

EVALUATION OF FUNDAMENTAL ORGANIC CONCEPTS

by

MATTHEW DAVISSON WODRICH

(Under the Direction of Paul von Ragué Schleyer)

ABSTRACT

The concept of protobranching, defined as the net stabilization provided by 1,3-alkyl-alkyl interactions in all branched and *n*-alkanes except methane and ethane, and its implications are highlighted. Protobranching is assessed via Pople's isodesmic bond separation energy and has an average value of 2.8 kcal/mol for *n*-alkanes. Protobranching has a significant impact on the quantification of physical organic phenomena, including ring/cage strain, conjugation and hyperconjugation, and aromatic resonance energies. Historically, these quantities have been evaluated using propane and larger alkanes (both linear and branched) as reference compounds. However, the inherent stabilization within these "reference" compounds has not previously been considered. Reevaluated energies for the above mentioned phenomena are discussed. Protobranching has also been utilized to create a new isodesmic additivity scheme, capable of calculating heats of formation of alkanes, alkyl radicals, alkenes, and alkynes to high accuracy. Data fitting schemes based on geminal interactions are also explored. The ability of computational methods (HF, DFT, and post-HF) to compute the magnitude of protobranching stabilization is investigated. Pople's isodesmic bond separation reactions of *n*-alkanes (propane to decane) show systematic underestimation for all DFT functionals tested; they are unable to accurately account for the protobranching stabilization. In the final chapter, double aromaticity, the existence of two mutually orthogonal Hückel frameworks within the same molecule, of small carbon, boron, and borocarbon monocycles is analyzed using refined NICS techniques. Double aromaticity is confirmed in C₆ and C₁₀, as had been previously hypothesized. C₈ and C₁₂ are shown to be doubly antiaromatic. Select boron and borocarbon compounds are also shown to be doubly aromatic.

INDEX WORDS: COMPUTATIONAL CHEMISTRY, DENSITY FUNCTIONAL THEORY, PROTOBRANCHING, CONJUGATION, HYPERCONJUGATION, RESONANCE ENERGY, AROMATIC STABILIZATION ENERGY, AROMATICITY, DOUBLE AROMATICITY, BOROCARBON, ISODESMIC, HOMODESMOTIC, BOND SEPARATION ENERGY, ADDITIVITY SCHEME, HYDROCARBON

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DEDICATION

For my parents Dave and Sue Wodrich, because, “everyone gets a Ph.D.”

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 PREAMBLE

Chemists have long been interested in the determination of fundamental molecular properties, including molecular strain, aromatic resonance energy, and other stabilizing or destabilizing energetic effects. Typically, such effects cannot be measured directly by experiment, for example no instrument can tell you the resonance energy of benzene or the ring strain of cyclopropane. Such energies must be determined using alternate techniques. Generally, chemical equations are written, which compare the feature of interest to various “reference” compounds. Using the relevant heats of formation (or computed energies) a numeric value for the phenomena in question can be obtained. Clearly, numerous equations could be written, the result being a wide range of values. The problem lies in the choice of “reference” compounds, which ideally contain minimal perturbing effects. The importance of these choices is highlighted in this dissertation.

In addition to making use of available thermochemical data, computations are also of significant importance. The use of computations within the chemistry community has grown drastically over the past decade. This enhancement has been fueled by notable increases in computer speed, reduction in cost, and the awarding of the 1998 Nobel Prize in chemistry to John Pople and Walter Kohn. Since its advent, the field has branched considerable. Computations are no longer limited to small molecules, today proteins are regularly modeled using molecular mechanics, while the study of medium sized systems (~150 atoms) can even be accomplished using quantum techniques. In this dissertation, the majority of work has been conducted using density functional theory and makes use

of a small amount of Hartree-Fock and post Hartree-Fock *ab initio* methods. Below is a brief introduction into the theory behind the calculations that make up a significant portion of this work.

1.2 HARTREE-FOCK THEORY

The central theorem of quantum chemistry is Schrödinger's equation:

$$\hat{H}\Psi_i(x_1, x_2, \dots, x_N, R_1, R_2, \dots, R_M) = E_i \Psi_i(x_1, x_2, \dots, x_N, R_1, R_2, \dots, R_M), i = 1, 2, \dots, \infty \quad (1.2.1)$$

Where $\hat{H}$ is the Hamiltonian operator for an M nuclei and N electron molecular system.

The Hamiltonian represents the total energy in the form:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \quad (1.2.2)$$

Where A and B run over all M nuclei, while i and j represent the N electrons in the system. The first two terms of the Hamiltonian represent the electron and nuclear kinetic energy respectively, while the later three terms include the nuclear-electron attraction, as well as the electron-electron and nuclear-nuclear repulsions. The Born-Oppenheimer approximation allows for the simplification of the Hamiltonian into the Electronic Hamiltonian resulting from the significant mass difference between electrons and nuclei. This approximation allows the consideration that electrons move in a field of fixed nuclei. The Electronic Hamiltonian is represented by:

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.2.3)$$

Hartree first proposed an approximation for the atomic wave function in 1928.^[1] However, this approximation contained problems, namely it assumes electrons can be described independently of one another, and it is not anti-symmetric. The anti-symmetry problem was solved by Fock and independently by Slater,^[2] who proposed the use of an anti-symmetric determinant (now called the Slater determinant).

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(\vec{x}_2) & \cdots & \phi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{x}_N) & \phi_2(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix} \quad (1.2.4)$$

By minimizing the total energy of the Slater determinant using the interacting Hamiltonian, and enforcing orthogonality between the single-electron spin orbitals, one obtains the Hartree-Fock (HF) approximation. The expectation value of the total energy of the Hamiltonian is given by:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (1.2.5)$$

where H_i is an element of the one electron operator, J_{ij} is the Coulomb interaction of electrons i and j , and K_{ij} is the exchange integral.

$$H_i = \int \phi_i^*(\vec{r}) \left[-\frac{1}{2} \nabla_i^2 + \sum_{A=1}^M \frac{Z_A}{|\vec{r} - \vec{r}_{Ai}|} \right] \phi_i(\vec{r}) d\vec{r} \quad (1.2.6)$$

$$J_{ij} = \iint \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (1.2.7)$$

$$K_{ij} = \iint \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_i(\vec{r}_2) \phi_j(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \quad (1.2.8)$$

1.3 POST-HARTREE-FOCK METHODS

The use of perturbational methods provides a correction to the Hartree-Fock approximation. Møller-Plesset perturbation theory allows for the calculation of correlation energy, and is generally employed at the second order (MP2). The coupled-cluster methods (i.e. CCSD and CCSD(T)) also account for correlation energy, and use a linear combination of determinants to create the trial wave function. Methods like coupled-cluster progressively approach the “true” answer to the Schrödinger equation as more corrections are added (i.e. CCSD $\rightarrow$ CCSDT $\rightarrow$ CCSDTQ), but such corrections remain extremely computational expensive for even moderate sized molecular systems.

1.4 DENSITY FUNCTIONAL THEORY

The theory of density functionals is based on a rather simply premise, that one can describe all ground-state properties of an atomic or molecular system if the electron density $\rho(\mathbf{r})$ is known. In 1927, Thomas^[3] and Fermi^[4] were the first to attempt replacing the wave function with the electron density. This model (Equation 1.4.1) was based on a quantum statistical model of electrons in a fictitious uniform electron gas and provides a simple expression for the kinetic energy while treating nuclear-nuclear and electron-nuclear interactions in a classical way.

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} \quad (1.4.1)$$

In 1951, Slater developed the $X\alpha$ method^[5] as a way to approximate the non-local exchange contribution stemming from the anti-symmetry of the wave function in the Hartree-Fock method. While the intent was not to describe physical properties in terms of the electron density, Slater’s method exploits the electron density as its central quantity.

This work provides an expression for the exchange energy in terms of the electron density, and is given in equation 1.4.2.

$$E_{x\alpha}[\rho] \equiv C_x \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1 \quad (1.4.2)$$

Slater's work allows for the replacement of the complicated non-local exchange term in Hartree-Fock theory by a local term relying only on the electron density. Equation 1.4.2 was then refined with the addition of a semiempirical parameter, α , which could be adjusted to improve the quality of the approximation (Equation 1.4.3).

$$E_{x\alpha}[\rho] = -\frac{9}{8} \left(\frac{3}{\pi} \right)^{1/3} \alpha \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1 \quad (1.4.3)$$

Despite this earlier work, today the Hohenberg-Kohn theorem is widely regarded as the foundation of density functional theory.^[6] This proof relates the ground-state electronic energy, via the Hamiltonian, to a unique electron density ρ . *"The external potential $V_{ext}(\vec{r})$ is a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$."* Following this proof leads to an expression for electronic energy based on the electron density (Equation 1.4.4).

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + T[\rho_0] + E_{ee}[\rho_0] \quad (1.4.4)$$

Where $\int \rho_0(\vec{r}) V_{Ne} d\vec{r}$ (the potential energy due to nuclei-electron attraction) is system dependent while $T[\rho_0] + E[\rho_0]$ (independent of N , R_A and Z_A) is universally valid. Collecting the kinetic energy term (T) and the electron-electron energy term (E_{ee}) together we arrive at the Hohenberg-Kohn functional $F_{HK}[\rho_0]$, given by Equation 1.4.5.

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}[\rho_0] \quad (1.4.5)$$

If the Hohenberg-Kohn functional were known exactly, this would allow for the exact solution of the Schrödinger equation! Unfortunately, the true form of the Hohenberg-Kohn functional is unknown, and thus we must resort to approximations of this quantity.

The work of Kohn and Sham^[7] allowed a practical approach on how to approximate the universal Hohenberg-Kohn functional. Kohn and Sham proposed building a set of orbitals to form a non-interacting reference system. This system allows for the computation of the kinetic energy term to good accuracy. The remaining portion (relatively small compared to that calculated exactly) is left to be determined by the approximate functional. Thus, Kohn and Sham effectively have split the universal functional into a portion computed exactly, and the remaining exchange correlation energy (Equation 1.4.6 and 1.4.7).

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] \quad (1.4.6)$$

where

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{ncl}[\rho] \quad (1.4.7)$$

The calculation of this exchange-correlation energy remains unknown, however, several approaches have been developed for its approximation.

1.4.1 THE LOCAL DENSITY APPROXIMATION

Local density approximation (LDA)^[7] is based upon the model system of a hypothetical homogenous uniform electron gas.^[8] Within LDA, functionals follow the form

$$E_{xc}^{LDA}[\rho] = \int f(\rho(\vec{r})) d\vec{r} \quad (1.4.8)$$

with f being a function of ρ , the electron density. The exchange energy adopts the form of

$$E_x^{Dirac}[\rho] = -C_x \int \rho^{4/3}(\vec{r}) d^3r \quad (1.4.9)$$

from the homogenous uniform electron gas, where $C_x = (3/4)(3/\pi)^{1/3}$. Amongst the most popular parameterization is the VWN functional of Vosko, Wilk, and Nussair^[9] based on the Monte Carlo data of the uniform electron gas by Ceperley.^[10]

LDA has been used widely in the world of solid-state physics as well as materials science. Its use in chemistry must be cautious, as it has been shown to systematically overbind molecules, as well as provide mean absolute errors of ~ 100 kcal/mol for the heats of formations of molecules.^[11-13]

1.4.2 GENERALIZED GRADIENT APPROXIMATION

The generalized gradient approximation (GGA) employs the electron density and its derivatives to account from the inhomogeneity of ρ . GGA functionals have the form

$$E_{xc}^{GGA}[\rho] = \int f(\rho(\vec{r}), |\nabla\rho(\vec{r})|) d\vec{r} \quad (1.4.10)$$

where f is a function of the electron density, ρ , and its first derivative, $\nabla\rho$. Two correlation functionals in common use are the P86 of Perdew,^[14,15] and LYP of Lee, Yang, and Parr.^[16]

The exchange energy follows the form

$$E_x^{GGA}[\rho] = -C_x \int \rho^{4/3}(\vec{r}) F(s(\vec{r})) d\vec{r} \quad (1.4.11)$$

where $C_x = (3/4)(3/\pi)^{1/3}$ and $F(s)$ is the enhancement factor with $s = \frac{|\nabla\rho|}{(2\rho k_F)}$ and

$k_F = (3\pi^2\rho)^{1/3}$. Three of the most popular exchange functionals are B88 of Becke (equation 1.4.12),^[17] PW91 of Perdew and Wang (equation 1.4.13),^[18-20] and PBE of Perdew, Burke, and Ernzerhof (equation 1.4.14).^[21,22]

$$F^{B88}(s) = 1 + \frac{0.0042}{2^{1/3}C_x} \frac{b^2 s^2}{1 + 0.0252bs \arcsin(bs)} \quad (1.4.12)$$

$$F^{PW91}(s) = \frac{1 = 0.19645s \arcsin(7.7956s) + \left(0.2743 - 0.1508e^{-100s^2}\right)s^2}{1 + 0.19645s \arcsin(7.7956s) + 0.004s^4} \quad (1.4.13)$$

$$F^{PBE}(s) = 1 + 0.804 - \frac{0.804}{1 + \frac{0.21951}{0.804}s^2} \quad (1.4.14)$$

GGA represents a significant improvement for chemical applications, heat of formation mean absolute errors are reduced from ~ 100 kcal/mol in LDA to 5-10 kcal/mol in GGA.^[11-13]

1.4.3 HYBRID FUNCTIONALS

Due to the exact description of exchange in the Hartree-Fock formalism, Becke concluded that a fraction of exact exchange could be mixed with LDA or GGA exchange-correlation functionals, also known as hybrid functionals. This type of functional is, by far, the most used in the chemical community. In particular, the popular B3LYP,^[16,17,23] which is given by

$$E_{xc}^{B3LYP}[\{\phi_i\}] = E_x^{Dirac}[\rho] + E_c^{VWN3}[\rho] + 0.72(E_x^{B88}[\rho] - E_x^{Dirac}[\rho]) + 0.81(E_c^{LYP}[\rho] - E_c^{VWN3}[\rho]) + 0.2(E_x^{HF}[\{\phi_i\}] - E_x^{Dirac}[\rho]) \quad (1.4.15)$$

Other popular hybrid functionals include PBE0^[24,25] as well as B97-2.^[26] The later is known to be among the best functionals for predicting thermochemical properties,^[27] which are underestimated by GGA functionals.

1.4.4 META-GENERALIZED GRADIENT APPROXIMATION

The exchange-correlation energy of meta-GGA functionals make use of the electron density ρ , its first derivative $\nabla\rho$, and its second derivative, $\nabla^2\rho$ as well as the kinetic

energy density $\tau = \left(\frac{1}{2}\right) \sum_{i=1}^N \nabla\phi_i^* \cdot \nabla\phi_i$. These functionals take the form of

$$E_{xc}^{MGA}[\rho] = \int f(\rho(\vec{r}), |\nabla\rho(\vec{r})|, \nabla^2\rho(\vec{r}), \tau(\vec{r})) d\vec{r} \quad (1.4.16)$$

Popular MGGA functionals include VSXC of van Voorhis and Scuseria,^[28] as well as TPSS of Perdew.^[29]

1.5 CHAPTER SUMMARY

1.5.1 THE CONCEPT OF PROTOBRANCHING AND ITS MANY PARADIGM SHIFTING IMPLICATIONS FOR ENERGY EVALUATIONS

The new concept of protobranching is introduced and its implications discussed. Protobranching is defined as the net stabilizing 1,3-alkyl-alkyl interactions found in normal, branched, and most cycloalkanes, but not in methane or ethane. The protobranching stabilization is appreciable, 2.8 kcal/mol, and is easily assessed via Pople's isodesmic bond separation reaction. Because of protobranching stabilization, traditional equations for the evaluation of the branching effect, ring and cage strain, conjugation and hyperconjugation, and the resonance and aromatic stabilization energy of benzene must be reevaluated. Furthermore, the new block-localized wave function technique, which localizes the π bonds and precludes their conjugative interactions, provides alternative theoretically based estimates for hyperconjugation, conjugation, and aromatic resonance energies. Tests show several density functionals to underestimate the branching stabilization.

1.5.2 NEW ADDITIVITY SCHEMES FOR HYDROCARBON ENERGIES

A new isodesmic additivity scheme has been created based on energetic relationships of simple alkanes, alkyl radical, alkenes and alkynes. This scheme accurately reproduces experimental heats of formation for all systems studied, and makes use of conventional physical organic interpretations of the branching effect and hyperconjugation.

Furthermore, statistical data fitting to experimental heats of formation can be done to chemical accuracy using only four parameters. Several other data fitting schemes are also presented.

1.5.3 SYSTEMATIC ERRORS IN COMPUTED ALKANE ENERGIES USING B3LYP AND OTHER POPULAR DFT FUNCTIONALS

Isodesmic bond separation reaction energies have been calculated on normal alkanes using 16 different density functionals, as well as Hartree-Fock, MP2, CCSD(T), and G3 theory. All density functionals are shown to systematically underestimate the stabilization provided from protobranching interactions. The newly designed functionals designed for the purpose of describing weak interactions agree better with experiment, but still underestimate the stabilization. In contrast, G3 and CCSD(T) provide excellent agreement with experimental data, while MP2 overestimates. The popular B3LYP functionals is amongst the worst performers.

1.5.4 DOUBLE AROMATICITY IN CARBON, BORON, AND BOROCARBON RINGS

The aromaticity and double aromaticity of small carbon, boron, and borocarbon monocycles are probed using nucleus-independent chemical shifts (NICS) and refined NICS techniques. Double aromaticity, the presence of two orthogonal Hückel frameworks within the same molecule, is seen in $C_6H_3^+$, C_6^{4+} , $C_4B_4^{4+}$, C_6 , C_5B_2 , C_4B_4 , C_2B_8 , B_{10}^{2-} , B_{12} , C_{10} , C_9B_2 , C_8B_4 , C_7B_6 , C_6B_8 , and C_{14} . Double antiaromaticity is seen in C_8 and C_{12} , while mixed π /radial aromatic/antiaromatic systems are seen in C_7 and C_9 .

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CHAPTER 2

THE CONCEPT OF PROTOBRANCHING AND ITS MANY PARADIGM SHIFTING IMPLICATIONS FOR ENERGY EVALUATIONS[†]

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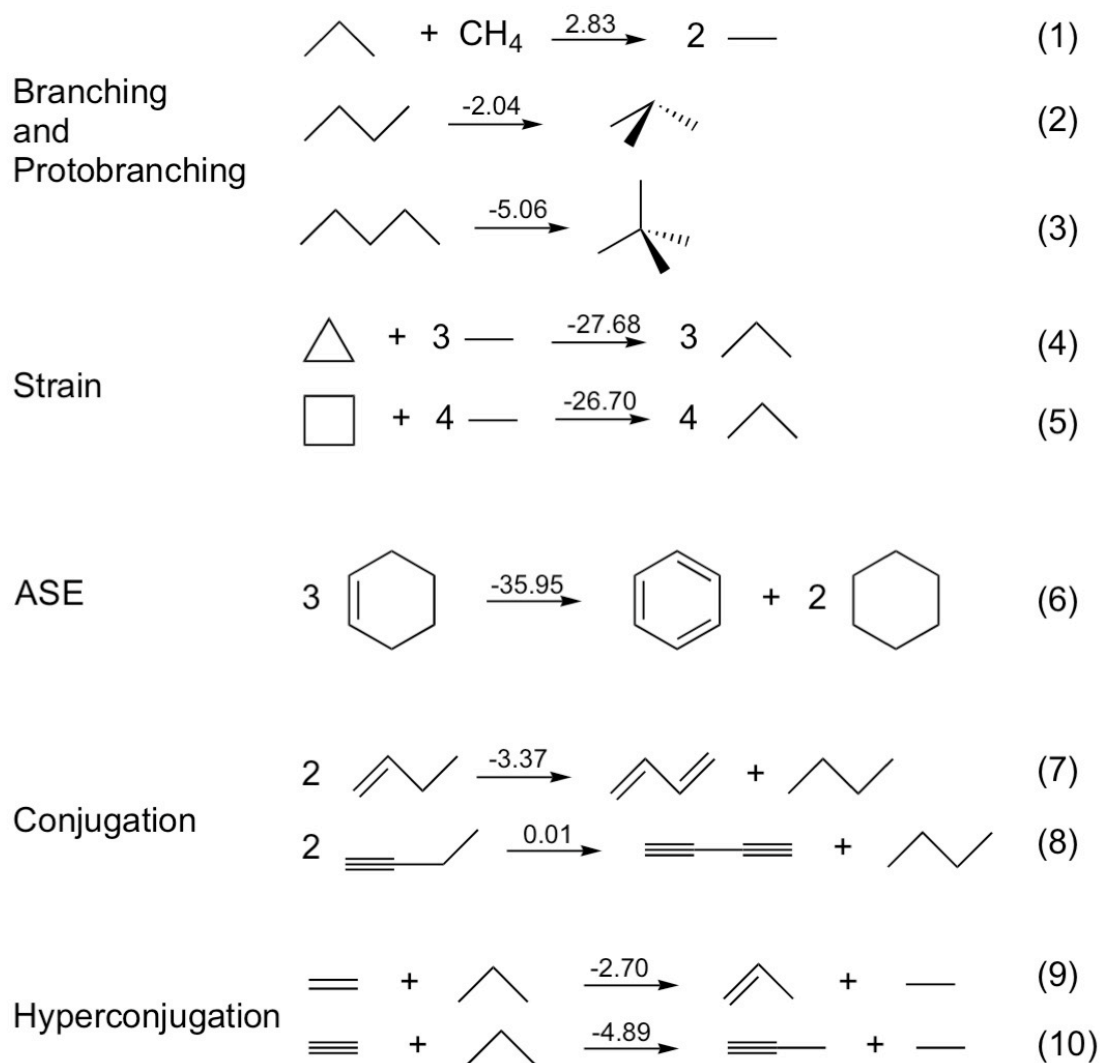
2.1 ABSTRACT

Topologically branched alkanes like isobutane and neopentane are more stable than their straight chain isomers, *n*-butane and *n*-pentane (by 2.04 and 5.06 kcal/mol, respectively, experimentally). Historically, this “branching effect” has been attributed largely to the greater number of attractive intramolecular 1,3–methyl or alkyl group interactions in branched species. There are three such stabilizing 1,3–interactions in isobutane and six in neopentane. Although fewer in number, the same type of 1,3-alkyl-alkyl interactions (which we name “protobranching”) also stabilize *n*-alkanes relative to methane and ethane. There is one protobranch in propane, two in *n*-butane, three in *n*-pentane, etc. While the energy of each protobranch is appreciable (2.8 kcal/mol on average, for the *n*-alkanes and cyclohexane), this has not been taken into account in conventional energy evaluations based on alkane reference standards and experimental energy data, e.g., of the strain of small rings, as well as the stabilizations due to conjugation, hyperconjugation, and aromaticity. When protobranching is considered, the ring strain of cyclopropane is reduced from 27.7 kcal/mol (based on three propane reference molecules, each stabilized by one protobranch) to 19.2 kcal/mol (Pople’s bond separation energy). When protobranching is considered, evaluations of the energies of hyperconjugation (5.5 and 7.7 kcal/mol for alkyl group stabilization of alkenes and alkynes, respectively) are considerably larger than the traditional estimates. Previous evaluations of the resonance energy (RE) of benzene were based on equations that gave widely diverging results. After adjusting for conjugation, hyperconjugation, and protobranching, all these equations give RE ~65 kcal/mol. The BLW (block localized wavefunction) method, which localizes the π bonds and precludes their conjugative interactions, provides alternative theoretically

based estimates for hyperconjugation, conjugation, and aromatic resonance energies. Protobranching is seriously underestimated by theoretical computations at levels (HF, DFT). Consequently, such levels, including the popular B3LYP functional, give bond separation energies, which, with larger molecules, differ increasingly greatly from experimental values.

2.2 INTRODUCTION

Many highly important chemical concepts such as aromaticity (Faraday, 1825;^[1] Kekulé, 1866)^[2], ring strain (Baeyer, 1885),^[3] conjugation (Thiele, 1899),^[4] alkane branching (Rossini, 1934;^[5] Nenitzescu, 1935)^[6] and hyperconjugation (Mulliken, 1939),^[7,8] depend upon the use and choice of reference compounds for their quantitative evaluation. Most of these are not directly measurable experimentally. Nevertheless, the quantities associated with these concepts are very significant for interpreting the behavior of molecules. Consequently, the availability of accurate thermochemical data dating from the 1930s stimulated chemists to devise evaluation methods to estimate energies attributed to these effects. Necessarily, these methods as well as the molecules used as references or models depend on arbitrary choices, however reasonable they may appear to be. The conventional equations most often employed for this purpose are illustrated in Scheme 2.1 Many other defining equations have been or might be employed.



Scheme 2.1. Conventional equations for the evaluation of protobranching (Eq 1), branching (Eq 2 and 3), ring strain (Eq 4 and 5), aromatic stabilization energy (Eq 6), conjugation (Eq 7 and 8), and hyperconjugation (Eq 9 and 10). Values in kcal/mol are based on experimental heats of formation at 298K.^[9]

The main purpose of this paper is to reexamine and reevaluate all of the energies in Scheme 2.1 based on a uniform treatment, which avoids what we perceive to be perturbing effects that “contaminate” their assessment. Our reevaluations result in substantial changes from the conventional values given in Scheme 2.1. In particular, note that propane, unbranched alkanes, and cyclohexane are employed as reference

compounds in all these equations, except equation 1. We argue that such alkanes are biased choices for the purpose since they benefit from stabilizing interactions, which are absent from the molecules being evaluated.^[10,11] Ideally, the best model reference compounds not only lack the feature of interest, but also all other perturbing effects as much as possible. While chemical knowledge has been refined enormously since the pioneering thermochemical evaluations of the 1930's, early equations to evaluate energies (Scheme 2.1) are still commonly cited. However, "perturbing effects," which were not known at the time, contaminate these evaluations. The present paper emphasizes a perturbing effect, "protobranching,"^[10-12] whose origin is the same as the well known branching effect. Protobranching stabilizes propane by an attractive 1,3-methyl-methyl interaction (Equation 1). In a similar manner, isobutane is stabilized by three 1,3-methyl-methyl interactions and neopentane by six 1,3-methyl-methyl interactions (Figure 2.1). These branched alkanes are more stable than their normal isomers, but the later also are stabilized by protobranching. *n*-Butane have two and *n*-pentane three stabilizing protobranching (1,3-alkyl-alkyl) interactions respectively. Homologation of any alkane, in either a *linear* or branched fashion, results in a larger number of stabilizing 1,3-alkyl-alkyl protobranching interactions. Although protobranching as a thermochemical effect, was recognized fifty years ago,^[13-15] its consequences have not been fully appreciated. We define protobranching as the net stabilizing 1,3-alkyl-alkyl interactions existing in normal, branched, and most cycloalkanes, but not in methane and ethane.

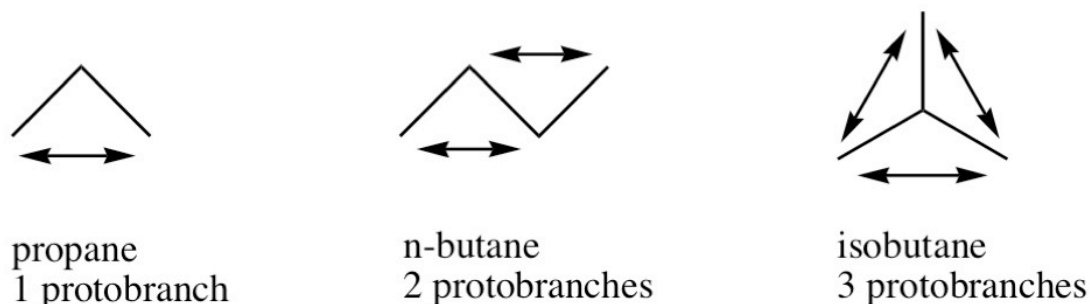


Figure 2.1. Protobranching interactions in propane (1), *n*-butane (2), and isobutane (3). Similarly, neopentane and cyclohexane have six protobranching interactions each. While branched alkanes have a greater number of protobranches, attractive 1,3-alkyl-alkyl interactions also are present in linear alkanes.

