

## Crystal Structure of the 1:1 Addition Compound Between Durene and Hexafluorobenzene

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The 1:1 addition compound between durene and hexafluorobenzene crystallizes at +20 °C in the monoclinic space group  $C2/m$  with cell parameters  $a = 9.478 \text{ \AA}$ ,  $b = 15.771 \text{ \AA}$ ,  $c = 7.232 \text{ \AA}$ ,  $\beta = 133.46^\circ$ . The structure is disordered. The partner molecules are stacked alternately in infinite columns and the mean separation between the molecular planes is 3.51 Å. The benzene rings of the partner molecules are twisted 19° relative to each other. At lower temperatures the crystals are triclinic. Analysis of poor intensity data taken at -100 °C shows that the benzene rings of the partner molecules are nearly parallel at this temperature.

The crystal structures of the 1:1 addition compounds of hexafluorobenzene (HFB) with *p*-xylene<sup>1</sup> and mesitylene<sup>2</sup> are quite different from that of its addition compound with hexamethylbenzene.<sup>3,4</sup>

While the two former structures indicate little or no contribution of charge-transfer forces, the latter shows similarity to structures of charge-transfer complexes. To obtain more information about how the number of methyl groups in compounds of this kind affect their structure, the crystal structure of the 1:1 compound between durene and HFB was investigated.

### DESCRIPTION OF THE CRYSTALS. CRYSTAL DATA

At +20 °C the crystals are monoclinic and the following cell parameters were found:  $a = 9.478 \pm 0.004 \text{ \AA}$ ,  $b = 15.771 \pm 0.003 \text{ \AA}$ ,  $c = 7.232 \pm 0.003 \text{ \AA}$ ,  $\beta = 133.36 \pm 0.03^\circ$ . This face-centered cell was chosen in order to have an axis ( $c$ ) in the direction along which the crystals are elongated. Another face-centered cell with

a  $\beta$ -angle of 130.63° in which this direction is along [101] could have been chosen. Assuming two molecules of each kind in the cell the calculated density is 1.36 g/cm<sup>3</sup>.

Of the reflections  $hkl$  those with  $h + k = 2n + 1$  are absent, and as both the molecules may have centres of symmetry, the space group was assumed to be  $C2/m$ .

When the crystals are cooled to -50 °C twins of a triclinic modification are obtained. The twin plane corresponds to (010) in the monoclinic form. No exact determination of the transition point has been made. NMR measurements<sup>5</sup> show a rapid decrease in the proton second moment when the temperature is increased above 250 K indicating that the transition may occur at this temperature. Cell parameters of the triclinic modification have not been determined, but the diagrams indicate no doubling of any axes and only moderate changes of the cell parameters relative to those of the monoclinic cell.

### EXPERIMENTAL

The crystals were obtained by evaporating the solvent from an ether solution of the two components at -25 °C. They are unstable on exposure to the atmosphere and were kept in sealed glass capillaries.

The cell parameters and the intensities for the monoclinic form were measured at the University of Bergen on a paper-tape controlled Siemens AED diffractometer using  $MoK\alpha$  radiation. Six reflections were used for the least squares refinement of the cell parameters. The intensity data were collected using a five-value scan technique.<sup>6</sup> 311 reflections whose intensities were more than two times the standard deviations were regarded as observed. The in-

tensities of two standard reflections which were measured at intervals of 50 reflections were approximately constant during the first 70 % of the data collection time, but decreased to less than half of their original values during the rest of the time. The crystals are thus not very stable even in sealed capillaries when exposed to the X-ray beam.

The computer program used for the data reduction has been written at the Weizmann Institute of Science, Rehovoth, and has been modified for Univac 1110 by L. M. Milje and K. Åse. The diffractometer programs have been written by K. Maartmann-Moe. All the other programs used in this work are described in Ref. 7. The atomic form factors are given in Ref. 8. The weight factors used in the least squares refinement are  $(I_t - I_b)^2 / [I_t + I_b + k^2(I_t - I_b)]$  where  $k$ , which is the standard deviation in the scaling curve, was estimated to be 0.015. The dimensions of the crystal were approximately  $0.1 \times 0.2 \times 0.3 \text{ mm}^3$  and absorption corrections were found to be unimportant and not performed. The effect of secondary extinction seems to be small and was not corrected for.

