Chapter III

About Benzene, Prismane and Some Related Molecules

3.1. Benzene, the epitome of aromaticity

Benzene, the paradigm of aromaticity, was isolated by Faraday in 1825. Kekule first suggested the cyclic structure of benzene in 1865 and applied the term ‘aromatic’ to compounds containing benzene ring. A year later Erlenmeyer designated as aromatic those compounds with reactivities similar to benzene. At that time all unsaturated systems with cyclic conjugation were considered to be aromatic until Willstatter showed that cyclooctatetraene has no chemical similarity to benzene. Robinson’s 1925 concept of aromatic sextet was followed in 1931 by MO calculations and Hückel rule stating that planar monocyclic systems with \((4n+2)\pi\) electrons are more stable than those with \(4n\ \pi\) electrons.

With new experimental techniques and with the dramatic development of quantum theory, new interpretations to aromaticity have emerged.

3.2. Quantitative criteria of aromaticity

Aromaticity is essentially an ‘excess’ property and is a deviation from an additive scheme. Hence most quantitative measures of aromaticity are based on an assumption of some reference state.

3.2.1. Energy criteria

Resonance energy was the first quantitative measure of aromaticity. Stabilization can be measured experimentally or estimated theoretically by different models. The experimental value obtained from group-additivities of Cohen and Benson and applied to heats of formation of benzene (as aromatic) and cyclohexatriene (olefinic) is 21 kcal/mol. Inadequacy in selection of proper and sufficiently well defined reference state, limited precision and accuracy of the energy determination, the perturbation of derived energy by extraneous effects
such as strain or change in hybridisation makes the estimation of stabilization energy difficult.

Theoretical models also lack generality due to the arbitrary reference state and due to a strong dependence on the level of theory applied. For deriving stabilization energy theorists employ homodesmic or isodesmic reactions. Even with the highest available level of theory, one may end up with variable results, since they depend heavily on the formulation of the given reaction.

3.2.2. Geometric criteria

Experimentally all C-C bonds in benzene are of equal length, 1.3989 Å. Bond length alternation is assumed to be associated with decrease of aromatic characters. It is best described by statistical function of the variance of bond lengths. An obvious limitation of this index is that it cannot be applied to heterocycles since length of different types of bonds cannot be averaged. To overcome this limitation Bird\textsuperscript{37} replaced bond lengths by Gordy's bond order and applied the same procedure. The above procedures suffer from some disadvantage. According to them, any π electron system with equal bond lengths is aromatic which fails in examples like radialene\textsuperscript{38} with all C-C bonds lengths around 1.52 Å. Similarly the pentagonal ring in the C\textsubscript{60}\textsuperscript{39} has a C\textsubscript{5} symmetry, but is not certainly aromatic. The concept of optimal interatomic distance for an aromatic molecule with π electron delocalisation was successfully explained by HOMA model\textsuperscript{40} (Harmonic Oscillator Model of Aromaticity)

\[
\text{HOMA} = 1 - \left[ \frac{2}{N} \sum (R_{opt} - R) \right] = 1 - \alpha (R_{opt} - R_{av})^2 - (\alpha/N) \sum (R_{av} - R)^2 = 1 - EN - GEO...
\] (3.1)

Here two effects, which decrease aromaticity, are taken into account. 1. Increase in bond length alternation (GEO term) and 2. Increase in mean bond length in the system (EN term). \(N\) is the number of bonds taken into summation and \(\alpha\) an empirical constant chosen to scale HOMA = 0 for the hypothetical
Kekule structure of an aromatic system. HOMA = 1 for the system with all bonds equal to the optimal value $R_{opt}$. The average bond length is $R_{AV}$ where as $R_i$ is a running bond length. The terms GEO and EN are both energetic in nature. Increase in bond length alternation as also extension of bond length are expensive energetically. Thus both terms are associated with decrease in aromaticity. The HOMA model has been successful in explaining the aromatic character of many molecules.

3.2.3 Magnetic criteria

$^1H$ NMR Spectroscopy is very useful for studying aromatic character. Exocyclic protons exhibit characteristic diatropic chemical shifts due to the induction of diamagnetic ring-current in cyclic $\pi$ systems. In higher $(4n+2)\pi$ annulenes, endocyclic protons show correspondingly high field (paratropic) shifts if measured at low temperatures where as for $4n \pi$ annulenes, these effects are reversed.

