Chapter V

Hexasilabenzene and Hexasilaprismane and Their Phospha
Analogues

5.1. Introduction

Silicon occupies a special position in chemistry. The tetra covalency of silicon in many of its compounds which show remarkable stability resembles that of carbon in saturated carbon compounds. On the other hand, its lack of ability to form stable multiple bonded compounds, its poor ability to catenate, its many crystalline compounds and its ability to expand its coordination sphere are all different from carbon. Its chemistry may be said to lie between that of organic and inorganic compounds. Moreover, silicon is the second most abundant element on the earth's crust, and is today, the vital component of microchip technological development. Thus there is an expanding interest in silicon chemistry.

Carbon plays a pivotal role in organic chemistry. There has been a considerable interest in replacing the skeletal carbons in molecules by heavier group 14 atoms, especially silicon. Benzene is unique among conjugated compounds because of its special stability. This has been attributed to its aromaticity. Silicon is contiguous to carbon in group 14 and it is natural to ask whether hexasilabenzene Si₆H₆ also has an aromatic structure since it also contains six π electrons. But computational calculations at higher level of theory reveal that the planar D₆h structure is not a minimum on the Si₆H₆ potential energy surface, but corresponds to a transition structure with one single imaginary b₂g frequency. The displacement along the b₂g vibrational mode leads to a minimum which is a chair-like puckered D₃d structure.

Another interesting point to be noted is the relative stabilities of its valence isomers. Benzene is 85 – 130 kcal/mol more stable than its valence isomers such as Dewar benzene (C₂ᵥ), benzvalene (C₂ᵥ) and prismane (D₃h). In
contrast, the Si₆H₆ valence isomers lie very close in stability to hexasilabenzene and are progressively favoured as the number of double bonds decrease. Thus hexasilaprismane which is about 13 kcal/mol more stable than hexasilabenzene becomes the most stable Si₆H₆ isomer. The dramatic difference between C₆H₆ isomers and their silicon analogues are ascribed to the fact that silicon atoms have a tendency to have saturated bonds and are capable of forming less strained compounds.

There are earlier studies on the stabilities of hexasilabenzene and hexasilaprismane. One can naturally assume that just like the stability patterns emerging for azabenzenes and azaprismanes in skeletally substituted hexasilabenzene and hexasilaprismane also, patterns of stability will become evident. The SiH units of hexasilabenzene and hexasilaprismane are progressively replaced with phosphorus and the relative stabilities of these molecules are investigated. This chapter includes the findings so obtained and the attempts to give meaning to these findings.

5.2. The method

Ab initio calculations are done using Gaussian 98 program. Full geometry optimisation was carried out at HF/6-31G** level in each case under symmetry constraints indicated. Single point calculations on HF/6-31G** optimised structures were carried out to get MP2/6-31G** energies. All the stationary points are characterised by carrying out vibration frequency calculations at HF/6-31G**. Most of the molecular structures under study are found to be minima on the potential energy surface since they have no imaginary frequencies. But in some cases, structures are not minima because they have one or more imaginary frequencies.
5.3. Results and discussion

5.3.1. Hexasilabenzene and hexasilaprismane

Hexasilaprismane is found to be 11.7 kcal/mol more stable than hexasilabenzene at MP2/6-31G** level. Hexasilabenzene shows a small imaginary frequency, indicating that the planar form is not a true minimum although close to it. Structure and other details of energy are given in Table 5.1.

Table 5.1

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<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>Rel. energy kcal/mol</th>
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Here we find a reversal in relative energies from that of benzene and prismane where benzene is far more stable than prismane. In the case of hexasilabenzene and hexasilaprismane also, factors like bond strength, resonance and strain can decide the relative energies. Unlike benzene, resonance stability of hexasilabenzene is small due to the poor $\pi$ orbital overlapping capacity of silicon. Also, strain in hexasilaprismane is reduced due to the stronger reluctance of silicon atom to form hybrid orbitals; that is, an increasing tendency to maintain (ns$^2$) (np$^3$) valence electron configuration, even in compounds. This property of silicon is favourable for making $90^\circ$ bond angles with low strain in four-membered rings. Also, silicon atoms have a tendency to prefer saturated bonds, unlike carbon. All these factors combined
makes hexasilaprismane more stable than hexasilabenzene, although by only a few kcal/mol.

