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Crystallographic Studies of Addition Compounds of Hexafluorobenzene. Crystal Structure of the 1:1 Adduct with *N,N*-Dimethylaniline

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The 1:1 addition compound between *N,N*-dimethylaniline and hexafluorobenzene crystallizes at room temperature in a monoclinic cell. A lattice with space group $I2/m$ and $a = 6.927$ (1), $b = 14.833$ (2), $c = 7.071$ (1) Å, $\beta = 103.67$ (1)° was chosen rather than a Bravais lattice with space group $C2/m$. The structure was refined to $R = 0.060$ for 280 counter data. The structure is disordered with the *N,N*-dimethylaniline molecule in two different orientations. The partner molecules are stacked alternately in infinite columns, and the mean separation between the molecular planes is 3.52 Å. The benzene rings of the partner molecules overlap in a way which is often found in charge-transfer complexes.

Introduction

The structures of the addition compounds between hexafluorobenzene (HFB) and the symmetrically methylated benzenes *p*-xylene, mesitylene, durene and hexamethylbenzene have been reported (Dahl, 1975 and references therein). In all these compounds the molecules are stacked alternately in infinite columns. With regard to interplanar distances (Table 1) and overlap (Fig. 1) a clear trend is observed: The *p*-xylene and mesitylene compounds have the largest interplanar

distances, and overlap with the benzene rings twisted 30° relative to each other. Further increase in the number of methyl groups gradually shortens the interplanar distance and alters the relative orientation of the benzene rings towards parallelism.

No charge-transfer bands have been observed in spectra of addition compounds between HFB and aromatic hydrocarbons in solution (Beaumont & Davis, 1967; Swinton, 1974). However, a short interplanar distance and an overlap like that of the hexamethylbenzene compound may be considered as typical features of charge-transfer complexes. As methyl groups are known to increase the donor strength of an aromatic hydrocarbon (Herbstein, 1971), the observed trend has been interpreted as being due to charge-transfer forces in the compounds with more than three methyl groups (Dahl, 1975).

As distinct from the compounds mentioned above, addition compounds between HFB and aromatic amines in solution show charge-transfer bands (Beau-

Table 1. Mean interplanar distance in addition compounds between HFB and methylated benzenes

| | Temperature (°C) | Distance (Å) |
|-----------------------|------------------|--------------|
| <i>p</i> -Xylene–HFB | 20 | 3.55 |
| Mesitylene–HFB | –35 | 3.56 |
| Durene–HFB | 20 | 3.51 |
| Hexamethylbenzene–HFB | –40 | 3.43 |

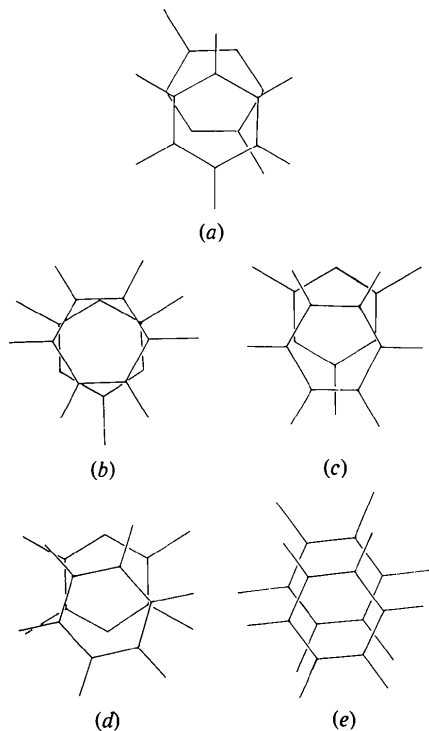


Fig. 1. Overlap diagrams of (a) *p*-xylene-HFB, (b) and (c) mesitylene-HFB, (d) durene-HFB (monoclinic form) and (e) hexamethylbenzene-HFB (triclinic form).

mont & Davis, 1967). Crystal structures of some complexes between aromatic amines and π -acceptors indicate n - π interaction (Ohashi, 1973). This kind of interaction may most clearly be seen from the crystal structure if the amine has no centre of symmetry. For the purpose of elucidating the nature of complexes between HFB and aromatic amines and throwing light on the results of the investigations of the addition compounds with methylated benzenes, the structure of the addition compound between HFB and *N,N*-dimethylaniline (DMA) was determined.

