

Crystal Structure of the 1:1 Complex between N,N,N',N' -Tetramethyl-*p*-phenylenediamine and Hexafluorobenzene

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The 1:1 complex between N,N,N',N' -tetramethyl-*p*-phenylenediamine and hexafluorobenzene crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a=6.547(2)$ Å, $b=7.233(4)$ Å, $c=9.567(3)$ Å, $\alpha=104.07(5)^\circ$, $\beta=107.74(3)^\circ$, $\gamma=94.55(5)^\circ$. The structure was refined to $R=0.077$ for 206 observed reflections. The structure is disordered with the hexafluorobenzene molecule in two different orientations. The partner molecules are stacked alternately in infinite columns, and the mean separation between the molecular planes is 3.43 Å. The N atoms have a partially tetrahedral geometry which indicates that the complex has a considerable $n-\pi$ character.

In all the known crystal structures of addition compounds of hexafluorobenzene (HFB) with aromatic hydrocarbons and aromatic amines the molecules are stacked alternately in infinite columns.^{1–3} Charge-transfer bands in solution have been found in the spectra of the compounds with aromatic amines, but not in the spectra of those with aromatic hydrocarbons.^{4,5} A possible influence of charge-transfer forces on the crystal structures even of some of the latter compounds has been discussed.³

The crystal structure of the complex between N,N -dimethylaniline (DMA) and HFB has been published recently.¹ The charge-transfer band of this complex is observed at a somewhat shorter wavelength than that of the complex between N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD) and HFB,⁴ which indicates that the second dimethylamino group increases the charge-transfer interaction. The present investigation was carried out in order to study the effect on the crystal structure of the second dimethylamino group.

EXPERIMENTAL

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

Preliminary investigations indicated that all the crystals were of poor quality, consisting of several individuals with slightly different orientations. The crystal chosen for data collection had the dimensions $0.2 \times 0.3 \times 0.07$ mm in the axial directions.

The cell parameters and the intensities were measured on an Enraf-Nonius CAD4 diffractometer using $\text{MoK}\alpha_1$ radiation ($\lambda=0.70926$ Å) and $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å). Because of the poor quality of the crystal it was rather difficult to find the orientation matrix. The matrix and the cell parameters finally arrived at were determined from the setting angles of 22 reflections. The reasonable standard deviations of the cell parameters and the fact that most of the reflections found in the data collection were well centered, indicate that the matrix and the cell parameters are approximately correct.

The intensities were collected by an $\omega/2\theta$ scan at a rate in ω of $0.3-2.0^\circ \text{ min}^{-1}$. 206 reflections with $I > 2.5\sigma(I)$ were used for the structure determination. Lp and absorption corrections were performed.

CRYSTAL DATA

N,N,N',N' -Tetramethyl-*p*-phenylenediamine hexafluorobenzene, $\text{C}_{10}\text{H}_{16}\text{N}_2 \cdot \text{C}_6\text{F}_6$, F.W. = 350.34. Space group $P\bar{1}$ or $P1$, $a=6.547(2)$ Å, $b=7.233(4)$ Å, $c=9.567(3)$ Å, $\alpha=104.07(5)^\circ$, $\beta=107.74(3)^\circ$, $\gamma=94.55(5)^\circ$, $V=412.6$ Å³, Z (assumed)=1, $D_x=1.41$ g cm⁻³ (not measured), $\mu(\text{MoK}\alpha)=1.44$ cm⁻¹.

STRUCTURE DETERMINATION AND REFINEMENT

A trial structure which could be used as a starting point for further refinement was found by packing considerations. During the refinement it became clear that the molecules are situated in centres of symmetry and that the correct space group is $P\bar{1}$.

It turned out to be impossible to refine any ordered structure to an R below 0.20. A difference Fourier map clearly indicated orientational disorder of the HFB molecule. This molecule was therefore assumed to have two orientations, with different occupancies as they are not related by symmetry. The occupancy factor which thus is a variable parameter turned out to be strongly correlated to the thermal parameters of the HFB molecule in both orientations and to the positional parameters of the orientation with lowest occupancy. The occupancy factor was therefore not refined the ordinary way, but was given a series of values, each of which were kept constant during a least squares refinement of the structure. Nearly equal values of the isotropic thermal parameters for the two orientations were obtained when the occupancy factors were 62 and 38 %, respectively. For this reason these factors were assumed to be approximately correct and were not refined any further.