5.3.2. Monophosphapentasilabenzenze and monophosphapentasilaprismane

Monophosphapentasilaprismane 4.b is found to be more stable than monophosphapentasilabenzenze 3.b by 12.1 kcal/mol. 3.b is not a true minimum in the potential energy surface since it shows one imaginary frequency. One can assume that factors that make hexasilaprismane more stable than hexasilabenzene are responsible for the greater stability of 4.b also. Structure and details of energy are given in table 5.2.

Table 5.2

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5.3.3. Diphosphatetrasilabenzenze and diphosphatetrasilaprismane

Diphosphatetrasilabenzenze has three isomers. The ortho 3.c1, the meta 3.c2, and the para 3.c3. Diphosphatetrasilaprismane also has got the same number of isomers, 4.c1, 4.c2 and 4.c3. Unlike diazabenzenze and diazaprismane isomers, where diazaprismane isomers have far higher relative energies than diazabenzenze isomers the relative energies of diphosphatetrasilabenzenze and diphosphatetrasilaprismane isomers are quite close. In fact, in some cases they overlap. Thus the planar isomer 3.c1 with C2v symmetry has a relative energy of 27.3 kcal/mol at MP2/6-31G** level of
theory. $\textbf{3.c2}$ with $C_{2v}$ symmetry is more stable with 12.4 kcal/mol at the same level of theory and $\textbf{3.c3}$ with $D_{2h}$ symmetry has a relative energy of 15.1 kcal/mol. Vibrational frequency calculations show that $\textbf{3.c2}$ is not a true minimum on the potential energy surface at HF/6-31G** level.

Of the three diphosphatetrasilaprismanes, isomer $\textbf{4.c1}$ with $C_{2v}$ symmetry has a relative energy of 15.1 kcal/mol at MP2/6-31G** level of theory. $\textbf{4.c2}$ with $C_5$ symmetry is slightly more stable with 13.6 kcal/mol at the same level of theory. Of all the isomers, planar and non planar, isomer $\textbf{4.c3}$ is the most stable in agreement with the general trend that phosphasilaprismanes are more stable than phosphasilabenzene isomers. Vibrational frequency calculations show that all structures are minima since there are no imaginary frequencies. Structures and energy details are given in Table 5.3.
Relative stabilities of diphosphatetrasilabenzene isomers

The stability pattern of diphosphatetrasilabenzene isomers is similar to that of diazabenzene isomers and that of diphosphatetrasilaprismane isomers is similar to that of diazaprismanes. The factors that can determine the relative energies of diphosphatetrasilabenzenes are

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Relative stabilities of diphosphatetrasilabenzene isomers

The stability pattern of diphosphatetrasilabenzene isomers is similar to that of diazabenzene isomers and that of diphosphatetrasilaprismane isomers is similar to that of diazaprismanes. The factors that can determine the relative energies of diphosphatetrasilabenzenes are
1. Electrostatic interactions

Electrostatic interaction can give the simplest explanation for the relative stabilities of the various isomers. The ortho isomer \(3.c1\) with highest electrostatic repulsion is the least stable isomer. Isomers \(3.c2\) and \(3.c3\) with attractive interactions are more stable.

2. Topological Charge stabilisation

Gimrac's rule of topological charge stabilisation (TCS) can be used in this context also to explain the relative stabilities of the isomers. According to this rule, the more electronegative atoms try to occupy sites with higher electron density. The charge analysis on the mono skeletally phosphorus substituted hexasilabenzene is done using Mulliken and natural population analyses. Since phosphorus is more electronegative than silicon, it prefers to occupy the site with higher electron density. Thus, the preference for the meta position is the highest, followed by para. The least preferred is the ortho position. This explains the relative stabilities of the isomers, and theoretical calculations also support this observation.

