Chapter VI
Substituent Effect on Benzene and Prismane

6.1. Introduction

Benzene and prismane are molecules of great theoretical and experimental interest. Benzene is known to chemists even from earlier days and is the true symbol of aromaticity. On the other hand, prismane is specially noted for its existence in spite of the fact that the molecule is highly strained.

Strain is an important concept in organic chemistry. This concept was introduced to explain the relative instability of geometrically constrained organic compounds by von Baeyer. Now it is discussed in terms of bond length and bond angle distortions as well as torsional terms and non-bonded interactions.

Closely associated with the concept of strain is the strain alleviating or strain-increasing effects of substituents. Substitution using various groups changes the strain energies of small rings. Previous experimental and computational investigations show that large bulky substituents, e.g.; C(CH₃)₃ and Si(CH₃)₃ can stabilise highly strained (CH)n molecules.

There are a few studies on the effectiveness on alkyl and silyl substituents in imparting thermodynamic stability to cyclic molecules.

In the present study, the effect of methyl and silyl substitution on the stability of benzene ring and prismane skeleton is investigated. Also, effect of persubstitution using various groups is also studied.

6.2. Effect of substitution using methyl groups

The hydrogen atoms of benzene and prismane are progressively replaced with methyl groups. The following isodesmic reaction is used to calculate the stability of benzene and prismane skeleton due to substitution.
\[(\text{CH})_n + n \text{CH}_3\text{CH}_3 \rightarrow C_6H_{6-n}(\text{CH}_3)_n + n \text{CH}_4\]

where \(n\) varies from one to six.

Energies of the reactant and product molecules are calculated at HF/6-31G** level using geometries optimised at the same level. \(\Delta E\) in each case is calculated and recorded.

### 6.2.1. Monomethylbenzene and monomethylprismane

Calculations at HF/6-31G** level show that in monomethylbenzene, the benzene nucleus is stabilised by 2.2 kcal/mol. The additional stability is due to the electron-donating inductive effect and hyperconjugation of the methyl group.

In monomethylprismane, the prismane skeleton is stabilised by 1.9 kcal/mol. Electron-donating groups decrease the strain of molecules like prismane. The relative stability of monomethylbenzene is 125.2 kcal/mol with respect to monomethylprismane. Detailed structure and energy details are given in table 6.1.

### Table 6.1

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>(\Delta E)-kcal/mol</th>
<th>Relative energy-kcal/mol</th>
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6.2.2. Dimethylbenzene and dimethylprismane

Of the three isomers of dimethylbenzene, in the ortho isomer 5.b1, the benzene nucleus is stabilised by 3.7 kcal/mol at HF/6-31G** level. In the meta isomer 5.b2 and the para isomer 5.b3 the nucleus is stabilised by 4.3 and 4.2 kcal/mol respectively.

The smaller stability of the ortho isomer is due to the interaction between the two methyl groups at the ortho position. The meta and para isomers have no such interaction and are more stable, although the difference is extremely small.

In dimethylprismane isomer 6.b1 with $C_2\nu$ symmetry, calculations at HF/6-31G** show that the prismane skeleton is stabilised by 9.1 kcal/mol. Isomer 6.b2 of Cs symmetry also records the same value of 9.1 kcal/mol. In isomer 6.b3 with $C_2$ symmetry, the nucleus is stabilised by 9.3 kcal/mol. These values indicate that in prismane, stability is practically independent of the position of substitution while in benzene isomers, it is affected by the position of substitution.

Of the three dimethylbenzene isomers, 5.b2 is the stablest. 5.b1 and 5.b3 have close relative energies of 0.1 and 0.6 kcal/mol respectively. The dimethylprismane isomers 6.b1, 6.b2 and 6.b3 have almost the same relative energies, values being 120.1, 120.1 and 119.9 kcal/mol respectively. Structure and energy details are given in table 6.2.
Table 6.2

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<th>Species</th>
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6.2.3. Trimethylbenzene and trimethylprismane

Calculations at HF/6-31G** level show that in 1,2,3-trimethylbenzene isomer 5.c1, the benzene nucleus is stabilised by 3.6 kcal/mol. In the 1,2,4-trimethyl isomer, the nucleus is stabilised by 4.6 kcal/mol and in 1,3,5-trimethyl isomer 5.c3, it is stabilised by 6.7 kcal/mol. The first isomer with a methyl group which is ortho to two other methyl groups is the least stable variety since the ortho interaction is strongest in this compound. The isomer 5.c3 with all methyl groups at meta positions exhibits special stability. Isomer 5.c2 with only one ortho interaction and one meta interaction comes in between as far as stability is concerned.

