Crystal Structure of the 1:1 Complex between *N,N*-Dimethylaniline and Fluoranil

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a=6.863(1)$ Å, $b=6.987(2)$ Å, $c=8.116(1)$ Å, $\alpha=110.81(1)°$, $\beta=99.87(1)°$, $\gamma=105.38(2)°$. The structure was refined to $R=0.059$ for 307 observed reflections. The structure is disordered with the *N,N*-dimethylaniline molecule in two equivalent orientations. The N atoms have a partially tetrahedral geometry. The partner molecules are stacked alternately in infinite columns. The structure indicates a strong $n-\pi^*$ interaction with the fluoranil molecule on one side of the *N,N*-dimethylaniline molecule and a weaker interaction with that on the other side. The corresponding interplanar distances are 3.24(1) and 3.46(1) Å.

The crystal structures of the electron donor–acceptor complexes of hexafluorobenzene with *N,N*-dimethylaniline (DMA)[1] and *N,N*-dimethyl-*p*-toluidine[2] show that the N atoms in both complexes have a planar geometry which indicate that the amine functions as a π-donor. The contacts with the acceptor molecules on different sides in the stack are related by symmetry and therefore equivalent.

Fluoranil and hexafluorobenzene are very similar with respect to molecular shape. However, fluoranil has a considerably greater electron affinity, hexafluorobenzene may possibly be a σ^*-acceptor rather than a π^*-acceptor[3] and electron distribution as well as polarizability of the two molecules are probably rather different. A comparison of the structures of their DMA complexes, where the steric requirements are nearly the same, should therefore show effects of these chemical differences. The present investigation was carried out in order to study such effects.

EXPERIMENTAL

Dark blue crystals of satisfactory quality were obtained after several attempts by evaporation of a solution of the two components in acetone. All the samples consisted of several individuals, some of these being twins with (001) as the twin plane. Although they were kept in glass capillaries the crystals broke down after a couple of weeks. The shape of the crystal chosen for data collection was nearly cubic with edges of 0.2 mm approximately in the axial directions.

The cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer using CuKα radiation ($\lambda=1.54178$ 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 $0.3-2.9°$ min^{-1}. There was a continous reduction of the intensities of the standard reflections down to 54 % of their original values during the data collection. 307 reflections with $I>1.5\sigma$ (I) were used for the structure determination. Absorption corrections were not performed.

CRYSTAL DATA

N,N-Dimethylaniline fluoranil, $C_8H_{11}N.C_6F_4O_2$, F.W. $=301.24$. Space group $P\bar{1}$, $a=6.863(1)$ Å, $b=6.987(2)$ Å, $c=8.116(1)$ Å, $\alpha=110.81(1)°$, $\beta=99.87(1)°$, $\gamma=105.38(2)°$, $V=335.2$ Å^3, $Z=1$, $D_x=1.49$ g cm^{-3}, $\mu(\text{Cu}K\alpha)=12.4$ cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

By the transformation $a'=b$, $b'=a+b+2c$, $c'=a$ the cell may be converted into a pseudo-monoclinic

cell not very different from the monoclinic cell of DMA-hexafluorobenzene. A trial structure, based on the assumption that the molecular packing is similar in the two complexes, could be used as a starting point for the refinement. The O atoms were distinguished from the F atoms after some refinement because of their shorter distance to the ring C atoms. The DMA-hexafluorobenzene structure is disordered with two orientations of the DMA molecule, related by a mirror plane. In the present triclinic case two space groups are possible. One of these, $P1$, requires no disorder, whereas the other one, $P\bar{1}$, requires two orientations of the DMA molecule, related by a centre of symmetry. Refinements, based on both these space groups, clearly showed that the latter is the correct one.

