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Crystal Structure of the 1:1 Addition Compound between *p*-Xylene and Hexafluorobenzene

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The 1:1 addition compound between *p*-xylene and hexafluorobenzene crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 6.844$ Å, $b = 7.327$ Å, $c = 7.318$ Å, $\alpha = 102.42°$, $\beta = 98.13°$, $\gamma = 102.86°$. The crystals show a great tendency to form twins. The partner molecules are stacked alternately in infinite columns. An angle of 5.3° has been found between the molecular planes, whose mean separation within the stack is 3.55 Å. The benzene rings of the partner molecules are twisted 30° relative to each other.

The crystal structures of the 1:1 addition compounds of hexafluorobenzene (HFB) with mesitylene and hexamethylbenzene show considerable differences in interplanar distances and relative orientations of the molecules.[1] As the structure of the mesitylene compound is less similar to typical charge-transfer complexes, the differences may be explained from the higher ionisation potential of the "donor" in this compound.

To test the tenability of this reasoning, the structure of the addition compound between HFB and *p*-xylene, whose ionisation potential is still higher, was investigated.

DESCRIPTION OF THE CRYSTALS. CRYSTAL DATA

X-Ray diagrams taken at room temperature show that most of the crystals are twins of the pseudo-merohedral type.[2] The single crystals obtained were transformed into twins when exposed to the X-ray beam for a few hours.

The crystals are triclinic and the following cell parameters were found: $a = 6.844 \pm 0.008$ Å, $b = 7.327 \pm 0.007$ Å, $c = 7.318 \pm 0.009$ Å, $\alpha = 102.42 \pm 0.10°$, $\beta = 98.13 \pm 0.06°$, $\gamma = 102.86 \pm 0.10°$. Assuming one molecule of each kind in the cell calculated density is 1.42 g/cm³. The twin plane is $(1\bar{1}0)$ and the obliquity is 4.5°.

EXPERIMENTAL

Needle-shaped crystals were obtained by mixing equimolecular amounts of the two components, followed by crystallization and sublimation.

The crystals whose melting point is 27.4 °C,[3] are unstable at room temperature even when kept in sealed capillaries and are completely destroyed due to sublimation after a few days' exposure to the X-ray beam. When cooled below room temperature the crystals are damaged. The intensity data were therefore collected at room temperature and several crystals had to be used.

Cu$K\alpha$-radiation was used for all the diagrams. Cell dimensions were determined from oscillation diagrams which could be indexed, taken about the *c*-axis and using NaCl ($a = 5.6395$ Å) as calibrating substance, and from precession diagrams of the $0kl$- and $h0l$-zone.

The intensity data were collected from Wesisenberg diagrams taken about the *c*-axis. To avoid overlap of reflections from different individuals of the twin crystals and also to decrease the exposure time non-integrated diagrams were used. The precession diagrams mentioned above and oscillation diagrams taken about the *c*-axis were used to calculate interlayer scale factors. All the 329 observed reflections were measured visually, and the intensities of those having important spot-elongation were corrected for this effect.[4] All the crystals used were so small that absorption correction was found to be unimportant and was not performed.

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 1/2 F_{min} and are marked with asterisks.

