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Crystal Structure of the Trigonal Form of the 1:1 Complex Between Hexamethylbenzene and Hexafluorobenzene

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A 1:1 addition compound between hexamethylbenzene and hexafluorobenzene has been prepared. Above ~0°C the crystals are trigonal with space group $R\bar{3}m$. By cooling below this temperature they are transformed into a triclinic modification. The structure of the trigonal modification at ~5°C has been determined and found to be disordered. The partner molecules are stacked alternately in infinite columns with some disorder in the stacking sequence. The separation of the molecular centres within the stack is 3.56 Å, but as the hexafluorobenzene molecule shows disorder due to tilting, smaller distances between fluorine atoms and methyl carbon atoms are present. Possible interactions between methyl groups and fluorine atoms are discussed.

Aromatic hydrocarbons, known as π-electron donors in charge-transfer complexes, form addition compounds with hexafluorobenzene both in solid,[1] liquid [2] and probably gas [3] phase. As spectroscopic [4] and dipole [2] measurements do not indicate any electron transfer in these compounds, the crystal structure of the 1:1 complex between mesitylene and hexafluorobenzene was investigated in order to get information about the intermolecular forces present.[5] It was found that the interaction between methyl groups and fluorine atoms may possibly be of importance for the complex formation. In the present paper the structure of a similar complex is reported.

From a solution of hexamethylbenzene in hexafluorobenzene needle-shaped crystals of an addition compound with melting point ~131°C were formed by evaporation of the excess solvent. Like other solid complexes with hexafluorobenzene the crystals are very unstable on exposure to the atmosphere at room temperature.[6] Crystals made from ether solutions with the two components present in varying proportions all give the same X-ray diagrams as those made from the hexafluorobenzene solution. It was therefore concluded that the compound is a stoichiometric complex rather than mixed crystals.

X-Ray diagrams taken at room temperature show great thermal damping and the strong diffuse scattering which is characteristic for complexes with

hexafluorobenzene.[6] These effects are markedly reduced when the crystals are cooled below 0°C, but at these temperatures the diagrams show separated reflexions in each of the regions where a single reflexion is present in the room-temperature diagrams. This can be satisfactorily explained assuming phase transformation by cooling into a slightly different, less symmetrical form and formation of repeated twin crystals. The case is not very different from that reported by Herbstein [7] for 1,2,4,5-tetrachlorobenzene. Even crystals which were prepared at a temperature below the transition point turned out to consist of repeated twins. As a structure analysis of the low-temperature form thus seemed to be difficult, it was decided, as a first step, to investigate the structure above 0°C.

EXPERIMENTAL

The crystals used in the structure analysis were made by slowly evaporating the excess solvent from a solution of hexamethylbenzene in hexafluorobenzene at ~5°C. X-Ray diagrams showed that the crystals are rhombohedral with the hexagonal *c*-axis along the needle axis. The data given in this paper all refer to hexagonal axes. Of the two possible space groups, $R3m$ and $R\bar{3}m$, the latter was chosen because both of the partner molecules may have centres of symmetry. Cell dimensions at 5°C were determined from an oscillation diagram about the *c*-axis and a Weissenberg diagram about the *a*-axis, using KCl as calibrating substance. The values arrived at were: $a = 14.596 \pm 0.012$ Å, $c = 7.124 \pm 0.007$ Å. If the cell is assumed to contain three molecules of each kind, the calculated density is 1.32 g/cm³ which is a reasonable value.

The intensity data were collected from integrated Weissenberg-diagrams taken at 5°C, mainly about the *c*-axis. Zero and third level diagrams taken about the *a*-axis were used to calculate interlayer scale factors. To confirm the correctness of the scale factors, a diagram was taken about the *c*-axis which registered the zero and first layer simultaneously. Cu$K\alpha$-radiation was used for all the diagrams. Absorption corrections had to be performed on the data from diagrams taken about the *a*-axis, but considered unimportant and not performed on the data from the other diagrams. Of the 81 independent reflexions observed, the strong ones were measured photometrically, the weak ones visually.

