

A theoretical study on the specific interaction of hexafluorobenzene with benzene and *p*-xylene

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Abstract. A CNDO/2 study has been carried out for $C_6F_6 + C_6H_6$ and $C_6F_6 + C_6H_4$ composites and individual molecules. The favoured configurations of the adducts have been decided on the basis of energy calculations of various geometries. For the $C_6F_6 + C_6H_6$ adduct the lowest energy corresponds to the configuration in which the molecular planes are parallel to each other with a twist angle of 30° . For the $C_6F_6 + C_6H_4$ adduct lowest energy corresponds to a geometry in which the two molecular planes are inclined by a small angle with the angle of twist between the molecular planes being 30° . It is shown that the complexes are not of the charge transfer type.

Keywords. CNDO study; benzene; hexafluorobenzene; *p*-xylene; charge transfer.

1. Introduction

The formation of complexes between hexafluorobenzene and alkyl benzenes is quite well-known (Patrick and Prosser 1960; Duncan *et al* 1966; Boeyens and Herbstein 1966). However, the nature of the specific interaction has not been well understood. It was earlier suggested (Patrick and Prosser 1960; Fenby *et al* 1966) that this has the nature of electron transfer interaction with benzene acting as donor and hexafluorobenzene as an acceptor. Thermodynamic studies on alkyl benzenes + hexafluorobenzene showed (Fenby and Scott 1967; Duncan *et al* 1966) that the excess enthalpy became more negative with the substitution of alkyl group in benzene. This was taken as an evidence for the charge transfer type of interaction because alkyl substitution also increased the electron donating power of the alkyl benzenes. However, no charge transfer bands were observed spectroscopically. As a matter of fact more recent (Gaw and Swinton 1968) thermodynamic studies and calculations based on quadrupole interactions (Broth and Swinton 1974) indicate that these interactions arise principally from electrostatic forces. Depolarised Rayleigh light scattering study (Brown *et al* 1978) gives indirect evidence for the existence of $C_6H_6 + C_6F_6$ adduct with their planes parallel to each other even in the liquid solutions. In the absence of any unequivocal experimental evidence we report the CNDO/2 calculations (Pople and

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Beveridge 1970) on the energies and charge distributions of the benzene (*p*-xylene) and hexafluorobenzene molecules separately and also for the composite molecules in which the distance between the centres of mass of C_6H_6 (C_6H_{10}) and C_6F_6 and their relative orientations have been varied.

2. Geometries

The following relative orientations (figure 1) of benzene (*p*-xylene) with respect to hexafluorobenzene in the complex have been considered:

(i) Those in which the benzene (*p*-xylene) and hexafluorobenzene molecules were in the same plane as shown in figures 1a and 1b.

