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***Ab Initio* Analysis of the Energy and Geometry During the Rearrangement of
Cyclopentadienylboranes and the Evaluation of the DAPSIC Computer Tutorial**

Brian Hill

A Dissertation Presented to the Graduate Faculty of Middle Tennessee State University in
Partial Fulfillment of the Requirements for the Doctorate of Arts Degree

December, 1999

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Cyclopentadienylboranes and the Evaluation of the DAPSIC Computer Tutorial**


Brian Hill

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Approved:




Dr. William H. Ilsley - Major Professor



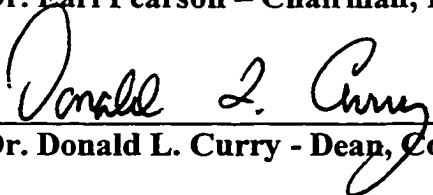
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ABSTRACT

***Ab Initio* Analysis of the Energy and Geometry During the Rearrangement of Cyclopentadienylboranes and the Evaluation of the DAPSIC Computer Tutorial**

By Brian Hill

The equilibrium and transition state geometries of the degenerate 1,5-sigmatropic rearrangement of cyclopentadienylborane, cyclopentadienyldifluoroborane, cyclopentadienyldichloroborane, pentamethylcyclopentadienylborane, pentamethylcyclopentadienyldifluoroborane, and pentamethylcyclopentadienyldichloroborane were optimized using *ab initio* (RHF/3-21G*, RHF/6-31G*, RMP2/3-21G*, and RMP2/6-31G*) calculations. Activation energies were predicted and compared with previously published experimental data [P. Jutzi, B. Krato, M. Hursthouse, A. J. Howes, *Chem. Ber.* (1987), 120, 565-574.] The molecule optimized to an asymmetrical geometry with the boron atom shifted away from its symmetric η^1 position and toward one of the two neighboring carbons. This geometry was predicted for each molecule at each level of theory except for $C_5H_5BH_2$ at the RMP2/6-31G* level and $C_5H_5BH_2$ at the RHF/6-31G* level. This geometry was also predicted for bis(pentamethylcyclopentadienyl)fluoroborane.

Also, a computer aided instruction program called DAPSIC was evaluated for effectiveness in introductory college chemistry classes at MTSU. DAPSIC was designed to teach unit conversions using the factor-label method (also known as dimensional analysis or unit analysis.) Student performance on a brief quiz before and after using DAPSIC was compared with student performance on a brief quiz before and after doing an equivalent worksheet assignment. In the chemistry class intended for non-majors, the improvement in the quiz scores of students who used DAPSIC was significantly greater than the improvement in the quiz scores of students who used the worksheet. No significant difference was seen in the chemistry major's introductory class. In both classes, students over age 22 who used DAPSIC also showed significantly greater improvement over students age 22 who used the worksheet.

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Part A

***Ab Initio* Analysis of the Energy and Geometry**

During the Rearrangement of Cyclopentadienylboranes

Chapter 1 Introduction

Background

This dissertation summarizes the efforts undertaken by the author to model the 1,5-sigmatropic rearrangement of cyclopentadienylboranes using *ab initio* quantum mechanical techniques, and to evaluate the results against previously published empirical data [1]. These results will also be evaluated against previously modeled semi-empirical quantum chemistry calculations [2]. The goal of this work was to attempt to reproduce the previously published results, and if possible to improve upon them. The 1,5-sigmatropic rearrangement of cyclopentadienylboranes has previously been studied experimentally and theoretically, although it has not been studied using *ab initio* methods.

In 1963 Miranov and co-workers discovered that cyclopentadiene (C_5H_6) could undergo rearrangement[3]. At -10 °C this molecule has a stable structure. At 60 °C, however, a hydrogen atom can shift its bond from one carbon to an adjacent carbon on the same molecule. This produces a molecule identical to the original but with hydrogen atoms shifted to different positions within the molecule. This rearrangement is an example of a 1,5-sigmatropic suprafacial shift [4], and has alternatively been referred to as a "merry-go-round" circumambulatory rearrangement [5] or "ring whizzing" [6]. This molecule can also be described as "fluxional" in that its structure and bonding will change rapidly during long-duration experimental techniques (e.g., NMR spectroscopy) while

maintaining only one equilibrium structure seen by short-duration experimental techniques (i.e. X-ray crystallography) [7]. This rearrangement has been further studied experimentally [8] and has been analyzed theoretically [9].

Fluxional behavior has also been observed for substituted cyclopentadienes [6,10,11,12]. In Figure 1, a migrating substituent (here labeled “M”) has replaced an allylic hydrogen. The mechanism shown in Figure 1 describes a degenerate 1,5-sigmatropic rearrangement, since the molecular geometry is the same before and after rearrangement. Other (non-degenerate) mechanisms may be available for rearrangement,

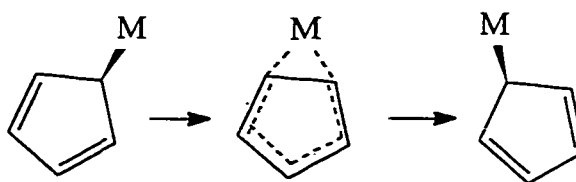


Figure 1
1,5-Sigmatropic rearrangement of substituted cyclopentadiene

but degenerate rearrangement has been observed in a number of different compounds [11,13]. This behavior has been modeled for a number of different substituents [14].

Cyclopentadienylborane is one substituted cyclopentadiene that has been investigated in terms of its ability to undergo a 1,5-sigmatropic rearrangement [1,11]. A search of *Chemistry Abstracts*, however, reveals no evidence that cyclopentadienylborane has ever been synthesized [15]. However, this molecule has been used as a model for theoretical investigations of cyclopentadienylboranes with further substitutions. In 1984

Wolfgang Schoeller modeled this rearrangement for this class of molecules using MNDO (a semi-empirical technique) [1]. *Ab initio* techniques have the distinction that, unlike semi-empirical techniques, they are based only on a few measured fundamental physical constants (mass of an electron, charge of an electron, etc.) This method is therefore more likely to be reliably applicable to molecules that are different from the ones used to generate semi-empirical parameters [16]. Since there had been no previously published *ab initio* studies of cyclopentadienylboranes, the decision was made to model theoretically this same rearrangement, but using *ab initio* methods not commonly available at the time of the previous study [1].

There were several reasons for the decision to study cyclopentadienylboranes. Boron is an element found in electron deficient molecules with unusual bonding (such as may be seen in organometallic compounds), yet at the same time has a low atomic number (and is therefore easy to handle computationally). These molecules have not been examined in great detail by many researchers, although there recently has been some renewed interest in related compounds [17-19]. Also, examining this system may serve as a useful first step for further investigations of larger systems (e.g., cyclopentadienyl-mercury compounds previously studied at this university [20]). Compounds similar to these have been shown to optimize to different geometries at different levels of *ab initio* theory [21]. An *ab initio* study of this system would arguably be useful for assessing the accuracy of different levels of theory for modeling systems of this type. Finally, if the *ab initio* predictions about cyclopentadienylboranes give good agreement with experimental

evidence, then a more thorough analysis of the bonding in these molecules [22] can be applied with greater confidence.

Schoeller's initial theoretical treatment of this molecule was based on an analysis using the rules of conservation of orbital symmetry [4]. Woodward and Hoffmann predicted that suprafacial 1,5-sigmatropic rearrangements are allowed if the substituent migrates with retention of configuration at the migrating center. If the substituent migrates with inversion of configuration (i.e., through opposite ends of a p orbital), the expected reaction would be a suprafacial 1,3-sigmatropic rearrangement [4,12]. Schoeller's analysis and subsequent calculations, however, suggest that the 1,5-sigmatropic rearrangement proceeds through an inversion of configuration at the migrating boron atom. His predicted mechanism appears to imply that the two hydrogens on the BH_2 substituent will exchange places on each 1,5-sigmatropic shift.

This prediction appears to contradict the Woodward-Hoffmann prediction. However, Schoeller's prediction is consistent with Woodward-Hoffmann's prediction if



Figure 2
Unoccupied orbitals of a BH_2^+ fragment
(bent here, since it is bent when attached to cyclopentadienide).

one considers that there are two orbitals of the BH_2^+ fragment (i.e. if the orbitals were to be separated from the rest of cyclopentadienylborane) that may be involved in the interaction (see Figure 2). Schoeller labels these two orbitals σ and p . Schoeller's predicted equilibrium geometry can be explained in terms of a bonding interaction between a (σ) unoccupied orbital of the BH_2^+ fragment and one of the two (degenerate) highest occupied molecular orbitals of the ring (pictured as the sum of atomic orbitals in



Figure 3
Degenerate highest occupied
molecular orbitals of cyclopentadienide

Figure 3). As the molecule proceeds towards the transition state, the other (p) unoccupied orbital of the BH_2^+ may be able to interact with the other degenerate highest occupied molecular orbital of the ring. It is therefore possible that this overlap can continue until it is responsible for the new bond in the final equilibrium geometry; the previous bonding interaction having been broken. Although Schoeller does not state this prediction explicitly, his proposed mechanism would appear to require that, as the molecule proceeds from one equilibrium geometry to the next, the highest occupied molecular orbital and the second highest molecular orbital will exchange places. Although this

model may have some possible theoretical problems, in principle it can be tested. An alternative explanation for his mechanism would be a form of subjacent orbital control [23] (i.e., interactions involving orbitals other than the highest occupied molecular orbital and the lowest unoccupied molecular orbital).

Review of Literature

Although cyclopentadienylborane has not been synthesized [15], a variety of substituted cyclopentadienylbornanes have been synthesized and studied [24-30]. Many of these compounds are highly fluxional, and activation energy data are available for some of these molecules [2]. Some of these compounds have been used to produce cyclopenta-dienylboronium ions, which have been noted to adopt an η^5 structure [31, 32]. Consideration of the geometry of these η^5 compounds, however, is beyond the scope of this work.

The 1,5-sigmatropic rearrangement has been successfully modeled using *ab initio* techniques [33]. Not surprisingly, more accurate predictions are encountered at higher levels of theory. However, some useful results have been obtained at comparatively modest levels of theory. For example, for the 1,5-sigmatropic rearrangement of hydrogen in *cis*-1,3-pentadiene, the RMP2/6-31G* level was found to predict the activation energy within experimental error [33]. This level of theory was not sufficient for all rearrangements. For example, the walk-rearrangement of bicyclo[2.1.0]pent-2-ene required modeling at the RMP4/6-31G* level to successfully predict the activation energy [33].

Although the Hartree-Fock level is sufficient for predicting many equilibrium geometries, activation energy calculation requires some form of consideration of electron correlation, since the transition state geometry is more affected by electron correlation effects than the equilibrium geometry [33]. A discussion of the details of these computational methods is found at the end of this chapter.

Although cyclopentadienylboranes have not been modeled using *ab initio* methods, a number of related compounds have been studied using these methods. *Ab initio* calculations have been employed to successfully model some experimental results in various cyclopentadienyl organometallic compounds [34-38]. The *ab initio* analysis of the geometry and behavior of other group 13 analogs of cyclopentadienylborane are here reviewed.

One early attempt to model these compounds was made by Anh, et. al. [14]. They noted that the $C_5H_5CH_2^+$ substituent was isoelectronic with $C_5H_5BH_2$. Extended Huckel calculations for $C_5H_5CH_2^+$ suggested that either the η^1 or η^2 geometry would be much lower in energy than the η^3 or η^5 geometry. The energy depended strongly on the orientation of the CH_2 substituent. The lowest energy geometry predicted was η^2 , with the CH_2 substituent oriented within the plane bisecting the ring. Anh, et. al noted that this geometry was consistent with the geometry already seen in $C_5H_5Al(CH_3)_2$ [14].

Like cyclopentadienylboranes, cyclopentadienyl aluminum compounds tend to be highly fluxional [39]. As such detailed information about the rearrangement mechanism is difficult to obtain. Bonding ranging from η^1 [39], η^2 [14], η^3 [40], to η^5 [41] is

observable in cyclopentadienylaluminum compounds. Also, asymmetrical geometries similar to those seen in cyclopentadienylboranes [2] have been observed in these compounds[39]. In one η^1 aluminum compound ($[\text{Al}(\text{C}_2\text{B}_9\text{H}_{11})_2]^+$) *ab initio* calculations were able to successfully predict both structural and NMR data [41]. However, RHF/3-21G* and RHF/6-31G* predictions of the hapticity of the equilibrium geometry of $\text{Al}(\text{C}_5\text{H}_5)_3$ do not match the X-ray crystallographic data [39]. This discrepancy could have been due to intermolecular steric constraints in the solid phase, since the unit cell observed had two different conformations present. Fisher, et. al, suggested the need to perform calculations at least at the MP2 level to successfully predict the geometry of this compound [39]. Their calculations did, however, successfully model the metal-ring distances seen in this molecule. These results also predicted that the energy differences between the different possible hapticities of the metal-ring bonding were small. NMR measurements support this prediction; $\text{Al}(\text{C}_5\text{H}_5)_3$ and related methyl substituted compounds were fluxional at -100 degrees Celsius [39].

Cyclopentadienyl gallium compounds analogous to cyclopentadienylboranes have been synthesized and characterized. The molecule $\text{C}_5\text{Me}_5\text{GaCl}_2$ was used to synthesize $\text{Ga}(\text{C}_5\text{Me}_5)_3$, although attempts to obtain X-ray crystallographic data on this molecule were unsuccessful [42]. In 1998 Jutzi, et. al. used $\text{C}_5\text{Me}_5\text{GaI}_2$ to synthesize $(\text{C}_5\text{Me}_5)\text{Ga}$, which then was used as an electron donating ligand in other organometallic compounds [43]. (Note that gallium, unlike boron, can form 1+ oxidation state compounds here). In $(\text{C}_5\text{Me}_5)\text{Ga}$, and in most molecules examined involving a $(\text{C}_5\text{Me}_5)\text{Ga}$ ligand, the gallium

atom occupied an η^5 position over the cyclopentadienyl ring. The exception was $\text{Fe}_2(\mu\text{-C}_5\text{Me}_5\text{Ga})_3(\text{CO})_6$, in which one gallium exhibited η^3 bonding. Both $\text{C}_5\text{Me}_5\text{GaCl}_2$ and $(\text{C}_5\text{Me}_5)_2\text{GaCl}$ have gallium bound η^1 to the cyclopentadienyl ring [40], although both form dimers in solid state bridging through chlorine atoms. An *ab initio* analysis of these compounds would probably be of interest. Unfortunately, a search of Chemistry Abstracts did not yield any recent papers involving *ab initio* calculations of cyclopentadienyl gallium compounds.

In contrast to gallium, cyclopentadienyl indium compounds have been optimized using *ab initio* techniques. In 1989 Beachley, et al. examined $\text{In}(\text{C}_5\text{Me}_5)$ using X-ray crystallography, electron diffraction, and Hartree-Fock *ab initio* calculations [44]. In contrast to cyclopentadienylborane, this compound involves a group 13 element in the +1 oxidation state, and an approximately η^5 orientation with respect to the ring. (The molecule $\text{In}(\text{C}_5\text{Me}_5)\text{Cl}_2$ was synthesized, but was found to decompose spontaneously in solution.) The geometry of $\text{In}(\text{C}_5\text{Me}_5)$ was optimized using two different basis sets, with the smaller basis set predicting geometry closer to experimental results than the larger basis set. Both basis sets did, however, predict that $\text{In}(\text{C}_5\text{Me}_5)$ has a shorter indium-ring centroid distance than $\text{In}(\text{C}_5\text{H}_5)$, a prediction that was confirmed experimentally. All calculations in this paper assumed symmetry, even though X-ray crystallographic data indicated that the indium atom is displaced slightly from the axis.

In 1997, Hinderling, et al. examined several indium (III) pentamethylcyclopentadienyl cationic species using density functional theory (DFT) calculations [45].

They examined possible intermediates in the reaction of $[(C_5Me_5)In(P(CH_3)_3)(CH_3)]^+$ with benzene to produce $[(C_5Me_5)In(P(CH_3)_3)(C_6H_5)]^+$ and CH_4 . They used density functional theory calculations to optimize the geometries. Their results predicted relative energies inconsistent with their experimental results, although they noted that their results were close enough together in energy to argue that their putative mechanism was plausible. They did, however, note that the optimized geometries obtained using density functional theory were in general consistent with the Hartree-Fock optimizations they had obtained previously.

Both indium studies mentioned the computational difficulties associated with calculations involving large molecules containing heavy atoms (and thus involving relativistic effects). These problems would only be magnified for thallium containing molecules. As such, this review of the literature will not consider cyclopentadienyl-thallium molecules other than to note that both cyclopentadienylthallium and pentamethylcyclopentadienylthallium have been synthesized [46].

In addition to group 13 molecules, *ab initio* calculations have been performed for cyclopentadienyl silicon molecules. Silicon is diagonally related to boron on the periodic table. Silicon, like boron, is a metalloid noted to have a preference for sigma bonding [39]. Semi-empirical calculations of $Si(C_5H_5)_2$ suggested that this molecule would adopt a "bent sandwich" (low symmetry) η^5 geometry, similar to the geometry seen in $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ [47]. This same geometry was later seen by X-ray crystallography and electron diffraction in $Si(C_5Me_5)_2$ [48]. MNDO calculations were

unable to predict the observed geometry of this molecule, but HF/STO-3G and HF/STO-3G* calculations were able to predict that the equilibrium geometry would adopt a "bent sandwich" conformation [48]. Subsequent HF and MP2 calculations by Lee, et. al. on $\text{Si}(\text{C}_5\text{H}_5)_2$ suggested that this molecule would adopt a conformation with low symmetry [21]. Preliminary calculations suggested that the lowest energy triplet state would be significantly higher in energy than the singlet state; Lee, et al. did not pursue triplet state geometries further [21]. At higher levels of theory the energy difference between the "bent sandwich" and the higher symmetry η^5 conformers was smaller. Lee, et. al noted the possibility that the higher symmetry conformer might be predicted to be the global minimum if higher levels of theory or larger basis sets were used [21].

In summary, *ab initio* calculations have been used to model the geometry and properties of various molecules similar to cyclopentadienylborane, with varying degrees of success. A variety of hapticities for these molecules have been predicted for equilibrium and transition state geometries for these molecules. Unusual asymmetric geometries have been observed for some of these compounds. It would therefore appear to be reasonable to use these *ab initio* techniques to model various possible geometries of cyclopentadienylboranes, in order to attempt to model the 1,5-sigmatropic rearrangement of these molecules.

Purpose and Objectives

The purpose of this study was to model the degenerate 1,5-sigmatropic rearrangement of cyclopentadienylborane and some related compounds, using *ab initio* techniques.

The objective was to predict and analyze the geometry and energy of the equilibrium and transition states geometries of these molecules. The overall goal was to determine the mechanism for this rearrangement, and to compare these predictions with previously reported experimental data [2].

The following molecules were selected to be investigated: cyclopentadienylborane ($C_5H_5BH_2$), (1); cyclopentadienyldifluoroborane ($C_5H_5BF_2$), (2); cyclopentadienyldichloroborane ($C_5H_5BCl_2$), (3); pentamethylcyclopentadienylborane ($C_5Me_5BH_2$), (4); pentamethylcyclopentadienyldifluoroborane ($C_5Me_5BF_2$), (5); pentamethylcyclopentadienyldichloroborane ($C_5Me_5BCl_2$), (6); bis(pentamethylcyclopentadienyl)fluoroborane ($(C_5Me_5)_2BF$), (7). This set of molecules was selected in order to span both the parent molecule (1) and the molecules for which empirical data is available (5-7). Substituent effects due to methyl, fluorine, and chlorine at relevant sites on cyclopentadienylborane could also be compared from the molecules chosen in this study.

The energy of each molecule was optimized in order to obtain the lowest energy conformation (anticipated to be the η^1 conformation of this molecule). All molecules except (7) were optimized while constraining the geometry to an η^2 conformation (anticipated to be the transition state of this molecule in the degenerate 1,5-sigmatropic rearrangement). Vibrational analysis was performed on both conformations in order to estimate the zero point vibrational energy corrections to the calculated energies of these two conformations, and to verify that the putative transition state possessed only one imaginary vibrational mode (e.g. that it does in fact have a defining characteristic of a

transition state.) For molecule (1), additional optimizations were performed to scan for effects of the H-B-C-H dihedral angle and the B-C distance on the energy and optimized geometry of this molecule.

These molecules were optimized using the following computational methods: MNDO (reproducing results obtained previously), RHF/3-21G* (an *ab initio* method with a small basis set), RHF/6-31G* (an *ab initio* method with a larger basis set), RMP2/3-21G* (an *ab initio* technique correcting for electron correlation effects), and RMP2/6-31G* [49]. RMP2/6-31G* has produced useful results for cyclopentadiene [2] and for cyclopentadienylaluminum [39], but was found to be beyond the limits of our currently available computer facilities for molecules 4-7. All methods were applied to molecules 1-3, and all methods except RMP2/6-31G* were applied to molecules 4-7.

Schoeller's study [1] of these molecules assumed that both the equilibrium and transition state geometries would possess C_s symmetry (i.e. there would be a plane of symmetry through the boron atom). X-ray crystallographic data for crystals of molecule (7), however, indicates that the cyclopentadienylborane unit within these molecules may not possess C_s symmetry [2]. As such, no assumptions were made about the symmetry of the equilibrium geometry, and the only assumption that was made about the transition state geometry was that the boron atom was equidistant between the two adjacent carbons [50]. Frequency analysis was used to verify that the transition state had only one imaginary frequency.

Various geometries were selected to be explored as candidates for the equilibrium and transition state geometries for these molecules. The mechanism previously

postulated for the 1,5-sigmatropic rearrangement has been assumed to involve an η^1 equilibrium geometry and an η^2 transition state geometry; however, the possibility of a stable η^2 equilibrium geometry for some molecules of this type has previously been suggested [1,14,51]. Therefore, other hapticities were selected to be examined. No transition state was calculated for (7), however, the equilibrium geometry was generated for comparison with X-ray crystallographic data for this molecule [2]. Activation energies were calculated for (1-6) at all available levels of theory; in particular activation energies for the rearrangement of molecules 5-6 were predicted for comparison with experimental values [2]. These comparisons in turn were intended to be used to evaluate which method of calculation produced the most accurate predictions. Comparisons of the predictions for different molecules by the same method were used to evaluate the effects of fluorine, chlorine, and methyl substitutions on this rearrangement. Finally, various geometries between the equilibrium and transition state geometries were generated for the purpose of determining whether or not the predicted mechanism involves the two identical boron substituents exchanging positions at each step as implied by the previous study [1].

Overview of Quantum Mechanics and *Ab Initio* Molecular Orbital Theory

In order to predict the activation energy for the rearrangement of cyclopentadienylboranes, a theoretical model is needed. The previous study of this system employed the MNDO semi-empirical method [1], which although quantum mechanical,

depends somewhat on measured spectroscopic quantities which are then assumed to be generally valid for all molecules [52]. In contrast, this study employed two *ab initio* quantum mechanical methods -- Restricted Hartree-Fock (RHF) and restricted second-order Moller-Plesset perturbation theory (RMP2). These are both *a priori* methods (i.e. they do not require any empirical data beyond the mass and charge of an electron, the mass and charge of the nuclei of the elements, and Planck's constant). The history and development of quantum mechanics and *ab initio* molecular orbital theory in general are covered in undergraduate physical chemistry textbooks [53-55], books provided with molecular modeling software [56,57], and other references [58-60]. Since these methods are used in most of the calculations discussed in this research, an overview of their derivation is also included here.

In 1925 Clifton Davidson and Lester Germer demonstrated that electrons in motion can form diffraction patterns and therefore can have wavelike properties [61]. The wavelength of matter in motion had previously been predicted theoretically by deBroglie [62]. In 1926, Erwin Schrodinger produced a wave equation in order to explain the wavelike properties of matter. In a simplified form, for a single particle in one dimension, the equation is [63]:

$$-\frac{1}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = -\frac{1}{i} \frac{\partial \Psi}{\partial t} \quad (1)$$

where x is the spatial coordinate, m is the mass of the particle, t is the time coordinate, i equals $(-1)^{1/2}$ and V is the potential energy of the particle (which may be function of both

x and t). This equation is conveniently expressed in a particular system of units called “atomic units” [64]. The wavefunction Ψ is a complex function (of both x and t) that, according to the standard interpretation of quantum theory, contains a complete description of the behavior of the particle [65]. Max Born in particular postulated that $\Psi^*\Psi$ is proportional to the probability of finding the particle at a particular location [66]. In order to be an acceptable wavefunction, Ψ must be single valued, continuous, finite and differentiable at each value of x and t [67]. Additionally, in order for $\Psi^*\Psi$ to equal to the probability of finding the particle at a particular location, the function Ψ must be normalized (that is, $\int \Psi^*\Psi dx=1$) [67]. Beyond that, given any arbitrarily chosen initial $\Psi(x, t=0)$, one can predict the subsequent values of $\Psi(x, t>0)$.

Wavefunctions that represent particles with observable properties in real time (that is, particles in stable systems where V is not a function of time) have the additional restriction that $\Psi^*\Psi$ is to be independent of time (that is, that the probability of finding a particle at a particular location remains constant with respect to t). In other words, the function Ψ will be of the form [68]:

$$\Psi(x, t) = \psi(x)\psi'(t) \quad (2)$$

where ψ is a function only of x, and ψ' is a function only of t. With this substitution, Equation 1 can thus be rearranged in order to separate the variables [69]:

$$\frac{1}{\psi} \left(-\frac{1}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \right) = \frac{1}{\psi'} \left(-\frac{1}{i} \frac{\partial \psi'}{\partial t} \right) = E \quad (3)$$

Both sides of this equation are independent and must therefore be equal to a constant (here labeled “E”). The time dependent portion of this equation can then be removed and the rest reorganized into the form [69]:

$$-\frac{1}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi \quad (4)$$

Functions that fit this restriction are called eigenfunctions and E is referred to as the eigenvalue (corresponding to the energy of the system).

For an electron (with $m=1$) in three spatial dimensions, Equation 4 becomes:

$$-\frac{1}{2} \nabla^2 \psi + V\psi = E\psi \quad \left(\text{where } \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (5)$$

where x, y, and z are the Cartesian coordinates of the electron, and where V is a function of all three coordinates [70]. This equation can be used to model, for example, the hydrogen atom with a proton at the origin (where $V=-(x^2+y^2+z^2)^{-1/2}$). This model can also be used to predict eigenvalues for the energy of an electron in a hydrogen atom which are in general consistent with experimental results [71].

The actual hydrogen atom is of course a two-particle system, but since the proton is much heavier than the electron, this system can be approximated by assuming that the nucleus is stationary and located at the origin. (The assumption that the electron mass is equal to the reduced mass of an electron-proton system leads to an error of less than

0.1%. One need not make this assumption, however, since this particular system can be solved exactly. [71].)

In principle, Equation 5 can be solved for any system with one electron. The H_2^- ion, for example, can be modeled by the following equation:

$$-\frac{1}{2} \left(\nabla_{\text{electron}}^2 \psi + \frac{1}{M_p} \nabla_{HA}^2 \psi + \frac{1}{M_p} \nabla_{HB}^2 \psi \right) + V\psi = E\psi \quad (6)$$

$$\left(\text{where } V = \frac{-1}{r_{1A}} + \frac{-1}{r_{1B}} + \frac{1}{r_{AB}} \right)$$

where the “del-squared” operators represent the second derivatives of ψ with respect to the coordinates of the electron, the first hydrogen, and the second hydrogen, respectively. The variable M_p represents the mass of a proton and r represents the distance between the particles listed in the subscript [72]. Since this system contains three particles, it cannot be solved exactly. However, a good approximation may be made by assuming that, since the nuclei are much heavier than the electrons, they can be assumed to remain stationary. (This assumption is known as the Born-Oppenheimer approximation [73].) By assuming that the nuclear energy is constant, the rest of the equation can be solved for constant nuclear coordinates to give the electronic wavefunction and energy [73]:

$$-\frac{1}{2} \nabla_{\text{electron}}^2 \psi + V\psi = E_{\text{electron}} \psi \quad (7)$$

$$\left(\text{where } V = \frac{-1}{r_{1A}} + \frac{-1}{r_{1B}} \right)$$

where both V and ψ now are functions only of the coordinates of the electron, and E_{electron} represents the energy only of the electron. The nuclear potential energy can then be added in order to determine the energy of the ion for a given internuclear distance. This internuclear distance can be varied, and the energy can be calculated for each value. The equilibrium internuclear distance is then the one with the lowest energy. The process of varying nuclear coordinates in order to find an energy minimum is referred to as geometry optimization. The nuclear kinetic energy cannot in fact be equal to zero, so the actual energy will also include zero point vibrational energy. [74].

Equation 7 can be expanded to include systems of more than one electron. For example, for the H_2 molecule with two electrons the expanded equation must include some additional terms:

$$-\frac{1}{2}(\nabla_{\text{electron1}}^2 \psi + \nabla_{\text{electron2}}^2 \psi) + V\psi = E_{\text{electron}} \psi \quad (8)$$

$$\left(\text{where } V = \frac{-1}{r_{1A}} + \frac{-1}{r_{1B}} + \frac{-1}{r_{2A}} + \frac{-1}{r_{2B}} + \frac{1}{r_{12}} \right)$$

where terms have now been added which are functions of the coordinates of electron 2, and both V and ψ are now functions of six spatial coordinates [75].

For molecules beyond H_2 , the general form of Equation 8 is:

$$-\frac{1}{2} \left(\sum_{\text{All elect.}} \nabla_i^2 \psi \right) + V\psi = E\psi \quad (9)$$

$$\left(\text{where } V = \sum_{\text{All elect.}} \sum_{\text{All nucl.}} \frac{-Z_I}{r_{iI}} + \sum_{\text{All elect. pairs}} \frac{1}{r_{ij}} \right)$$

where Z_I is the atomic number, r_{iI} is the distance from an electron to a nucleus, and r_{ij} is the distance between two electrons [76]. For N electrons, ψ and V will be functions of $3N$ spatial coordinates. This is the electronic time-independent Schrodinger equation for a generalized molecule.

Two complexities are introduced with the introduction of multielectron systems. First, solving ψ for a system with many variables is prohibitively complex. This equation would be simplified considerably if each term involved the Cartesian coordinates of only one electron. If this separation of variables was possible, this multielectron wavefunction then becomes the product of individual single electron wavefunctions (usually referred to as orbitals, and in a multinuclear system referred to as molecular orbitals). Stated mathematically, the multielectron wavefunction could potentially have the form:

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots) = \phi_1(x_1, y_1, z_1) \phi_2(x_2, y_2, z_2) \dots \quad (10)$$

where $\phi_1(x_1, y_1, z_1)$ is a single electron wavefunction for electron 1, $\phi_2(x_2, y_2, z_2)$ is a single electron wavefunction for electron 2 etc. [77]. This initial equation is inadequate, however, since it does not take into account the fact that each electron is indistinguishable

from all other electrons, the existence of electron spin, and the requirements of the Pauli Exclusion principle [78]. However, this problem can be remedied by introducing a spin coordinate for each electron, by creating spin orbitals (multiplying each spatial orbital by a function of the spin coordinate), and by adding or subtracting terms in which the coordinates of the electrons are exchanged [79]. (This process is simplified somewhat if we assume a “restricted” case for an even electron singlet state molecule, in which each spatial orbital can be used to define two spin orbitals.) The process of generating an acceptable multielectron wavefunction from single spatial molecular orbitals is straightforward and described in detail in standard references [80]. Here it is sufficient to note that, if molecular (spatial) orbitals are known, a multielectron wavefunction can be generated automatically. But, again, the concept of single electron orbitals is only strictly valid to the extent that the multielectron wavefunction can be separated into terms containing only single electron coordinates.

The process of calculating each orbital would also be prohibitively complicated unless some assumption about the form of the molecular orbital function is made. In principle, any function can be defined by assigning a numerical value to each particular coordinate. Since the number of coordinates is infinite, an infinite number of numerical values are required to describe a function completely. Equivalently, any function may be described as the linear combination of a set of basis functions, provided that the basis set is complete. A complete basis set is infinite, so an infinite number of numerical coefficients must be assigned in order to completely describe any function [81]. For practical reasons, the number of numerical values used to describe an orbital must be

finite. Since the basis set used to define a molecular orbital must be limited, the basis set selected for use ideally should have a demonstrated record of modeling the properties of different molecules with acceptable accuracy within acceptable size limits. One set that has been used extensively has been gaussian functions [82]; e.g. functions of the following form:

$$g(x, y, z) = c x^n y^m z^l \exp(-\alpha r^2) \quad (11)$$

where r equals $(x^2+y^2+z^2)^{1/2}$; m , n , and l are non-negative integers, and c is the constant required for normalization. The relative sharpness of the function is determined by α . Specified sets of these functions centered at each atom with specific values for α are given labels used to identify them in research literature. The two sets used in this research are 3-21G* and 6-31G* [49]. The latter has been used with acceptable accuracy to model equilibrium and transition state geometries of small molecules [83], the former is smaller and therefore more practically convenient to use.

Once a basis set has been selected, molecular orbitals may be generated by assigning coefficients to each basis set function. Multielectron wavefunctions may then be generated from these molecular orbitals. The variational principle [84] states that it is possible to determine the coefficients that will give the best approximation of the true wavefunction. If both sides of Equation 9 are multiplied by the complex conjugate of ψ , and both sides are integrated over all electron coordinates, then the right-hand side of Equation 9 will be equal to the expected (average) value of the energy of the electrons. If

the wavefunction was exactly correct, this value would simply be the eigenvalue of this equation. For any inexact wavefunction, the expected value for the energy will be higher than the true eigenvalue. Therefore, the best approximation of the true wavefunction is the one that yields the minimum for the expected energy value [85]. In principle, the coefficients may be varied randomly and those particular coefficients that generate the minimum expected value for the energy can eventually be noted. In practice, there exist practical methods of generating these coefficients automatically [86].

Unfortunately, these wavefunctions cannot simply be inserted into Equation 9 in its current form and solved, due to the second complexity introduced in multielectron systems. The second of the two complexities is the fact that electron-electron repulsions are included in the potential function V in Equation 9. In order for the molecular orbital assumption to be strictly valid, each term in Equation 9 must only depend on one set of electron coordinates. The last set of terms in V in Equation 9, however, depends on the coordinates of two electrons. One approximation that allows for the separation of electron coordinates is called the Hartree-Fock approximation [87]. In this method, the electron repulsion potential energy of electron 1 is assumed to be equal to its average repulsion from other electrons over all space. Stated mathematically for one electron in a two electron system [88]:

$$V_{Coulomb12} \phi_1(coord1) = \left\{ \int d(coord2) |\phi_2(coord2)|^2 \left(\frac{1}{r_{12}} \right) \right\} \phi_1(coord1) \quad (12)$$

where ϕ_1 and ϕ_2 are the two molecular orbitals, and “coord1 and “coord2” are the coordinates (spatial and spin) for the two electrons. In order to find the total electron repulsion potential energy, it is necessary to add the potential energy contribution for each pair of electrons; however, in order for the final wavefunction to be antisymmetric (as required by the Pauli principle), exchange terms of the following form must be subtracted as well [89]:

$$V_{\text{Exchange}12} \phi_1(\text{coord1}) = \left\{ \int d(\text{coord2}) \phi_2^*(\text{coord2}) \phi_1(\text{coord2}) \left(\frac{1}{r_{12}} \right) \right\} \phi_2(\text{coord1}) \quad (13)$$

Note that if both electrons have opposite spins, $V_{\text{exchange}12}$ will equal zero. If terms of these two types are substituted in place of the last set of terms in Equation 8, then the molecular orbital approximation is valid since all electron coordinates are separable. This form of Equation 9 could in principle be solved. Unfortunately, the integrals in Equation 12 and 13 require that the molecular orbitals already be defined before this equation can be solved. In practice, an initial guess is made for each molecular orbital, and then this form of Equation 9 is used to generate better approximations for the orbitals. If the initial guess is sufficiently correct, the approximations will eventually converge to a final answer [90]. The Hartree-Fock method can thus be used to generate molecular orbitals for a particular molecule.

Even with a complete (infinite) basis set, the Hartree-Fock method cannot generate exact solutions to the Schrodinger equation [91]. The Hartree-Fock assumption

is inherently flawed, since it assumes that the motion of electrons of opposite spin is not correlated. An example of this flaw may be seen in Equation 12. The value of ϕ_2 squared (i.e. the probability of finding electron 2 at a particular location x_2, y_2, z_2) is assumed here to be independent of the location of electron 1. In a real system, since electrons repel each other, if electron 1 happens to be close to x_2, y_2, z_2 (i.e. where $1/r_{12}$ is largest), then the probability of finding electron 2 there will be substantially reduced. Therefore, the Hartree-Fock value predicted for the energy will be an overestimate of the actual energy.

The difference between the actual eigenvalue and the Hartree-Fock predicted energy is called the correlation energy [92]. There exist a number of different methods for estimating this quantity (Equation 10). They assume that the Hartree-Fock generated molecular orbitals (and therefore Hartree-Fock generated multielectron wavefunctions) can be modified in order to account for electron correlation effects. These molecular orbitals can then be used to generate a multielectron wavefunction that is closer to an exact solution to the Schrodinger equation (Equation 9), which in turn can be used to determine an expected value for the energy that is closer to the true eigenvalue of the system [93]. Such a multielectron wavefunction in principle could be generated from any complete basis set of multielectron functions. One convenient set is the set of all possible ground and excited state multielectron wavefunctions generated by the Hartree-Fock solutions (i.e. multielectron wavefunctions generated by placing electrons in all possible molecular orbitals, not just the lowest energy orbitals). Stated mathematically [94], this becomes:

$$\psi^{EC} = \sum_{n=0}^{\text{All Substitutions}} c_n \psi_n^{HF} \quad (14)$$

where a "substitution" refers to removing an electron from a low energy occupied orbital and placing it in a higher energy unoccupied orbital; and where the resulting multielectron wavefunction, corrected for electron correlation, is a linear combination of all possible Hartree-Fock multielectron wavefunctions (including, where $n = 0$, the ground state Hartree-Fock solution). The problem is therefore reduced to determining the coefficients in Equation 14. Applying the variational principle and finding energy minimizing coefficients for Equation 14 (a method called configuration interaction) is theoretically possible, but usually impractical [95].

One alternative approach to solving for the correlation energy and the corrected multielectron wavefunction is called Moller-Plesset perturbation theory [96].

Perturbation theory is a general mathematical method for introducing successive order corrections for an approximate mathematical solution [97]. According to perturbation theory, it can be shown [98,99] that the first-order correction to the wavefunction will have coefficients of the following form:

$$c_n = \frac{1}{E_n - E_0} \int \psi_n^* \frac{1}{r} \psi_0 d(\text{coordinates}) \quad (15)$$

where E_0 is the sum of all the single electron energies for all occupied orbitals in the ground state, E_n is the sum of all the single electron energies for all occupied orbitals in

the excited state (i.e. for ψ_n in Equation 14), r is the distance between electrons, and the integral is integrated over all coordinates for each electron. This integral can be simplified by noting that for the first-order correction, the integral will be non-zero only for ψ_n that has two electrons in non-ground state molecular orbitals [100]. With this simplification, it is possible to reduce the integral in Equation 15 to the following form [101]:

$$\begin{aligned} \int \psi_n^* \frac{1}{r} \psi_0 d(\text{coordinates}) = & \\ \int d(\text{coord1}) d(\text{coord2}) \phi_i^*(\text{coord1}) \phi_j^*(\text{coord2}) \frac{1}{r_{12}} \phi_k(\text{coord1}) \phi_l(\text{coord2}) & \\ - \int d(\text{coord1}) d(\text{coord2}) \phi_i^*(\text{coord1}) \phi_j^*(\text{coord2}) \frac{1}{r_{12}} \phi_l(\text{coord1}) \phi_k(\text{coord2}) & \quad (16) \end{aligned}$$

where “coord 1 and “coord 2” are the coordinates (spatial and spin) for two electrons, ϕ_i and ϕ_j are the two orbitals which are occupied in ψ_n but not in ψ_0 , and ϕ_k and ϕ_l are the two orbitals which are occupied in ψ_0 but not in ψ_n . Each term is an integral over all six spatial coordinates (and two spin coordinates).

The coefficients generated from Equations 15 and 16 can then be used to generate a first-order corrected multielectron wavefunction. This wavefunction, in turn, can be used to generate the second-order correlation energy. The sum of the unperturbed and first-order Moller-Plesset energies is equivalent to the Hartree-Fock energy [102]. The sum of all three, then, is the second-order Moller-Plesset energy expected value. Since this is not a variational process, it is possible that this value may be lower than the actual

eigenvalue [103]; however, values closer to the actual eigenvalue may be generated by higher order corrections [104].

Again, once the total electron energy for a given molecule is known, the nuclear energy can also be calculated to determine the total energy. The geometry can be optimized to minimize this energy (with or without a geometric constraint). Once the equilibrium geometry is determined, the zero-point vibrational energy can be estimated from the second derivatives of the potential energy with respect to each nuclear coordinate [105], together with a normal mode analysis [106]. For an equilibrium geometry, all normal modes will have real frequencies. For a transition state geometry, one normal mode will be imaginary (and may be omitted from the calculation of the zero-point energy [107]).

In summary, this research will use restricted Hartree-Fock energies and restricted second-order Moller-Plesset energies to estimate the energy of each molecule examined. These methods will be used with either a 3-21G* or 6-31G* basis set to generate energy optimized geometries for each molecule. Whenever practically feasible, the actual energy of the molecule will be estimated by also including the zero-point vibrational energy. These quantities will be compared with experimental results when available.

Because of limitations on computational resources, the following assumptions will be made: This research assumes that the time-independent, non-relativistic Schrodinger equation is adequate for modeling these molecules. An analysis of molecules involving elements beyond the third row of the periodic table would need to account for relativistic effects in some way [108], but no such elements are found in the

molecules under consideration here. This research also assumes the Born-Oppenheimer approximation of separation of nuclear and electronic wavefunctions to be adequate, and that the multielectron wavefunction can be approximated with adequate accuracy from determinants of molecular orbitals. Furthermore, this research will assume that all molecules encountered will be in the singlet state, and that two spin orbitals can be generated from the same spatial orbital (i.e. that “restricted” methods are valid.) Finally, this research will assume that the 6-31G* basis set, together with second-order Moller-Plesset analysis, will be able to estimate the energy differences between different molecular geometries. These assumptions will place limits on the reliability of the conclusions reached by this research. All conclusions reached herein may someday be re-examined when computational resources do not mandate that some or all of these assumptions be made (even as this research is a re-examination of a previous work [1], using tools not commonly available when the previous research was published).

Chapter 2 Experimental Methodology

Definition of Terms and Labels Used in This Study

This study employs certain non-SI units, in order to facilitate comparisons with previous studies. Non-SI units employed here are defined so that conversions can be easily made. This study will use the conversion factor that one Hartree is equal to 627.5095 kilocalories per mole [64], and that one calorie is defined as 4.184 Joule [109]. One Ångstrom (1 Å) is of course equal to 10^{-10} meters, and one Bohr is equal to 0.52918 Å.

For the presentation of numerical data, the following convention is employed: All distances will be reported to the nearest 0.001 Å and all angles are reported to the nearest 0.1 degrees, as has been done in a previous study [110].

Abbreviations relating to calculation methods will be used here in the same sense as defined in the user's manual of each program [56-57]. The phrase "at this level" will be used to designate a particular method of calculation (i.e. RHF, or RMP2) together with a particular basis set (i.e. 3-21G* or 6-31G*).

This study will examine substitutions on 2,4-cyclopentadien-1-ylborane, here referred to simply as cyclopentadienylborane (1). The molecule can be subdivided into a cyclopentadienyl fragment and a BH₂ (or BX₂, where X is a halogen) fragment. "The ring" will be used in this study to refer to the five carbons of the cyclopentadienyl substituent. Physical descriptions of the geometry in this study will use the atomic labels shown in Figure 4:

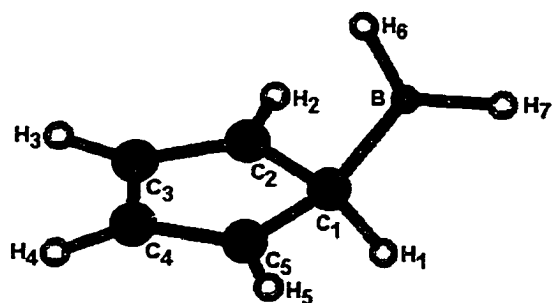


Figure 4
Atomic notation system used in this study.

"C1" will be used to refer to the carbon atom nearest to the boron atom, or to the left carbon atom if two are equidistant. "C2" and "C5" will be the two carbons neighboring C1; if one of these two is closer to the boron atom, that carbon atom will be designated "C2". "C3" and "C4" will designate the two remaining carbons numbered in order around the ring. Hydrogens bound to the ring will be assigned the same numerical designation as the carbon to which it is bound ("H1" is bound to C1, etc.) The two hydrogens of the BH₂ unit will be designated "H6" and "H7". If the hydrogens are not symmetrically placed, the hydrogen that is closest to the center axis of the ring will be designated "H6". For molecules with H6 and H7 substituted with a halogen (2 or 3), the "H" in this label will be substituted with either "F" or "Cl". "X" will refer to a generalized halogen (in this case, either fluorine or chlorine).

In order to make the display of molecules consistent, the molecule will be displayed so that the carbons are in counterclockwise order when viewed from the boron atom. For certain optimized molecules, the molecule was reflected so that the mirror

image is seen in the displayed figure. The assumption is made that reflection will not alter the energy of the molecule. This assumption was tested for molecule **5** at RHF/3-21G*, and both the molecule and its mirror image optimized to exactly the same value.

Several qualitative descriptions will be used relative to positions around the ring. "The plane of the ring" will here refer to the plane in space that most nearly contains all five carbons of the ring. This term will be used qualitatively only, since in fact the ring may not be exactly planar. The term "planar hydrogen" will be used to describe the hydrogen on a methyl group that is oriented in or closest to the plane of the ring. "The central axis of the ring" will refer to a line normal to the plane of the ring that contains the centroid of the ring. "Axial hydrogen" will refer to the hydrogen on a methyl group that is oriented along or approximately along the axis of a ring. The axis of the ring defines two different directions. "Up" will define the direction along this axis from the ring to the boron, and "down" will define the opposite direction. "A plane bisecting the ring" will refer to a plane perpendicular to the plane of the ring that contains both a carbon atom and the midpoint of the two carbon atoms on the opposite side of the ring. "The plane bisecting the ring" will refer to the one plane bisecting the ring that is closest to the boron atom. None of these definitions will be used for calculations; they are intended simply to provide a qualitative description of orientations around the ring.

This study will also examine (1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-boranes (here referred to simply as pentamethylcyclopentadienylboranes). For these molecules, the labels "H1" through "H5" will be replaced with "Me1" through "Me5", where "Me" refers to a methyl (CH_3 -) substituent. Distances and angles involving

methyls will be labeled using “Me1” through “Me5”, with the understanding that these refer to the distances and angles involving the location of the carbon of the methyl group. Two halogen substitutions will also be examined in this study: difluoro(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-borane (**5**) and dichloro(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-borane (**6**).

This study will also examine fluorobis(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-borane (**7**). This molecule contains two cyclopentadienyl units; the atoms of one unit will arbitrarily be chosen to have the labels described above, the other will have primed labels (C1', H1', etc).

Distances and angles will be named in accordance with the standard conventions used by Spartan. The distance between two atoms will be named by designating labels of the two atoms (i.e. distance C1-C2 will designate the distance between these two atoms). Angles will be designated by listing the three atoms involved, with the second atom listed referring to the atom at the vertex of the angle (i.e. angle B-C1-C2 will refer to the angle between the line containing B and C1 and the line containing C1 and C2). Note that angles defined by this convention will range from 0 degrees to 180 degrees.

Dihedral angles will also be named in accordance with the standard convention used by Spartan. They will be designated by listing the four atoms involved. The second and third atoms listed define an axis. If all atoms are projected onto a plane which contains atom three and which is normal to that axis, the dihedral angle is the angle from the projection of the line containing atoms one and two to the projection of the line containing atoms three and four. If this plane is viewed from the position of atom two, a

positive dihedral angle is defined by a clockwise rotation from the projection of the atom one - atom two line to the projection of the atom three - atom four line. Note that dihedral angles can be positive, negative, or zero. Note also that if three of these four atoms are co-linear, the dihedral angle will be undefined.

In addition to measuring and comparing the distances and angles of molecules, a simple test will be used to compare molecules. In this study, two geometries will be described as "essentially identical" when they can be displayed superimposed using Spartan without any visible differences between the bonds.

The symbol η will be used to describe the hapticity of the binding of a substituent. One source defines this term as the number of ligand atoms within bonding distance of a particular atom [111]. Unfortunately, in order to apply this definition, the absolute limit of the binding distance must be known. This difficulty has been noted by other authors [21,39]. To avoid the difficulties associated with defining this limit, hapticity will here be defined in terms of the location of the boron atom relative to the location of the five carbons of the ring. This description is intended to provide a convenient qualitative description of the geometries of these molecules.

The following particular conformation descriptions will be used for the purpose of this study:

" η^1 ": This description refers to a conformation in which the boron atom is located within the plane bisecting the ring, and is closer to one carbon than to any centroid. (A "centroid" here is defined as a location in space defined by averaging

the location of two or more carbon atoms).

" η^2 ": This description refers to a conformation in which the boron atom is located over the midpoint (two-atom centroid) of two neighboring carbons. Implied in this definition is that the B-C1 distance equals the B-C2 distance, and that the molecule does not otherwise fit the definition of η^4 or η^5 .

" η^3 ": This description refers to a conformation in which the boron atom is located over the centroid defined by three neighboring ring carbons. The distance from the boron atom to the centroid is smaller than the distance from boron to any particular carbon. For the purposes of this study, it will be sufficient to note that if the sum of angles B-C1-C2 and B-C1-C5 is greater than 180 degrees, the molecule is definitely not η^3 . A more exact definition is not required for this study.

" η^4 ": This description refers to a conformation in which the boron atom is located over the centroid defined by four neighboring ring carbons. The distance from the boron atom to this centroid is shorter than the distance from boron to any particular ring carbon. The distance from boron to this centroid is also shorter than the distance from boron to the centroid of any two or three neighboring ring carbons. Previous studies have not required extensive use of this term [14].

" η^5 ": This description refers to a conformation in which all B-C distances are the same. The boron atom is located along the center axis of the ring. This definition implies that the boron atom is closer to the centroid of the five ring carbons than

to any particular carbon atom on the ring.

Each one of these descriptions implies constraints on the symmetry of the molecule it describes; however, it is possible that in some molecules this symmetry may be distorted. Consider, for example, a sandwich compound involving a metal atom bound to *t*-butylcyclopentadiene. It would be reasonable to assume that, although the metal atom might be located approximately over the five-carbon centroid, not all B-C distances will be the same. Since the ligand is asymmetrical, it may be assumed that steric forces (for example) may cause the metal atom to be located asymmetrically. Arguably, this asymmetry would be lost if the cyclopentadienyl substituent were again made symmetrical. This same asymmetry may possibly be seen in an otherwise symmetrical compound in the solid state; crystal packing forces may distort symmetry.

It is also possible that loss of symmetry may arise fundamentally from the bonding of the boron atom to the ring, rather than out of any steric forces distorting the otherwise symmetric bonding of the boron atom to the molecule. Such asymmetrical bonding has for other molecules been implied by the use of the prefix “ $\eta^{1.5}$ ” [39]. This term has been used to imply a bonding that is between η^1 and η^2 ; possibly also to imply a ligand-metal interaction involving exactly three electrons. Arguably, this nomenclature implies an unwarranted degree of precision (e.g. $\eta^{1.5}$ as opposed to $\eta^{1.4}$ or $\eta^{1.6}$); for this reason this term will be avoided here. Instead, “*abgekippt*”, a term previously applied to one of these molecules by Jutzi, et. al., will be used [2]. This term was apparently coined to describe the geometry of $(C_5Me_5)_2BF$, which appeared to be “toppled over”

(approximate English translation.)

An *abgekippt* conformation will here be defined as a conformation in which the boron atom is located closer to one carbon than to any centroid, but is not located within the plane bisecting the ring. This asymmetry appears in the gas phase with a symmetric (cyclopentadienyl or pentamethylcyclopentadienyl) ring substituent. Furthermore, the substitution of methyl for hydrogens on the cyclopentadienyl ring will not dramatically increase the relative degree of asymmetry (as would be expected if steric interactions were responsible for the asymmetry).

The term “optimize” will be reserved exclusively to refer to the unconstrained process of finding the lowest energy conformation of a molecule, as described in each program’s users manual. If there is a constraint on the optimization process, a prefix will be added to the word “optimize” in order to contrast it with unconstrained optimization. For example, the term “ η^2 -optimize” will designate that the process of optimization was constrained to maintain an η^2 geometry at all times.

The descriptive labels η^1 - η^5 are here assigned only on the basis of the location of the boron atom and five carbon atoms; these conformations can be further subdivided in terms of the orientation of the two substituents on the boron atom. For consistency, this study will use the terms first used in Schoeller's paper [1]. If the substituents are oriented within the plane bisecting the ring, the geometry will be designated the “inversion” conformation. If the substituents are oriented symmetrically away from this plane, the geometry can be designated as the “retention” conformation.

The use of the terms "retention" and "inversion" to describe conformations appears to be used ambiguously in Schoeller's paper [1]. Moreover, one could argue that there is an inherent ambiguity to these terms since they refer to the molecular orbitals of fragments of molecules (which cannot be observed experimentally). The standard 1,5-sigmatropic rearrangement mechanism is predicted to occur with retention of configuration (i.e. from a "retention" equilibrium geometry through a "retention" transition state geometry) since the orbitals involved in the transition do not change sign [4]; however, an alternative prediction might be possible with a BH_2 substituent. Predictions of this type are ultimately verified in terms of the relative motion of nuclei within a molecule (which can be more easily observed experimentally). In order to describe what is experimentally observable, mechanisms in this study will be discussed here exclusively in terms of the motion of nuclei. However, the terms "retention" and "inversion" will be retained as a convenient label for these geometries.

The conformations of pentamethylcyclopentadienylboranes can also be subdivided on the basis of the relative orientation of the methyls. A complete analysis of the effect of methyl orientation on the energy of these molecules is outside the scope of this research. However, consideration of the orientations of the methyls is needed in order to assure that the energy of the optimized molecules accurately represents the actual equilibrium geometry of the molecule, rather than a local minimum with a higher energy due to a locked methyl orientation. Also, in order to make comparisons between different molecules, the methyl orientations should at least be qualitatively similar. Some effort here will be made to identify the optimized orientations seen in these molecules.

For brevity, an abbreviated means of describing these orientations is here adopted. A complete set of labels for every possible orientation is not needed here, four labels will be sufficient to facilitate discussion of the results seen in this study. A conformation will be named an “audience” conformation (see Figure 5) if Me1 has a hydrogen that is

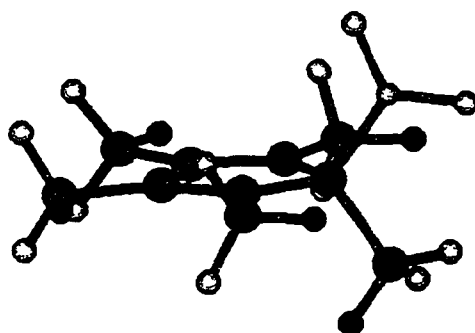


Figure 5
“Audience” conformation
(axial and planar hydrogens identified in black)

oriented downward approximately perpendicular to the plane of the ring, and all other methyls have a hydrogen oriented in the plane of the ring and facing C1. A conformation that has the same orientation of Me1, Me3, and Me4 but has Me2 and Me5 rotated 180 degrees will be named a “chat” conformation (See Figure 6). A conformation will be named an “archive” conformation (see Figure 7) if Me1 and Me2 each have one hydrogen that is oriented downward approximately perpendicular to the plane of the ring, Me3 and Me5 each have a hydrogen oriented in the plane of the ring pointing away from C4, and

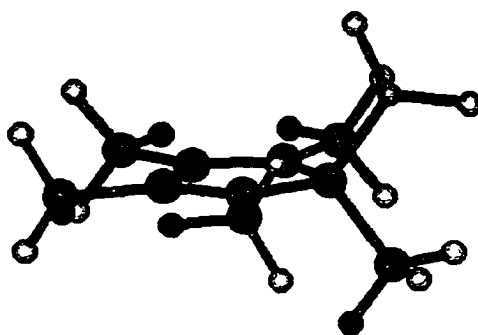


Figure 6
“Chat” conformation
(axial and planar hydrogens identified in black)

Me4 has one hydrogen oriented upward approximately perpendicular to the plane of the ring. Finally, a conformation will be named a “fence and gate” conformation (see Figure

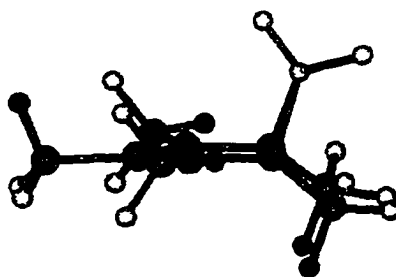


Figure 7
“Archive” conformation
(axial and planar hydrogens identified in black)

8) if all methyl groups have one hydrogen oriented approximately axially, with the axial hydrogen of Me4 pointing upward and all others pointing downward. These four labels are not intended to provide exact definitions of the conformations of each molecule.

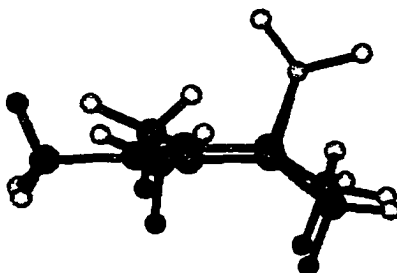


Figure 8
“Fence and Gate” conformation
(axial and planar hydrogens identified in black)

Rather, these labels are intended as starting points for further discussion of the optimized conformation; distortions away from these descriptions will be noted.

Methodology

Three commercially available quantum chemistry software packages were used in this study: HyperChem [112], Spartan [113], and Gaussian [114]. All three can be used to construct molecules (i.e. define a set of Cartesian coordinates and accompanying atomic numbers, along with the number and spin of accompanying electrons), to optimize these molecules, and to calculate observable quantities associated with these molecules. Unless otherwise specified, the standard procedures were used for each program.

The following computers were used for this study. Spartan 5.0 was run on an SGI O2 workstation at MTSU [115]. Gaussian 94W and HyperChem 4.5 were run primarily on a 233MHz Pentium PC at MTSU with 128 MB RAM, and 4 GB available disk space.

Other PC's were also used at MTSU and Bryan College. For certain molecules, Gaussian 98 was also run on the NCSA HP Exemplar Array at the University of Illinois [116].

Each initial molecule was built using the "build molecule" function of HyperChem or Spartan. Both programs feature a "Build" function that allows users to construct 3D molecules from 2D sketches on screen. Both add hydrogens automatically. Both programs were tested by drawing and building cyclopentadiene several times; the same starting point 3D geometry was produced repeatedly.

To constrain a dihedral angle using HyperChem the following non-standard procedure was employed. The select tool was used to select atoms H7, B, C1, H1 (or the equivalent atoms in molecules other than $C_5H_5BH_2$.) The "Name Selection" function was used to assign this dihedral angle a name. The "Restrains" function was then used to assign a restrained value of this named dihedral to 0.0 degrees; the force constant was assigned the non-default value equal to 1000 kilocalories per mole per Ångstrom. Default values were used for all other parameters. The molecule was then optimized while maintaining the desired geometry. Once optimized, the restraint was removed in order to calculate the single point energy.

When using HyperChem, the following procedure was employed to η^2 -optimize a geometry (i.e. to optimize a molecule with η^2 geometry). The atoms B and C2 were selected and named, then the atoms B and C1 were named. Both named selections were restrained to the same value, and the force constant of each was assigned the non-default value equal to 10000 kilocalories per mole per Ångstrom. The molecule was then

optimized, the restraints were then removed, and the single point energy was calculated. The B-C distance was subsequently varied until a minimum energy was observed.

When using Gaussian 94W or 98, an alternative procedure was used to η^2 -optimize a geometry. A Z-matrix was constructed for this molecule that specified both the distance B-C1 and distance B-C2 by the same variable name ("RBC1"). Values for the other distances, angles, and dihedral angles were measured using previously built molecules. These molecules were then optimized with Gaussian 94W or 98 using the "Opt=z-matrix" or the "popt" keyword to assure that the B-C1 distance remained equal to the B-C2 distance as all other parameters optimize. Cartesian coordinates generated in the output file from Gaussian 94W or 98 were exported to HyperChem formatted files, and geometric measurements were made using HyperChem.

Alternative starting geometries (including η^3 , η^4 , and η^5 geometries) were generated, and optimized with or without constraints. Standard procedures using Spartan 5.0 were used to optimize these molecules. The results were then compared to those previously generated to determine if other local minima were available to this molecule.

Unless otherwise specified, the RMP2 calculations used a frozen core approximation without effective core potentials. When effective core potentials are used, the pseudopotential "LANL2" as defined by Gaussian 94W or 98, was employed. Pseudopotentials have been shown to produce surprisingly accurate results [117].

Vibrational frequency calculations were performed using either Gaussian 94W or 98 or Spartan 5.0. The zero-point vibrational energy correction for the equilibrium and

transition state energy was calculated for (5-6), in order to obtain an accurate prediction for the activation energies. All activation energy measurements were converted from atomic units to kcal/mole.

Molecular orbitals and electron density were examined using Spartan 5.0. In particular, the electron density was examined in order to identify the bond critical points of the molecule. The bond critical point is the point between atoms where the electron density reaches a minimum on a line connecting two atoms, and is at a maximum along the directions perpendicular to that line. (For a discussion of bond critical points, other topological features of the electron density scalar field, and in general of the theory of atoms in molecules, see reference 118). The electron density was mapped using Spartan 5.0 to attempt to qualitatively characterize the bond critical point or points present between the boron atom and the two adjacent carbons as this reaction proceeds [22]. All figures displaying molecular geometry were made using HyperChem 4.5, and all figures displaying molecular orbitals and electron densities were made using Spartan 5.0.

X-ray crystallographic data obtained from a previous reference [2] for $(C_5Me_5)_2BF$ were converted to Cartesian coordinates, and then imported into HyperChem, which was used to measure distances and angles.

Assumptions and Limitations

In addition to the standard assumptions of quantum mechanics discussed in Chapter 1 in the discussion of *ab initio* molecular orbital theory, this study also assumes that programs such as Gaussian, HyperChem, and Spartan are able to accurately calculate

and optimize MNDO, RHF, and RMP2 energies for the molecules of interest.

Furthermore, this study assumes that a finite set of carefully selected starting geometries are sufficient to obtain the global minimum geometry for these molecules. This is particularly problematic for the pentamethylcyclopentadienyl derivatives. A limited attempt was made to determine if different starting geometries of the different methyl groups would produce local minima with significantly different energies, or instead if they would all optimize to the same global minimum geometry. All possible geometries, however, were not examined. It is therefore possible that the optimized geometries for the pentamethylcyclopentadienyl derivatives may not represent the true global minima.

Certain assumptions needed to be made when comparing these results with previously published empirical data. Primarily, it was assumed that the published data were accurate. A critique of these experimental methods is outside the scope of this study. Additionally, it was assumed that the experimental conditions would not significantly affect these calculations; that solid-phase crystallographic data for $(C_5Me_5)_2BF$ were indeed comparable with gas-phase calculations for the same molecule, and that liquid phase measurements of the activation energy of $C_5Me_5BF_2$ and $C_5Me_5BCl_2$ in toluene were indeed comparable with gas-phase calculations for the same molecules. There is some evidence that rearrangements of this type are comparatively insensitive to solvent effects [50].

Chapter 3

Results and Discussion

Overview

In this chapter, the results of optimizations and analyses of cyclopentadienylborane (**1**) (the parent molecule for this class of molecules) are first discussed. This molecule has not been synthesized or observed, so no empirical data is available for this molecule for comparison with theoretical predictions. However, the results obtained here are used for comparison with other molecules of this class for which there are empirical data. This molecule is examined more closely than the various substituted cyclopentadienes, since as the smallest molecule of this class its calculations are simplest and the least expensive. Several angle and distance scans are examined for this molecule to explore constraints on structure.

The effect of substitutions on the geometry of cyclopentadienylborane is next examined. The effects of three different single type substitutions are examined: BF_2 in place of BH_2 , BCl_2 in place of BH_2 , and pentamethylcyclopentadienyl in place of cyclopentadienyl. For each, the effects on the geometry and the relative energy of the equilibrium and transition state geometries are examined.

Finally, the effects of more than one type of substitution on the energy and geometry of cyclopentadienylborane are examined. Specifically, three molecules are examined: $\text{C}_5\text{Me}_5\text{BF}_2$ (**5**), $\text{C}_5\text{Me}_5\text{BCl}_2$ (**6**), and $(\text{C}_5\text{Me}_5)_2\text{BF}$ (**7**). These three molecules have been synthesized, and some empirical data are available for each [2].

Semi-Empirical and *Ab Initio* Studies of Unsubstituted Cyclopentadienylborane

MNDO Calculations for $C_5H_5BH_2$

HyperChem was used to construct a cyclopentadienylborane molecule having the starting geometry shown in Figure 9a. This molecule was optimized using MNDO to the η^1 -retention conformation shown in Figure 9b. A molecule constrained to η^1 -inversion geometry was then constructed using HyperChem. This molecule was then optimized to produce the structure shown in Figure 9c. The optimized geometry of both

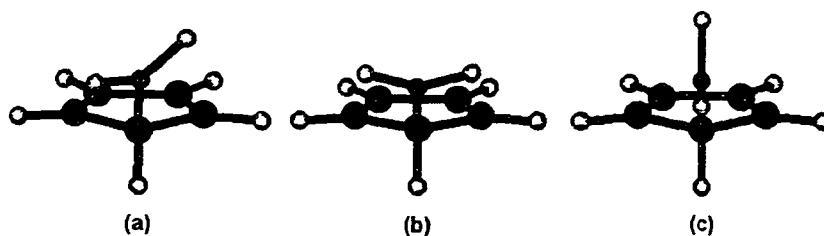


Figure 9
Geometry of $C_5H_5BH_2$
(a) HyperChem-generated starting point geometry,
(b) optimized using MNDO, (c) optimized using MNDO,
while restraining the H-B-C-H dihedral angle to zero degrees.

conformations matched the data published by Schoeller to within ± 0.005 Å and ± 0.1 degrees. As previously reported, the η^1 -retention conformation was lower in energy than the η^1 -inversion conformation. The difference in energy obtained here was 0.75 kcal/mole, compared to 0.70 kcal/mole reported previously by Schoeller [1].

Schoeller performed his optimization assuming C_s symmetry. However, no

symmetry constraints were used here. To confirm that the optimized molecule corresponded to a symmetrical conformation, the molecule was re-optimized with dihedral angles restrained to values ranging from 0 degrees to 90 degrees (in ten degree increments). These values descended from a maximum at 0 degrees down to a minimum at 88.1 degrees (the dihedral angle seen for the molecule in Figure 9b). The MNDO calculations performed using HyperChem were able to reproduce Schoeller's results exactly [1]. The equilibrium geometry for this molecule, as predicted by MNDO, was concluded to be the η^1 -retention conformation.

An η^2 -constrained cyclopentadienylborane molecule was built, with the B-C1 and B-C2 distances constrained to 2.0 Å and optimized using MNDO. This process was repeated for various boron-carbon distances until a minimum energy was found at a boron-carbon distance equal to 1.667 Å (± 0.001 Å). Data published by Schoeller for the η^2 -transition state for the 1,5-sigmatropic rearrangement [1] matched the data obtained here within ± 0.005 Å and ± 0.1 degrees. When the constraints were removed, this molecule optimized back to a geometry essentially identical to that seen in Figure 9b. A summary of the MNDO results of this study compared with the MNDO results published by Schoeller is presented in Table 1.

RHF/3-21G* Calculations for $C_5H_5BH_2$

A Z-matrix was constructed using parameters taken from the MNDO optimized C_5 -symmetric conformations of $C_5H_5BH_2$ discussed previously. These geometries are shown in Figures 10a and 11a, respectively. Both starting point geometries were

optimized at the RHF/3-21G* level with Gaussian 94W. The results are shown in Figures 10b and 11b. The conformation shown in Figure 10b is lower in energy (-216.82471 Hartrees) than the conformation shown in Figure 11b (-216.82149 Hartrees). This is

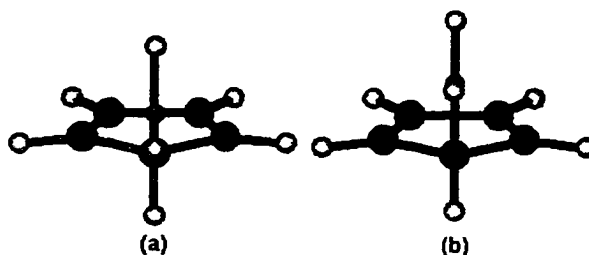


Figure 10
Geometry of $C_5H_5BH_2$ (η^1 -inversion)
(a) optimized using MNDO (starting point for *ab initio* optimization), (b) optimized at the RHF/3-21G* level.

opposite the results obtained using MNDO. As seen in these Figures, the primary effect of optimization at the RHF/3-21G* level is the shifting of the boron atom up and away from the plane of the ring, relative to its position when optimized using MNDO.

Frequency analysis of the molecules in Figures 10b and 11b each showed one imaginary frequency. The frequencies of the imaginary modes for the molecules shown in Figures 10b and 11b were reported to be -164.54 cm^{-1} and -92.52 cm^{-1} , respectively. Animation of these modes shows motion of the boron atom away from the plane bisecting the ring. Since both have imaginary frequency modes, neither of these conformations represent a true local minimum, both of these geometries represent

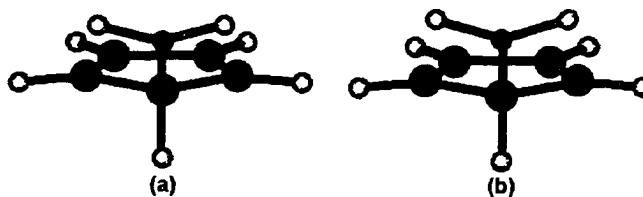


Figure 11
Geometry of $C_5H_5BH_2$ (η^1 -retention)
(a) optimized using MNDO (starting point for *ab initio* optimization), (b) optimized at the RHF/3-21G* level.

saddlepoint geometries rather than local minima. In neither case was there any constraints specified in the Gaussian job.

Other starting point geometries of this molecule were optimized at the RHF/3-21G* level (using Gaussian 94W and Spartan 5.0). The starting points and resultant geometries are shown in Figure 12. Each of these refined to a geometry essentially identical to that shown in Figure 12a or to its mirror image. The energy of this *abgekippt* conformation is lower than those listed in Figures 10 and 11. Notably, attempts to further refine the molecules shown in Figures 10b and 11b resulted in this geometry as well. Some of these molecules were optimized using Spartan 5.0 and some were optimized using Gaussian 94W. All optimized molecules were essentially identical nonetheless. The average of all of the reported energies of all of these optimized molecules was -216.8254672 Hartrees. The standard deviation was 0.0000038 Hartrees. This geometry was therefore reproducible, and had an energy (to eight significant figures) equal to -216.82547 Hartrees. A summary of the *ab initio* predicted energies for this and all other molecules examined in this study is presented in Table 2. Frequency analysis confirmed

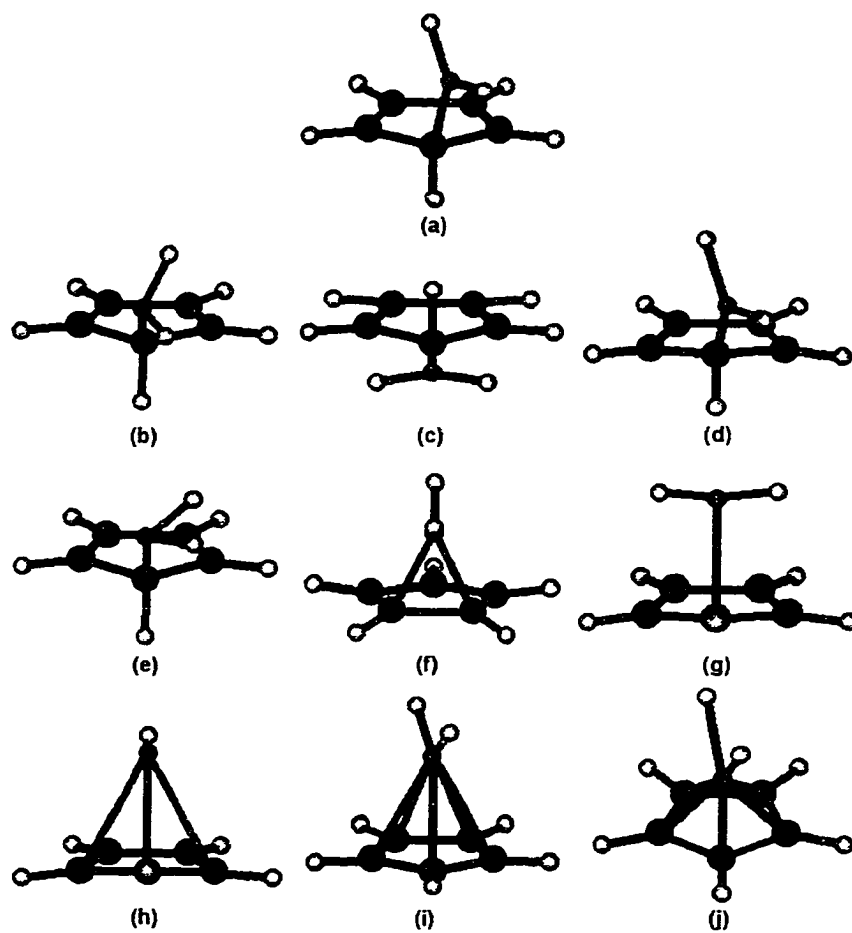


Figure 12
Geometries of $C_5H_5BH_2$
(a) optimized at the RHF/3-21G* level (*abgekippt*),
(b-j) various starting points used to generate the
optimized geometry shown in (a).

that this conformation represents a local minimum (lowest vibrational frequency = 151.49 cm^{-1}). Animation of this mode showed motion of the boron atom in the approximate direction of C2. The molecule shown in Figure 12a was re-optimized using MNDO with Spartan 5.0. The resulting molecule had a geometry that was essentially identical to the η^1 -retention configuration shown in Figure 9b.

Some bond distances and angles for *abgekippt* $\text{C}_5\text{H}_5\text{BH}_2$ (Figure 12a) are given in Table 3. The two H-B-C-H dihedral angles are -158.6 and 24.9 degrees. The hydrogens are therefore asymmetrically placed relative to the rest of the molecule. Additionally, the boron atom is shifted to an asymmetrical location relative to the ring. The distances from the boron atom to the nearest neighboring carbons C2 and C5 are 2.323 Å and 2.546 Å, respectively. The carbon-carbon bond distances of the ring are also asymmetrical. The two distances from C1 to its two neighboring carbons C2 and C5 are 1.527 and 1.502 Å, respectively.

An attempt was made to find a stable η^3 geometry for $\text{C}_5\text{H}_5\text{BH}_2$. Spartan was

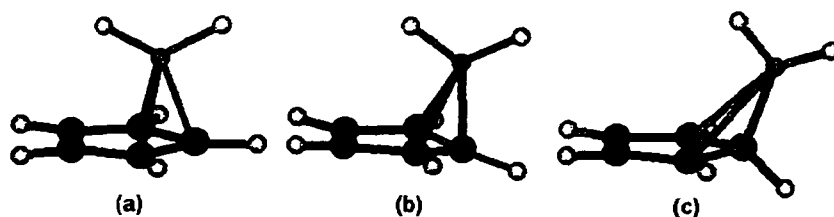


Figure 13
Geometry of $\text{C}_5\text{H}_5\text{BH}_2$ (initial η^3 conformation). (a) starting geometry, (b) optimized at the RHF/3-21G* level, while constraining C_5 symmetry and constraining bond distances $\text{B-C2} = \text{B-C5} = 2.0285$, (c) RHF/3-21G* optimized, without constraints. Although B-C2 and B-C5 links are shown, the B-C2 and B-C5 distances for (c) are identical to those unbonded distances shown in Figure 12a.

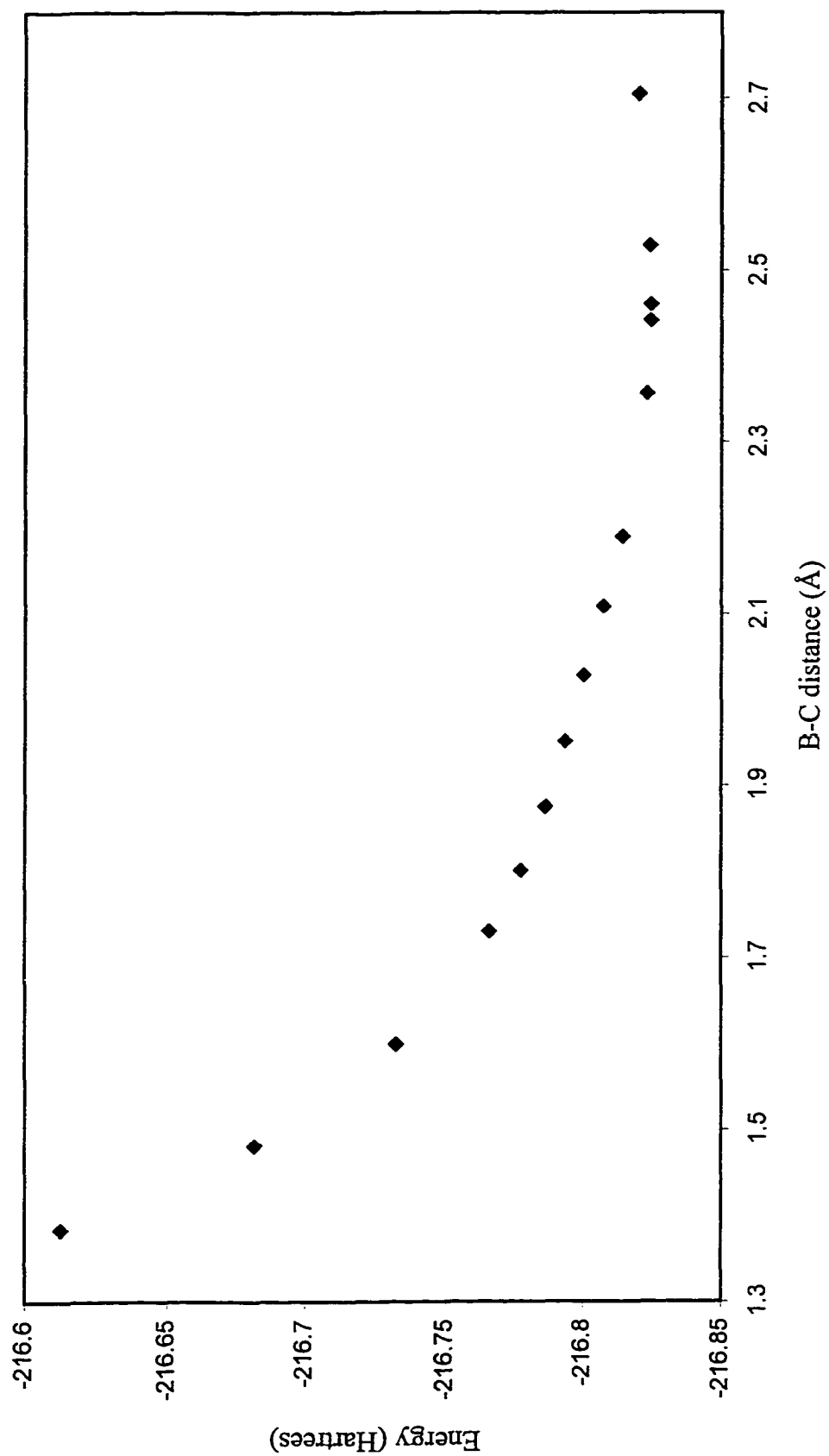


Figure 14
Energy (RHF/3-21G*) vs B-C2
(=B-C5) distance for η^3 -optimized $C_5H_5BH_2$

used to produce a planar cyclopentadienide ring. A ligand point was then defined as the centroid of carbons 1, 2, and 5. A BH_2 substituent was then added above this point. The resulting starting point geometry is shown in Figure 13a. Both the B-C2 distance and the B-C5 distance were constrained to the same value, and the molecule was optimized at the RHF/3-21G* level while maintaining symmetry. This η^3 -optimized molecule is shown in Figure 13b. This process was repeated for several different constrained values of the boron-carbon distance. A plot of the η^3 -optimized energy vs. the B-C2 distance is shown in Figure 14. Note that the lowest energy is seen at a B-C2 distance of 2.461 Å. This corresponds to the value found for the η^1 molecule shown in Figure 10b. Since there are no other minima on this graph, no local minimum η^3 geometry is seen for this molecule using this method.

A frequency analysis was performed on one of these molecules (B-C = 2.028 Å). Two imaginary frequencies (reported as -314.82 cm^{-1} and -156.01 cm^{-1}) were found. Animation of both of these imaginary modes showed motion of the boron atom approximately parallel to the plane of the ring. This conformation therefore represents a second-order saddle point rather than a local minimum. This geometry was then re-optimized, without any distance or symmetry constraints, using a maximum step size 1/10th the Spartan default value. The resulting geometry, shown in Figure 13c, is essentially identical to that of the molecule shown in Figure 12a.

An attempt was also made to find a stable η^5 geometry for this molecule. Spartan was used to produce a cyclopentadienyl ring with an η^5 bound BH_2 substituent, as shown in Figure 15a. The five boron-carbon distances were constrained to the same value, and

the molecule was optimized with no constraints on symmetry. The resulting geometry is shown in Figure 15b. This process was repeated for several different boron-carbon distances. A graph of the optimized energy vs. the boron-carbon distance is shown in Figure 16. The minimum energy is at a boron-carbon distance of approximately 1.9 Å. Frequency analysis of this molecule showed three imaginary frequencies (reported as -670.51, -329.72, and -287.99 cm^{-1}). Animation of these modes showed motion of the boron atom approximately parallel to the ring. This molecule was then optimized without constraints (with an optimization step size set to 1/10th of the default value). It optimized to an *abgekippt* geometry essentially identical to that of the molecule shown Figure 12a. Therefore, no local minimum η^5 geometry is seen for this molecule at this level of theory.

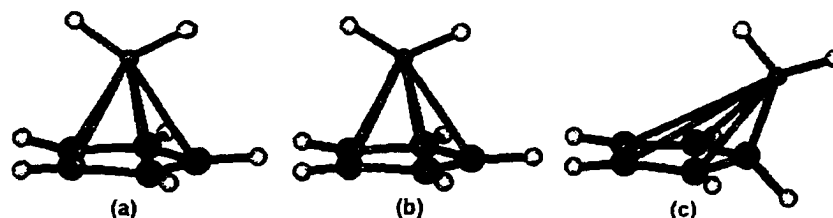


Figure 15

Geometry of $\text{C}_5\text{H}_5\text{BH}_2$

(a) starting point, with all five BC distances set equal, (b) optimized at the RHF/3-21G* level, constraining all five B-C bond distances, (c) optimized at the RHF/3-21G* level, without constraints. Although five B-C links are shown, all B-C distances for Figure 15c are identical to distances shown in Figure 12a.

An attempt was made to find a stable η^2 geometry for this molecule. Parameters for the η^2 Z-matrix were taken from the η^2 -optimized molecule previously obtained using

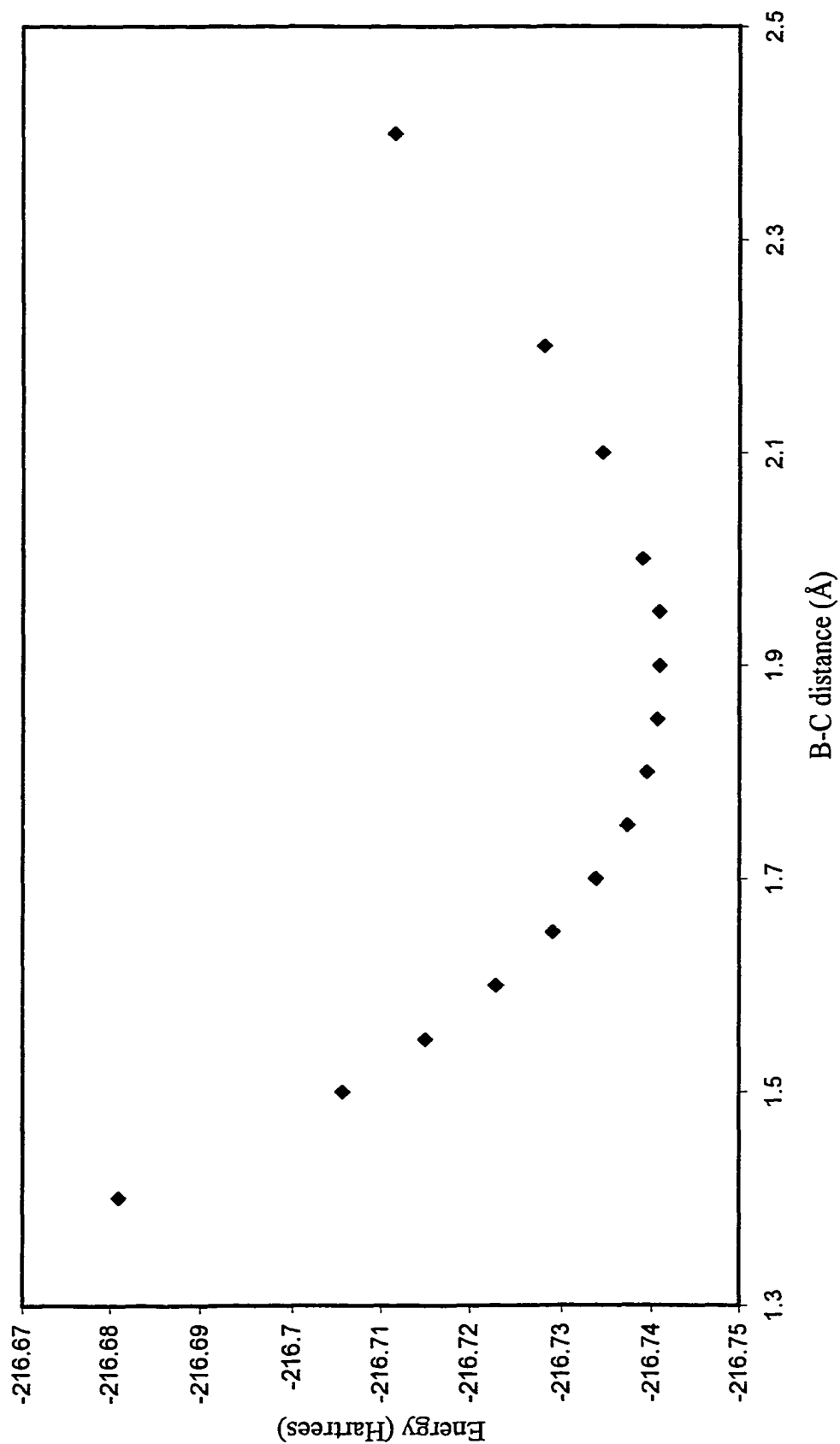


Figure 16
Energy (RHF/3-21G*) vs. boron-carbon
distance for η^5 -optimized $C_5H_5BH_2$

MNDO shown in Figure 17a. This molecule was then η^2 -optimized using Gaussian 94W. The resulting geometry is shown in Figure 17b. A summary of selected distances and angles for the molecule is presented in Table 4. Frequency calculation yielded one imaginary frequency (reported by Gaussian 94W as -438.35 cm^{-1}). This molecule was then re-optimized without any constraints. The resulting geometry was essentially identical to the *abgekippt* geometry exhibited by the molecule shown in Figure 12a.