We emphasize that protobranching is directly related to the well known branching effect in alkanes. Branched alkanes were discovered in the 1930's to be more stable than *n*-alkanes through two independent lines of investigation, direct isomerization reactions, e.g., the AlCl_3 -catalyzed conversion of *n*-butane to isobutane,^[16,17] and the systematic thermochemical investigations sponsored by the American Petroleum Institute.^[5] The heat of formation of isobutane is 2.0 kcal/mol lower than *n*-butane, and neopentane is favored by 5.1 kcal/mol over *n*-pentane (Scheme 2.1, Equations 1 and 2). However, because of the stability of protobranching, the branching energies given by Equations 2 and 3 are underestimated since *n*-alkanes contain the same stabilization.

2.2.1. RELATIONSHIPS AND INTERPRETATIONS OF HYDROCARBON ENERGIES

Fajans' 1920 assumption^[18] that C-C and C-H bond energies were constant was negated in the 1930's when accurate thermochemical data became available.^[5] Although having the same number of two-atom CC and CH interactions, branched alkanes are more stable

than their normal alkane isomers. Starting with Eyring^[19] and continuing today, numerous research groups considered the energetic consequences of three-atom CCC, CCH, HCH interactions.^[15] However, the quantities and even the signs associated with such terms varied widely and are still disputed.^[20-22] Gronert's recent ad hoc treatment^[20,21] assumes that these three-atom interactions are all repulsive, but Wodrich and Schleyer^[22] found that a single attractive term reproduced an extended set of data equally well. Note that, these next-nearest-neighbor interactions are inherently incapable of accounting for the rotational barrier of ethane ("eclipsing strain") or the higher energies of gauche over anti-butane and of cis over trans 2-butene ("steric repulsion"). Grimme's analysis^[23] indicated that interpair correlations between orbitals of the same type (CC/CC and CH/CH) favored the branched form while CC/CH correlations lowered the energy of the linear isomer. He found that medium range (vicinal) interpair correlations

CH bond energies may typically be derived by taking $\frac{1}{4}$ the atomization energy (AE) of methane. Assuming that these CH bond energies are the same, the CC bond energy in ethane can be calculated from its AE. However, this treatment assumes that there are no three-atom (or higher) contributions arising from HCH interactions in methane and ethane or from HCC as well as HCCH interactions in the later. There is no satisfactory way to account for the rotational barrier of ethane on the basis of two- and three-atom interactions if these are assumed to be structure/conformation independent.

Two many two-atom, three-atom, four-atom, and higher terms are needed for a complete and trustworthy dissection for all the individual interaction energies of even a molecule as simple as propane. Molecular mechanics (MM) is the best approach along such phenomenological lines, but the same reservations apply. Although capable of

reproducing energies as well as many other physical properties very accurately, the success of MM depends on the empirical adjustment of many parameters as well as the assumptions of its basic methodology.

Quantum mechanics (QM) also can achieve high accuracy, but has still not solved the “alkane chain branching mystery” satisfactorily. Pitzer and Catalanos’^[24] 1956 analysis of neo vs. *n*-pentane, iso- vs. *n*-butane as well as propane vs. methane and ethane (our “protobranching”) attributed the energy differences to zero-point, thermal, and van der Waals attractive (London dispersion^[25]) effects. Indeed, HF and DFT levels, which do not describe dispersion, fail badly in reproducing the butane and pentane isomerization energies, as well as their isodesmic BSE’s and that of propane. In contrast, MP2, as well as CCSD(T) and other higher level correlation methods, succeed very well with all of these tasks.

Nevertheless, Pitzer’s “dispersion” explanation does not suffice. HF and DFT methods lack dispersion, but reproduce some “long range” effects, such as those responsible for the ethane and butane rotational barriers, as well as the 2-butene isomer differences quite well. Grimme^[23] considers “middle range” correlation effects to be more important than those at “long range,” but his recent conclusions also are subject to criticism.

We stress that we *are not* concerned with the details of these issues here. Instead, the primary purpose of this paper is to consider the consequences of the realization that propane and higher *n*-alkanes benefit from the same net stabilizing influences (whatever their detailed nature may be) that are responsible for the “branching effect” exemplified by isobutane and neopentane. Because of “contamination” by this “protobranching”

stabilization, we argue that *n*-alkane, cyclohexane, and other hydrocarbons are seriously compromised as reference molecules for the evaluation of energies associated with the basic concepts of ring strain, hyperconjugation, conjugation, and aromaticity. Their conventionally evaluated energies can change two-fold when protobranching is taken into account. All the energies employed in this paper (unless otherwise noted) are based on the experimental heats of formation at 298K given in the NIST compilation. Although superior conceptually, 0K data is much less readily available and has not generally been employed in the prior literature.

“Protobranching” describes the net stabilizing interactions between 1,3-disposed methyl and/or alkyl groups in propane, the higher *n*-alkanes, and cyclohexane. Protobranching depicts the total sum of all the individual interactions of the carbons and hydrogens of methyl and methylene groups. Their equivalence is assumed, since the average value for protobranching in these molecules is found to be the same (see ca. Table 2.1). According to the long-held tenets of conformation analysis, saturated hydrocarbons are considered to be “strain free” if they do not possess abnormal bond lengths or angles, eclipsed conformations, or closely-approaching atoms. However, Pople’s isodesmic bond separation energies^[26-28] (based on methane and ethane, see later discussion) reveal that all these “strain free” molecules benefit from protobranching stabilization and, in that sense, have “negative strain.”

While the name, “protobranching,” and its ramifications discussed in this paper are new, antecedents go back to the 1930’s. T. L. Allen deduced a value of 2.3 ± 0.3 kcal/mol, which is very similar to our 2.83 kcal/mol protobranching value (revised for branching) based on Pople’s BSE concept. George and Trachtman^[29,30] have discussed the

differences between Pople's isodesmic BSE evaluations and the results of their homodesmotic scheme at length.

We now discuss the many ramifications of the protobranching concept. This paper considers the evaluation of energies associated with 1) straight and branched hydrocarbons, 2) ring and cage strain, 3) resonance and aromatic stabilization energy, 4) hyperconjugation in alkenes and alkynes.

2.3 RESULTS AND DISCUSSION

2.3.1 EVALUATION OF PROTOBRANCHING ENERGIES OF STRAIGHT AND BRANCHED ALKANES

We quantify protobranching (and other interactions) by means of Pople's isodesmic bond separation reactions (BSE):^[26-28] defined as a reaction in which "all formal bonds between heavy (non-hydrogen) atoms are separated into the simplest parent (two-heavy-atom) molecules containing these same kinds of linkages."^[28] BSE reactions involving hydrocarbons are balanced by methane; there are the same number of CC single, double, and triple bonds on both sides of the equation. For example, we employ the BSE equation to evaluate the protobranching of propane (Equation 1, Scheme 2. 1).

The bond separation energies (BSE) provided in Table 2.1 make use of NIST 298K experimental data to evaluate protobranching in a number of "strain free" linear, branched, and cyclic alkanes. When compared with methane and ethane, propane (as well as higher alkanes) is stabilized appreciably by protobranching. The average value for

each protobranch (ca. 2.8 kcal/mol) is remarkable constant (Table 2.1, last column) for the higher *n*-alkanes as well as cyclohexane.^[31]

Table 2.1. Evaluation of bond separation energies for saturated hydrocarbons (in kcal/mol). NIST 298K thermochemical data were employed.

<u>Molecule</u>	<u>Bond Separation Reaction</u>	<u>Total Reaction Energy</u>	<u>Number of Protobranches</u>	<u>Energy per Protobranch</u>
propane	$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_4 \rightarrow 2 \text{CH}_3\text{CH}_3$	2.83	1	2.83
<i>n</i> -butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3 + 2 \text{CH}_4 \rightarrow 3 \text{CH}_3\text{CH}_3$	5.69	2	2.84
<i>n</i> -pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3 + 3 \text{CH}_4 \rightarrow 4 \text{CH}_3\text{CH}_3$	8.59	3	2.86
<i>n</i> -hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3 + 4 \text{CH}_4 \rightarrow 5 \text{CH}_3\text{CH}_3$	11.32	4	2.83
<i>n</i> -heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3 + 5 \text{CH}_4 \rightarrow 6 \text{CH}_3\text{CH}_3$	14.61	5	2.92
cyclohexane	$(\text{CH}_2)_6 + 6 \text{CH}_4 \rightarrow 6 \text{CH}_3\text{CH}_3$	16.53	6	2.76
isobutane	$\text{CH}(\text{CH}_3)_3 + 2 \text{CH}_4 \rightarrow 3 \text{CH}_3\text{CH}_3$	7.73	3	2.58
isopentane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3 + 3 \text{CH}_4 \rightarrow 4 \text{CH}_3\text{CH}_3$	10.94 ^a	4	2.74
neopentane	$\text{C}(\text{CH}_3)_4 + 3 \text{CH}_4 \rightarrow 4 \text{CH}_3\text{CH}_3$	13.65	6	2.28

^a To compensate for the skew interaction in isopentane, 0.7 kcal/mol was added.

The branching stabilization per protobranch in isobutane and neopentane is somewhat attenuated. Protobranching is a net favorable composite of attractions (larger) and repulsions (smaller). The repulsion contributions increase somewhat in branched hydrocarbons, since the methyl groups are in closer proximity (note the C-C-C bond angle trend 112.7° in propane, 111.0° in isobutane, and 109.5° in neopentane).^[32] This results in attenuation of the average value of the protobranching interaction in branched hydrocarbons, to 2.58 and 2.28 kcal/mol in isobutane and neopentane, respectively (Table 2.1).

2.3.2 COMPUTATIONAL MODELS

In historical terms, the origin of the branching stabilization, and thus the origin of protobranching as well, has been thought to arise from intramolecular van der Waals interactions.^[24] The use of *ab initio* methods would, at least in part, allow us to gauge the degree to which this is true. Post Hartree-Fock *ab initio* methods, such as MP2, explicitly account for electron correlation. In contrast, Hartree-Fock (HF) does not. Thus, one can gain at least partial insight into the role of dispersion and correlation in branching stabilization by examining differences between these two theoretical levels. Density functional theory (DFT) provides insight as well. Various functionals include different degrees of correlation. In general, these functionals perform poorly for long-range correlation and thus van der Waals interactions. While overcoming this van der Waals problem is the topic of much current research in the field,^[33-37] satisfactory density functionals are not in common use. Within the context of DFT, Grimme's^[23] recent analysis of failure for alkane isomerizations points to the density functionals neglect of "medium-range" electron correlation effects as the source of error in predicting isomer energy differences. Other problems in describing hydrocarbon properties have also recently been emphasized in the literature. Check and Gilbert's analysis of homolytic C-C bond breaking energies of methyl-substituted ethane show B3LYP to have increasing errors as the number of methyl group substitutions is increased.^[38] We have recently tested a large number of density functionals by computing the Pople bond separation reaction energies of *n*-alkanes (propane through decane). We found that all functionals systematically underestimate the energy of these reactions.^[12] Schreiner et al.^[39] found that DFT incorrectly assigns the lowest energy isomers for a number of large

hydrocarbon compounds, generally underestimating the energy of structures containing only single bonds and small rings. Cage systems, like those studied by Schreiner, as well as *n*-alkanes all possess stabilization from protobranching. It can clearly be seen from the above-mentioned studies that current density functionals are unable to accurately describe the stability inherent in hydrocarbon branching. Furthermore, it seems that even in the world of methodological development, there is no consensus on the physical origins of branching stabilization, or how best to design functionals to accurately handle it.

Despite shortcomings, computational data can provide insight into the preference of protobranching in small molecules. Therefore, we have used Gaussian 98^[40] and 03^[41] at HF, DFT, and MP2 levels with the 6-311++G(d,p) basis set to complement experimental data. Computed energies include zero-point vibrational energies (ZPE) and thermal corrections to 298K, unless otherwise stated.

Quantum mechanical assessments of the branching effect (Table 2.2) include HF, DFT, and correlated *ab initio* methods. The HF energy of isobutane vs. *n*-butane is only 0.40 kcal/mol. Inclusion of ZPE and thermal corrections to 298K adds an additional stabilization of 0.34 kcal/mol, but the sum, 0.74 kcal/mol, is much less than the experimental value, 2.04 kcal/mol. DFT methods describe electron correlation based only on the local density: nonlocal effects are only partially incorporated into DFT calculations when the electron density gradient is considered.^[42] Like HF, DFT systematically underestimates the branching stabilization. Even the widely used B3LYP functional underestimates the stabilization of propane by over 1 kcal/mol!^[12] A more thorough evaluations of density functionals is given in reference ^[12]. Not surprisingly,

contrasting behavior is seen in the post-HF *ab initio* methods MP2 and CCSD(T):^[43] with both agreeing to within 0.25 kcal/mol for propane.

2.3.3 BENSON AND PROTOBRANCHING-CORRECTED GROUP INCREMENTS

Benson's well-known group enthalpy increments are based on average experimental values, and generally estimate 298K heats of formation of hydrocarbons with high accuracy.^[44] The alkane group increments, $C-(C)(H)_3 = -10.0$, $C-(C)_2(H)_2 = -5.0$, $C-(C)_3(H) = -2.4$, and $C-(C)_4 = -0.1$ kcal/mol can be extended by including the heat of formation of CH_4 , -17.9 kcal/mol. Instead of progressing regularly, the changes in the increments as each C-H is sequentially replaced with a C-C decrease steadily, from 7.9 kcal/mol between the heat of formation of CH_4 and the first Benson increment CH_3 , to 5.0 kcal/mol for CH_3 and CH_2 , 2.6 kcal/mol for CH_2 and CH , and 2.3 kcal/mol for CH to C (see Table 2.3 and Figure 2.2). Protobranching is responsible for this attenuation. The CH_3 increment is based on ethane, which, like methane, lacks protobranching. In contrast, propane, the simplest alkane with a CH_2 group, is stabilized by one protobranch (2.8 kcal/mol). Taking this into account, Benson's 5.1 kcal/mol difference between the CH_3 and CH_2 increments is increased to 7.9 kcal/mol, the same as for CH_4 vs. CH_3 ! The "expected increment" data in the fourth column of Table 2.3 assumes that this 7.9 kcal/mol progression continues to the CH and C groups (see Figure 2.2, upper line).

Table 2.2. Performance of various theoretical levels in evaluating branching stabilization. The 6-311++G(d,p) basis set was used throughout. E_0 is the quantity given by the electronic energies. ZPE/Thermal is the contribution to branching stabilization from scaled zero-point vibrational and thermal corrections to 298K.

Method	propane + methane $\rightarrow$ 2 ethane			<i>n</i> -butane + 2 methane $\rightarrow$ 3 ethane			isobutane + 2 methane $\rightarrow$ 3 ethane			isobutane $\rightarrow$ <i>n</i> -butane			neopentane $\rightarrow$ <i>n</i> -pentane		
	E_0	ZPE/Thermal	$E_0 +$ ZPE/Thermal	E_0	ZPE/Thermal	$E_0 +$ ZPE/Thermal	E_0	ZPE/Thermal	$E_0 +$ ZPE/Thermal	E_0	ZPE/Thermal	$E_0 +$ ZPE/Thermal	E_0	ZPE/Thermal	$E_0 +$ ZPE/Thermal
HF	0.96	0.47	1.43	1.84	0.93	2.77	2.24	1.27	3.51	0.40	0.34	0.74	0.53	0.87	1.40
BLYP	1.12	0.41	1.53	2.14	0.83	2.97	2.61	1.13	3.74	0.47	0.30	0.77	0.65	0.52	1.17
B3LYP	1.22	0.45	1.67	2.35	0.89	3.24	2.95	1.20	4.15	0.60	0.31	0.91	1.07	0.61	1.68
mPW1PW91	1.34	0.47	1.81	2.62	0.80	3.42	3.36	1.27	4.63	0.74	0.34	1.08	1.68	0.64	2.32
PW91	1.52	0.44	1.96	2.97	0.89	3.86	3.83	1.22	5.05	0.87	0.33	1.20	1.91	0.51	2.42
BHandH	2.32	0.56	2.88	4.60	1.11	5.71	6.29	1.51	7.80	1.69	0.40	2.09	4.34	0.80	5.14
MP2	2.34	0.52	2.86	4.69	1.03	5.72	6.65	1.42	8.07	1.95	0.39	2.34	5.41	--	--
CCSD(T)	2.09	0.52	2.61	4.18	1.03	5.21	5.84	1.42	7.26	1.66	0.39	2.05	4.47	--	--
Experiment			2.83			5.69			7.73			2.04			5.06

The difference between these idealized and Benson's practical increments (Table 2.3, column 2) are a measure of the total protobranching energy. Isobutane and neopentane, the simplest alkanes with CH and C groups, have three and six protobranches, respectively. However, their average stabilization energies per protobranch (Table 2.3, last column) are somewhat attenuated relative to the CH₂ value due to the greater Pauli repulsion resulting from the closer proximity of the methyl groups in branched as compared to *n*-alkanes (see discussion above).^[45]

Table 2.3. Benson group increments for 298K alkanes and values expected on the basis of a regular progression. Differences between Benson and expected values are used to evaluate protobranching. All data in kcal/mol.

Alkane Group	Benson Group Increments, 1993, 298K	Difference of Benson Group Increments	Increments expected from a regular progression ^a	Difference between expected and Benson increments	Number of protobranches	Energy per protobranch
CH ₄	(-17.9) ^b	--	(-17.9) ^b	0	0	--
C-(C)(H) ₃	-10.0	7.9	-10.0	0	0	--
C-(C) ₂ (H) ₂	-5.0	5.0	-2.1	2.9	1	2.9
C-(C) ₃ (H)	-2.4	2.6	+5.8	8.2	3	2.7
C-(C) ₄	-0.1	2.3	+13.7	13.8	6	2.3

a) These expected values are derived by adding 7.9 kcal/mol sequentially.

b) Not a true Benson increment, but is the 298K heat of formation of methane.

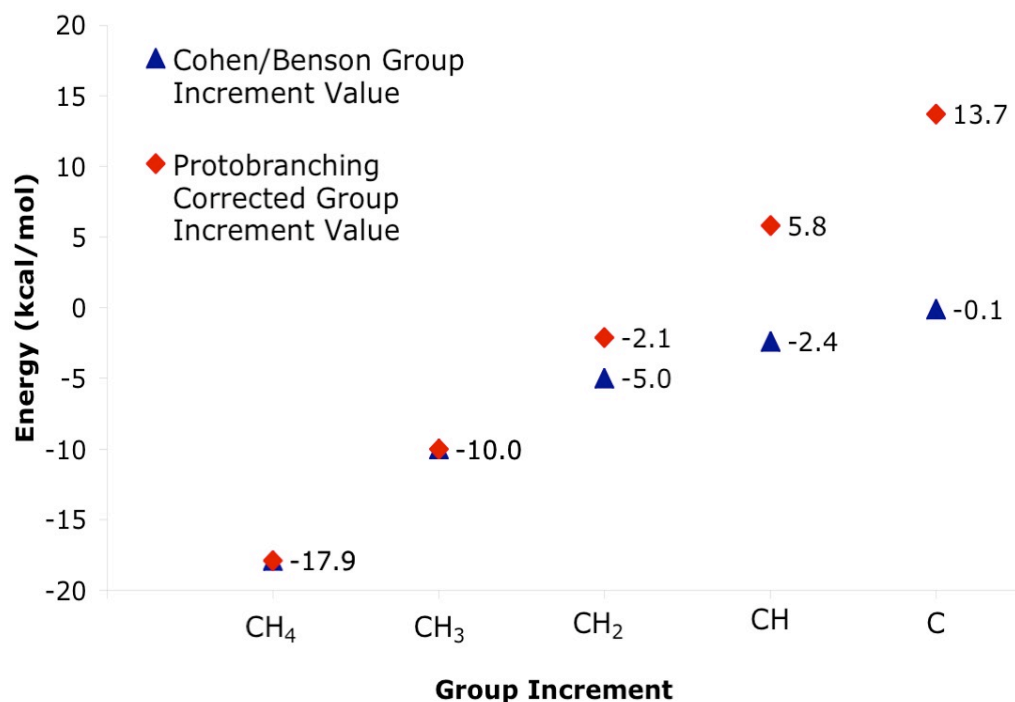


Figure 2.2. Benson group increment values and protobranching corrected group increment values.

2.3.4 PROTOBRANCHING AND RING/CAGE STRAIN ENERGIES

Strain is a virtual quantity; its evaluation depends on comparisons with models assumed to be “strain-free.” As originally conceived by Bayer in 1885,^[3] ring strain was based on CCC bond angle deviations from tetrahedral in cyclic alkanes, which he assumed to be planar. All cycloalkane rings (except cyclopropane) are now known to favor non-planar conformations, which, for cyclohexane and the larger rings minimize angle strain. The non-planar preference of cyclopentane (which would have nearly perfect 108° CCC angle in D_{5h} symmetry) was rationalized by Pitzer’s concept of torsional strain.^[46,47] All C-H bonds are eclipsed in the planar geometries of cycloalkanes; hence, both cyclopentane

and even cyclobutane pucker as a consequence. Eclipsing is responsible for some of the strain of cyclopropane.

The conventional definition of strain energy employs propane or other *n*-alkanes as “strain-free” models; such alkanes prefer staggered conformations energetically and are assumed not to possess other perturbing effects. For example, the conventional evaluation of the strain in cyclopropane (Equation 4, Scheme 2.1) is based on these assumptions. However, we have shown above that (unlike cyclopropane) propane and higher alkanes are stabilized by protobranching; in that sense these commonly used reference molecules have “negative strain.” The conventional ring strain definition is flawed when the same structural features are not present in the rings as in the *n*-alkanes. Cyclopropane is a case in point; no protobranching 1,3-alkyl-alkyl interactions are present since all carbon atoms are directly bonded to one another. Hence, the traditional homodesmotic evaluation (27.7 kcal/mol using experimental data, Equation 4) overestimates the ring strain. Each of the three propanes on the left side is stabilized by a protobranch and this substantial (8.5 kcal/mol) perturbation is not balanced on the right side. Pople’s isodesmic BSE (Equation 11) does not suffer from this imbalance and provides a much smaller estimate of the strain energy in cyclopropane (19.2 kcal/mol). We argue that the strain energy of cyclopropane is really 8.5 kcal/mol less than the conventional value.



Furthermore, cyclopropane is the only cycloalkane with fully eclipsed C-H bonds. Based on the 2.9 kcal/mol ethane rotation barrier,^[48] each pair of eclipsed vicinal C-H

bonds can be assigned a torsional strain of ca. 1 kcal/mol. Consequently, the eclipsing strain in cyclopropane could be as large as 6 kcal/mol (the bending of the H's away from one another may reduce this amount). Hence, the angle strain of the carbon skeleton of cyclopropane may actually be as low as 13 kcal/mol! This is less than half of the conventionally accepted (total) strain energy of cyclopropane.

Exner and Schleyer analyzed the energy contributions of cyclopropane most recently.^[49] The large reduction of the strain energy (to 13, 19, or even to the conventional 28 kcal/mol) is due to the σ -aromatic stabilization, which is now firmly established in cyclopropane.^[50] Comparing the Baeyer angle strain of planar silicon and planar carbon rings (Figures 2.3 and 2.4, respectively) shows the unusual nature of cyclopropane. As Baeyer strain is only concerned with deviations from the idealized sp^3 hybridized bond angle, one expects “V-shaped” or parabolic curves when strain energies are plotted against the size of *planar* rings. The behavior of the planar Si_nH_{2n} rings (Figure 2.3) is just as Baeyer predicted. However, the left side of the corresponding graph (Figure 2.4) for planar carbon rings is quite different, as the strain energy of cyclopropane is much less than expected on the basis of its 60° CCC angles and eclipsed vicinal C-H interactions. Stabilization by σ -aromaticity is responsible for the abnormal behavior of cyclopropane.

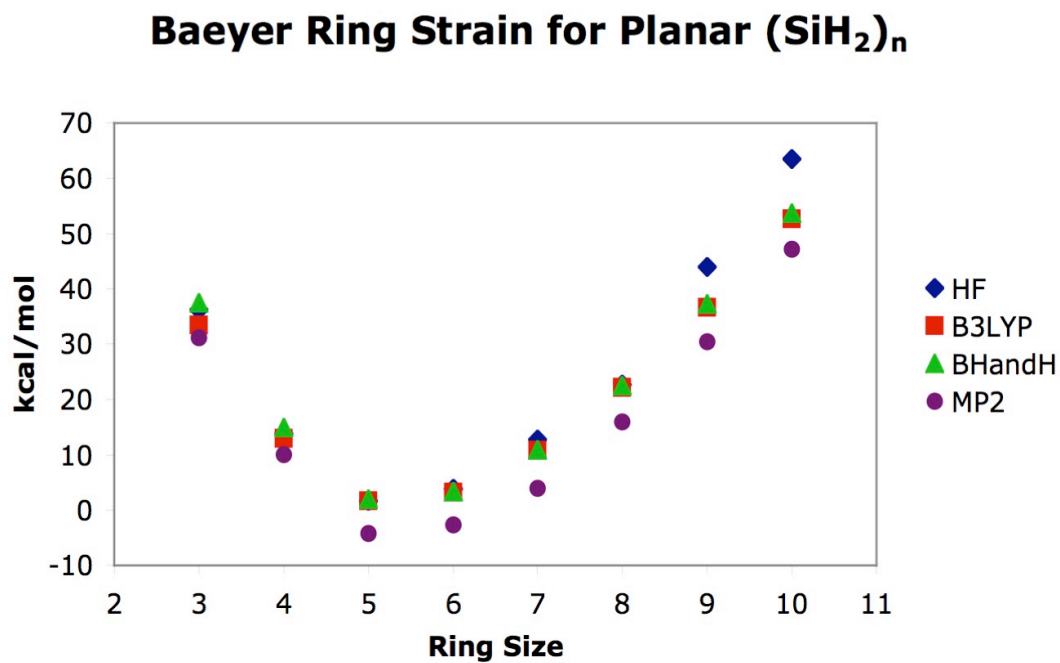


Figure 2.3. Baeyer (angle) ring strain for planar (SiH₂)_n rings as computed by the BSE equation $n \text{ Si}_2\text{H}_6 \rightarrow n \text{ SiH}_4 + (\text{SiH}_2)_n$. Si-H bonds are partially ionic and silicon does not rehybridize when the ring bond angles are deformed. Hence, the strain of small silicon rings follows Baeyer's expectation.