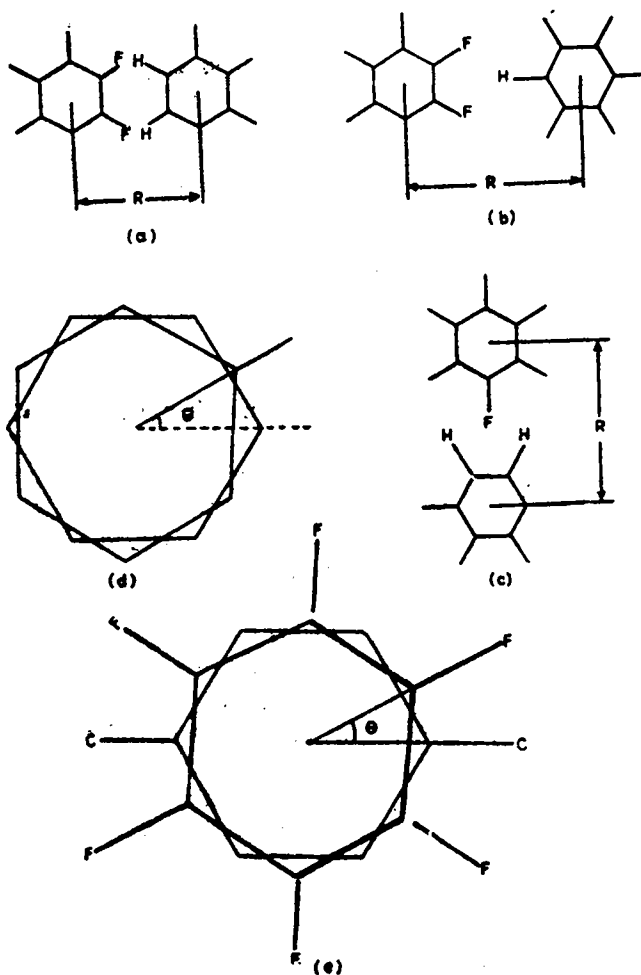


Figure 1. Geometrical models for the benzene (*p*-xylene)-hexafluorobenzene complexes.

(ii) Those in which the six-fold axis of benzene (*p*-xylene) lies in the molecular plane of hexafluorobenzene and one of the fluorine atom points towards the centre of the benzene molecule (figure 1c). For this configuration the HFB molecular plane has been rotated around the two-fold axis passing through the fluorine atom pointing towards benzene ring by 0 to 30°.

(iii) Those in which the molecules are placed one above the other and the twist angle between the molecular planes has been varied from 0 to 30° (figure 1d)

(iv) Those in which the molecular planes are inclined to each other (figure 1e). For symmetry consideration this was considered only for the hexafluorobenzene/*p*-xylene complex.

The energy of the molecular systems hexafluorobenzene and benzene (*p*-xylene) has been calculated as a function of the distance between the interacting molecules for all the above configurations. The molecular geometries of benzene (*p*-xylene) and hexafluorobenzene in the complex are assumed to be those of the isolated molecules ($R_{CC} = 1.397$ Å, $R_{CH} = 1.10$ Å, $R_{CF} = 1.37$ Å, and $R_{CC'} = 1.52$ Å). The intermolecular interaction energy (ΔE) is defined by the difference:

$\Delta E = \text{Energy of composite molecule} - \text{the sum of the energies of isolated molecules.}$

3. Results and discussion

The results obtained for the various configurations of different classes are summarised in tables 1 and 2. It is found that the configurations falling in categories (i) and (ii) have the least stabilization energy. The intermolecular distances for these configurations were also varied but only the distances corresponding to the lowest energy is recorded for these geometries. Configurations with $\theta = 30^\circ$ were found to be the most stable from category (iii) for benzene + hexafluorobenzene complex. A plot of ΔE vs. R for this is shown in figure 2 which shows a

Table 1. CNDO stabilization energy for the benzene-hexafluorobenzene adduct, as a function of distance (R) and geometry.

Geometry	θ/degree	$R/\text{Å}$	$-\Delta E \times 10^3/\text{a.u.}$	
I	(a)	...	7.30	0.576
	(b)	...	5.50	0.400
II	0	3.00	5.400	
	15	3.00	5.372	
	30	3.00	0.123	
III	0	3.00	0.654	
	15	3.00	5.911	
	30	3.00	6.119	
	30	2.65	7.045	

Table 2. Stabilization energy $-\Delta E \times 10_3$ for *p*-xylene-hexafluorobenzene system at various tilt angles (ϕ) between the molecular planes [twist angle (θ) being 30°].

$d/\text{\AA}$	ϕ			
	0°	4°	6°	8°
2.60		2.315		
2.70		2.860	3.215	
2.80	2.396	2.843	3.168	3.046
2.90		2.555	2.803	3.625
3.00	1.910	2.163	2.317	
3.10		1.759		