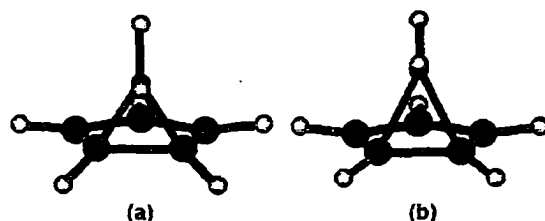


Figure 17
Geometry of $\text{C}_5\text{H}_5\text{BH}_2$ (η^2 -constrained)
(a) η^2 -optimized using MNDO (starting point for further optimization), (b) η^2 -optimized at the RHF/3-21G* level.

A scan of the optimized energy versus the B-C2 distance was performed next. A new Z-matrix was constructed, assigning the B-C1 distance as a variable and holding the B-C2 distance constant. Parameters from the previously η^2 -optimized molecule were added to this new Z-matrix, and the molecule was re-optimized while holding the B-C2 distance constant. This process was repeated for B-C2 distances ranging from 1.783 Å (the distance in the η^2 -optimized molecule) to 2.38 Å. The maximum (-216.81424 Hartrees) is at the distance found in the η^2 -optimized molecule. The minimum (-216.82547 Hartrees) is at 2.323 Å, the B-C2 distance in the *abgekippt* molecule.

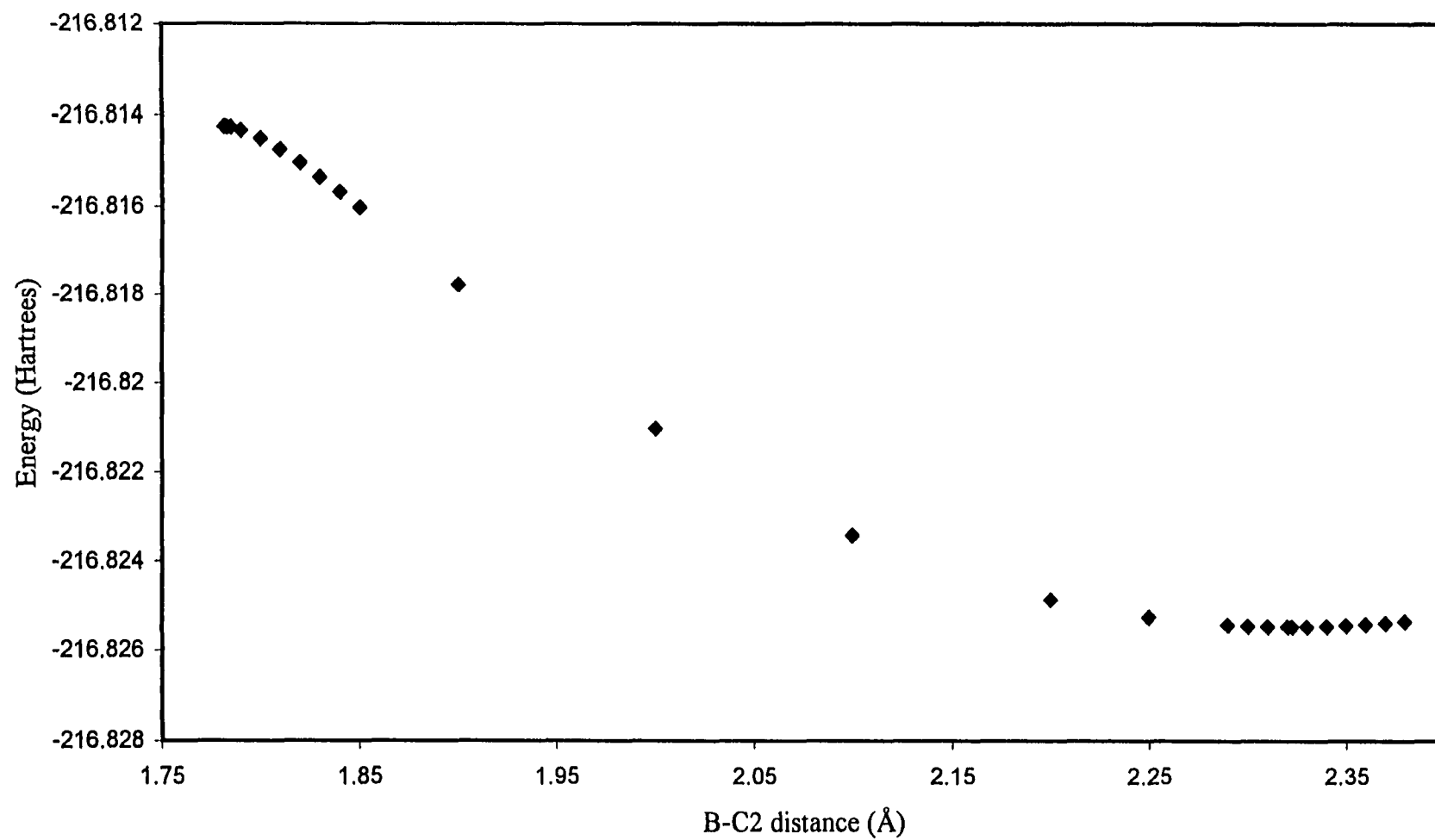


Figure 18
Energy (RHF/3-21G*) vs. constrained
B-C2 distance for η^2 -optimized $C_5H_5BH_2$

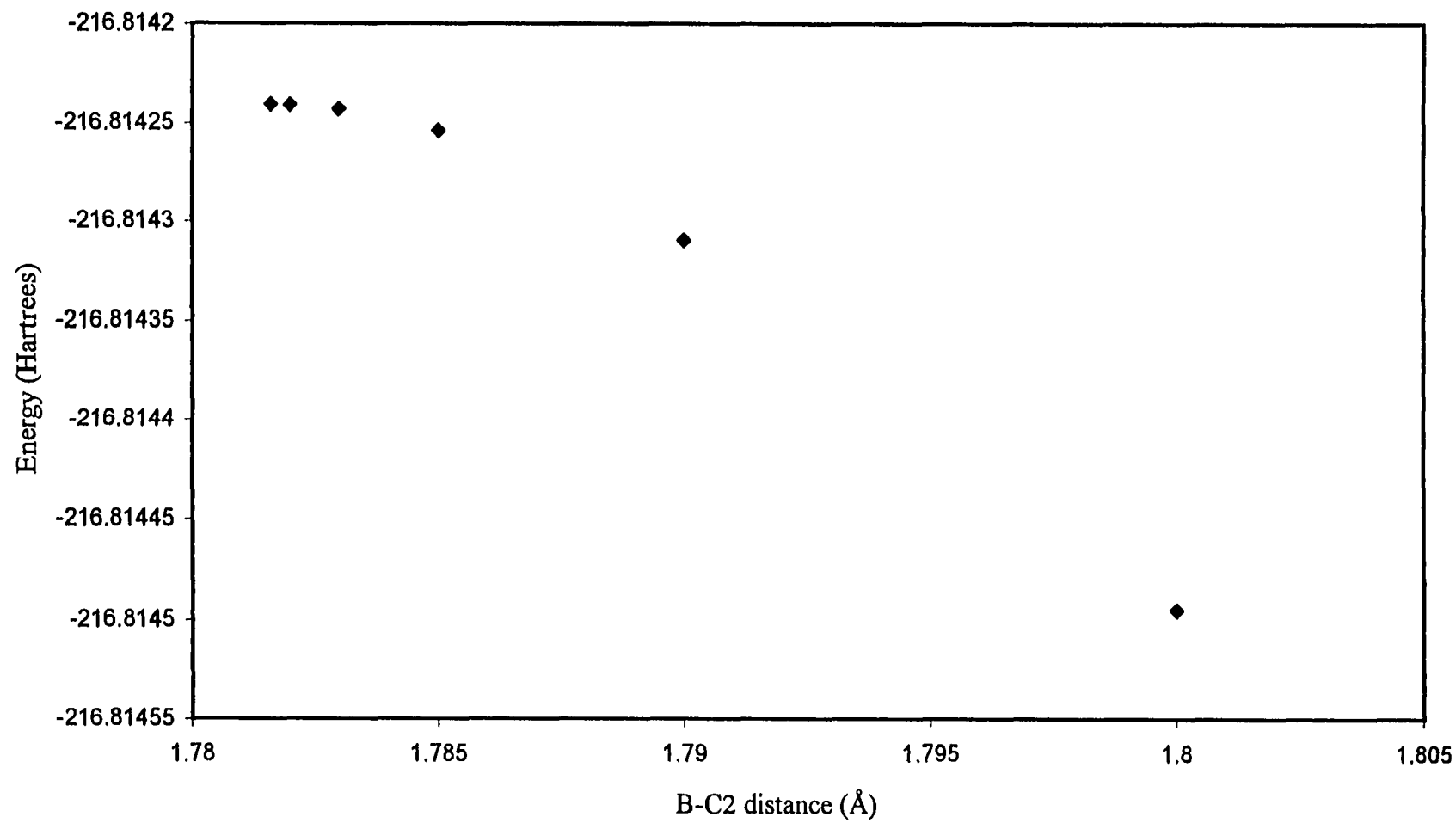


Figure 19
Energy (RHF/3-21G*) vs. constrained B-C2 distance
for η^2 -optimized $C_5H_5BH_2$ (expanded to show detail)

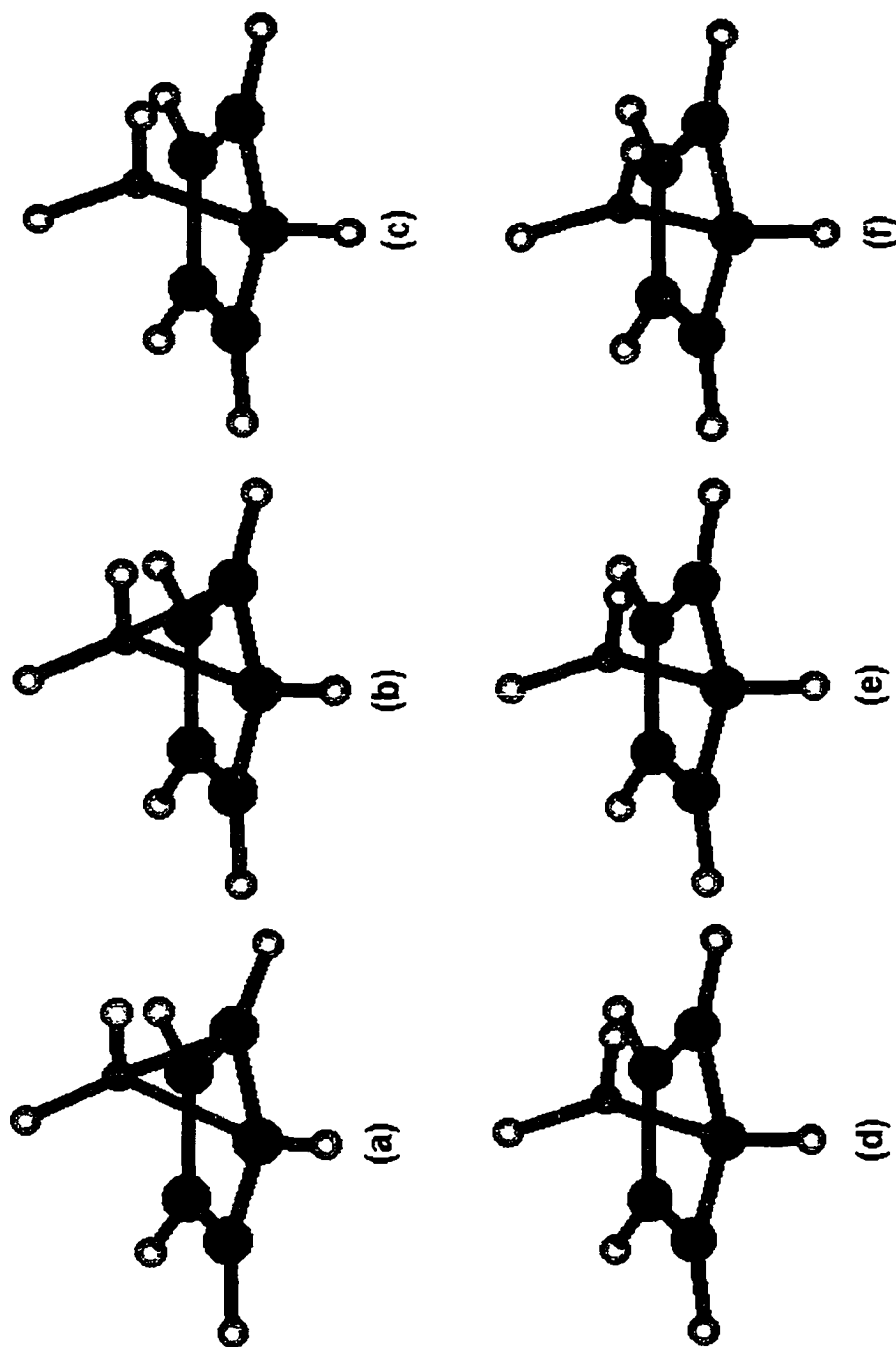


Figure 20
Geometry of $C_5H_5BH_2$
Optimized at the RHF/3-21G* level with
B-C2 distance constrained to the following values:
(a) 1.8 Å, (b) 1.9 Å, (c) 2.0 Å, (d) 2.1 Å, (e) 2.2 Å, (f) 2.3 Å

A plot of the RHF/3-21G* energy of these molecules vs. the constrained B-C2 distance is shown in Figure 18. Figure 19 shows the data points from Figure 18 in the region around the maximum. The optimized geometries for various points on this graph are shown in Figure 20. The boron atom moves from its position in the η^2 geometry smoothly to its position in the *abgekippt* geometry, and the hydrogens move without exchanging positions. The B-C5 distance remained nearly constant for all these geometries. These results support a mechanism for the 1,5-sigmatropic rearrangement in which the two hydrogen atoms on boron do not exchange positions.

A scan of the energy vs. the H-B-C-H dihedral angle was also performed. A Z-matrix was constructed for the molecule shown in Figure 12a, but allowing the H7-B-C1-H1 dihedral angle to be constrained to a particular value. This molecule was optimized for different values for this dihedral angle. For each starting point, the H6-B-C1-H1 dihedral angle was allowed to vary, but was initially set to the H7-B-C1-H1 dihedral angle minus 180 degrees. The plot of these data is shown in Figure 21. The minimum at 24.9 degrees is the *abgekippt* geometry. The maxima at zero degrees and 88.1 degrees are the η^1 -retention geometry and the η^1 -inversion geometry, respectively.

Of all of these optimizations, the only ones that produced stable local minima were those that are essentially identical to Figure 12a. These results indicate that the equilibrium geometry of cyclopentadienylborane, as predicted at the RHF/3-21G* level, is an *abgekippt* conformation.

Three transition state geometries (first-order saddle points) were predicted at the RHF/3-21G* level. The η^2 geometry shown in Figure 17b represents the transition state

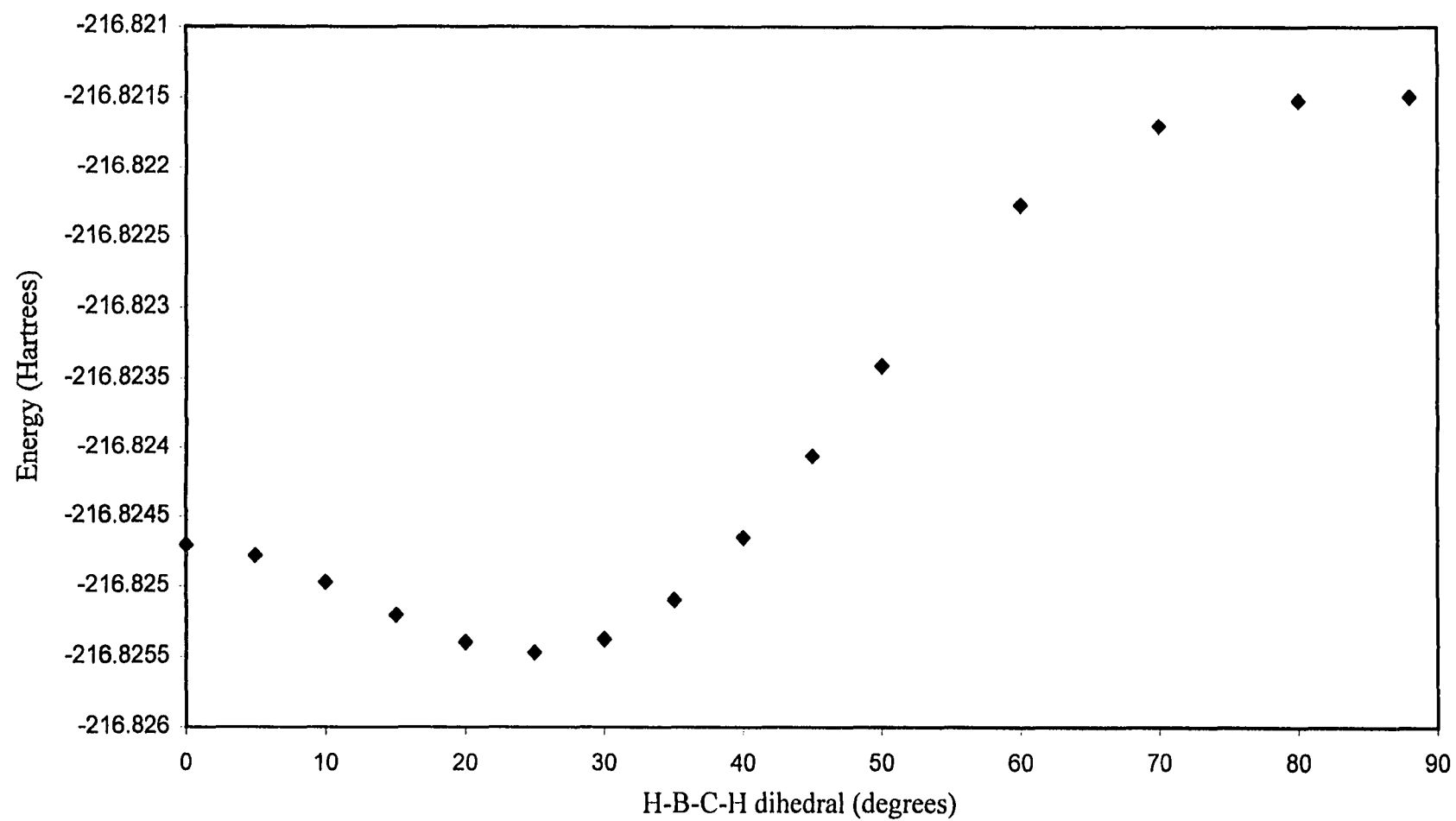


Figure 21
Energy (RHF/3-21G*) vs. constrained
H7-B-C1-H1 dihedral angle for otherwise optimized $C_5H_5BH_2$

for the 1,5-sigmatropic rearrangement of the BH_2 substituent from C1 to C2. This can be seen in the plot in Figure 18. The horizontal axis of this graph represents half of the expected reaction coordinate for this rearrangement. The curve is smooth from the minimum energy η^2 geometry to the maximum at the *abgekippt* geometry, with no other local minima seen along this pathway. This plot reveals an activation energy for the rearrangement of cyclopentadienylborane of 0.01123 Hartrees, or 7.045 kcal/mol (as predicted at the RHF/3-21G* level). This is lower than the 18.00 kcal/mole previously found using MNDO [1]. These energies were recalculated and corrected for zero-point energy. The zero-point energy of *abgekippt* $\text{C}_5\text{H}_5\text{BH}_2$ was calculated to be 0.11142 Hartrees, or 69.916 kcal/mole. The zero-point energy of η^2 -optimized $\text{C}_5\text{H}_5\text{BH}_2$ was calculated to be 0.11139 Hartrees, or 69.900 kcal/mole. The one imaginary frequency in the η^2 molecule was ignored when calculating this quantity. With these added zero-point energies, the activation energy predicted at the RHF/3-21G* level is 7.03 kcal/mole. A summary of these and other equilibrium and zero-point energies is presented in Table 2.

The η^1 symmetric geometry shown in Figure 10b represents another transition state. It is the saddle point in the rearrangement of the BH_2 substituent from the *abgekippt* position on C1 leaning toward C2 to the *abgekippt* position on C1 leaning toward C5. These two equilibrium geometries are degenerate and enantiomeric. Between them is a small but calculable activation energy of 0.00076 Hartrees, or 0.48 kcal/mol. This activation energy (not corrected for zero-point energy) can be seen in the plot in Figure 21 as the energy between the equilibrium geometry and the maximum with the H-B-C-H dihedral angle equal to 0.0 degrees.

Examination of the geometries shown in Figure 20 shows that at all points H6 remains oriented approximately axial to the ring, and H7 remains oriented equatorially. However, in an equilibrium geometry, it should be possible for the BH₂ substituent to rotate, exchanging positions between the H6 and H7. The transition state for this rearrangement is the η^1 -retention conformation shown in Figure 11b. The activation energy for this rearrangement can be seen in the plot in Figure 21 as the energy difference between the equilibrium geometry and the maximum at 88 degrees. The predicted barrier to rotation is therefore 0.00398 Hartrees or 2.50 kcal/mol. The η^3 and η^5 geometries were found to be significantly higher in energy and were not first order saddle points. It is therefore unlikely that the rearrangement of BH₂ in cyclopentadienylborane would proceed through an η^3 or η^5 geometry.

RHF/6-31G* Calculations for C₅H₅BH₂

The molecule previously optimized at the RHF/3-21G* level was re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 22b. Geometric parameters for this molecule are presented in Table 3. The overall geometry is similar to the geometry seen in the molecule optimized at the RHF/3-21G* level. Notable differences between these two geometries include the following: the C1-C2 bond distance is over 1% shorter at the RHF/6-31G* level, the boron atom is shifted closer to H1 (seen in the decrease in the B-H1 distance and the B-C1-H1 angle, and also the increase in the B-C2 and B-C5 distances and B-C1-C2 and B-C1-C5 angles), and the BH₂ substituent is

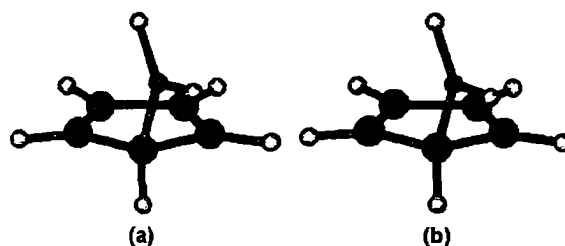


Figure 22
Geometry of $C_5H_5BH_2$
(a) optimized at the RHF/3-21G* level (starting point for
further optimization), (b) optimized at the RHF/6-31G* level.

rotated further away from the plane of symmetry (seen in the H-B-C-H dihedrals). The nine other starting points shown in Figure 12, when optimized at the RHF/6-31G* level, each resulted in either an *abgekippt* geometry or an η^1 -retention geometry. These two geometries represent possible local minima at this level of theory.

An attempt was made to produce a stable η^3 geometry, as was previously done at the RHF/3-21G* level. A plot of the energy vs. the constrained B-C2 (= B-C5) distances is shown in Figure 23. As with the equivalent plot at the RHF/3-21G* level, no evidence is seen for an η^3 local minimum. Frequency analysis of the η^3 -optimized geometry, with the B-C2 distance constrained to 2.028 Å, showed two imaginary frequencies. One imaginary frequency, reported at -319.12 cm^{-1} , showed motion of the boron atom away from the plane bisecting the ring. The other imaginary frequency, reported at -232.79 cm^{-1} , showed motion of the boron atom parallel to the plane of the ring within the bisecting plane. The lowest real frequency (at 480.68 cm^{-1}) also showed boron "bond wagging" motion (i.e. motion involving constant bond length). This geometry was re-

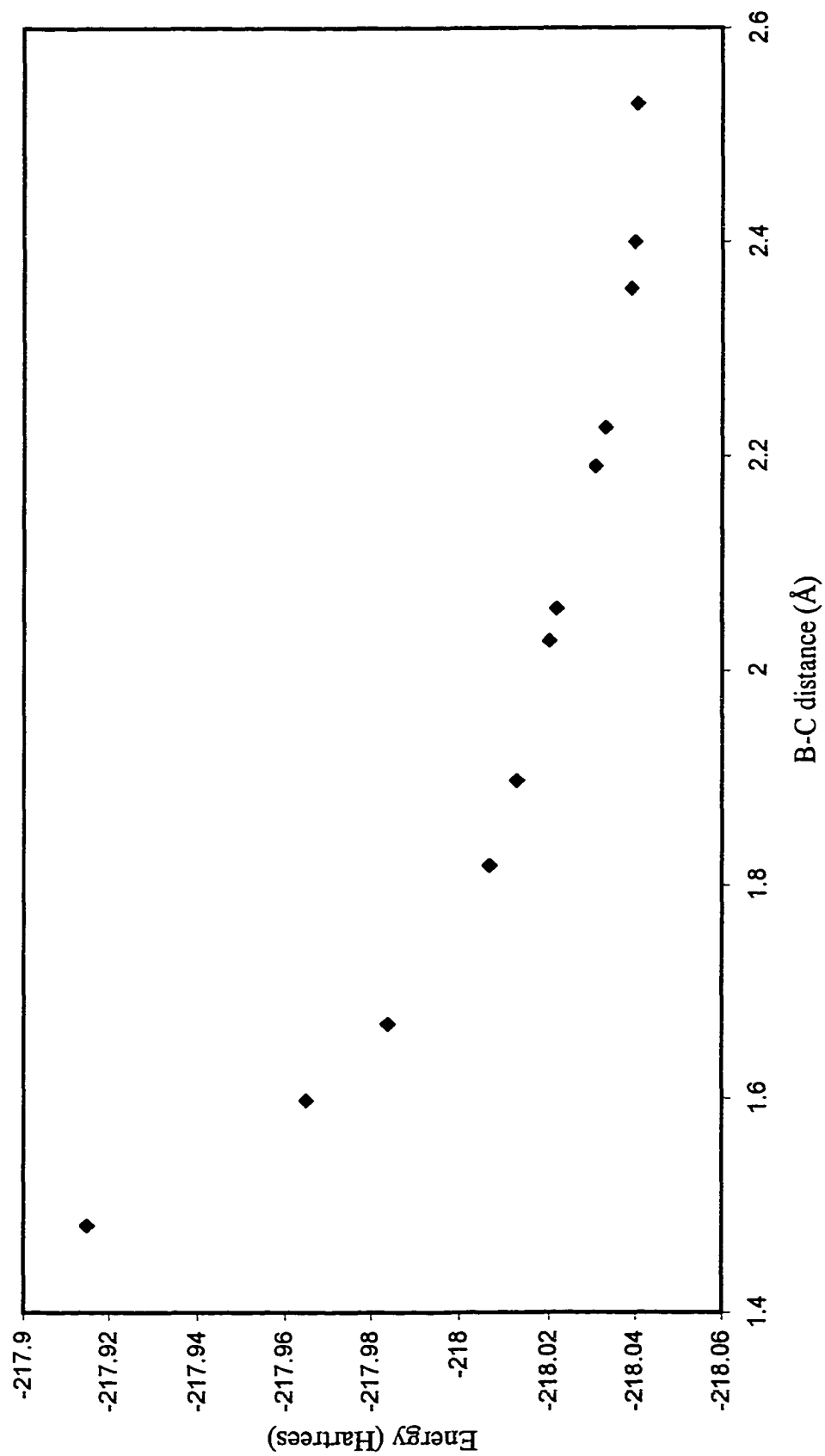


Figure 23
Energy (RHF/6-31G*) vs. B-C2
(=B-C5) distance for η^3 -optimized $C_5H_5BH_2$

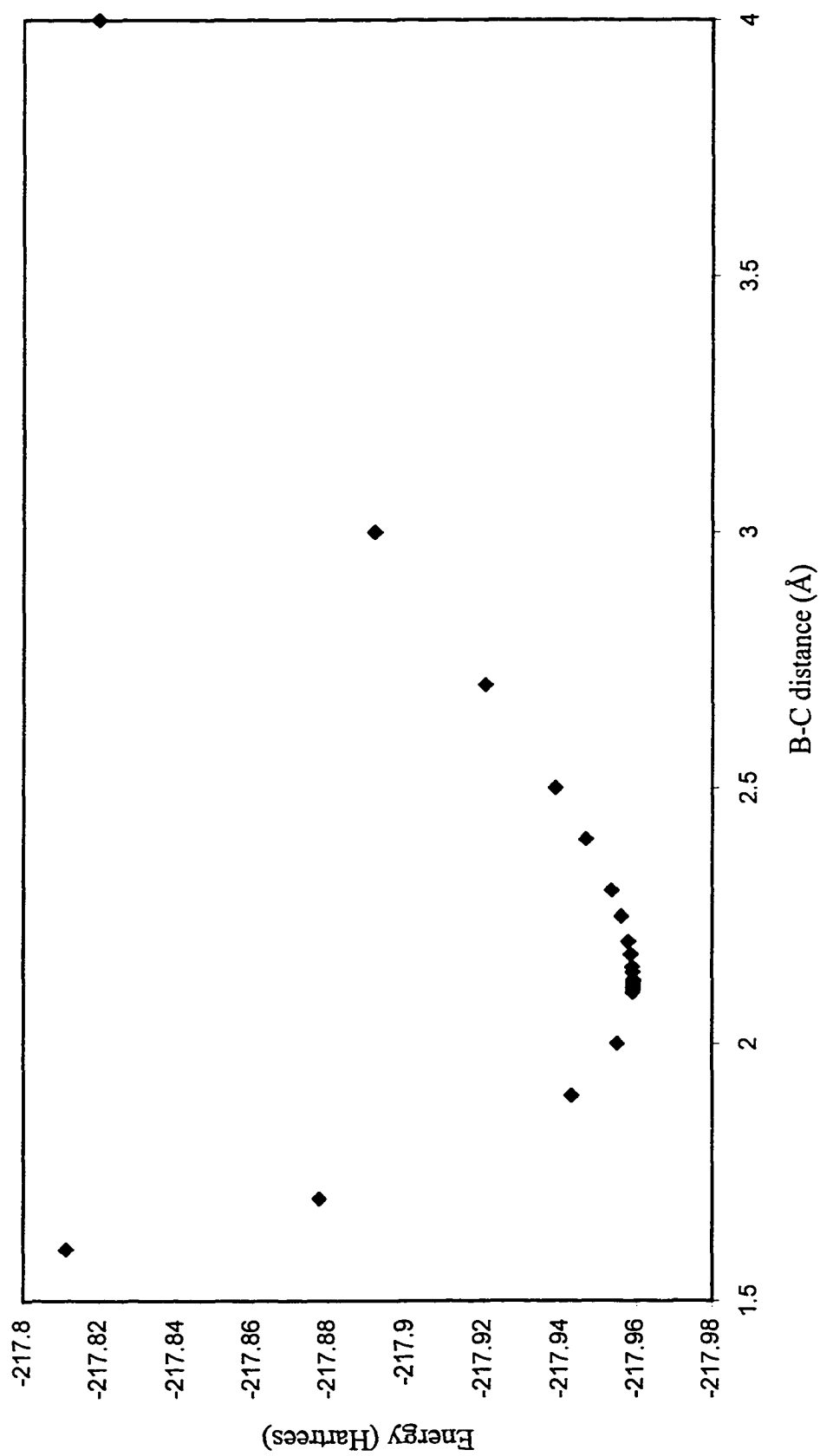


Figure 24
Energy (RHF/6-31G*) vs. constrained
boron-carbon distance for η^5 -optimized $C_5H_5BH_2$

optimized without constraints. The resulting geometry was *abgekippt* (superimposable with Figure 12a). This η^3 -constrained geometry therefore represents neither a local minimum nor a first order saddle point.

An attempt was made to produce a stable η^5 geometry. The five boron-carbon distances were constrained to the same value, and the molecule was optimized with no constraints on symmetry. This process was repeated for several different boron-carbon distances. A plot of the optimized energy vs. the boron-carbon distance is shown in Figure 24. The lowest energy of the molecules optimized was the one with a constrained boron-carbon distance equal to 2.123 Å. Frequency analysis of this geometry showed three imaginary frequencies (reported as -682.99 cm^{-1} , -317.12 cm^{-1} , and -281.85 cm^{-1}). Animation of these modes resembled the modes seen at the RHF/3-21G* level for the same structure. This molecule was re-optimized without any constraints. The resulting geometry was an η^1 -retention geometry. This geometry therefore represents neither a local minimum nor a first-order saddle point.

An attempt was also made to produce a stable η^2 geometry. Optimized parameters from the η^2 -optimized $\text{C}_5\text{H}_5\text{BH}_2$ molecule obtained at the RHF/3-21G* level were entered back into the Z-matrix. The molecule was then η^2 -optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 25b and geometric parameters are listed in Table 4. The RHF/6-31G* η^2 -optimized geometry was essentially identical to that found at the RHF/3-21G* level for most atoms. However, the following differences were noted: the boron atom is somewhat closer to the ring (as seen in the decrease in the B-C2, B-C5, B-C5, and B-H1 distances) and the BH_2 substituent

has rotated farther away from the plane bisecting the molecule.

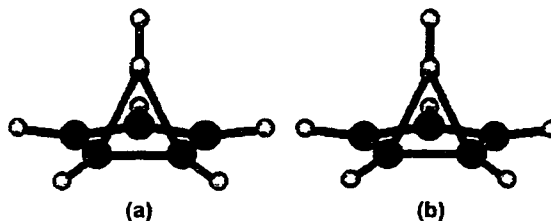


Figure 25
Geometry of $C_5H_5BH_2$
(a) η^2 -optimized at the RHF/3-21G* level (starting point for
further optimization), (b) η^2 -optimized at the RHF/6-31G* level.

The *abgekippt* geometry was re-optimized with the H7-B-C1-H1 dihedral angle constrained to particular values, as was previously done at the RHF/3-21G* level. The plot of the energy vs. the constrained dihedral angle is shown in Figure 26. At the RHF/6-31G* level, there is a maximum between the equilibrium geometry (H7-B-C1-H1 = 26.3 degrees) and the η^1 -retention conformation. The η^1 -retention conformation was therefore shown to be a local minimum. Subsequent optimization of this geometry without constraints confirmed this prediction. Comparison of the energy at 0 degrees with the equilibrium geometry indicates that the activation energy for interconversion between the two enantiomeric *abgekippt* conformations is 0.00081 Hartrees, or 0.51 kcal/mole. Comparison of the energy at 70 degrees (approximately at the maximum) with the equilibrium geometry gives an estimated energy barrier to rotation of 0.00215 Hartrees, or 1.35 kcal/mole.

For these molecules, interatomic distances were plotted as a function of the

constrained H7-B-C1-H1 dihedral angle. A plot of boron-nearest neighbor distance is shown in Figure 27. The B-H1 distance is relatively short for the η^1 -retention local minimum, and the B-C2 distance is relatively short for the *abgekippt* local minimum. A plot of the distance from C1 to these three atoms is shown in Figures 28 and 29. Both of these local minima therefore may involve some interaction of the boron atom with a nearest neighboring atom. The C1-H1 bond length increases as the geometry approaches the η^1 -retention minimum. This bond lengthening would be expected in a mechanism for 1,5-sigmatropic shift of H1 instead of BH₂. Also, the C1-C5 bond length decreases as the geometry approaches the *abgekippt* minimum. The C1-C2 distance is also affected by a change in the dihedral angle, although the exact relationship is not clearly demonstrated by this plot.

Frequency analysis of the *abgekippt*, η^1 -retention and η^1 -inversion molecule was performed. Frequency analysis was also performed on the molecule with the H-B-C-H dihedral angle constrained to 70 degrees. This geometry was estimated to be close to the transition state on the maxima of the graph in Figure 26, although it does not represent a true optimized saddle point (for this molecule, the first derivative of the energy with respect to the dihedral angle was reported by Gaussian 94W as 0.0003 Hartrees per Bohr, close to but not equal to zero). Both local minima (*abgekippt* and η^1 -retention) had three frequencies below 400 cm⁻¹, which when animated all showed boron "bond wagging" motion (the boron-carbon distance stayed approximately the same and the boron atom shifted position relative to the ring while the B-C1 distance remained approximately constant). The other two geometries both showed one imaginary frequency (reported

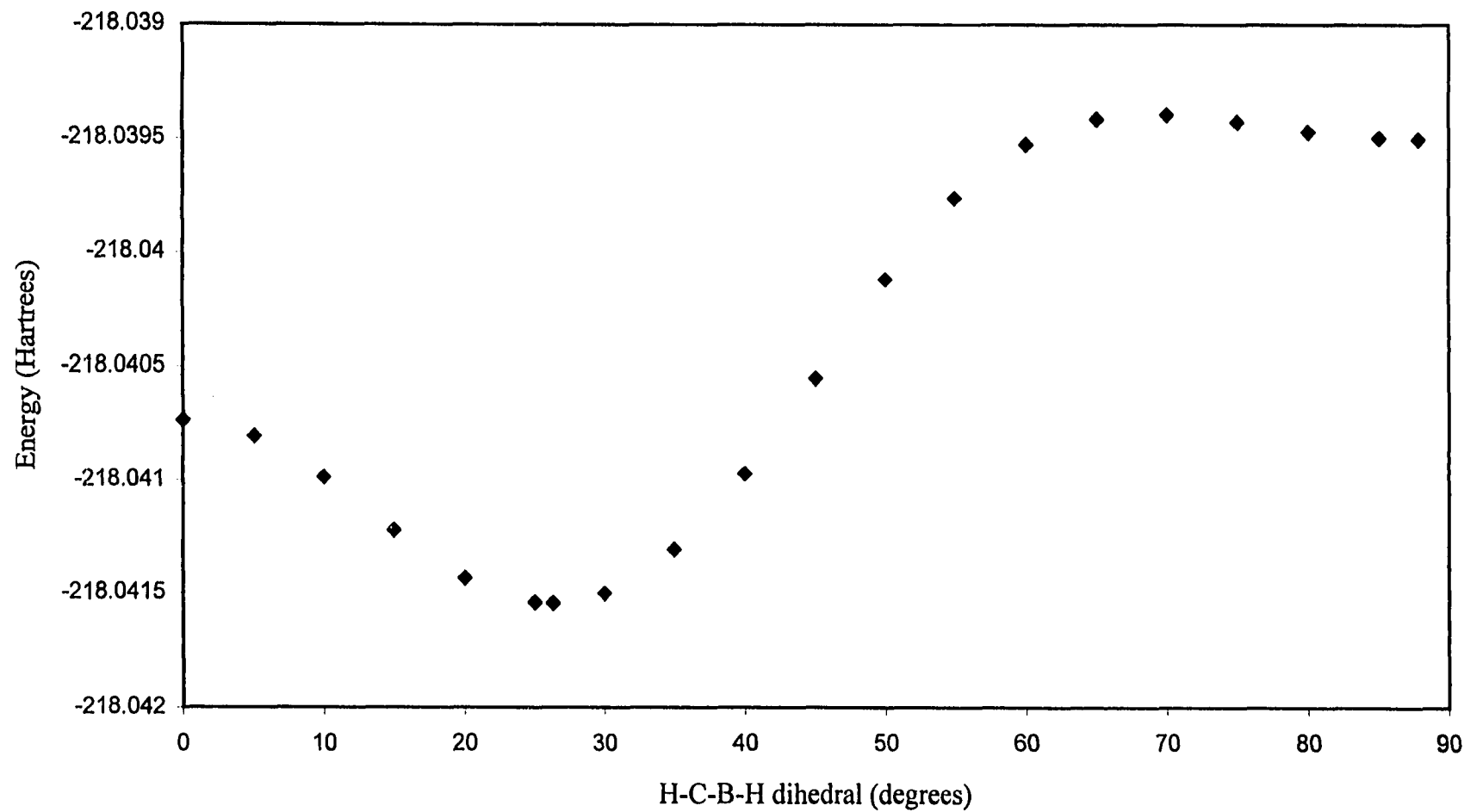


Figure 26
Energy (RHF/6-31G*) vs constrained
H7-B-C1-H1 dihedral angle in otherwise optimized C₅H₅BH₂

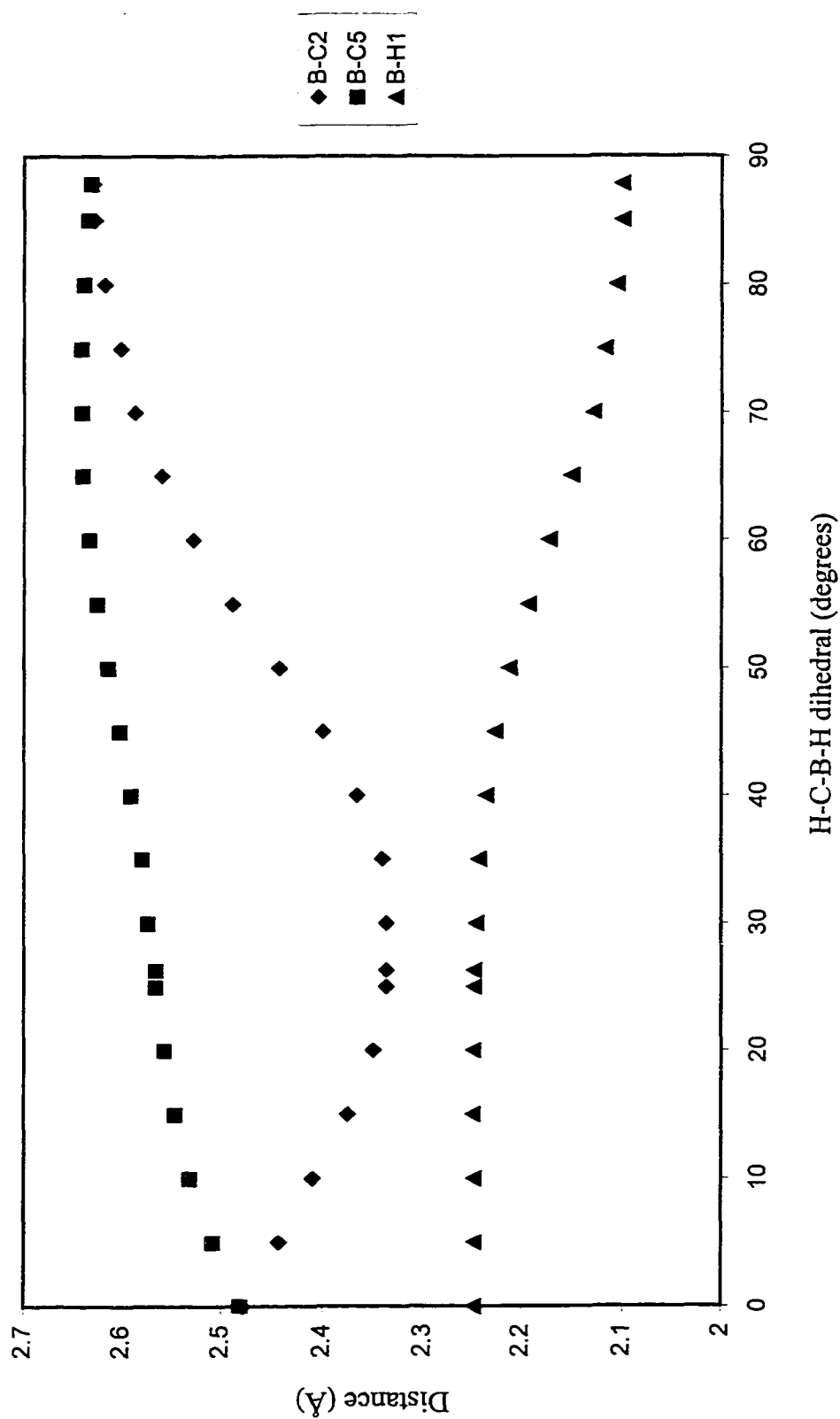


Figure 27
 Boron-nearest neighbor distance vs. constrained
 H7-B-C1-H1 dihedral angle in otherwise optimized $C_5H_5BH_2$

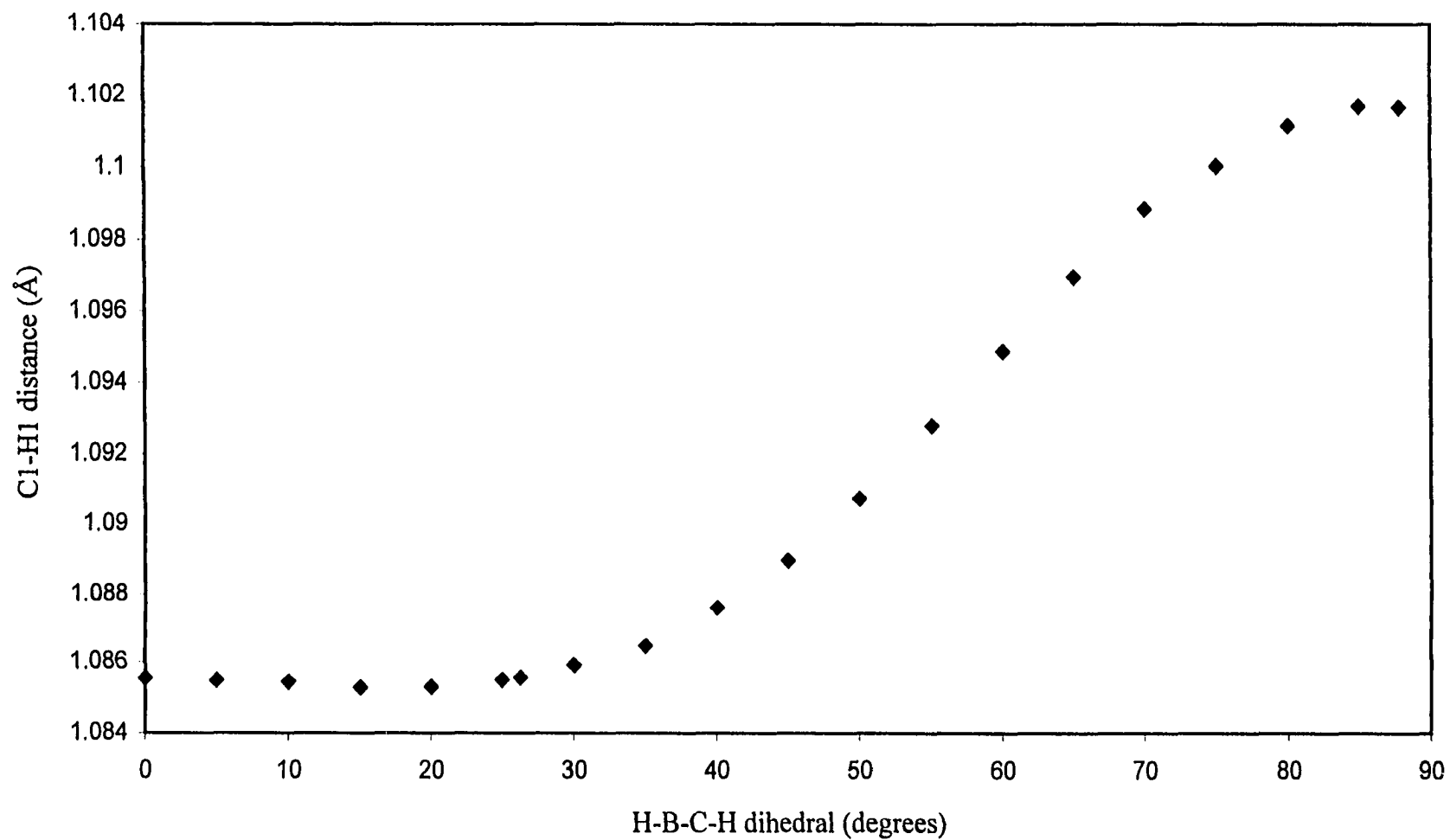


Figure 28
C1-H1 distance vs. constrained
H7-B-C1-H1 dihedral angle in otherwise optimized C₅H₅BH₂

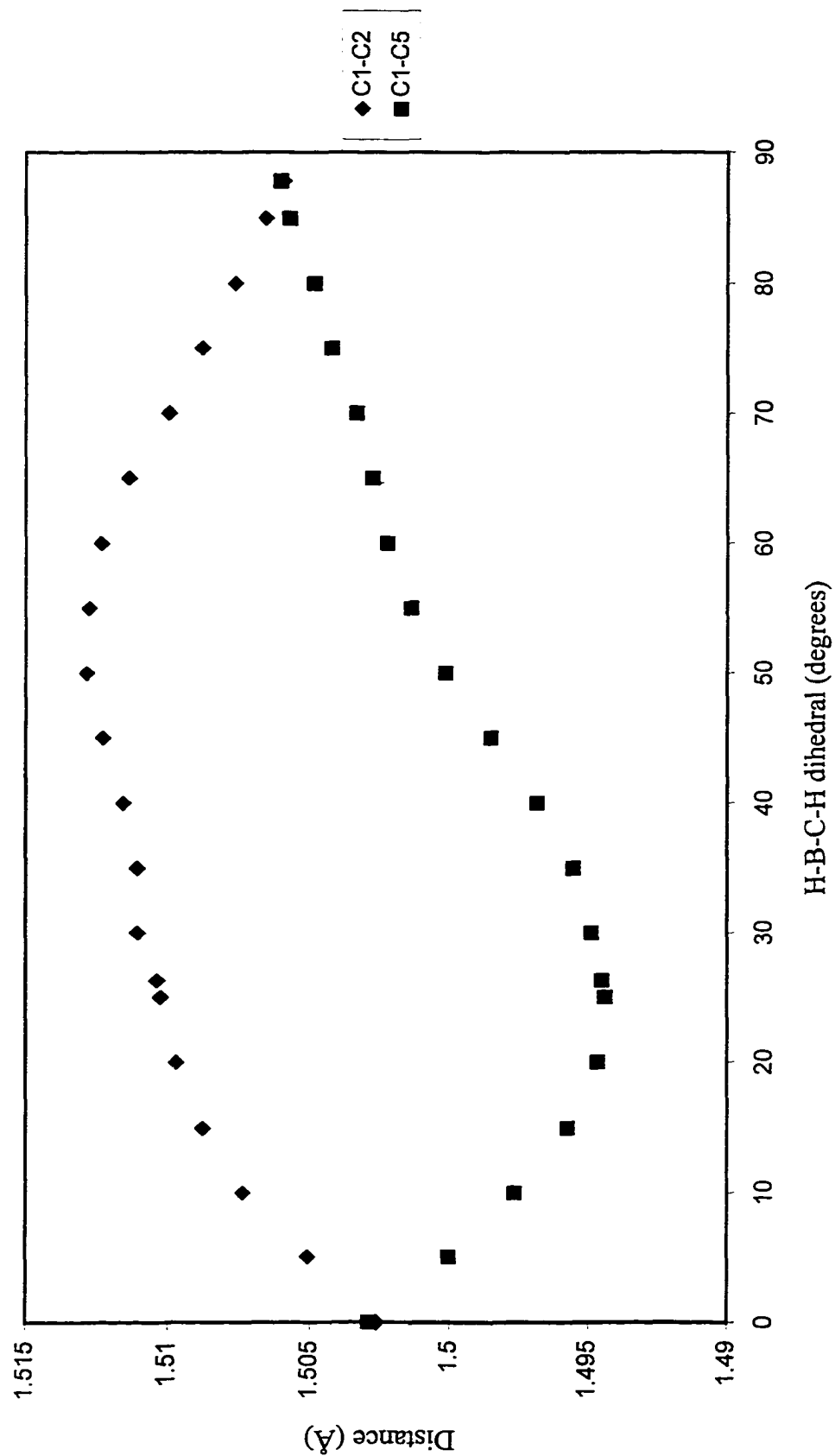


Figure 29
Carbon-carbon distance vs. constrained
H7-B-C1-H1 dihedral angle in otherwise optimized $C_5H_5BH_2$

as -171.46 cm^{-1} for the η^1 -inversion geometry and -112.95 cm^{-1} for the molecule with the dihedral angle constrained to 70 degrees) and two frequencies below 400 cm^{-1} (173.74 cm^{-1} and 368.31 cm^{-1} for the η^1 -inversion, and 192.74 cm^{-1} and 299.13 cm^{-1} for the molecule with the dihedral angle constrained to 70. degrees). Animation of these modes all showed boron "bond wagging" motion.

For the *abgekippt* position, the three frequencies were at 138.87, 216.73, and 345.80 cm^{-1} . These modes were also animated to reveal motion. In the lowest frequency mode the boron atom moved in the direction of C3 rather than C2. Since in the η^2 conformation (putative transition state for the 1,5-sigmatropic rearrangement) the boron atom is located closer to the axis of the ring than in the *abgekippt* position, this mode is not inconsistent with motion towards the η^2 geometry. Animation of this mode also showed motion of C2 and C5 parallel and opposite the motion of the boron atom. Such a mode would be expected since the B-C2 distance must decrease in order to achieve an η^2 geometry. Animation of the other two modes showed boron motion in a direction approximately perpendicular to the plane bisecting the ring.

For the other local minimum, the η^1 -retention geometry, animation revealed two modes (108.01 cm^{-1} , 302.45 cm^{-1}) with the boron atom moving perpendicular to the plane bisecting the rings, and one mode (164 cm^{-1}) with the boron atom moving parallel to the plane of the ring and towards the axis of the ring. The lowest frequency mode showed not only motion of the boron atom, but also rotation of the BH_2 substituent. This mode is therefore consistent with motion of the BH_2 substituent towards its *abgekippt* position.

Frequency analysis was also performed on the η^2 molecule. This analysis

revealed one imaginary mode, consistent with the prediction that this geometry is a first-order saddle point. The imaginary frequency was reported as -397.24 cm^{-1} . Animation of this mode showed motion of the boron atom parallel to the C1-C2 bond. The C1-C2 bond length remained approximately constant. The other carbon-carbon bond distances varied in an alternating pattern (i.e. while the C2-C3 and C4-C5 distances shortened, the C3-C4 and C5-C1 distances lengthened.) This mode is consistent with the putative mechanism of 1,5-sigmatropic rearrangement. As the boron atom shifts from C1 to C2, the positions of the shorter (double) bonds of the ring also shift.

Two real vibrational modes below 400 cm^{-1} were also reported. Animation of the mode at 330.18 cm^{-1} showed motion of the boron atom parallel to the plane of the ring and towards the axis of the ring. Animation of the mode at 371.05 cm^{-1} showed motion of the boron atom parallel to the C1-C2 bond. Unlike in the imaginary mode, the B-C2 and B-C5 distances remained fixed, while these three atoms moved relative to the rest of the ring.

The LUMO, HOMO, and HOMO-1 of both the *abgekippt* and η^2 geometries were displayed graphically using Spartan 5.0. Surfaces for these molecular orbitals are shown in Figures 30, 31, and 32; respectively. Default values were used for the Spartan 5.0 display parameters. For comparison, Figure 33 displays the orientations of the framework of the molecules without any molecular orbital plots to block the view.

The LUMO seen in both molecules resembles Schoeller's description of the BH_2^+ substituent's "p" fragment orbital [1]. To a small extent in the *abgekippt* geometry, and to a larger extent in the η^2 geometry, it is able to overlap one of the two degenerate

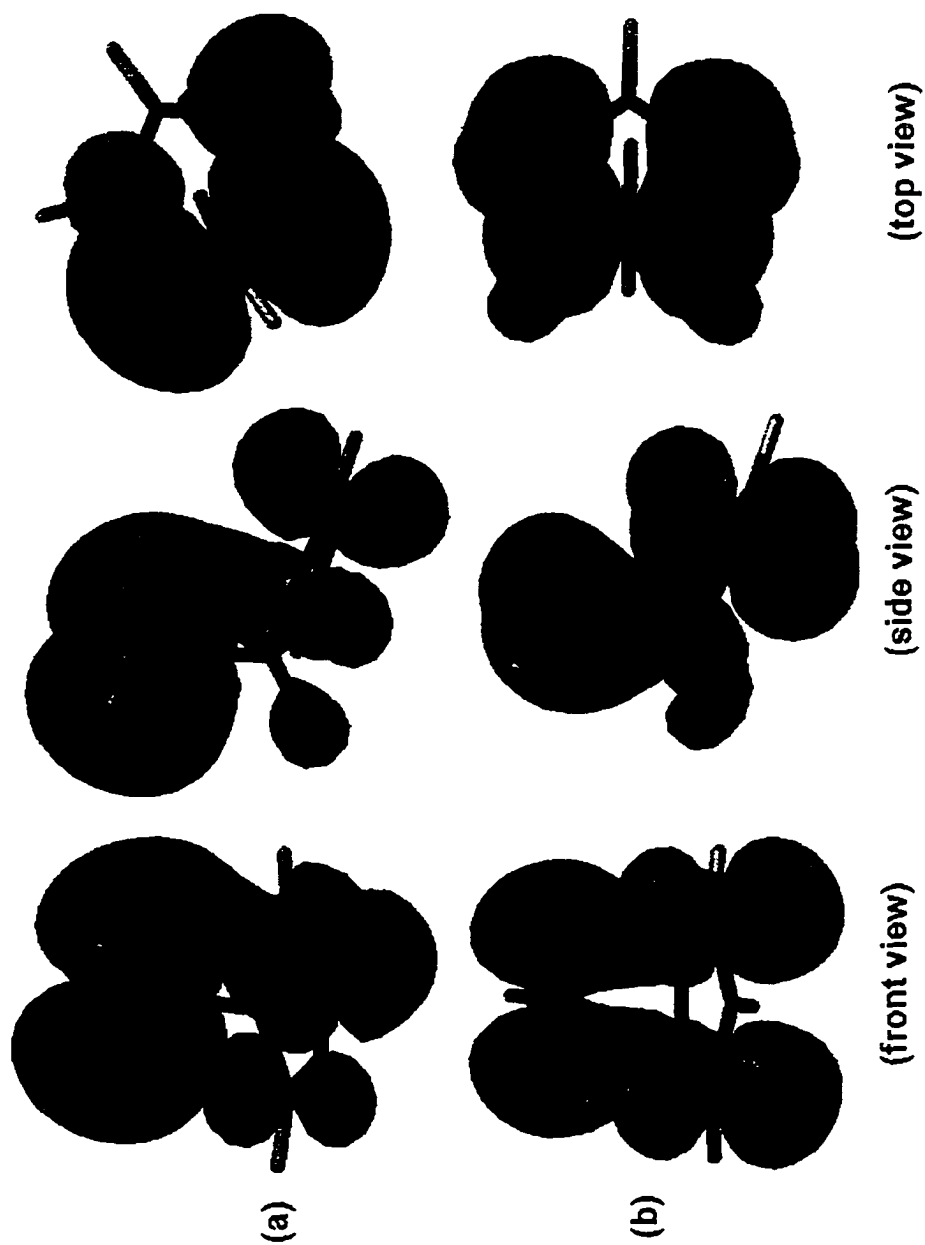


Figure 30
Isosurface of LUMO of $C_5H_5BH_2$
(RHF/6-31G*) (a) ground state, (b) η^2 -optimized

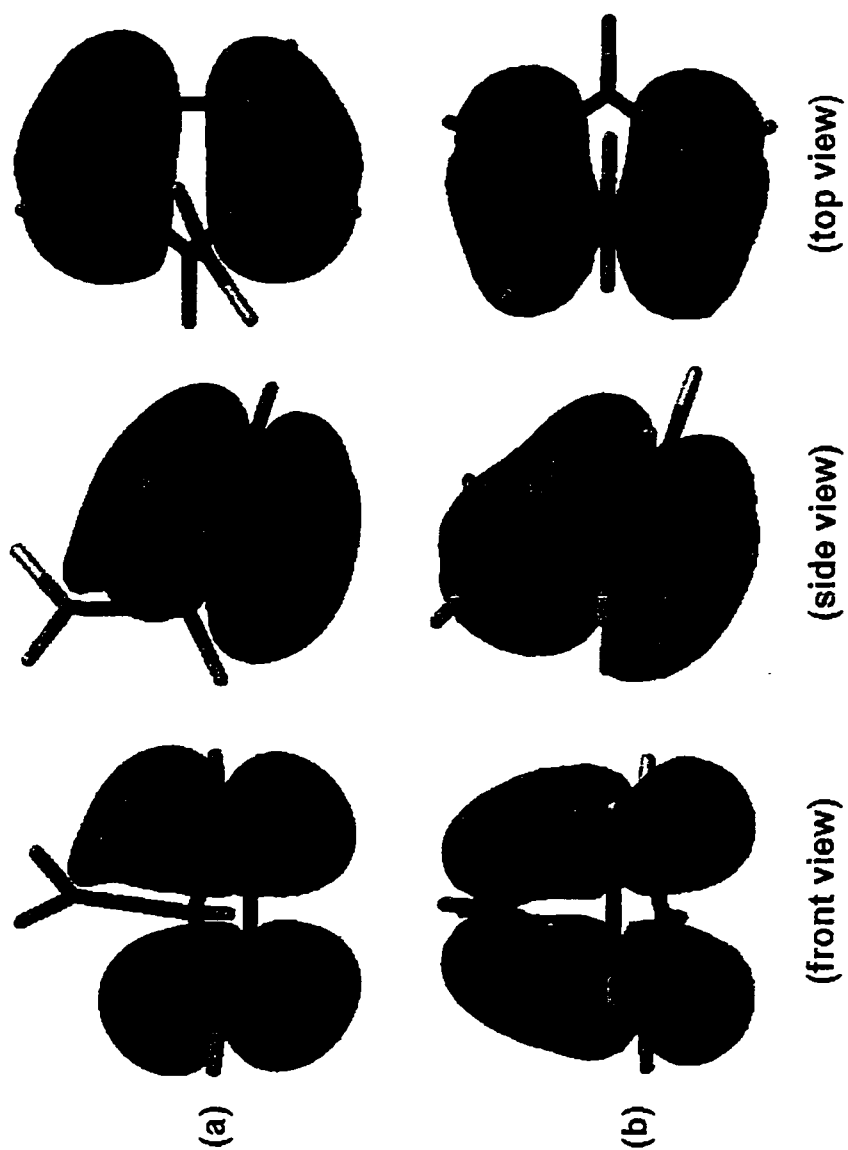


Figure 31
Isosurface of HOMO of $C_5H_5BH_2$
(RHF/6-31G*) (a) ground state, (b) η^2 -optimized

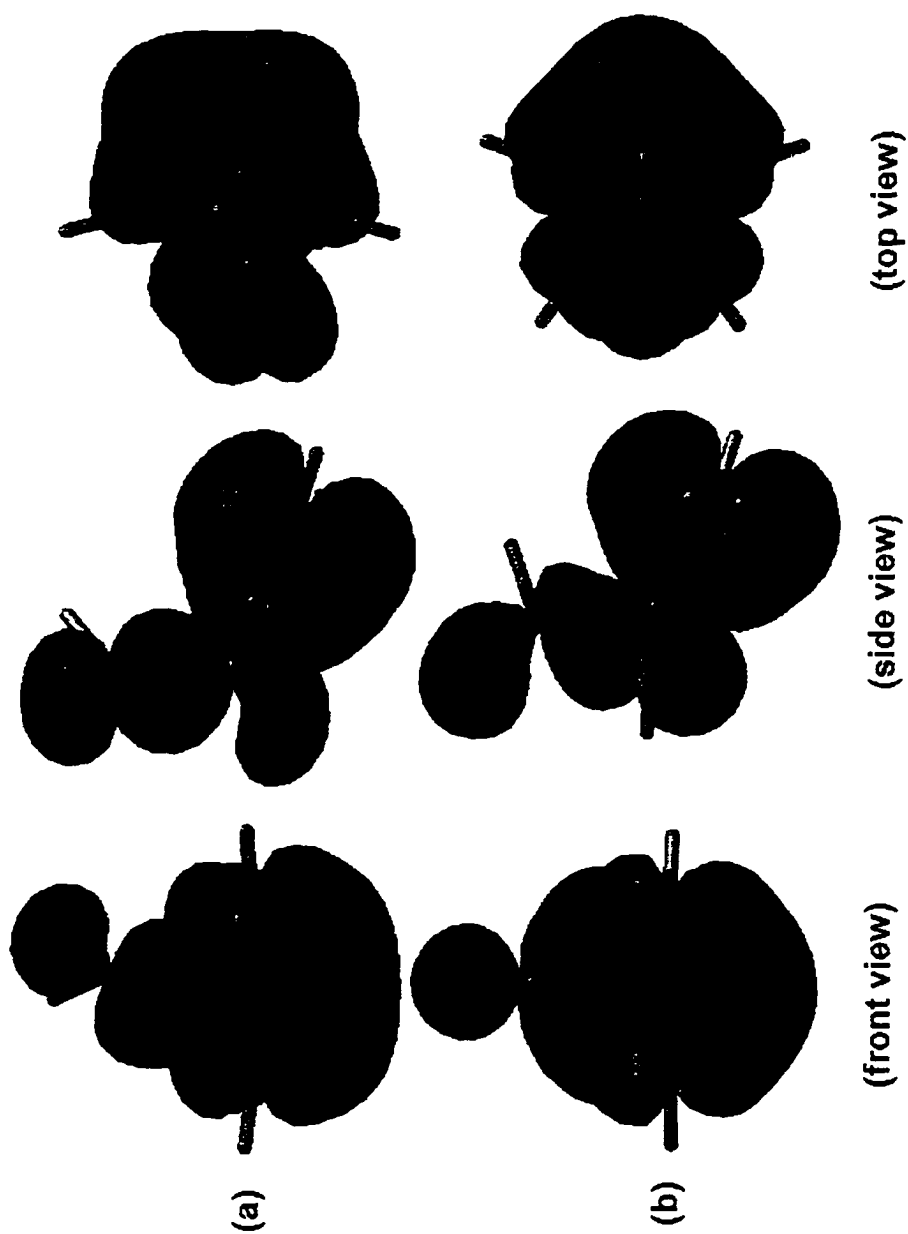


Figure 32
Isosurface of HOMO-1 of $C_5H_5BH_2$
(RHF/6-31G*) (a) ground state, (b) η^2 -optimized

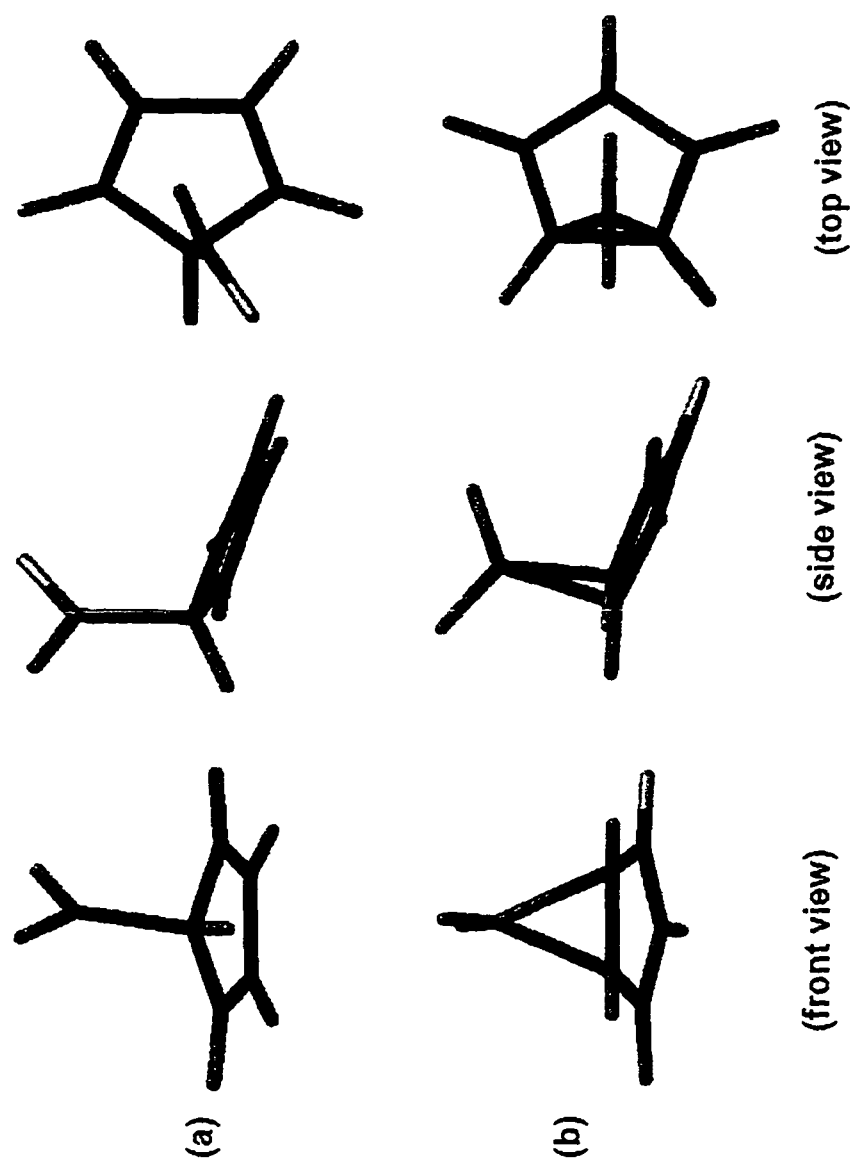


Figure 33
Geometry of $C_5H_5BH_2$ (RHF/6-31G*,
without isosurfaces), (a) ground state, (b) η^2 -optimized

lowest unoccupied fragment orbitals of the cyclopentadienide fragment. The HOMO matches Schoeller's description of one of the degenerate highest occupied fragment orbitals, although it also overlaps with Schoeller's "p" fragment orbital. The overlap is substantial in the η^2 geometry. The overlap in the equilibrium geometry is less apparent. However, the shapes of the lobes of the orbital closest to the boron atom are different. The lobe closer to C2 is distorted outward pointing toward the boron atom. This distortion can be described as resulting from the overlap between Schoeller's "p" fragment orbital. Figure 34 shows the top view of an isosurface plot of the HOMO for the *abgekippt* geometry displayed at an iso value equal to $0.021189 \text{ Bohr}^{-3/2}$ (as opposed

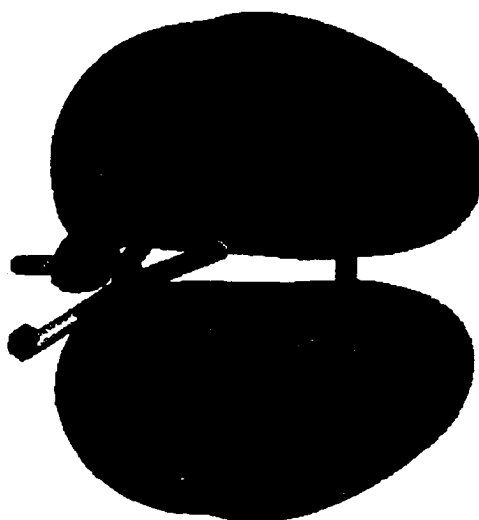


Figure 34
Isosurface of HOMO of $\text{C}_5\text{H}_5\text{BH}_2$ (RHF/6-31G*)
equilibrium geometry (displayed using $\text{Iso} = 0.021189 \text{ Bohr}^{-3/2}$).

to the default value of $0.032 \text{ Bohr}^{-3/2}$ used in Figures 30, 31, and 32.) The asymmetric distortion of this orbital can be more clearly seen at this value.

This overlap is promoted by the orientation of the boron atom away from the plane bisecting the ring. The HOMO for the *abgekippt* structure is shown in Figure 35a. For comparison, the HOMO for the η^1 -inversion structure is shown in Figure 35b. The distortion seen in Figure 35a is largely absent in Figure 35b. The distorted HOMO in

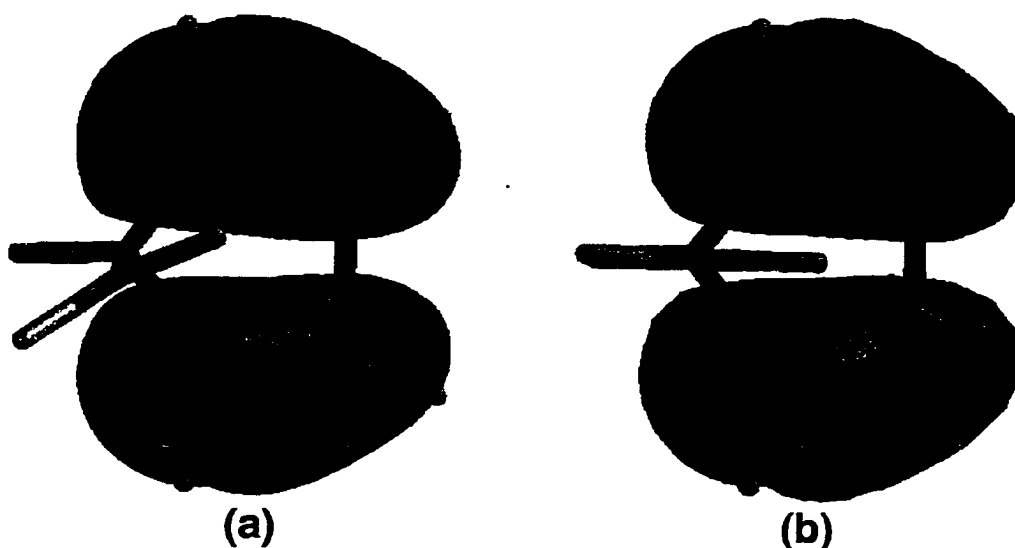


Figure 35
Isosurface of HOMO of $C_5H_5BH_2$
(RHF/6-31G*) (a) equilibrium geometry, (b) η^1 -inversion

Figure 35a is somewhat lower in energy than the undistorted HOMO in Figure 35b (eigenvalue = -0.39186 Hartrees, vs. -0.30997 Hartrees). Interactions of this type may explain why the *abgekippt* geometry is lower in energy than the η^1 -inversion geometry.

The HOMO-1 is in essence describable by an overlap of the other degenerate highest occupied fragment orbital of the cyclopentadienide fragment with Schoeller's "sigma" fragment orbital [1]. The overall shape of this molecular orbital, displayed for

the *abgekippt* geometry, is similar to that displayed for the η^2 geometry. Although the difference in energy between HOMO and HOMO-1 is smaller for the η^2 geometry than for the *abgekippt* geometry, they remain separated by 0.004 Hartrees. These orbitals are therefore not degenerate. The RHF/6-31G* results therefore do not show any evidence of the equilibrium geometry HOMO-1 becoming higher in energy than HOMO during 1,5-sigmatropic rearrangement.

The electron densities were calculated for the *abgekippt*, the η^1 -inversion, and the η^2 geometries. Isosurfaces of the electron density at various values of ρ are shown in Figure 36. The location of the bonding critical points can be inferred from these figures. A region where the isosurface narrows to a very thin, “hour glass” shaped cylinder must contain a critical point [118]. Alternatively, a critical point must be located between two regions of an isosurface that approach each other and almost touch (e.g. that resemble a stalactite and stalagmite approaching each other.) The plots of $\rho = 0.174 \text{ Bohr}^{-3}$ show the critical points for the B-C1 bond in the two η^1 geometries. The electron density is somewhat higher for the *abgekippt* molecule than for η^1 -inversion geometry. The plot of $\rho = 0.118 \text{ Bohr}^{-3}$ for the η^2 geometry shows a critical point between the boron atom and the midpoint of the C1-C2 bond. Close examination of this critical point suggest that it may have non-zero ellipticity, since the isosurface immediately beneath it appears highly asymmetric. The isoelectronic $\text{C}_5\text{H}_5\text{CH}_5^+$ cation has been shown to have separate bond critical points for B-C1 and B-C2 and both showed ellipticity, consistent with the homoaromaticity of this cation [119]. The plot at $\rho = 0.254 \text{ Bohr}^{-3}$ shows critical points

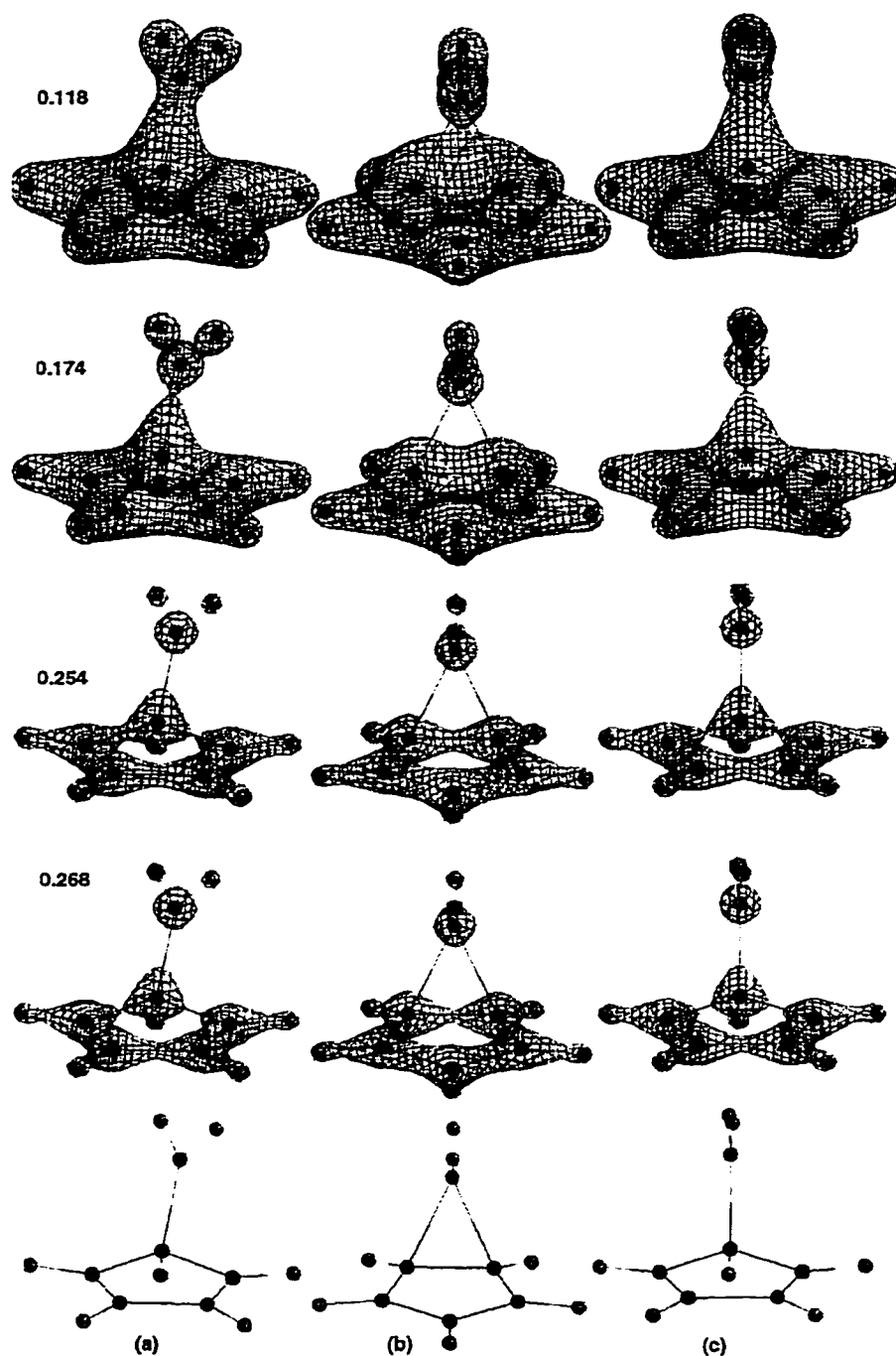


Figure 36

Electron density isosurfaces of $C_5H_5BH_2$ (RHF/6-31G*) for (a) *abgekippt* geometry, (b) η^2 geometry, and (c) η^1 -inversion geometry. Plots shown are $\rho = 0.118 \text{ Bohr}^{-3}$ (top), $\rho = 0.174 \text{ Bohr}^{-3}$, $\rho = 0.254 \text{ Bohr}^{-3}$, and $\rho = 0.268 \text{ Bohr}^{-3}$. The geometry without isosurfaces is also shown.

for the C1-C5 and the C1-C2 bonds in the η^1 -inversion. Examination of the plot for the *abgekippt* geometry shows that the electron density for the C1-C2 bond is less than 0.254 Bohr⁻³ and the electron density for the C1-C5 bond is greater than 0.254 Bohr⁻³. Finally, the plot at $\rho = 0.268$ Bohr⁻³ shows that the bond critical point between C1 and C2 in the η^2 geometry is slightly greater than that value, and that the bond critical point between C1 and C5 in the *abgekippt* molecules is less than that value. The difference between the η^2 geometry and the *abgekippt* equilibrium geometry was 6.07 kcal/mole. The energies for the *abgekippt* and η^2 molecules were corrected for zero-point vibrational energy. The zero-point energies and the corrected energies are listed in Table 2. With the correction for zero-point energy, the activation energy predicted at the RHF/6-31G* level was 6.00 kcal/mole.

RHF/6-311G** Calculations for C₅H₅BH₂

The η^2 geometry of C₅H₅BH₂ was optimized at the RHF/6-311G** level with Spartan 5.0 using its transition state optimization task feature. Optimization required six cycles and over 18 days. The resulting geometry was essentially identical to the geometry seen at the RHF/6-31G* level that was used as the starting point. The results are summarized in Table 4. No further calculations were done on C₅H₅BH₂ at the RHF/6-311G** level.

RMP2/3-21G* Calculations for C₅H₅BH₂

The optimized geometry of C₅H₅BH₂ at the RMP2/3-21G* level was calculated

using both Spartan 5.0 and Gaussian 94W, starting with the geometry optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 37. The calculated MP2 (frozen core) energy was -217.31895 Hartrees (HF energy was -216.81975 Hartrees). This geometry is *abgekippt*. The distance from the boron atom to C1 is closer than the distance from the boron atom to the midpoint of C1-C2 of (1.720 Å). The geometry is more pronouncedly asymmetrical than the RHF optimized geometry. In general this geometry is closer to the η^2 geometry than the RHF optimized geometry.

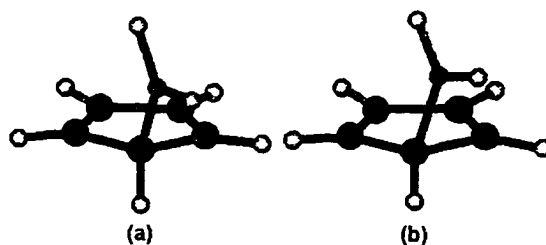


Figure 37
Geometry of $C_5H_5BH_2$
(a) optimized at the RHF/6-31G* level (starting point for
further optimization), (b) optimized at the RMP2/3-21G* level

Different starting point geometries were created with the H7-B-C1-H1 dihedral angle ranging from 5 to 85 degrees. Each was optimized at the RMP2/3-21G* level without constraints. For each geometry, the resulting MP2 energy was reported to be $-217.3189467 \pm 0.0000002$ Hartrees (-217.31895 Hartrees, rounded to eight significant figures.)

Molecular orbital surfaces were displayed for this geometry. Figure 38 shows surface plots of LUMO, HOMO, and HOMO-1. (It should be noted that, for a correlated

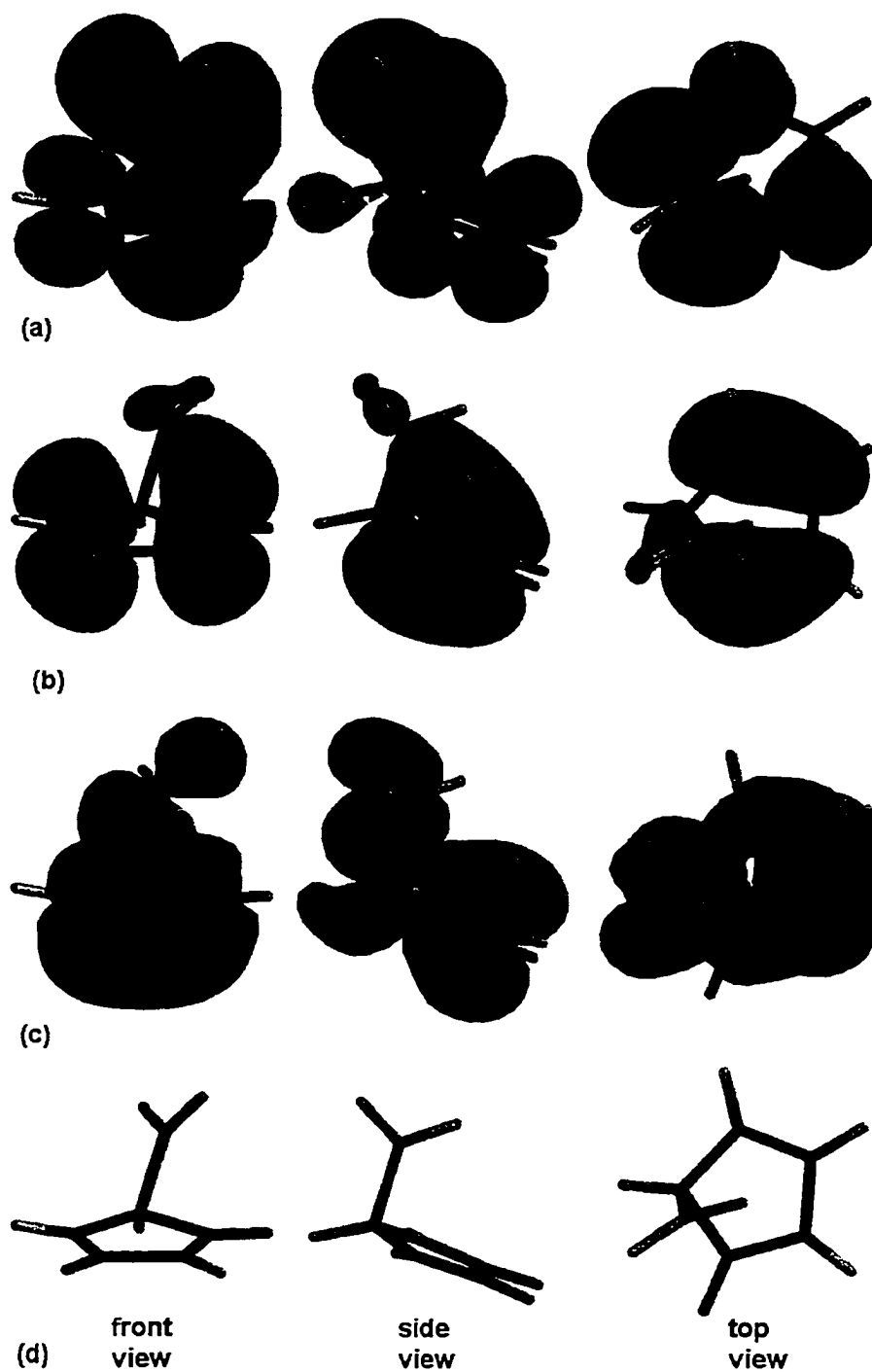


Figure 38
Molecular orbital isosurfaces for $C_5H_5BH_2$
(RMP2/3-21G*). Isosurfaces shown are (a) LUMO, (b) HOMO,
and (c) HOMO-1. The geometry without isosurfaces (d) is also shown.

multielectron wavefunction, the significance of individual molecular orbitals is open to question.) In general, these plots resemble those seen for the orbitals calculated at the RHF/6-31G* level, but the distortions seen particularly in HOMO are more clearly evident in the orbitals calculated at the RMP2/3-21G* level.

Electron density isosurfaces were also plotted for this geometry. Figure 39 shows

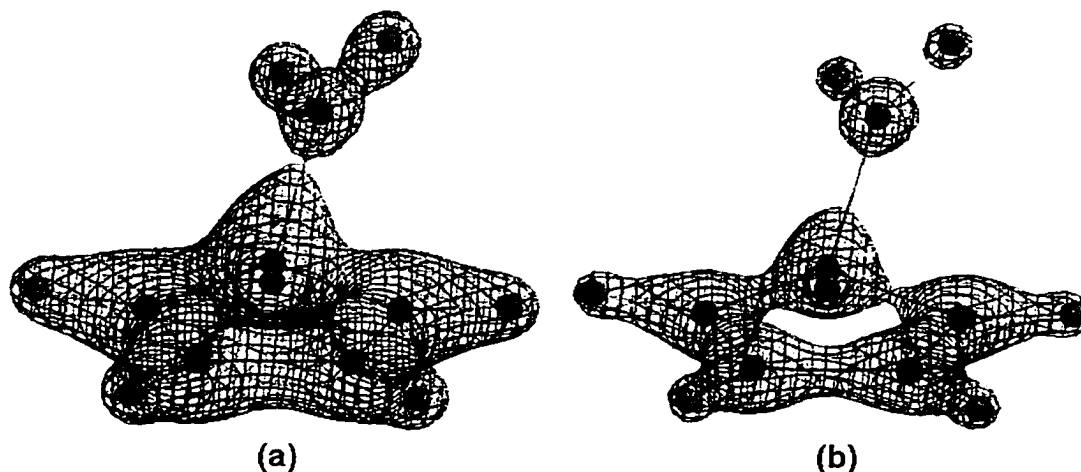


Figure 39
Electron density isosurface of
 $\text{C}_5\text{H}_5\text{BH}_2$ (RMP2/3-21G*), (a) $\rho = 0.145 \text{ Bohr}^{-3}$, (b) $\rho = 0.22 \text{ Bohr}^{-3}$

surface plots at $\rho = 0.145 \text{ Bohr}^{-3}$ and 0.22 Bohr^{-3} isosurfaces. Both show a reduction in the electron density at the critical point, compared with the equivalent results at the RHF/6-31G* level. This is consistent with a previous study showing that electron correlation consideration changes the magnitude of the electron density but generally does not affect the number or kind of the critical points [120].

