I have applied density functional theory (DFT) to various problems in organic and inorganic chemistry. The use of various DFT levels has rigorously been tested to assess the reliability of these methods to accurately compute structures and energies. The B3LYP DFT theory with a reasonably large basis sets is sufficiently accurate. In few cases, however, B3LYP leads to serious errors in predicting the ground state structures.

Work employing the B3LYP method to investigate the reaction of phosphaethene with 1,3-dienes revealed that the structures of the reactants and products and their energies were sufficiently accurate to explain the experimental regioselectivities. Additionally the B3LYP method also accurately reproduce the $^1$H NMR chemical shifts. In the study regarding the stability of $[4n]$annulenes (antiaromatic hydrocarbons), the use of an appropriate isodesmic equation can give B3LYP stabilization energies which are in excellent agreement with those given by other methods. In these cases, results from B3LYP-DFT were sufficiently accurate and reliable.

Computationally challenging for all the DFT methods was the prediction of structures and energies of $[4n+2]$annulenes. The widely accepted X-ray and B3LYP indicated CC bond
equalized structures of [14]-, [18]-, and [22]annulenes are found to be incorrect since the computed proton chemical shifts using these geometries gave $\delta$ $^1$Hs which are in gross disagreement with the experimental values. Instead lower symmetry structures with CC bond alternation are given by KMLYP and BHLYP DFT methods. These lower symmetry structures are found to be more stable, as also confirmed by the CCSD(T) method, and give proton chemical shifts in excellent agreement with experimental values.

Our application of the B3LYP level to various problems indicates that this method, in general, is reliable for computing accurate structures and energies. However, in a few cases caution is indicated when applying the B3LYP method, this study suggests that the KMLYP is capable of predicting structures more reliably than the B3LYP method. We also propose that data sets containing aromatic annulenes (larger than benzene) could serve as the basis for developing even better hybridizations of density functional and other methods.

INDEX WORDS: Density Functional Theory, Diels-Alder Reaction, Radical Cation Mechanism, Nucleus Independent Chemical Shifts (NICS), Magnetic Susceptibilities, $^1$H NMR Chemical Shifts, Aromaticity, Antiaromaticity, Nonclassical Carbocations
STRUCTURES, ENERGETICS, AND MAGNETIC PROPERTY EVALUATIONS USING
DENSITY FUNCTIONAL THEORY

by

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DEDICATION

---- to all my teachers
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I am grateful to so many people, who have helped me at different times during my entire career. I hope that I can acknowledge them all. I will start with the obvious, my parents. I truly appreciate your patience and your willingness to help me on several occasions since the day I was born. I also am truly grateful for your encouragement and for nurturing my desire towards science. I am very sure that you are the very best parents. I would also like to acknowledge my in-laws for their patience and for putting faith in me. Your mails at times have really relieved me from a lot of stress. Your philosophical teachings have benefited me.

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CHAPTER 1
INTRODUCTION

The scope of chemistry extends far beyond Nature. Chemists use their intellectual skills and indigenous methods to design and synthesize molecules of great complexity. I was (also am) a synthetic chemist, before joining the Schleyer group, and on entering the domain of computational chemistry, I often asked myself “if all the synthesis and characterization of compounds can be done in laboratories, then why is there a need to study molecules computationally?” But what forced my inclination towards theoretical chemistry was an impressive statement by Paul Schleyer “(the purpose of computational chemistry is) to model all aspects of chemistry by calculation rather than experiment.”

The laws of physics in mathematical terms allow analysis of chemical principles and most importantly the properties of structures. The field of computational chemistry aids the experimentalist by making predictions that will save time, effort and chemicals. While experiments are difficult (and sometimes even dangerous or impossible), costly, and time consuming, theoretical computations provide a valuable alternative for structure determination of molecules. In addition, short lived intermediates and also transition states are extremely difficult to characterize experimentally. Computational chemistry offers an impressive ability to study structures in a general and systematic way. Presently available programs possess the capability to provide convenient ways to obtain accurate geometric and also spectroscopic details. The impact of quantum chemistry in present-day research led to the 1998 Chemistry Nobel Prize for two
pioneers in computational chemistry namely, Professor J. A. Pople[1] and the founding father of
density functional theory (DFT), Professor W. Kohn[2].

While exact and highly correlated methods can allow computations to experimental
accuracy, use of these methods for very large molecules is not feasible. Since many molecules
that are of interest and importance are “large”, the scrutiny and computational characterization
for these molecules are important. This dissertation mainly focuses on the B3LYP DFT method
as a tool for solving problems on various “aromatic”[3] systems. For a vast majority of structures
B3LYP provides sufficiently accurate structures and energies. However, for a few large aromatic
systems, the use of the B3LYP functional is severely discouraged and alternative methods, e.g.
KMLYP and BHLYP, have been proposed. Incidentally, owing to time constraints, the validity
of the newly introduced KMLYP method could be tested only on few molecules, where the
performance of this functional has superseded the other available, older DFT methods.

1.1 EQUATIONS OF DFT

1.1.1 HISTORY OF DFT

The “story of DFT”, the basic idea that the electron density, $\rho(r)$, at each point $r$ determines the
ground-state properties of atomic and molecular systems, dates back before the origination of
Hartree-Fock theory (HF) [4, 5], the theory considered as the starting point for quantum
chemistry. In late 1920’s and 1930’s Thomas, Fermi, Dirac, and von Weiszäcker derived an
expression for the kinetic energy based on the density of the electrons in an infinite potential; the
theory holds for free electron gases[6- 9]. An important step towards the use of DFT occured
when Slater, in 1951, proposed the X$\alpha$ method where the use of a simple, one parameter
approximate exchange correlation functional was expressed in the form of an exchange-only functional[10]. The biggest advance occurred in 1964 with the Hohenberg and Kohn theorems, which stated that energy and all other electronic properties of the ground state are uniquely determined by its charge density[11]. In 1965 Kohn and Sham formulated the DFT equations to allow exact solution of the kinetic energy functional and introduced the Kohn-Sham orbitals to DFT[12]. This point paved the way to a computational breakthrough for DFT. Around 1995, DFT via the Kohn-Sham formalism was introduced into Pople’s GAUSSIAN, the most popular program in use. Undoubtedly, this further promoted the use of DFT as computationally attractive alternative to existing other wavefunction techniques.

1.1.2 PRESENT STATUS OF DFT[13]

DFT employs the square of the wavefunction based on the electronic density and includes some electron correlation to the total energy. The equations are similar to those for HF theory. It is conceptually useful to partition the total electronic energy of a given system into five components: (1) the kinetic energy of the electrons, (2) Coulomb energy of the electrons due to their attraction to the nuclei, (3) electron-electron Coulomb repulsion which assumes that each electron moves independently (which they don’t) and that each electron is repelled by itself (which it doesn’t), and (4, 5) two more terms which corrects for two false assumptions in (3). The last two terms are collectively termed as $E_{xc}$, which accounts for some correlation in DFT. The $E_{xc}$ part includes some part of the kinetic energy correlation energy since determination of electron kinetic energy in terms of a finite set of orbitals based on the density omits a small proportion of the energy. A major contribution to $E_{xc}$ consists of the correction for the self-repulsions of the electrons, also known as the exchange energy.
From the HF theory the electronic Hamiltonian is:

\[ \hat{H}_e = -\sum_i^{N} \frac{1}{2} \nabla^2_i + \sum_{i<j}^{N} \frac{1}{r_{ij}} - \sum_A^{M} \sum_i^{N} \frac{Z_A}{|R_A - r_i|} \]  

(1.1)

The result is:

\[ E_{HF} = T + J + V_{ne} \]  

(1.2)

The energy expression, after expansion of orbitals in terms of density, becomes:

\[ E_{DFT}[\rho] = T_s[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \]  

(1.3)

where:

\[ E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) = (T[\rho] - T_s[\rho]) + K[\rho] \]  

(1.4)

The correlation energy is \( T[\rho] - T_s[\rho] \) and the exchange energy is \( K[\rho] \).

The orbitals are then constrained to be orthogonal and optimized using Lagrange’s method of undetermined multipliers:

\[ L[\rho] = E_{DFT}[\rho] + \sum_{ij}^{N} \lambda_{ij} \langle \phi_i | \phi_j \rangle - \delta_{ij} \]  

(1.5)

A set of equations with an effective one-electron operator is produced:

\[ \hat{h}_{KS} = -\frac{1}{2} \nabla^2 + V_{ne} + \int \frac{\rho(\hat{r}^*)}{|\hat{r}^* - \hat{r}|} d\hat{r}^* + V_{xx}(\hat{r}) \]  

(1.6)

As fore mentioned, exchange energy is the largest contributor to \( E_{xc} \).

1.1.3 FUNCTIONALS

Various exchange and correlation functionals have been designed, which treat the exchange correlation “corrections” in different ways. One of the earliest and most widely used in chemistry is the Local Spin Density Approximation (LSDA), which treats electron density locally as a uniform gas with the introduction of a spin polarization parameter. This functional employs the
1980 correlation functional of Vosko, Wilk, and Nusair[14] and the exchange functional of Slater[15]. However, this correlation functional over-binds the molecules and total energies are in error by up to 10%. Additionally, correlation energies are overestimated by up to a factor of two. Two families of functionals, which add correction to the LSDA approximation, have emerged: the Generalized Gradient Approximation (GGA) and the hybrid functionals. The data presented in this thesis use the following functionals: the GGA exchange functionals, which is the “B” functional[16]. The GGA correlation functionals employed Becke’s three parameter “B3”[17] and half and half “BH” functionals[18]. These exchange and correlation functionals[19] combine to give different functionals: BLYP, B3LYP, BHLYP. In general, the best results were obtained with B3LYP functionals. However, in the sixth chapter, the B3LYP method is demonstrated to fail severely in giving the correct electronic structure of large aromatic annulenes. On the other hand, the performance of newly introduced KMLYP functional’s is superior[20]. The B3LYP[17] exchange functional is 20% HF exchange and 80% Slater LSDA exchange. In addition, 72% of the Becke88 exchange gradient correction is included. The correlation functional in KMLYP consists of 81% LYP and 19% VWN correlation functional. In contrast KMLYP uses a higher percentage of exact exchange, 55.7% HF exchange, along with 44.3% Slater exchange. In addition, KMLYP includes 44.8% LYP and 55.2% VSN correlation functional.
1.2 COMPUTATIONAL DETAILS

The Gaussian-94[21] and Gaussian-98 [22] suite of programs were used for most of the work described in this thesis. The Pople’s double and triple zeta basis sets, 6-31G* and 6-311+G**, respectively, were used for all the structures, to maintain consistency. The $^1$H NMR chemical shifts and its dissection into (localized MO’s) LMO’s for some structures were computed using the demon-Master NMR program[23] at the SOS-DFPT[24] level with the Perdew-Wang-91 (PW91)[25] exchange correlation functional and the IGLO-III TZ2P[26] basis set (recommended options). The magnetic susceptibilities were computed by the CSGT[27] method and $^1$H NMR chemical shifts (and nucleus independent chemical shifts, NICS[28]) were computed using the GIAO[29] method implemented in Gaussian-98 program package.

1.3 OVERVIEW OF CHAPTERS

1.3.1 DIELS-ALDER REACTION OF PHOSPHAETHENE WITH 1,3-DIENES

The DFT- B3LYP/6-311+G** computations on Diels-Alder (DA) reaction of phosphaethene with various 1,3-dienes and with isoprene reveal that asynchronous transition states (TS) are involved. The activation energies of these reactions, computed at fore mentioned level, are much lower than that of the parent ethane- butadiene Diels-Alder reaction, although the exothermicities of all lie in the same range. DFT studies also indicate that the lower activation energies in the former reactions are attributed to weakness of the C=P $\pi$ bond relative to the C=C $\pi$ bonds[30]. Regioselectivities of the phosphaethene-isoprene cycloadditions cannot be explained based on the neutral DA reactions. However, UB3LYP/6-311+G** computations on radical cation
reactions of phosphaethene with isoprene, which proceed stepwise with open chain intermediates, could account for the high stereoselectivities that have been experimentally observed in some cases. The DFT computed $^1$H NMR chemical shifts and NICS were used to quantify the aromaticity of the transition states.

1.3.2 HOW DO RING CURRENTS AFFECT THE $^1$H NMR CHEMICAL SHIFTS?

Chapter 3 further explores the use of DFT methods employed in the IGLO program to assess the ring current effects on $^1$H NMR chemical shifts. The conventional explanation, based on the Pople’s ring current model, states that Hs of benzene are deshielded from the ring currents[32]. The \textit{ab initio} IGLO program, which can dissect the total contributions into $\sigma$ and $\pi$ contributions, reveal that the downfield $\delta$ $^1$H of benzene does not arise from deshielding ring current effects; the shielding is less than the $\pi$ contributions to vinyl Hs. Enhanced $\sigma$ CC influences are responsible for the more downfield $\delta$ $^1$Hs of the inner protons of naphthalene and anthracene. It is widely accepted that ring currents in acetylene are responsible for upfield chemical shifts of Hs as compared to the protons of alkene[33]. Our analyses of the ring currents indicate no evidence for "ring currents" in acetylene.

1.3.3 ON THE STABILITY OF [4n]ANNULENES

The [4n]annulenes, the unfavorable counterparts of the stabilized [4n+2]$\pi$-electron aromatics, were described to be destabilized. The B3LYP/6-31G* stabilization energies of planar [4n]annulenes, evaluated by a “new” indene-isoindene isomerization method, revealed that all of the 4n $\pi$-electron rings, except for cyclobutadiene, are only slightly destabilized. Planar cyclooctatetraene prefers the D$_{4h}$ form, which is expected to be antiaromatic. Thus the D$_{2d}$ (most
stable tub form of cyclooctatetraene) – $D_{4h}$ energy difference gives an upper bound to the
antiaromatic destabilization energy, which is known to be 10 kcal/mol from the NMR
measurements on cyclooctatetraene derivatives[34]. This value is well reproduced by the DFT
computations on the parent cyclooctatetraene itself. The DFT computed energies and magnetic
properties, demonstrate that the antiaromatic character of the larger systems with $4n \pi$-electrons
is best described by magnetic properties rather than energies.

The subsequent two chapters deal with the application of B3LYP DFT method in
predicting the stabilization energies of aromatic annulenes and verifying if this method is
appropriate for predicting a correct electronic structure of several aromatic annulenes.

1.3.4 HOW AROMATIC ARE LARGE (4n+2)$\pi$ ANNULENES?
The energy and magnetic properties of [4n+2] annulenes optimized at HF and B3LYP are
compared. The total aromatic stabilization energies (ASE is the (de) stability of a cyclic
conjugated polyene with respect to its non-aromatic isomer) of [n= 6 to 66]annulenes, computed
at B3LYP/6-31G*, are found to converge to 22 kcal/mol for [66]annulene. However, the ASEs
per $\pi$-electron show a significant decrease with the increase in ring size. The HF method prefers
structures, which are bond length alternating starting after [10]annulene, while the B3LYP
method favors bond equalized structures up to [30]annulene. Bond length alternation (which as
indicated above depends on the theoretical level) only reduces the stabilization energies
somewhat but is found to considerably influence the magnetic properties (NICS, proton chemical
shifts, and magnetic susceptibilities). Only magnetic properties, but not the stabilization energies,
show that the aromaticities of large annulenes decrease slowly and then nearly vanish (at
[66]annulene). All the data presented demonstrate that the magnetic properties, unlike stabilization energies, are very sensitive to geometries.

1.3.5 [18]ANNULENE HAS ALTERNATING, RATHER THAN EQUALIZED CC BOND LENGTHS

The $^1$H NMR chemical shifts of various arenes computed by GIAO-B3LYP/6-311+G** are generally found to be within 0.2 to 0.5 ppm of the experimental values[35]. Schleyer and Bühl have established that an excellent agreement between the computed and experimental chemical shifts is found only when the geometries are correct[36]. Based on the above facts, the widely accepted X-ray[37] and the B3LYP optimized D$_{6h}$ (bond length-equalized) structure[38] of [18]annulene cannot be correct as the computed chemical shifts using the fore mentioned method are in gross disagreement with the experimental values. Additionally, B3LYP predictions that [14]- and [22]annulenes have highly symmetric structures are also incorrect since these CC bond-length equalized structures give chemical shifts that are far from the experimental values[39]. KMLYP and BHLYP methods predict that [14]-, [18]-, [22]annulenes with CC bond alternation (lower symmetry) geometries are energetically more stable. Additionally, these lower symmetry structures give $\delta$ $^1$H’s agreeing within 0.7 ppm of the experimental values. The X-ray crystallographic findings and also the data can be reconciled by assuming superpositions or rapid dynamic equilibria of the lower symmetry [18]annulene structure. The computed downfield and upfield chemical shifts of the outer and inner protons, respectively, demonstrates that the bond alternation in [14]-, [18]-, and [22]annulenes does not eliminate aromaticity.
1.4 REFERENCES


CHAPTER 2

DIELS–ALDER REACTION OF PHOSPHAETHENE WITH 1,3-DIENES∗

Computations on the Diels–Alder (DA) reactions of phosphaethene with 1,3-butadiene and with isoprene reveal asynchronous transition structures. The DFT (B3LYP/6-311+G**) activation energies of these reactions, 12 to 14 kcal mol\(^{-1}\), are much lower than that of the parent ethene-butadiene reaction, 28 kcal mol\(^{-1}\), even though the exothermicities of all lie in the same range, -29 to -33 kcal mol\(^{-1}\). The transition states (TS) for the phosphethene-butadiene or isoprene DA reactions are earlier than the TS’s of the butadiene-ethene cycloaddition. Due to the weaker C=P than the C=C \(\pi\) bonds, the energies required to reach the phosphaethene TS’s are much less than the carbocyclic cases. The computed \(^1\)H NMR chemical shifts and Nucleus Independent Chemical Shifts (NICS) quantify the aromatic character of the transition states. Regioselectivities of the neutral phosphaethene-isoprene DA reactions are modest, at best. However, computations on radical-cation DA reactions of phosphaethene with isoprene, which proceed step-wise with open chain intermediates, can account for the high regioselectivities, which have been observed in some cases.
2.2 INTRODUCTION

The Diels-Alder (DA) reaction, perhaps the most widely used synthetic method for the construction of six-membered rings[1], also has been central in the development of theoretical models of pericyclic reactions[2]. The availability of new classes of organophosphorus compounds with >C=P- functionalities, namely phosphaalkenes[3-7], heterophospholes[6,8-10], anellated azaphospholes[11-14], and phosphinines[15], has further enlarged the scope of the DA reaction. A number of [4+2] cycloadditions have been carried out successfully using these phosphorus compounds, mostly as dienophiles, but in some cases as diene components as well. Unlike the phosphaalkenes, which have a strong tendency to undergo [2+2] dimerization unless bulky substituents are present[3,5, 16], the DA reaction of the parent phosphaethene, generated in situ, with 2,3-dimethyl-1,3-butadiene leads to a tetrahydrophosphinine[17]. Likewise, the behavior of the phosphabutadienes are governed by the nature of the substituents: they may dimerize in the [2+2] mode[18] or may undergo [4+2] cycloadditions acting as dienophiles[19]. The DA reactions involving the >C=P- functionality of a few heterophospholes have been reported[8-10, 16]. In some cases, the phosphabutadiene system within the heterophosphole ring acts as a diene component[20-22].

