Crystal Structure of the Disordered, Trigonal Form of the 1:1 Complex between Hexamethylbenzene and Fluoranil at 23 and −50 °C

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The title compound crystallizes at temperatures above −100 °C in the space group $R\bar{3}m$. The hexagonal axes are, at 23 °C, a = 14.584(2), c = 6.710(5) Å and, at −50 °C, a = 14.525(6), c = 6.634(3) Å. The structure is disordered at both temperatures and was determined by X-ray methods using constrained refinement. Different models were used for the disorder. The best results were obtained with a model where the fluoranil molecule has the same three equivalent major orientations and the same three equivalent minor orientations at both temperatures. The occupancy factors for the major orientations are largest in the low temperature structure. The final R for the room-temperature structure is 0.050 for 159 observed reflections and for the low-temperature structure 0.053 for 211 observed reflections. At both temperatures the molecules are stacked alternately in infinite columns with an interplanar distance of $c/2$. The molecules overlap with the ring centres directly superposed and the ring of the fluoranil molecule in the major orientations twisted 30° relative to that of the hexamethylbenzene molecule.

Many molecular complexes of hexafluorobenzene crystallize at room temperature in the trigonal space group $R\bar{3}m$, or possibly a closely related one.[1] The structures of two of these, the complexes of hexafluorobenzene with deuteriobenzene and hexamethylbenzene, have been published and are both highly disordered.[2,3] For the complex with hexamethylbenzene, the ordered, triclinic low-temperature structure has also been published.[4]

Preliminary investigations show that also some complexes of fluoranil crystallize in this, or a closely related, space group. Among these complexes is that with hexamethylbenzene, which is of interest as part of a systematic comparison of complexes of hexafluorobenzene and fluoranil with the same partner molecules. Although the structure was expected to be highly disordered, it was considered possible to refine it using the Oxford CRYSTALS package,[5] which is well suited for constrained refinement of disordered structures.

The crystals of this complex undergo no phase transition when cooled to −100 °C, but the quality is markedly reduced below −50 °C. Below −100 °C the crystals are completely destroyed. In order to study the temperature dependence of the disorder, data were taken both at room temperature and at −50 °C.

Experimental

Red, needle-shaped crystals of the title compound were formed by evaporation of a solution of the two components in acetone. Although they were kept in sealed glass capillaries the crystals broke down after approximately one month. For the cell parameter and X-ray intensity measurements an Enraf–Nonius diffractometer and cooling device were used. Crystal and experimental data are given in Table 1.

Several space groups are possible from the systematic absences. All these require disorder with at least three orientations of the fluoranil molcule. This is sufficient even for the most symmetrical one, $R\bar{3}m$, which was assumed to be the correct space group. This, and the assumption that the the molecules occupy the centres of symmetry (0,0,0) and (0,0,1/2), was confirmed in the refinement.

From a Patterson map and by trial and error it was found that the non-H part of the hexamethylbenzene molecule has one single orientation with the C–CH_3 bonds along the twofold axes [1 0 0], [1 1 0] and [0 1 0], and that orientational disorder with six orientations had to be introduced for the fluoranil molecule, twice the minimum number necessary from the space group symmetry. Two models for this disorder are possible. In model A (Fig. 1) the three equivalent orientations with the C=O bonds along [2 1 0], [1 2 0] and [1−1 0] are not equivalent to those with the C=O bonds along [1 0 0], [1 1 0] and [0 1 0]. In model B all six general orientations in the plane (0 0 1) are equivalent.

Constrained refinements based on each of these models were performed both for the room-temperature structure and for the low-temperature structure. Because of the

Table 1. Crystal and experimental data for hexamethylbenzene–fluoranil.[a]

Temperature/°C	23	−50
Crystal size along *a, b, c*/mm	0.2×0.2×0.6	0.1×0.3×0.5
No. of reflections for cell dimensions	25	20
a/Å	14.584(2)	14.525(6)
c/Å	6.710(5)	6.634(3)
V/Å^3	1236.0(9)	1212.1(11)
D/g cm^{-3}	1.380	1.407
D_m (flotation)/g cm^{-3}	1.36	
μ (Mo K_α) (cm^{-1})	1.30	1.32
Min. scan speed in ω/° min^{-1}	0.3	1.2
Max. scan speed in ω/° min^{-1}	1.0	2.9
No. of observed reflections [$I>1.5\sigma(I)$]	159	212
Intensity loss in data collection (%)	5	0
Max. sinθ/λ for observed reflections	0.594	0.680

[a]At both temperatures: formula unit $C_{12}H_{18}{\cdot}C_6F_4O_2$, M_r = 342.33, space group $R\bar{3}m$ (No. 166), hexagonal axes are given, Z = 3, radiation Mo K_α, λ = 0.71069 Å, scan mode ω/2θ, no absorption corrections.