In trimethylprismane isomer 6.c1 with C_{3v} symmetry, the prismane skeleton is stabilised by 13.1 kcal/mol at HF/6-31G** level. In the isomer 6.c2 with Cs symmetry, there is a slightly higher stabilisation, the value being 13.6 kcal/mol. Isomer 6.c3 also records a close value of 13.4 kcal/mol. In this case also, stabilisation is not much dependent on the position of substitution with methyl groups.

Trimethylbenzene isomers differ only slightly in their relative stabilities. Isomer 5.c3 is the most stable one. The relative energy of 5.c2 is 2.0 kcal/mol, while 5.c3 is the least stable, its value being 3.1 kcal/mol. Trimethylprismane isomers have close relative energies although remarkably higher than trimethylbenzene isomers. The relative energies of 6.c1, 6.c2 and 6.c3 are 118.7, 117.9 and 116.4 kcal/mol respectively. Details are given in table 6.3.
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<tr>
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6.2.4. Tetramethylbenzene and tetramethylprismane.

In the 1,2,3,4-tetramethylbenzene isomer \(5.d1\), the benzene nucleus is stabilised by 3.5 kcal/mol. In the 1,2,3,5-tetramethyl benzene isomer \(5.d2\), the nucleus is stabilised by 5.8 kcal/mol. In the 1,2,4,5-tetramethyl benzene isomer \(5.d3\), the value is 7.4 kcal/mol. The isomer \(5.d1\) with larger number of ortho interaction and smaller meta interactions is the least stable isomer. Isomers \(5.d2\) and \(5.d3\) with smaller number of ortho interactions and larger number of meta interactions are more stable.

At HF/6-31G** level in prismane isomer \(6.d1\), prismane skeleton is stabilised by 17.4 kcal/mol. In isomer \(6.d2\), the prismane skeleton is stabilised by 17.7 kcal/mol. Isomer \(6.d3\) records a close value of 17.5 kcal/mol. In these isomers also, calculations reveal that stability is independent of the position of substitution.

In tertramethylbenzene isomer, the relative energies vary only a little. Isomer \(5.d3\) is the most stable isomer. The relative energies of \(5.d1\) and \(5.d2\) are 4.0 and 1.6 kcal/mol respectively. The tetramethylprismane isomers have remarkably higher relative energies. Thus, isomers \(6.d1\), \(6.d2\) and \(6.d3\) have close relative energies of 114.8, 114.5 and 114.8 kcal/mol respectively. Details are given in table 6.4.
## Table 6.4

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6.2.5. Pentamethylbenzene and pentamethylprismane

Calculations at HF/6-31G** level show that in pentamethylbenzene with Cs symmetry, the benzene nucleus is stabilised by 3.2 kcal/mol. The stability is less than expected since the number of ortho interactions considerably increase here.

In pentamethylprismane, however, calculations show that prismane skeleton is stabilised by 21.4 kcal/mol.

5.e is more stable than 6.e by 106.6 kcal/mol. Detailed structure and energy details are given in table 6.5.

Table 6.5

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
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6.2.6. Hexamethylbenzene and hexamethylprismane

In hexamethylbenzene, the benzene nucleus is destabilised by 8.4 kcal/mol. This is a reversal from the general trend and can be due to the increased ortho interactions.