Remarkably, complete regioselectivity has been reported in the DA reaction of 2-acetyl-2H-1,2,3-diazaphospholes with isoprene (Scheme 2.1): “the other isomer was not detected” in the $^{31}$P NMR signals of the product[23]. However, the analytical methods used to purify the products and the limits of detectability were not mentioned in the reference. 1,3-Azaphospholo[5,1-a]isoquinoline undergoes DA reactions with 2,3-dimethyl-1,3-butadiene[24] and with isoprene[25]; 62 to 100% regioselectivity was observed in the latter case, depending on
the conditions (Scheme 2.2). Experimentally, the DA reactions of 1,3-azaphospholo[5,1-
b]benzothiazoles[26], 1,4,2-diazaphospholo[5,4-b]benzothiazoles, thiazolines[27] and 1,4,2-
diazaphospholo[4,5-a]pyridines[28] with isoprene showed 70 to 100% regioselectivity (Scheme
2.3).

Many ab initio[29-32] and semiempirical[33-46] calculations on the DA cycloadditions
have been reported. The prototype DA cycloaddition of 1,3-butadiene with ethene has been
computed theoretically at different levels and a well-defined synchronous transition state, TS₁,
has been established[47]. However, unsymmetrical reactants (e.g. isoprene, acrolein) involve
asynchronous transition states, i.e. the lengths of two newly forming bonds differ significantly
in the TS. Asynchronicity of such transition states has been established both by experimental[48]
and by theoretical methods[49-51].

In contrast, theoretical studies of DA reactions involving phosphorus and the aromaticity
of their transition states are scarce. The DA cycloadditions of phospha-1,3-butadienes with
ethene were computed to be very exothermic with low activation energies[52]. Ab initio
investigations of the [2+4] cycloadditions of phosphaethene with 2H-phosphole[53] and with 1,3-
butadiene[54-57] revealed such low activation energies and a preference for endo approach. It
was concluded that the presence of phosphorus in a DA reactant lowers the activation energy
relative to that of the hydrocarbon systems, due to the weaker C=P than C=C π bond[52]. We
have now carried out ab initio calculations on the prototype DA reactions of phosphaethene with
1,3-butadiene and with isoprene at the B3LYP/6-311+G** DFT level to ascertain the nature of
the transition states and to examine the regioselectivity. The aromaticity of the transition states
have been established by computations of the ¹H NMR chemical shifts[58], the magnetic
susceptibility exaltations[59], and the NICS[60] values. The DA reactions of isoprene with
phosphaethene and related systems, proceeding through a concerted TS, shows no appreciable regioselectivity. Alternatively, we show that reactions proceeding through radical-cation mechanisms can give products with high regioselectivity.

Some pericyclic reactions may be prohibitively slow or may not give the desired products. Lewis acids or catalytic agents may assist by complexation, thereby reducing the electron density of one reactant. Alternatively, one electron may be removed from the system by an oxidizing agent; this may accelerate the reaction[61]. This approach has been termed as “hole catalysis” by Bauld[62]. Radical cation reactions, which do not need to be electrocyclic, generally have low activation energies but nevertheless show high degrees of regio- and stereoselectivity[63]. Radical cation reactions thus complement neutral reactions. The DA reactions of ethene with butadiene radical-cation have been investigated theoretically recently[64]. A stepwise addition involving open chain intermediates but leading to a DA-like product, cyclohexene radical cation, was found to have a total activation barrier of only 6.3 kcal mol\(^{-1}\) and exothermicity of 45.6 kcal mol\(^{-1}\)[64]. All the TS’s and intermediates were found to have lower energy than the separated starting reactants.

We have now investigated, similarly, the stepwise reaction of the isoprene radical cation with phosphaethene with density functional theory at the UB3LYP/6-311+G** level. A reaction pathway leading to the radical cation DA products was shown to be possible.
Scheme 2.1

Scheme 2.2

Scheme 2.3

<table>
<thead>
<tr>
<th></th>
<th>Y</th>
<th>X</th>
<th>CR'/S/Se</th>
<th>100%</th>
<th>0-30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td></td>
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</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3 COMPUTATIONAL METHODS

All results were obtained with the GAUSSIAN 94 [65] and GAUSSIAN 98 [66] series of programs. Reactants and products as well as transition structures resulting from the Diels-Alder reaction of phosphaethene with 1,3-dienes were optimized initially at HF/6-31G* and finally at the B3LYP/6-311+G** DFT level. The frequencies were computed at B3LYP/6-31G*; the transition structures were confirmed by the presence of one imaginary frequency. Unscaled zero point energy corrections (ZPE) from the same level were applied to the B3LYP/6-311+G** energies. The potential energy surface along the reaction course (s) for the parent as well as phosphaethene and butadiene DA reaction is computed at B3LYP/6-311+G**. The bond orders, of the various bonds, in TS’s were evaluated using the NBO program[67] as implemented in Gaussian-98 package.

For the radical cation reactions, the geometries of all the reactants and of all the intermediates and TS’s and of all the products were optimized with 6-31G* and 6-311+G** basis sets and Becke’s three parameter hybrid functional in conjunction with correlation functional of Lee, Yang and Parr (UB3LYP) as implemented in Gaussian-98. The frequencies were computed at UB3LYP/6-31G* and unscaled zero point corrections from the same level were applied to the UB3LYP/6-311+G** energies.

The magnetic susceptibilities were computed by the CSGT method[59a, b] at B3LYP/6-31+G*// B3LYP/6-311+G**. NICS values were obtained at GIAO-B3LYP/6-31+G* // B3LYP/6-311+G**[59c]. Dissected NICS[60] and the proton chemical shifts[58] were evaluated using the deMon-Master NMR program[68], at SOS-DFPT[69] level with the Perdew-Wang-
91(PW91) [70a, b] exchange correlation functional and the IGLO-III TZ2P basis set[70c] (recommended options).

2.4 RESULTS AND DISCUSSION

The first part of the study involved the parent and six other DA reactions, as summarized in Table 2.1. Note that reaction 1 is the parent Diels-Alder reaction of butadiene with ethene.

2.4.1 GEOMETRIES:

The B3LYP/6-311+G** optimized geometries of the reactants, phosphaethene (1), 1,3-butadiene (2) and isoprene (3) (Figure 2.1), the products (4-9) (Figure 2.2), as well as the transition structures, TS1, TS2-7 (Figure 2.3), show the change in bond lengths along the reaction course.

Table 2.1. Activation energies ($\Delta E_a$, kcal mol$^{-1}$) and exothermicities ($\Delta E_{rxn}$, kcal mol$^{-1}$) for the reactions 1-7 between phosphaethene (1) and 1,3-dienes (2, 3).

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
<th>$\Delta E_a$</th>
<th>$\Delta E_{rxn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Butadiene+ Ethene $\rightarrow$ TS$_1$</td>
<td>28.00</td>
<td>-29.19</td>
</tr>
<tr>
<td>2.</td>
<td>1(endo) + 2 $\rightarrow$ TS$_2$ $\rightarrow$ 4</td>
<td>12.41</td>
<td>-29.71</td>
</tr>
<tr>
<td>3.</td>
<td>1(exo) + 2 $\rightarrow$ TS$_3$ $\rightarrow$ 5</td>
<td>14.48</td>
<td>-32.15</td>
</tr>
<tr>
<td>4.</td>
<td>1(endo) + 3 $\rightarrow$ TS$_4$ $\rightarrow$ 6 (P:Me, 1:4)</td>
<td>12.46</td>
<td>-30.84</td>
</tr>
<tr>
<td>5.</td>
<td>1(endo) + 3 $\rightarrow$ TS$_5$ $\rightarrow$ 7 (P:Me, 1:3)</td>
<td>12.30</td>
<td>-31.01</td>
</tr>
<tr>
<td>6.</td>
<td>1(exo) + 3 $\rightarrow$ TS$_6$ $\rightarrow$ 8 (P:Me, 1:4)</td>
<td>14.47</td>
<td>-33.11</td>
</tr>
<tr>
<td>7.</td>
<td>1(exo) + 3 $\rightarrow$ TS$_7$ $\rightarrow$ 9 (P:Me, 1:3)</td>
<td>14.12</td>
<td>-33.03</td>
</tr>
</tbody>
</table>
Figure 2.1. Bond lengths (B3LYP/6-311+G**) and $^1$H NMR chemical shifts (GIAO-B3LYP/6-31+G**//B3LYP/6-311+G**, in δ ppm) of the reactants.

The computed lengths of the PC double bond in 1 (1.67 Å) and the PC single bond in 4-9 (1.86 – 1.89 Å) are very close to the experimental values of related compounds[5c, 71]. The PC bond lengths in the phosphaethene moiety in the transition structures TS$_2$-TS$_7$ (~1.71 Å) are intermediate between C= P and C-P bond lengths. The central CC bonds of 1,3-butadiene (1.47 Å) and of isoprene (1.48 Å) shorten on reaction with phosphaethene (~1.40 Å in TS$_2$-TS$_7$) and become typical CC double bonds (~1.33 Å) in the products. The newly forming, C1-C6, bond lengths in TS$_2$-TS$_7$ are slightly longer (~0.1 to 0.2 Å) than those in the prototype ethene-butadiene DA cycloaddition TS$_1$. Although the two newly forming bonds, PC and CC in TS$_2$-TS$_7$, do not differ significantly in their lengths in the transition structures, the PC bonds (~1.88
Å) are, as expected, longer than the CC bonds (~1.53 Å) in the products. Furthermore, PC bonds are slightly longer in the exo approach transition structures relative to those from the endo approach transition structures.

Figure 2.2. Geometries (B3LYP/6-311+G**) and $^1$H chemical shifts in ppm (GIAO- B3LYP/6-31+G*/ B3LYP/6-311+G**) of the products of the reactions of phosphaethene with 1,3-butadiene and with isoprene.
Figure 2.3. Bond lengths (B3LYP/6-311+G**, in Å) and ¹H NMR chemical shifts as well as NICS (GIAO- B3LYP/6-31+G* //B3LYP/6-311+G**, in ppm) of the transition states obtained in Diels-Alder reactions of phosphethene with butadiene, TS₂, TS₃, and isoprene, TS₄, TS₅, TS₆, and TS₇. In all the TS's, C₂-C₃-P₅-C₆ are in one plane. The dotted lines denote the mobile electron localization as given by the dissected NICS (IGLO method) computations.

While phosphethene is planar, the 4-phosphacyclohexene rings in the products 4-9 are puckered. The C-C=C-C substructures of these rings are almost planar, with dihedral angles of
0.6-1.2°, but there is considerable folding involving phosphorus. The C3-C4-P5-C6 dihedral angle, for example, is 39.9° in 4. The CPC angle in 4 is 99.1° which is in conformity with the usual small angles at phosphorus in rings[8, 72, 73]. In the transition states, the phosphaethene and diene fragments approach each other in distinctly non parallel planes, although the values of the C2-C3-P5-C6 dihedral angles are small, e.g. 6.5° in TS₁ and 5.0° TS₅. The diene moieties in the transition structures (TS₂ through TS₇) are nearly planar, the CCCC dihedral angle is close to zero.

2.4.2 ENERGIES:
The activation, ΔEₐ, and reaction energies, ΔE_rxn, of reactions 1-7 are given in Table 2.1. While the exothermicities of the DA reactions of ethene with 1,3-butadiene and with phosphabutadienes, reported earlier[52], are quite similar, the ΔEₐ for the latter are smaller. Our results are parallel: the presence of phosphorous in the dienophile lowers the activation barriers (which ranges from 12.3 to 14.5 kcal mol⁻¹) for reactions 2-7, as compared to ΔEₐ for the prototype ethene-butadiene cycloaddition, but the ΔE_rxn values (Table 2.1) are in the same range. The difference in ΔEₐ between the carbocyclic and phospha DA reactions has been attributed to the weakness[74] of the C=P π bond relative to the C=C π bond.

The bond orders (Scheme 2.4) of the synchronous TS₁ for the parent DA reaction as well as for asynchronous TS₂-TS₇ show that the extent of double bond formation on C2-C3 is greater in TS₁. Also the extent of bond formation between C1-C6 and C4-C5 is somewhat larger in TS₁ as compared to that between C1-C6 and C4-P5 in TS₂-TS₇. Consequently, the TS’s for phosphaethene-butadiene or isoprene DA reactions are “earlier” than the TS₁ of ethene-butadiene cycloaddition, Figure 2.4, (the reaction course “s”, in Figure 2.4, is defined as s=(d₉-d)/(d₉-d₉);
where \( d \) is the distance between \( C_1-C_4 \) and \( C_5-C_6 \) midpoints, \( d_R \) and \( d_p \) are the respective distances in the optimized reactant and product geometry. Hence the energy necessary for reorganization of all bonds in reactions 2 to 7 is less than that needed in reaction 1. Since C-P \( \pi \) bonds are weaker than the C-C \( \pi \) bonds[74], the C=P bond reorganization energy also is less than that for C=C. Hence, \( \Delta E_a \) is smaller for reactions 2 to 7 than for reaction 1. Also, note the smaller HOMO-LUMO gap between diene and phosphaethene (the FMO gap between butadiene and ethene is 6.26 e.v. and between butadiene and phosphaethene is only 4.35 e.v.). Hence, based on the FMO theory, DA reactions 2 to 7 should be faster and occur with lower activation barriers as compared to reaction 1.

On going from the reactants to the product in the parent DA reaction, two C=C bonds are converted into four C-C bonds. An estimate of the exothermicity, via bond energies (obtained from ref. 74b), gives an enthalpy of \(-37.8\) kcal mol\(^{-1}\). A similar estimate for the phosphaethene-butadiene or isoprene system gives an exothermicity of \(-35.7\) kcal mol\(^{-1}\). The exothermicities of reaction 1 and of reactions 2 to 7, evaluated via bond energies, are in close agreement, as are the \( \Delta E_{rxn} \) values in Table 2.1.

2.4.3 STEREOSELECTIVITY AND REGIOSELECTIVITY:
The \(-2\) kcal mol\(^{-1}\) lower activation energies for reactions 2, 4 and 5 indicate that the approach of the reactants with an endo P-H group is kinetically more favorable than attack with an exo P-H. A similar effect was noted in the DA reactions of ethene with 1-phosphabutadienes[52]. The preference for the endo transition state, in our cases, is due to the orientation of the phosphorus lone pair away from the butadiene. Houk and coworkers demonstrated[75] the powerful
stereochemical control of dienophile heteroatom lone pairs in the DA reactions of formaldehyde, diazene, formaldimine, and nitrosylhydride with butadiene.

Figure 2.4. Intrinsic reaction coordinate (IRC) of [4+2] Diels Alder reaction of butadiene with ethene and with phosphaethene at B3LYP/6-311+G**.

These reactions have larger activation barriers than phosphaethene-butadiene cycloaddition since the C-N π bond (80.8 kcal mol\(^{-1}\)) is much stronger[74b, 74c] than C=P bond (49.4 kcal mol\(^{-1}\)). The \(~2\) kcal mol\(^{-1}\) greater \(\Delta E_{\text{rxn}}\) of the exo additions, 3, 6 as well as 7 (Table 2.1), however, show that the product structures resulting from these exo reactions are thermodynamically more stable than those resulting from the endo additions.
Scheme 2.4. NBO bond order of reactants as well as TS’s of the Diels-Alder reactions of ethene with butadiene as well as phosphethene with butadiene and with isoprene.

Cossio et. al pointed out that although the transition state aromaticity was important, this does not determine the regioselectivity of the reaction[76b]. In our cases, the energies of the
alternative transition structures $\text{TS}_4$ and $\text{TS}_5$, on the one hand, and $\text{TS}_6$ and $\text{TS}_7$, on the other, do not differ significantly. While $\text{TS}_5$ and $\text{TS}_7$, which correspond to the preferred regioisomers, are lower in energy, the differences are only 0.16 and 0.35 kcal mol$^{-1}$, respectively.

Experimentally, the DA reactions of isoprene with 2-acetyl-2H-1,2,3-diazaphosphole[23] and with 1,4,2-diazaphospholo[4,5-$\alpha$]pyridine[28] were reported to produce the meta regioproduct exclusively. To rationalize these results, we have computed the activation barriers for the concerted TS’s of the DA reactions of isoprene with 2H-1,2,3-diazaphosphole ($\text{10}$), 2-acetyl-2H-1,2,3-diazaphosphole ($\text{11}$), 1,4,2-diazaphospholo[4,5-$\alpha$]pyridine ($\text{12}$), and phosphacetylene ($\text{13}$). We have computed the activation energies, $\Delta E_a$, of the TS’s for the DA reactions resulting from exo and from endo approach of both the reactants (reactions 8 through 19) as summarized in Table 2.2.

For comparison, we also computed the activation barriers of reactions 22 and 23, as well as those for the DA reaction of butadiene with acetylene (reaction 20) and with phosphacetylene (reaction 21).