STRUCTURE DETERMINATION AND REFINEMENT

If the structure is ordered, only a limited number of arrangements of the molecules are possible. The partner molecules have to occupy the centres of symmetry at (0,0,0) and (0,0,$\frac{1}{2}$). Not considering the hydrogen atoms the molecules may be assumed to be planar and situated in the planes (x,y,0) and (x,y,$\frac{1}{2}$). Two orientations are possible for each of the molecules, one with the C–F bonds or C–CH_3 bonds directed along the *a*-axis and directions equivalent to this (orientation A), the other with these bonds along the reciprocal *a*-axis and the equivalent directions (orientation B). Structure factor calculations did not give promising results for any of the four structures derived in this way. By combining two of the structure factor sets, however, a much better *R*-value was obtained, indicating that the hexamethylbenzene molecule has orientation A, while the hexafluorobenzene molecule has both of the two possible orientations. Giving orientation A for hexafluorobenzene a statistical weight of 60 %, an *R*-value of 33 % was obtained. Thermal parameters were introduced assuming the molecules to have a considerable degree

Table 1. Observed and calculated structure factors, ten times the absolute values. The columns listed are h, k, l, F_o, and F_c. Unobserved reflexions have F_o-values like $\frac{1}{2}F_{min}$ and are marked with asterisks.

3	0	0	415	- 389	3	2	1	67	- 68	1	2	2	117	- 112	5	2	3	18	- 50 *
6	0	0	59	66	6	2	1	21	2 *	4	2	2	176	- 147	0	3	3	62	43
9	0	0	154	176	1	3	1	188	192	7	2	2	21	- 23 *	3	3	3	91	- 92
12	0	0	43	39	4	3	1	193	- 181	2	3	2	209	- 192	1	4	3	15	19 *
1	1	0	1182	1189	7	3	1	25	24 *	5	3	2	201	- 193	2	5	3	18	- 48 *
4	1	0	248	223	2	4	1	209	- 187	8	3	2	46	51	0	6	3	17	- 2 *
7	1	0	188	- 200	5	4	1	91	77	0	4	2	57	45	0	9	3	44	58
10	1	0	146	175	8	4	1	55	- 43	3	4	2	299	- 280	1	10	3	46	41
2	2	0	655	- 643	0	5	1	65	61	6	4	2	22	36 *	1	0	4	329	365
5	2	0	319	- 282	3	5	1	21	- 5 *	1	5	2	16	6 *	4	0	4	12	- 28 *
8	2	0	116	111	1	6	1	70	- 84	4	5	2	75	- 56	10	0	4	38	65
3	3	0	435	- 405	4	6	1	24	15 *	2	6	2	163	- 154	2	1	4	80	75
6	3	0	86	- 94	2	7	1	52	69	0	7	2	136	- 129	5	1	4	72	- 68
9	3	0	39	33	5	7	1	78	- 78	3	7	2	68	38	0	2	4	171	184
4	4	0	371	- 339	0	8	1	80	81	1	8	2	64	53	3	2	4	77	- 62
7	4	0	64	57	1	9	1	90	96	2	9	2	100	95	6	2	4	34	- 37
5	5	0	84	94	0	11	1	74	45	0	10	2	159	168	1	3	4	12	- 14 *
1	0	1	167	- 139	2	0	2	412	424	0	0	3	48	43	4	3	4	107	- 84
4	0	1	257	271	5	0	2	152	157	3	0	3	33	29	2	4	4	95	- 81
7	0	1	21	- 48 *	8	0	2	20	- 31 *	6	0	3	17	- 13 *	0	5	4	53	- 51
10	0	1	107	96	11	0	2	83	101	9	0	3	63	57	3	5	4	59	- 52
2	1	1	27	26	0	1	2	1647	1839	1	1	3	9	9 *	1	6	4	57	- 54
5	1	1	88	- 99	3	1	2	162	- 163	4	1	3	15	12 *	1	9	4	57	60
8	1	1	97	101	6	1	2	129	- 137	10	1	3	62	43	0	1	5	46	58
0	2	1	102	- 96	9	1	2	130	150	2	2	3	12	- 3 *	0	0	6	58	54