![Fig 5.1 Mulliken and natural atomic charges on monophosphapentasilabenzene at HF/6-3G** level.](image)

Relative stabilities of diphosphatetrasilaprismane isomers

Of the various energies that contribute to the relative stability, the total bond strength\(^67\) can be the most significant one. Isomers \(4.c1\) and \(4.c2\) with four Si-Si bonds, four Si-P bonds and one P-P bond have a total bond energy of 419 kcal/mol and total electronic energies are also close. But isomer \(4.c3\) with
three Si-Si and six Si-P bonds is calculated to have a total bond strength of 432 kcal/mol, explaining its higher stability.

5.3.4. Triphosphatrisilaprismane and triphosphatrisilabenzene

Triphosphatrisilabenzene has three isomers. The number of isomers for triphosphatrisilaprismane is also the same. Contrary to the general trend, of all the six isomers, the planar isomer 3.d3 with D$_{3h}$ symmetry is the most stable isomer at MP2/6-31G** level. Isomer 3.d1 has a relative energy of 31.7 kcal/mol and is the least stable of all isomers. 3.d2 has a relative energy of 20.7 kcal/mol at MP2 level. Isomer 3.d2 shows three imaginary frequencies, indicating it is not minimum on the potential energy surface. But 3.d3 and 3.d1 show no such imaginary frequencies, and their structures are true minima on the potential energy surface.

Triphosphatrisilaprismane isomer 4.d2 with Cs symmetry is the most stable non planar isomer, with a relative energy of 0.3 kcal/mol at MP2/6-31G** level and is close in relative stability to the isomer 3.d3. Isomer 4.d1 with C$_{3v}$ symmetry is considerably less stable with relative energy 28.9 kcal/mol at the same level. 4.d3 with C$_1$ symmetry is having a relative energy of 15.4 kcal/mol. Vibrational frequencies show that all the three isomers are minima on their potential energy surface since there are no imaginary frequencies. The structure and energy details are given in Table 5.4.
Table 5.4

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<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
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Relative stabilities of triphosphatrisilabenzenes

Triphosphatrisilabenzenes isomer 3.d3 is the most stable of all the six isomers, in contrast to the general trend where non-planar isomers are more stable. The additional stability of 3.d3 can be explained by electrostatic interaction. The molecule has a significant charge alternation and it is reminiscent of borazine, \(B_3N_3H_6\), than of benzene itself. When we come to 3.d1
such attractive interactions decrease and the relative stability is also decreased. In the case of 3.d1 the interaction becomes more repulsive in nature and it becomes the least stable isomer. This observation is confirmed by theoretical calculations.

Topological charge stabilisation can also be used to predict the relative stabilities of triphosphatrisilabenzenes. The charge analysis on the mono-skeletally phosphorus substituted hexasilabenzenes is done using Mulliken and natural population analyses. Since phosphorus is more electronegative than silicon, phosphorus prefers to occupy sites with higher electron density. Thus in isomer 3.d3, the two incoming phosphorus atoms occupy the meta position with respect to the existing P atom where the electron density is the maximum and is the most stable isomer. In the second isomer 3.d2, one incoming phosphorus goes to the meta position, where the electron density is the maximum and the second phosphorus atom goes to the less preferred para position. In the least stable isomer 3.d1, one incoming phosphorus atom occupies the meta position and the second one the least preferred ortho position. This is confirmed by theoretical calculations.

\[ \text{Fig 5.2 Mulliken and natural atomic charges on monophosphapentasilabenzenes at HF/6-3G** level.} \]

**Relative stabilities of triphosphatrisilaprismanes**

Of the various types of energies, total bond strength can be the most significant factor which decides the relative stabilities. Isomer 4.d1 with three Si-Si bonds, three P-P bonds and three Si-P bonds has a total bond energy of 402 kcal/mol. Isomer 4.d3 of C₁ symmetry having two Si-Si bonds, two P-P bonds and five Si-P bonds has a total bond energy of 422 kcal/mol. 4.d2 with
Cs symmetry having one Si-Si bond, one P-P bond and seven Si-P bonds has a total bond strength of 432 kcal/mol and is the most stable non-planar isomer. Total bond strengths are in agreement with relative energies of these isomers.