The geometries of the TS’s for all the reactions (8 through 23) are displayed in Figure 2.5. Table 2.2 shows that the activation barriers (for the same dienophile) for exo and for endo approach of the reactants are quite similar. $\Delta E_{\text{rxn}}$ of these reactions (Table 2.2) are exothermic, except that reactions 8 through 11 become slightly endothermic when the ZPE corrections ($\Delta E_{\text{rxn}+\text{ZPE}}$) are applied. $\Delta E_a$ and $\Delta E_{\text{rxn}}$ show that the TS’s for the endo approach of the reactants for all the reactions (8 through 19, in Table 2.2) are favored slightly (by about 0.3 to 0.9 kcal mol$^{-1}$) over those for the exo approach. The endo TS’s are thus kinetically preferred.
Table 2.2. Activation energies (\(\Delta E_a\), kcal mol\(^{-1}\)), ZPE corrected activation energies (\(\Delta E_{a+ZPE}\), in kcal mol\(^{-1}\)), exothermicities (\(\Delta E_{rxn}\), kcal mol\(^{-1}\)) and ZPE corrected exothermicities \(^b\) (\(\Delta E_{rxn+ZPE}\), kcal mol\(^{-1}\)) for the DA reactions of isoprene (3) with 2H-1,2,3-diazaphosphole (10), reaction 8-11, with 2-acetyl-2H-1,2,3-diazaphosphole (11), reactions 12 through 15, with 1,4,2-diazaphospholo[4,5-\(\alpha\)]pyridine (12), reactions 16-19, and with phosphacetylene (13), reactions 22 and 23, and also for the DA reaction of butadiene (2) with acetylene, reaction 20, and with phosphacetylene, reaction 21.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
<th>(\Delta E_a)</th>
<th>(\Delta E_{a+ZPE})</th>
<th>(\Delta E_{rxn})</th>
<th>(\Delta E_{rxn+ZPE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>8. 10 (endo) + 3 → TS(_8) → 14-meta-endo</td>
<td>27.08</td>
<td>27.48</td>
<td>-2.40</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>9. 10 (endo) + 3 → TS(_9) → 15-para-endo</td>
<td>27.73</td>
<td>28.19</td>
<td>-2.11</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>10. 10 (exo) + 3 → TS(_{10}) → 16-meta-exo</td>
<td>26.87</td>
<td>27.38</td>
<td>-1.52</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>11. 10 (exo) + 3 → TS(_{11}) → 17-para-exo</td>
<td>27.69</td>
<td>28.20</td>
<td>-1.77</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>12. 11 (endo) + 3 → TS(_{12}) → 18-met-exo</td>
<td>14.84</td>
<td>15.88</td>
<td>-16.91</td>
<td>-13.62</td>
<td></td>
</tr>
<tr>
<td>14. 11 (exo) + 3 → TS(_{14}) → 20-met-exo</td>
<td>15.43</td>
<td>16.30</td>
<td>-15.80</td>
<td>-12.47</td>
<td></td>
</tr>
<tr>
<td>15. 11 (exo) + 3 → TS(_{15}) → 21-para-exo</td>
<td>16.67</td>
<td>17.58</td>
<td>-15.59</td>
<td>-12.25</td>
<td></td>
</tr>
<tr>
<td>16. 12 (endo) + 3 → TS(_{16}) → 22-met-exo</td>
<td>22.33</td>
<td>22.95</td>
<td>-11.80</td>
<td>-8.56</td>
<td></td>
</tr>
<tr>
<td>17. 12 (endo) + 3 → TS(_{17}) → 23-para-exo</td>
<td>23.71</td>
<td>24.47</td>
<td>-11.14</td>
<td>-7.91</td>
<td></td>
</tr>
<tr>
<td>18. 12 (exo) + 3 → TS(_{18}) → 24-met-exo</td>
<td>23.00</td>
<td>23.49</td>
<td>-10.71</td>
<td>-7.52</td>
<td></td>
</tr>
<tr>
<td>19. 12 (exo) + 3 → TS(_{19}) → 25-para-exo</td>
<td>23.71</td>
<td>24.31</td>
<td>-10.28</td>
<td>-7.02</td>
<td></td>
</tr>
<tr>
<td>20. Acetylene + 2 → TS(_{20}) → 26</td>
<td>25.65</td>
<td>27.40</td>
<td>-54.05</td>
<td>-47.47</td>
<td></td>
</tr>
<tr>
<td>21. 13 + 2 → TS(_{21}) → 27</td>
<td>15.40</td>
<td>15.74</td>
<td>-35.41</td>
<td>-31.31</td>
<td></td>
</tr>
<tr>
<td>22. 13 + 3 → TS(_{22}) → 28-met</td>
<td>15.66</td>
<td>16.49</td>
<td>-36.12</td>
<td>-32.35</td>
<td></td>
</tr>
<tr>
<td>23. 13 + 3 → TS(_{23}) → 29-para</td>
<td>15.84</td>
<td>16.67</td>
<td>-36.13</td>
<td>-32.44</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.5. continued on next page
Figure 2.5. continued on next page
Figure 2.5 continued on next page
Figure 2.5. Bond lengths (B3LYP/6-311+G**, in Å) of the transition states obtained by Diels-Alder reactions of isoprene with 2H-1,2,3-diazaphosphole (10), TS8 through TS11, with 2-acetyl-2H-1,2,3-diazaphosphole (11), TS12 through TS15, with 1,4,2-diazaphospholo[4,5-a]pyridine (12), TS16 through TS19, and with phosphacetylene (13), TS22 and TS23, and of the TS’s obtained by the Diels-Alder reaction of butadiene with acetylene, TS20, and phosphacetylene, TS21.

The activation barriers (ΔEa in Table 2.2) suggest that, for the endo approach of the reactants, TS’s leading to the meta products are preferred (by 0.7 kcal mol⁻¹) over the TS’s leading to the para products. The same energetic preference for the TS’s leading to the meta product, is found for the exo approach of the reactants. Similarly, the exothermicities (ΔErxn in
Table 2.2) of the reactions 8 through 19 show that the meta products are preferred, but only by about 0.2 to 0.7 kcal mol$^{-1}$, over the para products. The DA reactions of isoprene with phosphacetylene (reaction 22 and 23) also show that the activation barriers leading to the meta product are only preferred slightly (0.2 kcal mol$^{-1}$) than those leading to the para products. Also, the exothermicities of reactions 22 and 23 are almost the same. These isoprene reactions, 22 and 23, have activation barriers and exothermicities similar to that of butadiene reaction 21. As pointed out earlier, the presence of phosphorus in one of the reactants lowers the activation barrier as compared to that in the carbocyclic case, reaction 20.

The computed activation barriers and exothermicites of reactions 8 through 19 as well as 22 and 23, suggest that the experimentally observed regioselectivity of products cannot be accounted by the closed shell pericyclic mechanism (concerted [4+2] DA cycloaddition). Also, reactions 12 through 19 would not proceed unless small amount of catalyst is added. This provides a hint that another mechanism may be operative in such cases.

### 2.4.4 RADICAL CATION REACTIONS:

It is known that radical cation DA reactions generally have low activation barriers but nevertheless show high regio- and stereoselectivities[63]. The dissociation of ionized cyclohexene into the butadiene radical cation and ethene, by field ionization mass spectrometry[77, 78], found, in addition to the butadiene radical cation, other intermediates. These were generated by hydrogen scrambling, proposed to result from successive 1,3 allylic rearrangements. Hofmann and Schaefer investigated the reaction pathways connecting ethene and butadiene radical cation theoretically[64]. A stepwise addition involving an ion-molecule complex was involved and the reaction was predicted to have a low activation barrier, only 6.3
kcal mol\(^{-1}\). In addition, these authors investigated pathways different addition of the butadiene radical cation to ethene leading to the DA product\[64\].

\[\text{chart 2.1}\]
Figure 2.6. Optimized geometries (at UB3LYP/6-311+G**) of various stationary points and transition structures for the radical cation reaction of isoprene$^+$ with phosphaethene leading to the DA radical cation products.
We have investigated the radical cation pathway of phosphaethene with isoprene leading to the DA products, Chart 2.1. The geometries of all the intermediates and the TS’s are displayed in Figure 2.6. For all the reactions (24 through 27) our computations show that the highly reactive isoprene radical cation reacts with phosphaethene, without a barrier, to give a gauche-out intermediate (all attempts to locate a TS, leading to the gauche-out intermediate, at UHF/6-31G* and at UB3LYP/6-31G* failed). This intermediate passes over a barrier, TS (rotation around the C-P bond), to give a gauche-in intermediate. The later intermediate then goes over another TS finally to give a DA cyclized radical cation product. As shown in Chart 2.1, the formation of first intermediates, int1, from isoprene radical cation and phosphaethene, are very exothermic for all the reactions (24 through 27). Similarly, for all these reactions the evolution of the DA-like radical cation products from the second intermediates, int2, are also very exothermic, Chart 2.1. Note that all the energies in Chart 2.1 are relative to isoprene radical cation and phosphaethene.

Reactions 26 and 27, in Chart 2.1, have high barriers, ~5.5 kcal mol\(^{-1}\) and ~7.1 kcal mol\(^{-1}\), for the formation of the int2-in from int1-out as compared to that for reaction 25, 0.2 kcal mol\(^{-1}\). Also, for reaction 24, the barriers for the formation of the int2 and of radical cation product, 0.7 and 3.8 kcal mol\(^{-1}\), are relatively higher than that needed for reaction 25, 0.2 and 3.4 kcal mol\(^{-1}\). Thus reaction 25, leading to meta-endo radical-cation product, has negligible barriers along the reaction course and hence is the preferred pathway.

As evident from Chart 2.1 and Figure 2.6, the formation of int2 from int1 involves the rotation around the C-P bond: surprisingly for the exo approach of the reactants, this barrier, TS\(_1\), is higher. To investigate the origin of this high barrier, viz 5.5 kcal mol\(^{-1}\), we have computed the DA reaction of butadiene\(^{+}\) with phosphaethene, Chart2.2.
Chart 2.2

Reaction 28

Reaction 29

TS\textsubscript{3}-exo-in/out

TS\textsubscript{3}-endo-in/out

int\textsubscript{3}-endo-out

int\textsubscript{3}-exo-out

TS\textsubscript{3}-exo-in/out

TS\textsubscript{3}-endo-in/out

int\textsubscript{3}-endo-out

int\textsubscript{3}-exo-out

Chart 2.2
For the exo addition of the reactants, reaction 29 (the formation of the intermediate \textbf{int}_3-\textbf{exo-out}) is more exothermic, 3.5 kcal mol\(^{-1}\), than reaction 28 (\textbf{int}_3-\textbf{endo-out}). The population analysis (NPA), Chart 2.2, shows that charges in \textbf{int}_3-\textbf{exo-out} are more electronically delocalized and hence this intermediate is preferred over \textbf{int}_3-\textbf{endo-out}. However the barrier, 5.5 kcal mol\(^{-1}\), for reaction 29 (exo addition), to form \textbf{TS}_3, is higher than that for reaction 28, 0.9 kcal mol\(^{-1}\) in Chart 2.2. The population analysis on these TS’s shows that the \textbf{TS}_3-\textbf{endo-in/out} is preferred because the charge is more delocalized over this structure as compared to that over \textbf{TS}_3-\textbf{exo-in/out}. Hence the endothermicity is low for the formation of the former TS, \textbf{TS}_3-\textbf{endo-in/out}.

2.4.5 AROMATICITY OF THE CONCERTED TRANSITION STATES:

Jiao and Schleyer\cite{79} analyzed the aromaticity of pericyclic transition states systematically on the basis of geometric, energetic, and magnetic criteria. The aromatic transition structures exhibit exalted magnetic susceptibilities, magnetic susceptibility anisotropies, as well as abnormal \(^1\)H NMR chemical shifts.

Schleyer et al.\cite{60a} also developed a simple and effective criterion for determining aromaticity of different systems, the nucleus independent chemical shifts (NICS), which is the negative of the computed magnetic shieldings at or above the ring centers. NICS, as an indicator of aromaticity, agrees well with the energetic, geometric, and magnetic criteria, in many related systems and does not require increment systems or other reference molecules (although comparisons are helpful for interpretation) \cite{60c}. NICS also is effective for assessing the aromaticity of the individual rings in polycyclic systems\cite{80}. Cossio et al.\cite{81} extended the NICS criterion to the characterization of in-plane aromaticity of the transition states in 1,3-dipolar cycloadditions. NICS values have also been used to determine the aromaticity and
antiaromaticity of transition states[76, 82]. As shieldings arise from the contributions of the core and various bonding electrons as well as from the mobile electrons (ring currents), we have used dissected NICS (separation of total NICS into $\pi$, $\sigma$ and core electron components inherent in the IGLO localization method) to evaluate the delocalized electron contribution (aromaticity) to the total value[60b, 60c].

A common difficulty in the calculation of magnetic properties is that gauge invariance is not guaranteed i.e., the computational result may depend on the position of the molecule in the cartesian frame. To overcome this problem, Gauge-Independent Atomic Orbital (GIAO) and Individual Gauge for Localized Orbital (IGLO), methods are employed. Unlike GIAO (a method in which each atomic orbital has its own local gauge origin), IGLO (localized molecular orbitals associated with individual gauge origins) gives an interpretative framework based on contributions from each localized orbital e.g. lone pairs, core and the bonding electrons. Since, Kutzelnigg’s original IGLO program employed the Boys[83a] localization method (which represented double bonds by two equivalent $\tau$ (banana) orbitals), Pipek-Mezey localization, which provides $\pi$ and $\sigma$ separation[83b], was employed here.

However, all localization schemes necessarily are arbitrary in treating inherently delocalizated systems, like aromatic TS’s. The nature of the localized orbitals, given by the program, sometimes seems counterintuitive. But the localization scheme generally reflects shorter distances and higher electron densities.

For example: $\text{TS}_1$ in Figure 2.3 shows the localized structure of the synchronous TS for the cycloaddition of butadiene with ethene. The Pipek-Mezey localization of the six mobile electrons, shown by dotted lines, reflects greater electron density in the regions of the C1-C2, C3-C4 and C6-C5. This localized structure, $\text{TS}_1$, can be considered to be akin to a “resonance
hybrid” of the TS (Scheme 2.5). The cyclic six electron delocalization, \( \text{a} \), can be represented in terms of such “resonance hybrids” involving \( \text{b} \) and \( \text{c} \). The resonance hybrid weights of these competing structures can be evaluated by the NBO program[84]. One of the later pair, \( \text{c} \), is chosen by the Pipek-Mezey localization scheme because the C1-C2 and C5-C6 distances are shorter than the C2-C3 and C1-C6 distances. In the IGLO output, one can differentiate \( \sigma \) bonds from the mobile electrons (or \( \pi \) bonds) by analyzing the shielding tensors. Generally, \( \sigma \) bonds have small shielding tensors for in-plane, \( \sigma_{xx} \) and \( \sigma_{yy} \), and out of plane component, \( \sigma_{zz} \), whereas mobile electrons have large out of plane shielding tensor, \( \sigma_{zz} \) (and small \( \sigma_{xx} \) and \( \sigma_{yy} \)).

![Scheme 2.5](image)

Table 2.3 compares NICS values at the geometrical heavy-atom centers of the TS’s. NICS given by the GIAO and IGLO methods agree. \( \text{TS}_2 \) through \( \text{TS}_7 \) have large negative NICS (-16.8 to –17.2). The NICS values suggest strong ring currents in the TS’s. The NICS values for \( \text{TS}_2 \) through \( \text{TS}_7 \) are slightly reduced than that in the parent DA reaction \( \text{TS}_1 \). Additionally, the dissected NICS (Table 2.3) at the centers of \( \text{TS}_2 \) through \( \text{TS}_7 \) show diatropic contributions (from –11.8 to –13.4) from six mobile electrons. Thus the dissected NICS values also confirm the aromaticity of these TS’s. The contributions from the six mobile electrons in \( \text{TS}_2 \) through \( \text{TS}_7 \) are less than –20.7, for benzene and are also less than –14.0, for \( \text{TS}_1 \). This decrease in the six mobile electrons contributions indicates a smaller ring current than that in benzene.
Table 2.3. Computed magnetic susceptibility exaltations (Λ, cgs.ppm), GIAO-NICS(0) at the center of the TS and six mobile electron contributions to dissected NICS for the reactions between phosphaethene 1 and 1,3-dienes 2, 3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Λ</th>
<th>GIAO-NICS(0) (IGLO-NICS(0))</th>
<th>Mobile electron contribution to IGLO-NICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>-15.8</td>
<td>-8.0 (-8.8)</td>
<td>-20.7</td>
</tr>
<tr>
<td>1</td>
<td>-19.3</td>
<td>-18.5 (-19.4)</td>
<td>-14.0</td>
</tr>
<tr>
<td>2</td>
<td>-24.7</td>
<td>-17.0 (-18.0)</td>
<td>-12.5</td>
</tr>
<tr>
<td>3</td>
<td>-24.3</td>
<td>-16.8 (-17.7)</td>
<td>-13.0</td>
</tr>
<tr>
<td>4</td>
<td>-23.9</td>
<td>-17.2 (-18.0)</td>
<td>-12.8</td>
</tr>
<tr>
<td>5</td>
<td>-23.0</td>
<td>-16.8 (-17.7)</td>
<td>-12.7</td>
</tr>
<tr>
<td>6</td>
<td>-22.7</td>
<td>-17.0 (-17.7)</td>
<td>-13.4</td>
</tr>
<tr>
<td>7</td>
<td>-22.8</td>
<td>-17.0 (-17.7)</td>
<td>-13.1</td>
</tr>
</tbody>
</table>

The calculated $^1$H NMR chemical shifts of the reactants are in good agreement with the experimental values[85]. The changes observed in the NMR chemical shifts of the terminal protons of the diene along the reaction path are of particular interest[79c]. The outer protons on C1 and C4 (in TS$_2$ through TS$_7$) are only slightly downfield, 5.5 to 6.3 ppm, as compared to that in 1,3-butadiene, 5.2 ppm. However, the inner protons (of C$_1$ and C$_4$) in TS$_2$ through TS$_7$, 0.7 to 1.2 ppm, show large upfield shifts as compared to the reactants, 5.9 ppm (Figure 2.1 and Figure 2.3). The $^1$H NMR chemical shifts of these inner protons fall in the range expected for a non-aromatic ring in the products, Figure 2.2. On the other hand, the chemical shifts of the protons attached to C$_2$ and C$_3$ do not change much along the reaction path and in the products have values expected for vinylic protons. The proton attached to P experiences large changes in chemical shift along the reaction path and is also affected by the (exo and endo) approach of the two reactants. As expected, from its inner location, this δH is more upfield, about 0.7 to 0.8 ppm, in the transition state resulting from the endo approach but is in the range for protons bound to tri-coordinate phosphorus in the products. The inner proton attached to C$_6$, in TS$_2$ through TS$_7$, is also shifted upfield, 3.1 to 5.1 ppm, as compared to 8.7 ppm, in the phosphaethene. Thus all
“inner” protons on both, diene as well as dienophile, show pronounced chemical shifts due to electronic effects arising from delocalization.

Jiao and Schleyer[79a, 79c] also applied magnetic susceptibility exaltation criteria to demonstrate the cyclic delocalization in pericyclic TS’s. The calculated total magnetic susceptibility (including paramagnetic, diamagnetic and non-local contributions) for such TS’s is quite different from that of the reactants. This difference was taken to be the magnetic susceptibility exaltation of the TS’s. The magnetic susceptibility exaltations (ranging from -22.7 to –24.7 cgs ppm, Table 2.3) for TS₂ through TS₇ are higher than -19.3 cgs ppm, for TS₁, and are also higher than -15.8 cgs.ppm, for the benzene. Thus the magnetic susceptibility exaltation values of TS₂ through TS₇ also demonstrate the aromaticity of these TS’s.

2.5 CONCLUSIONS

The [2+4] cycloadditions of phosphaethene with 1,3-dienes occur via aromatic transition structures. The ¹H NMR chemical shifts, the magnetic susceptibility exaltations, and the NICS values at the center of these asynchronous TS’s show the presence of ring currents circulating along the molecular perimeters. Evaluations of the bond orders of all the TS’s (TS₁ and TS₂ through TS₇) as well as IRC suggest that TS’s resulting from DA reactions of phosphethene with butadiene and with isoprene are earlier than the TS₁ of the parent DA reaction. Hence the activation barriers for forming TS₂ through TS₇ of phosphethene-butadiene or isoprene, are much lower than that needed for forming the parent DA TS₁. However, the exothermicities of phosphethene cycloadditions with butadiene or with isoprene and the DA of butadiene with ethene are in the same range.
The computed regioselectivities of the products for reactions 4 through 7 (cycloaddition of phosphaethene with isoprene) are all quite low: the differences in the barriers leading to regioisomeric products are less than 0.4 kcal mol\(^{-1}\). Computational investigations of the DA reactions of isoprene with 2H-1,2,3-diazaphospholes, with 2-acetyl-2H-1,2,3-diazaphosphole, with 1,4,2-diazaphospholo[4,5-\(a\)]pyridine, and with phosphacetylene show that the regioisomeric, meta and para, products should be formed in roughly 2:1 ratios. In contrast, experimentalists failed to detect the para regioisomer (such conclusions were based on the presence of only one \(^{31}\)P NMR signal in the products) [23]. In addition, it was reported that the reaction could not proceed without adding catalysts.

