

Solid Addition Complexes of Tetramethylbenzenes with Fluoranil and Hexafluorobenzene. Crystal Structure of the 1:1 Complex between Durene and Fluoranil

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The 1:1 complex between durene and fluoranil crystallizes in the triclinic space group $P\bar{1}$ with $a=6.820(1)$ Å, $b=7.161(1)$ Å, $c=8.908(1)$ Å, $\alpha=109.57(1)^\circ$, $\beta=106.60(1)^\circ$, $\gamma=99.05(1)^\circ$. The structure was refined to $R=0.087$ for 1127 observed reflections. The partner molecules are stacked alternately in infinite columns and the mean separation between the molecular planes is 3.383(3) Å. Although the cell, after transformation, is not very different from that of the monoclinic form of the complex between durene and hexafluorobenzene, the interplanar distance and overlap of the molecules are somewhat different in the two complexes. Detailed crystal structure determinations of the complexes of 1,2,3,5-tetramethylbenzene with fluoranil and hexafluorobenzene have not been possible, but it is concluded that these structures are disordered and quite similar, and that the mean separation of the molecular planes in the fluoranil complex is 3.42 Å, shorter than that in the hexafluorobenzene complex.

Several crystal structures of addition complexes between benzene derivatives and hexafluorobenzene have been investigated.^{1,2} Fluoranil has a molecular shape very similar to that of hexafluorobenzene, whereas its electron affinity is considerably greater.^{3,4} Hexafluorobenzene may possibly be a σ^* -acceptor rather than a π^* -acceptor.^{5,6} A comparison of the structures of complexes of these molecules with the same donor, should therefore show differences which are due to chemical, not steric, effects. For this purpose, the complexes of *N,N*-dimethylaniline with hexafluorobenzene and fluoranil have been investigated earlier.^{2,7}

The nature of the addition compounds between hexafluorobenzene and methylated benzenes has been discussed, as no charge transfer bands have been observed in their spectra.⁸ Preliminary X-ray investigations show that these compounds usually have cell dimensions very similar to those of the corresponding fluoranil complexes. In many cases the space group is $R\bar{3}m$ and the symmetry requires that the structures are disordered.

The 1,2,3,5-tetramethylbenzene complexes of hexafluorobenzene and fluoranil are isomorphous with a space group symmetry which not requires disorder. These compounds were therefore regarded as suitable for the purpose of this investigation. So was also the complex between durene and fluoranil. The complex between durene and hexafluorobenzene has been investigated earlier.¹

Table 1. Crystal data.

	1,2,3,5-Tetramethyl- benzene-hexafluoro- benzene	1,2,3,5-Tetramethyl- benzene-fluoranil	Durene-fluoranil
Formula	C ₁₀ H ₁₄ · C ₆ F ₆	C ₁₀ H ₁₄ · C ₆ F ₄ O ₂	C ₁₀ H ₁₄ · C ₆ F ₄ O ₂
F.W.	320.28	314.28	314.28
Space group	<i>P</i> 2 ₁ / <i>m</i> or <i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>m</i> or <i>P</i> 2 ₁	\bar{P}
<i>a</i> (Å)	7.119(1)	6.832(1)	6.820(1)
<i>b</i> (Å)	14.138(1)	13.972(1)	7.161(1)
<i>c</i> (Å)	8.227(1)	8.519(1)	8.908(1)
α (°)	90	90	109.57(1)
β (°)	98.94(1)	105.56(1)	106.60(1)
γ (°)	90	90	99.05(1)
<i>V</i> (Å ³)	817.9	783.3	377.1
<i>Z</i>	2	2	1
<i>D</i> _x (gcm ⁻³)	1.300	1.332	1.384
<i>D</i> _m (flotation)(gcm ⁻³)		1.35	1.35
μ (CuK α)(cm ⁻¹)	11.21	10.62	11.03

EXPERIMENTAL

Needle-shaped crystals of the 1,2,3,5-tetramethylbenzene-hexafluorobenzene complex were formed from a solution in dichloromethane. The X-ray intensities of reflections with odd *h*-values (*a* being the needle axis) turned out to be very weak, different in different crystals and to decrease rapidly when the crystals were exposed to X-rays. For this reason no complete data set for this complex was collected.

Needle-shaped crystals of the fluoranil complexes of durene and 1,2,3,5-tetramethylbenzene were formed by evaporation of the solvent from solutions of the components in acetone. The dimensions of the durene-fluoranil crystals used for data collection were 0.35 × 0.1 × 0.1 mm in the axial directions.

Cell parameters and X-ray intensities were measured on an Enraf-Nonius CAD4 diffractometer using CuK α radiation ($\lambda = 1.5418$ Å). The cell parameters for each compound were determined from the setting angles of 25 reflections. The crystal data are given in Table 1. Using the matrix

$$\begin{pmatrix} -1 & -1 & 0 \\ 0 & 1 & 2 \\ 1 & 0 & 0 \end{pmatrix}$$

the cell of the durene-fluoranil complex may be transformed to a pseudo-monoclinic cell very similar to the monoclinic room temperature cell of the durene-hexafluorobenzene complex.