Calculations show that in hexamethylprismane, the general trend continues and the prismane skeleton is stabilised by 25.1 kcal/mol. 5.f is more stable than 6.f by 91.3 kcal/mol. Details are given in table 6.6.
6.3. Effect of substitution using silyl groups

The hydrogen atoms of benzene and prismane are progressively replaced with silyl groups. The following isodesmic reaction is used to calculate the stability of benzene nucleus and prismane skeleton due to substitution using silyl groups.

\[(\text{CH})_n + n \text{CH}_3\text{SiH}_3 \rightarrow C_n\text{H}_{6-n} (\text{SiH}_3)_n + n \text{CH}_4\]

where \(n\) varies from 1 to 6.

Energies of reactant and product molecules are calculated at HF/6-31G** level using geometries optimised at the same level. \(\Delta E\) is calculated and recorded.

### Table 6.6

<table>
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6.3.1. Monosilylbenzene and monosilylprismane

In monosilylbenzene, the benzene nucleus is destabilised by a small quantity of 0.3 kcal/mol.

But in monosilylprismane, the prismane skeleton is stabilised by 2.5 kcal/mol. In strained systems, substitution using electron-releasing groups reduce the strain. 7.a is more stable than 8.a by a remarkably high energy of 121.9 kcal/mol. Energy details are given in table 6.7.
6.3.2. Disilylbenzene and disilylprismane

Of the three isomers of disilylbenzene, in isomer 7.b1, the ortho variety, benzene nucleus is destabilised by 3.5 kcal/mol. Calculations show that in the meta isomer 7.b2, the ring is destabilised by a small quantity of 0.8 kcal/mol. The para isomer 7.b3 also records the same value of 0.8 kcal/mol.

Calculations at HF/6-31G** level show that in disilylprismane isomer 8.b1, the prismane skeleton is stabilised by 7.8 kcal/mol. In isomer 8.b2, the value is 7.2 kcal/mol. In isomer 8.b3, the skeleton is stabilised by 8.5 kcal/mol. In disilylprismanes, 7.b2 and 7.b3 are the most stable isomers. 7.b1 is having a slightly higher relative energy of 2.7 kcal/mol. Disilylprismane isomers 8.b1, 8.b2 and 8.b3 have close relative energies of 116.1, 116.7 and 115.4 kcal/mol respectively. Energy and other details are given in table 6.8.

### Table 6.7

<table>
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</table>

### Notes

- Sl. No: Sequential number
- Species: Structural representation
- Energy (HF/6-31G**): Total energy in Hartrees
- ΔE-kcal/mol: Energy difference in kcal/mol
- Relative energy-kcal/mol: Relative energy in kcal/mol
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6.3.3. Trisilylbenzene and trisilylprismane

Of the three isomers of trisilylbenzene, in 1,2,3-trisilylbenzene 7.c1, the benzene nucleus is destabilised by 7.8 kcal/mol. In the 1,2,4-trisilylbenzene isomer, the benzene nucleus is destabilised by 4.6 kcal/mol. Calculations show that in 1,3,5-trisilylbenzene, this value is 1.3 kcal/mol. Trisilylbenzene isomers also show the same pattern of stability as trimethylbenzene isomers. Thus, 7.c1 with one silyl group ortho to two other silyl groups, is the least stable variety. The isomer 7.c3 with all silyl groups at meta positions shows special stability as shown by calculations. Isomer 7.c2 comes in between in stability.

In the trisilylprismane isomer 8.c1, the prismane skeleton is stabilised by 8.9 kcal/mol. In isomer 8.c2, it is stabilised by 11.5 kcal/mol. Calculations show that for 8.c3, the prismane skeleton is stabilised by 10.8 kcal/mol.

Trisilylbenzene isomer 7.c3 is the stablest isomer. 7.c2 and 7.c1 have relative energies of 6.5 kcal/mol and 3.3 kcal/mol respectively. Trisilylprismane isomer 8.c1 has a relative energy of 114.5 kcal/mol while 8.c2 and 8.c3 show extremely close values of 112.0 and 112.7 kcal/mol respectively. Details are given in table 6.9.
Table 6.9

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6.3.4. Tetrasylylbenzene and tetrasylylprismane

Calculations at HF/6-31G** level show that in 1,2,3,4-tetrasylylbenzene isomer 7.d1, the benzene nucleus is destabilised by 14.1 kcal/mol. In the 1,2,3,5-tetrasylylbenzene, the nucleus is destabilised by 9.8 kcal/mol. In the 1,2,4,5-teramethylbenzene isomer, the nucleus is destabilised by 7.6 kcal/mol.

