THEORETICAL STUDIES ON AROMATICITY AND THE ELECTRONIC STRUCTURE OF METAL-SILICON MULTIPLE BONDING

A Thesis
Submitted for the Degree of
Doctor of Philosophy

By

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Dedicated to the Memory of
Ms. Nuzat Jahan

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Statement

I hereby declare that the work embodied in the thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, India under the supervision of **Professor Eluvathingal D. Jemmis**.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

B. Kiran
Boggavarapu Kiran

Certificate

Certified that the work contained in the thesis entitled **Theoretical Studies on Aromaticity and the Electronic Structure of Metal-Silicon Multiple Bonding** has been carried out by **Mr. Boggavarpu Kiran** under my supervision and the same has not been submitted elsewhere for any degree.

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Abbreviations

MO	Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
EH	Extended Hückel
FMO	Fragment Molecular Orbital
HF	Hartree-Fock
DFT	Density Functional Theory
NBO	Natural Bond Orbital
WBI	Wiberg Bond Index
CP	Cyclopropane
CB	Cyclobutane
DFCP	1,1-Diflurocyclopropane
BH	Bicyclo[2.1.1]hexane
Cp	Cylopentadienyl anion
B3LYP	Becke-3-Lee-Yong-Parr

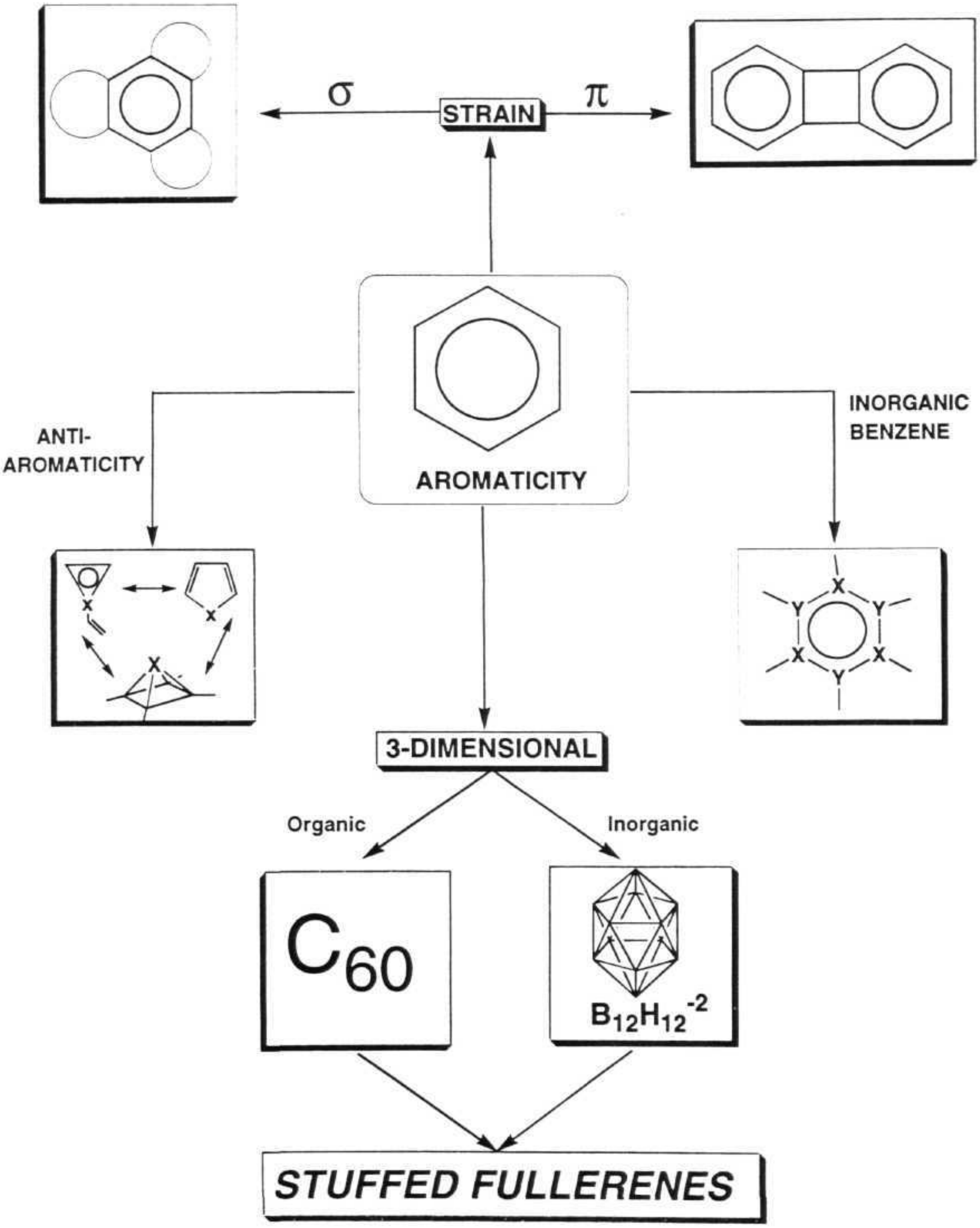
Chapter 0

Introduction

[0.1] General Theme of the Thesis

The concept of aromaticity is central to chemistry. As the name implies, all compounds with pleasant olfactory properties were classified as aromatic in the first half of the nineteenth century. This was the first working principle used to distinguish between aromatic and aliphatic compounds. Today, our understating of the molecular and the electronic structure of chemical compounds is far more sophisticated than that of early 1800's. Despite these tremendous advances, a precise and generally acceptable definition of aromaticity remains elusive. Part of the problem stems from the fact that aromaticity is not an observable quantity. One can not devise an experiment to 'measure' aromaticity. Consequently, many definitions exist.

From the beginning, theory has played a significant role in both understanding and quantifying aromaticity. The birth of quantum mechanics and its application to chemical problems in the first half of the twentieth century gave a basis for several empirical rules and models. Present theoretical methods and computational techniques allow reliable predictions of the structure and the properties of moderately large molecules with reasonable accuracy. These developments provided a new understanding to the concept. In addition, theoretical methods have inherent advantage of being able to study model systems which are otherwise not accessible to experiments. This thesis attempts such a theoretical study on aromaticity in a variety of chemical environments. It also contains structural and electronic study by ab initio methods on silylynes. A schematic theme of the thesis is presented in the next page, followed by a brief description of the problems studied.



Schematic Theme of the Thesis

The first chapter deals with the effect of strain, both σ and π, on aromaticity in annelated benzenes. In the first section, evolution of C-C bonds lengths in multi-annelated benzenes from the corresponding mono-annelated systems is considered. A bond increment scheme corresponding to each type of the ring is devised. This is found to be valid for both experimental and theoretical structures. Efforts were also made to understand the role of σ and π bonds in the bond length variations from the model study on the hypothetical planar cyclohexane.

The second section attempts a systematic study of the effect of strained ring annelation to monocyclic 6π electron systems of 5, 6 and 7 membered rings. The study has been done using structural, energetic and magnetic criteria. We find that strain and aromaticity are not correlated. That is, addition of more strain to the system does not necessarily decrease the aromaticity correspondingly. Last section discusses the relation between the total number of π electrons present in the systems and its aromaticity. For example, biphenylene has 12 (4n) π electrons; but is aromatic. Interesting magnetic behaviour of its isoelectronic analogues is discussed in this section. The study also includes [3]phenylene and its analogues in both linear and bent geometries. We find that, it is possible to devise systems with the same number of electrons which exhibit aromaticity, nonaromaticity and antiaromaticity.

Despite the equal B-N bond lengths, borazine, the inorganic benzene, is not aromatic. The first section of chapter 2, discusses the relationship between the resonance energy and magnetic criteria of aromaticity in $X_3Y_3H_6$ (X = B, Al, and Ga; Y = N, P, and As), $X_3Z_3H_3$ (Z = O, S, and Se) and Phoshazenes. We find that despite the equal resonance energy of borazine and boraphosphazine, the former is not aromatic while the later is. Aromaticity is often associated with thermodynamic stability. C_4H_4X (X = BH, AlH, CH^+, C, SiH^+, Si, N^+ and P^+) systems provide a unique opportunity to test the relative energies of various aromatic and antiaromatic isomers. We have found that, second section of chapter, under favourable conditions antiaromatic isomers can be thermodynamically more stable than the aromatic ones.

The chemistry of 3-dimensional aromatic compounds is also well established. C_{60} is a 3-dimensional aromatic compound. A similar icosahedral skeleton, B_{60} can be seen as a part of the structure of elemental boron. Unlike C_{60}, B_{60} does not exist as an isolated molecule. We have studied the possibility of stuffing C_{60} and higher fullerenes with icosahedral units based on electron counts. These are discussed in chapter 3. $B_{12}H_{12}^{-2}$ is a stable aromatic icosahedral dianion. $C_2B_{10}H_{12}$, the neutral analogue, exists in three isomeric forms (ortho, para and meta). Several isoelectronic heteroboranes are also known. We have studied, in the second section, the relative stabilities of $X_2B_{10}H_{10}$ (X = CH, SiH, N, P and Sb) and unravelled a new isomer for X=N. *o*-Carborane is often compared in reactivity to benzene. Jones and coworkers have shown that the analogy extends even to their dehydroderivatives, $C_2B_{10}H_{10}$ and benzyne. Seyferth and coworkers have recently synthesised a derivative of 1,2-$Si_2B_{10}H_{10}R_2$ whose structure is similar to that of *o*-carborane. However, we show in the third section, that its dehydroderivative should behave differently.

The contrasting behaviour of C and Si found in the last section is not restricted to the main group alone. We have found, in chapter 4, that with certain complexes the Si prefers divalency over triple bond. The structure and bonding of several M≡ Si systems were studied. Both Fischer and Schrock complexes of Ti, W, Re and Os complexes were considered. Despite the weak M≡Si bond, with certain metal and ligand combinations it should be possible to realize this experimentally.

[0.2] The History of Aromaticity

The story of aromaticity began prior to the isolation of benzene. In the beginning, all pleasant smelling molecules, including 'essential oils' were classified as aromatic. With the development of accurate combustion analysis (1800-1830) aromatic compounds were catalogued from a compositional point of view. They were characterized by their relatively high carbon-hydrogen ratios. Benzene is first isolated by Michael Faraday in 1825 as a pyrolysis product of whale oil.[1] This was recognised as the parent molecule of the aromatic species. Subsequently, pyrolysis of petroleum products also qualified as benzene derivatives.[2] Thus, benzene or phenyl nucleus had been identified as the simplest aromatic entity and assumed to be present in every aromatic compound. Attention naturally turned to the structure of benzene.

Initial attempts to place aromaticity on a structural basis was made by Loschmidt in 1861.[3] He made a highly imaginative but little publicised attempt to propose structures for 368 substances, out of which 121 were considered to be aromatic.[3] Large number of Loschmidt's structures are remarkably similar to those accepted today. Interestingly, he did not subscribe to the notion that the benzene nucleus contained unsaturated carbon-carbon bonds. However, the description of aromatic substances advanced from compositional basis to structural basis with Loschmidt.

In 1865 August Kekule made a far reaching proposal about the nature of the phenyl nucleus.[4] He consolidated all the known facts about aromatics known so far. All aromatic compounds are relatively richer in carbon than the corresponding aliphatic compounds. The simplest of them contains at least six carbon atoms. All rearrangement products of aromatic substances belong to the same family. All the carbon atoms in benzene are equivalent. Compiling all these facts with imagination he concluded, that the benzene structure consists of a cycle of six carbon atoms with alternating single and double bonds. The six remaining valences were assigned for bonding to atoms external to the six carbon nucleus.

At the same time, Erlenmeyer proposed a chemical basis for aromaticity, which is used even today.[5] He noticed that all aromatic substances undergo substitution rather than addition. Putting this in his own words "If the expression 'aromatic' is to be given any scientific meaning, it must be applied to all those substances which are related in a *chemical sense* as is the case for the earlier so called aromatic compounds". Interestingly, the Kekule formula fails to explain the reactivity difference between typical unsaturated substances and the phenyl nucleus. The rebirth of Kekule formula has to wait till the advent of quantum mechanics in the 1920's.

Prior to the quantum mechanical treatment of benzene, Pascal (1910) had identified that aromatic compounds have exalted diamagnetic susceptibilities.[6] This advanced the concept of aromaticity from 'chemical sense' to 'magnetic sense'. Soon after the discovery of the electron, chemical formulae were to be reorganised as electron formulae. After the development of notions such as ionic bond, shared electron pair bond, the octet rule and the Molecular Orbital (MO) and Valence Bond (VB) theories, there was a revival of the benzene problem. Although Armit and Robinson were usually credited for proposing the 'aromatic sextet' rule in 1925, in fact it was first proposed by Crocker of MIT in 1922.[7] He proposed that each of the monocyclic aromatic compounds shared the stable group of six aromatic electrons in the ring. In 1925, Robinson named Crocker's stable electron sextet as the aromatic sextet.[8] He noted it as a new entity like electron pair and the electron octet rule which imparts stability to the systems.

Next major impetus to the problem was given by Huckel in 1931.[9] In his quantum mechanical treatment of the benzene problem, he tried to explain why benzene is stable with six π electrons. Huckel examined both the VB and MO theories and found that the MO method could explain the stability of the aromatic sextet. His 4n+2 rule is more broadly applicable than the aromatic sextet rule.

In 1933, Pauling applied resonance theory (VB method) to the benzene problem.[10] Pauling examined the stability of the six π electrons of benzene, and concluded that the stabilization of benzene was due to the contributions from five canonical resonance structures. In addition to the resonance theory, Pauling also proposed the 'ring current theory'- free electron circulation around the benzene ring. Interestingly, this theory is still in use. After this, all the subsequent major theories are based on 'magnetic' properties of the aromatic compounds.

In 1937, London tried to explain the π electron current contribution to magnetic susceptibility.[11] After a gap of 20 years, Pople studied the ring current effects on NMR chemical shifts.[12] In 1969, Dauben made a modern study on diamagnetic susceptibility exaltation, which is by far the best method to identify whether a given molecule is aromatic or not.[13] In 1980, quantum mechanical calculation of magnetic properties were done by Kutzelnigg.[14] In 1996, Schleyer proposed a new method, Nucleus Independent Chemical Shift (NICS), to quantify aromaticity.[15]

[0.3] Criteria Used to Define Aromaticity

Aromaticity is not an experimentally observable quantity. Despite this limitation, a host of criteria has been developed to quantify aromaticity. These criteria can be classified into chemical, structural and magnetic criteria of aromaticity. In the following sections we will examine the advantages and disadvantages of these criteria.

[0.3.1] Chemical Behaviour

The reactivity of aromatic compounds is quite different from that of the olefins. Normally, aromatic compounds prefer electrophilic substitution over addition. However, this behaviour is not universal. Many benzenoid hydrocarbons have long been known to undergo addition rather than substitution reactions. For example, phenanthracene adds bromine; anthracene serves as diene in Diels-Alder reactions. Electrophilic substitution is impossible with fullerenes which are aromatic. On the other hand, sterically crowded olefins can undergo substitution instead of addition. Aromaticity is usually attributed to the ground state but the reactivity of molecules depend on many factors which are not necessarily related to the ground state. Thus, this criterion cannot be applied to all the substances which can be classified as aromatic.

[0.3.2] Structural Criteria

The C-C bond lengths in benzene are equal and intermediate between single and double bond lengths. Based on these observations, several structural criteria have been developed to quantify aromaticity.[16] Since for most of the compounds a precise measurement of bond lengths is possible from experiments, aromaticity index based on equal or near equal bond lengths have become very popular. However, the geometric criterion has several limitations. For example, the cyclopentadienyl cation ($C_5H_5^+$ (D_{5h} triplet)) is highly antiaromatic, with C-C bond length of 1.425 Å; which can be hardly differentiated from that of the aromatic D_{5h} cyclopentadienyl anion, which has 1.414 Å.[17] Bond length equalization is not only found in cyclic systems but also in acyclic compounds. The allyl cation is a simple example. Alternating bond lengths are also found in highly aromatic substances. For example, in tetracene the maximum differences of bond lengths is 0.085 Å. The geometric criterion has other fundamental limitations.

The changes in bond length of an aromatic compound are not entirely due to the π electrons. There is a substantial contribution from the σ electrons as well. In fact, there was a long and lively debate on the origin of equal bond length in benzene.[18] The widely held opinion was that, the cyclic delocalization of six π electrons is responsible for the equal bond lengths. Shaik and others have argued that the π electrons in benzene have inherent distortive tendency, and that it is the σ frame work that retains the equal bond lengths.[18] Recent experimental verifications on the first excited state of benzene have proved this argument.[19] Normally frequency reduction occurs on excitation, but in benzene the first excited state results in frequency exaltation. This exaltation, Shaik argues, is a result of the distortive tendency of π electrons. He further observed that, this behaviour is not confined to benzene alone, all the delocalized structures exhibit similar behaviour.

[0.3.3] Energetic Criteria

Aromatic compounds enjoy extra stability compared to the corresponding acyclic counterparts. This energy is estimated using homo- or isodesmoitic equations.[20] Consider the estimates of the resonance energy of benzene using different reference systems (Eq. 1-5 values of the reference compounds are taken from the experimental heat of formation).[17]

3 cyclohexene = benzene + 2 cyclohexane $\Delta H = -35.2$ kcal/mol Eq. 1
3 ethylene + 3 C_2H_6 = benzene + 6 methane $\Delta H = -64.2$ kcal/mol Eq. 2
3 ethylene + cyclohexane = benzene +3 C_2H_6 $\Delta H = -48.9$ kcal/mol Eq. 3
3 trans-butadiene = benzene + 3 ethylene $\Delta H = -21.7$ kcal/mol Eq. 4
$3\ C_6H_8 + C_6H_{12} = C_6H_6 + 3\ C_6H_{10}$ $\Delta H = -35.2$ kcal/mol Eq. 5

From the above equations it is obvious that the choice of reference systems is very crucial in the estimation of stabilization energy. Moreover, it is very difficult to develop an energy equation for some of the molecules. A good example is C_{60}.

The overall stability of a molecule is not entirely due to its aromaticity; strain, changes in the hybridization and other effects also contribute. Often it is very difficult to separate them. These effects may counterbalance or override the influence of aromaticity, in certain cases.

[0.3.4] Magnetic Criteria

Molecules with cyclic conjugated π electron systems have specific magnetic properties different form those of other π electrons systems. In particular, the deshielding of protons attached to the ring carbons as compared to the noncyclic conjugated π systems, a pronounced anisotropy of the susceptibility, and stronger diamagnetic susceptibility than expected from additivity rules like those of Pascal are some the important manifestation of the 'aromatic π electrons'.[6] Nuclear magnetic chemical shifts and magnetic susceptibility require special attention.

[0.3.4.1] Chemical Shifts

^{1}H-NMR chemical shifts are perhaps the most widely used tool for the characterization of aromatic compounds. Pople suggested that the 2 ppm greater deshielding of the benzene protons (7.26) relative to those of ethylene (5.28) may be a manifestation of the molecular ring current induced by an external magnetic field.[12] The effects inside the rings are much larger than those on the outside and the differences between aromaticity and antiaromaticity is dramatic. In the aromatic [18]annulene, the measured ^{1}H-NMR chemical shifts of 9.28 ppm (outer protons) and -2.99 ppm (inner protons) are in sharp contrast to the values for the antiaromatic [18]annulene dianion -1.13 ppm (outer), 28.1 ppm (inner) and 29.5 ppm (inner).[21] However, this criterion is not a general one. Some aromatic molecules like C_{60} and oxocarbons do not have hydrogens.

[0.3.4.2] Magnetic Susceptibility

Magnetic susceptibility is a measure of the extent to which a material is either attracted to or repelled by a magnetic field. It is measured by the force exerted on a sample by a field of known strength. A material repelled by a magnetic field is said to be diamagnetic; one attracted is paramagnetic. It is expressed as susceptibility per mole χ_M which has the units cm^3mole^{-1}. It is the average of three orthogonal contributions; $\chi_M = 1/3\ (\chi_x + \chi_y + \chi_z)$.

The first systematic and extensive investigation on the magnetic properties of organic compounds was made by Pascal during the first quarter of this century.[6] He observed that the magnetic susceptibilities of organic compounds are approximately additive function of their constituent group values. Based on this he developed a scheme of atomic increments for magnetic susceptibilities. However, he found that the double bonds on benzene had to be handled differently form those of ordinary olefins. Thus, benzene possesses a rather large magnetic susceptibility than was expected from a comparison with the values of alkenes. Therefore a special constant, Λ, has to be added to the aromatic systems for correct predictions. This exaltation was later recognized, as a measure of aromaticity. Magnetic susceptibility exaltation arises as a consequence of the special properties of fully delocalized electrons. External magnetic fields act on these electrons to induce an opposing field much larger than those induced in the electrons of ordinary covalent bonds. The exaltation (Λ) is the difference between molar susceptibility (χ_M) of the system under consideration and the sum of the contributions from a reference nonaromatic molecules ($\chi_{M'}$) (Eq. 6)

$$\Lambda = \chi_M - \chi_{M'} \qquad \text{Eq. 6}$$

This criteria has been widely used. Systematic study by Dauben and others on a variety of molecules has proved its validity.[13] The advantage with MSE is that the values are comparable across the systems. However, one shortcoming of this method is the choice of the reference systems. To get the exaltation it is necessary to develop increment values from various reference systems which are not aromatic. This makes the definition not require.

[0.3.4.3] NICS

Recently Schleyer and coworkers have developed another criterion, Nucleus Independent Chemical Shift.[15] The absolute magnetic shielding computed at ring centres (nonweighted mean of the heavy atom coordinates) reflect the aromatic/antiaromatic nature of the system. To correspond to the familiar NMR chemical shifts convention, the signs of the computed values are reversed. Negative NICSs denote aromaticity; positive NICSs antiaromaticity. The advantage with this method is that the ring currents of individual rings in a polycyclic systems can be estimated. However, NICS is not an experimental observable. It also depends on the ring size which makes the comparisons between the different rings difficult.

It is clear from the above discussion that each criterion has its own strengths and weakness. A complex phenomenon like aromaticity requires a multi-dimensional approach. Schleyer and others have shown that the geometric, energetic and magnetic criteria, are necessary for a better understanding of aromaticity in a given system.[16(c)] Even with all these criteria, it is difficult to answer the question 'is this molecule aromatic?' without resorting to some arbitrary cut off mark. All these criteria gives a gradation of values; it is always possible (the thesis provides many such examples) to find systems that stay somewhere between the well defined regions of aromatic, nonaromatic and antiaromatic systems.

[0.4] Methodology

Broadly, there are three path ways adopted for structure, energy and property calculations. They are molecular mechanics, semiempirical (MNDO and AM1) and ab initio (HF and DFT) methods. Each one has its own advantages, disadvantages and limitations. The applicability of each method depends on the nature of the problem at hand and the computer resources available.

[0.4.1] Molecular Mechanics

Even today molecular mechanics (MMX) is the only choice of method to handle molecules consisting of hundreds or thousands of atoms.[22] For example, consider a polypeptide or protein, ignoring the side chain conformation and conformation of each peptide bond, a molecule with n amino acid residues has 3^{2n} possible conformations with local energy minima. For $n = 25$, this is $3^{50} \cong 10^{24}$ conformations to be examined. No other method could do it at present.

Molecular mechanics considers atoms as spheres and bonds as springs. The mathematics of spring deformation can be used to describe the ability of bonds to stretch, bend and twist. Non-bonded atoms (greater than two bonds apart) interact through van der Walls attraction, steric repulsion and electrostatic attraction/repulsion.

A simple MMX energy equation is given by E = Stretching Energy + Bending Energy + Torsion Energy + Non-bonded Interaction Energy. This equation together with the parameters required to describe the behaviour of different kinds of atoms and bonds consists of a force filed. Many different force fields are now available.

Molecular mechanics is very fast and with a good parameter set reasonably accurate results can be obtained. But there are several limitations. Molecular mechanics is not quantum mechanical method, since it does not deal with an electronic Hamiltonian or wave function. Since it needs sufficient data to choose values for the parameters, it cannot be applied to novel types of compounds.

[0.4.2] Semiempirical Methods

Semiempirical methods broadly fall into two categories; those using a Hamiltonian that is the sum of one-electron terms and those using a Hamiltonian that includes two-electron repulsion terms as well as one-electron terms. The Huckel and Extended Huckel (EH)[23] methods are one-electrons theories, whereas the Pariser-Parr-Pople (PPP),[24] MNDO,[25] AM1,[26] PM3[27] are two-electron theories.

The simplest one-electron semiempirical MO method for non-planar molecules is the extended Huckel theory.[23] The EH method begins with the approximation of treating the valence electrons separately from the rest. Each valence MO contains contributions from the valence AOs. The AOs are usually Slater-type orbitals with fixed orbital exponents. A major difference between EH and simple Huckel is that in EH *all* overlap integrals are explicitly evaluated using the forms chosen for the AOs at the internuclear distances selected. The total valence-electron energy is given as the sum of orbital energies.

This method is particularly popularised by Hoffmann and his co-workers. They have shown that, with the help of reasonable starting geometries (often using coordinates from X-ray) an excellent understanding, of course qualitatively, of the electronic structure of rather complex molecules (inorganic complexes, clusters etc.) could be obtained with this very simple method. This model is very good for analysing the properties based on overlap of orbitals Walsh diagrams and fragment molecular orbitals method (in which a complex molecule is constructed from simple fragments). EH often provide a connection between an orbital description and chemical intuition. Despite these obvious and very useful advantages, the method should not be misused. Electron-electron repulsion terms were not used in the formalism. Therefore, the results heavily depend on the geometry given. EH works well for angular changes, dihedral angle variations, for relative energy level ordering and for the qualitative analysis of electronic structure. EH should not used for calculating activation energies for reactions where bonds are made or broken. It also does not work well for spectroscopic properties, excitation energies etc.

The second category of semiempirical methods share many common approximations. The most important ones are given below.

1. Elimination of overlap between functions on different atoms (the "NDDO approximation"). Thus, instead of solving $|H - ES| = 0$ the expression $|H - E| = 0$ in which H is the secular determinant, S is the overlap matrix, and E is the set of eigenvalues is solved. This is rather a drastic approximation but reduces the computational effort.

2. Restriction to a minimal valence basis set of atomic functions one s orbital and three p orbitals (p_x, p_y and p_z) per atom for maingroup elements. Inner shell (core) functions are not included explicitly. Because of this, the cost of doing a calculation involving a second-row element is no more than that incurred for the corresponding first-row element.

3. They are all self-consistent field (SCF) methods. The basic idea of SCF method is simple. By making an initial guess at the spin orbitals, one can calculate the average field seen by each electron and then solve the eigenvalue equation for a new set of spin orbitals. Using these new spin orbitals one can obtain new fields and repeat the procedure until self-consistency is reached.

4. Additional numerical approximations to further simplify the calculations and more importantly introduction of adjustable parameters to reproduce specific experimental data. These distinguish among the various semi-empirical methods currently available.

In general these methods have certain advantages over costly but more accurate ab initio methods. The obvious advantage is that they consume much less CPU time compared to ab initio calculations. Often (but not always) these methods are better than minimal basis ab initio HF calculations. These are particularly useful when handling very large molecules such as fullerenes for which even a moderately accurate ab initio calculations are prohibitively expensive. The problem with these methods is that their successes or failures are to be judged from previous experience. There is no systematic way of improving the results.

[0.4.3] Ab Initio Methods

To begin with, the name ab initio does not imply 100% accurate.[28] But one can systematically improve the results to get the desired accuracy. In contrast to the semiempirical methods ab initio methods use the correct Hamiltonian and does not use experimental data other than the values of the fundamental physical constants. Several approximations are used instead. Since different approximations lead to different kind of results, the obvious problem is to choose the correct (which agrees with experiments and goes beyond it) method for a given problem. Number of theoretical groups over the years have done systematic study on several molecules and come up with certain core requirements for the correct description of the electronic structure. Large and flexible basis set and inclusion of electron correlation are two such important requirements.

[0.4.3.1] Basis Sets

The choice of basis set is very important.[28] Although any basis set that sufficiently spans the space of electron distribution could be used, the concept of Molecular Orbitals as Linear Combinations of Atomic Orbitals (LCAO) suggests a very natural set of basis functions: AO type functions concentrated on each nuclei. One obvious choice is the exact hydrogen AO's known as Slater-type orbitals (STO). However, the computation of the integrals is greatly simplified by using gaussian-type orbitals (GTO) for basis functions.

For a better representation of the cusp in the electron density distribution at the nuclei, GTO basis sets are constructed from fixed linear-combinations of Gaussian functions, contracted GTO's (CGTO).[29] The earliest CGTO basis sets were constructed from *N* GTOs that best fit the desired STO. These are called STO-*N*G basis sets. To achieve accurate properties for some molecules it was necessary to include basis functions of higher angular momentum than any of the occupied (i.e. d-functions on C, f-functions on Fe etc.) orbitals. Such basis functions are called polarization functions because they increase the flexibility of molecular orbitals. For molecules with highly diffuse electron densities, such as s anions or molecules in Rydberg states, it is usually necessary to include basis functions with very small exponents. These are called diffuse functions.

A large number of Gaussian-type basis have been developed with differing strengths. The two most popular families of basis sets are those Huzinaga and Dunning (HD) and by Pople. Basis sets are usually described by how many gaussians per contracted GTO (CGTO), and by the number of CGTOs for each atomic orbital in an occupied shell (i.e. 1s, 2s, 2px, 2py, 2pz for all second-row atoms). A "minimal" basis set contains only one basis function per AO.

In the Huzinaga-Dunning basis sets, the number of CGTOs per atomic orbital is known as the zeta value.[30] Hence, the double zeta basis set would have two CGTOs per AO. E.g. for carbon a double zeta (DZ) basis would contain 10 basis functions. Similarly triple-zeta and other higher-order zeta could be obtained. The contraction of HD basis sets is described by a list of the total number of Gaussian functions of each type (s, p, d etc.) and the resulting number of CGTOs of each type.

The Pople family of basis sets include the set of STO-*N*G minimal basis sets and a large number of split-valence basis sets.[31] The later have one basis function for the core orbitals and two or more CGTOs for the valence orbitals. The standard Pople nomenclature is *L-M1M2M3G*, *L* is the number of primitive functions in the single core basis function. The number of *Mi* 's indicate how many separate basis functions describe the valence region, and the value *Mi* indicates the number of primitive functions in that basis function. For example, in a 6-311G basis set for oxygen, the core 1s orbital is described by one basis function consisting of 6 primitive gaussians. There are three of each of the valence 2s and 2p orbitals, the first containing 3 primitives and next tow consists of only one gaussian function each. Polarization on the non-hydrogen atoms is indicated by adding a single "*" to the description, or "**" if the hydrogens have p-type basis functions. Similarly the presence of diffuse functions is indicated by a "+" or "++" before the G, 6-311++G**. The most commonly used and found to describe the properties basis set is 6-31G*.

Majority of the ab initio calculations are confined to molecules of the light atoms; that is the first and second full rows of the periodic table. Heavy atom calculations pose two problems; one large number of two-electron integrals and relativistic effects. To circumvent these bottlenecks the use of pseudopotentials were devised. The basic idea of the pseudopotential approximation was introduced in the 1935 by Hellmann, who proposed that the chemically inert core electrons can be replaced by a suitably chosen function called pseudopotential.[32] The central idea was the replacement of the core electrons by a linear combination of Gaussian functions, called potential functions which are parameterized using data from all electron atom calculations as a reference. There are two different types of pseudopotential methods are available. One is usually called "ab initio model potential" (AIMP) and the other is "effective core potential" (ECP).[33,34]

The difference between the model potential and the effective core potential is that the valence orbitals of the AIMP approximation retain the correct nodal structure. In contrast, the pseudo-orbitals of the ECP methods are smoothed out in the core region. For example, the 4s valence orbitals of the Ti atom would become the lowest lying s orbital in an AIMP calculation (the 1s, 2s and 3s core orbitals being represented by the potential functions) but the radial part of the 4s function would still have three nodes. In ECP, the 4s valence orbital of Ti would have no node, the 5s orbital would have one node so on. The nodeless pseudo-orbitals have the benefit of allowing the basis set to be reduced in size, offering an additional economic advantage. Does the correct nodal property of the AIMP valence orbitals lead to better results? Model potentials do not give better geometries or bond energies than the ECP methods using valence basis sets of similar quality.

The two most important parameters for selecting select a suitable pseudopotential are the core size and the number of basis functions for the valence orbitals. In general, small core size and double zeta treatment of valence orbitals would give best results in terms of accuracy versus CPU time. The $(n - 1)s^2$, $(n - 1)p^6$, $(n - 1)d^x$, ns^y electrons of the transition metal should be treated explicitly in the ECP method. Correlation energy must be included in the geometry optimisation of transition metal complexes.

[0.4.2.2] Electron Correlation

Near HF limit basis set also does not ensure reliable results in ab initio calculations. Inclusion of correlation energy is necessary for the correct description of electronic structure.[35] Within the HF approximation electron interact with each other only via the average electron density. In reality, there is an instantaneous repulsion between the electrons. The energy change caused by these instantaneous interactions is called the correlation energy. Of course, the HF approximation has some correlation built-in but is not sufficient. An explicit inclusion of correlation energy is necessary.

There has been many methods developed to calculate the correlation energy. The most popular strategies are: perturbation theories, configuration interaction, coupled cluster, MCSCF, GVB and density functional theory. Out of these, Density Functional methods are more promising and computationally cost effective.