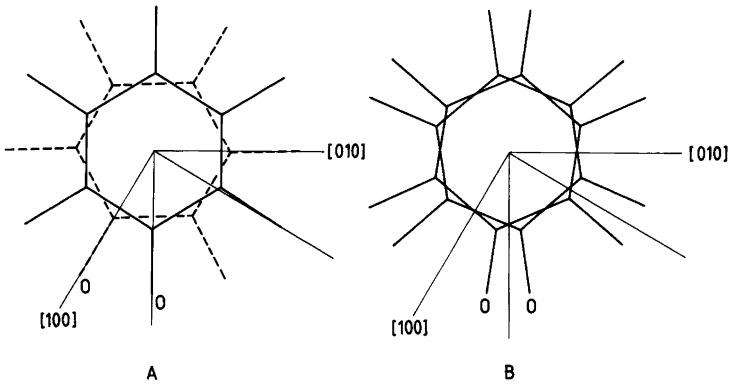

Fig. 1. The two possible models for the disorder of the fluoranil molecule. For each model only two of the six orientations of the molecule are shown.

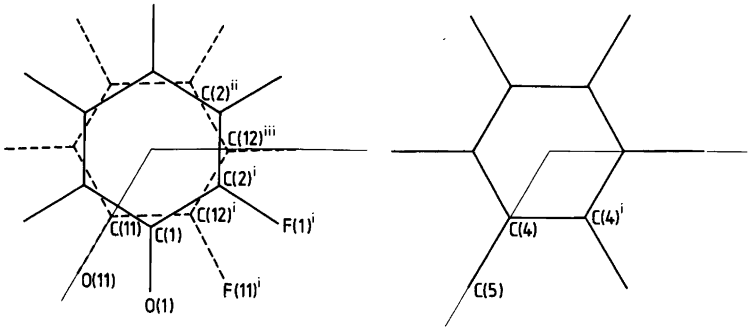

Fig. 2. Atom-labelling scheme. Symmetry code: (i): *x*−*y*,*x*,*z*; (ii): *y*−*x*,*y*,*z*; (iii): *y*,*x*,*z*.

pseudo-symmetry of the fluoranil molecule, atoms from 3 different orientations of this molecule occupy approximately the same positions. For these approximately overlapping atoms the thermal parameters were constrained to be exactly equal. All further constraints, which also refer to the fluoranil molecule, were not absolute, but were treated as extra observations and added to the structure factors in the least-squares refinement.[6] They were given standard deviations of 0.01 Å for bond distances, 1.0° for bond angles and 0.01 Å^2 for U-values. For both models the bond angles were constrained to be as in the pure compound,[7] and the bond distances at 23 and −50 °C to be 2.0 and 1.5 %, respectively, shorter than those of the pure compound, in order to compensate the effect of the librational motion. For the atoms O(1) and O(11) and for C(1) and C(11) the U_{33}-values were constrained to be equal. For each of these pairs of atoms, the thermal vibrations along their interatomic vectors were also constrained to be equal.

As there were no indications of disorder due to tilting of the molecular planes, the *z*-coordinates for all non-H atoms were kept constant in the refinement. All parameters of the H atoms were kept constant. Their positions were calculated assuming C–H distances of 1.0 Å and disorder due to rotation about the C–CH_3 bond. They were given isotropic *U*-values of 0.14 Å^2 for the room-temperature structure and 0.09 Å^2 for the low-temperature structure.

The number of parameters refined and the number of constraints was 40 and 16, respectively, for model A, and 35 and 11 for model B. The degrees of freedom were thus the same for both models. It was difficult to find a weighting scheme which gave approximately the same value for $w\Delta F^2$ for different categories of reflections. The best results were obtained when $w = \sin^2\theta/\lambda^2$ was used. One reflection of the low-temperature data (−2 2 2) was found to have large systematic errors and was left out in the refinement.