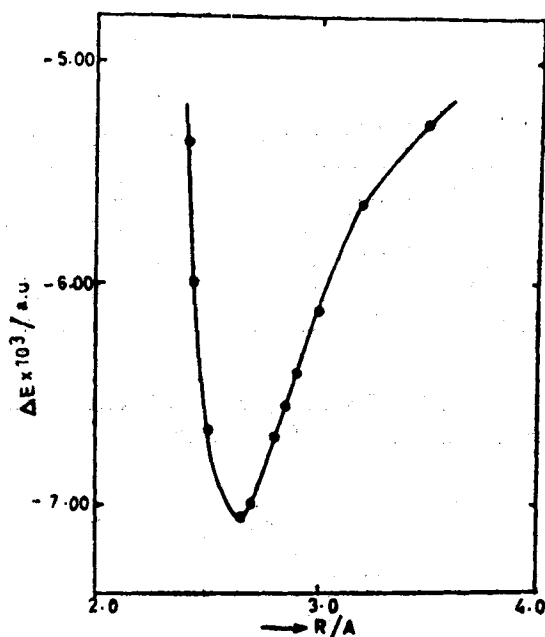


Figure 2. CNDO stabilization energies for benzene-hexafluorobenzene as a function of distance between the two molecules.

minimum at $R = 2.65 \text{ \AA}$. Crystallographic studies (Dahl 1972, 1975) on some of the alkyl benzenes and hexafluorobenzene adducts also indicate that these molecules are alternatively stacked on one another and the relative orientation of their rings is such that carbon atoms of the two rings do not lie directly under each other. Actually the two rings have relative orientation of 30° . However,

for HFB-*p*-xylene complex, the most stable geometry is that in which the molecular planes of both the molecules are twisted by 30° and are inclined by a small angle ϕ (figure 1e). It was found that the maximum stabilization takes place at $\phi \approx 6^\circ$ (table 2). This is consistent with the crystallographic studies (Dahl 1975) in which the inclination angle of 5.4° is reported.

The charges on various atoms in the isolated molecules and in the composite molecules for stabilized geometries are given in figure 3. It can be seen that there is very little intermolecular charge transfer. There is only intramolecular adjustment of charges on atoms on each molecule. It is also apparent from the HOMO and LUMO of the molecules (figure 4) that the charge transfer from benzene (*p*-xylene) to hexafluorobenzene is not energetically favoured.