No H positions could be found from a difference map. Their positions were therefore calculated with C–H distances of 1.0 Å and disorder due to rotation of the methyl groups assumed. The isotropic B values used were 10 for methyl H atoms and 5 for H atoms bound directly to the ring. The parameters of the H atoms were kept constant in the refinement, but were included in the structure factor calculations. Even the positional and thermal parameters of the C atoms of the HFB molecule in the minor orientation were kept constant in the least squares refinement as they are strongly correlated to other parameters. They were, however, adjusted during the refinement in such a way that the positions were reasonable relative to the F positions and the thermal parameters had approximately the average value of those of the C atoms in the major orientation.

In the last part of the refinement, anisotropic thermal parameters were used for the F atoms in both orientations of the HFB molecule and for the N and C atoms of the dimethylamino group. Cycles in which all thermal parameters were kept constant, and cycles in which all the positional parameters were kept constant, were performed alternately until no significant shifts were observed.

The final R is 0.077 and $R_w = [\sum w(F_o - F_c)^2 / \sum wF^2]^{1/2} = 0.044$. A list of observed and calculated structure factors may be obtained from the author

Table 1. Positional and thermal parameters. The anisotropic temperature factor is $\exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$. Standard deviations in parentheses are given for those parameters which have been refined.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F1	0.1313(26)	0.6726(25)	0.2973(19)	0.148(21)	0.112(20)	0.071(21)	0.048(15)	0.026(13)	0.018(14)
F2	0.4072(26)	0.6987(26)	0.1389(20)	0.074(16)	0.138(27)	0.117(21)	-0.035(16)	0.021(16)	0.019(17)
F3	0.2645(28)	0.5270(30)	-0.1674(20)	0.099(17)	0.098(23)	0.180(24)	0.003(16)	0.074(20)	0.035(19)
F4	-0.0134(51)	0.5980(46)	0.2792(40)	0.174(36)	0.105(41)	0.153(41)	0.053(30)	0.109(30)	0.043(31)
F5	0.3632(46)	0.7381(46)	0.2426(36)	0.114(30)	0.161(43)	0.153(35)	0.045(28)	0.055(29)	0.076(29)
F6	0.3725(39)	0.6136(44)	-0.0562(33)	0.112(28)	0.101(37)	0.183(45)	-0.035(26)	0.072(33)	0.085(28)
N	0.2431(20)	0.2010(19)	0.3097(15)	0.035(11)	0.119(18)	0.057(14)	-0.011(12)	-0.003(10)	0.007(12)
C10	0.1428(26)	0.2053(29)	0.4234(19)	0.130(20)	0.168(26)	0.098(22)	-0.032(17)	0.088(18)	0.014(18)
C11	0.4639(28)	0.2343(29)	0.3564(15)	0.116(18)	0.147(23)	0.046(19)	-0.037(16)	-0.004(15)	0.049(15)

	x	y	z	B		x	y	z	B
C1	0.080(6)	0.583(5)	0.150(4)	8.9(1.3)	C6	0.186	0.555	-0.028	6.3
C2	0.225(5)	0.604(4)	0.073(3)	4.4(9)	C7	-0.0822(31)	0.0276(28)	0.1198(22)	5.6(6)
C3	0.141(5)	0.522(4)	-0.088(4)	4.7(9)	C8	0.1326(31)	0.0996(26)	0.1611(20)	6.0(6)
C4	-0.007	0.550	0.144	6.3	C9	0.1987(20)	0.0732(22)	0.0298(21)	3.2(4)
C5	0.177	0.618	0.118	6.3					

Table 2. Bond distances (Å) and angles (°). Atoms marked by primes are related to those in the asymmetric unit by a centre of symmetry. Standard deviations in parentheses are given where all positions involved have been refined.