of libration movement and especially great vibration amplitudes in the direction [001]. Without any refinement of the parameters the R-value was lowered to 19 %. As structure factors calculated at this stage turned out to be too high for reflexions having odd l-values, it was believed to be some

Table 2. Coordinates and statistical weight of the atomic positions. Estimated standard deviations in parentheses. The 12 % of the molecules displaced due to disorder in the stacking sequence are not included.

	x	y	z	Statistical weight
Cl	0.945 (.0006)	.0	.0	1
C2	.2041 (.0009)	.0	.0	1
C3	.0923 (.0017)	.0	.5	.673 (.010)
F1	.1793 (.0010)	.0	.4325 (0.029)	.337
C4	.1064 (.0114)	.0532	.5	.327
F2	.2084 (.0052)	.1042	.5	.163

Anisotropic thermal parameters according to the expression: $\exp -(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$. Estimated standard deviations in parentheses.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	.0093 (.0006)	.0122 (.0009)	.0520 (.0039)	.0122	−.0009	− 0019 (.0035)
C2	.0143 (.0009)	.0290 (.0022)	.1082 (.0094)	.0290	−0.022	−.0044 (.0068)
C3	.0213 (.0021)	.0281 (.0042)	.0652 (.0100)	.0281	.0013	.0025 (.0089)
F1	.0184 (.0010)	.0381 (.0025)	.0669 (.0100)	.0381	.0011	.0023 (.0087)
C4	.0162	.0177	.0922	.0162	.0000	.0000
F2	.0162	.0281	.1341	.0162	.0000	.0000

disorder in the stacking sequence. Placing 12 % of the hexafluorobenzene molecules around the centres of symmetry formerly occupied by hexamethylbenzene and *vice versa*, the calculated structure factors were reduced by 24 % for reflexions with odd l-values while the other structure factors remained unaltered. By this the R-value was lowered to 15.3 %. No further refinement of the degree of this disorder was performed.

In the least squares refinement only observed reflexions were included. The weight factors chosen were $A(F_o)^{-0.7}$ for reflexions with structure factors greater than $\sim 4|F_{min}|$, while a constant weight was used for the weaker reflexions. Hydrogen atoms with positions calculated assuming disorder due to rotation of the methyl groups were included in the structure factor calculations.

In the first three refinement cycles all positional parameters of the fluorine and carbon atoms, the relative weight of the two orientations of the hexafluorobenzene molecule and the scale factor were varied, the thermal parameters being kept constant. The positional parameters given in Table 2 for the hexafluorobenzene atoms in orientation B are those resulting from this refinement. As the molecule in orientation B is assumed to be planar no refinement of the z-parameters has been performed although they are not fixed by the space group symmetry. In the next three cycles the positional and thermal parameters were varied for the carbon atoms of hexamethylbenzene and for all atoms of hexafluorobenzene in orientation A. The scale factor was kept constant to avoid correlation with the thermal parameters. This refinement in which 20 parameters were varied gave an R-value of 9.7 %. Analysis of the vibration ellipsoids showed an r.m.s. amplitude of 0.681 Å for the fluorine atoms approximately in the [001]-direction, while no other r.m.s. amplitudes were greater than 0.55 Å. To see if this is due to disorder, separated half fluorine atoms were placed at equal distance above and below the plane $(x,y,\frac{1}{2})$. Starting with a separation of 0.71 Å, three refinement cycles were performed in which the z-value for a half fluorine atom was varied in addition to the parameters varied in the preceding cycles. This lowered the conventional R-value to 9.0 %, while the weighted R-value was lowered from 12.5 % to 11.3 %. As this lowering was due to one additional parameter only, the presence of fluorine positions out of the plane $(x,y,\frac{1}{2})$ might be regarded as proved. The separation arrived at between the two half fluorine atoms was 0.96 Å, the r.m.s. vibration amplitude in the [001]-direction was 0.414 Å. The correlation between z and B_{33} of the fluorine atom in this refinement was 0.418. Between z of the fluorine atom and B_{33} of the carbon atom of hexafluorobenzene the correlation was 0.666.