In 1964, Hohenberg and Kohn proved that the ground-state molecular energy and other molecular electronic properties are uniquely determined by the electron probability density $\rho(x, y, z)$, a function of only three variables.[36] In DFT methods the electron density rather than the wavefunction is the basis of the calculation. The computational effort of DFT methods scales formally with N^3 as opposed to N^4 for the HF method. The problem with the DFT methods is that the exact functional is not known; it can be guessed only by trial and error. However, recent progress in developing new functional, in particular gradient corrected functional and hybrid (HF + density) functional is impressive. The most popular hybrid method and extensively used in the thesis is B-LYP/HF procedure. In this method the exchange energy is replaced by an exchange-correlation functional from Becke and Lee-Yang-Parr approximations using the electron density from HF. This functional is sum of parallel-spin and antiparallel-spin parts. The parallel spin part is know as Becke exchange functional and the antiparallel part is known as Lee, Yang, Parr correlation function. If Becke's 3 parameter functional are used, this method is known as Becke3LYP.[37] Most of the times the geometries, relative energies and other molecular properties obtained at this level are comparable with results from MP2 calculations.[38]

[0.4.3.3] Methodology Used in the Thesis

In this thesis, a variety of methods have been used depending on the problem and the resources available. We have found that for reliable geometries, relative energies and vibrational analysis, hybrid density functional method Becke3LYP with 6-31G* basis is good from cost Vs efficiency point of view. Therefore, whenever possible (first two chapters and part of the third chapter) this method has been extensively used. Stuffed fullerenes (third chapter) have more than 100 heavy atoms. With the present resources at hand, it is impossible for us, to use any kind of ab initio methods. Therefore, semiempirical methods have been applied to find the feasibility of stuffing fullerenes. Transition metals still pose challenges to computational chemists. B3LYP method with relativistic pseudopotential basis set for the transition metals often give reliable results. Thus, Stevens pseudopotentials on the transition metals and heavier elements and 6-31G* basis set for the first and second row elements were used in chapter IV. For qualitative understanding, EHMO calculations have been performed on the ab initio optimized geometries. All the ab initio calculations were done using G94,[39] semiempirical calculations with MOPAC93,[40]. Extended Huckel calculations have been performed using CACAO.[41]

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Chapter 1

Localization or Delocalization: The Effect of Strained Ring Annelation on Aromatic Systems

[1.0] Abstract

A bond-increment-scheme, which depends on the sign and magnitude of a, b, c and d in **6**, decides the extent of bond length alternation in **5**. This scheme is found to be valid for a large number of experimental and theoretical structures. We have also observed that, the nonbonded C---C repulsive interactions between the bridge-heads of bicyclo[2.1.1]hexane and related systems are responsible for the observed large bond length variations. From the model studies, we have found that the σ orbitals transmit the effect of small ring annelation to the adjacent bond only, while the delocalized π orbitals play a major role in transmitting the perturbation to the third and fourth bonds.

The variation in bond lengths alone cannot unequivocally reflect the changes in localization (or delocalization). Energetic and magnetic criteria are also equally important in this regard. We have studied the localization in several 6π aromatic systems, cylopentadienyl anion, thiophene, benzene and tropilum cation, using all the three criteria. These systems are annelated by cyclopropane (CP), 1,1-diflurocyclopropane (DFCP), cyclobutane (CB) and bicyclo[2.1.1]hexane (BH).

Five membered rings are maximum affected by the annelation of small rings while six and seven membered rings are least perturbed. In case of cyclopentadienyl anion and its neutral analogs, bisannelation of CP and DFCP has maximum effect on the ring current as observed from MSE and NICS. This effect is *not* reflected in the bond lengths of the corresponding annelated systems. For benzene, despite the accumulation of substantial strain by the annelation of small rings, no noticeable decrease in the delocalization is observed. However, trisannelation of BH decreased the aromaticity to half the value of benzene. The strain accumulated by the trisannelation of the same is small compared to cyclopropane. This

indicates that there is no direct correlation between the strain and the delocalization in aromatic rings. Thus, the original claim of Mills-Nixon that the annelation of small rings to aromatic systems decreases the delocalization is questioned. Tropilium cation is least perturbed by any of these annelations. Instead, annelation of small rings stabilizes this cation. For example, triscyclobutatropilium cation is more stable than the tropilium cation! As the ring size increases, annelation of small rings is necessary to stabilize the planar delocalized rings.

Biphenylene, **1**, is aromatic. Chemically, it behaves like any other tri-cyclic aromatic compound. The MSE **1** is equal to that of benzene. Norbiphenylene anion, **2**, is isoelectronic to **1** but not aromatic. Both MSE and NICS indicates the presence of no ring current in **2**. This is in agreement with the experimental observation that **2** quickly dimerizes, like cyclobutadienes. This is due to the charge shift from 5 to 6 membered ring in **2**. Similar study on **3**, a neutral analog of **2,** which is found to be aromatic, confirms the role of charge in **2**. Similar behaviour is observed for **6**, the tropilium analogue of **2**. Annelation of seven and five membered rings, **7**, show unusual magnetic properties. **7** is antiaromatic. Both 5 and 7 membered rings in **7** show significant paramagnetic ring current. Thus, for a given number of π electrons aromatic, nonaromatic and antiaromtic systems exist. It is not possible to predict the aromatic behaviour of a given system from the total π electron count alone. This is found to be true for the [3]phenylene and its isoelectronic systems, which posses 18 π electrons.

[1.1] Bond Localization in Annelated Benzenes - An Additivity Scheme

[1.1.1] Introduction

Intensive research is going on to trap the elusive cyclohexatriene, one of the resonance structures of benzene.[1] The idea of annelation of strained rings to localize the bonds in benzene has been around for a long time. During the days of the oscillation model for benzene, **1**, Mills and Nixon[2] suggested that the two principal Kekule structures could be trapped by small ring annelation. Despite the failure of the oscillation model and the subsequent rejection of the MN effect, the possibility of synthesizing annelated benzenes with significantly different C-C bond lengths continues to fascinate chemists. There has been two different approaches to this problem. One method is based on the annelation by antiaromatic cyclobutadiene rings, pioneered by Vollhardt.[1d,3] The attempt to avoid antiaromaticity following the conjugation leads to the localization of the π bonds in benzene, so that the canonical structures with cyclobutadienoid rings contribute minimum. Several molecules have been synthesized in this category.[4] For example, [4]phenylene,[5] **2,** where the bond lengths of the central benzene ring differ by 15.2pm, has the maximum bond length alternation known so far. A different strategy has been adopted by Siegel,[6] who used annelation by strained nonconjugating bicyclic systems. The recent structural study of strained bicyclic systems such as bicyclo[2.1.1]hexene[7], **3**, and oxanorbornadiene[8] have shown that substantial bond length variations can be realized even without extension of conjugation in benzene and other related systems such as [14]annulenes.[9]

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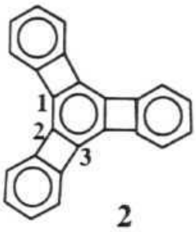

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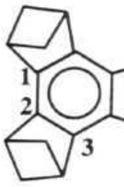

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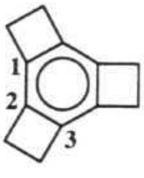

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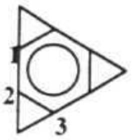

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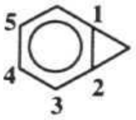

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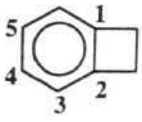

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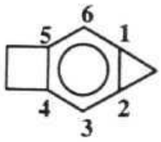

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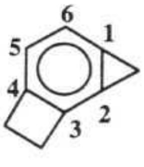

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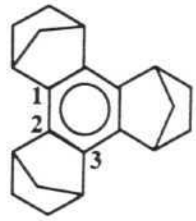

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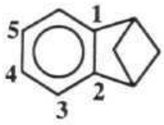

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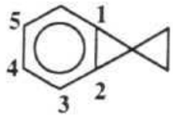

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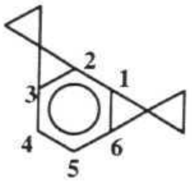

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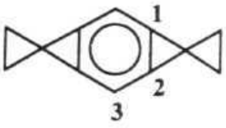

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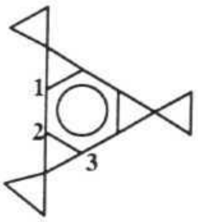

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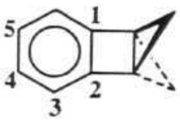

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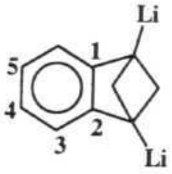

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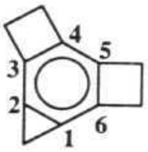

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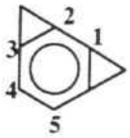

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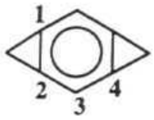

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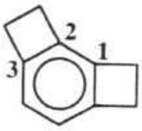

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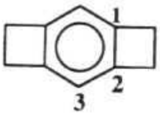

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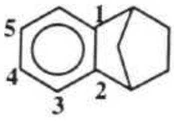

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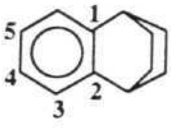

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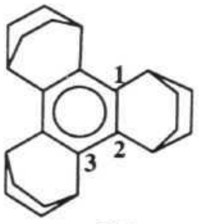

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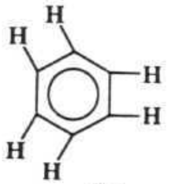

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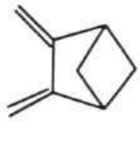

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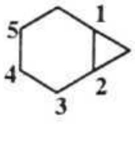

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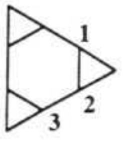

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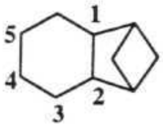
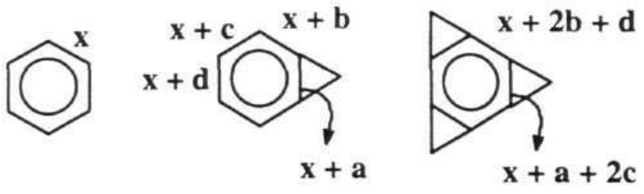


31

There have been many earlier attempts to induce bond length variations in benzene by annelating strained rings.[10] Tris-cyclobutabenzene, **4,** for example, gave a difference in C-C bond lengths of 2.3pm.[10] On the other hand tris-cyclopropabenzene, **5,** is calculated to give no bond length alternation, though all bonds were shortened.[11] This is surprizing because mono-cyclopropabenzene,[12] **6,** had shown large variation of bond lengths compared to mono-cyclobutabenzene,[13] **7.** In most of the annelated systems we have observed systematic variation in bond lengths on going from mono-annelation to tris-annelation. In this section, we analyze and explain the variations brought by the annelation of nonconjugating strained rings and show that these are additive. The additive nature of bond length variations is demonstrated for experimentally known structures. An internally consistent set of values is obtained for structures calculated at the Hatree Fock level using the 6-31G* basis set[14].

[1.1.2] Results and Discussion

The extent of C-C bond length variations in benzene on annelation of a ring can be expressed in relation to the parent benzene. For example the annelated bond, C_1-C_2, in cyclopropabenzene, **6**, is shortened by 5.0pm, from the reference bond length 138.4pm (X-ray) (Table 1) of benzene. Similarly C_2-C_3 bond decreases by 2.1pm. These and other changes (a, b, c and d) are characteristic of cyclopropane annelation, Scheme 1 . Sets of a-d values obtained for different rings are given in Table 2.



1 **6** **5**

Scheme 1

Table 1 Experimental bond lengths of annelated benzenes from X-ray studies along with Bond Increment Scheme (BIS) values , Theoretical values at the HF/6-31G* level along with BIS values.

Structure		**Expt.**	**BIS(Expt.)**	**HF/6-31G***	**BIS(6-31G*)**
1[a]	C_1-C_2	138.4	138.4	138.6	138.6
3[b]	C_1-C_2	143.8	------	144.0	144.1
	C_2-C_3	134.9	------	134.4	133.7
4	C_1-C_2	141.3	142.3	139.1	139.4
	C_2-C_3	139.0	140.1	137.8	137.9
7	C_1-C_2	134.9	134.9	133.5	133.8
	C_2-C_3	138.5	137.9	137.8	137.7
	C_3-C_4	140.5	138.8	139.3	139.2
	C_4-C_5	139.9	140.3	138.9	138.9
8	C_1-C_2	135.1	135.0	133.9	133.9
	C_2-C3	136.3	136.4	136.7	136.2
	C3-C4	139.3	139.4	139.0	139.4
	C4-C5	138.4	139.1	138.5	138.7
	C5-C6	140.1	140.3	140.7	140.7
	C6-C1	136.8	137.8	137.6	137.6
10	C1-C2	141.7	------	141.6	141.7
	C2-C3	137.9	------	136.4	136.3
18	C1-C2	136.3	136.6	134.5	134.6
	C2-C3	137.2	137.9	136.9	136.7
	C3-C4	141.1	141.0	139.7	140.0
	C4-C5	138.5	137.9	137.8	138.2
21	C1-C2	139.9	140.6	138.6	138.6
	C2-C3	139.4	140.1	138.5	138.5
	C4-C5	138.2	140.0	138.3	138.7
	C5-C6	141.3	141.6	140.0	138.6
22	C1-C2	140.2	140.7	138.6	138.7
	C2-C3	138.5	138.7	137.3	137.0
25.	C_1-C_2	140.8	------	140.6	140.4
	C_2-C_3	137.9	------	138.0	137.6

[a] this work , [b]structures **3, 4, 7, 8, 9, 17, 20, 21 and 24** are taken form ref. 1(a).

These variations are found to be additive in multi-annelated molecules. For example cyclopropane and cyclobutane in **8** are trans to each other. The C_1-C_2 bond annelated to cyclopropane should decrease by 5.0pm, (138.4 - 5.0). But C_1-C_2 bond is also trans to the cyclobutane, so it is elongated by 1.5pm (Table 2). The net effect is that the bond length is brought to 133.9pm (138.4 - 5.0 + 1.5). This is identical to the X-ray value of 133.9pm (Table 1). Similarly the C_4-C_5 bond length comes to 139.7pm (138.4 + 0.7 + 0.6) compared to 139.9pm obtained from X-ray studies (Table 1). When cyclopropane and cyclobutane are annelated asymmetrically as in **9,** all the bond lengths can be predicted by the bond increment scheme (BIS) (Table 1). Standard deviation of the difference between BIS(X-ray) and X-ray bond lengths is 0.43pm. The corresponding value for BIS(HF/6-31G*) and HF/6-31G* bond lengths is 0.32pm. In general, the maximum deviation of the BIS bond lengths from the observed ones is less than 1pm.

Table 2 Bond length increments in benzene annelated by different rings[a]. These values are obtained by subtracting the bond lengths form the standard benzene value 138.4pm, for X-ray and 138.6pm for HF/6-31G* geometries. Negative sign indicates shortening and positive sign indicates lengthening from the standard values.

Rings	**a**	**b**	**c**	**d**
Cyclopropane	-5.0 (-5.4)[b]	-2.1 (-1.6)[b]	0.3 (1.4)[b]	0.6 (0.9)[b]
Cyclobutane	0.7 (-0.6)[b]	0.1 (-0.8)[b]	1.6 (0.7)[b]	1.5 (0.6)[b]
[2.1.1]hexane[b]	1.7	-2.0	1.9	-0.9
[2.2.1]hexane[b]	1.1	-1.0	1.0	-0.3
[2.2.2]hexane[b]	1.0	-0.4	0.4	-0.2
Spiropentane[b]	-4.0	-0.17	1.6	0.6

[a] The bond lengths data for **6, 7, 11, 12, 23, and 24** are not given in the tables **1** or **3**. The same can be generated by adding corresponding **a, b, c** and **d** to 138.4pm for X-ray and 138.6pm for HF/6-31G* values. [b]Corresponds to HF/6-31G* values.

Equal bond lengths observed in tris-cyclopropabenzene, **5,** can now be understood from the BIS. The C_1-C_2 bond length would be 136.0pm (138.6 - 5.4 + 1.4 + 1.4), and C_2-C_3 bond length 136.3pm (138.6 - 1.6 - 1.6 + 0.9). Since annelation of cyclopropane does not induce alternating bond lengths (Table 2), large variations cannot be realized on tris-annelation. The large localization observed in **3** is a result of alternating signs (-ve., +ve., -ve., and +ve.) of a-d parameters in **11.** The effect of spiropentane annelation to benzene has also been studied (**12, 13, 14** and **15**), (Table 3) which follows the BIS. The success of BIS over a large number of known and calculated molecules shows that the bond length variations in the annelated benzenes are additive.

One of the earlier attempts to explain the bond length variations on annelation by small rings considered the angularly constrained benzene as a model.[15] When the CCH angle is 90.0°, **26,** the C-C bond lengths differed by as much as 20pm. The lack of corresponding difference in **4,** is attributed to cyclobutane banana bonds. We find that the dramatic bond length differences observed in the model, **26,** are not from the small CCH angle, but from the H---H repulsive interactions operating at that short distance. These are removed on going to **4,** where H---H repulsive interactions are eliminated by forming the C-C bonds, so that there is little bond length alternation. A similar repulsive force is also the key in causing the significant C-C bond length variations in benzene annelated by [2.1.1]hexane, **3**. Here the repulsion is between the bridge-head carbons which elongates the ipso bond. Earlier, in an attempt to explain the differences in reactivity between bicylco[2.1.1]hexene, **27,** and 2,3-bismethylene[2.1.1]hexane. **28,** Jorgensen and Borden[16] considered the interaction of ethylene and butadiene with cyclobutane ring. This filled-filled repulsive interaction is found to be the major destbilizing factor for **27** compared to **28**. The magnitude of this interaction in **11** is intermediate between those in **27** and **28**. So the extrastability of butadiene with cyclobutane is used to explain the elongation of the ipso bond in **11,** however this is not the complete story. This interaction alone will not explain the variation of the annelated bond length as a function of the size of the bicyclic ring. If the repulsive interactions between bridgehead carbons is really operative, increasing the distance between them should result in the decrease of the bond length variations. This is indeed found to be true in going from **3** to **10** and **25**. One of the ways of eliminating the repulsions between the bridge-head carbons is to form a bond between the bridge heads as in **16**, which will remove the repulsive interactions. Despite the high strain (455 kj/mol for [2.1.1]propellane compared. to 155 kj/mol for [2.1.1]hexane), our calculations show that **16** has negligible variations in the C-C bond lengths (Table 3). This is similar to the small deviations found for cyclobutane annelations. Further support for this comes from calculations on the dilithioderivative, **17** (of **11**), which has larger bridge-head C-C repulsions from the increased negative charge on the bridge-head carbons than that in **11.** Thus the largest variation observed by any mono-annelation is seen in **17** (Table 3.).

The annelated rings considered here perturb the σ frame work of the benzene. If σ orbitals alone are responsible for the observed bond length alternation how are the remote bonds getting affected? To understand the role of σ and π orbitals in bringing out the characteristic bond length variations, we have done a model study on cyclohexane where the six carbons are constrained to one plane. When cyclopropane is annelated, the nature of the variation in bond parameters in **29** is similar to that in **6**, (C_1-C_2=149.8pm, C_2-C_3=151.8pm, C_3-C_4=155.2pm and C_4-C_5=155.6pm; compared to the C_1-C_2 distances in planar cyclohexane 154.9pm). Again, on tris-annelation of planar cyclohexane by cyclopropane no bond alternation is found, **30**. Annelation by [2.1.1]hexane (C_1-C_2=157.0pm, C_2-C_3=154.4pm, C_3-C_4=155.1pm and C_4-C_5=155.0pm, **31**) showed similar patterns for the ipso and adjoint bond lengths as found in the corresponding benzene systems. As anticipated, the σ bonds do not transmit the effects beyond two bonds. The significant bond length variations found on remote bonds as in **6** and other mono-annelated rings shows the importance of the transmission of the perturbation at C_1-C_2 to the rest of the ring by the conjugated π-system. This is carried over on multi-annelation as well. These results are in agreement with the school of thought put forward by Shaik and co-workers that the equal bond lengths in benzene is due to the σ frame[17]. We also note that the bond length alternations calculated for annelated cyclohexane systems is further enhanced by the localizing nature of the π frame work in the benzene skeleton.

Table 3 Theoretical bond lengths at HF/6-31G* along with BIS values.

Structure		**HF/6-31G***	**BIS (6-31G*)**
5[a]	C_1-C_2	135.9	136.0
	C_2-C_3	135.6	136.3
13[b]	C_1-C_2	135.8	136.2
	C_2-C_3	135.5	135.2
	C_4-C_5	137.0	137.5
	C_5-C_6	142.2	141.8
14[b]	C_1-C_2	134.7	135.2
	C_2-C_3	138.6	138.5
15[b]	C_1-C_2	138.2	137.8
	C_2-C_3	134.7	135.8
19[b]	C_1-C_2	134.2	134.6
	C_2-C_3	136.0	135.4
	C_4-C_5	137.6	137.9
	C_5-C_6	141.6	141.4

[a] Structure **5** is taken form ref. 1(a), [b]This work.

[1.1.3] Conclusions

The bond increment scheme presented here predicts the geometries of multi-annelated benzenes from those of the mono-annelated ones. The bond length variations or the lack of it is a result of this additivity. The nonbonded C---C repulsions at the bridge head positions of the bicyclic systems such as [2.1.1]hexane causes the C-C bond length variations. Studies on model planar cyclohexane indicate that small ring annelation effects the σ system and the π system carries the perturbation to the rest of the benzene.

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[1.2] The Effect of Strained Ring Annelation in 5, 6 and 7 Membered Ring Six-π Aromatic Systems.

[1.2.1] Introduction

In the previous section, we have seen the evolution of bond lengths in multi-annelated benzenes from the corresponding mono-annelations. The bond increment scheme described there explains the origin of bond length variations which is characteristic of each annelation. However, there are several questions yet to be answered satisfactorily. How good is the bond length criteria in understanding the changes of delocalization in annelated systems? What is the relation between strain and aromaticity? How are these effects manifested as a function of size and charge of the 6π electron rings? In this section an attempt will be made to address some of these questions.

The strained rings considered are cyclopropane (CP), cyclobutane (CB) and bicyclo[2.1.1]hexane (BH). Annelation by cyclopropane imparts maximum strain and subsequently should show maximum bond length alternation (BLA). However, structural studies on mono-cyclopropa-arenes and the multi-annelated systems have shown that the BLA observed in these molecules is not chemically significant.[1] The same is also true for cyclobutane annelation.[2] Bicyclic systems have a different story. Significant BLA can be achieved in benzene and other aromatic ring systems by annelation of bicyclic systems.[3] Initial studies on BLA or MN effect were mainly focused on benzene. Later, several other aromatic ring systems, such as polycyclic-arenes,[4] hetero aromatic five and six membered rings,[5] cyclopentadienyl anion,[6] tropilium cation[7,8] have been studied by annelating with various strained rings.

So far the studies on MN effect are focused on the structural aspects of the annelated rings.[9] As noted in the chapter 0, estimates of aromaticity from the structural criterion alone are inadequate. Bond lengths are determined by both σ and π effects. Aromaticity depends on the delocalization of 4n+2 π electrons in a ring. Methods based on magnetic properties, such as anisotropies, MSE and NICS etc., which will estimate the variations in ring current, are necessary for proper understanding of the MN effect.

In this chapter, we have studied the effect of several strained rings annelated to cyclopentadienyl anion, thiophene, benzene and tropilium cation. The rings that are considered for annelation are cyclopropane, 1,1-diflurocyclopropane (DFCP), cyclobutane and bicyclo[2.1.1]hexane. Estimations of aromaticity are made from structural, energetic and magnetic criteria.

The hybrid HF-Density functional calculations using Becke3LYP correlation functional and 6-31G* basis set is used for all molecules considered here.[10] Full geometry optimizations were done for all molecules and vibrational frequencies were calculated to establish the nature of the stationary points. All calculations were performed using Gaussian 94 series of programmes.[11] NBO analysis is used to gain further insight into the bonding.[12] The magnetic susceptibility tensors were computed with CSGT-B3LYP/6-31G*//B3LYP-6-31G*[13] and NICS values were at GIAO-HF/6-31G*//B3LYP-6-31G*[14] method.

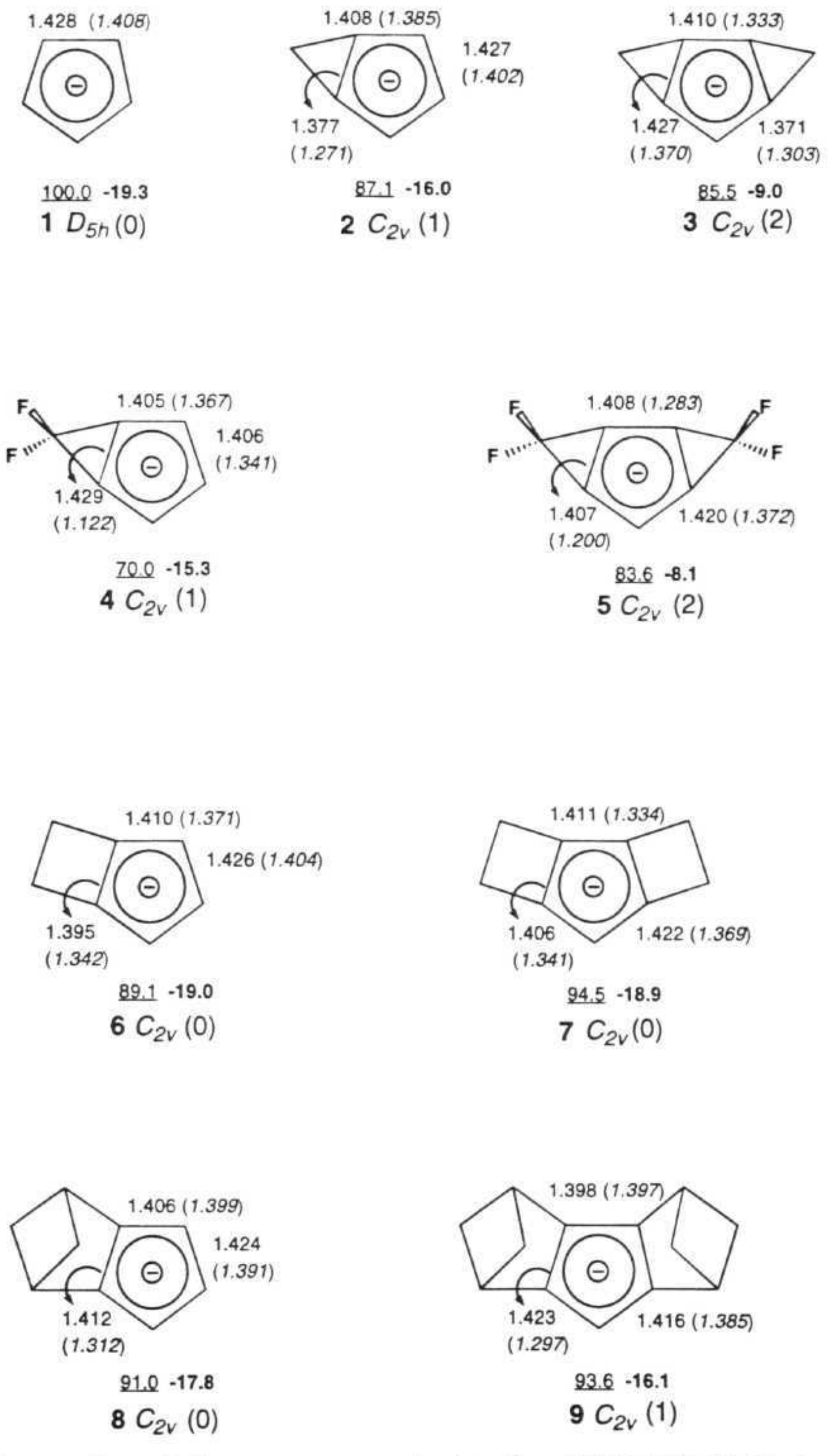
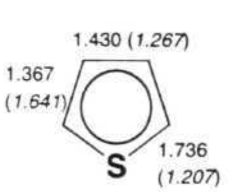
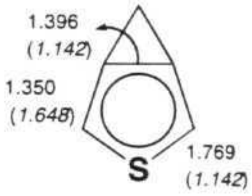


Fig. 1 Geometries of the structures calculated at B3LYP/6-31G* level. Bond lengths (Å), WBI (parenthesis), BAI_{WBI} (underline) and NICS values (bold) along with point group(italics) and NIMG(parenthesis) are given.



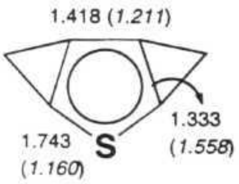
54.5 **-14.3**

10 C_{2v} (0)



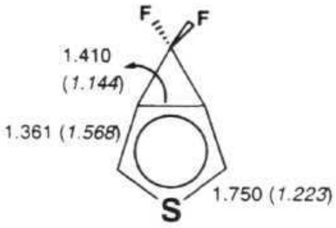
46.8 **-11.5**

11 C_{2v} (0)



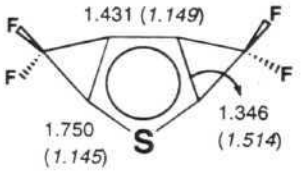
59.6 **-7.9**

12 C_{2v} (2)



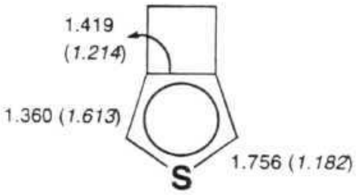
57.8 **-13.0**

13 C_{2v} (0)



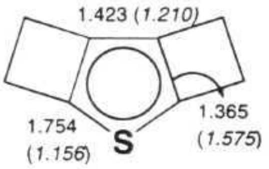
59.1 **-8.4**

14 C_{2v} (2)



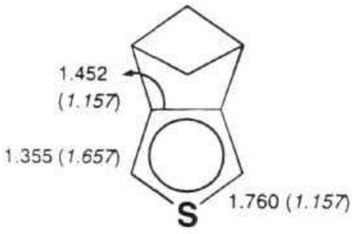
55.5 **-15.1**

15 C_{2v} (0)



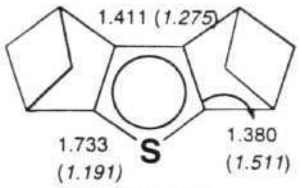
57.5 **-12.6**

16 C_{2v} (0)



46.6 **-12.5**

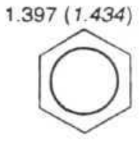
17 C_{2v} (0)



69.3 **-12.7**

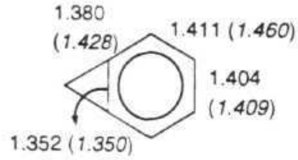
18 C_{2v} (0)

Fig. 1 contd.



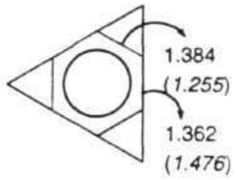
100.0 **-11.5**

19 D_{6h} (0)



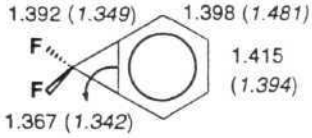
91.5 **-11.1**

20 C_{2v} (0)



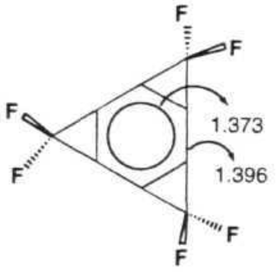
75.7 **-12.5**

21 D_{3h} (0)



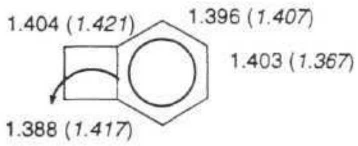
88.1 **-10.5**

22 C_{2v} (0)



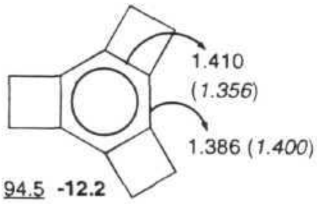
80.1 **-8.0**

23 D_{3h} (0)



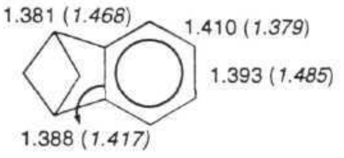
94.0 **-11.7**

24 C_{2v} (0)



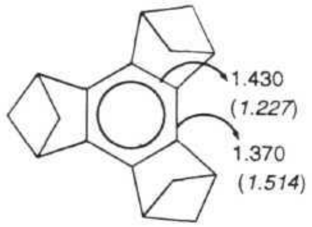
94.5 **-12.2**

25 D_{3h} (0)



84.5 **-11.0**

26 C_{2v} (0)



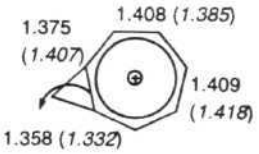
68.6 **-6.7**

27 D_{3h} (0)

Fig. 1 contd.

