

Crystal Structure of the Triclinic Form of the 1 : 1 Complex Between Hexamethylbenzene and Hexafluorobenzene at -40°C

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The crystal structure at -40°C of the 1 : 1 addition compound between hexamethylbenzene and hexafluorobenzene in the triclinic form, stable below 0°C , has been determined. The partner molecules are stacked alternately in infinite columns. An angle of 3.6° has been found between the molecular planes, whose mean separation within the stack is 3.43 \AA . The formation of repeated twins by phase transformation from the trigonal to the triclinic form is described and the relation between the structures in these modifications is discussed. Attention is given to the relatively great differences between the structures of this complex at -40°C and that of the complex between mesitylene and hexafluorobenzene at approximately the same temperature.

The crystal structure of the 1 : 1 complex between mesitylene and hexafluorobenzene (HFB)¹ shows some features not usually found in $\pi-\pi$ complexes. The lack of traceable charge-transfer bonds in the spectra of complexes between HFB and aromatic hydrocarbons^{2,3} also indicates some difference between these complexes and ordinary $\pi-\pi$ complexes.

To obtain more information about the intermolecular forces present in this type of complexes, the 1 : 1 complex between hexamethylbenzene (HMB) and HFB has been studied.⁴ The crystals were found to be trigonal at room temperature and transformed into repeated twins of a triclinic modification when cooled below 0°C . The structure of the trigonal form is disordered and the model arrived at shows several orientations of the HFB-molecule. The structure of the triclinic modification at -40°C is presented in the present paper.

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DESCRIPTION OF THE TWINNING. CRYSTAL DATA

X-Ray diagrams taken when a crystal is cooled below 0°C show two or more reflections near the spot where a single reflection is present in the room-temperature diagrams. After heating above 0°C the same single crystal diagrams are obtained as before the cooling. The number of separated reflections is not the same each time the crystal is cooled down. The separation is very small just below 0°C, but increases when the temperature is lowered. This dependence on temperature is relatively small below $\sim -30^\circ\text{C}$. One crystal, which was kept at -80°C , was damaged after a few days. Crystals which have not been heated above 0°C give the same separated reflection as those described.

These observations are satisfactorily explained when it is assumed that phase transformation into a triclinic, pseudo-trigonal modification occurs and repeated twins are formed. The following cell parameters were found at -40°C . $a = 8.740 \pm 0.010 \text{ \AA}$, $b = 8.834 \pm 0.011 \text{ \AA}$, $c = 7.149 \pm 0.012 \text{ \AA}$, $\alpha = 110.82 \pm 0.06^\circ$, $\beta = 107.34 \pm 0.07^\circ$, $\gamma = 111.14 = 0.05^\circ$. Although the diagonal [111] is shorter (8.248 Å) than the a - and b -axes, this cell was chosen as the molecular planes turned out to be not far from parallel to (001). A cell based on the corresponding vectors $\mathbf{a}' = \frac{1}{3}\mathbf{a} + \frac{2}{3}\mathbf{b} - \frac{1}{3}\mathbf{c}$, $\mathbf{b}' = \frac{2}{3}\mathbf{a} - \frac{1}{3}\mathbf{b} - \frac{1}{3}\mathbf{c}$, $\mathbf{c}' = \mathbf{c}$ in the trigonal modification has the parameters $a' = b' = 8.755 \text{ \AA}$, $c' = 7.124 \text{ \AA}$, $\alpha' = \beta' = 105.74^\circ$, $\gamma' = 112.94^\circ$. Assuming one molecule of each kind in the cell the calculated density at -40°C is 1.39 g/cm^3 . The corresponding value found for the trigonal modification is 1.32 g/cm^3 .