For the room-temperature structure the final $R = 0.0498$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF^2]^{1/2} = 0.0513$ for model A, $R = 0.0537$ and $R_w = 0.0556$ for model B. For the low-temperature structure $R = 0.0528$ and $R_w = 0.0612$ for model A, $R = 0.0543$ and $R_w = 0.0628$ for model B. From these results and arguments given in the discussion it was concluded that model A is more correct than B at both temperatures. Only the results obtained using model A are therefore presented here. The maximum electron densities in the final difference maps were 0.16 and 0.15 e Å^{-3} for the room-temperature and the low-temperature structure, respectively.

Lists of observed and calculated structure factors, anisotropic temperature factors for the non-H atoms and calculated positional parameters for the H atoms may be obtained from the author on request. The final positional parameters and U_{eq}-values for the non-H atoms are given in Table 2. Bond distances, uncorrected and corrected for librational motion,[8] bond angles, and distances and angles to which they were constrained are given in Table 3. The molecular packing is shown in Fig. 3.

Scattering factors were taken from Ref. 9. All calculations were performed on a Vax 8600 computer at the University of Tromsø. The computer programs used are included in the Oxford CRYSTALS package.

Table 2. Positional parameters and equivalent isotropic temperature factors (Å^2). Standard deviations are in parentheses. Occupancy factors at 23 °C are 0.235(5) for O(1)–C(2) and 0.099(5) for O(11)–C(12), at −50 °C 0.298(4) for O(1)–C(2) and 0.036(4) for O(11)–C(12).

Atom	*x*	*y*	*z*	B_{eq}[a]
23 °C				
O(1)	0.2061(18)	0.1030(9)	0	0.180(5)
F(1)	0.2136(9)	0.1065(18)	0	0.180(5)
C(1)	0.1117(17)	0.0558(8)	0	0.093(4)
C(2)	0.1107(9)	0.0587(10)	0	0.093(4)
O(11)	0.1784(16)	0	0	0.204(7)
F(11)	0.1832(16)	−0.0008(18)	0	0.204(7)
C(11)	0.0969(15)	0	0	0.116(11)
C(12)	0.0969(12)	0.0036(7)	0	0.116(11)
C(4)	0.0953(3)	0	0.5	0.074(1)
C(5)	0.1986(3)	0	0.5	0.126(2)
−50 °C				
O(1)	0.2079(19)	0.1040(9)	0	0.116(3)
F(1)	0.2161(8)	0.1079(18)	0	0.116(3)
C(1)	0.1124(17)	0.0562(9)	0	0.063(1)
C(2)	0.1118(9)	0.0593(10)	0	0.063(1)
O(11)	0.1801(16)	0	0	0.139(14)
F(11)	0.1855(16)	−0.0007(19)	0	0.139(14)
C(11)	0.0977(15)	0	0	0.056(9)
C(12)	0.0982(12)	0.0037(7)	0	0.056(9)
C(4)	0.0960(2)	0	0.5	0.042(1)
C(5)	0.2000(3)	0	0.5	0.073(1)

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij}\, a^*_i\, a^*_j\, a_i\, a_j\, \cos\alpha_{ij}$

Table 3. Bond distances (Å), uncorrected and corrected for librational motion, and bond angles(°). Standard deviations are in parentheses.

	23 °C		−50 °C		Constrained to[a]
	Uncorrected	Corrected	Uncorrected	Corrected	
O(1)–C(1)	1.192(9)	1.219	1.201(9)	1.219	1.215
O(11)–C(11)	1.189(9)	1.211	1.196(10)	1.213	1.215
F(1)^i–C(2)^i	1.301(7)	1.330	1.313(7)	1.333	1.323
F(11)^i–C(12)^i	1.291(9)	1.315	1.301(10)	1.319	1.323
C(1)–C(2)^i	1.447(8)	1.480	1.454(7)	1.476	1.475
C(11)–C(12)^i	1.440(9)	1.466	1.450(9)	1.471	1.475
C(2)^i–C(2)^{ii}	1.312(9)	1.342	1.319(9)	1.339	1.339
C(12)^i–C(12)^{iii}	1.309(9)	1.334	1.318(10)	1.337	1.339
C(4)–C(5)	1.506(6)	1.522	1.510(6)	1.521	
C(4)–C(4)^i	1.390(4)	1.406	1.395(3)	1.404	
O(1)–C(1)–C(2)^i	121.4(9)		121.3(9)		121.55
O(11)–C(11)–C(12)^i	121.8(1.0)		121.6(1.0)		121.55
F(1)^i–C(2)^i–C(2)^{ii}	122.4(1.0)		122.3(1.0)		122.4
F(11)^i–C(12)^i–C(12)^{iii}	122.5(1.0)		122.4(1.0)		122.4

[a] Uncorrected distances are constrained to be 2.0 % shorter at 23 °C and 1.5 % shorter at −50 °C than those given here.