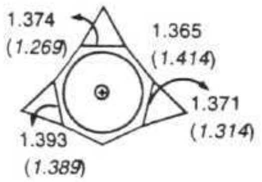
100.0 **-6.7**

28 D_{7h} (0)



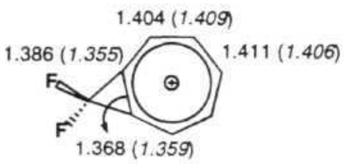
92.8 **-7.6**

29 C_{2v} (0)



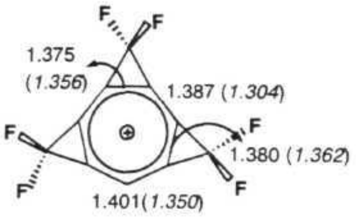
87.0 **-4.7**

30 C_{2v} (0)



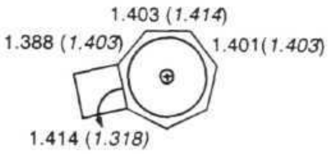
94.5 **-7.8**

31 C_{2v} (0)



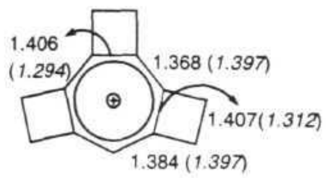
94.9 **-5.9**

32 C_{2v} (0)



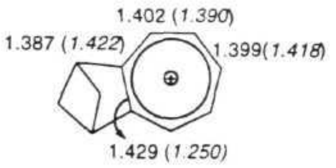
90.9 **-8.2**

33 C_{2v} (0)



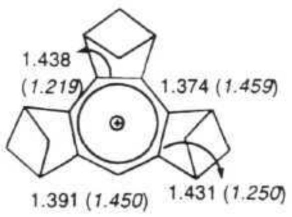
89.8 **-8.3**

34 C_{2v} (0)



87.1 **-7.1**

35 C_{2v} (0)



77.1 **-7.0**

36 C_{2v} (0)

Fig.1 contd.

Table 1 Various criteria of aromaticity for the structures **1-36**.

	BAI$_{org}$[a]	BAI$_{WBI}$[b]	SE[c]	χ_{tot}[d]	$\chi_{anis.}$	NICS[e]
1	100.0	100.0	7.7	46.9	23.9	-19.3
2	87.1	87.1	-30.7	49.9	29.2	-16.0
3	85.5	85.5	-67.6	50.6	26.7	-6.7
4	70.0	70.0	3.2	61.6	31.1	-15.3
5	83..6	83.6	-22.2	77.1	37.6	-8.1
6	94.5	94.5	-10.2	56.5	20.9	-19.0
7	96.8	96.8	-24.2	65.4	19.7	-18.9
8	93.5	91.3	8.7	65.3	22.2	-17.8
9	91.1	90.1	9.7	83.8	20.0	-16.0
10	57.3	54.5	15.3	47.4	25.9	-14.3
11	39.0	46.8	-21.3	50.4	24.9	-11.5
12	42.0	59.6	-58.7	50.6	29.3	-7.9
13	50.0	57.8	-15.7	63.4	32.8	-13.0
14	44.1	59.1	-50.4	77.9	34.2	-8.4
15	47.5	55.5	-0.4	59.6	20.7	-15.1
16	50.0	57.3	-14.7	67.7	19.9	-12.6
17	43.0	46.6	4.1	46.6	27.3	-12.5
18	62.7	69.3	-5.9	69.3	25.4	-12.7
19	100.0	100.0	24.2	46.1	34.9	-11.5
20	80.4	91.5	-2.0	51.9	36.6	-11.1
21	90.9	75.7	-48.7	52.6	35.5	-12.5
22	85.4	88.1	5.2	62.3	37.4	-10.5
23	90.4	91.3	10.1	58.6	34.3	-8.0
24	94.6	94.0	15.5	57.7	30.4	-11.7
25	89.9	94.5	1.3	60.1	32.5	-12.2
26	89.2	84.5	16.7	67.3	33.0	-11.0
27	74.7	68.6	8.9	63.4	32.1	-6.7
28	100.0	100.0	39.5	45.5	49.5	-6.7
29	81.8	92.8	33.9	50.3	47.8	-7.6
30	91.4	87.0	12.5	58.9	42.7	-4.7
31	85.9	94.5	15.6	61.3	52.3	-7.8
32	91.9	94.9	-43.4	93.8	52.3	-5.9
33	92.2	90.9	46.9	57.4	47.8	-8.2
34	86.2	89.8	56.1	80.5	34.2	-8.3
35	87.1	84.6	57.4	65.6	47.3	-7.1
36	77.1	77.1	84.7	108.9	39.4	-6.3

[a] Bird's Aromatic Index (BAI) calculated with the geometries at B3LYP/6-31G*. [b] BAI calculated using Wiberg Bond Index (WBI). [c] Strain Energies (kcal/mol) calculated using Eq. 1. [d] χ total is average of all the eigen vectors calculated at CSGT-B3LYP/6-31G*//B3LYP/6-31G*. [e] Nucleus Independent Chemical Shift calculated by GIAO-HF/6-31G*//B3LYP/6-31G*

[1.2.1] Results and Discussion

[1.2.1.1] Structural Criteria

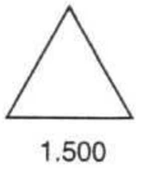
The changes in the C-C bond lengths of the annelated system from the standard value determines the extent of localization or delocalization. Since the calculated bond lengths can be directly correlated to the experimental values, this criterion is very important in understanding the MN effect. Bird's Aromaticity Index (BAI) as a geometrical measure for aromaticity is well established.[15] Originally, $BAI_{org.}$ had been devised based on the statistical evaluation of the deviations in peripheral bond orders. The bond orders are derived from the experimentally determined bond lengths by an empirical way.[15] We made a slight modification. Instead of using empirically derived bond orders, we have used Wiberg bond orders, to evaluate the index, BAI_{WBI}. This modification has certain advantages over the original method. The use of bond orders derived from the wave functions (such as WBI) eliminates the necessity of empirically derived constants and makes the index more uniform. Since the internuclear distances do not necessarily reflect the true nature of the bond, any index based on these distances may not reflect the real localization or delocalization from the electronic point of view. This is more true in the case of MN effect. Since three membered rings have bent bonds, estimates based on internuclear distances are misleading. Therefore, the proposed modification imparts uniformity and reliability to the Bird's criterion. BAI_{WBI} is used in the discussion unless otherwise stated. Table 1 lists various criteria, $BAI_{org.}$, BAI_{WBI}, strain energies, magnetic susceptibility, anisotropy and NICS for the structures **1-36** (Figure 1).

Short bonds are the common feature of three membered rings.[16] Annelation of cyclopropane shortens the annelated C-C bond. However, from the WBI, it has the smallest bond order (Table 1). The ipso bond (the bond adjacent to the annelated bond) also gets shortened but it has larger bond order. The changes occurred at the remaining bonds are minor and depends on the symmetry and the size and charge of the ring.

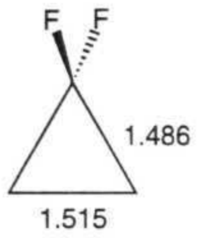
Despite these apparent changes in the bond lengths, annelation of cyclopropane did not effect the delocalization much. A moderate decrease in the Bird's criteria indicates this change more quantitatively. A maximum decrease of 15% in BAI_{WBI} is observed for **2** (Table 1). As anticipated, the BAI_{WBI} increases slightly, implying an increase in the delocalization with the size of the ring.

Annelation of additional cyclopropanes brings extra strain but only modest change in the corresponding bond distances (Table 1). For cyclopentadienyl anion, additional cyclopropane annelation decreases delocalization by only 2% (Table 1). The changes are more dramatic for thiophene; instead of decreasing the delocalization, additional cyclopropane actually enhances it (Table 1). This means that, from a structural point of view, more strain is enhancing the delocalization. This goes against the original anticipation of MN. Interestingly, this difference is not seen in the BAI_{org}. The differences between $BAI_{org.}$ and BAI_{WBI} are more pronounced only for three membered rings. There is a notable amount of decrease in the delocalization for both six and seven membered rings upon annelation of three CPs; ~ 25% decrease for **21** and ~15% decrease in **30**. However, the effect of cyclopropanes on delocalization is not additive in nature, i.e., by annelation of more number of cyclopropanes the effects are not adding up. Thus, structurally, annelation of cyclopropanes does not bring significant localization.

Fluorines and hydrogens differ substantially in their effects. Replacement of hydrogens by fluorines increases distal bond length, **37** and **38**. Maksic and coworkers have found that when **38** is annelated to benzene, a reverse MN effect is



37



38

operative.[9] In the present study (Table 1) we observed that annelation of both CP and DFCP can have varied effect on the BLA. Annelation of DFCP to **1** decreases the delocalization to a maximum extent, as much as 30% (Table 1). Compared to this, additional DFCP on cyclopentadienyl anion, **5**, enhances the delocalization (Table 1). Unlike CP, annelation of either mono- or di- DFCP to thiophene increases the delocalization. Both six and seven membered rings are not affected much upon annelation of DFCP (Table 1). Thus, DFCP does not decrease the delocalization as much as the CP does except for **4**.

Strain energies for cyclobutane and cyclopropane are very similar. Yet, they affect differently on annelation to an aromatic system. In all the systems that have been considered here, not more than 5% decrease in the delocalization is observed upon cyclobutane annelation. This is found to be true for both mono- as well as multi-annelated cyclobutanes. Therefore, larger rings, such as cyclopentane, cyclohexane etc., are not expected to produce significant impact on the bond lengths.

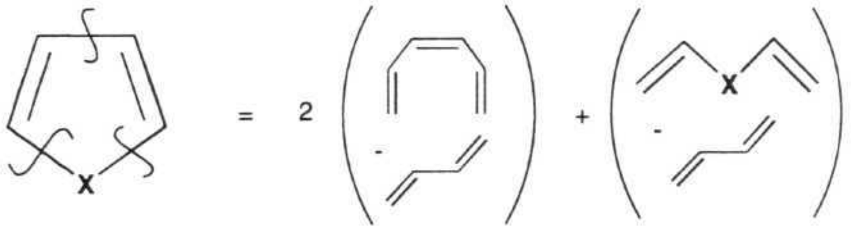
Among the bicyclic systems, bicyclo[2.1.1]hexane is expected, due to the shortest distance between the bridge-head carbon atoms, to induce maximum BLA. Except for benzene, there is no significant effect on annelation of bicyclo[2.1.1]hexane to 5, 7, and thiophene ring systems. In fact, for thiophene bis-annelation, **18**, enhances the delocalization instead of decreasing (Table 1) (cf. **12**). Tris-annelation of bicyclo[2.1.1]hexane to benzene, **27**, had produced maximum localization among the non-conjugating rings because of the alternating sign of a, b, c and d parameters discussed in chapter 1. A drop of 30% in delocalization is observed for **10**.

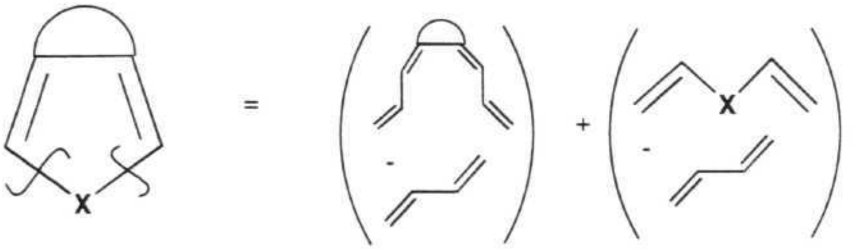
In conclusion, from the bond length criterion, altogether only a few systems appear to have localized picture. The criteria $BAI_{org.}$ and BAI_{WBI} differ substantially in certain cases. All the problem cases involve three-membered ring annelations. In those cases, the BAI_{WBI} is more reliable than BAI_{org}. The maximum localization for cyclopentadienyl anion is observed with DFCP annelation, **4**,. Tris-annelation of bicyclo[2.1.1]hexane to benzene, **27**, has the maximum effect. Surprisingly, for tropilium cation annelation by all kinds of rings have only a marginal effect. In case of thiophene, except cyclopropane other rings have not perturbed the delocalization much. In fact, with some of the rings, **12** and **18**, delocalization has increased upon annelation (Table 1).

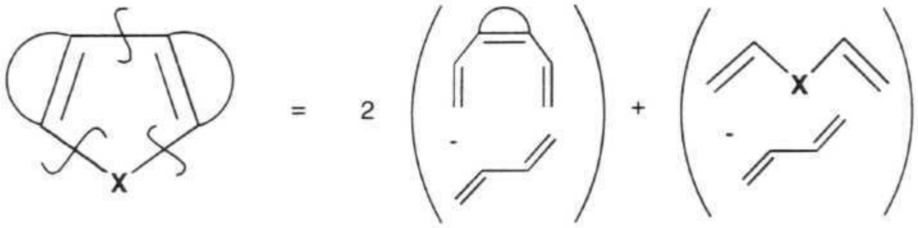
Not all rings impart equal strain to the systems. To verify the original claim of MN that the ring which imparts maximum strain should correspondingly induce more localization, it is necessary to quantify the strain that the aromatic ring experiences. Following section attempts to estimate the strain quantitatively.

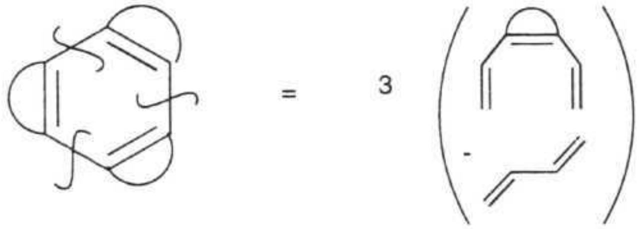
[1.2.2.2] Strain Energies:

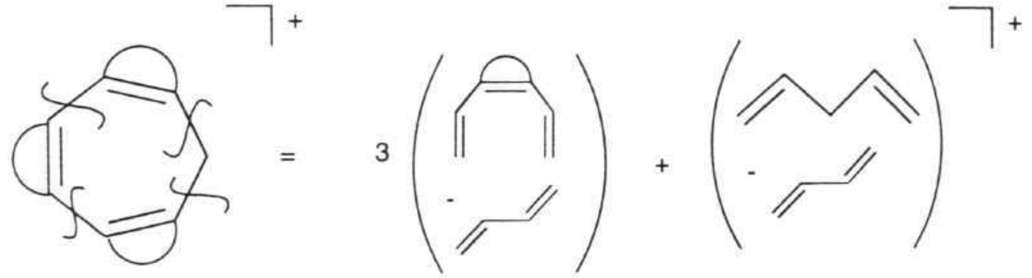
Several methods are available to estimate the strain energies. We adopt a strategy based on homodesmoitic equation (Eqs. 1-5) where the annelated ring kept undisturbed.[17] This ensures that the strain exerted by the annelated ring on the aromatic system can be isolated. The energies from Eqs.1-5 also include the resonance energy of the aromatic ring. Table 1 lists the strain energies calculated by the Eq. 1-5 for all the systems under consideration.


Eq. 1


Eq. 2


Eq. 3


Eq. 4


Eq. 5

X = CH$^-$, S ⌒ **= CH$_2$, CF$_2$, CH$_2$-CH$_2$, CH(CH$_2$)(CH$_2$)CH**

For cyclopentadienyl the reaction energy for Eq.1 is endothermic, by 5 Kcal/mol. This energy is the sum of aromatic stabilization energy (ASE) plus strain energy of five membered ring. Schleyer had calculated, using a different isodesmoitic equation, that the ASE for **1** is 20 Kcal/mol at MP2/6-31G* level of theory.[26] This indicates that the cyclopentadienyl anion is strained by approximately 15 Kcal/mol. This strain is mostly from bond angles, as they deviate from sp^2 ideal angle. The strain is reduced for thiophene compared to **1** (Table 1). As the size of the ring increases, from benzene to tropilium ion, the energy from the isodesmoitic equations becomes more endothermic indicating less strain and more stabilization from aromatic resonance energy. In addition, the charge on the system also influences the energy of the equation. It is well known that the spread of the positive charge over a large basin is more stabilizing.

Annelation of three membered ring exerts maximum strain to the aromatic system. The homodesmoitic equation becomes more exothermic for CP and DFCP. The strain energy per cyclopropane annelation linearly varies with H-C-C angle of the aromatic ring. For **1**, annelation of one cyclopropane imparts 38 Kcal/mol strain energy (Table 1). For thiophene the same is 36 Kcal/mol. This energy comes down to 26 Kcal/mol for benzene and in case of tropilium ion a modest strain of 5.6 Kcal/mol is observed. Thus, maximum strain is observed for **1** and minimum at **27**. Unlike the bond length variations, which does not vary smoothly with the additional CPs, the strain energy increases more or less uniformly with each annelation of CPs(Table 1).

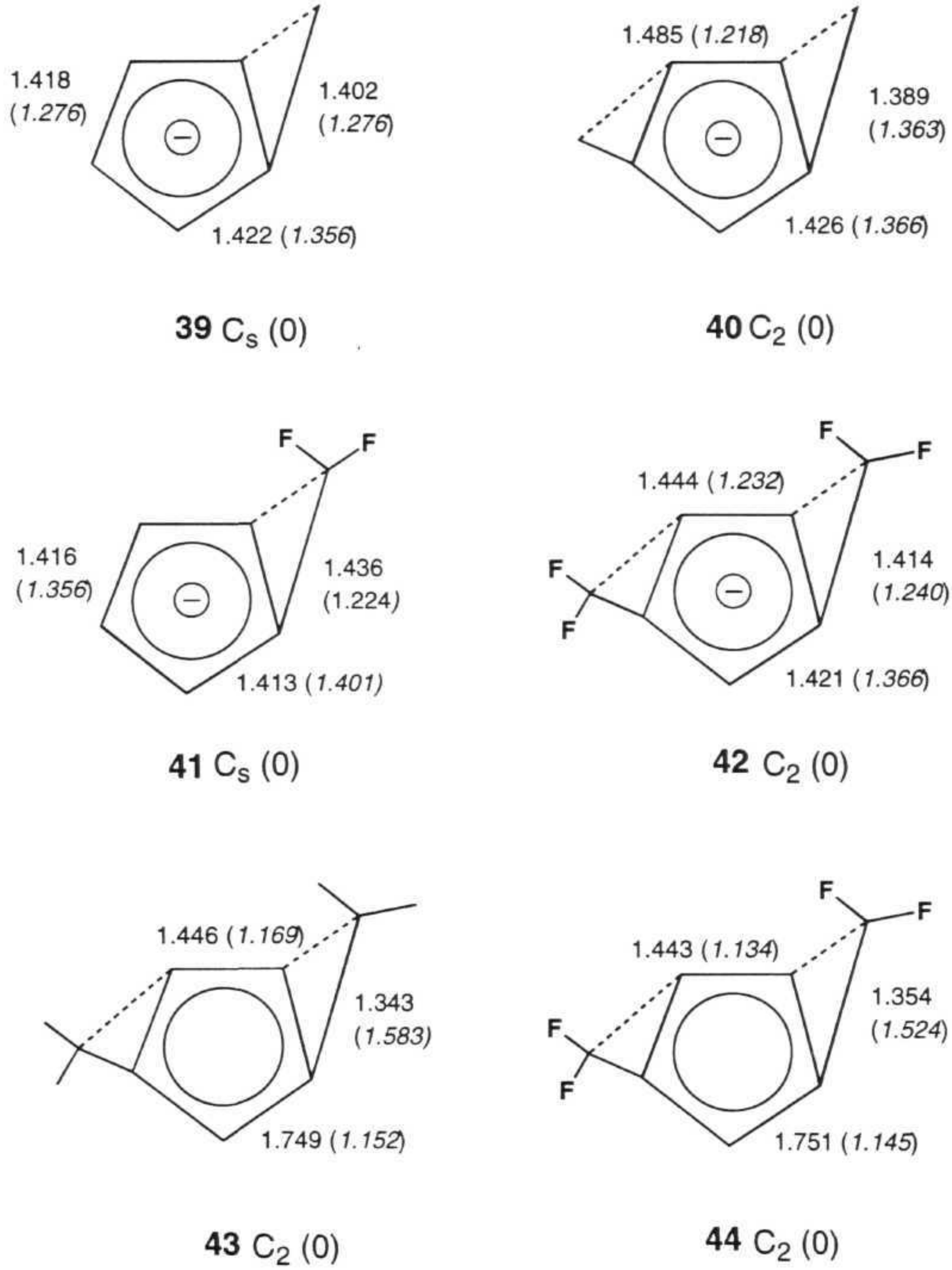


Fig 2. Minimum Energy Structures Optimized at B3LYP/6-31G*

Annelation of DFCP has very similar effect as that of CP but for an important difference. Unlike CP, there is no strict correlation of strain induced by each DFCP to that of the ring size. One DFCP exerts only 4 Kcal/mol strain on cyclopentadienyl anion. Where as for thiophene one DFCP puts up as much as 31 Kcal/mol strain. For benzene and tropilium cation the strain energies per DFCP are 19 and 24 Kcal/mol. The strain is unusually low for **4** and high for **31**. This is because of the fact that the carbon atom in DFCP experiences more positive charge by virtue of the two fluorine atoms. This is being reduced in **4** and enhanced in **31**, resulting in the decrease and increase of strain from the expected values.

The high strain exerted by the three membered rings is also reflected in the stability of these rings. For cyclopentadienyl anion, all the structures with CP and DFCP are not minima. Structures **2** and **4** are transition states; **3** and **5** are second order stationary points (Table 1). Interestingly, for thiophene **11** and **13** are minima but **12** and **14** are second order stationary points. All the imaginary frequencies correspond to the out-of-plane movement of the three membered rings. The optimized minimum energy structures are depicted in the Fig 2. Energetically, **39** is 7.2 Kcal/mol lower than **2**; annelation of two CPs, **41**, lowers the relative energy by two times, 15.3 Kcal/mol. A modest stabilization is observed for the annelation of DFCPs. Structures **40** is lower in energy only by 1.2 Kcal/mol and **42** by 3.1 kcal/mol with respect to **4** and **5**. A similar behaviour is also observed for thiophene. **43** is 7.5 and **44** is 2.1 Kcal/mol lower in energy compared to **12** and **14**.

Annelation of the next higher ring, cyclobutane, does not induce as much as strain as that of CP. Instead, it can stabilize larger rings. There is a gradual decrease in strain with the decrease in the size of the aromatic ring. Starting from the highest strain per cyclobutane, 18 Kcal/mol, for **1**, the strain decreases to 16 and 9

Kcal/mol for thiophene, and benzene respectively. In tropilium cation, annelation of cyclobutane *stabilizes* the system by 7 Kcal/mol. Schleyer and co-workers have recently reported that annelation of CP and CB stabilizes the planar form of [10]annulene.[18] This is due to the fact that H-C-C angles of cyclopropene and cyclobutene are not very different from large C-C-C angle in [10]annulene. Therefore, the total strain of the system is reduced considerably. We see that the same is also true for **33**. Thus, the stabilization of large aromatic rings by small ring annelation starts from tropilium cation.

Bicyclo[2.1.1]hexane has considerable amount of inherent strain, 37 Kcal/mol which is more than that of CP or CB.[19] Despite this, annelation of BH to aromatic rings does not induces as much strain as that of CP and CB. Maximum strain is experienced by thiophene, 11 Kcal/mol (Table 1). Surprisingly, slight stabilization is observed for cyclopentadienyl anion, due to the negative charge distribution to the bicyclic ring. In case of benzene the strain by bicyclic[2.1.1]hexane annelation is about 8 Kcal/mol for **26**. Trisannelation of BH, **27**, increases the strain by 15.3 Kcal/mol. However, compared to the **21**, which is maximum strained, **27** has more localized bonds. This indicates that increased strain does not necessarily induce large BLA. Huge stabilization by BH annelation, around 17 Kcal/mol per ring, is realized for tropilium cation. Thus, higher rings can be made more stable by the bicyclic ring annelations. These are better than CB and CP annelations.

Since, all aromatic rings posses 'ring currents', it is necessary to understand how the ring current is getting affected by the strained ring annelations. In the following section we try to evaluate the ring currents for the systems under consideration.

[1.2.2.3] Magnetic Criterion:

The concept of ring current is widely used in chemistry as a necessary property of aromaticity. The effect of ring current is manifested in several ways. Abnormal low-field chemical shift of the protons attached to aromatic ring is one such property. Despite its wide usage and practicality, the ^1H chemical shift are less sensitive to the subtle changes in the aromatic ring and also obviously limited to the only systems that have aromatic protons. In addition, as Kutzelnigg pointed out, not only ring currents but also charge, strain and other factors influence the 2 ppm difference between olefinic and aromatic protons.[20] Therefore, this criterion is not useful to the present problem. Another prominent effect of ring current is the marked anisotropy of the magnetic susceptibility. In aromatic systems, the out-of-molecular plane susceptibility is large compared to the in-plane susceptibilities. We have calculated the magnetic susceptibilities of all the molecules that are considered here and the results are given in the table 1.

As anticipated large anisotropies can be seen (Table 1) for all the aromatic systems under consideration. Our results are in good agreement with the earlier results on some of the molecules.[21] As the size of the aromatic ring increases the absolute value of the anisotropy also increases. Interestingly, all the annelated rings have larger anisotropies compared to the corresponding parent aromatic ring except for cyclobutane. However, this does not imply that the annelated rings are more aromatic. Several authors have recognised that the large anisotropy can be realised even in the absence of any 'ring current' for certain systems.[20,22] Therefore, large anisotropies are not entirely due to the ring current, especially in strained systems.

To probe aromaticity in these systems NICS method has been used.[23] NICS values depend on the size of the aromatic ring. Consider the systems, **1**, **10**, **19** and **28**. As the size of the ring increases from 5, 6 to 7, the absolute NICS value decreases. This does not necessarily mean that the 'aromaticity' in these systems differ by that much magnitude. It only indicates that the ring current calculated by NICS value depends on the size of the ring. Therefore, for meaningful results it is best if the comparisons were made within the same ring.

Annelation of one cyclopropane, has no dramatic effect on the ring current on any kind of aromatic system. As one goes from 5, 6 to 7 membered rings there is a gradual increase in the NICS value, indicating that the larger systems gain ring current by CP annelation (Table 1). The same is true for DFCP annelation also. Multi-annelation of three membered rings have dramatic effect on the ring current of the five membered rigs. Annelation of two cyclopropanes or two DFCP to **1**, **10** has decreased the aromaticity considerably, (more than 50%) (Table 1). Unlike mono-annelation, there is no gradual change in the NICS values as a function of the ring size (Table 1) for multi-annelation. Though there is a small decrease of NICS value for **21, 23, 30** and **32**, it is not chemically significant. NICS values do not always run parallel with the strain energies. This is because the most strained species (Table 1) are not always least aromatic. In five membered rings it is true that strain decreases the ring current but for six and seven membered rings despite the large strain the aromaticity has not decreased considerably (Table 1). This implies that strain and aromaticity are not linearly related. Strain, in the present systems, is mostly from the constrained bond angles but the changes in ring current are not entirely due to the strain in these systems.

Annelation of cyclobutanes has no effect on the NICS values for any aromatic ring system considered here. In tune with the stabilization observed upon multi-annelation of cyclobutanes to tropilium cation, the NICS values also found to increase, leading to 'more' aromaticity, as the size of the ring increases (Table 1). The effect of bicyclo[2.1.1]hexane is different for different systems. The ring currents of neither five membered ring nor the seven membered ring are affected by the bicyclo[2.1.1]hexane annelation (Table 1). However, for six membered ring, **27**, nearly a 40% drop in NICS value is observed.

[1.2.3] Conclusions:

Structural criteria are inadequate to understand aromaticity. However, it is advantageous to use wave function derived bond orders than the internuclear bond lengths in calculating Bird's Aromaticity Index. Strain energies vary smoothly as a function of the size of the annelating ring and also the aromatic ring being annelated. Cyclopropane gives maximum strain followed by CB and BH. 1,1-Diflurocyclopropane follows the trends of CP in neutral compounds but for the charged systems the behaviour is different. For negatively charged ions (**4**) strain is less than anticipated and for cations (**31**) it is more than expected. Interestingly, annelation of CB or BH can be stabilizing also. For tropilium cation, annelation by CB and BH stabilizes the cation compared to the parent one. From NICS values, only a few systems are found affected by the annelation of strained rings. In five membered rings, annelation of CPs and DFCPs brought maximum localization (**3, 5, 12** and **14**). Higher rings (6 and 7) were only marginally perturbed by the strained ring annelation. Not withstanding the original claim of Mills-Nixon, strain and aromaticity are not directly related. More strain does not necessarily imply greater decrease in the ring current.

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[1.3] Aromaticity, Nonaromaticity and Antiaromaticity: The Many Faces of Cyclic 4n+2 π Electrons.

[1.3.1] Introduction

In the last section we have examined the effect of annelation of nonconjugative strained systems on aromatic rings. Annelation of rings that will directly interact with the aromatic π electrons are also equally, if not more, effective in localizing the bonds. However, annelation of these rings increases the total number of π electrons in the system. Then the aromatic nature of the total system itself is perturbed. For example, biphenylene, **1**, is a 4n electron system (total 12 π electrons) which is aromatic.[1] Each benzene ring preserves its own ring current, albeit less than that of free benzene. Does it imply that annelation of any two 4n+2 π system retains aromaticity? What is the relationship between the total number of π electrons and aromaticity in these systems? Our theoretical investigations at Becke3LYP/6-31G* level of theory,[2] on a set of isoelectronic molecules, **1-16,** reveals that for a given number of 4n or 4n+2 π electrons it is *not* possible in general to ascertain its aromaticity. The systems can be aromatic, nonaromatic and antiaromatic depending on the nature of the annelating rings.

[1.3.2] Results and Discussion

While no calculations exist on many of the compounds under study, biphenylene, **1**, and its higher analogues, **9** and **10**, are subjected to many theoretical[3] and experimental studies.[4] There is a remarkable agreement between various theoretical methods that **1** is aromatic.[3] Chemically it behaves like any other tricyclic aromatic hydrocarbon.[4] The aromaticity of **1** is also reflected in the high value of magnetic susceptibility exaltation (MSE),[5] -14.0 (Table 1).[3] This value is close to that of benzene, -17.2. From NICS data,[6] which allows to measure the ring current of individual rings, each benzene ring in **1** is half aromatic (Table 1).[3]


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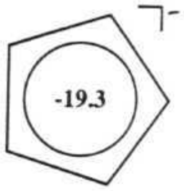
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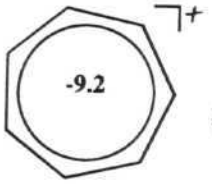
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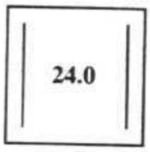
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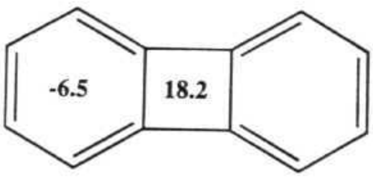
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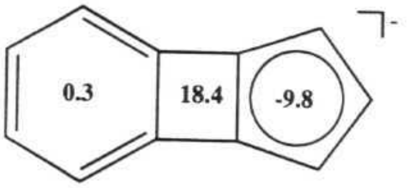
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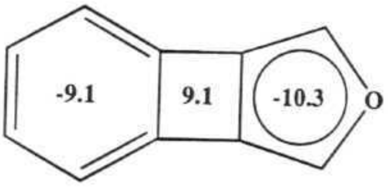
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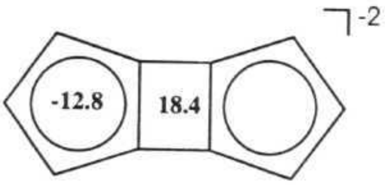
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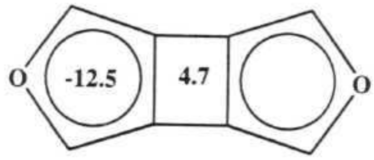
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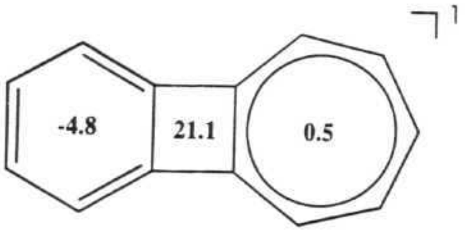
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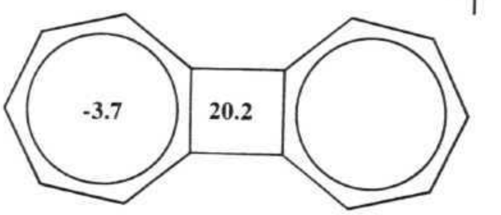
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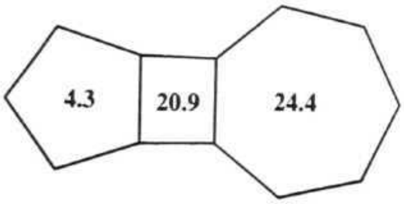
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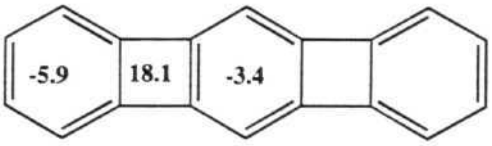
20.9
24.4

8

Recent NMR experiments by Mitchel also came to the same conclusion that on a relative scale of aromaticity **1** is half as aromatic as benzene.[1(d)]

Contrasting behaviour is observed when one of the benzene ring in **1** is replaced by cyclopentadienyl anion, resulting in norborphenylene, **2**. Obviously, both **1** and **2** are isoelectronic. Norborphenylene, **2**, has been prepared by Carvo and co-workers but due to its quick dimerization no detailed information is available.[7] Our calculations on **2** reports very interesting magnetic properties. In contrast to **1**, calculations suggest that **2** is not aromatic. The MSE data does not indicate the presence of appreciable ring current in the molecule. In agreement with the MSE, NICS values for 6 and 5 membered rings in **2** also indicate diminished ring currents (Table 1). This may be due to the shift of the negative charge from five membered ring to the six membered ring. Maximum negative charge, from Natural Population Analysis (NPA),[8] is spread over five and six membered rings. This has dual consequences. There is a net increase in the effective number of π electrons at the six membered ring and simultaneous decrease at the five membered ring. Consequently **2** is nonaromatic. Further support came from studying the neutral system **3** where the five membered ring is replaced by furan. Structure **3** is aromatic. High aromaticity is indicated by the considerably larger MSE value (Table 1) and both the 5 and 6 membered rings have significant ring currents as seen from NICS values (Table 1). The restoration of ring current in **3** supports the argument based on charge. The four membered rings in all of these molecules have substantial antiaromaticity with the possible exception of **3**.