In order to reduce the number of variable parameters in the least-squares refinement and to avoid strong correlation due to small separation of atoms from different orientations of the DMA molecule, constrained refinement of the phenyl ring of this molecule was used. All bond distances and angles in the ring were fixed to 1.39 Å and 120°. A series of cycles in which the positional, orientational and thermal parameters of the phenyl group were refined while all parameters of the dimethyl-amino group were kept constant, followed by cycles in which the parameters of the C and N atoms of the dimethylamino group were refined with those of the phenyl group being fixed, were performed until no significant shifts were observed.

No H atoms could be found from a difference map. Their positions were therefore calculated with $C-H$ distances of 0.95 Å and disorder due to rotation of the methyl groups assumed. The isotropic B values used were 9 Å^2 for methyl H atoms and 7 Å^2 for H atoms bound directly to the ring. The parameters of the H atoms were not refined, but included in the structure factor calculations.

The weights used in the final part of the refinement were $w = XY$, where $X = 1$ for $\sin \theta > 0.3$, else $X = \sin \theta/0.3$, $Y = 1$ for $|F_o| < 7.5$, else $Y = 7.5/|F_o|$. The final R is 0.059 and $R_w = [\Sigma w(F_o - F_c)^2/wF^2]^{\frac{1}{2}} = 0.074$. A list of observed and calculated structure factors may be obtained from the author upon request. The final parameters are given in Table 1. Bond distances and angles are shown in Fig. 1. The disorder of the DMA molecule and the overlap diagrams of the complex are shown in Fig. 2. The packing of the molecules and some intermolecular distances are shown in Fig. 3.

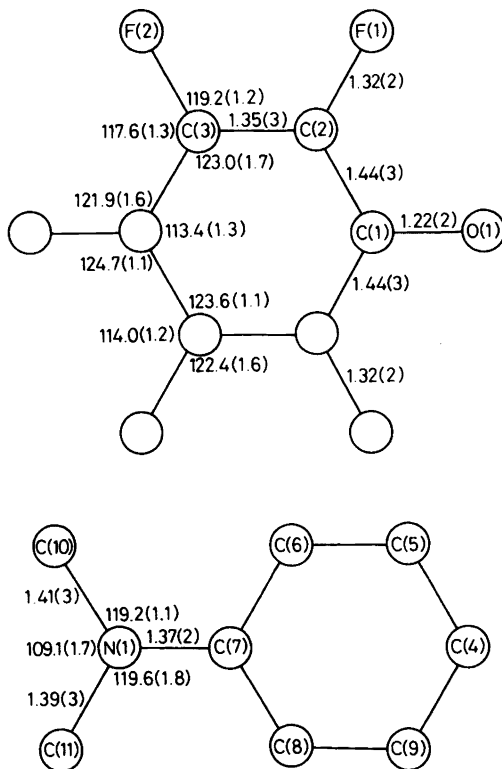Scattering factors for the H atoms are taken

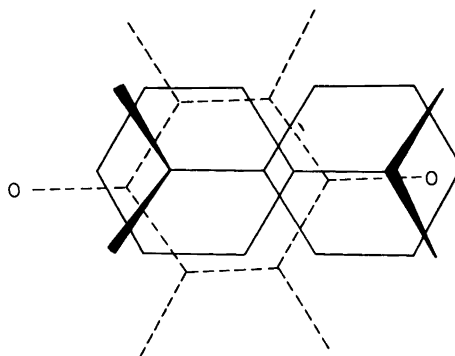Fig. 1. Bond distances (Å) and angles (°). Standard deviations in parentheses.