The $\text{C}_5\text{H}_5\text{BH}_2$ molecule was η^2 -optimized at the RMP2/3-21G* level, using the η^2 -optimized geometry obtained at the RHF/6-31G* level as a starting point. The results

are shown in Figure 40b. In general, the η^2 -optimized geometry resembled the geometry seen at the RHF/6-31G* level for the same molecule (Figure 25b), with all bond distances somewhat longer, and with H6 shifted somewhat closer to the ring. Again, the energies for HOMO and HOMO-1 were close but not identical. The difference in energy between the two orbitals was 0.00329 Hartrees.

The difference in energy between the unconstrained optimized (*abgekippt*) molecule and the η^2 -optimized molecule, corrected for zero-point energies, was

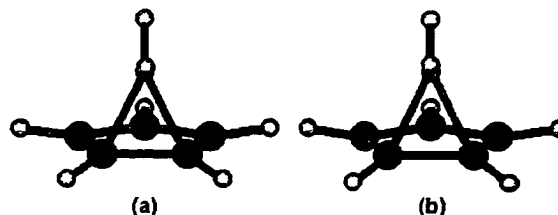


Figure 40
Geometry of $C_5H_5BH_2$
 (a) η^2 -optimized at the RHF/6-31G* level (starting point for further optimization), (b) η^2 -optimized at the RMP2/3-21G* level.

1.34 kcal/mole. The zero-point vibrational energy of the η^2 -optimized geometry was greater than the zero-point vibrational energy of the equilibrium geometry.

RMP2/6-31G* Calculations for $C_5H_5BH_2$

The optimized geometry of $C_5H_5BH_2$ was calculated at the RMP2/6-31G* level using both Spartan 5.0 and Gaussian 94W, starting with the *abgekippt* geometry optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 41. The

calculated RMP2 energy was -218.76255 Hartrees (HF energy was -218.03049 Hartrees).

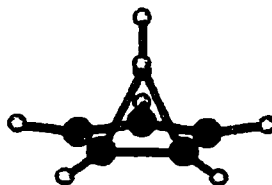


Figure 41
Geometry of $C_5H_5BH_2$ (optimized
without constraint at the RMP2/6-31G* level).

The same results were obtained when the geometry η^2 -optimized at the RHF/6-31G* level was used as a starting point. Unlike the predictions at the RHF/3-21G*, RHF/6-31G*, and RMP2/3-21G* levels, the prediction at the RMP2/6-31G* level is that the η^2 geometry is the equilibrium geometry.

A distance scan was performed, starting with the optimized geometry and varying the B-C2 distance. Some of the resulting geometries are shown in Figure 42. The energy rises uniformly as the B-C2 distance increases up to 2.27 Å. Beyond 2.27 Å, the boron atom shifts to the other side of the ring (i.e. the constrained distance becomes the B-C5 distance rather than the B-C2 distance.) The geometry at a B-C2 distance of 2.3 Å was subsequently optimized without constraints. The resulting geometry was η^2 and the energy was the same as that seen for the molecule shown in Figure 41. A plot of the energy vs. the constrained B-C2 distance is shown in Figure 43. Beyond 2.3 Å, the energy decreased dramatically since the boron atom was shifted toward the other side of carbon 1. There is no indication of a stable *abgekippt* geometry. Instead, there appears to be a smooth transition from the η^2 equilibrium geometry to an η^1 -inversion transition

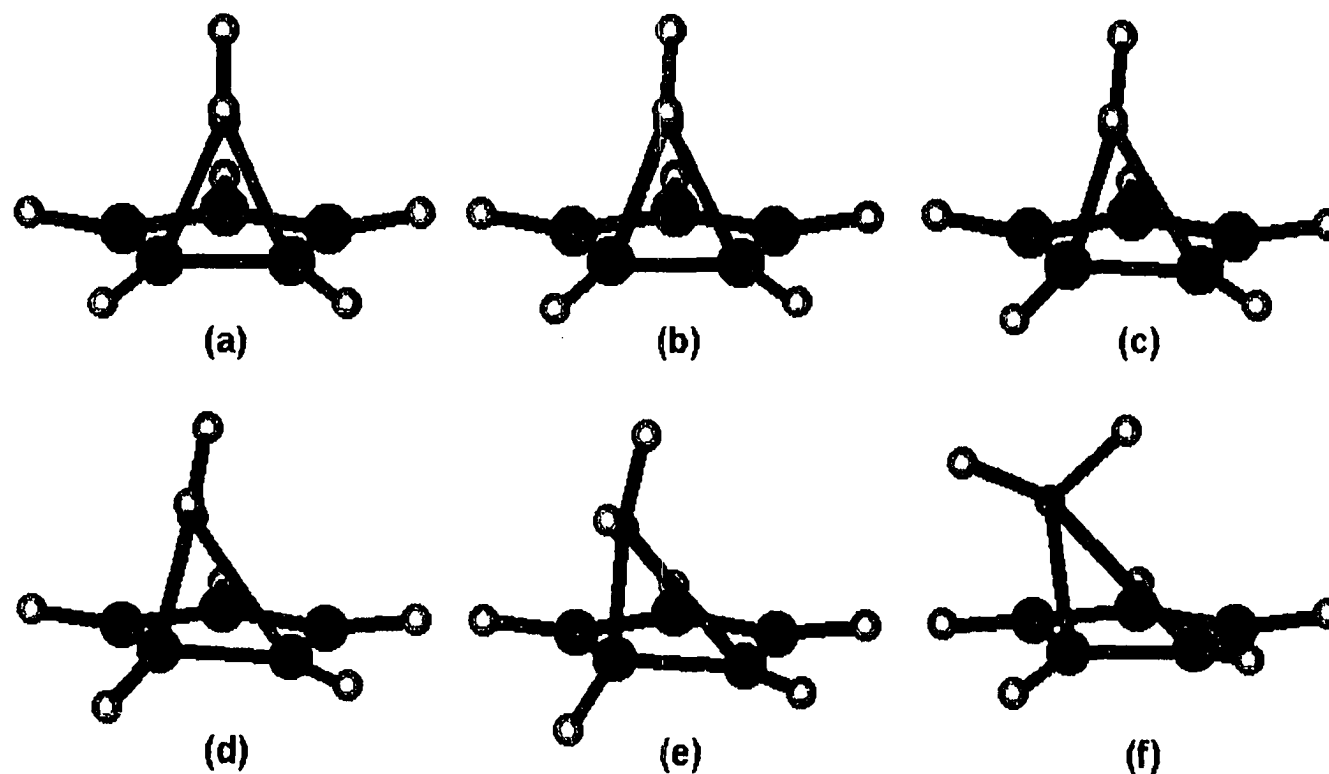


Figure 42
Geometry of $C_5H_5BH_2$ (optimized at the
RMP2/6-31G* level with constrained B-C2 distance)
(a) unconstrained ground state, (b) B-C2 = 1.8 Å, (c) B-C2 = 1.9 Å,
(d) B-C2 = 2.0 Å, (e) B-C2 = 2.2 Å, (f) B-C2 = 2.3 Å. Note that for B-C2 =
2.3 Å the boron atom has shifted towards the midpoint of the next carbon-carbon bond.

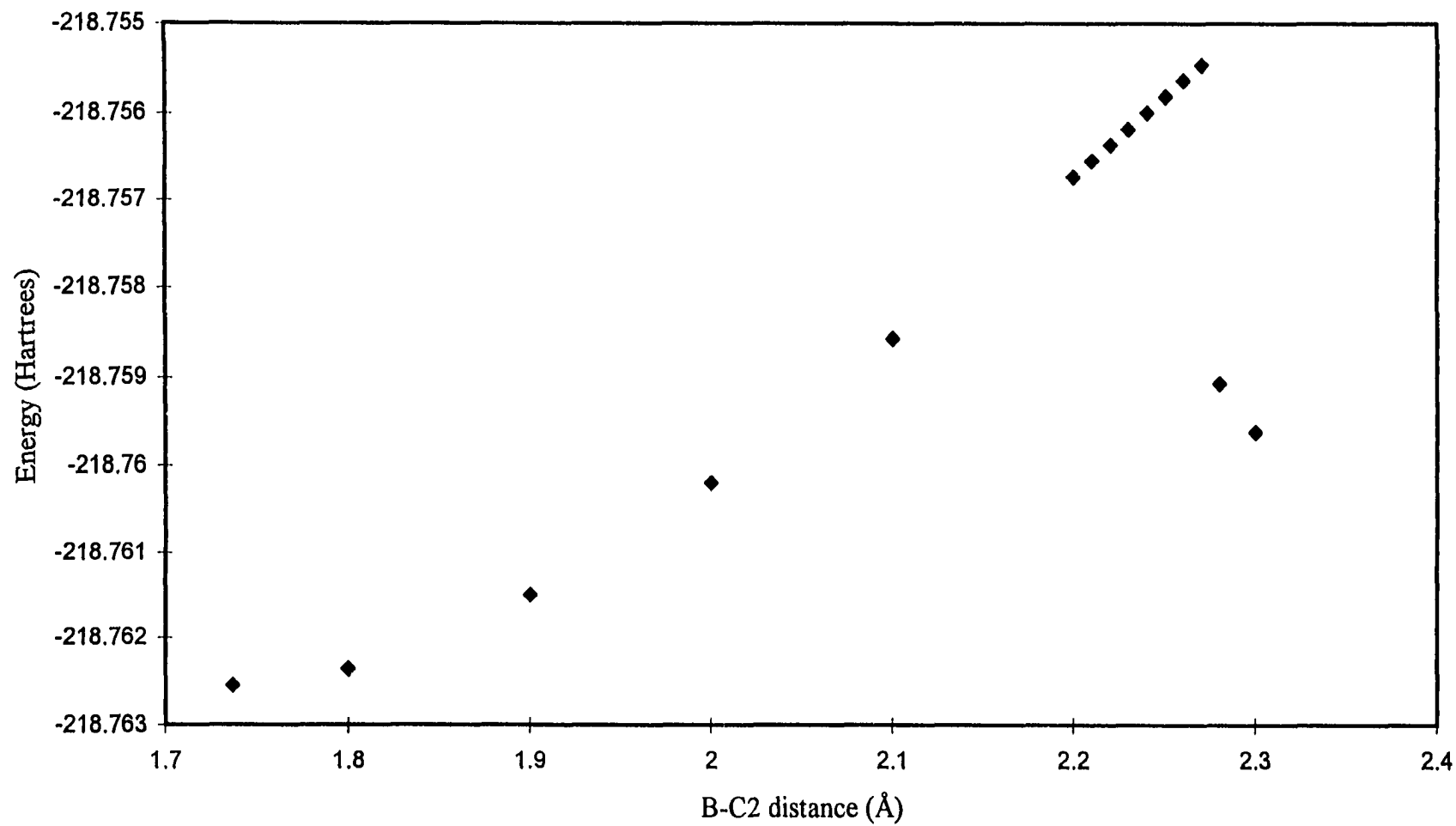


Figure 43
Energy (RMP2/6-31G*) vs. constrained
B-C2 distance for otherwise optimized $C_5H_5BH_2$

state geometry. A scan of the energy vs. the constrained B-C2 distance yielded a maximum at B-C2 = 2.27 Å and an energy of -218.75546 Hartrees. The energy difference between these two geometries is 0.00709 Hartrees, or 4.45 kcal/mole.

Table 1
MNDO energies and η^2 B-C bond lengths.
 (All energies are in kcal/mole, all distances are in Ångstroms.)

Molecule	Energy (η^1)	Energy (η^2)	Δ Energy ($\eta^2 - \eta^1$)	Δ Energy previously reported [1]	η^2 B-C bond length	η^2 B-C bond length reported previously [1]
C ₅ H ₅ BH ₂	-1315.6	-1297.5	18.0	18.0	1.667	1.67
C ₅ H ₅ BF ₂	-1430.9	-1397.1	33.7	33.6	1.75	1.75
C ₅ H ₅ BCl ₂	-1335.4	-1312.0	23.4	22.9	1.67	1.67
C ₅ Me ₃ BH ₂	-2722.1	-2707.0	15.2	16.5	1.69	1.68
C ₅ Me ₃ BF ₂	-2836.4	-2804.1	32.2	31.8	1.77	1.78
C ₅ Me ₃ BCl ₂	-2740.4	-2718.6	21.8	18.9	1.68	1.68

Table 2
Equilibrium and zero-point
energies (All energies are in Hartrees)

Molecule	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*	RMP2/6-31G*
C₅H₅BH₂ (unconstrained) (1)				
Equilibrium Energy	-216.82547	-218.04154	-217.31895	-218.76255
Zero-Point Energy	0.11142	0.11103	0.10483	0.10626
C₅H₅BH₂ (η^2-optimized)				
Equilibrium Energy	-216.81424	-218.03186	-217.31681	-218.76255
Zero-Point Energy	0.11139	0.11092	0.10484	0.10626
C₅H₅BF₂ (unconstrained)				
Equilibrium Energy	-413.65590	-415.91408	-414.37942	-416.96215
Zero-Point Energy	0.10038	0.09968	0.09374	0.09398
C₅H₅BF₂ (η^2-optimized)				
Equilibrium Energy	-413.62913	-415.88498	-414.36151	-416.95371
Zero-Point Energy	0.09938	0.09859	0.09306	0.09345
C₅H₅BCl₂ (unconstrained)				
Equilibrium Energy	-1135.95473	-1135.95530	-1131.33902	-1136.93029
Zero-Point Energy	0.09650	0.09658	0.09015	0.09092
C₅H₅BF₂ (η^2-optimized)				
Equilibrium Energy	-1135.92951	-1135.93013	-1131.32750	-1136.92649
Zero-Point Energy	0.09506	0.09530	0.08974	0.09074
C₅Me₅BH₂ (unconstrained)				
Equilibrium Energy	-410.932516	-413.22622	-411.90123	N/A
Zero-Point Energy	0.25997	0.25977	0.24790	N/A
C₅Me₅BH₂ (η^2-optimized)				
Equilibrium Energy	-410.92085	-413.21714	-411.90010	N/A
Zero-Point Energy	0.25929	0.25908	0.24773	N/A
C₅Me₅BF₂ (unconstrained)				
Equilibrium Energy	-607.76936	-611.10052	-608.96669	N/A
Zero-Point Energy	0.24969	0.24888	0.23736	N/A
C₅Me₅BF₂ (η^2-optimized)				
Equilibrium Energy	-607.74224	-611.07104	-608.96669	N/A
Zero-Point Energy	0.24745	0.24664	0.23630	N/A
C₅Me₅BCl₂ (unconstrained)				
Equilibrium Energy	-1324.68991	-1331.13955	-1325.92565	N/A
Zero-Point Energy	0.24558	0.24542	0.23332	N/A
C₅Me₅BCl₂ (η^2-optimized)				
Equilibrium Energy	-1324.66772	-1331.13955	-1325.92565	N/A
Zero-Point Energy	0.24345	0.24542	0.23332	N/A

(Note: (1) C₅H₅BH₂ optimized to an η^2 geometry without constraint at RMP2/6-31G*.)

Table 3
C₅H₅BH₂ optimized geometry - η^1 and *abgekippt* results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1	1.593	1.587	1.616
C1-C2	1.527	1.510	1.523
C2-C3	1.340	1.338	1.386
C3-C4	1.465	1.461	1.458
C4-C5	1.337	1.335	1.378
C1-C5	1.502	1.494	1.498
B-H6	1.186	1.188	1.195
B-H7	1.191	1.192	1.200
C1-H1	1.082	1.086	1.088
C2-H2	1.069	1.073	1.083
C3-H3	1.069	1.074	1.084
C4-H4	1.069	1.074	1.083
C5-H5	1.070	1.074	1.083
Other distances			
B-C2	2.323	2.336	2.114
B-C5	2.546	2.567	2.520
B-H1	2.276	2.247	2.320
Selected angles			
B-C1-C2	96.2	97.9	84.6
B-C1-C5	110.7	112.8	108.0
B-C1-H1	115.3	113.1	116.8
H6-B-C1	119.0	120.2	118.4
H7-B-C1	120.9	120.3	120.2
H6-B-H7	120.0	119.4	121.3
H1-C1-C2	114.5	113.8	118.0
H1-C1-C5	115.8	115.1	119.9
Selected dihedral angles			
H6-B-C1-H1	-158.6	-157.3	-156.6
H7-B-C1-H1	24.9	26.4	22.0

(Note: RMP2/6-31G* optimization resulted in an η^2 geometry which is listed on Table 4)

Table 4
C₅H₅BH₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RHF/6-311G**	RMP2/3-21G*	RMP2/6-31G*
Bond distances					
B-C1 (= B-C2)	1.782	1.752	1.757	1.786	1.737
C1-C2	1.472	1.455	1.454	1.480	1.450
C2-C3	1.414	1.411	1.411	1.440	1.424
C3-C4	1.393	1.390	1.390	1.414	1.400
C4-C5	1.393	1.390	1.390	1.414	1.400
C5-C1	1.414	1.411	1.410	1.440	1.424
B-H6	1.179	1.182	1.181	1.191	1.189
B-H7	1.189	1.193	1.193	1.199	1.197
C1-H1	1.068	1.073	1.072	1.082	1.084
C2-H2	1.068	1.073	1.072	1.082	1.084
C3-H3	1.069	1.074	1.074	1.083	1.086
C4-H4	1.067	1.0737	1.072	1.082	1.084
C5-H5	1.069	1.073	1.073	1.083	1.086
Other distances					
B-C5	2.538	2.513	2.513	2.567	2.513
B-H1	2.389	2.350	2.348	2.407	2.338
Selected angles					
B-C1-C2	65.6	65.5	65.6	65.5	65.3
B-C1-C5	104.6	104.7	104.6	105.0	104.9
B-C1-H1	111.5	110.3	109.8	111.8	109.8
H6-B-C1	116.0	117.7	117.5	114.7	116.4
H7-B-C1	115.8	115.2	115.1	116.4	115.8
H7-B-H6	122.6	121.4	121.8	123.4	122.2
H1-C1-C2	124.9	125.3	125.4	124.4	124.9
H1-C1-C5	125.9	125.9	125.9	125.8	126.0
Selected dihedrals					
H6-B-C1-H1	-137.5	-135.6	-135.5	-138.8	-136.6
H7-B-C1-H1	17.1	18.2	18.6	16.0	17.4
H6-B-C4-H4	-0.1	0.0	0.0	0.0	0.0
H7-B-C4-H4	180.0	-179.9	180.0	-179.9	180.0

(Note: RMP2/6-31G* results represents unconstrained optimization. All other results represent η^2 -optimization.)

Semi-empirical and *Ab Initio* Studies of $C_5H_5BF_2$

MNDO Calculations for $C_5H_5BF_2$

A molecule of $C_5H_5BF_2$ (**2**) was constructed using HyperChem, and optimized using MNDO. The resulting geometry is shown in Figure 44. The energy was reported by HyperChem as -1430.9 kcal/mole and the F-B-C-H dihedral angle is -28.9 degrees. Alternative starting point geometries were created with the F-B-C-H dihedral angle set to 0. and 90. degrees. These molecules were optimized without constraints, producing molecules retaining the initial symmetry. The energies of the η^1 -retention and η^1 -inversion geometries were -1430.7 and -1430.8 kcal/mole, respectively. Since both of these values are higher than the energy of the molecule shown in Figure 44, the actual MNDO optimized equilibrium geometry is therefore different from that reported by Schoeller [1] assuming C_s symmetry.

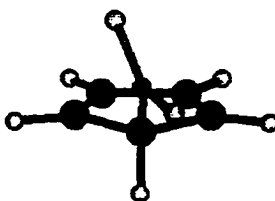


Figure 44
Geometry of $C_5H_5BF_2$, optimized using MNDO.

Another molecule was created, and η^2 -optimized with a boron-carbon bond length of 1.75 Å. The energy was reported as -1397.1 kcal/mole. The energy increased when the molecule was η^2 -optimized with a bond length of either 1.74 or 1.76 Å.

RHF/3-21G* Calculations for C₅H₅BF₂

A Z-matrix was constructed for C₅H₅BF₂ using parameters taken from the molecule optimized using MNDO. This molecule was then optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 45. A summary of selected distances and angles for this molecule is presented in Table 5. The geometry was found to be *abgekippt*. Although the geometry of this molecule differs from the geometry of *abgekippt* C₅H₅BH₂ at the same level. The B-C1 bond distance is over 1% shorter, and the other bond distances within the ring are all within 1% of the distances in C₅H₅BH₂. The B-C2, B-C5, and B-H1 distances are all over 1% different, as are the angles involving C1 and these atoms. These differences indicate that the position of the boron atom has shifted away from C2 and C5 and toward H1. The BF₂ substituent's orientation is also substantially different than that of the BH₂ substituent in C₅H₅BH₂. The

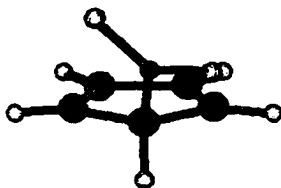


Figure 45
Geometry of C₅H₅BF₂,
(optimized at the RHF/3-21G* level).

F7-B-C1-H1 dihedral angle is nearly 60 degrees, over twice as large as the corresponding H7-B-C1-H1 dihedral angle in C₅H₅BH₂. Although both C₅H₅BF₂ and C₅H₅BH₂ exhibit *abgekippt* geometry at this level of theory, the C₅H₅BF₂ geometry more closely resembles

an η^1 -retention geometry than does $\text{C}_5\text{H}_5\text{BF}_2$.

The $\text{C}_5\text{H}_5\text{BF}_2$ molecule was η^2 -optimized for two different starting geometries. A molecule was built using HyperChem, and was η^2 -optimized using MNDO. Geometric parameters from this molecule were entered into a Z-matrix for an η^2 -constrained $\text{C}_5\text{H}_5\text{BF}_2$ molecule. This molecule was then η^2 -optimized at the RHF/3-21G* level using Gaussian 94W. The resulting geometry is shown in Figure 46. A summary of selected distances and angles for this molecule is presented in Table 6. A new Z-matrix was written for an η^2 -constrained $\text{C}_5\text{H}_5\text{BF}_2$ molecule, with parameters taken from $\text{C}_5\text{H}_5\text{BH}_2$ optimized at the RHF/3-21G* level. This geometry was also η^2 -optimized at the RHF/3-21G* with the boron-fluorine distance set to 1.35 Å. The resulting geometry was essentially identical to that shown in Figure 46. The energies of these two geometries differed by less than 0.00001 Hartrees.

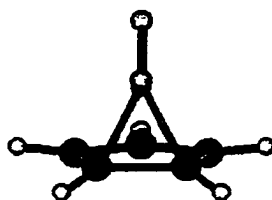


Figure 46
Geometry of $\text{C}_5\text{H}_5\text{BF}_2$,
(η^2 -optimized at the RHF/3-21G* level)

The η^2 -optimized geometry for this molecule resembles the η^2 -optimized geometry of $\text{C}_5\text{H}_5\text{BH}_2$ at this level of theory, although the boron atom is closer to C1, H1, C2, and H2,

and further from the other carbons of the ring. The C1-C2 bond distance is also longer in $C_5H_5BF_2$ than in $C_5H_5BH_2$. Other geometric parameters for the boron atom and the ring resembled those of $C_5H_5BH_2$ at this level. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 16.17 kcal/mole.

The F-B-C-H dihedral angle was constrained to values between 0 and 90 degrees. The otherwise unconstrained $C_5H_5BF_2$ molecule was optimized. A plot of the energy vs. the F7-B-C1-H1 dihedral angle is shown in Figure 47. This plot indicates that, unlike $C_5H_5BF_2$ optimized at the RHF/3-21G* level, the η^1 -retention geometry is lower in energy than the η^1 -inversion geometry. The difference between the lowest energy and highest energy data points on this graph is only 0.00130 Hartrees, much less than in the corresponding graph for $C_5H_5BH_2$ (Figure 21). In the equilibrium geometry, the boron atom is shifted nearer to H1. It is located less asymmetrically relative to C2 and C5 than it is at other angles.

Frequency analysis of this molecule yielded no imaginary frequencies, and three frequencies under 400 cm^{-1} (18.68 cm^{-1} , 114.10 cm^{-1} , and 154.65 cm^{-1}). Animation of the lowest frequency mode showed rotation of the BF_2 substituent. Animation of the other two modes showed "bond wagging" motion. The low frequencies, relative to $C_5H_5BH_2$, would suggest that there is less interaction of the BX_2 substituent with the ring.

A $C_5H_5BF_2$ molecule was also η^5 -optimized using Spartan 5.0, with all boron-carbon distances constrained to 1.8, 2.0, and 3.0 Å. Of these three, the η^5 -molecule with

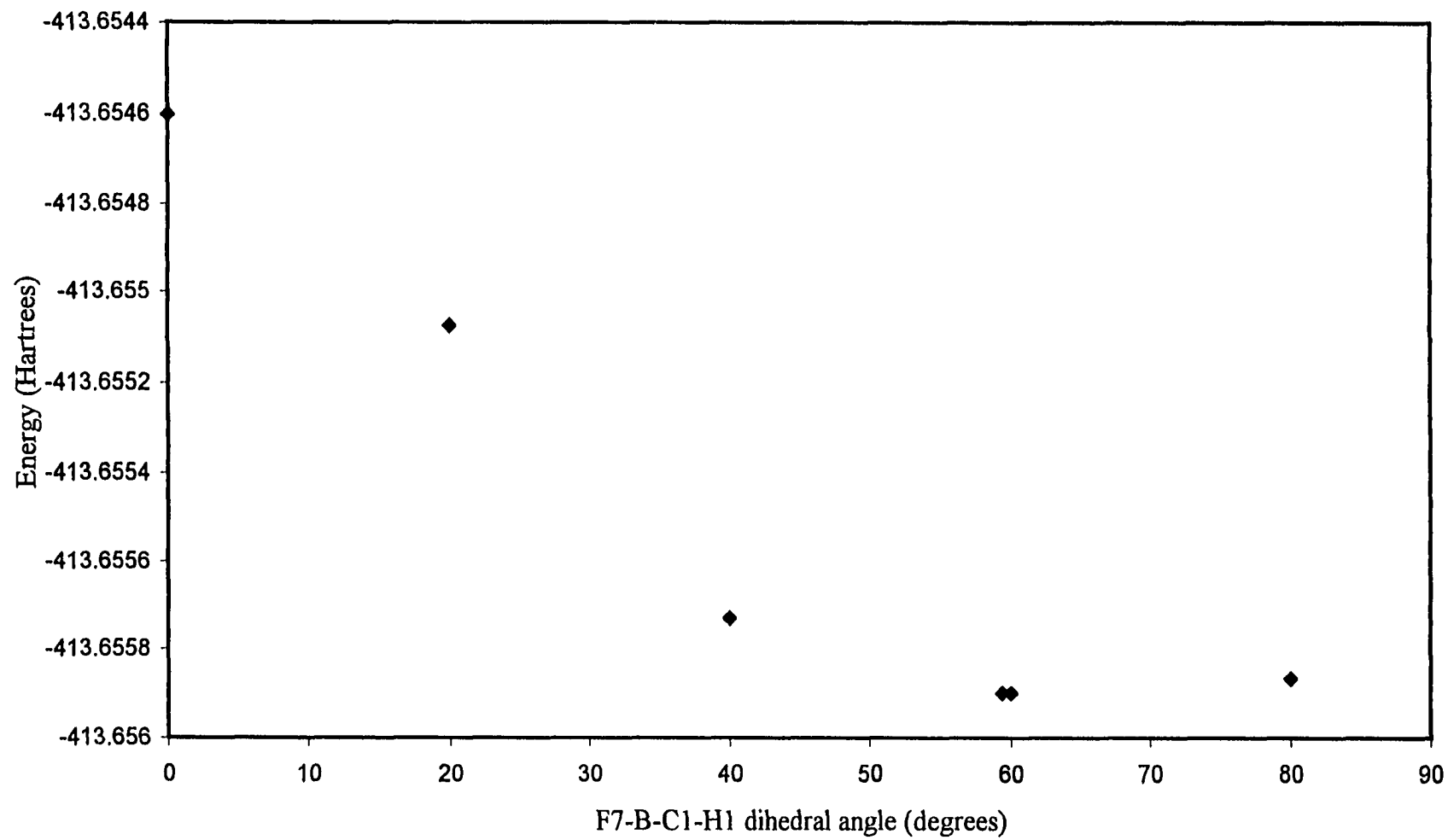


Figure 47
Energy (RHF/3-21G*) vs. constrained
F7-B-C1-H1 dihedral angle for otherwise optimized $C_5H_5BF_2$

boron-carbon distances constrained to 2.0 Å had the lowest energy (-413.54399 Hartrees). This molecule was then optimized, without constraints, to produce a geometry and energy essentially identical to the molecule shown in Figure 45. This result suggests that there is no stable η^5 local minimum for this molecule at this level of theory.

RHF/6-31G* Calculations for $C_5H_5BF_2$

A $C_5H_5BF_2$ molecule was optimized at the RHF/6-31G* level using Spartan 5.0. The resulting geometry is shown in Figure 48. This geometry was also optimized using Gaussian 94W, the energy calculated agreed with the value reported by Spartan 5.0 within 0.00002 Hartrees. Unlike the optimized geometries predicted for $C_5H_5BF_2$ using MNDO and at the RHF/3-21G* level, this molecule has an η^1 -retention geometry. The distances and angles, listed in Table 5, indicate that this molecule is approximately symmetrical. Both the B-H1 distances and the B-C1-H1 angles are smaller for the molecule optimized at the RHF/6-31G* level than for the molecule optimized at the RHF/3-21G* level.

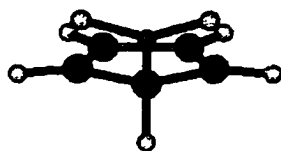


Figure 48
Geometry of $C_5H_5BF_2$, (optimized at
the RHF/6-31G* level without constraints).

Additionally, the boron-fluorine distances are shorter and the F-B-F angle is wider

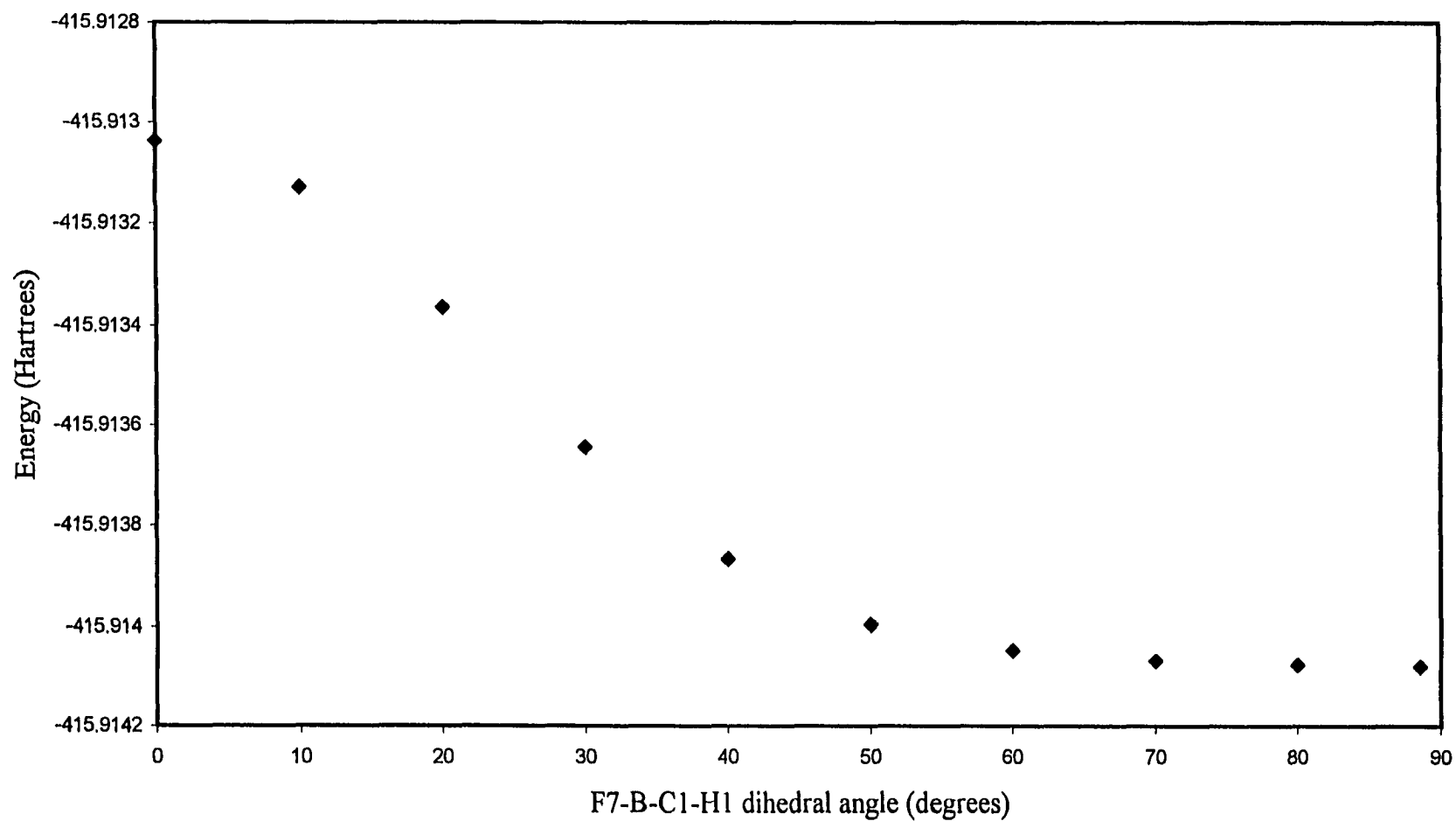


Figure 49
Energy (RHF/6-31G*) vs. constrained
F7-B-C1-H1 dihedral angle for otherwise optimized $C_5H_5BF_2$

compared to the molecule optimized at the RHF/3-21G* level. The F-B-C-H dihedral angle was constrained to values between 0. and 90. degrees. The otherwise unconstrained $C_5H_5BF_2$ molecule was optimized. The plot of the energy vs. the F-B-C-H dihedral angle is shown in Figure 49. This graph indicates that the η^1 -retention geometry is the lowest energy conformation. The difference between the lowest energy and highest energy data points on this graph is 0.00104 Hartrees. The molecule shown in Figure 46 was η^2 -optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 50. The geometry in general resembles the molecule η^2 -optimized at the RHF/3-21G* level, although the C1-C2 distance is over 1% longer. Additionally, the boron-fluorine distances are shorter in this molecule and the F-B-F angle is wider compared to the

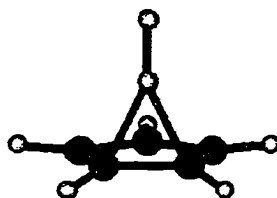


Figure 50
Geometry of $C_5H_5BF_2$,
(η^2 -optimized at the RHF/6-31G* level).

molecule η^2 -optimized at the RHF/3-21G* level. The difference in energy (corrected for zero-point energy) between the η^1 -retention molecule, optimized without constraints, and the η^2 -optimized molecule is 17.57 kcal/mole.

An η^5 geometry for this molecule was optimized using Spartan 5.0 at the RHF/6-

31G* level without constraints. Although the optimization was terminated before it reached convergence, the geometry that was produced from this incomplete optimization was recognizably η^1 . This result suggests that there is no stable η^5 local minimum for this molecule at this level of theory.

RMP2/3-21G* Calculations for $C_5H_5BF_2$

The molecule shown in Figure 45 was optimized at the RMP2/3-21G* level. The resulting geometry is shown in Figure 51. Like the RHF/3-21G* geometry, and unlike the RHF/6-31G* geometry, this geometry is *abgekippt*. The F-B-C1-H1 dihedral angles, however, more closely resemble those seen in $C_5H_5BH_2$ at this level than those seen in either of the RHF optimized geometries obtained for $C_5H_5BF_2$. The calculated energy was -414.37942 Hartrees.

Frequency analysis on the molecule shown in Figure 51 yielded no imaginary frequencies, five modes with frequencies below 400 cm^{-1} (40.5198 cm^{-1} , 99.8357 cm^{-1} , 158.3762 cm^{-1} , 344.3325 cm^{-1} , and 388.3708 cm^{-1}), and a zero-point vibrational energy of 1.21866 Hartrees.

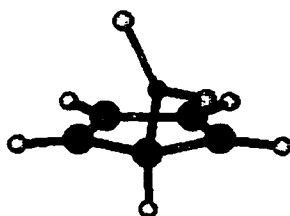


Figure 51
Geometry of $C_5H_5BF_2$,
(optimized at the RMP2/3-21G* level).

A Z-matrix was created for $C_5H_5BF_2$ with the F-B-C-H dihedral angle set to 85 degrees. This geometry was intended to provide a starting point that would optimize to an η^1 -retention geometry. After this geometry was optimized at this level, the energy and the F-B-C-H dihedral angles were essentially identical to those of the molecule shown in Figure 51. This result would indicate that the η^1 -retention geometry is not a local minimum for this molecule at this level of theory.

A Z-matrix was constructed using parameters taken from the $C_5H_5BF_2$ molecule η^2 -optimized at the RHF/3-21G* level. This molecule was then η^2 -optimized at the RMP2/3-21G* level. The resulting geometry is shown in Figure 52. This geometry resembles the η^2 -optimized geometry obtained at both the RHF/3-21G* and the RHF/6-31G* levels, although the carbon-carbon and the boron-fluorine bond lengths are uniformly somewhat longer. The carbon-carbon bond lengths were similar to the values seen in η^2 -optimized $C_5H_5BH_2$ at this level of theory. The difference in energy (corrected

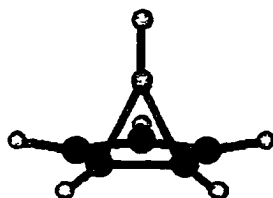


Figure 52
Geometry of $C_5H_5BF_2$,
(η^2 -optimized at the RMP2/3-21G* level).

for zero-point) between the *abgekippt* molecule, optimized without constraints, and the

η^2 -optimized molecule was 10.81 kcal/mole.

RMP2/6-31G* Calculations for C₅H₅BF₂

The molecule obtained at the RMP2/3-21G* level was re-optimized at the RMP2/6-31G* level. The resulting geometry is shown in Figure 53. This geometry is also *abgekippt*. Compared with the results obtained at the RMP2/3-21G* level, the boron

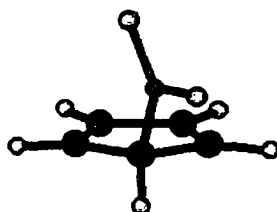


Figure 53
Geometry of C₅H₅BF₂, (optimized at the
RMP2/6-31G* level from *abgekippt* starting point).

atom is shifted closer to C2, C5, and H1 atoms, the H1 atom is shifted upwards towards the plane of the ring, and the C1-C2, C3-C4, C1-C5, and boron-fluorine distances are also over 1% shorter in this molecule.

An η^1 -retention starting point geometry was also optimized for this molecule at the RMP2/6-31G* level. The resulting geometry is shown in Figure 54. The energy for this molecule is 0.00196 Hartrees higher than that of the *abgekippt* molecule shown in Figure 53. This geometry therefore does not represent the global minimum energy conformation for this molecule at this level of theory.

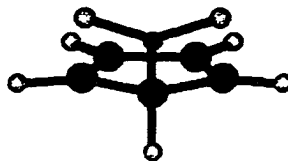


Figure 54
Geometry of $C_5H_5BF_2$, (optimized at the
RMP2/6-31G* level from η^1 -retention starting point).

The molecule previously η^2 -optimized at the RHF/6-31G* level was also η^2 -optimized at the RMP2/6-31G* level. The resulting geometry is shown in Figure 55. The geometry resembles the η^2 -optimized geometry found at the RMP2/3-21G* level,

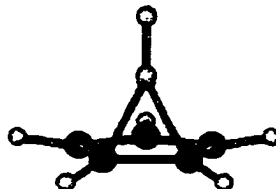


Figure 55
Geometry of $C_5H_5BF_2$,
(η^2 -optimized at the RMP2/6-31G* level).

although the B-C1, B-C2, C1-C2, B-H1 and boron-fluorine distances are somewhat shorter and the B-C1-H1 angle is smaller. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 4.96 kcal/mole.

Table 5
C₅H₅BF₂ optimized geometry - η^1 and *abgekippt* results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*	RMP2/6-31G*
Bond distances				
B-C1	1.564	1.578	1.575	1.576
C1-C2	1.531	1.508	1.549	1.505
C2-C3	1.331	1.330	1.363	1.362
C3-C4	1.478	1.472	1.484	1.452
C4-C5	1.331	1.330	1.363	1.361
C1-C5	1.513	1.508	1.522	1.488
B-F6	1.342	1.312	1.358	1.331
B-F7	1.345	1.312	1.361	1.337
C1-H1	1.090	1.096	1.096	1.096
C2-H2	1.069	1.073	1.083	1.085
C3-H3	1.069	1.074	1.083	1.085
C4-H4	1.069	1.074	1.083	1.085
C5-H5	1.069	1.073	1.083	1.085
Other distances				
B-C2	2.504	2.595	2.437	2.341
B-C5	2.581	2.594	2.578	2.545
B-H1	2.195	2.148	2.236	2.209
Selected angles				
B-C1-C2	108.0	114.4	102.5	98.9
B-C1-C5	114.0	114.4	112.7	112.3
B-C1-H1	110.3	105.5	112.5	110.3
F6-B-C1	124.0	121.7	123.5	122.9
F7-B-C1	121.1	121.7	121.4	120.2
F6-B-F7	114.9	116.5	115.0	116.9
H1-C1-C2	110.4	110.1	112.0	114.3
H1-C1-C5	111.8	110.1	113.9	116.1
Selected dihedral angles				
F6-B-C1-H1	-120.7	-88.4	-145.7	-152.6
F7-B-C1-H1	59.4	88.6	36.2	29.6

Table 6
C₅H₅BF₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*	RMP2/6-31G*
Bond distances				
B-C1 (= B-C2)	1.746	1.760	1.767	1.747
C1-C2	1.497	1.471	1.507	1.469
C2-C3	1.409	1.406	1.431	1.419
C3-C4	1.391	1.389	1.414	1.400
C4-C5	1.391	1.389	1.414	1.400
C5-C1	1.409	1.406	1.431	1.419
B-F6	1.354	1.319	1.366	1.340
B-F7	1.357	1.327	1.369	1.347
C1-H1	1.069	1.074	1.083	1.085
C2-H2	1.069	1.074	1.083	1.085
C3-H3	1.069	1.073	1.083	1.085
C4-H4	1.067	1.072	1.082	1.084
C5-H5	1.069	1.073	1.083	1.085
Other distances				
B-C5	2.561	2.567	2.609	2.576
B-H1	2.345	2.324	2.369	2.316
Selected angles				
B-C1-C2	64.6	65.3	64.8	65.1
B-C1-C5	108.0	107.8	108.9	108.5
B-C1-H1	110.5	107.8	110.1	107.4
F6-B-C1	122.7	123.1	122.2	122.2
F7-B-C1	115.6	114.1	115.7	114.4
F7-B-F6	114.7	116.4	115.2	116.9
H1-C1-C2	124.1	124.5	123.4	124.1
H1-C1-C5	126.3	126.5	126.2	126.5
Selected dihedrals				
F6-B-C1-H1	-133.2	-132.1	-134.4	-132.9
F7-B-C1-H1	15.8	18.7	15.2	18.0
F6-B-C4-H4	-0.1	0.0	0.0	0.0
F7-B-C4-H4	180.0	180.0	180.0	180.0

Semi-empirical and *Ab Initio* Studies of $C_5H_5BCl_2$

MNDO Calculations for $C_5H_5BCl_2$

A molecule of $C_5H_5BCl_2$ (**3**) was constructed using HyperChem, and optimized at the MNDO level. The resulting geometry is shown in Figure 56. This geometry is *abgekippt*, with a Cl-B-C-H dihedral angle of 27.2 degrees. The energy was reported to be -1335.38 kcal/mole. Alternative starting point geometries were created with Cl-B-C-H dihedral angles set to 0 and 90 degrees. These molecules were optimized without symmetry constraints at the MNDO level, producing molecules essentially identical to the molecule shown in Figure 56. The actual MNDO optimized equilibrium geometry is therefore different from that reported by Schoeller [1] assuming the C_s symmetry.

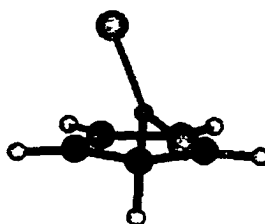


Figure 56
Geometry of $C_5H_5BCl_2$, (optimized using MNDO).

Another $C_5H_5BCl_2$ molecule was constructed using HyperChem with the B-C1 and B-C2 lengths constrained to 1.67 \AA (the η^2 -optimized bond length reported by Schoeller [1]) and η^2 -optimized. The resulting geometry is shown in Figure 57. The energy reported by HyperChem was -1312.0 kcal/mol. The molecule was re-optimized

with both of the constrained bond lengths increased and decreased by 0.01 Å. Both optimizations resulted in molecules with higher reported energy.

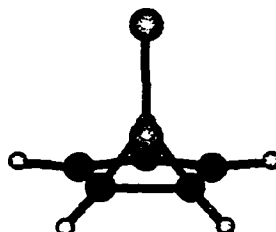


Figure 57
Geometry of $C_5H_5BCl_2$, (η^2 -optimized using MNDO).

RHF/3-21G* Calculations for $C_5H_5BCl_2$

The molecule optimized using MNDO was then optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 58. A summary of selected distances and angles for this molecule is found in Table 7. The geometry was found to be

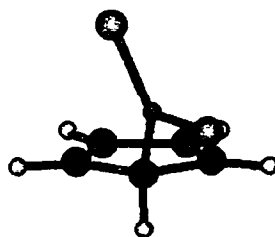


Figure 58
Geometry of $C_5H_5BCl_2$,
(optimized at the RHF/3-21G* level).

abgekippt and resembled the optimized geometry of $C_5H_5BH_2$ at this level. The B-Cl,

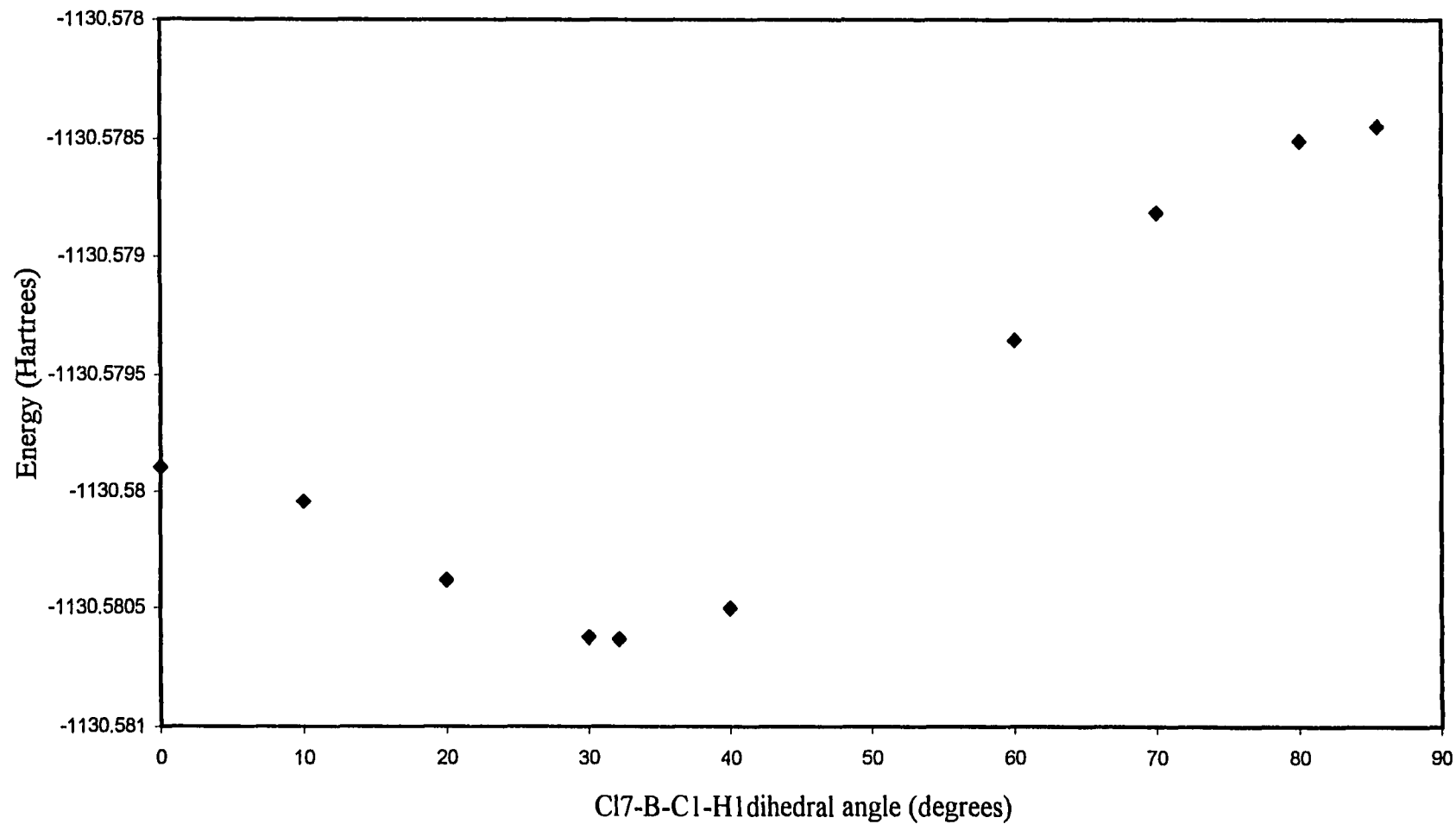


Figure 59
Energy (RHF/3-21G*) vs. constrained
Cl7-B-C1-H1 for otherwise optimized C₅H₅BCl₂

B-C2, and B-C5 distances, and the B-C1-C2 and B-C1-C5 angles are somewhat larger than in $C_5H_5BH_2$. The Cl-B-C1-H1 dihedral angle (for the equatorial chlorine) is 32.1 degrees. This is closer to the corresponding value in $C_5H_5BH_2$ (24.9 degrees) than the corresponding value in $C_5H_5BF_2$ (59.4 degrees). The Cl-B-C-H dihedral angle was constrained to values between 0 and 90 degrees. The otherwise unconstrained $C_5H_5BCl_2$ molecule was optimized. A plot of the energy vs. the Cl-B-C1-H1 dihedral angle is shown in Figure 59. This plot indicates that the *abgekippt* geometry is lower in energy than either the η^1 -retention or the η^1 -inversion geometry. The difference between the lowest energy and highest energy data points on this graph is 0.00218 Hartrees or 1.37 kcal/mole.

The $C_5H_5BCl_2$ molecule was η^2 -optimized at the RHF/3-21G* level, using parameters taken from $C_5H_5BH_2$. The Z-matrix for the η^2 -optimized geometry of $C_5H_5BH_2$ was altered, changing H6 and H7 to chlorine and setting the bond distances to an initial value of 1.8 Å. The resulting geometry is shown in Figure 60. A summary

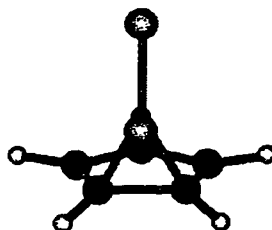


Figure 60
Geometry of $C_5H_5BCl_2$,
(η^2 -optimized at the RHF/3-21G* level).

of selected distances and angles for this molecule is found in Table 8. This geometry is similar to the geometry found for $C_5H_5BF_2$ at this level of theory, although the boron atom is bent slightly farther away from the axis of the ring. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 14.92 kcal/mole.

An η^5 geometry for this molecule was constructed using Spartan 5.0. This molecule was then optimized at the RHF/3-21G* level without constraints, to produce a geometry that was recognizably *abgekippt*. This result suggests that there is no stable η^5 local minimum for this molecule at this level of theory.

RHF/6-31G* Calculations for $C_5H_5BCl_2$

The molecule previously optimized at the RHF/3-21G* level was re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 61. This geometry is

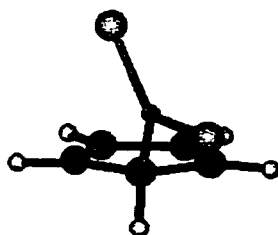


Figure 61
Geometry of $C_5H_5BCl_2$,
(optimized at the RHF/6-31G* level).

abgekippt and resembles the starting point geometry. The most notable difference is that the boron atom is somewhat further away from C2 and somewhat closer to H1.

The molecule η^2 -optimized at the RHF/3-21G* level was also re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 62. In general, this geometry also resembles the starting geometry. The most notable differences here, however, is that the boron atom is closer to C1 and C2, and that H1 is shifted upwards toward the plane of the ring. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 14.99 kcal/mole.

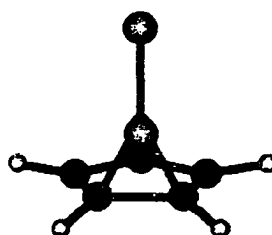


Figure 62
Geometry of $C_5H_5BCl_2$,
(η^2 -optimized at the RHF/6-31G* level).

An η^5 geometry for this molecule was constructed using Spartan 5.0. This molecule was then optimized at the RHF/6-31G* level without constraints, to produce a geometry that was recognizably *abgekippt*. This result suggests that there is no stable η^5 local minimum for this molecule at this level of theory.

RMP2/3-21G* Calculations for C₅H₅BCl₂

The C₅H₅BCl₂ molecule was optimized at the RMP2/3-21G* level, using the RHF/6-31G* optimized geometry of C₅H₅BH₂ as a starting point, but with chlorines substituted for H6 and H7 and with the B-Cl distances set to 1.9 Å. The resulting geometry is shown in Figure 63. The geometry is *abgekippt* and in general resembles the RMP2/3-21G* optimized geometry for C₅H₅BF₂. The boron atom and ring bond distances are all within 1% of the corresponding values for C₅H₅BF₂. The chief differences are that boron atom is bent approximately 2% closer to C2, that H1 is shifted closer to the plane of the ring, and that the Cl-B-Cl-H1 angles are somewhat closer to the symmetric values than the F-B-Cl-H1 angles.

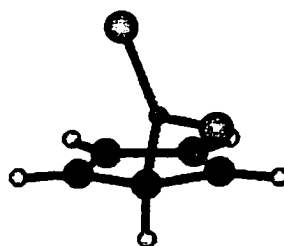


Figure 63
Geometry of C₅H₅BCl₂,
(optimized at the RMP2/3-21G* level).

The molecule previously η^2 -optimized at the RHF/6-31G* level of theory was η^2 -optimized at the RMP2/3-21G*. Initially the molecule was optimized using pseudopotentials for chlorine core electrons, then the molecule was re-optimized without pseudopotentials. The resulting geometry is shown in Figure 64. This geometry is very

similar to the η^2 -optimized geometry for $C_5H_5BF_2$ at this level. The chief difference being that Cl7 was bent closer to the ring and farther away from the other chlorine. The

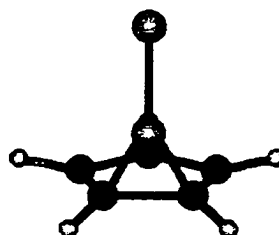


Figure 64
Geometry of $C_5H_5BCl_2$, (η^2 -optimized at the RMP2/3-21G* level using LANL2 pseudopotential).

difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 6.98 kcal/mole.

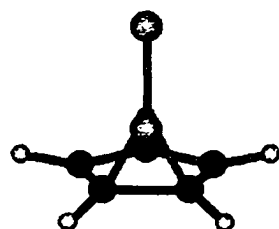


Figure 65
Geometry of $C_5H_5BCl_2$, (η^2 -optimized at the RMP2/3-21G* level without using pseudopotential).

RMP2/6-31G* Calculations for $C_5H_5BCl_2$

The RMP2/3-21G* optimized molecule was re-optimized at the RMP2/6-31G*

level. The resulting geometry is shown in Figure 66. This geometry was found to be *abgekippt*. The boron atom was shifted closer to both C2 and C5 than in the RMP2/3-

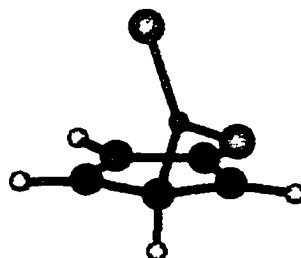


Figure 66
Geometry of $C_5H_5BCl_2$,
(optimized at the RMP2/6-31G* level).

21G* optimized molecule. Also, compared to the molecule optimized at the RMP2/3-21G* level, H1 is shifted upwards towards the plane of the ring and is located closer to the boron atom than it is in the RMP2/3-21G* molecule. The C1-C2, C3-C4, and C1-C5 distances are over 1% shorter in this molecule.

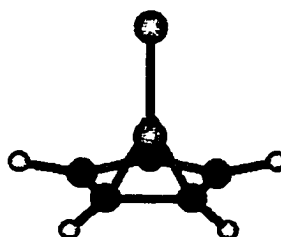


Figure 67
Geometry of $C_5H_5BCl_2$,
(η^2 -optimized at the RMP2/6-31G* level).

The RMP2/3-21G* η^2 -optimized molecule was also η^2 -optimized at the RMP2/6-31G* level. The resulting geometry is shown in Figure 67. The geometry resembles the η^2 -optimized geometry at the RMP2/3-21G* level, although the B-C1, B-C2, C1-C2, B-H1 and B-C5 distances are somewhat shorter and the B-C1-H1 angle is smaller. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 2.27 kcal/mole.

Table 7
C₅H₅BCl₂ optimized geometry - η^1 and *abgekippt* results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*	RMP2/6-31G*
Bond distances				
B-C1	1.576	1.581	1.584	1.577
C1-C2	1.537	1.519	1.550	1.505
C2-C3	1.331	1.331	1.366	1.365
C3-C4	1.476	1.469	1.481	1.449
C4-C5	1.331	1.330	1.365	1.363
C1-C5	1.512	1.503	1.519	1.484
B-Cl6	1.757	1.757	1.758	1.746
B-Cl7	1.769	1.767	1.769	1.756
C1-H1	1.086	1.089	1.095	1.095
C2-H2	1.069	1.073	1.083	1.084
C3-H3	1.069	1.074	1.084	1.086
C4-H4	1.069	1.084	1.083	1.085
C5-H5	1.069	1.073	1.083	1.085
Other distances				
B-C2	2.457	2.484	2.377	2.282
B-C5	2.604	2.621	2.596	2.565
B-H1	2.215	2.189	2.245	2.215
Selected angles				
B-C1-C2	104.2	106.5	98.7	95.5
B-C1-C5	114.9	116.4	113.5	113.8
B-C1-H1	111.2	108.8	112.5	110.7
Cl6-B-C1	122.8	123.2	112.5	123.3
Cl7-B-C1	119.2	119.2	119.1	118.6
Cl6-B-Cl7	117.9	117.5	118.3	118.1
H1-C1-C2	111.3	110.9	113.3	114.8
H1-C1-C5	112.7	111.9	114.8	116.3
Selected dihedral angles				
Cl6-B-C1-H1	-150.4	-148.3	-151.8	-152.7
Cl7-B-C1-H1	32.1	34.0	30.3	28.0

Table 8
C₅H₅BCl₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G* (a)	RMP2/3-21G* (b)	RMP2/6-31G*
Bond distances					
B-C1 (= B-C2)	1.753	1.734	1.776	1.767	1.743
C1-C2	1.493	1.473	1.498	1.499	1.465
C2-C3	1.415	1.412	1.436	1.436	1.421
C3-C4	1.390	1.388	1.414	1.413	1.400
C4-C5	1.390	1.388	1.414	1.413	1.400
C5-C1	1.415	1.412	1.436	1.436	1.421
B-Cl6	1.784	1.790	1.776	1.791	1.767
B-Cl7	1.799	1.801	1.787	1.802	1.776
C1-H1	1.069	1.073	1.083	1.083	1.085
C2-H2	1.069	1.072	1.083	1.083	1.085
C3-H3	1.069	1.073	1.083	1.083	1.086
C4-H4	1.067	1.072	1.082	1.082	1.084
C5-H5	1.069	1.073	1.083	1.083	1.086
Other distances					
B-C5	2.598	2.583	2.637	2.629	2.604
B-H1	2.350	2.323	2.369	2.365	2.315
Selected angles					
B-C1-C2	64.8	64.9	65.1	64.9	65.1
B-C1-C5	109.7	109.9	109.9	109.9	110.3
B-C1-H1	110.4	109.4	109.5	109.8	107.6
Cl6-B-C1	123.9	125.0	122.6	122.8	123.3
Cl7-B-C1	113.5	113.5	113.8	114.1	113.8
Cl7-B-Cl6	115.8	114.6	117.1	116.4	116.4
H1-C1-C2	124.4	109.4	123.8	123.9	124.5
H1-C1-C5	125.3	109.9	125.5	125.5	125.4
Selected dihedrals					
Cl6-B-C1-H1	-132.2	-130.6	-133.6	-133.3	-131.7
Cl7-B-C1-H1	17.6	18.5	17.3	17.0	18.8
Cl6-B-C4-H4	0.0	0.0	0.0	0.0	0.0
Cl7-B-C4-H4	179.9	-179.9	180.0	-179.9	-179.9

(a) RMP2/3-21G* without pseudopotential. (b) RMP2/3-21G* with LANL2 pseudopotential

Semi-empirical and *Ab Initio* Studies of $C_5Me_5BH_2$

MNDO Calculations for $C_5Me_5BH_2$

A molecular geometry for pentamethylcyclopentadienylborane (4) was constructed using HyperChem. The geometry was then optimized using MNDO. The resulting geometry is shown in Figure 68. This geometry is not symmetrical, and therefore differs from the results previously published by Schoeller [1]. The η^1 -inversion and η^1 -retention starting point geometries both optimized to an *abgekippt* conformation.

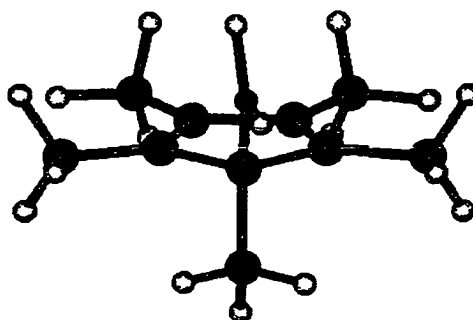


Figure 68
Geometry of $C_5Me_5BH_2$, (optimized using MNDO).

The orientation of the methyls in Figure 68 approximates the “audience” conformation described in Chapter 2 on page 40. The planar hydrogens of methyls 2 and 5 are tipped upward slightly toward the boron atom. The dihedral angles of these two methyls were similar but not symmetrical.

Different starting point geometries for this molecule were optimized in an attempt to find other local minima with different orientations of the methyl groups. The molecule

in Figure 68 was then altered so that the dihedral angles of the methyl hydrogens were rotated 60 degrees, and the molecule was subsequently re-optimized. This was done for each methyl group individually, for each two adjacent methyls, for methyl 1 with both of its two neighboring methyls, and for all five methyls simultaneously. In each case the re-optimized geometry returned to the orientation described above for the molecule shown in Figure 68. No other local minima involving different orientations of the methyl groups were found here for this molecule at this level of theory.

A new model for this molecule was constructed using HyperChem with the B-C1 and B-C2 bond distances constrained to 1.69 Å and η^2 -optimized. The resulting geometry is shown in Figure 69. The calculated energy for this molecule was lower than the calculated energy for the same molecule optimized with the B-C1 and B-C2 bond lengths constrained to 1.68 Å or 1.70 Å. The orientation of the methyls approximated the “fence and gate” conformation described in Chapter 2 on page 42.

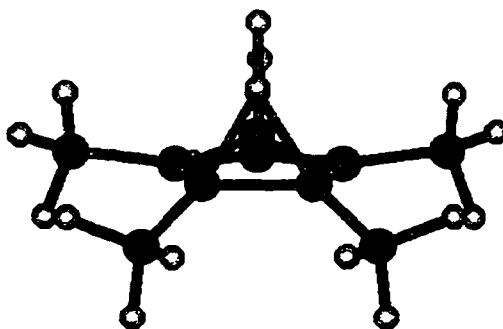


Figure 69
Geometry of $C_5Me_5BH_2$, (η^2 -optimized using MNDO).

The geometry of the molecule shown in Figure 69 was altered so that the methyl

dihedral angles were rotated 60 degrees, and the molecule was then re-optimized. This was done for each methyl individually and for all methyls simultaneously. In each case the re-optimized geometry returned to the original orientation. No other local minima involving different orientations of the methyl groups were found for this molecule at this level of theory.

RHF/3-21G* Calculations for $C_5Me_5BH_2$

The geometry shown in Figure 68 was optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 70. A summary of selected distances and angles for this molecule is presented in Table 9. The optimized geometry and energy were essentially identical for molecules optimized with Spartan 5.0 and Gaussian 94W. The

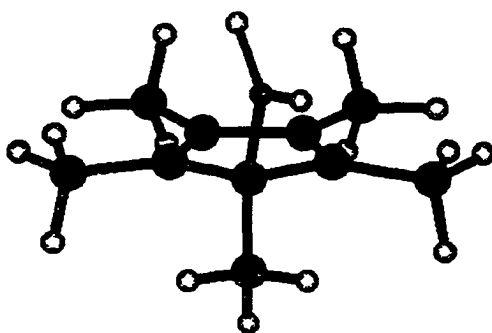


Figure 70
Geometry of $C_5Me_5BH_2$,
(optimized at the RHF/3-21G* level).

geometry was found to be *abgekippt*. The bond distances and angles were almost all within 1% of the corresponding distances and angles of $C_5H_5BH_2$ optimized at this level. The only exceptions were that the B-C1-C5 angle was smaller and the B-C1-Me1 angle

was larger than the corresponding B-C1-C5 and B-C1-H1 angles of $C_5H_5BH_2$. The methyls are oriented in the "chat" conformations as described in Chapter 2 on page 41, although the planar hydrogens of methyls 2 and 5 are tipped upward slightly.

Different starting point geometries for this molecule were optimized in an attempt to find other local minima with different orientations of the methyl groups. The dihedral angle of the methyl hydrogens was rotated 60 degrees, and the molecule was re-optimized. This was done for each methyl group individually, for methyls 1 and 2 simultaneously, for methyls 2 and 3, for methyls 3 and 4, for methyls 2 through 4, for methyls 2 through 5, and for all five methyls. All except one returned to a geometry with the same energy as the molecule shown in Figure 70 (within 0.00005 Hartrees) and the same orientation of the methyls. The exception was the starting point with methyl 2 rotated. The optimized orientation for these hydrogen was rotated approximately 56 degrees further than the orientation exhibited by the molecule in Figure 70, and the energy was 0.0006 Hartrees higher than in that of the molecule shown in Figure 70. Frequencies calculated for this alternate geometry yielded one imaginary frequency (reported by Gaussian 94W as -70.8058 cm^{-1}), indicating that this geometry was not a local minimum. The geometry in Figure 70 represents the lowest energy conformation of this molecule at this level of theory found from these starting points.

Another starting point geometry was produced by rotating the BH_2 substituent of the molecule in Figure 68 to produce an η^1 -inversion starting geometry. This starting point geometry was then optimized at the RHF/3-21G* level. The resulting geometry was visibly *abgekippt*.

An additional starting point geometry was produced by rotating the BH₂ substituent of the molecule in Figure 68 to produce an η^1 -retention starting point. This geometry was also optimized at the RHF/3-21G* level. The geometry remained η^1 -retention, and the methyl groups rotated to a “chat” conformation. This geometry was 1.91 kcal/mole higher in energy than the *abgekippt* geometry shown in Figure 70. Frequency analysis yielded one imaginary frequency (reported as -36.9618 cm^{-1}) for this geometry. This conformation, therefore, does not represent a local minimum.

An η^2 geometry was constructed for this molecule by substituting methyls for the ring hydrogens of the C₅H₅BH₂ molecule previously η^2 -optimized at this level of theory. The resulting molecule was then η^2 -optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 71. A summary of selected distances and angles for this

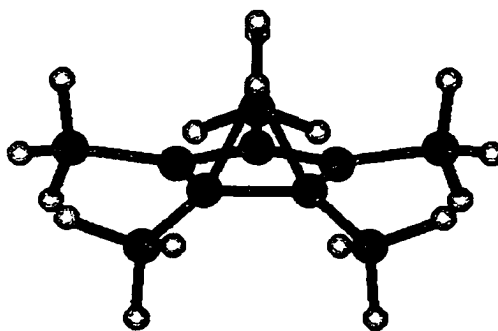


Figure 71
Geometry of C₅Me₅BH₂,
(η^2 -optimized at the RHF/3-21G* level).

molecule is presented in Table 10. In general, this geometry resembled the geometry of η^2 -optimized C₅H₅BH₂. However, the B-C1 distance was somewhat shorter than in

$C_5H_5BH_2$. On the other hand, the B-C1-Me1 and H6-B-C1 bond angles were slightly larger than the corresponding angles in $C_5H_5BH_2$, and the B-C1-C5 bond angle was smaller than in $C_5H_5BH_2$.

The orientation of the methyls in η^2 -optimized $C_5Me_5BH_2$ approximates the “archive” conformation described in Chapter 2. The planar hydrogens of methyls 3 and 5 are tipped upward approximately 7. degrees from the ring. This rotation is much less than that seen in the molecule η^2 -optimized using MNDO.

The molecule shown in Figure 71 was then altered so that the orientation of every methyl was rotated by 60 degrees. This altered geometry was again η^2 -optimized. The methyl orientations and the energy returned to that exhibited by the original molecule. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 6.89 kcal/mole.

An η^5 geometry for this molecule was constructed using Spartan 5.0. This molecule was then optimized at the RHF/3-21G* level without constraints. The resulting geometry was recognizably *abgekippt*. This result suggests that there is no stable η^5 local minimum for this molecule at this level of theory.

RHF/6-31G* Calculations for $C_5Me_5BH_2$

The molecule previously optimized at the RHF/3-21G* level was then optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 72. This geometry is *abgekippt* and resembles the starting point geometry. The only notable difference is

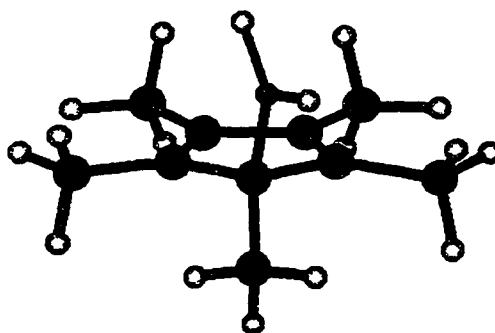


Figure 72
Geometry of $C_5Me_5BH_2$, (optimized at the RHF/6-31G* level using optimized geometry at the RHF/3-21G* level as a starting geometry).

that methyl 1 is shifted upward toward the plane of the ring somewhat, relative to the geometry found at the RHF/3-21G* level. The orientation of the hydrogens on the methyls approximated the “chat” conformation seen in the starting point geometry.

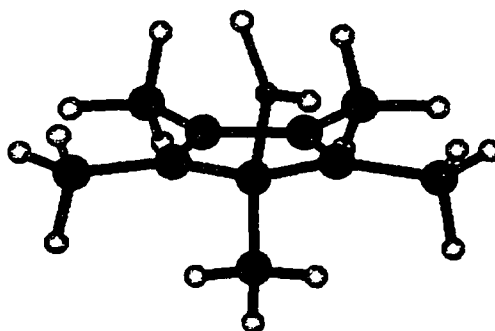


Figure 73
Geometry of $C_5Me_5BH_2$, (optimized at the RHF/6-31G* level, using η^1 -retention geometry as the starting geometry).

An η^1 -retention starting point geometry was also constructed using HyperChem, and optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 73. The energy and geometry are essentially identical to that exhibited by the molecule

shown in Figure 72.

The $\text{C}_5\text{Me}_5\text{BH}_2$ molecule, η^2 -optimized at the RHF/3-21G* level, was re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 74. The geometry resembles the starting geometry. The chief differences are that the boron atom is shifted slightly closer to C1 and C2, that the H6-B-C1 angle is somewhat larger, and that the H6-B-H7 angle is somewhat smaller than in the molecule η^2 -optimized at the RHF/3-21G* level. The orientation of the methyl groups resembles the “archive” conformation seen in the starting geometry. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 5.26 kcal/mole.

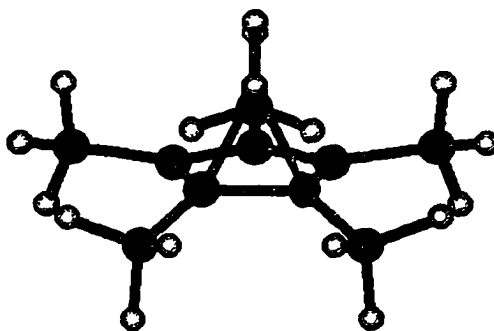


Figure 74
Geometry of $\text{C}_5\text{Me}_5\text{BH}_2$,
(η^2 -optimized at the RHF/6-31G* level).

An η^5 geometry for this molecule was constructed using Spartan 5.0. This molecule was optimized without constraints at the then RHF/6-31G* level to produce a geometry that was recognizably *abgekippt*. This result suggests that there is no stable η^5

local minimum for this molecule at this level of theory.

RMP2/3-21G* Calculations for $C_5Me_5BH_2$

The molecule optimized at the RHF/3-21G* level was re-optimized at the RMP2/3-21G* level. The resulting geometry is shown in Figure 75. This geometry is recognizably *abgekippt*. The boron atom is shifted over 10% closer to C2 than in either of the molecules optimized at the RHF/3-21G* or the RHF/6-31G* level. It is also somewhat closer to C5 and farther from the carbon in methyl 1. The C2-C3 and C4-C5 bond lengths are also somewhat longer. The other most obvious difference between this geometry and either of the restricted Hartree-Fock geometries is placement of methyl 2. The carbon of methyl 2 is shifted downwards away from the plane of the ring, and the

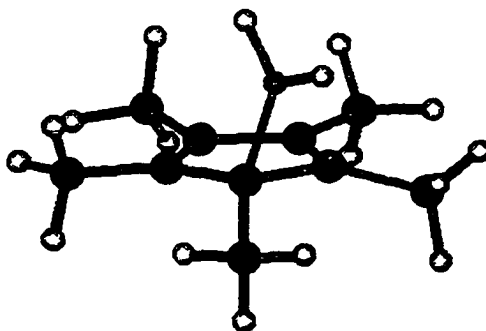


Figure 75
Geometry of $C_5Me_5BH_2$,
(optimized at the RMP2/3-21G* level).

orientation of the hydrogens is different from that seen in the starting point geometry.

The location and orientation of methyl 2 in this molecule in general resemble that seen in

the “archive” conformation seen in the η^2 -optimized molecule. All other methyl orientations approximated the “chat” conformation. The distance from the C1-C2 centroid to the boron atom is 1.665 Å. This is slightly longer than the B-C1 distance, so this geometry is still classified as *abgekippt*. However, it strongly resembles an η^2 geometry.

The molecule η^2 -optimized at the RHF/6-31G* level was re-optimized at the RMP2/3-21G* level. The resulting geometry, shown in Figure 76, resembles the geometry η^2 -optimized at the RHF/3-21G* level, although the carbon-carbon bond lengths of the ring are somewhat longer. The difference in energy (corrected for zero-point) between the *abgekippt* molecule and the η^2 -optimized molecule was 0.60 kcal/mole.

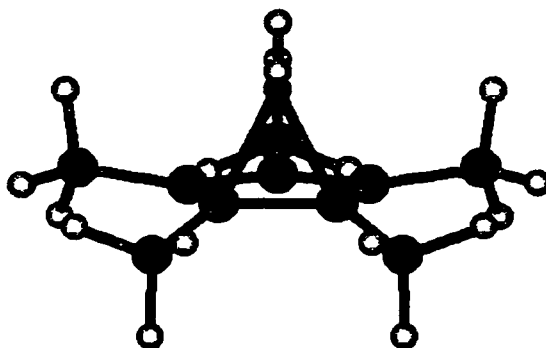


Figure 76
Geometry of $C_5Me_5BH_2$
(η^2 -optimized at the RMP2/3-21G* level)

Table 9
C₅Me₅BH₂ optimized geometry - η^1 and *abgekippt* results
(All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1	1.588	1.588	1.624
C1-C2	1.536	1.522	1.520
C2-C3	1.340	1.342	1.398
C3-C4	1.480	1.476	1.459
C4-C5	1.337	1.338	1.384
C1-C5	1.514	1.507	1.500
B-H6	1.187	1.189	1.196
B-H7	1.193	1.194	1.204
C1-Me1	1.539	1.534	1.532
C2-Me2	1.509	1.507	1.519
C3-Me3	1.506	1.503	1.514
C4-Me4	1.506	1.504	1.517
C5-Me5	1.505	1.503	1.514
Other distances			
B-C2	2.342	2.335	2.016
B-C5	2.528	2.523	2.494
B-Me1	2.672	2.641	2.732
Selected angles			
B-C1-C2	97.1	97.3	79.7
B-C1-C5	109.1	109.2	105.9
B-C1-Me1	117.4	115.5	119.9
H6-B-C1	119.6	120.3	119.3
H7-B-C1	120.9	120.8	119.3
H6-B-H7	119.4	118.9	121.1
Me1-C1-C2	113.7	114.7	119.3
Me1-C1-C5	114.8	115.4	120.2
Selected dihedral angles			
H6-B-C1-Me1	-157.6	-157.0	-151.5
H7-B-C1-Me1	25.7	26.0	22.7

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Table 10
C₅Me₅BH₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1 (= B-C2)	1.762	1.737	1.773
C1-C2	1.481	1.467	1.486
C2-C3	1.424	1.424	1.448
C3-C4	1.395	1.394	1.416
C4-C5	1.395	1.394	1.415
C5-C1	1.424	1.424	1.448
B-H6	1.182	1.185	1.194
B-H7	1.193	1.197	1.203
C1-Me1	1.515	1.514	1.522
C2-Me2	1.515	1.514	1.522
C3-Me3	1.504	1.502	1.514
C4-Me4	1.508	1.507	1.516
C5-Me5	1.504	1.502	1.514
Other distances			
B-C5	2.501	2.479	2.534
B-Me1	2.783	2.760	2.799
Selected angles			
B-C1-C2	65.1	65.0	65.2
B-C1-C5	102.9	102.9	103.3
B-C1-Me1	116.1	116.0	116.1
H6-B-C1	117.6	118.8	116.1
H7-B-C1	115.2	115.2	115.8
H7-B-H6	121.3	119.9	122.4
Me1-C1-C2	124.4	124.8	123.8
Me1-C1-C5	125.2	124.9	125.1
Selected dihedrals			
H6-B-C1-Me1	-138.2	-137.0	-139.7
H7-B-C1-Me1	15.3	15.5	14.4
H6-B-C4-Me4	0.0	0.0	0.1
H7-B-C4-Me4	180.0	180.0	-179.7

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Semi-empirical and *Ab Initio* Studies of $C_5Me_5BF_2$

MNDO Calculations for $C_5Me_5BF_2$

A $C_5Me_5BF_2$ (**5**) molecule was built using HyperChem and optimized using MNDO. The resulting geometry is shown in Figure 77. This geometry was found to be essentially identical to the η^1 -inversion geometry described by Schoeller [1]. Starting geometries that were η^1 -retention and *abgekippt* were also built and optimized. Each optimized to a geometry that may be described as η^1 -inversion. The orientations of the methyls in the optimized molecule resemble the “audience” conformation seen previously in $C_5Me_5BH_2$ optimized using MNDO.

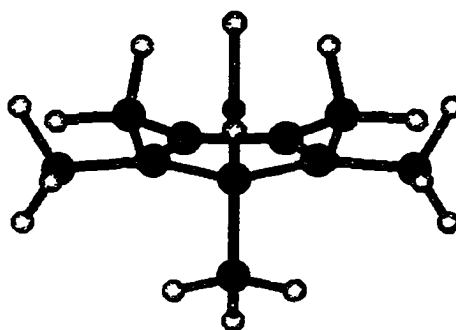


Figure 77
Geometry of $C_5Me_5BF_2$, (optimized using MNDO).

A $C_5Me_5BF_2$ molecule was built with the B-C1 and B-C2 bond distances constrained to 1.77 Å, and optimized using MNDO. The geometry is shown in Figure 78. When re-optimized with boron-carbon distances constrained to 1.76 Å or to 1.78 Å (the boron-carbon distance previously reported for the MNDO optimized transition state

[1]), the energy was higher than for the molecule shown in Figure 78. The orientation of the methyls resembled the “fence and gate” conformation seen in $\eta^2\text{-C}_5\text{Me}_5\text{BH}_2$ using MNDO.

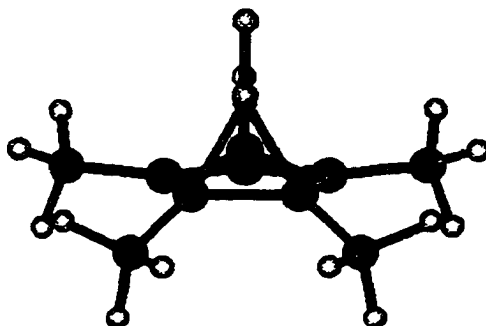


Figure 78
Geometry of $\text{C}_5\text{Me}_5\text{BF}_2$, (η^2 -optimized using MNDO).

RHF/3-21G* Calculations for $\text{C}_5\text{Me}_5\text{BF}_2$

The $\text{C}_5\text{Me}_5\text{BF}_2$ molecule optimized using MNDO was re-optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 79. A summary of selected distances and angles for this molecule is presented in Table 11. Additionally, an alternate starting geometry was taken from $\text{C}_5\text{Me}_5\text{BH}_2$ optimized at the RHF/3-21G* level with the two hydrogens bound to the boron atom changed to fluorines and the boron-fluorine distance reset to 1.3 Å. This molecule was then optimized at the RHF/3-21G* level. The results were essentially identical to the molecule shown in Figure 79. This geometry was found to be *abgekippt* and resembled the geometry found for $\text{C}_5\text{H}_5\text{BF}_2$ optimized at the RHF/3-21G* level more closely than it resembles the geometry of $\text{C}_5\text{Me}_5\text{BH}_2$ optimized at this level. The main difference between the optimized geometries of $\text{C}_5\text{Me}_5\text{BF}_2$ and

$C_5H_5BF_2$ is that the boron atom is shifted closer to the center of the ring in the latter (both B-C1-C2 and B-C1-C5 angles are smaller, and B-C1-Me1 angle is larger.) The orientations of the methyls on the molecule shown in Figure 79 resemble the “chat” conformation seen at this level for $C_5Me_5BH_2$, although Me2 is rotated farther away from its symmetric position in $C_5Me_5BF_2$. This optimized geometry was altered in an attempt

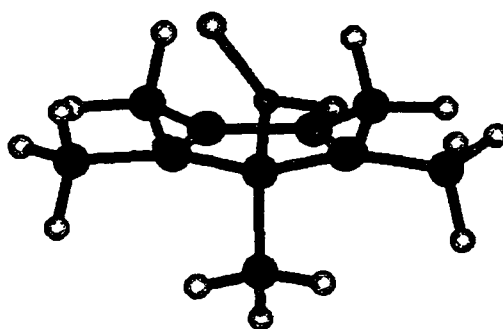


Figure 79
Geometry of $C_5Me_5BF_2$,
(optimized at the RHF/3-21G* level).

to find other local minima with different orientations of the methyl groups. The dihedral angle of the methyl hydrogens was rotated 60. degrees, and the molecule was re-optimized. This was done for each methyl group individually, for methyls 1 and 2 simultaneously, for methyls 1 through 3, for methyls 1 through 4, for methyls 2 and 3, for methyls 2 through 4, for methyls 3 and 4, and for all five methyls. All returned to a geometry that was essentially identical to the starting point geometry. No other local minima were seen for this molecule at this level of theory.

The $C_5Me_5BH_2$ molecule η^2 -optimized at the RHF/3-21G* level was also

modified. The two hydrogens bound to boron were changed to fluorines, and the boron-fluorine distance were reset to 1.3 Å. This modified geometry was then η^2 -optimized at this level. The resulting geometry is shown in Figure 80. A summary of selected bond distances and angles for this molecule is presented in Table 12. The B-C1 distance is shorter and the C1-C2 distance is longer in this molecule than in either η^2 -optimized $\text{C}_5\text{Me}_5\text{BH}_2$ or $\text{C}_5\text{H}_5\text{BF}_2$ at this level of theory. The B-C1-C5 angle is larger than in $\text{C}_5\text{Me}_5\text{BH}_2$ but smaller than in $\text{C}_5\text{H}_5\text{BF}_2$. The geometry of this molecule approximates the “archive” conformation seen previously for η^2 -optimized $\text{C}_5\text{Me}_5\text{BH}_2$. The planar hydrogens of methyls 3 and 5 are rotated slightly downward away from the boron atom (as opposed to slightly upwards as seen in η^2 -optimized $\text{C}_5\text{Me}_5\text{BH}_2$). The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 15.61 kcal/mole.

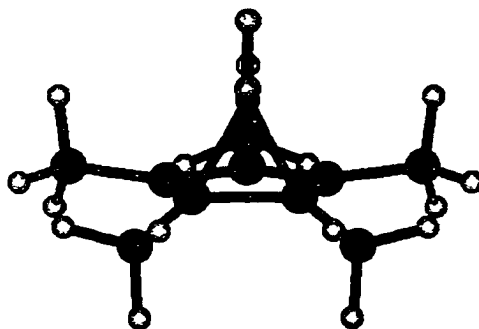


Figure 80
Geometry of $\text{C}_5\text{Me}_5\text{BF}_2$,
(η^2 -optimized at the RHF/3-21G* level).

An η^5 geometry for this molecule was constructed using Spartan 5.0 and

optimized at the RHF/3-21G* level without constraints, to produce a geometry that was recognizably *abgekippt*. This result suggests that there is no stable η^5 local minimum for this molecule at this level.

RHF/6-31G* Calculations for $C_5Me_5BF_2$

The molecule optimized at the RHF/3-21G* level was re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 81. The geometry was found to be *abgekippt* with bond angles and distances resembling those seen for $C_5Me_5BF_2$ optimized at the RHF/3-21G* level, although the B-C1 distance is longer and both boron-fluorine distances are shorter. The orientation of the methyl groups approximated the “chat” conformation. The molecule shown in Figure 81 was re-optimized using MNDO. The subsequent geometry closely resembled the molecule shown in Figure 77.

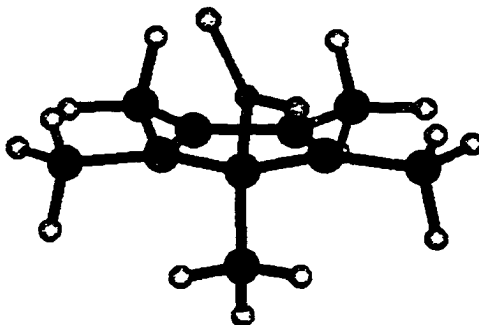


Figure 81
Geometry of $C_5Me_5BF_2$,
(optimized at the RHF/6-31G* level).