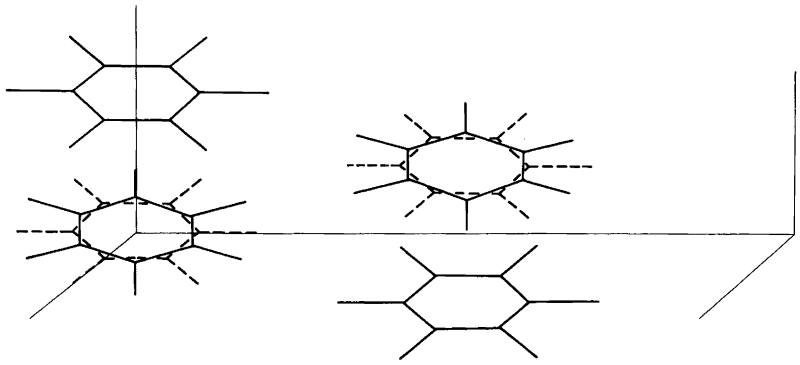

Fig. 3. The molecular packing. The average of the three major orientations of the fluoranil molecule is shown with full lines, the average of the three minor orientations with broken lines.

Discussion

For several hexafluorobenzene complexes there have been problems similar to those described here in finding the best model for the disorder. For the monoclinic forms of the complexes with durene[10] and *N,N*,3,5-tetramethylaniline[11] models similar to B with two equivalent, general orientations of the hexafluorobenzene molecule gave the lowest *R*-values. These models also gave considerably lower maximum values for the anisotropic thermal vibrations of the F-atoms than the alternative models with two non-equivalent orientations. For the present structure the corresponding maximum values were considerably lower at both temperatures when model A was used. For the trigonal form of the hexamethylbenzene–hexafluorobenzene complex it has been concluded earlier that a model corresponding to A gives the best results.[3] Rerefinement of this structure using the CRYSTALS package showed, however, that it is impossible to decide which is the best model from the old film data.

If B were the correct model for the disorder, the effect of cooling would be a rotation of the fluoranil molecule, leading to a decrease in the angle between two neighbouring orientations from 17(2)° at 23 °C to 7(2)° at −50 °C. With model A the orientations are not altered, but the sum of the occupancy factors for the three major orientations increase from 0.704(15) at 23 °C to 0.893(12) at −50 °C. The result obtained with model A seems thermodynamically more reasonable. If the angle between two orientations in model B were 0 and if the sum of the occupancy factors for the major orientations in model A were 1, the two models would be identical. The models are thus not very different at −50 °C, which is reflected by the small difference in the *R*-values at this temperature.

All U_{33}-values seem reasonable and indicate no additional disorder due to tilting of the molecular planes, which was observed in the trigonal form of the corresponding hexafluorobenzene complex. The interplanar distance is thus *c*/2. This distance both at 23 and −50 °C, 3.355(3) and 3.317(1) Å, respectively, is considerably smaller than in the low-temperature form of the corresponding hexafluorobenzene complex. In the fluoranil complex with durene the interplanar distance is 3.383(3) Å.[12] This indicates that an increasing number of methyl groups in methylated benzenes has the effect of shortening the interplanar distance in complexes with fluoranil. The same trend has been found for complexes with hexafluorobenzene.[1]

The shortest distance in the stack from atoms of the major orientations of fluoranil to non-H atoms of hexamethylbenzene, from C(2) to C(4), is 3.422(3) Å at 23 °C and 3.385(1) Å at −50 °C. None of the distances between different stacks are shorter than the van der Waals distances.

The molecules overlap with the ring centres directly superposed and with the ring of the fluoranil molecule in the major orientations twisted 30° relative to that of the hexamethylbenzene molecule. When the overlapping molecules in the hexamethylbenzene–hexafluorobenzene complex are viewed perpendicular to the molecular planes, a considerable displacement of the ring centres is observed and the rings are nearly parallel. Similar differences in the molecular overlap have been observed for the complexes of durene with fluoranil and hexafluorobenzene. Fluoranil and hexafluorobenzene have approximately the same molecular shape. The differences in molecular overlap are therefore probably not the result of steric effects, but indicate differences in the nature of the intermolecular interactions, and may possibly be connected with the fact that fluoranil is a much stronger electron donor than hexafluorobenzene.

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