Schleyer et al$^{41}$ have introduced the NICS parameter (Nucleus Independent Chemical Shift) which is a useful tool for theoretical characterisation of magnetic properties related to aromaticity of ring systems. The more negative the NICS values, the more aromatic the system. NICS too has its inherent limitations. Thus it overestimates the aromaticity of cyclopentadienyl anion and underestimates that for cyclopentatrienyl cation with the same number of $\pi$ electrons.

3.2.4 Criteria of chemical reactivity

Aromatic systems have a tendency to retain the $\pi$ electron system. However it is difficult to be expressed quantitatively. Thermodynamic stability is usually the reason for an aromatic system to prefer the reactions in which $\pi$ electrons are retained. Typical reaction of this type are electrophilic substitution, the rates of which may be affected greatly by small changes in $\pi$ electron systems due to substituent or topological effects. Unlike thermodynamic stability which is
a unique property of the ground state, kinetic stability depends on energy of the ground state, transitional states and intermediate state leading to stable products.

3.3. Azabenzenes

The replacement of all CH units by isoelectronic hetero atoms such as N, P, SiH and As, which results in N₆, P₆, Si₆H₆, As₆ received attention due to their inherent symmetry. In sharp contrast to benzene, none of them have the planar π system as global minima on their respective potential energy surface. Molecules derived from benzene by replacing two CH units by isoelectronic Nitrogen bearing a lone pair were subjected to extensive theoretical and experimental studies. Thus pyrimidine, pyridazine and pyrazine constitute the most important species possessing fully delocalised structures. Single point energies at MP3, MP4SDQ, CCSD and CCSD(T) levels show trends that are similar to that of MP2 level using 6-31G* basis set. The relative energies of ortho, meta and para are found to be 0.0, -92.3 and -76.9 kJ/mol respectively, at MP2/6-31G* level of theory. Factors that control the relative stabilities of the positional isomers are

a) Repulsion between the lone pairs.

Repulsion between lone pairs appears to be the most straightforward factor which accounts for the lower stability of the ortho isomers

b) Bond strengths in the twin VB structures:

One factor that distinguishes the stability of ortho isomer from the meta and para isomers is the bond strengths in twin Kekule structures and their resonance energies as noticed by Hiberty et al. Sums of bond strengths for the twin Kekule forms of each isomer is calculated.

Both the Kekule forms of meta and para isomers will have the identical bond strengths while those of the ortho isomer have different bond strengths.
c) Topological charge stabilization

Gimrac's\textsuperscript{45} rule of TCS shows great success in predicting the relative stabilities of the positional isomers. According to the model the more electronegative atoms occupy sites with higher electron density and less electronegative atoms occupy site with less electron density. The rule is applied to predicating the relative preference for further substitution on mono substituted benzene. The charge analysis on mono substituted benzene isomers are done using Mulliken and Natural population analyses which give preference for the occupation site to the second substituent. Since nitrogen is more electronegative than carbon and since it prefers to occupy a site with higher electron density, preference for the meta position is the highest, followed by para and ortho position. This clearly explains the stabilities of these isomers. The application of TCS successfully explains the relative stabilities of positional isomers involving different hetero atoms in general.

![Fig (3.8) Mulliken and natural atomic charges (values in parentheses) of the mono substituted isomers at HF/6-31G* level on MP2/6-31G* geometries.](image)

3.4. Hexaazabenzene

While the N\textsubscript{6} benzene like D\textsubscript{oh} structure\textsuperscript{46} corresponds to a minimum at the Hartree Fock level, it is a second order saddle point (with two degenerate imaginary frequencies) at MP2/6-31G* level.
The twist boat $D_2$ minimum is more stable than the planar variety by 1.6 Kcal/mol at MP2/6-31G* level.

3.5. Phosphabenzences

The carbon-phosphorous analogy is a powerful concept in heterochemistry, even more useful than carbon silicon analogy although the latter atoms belong to the same column of the periodic table. The analogy is general and applies to aromatic systems leading to the family of phosphinines by replacement of one or several CH entities by P atom in benzene rings. Phosphinines have been discovered by Markl in 1966. Monophosphinines are well known and display an aromatic stability that is just slightly less than benzene.

In diphosphinines, ortho, meta and para, all the C-C bond lengths are very close to the value of 1.4 Å which typifies the benzene ring indicating the absence of any phenomenon of bond fixation (preference of one Kekule structure over the other) and that resonance fully takes place in planar disphosphinines. The P-P and P-C bond lengths of these isomers lie between accepted values for the corresponding single and double bonds. Using geometries optimised at the
MP2/6-31G** level, the order of the stabilities of the three planar isomers has been calculated from HF to MP4. The results confirm that electron correlation effects, though not negligible, have a rather weak effect on the relative energies, which do not differ much from HF to MP2. The MP2 and MP4 results are practically the same showing an excellent convergence of Moller-Plesset series. All in all the MP2 results are in excellent agreement with higher levels showing that more elaborate treatments of electron correlation are insignificant as far as differences between absolute energies are concerned.