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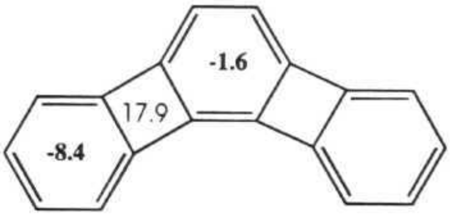

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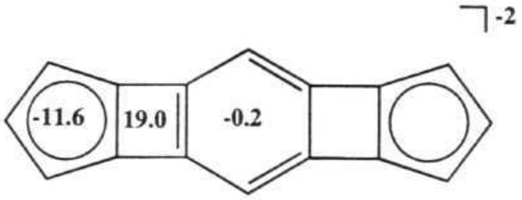

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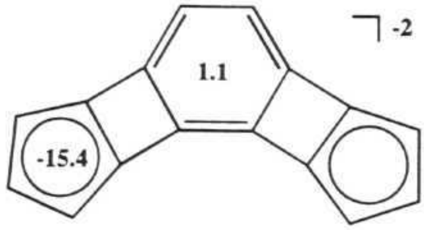

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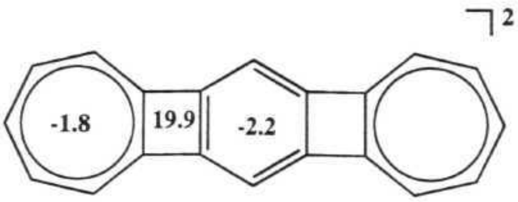

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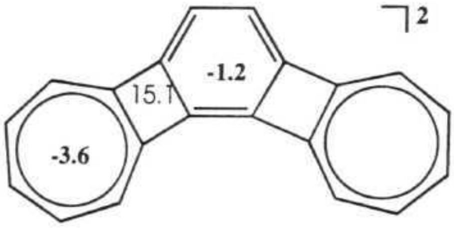

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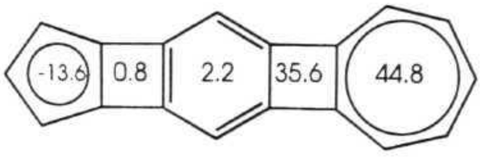

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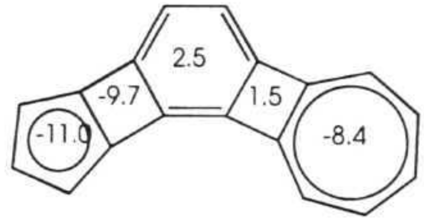

16

Replacement of the two 6 membered rings in **1** by cyclopentadienyl rings, **4**, shows yet another behaviour. Despite each five membered ring in **4** being aromatic, from NICS, (Table 1), the total system is nonaromatic as indicated by the small MSE value (Table 1). However **5**, the neutral analogue of **4**, restores the aromaticity as in **3**.

This unusual behaviour is not just confined to the systems with negative charge alone; annelation of tropilium cation to benzene, **6**, also follows the same pattern. Structure **6** is also not aromatic (Table 1). Neither of the rings, 7 or 6, have appreciable ring currents, from NICS data (Table 1). Interestingly, **6** has been synthesized and found to be a stable molecule.[9] All the ring protons resonate around 7 - 8 ppm relative to the TMS standard, despite the absence of ring current. The spread of charge over the ring is one of the reasons attributed for the observed behaviour. This example emphasises the fact that the ^{1}H NMR chemical shifts which may resonate at the so called aromatic region does not necessarily reflect the presence or absence of ring current. Unlike the dianion **4**, annelation of two tropilium cations, **7**, shows the presence of considerable ring current. The MSE value of **7** is close to the value of tropilium cation. This behaviour parallels that of **1**. Both are only half as aromatic in comparison to their parent molecules.

We have also studied an isomer of biphenylene, **8**, a neutral compound comprising 5 and 7 membered rings. Structure **8**, can be viewed as an annelation of cyclopentadienyl anion and tropilium cation. Interestingly, **8**, is highly antiaromatic, with large +ve MSE value, 49.0 (Table 1). The strong antiaromaticity is reflected in all the rings. Each ring in **8** is strongly antiaromatic, with huge paratropic NICS values (Table 1). Energetically **8** is 49.6 kcal/mol higher than **1** (Table 1).

This kind of behaviour is not limited to the systems with 4n π electrons, which may have inherent tendency to be anti(or non)aromatic. The next higher homologue, [3]phenylene and the isoelectronic analogues, which posses 4n+2 (18) π electrons also behaves in a similar way. That is, apriory prediction of their aromatic is not possible. We have considered the linear **9** and the angular **10** forms of [3]phenylene and its isoelectronic analogs. In agreement with the earlier work, **10** is thermodynamically more stable than the **9**.[4] As anticipated MSE data indicates that **10** is more aromatic than **9**. Interestingly, according to the NICS data, the middle ring in both **9** and **10** does not show any ring current (Table 1). However, the terminal benzene rings gain considerable ring current in **10** compared to **9**.

Replacement of the two terminal benzene rings by cyclopentadienyl rings give rise to **11** and **12**. Both have very different aromatic properties. While the linear arrangement does not show any exaltation, the angular structure is considerably aromatic. Interestingly, the NICS value of the four membered ring in **12** is notably reduced compared to **11**. Thermodynamically **12** is more stable than **11** (Table 1).

A similar behaviour is observed for **13** and **14**, which have terminal tropilium cations. The angular annelation, **14** is more aromatic than **13**. However, **13** is more stable than the angular one **14**, contrary to the stabilities of **9** - **10** and **11** - **12** (Table 1). We have also studied two isomers of **9** and **10**, comprising 5, 6 and 7 membered rings, **15** and **16**. The liner arrangement, **15**, showed significant antiaromaticity (Table 1). Thermodynamically **15** is 63.4 kcal/mol higher in energy than **10**. Contrary to the expectations, the angular arrangement **16** is most aromatic of the 18 π electron systems studied so far. However, **16** is not the most stable arrangement (Table 1). This implies that the most stable isomer need not be most aromatic.

[1.3.3] Conclusions

The aromaticity in the 4n+2 annelated systems does not depend on the number of π electrons. The aromatic nature of a given system depends on the size, type and charge of the ring. This study further emphasises the fact that the thermodynamic stability of a given system depends on many factors and aromaticity is one among them.

Table 1 Various criteria, magnetic susceptibilities and relative energies for the systems **1** - **16.**

Molecule	χ	$\chi_{\perp}$	$\chi_{\parallel}$	**MSE**	**NICS**	**RE**
Benzene	-46.1	-92.7	-22.8	-17.2	11.5	
$C_5H_5^-$	-46.9	-78.7	-31.0	-14.4	19.3	
Furan	-45.5	-61.1	-24.1	-9.7	13.8	
$C_7H_7^+$	-36.4	-111.5	-12.5	-21.1	9.2	
C_4H_4	-7.6	7.0	-15.0	12.0	-24.0	
1	-63.4	109.4	40.5	-13.4	(6)-6.5; (4) 18.2	0.0
2	-50.4	54.0	48.6	4.0	(6) 0.3;(5) -9.8;(4) 18.4	
3	-62.6	101.8	43.1	-14.1	(6) -9.1;(5) -10.3;(4) 9.1	
4	-63.6	76.4	57.0	-5.7	(5) -12.8;(4) 18.4;	
5						
6	-48.2	84.3	30.2	-2.2	(6) -4.8;(7) 0.5;(4) 21.1	
7	-59.4	138.2	20.1	-17.7	(7) -3.7;(4) 20.2	
8				49.0	(7) 24.4; (5) 4.3; (4)20.9	49.0^b
9	-83.1	-133.8	-57.7	-10.5	(6)^a -3.4; (6) -5.9; (4) 18.1	0.0
10	-91.9	-159.4	-58.2	-19.3	(6)^a -1.6; (6) -8.4 (4) 13.3	-2.5
11	-76.7	-81.5	-74.2	3.0	(6) -0.2; (5) -11.6; (4) 19.0	0.0
12	-95.0	-134.0	-75.6	-15.3	(6) 1.1; (5) -15.4 (4) 6.8	-11.1
13	-70.8	-138.1	-37.1	-7.3	(6) -2.2; (7) -1.8; (4) 19.9	0.0
14	-79.9	-164.9	-37.4	-16.4	(6) -1.2; (7) -3.6 (4) 16.8	4.1
15	59.2	288.9	-55.7	130.2	(6) 2.2 (4) 0.8 (5) -13.6 (7) 44.8 (4) 35.6	63.4^c
16	-107.8	-211.0	-56.2	-36.8	(6) 2.5 (4) -9.7 (5) -11.5 (7) -8.4 (4) 1.5	56.6^c

[a] middle six membered ring; [b] relative to **1**; [c] relative to **9**.

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Chapter 2

Stability Vs Aromaticity in Inorganic Benzenes and Monohetero Aromatic Systems

[2.0] ABSTRACT:

A systematic estimation of aromaticity in $X_3Y_3H_6$, **1**, (X= B, Al and Ga; Y= N, P and As), $P_3N_3H_6$, **2**, and $X_3Z_3H_3$, **3**, (Z= O, S and Se) has been done using structural, energetic and magnetic criteria. Estimates based on aromatic stabilization energy (ASE) calculations predict that **1BN** (**1**, X = B and Y = N) and **1BP** are equally aromatic. Contrary to this MSE and NICS indicate that **1BN** is not aromatic while **1BP** is. This emphasizes the fact that energetic and magnetic criteria need not go parallel. Based on MSE and NICS values, all **1XP** compounds show strong aromatic character; **1XAs** are border-line aromatic while **1XN** compounds are non-aromatic. Despite being aromatic all **1XP** and **1XAs** compounds are found to prefer non-planar geometries. Contrary to the MSE predictions, NICS values indicate that none of the compounds **3** is aromatic. Despite the existence of a large number of well established structures and substantial aromatic stabilization energy, phosphazenes, **2**, are not aromatic from NICS data.

Ab initio studies at the B3LYP/6-311++G** level have been done on the aromatic and antiaromatic isomers of C_4H_4X (X = BH, AlH, CH^+, SiH^+, C, Si, N^+ and P^+), **1, 2, 3** and **4**. Contrary to the general belief that aromatic isomers are more stable than antiaromatic ones, we find that, **4BH**, **4AlH** and **4SiH⁺** are thermodynamically more stable than the corresponding aromatic **1, 2** and **3** isomers. However, for C, Si, N^+ and P^+ the aromatic isomers, **1**, are more stable. All the type **3** structures except **3AlH** and **3SiH⁺** are minima. The minimum energy structures, **6AlH** and **6SiH⁺** show novel bonding characteristics.

[2.1] Aromaticity in $X_3Y_3H_6$ (X= B, Al and Ga; Y= N, P and As), $X_3Z_3H_3$ (Z= O, S and Se) and Phosphazenes.

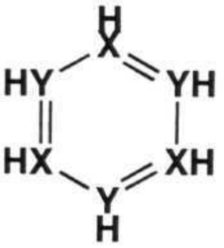
[2.1.1] Introduction

Inorganic cyclic ring systems that are isoelectronic to benzene have been known for many years. Borazine, **1BN** (**1**, X=B and Y=N) and phosphazene, **2**, are text book examples.[1] Numerous derivatives of **1BN** have been synthesized and well characterised.[2] Planarity, equal bond lengths and the similarity in physical properties with benzene gave the name 'inorganic benzene' to borazine. However, the chemical properties of borazine are quite different from benzene.[1,3] Borazine readily undergoes several polar addition reactions which are extremely difficult with benzene. Theoretical calculations have shown that the π electrons are localized on nitrogen atoms making it basic; boron as expected is acidic in nature.[3] Power's group has synthesized several heavier analogs of borazine; **1BP**, **1GaP, 1AlN** and **1GaN**.[4] A few of the group 16 analogs of the borazine family, $X_3Z_3H_3$ (X= B, Al and Ga; Z=O, S and Se), **3**, are also known; boraxine, **3BO** and the B-S analog, **3BS** are well characterized examples.[5] Phosphazenes, **2**, represent another class of inorganic benzenes where the hyper-valent phosphorus is involved in the delocalization.[6] The extent of aromaticity in these systems is of current interest.

Several attempts have been made to estimate the aromaticity in these systems.[7,8] Aromatic stabilization energy (ASE) calculations based on homodesmotic equations (Eq. 1) have shown that **1BN** and **1BP** have nearly equal stabilization (10.1 and 11.2 kcal/mol, respectively) which are close to half of the value for benzene (22.2 kcal/mol) (at MP4/6-31G*//HF/6-31G*).[7b] However, magnetic susceptibility exaltation (MSE) data, based on group increment values, indicate that **1BN** is not aromatic (-1.7), compared to benzene (-13.7).[8] No MSE data exists for **1BP**. Both **1BN** and **1BP** form metal complexes of the type $(B_3Y_3H_6)Cr(CO)_3$ but they differ substantially in the mode of bonding.[9,10] Borazine metal complex, **4BN**, is puckered, indicating the preference for σ type of bonding where the lone pairs of N interacts with the metal. The phosphorous analog, **5BP**, is more like benzene complex, **5CC.** This is an indication that the π delocalization is more than that in **1BN**, which is not reflected in ASE estimates. Are aromatic stabilization energies good indicators of aromaticity?

Phosphazenes, $P_3N_3R_6$, **2**, present a similar dilemma.[6] The planarity, equal and short PN bond distances, high stability and extreme reluctance to reduction resemble that of aromatic compounds. But there exists a significant difference. The delocalization here is from $d\pi$-$p\pi$ overlap. Can this overlap be sufficient enough to make the derivatives of **2** aromatic? What is the extent of delocalization present in these systems?

Any criteria of aromaticity provides a spectrum of values. How do we draw the line of demarcation between aromatic and nonaromatic compounds? To make the discussion tractable we arbitrarily assign the convention that if a molecule has less than half the magnitude of property in comparison to that of benzene, it is not aromatic. Currently there exists no comparison of aromaticity based on the structural, energetic and magnetic criteria for the inorganic benzenes. Theoretical studies that are directed to address aromaticity in **3** are almost non-existent. Several theoretical studies exist in the literature on **2** to understand the bonding and the role of 'd' orbital participation in bonding.[18] But relatively little work has been done on the aromaticity of these class of compounds.



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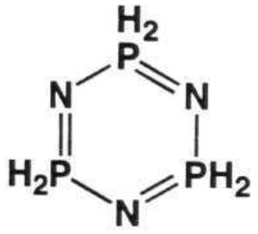

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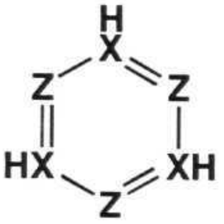

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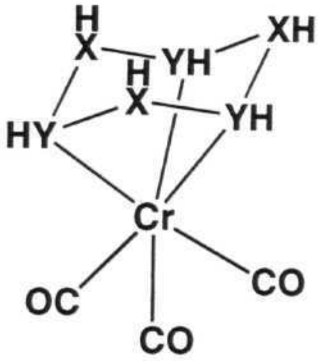

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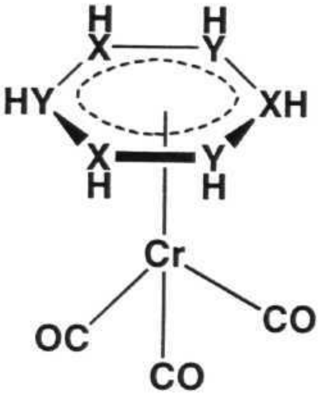

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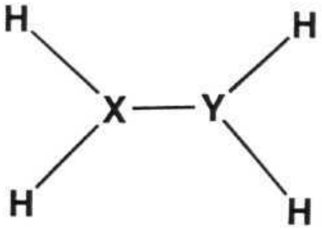

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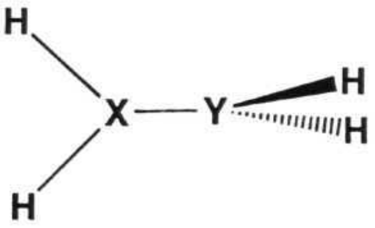

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In this section, structural, energetic and magnetic criteria have been used to ascertain the relative aromaticity of $X_3Y_3H_6$ (X = B, Al, and Ga; Y = N, P and As), $X_3Z_3H_3$ (X = B, Al, and Ga; Z = O, S and Se) and $P_3N_3H_6$.

The hybrid HF-Density functional calculations using Becke, Yang and Parr correlation functional and 6-31G* basis set (B3LYP/6-31G*) is used for all the molecules considered here.[19] Full geometry optimizations were done for all molecules and vibrational frequencies were calculated to establish the nature of stationary points. All calculations were performed using Gaussian 94 series of programmes.[20] The total energies of $X_3Y_3H_6$ and $X_3Z_3H_3$ along with benzene are given in Tables 1, 2 and 3. We have used the energies and properties of the optimized planar form of the rings in establishing the aromaticity index. This is because, for most systems, the experimentally known structures are planar. Comparisons can be easily made across the ring systems if all of them have planar geometries.

NBO analysis is used to gain further insight into the bonding in these molecules, using the standard routine given in Gaussian 94 programmes.[21] The non-NRT (Natural Resonance Theory) bond indices namely Wiberg bond indices (WBI) has been used to gauge the bond strengths.[21]

The NMR shielding tensors were computed at two different methods, (1) the Gauge-Independent Atomic Orbital (GIAO) and (2) the Continuous Set of Gauge Transformations (CSGT) methods.[22,23] The magnetic susceptibility tensors were computed with CSGT-B3LYP/6-31G*//B3LYP-6-31G* and the NICS values at the GIAO-HF/6-31G*//B3LYP-6-31G* method by placing a ghost atom (symbol Bq for Gaussian 94 input) at the geometrical center of the molecule.[16]

Table 1. Total Energies of $X_3Y_3H_6$ (**1**) along with Zero Point Energies (ZPE) calculated at B3LYP/6-31G* level.

Structure	**Total Energy (a.u)**	**ZPE (Kcal/mol)**
1BN	-242.67016	58.63
1BP	-1102.24107	43.25
1BAs	-6779.43801	40.12
1AlN	-895.37568	43.58
1AlP	-1755.04751	32.04
1AlAs	-7432.31683	29.60
1GaN	-5936.79088	43.64
1GaP	-6796.52559	31.79
1GaAs	-12473.80812	29.11

Table 2. Total Energies of $X_3Z_3H_3$ (**3**) along with Zero Point Energies (ZPE) calculated at B3LYP/6-31G* level.

Structure	**Total Energy (a.u)**	**ZPE (Kcal/mol)**
1BO	-302.31918	34.71
1BS	-1271.08422	26.62
1BSe	-7274.64758	26.60
1AlO	-955.09713	22.42
1AlS	-1923.94340	18.36
1AlSe	-7927.56413	17.16
1GaO	-5996.45424	21.14
1GaS	-6965.39015	17.71
1GaSe	-12969.03532	16.57

Table 3 Important parameters for Benzene (**1CC**), Ethylene (**6CC**) and 1,3-butadiene (**8CC**) calculated at B3LYP/6-31G* level.

	1CC	6CC	8CC
Energy (a.u)	-232.24886	-78.58746	-155.99214
Susceptibility ε_1	92.56	19.35	34.24
ε_2	22.82	10.18	18.00
ε_3	22.82	9.53	16.18
ASE (kcal/mol)	21.9		
MSE ($\Lambda_{av.}$)	-16.7		
NICS	-11.5		

Table 4. X-Y Bond lengths (Å) and Wiberg Bond Index (WBI) of $XH_2YH_2\|$ (**6**), $X_3Y_3H_6$ (**1**) and $XH_2YH_2\perp$ (**7**) systems.

Structure	Z = N	Z = P	Z = As
7BZ	1.473 (0.88)	1.967 (1.05)	2.060 (1.05)
1BZ	1.431(1.00)[1.429][a]	1.841 (1.35) [1.840][d]	1.915 (1.35)
6BZ	1.393 (1.26)	1.796 (1.63)	1.871(1.64) [1.926][e]
7AlZ	1.809 (0.57)	2.371 (0.82)	2.439 (0.84)
1AlZ	1.801(0.56)[1.782][b]	2.268 (0.92)	2.325 (0.95)
6AlZ	1.780 (0.77)	2.235 (1.07)	2.281 (1.04)
7GaZ	1.897 (0.65)	2.352 (0.86)	2.423 (0.87)
1GaZ	1.848(0.72) [1.859][c]	2.234 (1.01)	2.296 (1.04)
6GaZ	1.832 (0.87)	2.208 (1.19)	2.265 (1.23)

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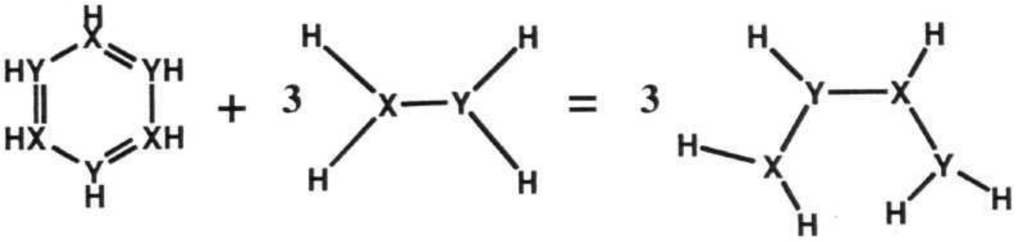
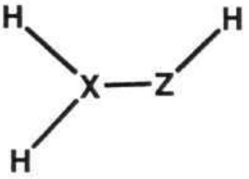


Eq. 1

1 6 8



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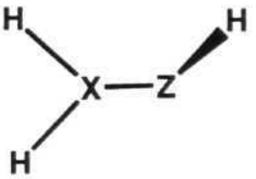

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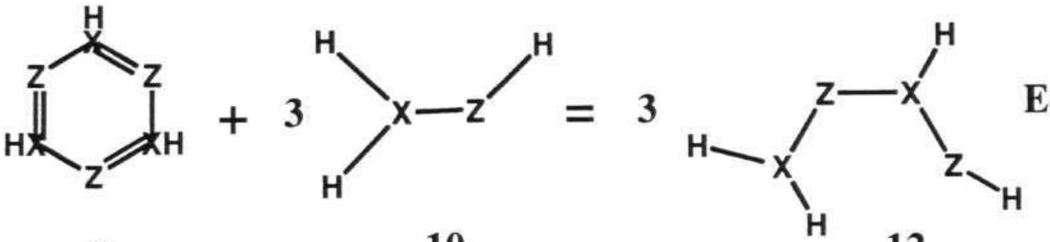
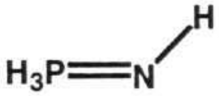


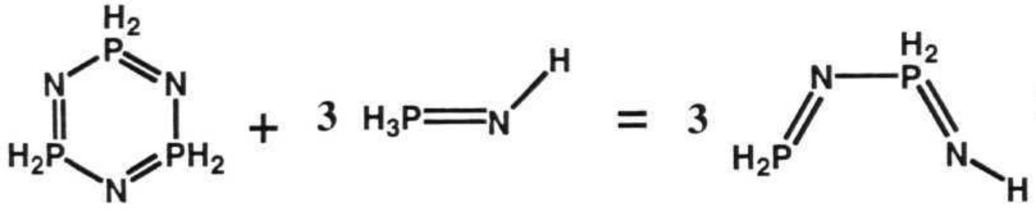
Eq. 2

3 10 12



$H_4P{-}NH_2$

13 14



Eq. 3

2 13 15

[2.1.2] Results and Discussion:

[2.1.2.1] *$X_3Y_3H_6$ systems*:

Structural Criteria: In the discussion of relative aromaticity of inorganic benzenes, it is useful to start with the structural data. The bond length equalization which is the hallmark of aromaticity for hydrocarbons has also been observed in borazine and the related systems. In borazine the B-N bond length is intermediate between single and double bond lengths. For comparison X-Y bond lengths in XH_2YH_2 (**6**) and XH_2YH_2 (**7**) as well as WBI are given in Table 4.[21]

In general, the X-Y distance in $X_3Y_3H_6$ systems is calculated to be intermediate between single and double bond lengths for all the X and Y considered here (Table 4). As the size of the atoms increases the X-Y distances tend to increase. Thus, the structural data point to a delocalized description for six membered rings. To gain further insight into the bonding between the X-Y bond pairs Wiberg bond orders have been calculated.[21] For polar bonds the bond orders will be less than the corresponding covalent bond orders. The WBI indicates that the bond order decreases with the increase in the electronegativity difference between X and Y (Table 4). For most of the compounds under the present study, the X-Y single bond order, as modelled by $XH_2YH_2\perp$, **7**, is less than one. For X=Y (**6**) double bonds, WBI is much less than two. The WBI for **1BP** is highest of all; reflecting the enhanced delocalization in comparison with other compounds. This indicates **1BP** to be the most aromatic among the systems considered here. However, the bond-length criteria alone is not sufficient to probe aromaticity.[8]

Energetic Criteria: Traditionally, aromatic stabilization energy is associated with the aromaticity of the chemical systems under consideration. Homodesmotic equations, which preserve similar bond types on both sides, have

been widely used to estimate aromatic stabilization energies.[12] The accuracy of the ASE calculation depends on the reference systems considered. For benzene, homodesmotic equation consisting of the ethylene and cis-1,3-butadiene is found to give best results.[8] Similar equations were applied to several inorganic ring systems such as Si_6H_6 and P_6 with considerable success.[11a,b, 24]
Earlier, aromatic stabilization energy calculations using Eq. 1, have been performed on **1BN**, **1BP** and **1AlN**.[7b] As anticipated from the electronegativity difference between the bond pairs, **1AlN** has very low aromatic stabilization energy. Surprisingly, despite the different bond polarities, both borazine and boraphosphabenzene, possess very similar aromatic stabilization energies. We used similar equation (Eq. 1) for estimating the aromaticity for $X_3Y_3H_6$. The calculated energy values are depicted in Table 5. In the estimation of energies planar geometries were used for all of the reference systems, even though some of these were not minima.

In agreement with the earlier work, both **1BN** and **1BP** have very similar aromatic stabilization energies.[7b] **1AlN** has very small ASE in accordance with the electronegativity difference between the aluminium and nitrogen. In general, as the electronegativity difference between the X-Y pairs increases the ASE decreases. This is in tune with the observation that overlap of orbitals centred on atoms decreases with increasing electronegativity difference. However, the delocalization is not the only factor that contributes to the final value of the aromatic stabilization energy. Strain and other factors would also influence. It is extremely difficult to delineate these contributions from the total value of Eq. 1. Hence, the energy criteria need not necessarily reflect the relative aromaticity of the systems considered. The next section considers studies based on magnetic properties of $X_3Y_3H_6$ systems.

Table 5. Aromatic stabilization Energies (ASE) (in Kcal/mol) and Magnetic Susceptibility Exaltation (Λ) values (in cgs units) calculated at B3LYP/6-31G* level and Nucleus Independent Chemical Shift (NICS) values of $X_3Y_3H_6$ systems at GIAO-Hf/6-31G*//B3LYP/6-31G* level.

Structure	**Y = N**	**Y = P**	**Y = As**
1BY; ASE	9.6	10.4	8.7
Λ	-5.9	-17.8	-20.3
NICS	-2.1	-7.9	-8.3
1AlY; ASE	2.0	2.8	-0.7
Λ	-4.5	-9.7	-12.1
NICS	-2.2	-4.9	-5.6
1GaY; ASE	5.7	3.2	2.4
Λ	-1.3	-10.0	-12.9
NICS	-1.5	-5.3	-6.0

Magnetic Criteria: Aromatic compounds have very large out-of-plane susceptibilities in comparison to the in-plane components. The magnetic susceptibility data for $X_3Y_3H_6$ systems along with the values for **6** and **8**, which are necessary for the increment scheme is given in Table 5. Almost all compounds have large out-of-plane susceptibilities (ε_1) except for **1AlN**. The magnetic susceptibility exaltation was successfully applied by Dauben and coworkers for a large number of hydrocarbons. For the present systems, the MSE, Λ, is defined according to Eq.1 (Table 6). These can be compared to the MSE value of -16.7 calculated for benzene (Table 3). According to this **1BN** is not aromatic which in accordance with earlier results (Table 5).[8] This contrasts with the comparable ASE values of **1BN** and **1BP**. Further estimates of aromaticity can be made from NICS.[16] These are given along with the exaltation data (Table 5). The NICS values reflect the same trends as that of MSE. Large NICS values can be seen for **1BP** and **1BAs** compounds. The compounds involving Al, Ga, P and As are border-line aromatics.

Table 6 Magnetic Susceptibility Data (in ppm cgs units with the signs reversed) for $X_3Y_3H_6$ (**1**), **6** and **8**, calculated at CSGT-B3LYP/6-31G* level.

Structure	ε_1	ε_2	ε_3	$\chi_{av.}$
6BN	17.22	13.17	9.76	13.38
8BN	31.90	22.19	18.65	24.25
1BN	57.48	29.03	29.03	38.51
6BP	25.89	19.23	18.31	21.14
8BP	46.25	34.55	33.15	37.98
1BP	113.17	45.87	45.87	68.30
6BAs	35.44	29.51	28.93	31.29
8BAs	65.34	55.09	52.49	57.64
1BAS	147.57	75.25	75.25	99.36
6AlN	23.63	17.65	17.33	19.34
8AlN	41.15	35.33	32.25	36.24
1AlN	57.54	57.54	48.79	54.62
6AlP	31.28	25.52	22.69	26.50
8AlP	56.10	49.48	44.10	49.89
1AlP	86.76	76.36	76.36	79.83
6AlAs	43.38	35.65	32.62	37.22
8AlAs	78.92	69.25	63.53	70.56
1AlAs	121.25	107.53	107.53	112.10
6GaN	31.63	29.84	28.90	30.12
8GaN	58.90	57.73	56.06	57.78
1GaN	83.69	83.59	83.59	83.62
6GaP	42.06	38.30	34.94	38.77
8GaP	77.22	74.65	68.03	73.30
1GaP	121.52	111.15	111.15	114.61
6GaAs	52.12	48.20	45.16	48.49
1GaAs	157.22	136.24	136.24	143.23

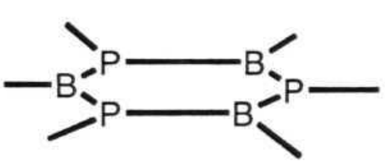
Though not exact, there is a good correlation between the electronegativity difference between the heavy atoms involved in the ring and various parameters of aromaticity. Thus, the top right side of the table 5 gives the systems with highest aromaticity. The bottom left has the least aromatic candidates. These are also the ones with extreme electronegativity differences. There is a progressive increase in aromaticity from nitrogen to phosphorous to arsenic in these systems. According to the yardstick of 50% value of benzene, all the $X_3Y_3H_6$ systems except X = N are aromatic.

Planarity Vs. Non-Planarity: We have noticed in the previous section that the phosphorus and arsenic compounds of B, Al and Ga are aromatic or quasi-aromatic. However, all of them are third-order stationery points on the B3LYP/6-31G* potential energy surface, with the imaginary frequencies corresponding to the out of plane movement of P or As atoms. These distortions are expected to decrease the π interaction with the neighbouring groups. What are the overriding factors responsible for the ring puckering?

Table 7 Total and Relative Energies (with respect ot the planar structures, **1XY** of Table 1) of the optimized structures of $X_3Y_3H_6$ (**1**) systems calculated at B3LYP/6-31G* level.

Structure	Total Energy (ZPE)	RE
9BP	-1102.24108 (43.05)	0.71
9BAs	-6779.46291 (41.74)	15.64
9AlP	-1775.06243 (32.58)	9.36
9AlAs	-7432.34085 (30.17)	15.07
9GaP	-6796.55234 (31.11)	16.90
9GaAs	-12473.84769 (29.95)	24.83

To understand these factors, we have optimized the structures without any symmetry constraints (C_1 symmetry), **9**, (Fig 1). The total and relative energies are given in Table 7. In agreement with the experimentally observed planar geometry of the derivatives of **1BP**, the C_1 symmetry structure is energetically and structurally very close to the planar optimized geometry. This is in contrast to the earlier result (HF/6-31G*) where, the non-planar structure is calculated to be 5 kcal/mol lower in energy than the planar one.[7b]



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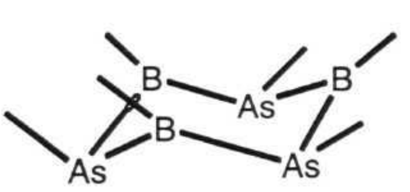

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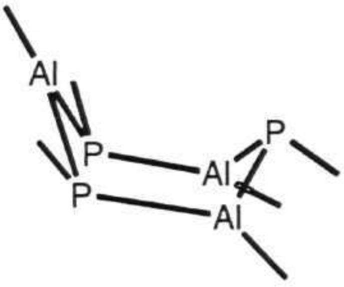

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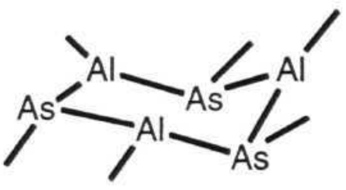

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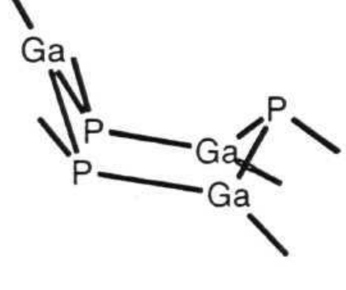

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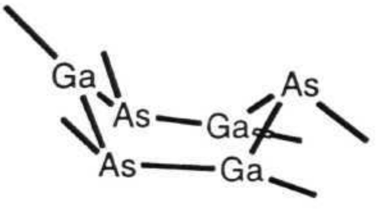

9GaAs

Table 8. Inversion Barriers of YH_3 systems calculated at B3LYP/6-31G* level

Y	T.E. $YH_3(C_{3v})$	T.E. YH_3 (D_{3h})	RE
N	-56.54795	-56.53773	6.42
P	-343.14028	-343.08361	35.56
As	-2235.53747	-2235.46418	45.99

Except **1BP**, all the structures in Table 7 are puckered to a large extent and substantially lower in energy (Table 7). The solid state structure of **1GaP** has a boat conformation with average Ga-P distance of 2.310 Å. We have located a similar kind of boat conformation, **9GaP**, with the average Ga-P distance 2.296 Å. The non-planarity in these compounds is not only due to the small ASE value, but also due to the large inversion barriers of PH_3 and AsH_3 (Table 8). The inversion barrier for ammonia is very small in comparison to other group members. Therefore, all the nitrogen compounds are planar, whereas the remaining structures are puckered. Additionally, the ASE (Table 5) is small except for **1BP**. In other words, the gain in delocalization in the planar geometry is not sufficient to compensate the preference for pyramidalization.

