Crystal Structure of the 1:1 Complex Between

Mesitylene and Hexafluorobenzene

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The crystal structure of the complex between mesitylene and hexafluorobenzene at −35°C has been determined. The final R-value is 10.6 %. The partner molecules are stacked alternately along the c-axis, and the distance between the nearly parallel molecular planes is 3.56 Å. The rings are twisted 30° relative to each other about the plane normal.

Structure determinations of molecular donor-acceptor complexes between aromatic partners have shown as general characteristics that the molecules are stacked alternately in infinite columns and that the molecular planes are exactly or nearly parallel.[1,2] Other characteristics, however, like distances between the molecular planes and relative orientations of the molecules, vary in the different complexes and are difficult to fit into a coherent pattern. One reason for this may be the existence in many of these complexes of localized intermolecular forces in addition to the delocalized $\pi - \pi$ donor-acceptor bonds. Structures of this type may thus provide information not only about $\pi - \pi$ donor-acceptor bonds, but also about other kinds of weak intermolecular forces.

In complexes between hexafluorobenzene and a partner having methyl groups, interactions between fluorine atoms and methyl groups may be possible. Spectroscopic measurements have not given any indications of charge-transfer bonds in complexes between hexafluorobenzene and aromatic hydrocarbons.[3,4] The only X-ray crystallographic work reported until now on complexes with hexafluorobenzene is cell dimension and space group determinations of complexes with anthracene, perylene and pyrene.[5] The existence of the 1:1 complex between mesitylene and hexafluorobenzene was first reported by Patrick and Prosser.[6] Later, an NMR investigation of this complex has shown that thermal reorientation of both partners occurs at room temperature and of hexafluorobenzene even at 77°K.[7]

X-Ray diagrams of the complex taken at room temperature show strong diffuse scattering and unusually great thermal damping. These effects are markedly reduced when the crystal is cooled to −35°C. The cooling does not

result in any change in space group, but the a- and b-axes decrease approximately 1 %. As the structure thus seemed to be much more rigid at $-35°C$, it was decided to take the intensity diagrams at this temperature.

EXPERIMENTAL. STRUCTURE DETERMINATION

Needle-shaped crystals of the complex were grown from gas phase at room temperature by placing the two volatile partner compounds under a bell jar. On exposure to the atmosphere the complex is extremely unstable at room temperature, and the crystals had to be transferred to glass capillaries at low temperature.

Cell dimensions were determined from oscillation diagrams taken at $-35°C$, using KCl as calibrating substance. They were found to be: $a = 15.519 \pm 0.003$ Å, $b = 13.441 \pm 0.005$ Å, $c = 7.198 \pm 0.010$ Å. If the cell is assumed to contain four molecules of each kind, the calculated density is 1.35 g/cm³ which seems reasonable.

The intensity data were collected from integrated Weissenberg diagrams, taken at $-35°C$ about the c-axis which was parallel to the needle axis, using CuKα-radiation. 395 reflexions were observed. The strong reflexions were measured photometrically, the weak ones visually. Absorption corrections were found unnecessary and were not applied. Two space groups, $Pnma$ and $Pna2_1$, are possible from the extinction rules. A three-dimensional Patterson-synthesis indicated that the centrosymmetrical $Pnma$ is the correct one, and the structure determination was based on this assumption.

From a three-dimensional sharpened Patterson synthesis, regions of the cell could be found where the molecules had to be situated, but a more detailed interpretation turned out to be difficult. A computer program which moves the molecules in steps, calculating the R-value after each step, was therefore employed. The molecules were moved in the regions found from the Patterson synthesis and different orientations of the molecules relative to the mirror plane parallel with (010), in which they had to be situated, were tried. Only the $hk0$ and $h0l$ reflexions were used in these calculations. The best structure gave an R-value for all observed reflexions of 29 %. The corresponding Fourier-synthesis seemed promising, and least squares refinement was therefore started at this stage.

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

LEAST SQUARES REFINEMENTS

The weight factors (W) chosen were $W = A1$ for an observed structure factor with $F_o \lesssim FB$, and $W = A2(F_o)^{B2}$ for $F_o > FB$. Using a value of -1.0 for B2, the mean values of $W^2(\Delta F)^2$ remained nearly constant for different intensity intervals. Except in the last cycle of the refinement process, only observed reflexions, 395 in all, were included.

As a first step, three refinement cycles were carried out in which the positional parameters and isotropic thermal damping parameters of the fluorine and the carbon atoms were varied. Hydrogen atoms not belonging to methyl groups were also included in the structure factors. Their positions were calculated assuming a C$-$H distance of 1.00 Å, and they were given a B-value of 9.0 Å². The structure factors calculated after this refinement were used to derive interlayer scale factors, requiring that for each layer $\sum |F_o| = \sum |F_c|$. Three more refinement cycles were then carried out, and the R-value arrived at was 18.5 %. The resulting thermal parameters were considerably greater for the hexafluorobenzene atoms than for the mesitylene atoms, and for the former, anisotropic thermal parameters were introduced and varied together with the parameters mentioned before. The resulting R-value was 13.2 %. Anisotropic thermal parameters were then introduced also for the carbon atoms

Table 1. Observed and calculated structure factors, 10 times the absolute values. The columns listed are h, k, l, F_o, and F_c. Unobserved reflexions have F_o-values like $1/2\,F_{min}$ and are marked with asterisks.