A mechanistic alternative, computations on a step-wise addition of isoprene radical cation with phosphaethene, show that TS’s leading to meta-endo radical cation product have negligible barriers along the reaction course and hence would be the preferred pathway.

In conclusion, the computations of the activation barriers of the TS’s for the concerted DA reactions of isoprene with phosphaethene (reactions 4 through 7) and other dienophiles (reactions 8 through 23) do not account for the regioselectivity of the products observed experimentally in some reactions. High regioselectivities, e.g. of reactions 8 through 19, might result via a radical cation mechanism.

2.6 ACKNOWLEDGEMENTS

I sincerely thank Dr. Y. Yamaguchi and Dr. M. Manoharan for helpful discussions.


[58] The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from proton shieldings of TMS, 31.31 ppm.


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CHAPTER 3

HOW DO RING CURRENTS AFFECT THE $^1$H NMR CHEMICAL SHIFTS?*  

Conventional explanations of proton NMR chemical shifts need fundamental revisions. Ab initio (IGLO) analyses reveal that the downfield $\delta^1H$ of benzene is not due to deshielding ring current effects; the shielding is less than the $\pi$ contribution to vinyl $^1H$s. Enhanced deshielding CC influences are responsible for the more downfield $\delta^1H$s of the inner protons of naphthalene and anthracene. Double $\pi$ effects shield ethynyl Hs; there is no evidence for a special "ring current influence."
3.2 INTRODUCTION

The conventional explanation for the unusual downfield chemical shift of arene hydrogens needs a fundamental revision: arene hydrogens are NOT deshielded by the ring current effects. The conventional explanation is based on Pople’s ring current model[1] typically illustrated as in Figure 3.1a in almost all NMR monographs and organic textbooks, where the Hs are located in the deshielding region around benzene[2]. This scheme was based on the “Pauling-Lonsdale-London π model” and ignores other possible local contributions from the σ CH and CC bonds[3]. Musher’s suggestion[4] that local contributions, rather than ring currents, were responsible for the downfield ¹H shifts in aromatic hydrocarbons has been criticized[1c-e, 5] and supported[6,7].

McConnell’s equation[8] predicts the directional dependence of the NMR shielding tensors experienced by a nucleus in proximity to an anisotropic group. Evaluation of the sign of the shielding effect calculated by this equation gives rise to the familiar “shielding cone” depictions not only for benzene (Figure 3.1a) but also for other molecules[9] modeling functional groups (Figure 3.2a). Unfortunately, these depictions also result in incorrect predictions at variance with the shielding surfaces computed by ab initio and density functional methods[10].
Figure 3.1. Comparison of the conventional ring current model (B₀ and B' are the applied and induced magnetic fields respectively) with the shielding environment computed by the IGLO method. Red and green color dots represent magnetically shielded and deshielded points, respectively.

Figure 3.2a. Classical anisotropy (shielding (+) and deshielding (-)) cones for ethene and ethyne

Figure 3.2b. Computed shielding environments of (a) ethane (b) ethene and (c) ethyne
These modern computations[10] show (see Figure 3.1b) that the deshielding zone of benzene is weak in magnitude and begins farther away from the ring center than in Figure 3.1a. Schleyer et al.’s grid[10a] and Klod and Kleinpeter’s informative graphical representations[10b, 10d] of the shielding environments of various molecules showed that the deshielding zone in benzene starts near 3.5Å away from the center of the ring. Hence, the Hs fall into the shielding rather than into the deshielding cone. This paper analyses, in detail, the reasons for difference in the chemical shifts between arene and vinyl Hs. (Note that magnetic “shieldings” are absolute values and have the opposite sign convention than chemical “shifts”, which are measured experimentally relative to a chosen standard.)

A similar study was first reported by Fleischer, Kutzelnigg, Lazzeretti, and Mühlknkamp[7] in 1994. They employed the individual gauge for localized orbitals (IGLO) method[11] to study the ring current and local effects on the $^1$H NMR chemical shieldings of benzene and related olefins. The IGLO method dissects total shieldings into individual CC($\pi$), CC($\sigma$), CH, lone-pair, and core electron localized molecular orbital (LMO) contributions. After a complicated analysis, Kutzelnigg et al. concluded that ring currents are present in benzene but have “only a small effect on the $^1$H shift. So Musher is somehow right that a description of the magnetic properties of benzene is possible in terms of localized quantities.” These conclusions have been ignored until very recently[10]. Textbooks continue to repeat the conventional explanation.
3.3 THEORETICAL METHODS

All the structures from Table 3.1 were fully optimized at the B3LYP/6-311+G** DFT level using the GAUSSIAN 98 suite[12] of program. All the structures showed real vibrational frequencies at B3LYP/6-31G*. The dissection of the proton chemical shifts[58] into various localized molecular orbitals (LMO) components were evaluated using the deMon-Master NMR program[13], at SOS-DFPT level with the Perdew-Wang-91(PW91) exchange correlation functional and the IGLO-III TZ2P basis set (recommended options).

3.4 RESULTS AND DISCUSSION

The data in Table 3.1 documents the good agreement of the IGLO-computed[14] proton chemical shifts with the experimental[2, 15] values and provides the details of the LMO dissection. The contribution of the intrinsic CH bond itself to the H shielding is by far the largest. However, these contributions are almost the same in different hydrocarbon environments. The exceptions are acetylene and the 3-membered rings, evidently due to the influence of the essentially sp C-H bond hybridization. The very small core (carbon 1s) electron contributions can be ignored. Likewise, non-vicinal CHs have negligible shielding effects. Hence, variations in hydrogen chemical shifts are mainly due to differences in the CC(π) and the CC(σ) contributions.

Ethene and ethyne: Contrary to the usual depiction of completely different shielding environments of ethene and ethyne (Figure 3.2a), attributed to an alleged “ring current effect” in ethyne, the computed shielding environments (Figure 3.2b) show no qualitative differences
among ethane, ethane, and ethyne[10b]. There are no discernable “ring current” effects in ethyne nor any indication of the “shielding-deshielding” cones depicted in Figure 3.2a. The upfield hydrogen chemical shift in C2H2 is not due to the alleged special “diatropic ring current effects,” but primarily to normal $\pi$ shielding influences. The IGLO dissection, Table 3.1, reveals that the CC($\pi$) shielding of the Hs per $\pi$ bond is the same in ethene (2.6 ppm) and in ethyne (2.5 ppm for each of the two $\pi$-bonds). The total 5.0 ppm $\pi$ effect in ethyne is additive rather than enhanced as one would expect if special “ring currents” were operative.

Table 3.1. LMO Contributions, Evaluated at the PW91/IGLO-III//B3LYP/6-311+G** IGLO level, of Various LMO’s (CH(main), CC($\pi$), CC($\sigma$), CH$_{\text{other}}$ and Core) to the Total Proton Shieldings. $\delta_{\text{calc}}$ ($\delta_{\text{obs}}$), in ppm, are the Computed (Experimental) Chemical Shifts Relative$^{12}$ to TMS.

<table>
<thead>
<tr>
<th>ring</th>
<th>Total shielding</th>
<th>$\delta_{\text{calc}}$ ($\delta_{\text{obs}}$)</th>
<th>CH (main)</th>
<th>CC ($\pi$)</th>
<th>CC ($\sigma$)</th>
<th>CH$_{\text{other}}$</th>
<th>core</th>
</tr>
</thead>
<tbody>
<tr>
<td>H _ H _ H _ H</td>
<td>30.5</td>
<td>0.8 (0.88)</td>
<td>25.5</td>
<td>-</td>
<td>1.3</td>
<td>3.7</td>
<td>0.0</td>
</tr>
<tr>
<td>H _ H _ _ H</td>
<td>25.8</td>
<td>5.5 (5.84)</td>
<td>26.0</td>
<td>2.6</td>
<td>-1.9</td>
<td>-0.8</td>
<td>-0.1</td>
</tr>
<tr>
<td>H _ _ _ _ H</td>
<td>29.8</td>
<td>1.5 (2.88)</td>
<td>23.8</td>
<td>5.0</td>
<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>H _ _ _ _ _</td>
<td>20.9</td>
<td>10.4 (10.3)</td>
<td>23.1</td>
<td>1.6</td>
<td>-3.6</td>
<td>-0.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>=CH</td>
<td>24.1</td>
<td>7.2 (7.06)</td>
<td>24.5</td>
<td>2.5</td>
<td>-2.7</td>
<td>0.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>&gt;CH$_2$</td>
<td>30.4</td>
<td>0.9 (0.93)</td>
<td>26.0</td>
<td>-1.7</td>
<td>4.2</td>
<td>1.9</td>
<td>0.0</td>
</tr>
<tr>
<td>=CH</td>
<td>25.0</td>
<td>6.3 (6.03)</td>
<td>26.1</td>
<td>2.4</td>
<td>-3.4</td>
<td>0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>&gt;CH$_2$</td>
<td>28.7</td>
<td>2.6 (2.57)</td>
<td>25.4</td>
<td>-0.6</td>
<td>2.3</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>_ _ _</td>
<td>25.4</td>
<td>5.9 (5.76)$^b$</td>
<td>25.5</td>
<td>2.8</td>
<td>-2.9</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>H$_{\text{imr}}$</td>
<td>24.6</td>
<td>6.7 (6.36)</td>
<td>25.3</td>
<td>2.8</td>
<td>-3.5</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>=CH</td>
<td>25.3</td>
<td>6.0 (5.59)</td>
<td>26.2</td>
<td>2.9</td>
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</tr>
<tr>
<td></td>
<td>δ  (ppm)</td>
<td>J  (Hz)</td>
<td>δ  (ppm)</td>
<td>J  (Hz)</td>
<td>δ  (ppm)</td>
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<td>0.0</td>
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<td>-0.5</td>
<td>0.6</td>
<td>4.0</td>
<td>0.1</td>
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<tr>
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<td>-4.3</td>
<td>0.0</td>
<td>-0.2</td>
<td>Hα</td>
</tr>
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<td>8.4</td>
<td>25.7</td>
<td>-4.1</td>
<td>-0.1</td>
<td>-0.2</td>
<td>Hβ</td>
</tr>
<tr>
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<td>8.8</td>
<td>25.7</td>
<td>-4.8</td>
<td>0.2</td>
<td>-0.2</td>
<td>Hγ</td>
</tr>
<tr>
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<td>9.5</td>
<td>25.7</td>
<td>-4.3</td>
<td>-0.1</td>
<td>0.0</td>
<td>H1</td>
</tr>
<tr>
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<td>9.6</td>
<td>25.8</td>
<td>-4.2</td>
<td>-0.2</td>
<td>-0.1</td>
<td>H2</td>
</tr>
<tr>
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<td>-5.8</td>
<td>25.1</td>
<td>4.7</td>
<td>2.6</td>
<td>4.7</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

*Enhanced by geminal CH effects.*

*Based on δ 7.27 for benzene and the experimentally[15b] observed difference of 1.51 ppm between CBD and benzene in a clathrate.*
Benzene: Statements like “the downfield chemical shift of the arene protons (δ~7.3) relative to those of vinylic protons (cyclohexene δ~5.6) is because arene protons lie in the deshielding zone (Figure 3.1a)” are incorrect[2b, 2c, 16]. Figure 3.1b shows the arene protons to lie in the shielding rather than the deshielding zone! The CC(π) bonds shield the benzene Hs by +1.9 ppm (Table 3.1).

Why then are the benzene protons deshielded (by 1.7 ppm, experimental) relative to the vinyl protons in cyclohexene? Comparison of the data for both hydrocarbons in Table 3.1 reveals that small differences in all the CC(σ) and the C-H contributions together account for only about half of the total deshielding. The other half is due to the 1.0 ppm decrease in the π-bond shielding of benzene (1.9 ppm) relative to cyclohexene (2.9 ppm).

Toluene: Note that the methyl Hs in toluene do lie in the deshielding ring current zone of benzene. However, the paratropic CC(π) contribution, -0.5 ppm (Table 3.1), to the total methyl hydrogen shielding is small.

Naphthalene and anthracene: The proton chemical shifts of polycyclic arenes often vary in systematic ways. Thus, the benzene (δ 1H 7.3) and the outer β-protons of naphthalene and anthracene (both δ 1H 7.3) resonate at ca. 0.5 ppm higher fields than the inner α-protons (Table 3.1). The γ-Hs on the central ring of anthracene (δ 1H 8.3) are deshielded even more. Although Blustin[6] rationalized these trends by employing Musher’s localized model[4], Haigh and Mallion[17] showed that the chemical shifts predicted by the traditional ring current model also agree with experimental values. According to the currently accepted explanation, paratropic ring current contributions from adjacent rings help deshield the α-protons in naphthalene and anthracene and the Hγs to a greater extent in the latter[1d].
As in benzene, the CC(\(\pi\)) contributions in Table 3.1 shield all the naphthalene and anthracene Hs. While the shielding is 0.2-0.3 less for H_\(\alpha\) and 0.5 ppm less for H_\(\gamma\) than for H_\(\beta\), larger differences, 0.7 and 1.2 ppm, respectively, are found in the deshielding CC(\(\sigma\)) contributions. A more detailed analysis shows that the larger CC(\(\sigma\)) differences depend on the number of non-adjacent CC bonds; there are two for H_\(\beta\)s, three for H_\(\alpha\)s, and four for H_\(\gamma\)s. Hence, \(\sigma\) rather than \(\pi\) effects are primarily responsible for the \(\delta\) \(^1\)H variations in these acene systems.

![Dissected CC(\(\pi\)) shielding grids](image)

Figure 3.3. Dissected CC(\(\pi\)) shielding grids (evaluated from the IGLO output) of acetylene, benzene, cyclobutadiene, and \textit{trans}-dihydropyrene. Red and green dots represent magnetically shielded and deshielded points, respectively. Note that all the Hs are shielded by the \(\pi\) effect.

\textit{trans}-Dihydropyrenes: The [14]\(\pi\)-electron \textit{trans}-dihydropyrenes, 15,16-dihydropyrene and 15,16-dimethylidihydropyrene[18] are employed as probes to study ring current effects
experimentally[19]. The downfield-shifted perimeter protons are believed to lie in the deshielding zone while those associated with the inner carbons lie in the shielding zone and are shifted to high fields. As Table 3.1 reveals, all the protons of trans-dimethylidihydropyrene, outer as well as inner, are in the ring current shielding zone (note the CC(π) contributions in Table 3.1). Hence the shielding-deshielding cone also is farther away from the center[16] of these annulenes than has been supposed. While the CC(σ) deshielding of all the outer protons (H1, H2, H3) is almost the same, the CC(π) shielding of H1 is ~1 ppm larger than H2 and H3.

The ring currents influence on the inner protons of trans-dihydropyrene[18] and on the methyl protons (HCH3) in trans-dimethylidihydropyrene, which are near the aromatic ring center, are much more pronounced. Both H4 [18] and CH3 are strongly shielded, not only by the CC(π) but also by the CC(σ) and the CHother contributions (Table 3.1).

Cyclopropene and the cyclopropenium ion: The three-membered rings in Table 3.1 exhibit unusually deshielded proton chemical shifts, δ 10.3 for the cyclopropenium cation and δ 7.06 for the =C-Hs of cyclopropene (i.e., in the “aromatic region”). However, the π-contributions are shielding in both cases. The observed deshielding arises from the paratropic CC(σ) contributions and the lower inherent main CH bond shieldings. The latter effect evidently is due, as in ethyne, to the essentially sp hybridization of the CH bonding.

Cyclobutadiene and benzocyclobutadiene: Contrary to the expectation that the paramagnetic ring currents of anti-aromatic compounds[20] should shield the cyclobutadiene (CBD) protons, these δ Hs are not found upfield. Instead they appear in the vinyl H regions because the paratropic contributions from the π-bonds at the ring center in CBD are close to zero[10a, 16]. The experimentally measured[15b] upfield proton chemical shift of CBD relative to benzene in a clathrate, 1.51 ppm, is in agreement with the computed difference, 1.6 ppm
(Table 3.1). Moreover, the computed proton chemical shifts for CBD, $\delta$ 5.9, is close to $\delta$ 5.38, measured[21] for the tri-$t$-butyl-cyclobutadiene ring H. The slight upfield shift of the CBD Hs is due to increase in the $\pi$-bond shielding (2.8 ppm) relative to that in cyclobutene (2.4 ppm). Note that the total $\text{CC}(\sigma)$, $\text{CH}_{\text{other}}$, and intrinsic CH contribution in both these cases are almost the same.

The greater downfield chemical shift of benzocyclobutadiene protons (H 4MR) relative to those of CBD is attributed (Table 3.1) to the larger paratropic contributions from the $\sigma$ C-C bonds. Also note that the total $\text{CC}(\pi)$, $\text{CH}_{\text{other}}$, and core contribution are nearly the same for both these hydrocarbons.

### 3.5 CONCLUSIONS

We conclude that the deshielding cone of benzene actually begins farther away (at over 3 Å) from the ring center[10a, 10b] than the Johnson-Bovey prediction[9]. Consequently, the protons are shielded and not “deshielded” by the $\pi$ ring current. However, this diatropic effect is 1.0 ppm less than the $\pi$ shielding of the vinyl protons of cyclohexene by the C=C double bond. Small differences in the CH and CC(s) shielding also contribute to the $\delta^1H$ of benzene. Likewise, the protons of cyclobutene and CBD are also in the shielding zone; the higher field chemical shift of the CBD Hs is due to the increase in $\pi$ bond shielding relative to cyclobutene. Although arene proton chemical shifts have long served as a major criterion of aromaticity, the findings in this paper and the related literature[10] undermine at least part of the theoretical basis for this connection.
No direct relationship between external arene H chemical shifts and other magnetic, geometric, and energetic aromaticity criteria is apparent from the data in Table 3.1. Neither the NICS(1) of benzene (-10.6) [22], naphthalene (-10.8), and anthracene (-9.9 outer rings, -13.1 inner ring) nor the HOMA values[22] parallel the proton shifts. The ASE/electron for naphthalene and anthracene are not larger than benzene, but the Hs are farther downfield. The ASE/electron of the trans-dimethyldihydropyrene [14]annulene perimeter is less than benzene, but the H shifts are farther downfield. Likewise, the outer H chemical shifts of [18]annulene (δ = 9.2) [15a] are among the most deshielded of any aromatic hydrocarbon, but the ASE/e is much less[23] than benzene's.