0	1	0	312.	304.	
0	2	0	172.	-176.	
0	3	0	82.	-81.	
0	4	0	78.	-75.	
0	5	0	47.	47.	
0	6	0	18.	11.	
1	-5	0	8.	1.	*
1	-4	0	49.	-36.	
1	-3	0	68.	57.	
1	-2	0	112.	-115.	
1	-1	0	232.	244.	
1	0	0	288.	283.	
1	1	0	89.	-97.	
1	2	0	43.	35.	
1	3	0	131.	-129.	
1	4	0	18.	-19.	
1	5	0	48.	53.	
2	-6	0	22.	22.	
2	-5	0	16.	*	
2	-4	0	62.	-51.	
2	-3	0	61.	-55.	
2	-2	0	115.	-106.	
2	-1	0	100.	-90.	
2	0	0	169.	-166.	
2	1	0	5.	-6.	*
2	2	0	6.	26.	*
2	3	0	68.	-66.	
3	-5	0	19.	21.	
3	-4	0	24.	-6.	
3	-3	0	87.	-85.	
3	-2	0	69.	-72.	
3	-1	0	48.	46.	
3	0	0	57.	-49.	
3	1	0	130.	-128.	
3	2	0	70.	-57.	
3	4	0	24.	19.	
4	-5	0	19.	20.	
4	-4	0	48.	51.	
4	-3	0	8.	5.	*
4	-2	0	58.	-51.	
4	-1	0	49.	-40.	
4	0	0	58.	-50.	
4	1	0	17.	7.	
4	2	0	36.	42.	
4	3	0	19.	17.	
5	-3	0	19.	27.	
5	-2	0	9.	8.	*
5	-1	0	8.	2.	*
5	0	0	29.	29.	
5	1	0	44.	46.	
5	3	0	18.	-6.	
-5	1	1	8.	10.	*
-5	2	1	8.	-1.	*
-5	3	1	9.	-7.	*
-5	4	1	9.	6.	*
-4	-4	1	36.	-38.	
-4	-2	1	34.	28.	
-4	-1	1	36.	40.	
-4	0	1	20.	19.	
-4	1	1	38.	-40.	
-4	2	1	15.	14.	
-4	3	1	19.	20.	
-4	4	1	8.	-6.	*
-3	-5	1	19.	-21.	
-3	-3	1	29.	28.	
-3	-2	1	44.	-39.	
-3	-1	1	44.	46.	
-3	0	1	50.	-52.	
-3	1	1	116.	-133.	
-3	2	1	47.	41.	
-3	3	1	44.	52.	
-3	4	1	16.	11.	
-3	5	1	19.	-27.	
-3	6	1	19.	-20.	
-2	-4	1	36.	32.	
-2	-3	1	71.	-74.	
-2	-2	1	138.	-136.	
-2	-1	1	99.	100.	
-2	0	1	31.	43.	
-2	1	1	127.	151.	
-2	2	1	30.	-34.	
-2	3	1	112.	-106.	
-2	4	1	15.	14.	
-2	5	1	18.	-18.	
-1	-4	1	46.	48.	
-1	-3	1	36.	38.	
-1	-2	1	113.	123.	
-1	-1	1	91.	-96.	
-1	0	1	103.	-126.	
-1	1	1	143.	149.	
-1	2	1	118.	-105.	
-1	3	1	56.	-53.	
-1	4	1	37.	33.	
-1	5	1	8.	-6.	*
0	-4	1	41.	39.	
0	-3	1	28.	-26.	
0	-2	1	40.	39.	
0	-1	1	89.	-99.	
0	0	1	201.	-204.	
0	2	1	144.	116.	
0	3	1	95.	97.	
0	4	1	16.	16.	
0	6	1	19.	27.	
1	-5	1	8.	11.	*
1	-4	1	46.	-47.	
1	-3	1	167.	-178.	
1	-2	1	126.	117.	
1	-1	1	176.	188.	
1	0	1	102.	99.	
1	1	1	64.	43.	
1	2	1	178.	-186.	
1	3	1	17.	12.	
1	4	1	21.	11.	
2	-3	1	47.	51.	
2	-2	1	5.	-12.	*
2	-1	1	161.	-153.	
2	0	1	89.	95.	
2	1	1	75.	-68.	
2	2	1	102.	-85.	
2	3	1	46.	44.	
2	4	1	22.	-26.	
3	-3	1	64.	59.	
3	-2	1	85.	-76.	
3	-1	1	81.	-79.	
3	0	1	83.	84.	
3	1	1	48.	41.	
3	2	1	50.	44.	
3	3	1	42.	-38.	