Here also, the pattern of stability is similar to that of tetramethylbenzene isomers.

In tetrasylylprismane isomer 8.d1, the prismane skeleton is stabilised by 12.5 kcal/mol. In the isomer 8.d2, it is stabilised by 13.8 kcal/mol, and in 8.d3, the value is 12.9 kcal/mol. The energy values once again suggest that in prismane isomers, the stability is unrelated to the position of substitution using silyl groups. 7.d2 has a relative energy of 2.2 kcal/mol, while 7.d1 has a slightly higher energy of 6.5 kcal/mol. Calculations show that 7.d3 is the most stable isomer. In tetrasylylprismane isomers, the relative energies are quite close. Thus, 8.d1, 8.d2 and 8.d3 have relative energies 104.7, 103.4 and 104.2 kcal/mol respectively. Energy and other details are given in table 6.10.
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</table>
6.3.5. Pentasilylbenzene and pentasilylprismane

In pentasilylbenzene, calculations show that the benzene nucleus is destabilised by 18.1 kcal/mol. Calculations at HF/6-31G** level shows that in pentasilylprismane, the prismane skeleton is stabilised by 14.8 kcal/mol.

The relative energy of 8.e with respect to 7.e is found to be 91.9 kcal/mol. Structure and energy details are shown in table 6.11.

**Table 6.11**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.e</td>
<td></td>
<td>-1681.08582</td>
<td>18.1</td>
<td>0.0</td>
</tr>
<tr>
<td>8.e</td>
<td></td>
<td>-1680.93930</td>
<td>-14.8</td>
<td>91.9</td>
</tr>
</tbody>
</table>

6.3.6. Hexasilylbenzene and hexasilylprismane

At HF/6-31G** level in hexasilylbenzene, the benzene nucleus is destabilised by 63.4 kcal/mol.

In hexasilylprismane, the general trend is continued and the prismane nucleus is stabilised by 15.7 kcal/mol. Hexamethylprismane has a relative stability of 45.7 kcal/mol with respect to hexamethylbenzene. Details are given in table 6.12.
6.4. Persubstituted benzene and prismane

Benzene and prismane are persubstituted using atoms and groups like F, Cl, CF₃, CCl₃, SiF₃ and SiCl₃. Isodesmic reaction is used to calculate the stability of the benzene nucleus and prismane skeleton.

\[ \text{C}_6\text{H}_6 + 6 \text{CH}_3\text{X} \rightarrow \text{C}_6\text{X}_6 + 6\text{CH}_4 \]

where X is any of the above-mentioned groups. Energies of all the molecules are calculated at HF/6-31G** level using geometries optimised at the same level. \( \Delta E \) is calculated as the difference in total energy of the products and that of the reactants.

6.4.1. Hexafluorobenzene and hexafluoroprismene

Calculations at HF/6-31G** level show that in hexafluorobenzene, the benzene nucleus is stabilised by 7.2 kcal/mol.

In hexafluoroprismene the prismane skeleton is destabilised by 3.5 kcal/mol. In strained systems, electron-withdrawing groups decrease the stability. 13.a is more stable than 14.a by 135.6 kcal/mol. Detailed structures and energies are given in table 6.13.
Table 6.13

R=F

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.a</td>
<td><img src="image1.png" alt="Image" /></td>
<td>-823.75357</td>
<td>-7.2</td>
<td>0.0</td>
</tr>
<tr>
<td>14.a</td>
<td><img src="image2.png" alt="Image" /></td>
<td>-823.53747</td>
<td>3.5</td>
<td>135.6</td>
</tr>
</tbody>
</table>

6.4.2. Hexachlorobenzene and hexachloroprismane

Calculations at HF/6-31G** level show that in hexachlorobenzene, the benzene nucleus is destabilised by 24.9 kcal/mol.