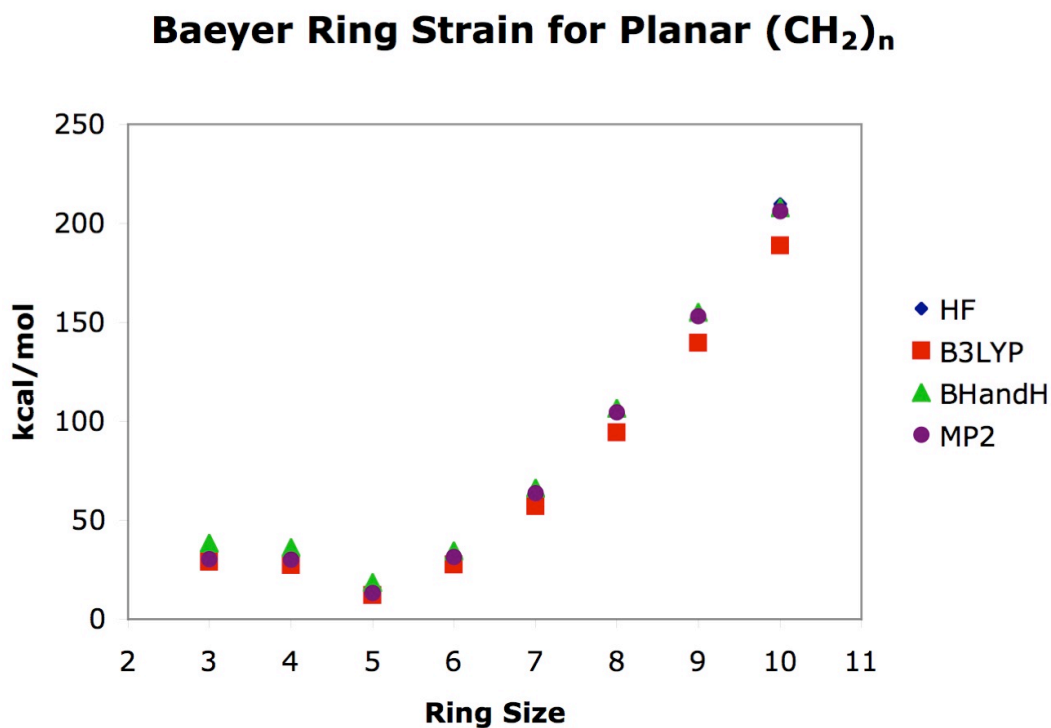


Figure 2.4. Baeyer ring strain for planar (CH₂)_n rings, as computed by the BSE equation, $n \text{ C}_2\text{H}_6 \rightarrow n \text{ CH}_4 + (\text{CH}_2)_n$. Note the marked deviation of cyclopropane from Baeyer's expectations and from the behavior of trisilacyclopropane (Figure 2.3).

HF, B3LYLP, and MP2 computations with the 6-311++G(d,p) basis set show all three methods perform well for cyclopropane (Table 2.4). The nearly equal energy computed by these three methods leads us to conclude that protobranching in cyclopropane is small or nonexistent.

Table 2.4. Strain energies of cyclopropane based on the BSE Equation 11. E_0 (the electronic) and ZPE/Thermal energies (the scaled zero-point and thermal corrections to 298K) are in kcal/mol. The 6-311++G(d,p) basis set was employed uniformly.

Level	Energies based on Equation 11		
	E_0	ZPE/Thermal	$E_0 + \text{ZPE/Thermal}$
HF	-24.65	4.28	-20.37
B3LYP	-23.15	4.16	-18.99
MP2	-23.43	4.15	-19.28
Experiment			-19.19

The evaluation of the cyclobutane strain is problematic. While there are four CH_2 groups, only two unique 1,3-alkyl-alkyl cross-ring interactions are present.^[51-53] The conventional homodesmotic evaluation, Equation 5 (Scheme 2.1), overestimates the strain since there are four propanes (each stabilized by one protobranch) on the left side; the 5.66 kcal/mol correction applied to Equation 12 results in a cyclobutane strain energy of 21.0 kcal/mol. The BSE Equation 13 gives 15.4 kcal/mol using experimental data, but underestimates the strain due to the presence of the stabilizing protobranching in cyclobutane.



The data in Table 2.5 analyze protobranching in cyclobutane by computing the BSE at HF, B3LYP, and MP2 theoretical levels. In contrast to the BSE of cyclopropane, not all methods perform the same for cyclobutane, the behavior is similar to that of other linear and branched alkanes. We therefore conclude that cyclobutane is stabilized by protobranching interactions.

Table 2.5. Cyclobutane BSE evaluations of Equation 13 (in kcal/mol). E_0 is the electronic energy. ZPE/Thermal is the scaled zero-point vibrational and thermal corrections to 298K.

	Energies based on Equation 13		
	E_0	ZPE/Thermal	$E_0 + \text{ZPE/Thermal}$
HF/6-311++G(d,p)	-22.53	4.46	-18.06
B3LYP/6-311++G(d,p)	-20.86	4.32	-16.54
MP2/6-311++G(d,p)	-19.25	4.55	-14.70
Experiment			-15.38

Equation 14 evaluates the conventional strain energies of the cycloalkanes. With the exception of cyclopropane and cyclobutane (discussed above), this assessment balances protobranching on the left and right sides of the equation. Thus, the six protobranches of cyclohexane are mirrored by the six protobranches in the six propane molecules. The isodesmic BSE, Equation 15, is not protobranching balanced and gives the total stabilization or destabilization inherently present within the molecule being evaluated. Thus, on the basis of methane and ethane (Equation 15), cyclohexane (BSE - 16.53 kcal/mol) is highly stabilized. The differences in these definitions have been discussed in detail by George et al.,^[29] and are clearly shown in Figure 2.5.



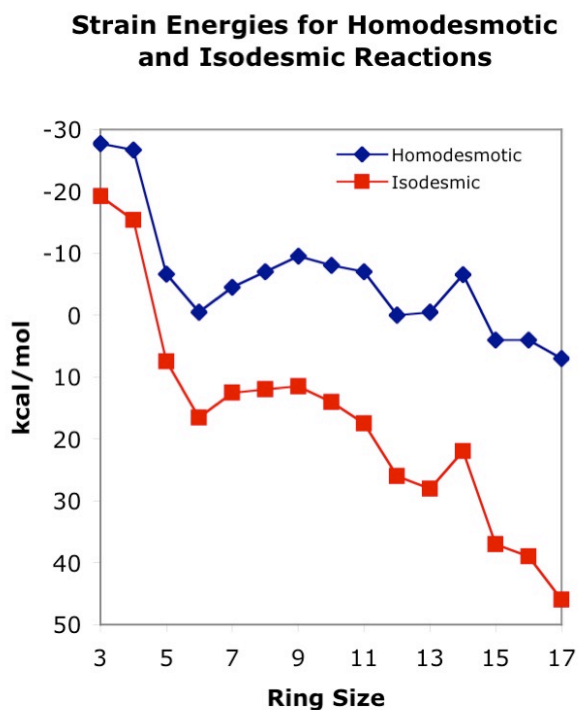


Figure 2.5. Comparison plots (derived from George et al.),^[29] based on experimental data) of the strain energies (in kcal/mol) given by the homodesmotic (Equation 14, blue points) and isodesmic reactions (Equation 15, red points), as a function of cycloalkane ring size.

The tetrahedrane, cubane, dodecahedrane, norbornane, adamantane, and tetramethyladamantane cage systems also illustrate the importance of protobranching on the evaluation of strain. Despite the very large conventionally estimated strain energy of 136.34 kcal/mol (Equation 16),^{[54][55]} large diatropic NICS values in the center indicate that tetrahedrane is aromatic.^[56,57] Like cyclopropane, tetrahedrane is devoid of protobranching. Hence, the strain energy, based on the conventional CH group increment, is overestimated by 30.92 kcal/mol. Applying the isodesmic BSE (Equation 17) removes the effects of protobranching from Equation 16, and gives our recommended tetrahedrane

strain energy, 105.42 kcal/mol. Although large, this value is far less than that expected on the basis of extreme angle deformations.

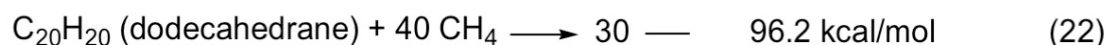
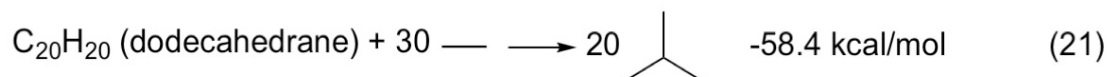


Cubane has 12 1,3-alkyl-alkyl interactions, counting two for each face. This is half the number present in eight isobutane molecules. Thus, the conventional strain evaluation of 164.8 kcal/mol, given by Equation 18 is overestimated by ca. 30 kcal/mol.^[58] Instead, Equation 19 uses twelve protobranches to balance the protobranching in cubane, and the strain is reduced to 133.9 kcal/mol. However, the BSE (Equation 20) finds the total destabilization of cube to be only 102.9 kcal/mol.

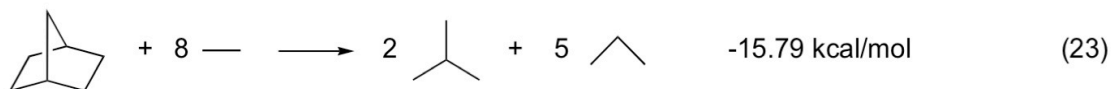


Dodecahedrane has 60 1,3-alkyl-alkyl interactions, five for each of the 12 faces (or three for each of the 20 vertexes). The conventional strain estimate, 58.4 kcal/mol (Equation 21), is based on 20 isobutane reference molecules, but each of these is stabilized substantially (7.73 kcal/mol, Table 2.2) by protobranching. Since about 30 kcal/mol of the conventional strain energy can be ascribed to the 30 eclipsed vicinal C-H

interactions, the “neglect of protobranching” error can easily account for the remainder. Indeed, BSE Equation 22 shows dodecahedrane to be stabilized by 96.2 kcal/mol, relative to methane and ethane! This value is similar to the sum of the stabilization energies of 12 cyclopentanes computed by BSE (cf. Figure 2.5).



Similarly, the strain energy of norbornane can be evaluated by the homodesmotic equation 23, which matches each of the six isobutane like and five propane like protobranching interactions. This gives a strain of 15.79 kcal/mol. However, if one considers the isodesmic equation 24, norbornane is stabilized by 13.82 kcal/mol as a result of protobranching interactions.



Adamantane and tetramethyladamantane are molecules which are thought to contain little or no strain energy,^[59] shown by equations 25 and 26. However, the reference propane, isobutane, and neopentane are greatly stabilized by protobranching. Thus, the BSE value (Equations 27 and 28) show both cages to be strongly stabilized. BSE evaluations at HF, B3LYP, and MP2 levels show the underestimation of the branching stability by DFT in adamantane and tetramethyladamantane (Table 2.6).

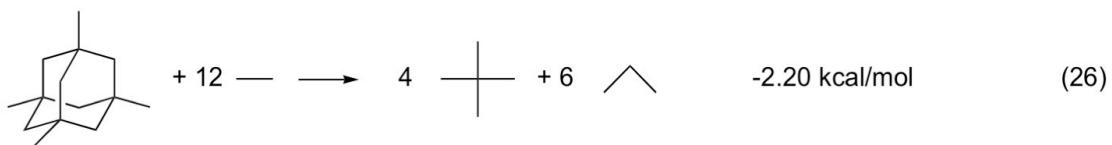
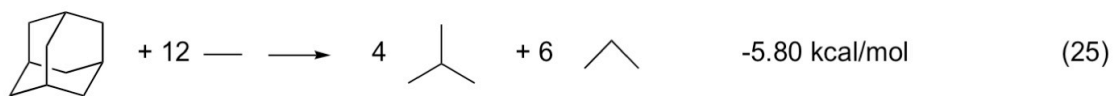
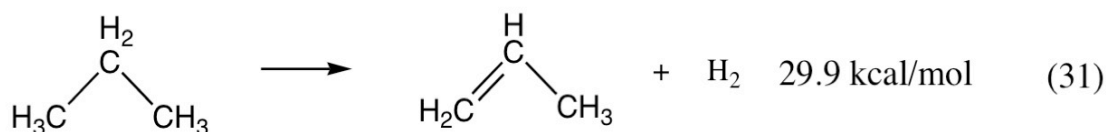
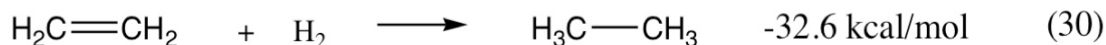


Table 2.6. BSE evaluations of Equations 17, 20, 22, 24, 27 and 28 (in kcal/mol). E_0 is the electronic energy. ZPE/Thermal is the scaled zero-point vibrational and thermal corrections to 298K.

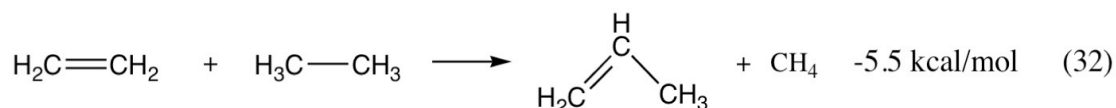
Tetrahedrane	E_0	ZPE/Thermal	E_0 +ZPE/Thermal
(based on Equation 17)			
HF/6-311++G(d,p)	-126.97	14.70	-112.27
B3LYP/6-311++G(d,p)	-117.07	14.68	-102.39
MP2/6-311++G(d,p)	-123.45	15.73	-107.72
Cubane			
(based on Equation 20)			
HF/6-311++G(d,p)	-137.93	22.59	-115.34
B3LYP/6-311++G(d,p)	-127.20	22.71	-104.49
MP2/6-311++G(d,p)	-126.18	24.60	-101.58
Experiment			-102.9
Dodecahedrane			
(based on Equation 22)			
HF/6-311++G(d,p)	2.80	43.80	46.60
B3LYP/6-311++G(d,p)	13.40	43.33	56.73
MP2/6-31G(d)			
Experiment			96.2
Norbornane			
(based on Equation 24)			
HF/6-311++G(d,p)	-6.04	8.36	2.32
B3LYP/6-311++G(d,p)	-4.07	8.31	4.24
MP2/6-311++G(d,p)	7.31	9.09	16.40
Experiment			13.82
Adamantane			
(based on Equation 27)			
HF/6-311++G(d,p)	11.04	12.35	23.39
B3LYP/6-311++G(d,p)	13.29	11.80	25.09
MP2/6-311++G(d,p)	33.52	13.50	47.02
Experiment			42.10
Tetramethyladamantane			
(based on Equation 28)			
HF/6-311++G(d,p)	19.44	16.44	35.88
B3LYP/6-311++G(d,p)	24.36	15.16	39.52
MP2/6-31G(d)	61.63	17.27	78.99
Experiment			69.38

2.3.5 THE EFFECT OF PROTOBRANCHING ON HYPERCONJUGATION AND CONJUGATION ENERGY ESTIMATION

Mulliken's concept of hyperconjugation^[7,8] was described as the stabilization resulting from the interaction of the low lying π^* orbital of an olefin with an occupied orbital of an alkyl substituent having correct symmetry. The conventional evaluations of the energies of hyperconjugation are based on comparisons of the differences in heats of hydrogenation of alkenes with ethene and alkynes with ethyne.^[60] Thus the sum of Equation 30 and Equation 31 (given directly by Equation 8) is the commonly quoted value for the hyperconjugation stabilization by a methyl (or other alkyl group) on a CC double bond. A similar procedure gives Equation 9 for alkynes. We now argue that the values derived from Equation 8 and 9 are too low since the reference compound in both these equations, propane, is stabilized by protobranching.



We have recently analyzed hyperconjugation using isodesmic equations and by describing the virtual states where the hyperconjugative interactions in 1-butene and 1-butyne were absent.^[61] However, the equations employed did not compensate for protobranching. To illustrate, Equation 9 can be derived conceptually in a different way by adding Equation 1 and 32.



Equation 32 gives the revised value for alkene hyperconjugation directly. Similarly, Equation 33 applies to alkyne hyperconjugation. Both these BSE-based values assume that no protobranching corrections are needed for propyne (readily understood in view of the 180° bond angle and the C(1)-C(3) distance) and for propene (which is more problematic).



Do propene (and other olefins) have stabilizing protobranching type 1,3-interactions? Analysis of the bond separation energies (BSE) at HF, B3LYP, and MP2 with the 6-311++G(d,p) basis set are given for propene in Table 2.7 and for propane in Table 2.2. The similar performance of these three methods to that of cyclopropane (which contains no protobranching interactions) indicates no protobranching is present. While the HF predicts the stability of propene to be over 1kcal/mol lower than MP2, we conclude that this results from poor description of hyperconjugation, and does not arise from the presence of protobranching. The conclusion is supported by the nearly identical predictions of B3LYP and MP2. We concluded that little or no protobranching is present in propene. Instead, we assume that the hyperconjugation energies, which benefit from $\pi \rightarrow \sigma^*_{\text{CH}_3}$ as well as Mulliken's $\pi^* \leftarrow \sigma_{\text{CH}_3}$ stabilization, includes all 1,3 contributions. Hence, we do not apply explicit protobranching corrections to the C=C-C moieties of olefins. As an illustration, we assume cyclohexene to have two hyperconjugation and four protobranching interactions.

Table 2.7. BSE analysis of propene. The E_0 (electronic) and the ZPE/Thermal (scaled zero-point vibrational and thermal corrections to 298K) are in kcal/mol. All computations used the 6-311++G(d,p) basis set.

Level	propene + methane $\rightarrow$ ethene + ethane		
	E_0	ZPE/Thermal	E_0 + ZPE/Thermal
HF	3.74	0.54	4.28
B3LYP	4.70	0.50	5.20
MP2	4.99	0.40	5.39
Experiment			5.71

We have also made use of an entirely different approach to quantify the effect of electron delocalization on unsaturated systems, the block-localized wave function (BLW) method of Mo et al.^[62,63] BLW is closely associated with valence bond (VB) theory and can be employed at the practicable HF and DFT levels, because of error cancellation. The wave function of the major contributor to a resonance hybrid, e.g., a localized, non-conjugating cyclohexatriene, can be optimized self-consistently. In effect, BLW “turns off” the π conjugation in butadiene, the hyperconjugation in propene, and the aromaticity in benzene, but the sigma framework remains essentially intact. As an illustration, Equation 33 is not balanced with regard to the number of $C(sp^2)$ -X and $C(sp^3)$ -X bonds (X=H or C), but the BLW method applied to propene does not have this fault. BLW thus affords a considerable conceptual advantage over conventional delocalization energy assessments using thermochemical data and isodesmic or homodesmotic reactions. Such reactions attempt to approximate a virtual Lewis structure (the most stable resonance structure), in which the effects of electron delocalization are absent, as a composite of non-delocalized model reference compounds. In contrast, the difference between the

BLW and HF (or KS) wave functions *of the same compound* gives the resonance energy (following the Pauling-Wheland definition) directly. The BLW method already has been applied to many molecules,^[63-68] including the evaluation of the hyperconjugation of propene and the aromaticity of benzene.

The validity of our revised hyperconjugation energy of propene is substantiated by the BLW method. For propene, the delocalized (HF or KS) and localized (BLW) wave functions can be expressed as

$$\Psi(\text{del}) = \hat{A}(\sigma' 1a''^2 2a''^2)$$

and

$$\Psi(\text{loc}) = \hat{A}(\sigma' \pi_{C=C}^2 \pi_{CH_3}^2)$$

where $\pi_{C=C}$ and π_{CH_3} are group orbitals expanded in $\text{CH}_2=\text{CH}$ and CH_3 groups, and are nonorthogonal. In contrast, $1a''$ and $2a''$ are delocalized for the whole system and orthogonal. The energy difference between these two functionals, which are independently optimized self-consistently, represents the vicinal interaction between the π double bond and the adjacent methyl group, or more simply the hyperconjugation of the methyl group. Using the 6-311+G(d,p) basis set the adiabatic hyperconjugation energy is estimated to be -5.5 or -6.3 kcal/mol at the HF or DFT (B3LYP) level, in agreement with the -5.5 kcal/mol obtained in Equation 32.

Recently Rogers et al. developed an increment scheme for estimating the heats of formation of polyynes.^[69] While the increment scheme reproduces both theoretically and experimentally derived heats of formation accurately, we criticize the evaluation methods to achieve these increments. Our derivation of the energies of protobranching,

hyperconjugation, conjugation, as well as what we have termed “cross-hyperconjugation” for Rogers’ compounds, gives a different perspective.

The BSE of *n*-pentane (8.59 kcal/mol), 1-pentyne (13.24 kcal/mol), and 1,3-pentadiyne (23.67 kcal/mol) were computed using G3(MP2) data.^[70] The BSE for *n*-pentane provides 2.86 kcal/mol per protobranching stabilization. Hyperconjugation (7.58 kcal/mol) is given by the BSE of 1-pentyne after correction for the two protobranches present. Diyne conjugation stabilization is 16.09 kcal/mol, based on the BSE of 1,3-pentadiyne after subtracting the value of a methyl hyperconjugation.

Cross hyperconjugation, involving the attenuated interaction of a methylene group situated between two triple bonds, is present in 1,4-hexadiyne. Its BSE, 21.51 kcal/mol, minus the methyl hyperconjugation, defines this stabilization, 13.93 kcal/mol. This is only about 1.2 kcal/mol less than two individual alkyne hyperconjugations (2×7.58 kcal/mol = 15.16 kcal/mol), in sharp contrast to the 3.9 kcal/mol *destabilization* assigned by Rogers et al. An extensive list of BSE values of unsaturated compounds is given in Table 2.8.

While Rogers et al.’s self-consistent increment scheme accurately reproduces experimental heats of formation, we take issue with their derivation of the stabilization energy values for conjugation and cross hyperconjugation. Since hyperconjugation was not considered, the 0.9 kcal/mol attributed to “conjugation” and the 3.9 kcal/mol destabilization due to “attenuation” do not represent the uncontaminated values. Fortuitous cancellation can result in data-fitting schemes, which predict accurate values of heats of formation, but do not have interpretive significance.^[20] Dienes are stabilized much more than 0.9 kcal/mol by conjugation; the BSE value is 15.1 kcal/mol.

Based on the BLW method, the Pauling-Wheland resonance (conjugation) energy in 1,3-butadiyne is even larger, 20.1 kcal/mol at the HF/6-311+G(d,p) level (26.2 kcal/mol at B3LYP/6-311+G(d,p) level). The BLW resonance energy of anti-1,3-butadiene (9.9 kcal/mol at the HF/6-311+G(d,p) level and 12.2 kcal/mol at the B3LYP/6-311+G(d,p) level) is half as large. The difference between the BSE and BLW diyne estimates (see summary Table 2.9 in the Conclusions) may be due to differences in the carbon hybridization in the isodesmic bond separation reactions.

Table 2.8. Evaluation of bond separation energies for unsaturated hydrocarbons (in kcal/mol). NIST thermochemical data at 298K were employed.

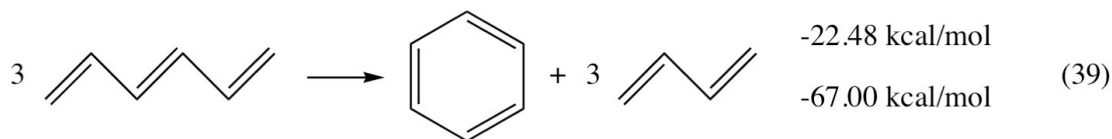
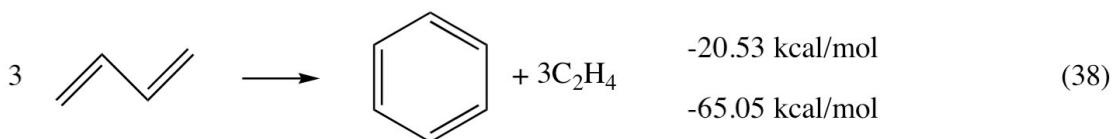
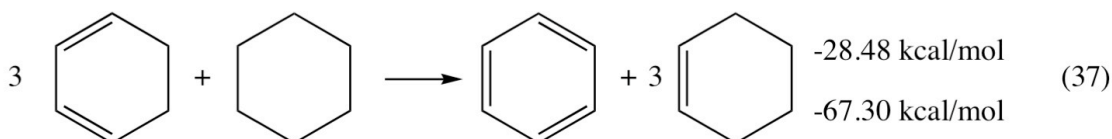
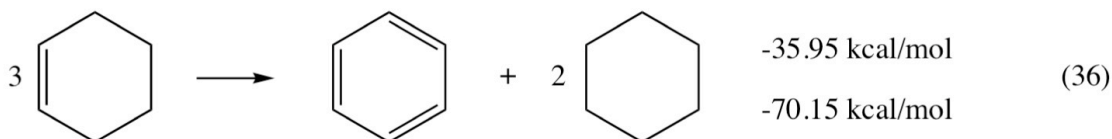
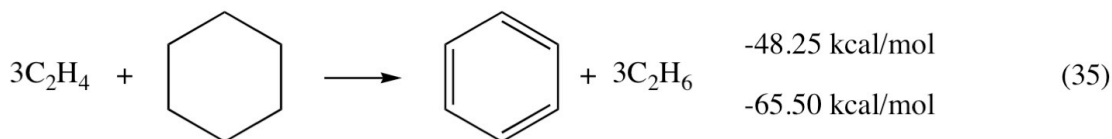
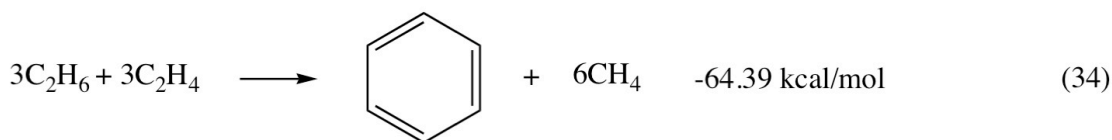
Molecule	PB	Alkene HC	Alkyne HC	Alkene CHC	Alkyne CHC	Alkene Conj	Alkyne Conj	Est Energy	Bond Separation Energy
propane	1	--	--	--	--	--	--	2.83	2.83
propene	--	1	--	--	--	--	--	5.71	5.71
propyne	--	--	1	--	--	--	--	7.81	7.81
1-butene	1	1	--	--	--	--	--	8.54	8.58
trans-2-butene	--	2	--	--	--	--	--	11.42	11.01
2-methyl-1-propene	1	2	--	--	--	--	--	14.25	12.54
anti-1,3-butadiene	--	--	--	--	--	1	--	14.84	14.84
syn-1,3-butadiene	--	--	--	--	--	1	--	12.94	12.94
1-butyne	1	--	1	--	--	--	--	10.64	10.41
2-butyne	--	--	2	--	--	--	--	15.62	15.21
1,3-butadiyne	--	--	--	--	--	--	1	15.12	15.12
trans-1,3-pentadiene	--	1	--	--	--	1	--	20.55	20.50
1,4-pentadiene	1	--	--	1	--	--	--	13.26	13.26
1,3-pentadiyne	--	--	1	--	--	--	1	22.93	23.67
1-pentene	2	1	--	--	--	--	--	11.37	11.19
trans-2-pentene	1	2	--	--	--	--	--	14.25	14.00
1-pentyne	2	--	1	--	--	--	--	13.47	13.24
2-pentyne	1	--	2	--	--	--	--	18.45	16.94

1-hexene	3	1	--	--	--	--	--	14.20	14.35
3-hexene	2	2	--	--	--	--	--	17.08	16.95
cyclohexene	4	2	--	--	--	--	--	22.74	20.72
1,3-cyclohexadiene	2	2	--	--	--	1	--	30.02	27.28
1,4-hexadiyne	--	--	1	--	1	--	--	21.72	21.72
1,5-hexadiyne	2	--	2	--	--	--	--	21.28	20.52
1,3,5-hexatriyne	--	--	--	--	--	--	2	30.24	30.65
3-heptyne	3	--	2	--	--	--	--	24.11	23.04
1,3-heptadiyne	2	--	1	--	--	--	1	28.59	29.37
1,3,6-heptatriyne	--	--	--	--	1	--	1	29.03	29.50

2.3.6. PROTOBRANCHING AND AROMATIC RESONANCE (RE) AND STABILIZATION ENERGIES (ASE)

Kistiakowsky's seminal evaluation of the resonance energy of benzene (Equation 6, Scheme 2.1)^[71] has previously been criticized.^[67] His 36 kcal/mol value,^[71] based on the heats of hydrogenation of benzene and cyclohexene, is badly flawed, since the three reference cyclohexenes on the right side are stabilized considerably by hyperconjugation (a concept unknown at that time), for which there is no compensation on the left side. Consequently, *the RE of benzene must be much larger than 36 kcal/mol.*

Many model reactions (isodesmic, homodesmotic, etc.) have been used to estimate the resonance energy (RE) as well as the aromatic stabilization energy (ASE) of benzene.^[72] According to Pauling and Wheland resonance energy is defined as the difference between the actual energy of a molecule and the virtual energy of the most stable resonance contributor.^[73-77] Since the real reference molecules chosen to approximate the virtual energy of a non-resonating cyclohexatriene are never free from other stabilizing or destabilizing interactions, these perturbing features ("contaminations") should be balanced in the defining equations as completely as possible. Unfortunately, Equations 35-39 Scheme 2.2 fail to balance the stabilization from conjugation, hyperconjugation, and protobranching interactions.