At all computation levels, the ortho isomer 2.11a is found to be the most stable while the meta 2.11b and the para 2.11c isomers are rather close together in energy and both lie a few kcal/mol above the 2.11a. The various Kekule structures 1-3 have the sums of bond strengths as follows.

![Fig. (2.11)](image)

It is seen that all the Kekule structures have the same energies in b and c. Assuming the resonance energy to be the same, 22 kcal/mol in both systems, the para and meta isomers are predicted to have about the same relative energies in agreement with computation.
Another interesting observation is the reactivity of the para isomer 2.12c which suggests some diradical character. A good indication of this property for a molecule is the singlet-triplet energy gap; the smaller the gap the larger the diradical character in the singlet ground state. The singlet triplet gap has been calculated for the three planar isomers at MP2 level. The gap amounts to 73.4, 74.3 and 66.3 kcal/mol for a, b and c respectively, showing a large diradical character for the para isomers than for the other two. Once again this computation of result can be understood in terms of relative stabilities of Kekule structures using standard bond strengths. The relative energies of the various diradical structures can be estimated and compared. The lowest diradical structure is indicated below for each isomer, showing that the lowest diradical structure among all possibilities is indeed found in 1,4-diphosphabenzene 2.12c with odd electrons located on the phosphorous atoms.

![Diagram of diradical structures for P6 isomers](image)

Fig (2.12)

3.6. Hexaphosphabenzene

Among the various valence isomers of P6, cyclic P6 (hexaphosphabenzene) is of special interest since it could share the aromatic structure of benzene, all six CH units in C6H6 being replaced by isoelectronic Phosphorous atoms. Sherer and co-workers have succeeded in preparing a triple-decker sandwich complex from the reaction of P4 with $[\eta^5 C_5 Mo (CO)_2]_2 - Mo\equiv Mo$ and found that its crystal structure involves a planar P6 ring. Calculation by Nagase and Ito at HF/6-31G revealed that the structure is having D6h symmetry as expected. At HF/6-31G level the P-P bond length of cyclic P6 (D6h) is found to be intermediate between single
and double bond values suggesting that there is significant \( \pi \) electron conjugation in the molecule. At HF/6-31G level, the resonance energy of hexaphosphabenzene is 14.9 kcal/mol. This value although significant is small when compared with value of 24.7 Kcal/mol for benzene, calculated at the same level.

In order to ascertain whether hexaphosphabenzene is an observable species, it has to be seen whether the decomposition \( \text{P}_6 \rightarrow 3 \text{P}_2 \) is hindered by a barrier. The decomposition proceeds via a \( \text{D}_{3\text{h}} \) transition structure. The barrier is calculated to be sizeable as much as 20.2 kcal/mol. The relatively high value makes hexaphosphabenzene kinetically stable.

### 3.7. Hexasilabenzene

Carbon compounds have played a central role in organic chemistry. There has been considerable interest in replacing skeletal carbon by heavier group 14 atoms especially silicon in the expectations of novel chemical properties. This can lead to a comparison between properties like aromaticity, strain and bonding in carbon and silicon compounds. Benzene is unique among conjugated compounds with respect to its stability and reactivity. This is mainly attributed to its aromaticity, which has already been discussed.

Silicon is contiguous to carbon in group 14. Thus it is expected that hexasilabenzene (Si\(_6\)H\(_6\)) also has an aromatic structure of \( \text{D}_{6\text{h}} \) symmetry since it contains six \( \pi \) electrons. The minimum energy structure has been calculated to be planar with \( \text{D}_{6\text{h}} \) symmetry at the HF level. But calculations at higher level reveal that planar \( \text{D}_{6\text{h}} \) is not a minimum on the potential energy surface but corresponds to a transition structure with one imaginary \( b_{2g} \) vibrational mode which leads to a minimum, which is a chair-like puckered structure of \( \text{D}_{3\text{d}} \) symmetry. It is well known that the SiH\(_3\) radical takes a non-planar and pyramidal structure unlike the CH\(_3\) radical. Deviation from planarity is however relatively small and gain in energy is only about 1 kcal/mol probably because \( \pi \) bonding becomes unfavourable upon pyramidisation.
3.8. Prismane

Tetrahedrane, prismane and cubane are some of the most strained organic compounds. Prismane is estimated to have a strain energy of 130 Kcal/mol. Yet the molecule has been prepared and is found to be stable.