Experimental

The crystals were obtained by evaporation at -20°C of a solution of the two components in dichloromethane. The crystals are unstable in air and were sealed in glass capillaries.

Weissenberg diagrams taken at different temperatures show that a phase transition takes place between -60 and -100°C . The low-temperature cell seems to be closely related to that at room temperature, but some of the axes are doubled. No further studies of the low-temperature form have been made, and all data given here refer to the room-temperature form.

The systematic extinctions were found from

Weissenberg diagrams; the cell parameters and the intensities were measured on an Enraf-Nonius CAD-4 diffractometer. For the least-squares refinement of the cell parameters θ values of 25 reflexions, measured with $\text{Mo } K\alpha_1$ radiation ($\lambda = 0.70926 \text{ \AA}$), were used. As a *C*-centred monoclinic cell has a very large β angle, an *I*-centred cell was chosen for the structure determination.

The crystal data are: $\text{C}_8\text{H}_{11}\text{N} \cdot \text{C}_6\text{F}_6$, monoclinic. Cell used: space group *Im* or *I2/m*, $a = 6.927(1)$, $b = 14.833(2)$, $c = 7.071(1) \text{ \AA}$, $\beta = 103.67(1)^\circ$. Conventional cell: space group *Cm* or *C2/m*, $a = 6.927(1)$, $b = 14.833(2)$, $c = 8.754(1) \text{ \AA}$, $\beta = 128.08(1)^\circ$. $V = 669.6 \text{ \AA}^3$, $Z = 2$ (assumed). $D_c = 1.46 \text{ g cm}^{-3}$ (not measured), $\mu(\text{Mo } K\alpha) = 1.63 \text{ cm}^{-1}$.

The intensities were collected by an $\omega/2\theta$ scan with $\text{Mo } K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). 280 reflexions with $I > 2.5\sigma(I)$ were used for the structure determination.

Most of the crystals obtained were needle shaped. The one used for data collection was, however, not far from spherical with radius $\sim 0.1 \text{ mm}$. Absorption corrections were therefore not performed.

Structure determination and refinement

The length of *c* and the observation that the needle axis of the crystals is along [001] indicated that the molecules are stacked along this direction. None of the possible ordered structures were found to be correct and disorder had to be introduced. With two orientations of the DMA molecule assumed, related by the mirror plane (010) as indicated in Fig. 2, satisfactory *R* values were obtained. Least-squares refinement clearly indicated that the DMA molecule is situated on a twofold axis and that the correct space group is *I2/m*.

In the last part of the refinement all positional and anisotropic thermal parameters of the HFB molecule were varied independently. Because of the small separation between the atomic positions of DMA molecules in different orientations, only isotropic thermal parameters could be used for the C and N atoms of this molecule. Cycles in which these parameters were kept constant, and cycles in which

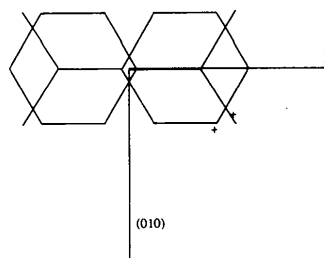


Fig. 2. The two orientations of the DMA molecule. The + marks indicate the positions to which the neighbouring ring C atom and methyl C atom moved during the refinement.

Table 2. *Final atomic parameters*

Anisotropic thermal parameters ($\times 10^3$) are defined by
 $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.
 Anisotropic and isotropic thermal parameters are in \AA^2 .