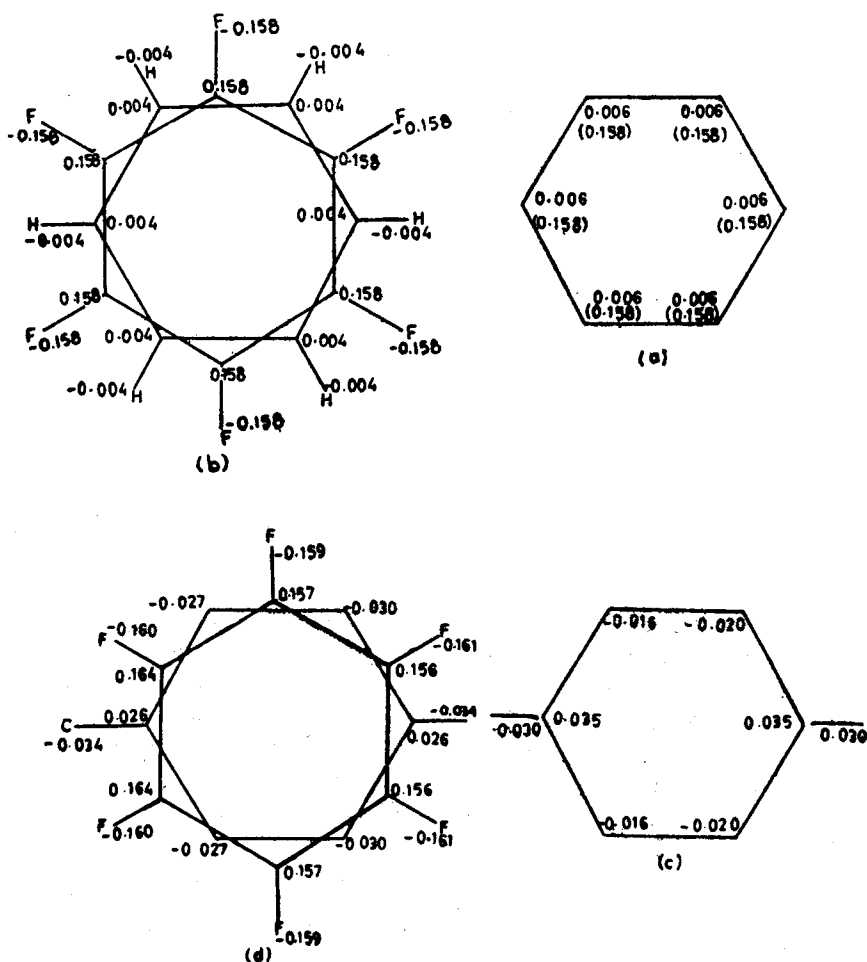


Figure 3. (a) Charges on carbon atoms in benzene molecule. The values in parenthesis indicate the charges on carbon atoms in hexafluorobenzene. (b) Charges on various atoms in the composite molecule $C_6H_6 + C_6F_6$. (c) Charges on carbon atoms in *p*-xylene. (d) Charges on various atoms in the composite molecule $C_8H_{10} + C_6F_6$.

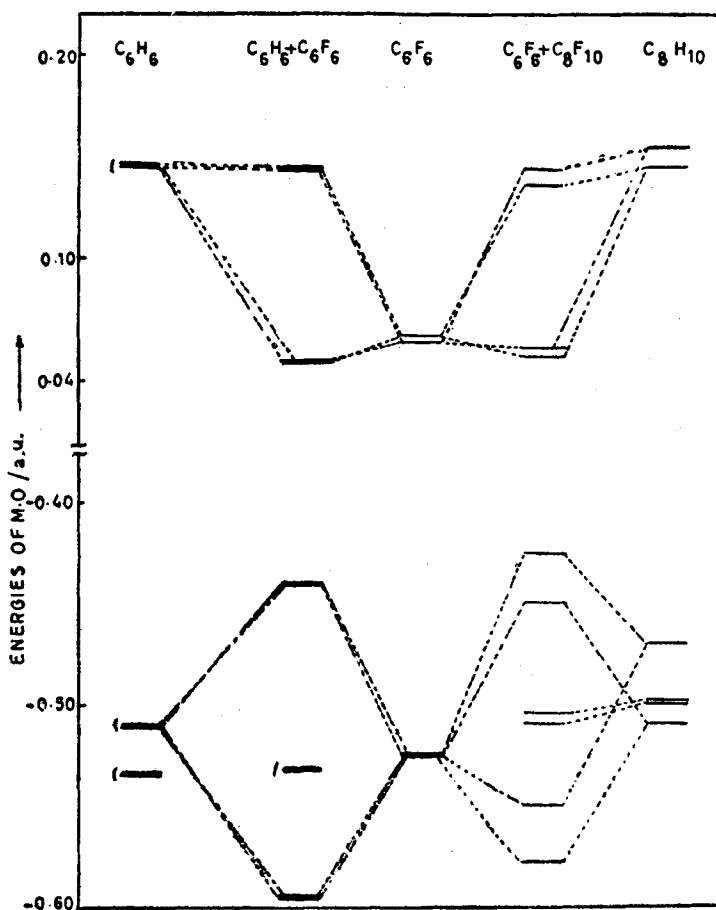


Figure 4. Energies of HOMO and LUMO of benzene (*p*-xylene) and hexafluorobenzene and their adducts.

We have carried out the correlation of the molecular orbitals of the composite molecule with the molecular orbitals of the individual hexafluorobenzene and benzene (*p*-xylene) molecules. It is evident from figure 4 that the interaction of highest occupied molecular orbitals play insignificant role in stabilization. Actually this leads to slight destabilization. It was noted for both the complexes that the stability arises due to the interaction of some lower molecular orbitals.

The theoretical calculations agree with the crystallographic studies regarding the configuration of the complexes. The calculated intermolecular distances are small. This, however, is a general weakness of CNDO method. Our calculations also explain the results of depolarized Rayleigh scattering study of benzene+hexafluorobenzene system.

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