

Stereochemical calculations on substituted benzene and benzene-like compounds*

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Abstract. Semi-empirical calculations have been done on hexaphenyl benzene, triphenyl benzene and *s*-triphenyl triazine free molecules and the results are compared with x-ray crystal structure studies. The conformation of isolated molecule differs from that found in crystals. The agreement improves when packing forces are also included in the minimum energy calculations.

Keywords. Semi-empirical calculation; conformation of tri and hexa substituted benzene; packing forces.

1. Introduction

The arrangement of aromatic ring systems connected with single bonds have been studied in the past (Almenningen *et al* 1958; Bastiansen 1952). In our earlier investigation on the structure of 3, 3'-dibromobenzophenone (Vasantha Pattabhi and Venkatesan 1973) we have observed that the conformation of the molecules in crystalline environment is not the same as for an isolated molecule. In continuation of the studies on the influence of packing on the conformation of molecules we have studied the arrangement of aromatic rings in an overcrowded neighbourhood in the case of hexaphenyl benzene (I), triphenyl benzene (II) and *s*-triphenyl triazine (III). Crystal structures of these compounds have been determined by Bart 1968, Farag 1954 and Damiani *et al.* 1965, respectively. Crystal structure of triphenyl benzene has been redetermined recently by Lin (1975). Results obtained from the present study have been compared with the experiment.

2. Semi-empirical calculations

In this method the potential energy is minimised for an isolated molecule varying the rotational parameters about the single bonds. The total energy of an isolated molecule was calculated using the following equation,

$$E_{iso} = E_{\pi} + E_{nb}$$

where E_{π} is π -electron energy and E_{nb} is that due to non-bonded interactions. Kitaigorodskii potential function (Kitaigorodskii 1961) was used in the calculation of E_{nb} , given by

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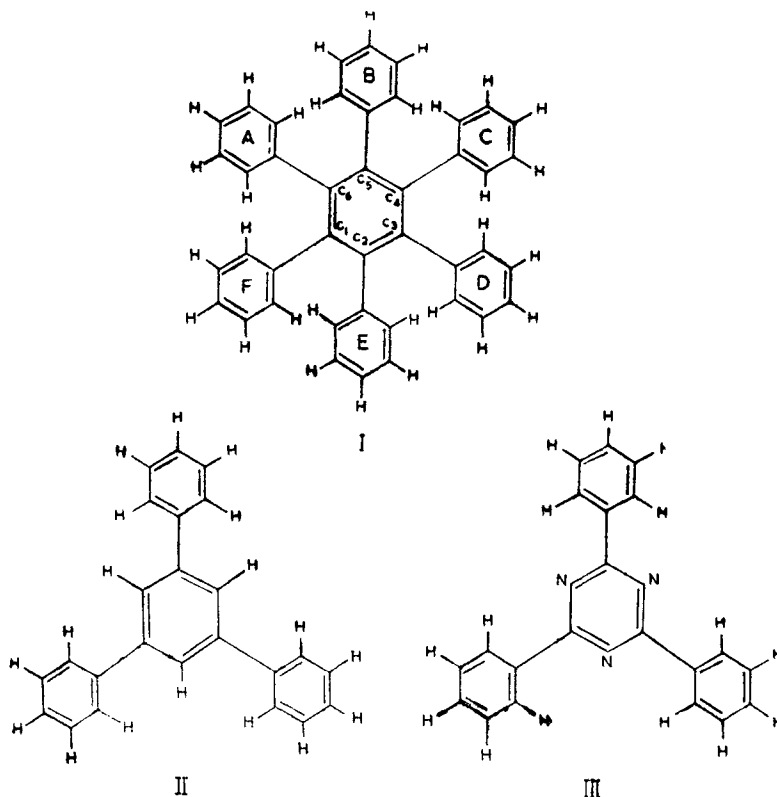


Figure 1. I. Hexaphenyl benzene
 II. Triphenyl benzene
 III. *s*-triphenyl triazine.

$$V_{nb}(i, j) = 3.5 [8600 \exp(-13Z) - 0.04/Z^6]$$

where $Z = r_{ij}/r_0$; r_0 -equilibrium distance that characterises any interaction. The r_0 values corresponding to the equilibrium distance used in this calculation are given in table 1. Assuming that the atoms are 'pressed' on entering the crystal, equilibrium distances between various atoms (r_0) are taken to be slightly larger (about 10%) than the usual sum of the van der Waal's radii.

The π -electron energy was calculated using the Hückel Molecular Orbital method (HMO). The constants used in the present study closely correspond to those given by Streitwieser (1961). Non-bonded as well as π -electron energies were calculated at 10° interval and the values of interest alone are listed in tables 2 (a), (b) and (c). E_π was not included in the case of hexaphenyl benzene as bond lengths obtained from x-ray studies do not indicate significant π -bonding (Bart 1968).