F1-C1	1.32(5)	F1-C1-C2	121(3)
F2-C2	1.22(5)	C3'-C1-C2	128(3)
F3-C3	1.27(5)	F2-C2-C3	123(3)
C1-C2	1.39(6)	C1-C2-C3	115(3)
C2-C3	1.42(6)	F3-C3-C2	120(3)
C3-C1'	1.45(6)	C2-C3-C1'	116(3)
F4-C4	1.27	F4-C4-C5	119
F5-C5	1.45	C6'-C4-C5	122
F6-C6	1.38	F5-C5-C6	121
C4-C5	1.38	C4-C5-C6	118
C5-C6	1.38	F6-C6-C5	119
C6-C4'	1.36	C5-C6-C4'	120
C7-C8	1.36(4)	C9'-C7-C8	120.4(2.0)
C8-C9	1.42(3)	C7-C8-C9	110.6(1.4)
C9-C7'	1.38(5)	C8-C9-C7'	128.7(1.5)
N-C8	1.37(5)	N-C8-C9	129.9(1.7)
N-C10	1.43(3)	C8-N-C10	119.8(1.4)
N-C11	1.36(3)	C8-N-C11	118.0(1.5)
		C10-N-C11	117.8(1.2)

upon request. The final parameters are given in Table 1. Bond distances and angles are given in Table 2. The two orientations of the HFB molecule and the overlap diagram of the complex is shown in Fig. 1. The packing of the molecules is shown in Fig. 2.

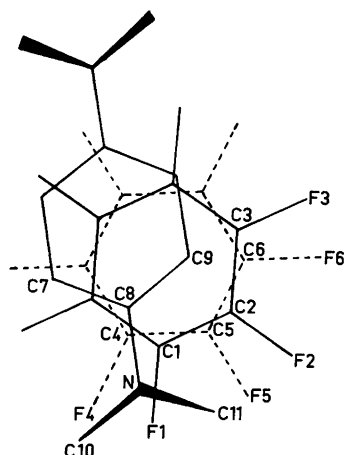


Fig. 1. The overlap of the molecules, viewed perpendicular to the average molecular plane. Both the major orientation (solid line) and the minor orientation (broken line) of the HFB molecule are included. The unequal degree of out of plane position of the methyl C atoms is indicated.

Scattering factors used for the F, N and C atoms are taken from Ref. 6, those used for the H atoms are taken from Ref. 7. The computer program used for data reduction has been written at the University of Lund and modified at the University of Tromsø for the Univac 1110. The other programs used are included in the X-RAY 76 system.⁸

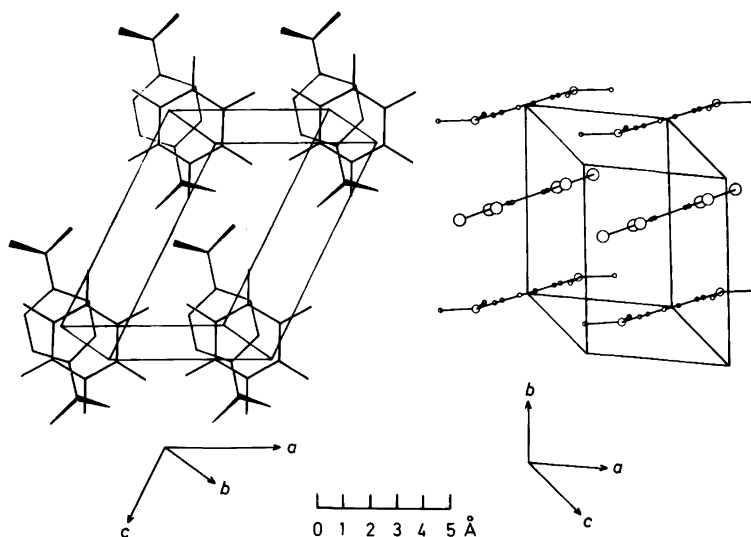


Fig. 2. The packing of the molecules, viewed perpendicular to, and along the average molecular plane. Only the major orientation of the HFB molecule is shown.

Table 3. Distances (Å) from the least-squares planes of the molecules. With the exceptions of C10 and C11 the atoms included are those defining the planes.

