

those observed in these other structures. However, the angles, Table 7, show a larger range of values, 89–152°, than found, for example, in the octanediol, 100–114°. The H atoms generally were found in appropriate hydrogen-bonding positions but due to the lower quality of the data they cannot unambiguously be assigned to these positions.

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References

- ARISON, B. H. & BECK, J. L. (1973). *Tetrahedron*, **29**, 2743–2746.
- AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701–704.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- COCHRAN, A. & DOUGLAS, A. S. (1955). *Proc. R. Soc. London Ser. A*, **227**, 486–500.
- DATTAGUPTA, J. K. & SAHA, N. N. (1975). *J. Cryst. Mol. Struct.* **5**, 177–189.
- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* **A29**, 231–234.
- DEGELH, R. & MARSH, R. E. (1959). *Acta Cryst.* **12**, 1007–1014.
- FOLK, R. M., PETERS, A. C., PAVKOV, K. L. & SWENBERG, J. A. (1974). *Cancer Chemother. Rep. Part 3*, **5**, 37–41.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GITTERMAN, C. O., RICKES, E. L., WOLF, D. E., MADAS, J., ZIMMERMAN, S. B., STOUT, T. H. & DEMNY, T. C. (1970). *J. Antibiot.* **23**, 305–310.
- HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45–55.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–101, 149–150. Birmingham: Kynoch Press.
- JEFFREY, G. A. (1969). *Acc. Chem. Res.* **2**, 344–352.
- JEFFREY, G. A. & MASTROPAOLO, D. (1978). *Acta Cryst.* **B34**, 552–556.
- JEFFREY, G. A. & SHEN, M. S. (1972). *J. Chem. Phys.* **57**, 56–61.
- KIM, H. S. & JEFFREY, G. A. (1970). *J. Chem. Phys.* **53**, 3610–3615.
- KOCH, M. J. H. (1974). *Acta Cryst.* **A30**, 67–70.
- PETTIT, G. R., VON DREELE, R. B., HERALD, D. L., EDGAR, M. T. & WOOD, H. B. JR (1976). *J. Am. Chem. Soc.* **98**, 6742–6743.
- RAMACHANDRAN, G. N. & VENKATACHALAM, C. M. (1968). *Biopolymers*, **6**, 1255–1262.
- ROLLETT, J. S. & CARRUTHERS, R. S. (1974). Private communication.
- SCHWARZENBACH, D. (1968). *J. Chem. Phys.* **48**, 4134–4140.
- SLETTEN, E. (1970). *J. Am. Chem. Soc.* **92**, 172–177.
- SMAIL, E. J. & SHELDRIK, G. M. (1973). *Acta Cryst.* **B29**, 2027–2028.
- TARNOWSKI, G. S., SCHMID, F. A., HUTCHISON, D. J. & STOCK, C. C. (1973). *Cancer Chemother. Rep. Part 1*, **57**, 21–27.
- WELLS, A. F. (1967). *Structural Inorganic Chemistry*, 3rd ed., p. 57. Oxford Univ. Press.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

Acta Cryst. (1981). **B37**, 98–101

Structure of the 1:1 Complex Between *N,N*-Dimethyl-*p*-toluidine and Hexafluorobenzene

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Abstract

The 1:1 complex between *N,N*-dimethyl-*p*-toluidine, $C_9H_{13}N$, and hexafluorobenzene, C_6F_6 , crystallizes in a monoclinic cell. In order to avoid a too oblique β angle a lattice with space group $I2/m$ and $a = 6.566$ (2), $b = 16.539$ (5), $c = 7.206$ (3) Å, $\beta = 97.97$ (3)° was chosen rather than the conventional Bravais lattice with space group $C2/m$ and $a = 6.566$ (2), $b = 16.539$ (5),

$c = 9.051$ (3) Å, $\beta = 127.96$ (3)°. $V = 775.0$ Å³, $Z = 2$ (assumed), $D_c = 1.38$ Mg m⁻³ (not measured). The structure was refined by constraints to $R = 0.078$ for 164 observed reflections. The structure is disordered with the *N,N*-dimethyl-*p*-toluidine molecule in two equivalent orientations. The thermal vibrations of the hexafluorobenzene molecule are unusually large, especially along [010]. The partner molecules are stacked alternately with an interplanar distance of 3.50 Å. The overlap of the benzene rings of the partner molecules is very similar to that observed in other complexes of hexafluorobenzene with π donors, and the

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difference from that of the complex with *N,N*-dimethylaniline can be explained from differences in the steric requirements.