3.6 ACKNOWLEDGEMENTS

I would like to thank Ned H. Martin, Rainer Herges, and Thomas Heine as well as S. Klod and E. Kleinpeter for helpful discussions. The University of Georgia and the National Science Foundation Grant CHE-0209857 provided financial support.

3.7 REFERENCES


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[16] For a comparison of CC(π) shielding grids of benzene, acetylene, cyclobutadiene, and trans-dihydropyrene, see Figure 3.3.


[18] A detailed IGLO analysis of 15,16-dihydropyrene was given in the SI of published manuscript and compiled in Table 3.1 of this chapter.


CHAPTER 4

ON THE STABILITY OF [4n]ANNULENES*

4.1 ABSTRACT

The stabilization energies (B3LYP/6-31G*) of planar \([4n]\)annulenes, evaluated by a new indene-isoisindene isomerization method, reveal that all \(4n\) \(\pi\)-electron rings larger than the energetically unfavorable cyclobutadiene are only slightly destabilized by the \(\pi\)-electron interactions. Cyclooctatetraene prefers the "tub" conformation because of strain effects. Generally, the antiaromatic character of the larger systems with \(4n\) \(\pi\) electrons is revealed best by their magnetic properties, rather than their energies.
4.2 INTRODUCTION

Originally, [4n]annulenes, the unfavorable counterparts of the stabilized [4n+2]π electron aromatics, were described as being pseudoaromatic[1], i.e., they were expected to lack special conjugative stabilization and to resemble polyenes. In a pioneering series of investigations, Breslow provided convincing evidence that π electron interactions destabilize small 4π electron systems like the cyclopropenyl anion, cyclobutadiene (CBD) and the cyclopentadienyl cation. He coined the term “antiaromatic” to describe [4n] systems generally[2]. However, in his 1973 account[3], Breslow conceded that “there is no strong evidence yet for conjugative destabilization in the [larger] 4n systems relative to normal compounds” although [4n] are clearly less stable than [4n+2] systems. Wiberg’s authoritative review of antiaromaticity in 2001 concluded, “when the ring size becomes larger, the antiaromatic character is decreased and is smaller even with cyclooctatetraene”[4]. Due to the ring strain complications associated with the larger [4n]annulenes, Wiberg was unable to evaluate their π energy contributions. We have overcome this problem in the present paper and show that except for CBD, the larger [4n] π-electron systems are only slightly destabilized.

The first uniform evaluations of the energies of [n]annulenes of increasing size were carried out in the early days of organic electronic structure theory using Hückel theory and its subsequent refinements[5]. The “resonance energy per electron” (REPE) of Dewar[5b], employed extensively by Hess and Schaad (HS) [5c], is representative. Their results indicate the aromaticity of benzene to be very high, while that of the larger [4n+2]annulenes decreases steadily. Conversely, the antiaromatic character of the larger [4n]annulenes is predicted by their REPEs to become less and less negative from the high cyclobutadiene value. This work
contributed to the firmly embedded popular view that planar antiaromatic systems are destabilized.

However, evidence[6] to the contrary, particularly dealing with cyclooctatetraene (COT), has existed for a long time. The strongly twisted double bond conformations of the most stable tub form (D$_{2d}$) preclude $\pi$ interactions. Planar COT is known to prefer D$_{4h}$ symmetry with alternating single and double bonds. Since the D$_{4h}$ form is expected to be “antiaromatic,” the D$_{2d}$–D$_{4h}$ energy difference, gives an upper bound to the antiaromatic destabilization energy. This is known from NMR measurements on COT derivatives to be about 10 kcal/mol[7], a value that can very well be reproduced by DFT computations on C$_8$H$_8$ itself.[8] However, at least part of this ca. 10 kcal/mol difference is due to the increase in the strain energy in going from tub to the planar form.

The COT strain energy has been computed by molecular mechanics, which do not take the electronic repulsions inherent in the antiaromaticity concepts, into account. Based on MM2, MM3, and MM4 results, Allinger and co-workers concluded that the ca. 10 kcal/mol COT inversion barrier is due almost completely to strain rather than to electronic effects[9]. Our present MM4 re-examination gives a 0.9 kcal/mol D$_{4h}$ COT destabilization energy.

4.3 METHODS

All the structures were fully optimized at B3LYP/6-31G* DFT level using the Gaussian 98 package[10]. The magnetic susceptibilities were computed by the CSGT method at B3LYP/6-31+G*// B3LYP/6-31G*[11]. NICS(0), NICS(0)$_n$, and the proton chemical shifts were evaluated
using the deMon-Master NMR program, at SOS-DFPT level with the Perdew-Wang-91(PW91)
exchange correlation functional and the IGLO-III TZ2P basis set (recommended options).[12]

We have applied the recently introduced Schleyer and Pühlhofer (SP) isomerization
stabilization energy (ISE) method[13], but with the appropriate corrections, to investigate the
REs of [4n]annulenes, equation 4.1 and Scheme 4.1. The data, computed at B3LYP/6-31G*+ZPE on assumed planar structures, indicate destabilizations of less than 1 kcal/mol for
COT and small destabilizations also for [12]-, [16]-, [20]-, and [24]annulenes, Scheme 4.1. The
small destabilization of planar COT is in complete agreement with the existing thermodynamic
conclusions.[6, 9]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_3
\end{align*}
\]

Equation 4.1

We now introduce a new “indene (a)-isoindene (b)” ASE (aromatic stabilization energy)
evaluation method, illustrated by equation 4.2, which employs fused five membered ring
appendages. This approach (designated ISE$_{II}$) is homodesmotic and has the advantage that all
carbons in the [n]annulene moiety are sp$^2$ hybridized in both isomers.
Scheme 4.1. $ISE_{SP}$ computed by Schleyer-Pühlhofer procedure at B3LYP/6-31G*+ZPE. Planar geometries were employed to evaluate $ISE_{SP}$. Energies given in kcal/mol.
However, like $\text{ISE}_{\text{sp}}$, $\text{ISE}_{\text{II}}$ requires the application of syn-anti corrections.[13, 14] These arise because s-cis (syn) butadiene conformations are considerably less stable than the s-trans (anti) forms.[13] Note that isoindene (b) has two more anti conformations (which needs corrections)[15] than indene (a), but the syn-anti relationships in the [12]-, [16]-, and [20] annulene counterparts (Scheme 4.2) are just the reverse. Syn-anti corrections in both the $\text{ISE}_{\text{II}}$ and $\text{ISE}_{\text{sp}}$[16] methods also may be evaluated, as shown in equation 4.3 for [12]annulene, by employing the dihydro derivatives of the fused bicyclic annulene and its non-aromatic isomer as conjugated reference species. Such corrections have been applied to the $\text{ISE}_{\text{II}}$ data[17] in Table 4.1 and in Scheme 4.2.

The benzene $\text{ISE}_{\text{II}}$, computed at B3LYP/6-31G* + ZPE by equation 4.2 is 29.0 kcal/mol, nearly the same as obtained from experimental data.[18] The benzene $\text{ISE}_{\text{sp}}$ from equation 4.1 is
somewhat larger, but both exceed Dewar-de Llano resonance energy of 17 kcal/mol considerably. This Dewar-de Llano RE does not include the syn-anti corrections.

Scheme 4.2. Comparison of $\text{ISE}_{\text{SP}}$, $\text{ISE}_{\text{II}}$ (uncorrected), and $\text{ISE}_{\text{II}}$ (corrected) (kcal/mol) at B3LYP/6-31G* + ZPE. All the energies are reported in kcal/mol. Planar geometries were employed.
4.4 RESULTS AND DISCUSSION

4.4.1 GEOMETRIES

The [4n]annulene geometries and energies were evaluated by imposing planarity in order to maximize the $\pi$ interactions. While all the larger [4n]annulenes have non-planar minima, the planar restriction is not unrealistic.[6] All the [4n]annulenes favor bond-alternating geometries at B3LYP/6-31G*, Figure 4.1. The difference in lengths between the longest and shortest bonds ($\Delta r$, see Table 4.1 and Figure 4.1) provides a geometric aromaticity index. This may be compared to the computed 0.078 Å single-double bond difference in the interior of long chain conjugated polyenes. With the exception of COT ($\Delta r$ 0.130 Å), there is a regular decrease from the large $\Delta r$ of cyclobutadiene (0.243 Å) to 0.087 Å for [24]annulene, Figure 4.1.

4.4.2 ENERGIES

The [4n]annulene ISE$_{sp}$'s, computed by the SP method with corrections (Table 4.1 and Scheme 4.1 and 4.2), agree very well with the ISE$_{II}$ (corrected) results. As we concluded earlier,[19] Dewar’s $\pi$-approximation largely underestimates the REs for [4n+2]annulenes. Examples are his unrealistically low 2.8 kcal/mol RE for [18]annulene,[5c, 20, 21] and his prediction that the RE of large aromatic annulenes should decrease to 2.8 kcal/mol. We confirmed Choi and Kertesz’s finding[21b] that these energies approach a much higher constant value.
Table 4.1. The Difference Between Shortest and Longest [4n]Annulene Bond Length (Δr), Hess-Schaad Resonance Energies per π-Electron (REPE), Syn-Anti Corrected Isomerization Stabilization Energies (kcal/mol) Evaluated by the Schleyer- Pühlhofer Method (ISE_{Spcorr}, Scheme 4.1) and the Indene- Isoindene approach (ISE_{Iicorr}, Scheme 4.2), Magnetic Susceptibility Exaltations (Λ, cgs. ppm), as well as Averaged Inner (δ H_{inner}) and Outer (δ H_{Outer}) ^1H NMR Chemical Shifts of the Antiaromatic [4n]annulenes in Planar Bond Alternating Geometries.

<table>
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<tr>
<th></th>
<th>Δr</th>
<th>REPE</th>
<th>ISE_{Spcorr}</th>
<th>ISE_{Iicorr}</th>
<th>Λ</th>
<th>NICS</th>
<th>NICS</th>
<th>δ H_{inner}</th>
<th>δ H_{Outer}</th>
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<td>-3.1</td>
<td>-407.3</td>
<td>19.3</td>
<td>18.1</td>
<td>33.0</td>
<td>-1.9</td>
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</tbody>
</table>

REPE in units of β are taken from reference 5c. ISE_{Spcorr} and ISE_{Iicorr} evaluated at B3LYP/6-31G*+ ZPE (B3LYP/6-31G*) + syn-anti corrections. Λ = χ_M - χ'_M. Magnetic susceptibilities of parent [4n]annulenes, χ_M, at CSGT-B3LYP/6-31+G*//; magnetic susceptibilities of nonaromatic models, χ'_M, evaluated using increments (see reference 22). NICS(0), NICS(0)\_\alpha, H_{outer}, and H_{inner} at IGLO/TZ2P//B3LYP/6-31G*.^a Taken from reference 13. ^b Syn-anti correction of 7.2 kcal/mol made to ISE_{Iicorr}. ^c Taken from reference 19.
The negative REPEs derived from application of the Dewar reference within the framework of the Hückel method,[5d] as noted above, indicate all [4n]annulenes to be
destabilized (Table 4.1 and Figure 4.2, which include benzene). The large [4n]annulenes also are destabilized, but only to a small extent. Both ISEs exhibit progressions to more positive values with increasing ring size. In accord with the earlier molecular mechanics[9] and ab initio investigations,[22] but in disagreement with the large REPE destabilization, planar D$_{4h}$ COT, perhaps the best studied [4n]annulene, is only destabilized minimally. At least part of the disagreement between the REPE and ISE methods is due to the different choice of reference structures. The REPE method, being based on Hückel $\pi$ energies, uses linear polyenes and does not take syn and anti energy differences into account. These energy differences are an essential component of the ISE method; therefore, the idealized reference structures proposed by Dewar are not employed.

![Figure 4.2](image-url)

**Figure 4.2.** ISE per $\pi$-electron (ISEPE) of the [n]annulenes computed by the Schleyer-Pühlhofer (ISE$_{SP}$) and by the indene-isoiindene (ISE$_{II}$) methods compared with scaled REPEs.

Contrary to Breslow’s antiaromaticity definition that “a cyclic conjugated system has its $\pi$ electron energy higher than that of a suitable reference compound which is not cyclically
delocalized,”[2] we find that the [4n]annulenes, with the exception of CBD, are not destabilized appreciably.

4.4.3 MAGNETIC PROPERTIES

In contrast to the energies, more sensitive measures of [n]annulene aromaticity or antiaromaticity are provided by the magnetic criteria (Λ,[23] 1H NMR chemical shifts, as well as NICS[24] and its dissection). These properties are influenced directly by the special ring current effects attributable to cyclic π-electron conjugation. Like our aromatic annulene results,[19] we now find the magnetic properties of [4n]annulenes to be more sensitive than the energies.

Although the magnetic susceptibility exaltation, Λ, for only a few [4n]annulenes are known experimentally,[23a] Λ is closely associated with aromaticity. The computed[25] Λ of D₄h COT is large and negative (-79.4 cgs. ppm, Table 4.1). The data in Table 4.1 show an increase in Λ from [8]- to [24]annulene. However, recall that Λ for cyclic conjugated systems depend on the square of the ring area.[19] Nevertheless, the negative [24]annulene Λ indicates unfavorable cyclic π-electron interactions and antiaromaticity in [4n]annulenes.

The computed proton chemical shifts, also summarized in Table 4.1, are extremely sensitive to the geometries and to the cyclic π-electron currents. In contrast to the large antiaromatic destabilization of CBD, its protons (δ 5.9) appear[26] in the olefinic region. COT (δ 2.0) and the outer Hs of [12]-, [16]-, [20]-, and [24]annulene are displaced upfield (δ -1.9 to +2.8) while the inner protons are strongly deshielded (downfield) (δ ~33). The computed downfield chemical shifts of the inner Hs and the upfield chemical shifts of the outer Hs, indicate strong paratropic ring currents in [4n]annulenes and the expected “antiaromatic” behavior.
Understandably, the NICS\textsuperscript{[27]} in the ring centers and above mirror the behavior of the chemical shifts of the inner protons. The [4n]annulenes NICS(0) are large and positive due to the strong induced paratropic ring currents arising from cyclic $\pi$-electron interaction. D\textsubscript{4h} COT shows the largest NICS(0) value in the [4n]annulenes set, Table 4.1. NICS(0) decreases, but only slightly, with increasing ring size. Similar to the $\Lambda$ data, the large positive NICS(0) values indicate strong paratropic ring currents in [4n]annulenes, Table 4.1. Since NICS(0) include both $\sigma$ and $\pi$ contributions, dissected NICS values\textsuperscript{[24b]} are more instructive in assigning the paratropic $\pi$-bond contributions. The CBD NICS(0)$_{\pi}$ value (-0.2) is exceptional in showing no net $\pi$ contributions.\textsuperscript{[24c]} The other [4n]annulenes have large and positive $\pi$ contributions. Like NICS(0), NICS(0)$_{\pi}$ also is largest at the center of D\textsubscript{4h} COT, but the NICS(0)$_{\pi}$ values of the other [4n]annulenes are nearly the same.

4.5 CONCLUSIONS

In conclusion, SPs ISE procedure gives reliable and consistent data for [4n]annulenes if appropriate corrections are applied. The reliability of SPs method also is confirmed by the close agreement with the newly introduced ISE\textsubscript{II} (indene-isoindene) approach, which is fully homodesmotic.

The [4n]annulene antiaromaticity criteria give somewhat inconsistent results. CBD is exceptional in having a uniquely large destabilization energy and negative $\Lambda$, but exhibiting olefinic proton chemical shifts and a near zero NICS(0)$_{\pi}$ value. D\textsubscript{4h} COT has a near zero stabilization energy, but also the largest NICS(0) and NICS(0)$_{\pi}$ values. Otherwise, there are regular progressions in the degree of bond alternation with ring size, but no notable differences
in the remaining properties listed in Table 4.1.

Remarkably, the destabilizing effects in larger [4n] systems are insignificant. This finding undermines definitions of antiaromaticity based on energy for systems with more than 4 π electrons. The degree of bond alternation of the antiaromatics is larger than for conjugated olefins. While ISE does not reveal significant antiaromatic behavior for COT and the larger [4n]annulenes, the computed proton chemical shifts, \( \Lambda \), and NICS reveal strong paratropic ring currents in these larger [4n]annulenes.

Consequently, the [4n]annulene aromaticity indices can be regarded as statistically multidimensional.[28] The best antiaromaticity indicators appear to be the proton chemical shifts and the closely related NICS, rather than energies. For example, planar \( D_{4h} \) COT is non-aromatic energetically, but exhibits an upfield proton chemical shift (\( \delta 2.0 \)) and a positive NICS indicating antiaromaticity. Similar antiaromatic behavior also is shown by the larger [4n]annulenes. The term “antiaromaticity,” applied to [4n]annulenes with \( n>1 \), is better based on magnetic behavior, rather than energetic destabilization.

4.6 ACKNOWLEDGEMENTS

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4.7 REFERENCES


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(i) The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from the proton shieldings of TMS, 31.31 ppm.


[14] The correction evaluations to $ISE_{sp}$ and $ISE_{II}$ were applied by similar equations as depicted in equation 4.3.

[15] When fused to an arene, the cyclopentene moiety is taken by our convention to have a syn conformation irrespective of the Kekulé form of the aromatic ring.

[16] (a) Syn-anti corrections for SP’s ISE method were evaluated as the energy difference between the dihydrogen derivative of methyl-[4n]annulene and their respective non-aromatic isomer.

[17] All energies refer to forced C₃ geometries optimized at B3LYP/6-31G* using Gaussian 98. Zero point energies computed at B3LYP/6-31G* were applied.


[25] Evaluations ($\Lambda = \chi_M - \chi'_M$) are based on the difference between the magnetic susceptibilities of an antiaromatic compound ($\chi_M$) and their closely related non-aromatic model ($\chi'_M$). $\chi'_M$ was based on increment scheme, which is based on magnetic susceptibilities of ethylene and butadiene. The $\mathrm{CH}_2=$ and $=\mathrm{CH}-$ increments are $-7.3$ and $-5.1$ cgs.ppm, respectively.


[27] The negative value of absolute magnetic shieldings calculated at revealing points (generally center of the ring) in [n]annulene system.