[2.1.2.2] *$X_3Z_3H_3$ systems*:

$X_3Z_3H_3$, **3**, (X = B, Al and Ga; Z = O, S and Se) form another group of 6π electron systems. One lone pair of the group 16 elements is in the plane of the ring and the other lone pair perpendicular to the ring. The well known example in this category is boraxine, $B_3O_3H_3$, **3BO**. The sulphur analog of boraxine is also experimentally known. However, little work has been done on these systems addressing the question of aromaticity. In quantifying aromaticity here, we have essentially used the same methodology as used for $X_3Y_3H_6$ systems.

Table 9. X-Z Bond lengths (Å) and Wiberg Bond Index (WBI) of $XH_2ZH\parallel$ (**10**), $X_3Z_3H_3$ (**3**) and $XH_2ZH\perp$ (**11**) systems calculated at B3LYP/6-31G* level.

Structure	Z = O	Z = S	Z = Se
11BZ	1.364 (0.94)	1.873 (1.16)	2.006 (1.16)
3BZ	1.377 (0.88) [1.383][a]	1.811 (1.26) [1.795][b]	1.928 (1.29)
10BZ	1.354 (1.08)	1.783 (1.43)	1.899 (1.47)
11AlZ	1.697 (0.58)	2.233 (0.77)	2.342 (0.82)
3AlZ	1.721 (0.56)	2.193 (0.82)	2.305 (0.90)
10AlZ	1.714 (0.64)	2.199 (0.90) [2.194][c]	2.300 (0.98)
11GaZ	1.816 (0.64)	2.256 (0.81)	2.358 (0.86)
3GaZ	1.808 (0.63)	2.204 (0.88)	2.307 (0.95)
10GaZ	1.810 (0.73)	2.207 (0.98) [2.208][c]	2.304 (1.05)

[a] Boese, R., Polk, M., Blaser, D. *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 245. [b] Huttner, G. and Kreig, B.; *Chem. Ber.* **1972**, *105*, 3437. [c] Wehmschulte, R. J.; Senge, K. R,; Power, P. P.; *Inorg. Chem.*, **1995**, *34*, 2593.

Bond lengths along with WBI of $X_3Z_3H_3$, **3**, $XH_2ZH\parallel$, **10**, and $XH_2ZH\perp$, **11**, are given in the Table 9. Unlike the bond lengths in $X_3Y_3H_6$ systems (Table 4), the X-Z bond lengths fall in a short range. The WBI shows a slightly different picture. The bond orders do not linearly vary with the bond distances. Nevertheless, the differences between various bond types (single, aromatic and double) have very small differences. It is difficult to categorize these systems as aromatic or otherwise based on bond-lengths.

Aromatic stabilization energies have been calculated using Eq. 2, similar to that used for $X_3Y_3H_6$ systems. Magnetic susceptibility data for the reference compounds are given in the Table 10. The exaltation is also calculated using the same equation and NICS has been calculated similarly. Aromatic stabilization energies, MSE data and NICS values are given in the Table 11.

Table 10 Magnetic Susceptibility Data (in ppm cgs units with the signs reversed) for**3**, **10** and **12** calculated at CSGT-B3LYP/6-31G* level.

Structure	ε_1	ε_2	ε_3	$\chi_{av.}$
10BO	13.60	12.46	6.63	10.90
12BO	25.93	20.11	15.97	20.67
3BO	44.04	29.79	29.79	34.54
10BS	26.35	18.20	14.63	19.73
12BS	53.01	35.93	25.17	38.04
3BS	101.08	45.38	45.38	63.95
10BSe	36.77	27.18	23.50	29.15
12BSe	74.02	54.45	43.13	57.20
3BSe	138.50	72.48	72.48	94.49
10AlO	21.96	15.21	14.49	17.22
12AlO	35.99	34.22	24.79	31.67
3AlO	56.54	56.54	45.12	52.73
10AlS	32.00	24.17	23.84	26.67
12AlS	62.14	48.54	46.89	52.52
3AlS	87.77	87.77	87.15	87.56
10AlSe	40.80	35.90	34.14	36.95
12AlSe	83.03	73.59	66.32	74.31
3AlSe	123.02	117.17	117.17	119.12
10GaO	28.97	26.96	25.51	27.15
12GaO	53.29	50.31	48.37	50.67
3GaO	80.19	80.19	69.64	76.67
10GaS	42.01	36.91	34.52	37.81
12GaS	79.18	72.50	67.84	73.17
3GaS	113.48	113.19	113.19	113.29
10GaSe	50.23	48.85	44.16	47.75
3GaSe	149.79	138.06	138.06	141.97

Table 11. Aromatic stabilization Energies (ASE) (Kcal/mol) and Magnetic Susceptibility Exaltation (Λ) values (in cgs units) calculated at B3LYP/6-31G* level and Nucleus Independent Chemical Shift (NICS) values of $X_3Z_3H_3$ systems at GIAO-HF/6-31G*//B3LYP/6-31G* level.

Structure	**Z = O**	**S**	**Se**
3BZ; ASE	4.2	8.1	3.5
Λ	-5.2	-9.0	-10.3
NICS	0.4	0.9	0.0
3AlZ; ASE	-5.8	1.2	-0.1
Λ	-9.4	-10.0	-7.0
NICS	-2.3	-2.9	-1.9
3GaZ; ASE	3.3	-2.8	-3.3
Λ	-6.2	-7.2	-7.4
NICS	-1.8	-1.8	-1.0

Several interesting points emerge from Table 11. Except for **1BS**, the aromatic stabilization energy for the remaining systems is very small, less than 5 kcal/mol. It is destabilizing (Eq. 2 is endothermic) for **3AlO, 3GaS** and **3GaSe**. The magnetic susceptibilities of **3, 10** and **12** (Table 10) show some unusual properties. As in **1** the out-of-plane susceptibilities of **3** are also large compared to the in-plane values, except for **1AlN**. For Al-O, Ga-O, Al-S and Ga-S compounds the out-of-plane values are less than the in-plane values.

The trends in MSE data differ from those obtained from aromatic stabilization energy results. For most compounds the MSE is more than half of the value for benzene,. indicating these systems are aromatic according to our operational definition. However, NICS presents a different picture. Almost all the compounds have very low NICS values indicating that these are not aromatic.

[2.1.2.3] *Phosphazenes:*

Phosphazenes, $P_3N_3R_6$, **2**, represent yet another class of inorganic benzenes where, unlike earlier systems, $d\pi$-$p\pi$ interactions are invoked to justify delocalization. Numerous derivatives of **2** have been synthesized and well characterised.[25] The bonding in these compounds have attracted several theoretical studies. One of the successful models for bonding in **2** is Dewar's island model.[16a] In this model, the d_{xz} and d_{yz} orbitals are hybridized to give two orbitals which are directed toward the adjacent nitrogen atoms. This allows the formation of three-centre bonds about each nitrogen. Trinquier had explained the bonding without the participation of 'd' orbitals of phosphorous.[16b]

Formally, aromaticity in these compounds arises from the fact that the nitrogen p_z orbital, which is perpendicular to ring, participates in the delocalization with the phosphorus d_{xz} and d_{yz} orbitals. The important parameters of $P_3N_3H_6$, **2**, along with the reference compounds are given in Table 12. For the single and double bonds we have taken PH_4NH_2 (**13**) and PH_3NH (**14**). The homodesmotic Eq. 3 is used to calculated ASE and MSE.

Table 12 Important parameters for $P_3N_3H_6$ (**2**), **13** and **15** calculated at B3LYP/6-31G* level.

	2	**13**	**15**
Energy (a.u)	-1191.88320	-398.44640	-795.73584
Susceptibility ε_1	38.39	20.64	34.13
ε_2	38.23	16.69	33.27
ε_3	38.23	14.58	24.858
ASE (kcal/mol)	9.3		
MSE ($\Lambda_{av.}$)	-2.1		
NICS	-2.2		

The average P-N bond length in the derivatives of **2** is 1.582 Å; the optimized P-N bond length for **2** is 1.605 Å.[26] This bond length is intermediate between P-N single bond length of 1.697 Å in PH_4NH_2, **13**, and P-N double bond length 1.574 Å as seen in PH_3NH, **14**. The aromatic stabilization energy from the Eq. 4 is 9.3 kcal/mol. Since the P-N-P and N-P-P bond angles are very close to the 120°, the strain energy contribution to the total aromatic stabilization energy will be minimum. Despite the substantial aromatic stabilization energy, the MSE and NICS data does not support aromaticity. Both show that **2** is not aromatic. Thus, large ASE value does not necessarily indicate that the system under study is aromatic.

[2.1.3] Conculsions

The aromaticity in $X_3Y_3H_6$, $X_3Z_3H_3$ and $P_3N_3H_6$ systems have been studied using structural, energetic and magnetic criteria. All these criteria can diverge quite strongly from each other. Despite equal aromatic stabilization energies, **1BN** is not aromatic but **1BP** is substantially aromatic form the MSE and NICS data. The MSE and NICS data also do not always parallel each other. This has been the case for the $X_3Z_3H_3$ systems. While ASE and MSE relay on the choice of reference systems, the NICS values do not require a reference system. Based on NICS values phosphazene (**2**) and $X_3Z_3H_3$ (**3**) are not aromatic. However, NICS is no experimentally observable quantity. A judicious use all criteria is needed in gauging aromaticity of these systems.

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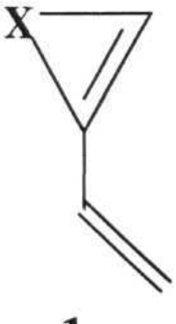
[2.2] Can Antiaromatic Isomers be More Stable Than the Aromatic Ones?

[2.2.1] Introduction

One of the characteristics of aromatic compounds have been their extra stability.[1] Among the possible 256 isomers for C_6H_6 with carbon valence ≤ 4, benzene is the most stable arrangement.[2] Similarly, the story of the isolation of cyclobutadiene, an isomer of C_4H_4, itself is a testimonial to the instability of antiaromatic compounds.[3] Despite the aromatic stabilization certain systems are thermodynamically less stable. For example, in Si_6H_6, non-aromatic hexasila[3]prismane is calculated to be more stable than the hexasilabenzene.[4] There are a few examples in heterobicyclic compounds, where the most stable isomer is the least aromatic.[5] All these examples are confined to aromatic Vs non-aromatic isomers only. We show here that under suitable circumstances antiaromatic isomers can also be more stable than the aromatic isomers.



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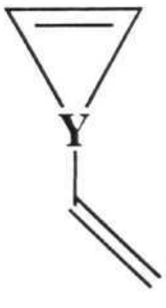

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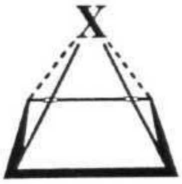


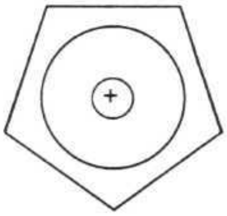
3

4

X = BH, AlH, CH^+, SiH^+, C, Si, N^+ and P^+

Y = B, Al and Si^+

The potential energy surface of C_4H_4X offers a unique opportunity where 2-D aromatic (**1, 2**), 3-D aromatic (**3**) and 2-D antiaromatic (**4**) structures can be realized. Understanding the stabilities of these isomers will provide insight into the interplay between aromaticity and antiaromaticity. Some of these isomers are known to exist. All the three isomers of $C_5H_5^+$, that are considered here are known experimentally.[6] C_5H_4, **4C**, is known to exist in solution,[7] and a dilithium derivative of **4Si** has been recently characterized.[8] Tetra-phenyl derivatives of **4B** and **5Al** are known experimentally as stable compounds.[9]



5

For $C_5H_5^+$, besides the three isomers (**1, 3** and **4**) listed above, cyclopentadienyl cation with triplet ground state, **5**, is also one of the low energy isomer.[10] For a long time, there was a controversy over the most stable isomer of $C_5H_5^+$. Experimental verifications point out that **1CH$^+$** is more stable by 9.60 kcal mol^{-1}, than the **5**.[6] However, calculations at QCISD(T)/6-31G(d,p)//MP2/6-31G(d,p) predict the **5** is 2.0 kcal mol^{-1} lower in energy than vinylcyclopropynyl cation, **1CH$^+$**.[11] Recent calculations at G2 level of theory reversed the QCISD(T) predictions and confirmed that **1CH$^+$** is 2.1 kcal mol$^-$ lower in energy than **5**.[10] Both theory and experiment agree that **3CH$^+$** and **4CH$^+$** are higher energy isomers.[10]

When one of the CH groups in $C_5H_5^+$ is replaced by a hetero group, the relative stabilities of the resulting isomers differ substantially. We have done a limited survey on the relative stability of the structures **1, 2, 3** and **4**. Calculations were done at Becke3LYP/6-311++G** level of theory[12] using the Gaussian 94 programme.[13] Frequency calculations were also done at the same level of theory to ascertain the nature of the stationary points. NBO analysis is used to understand the bonding in these compounds.[14]

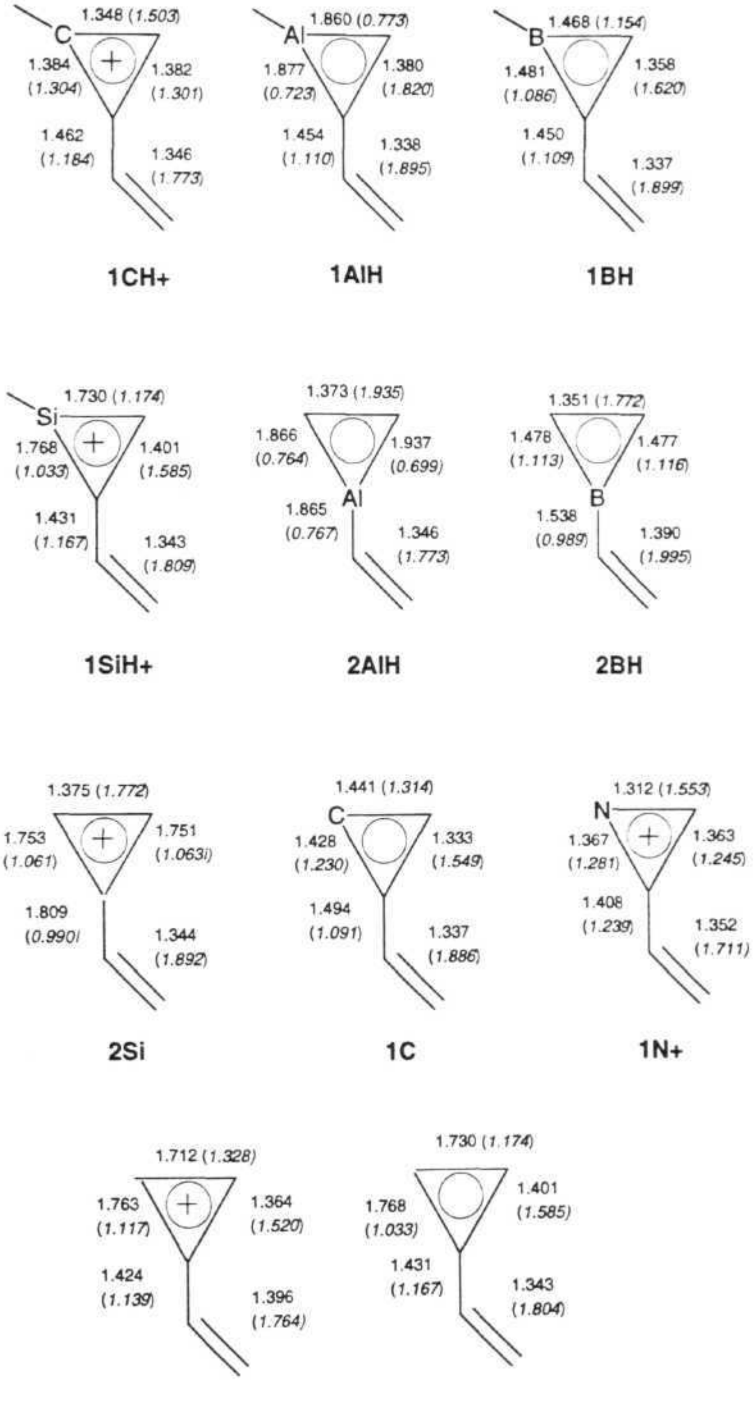
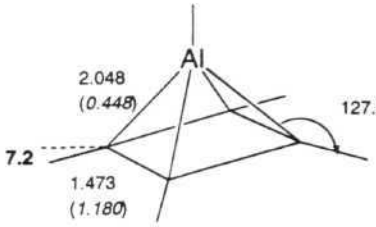
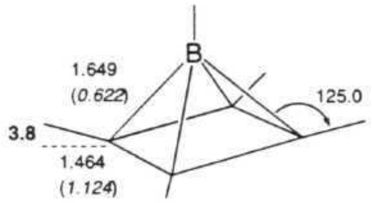


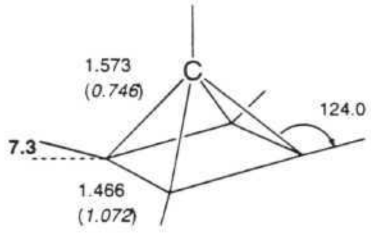
Fig. 1 Bond lengths along with WBI (parenthesis)



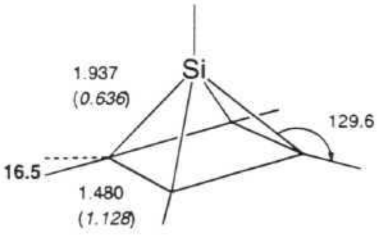
3AlH



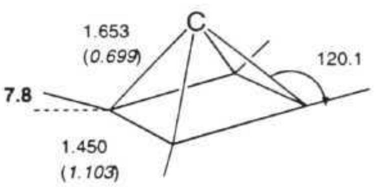
3BH



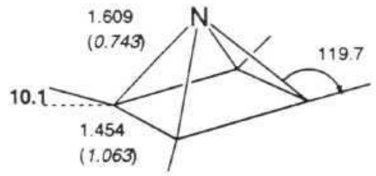
3CH+



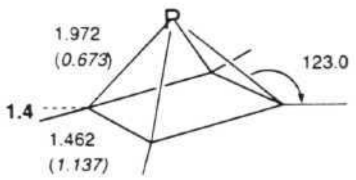
3SiH+



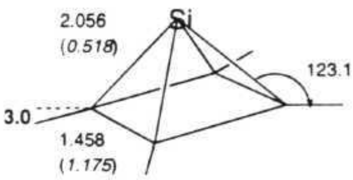
3C



3N+

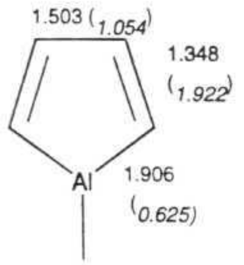


3P+

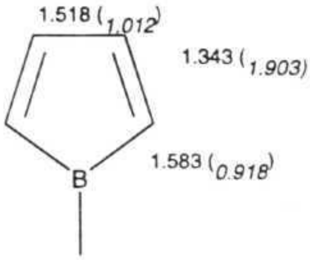


3Si

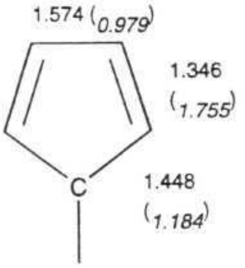
Fig. 2 Bond lengths along with WBI (parenthesis)



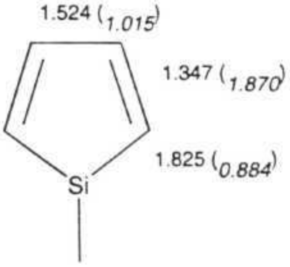
4AlH



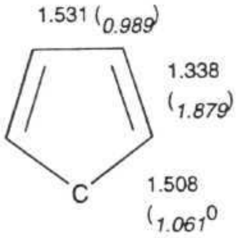
4BH



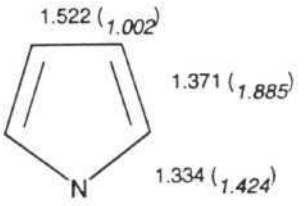
4CH+



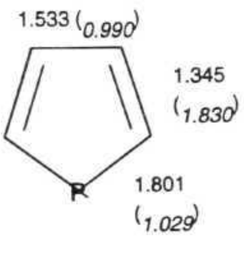
4SiH+



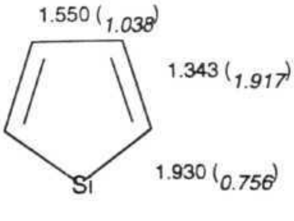
4C



4N+



4P+



4Si

Fig. 4 Bond lengths along with WBI (parenthesis)

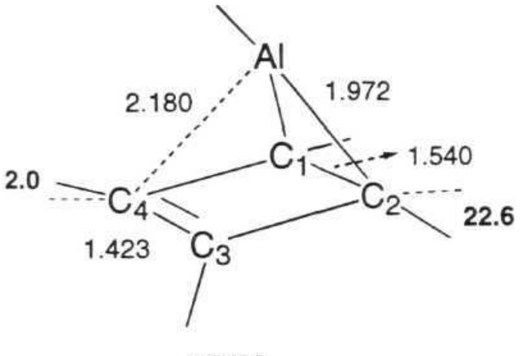
Table 1 Relative Energies (Kcal mol^{-}) and NIMG (parenthesis) of **1**, **2**, **3** and **4**.

X(Y)	**1X**	**2Y**	**3X**	**4X**	**X**	**1X**	**3X**	**4X**
BH(B)	3.1 (0)	0.0 (0)	16.9 (0)	-4.5 (0)	**C**	0.0 (0)	22.3 (0)	18.1 (1)
$CH^+(C^+)$	0.0 (0)	0.0 (0)	26.9 (0)	8.5 (0)	**N^+**	0.0 (0)	33.0 (0)	1.2 (1)
AlH(Al)	0.1 (0)	0.0 (0)	12.3 (2)	-27.1 (0)	**Si**	0.0 (0)	5.2 (0)	0.1 (1)
$SiH^+(Si^+)$	6.2 (0)	0.0 (0)	18.8 (2)	-18.5 (0)	**P^+**	0.0 (0)	4.1 (0)	5.0 (0)

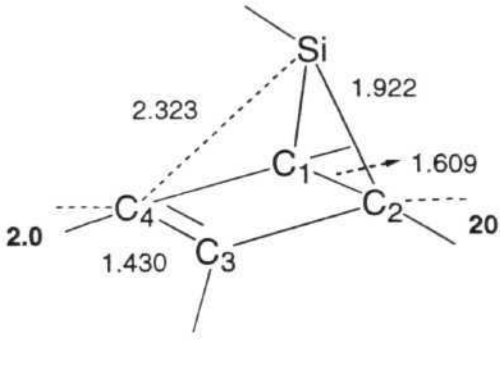
[2.2.2] Results and Discussion:

Energetics: Table 1 lists the relative energies of the various isomers considered along with the number of imaginary frequencies. Our present level calculations predict that **5** is 2.0 kcal mol^{-1} is more stable than the **1CH$^+$**. The pyramidal cation, **3CH$^+$** and the C_{2v} singlet structure are higher in energy than **1CH$^+$** (Table 1). Replacement of one CH^+ group by various hetero groups (BH, AlH, and SiH^+) dramatically reverses the trends. The most stable isomer for all of the hetero systems considered here is the antiaromatic **4** (Table 1). Among the boron analoges, antiaromatic **4BH** is 4.5 kcal mol^{-1} stable than the most stable aromatic isomer **2B**. The 3-D aromatic counter part, **3B**, is the least stable one among the considered aromatic isomers. Structure **1BH** is 3.13 Kcal mol^{-} higher in energy than the corresponding isomer **2B**. Large stabilization of the isomer **4** has been observed for **4AlH** and **4SiH$^+$** (Table 1). Both **1AlH** and **2Al** are isoenergetic but for silicon, **1SiH$^+$** is 6.17 Kcal mol^{-} is higher in energy than **2Si$^+$**.

For both silicon and aluminium, the 3-D aromatic isomer, **3**, has two imaginary frequencies (Table 1). These frequencies correspond to the movement of the apex hydrogen atom away from the mean position. Following these imaginary frequencies lead to **6AlH** and **6SiH$^+$**. The hetero atom has moved from the central position making sigma bonds with two adjacent carbon atoms, thus forming a three membered ring. The apex hydrogen bent sufficient enough to be in the plane of Al and two basal carbon atoms, **6AlH**. This makes the tricoordinated aluminium planar. The empty orbital of the Al will have then a chance to interact with the π orbitals of the remaining carbon atoms. Accordingly, from the Wiberg Bond Index (WBI) the bond order between Al-C_3 is 0.325 and Al-C_1 is 0.567. **6SiH$^+$** has very similar structure with slight difference. The apex hydrogen has bent too far away from the mean position. This makes the silicon nonplanar with respect to its coordination. The Si moved slightly away from the weakly-bonding carbon atoms. This is clearly reflected in the distance between the Si-C_1(1.922 Å with WBI 0.678) and Si-C_3 (2.323 Å and WBI 0.321). In both the cases the hydrogens attached to the basal carbon atoms have adjusted so as to maximise the interaction with the apex hetero atom. In case of **6AlH** the C_3 and C_4 hydrogen bent 5° *above* the basal plane and hydrogens of C_1 and C_2 have bent 22.6° *below* the plane. For **6SiH$^+$** the same is 2° and 20° respectively.



6AlH



6SiH+

Not all hetero atoms destabilize the aromatic isomers. With another set of isoelectronic hetero atoms the trends can be reversed back again. In view of the fact that BH is isolobal to Si,[15] we have calculated the structures **1, 3** and **4** where X = C, Si, N^+ and P^+. The results of the calculations are given in the table 1. Surprisingly, contrary to the earlier hetero groups, the 2-D aromatic isomer, **1**, is more stable than the antiaromatic isomer for all the hetero atoms considered. However, for silicon, both **1Si** and **4Si** are isoenergetic. Except for P^+, the 3-D isomer is higher in energy compared to the other two isomers. **3P+**, is 9.1 Kcal mol^- lower in energy than **4P+**.

Structural Properties:

Structural parameters of the investigated compounds along with the corresponding WBI are given in the Figs. 1 to 3. Though structural criteria has its own limitation in understanding the nature of aromaticity, equal or near equal bond lengths in the aromatic ring denotes effective π delocalization. Similarly, well separated single and double bonds represent antiaromaticity. A closer look at the bond lengths for the structures **1** and **2** would indicate that not all isoelectronic aromatic molecules enjoy equal or near equal bond lengths. While **1CH+** with near equal bond lengths is situated at one end of the spectrum and **1AlH** and **2AlH** with maximum difference between the bond lengths is at the other. Remaining systems, BH, SiH^+, C, Si, N^+ and P^+ fall somewhere in between for **1** and **2**. This change can be clearly seen from the WBI. The X-C bond orders for the bonds in three membered ring for most of the systems are only marginally more than one. While a fully delocalized system demands even a larger bond order for the same.

Stability of the pyramidal systems, **3**, depend on the favourable overlap between the 'ring' and 'cap' orbitals.[17] This in turn depends on their relative sizes. A better way to understand the relative sizes of the various hetero groups is to monitor the movement of basal hydrogens (hydrogens which are attached to the ring carbon atoms). The deviations of the hydrogens from the plane of the four membered ring are given (bold letters) along with the bond lengths in Fig. 2. If the cap is small, to maximize the interaction with the cap, the basal hydrogens bent towards the cap and if the cap is large they bent the other way. The smallest of all the caps is N^+

and the largest is SiH^+. Remaining groups fall in between. The optimum size is obtained with P^+ group where the hydrogens have deviated marginally (1.4°) out of the plane. Therefore, **$3P^+$** should be most stable among the pyramidal systems. However, none of these three-dimensional aromatic systems are more stable than their planar counter parts.

Magnetic Properties: The aromatic or antiaromatic nature of the π electrons in a ring are best described by their magnetic behaviour especially from the exaltation data.[16] The exaltation data for **1, 2** and **4** are given in table 2. There are highly aromatic and antiaromatic isomers among the carbon analoges. But the substitution of a hetero atom in the aromatic ring decreases it, as seen from the exaltation data (Table 2). Since the Al-C bond is much longer than the C-C distance and is more polar, **1AlH**, and **2Al** are least aromatic. Similarly, **4AlH** is also least antiaromatic. This behaviour is also seen in BH and SiH analogs as well. However, substitution by etero groups such as C, Si, N^+ and P^+ makes the three membered ring more aromatic (Table 2). From the exaltation data, **$1N^+$, 1Si** and **$1P^+$** are more aromatic than **1C**. At the same time, **$4N^+$** and **4Si** are less antiaromatic. However, **$4P^+$** is the most antiaromatic isomer (Table 2). In the absence of any aromatic stabilization or antiaromatic destabilization, other factors, especially strain, will dominate the relative stabilities. Since, three membered rings are the most strained rings, all its isomers will be higher in energy than the other rings. Therefore, substitution of BH, AlH and SiH in a three membered ring lowers the aromaticity and increases the strain which makes the rings less stable compared to others. Since aromaticity has not been affected by the divalent groups, C, Si, N^+ and P^+, the corresponding rings are not destabilized relative to the other rings.

Table 2 Magnetic susceptibilities, calculated (χ_M) and from group increments ($\chi_{M'}$) along with the exaltations Λ (χ_M - $\chi_{M'}$) (ppm cgs)[a]

X(Y)		**1X**	**2Y**	**4X**	**X**	**1X**	**4X**
BH(B)	χ_M	-31.6	-30.9	-18.8	**C**	-30.2	-20.4
	$\chi_{M'}$	-19.3	-19.3	-25.6		-19.4	-20.6
	Λ	-12.3	-11.6	6.8		-10.8	0.2
$CH^+(C^+)$	χ_M	-27.5	----	25.6	**N^+**	-21.8	3.2
	$\chi_{M'}$	-14.2	----	-20.3		-6.7	-0.4
	Λ	-13.3	----	45.9		-15.1	3.6
AlH (Al)	χ_M	-33.8	-31.4	-29.1	**Si**	-34.4	-16.4
	$\chi_{M'}$	-24.1	-24.1	-30.2		-13.6	-19.9
	Λ	-9.7	-7.3	1.1		-20.8	3.5
$SiH^+(Si^+)$	χ_M	-30.3	-30.3	-19.0	**P^+**	-29.8	21.0
	$\chi_{M'}$	-20.4	-20.4	-26.7		-12.3	-18.6
	Λ	-9.9	-9.9	7.7		-17.5	39.6

[a] NMR computations at CSGT-B3LYP/6-311++G**//B3LYP/6-311++G**

[2.2.3] Conclusions

We have presented two sets of examples where depending on the nature of the substitution different isomers, aromatic or antiaromatic, get more stabilized relative to other isomers. The notion that the aromatic isomers are always thermodynamically more favourable than the antiaromatic isomers need not hold good in all cases. The stability of an isomer depends on several factors such as strain, overlap, hybridization, delocalization etc. The total energy, indeed, represents all these effects. Aromaticity and antiaromaticity contributes, among other factors, to the stability of the molecules.

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Chapter 3

Aromaticity in Three Dimensional Molecules

[3.0] Abstract

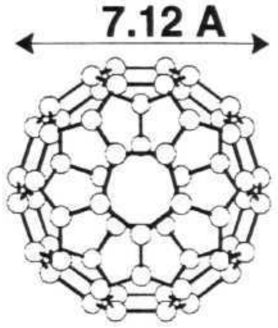
We have found a novel way of stuffing fullerenes following the structure of elemental boron. This makes use of pentagonal rings of the surface for anchoring hapta-five groups. The diameter of C_{60} is not large enough to accommodate $C_2B_{10}@B_{12}$ unit. Higher fullerenes such as C_{80} and Si_{60} are also considered. $C_2B_{10}@C_{12}@C_{56}B_{24}$ and two isomer of stuffed Si_{60}, $Si_2B_{10}@Si_{12}@Si_{38}B_{22}$ and $Si_2B_{10}@B_{12}@Si_{50}B_{10}$ were calculated to be minima on the MNDO potential energy surface.