Introduction

Crystal structures of molecular complexes of hexafluorobenzene (HFB) with partners which are closely related to each other seem to form a more coherent pattern than the majority of the known crystal structures of electron-donor-acceptor complexes between aromatic molecules (Dahl, 1977; Herbstein, 1971; Prout & Kamenar, 1973). This may in part be due to the small size of the F atoms and the disc shape of the HFB molecule, which reduce the importance of steric hindrance for the molecular packing. The same features of the HFB molecule may also explain the unusually large anisotropic thermal motion and the frequent occurrence of disorder in these complexes. These structures may thus be of importance both for elucidating the nature of the intermolecular forces in electron-donor-acceptor complexes and for studying the crystalline state of molecular compounds.

In the HFB complex with *N,N*-dimethylaniline (DMA) (Dahl, 1977) the benzene rings of adjacent molecules within the stack overlap approximately as in the complex with hexamethylbenzene (Dahl, 1973), and this overlap seems to be typical for HFB complexes with π donors. In the complex with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Dahl, 1979) the overlap is somewhat different, but here the partially tetrahedral geometry of the N atoms indicates that the amine is an *n*-donor. *N,N*-Dimethyl-*p*-toluidine (DMT) has a donor strength and a molecular shape somewhere between the two amines mentioned above. The structure of its HFB complex was determined in order to help complete the picture of this class of complexes.

Experimental

The crystals are very unstable when exposed to the atmosphere and were therefore formed by evaporation of the excess HFB from a mixture of the two components in a capillary, which was then sealed immediately. All the crystals were very thin plates with face (010) and the one used for data collection was $0.3 \times 0.01 \times 0.5$ mm in the axial directions.

The systematic extinctions, found from Weissenberg diagrams, are $h + k + l = 2n + 1$, which indicated the space group to be *Im*, *I2* or *I2/m*. The cell parameters and intensities were measured on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters were determined from the setting angles

of 25 reflections. The intensities were collected by an $\omega/2\theta$ scan at a rate in ω of $0.3\text{--}1.0^\circ \text{ min}^{-1}$, and all reflections were measured twice. In spite of this, only 165 reflections had $I > 1.5\sigma(I)$ and were used for the structure determination. Absorption corrections were not performed.

Structure determination and refinement

The cell dimensions and the systematic extinctions indicated that the structure is not very different from that of the DMA-HFB complex, which has the space group *I2/m*. Attempts to use the other possible, less symmetrical, space groups confirmed that the space group is *I2/m* even for this complex. The structure is therefore disordered with two orientations of the DMT molecule, related by the mirror plane (010). The assumption that this molecule occupies approximately the same space in the two orientations made it possible to derive a trial structure which could be used as a starting point for further refinement.

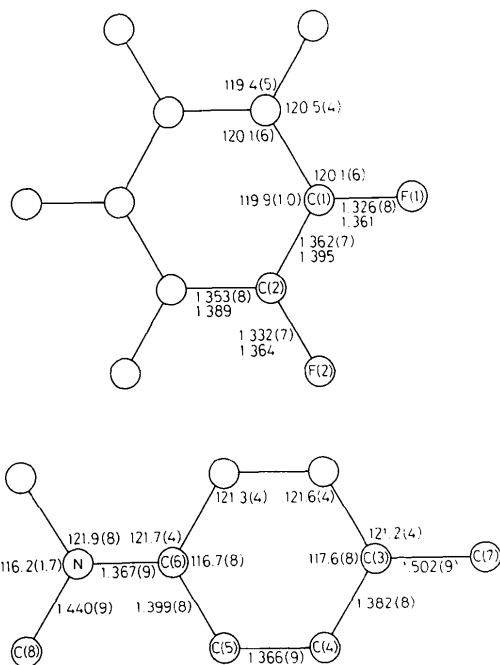
Because of the small number of observed reflections constrained refinement was used (Waser, 1963). Both the HFB molecule and the non-hydrogen part of the DMT molecule were constrained to be planar, as the space-group symmetry excludes the possibility of a tetrahedral geometry of the N atoms. Angles and bond distances of the HFB molecule were constrained to be the same as those not corrected for librational motion in the DMA-HFB complex, as the effect of the librational motion was assumed to be approximately the same in both complexes. For bond distances and angles in the DMT molecule the structure of *p*-(*N,N*-dimethylamino)benzoic acid (Colapietro, Domenicano & Marciante, 1978) was used as a model, and the C(3)-C(7) distance (Fig. 1) was constrained to be 1.50 Å. The thermal vibrations of atoms linked by a covalent bond were constrained to be equal in the bond direction, except for C(3)-C(4), C(5)-C(6) and N-C(8), where this would have been unreasonable because of the difficulties mentioned below in the refinement of some of the thermal parameters.