For both fluoranil complexes the intensities were collected by an $\omega/2\theta$ scan at a rate in ω of 0.3–2.0 min.⁻¹ 296 reflections for 1,2,3,5-tetramethylbenzene-fluoranil and 1127 for durene-fluoranil had $I > 1.5\sigma(I)$ and were used for the structure determination. Lp and absorption corrections were performed.

ON THE STRUCTURES OF THE 1,2,3,5-TETRAMETHYLBENZENE COMPLEXES WITH FLUORANIL AND HEXAFLUOROBENZENE

The structure of the 1,2,3,5-tetramethylbenzene-fluoranil complex could not be refined to an *R* below 17%. One reason for this was that the reflections from crystal planes nearly perpendicular to the needle axis were strongly extended and therefore observed too weak

Table 2. Positional parameters and equivalent or isotropic temperature factors (\AA^2).
 $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$. Standard deviations in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U_{iso}
O(1)	0.1340(6)	0.1047(8)	0.3348(4)	0.144(3)
F(1)	0.1908(5)	0.4001(5)	0.2180(5)	0.200(3)
F(2)	0.0575(6)	0.2935(6)	-0.1218(6)	0.162(3)
C(1)	0.0715(6)	0.0560(8)	0.1799(6)	0.094(3)
C(2)	0.0991(6)	0.2064(7)	0.1115(6)	0.094(3)
C(3)	0.0330(7)	0.1571(8)	-0.0578(7)	0.093(3)
C(4)	0.5529(8)	-0.1391(9)	0.2761(6)	0.140(4)
C(5)	0.6972(7)	0.3067(8)	0.3522(5)	0.118(3)
C(6)	0.5267(5)	-0.0637(6)	0.1358(4)	0.073(2)
C(7)	0.5965(5)	0.1443(6)	0.1692(4)	0.074(2)
C(8)	0.5684(5)	0.2025(5)	0.0340(5)	0.075(2)
H(1)	0.610(5)	0.335(5)	0.047(4)	0.083(9)
H(2)	0.481(9)	-0.097(9)	0.342(7)	0.164(18)
H(3)	0.499(9)	-0.278(10)	0.256(7)	0.170(19)
H(4)	0.696(9)	-0.113(8)	0.341(6)	0.152(16)
H(5)	0.818(6)	0.279(6)	0.414(5)	0.112(12)
H(6)	0.771(6)	0.431(6)	0.348(5)	0.114(12)
H(7)	0.602(7)	0.313(7)	0.409(5)	0.124(13)

relative to the other reflections. A correction for this effect was performed. In addition, the structure turned out to be highly disordered with both partner molecules in more than one orientation. The only conclusions concerning the structure drawn here is that the partner molecules are stacked alternately in infinite columns and the average distance between the molecular planes, which are well determined, is 3.42 Å.

The weak intensities of reflections with odd *h*-values of the 1,2,3,5-tetramethylbenzene-hexafluorobenzene complex is believed to be due to a kind of disorder where stacks are translated along the *a*-axis by half of its length, rather than to disorder in the stacking sequence. No attempt was made to determine the structure, but the similarity in the cell dimensions of the two 1,2,3,5-tetramethylbenzene complexes (Table 1) and the observed similarities in the intensities of reflections with even *h*-values indicate that the structures are not very different. As the *a*-axis is 0.287 Å longer in the hexafluorobenzene complex the mean distance between the molecular planes is probably well above 3.50 Å.

STRUCTURE DETERMINATION OF THE DURENE-FLUORANIL COMPLEX

From a Patterson map and subsequent Fourier maps all non-hydrogen atoms could be located. All H atoms were found from a difference map.

During the least squares refinement it was observed that the intensities of reflections with odd *h*-values were too low. For these reflections $\Sigma F_c = \Sigma F_o$ after increasing their F_o -values by 5 %, and this was done in the final refinement cycles. This effect may be explained in the same way as that observed for the 1,2,3,5-tetramethylbenzene-hexafluorobenzene complex.

In the last part of the least squares refinement all atomic positions and thermal parameters, anisotropic for non-hydrogen atoms and isotropic for H atoms, were varied. In