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|------|------------|------------|------------|----------|----------|----------|----------|----------|----------|
| F(1) | 0 | 0.1814 (3) | 0.5 | 258 (4) | 121 (3) | 190 (3) | 0 | 108 (3) | 0 |
| F(2) | 0.3425 (4) | 0.0906 (2) | 0.6199 (4) | 135 (2) | 266 (3) | 175 (2) | -78 (2) | 42 (2) | -36 (2) |
| C(1) | 0 | 0.0917 (5) | 0.5 | 148 (7) | 111 (7) | 96 (5) | 0 | 53 (5) | 0 |
| C(2) | 0.1727 (7) | 0.0456 (3) | 0.5609 (7) | 99 (3) | 170 (6) | 95 (3) | -27 (3) | 32 (2) | -12 (3) |

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> | | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|------|-------------|------------|-------------|----------|------|-------------|--------------|-------------|----------|
| C(3) | 0 | 0.1768 (9) | 0 | 13.9 (4) | C(6) | 0 | -0.0089 (16) | 0 | 7.1 (2) |
| C(4) | 0.2032 (12) | 0.1271 (8) | 0.0578 (15) | 13.1 (3) | C(7) | 0.1496 (12) | -0.1538 (6) | 0.0457 (13) | 9.0 (3) |
| C(5) | 0.1767 (8) | 0.0337 (4) | 0.0544 (7) | 9.1 (2) | N(1) | 0 | -0.1079 (8) | 0 | 9.9 (3) |

the positional parameters were kept constant, were performed alternately until no significant shifts were observed.

No H positions could be found from a difference map. These positions were thus calculated with disorder due to rotation of the methyl groups assumed. The parameters of the H atoms were kept constant in the refinement, but were included in the structure factor calculations. As the effect of extinction is significant, an isotropic secondary extinction parameter was varied in the last refinement cycles, assuming a constant value of the mean path length. The final R is 0.060 and $R_w = [\sum w(F_o - F_c)^2 / \sum wF^2]^{1/2} = 0.028$. The final parameters are given in Table 2.*

Rigid-body-motion analysis of HFB showed that the largest r.m.s. angle of libration is 9.3° . The corresponding librational axis is approximately perpendicular to the molecular plane. Bond distances, with the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32608 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond distances (Å) and angles (°)*

Values on second line are corrected for librational motion.
 Symmetry code: (i) \bar{x}, y, \bar{z} ; (ii) x, \bar{y}, z .

| | | | |
|--------------------------|-----------|-------------------------------|-----------|
| F(1)-C(1) | 1.330 (9) | F(1)-C(1)-C(2) | 120.2 (3) |
| | 1.355 | C(2)-C(1)-C(2) | 119.5 (6) |
| F(2)-C(2) | 1.330 (5) | F(2)-C(2)-C(1) | 119.7 (4) |
| | 1.357 | F(2)-C(2)-C(2 ⁱⁱ) | 120.0 (4) |
| C(1)-C(2) | 1.356 (6) | C(1)-C(2)-C(2 ⁱⁱ) | 120.2 (5) |
| | 1.383 | C(4)-C(3)-C(4) | 123 (1) |
| C(2)-C(2 ⁱⁱ) | 1.354 (6) | C(3)-C(4)-C(5) | 111 (1) |
| | 1.379 | C(4)-C(5)-C(6) | 125 (1) |
| C(3)-C(4) | 1.56 (1) | C(5)-C(6)-C(5) | 124 (2) |
| C(4)-C(5) | 1.40 (1) | C(5)-C(6)-N | 118 (1) |
| C(5)-C(6) | 1.35 (1) | C(6)-N-C(7) | 124 (1) |
| C(6)-N | 1.47 (3) | C(7)-N-C(7) | 112 (1) |
| N-C(7) | 1.22 (1) | | |