[28] Such conclusions also were made from a study of aromatic systems comprising of 105 compounds. For e.g. see Cyrański, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* 2002, 67, 1333.
CHAPTER 5

HOW AROMATIC ARE LARGE (4n+2)π ANNULENES?*

4.1 ABSTRACT

While the total aromatic stabilization energies (ASE) of the [n]annulenes, C₆H₆ to C₆₆H₆₆, converge to ca 22 kcal/mol, the ASE’s per $\pi$ electron decrease markedly. Bond length alternation (which depends on the theoretical level) only reduces stabilization somewhat, but influences the magnetic properties (NICS, proton chemical shifts, and magnetic susceptibilities) considerably. Nevertheless, these magnetic criteria, when based on the most realistic structures, agree that the aromaticities of the larger annulenes decrease and then nearly vanish.
The theory of bonding in cyclic fully conjugated polyenes (annulenes),[1] first developed by Hückel[2] and later refined by Longuet-Higgins and Salem[3] as well as by Coulson and Dixon,[4] predicts “delocalized” structures (highly symmetrical) for the smaller aromatic [n]annulenes but “localized” structures with bond alternating geometries for higher homologs. Shaik and his associates have developed the view that the \( \pi \) interactions in benzene favor bond alternation, but the \( \sigma \)-framework imposes \( D_{6h} \) symmetry.[5] Kuhn,[6] Dewar[7] and others,[8] proposed that bond length alternation in higher \((4n+2)\pi\)-electron annulenes should set in beyond a certain size.[9] However, the critical value of “n”, where the bond alternating [n]annulene geometries become more stable than the more symmetrical alternatives, has still not been established with certainty, either experimentally or computationally.[10] The theoretical results depend strongly on the method employed. Hartree-Fock levels favor bond-alternating geometries for all annulenes other than benzene. Methods including electron correlation favor more symmetrical geometries, but, as exemplified by two systematic studies, the results vary considerably. Using the semi-empirical MNDOC method Yoshizawa found [30]annulene to prefer a bond alternating \( D_{3h} \) geometry over the \( D_{6h} \) structure by 4.6 kcal/mol.[11] However, Choi and Kertsez (CK) reported that this energy difference was only 0.1 kcal/mol at B3LYP/6-31G*.[12] Bond alternating forms generally became progressively more stable in higher [n]annulenes (for example, \( n=42, 54, \) and 66). Recently, Kiran et al. demonstrated that symmetrically-placed methylene bridges result in delocalized \( D_{6h} \) over \( D_{3h} \) structure for [30]- and [42]annulene but such modified [56]- and [66]annulenes still favor bond alternating geometries.[13]
Resonance energies (RE), evaluated from experimental or theoretical data, were the first quantitative measures of aromaticity. While the early estimate (36 kcal/mol) of the aromatic stabilization energy (ASE) of benzene, [6]annulene, is not far from the 32.2 kcal/mol, value we now favor, such energetic evaluations are more difficult for higher annulenes.

Dewar estimated a very small RE for [18]annulene (only 2.9 kcal/mol) based on PMO theory. An “experimental value” based on an energy comparison with benzene, gave 100 kcal/mol! In sharp contrast, both Siegel and Baldridge as well as CK reported RE ca. 18 kcal/mol, evaluated by comparing [18]annulene with hexatriene and butadiene. However, this procedure is unsatisfactory since the reference molecules do not mimic the HH repulsions and other strain effects in the constricted annulene geometry. Employing the energies of molecular fragments based on the optimized geometries of [18]annulenes, CK derived a significantly higher ASE, 39.1 kcal/mol, but considered this value to be suspect. However, the same fragment method appeared to give reliable results for the larger, less strained annulenes. On this basis, CK concluded that ASE’s of larger annulenes approached a constant value near 23 kcal/mol. This contradicts Dewar’s prediction that large annulenes (n ≥ 30) should have very small RE’s. CK also reported NICS for the [14]-, [18]-, [22]-, [26]-, [30]-, [42]-, [54]-, and [66]annulenes. We now extend their study by comparing the energies as well as the magnetic properties of both bond alternating and bond equalized structures of the same set of annulenes.

Our computations of the magnetic susceptibility exaltations, Λ, the 1H NMR chemical shifts of the inner and outer protons, as well as NICS and its dissection, employed both the bond alternating Hartree-Fock and the more regular geometries (obtained by B3LYP optimization or by imposing higher symmetry constraints). The isomerization stabilization energy (ISE) method was used to evaluate the ASE’s at three different levels. The HF/6-
31G*//HF/6-31G* and the B3LYP/6-31G*/B3LYP/6-31G* data are given in Scheme 5.1. These levels are designated HF//HF and B3LYP//B3LYP subsequently in text and HF//HF and B3//B3 in Table 5.1. We also employed the more localized HF geometries for single point ISE evaluations (B3LYP/6-31G*///HF/6-31G*; designated B3LYP//HF in text and referred as B3//HF in Table 5.1); the results are compared with the fully optimized B3LYP//B3LYP data in Table 5.1. The same ISE equations were used to evaluate the annulenes Λ’s.

4.3 COMPUTATIONAL METHODS

All the [n]annulene structures were optimized at the B3LYP/6-31G* DFT level using the Gaussian 98 package[23]. Energies were evaluated at B3LYP/6-31G*+ ZPE (at the same level). Magnetic susceptibilities were computed by the CSGT-B3LYP /6-31+G*/// for n≤30 and at CSGT-B3LYP /6-31G*/// for n>30.[24] NICS(0), NICS(π), and the inner and outer proton chemical shifts were evaluated using the deMon-Master NMR program, at SOS-DFPT level with the Perdew-Wang-91(PW91) exchange correlation functional and the IGLO-III TZ2P basis set for n≤30 [25] and at GIAO-B3LYP/6-31G* for n>30.[26]

4.4 RESULTS AND DISCUSSION

4.4.1 GEOMETRIES AND ENERGIES

All the [n]annulenes (n≥10) favor bond-alternating structures at the HF//HF level (Table 5.1). In contrast, lower energy bond-alternating minima are found only for the higher [n]annulenes (n≥30) at B3LYP//B3LYP.[27] In these annulenes, the D_{6h} forms were obtained by imposing
symmetry. The geometries of few representative \([4n+2]\pi\) annulenes are given in Figure 5.1.

Notably, these \(D_{6h}\) forms were only 0.26 \([n=30]\) to 6.1 kcal/mol \([n=66]\) higher in energy than the \(D_{3h}\) minima (\(E_{rel}\), Table 5.1). In contrast, the B3LYP//HF single point relative energies (Table 5.1) increased steadily from 2.92 \([n=10]\) to 28.33 kcal/mol \([n=66]\). However, this increase was not due solely to the decrease in resonance energy in bond-localized geometries. Geometrical parameters at HF are not optimum for B3LYP energy evaluations.

The ISE evaluations are more instructive. The ISE’s of many of the annulenes at HF//HF (Scheme 5.1) and of all the annulenes at B3LYP//HF (Table 5.1) are only slightly smaller than those evaluated at B3LYP//B3LYP. The deviations, the ISE data at HF//HF, start at \([n=10]\), but then become progressively smaller as \(n\) increases (Scheme 5.1). Notably, the ISE’s of large annulenes approach plateaus of 18 (HF//HF) and 22 kcal/mol (B3LYP//B3LYP) (Scheme 5.1). Note that these plateaus, which match CK’s.[12a] are much larger than Dewar’s predicted ca. 2.8 kcal/mol. However, the \(ISE\) per \(\pi\)-electron, a more important measure of aromaticity of such different systems, decreases markedly with increasing annulene ring size (Figure 5.2).
Figure 5.1. (continued on next page).
Figure 5.1. B3LYP/6-31G* and HF/6-31G* (in parenthesis) of some of the representative [4n+2]π annulenes. All the bond lengths are in Å.

Note that the ISE-based stabilizations (Scheme 5.1, Table 5.1) at the HF//HF level are almost as large as those at B3LYP//B3LYP, despite the different preferences for bond alternating geometries, \([n>6]\) at HF//HF and \([n\geq30]\) at B3LYP//B3LYP. Consequently, “bond localization” in these B3LYP optimized large annulenes does not result in a major loss of stabilization energy. The same conclusion has been reached for benzene, after imposition of Kekulé cyclohexatriene geometries (Table 5.1).[20a, 20b, 28]
Table 5.1. Relative energies ($E_{\text{rel}}$, kcal/mol), total NICS(0) and dissected $\pi$-contributions (at the ring centers), magnetic susceptibility exaltations ($\Lambda$, cgs.ppm), as well as averaged inner and outer $^1$H NMR chemical shifts of the [n]annulenes. Values in parentheses are the isomerization stabilization energies (ISE, kcal/mol) and magnetic susceptibility exaltations ($\Lambda$, cgs.ppm), evaluated using the [n]annulene derivatives in Scheme 5.1.

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$^a$ $\Lambda=\chi_m^\infty - \chi_M$. Magnetic susceptibilities of aromatic annulenes, $\chi_M$, at CSGT-B3LYP/6-31+G*// (for $n \leq 30$) and at CSGT-B3LYP/6-31G*// (for $n > 30$); magnetic susceptibilities of non-aromatic annulenes, $\chi_M$ evaluated by using increments (see footnote 31). $^b$ $\Lambda$ based on Scheme 5.1 at CSGT-B3LYP/6-31+G*// for $n \leq 30$ and at CSGT-B3LYP/6-31G* for $n > 30$. $^c$ With fixed 1.449 and 1.350 Å CC lengths.
Scheme 5.1. ISE and $\text{ISE}_{\text{HF}}$ (in kcal/mol, ZPE corrected) at B3LYP/6-31G*/B3LYP/6-31G* and HF/6-31G*/HF/6-31G* energies, respectively. $C_s$ geometries were used.
The computed B3LYP ISE’s of [18]annulene, 27.4 kcal/mol on the more regular //B3LYP structures and 21.9 kcal/mol on the //HF geometries (Table 5.1), lie between CK’s two ASE estimates, 16.4 and 39.1 kcal/mol. Although our B3LYP//B3LYP ISE’s for [42]-, [54]-, and [66]annulene (22.9, 22.5 and 22.4 kcal/mol, Table 5.1) are in remarkably good agreement with the B3LYP CK values (23.2, 22.6 and 23.1 kcal/mol respectively. However, CK’s procedure, when applied to the HF//HF data, gives ASE values that are in gross disagreement with our ISE’s. Because of the close relationship of the structures involved, the ISE method deals with strained molecules more effectively.[16, 22]

Figure 5.2. ISE per π-electron, computed using Scheme 5.1, (at B3LYP//B3LYP) versus the ring size for annulenes.

4.4.2 Magnetic Properties.
Arguably, magnetic criteria (Λ, ¹H NMR chemical shifts,[29] as well as NICS and its dissection into π-contributions) provide the best measures of aromaticity since they are based directly on the special “ring current” effects due to cyclic electron delocalization. The magnetic properties
are influenced by the geometries much more than the energies. Dramatic differences are to be found in Table 5.1.

Magnetic susceptibility exaltations, $\Lambda$, are well established to be closely associated with aromaticity.[21] Evaluations ($\Lambda = \chi_M - \chi'_M$) are based on the bulk magnetic susceptibilities of an annulene ($\chi_M$) and its non-aromatic model ($\chi'_M$). The remarkable agreement of annulene $\Lambda$ values computed by the equations of Scheme 5.1 (values in parentheses in Table 5.1) as well as $\Lambda$'s using increments[30] validate the use of the ISE equations for $\Lambda$ estimations. The $\Lambda$'s (Table 5.1) for B3LYP optimized annulenes generally are very large. But this does not mean that, e.g. [66]annulene with $\Lambda$=-760.3 cgs.ppm, is much more aromatic than benzene, $\Lambda$=-15.8 cgs.ppm. The ring current contribution to the total $\chi$ of a cyclic compound is proportional to the product of the square of the ring area ($\theta^2$) and ASE; $\chi \sim \theta^2$ ASE.[1a, 31] Due to the greater ring area as well as to the cyclic electron delocalization, $\Lambda$'s for the large B3LYP optimized annulenes are much larger than those for the small annulenes. The expected relationship is demonstrated by Figure 5.3, but only for [n≤30]annulenes, where $\Lambda$ is proportional to the product of $\theta^2$ and ISE.[32] The curve shown then falls off for D$_{3h}$ [42]-, [54]-, and [66]annulene. However, the much larger $\Lambda$'s for their D$_{6h}$ forms (-10,127.6 for [66]annulene!) continue the initial trend in Figure 5.3.

The computed proton chemical shifts also are quite sensitive to the geometry. As is well known, the $\delta^1$H's of the inner and the outer protons in annulenes can differ dramatically (Table 5.1) from those of normal alkenes ($\delta$=5.6 for cyclohexene). The outer H's are downfield (also from those of benzene, $\delta$= 7.2) whereas the inner H's are upfield, evidently due to the strong diatropic ring currents in these annulenes. The $\delta^1$H's computed on the most symmetrical B3LYP geometries (Table 5.1) show steady increases to very large negative ($H_{inner}$) and positive ($H_{outer}$) values, but these are far away from the experimental $\delta^1$H's.
The behavior of the computed $\delta_1^1\text{H}$’s using the bond localized HF-optimized annulene geometries is quite different. The inner-outer $\delta_1^1\text{H}$ difference is largest for \([n=10]\)) but then decreases with increasing ring size, slowly at first and then rapidly to the vanishing point. There is no $\delta_1^1\text{H}$ difference between the olefin-like outer and the inner proton chemical shifts for \([54]-\)and \([66]\)annulene using the $D_{3h}$ HF geometries. The less bond length-alternating B3LYP-optimized $D_{3h}$ \([n>30]\)annulene geometries result in intermediate behavior: the inner-outer $\delta_1^1\text{H}$ differences decrease steadily with ring size.

Note that the computed $^1\text{H}$ NMR chemical shifts of \([18]\)annulene, both for the outer ($\delta=11.8$) and especially the inner ($\delta=-11.2$) protons, are in gross disagreement with the latest experimental values, $\delta 9.2$ and -2.96.[33] As pointed out by CK, such discrepancies also are found for the B3LYP-optimized larger annulenes. The $//HF$ geometries give computed proton chemical shifts data, e.g., $\delta 8.8$ and -1.6 for $D_{3h}$ \([18]\)annulene, which is in much closer agreement.
with experiment, Table 5.1.[10] Consequently, the proton chemical shifts computed for [18]annulene using the //B3LYP geometry grossly disagree with the experimental values.

The NICS values (Table 5.1) also depend markedly on the geometry for \([n>10]\). Understandably, NICS(0) in the annulene centers (as well as its dissected \(\pi\) contribution, NICS(\(\pi\))) mirrors the behavior of the inner proton chemical shifts: the magnitudes are largest for the \(D_{6h}\) geometries, smaller for the //B3LYP \(D_{3h}\) minima, and smallest to negligible for the //HF geometries.

NICS often correlates well with energies (as well as with geometries and with other magnetic criteria); general agreement is found here.[20b, 34] The negative NICS(0) and NICS(\(\pi\)) values (Table 5.1) indicate that the highest symmetry (bond equalized) annulene geometries are all aromatic. NICS(0) reaches a constant value of about \(-17\) which appears to mirror the ISE leveling (Table 5.1). However, neither the NICS(0) values for the HF-optimized nor for the \(D_{3h}\) B3LYP minima agree. These values decrease rather rapidly with increasing size, sooner along the HF than the B3LYP series. This follows the ISE/electron behavior of Figure 5.2 and also is evident from \(\Lambda\) and the \(^1\)H chemical shifts. However, the \(\Lambda\), ISE and the \(^1\)H NMR chemical shift, but NOT NICS(0) predict that the B3LYP-optimized \(D_{3h}\) “bond alternating” structure of [66]annulene retains “significant aromatic character.” Although the HF-optimized “bond alternating” [54]- and [66]-annulenes have large ISE’s, the \(\Lambda\)’s, \(^1\)H NMR chemical shift differences, and NICS (Table 5.1) are very small; evidently these annulenes behave more like cyclized long chain polyenes.
4.5 CONCLUSIONS

Despite the divergence in the data at different levels and geometries, we conclude that the best interpretations of all the criteria investigated agree in revealing the major trends along the [n]annulene series. Structurally, the trend towards greater bond alternation follows the increases in ring size. The onset of bond alternation occurs at \([n=10]\) at HF/6-31G* but at \([n=30]\) at B3LYP/6-31G*. However, there is a evidence that the latter DFT level may favor the higher symmetry annulene structures excessively.[35] The ISE method gives consistent and evidently reliable energies, particularly for the strained systems where other ASE evaluations are problematical. The ISE per \(\pi\)-electron decreases to very small values with increasing ring size (Figure 5.2). The \(\Lambda\), NICS and the \(^1\)H NMR chemical shifts depend markedly on the annulene geometries, but the more realistic lower-symmetry structures also follow the trend to smaller aromaticity. The HF \(D_{3h}\) forms of the largest annulenes show non-aromatic \(\delta\) \(^1\)H behavior; also, their ISE/electron, \(\Lambda\), and NICS values are quite small.

The ISE differences, based on bond equalized (B3LYP) and bond localized (HF) optimized structures, are small. In contrast, the magnetic criteria are very sensitive to the geometries. Neither B3LYP nor HF geometries give computed proton chemical shift in agreement with experiment. We intend, in future, to employ this sensitivity, along with experimental data comparisons, to establish the reliability of structures computed at various theoretical levels.
4.6 ACKNOWLEDGEMENTS

We thank Norman L. Allinger for helpful discussions. The University of Georgia and National Science Foundation Grant CHE-0209857 provided financial support.

4.7 REFERENCES


We will address this problem in the subsequent chapter. See reference 11 and 12 for recent discussions.


[22] The ISE method\(^\text{16}\) compares the computed energy of a methyl derivative of a given aromatic system with its structurally closely related non-aromatic exocyclic methylene isomer. See Scheme 5.1.


(i) The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from the proton shieldings of TMS, 31.31 ppm.

[26] (a) Wolinski, K.; Hilton, J. F.; Pulay, P. J. Am. Chem. Soc. 1990, 112, 8251. (b) The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from the proton shieldings of TMS, 31.98 ppm.

[27] At B3LYP//B3LYP a slight C-C bond alternation, 0.04Å, sets in at [30]annulene.


[29] Dissected NICS and $^1$H NMR chemical shift computed using the deMon NMR program, which employs the Pipek-Mezey $\sigma, \pi$ localization.

[30] Our increment scheme was based on magnetic susceptibilities of ethylene and butadiene. The CH$_2$= and =CH- increments are −7.3 and −5.1 cgs.ppm, respectively.


[32] The approximate ring areas were evaluated by dividing the annulene into triangular, rectangular, and trapezoidal subunits.