As the last step in the refinement two cycles were performed where the only parameters varied were the scale factor and the relative weight of the two orientations of hexafluorobenzene. This gave a conventional R-value of 8.9 % and weighted R-value of 11.1 %. The relative weight of orientation A arrived at was 67.3 %. As only the strongest reflexion indicates secondary extinction, no correction for this effect was performed.

All programs used in this work have been written or revised by crystallographers at the University of Oslo.[8] The atomic form factors used are those given by Hanson *et al.*[9]

DISCUSSION

Observed and calculated structure factors are given in Table 1, positional and thermal parameters and statistical weight factors in Table 2, and interatomic distances in Table 3. Assuming the hexafluorobenzene molecule

Table 3. Interatomic distances (Å). Estimated standard deviations in parentheses.

	Uncorrected values	Corrected values
C1 – C1′	1.38 (.01)	1.40
C1 – C2	1.60 (.02)	1.60
C3 – C3′	1.35 (.03)	1.35
C3 – F1	1.36 (.03)	1.29
C4 – C4′	1.35 (.14)	
C4 – F2	1.29 (.16)	

in orientation B to be planar and not considering the displacements of the fluorine atoms from the plane $(x,y,\frac{1}{2})$ in orientation A, all intramolecular angles are fixed by symmetry and have "normal" values. The principal axes of the vibration ellipsoids are given in Table 4. A rigid body analysis of the hexamethylbenzene molecule gave an r.m.s. value of 0.0040 Å for ΔU(i,j), which seems reasonable in view of the high U(i,j)-values. The corrected values of the interatomic distances in hexamethylbenzene in Table 3 are those resulting from this rigid body analysis. It seems reasonable to believe that the displacements of the fluorine atoms from the plane $(x,y,\frac{1}{2})$ are due to tilting of the whole molecule rather than only to bending of the bond angles.

Table 4. Principal axes of the thermal vibration ellipsoids.

	r.m.s. amplitudes Å	B-values Å²	Components of the r.m.s. amplitudes (Å) $U(x)$	$U(y)$	$U(z)$
C1	.366	10.6	.026	.052	.364
	.314	7.8	.180	.360	.038
	.261	5.4	.261	0	0
C2	.529	22.1	.066	.131	−.517
	.482	18.4	.272	.544	.103
	.276	6.0	.276	0	0
C3	.478	18.0	.274	.549	.046
	.409	13.2	.022	.045	−.407
	.393	12.2	.393	0	0
F1	.555	24.4	.320	.641	.021
	.414	13.6	.009	.018	−.414
	.309	7.5	.309	0	0
C4	.487	18.7	.0	.0	.487
	.384	11.6	0	.384	0
	.362	10.4	.418	.209	.0
F2	.587	27.2	.0	.0	.587
	.509	20.5	0	.509	0
	.362	10.4	.418	.209	0

Introduction of a similar displacement of the C3-atoms in the refinement leads to unacceptable correlations between the parameters, making further analysis of this from the data impossible. The corrected values of the interatomic distances in hexafluorobenzene in Table 3 are calculated assuming a straight line running from the centre of symmetry through C3 to the calculated position of F1.