Ab initio theoretical studies on $X_2B_{10}H_{10}$ (X= CH, SiH, N, P and Sb) have been done for ortho- **1**, para- **2** and meta- **3**. Unlike lower-vertex heteroboranes, all the hetero derivatives have shown similar trends in the relative stabilities, 1,12- isomer being more stable followed by 1,7- and 1,2- isomers, except for N and Sb. No conventional 1,2-isomer for N could be found. Instead, a new nido isomer, **8**, which is 18.1 kcal/mol higher in energy than the most stable isomer has been located. Any hetero group substitution to icosahedral $B_{12}H_{12}^{2-}$ is found to be thermodynamically destabilizing.

Despite the structural similarity between o-carborane and the corresponding Si analog, B3LYP/6-31G* calculations indicate that their dehydro-derivatives have no parallels. The 1,2-Dehydro-o-Carborane has a strained C-C π bond and comparable in reactivity to that of benzyne. However, Si analog, **5**, is calculated to be a transition state. A distorted structure **6**, is 5.2 kcal/mol lower in energy has on one Si pushed outside the icosahedral skeleton and the other Si pushed inside. The bonding in 6 has close similarities with the mono-bridged Si_2H_2.

[3.1] Elemental Boron Route to Stuffed Fullerenes

[3.1.1] Introduction



1, C_{60}

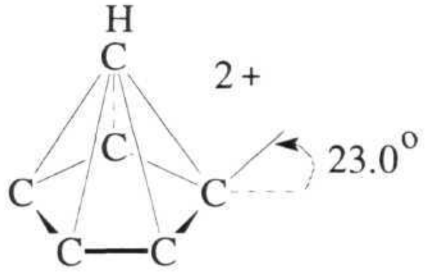
One of the most important discoveries in the last ten years in chemistry is that of fullerenes, polyhedral allotropes of carbon.[1] A lot of chemistry has been done already with C_{60} (1) and higher fullerenes.[2] Fullerenes have shown remarkable properties as materials, as organic compounds where the double bonds yielded to many organic reactions and as ligands in transition metal chemistry.[3] An equally intriguing area of research in fullerenes is the chemistry within.[4] The space within fullerenes is large. For example C_{60} has a diameter of 7.12 Å.[5] The first fullerene with an encapsulated metal atom inside was observed soon after the discovery of fullerenes.[6] Several mono-metallofullerenes $M@C_n$ (M = Sc, Y, La, Fe, and Co; n = 60, 70, 74, 82, 84 etc.)[7] and di-metal species $M_2@C_n$ (M = Sc, Y, La, and U; n = 60, 80, 82, 84)[8] and a few tri-metal species such as scandium metallofullerene have been characterized.[9] Interestingly a few noble gas elements have also been trapped inside the fullerene cage, which made the observation of unusual physical and chemical properties of isolated atoms encircled by a π electron cloud possible.[10]

There is a good deal of evidence from spectroscopic techniques that the charge has been transferred from the encapsulated metal atoms to the fullerene surface.[11] With two or three metal atoms inside, it is rather difficult to locate the position of the atoms. It is assumed that these atoms will form clusters with weak metal-metal bonds. The clusters also donate electrons to the cage.[12] There is a limit on the size of the atoms that can be encapsulated into a particular cage. Calculations have shown that noble gas elements in the range of $1.01 < R^* < 1.28$, where R^* is the reduced radius of the nobel gas atom will be profitably encapsulated by C_{60}. Obviously Kr and Xe falls outside this range. In tune with this we find no experimental evidence for endohedral chemistry with Kr and Xe.[12]

A few atoms do not fill the available space. To utilize the entire space a systematic chemical binding beginning from the endohedral surface is required. Six and five membered rings present in fullerenes provide ample opportunity to do this. In this section we present possibilities to stuff fullerenes covalently with hetero atoms in a novel way.[13] We also present semi-empirical quantum-chemical calculations to support the proposal.[14]

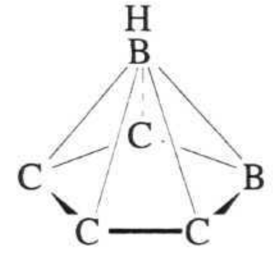
[3.1.2] Pentahapto Bonding

Five membered rings are known to form pentagonal pyramidal compounds if there are six interstitial electrons. For example $C_6H_6^{2+}$ (**2**) has C_{5v} symmetry. The electronic structure is best described by constructing it from a C_5H_5 ring and CH^{2+} cap conceptually. Orbital interactions, now well known, between the π MO's of C_5H_5 of (**2**) and the s-p orbitals of CH^{2+}, lead to three stable delocalized MO's.[15] Six electrons are available from the two fragments (five from C_5H_5 and one form CH^{2+}) to fill these, explaining the stability of the C_{5v} structure. Theoretical studies at various levels have shown that the C-H bonds of the C_5H_5 ring are bent towards the CH cap by an angle of 23°. Such pyramidal compounds are fairly common. There is an X-ray structure corresponding to $C_5H_5B\text{-}I^+$.[16] Calculations on $C_5H_5BH^+$ have shown similar electronic structure and C-H out of



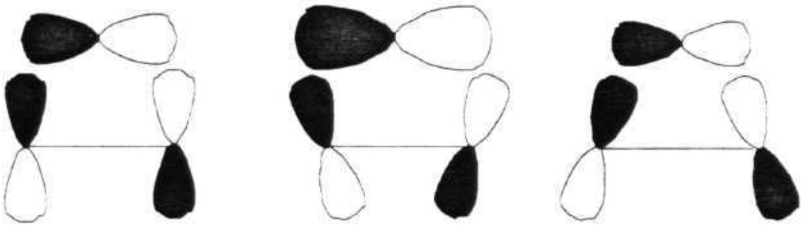
2, $C_6H_6^{2+}$

plane bending. A neutral analog is $C_4B_2H_6$ (**3**).[17] Here C_4BH_5 ring is capped by a BH group. This is the most stable isomer calculated.



3, $C_4B_2H_6$

The extra stability of the isomer where BH is in the capping position in comparison to another isomer where the CH caps a $C_3B_2H_5$ ring, is due to the better overlap of the ring π orbitals with the orbitals of capping group. In fact the out of plane bending of ring CH and BH bonds is an attempt to redirect the ring orbitals for better overlap with the cap (**4**).[18] How do we use these ideas in stuffing fullerenes? In a formal way each five membered ring in C_{60} can be assigned five π electrons. Therefore it requires only one more electron from the cap for completion of six interstitial electrons. Obviously CH^{2+} and BH^+ that we discussed for capping the C_5H_5 ring can be used here as well. The calculated angle of 23° for the CH out of plane bending in **2** should be compared to the 31.2°, made by the bonds emanating from five membered ring in C_{60} with the adjacent rings.



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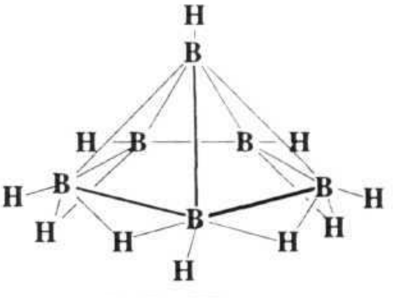
Let us now consider CH^{2+} as a capping group for each of the 12 five membered rings in C_{60}. This results in the impossible $H_{12}C_{12}@C_{60}{}^{24+}$. The resulting CH groups which are bonded in pentahapto fashion are pointed towards the centroid of C_{60}. The charge can be reduced into half by replacing each CH^{2+} by BH^+ ($H_{12}B_{12}@C_{60}{}^{12+}$). The 12 BH or CH groups sticking towards the center will create undue steric congestion. It would be ideal if these groups can be tied with an icosahedral unit so that the overall symmetry is maintained. Where do we look for an icosahedron that serves the purpose?

[3.1.3] Tying the Inverted Umbrellas

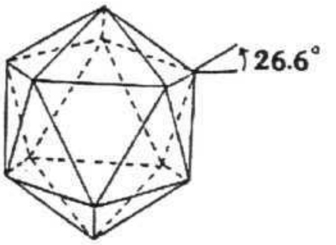
As a family of compounds boranes offer representatives of almost all polyhedral arrangements. The most commonly found borane dianions are based on the trigonalbipyramid, the octahedron, the pentagonalbipyramid and the icosahedron.[19] Amongst these the octahedron ($B_6H_6^{2-}$)and the icosahedron ($B_{12}H_{12}^{2-}$) are more stable than the trigonalbipyramidal $B_5H_5^{2-}$ and the pentagonalbipyramidal $B_7H_7^{2-}$ arrangements.[20, 21] This is not a size effect; $B_6H_6^{2-}$ is experimentally known to be more stable than either $B_5H_5^{2-}$ or $B_7H_7^{2-}$. In fact $B_{12}H_{12}^{2-}$ is the most stable one.

[3.1.4] Stability of $B_{12}H_{12}^{2-}$ and the Structure of Elemental Boron



5, B_6H_{10}

The concept of orbital compatibility mentioned earlier can be used to explain the extra stability of $B_{12}H_{12}^{2-}$. $B_{12}H_{12}^{2-}$ can be made up of two $B_6H_6^-$ pentagonal pyramidal units. The electronic structure of pentagonal pyramid demands six delocalized electrons. An all-boron example is B_6H_{10} (**5**), well characterized experimentally.[22] This has four B-B bridging hydrogens. The terminal BH bonds of B_5 ring are bent towards the BH cap by an angle of 25°. The structure of icosahedron dictates an angle of 26.6° for the BH bonds and the corresponding B_5 plane (**6**). This is very close to the ideal angle necessary for optimal overlap as in B_6H_{10}. In addition the icosahedral symmetry demands that every bond in $B_{12}H_{12}^{2-}$ is equivalent so that $B_{12}H_{12}^{2-}$ is unusually stable. In fact the most stable polymorph of elemental boron, β rhombohedral form, takes advantage of this extra stability in the following way.[23] The unit cell has 105 atoms. The structure begins with an icosahedral B_{12}. Ideally 12 icosahedral B_{12} units have to be attached to the central B_{12} to gain maximum advantage. However space does not permit this. Instead the structure begins by having 12 half icosahedra (inverted pentagonal pyramids of B_6 units) emanating from each boron atom of the central B_{12} unit (**7**). These five membered rings are connected to each other by B-B σ bonds. If the 12 five membered rings are connected this way, we have a surface that has the same topology of C_{60}. This gives B_{84} unit (**8**).



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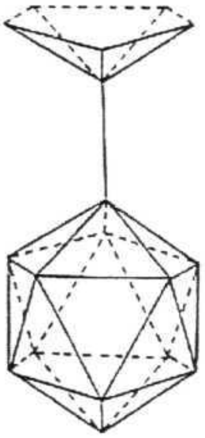

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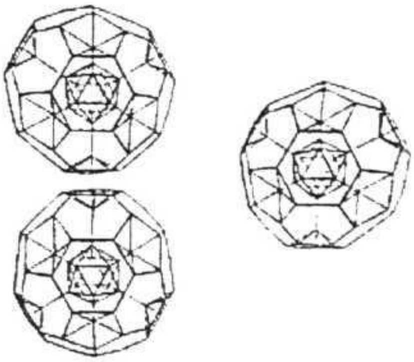
Obviously this structure is highly electron deficient. The central B_{12} unit requires two more electrons to make it isoelectronic to $B_{12}H_{12}^{2-}$. In addition the 12 half icosahedra are also electron deficient. We have already seen that a pentagonal pyramid arrangement requires six delocalized electrons between the ring and the cap. The pyramidal B_6 units in B_{84} has only two electrons. Boron tries to overcome electron deficiency by associating the B_{84} unit to form the β rhombohedral structure. In the three dimensional structure, six of the five membered rings of the B_{84} units finds five membered ring partners in the neighbouring B_{84} unit which completes the icosahedron (**9**). In the unit cell the remaining 21 atoms bind the other five membered rings. This view of structure of elemental boron helps us in redefining the question of stuffing C_{60} as an exercise in making B_{84} electron sufficient.

We have seen that a B_{12} unit may be used to tie the 12 endohedral B-H bonds in $H_{12}B_{12}@C_{60}^{12+}$. Then the structure becomes $B_{12}@B_{12}@C_{60}^{10+}$. This corresponds to an electron sufficient equivalent of B_{84}. To make it more realistic in terms of charge, let us replace 10 carbon atoms from different five membered rings by 10 boron atoms. The resulting formula is $B_{12}@B_{12}@C_{50}B_{10}$. This does not yet achieve the aim.



[3.1.5] Space Requirements and Stuffing of C_{60}

The only problem with the above stuffed fullerene $B_{12}@B_{12}@C_{50}B_{10}$ is lack of space. The dimensions of C_{60} or $C_{50}B_{10}$ cage are not sufficient to accommodate icosahedral $B_{12}@B_{12}$ unit. The distance between the centroid to the center of five membered rings in C_{60} is about 3.33 Å. The radius of icosahedral B_{12}, 1.68 Å, the B-B single bond length, 1.76 Å, and the standard ring cap distance in $B_2C_4H_6$, 1.29 Å, add up to 4.73 Å.[24] Minor advantages are obtained by reorganizations such as $B_{12}@C_{12}@C_{38}B_{22}$. Substitution of carbon atoms on the fullerene cage by boron atoms increases the size of the fullerene because C-B bond is longer than C-C bond. However these changes are still not sufficient. There are several ways to proceed at this stage. Atoms larger than carbon in the outer surface can accommodate the inner boron units. Alternatively larger carbon fullerene cages of icosahedral symmetry can be considered. We have considered a higher fullerene cage C_{80} and a non-carbon fullerene Si_{60} for stuffing. Semi-empirical MNDO studies have been performed on stuffed C_{80} and Si_{60}.

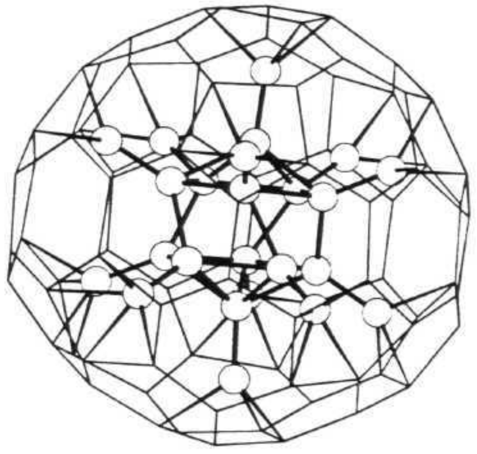


Fig **1** Optimized geometry of $C_2B_{10}@C_{12}@C_{56}B_{24}$. Outer $C_{56}B_{24}$ shell is shown as lines and inner $C_2B_{10}@C_{12}$is shown as circles for clarity

C_{80} is the next higher fullerene which has I_h symmetry.[25] The critical diameter required for stuffing C_{80} with $C_2B_{10}@B_{12}$ in fullerenes is about 9.5 Å. The diameter of I_h-C_{80} is 7.87 Å. HOMO of the I_h-C_{80} is fourfold degenerate with two electrons and LUMO is also fourfold degenerate. There are seven possible isomers within the isolated-pentagon rule.[27] Ab initio calculations have shown that I_h-C_{80} has the largest bond energy among the seven isomers. The diameter of C_{80} is still shorter than the required value. It is felt that $C_2B_{10}@C_{12}$ instead of $C_2B_{10}@B_{12}$ and corresponding changes in the outer shell to $C_{56}B_{24}$ might help in adjusting the estimated difference of 1.5 Å. $C_2B_{10}@C_{12}@C_{56}B_{24}$ (Fig **1**) has been optimized by semi-empirical MNDO method without any symmetry constraints. It was calculated to be a minimum on the potential energy surface. The important parameters along with I_h-C_{80} are given in Table **1.** Essentially the HOMO and LUMO energies have not been changed after stuffing, the HOMO-LUMO gap is 4.52 eV for the stuffed fullerene and 4.40 eV for I_h-C_{80}.

Table 1. Important parameters of $C_2B_{10}@C_{12}@C_{56}B_{24}$, and C_{80}. Distances are in Å, Heats of formation in kcal/mol and HOMO and LUMO energies are given in eV.

	$C_2B_{10}@C_{12}@C_{56}B_{24}$	$C_{80}(I_h)$
Heat of formation	2197.3	1060.2
HOMO	-8.26	-8.38
LUMO	-3.74	-3.98
Δ(LUMO-HOMO)	4.52	4.40
$C\text{-}C_{av.}$	1.52	1.45
$C\text{-}B_{av.}$	1.60	--

The average C-C bond length on the surface of stuffed fullerene is 1.52 Å, which is longer than the C-C bond length, 1.46 Å, found in $C_4B_2H_6$ and also longer than I_h-C_{80} average C-C bond length of 1.45 Å. The average C-B bond length in the pyramidal structure is 1.60 Å compared to 1.54 Å in the $C_4B_2H_6$. The B-B bond lengths in icosahedral inner core have not been changed much compared to the $B_{12}H_{12}^{2-}$ at the same level, 1.67 Å Vs 1.68 Å. We feel that heterofullerenes of this type should be viable species.

[3.1.6] Stuffing Si_{60}

Silicon analogs of fullerenes are not known. There is mass spectral evidence for the existence of Si_{60}^+, but the structure is not known in detail.[27] Icosahedral Si_{60} is calculated to be a minimum by a variety of quantum-mechanical methods.[28] Other isomers of Si_{60} are higher in energy than the I_h-Si_{60}. We have studied the possibility of stuffing icosahedral Si_{60}. $B_{12}@Si_{12}@Si_{38}B_{22}$ structure has the component distance adding up to the required value for Si_{60}. The radius of B_{12} icosahedron (1.68 Å), B-Si bond length (2.22 Å) and the boron apex to the Si_4B

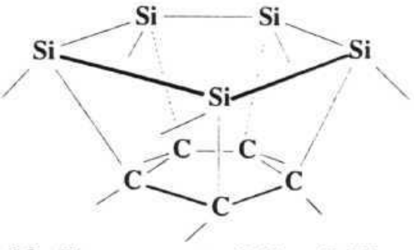
ring distance (1.50 Å) add up to 5.40 Å which is not far from the distance between the centroid to the center of five-membered ring in Si_{60} (5.15Å). We have selected two isomers $Si_2B_{10}@Si_{12}@Si_{38}B_{22}$ and $Si_2B_{10}@B_{12}@Si_{50}B_{10}$ for study. Both the structure are minima on the MNDO potential energy surface. The latter one is more stable by about 300 kcal/mol (Table **2**).

Table **2.** Important parameters of two isomers of Si_{60} stuffed fullerene. Distances are in Å. Heats of formation in kcal/mol and HOMO and LUMO energies are given in eV.

	$Si_2B_{10}@B_{12}@Si_{48}B_{12}$	$Si_2B_{10}@Si_{12}@Si_{36}B_{24}$	Si_{60}
Heat of formation	1354.8	1667.7	812.6
HOMO	-7.17	-6.02	-7.23
LUMO	-1.39	-0.86	-1.50
Δ (LUMO-HOMO)	5.76	5.16	5.73
$Si\text{-}Si_{av.}$	2.17	2.21	1.92
$Si\text{-}B_{av.}$	1.95	1.90	---

The HOMO and LUMO energies of the most stable isomer are comparable to I_h-Si_{60}.[29] The average Si-Si bond length on the surface is 2.21 Å compared to 1.97 Å in Si_{60}. B-Si bond length is 2.23 Å compared to 2.20 Å found in $Si_4B_2H_6$. The average B-Si bond length of pyramidal B atom to the Si in five membered ring is 2.22 Å.

There is another kind of stuffing possible with Si_{60}.[29] The diameter of Si_{60} (5.55 Å calculated at PM3) is sufficient enough to accommodate C_{60} (3.56 Å observed) inside the cage. It can be regarded as a formal polymorph of silicon carbide designated as



10, Fragment of $C_{60}@Si_{60}$

I_h-$(SiC)_{60}$ (**10**). Energetically $(SiC)_{60}$ is 552 kcal/mol lower than the sum of heats of formation calculated for C_{60} and Si_{60} at PM3 level of theory. The HOMO-LUMO gap is intermediate between C_{60} and Si_{60}. $(SiC)_{60}$ has only Si-C, C-C and Si-Si σ bonds with the bond order of 0.887, 0.972 and 0.929 respectively. This would however leave the question of stuffing the inside C_{60}.

[3.1.7] Conclusions

We have presented here a novel way of stuffing fullerenes on the lines of the structure of elemental boron. This makes use of pentagonal rings of the surface for anchoring hapta-five groups The dimensions of C_{60} are not sufficient enough to accommodate $C_2B_{10}@B_{12}$ unit. Higher fullerenes such as C_{80} and Si_{60} are considered further. $C_2B_{10}@C_{12}@C_{56}B_{24}$ and two isomers of stuffed Si_{60}, $Si_2B_{10}@Si_{12}@Si_{38}B_{22}$ and $Si_2B_{10}@B_{12}@Si_{50}B_{10}$ were calculated to be minima on the MNDO potential energy surface. We refrain from speculating the properties of these structural candidates.

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[3.2] Ab Initio Studies on Disubstituted-*closo*-Icosahedral Heteroboranes, $X_2B_{10}H_{10}$ (X = CH, SiH, N, P and Sb).

[3.2.1] Introduction

Polyhedral boranes have been a fascinating area of research for many years. The icosahedral $B_{12}H_{12}^{2-}$ is one of the earliest known stable dianions[1]. Several recent developments have added a renewed interest in the chemistry of boranes. New icosahedral monoanions have been synthesized and used as weakly nucleophilic units to stabilize naked cations[2]. The neutral analogs of $B_{12}H_{12}^{2-}$ such as carboranes have also provided exciting new chemistry. Following the similarity of benzene and o-carborane[3], an equivalent of benzyne (1,2-dehydrobenzene), 1,2-$C_2B_{10}H_{10}$ has been synthesized[4]. Properties of 1,2-$C_2B_{10}H_{10}$ are comparable to those of benzyne[5]. The strucutral consequences of such unsaturation in polydedral systems are discussed in chapter 3.3. Other heterosubstituted icosahedral boranes have been targets of synthesis. A disila analog of o-carborane, 1,2-$(SiMe)_2B_{10}H_{10}$, has been obtained recently[6]. The dianions $XB_{11}H_{11}^{2-}$ and the monoanions $CH_3XB_{11}H_{11}^{1-}$ (X =Si, Ge, and Sn) are also known[7]. Several neutral derivatives of 1,2-$X_2B_{10}H_{10}$ and 1,2-$XYB_{10}H_{10}$ (X and Y = P, As, Sb and Pb), $CH_3SiSnB_{10}H_{10}$ and $CH_3SiSbB_{10}H_{10}$ have been synthesized[8]. Incorporation of nitrogen as a heterovertex in the boron polyhedral cage is not common. So far only one icosahedral azaborane, 1-$NB_{11}H_{12}$, has yielded to synthesis[9].

More than one hetero group substitution in the icosahedral skeleton brings in the interesting question of isomer stabilities. For disubstituted icosahedral systems the three possible isomers are ortho (1,2-), **1**, meta (1,7-), **2**, and the para (1,12-), **3**, prefixes following the system used in the 2-dimensionally aromatic benzene


1


2


3

derivatives. The distinction to be noted here is that in the ortho, meta and para benzenes, the carbon skeleton is intact. The ortho, meta and para nomenclature in the icosahedral boranes refer to the replacement of the BH atoms with other hetero atoms. The most studied disubstituted boranes are the carboranes. The three isomers of $C_2B_{10}H_{12}$ have been known for a long time and are well characterized structurally. Thermal isomerization and equilibrium studies involving the three species are known. The 1,2- isomer, **1CH** (structure **1** with X = CH, unlabeled vertices refer to BH) is the least stable one and isomerizes to the next stable meta isomer, **2CH**, at 500 °C. This in turn goes to the most stable 1,12- isomer above 615 °C[10]. Theoretical studies at various levels have confirmed these relative energies[11]. The disilaborane, 1,2-$Si_2B_{10}H_{12}$ is much more reactive, the only known derivative $(SiMe)_2B_{10}H_{10}$ decomposes above 230 °C. The ortho isomer of $P_2B_{10}H_{10}$ is also known but requires temperatures in the range of 560-590 °C for conversion to the 1,7- isomer[12].

Several strategies has been suggested to explain the relative stabilities of the positional isomers of the dihetero boranes all of which adhere to the same electron count. The most dominant hetero substituent in borane chemistry has been carbon and hence these rules have been based predominantly on carboranes. Early on Williams suggested that the isomer with the more electronegative atoms as far apart as possible will be more favourable[13]. While this was found to be successful for many carboranes, there were ambiguities for other heterosubstituted boranes.

Gimarc's topological charge stabilization model suggested that the electronegative atoms tend to occupy the places of maximum charge density calculated for the parent borane[14]. Though this model has done well in several inorganic ring systems and carboranes it failed to predict the relative stabilities of lower vertex heteroboranes[15]. One of us suggested a criterion based on the orbital compatibility which matches the diffuse nature of the orbitals of the hetero groups vis-à-vis the skeletal rings[16]. This is successful in predicting the relative stabilities of several hetero substituted lower vertex boranes. Especially important were the correct predictions that the order of the relative of stabilities of 5, 6 and 7 vertex *closo* boranes will be reversed on going to the corresponding silaboranes[17].

Is the concept of orbital compatibility applicable to higher vertex boranes as well? What is in store for other substituents such as N, P and Sb. In the present study the structures and relative stabilities of *closo*-$X_2B_{10}H_{10}$ (X= CH, SiH, P, N and Sb) are examined by *ab initio* methods. Another point of interest is the aromaticity of *closo*-boranes. NICS has been used in the present study to estimate the relative aromaticity of various heteroboranes.[18]

Hartree Fock calculations using 6-31G* basis set has been used for all the structures considered except for isomers of Sb where the LANL1DZ basis set is employed. Frequency calculations are done on all the isomers to ascertain the nature of the stationary points except for the isomers of $Sb_2B_{10}H_{10}$. All the isomers reported correspond to minima on the potential energy surface. Single point MP2 calculations were done on HF geometries. In the discussion MP2 relative energies are used unless otherwise specified. All the calculations were performed by the Gaussian94 series of programs[19].

Table 1. Total Energies (a.u.) and Relative Energies (kcal/mol) (ZPE corrected) (MP2 values in parenthesis) of disubstituted icosahedral heteroboranes $X_2B_{10}H_{10}$.

	HF/6-31G*	MP2//HF	ZPE(NIMAG)	RE
1BH	-303.28332	-304.44372	100.10 (0)	--------
8a	-361.54432	-362.80956	97.44 (0)	18.0 (23.0)
2N	-361.57306	-362.84330	100.30 (0)	0.0 (1.8)
3N	-361.57188	-362.84621	100.25 (0)	0.8 (0.0)
1CH	-329.62084	-330.83000	117.54 (0)	20.3 (22.8)
2CH	-329.64938	-330.85539	117.83 (0)	2.4 (4.2)
3CH	-329.64938	-330.86116	117.91 (0)	0.0 (0.0)
1P	-934. 17726	-935.36600	96.21 (0)	10.1 (8.4)
2P	-934.18963	-935.37608	96.38 (0)	2.3 (2.1)
3P	-934.19336	-935.39935	96.45 (0)	0.0 (0.0)
1SiH	-831.69385	-832.82773	106.12 (0)	4.2 (3.6)
2SiH	-831.69858	-832.83203	106.13 (0)	1.2 (0.9)
3SiH	-831.70048	-832.83349	106.16 (0)	0.0 (0.0)
1Sb	-263.04968	--------------	----------	0.0
2Sb	-263.04587	--------------	----------	1.8
3Sb	-263.04869	--------------	----------	0.6

a **1N** collapses to **8**.

[3.2.2] Results and Discussion

Table 1 gives the relative energies of the *closo*-hetero-icosahedral systems, $X_2B_{10}H_{10}$ (X= N, CH, SiH, P and Sb). In agreement with the earlier theoretical and experimental studies, the 1,12- isomer of $C_2B_{10}H_{12}$ is more stable followed by the 1,7- and 1,2- isomers. The C-C bond distance in **1CH** is 1.609 Å (1.624 Å, X-ray) which is longer than the normal Csp^3-Csp^3 distance of 1.540 Å. This bond length is intermediate between the C-C bond lengths of **7CH**, 1.538 Å and **5CH**, 1.628 Å. The demand of an icosahedral skeleton cannot be met by the regular C-C bond length, which is smaller than the normal B-B bond. This causes unusual strain in the 1,2- isomer resulting in stretching the C-C bond. This is also reflected in the Wiberg Bond Index (WBI) 0.752 of C-C bond in **1CH**. However, the stretched C-C bond is not very reactive. Numerous derivatives of 1,2- $C_2B_{10}H_{12}$ are known to be very stable and to participate in reactions without the rupture of the C-C bond. In general, both 1,7- and 1,12- isomers differ by only a small amount of energy due to the structural similarity between them.

The reversal of trends observed on going from C to Si in the lower vertex (5,6 and 7) boranes is not seen with icosahedral skeleton. The relative energies of $Si_2B_{10}H_{12}$ fall in a narrow range (Table 1) but the trends are similar to those of carboranes. This is not contrary to the overlap matching criteria. The highly symmetric icosahedral skeleton provides the same five membered ring when any vertex is removed. Substitution of one hetero atom in the rigid skeleton does not change this picture substantially. The Si-Si bond distance (2.308 Å, X-ray[6]) in **1SiH** is reproduced at the present theoretical level. This bond length is slightly shorter than the normal Si-Si bond length, 2.348 Å, and longer than the Si-Si bond length in **7SiH**, 2.106 Å and **5SiH**, 2.228 Å. This compressed Si-Si distance is not an indication of the strength of the bond, as the WBI is only 0.508, reflecting the participation of the Si-Si σ bond in the skeletal multicentre bonding. In contrast to the C-C stretching in **1CH**, the Si atoms are forced to be closer by the rigid icosahedral frame work in **1SiH**. However, **1SiH** is thermally less stable than **1CH**; at 500°C **1CH** rearranges to **2CH** but above 230°C **1SiMe** decomposes. Despite the similarity between **1CH** and **1SiH**, they differ substantially in the charge distribution. Consistent with the electronegativity differences, there is a polarization of the negative charge on the carbon atoms in **1CH**, while positive charge is localized at the silicon atoms in **1SiH**. This difference in charge distribution is reflected in their reactivity towards electrophiles and nucleophiles. The dimethyl derivative of **1SiH** is attacked by nucleophilic bases resulting in the loss of a MeSi vertex, whereas in **1CH** a B atom adjacent to the two C atoms reacts with the nucleophiles.[6] The remaining two isomers, **2SiH** and **3SiH**, have not been synthesized. Our theoretical results indicate that both the isomers are very close in energy and should be amenable to the synthesis.

Similar trends in the relative stabilities continue for group-15 elements as well. The 1,12- isomer of $P_2B_{10}H_{10}$ is the most stable one followed by 1,7- and 1,2- isomers. However, the energy difference between **1P** and **3P** is half of what is found for the corresponding carboranes (Table 1). The P-P bond length in **1P** of 2.293 Å, compares well with the X-ray value of 2.284 Å[12]. This length is slightly longer than the normal P-P bond length of 2.258 Å; while the corresponding bond length in 1,2-$P_2B_4H_4$ is 2.222 Å. The WBI of P-P bond in **1P** is 0.5081.

One interesting aspect concerning the X-X internuclear distances in 1,2-disubstituted hetero boranes is that these increase or decrease in length from their standard values to accommodate the boron skeleton. The C-C internuclear distance in **1CH** is elongated compared to the normal C-C distance due to the very small size of the CH group vis-à-vis BH. The size of the orbitals of the P is close to that of the BH, and there is only a slight elongation in the P-P distance in **1P**. On the other hand, SiH group is slightly larger than the BH group. Consequently there is a compression of the Si-Si internuclear distance in **1SiH**. These size differences are also reflected in the relative stabilities of the isomers. As the difference between the size of the hetero group vis-à-vis BH decreases, the relative stabilities of the isomers also decrease. The dramatic effect of the size difference of the hetero atom can be seen with nitrogen as substituent in the icosahedral skeleton.

4

X= SiH

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X= CH

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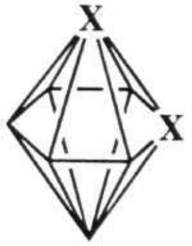

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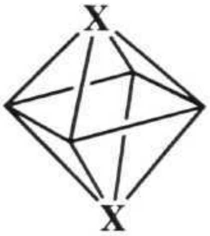

6

X= SiH

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X= CH

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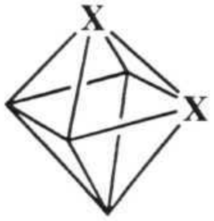

7

Unlike **1P**, we could not locate a stationary point corresponding to the conventional 1,2- isomer of $N_2B_{10}H_{10}$. The C-C distance in **1CH** is calculated to be 1.609 Å (1.624 Å from X-ray). This is already too short in comparison to the B-B distance (1.795 Å) expected for the icosahedral skeleton. The N-N distance in **1N**, anticipated to be much shorter, is not able to withstand the strain of the icosahedral skeleton. Despite the electron count appropriate for a *closo* arrangement, the N-N distance in **1N** on optimization is stretched to 2.453 Å, with practically no bonding interaction (WBI = 0.036). This is not comparable to the *nido* structure on B_4N_2 skeleton[20]. Structure **8** is 18.1 kcal/mol higher in energy than the 1,7- isomer. At the HF/6-31G* level of theory the 1,7- isomer is more stable than the 1,12- isomer. Single point calculations at the MP2/6-31G*//HF/6-31G* indicate that the 1,7- isomer is lower in energy that the 1,12- isomer. Obviously, these two isomers are very close in energy.