HFB major orientation		HFB minor orientation		TMPDA	
F1	0.05	F4	-0.04	C7	0.02
F2	-0.01	F5	0.04	C8	-0.04
F3	0.00	F6	-0.04	C9	0.02
C1	-0.03			N	0.01
C2	-0.04			C10	-0.08
C3	0.05			C11	-0.34

DISCUSSION

Because of the large standard deviations in the parameters and the high correlation between some of the parameters, many of the results must be regarded as very uncertain and will not be subject to any further comments. However, some conclusions about the structure, essential for a discussion of the nature of this complex, may safely be drawn.

It appears from Fig. 2 that the molecules are stacked alternately in infinite columns. The intermolecular distances indicate normal van der Waals forces between the stacks. It may, however, be noted that the thermal motion of this complex is considerably less than that found in other addition compounds of HFB, which indicates a difference in the strength or the nature of the intermolecular forces.

The deviations from least squares planes of the molecules, shown in Table 3, are not significant for those atoms defining the planes. The distances to the methyl C atoms, however, clearly show that the N atom has a partially tetrahedral geometry, which indicates that the TMPD molecule functions as an *n*-donor. The difference between these two distances shows that the amino group is slightly twisted relative to the aromatic ring. It appears from Figs. 1 and 2 that this twisting moves the lone pair electrons of the N atom towards a C-F bond of the adjacent HFB molecule in the major orientation.

In the complex between DMA and HFB all non-hydrogen atoms of the amine were found to be co-planar, which indicates a π - π interaction. However, the geometry of the N atoms shows that aromatic amines function as *n*-donors in the complexes of 1,2,4,5-tetracyanobenzene with TMPD, *N,N*-dimethyl-*p*-phenylenediamine, and *p*-phenylenediamine, respectively,⁹ and in the complex between TMPD and sulfur dioxide.¹⁰

It may also be noted that the overlap between the TMPD molecule and the HFB molecule in the major orientation (Figs. 1 and 2) is very similar to that between the partner molecules in the complex between TMPD and 1,2,4,5-tetracyanobenzene,⁹ which seems to confirm that the intermolecular forces are of the same kind.

The angle between the stack axis and the plane normals of the molecular planes is 16.4, 19.8 and 21.0° for TMPD and HFB in the major and minor orientation, respectively. The difference between the two latter values is not significant. The mean separation between the molecular planes is 3.43 Å, (standard deviation <0.005 Å), which is 0.09 Å shorter than in the DMA-HFB complex. Steric factors as well as stronger interaction may contribute to this shortening. The N-CH₃ bonds are pointing away from the molecular plane of the nearest HFB molecule, and no H atoms may therefore be within the van der Waals distance from this molecule during rotation of the methyl groups, as distinct from what was found in the DMA-HFB complex.

The interplanar distance in this complex is the same as that in the complex between hexamethylbenzene and HFB at -40 °C,² in which the steric hindrance is considerable and the charge-transfer interaction would be expected to be weaker. This observation is surprising, even when the effect of the different temperatures is taken into consideration.

Acknowledgements. The author thanks cand. real. Lars K. Hansen for help in the use of the diffractometer, and Dr. C. K. Prout for assistance given by the Chemical Crystallography Laboratory, University of Oxford, where the manuscript was prepared.

REFERENCES

1. Dahl, T. *Acta Crystallogr. B* 33 (1977) 3021.
2. Dahl, T. *Acta Chem. Scand.* 27 (1973) 995.
3. Dahl, T. *Acta Chem. Scand. A* 29 (1975) 699 and reference therein.
4. Beaumont, T. G. and Davis, K. M. C. *J. Chem. Soc. B* (1967) 1131.
5. Swinton, F. L. In Foster, R., Ed., *Molecular Complexes*, Vol. 2, Elek, London 1974.
6. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
8. Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. and Flack, H. *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
9. Ohashi, Y. *Acta Crystallogr. B* 29 (1973) 2863.
10. Childs, J. D., van der Helm, D. and Christian, S. D. *Inorg. Chem.* 14 (1975) 1386.

Received April 6, 1979.