The Fourier map (Fig. 1) and the thermal parameters indicate great thermal movement, and in agreement with NMR results for other complexes

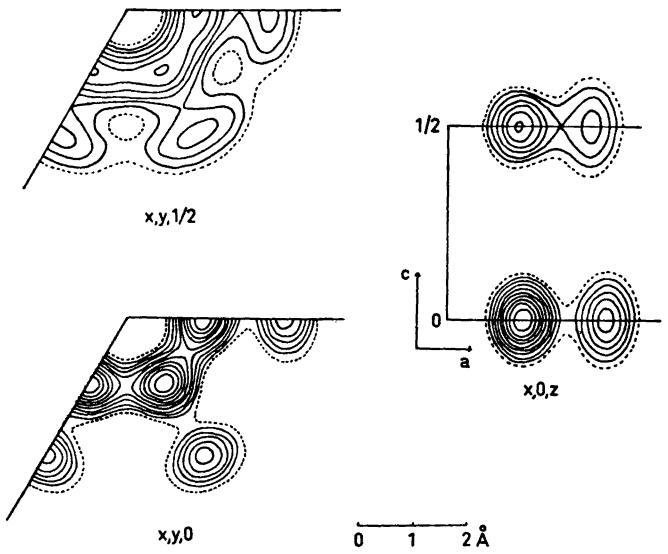

Fig. 1. Sections through a three-dimensional Fourier-map. Contour intervals of 1/4 e/Å^3 and lowest contour (broken line) at 1 e/Å^3.

with hexafluorobenzene [10] it seems reasonable to believe that reorientation occurs for the hexafluorobenzene molecule and probably also for the hexamethylbenzene molecule. Possibly more minima of energy are present in the structure than those arrived at in this work. An attempt to replace the orientations A and B of hexafluorobenzene by two equivalent orientations rotated a small angle from orientation A did not give a satisfactory R-value. A difference synthesis gave no clear indications of any extra orientations of the molecules. It seems therefore difficult to obtain a better model of the structure from the data than that obtained in this work, shown in Fig. 2.

The distance between the molecular centres within the stack is 3.56 Å, and no calculated C–C or C–F distances between different stacks are less than 3.65 Å. The only possible localized intermolecular forces present are therefore between fluorine atoms and methyl groups within the stack. The positions of C2 and F1 in Table 2 give a C–F distance of 3.08 Å and a F–H separation which must be less than normal van der Waals distance. These calculations

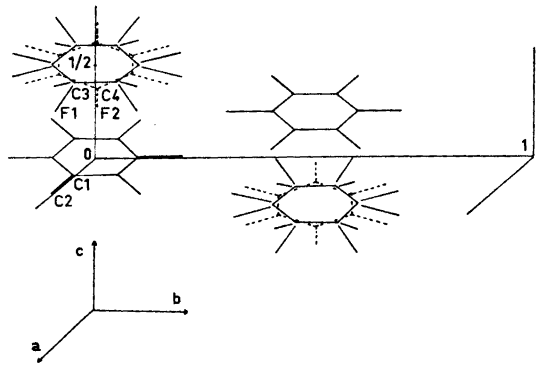

Fig. 2. A schematic representation of the structure, indicating orientation B of hexafluorobenzene with broken lines and the disorder of the fluorine positions with a double set of C – F bonds in orientation A.

are of limited value, however, because the fluorine positions must be still more disordered if the hexafluorobenzene molecule is tilted, and it may be suspected that some disorder of similar kind is present in the hexamethylbenzene molecule, too. The only conclusion which may be safely drawn is that hexafluorobenzene is tilted more than hexamethylbenzene and that the distance C2 – F1 therefore is less than the separation between the molecular centres.

It would be of interest to determine the structure of this compound also in the low-temperature form. From the results of the high-temperature analysis one may assume the phase transformation to be of the order-disorder type which seems to be characteristic for many $\pi-\pi$ complexes.[11] Some attempts have been made to find a set of reflexions in the low-temperature diagrams which corresponds to one individual in the twin crystals. The crystals have been found to be triclinic, and the work will be continued.

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