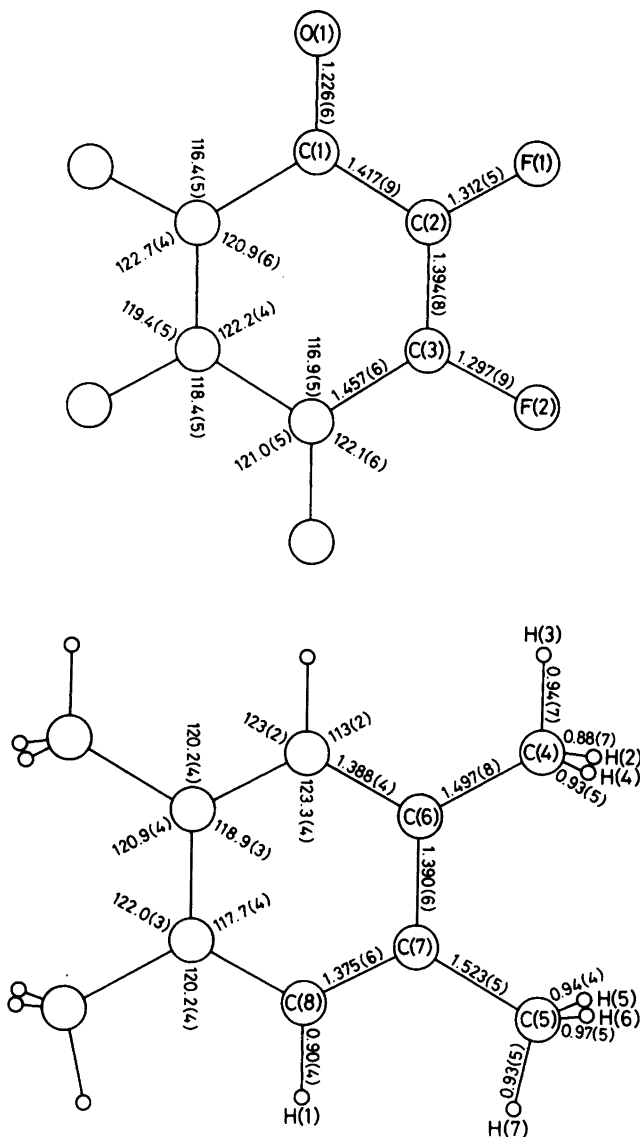


Fig. 1. Bond distances (Å) and angles (°). Standard deviations in parentheses.

addition, an isotropic extinction parameter was refined as the effect of extinction turned out to be important. The weights used were $w=XY$ with $X=1$ for $\sin \theta > 0.50$, else $X=\sin \theta / 0.50$, $Y=1$ for $|F_o| < 4$, else $Y=4/|F_o|$. The final $R=0.087$ and $R_w=[\sum w(F_o - F_c)^2 / \sum w F_c^2]^{1/2} = 0.099$. Lists of observed and calculated structure factors and anisotropic temperature factors may be obtained from the authors on request. The final positional parameters and U_{eq} or U_{iso} values are given in Table 2.

Scattering factors for the H atoms are taken from Ref. 9, those used for the other atoms are taken from ref. 10. All calculations have been performed at the CYBER 171 MP at the

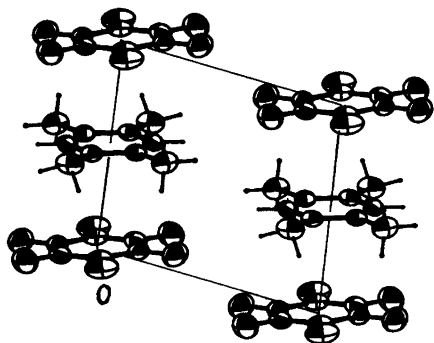


Fig. 2. The packing of the molecules viewed perpendicular to (001).

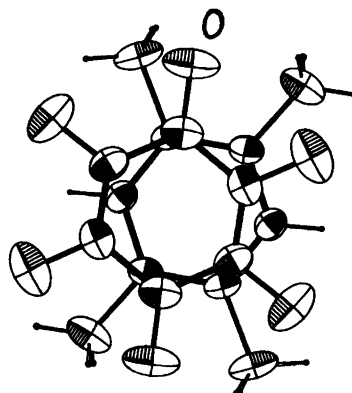


Fig. 3. The overlap of the molecules, viewed perpendicular to the average molecular plane.

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.¹¹

DISCUSSION OF THE STRUCTURE OF THE DURENE-FLUORANIL COMPLEX

The relatively high *R*-value is probably a result of various crystallographic peculiarities occurring in this class of complexes, some of which have been described earlier in this article. No bond distances and angles (Fig. 1), apart from those involving H atoms, deviate significantly from those observed in the pure components.^{12,13} and no atoms apart from methyl H atoms deviate significantly from least squares planes through the molecules.

The molecular packing is shown in Fig. 2. The partner molecules are stacked alternately in infinite columns. The angles between the stack axis and the plane normals of the molecular planes are $6.0(3)^\circ$ for durene and $8.4(2)^\circ$ for fluoranil. The angle between the molecular planes is $2.4(3)^\circ$. The mean interplanar distance is $3.383(3)$ Å, which is 0.13 Å shorter than that observed in the corresponding hexafluorobenzene complex and indicates that the present complex is considerably stronger. The shortest distance between non-hydrogen atoms of adjacent molecules in the stack, $3.378(9)$ Å, is between C atoms of the benzene rings. No distances between such molecules involving H atoms are within the van der Waals distance. No intermolecular distances between different stacks are within the van der Waals distance.

The overlap of the molecules is shown in Fig. 3. The molecular centres are situated more directly over each other than in the durene-hexafluorobenzene complex. The rings are twisted 27° relative to each other. In the room-temperature form of the hexafluorobenzene complex the rings are twisted 19° , whereas they are more parallel in the low-temperature form. In complexes between π -donors and hexafluorobenzene an increased strength of the complex seems to favour a parallel orientation of the rings. From the present work it is concluded that this pattern is not observed when the class of complexes is extended to include fluoranil complexes.

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