Scheme 2.2. Equations that have been employed to evaluate the resonance energy of benzene. The upper values are the original RE estimates. The lower values are the RE's after correction for the perturbing effects of protobranching, hyperconjugation, and conjugation.

A second set of ASE evaluations, devised to compare benzene with conjugation but non-aromatic reference molecules, have been widely discussed in the literature.^[78] Consequently, the various equations used to estimate the stabilization of the benzene RE and ASE give very different values. The wide divergence of benzene stabilization energies often has been mentioned disparagingly in critical appraisals of the aromaticity

concept. Remarkably, when hyperconjugation, protobranching, and conjugation adjustment are applied, the various aromaticity evaluations (Equations 34-39) yield surprisingly consistent resonance energies!

The BSE (Equation 34 of Scheme 2.2) gives a RE equal to 64.39 kcal/mol and requires no modification for hyperconjugation and protobranching, as these are not involved. Equation 35, evaluated directly using 298K experimental data, gives a much lower value, 48.25 kcal/mol. However, the stabilizing 1,3-alkyl-alkyl protobranching interactions of the cyclohexane reference molecule should be considered. Adding the stabilization from protobranching corrects the Equation 35 RE to 65.50 kcal/mol. This is nearly identical with the RE from Equation 34!

Kistiakowsky originally applied isodesmic Equation 36 to give the RE of benzene.^[71] However, the flaws in this equation are now apparent. While protobranching is balanced (four for each of the three cyclohexenes on the left vs. six each for the two cyclohexanes on the right side), the total of six stabilizing hyperconjugative interactions on the left side (worth 5.7 kcal/mol each, see above) have no counterpart on the right. When this hyperconjugation stabilization is taken into account, the RE given by Equation 36 increases from 36.0 to 70.2 kcal/mol.

Equation 37 was devised to estimate the ASE of benzene, but also can serve (after correction) to assess its RE. The total of six hyperconjugative and twelve protobranches are balanced, but three uncompensated syn-type conjugation interactions (worth 12.94 kcal/mol each) are present on the left side. Their consideration results in a benzene RE of 67.3 kcal/mol. The three uncompensated conjugations in Equation 38 and 39 stabilize the left sides by 44.52 kcal/mol; when this is taken into account, the RE of Equation 38 is

increased from 20.5 to 65.1 kcal/mol and of Equation 39 from 22.5 kcal/mol to 67.0 kcal/mol.

Clearly contributions from conjugation, hyperconjugation, and protobranching should be considered when evaluating resonance energies. After correcting for these effects, the inconsistencies in RE's given by Equation 34-39 largely vanish (Figure 2.6).

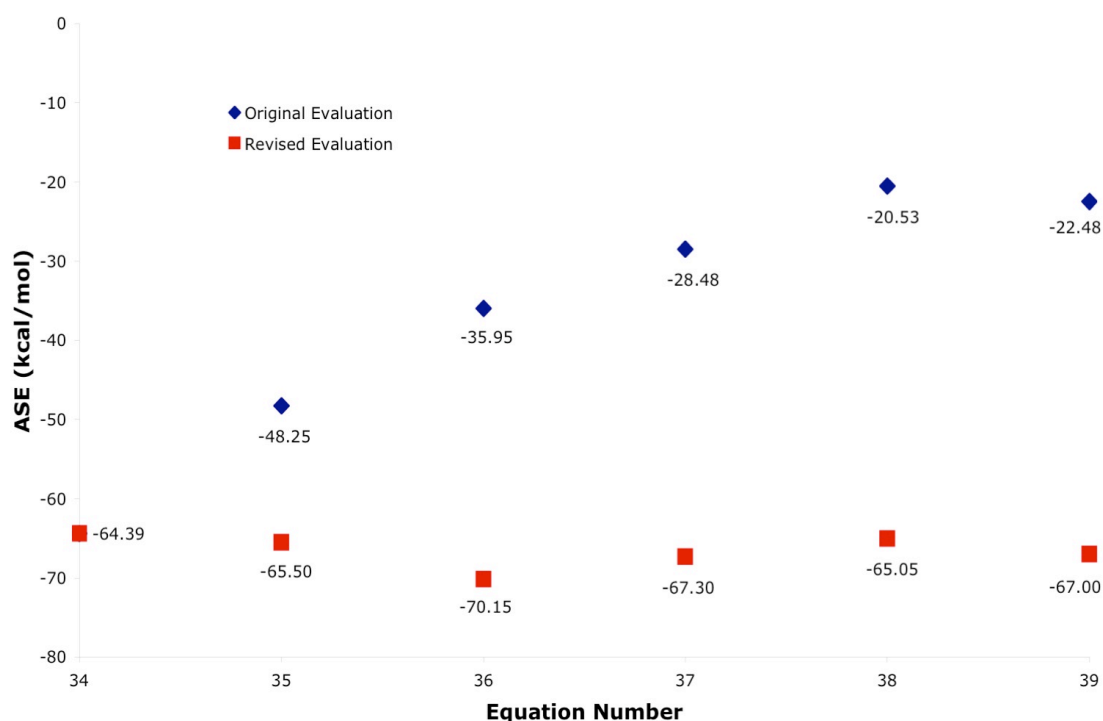
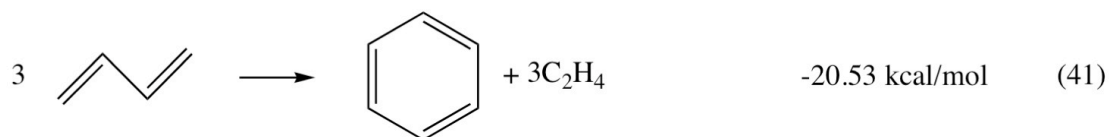
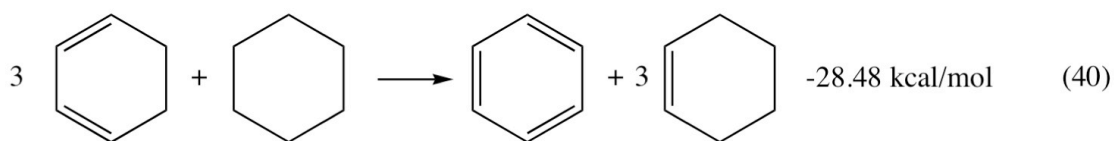


Figure 2.6. Original values and stabilization revised values for aromatic stabilization energies calculated by various equations (Scheme 2.2).

Dewar's original definition of the aromatic stabilization energy (ASE), Equation 40 in Scheme 2.3, is intended to estimate the extra resonance energy due to the cyclic electron delocalization.^[79] The ASE of Equation 40 is 20.53 kcal/mol. However, benzene only has *syn* conformations, which, for 1,3-butadiene, are 3.0 kcal/mol higher in energy

than the *anti* conformations. Equation 41, employing the 1,3-cyclohexadiene as the reference, removes the syn/anti discrepancy (as well as balances all protobranching and hyperconjugation interactions) and results our recommended ASE value, of 28.48 kcal/mol. This value agrees well with the mathematical derivation of Dewar resonance energy, 32.7 kcal/mol, obtained by Fishtik and Datta.^[80]



Scheme 2.3. Equations used to evaluate aromatic stabilization energy of benzene.

2.4 CONCLUSIONS

Protobranching is a simple concept with remarkably broad, paradigm shifting implications for energy evaluations in organic chemistry. Protobranching extends the well-established concept of branching to n-alkanes and to cycloalkanes. The consequences for energetic analysis are fundamental: n-alkanes larger than ethane and cyclohexane can no longer be considered “strain-free” reference molecules. All interactions, other than the one of interest, should be balanced in reference molecules, but this is difficult to realize in larger systems. Unblemished energetic analysis requires the elimination of all contaminants, either stabilizing or destabilizing, with reference molecules. This can be achieved best by using simple molecules (methane, ethane, ethene, etc.), which provide references that lack perturbing effects (e.g., conjugation, hyperconjugation, and strain, as well as protobranching). The recognition of protobranching adds another effect that should be considered. If this is not done, incomplete and potentially misleading energetic analyses will result.

The protobranching concept accounts for the very large errors, e.g., in estimates of branching energies as well as the heats of formation of the larger n-alkanes by HF and B3LYP as well as other DFT functionals. Application of the protobranching concept reduces the conventional strain energy of cyclopropane from 27.7 to 19.2 kcal/mol, and also reduces the conventional ring strain estimates of cyclobutane, tetrahedrane, and cubane to much smaller values.

Protobranching also helps reconcile the inconsistent values, ranging from 19.3 to 66.9 kcal/mol, for the benzene stabilization energy given by many literature schemes.^[78] Agreement is achieved when conjugation, hyperconjugation, and protobranching

corrections are applied. Kistiakowsky's classical resonance energy,^[71] 36 kcal/mol, is underestimated due to the neglect of hyperconjugation; we recommend the BSE value of 64.4 kcal/mol instead. The ASE of benzene is revised from 20.5 to 28.8 kcal/mol.

When protobranching is taken into account, the conventional hyperconjugative stabilization of an alkene by an alkyl group more than doubles, from 2.5 to 5.5 kcal/mol. The BLW value is 5.5 kcal/mol (6.3 kcal/mol B3LYP). The alkyl group alkyne hyperconjugation increases from 5.0 to 7.7 kcal/mol, based on BSE; the BLW value is even larger (10.5 kcal/mol HF, 12.5 kcal/mol B3LYP). Consideration of protobranching increases estimation of the conjugation energy of dienes from 3.7 to 14.8 kcal/mol (BLW 9.9 kcal/mol HF, 12.2 kcal/mol B3LYP) and diynes from 0.2 to 15.1 kcal/mol (BLW 20.1 kcal/mol HF, 26.2 kcal/mol B3LYP). Table 2.9 summarizes our major thermochemical and BLW evaluations with the conventional values.

Table 2.9. Summary of conventional, revised, and BLW (at HF and B3LYP) energy evaluations of strain, hyperconjugation, conjugation, and benzene aromaticity (kcal/mol).

<i>Property</i>	<i>Conventional Evaluation</i>	<i>Revised Evaluation (Based on BSE)</i>	<i>BLW Evaluation (B3LYP)</i>
Ring/Cage Strain			
cyclopropane	27.7	19.2	--
cyclobutane	26.8	21.0 ^a	--
tetrahedrane	136.3	105.4	--
cubane	164.8	102.9 ^a	--
Hyperconjugation			
propene	2.5	5.7	5.4 (6.3)
propyne	5.0	7.8	10.5 (12.5)
Conjugation			
butadiene	3.7	14.8	9.9 (12.2)
butadiyne	0.2	15.1	20.1 (26.2)
Aromaticity of			
ASE	20.5	28.8	--
RE	36.0	64.4	57.5 (63.2)

^a Corrected for protobranching; see text.

2.6 ACKNOWLEDGMENTS

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CHAPTER 3

NEW ADDITIVITY SCHEMES FOR HYDROCARBON ENERGIES[†]

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3.1. ABSTRACT

A new isodesmic additivity scheme based on the energetic relationships among the simplest hydrocarbon molecules reproduces the experimental heats of formation for a broad range of unstrained hydrocarbons with remarkable accuracy. The stabilizations of radicals, double, and triple CC bonds by alkyl substituents (hyperconjugation), as well as the stabilization by 1,3-alkyl group interactions at the same carbon (branching) support conventional interpretations. Statistical data fitting can also be achieved by using only four adjustable parameters.

3.2. INTRODUCTION

Decades of meticulous experimental measurements provided accurate thermochemical data for a large number of hydrocarbons.^[1] Regularities in these data have been expressed by many quantitative relationships, most notably the extensive group increment scheme developed and refined by Benson.^[2] Assuming additivity, increment values for e.g., C-(C)(H)₃, C-(C)₂(H)₂ and many other hydrocarbon groups reproduce the known heats of formation (ΔH_f) remarkably well (see the selection in Table 3.1). Deviations from additivity can be used, for example, to evaluate “strain” but the main purpose of these increments is predictive, rather than interpretive. The many increment types required by Benson’s method are evaluated by averaging all the available experimental data. In the present context, Benson’s method requires nine group enthalpy increments for the selection of alkanes, alkenes, and alkynes listed in Table 3.1, a separate value for methane, and a special treatment for the alkyl radicals.^[2]

Table 3.1. Heats of formation of Gronert's strain-free hydrocarbons as well as alkynes, in kcal/mol. Molecules shown in bold font were used to derive the isodesmic parameters and attenuation coefficients employed in Scheme 3.2 and Table 3.2.

Molecule	Experimental Refs. 1, 7	Benson ^[2]	Benson Deviation	Gronert ^{a,b}	Gronert Deviation	Isodesmic	Isodesmic Deviation
methane	-17.89	--	--	-17.3	0.6	-17.89	0.0
ethane	-20.04 ± 0.07	-20.00	0.0	-20.4	0.3	-20.04	0.0
propane	-25.02 ± 0.12	-25.00	0.0	-25.3	0.3	-25.02	0.0
n-butane	-30.03 ± 0.16	-30.00	0.0	-30.2	0.2	-30.00	0.0
isobutane	-32.07 ± 0.15	-32.40	0.3	-31.9	0.2	-32.08	0.0
n-pentane	-35.08 ± 0.14	-35.00	0.1	-35.1	0.0	-34.98	0.1
isopentane ^c	-36.73 ± 0.14	-36.60	0.1	-36.8	0.1	-37.06	0.3
Neopentane	-40.14 ± 0.15	-40.10	0.0	-40.3	0.2	-39.98	0.2
n-hexane	-39.96 ± 0.19	-40.00	0.0	-40.0	0.0	-39.96	0.0
n-heptane	-44.89 ± 0.19	-45.00	0.1	(-45.1)	0.2	-44.94	0.1
Cyclohexane	-29.43 ± 0.19	-29.30 ^d	0.1	-29.3	0.1	-29.88	0.5
trans-decalin	-43.54 ± 0.55	-44.80	1.3	(-41.8)	2.8	-43.89	0.4
methyl radical	35.05 ± 0.07 ⁱ	--	--	34.9	0.1	35.05	0.0
ethyl radical	29.0 ± 0.4 ⁱ	28.4	0.0	29.1	0.1	29.00	0.0
n-propyl radical	23.9 ± 0.5	23.4	0.5	24.2	0.3	24.02	0.1
isopropyl radical	21.5 ± 0.4 ⁱ	21.0	1.0	21.6	0.1	21.29	0.2
sec-butyl radical	16.1 ± 0.5 ⁱ	16.0	0.0	16.7	0.6	16.31	0.2
tert-butyl radical	12.3 ± 0.4 ⁱ	11.0	1.3	12.2	0.1	12.40	0.1
cyclohexyl radical	No data	16.0	--	(17.5)	--	16.43	--
Ethene	12.54	12.54	0.0	12.5	0.0	12.54	0.0
Propene	4.88	4.82	0.1	4.9	0.0	4.88	0.0
1-butene	-0.15 ± 0.19	-0.18	0.0	0.1	0.3	-0.10	0.1
E-2-butene	-2.58 ± 0.24	-2.90	0.3	-2.6	0.0	-2.78	0.2
2-methylpropene	-4.29 ± 0.26	-3.54	0.8	-4.3	0.0	-4.29	0.0
2-methyl-2-butene	-9.92 ± 0.21	-10.12	0.2	-10.1	0.2	-10.25 ^e	0.3
tetramethylethylene	-16.80 ± 0.36	-17.42	0.6	(-21.6)	4.8	-17.06 ^e	0.3
Acetylene	54.19 ± 0.19	54.20	0.0	--	--	54.19	0.0
Propyne	44.32 ± 0.21	44.40	0.1	--	--	44.32	0.0
1-butyne	39.48 ± 0.21	39.66	0.2	--	--	39.34	0.2
2-butyne	34.68 ± 0.24	34.60	0.1	--	--	34.45	0.2
1-pentyne	34.50 ± 0.50	34.67	0.2	--	--	34.36	0.1
2-pentyne	30.80 ± 0.50	29.86	0.9	--	--	29.47	1.3
3-methyl-1-butyne	32.60 ± 0.50	32.86	0.3	--	--	32.28	0.3
3,3-dimethyl-1-butyne	25.36	25.72	0.4	--	--	24.38	1.0

a) Data given by Gronert (reference 3) or (in parentheses) derived here from his scheme. b) Acetylenes were not considered by Gronert. c) Isopentane is strained, but the gauche interaction is ignored. d) Benson's 0.7 kcal/mol strain correction was included. e) Including 2.03 kcal/mol *cis* strain corrections. See text.

Recently, Gronert^[3] devised a new additivity scheme based on fewer parameters, which is remarkable in reproducing accurately the ΔH_f 's of diverse unstrained hydrocarbons, alkanes, alkyl radicals, and alkenes (Table 3.1), by means of a unified treatment (Scheme 3.1a). But Gronert went far beyond this empirical success to claim validity for the assumptions he employed (notably geminal *repulsions*) in devising his scheme and to question well-established concepts like hyperconjugation. We now analyze Gronert's treatment in detail and show that the simpler Scheme 3.1b, with a single, *attractive* geminal term, is able to reproduce the same set of experimental data satisfactorily. Our second treatment, Scheme 3.2, based on conventional reasoning, performs equally well.

Gronert's Scheme 3.1a is easy to use in practice. It depends on the number of each kind of bond (two-atom terms) and 1,3-geminal combination (three-atom terms). The H atom $\Delta H_f = 52.1$ kcal/mol, used in the one-atom $f(C,H)$ term, is the only directly employed experimental value. In contrast, Gronert did not employ the experimental $DH_f = 170.6$ kcal/mol for the C atom, but increased its value to 231.3 kcal/mol by adding 60.7 kcal/mol (the bond dissociation energy of the excited C–H quartet state). Gronert then derived his C–C, C=C, and C–H bond energies arbitrarily by statistical fitting; the resulting values are very far from conventional estimates (see discussion below). The values of these bond energies are artificially *assumed to be the same for all hydrocarbons* (independent of carbon hybridization, etc.) and serve to decrease the total energy.

Three additional statistically derived CCC, CCH, and HCH three-atom geminal interaction terms increase the energy. These terms *depend only on the number of each type of geminal unit, and are independent of the actual structure*.

Scheme 3.1. (a) Gronert's method for evaluating alkane, cycloalkane, alkene, and alkyl radical heats of formation. (b) Four-parameter simplification employing experimental H and C data. (See Tables 3.5 and 3.19.)

$$\Delta H_f = n_{C-C}E_{C-C} + n_{C=C}E_{C=C} + n_{C-H}E_{C-H} + n_{C-C-C}E_{C-C-C} + \\ n_{C-C-H}E_{C-C-H} + n_{H-C-H}E_{H-C-H} - f(C,H)$$

a) Gronert's evaluation (including CH and CH₂): $f(C,H) = (170.6 + E_c)n_C + 52.1 n_H$, $E_{C-C} = -146.0$, $E_{C=C} = -66.2$, $E_{C-H} = -124.2$, $E_{C-C-C} = 10.2$, $E_{C-C-H} = 9.3$, $E_{H-C-H} = 6.6$, and $E_C = 60.7$ kcal/mol.

b) Four-parameter simplification (excluding CH and CH₂): $f(C,H) = (170.6 n_C + 52.1 n_H)$, $E_{C-C} = -85.59$, $E_{C-H} = -96.07$, $E_{C=C} = -64.34$, $E_{H-C-H} = -1.97$

To summarize, Scheme 3.1a achieves its diversity of application and accuracy by employing the fixed values of seven arbitrarily derived terms. The value for $f(\text{C})$ is set *ad hoc* and the values of the other terms are determined empirically as best fit averages of the experimental hydrocarbon heats of formation shown in Table 3.1. Only $f(\text{H})$ is based directly on the experimental ΔH_f value.

Gronert conceded that his derived C–C and C–H bond energy values are far larger than those commonly accepted in the literature. For instance, the conventional average C–H bond energy (BE) of methane (99.2 kcal/mol) is $\frac{1}{4}$ the experimental atomization energy (396.9 kcal/mol). Gronert's C–H value is 124.2 kcal/mol. Assuming that ethane has the same C–H BE as methane (an assumption Gronert adopts), the experimentally-based C–C BE of ethane is 78.5 kcal/mol.^[4] The experimental CC bond dissociation energy (BDE) of ethane into two methyl radicals is 91.4 kcal/mol. Gronert's 146.0 kcal/mol C–C value is much larger than both the ethane BE and BDE, and has no independent support. As the one-atom and two-atom terms in Scheme 3.1a result in ΔH_f 's that are far too negative, Gronert compensates for the gross overestimation by “repulsive” (positive) 1,3 geminal C–C–C, C–C–H, and H–C–H terms, which are adjusted to give the best overall data fit. His 1,3 “repulsion” concept was then employed to challenge hyperconjugation as well as the conventional interpretation of the stabilization of branched alkanes as a net attractive effect, e.g., isobutane and neopentane, are usually interpreted as having a greater number of net attractive interactions among 1,3-groups than their less stable n-alkane isomers.

Gronert's detailed reasoning and justification notwithstanding, the quantitative success of his treatment is the chief evidence favoring his iconoclastic interpretation of branching and his contest of hyperconjugation. However, statisticians warn us that good correlations

do not necessarily establish causal relationships.^[5] We argue that Gronert's overestimation of bond energies masks the stabilizing influence of hyperconjugation and branching. Indeed, we have found that many different values of the Gronert terms give satisfactory to excellent ΔH_f estimates, when compared with experiment. Table SI-2 summarizes some of the alternative parameter sets we have devised by statistical data fitting^[6-8] (details are given in Section 3.8.1, Table 3.4 and in Tables 3.5-3.19), many showing good correlation with experiment. We use the experimental ΔH_f 's for C and H atoms; this results in CH and CC bond energies close to the conventional estimates. When the exceptional ^4CH excited state and the $^3\text{CH}_2$ molecules are removed from the set, data fitting for the remaining 22 alkanes, alkenes, and free radicals is achieved remarkably well *with only four adjustable parameters* – the minimum number chemically plausible – the two atom C–H, C–C, and C=C terms as well as a single three-atom HCH term, which has a negative (i.e., *attractive*) value. *But no significance can be attached to the values obtained from all such empirical fitting schemes.*

We now propose a new approach to an additivity scheme, which makes use of conventional considerations and does not require data fitting (Scheme 3.2).

Scheme 3.2. Generalized isodesmic method for calculating heats of formation of unstrained alkanes, alkenes, alkynes, and alkyl radicals (in kcal/mol). See the text and the parameters in Table 3.2 for details of the applications and the evaluations.

$$\Delta H_f = \text{base} - 2.15n(\text{CH}_2) - 1,3\text{CCC branching attraction} - \text{hyperconjugation}$$

Our new isodesmic additivity method (Scheme 3.2) for a wider set of hydrocarbons including alkynes (Table 3.1) is based almost entirely on experimental data for the

simplest molecules (methane, ethane, propane, ethene, propene, ethyne, propyne, as well as the methyl and ethyl radicals). Scheme 3.2 reproduces the heats of formation of hydrocarbons with accuracies equal to Gronert's Scheme 3.1a *without using data averaging*. All the 1,3-interactions in our scheme are stabilizing (rather than destabilizing) and provide *support the conventional concepts of branching and hyperconjugation*. The only adjustable parameters arise in Scheme 3.2 from the reasonable assumption that the magnitude of stabilizing effects at a given carbon are attenuated when more than one substituent contributes.

The ΔH_f 's (in kcal/mol) of the molecules chosen as the appropriate base (methane (-17.89), ethene (+12.54), ethyne (+54.19), and the methyl radical (+35.05)) are elaborated by the formal addition of one or more $[\text{CH}_2]$ units. The -2.15 $[\text{CH}_2]$ increment in Scheme 3.2 (the difference in the heats of formation of CH_4 (-17.89) and C_2H_6 (-20.04), Reaction 1, Table 3.2) is employed universally in our method for each additional $[\text{CH}_2]$ unit in larger unstrained molecules. Like all the values used in Scheme 3.2 and Table 3.2, it is *not* derived by averaging.

Table 3.2. Parameters employed in Scheme 3.2. Experimental ΔH_f data (in kcal/mol) were used for their evaluation.

Reaction	Energy	Attenuation	Interaction
1) $C_2H_6-CH_4 \rightarrow [CH_2]^a$	2.15	None	
2) $C_3H_8+CH_4 \rightarrow 2 C_2H_6$	2.83	$(0.955)^{N-1(b)}$	1,3-CCC Branching
3) $C_2H_5\cdot + CH_4 \rightarrow C_2H_6 + CH_3\cdot$	3.90	$(0.85)^{N-1(c)}$	Alkyl radical HC
4) propene + $CH_4 \rightarrow C_2H_6 + C_2H_4$	5.51	$(0.88)^{N-1(d)}$	Alkene HC
5) propyne + $CH_4 \rightarrow C_2H_6 + CH_4$	7.72	None	Alkyne HC

a) Value of the $[CH_2]$ unit to be added to the base. The methane-bound $-15.74 [H_2]$ unit (via $[CH_2] + [H_2] = CH_4$) is used to correct for the stoichiometric differences of polycycles.

b) Derived from the difference per 1,3-CCC in propane and isobutane.

c) Derived from the difference per hyperconjugation (HC) in the ethyl and isopropyl radicals.

d) Derived from the difference per hyperconjugation (HC) in propene and 2-methylpropene.

Table 3.2 summarizes the derivation and the parameters employed in our Scheme 3.2. The parameters are based on the five bond separation energies of equations 1-5, and a uniform attenuation treatment.

However, the $[CH_2]$ incorporation that extends ethane to propane introduces a new type of 1,3CCC interaction, not present in methane or ethane. Were there a linear progression from methane and ethane, the ΔH_f of propane would be $-20.04 - 2.15 = -22.19$ kcal/mol. Instead, its experimental ΔH_f (-25.02) is -2.83 kcal/mol more negative (Reaction 2, Table 3.2). This -2.83 *net attraction* value is employed universally as the 1,3CCC term in Scheme 3.2, not only to other unstrained straight chain and cyclic hydrocarbons but also to all situations not involving branching or hyperconjugation. Examples are the 1,3CCC methyl–methyl interactions in 2-methylpropene and in the isopropyl radical. Contrary to Gronert’s geminal terms, the our 1,3CCC interactions based on propane *reduce* the total energy and are *net stabilizing*.^[9]

3.3. BRANCHING AND ATTENUATION

Chain branching results in multiple 1,3–interactions at the same carbon. Three 1,3CCC interactions are present in isobutane and in the t–butyl radical. Six 1,3CCC interactions are present in neopentane. Attenuation effects, which are common in chemistry, occur: the second (and subsequent) substituent stabilizes less effectively than the first. The -2.83 kcal/mol 1,3CCC stabilization value is attenuated somewhat in branched molecules. This attenuation can be expressed by a single term, $(0.955)^{N-1}$, which employs a coefficient *based on isobutane, the smallest branched chain alkane*, and an exponent, $N-1$, where N is the number of 1,3–CCC interactions at the same carbon. Note that the 0.955 attenuation coefficient gives excellent agreement for neopentane, the most highly branched example in Table 3.1.

3.4. HYPERCONJUGATION IN ALKENES, ALKYNES, AND ALKYL RADICALS

Alkyl substituents stabilize unsaturated functional groups by electron donation. Such “hyperconjugative” interactions (last term, Scheme 3.2) are evaluated simply from by the BSE equations (3) – (5) in Table 3.2. Thus, the alkyl group stabilization is 5.51 kcal/mol for an alkene (based on propene), is 7.72 kcal/mol for an alkyne (based on propyne), and 3.90 kcal/mol for a alkyl radical (based on the ethyl radical) due to hyperconjugation. (Note that “hyperconjugation,” as defined here (Table 3.2), includes all the 1,3–CCC interactions involving the two unsaturated carbons. Consequently, the -2.83 kcal/mol branching term is NOT applied in such instances.) However, attenuation is present, as two (or more) alkyl groups attached to the same carbon are not as effective as the first.