For the low-temperature diagrams an ENRAF-NONIUS  $\text{N}_2$  gas-flow cooling device was used. A considerable number of crystals were destroyed or moved in the capillary before any diagram could be obtained, and data for a complete structure determination was therefore not taken. A zero-layer Weissenberg diagram was eventually obtained, taken at  $-100^\circ \text{C}$  with  $30^\circ$  rotation about the direction corresponding to the  $c$ -axis of the monoclinic cell. Using reflections from both individuals of the twin crystal, a rough visual intensity estimation of 29 observed reflections was made. Six low-angle unobserved reflections were also included in the data.

### STRUCTURE DETERMINATION OF THE MONOCLINIC FORM

None of the possible ordered structures were found to be correct and disorder had to be introduced. An attempt was made to refine a

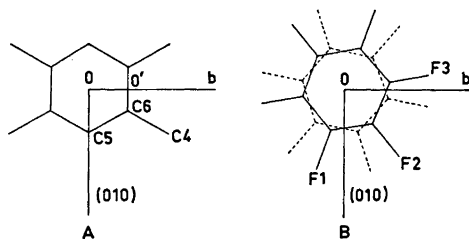


Fig. 1. The orientation of the molecules in the monoclinic form.

structure based on a model in which the durene molecule has the orientation shown in Fig. 1A and the HFB molecule has two non-equivalent orientations, each with one of its mirror planes in (010). As the  $R$ -value obtained was not below 10 % and the thermal vibration parameters were unreasonably large, this model was assumed to be incorrect.

Satisfactory results were obtained using a model with the durene molecule oriented as in Fig. 1A, and with the HFB molecule in the two equivalent orientations indicated in Fig. 1B.

During the least squares refinement the following restrictions were put on the geometry of the molecules:

Durene:  $\angle \text{OC}_6\text{C}_4 = 180^\circ$ ,  $\text{C}_4 - \text{C}_6 / \text{C}_6 - \text{O} = 1.52/1.40$ ,<sup>9</sup>  $\text{C}5 - \text{O} / \text{C}6 - \text{O}' = 2$  HBF (for all C-F bonds):  $\angle \text{OCF} = 180^\circ$ ,  $\text{F} - \text{C} / \text{C} - \text{O} = 1.326/1.394$ .<sup>10</sup>

In the last refinement cycles all positional and thermal parameters were varied, giving 65 independent parameters. H-atoms with positions calculated assuming disorder due to rotation of the methyl groups were included in the structure factor calculations. A conventional  $R$ -value of 7.9 % was obtained ( $R_w = 6.8 \%$ ).

Observed and calculated structure factors are given in Table 1, positional and thermal parameters in Table 2, bond distances and angles and intermolecular distances in Table 3 and principal axes of the vibration ellipsoids in Table 4. Sections through a three-dimensional Fourier map along the molecular planes are shown in Fig. 3 and the packing of the molecules is shown in Fig. 4.

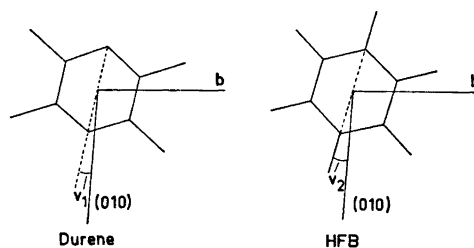


Fig. 2. The orientation of the molecules in the triclinic form.