For some parameters absolute constraints were used. As C(3) and N occupy approximately the same position, the shifts in their thermal parameters were set equal. U_{12} and U_{23} for C(5) were set to zero as this atom is situated near a mirror plane. The H atoms were included in the structure factor calculations, but their parameters were kept constant in the refinement. Their positions were calculated with C-H = 0.95 Å and disorder due to rotation of the methyl groups was assumed. The isotropic U values used were 0.18 \AA^2 for methyl H atoms and 0.14 \AA^2 for those bound directly to the ring.

With these assumptions 70 parameters were varied in the refinement, and 31 constraints were included in

Table 1. Positional parameters and equivalent isotropic temperature factors (\AA^2) (Hamilton, 1959)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
F(1)	0	0.1624 (8)	0.5	18.6
F(2)	0.3475 (12)	0.0805 (7)	0.6275 (10)	18.0
C(1)	0	0.0822 (8)	0.5	12.4
C(2)	0.1752 (13)	0.0409 (2)	0.5640 (11)	11.2
C(3)	0	0.1263 (13)	0	9.7
C(4)	0.1772 (11)	0.0830 (12)	0.0591 (11)	9.2
C(5)	0.1785 (10)	0.0004 (12)	0.0596 (11)	7.9
C(6)	0	-0.0440 (12)	0	8.6
C(7)	0	0.2171 (14)	0	15.1
C(8)	0.1834 (20)	-0.1727 (13)	0.0604 (13)	14.3
N	0	-0.1267 (13)	0	13.1

Fig. 1. Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses. Distances on the second line are corrected for librational motion.

the observations in addition to the reflections. During the refinement it became obvious that $F(020)$ had a systematic error, possibly as a result of the low θ angle of this reflection, and it was omitted in the last cycles.

The weights used in the final part of the refinement were $w = 1/\sum_{r=1}^n A_r T_r(x)$, where $T_r(x)$ is the Chebyshev polynomial and x is $|F_o|/|F_o(\max)|$ (Rollett, 1965; Carruthers & Watkin, 1979). Four coefficients (A_r) were used, with the values 6.46, 1.08, -7.35 and -1.68. The final R is 0.078 and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.087$. The final parameters are given in Table 1.

Bond distances, with the inclusion of those corrected for librational motion of the HFB molecule, and

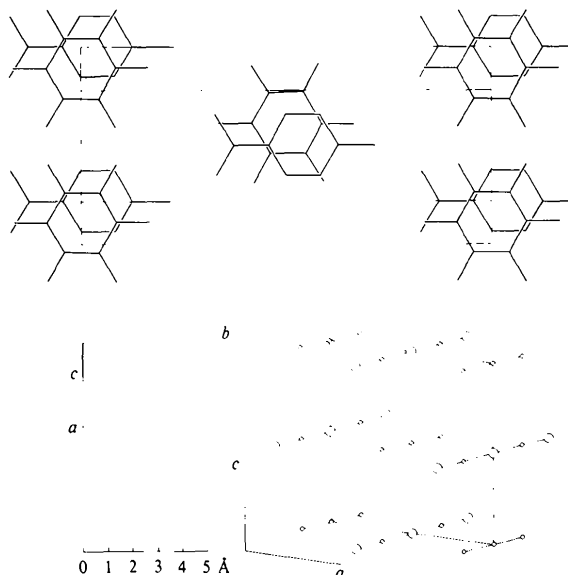


Fig. 2. The packing of the molecules viewed perpendicular to the average molecular plane and perpendicular to (010). Only one of the equivalent orientations of the DMT molecule is shown.

angles are shown in Fig. 1. The packing of the molecules is shown in Fig. 2.

All calculations were performed on the Oxford ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1975). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).†

Discussion

No bond distances or angles deviate significantly from the models to which they were constrained, the largest deviations being 0.007 \AA and 0.6° for HFB (uncorrected values) and 0.011 \AA and 0.4° for DMT.

It appears from Table 1 that the thermal vibrations are unusually large, especially for the HFB molecule. Rigid-body-motion analysis of this molecule showed r.m.s. angles of libration of 11.1, 7.1 and 5.8° about the principal librational axes, with the largest axis approximately perpendicular to the molecular plane and the smallest one along [010]. R.m.s. amplitudes of translation are 0.438, 0.332 and 0.205 \AA along the principal translational axes, with the largest and the smallest one along [010] and approximately along c^* , respectively. Bond distances of HFB corrected for librational motion all seem reasonable. Both the shape of the crystals and the extremely large translational

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35652 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