Assuming the planes (100), (010), and ($\bar{1}\bar{1}0$) to be possible twin planes, all the reflections could be indexed. Following Friedel's classification the twins are of the pseudo-merohedral type.⁵ The obliquity is 2.1° , 5.2° , and 7.1° when the twin plane is ($\bar{1}\bar{1}0$), (100), and (010), respectively. Even when the temperature is lowered very slowly through the transition point, the probability for each of these planes to be twin plane seems to be approximately equal. The corresponding planes in the trigonal modification are all mirror planes. The direction of the c -axis, which is along the needle axis, seems to be unaltered relative to the outer shape of the crystal during the phase transformation.

EXPERIMENTAL

Needle-shaped crystals were obtained from an ether solution of the two components at -30°C . The crystals are unstable on exposure to the atmosphere and were kept in sealed glass capillaries.

Cu $K\alpha$ -radiation was used for all the diagrams, which were taken at -40°C after cooling the crystal slowly down from room temperature. Cell parameters were determined from Weissenberg diagrams taken about the c -axis and a direction corresponding to the a -axis in the trigonal modification. Diagrams were taken on the same films at room temperature at which accurate cell parameters were known, in order to calibrate the camera radius.

The intensity data were collected from Weissenberg diagrams taken mainly about the c -axis. One diagram taken about a direction corresponding to the a -axis in the trigonal form, and one about the c -axis which registered the zero and first layer simultaneously were taken to calculate interlayer scale factors. To avoid overlap of reflections from different individuals of the twin crystals, it was necessary to use non-integrated diagrams. All the 343 observed reflections were measured visually, and the intensities of those having important reflection spot extension were corrected for this effect.⁶ Absorption correction was considered unimportant and not performed.

STRUCTURE DETERMINATION

As both the partner molecules may have centres of symmetry, the space group $P\bar{1}$ was assumed. From a three-dimensional, sharpened Patterson synthesis the orientations of the molecules, which seemed to be approximately equal, were found. The HFB- and the HMB-molecule were placed in the centres of symmetry $(0,0,\frac{1}{2})$ and $(0,0,0)$, respectively. Structure factors based on the F- and C-atoms were calculated, giving an R -value of 28 %, and least squares refinement was started.

73 low-angle reflections, which with certainty could be classified as unobserved, were given values of $\frac{1}{4} I_{\min}$ for I_o and included in the least squares refinement. The R -values given below are calculated from the observed reflections only. The weight factors chosen were $A(F_o)^{-0.6}$ for reflections with $F_o > \sim 3 |F_{\min}|$, while a constant weight was used for the weaker observed reflections and $\frac{1}{3}$ of this weight for the unobserved reflections. Hydrogen atoms with positions calculated assuming disorder due to rotation of the methyl groups were included in the structure factor calculations.

An R -value of 12.0 % was arrived at when positional and anisotropic thermal parameters were varied for the F-atoms and the methyl C-atoms, while positional and isotropic thermal parameters were varied for the ring C-atoms. To obtain more reasonable atomic positions and to allow introduction of anisotropic thermal parameters also for the ring C-atoms without varying too many parameters independently, some restrictions were put on the geometry of the molecules in the last four refinement cycles. Straight lines were assumed to run along the C-F bonds and the C-CH₃ bonds through the centres of the molecules. The quotient between the length of each of these bonds and the distance of the corresponding ring C-atom from the centre of the molecule was kept constant, with a value of 1.326/1.394 for the HFB-molecule⁷ and 1.52/1.40 for the HMB-molecule.⁸ As anisotropic thermal parameters were varied for all the F- and C-atoms, the scale factor was kept constant to avoid correlation with these parameters. 90 parameters were varied independently in these cycles which gave a conventional R -value of 8.2 %. When the unobserved reflections also are included, the conventional R -value is 10.1 %, while the weighted R -value is 11.3 %.

Difference syntheses gave no indication neither of positions of the H-atoms nor of any disorder in the structure. Rigid body analysis of the thermal vibrations was performed but the results were not good enough to justify any correction for this effect. No effect of secondary extinction has been found.

All programs used are described in Ref. 9, and the atomic form factors are given in Ref. 10.