In hexachloroprismane, the skeleton is destabilised by 3.0 kcal/mol at the same level of theory. 16.a is less stable than 15.a by 102.9 kcal/mol. Details are given in table 6.14.

Table 6.14

R=Cl

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.a</td>
<td><img src="image3.png" alt="Image" /></td>
<td>-2984.05128</td>
<td>24.9</td>
<td>0.0</td>
</tr>
<tr>
<td>16.a</td>
<td><img src="image4.png" alt="Image" /></td>
<td>-2983.88722</td>
<td>3.0</td>
<td>102.9</td>
</tr>
</tbody>
</table>
6.4.3. Persubstitution using CF₃ groups

In hexakis(trifluoromethyl)benzene, the benzene nucleus is destabilised by 124.4 kcal/mol.

Calculations at HF/6-31G** level shows that in hexakis(trifluoro)prismane, the prismane skeleton is less stable by 22.1 kcal/mol. The relative stability of 13.b with respect to 14.b is found to be 22.4 kcal/mol. Details are given in table 6.15.

Table 6.15
R=CF₃

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy-kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.b</td>
<td><img src="image" alt="13.b" /></td>
<td>-2244.25777</td>
<td>124.4</td>
<td>0.0</td>
</tr>
<tr>
<td>14.b</td>
<td><img src="image" alt="14.b" /></td>
<td>-2244.22199</td>
<td>22.1</td>
<td>22.4</td>
</tr>
</tbody>
</table>

6.4.4. Persubstitution using CCl₃ groups

In hexakis(trichloromethyl)benzene, the benzene nucleus is destabilised by 387.9 kcal/mol. Calculations at HF/6-31G** show that in hexakis(trichloromethyl)prismane, the prismane skeleton is destabilised by 148.0 kcal/mol. The relative stability of 15.b with respect to 16.b is 115.1 kcal/mol. Details are given in table 6.16.
Table 6.16

R=CCl₃

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy-kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.b</td>
<td><img src="image1" alt="Image" /></td>
<td>-8724.37062</td>
<td>387.9</td>
<td>0.0</td>
</tr>
<tr>
<td>16.b</td>
<td><img src="image2" alt="Image" /></td>
<td>-8724.55409</td>
<td>148.0</td>
<td>115.1</td>
</tr>
</tbody>
</table>

6.4.5. Persubstitution using SiF₃ groups

At HF/6-31G** level, in hexakis(trifluorosilyl)benzene, the benzene nucleus is destabilised by 59.6 kcal/mol. At the same level of theory, in hexakis(trifluorosilyl)prismane, the prismane skeleton is destabilised by 5.2 kcal/mol. The relative energy of 14.c is found to be 70.4 kcal/mol with respect to 13.c. Detailed structure and energies given is given in table 6.17.

Table 6.17

R=SiF₃

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy-kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.c</td>
<td><img src="image3" alt="Image" /></td>
<td>-3751.88831</td>
<td>59.6</td>
<td>0.0</td>
</tr>
<tr>
<td>14.c</td>
<td><img src="image4" alt="Image" /></td>
<td>-3751.77601</td>
<td>5.2</td>
<td>70.4</td>
</tr>
</tbody>
</table>
6.4.6. Persubstitution using SiCl₃ groups

Theoretical calculations show that in hexakis(trichlorosilyl)benzene, the benzene nucleus is destabilised by 227.3 kcal/mol.

In hexakis(trichlorosilyl)prismane, the prismane skeleton is less stable by 61.7 kcal/mol. 16.c is 40.8 kcal/mol destabilised than 15.c. Details are given in table 6.18.