An η^1 -retention starting point geometry was constructed using Spartan 5.0, and optimized at the RHF/6-31G* level while restraining one F-B-C1-Me1 dihedral angle to

87. degrees. This molecule had two imaginary frequencies (reported as -276.50 cm^{-1} and -52.39 cm^{-1}). The constraint was then removed, and the molecule re-optimized.

Although the optimization was terminated before convergence criteria were met, the molecule moved from an η^1 -retention geometry to an *abgekippt* geometry during optimization.

The molecule η^2 -optimized at the RHF/3-21G* level was then η^2 -optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 82. The geometry resembles that obtained at the RHF/3-21G* level, although the B-C1 distance is longer and the C1-C2 and boron-fluorine distances are shorter. The orientation of the methyl groups approximates the “archive” conformation.

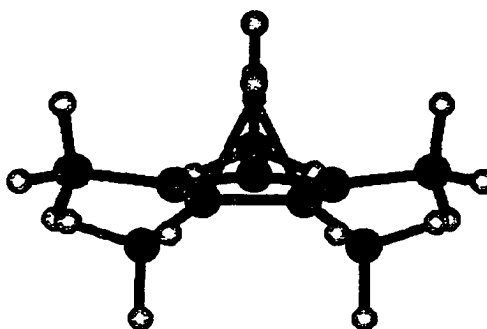


Figure 82
Geometry of $\text{C}_5\text{Me}_5\text{BF}_2$,
(η^2 -optimized at the RHF/6-31G* level).

The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 17.10 kcal/mole.

RMP2/3-21G* Calculations for $C_5Me_5BF_2$

The molecule optimized at the RHF/6-31G* level was re-optimized at the RMP2/3-21G* level. The resulting geometry is shown in Figure 83. In general, the bond angles and distances most closely resemble the same molecule optimized at the RHF/3-21G* level. Compared with the geometries optimized at either the RHF/3-21G* level or the RHF/6-31G* level, this molecule has longer C2-C3, C4-C5 bonds, longer boron-fluorine bonds, a shorter B-C2 distance, and a smaller B-C1-C2 angle. The orientation of the methyls approximates the “chat” conformation, although methyl 2 is rotated significantly toward its “archive” conformation.

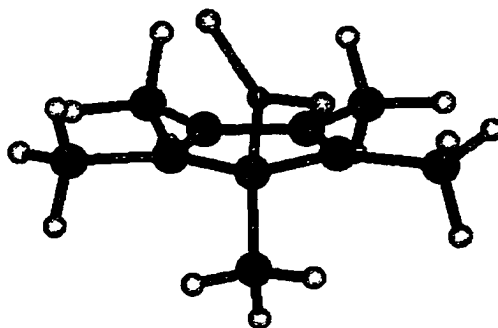


Figure 83
Geometry of $C_5Me_5BF_2$,
(optimized at the RMP2/3-21G* level).

The molecule η^2 -optimized at the RHF/6-31G* level was then η^2 -optimized at the RMP2/3-21G* level. The resulting geometry is shown in Figure 84. Compared with the geometries optimized at either restricted Hartree-Fock level, the carbon-carbon bond distances and the boron-carbon distances are somewhat longer. Otherwise, this geometry

resembles those seen for this molecule at previous levels. The orientation of the methyls approximated the “archive” conformation.

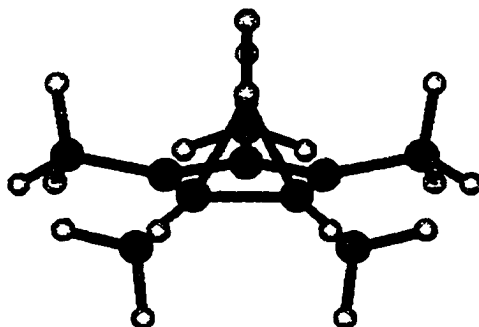


Figure 84
Geometry of $C_5Me_5BF_2$,
(η^2 -optimized at the RMP2/3-21G* level).

The molecules shown in Figure 83 and Figure 84 were re-optimized, this time using full RMP2/3-21G* (as opposed to a frozen core approximation). Gaussian 94W reported that the frozen core optimized starting point geometries already met the criteria for optimization using full MP2. The calculated full RMP2/3-21G* energies was reported to differ from the frozen core RMP2/3-21G* energies by less than 1.5×10^{-8} Hartrees. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 9.83 kcal/mole.

Table 11
C₅Me₅BF₂ optimized geometry - η^1 and *abgekippt* results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1	1.561	1.583	1.566
C1-C2	1.539	1.528	1.552
C2-C3	1.333	1.335	1.366
C3-C4	1.489	1.484	1.492
C4-C5	1.333	1.334	1.366
C1-C5	1.518	1.514	1.525
B-F6	1.345	1.313	1.360
B-F7	1.350	1.317	1.366
C1-Me1	1.551	1.542	1.554
C2-Me2	1.507	1.505	1.516
C3-Me3	1.505	1.503	1.515
C4-Me4	1.505	1.503	1.515
C5-Me5	1.504	1.502	1.512
Other distances			
B-C2	2.474	2.470	2.431
B-C5	2.550	2.553	2.551
B-Me1	2.587	2.587	2.617
Selected angles			
B-C1-C2	105.9	105.1	102.5
B-C1-C5	111.8	111.0	111.2
B-C1-Me1	112.5	111.8	114.0
F6-B-C1	124.6	123.3	124.3
F7-B-C1	121.1	121.0	121.0
F6-B-F7	114.3	115.7	114.7
Me1-C1-C2	110.9	112.4	111.4
Me1-C1-C5	112.8	113.5	113.7
Selected dihedral angles			
F6-B-C1-Me1	-134.0	-146.5	138.3
F7-B-C1-Me1	46.6	35.1	-43.3

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Table 12
C₅Me₅BF₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1 (= B-C2)	1.725	1.744	1.752
C1-C2	1.508	1.486	1.524
C2-C3	1.419	1.418	1.438
C3-C4	1.394	1.394	1.417
C4-C5	1.394	1.394	1.417
C5-C1	1.419	1.418	1.438
B-F6	1.361	1.331	1.371
B-F7	1.367	1.336	1.379
C1-Me1	1.516	1.515	1.523
C2-Me2	1.516	1.515	1.523
C3-Me3	1.503	1.502	1.514
C4-Me4	1.507	1.506	1.516
C5-Me5	1.503	1.502	1.513
Other distances			
B-C5	2.513	2.515	2.559
B-Me1	2.733	2.748	2.747
Selected angles			
B-C1-C2	64.1	64.8	64.4
B-C1-C5	105.7	104.9	106.3
B-C1-Me1	114.8	114.7	113.9
F6-B-C1	123.7	123.4	123.3
F7-B-C1	115.3	115.2	115.1
F7-B-F6	113.5	114.5	114.4
Me1-C1-C2	123.2	123.9	122.7
Me1-C1-C5	126.1	125.4	126.2
Selected dihedrals			
F6-B-C1-Me1	-134.6	-134.4	-135.3
F7-B-C1-Me1	13.2	14.7	13.3
F6-B-C4-Me4	0.0	-0.1	0.0
F7-B-C4-Me4	180.0	180.0	-179.9

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Semi-empirical and *Ab Initio* Studies of $C_5Me_5BCl_2$

MNDO Calculations for $C_5Me_5BCl_2$

A $C_5Me_5BCl_2$ molecule (6) was built using HyperChem and optimized using MNDO. The resulting geometry, as shown in Figure 85, was essentially identical to the η^1 -inversion conformation described by Schoeller [1]. The orientations of the methyls in the optimized molecule resemble the “audience” conformation seen in $C_5Me_5BH_2$ and $C_5Me_5BF_2$ optimized using MNDO.

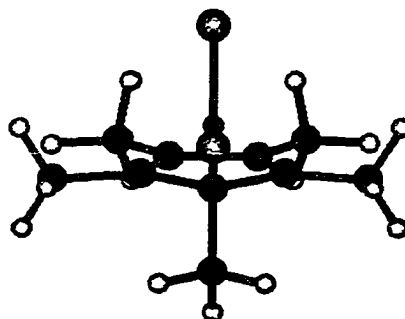


Figure 85
Geometry of $C_5Me_5BCl_2$, (optimized using MNDO).

A $C_5Me_5BCl_2$ molecule was then built with the B-C1 and B-C2 bond distances constrained to 1.68 Å, and optimized using MNDO. The geometry is shown in Figure 86. The molecule was then re-optimized with boron-carbon distances constrained to 1.67 Å (the value previously reported [1]) and 1.69 Å. In both cases the energy was found to be higher than for the molecule shown in Figure 86. The orientation of the methyls in Figure 86 resembles the “fence and gate” conformation seen in both $C_5Me_5BH_2$ and

$C_5Me_5BF_2$ η^2 -optimized using MNDO.

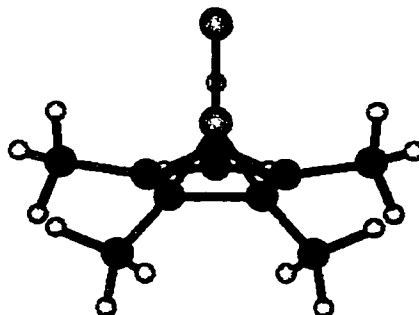


Figure 86
Geometry of $C_5Me_5BCl_2$, (η^2 -optimized using MNDO).

RHF/3-21G* Calculations for $C_5Me_5BCl_2$

The geometry optimized using MNDO was re-optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 87. A summary of selected bond distances and angles for this molecule is presented in Table 13. The geometry of this

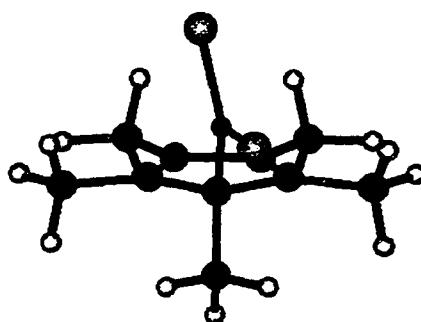


Figure 87
Geometry of $C_5Me_5BCl_2$,
(optimized at the RHF/3-21G* level).

molecule resembles the geometry of both $C_5H_5BCl_2$ and $C_5Me_5BH_2$ optimized at the

RHF/3-21G* level. The most notable difference is that the boron atom is farther from C2 and C5 in this molecule than in $C_5Me_5BH_2$, and the boron atom is closer to C5 in this molecule than in $C_5H_5BCl_2$. The orientation of the methyls approximates the “chat” conformation.

The $C_5Me_5BCl_2$ molecule previously η^2 -optimized using MNDO was η^2 -optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 88. A summary of selected distances and angles for this molecule is presented in Table 14. The geometry seen in Figure 88 closely resembles the geometry of η^2 -optimized $C_5Me_5BF_2$ at

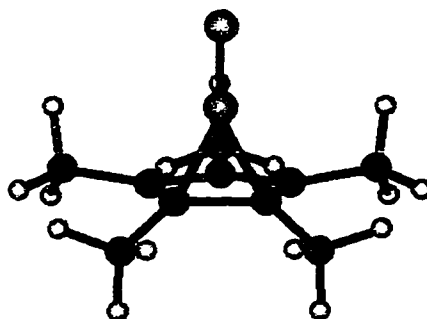


Figure 88
Geometry of $C_5Me_5BCl_2$,
(η^2 -optimized at the RHF/3-21G* level).

this level. The bond angles and distances of this molecule are within 1% of the values seen in $C_5Me_5BF_2$ for all atoms except the carbon of methyl 1. The C1-Me1 bond distance is somewhat longer in $C_5Me_5BCl_2$, and the methyl is shifted somewhat closer to carbon 5. The orientation of the hydrogens on the methyls approximates the “archive” conformation, but with the planar hydrogens of methyls 3 and 5 rotated downward.

Frequency analysis of this molecule yields one imaginary frequency (reported by Gaussian 94W as -296.0828 cm^{-1}) as expected for a transition state. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 12.59 kcal/mole.

An η^5 geometry for this molecule was constructed using Spartan 5.0. This molecule was then optimized at the RHF/3-21G* level without constraints, to produce a geometry that was recognizably *abgekippt*. This result suggests that there is no stable η^5 local minimum for this molecule at this level.

RHF/6-31G* Calculations for $C_5Me_5BCl_2$

The $C_5Me_5BCl_2$ molecule previously optimized at the RHF/3-21G* level was re-optimized at the RHF/6-31G* level. The resulting geometry, shown in Figure 89, was *abgekippt*.

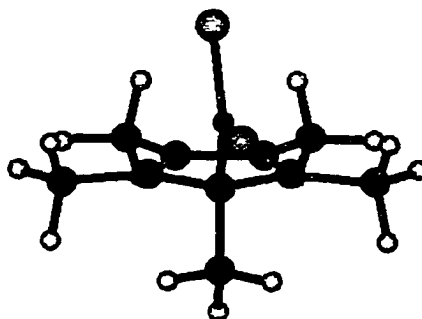


Figure 89
Geometry of $C_5Me_5BCl_2$,
(optimized at the RHF/6-31G* level).

Compared to the molecule optimized at the RHF/3-21G* level, the boron atom is shifted

farther away from C2 (as seen both in a longer B-C2 distance and a larger B-C1-C2 and B-C1-H2 angle). All other parameters were within 1% of the other molecule. The orientation of the methyls approximates the “chat” conformation. Frequency analysis of this molecule yielded no imaginary frequencies. The lowest frequency reported was 11.492 cm^{-1} .

The $\text{C}_5\text{Me}_5\text{BCl}_2$ molecule η^2 -optimized at the RHF/3-21G* level was then η^2 -optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 90. The bond angles and distances were all within 1% of the values seen in the molecule η^2 -optimized at the RHF/3-21G* level except that the Cl-B-Cl was somewhat narrower at the RHF/6-31G* level. This leads also to a somewhat larger Cl-B-Cl-Me1 dihedral angle. Frequency analysis of this molecule yields one imaginary frequency (reported by Gaussian 94W to be -236.8351 cm^{-1}). Orientation of the hydrogens on the methyls

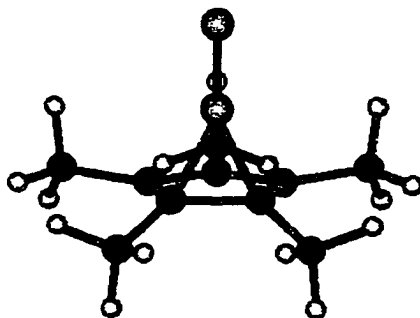


Figure 90
Geometry of $\text{C}_5\text{Me}_5\text{BCl}_2$,
(η^2 -optimized at the RHF/6-31G* level).

resembles the “archive” conformation seen in this molecule at RHF/3-21G*. The

difference in energy (corrected for zero-point energy) between these two conformations was 12.45 kcal/mole.

RMP2/3-21G* Calculations for $C_5Me_5BCl_2$

The molecule previously optimized at the RHF/6-31G* level was re-optimized at the RMP2/3-21G* level. Initially, the molecule was optimized using LANL2 pseudopotentials for the core electrons. This geometry was then further optimized without pseudopotentials. The resulting geometry is shown in Figure 91. In general, the bond angles and distances most closely resembles the same molecule optimized at the RHF/3-21G* level. Compared with the geometries optimized at the RHF/3-21G* and

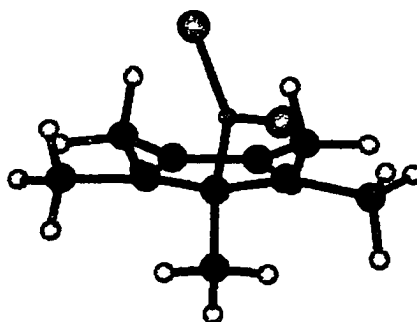


Figure 91
Geometry of $C_5Me_5BCl_2$,
(optimized at the RMP2/3-21G* level).

RHF/6-31G* levels, this molecule has longer C2-C3, C4-C5 bonds, a shorter B-C2 distance, and a smaller B-C1-C2 angle. The orientation of the methyls approximated the “chair” conformation, although methyl 2 is rotated somewhat upward and the planar hydrogen of methyl 5 is rotated somewhat downward. Like $C_5Me_5BH_2$ at this level, and

unlike $\text{C}_5\text{Me}_5\text{BF}_2$ at this level, the carbon of methyl 2 is shifted downward away from the plane of the ring.

The molecule previously η^2 -optimized at the RHF/6-31G* level was then η^2 -optimized at the RMP2/3-21G* level using LANL2 pseudopotentials. This molecule was then η^2 -optimized without pseudopotentials. The resulting geometry is shown in Figure 92. Compared to the same molecule η^2 -optimized at the RHF/3-21G* or the RHF/6-31G* level, the boron-carbon and carbon-carbon distances are somewhat longer. This geometry closely resembles the geometry of η^2 -optimized $\text{C}_5\text{Me}_5\text{BF}_2$ at the same level, although methyl 1 and methyl 2 are shifted somewhat farther away from the ring. The orientations of the methyl hydrogens resemble the “archive” conformation seen for this molecule at previous levels. The difference in energy (corrected for zero-point) between the *abgekippt* molecule, optimized without constraints, and the η^2 -optimized molecule was 3.75 kcal/mole.

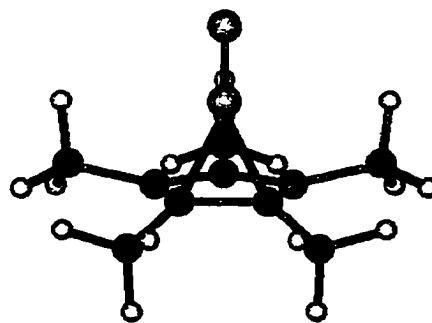


Figure 92
Geometry of $\text{C}_5\text{Me}_5\text{BCl}_2$,
(η^2 -optimized at the RMP2/3-21G* level).

Table 13
C₅Me₅BCl₂ optimized geometry - η^1 and *abgekippt* results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RP2/3-21G *
Bond distances			
B-C1	1.580	1.593	1.580
C1-C2	1.541	1.527	1.554
C2-C3	1.333	1.334	1.373
C3-C4	1.487	1.483	1.483
C4-C5	1.332	1.333	1.369
C1-C5	1.526	1.521	1.524
B-Cl6	1.763	1.765	1.765
B-Cl7	1.771	1.768	1.774
C1-Me1	1.547	1.542	1.547
C2-Me2	1.506	1.504	1.516
C3-Me3	1.505	1.503	1.515
C4-Me4	1.505	1.503	1.515
C5-Me5	1.505	1.503	1.512
Other distances			
B-C2	2.479	2.505	2.344
B-C5	2.556	2.548	2.536
B-Me1	2.644	2.629	2.668
Selected angles			
B-C1-C2	105.2	106.8	96.8
B-C1-C5	110.8	109.8	109.5
B-C1-Me1	115.4	114.0	117.1
Cl6-B-C1	121.8	121.9	122.8
Cl7-B-C1	121.5	122.2	120.4
Cl6-B-Cl7	116.6	115.9	116.8
Me1-C1-C2	111.1	111.7	113.4
Me1-C1-C5	111.4	111.6	114.7
Selected dihedral angles			
Cl6-B-C1-Me1	-164.9	-171.7	-154.0
Cl7-B-C1-Me1	17.3	9.6	26.4

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Table 14
C₅Me₅BCl₂ η^2 -optimized geometry results
 (All distances are in Ångstroms, and all angles are in degrees)

Parameters	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances			
B-C1 (= B-C2)	1.723	1.710	1.762
C1-C2	1.505	1.491	1.504
C2-C3	1.431	1.430	1.445
C3-C4	1.392	1.392	1.415
C4-C5	1.392	1.392	1.415
C5-C1	1.431	1.430	1.445
B-Cl6	1.816	1.821	1.799
B-Cl7	1.812	1.816	1.796
C1-Me1	1.518	1.518	1.523
C2-Me2	1.518	1.518	1.523
C3-Me3	1.499	1.498	1.509
C4-Me4	1.507	1.505	1.514
C5-Me5	1.498	1.498	1.509
Other distances			
B-C5	2.534	2.526	2.561
B-Me1	2.787	2.777	2.805
Selected angles			
B-C1-C2	64.1	64.2	64.7
B-C1-C5	106.6	106.8	105.5
B-C1-Me1	118.5	118.6	117.1
Cl6-B-C1	123.3	124.3	122.1
Cl7-B-C1	116.6	116.7	116.5
Cl7-B-Cl6	112.5	111.3	114.4
Me1-C1-C2	124.1	124.5	123.6
Me1-C1-C5	123.2	122.6	124.1
Selected dihedrals			
Cl6-B-C1-Me1	-134.9	-133.8	-136.3
Cl7-B-C1-Me1	12.4	12.8	12.8
Cl6-B-C4-Me4	0.0	-0.1	0.0
Cl7-B-C4-Me4	180.0	179.9	180.0

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Semi-empirical and *Ab Initio* Studies of $(C_5Me_5)_2BF$

MNDO Calculations for $(C_5Me_5)_2BF$

A $(C_5Me_5)_2BF$ molecule (**7**) was built using HyperChem 4.5. Optimization of this molecule using MNDO produced the geometry shown in Figure 93b. This geometry did not resemble the X-ray crystallographic data reported for this molecule [2] as shown in Figure 93a. The cyclopentadienyl rings were oriented away from each other relative to the boron atom. A new starting geometry was constructed for this molecule with the two cyclopentadienyl rings parallel to each other. This molecule was then optimized using MNDO. The resulting geometry, shown in Figure 93c, resembled the X-ray crystallographic data, although it was 0.81 kcal/mole higher in energy than the other optimized conformation. The bond distances for this molecule were within 5% of the values seen in the X-ray crystallographic data [2]. The average B-C1-C2 angle and the B-C2 distance were both over 5% larger than the values seen in the X-ray crystallographic data [2]. A summary of selected distances and angles for the molecule is presented in Table 15. The percent errors (relative to empirical values) are found in Table 16. The methyl orientations for both MNDO optimized molecules approximates the “audience” conformation. There is no X-ray crystallographic data available on the actual location of the methyl hydrogens.

Both the X-ray crystallographic data [2] and the molecule optimized using MNDO shown in Figure 93c have approximately but not exactly C_2 symmetry. The geometric parameters listed in Table 15 represent the average for both rings.

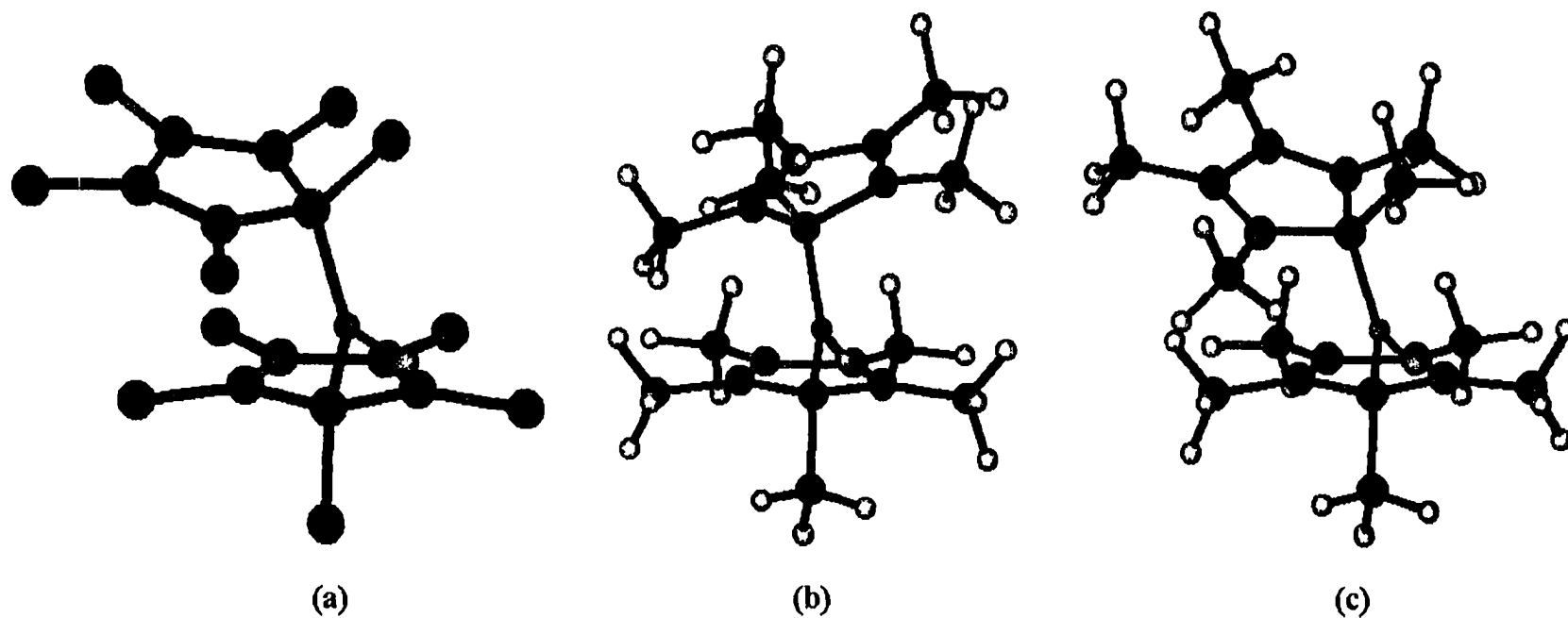


Figure 93
Geometry of $(C_5Me_5)_2BF$,
(a) coordinates from previously published X-ray crystallographic
data [2], (b) optimized using MNDO with the rings oriented away from each
other, (c) optimized using MNDO with the rings oriented towards each other.

RHF/3-21G* Calculations for $(C_5Me_5)_2BF$

The molecule previously optimized using MNDO was re-optimized at the RHF/3-21G* level. The resulting geometry is shown in Figure 94. For most of the parameters listed in Table 15, the molecule optimized at the RHF/3-21G* level is closer to the X-ray crystallographic data [2] than the molecule optimized using MNDO. The exceptions are as follows: the boron-fluorine distance, the F-B-C1 angle, the C1-B-C1' angle, the B-C1-C5 angle, and the C5-Me5 distance. In particular, the values obtained from the molecule optimized at the RHF/3-21G* level for the B-C2 and C5-C5' distances, the B-C1-C2 angle, and the C5-C1-C1'-C5' and C2-C1-C1'-C2' dihedral angles were much closer to the X-ray crystallographic data values [2] than were the values obtained using MNDO. The methyl orientations for both pentamethylcyclopentadienyl substituents approximated the "chat" conformation seen in previous molecules, although the planar hydrogen of methyl 2 was rotated upward more than methyl 5.

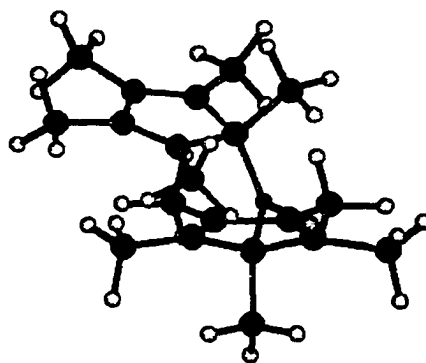


Figure 94
Geometry of $(C_5Me_5)_2BF$,
(optimized at the RHF/3-21G* level).

RHF/6-31G* Calculations for $(C_5Me_5)_2BF$

This molecule, optimized at the RHF/3-21G* level, was then re-optimized at the RHF/6-31G* level. The resulting geometry is shown in Figure 95. For most of the parameters listed in Table 15, the geometry obtained at the RHF/6-31G* level is closer to the X-ray crystallographic geometry [2] than the geometry optimized using MNDO. The exceptions are as follows: the F-B-C1 angle, the C1-B-C1' angle, the B-C1-C5 angle, and the B-C1-Me1 angle. The degree to which each of these values varied from the empirical values is summarized in Table 16. In particular, the values obtained at the RHF/6-31G* level for the B-C2 and C5-C5' distances, the B-C1-C2 angle, and the C5-C1-C1'-C5' and C2-C1-C1'-C2' dihedral angles are much closer to the X-ray crystallographic data values [2] than are the values obtained using MNDO.

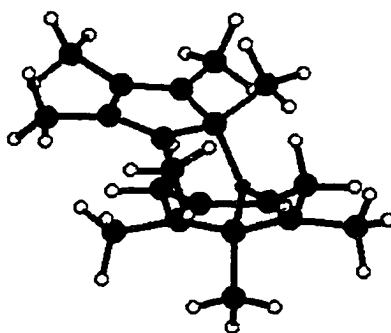


Figure 95
Geometry of $(C_5Me_5)_2BF$,
(optimized at the RHF/6-31G* level).

Compared to the RHF/3-21G* values, all listed values for the molecule optimized at the RHF/6-31G* level were closer to the X-ray crystallographic data values [2] except

for the B-C1, C2-H2, C3-H3, B-C2, and B-C5 distances. However, the other distances and angles for the molecule optimized at the RHF/6-31G* level are further from the X-ray crystallographic data values [2] except for the B-Me1 distance, the Me1-C1-C2 angle, the C2-C1-C1'-C2' dihedral angle, and the C5-C1-C1'-C5' dihedral angle. The methyl orientations for both pentamethylcyclopentadienyl substituents approximate the “chat” conformation seen in the molecule optimized at the RHF/3-21G* level, although the planar hydrogen of methyl 2 is rotated downward.

RMP2/3-21G* Calculations for $(C_5Me_5)_2BF$

The molecule previously optimized at the RHF/6-31G* level was then re-optimized using Gaussian 98 at the RMP2/3-21G* level. The resulting geometry is

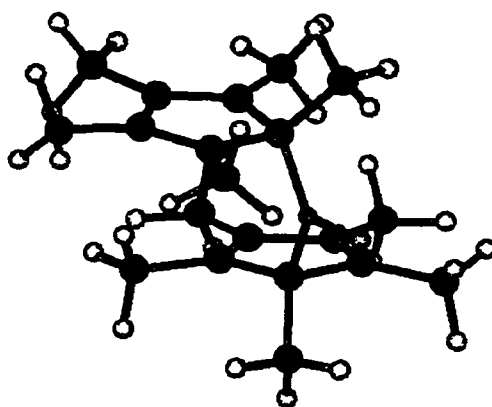


Figure 96
Geometry of $(C_5Me_5)_2BF$,
(optimized at the RMP2/3-21G* level).

shown in Figure 96. Compared to the values obtained at the RHF/6-31G* level, all listed

bond distances obtained at the RMP2/3-21G* level are less close to the X-ray crystallographic data values [2] except the B-C1 and C3-Me3 distances. However, all listed bond angles obtained at the RMP2/3-21G* level are closer to the X-ray crystallographic data values [2] except for the B-C1-Me1 angle. In general, the geometric parameters seen in the geometries optimized at the RMP2/3-21G* and RHF/6-31G* levels approximate the X-ray crystallographic data values [2] closer than the values obtained using MNDO or at the RHF/3-21G* level, although a few exceptions are noted in Table 15. The methyl orientations for both pentamethylcyclopentadienyl substituents approximates the “chat” conformation seen in the previous levels, although the planar hydrogen of Me2 is rotated upward.

Table 15
 $(C_5Me_5)_2BF$ geometry
 (All distances are in Ångstroms, all angles are in degrees. Boldface italicised quantities represents the theoretical predictions closest to the corresponding empirical value [2].)

Parameter	Empirical [2]	MNDO	RHF /3-21G*	RHF /6-31G*	RMP2 /3-21G*
Bond distances					
B-C1	1.582	1.636	1.587	1.605	1.585
C1-C2	1.525	1.549	1.542	1.530	1.554
C2-C3	1.339	1.376	1.335	1.337	1.372
C3-C4	1.458	1.488	1.486	1.481	1.484
C4-C5	1.341	1.375	1.334	1.334	1.370
C1-C5	1.494	1.542	1.516	1.511	1.520
B-F	1.344	1.317	1.378	1.338	1.398
C1-Me1	1.545	1.560	1.556	1.549	1.555
C2-Me2	1.511	1.499	1.510	1.506	1.518
C3-Me3	1.514	1.498	1.506	1.504	1.517
C4-Me4	1.504	1.498	1.506	1.504	1.515
C5-Me5	1.499	1.498	1.505	1.504	1.511
Other distances					
B-C2	2.409	2.597	2.488	2.498	2.377
B-C5	2.614	2.698	2.645	2.659	2.628
B-Me1	2.584	2.652	2.595	2.585	2.629
C1-C1'	2.902	2.986	2.929	2.964	2.898
C5-C5'	3.193	3.493	3.248	3.299	3.080
Selected bond angles					
B-C1-C2	101.6	109.2	105.3	105.6	98.5
B-C1-C5	116.3	116.1	116.9	117.1	115.7
B-C1-Me1	111.5	112.2	111.3	110.0	113.7
C1'-B-C1	133.1	131.7	134.7	134.8	132.2
F-B-C1	113.5	114.2	112.6	112.6	113.9
Me1-C1-C2	112.4	109.5	109.8	111.2	111.5
Me1-C1-C5	111.9	107.7	110.6	110.3	113.0
Selected bond dihedral angles (absolute value)					
C1'-B-C1-Me1	146.9	153.0	142.0	141.3	145.9
F-B-C1-Me1	33.1	27.0	38.0	38.7	34.1
C2-C1-C1'-C2'	176.4	155.6	175.4	176.3	176.0
C5-C1-C1'-C5'	30.2	51.3	24.2	25.6	23.0

(Note: the symbol "Me1" here represents the carbon of methyl 1.)

Table 16
(C₅Me₅)₂BF optimized geometry
percent error (relative to empirical values [2])

Parameters	MNDO	RHF/3-21G*	RHF/6-31G*	RMP2/3-21G*
Bond distances				
B-C1	3.44	0.32	1.49	0.18
C1-C2	1.56	1.12	0.35	1.88
C2-C3	2.73	0.30	0.19	2.46
C3-C4	2.05	1.92	1.56	1.82
C4-C5	2.58	0.50	0.50	2.20
C1-C5	3.22	1.46	1.14	1.71
B-F	2.04	2.47	0.46	3.97
C1-Me1	1.00	0.72	0.28	0.62
C2-Me2	0.83	0.08	0.37	0.47
C3-Me3	1.05	0.51	0.65	0.17
C4-Me4	0.40	0.14	0.02	0.78
C5-Me5	0.06	0.41	0.36	0.80
Other distances				
B-C2	7.84	3.29	3.69	1.31
B-C5	3.20	1.19	1.72	0.55
B-Me1	2.60	0.43	0.01	1.72
C1-C1'	2.90	0.95	2.14	0.13
C5-C5'	9.39	1.73	3.33	3.54
Selected bond angles				
B-C1-C2	7.47	3.62	3.86	3.12
B-C1-C5	0.21	0.50	0.62	0.58
B-C1-Me1	0.53	0.13	1.32	2.01
C1'-B-C1	1.03	1.27	1.30	0.62
F-B-C1	0.61	0.75	0.76	0.36
Me1-C1-C2	2.59	2.37	1.10	0.79
Me1-C1-C5	3.80	1.18	1.45	0.93
Selected bond dihedral angles (absolute value)				
C1'-B-C1-Me1	4.18	3.27	3.78	0.63
F-B-C1-Me1	18.53	14.49	16.76	2.79
C2-C1-C1'-C2'	11.77	0.58	0.05	0.24
C5-C1-C1'-C5'	69.80	19.79	15.14	23.92

Chapter 4

Conclusions

The molecular geometries found for $C_5H_5BH_2$ and $C_5Me_5BCl_2$, optimized using MNDO, are consistent with results previously reported [1]; however, the geometries of the other molecules examined are not. The molecular geometries found for $C_5H_5BF_2$, $C_5H_5BCl_2$, and $C_5Me_5BH_2$, optimized using MNDO, are found to be asymmetric. In contrast, Schoeller [1] only considered symmetric conformations. For both $C_5Me_5BH_2$ and $C_5Me_5BF_2$ the boron-carbon bond length in the η^2 conformation is found to differ with the previously reported value by 0.01 Å. Since the equilibrium geometries for several of these molecules differ from previously reported values, the difference between the energies of the equilibrium and transition states geometries are expected to differ from reported values [1]. These values are given in Table 16. For $C_5Me_5BCl_2$, the activation energy found here does not match the value reported previously [1], even though the boron-carbon bond lengths for the η^2 conformation match previous results. However, a better agreement with Schoeller's results is obtained when the equilibrium geometry is assumed to be a η^1 -retention geometry. Further inspection of Schoeller's results yields similar inconsistencies for the data obtained for $C_5H_5BF_2$ and $C_5H_5BCl_2$. The η^1 -retention conformation was reported to be higher in energy than the η^1 -inversion conformation, but the η^1 -retention conformation appears to have been used when calculating the difference in energy. A full analysis of these molecules using MNDO is

outside the scope of this research, however, further re-examination of the previously published MNDO results would appear to be warranted.

In general, the molecules examined optimized to *abgekippt* equilibrium geometries. No equilibrium η^3 or η^5 geometries were found. For all geometries identified in this study as *abgekippt*, the sum of angles B-C1-C2 and B-C1-C5 is greater than 180. degrees. This indicates that these geometries are not in fact η^3 . The only equilibrium η^2 geometry found was for $C_5H_5BH_2$. The $C_5H_5BH_2$ molecule was predicted to have an η^2 equilibrium geometry at the RMP2/6-31G* level. Since this represents the most accurate model used in this research, the η^2 conformation may indeed be the actual equilibrium geometry for this molecule. Of all of these molecules, only one is predicted to have a symmetrical η^1 equilibrium geometry. The $C_5H_5BF_2$ molecule is predicted to have an η^1 -retention equilibrium geometry at the RHF/6-31G* level. However, since this geometry is not seen at the RMP2 level, the symmetrical equilibrium geometry for this molecule may not represent the actual equilibrium geometry of the molecule. For all other cases, the equilibrium geometry was found to be asymmetric. Although these results do not exclude the possibility that higher levels of theory may predict an η^2 equilibrium geometry for one or more of these molecules, these results suggest that an *abgekippt* equilibrium geometry is a reasonable possibility for this class of molecules. Moreover, the *abgekippt* conformations of these molecules tend to resemble the equilibrium geometry of $(C_5Me_5)_2BF$, for which there is empirical evidence of an

abgekippt equilibrium geometry [2]. This similarity suggests that this geometry may be a general characteristic of this class of molecules.

Comparison of the *ab initio* and MNDO predictions for the geometry of $(C_5Me_5)_2BF$ with the X-ray crystallographic data [2] suggests that the available *ab initio* methods are in general more accurate than MNDO, and that the asymmetry previously observed in this compound is the result of the bonding within the molecule, as opposed to the result of interactions between molecules packed in the solid state. *Ab initio* and MNDO predictions of the relative methyl orientations differ for these molecules; MNDO uniformly predicted “audience” conformations for the equilibrium geometry and “fence and gate” conformations for the transition state geometry, whereas *ab initio* methods predicted “chat” conformations for the equilibrium geometry and “archive” conformations for the transition state geometry. Unfortunately, there is no empirical data available upon which to evaluate the MNDO vs. *ab initio* predictions.

Comparisons of the different *abgekippt* geometries have been previously discussed in detail in Chapter 3. However, there are a few generalizations that are common to all of these geometries. *Abgekippt* geometries are, according to the definition given on page 38, asymmetric with respect to the placement of the boron atom relative to the plane bisecting the ring. This asymmetry can be seen in both the B-C1-C2 angle (compared with the B-C1-C5 angle) and the B-C2 distance (compared with the B-C5 distance). Other asymmetries may be noted in these molecules. The C1-C2 bond length is increased relative to the C1-C5 bond length, the H1-C1-C2 angle is increased relative to the H1-C1-C5 angle, and the plane of the BH_2 (or BX_2) group is rotated approximately

perpendicular to the B-C1-C2 plane. These asymmetries become more pronounced as the molecule approaches the η^2 geometry (the putative transition state of the 1,5-sigmatropic rearrangement). The *abgekippt* geometry may then be viewed as an intermediate between a purely η^1 geometry and a purely η^2 geometry.

In order to compare the relative asymmetries of the *abgekippt* equilibrium geometry for each molecule, three asymmetry measures are here defined. The asymmetry of the boron atom's position is defined in two ways: "B-C1-C2 % asymmetry" is defined as the difference between the B-C1-C5 angle and the B-C1-C2 angle, divided by the average of the two angles (and multiplied by 100%). "B-C2 % asymmetry" is defined as the difference between the B-C5 and the B-C2 distances, divided by the average of the two distances (and multiplied by 100%). The asymmetry of the carbon-carbon bond distances is also considered for comparison: "C1-C2 % asymmetry" is defined as the difference between the C1-C2 and the C1-C5 distances, divided by average of the two distances (and multiplied by 100%). In Tables 17-22, these three quantities are listed and compared with the activation energies predicted for each molecule at each level. For comparison, these quantities can be calculated from empirical data [2] for molecule (7): B-C2% = 8.177, B-C1-C2% = 13.486, C1-C2% = 2.032 . These quantities can also be calculated from empirical data for a related compound $C_5Me_5B(Cl)As(t-Bu)_2$ [18]: B-C2% = 8.206, B-C1-C2% = 11.108, C1-C2% = 0.025 .

Table 17 shows the effects of different levels of theory on the predictions for $C_5H_5BH_2$. For these molecules, the activation energy decreases when a larger basis set is

used (e.g. from 3-21G* to 6-31G*), and the activation energy also decreases when electron correlation effects are considered (e.g. from RHF to RMP2.) Electron correlation effects appear to have a greater effect than the size of the basis set. The extreme example of this effect is seen at the RMP2/6-31G* level. The activation energy (as defined for the 1,5-sigmatropic rearrangement) disappears at this level since the η^2 conformation here is predicted to be the equilibrium geometry. The asymmetry of the

Table 17
C₅H₅BH₂ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	7.05	6.07
ΔZPE ^b	0.02	0.07
E_a ^c	7.03	6.00
C1-C2 % asym ^d	1.64	1.07
B-C2 % asym. ^e	9.18	9.44
B-C1-C2 % asym. ^f	13.98	14.19
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	1.34	N/A
ΔZPE ^b	-0.01	
E_a ^c	1.34	
C1-C2 % asym ^d	1.66	
B-C2 % asym. ^e	17.54	
B-C1-C2 % asym. ^f	24.28	

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

boron atom's position (i.e. "B-C2 % asymmetry" and "B-C1-C2 % asymmetry") increased when a larger basis set is used and decreases when electron correlation effects are added. In contrast, the C1-C2 bond asymmetry is not consistent with this trend. The asymmetry

decreases for the larger basis set, but increases when electron correlation is considered.

The asymmetry of the RMP2/6-31G* equilibrium geometry is not considered here, since it is not an *abgekippt* geometry.

Table 18
C₅H₅BF₂ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	16.80	18.26
ΔZPE ^b	0.63	0.69
E_a ^c	16.17	17.57
C1-C2 % asym ^d	1.14	-0.001
B-C2 % asym. ^e	2.99	-0.01
B-C1-C2 % asym. ^f	5.33	-0.01
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	11.24	5.30
ΔZPE ^b	0.43	0.33
E_a ^c	10.81	4.96
C1-C2 % asym ^d	1.74	1.18
B-C2 % asym. ^e	5.64	8.33
B-C1-C2 % asym. ^f	9.45	12.72

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 18 shows the effects of different levels of theory on the predictions for C₅H₅BF₂. For the restricted Hartree-Fock levels, unlike C₅H₅BH₂, the activation energy increases as a larger basis set is used. In this case, however, the equilibrium geometry is predicted to have an η^1 -retention geometry, not an *abgekippt* geometry. The unusually short B-H1 distance suggests that a different sort of bonding interaction is responsible for this geometry. For all other comparisons, the trends seen in C₅H₅BH₂ are also seen in

$C_5H_5BF_2$ (i.e. at higher levels of theory, the predicted activation energy decreases and the asymmetry of the boron atom's position increases.)

Table 19
 $C_5H_5BCl_2$ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	15.83	15.80
ΔZPE ^b	0.90	0.80
E_a ^c	14.92	14.99
C1-C2 % asym ^d	1.60	1.01
B-C2 % asym. ^e	5.81	5.35
B-C1-C2 % asym. ^f	9.76	8.80
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	7.23	2.39
ΔZPE ^b	0.26	0.11
E_a ^c	6.98	2.27
C1-C2 % asym ^d	2.02	1.42
B-C2 % asym. ^e	8.78	11.65
B-C1-C2 % asym. ^f	14.00	17.47

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 19 shows the effects of different levels of theory on the predictions for $C_5H_5BCl_2$. As with both $C_5H_5BH_2$ and $C_5H_5BF_2$, the effect of considering electron correlation has a larger effect on the activation energy and percent asymmetry than the effect of the size of the basis set. Also, as with the previous molecules, as the activation energy decreases there is a corresponding increase in the asymmetry of the boron atom's position (but not necessarily an increase in the C1-C2 % asymmetry).

Table 20
C₅Me₅BH₂ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	7.32	5.70
ΔZPE ^b	0.43	0.43
E_a ^c	6.89	5.26
C1-C2 % asym ^d	1.46	1.00
B-C2 % asym. ^e	7.62	7.76
B-C1-C2 % asym. ^f	11.65	11.55
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	0.71	N/A
ΔZPE ^b	0.11	
E_a ^c	0.60	
C1-C2 % asym ^d	1.33	
B-C2 % asym. ^e	21.22	
B-C1-C2 % asym. ^f	28.25	

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 20 shows the effects of different levels of theory on the predictions for C₅Me₅BH₂. For this molecule and for the other pentamethylcyclopentadienyl compounds, predictions at the RMP2/6-31G* level are not available here. At the restricted Hartree-Fock level, an increase in the size of the basis set results in a small decrease in the activation energy, and a negligible effect on the asymmetry of the boron atom's position (the B-C2 asymmetry increased but the B-C1-C2 asymmetry decreases.) Also, as with the previous molecules, consideration of electron correlation results in a much larger decrease in activation energy combined with a large increase in the asymmetry of the boron atom's position (but not in the C1-C2 bond asymmetry).

Table 21
C₅Me₅BF₂ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	17.02	18.50
ΔZPE ^b	1.41	1.40
E_a ^c	15.61	17.10
C1-C2 % asym ^d	1.37	0.89
B-C2 % asym. ^e	3.04	3.34
B-C1-C2 % asym. ^f	5.47	5.51
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	10.50	N/A
ΔZPE ^b	0.67	
E_a ^c	9.83	
C1-C2 % asym ^d	1.77	
B-C2 % asym. ^e	4.82	
B-C1-C2 % asym. ^f	8.23	

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 21 shows the effects of different levels of theory on the predictions for C₅Me₅BF₂. Like C₅H₅BF₂, and unlike the other molecules in this study, at the restricted Hartree-Fock level increasing the size of the basis set resulted in an increase in the activation energy. Unlike all other molecules, this increase in activation energy is accompanied by a slight increase in the asymmetry of the boron atom's position. The reason for this increase is not clear. However, like all other molecules considered in this study, consideration of electron correlation resulted in a much larger change in the activation energies and the asymmetry of the boron atom's position.

Table 22
C₅Me₅BCl₂ energy (kcal/mole) and percent
asymmetry summary (at different levels of theory)

Parameter	RHF/3-21G*	RHF/6-31G*
ΔE (equilibrium) ^a	13.93	13.77
ΔZPE ^b	1.34	1.32
E_a ^c	12.59	12.45
C1-C2 % asym ^d	0.97	0.39
B-C2 % asym. ^e	3.08	1.68
B-C1-C2 % asym. ^f	5.19	2.74
Parameter	RMP2/3-21G*	RMP2/6-31G*
ΔE (equilibrium) ^a	4.04	N/A
ΔZPE ^b	0.30	
E_a ^c	3.75	
C1-C2 % asym ^d	1.96	
B-C2 % asym. ^e	7.86	
B-C1-C2 % asym. ^f	12.34	

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 22 shows the effects of different levels of theory on the predictions for C₅Me₅BCl₂. Unlike all other molecules, at the restricted Hartree-Fock level there is a slight decrease in the activation energy accompanied by a decrease in the asymmetry of the boron atom's position. However, like all other molecules considered in this study, consideration of electron correlation results in a much larger change in the activation energy and the asymmetry of the boron atom's position.

For each molecule listed in Tables 17-22, the bottom right box (RMP2/6-31G*) should be expected to be closest to the exact solution to Schrodinger's equation [56]. This method produced the smallest activation energy prediction for each molecule for which it was available. Notably, the RMP2/6-31G* results are more closely

approximated by RMP2/3-21G* than by RHF/6-31G*. Basis set effects do not appear to be as important as electron correlation effects for these molecules. For molecules that were not fully analyzed at the RMP2/6-31G*, the RMP2/3-21G* prediction is probably the best approximation available. For each molecule, these predictions also represent the largest asymmetry of the boron atom's position. The C1-C2 asymmetry, in contrast, does not display a uniform trend on Tables 17-22.

For $C_5Me_5BF_2$ (5) and $C_5Me_5BCl_2$ (6), the activation energy for rearrangement has been measured [2]. The activation energy of $C_5Me_5BF_2$ is reported to be 12.8 ± 2.0 kcal/mole [2]. Each *ab initio* result is closer to the empirical value [2] than the value obtained using MNDO (32.2 kcal/mole). None of the *ab initio* results, however, are within experimental error of the empirical result. The empirical value [2] is approximately halfway between the value predicted at the RHF/3-21G* level and the value predicted at the RMP2/3-21G* level. The trends observed in Tables 17-19 suggest however, that the activation energy predicted at the RMP2/6-31G* level will be smaller than the activation energy predicted at the RMP2/3-21G* level (and therefore further from the empirical result). The activation energy for $C_5Me_5BCl_2$ was reported to be less than 5 kcal/mole [2]. Again, each *ab initio* result is closer to the empirical value [2] than the value predicted using MNDO (21.7 kcal/mole). The value predicted at the RMP2/3-21G* level (3.7 kcal/mole) is within experimental error of the empirical value [2].

The data presented in Tables 17-22 are re-organized in order to present the effects of substituents on the activation energy and the relative asymmetry of these molecules.

These comparisons are found in Tables 23-28.

Table 23
Summary of results optimized at the
RHF/3-21G* level: energy (kcal/mole) and percent
asymmetry (for fluorine and methyl substitutions)

Parameter	C ₅ H ₅ BH ₂	C ₅ H ₅ BF ₂
ΔE (equilibrium) ^a	7.05	16.80
ΔZPE ^b	0.02	0.63
E _a ^c	7.03	16.17
C1-C2 % asym ^d	1.64	1.14
B-C2 % asym. ^e	9.18	2.99
B-C1-C2 % asym. ^f	13.98	5.33
Parameter	C ₅ Me ₅ BH ₂	C ₅ Me ₅ BF ₂
ΔE (equilibrium) ^a	7.32	17.02
ΔZPE ^b	0.43	1.41
E _a ^c	6.89	15.61
C1-C2 % asym ^d	1.46	1.37
B-C2 % asym. ^e	7.62	3.04
B-C1-C2 % asym. ^f	11.65	5.48

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 23 shows the effects of fluorine and methyl substitutions at the RHF/3-21G* level. Substituting BF₂ for BH₂ results in a substantial increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Substituting C₅Me₅ for C₅H₅ resulted in a decrease in the activation energy. For BH₂, this effect is accompanied by a decrease in the asymmetry of the boron atom's position, and for BF₂ this effect is accompanied by an increase in the asymmetry of the boron atom's position.

Table 24
Summary of results optimized at the
RHF/6-31G* level: energy (kcal/mole) and percent
asymmetry (for fluorine and methyl substitutions)

Parameter	$C_5H_5BH_2$	$C_5H_5BF_2$
ΔE (equilibrium) ^a	6.07	18.26
ΔZPE ^b	0.07	0.69
E_a ^c	6.00	17.57
C1-C2 % asym ^d	1.07	-0.001
B-C2 % asym. ^e	9.44	-0.01
B-C1-C2 % asym. ^f	14.19	-0.01
Parameter	$C_5Me_5BH_2$	$C_5Me_5BF_2$
ΔE (equilibrium) ^a	5.70	18.50
ΔZPE ^b	0.43	1.40
E_a ^c	5.26	17.10
C1-C2 % asym ^d	1.00	0.89
B-C2 % asym. ^e	7.76	3.34
B-C1-C2 % asym. ^f	11.55	5.51

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 24 shows the effects of fluorine and methyl substitutions at the RHF/6-31G* level. Again, substituting BF_2 for BH_2 results in a substantial increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Again, substituting C_5Me_5 for C_5H_5 resulted in a decrease in the activation energy. For BH_2 , this effect is accompanied by a decrease in the asymmetry of the boron atom's position, and for BF_2 this effect is accompanied by an increase in the asymmetry of the boron atom's position. This increase is not surprising, since the predicted equilibrium geometry for $C_5H_5BF_2$ at this level has an η^1 -retention geometry, not an *abgekippt* geometry.

Table 25
Summary of results optimized at the
RMP2/3-2G* level: energy (kcal/mole) and percent
asymmetry (for fluorine and methyl substitutions)

Parameter	C ₅ H ₅ BH ₂	C ₅ H ₅ BF ₂
ΔE (equilibrium) ^a	1.34	11.24
ΔZPE ^b	-0.01	0.43
E _a ^c	1.34	10.81
C1-C2 % asym ^d	1.66	1.74
B-C2 % asym. ^e	17.54	5.64
B-C1-C2 % asym. ^f	24.28	9.45
Parameter	C ₅ Me ₅ BH ₂	C ₅ Me ₅ BF ₂
ΔE (equilibrium) ^a	0.71	10.50
ΔZPE ^b	0.11	0.67
E _a ^c	0.60	9.83
C1-C2 % asym ^d	1.33	1.77
B-C2 % asym. ^e	21.22	4.82
B-C1-C2 % asym. ^f	28.25	8.23

a) η^1 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^1 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 25 shows the effects of fluorine and methyl substitutions at the RMP2/3-21G* level. Again, substituting BF₂ for BH₂ results in a substantial increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Substituting C₅Me₅ for C₅H₅ results in a decrease in activation energy. For BH₂, this effect is accompanied by a increase in the asymmetry of the boron atom's position, and for BF₂ this effect is accompanied by a decrease in the asymmetry of the boron atom's position.

Table 26
Summary of results optimized at the
RHF/3-21G* level: energy (kcal/mole) and percent
asymmetry (for chlorine and methyl substitutions)

Parameter	$C_5H_5BH_2$	$C_5H_5BCl_2$
ΔE (equilibrium) ^a	7.05	15.83
ΔZPE ^b	0.02	0.90
E_a ^c	7.03	14.92
C1-C2 % asym ^d	1.64	1.60
B-C2 % asym. ^e	9.18	5.81
B-C1-C2 % asym. ^f	13.98	9.76
Parameter	$C_5Me_5BH_2$	$C_5Me_5BCl_2$
ΔE (equilibrium) ^a	7.32	13.93
ΔZPE ^b	0.43	1.34
E_a ^c	6.89	12.59
C1-C2 % asym ^d	1.46	0.97
B-C2 % asym. ^e	7.62	3.08
B-C1-C2 % asym. ^f	11.65	5.19

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 26 shows the effects of chlorine and methyl substitutions at the RHF/3-21G* level. As with BF_2 , substituting BCl_2 for BH_2 results in an increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Substituting C_5Me_5 for C_5H_5 resulted in a decrease in the activation energy and a decrease in the asymmetry of the boron atom's position.

Table 27
Summary of results optimized the
RHF/6-31G* level: energy (kcal/mole) and percent
asymmetry (for chlorine and methyl substitutions)

Parameter	$C_5H_5BH_2$	$C_5H_5BCl_2$
ΔE (equilibrium) ^a	6.07	15.80
ΔZPE ^b	0.07	0.80
E_a ^c	6.00	14.99
C1-C2 % asym ^d	1.07	1.01
B-C2 % asym. ^e	9.44	5.35
B-C1-C2 % asym. ^f	14.19	8.80
Parameter	$C_5Me_5BH_2$	$C_5Me_5BCl_2$
ΔE (equilibrium) ^a	5.70	13.77
ΔZPE ^b	0.43	1.32
E_a ^c	5.27	12.45
C1-C2 % asym ^d	1.00	0.39
B-C2 % asym. ^e	7.76	1.68
B-C1-C2 % asym. ^f	11.55	2.74

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 27 shows the effects of chlorine and methyl substitutions at the RHF/6-31G* level. Again, substituting BCl_2 for BH_2 results in an increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Substituting C_5Me_5 for C_5H_5 resulted in a decrease in the activation energy and a decrease in the asymmetry of the boron atom's position.

Table 28
Summary of results optimized the
RMP2/3-21G* level: energy (kcal/mole) and percent
asymmetry (for chlorine and methyl substitutions)

Parameter	$C_5H_5BH_2$	$C_5H_5BCl_2$
ΔE (equilibrium) ^a	1.34	7.23
ΔZPE ^b	-0.01	0.26
E_a ^c	1.34	6.98
C1-C2 % asym ^d	1.66	2.02
B-C2 % asym. ^e	17.54	8.78
B-C1-C2 % asym. ^f	24.28	14.00
Parameter	$C_5Me_5BH_2$	$C_5Me_5BCl_2$
ΔE (equilibrium) ^a	0.71	4.05
ΔZPE ^b	0.11	0.30
E_a ^c	0.60	3.75
C1-C2 % asym ^d	1.33	1.96
B-C2 % asym. ^e	21.22	7.86
B-C1-C2 % asym. ^f	28.25	12.34

a) η^2 -optimized energy minus unconstrained optimized energy

b) zero point energy of unconstrained molecule minus zero point energy of η^2 -optimized molecule

c) " ΔE (equilibrium)" plus " ΔZPE "

d) (C1-C2 minus C1-C5) / (average of C1-C2 and C1-C5) x 100%

e) (B-C5 minus B-C2) / (average of B-C2 and B-C5) x 100%

f) (B-C1-C5 minus B-C1-C2) / (average of B-C1-C2 and B-C1-C5) x 100%

Table 28 shows the effects of chlorine and methyl substitutions at the RMP2/3-21G* level. Again, substituting BCl_2 for BH_2 results in an increase in the activation energy and a decrease in the asymmetry of the boron atom's position. Substituting C_5Me_5 for C_5H_5 resulted in a decrease in activation energy. For BH_2 , this effect is accompanied by an increase in the asymmetry of the boron atom's position, and for BF_2 this effect is accompanied by a decrease in the asymmetry of the boron atom's position.

Comparison of Tables 23-28 shows that halogen substitution uniformly results in an increase in the activation energy. The same effect is also seen in the results obtained using MNDO, as seen here and as previously reported [1]. Tables 23-28 also show that halogen substitution uniformly results in a decrease in asymmetry of the boron atom's

position. No uniform trend is observed in the effect of halogen substitution on the C1-C2 percent asymmetry. Also, no uniform effect is seen in the effect of methyl substitution effect on the asymmetry of the boron atom's position. Methyl substitution does, however, uniformly decrease the activation energy.

Finally, examination of the *ab initio* results, including the constrained distance scans, suggests that the mechanism for the 1,5-sigmatropic rearrangement does not involve an exchange between the two identical substituents on boron. For all RMP2 results, the identical substituents on boron were oriented with the plane bisecting the ring rather than with the plane of the ring. A similar result has been noted in cyclopentadienylaluminum compounds [39]. The transition state geometry had a similar substituent placement, suggesting that switching of identical substituents on rearrangement is not required. The scans of the energy vs. the constrained B-C2 distance also support this model. This mechanism is consistent with the Woodward-Hoffmann rules [4] that predict that this mechanism will proceed with a retention of configuration, as described in the Chapter 1. This prediction is in contrast with the predictions previously reported in the literature for this class of compound [1,11]. Unfortunately, the barrier to rotation of the BH₂ substituent (and presumably of the BF₂ and BCl₂ substituents) is relatively small, so it may not be possible to test this prediction experimentally.

Because of the relative paucity of empirical data on these compounds, the evaluation of these *ab initio* predictions is at best provisional. Additional empirical data

may become available in the future, and these theoretical results may assist in future evaluation.

Part B

Evaluation of the DAPSIC computer tutorial

Chapter 1

Introduction

Background

In connection with the author's graduate work at MTSU, several computer programs relevant to the teaching of undergraduate students were written. These include the following: a laboratory experiment for the advanced inorganic lab for teaching molecular orbital theory, a utility program to determine the symmetric point group for a given molecule, a program to display the effects of various symmetry operations on an ethane molecule, and a computer tutorial to teach unit conversions (see Appendix B). It was noted that unit conversions were employed when calculating the energy of activation of the rearrangement of cyclopentadienylboranes. In an effort to make this research also relevant to the teaching of undergraduates, the author tested the effectiveness of one of these programs as a method of teaching unit conversion problems to introductory chemistry students.

One of the first tasks of an introductory college chemistry course is to teach students to be able to convert measurements from one type of unit to another. Unit conversion has been presented within the first two chapters in a variety of introductory chemistry textbooks over the past six decades [121-127]. These calculations are required of students who wish to understand or do research in chemistry similar to the research described in part A; for example, they must be able to convert energy units from Hartrees/particle to kcal/mole. One method for solving problems of this type is known alternately as the "factor label method", "dimensional analysis", or "unit analysis" [128-

130]. Although there are legitimate criticisms of this method as it is usually presented [131,132], the factor label method remains one of the most popular ways of presenting stoichiometric problem solving in chemistry [131]. There is evidence that this method is effective [133]. This method is presented throughout a typical college chemistry course for solving a variety of types of problems [134]. The task of learning unit conversion is thus seen by many to be of fundamental importance in undergraduate chemistry.

Presuming that there is fundamental importance to teaching a systematic method of problem solving in chemistry, then the strategy for teaching this method should be selected and evaluated carefully. The factor label method is presented initially in lecture at Bryan College. Students are then required to solve problems during the first laboratory period. The course instructor observes students solving problems during this laboratory period to determine whether or not students are applying the method properly and calculating the correct answer. Those students who are having difficulty can then be given further explanation and guidance. This particular teaching method was selected at Bryan College in order to insure that students actively attempt to apply the factor label method to problems early in the course in an environment where assistance is available. Unfortunately, devoting the first laboratory period to teaching the factor label method means omitting one other laboratory experiment. As the number of laboratory skills expected of an introductory chemistry course increases, this practice may have to be abandoned. Also, teaching the factor label method during the first laboratory period appears to be ineffective in labs with a high student-to-teacher ratio; not all students appear to receive the individualized attention they need. This method may possibly be

intimidating to a student who does not wish to practice a new skill under the close supervision of the instructor. A certain percentage of students add the course late and miss the first laboratory period entirely. These difficulties suggest that alternatives should be investigated.

A traditional approach to teaching the factor label method is to give solved examples and worksheets with answers for students to do for homework [130]. This approach has the possible advantage of providing a less stressful environment for practicing this method at an individualized pace. Unfortunately, unsupervised students have at times been observed to ignore the unit labels entirely, and therefore to not learn to apply the factor label method. Those who do so are often unable to answer these types of questions correctly on the first exam. Therefore, some form of interactive instruction may possibly be essential for students who lack experience or confidence in dealing with mathematics. Despite these potential disadvantages, a set of worksheets has been written by the author. Should the first lab no longer be available for factor label method practice, these worksheets would be used in its place. A copy of these worksheets is found in Appendix C.

The non-traditional teaching method, computer-aided instruction (CAI), may have some potential advantages over both Bryan College's current teaching method and the use of worksheets. Computers are available at Bryan at times when an instructor would be unavailable. A CAI program can be designed to provide feedback beyond the simple correct answers an answer key to a worksheet is able to provide. This feedback may presumably occur in a less stressful manner, since "some students who are embarrassed

to show their 'ignorance' to a teacher or tutor are willing to do so to a computer" [135]. A number of computer programs have been available for teaching chemistry for many years [136-138]; however none of these were judged by Bryan College's chemistry faculty to substitute for the instruction that Bryan students are currently receiving. A new computer tutorial called "Dimensional Analysis Problem Solving in Chemistry" (DAPSIC) is being developed by the author in an attempt to model the instruction currently being given to Bryan students. A preliminary version of this computer program is now available. A copy of the instructions for use of this program is found in Appendix C, and a full text copy of this program is found in Appendix B.

DAPSIC is designed with the intention of focusing students' attention on the factor label method as opposed to the memorization of conversion factors or the arithmetic of the calculations involved. Students are forced to attend to the methodology of the factor label method, since DAPSIC requires a decision and a mouse-click for each separate step in the method. This program requires students to choose which unit conversion factors will be applied to a given problem before the actual numerical values of these conversion factors are displayed. Once the student decides that the calculation has been set up properly, DAPSIC immediately displays the results of the arithmetic calculation automatically. This tutorial is thus intended to focus the student entirely on the mechanics of selecting unit factors, choosing which units to put where, crossing out any unit labels that are found in both the numerator and denominator, and checking whether or not the problem is finished. (The process of dividing out the units is often incorrectly referred to by chemists as "canceling" the units [131]; this word was used

within DAPSIC and related materials in order to maintain consistency with other chemistry educational materials. The process was described using this term in the DAPSIC program and in the worksheets.) DAPSIC, then, intentionally forces students to be actively involved in each logical step in the thought process necessary to solve conversion problems using this method.

DAPSIC was written specifically to target those students who might otherwise be expected to have difficulty with the factor label method. In particular, students who may benefit from the rigorous practice include high school students who have not had chemistry, college students who did not take chemistry in high school, and older students who have not had chemistry for many years and have need of review. Since in DAPSIC the process of solving problems is simplified to mouse clicking, it was anticipated that students could solve more problems in a shorter amount of time. Some students seem to require a large number of practice problems before they are comfortable with the factor label method. These students also seem to need practice setting up the method. DAPSIC differs from other factor label method tutorial programs available [128,130,138] by focusing student attention on the method.

Now that the development of DAPSIC is at the field testing stage, the opportunity exists to begin to compare this method of instruction with the traditional worksheet method. The goal of each of these methods of instruction is to produce a measurable improvement in a student's ability to solve unit conversion problems. It was anticipated that DAPSIC would primarily benefit these groups of students who's experience in chemistry is limited. The research described herein is a preliminary assessment of the

effectiveness of DAPSIC compared with the traditional worksheet method. Thus, the results of this study will be useful as the decision of whether or not to continue to develop DAPSIC is made. If so, once a final version of DAPSIC has been developed, it is anticipated that a thorough and systematic evaluation of CAI for teaching factor label method calculations will be attempted at some future date. It is anticipated that a fuller version of DAPSIC (one that covers more content areas) may be of benefit to a wider group of students if the program is tested again in the future.

Purpose of This Study

The purpose of this research was to compare two methods of instruction. Primarily, the study compared the effectiveness of a particular CAI method of teaching factor label method calculations with the effectiveness of an equivalent worksheet assignment. An attempt was made to determine which of these methods of instruction produced improvement in problem solving ability in a greater number of students. The results of this research will be used in the future to decide whether or not to continue the development of DAPSIC. This research also examined student feedback about the tutorial to answer four research questions relating to student attitudes toward these methods. Finally, this study obtained suggestions and information for further revisions of DAPSIC.

Significance of This Study

This study provided information to determine which of two possible teaching approaches resulted in a greater average test score improvement. Although this particular research project was not designed to be generalized to settings outside of college chemistry education, researchers comparing different teaching methods in other settings may find the information in this study useful.

This study was intended to aid in the selection of teaching methods at Bryan College. Further development of DAPSIC would require time and resources available at Bryan College. This study is intended to assure that these resources are used wisely. Other colleges who are developing or considering development of similar tutorials may find the results of the study useful. Ultimately, students in general may be the beneficiaries of any improvement in the selection of effective teaching methods.

The scope of this research was intentionally limited to one particular CAI method for teaching one particular skill. However, the results of this study may be helpful to those seeking to address the effectiveness of CAI in general. This program has features that differ from other CAI programs; future research may be needed to compare these features with those of other computer tutorials. If, in the future, the DAPSIC tutorial is fully developed, this program may be used in further research comparing differently designed tutorials (e.g. comparing DAPSIC with modified versions of DAPSIC which have different design features.) Future program developers may benefit from comparison of differing designs in CAI programs.

Hypothesis and Research Questions

The null hypothesis for this research is stated as follows: Students who use the DAPSIC computer tutorial and students who use an equivalent worksheet assignment will show no statistically significant difference in student ability to answer unit conversion problems. This hypothesis was tested using two different groups of students: students who enroll in a chemistry course intended for chemistry majors and pre-medicine students (CHEM 121), and students who enroll in a chemistry course designed for those who will not continue in the study of chemistry (CHEM 111). This hypothesis was also tested using a subgroup within these two groups; those students who met specific criteria for identification as “at risk” chemistry students. The definition of “at-risk” students that was used in this study is given in the next section.

The data used to test this hypothesis were also examined to determine if any other identifiable subgroup responded to these two methods differently from the group as a whole.

Student feedback was solicited to address the following research questions: Do students respond favorably or unfavorably to the computer tutorial? Do they respond more favorably to the computer tutorial or the worksheets? Are students able to recognize the design rationale behind the computer tutorial? Do they express a willingness to continue to use tutorials of this type?

Definition of Terms

For the purposes of this study, “**effectiveness**” of these teaching methods was defined as follows: Each student was given a pre-treatment quiz at the beginning of the

study. The teaching method in question was then applied. Afterwards, a post-treatment quiz was given to each student. A gain score was calculated by subtracting the pre-treatment quiz score from the post-treatment quiz score. If the mean gain score for a group of students was positive, then the teaching method was considered effective for that group of students. One teaching method was identified "**more effective**" if there was a significant difference between the gain scores of the two groups of students using the two different teaching methods.

For the purposes of this study, "**at-risk students**" was defined as follows:

Students were identified "at-risk" if they met one or more of the following criteria: (a) they have never had chemistry in high school, (b) they reported that their ACT score was below 18 or that their SAT score was below 880, or (c) they reported on the questionnaire that they disagreed or strongly disagreed with the statements "I feel confident that my math background is adequate in order to do well in this chemistry course," "In general, I enjoy math and science courses," or "I felt confident in my ability to do unit conversion problems before I enrolled in this chemistry course".

A few additional terms were defined for the purpose of this study. "**Gain score**" was defined as the difference between a post-treatment quiz grade and a pre-treatment grade. "**Computer Aided Instruction (CAI)**" was defined as any technique that uses a computer program to assist in a specific instructional task. The "**factor label method**" was described in detail in one of the handouts given to students in this study (see Appendix C).

Limitations of This Study

For practical reasons, this study was limited to a specific group of students. In order to obtain a sample size sufficiently large to justify statistical analysis, this study was performed at Middle Tennessee State University (MTSU) rather than Bryan College. Volunteer students were from CHEM 111 and CHEM 121 at MTSU from the spring of 1997 and the spring of 1998. Generalization of the results of this study beyond this specific group of students would be difficult to justify.

Furthermore, since students' participation in this project was voluntary, the population for this study consisted of those students enrolled in these two courses during these two years who were willing to volunteer for this testing. Since no information was available on students who chose not to participate, it is not possible to determine whether or not this sample population is representative of chemistry students in general.

Since the researcher was not the instructor for the classes and there were several sections of each course involved, the setting of the testing for CHEM 121 was not consistent. Different computer labs were used based on availability of facilities for CHEM 121. For CHEM 111 the test was completed as an outside assignment, since testing for this class was not performed during the regular laboratory period. Students were given suggested time limits for each part, but no attempt was made to enforce these limits. Although students were asked not to change their answers in the pre-treatment quiz after they had completed the post-treatment quiz, no attempt was made to prevent students from altering their answers to the pre-treatment quiz retroactively. Some

calculators were available for students who did not have calculators; however, no attempt was made to hold constant the type of calculator available during testing.

Chapter 2

Review of Literature

Background

Computer aided instruction (CAI) has been extensively researched and reviewed; however, the results of experimental research on the effectiveness of CAI have not been uniform. This review of the literature will focus on the development of CAI and CAI research, particularly relating to the teaching of chemical and mathematical problem solving at the college level. Although generalizations about the effectiveness of CAI are inconsistent in the research literature, there have been several studies that have shown that some specific CAI application has resulted in significantly improved performance when compared with traditional teaching methods. These findings suggest that an experiment to test the effectiveness of a CAI program for teaching college-level chemistry problem solving may be of interest.

The Development of CAI

The concept of CAI has grown steadily from its roots early in this century [139]. In 1926 S. L. Pressley envisioned the design of mechanical devices that would allow students to drill and practice basic skills and memorized information [139]. He believed such a device would save teachers time and allow students to work on specific questions until a correct answer was obtained. In the 1950s B. F. Skinner noted that such a device had the advantage of immediate reinforcement of correct answers [139]. Both Pressley

and Skinner noted that students could proceed at an individualized pace. As computer systems began to be used to implement this prescription, other potential advantages of CAI were noted. As such, some authors have predicted that the intrinsic benefits of CAI will lead eventually to revolutionary changes in education comparable to a “second renaissance” [140].

The optimism over the potential of CAI has been dampened by the limitations of the computer technology developed over the same period. Some of the early mainframe computers were used for instructional purposes [141]; however, the limited availability, high cost, and complexity of using these systems prevented wide implementation of early CAI. Nonetheless, some early systems were implemented with demonstrable success [142]. As the price of computers decreased, cost effective CAI became a possibility. In particular, microcomputers such as the APPLE II and the TRS-80 developed in the 1970s made common implementation of CAI a possibility [136-138] and led to the development of a wide variety of programs designed to teach topics in specific subjects such as chemistry [143]. Some people felt that these systems suffered from many of the same disadvantages as the mainframes that they largely replaced; programs written for them were menu driven and required external documentation to learn to use [144]. With the introduction of the Apple Macintosh and Microsoft Windows in the 1980s came the concept of a graphical user interface (GUI) system [144]. In this environment, program execution is more directly under the control of the user. Instead of having to look up a specific computer command in a manual, the user can control the program execution by

the click of a mouse button. Thus the graphical user interface system represented a new opportunity for CAI systems to overcome the limitations of computer technology.

The Effectiveness of CAI

During the development of CAI, numerous studies examined the effectiveness of CAI in comparison to traditional teaching methods. In general, several reviews of this research have indicated a lack of evidence for the effectiveness of CAI [145]. Jamieson, et. al. note that “findings of no significant difference dominate the research literature in this area.”[146]. These results would tend to question the optimism over the inherent advantage of CAI in terms of measurable student performance, since research tended to show that students who were taught with traditional methods of instruction performed nearly as well on tests as students who used CAI [147]. Nonetheless, some meta-analysis of this research identifies some potential strengths of CAI. One study by P. K. Burns and W. C. Bozeman in 1981 [148], which synthesized results from 40 previous studies involving mathematics CAI programs that were used as a supplement to traditional methods, found a small but statistically significant improvement in measurable student achievement among high ability and disadvantaged students using CAI. Another study by J. A. Kulik, C. C. Kulik, and P. Cohen in 1980 [147] synthesized results from 54 previous CAI programs at the college level and found that, in general, CAI performance was somewhat superior to traditional methods. However, only fourteen of these 54 studies found a significant difference between CAI and traditional methods, and one of those fourteen studies found that the traditional method was superior to CAI. While CAI

was not uniformly found to be dramatically superior to traditional methods of instruction, as some early proponents of CAI initially anticipated, these results suggest that CAI may be of value. In fact, CAI may be of value for other practical reasons and may be used successfully for instructional purposes, even if it is not inherently superior to traditional methods of instruction.

Although research arguably has not demonstrated that CAI is inherently superior to non-CAI, some studies have found statistically significant improvement with specific CAI implementations. Thus, the focus of research can now potentially shift to studying what types of CAI are most effective. K. F. Matta and G. M. Mann in 1989 noted that although CAI research remains popular, “the focus has shifted from assessing the relative effectiveness of CAI (in comparison to traditional classroom teaching) to identifying factors that influence the success of CAI implementation.” [142]. An example of this approach is a study of CAI for adult professionals conducted by D. S. Shaw in 1992. Shaw tested the effectiveness of CAI training in the use of AutoCAD among adult professional designers [149] and found no significant difference in test scores of those who used CAI and those who were trained in other methods. However, in interviews and surveys she was able to identify features of the program that were considered to be unproductive for its specific target audience. This information could arguably lead to the development of improved CAI. She noted, “The most important lesson we have learned in the last 6 years of research is that CAI for adults must be quite different from CAI for children to be effective” [149]. Additionally, H. J. Becker notes that most CAI research that has been reviewed was done early in the development of computer technology; and

proposes that new methodologically rigorous experiments be conducted using modern CAI systems [145].

The Effectiveness of CAI in Chemistry

In contrast to CAI research in other fields, CAI research in chemistry is meager, and CAI research in the teaching of mathematical problem solving in chemistry is even more meager. Research does suggest that CAI may be more effective than traditional methods in teaching the writing of chemical formulas [150], the use of laboratory equipment [151], and the nomenclature and reactions of organic chemistry [152]. Conversely, other studies suggested that traditional methods of instruction are more effective than CAI for teaching details about the quantum mechanical description of atoms and bonding [153] and the writing of chemical formulas and nomenclature [154]. However, none of these examples deal with the use of CAI to teach mathematical problem solving in chemistry.

One investigation of CAI applied to mathematical problem solving in chemistry suggests, but does not prove, that CAI is effective. CAI was implemented with a change in curriculum in a physical chemistry course at the U.S. Air Force Academy in 1985-1987 [155]. The effects of the overall implementation of personalized instruction, which involved individualized tutoring and mini-lectures in addition to CAI were identified. Standardized tests were given after the implementation of personalized instruction. The scores for the two years after implementation were in general higher than scores for the 12 years preceding the change. No pretest was administered to control for changes in

composition of students in class from year to year. Also, the design of the study did not allow for distinguishing between the effects of CAI and the effects of the change in lecture format. The authors expressed the opinion that CAI was essential to the overall implementation of the change in curriculum; however, this finding cannot be regarded as having been proven experimentally.

Yalcinalp, et. al. used a true-experimental design to determine whether the use of CAI had any effect on student learning of mole calculations in chemistry [156]. The researchers divided chemistry students in a high school in Turkey randomly into two groups. For 4 weeks one group used CAI and the other was given an extra teacher-led recitation while receiving the same classroom instruction from the same teacher. Both groups were given pre-tests and post-tests measuring students' proficiency in solving mole calculations. Before the study, there were no significant differences between the performances of the two groups. At the end of the study, the CAI groups were found to have scored significantly higher than the recitation group. One feature noted in this study was that CAI was regularly scheduled and teacher supervised. This true-experimental design study demonstrates that it is possible for CAI to significantly improve interactive teacher-led recitations in chemistry.

The Effectiveness of CAI for Teaching the Factor Label Method

The effectiveness of the factor label method for solving of problems in chemistry has been investigated. In 1983 students in Indiana high schools were taught the mole concept using different instructional books [157]. Each book presented either the factor

label method or the method of proportionality to teach this topic. Books were randomly distributed to students. Post-test scores for those who used the factor label method had higher scores than those that used proportionality. In 1986, D. M. Bunce, H. Heikkinen compared the factor label method with an alternative teaching strategy in a college chemistry course at the University of Maryland [158]. The study found both methods to be equally effective. These studies support the conclusion that the factor label method itself would appear to be an effective method of solving chemistry problems.

Since the factor label method is traditionally taught to college chemistry students, a CAI program to assist in teaching this concept might be beneficially implemented. To date, only one study has examined the effectiveness of CAI for teaching chemistry problem solving using the factor label method [128]. In 1988 Myra H. Hauben and James. D Lehman asked "underprepared" students at Purdue University to participate in a Saturday session outside of class to learn dimensional analysis. These students were randomly divided into two groups; one group used a CAI program and the other group used a "paper and pencil version" covering the same content. A quiz was given two days later, which was "subdivided into an easy item score and a hard (more complex) item score" [128]. An ANOVA indicated that there was a significant difference in achievement between the two groups on the easy item score but not on the hard item score. Students in the CAI group scored higher on the easy items but lower on the hard items. In the opinions of the authors of this paper, "... there was probably no real difference among the groups" [128]. This study suggests that CAI is not a more effective technique for teaching factor label method calculations.

There appear to be some differences between DAPSIC used in this study and the CAI program used in Hauben and Lehman's study [128]. DAPSIC was written for Windows 3.1 and Windows 95 [159] and was designed to take advantage of the graphical user interface environment. Hauben's CAI program was written for the APPLE IIe computer, which predated the development of graphical user interface (GUI) systems. Almost ten years separate the two programs, during which time the familiarity of students with computer use would have improved. Finally, Hauben's CAI program focuses solely on numerical answers and does not emphasize the method of dimensional analysis. According to their description of the program, answers that have no units were not considered wrong. The method of dimensional analysis is presented by their program only in three solved answers and not in the actual problems which students solve. These differences in design features of the two programs suggest a study to re-examine the effectiveness of this particular CAI program for teaching the factor label method may be important.

Finally, there are some features of the research methods used in Hauben and Lehman's study [128] that were not necessary to repeat in the testing of DAPSIC. Their study was administered on Saturday rather than during the regular laboratory time. Their research used a "post-test only" experimental design with no assessment of individual student achievement before the tutorial or to calculate a gain score for each individual student. The quiz was administered two days after the tutorial rather than immediately after the tutorial. Finally, there were some additional features of their study that were open to possible criticism. Hauben and Lehman compared the results of both treatment

groups with the results of a "no treatment control" group made up of randomly selected students who agreed to participate in the study but who did not attend the Saturday session. This group arguably does not represent a random control since there may be significant differences between the "no-show" students and those who actually participated. A re-examination of the effectiveness of a CAI program should correct these features in the experimental design.

To summarize, although there have been studies of the effectiveness of CAI, the results of these studies to date have been inconsistent. Further CAI research would appear to be warranted. Also, there have been comparatively few studies investigating CAI for the teaching of chemistry. Therefore, the testing of DAPSIC seeks to investigate a less thoroughly studied application of CAI using a newer type of program and a somewhat different experimental methodology. The results of this study can then be made available for comparison with other CAI experimental results.

Chapter 3 Methodology

Background

This research was designed to compare the effectiveness of DAPSIC with the effectiveness of an equivalent worksheet method. The results of this research were to be used to decide whether or not to continue the development of DAPSIC.

Permission to conduct this study was obtained from the MTSU Human Subject Research Review Board (see Appendix F). The researcher then obtained permission to ask for volunteers from students in Chemistry 111 and 121 at MTSU. The study was conducted during the first week of labs in these classes during the beginning of Spring semester of 1997 and 1998.

Research Design

The experimental design chosen was a variation of the "pretest-posttest control group design" [160]. The design varied in that both groups selected received a different treatment. "There is no control group as it is typically defined, but this design allows the researcher to compare the differential effects of both forms of experimental treatment" [161]. In this study, volunteer students were divided into two groups. Both groups signed a consent form, and then took a pre-treatment quiz (see Appendix C). Group A worked on a worksheet with an answer key, while group B worked on the DAPSIC tutorial. Both groups then took a post-treatment quiz (see Appendix C). After the quiz,

group A was given the opportunity to use the DAPSIC tutorial, and group B was given the opportunity to review the worksheet. After both groups had used and reviewed both methods, they filled out a student questionnaire (see Appendix C). Since there is no group of subjects that take the pre-test and then immediately take the post-test without any further instruction, this study will not be able to compare the effects of an instructional method with the effects of no instructional method. The only valid comparison is the effect of one instructional method vs. the effect of the other instructional method. This design was selected in order to make this comparison.

Hauk, et al. noted that the “only threat to internal validity that is not controlled by the pretest-posttest control group design is mortality.” [161] All CHEM 121 students who volunteered did in fact complete the study, and thus mortality threat was not a factor for this group in the results. Two students, after they had completed the tutorial, chose not to give their consent to participation, and data for these two students were destroyed. CHEM 111 students did not complete this study under the same supervision. Each student completed all tasks individually and returned the materials to the lab instructor when completed. No record was kept of the number of students who volunteered for the study. Since there are no data on mortality for this population, the validity of conclusions drawn from CHEM 111 is open to question.

Sample

Students enrolled in the two introductory chemistry courses (CHEM 111 and CHEM 121) at MTSU during the spring of 1997 and 1998 were invited to participate in

this study. Participation was voluntary. The two instructors supervising these laboratory courses (Dr. Gary White and Dr. Judith Iriarte-Gross) reported afterwards that they thought students in those two years seemed fairly typical of students they had seen other years; however, other information is not available to confirm these impressions.

According to MTSU student profiles [162], there were 16639 students enrolled at MTSU during the spring semester of 1997 and 16394 students enrolled at MTSU during the spring of 1998. The total number of students enrolled in 100 level chemistry during Spring 1997 and Spring 1998 was 1375 and 1340, respectively. Freshman intending to major in chemistry during Spring 1997 and Spring 1998 numbered 212 and 201, respectively. During Spring 1997 there were enrolled 3340 student under the age of 21, 6707 students between age 21 and 24, and 6592 students over the age of 24. During Spring 1998 there were enrolled 3605 student under the age of 21, 6940 students between age 21 and 24, and 6389 students over the age of 24. According to Lovejoy's College Guide [163] the average composite ACT score at MTSU for 1997 was 21.

Instrumentation

The DAPSIC computer tutorial was written by the researcher in Visual Basic 3.0 [164] for use in personal computers operating under either Windows 3.1 or Windows95 [159]. This computer tutorial presents a problem to the subject, then allows the subject to repeatedly select an appropriate conversion factor, multiply the starting quantity by this conversion factor, and identify the units of the product. A text version of this program is included in Appendix B.

The researcher wrote the practice problems included in the tutorial and the worksheet. This set of problems was compared by the researcher with problems in several introductory chemistry textbooks [121-127] and was believed by the researcher to be a typical problems set for teaching factor label method in an introductory chemistry course. These problems were also reviewed for content validity by a group of Bryan College volunteer students and teaching assistants, who also felt that these problems were representative of the type of problems typically encountered by introductory chemistry students. The problems were classified into simple metric-English conversions, multi-step unit conversions, and conversions involving density units. Even though problems involving calculation of square or cubic units from linear units may typically be solved using the factor label method, they were intentionally omitted from the study assignment since the current version of DAPSIC cannot handle square or cubic units. Problems involving temperature unit conversion were intentionally omitted since these problems are solved using a formula rather than a unit factor [165].

The quiz questions used to assess student achievement were taken from the original set of problems written in the development of DAPSIC. Originally, a quiz with five questions was intended to be used as both the pre-test and the post-test quiz. However, before the study began, the researcher removed two of the questions from the pre-test quiz. Only responses to the three questions found in both quizzes were graded and analyzed.

The researcher designed a questionnaire for student feedback. This questionnaire contained demographic questions, attitude questions, and a space for free response. The

demographic information and three of the attitude questions were included to identify “at-risk” students. The other questions were included to determine if the student felt that the CAI and worksheet practice was helpful, if the student felt the CAI tutorial was more beneficial than the worksheet, if they felt comfortable working with computer tutorials in general and with DAPSIC in particular, and if they felt that this type of computer tutorial should continue to be used. These questions were selected to quantify general student attitudes; more specific student feedback was obtained through the free response portion of the questionnaire.

The program, instructions, worksheets, and quizzes were all reviewed by teaching assistants and volunteer students at Bryan College prior to the beginning of this study in an effort to verify content validity. These materials were deemed appropriate for this study with minor revisions made based on their suggestions. A copy of the final form of all printed material used in this study is included in Appendix C.

Procedure

The activities for the students were designed so that all students could complete all quizzes, tutorials, and questionnaires within 2 hours. The length of time allocated for this study was the same as the time allocated for Hauben and Lehman's study [128] and approximately the same as the time allocated for the worksheet currently being used at Bryan College.