8

When the X group is too diffuse compared to BH, as in $Sb_2B_{10}H_{10}$, all the isomers are found to be of equal energy (Table 1). The 1,2- isomer is slightly more stable than the 1,12- isomer. The 1,7- isomer is the least stable one. Unlike lower vertex heteroboranes, the icosahedral cage absorbs differences between the various hetero groups until the difference becomes too large as in the case of nitrogen and antimony.

[3.2.3] Bonding in $X_2B_{10}H_{10}$ Systems

Icosahedral $B_{12}H_{12}^{2-}$ is exceptionally stable. A three-dimensional network comprising of icosahedral B_{12} can be seen as a part of the stable form of elemental boron[21]. It has been argued that BH is perfectly suited as a 'cap' to the B_5 plane of icosahedral skeleton[22]. Let us consider the nature of the p orbitals in any of the B_5 rings in the skeleton. The geometry of the icosahedron does not permit the B-H hydrogen atoms to lie on the B_5 plane. They are bent by an angle of 26.6° towards the `cap'. This bending rehybridizes the p orbitals of the B_5 plane and orient them towards the cap. This is absent in either $B_6H_6^{2-}$ or $B_7H_7^{2-}$, where the p orbitals are perpendicular to B_4 and B_5 planes respectively. Thus, the effective diffuse nature of the B_5 plane in an icosahedron is intermediate between B_4 and B_5 rings, which favours the BH group to fit exactly with the ring. This is one of the reasons attributed for the extraordinary stability of $B_{12}H_{12}^{2-}$. Thus, any other cap which is different from B-H should destabilize the icosahedral cage. The extent of destabilization again depends on how much the size of the hetero group differs from B-H. This can be understood from the following equation (1).

$$B_{12}H_{12}^{2-} + 2XH_3 \rightarrow 1,12\text{-}\ X_2B_{10}H_{10} + 2\ BH_4^- \qquad (1)$$

X	CH	SiH	P	N
ΔE kcal/mol	56.67	64.57	34.94	94.10

Clearly, all the hetero caps are destabilizing, two, N and SiH, being the worst; the smallest and the largest in relation to BH. This is because the orbitals of N are too small and those SiH too large to effectively cap B5 ring of the icosahedron. This is to be contrasted with the similar kind of equations for $B_6H_6^{2-}$ and $B_7H_7^{2-}$ (eq. (2) and (3)).

$$B_6H_6^{2-} + 2XH_3 \rightarrow 1{,}6\ X_2B_4H_4 + 2\ BH_4^- \tag{2}$$

X	CH	SiH	P
ΔE kcal/mol	-36.67	-11.11	-72.45

$$B_7H_7^{2-} + 2XH_3 \rightarrow 1{,}7\text{-}\ X_2B_5H_5 + 2\ BH_4^- \tag{3}$$

X	CH	SiH	P
ΔE kcal/mol	41.72	-20.40	-37.67

For the octahedron, substitution by hetero groups is exothermic, more so for phosphorus. Pentagonal-bipyramidal substitution by carbon is endothermic, because CH is too small to cap a five membered ring, but is exothermic for substitution by silicon and phosphorous (3). Both 1,6 $N_2B_4H_4$ and 1,7- $N_2B_5H_5$ are higher order stationary points for nitrogen; therefore were not considered. The conclusion from the above equations is that any substitution in the icosahedral skeleton is destabilizing and the reverse is true for the octahedron.

Table 2. NICS values of various isomers.[a]

Isomer	1,2	1,7	1,12
BH	-34.27		
N	-9.19	-31.79	-35.21
CH	-34.18	-34.16	-35.37
P	-32.17	-31.09	-29.66
SiH	-34.26	-34.56	-34.21

[a] The NICS values were calculated by placing the ghost atom at the origin.

The calculated NICS values of various molecules are given in Table 2.[23] Surprisingly, NICS values are similar for all of the isomers except **1N**. This is anticipated because **1N** has a *nido*-structure and hence delocalization will be less. Thus, aromaticity is not affected by the hetero atom substitution but we have seen that hetero substitution is destabilizing thermodynamically. There is a growing body of evidence to support the fact that the thermodynamic stability need not be associated with aromaticity; strain and other factors also influence thermodynamic stabilities. The geometry of hetero substituted icosahedral systems tend to adjust so as to retain maximum delocalization possible.

[3.2.4] Conclusions

$B_{12}H_{12}^{2-}$ favors no substitution. Any hetero atom substitution is destabilizing. It appears that the hetero group substitution does not affect the aromaticity and the geometries tend to adjust to retain maximum delocalization. The finer differences observed in lower vertex boranes for C, Si and other elements are found to be absent in the $X_2B_{10}H_{10}$ systems.

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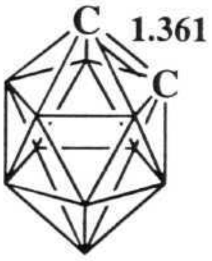
[3.3] Structure and Bonding in $X_2B_{10}H_{10}$ (X = C and Si). The Kinky Surface of 1,2-Dehydro-*o*-Disilaborane.

[3.3.1] Introduction

The chemistry of o-carborane, **1**, has several parallels with benzene.[1-3] Jones and co-workers[4] have brought out yet another amazing parallel between these two prototypes: the 1,2-Dehydro-o-carborane, **2**, is shown to be comparable in reactivity to 1,2-Dehydro-benzene (benzyne), **3**. Derivatives of disila-analogs should provide equally interesting chemistry. Seyferth and co-workers[5] have synthesized a dimethyl derivative of **4**. Despite the structural similarity between **1** and **4**, they differ substantially in their reactivity patterns. Nucleophilic bases attack the dimethyl derivative of **4** resulting in the loss of an MeSi vertex, whereas in **1** the reaction is centred on a boron adjacent to the carbon.[6] Will the behaviour of $B_{10}Si_2H_{10}$ follow that of the carbon analog? The structure of Si_2H_4 contrast dramatically with that of ethylene.[7,8] Constraints of an icosahedral skeleton make any guess on the structure of the $B_{10}Si_2H_{10}$ even more hazardous. This section compares the C-C double bonds in **2** and **3** and unravel an unexpected kinky structure for $B_{10}Si_2H_{10}$.

1



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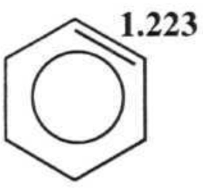

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4

Distances at B3LYP/6-31G*

[3.3.2] Results and Discussion

The structures **1-6** and **11** were optimized at the HF/6-31G* and B3LYP/6-31G* levels of theory.[9,10] Total energies and important parameters are given in Table 1. Unless otherwise stated, B3LYP energies and bond parameters have been used in the discussion. The structure of o-carborane has been studied by several theoretical methods.[11] The structure is calculated to be a minimum at the B3LYP/6-31G* level with a C-C distance, 1.622 Å, comparable to the experimental value (Table 1) and to the previous theoretical studies. The Wiberg Bond Index[12] (WBI) of 0.74 reflects the stretched and delocalized nature of the C-C bond. For comparison, WBI for C-C bond in ethane is 1.00. The 1,2-Dehydro-o-carborane, **2**, is also calculated to be a minimum with a C-C distance of 1.361 Å. This is much longer than the corresponding C-C distance in benzyne but no direct comparison can be made as there is no previous theoretical or experimental estimate.

The frontier orbitals of **2** and **3** are the π and the π^* levels. The LUMO energies for **2**, **3** and ethylene are -0.1438, -0.0702 and 0.0188 au respectively. Therefore, in Diels-Alder reactions, the reactivity towards normal dienes is expected to be in the order **2** > **3** > C_2H_4, if steric considerations are not taken into account. The π bonds in **2** and **3** are destabilized in relation to ethylene by similar amounts, Eq. (1) and (2). These are in tune with the observed experimental reactivities.[4b]

$$C_2H_6 + \mathbf{2} \text{------------>} \mathbf{1} + C_2H_4 \quad -57.4\ \text{kcal/mol} \quad (1)$$
$$C_2H_6 + \mathbf{3} \text{------------>} C_6H_6 + C_2H_4 \quad -60.1\ \text{kcal/mol} \quad (2)$$

The calculated Si-Si distances in **4** of 2.309 Å (HF) and 2.312 Å (B3LYP) are comparable to the experimental distance of 2.308 Å (Table 1). This is shorter than the Si-Si bond distance in $(CH_3)_6Si_2$, 2.340 Å.[13] The dehydro structure **5** is calculated to have an Si-Si distance of 2.164 Å at HF level and 2.229 Å at B3LYP level of theory. In contrast to the increase in the Si=Si distance in **5** on going to the B3LYP level, the B-B bonds which are involved heavily in the multicentre bonding of the cage are shortened at this level, (HF av. B-B=1.825 Å; B3LYP av. B-B=1.809 Å). The influence of the icosahedral skeleton in determining the relative π bond strengths is demonstrated by Eq. (3) and (4).

$$H_2Si{=}SiH_2 + C_2H_6 \text{ ----> } Si_2H_6 + H_2C{=}CH_2 \quad -19.0 \text{ kcal/mol} \tag{3}$$

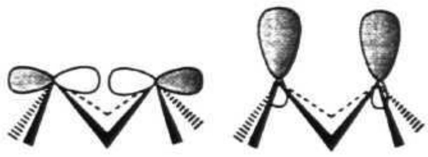
$$\mathbf{1} + \mathbf{5} \text{ -----> } \mathbf{2} + \mathbf{4} \quad 36.6 \text{ kcal/mol} \tag{4}$$

The exothermicity of eq. (3) is attributed among other factors to the strong C-C π bonds. However, the eq. (4) is endothermic. A probable explanation for the reversal could be obtained from the structural details of the icosahedral skeletons. The B-B distance in $B_{12}H_{12}^{2-}$ is 1.800 Å. To accommodate this skeletal distance the C-C bond in **1** is stretched to 1.624 Å. The strain goes up further in **2**, because the C-C double bond is energetically more expensive to stretch. The calculated distance of 1.361 Å in **2** is only marginally longer than that in ethylene. The structure is distorted considerable from an ideal skeleton. Another source of strain is the pyramidalization of the carbon in **2**. A contraction, instead of elongation, is in order in **4**; the Si-Si distance decreases to 2.312 Å. This is still far form the standard icosahedral value of 1.800 Å in $B_{12}H_{12}^{-2}$. Further reduction of strain is achieved in the silicon system by introducing the double bond (**5**). In addition, the pyramidalization at Si is less demanding energetically. Thus, the combination of **1** and **5** is better compared to **2** and **4**. Despite this **5** is calculated to be a transition state. Following the imaginary frequency led to an unusual structure **6** with C_s symmetry.

5 **6** **11**

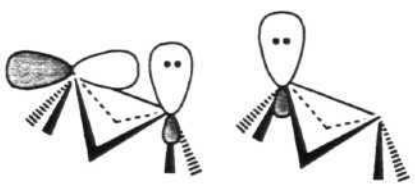
Distances at B3LYP/6-31G* except for 11 (HF/6-31G*)

The surface of **6** is kinky. One Si atom has gone out of the icosahedral surface (Si_{out}) and the other has gone slightly in (Si_{in}). The average Si-B bond distance of 2.121 Å in **5** has gone to 2.360 Å for the Si_{out} and 2.043 Å for the Si_{in}. The Si-Si distances and WBI's in **4** (2.309 Å, 0.57) and **6** (2.300 Å, 0.67) are comparable. However, the Si-Si bond in **6** is very different from that of **4**. The results indicate that a good approximation to bonding can be obtained starting with the interaction of two sp^2 hybrid Si groups. In a symmetrical arrangement as in **5**, there is a sigma orbital and a π orbital, **7**. In **6**, one Si goes up and the other goes down, resulting in two different MO's (**8**). The σ MO, **8a**, arises from the interaction of the p orbital on Si_{out} with the sp^n hybrid on Si_{in}. A lone pair formed on Si_{out} is the HOMO, **8b**. There are a few examples in literature where the p orbital of one Si accepting electrons from the hybrid orbital of the adjacent Si. Mono-bridged Si_2H_2 (**9**) presents the closest comparison.[14] Even though the environment around Si is very different in **6** and **9**, the Si_2H_2 structure presents such an interaction.[14] The Si_2 unit in **6** can also be compared to that in Si_2H_4, **10**. The trans structure **10** is calculated to be more favourable than the cis structure; the latter is not even a stationary point.[8(b)] However, the constraints of the B_{10} template forces a cis arrangement with the unusual bonding pattern, **8a,b**.



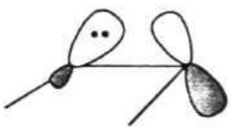
a **b**

7



a **b**

8



9

10

This bonding arrangement also satisfies the electron count (2n+2 electrons) needed for closo-structures.[15] In **6**, this has been achieved by the participation of all the four valence electrons of one Si atom (Si_{in}) and two valence electrons of the other Si (Si_{out}) for skeletal bonding. There is another structure, **11**, on the HF potential energy surface, corresponding to two lone pairs, one on each Si atom. Structure **11** is 9 kcal/mol higher in energy than **5**, with an Si-Si distance of 2.604 Å but without any bonding interaction. However, **11** is a third order stationary point at the HF level. This structure may become more important for the heavier analogs. It collapses to **5** at the B3LYP level. In view of their reactivity and novel bonding characteristics, **6** is an exciting target for experiments.

[3.3.3] Conclusions

The structure and reactivity of $Si_2B_{10}H_{10}$ differs substantially from those of $C_2B_{10}H_{10}$. The preference of Si for divalency is firmly established.

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Chapter 4

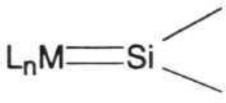
Structure and Bonding in Silylynes

[4.0]Abstract

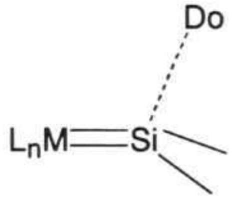
Density functional theory (DFT) calculations were performed on a variety of silylyne complexes of Ta, W, Re and Os metals. The ligands around each metal were designed to give both the Fischer and the Schrock complexes. Fragment Molecular Orbital analysis was also carried out for a qualitative understanding. The conventional M≡Si bond is found to be the favoured arrangement for most of the systems studied. Our study reveals that the Schrock complexes are preferred over the corresponding Fischer complexes for all metals. In general, the metal silicon π bonds are much weaker than the metal-carbon π bonds. With certain metals, the low-valent bonding mode for SiH was observed. There is no stationary point corresponding to the linear Os-Si-H arrangement, **12Si**. The linear structure, upon optimization, collapsed to **13Si**. The minimum energy structure, **13Si**, contains a divalent silicon with a lone pair.

[4.1] Introduction

Compounds containing silicon double bonds with main group elements and transition metals (silylenes, **1a** and **1b**) are well known.[1] Silylenes have rich coordination chemistry compared to carbenes. In contrast, there is no known example of a stable complex with M≡Si, where M is a transition metal.[1(a)] There is an example of donor-stabilized Ru-Silylyne complex $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2RuSi\{(biphe)(SC_6H_4\text{-}4\text{-}Me)\}][OTf]_2$, known experimentally.[2] This has a tetra-co-ordinated Si. Recently, Power's group had synthesized a base free Mo-Germylyne complex $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3\text{-}2,6\text{-}Mes_2$.[3] These examples indicate that it should be possible to realize stable M≡Si bond. What are the ideal metal-ligand combinations for this purpose? How does one electronically tune the M≡Si bond?



1a



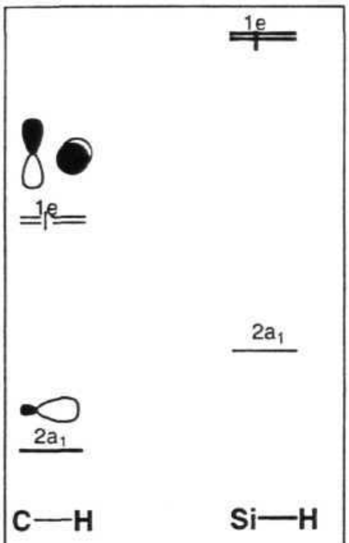
1b

In the main group silicon chemistry, the preference of Si for divalency over multiple bonding is well established. The potential energy surface of Si_2H_2 depicts the variety of bonding modes it can exhibit.[4] No well established example of formal Si≡X (X = main group element) bond is available except for HSi≡N which was characterized spectroscopically.[5] Can the widely present divalency in the main group silicon chemistry be realized in transition-metal systems as well?

In this chapter, we explore the electronic structure and the bonding in silylynes. We have modeled both the Fischer and the Schrock types of silylynes with Ta, W, Re and Os metals. Though formal silicon triple bond is possible with suitable metal-ligand combinations, the preference for divalency is firmly established with certain metal systems.

Structures **4-13** were optimized using hybrid density functional method B3LYP.[6] For the elements, Ta, W, Re, Os and Cl, Steven's relativistic core potentials along with the split-valence basis sets (4111,411,311)[7] were used. 6-31G* basis sets were used for the remaining elements. The optimizations and the frequency calculations were done using G94 suite of programs.[8]

[4.2] Comparison of CH and SiH ligands:



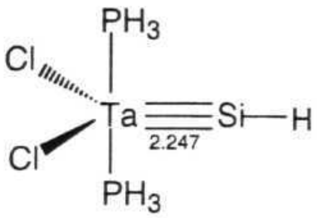
2 **3**

Scheme 1 Schematic representation of C-H and Si-H orbital levels.

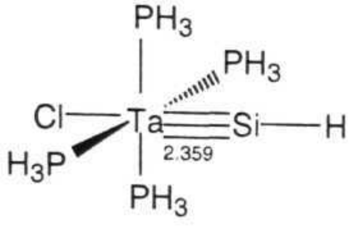
Let us begin by comparing the MO pattern of SiH with that of the well known CH orbitals. Both the species are known spectroscopically. With 3 valence electrons and 3 orbitals, several different occupancies and spin states can be constructed for these systems. The ground state for both the species is a $^2\Pi$ state. The excited states, $^4\Sigma^-$, where three valence electrons occupy three different orbitals, are around 17.2 and 25.1 kcal/mol higher in energy for CH and SiH respectively.[9] Inclusion of correlation energy with large basis sets is necessary to reproduce this difference. Calculations for CH at HF/6-31G** incorrectly predicts the $^4\Sigma^-$ state to be more stable than the $^2\Pi$ state by about 7 kcal/mol.[9] Calculations at B3LYP/6-31G*, however, correctly predicts the energy level ordering with a difference of 20.4 and 42.4 kcal/mol for CH and SiH respectively. Therefore, we used the B3LYP level of theory in the present problem.

The basic MO pattern is similar for both the ligands (Scheme 1). However, the two systems differ significantly in the relative position of the energy levels of the valence orbitals. The donor σ orbital of the SiH group is very high in energy compared to the corresponding σ orbital of the CH group. The π acceptor orbitals of SiH are also pushed up in energy relative to that of the CH group. These restrict the type of metal fragments that can have good overlap with the SiH.

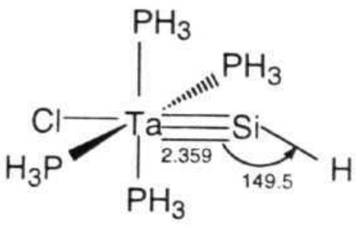
Carbyne complexes are broadly classified into two classes, Fischer and Schrock.[10] The Fischer carbynes are characterized by the low oxidation state of the metal, π-acceptor ligands on the metal and π-donor groups on the carbon atom. High oxidation state metals with typical σ bonding ligands and H or alkyl substituted carbon are the characteristics of the Schrock complexes. These characteristics are also reflected in the energy levels of the metal and the ligand (C-R) fragments. Typical Fischer carbyne metal fragments have low lying donor-acceptor orbitals in comparison to the Schrock type of metal fragments. It is possible to predict what kinds of metal fragments are electronically better suited for CR or SiR. If symmetry permits, orbitals closer in energy interact better with one another. Since the donor σ and the acceptor π orbitals of SiH are higher in energy than the corresponding CH orbitals (Scheme 1), SiH interacts better with the Schrock kind of metal fragments. Conversely, CH interacts better with Fischer type of complexes. Interestingly, the preference of CH for Fischer kind of metal fragments is also reflected in their abundance. Around 80% of all known carbyne complexes are of Fischer type! However, this classification is not very rigid. There are many borderline cases where this classification does not hold good.



4Si

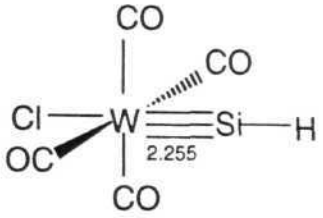


5Si

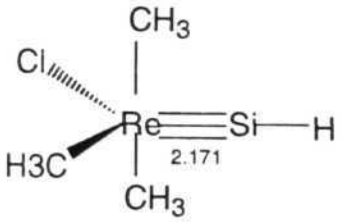


6Si

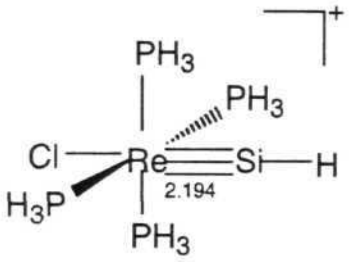
7Si



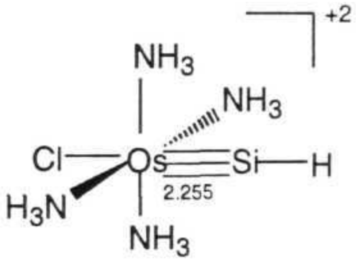
8Si



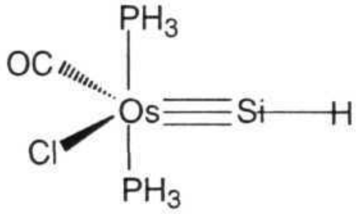
9Si



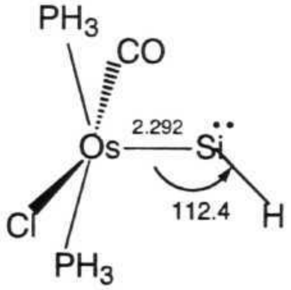
10Si



11Si



12Si



13Si

[4.3] Electron Count of the Systems:

There are several ways of counting the number of electrons in a given metal complex. The CH ligand can be treated as CH^{+}, CH, and CH^{-3} with 2, 3 and 6 valence electrons respectively.[10] The same is true for SiH as well. Since the SiH orbitals are much higher in energy than the orbitals of the metal fragment, it will be more appropriate to treat SiH as SiH^{+}. However, for the sake of uniformity, we have considered both CH and SiH as CH^{-3} and SiH^{-3} ligands. Rest of the ligands are considered with their standard electron count. It should, however, be remembered that the fragmentation of the complex and the assignment of the oxidation states are only for our convenience in understanding. The total electronic distribution of a given complex is more important than the convention of electron count adopted for the individual atoms or groups in the system.

The silylynes are chosen in such a way that the corresponding carbyne complexes are known experimentally or, at least, a close alternative exists for that particular metal. In the absence of any corresponding carbyne complex, arbitrary ligands that are supposed to mimic either the Fischer or the Schrock type were chosen. In the following sections the geometric, electronic and reactivity patterns of each metal complex are discussed individually. Comparisons are also made with the corresponding carbyne complexes.

[4.4] Tantalum-Silylyne Complexes:

There are only three tantalum carbyne complexes known and well characterized by X-ray analysis.[11] Two of them correspond to the Schrock type and the third one to the Fischer type. We have considered two types of Ta complexes, **4Si** and **5Si** for the present study. Structure **4Si** is derived from the corresponding carbyne complex, **4C**, where one cyclopentadienyl ligand is replaced by Cl ligand. This complex represents the Schrock type. Structure **5Si** is also derived from the corresponding carbyne complex, **5C**, and characterizes the Fischer type. Both of these are 18 electron complexes with d^0 and d^2 electron count for the metal respectively.

Structure **4Si** is a minimum in trigonal bipyramidal geometry with the Ta≡Si distance 2.247 Å. Gordon and Cundari have calculated, using effective core potentials at the GVB level of theory, model Ta-silylene complexes with H and Cl ligands on Ta.[12] The average Ta=Si bond length in these complexes is 2.495 Å. This length is shorter than the average Ta-Si single bond length, 2.651 Å, available from X-ray data.[13] Considering that the present calculations are reliable and comparable to the X-ray values, a decrease of 0.404 Å from the average Ta-Si bond length certainly signifies the presence of a triple bond. To appreciate the numbers further, consider the bond lengths of Si_2H_6 (2.351 Å), Si_2H_4 (2.142 Å) and Si_2H_2 (1.974 Å).[4] Here, the difference between the bond lengths of single and triple bonds is 0.377 Å which is not far from the 0.4 Å difference obtained for **4Si**. The remaining bond lengths, viz. Ta-Cl (2.456 Å) and Ta-P (2.632 Å) are in good agreement with the average X-ray values Ta-C (2.399 Å) and Ta-PMe_3(2.589 Å).[14]

The natural population analysis (NPA),[15] shows Ta in **4Si** to have slight negative charge (-0.03) and Si to possess considerable amount of positive charge (0.28). The positive charge on the Si atom implies the flow of electrons from the SiH ligand to the metal. This is contrary to the expectation for a Schrock kind of complex. In the ideal Schrock carbyne complex, the C atom is nucleophilic with negative charge developed on it. This results from the drift of charge from the high lying metal orbitals to the low lying CH orbitals. The reversal observed for **4Si** is due to the high energy SiH orbitals. For a better understanding of the electronic structure, an interaction diagram for **4Si** is constructed (Fig. 1) using the Fragment Molecular Orbital approach from EH calculations.

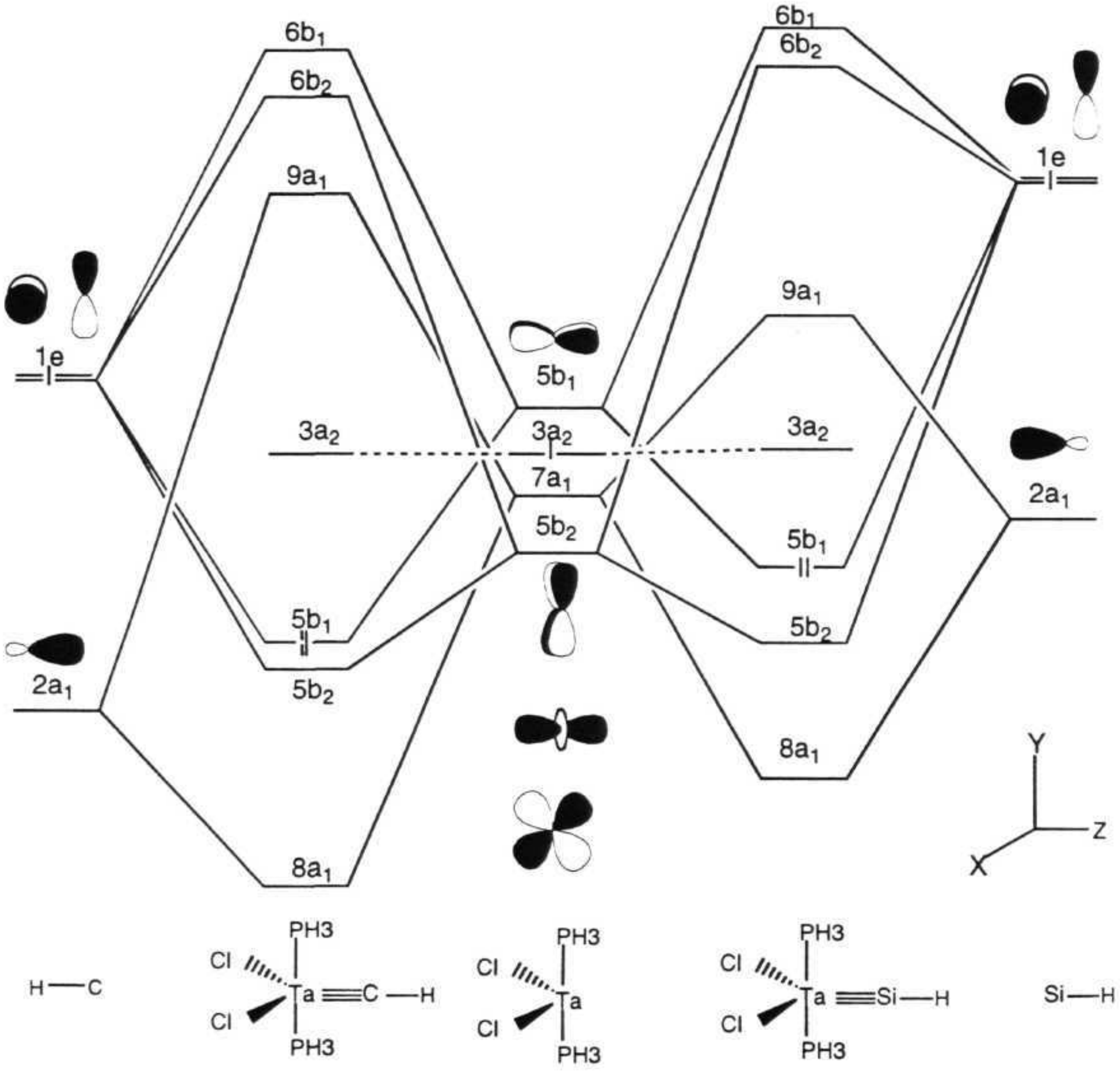


Fig. 1 Interaction diagram for **4C** and **4Si**

The complex **4Si** is fragmented into $Cl_2Ta(PH_3)_2$ and SiH. For comparison, interaction of the corresponding carbyne complex with standard geometry is also given (Fig. 1). The frontier orbitals of the TBP fragment, $Cl_2Ta(PH_3)_2$, are well known. It should be remembered that there are three valence orbitals with the right symmetry to interact with the ligand (CH or SiH) σ and π orbitals (Fig. 1). Significant differences are there between the carbyne and the silylyne complexes.

The LUMO, $3a_2$, in both the compounds is a non bonding metal orbital. Since the CH orbitals are lower in energy than those of SiH, the CH π orbitals have stronger interaction with the metal orbitals. One way to understand the strength of this interaction is to look at the orbital coefficients of the metal and the ligand. Since the ab initio wave functions are too complex to use for this purpose, we have used percentage of orbital coefficients derived from extended Hückel theory (EHT) calculations. In the present set of complexes, **4Si** and **4C**, the two π bonds are, by virtue of symmetry, not equivalent. Therefore, they have different π orbital coefficients. The metal to ligand coefficient ratio for **4C** is 31:52 for $5b_2$ and 51:37 for $5b_1$ (Fig. 1) respectively. The same for **4Si** is 54:28 and 76:16 respectively. Strong interaction will develop if the coefficients of the interacting fragments are large and equal. Clearly, the π bonds in **4C** are stronger than those in **4Si**. However, the second π bond, $5b_1$, is significantly weaker than the first one for both these complexes. These also explain the reversal of charges at the metal and ligand in these complexes.

Another consequence of this weak interaction is reflected in their HOMO-LUMO gap. The HOMO-LUMO gap, (ΔHL), is a good indicator of the kinetic stability. It is apparent from Fig. 1 that **4Si** is kinetically unstable due to the small ΔHL compared to that of the carbyne complex. In addition, the bonding π

orbitals in **4Si** have significant contribution from the metal fragment and the π^* orbitals have large MO coefficients of Si. As a result, the external base pairs (mostly the solvents molecules) tend to co-ordinate with the Si. Majority of the silylene (M=Si) complexes are thus base stabilized. Silylyne complexes also should benefit from such stabilizations.