The attenuation terms are $(0.88)^{N-1}$ for alkenes (based on isobutene) and $(0.85)^{N-1}$ for alkyl radicals (based on isopropyl).

Due to its *cis* interaction, 2-methyl-2-butene, included by Gronert, is not strain-free. A 2.03 kcal/mol strain correction is deduced from our treatment. Applying this correction twice gives a good isodesmic result for tetramethylethylene, in contrast to Gronert's method (Table 3.1).

3.5. METHOD OF APPLICATION

In practice, Scheme 3.2 is evaluated quite simply by using the parameters in Table 3.2. The ΔH_f of a hydrocarbon is computed from its appropriate base, its stoichiometry, and its connectivity. Details for the derivation of each hydrocarbon ΔH_f in Table 3.1 are given in Table SI-1 in simplified form, with separate entries depending on the number of 1,3CCC interactions.

3.6. CYCLIC MOLECULES

The same approach applies to unstrained acyclic, cyclic, and polycyclic alkanes, but the variations in stoichiometry must be taken into account. The C_nH_{2n+2} alkanes are based on methane ($\Delta H_f = -17.89$), but the C_nH_{2n} cycloalkanes have two fewer H's for the same number of carbons, and need no base. Instead, the -2.15 kcal/mol value for each $[CH_2]$ unit is used directly, e.g., six times for cyclohexane. The -2.83 term is employed six times as well, as there are six 1,3-CCC interactions around the six membered ring. The resulting -29.88 ΔH_f estimate matches compared the experimental -29.43 ± 0.19 kcal/mol. The ΔH_f evaluation of C_nH_{2n-2} bicycloalkanes employs the 15.74 kcal/mol $[H_2]$

unit as the base (See Table 3.2, footnote a). Our -43.89 estimate for trans-decalin (Table 3.1) agrees better with experiment ($\Delta H_f = -43.54 \pm 0.55$) than the -41.8 calculated using Gronert's scheme. The splendid overall performance of our isodesmic method is illustrated in the abstract figure.

Gronert's Scheme 3.1a also gives good results. It employs seven adjusted parameters, but these are ad hoc and are derived by data averaging. If CH and CH₂ are removed from Gronert's data set, our simplified data-fitting Scheme 3.1b requires only four adjusted parameters to give satisfactory results. Our alternative treatment, Scheme 3.2, is based on the well-established theoretical concepts of branching, hyperconjugation, and attenuation and depends only on the energetic relationships among the simplest hydrocarbon molecules. The parameters are not averaged and are applied universally to reproduce experimental heats of formation for acyclic and cyclic alkanes, alkyl free radicals, alkenes, and alkynes very accurately (Table 3.1 and Figure 3.1).

3.7. ACKNOWLEDGMENTS

We thank C. Corminboeuf, N. L. Allinger, W. T. Borden, P. Jarowski, B. N. Papas, and S. Gronert for comments, suggestions, and assistance.

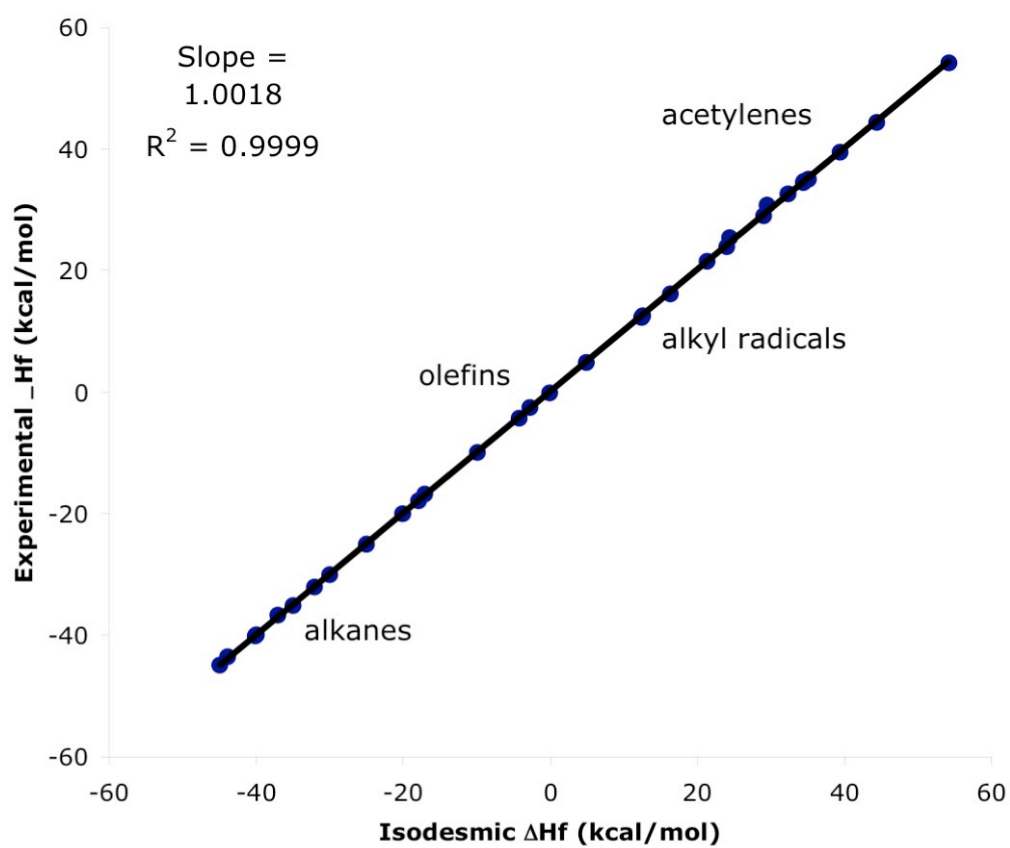


Figure 3.1. Performance of our new isodesmic additivity scheme.

3.8. SUPPORTING INFORMATION

Table 3.3. Table used to derive values for heats of formation using the isodesmic additivity scheme. The number in each column represents the number of each specific interaction present in the molecule of interest. This number is then multiplied by the value for the interaction located at the top of each column. The value of the summed interactions is then subtracted from the base value, giving ΔH_f . All values in kcal/mol.

	base	# of extra CH ₂ (2.15 kcal/mol)	# of primary branches (2.83 kcal/mol)	# of tertiary branches ^a (7.74 kcal/mol)	# of quarternary branches ^b (13.49 kcal/mol)	# primary radical HC (3.90 kcal/mol)	# of secondary radical HC ^c (6.63 kcal/mol)	# of tertiary radical HC ^d (8.45 kcal/mol)	# of primary olefin HC (5.51 kcal/mol)	# of secondary olefin HC ^e (9.70 kcal/mol)	# of acetylene HC (7.72 kcal/mol)	syn olefin correction (2.03 kcal/mol)	Total ΔH_f
methane	-17.89	--	--	--	--	--	--	--	--	--	--	--	-17.89
ethane	-17.89	1	--	--	--	--	--	--	--	--	--	--	-20.04
propane	-17.89	2	1	--	--	--	--	--	--	--	--	--	-25.02
n-butane	-17.89	3	2	--	--	--	--	--	--	--	--	--	-30.00
isobutane	-17.89	3	--	1	--	--	--	--	--	--	--	--	-32.08
n-pentane	-17.89	4	3	--	--	--	--	--	--	--	--	--	-34.98
isopentane	-17.89	4	1	1	--	--	--	--	--	--	--	--	-37.06 ^f
neopentane	-17.89	4	--	--	1	--	--	--	--	--	--	--	-39.98
n-hexane	-17.89	5	4	--	--	--	--	--	--	--	--	--	-39.96
n-heptane	-17.89	6	5	--	--	--	--	--	--	--	--	--	-44.94
cyclohexane	0.0	6	6	--	--	--	--	--	--	--	--	--	-29.88
decalin	15.74	10	8	2	--	--	--	--	--	--	--	--	-41.73
methyl radical	35.05	--	--	--	--	--	--	--	--	--	--	--	35.05
ethyl radical	35.05	1	--	--	--	1	--	--	--	--	--	--	29.00
propyl radical	35.05	2	1	--	--	1	--	--	--	--	--	--	24.02
isopropyl radical	35.05	2	1	--	--	--	1	--	--	--	--	--	21.29
sec-butyl radical	35.05	3	2	--	--	--	1	--	--	--	--	--	16.31
tert-butyl radical	35.05	3	--	1	--	--	--	1	--	--	--	--	12.40
cyclohexyl radical	50.79 ^g	5	6	--	--	--	1	--	--	--	--	--	16.43
ethene	12.54	--	--	--	--	--	--	--	--	--	--	--	12.54
propene	12.54	1	--	--	--	--	--	--	1	--	--	--	4.48
1-butene	12.54	2	1	--	--	--	--	--	1	--	--	--	-0.10
E-2-butene	12.54	2	--	--	--	--	--	--	2	--	--	--	-2.78
2-methylpropene	12.54	2	1	--	--	--	--	--	--	1	--	--	-4.29
2-methyl-2-butene	12.54	3	2	--	--	--	--	--	1	1	--	1	-9.92
tetramethylethene	12.54	4	2	--	--	--	--	--	--	2	--	2	-17.06
ethyne	54.19	--	--	--	--	--	--	--	--	--	--	--	54.19
propyne	54.19	1	--	--	--	--	--	--	--	--	1	--	44.32
1-butyne	54.19	2	1	--	--	--	--	--	--	--	1	--	39.34
2-butyne	54.19	2	1	--	--	--	--	--	--	--	2	--	34.45
1-pentyne	54.19	3	2	--	--	--	--	--	--	--	1	--	34.36
2-pentyne	54.19	3	1	--	--	--	--	--	--	--	2	--	29.47

3-methyl-1-butyne	54.19	3	--	1	--	--	--	--	--	--	1	--	32.28
3,3-dimethyl-1-butyne	54.19	4	--	--	1	--	--	--	--	--	1	--	24.38

a) # of tertiary branches = $(0.955)^2 (2.83)(3) = 7.74$ kcal/mol, **b)** # of quaternary branches = $(0.955)^5 (2.83)(6) = 13.49$ kcal/mol, **c)** # of secondary radical hyperconjugation interactions = $(0.85)(3.90)(2) = 6.63$ kcal/mol, **d)** # of tertiary radical hyperconjugation interactions $(0.85)^2 (3.90)(3) = 8.45$ kcal/mol, **e)** # of secondary olefin hyperconjugation interactions, $(0.88)(5.51)(2) = 9.70$ kcal/mol, **f)** This molecule is strained but, following Gronert, the gauche interaction is ignored. **g)** Base value derived from the heat of formation of the methyl radical (35.05 kcal/mol) plus the value of removing of an $[H_2]$ unit (15.74 kcal/mol).

3.8.1. COMMENTS ON THE STATISTICAL ANALYSES IN TABLE 3.4

Employing the Excel program, we analyzed Gronert's treatment (Scheme 3.1) and many variations based on the same structure-based parameters he employed. The objective was to fit the 298 K experimental heats of formation of a set of 24 essentially strain-free alkanes, alkenes, and alkyl radicals. Gronert included two more "exotic" hydrocarbons, the triplet ground state of methylene, $^3\text{CH}_2$, and the quartet excited state of methylidyne, ^4CH .

Gronert employed eight parameters to fit this data set: 2 one-atom, 3 two-atom, and 3 three-atom terms. Only one value was used for each of these terms. Its experimental heat of formation, 52.1 kcal/mol, was fixed for the hydrogen atom. But for the carbon atom parameter, Gronert employed an artificial value, 231.3 kcal/mol, which is the sum of the experimental heat of formation of the C atom (170.6) and of the bond dissociation energy of the ^4CH quartet (60.7 kcal/mol). This artificial C parameter automatically results in a perfect fit between the "derived" and experimental ^4CH value. Gronert's scheme (see Table 3.5) achieves a low mean unsigned deviation (MUD) by using the six remaining variables, i.e., the 3 two-atom (C-C, C=C, and C-H) and the 3 three-atom (CCC, CCH, and HCH) terms. The molecular connectivity determines how many times each of these terms is used. Tables 3.5-3.19 provide all the details. Table 3.4 summarizes the performance of each of the treatments used in these Tables.

Gronert's statistical fitting (run 3) is only improved trivially by using the Excel program (run 4). The same is true in run 5, where Gronert's fixed 231.3 value is allowed to vary, and in run 6, where the 52.1 H atom constraint is lifted.

If a much smaller arbitrary 200 kcal/mol (instead of 231.3) value for C is fixed (run 7), the MUD deteriorates (but only to 1.02 kcal/mol) due almost entirely to the ^4CH (as expected) and the $^3\text{CH}_2$ errors. If the C atom parameter is fixed to the 170.6 kcal/mol experimental ΔH_f (run 8), these deviations are much larger and MUD becomes 1.84 kcal/mol.

Instead of including ^4CH excited state, runs 9 and 10 employed the experimental ^2CH ground state $\Delta H_f = 142.00$ kcal/mol instead. All eight parameters were allowed to vary in run 9; MUD was only 0.40 kcal/mol! However, if C and H were fixed to the experimental values, MUD increased, but only to 1.12 kcal/mol. As also is shown by comparing the individual errors in Tables 8 vs. 10, the ground state ^2CH ΔH_f is matched more closely than the ^4CH ΔH_f when the experimental C and H energies are employed.

Since CH is only distantly related to the usual hydrocarbons, we removed it from the test set entirely in runs 11-13 (but retained $^3\text{CH}_2$). The MUD values improved and became comparable to those of typical experimental ΔH_f determinations. Run 13, using the C and H ΔH_f 's, is the most significant; the 0.60 kcal/mol MUD is due mostly to the large $^3\text{CH}_2$ deviation, 9.5 kcal/mol.

We next omitted $^3\text{CH}_2$ from our data set. Runs 14-16 gave slightly better results than Gronert's MUD. This performance is particularly noteworthy for Run 16 where C and H were fixed to their ΔH_f values. Most remarkably, run 17 achieves experimental accuracy (MUD=0.50 kcal/mol) by using only four variables! The CCC and CCH three-atom terms are omitted, and C and H are fixed to their ΔH_f values. Four variables are the minimum number chemically plausible. These represent the three types of bonds, C-H,

C–C, and C=C, and only one other “structural parameter,” which depends on the number of HCH units in a molecule.

As we regard this as an exercise in data fitting, we attach no significance to any of the values. For example, all the CH bonds in the various positions and in the different types of molecules do not have the same energy, and the same is true of the C–C and C=C bonds as well as the HCH units. Nevertheless, it is striking that the C=C values in *all* the runs are nearly the same, and that the C–H and C–C energies from runs 8, 10, 13, and 15-17 are also in line with typical values of “bond energies” given in compilations. This agreement with conventional assessments contrasts sharply with Gronert’s C–H and C–C parameters (Run 3) that are nearly twice as large. Gronert’s CCC (10.2), CCH (9.3), and HCH (6.6 kcal/mol) three-atom terms (Run 3) are all appreciably positive, and he considers these to have chemical significance (i.e., to be *repulsive*). In contrast, many of the three atom terms in Runs 8, 10, 13-17 have *negative values or are very small*. Run 17 achieves a good MUD with a single, negative HCH (i.e., *attractive*) value (–1.97

Table 3.4. Summary of values (in kcal/mol) from Tables 3.5-3.19. Fixed parameters are given in red; experimental data are in bold font. The value Gronert used are in italics. Parameters in black were free to vary. Data fitting were done using Excel.

Run	C	H	CH	CC	HCH	CCH	CCC	C=C	Mean Unsigned Deviation
⁴CH and ³CH₂									
3 Gronert	<i>231.3</i>	<i>52.1</i>	<i>-124.2</i>	<i>-146.0</i>	<i>6.6</i>	<i>9.3</i>	<i>10.2</i>	<i>-66.2</i>	0.22
4 Stat. Av.	<i>231.3</i>	<i>52.1</i>	-124.38	-146.36	6.78	9.40	10.33	-65.83	0.19
5 Expt ΔH _f H	231.71	<i>52.1</i>	-124.61	-146.74	6.88	9.47	10.38	-65.86	0.18
6 None fixed	231.88	-36.34	-36.34	-146.86	6.95	9.52	10.40	-65.81	0.18
7 Arbitrary C	<i>200.0</i>	<i>52.1</i>	-108.44	-115.18	1.38	4.10	5.16	-66.09	1.02
8 Expt ΔH _f C	<i>170.6</i>	<i>52.1</i>	-93.73	-85.54	-3.54	-0.84	0.19	-66.17	1.84
²CH and ³CH₂									
9 None fixed	196.91	66.94	-121.80	-112.25	0.91	3.64	4.70	-65.93	0.40
10 Expt ΔH _f C	<i>170.6</i>	<i>52.1</i>	-93.77	-85.83	-3.50	-0.78	0.28	-66.02	1.12
No CH									
11 None fixed	219.90	51.84	-118.19	-135.03	4.72	7.43	8.46	-66.04	0.24
12 Arbitrary C	<i>200.0</i>	<i>52.1</i>	-108.64	-115.09	1.50	4.16	5.11	-65.86	0.40
13 Expt ΔH _f C	<i>170.6</i>	<i>52.1</i>	-93.75	-85.75	-3.52	-0.80	0.25	-66.08	0.60
No CH or CH₂									
14 None fixed	175.60	-22.20	-22.20	-90.70	-2.52	0.11	1.06	-65.83	0.19
15 Expt ΔH _f H	175.59	<i>52.1</i>	-94.01	-85.69	-3.34	-0.72	0.22	-65.84	0.19
16 Expt ΔH _f C	<i>170.6</i>	<i>52.1</i>	-94.01	-85.67	-3.34	-0.72	0.21	-68.83	0.19
17 No CCH, CCC	<i>170.6</i>	<i>52.1</i>	-96.07	-85.59	-1.97	<i>0.0</i>	<i>0.0</i>	-64.34	0.50

Table 3.5. Gronert's scheme. Average deviation is 0.22 kcal/mol.

Molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.3	-17.9	0.6
ethane	2	6	6	1	6	6	0	0	-20.4	-20.0	0.4
propane	3	8	8	2	7	10	1	0	-25.3	-25.0	0.3
n-butane	4	10	10	3	8	14	2	0	-30.2	-30.0	0.2
isobutane	4	10	10	3	9	12	3	0	-31.9	-32.1	0.2
n-pentane	5	12	12	4	9	18	3	0	-35.6	-35.1	0.5
isopentane	5	12	12	4	10	16	4	0	-36.8	-36.7	0.1
neopentane	5	12	12	4	12	12	6	0	-40.3	-40.1	0.2
n-hexane	6	14	14	5	10	22	4	0	-39.9	-40.0	0.1
cyclohexane	6	12	12	6	6	24	6	0	-29.3	-29.4	0.1
methyl radical	1	3	3	0	3	0	0	0	34.9	35.1	0.2
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.6	21.5	0.1
sec-butyl radical	4	9	9	3	7	12	2	0	16.7	16.1	0.6
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	93.8	93.3	0.5
^4CH	1	1	1	0	0	0	0	0	159.2	159.2	0.0
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	4.9	4.9	0.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.1	-0.2	0.3
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-10.1	-9.9	0.2
$E_{\text{interaction}}$ (kcal/mol)	231.3	52.1	-124.2	-146.0	6.6	9.3	10.2	-66.2			

Table 3.6. Scheme where C = 231.3 and H =52.1, all other parameters free to vary. Average deviation is 0.19 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	34.8	35.1	0.3
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
³ CH ₂	1	2	2	0	1	0	0	0	93.5	93.3	0.2
⁴ CH	1	1	1	0	0	0	0	0	159.1	159.2	0.1
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
<i>E</i> _{interaction} (kcal/mol)	231.3	52.1	-124.38	-146.36	6.78	9.40	10.33	-65.83			

Table 3.7. Scheme where H=52.1, all other parameters free to vary. Average deviation is 0.18 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.0	-35.1	0.1
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.5	-29.4	0.1
methyl radical	1	3	3	0	3	0	0	0	34.8	35.1	0.3
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	93.6	93.3	0.3
^4CH	1	1	1	0	0	0	0	0	159.2	159.2	0.0
ethene	2	4	4	1	2	4	0	1	12.4	12.5	0.1
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-10.0	-9.9	0.1
$E_{\text{interaction}}$ (kcal/mol)	231.71	52.1	-124.61	-146.74	6.88	9.47	10.38	-65.86			

Table 3.8. No fixed parameters. Average deviation is 0.18 kcal/mol.

Molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutene	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.0	-35.1	0.1
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	34.7	35.1	0.6
ethyl radical	2	5	5	1	4	5	0	0	28.9	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.0	23.9	0.1
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.5	16.1	0.4
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	93.5	93.3	0.2
^4CH	1	1	1	0	0	0	0	0	159.2	159.2	0.0
ethene	2	4	4	1	2	4	0	1	12.4	12.5	0.1
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-10.0	-9.9	0.1
$E_{\text{interaction}}$ (kcal/mol)	231.88	-36.34	-36.34	-146.86	6.95	9.52	10.40	-65.81			

Table 3.9. Scheme where H=52.1, C=200.0, all other parameters free to vary. Average deviation is 1.02 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.4	-20.0	0.4
propane	3	8	8	2	7	10	1	0	-25.3	-25.0	0.3
n-butane	4	10	10	3	8	14	2	0	-30.2	-30.0	0.2
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.1	35.1	0.0
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	88.7	93.3	4.6
^4CH	1	1	1	0	0	0	0	0	143.7	159.2	15.5
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	200.0	52.1	-108.44	-115.18	1.38	4.10	5.16	-66.09			

Table 3.10. Scheme where C = 170.6 and H = 52.1, all other parameters free to vary. Average deviation is 1.84 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.4	-20.0	0.4
propane	3	8	8	2	7	10	1	0	-25.3	-25.0	0.3
n-butane	4	10	10	3	8	14	2	0	-30.2	-30.0	0.2
isobutane	4	10	10	3	9	12	3	0	-31.9	-32.1	0.2
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.8	-36.7	0.1
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.1	35.1	0.0
ethyl radical	2	5	5	1	4	5	0	0	29.2	29.0	0.2
propyl radical	3	7	7	2	5	9	1	0	24.3	23.9	0.4
isopropyl radical	3	7	7	2	6	8	1	0	21.6	21.5	0.1
sec-butyl radical	4	9	9	3	7	12	2	0	16.7	16.1	0.6
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	83.8	93.3	9.5
^4CH	1	1	1	0	0	0	0	0	129.0	159.2	30.2
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	170.6	52.1	-93.73	-85.54	-3.53	-0.84	0.19	-66.17			

Table 3.11. Scheme using ^2CH and $^3\text{CH}_2$ and no fixed parameters. Average deviation is 0.40 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.0	35.1	0.1
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.4	21.5	0.1
sec-butyl radical	4	9	9	3	7	12	2	0	16.5	16.1	0.4
tert-butyl radical	4	9	9	3	9	9	3	0	12.1	12.3	0.2
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	88.1	93.3	5.2
^2CH	1	1	1	0	0	0	0	0	142.1	142.0	0.1
ethene	2	4	4	1	2	4	0	1	12.6	12.5	0.1
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	196.91	66.94	-121.80	-112.25	0.91	3.64	4.70	-65.93			

Table 3.12. Scheme using ^2CH and $^3\text{CH}_2$, $\text{C}=170.6$, $\text{H}=52.1$, all other parameters free to vary. Average deviation is 1.12 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.1	35.1	0.0
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	83.8	93.3	9.5
^2CH	1	1	1	0	0	0	0	0	128.9	142.0	13.1
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	170.6	52.1	-93.77	-85.83	-3.50	-0.78	0.28	-66.02			

Table 3.13. Scheme with no CH, and no fixed parameters. Average deviation is 0.24 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.2	-30.0	0.2
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.1	35.1	0.0
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	91.9	93.3	1.4
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	219.90	51.84	-118.19	-135.03	4.72	7.43	8.46	-66.04			

Table 3.14. Scheme with no CH, C=200.0, and H=52.1, all other parameters free to vary. Average deviation is 0.40 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.9	-32.1	0.2
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.8	-36.7	0.1
neopentane	5	12	12	4	12	12	6	0	-40.2	-40.1	0.1
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	34.9	35.1	0.2
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	88.4	93.3	4.9
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	6.0	4.9	1.1
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.1	-0.2	0.3
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-10.0	-9.9	0.1
$E_{\text{interaction}}$ (kcal/mol)	200.0	52.1	-108.64	-115.09	1.50	4.16	5.11	-65.86			

Table 3.15. Scheme with no CH, C=170.6, and H=52.1, all other parameters free to vary. Average deviation is 0.60 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.2	-30.0	0.2
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.1	-35.1	0.0
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	35.1	35.1	0.0
ethyl radical	2	5	5	1	4	5	0	0	29.1	29.0	0.1
propyl radical	3	7	7	2	5	9	1	0	24.2	23.9	0.3
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
$^3\text{CH}_2$	1	2	2	0	1	0	0	0	83.8	93.3	9.5
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.7	-2.6	0.1
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.4	-4.3	0.1
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	170.6	52.1	-93.75	-85.75	-3.52	-0.80	0.25	-66.08			

Table 3.16. Scheme where CH and $^3\text{CH}_2$ have been removed, all other parameters free to vary. Average deviation is 0.19 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.0	-35.1	0.1
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	34.8	35.1	0.3
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.2	12.3	0.1
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	175.60	-22.20	-22.20	-90.70	-2.52	0.11	1.06	-65.83			

Table 3.17. Scheme with CH and $^3\text{CH}_2$ removed, H = 52.1, all other parameters free to vary. Average deviation is 0.19 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.0	-35.1	0.1
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.5	-29.4	0.1
methyl radical	1	3	3	0	3	0	0	0	34.9	35.1	0.2
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-10.0	-9.9	0.1
$E_{\text{interaction}}$ (kcal/mol)	170.59	52.1	-94.01	-85.69	-3.34	-0.72	0.22	-65.84			

Table 3.18. Scheme with CH and $^3\text{CH}_2$ removed, C = 170.6 and H = 52.1, all other parameters free to vary. Average deviation is 0.19 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.3	-20.0	0.3
propane	3	8	8	2	7	10	1	0	-25.2	-25.0	0.2
n-butane	4	10	10	3	8	14	2	0	-30.1	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-35.0	-35.1	0.1
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.1	-40.1	0.0
n-hexane	6	14	14	5	10	22	4	0	-40.0	-40.0	0.0
cyclohexane	6	12	12	6	6	24	6	0	-29.5	-29.4	0.1
methyl radical	1	3	3	0	3	0	0	0	34.8	35.1	0.3
ethyl radical	2	5	5	1	4	5	0	0	29.0	29.0	0.0
propyl radical	3	7	7	2	5	9	1	0	24.1	23.9	0.2
isopropyl radical	3	7	7	2	6	8	1	0	21.5	21.5	0.0
sec-butyl radical	4	9	9	3	7	12	2	0	16.6	16.1	0.5
tert-butyl radical	4	9	9	3	9	9	3	0	12.3	12.3	0.0
ethene	2	4	4	1	2	4	0	1	12.5	12.5	0.0
propene	3	6	6	2	4	7	1	1	5.9	4.9	1.0
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.6	-2.6	0.0
1-butene	4	8	8	3	5	11	2	1	0.0	-0.2	0.2
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-9.9	-9.9	0.0
$E_{\text{interaction}}$ (kcal/mol)	170.6	52.1	-94.01	-85.68	-3.34	-0.72	0.21	-65.83			

Table 3.19. Scheme with CH and $^3\text{CH}_2$ removed, C = 170.6, H = 52.1, CCH = 0.0, CCC = 0.0, all other parameters free to vary. Average deviation is 0.50 kcal/mol.

molecule	# C	# H	# CH	# CC	# HCH	# CCH	# CCC	# C=C	Calc. Hf	Expt Hf	deviation
methane	1	4	4	0	6	0	0	0	-17.1	-17.9	0.8
ethane	2	6	6	1	6	6	0	0	-20.0	-20.0	0.0
propane	3	8	8	2	7	10	1	0	-24.9	-25.0	0.1
n-butane	4	10	10	3	8	14	2	0	-29.9	-30.0	0.1
isobutane	4	10	10	3	9	12	3	0	-31.8	-32.1	0.3
n-pentane	5	12	12	4	9	18	3	0	-34.8	-35.1	0.3
isopentane	5	12	12	4	10	16	4	0	-36.7	-36.7	0.0
neopentane	5	12	12	4	12	12	6	0	-40.7	-40.1	0.6
n-hexane	6	14	14	5	10	22	4	0	-39.7	-40.0	0.3
cyclohexane	6	12	12	6	6	24	6	0	-29.4	-29.4	0.0
methyl radical	1	3	3	0	3	0	0	0	32.8	35.1	2.3
ethyl radical	2	5	5	1	4	5	0	0	27.9	29.0	1.1
propyl radical	3	7	7	2	5	9	1	0	23.0	23.9	0.9
isopropyl radical	3	7	7	2	6	8	1	0	21.0	21.5	0.5
sec-butyl radical	4	9	9	3	7	12	2	0	16.1	16.1	0.0
tert-butyl radical	4	9	9	3	9	9	3	0	12.1	12.3	0.2
ethene	2	4	4	1	2	4	0	1	11.4	12.5	1.1
propene	3	6	6	2	4	7	1	1	5.6	4.9	0.7
<i>E</i> -2-butene	4	8	8	3	6	10	2	1	-2.3	-2.6	0.3
1-butene	4	8	8	3	5	11	2	1	-0.3	-0.2	0.1
2-methylpropene	4	8	8	3	7	8	3	1	-4.3	-4.3	0.0
2-methyl-2-butene	5	10	10	4	9	9	6	1	-11.1	-9.9	1.2
$E_{\text{interaction}}$ (kcal/mol)	170.6	52.1	-96.07	-85.59	-1.97	0.0	0.0	-64.34			

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CHAPTER 4

SYSTEMATIC ERRORS IN COMPUTED ALKANE ENERGIES USING B3LYP AND OTHER POPULAR DFT FUNCTIONALS[†]

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4.1. ABSTRACT

Energies computed by B3LYP and other popular DFT functionals are flawed by systematic errors, which can become considerable for larger molecules. These errors, predominantly due to inadequacies in assessing longer-range non-bonded attractive effects (dispersion), are illustrated by the isodesmic stabilization energies of *n*-alkanes (based on methane and ethane, which have no stabilizing 1,3-alkyl group interactions). Newer functionals, designed to describe weak interactions, give somewhat better agreement with experiment, but are not fully satisfactory.