3	4	1	45.	-50.	
4	-2	1	16.	18.	
4	-1	1	28.	27.	
4	0	1	8.	6.	*
4	1	1	8.	*	*
4	2	1	9.	-7.	*
4	3	1	24.	-30.	
5	-3	1	18.	-19.	
5	-2	1	28.	-23.	
5	-1	1	9.	-9.	*
5	1	1	19.	24.	
-5	-2	2	21.	28.	
-5	2	2	9.	-4.	*
-4	-2	2	30.	-33.	
-4	-1	2	57.	-59.	
-4	0	2	6.	-1.	*
-4	1	2	8.	-14.	*
-4	2	2	45.	-47.	
-4	3	2	9.	-3.	*
-4	4	2	9.	20.	*
-3	-3	2	30.	-22.	
-3	-2	2	19.	-17.	
-3	-1	2	51.	-54.	
-3	0	2	33.	-35.	
-3	1	2	53.	-56.	
-3	2	2	60.	-65.	
-3	3	2	44.	-41.	
-3	4	2	9.	-14.	*
-2	-5	2	21.	22.	
-2	-4	2	45.	-46.	
-2	-3	2	24.	-22.	
-2	-2	2	6.	-6.	*
-2	-1	2	53.	-59.	
-2	0	2	36.	43.	
-2	1	2	43.	-44.	
-2	2	2	6.	6.	*
-2	3	2	16.	-9.	
-2	4	2	31.	-25.	
-2	5	2	10.	15.	*
-1	-6	2	21.	25.	
-1	-4	2	79.	-82.	
-1	-3	2	67.	-65.	
-1	-2	2	64.	-67.	
-1	-1	2	480.	533.	
-1	0	2	523.	664.	
-1	1	2	60.	-51.	
-1	2	2	66.	-64.	
-1	3	2	84.	-70.	
-1	4	2	8.	-3.	*
-1	5	2	31.	27.	
0	-5	2	26.	-20.	
0	-4	2	7.	-2.	*
0	-3	2	6.	-19.	*
0	-2	2	19.	13.	
0	-1	2	422.	576.	
0	0	2	182.	207.	
0	1	2	104.	-80.	
0	2	2	64.	-58.	
0	3	2	111.	-112.	
0	4	2	48.	53.	
0	5	2	24.	25.	
1	-5	2	21.	-22.	
1	-4	2	16.	-19.	
1	-3	2	68.	-70.	
1	-2	2	65.	-63.	
1	-1	2	76.	-76.	
1	0	2	140.	-135.	
1	1	2	117.	108.	
1	2	2	70.	-48.	
1	3	2	56.	-46.	
1	4	2	41.	45.	
2	-4	2	60.	-58.	
2	-3	2	87.	-103.	
2	-2	2	6.	-8.	*
2	-1	2	24.	-17.	
2	0	2	87.	-96.	
2	1	2	101.	-92.	
2	2	2	75.	-72.	
2	3	2	22.	18.	
3	-3	2	63.	-47.	
3	-2	2	50.	-45.	
3	-1	2	60.	-60.	
3	0	2	76.	-85.	
3	1	2	8.	-5.	*
3	2	2	29.	35.	
3	3	2	32.	25.	
4	-2	2	8.	-16.	*
4	-1	2	8.	-1.	*
4	0	2	46.	56.	
4	1	2	49.	59.	
5	-2	2	24.	22.	
-5	2	3	16.	6.	
-4	0	3	61.	-46.	
-4	1	3	7.	-15.	*
-4	2	3	26.	28.	
-4	3	3	8.	13.	*
-3	-3	3	65.	-48.	
-3	-2	3	13.	-11.	
-3	-1	3	25.	14.	
-3	0	3	6.	*	*
-3	1	3	35.	34.	
-3	2	3	26.	-20.	
-3	3	3	7.	-6.	*
-3	4	3	8.	-8.	*
-2	-5	3	16.	18.	
-2	-2	3	30.	32.	
-2	-1	3	54.	-58.	
-2	0	3	46.	44.	
-2	1	3	23.	24.	
-2	2	3	75.	-91.	
-2	3	3	13.	-1.	
-2	4	3	7.	-2.	*
-1	-5	3	18.	22.	
-1	-4	3	17.	18.	
-1	-3	3	25.	28.	
-1	-2	3	30.	-33.	
-1	-1	3	140.	-160.	
-1	0	3	21.	20.	
-1	1	3	47.	51.	
-1	2	3	38.	41.	
-1	3	3	43.	43.	
-1	4	3	7.	-7.	*
0	-4	3	52.	-62.	
0	-3	3	33.	-34.	
0	-2	3	63.	74.	
0	-1	3	66.	72.	
0	0	3	103.	91.	