Fig. 2. The overlap of the molecules, viewed perpendicular to the average molecular plane. Both the equivalent orientations of the DMA molecule is shown. The one with the amino group on the left side is in closest contact with fluoranil molecule.
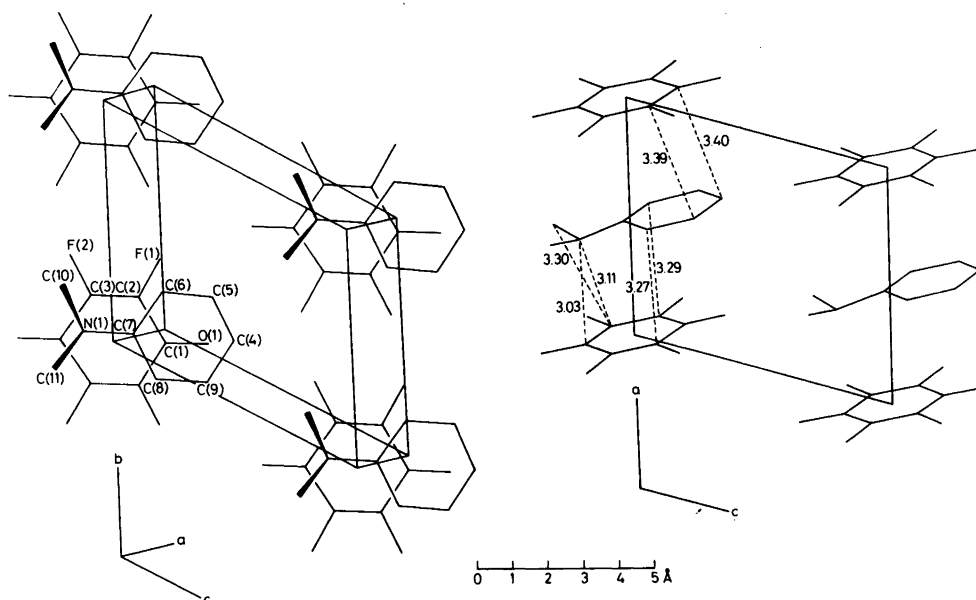
Fig. 3. The packing of the molecules, viewed perpendicular to the average molecular plane and along [010]. Only one of the equivalent orientations of the DMA molecule is shown. Some short intermolecular distances (Å) are given.

from Ref. 4, those used for the other atoms are taken from Ref. 5. All calculations have been performed at the CYBER 171 MP at the University of Tromsø. The computer program used for data reduction has been written at the University of Lund and modified at the University of Tromsø. The other programs used are included in the X-RAY 76 system.[6]

Table 1. Positional and thermal parameters. The anisotropic temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)]$. Standard deviations are given in parentheses. For the rigid group C(4–9) standard deviations are approximately 0.006 Å for the position of the centre of gravity and 0.8° for the Euler angles. Occupancy factors for C(4–11) and N(1) are 0.5.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.1944(13)	0.1707(14)	0.3634(12)	0.119(8)	0.135(7)	0.090(5)	0.055(5)	0.013(5)	0.044(5)
F(1)	0.2172(11)	0.4343(11)	0.1892(10)	0.132(6)	0.079(5)	0.179(6)	0.033(4)	0.046(5)	0.048(4)
F(2)	0.0230(11)	0.2640(11)	−0.1771(10)	0.151(7)	0.141(5)	0.187(7)	0.079(5)	0.080(5)	0.122(5)
C(1)	0.1024(19)	0.0961(20)	0.1992(19)	0.068(9)	0.077(10)	0.105(9)	0.030(8)	0.028(8)	0.041(9)
C(2)	0.1088(19)	0.2223(18)	0.0919(22)	0.103(10)	0.053(7)	0.125(11)	0.035(7)	0.066(9)	0.043(8)
C(3)	0.0166(20)	0.1340(24)	−0.0918(23)	0.100(10)	0.106(12)	0.114(10)	0.062(9)	0.069(9)	0.083(9)
C(10)	0.3761(34)	0.0395(37)	−0.3006(27)	0.104(19)	0.153(19)	0.084(16)	0.060(16)	0.051(14)	0.081(16)
C(11)	0.2826(37)	−0.3076(41)	−0.3191(29)	0.110(21)	0.106(18)	0.075(16)	0.025(16)	0.010(15)	0.005(14)
N(1)	0.3414(24)	−0.0880(24)	−0.2003(19)	0.095(15)	0.081(11)	0.066(11)	0.029(10)	0.015(10)	0.028(9)

	x	y	z	B		x	y	z	B
C(4)	0.6780	0.1487	0.3495	7.8(6)	C(7)	0.4706	−0.0098	−0.0237	5.1(4)
C(5)	0.6869	0.2921	0.2659	8.2(6)	C(8)	0.4616	−0.1533	0.0599	5.6(4)
C(6)	0.5832	0.2129	0.0793	6.2(4)	C(9)	0.5653	−0.0740	0.2465	8.6(6)