4.2. INTRODUCTION

Kohn-Sham density functional theory has become the standard computational chemistry method. Based on its superior performance in numerous energy assessments of small molecules, B3LYP is the most widely used functional. B3LYP reproduces the geometries of smaller and larger molecules very well. Despite such successes, there is increasing awareness that B3LYP can fail badly in describing the energies of van der Waals molecules, hydrogen bonded systems, reaction barrier heights, and larger molecules.^[1-4] B3LYP computations of even the most basic organic molecules, the *n*-alkanes, result in systematic errors in the predicted heats of formation^[5-8] and bond energies.^[9-12] Redfern *et al.*^[13] reported increasing deviations between B3LYP and G3 theory as the *n*-alkane chain is lengthened (Figure 1). Errors in B3LYP computations of experimental homolytic C–C bond breaking energies of methyl-substituted ethanes and the relative stabilities of isomers become more serious as the molecules become larger.^[14-16] The “cumulative effect of the errors in large molecules”^[7] “discourage the use of the B3LYP model for

reaction energy calculations of organic compounds containing more than four carbon atoms.”^[14] Possible origins of these shortcomings (e.g., dispersion) have been considered,^[14,16] but the problems have not been overcome.

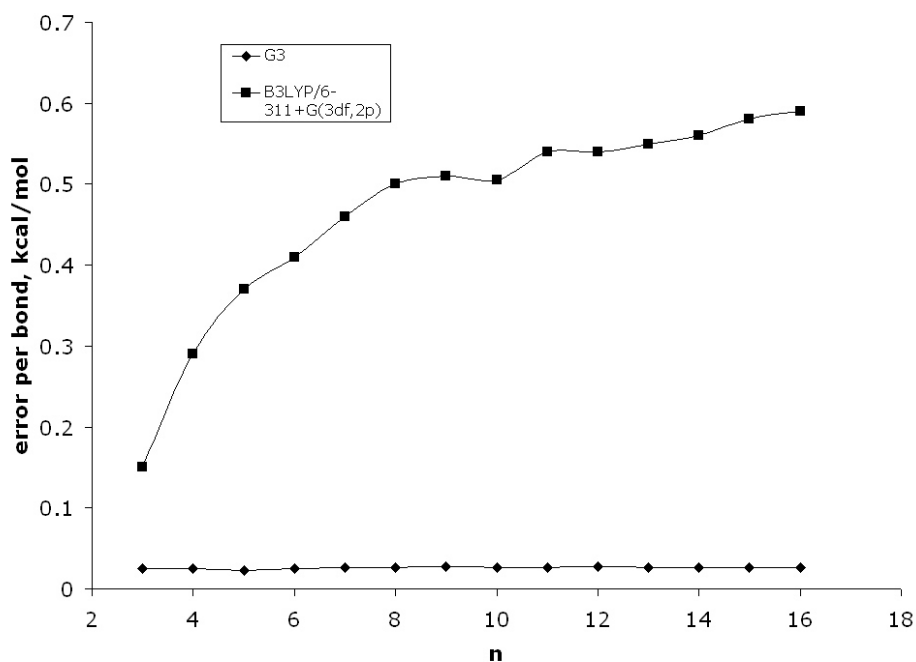


Figure 4.1. Error per bond in calculated enthalpies of formation for *n*-alkanes.

Reproduced from Reference 4.

We computed the isodesmic stabilization energies (Equation 1) of the linear conformations of the *n*-alkanes in order to assess and to help understand the errors given by numerous early and more recent DFT functionals. Figure 2 compares the results against the experimental data and emphasizes the poor performance of most of the functionals with these basic organic molecules.



4.3. METHODS

Our computations with the Gaussian 98,^[17] Gaussian 03,^[18] and Molpro^[19] programs employed one LDA functional (SVWN5),^[20,21] the widely-used hybrid GGA, B3LYP,^[22,23] and several pure GGA functionals (BP86,^[24,25] OLYP,^[23,26,27] PBE,^[28] PW91,^[29] and HCTH).^[30] In addition, we ascertained the performance of the more recently proposed hybrid GGA's (B97-1^[30] and mPW1PW91),^[31] the kinetic-energy dependent meta-GGA (TPSS),^[32,33] and the hybrid meta-GGA functionals (TPSS1KCIS,^[32-37] PBE1KCIS,^[28,34-36,38] MPW1B95,^[31,39,40] MPWB1K,^[31,39,40] MPW1K,^[31,41] and B1B95).^[24,39] The 6-311+G(d,p) basis set was used with all these functionals for uniformity. In addition, comparison with HF, MP2, G3,^[42] and CCSD(T) data were obtained (also included in Figure 2). The computed energies refer to the linear zig-zag *n*-alkane conformations and include zero-point vibrational corrections for comparison with the experimental heats of formation at 0 K.^[43]

4.4. RESULTS AND DISCUSSION

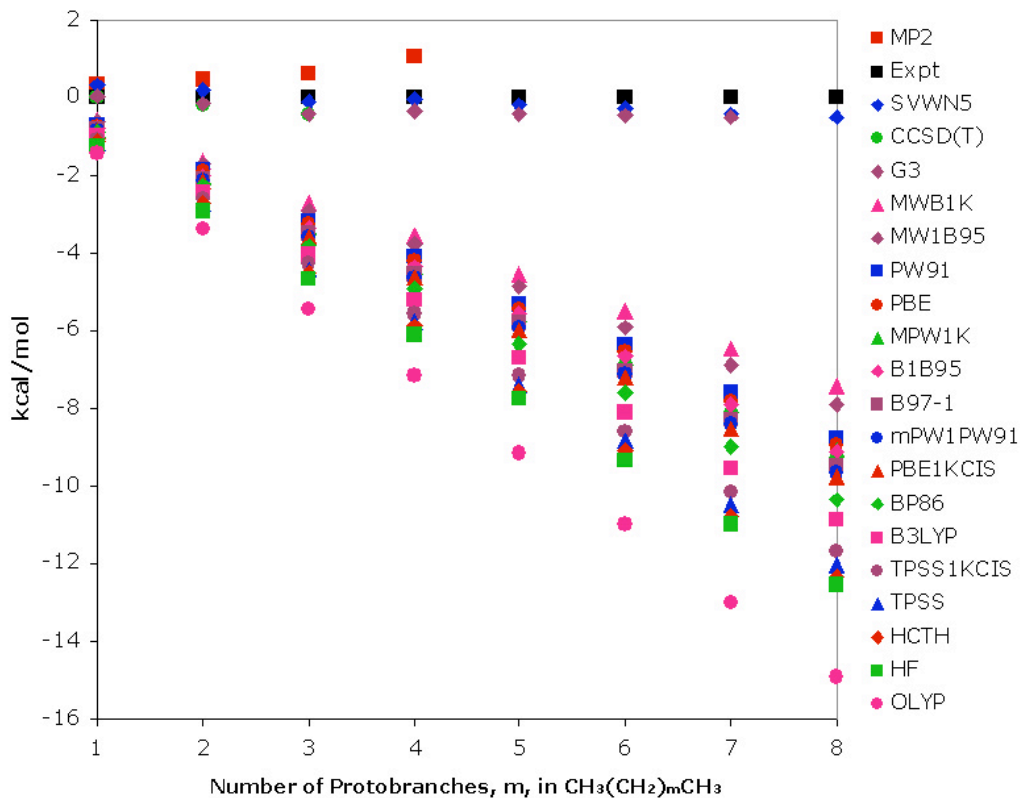


Figure 4.2. Deviations of various DFT functionals from experimental (0 K) protobranching stabilization energies. Negative values denote underestimation. Stabilization energies are based on Equation 1. CCSD(T) and MP2 refer to CCSD(T)/aug-cc-pVTZ//MP2/6-311+G(d,p) and MP2/aug-cc-pVTZ//MP2/6-311+G(d,p), respectively, and include MP2/6-311+G(d,p) zero-point corrections. All other computations employed the 6-311+G(d,p) basis set .

We attribute the increasingly large discrepancies between the computed and experimental energies apparent in Figures 1 and 2 to “protobranching.”^[44-46] Protobranching, defined as the stabilizing interactions between two 1,3-disposed methyl (or methylene) groups in propane, higher linear, and branched alkanes, offers new insight into hydrocarbon stabilization. Each homologation of linear alkanes results in a further stabilization of ca. 2.8 kcal/mol, relative to methane and ethane (evaluated using Pople’s

isodesmic bond energy (BSE) separation reaction, Eq. 1,^[47-49] where m also gives the number of protobranches). Topologically branched alkanes like isobutane and neopentane have more protobranches and are stabilized to an even larger extent than linear alkanes.^[44-46] These 1,3 stabilizations between geminal groups can be attributed predominantly to attractive intramolecular van der Waals interactions arising from London dispersion forces^[50,51] (i.e. long range R^{-6} electron correlation effects). However, Grimme's^[16] very recent analysis points instead to the greater importance of medium-range electron correlation differences. Hartree-Fock (HF), B3LYP, and many other functionals give unsatisfactory results (Figure 1 and 2) since they strongly underestimate the 1,3 stabilization effects.

The Hartree-Fock approximation completely neglects dynamic electron correlation. B3LYP as well as most well-established density functionals only use local electron densities to describe correlation and do not account for medium^[16] and longer-range dispersion interactions.^[52] However, the design of DFT functionals that perform well for weak interactions is the goal of much current research.^[16,38,53-56] DFT energies are affected by additional sources of error. For instance, correlation functionals that eliminate the “self-exchange” problem are being sought.^[39] This error (not shared by Hartree-Fock), arises from the spurious interaction of an electron with itself.

Nearly all the DFT functionals systematically underestimate the energies of n -alkane chains (Figure 2). Shockingly, the widely used B3LYP is among the worst functionals and underestimates each protobranching stabilization by 1.33 kcal/mol on average. Note that this 40% underestimation is comparable to the 47% of HF. OLYP, the poorest performer in our set, underestimates the stabilization energy by 1.8 kcal/mol on

average. Indeed, the exchange functional for OLYP was fit with a restricted set of data which lacked weakly bonded systems.^[27] Other functionals, including the non-empirical TPSS meta-GGA, and the semi-empirical HCTH GGA underestimate branching, their mean absolute deviations (MAD) range from 1.10 to 1.50 kcal/mol. Although the LDA approximation generally strongly overestimates weak interaction energies,^[5,57-59] SVWN5 performs best here (Figure 2). Similarly small errors have been reported before for propane, butane, and isobutane, *provided that error-cancelling isodesmic evaluations (cf., Equation 1) were employed.*^[7] Of course, caution must be exercised because of the well documented deficiencies of LDA.^[5,7,52]

The PW91 and the closely related “parameter-free” PBE exchange correlation GGA functionals describe the binding in attractive van der Waals regions more accurately;^[60] their MADs are 1.05 and 1.08 kcal/mol, respectively, per protobranch. Somewhat better results are given by the recently developed hybrid meta-GGAs, MPW1B95 and MPW1B1K of Zhao and Truhlar, designed partially for the description of weakly interacting systems.^[53] Not surprisingly, these new functionals outperform B3LYP and other early functionals. However, significant errors (which are cumulative, Figure 2) still remain.

Unlike DFT, both MP2 and CCSD(T) results depend on basis set size.^[61] The expected overestimation^[62-64] of the branching stabilization is found at MP2/aug-cc-pVTZ, but not at the lower MP2/6-311+G(d,p) level. This suggests the possible existence of an intramolecular basis set superposition error. Similarly, CCSD(T)/6-311+G(d,p) results diverge somewhat from experiment but aug-cc-pVTZ values parallel those of

experiment. Obviously, computational expense precludes application to longer *n*-alkane chains.

Figure 2 emphasizes the regularity of the increasingly large deviations from the experimental BSE stabilizations as the *n*-alkane chain is lengthened. Check and Gilbert^[14] also noted regularities in the computed bond dissociation energies of the central C-C bond of ethane as the number of methyl substituents increases. The B3LYP error increases to 21.1 kcal/mol for 2,2,3,3-tetramethylbutane; its high degree of branching enhances the long-range attractions. B3LYP fails as a consequence. Indeed, most of the functionals in Figure 2 systematically underestimate weak long-range interactions. Their poor performance appears to arise principally from their inadequacies in accounting for long and medium-range electron correlation effects.^[16]

The adjacent paper by Schreiner *et al.*^[15] illustrates the problems in reproducing the experimental relative energies of hydrocarbons, especially when isomers having a different blend of single and multiple CC bonds are compared, at various DFT and ab initio levels. The preferred geometries of [n]annulenes were found earlier to depend strongly on the level of theory employed.^[65]

Curtiss, *et al.*^[7] have noted that homodesmotic energy evaluations improve the accuracy of B3LYP for large molecules. However, for alkanes this only arises through cancellation of the protobranching errors (Equation 2, where m also is the number of protobranches).



Linear and branched alkanes larger than ethane are stabilized by intramolecular 1,3 “protobranching” interactions between alkyl groups. The most commonly used DFT functionals, notably B3LYP, underestimate the protobranching stabilization mainly due to their inadequate descriptions of long-range non-bonded interactions. We join with others^[15] to discourage the use of B3LYP energy data for larger molecules. Unfortunately, the DFT alternatives are only somewhat better, but are not yet fully satisfactory.

The recent hybrid meta-GGA functionals of Zhao and Truhlar, as well as other recently proposed van der Waals-corrected DFT functionals^[53-56] with the correct R^{-6} asymptotic behavior, may provide more accurate assessments of weakly-bound systems and better descriptions of intramolecular non-bonded interactions at considerably less computational cost than post-HF wavefunction methods. However, even the best-performing MPW1B95 and MPWB1K hybrid meta-GGA functionals^[31,39,40] do not evaluate the energies of *n*-alkane chains accurately, and only offer some improvement over B3LYP for larger molecules. We hope that Check and Gilbert’s pessimistic admonition, “a computational chemist cannot trust a one-type DFT calculation”^[14] can be overcome eventually.

4.5. ACKNOWLEDGMENTS

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CHAPTER 5

AROMATICITY AND DOUBLE AROMATICITY IN MONOCYCLIC BORON, CARBON, AND BOROCARBON COMPOUNDS[†]

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5.1 ABSTRACT

The double aromatic character of selected monocyclic carbon, boron, and borocarbon rings is demonstrated by refined nucleus-independent chemical shift (NICS) analyses involving the contributions of individual canonical MOs and their out-of-plane NICS tensor component (CMO-NICS_{zz}). Double aromaticity results from two mutually orthogonal Hückel p AO frameworks in a single molecule. The familiar π orbitals are augmented by the in-plane delocalization of electrons occupying sets of radial p orbitals. Such double aromaticity is present in $C_6H_3^+$, C_6^{4+} , $C_4B_4^{4+}$, C_6 , C_5B_2 , C_4B_4 , C_2B_8 , B_{10}^{2-} , B_{12} , C_{10} , C_9B_2 , C_8B_4 , C_7B_6 , C_6B_8 , and C_{14} . Monocyclic C_8 and C_{12} are doubly anti-aromatic, since both the orthogonal π and radial Hückel sets are paratropic. Planar C_7 and C_9 monocycles have mixed π aromatic/radial antiaromatic systems.

5.2 INTRODUCTION

Double aromaticity,^[1] as originally conceived by Chandrasekhar, Jemmis, and Schleyer in 1979, is defined as the existence of two mutually orthogonal Hückel framework MO sets in a single molecule. Both of these orthogonal systems can stabilize molecules. The usual $4n+2$ π electron system perpendicular to the plane is augmented by an in-plane $4n+2$ electron system comprised of radial (inward-pointing) p AO's. The $C_6H_3^+$ ion (Figure 5.1) provided the first theoretical evidence for double aromaticity; it benefits from having 6π electrons as well as from the in-plane 3-center-2-electron interaction of the three radial p atomic orbitals on the bare 1,3, and 5 carbon atoms. Nelson and Kentämaa's mass spectral experiments have identified this species.^[2] The $C_6H_3^+$ ion^[3] opened the fields of

double and in-plane aromaticity, concepts that have received significant theoretical attention since.^[3-23]

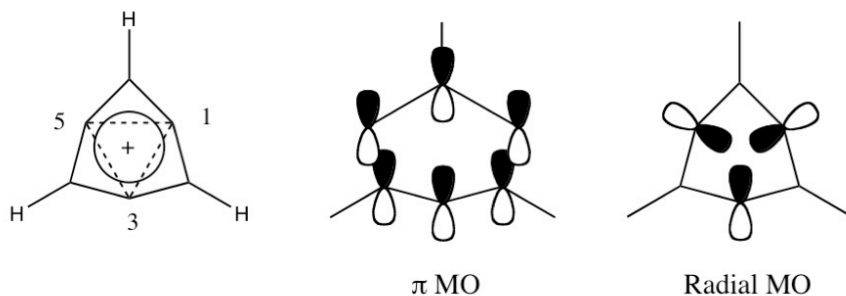


Figure 5.1. The planar $C_6H_3^+$ doubly aromatic ion comprised of 6π electrons and 2 radial in-plane electrons.

Further early examples of double aromaticity included $C_{10}H_5^-$ ($10\pi + 6$ rad) and C_8H_4 ($10\pi + 2$ rad) (Figure 5.2).^[3] More recently, Schleyer et al.,^[24] analyzed the structures and magnetic properties of 3,5-dehydrophenyl cation and the closely related cyclo[6]carbon (C_6) in greater detail. The six membered rings of both species had equal CC bond lengths,^[25-27] and enhanced magnetic susceptibility anisotropy.

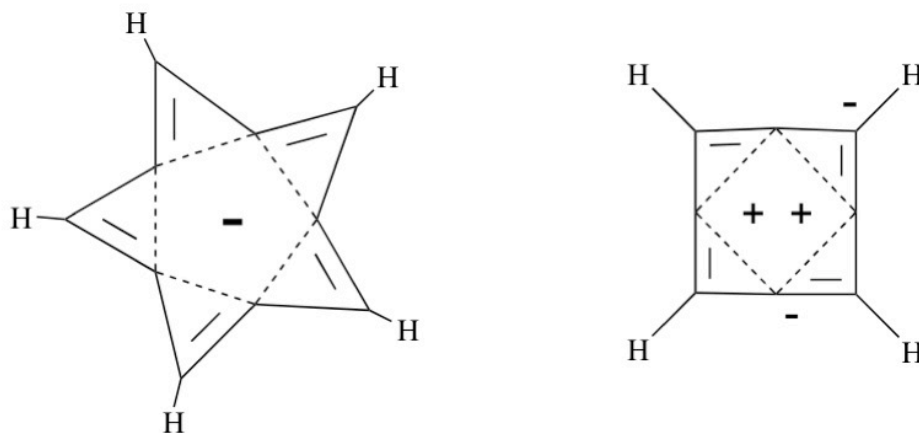


Figure 5.2. Double aromatic structures of $C_{10}H_5^-$ ($10\pi + 6$ rad) and C_8H_4 ($10\pi + 2$ rad).

Carbon clusters have been extensively studied experimentally,^[28-42] particularly those larger clusters serving as precursors to fullerenes and nanotubes.^[43-45] Several mass spectrometry studies have shown the presence of “magic peaks”, which appear as above average abundances for certain stoichiometries. Photoelectron spectra of monocyclic C_n^- have also shown clear differences between clusters with $n=4N$ and $4N+2$ carbon atoms respectively.^[46-48] Such distinctive patterns likely suggest certain stoichiometric structures to have an enhanced stability.

Along with extensive experimental studies of carbon clusters, many theoretical calculations probing electronic properties and structures have been made, originating with Pitzer and Clementi.^[49] Using a refined Hückel p-electron model, they predicted that C_n clusters would be linear and that rings might be formed around $n=10$. In 1966, these predictions were corroborated by Hoffmann’s extended Hückel theory.^[50] Another significant paper appeared in 1977, in which Slanina and Zahradnik considered both linear and cyclic geometries of C_n ($n = 4-7$) clusters using Dewar et al.’s MINDO/2 method.^[51] This first comprehensive examination of structures indicated that 3-dimensional and monocyclic were nearly always preferred over linear species. In the middle 1970’s, the Schleyer-Pople group was also interested in the possibility that rings with $4N+2$ carbons might be “doubly aromatic,” stabilized by both perpendicular and in-plane Hückel systems, but the limited computational resources of the day (E. M. Engler, at IBM, did succeed in computing C_{10} at STO-3G)^[52] did not permit reliable tests and developments of this idea using *ab initio* methods. Since then, extensive *ab initio* studies have confirmed that an energetic competition exists between linear (triplet) and cyclic (singlet) isomers of medium-size C_n clusters.^[53] Most recent theoretical analysis have

shown that the monocyclic C_6 and C_{10} singlet states are lower in energy than their linear counterparts.^[12,28,53-65] Interestingly, the lowest energy structures for C_6 and C_{10} correspond to the bond angle alternating polyallene D_{3h} and D_{5h} rather than the full D_{6h} and D_{10h} symmetry (equal bond lengths and angles), which are transition states. Despite a sizable HOMO-LUMO gap, the symmetry of their frontier molecular orbitals allows for a second-order Jahn-Teller distortion.^[13,66,67] Alternatively, rings with $4N$ carbon atoms generally display a strong first-order Jahn-Teller distortion leading to C_{2nh} polyyne structures^[61,65,68] which are doubly antiaromatic according to the Hückel rule. However, the question has been raised whether it is possible for a formally doubly antiaromatic molecule ($4n+4m$) to become doubly aromatic by using alternative electronic configurations with $4n+2$ and $4m-2$ electrons in the two orthogonal frameworks.^[11]

Boron, as well as borocarbons (a binary compounds comprised only of boron and carbon atoms), constitute other classes of related molecules. Unlike carbon clusters, borocarbons have received remarkably little attention as a class, despite several examples of remarkable structures.^[69-73] Three C_3B_4 isomers, for example, have planar hexacoordinate carbons.^[73] In contrast, binary combinations of carbon with lithium, nitrogen, oxygen, fluorine and other main group elements have been studied in detail. Boron carbide,^[74-86] one of the hardest materials known, having a number of important uses, has received the most attention. Diatomic and larger BC clusters have been studied using mass spectrometry^[87,88] and EPR.^[89-91] Other studies have probed the structure of B_nC_m ($n+m = 2-5$) clusters.^[92-101] Park^[102] described structural and bonding trends in a series of isoelectronic borocarbon compounds. Potential energy surface investigations reveal that the global isomers of $B_7C_1^{1-}$, B_6C_2 , and $B_5C_3^{1+}$ all prefer monocyclic rings

surrounding a heptacoordinate boron atom. Many other borocarbons have been found computationally to have planar terta-, penta-, and hexa-coordinate carbon structures.^[69,70,73,103-107]

Further analysis of molecular properties allows for the corroboration of electron delocalization in orthogonal planes within these structures. Recently, Martín-Santamaría and Rzepa^[14] studied double aromaticity and double anti-aromaticity in small carbon rings using nucleus-independent chemical shifts (NICS). Introduced in 1996 by Schleyer et al.,^[108] NICS provides a simple and effective magnetic aromaticity index; negative (diatropic) NICS values (usually depicted by red dots) indicate magnetic aromaticity, while positive (paratropic) values (green dots) indicate magnetic anti-aromaticity. Typically, the magnetic environments of molecules are probed by computing a number of NICS points; those designated NICS(0) are computed at the geometric centers of rings while NICS(1) are computed at 1 Å above the geometric center. Using isotropic NICS(0) calculations, Martín-Santamaría and Rzepa's results suggested D_{5h} -C₁₀, D_{7h} -C₁₄, 1,6-C₈N₂, 1,7-C₁₀B₂, C_s-quintet C₁₂, C₁₁H₂, and bicyclic C₁₉ to be doubly aromatic. Their conclusions, however, were based only on isotropic NICS values and employed no dissection to probe the aromaticity of each individual orthogonal Hückel framework. The bond angle alternating polyallene D_{5h} -C₁₀ has overall aromatic character, but its NICS(0) = -28.9 is only on par with, not greater than, that of aromatic C_{2v} [10]-annulene (-28.6).^[109] However, if one considers the D_{10h} C₁₀H₁₀, doubly aromatic D_{5h} -C₁₀ is shown to have a greater isotropic NICS value (-13.2 vs. -28.9, see later discussion). The difference in the isotropic NICS(0) value is clearly due the in-plane radial 10 electron system present in D_{5h} -C₁₀ but not in C₁₀H₁₀! In contrast, the NICS(0) value of the polyallene D_{7h} -

C_{14} (-35.6) is much larger than that of both the D_{2h} [14]-annulene (-13.4) and the D_{14h} $C_{14}H_{14}$ (-15.8), one could also conclude that the enhanced isotropic NICS(0) value of D_{7h} - C_{14} is due to its additional in-plane aromatic system. Hofmann and Berndt^[110] established the double aromaticity of small boron systems, using enhanced NICS values as a criterion, and determined that the two-electron delocalization was the key to understanding their unusual structures. Double aromatic molecules were designed with two in-plane delocalized electrons using anionic B_3 , neutral B_3 , and CB_2 subunits (Figure 5.3).