Before the study began, all papers needed for student use were collated into sets and stapled together. Two different sets of papers were produced, one for group A and

one for group B. The first page was identical for both groups. The second page of each set of papers informed the student which group they would be in, along with instructions relevant to each group. All subsequent pages were identical for each group; the only difference was in the order in which they were arranged. The group A sets of papers and the group B sets of papers were assembled into a single stack according to the following procedure. Digits were read sequentially from a random number table [166]. If the next digit was even, a group A paper set was added to the stack followed by a group B paper set. If the next digit was odd, a group B paper was added to the stack followed by a group A paper. The stack of papers was then taken to the location of the testing. CHEM 121 students were given sets of papers from this stack in the order in which they entered the room for testing. Papers for CHEM 111 were arranged using the same procedure, and CHEM 111 students were given sets of papers from the stack in the order in which they volunteered to participate in the study. Neither the students nor the person administering the study could see to which group a particular student was assigned until after the papers were distributed. This procedure was intended to separate the students randomly while still maintaining approximately equal populations in the two groups.

This study was administrated differently in CHEM 111 and CHEM 121. CHEM 121 students, during the first laboratory period of the semester, were invited to participate in this study in place of the regularly scheduled laboratory experiment. Approximately 20% of each lab section volunteered for this study. Those who chose to participate completed the tutorials, took the quizzes, and filled out the questionnaire in a computer laboratory under the direct supervision of the researcher. CHEM 111 students, during the

first laboratory period of the semester, were invited to participate in this study during their free time at some point during the semester. Students who volunteered for the study were given a set of papers and a disk. Once students finished the assigned tasks, they returned their papers to their laboratory instructor.

The timeline for the study was as follows: Students read and signed the consent form (approximately 5 minutes). They then read the general direction sheet (5 minutes). Students took the pre-tutorial quiz (3 questions, suggested time limit - 15 minutes). Group A students then did the worksheets; group B students did the computer tutorial (suggested time limit - 30 minutes.) The post-treatment quiz was then administered (5 questions, suggested time limit - 30 minutes). Group A then reviewed the computer tutorial while group B reviewed the worksheet (no time limit). Both groups then completed the questionnaire (no time limit.) Most students were able to finish this assignment in approximately 2 hours.

Once the assignment was completed, the pre-test and post-test quizzes were graded by the researcher. The stapled sets of papers were then folded over so that the quiz page was visible and the page identifying the group was not visible. All sets of papers were folded before any were graded. This process was followed for both the pre-test quiz and the post-test quiz.

Justification of Statistical Techniques

A t-test was performed on the data by Dr. Toto Sutarso of the Office of Information Technology MTSU to determine whether there was a significant difference

in the mean gain scores of these two groups. For studies involving a small sample size, this statistical test is appropriate [167]. A probability of 0.05 was considered sufficient to reject the null hypothesis in each case.

The researcher tabulated the results of the student feedback questionnaire items and performed a content analysis on the questionnaire open responses. Content analysis is used since it is a frequently used method to systematically identify characteristics of written documents [168]. The content analysis was performed to identify the major themes expressed by students and to tabulate the number of positive vs. negative comments recorded.

Chapter 4

Data Analysis

Demographic Information on the Sample

Of the 104 participants who signed the consent form and handed in their sheets, there were results from 65 CHEM 121 students and 39 CHEM 111 students. Of the CHEM 121 students, 25 (38%) reported that they were freshman, 23 (35%) sophomores, 13 (20%) juniors, 3 (5%) seniors, and 1 (2%) student reported “other” for college level. Of the CHEM 111 students, 10 (26%) reported that they were freshman, 13 (33%) sophomores, 10 (26%) juniors, 4 (10%) seniors, and 2 (5%) students reported “other” for college level. There were 40 students younger than age 23 in CHEM 121 (61% of this class), and 23 students younger than age 23 in CHEM 111 (59% of this class). The demographic information collected on each student is tabulated in Appendix D.

Gain Scores

The quiz results are listed in Tables 29-37. The scores for the pre-test and post-test can range from 0 (no correct answers) to 3 (all correct answers), while the gain scores (pre-test score minus post-test score) can range from -3 to +3. A negative gain score implies that student answered more questions incorrectly on the post-test quiz than on the pre-test quiz. The null hypothesis given in Chapter 1 can then be restated using this definition of gain score: For a specific group of students, the mean gain score for group A will equal the mean gain score for group B. This null hypothesis can be tested for both

classes, and for groups of students within each class. All raw scores for all students are tabulated in Appendix D.

The gain score results for all CHEM 121 students are given in Table 29. The mean gain score of students who used the worksheet was zero, suggesting that the tutorial had no net improvement in student performance. The mean gain score of students who used DAPSIC was 0.21, suggesting that the tutorial may have had a positive impact on these students. However, the t-test results ($t=-1.519$, $P=0.134$) indicate that there is a probability of over 13% that these two populations did in fact have identical mean gain scores. Since this probability is not less than 5%, the null hypothesis is accepted for CHEM 121 students.

Table 29
Gain score results: all CHEM 121 students

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	36	1.81	1.81	0.00	0.68
Group B (DAPSIC)	29	1.93	2.14	0.21	0.41
t-test results	n=65	$t=-1.519$	$P(t)=0.134$	Null Hypothesis accepted	

Results for "at-risk" CHEM 121 students are shown in Table 30. Thirty-nine students were identified as "at-risk" according to the criteria defined in Chapter 1 (no high school chemistry, low ACT or SAT scores, and/or reported a lack of confidence in abilities on questionnaire.) There was a higher gain score (0.13) for group A and a slightly higher gain score (0.25) for group B, indicating that both groups were benefiting

from both methods of instruction. The gain scores of groups A and B differed less for "at-risk" CHEM 121 students than for CHEM 121 students in general. Based on the t-test results ($t=-0.654$, $P=0.517$) the null hypothesis was also accepted for this group.

Table 30
Gain score results: "at risk" CHEM 121 students

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	23	1.57	1.70	0.13	0.69
Group B (DAPSIC)	16	1.69	1.94	0.25	0.45
t-test results	n=39	$t=-0.654$	$P(t)=0.517$	Null Hypothesis accepted	

After the results were initially reviewed, it was noted that older and younger students seemed to respond differently to this study. Therefore it seemed reasonable to examine CHEM 121 students in age subgroups. This group was therefore divided into those younger than age 23 (40 students, 61.5% of the overall group) and those older than age 22 (25 students, 38.5% of the overall group). Age 22 was assumed to be the age at which a traditional student (who enrolls in college immediately after high school) is expected to graduate from college. As shown in Table 31, for the forty younger students there was almost no difference in the mean gain scores of the two groups. This subgroup was the only sample in this study that had a higher mean gain score for group A than group B. The results of the t-test ($t=0.235$, $P=0.816$) caused the acceptance of the null hypothesis.

Table 31
Gain score results: CHEM 121 students age 22 or younger

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	21	1.62	1.76	0.14	0.65
Group B (DAPSIC)	19	2.15	2.26	0.11	0.32
t-test results	n=40	t=0.235	P(t)=0.816	Null Hypothesis accepted	

Results for older students are shown in Table 32. For the twenty-five older students the t-test results ($t=2.51$, $P=0.020$) indicated that there was sufficient difference in the means to reject the null hypothesis. The mean gain score for group A was negative for older CHEM 121 students; suggesting that for them the worksheet assignment was more confusing than helpful. The mean gains score for group B was almost twice as large as the mean gain score for CHEM 121 students in general.

Table 32
Gain score results: CHEM 121 students age 23 or older

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	15	2.07	1.87	-0.20	0.68
Group B (DAPSIC)	10	1.50	1.90	0.40	0.52
t-test results	n=25	t=-2.510	P(t)=0.020	Null Hypothesis rejected	

The results for all thirty-nine CHEM 111 students are given in Table 33, respectively. For this class, the null hypothesis was rejected ($P<0.05$). There was a

negative mean gain score for group A and a positive mean gain score for group B indicating that DAPSIC tended to raise student achievement, whereas the worksheet tended to lower achievement.

Table 33
Gain score results: all CHEM 111 students

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	18	2.00	1.94	-0.06	0.64
Group B (DAPSIC)	21	1.86	2.33	0.48	0.68
t-test results	n=39	t=-2.525	P(t)=0.016	Null Hypothesis rejected	

Of the thirty-nine CHEM 111 students, twenty-seven (69.2%) were identified as "at risk". The results for these students are given in Table 34. For this group, the null hypothesis was also rejected ($P < 0.05$). Again, there was a negative mean gain score for group A and a positive mean gain score for group B indicating that DAPSIC tended to raise student achievement, whereas the worksheet tended to lower achievement.

Table 34
Gain score results: "at risk" CHEM 111 students

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	12	2.17	2.00	-0.17	0.58
Group B (DAPSIC)	15	1.73	2.20	0.47	0.74
t-test results	n=27	t=-2.492	P(t)=0.020	Null Hypothesis rejected	

As with CHEM 121 students, CHEM 111 students were also examined in age subgroup. The results for the twenty-three CHEM 111 students age 22 or younger are given in Table 35. The younger students in group B had a higher mean gain score (0.33) than the younger students in group A (0.00), but the difference between the two was smaller than for CHEM 111 students in general. The null hypothesis was accepted for this subgroup ($t=-1.245$, $P=0.227$).

Table 35
Gain score results: CHEM 111 students age 22 or younger

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	11	2.00	2.00	0.00	0.63
Group B (DAPSIC)	12	2.08	2.41	0.33	0.65
t-test results	n=23	$t=-1.245$	$P(t)=0.227$	Null Hypothesis accepted	

The results for CHEM 111 students over age 23 are shown in Table 36. As with CHEM 121, the sixteen older students showed a greater difference between the mean gain scores of groups A and B than did students in general, "at-risk" students, or younger students. For older students in CHEM 111, the difference between the mean gain scores of groups A and B was even larger than the corresponding difference in older CHEM121 student. Based on the t-test results ($t=-2.303$, $P=0.038$, the null hypothesis was rejected) for older CHEM 111 students.

Table 36
Gain score results: CHEM 111 students age 23 or older

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	7	2.00	1.86	-0.14	0.69
Group B (DAPSIC)	9	1.55	2.22	0.67	0.71
t-test results	n=16	t=-2.303	P(t)=0.038	Null Hypothesis rejected	

According to MTSU chemistry professors Dr. William Ilsley, Dr. Gary White, and Dr. Judith Iriarte-Gross, CHEM 121 students are ordinarily expected to have previously had high school chemistry, but CHEM 111 students are not necessarily expected to have previously had chemistry in high school. Therefore it seemed reasonable to also examine the subset of CHEM 111 students who reported that they had never had high school chemistry. Results for the ten students who reported that they had had no chemistry in high school are given in Table 37. This subgroup was the smallest

Table 37
Gain score results: CHEM 111 students who reported never having had high school chemistry

Subject Group	Number of subjects	Pre-Test mean score	Post-Test mean score	Gain Score Mean	Gain Score Std. Dev.
Group A (worksheet)	3	2.33	2.00	-0.67	0.58
Group B (DAPSIC)	7	1.29	2.29	1.00	0.82
t-test results	n=10	t=-3.669	P(t)=0.012	Null Hypothesis rejected	

subgroup examined in this study. For this subgroup, the null hypothesis was rejected ($t=3.669$, $P=0.012$). This subgroup had the largest difference between the mean gain scores of group A (-0.67) and B (1.00) of any subgroup examined in this study. The mean gain score for the DAPSIC students in this subgroup indicated that average student answered one additional question correctly as a result of using the DAPSIC tutorial.

Questionnaire Item Responses

A summary of student responses to the questionnaire items 1 through 9 is given in Table 38 and Table 39. For each statement, students were asked to circle "strongly agree", "agree", "disagree", "strongly disagree", or "no opinion". Questionnaire items were categorized as reflecting student attitudes in general (Table 38) and student attitudes concerning the tutorial specifically (Table 39). Student responses to questionnaire items are tabulated in Appendix D.

General student attitudes were addressed by questionnaire items 1, 2, 3, and 6. A majority of students in both classes indicated that they felt confident in their mathematics background (81.6% for CHEM 121, 79.5% for CHEM 111) and that they enjoyed mathematics and science courses (84.6% for CHEM 121, 82.0% for CHEM 111). Also, a majority of students in both classes indicated that they felt comfortable working with computer tutorials and educational software (92.3% in CHEM 121, 84.6% in CHEM 111). Responses to questionnaire item 3 indicate that approximately half of each class felt confident in their ability to do this type of unit conversion problem prior to the study (50.7% for CHEM 121, 43.6% for CHEM 111) while approximately half expressed a

Table 38
Student responses to
questionnaire items: general attitudes

1: "I feel confident that my math background is adequate in order to do well in this chemistry course."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	19	29.2%	12	30.8%
Agree	34	52.4%	19	48.7%
Disagree	8	12.3%	6	15.4%
Strongly disagree	1	1.5%	2	5.1%
No opinion	3	4.6%	0	0.0%

2: "In general, I enjoy math and science courses."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	20	30.8%	7	17.9%
Agree	35	53.8%	25	64.1%
Disagree	8	12.3%	4	10.3%
Strongly disagree	0	0.0%	1	2.6%
No opinion	2	3.1%	2	5.1%

3: "I feel confident in my ability to do unit conversion problems before I enrolled in this chemistry course."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	9	13.8%	8	20.5%
Agree	24	36.9%	9	23.1%
Disagree	27	41.6%	13	33.3%
Strongly disagree	4	6.2%	9	23.1%
No opinion	1	1.5%	0	0.0%

6: "I feel comfortable working with computer tutorial/educational software in general."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	28	43.1%	13	33.3%
Agree	32	49.2%	20	51.3%
Disagree	4	6.2%	6	15.4%
Strongly disagree	1	1.5%	0	0.0%
No opinion	0	0.0%	0	0.0%

Table 39
Student responses to questionnaire
Items: tutorial and worksheet attitudes

4: "I feel that it was helpful to me to do the practice problems in this study (both on paper and on computer)."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	33	50.8%	20	51.3%
Agree	28	43.1%	17	43.5%
Disagree	2	3.1%	1	2.6%
Strongly disagree	1	1.5%	0	0.0%
No opinion	1	1.5%	1	2.6%

5: "I feel that working problems on the computer was more beneficial than working problems on paper."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	17	26.2%	9	23.1%
Agree	23	35.4%	11	28.2%
Disagree	14	21.5%	11	28.2%
Strongly disagree	5	7.7%	0	0.0%
No opinion	6	9.2%	8	20.5%

7: "I was able to understand how to use this computer tutorial."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	33	50.8%	15	38.5%
Agree	31	47.7%	16	41.0%
Disagree	1	1.5%	5	12.8%
Strongly disagree	0	0.0%	2	5.1%
No opinion	0	0.0%	1	2.6%

8: "I would continue to use computer tutorials of this type in this course if given the opportunity to do so."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	32	49.2%	13	33.3%
Agree	26	40.0%	18	46.2%
Disagree	3	4.6%	5	12.8%
Strongly disagree	0	0.0%	0	0.0%
No opinion	4	6.2%	3	7.7%

9: "I would recommend that this computer tutorial continue to be offered as part of this course next year."

Response	CHEM 121		CHEM 111	
	Number	Percent	Number	Percent
Strongly agree	35	53.8%	15	38.5%
Agree	25	38.5%	18	46.2%
Disagree	1	1.5%	4	10.3%
Strongly disagree	0	0.0%	0	0.0%
No opinion	4	6.2%	2	5.1%

lack of confidence in their ability to do these problems (47.8% in CHEM 121, 56.4% in CHEM 111).

Attitudes toward the DAPSIC tutorial and the worksheet assignment were addressed by questionnaire items 4, 5, 7, 8, and 9. A majority of students felt that they could understand how to use DAPSIC, would be willing to use tutorials of this type in the future, and would recommend future use of this tutorial in their current course. Over 90% agreed that doing the practice problems in this study was helpful to them. However, both classes were approximately evenly split as to whether the computer tutorial was more helpful than the worksheet. Even though most students felt that tutorials of this type should continue to be available, they were less confident that it was helping them more than paper and pencil assignments.

Questionnaire Open Responses

At the end of the student questionnaire, students were invited to add comments or suggestions about the study and about DAPSIC. Over 60% of the students in both classes chose to do so. After all student responses were collected, content analysis was performed by the researcher: All responses were read three times. During the second reading the major themes and categories were identified. These categories are listed in Table 40; most categories directly or indirectly related to the relative merits of DAPSIC. On the third reading, all comments were placed into their appropriate categories and the number of comments in each category was recorded. In all, 167 separate comments were identified by the researcher (65 from CHEM 111 students and 102 from CHEM 121

students). The largest single category identified who would or would not benefit from using DAPSIC. Some students identified themselves as having benefited personally, some commented about students in general, others felt that students other than themselves might be helped by this software. One comment in the latter category was: "It may be more appropriate for high school students than college students. A list of all comments is found in Appendix E.

Table 40
Questionnaire open response
content analysis: categories of comments

Total students who made comments: CHEM 111: 25 students (64% of participating students)
 CHEM 121: 41 students (63% of participating students)

Response	Chem121		Chem111	
	Number of responses	Percent of responses	number of responses	percent of responses
Identifying who would/would not benefit from DAPSIC	22	21.6%	11	16.9%
Discussing design concept of DAPSIC	21	20.6%	7	10.7%
Comparing DAPSIC with worksheet	13	12.7%	4	6.2%
Stating non-specific encouraging comments	12	11.8%	10	15.4%
Using DAPSIC	9	8.8%	10	15.4%
Suggesting improvements for DAPSIC	9	8.8%	8	12.3%
Disclosing the student's background or abilities	6	5.9%	7	10.8%
Complaining about confusing aspects of DAPSIC	4	3.9%	6	9.2%
Other	6	5.9%	2	3.1%
Total Responses:	102	100%	65	100%

Of these 167 comments, there were 135 comments specifically relating to DAPSIC that could be classified as positive and negative. The 78 positive comments (57.8%) outnumbered the 57 negative comment (42.2%) for both classes. Positive comments tended to be non-specific or general; for example, "I liked this program a lot".

The negative comments, however, were usually longer and more specific; for example, "The software/program seems to make problem solving almost too easy by giving a finite number of options from which to choose." The positive comments are summarized in Table 41 and the negative comments in Table 42.

Of these comments about DAPSIC, the comments specifically relating to the design concept of this program were separated out and examined separately. These comments, whether positive or negative, reflect that students perceived the approach used in this tutorial as somehow different. For example students were able to identify the program as forcing a step-by-step approach. One student responded positively: "I think I may have done better on the test had I done the computer test first where a definite pattern is observed.... It makes it clear how to solve measurements. Puts more emphasis on setting up the problem rather than the multiplying." Another student responded negatively to the same idea: "It provides more of a challenge for me to have to conceptualize what I am doing. After a while the conversion process seemed almost mechanical on the computer and I easily lost track of the 'big picture' of the problem." Other design features that were noted were that DAPSIC did not require the memorization of numerical quantities, that it focused on method by automating the calculations, and that it required students to continue working until a correct answer was reached (as opposed to guessing and possibly getting the answer wrong.) These design features were noticeable enough to provoke student comments.

Table 41
Questionnaire open response content
analysis: positive comments about the DAPSIC tutorial

Response	CHEM 121		CHEM 111	
	Number of responses	Percent of positive responses	number of responses	percent of positive responses
Non-specific encouraging comments	12	24.5%	10	34.4%
Program was useful (non-specific)	11	22.5%	6	20.6%
Program in general was easy to use	4	8.2%	4	13.7%
Keep the program for present or future students	5	10.2%	2	6.9%
A forced step-by-step approach is helpful	6	12.3%	0	0.0%
Focusing on method by automating mechanics is helpful	1	2.0%	2	6.9%
Computer was preferable to worksheet	2	4.1%	1	3.5%
Program help me build confidence	1	2.0%	1	3.5%
Program helped me understand	2	4.1%	0	0.0%
Forcing cancellation of units is helpful	2	4.1%	0	0.0%
Program helpful for those less experienced than me	1	2.0%	1	3.5%
Program should be optional	1	2.0%	1	3.5%
Building from simple to complex problems is helpful	0	0.0%	1	3.5%
Someone with a different learning style might benefit	1	2.0%	0	0.0%
Total Positive Responses:	49	100%	29	100%

Table 42
Questionnaire open response content
analysis: negative comments about the DAPSIC tutorial

Response	CHEM 121		CHEM 111	
	Number of responses	Percent of negative responses	number of responses	percent of negative responses
Computer program problems	11	30.5	11	52.3
Method problems	12	33.4	5	23.8
Computer should not replace worksheet	11	30.5	3	14.3
Aversion to forced step-by-step approach	2	5.6	1	4.8
Program in general did not help me	0	0.0	1	4.8
Total Negative Responses	36	100%	21	100%

Chapter 5

Discussion and Conclusions

The Effectiveness of DAPSIC – Student Performance

The gain score results of the pre-test and post-test were not significantly different for the two groups in CHEM 121. As such, there is not sufficient evidence to conclude that DAPSIC is any more effective than an equivalent worksheet assignment for this group. This conclusion is reached both for CHEM 121 students in general, and for "at risk" CHEM 121 students. These results mirrored those obtained in Hauben and Lehman's previous study [128]. One unanticipated result was observed, however. DAPSIC does appear to be more effective than the worksheet for the older students in CHEM 121. Students who were older than the traditional college age students seemed to benefit much more from this tutorial. Although this result was not originally anticipated, in retrospect it is reasonable since returning students who need review in chemistry was one of the groups originally targeted in the development of DAPSIC.

Of the two courses examined in this study, the study of CHEM 121 should be considered more valid. For this class, the study was directly supervised by the researcher. There are data on essentially all of the CHEM 121 students who volunteered to participate in the study. The conditions in CHEM 121 resembled the intended use of DAPSIC. For these reasons, the study for CHEM 121 was considered to have internal validity, whereas conclusions drawn from CHEM 111 may be considered suspect. Since this program was designed to target "at risk" students, and since more "at risk" students are found in CHEM 111 than CHEM 121, further study is needed.

The gain score results for CHEM 111 did show significant differences between the groups. This result, however, may be misleading. Since students in both groups A and B were at liberty at any time to discontinue the study, those who decided that the computer tutorial was not beneficial may have simply decided that they would not turn in the materials to the instructor. As such, the actual population may have consisted only of those students who felt positively about the computer software, and thus affected the validity of the study. It is recommended that the effectiveness of the DAPSIC tutorial be investigated in CHEM 111 using more controlled experimental conditions. Ideally, this study should be repeated for CHEM 111 using the methodology used previously for CHEM 121.

The analysis of results for CHEM 111 students does suggest that the difference in procedure may not have been primarily responsible for the difference in gain score results. Both classes showed greater gain scores in group A than in group B, and both showed a greater gain score difference among the "at risk" students. Both classes showed the same trend relative to age; traditional college age students tended to respond more favorably to the worksheet, and older returning students tended to respond more favorably to DAPSIC. The responses to the questionnaire for both classes tended to be similar. These similarities between CHEM 121 and CHEM 111 results suggest that the differences between the two classes may not be entirely the result of a non-representative sample of students.

The difference in gain score results between CHEM 121 and CHEM 111 may instead reflect a fundamental difference in preparation and experience between students

in CHEM 121 and CHEM 111. Students in CHEM 111 are not chemistry majors; as such they may possibly be less experienced in unit conversion specifically and in mathematics in general. They may be more willing to learn from a computer tutorial than their counterparts in CHEM 121. Since they are less experienced in chemistry, a short practice session may be more beneficial to them than to CHEM 121 students. Therefore, the difference in student preparation may lead to DAPSIC having more effectiveness in CHEM 111 than CHEM 121.

Based on this preliminary assessment, the researcher is not able to conclude that DAPSIC is a more effective teaching method for students in general. However, it appears to be effective for a certain portion of the student population, including the "at risk" students that DAPSIC was written to target. A difference in DAPSIC's effectiveness between "at risk" students and students in general was anticipated based on the target audience of DAPSIC's design; therefore, the results of this study are not unforeseen. A more thorough study using an improved version of DAPSIC, a longer time period, and a careful control of procedures would be informative. Any further study should examine both classes using the same experimental procedure, and should specifically address the effect of DAPSIC on different age students. The quizzes used to assess student achievement should be revised. The pre-test and post-test questions should not be the same, more questions should be used, and more attention should be given to establishing the validity of the tests. Finally, a larger sample should be obtained for both classes.

The Effectiveness of DAPSIC – Student Attitudes

Some general conclusions may be drawn from the responses to the questionnaire relating to the following research questions.

“Do students respond favorably or unfavorably to the computer tutorial?”

Although a number of students responded very unfavorably to the computer tutorial, a majority of students and a majority of comments were in favor of the computer tutorial. Most students seemed to feel that the tutorial was of some value to them.

“Do they respond more favorably to the computer tutorial or the worksheets?”

Although over half of the students favored the tutorial, a very substantial minority did not. The free responses and the questionnaire items indicated that there was no general consensus that the computer tutorial was more effective than the worksheet.

Interestingly, there was no consensus that the computer tutorial was more effective among CHEM 111 students, even though there is evidence that the computer tutorial was in fact more helpful than the worksheet for this class.

“Are students able to recognize the design rationale behind the computer tutorial?” More students commented on the design of the tutorial than any other category listed. Whether they commented on it positively or negatively, most students were able to recognize that the program was designed to focus on the step-by-step mechanics of problem solving as opposed to memorization or simple arithmetic.

“Do they express a willingness to continue to use tutorials of this type?” Most students indicated both that they would continue personally to use tutorials of this type and that they would recommend that others use it. Apparently, many of the students who

did not believe that the computer tutorial was more effective than worksheets still felt that the computer tutorial was of value.

Proposed Revisions of DAPSIC

This study was a preliminary assessment of DAPSIC in its current form. Although these results do not clearly demonstrate any superiority of DAPSIC over an equivalent worksheet assignment, some of the results suggest that DAPSIC may be a promising alternative worth developing. This researcher therefore plans to continue personally to develop DAPSIC in the future as time permits. The goal of this future development is to produce a computer tutorial that can clearly be demonstrated to be more effective than an equivalent worksheet assignment, particularly for “at risk” students. This preliminary study is therefore encouraging, since this group seems to be benefiting from the current version of DAPSIC. Students who learn effectively from worksheet assignments currently used at Bryan College will probably continue to prefer the traditional assignments. However, there are some students who do not seem to be benefiting from the traditional assignment. The ultimate aim of the development of DAPSIC is to give them an alternative.

In addition to expanding the content area addressed by DAPSIC to include conversions involving Hartrees, calories, and Joules, some features of the current form of DAPSIC will be revised. Certain revisions are needed to correct problems with program execution. However, the basic design concept of DAPSIC will be preserved. Although not all students responded positively to the focus on method, students who responded to

the subject on the questionnaire noted that the program encouraged them to think differently. One student stated, “The software makes it much easier to catch your mistakes and you have to follow through with each part of the conversion, so it was helpful.” This emphasis appears to be valuable; as such the researcher will attempt to retain this emphasis as DAPSIC is modified. Students who originally were not challenged by the current version of DAPSIC may benefit more from application of the factor label method to less familiar subject areas.

Students identified the following problems: (1) The “information in problem text” feature was confusing and the directions for use of this feature will need to be clarified. (2) Larger fonts will be used for the problem solving area since students had difficulty reading them. (3) The method of organizing the conversion factors used in this program will be explained more clearly or revised, since some students reported that they had difficulty with this feature. (4) More “help” buttons should be included, to help students who find difficulties with particular steps. (5) Finally, the selection of problems to solve is currently manual and was confusing to some students. A future version of DAPSIC might automatically select the next problem in sequence, unless the student chooses to skip to a certain problem. Students who are able to demonstrate that they can solve easy problems could automatically be directed to more challenging problems. These revisions to DAPSIC are relatively minor, and can be accomplished with a minimum of effort.

Some means of student self-assessment should be included in the program. A distressing number of students seemed unaware that they were not solving the quiz problems correctly on paper. Some student comments reflected this misperception. One

particular student wrote, “This tutorial makes conversion too easy. A person's mathematical ability is negated by this program. The only skill necessary (sic) to use this program is the ability to negate like standards of measurement. If the idea is to create easy conversion without math then this program is excellent, but I feel it may be too easy and contribute to the ‘Dumbing down of society’ which seems to be so prevalent today. Shouldn't chemistry be more than clicking ‘yes’ or ‘no’?” Ironically, the persuasiveness of this student’s criticism is diminished by the fact that this particular student scored only 33% on both quizzes. Students are perhaps not receptive to learning a different method unless they are first able to see whether or not the method they are currently using is working for them. Including some form of computer graded pre-test might allow students to assess for themselves whether or not they have mastered unit conversion. Feedback would benefit those students who do not need much practice because they have already mastered unit conversion. It would also benefit those students who think they have mastered this skill but have not.

Revisions of DAPSIC are needed in order for students to see the connection between the method used on the computer and the method used on paper and pencil. A few of the responses to the questionnaire suggest that some students thought that the purpose of this program was to show how to use a computer. DAPSIC should offer some connection between work done using mouseclicks and work done using paper and pencil. Perhaps the program could at some point require students to type in the correct conversion factor rather than selecting it. Perhaps the program could have certain problems at the end of each section that can only be solved using pencil and paper. As a

student solves problems correctly, there could perhaps be a transition from maximum automation and minimum automation. DAPSIC needs to be revised to communicate to students the tutorial goal of providing an opportunity for them to learn a technique that they can use without a computer, rather than to learn how to use a computer.

DAPSIC might also be re-examined to relate it to a greater range of students. Since this program is inherently visual, providing auditory signals or providing a component that must be solved using paper and pencil would benefit those who are not visual learners. This program is a tutorial teaching a step-by-step method. Some of the most emotional responses on the questionnaire were from students who seemed offended that an intuitive approach was not applicable to these problems. Some opportunity to guess the correct answer to a question initially may provide some feedback to students who are offended by a step-by-step method. These students may then be able to compare the factor label method with whatever intuitive method they are using (and if the intuitive method is not consistently effective allow them to consider for themselves whether an alternative method might be desirable to learn.).

Further Investigations of CAI

If a revised version of DAPSIC is deemed worthy of further evaluation, the evaluation method should be revised in light of the experience gained from conducting this current study. A more thorough study would be necessary in order to establish the relative effectiveness of DAPSIC with any reliability. The current study suffered from time constraints. A longer duration study was initially desired, but financial and

logistical limitations required this study to only involve one brief treatment. Also, the experimental method used for CHEM 111 was inherently suspect, since these students were not supervised in any way during the study and no measure of the number of students who started but did not complete the study is available. Greater attention should also be given in the future to establishing the content validity of the quiz and practice problems.

This researcher made an unfortunate decision as the instruments for conducting this study were being developed. At first, a single quiz containing five of these problems was written and included in the application made to the Human Subjects Review Board. Unfortunately, the quiz was never subsequently revised to produce different pre-treatment and post-treatment quizzes, nor were additional quiz questions written and included. Also, when the instruments were first pre-tested at Bryan College, it was felt that the duration of the study was too long. The researcher decided at that point to remove two of the questions from the pre-treatment quiz. Since a three-question test is inherently a weak instrument for evaluating a student's ability to solve factor label method problems, longer quizzes and different questions for pre-and post-test quizzes should be used in future testing.

One unexpected observation made here may be of particular interest to other researchers - the observation that older students and younger students responded differently to DAPSIC. The researcher had previously expected that the younger students were more likely to benefit from a computer tutorial. The reverse seems to be a consistent observation of this study. An explanation of why older students seem to

benefit more from DAPSIC is not obvious to this researcher. Future CAI researchers may find this a fruitful area of investigation.

DAPSIC differs in some ways from other CAI programs currently available, since it focuses rigorously on teaching methodology. If DAPSIC is ever fully developed, there also may be the opportunity to test the relative effectiveness of DAPSIC vs. other CAI programs such as the one tested in Hauben and Lehman's previous study [128]. Developers of future CAI tutorials may someday benefit from efforts to identify design features that are effective in current CAI programs such as DAPSIC.

Appendix A

Selected Optimized Molecular Geometries

Cartesian coordinates of the molecules listed in Table 1-2 and Table 15-16 are listed here. This includes all ground and transition state geometries for the 1,5-sigmatropic rearrangement of (1-6), and all ground state geometries for (7). Each of the following molecules was either optimized or η^2 -optimized using MNDO, RHF, or RMP2. Each is labeled with the figure number used in the text.

The file formats used by HyperChem 4.5 or 5.1 are used here to specify the molecule. This format was selected since it allows for specifying the coordinates more precisely than Brookhaven's Protein Data Base format.

The files list the default forcefield "mm+". This default was not changed, since the coordinates were not originally generated using Hyperchem.

Figure 9b: MNDO optimized $C_5H_5BH_2$

```
forcefield mm+
sys 0
view 40 0.21666 55 15 0.9427005 -0.2540743 0.2162452 -0.3333226 -0.6889315 0.6436377 -0.01455367 -0.678837 -0.7341447
1.3945 -0.4272 -54.363
seed -1111
mol 1
atom 1 - C CX - -0.07707262 -2.675775 -0.9460849 0.2577277 3 2 s 5 d 7 s
atom 2 - C CX - -0.07721186 -1.285031 -1.435381 0.2556032 3 1 s 3 d 8 s
atom 3 - C CX - -0.0947361 -0.4395003 -0.371088 0.1656344 3 2 d 4 s 9 s
atom 4 - C CT - -0.06807518 -1.234899 0.9290357 0.09424353 4 3 s 5 s 6 s 10 s
atom 5 - C CX - -0.09477377 -2.66896 0.4132636 0.1690558 3 4 s 1 d 11 s
atom 6 - B ** -0.1799684 -0.8968079 1.897711 -1.06542 3 4 s 12 s 13 s
atom 7 - H HC - 0.07314676 -3.536067 -1.599046 0.3263472 1 1 s
atom 8 - H HC - 0.07314348 -1.02291 -2.483228 0.3225282 1 2 s
atom 9 - H HC - 0.07280242 0.6423935 -0.3867964 0.1536776 1 3 s
atom 10 - H HC - 0.06901604 -1.009985 1.564173 0.9953812 1 4 s
atom 11 - H HC - 0.07283217 -3.522394 1.078398 0.1601427 1 5 s
atom 12 - H H - 0.06449258 0.1770843 1.962471 -1.498837 1 6 s
atom 13 - H H - 0.06454742 -1.692509 2.629448 -1.485843 1 6 s
endmol 1
```

Figure 17a: MNDO η^2 -optimized $C_5H_5BH_2$

```
forcefield mm+
sys 0
view 40 0.32452 55 15 1 0 0 0 1 0 0 0 1 -5.6992e-018 -0.40034 -55.07
seed -1111
mol 1
atom 1 C C ** h 0 -0.77 -0.4078745 0.6628744 4 2 s 5 s 6 s 9 s
atom 2 C C ** h 0 0.77 -0.4078745 0.6628744 4 1 s 3 s 13 s 6 s
atom 3 C C ** h 0 1.153 -0.06815934 -0.6924849 3 2 s 4 s 12 s
atom 4 C C ** h 0 1.950951e-016 0.1339685 -1.487394 3 3 s 5 s 11 s
atom 5 C C ** h 0 -1.153 -0.06815934 -0.6924849 3 1 s 4 s 10 s
atom 6 B B ** h 0 -1.494194e-016 0.8004946 1.514443 4 1 s 7 s 8 s 2 s
```



```

atom 7 H H ** h 0 -3.766644e-017 1.881412 1.079725 1 6 s
atom 8 H H ** h 0 -3.017121e-016 0.6883393 2.672365 1 6 s
atom 9 H H ** h 0 -1.377 -1.080729 1.271723 1 1 s
atom 10 H H ** h 0 -2.177 0.04329887 -1.03138 1 5 s
atom 11 H H ** h 0 3.419232e-016 0.4159287 -2.531535 1 4 s
atom 12 H H ** h 0 2.177 0.04329887 -1.03138 1 3 s
atom 13 H H ** h 0 1.377 -1.080729 1.271723 1 2 s
endmol 1

```

Figure 12a: RHF/3-21G* optimized C₅H₅BH₂

forcefield mm+

sys 0

view 40 0.30358 55 15 1 0 0 0 1 0 0 0 1 0.0885 -0.0835 -55.347

seed -1111

mol 1

res 1 UNK 1 --

```

atom 1 C C CR h 0 1.133036 -0.2806285 -0.1065478 3 2 s 5 s 10 s
atom 2 C C C4 h 0 -0.04454084 -0.5719029 0.8206633 4 1 s 3 s 6 s 9 s
atom 3 C C CR h 0 -1.219196 -0.2657112 -0.06377643 3 2 s 4 s 13 s
atom 4 C C CR h 0 -0.7998135 0.2232229 -1.235319 3 3 s 5 s 12 s
atom 5 C C CR h 0 0.6653936 0.2183549 -1.258923 3 1 s 4 s 11 s
atom 6 B B B3 h 0 0.2285995 0.630362 1.829299 3 2 s 7 s 8 s
atom 7 H H H h 0 -0.1326889 1.720417 1.53492 1 6 s
atom 8 H H H h 0 0.8419272 0.456661 2.835196 1 6 s
atom 9 H H H h 0 -0.03256128 -1.559086 1.263291 1 2 s
atom 10 H H H h 0 2.156445 -0.4460129 0.1558358 1 1 s
atom 11 H H H h 0 1.257741 0.5432255 -2.087274 1 5 s
atom 12 H H H h 0 -1.413685 0.576014 -2.036089 1 4 s
atom 13 H H H h 0 -2.235703 -0.3832584 0.2501116 1 3 s
endres 1
endmol 1

```

Figure 17b: RHF/3-21G* η^2 -optimized C₅H₅BH₂

forcefield mm+

sys 0

view 40 0.32894 55 15 1 0 0 0 1 0 0 0 1 0.00010696 -0.50725 -55.026

seed -1111

mol 1

```

atom 1 C C ** h 0 -0.7364017 -0.4629477 0.6781194 4 2 s 5 s 10 s 11 s
atom 2 C C ** h 0 -1.128359 -0.1301245 -0.6389353 3 1 s 3 s 6 s
atom 3 C C ** h 0 -0.0009327757 0.06275497 -1.432449 3 2 s 4 s 7 s
atom 4 C C ** h 0 1.128641 -0.1303012 -0.6402598 3 3 s 5 s 8 s
atom 5 C C ** h 0 0.7365983 -0.4634083 0.6772929 4 1 s 4 s 9 s 11 s
atom 6 H H ** h 0 -2.141607 -0.00237331 -0.9551998 1 2 s
atom 7 H H ** h 0 -0.001696518 0.3896458 -2.448281 1 3 s
atom 8 H H ** h 0 2.141393 -0.001816379 -0.9578115 1 4 s
atom 9 H H ** h 0 1.349237 -0.9408374 1.410527 1 5 s
atom 10 H H ** h 0 -1.346762 -0.9428076 1.41235 1 1 s
atom 11 B B ** h 0 0.0004640813 1.028105 1.316482 4 1 s 12 s 13 s 5 s
atom 12 H H ** h 0 0.0006664004 1.957303 0.5905324 1 11 s
atom 13 H H ** h 0 0.001175592 1.140216 2.500321 1 11 s
endmol 1

```

Figure 22b: RHF/6-31G* optimized C₅H₅BH₂

forcefield mm+

sys 0

view 40 0.30531 55 15 1 0 0 0 1 0 0 0 1 0.046344 -0.082462 -55.373

seed -1111

mol 1

```

atom 1 -C ** -0 -1.218735 -0.2378948 -0.0677791 3 2 s 3 s 12 d
atom 2 -H ** -0 -2.239496 -0.3304037 0.2522328 1 1 s
atom 3 -C ** -0 -0.0481175 -0.5489053 0.8077264 4 4 s 7 s 1 s 8 s
atom 4 -B ** -0 0.2457811 0.5941862 1.867953 3 3 s 5 s 6 s
atom 5 -H ** -0 0.8756358 0.3559478 2.851747 1 4 s
atom 6 -H ** -0 -0.1062054 1.708997 1.655342 1 4 s
atom 7 -H ** -0 -0.04951445 -1.544073 1.241449 1 3 s
atom 8 -C ** -0 1.119571 -0.2856902 -0.1133997 3 9 s 3 s 10 d

```

```

atom 9 - H ** - 0.2146809 -0.4491049 0.1516064 1 8 s
atom 10 - C ** - 0.6620079 0.2063738 -1.270442 3 11 s 8 d 12 s
atom 11 - H ** - 0.1263124 0.5156286 -2.105388 1 10 s
atom 12 - C ** - 0.7986045 0.2308749 -1.245532 3 13 s 10 s 1 d
atom 13 - H ** - 0.141599 0.5835251 -2.050189 1 12 s
endmol 1

```

Figure 25b: RHF/6-31G* η^2 -optimized $C_5H_5BH_2$

```

forcefield mm+
sys 0
view 40 0.32467 55 15 1 0 0 0 1 0 0 0 1 0.00057108 -0.38415 -55.121
seed -1111
mol 1
res 1 UNK 1 --
atom 1 H H H h 0 -0.0003801583 1.864211 0.859916 1 5 s
atom 2 H H H h 0 2.140428 0.1379685 -0.9416218 1 8 s
atom 3 C C C4 h 0 0.728349 -0.5434506 0.6096345 4 4 s 5 s 8 s 9 s
atom 4 C C C4 h 0 -0.7266502 -0.5444093 0.6114998 4 3 s 5 s 6 s 10 s
atom 5 B B B4 h 0 0.0009167482 0.8259392 1.424236 4 1 s 3 s 4 s 13 s
atom 6 C C C R h 0 -1.1244 -0.04467296 -0.6469279 3 4 s 7 s 11 s
atom 7 C C C R h 0 -0.0008565019 0.2491497 -1.411204 3 6 s 8 s 12 s
atom 8 C C C R h 0 1.123598 -0.04475237 -0.6493111 3 2 s 3 s 7 s
atom 9 H H H h 0 1.347741 -1.095008 1.290126 1 3 s
atom 10 H H H h 0 -1.345258 -1.095907 1.292753 1 4 s
atom 11 H H H h 0 -2.14157 0.1380871 -0.9359875 1 6 s
atom 12 H H H h 0 -0.00242579 0.7230269 -2.373514 1 7 s
atom 13 H H H h 0 0.002647388 0.7664109 2.615991 1 5 s
endres 1
endmol 1

```

Figure 37b: RMP2/3-21G* optimized $C_5H_5BH_2$

```

forcefield mm+
sys 0
view 40 0.3018 55 15 1 0 0 0 1 0 0 0 1 0.073436 -0.15615 -55.284
seed -1111
mol 1
atom 1 - C ** - 0.6607243 0.1878168 -1.216721 3 2 s 5 s 6 s
atom 2 - C ** - 0.7974965 0.1913367 -1.227979 3 1 s 3 s 8 s
atom 3 - C ** - 0.125687 -0.3075904 -0.0280239 3 2 s 4 s 9 s
atom 4 - C ** - 0.09353191 -0.5983073 0.8705355 4 3 s 5 s 10 s 11 s
atom 5 - C ** - 0.1117085 -0.3300083 -0.01470267 3 4 s 1 s 7 s
atom 6 - H ** - 0.1287291 0.5225563 -2.035595 1 1 s
atom 7 - H ** - 0.2143328 -0.5417933 0.2583124 1 5 s
atom 8 - H ** - 0.1407187 0.5727846 -2.037425 1 2 s
atom 9 - H ** - 0.22902 -0.3807691 0.2880522 1 3 s
atom 10 - H ** - 0.09121737 -1.49893 1.480307 1 4 s
atom 11 - B ** - 0.03285779 0.7799699 1.601832 3 4 s 12 s 13 s
atom 12 - H ** - 0.9879858 0.7555877 2.604543 1 1 s
atom 13 - H ** - 0.05236298 1.811232 1.133989 1 11 s
endmol 1

```

Figure 40: RHF/3-21G* η^2 -optimized $C_5H_5BH_2$

```

forcefield mm+
sys 0
view 40 0.32203 55 15 1 0 0 0 1 0 0 0 1 -8.1275e-005 -0.35608 -55.126
seed -1111
mol 1
atom 1 - C ** - 0.1148609 -0.1257209 -0.6511893 3 2 s 5 d 8 s
atom 2 - C ** - 0.7401784 -0.4722023 0.6850268 4 1 s 3 s 9 s 10 s
atom 3 - C ** - 0.7401186 -0.4722392 0.6851342 4 2 s 4 d 13 s 10 s
atom 4 - C ** - 0.1148718 -0.1255976 -0.651021 3 3 d 5 s 6 s
atom 5 - C ** - 0.000101239 0.08020359 -1.449903 3 4 s 1 d 7 s
atom 6 - H ** - 0.2174746 0.03496397 -0.9594278 1 4 s
atom 7 - H ** - 0.7574453e-005 0.4349104 -2.472241 1 5 s
atom 8 - H ** - 0.2174584 0.03487657 -0.959766 1 1 s
atom 9 - H ** - 0.1351009 -0.976451 1.422354 1 2 s
atom 10 - B ** - 0.4004083e-005 1.014313 1.341756 4 2 s 11 s 12 s 3 s

```

```

atom 11 - H ** -0 -0.0008913504 1.942002 0.5946654 1 10 s
atom 12 - H ** -0 0.0003577647 1.12829 2.534846 1 10 s
atom 13 - H ** -0 1.350609 -0.9768204 1.422502 1 3 s
endmol 1

```

Figure 41: RMP2/6-31G* optimized $C_5H_5BH_2$ (Optimized to an η^2 geometry)

```

forcefield mm+
sys 0
view 40 0.33276 55 15 1 0 0 0 1 0 0 0 1 8.2032e-005 -0.50964 -55.015
seed -1111
mol 1
atom 1 - B B3 -0 0.000597604 0.9934502 1.301019 4 2 s 3 d 5 s 6 s
atom 2 - H H -0 0.0006441292 1.933485 0.573915 1 1 s
atom 3 - H H -0 -0.0002304823 1.108606 2.492523 1 1 d
atom 4 - C C3 -0 -1.135729 -0.1290317 -0.6402063 3 5 s 8 s 13 s
atom 5 - C C3 -0 -0.7253729 -0.4588909 0.6825477 4 4 s 6 s 1 s 9 s
atom 6 - C C3 -0 0.7251613 -0.4585791 0.6827949 4 5 s 7 s 1 s 10 s
atom 7 - C C3 -0 1.135499 -0.1295893 -0.6407648 3 8 s 6 s 11 s
atom 8 - C C4 -0 1.89215e-005 0.06473906 -1.436272 3 7 s 4 s 12 s
atom 9 - H H -0 -1.345563 -0.9130647 1.447571 1 5 s
atom 10 - H H -0 1.344982 -0.9142076 1.44724 1 6 s
atom 11 - H H -0 2.164146 0.03523422 -0.9466259 1 7 s
atom 12 - H H -0 -0.0001228782 0.4141977 -2.462429 1 8 s
atom 13 - H H -0 -2.164311 0.03661115 -0.9458871 1 4 s
endmol 1

```

Figure 44: MNDO optimized $C_5H_5BF_2$

```

forcefield mm+
sys 0
view 40 0.30937 55 15 1 0 0 0 1 0 0 0 1 -1.0535 -0.1477 -54.687
seed 0
mol 1
atom 1 - C C3 -0 -0.1095152 -0.1385528 -0.05586565 -0.9545673 3 2 d 5 s 9 s
atom 2 - C C3 -0 -0.05682278 0.2780739 0.3424222 -2.18869 3 1 d 3 s 10 s
atom 3 - C C3 -0 -0.06407452 1.753514 0.3459164 -2.224517 3 2 s 4 d 11 s
atom 4 - C C3 -0 -0.09969473 2.229638 -0.04976774 -1.011352 3 3 d 5 s 12 s
atom 5 - C C4 -0 -0.004720688 1.070098 -0.3604727 -0.06863127 4 4 s 1 s 6 s 13 s
atom 6 - B B3 -0 0.33391 1.041833 0.4600923 1.300625 3 7 s 8 s 5 s
atom 7 - F F -0 -0.183382 1.539892 1.671979 1.45982 1 6 s
atom 8 - F F -0 -0.1882839 0.4990932 -0.02411351 2.404232 1 6 s
atom 9 - H H -0 -0.07922119 -1.155597 -0.1827809 -0.6078859 1 1 s
atom 10 - H H -0 -0.07835561 -0.3379184 0.6153133 -3.035868 1 2 s
atom 11 - H H -0 -0.0784933 2.32623 0.6214237 -3.100538 1 3 s
atom 12 - H H -0 -0.07806826 3.262646 -0.1656908 -0.7110396 1 4 s
atom 13 - H H -0 -0.05844587 1.085479 -1.446589 0.1876605 1 5 s
endmol 1

```

Figure 45: RHF/3-21G* optimized $C_5H_5BF_2$

```

forcefield mm+
sys 0
view 40 0.30722 40 15 0.4054019 0.08531322 0.9101488 -0.6347873 -0.6901658 0.3474424 0.657795 -0.7186048 -0.2256388
0.07514 -0.0051533 -40.113
mol 1
atom 1 - C ** -0 -1.934798 -0.769181 -0.503074 3 2 d 5 s 7 s
atom 2 - C ** -0 -0.807363 -1.241736 0.022265 3 1 d 3 s 8 s
atom 3 - C ** -0 -0.06795 -0.106353 0.734574 4 2 s 4 s 10 s 11 s
atom 4 - C ** -0 -1.013099 1.058235 0.532277 3 3 s 5 d 9 s
atom 5 - C ** -0 -2.065407 0.668304 -0.18267 3 4 d 1 s 6 s
atom 6 - H ** -0 -2.885696 1.280341 -0.489988 1 5 s
atom 7 - H ** -0 -2.651739 -1.328271 -1.065178 1 1 s
atom 8 - H ** -0 -0.434033 -2.241969 -0.023175 1 2 s
atom 9 - H ** -0 -0.820783 2.040229 0.907256 1 4 s
atom 10 - H ** -0 0.064189 -0.341819 1.790809 1 3 s
atom 11 - B ** -0 1.322147 0.076158 0.041228 3 3 s 12 s 13 s
atom 12 - F ** -0 2.226642 -0.919023 0.025057 1 11 s
atom 13 - F ** -0 1.71214 1.202921 -0.574624 1 11 s
endmol 1

```

Figure 46: RHF/3-21G* η^2 -optimized $C_3H_5BF_2$

forcefield mm+

sys 0

view 40 0.34075 40 15 -0.464133 0.5426189 -0.7001038 0.4766464 0.8192006 0.3189334 0.7465847 -0.1856745 -0.6388554 -0.12987 0.048244 -40.065

mol 1

atom 1 - C ** -0 0.179411 -0.889092 -0.747984 4 2 s 3 s 6 s 9 s

atom 2 - B ** -0 -1.018719 0.13852 -0.000471 3 1 s 12 s 13 s

atom 3 - C ** -0 0.179237 -0.887549 0.749437 3 1 s 4 d 10 s

atom 4 - C ** -0 1.268125 -0.07831 1.130864 3 3 d 5 s 11 s

atom 5 - C ** -0 1.915291 0.409146 -0.000249 3 4 s 6 d 8 s

atom 6 - C ** -0 1.268436 -0.080383 -1.130533 3 5 d 1 s 7 s

atom 7 - H ** -0 1.513419 0.167914 -2.140609 1 6 s

atom 8 - H ** -0 2.726965 1.101858 -0.001338 1 5 s

atom 9 - H ** -0 -0.292322 -1.639933 -1.345693 1 1 s

atom 10 - H ** -0 -0.292632 -1.636842 1.34899 1 3 s

atom 11 - H ** -0 1.512879 0.171418 2.14064 1 4 s

atom 12 - F ** -0 -0.928691 1.4891 -0.001212 1 2 s

atom 13 - F ** -0 -2.286611 -0.344643 0.000229 1 2 s

endmol 1

Figure 48: RHF/6-31G* optimized $C_3H_5BF_2$

forcefield mm+

sys 0

view 40 0.22999 40 15 0.9995436 0.02295201 0.01964247 -0.02978068 0.8578094 0.5131045 -0.005072713 -0.5134552 0.8581014 0.022682 0.37766 -40.265

mol 1

atom 1 - C ** -0 -0.7318435 -0.5081381 -1.267645 3 2 d 5 s 7 s

atom 2 - C ** -0 -1.161331 -0.1604542 -0.0582505 3 1 d 3 s 8 s

atom 3 - C ** -0 0.020219 0.055338 0.8531038 4 2 s 4 s 10 s 11 s

atom 4 - C ** -0 1.186755 -0.2546037 -0.050392 3 3 s 5 d 9 s

atom 5 - C ** -0 0.7388816 -0.5671117 -1.262718 3 4 d 1 s 6 s

atom 6 - H ** -0 1.339791 -0.8261415 -2.114097 1 5 s

atom 7 - H ** -0 -1.345869 -0.7185453 -2.123058 1 1 s

atom 8 - H ** -0 -2.180439 -0.0320672 0.2513816 1 2 s

atom 9 - H ** -0 2.210791 -0.2080689 0.2660154 1 4 s

atom 10 - H ** -0 -0.0111906 -0.6574542 1.684839 1 3 s

atom 11 - B ** -0 0.0750176 1.48305 1.523244 3 3 s 12 s 13 s

atom 12 - F ** -0 1.213142 2.05111 1.845485 1 11 s

atom 13 - F ** -0 -1.016416 2.139174 1.839759 1 11 s

endmol 1

Figure 50: RHF/6-31G* η^2 -optimized $C_3H_5BF_2$

forcefield mm+

sys 0

view 40 0.45048 40 15 -0.4704175 -0.4373162 -0.7664607 -0.3444263 0.8906659 -0.2967907 0.8124518 0.1243737 -0.569608 -0.10692 -0.03163 -40.053

mol 1

atom 1 - C ** -0 1.265532 -0.083799 -1.12798 3 2 s 5 s 12 s

atom 2 - C ** -0 1.910268 0.409796 -0.000779 3 1 s 3 s 11 s

atom 3 - C ** -0 1.264234 -0.076869 1.12899 3 2 s 4 s 10 s

atom 4 - C ** -0 0.182175 -0.884441 0.737721 4 3 s 5 s 6 s 9 s

atom 5 - C ** -0 0.182435 -0.888638 -0.732978 4 4 s 1 s 6 s 13 s

atom 6 - B ** -0 -1.028078 0.157647 -0.000823 4 5 s 7 s 4 s 8 s

atom 7 - F ** -0 -0.940412 1.474101 -0.004303 1 6 s

atom 8 - F ** -0 -2.253188 -0.351503 0.000747 1 6 s

atom 9 - H ** -0 -0.332473 -1.601477 1.348785 1 4 s

atom 10 - H ** -0 1.499068 0.180841 2.143831 1 3 s

atom 11 - H ** -0 2.717657 1.115736 -0.002974 1 2 s

atom 12 - H ** -0 1.50205 0.167284 -2.144085 1 1 s

atom 13 - H ** -0 -0.331373 -1.610299 -1.339281 1 5 s

endmol 1

Figure 51: RMP2/3-21G* optimized $C_3H_5BF_2$

forcefield mm+

sys 0

```

view 40 0.48066 40 15 -0.1580445 -0.1010754 -0.9822452 0.9194109 -0.3778779 -0.1090499 -0.3601465 -0.9203217 0.1526514 -
0.10724 -0.043799 -40.112
mol 1
atom 1 - B ** - 0 -1.290003 -0.119338 0.03275 3 2 s 4 s 5 s
atom 2 - C ** - 0 0.03932 0.211873 0.809284 4 1 s 3 s 6 s 12 s
atom 3 - H ** - 0 -0.150034 0.599575 1.817046 1 2 s
atom 4 - F ** - 0 -2.405149 0.647466 0.175132 1 1 s
atom 5 - F ** - 0 -1.409045 -1.148145 -0.844933 1 1 s
atom 6 - C ** - 0 1.04481 -0.929779 0.766882 3 2 s 7 s 8 s
atom 7 - H ** - 0 0.912697 -1.859344 1.306124 1 6 s
atom 8 - C ** - 0 2.068039 -0.615969 -0.077433 3 6 s 9 s 10 s
atom 9 - H ** - 0 2.90962 -1.250816 -0.325727 1 8 s
atom 10 - C ** - 0 1.855732 0.748833 -0.619844 3 8 s 11 s 12 s
atom 11 - H ** - 0 2.52806 1.249438 -1.306158 1 10 s
atom 12 - C ** - 0 0.706997 1.270217 -0.103089 3 10 s 13 s 2 s
atom 13 - H ** - 0 0.288022 2.252898 -0.281625 1 12 s
endmol 1

```

Figure 52: RHF/3-21G* η^2 -optimized $C_5H_5BF_2$

forcefield mm+

sys 0

```

view 40 0.24811 40 15 0.674267 0.1587708 0.7212183 -0.3626936 0.9219121 0.1361302 -0.6432864 -0.3533693 0.6792001
0.036046 -0.010718 -40.062

```

```

mol 1
atom 1 - C ** - 0 -0.178658 -0.89333 0.75398 4 2 s 8 s 9 s 5 s
atom 2 - B ** - 0 1.038994 0.14228 -8e-005 4 1 s 3 s 4 s 5 s
atom 3 - F ** - 0 0.937442 1.504064 -0.000631 1 2 s
atom 4 - F ** - 0 2.317933 -0.34705 0.000103 1 2 s
atom 5 - C ** - 0 -0.178671 -0.894044 -0.753137 4 2 s 6 s 10 s 1 s
atom 6 - C ** - 0 -1.290783 -0.086603 -1.151847 3 5 s 7 s 11 s
atom 7 - C ** - 0 -1.943784 0.410053 -0.000209 3 6 s 8 s 12 s
atom 8 - C ** - 0 -1.290765 -0.085484 1.151892 3 7 s 1 s 13 s
atom 9 - H ** - 0 0.301299 -1.659517 1.349654 1 1 s
atom 10 - H ** - 0 0.301314 -1.660931 -1.347891 1 5 s
atom 11 - H ** - 0 -1.516902 0.188368 -2.174484 1 6 s
atom 12 - H ** - 0 -2.766225 1.113529 -0.000472 1 7 s
atom 13 - H ** - 0 -1.516863 0.190482 2.174267 1 8 s
endmol 1

```

Figure 53: RMP2/6-31G* optimized $C_5H_5BF_2$

forcefield mm+

sys 0

```

view 40 0.33317 40 15 -0.6463622 -0.2525794 -0.7200136 0.3011767 0.7825538 -0.5448873 0.7010767 -0.5690458 -0.4297421 -
0.13824 -0.036465 -40.1

```

```

mol 1
atom 1 - C ** - 0 0.039082 0.236756 0.835831 4 2 s 5 s 6 s 9 s
atom 2 - C ** - 0 0.62762 1.250567 -0.10828 3 1 s 3 s 13 s
atom 3 - C ** - 0 1.761297 0.727444 -0.652112 3 2 s 4 s 12 s
atom 4 - C ** - 0 2.021286 -0.573098 -0.06158 3 3 s 5 s 11 s
atom 5 - C ** - 0 1.046211 -0.857954 0.843793 3 4 s 1 s 10 s
atom 6 - B ** - 0 -1.250744 -0.142058 0.013739 3 1 s 7 s 8 s
atom 7 - F ** - 0 -1.259976 -1.093054 -0.917811 1 6 s
atom 8 - F ** - 0 -2.390922 0.528847 0.204418 1 6 s
atom 9 - H ** - 0 -0.24037 0.641323 1.814811 1 1 s
atom 10 - H ** - 0 0.950451 -1.767143 1.427314 1 5 s
atom 11 - H ** - 0 2.863133 -1.210035 -0.312679 1 4 s
atom 12 - H ** - 0 2.386602 1.207617 -1.398125 1 3 s
atom 13 - H ** - 0 0.179002 2.214099 -0.325394 1 2 s
endmol 1

```

Figure 55: RHF/6-31G* η^1 -optimized $C_5H_5BF_2$

forcefield mm+

sys 0

```

view 40 0.30359 40 15 0.6784625 0.008211046 0.7345891 -0.2263968 0.9536069 0.1984397 -0.6988799 -0.3009425 0.6488455
0.03114 0.00058003 -40.063

```

```

mol 1
atom 1 - C ** - 0 -0.164964 -0.885604 0.735833 4 2 s 3 s 6 s 8 s

```

```

atom 2 - B ** - 0 1.025564 0.159368 -0.000172 3 1 s 11 s 12 s
atom 3 - C ** - 0 -0.164886 -0.887508 -0.733593 3 1 s 4 s 13 s
atom 4 - C ** - 0 -1.270419 -0.097295 -1.140743 3 3 s 5 s 10 s
atom 5 - C ** - 0 -1.919572 0.392185 -0.000546 3 4 s 6 s 9 s
atom 6 - C ** - 0 -1.270418 -0.094252 1.140935 3 5 s 1 s 7 s
atom 7 - H ** - 0 -1.493215 0.181543 2.166513 1 6 s
atom 8 - H ** - 0 0.368635 -1.608192 1.34464 1 1 s
atom 9 - H ** - 0 -2.749056 1.090703 -0.001494 1 5 s
atom 10 - H ** - 0 -1.493127 0.176098 -2.166988 1 4 s
atom 11 - F ** - 0 0.900918 1.493295 -0.001707 1 2 s
atom 12 - F ** - 0 2.278165 -0.336694 0.000317 1 2 s
atom 13 - H ** - 0 0.368756 -1.611551 -1.340622 1 3 s
endmol 1

```

Figure 56: MNDO optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.22481 55 15 1 0 0 0 1 0 0 0 1 1.0623 0.22483 -54.986

seed 0

mol 1

```

atom 1 - B B3 - 0.1854432 -1.921125 0.8887267 -0.2249625 3 2 s 3 s 8 s
atom 2 - Cl CL - -0.1141047 -1.136842 1.232333 -1.777995 1 1 s
atom 3 - Cl CL - -0.1245885 -3.654032 1.276433 -0.142157 1 1 s
atom 4 - C C3 - -0.1048856 -1.150357 -1.257052 0.9413295 3 5 d s 9 s
atom 5 - C C3 - -0.05417824 0.1341267 -1.700103 1.037905 3 4 d s 10 s
atom 6 - C C3 - -0.063591 1.040325 -0.5421607 1.164229 3 5 s 7 d 11 s
atom 7 - C C3 - -0.09450436 0.3053551 0.604388 1.144071 3 6 d s 12 s
atom 8 - C C4 - -0.01364326 -1.179222 0.272656 1.009159 4 7 s 4 s 13 s
atom 9 - H H - 0.08118916 -2.052062 -1.849109 0.8586986 1 4 s
atom 10 - H H - 0.07931799 0.4780213 -2.726529 1.034509 1 5 s
atom 11 - H H - 0.07932526 2.114159 -0.6357284 1.261895 1 6 s
atom 12 - H H - 0.07961643 0.661269 1.622528 1.229143 1 7 s
atom 13 - H H - 0.06460381 -1.713863 0.6014253 1.933356 1 8 s
endmol 1

```

Figure 57: MNDO η^2 -optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.28396 55 15 -0.8947563 -0.22981 -0.3828819 0.3046865 0.312648 -0.8996763 0.3264618 -0.9216499 -0.2097237 -1.8757
-0.72411 -54.889

seed 0

mol 1

```

atom 1 - Cl CL - -0.1815877 -1.643486 1.170989 -1.688376 1 2 s
atom 2 - B B3 - 0.0827632 -1.420761 0.2162926 -0.1654731 4 1 s 3 s 4 s 8 s
atom 3 - Cl CL - -0.1681337 -2.048885 -1.473089 -0.3124532 1 2 s
atom 4 - C C4 - -0.1603894 -1.499181 0.9290483 1.342976 4 5 s 8 s 2 s 9 s
atom 5 - C C3 - 0.1353531 -1.399992 2.374405 1.429472 3 4 s 6 d 10 s
atom 6 - C C3 - -0.1724529 -0.1084806 2.797749 1.038983 3 5 d 7 s 11 s
atom 7 - C C3 - 0.1353471 0.6682152 1.670116 0.6856009 3 6 s 8 d 12 s
atom 8 - C C3 - -0.1603785 -0.1121029 0.4567031 0.8440822 4 7 d 4 s 13 s 2 s
atom 9 - H H - 0.1092601 -2.099296 0.3763825 2.070637 1 4 s
atom 10 - H H - 0.08842778 -2.215203 3.026277 1.724198 1 5 s
atom 11 - H H - 0.09410524 0.2281118 3.826177 1.001157 1 6 s
atom 12 - H H - 0.08842796 1.688992 1.696759 0.3199835 1 7 s
atom 13 - H H - 0.1092579 0.3696487 -0.4643606 1.182653 1 8 s
endmol 1

```

Figure 58: RHF/3-21G* optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.24819 40 15 0.1991336 0.2819671 0.938531 -0.6757473 0.7331137 -0.07687537 -0.7097262 -0.6189013 0.3365261
0.11871 0.13514 -40.166

mol 1

```

atom 1 - C ** - 0 -0.529512 -0.638288 0.654942 4 2 s 5 s 6 s 11 s
atom 2 - C ** - 0 -1.146429 -1.217825 -0.627532 3 1 s 3 s 10 s
atom 3 - C ** - 0 -2.316917 -0.625573 -0.855515 3 2 s 4 s 9 s
atom 4 - C ** - 0 -2.604716 0.336817 0.225307 3 3 s 5 s 13 s

```

```

atom 5 - C ** -0 -1.602934 0.328539 1.10176 3 4 s 1 s 12 s
atom 6 - B ** -0 0.811186 0.034822 0.170416 3 1 s 7 s 8 s
atom 7 - Cl ** -0 2.286592 -0.938195 0.088406 1 6 s
atom 8 - Cl ** -0 0.898071 1.707769 -0.359318 1 6 s
atom 9 - H ** -0 -2.970361 -0.819317 -1.679198 1 3 s
atom 10 - H ** -0 -0.674807 -1.977869 -1.212658 1 2 s
atom 11 - H ** -0 -0.336231 -1.418004 1.386227 1 1 s
atom 12 - H ** -0 -1.522973 0.919738 1.988805 1 5 s
atom 13 - H ** -0 -3.487779 0.936553 0.276478 1 4 s
endmol 1

```

Figure 60: RHF/3-21G* η^2 -optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.32515 40 15 -0.2285548 0.2611032 -0.9378634 -0.1710634 0.9376028 0.3027183 0.9583841 0.2296218 -0.1696284 -0.092158 0.022746 -40.084

mol 1

```

atom 1 - B ** -0 -0.594819 0.005318 -9.7e-005 4 5 s 4 s 7 s 8 s
atom 2 - C ** -0 2.403801 0.097813 -0.000547 3 3 s 6 s 13 s
atom 3 - C ** -0 1.719252 -0.337268 1.128727 3 2 s 4 s 9 s
atom 4 - C ** -0 0.570619 -1.069761 0.747317 4 3 s 5 s 1 s 10 s
atom 5 - C ** -0 0.570481 -1.071304 -0.745503 4 4 s 6 s 1 s 11 s
atom 6 - C ** -0 1.719109 -0.339672 -1.128751 3 5 s 2 s 12 s
atom 7 - Cl ** -0 -2.27204 -0.644404 2.4e-005 1 1 s
atom 8 - Cl ** -0 -0.450897 1.783934 -0.00058 1 1 s
atom 9 - H ** -0 1.97773 -0.102998 2.138879 1 3 s
atom 10 - H ** -0 0.072992 -1.796352 1.353242 1 4 s
atom 11 - H ** -0 0.072884 -1.799868 -1.349065 1 5 s
atom 12 - H ** -0 1.977343 -0.107716 -2.139498 1 6 s
atom 13 - H ** -0 3.263516 0.729476 -0.001078 1 2 s
endmol 1

```

Figure 61: RHF/6-31G* optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.20041 40 15 -0.1367119 0.6383515 0.7575072 -0.9234165 0.1947132 -0.3307395 -0.3586248 -0.7447107 0.5628447 0.080123 -0.16886 -39.995

mol 1

```

atom 1 - Cl ** -0 1.005458 1.69812 -0.369903 1 2 s
atom 2 - B ** s 0 0.821253 0.032885 0.16022 3 1 s 5 s 10 s
atom 3 - C ** -0 -0.735811 -1.977173 -1.182386 1 6 s
atom 4 - C ** -0 -1.61078 0.400929 1.06544 3 5 s 8 s 13 s
atom 5 - C ** s 0 -0.558944 -0.580054 0.628002 4 4 s 6 s 2 s 9 s
atom 6 - C ** -0 -1.196025 -1.200229 -0.603063 3 5 s 7 s 3 s
atom 7 - C ** -0 -2.375314 -0.625324 -0.825503 3 6 s 8 s 11 s
atom 8 - C ** -0 -2.637775 0.372539 0.220765 3 7 s 4 s 12 s
atom 9 - H ** -0 -0.366934 -1.33611 1.38769 1 5 s
atom 10 - Cl ** s 0 2.250575 -1.004413 0.105374 1 2 s
atom 11 - H ** -0 -3.048837 -0.857124 -1.629046 1 7 s
atom 12 - H ** -0 -3.52542 0.973653 0.278522 1 8 s
atom 13 - H ** -0 -1.508803 1.032142 1.927264 1 4 s
endmol 1

```

Figure 62: RHF/6-31G* η^2 -optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

view 40 0.44222 40 15 -0.1137629 0.2093004 -0.9712113 0.3051629 0.9376628 0.1663252 0.9454807 -0.277456 -0.170542 -0.097857 0.018544 -40.082

mol 1

```

atom 1 - H ** -0 1.971925 -0.086306 -2.1389 1 8 s
atom 2 - H ** -0 3.263475 0.754108 0.000648 1 11 s
atom 3 - H ** -0 0.067541 -1.779282 1.349115 1 9 s
atom 4 - H ** -0 1.970768 -0.086245 2.139392 1 10 s
atom 5 - B ** -0 -0.579434 -0.003151 -0.000616 3 6 s 12 s 13 s
atom 6 - C ** -0 0.579091 -1.06272 -0.736861 4 5 s 7 s 8 s 9 s
atom 7 - H ** -0 0.06838 -1.779856 -1.349378 1 6 s
atom 8 - C ** -0 1.723449 -0.330998 -1.123955 3 6 s 11 d 1 s

```

```

atom 9 - C ** -0 0.578697 -1.062461 0.736622 3 6 s 10 d 3 s
atom 10 - C ** -0 1.72283 -0.330925 1.124308 3 9 d 11 s 4 s
atom 11 - C ** -0 2.409221 0.106634 0.00031 3 10 s 8 d 2 s
atom 12 - Cl ** -0 -0.481275 1.784445 -0.000113 1 5 s
atom 13 - Cl ** -0 -2.255469 -0.662318 9.3e-005 1 5 s
endmol 1

```

Figure 63: RMP2/3-21G* optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.38264 40 15 0.3306121 -0.1829451 0.9258654 -0.5650483 0.7473984 0.3494511 -0.7559207 -0.6386914 0.1437261
0.072106 0.019624 -40.1

```

mol 1

```

atom 1 - C ** -0 -2.571377 0.278661 0.195673 3 2 s 5 s 6 s
atom 2 - C ** -0 -2.208789 -0.619324 -0.924203 3 1 s 3 s 7 s
atom 3 - C ** -0 -1.027658 -1.246373 -0.645301 3 2 s 4 s 8 s
atom 4 - C ** -0 -0.495758 -0.721016 0.712157 4 3 s 5 s 9 s 11 s
atom 5 - C ** -0 -1.609804 0.207933 1.162256 3 4 s 1 s 10 s
atom 6 - H ** -0 -3.463613 0.892004 0.225602 1 1 s
atom 7 - H ** -0 -2.810489 -0.768372 -1.812998 1 2 s
atom 8 - H ** -0 -0.510529 -1.985663 -1.244527 1 3 s
atom 9 - H ** -0 -0.249626 -1.520502 1.419464 1 4 s
atom 10 - H ** -0 -1.581795 0.760643 2.093121 1 5 s
atom 11 - B ** -0 0.789619 0.041225 0.186328 3 4 s 12 s 13 s
atom 12 - Cl ** -0 0.747743 1.720783 -0.330181 1 1 s
atom 13 - Cl ** -0 2.319803 -0.837461 0.058663 1 1 s
endmol 1

```

Figure 65: RHF/3-21G* η^1 -optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.32691 40 15 0.2033492 0.09624277 0.9743646 0.08275263 0.989907 -0.1150484 -0.9756029 0.1040262 0.1933325
0.060208 -0.0072712 -40.073

```

mol 1

```

atom 1 - C ** -0 -0.556787 -1.086685 0.749135 4 2 s 3 s 7 s 8 s
atom 2 - C ** -0 -0.556731 -1.086923 -0.748796 4 1 s 6 s 12 s 3 s
atom 3 - B ** -0 0.619677 0.012784 3.8e-005 4 1 s 4 s 5 s 2 s
atom 4 - Cl ** -0 0.414592 1.777099 -9e-005 1 3 s
atom 5 - Cl ** -0 2.293811 -0.613622 2e-006 1 3 s
atom 6 - H ** -0 -0.034574 -1.819284 -1.351617 1 2 s
atom 7 - H ** -0 -0.034766 -1.818823 1.352345 1 1 s
atom 8 - C ** -0 -1.724587 -0.354562 1.15086 3 1 s 9 s 10 s
atom 9 - H ** -0 -1.96671 -0.095515 2.174347 1 8 s
atom 10 - C ** -0 -2.413324 0.091699 -0.000127 3 8 s 11 s 12 s
atom 11 - H ** -0 -3.28324 0.735566 -0.000158 1 10 s
atom 12 - C ** -0 -1.724478 -0.354969 -1.150916 3 10 s 2 s 13 s
atom 13 - H ** -0 -1.966509 -0.096353 -2.174533 1 12 s
endmol 1

```

Figure 66: RMP2/6-31G* optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.26149 40 15 0.1508403 -0.3380854 0.9289486 -0.1708409 0.9166463 0.3613488 -0.973684 -0.2132084 0.08050839
0.075834 0.031478 -40.098

```

seed -1111

mol 1

```

atom 1 - C ** -0 -2.53049 0.238579 0.192192 3 2 s 3 s 8 s
atom 2 - H ** -0 -3.422704 0.85439 0.240267 1 1 s
atom 3 - C ** -0 -1.602225 0.096421 1.179523 3 1 s 4 s 5 s
atom 4 - H ** -0 -1.597427 0.595722 2.142369 1 3 s
atom 5 - C ** -0 -0.499052 -0.766024 0.689337 4 3 s 6 s 7 s 11 s
atom 6 - H ** -0 -0.193111 -1.583976 1.349773 1 5 s
atom 7 - C ** -0 -0.961507 -1.197245 -0.67627 3 5 s 8 s 10 s
atom 8 - C ** -0 -2.134634 -0.556464 -0.952595 3 7 s 1 s 9 s
atom 9 - H ** -0 -2.697314 -0.639166 -1.877355 1 8 s
atom 10 - H ** -0 -0.424059 -1.890051 -1.314351 1 7 s
atom 11 - B ** -0 0.758122 0.036594 0.177999 3 5 s 12 s 13 s

```



```
atom 12 - Cl ** - 0 0.699664 1.719962 -0.282559 1 1 1 s
atom 13 - Cl ** - 0 2.295127 -0.80299 0.045863 1 1 1 s
endmol 1
```

Figure 67: RHF/6-31G* η^2 -optimized $C_5H_5BCl_2$

forcefield mm+

sys 0

```
view 40 0.30954 40 15 0.4420899 0.3392989 0.8303209 -0.4735987 0.8744392 -0.1051678 -0.7617485 -0.3467453 0.5472722
0.058319 -0.0225 -40.061
```

seed -1111

mol 1

```
atom 1 - H ** - 0 -3.268527 0.73429 -0.000857 1 2 s
atom 2 - C ** - 0 -2.395799 0.090694 -0.000432 3 1 s 3 s 9 s
atom 3 - C ** - 0 -1.71202 -0.350564 1.138271 3 2 s 4 s 5 s
atom 4 - H ** - 0 -1.948004 -0.085954 2.164308 1 3 s
atom 5 - C ** - 0 -0.555185 -1.070118 0.733154 4 3 s 6 s 7 s 11 s
atom 6 - H ** - 0 -0.00512 -1.774178 1.348083 1 5 s
atom 7 - C ** - 0 -0.555061 -1.071109 -0.731868 4 5 s 8 s 9 s 11 s
atom 8 - H ** - 0 -0.004926 -1.776568 -1.345127 1 7 s
atom 9 - C ** - 0 -1.711739 -0.352098 -1.138364 3 7 s 10 s 2 s
atom 10 - H ** - 0 -1.947423 -0.089063 -2.164869 1 9 s
atom 11 - B ** - 0 0.602101 0.007015 1.2e-005 4 5 s 7 s 12 s 13 s
atom 12 - Cl ** - 0 2.263363 -0.619898 -6e-006 1 1 1 s
atom 13 - Cl ** - 0 0.427361 1.765519 -0.000357 1 1 1 s
endmol 1
```

Figure 68: MNDO optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

```
view 40 0.18646 55 15 0.2298592 -0.6797328 0.6965112 0.8951399 0.4285368 0.1228041 -0.3819547 0.5952473 0.7069591 -
0.56295 -3.8773 -51.403
```

mol 1

```
atom 1 - C C3 - -0.0734148 -6.588976 0.4551771 -0.02499386 3 2 s 5 d 8 s
atom 2 - C C3 - -0.08397484 -5.183622 -0.03289329 -0.001783633 3 1 s 3 d 6 s
atom 3 - C C3 - -0.0994997 -4.328643 1.044554 -0.001333011 3 2 d 4 s 7 s
atom 4 - C C4 - -0.07392979 -5.14055 2.356594 -0.03525427 4 3 s 5 s 10 s 11 s
atom 5 - C C3 - -0.1098037 -6.594873 1.831036 -0.03622106 3 4 s 1 d 9 s
atom 6 - C C4 - -0.08654642 -4.8231 -1.486125 0.01821393 4 2 s 12 s 13 s 14 s
atom 7 - C C4 - -0.08404827 -2.831899 1.012335 0.02600739 4 3 s 15 s 16 s 17 s
atom 8 - C C4 - -0.08480597 -7.772372 -0.4627734 -0.03079935 4 1 s 18 s 19 s 20 s
atom 9 - C C4 - -0.08320737 -7.794217 2.727483 -0.06528839 4 5 s 21 s 22 s 23 s
atom 10 - C C4 - -0.07623243 -4.824461 3.192564 -1.298387 4 4 s 24 s 25 s 26 s
atom 11 - B B3 - -0.1909876 -4.940331 3.136794 1.315843 3 4 s 27 s 28 s
atom 12 - H H - -0.001072645 -5.211111 -2.004078 -0.8844852 1 6 s
atom 13 - H H - -0.004860759 -3.728074 -1.657924 0.0403148 1 6 s
atom 14 - H H - -0.0008649826 -5.24658 -1.989612 0.9130054 1 6 s
atom 15 - H H - -0.001285136 -2.42758 0.5927537 -0.9201798 1 7 s
atom 16 - H H - -0.005530119 -2.382088 2.017658 0.1563249 1 7 s
atom 17 - H H - -0.000369072 -2.45722 0.3860568 0.8635873 1 7 s
atom 18 - H H - -0.004573822 -8.736979 0.07809077 -0.1086062 1 8 s
atom 19 - H H - -0.0002036095 -7.72927 -1.164419 -0.8904585 1 8 s
atom 20 - H H - -0.0002208948 -7.811822 -1.063384 0.9027277 1 8 s
atom 21 - H H - -0.001739442 -8.345452 2.619799 -1.024136 1 9 s
atom 22 - H H - -0.001265526 -8.497227 2.48549 0.7603845 1 9 s
atom 23 - H H - -0.003407001 -7.535401 3.800321 0.04235738 1 9 s
atom 24 - H H - -0.004479289 -4.986063 2.605433 -2.225614 1 10 s
atom 25 - H H - -0.006404042 -5.462365 4.097188 -1.363315 1 10 s
atom 26 - H H - -0.00840199 -3.77142 3.540493 -1.303922 1 10 s
atom 27 - H H - -0.06122375 -4.969677 2.584465 2.335887 1 11 s
atom 28 - H H - -0.06579375 -4.77069 4.284762 1.332646 1 11 s
endmol 1
```

Figure 69: MNDO η^2 -optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

```

view 40 0.18646 55 15 0.7252973 -0.1245279 0.6770796 -0.6111982 0.3361476 0.7165483 -0.316829 -0.9335404 0.1676957
0.64847 0.0091497 -54.129
seed 0
mol 1
atom 1 - C C3 -0.1336474 -2.080974 -0.9209467 -0.2007426 3 2 s 5 d 7 s
atom 2 - C C3 -0.216548 -2.121553 0.4929636 -0.00614875 3 1 s 3 d 6 s
atom 3 - C C3 -0.1338887 -0.7902676 0.9785661 0.1685312 3 2 d 4 s 10 s
atom 4 - C C4 -0.1857109 0.1611747 -0.1369169 0.1495367 4 3 s 5 s 9 s 11 s
atom 5 - C C3 -0.1858358 -0.7011403 -1.406022 -0.0978912 3 4 s 1 d 8 s
atom 6 - C C4 -0.09574604 -3.360575 1.334388 -0.01821376 4 2 s 12 s 13 s 14 s
atom 7 - C C4 -0.04795289 -3.261812 -1.788486 -0.520822 4 1 s 15 s 16 s 17 s
atom 8 - C C4 -0.1150832 -0.3988008 -2.773886 0.4748737 4 5 s 18 s 19 s 20 s
atom 9 - C C4 -0.1151423 1.415176 -0.1040486 0.9962412 4 4 s 21 s 22 s 23 s
atom 10 - C C4 -0.04797745 -0.4023167 2.42181 0.2951512 4 3 s 24 s 25 s 26 s
atom 11 - B B3 -0.0500021 0.2250869 -0.8343644 -1.376924 3 4 s 27 s 28 s
atom 12 - H H -0.004041791 -4.236056 0.7868289 0.3881439 1 6 s
atom 13 - H H -0.004025459 -3.250666 2.24724 0.6025791 1 6 s
atom 14 - H H -0.0006716251 -3.611755 1.65697 -1.051236 1 6 s
atom 15 - H H -0.01223981 -3.987738 -1.272946 -1.182615 1 7 s
atom 16 - H H -0.01961327 -2.968316 -2.723413 -1.038791 1 7 s
atom 17 - H H -0.01927614 -3.789785 -2.068615 0.4161054 1 7 s
atom 18 - H H -0.01758981 -0.7770687 -2.855775 1.517021 1 8 s
atom 19 - H H -0.009929657 -0.8761701 -3.578416 -0.1223476 1 8 s
atom 20 - H H -0.003950775 0.6860404 -2.997849 0.500109 1 8 s
atom 21 - H H -0.01763189 1.159537 0.003068429 2.072829 1 9 s
atom 22 - H H -0.003886819 2.026119 -1.022636 0.8931798 1 9 s
atom 23 - H H -0.009832859 2.070755 0.7471508 0.7179095 1 9 s
atom 24 - H H -0.01910257 -0.5577591 2.765161 1.340584 1 10 s
atom 25 - H H -0.01918232 0.6604237 2.597692 0.0346183 1 10 s
atom 26 - H H -0.01283616 -1.005062 3.070677 -0.3732519 1 10 s
atom 27 - H H -0.05448079 -0.3193666 -0.2936298 -2.254416 1 11 s
atom 28 - H H -0.04456878 1.185165 -1.433411 -1.649165 1 11 s
endmol 1

```

Figure 70: RHF/3-21G* optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

```

view 40 0.32259 40 15 0.4561642 -0.3819093 0.8037783 0.8803601 0.06180013 -0.4702624 0.129924 0.9221312 0.3644088
0.0045912 -0.011708 -39.999

```

mol 1

```

atom 1 - H ** -0.0714197 -0.602215 2.456688 1 17 s
atom 2 - H ** -0.2676934 -0.47552 1.861772 1 17 s
atom 3 - H ** -0.2256757 1.983672 -1.079855 1 15 s
atom 4 - H ** -0.07768 3.253365 -0.039844 1 16 s
atom 5 - H ** -0.2102361 2.435199 0.766265 1 16 s
atom 6 - H ** -0.2004245 2.428981 -0.983967 1 16 s
atom 7 - H ** -0.3061225 -1.42209 -0.067551 1 14 s
atom 8 - H ** -0.3213358 0.074042 0.832807 1 14 s
atom 9 - H ** -0.3199733 0.102173 -0.920738 1 14 s
atom 10 - H ** -0.008836 -3.123394 0.827913 1 13 s
atom 11 - H ** -0.1648157 -0.824606 -1.987877 1 23 s
atom 12 - H ** -0.2239489 -2.075402 -0.89941 1 23 s
atom 13 - C ** -0.504021 -2.671417 -0.026776 4 19 s 10 s 25 s 26 s
atom 14 - C ** -0.2770081 -0.380775 -0.048231 4 20 s 9 s 8 s 7 s
atom 15 - C ** -0.1779393 2.017736 -0.104327 4 22 s 3 s 27 s 28 s
atom 16 - C ** -0.1415458 2.381761 -0.072858 4 21 s 6 s 5 s 4 s
atom 17 - B ** -0.1519667 -0.560859 1.585748 3 18 s 2 s 1 s
atom 18 - C ** -0.1039295 -0.542372 0.072556 4 17 s 19 s 22 s 23 s
atom 19 - C ** -0.0332778 -1.175774 -0.020558 3 18 s 20 s 13 s
atom 20 - C ** -0.1271973 -0.224825 -0.034274 3 19 s 21 s 14 s
atom 21 - C ** -0.0620467 1.104009 -0.024229 3 20 s 22 s 16 s
atom 22 - C ** -0.0711055 0.95646 -0.005039 3 21 s 18 s 15 s
atom 23 - C ** -0.2042273 -1.01311 -0.995409 4 18 s 24 s 12 s 11 s
atom 24 - H ** -0.2987088 -0.492468 -0.891746 1 23 s
atom 25 - H ** -0.070188 -3.103745 -0.923882 1 13 s
atom 26 - H ** -0.1547117 -2.955238 0.007605 1 13 s
atom 27 - H ** -0.255597 1.883329 0.641301 1 15 s

```

atom 28 - H ** - 0 1.363878 3.008054 0.026649 1 15 s
endmol 1

Figure 71: RHF/3-21G* η^2 -optimized $C_5Me_5BH_2$
forcefield mm+

sys 0
view 40 0.33411 40 15 -0.5478237 0.7305878 -0.4075913 -0.8342807 -0.5132899 0.2012689 -0.06216785 0.4503054 0.8907077 -
0.0042366 -5.5962e-005 -40.001
mol 1
atom 1 - H ** - 0 0.161611 3.241887 0.18062 1 17 s
atom 2 - H ** - 0 0.164739 -3.241705 0.180434 1 18 s
atom 3 - H ** - 0 -2.006343 2.597507 -0.023333 1 16 s
atom 4 - H ** - 0 -2.141508 1.668874 -1.511587 1 16 s
atom 5 - H ** - 0 -3.016493 1.176084 -0.071521 1 16 s
atom 6 - H ** - 0 -2.004343 -2.599082 -0.022967 1 19 s
atom 7 - H ** - 0 -2.139639 -1.671267 -1.511731 1 19 s
atom 8 - H ** - 0 -3.015438 -1.178357 -0.072203 1 19 s
atom 9 - H ** - 0 -2.105168 -0.001347 2.071078 1 15 s
atom 10 - C ** - 0 -0.908132 0.740071 -0.011548 4 11 s 14 s 15 s 16 s
atom 11 - C ** - 0 0.459332 1.131414 -0.089263 3 10 s 12 s 17 s
atom 12 - C ** - 0 1.273619 0.000638 -0.148385 3 11 s 13 s 23 s
atom 13 - C ** - 0 0.460356 -1.130932 -0.089514 3 12 s 14 s 18 s
atom 14 - C ** - 0 -0.907416 -0.740878 -0.011729 4 13 s 10 s 19 s 15 s
atom 15 - B ** - 0 -1.01602 -0.00065 1.583471 4 10 s 9 s 20 s 14 s
atom 16 - C ** - 0 -2.086158 1.596236 -0.429559 4 10 s 5 s 4 s 3 s
atom 17 - C ** - 0 0.959805 2.54872 -0.043442 4 11 s 1 s 26 s 27 s
atom 18 - C ** - 0 0.962278 -2.547717 -0.043389 4 13 s 2 s 21 s 22 s
atom 19 - C ** - 0 -2.084706 -1.598069 -0.42972 4 14 s 8 s 7 s 6 s
atom 20 - H ** - 0 -0.042008 -0.00025 2.253716 1 15 s
atom 21 - H ** - 0 1.735941 -2.661306 0.707649 1 18 s
atom 22 - H ** - 0 1.388422 -2.820246 -1.004819 1 18 s
atom 23 - C ** - 0 2.781536 0.001152 -0.114553 4 12 s 24 s 25 s 28 s
atom 24 - H ** - 0 3.15793 -0.000749 0.905598 1 23 s
atom 25 - H ** - 0 3.180563 -0.871415 -0.618689 1 23 s
atom 26 - H ** - 0 1.385243 2.82157 -1.005095 1 17 s
atom 27 - H ** - 0 1.733621 2.663227 0.707287 1 17 s
atom 28 - H ** - 0 3.179882 0.876019 -0.61518 1 23 s
endmol 1

Figure 72: RHF/6-31G* optimized $C_5Me_5BH_2$
forcefield mm+

sys 0
view 40 0.31325 40 15 0.8289684 -0.4125182 -0.3776773 -0.3056484 0.231385 -0.9236017 0.4683914 0.881073 0.06572532 -
0.0050174 -0.0095954 -39.991
mol 1
atom 1 - H ** - 0 2.694599 -0.323152 1.85131 1 17 s
atom 2 - H ** - 0 0.74908 -0.551123 2.462332 1 17 s
atom 3 - H ** - 0 -3.214345 -0.115892 0.843318 1 23 s
atom 4 - H ** - 0 -3.216337 -0.065747 -0.904039 1 23 s
atom 5 - H ** - 0 -2.983395 -1.588096 -0.074356 1 23 s
atom 6 - H ** - 0 0.094268 -3.103294 -0.933603 1 24 s
atom 7 - H ** - 0 0.168759 -3.122162 0.812151 1 24 s
atom 8 - H ** - 0 -1.380414 -3.035734 0.00585 1 24 s
atom 9 - H ** - 0 3.02558 -0.337959 -0.850365 1 25 s
atom 10 - H ** - 0 2.155671 2.100112 -1.083034 1 21 s
atom 11 - H ** - 0 1.192744 3.07736 0.002435 1 21 s
atom 12 - H ** - 0 -2.224539 2.32559 0.776859 1 22 s
atom 13 - H ** - 0 -0.957637 3.208479 -0.049164 1 22 s
atom 14 - H ** - 0 -2.152829 2.318139 -0.969039 1 22 s
atom 15 - C ** - 0 0.655833 0.989172 -0.016221 3 16 s 20 s 21 s
atom 16 - C ** - 0 1.058391 -0.476532 0.066503 4 15 s 17 s 18 s 25 s
atom 17 - B ** - 0 1.540902 -0.46766 1.57923 3 16 s 2 s 1 s
atom 18 - C ** - 0 -0.266996 -1.187874 -0.026861 3 16 s 19 s 24 s
atom 19 - C ** - 0 -1.260041 -0.291458 -0.038266 3 18 s 20 s 23 s
atom 20 - C ** - 0 -0.683627 1.066782 -0.028732 3 19 s 15 s 22 s
atom 21 - C ** - 0 1.660282 2.10823 -0.114929 4 15 s 11 s 10 s 26 s
atom 22 - C ** - 0 -1.543434 2.299366 -0.069456 4 20 s 14 s 13 s 12 s