CHAPTER 6

[18]ANNULENE HAS ALTERNATING, RATHER THAN EQUALIZED CC BOND LENGTHS

The widely accepted (X-ray and theoretical B3LYP and MP2) D\textsubscript{6h} CC bond length-equalized structure of [18]annulene cannot be correct. The X-ray geometry used to compute the proton NMR chemical shifts by the highly accurate GIAO/B3LYP/6-311+G** method gives inner \( \delta_{1H} \) and outer \( \delta_{1H} \) hydrogen's in gross disagreement with the experimental values of -3.0 and 9.3, respectively. The higher symmetry [14]- and [22]annulene structures can be ruled out similarly. The hydrogen chemical shifts, particularly of the inner H’s, are highly sensitive to small changes in geometry. Lower symmetry, single bond-double bond alternating structures of these three annulenes, computed to be the most stable forms with the KMLYP and BHandHLYP density functionals, result in \( \delta_{1H} \)’s agreeing within 0.7 ppm of the experimental values. It is shown that the X-ray crystallographic data can be reconciled with the computed C\textsubscript{2} [18]annulene minimum by assuming a 50:50 superposition or a rapid dynamic equilibrium in the solid state. The preference for bond-alternating structures (\( \Delta r_{cc} = 0.1 \) Å) begins quite early along the 4n+2 Hückel \( \pi \) electron series, at [14]annulene. Bond alternation does not eliminate aromaticity. The descriptive terms, “delocalized” and “localized,” used to designate CC bond length equalized and alternating geometries, are misleading and should be abandoned.
[18]Annulene (C₁₈H₁₈) is the critical signpost[1] along the 4n+2 π electron Hückel[2] route from benzene to the larger aromatic (CH)ₖ rings. For over four decades, [18]annulene has been assigned the same essential six-fold symmetry as benzene: “the bonds do not alternate in length.”[1] However, geometries with nearly equal C-C bond lengths are not expected for the still larger [4n+2]annulenes. Since the aromatic stabilization energy per carbon decreases with increasing size[3, 4], very large annulenes should approach the behavior of polyolefins. This was first predicted[5] in 1959 by Longuet-Higgins and Salem, who guessed that C-C bond length-alternation might begin with [30]annulene. Indeed, this result was obtained at the DFT-B3LYP and MP2 theoretical levels in the comprehensive annulene survey of Choi and Kertesz (CK) in 1998.[4] In contrast, we show here that this crossover point occurs much earlier, at [14]annulene, which, along with [18]annulene, has alternating rather than equalized CC bond lengths.

As stressed by Shaik, Hiberty, et al.,[6] the σ-framework of aromatic compounds favors regular geometries, but the π components favor localization in double bonds due to greater overlap of adjacent p orbitals. There are two competing tendencies. The preference for pair-wise interactions when CC distances are shorter competes with the gain in aromatic stabilization energy when the CC separations are equalized, but longer. However, the gain in the aromatic stabilization energy is the weaker of these two π effects: cyclic electron delocalization is not eliminated, but only reduced slightly by bond alternation[3]. Thus, benzene, rather than being the aromatic prototype in this sense, is the exception! Benzene favors the highly symmetric D₆h structure[7] solely due to its σ-skeleton.[6] Naphthalene and virtually all other polybenzenoid hydrocarbons exhibit appreciable CC bond length differences. In the larger annulenes, the
preference for a bond alternating or a higher symmetry structure will depend on Shaik-Hiberty’s “fine balance of σ-resistance and π distortivity.” Hence, it is important to establish the point in the annulene progression at which the σ-skeleton ceases to be the dominating influence and is replaced by the inherent predilection for double bond localization.

The structure of [18]annulene, the most extensively investigated higher Hückel monocycle, is of critical importance in this context. But the seemingly secure and currently accepted experimental and theoretical conclusion that [18]annulene (C_{18}H_{18}) has a D_{6h} structure cannot be correct! Like benzene, [18]annulene belongs to the [4n+2]aromatic subgroup with 6(2p+1) π electrons (where “p” is an integer), which permits the highly symmetrical D_{6h} point group. However, the chemistry of C_{18}H_{18} differs markedly than that of benzene: [18]annulene undergoes reactions typical of localized π-systems. The 1965 X-ray structure determination at 80 K favored D_{6h} symmetry with somewhat different (but not alternating) 1.382 and 1.419 Å lengths for the 12 inner and the six outer C-C bonds, respectively. The 1995 X-ray reinvestigation at 111 K revealed some disorder in the [18]annulene crystal but gave CC lengths of 1.385 and 1.405 Å and confirmed the essential D_{6h} symmetry. Electron correlated MP2 and B3LYP computations reproduced the X-ray structure well and supported the experimental conclusions that C_{18}H_{18} has a “highly delocalized D_{6h} structure.” Other indirect evidence based on IR, UV-visible, fluorescence and photoelectron spectroscopy also was consistent with a D_{6h} structure. However, data from such methods are not sensitive to geometry changes. In sharp contrast, the proton chemical shifts respond markedly even to slight variations in structure.

Bühl and Schleyer (BS) established and validated the use of ab initio/GIAO/NMR methods for structural determinations. Based on the comparison of experimental and
computed chemical shifts for a large number of boranes, carboranes, and non-classical carbocation systems, BS found excellent agreement between the experimental and computed chemical shifts only when the geometries were correct,[13] and revealed many errors in experimental structures. The $^1$H NMR chemical shifts of many arenes computed by GIAO-B3LYP/6-311+G** are generally within 0.2 to 0.5 ppm of the experimental values.[14] Hence, accurate structures of [n]annulenes may be established by comparing computed with experimental chemical shifts. Excellent agreement is expected only when the geometries are correct. Our results using this procedure demonstrate that [18]annulene cannot have a D$_{6h}$ structure. The evidence is decisive: the computed proton chemical shifts using the X-ray geometry[15] are in gross disagreement with those measured[8d, 16] experimentally. CK noted[4] that the proton chemical shifts for all the higher aromatic annulenes, computed using the B3LYP/6-31G* geometries, were far from the available experimental NMR data, stating “the origin of this discrepancy is not clear.” Our explanation is simple: neither the X-ray nor the B3LYP geometries are correct.

6.3 COMPUTATIONAL METHODS

All the [n]annulene structures were fully optimized both using regular as well as the imposed higher symmetry geometry at the B3LYP/6-311+G**, KMLYP/6-311+G**,[17] and BHandHLYP/6-311+G** DFT level using the Gaussian 98 package.[18] Energies were evaluated at B3LYP/6-311+G**. The frequencies were computed at the respective DFT level with the 6-311+G** basis set; the ground state structures, transition states and higher order saddle point structures were confirmed by the presence of imaginary (or real) vibrational
frequencies. Single point energies of D$_{6h}$ and C$_2$ [18]annulene structures were computed using CCSD augmented by a perturbative treatment of triple excitations, CCSD(T),[19] with the DZP(C)+DZ(H) (fc) and the DZ (fc) basis sets using the local version of the ACESII program[20]. The $^1$H NMR chemical shifts were computed at GIAO-B3LYP/6-311+G**// using the DFT/6-311+G** geometry.[21] The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from the proton shieldings of TMS, 31.98 ppm.

6.4 RESULTS AND DISCUSSION

6.4.1 [18]ANNULENE:
The $^1$H NMR chemical shifts computed using the lowest energy B3LYP D$_{6h}$ [18]annulene geometry (–11.0 inner and 11.5 outer H’s; Figure 6.1 and Table 6.1), deviate impossibly far from the experimental values[16], –3.0 and 9.3, respectively. The same is true of the D$_{6h}$–imposed geometries, optimized at the BHLYP and KMLYP DFT levels we favor. Moreover, the D$_{6h}$ structure is a transition state, rather than a minimum, at BHLYP and KMLYP. These results exclude the “highly delocalized” D$_{6h}$ structure for the [18]annulene.

At the KMLYP and BHLYP levels, lower symmetry (D$_{3h}$, D$_3$, and C$_2$) [18]annulene structures are more stable than D$_{6h}$, but C$_2$ is the only minimum (Table 6.1). Although the computed $\delta$H’s of the outer protons of D$_{3h}$ and D$_3$ structures are acceptable compared with experiment (Table 6.1), the chemical shifts of inner protons of the D$_3$ ($\delta$H$_{\text{inner}}$ = –4) and D$_{3h}$ ($\delta$H$_{\text{inner}}$ = –5) structures differ by 1 and 2 ppm. In contrast, the bond length alternating C$_2$ KMLYP and BHLYP minima give[22] outer and inner proton chemical shifts (8.9 and -2.5 KMLYP; 9.2 and -2.8 BHLYP, Figure 6.1) remarkably close to the experimental data, 9.3 and -3.0.
Table 6.1. Theoretical results for the [18] annulene, Figure 6.1. The 6-311+G** basis set was used throughout. PG is the point group. $\Delta r$ (in Å) is the difference between the shortest and the longest C-C bond length. $E_{\text{rel}}$ is the relative energy (in kcal/mol) with respect to the energetically most stable structure, at various levels of theory. $\nu$ gives the imaginary or the smallest real vibrational frequency. $\delta H_{\text{inner}}$ and $\delta H_{\text{outer}}$ are the GIAO $^1$H chemical shifts, in ppm, evaluated relative to TMS.

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<td>$D_3$</td>
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<td>0.4</td>
<td>$23.7i, 22.6i$</td>
<td>-4.3 to -4.6</td>
<td>9.5 to 9.7</td>
<td></td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.100</td>
<td>0.0</td>
<td>74.0</td>
<td>-2.7 to -2.9</td>
<td>8.9 to 9.4</td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td>0.042</td>
<td>0.0</td>
<td>74.0</td>
<td>-2.7 to -2.9</td>
<td>8.9 to 9.4</td>
<td></td>
</tr>
</tbody>
</table>

In addition to this NMR evidence, $C_2$ [18]annulene is appreciably lower in energy than the $D_{6h}$ form at KMLYP and BHLYP as well as at MPW1PW91 (Table 6.2). The same is true at the current cutting edge of theory: single point energy comparisons using the highly correlated CCSD(T) method (with the DZP(C)+DZ(H) and DZ basis sets) also predict the $C_2$ form to be more stable than the $D_{6h}$ structure. The different energy ordering at B3LYP and at MP2 (Table 6.2) is suspect: Schaefer and coworkers[23] have stressed that these methods “overestimate the delocalization.” While the KMLYP and BHLYP energy differences between the $C_2$ and the $D_3$ and $D_{3h}$ geometries are small (Table 6.1), the $D_3$ and $D_{3h}$ forms are higher order saddle points rather than minima. $D_{6h}$ [18]annulene is a transition structure, rather than a minimum. The eigenvectors of the sizable imaginary frequencies, $1218i$ at KMLYP and $1073i$ cm$^{-1}$ at BHLYP (Table 6.1), indicate the strong preference for C-C bond alternation. Hence, we conclude that
[18]annulene prefers a bond alternating C$_2$ (or closely related) geometry over the currently accepted bond equalized D$_{6h}$ (or slightly non-planar) structure.[8b, 16]

Figure 6.1. Optimized geometry and chemical shifts (bold) of [18] annulene. The high symmetry structure on the left were optimized at B3LYP/6-311+G** (the figures in parenthesis are the X-ray data) and the corresponding lower symmetry structures on right at KMLYP/6-311+G** and BHLYP/6-311+G** (in parenthesis). The experimental NMR values of the inner and outer protons are –2.99 and 9.3, respectively.

According to Gorter et al.[9b], the X-ray diameters excluded the possibility of an alternative bond alternating D$_{3h}$ structure for [18]annulene because a 50:50 inversion disorder model (based on an early[24] HF/6-31G* geometry) had “calculated ring diameters up to 0.20Å too large” (Table 6.3). In contradiction, the data in Table 6.3 demonstrate that the 50:50 inversion disorder C$_2$ (or D$_{3h}$) model of [18]annulene cannot be excluded, since the computed major and minor ring diameters for the C$_2$, D$_{3h}$, as well as the D$_{6h}$ structures have deviations less than 0.06 Å from the experimental values. Furthermore, the 50:50 C$_2$ [18]annulene superposition shown in Figure 6.2 also yields an averaged “D$_{6h}$ structure” with internal (1.379Å) and external (1.392Å) CC bond lengths close to the reputed X-ray distances[9b], 1.385 and 1.405 Å,
respectively. Consequently we believe that the X-ray evidence cannot exclude 1:1 inversion disorder for a bond alternating C₂ (or D₆h) [18]annulene structure.[7]

Table 6.2. Single point energy C₂ vs. D₆h [18]annulene energy differences, E_{rel}, in kcal/mol. Positive values of E_{rel} indicate that the C₂ structure is more stable whereas negative E_{rel}'s signify the greater stability of D₆h.

<table>
<thead>
<tr>
<th>Level</th>
<th>C₂</th>
<th>D₆h</th>
<th>E_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/6-311+G**//KMLYP/6-311+G**</td>
<td>-692.11092</td>
<td>-692.07832</td>
<td>20.45</td>
</tr>
<tr>
<td>KMLYP/6-311+G**//KMLYP/6-311+G**</td>
<td>-695.38249</td>
<td>-695.37735</td>
<td>3.22</td>
</tr>
<tr>
<td>CCSD(T)/DZP(C)+DZ(H)(fc)//KMLYP/6-311+G**</td>
<td>-694.47008</td>
<td>-694.46674</td>
<td>2.10</td>
</tr>
<tr>
<td>CCSD(T)/DZ(fcc)//KMLYP/6-311+G**</td>
<td>-693.44243</td>
<td>-693.43812</td>
<td>2.70</td>
</tr>
<tr>
<td>B3LYP/6-311+G**//KMLYP/6-311+G**</td>
<td>-696.34217</td>
<td>-696.33821</td>
<td>2.49</td>
</tr>
<tr>
<td>MPW1PW91/6-311+G**//KMLYP/6-311+G**</td>
<td>-696.61875</td>
<td>-696.61819</td>
<td>0.35</td>
</tr>
<tr>
<td>B3LYP/6-311+G**//KMLYP/6-311+G**</td>
<td>-696.80933</td>
<td>-696.81557</td>
<td>-3.91</td>
</tr>
<tr>
<td>BLYP/6-311+G**//KMLYP/6-311+G**</td>
<td>-696.48006</td>
<td>-696.49043</td>
<td>-6.51</td>
</tr>
<tr>
<td>BP86/6-311G*//KMLYP/6-311+G**</td>
<td>-696.78056</td>
<td>-696.79173</td>
<td>-7.00</td>
</tr>
<tr>
<td>MP2/6-31G*//KMLYP/6-311+G**</td>
<td>-694.23195</td>
<td>-694.29035</td>
<td>-15.06</td>
</tr>
</tbody>
</table>

Dynamic disorder is a further complication. D₆h [18]annulene is a transition state joining the two C₂ structures with an interconversion barrier of only ca. 3 kcal/mol at KMLYP and BHLYP (2.1 kcal/mol at our highest CCSD(T) level, Table 6.2). Hence, the symmetrization of [18]annulene takes place rapidly even at 111 K (the 1995 X-ray investigation temperature). This may result in a time averaged D₆h structure and, at least, compromises the interpretation of the experimental data. Haddon[10] also pointed out that “unfortunately the X-ray study cannot be regarded as definitive in the present case” since the “C-C distances are averaged over time and over a large number of unit cells by the diffraction process.”

Although the agreement between the experimental[1] and computed[11a] IR spectra (BLYP/6-311G*) for D₆h [18]annulene was said to lend “further support to the delocalized structure,” not only the D₆h, but also the D₃h, D₃, and particularly the C₂ optimized [18]annulene
structures all give computed IR frequencies in the same range. Unlike the NMR data, the low-resolution experimental IR spectrum does not permit differentiation among the geometrical alternatives. The same insensitivity characterizes other spectroscopic methods which have been applied to [18]annulene.[12]

Table 6.3. Comparison of C–C major and minor bond distances (in Å) across the ring for the X-ray [18]annulene structure with those computed at different levels of theory.

<table>
<thead>
<tr>
<th>C–C distances across the ring</th>
<th>Deviations from X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minor</td>
</tr>
<tr>
<td>X-ray</td>
<td>D₆h</td>
</tr>
<tr>
<td>//HF/6-31G*</td>
<td>D₆h</td>
</tr>
<tr>
<td>//B3LYP/6-311+G**</td>
<td>D₆h</td>
</tr>
<tr>
<td>//KMLYP/6-311+G**</td>
<td>D₆h</td>
</tr>
<tr>
<td>1:1 Distortion models:</td>
<td></td>
</tr>
<tr>
<td>//HF/6-31G*</td>
<td>D₃h</td>
</tr>
<tr>
<td>//KMLYP/6-311+G**</td>
<td>D₃h</td>
</tr>
<tr>
<td>//KMLYP/6-311+G**</td>
<td>C₂</td>
</tr>
<tr>
<td>//BHLYP/6-311+G**</td>
<td>C₂</td>
</tr>
</tbody>
</table>

Figure 6.2. 1:1 Inversion disorder (superposition) of KMLYP and BHLYP optimized C₂ [18]annulene. The figures in parentheses are the corresponding BHLYP geometries while those in bold are the 1995 X-ray data measured at 111 K.
6.4.2 [14]Annulene:

Although the highest possible symmetry of [14]annulene is \( D_{2h} \), this lower homolog of \( C_{18}H_{18} \) suffers from more severe non-bonding repulsions among the intra-annular hydrogens. These are ameliorated in non-planar geometries. The X-ray structure determination\([25]\) at 283–303 K found \( C_{2h} \) symmetry and moderate C-C bond alternation (\( \Delta r = R_{\text{single}} - R_{\text{double}} = 0.057 \AA \), the same as the perimeter of naphthalene). However, the \(^1\text{H} \) NMR chemical shifts of the inner hydrogens (\( \delta H_{\text{inner}} = -5.4 \) to \(-7.0 \)) computed using the X-ray geometry\([15]\) are far away from the measured 0.0 ppm value\([8d]\). Hence, the experimental structure of [14]annulene also requires revision.

![Figure 6.3. Optimized geometry and chemical shifts (bold) of [14]annulene. The high symmetry structures on the left were optimized at B3LYP/6-311+G** (the figures in parenthesis are the X-ray data) and the corresponding lower symmetry structures on right at KMLYP/6-311+G** and BHLYP/6-311+G** (in parenthesis). The experimental NMR values of inner and outer protons are 0.0 and 7.6, respectively.](image)

All the DFT energies (Table 6.4) find the \( C_{2h} \) form to be slightly more stable (2.5 kcal/mol) than the \( D_2 \). However, the local \( C_{2h} \) B3LYP/6-311+G** minimum also gives computed proton chemical shifts far away from the experimental values. The \( C_{2h} \) form is a transition state at both BHLYP and KMLYP; the single imaginary frequency (> 600i cm\(^{-1}\)) leads to the most stable
The computed $^1$H NMR chemical shifts of the C$_s$ inner ($\delta$= 0.0 to –0.4) and outer ($\delta$= 7.4 to 8.1) protons are in spectacular agreement with experiment, Table 6.4. Note that the substantial ($\Delta r = 0.10$ Å) C-C bond alternation in the optimized C$_s$ structure (Table 6.4 and Figure 6.3) is nearly twice as large as the X-ray finding. We conclude that the currently accepted delocalized C$_{2h}$ structure of [14]annulene is not correct; instead, a bond length alternating C$_s$ geometry is favored.

Table 6.4. Theoretical results for the [14] annulene, Figure 6.3. The 6-311+G** basis set was used throughout. PG is the point group. $\Delta r$ (in Å) is the difference between the shortest and the longest C-C bond length. $E_{\text{rel}}$ is the relative energy (in kcal/mol) with respect to the energetically most stable structure, at various levels of theory. $\nu$ gives the imaginary or the smallest real vibrational frequency. $\delta H_{\text{inner}}$ and $\delta H_{\text{outer}}$ are the GIAO $^1$H chemical shifts, in ppm, evaluated relative to TMS.