0	1	3	23.	-19.	
0	2	3	4.	-7.	*
0	3	3	18.	11.	
0	4	3	7.	6.	*
0	5	3	19.	27.	
1	-4	3	14.	-13.	
1	-3	3	33.	35.	
1	-2	3	4.	- *	*
1	-1	3	9.	11.	
1	0	3	35.	31.	
1	1	3	126.	-122.	
1	2	3	29.	-22.	
1	3	3	7.	9.	*
1	5	3	16.	11.	
2	-4	3	33.	39.	
2	-3	3	12.	5.	
2	-2	3	117.	-117.	
2	-1	3	5.	4.	*
2	0	3	67.	56.	
2	1	3	12.	7.	
2	2	3	15.	19.	
2	3	3	45.	-52.	
2	4	3	19.	-21.	
3	-4	3	8.	8.	*
3	-3	3	13.	-2.	
3	-2	3	6.	-3.	*
3	-1	3	37.	33.	
3	0	3	6.	5.	*
3	1	3	7.	8.	*
3	2	3	24.	-29.	
3	3	3	32.	-38.	
4	-3	3	18.	-19.	
4	-2	3	15.	-13.	
4	-1	3	8.	-4.	*
4	0	3	7.	15.	*
4	1	3	16.	24.	
5	-3	3	18.	-21.	
5	0	3	22.	27.	
-4	-2	4	27.	-23.	
-4	0	4	17.	-17.	
-4	1	4	33.	-29.	
-3	-4	4	23.	-17.	
-3	-3	4	20.	-12.	
-3	-2	4	30.	-21.	
-3	-1	4	20.	-18.	
-3	0	4	21.	-18.	
-3	1	4	20.	-17.	
-3	3	4	18.	-17.	
-2	-4	4	34.	-35.	
-2	-3	4	36.	-28.	
-2	-2	4	43.	39.	
-2	-1	4	182.	198.	
-2	0	4	92.	96.	
-2	1	4	22.	-17.	
-2	2	4	35.	-29.	
-2	3	4	25.	-23.	
-1	-3	4	20.	-12.	
-1	-2	4	141.	162.	
-1	-1	4	270.	276.	
-1	0	4	36.	32.	
-1	1	4	41.	-44.	
-1	2	4	56.	-62.	
-1	4	4	19.	32.	
0	-3	4	37.	-31.	
0	-2	4	39.	48.	
0	-1	4	9.	-6.	
0	0	4	27.	-16.	
0	1	4	23.	19.	
0	2	4	53.	-58.	
0	3	4	9.	19.	*
1	-5	4	25.	-20.	
1	-4	4	52.	-53.	
1	-3	4	39.	-43.	
1	-2	4	6.	-15.	*
1	-1	4	65.	-60.	
1	0	4	39.	-29.	
1	1	4	64.	-58.	
1	2	4	33.	-32.	
1	3	4	26.	28.	
2	-4	4	23.	-19.	
2	-3	4	34.	-31.	
2	-2	4	41.	-38.	
2	-1	4	75.	-71.	
2	0	4	65.	-62.	
2	1	4	17.	-14.	
2	2	4	26.	30.	
3	-3	4	22.	-12.	
3	-2	4	27.	-23.	
3	-1	4	9.	- *	*
3	0	4	39.	44.	
3	1	4	41.	39.	
4	-3	4	19.	21.	
4	0	4	28.	22.	
-4	1	5	13.	8.	
-3	-1	5	11.	-10.	
-3	0	5	17.	18.	
-3	1	5	15.	-10.	
-3	2	5	18.	-15.	
-2	-2	5	56.	-40.	
-2	-1	5	31.	-18.	
-2	0	5	29.	23.	
-2	2	5	16.	11.	
-1	-4	5	18.	-14.	
-1	-2	5	12.	4.	
-1	-1	5	46.	38.	
-1	0	5	18.	29.	
-1	2	5	12.	11.	
-1	4	5	14.	16.	
0	-3	5	23.	22.	
0	-2	5	22.	21.	
0	-1	5	28.	26.	
0	0	5	20.	-15.	
0	1	5	35.	-33.	
0	2	5	8.	-5.	
1	-4	5	14.	16.	
1	-3	5	16.	-16.	
1	-2	5	39.	-33.	
1	-1	5	15.	16.	
1	0	5	8.	-5.	
1	2	5	14.	-10.	
1	3	5	24.	-20.	
2	-3	5	12.	-19.	
2	-1	5	22.	18.	
2	2	5	28.	-33.	
2	3	5	12.	-18.	
3	-3	5	14.	-13.	
3	0	5	19.	17.	
4	-3	5	16.	-16.	
4	-1	5	22.	22.	
4	0	5	22.	26.	