```

atom 23 - C ** -0 -2.744611 -0.533203 -0.043761 4 19 s 5 s 4 s 3 s
atom 24 - C ** -0 -0.356277 -2.688419 -0.03531 4 18 s 8 s 7 s 6 s
atom 25 - C ** -0 2.111373 -0.91075 -0.961129 4 16 s 9 s 27 s 28 s
atom 26 - H ** -0 2.439851 2.030994 0.636593 1 21 s
atom 27 - H ** -0 1.746619 -0.773598 -1.975138 1 25 s
atom 28 - H ** -0 2.372451 -1.957514 -0.839288 1 25 s
endmol 1

```

Figure 74: RHF/6-31G* η^2 -optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

```

view 40 0.34164 40 15 -0.5174497 0.8054582 -0.288934 -0.8556644 -0.4906537 0.1646128 -0.009177773 0.3324094 0.9430905 -
0.0039562 0.00063231 -40.001

```

mol 1

```

atom 1 - H ** -0 -2.103081 -0.003719 2.047768 1 19 s
atom 2 - H ** -0 -0.051405 -0.000302 2.253384 1 19 s
atom 3 - H ** -0 0.190129 -3.223733 0.305171 1 27 s
atom 4 - H ** -0 1.814532 -2.642186 0.617646 1 27 s
atom 5 - H ** -0 1.267369 -2.867694 -1.030148 1 27 s
atom 6 - H ** -0 -1.995703 -2.601917 -0.012709 1 24 s
atom 7 - H ** -0 -2.141155 -1.68907 -1.504326 1 24 s
atom 8 - H ** -0 -3.01207 -1.188107 -0.068879 1 24 s
atom 9 - H ** -0 -2.151923 1.673472 -1.505579 1 23 s
atom 10 - H ** -0 -2.003067 2.595558 -0.020065 1 23 s
atom 11 - H ** -0 0.1768 3.224008 0.308915 1 26 s
atom 12 - H ** -0 1.251586 2.87503 -1.0302 1 26 s
atom 13 - H ** -0 1.804798 2.649955 0.615694 1 26 s
atom 14 - H ** -0 3.190951 -0.861848 -0.623192 1 25 s
atom 15 - H ** -0 3.168175 -0.003236 0.903196 1 25 s
atom 16 - H ** -0 3.187978 0.882262 -0.607796 1 25 s
atom 17 - C ** -0 -0.90766 0.731683 -0.013548 4 18 s 19 s 22 s 23 s
atom 18 - C ** -0 -0.904547 -0.735325 -0.013401 4 17 s 20 s 24 s 19 s
atom 19 - B ** -0 -1.010783 -0.001886 1.557403 4 17 s 18 s 2 s 1 s
atom 20 - C ** -0 0.462262 -1.126488 -0.08881 3 18 s 21 s 27 s
atom 21 - C ** -0 1.277341 0.002786 -0.152236 3 20 s 22 s 25 s
atom 22 - C ** -0 0.457575 1.128665 -0.088708 3 21 s 17 s 26 s
atom 23 - C ** -0 -2.08333 1.592395 -0.423362 4 17 s 10 s 9 s 28 s
atom 24 - C ** -0 -2.076619 -1.601374 -0.422379 4 18 s 8 s 7 s 6 s
atom 25 - C ** -0 2.783558 0.005146 -0.114757 4 21 s 16 s 15 s 14 s
atom 26 - C ** -0 0.946529 2.548209 -0.03884 4 22 s 13 s 12 s 11 s
atom 27 - C ** -0 0.957659 -2.543751 -0.039284 4 20 s 5 s 4 s 3 s
atom 28 - H ** -0 -3.016603 1.179288 -0.063943 1 23 s
endmol 1

```

Figure 75: RMP2/3-21G* optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

```

view 40 0.33251 40 15 0.5147273 -0.1077396 0.8505575 0.8494893 -0.06997654 -0.5229448 0.1158609 0.9917134 0.05550477
0.0033663 -0.0099827 -39.998

```

mol 1

```

atom 1 - C ** -0 -1.298088 -0.085464 -0.115933 3 2 s 5 s 6 s
atom 2 - C ** -0 -0.508396 1.140751 -0.072087 3 1 s 3 s 7 s
atom 3 - C ** -0 0.853334 0.829209 -0.029387 3 2 s 4 s 9 s
atom 4 - C ** -0 0.969455 -0.684061 0.058333 4 3 s 5 s 10 s 26 s
atom 5 - C ** -0 -0.442086 -1.172082 -0.082931 3 4 s 1 s 8 s
atom 6 - C ** -0 -2.81448 -0.088759 -0.094625 4 1 s 11 s 12 s 13 s
atom 7 - C ** -0 -1.124295 2.523926 -0.086077 4 2 s 17 s 18 s 19 s
atom 8 - C ** -0 -0.79364 -2.643341 -0.026091 4 5 s 14 s 15 s 16 s
atom 9 - C ** -0 2.020623 1.77326 -0.262741 4 3 s 20 s 21 s 22 s
atom 10 - C ** -0 2.107137 -1.39253 -0.683628 4 4 s 23 s 24 s 25 s
atom 11 - H ** -0 -3.216999 0.541084 -0.897577 1 6 s
atom 12 - H ** -0 -3.195564 0.29245 0.861647 1 6 s
atom 13 - H ** -0 -3.200993 -1.103649 -0.23385 1 6 s
atom 14 - H ** -0 -1.872835 -2.789636 -0.141273 1 8 s
atom 15 - H ** -0 -0.490502 -3.082124 0.932593 1 8 s
atom 16 - H ** -0 -0.285969 -3.194089 -0.828334 1 8 s
atom 17 - H ** -0 -1.843949 2.634197 0.734942 1 7 s

```

```

atom 18 - H ** - 0 -1.657955 2.698357 -1.029317 1 7 s
atom 19 - H ** - 0 -0.354648 3.294507 0.022615 1 7 s
atom 20 - H ** - 0 1.809457 2.768581 0.14496 1 9 s
atom 21 - H ** - 0 2.219253 1.874078 -1.337515 1 9 s
atom 22 - H ** - 0 2.928841 1.398585 0.219868 1 9 s
atom 23 - H ** - 0 1.966385 -1.307439 -1.767807 1 10 s
atom 24 - H ** - 0 3.074225 -0.953583 -0.415879 1 10 s
atom 25 - H ** - 0 2.130125 -2.454549 -0.414051 1 10 s
atom 26 - B ** - 0 1.147526 -0.286762 1.623391 3 4 s 27 s 28 s
atom 27 - H ** - 0 0.180878 -0.224082 2.324402 1 26 s
atom 28 - H ** - 0 2.255237 -0.164329 2.078621 1 26 s
endmol 1

```

Figure 76: RHF/3-21G* η^2 -optimized $C_5Me_5BH_2$

forcefield mm+

sys 0

view 40 0.27317 55 15 1 0 0 0 1 0 0 0 1 -0.00088083 -0.34391 -55.086

seed -1111

mol 1

```

atom 1 - H ** - 0 -0.8860905 0.1929666 -3.263548 1 24 s
atom 2 - H ** - 0 -2.801196 -0.4164395 -1.804937 1 23 s
atom 3 - H ** - 0 -2.728097 1.269929 -1.253596 1 23 s
atom 4 - H ** - 0 -3.284108 -0.00396095 -0.1459323 1 23 s
atom 5 - H ** - 0 2.721398 1.262937 -1.279209 1 25 s
atom 6 - H ** - 0 2.808504 -0.4359026 -1.788948 1 25 s
atom 7 - H ** - 0 3.282346 0.02054687 -0.1388449 1 25 s
atom 8 - H ** - 0 2.617718 -0.5603577 1.926606 1 26 s
atom 9 - H ** - 0 1.615675 -2.023204 1.753675 1 26 s
atom 10 - H ** - 0 1.183262 -0.7692892 2.941465 1 26 s
atom 11 - H ** - 0 -0.001184842 2.156988 0.5537432 1 13 s
atom 12 - H ** - 0 0.001538342 1.517635 2.554088 1 13 s
atom 13 - B ** - 0 0.0001175482 1.288679 1.372897 4 12 s 11 s 17 s 18 s
atom 14 - H ** - 0 -1.612819 -2.023885 1.755591 1 22 s
atom 15 - H ** - 0 -2.617548 -0.5625743 1.926203 1 22 s
atom 16 - H ** - 0 -1.183406 -0.7677844 2.942168 1 22 s
atom 17 - C ** - 0 -0.7428373 -0.2452853 0.886189 4 18 s 21 s 22 s 13 s
atom 18 - C ** - 0 0.7429068 -0.2452895 0.8859497 4 17 s 19 s 26 s 13 s
atom 19 - C ** - 0 1.150411 0.002481609 -0.4811983 3 18 s 20 s 25 s
atom 20 - C ** - 0 -0.0003356203 0.1433206 -1.293608 3 19 s 21 s 24 s
atom 21 - C ** - 0 -1.150786 0.001370295 -0.4812638 3 20 s 17 s 23 s
atom 22 - C ** - 0 -1.590113 -0.9431275 1.941115 4 17 s 16 s 15 s 14 s
atom 23 - C ** - 0 -2.574174 0.2279333 -0.9460129 4 21 s 4 s 3 s 2 s
atom 24 - C ** - 0 -0.0001422169 0.5785224 -2.746037 4 20 s 27 s 28 s 1 s
atom 25 - C ** - 0 2.573744 0.2277218 -0.9468306 4 19 s 7 s 6 s 5 s
atom 26 - C ** - 0 1.590924 -0.9427199 1.940475 4 18 s 10 s 9 s 8 s
atom 27 - H ** - 0 0.8880316 0.1962763 -3.262162 1 24 s
atom 28 - H ** - 0 -0.00220059 1.673154 -2.833522 1 24 s
endmol 1

```

Figure 77: MNDO optimized $C_5Me_5BF_2$

forcefield mm+

sys 0

view 40 0.18646 55 15 0.1116997 -0.05819017 0.9920369 -0.9911492 -0.07859055 0.1069899 0.07173906 -0.9952072 -0.06645373
0.96023 0.056016 -54.432

mol 1

```

atom 1 - C C3 - -0.06695986 -2.443292 -0.208559 0.3171189 3 2 s 5 d 10 s
atom 2 - C C3 - -0.0669837 -2.429221 1.281401 0.3450617 3 1 s 3 d 6 s
atom 3 - C C3 - -0.1207156 -1.128514 1.723852 0.3841365 3 2 d 4 s 7 s
atom 4 - C C4 - -0.002517223 -0.1673355 0.5135623 0.4074867 4 3 s 5 s 8 s 11 s
atom 5 - C C3 - -0.1207309 -1.151198 -0.6766645 0.3396764 3 4 s 1 d 9 s
atom 6 - C C4 - 0.08292127 -3.676763 2.110081 0.3267184 4 2 s 14 s 15 s 16 s
atom 7 - C C4 - 0.08306646 -0.6588855 3.145395 0.4192545 4 3 s 17 s 18 s 19 s
atom 8 - C C4 - 0.06524277 0.6532044 0.4816104 1.721826 4 4 s 20 s 21 s 22 s
atom 9 - C C4 - 0.08304524 -0.7085626 -2.107168 0.3222929 4 5 s 23 s 24 s 25 s
atom 10 - C C4 - 0.08292651 -3.706321 -1.012178 0.2685081 4 1 s 26 s 27 s 28 s
atom 11 - B B3 - 0.3325882 0.7495157 0.5294741 -0.9295301 3 4 s 12 s 13 s

```

```

atom 12 - F F - -0.1825471 0.2518225 0.5573512 -2.152671 1 1 1 s
atom 13 - F F - -0.1866884 2.070837 0.5161207 -0.9230784 1 1 1 s
atom 14 - H H - 0.001039267 -4.333033 1.859744 1.1869 1 6 s
atom 15 - H H - -0.002082586 -3.471795 3.197833 0.386199 1 6 s
atom 16 - H H - 0.003680468 -4.251717 1.938986 -0.6078737 1 6 s
atom 17 - H H - 0.002991676 -0.9679356 3.640738 1.364707 1 7 s
atom 18 - H H - -0.003432751 0.4437876 3.238289 0.3490438 1 7 s
atom 19 - H H - 0.003612518 -1.082764 3.728846 -0.425704 1 7 s
atom 20 - H H - 0.003389478 -0.01575753 0.4716677 2.606878 1 8 s
atom 21 - H H - 0.001170039 1.298241 -0.417695 1.785145 1 8 s
atom 22 - H H - 0.001158535 1.315111 1.365628 1.81791 1 8 s
atom 23 - H H - -0.003413081 0.3923815 -2.218282 0.251495 1 9 s
atom 24 - H H - 0.002979755 -1.030018 -2.631875 1.24755 1 9 s
atom 25 - H H - 0.003626347 -1.140586 -2.650171 -0.5452072 1 9 s
atom 26 - H H - 0.003582954 -4.287885 -0.7813553 -0.6489468 1 10 s
atom 27 - H H - -0.002059221 -3.521343 -2.10512 0.2674878 1 10 s
atom 28 - H H - 0.001108468 -4.3485 -0.7957325 1.148361 1 10 s
endmol 1

```

Figure 78: MNDO η^2 -optimized $C_5Me_5BF_2$

forcefield mm+

sys 0

view 40 0.19196 55 15 -0.08022925 0.9918931 0.09854658 0.0993332 -0.09041711 0.9909378 0.9918145 0.08929108 -0.09127383
0.1092 0.09342 -55.052

seed -1111

mol 1

```

atom 1 - C C4 - 0.03774452 -1.211156 -0.7972606 0.5770897 3 2 s 5 s 10 s
atom 2 - C C4 - -0.1429086 -0.7778077 -1.150181 -0.7357145 3 1 s 3 s 6 s
atom 3 - C C4 - 0.03762627 -0.6956078 0.02855487 -1.535739 3 2 s 4 s 7 s
atom 4 - C C4 s -0.155808 -1.126147 1.185382 -0.7569109 4 3 s 5 s 8 s 11 s
atom 5 - C C4 - -0.1555929 -1.468104 0.6380669 0.6433975 4 4 s 1 s 9 s 11 s
atom 6 - C C4 - 0.08848691 -0.4399878 -2.535657 -1.196652 4 2 s 14 s 15 s 16 s
atom 7 - C C4 - 0.06306672 -0.1969979 0.08928088 -2.948087 4 3 s 17 s 18 s 19 s
atom 8 - C C4 - 0.1030285 -1.836217 2.341056 -1.432639 4 4 s 20 s 21 s 22 s
atom 9 - C C4 - 0.103044 -2.562937 1.178721 1.540853 4 5 s 23 s 24 s 25 s
atom 10 - C C4 - 0.06307006 -1.338485 -1.74082 1.734901 4 1 s 26 s 27 s 28 s
atom 11 - B B4 s 0.291342 0.01919786 1.590829 0.5302115 4 4 s 12 s 13 s 5 s
atom 12 - F F - -0.2058864 1.219614 1.010228 0.596088 1 1 1 s
atom 13 - F F - -0.2028422 0.04632189 2.830609 1.021432 1 1 1 s
atom 14 - H H - -0.00161314 -0.668712 -2.6813 -2.272502 1 6 s
atom 15 - H H - 0.006137311 0.6399831 -2.748046 -1.046671 1 6 s
atom 16 - H H - -0.001607299 -1.016363 -3.309066 -0.6487808 1 6 s
atom 17 - H H - 0.01347852 -1.005536 -0.2028189 -3.652293 1 7 s
atom 18 - H H - 0.01183939 0.1470646 1.104405 -3.23079 1 7 s
atom 19 - H H - 0.01044291 0.6625315 -0.5931851 -3.111237 1 7 s
atom 20 - H H - -0.005735278 -2.718723 1.970945 -1.997884 1 8 s
atom 21 - H H - 0.00826776 -2.205229 3.105225 -0.7208855 1 8 s
atom 22 - H H - -0.001935363 -1.168106 2.86374 -2.148028 1 8 s
atom 23 - H H - -0.005740523 -3.527308 0.6741892 1.31565 1 9 s
atom 24 - H H - -0.001909971 -2.330159 1.006262 2.61202 1 9 s
atom 25 - H H - 0.008230627 -2.731263 2.266746 1.420027 1 9 s
atom 26 - H H - 0.01065165 -0.5102109 -2.47893 1.756472 1 10 s
atom 27 - H H - 0.01167786 -1.320409 -1.216582 2.71138 1 10 s
atom 28 - H H - 0.01344484 -2.296098 -2.3008 1.669149 1 10 s
endmol 1

```

Figure 79: RHF/3-21G* optimized $C_5Me_5BF_2$

forcefield mm+

sys 0

view 40 0.25236 40 15 0.9119169 0.3788526 0.1577286 -0.1248479 -0.1100129 0.9860579 0.3909228 -0.9188949 -0.05302364
0.026274 -0.097567 -40.054

mol 1

```

atom 1 - H ** - 0 0.477982 0.10592 2.628306 1 14 s
atom 2 - H ** - 0 1.602319 2.494923 -0.156675 1 21 s
atom 3 - H ** - 0 0.266203 -2.819294 1.496465 1 24 s
atom 4 - H ** - 0 0.588641 -2.944741 -0.226931 1 24 s
atom 5 - H ** - 0 -1.029704 -3.218792 0.388185 1 24 s

```

```

atom 6 - H ** -0 -2.102122 2.889652 -0.513056 1 22 s
atom 7 - H ** -0 -3.244013 1.827205 0.288457 1 22 s
atom 8 - H ** -0 -2.897293 1.612724 -1.416803 1 22 s
atom 9 - H ** -0 -3.669411 -0.766239 0.363008 1 23 s
atom 10 - H ** -0 -3.216243 -0.982527 -1.317399 1 23 s
atom 11 - H ** -0 -2.888291 -2.249376 -0.150844 1 23 s
atom 12 - C ** -0 0.667344 -0.113495 0.485195 4 13 s 14 s 17 s 20 s
atom 13 - B ** -0 1.760469 -0.256547 -0.620035 3 12 s 15 s 16 s
atom 14 - C ** -0 1.269574 -0.081945 1.914302 4 12 s 1 s 27 s 28 s
atom 15 - F ** -0 2.876047 0.502602 -0.599143 1 13 s
atom 16 - F ** -0 1.689747 -1.106217 -1.659772 1 13 s
atom 17 - C ** -0 -0.429093 -1.152637 0.332251 3 12 s 18 s 24 s
atom 18 - C ** -0 -1.568805 -0.554842 -0.013222 3 17 s 19 s 23 s
atom 19 - C ** -0 -1.347052 0.914818 -0.110287 3 18 s 20 s 22 s
atom 20 - C ** -0 -0.075807 1.198312 0.174496 3 19 s 12 s 21 s
atom 21 - C ** -0 0.607066 2.538828 0.267447 4 20 s 2 s 25 s 26 s
atom 22 - C ** -0 -2.457002 1.86976 -0.458438 4 19 s 8 s 7 s 6 s
atom 23 - C ** -0 -2.909674 -1.177976 -0.294241 4 18 s 11 s 10 s 9 s
atom 24 - C ** -0 -0.139158 -2.617485 0.509424 4 17 s 5 s 4 s 3 s
atom 25 - H ** -0 0.706192 2.847939 1.304621 1 21 s
atom 26 - H ** -0 0.048452 3.303802 -0.255554 1 21 s
atom 27 - H ** -0 2.014493 0.699593 1.997419 1 14 s
atom 28 - H ** -0 1.743937 -1.025545 2.159649 1 14 s
endmol 1

```

Figure 80: RHF/3-21G* η^2 -optimized $C_5Me_5BF_2$
forcefield mm+

```

sys 0
view 40 0.26783 40 15 0.9661399 0.2580023 -0.002921141 -0.002772097 -0.0009414447 -0.9999957 -0.258004 0.9661438 -
0.0001943596 0.018698 -0.077208 -39.935
mol 1
atom 1 - H ** -0 1.613998 2.62451 -0.881896 1 21 s
atom 2 - H ** -0 1.616309 -2.623358 -0.880446 1 20 s
atom 3 - H ** -0 2.675241 -1.237825 -0.875745 1 20 s
atom 4 - H ** -0 1.613742 -1.520332 -2.251443 1 20 s
atom 5 - H ** -0 -2.064307 -2.741935 -0.819996 1 19 s
atom 6 - H ** -0 -0.45457 -3.264425 -0.357453 1 19 s
atom 7 - H ** -0 -1.578858 -2.693788 0.86545 1 19 s
atom 8 - H ** -0 -3.510203 -0.874598 -0.290928 1 18 s
atom 9 - H ** -0 -3.510348 0.873816 -0.290845 1 18 s
atom 10 - H ** -0 -3.165419 -0.000445 1.191826 1 18 s
atom 11 - H ** -0 -1.583313 2.692386 0.864785 1 17 s
atom 12 - C ** -0 -0.744282 1.134222 -0.335216 3 13 s 16 s 17 s
atom 13 - C ** -0 0.612011 0.7544 -0.50939 4 12 s 14 s 21 s 22 s
atom 14 - C ** -0 0.612221 -0.754018 -0.509654 4 13 s 15 s 20 s 22 s
atom 15 - C ** -0 -0.743956 -1.134335 -0.335616 3 14 s 16 s 19 s
atom 16 - C ** -0 -1.54794 -0.000197 -0.226716 3 15 s 12 s 18 s
atom 17 - C ** -0 -1.233656 2.543147 -0.152315 4 12 s 11 s 25 s 26 s
atom 18 - C ** -0 -3.016044 -0.000371 0.115544 4 16 s 10 s 9 s 8 s
atom 19 - C ** -0 -1.23267 -2.543482 -0.152696 4 15 s 7 s 6 s 5 s
atom 20 - C ** -0 1.694672 -1.583144 -1.171661 4 14 s 4 s 3 s 2 s
atom 21 - C ** -0 1.694109 1.583971 -1.171443 4 13 s 27 s 28 s 1 s
atom 22 - B ** -0 1.079943 -2e-006 0.969477 4 13 s 23 s 24 s 14 s
atom 23 - F ** -0 0.312274 -0.00044 2.093474 1 22 s
atom 24 - F ** -0 2.422167 0.00026 1.226016 1 22 s
atom 25 - H ** -0 -0.454929 3.264358 -0.353683 1 17 s
atom 26 - H ** -0 -2.063044 2.742227 -0.822259 1 17 s
atom 27 - H ** -0 1.614393 1.519461 -2.251213 1 21 s
atom 28 - H ** -0 2.674835 1.240427 -0.873971 1 21 s
endmol 1

```

Figure 81: RHF/6-31G* optimized $C_5Me_5BF_2$

forcefield mm+

sys 0

```

view 40 0.37576 40 15 0.6395549 0.619423 0.4552852 0.5652247 -0.7803141 0.2676395 0.5210475 0.08616824 -0.849167 0.06246 -
0.57613 -39.821

```

mol 1

```

atom 1 - C ** - 0 -1.335815 0.91269 -0.071014 3 2 s 5 s 6 s
atom 2 - C ** - 0 -1.556429 -0.55253 0.003551 3 1 s 3 s 7 s
atom 3 - C ** - 0 -0.414754 -1.153782 0.340761 3 2 s 4 s 8 s
atom 4 - C ** - 0 0.680968 -0.118924 0.486848 4 3 s 5 s 9 s 10 s
atom 5 - C ** - 0 -0.062796 1.188923 0.221529 3 4 s 1 s 11 s
atom 6 - C ** - 0 -2.444436 1.870376 -0.407684 4 1 s 15 s 16 s 17 s
atom 7 - C ** - 0 -2.895995 -1.17312 -0.279872 4 2 s 18 s 19 s 20 s
atom 8 - C ** - 0 -0.140181 -2.619441 0.523988 4 3 s 21 s 22 s 23 s
atom 9 - B ** - 0 1.735742 -0.23851 -0.687431 3 4 s 24 s 25 s
atom 10 - C ** - 0 1.361539 -0.136568 1.87079 4 4 s 26 s 27 s 28 s
atom 11 - C ** - 0 0.608222 2.530902 0.33837 4 5 s 12 s 13 s 14 s
atom 12 - H ** - 0 -0.020133 3.326602 -0.039937 1 11 s
atom 13 - H ** - 0 0.841232 2.763176 1.37474 1 11 s
atom 14 - H ** - 0 1.545548 2.566099 -0.208447 1 11 s
atom 15 - H ** - 0 -3.249115 1.804902 0.319714 1 6 s
atom 16 - H ** - 0 -2.104139 2.896941 -0.429694 1 6 s
atom 17 - H ** - 0 -2.873891 1.642781 -1.379454 1 6 s
atom 18 - H ** - 0 -3.65872 -0.780132 0.386968 1 7 s
atom 19 - H ** - 0 -3.218448 -0.958829 -1.295302 1 7 s
atom 20 - H ** - 0 -2.879025 -2.248241 -0.161395 1 7 s
atom 21 - H ** - 0 -1.024327 -3.220899 0.358885 1 8 s
atom 22 - H ** - 0 0.621911 -2.966111 -0.169922 1 8 s
atom 23 - H ** - 0 0.217493 -2.834095 1.527723 1 8 s
atom 24 - F ** - 0 1.488341 -0.858226 -1.818064 1 9 s
atom 25 - F ** - 0 2.92591 0.317546 -0.589843 1 9 s
atom 26 - H ** - 0 2.109974 0.642728 1.951387 1 10 s
atom 27 - H ** - 0 1.859103 -1.082883 2.057936 1 10 s
atom 28 - H ** - 0 0.62363 0.015474 2.651522 1 10 s
endmol 1

```

Figure 82: RHF/6-31G* η^2 -optimized $C_5Me_5BF_2$
forcefield mm+

```

sys 0
view 40 0.24325 40 15 0.2501426 -0.3210673 0.9134246 0.9656889 0.01470962 -0.2592849 0.06981177 0.9469421 0.3137307
0.035867 -0.044682 -40.004
mol 1
atom 1 - H ** - 0 -1.998411 -2.77157 -0.885248 1 17 s
atom 2 - H ** - 0 -0.427006 -3.26396 -0.287632 1 17 s
atom 3 - H ** - 0 -1.648925 -2.682479 0.827241 1 17 s
atom 4 - H ** - 0 -3.510075 -0.867338 -0.29242 1 16 s
atom 5 - H ** - 0 -3.158982 -0.013683 1.195807 1 16 s
atom 6 - H ** - 0 -3.505893 0.879526 -0.269946 1 16 s
atom 7 - C ** - 0 0.616493 0.743075 -0.518271 4 8 s 11 s 12 s 22 s
atom 8 - C ** - 0 0.616079 -0.742769 -0.51879 4 7 s 9 s 12 s 18 s
atom 9 - C ** - 0 -0.735759 -1.131643 -0.340631 3 8 s 10 s 17 s
atom 10 - C ** - 0 -1.541077 0.000666 -0.230419 3 9 s 11 s 16 s
atom 11 - C ** - 0 -0.735385 1.132608 -0.339988 3 10 s 7 s 15 s
atom 12 - B ** - 0 1.073186 -0.000502 0.991803 4 7 s 8 s 13 s 14 s
atom 13 - F ** - 0 0.296133 -0.000629 2.073019 1 12 s
atom 14 - F ** - 0 2.383307 -0.001282 1.252007 1 12 s
atom 15 - C ** - 0 -1.220517 2.543123 -0.16074 4 11 s 26 s 27 s 28 s
atom 16 - C ** - 0 -3.005701 -0.000187 0.119159 4 10 s 6 s 5 s 4 s
atom 17 - C ** - 0 -1.222045 -2.541716 -0.161584 4 9 s 3 s 2 s 1 s
atom 18 - C ** - 0 1.695863 -1.588938 -1.162117 4 8 s 19 s 20 s 21 s
atom 19 - H ** - 0 2.682948 -1.206852 -0.941595 1 18 s
atom 20 - H ** - 0 1.5782 -1.607059 -2.242177 1 18 s
atom 21 - H ** - 0 1.662547 -2.611641 -0.805653 1 18 s
atom 22 - C ** - 0 1.69658 1.588702 -1.161809 4 7 s 23 s 24 s 25 s
atom 23 - H ** - 0 1.661556 2.612221 -0.80792 1 22 s
atom 24 - H ** - 0 1.580814 1.604076 -2.242123 1 22 s
atom 25 - H ** - 0 2.683704 1.208249 -0.938587 1 22 s
atom 26 - H ** - 0 -0.425648 3.264847 -0.290684 1 15 s
atom 27 - H ** - 0 -1.999444 2.772505 -0.88174 1 15 s
atom 28 - H ** - 0 -1.643438 2.685358 0.829566 1 15 s
endmol 1

```

Figure 83: RMP2/3-21G* optimized $C_5Me_5BF_2$


```

forcefield mm+
sys 0
view 40 0.24573 40 15 0.180529 -0.07168167 -0.9809541 0.9341952 -0.2995272 0.1938113 -0.3077151 -0.9513912 0.01289132
0.073444 -0.063701 -39.959
mol 1
atom 1 - H ** - 0 0.219821 3.301609 -0.235396 1 15 s
atom 2 - H ** - 0 -1.949644 2.98529 -0.508485 1 16 s
atom 3 - H ** - 0 -2.849944 1.737811 -1.398182 1 16 s
atom 4 - H ** - 0 -3.166034 1.999676 0.329139 1 16 s
atom 5 - H ** - 0 -3.248456 -0.902058 -1.332526 1 14 s
atom 6 - H ** - 0 -3.732418 -0.618852 0.352457 1 14 s
atom 7 - H ** - 0 -2.977984 -2.158791 -0.108217 1 14 s
atom 8 - H ** - 0 0.255873 -2.888989 1.459842 1 26 s
atom 9 - H ** - 0 -1.164192 -3.20302 0.442381 1 26 s
atom 10 - H ** - 0 0.432818 -2.994293 -0.308302 1 26 s
atom 11 - H ** - 0 1.7496 -1.142893 2.166309 1 22 s
atom 12 - H ** - 0 2.135533 0.584152 1.97591 1 22 s
atom 13 - H ** - 0 0.563566 0.091984 2.668821 1 22 s
atom 14 - C ** - 0 -2.96797 -1.078539 -0.286377 4 18 s 7 s 6 s 5 s
atom 15 - C ** - 0 0.747853 2.510104 0.307457 4 20 s 1 s 27 s 28 s
atom 16 - C ** - 0 -2.380416 1.981137 -0.436839 4 17 s 4 s 3 s 2 s
atom 17 - C ** - 0 -1.313902 0.963114 -0.087163 3 18 s 20 s 16 s
atom 18 - C ** - 0 -1.600187 -0.498263 0.010956 3 17 s 19 s 14 s
atom 19 - C ** - 0 -0.460749 -1.160237 0.370355 3 18 s 21 s 26 s
atom 20 - C ** - 0 0.001146 1.195291 0.201929 3 17 s 21 s 15 s
atom 21 - C ** - 0 0.683622 -0.162935 0.516809 4 19 s 20 s 22 s 23 s
atom 22 - C ** - 0 1.331392 -0.157927 1.929291 4 21 s 13 s 12 s 11 s
atom 23 - B ** - 0 1.712574 -0.303732 -0.65533 3 21 s 24 s 25 s
atom 24 - F ** - 0 2.883127 0.400907 -0.652417 1 23 s
atom 25 - F ** - 0 1.522917 -1.086371 -1.751554 1 23 s
atom 26 - C ** - 0 -0.222295 -2.647594 0.501706 4 19 s 10 s 9 s 8 s
atom 27 - H ** - 0 1.75291 2.407841 -0.114903 1 15 s
atom 28 - H ** - 0 0.850324 2.823456 1.3548 1 15 s
endmol 1

```

Figure 84: RHF/3-21G* η^2 -optimized $C_5Me_5BF_2$

```

forcefield mm+
sys 0
view 40 0.19909 40 15 -0.2043228 0.5117083 -0.8345099 -0.6447364 0.5711267 0.5080642 0.7365916 0.641848 0.2132228 -
0.11214 -0.013574 -39.995
seed -1111
mol 1
atom 1 - H ** - 0 0.489006 -3.2961 -0.469395 1 6 s
atom 2 - H ** - 0 1.407478 -2.742112 0.948829 1 6 s
atom 3 - H ** - 0 3.187999 0.001238 1.184179 1 7 s
atom 4 - H ** - 0 1.393678 2.746555 0.949209 1 8 s
atom 5 - C ** - 0 -1.720356 -1.580584 -1.171008 4 11 s 19 s 20 s 21 s
atom 6 - C ** - 0 1.231506 -2.570735 -0.121485 4 12 s 18 s 2 s 1 s
atom 7 - C ** - 0 3.045869 0.001187 0.095829 4 13 s 26 s 27 s 3 s
atom 8 - C ** - 0 1.227945 2.572043 -0.122248 4 14 s 25 s 4 s 28 s
atom 9 - C ** - 0 -1.722046 1.578048 -1.171805 4 10 s 22 s 23 s 24 s
atom 10 - C ** - 0 -0.61486 0.756219 -0.52623 4 11 s 14 s 9 s 15 s
atom 11 - C ** - 0 -0.614123 -0.757317 -0.525592 4 10 s 12 s 5 s 15 s
atom 12 - C ** - 0 0.758818 -1.154517 -0.369634 3 11 s 13 s 6 s
atom 13 - C ** - 0 1.571785 0.000743 -0.258692 3 12 s 14 s 7 s
atom 14 - C ** - 0 0.75764 1.155058 -0.370474 3 13 s 10 s 8 s
atom 15 - B ** - 0 -1.081925 -0.000141 0.982911 4 11 s 16 s 17 s 10 s
atom 16 - F ** - 0 -0.290208 0.00111 2.102427 1 15 s
atom 17 - F ** - 0 -2.436334 -0.001064 1.243127 1 15 s
atom 18 - H ** - 0 2.170764 -2.75899 -0.65508 1 6 s
atom 19 - H ** - 0 -1.599644 -2.640448 -0.921956 1 5 s
atom 20 - H ** - 0 -1.68639 -1.467854 -2.26032 1 5 s
atom 21 - H ** - 0 -2.69911 -1.256841 -0.805617 1 5 s
atom 22 - H ** - 0 -1.685677 1.468117 -2.261332 1 9 s
atom 23 - H ** - 0 -1.604881 2.637624 -0.919825 1 9 s
atom 24 - H ** - 0 -2.700594 1.250644 -0.809145 1 9 s
atom 25 - H ** - 0 2.172268 2.758647 -0.647332 1 8 s

```

```

atom 26 - H ** - 0 3.54067 0.888359 -0.314656 1 7 s
atom 27 - H ** - 0 3.541022 -0.885807 -0.31463 1 7 s
atom 28 - H ** - 0 0.488839 3.296387 -0.479435 1 8 s
endmol 1

```

Figure 85: MNDO optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.18646 55 15 0.4086601 0.8076134 0.4251559 -0.8763189 0.4773913 -0.06451999 -0.2550729 -0.3462054 0.9028176
1.4832 -0.051381 -54.909

```

seed 0

mol 1

```

atom 1 - C C3 - -0.06495953 -2.404251 0.3314435 0.5830811 3 2 s 5 d 10 s
atom 2 - C C3 - -0.06498623 -2.379755 1.821059 0.6230526 3 1 s 3 d 6 s
atom 3 - C C3 - -0.1163244 -1.07636 2.255622 0.6685939 3 2 d 4 s 7 s
atom 4 - C C4 - -0.01058674 -0.1238154 1.036653 0.6888523 4 3 s 5 s 8 s 11 s
atom 5 - C C3 - -0.1163449 -1.115896 -0.1475555 0.6046899 3 4 s 1 d 9 s
atom 6 - C C4 - 0.08265328 -3.621591 2.658542 0.6092746 4 2 s 14 s 15 s 16 s
atom 7 - C C4 - 0.08248997 -0.5957107 3.673115 0.7179061 4 3 s 17 s 18 s 19 s
atom 8 - C C4 - 0.06743765 0.6838606 0.9883178 2.011565 4 4 s 20 s 21 s 22 s
atom 9 - C C4 - 0.08246827 -0.6822103 -1.580724 0.578558 4 5 s 23 s 24 s 25 s
atom 10 - C C4 - 0.08265805 -3.672979 -0.4627728 0.5258979 4 1 s 26 s 27 s 28 s
atom 11 - B B3 - 0.1909692 0.766697 1.05686 -0.6294211 3 4 s 12 s 13 s
atom 12 - Cl CL - -0.1194053 0.06105138 1.112538 -2.261727 1 11 s
atom 13 - Cl CL - -0.1253829 2.545262 1.02633 -0.6190416 1 11 s
atom 14 - H H - 0.001351058 -4.281314 2.405249 1.46593 1 6 s
atom 15 - H H - -0.001541018 -3.409165 3.744251 0.6785855 1 6 s
atom 16 - H H - 0.004273891 -4.195535 2.499292 -0.3280091 1 6 s
atom 17 - H H - 0.00324887 -0.8969124 4.159158 1.670742 1 7 s
atom 18 - H H - -0.001799226 0.5072567 3.757967 0.643445 1 7 s
atom 19 - H H - 0.004573524 -1.019241 4.269796 -0.1178464 1 7 s
atom 20 - H H - 0.003575385 0.003439355 0.9763074 2.888146 1 8 s
atom 21 - H H - 0.002758384 1.320014 0.08309913 2.075466 1 8 s
atom 22 - H H - 0.002748191 1.349389 1.867478 2.122689 1 8 s
atom 23 - H H - -0.001781702 0.4176506 -1.697826 0.50199 1 9 s
atom 24 - H H - 0.003235757 -1.002913 -2.107114 1.503173 1 9 s
atom 25 - H H - 0.004591286 -1.121853 -2.117273 -0.2890413 1 9 s
atom 26 - H H - 0.00417012 -4.250908 -0.2205755 -0.3908977 1 10 s
atom 27 - H H - -0.001514673 -3.495724 -1.556928 0.5168396 1 10 s
atom 28 - H H - 0.001423657 -4.315205 -0.248398 1.406212 1 10 s
endmol 1

```

Figure 86: MNDO η^2 -optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.17651 55 15 0.944251 0.2153271 -0.2490467 -0.3286142 0.6625416 -0.6730909 0.02006921 0.717407 0.6963651 -1.0245
-0.55041 -54.999

```

seed -1111

mol 1

```

atom 1 - C C4 - -0.1656389 -0.2913754 -0.1661282 -0.809755 4 2 s 5 s 10 s 11 s
atom 2 - C C3 - -0.1329603 -0.2395418 1.303678 -0.870611 3 1 s 3 d 6 s
atom 3 - C C3 - -0.1873288 1.095688 1.760113 -0.661238 3 2 d 4 s 7 s
atom 4 - C C3 - -0.1330013 1.936136 0.6430867 -0.3768392 3 3 s 5 d 8 s
atom 5 - C C3 - -0.1656046 1.17034 -0.6099467 -0.4781006 4 4 d 1 s 9 s 11 s
atom 6 - C C4 - 0.04504776 -1.438935 2.182332 -1.067571 4 2 s 14 s 15 s 16 s
atom 7 - C C4 - 0.08877206 1.538471 3.191985 -0.698612 4 3 s 17 s 18 s 19 s
atom 8 - C C4 - 0.04504943 3.378737 0.7195715 0.02616249 4 4 s 20 s 21 s 22 s
atom 9 - C C4 - 0.1046312 1.851201 -1.838333 -1.054496 4 5 s 23 s 24 s 25 s
atom 10 - C C4 - 0.1046236 -1.224861 -0.9043708 -1.752243 4 1 s 26 s 27 s 28 s
atom 11 - B B3 - 0.0819149 0.009628505 -0.7814585 0.7243024 4 1 s 12 s 13 s 5 s
atom 12 - Cl CL - -0.1988277 0.001968657 0.2929734 2.19549 1 11 s
atom 13 - Cl CL - -0.1728315 -0.5918283 -2.432164 1.16635 1 11 s
atom 14 - H H - 0.02544552 -2.386646 1.661025 -0.8262482 1 6 s
atom 15 - H H - 0.02051842 -1.396331 3.084455 -0.4231535 1 6 s
atom 16 - H H - 0.02234322 -1.49283 2.516777 -2.126133 1 6 s
atom 17 - H H - 0.01068968 1.445764 3.660604 0.3039794 1 7 s

```

```

atom 18 - H H - 0.000235498 2.59469 3.289892 -1.023338 1 7 s
atom 19 - H H - 0.0002190471 0.9364226 3.791867 -1.411653 1 7 s
atom 20 - H H - 0.02061594 3.568657 1.573745 0.7082704 1 8 s
atom 21 - H H - 0.02537858 3.717113 -0.1936822 0.5549275 1 8 s
atom 22 - H H - 0.02231956 4.016684 0.8488892 -0.8747238 1 8 s
atom 23 - H H - 0.001781702 2.635803 -2.219218 -0.3688018 1 9 s
atom 24 - H H - 0.01472408 1.151319 -2.675217 -1.242435 1 9 s
atom 25 - H H - -0.01327312 2.333678 -1.594994 -2.025901 1 9 s
atom 26 - H H - -0.01327205 -1.07101 -0.5617353 -2.798455 1 10 s
atom 27 - H H - 0.01473862 -1.071266 -2.000681 -1.745775 1 10 s
atom 28 - H H - 0.001767159 -2.286612 -0.7238731 -1.48585 1 10 s
endmol 1

```

Figure 87: RHF/3-21G* optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

view 40 0.27209 40 15 -0.7233417 0.4571445 -0.5174897 0.6576765 0.6844255 -0.3146797 0.2103291 -0.5679618 -0.7957268 -0.17543 0.017869 -40.157

seed -1111

mol 1

```

atom 1 - H ** - 0 3.161817 -2.303023 0.067287 1 17 s
atom 2 - H ** - 0 4.022659 -0.8037 0.359287 1 17 s
atom 3 - H ** - 0 3.437497 -1.180911 -1.250719 1 17 s
atom 4 - H ** - 0 3.693146 1.735863 -0.039462 1 18 s
atom 5 - H ** - 0 2.517512 2.78672 -0.807415 1 18 s
atom 6 - H ** - 0 3.138547 1.390641 -1.666947 1 18 s
atom 7 - C ** - 0 0.489095 1.264645 0.215687 3 8 s 11 s 19 s
atom 8 - C ** - 0 1.721872 0.900132 -0.137695 3 7 s 9 s 18 s
atom 9 - C ** - 0 1.906946 -0.554297 0.111401 3 8 s 10 s 17 s
atom 10 - C ** - 0 0.784297 -1.066236 0.613779 3 9 s 11 s 16 s
atom 11 - C ** - 0 -0.270608 0.029295 0.735472 4 10 s 7 s 12 s 15 s
atom 12 - B ** - 0 -1.441052 -0.202411 -0.300932 3 11 s 13 s 14 s
atom 13 - Cl ** - 0 -1.138159 -0.826442 -1.921998 1 12 s
atom 14 - Cl ** - 0 -3.119074 0.206639 0.089808 1 12 s
atom 15 - C ** - 0 -0.713385 0.225504 2.204693 4 11 s 23 s 24 s 25 s
atom 16 - C ** - 0 0.486085 -2.484626 1.01809 4 10 s 20 s 21 s 22 s
atom 17 - C ** - 0 3.204009 -1.254644 -0.192976 4 9 s 3 s 2 s 1 s
atom 18 - C ** - 0 2.827163 1.757397 -0.69376 4 8 s 6 s 5 s 4 s
atom 19 - C ** - 0 -0.141949 2.632298 0.18755 4 7 s 26 s 27 s 28 s
atom 20 - H ** - 0 1.3501 -3.122307 0.891095 1 16 s
atom 21 - H ** - 0 0.185048 -2.53626 2.059844 1 16 s
atom 22 - H ** - 0 -0.319541 -2.900842 0.41899 1 16 s
atom 23 - H ** - 0 0.162715 0.419299 2.811303 1 15 s
atom 24 - H ** - 0 -1.212373 -0.658787 2.583197 1 15 s
atom 25 - H ** - 0 -1.398068 1.057633 2.300475 1 15 s
atom 26 - H ** - 0 -0.425928 2.946266 1.187245 1 19 s
atom 27 - H ** - 0 -1.037894 2.651376 -0.426341 1 19 s
atom 28 - H ** - 0 0.541846 3.369925 -0.209385 1 19 s
endmol 1

```

Figure 88: RHF/3-21G* η^2 -optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

view 40 0.26117 40 15 0.1530636 0.06429977 0.9861223 0.9359193 0.310887 -0.1655425 -0.3172169 0.9482694 -0.01259391 0.089398 -0.072295 -40.006

seed -1111

mol 1

```

atom 1 - H ** - 0 -0.797954 3.260202 -0.583482 1 10 s
atom 2 - H ** - 0 -1.537691 2.677304 0.900266 1 10 s
atom 3 - H ** - 0 -2.472398 2.725541 -0.584895 1 10 s
atom 4 - H ** - 0 -3.79299 -0.866865 -0.037931 1 7 s
atom 5 - H ** - 0 -3.78478 0.88029 -0.013676 1 7 s
atom 6 - H ** - 0 -3.215697 -0.015321 1.385366 1 7 s
atom 7 - C ** - 0 -3.237615 -0.000321 0.299348 4 12 s 6 s 5 s 4 s
atom 8 - H ** - 0 -2.478094 -2.719503 -0.581502 1 27 s
atom 9 - H ** - 0 -1.527782 -2.680701 0.893907 1 27 s
atom 10 - C ** - 0 -1.487029 2.535169 -0.17626 4 11 s 3 s 2 s 1 s

```

```

atom 11 - C ** -0 -1.053828 1.13122 -0.471311 3 12 s 15 s 10 s
atom 12 - C ** -0 -1.839508 0.000902 -0.261776 3 11 s 13 s 7 s
atom 13 - C ** -0 -1.054365 -1.129184 -0.474493 3 12 s 14 s 27 s
atom 14 - C ** -0 0.272422 -0.751205 -0.852944 4 13 s 15 s 16 s 24 s
atom 15 - C ** -0 0.272759 0.753496 -0.851013 4 14 s 11 s 17 s 24 s
atom 16 - C ** -0 1.156008 -1.60037 -1.748927 4 14 s 21 s 22 s 23 s
atom 17 - C ** -0 1.156364 1.604176 -1.745512 4 15 s 18 s 19 s 20 s
atom 18 - H ** -0 0.749214 1.635638 -2.750809 1 17 s
atom 19 - H ** -0 2.158745 1.206774 -1.794665 1 17 s
atom 20 - H ** -0 1.228706 2.616376 -1.367513 1 17 s
atom 21 - H ** -0 0.745012 -1.636119 -2.75251 1 16 s
atom 22 - H ** -0 1.234527 -2.611284 -1.368635 1 16 s
atom 23 - H ** -0 2.156327 -1.198446 -1.80317 1 16 s
atom 24 - B ** -0 0.981431 -0.000781 0.526222 4 14 s 15 s 25 s 26 s
atom 25 - Cl ** -0 0.210811 -0.003735 2.170352 1 24 s
atom 26 - Cl ** -0 2.792104 -0.000622 0.607332 1 24 s
atom 27 - C ** -0 -1.488038 -2.533505 -0.18247 4 13 s 28 s 9 s 8 s
atom 28 - H ** -0 -0.804875 -3.258163 -0.600343 1 27 s
endmol 1

```

Figure 89: RHF/6-31G* optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

view 40 0.31047 40 15 -0.1243728 -0.1132286 -0.9857538 -0.9921591 0.02651902 0.1221349 0.01231207 0.993215 -0.115639 -0.13999 -0.075112 -40.046

seed -1111

mol 1

```

atom 1 - H ** -0 -1.306266 -0.7326748 -2.496856 1 12 s
atom 2 - H ** -0 -1.352945 1.005227 -2.349389 1 12 s
atom 3 - H ** -0 0.1353713 0.2107609 -2.844605 1 12 s
atom 4 - H ** -0 -0.1200262 2.886117 -1.417718 1 13 s
atom 5 - H ** -0 -0.7114399 2.767036 0.2232056 1 13 s
atom 6 - B ** -0 -1.450157 -0.112234 0.321781 3 7 s 25 s 26 s
atom 7 - C ** -0 -0.26097 0.02225501 -0.729011 4 8 s 11 s 12 s 6 s
atom 8 - C ** -0 0.6534457 -1.182293 -0.5182064 3 7 s 9 s 16 s
atom 9 - C ** -0 1.839526 -0.7606595 -0.07617196 3 8 s 10 s 15 s
atom 10 - C ** -0 1.831951 0.7181538 0.03311641 3 9 s 11 s 14 s
atom 11 - C ** -0 0.6401703 1.18456 -0.3411669 3 10 s 7 s 13 s
atom 12 - C ** -0 -0.729166 0.132232 -2.194085 4 7 s 3 s 2 s 1 s
atom 13 - C ** -0 0.1617377 2.608057 -0.405704 4 11 s 24 s 5 s 4 s
atom 14 - C ** -0 3.033276 1.489226 0.5038102 4 10 s 23 s 27 s 28 s
atom 15 - C ** -0 3.051494 -1.578733 0.2718344 4 9 s 20 s 21 s 22 s
atom 16 - C ** -0 0.1999941 -2.586656 -0.8086795 4 8 s 17 s 18 s 19 s
atom 17 - H ** -0 0.9742003 -3.309529 -0.5888876 1 16 s
atom 18 - H ** -0 -0.07169929 -2.706606 -1.853871 1 16 s
atom 19 - H ** -0 -0.6730953 -2.862687 -0.221747 1 16 s
atom 20 - H ** -0 3.336286 -1.426611 1.309263 1 15 s
atom 21 - H ** -0 3.903384 -1.292676 -0.3389207 1 15 s
atom 22 - H ** -0 2.88441 -2.637661 0.1287517 1 15 s
atom 23 - H ** -0 2.854595 2.555933 0.5128291 1 14 s
atom 24 - H ** -0 0.9229077 3.303121 -0.07730245 1 13 s
atom 25 - Cl ** -0 -1.169659 -0.03566537 2.062482 1 6 s
atom 26 - Cl ** -0 -3.124498 -0.3807814 -0.1801077 1 6 s
atom 27 - H ** -0 3.314213 1.193326 1.510835 1 14 s
atom 28 - H ** -0 3.891972 1.303622 -0.1355934 1 14 s
endmol 1

```

Figure 90: RHF/6-31G* η^2 -optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

view 40 0.39375 40 15 -0.2755444 -0.01192288 -0.9612144 -0.9612281 0.01461298 0.275367 0.0107631 0.9998222 -0.01548715 0.056085 -0.20615 -40.006

seed -1111

mol 1

```

atom 1 - H ** -0 0.77293 -3.257938 -0.523134 1 25 s
atom 2 - H ** -0 2.445994 -2.740095 -0.654595 1 25 s
atom 3 - H ** -0 1.627434 -2.667885 0.892079 1 25 s

```

```

atom 4 - H ** -0.3801783 -0.870375 0.000635 1 24 s
atom 5 - H ** -0.3797772 0.875654 0.011238 1 24 s
atom 6 - H ** -0.3223215 -0.007222 1.411206 1 24 s
atom 7 - H ** -0.2435177 2.747236 -0.670292 1 23 s
atom 8 - H ** -0.0764139 3.25804 -0.494013 1 23 s
atom 9 - H ** -0.1654748 2.659596 0.895199 1 23 s
atom 10 - H ** -0 -0.677967 -1.697114 -2.73745 1 26 s
atom 11 - H ** -0 -1.26105 -2.598299 -1.344943 1 26 s
atom 12 - H ** -0 -2.113519 -1.178731 -1.878056 1 26 s
atom 13 - H ** -0 -1.257511 2.603139 -1.340168 1 22 s
atom 14 - B ** -0 -0.983104 -0.000412 0.509235 4 15 s 19 s 20 s 21 s
atom 15 - C ** -0 -0.262503 0.74653 -0.849142 4 16 s 19 s 14 s 22 s
atom 16 - C ** -0 1.059862 1.126427 -0.458127 3 15 s 17 s 23 s
atom 17 - C ** -0 1.848932 -4.2e-005 -0.245121 3 16 s 18 s 24 s
atom 18 - C ** -0 1.059678 -1.125647 -0.461382 3 17 s 19 s 25 s
atom 19 - C ** -0 -0.262812 -0.744207 -0.851032 4 18 s 15 s 14 s 26 s
atom 20 - Cl ** -0 -0.26161 -0.003385 2.181492 1 14 s
atom 21 - Cl ** -0 -2.798137 0.000119 0.574587 1 14 s
atom 22 - C ** -0 -1.128077 1.608344 -1.749642 4 15 s 13 s 27 s 28 s
atom 23 - C ** -0 1.4959 2.530887 -0.172013 4 16 s 9 s 8 s 7 s
atom 24 - C ** -0 3.242056 -0.000561 0.324369 4 17 s 6 s 5 s 4 s
atom 25 - C ** -0 1.49424 -2.530988 -0.17775 4 18 s 3 s 2 s 1 s
atom 26 - C ** -0 -1.128979 -1.603447 -1.753447 4 19 s 12 s 11 s 10 s
atom 27 - H ** -0 -0.678027 1.701966 -2.734086 1 22 s
atom 28 - H ** -0 -2.113663 1.185826 -1.873412 1 22 s
endmol 1

```

Figure 91: RMP2/3-21G* optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.34619 40 15 -0.004413691 0.09889195 0.9950883 -0.9893568 -0.1451637 0.01003809 0.1454434 -0.9844531 0.09848007
-0.12547 0.11216 -40.082

```

seed -1111

mol 1

```

atom 1 - H ** -0 -0.156932 -2.651347 2.348768 1 19 s
atom 2 - H ** -0 1.482523 1.123048 2.301629 1 17 s
atom 3 - H ** -0 1.540738 -0.6370358 2.54108 1 17 s
atom 4 - H ** -0 0.06616977 0.2729461 2.976997 1 17 s
atom 5 - H ** -0 -0.7589645 -3.436345 0.8740315 1 19 s
atom 6 - H ** -0 0.9217852 -2.876063 0.9592663 1 19 s
atom 7 - H ** -0 0.3003679 2.851906 1.20147 1 24 s
atom 8 - H ** -0 0.4936747 2.670776 -0.557907 1 24 s
atom 9 - H ** -0 -1.06374 3.188771 0.1177472 1 24 s
atom 10 - H ** -0 -3.236569 -1.750583 -1.177948 1 21 s
atom 11 - H ** -0 -2.679933 -2.900353 0.05658077 1 21 s
atom 12 - H ** -0 -3.802938 -1.596701 0.4981379 1 21 s
atom 13 - C ** -0 0.310041 -0.006873024 0.844261 4 14 s 17 s 18 s 23 s
atom 14 - B ** -0 1.331451 -0.341803 -0.31365 3 13 s 15 s 16 s
atom 15 - Cl ** -0 2.873398 -1.140042 0.05195785 1 14 s
atom 16 - Cl ** -0 1.012154 0.03577644 -2.008035 1 14 s
atom 17 - C ** -0 0.893449 0.199958 2.262142 4 13 s 4 s 3 s 2 s
atom 18 - C ** -0 -0.5486341 -1.295699 0.7107932 3 13 s 19 s 20 s
atom 19 - C ** -0 -0.1071993 -2.64099 1.251883 4 18 s 6 s 5 s 1 s
atom 20 - C ** -0 -1.76537 -0.9440624 0.1813863 3 18 s 21 s 22 s
atom 21 - C ** -0 -2.938066 -1.852626 -0.1269342 4 20 s 12 s 11 s 10 s
atom 22 - C ** -0 -1.820139 0.5227243 -0.03053056 3 20 s 23 s 25 s
atom 23 - C ** -0 -0.6434918 1.088728 0.3817258 3 22 s 13 s 24 s
atom 24 - C ** -0 -0.2023875 2.531721 0.2804692 4 23 s 9 s 8 s 7 s
atom 25 - C ** -0 -3.021755 1.212665 -0.643368 4 22 s 26 s 27 s 28 s
atom 26 - H ** -0 -3.152328 0.9080291 -1.689632 1 25 s
atom 27 - H ** -0 -3.938329 0.9583942 -0.09692246 1 25 s
atom 28 - H ** -0 -2.898249 2.300215 -0.6186463 1 25 s
endmol 1

```

Figure 92: RHF/3-21G* η^2 -optimized $C_5Me_5BCl_2$

forcefield mm+

sys 0

```

view 40 0.27179 40 15 0.2486673 -0.03789338 0.9678474 0.9659287 -0.06430569 -0.250692 0.07173767 0.9972105 0.02061158
0.049989 -0.06774 -40.002
seed -1111
mol 1
atom 1 - C ** -0 -1.040249 1.152461 -0.540903 3 2 s 5 s 17 s
atom 2 - C ** -0 -1.83524 0.000163 -0.33181 3 1 s 3 s 18 s
atom 3 - C ** -0 -1.040424 -1.152056 -0.541878 3 2 s 4 s 19 s
atom 4 - C ** -0 0.304817 -0.751701 -0.887471 4 3 s 5 s 6 s 10 s
atom 5 - C ** -0 0.304838 0.752239 -0.88699 4 4 s 1 s 6 s 9 s
atom 6 - B ** -0 0.961145 -0.000204 0.564402 4 5 s 4 s 7 s 8 s
atom 7 - Cl ** -0 0.070997 -0.001069 2.127224 1 6 s
atom 8 - Cl ** -0 2.749612 -0.000125 0.728586 1 6 s
atom 9 - C ** -0 1.258817 1.594409 -1.723665 4 5 s 14 s 15 s 16 s
atom 10 - C ** -0 1.258595 -1.593207 -1.725063 4 4 s 11 s 12 s 13 s
atom 11 - H ** -0 0.968474 -1.532234 -2.780547 1 10 s
atom 12 - H ** -0 2.288502 -1.244036 -1.616452 1 10 s
atom 13 - H ** -0 1.220634 -2.640785 -1.40742 1 10 s
atom 14 - H ** -0 0.967139 1.536654 -2.778899 1 9 s
atom 15 - H ** -0 2.288249 1.243142 -1.617385 1 9 s
atom 16 - H ** -0 1.223165 2.64123 -1.403256 1 9 s
atom 17 - C ** -0 -1.450808 2.557248 -0.171619 4 1 s 23 s 24 s 25 s
atom 18 - C ** -0 -3.239399 0.000149 0.235221 4 2 s 20 s 21 s 22 s
atom 19 - C ** -0 -1.450809 -2.557002 -0.17304 4 3 s 26 s 27 s 28 s
atom 20 - H ** -0 -3.79002 0.888048 -0.093919 1 18 s
atom 21 - H ** -0 -3.208062 -0.001081 1.332559 1 18 s
atom 22 - H ** -0 -3.790878 -0.886487 -0.095889 1 18 s
atom 23 - H ** -0 -0.778133 3.295014 -0.619851 1 17 s
atom 24 - H ** -0 -1.421826 2.677664 0.921057 1 17 s
atom 25 - H ** -0 -2.472181 2.764159 -0.51213 1 17 s
atom 26 - H ** -0 -1.417714 -2.678877 0.919365 1 19 s
atom 27 - H ** -0 -2.473677 -2.7625 -0.509846 1 19 s
atom 28 - H ** -0 -0.780563 -3.2948 -0.624862 1 19 s
endmol 1

```

Figure 93c: MNDO optimized (C₅Me₅)₂BF

forcefield mm+

sys 0

```

view 40 0.15023 55 15 0.1964421 0.7414819 -0.6415723 -0.9254008 0.3564854 0.1286523 0.3241046 0.5684389 0.7561968 3.3678 -
1.558 -54.002

```

seed 0

mol 1

```

atom 1 - C C3 -0.08822298 2.599573 2.795734 -0.4005592 3 2 s 4 d 7 s
atom 2 - C C3 -0.07422781 1.878464 4.088424 -0.2501684 3 1 s 3 d 6 s
atom 3 - C C3 -0.1200891 0.7227677 3.885047 0.4677688 3 2 d 5 s 9 s
atom 4 - C C3 -0.09618902 1.884056 1.802812 0.2268838 3 1 d 5 s 8 s
atom 5 - C C4 -0.03107548 0.6034061 2.390106 0.854796 4 4 s 3 s 10 s 11 s
atom 6 - C C4 -0.08501816 2.405327 5.385434 -0.783865 4 2 s 23 s 24 s 25 s
atom 7 - C C4 -0.08799291 3.914581 2.673754 -1.106709 4 1 s 26 s 27 s 28 s
atom 8 - C C4 -0.08649254 2.320313 0.3824704 0.4154412 4 4 s 29 s 30 s 31 s
atom 9 - C C4 -0.08211231 -0.2490737 4.945282 0.8891393 4 3 s 32 s 33 s 34 s
atom 10 - C C4 -0.06422186 0.7238305 2.241305 2.403457 4 5 s 35 s 36 s 37 s
atom 11 - B B3 -0.2363272 -0.8128916 1.798005 0.2885358 3 5 s 15 s 22 s
atom 12 - C C3 -0.07422781 -0.03634636 -0.5904855 -2.25548 3 13 s 16 d 18 s
atom 13 - C C3 -0.08822536 0.2378548 0.6740649 -2.989914 3 12 s 14 d 17 s
atom 14 - C C3 -0.09618759 -0.4371134 1.706297 -2.381259 3 13 d 15 s 21 s
atom 15 - C C4 -0.03107452 -1.228378 1.17757 -1.167337 4 14 s 16 s 20 s 11 s
atom 16 - C C3 -0.1200867 -0.8774129 -0.3306577 -1.198347 3 15 s 12 d 19 s
atom 17 - C C4 -0.08799362 1.096049 0.7346008 -4.215723 4 13 s 38 s 39 s 40 s
atom 18 - C C4 -0.08501768 0.5140004 -1.917928 -2.679343 4 12 s 41 s 42 s 43 s
atom 19 - C C4 -0.08211303 -1.442461 -1.347429 -0.253349 4 16 s 44 s 45 s 46 s
atom 20 - C C4 -0.06422091 -2.746936 1.365836 -1.47317 4 15 s 47 s 48 s 49 s
atom 21 - C C4 -0.08649111 -0.528531 3.116893 -2.87634 4 14 s 50 s 51 s 52 s
atom 22 - F F -0.1719084 -1.796947 1.825857 1.163261 1 11 s
atom 23 - H H -0.001153827 2.714289 5.29442 -1.84605 1 6 s
atom 24 - H H -0.004479408 1.658503 6.203809 -0.7415439 1 6 s
atom 25 - H H -0.0003966689 3.288724 5.717617 -0.1973712 1 6 s

```

```

atom 26 - H H - -0.002283931 4.684123 3.314672 -0.6260015 1 7 s
atom 27 - H H - -0.004648089 4.312398 1.639092 -1.10422 1 7 s
atom 28 - H H - -0.001667976 3.826828 2.981496 -2.170145 1 7 s
atom 29 - H H - -0.002762437 3.199538 0.3344396 1.095418 1 8 s
atom 30 - H H - -0.005188942 1.533886 -0.257077 0.8623551 1 8 s
atom 31 - H H - 0.001398385 2.617273 -0.08848735 -0.5442529 1 8 s
atom 32 - H H - -0.002179861 -0.6702392 5.478479 0.01005422 1 9 s
atom 33 - H H - 0.0009291768 -1.109527 4.553966 1.466505 1 9 s
atom 34 - H H - -1.001358e-005 0.250456 5.700704 1.533951 1 9 s
atom 35 - H H - -0.001414418 1.713291 2.591885 2.763521 1 10 s
atom 36 - H H - 0.0009220243 -0.03976874 2.830791 2.948959 1 10 s
atom 37 - H H - -0.006100416 0.610353 1.185494 2.723125 1 10 s
atom 38 - H H - -0.002282739 0.6881599 0.08373992 -5.018255 1 17 s
atom 39 - H H - -0.004648924 1.172946 1.755917 -4.639742 1 17 s
atom 40 - H H - -0.001669645 2.13165 0.3997001 -3.995104 1 17 s
atom 41 - H H - -0.001152396 1.607392 -1.866605 -2.863307 1 18 s
atom 42 - H H - -0.004479766 0.3586759 -2.710918 -1.920189 1 18 s
atom 43 - H H - 0.0003960729 0.02471274 -2.261063 -3.616129 1 18 s
atom 44 - H H - -1.0252e-005 -2.047872 -2.100069 -0.8037882 1 19 s
atom 45 - H H - -0.002180815 -0.6357379 -1.891265 0.2832266 1 19 s
atom 46 - H H - 0.0009286404 -2.103832 -0.9131303 0.5217847 1 19 s
atom 47 - H H - -0.001414537 -2.999944 0.9944122 -2.48787 1 20 s
atom 48 - H H - 0.0009221435 -3.396139 0.816277 -0.7627677 1 20 s
atom 49 - H H - -0.00609982 -3.044206 2.433249 -1.427761 1 20 s
atom 50 - H H - -0.002762675 -1.099226 3.156196 -3.830527 1 21 s
atom 51 - H H - -0.005188704 -1.043913 3.793201 -2.166263 1 21 s
atom 52 - H H - 0.001399457 0.4736609 3.551176 -3.071299 1 21 s
endmol 1

```

Figure 94: RHF/3-21G* optimized (C₅Me₅)₂BF

forcefield mm+

sys 0

view 40 0.14951 40 15 0.6368364 0.4529468 -0.623922 -0.4703137 0.8694589 0.1511498 0.6109373 0.1971814 0.7667302 -1.0341 -1.5948 -40.458

seed -1111

mol 1

```

atom 1 - H ** - 0 1.204574 2.20668 3.304047 1 45 s
atom 2 - H ** - 0 -0.3698714 1.528631 2.922456 1 45 s
atom 3 - H ** - 0 -0.1963958 3.25205 3.171246 1 45 s
atom 4 - H ** - 0 3.058538 1.499379 1.052081 1 52 s
atom 5 - H ** - 0 2.650356 -0.042849 0.2994676 1 52 s
atom 6 - H ** - 0 2.136749 0.2909192 1.942517 1 52 s
atom 7 - H ** - 0 -0.5497187 5.485396 0.4046358 1 47 s
atom 8 - H ** - 0 1.117094 5.720703 0.8959256 1 47 s
atom 9 - H ** - 0 0.230587 4.969029 -2.007912 1 49 s
atom 10 - H ** - 0 1.919729 5.146505 -1.574908 1 49 s
atom 11 - H ** - 0 -0.0553665 5.099458 2.04178 1 47 s
atom 12 - H ** - 0 1.452171 4.010242 -2.825989 1 49 s
atom 13 - H ** - 0 1.592205 1.811473 -3.051455 1 51 s
atom 14 - H ** - 0 2.9001 1.221437 -2.043845 1 51 s
atom 15 - H ** - 0 1.423687 0.2985125 -2.178611 1 51 s
atom 16 - H ** - 0 -1.590957 2.74444 -0.9547376 1 34 s
atom 17 - H ** - 0 -2.917147 3.479098 -0.0805501 1 34 s
atom 18 - H ** - 0 -3.240719 2.228765 -1.266013 1 34 s
atom 19 - H ** - 0 -3.40584 -0.7084576 -0.6771767 1 41 s
atom 20 - H ** - 0 -2.243906 -0.0235117 -1.810216 1 41 s
atom 21 - H ** - 0 -1.892097 -1.547636 -1.017881 1 41 s
atom 22 - H ** - 0 -0.5098974 -2.198443 1.317224 1 40 s
atom 23 - H ** - 0 -2.180106 -2.705582 1.370823 1 40 s
atom 24 - H ** - 0 -1.356032 -2.261717 2.853317 1 40 s
atom 25 - H ** - 0 -3.88631 3.401828 1.859619 1 36 s
atom 26 - H ** - 0 -3.284379 2.842405 3.408436 1 36 s
atom 27 - H ** - 0 -4.749207 2.152184 2.735495 1 36 s
atom 28 - H ** - 0 -2.756629 -1.140561 4.149562 1 38 s
atom 29 - H ** - 0 -4.196566 -0.182558 3.860466 1 38 s
atom 30 - H ** - 0 -2.771707 0.5677358 4.552625 1 38 s
atom 31 - B ** - 0 -0.1138552 0.2689569 0.1255013 3 32 s 42 s 43 s

```

```

atom 32 - C ** -0 -1.688887 0.1869635 0.2994008 4 31 s 33 s 41 s 39 s
atom 33 - C ** -0 -2.419112 1.488111 0.5686594 3 32 s 34 s 35 s
atom 34 - C ** -0 -2.548243 2.548459 -0.4913674 4 33 s 18 s 17 s 16 s
atom 35 - C ** -0 -2.944426 1.468112 1.794707 3 33 s 36 s 37 s
atom 36 - C ** -0 -3.761532 2.528216 2.484597 4 35 s 27 s 26 s 25 s
atom 37 - C ** -0 -2.623599 0.172463 2.447553 3 35 s 38 s 39 s
atom 38 - C ** -0 -3.110948 -0.1696965 3.831148 4 37 s 30 s 29 s 28 s
atom 39 - C ** -0 -1.913822 -0.5898937 1.612446 3 37 s 40 s 32 s
atom 40 - C ** -0 -1.458614 -2.016904 1.803604 4 39 s 24 s 23 s 22 s
atom 41 - C ** -0 -2.3504 -0.5775552 -0.8836678 4 32 s 21 s 20 s 19 s
atom 42 - F ** -0 0.421645 -0.8842385 -0.4046031 1 31 s
atom 43 - C ** -0 0.9869072 1.37264 0.4225036 4 31 s 44 s 50 s 52 s
atom 44 - C ** -0 0.5670922 2.545231 1.287075 3 43 s 45 s 46 s
atom 45 - C ** -0 0.2817244 2.375208 2.754766 4 44 s 3 s 2 s 1 s
atom 46 - C ** -0 0.5811684 3.667925 0.5667222 3 44 s 47 s 48 s
atom 47 - C ** -0 0.2539699 5.070452 1.006031 4 46 s 11 s 8 s 7 s
atom 48 - C ** -0 1.009239 3.357478 -0.8218233 3 46 s 49 s 50 s
atom 49 - C ** -0 1.161806 4.427242 -1.871348 4 48 s 12 s 10 s 9 s
atom 50 - C ** -0 1.260612 2.051176 -0.9349532 3 48 s 51 s 43 s
atom 51 - C ** -0 1.818792 1.303602 -2.122394 4 50 s 15 s 14 s 13 s
atom 52 - C ** -0 2.297774 0.7329501 0.9650405 4 43 s 6 s 5 s 4 s
endmol 1

```

Figure 95: RHF/6-31G* optimized (C₅Me₅)₂BF

forcefield mm+

sys 0

view 40 0.41426 55 15 0.05941182 -0.3333732 0.9409212 0.8304488 0.5395456 0.1387274 -0.5539178 0.7731448 0.3089047
0.29034 -0.336 -52.701

seed -1111

mol 1

```

atom 1 - B B3 -0 -0.1065325 0.2554567 0.1216498 3 2 s 13 s 10 s
atom 2 - F F -0 0.4139057 -0.8656406 -0.3909064 1 1 s
atom 3 - C C4 -0 -1.424184 -1.99333 1.843009 4 4 s 39 s 38 s 40 s
atom 4 - C C3 -0 -1.920852 -0.5904009 1.614854 3 3 s 5 s 10 s
atom 5 - C C3 -0 -2.633125 0.1767575 2.445907 3 4 s 6 s 7 s
atom 6 - C C3 -0 -3.099916 -0.1383035 3.840562 4 5 s 43 s 42 s 41 s
atom 7 - C C3 -0 -2.960598 1.458633 1.781124 3 9 s 8 s 5 s
atom 8 - C C4 -0 -2.434293 1.465432 0.5553665 3 10 s 7 s 11 s
atom 9 - C C4 -0 -3.790639 2.522888 2.444719 4 7 s 44 s 45 s 46 s
atom 10 - C C4 -0 -1.699016 0.1690367 0.3049238 4 1 s 12 s 4 s 8 s
atom 11 - C C4 -0 -2.597537 2.508629 -0.5158713 4 8 s 49 s 48 s 47 s
atom 12 - C C4 -0 -2.330329 -0.5842681 -0.8927231 4 10 s 50 s 52 s 51 s
atom 13 - C C4 -0 1.005892 1.375891 0.4117642 4 1 s 14 s 16 s 21 s
atom 14 - C C3 -0 0.5986471 2.538262 1.287742 3 13 s 17 s 18 s
atom 15 - C C3 -0 1.764372 1.314712 -2.145395 4 21 s 29 s 30 s 31 s
atom 16 - C C3 -0 2.294626 0.7138542 0.9609903 4 13 s 32 s 34 s 33 s
atom 17 - C C3 -0 0.6035012 3.666269 0.5755221 3 20 s 14 s 19 s
atom 18 - C C4 -0 0.3518799 2.377135 2.762617 4 14 s 36 s 37 s 35 s
atom 19 - C C4 -0 0.2891634 5.06188 1.039428 4 17 s 24 s 23 s 25 s
atom 20 - C C4 -0 1.01234 3.363866 -0.8150589 3 21 s 17 s 22 s
atom 21 - C C4 -0 1.264153 2.056666 -0.934276 3 13 s 20 s 15 s
atom 22 - C C4 -0 1.126905 4.437346 -1.862672 4 20 s 28 s 27 s 26 s
atom 23 - H H -0 1.148763 5.718131 0.9272388 1 19 s
atom 24 - H H -0 -0.0024519 5.083286 2.08123 1 19 s
atom 25 - H H -0 -0.5213528 5.498235 0.4611026 1 19 s
atom 26 - H H -0 1.84045 5.200314 -1.562983 1 22 s
atom 27 - H H -0 0.1732247 4.936547 -2.014491 1 22 s
atom 28 - H H -0 1.446479 4.045685 -2.81881 1 22 s
atom 29 - H H -0 1.977869 1.991087 -2.962594 1 15 s
atom 30 - H H -0 1.051309 0.5803675 -2.507884 1 15 s
atom 31 - H H -0 2.680355 0.7746915 -1.923138 1 15 s
atom 32 - H H -0 3.077482 1.458747 1.062875 1 16 s
atom 33 - H H -0 2.652776 -0.0708956 0.3077735 1 16 s
atom 34 - H H -0 2.125205 0.2717976 1.9385 1 16 s
atom 35 - H H -0 1.289394 2.375392 3.31498 1 18 s
atom 36 - H H -0 -0.1522866 1.444372 2.981645 1 18 s
atom 37 - H H -0 -0.2579396 3.178985 3.159548 1 18 s

```



```

atom 38 - H H -0 -1.772211 -2.663386 1.062163 1 3 s
atom 39 - H H -0 -1.774816 -2.387574 2.787761 1 3 s
atom 40 - H H -0 -0.340026 -2.056318 1.845684 1 3 s
atom 41 - H H -0 -2.715076 0.5871647 4.552771 1 6 s
atom 42 - H H -0 -2.781957 -1.118676 4.168518 1 6 s
atom 43 - H H -0 -4.184176 -0.1032195 3.906224 1 6 s
atom 44 - H H -0 -3.911598 3.391859 1.811377 1 9 s
atom 45 - H H -0 -3.338533 2.853886 3.376309 1 9 s
atom 46 - H H -0 -4.784313 2.154072 2.687155 1 9 s
atom 47 - H H -0 -1.701388 2.605766 -1.115631 1 11 s
atom 48 - H H -0 -2.819288 3.48329 -0.0995515 1 11 s
atom 49 - H H -0 -3.411226 2.24834 -1.189842 1 11 s
atom 50 - H H -0 -2.217292 -0.0225012 -1.815294 1 12 s
atom 51 - H H -0 -3.39174 -0.7305827 -0.7188032 1 12 s
atom 52 - H H -0 -1.871998 -1.552631 -1.044109 1 12 s
endmol 1

```

Figure 96: RMP2/3-21G* optimized (C₃Me₃)₂BF

forcefield mm+

sys 0

view 40 0.21364 40 15 -0.4753503 -0.8791536 0.03363021 -0.6361423 0.3170484 -0.7034225 0.607754 -0.3557658 -0.7099759 -0.024986 -0.02684 -40.027

seed -1111

mol 1

```

atom 1 - H ** -0 -0.3476569 3.264883 1.96002 1 33 s
atom 2 - H ** -0 -1.758143 0.9135526 1.286328 1 48 s
atom 3 - H ** -0 -2.229026 2.311443 0.2940932 1 48 s
atom 4 - H ** -0 -3.202429 0.8263814 0.2453504 1 48 s
atom 5 - H ** -0 0.6869711 -2.513248 3.604784 1 31 s
atom 6 - H ** -0 -0.3752912 -2.926455 2.247941 1 31 s
atom 7 - H ** -0 -1.015582 -2.008632 3.629903 1 31 s
atom 8 - H ** -0 -1.285886 3.398945 -1.278141 1 47 s
atom 9 - H ** -0 0.3475667 3.264927 -1.959953 1 47 s
atom 10 - H ** -0 -1.071114 3.148937 -3.023125 1 47 s
atom 11 - H ** -0 2.228918 2.311509 -0.2940235 1 29 s
atom 12 - H ** -0 1.758167 0.9135873 -1.286268 1 29 s
atom 13 - H ** -0 3.20243 0.8265176 -0.2452445 1 29 s
atom 14 - H ** -0 1.170002 0.02856185 -4.478412 1 46 s
atom 15 - H ** -0 1.463234 1.620602 -3.743743 1 46 s
atom 16 - H ** -0 -0.00820537 1.339163 -4.69686 1 46 s
atom 17 - H ** -0 -2.968241 -1.537716 -0.1839474 1 49 s
atom 18 - H ** -0 -2.149293 -2.678483 -1.27619 1 49 s
atom 19 - H ** -0 -2.968165 -1.2357 -1.943454 1 49 s
atom 20 - H ** -0 -1.170096 0.02843615 4.47839 1 32 s
atom 21 - H ** -0 0.008088454 1.339046 4.696902 1 32 s
atom 22 - H ** -0 -1.463331 1.620492 3.743755 1 32 s
atom 23 - H ** -0 2.149325 -2.678482 1.276141 1 30 s
atom 24 - H ** -0 2.968193 -1.235724 1.943462 1 30 s
atom 25 - H ** -0 2.968267 -1.537664 0.183945 1 30 s
atom 26 - H ** -0 -0.6869681 -2.5132 -3.604783 1 45 s
atom 27 - H ** -0 0.375352 -2.926385 -2.247986 1 45 s
atom 28 - H ** -0 1.015568 -2.008529 -3.629962 1 45 s
atom 29 - C ** -0 2.178588 1.216905 -0.3231637 4 35 s 13 s 12 s 11 s
atom 30 - C ** -0 2.378493 -1.622593 1.104176 4 34 s 25 s 24 s 23 s
atom 31 - C ** -0 -0.1422704 -2.150296 2.982557 4 38 s 7 s 6 s 5 s
atom 32 - C ** -0 -0.6896546 0.8798431 3.984772 4 37 s 22 s 21 s 20 s
atom 33 - C ** -0 0.6799899 2.885246 2.032189 4 36 s 1 s 51 s 52 s
atom 34 - C ** -0 1.066467 -0.797914 0.9808419 4 35 s 38 s 30 s 39 s
atom 35 - C ** -0 1.316055 0.6903061 0.7997597 3 34 s 36 s 29 s
atom 36 - C ** -0 0.7163314 1.385687 1.816842 3 35 s 37 s 33 s
atom 37 - C ** -0 0.03754063 0.4332098 2.730916 3 36 s 38 s 32 s
atom 38 - C ** -0 0.233634 -0.851607 2.291312 3 37 s 34 s 31 s
atom 39 - B ** -0 1.500102e-005 -1.439467 5.998887e-006 3 34 s 41 s 50 s
atom 40 - C ** -0 -0.2336387 -0.851555 -2.291312 3 41 s 44 s 45 s
atom 41 - C ** -0 -1.066441 -0.797911 -0.9808159 4 40 s 42 s 49 s 39 s
atom 42 - C ** -0 -1.316081 0.6902978 -0.7997124 3 41 s 43 s 48 s
atom 43 - C ** -0 -0.7163873 1.385714 -1.816786 3 42 s 44 s 47 s

```

```
atom 44 - C ** - 0 -0.03759429 0.4332722 -2.730897 3 43 s 40 s 46 s
atom 45 - C ** - 0 0.1422851 -2.150225 -2.982585 4 40 s 28 s 27 s 26 s
atom 46 - C ** - 0 0.689562 0.8799499 -3.98476 4 44 s 16 s 15 s 14 s
atom 47 - C ** - 0 -0.6800779 2.88528 -2.032099 4 43 s 10 s 9 s 8 s
atom 48 - C ** - 0 -2.178614 1.216842 0.3232364 4 42 s 4 s 3 s 2 s
atom 49 - C ** - 0 -2.378467 -1.622603 -1.10418 4 41 s 19 s 18 s 17 s
atom 50 - F ** - 0 2.088336e-005 -2.83715 -5.698581e-006 1 39 s
atom 51 - H ** - 0 1.070989 3.148882 3.023235 1 33 s
atom 52 - H ** - 0 1.285816 3.398941 1.278267 1 33 s
endmol 1
```

Appendix B

DAPSIC 2.0 Program

The following is the text of a Visual Basic 3.0 program that was written to tutor students in the factor label method. The evaluation of this program is described in Part B of this text. This program was written by the author while matriculating at MTSU.

The program referred to as "DAPSIC" is actually two separate programs. "DAPSIC" is a program that handles the selection of problems. Once a problem has been selected, a program called "DAPSIC03" handles the mechanics of solving the problem.

Included here are the text files for both "DAPSIC" and "DAPSIC03", along with a sample problem and a sample list of problems:

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```
PROGRAM: DAPSIC
FILE: DAPSIC.MAK
FRMABOUT.FRM
INTERN1.BAS
FRMINTRO.FRM
FRMWHAT.FRM
ProjWinSize=71,384,252,376
ProjWinShow=2
IconForm="frmAbout"
Title="DAPSIC - select problem"
ExeName="DAPSIC.EXE"
Path="Q:\DAPSIC~9\DAPSICSL"
```

```
FILE: INTERN1.BAS
Option Explicit

' drivechange <-- search for this word to change drives
'Const FILELIST = "a:lstprob.txt"
'Const FILELIST = "b:blstprob.txt"
Const FILELIST = "\listprob.txt"
'debug line

' the drive is found in frmIntro under gotoprob

Global fileName As String
```

```

Global probList(50), probDisc(50) As String
Global probLevel(50) As Integer
Global probMap(50) As Integer
Global probProgressNumber As Integer
Global lineOfText As String
Global dummyvar
Global sigFigFlag As Integer
Global levelFlag As Integer
Global CurrentPath As String
Global CurrentLevel As Integer
Global FirstTimeUserFlag As Integer
'Global HintFlag As Integer
'Global hintProgress As Integer ' true if you have reached a point where a new hint
window needs to be shown.
'Global hintNumber, HintMax As Integer
'Global HintText(1 To 50) As String
'Global DoThisText(1 To 50) As String
'Global HintCommand(1 To 50) As Integer

'Global flashState1, flashState2, flashState3, flashState4 As Integer
'Global OnSwitchForArrow(0 To NUMBEROFARROWS) As Integer

'make all forms modal!