3.8.1. Synthesis of prismane

Prismane has been synthesized by Katz and Acton. Benzvalene (2.13a) on combining with 4-phenyltriazolinedione (ice cooled, then set at room temperature for 1 hr) gives, after passage through silica gel using CHCl₃ eluent, in 50-60% yield a 1:1 adduct, m.p 173-175°, of structure 2.13b. Refluxing with KOH in CH₃OH – H₂O (85:15 v/v) for 24 hr, extraction and treatment with acidic CuCl₂ then gives a cuprous chloride derivative, which with aqueous NaOH gives azo compound 2.13c (65% yield after crystallization from pentane sublimation). Prismane was isolated in 1.8% yield after photolysing 3.2g of 2.13c as a 0.19 M solution in isobutane at 35°, evaporating solvent, distilling at 10⁻⁴ Torr. It is an explosive colourless liquid. Stable at room temperature. At 90° in Toluene it decomposes with a half-life of 11 hr, giving benzene. It is therefore unnecessary to cool the reaction mixture in which prismane is prepared. In fact, it is essential that for the success of the synthesis that during the photolysis the aza compound 2.13c be heated.

![Chemical diagram](image)

Fig (2.13)
Early calculations by Newton and Schulman\textsuperscript{50} shows the hybridisation of CH bond in prismane to be 36.4% s character. The $J_{\text{CH}}$ in prismane is very high (calcd. 189 Hz; exptl. 182 Hz), reflecting high degree of angle strain. The $J_{\text{CC}}$ for three-membered ring in prismane (10.4Hz) is close to cyclopropane itself (calcd. 13.2 Hz; exptl 10.0Hz). The $J_{\text{CC}}$ values for the four-membered rings in prismane (39.7Hz) and Dewar benzene (41.5Hz) are close to the analogous value for the side bond in bicyclo [2,1,0] pentane (calcd 37.1 Hz; exptl 36.7 Hz).

Although the hybridisation of C-C bonds in the three-membered rings of prismane is similar to that in cyclopropane, the lowest I.P. of prismane (8.4 eV) is appreciably smaller than the corresponding cyclopropane value.

The calculated electrostatic potential of prismane show interesting and significant features of negative regions associated with C-C bonds; the most negative points being near the midpoint of bonds\textsuperscript{51}. While this is not typical of chemical bonds in general, we find it to be the characteristic of C-C bonds of strained hydrocarbons. These bonds can accordingly serve as initial sites for electrophilic attack as proved in the laboratory.

### 3.9. Aza analogues of prismane

Aza analogues of prismane are obtained by replacing one or more CH units of prismane with nitrogen. Early studies show that there is a shortening of both C-C and C-N bonds as the number of nitrogen increases\textsuperscript{52}. Finally, the N-N distances are again unusually long, in the 1.58-1.60 Å range. In isomeric compounds, the one having the fewest N-N bonds is the most stable isomer. Unlike heterocyclic aromatic systems, in polyazaprismane the N-N distances are unusually long. This suggests that the instability resulting from adjacent nitrogens in strained molecules may be due to a tendency for the N-N bonds to rupture.

Due to the electron-withdrawing power of nitrogen, the negative C-C bond potentials are greatly weakened in monoazaprismane. Thus reactivities of C-C
bonds towards electrophiles can be expected to greatly diminish as the number of nitrogen increases.

But the azaprismanes do show strong and extensive negative regions associated with the nitrogen which can be attributed to their lone pairs. These basic sites are expected to be important elements of the reactive behaviour of aza systems. These negative sites become progressively weaker as the number of nitrogen in the molecule increases. As more of them compete for the available polarisable electronic charge, each receives only a smaller share of it.

3.10. Silaprismane

Of the various silaprismanes possible, the most studied is the hexasilaprismane. An important point to be noted is the relative stabilities of the valence isomers. Benzene is 85-120 kcal/mol more stable than its valence isomers such as Dewar benzene, benzvalene and prismane. In contrast Si₆H₆ valence isomers are close in stability to hexasilabenzene and are progressively favoured as the number of double bond decrease. Thus hexasilaprismane is nearly 13.4 kcal/mol more stable than hexasilabenzene and is the most stable Si₆H₆ isomer. The dramatic difference between C₆H₆ isomers and their heavier analogues are ascribed to the fact that the heavier atoms have a strong tendency to have saturated bonds and are capable of forming less strained compounds.