If the angles of rotation, about the single bonds connecting the benzene and phenyl rings are denoted as θ_1, θ_2 , etc., then we observe from tables 2 (a), (b) and (c) that for a free molecule, the θ values corresponding to the minimum value of E_{iso} are:

$$\theta_1 = \theta_2 = \theta_3 = \theta_4 = \theta_5 = \theta_6 = 74^\circ \text{ for hexaphenyl benzene;}$$

Table 1. Constants used for Kitaigorodskii's potential function

| Atom pair | r_0 (Å) |
|---------------------|-----------|
| H...H | 2.6 |
| H _j ...C | 3.15 |
| H...N | 3.0 |
| C...C | 3.80 |
| C...N | 3.52 |
| N...N | 3.30 |
| H...Br | 3.50 |
| H...O | 2.90 |
| C...O | 3.44 |
| C...Br | 4.00 |
| N...O | 3.20 |
| N...Br | 4.00 |
| O...O | 3.11 |
| O...Br | 3.70 |
| Br...Br | 4.30 |

Table 2a. Hexaphenyl benzene: Total energy (KCal. Mole⁻¹) of isolated molecule and after packing

| θ_1 | θ_2 | θ_3 | θ_4 | θ_5 | θ_6 | E_{nb} (E_{iso}) | Packing energy | E Total |
|------------|------------|------------|------------|------------|------------|---------------------------|-------------------|--------------|
| 60° | 60° | 60° | 60° | 60° | 60° | -10.16 | -45.54 | -55.70 |
| 63 | 63 | 63 | 63 | 63 | 63 | -11.74 | -46.19 | -57.93 |
| 65 | 65 | 65 | 65 | 65 | 65 | -12.54 | -46.38 | -58.92 |
| 68 | 68 | 68 | 68 | 68 | 68 | -13.45 | -46.33 | -59.78 |
| 70 | 70 | 70 | 70 | 70 | 70 | -13.92 | -46.09 | -60.01 |
| 72 | 72 | 72 | 72 | 72 | 72 | -14.29 | -45.65 | -59.94 |
| 74 | 74 | 74 | 74 | 74 | 74 | -14.73 | -44.56 | -59.29 |
| 60 | 62 | 62 | 60 | 62 | 62 | -10.90 | -45.78 | -56.68 |
| 62 | 62 | 60 | 60 | 62 | 62 | -10.90 | -45.91 | -56.81 |
| 65 | 65 | 65 | 70 | 70 | 65 | -12.98 | -46.44 | -59.42 |
| 66 | 68 | 68 | 62 | 71 | 67 | -13.02 | -46.74 | -59.76 |
| 68 | 68 | 62 | 71 | 67 | 66 | -13.02 | -46.08 | -59.10 |
| 70 | 70 | 60 | 70 | 65 | 70 | -12.99 | -46.78 | -59.77 |

$\theta_1 = \theta_2 = \theta_3 = 50^\circ$ for triphenyl benzene;

and $\theta_1 = \theta_2 = \theta_3 = 0^\circ$ for *s*-triphenyl triazine.

Almenningen *et al* (1958) have done electron diffraction studies of hexaphenyl

Table 2 (b). Triphenyl benzene: Total energy (K. Cal. Mole⁻¹) of the isolated molecule (E_{180}) and after packing

| θ_1 | θ_2 | θ_3 | E_{nb} | E_{π} | E_{180} | Packing energy | E Total |
|------------|------------|------------|----------|-----------|-----------|----------------|-----------|
| 0° | 0° | 0° | 10.56 | -592.85 | -582.29 | | |
| 10 | 10 | 10 | 8.62 | -590.87 | -582.25 | | |
| 20 | 20 | 20 | 4.40 | -589.82 | -585.42 | | |
| 30 | 30 | 30 | 0.51 | -587.30 | -586.79 | 13.61 | -573.18 |
| 40 | 40 | 40 | -2.06 | -584.75 | -586.81 | 82.1 | -504.71 |
| 50 | 50 | 50 | -3.55 | -583.31 | -586.86 | | |
| 60 | 60 | 60 | -4.39 | -581.78 | -586.17 | | |
| 70 | 70 | 70 | -4.85 | -581.11 | -585.96 | | |
| 80 | 80 | 80 | -5.09 | -580.57 | -585.66 | | |
| -34 | 27 | -24 | 1.12 | -587.81 | -586.69 | -35.97 | -622.66 |
| -30 | 20 | -20 | 3.02 | -588.82 | -585.80 | -34.71 | -620.51 |
| 40 | 30 | 30 | -0.43 | -586.56 | -586.99 | -36.94 | -623.93 |