Sub InitIt ()
    'CurrentPath = App.path
    CurrentPath = "C:\da\dapsic"
    CurrentLevel = 1
    FirstTimeUserFlag = False
End Sub

Sub logit (dummy As String)

' drivechange
'   Open "a:logfile.txt" For Append As #3
'   Open "b:logfile.txt" For Append As #3
    Open CurrentPath & "\logfile.txt" For Append As #3

    Print #3, dummy; " " & Time$
    Close #3
End Sub

Static Sub UpdateList ()
Dim dummy As String
Dim i As Integer
If Dir$(CurrentPath & FILELIST) = "" Then
    MsgBox "This file was not found:" & CurrentPath & FILELIST
Else
    i = 0
    Open CurrentPath & FILELIST For Input As #1
    Do While (Not (EOF(1))) And (i < 51)
        Input #1, dummy
        probDisc(i) = dummy
        Input #1, dummy
        probList(i) = dummy
        Input #1, dummy
        probLevel(i) = CInt(dummy)
        i = i + 1
    Loop
    If i <= 50 Then probList(i) = "ENDOF LIST"
    probProgressNumber = 0
    Close #1
End If
End Sub

```

FILE: FRMABOUT.FRM

```

VERSION 2.00
Begin Form frmAbout
    Caption           = "DAPSIC - Introductory menu"
    ClientHeight      = 6555
    ClientLeft        = 825
    ClientTop         = 255
    ClientWidth       = 7650
    ControlBox        = 0 'False
    Height            = 6960
    KeyPreview        = -1 'True
    Left              = 765
    LinkTopic         = "Form3"
    MaxButton         = 0 'False
    MinButton         = 0 'False
    ScaleHeight       = 6555
    ScaleWidth        = 7650
    Top               = -90
    Width             = 7770
    Begin CommandButton Command1
        Caption       = "Quit"
        Height        = 675
        Left          = 6600
        TabIndex      = 9
        Top           = 5520
        Width         = 495
    End
    Begin TextBox Text1
        Height        = 288
        Left          = 2580
        TabIndex      = 1
        Top           = 5100
        Width         = 4452
    End
    Begin CommandButton cmdFirstTime
        Caption       = "Click here if this is your first time using this program"
        Height        = 675
        Left          = 480
        TabIndex      = 3
        Top           = 3060
        Width         = 6735
    End
    Begin CommandButton cmdStart
        Caption       = "Click here to go to problem list"
        Enabled       = 0 'False
        Height        = 675
        Left          = 480
        TabIndex      = 2
        Top           = 5520
        Width         = 5955
    End
    Begin Label Label9
        BorderStyle   = 1 'Fixed Single
        Caption       = "Middle Tennessee State University"
        ForeColor     = &H000000FF&
        Height        = 255
        Left          = 2640
        TabIndex      = 12
        Top           = 2460
        Width         = 4635
    End
    Begin Label Label8
        BorderStyle   = 1 'Fixed Single
        Caption       = "Dr. William Ilsley"
        ForeColor     = &H000000FF&
        Height        = 255
        Left          = 2640
        TabIndex      = 11
        Top           = 2160
    End

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        Width          = 4635
    End
    Begin Label Label7
        Caption         = "This copy is registered to:"
        Height          = 195
        Left             = 240
        TabIndex        = 10
        Top              = 2160
        Width           = 2295
    End
    Begin Line Line1
        X1               = 180
        X2               = 7260
        Y1               = 2820
        Y2               = 2820
    End
    Begin Label Label6
        Caption         = "(All rights reserved. Please be nice to a poor grad student
with a family to feed, and refrain from making copies of this program. I'd do the same
for you. Thanks.)"
        Height          = 435
        Left             = 180
        TabIndex        = 8
        Top              = 1560
        Width           = 7095
    End
    Begin Label Label5
        Caption         = "DAPSIC: Dimensional Analysis Problem Solving In Chemistry"
        FontBold        = -1 'True
        FontItalic      = 0 'False
        FontName        = "MS Sans Serif"
        FontSize        = 18
        FontStrikethru   = 0 'False
        FontUnderline    = 0 'False
        Height          = 975
        Left             = 240
        TabIndex        = 7
        Top              = 120
        Width           = 7155
    End
    Begin Label Label4
        Caption         = "Enter your name here:"
        Height          = 255
        Left             = 480
        TabIndex        = 6
        Top              = 5100
        Width           = 1995
    End
    Begin Label Label3
        Caption         = "Copyright 1996 Brian Hill"
        FontBold        = -1 'True
        FontItalic      = 0 'False
        FontName        = "MS Sans Serif"
        FontSize        = 9.75
        FontStrikethru   = 0 'False
        FontUnderline    = 0 'False
        Height          = 255
        Left             = 2460
        TabIndex        = 5
        Top              = 1140
        Width           = 2715
    End
    Begin Label Label2
        Caption         = "DAPSIC was developed by Brian Hill under the direction of Dr.
William Ilsley. It was written for CHEM 760 at Middle Tennessee State University. This
work was supported financially by Bryan College."
        Height          = 675
        Left             = 480

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        TabIndex      = 4
        Top           = 4260
        Width         = 6615
    End
    Begin Label Label1
        Caption       = "Modules 1-3, version 2.1 Last revision 6/19/97"
        Height        = 255
        Left          = 1620
        TabIndex      = 0
        Top           = 3900
        Width         = 4095
    End
End
Option Explicit

Sub cmdFirstTime_Click ()
    MsgBox "Help screen under construction. Sorry for the delay."
    firstTimeUserFlag = True
    frmWhat.Show 1
    text1.SetFocus
End Sub

Sub cmdStart_Click ()
    frmAbout.Hide
    logit (text1.Text)
    UpdateList
    frmIntro.Show 1
End Sub

Sub Command1_Click ()
    End
End Sub

Sub Form_KeyPress (keyascii As Integer)
    If keyascii = 13 Then
        cmdStart_Click
        keyascii = 0
    End If
End Sub

Sub Form_Load ()
    InitIt
End Sub

Sub Text1_Change ()
    cmdStart.Enabled = True
End Sub

```

FILE: FRMINTRO.FRM

VERSION 2.00

```

Begin Form frmIntro
    Caption       = "DAPSIC, problem list"
    ClientHeight  = 5985
    ClientLeft    = 1935
    ClientTop     = 630
    ClientWidth   = 5865
    ControlBox    = 0 'False
    Height        = 6675
    Left          = 1875
    LinkTopic     = "Form3"
    MaxButton     = 0 'False
    MinButton     = 0 'False

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```

ScaleHeight      = 5985
ScaleWidth       = 5865
Top              = 0
Width           = 5985
Begin OptionButton Option1
    Caption       = "(I wish to see all levels, please)"
    Height        = 255
    Index         = 0
    Left          = 180
    TabIndex      = 9
    Top           = 1080
    Width         = 4035
End
Begin OptionButton Option1
    Caption       = "Level 3 - Density and other substance specific problems"
    Height        = 255
    Index         = 3
    Left          = 180
    TabIndex      = 8
    Top           = 840
    Width         = 5235
End
Begin OptionButton Option1
    Caption       = "Level 2 - Multistep unit conversion"
    Height        = 255
    Index         = 2
    Left          = 180
    TabIndex      = 7
    Top           = 600
    Width         = 4455
End
Begin OptionButton Option1
    Caption       = "Level 1 - Basic Metric / English conversion"
    Height        = 255
    Index         = 1
    Left          = 180
    TabIndex      = 6
    Top           = 360
    Width         = 4035
End
Begin CommandButton cmdNextOne
    Caption       = "Do this problem"
    Height        = 435
    Left          = 180
    TabIndex      = 3
    Top           = 5400
    Width         = 3615
End
Begin CommandButton cmdQuit
    Caption       = "Quit"
    Height        = 435
    Left          = 3960
    TabIndex      = 1
    Top           = 5400
    Width         = 1575
End
Begin ListBox lstProb
    Height        = 2955
    Left          = 180
    TabIndex      = 0
    Top           = 2400
    Width         = 5415
End
Begin Label Label3
    Caption       = "Level:"
    Height        = 255
    Left          = 120
    TabIndex      = 5

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        Top          = 60
        Width        = 1875
    End
    Begin Line Line1
        BorderWidth   = 2
        X1            = 120
        X2            = 5760
        Y1            = 1500
        Y2            = 1500
    End
    Begin Label Label2
        Caption       = "PLEASE DO AT LEAST THOSE MARKED WITH AN ASTERISK (****) .
OTHERS ARE OPTIONAL."
        FontBold      = -1 'True
        FontItalic    = 0  'False
        FontName      = "MS Sans Serif"
        FontSize      = 9.75
        FontStrikethru = 0  'False
        FontUnderline = 0  'False
        Height       = 435
        Left         = 180
        TabIndex     = 4
        Top          = 1920
        Width        = 5415
    End
    Begin Label Label1
        Caption       = "List of problems: (double click on one to select)"
        FontBold      = -1 'True
        FontItalic    = 0  'False
        FontName      = "MS Sans Serif"
        FontSize      = 8.25
        FontStrikethru = 0  'False
        FontUnderline = -1 'True
        Height       = 195
        Left         = 180
        TabIndex     = 2
        Top          = 1680
        Width        = 5235
    End
    Begin Menu mnuDummy1
        Caption       = "&File"
        Begin Menu mnuQuitting
            Caption    = "&Quit"
        End
    End
    Begin Menu mnuDummy2
        Caption       = "&Parameters"
        Begin Menu mnuSigFig
            Caption    = "&Significant Figures"
        End
    End
End
Option Explicit

Sub cmdNextOne_Click ()
    gotoProb
End Sub

Sub cmdQuit_Click ()
    End
End Sub

Sub cmdStartProb_Click ()
    If lstProb.ListIndex > 0 Then
        'lstProb.listIndex = lstProb.listIndex + 1
        probProgressNumber = probProgressNumber - 1
        displayList
    End If
End Sub

```

```

        gotoProb
End Sub

Sub displayLevel ()

    option1(currentLevel).Value = True
End Sub

Static Sub displayList ()
Dim i, j As Integer
    'HintFlag = False
    mnuSigFig.Checked = sigFigFlag
    lstProb.Clear
    i = 0
    j = 0
    Do Until (probDisc(i) = "ENDOF LIST") Or (probDisc(i) = "") Or (i > 50)
        If (currentLevel = 0) Or Abs(probLevel(i)) = currentLevel Then
            lstProb.AddItem probDisc(i)
            probMap(j) = i
            j = j + 1
        End If
        i = i + 1
    Loop
    If lstProb.ListCount > 0 Then lstProb.ListIndex = probProgressNumber
    'If (lstProb.ListIndex < (lstProb.listCount - 1)) Or (probProgressNumber = 0) Then
cmdNextOne.Enabled = True Else cmdNextOne.Enabled = False
End Sub

Sub Form_Activate ()
    displayLevel
    displayList
End Sub

Sub Form_Load ()
    sigFigFlag = False
    levelFlag = 2
End Sub

Static Sub gotoProb ()
'Static message As Integer

    filename = probList(probMap(lstProb.ListIndex))
    probProgressNumber = lstProb.ListIndex
    'MsgBox fileName
    Open CurrentPath & "\" & filename For Input As #1

' drivechange
'    Open "a:PROBBUF.TXT" For Output As #2
'    Open "b:PROBBUF.TXT" For Output As #2
    Open CurrentPath & "\PROBBUF.TXT" For Output As #2

    Print #2, "This will determine which module is used."
    If sigFigFlag = True Then Print #2, CStr(probLevel(lstProb.ListIndex)) Else Print
#2, CStr(-1 * probLevel(lstProb.ListIndex))
    Do While Not (EOF(1))
        Input #1, lineOfText
        Print #2, lineOfText
    Loop
    Close #1
    Close #2
    logit (filename)
    'MsgBox "reached this point"
    If probProgressNumber < lstProb.ListCount - 1 Then probProgressNumber =
probProgressNumber + 1

```

```

        'If (probProgressNumber = 0) And (lstProb.ListCount > 1) Then probProgressNumber
= 1
        displayList

' drivechange
'     dummyvar = Shell("a:daprun.exe", 1)
'     dummyvar = Shell("b:bdaprun.exe", 1)
        dummyvar = Shell(CurrentPath & "\daprun.exe", 1)

        'frmIntro.Hide
        'copy the file

        'shell
        'If sigFigFlag = True Then MsgBox "sigfig on" Else MsgBox "sigfig off"
        'MsgBox CStr(levelFlag)

End Sub

Sub lstProb_DblClick ()
    gotoProb
End Sub

Sub mnuLevel_Click (index As Integer)
    levelFlag = index
    displayList
End Sub

Sub mnuQuitting_Click ()
    End
End Sub

Sub mnuSigFig_Click ()
    If sigFigFlag = True Then sigFigFlag = False Else sigFigFlag = True
    displayList
End Sub

Sub Option1_Click (index As Integer)
    If index <> currentLevel Then probProgressNumber = 0
    currentLevel = index
    displayList
End Sub

```

FILE: FRMWHAT.FRM

VERSION 2.00

Begin Form frmWhat

```

    Caption           = "Dapsic:  What is dimensional analysis?"
    ClientHeight      = 6720
    ClientLeft        = 75
    ClientTop         = 375
    ClientWidth       = 9495
    ControlBox        = 0 'False
    Height            = 7125
    Left              = 15
    LinkTopic         = "Form1"
    MaxButton         = 0 'False
    MinButton         = 0 'False
    ScaleHeight       = 6720
    ScaleWidth        = 9495
    Top               = 30
    Width             = 9615
    WindowState       = 2 'Maximized
Begin CommandButton Command1
    Caption           = "Done"
    Height           = 855
    Left             = 8460
    TabIndex         = 0

```

```

Top          = 5640
Width        = 855
End
Begin Label Label13
Caption      = "Dimensional analysis, then, is the method of solving
conversion problems using unit factors. The unit factor involved may be a metric to
English conversion factor, or an English to English conversion factor, or even a factor
given in the text of a problem. Often, more than one unit factor may be needed to solve
a problem. In any case, you can multiply and cancel units to solve a particular
problem."
Height       = 1035
Left         = 180
TabIndex     = 17
Top          = 5640
Width        = 7875
End
Begin Line Line4
X1           = 180
X2           = 9420
Y1           = 5520
Y2           = 5520
End
Begin Line Line3
X1           = 120
X2           = 9420
Y1           = 960
Y2           = 960
End
Begin Label Label12
Caption      = "3.66 inches is the correct answer, rounded to three
significant figures. "
Height       = 255
Left         = 180
TabIndex     = 19
Top          = 5220
Width        = 7815
End
Begin Label Label11
Caption      = "3.66 in. "
FontBold     = -1 'True
FontItalic    = 0 'False
FontName     = "MS Sans Serif"
FontSize     = 12
FontStrikethru = 0 'False
FontUnderline = 0 'False
Height       = 315
Left         = 6900
TabIndex     = 22
Top          = 4620
Width        = 1275
End
Begin Label Label4
Caption      = "="
Height       = 195
Index        = 6
Left         = 6540
TabIndex     = 30
Top          = 4680
Width        = 255
End
Begin Label Label4
Caption      = "="
Height       = 195
Index        = 5
Left         = 3960
TabIndex     = 29
Top          = 4680
Width        = 255

```

```

End
Begin Label Label10
  Caption      = "cm."
  FontBold     = -1 'True
  FontItalic   = 0  'False
  FontName     = "MS Sans Serif"
  FontSize     = 8.25
  FontStrikethru = -1 'True
  FontUnderline = 0  'False
  Height       = 255
  Index        = 1
  Left         = 4860
  TabIndex     = 28
  Top          = 4500
  Width        = 375
End
Begin Label Label10
  Caption      = "cm."
  FontBold     = -1 'True
  FontItalic   = 0  'False
  FontName     = "MS Sans Serif"
  FontSize     = 8.25
  FontStrikethru = -1 'True
  FontUnderline = 0  'False
  Height       = 255
  Index        = 0
  Left         = 5400
  TabIndex     = 27
  Top          = 4860
  Width        = 375
End
Begin Label Label4
  Caption      = "x"
  Height       = 195
  Index        = 3
  Left         = 5340
  TabIndex     = 26
  Top          = 4500
  Width        = 195
End
Begin Label Label3
  Caption      = "2.54"
  Height       = 255
  Index        = 7
  Left         = 4920
  TabIndex     = 25
  Top          = 4860
  Width        = 795
End
Begin Line Line2
  Index        = 2
  X1           = 4380
  X2           = 6180
  Y1           = 4800
  Y2           = 4800
End
Begin Label Label5
  Caption      = "1 in."
  Height       = 255
  Index        = 3
  Left         = 5640
  TabIndex     = 24
  Top          = 4500
  Width        = 495
End
Begin Label Label3
  Caption      = "9.29"
  Height       = 255

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        Index      = 5
        Left       = 4380
        TabIndex   = 23
        Top        = 4500
        Width      = 795
    End
    Begin Label Label4
        Caption     = "x"
        Height      = 195
        Index       = 4
        Left        = 2820
        TabIndex    = 21
        Top         = 4680
        Width       = 195
    End
    Begin Label Label3
        Caption     = "2.54 cm. "
        Height      = 255
        Index       = 6
        Left        = 3060
        TabIndex    = 20
        Top         = 4860
        Width       = 795
    End
    Begin Line Line2
        Index       = 1
        X1          = 3060
        X2          = 3900
        Y1          = 4800
        Y2          = 4800
    End
    Begin Label Label5
        Caption     = "1 in."
        Height      = 255
        Index       = 2
        Left        = 3060
        TabIndex    = 18
        Top         = 4500
        Width       = 495
    End
    Begin Label Label3
        Caption     = "9.29 cm. "
        Height      = 255
        Index       = 4
        Left        = 1920
        TabIndex    = 16
        Top         = 4560
        Width       = 795
    End
    Begin Label Label9
        Caption     = "Now let's get back to converting 9.29 cm to inches. Since our
unit factor is equal to 1, we can multiply 9.29 cm by this quantity, and its value will
not change. We can also cancel out the unit ""cm""; since it appears in both the
numerator and denominator, it will cancel:"
        Height      = 615
        Left        = 180
        TabIndex    = 15
        Top         = 3840
        Width       = 9135
        WordWrap    = -1 'True
    End
    Begin Label Label8
        Caption     = "The fraction we obtain (1 in / 2.54 cm) is called a unit
factor. It is numerically equal to 1. (Since 2.54 cm = 2.54 cm, the numerator and
denominator on the left will cancel.) "
        Height      = 495
        Left        = 180
        TabIndex    = 14

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        Top          = 3300
        Width        = 9075
    End
    Begin Label Label7
        Caption       = "1"
        Height        = 255
        Index         = 0
        Left          = 4980
        TabIndex      = 13
        Top           = 2820
        Width         = 315
    End
    Begin Label Label4
        Caption       = "="
        Height        = 195
        Index         = 2
        Left          = 5340
        TabIndex      = 12
        Top           = 2820
        Width         = 255
    End
    Begin Label Label3
        Caption       = "2.54 cm. "
        Height        = 255
        Index         = 3
        Left          = 5640
        TabIndex      = 11
        Top           = 3000
        Width         = 795
    End
    Begin Label Label3
        Caption       = "2.54 cm. "
        Height        = 255
        Index         = 2
        Left          = 3720
        TabIndex      = 10
        Top           = 3000
        Width         = 795
    End
    Begin Line Line2
        Index         = 0
        X1            = 5640
        X2            = 6480
        Y1            = 2940
        Y2            = 2940
    End
    Begin Line Line1
        Index         = 0
        X1            = 3720
        X2            = 4560
        Y1            = 2940
        Y2            = 2940
    End
    Begin Label Label5
        Caption       = "1 in."
        Height        = 255
        Index         = 1
        Left          = 5640
        TabIndex      = 9
        Top           = 2640
        Width         = 495
    End
    Begin Label Label4
        Caption       = "="
        Height        = 195
        Index         = 1
        Left          = 4680
        TabIndex      = 8

```

```

    Top          = 2820
    Width        = 255
End
Begin Label Label3
    Caption      = "2.54 cm. "
    Height       = 255
    Index        = 1
    Left         = 3720
    TabIndex     = 7
    Top          = 2640
    Width        = 795
End
Begin Label Label6
    Caption      = "Now let's divide both sides of this equation by 2.54 cm.
(Note: we divide not just by 2.54, but by 2.54 cm. The unit may be regarded as part of
this quantity and may NOT be omitted). We will obtain the following:"
    Height       = 435
    Left         = 120
    TabIndex     = 6
    Top          = 2160
    Width        = 9315
End
Begin Label Label5
    Caption      = "1 in."
    Height       = 255
    Index        = 0
    Left         = 5160
    TabIndex     = 5
    Top          = 1800
    Width        = 495
End
Begin Label Label4
    Caption      = "="
    Height       = 195
    Index        = 0
    Left         = 4680
    TabIndex     = 4
    Top          = 1800
    Width        = 255
End
Begin Label Label3
    Caption      = "2.54 cm. "
    Height       = 255
    Index        = 0
    Left         = 3720
    TabIndex     = 3
    Top          = 1800
    Width        = 795
End
Begin Label Label2
    Caption      = "How many inches is equal to 9.29 centimeters? To solve this
problem, we need to know that 1 inch is equal to 2.54 centimeters. (This is one of three
metric to English conversion factors you will use in this tutorial). Expressed
mathematically, we can say: "
    Height       = 675
    Left         = 120
    TabIndex     = 2
    Top          = 1020
    Width        = 9315
End
Begin Label Label1
    Caption      = "Dimensional analysis (also known as factor label method or
unit analysis) is a useful method for solving a variety of problems in chemistry. To
illustrate this method, let's examine a metric to English conversion problem:"
    FontBold     = -1 'True
    FontItalic   = 0 'False
    FontName     = "MS Sans Serif"
    FontSize     = 9.75

```



```

        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height         = 795
        Left           = 120
        TabIndex        = 1
        Top            = 120
        Width          = 9315
    End
End
Option Explicit

Sub Command1_Click ()
    frmWhat.Hide
End Sub

```

PROGRAM: DAPSIC03
FILE: DAPSIC03.MAK

```

INTERN.FRM
INTERN1.BAS
INTERN2.FRM
FRMMETEN.FRM
FRMENGEN.FRM
FRMMETME.FRM
FRMGETST.FRM
FRMSTAR2.FRM
FRMDENSE.FRM
FRMSUBST.FRM
FRMINTEX.FRM
ProjWinSize=74,319,252,376
ProjWinShow=2
IconForm="Form1"
Title="DAPSIC - problem mode"
ExeName="DAPRUN.EXE"
Path="Q:\DAPSIC-9\DAPSICRN"

```

FILE: INTERN.BAS

```

Option Explicit

' drivechange
'Const FILENAME = "a:probbuf.txt"
'Const FILENAME = "b:probbuf.txt"
Const FILENAME = "\probbuf.txt"

'drivechange
' DON'T FORGET TO CHANGE LSTPROB.TXT and BLSTPROB.TXT

Type nextToTheLine
    num As Double
    sigfig As Integer
    exp As Integer
    unit As String
    unitCanceled As Integer
    stuff As String
    stuffCanceled As Integer
End Type

Type betweenTheParenthesis
    n As nextToTheLine
    d As nextToTheLine
End Type

```

```

Global StartingPoint As betweenTheParenthesis
Global studentAnswer As betweenTheParenthesis
Global correctAnswer As betweenTheParenthesis
Global bufferFactor As betweenTheParenthesis
Global unitFactor(1 To 13) As betweenTheParenthesis
Global givenInfo(1 To 4) As betweenTheParenthesis
Global keyPhrase(1 To 6) As String
Global numberOfGivenInfo As Integer

Global currentFactor As betweenTheParenthesis
Global nullFactor As betweenTheParenthesis

Global ProblemText As String
Global UnitFindingStage As Integer
Global NumberFactorsSoFar As Integer

Global LevelFlag As Integer
Global sigFigFlag As Integer
'Global fileName As String
'Global probList(50), probDisc(50) As String
Global probProgressNumber As Integer

Global isOn(0 To 3) As Integer
Global newProblemFlag As Integer
Global currentPath As String
'Global HintFlag As Integer
'Global hintProgress As Integer ' true if you have reached a point where a new hint
window needs to be shown.
'Global hintNumber, HintMax As Integer
'Global HintText(1 To 50) As String
'Global DoThisText(1 To 50) As String
'Global HintCommand(1 To 50) As Integer

'Global flashState1, flashState2, flashState3, flashState4 As Integer
'Global OnSwitchForArrow(0 To NUMBEROFARROWS) As Integer

'make all forms modal!

Static Function almostSameThing (dummy1 As betweenTheParenthesis, dummy2 As
betweenTheParenthesis) As Integer
Dim foundADifference As Integer
    foundADifference = False

    If sci(dummy1.d.num, dummy1.d.sigfig) <> sci(dummy2.d.num, dummy2.d.sigfig) Then
foundADifference = True
    If dummy1.n.unit <> dummy2.n.unit Then foundADifference = True
    If dummy1.d.unit <> dummy2.d.unit Then foundADifference = True

    almostSameThing = Not (foundADifference)

End Function

Sub InitIt ()
    'currentPath = app.path
    currentPath = "C:\da\dapsic"
End Sub

Static Sub initNullFactor ()
    nullFactor.n.num = 1
    nullFactor.n.sigfig = 9
    nullFactor.n.unit = " "
    nullFactor.n.unitCanceled = False
    nullFactor.n.stuff = " "
    nullFactor.n.stuffCanceled = False

    nullFactor.d = nullFactor.n

```

```

End Sub

Static Sub InitStartingPoint ()
Dim i As Integer
    i = readFromFile()
    NumberFactorsSoFar = 0
End Sub

Static Sub InitStudentAnswer ()
    studentAnswer = nullFactor
End Sub

Static Sub InitUnitFactor ()
Dim i As Integer
    For i = 1 To 13
        unitfactor(i) = nullFactor
    Next i
End Sub

Sub logit (dummy As String)

' drivechange
'   Open "a:logfile.txt" For Append As #3
'   Open "b:logfile.txt" For Append As #3
    Open currentPath & "\logfile.txt" For Append As #3

    Print #3, dummy & Time$
    Close #3
End Sub

Static Function readFromFile () As Integer
Dim dummyFactor As betweenTheParenthesis
Dim dummy1 As String
Dim i As Integer
    If (Dir$(currentPath & FILENAME) = "") Then
        MsgBox "Unable to open file"
        readFromFile = False
    Else
        Open currentPath & FILENAME For Input As #1
        Line Input #1, dummy1
        Line Input #1, dummy1
        sigFigFlag = CInt(dummy1) / Abs(CInt(dummy1))
        If sigFigFlag = -1 Then sigFigFlag = False Else sigFigFlag = True
        LevelFlag = Abs(CInt(dummy1))
        Line Input #1, dummy1
        Line Input #1, dummy1
        ProblemText = dummy1
        Line Input #1, dummy1
        Line Input #1, dummy1
        numberOfGivenInfo = CInt(dummy1) - 2
        For i = 1 To numberOfGivenInfo + 2
            Line Input #1, dummy1
            dummyFactor = nullFactor
            Line Input #1, dummy1
            Line Input #1, dummy1
            keyPhrase(i) = dummy1
            Line Input #1, dummy1
            Line Input #1, dummy1
            dummyFactor.n.num = CDb1(dummy1)
            Line Input #1, dummy1
            Line Input #1, dummy1
            dummyFactor.n.sigfig = CInt(dummy1)
            dummyFactor.n.exp = 0
            Line Input #1, dummy1
            Line Input #1, dummy1
            dummyFactor.n.unit = dummy1 & " "
            dummyFactor.n.unitCanceled = False
        Next i
    End If
End Function

```

```

        Line Input #1, dummy1
        Line Input #1, dummy1
        dummyFactor.n.stuff = dummy1 & " "
        dummyFactor.n.stuffCanceled = False
        Line Input #1, dummy1
        Line Input #1, dummy1
        dummyFactor.d.num = CDBl(dummy1)
        Line Input #1, dummy1
        Line Input #1, dummy1
        dummyFactor.d.sigfig = CInt(dummy1)
        dummyFactor.d.exp = 0
        Line Input #1, dummy1
        Line Input #1, dummy1
        dummyFactor.d.unit = dummy1 & " "
        dummyFactor.d.unitCanceled = False
        Line Input #1, dummy1
        Line Input #1, dummy1
        dummyFactor.d.stuff = dummy1 & " "
        dummyFactor.d.stuffCanceled = False
        If i = 1 Then correctAnswer = dummyFactor
        If i = 2 Then StartingPoint = dummyFactor
        If i > 2 Then givenInfo(i - 2) = dummyFactor
    Next i
    Close #1
    readFromFile = True
End If
End Function

Static Function sameThing (dummy1 As betweenTheParenthesis, dummy2 As
betweenTheParenthesis) As Integer
Dim foundADifference As Integer
    foundADifference = False

    If sci(dummy1.n.num, dummy1.n.sigfig) <> sci(dummy2.n.num, dummy2.n.sigfig) Then
foundADifference = True
    If sci(dummy1.d.num, dummy1.d.sigfig) <> sci(dummy2.d.num, dummy2.d.sigfig) Then
foundADifference = True
    If dummy1.n.unit <> dummy2.n.unit Then foundADifference = True
    If dummy1.d.unit <> dummy2.d.unit Then foundADifference = True

    sameThing = Not (foundADifference)

End Function

Static Function sci (dummy As Double, dummy2 As Integer) As String
Dim num1, num3 As Double, expl As Integer, sigFig1 As Integer
Dim num2, num4, num5 As Long, dummySci, dummySci1 As String
Dim mustShowSciFlag As Integer
Dim calculatorLength As Integer
If dummy = 0 Then
    sci = "zero!"
Else
    mustShowSciFlag = False
    num1 = dummy
    expl = 0
    sigFig1 = dummy2
    If sigFig1 > 9 Then sigFig1 = 9
    Do While num1 >= 10
        num1 = num1 / 10
        expl = expl + 1
    Loop
    Do While num1 < 1
        num1 = num1 * 10
        expl = expl - 1
    Loop
    If sigFig1 > 8 Then
        'sigFig1 = 9
        dummySci = CStr(dummy)

```

```

        If InStr(dummySci, "E") <> 0 Then
            calculatorLength = InStr(dummySci, "E") - 1
            If calculatorLength > 9 Then calculatorLength = 9
            dummySci1 = Left$(dummySci, calculatorLength) & "x10^"
            dummySci1 = dummySci1 & Right$(dummySci, Len(dummySci) - InStr(dummySci,
"E"))
            dummySci = dummySci1
        End If
        sci = dummySci
    Else
        If sigFig1 > 0 Then
            num1 = num1 * (10 ^ (sigFig1 - 1))
            num2 = CLng(num1)
            num5 = Fix(num1)
            If Len(CStr(num2)) > Len(CStr(num5)) Then
                num2 = num2 \ 10
                expl = expl + 1
            End If
            num3 = num2 / (10 ^ (sigFig1 - 1)) * (10 ^ expl)
            dummySci = CStr(num1)
            If (expl < 4) And (expl > -3) And (Right(dummySci, 1) <> "0") And
(Len(dummySci) < sigFig1) Then
                num1 = num2 / (10 ^ (sigFig1 - 1)) * (10 ^ expl)
                sci = CStr(num1)
            Else
                dummySci = CStr(num2)
                dummySci1 = Left$(dummySci, 1)
                If Len(dummySci) > 1 Then
                    dummySci1 = dummySci1 & "."
                    dummySci1 = dummySci1 & Right$(dummySci, Len(dummySci) - 1)
                End If
                If expl <> 0 Then
                    dummySci1 = dummySci1 & "x10^"
                    dummySci1 = dummySci1 & CStr(expl)
                End If
                sci = dummySci1
            End If
        Else
            sci = "!!Error!!"
        End If
    End If
End If

' revise this to handle negative numbers!
End Function

Static Function squish (dummy1 As Double) As Double
Dim dummyString As String
Dim dummy2 As Double

    dummyString = CStr(dummy1)
    dummy2 = CDbl(dummyString)
    squish = dummy2
End Function

```

FILE: INTERN.FRM

VERSION 2.00

Begin Form Form1

```

BackColor      = &H00E0FFFF&
Caption        = "DAPSIC, main window"
ClientHeight   = 4860
ClientLeft     = 60
ClientTop      = 360
ClientWidth    = 9495
ControlBox     = 0 'False

```

```

Height      = 5265
Left        = 0
LinkTopic   = "Form1"
MaxButton   = 0 'False
MinButton   = 0 'False
ScaleHeight = 4860
ScaleWidth  = 9495
Top         = 15
Width       = 9615
Begin ListBox LstSigFig
  Height      = 420
  Left        = 6840
  TabIndex    = 37
  Top         = 300
  Width       = 1695
End
Begin CommandButton cmdQuit
  Caption     = "Quit"
  Height      = 795
  Left        = 8640
  TabIndex    = 21
  Top         = 60
  Width       = 675
End
Begin CommandButton cmdUndo
  Caption     = "Undo change"
  Height      = 375
  Left        = 3360
  TabIndex    = 20
  Top         = 60
  Width       = 1695
End
Begin CommandButton cmdCheckAnswer
  Caption     = "Check answer"
  Height      = 375
  Left        = 3360
  TabIndex    = 19
  Top         = 480
  Width       = 1695
End
Begin CommandButton cmdMultiply
  Caption     = "Multiply"
  Height      = 375
  Left        = 1740
  TabIndex    = 17
  Top         = 480
  Width       = 1575
End
Begin CommandButton cmdCancelUnits
  Caption     = "Cancel units"
  Height      = 375
  Left        = 1740
  TabIndex    = 11
  Top         = 60
  Width       = 1575
End
Begin CommandButton cmdGetFactor
  Caption     = "Get Unit Factor"
  Height      = 375
  Left        = 120
  TabIndex    = 4
  Top         = 480
  Width       = 1575
End
Begin CommandButton cmdNewProblem
  Caption     = "Start over again"
  Height      = 375
  Left        = 120

```

```

        TabIndex      = 0
        Top           = 60
        Width         = 1575
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to NINE significant digits.)"
        Height         = 615
        Index          = 9
        Left           = 6120
        TabIndex       = 84
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to EIGHT significant digits.)"
        Height         = 615
        Index          = 8
        Left           = 6120
        TabIndex       = 92
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to SEVEN significant digits.)"
        Height         = 615
        Index          = 7
        Left           = 6120
        TabIndex       = 91
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to SIX significant digits.)"
        Height         = 615
        Index          = 6
        Left           = 6120
        TabIndex       = 90
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to FIVE significant digits.)"
        Height         = 615
        Index          = 5
        Left           = 6120
        TabIndex       = 89
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to FOUR significant digits.)"
        Height         = 615
        Index          = 4
        Left           = 6120
        TabIndex       = 88
        Top            = 300
        Width          = 2415
    End
    Begin Label lblSigIdent
        BackStyle      = 0 'Transparent
        Caption        = "(Answer rounded to THREE significant digits.)"
        Height         = 615

```

```

        Index      = 3
        Left       = 6120
        TabIndex   = 87
        Top        = 300
        Width      = 2415
    End
    Begin Label lblSigIdent
        BackStyle   = 0 'Transparent
        Caption     = "(Answer rounded to TWO significant digits.)"
        Height      = 615
        Index       = 2
        Left        = 6120
        TabIndex    = 86
        Top         = 300
        Width       = 2415
    End
    Begin Label lblSigIdent
        BackStyle   = 0 'Transparent
        Caption     = "(Answer rounded to ONE significant digit.)"
        Height      = 615
        Index       = 1
        Left        = 6120
        TabIndex    = 85
        Top         = 300
        Width       = 2415
    End
    Begin Line Line6
        Index      = 3
        X1         = 6960
        X2         = 9420
        Y1         = 4500
        Y2         = 4500
    End
    Begin Line Line6
        Index      = 2
        X1         = 6960
        X2         = 9420
        Y1         = 3900
        Y2         = 3900
    End
    Begin Line Line6
        Index      = 1
        X1         = 6960
        X2         = 9420
        Y1         = 3300
        Y2         = 3300
    End
    Begin Line Line5
        Index      = 3
        X1         = 4320
        X2         = 6780
        Y1         = 4500
        Y2         = 4500
    End
    Begin Line Line5
        Index      = 2
        X1         = 4320
        X2         = 6780
        Y1         = 3900
        Y2         = 3900
    End
    Begin Line Line5
        Index      = 1
        X1         = 4320
        X2         = 6780
        Y1         = 3300
        Y2         = 3300
    End
End

```



```

Begin Line Line3
  Index      = 3
  X1         = 1680
  X2         = 4140
  Y1         = 4500
  Y2         = 4500
End
Begin Line Line3
  Index      = 2
  X1         = 1680
  X2         = 4140
  Y1         = 3900
  Y2         = 3900
End
Begin Line Line3
  Index      = 1
  X1         = 1680
  X2         = 4140
  Y1         = 3300
  Y2         = 3300
End
Begin Label lblUnit
  BackStyle  = 0 'Transparent
  Caption    = "mmol NH4C2H3O2"
  FontBold   = 0 'False
  FontItalic = 0 'False
  FontName   = "Small Fonts"
  FontSize   = 6
  FontStrikethru = 0 'False
  FontUnderline = 0 'False
  Height     = 195
  Index      = 29
  Left       = 8220
  TabIndex   = 42
  Top        = 4560
  Width      = 1095
End
Begin Label lblUnit
  BackStyle  = 0 'Transparent
  Caption    = "mmol NH4C2H3O2"
  FontBold   = 0 'False
  FontItalic = 0 'False
  FontName   = "Small Fonts"
  FontSize   = 6
  FontStrikethru = 0 'False
  FontUnderline = 0 'False
  Height     = 195
  Index      = 28
  Left       = 8220
  TabIndex   = 43
  Top        = 4260
  Width      = 1095
End
Begin Label lblNum
  Alignment  = 1 'Right Justify
  BackStyle  = 0 'Transparent
  Caption    = "1.23456789E-04"
  FontBold   = 0 'False
  FontItalic = 0 'False
  FontName   = "Small Fonts"
  FontSize   = 6
  FontStrikethru = 0 'False
  FontUnderline = 0 'False
  Height     = 195
  Index      = 29
  Left       = 7080
  TabIndex   = 44
  Top        = 4560

```

```

        Width          = 1035
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle        = 0 'Transparent
        Caption          = "1.23456789E-04"
        FontBold         = 0 'False
        FontItalic        = 0 'False
        FontName          = "Small Fonts"
        FontSize          = 6
        FontStrikethru    = 0 'False
        FontUnderline     = 0 'False
        Height           = 195
        Index            = 28
        Left              = 7080
        TabIndex          = 45
        Top               = 4260
        Width            = 1035
    End
    Begin Label lblUnit
        BackStyle        = 0 'Transparent
        Caption          = "mmol NH4C2H3O2"
        FontBold         = 0 'False
        FontItalic        = 0 'False
        FontName          = "Small Fonts"
        FontSize          = 6
        FontStrikethru    = 0 'False
        FontUnderline     = 0 'False
        Height           = 195
        Index            = 27
        Left              = 5580
        TabIndex          = 46
        Top               = 4560
        Width            = 1095
    End
    Begin Label lblUnit
        BackStyle        = 0 'Transparent
        Caption          = "mmol NH4C2H3O2"
        FontBold         = 0 'False
        FontItalic        = 0 'False
        FontName          = "Small Fonts"
        FontSize          = 6
        FontStrikethru    = 0 'False
        FontUnderline     = 0 'False
        Height           = 195
        Index            = 26
        Left              = 5580
        TabIndex          = 47
        Top               = 4260
        Width            = 1095
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle        = 0 'Transparent
        Caption          = "1.23456789E-04"
        FontBold         = 0 'False
        FontItalic        = 0 'False
        FontName          = "Small Fonts"
        FontSize          = 6
        FontStrikethru    = 0 'False
        FontUnderline     = 0 'False
        Height           = 195
        Index            = 27
        Left              = 4440
        TabIndex          = 48
        Top               = 4560
        Width            = 1035
    End
End

```

```

Begin Label lblNum
  Alignment      = 1 'Right Justify
  BackStyle      = 0 'Transparent
  Caption        = "1.23456789E-04"
  FontBold       = 0 'False
  FontItalic     = 0 'False
  FontName       = "Small Fonts"
  FontSize       = 6
  FontStrikethru = 0 'False
  FontUnderline  = 0 'False
  Height         = 195
  Index          = 26
  Left           = 4440
  TabIndex       = 49
  Top            = 4260
  Width          = 1035
End
Begin Label lblUnit
  BackStyle      = 0 'Transparent
  Caption        = "mmol NH4C2H3O2"
  FontBold       = 0 'False
  FontItalic     = 0 'False
  FontName       = "Small Fonts"
  FontSize       = 6
  FontStrikethru = 0 'False
  FontUnderline  = 0 'False
  Height         = 195
  Index          = 25
  Left           = 2940
  TabIndex       = 50
  Top            = 4560
  Width          = 1095
End
Begin Label lblUnit
  BackStyle      = 0 'Transparent
  Caption        = "mmol NH4C2H3O2"
  FontBold       = 0 'False
  FontItalic     = 0 'False
  FontName       = "Small Fonts"
  FontSize       = 6
  FontStrikethru = 0 'False
  FontUnderline  = 0 'False
  Height         = 195
  Index          = 24
  Left           = 2940
  TabIndex       = 51
  Top            = 4260
  Width          = 1095
End
Begin Label lblNum
  Alignment      = 1 'Right Justify
  BackStyle      = 0 'Transparent
  Caption        = "1.23456789E-04"
  FontBold       = 0 'False
  FontItalic     = 0 'False
  FontName       = "Small Fonts"
  FontSize       = 6
  FontStrikethru = 0 'False
  FontUnderline  = 0 'False
  Height         = 195
  Index          = 25
  Left           = 1800
  TabIndex       = 52
  Top            = 4560
  Width          = 1035
End
Begin Label lblNum
  Alignment      = 1 'Right Justify

```

```

BackStyle      = 0 'Transparent
Caption        = "1.23456789E-04"
FontBold       = 0 'False
FontItalic     = 0 'False
FontName       = "Small Fonts"
FontSize       = 6
FontStrikethru = 0 'False
FontUnderline  = 0 'False
Height         = 195
Index          = 24
Left           = 1800
TabIndex       = 53
Top            = 4260
Width          = 1035
End
Begin Label lblUnit
BackStyle      = 0 'Transparent
Caption        = "mmol NH4C2H3O2"
FontBold       = 0 'False
FontItalic     = 0 'False
FontName       = "Small Fonts"
FontSize       = 6
FontStrikethru = 0 'False
FontUnderline  = 0 'False
Height         = 195
Index          = 23
Left           = 8220
TabIndex       = 57
Top            = 3960
Width          = 1095
End
Begin Label lblUnit
BackStyle      = 0 'Transparent
Caption        = "mmol NH4C2H3O2"
FontBold       = 0 'False
FontItalic     = 0 'False
FontName       = "Small Fonts"
FontSize       = 6
FontStrikethru = 0 'False
FontUnderline  = 0 'False
Height         = 195
Index          = 22
Left           = 8220
TabIndex       = 58
Top            = 3660
Width          = 1095
End
Begin Label lblNum
Alignment      = 1 'Right Justify
BackStyle      = 0 'Transparent
Caption        = "1.23456789E-04"
FontBold       = 0 'False
FontItalic     = 0 'False
FontName       = "Small Fonts"
FontSize       = 6
FontStrikethru = 0 'False
FontUnderline  = 0 'False
Height         = 195
Index          = 23
Left           = 7080
TabIndex       = 59
Top            = 3960
Width          = 1035
End
Begin Label lblNum
Alignment      = 1 'Right Justify
BackStyle      = 0 'Transparent
Caption        = "1.23456789E-04"

```

```

FontBold      = 0  'False
FontItalic    = 0  'False
FontName      = "Small Fonts"
FontSize      = 6
FontStrikethru = 0  'False
FontUnderline = 0  'False
Height        = 195
Index         = 22
Left          = 7080
TabIndex      = 60
Top           = 3660
Width         = 1035
End
Begin Label lblUnit
  BackStyle    = 0  'Transparent
  Caption      = "mmol NH4C2H3O2"
  FontBold     = 0  'False
  FontItalic   = 0  'False
  FontName     = "Small Fonts"
  FontSize     = 6
  FontStrikethru = 0  'False
  FontUnderline = 0  'False
  Height       = 195
  Index        = 21
  Left         = 5580
  TabIndex     = 61
  Top          = 3960
  Width        = 1095
End
Begin Label lblUnit
  BackStyle    = 0  'Transparent
  Caption      = "mmol NH4C2H3O2"
  FontBold     = 0  'False
  FontItalic   = 0  'False
  FontName     = "Small Fonts"
  FontSize     = 6
  FontStrikethru = 0  'False
  FontUnderline = 0  'False
  Height       = 195
  Index        = 20
  Left         = 5580
  TabIndex     = 62
  Top          = 3660
  Width        = 1095
End
Begin Label lblNum
  Alignment    = 1  'Right Justify
  BackStyle    = 0  'Transparent
  Caption      = "1.23456789E-04"
  FontBold     = 0  'False
  FontItalic   = 0  'False
  FontName     = "Small Fonts"
  FontSize     = 6
  FontStrikethru = 0  'False
  FontUnderline = 0  'False
  Height       = 195
  Index        = 21
  Left         = 4440
  TabIndex     = 63
  Top          = 3960
  Width        = 1035
End
Begin Label lblNum
  Alignment    = 1  'Right Justify
  BackStyle    = 0  'Transparent
  Caption      = "1.23456789E-04"
  FontBold     = 0  'False
  FontItalic   = 0  'False

```

```

    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 20
    Left          = 4440
    TabIndex      = 64
    Top           = 3660
    Width         = 1035
End
Begin Label lblUnit
    BackStyle     = 0 'Transparent
    Caption       = "mmol NH4C2H3O2"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 19
    Left          = 2940
    TabIndex      = 65
    Top           = 3960
    Width         = 1095
End
Begin Label lblUnit
    BackStyle     = 0 'Transparent
    Caption       = "mmol NH4C2H3O2"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 18
    Left          = 2940
    TabIndex      = 66
    Top           = 3660
    Width         = 1095
End
Begin Label lblNum
    Alignment     = 1 'Right Justify
    BackStyle     = 0 'Transparent
    Caption       = "1.23456789E-04"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 19
    Left          = 1800
    TabIndex      = 67
    Top           = 3960
    Width         = 1035
End
Begin Label lblNum
    Alignment     = 1 'Right Justify
    BackStyle     = 0 'Transparent
    Caption       = "1.23456789E-04"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6

```

```

    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 18
    Left           = 1800
    TabIndex       = 68
    Top            = 3660
    Width          = 1035
End
Begin Label lblUnit
    BackStyle      = 0 'Transparent
    Caption        = "mmol NH4C2H3O2"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 17
    Left           = 8220
    TabIndex       = 72
    Top            = 3360
    Width          = 1095
End
Begin Label lblUnit
    BackStyle      = 0 'Transparent
    Caption        = "mmol NH4C2H3O2"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 16
    Left           = 8220
    TabIndex       = 73
    Top            = 3060
    Width          = 1095
End
Begin Label lblNum
    Alignment      = 1 'Right Justify
    BackStyle      = 0 'Transparent
    Caption        = "1.23456789E-04"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 17
    Left           = 7080
    TabIndex       = 74
    Top            = 3360
    Width          = 1035
End
Begin Label lblNum
    Alignment      = 1 'Right Justify
    BackStyle      = 0 'Transparent
    Caption        = "1.23456789E-04"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False

```

```

        Height      = 195
        Index       = 16
        Left        = 7080
        TabIndex    = 75
        Top         = 3060
        Width       = 1035
    End
    Begin Label lblUnit
        BackStyle    = 0 'Transparent
        Caption      = "mmol NH4C2H3O2"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height      = 195
        Index       = 15
        Left        = 5580
        TabIndex    = 76
        Top         = 3360
        Width       = 1095
    End
    Begin Label lblUnit
        BackStyle    = 0 'Transparent
        Caption      = "mmol NH4C2H3O2"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height      = 195
        Index       = 14
        Left        = 5580
        TabIndex    = 77
        Top         = 3060
        Width       = 1095
    End
    Begin Label lblNum
        Alignment    = 1 'Right Justify
        BackStyle    = 0 'Transparent
        Caption      = "1.23456789E-04"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height      = 195
        Index       = 15
        Left        = 4440
        TabIndex    = 78
        Top         = 3360
        Width       = 1035
    End
    Begin Label lblNum
        Alignment    = 1 'Right Justify
        BackStyle    = 0 'Transparent
        Caption      = "1.23456789E-04"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height      = 195
        Index       = 14

```



```

        Left          = 4440
        TabIndex      = 79
        Top           = 3060
        Width         = 1035
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption        = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height         = 195
        Index          = 12
        Left           = 2940
        TabIndex       = 80
        Top            = 3060
        Width          = 1095
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption        = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height         = 195
        Index          = 13
        Left           = 2940
        TabIndex       = 81
        Top            = 3360
        Width          = 1095
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle       = 0 'Transparent
        Caption         = "1.23456789E-04"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height         = 195
        Index          = 12
        Left           = 1800
        TabIndex       = 82
        Top            = 3060
        Width          = 1035
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle       = 0 'Transparent
        Caption         = "1.23456789E-04"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height         = 195
        Index          = 13
        Left           = 1800
        TabIndex       = 83

```

```

        Top          = 3360
        Width        = 1035
    End
    Begin Label Label13
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 3
        Left          = 1500
        TabIndex      = 71
        Top           = 4380
        Width         = 135
    End
    Begin Label Label14
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 3
        Left          = 4140
        TabIndex      = 70
        Top           = 4380
        Width         = 135
    End
    Begin Label Label15
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 3
        Left          = 6780
        TabIndex      = 69
        Top           = 4380
        Width         = 135
    End
    Begin Label Label13
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 2
        Left          = 1500
        TabIndex      = 56
        Top           = 3780
        Width         = 135
    End
    Begin Label Label14
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 2
        Left          = 4140
        TabIndex      = 55
        Top           = 3840
        Width         = 135
    End
    Begin Label Label15
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 2
        Left          = 6780
        TabIndex      = 54
        Top           = 3780
        Width         = 135
    End
    Begin Label Label13
        BackStyle     = 0 'Transparent
        Caption       = "X"
        Height        = 255
        Index         = 1

```

```

        Left          = 1500
        TabIndex      = 41
        Top           = 3180
        Width         = 135
    End
    Begin Label Label4
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Index          = 1
        Left           = 4140
        TabIndex       = 40
        Top            = 3180
        Width          = 135
    End
    Begin Label Label5
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Index          = 1
        Left           = 6780
        TabIndex       = 39
        Top            = 3180
        Width          = 135
    End
    Begin Label Label6
        Caption        = "Significant Digits:"
        Height         = 255
        Left           = 6840
        TabIndex       = 38
        Top            = 60
        Width          = 1695
    End
    Begin Label Label5
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Index          = 0
        Left           = 6780
        TabIndex       = 36
        Top            = 2580
        Width          = 135
    End
    Begin Label Label4
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Index          = 0
        Left           = 4140
        TabIndex       = 35
        Top            = 2580
        Width          = 135
    End
    Begin Label Label3
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Index          = 0
        Left           = 1500
        TabIndex       = 34
        Top            = 2580
        Width          = 135
    End
    Begin Label Label2
        BackStyle      = 0 'Transparent
        Caption        = "X"
        Height         = 255
        Left           = 5100

```

```

        TabIndex      = 33
        Top           = 1980
        Width         = 135
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption        = "mmol NH4C2H3O2"
        FontBold       = 0 'False
        FontItalic     = 0 'False
        FontName       = "Small Fonts"
        FontSize       = 6
        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height        = 195
        Index          = 11
        Left           = 8220
        TabIndex      = 1
        Top           = 2760
        Width         = 1095
    End
    Begin Line Line6
        Index          = 0
        X1             = 6960
        X2             = 9420
        Y1             = 2700
        Y2             = 2700
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption        = "mmol NH4C2H3O2"
        FontBold       = 0 'False
        FontItalic     = 0 'False
        FontName       = "Small Fonts"
        FontSize       = 6
        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height        = 195
        Index          = 10
        Left           = 8220
        TabIndex      = 2
        Top           = 2460
        Width         = 1095
    End
    Begin Label lblNum
        Alignment      = 1 'Right Justify
        BackStyle      = 0 'Transparent
        Caption        = "1.23456789E-04"
        FontBold       = 0 'False
        FontItalic     = 0 'False
        FontName       = "Small Fonts"
        FontSize       = 6
        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height        = 195
        Index          = 11
        Left           = 7080
        TabIndex      = 5
        Top           = 2760
        Width         = 1035
    End
    Begin Label lblNum
        Alignment      = 1 'Right Justify
        BackStyle      = 0 'Transparent
        Caption        = "1.23456789E-04"
        FontBold       = 0 'False
        FontItalic     = 0 'False
        FontName       = "Small Fonts"
        FontSize       = 6

```

```

    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 10
    Left           = 7080
    TabIndex       = 6
    Top            = 2460
    Width          = 1035
End
Begin Label lblUnit
    BackStyle      = 0 'Transparent
    Caption        = "mmol NH4C2H3O2"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 9
    Left           = 5580
    TabIndex       = 7
    Top            = 2760
    Width          = 1095
End
Begin Line Line5
    Index          = 0
    X1             = 4320
    X2             = 6780
    Y1             = 2700
    Y2             = 2700
End
Begin Label lblUnit
    BackStyle      = 0 'Transparent
    Caption        = "mmol NH4C2H3O2"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 8
    Left           = 5580
    TabIndex       = 8
    Top            = 2460
    Width          = 1095
End
Begin Label lblNum
    Alignment      = 1 'Right Justify
    BackStyle      = 0 'Transparent
    Caption        = "1.23456789E-04"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 9
    Left           = 4440
    TabIndex       = 9
    Top            = 2760
    Width          = 1035
End
Begin Label lblNum
    Alignment      = 1 'Right Justify
    BackStyle      = 0 'Transparent

```

```

Caption      = "1.23456789E-04"
FontBold     = 0   'False
FontItalic   = 0   'False
FontName     = "Small Fonts"
FontSize     = 6
FontStrikethru = 0   'False
FontUnderline = 0   'False
Height       = 195
Index        = 8
Left         = 4440
TabIndex     = 10
Top          = 2460
Width        = 1035
End
Begin Label lblUnit
  BackStyle   = 0   'Transparent
  Caption     = "mmol NH4C2H3O2"
  FontBold    = 0   'False
  FontItalic  = 0   'False
  FontName    = "Small Fonts"
  FontSize    = 6
  FontStrikethru = 0   'False
  FontUnderline = 0   'False
  Height      = 195
  Index       = 7
  Left        = 2940
  TabIndex    = 12
  Top         = 2760
  Width       = 1095
End
Begin Line Line3
  Index       = 0
  X1          = 1680
  X2          = 4140
  Y1          = 2700
  Y2          = 2700
End
Begin Label lblUnit
  BackStyle   = 0   'Transparent
  Caption     = "mmol NH4C2H3O2"
  FontBold    = 0   'False
  FontItalic  = 0   'False
  FontName    = "Small Fonts"
  FontSize    = 6
  FontStrikethru = 0   'False
  FontUnderline = 0   'False
  Height      = 195
  Index       = 6
  Left        = 2940
  TabIndex    = 13
  Top         = 2460
  Width       = 1095
End
Begin Label lblNum
  Alignment   = 1   'Right Justify
  BackStyle   = 0   'Transparent
  Caption     = "1.23456789E-04"
  FontBold    = 0   'False
  FontItalic  = 0   'False
  FontName    = "Small Fonts"
  FontSize    = 6
  FontStrikethru = 0   'False
  FontUnderline = 0   'False
  Height      = 195
  Index       = 7
  Left        = 1800
  TabIndex    = 14
  Top         = 2760

```

```

        Width          = 1035
End
Begin Label lblNum
    Alignment          = 1 'Right Justify
    BackStyle          = 0 'Transparent
    Caption             = "1.23456789E-04"
    FontBold           = 0 'False
    FontItalic         = 0 'False
    FontName            = "Small Fonts"
    FontSize           = 6
    FontStrikethru     = 0 'False
    FontUnderline      = 0 'False
    Height             = 195
    Index              = 6
    Left               = 1800
    TabIndex           = 15
    Top                = 2460
    Width              = 1035
End
Begin Label lblUnit
    BackStyle          = 0 'Transparent
    Caption             = "mmol NH4C2H3O2"
    FontBold           = 0 'False
    FontItalic         = 0 'False
    FontName            = "Small Fonts"
    FontSize           = 6
    FontStrikethru     = 0 'False
    FontUnderline      = 0 'False
    Height             = 195
    Index              = 5
    Left               = 6540
    TabIndex           = 16
    Top                = 2160
    Width              = 1095
End
Begin Line Line2
    X1                 = 5280
    X2                 = 7740
    Y1                 = 2100
    Y2                 = 2100
End
Begin Label lblUnit
    BackStyle          = 0 'Transparent
    Caption             = "mmol NH4C2H3O2"
    FontBold           = 0 'False
    FontItalic         = 0 'False
    FontName            = "Small Fonts"
    FontSize           = 6
    FontStrikethru     = 0 'False
    FontUnderline      = 0 'False
    Height             = 195
    Index              = 4
    Left               = 6540
    TabIndex           = 32
    Top                = 1860
    Width              = 1095
End
Begin Label lblNum
    Alignment          = 1 'Right Justify
    BackStyle          = 0 'Transparent
    Caption             = "1.23456789E-04"
    FontBold           = 0 'False
    FontItalic         = 0 'False
    FontName            = "Small Fonts"
    FontSize           = 6
    FontStrikethru     = 0 'False
    FontUnderline      = 0 'False
    Height             = 195

```

```

        Index          = 5
        Left           = 5400
        TabIndex       = 31
        Top            = 2160
        Width          = 1035
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle       = 0 'Transparent
        Caption         = "1.23456789E-04"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru   = 0 'False
        FontUnderline    = 0 'False
        Height          = 195
        Index           = 4
        Left            = 5400
        TabIndex       = 30
        Top             = 1860
        Width           = 1035
    End
    Begin Label lblUnit
        BackStyle       = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru   = 0 'False
        FontUnderline    = 0 'False
        Height          = 195
        Index           = 3
        Left            = 3840
        TabIndex       = 29
        Top             = 2160
        Width           = 1095
    End
    Begin Line Line1
        X1              = 2640
        X2              = 5100
        Y1              = 2100
        Y2              = 2100
    End
    Begin Label lblUnit
        BackStyle       = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru   = 0 'False
        FontUnderline    = 0 'False
        Height          = 195
        Index           = 2
        Left            = 3840
        TabIndex       = 28
        Top             = 1860
        Width           = 1095
    End
    Begin Label lblNum
        Alignment       = 1 'Right Justify
        BackStyle       = 0 'Transparent
        Caption         = "1.23456789E-04"
        FontBold        = 0 'False
        FontItalic      = 0 'False
        FontName        = "Small Fonts"

```



```

        FontSize      = 6
        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height         = 195
        Index          = 3
        Left           = 2760
        TabIndex       = 27
        Top            = 2160
        Width          = 1035
    End
    Begin Label lblNum
        Alignment      = 1 'Right Justify
        BackStyle       = 0 'Transparent
        Caption         = "1.23456789E-04"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height          = 195
        Index           = 2
        Left            = 2760
        TabIndex        = 26
        Top             = 1860
        Width           = 1035
    End
    Begin Label lblUnit
        BackStyle       = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height          = 195
        Index           = 0
        Left            = 1260
        TabIndex        = 25
        Top             = 1860
        Width           = 1095
    End
    Begin Line Line4
        X1              = 60
        X2              = 2460
        Y1              = 2100
        Y2              = 2100
    End
    Begin Label lblUnit
        BackStyle       = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height          = 195
        Index           = 1
        Left            = 1260
        TabIndex        = 24
        Top             = 2160
        Width           = 1095
    End
    Begin Label lblNum
        Alignment      = 1 'Right Justify
        BackStyle       = 0 'Transparent

```

```

Caption      = "1.23456789E-04"
FontBold     = 0 'False
FontItalic   = 0 'False
FontName     = "Small Fonts"
FontSize     = 6
FontStrikethru = 0 'False
FontUnderline = 0 'False
Height       = 195
Index        = 0
Left         = 120
TabIndex     = 23
Top          = 1860
Width        = 1035
End
Begin Label lblNum
Alignment    = 1 'Right Justify
BackStyle    = 0 'Transparent
Caption      = "1.23456789E-04"
FontBold     = 0 'False
FontItalic   = 0 'False
FontName     = "Small Fonts"
FontSize     = 6
FontStrikethru = 0 'False
FontUnderline = 0 'False
Height       = 195
Index        = 1
Left         = 120
TabIndex     = 22
Top          = 2160
Width        = 1035
End
Begin Label lblProblem
BorderStyle  = 1 'Fixed Single
ForeColor    = &H00FF0000&
Height       = 795
Left         = 120
TabIndex     = 18
Top          = 960
Width        = 9315
WordWrap     = -1 'True
End
Begin Label Label1
BackStyle    = 0 'Transparent
Caption      = "X"
Height       = 255
Left         = 2520
TabIndex     = 3
Top          = 1980
Width        = 135
End
End
Option Explicit

Sub cmdCancelUnits_Click ()
Static somethingCanceled As Integer
Static i As Integer
Static j As Integer

If numberFactorsSoFar > 0 Then
    somethingCanceled = False

' insert something checking for is it already canceled
For i = 1 To numberFactorsSoFar
    If (startingPoint.n.unit = unitFactor(i).d.unit) And
(startingPoint.n.unitCanceled = False) And (unitFactor(i).d.unitCanceled = False) Then
        startingPoint.n.unitCanceled = True
        unitFactor(i).d.unitCanceled = True
        somethingCanceled = True

```

```

        End If
        If (startingPoint.d.unit = unitFactor(i).n.unit) And
(startingPoint.d.unitCanceled = False) And (unitFactor(i).n.unitCanceled = False) Then
            startingPoint.d.unitCanceled = True
            unitFactor(i).n.unitCanceled = True
            somethingCanceled = True
        End If
    Next i

    If numberFactorsSoFar > 1 Then
        For i = 2 To numberFactorsSoFar
            For j = 1 To (numberFactorsSoFar - 1)
                If (unitFactor(j).n.unit = unitFactor(i).d.unit) And
(unitFactor(j).n.unitCanceled = False) And (unitFactor(i).d.unitCanceled = False) Then
                    unitFactor(j).n.unitCanceled = True
                    unitFactor(i).d.unitCanceled = True
                    somethingCanceled = True
                End If
                If (unitFactor(j).d.unit = unitFactor(i).n.unit) And
(unitFactor(j).d.unitCanceled = False) And (unitFactor(i).n.unitCanceled = False) Then
                    unitFactor(j).d.unitCanceled = True
                    unitFactor(i).n.unitCanceled = True
                    somethingCanceled = True
                End If
            Next j
        Next i
    End If

    If somethingCanceled = False Then
        MsgBox "Nothing Canceled. Check for possible error."
    Else
        studentAnswer = nullFactor
    End If
    ' Hintprogress?
    DisplayFactors
End If
If numberFactorsSoFar = 0 Then

    MsgBox "Give me something to cancel first, then I'll try to cancel it."
End If
'If HintFlag = True Then
'HintProgress = False
'timer1.Enabled = True
'End If
End Sub

Sub cmdCheckAnswer_Click ()
    If sameThing(studentAnswer, correctAnswer) = True Then
        frmSubstance.lstSub.Clear
        logit ("Completed")
        MsgBox "Good job!"
        End
    Else
        If sameThing(studentAnswer, nullFactor) = True Then
            MsgBox "Multiply it out first, then check."
        Else
            If almostSameThing(studentAnswer, correctAnswer) = True Then MsgBox "Almost.
Check your significant digits!" Else MsgBox "No. Keep trying."
        End If
    End If
End Sub

Sub cmdGetFactor_Click ()
    unitFindingStage = 0
    currentFactor = nullFactor
    If numberFactorsSoFar >= 13 Then
        MsgBox "Sorry, you have exceeded the limits of this program. Try clicking 'Undo'
to remove unneeded unit factors."
    End If
End Sub

```

```

Else
    form2.Show 1
    If Not (sameThing(currentFactor, nullFactor)) Then
        numberFactorsSoFar = numberFactorsSoFar + 1
        unitFactor(numberFactorsSoFar) = currentFactor
        studentAnswer = nullFactor
    End If
End If
'HintProgress????
DisplayFactors

End Sub

Sub cmdMultiply_click ()
Static dummyString As String
Static i As Integer
    studentAnswer.n.sigfig = 9
    studentAnswer.d.num = 1
    studentAnswer.n.num = startingPoint.n.num / startingPoint.d.num
    'If startingPoint.n.sigFig < studentAnswer.n.sigFig Then studentAnswer.n.sigFig =
startingPoint.n.sigFig
    'If startingPoint.d.sigFig < studentAnswer.n.sigFig Then studentAnswer.n.sigFig =
startingPoint.d.sigFig

    If numberFactorsSoFar > 0 Then
        For i = 1 To numberFactorsSoFar
            studentAnswer.n.num = studentAnswer.n.num * unitFactor(i).n.num /
unitFactor(i).d.num
            'If unitFactor(i).n.sigFig < studentAnswer.n.sigFig Then
studentAnswer.n.sigFig = unitFactor(i).n.sigFig
            'If unitFactor(i).d.sigFig < studentAnswer.n.sigFig Then
studentAnswer.n.sigFig = unitFactor(i).d.sigFig
        Next i
    End If

    dummyString = ""
    If startingPoint.n.unitCanceled = False Then dummyString = dummyString &
startingPoint.n.unit
    If numberFactorsSoFar > 0 Then
        For i = 1 To numberFactorsSoFar
            If unitFactor(i).n.unitCanceled = False Then dummyString = dummyString &
unitFactor(i).n.unit
        Next i
    End If
    studentAnswer.n.unit = dummyString

    dummyString = ""
    If startingPoint.d.unitCanceled = False Then dummyString = dummyString &
startingPoint.d.unit
    If numberFactorsSoFar > 0 Then
        For i = 1 To numberFactorsSoFar
            If unitFactor(i).d.unitCanceled = False Then dummyString = dummyString &
unitFactor(i).d.unit
        Next i
    End If
    studentAnswer.d.unit = dummyString
    If sigFigFlag = True Then
        studentAnswer.n.sigfig = 1stSigFig.ListIndex
    Else
        studentAnswer.n.sigfig = correctAnswer.n.sigfig
    End If
    If studentAnswer.n.sigfig = 0 Then studentAnswer.n.sigfig = 9
    ' Hintprogress????
    DisplayFactors
    'If HintFlag = True Then
        'HintProgress = False
        'timer1.Enabled = True

```

```

'End If
End Sub

Sub cmdNewProblem_click ()
    initNullFactor
    InitStartingPoint
    InitUnitFactor
    InitStudentAnswer
    updateSigFig
    DisplayFactors
End Sub

Sub cmdQuit_Click ()
    logit ("Exit")
End
End Sub

Sub cmdUndo_Click ()
    Static i As Integer
    Static foundOne As Integer

    If numberFactorsSoFar > 0 Then
        If unitFactor(numberFactorsSoFar).n.unitCanceled = True Then
            If (startingPoint.d.unit = unitFactor(numberFactorsSoFar).n.unit) And
                (startingPoint.d.unitCanceled = True) Then
                startingPoint.d.unitCanceled = False
            Else
                If numberFactorsSoFar > 1 Then
                    foundOne = False
                    i = 0
                    Do
                        i = i + 1
                        If (unitFactor(i).d.unit = unitFactor(numberFactorsSoFar).n.unit)
                            And (unitFactor(i).d.unitCanceled = True) Then
                            unitFactor(i).d.unitCanceled = False
                            foundOne = True
                        End If
                    Loop Until (foundOne = True) Or (i = (numberFactorsSoFar - 1))
                End If
            End If
        End If
        If unitFactor(numberFactorsSoFar).d.unitCanceled = True Then
            If (startingPoint.n.unit = unitFactor(numberFactorsSoFar).d.unit) And
                (startingPoint.n.unitCanceled = True) Then
                startingPoint.n.unitCanceled = False
            Else
                If numberFactorsSoFar > 1 Then
                    foundOne = False
                    i = 0
                    Do
                        i = i + 1
                        If (unitFactor(i).n.unit = unitFactor(numberFactorsSoFar).d.unit)
                            And (unitFactor(i).n.unitCanceled = True) Then
                            unitFactor(i).n.unitCanceled = False
                            foundOne = True
                        End If
                    Loop Until (foundOne = True) Or (i = (numberFactorsSoFar - 1))
                End If
            End If
        End If

        unitFactor(numberFactorsSoFar) = nullFactor
        numberFactorsSoFar = numberFactorsSoFar - 1
        studentAnswer = nullFactor
        DisplayFactors
    End If
End Sub

```

```

Static Sub DisplayFactors ()
Dim i As Integer
Dim listFig As Integer
Dim ilimit As Integer
'MsgBox "#" & startingPoint.n.unit & "#"
If startingPoint.n.unit = " " Then lblNum(0).Caption = "" Else lblNum(0).Caption =
sci(startingPoint.n.num, startingPoint.n.sigfig)
lblUnit(0).Caption = startingPoint.n.unit
lblUnit(0).FontStrikethru = startingPoint.n.unitCanceled

If startingPoint.d.unit = " " Then lblNum(1).Caption = "" Else lblNum(1).Caption =
sci(startingPoint.d.num, startingPoint.d.sigfig)
lblUnit(1).Caption = startingPoint.d.unit
lblUnit(1).FontStrikethru = startingPoint.d.unitCanceled

If numberFactorsSoFar > 9 Then ilimit = 13
If numberFactorsSoFar < 10 Then ilimit = 10
If numberFactorsSoFar < 7 Then ilimit = 7
If numberFactorsSoFar < 4 Then ilimit = 4
showline ((ilimit - 4) \ 3)
For i = 1 To ilimit
If unitFactor(i).n.unit = " " Then lblNum(2 * i).Caption = "" Else lblNum(2 *
i).Caption = sci(unitFactor(i).n.num, unitFactor(i).n.sigfig)
lblUnit(2 * i).Caption = unitFactor(i).n.unit
lblUnit(2 * i).FontStrikethru = unitFactor(i).n.unitCanceled

If unitFactor(i).d.unit = " " Then lblNum(2 * i + 1).Caption = "" Else lblNum(2 *
i + 1).Caption = sci(unitFactor(i).d.num, unitFactor(i).d.sigfig)
lblUnit(2 * i + 1).Caption = unitFactor(i).d.unit
lblUnit(2 * i + 1).FontStrikethru = unitFactor(i).d.unitCanceled
Next i

If sigFigFlag = True Then
listFig = lstSigFig.ListIndex
Else
listFig = correctAnswer.n.sigfig
End If
If listFig = 0 Then listFig = 9
If studentAnswer.n.unit = " " Then lblNum((2 * ilimit) + 2).Caption = "" Else
lblNum((2 * ilimit) + 2).Caption = sci(studentAnswer.n.num, listFig)
lblUnit((2 * ilimit) + 2).Caption = studentAnswer.n.unit
lblUnit((2 * ilimit) + 2).FontStrikethru = studentAnswer.n.unitCanceled

If studentAnswer.d.unit = " " Then lblNum((2 * ilimit) + 3).Caption = "" Else
lblNum((2 * ilimit) + 3).Caption = sci(studentAnswer.d.num, 9)
lblUnit((2 * ilimit) + 3).Caption = studentAnswer.d.unit
lblUnit((2 * ilimit) + 3).FontStrikethru = studentAnswer.d.unitCanceled

lblProblem.Caption = problemText
HandleSigFig
'If SigFigFlag = False Then MsgBox "No Sig Fig"
'showHint
End Sub

Sub Form_Activate ()
If newProblemFlag = True Then
cmdNewProblem_click
newProblemFlag = False
End If
DisplayFactors
End Sub

Sub Form_Load ()
InitIt
cmdNewProblem_click
End Sub

```

```

Sub HandleSigFig ()
Static visibleSigFig As Integer
    lblSigIdent(1).Visible = False
    lblSigIdent(2).Visible = False
    lblSigIdent(3).Visible = False
    lblSigIdent(4).Visible = False
    lblSigIdent(5).Visible = False
    lblSigIdent(6).Visible = False
    lblSigIdent(7).Visible = False
    lblSigIdent(8).Visible = False
    lblSigIdent(9).Visible = False

    If sigFigFlag = True Then
        label6.Visible = True
        lstSigFig.Visible = True
    Else
        lstSigFig.Visible = False
        label6.Visible = False
        visibleSigFig = correctAnswer.n.sigfig
        If visibleSigFig < 1 Or visibleSigFig > 9 Then visibleSigFig = 9
        lblSigIdent(visibleSigFig).Visible = True

    End If
End Sub

Sub LstSigFig_Click ()
    cmdMultiply_click
End Sub

Static Sub showline (dummy As Integer)
Dim i As Integer
    For i = 0 To 3
        If i = dummy Then label5(i).Caption = "=" Else label5(i).Caption = "X"
        If i > dummy Then isOn(i) = False Else isOn(i) = True
        label3(i).Visible = isOn(i)
        label4(i).Visible = isOn(i)
        label5(i).Visible = isOn(i)
        line3(i).Visible = isOn(i)
        line5(i).Visible = isOn(i)
        line6(i).Visible = isOn(i)
    Next i
    For i = 6 To 11
        lblNum(i).Visible = isOn(0)
        lblUnit(i).Visible = isOn(0)
    Next i
    For i = 12 To 17
        lblNum(i).Visible = isOn(1)
        lblUnit(i).Visible = isOn(1)
    Next i
    For i = 18 To 23
        lblNum(i).Visible = isOn(2)
        lblUnit(i).Visible = isOn(2)
    Next i
    For i = 24 To 29
        lblNum(i).Visible = isOn(3)
        lblUnit(i).Visible = isOn(3)
    Next i

End Sub

Static Sub updateSigFig ()
    lstSigFig.Clear
    lstSigFig.AddItem "(exact)"
    lstSigFig.AddItem "1"
    lstSigFig.AddItem "2"
    lstSigFig.AddItem "3"

```

```

    lstSigFig.AddItem "4"
    lstSigFig.AddItem "5"
    lstSigFig.AddItem "6"
    lstSigFig.AddItem "7"
    lstSigFig.ListIndex = 0
End Sub

```

FILE: INTERN2.FRM

VERSION 2.00

```

Begin Form Form2
    BackColor      = &H00C0E0FF&
    Caption        = "DAPSIC, unit factors"
    ClientHeight   = 2835
    ClientLeft     = 120
    ClientTop      = 4335
    ClientWidth    = 9330
    ControlBox     = 0 'False
    Height         = 3240
    Left           = 60
    LinkTopic      = "Form2"
    MaxButton      = 0 'False
    MinButton      = 0 'False
    ScaleHeight    = 2835
    ScaleWidth     = 9330
    Top            = 3990
    Width          = 9450
    Begin CommandButton cmdFormShow
        Caption      = "Density Table"
        Height       = 315
        Index        = 4
        Left         = 6720
        TabIndex     = 27
        Top          = 60
        Width        = 1815
    End
    Begin CommandButton cmdFormShow
        Caption      = "Info in problem text"
        Height       = 315
        Index        = 3
        Left         = 6720
        TabIndex     = 26
        Top          = 420
        Width        = 1815
    End
    Begin CommandButton cmdFormShow
        Caption      = "English- English"
        Height       = 315
        Index        = 2
        Left         = 4800
        TabIndex     = 25
        Top          = 420
        Width        = 1815
    End
    Begin CommandButton cmdFormShow
        Caption      = "Metric - Metric"
        Height       = 315
        Index        = 1
        Left         = 960
        TabIndex     = 24
        Top          = 420
        Width        = 1815
    End
    Begin CommandButton cmdFormShow
        Caption      = "Metric - English"
        Height       = 315

```



```

        Index          = 0
        Left           = 2880
        TabIndex       = 23
        Top            = 420
        Width          = 1815
    End
    Begin CommandButton cmdGoBack
        Caption         = "No"
        Height          = 315
        Left            = 8400
        TabIndex        = 0
        Top             = 1200
        Width           = 495
    End
    Begin CommandButton cmdContinue
        Caption         = "Yes"
        Height          = 315
        Left            = 7740
        TabIndex        = 17
        Top             = 1200
        Width           = 555
    End
    Begin CommandButton cmdCancel
        Caption         = "Cancel"
        Height          = 375
        Left            = 7080
        TabIndex        = 16
        Top             = 1920
        Width           = 1215
    End
    Begin CommandButton cmdOkay
        Caption         = "Okay"
        Height          = 375
        Left            = 7080
        TabIndex        = 15
        Top             = 2340
        Width           = 1215
    End
    Begin OptionButton Option1
        Caption         = "I like this one"
        Height          = 255
        Index           = 1
        Left            = 4620
        TabIndex        = 14
        Top             = 2520
        Width           = 1815
    End
    Begin OptionButton Option1
        Caption         = "I like this one"
        Height          = 255
        Index           = 0
        Left            = 1140
        TabIndex        = 13
        Top             = 2520
        Width           = 1815
    End
    Begin Label Label5
        BackStyle       = 0 'Transparent
        Caption         = "Click on the type of identity you wish to find:"
        Height          = 195
        Left            = 960
        TabIndex        = 22
        Top             = 120
        Width           = 4215
    End
    Begin Line Line4
        X1              = 120
        X2              = 9180

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        Y1          = 780
        Y2          = 780
    End
    Begin Line Line1
        X1          = 120
        X2          = 9180
        Y1          = 1560
        Y2          = 1560
    End
    Begin Label Label4
        BackStyle    = 0 'Transparent
        Caption      = "You now have two different choices of conversion factors.
Select the one you wish to use:"
        Height       = 255
        Left         = 180
        TabIndex     = 21
        Top          = 1620
        Width        = 8115
    End
    Begin Label Label3
        BackStyle    = 0 'Transparent
        Caption      = "This is the identity that you have selected:"
        Height       = 255
        Left         = 180
        TabIndex     = 2
        Top          = 900
        Width        = 3675
    End
    Begin Label lblNum
        Alignment    = 1 'Right Justify
        BackStyle    = 0 'Transparent
        Caption      = "1.23456789E-04"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height       = 195
        Index        = 5
        Left         = 4320
        TabIndex     = 3
        Top          = 1920
        Width        = 1035
    End
    Begin Label lblNum
        Alignment    = 1 'Right Justify
        BackStyle    = 0 'Transparent
        Caption      = "1.23456789E-04"
        FontBold     = 0 'False
        FontItalic   = 0 'False
        FontName     = "Small Fonts"
        FontSize     = 6
        FontStrikethru = 0 'False
        FontUnderline = 0 'False
        Height       = 195
        Index        = 4
        Left         = 4320
        TabIndex     = 5
        Top          = 2280
        Width        = 1035
    End
    Begin Label lblNum
        Alignment    = 1 'Right Justify
        BackStyle    = 0 'Transparent
        Caption      = "1.23456789E-04"
        FontBold     = 0 'False
        FontItalic   = 0 'False

```

```

    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 3
    Left          = 960
    TabIndex      = 6
    Top           = 2280
    Width         = 1035
End
Begin Label lblNum
    Alignment     = 1 'Right Justify
    BackStyle     = 0 'Transparent
    Caption       = "1.23456789E-04"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 2
    Left          = 960
    TabIndex      = 7
    Top           = 1980
    Width         = 1035
End
Begin Label lblNum
    Alignment     = 1 'Right Justify
    BackStyle     = 0 'Transparent
    Caption       = "1.23456789E-04"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    ForeColor     = &H00FF0000&
    Height        = 195
    Index         = 1
    Left          = 6540
    TabIndex      = 8
    Top           = 960
    Width         = 1035
End
Begin Label lblUnit
    BackStyle     = 0 'Transparent
    Caption       = "mmol NH4C2H3O2"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"
    FontSize      = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height        = 195
    Index         = 4
    Left          = 5460
    TabIndex      = 9
    Top           = 2280
    Width         = 1095
End
Begin Label lblUnit
    BackStyle     = 0 'Transparent
    Caption       = "mmol NH4C2H3O2"
    FontBold      = 0 'False
    FontItalic    = 0 'False
    FontName      = "Small Fonts"

```

```

        FontSize      = 6
        FontStrikethru = 0 'False
        FontUnderline  = 0 'False
        Height         = 195
        Index          = 5
        Left           = 5460
        TabIndex       = 10
        Top            = 1920
        Width          = 1095
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        Height          = 195
        Index           = 3
        Left            = 2100
        TabIndex        = 11
        Top             = 2280
        Width           = 1095
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        ForeColor       = &H00FF0000&
        Height          = 195
        Index           = 1
        Left            = 7680
        TabIndex        = 19
        Top             = 960
        Width           = 1095
    End
    Begin Label lblUnit
        BackStyle      = 0 'Transparent
        Caption         = "mmol NH4C2H3O2"
        FontBold        = 0 'False
        FontItalic       = 0 'False
        FontName        = "Small Fonts"
        FontSize        = 6
        FontStrikethru  = 0 'False
        FontUnderline   = 0 'False
        ForeColor       = &H00FF0000&
        Height          = 195
        Index           = 0
        Left            = 5100
        TabIndex        = 20
        Top             = 960
        Width           = 1095
    End
    Begin Label Label2
        BackStyle      = 0 'Transparent
        Caption         = "Do you really want to use this identity?"
        Height          = 255
        Left            = 4080
        TabIndex        = 18
        Top             = 1200
        Width           = 3495
    End

```

```

End
Begin Label Label1
    BackStyle      = 0 'Transparent
    Caption        = "="
    ForeColor      = &H00FF0000&
    Height         = 255
    Left           = 6300
    TabIndex       = 12
    Top            = 960
    Width          = 135
End
Begin Line Line3
    X1              = 4200
    X2              = 6660
    Y1              = 2220
    Y2              = 2220
End
Begin Line Line2
    X1              = 840
    X2              = 3300
    Y1              = 2220
    Y2              = 2220
End
Begin Label lblUnit
    BackStyle      = 0 'Transparent
    Caption        = "mmol NH4C2H3O2"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    Height         = 195
    Index          = 2
    Left           = 2100
    TabIndex       = 4
    Top            = 1980
    Width          = 1095
End
Begin Label lblNum
    Alignment      = 1 'Right Justify
    BackStyle      = 0 'Transparent
    Caption        = "1.23456789E-04"
    FontBold       = 0 'False
    FontItalic     = 0 'False
    FontName       = "Small Fonts"
    FontSize       = 6
    FontStrikethru = 0 'False
    FontUnderline  = 0 'False
    ForeColor      = &H00FF0000&
    Height         = 195
    Index          = 0
    Left           = 3960
    TabIndex       = 1
    Top            = 960
    Width          = 1035
End
End
Option Explicit
Dim likeone As Integer
Dim reciprocal As Integer
Dim dummyFactor As BetweenTheParenthesis
Dim isStage(0 To 2) As Integer

Sub cmdCancel_Click ()
    currentFactor = nullFactor
    form2.Hide
End Sub

```

```

Sub cmdContinue_Click ()
Dim i As Integer
UnitFindingStage = 2
displayCurrent

End Sub

Sub cmdFormShow_Click (index As Integer)
If index = 0 Then
frmMetEng.Show 1
frmMetEng.Hide
End If
If index = 1 Then
frmMetMet.Show 1
frmMetMet.Hide
End If
If index = 2 Then
frmEngEng.Show 1
frmEngEng.Hide
End If
If index = 3 Then
frmInText.Show 1
frmInText.Hide
End If
If index = 4 Then
frmDense.Show 1
frmDense.Hide
End If
End Sub

Sub cmdGoBack_Click ()
currentFactor = nullFactor
UnitFindingStage = 0
displayCurrent
End Sub

Sub cmdOkay_Click ()
If likeOne = False Then
MsgBox "You must select one of the two options below."
Else
If reciprocal = True Then
dummyFactor.n = currentFactor.d
dummyFactor.d = currentFactor.n
currentFactor.n = dummyFactor.n
currentFactor.d = dummyFactor.d
End If
form2.Hide
End If
End Sub

Static Sub displayCurrent ()
Dim i As Integer
Dim howFar As Integer
cmdFormShow(0).Visible = True
If levelFlag = 1 Then
For i = 1 To 4
cmdFormShow(i).Visible = False
Next i
End If
If levelFlag = 2 Then
cmdFormShow(1).Visible = True
cmdFormShow(2).Visible = True
cmdFormShow(3).Visible = True
cmdFormShow(4).Visible = False
End If
If levelFlag = 3 Then

```

```

        For i = 1 To 4
            cmdFormShow(i).Visible = True
        Next i
    End If

    For i = 0 To 5
        lblNum(i).Visible = False
        lblUnit(i).Visible = False
    Next i
    toggleBoldness
    If UnitFindingStage = 2 Then cmdOkay.Enabled = True Else cmdOkay.Enabled = False
    If UnitFindingStage > 0 Then
        If UnitFindingStage = 1 Then howFar = 0 Else howFar = 4
        For i = 0 To howFar Step 2
            lblNum(i).Visible = True
            lblNum(i).Caption = currentFactor.n.num
            lblUnit(i).Visible = True
            lblUnit(i).Caption = currentFactor.n.unit
            lblUnit(i).FontStrikethru = currentFactor.n.unitCanceled

            lblNum(i + 1).Visible = True
            lblNum(i + 1).Caption = currentFactor.d.num
            lblUnit(i + 1).Visible = True
            lblUnit(i + 1).Caption = currentFactor.d.unit
            lblUnit(i + 1).FontStrikethru = currentFactor.d.unitCanceled
        Next i
    End If
End Sub

Sub Form_Activate ()
'Dim i As Integer

    displayCurrent

End Sub

Sub lblNum_Click (index As Integer)

    If index = 2 Or index = 3 Then
        option1_click (0)
    End If
    If index = 4 Or index = 5 Then
        option1_click (1)
    End If
End Sub

Sub option1_click (index As Integer)
likeone = True
If index = 0 Then reciprocal = False Else reciprocal = True
'If HintFlag = True Then
'HintProgress = False
'timer1.Enabled = True
'End If

End Sub

Static Sub toggleBoldness ()
Dim i As Integer
For i = 0 To 2
    If UnitFindingStage = i Then isStage(i) = True Else isStage(i) = False
Next i

    label5.FontBold = isStage(0)
    For i = 0 To 4
        cmdFormShow(i).Enabled = isStage(0)
    Next i

    label3.FontBold = isStage(1)

```

```

label2.FontBold = isStage(1)
cmdContinue.Enabled = isStage(1)
cmdGoBack.Enabled = isStage(1)

For i = 0 To 1
    option1(i).Visible = isStage(2)
Next i
label4.FontBold = isStage(2)
If isStage(2) = True Then
    likeone = False
    option1(0).Value = False
    option1(1).Value = False
End If

End Sub

```

FILE: FRMMETEN.FRM

VERSION 2.00

```

Begin Form frmMetEng
    BackColor      = &H00C0FFC0&
    Caption        = "Metric to English identities"
    ClientHeight   = 1065
    ClientLeft     = 3315
    ClientTop      = 6015
    ClientWidth    = 5820
    ControlBox     = 0 'False
    Height         = 1470
    Left           = 3255
    LinkTopic      = "Form3"
    MaxButton      = 0 'False
    MinButton      = 0 'False
    ScaleHeight    = 1065
    ScaleWidth     = 5820
    Top            = 5670
    Width          = 5940
    Begin CommandButton cmdCancel
        Caption     = "Cancel"
        Height      = 315
        Left        = 4200
        TabIndex    = 3
        Top         = 540
        Width       = 1215
    End
    Begin CommandButton cmdLQt
        Caption     = "L-qt"
        Height      = 315
        Left        = 1860
        TabIndex    = 2
        Top         = 540
        Width       = 855
    End
    Begin CommandButton cmdGLb
        Caption     = "g-lb"
        Height      = 315
        Left        = 1020
        TabIndex    = 1
        Top         = 540
        Width       = 735
    End
    Begin CommandButton cmdCmIn
        Caption     = "cm-in"
        Height      = 315
        Left        = 180
    End

```



```

        TabIndex      = 0
        Top           = 540
        Width         = 735
    End
    Begin Label Label1
        BackStyle      = 0 'Transparent
        Caption        = "Here are the available unit conversions.  Select one, or click
""Cancel"" if none of these are useful to you:"
        Height         = 435
        Left           = 180
        TabIndex       = 4
        Top            = 120
        Width          = 5295
    End
End
Sub cmdCancel_Click ()
    currentFactor = nullFactor
    UnitFindingStage = 0
    frmMetEng.Hide
End Sub

Sub cmdCmIn_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 2.54
    currentFactor.n.unit = "cm "
    currentFactor.d.num = 1
    currentFactor.d.unit = "in "
    goOn
End Sub

Sub cmdGLb_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 454
    currentFactor.n.sigfig = 3
    currentFactor.n.unit = "g "
    currentFactor.d.num = 1
    currentFactor.d.unit = "lb "
    UnitFindingStage = 1
    goOn
End Sub

Sub cmdLQt_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 1
    currentFactor.n.unit = "L "
    currentFactor.d.num = 1.1
    currentFactor.d.sigfig = 2
    currentFactor.d.unit = "qt "
    goOn
End Sub

Static Sub goOn ()
    If HintFlag = True Then HintProgress = True
    UnitFindingStage = 1
    frmMetEng.Hide
    If levelFlag = 3 Then frmSubstance.Show 1
End Sub

```

FILE: FRMENGEN.FRM
VERSION 2.00
 Begin Form frmEngEng