DISCUSSION

Observed and calculated structure factors are given in Table 1, positional and thermal parameters in Table 2, bond distances and angles in Table 3, and principal axes of the vibration ellipsoids in Table 4. Fig. 1 shows sections parallel to (001) through a three-dimensional Fourier map. The orientation

and packing of the molecules and intermolecular distances are shown in Fig. 2. Considering that corrections for librational motion have not been performed, all the bond distances and angles seem reasonable.

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 reflections have F_o -values like $\frac{1}{2}F_{\min}$ and are marked with asterisks.

0 1 0 375 390	-5 3 1 13 - 5 *	5 -3 1 26 21	1 -4 2 82 91	-4 -4 4 86 81
0 2 0 246 -242	-5 1 1 33 35 *	5 -2 1 41 46	1 -3 2 86 86	-4 -3 4 65 - 56
0 3 0 187 -205	-5 5 1 14 13 *	5 -1 1 28 19	1 -2 2 117 -115	-4 -2 4 59 -105
0 4 0 159 -164	-4 -2 1 14 17 *	5 0 1 16 - 21 *	1 -1 2 57 34	-4 -1 4 169 -111
0 5 0 51 51	-4 -1 1 59 59	6 -6 1 31 - 26	1 0 2 130 -130	-4 0 4 30 31
0 6 0 11 - 8 *	-4 0 1 11 - 16 *	6 -3 1 49 59	1 1 2 51 50	-4 1 4 11 - 17 *
0 7 0 29 - 34	-4 1 1 75 - 73	6 -2 1 30 21	1 2 2 51 39	-4 2 4 81 - 69
1 -7 0 46 - 67	-4 2 1 96 - 80	6 -1 1 36 21	1 3 2 37 - 32	-3 -6 4 66 64
1 -6 0 43 41	-4 3 1 40 - 31	-6 0 2 63 65	1 4 2 45 40	-3 -5 4 50 49
1 -5 0 11 - 7 *	-4 4 1 12 4 *	-7 2 2 120 117	2 -7 2 14 51 *	-3 -4 4 54 - 50
1 -4 0 190 -187	-4 5 1 31 28	-7 3 2 72 75	2 -6 2 13 - 3 *	-3 -3 4 34 26
1 -3 0 8 - 17 *	-4 6 1 46 56	-6 1 2 13 5 *	2 -5 2 50 - 49	-3 -2 4 9 1 *
1 -2 0 121 -128	-3 -3 1 48 55	-6 2 2 13 - 8	2 -4 2 82 80	-3 -1 4 77 - 81
1 -1 0 369 383	-3 -2 1 12 - 24 *	-6 3 2 13 - 7 *	2 -3 2 146 -146	-3 0 4 5 33 *
1 0 0 373 382	-3 -1 1 62 - 48	-6 4 2 38 36	2 -2 2 34 - 42	-3 1 4 58 - 44 *
1 1 0 139 -139	-3 0 1 17 10	-5 -2 2 53 51	2 -1 2 10 - 13 *	-3 2 4 13 6 *
1 2 0 206 211	-3 1 1 58 62	-5 -1 2 53 48	2 0 2 134 -131	-3 3 4 15 2 *
1 3 0 48 - 37	-3 1 1 18 14	-5 0 2 108 - 97	2 1 2 47 - 44	-2 -7 4 31 - 21
1 4 0 64 - 53	-3 2 1 10 - 13 *	-5 1 2 60 - 59	2 2 2 39 - 35	-2 -6 4 29 32
1 5 0 42 39	-3 3 1 44 - 48	-5 2 2 56 - 47	2 3 2 50 48	-2 -5 4 37 - 24
2 -6 0 26 33	-3 4 1 31 18	-5 3 2 101 - 97	2 4 2 60 62	-2 -4 4 61 - 61