There is an interesting contrast between silicon and carbon compounds. Tetrasilatetrahedrane is as highly strained as tetrahedrane. As the number of four-membered rings increases, however, the strain decreases significantly in silicon compounds, while it increases in carbon compounds. Thus hexasilaprismane is 32 kcal mol⁻¹ less strained than prismane, while octasilacubane with only four membered rings is 65 kcal mol⁻¹ less strained than cubane. The decrease in strain is due to a stronger reluctance of the heavier atoms to form hybrid orbitals; that is, an increasing tendency to maintain the (ns)² (np)² valence electron configuration even in compounds. Apparently this property of the heavier atoms is favourable
for making 90° bond angle in four membered rings\textsuperscript{54}. However, it becomes unfavourable is forming three-membraned rings with bond angles of 60° where hybrid orbitals with sufficiently high \( p \) character are essential for a description of the bent bond orbitals\textsuperscript{55}.

3.10.1. Synthesis of hexasilaprismane

Hexasilaprismane was synthesized by Sekiguchi et al\textsuperscript{56}. For the synthesis of strained polyhedranes proper choice of both starting compounds with suitable substituents and metal as reducing reagent is of crucial importance. Alkali metals are powerful reducing agents but sometimes cause the cleavage of the Si-Si bond. So the Mg/MgBr\(_2\) reagent that will not cleave the Si-Si bond is used.

The hexasilaprismane, hexakis(2,6-diisopropylphenyl)tetracyclo[2,2,0,0,0]
hexasilane (2.14c) was thus prepared by the dechlorinative coupling reaction of 1,2-bis(2,6-diisopropylphenyl)1,1,2,2-tetrachloridisilane (2.14a, 10.0 g, 19.2 mmol) with Mg (80 mmol/ MgBr\(_2\) (80 mmol) in THF. Purification by chromatography on silica gel with toluene gave 2.14c as orange crystals.
Contrary to other polyhedranes 2.14e is thermally and oxidatively fairly stable in the solid state, no change being observed even after a couple of months in air. The structure of 2.14e was elucidated by X-ray diffraction method. The skeleton is slightly distorted from the regular prismane structure made up from two triangular units (Si-Si; 2.374-2.387 Å av. 2.380 Å and Si-Si-Si; 59.8-60.3° av. 60.0°) and three rectangular units (Si-Si'; 2.365-2.389 Å av. 2.373 and Si-Si'; 89.6-90.5° av. 90.0°).

All the Si-Si bonds are elongated from the normal Si-Si bond length (2.34 Å) and are somewhat longer than those calculated for Si₆H₆ (2.359 Å for triangular units and 2.37 Å for rectangular units)⁵⁷.

3.11. Hexaphosphaprismane

In spite of the structural resemblance, the relative stability of P₆ isomers differ dramatically from that of N₆ isomers. As expected from the highly strained structures, the N₆ valence isomers are much more unstable than hexazabenzene. However, P₆ valence isomers are found to be almost as stable as hexaphosphabenzene⁵⁸. In order to give a satisfactory explanation, the strain energy of hexaphosphabenzene is estimated by using the following homodesmic reaction.

\[ P_6 + 9 \text{H}_2\text{PPH}_2 \rightarrow 6 \text{P( PH}_2)_3 \]

At HF/6-31G* the strain energy is found to be 43.5 kcal/mol.

The dimerisation 2HP=PH \rightarrow \text{cyclo (PH)}₄ is calculated and found that the reaction is 34.4 kcal/mol exothermic at HF/6-31G* level. Thus, it is shown that

\[ (\text{P=PH}) - 2 (\text{P-P}) = -17.2 \text{ kcal/mol} \]

This negative value corresponds to the fact that phosphorous is reluctant to form double bonds. Three double bonds are formally present in
hexaphosphabenzene. Upon going to its valence isomer three double bonds are transferred into six single bonds. And energy gain \((3 \times 17.2 = 51.6 \text{ kcal/mol})\) by this transformation is large enough to compensate a strain energy of 43.5 kcal/mol leading to a net stabilization of 8.1 kcal/mol. If a loss of resonance stabilisation \((15.2 \text{ kcal/mol at HF/6-31G level})\) is added, a small destabilization of 7.1 kcal/mol is obtained which agrees with the calculated value.

One may suspect that hexaphosphabenzene isomerises readily because of small energy separation from its valence isomers. However, the thermal isomerisations are symmetry-forbidden in terms of Woodward-Hoffmann rule. Thus hexaphosphabenzene is separated by considerable barriers from its valence isomers.