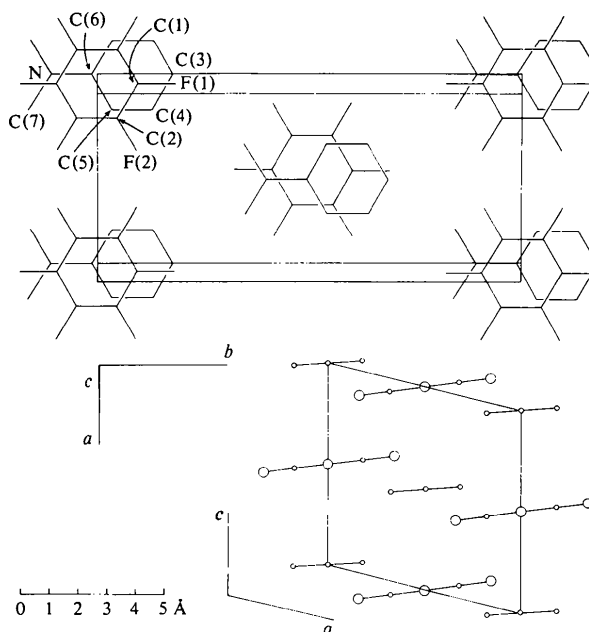


Fig. 3. The packing of the molecules viewed perpendicular to the average molecular plane and perpendicular to (010). Only one of the equivalent orientations of the DMA molecule is shown.

inclusion of those corrected for librational motion, and angles are given in Table 3. The packing of the molecules is shown in Fig. 3.

Scattering factors given by Doyle & Turner (1968) were used for the N and C atoms and those given by Stewart, Davidson & Simpson (1965) for the H atoms. The computer program used for data reduction was written at the University of Lund and modified for the Univac 1110 by L. K. Hansen and Leif Sæthre. The program used for rigid-body-motion analysis is that of Schomaker & Trueblood (1968) modified for the Univac 1110 by L. Milje. The other programs used are included in the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion

The corrected bond distances and angles of HFB are not significantly different from those found from gas-phase studies of the pure compound by electron diffraction (Almenningen, Bastiansen, Seip & Seip, 1964).

The geometry found for DMA must be considered in the light of the difficulties encountered in the refinement of the parameters. The parameters of C(4) and C(7) seem to have influenced each other strongly. It appears from Fig. 2 that the displacement of these atoms from their expected positions gives in the area an electron distribution which seems reasonable on account of anisotropic thermal motion. The unexpected positions may thus be an effect of not using anisotropic thermal parameters for these atoms in the refinement.

Interatomic distances between different stacks do not indicate strong interactions. If, however, the N—C(7) distance is increased to a normal value of 1.45 Å, a distance of 3.29 Å is found between F(1) and C(7), transformed to its equivalent position ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$). This contact between an F atom and a methyl group may be of the same kind as that observed in the addition compounds of HFB with mesitylene and durene (Dahl, 1975).

It follows from the space-group symmetry that the amino group is planar, and that the overlap on both sides of the DMA molecule is the same. This shows that DMA is a π -donor rather than an n -donor in this complex.

No atoms of HFB and no C or N atoms of DMA deviate significantly from appropriate least-squares planes. The angle between the plane normal and the stack axis is 7.1° for HFB and 3.9° for DMA. The mean distance between the molecular planes is 3.52 Å. This distance is relatively large compared with those found in other charge-transfer complexes (Prout & Kamenar, 1973). There is no intermolecular distance within the stack shorter than 3.55 Å between ring C atoms and 3.50 Å between F and ring C atoms. However, during rotation of methyl groups, methyl H atoms will be well within the van der Waals distance of 2.75 Å (Nyburg & Szymanski, 1968) from an F atom. The large interplanar distance is thus probably due to the bulky methyl groups.

The overlap is shown in Fig. 3. Such a diagram with the benzene rings parallel and a C—C bond of one ring

above the centre of the adjacent ring has been regarded as typical for a charge-transfer complex (Dahl, 1975). It may also be noted that the overlapping C—C bond of DMA is that nearest to the electron-donating amino group. It is therefore believed that the overlap is determined to a high degree by charge-transfer forces.

The results of this investigation throw light on the interpretation of the structures of addition compounds between HFB and methylated benzenes. An increase in the number of methyl groups above three in the methylated benzenes results in an interplanar distance shorter than that of the charge-transfer complex between HFB and DMA and an overlap more similar to that of this complex. This investigation thus seems to confirm that charge-transfer forces have an effect on the structure of addition compounds between HFB and the more highly methylated benzenes.

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