2 -5 0 83 - 75	-2 -4 1 44 51	-5 4 2 15 - 26 *	3 -7 2 144 138	-2 -3 4 52 63
2 -4 0 68 64	-2 -3 1 35 - 38	-5 5 2 14 15 *	3 -6 2 13 24 *	-2 -2 4 39 - 49
2 -3 0 206 204	-2 -2 1 90 - 73	-5 6 2 65 61	3 -5 2 85 - 87	-2 -1 4 125 142
2 -2 0 232 -244	-2 -1 1 51 54	-5 7 2 46 42	3 -4 2 161 -181	-2 0 4 175 185
2 -1 0 136 -136	-2 0 1 51 56	-4 -4 2 136 126	3 -3 2 112 -115	-2 1 4 11 2 *
2 0 0 255 -256	-2 1 1 7 24 *	-4 -3 2 15 61 *	3 -2 2 121 120	-2 2 4 25 - 21
2 1 0 6 - 24 *	-2 2 1 87 90	-4 -2 2 78 - 68	3 -1 2 47 - 55	-2 3 4 56 - 51
2 2 0 69 75	-2 3 1 24 - 17	-4 -1 2 235 -226	3 0 2 128 -127	-1 -8 4 33 - 39
2 3 0 71 67	-2 4 1 65 - 45	-4 0 2 188 -189	3 1 2 37 - 34	-1 -7 4 16 - 29 *
2 4 0 85 76	-2 5 1 27 13	-4 1 2 180 179	3 2 2 58 58	-1 -6 4 60 58
2 5 0 65 65	-1 -2 1 73 79	-4 2 2 80 - 79	4 -8 2 54 55	-1 -5 4 112 -107
3 -7 0 54 56	-1 -1 1 6 - 3 *	-4 3 2 142 -156	4 -7 2 92 94	-1 -4 4 120 -129
3 -6 0 72 65	-1 0 1 62 - 58	-4 4 2 59 - 58	4 -6 2 14 29 *	-1 -3 4 88 - 75
3 -5 0 66 - 62	-1 1 1 63 55	-4 5 2 14 8 *	4 -5 2 14 - 7 *	-1 -2 4 82 95
3 -4 0 64 51	-1 2 1 53 - 58	-4 6 2 65 72	4 -4 2 82 - 89	-1 -1 4 359 400
3 -3 0 203 -211	-1 3 1 31 29	-3 -5 2 122 129	4 -3 2 60 - 53	-1 0 4 144 142
3 -2 0 7 - 19 *	-1 4 1 34 - 36	-3 -4 2 111 107	4 -2 2 34 - 32	-1 1 4 51 - 44
3 -1 0 213 213	0 -6 1 54 - 45	-3 -3 2 83 - 84	4 -1 2 59 - 58	-1 2 4 45 - 45
3 0 0 205 -210	0 -5 1 13 48 *	-3 -2 2 95 95	4 0 2 16 19 *	-1 3 4 51 - 44
3 1 0 201 -208	0 -4 1 11 28 *	-3 -1 2 191 -179	4 1 2 26 *	0 -4 4 51 - 60
3 2 0 93 - 83	0 -3 1 9 - 46 *	-3 0 2 50 - 51	5 -5 2 38 43	0 -7 4 22 *
3 3 0 71 65	0 -2 1 38 38	-3 1 2 35 - 34	6 -4 2 62 64	0 -6 4 14 8 *
4 -7 0 115 118	0 0 1 139 - 99	-3 2 2 126 -136	6 -3 2 95 93	0 -5 4 128 -126
4 -6 0 103 108	0 1 1 19 - 13	-3 3 2 56 52	-4 1 3 44 - 47	0 -4 4 11 - 8 *
4 -5 0 82 84	0 2 1 18 48 *	-3 4 2 14 - 15 *	-4 2 3 28 - 31	0 -3 4 22 - 18
4 -4 0 146 - 148	0 3 1 27 - 25	-3 5 2 14 - 6 *	-3 -2 3 39 - 47	0 -2 4 182 189
4 -3 0 182 -191	0 4 1 34 39	-2 -5 2 64 72	-3 0 3 29 40	0 -1 4 138 133
4 -2 0 57 67	1 -5 1 38 42	-2 -4 2 85 - 80	-3 1 3 20 19	0 0 4 35 - 34
4 -1 0 56 - 60	1 -4 1 71 - 61	-2 -3 2 64 67	-3 2 3 27 36	0 1 4 14 - 4 *
4 0 0 153 -160	1 -3 1 44 39	-2 -2 2 198 286	-2 -2 3 40 - 35	0 2 4 15 - 18 *
4 1 0 11 - 9 *	1 -2 1 34 30	-2 -1 2 188 -193	-2 -1 3 54 53	1 -7 4 45 33 *