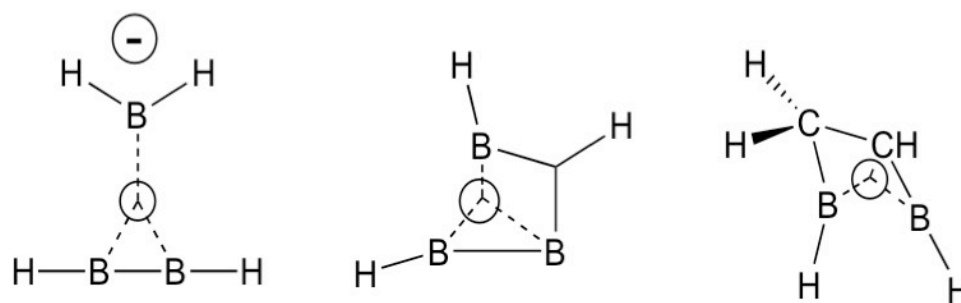


Figure 5.3. Double aromatic structures proposed by Hofmann and Berndt. Reproduced from Reference ^[110] and neutral CB_2 .

We now employ more refined NICS analyses,^[111-114] which allow the clear-cut assignment of double aromaticity through the analysis of individual MO contributions, to investigate a number of carbon, boron, and borocarbon rings.

5.3 METHODS

Carbon clusters and more generally sp bond systems are particularly challenging to model accurately due to their wide range of geometries and the occurrence of single,

double (polyallene) and triple bonds (polyacetylene) that results in a pronounced multireference character. The nature of the global minimum and the energy separation between the linear and cyclic C_n isomers is generally extremely sensitive to the computational level. Similarly, there has been a considerable discussion in the literature as to which ring structure: regular polygon or cummulenic (equal bonds, alternating angle) is the ground state. Despite these potential difficulties, geometries and relative energies obtained at the density functional levels are in reasonable agreements with high-order correlation methods (e.g. coupled-cluster expansion),^[55,61,63] while MP2 predictions were found to be qualitatively incorrect.^[63] In this paper, structures were optimized using the B3LYP^[115,116] hybrid density functional with the 6-311+G(d) basis set (6-311+G(d,p) for C_6H_6 , $C_{10}H_{10}$, $C_{14}H_{14}$, and $C_6H_3^+$) using Gaussian 98.^[117] Furthermore, comparisons with available CCSD(T) data are provided. All structures, unless otherwise noted, were characterized as local minima on the potential energy surface and contained no imaginary frequencies. NICS points were computed at geometric centers, NICS(0), and 1 Å above, NICS(1), using the Perdew-Wang-91 exchange-correlation functional^[118] with the triple- ζ GTO IGLO-III valence basis set using the deMon NMR program.^[119] NICS contributions of individual canonical molecular orbitals (CMO-NICS)^[120] were performed at PW91/IGLO-III using the NBO 5.0 program.^{[121][122]} Because isotropic NICS(0) values at ring centers do not reflect the “ring current” exclusively, we employed NICS_{zz} (the out-of-plane component of the NICS tensor), as a superior aromaticity measure due to its more accurate response to magnetic properties arising only from a magnetic field applied perpendicular to the molecular plane.^[111,112,114,123,124]

The carbon, boron, and borocarbon rings selected for study here had two potential “double aromatic” $4n+2$ or “double anti-aromatic” $4n$ electron Hückel systems (π and in-plane radial) based on simple electron counting. Two valence electrons of both boron and carbon are assigned to the σ framework. Thus, boron has one and carbon two available electrons for π and in-plane radial bonding. While many isomers are possible for each stoichiometry we have focused our evaluation to those being monocyclic and generally of higher symmetry.

5.4 RESULTS AND DISCUSSION

5.4.1 THE $C_6H_3^+$ ION

The distorted^[66] $C_6H_3^+$ ion (Figures 5.1 and 5.4), the first hypothesized doubly aromatic species, was predicted by Chandrasekhar, Jemmis, and Schleyer in 1979^[1] and further confirmed in 1994.^[24] We have now reexamined D_{3h} $C_6H_3^+$ using a combination of NICS, $NICS_{zz}$, and CMO- $NICS_{zz}$ to quantify the extent of its aromatic and doubly aromatic character. Large negative isotropic NICS(0) of -43.2 and NICS(1) (isotropic NICS taken at 1 Å above the ring center) of -20.0 values (Table 5.1) indicate the presence of a diatropic ring current. The large difference between isotropic NICS(0) and NICS(1) values is a probable indicator that the system contains a diatropic Hückel system in the molecular plane. If no diatropic in-plane radial system were present, one would expect the isotropic NICS(0) and NICS(1) values to be similar (as is the case for benzene NICS(0) = -7.5, NICS(1) = -9.6). The individual canonical molecular orbital contributions to NICS (CMO-NICS) as well as each out-of-plane NICS tensor component (CMO- $NICS_{zz}$), summarized in Table 5.1 and Figure 5.5, show the presence of a strongly aromatic 6-electron π system perpendicular to the molecular plane, $NICS_{\pi} = -32.76$ and a weakly aromatic two electron in-plane radial system, $NICS_{rad} = -3.59$ (Figure 5.4). The out-of-plane component of the NICS tensor for the π system in $C_6H_3^+$ is slightly weaker than that of benzene ($NICS_{zz} = -36.12$, while the $NICS_{radzz}$ contributes an additional -5.30). The remaining contributions to $NICS_{zz}$ arise from several diatropic low-lying orbitals, as well as minimal paratropic contributions from tangential orbitals (relative to C_6^{4+} and $C_4B_4^{4+}$, see subsequent paragraph). Thus, one expects $C_6H_3^+$ to be slightly more aromatic than benzene based on NICS.

Are the C_6^{4+} and $C_4B_4^{4+}$ monocycles further examples of “6+2” doubly aromatic systems, akin to $C_6H_3^+$? All three possess a single diatropic in-plane radial orbital; however, the overall aromatic character is dominated by the diatropic 6π electron system, which are very similar in all three ions ($NICS_{\pi_{zz}}$). As a result, the three species have relatively similar $NICS_{zz}$ values. However, the contradictory behavior of the $radial_{zz}$ and the total $NICS_{zz}$ remains puzzling: the system with the least negative $radial_{zz}$ value has the most negative $NICS_{zz}$ (Table 5.1). Such behavior is explained by the paratropicity of a low-lying tangential orbital, which contributes strongly in C_6^{4+} but only weakly in $C_6H_3^+$. Thus despite having a smaller $radial_{zz}$ values, the tangential orbital contribution in $C_6H_3^+$ (+7.66 ppm) has only a minimal effect on its $NICS_{zz}$ value while the large value of the C_6^{4+} tangential orbital (+24.59 ppm) has considerable impact on its total $NICS_{zz}$. The end result is total $NICS_{zz}$ values which contrast the sum of their π_{zz} and $radial_{zz}$ components. It should be noted, however, that Fowler has shown that low-lying orbitals have little or no effect on ring currents.^[125]

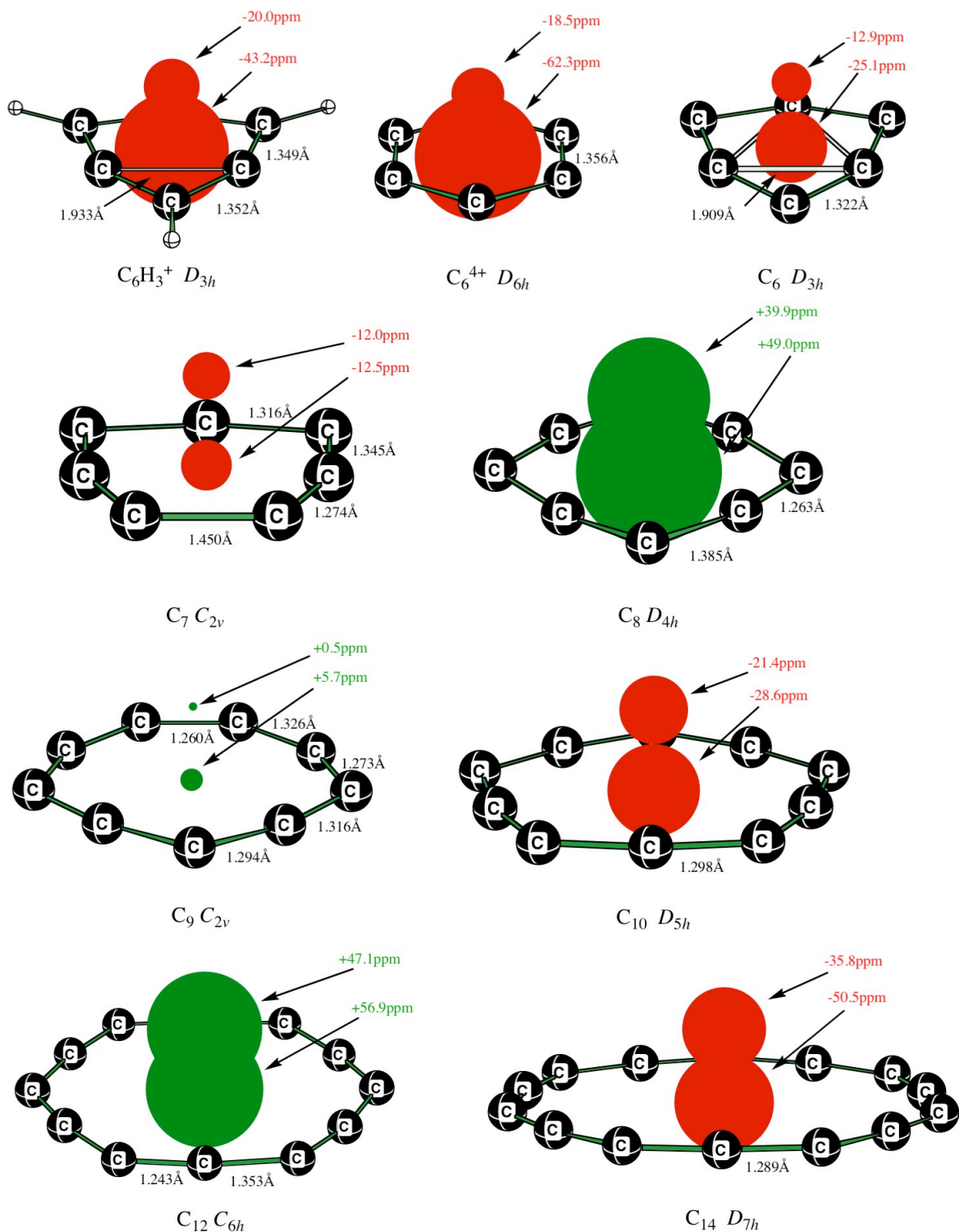


Figure 5.4. Geometries, point groups, and isotropic NICS values (red indicates diatropicity while green indicated paratropicity) of carbon clusters.

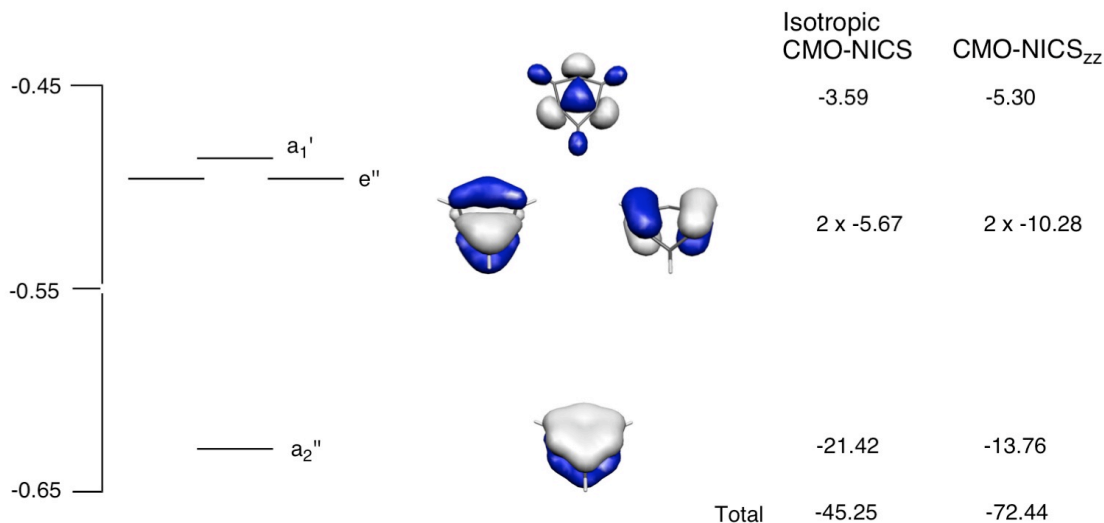


Figure 5.5. CMO-NICS plot of $C_6H_3^+$. CMO-NICS and CMO-NICS_{zz} contributions are listed on the right side in ppm; the “Total” listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

5.4.2 EVEN NUMBERD CARBON CLUSTER MONOCYCLICS

The most recent theoretical investigations conclude that cyclic C_6 prefers D_{3h} symmetry over both the D_{6h} and the linear chain forms (Figure 5.4).^[55,64] This geometrical preference can be attributed to a second-order Jahn-Teller effect.^[66] At the CCSD(T) level, Hutter and Lüthi^[55] predicted the D_{3h} global minimum to lie 8.3 kcal/mol below the regular hexagon D_{6h} transition state structure and obtained good agreement at the BP86/TZVP level for both geometries and energies. At the B3LYP/6-311+G(d) level, the interconversion barrier between the D_{3h} and D_{6h} structures is 13.62 kcal/mol.

The magnetic behavior of the global D_{3h} minimum is peculiar. The out-of-plane component of the NICS tensor for the π system (NICS _{π_{zz}}) is slightly larger than that of benzene, yet the in-plane system is paratropic at the ring center. This suggests that D_{3h} - C_6

is π aromatic and radial anti-aromatic. However, a grid of NICS_{zz} points, dissected into π and radial contributions, shows a clear change from paratropic within the central triangle to diatropic within the outer triangles and, as expected for aromatic systems, a deshielding zone outside the molecular framework (Figure 5.6). A possible explanation for this peculiar behavior is the presence of local diatropic ring currents within the three outer triangles, which necessarily causes the central triangle to be paratropic (Figure 5.7). Alternatively, similar paratropic $\text{NICS}_{\text{rad}zz}$ patterns are observed at the center of cyclopropane and, more generally, at the center of six σ -electrons D_{3h} aromatic rings.^[126] Akin to this set of σ -aromatic D_{3h} three membered rings, the paratropic shielding at the center of $D_{3h}\text{-C}_6$ arises essentially from the degenerate set of HOMOs with Möbius topology, as shown in Figure 5.8. While further analysis on this seemingly pathological NICS behavior are impending, the computation of isotropic $\text{NICS}(0)$, or even dissected NICS grids at several points is strongly recommended when determining the overall magnetic character of atypical molecules. The NICS_{zz} grid suggests that the D_{3h} structure of C_6 is doubly aromatic.

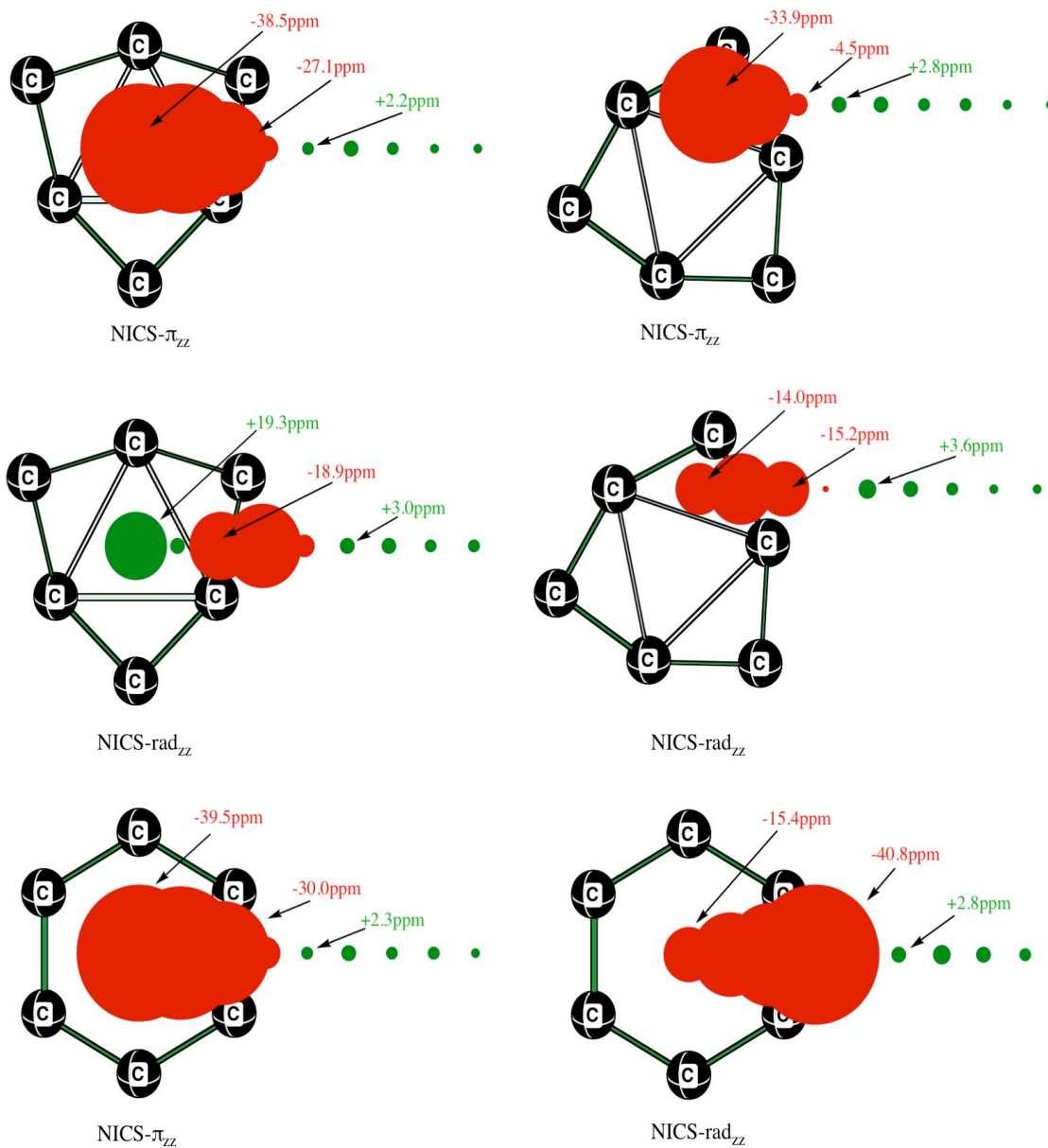


Figure 5.6. $NICS_{\pi_{zz}}$ and $NICS_{rad_{zz}}$ grids of C_6 (D_{3h} and D_{6h}). The $NICS_{\pi_{zz}}$ grids indicate the π systems to be diatropic within the molecular framework while the $NICS_{rad_{zz}}$ grids indicate the radial system is paratropic in the central triangle and diatropic in the outer triangles for D_{3h} and diatropic throughout for D_{6h} .

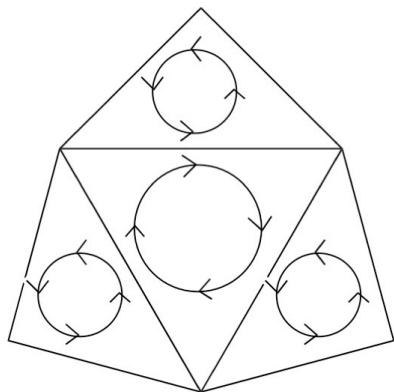


Figure 5.7. Proposed ring current model for the radial system of D_{3h} C_6 .

Although being a transition state, we have investigated the magnetic properties of the regular D_{6h} - C_6 structure. The isotropic NICS(0) value of D_{6h} - C_6 (−36.9) is appreciably larger than the −25.1 NICS(0) D_{3h} - C_6 (Table 5.1). Since archetype aromatic molecules generally exhibit special thermodynamic stability and a diatropic ring current, the enhanced diatropicity of the less stable D_{6h} structure appears surprising. However, several studies indicate that different aromaticity measures may provide divergent information.^[113,127] For instance, the lowest energy fused heterobicycles are not the most aromatic isomers.^[128] In addition, the differences in diatropicity of the D_{6h} and D_{3h} structures are less pronounced when considering larger shielding zones. The NICS_{zz} grids shown in Figure 5.6, clearly illustrate the overall diatropicity of both the D_{3h} and D_{6h} structures.

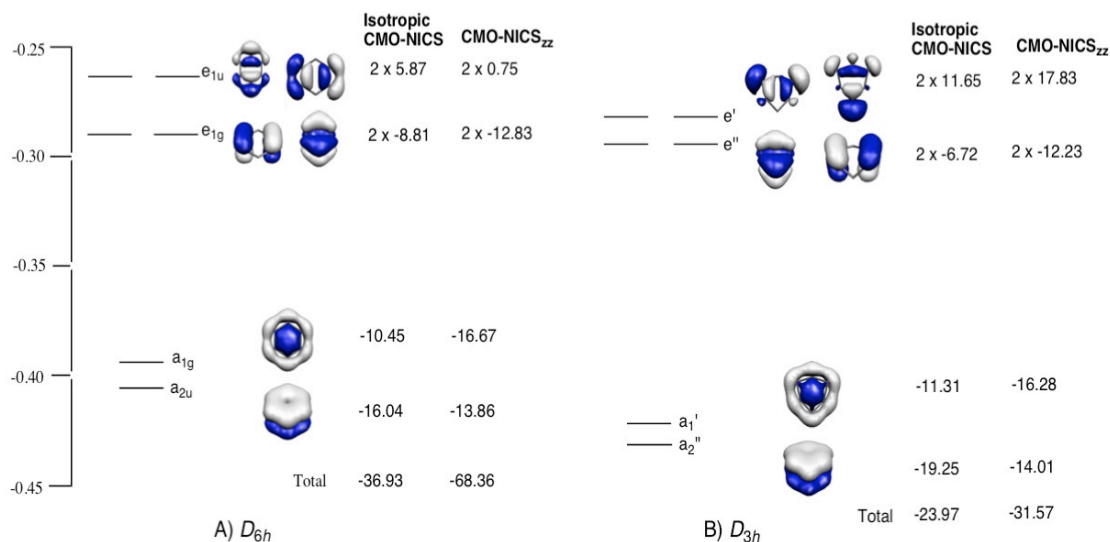


Figure 5.8. D_{6h} (A) and D_{3h} (B) CMO-NICS plots of C_6 . CMO-NICS and CMO-NICS_{zz} contributions are listed on the right side in ppm; the “Total” listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

Akin to C_6 , the C_{10} molecule has long been recognized to adopt a D_{5h} symmetry (vide supra) which is favored by several tens of kcal mol⁻¹ over the lowest energy linear isomer (Figure 5.9).^[53,58] The equivalent D_{5h} minima interconvert across the transition state of D_{10h} symmetry, corresponding to an energy barrier of about 1.0 kcal mol⁻¹ at the CCSD(T)/cc-pVTZ level.^[61] Similarly, B3LYP/6-311+G(d) optimization result in a polyacetylene D_{5h} - C_{10} stationary point with an interconversion barrier of about 2.5 kcal/mol, which demonstrates the floppy nature of these sp-carbon cluster. While C_{4n+2} clusters larger than C_{10} have been studied at less accurate theoretical levels, measured electronic spectra^[129] suggest these structures to be monocyclic rings, which likely exhibit double aromaticity. At the B3LYP/6-311+G(d) level, the D_{14h} - C_{14} transition state is roughly isoenergetic with the D_{7h} cumulenic energy minimum.

$\text{NICS}_{\pi\text{zz}}$ of both C_{10} and C_{14} are similar to those of their parent annulenes^[130] (i.e. $\text{C}_{10}\text{H}_{10}$ and $\text{C}_{14}\text{H}_{14}$), but their enhanced total NICS_{zz} indicate the presence of an additional diatropic subsystem. CMO-NICS and CMO- NICS_{zz} analysis indeed confirm that both carbon monocyclics are doubly aromatic, as has been previously hypothesized.^[13,14] Note the π MOs of both C_n and C_nH_n ($n=10,14$) systems contribute nearly equally, thus the $\text{NICS}_{\pi\text{zz}}$ values for both C_n and C_nH_n are nearly identical. However, C_{10} and C_{14} also contain a diatropic in-plane radial system, thus their total NICS_{zz} is much greater (>30 ppm) than that of their annulene analogues (Table 5.1).

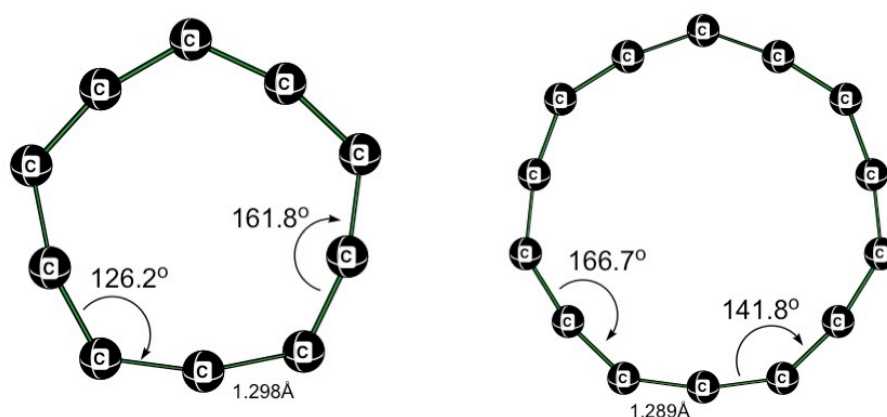


Figure 5.9. B3LYP/6-311+G(d) optimized bond angles of polyallene D_{5h} C_{10} and D_{7h} C_{14} .

C_8 is an interesting example of a double antiaromatic polyynic ring,^[53,54,57,61,68] possessing orthogonal “8 radial + 8 π ” electron systems (Figure 4). CCSD(T)/cc-pVDZ calculations predict the C_{4h} cyclic form to lie only 4 kcal mol⁻¹ below the linear structure.^[61] Alternatively, Hutter and Luthi identified a boat-like non-planar D_{4d} structure as a minimum.^[60] The energy difference between these two structures is less than 1 kcal/mol s at the B3LYP/aug-cc-PVTZ level^[54] once again reflecting the very floppy nature of these systems. At the PW91/IGLO-III//B3LYP/6-311+G(d) level, both the C_{4h}

and D_{4d} minima have small HOMO-LUMO energy separation (only 1.21 eV) resulting in a large paratropic HOMO-NICS (see SI for the D_{4d} structure).^[131] As expected, the highest lying π MO (the HOMO), and the highest in-plane radial orbital (HOMO-1), dominate the overall molecular paratropicity (Figure 5.10). The HOMO-NICS contribution +60.70 (+186.58 HOMO-NICS_{zz}) is very large, while the highest lying occupied orbital of the in-plane radial system also is strongly paratropic (CMO-NICS +16.47, CMO-NICS_{zz} +45.09). Not surprisingly, C_8 has a smaller ionization potential than C_6 or C_{10} .^[132] The polyynic C_{6h} ring was found to be lower in energy than the other C_{12} isomers at several DFT levels. However, uncertainties as to which structure is the minimum at higher theoretical levels remain.^[62] Regardless of the relative energies, the C_{6h} ring structure exhibits the same double antiaromatic character as C_8 (see Figure 5.11 and Table 5.1), no electronic rearrangement to a double aromatic configuration ($4n+2$, $4m-2$) is seen.