Table 2. Coordinates and anisotropic thermal parameters according to the expression:  $\exp - (B_{11}k^2 + B_{22}l^2 + B_{33}m^2 + B_{12}kl + B_{13}lm + B_{23}kl)$ , with estimated standard deviations in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
F 1	0.3578(29)	-0.0562(17)	0.7189(43)	0.067(5)	0.0323(33)	0.122(6)	0.031(5)	0.138(10)	0.018(7)
F 2	0.2826(31)	-0.1063(21)	0.6986(44)	0.074(7)	0.0260(22)	0.123(8)	-0.021(6)	0.134(15)	-0.014(7)
F 3	-0.0751(24)	0.1637(5)	0.5365(50)	0.138(12)	0.0117(4)	0.142(13)	0.038(4)	0.177(29)	0.023(6)
C 1	0.1834(15)	-0.0288(9)	0.6122(22)	0.086(8)	0.0175(32)	0.101(12)	0.026(9)	0.166(20)	0.021(9)
C 2	0.1448(16)	0.0544(11)	0.6018(22)	0.016(6)	0.0165(14)	0.063(10)	-0.010(4)	0.039(12)	-0.006(6)
C 3	-0.0386(12)	0.0839(2)	0.5187(26)	0.020(8)	0.0128(12)	0.067(7)	0.003(3)	0.052(14)	0.006(7)
C 4	0.2039(6)	0.1570(4)	0.1399(8)	0.145(4)	0.0148(6)	0.153(5)	-0.053(2)	0.222(8)	-0.027(2)
C 5	0.1955(6)	0	0.1342(7)	0.051(3)	0.0124(5)	0.070(4)	0	0.089(6)	0
C 6	0.0978(3)	0.0753(2)	0.0671(4)	0.066(2)	0.0087(3)	0.073(3)	-0.013(1)	0.108(5)	-0.007(2)

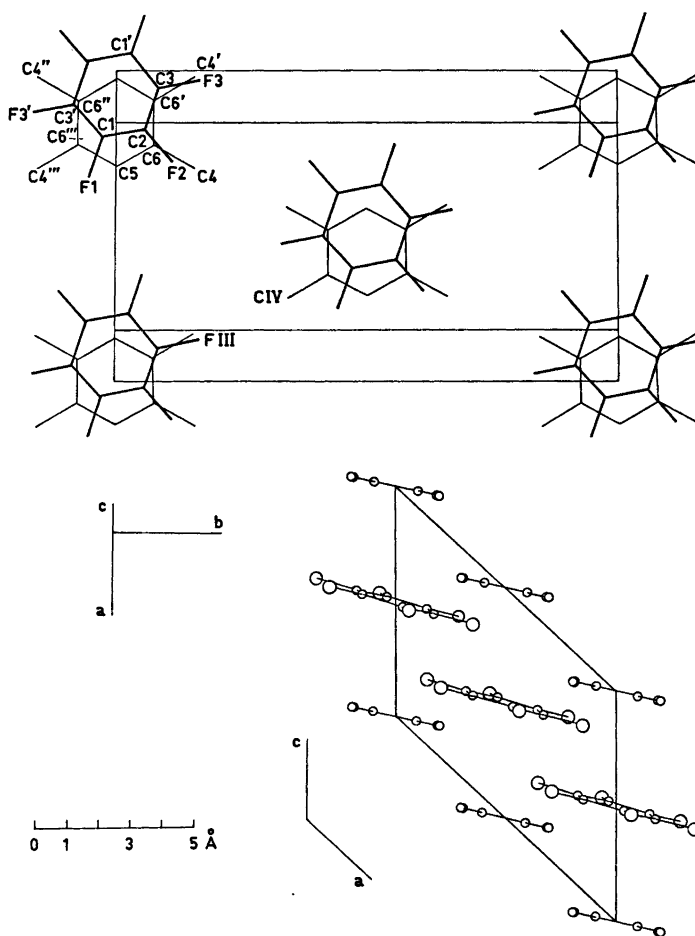


Fig. 4. The packing of the molecules viewed perpendicular to the plane of the durene molecule and perpendicular to (010). Only one of the equivalent orientations of the HFB-molecule is shown.

#### THE ORIENTATION OF THE MOLECULES IN THE TRICLINIC FORM

The space group of the triclinic crystals was assumed to be  $P\bar{1}$ . The axes are denominated as the corresponding axes of the monoclinic cell.