5.3.5. Tetraphosphadisilabenzenes and tetraphosphadisilaprismanes

There are three isomers of tetraphosphadisilabenzene and an equal number of tetraphosphadisilaprismanes. Tetraphosphadisilaprismane isomer 4.e2 of $C_2$ symmetry is the most stable isomer at MP2/6-31G** level, in confirmation with the general trend. 4.e1 with Cs symmetry has a relative energy of 15.9 kcal/mol at the same level of theory. Isomer 4.e3 with $C_{2v}$ symmetry is slightly less stable with a relative energy of 17.5 kcal/mol at the same level.

Tetraphosphadisilabenzene isomer 3.e1 with $C_{2v}$ symmetry has a relative energy of 26.7 kcal/mol at MP2 level. Isomer 3.e2 with same symmetry is more stable with relative energy of 12.5 kcal/mol. Isomer 3.e1 has five imaginary frequencies and is not a minimum on the potential energy surface. Structure and other energy details are given in Table 5.5.
Relative stabilities of tetraphosphadisilabenzenes

Relative stabilities of the isomers can be explained by electrostatic interactions and also topological charge stabilisation. Electrostatic charge repulsion is more in isomer 3.e1 and is less stable than 3.e2 where repulsive interactions are smaller.

Topological charge stabilisation can also be used to explain the relative stabilities of the isomers. Thus tetraphosphadisilabenzenes can be considered as a silicon substituted derivative of pentaphosphasilabenzenes. Atoms with lower
electro negativity prefer to remain positions with higher positive charge. Hence the SiH unit prefers to occupy the meta position and is the more stable isomer. The less preferred position is the ortho position. Theoretical calculations also confirm this observation.

The less preferred position is the ortho position. Theoretical calculations also confirm this observation.

![Fig 5.3](image)

**Fig 5.3 Mulliken and natural atomic charges on pentaphosphasilabenzenzene at MP2/6-3G** level.

**Relative stabilities of tetraphospha disilaprismane isomers**

The isomers of tetraphospha disilaprismane also vary in their relative energies. Total bond strength can be the most important factor that decides the relative energies in this case also. Thus the total bond energy of 4.e1 and 4.e3 with one Si-Si bond, four Si-P bonds and four P-P bonds are 410 kcal/mol. Their relative energies are also very close. Isomer 4.e2 with six Si-P bonds and three P-P bonds has a total bond strength of 429 kcal/mol. This gives 4.e2 a relative stability of 19 kcal/mol which is close to the theoretically calculated value.

**5.3.6. Pentaphosphasilabenzenzene and pentaphospha disilaprismane**

Pentaphosphasilaprismane is more stable than pentaphosphasilaprismane by 8.4 kcal/mol at MP2/6-31G** level. Pentaphosphasilabenzenzene also has five imaginary vibrational frequencies, indicating that it is not a true minimum. Structure and other energy details are given in Table 5.6.
Table 5.6

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5.4. Relative stabilities of ‘complement’ molecules

Just as in the case of azaprismanes and azabenzenes, we find that the relative energies of complement molecules of phosphasilabenzenes and phosphasilaprismanes are also quite close. Here complement molecules are formed when the SiH units of the molecule concerned are replaced with P and P with SiH units.

Diphosphatetrasilabenzenene isomer 3.c₁ of symmetry C₂ᵥ and its complement molecule 3.e₁ of the same symmetry have very close relative energies, the values being 27.3 and 26.7 kcal/mol respectively at MP2/6-31G** level of theory. Similarly, isomers 3.c₂ with symmetry C₂ᵥ and its complement 3.e₂ with the same symmetry have virtually the same relative energies, 12.4 and 12.6 kcal/mol respectively.

This relationship holds for phosphasilaprismane isomers also. Diphosphatetrasilaprismane isomer 4.c₁ of symmetry C₂ᵥ has a relative energy of 15.1 kcal/mol, and its complement of the same symmetry 4.e₃ has a relative energy of 17.5 kcal/mol. The isomer 4.e₂ with Cₛ symmetry has a relative energy of 13.6 kcal/mol and the complement molecule 4.e₁ has a close relative energy of 15.9 kcal/mol. The isomer 4.e₃ of C₂ symmetry and its complement isomer 4.e₂ are the most stable isomers at MP2/6-31G** level.
Monophosphapentasilabenzene 3.b and monophosphapentasilaprismane 4.b and their complement molecules pentaphosphasilabenzene 3.f and pentaphosphasilaprismane 4.d3 also hold the same relationship. While 3.b has a relative energy of 12.1 with respect to 4.b at MP2/6-31G** level of theory, its complement 3.f has a relative energy of 8.3 kcal/mol at the same level of theory, which is reasonably close.