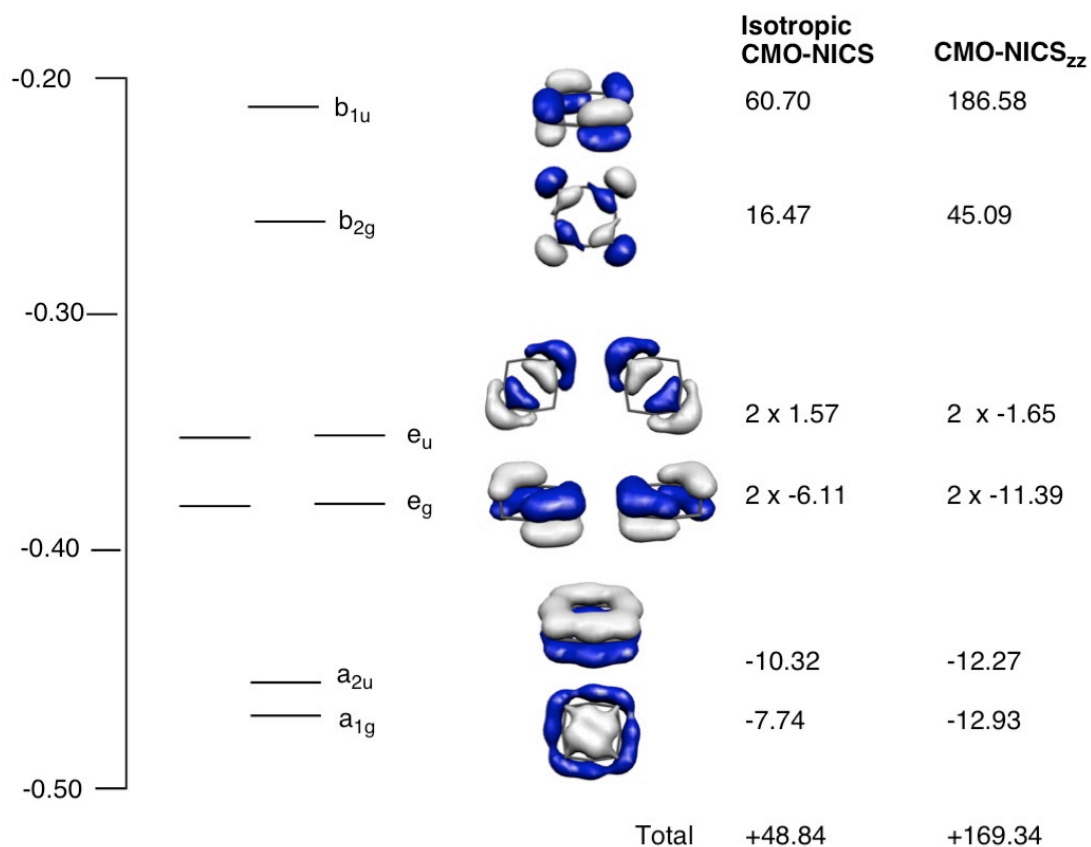


Figure 5.10. CMO-NICS and CMO-NICS_{zz} of doubly anti-aromatic C_8 . CMO-NICS and CMO-NICS_{zz} contributions are listed on the right side in ppm; the “Total” listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

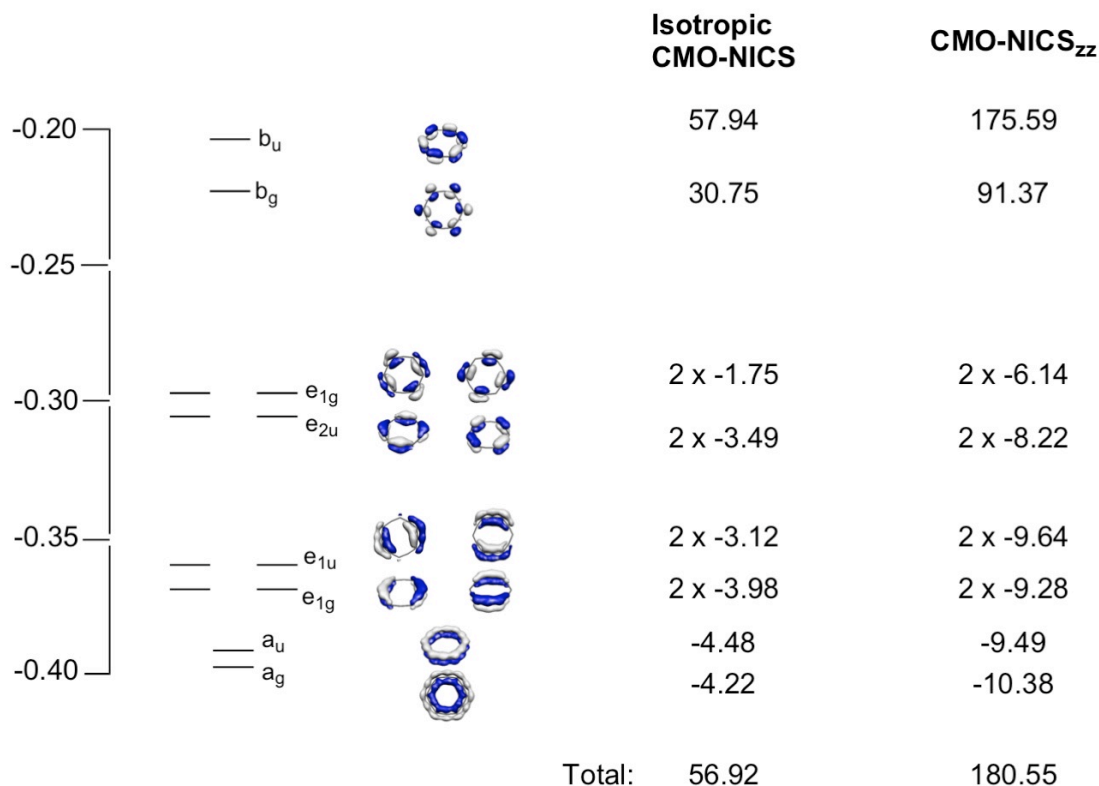


Figure 5.11. CMO-NICS and CMO-NICS_{zz} of doubly antiaromatic C₁₂. CMO-NICS and CMO-NICS_{zz} contributions are listed on the right side in ppm; the “Total” listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

5.4.3 ODD NUMBERED CARBON CLUSTER MONOCYCLICS

Martin et al.^[63] showed, using DFT and CCSD(T) calculations, that small monocyclic rings containing odd numbers of carbon atoms (C_n, n=5-9) are higher in energy than the corresponding linear structures. However, experimental evidence for cyclic C₇⁺ exists^[36] and small linear-cyclic isomerization energy (< 15 kcal mol⁻¹ at the CCSD(T) level) have been computed for C₇ and C₉.^[63] The π and radial electron counts of such “odd carbon” monocycles are not easy to assign *a priori*. Mixed aromatic/anti-aromatic electronic structures are possibilities. Cyclic C₇ and C₉ prefer C_{2v} over planar structures at both the

CCSD(T) and B3LYP levels.^[133] While D_{nh} triplet energies have been computed, these lie above the energy of the singlet species.^[63,134] We calculated CMO-NICS values for the C_7 and $C_9 C_{2v}$ monocycles (Figure 5.4 and Table 5.1). C_7 has negative overall isotropic NICS values, indicating a diatropic ring current. CMO-NICS/CMO-NICS_{zz} shows this system possesses a mixed aromatic/antiaromatic $6\pi/8$ in-plane system. Similarly, C_9 has mixed π aromatic/in-plane antiaromatic character with a “10+8” system. These systems parallel the mixed aromatic/anti-aromatic systems recently reported by Hofmann and Berndt (Figure 5.12).^[110]

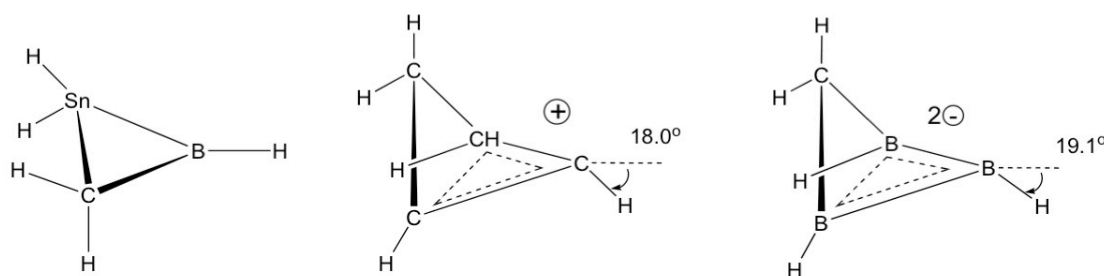


Figure 5.12. Mixed aromatic/antiaromatic systems reported by Hofmann and Berndt.^[110]

5.4.4 BORON AND BOROCARBON CLUSTERS

The previously described NICS analyses also establish double aromaticity in the two boron as well as the eight borocarbon rings (see Figure 5.13 and Table 5.1). C_4B_4 illustrates a “6+6” doubly aromatic borocarbon system (Figure 5.14). In contrast to C_6 , another “6+6” system (Figure 5.8) with somewhat smaller isotropic NICS(0) and NICS(1) values, the NICS(0)_{zz} of all three in-plane (radial) orbitals of C_4B_4 are diatropic. The enhanced diatropicity of the radial system compensates for the reduction in diatropic character of C_4B_4 ’s π system (see the CMO-NICS _{π_{zz}} data) as compared to both isomers of

C_6 (Figure 5.8). Degenerate in-plane radial HOMOs present the possibility of forming a “6+2” doubly aromatic system by removing four electrons from C_4B_4 . Indeed, CMO-NICS_{zz} shows $C_4B_4^{4+}$ to be doubly aromatic like C_6^{4+} . $C_4B_4^{4+}$ has slightly longer bond lengths than C_4B_4 (Figure 5.13), likely attributable to increased Coulomb repulsion and decreased in-plane bonding character. The in-plane radial system, which now has only two electrons, shows a significant decrease (10 ppm) in diatropic character of the out-of-plane component of the NICS tensor (NICS_{zz}). The two electron in-plane radial system has enhanced diatropicity (CMO-NICS_{radzz} = -13.45) relative to the prototype double aromatic $C_6H_3^+$ (-5.30) and is closer to the C_6^{4+} value (-15.99).

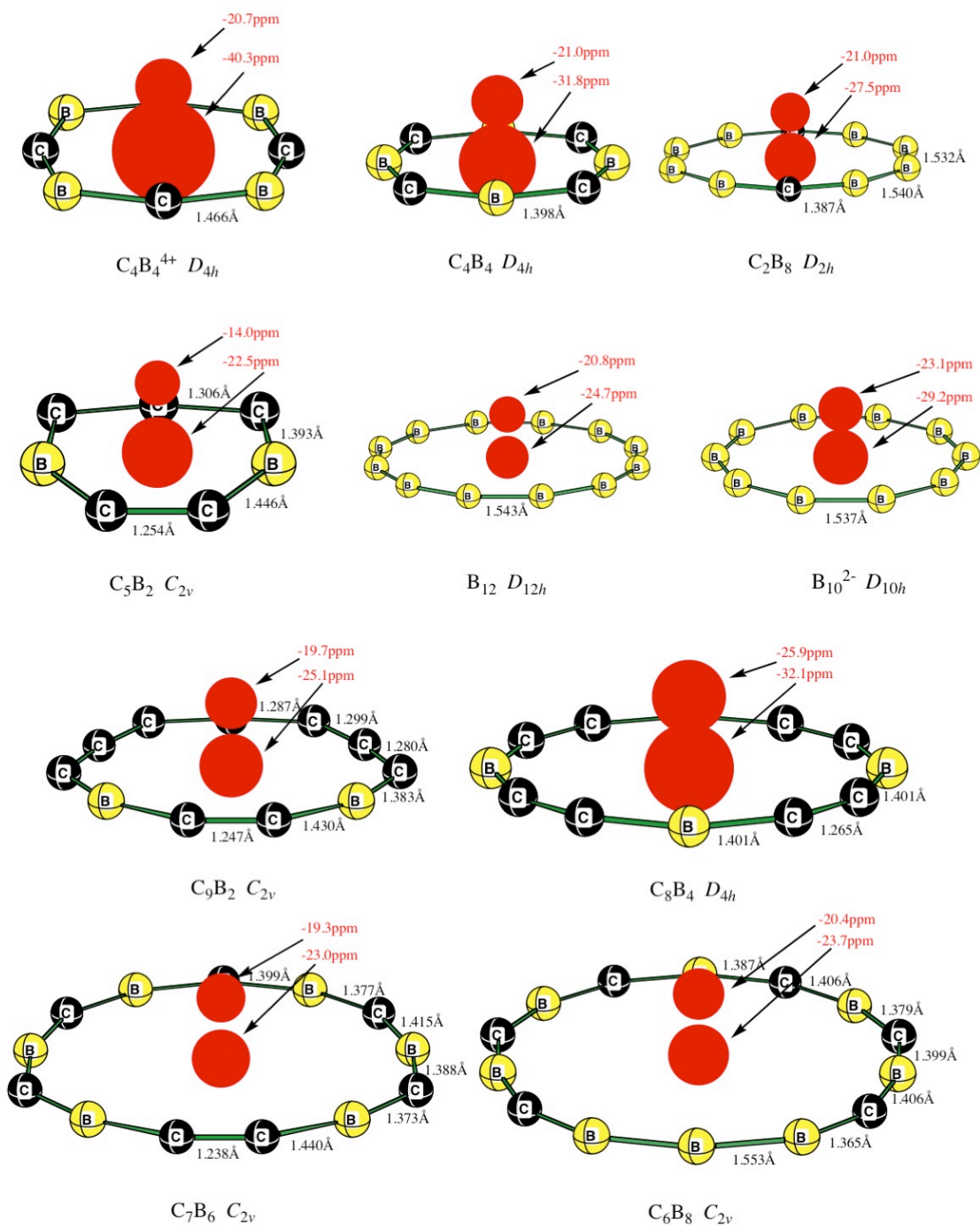


Figure 5.13. Geometries, point groups, and isotropic NICS values (red signifies diatropic) of various rings.

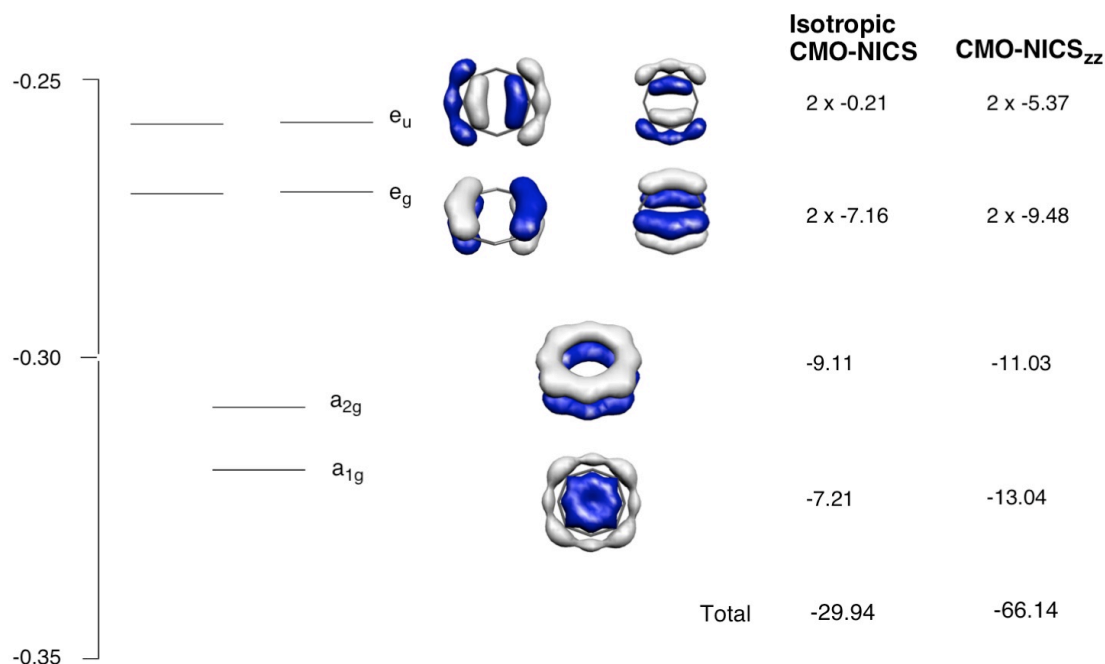


Figure 5.14. CMO-NICS and CMO-NICS_{zz} from canonical molecular orbitals of C₄B₄. CMO-NICS and CMO-NICS_{zz} contributions are listed on the right side in ppm; the “Total” listed at the bottom represents the contributions of *all* orbitals, not just those pictured. MO energies in a.u. are given on the left side.

Like D_{3h} -C₆, C₅B₂ has two orthogonal 6-electron systems, with both diatropic (the π system) and paratropic (in-plane radial system) character. Furthermore, NICS_{zz} grids show behavior similar to C₆; the in-plane radial system is paratropic at the center but becomes strongly diatropic at distances as close as 0.5 Å away. The perpendicular π system remains diatropic at all positions within the ring. The information obtained by using a NICS_{zz} grid allows us to conclude that, like C₆, C₅B₂ is doubly aromatic. The necessity of using such grids to identify the double aromaticity in C₆ and C₅B₂ makes these unique cases, as in general the dissection of NICS(0) values is sufficient to identify double aromaticity.

The larger borocarbons, with “10+10” double aromatic systems, show widely varying $\text{NICS}_{\pi_{zz}}$ values, all of which are smaller than those of D_{10h} [10]-annulene (-46.19). C_9B_2 has the most diatropic π system ($\text{NICS}_{\pi_{zz}} = -40.29$), but these values decrease in magnitude as more boron atoms are inserted into the ring (C_8B_4 , -37.20; C_7B_5 , -29.33, and C_6B_8 , -28.39). In contrast, the in-plane radial system ($\text{NICS}_{\text{rad}zz}$) values for C_9B_2 , C_7B_6 , and C_6B_8 range from -21.1 to -28.4. The highly symmetric D_{4h} C_8B_4 possesses an exceptionally diatropic in-plane radial system ($\text{NICS}_{\text{rad}zz}$ -42.92).

As expected from their electron count, the two monocyclic boron rings, B_{10}^{2-} and B_{12} are both doubly aromatic. In general, magnitudes of NICS_{zz} for both the perpendicular π system and the in-plane radial system are similar to other “6+6” borocarbons. Additionally, unlike the carbon monocyclic C_{10} , B_{10}^{2-} does not undergo a second-order Jahn-Teller distortion, favoring instead the fully symmetric D_{10h} .

5.4.5 GENERAL TRENDS

Isotropic NICS, NICS_{zz} and CMO- NICS_{zz} analysis values show the overall diatropic character of doubly aromatic compounds is greater than their singly aromatic counterparts. The second set of delocalized electrons, which occupy in-plane radial orbitals, increases the total ring current magnitude. Increasing ring size and number of Hückel electrons of carbon clusters results in larger NICS_{zz} values for each system (i.e. $\text{C}_{14} > \text{C}_{10} > \text{C}_6$). For borocarbons the larger rings have smaller NICS_{π} values ($\text{C}_6\text{B}_8 < \text{C}_7\text{B}_6 < \text{C}_8\text{B}_4 < \text{C}_9\text{B}_2$). The generally diatropic NICS_{zz} values for in-plane aromatic systems correlate weakly with the number of delocalized radial electrons. Systems with two in-plane radial electrons have smaller values than those with six in-plane electrons, etc.

However, several anomalies are found, including the radial $6e^-$ system of D_{3h} - C_6 , which behaves peculiarly at the ring center, and in the 10 radial electron C_8B_4 , which shows remarkable diatropic character equal to that of the 14 in-plane electron C_{14} . The number of delocalized electrons has some effect on NICS magnitude. The largest $NICS_{zz}$ value is found in the 14 π electron C_{14} (-56.7), however, 10 π electron values range from -28.6 to -40.3 and 6 π electron values from -23.9 to -39.5. Thus there is some degree of overlap between the diatropic magnitudes for 6 and 10 π electrons. The most diatropic in-plane radial system (-44.46) is also seen in C_{14} , which has 14 radial electrons illustrating the correlation between NICS values to electron number.

5.5 CONCLUSIONS

A majority of the monocyclic boron, carbon, and borocarbon rings we have studied possess negative isotropic NICS values (Table 5.1). More detailed CMO-NICS analysis of the contributions of individual MO's (π and in-plane radial) and, in particular their out-of-plane NICS tensor components (CMO-NICS_{zz}) provide clear evidence for double aromaticity (C_6 , C_6^{4+} , C_{10} , C_{14}) and double anti-aromaticity (C_8 , C_{12} which has two orthogonal eight electron systems), as well as mixed aromaticity/antiaromaticity (C_7 and C_9) (Table 5.1). Furthermore, CMO-NICS shows cyclic $C_4B_4^{4+}$, C_4B_4 , C_5B_2 , C_2B_8 , B_{12} , C_9B_2 , C_8B_4 , C_7B_6 , and C_6B_8 to be double aromatic species. These boron and borocarbon rings may possess exceptional stability, which might be confirmed by abundance mass spectrometry techniques, and constitute another class of compounds that meet the criteria of double aromaticity, as originally conceived by Chandrasekhar, Jemmis, and Schleyer.^[1]

5.6 ACKNOWLEDGMENTS

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Table 5.1. Point groups, NICS, and dissected NICS for relevant compounds.

Compound	Point Group	Electrons		NICS(0)	NICS(1)	NICS _{zz}	NICS(π)	NICS(rad)	NICS(π_{zz})	NICS(rad _{zz})
		π	rad							
C ₆ H ₃ ⁺	D _{3h}	6	2	-43.2	-20.0	-72.4	-32.76	-3.59	-34.32	-5.30
C ₆ ⁴⁺	D _{6h}	6	2	-62.3	-18.5	-67.5	-49.79	-9.82	-38.51	-15.99
C ₄ B ₄ ⁴⁺	D _{4h}	6	2	-40.3	-20.7	-56.1	-34.85	-7.17	-29.64	-13.45
C ₆ H ₆	D _{6h}	6	--	-7.5	-9.6	-14.9	-25.03	--	-36.12	--
C ₆	D _{6h}	6	6	-36.9	-17.6	-68.4	-33.66	+1.29	-39.52	-15.17
C ₆ ^a	D _{3h}	6	6	-25.1	-12.9	-31.6	-32.69	+11.98	-38.48	+19.36
C ₅ B ₂	C _{2v}	6	6	-22.5	-14.0	-42.2	-25.15	+6.01	-29.52	+5.91
C ₄ B ₄	D _{4h}	6	6	-31.8	-21.0	-66.1	-23.43	-7.63	-29.99	-23.78
C ₂ B ₈	D _{2h}	6	6	-27.5	-21.0	-57.6	-16.86	-9.01	-24.40	-23.82
B ₁₀ ²⁻	D _{10h}	6	6	-29.2	-23.1	-62.3	-17.89	-6.07	-26.29	-19.27
B ₁₂	D _{12h}	6	6	-24.7	-20.8	-55.1	-13.91	-9.63	-23.89	-25.32
C ₇	C _{2v}	6	8	-12.5	-12.0	-27.6	-25.59	+14.30	-36.68	+27.36
C ₈	D _{4h}	8	8	+48.8	+40.1	+169.3	+38.16	+11.87	+151.53	+28.86
C ₉	C _{2v}	10	8	+5.7	+0.5	+49.2	-30.09	+36.60	-53.37	+108.47
C ₁₀ H ₁₀	D _{10h}	10	--	-13.2	-12.3	-38.3	-29.21	--	-46.19	--
C ₁₀ ^a	D _{5h}	10	10	-28.2	-21.1	-69.5	-25.09	-3.86	-39.04	-13.89
C ₉ B ₂	C _{2v}	10	10	-25.1	-19.7	-62.9	-19.90	-6.77	-40.29	-21.11
C ₈ B ₄	D _{4h}	10	10	-32.1	-25.9	-79.2	-18.22	-14.81	-37.20	-42.92
C ₇ B ₆	C _{2v}	10	10	-23.0	-19.3	-56.5	-14.75	-9.15	-29.33	-26.16
C ₆ B ₈	C _{2v}	10	10	-23.7	-20.4	-59.4	-13.84	-10.16	-28.61	-28.39
C ₁₂	C _{6h}	12	12	+56.9	+47.1	+180.5	+38.52	+16.79	+131.10	+49.43
C ₁₄ H ₁₄	D _{14h}	14	--	-15.8	-14.5	-45.4	-19.56	--	-45.24	--
C ₁₄	D _{14h}	14	14	-40.8	-34.3	-114.1	-22.93	-21.28	-56.71	-63.95
C ₁₄ ^a	D _{7h}	14	14	-50.5	-35.8	-98.0	-22.78	-15.03	-56.26	-44.46

a) Polyallene structure.

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CHAPTER 6

CONCLUSIONS

The concept of protobranching and related applications to physical organic chemistry have been demonstrated in this dissertation. Its effects are far reaching as a result of the use of simple *n*-alkanes as reference values in nearly all energetic treatments of phenomena such as ring/cage strain, conjugation and hyperconjugation, and aromatic resonance energies. The benefits of Pople's isodesmic bond separation energies are also shown. These equations impose no interpretations by comparing the compound of interest directly to the simplest molecules of a particular class (i.e. methane and ethane for hydrocarbons). A dramatic illustration is provided in the aromatic resonance energy of benzene, where multiple chemical schemes give divergent information. However, when these schemes are corrected for the stabilizing interactions present, all agree to within several kcal/mol with the value give directly by the bond separation energy.

Using the knowledge of protobranching, as well as hyperconjugation, we have developed a simple additivity scheme that accurately reproduces experimental heats of formation of alkanes, alkyl radical, alkenes, and alkynes. In contrast to other recently proposed schemes such as those of Gronert, our additivity schemes makes use of well-established physical phenomena, such as the enhanced stability of branching and hyperconjugation.

Furthermore, protobranching has been extensively studied theoretically on model *n*-alkanes using Hartree-Fock, density functional theory, post Hartree-Fock methods, as well as the composite G3 method. HF and DFT methods are shown to systematically underestimate the branching stability. MP2, CCSD(T), and G3 all perform well, with MP2 slightly overestimating the stabilization. The performance of new functionals designed to account for weak interactions is only marginally better than those designed

for general application. Surprisingly, LDA shows the most accurate performance of those functionals tested, although this result should be regarded as dubious as problems with chemical applications of LDA have been well documented. The popular hybrid functional B3LYP is amongst the worst performers.

The double aromaticity of carbon, boron, and borocarbon monocyclic clusters has been studied using refined NICS techniques. Double aromaticity is the presence of two orthogonal Hückel frameworks in the same molecule, and is seen in all clusters studied that contain two “ $4n+2$ ” electron systems. These observations explain the presence of peaks of greater abundance (magic peaks) in mass spectral studies for C_6 , C_{10} , and C_{14} . Other boron and borocarbon compounds displaying double aromaticity are also likely candidates to be observed using mass spectrometry.

CHAPTER 7

LIST OF PUBLICATIONS

1. *Effects of halogen substitution on the properties of eight and nine-vertex polyhedral boranes.* C. Corminboeuf, **M. D. Wodrich**, R. B. King, P. v. R. Schleyer (To be submitted to *Inorganic Chemistry*).
2. *Double aromaticity in monocyclic carbon, boron, and borocarbon rings.* **M. D. Wodrich**, C. Corminboeuf, S. S. Park, P. v. R. Schleyer (To be submitted to *Chemistry – A European Journal*.)
3. *The concept of protobranching and its many paradigm shifting implications for energy evaluations.* **M. D. Wodrich**, C. S. Wannere, Y. Mo, P. D. Jarowski, K. N. Houk, P. v. R. Schleyer (To be submitted to *Chemistry – A European Journal*.)
4. *Systematic errors in computed alkane energies using B3LYP and other popular DFT functionals.* **M. D. Wodrich**, C. Corminboeuf, P. v. R. Schleyer *Organic Letters* **2006**, 8, 3631.
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