Table 6.18
R=SiCl₃

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Energy (HF/6-31G**) Hartrees</th>
<th>ΔE-kcal/mol</th>
<th>Relative energy-kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.c</td>
<td></td>
<td>-10232.07453</td>
<td>227.3</td>
<td>0.0</td>
</tr>
<tr>
<td>16.c</td>
<td></td>
<td>-10232.13962</td>
<td>61.7</td>
<td>40.8</td>
</tr>
</tbody>
</table>

6.5. AIM analysis

The total charge on the ring atoms in substituted prismanes are found using AIM analysis of the Gaussian 98 program. Calculations are done at HF/6-31G** level. Prismane, hexafluoroprismane, hexachloroprismane, hexamethylprismane and dimethylprismane are analysed. It is found that when ring-stabilizing groups are attached, the total positive charge on the ring decreases, and when ring-destabilizing groups are attached, the total positive charge increases. Detailed values are given in table 6.19.
6.6. Bond lengths in various persubstituted prismanes

The two types of bonds, the bonds in the triangular faces of prismane and the bonds connecting these triangular faces change in length with persubstitution. Prismane is persubstituted using F, Cl, CH₃, CF₃, SiH₃, SiF₃ and SiCl₃. The resulting bond lengths are given in table 6.20. Calculations are done at HF/6-31G** level.
<table>
<thead>
<tr>
<th>Species</th>
<th>Bond length a (Å)</th>
<th>Δa (Å)</th>
<th>Bond length b (Å)</th>
<th>Δb (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>1.54919</td>
<td>--</td>
<td>1.50682</td>
<td>--</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>1.54897</td>
<td>-2.2 x 10^-4</td>
<td>1.51235</td>
<td>5.53 x 10^-3</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>1.54546</td>
<td>-3.73 x 10^-3</td>
<td>1.5079</td>
<td>1.08 x 10^-3</td>
</tr>
<tr>
<td><img src="image4.png" alt="Image" /></td>
<td>1.55394</td>
<td>4.75 x 10^-3</td>
<td>1.51198</td>
<td>5.16 x 10^-3</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td>1.54626</td>
<td>-2.93 x 10^-3</td>
<td>1.50528</td>
<td>-1.54 x 10^-3</td>
</tr>
<tr>
<td><img src="image6.png" alt="Image" /></td>
<td>1.61466</td>
<td>6.54 x 10^-2</td>
<td>1.53836</td>
<td>3.15 x 10^-2</td>
</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td>1.5638</td>
<td>1.46 x 10^-2</td>
<td>1.52486</td>
<td>1.80 x 10^-2</td>
</tr>
<tr>
<td><img src="image8.png" alt="Image" /></td>
<td>1.56207</td>
<td>1.28 x 10^-2</td>
<td>1.52234</td>
<td>1.55 x 10^-2</td>
</tr>
<tr>
<td><img src="image9.png" alt="Image" /></td>
<td>1.59286</td>
<td>4.36 x 10^-2</td>
<td>1.53474</td>
<td>2.79 x 10^-2</td>
</tr>
</tbody>
</table>
6.7. Bond lengths in various persubstituted benzenes

Bond length of benzene changes with persubstitution using various groups. Calculations are done at HF/6-31G** level. Benzene is persubstituted using F, Cl, CH₃, CF₃, SiH₃, SiF₃ and SiCl₃. The resulting bond lengths are given in table 6.21.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Species</th>
<th>Bond length a (Å)</th>
<th>Δa (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.a</td>
<td><img src="image.png" alt="Image" /></td>
<td>1.38604</td>
<td>---</td>
</tr>
<tr>
<td>13.a</td>
<td><img src="image.png" alt="Image" /> R = F</td>
<td>1.37847</td>
<td>-7.57 x 10⁻³</td>
</tr>
<tr>
<td>15.a</td>
<td><img src="image.png" alt="Image" /> R = Cl</td>
<td>1.39068</td>
<td>4.64 x 10⁻³</td>
</tr>
<tr>
<td>13.b</td>
<td><img src="image.png" alt="Image" /> R = CF₃</td>
<td>1.4104</td>
<td>2.43 x 10⁻²</td>
</tr>
<tr>
<td>15.b</td>
<td><img src="image.png" alt="Image" /> R = CCl₃</td>
<td>1.42889</td>
<td>4.28 x 10⁻²</td>
</tr>
<tr>
<td>13.c</td>
<td><img src="image.png" alt="Image" /> R = SiF₃</td>
<td>1.40742</td>
<td>2.13 x 10⁻²</td>
</tr>
<tr>
<td>15.c</td>
<td><img src="image.png" alt="Image" /> R = SiCl₃</td>
<td>1.42188</td>
<td>3.58 x 10⁻²</td>
</tr>
</tbody>
</table>

Table 6.21 Bond lengths of persubstituted benzenes
It is interesting to compare the C-X distance in persubstituted prismane and the C-X distance in the corresponding strain-free species, where X can be various substituents. Calculations at HF/6-31G** level using H, CH₃, CF₃, CCl₃, SiH₃, SiF₃, and SiCl₃ are done and the results are given in tables 6.22.