4 2 0 33 41	1 1 1 52 - 54	-2 0 2 38 30	-2 1 3 30 37	-1 -6 4 51 - 36
4 3 0 55 60	1 0 1 16 - 16	-2 1 2 37 - 53	-2 2 3 29 - 34	-1 -5 4 12 2 *
4 4 0 55 47	1 1 1 92 83	-2 2 2 10 0 *	-1 -2 3 58 59	1 -4 4 52 49
4 5 0 20 31	1 2 1 74 - 68	-2 3 2 45 44	-1 0 3 73 - 77	1 -3 4 67 - 5
4 6 0 20 31	1 3 1 13 - 18 *	-2 4 2 75 - 74	0 -3 3 28 23	1 -2 4 28 - 5
4 7 0 52 50	1 4 1 29 22	-2 5 2 14 7 *	0 -2 3 36 38	1 -1 4 42 36
4 8 0 11 3 *	2 -6 1 50 - 19	-1 -6 2 14 12 *	0 -1 3 56 - 63	1 0 4 39 - 42
4 9 0 67 - 65	2 -5 1 12 - 19 *	-1 -5 2 14 10 *	1 -4 3 38 - 23	1 1 4 15 - 7 *
4 10 0 52 - 48	2 -4 1 73 - 70	-1 -4 2 173 -179	1 -2 3 21 21	1 3 4 29 29
4 11 0 50 58	2 -3 1 9 13 *	-1 -3 2 9 - 15 *	2 -4 3 38 - 46	2 -8 4 53 52
4 12 0 37 44	2 -2 1 54 43	-1 -2 2 121 -129	2 -1 3 33 - 32	2 -7 4 86 80
4 13 0 29 26	2 -1 1 92 90	-1 -1 2 439 424	-8 1 4 35 43	2 -6 4 14 - 19 *
4 14 0 27 33	2 0 1 9 16 *	-1 0 2 844 880	-8 2 4 78 76	2 -5 4 36 - 34
4 15 0 69 68	2 1 1 52 - 57	-1 1 2 40 52	-8 3 4 34 36	2 -4 4 91 - 91
4 16 0 83 80	2 2 1 38 - 45	-1 2 2 139 145	-7 4 4 12 - 46	2 -3 4 42 - 45
4 17 0 27 37	3 -6 1 59 48	-1 3 2 128 -135	-7 5 4 53 51	2 -2 4 29 37
4 18 0 41 - 47	3 -5 1 58 - 24	-1 4 2 58 - 65	-7 2 4 44 37	2 -1 4 54 - 54
4 19 0 36 42	3 -4 1 51 - 53	0 -7 2 47 - 54	-6 -2 4 30 24	2 0 4 56 - 48
4 20 0 49 48	3 -3 1 49 - 7 *	0 -6 2 75 85	-6 -1 4 33 33	2 3 4 38 33
4 21 0 97 113	3 -2 1 10 - 7 *	0 -5 2 74 74	-6 0 4 39 30	3 -6 4 95 92
4 22 0 31 57	3 -1 1 68 - 58	0 -4 2 235 -260	0 -4 2 38 - 24	3 -7 4 83 74
4 23 0 30 32	3 0 1 35 - 32	0 -3 2 139 -152	-6 2 4 31 - 28	3 -6 4 15 - 12 *
4 24 0 44 - 34	3 1 1 29 26	0 -2 2 24 - 31	-5 -4 4 79 68	3 -5 4 58 - 53
4 25 0 61 71	3 2 1 28 34	0 -1 2 911 799	-5 -3 4 36 40	3 -4 4 72 75
4 26 0 31 32	4 -6 1 32 42	0 0 2 425 414	-5 -1 4 109 -108	3 -3 4 14 - 4 *
4 27 0 1 20 - 8	4 -5 1 13 23 *	0 1 2 85 93	-5 0 4 58 - 46	3 -2 4 25 - 17 *
4 28 0 14 28 - 8	4 -3 1 35 - 33	0 2 2 12 - 10 *	-5 1 4 24 21	3 -1 4 49 - 40
4 29 0 1 31 35	4 -2 1 55 - 54	0 3 2 74 - 81	-5 2 4 68 - 63	4 -0 4 31 33
4 30 0 12 19 *	4 -1 1 13 - 11 *	0 4 2 14 - 7 *	-5 3 4 65 - 51	4 -1 4 33 12
4 31 0 12 12 *	5 0 1 14 12 *	1 -6 2 13 36 *	-5 4 4 32 29	5 -4 4 35 39
		1 -5 2 124 -123	-4 -5 4 135 150	5 -3 4 48 44
				6 -4 4 45 45