<table>
<thead>
<tr>
<th>PG</th>
<th>Level</th>
<th>$\Delta r$</th>
<th>$E_{\text{rel}}$</th>
<th>$\nu$</th>
<th>$\delta H_{\text{inner}}$</th>
<th>$\delta H_{\text{outer}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$</td>
<td>B3LYP</td>
<td>0.015</td>
<td>2.6</td>
<td>102.7</td>
<td>-6.7</td>
<td>9.0 to 9.7</td>
</tr>
<tr>
<td>C$_{2h}$</td>
<td>B3LYP</td>
<td>0.015</td>
<td>0.0</td>
<td>97.8</td>
<td>-6.0</td>
<td>8.9 to 9.5</td>
</tr>
<tr>
<td>D$_2$</td>
<td>KMLYP</td>
<td>0.013</td>
<td>5.3</td>
<td>741.0i</td>
<td>-7.0</td>
<td>8.7 to 9.4</td>
</tr>
<tr>
<td>C$_2$</td>
<td>KMLYP</td>
<td>0.105</td>
<td>1.7</td>
<td>97.8</td>
<td>0.4 to 1.0</td>
<td>7.3 to 7.9</td>
</tr>
<tr>
<td>C$_{2h}$</td>
<td>KMLYP</td>
<td>0.013</td>
<td>2.5</td>
<td>664.3i</td>
<td>-6.1</td>
<td>8.6 to 9.3</td>
</tr>
<tr>
<td>C$_s$</td>
<td>KMLYP</td>
<td>0.098</td>
<td>0.0</td>
<td>103.8</td>
<td>-0.0 to -0.4</td>
<td>7.4 to 8.1</td>
</tr>
<tr>
<td>D$_2$</td>
<td>BHLYP</td>
<td>0.014</td>
<td>5.0</td>
<td>680.5i</td>
<td>-7.0</td>
<td>8.8 to 9.5</td>
</tr>
<tr>
<td>C$_2$</td>
<td>BHLYP</td>
<td>0.109</td>
<td>1.9</td>
<td>98.1</td>
<td>0.4 to 1.0</td>
<td>7.4 to 8.0</td>
</tr>
<tr>
<td>C$_{2h}$</td>
<td>BHLYP</td>
<td>0.014</td>
<td>2.2</td>
<td>608.0i</td>
<td>-6.1</td>
<td>8.7 to 9.4</td>
</tr>
<tr>
<td>C$_s$</td>
<td>BHLYP</td>
<td>0.101</td>
<td>0.0</td>
<td>104.0</td>
<td>-0.1 to -0.4</td>
<td>7.6 to 8.2</td>
</tr>
<tr>
<td>C$_{2h}$</td>
<td>Expt.</td>
<td>0.056</td>
<td>-</td>
<td>0.0</td>
<td>7.6</td>
<td></td>
</tr>
</tbody>
</table>

6.4.3 [10]Annulene:

The second member of the neutral aromatic hydrocarbon series after benzene, [10]annulene, cannot adopt D$_{10h}$ symmetry due to ring strain. No X-ray structure[26] of [10]annulene is available, but computational studies reveal many possible (azulene-like, naphthalene-like, twist, boat, and heart) conformations all of which are non-planar. Employing the “cutting edge” CCSD(T) method, Schaefer and co-workers concluded that the non-aromatic twist C$_2$ form is
best[23, 27], Table 6.5. They demonstrated that HF underestimates, whereas MP2, B3LYP, and
several other DFT levels overestimate the degree of delocalization in the minimally non-planar
aromatic conformations, Table 6.5. In contrast, we find that the KMLYP and BHLYP methods,
which have a larger HF component than B3LYP, give optimized geometries and relative
energies, Table 6.5, of [10]annulene isomers which agree well[28] with the much more
computational-resource demanding CCSD(T). Consequently, we employed KMLYP and
BHLYP to optimize the [14]-, [18]-, and [22]annulenes, since this is not feasible at CCSD(T).

Table 6.5. Theoretical results for [10]annulene isomers. Except for the CCSD(T), the 6-311+G**
basis set was used throughout. The TZ2P CCSD(T)/ DZd CCSD(T) results are taken from [23].
$E_{rel}$ is the relative energy (in kcal/mol) with respect to the most stable [10]annulene conformation
at the specified level of theory (left-most column).

<table>
<thead>
<tr>
<th>(PG)</th>
<th>$E_{rel}$ Azulene-like ($C_2$)</th>
<th>$E_{rel}$ Boat ($C_2$)</th>
<th>$E_{rel}$ Heart ($C_2$)</th>
<th>$E_{rel}$ Naphthalene-like ($C_2$)</th>
<th>$E_{rel}$ Twist ($C_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>8.13</td>
<td>1.84</td>
<td>11.77</td>
<td>2.87</td>
<td>0.00</td>
</tr>
<tr>
<td>MP2</td>
<td>3.08</td>
<td>11.34</td>
<td>0.00</td>
<td>5.45</td>
<td>4.22</td>
</tr>
<tr>
<td>B3LYP</td>
<td>4.45</td>
<td>6.95</td>
<td>0.00</td>
<td>5.19</td>
<td>4.56</td>
</tr>
<tr>
<td>B3P86</td>
<td>3.36</td>
<td>8.18</td>
<td>0.00</td>
<td>4.84</td>
<td>4.61</td>
</tr>
<tr>
<td>B3PW91</td>
<td>3.38</td>
<td>7.56</td>
<td>0.00</td>
<td>3.44</td>
<td>4.35</td>
</tr>
<tr>
<td>MPWPW91</td>
<td>3.15</td>
<td>7.03</td>
<td>0.00</td>
<td>3.05</td>
<td>3.49</td>
</tr>
<tr>
<td>BHLYP</td>
<td>5.00</td>
<td>2.70</td>
<td>0.92</td>
<td>1.29</td>
<td>0.00</td>
</tr>
<tr>
<td>KMLYP</td>
<td>4.60</td>
<td>4.42</td>
<td>2.05</td>
<td>1.15</td>
<td>0.00</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>4.24</td>
<td>1.40</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Images of annulene isomers](image-url)
6.4.4 [22]Annulene:

Although [22]annulene was prepared by Sondheimer and co-workers[29] in 1971, its X-ray structure is not known. The NMR $^1$H chemical shifts of the inner and outer protons are −0.4 to −1.2 and 8.5 to 9.7, respectively. CK reported[4] a bond length equalized $D_{2h}$ structure at B3LYP/6-31G*, but the disagreement between the computed and experimental $^1$H chemical shifts (Table 6.6) clearly excludes such high symmetries for [22]annulene. The eigenvector of the large imaginary vibrational frequency of the $D_{2h}$ form ($\nu_I > 1600i$ cm$^{-1}$ at KMLYP and BHLYP) points toward bond-alternating structures.

The computed $^1$H NMR chemical shifts (Table 6.6) of the $C_2$ [22]annulene outer ($\delta_{\text{outer}} = 8.4$ to 9.5) and inner ($\delta_{\text{inner}} = -1.1$ to −1.4) protons agree with the experimental[29] NMR values; those computed for the higher-energy $C_{2v}$ forms differ by 2 ppm, Figure 6.3. Hence, we predict that [22]annulene favors a bond-alternating structure. By implication, this also should be true of all the higher annulenes.

Table 6.6. Theoretical results for the [22] annulene, Figure 6.3. The 6-311+G** basis set was used throughout. PG is the point group. $\Delta r$ (in Å) is the difference between the shortest and the longest C-C bond length. $E_{\text{rel}}$ is the relative energy (in kcal/mol) with respect to the energetically most stable structure, at various levels of theory (28). $\nu$ gives the imaginary or the smallest real vibrational frequency. $\delta H_{\text{inner}}$ and $\delta H_{\text{outer}}$ are the GIAO $^1$H chemical shifts, in ppm, evaluated relative to TMS.

<table>
<thead>
<tr>
<th>PG</th>
<th>Level</th>
<th>$\Delta r$</th>
<th>$E_{\text{rel}}$</th>
<th>$\nu$</th>
<th>$\delta H_{\text{inner}}$</th>
<th>$\delta H_{\text{outer}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{2h}$ B3LYP</td>
<td>0.014</td>
<td>48.3</td>
<td>$1840.0i$</td>
<td>-13.7 to -14.1</td>
<td>12.6 to 14.0</td>
<td></td>
</tr>
<tr>
<td>$D_{2h}$ KMLYP</td>
<td>0.013</td>
<td>6.4</td>
<td>$1840.0i$</td>
<td>-14.0 to -14.6</td>
<td>12.4 to 13.9</td>
<td></td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>0.100</td>
<td>0.2</td>
<td>22.0</td>
<td>-3.1 to -3.4</td>
<td>9.2 to 10.1</td>
<td></td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.103</td>
<td>0.0</td>
<td>46.6</td>
<td>-1.1 to -1.4</td>
<td>8.4 to 9.5</td>
<td></td>
</tr>
<tr>
<td>$D_{2h}$ BHLYP</td>
<td>0.014</td>
<td>5.4</td>
<td>$1605.8i$</td>
<td>-13.9 to -14.5</td>
<td>12.5 to 13.9</td>
<td></td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>0.101</td>
<td>0.2</td>
<td>$104.7i$</td>
<td>-3.0 to -3.3</td>
<td>9.3 to 10.1</td>
<td></td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.104</td>
<td>0.0</td>
<td>97.8</td>
<td>-1.1 to -1.5</td>
<td>8.6 to 9.3</td>
<td></td>
</tr>
<tr>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
<td>-0.4 to -1.2</td>
<td>8.5 to 9.7</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.4. Optimized geometry and chemical shifts (bold) of [22]annulene. The high symmetry structures on the left were optimized at B3LYP/6-311+G** and the corresponding lower symmetry structures on right at KMLYP/6-311+G** and BHLYP/6-311+G** (in parenthesis). The experimental NMR values of inner and outer protons are 0.0 and 7.6, respectively.

6.4.5 Other bridged annulenes:

The sort of bridging observed as in Vogel’s[30] 1,6-methano[10]annulene overcomes the strain and conformational flexibility problems for the larger annulenes, Figure 6.4. Both X-ray data and DFT computations[31] show various bridged [10]annulenes to have CC bond-equalized structures.[32] The same is true for many of the bridged [14]annulenes. The X-ray geometries of both bismethano[14]annulene conformers, syn and anti, are reproduced by B3LYP/6-31G* computations. While the syn form is aromatic, the small CC bond length range (1.427 to 1.389 Å) may be due, at least in part, to the restraints of the bridging CH₂ groups, Figure 6.4. Conversely, the non-aromatic behavior (1.486 to 1.356 Å CC range) of the anti conformer is partly due to the steric constraints of the bridges. KMLYP and BHLYP give geometries in equally good agreement with the X-ray data. Trans-dihydropyrene, another bridged [14]annulene, favors C_{2h} symmetry at B3LYP (the CC bond length range is only 1.393 to 1.401 Å) but a lower symmetry C₂ form (1.364 to 1.394 Å) at KMLYP, Figure 6.4.
Figure 6.5. B3LYP/6-311+G** and KMLYP/6-311+G** (in parentheses) optimized geometries of various bridged [4n+2]annulenes. All the bond lengths are given in Å.
In contrast, the bridged $[18]$annulene, hexahydrocoronene, behaves distinctly differently at B3LYP than at KMLYP and BHLYP, Figure 6.4. While the B3LYP structure is highly CC bond equalized at the $D_{3d}$ minimum, this $D_{3d}$ geometry is a transition state ($\nu = 1069i$ cm$^{-1}$) at KMLYP and BHLYP. Instead, the $D_3$ form, with moderate bond alternation ($\Delta r = 0.077$ Å), is a minimum at KMLYP and BHLYP. The inner 6-membered ring in hexahydrocoronene has essentially equal CC bond lengths due to the tendency of the $\sigma$-framework to favor regular geometries, Figure 6.4.

6.5 CONCLUSIONS

Our evidence establishes that the turning point from the more symmetrical to bond-alternating Hückel monocycles occurs at $[14]$annulene. The currently-accepted highest symmetry structures of $[14]$-, $[18]$-, and $[22]$annulene can be ruled out as they give computed $^1$H chemical shifts which disagree grossly with the experimental values. The correct structures, which can be obtained by optimization at the KMLYP and BHLYP DFT levels, give excellent $\delta$ $^1$H agreement. All three annulenes have lower symmetries and exhibit considerable CC bond length alternation ($\Delta r = 0.1$ Å, Table 6.1, 6.4 and 6.6). Nonetheless, they are clearly aromatic, judging from their abnormal inner and outer proton chemical shifts as well as their appreciable aromatic stabilization energies.$[3,4]$ Equal CC bond lengths in $[4n+2]\pi$ systems are not required for aromaticity, and actually reduce the stability of the $[14]$-, $[18]$-, and $[22]$annulenes by about 2.0, 2.8, and 5.8 kcal/mol, respectively (Table 6.1, 6.4 and 6.6). As we have noted here and earlier$[3]$, changes in geometry have much greater effects on the magnetic properties, which appear to be the most sensitive measures of the degree of delocalization. The commonly used descriptive terms, “localized,” for bond alternating$[3]$, and “delocalized,” for bond equalized, are deceptive
and misleading; they should be abandoned in the context of aromaticity or specified explicitly. The structures of fully conjugated 4n+2 \(\pi\) electron systems may have appreciable bond alternation and still be delocalized and aromatic[3]. Shaik- Hiberty[6] has emphasized the strong global distortive tendency of \(\pi\) components towards localized bonding. This is not overcome in the most symmetrical geometries of the [14]-, [18]-, and [22]annulenes by the modest gain in delocalization energy due to bond length equalization, even when combined with the preference of the \(\sigma\) CC bonds to have the same length.

6.6 ACKNOWLEDGEMENTS

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6.7 REFERENCES


[7] Ermer, O. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 782. Ermer has pointed out that X-ray diffraction studies not only are indecisive in differentiating D$_{3h}$ and D$_{6h}$ symmetries in benzene but also in solving the structures of higher [n]annulenes; “enhanced significance is to be assigned to theoretical calculations on a reliable quantum-mechanical basis.”


[10] In 1980, Haddon noted that the 1965 X-ray study of [18]annulene “cannot not be regarded as definitive” as the C-C distances are averaged over time. He also summarized the conflicting conclusions derived from the earlier theoretical as well as spectroscopic data including $^1$H NMR chemical shifts. See Haddon, R. C. *Chem. Phys. Lett.* **1980**, *70*, 210.


[15] The X-ray structures of [14]- and [18]annulene were retrieved from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk).


[17] KMLYP DFT method can be specified in the Gaussian-98 program by using the following keywords: # iop(5/45= 10000557) iop(5/46= 00000443) iop(5/47= 04481000).


[21] (a) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) The expected absolute proton shieldings, $\sigma$, were converted to chemical shifts, $\delta$, as the difference from the proton shieldings of TMS, 31.98 ppm.

[22] The upfield and the downfield chemical shift of the inner and the outer protons, respectively, document the strong diatropic ring currents of [18]annulene. In a closely related but non-aromatic structure, the outer as well as the inner protons are in the vinylic Hs region ($\delta \, ^1H \, 6.0$ to 7.4).


[28] Energies (Table 6.5) of all [10]annulene conformations employing various density functional methods with the 6-311+G** basis set. The CCSD(T) energies are taken from reference 23.


[31] 1,6-Methano- (C2v) and 1,5-methano-[10]annulenes (C1) both have delocalized structures but with moderate CC bond length differences (Δr = 0.039 and 0.061 Å, respectively, at KMLYP).

Applications of density functional theory have been made to various problems ranging from ground state structures to transition states. The commonly used B3LYP-DFT method is quite economical in correctly giving structures, energies, and various magnetic properties to a reasonable accuracy. However, the B3LYP method over-estimates the delocalization in larger aromatics by a substantial amount. The performance of the KMLYP level is superior to those of the other available DFT methods in predicting the accurate structures of large aromatic molecules. In particular, the structure and relative energies of various [10]annulene conformations evaluated by KMLYP are in excellent agreement with those given by highly correlated CCSD(T) level. However, the wide applicability and success of the KMLYP method to various systems (not considered in this dissertation) are still being surveyed by our group.

DFT computations on aromatic and non-aromatic molecules employing the IGLO program established that no direct relationship exists between the $^1$H NMR chemical shifts and other magnetic criteria, geometric, and energetic aromaticity criteria. The conventional explanation “benzene protons are downfield relative to vinylic protons is because arene protons lie in the deshielding zone of the $\pi$-ring currents” is incorrect. In contrast, our results indicated that the arene protons lie in the shielding zone.

Contrary to the common perception that [4n]annulenes, the unfavorable counterparts of aromatic hydrocarbons, are destabilized, the energetic criteria indicate that these antiaromatics
have insignificant destabilizing effects when the ring size is large. The B3LYP-DFT computed energies and magnetic properties, demonstrate that the antiaromatic character of the larger systems with 4n \( \pi \)-electrons is best described by magnetic properties rather than energies. Comparison of magnetic, structural, and energetic criteria demonstrated that various aromaticity indices are statistically multidimensional. However, the best antiaromaticity indicators for the largest [4n]annulenes are proton chemical shifts and NICS rather than energies.

Study on the [4n+2]\( \pi \) annulenes showed that the aromaticity per \( \pi \)-electron decreased with the increasing ring size of annulene. Although HF prefers a bond alternating structure at [10]annulene and B3LYP prefers a bond equalized structure even at [30]annulene, the ASE differences indicated by both these methods are rather insignificant; HF and B3LYP optimized structures show that total ASE of aromatic annulenes converges to 21 and 22 kcal/mol, respectively. The magnetic criteria (\( \Lambda \), NICS, and proton chemical shifts) depend markedly on the geometries and are regarded as more sensitive than the energies; significant aromaticity is retained by B3LYP optimized [66]annulene while HF optimized results demonstrate that [54]annulene is nonaromatic.

The sensitivity of \(^1\)H NMR chemical shifts was explored to deduce accurate structures of large [4n+2]annulenes. Neither HF nor B3LYP optimized [14]-, [18]-, and [22]annulene geometries give \(^1\)H NMR chemical shifts in agreement with the experiment. B3LYP method overestimated while HF level underestimated the degree of delocalization in aromatic systems. Consequently the B3LYP method predicted CC bond equalized aromatic structures for all these annulenes.

Optimization of [14]-, [18]-, and [22]annulenes with the KMLYP method, which incorporates suitable percentage of a HF component, showed that all of these annulenes prefer
lower symmetry, with single bond-double bond alternating geometries, which are more stable forms than their higher symmetry analogues. The annulene structures optimized at the KMLYP level give proton chemical shifts in excellent agreement with the experimental values; having maximum deviations less than 0.7 ppm.

The change from the more symmetrical to the C-C bond-alternating Hückel monocycles occurs at [14]annulene. DFT computations demonstrated that aromatic annulenes may have appreciable bond alternation and still be delocalized and aromatic.
CHAPTER 8

LIST OF PUBLICATIONS