**Table 6.22a**

<table>
<thead>
<tr>
<th>System</th>
<th>X − H</th>
<th>C−H Distance(Å)</th>
<th>C−H Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X = H</td>
<td>1.08442</td>
<td>1.0736</td>
</tr>
</tbody>
</table>

**Table 6.22b**

<table>
<thead>
<tr>
<th>System</th>
<th>X − F</th>
<th>C−F Distance(Å)</th>
<th>C−F Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X = F</td>
<td>1.3961</td>
<td>1.3161</td>
</tr>
</tbody>
</table>

**Table 6.22c**

<table>
<thead>
<tr>
<th>System</th>
<th>X − Cl</th>
<th>C−Cl Distance(Å)</th>
<th>C−Cl Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X = Cl</td>
<td>1.84925</td>
<td>1.7121</td>
</tr>
</tbody>
</table>
### Table 6.22d

<table>
<thead>
<tr>
<th>System</th>
<th>C-CH₃ Distance(Å)</th>
<th>C-CH₃ Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=CH₃</td>
<td>1.5662</td>
<td>1.49972</td>
</tr>
</tbody>
</table>

### Table 6.22e

<table>
<thead>
<tr>
<th>System</th>
<th>C-CF₃ Distance(Å)</th>
<th>C-CF₃ Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=CF₃</td>
<td>1.58118</td>
<td>1.49646</td>
</tr>
</tbody>
</table>

### Table 6.22f

<table>
<thead>
<tr>
<th>System</th>
<th>C-CCl₃ Distance(Å)</th>
<th>C-CCl₃ Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=CCl₃</td>
<td>1.66951</td>
<td>1.57076</td>
</tr>
</tbody>
</table>

### Table 6.22g

<table>
<thead>
<tr>
<th>System</th>
<th>C-SiH₃ Distance(Å)</th>
<th>C-SiH₃ Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=SiH₃</td>
<td>1.93429</td>
<td>1.87114</td>
</tr>
</tbody>
</table>
Table 6.22h

<table>
<thead>
<tr>
<th>System</th>
<th>C-SiF&lt;sub&gt;3&lt;/sub&gt; Distance(Å)</th>
<th>C-SiF&lt;sub&gt;3&lt;/sub&gt; Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=SiF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.88909</td>
<td>1.84459</td>
</tr>
</tbody>
</table>

Table 6.22i

<table>
<thead>
<tr>
<th>System</th>
<th>C-SiCl&lt;sub&gt;3&lt;/sub&gt; Distance(Å)</th>
<th>C-SiCl&lt;sub&gt;3&lt;/sub&gt; Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=SiCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.95038</td>
<td>1.90919</td>
</tr>
</tbody>
</table>

In all cases the C-X distance in persubstituted prismane is smaller than the C-X distance of the corresponding strain-free system.

6.7. Conclusion

In methyl substituted benzenes the benzene ring is stabilised due to substitution. But in the various isomers, the stability depends on the position of substitution. This is because there is an interplay between the energy-increasing ortho interaction and the energy-decreasing meta interaction. In the case of prismane also, the skeletal ring is stabilised with methyl substitution and stabilisation in increases as the number of methyl groups increases. In the silyl substituted benzenes, benzene ring in desatabilised and the destabilisation increases as the number of silyl substituents increases. But in this case also, stability of the isomers differ slightly. In silyl substituted prismanes, prismane nucleus is stabilised with silyl substitution and the stabilisation increases as the number of silyl groups increases. Here also, the various isomers show almost the same stability. In persubstituted benzene and prismane, generally the benzene and prismane nuclei are destabilised when substituted with electron-withdrawing groups.