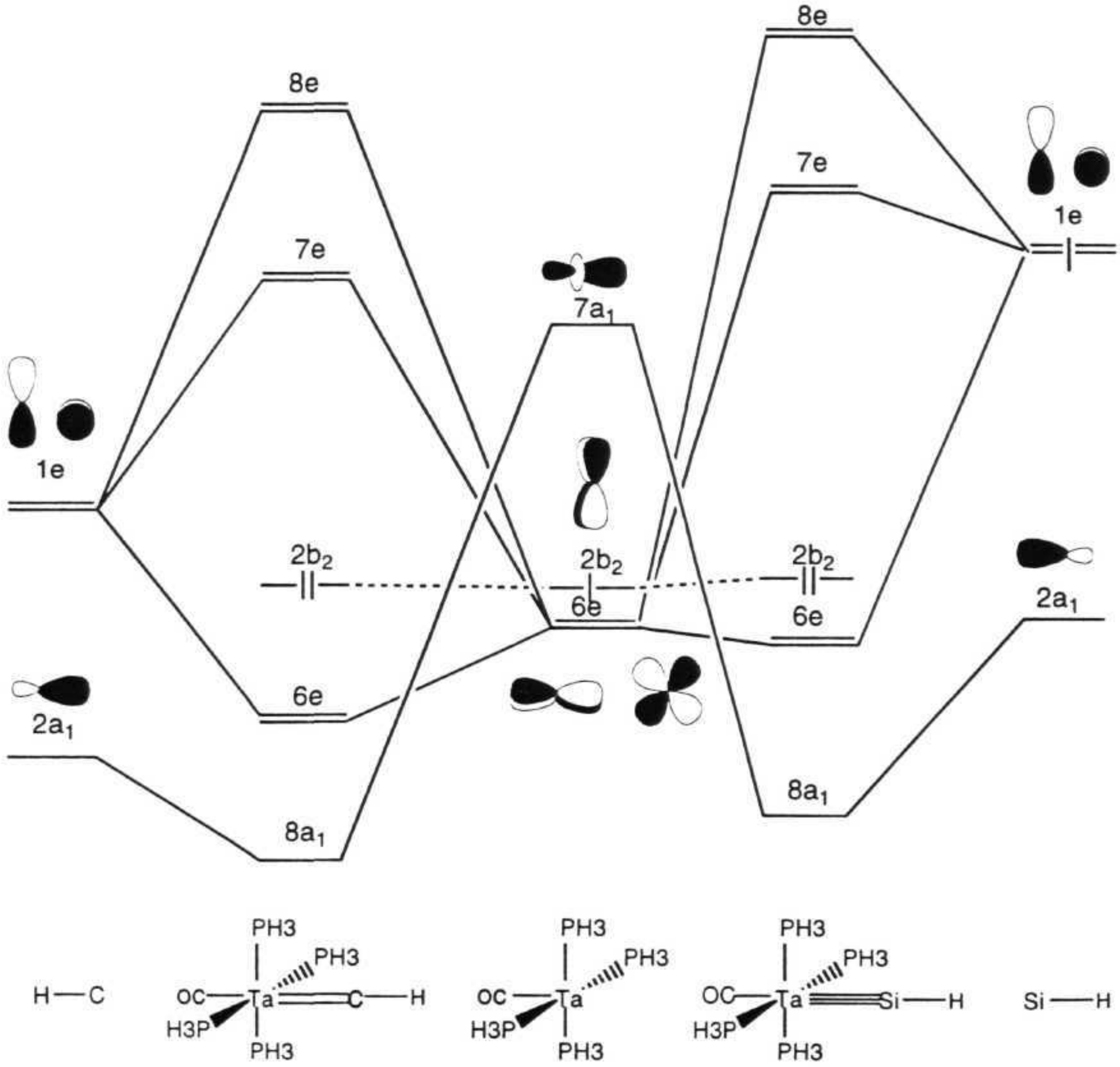


Fig. 2 Interaction diagram for **5C** and **5Si**

Addition of two more electrons to **4Si** should enhance the kinetic stability of the silylyne complex. One way to increase the number of 'd' electrons and to simultaneously maintain the total number of electrons constant is by removing anionic ligands and adding sufficient number of neutral ligands, as in **5Si**. Structure **5Si** can be derived from **4Si**, where the two Cl atoms are replaced by a CO and two PH_3 groups. It can be classified as Fischer type complex with 2d electron count.

Structure **5Si** is optimized in C_{4v} geometry. The Ta≡Si bond length is 2.354 Å, which is about 0.1 Å longer than the corresponding bond length in **4Si**. Electronically, **5Si** differs from **4Si** significantly. Due to the presence of the neutral ligands, the metal accumulates significant amount of negative charge (-0.493, from NPA). By virtue of the CO back donation, the metal orbitals with the right symmetry to interact with the ligand p orbitals, come down in energy compared to **4Si** making the interaction with SiH even worse (Fig. 2). Though the gap between $2b_2$ and 7e, ΔHL, is more for **5Si** compared to **4Si**, the π interactions are much weaker. The metal to ligand orbital coefficient ratio for **5Si,** 71:11, clearly reflects this. The corresponding ratio for **5C** is 54:31. Normally, the charge distribution in the Fischer complexes is $M^{\delta+}\equiv C^{\delta-}$. The charge on the Si atom, 0.44, however did not show the expected charge distribution. This is due to the fact that the valence orbitals of the SiH ligand are always higher in energy than the metal orbitals. Therefore, back donation from the metal to the Si rarely occurs. As a result, Si is always positive in these complexes.

5Si is not a minimum energy structure on the potential energy structure. It has two imaginary frequencies corresponding to the movement of hydrogen atoms attached to the silicon atom. We have optimized **5Si** without any symmetry constraints in C_1 symmetry which leads to **6Si**. It is 3.1 kcal/mol lower in energy than **5Si**. There is only one major geometrical change, the Ta-Si-H angle is reduced to 149.5° from linearity. However, this deformation has no effect on the charge distribution. Similarly, the relative ordering of the orbitals and their position do not change much.

[4.5] Tungsten-Silylyne Complexes:

Around 80% of the known carbyne complexes are from group 6 metals. The very first carbyne complex synthesized was with tungsten. A rich variety of Group 6 carbyne complexes with a variety of ligands and substituents are known and are well characterized. We have chosen two complexes for the present study, **7** and **8.** Structure **7,** represents the Schrock type with 12 electrons, whereas **8** is the analogy of a well known octahedral Fischer complex.

Structure **7Si** is optimized in C_{3v} geometry. The W≡Si bond length is 2.186 Å. Surprisingly, many Cr=Si complexes are known but no X-ray structure corresponding to W=Si complex is available for comparison. However, comparisons can be made with the W-Si bonds. The average W-Si bond length from X-ray crystal structures is 2.578 Å.[13] This is 0.392 Å longer than the calculated triple bond. The W-O bond length, 2.143 Å, is comparable to the average W-O bond length, 1.154 Å, obtained from X-ray.[14]

Structure **7Si**, a 12 electron complex, is a minimum on the potential energy surface. The charge distribution in **7Si** is quite interesting. Owing to the three OH groups, the metal is more positively charged (1.01, from NPA). This should make the silicon electrophilic as is observed with the corresponding carbyne complex. However, the Si atom in **7Si** is also positively charged (0.41, from

NPA). This behavior is typical of silylyne complexes, and Si can hardly acquire negative charge.

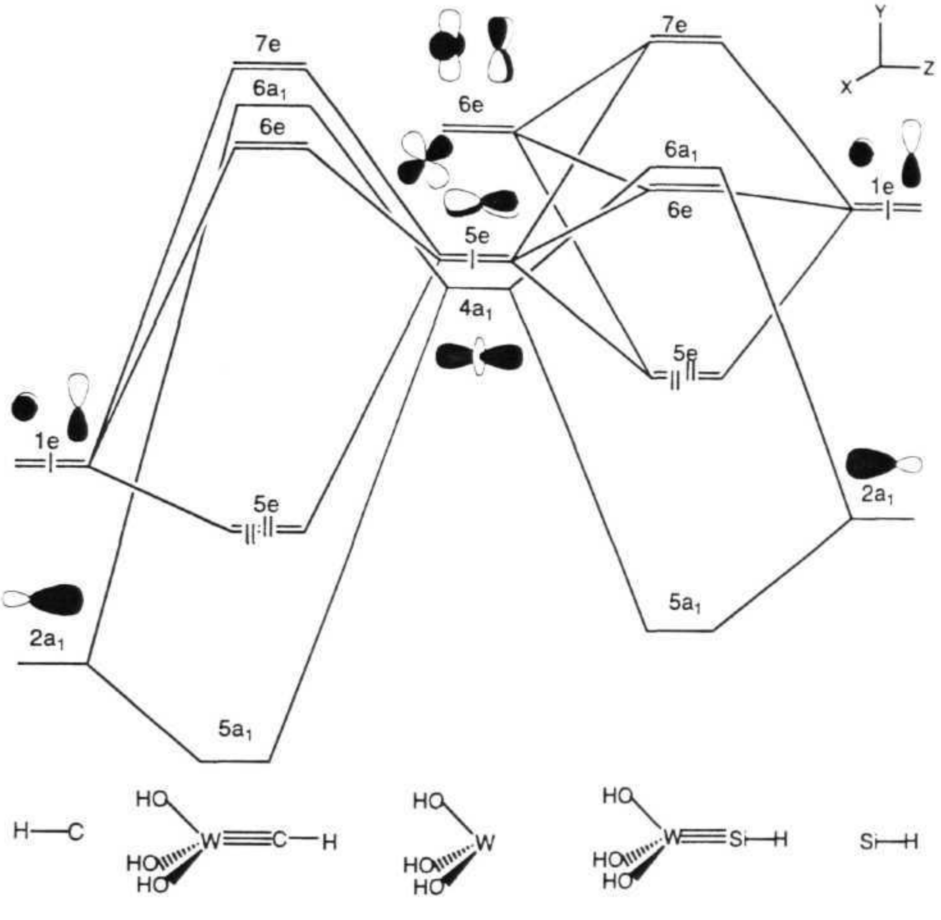


Fig. 3 Interaction diagram for **7C** and **7Si**

The presence of the electronegative ligands on tungsten pushes up the valence orbitals which, in turn, should interact better with the SiH ligand. The interaction diagram of **7C** and **7Si** is shown in Fig. 3. The valence orbitals of $W(OH)_3$ have been discussed earlier.[13] Typical Schrock type of interactions can be seen in fig. 3. The metal orbitals are higher in energy than those of CH, so the metal orbitals donate electrons to the CH making it electrophilic. This electrophilic nature of C is further reflected in making large electronic contribution to the π orbitals (Fig. 3), (28:68, metal to ligand). The higher metal orbitals are not energetically high enough to make the Si electrophilic. But, the interaction between the $W(OH)_3$ fragment and SiH are much better, 55:39, compared to that in **4Si** and **5Si**. We predict that this complex is a good candidate for synthesis.

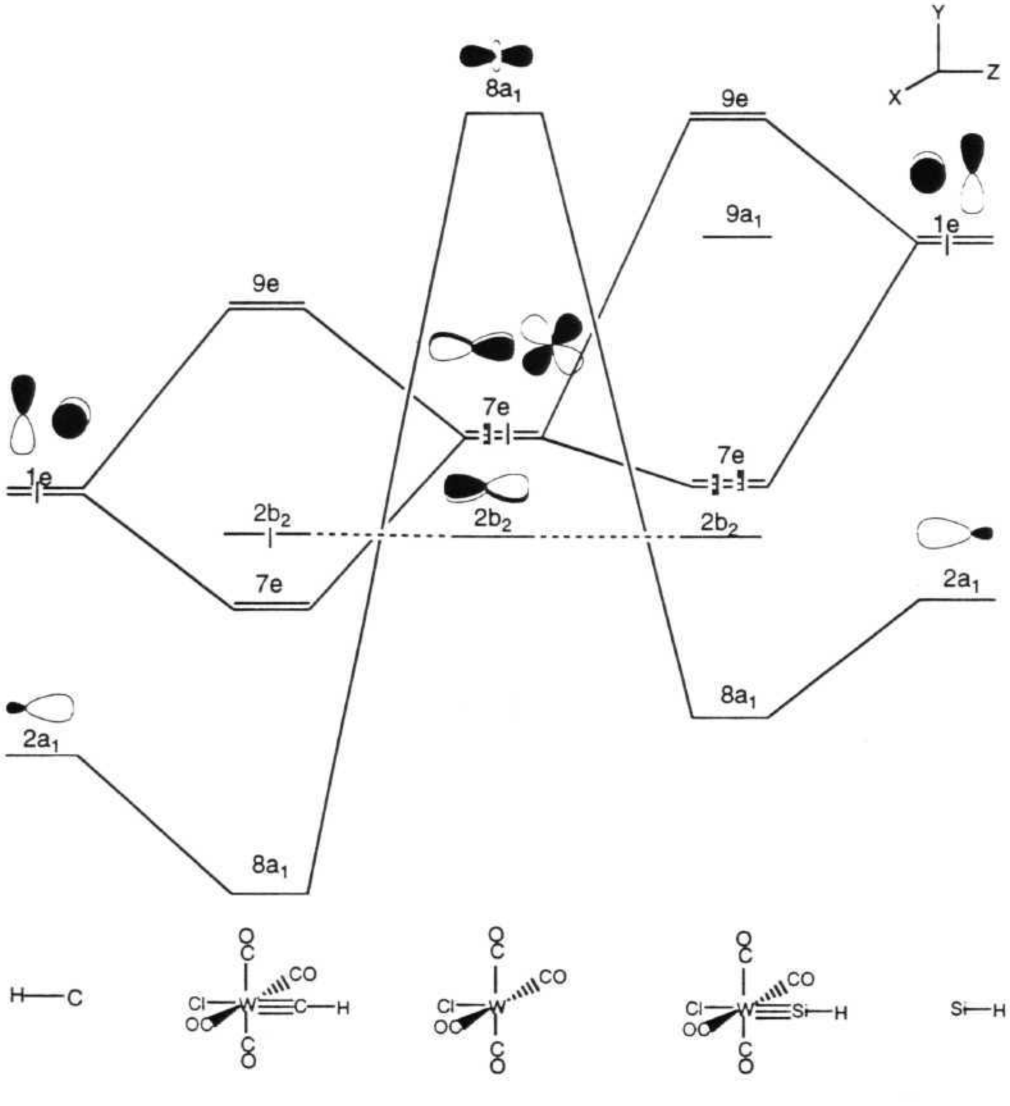


Fig. 4 Interaction diagram for **8C** and **8Si**

The discussion on silylynes is incomplete without **8**. Not only is the corresponding carbyne complex with phenyl substitution on the carbon and iodine in the trans position to it the first carbyne complex synthesized,[18] but also enormous amount of experimental chemistry has been developed subsequently. Structure **8Si** is a minimum in C_{4v} geometry. The W≡Si bond length of 2.255 Å is slightly longer than that in **7Si**. The charge distribution with W (-0.88) and Si (0.72) is quite anticipated .

The electronic structure of **8C** was discussed several times in the literature.[18] We have developed a similar interaction diagram, Fig. 4, comparing the carbyne and silylyne complexes. There are two π orbitals between the metal and the ligand. Interestingly, the HOMO of **8C** is a nonbonding metal orbital, $2b_2$, but the HOMO of **8Si,** is the degenerate π orbitals, due to the weak interactions. The metal to ligand orbital coefficient ratios for **8C** and **8Si** are 32:50 and 50:15 respectively. This implies that the well known metal fragment, $W(CO)_4Cl$, is not suitable for the SiH ligand.

[4.6] Rhenium-Silylyne Complexes

Not many rhenium carbyne complexes are known. Nevertheless, both Fischer and Schrock complexes were there among the known ones. We have selected two complexes, **9** and **10**, each one representing one category. The derivatives of both of these, **9C** and **10C**, are known experimentally and well characterized.[16]

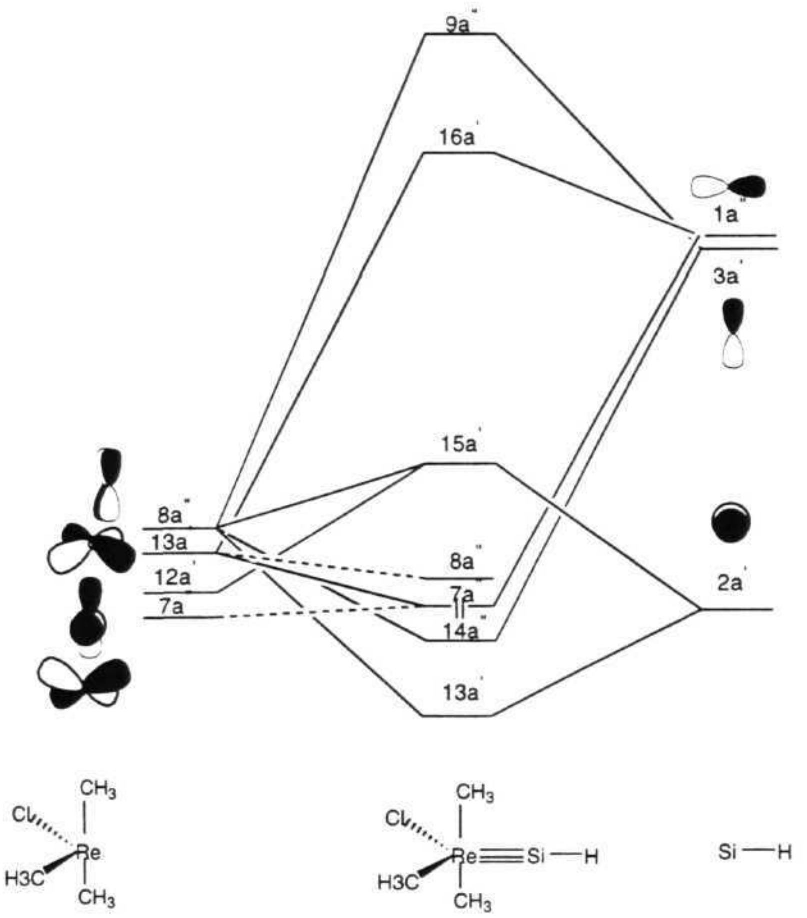


Fig. 5 Interaction diagram for 9Si

Structure **9Si**, is a minimum in C_{3v} geometry. The Re≡Si bond length is 2.171 Å. No complexes with Re=Si bonding are known for comparison. However, the average Re-Si bond length from X-ray structures is 2.511 Å.[19] The decrease in bond length for **9Si** is in line with the expectations. Structure **9Si** is a d^0 system. The charge distribution follows the expected trend, Re (-0.1) is slightly negatively and Si (0.3) is positively charged. The interaction diagram, Fig. 5, differs from the previous diagrams in one respect. The metal fragment orbitals are energetically not high enough to develop reasonable interaction with the SiH orbitals. This makes the interaction of π orbitals very weak (54:30 for **9C** and

78:10 for **9Si**). Therefore, not much stabilization is observed upon interaction with the SiH orbitals.

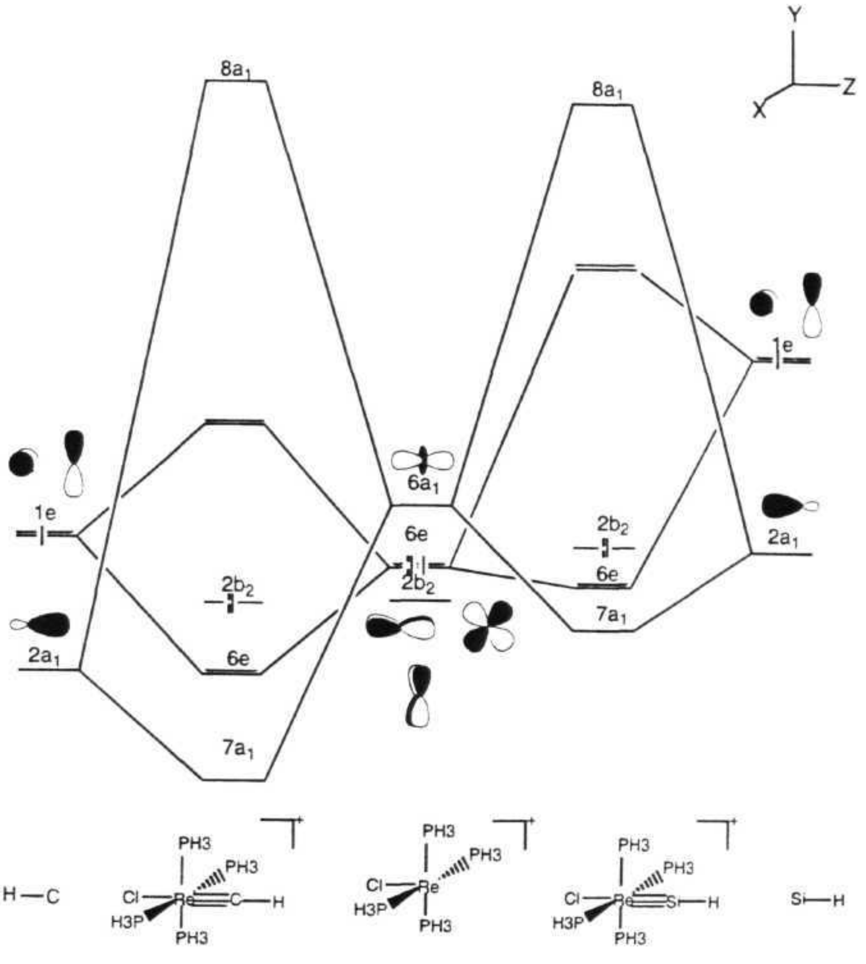


Fig. 6 Interaction diagram for **10C** and **10Si**

As a representative of the Fischer type complex, we have selected **10Si** for the study. **10Si** is a minimum in C_{4v} geometry, with Re≡Si bond length of 2.194 Å. This bond length is slightly longer than that of **9Si**. However, there is no perceptible change in the charge distribution, except that the Re atom has developed large negative charge (-1.0) compared to the Re atom in **9Si**. This can be understood from the increasing electron density at the metal center from the four PH_3 ligands. The charge on the Si atom in **10Si** has undergone hardly any change (0.41), indicating little change in the interaction with the metal fragment. In fact, the interaction diagram, Fig. 6, clearly depicts this. The metal $d\pi$ orbitals are hardly stabilized by the interaction with SiH π orbitals (ratios of coefficients, 82:10 for **10Si**). Therefore, electronically **10Si** is not a suitable candidate to stabilize the SiH ligand.

[4.1.5] Osmium-Silylyne complexes

Though only a few (more precisely five) X-ray structures of Osmium carbyne complexes are known, they assume very important position in the discussion of metal-carbyne complexes. Roper has prepared a series of Os-carbyne complexes in trigonal bipyramidal geometry, with the carbyne ligand in the equatorial position. These complexes show different reactivity patterns compared to the Fischer carbyne complexes with the group IV metals. We have considered two complexes, one of them, **11**, is of Schrock type and the other, **12**, represents the Roper complex.

Complex **11Si** is a minimum in C_{4v} geometry. It is an 18 electron complex with d^2 electron count. **11Si** is isoelectronic to **8Si,** with certain differences. **11Si** has amine groups instead of CO ligands, and is also dicationic. The $Os\equiv Si$ bond length is 2.179 Å, while the average Os-Si bond length from X-ray data is 2.471 Å.[20] The 0.308 Å difference between the single and the triple bond lengths is in accordance with the anticipation. The Os-Cl bond length (2.484 Å) is slightly longer than the average Os-Cl bond length, 2.368 Å, available from X-ray data.[14] Similarly, the Os-N bond length, 2.190 Å, is close to the average Os-N bond length of 2.136 Å.[14] The amine groups are bent away from the Os-Si-H, the N-Os-Si bond angle is 97.6°.

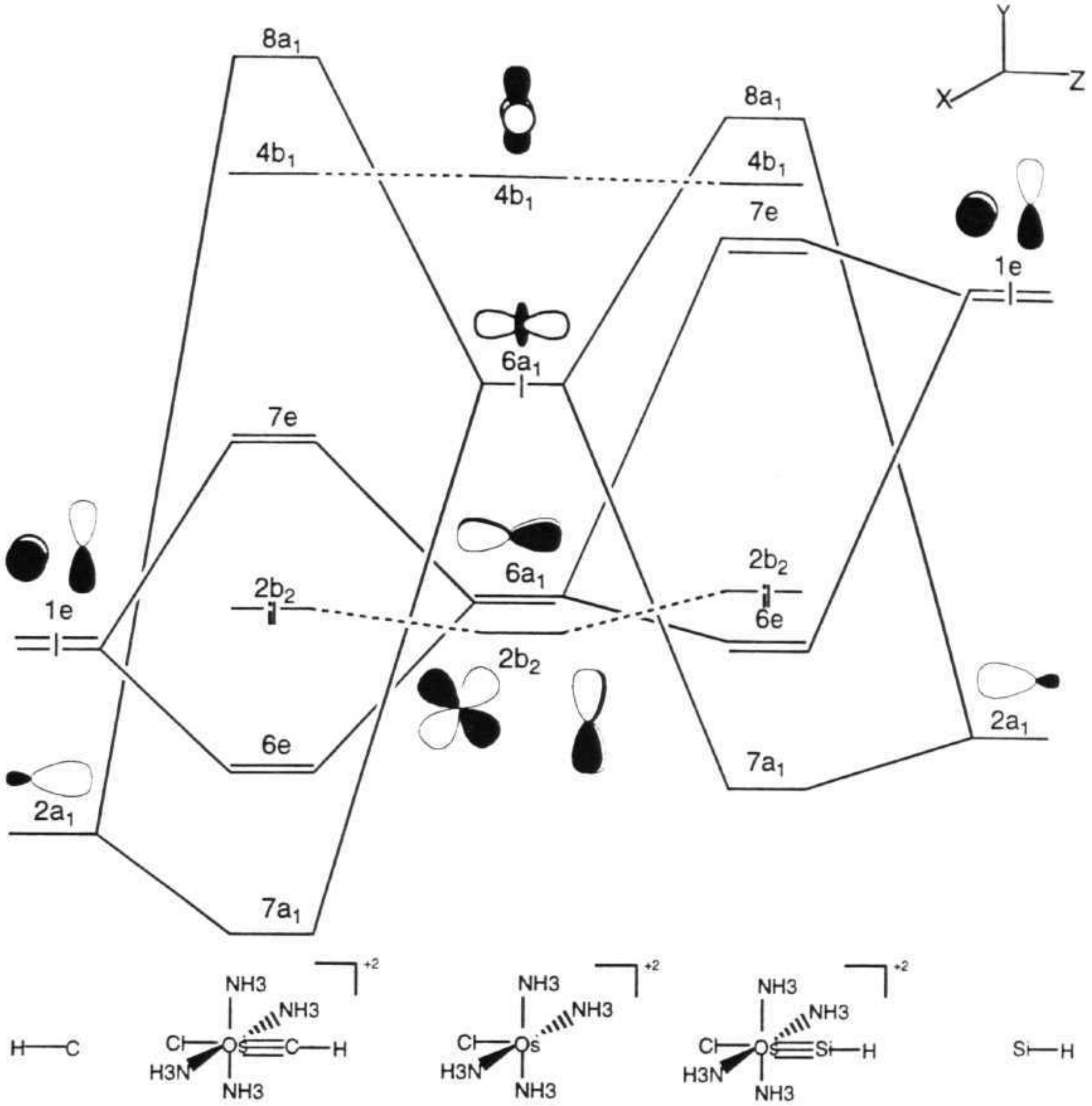


Fig. 7 Interaction diagram for **11C** and **11Si**

The natural charge distribution in **11Si** is as expected, Os (0.27) and Si (0.99). This distribution contrasts with **8Si** where the metal has negative charge and the Si is positively charged. The differences between **11Si** and **8Si** are due to the dicationic nature of **11Si**. The interaction diagram of **11Si**, Fig. 7, is very much similar to that of **8Si,** nevertheless, with some minor differences. Although the splitting pattern of the metal fragment, $ClOs(NH_3)_4^{+2}$ of **11Si** and that of $ClW(CO)_4$ of **8Si** are identical by symmetry, the frontier orbital energy levels are different. The Os metal orbitals are lower in energy than the W orbitals. As a result, the non-bonding orbital of the metal complex, $2b_2$, becomes the HOMO in **11Si**, whereas, it lies below the degenerate π orbitals in **8Si**. However, **8C** and **8Si** are similar with a non-bonding orbital as the HOMO followed by the π orbitals. Despite the shorter Os≡Si bond length, the π bonds are not strong enough. The metal to ligand contribution for **11Si** is 82:14 compared to 52:40 for the corresponding carbyne complex, **11C**.

We have considered another Os-complex, also known as the Roper complex, **12**, with d^4 electrons.[21] There is no stationary point corresponding to **12Si.** Optimization with a linear Os-Si-H geometry leads to **13Si.** Structure **13Si** is a minimum with C_s geometry. It has one carbonyl and a chloride ligand along with the carbyne (or silylyne) ligand in the equatorial plane and phosphine ligands at the axial positions. Compared to the carbon counterpart, this optimized structure has very unusual geometry. The major difference lies in the H-Si-Os angle which is 112.4° compared to 178.4° (available from X-ray) for **13C**.[14] The Os-Si bond length is 2.292 Å which is about 0.1 Å longer than what is found in **11Si**. The Os-Cl bond length, 2.520 Å, is slightly longer than the average Os-Cl bond length, 2.368 Å (from X-ray).[14] However, the Os-CO bond length is shortened to 1.848 Å from 1.902 Å, the average X-ray value.[14] The distance between the metal and the two axial phosphine ligands is also slightly elongated to 2.369 from 2.328 Å (X-ray average value).[14] The changes in bond lengths are accompanied by the equally interesting changes in the bond angles. The ligand CO vector makes an acute angle of 88.8° with Os-Si, a strong deviation from the standard angle (~120.0°). The Cl-Os-Si angle, 109.7°, is also deviated from the expected value. The axial phosphine ligands bend away (P-Os-Si angle is 98.0°) from the Os-Si vector. These structural changes reflect interesting electronic structure and are examined using FMO analysis.

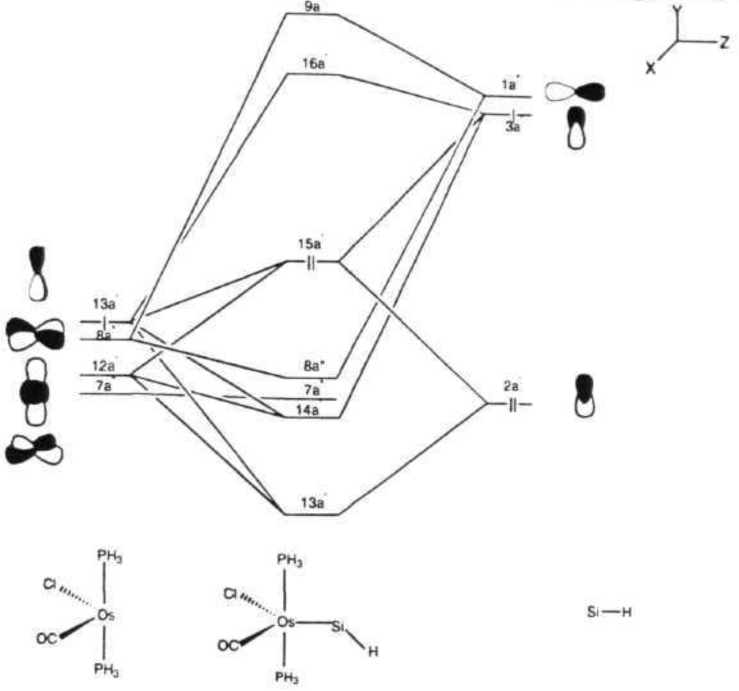


Fig. 8 Interaction diagram for **13Si**

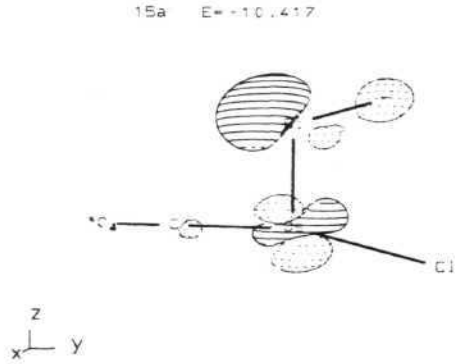


Fig. 9 Schematic representation of the orbital, 15a'. Axial PH_3 ligands are omitted for clarity.

As usual, **13Si** has been fragmented into $OsClCO(PH_3)_2$ and SiH. The interaction diagram is shown in Fig. 8. The HOMO, 15a', consists of a lone pair orbital on Si with a rearranged in-plane d-orbital interacting with the CO ligand, Fig 9. The lone pair on Si atom originates from the in-plane π orbital. Large deviation of the Os-Si-H angle from the linearity turns the otherwise regular π orbital into a lone pair orbital on Si. The corresponding in-plane d-orbital on the metal, d_{XZ}, rearranges as a result of this. The other ligands too adjust their position to maximize the interactions with the metal. The π orbital, 8a", also gets weakened due to the rearrangement of the orbitals in the equatorial plane.

[4.3] Conclusions

Our calculations reveal that the M≡Si bond can be stabilized using suitable metal templates. Owing to the high lying donor σ and acceptor π orbitals for SiH compared to CH, metal fragments with high energy valence levels are found to be better suited for SiH ligand. Thus, for each metal, Schrock type of metal fragments are more preferred than Fischer type. In general, the metal-silicon π bonds are much weaker than the corresponding metal-carbon π bonds. We identify **4Si**, **7Si**, **9Si** and **11Si** as better candidates for a stable M≡Si bond. Among these, **7Si** forms very stable π bonds. As in the main group chemistry, the preference for divalency over multiple bonding is also observed here. There is no stationary point corresponding to **12Si**. The minimum energy structure, **13Si**, has a lone pair on Si atom.

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List of Publications

1. "A Covalent Way to Stuff Fullerenes" **Current Science** 1994, 26, 766.
2. A chapter entitled "Elemental Boron Route to Stuffed Fullerenes" in **Computational Chemistry Reviews: Current Trends** Ed. Jerzy Leszczynski, World Scientific Publishers, Singapore, 1995.
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4. "H-Bridged Alternatives to the Homologues of Cyclopropane" **J. Mol. Str. (THEOCHEM)** 1996, 361, 205.
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8. "Structure and Bonding in $B_{10}Si_2H_{10}$ (X= C and Si). The Kinky Surface of 1,2-Dehydro-o-Disilaborane" **J. Am. Chem. Soc.** 1997, 119, 4076
9. "Relative Aromaticity in Inorganic 6π Six Membered Ring systems. A Structural, Energetic and Magnetic Study on $X_3Y_3H_6$ (X= B, Al and Ga; Y= N, P and As), $X_3Z_3H_3$ (Z= O, S and Se) and $P_3N_3H_6$ Systems" (accepted in **Inorg. Chem.**)

Manuscripts Under Preparation

10. "Ab Initio Studies on Structure and Bonding in Silylynes"

11. "Stability Vs Aromaticity. Can Antiaromatic Isomers be More Stable than the Aromatic Ones?"

12. "Aromaticity, Nonaromaticity and Antiaromaticity the Many faces of Cyclic 4n+2 π Electrons"

13. "Can Strained Ring Annelation Decrease the Aromaticity? A Systematic Study on 5, 6 and 7 membered ring 6π Aromatic Systems."