The experimental data obtained for this modification permit only determination of approximate orientations of the molecules projected along [001]. This was done by calculating a series of  $R$ -values for structures which were varied systematically by rotation of the molecules independently about their plane normal. Near the minimum value the rotations were made in steps of  $3^\circ$ . For each orientation

the coordinates were calculated using a value of  $86.3^\circ$  for  $\alpha^*$  (measured on the diagrams) and assuming the values of  $a^*$  and  $b^*$  to increase by 1.5% compared with those of the monoclinic cell. The angle between the  $c$ -axis and the molecular plane was assumed to be as in the monoclinic form for both molecules. Isotropic  $B$ -values,  $8 \text{ \AA}^2$  for the F-atoms and the methyl C-atoms and  $4 \text{ \AA}^2$  for the ring C-atoms, were used.

The lowest  $R$ -value, 20.9%, in which both observed and unobserved reflections are included, was obtained for the orientations shown in Fig. 2, the values of  $v_1$  and  $v_2$  being  $9^\circ$  and  $12^\circ$ , respectively. These orientations are be-

Table 3. Bond distances (Å) and angles (°) and intermolecular distances (Å). Values in parentheses are approximate standard deviations.

Distances in HFB (0.01–0.02)		Distances in durene (0.004)	
C3'–C1	1.35	C5–C6	1.373
C1–C2	1.35	C6–C6'	1.379
C2–C3	1.38	C4–C6	1.490
C1–F1	1.33		
C2–F2	1.27	Angles in durene (0.3)	
C3–F3	1.29	C6'''–C5–C6	119.7
		C5–C6–C6'	120.2
Angles in HFB (1.5)		C4–C6–C5	119.7
C3'–C1–C2	117.1	C4–C6–C6'	120.2
C1–C2–C3	122.4	Intermolecular distances (0.03)	
C2–C3–C1'	120.2	F1–C5	3.48
F1–C1–C3'	120.9	F1–C6'''	3.52
F1–C1–C2	122.0	F3'–C4''	3.62
F2–C2–C1	117.4	F3–C4'	3.64
F2–C2–C3	120.1	F2–C4	3.66
F3–C3–C2	121.8	C3'–C6''	3.48
F3–C3–C1'	117.9	C1–C6'''	3.51
		FIII–CIV	3.33

lieved to be correct within a few degrees. The benzene rings of the molecules are thus twisted  $\sim 3^\circ$  relative to each other about their plane normals.

## DISCUSSION

Where nothing else is stated the discussion refers to the structure of the monoclinic form.

Rigid body analysis of the thermal vibrations show the largest r.m.s. angle of libration to be  $11.8^\circ$  for both molecules, which is a slightly higher value than those found for the other addition compounds in this series. The largest axis of libration is nearly parallel to the *c*-axis for both molecules. No correction of the interatomic distances for this effect has been performed.

A distance of 3.33 Å is observed between an F-atom and a methyl C-atom belonging to different stacks. This distance is only 0.09 Å longer than the remarkably short contact of the same kind observed in the addition compound between HFB and mesitylene.<sup>2</sup> The corresponding angle C(ring)–C(methyl)⋯F is  $158.0^\circ$ .

Table 4. Principal axes of the thermal vibration ellipsoids.

	R.m.s. amplitudes Å	Components of the r.m.s. amplitudes (Å)		
		<i>U</i> ( <i>x</i> )	<i>U</i> ( <i>y</i> )	<i>U</i> ( <i>z</i> )
F 1	0.660	0.268	0.629	0.134
	0.405	0.379	–0.062	0.551
	0.325	0.300	–0.085	–0.019
F 2	0.590	0.256	–0.558	0.132
	0.410	0.264	0.035	0.542
	0.396	0.450	0.124	0.124
F 3	0.655	0.730	0.231	0.194
	0.447	0.244	0.118	0.561
	0.315	0.188	–0.283	0.153
C 1	0.534	0.496	0.395	0.350
	0.379	0.379	–0.253	0.326
	0.232	0.044	–0.024	–0.198
C 2	0.460	0.093	–0.455	0.045
	0.333	0.081	–0.005	0.383
	0.180	0.241	0.027	0.135
C 3	0.406	0.054	0.397	0.111
	0.320	0.135	–0.065	0.390
	0.204	0.266	–0.007	0.118
C 4	0.674	0.763	–0.339	0.345
	0.419	0.217	0.053	0.534
	0.307	0.181	0.262	0.034
C 5	0.395	0	0.395	0
	0.351	0.480	0	0.287
	0.291	0.049	0	0.323
C 6	0.424	0.507	–0.198	0.275
	0.303	0.208	0.252	0.220
	0.270	0.009	–0.083	0.263