Table 2. Coordinates and anisotropic thermal parameters according to the expression: $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$, with estimated standard deviations. All values multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
F1	2144 15	-1526 16	5243 17	726 38	985 49	1119 70	1191 81	1035 92	1127 91
F2	3637 13	2080 15	6324 17	283 22	860 42	790 49	82 48	396 55	622 70
F3	1535 14	3654 11	6087 14	999 45	244 20	708 48	274 48	820 74	517 52
C1	1099 8	-782 8	5124 9	380 46	624 63	565 87	580 99	647 112	771 126
C2	1863 7	1066 8	5678 9	319 45	332 44	595 78	32 79	325 102	687 100
C3	786 7	1872 6	5557 7	609 57	232 42	384 72	382 85	532 104	401 93
C4	2336 17	-1639 16	266 21	513 43	455 41	940 89	828 80	725 107	952 101
C5	4003 14	2353 15	1711 19	227 37	407 37	627 66	144 61	375 77	673 82
C6	1678 16	4026 18	1419 19	454 43	321 40	566 73	343 67	456 92	494 90
C7	1120 8	-786 8	127 10	340 37	270 31	382 61	437 62	383 78	426 74
C8	1919 7	1128 7	821 9	156 27	344 39	151 45	183 61	163 57	161 68
C9	805 8	1930 9	680 9	263 32	250 35	310 58	207 60	306 67	370 75