```

BackColor      = &H00C0FFC0&
Caption        = "English - English conversion"
ClientHeight   = 3150
ClientLeft     = 795
ClientTop      = 3480
ClientWidth    = 7365
ControlBox     = 0 'False
Height         = 3555
Left           = 735
LinkTopic      = "Form4"
MaxButton      = 0 'False
MinButton      = 0 'False
ScaleHeight    = 3150
ScaleWidth     = 7365
Top            = 3135
Width          = 7485
Begin CommandButton cmdYearDecade
    Caption      = "year-decade"
    Height       = 315
    Left         = 3240
    TabIndex     = 16
    Top          = 2580
    Width        = 1215
End
Begin CommandButton cmdDayYear
    Caption      = "day-year"
    Height       = 315
    Left         = 3240
    TabIndex     = 15
    Top          = 2220
    Width        = 1215
End
Begin CommandButton cmdDayWeek
    Caption      = "day-week"
    Height       = 315
    Left         = 3240
    TabIndex     = 14
    Top          = 1860
    Width        = 1215
End
Begin CommandButton cmdHourDay
    Caption      = "hour-day"
    Height       = 315
    Left         = 3240
    TabIndex     = 13
    Top          = 1500
    Width        = 1215
End
Begin CommandButton cmdMinHour
    Caption      = "min-hour"
    Height       = 315
    Left         = 3240
    TabIndex     = 12
    Top          = 1140
    Width        = 1215
End
Begin CommandButton cmdSMin
    Caption      = "s-min"
    Height       = 315
    Left         = 3240
    TabIndex     = 11
    Top          = 780
    Width        = 1215
End
Begin CommandButton cmdQtGal
    Caption      = "qt-gal"
    Height       = 315
    Left         = 1860

```

```

        TabIndex      = 10
        Top            = 2220
        Width          = 1215
    End
    Begin CommandButton cmdCupFloz
        Caption        = "cup-fl.oz"
        Height         = 315
        Left            = 1860
        TabIndex        = 9
        Top             = 2580
        Width           = 1215
    End
    Begin CommandButton cmdQtCup
        Caption        = "qt-cup"
        Height         = 315
        Left            = 1860
        TabIndex        = 8
        Top             = 1860
        Width           = 1215
    End
    Begin CommandButton cmdQtPtin
        Caption        = "qt-pint"
        Height         = 315
        Left            = 1860
        TabIndex        = 7
        Top             = 1500
        Width           = 1215
    End
    Begin CommandButton cmdLbTon
        Caption        = "lb-ton"
        Height         = 315
        Left            = 480
        TabIndex        = 6
        Top             = 2580
        Width           = 1215
    End
    Begin CommandButton cmdLbOz
        Caption        = "lb-oz"
        Height         = 315
        Left            = 480
        TabIndex        = 5
        Top             = 2220
        Width           = 1215
    End
    Begin CommandButton cmdFtMile
        Caption        = "ft-mile"
        Height         = 315
        Left            = 480
        TabIndex        = 4
        Top             = 1500
        Width           = 1215
    End
    Begin CommandButton cmdFtYd
        Caption        = "ft-yd"
        Height         = 315
        Left            = 480
        TabIndex        = 3
        Top             = 1140
        Width           = 1215
    End
    Begin CommandButton cmdCancel
        Caption        = "Cancel"
        Height         = 315
        Left            = 5940
        TabIndex        = 2
        Top             = 180
        Width           = 1215
    End
End

```

```

Begin CommandButton cmdInFt
    Caption      = "in-ft"
    Height       = 315
    Left         = 480
    TabIndex     = 1
    Top          = 780
    Width        = 1215
End
Begin Label Label1
    BackStyle    = 0 'Transparent
    Caption      = "Here are the available unit conversions.  Select one, or click
""Cancel"" if none of these are useful to you:"
    Height       = 435
    Left         = 300
    TabIndex     = 0
    Top          = 120
    Width        = 5295
End
End
Sub cmdCancel_Click ()
    currentFactor = nullFactor
    UnitFindingStage = 0
    frmEngEng.Hide
End Sub

Sub cmdCupFloz_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 12
    currentFactor.n.unit = "floz "
    currentFactor.d.num = 1
    currentFactor.d.unit = "cup "
    goOn
End Sub

Sub cmdDayWeek_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 7
    currentFactor.n.unit = "day "
    currentFactor.d.num = 1
    currentFactor.d.unit = "week "
    goOn
End Sub

Sub cmdDayYear_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 365.25
    currentFactor.n.unit = "day "
    currentFactor.d.num = 1
    currentFactor.d.unit = "year "
    goOn
End Sub

Sub cmdFtMile_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 5280
    currentFactor.n.unit = "ft "
    currentFactor.d.num = 1
    currentFactor.d.unit = "mile "
    goOn
End Sub

Sub cmdFtYd_Click ()

```

```

        currentFactor = nullFactor
        currentFactor.n.num = 3
        currentFactor.n.unit = "ft "
        currentFactor.d.num = 1
        currentFactor.d.unit = "yd "
        goOn

End Sub

Sub cmdHourDay_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 24
    currentFactor.n.unit = "hr "
    currentFactor.d.num = 1
    currentFactor.d.unit = "day "
    goOn

End Sub

Sub cmdInFt_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 12
    currentFactor.n.unit = "in "
    currentFactor.d.num = 1
    currentFactor.d.unit = "ft "
    goOn

End Sub

Sub cmdLbOz_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 16
    currentFactor.n.unit = "oz "
    currentFactor.d.num = 1
    currentFactor.d.unit = "lb "
    goOn

End Sub

Sub cmdLbTon_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 2000
    currentFactor.n.unit = "lb "
    currentFactor.d.num = 1
    currentFactor.d.unit = "ton "
    goOn

End Sub

Sub cmdMinHour_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 60
    currentFactor.n.unit = "min "
    currentFactor.d.num = 1
    currentFactor.d.unit = "hr "
    goOn

End Sub

Sub cmdQtCup_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 4
    currentFactor.n.unit = "cup "
    currentFactor.d.num = 1
    currentFactor.d.unit = "qt "
    goOn

End Sub

```

```

Sub cmdQtGal_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 4
    currentFactor.n.unit = "qt "
    currentFactor.d.num = 1
    currentFactor.d.unit = "gal "
    goOn

End Sub

Sub cmdQtPtin_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 2
    currentFactor.n.unit = "pint "
    currentFactor.d.num = 1
    currentFactor.d.unit = "qt "
    goOn

End Sub

Sub cmdSMin_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 60
    currentFactor.n.unit = "sec "
    currentFactor.d.num = 1
    currentFactor.d.unit = "min "
    goOn

End Sub

Sub cmdYearDecade_Click ()
    currentFactor = nullFactor
    currentFactor.n.num = 10
    currentFactor.n.unit = "year "
    currentFactor.d.num = 1
    currentFactor.d.unit = "decade "
    goOn

End Sub

Static Sub goOn ()
    If HintFlag = True Then HintProgress = True

    UnitFindingStage = 1
    frmEngEng.Hide
    If levelFlag = 3 Then frmSubstance.Show 1

End Sub

```

FILE: FRMMETME.FRM

VERSION 2.00

Begin Form frmMetMet

```

    BackColor      = &H00C0FFC0&
    Caption        = "Metric prefixes"
    ClientHeight   = 4020
    ClientLeft     = 1095
    ClientTop      = 1500
    ClientWidth    = 7365
    ControlBox     = 0 'False
    Height         = 4425
    Left           = 1035
    LinkTopic      = "Form3"
    MaxButton      = 0 'False
    MinButton      = 0 'False
    ScaleHeight    = 4020

```

```

ScaleWidth      = 7365
Top             = 1155
Width          = 7485
Begin CommandButton cmdOkay
  Caption       = "okay"
  Height        = 1215
  Left          = 6360
  TabIndex      = 8
  Top           = 1260
  Width         = 915
End
Begin CommandButton cmdCancel
  Caption       = "Cancel"
  Height        = 495
  Left          = 6360
  TabIndex      = 7
  Top           = 480
  Width         = 855
End
Begin Frame Frame2
  Caption       = "Base metric unit"
  Height        = 2955
  Left          = 3720
  TabIndex      = 1
  Top           = 360
  Width         = 2415
  Begin OptionButton OptBase
    Caption     = "Liters"
    Height      = 255
    Index       = 7
    Left        = 360
    TabIndex    = 21
    Top         = 2580
    Width       = 1455
  End
  Begin OptionButton OptBase
    Caption     = "candela"
    Height      = 255
    Index       = 6
    Left        = 360
    TabIndex    = 20
    Top         = 2280
    Width       = 1455
  End
  Begin OptionButton OptBase
    Caption     = "ampere"
    Height      = 255
    Index       = 5
    Left        = 360
    TabIndex    = 19
    Top         = 1980
    Width       = 1455
  End
  Begin OptionButton OptBase
    Caption     = "mole"
    Height      = 255
    Index       = 4
    Left        = 360
    TabIndex    = 18
    Top         = 1680
    Width       = 1455
  End
  Begin OptionButton OptBase
    Caption     = "kelvin"
    Height      = 255
    Index       = 3
    Left        = 360
    TabIndex    = 17

```

```

        Top          = 1380
        Width        = 1455
    End
    Begin OptionButton OptBase
        Caption       = "second"
        Height        = 255
        Index         = 2
        Left          = 360
        TabIndex      = 9
        Top           = 1080
        Width         = 1455
    End
    Begin OptionButton OptBase
        Caption       = "gram"
        Height        = 255
        Index         = 1
        Left          = 360
        TabIndex      = 6
        Top           = 780
        Width         = 1455
    End
    Begin OptionButton OptBase
        Caption       = "meter"
        Height        = 255
        Index         = 0
        Left          = 360
        TabIndex      = 5
        Top           = 480
        Width         = 1455
    End
End
Begin Frame Frame1
    Caption          = "Prefix"
    Height           = 3615
    Left             = 720
    TabIndex         = 0
    Top              = 360
    Width            = 2535
    Begin OptionButton OptPre
        Caption       = "nano"
        Height        = 255
        Index         = 9
        Left          = 240
        TabIndex      = 16
        Top           = 3240
        Width         = 1575
    End
    Begin OptionButton OptPre
        Caption       = "micro"
        Height        = 255
        Index         = 8
        Left          = 240
        TabIndex      = 15
        Top           = 2940
        Width         = 1575
    End
    Begin OptionButton OptPre
        Caption       = "milli"
        Height        = 255
        Index         = 7
        Left          = 240
        TabIndex      = 14
        Top           = 2640
        Width         = 1575
    End
    Begin OptionButton OptPre
        Caption       = "centi"
        Height        = 255

```



```

        Index      = 6
        Left       = 240
        TabIndex   = 13
        Top        = 2340
        Width      = 1575
    End
    Begin OptionButton OptPre
        Caption     = "deci"
        Height      = 255
        Index       = 5
        Left        = 240
        TabIndex    = 12
        Top         = 2040
        Width       = 1575
    End
    Begin OptionButton OptPre
        Caption     = "deka"
        Height      = 255
        Index       = 4
        Left        = 240
        TabIndex    = 11
        Top         = 1740
        Width       = 1575
    End
    Begin OptionButton OptPre
        Caption     = "hecto"
        Height      = 255
        Index       = 3
        Left        = 240
        TabIndex    = 10
        Top         = 1440
        Width       = 1575
    End
    Begin OptionButton OptPre
        Caption     = "kilo"
        Height      = 255
        Index       = 2
        Left        = 240
        TabIndex    = 4
        Top         = 1080
        Width       = 1575
    End
    Begin OptionButton OptPre
        Caption     = "mega"
        Height      = 255
        Index       = 1
        Left        = 240
        TabIndex    = 3
        Top         = 720
        Width       = 1575
    End
    Begin OptionButton OptPre
        Caption     = "giga"
        Height      = 255
        Index       = 0
        Left        = 240
        TabIndex    = 2
        Top         = 360
        Width       = 1575
    End
End
Begin Label Label1
    BackStyle      = 0 'Transparent
    Caption        = "Converts to and from base units: e.g. milligrams to grams,
meters to kilometers."
    Height         = 255
    Left           = 480
    TabIndex       = 22

```

```

        Top          = 60
        Width        = 6735
    End
End
Option Explicit

Const NUMPRE = 9
Const NUMBASE = 7
' NOTE: both of these are equal to the
'       number of possibilities - 1
'       because the first one is zero

Sub cmdCancel_Click ()
    currentFactor = nullFactor
    UnitFindingStage = 0
    frmMetMet.Hide

End Sub

Sub cmdOkay_Click ()
    Dim GoodPreFlag As Integer
    Dim goodBaseFlag As Integer

    currentFactor = nullFactor
    GoodPreFlag = False
    goodBaseFlag = False
    If optPre(0).Value = True Then
        currentFactor.n.num = 1
        currentFactor.d.num = 1000000000
        currentFactor.n.unit = "G"
        GoodPreFlag = True
    End If
    If optPre(1).Value = True Then
        currentFactor.n.num = 1
        currentFactor.d.num = 1000000
        currentFactor.n.unit = "M"
        GoodPreFlag = True
    End If
    If optPre(2).Value = True Then
        currentFactor.n.num = 1
        currentFactor.d.num = 1000
        currentFactor.n.unit = "k"
        GoodPreFlag = True
    End If
    If optPre(3).Value = True Then
        currentFactor.n.num = 1
        currentFactor.d.num = 100
        currentFactor.n.unit = "c"
        GoodPreFlag = True
    End If
    If optPre(4).Value = True Then
        currentFactor.n.num = 1
        currentFactor.d.num = 10
        currentFactor.n.unit = "da"
        GoodPreFlag = True
    End If
    If optPre(5).Value = True Then
        'currentFactor.n.num = 1
        'currentFactor.d.num = .1
        currentFactor.n.num = 10
        currentFactor.d.num = 1
        currentFactor.n.unit = "d"
        GoodPreFlag = True
    End If
    If optPre(6).Value = True Then
        'currentFactor.n.num = 1
        'currentFactor.d.num = .01

```

```

        currentFactor.n.num = 100
        currentFactor.d.num = 1
        currentFactor.n.unit = "c"
        GoodPreFlag = True
    End If
    If optPre(7).Value = True Then
        'currentFactor.n.num = 1
        'currentFactor.d.num = .001
        currentFactor.n.num = 1000
        currentFactor.d.num = 1
        currentFactor.n.unit = "m"
        GoodPreFlag = True
    End If
    If optPre(8).Value = True Then
        'currentFactor.n.num = 1
        'currentFactor.d.num = .000001
        currentFactor.n.num = 1000000
        currentFactor.d.num = 1
        currentFactor.n.unit = "mu"
        GoodPreFlag = True
    End If
    If optPre(9).Value = True Then
        'currentFactor.n.num = 1
        'currentFactor.d.num = .000000001
        currentFactor.n.num = 1000000000
        currentFactor.d.num = 1
        currentFactor.n.unit = "n"
        GoodPreFlag = True
    End If

    If optBase(0).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "m "
        currentFactor.d.unit = "m "
        goodBaseFlag = True
    End If
    If optBase(1).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "g "
        currentFactor.d.unit = "g "
        goodBaseFlag = True
    End If
    If optBase(2).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "sec "
        currentFactor.d.unit = "sec "
        goodBaseFlag = True
    End If
    If optBase(3).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "K "
        currentFactor.d.unit = "K "
        goodBaseFlag = True
    End If
    If optBase(4).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "mol "
        currentFactor.d.unit = "mol "
        goodBaseFlag = True
    End If
    If optBase(5).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "A "
        currentFactor.d.unit = "A "
        goodBaseFlag = True
    End If
    If optBase(6).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "cd "
        currentFactor.d.unit = "cd "
        goodBaseFlag = True
    End If
    If optBase(7).Value = True Then
        currentFactor.n.unit = currentFactor.n.unit & "L "
        currentFactor.d.unit = "L "

```

```

    goodBaseFlag = True
End If

    If goodBaseFlag = True And GoodPreFlag = True Then
        UnitFindingStage = 1
        frmMetMet.Hide
        If levelFlag = 3 Then frmSubstance.Show 1
    Else
        MsgBox "Please select both a prefix and a base unit"
    End If

End Sub

Sub Form_Activate ()
Dim i As Integer
    For i = 0 To NUMPRE
        optPre(i).Value = False
    Next i
    For i = 0 To NUMBASE
        optBase(i).Value = False
    Next i

End Sub

Sub OptBase_Click (index As Integer)
Dim i As Integer
    For i = 0 To NUMBASE
        If i = index Then optBase(i).Value = True Else optBase(i).Value = False
    Next i

End Sub

Sub OptPre_Click (index As Integer)
Dim i As Integer
    For i = 0 To NUMPRE
        If i = index Then optPre(i).Value = True Else optPre(i).Value = False
    Next i

End Sub

```

FILE: FRMGETST.FRM

VERSION 2.00

```

Begin Form frmGetStart
    Caption           = "Get a starting point"
    ClientHeight      = 2535
    ClientLeft        = 2640
    ClientTop         = 525
    ClientWidth       = 7365
    Height            = 2940
    Left              = 2580
    LinkTopic         = "Form3"
    ScaleHeight       = 2535
    ScaleWidth        = 7365
    Top               = 180
    Width             = 7485
    Begin CommandButton cmdTry
        Caption       = "How about this one?"
        Height        = 495
        Left          = 3780
        TabIndex      = 1
        Top           = 1740
        Width         = 2235
    End
    Begin TextBox Text1
        FontBold      = -1 'True
        FontItalic     = 0  'False
    End

```

```

        FontName      =    "MS Sans Serif"
        FontSize       =    12
        FontStrikethru  =    0    'False
        FontUnderline   =    0    'False
        Height         =    975
        Left            =    240
        MultiLine       =    -1    'True
        TabIndex        =    0
        Top             =    180
        Width           =    6015
    End
End
Option Explicit

Sub cmdTry_Click ()
    MsgBox "he picked " & text1.SelText
    frmGetStart.Hide
End Sub

Sub Form_Activate ()
    text1.Text = problemText
End Sub

```

FILE:FRMSTAR2.FRM

VERSION 2.00

Begin Form frmStart

```

BackColor      = &H00C0E0FF&
Caption        = "Extract Starting point from problem text"
ClientHeight   = 4695
ClientLeft     = 2025
ClientTop      = 1005
ClientWidth    = 5265
ControlBox     = 0 'False
Height         = 5100
Left           = 1965
LinkTopic      = "Form4"
MaxButton      = 0 'False
MinButton      = 0 'False
ScaleHeight    = 4695
ScaleWidth     = 5265
Top            = 660
Width          = 5385

```

Begin CommandButton cmdHelp

```

Caption        = "Refresh my memory, what is an ""extrinsic"" factor?"
Height         = 435
Left           = 180
TabIndex       = 5
Top            = 4080
Width          = 4935

```

End

Begin CommandButton cmdCancel

```

Caption        = "Cancel"
Height         = 375
Left           = 1080
TabIndex       = 3
Top            = 2640
Width          = 1335

```

End

Begin CommandButton cmdOkay

```

Caption        = "Okay"
Height         = 375
Left           = 2520
TabIndex       = 2
Top            = 2640
Width          = 1455

```

End

Begin TextBox Text1

```

Height         = 1575
Left           = 180
MultiLine      = -1 'True
TabIndex       = 0
Top            = 1020
Width          = 4935

```

End

Begin Label Label2

```

BackStyle      = 0 'Transparent
Caption        = "To select a factor: Click on the beginning of the first word,
and (while holding the mouse button down) move the cursor to the end of the last word.
Release the mouse button. The text you have selected will appear highlighted."

```

```

FontBold       = 0 'False
FontItalic     = 0 'False
FontName       = "MS Sans Serif"
FontSize       = 8.25
FontStrikethru = 0 'False
FontUnderline  = 0 'False
Height         = 915
Left           = 180
TabIndex       = 4
Top            = 3060
Width          = 4875

```

End

```

Begin Label Labell
    BackStyle      = 0 'Transparent
    Caption        = "Here's the text of the problem.  Select the starting point,
then click the OKAY button.  (NOTE:  If there is an ""extrinsic"" factor in this problem,
you will need to use that as your starting point."
    Height         = 915
    Left           = 180
    TabIndex       = 1
    Top            = 120
    Width          = 4815
End
End
Option Explicit

Sub cmdCancel_Click ()
    currentFactor = nullFactor
    UnitFindingStage = 0
    frmStart.Hide

End Sub

Sub cmdOkay_Click ()
    Dim i As Integer
    Dim gotOneFlag As Integer
    gotOneFlag = False
    If (ThisInText(2) = True) Then
        MsgBox "Be sure you are not confusing the answer with the starting point."
    Else
        If (ThisInText(1)) = True Then
            MsgBox "got the right one"
            gotOneFlag = True
        Else
            If (startingPoint.d.unit <> " ") And (numberOfGivenInfo > 2) Then
                For i = 3 To numberOfGivenInfo + 2
                    If (ThisInText(i) = True) And (gotOneFlag = False) Then
                        currentFactor = givenInfo(i - 2)
                        UnitFindingStage = 1
                        MsgBox "Swap out for original starting point"
                        gotOneFlag = True
                    End If
                Next i
            End If
        End If
        If gotOneFlag = True Then
            frmStart.Hide
            If currentFactor.n.stuff = " " And currentFactor.d.stuff = " " And levelFlag
= 3 Then frmSubstance.Show 1
        Else
            MsgBox "Sorry, I could not identify any useful relationship in what you
selected Be sure you are selecting ALL the information necessary."
        End If
    End If
End Sub

Sub Form_Activate ()
    If numberOfGivenInfo = 0 Then
        MsgBox "Sorry, there is no conversion factors given in text."
        frmStart.Hide
    Else
        text1.Text = problemText
    End If
End Sub

Sub Text1_Change ()
    text1.Text = problemText
End Sub

Static Function ThisInText (dummy As Integer) As Integer

```

```

Dim thisOneHereFlag, OtherOneIsnt, i As Integer
If text1.SelText <> "" Then
    OtherOneIsnt = True
    For i = 1 To numberOfGivenInfo + 2
        If i = dummy Then
            If InStr(text1.SelText, keyPhrase(i)) = 0 Then thisOneHereFlag = False Else
thisOneHereFlag = True
            Else
                If InStr(text1.SelText, keyPhrase(i)) <> 0 Then OtherOneIsnt = False
            End If
        Next i
        If (thisOneHereFlag = True) And (OtherOneIsnt = True) Then
            ThisInText = True
        Else
            ThisInText = False
        End If
    Else
        MsgBox "You must first select something in the text."
        ThisInText = False
    End If

End Function

```

FILE: FRMDENSE.FRM

VERSION 2.00

```

Begin Form frmDense
    BackColor      = &H00C0FFC0&
    Caption        = "Density table"
    ClientHeight   = 4845
    ClientLeft     = 2970
    ClientTop      = 2175
    ClientWidth    = 6450
    ControlBox     = 0 'False
    Height         = 5535
    Left           = 2910
    LinkTopic      = "Form3"
    MaxButton      = 0 'False
    MinButton      = 0 'False
    ScaleHeight    = 4845
    ScaleWidth     = 6450
    Top            = 1545
    Width          = 6570
    Begin CommandButton cmdGasoline
        Caption     = "gasoline"
        Height      = 375
        Left        = 3060
        TabIndex    = 14
        Top         = 900
        Width       = 1635
    End
    Begin CommandButton cmdAl
        Caption     = "aluminum"
        Height      = 375
        Left        = 4740
        TabIndex    = 13
        Top         = 480
        Width       = 1635
    End
    Begin CommandButton cmdAu
        Caption     = "gold"
        Height      = 375
        Left        = 4740
        TabIndex    = 12
        Top         = 900
    End

```



```

        Width          = 1635
    End
    Begin CommandButton cmdPb
        Caption          = "lead"
        Height           = 375
        Left             = 4740
        TabIndex         = 11
        Top              = 1320
        Width            = 1635
    End
    Begin CommandButton cmdEtOH
        Caption          = "alcohol"
        Height           = 375
        Left             = 3060
        TabIndex         = 10
        Top              = 480
        Width            = 1635
    End
    Begin CommandButton cmdIce
        Caption          = "ice"
        Height           = 375
        Left             = 4740
        TabIndex         = 9
        Top              = 60
        Width            = 1635
    End
    Begin CommandButton cmdWater
        Caption          = "water (liquid)"
        Height           = 375
        Left             = 3060
        TabIndex         = 8
        Top              = 60
        Width            = 1635
    End
    Begin CommandButton cmdCancel
        Caption          = "Cancel"
        Height           = 495
        Left             = 5160
        TabIndex         = 7
        Top              = 4200
        Width            = 1035
    End
    Begin CommandButton cmdGoBack
        Caption          = "No"
        Height           = 495
        Left             = 3720
        TabIndex         = 6
        Top              = 4200
        Width            = 675
    End
    Begin CommandButton cmdApply
        Caption          = "Yes"
        Height           = 495
        Left             = 2940
        TabIndex         = 3
        Top              = 4200
        Width            = 675
    End
    Begin CommandButton cmdMercury
        Caption          = "mercury"
        Height           = 375
        Left             = 3060
        TabIndex         = 1
        Top              = 1320
        Width            = 1635
    End
    Begin Label Label2
        BackStyle         = 0 'Transparent

```

```

Caption      = "Are you happy with this selection?"
Height       = 495
Left         = 120
TabIndex     = 5
Top          = 4200
Width        = 2355
End
Begin Label lblApply
BackStyle    = 0 'Transparent
Height       = 555
Left         = 180
TabIndex     = 4
Top          = 3540
Width        = 5895
End
Begin Label lblDensity
BackStyle    = 0 'Transparent
Height       = 735
Left         = 180
TabIndex     = 2
Top          = 2700
Width        = 5835
End
Begin Label Label1
BackStyle    = 0 'Transparent
Caption      = "Density are available for the following substances."
Height       = 495
Left         = 120
TabIndex     = 0
Top          = 60
Width        = 2715
End
Begin Menu mnuDummy
Caption      = "&Phrasing"
Begin Menu mnuPhrasing
Caption      = "&Mathematical"
Index       = 0
End
Begin Menu mnuPhrasing
Caption      = "&Verbose"
Index       = 1
End
Begin Menu mnuPhrasing
Caption      = "&Terse"
Index       = 2
End
End
End
Option Explicit
Dim phrasing As Integer

Sub cmdAl_Click ()
Const STUFFNAME = "aluminum "
CurrentFactor = nullFactor
CurrentFactor.n.num = 2.7
CurrentFactor.n.sigfig = 3
CurrentFactor.n.unit = "g " & STUFFNAME
CurrentFactor.n.stuff = STUFFNAME
CurrentFactor.d.num = 1
CurrentFactor.d.sigfig = 9
CurrentFactor.d.unit = "mL " & STUFFNAME
CurrentFactor.d.stuff = STUFFNAME
displayPhrase
End Sub

Sub cmdApply_Click ()
If CurrentFactor.n.unit = nullFactor.n.unit Then

```

```

        MsgBox "First make a selection, then click 'yes'"
    Else
        UnitFindingStage = 1
        frmDense.Hide
    End If

End Sub

Sub cmdAu_Click ()
Const STUFFNAME = "gold "
    CurrentFactor = nullFactor
    CurrentFactor.n.num = 19.32
    CurrentFactor.n.sigfig = 4
    CurrentFactor.n.unit = "g " & STUFFNAME
    CurrentFactor.n.stuff = STUFFNAME
    CurrentFactor.d.num = 1
    CurrentFactor.d.sigfig = 9
    CurrentFactor.d.unit = "mL " & STUFFNAME
    CurrentFactor.d.stuff = STUFFNAME
    displayPhrase

End Sub

Sub cmdCancel_Click ()
    CurrentFactor = nullFactor
    UnitFindingStage = 0
    frmDense.Hide

End Sub

Sub cmdEtOH_Click ()

Const STUFFNAME = "alcohol "
    CurrentFactor = nullFactor
    CurrentFactor.n.num = .789
    CurrentFactor.n.sigfig = 3
    CurrentFactor.n.unit = "g " & STUFFNAME
    CurrentFactor.n.stuff = STUFFNAME
    CurrentFactor.d.num = 1
    CurrentFactor.d.sigfig = 9
    CurrentFactor.d.unit = "mL " & STUFFNAME
    CurrentFactor.d.stuff = STUFFNAME
    displayPhrase

End Sub

Sub cmdGasoline_Click ()
Const STUFFNAME = "gasoline "
    CurrentFactor = nullFactor
    CurrentFactor.n.num = .71
    CurrentFactor.n.sigfig = 2
    CurrentFactor.n.unit = "g " & STUFFNAME
    CurrentFactor.n.stuff = STUFFNAME
    CurrentFactor.d.num = 1
    CurrentFactor.d.sigfig = 9
    CurrentFactor.d.unit = "mL " & STUFFNAME
    CurrentFactor.d.stuff = STUFFNAME
    displayPhrase
End Sub

Sub cmdGoBack_Click ()
    CurrentFactor = nullFactor
    displayPhrase
End Sub

Sub cmdIce_Click ()
Const STUFFNAME = "ice "

```

```

CurrentFactor = nullFactor
CurrentFactor.n.num = .92
CurrentFactor.n.sigfig = 2
CurrentFactor.n.unit = "g " & STUFFNAME
CurrentFactor.n.stuff = STUFFNAME
CurrentFactor.d.num = 1
CurrentFactor.d.sigfig = 9
CurrentFactor.d.unit = "mL " & STUFFNAME
CurrentFactor.d.stuff = STUFFNAME
displayPhrase

End Sub

Sub cmdMercury_Click ()
Const STUFFNAME = "mercury "
CurrentFactor = nullFactor
CurrentFactor.n.num = 13
CurrentFactor.n.sigfig = 2
CurrentFactor.n.unit = "g " & STUFFNAME
CurrentFactor.n.stuff = STUFFNAME
CurrentFactor.d.num = 1
CurrentFactor.d.sigfig = 9
CurrentFactor.d.unit = "mL " & STUFFNAME
CurrentFactor.d.stuff = STUFFNAME
displayPhrase
End Sub

Sub cmdPb_Click ()
Const STUFFNAME = "lead "
CurrentFactor = nullFactor
CurrentFactor.n.num = 11.34
CurrentFactor.n.sigfig = 4
CurrentFactor.n.unit = "g " & STUFFNAME
CurrentFactor.n.stuff = STUFFNAME
CurrentFactor.d.num = 1
CurrentFactor.d.sigfig = 9
CurrentFactor.d.unit = "mL " & STUFFNAME
CurrentFactor.d.stuff = STUFFNAME
displayPhrase

End Sub

Sub cmdWater_Click ()
Const STUFFNAME = "water "
CurrentFactor = nullFactor
CurrentFactor.n.num = 1
CurrentFactor.n.sigfig = 2
CurrentFactor.n.unit = "g " & STUFFNAME
CurrentFactor.n.stuff = STUFFNAME
CurrentFactor.d.num = 1
CurrentFactor.d.sigfig = 9
CurrentFactor.d.unit = "mL " & STUFFNAME
CurrentFactor.d.stuff = STUFFNAME
displayPhrase

End Sub

Static Sub displayPhrase ()
Dim densityString As String
If CurrentFactor.n.stuff <> " " Then
densityString = "The density of " & CurrentFactor.n.stuff
densityString = densityString & "= "
densityString = densityString & CStr(CurrentFactor.n.num)
densityString = densityString & " g/mL"
lblDensity.Caption = densityString
If phrasing = 0 Then
densityString = "This implies that: "
densityString = densityString & CStr(CurrentFactor.n.num)

```

```

        densityString = densityString & " g "
        densityString = densityString & CurrentFactor.n.stuff
        densityString = densityString & "= 1 mL "
        densityString = densityString & CurrentFactor.n.stuff
    End If
    If phrasing = 2 Then
        densityString = "This implies that 1 mL of "
        densityString = densityString & CurrentFactor.n.stuff
        densityString = densityString & "is equivalent to "
        densityString = densityString & CStr(CurrentFactor.n.num)
        densityString = densityString & " grams of "
        densityString = densityString & CurrentFactor.n.stuff
    End If
    If phrasing = 1 Then
        densityString = "This means that every one milliliter sample of "
        densityString = densityString & CurrentFactor.n.stuff
        densityString = densityString & "will always have a mass equal to "
        densityString = densityString & CStr(CurrentFactor.n.num)
        densityString = densityString & " grams."
    End If
    lblApply.Caption = densityString
Else
    lblDensity.Caption = ""
    lblApply.Caption = ""
End If

End Sub

Sub Form_Activate ()
    displayPhrase
End Sub

Sub Form_Load ()
    Dim i As Integer
    For i = 0 To 2
        If i = 0 Then mnuPhrasing(i).Checked = True Else mnuPhrasing(i).Checked = False
    Next i
    phrasing = 0
End Sub

Sub mnuPhrasing_Click (index As Integer)
    Dim i As Integer
    For i = 0 To 2
        If i = index Then mnuPhrasing(i).Checked = True Else mnuPhrasing(i).Checked =
False
    Next i
    phrasing = index
    displayPhrase
End Sub

FILE: FRMSUBST.FRM
VERSION 2.00
Begin Form frmSubstance
    BackColor       = &H00FFC0C0&
    Caption         = "Select substance"
    ClientHeight    = 4335
    ClientLeft      = 4200
    ClientTop       = 420
    ClientWidth     = 5325
    ControlBox      = 0 'False
    Height          = 4740
    Left            = 4140
    LinkTopic       = "Form3"

```

```

MaxButton      = 0   'False
MinButton      = 0   'False
ScaleHeight    = 4335
ScaleWidth     = 5325
Top            = 75
Width          = 5445
Begin CommandButton cmdCancel
  Caption      = "Cancel"
  Enabled      = 0   'False
  Height       = 435
  Left         = 2760
  TabIndex     = 3
  Top          = 3720
  Width        = 1575
End
Begin CommandButton cmdOkay
  Caption      = "Okay"
  Height       = 435
  Left         = 960
  TabIndex     = 2
  Top          = 3720
  Width        = 1455
End
Begin ListBox lstSub
  Height       = 1785
  Left         = 840
  TabIndex     = 1
  Top          = 840
  Width        = 3555
End
Begin Label Label2
  BackStyle    = 0   'Transparent
  Caption      = "To select a factor: Click on desired substance. The text you
have selected will appear highlighted. If there is only one substance, usually it will
automatically be selected for you."
  FontBold     = 0   'False
  FontItalic   = 0   'False
  FontName     = "MS Sans Serif"
  FontSize     = 8.25
  FontStrikethru = 0   'False
  FontUnderline = 0   'False
  Height       = 915
  Left         = 120
  TabIndex     = 4
  Top          = 2700
  Width        = 4875
End
Begin Label Label1
  BackStyle    = 0   'Transparent
  Caption      = "The identity you selected is true no matter what substance it
refers to. Select the substance that you would like this identity to apply to."
  Height       = 675
  Left         = 120
  TabIndex     = 0
  Top          = 120
  Width        = 5055
End
End
Sub cmdOkay_Click ()
  currentFactor.n.stuff = lstSub.List(lstSub.ListIndex)
  currentFactor.d.stuff = lstSub.List(lstSub.ListIndex)
  currentFactor.n.unit = currentFactor.n.unit & lstSub.List(lstSub.ListIndex)
  currentFactor.d.unit = currentFactor.d.unit & lstSub.List(lstSub.ListIndex)
  HintProgress = True
  frmSubstance.Hide
End Sub

Sub Form_Activate ()

```

```

    lstSub.Clear
    loadUpList
    If lstSub.ListCount > 0 Then lstSub.ListIndex = 0

End Sub

Static Sub loadSubstance (dummy As String)
Dim alreadyThereFlag As Integer
    If (dummy <> " ") And (dummy <> "") Then
        alreadyThereFlag = False
        If lstSub.ListCount > 0 Then
            For i = 0 To lstSub.ListCount - 1
                If lstSub.List(i) = dummy Then alreadyThereFlag = True
            Next i
        End If
        If alreadyThereFlag = False Then
            lstSub.AddItem dummy
        End If
    End If
End Sub

Static Sub loadUpList ()
    'If startingPoint.n.unitCanceled = False Then
    loadSubstance (startingPoint.n.stuff)
    'If startingPoint.d.unitCanceled = False Then
    loadSubstance (startingPoint.d.stuff)
    For i = 1 To numberFactorsSoFar
        'If unitFactor(i).n.unitCanceled = False Then
        loadSubstance (unitFactor(i).n.stuff)
        'If unitFactor(i).d.unitCanceled = False Then
        loadSubstance (unitFactor(i).d.stuff)
    Next i
    If lstSub.ListCount = 0 Then
        MsgBox "Error - this problem does not relate to any particular substance"
    End If
End Sub

```

FILE: FRMINTEX.FRM

VERSION 2.00

```

Begin Form frmInText
    BackColor      = &H00C0FFC0&
    Caption        = "Extract info from problem text"
    ClientHeight   = 3870
    ClientLeft     = 3960
    ClientTop      = 810
    ClientWidth    = 5265
    ControlBox     = 0 'False
    Height         = 4275
    Left           = 3900
    LinkTopic      = "Form4"
    MaxButton      = 0 'False
    MinButton      = 0 'False
    ScaleHeight    = 3870
    ScaleWidth     = 5265
    Top            = 465
    Width          = 5385
    Begin CommandButton cmdCancel
        Caption     = "Cancel"
        Height      = 375
        Left        = 1080
        TabIndex    = 3
        Top         = 2460
        Width       = 1335
    End
End

```

```

Begin CommandButton cmdOkay
    Caption      = "Okay"
    Height       = 375
    Left         = 2520
    TabIndex     = 2
    Top          = 2460
    Width        = 1455
End
Begin TextBox Text1
    Height       = 1575
    Left         = 120
    MultiLine    = -1 'True
    TabIndex     = 0
    Top          = 840
    Width        = 4935
End
Begin Label Label2
    BackStyle    = 0 'Transparent
    Caption      = "To select a factor: Click on the beginning of the first word,
and (while holding the mouse button down) move the cursor to the end of the last word.
Release the mouse button. The text you have selected will appear highlighted."
    FontBold     = 0 'False
    FontItalic   = 0 'False
    FontName     = "MS Sans Serif"
    FontSize     = 8.25
    FontStrikethru = 0 'False
    FontUnderline = 0 'False
    Height       = 915
    Left         = 180
    TabIndex     = 4
    Top          = 2940
    Width        = 4875
End
Begin Label Label1
    BackStyle    = 0 'Transparent
    Caption      = "Here's the text of the problem. Select the conversion factor
you wish to use to solve this problem, then click the OKAY button."
    Height       = 615
    Left         = 180
    TabIndex     = 1
    Top          = 180
    Width        = 4815
End
End
Option Explicit

Sub cmdCancel_Click ()
    currentFactor = nullFactor
    UnitFindingStage = 0
    frmInText.Hide
End Sub

Sub cmdOkay_Click ()
    Dim i As Integer
    Dim gotOneFlag As Integer
    gotOneFlag = False
    If (ThisInText(1) = True) Or (ThisInText(2) = True) Then
        MsgBox "Be sure you are not confusing the starting point or the answer with given
information."
    Else
        For i = 3 To numberOfGivenInfo + 2
            If (ThisInText(i) = True) And (gotOneFlag = False) Then
                currentFactor = givenInfo(i - 2)
                UnitFindingStage = 1
                gotOneFlag = True
            End If
        Next i
    End Sub

```



```

        If gotOneFlag = True Then
            frmInText.Hide
            If currentFactor.n.stuff = " " And currentFactor.d.stuff = " " And levelFlag
= 3 Then frmSubstance.Show 1
        Else
            MsgBox "Sorry, I could not identify any useful relationship in what you
selected Be sure you are selecting ALL the information necessary."
            End If
        End If
    End Sub

Sub Form_Activate ()
    If numberOfGivenInfo = 0 Then
        MsgBox "Sorry, there is no conversion factors given in text."
        frmInText.Hide
    Else
        text1.Text = problemText
    End If
End Sub

Sub Text1_Change ()
    text1.Text = problemText
End Sub

Static Function ThisInText (dummy As Integer) As Integer
Dim thisOneHereFlag, OtherOneIsnt, i As Integer
If text1.SelText <> "" Then
    OtherOneIsnt = True
    For i = 1 To numberOfGivenInfo + 2
        If i = dummy Then
            If InStr(text1.SelText, keyPhrase(i)) = 0 Then thisOneHereFlag = False Else
thisOneHereFlag = True
        Else
            If InStr(text1.SelText, keyPhrase(i)) <> 0 Then OtherOneIsnt = False
        End If
    Next i
    If (thisOneHereFlag = True) And (OtherOneIsnt = True) Then
        ThisInText = True
    Else
        ThisInText = False
    End If
Else
    MsgBox "You must first select something in the text."
    ThisInText = False
End If

End Function

```

SAMPLE LIST OF PROBLEMS

FILE: LSTPROB.TXT

*****Demonstration: Module 1

a:\lprobl.txt

1

1: Easy problem (Joanna)

a:\lprobla.txt

1

2 : Easy problem (gallon)

a:\lprob5.txt

1

3: Problem (meat)

a:\lprob3.txt

1

4 : Extra problem (soda)

```

a:\lprob4.txt
1
  5 :    Extra problem  (Nyssa)
a:\lprob2.txt
1
*****Demonstration: Module 2
a:\2problj.txt
2
*1*:    Easy problem  (prefix)
a:\2probl.txt
2
  2 :    Extra problem  (more prefix)
a:\2probla.txt
2
  3 :    Extra problem  (paper)
a:\2problb.txt
2
  4 :    Extra problem  (more paper)
a:\2problc.txt
2
*5*:    Given-info problem (cubits)
a:\2probl d.txt
2
*6*:    Denominator problem (speed)
a:\2prob6.txt
2
*7*:    Tougher problem (multistep)
a:\2prob2.txt
2
  8 :    Tougher problem (fishtank)
a:\2prob2a.txt
2
  9 :    Tougher problem (more fishtank)
a:\2prob2b.txt
2
 10 :    Tougher problem (ancient units)
a:\2prob2d.txt
2
*11*:   Long problem (Honda)
a:\2prob3.txt
2
 12 :   Long problem (beans)
a:\2prob4.txt
2
*13*:   Very long problem (fingernails)
a:\2prob5.txt
2
 14 :   Very long problem (more speed)
a:\2prob7.txt
2
 15 :   Tough problem (density)
a:\2prob8.txt
2
*****Demonstration: Module 3
a:\3problb.txt
3
*1*:    Easy problem  (aluminum)
a:\3probla.txt
3
  2 :    Problem  (mercury)
a:\3probl.txt
3
  3 :    Problem  (cost of gas)
a:\3problc.txt
3
  4 :    Problem  (Holston river)
a:\3prob2.txt
3

```

```

5 :    Tougher problem  (water freezing)
a:\3prob3.txt
3
6 :    Tougher problem  (alchemy)
a:\3prob5.txt
3
7 :    Tougher problem  (gasoline energy)
a:\3prob6.txt
3
8 :    One more problem (ancient units)
a:\3prob7.txt
3

```

SAMPLE PROBLEM

FILE: 3PROB6.TXT

```
' the next line is the text of the problem
```

```
-
```

One gram of gasoline (when burned) will produce 11.4 dietary Calories of energy. How many calories of energy can be produced from the gasoline in a 20.0 gallon gas tank?

```
' the number of factors to input
```

```
3
```

```
-----
' Key phrase for correct answer
```

```
How many calories of energ
```

```
'number- numerator- correct answer
```

```
590000
```

```
'sigfig- numerator- correct answer
```

```
2
```

```
'unit- numerator- correct answer
```

```
Calorie energy
```

```
'stuff- numerator- correct answer
```

```
energy
```

```
'number- denominator- correct answer
```

```
1
```

```
'sigfig- denominator- correct answer
```

```
99
```

```
'unit- denominator- correct answer
```

```
'stuff- numerator- correct answer
```

```
-----
' Key phrase for starting point
```

```
20.0 gallon ga
```

```
'number- numerator- starting point
```

```
20.0
```

```
'sigfig- numerator- starting point
```

```
3
```

```
'unit- numerator- starting point
```

```
gal gasoline
```

```
'stuff- numerator- starting point
```

```
gasoline
```

```
'number- denominator- starting point
```

```
1
```

```
'sigfig- denominator- starting point
```

```
99
```

```
'unit- denominator- starting point
```

```
'stuff- numerator- starting point
```

```
-----
' Key phrase for given info 1
```

```
ne gram of gasoline (when burned) will produce 11.4 dietary Calories of energ
```

```
'number- numerator- given info 1
```

```
11.4
```

```
'sigfig- numerator- given info 1
```

```

3
'unit- numerator- given info 1
Calorie energy
'stuff- numerator- given info 1
energy
'number- denominator- given info 1
1
'sigfig- denominator- given info 1
99
'unit- denominator- given info 1
g gasoline
'stuff- numerator- given info 1
gasoline

```

```

-----
' Key phrase for given info 2

```

```

'number- numerator- given info 2

'sigfig- numerator- given info 2
99
'unit- numerator- given info 2

'stuff- numerator- given info 2

'number- denominator- given info 2

'sigfig- denominator- given info 2
99
'unit- denominator- given info 2

'stuff- numerator- given info 2

```

```

-----
' Key phrase for given info 3

```

```

'number- numerator- given info 3

'sigfig- numerator- given info 3
99
'unit- numerator- given info 3

'stuff- numerator- given info 3

'number- denominator- given info 3

'sigfig- denominator- given info 3
99
'unit- denominator- given info 3

'stuff- numerator- given info 3

```

```

-----
' Key phrase for given info 4

```

```

'number- numerator- given info 4

'sigfig- numerator- given info 4
99
'unit- numerator- given info 4

'stuff- numerator- given info 4

'number- denominator- given info 4

'sigfig- denominator- given info 4
99
'unit- denominator- given info 4

```

'stuff- numerator- given info 4

Appendix C

DAPSIC Evaluation Handouts

The following pages contain the instructions, quizzes, worksheets, and feedback questionnaire that were given to the students in the evaluation of DAPSIC. Students in group A received the sheets in the following order: consent form, general directions, pre-tutorial quiz, worksheet, quiz, computer tutorial assignment, questionnaire. Students in group B received the sheets in the following order: consent form, general directions, pre-tutorial quiz, computer tutorial assignment, quiz, worksheet, questionnaire. The general directions sheet for each group was slightly different. Both versions are included here. All other sheets were identical for each group.

The consent form was originally written before obtaining permission from the instructors of CHEM 111 and CHEM 121. After the instructors reviewed the materials, they expressed an interest in having a fixed amount of academic credit for participation in the study (with the understanding that they would receive credit for an alternative assignment if they chose not to participate, and that they would still receive credit if they did the assignments but did not sign the consent form.) The consent form was altered accordingly. This modified version was approved by the chairman of the Human Subjects Review Board. The final version of the consent form is included here.

All sheets were written by the author while at MTSU.

USE OF THE DAPSIC TUTORIAL PROGRAM IN CHEMISTRY LAB
Consent and Release form

Dear Student,

I am currently working on my doctorate in Chemistry at MTSU. As part of my research I am developing a computer program called DAPSIC to provide students with practice solving unit conversion problems. To evaluate the effectiveness of this program compared to traditional methods of practicing this skill, I would like to invite you to participate in a study during this laboratory period.

Participation in this study is entirely voluntary; it will not be graded* as part of your chemistry course. You may choose to withdraw from this study at any time.

IF YOU CHOOSE TO PARTICIPATE:

During this laboratory period, you will be given a short quiz, testing your ability to do unit conversions. You will then be randomly assigned to one of two groups: Students in group A will be given a worksheet with practice problems to work through, with an answer key provided for checking answers. Students in group B will work through practice problems on the computer. After a period of time (no more than 1 hour) students will stop work and take a second short quiz. After the quiz students in group A will be provided an opportunity to use the computer, group B will be provided an opportunity to work through the worksheet. After all students have been exposed to both methods, you will be asked (on a questionnaire) your opinion about the use and usefulness of these two methods, and also some basic demographic information about yourself.

Results of this study will be summarized and included in my doctoral research. Summary results may be included in my dissertation, in a presentation at a professional meeting, or in part of a research paper in a professional journal.

Individual responses will remain completely confidential. Your name will not be included in any permanent records, and all documents (other than this consent form) identifying you will be destroyed after the results have been summarized.

IF YOU CHOOSE NOT TO PARTICIPATE:

~~This laboratory period is not considered part of the graded laboratory curriculum for this course;~~ therefore you may decline to participate without any affect on your grade.* No information about you will appear in the study.

_____ I give my consent to participate in this study. I maintain that I am doing so of my own free will. I understand that my grade in this class will not be affected by my participation in this study, and that I have the right to withdraw from this study at anytime.

_____ I choose NOT to participate in this study. I understand that my grade in this class will in no way be affected by my choice not to participate.

NAME: _____

SIGNATURE: _____

DATE: _____

* A certain number of points (probably 10) will be given to those who complete this assignment. An alternative assignment will be given to those who choose not to participate.

General Directions - Please read

You are in group: **A**

- 1) Please do these sheets in the order they are presented. (pre-test quiz, worksheet problems, quiz, computer tutorial, questionnaire). Do not skip ahead.
 - 2) IF YOU ARE NOT SURE HOW TO SOLVE A PARTICULAR PROBLEM, just put down your best guess and go on to the next problem. Do not spend very much time on any one problem. THERE ARE SUGGESTED TIME LIMITS FOR EACH ASSIGNMENT. You do not have to answer all questions to get credit for this assignment.
 - 3) Note that the computer tutorial problems are the same as the worksheet problems. You may do as many computer tutorial problems as you like; you need not re-do all problems.
 - 4) If you are using a floppy disk, please turn it in with the sheets once you have completed the assignment.
 - 5) If you have any comments or problems, please contact me (Brian Hill). My e-mail address is "hillbr@bryannet.bryan.edu".
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General Directions - Please read

You are in group: **B**

- 1) Please do these sheets in the order they are presented. (pre-test quiz, computer tutorial, quiz, worksheet problems, questionnaire). Do not skip ahead.
- 2) IF YOU ARE NOT SURE HOW TO SOLVE A PARTICULAR PROBLEM, just put down your best guess and go on to the next problem. Do not spend very much time on any one problem. THERE ARE SUGGESTED TIME LIMITS FOR EACH ASSIGNMENT. You do not have to answer all questions to get credit for this assignment.
- 3) Note that the computer tutorial problems are the same as the worksheet problems. You may do as many computer tutorial problems as you like; you need not re-do all problems.
- 4) If you are using a floppy disk, please turn it in with the sheets once you have completed the assignment.
- 5) If you have any comments or problems, please contact me (Brian Hill). My e-mail address is "hillbr@bryannet.bryan.edu".

DAPSIC: Chemistry tutorial worksheet

INTRODUCTION: Dimensional analysis (also known as factor label method or unit analysis) is a useful method for solving a variety of problems in chemistry. To illustrate this method, let's examine a metric to English conversion problem:

How many inches are equal to 9.29 centimeters? To solve this problem, we need to know that 1 inch is equal to 2.54 centimeters. (This is one of the three metric to English conversion factors you will use in this tutorial). Expressed mathematically, we can say:

$$2.54 \text{ cm} = 1 \text{ inch}$$

Now let's divide both sides of this equation by 2.54 cm. Note: we divide not just by 2.54, but by 2.54 cm. The unit may be regarded as part of this quantity and may NOT be omitted). We will obtain the following:

$$\frac{2.54 \text{ cm}}{2.54 \text{ cm}} = 1 = \frac{1 \text{ inch}}{2.54 \text{ cm}}$$

The fraction we obtain (1 in. / 2.54 cm.) is called a unit factor. It is numerically equal to 1, (Since 2.54 cm = 2.54 cm, the numerator and denominator on the left will cancel).

Now let's get back to converting 9.29 cm to inches. Since our unit factor is equal to 1, we can multiply 9.29 cm by this quantity, and its value will not change. We can also cancel out the unit "cm" - since it appears in both the numerator and denominator, it will cancel:

$$9.29 \text{ cm} \quad \times \quad \frac{1 \text{ inch}}{2.54 \text{ cm}} = \frac{9.29 \times 1 \times \text{inch} \times \cancel{\text{cm}}}{2.54 \cancel{\text{cm}}} = 3.66 \text{ inch}$$

3.66 inches is the correct answer, rounded to three significant figures.

Dimensional analysis, then, is the method of solving conversion problems using unit factors. The unit factor may be a metric to English conversion factor, or an English to English conversion factor, or even a factor given in the text of a problem. Often, more than one unit factor may be needed to solve a problem. In any case, you can multiply and cancel units to solve a particular problem.

CONVERSION FACTORSMetric-metric conversions:

$$1.1 \text{ qt} = 1 \text{ L} \quad 454 \text{ g} = 1 \text{ lb} \quad 2.54 \text{ cm} = 1 \text{ in}$$

Metric prefixes

$$1 \text{ centi} = 0.01 \quad 1 \text{ milli} = 0.001 \quad 1 \text{ kilo} = 1000$$

English conversions

$$1 \text{ ft} = 12 \text{ in} \quad 3 \text{ ft} = 1 \text{ yd} \quad 5280 \text{ ft} = 1 \text{ mile} \\ 4 \text{ qt} = 1 \text{ gal} \quad 16 \text{ oz} = 1 \text{ lb}$$

Time

$$60 \text{ sec} = 1 \text{ min} \quad 60 \text{ min} = 1 \text{ hr} \quad 24 \text{ hr} = 1 \text{ day} \quad 7 \text{ day} = 1 \text{ week} \quad 365 \text{ day} = 1 \text{ year}$$

Pre-tutorial Quiz

This pre-test is given to assess your current knowledge of unit conversion problems. Please answer the following questions. If you don't have a calculator, simply show how you would set up the calculation.

- 1) Convert 5.0 inches to centimeters

- 2) Convert 65 miles/hour to meters/second

- 3) It costs \$1.19 to purchase a 2 liter bottle of soda. Calculate the cost of 6.5 fl. oz. of this soda.

Given information

$$1 \text{ mile} = 5280 \text{ ft}$$

$$2.54 \text{ cm} = 1 \text{ inch}$$

$$1 \text{ ft} = 12 \text{ in}$$

$$1 \text{ m} = 100 \text{ cm}$$

$$1 \text{ cup} = 8 \text{ fl. oz.}$$

$$4 \text{ cup} = 1 \text{ qt}$$

$$1 \text{ liter} = 1.1 \text{ qt}$$

WORKSHEET PROBLEMS:

Do each of the following problems. After you are done, check your answers, Answers key is included on the last page).

- 1) When Joanna Hill was born she weighed 8.38 pounds. Convert this weight to grams.

- 2) A type of meat is sold for \$1.89 per pound. Convert this to dollars per gram (HINT! Note that now you need to cancel pounds from the denominator.)

- 3) Convert 500 centimeters to meters.

- 4) One cubit equals 18 inches. Convert 6.5 cubits to inches.

- 5) Convert 65 miles per hour to miles per minute

- 6) Convert 6.5 feet to meters. (NOTE: You will not be able to convert directly from feet to meters. You will need to convert to inches.)

- 7) A Honda Civic weighs 2500 lb. Calculate the mass in kg of 5 Hondas.

- 8) My fingernails grow at a rate of 1 mm every 1.5 weeks. Convert this velocity to miles per hour
- 9) Convert 250 mL of alcohol to grams, {HINT: You will need to use the density as a unit factor, Alcohol has a density of 0.789 g/mL.}
- 10) Convert 5.00 grams of aluminum to mL. (Density of aluminum = 2.7 g/mL)

ANSWER KEY:

(all answers rounded to the correct number of significant digits)

- 1) 3800 g
2) 0.00416 dollars per gram (in other words, 0.4 cents per gram)
3) 5.00 m
4) 117 in
5) 1.08 mile per minute
6) 2.0 m
7) 5700 kg
8) 2.47 times ten to the negative ninth miles per hr
9) 200 g alcohol
10) 1.85 mL aluminum

Quiz

Please answer the following questions. If you don't have a calculator, simply show how you would set up the calculation.

- 1) Convert 5.0 inches to centimeters

- 2) Convert 65 miles/hour to meters/second

- 3) It costs \$1.19 to purchase a 2 liter bottle of soda. Calculate the cost of 6.5 fl. oz. of this soda.

- 4) A tree grows 15 inches in a year. What is the speed of this growth in cm/hour?

- 5) An 8 foot board has a mass of 3 pounds. Calculate the mass in grams of a 10 cm section of this board.

Given information

1 mile = 5280 ft
2.54 cm = 1 inch
1 ft = 12 in
1 m = 100 cm
1 cup = 8 fl. oz.
4 cup = 1 qt
1 liter = 1.1 qt
1 year = 365 days
454 grams = 1 lb

Computer Tutorial Assignment

Directions:

- 1) Find a computer that runs either Windows 3.1 or Windows95. (NOTE: This disk was virus-checked when you received it. If you use it on more than one computer, be sure to virus-check it between uses.)
- 2) Start the program:
 - a) Windows 3. 1: Place the floppy disk in the drive. On screen you should see the window labeled "Program Manager". At the top of the menu you will see the menu (white rectangle with the words "File Option Window..." etc.) Click on "File", and you will see a new list. Click on the item labeled "Run". You will now see a textbox labeled "Command Line"; type "A:DAPSIC" in it, and click "OK".
If "A:DAPSIC" doesn't work, try "B:BDAPSIC". This is the version that will work on a B: drive.
 - b) Windows 95: Place the floppy disk in the drive. On screen you will either see an icon labeled "My Computer" or "A: Drive". If you see "My Computer", double click on it; you will now see a window with an icon labeled "A: Drive" or "Floppy Disk Drive". Double click on it.
You will now see the contents of the disk. Double click on the icon for "DAPSIC". If that doesn't work, try double clicking on the one labeled "BDAPSIC"; this is the version that works on a B: drive.
- 3) You should see a window labeled "DAPSIC: Dimensional Analysis Problem Solving In Chemistry." Look below it; you will see a space to enter your name. Please do so, then click "Go to problem list".
- 4) The first problem is labeled "*****Demonstration - Module 1 "; do this problem. Note that the text of the problem gives explicit step-by-step instructions; just follow these directions, and you should have no difficulty solving the problem.
- 5) Once you have finished with the demonstration problem, please do the other problems marked with an asterisk ("*"). This includes the demonstrations of the other modules.
- 6) When you are done, click "Quit". Don't forget to remove the floppy disk from the computer.

QUESTIONNAIRE

Name: _____

Age: _____

Year at school (freshman, sophomore, etc.): _____

Have you had chemistry in high school? _____

What was your last math course (either high school or college)? _____

SAT or ACT scores: _____

Have you had experience working with computers? _____

If so, circle those systems you have experience working with:

Macintosh Windows DOS Other(specify)

Circle your response to the following statements:

1) I feel confident that my math background is adequate in order to do well in this chemistry course.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

2) In general, I enjoy math and science courses.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

3) I felt confident in my ability to do unit conversion problems before I enrolled in this chemistry course.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

4) I feel that it was helpful to me to do the practice problems in this study (both on paper and on computer).

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

5) I feel that working problems on the computer was more beneficial than working problems on paper.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

6) I feel comfortable working with computer tutorial/educational software in general.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

7) I was able to understand how to use this computer tutorial.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

8) I would continue to use computer tutorials of this type in this course if given the opportunity to do so.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

9) I would recommend that this computer tutorial continue to be offered as part of this course next year.

STRONGLY AGREE, AGREE, DISAGREE, STRONGLY DISAGREE, NO OPINION

COMMENTS: Please list below any suggestions or comments you have about this study and this software...

Appendix D

DAPSIC Evaluation - Student Data

The following table lists the raw data obtained from the evaluation of DAPSIC.

St#: Student number (assigned in place of student name)

Cls: Chemistry class (either CHEM 111 or CHEM 121)

Grp: Group (A= worksheet first, B=DAPSIC first)

Pre-test: Questions 1, 2, and 3 of the pre-test quiz (r= answered correctly, w= answered incorrectly)

Post-test: Questions 1, 2, and 3 of the pre-test quiz (r= answered correctly, w= answered incorrectly)

Age: Age reported by student on questionnaire

HS chm: High school chemistry (y= student had chemistry in high school, n= student did not)

SAT/ACT: Score reported by student on questionnaire (nr= no response)

Questionnaire item: Answer circled by student for each questionnaire item:

1= Strongly Agree

2= Agree

3= Disagree

4= Strongly Disagree

5= No Opinion

Table D.1
Student Data from DAPSIC Evaluation

St#	Cls	Grp	Pre-test			Post-test			age	HS Chm	SAT/ACT	Questionnaire item								
			1	2	3	1	2	3				1	2	3	4	5	6	7	8	9
1	121	A	r	w	w	r	r	w	20	Y	nr	2	3	3	2	3	2	2	2	2
2	121	A	r	r	r	r	r	r	23	Y	29	1	1	1	2	3	2	2	2	2
3	121	A	r	r	r	r	r	r	19	Y	29	1	2	3	1	3	4	1	2	2
4	121	B	r	w	r	r	r	r	25	Y	nr	1	1	1	1	1	1	2	1	1
5	121	B	r	r	r	r	r	r	26	Y	19	2	2	3	1	2	2	2	1	1
6	121	B	r	r	r	r	r	r	19	Y	24	2	1	2	2	3	2	1	2	2
7	121	B	r	r	r	r	r	r	18	Y	26	2	1	3	1	5	2	2	2	2
8	121	A	r	w	r	r	r	r	22	Y	26	2	5	3	2	2	2	2	2	2
9	121	A	r	w	w	r	w	w	19	Y	22	2	2	3	1	1	1	1	1	1
10	121	B	r	w	w	r	w	w	19	Y	19	2	1	2	1	2	1	1	2	1
11	121	B	r	w	w	r	w	r	26	Y	1100	5	3	4	1	1	1	1	1	1
12	121	A	r	r	w	r	w	w	23	Y	nr	1	1	2	1	3	2	2	5	5
13	121	A	r	r	w	r	r	w	18	Y	23	2	2	2	1	3	1	1	2	2
14	121	B	r	w	r	r	w	r	18	Y	28	3	5	2	2	2	1	1	1	1
15	121	B	r	w	w	r	w	w	19	Y	20	2	2	3	2	2	2	2	1	1

Table D.1, Continued
Student Data from DAPSIC Evaluation

St#	cls	grp	Pre-test			Post-test			age	HS Chm	SAT/ACT	Questionnaire item								
			1	2	3	1	2	3				1	2	3	4	5	6	7	8	9
16	121	A	r	r	r	r	r	r	23	Y	29	2	2	2	1	1	1	1	1	1
17	121	A	r	w	w	r	w	w	18	Y	21	2	3	2	1	4	2	2	2	5
18	121	A	r	w	r	w	w	r	18	Y	30	1	2	1	1	2	2	2	2	2
19	121	A	r	r	r	r	r	r	32	Y	nr	2	2	2	2	3	2	2	3	2
20	121	B	r	r	r	r	r	r	20	Y	22	1	2	2	2	2	2	2	2	1
21	121	A	r	w	w	r	w	w	19	Y	23	2	2	3	2	5	2	1	2	2
22	121	A	r	r	w	r	r	w	20	Y	18	2	2	2	1	3	2	2	2	2
23	121	A	r	w	r	r	r	r	27	Y	24	5	1	3	2	5	2	2	1	2
24	121	A	r	w	w	r	r	r	18	Y	31	2	2	3	2	5	2	2	2	2
25	121	A	r	r	r	r	r	r	23	N	nr	3	3	3	1	2	3	2	1	1
26	121	B	r	r	w	r	r	w	20	Y	19	1	1	1	2	3	2	2	5	5
27	121	A	r	w	r	r	w	w	23	Y	19	2	1	3	1	2	1	2	2	1
28	121	A	r	w	w	r	w	w	19	Y	21	2	2	4	1	2	2	3	1	1
29	121	B	r	w	w	r	w	w	20	Y	16	1	2	2	4	1	1	1	1	1
30	121	B	r	w	r	r	r	r	19	Y	23	2	2	3	1	5	1	1	1	1
31	121	B	r	w	w	r	r	w	37	N	nr	3	2	3	2	3	1	1	2	1
32	121	A	r	w	w	r	w	w	27	Y	nr	2	2	4	2	5	2	2	5	5
33	121	B	r	w	w	r	w	w	24	Y	nr	1	1	2	1	2	1	1	1	1
34	111	B	w	w	r	w	w	r	19	Y	31	2	2	2	1	3	2	2	2	2
35	111	A	r	w	r	r	r	r	18	Y	30	2	2	2	2	5	2	5	2	2
36	111	B	r	w	r	r	r	r	18	Y	27	1	2	1	1	5	1	1	5	2
37	111	B	r	w	w	r	w	r	36	N	nr	3	2	3	3	3	3	3	2	3
38	111	B	r	w	w	r	r	r	45	N	nr	2	2	3	2	2	2	2	2	2
39	111	B	r	w	r	r	w	r	26	N	21	1	1	1	1	1	1	2	1	1
40	111	A	r	r	w	r	w	w	30	N	nr	2	2	4	1	2	2	3	2	2
41	111	B	r	w	w	r	r	r	19	N	23	2	2	3	1	1	1	1	1	1
42	111	A	r	r	r	r	r	r	21	Y	1024	1	1	3	2	3	2	3	2	2
43	111	A	r	r	r	r	r	r	19	Y	1150	1	5	1	5	2	3	4	3	2
44	111	B	r	r	w	r	r	w	20	Y	21	2	2	4	1	5	2	1	1	1
45	111	A	r	r	w	r	r	w	18	Y	21	2	5	3	2	2	2	2	1	1
46	111	B	r	r	r	r	r	r	20	Y	23	1	1	2	1	3	2	1	2	2
47	111	A	r	r	r	r	r	r	26	N	nr	2	2	2	1	1	1	1	1	1
48	111	B	r	w	w	r	w	w	35	N	nr	2	2	3	1	1	1	2	1	1
49	121	B	r	r	r	r	r	r	22	Y	32	1	1	1	2	1	1	1	1	2
50	121	A	r	r	r	r	r	r	19	Y	22	1	2	2	1	1	2	2	1	1
51	121	B	r	w	w	r	w	w	18	Y	21	3	2	3	1	1	1	1	1	1
52	121	B	r	r	w	r	r	w	18	Y	25	2	1	3	1	1	1	1	1	1
53	121	A	r	w	w	r	w	w	19	Y	nr	3	2	2	1	1	1	1	1	1
54	121	A	r	r	w	r	w	w	26	Y	31	2	2	2	2	4	2	2	2	2
55	121	B	r	w	w	r	w	w	25	Y	27	3	3	3	2	2	3	2	1	1
56	121	A	r	w	w	r	w	w	25	Y	21	4	3	4	2	2	2	2	2	2
57	121	B	r	w	w	r	w	w	25	N	18	2	3	1	1	4	1	1	1	1
58	121	A	r	w	r	r	w	w	20	N	25	2	1	2	2	3	1	2	2	2
59	121	B	r	w	r	r	w	r	19	Y	20	2	2	2	2	3	3	2	2	3
60	121	A	r	w	w	r	r	w	19	N	nr	2	2	3	1	1	1	1	1	1

Table D.1, Continued
Student Data from DAPSIC Evaluation

St#	cls	grp	Pre-test			Post-test			age	HS Chm	SAT/ ACT	Questionnaire item								
			1	2	3	1	2	3				1	2	3	4	5	6	7	8	9
61	121	B	r	w	r	r	r	r	21	Y	19	2	3	3	2	1	1	1	2	2
62	121	B	r	r	r	r	r	r	27	Y	nr	1	2	3	1	2	2	2	3	2
63	121	B	r	r	r	r	r	r	21	Y	24	1	2	2	1	2	1	1	1	1
64	121	B	r	r	r	r	r	r	21	Y	21	1	1	1	1	2	1	1	1	1
65	121	A	r	w	w	r	w	w	19	Y	21	2	2	3	1	1	1	1	1	1
66	121	B	r	w	w	r	w	r	32	Y	nr	2	1	2	2	3	1	1	1	1
67	121	A	r	r	w	r	r	w	22	N	1080	2	1	2	2	2	1	1	1	1
68	121	A	r	r	w	r	r	w	25	Y	nr	2	2	2	2	2	2	2	2	2
69	121	A	r	r	w	r	w	w	25	Y	1090	2	1	2	1	2	2	2	2	2
70	121	A	r	r	w	r	r	w	19	N	1100	3	2	3	1	2	2	1	1	1
71	121	B	r	r	r	r	r	r	22	Y	30	1	2	5	1	2	3	1	1	1
72	121	B	r	w	w	r	w	w	28	N	nr	2	2	3	3	4	2	2	1	1
73	121	A	r	w	w	r	w	r	29	Y	21	1	2	2	1	2	2	1	2	1
74	121	A	r	r	r	r	w	r	43	Y	nr	3	2	3	3	1	1	2	2	2
75	121	A	r	r	r	r	r	r	18	Y	19	2	2	2	1	2	2	1	2	2
76	121	A	r	w	w	r	w	w	19	Y	nr	1	1	3	2	1	2	1	1	1
77	121	B	r	w	r	r	w	r	19	Y	28	1	1	1	5	3	2	1	5	2
78	121	B	r	w	r	r	w	r	18	Y	24	5	2	3	2	1	1	1	1	1
79	121	A	r	w	w	r	w	w	27	Y	nr	2	2	3	2	1	1	2	1	1
80	121	A	r	w	w	r	w	w	19	Y	1170	1	1	1	2	4	2	1	3	2
81	111	B	r	r	r	r	r	r	22	Y	18	1	1	1	1	1	1	1	1	1
82	111	A	r	w	r	r	w	r	35	Y	nr	3	3	3	1	3	2	2	1	1
83	111	A	w	w	r	w	w	r	24	Y	18	1	2	2	2	3	2	2	2	1
84	111	B	r	w	r	r	r	r	27	N	nr	2	2	2	2	1	1	2	2	2
85	111	B	r	w	r	r	w	r	19	Y	19	3	3	4	2	2	3	3	3	2
86	111	B	r	w	w	r	w	w	20	Y	21	4	4	4	2	2	2	3	2	2
87	111	B	r	r	r	r	r	r	19	Y	28	1	2	3	1	2	1	1	1	1
88	111	B	r	r	r	r	r	r	46	Y	1200	2	2	4	1	2	3	2	2	2
89	111	A	r	r	r	r	w	r	19	Y	17	3	2	3	1	3	2	2	2	2
90	111	A	r	r	r	r	r	w	20	Y	21	2	2	2	2	5	2	1	2	2
91	111	B	r	w	r	r	r	r	20	Y	20	1	1	1	1	1	1	1	1	1
92	111	B	r	w	w	r	w	r	30	N	nr	3	3	4	1	1	1	1	2	1
93	111	B	r	w	w	r	w	w	35	Y	nr	4	2	4	1	5	1	1	1	1
94	111	B	r	r	r	r	r	r	21	Y	1100	1	2	1	2	3	2	2	2	2
95	111	A	r	w	w	r	w	w	20	Y	19	2	2	2	2	3	3	2	3	3
96	111	A	r	w	w	r	w	w	18	Y	20	2	2	2	2	3	2	2	3	3
97	111	A	r	w	w	r	w	w	20	Y	23	2	2	3	2	2	2	2	3	3
98	111	A	r	r	r	r	w	r	32	N	nr	3	3	4	1	2	1	1	1	1
99	111	A	w	w	w	r	w	w	19	Y	21	1	1	1	1	1	1	1	1	1
100	111	B	r	w	r	r	r	r	47	Y	1320	1	1	1	1	3	2	1	2	2
101	111	B	r	w	r	r	w	r	21	Y	21	2	2	3	2	5	2	1	2	2
102	111	A	r	w	r	r	r	r	49	Y	nr	2	2	4	2	5	2	2	5	5
103	111	A	w	w	r	r	w	w	32	Y	nr	2	2	3	2	5	3	4	5	5
104	111	A	r	r	r	r	r	r	20	Y	18	2	2	3	2	2	2	2	2	2

Appendix E

Student Questionnaire Open Response Comments

Subject headers in **BOLDFACE CAPITALS**; Subheading in **boldface lowercase**; Comments from Chem111 underlined; comments from Chem121 in *italics*.

COMMENTS AND SUGGESTIONS ABOUT SPECIFIC PARTS OF THE PROGRAM THAT WERE UNCLEAR OR NEEDED IMPROVING

———improve screen layout (so all information is available, clear, and intuitively organized)

Provide information on screen about unit cancellation when using reciprocal's (sic). I forgot and one of the problems took longer than it should because of this.

Some of the answers on the computer tutorial (when the computer did the multiplication were something like this: $\text{—cm}^3 \times 100$. That is not what I would have factored with a calculator.

In the tutorial, try a bigger font for the numbers.

The screens covered up the units so i (sic) had to return to the menu to reread them.

Don't forget the misspelling on the (Info in text window.

———Info in problem text – unclear directions

I had difficulty with getting the question specific conversions to come up when I followed the directions.

I did not understand how to use the info in text until it was discribed (sic) by the instructor.

improve the "conversion in question" function to make it un (sic) clear. i.e. clicking on a conversion should highlight the conversion. It should not be necessary to highlight the information.

Some special options were somewhat hidden (i.e. "extra information"). However, they were not impossible to find.

———add "help" buttons

An option ex: "Explain Method" would also be helpful - similar to what they offer on the Windows Algebra tutorial.

I just wish there was a part to help if you got stuck on a particular part and didn't know what to do.

You could use an (sic) direction window during the problem during the first problem.

———add significant digits tutorial

The only improvement would be to write in an extra choice. It would have helped me if I had been given a choice of answers and I had to choose the one with the correct number of significant digits. I know significant digits are a new concept for me and it would have helped me a lot in learning if that was incorporated into the software.

Computer automatically calculates the answer using the proper number of significant digits. Significant digit's proper use would be a good tutorial.

——improve the “Select Problem” window

Mark the test questions to make it clear which you have done.

Note in the instructions the the (sic) questions are indexed automatically.

——have transition to “worksheet” -type problem

Making the student do the multiplication w/ their own calculator would have made it more similar to the way we are required to do a conversion on the actual test.

PROGRAM (OR SOME ASPECT OF IT) WAS CONFUSING

——conversion factor organization

I was unable to get any other conversion factors setup other than Metric-English. Some of the problems required English-Metric and I was unable to make that choice at the conversion factor window.

My only problem with the computer was remembering what I had decided I needed to do w/ the equation while trying to figure out if what I knew I needed was english or metric.

The computer problem about the Honda was unsolvable. {NOTE: This problem can only be solved by finding the information in the problem text. Apparently this student was unable to figure out the instructions for this window.}

Some of the conversion steps and problems were confusing.

The metric-metric dialogue box was a little confusing I thought.

——non-specific

although I was a little unsure how to use it.

Finally, through trial and error, I was able to grasp the concept.

Tutorial was a little confusing at first.

——how program handles “canceling units”

I was a little confused about putting in the #;s into the equations and the cancel units function.

I did not know what to cross out. I thought the computer would do that.

PROGRAM IN GENERAL WAS EASY TO USE

The instructions listed here were simple enough -

The software was very self-explanitory (sic) and I had no problem with accessing it on the computer.

This was a very nice program, it was also very easy to understand. Very well done.

Once I got comfortable with the tutorial, it was fast and easy.

The software was easy to use and informative.

The program itself was simple enough to use.

It is a very easy-to-run program

The computer made converting look comparatively easy to do.

PROBLEMS WITH IMPLEMENTATIONS AND ENVIRONMENT

——program did not function

my computer would not let me get into "problem list" - I don't know why.

My disk would not work in several different computers.

I would like to try the rest of the program as I am not familiar with this concept.

——problem with where room/setting where computer was being used

The workers in the computer lab would rather socialize than help me figure out which computer this would work on.

I suggest that the environment be more conducive (sic) to test taking situations - it was very distracting.

I felt a bit nervous with the person conducting the study looking over my shoulder. I am not implying that it affected my performance, but it was a bit uncomfortable.

——too slow

Too many computer steps with lag time can cause breaks in train of thought.

It took a while to do the computer aided teaching. I don't know if there would be enough class time for it.

——computer with non-functioning mouse

(comment made next to item 7) ..._Only after model_ example & mouse wasn't working properly.

{Comment made by student using a computer with a non-functioning mouse...} Make sure to give proper verbal instructions or how to choose/calculate answers on computer. i.e. using tab keys.

——windows environment distracting

Getting through the mechanics of learning what boxes to click on the tutorial can distract initially from the subject matter being taught.

PERSONAL STATEMENTS OF BACKGROUND OR ABILITIES

———strong (high school background)

I believe this is because I have such a strong background in this from high school.

I was able to master converting units in high school, so in truth, this was a review for me.

———strong (computer background)

The computer was OK for me because I had done it before but I don't know if anyone would do so well.

———strong (other)

however, I figured the answers out (and got all but one right (out of 8)) by deciding which units needed to be canceled and not so much by actually _knowing_ or _realizing_ what I was doing. Hence, the less than dramatic improvement on the second quiz (sorry).

———weak (chemistry and math background)

I personally don't know the conversions well, not even what's "English-Eng", "Metric-Metric" or "Eng-Metric."

Being that I hadn't been in High School Chem. for 9 yrs., I hadn't realized everything I didn't retain.

I have never been very strong in math and have been out of school for 2 and a half years since I graduated with my first degree in communication disorders.

I have not had a chemistry course in five years so I was a little nervous going into this course in college. I had forgotten some of the things involved in this course.

———weak (computer background)

I am not a computer literate person at this time.

I lack computer skills and become over-whelmed pretty quickly with unfamiliar software.

——non-specific

- we need all the help we can get.

+ I need all the help I can get!

——weak (ability to follow directions)

I found that my understanding of the directions was lacking. I have trouble following directions.

COMPARISON WITH WORKSHEET

——worksheet/paper practice needed also (need a transition to “worksheet”-type problems)

I do think practicing on paper also helps, since we will not have the conversion figures to look back on during our tests.

Maybe do it on paper first, then the computer to check + work on setting up the problem.

I also think that it is important to be able to do the worksheet because it makes you think more directly about _which units to convert to._

——worksheet/paper practice needed also (computer learning should not replace paper and pencil learning)

I don't think it should take the place of good old paper, pencil, + calculator. Students may use it as a crutch.

I do _not_, however, feel that working through these problems, solely on a computer, would be beneficial. I think that both methods of problem solving are important.

I think they are both very helpful but that they need to be used in conjunction to get well-rounded practice.

——worksheet practice needed also (paper preferred for easy problems)

The software was helpful on the more complicated problems. The easier ones I would rather do on paper.

——worksheet/paper practice needed also (non-specific)

Both were helpful.

COMPARISON WITH WORKSHEET

——worksheet/paper works better for me (easier to think/organize on paper)

With the papers, I was able to see it all and visualize what steps I needed when.

I had to think more on the paper quiz in which I had to go through a series of conversions for each problem.

I guess that I am old fashioned in that I still like to sort things out on paper in order to work them out in my brain.

I think this software will be good for students that use it, but it is better for me to try and work the problems by hand because it forces me to think more about it.

——worksheet/paper works better for me (learn/remember better on paper)

I learn better by writing things, but I also learned and benefited from working with the software.

I have learned that through writing out problems and solving them by hand, I tend to remember the techniques used, for a much longer time.

COMPARISON WITH WORKSHEET

——computer better than worksheet (saves time)

When doing conversions on paper it takes time to do all of the math.

———computer better than worksheet (more comfortable)

I felt much more comfortable working with the computer program than on the first worksheet.

———computer better than worksheet (non-specific)

The commuter (sic) was more help.

COMMENTS ON THE DESIGN CONCEPT OF PROGRAM

———helpful (forcing step-by-step approach)

The software makes it much easier to catch your mistakes + you have to follow through with each part of the conversion, so it was very helpful.

The software was very helpful showing step by step how to get the answer.

The program helped me to learn to do it step-by-step.

This program allows for easy manipulation of each step of a problem without making a confusing mess of one's paper.

I felt that the computer was helpful in that it teaches how to move through the steps_ (find the conversion factor, cancel units, etc...)

In general, I think the easy flow of problem solving w/ this program will build confidence in the individuals abilities and provide a helpful tool for studying.

———helpful (focus on method by automating mechanics)

I found the computer tutorial very beneficial b/c I could cover more territory in less time.

on the computer the math is done for you therefore giving more time and practice with the conversions.

I think I may have done better on the test had I done the computer test first where a definite pattern is observed of "cancel, multiply, put the desired measurement in the proper place of the numerator or denominator to be canceled (sic)". It makes it clear how to solve measurements. Puts more emphasis on setting up the problem rather than the multiplication.

———helpful (forcing cancellation of units)

Before, I thought about it too much, then I saw it was somewhat just about cancelling the units.

The idea behind the program, showing the canceling of units, is excellent.

———helpful (build from simple to complex problems)

The problems were challenging and some were simple, that made for a good mixture.

COMMENTS ON THE DESIGN CONCEPT OF PROGRAM (STEP-BY-STEP APPROACH/FOCUS ON METHOD INSTEAD OF NUMBERS/LACK OF MEMORIZATION REQUIRED)

———unhelpful for me (lack of required memorization)

For me memorization is the key. If you don't know what goes where then it's hard to do the problems.

I feel more challenged if I have to come up with units/conversions on my own.

———unhelpful for me (forcing step-by-step approach)

The only thing that could be found useful was in setting up the problems, but I already knew how to do that.

The fact that each conversion I did was offered directly on the tutorial made it a little easy (each problem was 1 step conversion) which is good + bad.

———unhelpful for me (focus on method by automating mechanics)

It provides more of a challenge for me to have to conceptualize what I am doing. After a while the conversion process seemed almost mechanical on the computer and I easily lost track of the "big picture" of the problem.

———unhelpful for me (non-specific)

I personally found that the computer tutorial didn't help me.

COMMENTS ON THE DESIGN CONCEPT OF PROGRAM (STEP-BY-STEP APPROACH/FOCUS ON METHOD INSTEAD OF NUMBERS/LACK OF MEMORIZATION REQUIRED)

———flawed in principle (automation)

Since the program gave you everything you needed to do the work and then did all the work for you I did not find it very helpful at all.

The software/program seems to make problem solving almost _too_ easy by giving a finite number of options from which to choose.

but it mainly helps you to choose the right units. Therefore the computer does all the work and you loose focus on _solving_ the problem.

(comment entered next to the "disagree" circled for item 8) *I want to learn - not have the comp do it for me.*

This tutorial makes conversion too easy. A person's mathematical ability is negated by this program. The only skill neccessary (sic) to use this program is the ability to negate like standards of measurement.

If the idea is to create easy conversion without math then this program is excellent, but I feel it may be too easy and contribute to the "Dumbing down of society" which seems to be so prevalent today. Shouldn't chemistry be more than clicking "yes" or "no".

———flawed in principle (factor label method)

I was hoping the software would do more to help with things we are supposed to do in class. Dimensional analysis is not required - it is only a recomended (sic) way to do problems.

The program did not allow simple math steps such as multiplying an answer by 5! (At least, I couldn't figure out how to do this.)
{NOTE: multiplying by a number without a unit is not part of the factor label method.}

———flawed in principle (cannot get the answer wrong)

The computer program almost seemed too easy. It was if you couldn't get it wrong.

The computer wouldn't allow me to enter a mistake.

———flawed in principle (step by step)

I did fine one little glitch in the program; while converting in metric units, one cannot go from, for example, kg to decigrams. One would have to go from kg to grams, then from grams to decigrams. In another opinion, though, it might be considered easier to take the 2 steps to go from kg to decigrams.

"I BENEFITTED (OR COULD BENEFIT) PERSONALLY"

———review

It helped "freshen up" on my conversions.

It was a review that I needed and benefited from.

This program brought some of the conversion back to me and helped me realize how much more I could learn through a computer tutorial such as this.

In that sense, the program did help me, as a review.

Participating in this study has helped me tremendously. I think I got back a lot of what I learned years ago. Doing the tutorial in the computer definitely made the "post-quiz" much easier.

———practice

The program was excellent and the practice really helped. Thanks.

Excellent practice! A few hours a week of this, and I could get really good at unit conversions.

I found this study interesting and very helpful. I feel that the practice will help me in my chemistry class. Thank you.

——building confidence

I thought this program was a great help in confidence building for me in both math as it applies to chemistry and use of computers.

I fell (sic) more confident taking the quiz on paper after doing the problems on the computer.

——understand

However, I do feel that use of the program on a regular basis, and with time to reflect on the how's and why's of each problem, that my _understanding_ and _retention_ would increase _dramatically_.

I began to understand conversion better.

——other (helpful)

This computer tutorial was a big help to me

I feel this could be a very helpful method of study for myself or other students.

PROGRAM WOULD BE BENEFICIAL FOR STUDENTS IN GENERAL

——keep for present and future students

and I believe it could be beneficially used in future courses.

I feel confident that this tutorial will be helpful to further classes. Thanks.

If possible, why not give it a chance this semester.

Please start the program _THIS YEAR!_

I would 100% recommend the computer tutorial for next year.

I feel that the computer tutorial should be a part of the chemistry course in the future.

This computer program could be very beneficial to all students.

——other (helpful)

The software program helped a great deal.

It was helpful.

Very helpful

This tutorial was very helpful in unit conversions.

——study

I think anyone could benefit from this software and that students should be encouraged to use this type of information, especially for study purposes.

——practice

I feel, however, that it would be a great program for someone to get a lot of practice on doing conversion problems.

——review

I feel that the computer exercises were a good reminder of things like density conversions.

PROGRAM WOULD BE BENEFICIAL TO STUDENTS OTHER THAN ME

——good for those less experienced than me

I think that this program would only be helpful to people with a very limited knowledge of algebra because all it does is teach basic algebra.

It may be more appropriate for high school students than college students.

——should be optional

I feel that offering this as part of the course next year, as an optional activity, would be a nice idea. Some other people may find that it is very helpful.

(comment entered next to "agree" circled for item 9): *but _not_ mandatory -- this seems like the easy way out.*

——different learning style might benefit

However, someone else who could absorb and process information differently might have a different response.

NON-SPECIFIC ENCOURAGING COMMENTS (INCLUDING THOSE FOLLOWED BY CRITICISMS, QUALIFICATIONS, ETC.)

Excellent software though.

Overall, I think it is an excellent program. Good luck.

Good program!

Seems like your program is designed well.

Thank you for the opportunity.

Good work overall!!

I enjoyed using the computer program.

Good luck with your research!

Thank you for your work. Keep it up

I enjoyed the experience and I hope it expands.

It is a great program.

Other than this, I found the program to be excellent.

& I thoroughly enjoyed using it.

Good experiment.

I think that this is a _great_ idea.

Other than this, it was interesting.

I liked the computer program a lot.

This software is good for teaching conversions.

Great idea!!!

Good job!

Thanx for the practice!

Everything else is in very good.

OTHER COMMENTS

"Chemical Concepts" is available in the LRC and I have tried (sic) to use it. (about -2 hrs.), it's OK.

I feel exposure is the key to understanding chemistry. A computer tutorial would give extra information which might not be understood in a lecture or reading. A computer tutorial would give additional exposure to chemistry problems, making it more understandable.

The computer, on the other hand, helps with precision.

Note: Somethings like this is needed in the Georia Dept. of Transportation – they have recently switched construction projects over to metric measurements.

I only had problems with knowing what to multiply be (sic) sometimes (like on quiz #3+5). I didn't know where to factor in the 6.5 fl.oz.

The quiz I did before the computer exercise I fell (sic) I did awful on.

{Commenting on computer tutorials in general} More of them should be provided for science classes of this nature.

I think I would learn more with computer tutorials. It has so many options.

Appendix F

Permission from the Institutional Review Board

An application was made to the Middle Tennessee State University Institutional Review Board for permission to conduct the research described in Part B. A copy of the letter granting permission to conduct research on human subjects is included on the next page.

on-campus memo:



MEMO

TO: Brian Hill

FROM: JAMES V. BALCH
Basic and Applied Sciences Representative
Institutional Review Board

RE: Research Application
IRB Protocol No. 97018
Submitted for expedited review
on 9/6/96

DATE: September 9, 1996

This is to officially notify you that your research proposal,

An Evaluation of the Effectiveness of the DAPSIC Computer Tutorial Program

qualifies, in my opinion, for expedited review and is herewith approved by me as the representative from your college of the Institutional Review Board. Good luck as you pursue this project.

A handwritten signature in cursive script that reads "James V. Balch".
James V. Balch

/mh

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indices and found no reference to the cyclopentadienylborane isomer. The 1st-4th indices are not indexed by formulae; however, no reference to cyclopentadienylborane could be found in the subject index under "cyclopentadiene" or "borane".

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