Because of the restrictions put on the geometry of the durene molecule, all of its C-atoms are in the same plane. No atoms of the HFB molecule deviate significantly from the least squares plane through this molecule, the largest deviation being 0.038 Å. The angle between the *c*-axis and the plane normal, “the stacking angle”, is  $12.8^\circ$  for the durene molecule and  $15.4^\circ$  for the HFB molecule, and the angle between the molecular planes is  $3.6^\circ$ .

The mean distance between the molecular planes is 3.51 Å. The corresponding distances in the addition compounds of HFB with *p*-xylene,<sup>1</sup> mesitylene,<sup>2</sup> and hexamethylbenzene (triclinic form)<sup>4</sup> are 3.55 Å, 3.56 Å, and 3.43 Å, respectively. The standard deviations in these values are 0.005–0.01 Å. It seems reasonable to believe that the distance in the disordered trigonal form of the hexamethylbenzene-compound is shorter than 3.51 Å when the HFB molecule has its most probable orientation, although this distance has not been calculated exactly.<sup>3</sup> It

may therefore be concluded that the distance between the molecular planes in the durene-compound is shorter than in the *p*-xylene-compound and the mesitylene-compound, but longer than in both modifications of the hexamethylbenzene-compound.

The calculated angles between (010) and O-F1, O-F2 and O-F3 (Fig. 1 B) are 19.0, 40.2 and 77.7°, respectively. The two equivalent orientations of the HFB molecule are thus ~22° apart, and the benzene ring of this molecule is twisted ~19° relative to that of the durene molecule about its plane normal. During the transition between the monoclinic and the triclinic modification the durene molecule and the HFB molecule are rotated in opposite directions, 9 and 7°, respectively, relative to the mirror plane and twin plane (010). This finding and the large librational amplitudes in the monoclinic modification indicate very low barriers to rotation of the molecules in the crystals. However, the possibility of a more complicated disorder of the monoclinic form than that arrived at in this work should not be disregarded.

The relative orientation of the molecules in both modifications is thus different from that in the *p*-xylene-compound and the mesitylene-compound in which the benzene rings are twisted 30° relative to each other about their plane normals.<sup>1,2</sup> The nearly parallel orientation of the benzene rings in the low-temperature form is similar to that found in the low-temperature form of the hexamethylbenzene-compound.<sup>4</sup> The disordered room-temperature structure of these two compounds differ, however, as the largest proportion of the partner molecules is parallel in the hexamethylbenzene-compound.<sup>3</sup>

This work confirms, thus, that there is a close relationship between interplanar distance, relative orientation of the molecules and number of methyl groups in these addition compounds. In compounds with more than three methyl groups increasing number of such groups favours a short interplanar distance and a parallel orientation of the benzene rings, which overlap with a C—C bond of one ring approximately above the center of the adjacent ring. These are typical features of charge-transfer complexes.<sup>11</sup> Increasing numbers of methyl groups in

aromatic hydrocarbons also increase their donor strength in charge-transfer complexes.<sup>12</sup>

The nature of the HFB-compounds with aromatic hydrocarbons have been much discussed and it has been shown that the increased interaction caused by the methyl groups may be due to other factors than charge-transfer forces.<sup>13</sup> The lack of charge-transfer bands in their spectra<sup>14,15</sup> is the most important argument against the existence of charge-transfer forces in solutions of these compounds.

However, the variations in the crystal structures are difficult to explain by considering van der Waals forces only and the direction of the variations makes it reasonable to interpret them as being due to contribution of charge-transfer forces in crystals of compounds with more than three methyl groups.

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