Table 2 (c). S-Triphenyl triazine: Total energy (K. Cal. mole⁻¹) of the isolated molecule and after packing

| θ_1 | θ_2 | θ_3 | E_{nb} | E_{π} | E_{180} | Packing energy | E Total |
|------------|------------|------------|----------|-----------|-----------|----------------|-----------|
| 0° | 0° | 0° | -1.412 | -658.94 | -660.35 | -31.86 | -692.21 |
| 10 | 10 | 10 | -1.58 | -654.33 | -655.91 | -23.49 | -679.40 |
| 20 | 20 | 20 | -2.026 | -652.56 | -654.59 | | |
| 30 | 30 | 30 | -2.61 | -650.21 | -652.82 | | |
| 40 | 40 | 40 | -3.18 | -647.39 | -650.57 | | |
| 50 | 50 | 50 | -3.63 | -645.14 | -648.77 | | |
| 5 | 5 | 10 | -1.497 | -658.14 | -659.64 | -26.81 | -686.45 |
| 5 | 10 | 10 | -1.537 | -658.01 | -659.55 | -16.82 | -676.37 |
| 5 | 5 | 5 | -1.46 | -658.26 | -659.72 | -27.54 | -687.26 |
| 5 | -5 | 10 | -1.504 | -658.14 | -659.64 | -31.06 | -690.70 |

benzene vapour and they conclude that the peripheral rings are nearly orthogonal to the central ring, which would be expected if non-bonded interactions alone were considered. Calculations done by Guy (1949) indicate that the resonance energy reaches zero at angles of twist between 45° and 68°. Bastiansen (1952) examined the vapour of 1, 3, 5 triphenyl benzene by electron diffraction methods and found that the twist of the phenyl groups to be $46 \pm 5^\circ$. These results agree with results reported in this communication, though the minimum observed in the case of triphenyl benzene is rather flat.

However the observed twist angles obtained from crystal structure studies are unequal in all these cases and they are listed in table 3. We observe from this table that the conformation of the isolated molecule is different from that observed in crystal structure, even though the deviation in the case of *s*-triphenyl triazine is not significant. But it is known that each molecule in the crystal experiences a strain due to the surrounding molecule which causes distortion of the molecule, so that the crystal reaches the minimum of free energy. Hence it is essential to include packing forces also in the evaluation of total energy. This was achieved by placing the model molecule in the same orientation and position inside the crystal cell and intermolecular packing energy was calculated using Kitaigorodskii potential function for all the intermolecular contacts.

Table 3. Theoretical and experimental values of the twist angles

| Compound | | θ_1 | θ_2 | θ_3 | θ_4 | θ_5 | θ_6 | Reference |
|------------------------------|--------------|------------|------------|------------|------------|------------|------------|------------------------------|
| Hexaphenyl benzene | Theoretical | 72° | 72° | 72° | 72° | 72° | 72° | Bart 1968 |
| | Experimental | 68·8 | 68·5 | 62·0 | 70·7 | 67·3 | 65·9 | |
| Triphenyl benzene | Theoretical | -40 | 30 | -30 | | | | Lin 1975 |
| | Experimental | 40·7 | -37·2 | 36·1 | | | | |
| <i>s</i> -triphenyl triazine | Theoretical | 0 | 0 | 0 | | | | Damiani <i>et al</i> 1965 |
| | Experimental | -0·7 | 1·5 | -2·2 | | | | |

The intermolecular packing energies for the three compounds are listed in tables 2 (a), (b) and (c). The experimental and theoretical results are given in table 3 for comparison. Close packing of the molecule in the crystal lattice seems to demand observed changes in the conformation of the molecules.

In this connection, it is interesting to note from x-ray studies that the molecules of hexaphenyl benzene, triphenyl benzene and *s*-triphenyl triazine are packed in a similar fashion in the unit cell. They form layers parallel to the *bc* plane with one molecule overlapping the other to some extent.

In addition to the above calculation, the effect of cell length on packing has also been studied in the case of 3, 3'-dibromobenzophenone by varying the cell length along the needle axis. It is seen from this study that the minimum energy is obtained for the observed cell length only. Even though there are no short contacts for larger cell length the energy value for these is greater. In this case too the packing of the molecule seems to be important.

3. Conclusion

To summarise, we observe that the geometries of the isolated molecules of the three compounds, as calculated via semi-empirical methods are different from what one observes in the crystal structures of these compounds. This brings out the importance of the crystalline environment on the conformation of these molecules. While it is encouraging to note that the calculated molecular geometries of these molecules after packing agree with the experiments, the agreement must not be overestimated owing to the assumptions and approximations involved in the method of calculations. However, there is no doubt that the difference in conformation between the isolated molecule and the molecule as found in the crystal must originate from the influence of packing forces.

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