STRUCTURE DETERMINATION

As both the partner molecules may have centres of symmetry, the space group $P\bar{1}$ was assumed. Expecting one of the mirror planes of each molecule to coincide approximately with the twin plane, the possible orientations of the molecules were limited, and the correct orientations could be found from a sharpened three-dimensional Patterson synthesis. The HFB molecule and the *p*-xylene molecule were placed in $(0,0,\frac{1}{2})$ and $(0,0,0)$, respectively. Structure factors based on the F-and C-atoms were calculated, giving an R-value of 33 %, and least squares refinement was started.

During the least squares refinement, some restrictions were put on the geometry of the molecules. Straight lines were assumed to run along the C−F bonds and the $C-CH_3$ 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

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 in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
F1	0.2543(21)	−0.2289(19)	0.5279(17)	0.1012(58)	0.0938(55)	0.0998(50)	0.107(9)	0.061(8)	0.067(8)
F2	0.3867(17)	0.1557(17)	0.6872(14)	0.0619(38)	0.1074(52)	0.0557(30)	−0.029(7)	−0.009(5)	0.029(6)
F3	0.1358(19)	0.3819(16)	0.6676(15)	0.1313(62)	0.0496(31)	0.0662(35)	−0.018(7)	0.034(7)	−0.006(5)
C1	0.1303(11)	−0.1173(10)	0.5143(9)	0.0670(78)	0.0632(74)	0.0406(45)	0.061(12)	0.028(9)	0.047(9)
C2	0.1982(9)	0.0797(9)	0.5959(7)	0.0639(82)	0.0569(62)	0.0296(43)	−0.011(12)	0.006(9)	0.031(8)
C3	0.0696(10)	0.1957(8)	0.5859(7)	0.0889(92)	0.0498(75)	0.0302(45)	0.014(13)	0.025(10)	0.021(9)
C4	0.3324(28)	0.3445(27)	0.1886(19)	0.0910(86)	0.0758(72)	0.0471(49)	−0.067(14)	0.000(10)	0.000(9)
C5	0.1911(24)	−0.0163(34)	0.0540(19)	0.0515(59)	0.0688(69)	0.0266(37)	0.037(13)	0.007(7)	0.034(9)
C6	0.1594(13)	0.1652(13)	0.0904(9)	0.0636(79)	0.0530(65)	0.0229(35)	0.013(13)	0.013(8)	0.020(8)
C7	−0.0394(54)	0.1815(23)	0.0348(21)	0.0651(65)	0.0456(51)	0.0332(37)	0.015(11)	0.004(8)	0.015(7)

for the HFB molecule [5] and 1.52/1.40 for the *p*-xylene molecule.

Positional and anisotropic thermal parameters were varied for the F- and C-atoms. H-atoms with positions calculated assuming disorder due to rotation of the methyl groups were also included in the structure factor calculations.

For reflections with $F_o > \sim 3|F|_{min}$ the weight factors chosen were $A(F_o)^{-0.7}$ where A is constant. For the weaker reflections a constant weight was chosen.

55 unobserved low-angle reflections were given values of 1/4 I_{min} for I_o and included in the first cycles of the least squares refinement. In the last cycles only observed reflections were included. During the refinement it became obvious that the observed intensities of the 3 strongest reflections, $\bar{1}\bar{1}2$, $0\bar{1}2$, and $\bar{1}02$ were much too low. This may be due to secondary extinction, but may just as well be due to poorly estimated scale factors between the weakest diagrams of the second layer. It was considered that deleting these reflections from the refinement was more correct than performing corrections for secondary extinction.