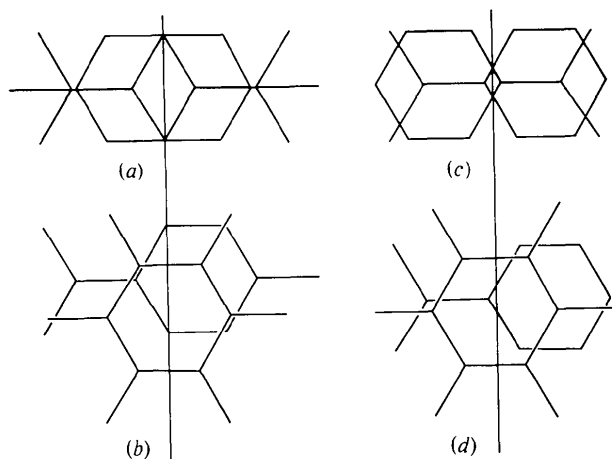


Fig. 3. The disorder of the donor molecule and the overlap of the partner molecules, viewed perpendicular to their average molecular plane, in the DMT-HFB complex (a and b) and in the DMA-HFB complex (c and d).

vibrations along [010] indicate a loose molecular packing in this direction, which is also apparent in Fig. 2. There are no interatomic distances which indicate strong interactions between the stacks in any direction.

Because of the constraints the deviations from planarity of HFB and the non-hydrogen part of DMT are very small and far from significant. The angle between the plane normal and the stack axis, the stacking angle, is 14.9° for HFB and 12.9° for DMT. The mean distance between the molecular planes is 3.50 \AA , which is significantly shorter than the corresponding distance of 3.52 \AA in the DMA-HFB complex. This shortening may be a result of the increased donor strength due to the additional methyl group in DMT. The shortest intermolecular distance in the stack between ring C atoms is 3.49 \AA and between F and ring C atoms 3.44 \AA . The shortest distance between F atoms and H atoms during rotation of the methyl groups is $\sim 2.6 \text{ \AA}$, which is within the van der Waals distance (Nyburg & Szymanski, 1968).

It appears from Fig. 3 that because the donor molecule occupies approximately the same space in both orientations and the HFB molecule is situated in the mirror plane, the overlap in the DMT-HFB complex has to be different from that in the DMA-HFB complex. It is, however, interesting to note that because of larger stacking angles in DMT-HFB, a C-C bond of one ring is still approximately above and parallel to a diagonal of the adjacent ring, in a similar way as in DMA-HFB. This similarity in spite of different steric requirements, and the fact that the same kind of overlap is observed in the hexamethylbenzene-

HFB complex, indicates that such an overlap is important in this class of complexes. As it is also observed in several $\pi-\pi^*$ complexes with other acceptors, it may be argued that this overlap is an important requirement for a maximum $\pi-\pi^*$ charge-transfer interaction. Theoretical calculations indicate, however, that such an interaction is not very sensitive to some smaller variations in the overlap (Mayoh & Prout, 1972). Moreover, various experimental results (Yim & Wood, 1976; Frazier, Christophorou, Carter & Schweinler, 1978) may indicate that HFB is a σ rather than π acceptor. This subject may be further elucidated by studying the effect on the structures of replacing HFB with fluoranil. A structure determination of the complex between DMA and fluoranil is now in progress.

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References

- CARRUTHERS, J. R. (1975). *CRYSTALS User Manual*, Oxford Univ. Computing Laboratory.
- CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* **A35**, 698-699.
- COLAPIETRO, M., DOMENICANO, A. & MARCIANTE, C. (1978). 9th Congr. Ital. Crystallogr. Assoc., Abstr.
- DAHL, T. (1973). *Acta Chem. Scand.* **27**, 995-1003.
- DAHL, T. (1977). *Acta Cryst.* **B33**, 3021-3024.
- DAHL, T. (1979). *Acta Chem. Scand. Ser. A*, **33**, 665-669.
- FRAZIER, J. R., CHRISTOPHOROU, L. G., CARTER, J. G. & SCHWEINLER, H. C. (1978). *J. Chem. Phys.* **69**, 3807-3818.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609-610.
- HERBSTEIN, F. H. (1971). *Perspectives in Structural Chemistry*, edited by J. D. DUNITZ & J. A. IBERS, Vol. IV, pp. 166-395. New York: John Wiley.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MAYOH, B. & PROUT, C. K. (1972). *J. Chem. Soc. Faraday Trans. 2*, **68**, 1072-1082.
- NYBURG, S. C. & SZYMANSKI, J. T. (1968). *Chem. Commun.* pp. 669-671.
- PROUT, C. K. & KAMENAR, B. (1973). *Molecular Complexes*, edited by R. FOSTER, Vol. I, pp. 151-207. London: Elek.
- ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, p. 40. Oxford: Pergamon.
- WASER, J. (1963). *Acta Cryst.* **16**, 1091-1094.
- YIM, M. B. & WOOD, D. E. (1976). *J. Am. Chem. Soc.* **98**, 2053-2059.