As in the case of azabenzenes and azaprismanes, here also these observations can give insights into the energy relationships of these molecules.

When we consider difference in bond energies between diphosphatetrasilaprismane isomers 4.c1 of C\textsubscript{2v} symmetry and isomer 4.c3 of C\textsubscript{2} symmetry.

\[
\text{total bond energy } 4.c3 - \text{total bond energy } 4.c1 = 2E_{\text{SiP}} - E_{\text{SiSi}} - E_{\text{PP}}
\]

where \(E_{\text{SiP}}\) is the strength of Si-P bond, \(E_{\text{SiSi}}\) is the strength of Si-Si bond and \(E_{\text{PP}}\) that of P-P bond. Similarly, when the difference in total bond energies of 4.e3 and 4.e2, the complement molecules of 4.c1 and 4.c3 are calculated,

\[
\text{total bond energy } 4.e3 - \text{total bond energy } 4.e2 = 2E_{\text{SiP}} - E_{\text{SiSi}} - E_{\text{PP}}
\]
Thus we find that the difference in total bond energies of 4.e1 and 4.e3 and the difference in total bond energies between their complement molecules 4.e3 and 4.e2 are the same. Since the difference in energy ΔE between 4.e1 and 4.e3 and between 4.e3 and 4.e2 are almost the same we can assume that the difference in other energies due to strain, electrostatic interaction between these molecules should also be the same.

This argument can be extended to phosphasilabenzenes also. When we calculate the difference in total bond energy between 3.c1 and 3.c2 we find that

[Diagram]

(3.c2)  (3.c1)

Fig 5.6

\[
\text{total bond energy } 3.c2 - \text{total bond energy } 3.c1 = 2E_{Si-P} - E_{Si-Si} - E_{P-P}
\]

where \( E_{Si-P} \) is the bond energy of Si=P, \( E_{Si-Si} \) is the bond energy of Si=Si and \( E_{P-P} \) is the bond energy of P=P.

Similarly when the difference between total bond energies of their complement molecules 3.e1 and 3.e2 are calculated.

[Diagram]

(3.e2)  (3.e1)

Fig 5.7

\[
\text{total bond energy } 3.e2 - \text{total bond energy } 3.e1 = 2E_{Si-P} - E_{Si-Si} - E_{P-P}
\]

which is the same difference in bond energies between 3.c2 and 3.c1. Since the difference in total energy ΔE between 3.c1 and 3.c2 and also between 3.e1 and 3.e2 are also practically the same, it can be assumed that the difference in
energies like resonance energy, strain and electrostatic energy should also be the same.

5.5. Conclusions

The present theoretical investigation into the relative stabilities of hexasilabenzenes and hexasilaprismanes and their phospha analogues leads to a few interesting conclusions. Unlike azabenzenes and azaprismanes, where azaprismanes are substantially higher in energy, phospha derivatives of hexasilaprismanes show higher stability although the values are not very high. Usually the most stable variety is the prismane variety with exception of tri-substituted isomers where the 1, 3, 5 triphosphatrisilabenzenes is the most stable variety. This can be attributed to the unusual stability of this isomer rather than the instability of the prismane isomers. Phospha analogues of hexasilaprismane vary considerably in their relative energies. Bond strength, in this context also seems to be the factor responsible for this variation.

Just as in the case of azaprismanes and azabenzenes, in the case of phospha analogues of hexasilabenzenes and hexasilaprismanes also the relative energies of complement molecules are close. Here also, the difference between bond strengths of two isomers and the difference in bond strengths of the complement molecules are the same. Since the difference between the total energy of these sets of isomers is also practically the same as shown by theoretical calculations, it can be assumed that the difference in other energies due to resonance, strain and electrostatic interactions should also be the same.