In the last refinement cycles 326 reflections were thus included, and 79 independent parameters were varied. The conventional R-value arrived at was 10.8 % ($R_w = 13.2$ %).

A difference synthesis gave no indications neither of the positions of the H-atoms nor of any disorder in the positions of the F- and C-atoms.

All programs used are described in Ref. 6, and the atomic form factors are given in Ref. 7.

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. The orientation and the packing of the molecules and intermolecular distances are shown in Fig. 1.

Rigid-body analysis of the thermal parameters gave r.m.s. discrepancies between observed and calculated amplitudes of vibration of 0.0117 Å for the HFB molecule and 0.0067 Å for the *p*-xylene molecule. In view of the large amplitudes these values seem reasonable. The direc-

Table 3. Bond distances (Å) and angles (°). Estimated standard deviations are from 0.01 to 0.02 Å for the distances, and approximately 1° for the angles. Bond distances corrected for libration are given in parentheses.

C3′–C1	1.39(1.41)	C3′–C1–C2	119.3
C1–C2	1.38(1.40)	C1–C2–C3	120.8
C2–C3	1.36(1.38)	C2–C3–C1′	119.8
C1–F1	1.31(1.31)	F1–C1–C3′	120.2
C2–F2	1.30(1.30)	F1–C1–C2	120.5
C3–F3	1.31(1.31)	F2–C2–C1	119.9
C7′–C5	1.37(1.39)	F2–C2–C3	119.2
C5–C6	1.37(1.40)	F3–C3–C2	120.0
C6–C7	1.40(1.42)	F3–C3–C1′	120.2
C6–C4	1.52(1.52)	C7′–C5–C6	123.4
		C5–C6–C7	118.0
		C6–C7–C5′	118.6
		C4–C6–C5	121.6
		C4–C6–C7	120.4

Table 4. Principal axes of the thermal vibration ellipsoids.

	R.m.s. amplitudes	Components of the r.m.s. amplitudes (Å)		
	Å	$U(x)$	$U(y)$	$U(z)$
F1	0.531	0.401	0.425	0.344
	0.477	0.146	0.149	−0.391
	0.368	−0.242	0.229	0.012
F2	0.577	−2.002	0.503	0.068
	0.405	0.171	0.097	−0.322
	0.311	0.277	0.173	0.207
F3	0.585	0.526	−0.157	0.113
	0.435	0.119	0.129	−0.364
	0.311	0.143	0.306	0.185
C1	0.418	0.323	0.371	0.168
	0.339	−0.223	0.157	0.161
	0.282	0.073	−0.099	0.236
C2	0.454	−0.288	0.289	0.076
	0.315	0.261	0.266	0.098
	0.260	0.017	−0.022	0.255
C3	0.457	0.433	−0.084	0.041
	0.343	0.152	0.358	0.079
	0.268	0.008	0.016	0.272
C4	0.602	0.392	−0.377	0.014
	0.384	0.146	0.123	−0.301
	0.279	0.202	0.222	0.193
C5	0.408	0.107	0.432	0.104
	0.339	0.322	0.002	−0.069
	0.240	0.083	0.004	0.238
C6	0.401	−0.293	0.216	0.013
	0.343	0.253	0.311	0.055
	0.235	0.028	0.027	0.243
C7	0.396	−0.358	0.088	0.060
	0.336	0.117	0.323	−0.051
	0.283	0.113	0.109	0.290

tion of the largest axis of libration is approximately perpendicular to the molecular plane for the HFB molecule and approximately along *c* for the *p*-xylene molecule. Bond distances corrected for libration are given in Table 3.

The largest deviation of the atoms from least squares planes through the molecules is 0.019 Å for the HFB molecule and 0.003 Å for the *p*-xylene molecule not including the H-atoms. These deviations from planarity are not significant. The angle between the *c*-axis and the plane normal of the molecular plane is 16.8° for the HFB molecule and 11.6° for the *p*-xylene molecule. The angle between the molecular planes is 5.3°. This non-parallelism has the effect of increasing the distance from the HFB molecule of the methyl group situated approximately above this molecule (Fig. 1).