The deviations from least squares planes through the molecules are 0.009 Å for all the methyl C-atoms, and 0.003 Å for all the ring C-atoms of the HMB-molecule, 0.003 Å for all the F-atoms, and 0.002 Å for all the ring C-atoms of the HFB-molecule. None of these deviations are significant. The angle between the *c*-axis and the plane normal of the molecular plane, "the stacking angle", is 14.4° for the HMB-molecule and 17.9° for the HFB-molecule. The angle between the molecular planes is 3.6°. The effect of this non-parallelism is to reduce the distances, 3.32 Å and 3.31 Å, from the plane of the HMB-molecule for two fluorine atoms, F2 and F3, respectively, situated approximately above the ring carbon atoms, and to increase the corresponding distances, 3.60 Å and 3.61 Å, for the two equivalent fluorine atoms situated approximately above the methyl groups. Steric hindrance may thus explain this finding. The mean separation between the molecular planes is 3.43 Å.

Table 3. Bond distances (Å) and angles (°). Estimated standard deviations are approximately 0.01 Å for the distances, and approximately 0.7° for the angles.

Distance		Angle	
C3' - C1	1.39	∠C3' - C1 - C2	120.3
C1 - C2	1.37	∠C1 - C2 - C3	120.9
C2 - C3	1.37	∠C2 - C3 - C1'	118.9
C1 - F1	1.30	∠F1 - C1 - C3'	119.7
C2 - F2	1.30	∠F1 - C1 - C2	120.0
C3 - F3	1.32	∠F2 - C2 - C1	119.8
C9' - C7	1.40	∠F2 - C2 - C3	119.3
C7 - C8	1.39	∠F3 - C3 - C2	120.4
C8 - C9	1.40	∠F3 - C3 - C1'	120.7
C7 - C4	1.51	∠C9' - C7 - C8	120.7
C8 - C5	1.51	∠C7 - C8 - C9	120.4
C9 - C6	1.53	∠C8 - C9 - C7'	118.9
		∠C4 - C7 - C9'	119.4
		∠C4 - C7 - C8	119.9
		∠C5 - C8 - C7	120.2
		∠C5 - C8 - C9	119.4
		∠C6 - C9 - C8	120.4
		∠C6 - C9 - C7'	120.7

Table 4. Principal axes of the thermal vibration ellipsoids.

	R.m.s. amplitudes Å	B-values Å ²	Components of the r.m.s. amplitudes (Å)		
			U(x)	U(y)	U(z)
F1	.508	20.4	.399	.605	.197
	.431	14.7	.189	.116	.500
	.350	9.7	-.293	.103	.032
F2	.568	25.5	-.099	.533	.033
	.383	11.6	.071	.138	.437
	.256	5.2	.308	.192	.114
F3	.572	25.8	.598	.002	.128
	.340	9.1	.123	.185	.408
	.221	3.8	.118	.250	.029
C1	.397	12.5	.195	.494	.230
	.308	7.5	.303	.048	.259
	.238	4.5	.131	.180	-.161
C2	.425	14.3	-.185	.291	.209
	.298	7.0	.279	.159	.332
	.162	2.1	.108	.147	-.023
C3	.416	13.6	.472	.090	.121
	.250	4.9	.110	.243	.277
	.204	3.3	.036	.156	-.090
C4	.406	13.1	.267	.342	.490
	.370	10.8	.349	.221	-.052
	.166	2.2	.072	-.119	.030

Table 4. Continued.

C5	.385	11.7	-.031	.364	.267
	.298	7.0	.216	.028	.302
	.202	3.2	.200	.166	.012
C6	.362	10.3	.356	-.014	.000
	.312	7.7	.192	.215	.383
	.271	5.8	.109	.284	-.012
C7	.302	7.2	.357	.261	.153
	.250	4.9	.008	.136	.269
	.194	3.0	.063	-.141	.060
C8	.334	8.8	.023	.346	.011
	.201	3.2	.242	.105	.081
	.156	1.9	.033	.075	.180
C9	.287	6.5	-.194	.150	.037
	.249	4.9	.250	.264	.245
	.190	2.8	.043	.081	-.137

As may be seen in the part of Fig. 2 showing the packing along $(1\bar{1}0)$, the plane normals of both molecules are lying approximately in this plane. The mutual displacement of centres of symmetry, relative to their positions in the trigonal form, is much greater in the neighbouring stacks shown in this figure than in the other pairs of neighbouring stacks. Molecules of different kinds belonging to this pair of stacks (*e.g.* situated in $(0,0,0)$ and $1,1,\frac{1}{2}$) are lying nearly in the same plane. Their interatomic distances, although shorter than between molecules belonging to other pairs of stacks, are not short enough to indicate any forces stronger than normal van der Waals interaction.