Table 2. Distances (Å) from the least-squares plane through the fluoranil molecule. Standard deviations in parentheses.

O(1)	0.017(9)	C(1)	−0.024(13)
F(1)	−0.002(8)	C(2)	−0.005(13)
F(2)	−0.012(8)	C(3)	0.031(14)

DISCUSSION

It appears from Table 2 that no atoms of the fluoranil molecule deviate significantly from a least squares plane through the molecule. In the DMA molecule, where the phenyl ring was constrained to be planar, the distances to N(1), C(10) and C(11) (Fig. 3) from this plane are −0.20, 0.05 and 0.20 Å, respectively. The amino group has thus a considerable degree of tetrahedral character. The unexpectedly large observed distance to N(1) has a standard deviation of 0.04 Å, mainly determined by the uncertainty in the orientation of the plane of the phenyl ring. The angle between this plane and that of the fluoranil molecule is 2.8°.

The distance to the neighbouring fluoranil molecule in the stack is shorter on one side of the DMA molecule than on the other side. The closest contact, which involves the lone pair electrons of the N atom, is shown in the lower right part of Fig. 3. The mean interplanar distance between the rings of this pair of molecules is 3.24(1) Å. The N atom is only 2.99(2) Å away from the plane of the fluoranil molecule, and some of its interatomic distances to this molecule (Fig. 3) are remarkably shoert. These distances and the geometry of the amino group indicate a strong $n - \pi^*$ interaction on this side of the DMA molecule.

The contact with the fluoranil molecule on the other side is shown in the upper right part of Fig. 3. The mean interplanar distance here is 3.46(1) Å. The interatomic distances between this pair of molecules correspond approximately to the van der Waals distances. No H atoms will be within the van der Waals distance from the fluoranil molecule on this side during rotation of the methyl groups. The longer intermolecular distances are therefore not a result of steric hindrance due to these groups.

The contact between a DMA molecule and a neighbouring fluoranil molecule depends on the orientation of the DMA molecule, and may be of one of the two kinds described above. The two kinds of overlap are shown in Fig. 2. That corresponding to the closest contact is characterized by the $C - N$ bond and a $C = O$ bond being localized approximately above the ring centres and nearly parallel to the diagonals of their respective adjacent rings. A similar overlap of $C = O$ bonds has been observed in many complexes with p-benzoquinone and its derivatives, and has been interpreted as an effect of dipole-induced dipole forces.[7] The facts that this overlap is observed only on one side of the DMA molecule, and that the $C = O$ group is not involved in any short intermolecular contacts, indicate that a similar interaction of this group is not very important in the present complex. It is therefore believed that the contact between the closest pair of molecules is dominated by the $n - \pi^*$ interaction.

The more distant pair of molecules have their rings nearly superimposed, which may indicate an important contribution of electrostatic forces in this interaction.

The conclusion is therefore that the DMA molecule has a strong $n - \pi^*$ charge-transfer interaction with the fluoranil molecule on one side in the stack, whereas the contact with that on the other side is mainly a van der Waals interaction with considerably less, or no contribution of charge-transfer forces. Because of the disorder, each fluoranil molecule may be involved either in two contacts of the same kind, or in one contact of each kind. The structure shows that the nature of this complex is different from that of the complex between DMA and hexafluorobenzene, and also demonstrates how the effect of charge-transfer interaction can be observed from the packing on different sides of an *n*-donor with lone pair electrons only on one side.

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