The mean separation between the molecular planes is 3.55 Å, not significantly shorter than the separation of 3.56 Å found in the compound between mesitylene and HFB.[8] The twisting of the benzene rings of approximately 30° relative to each other was found also in the mesitylene compound. As distinct from that observed in the mesitylene compound, no distances shorter than 3.59 Å (shown in Fig. 1) between F-atoms and methyl C-atoms of different stacks are present in this structure.

Assuming rotation of the methyl groups, the smallest distances possible were calculated between methyl H-atoms and the adjacent HFB molecule within the stack. These distances were compared with van der Waals distances, using a van der Waals radius of 1.55 Å for the F-atoms in directions approximately perpendicular to the C–F-bonds.[9] It was found that no distances could possibly be within the van der Waals distance neither in the *p*-xylene compound nor in the mesitylene compound. Similar calculations of the distances in the triclinic form of the addition compound between HFB and hexamethylbenzene show several distances from methyl H-atoms within the van der Waals distance both to F-atoms and to the benzene ring of HFB. In this compound the benzene rings have a nearly parallel orientation, and the mean separation between the molecular planes is 3.43 Å.[1]

The relative orientations of the molecules, the distances between the molecular planes, and the results of the more detailed analysis of the

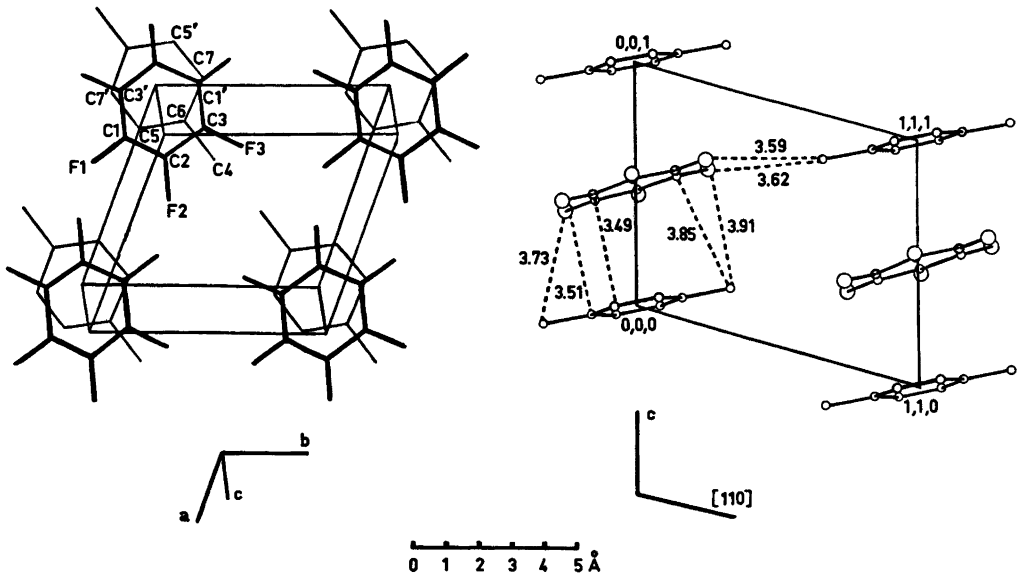

Fig. 1. The packing and the orientation of the molecules viewed perpendicular to the plane of the *p*-xylene molecule (left) and perpendicular to (1$\bar{1}$0) (right). Intermolecular distances, including the shortest ones, within the stack and between different stacks, are given.

intermolecular distances indicate that the intermolecular forces are of a similar kind in the *p*-xylene compound and the mesitylene compound, and that charge-transfer forces contribute little or nothing to these forces. The additional methyl groups in the hexamethylbenzene compound, however, seem to result in charge-transfer forces with considerable effect on the structure. Further informations on how the structure of these compounds varies with varying number of methyl groups were found to be of great interest, and a structure determination of the addition compound between HFB and durene is now going on. The distance between the molecular planes and the relative orientation of the molecules has been found to be something between that found in the hexamethylbenzene compound and that found in the two other addition compounds investigated. A full report of this structure will be published very soon.

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