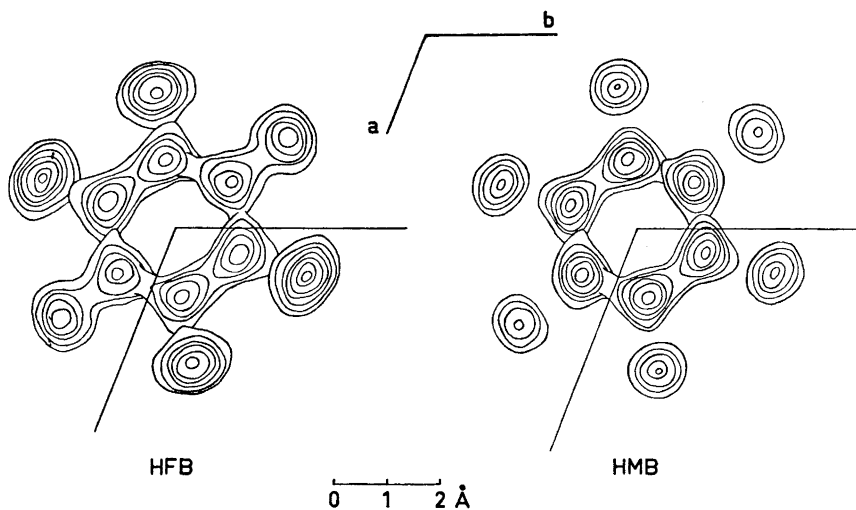


Fig. 1. Sections parallel to (001) , through a three-dimensional Fourier map viewed perpendicular to this plane. Contour intervals of $\frac{1}{2} e/\text{\AA}^3$, and lowest contour at $2 e/\text{\AA}^3$.

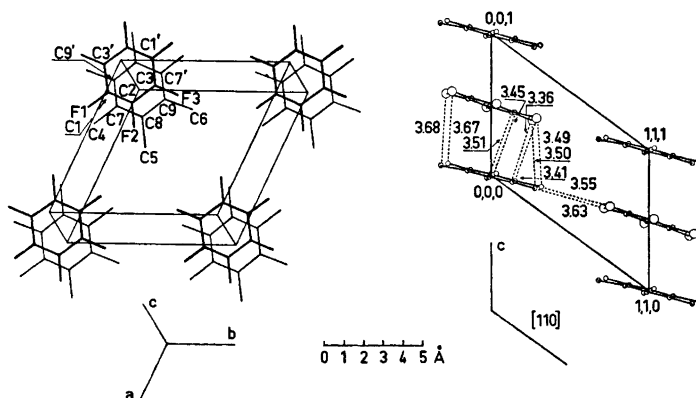


Fig. 2. The packing and the orientation of the molecules viewed perpendicular to the plane of the HMB-molecule (left) and perpendicular to (110) (right). Intermolecular distances within the stack and the shortest distances between different stacks are given.

The orientations of the molecules correspond very closely to that of the HMB-molecule and the most probable orientation of the HFB-molecule in the trigonal modification. Although only one orientation of the HFB-molecule is preferred, the thermal vibration ellipsoids indicate that reorientation of this molecule occurs also in the triclinic modification. The finding that the molecular planes are not parallel in the trigonal form due to tilting of the HFB-molecule is in accordance with this structure, but the stacking angle of the HMB-molecule adds weight to the suspicion that this molecule, too, is tilted in the trigonal form. Important interactions within the stack between methyl groups and fluorine atoms, whose existence was discussed in the report of the trigonal modification, are not confirmed in this work. No indications have been found of disorder in the stacking sequence like that found in the trigonal form.

A comparison of this structure with the structure of the complex between HFB and mesitylene at approximately the same temperature shows considerable differences. In spite of the greater number of methyl groups, the mean separation between the planes is 0.13 Å shorter in the HMB-complex, and the molecules, which have nearly the same orientation in this complex, are twisted 30° relative to each other in the mesitylene-complex. No short distance between a methyl group and a fluorine atom, like that found in the mesitylene-complex, is present in the HMB-complex. In general, the structure of the HMB-complex is much more similar to those of the majority of the $\pi - \pi$ complexes which have been investigated.¹¹ This finding may be interpreted as an indication that the dominating intermolecular forces are of the same kind as in this type of complexes.

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