h	k	l	F_o	F_c
0	2	0	1252	-1325
0	4	0	535	-549
0	6	0	488	508
0	8	0	194	-201
0	10	0	339	-355
0	12	0	44	39
2	0	0	896	1006
2	1	0	983	-1146
2	2	0	348	-275
2	3	0	592	-492
2	4	0	47	67
2	5	0	15	36 *
2	6	0	14	-18 *
2	7	0	439	-419
2	8	0	75	-55
2	9	0	119	-99
2	10	0	20	-30 *
2	11	0	99	99
4	0	0	221	-199
4	1	0	726	610
4	2	0	11	-52 *
4	3	0	224	-246
4	4	0	135	25
4	5	0	39	-61
4	6	0	142	-131
4	7	0	196	-199
4	8	0	43	15
4	9	0	19	-1 *
4	10	0	20	-10 *
4	11	0	21	26 *
4	12	0	58	53
6	0	0	167	-144
6	1	0	446	-404
6	2	0	244	-268
6	3	0	286	-294
6	4	0	373	403
6	5	0	84	76
6	6	0	224	-244
6	7	0	73	-86
6	8	0	47	-42
6	9	0	88	-90
6	10	0	86	74
6	11	0	129	-128
8	0	0	274	-264
8	1	0	387	-399
8	2	0	147	121
8	3	0	219	208
8	4	0	18	-21 *
8	5	0	63	69
8	6	0	20	-39 *
8	7	0	47	-44
8	8	0	81	48
8	10	0	101	119
10	0	0	88	103
10	1	0	150	-135
10	2	0	81	-98
10	3	0	38	-27
10	4	0	96	78
10	5	0	280	273
10	6	0	89	-93
10	7	0	61	-69
10	8	0	68	73
12	0	0	20	24 *
12	1	0	190	190
12	2	0	20	-29 *
12	3	0	73	-61
12	4	0	133	132
12	5	0	91	-90
12	6	0	91	-111
12	7	0	89	83
14	0	0	105	100
14	1	0	91	108
14	2	0	63	-67
14	3	0	43	-49
14	5	0	51	57
0	3	1	431	-428
0	4	1	204	284
0	5	1	242	-237
0	7	1	22	56 *
0	9	1	69	-74
0	11	1	54	48
0	13	1	150	-192
1	1	1	146	151
1	2	1	87	46
1	3	1	140	-124
1	4	1	329	279
1	5	1	98	108
1	6	1	113	-115
1	7	1	112	-120
1	8	1	55	3
1	9	1	24	48 *
1	10	1	53	-60
1	11	1	78	-77
1	12	1	111	115
2	1	1	206	-189
2	2	1	75	-111
2	3	1	323	-258
2	4	1	274	-283

h	k	l	F_o	F_c
2	5	1	217	227 *
2	6	1	109	106
2	7	1	102	-85
2	8	1	51	55
2	9	1	55	40
2	10	1	24	-36 *
2	11	1	25	-12 *
2	12	1	71	45
3	0	1	298	189
3	1	1	230	255
3	2	1	310	290
3	3	1	59	-35
3	4	1	170	152
3	5	1	664	-650
3	6	1	186	-198
3	7	1	19	9 *
3	8	1	91	-73
3	9	1	69	45
3	10	1	73	-78
3	11	1	76	-46
4	0	1	12	29 *
4	1	1	69	-25
4	2	1	378	-346
4	3	1	14	29 *
4	4	1	384	-385
4	5	1	92	-11
4	6	1	232	239
4	7	1	20	6 *
4	8	1	75	85
4	9	1	23	-7 *
4	10	1	74	68
4	11	1	54	26
5	0	1	202	-210
5	1	1	124	-154
5	2	1	240	-218
5	3	1	263	-287
5	4	1	248	-223
5	5	1	69	-40
5	6	1	240	207
5	7	1	114	-104
5	8	1	22	33 *
5	9	1	135	-113
5	10	1	25	25 *
5	11	1	100	99
6	0	1	53	-21
6	1	1	264	273
6	2	1	134	-141
6	3	1	270	292
6	4	1	150	162
6	5	1	19	-46 *
6	6	1	106	-95
6	7	1	46	50
6	8	1	23	13 *
6	9	1	119	116
6	10	1	54	58
7	0	1	498	-488
7	1	1	197	186
7	2	1	68	-69
7	3	1	83	-98
7	4	1	254	271
7	5	1	150	149
7	6	1	173	-137
7	7	1	23	21 *
7	8	1	93	-92
7	9	1	25	11 *
7	10	1	164	158
8	0	1	212	264
8	1	1	72	63
8	2	1	57	-79
8	3	1	164	166
8	4	1	61	42
8	5	1	59	-51
8	6	1	23	19 *
8	7	1	24	-37 *
8	8	1	25	44 *
8	9	1	77	77
8	10	1	63	-64
9	0	1	183	164
9	1	1	61	80
9	2	1	100	-90
9	3	1	58	55
9	4	1	65	-64
9	5	1	119	-135
9	6	1	129	113
9	7	1	60	29
9	8	1	25	15 *
9	9	1	89	88
10	0	1	46	2
10	1	1	46	-51
10	2	1	22	-9 *
10	3	1	48	-55
10	4	1	23	17 *
10	5	1	167	180
10	6	1	25	38 *
10	7	1	88	-64
10	8	1	26	-17 *
11	0	1	49	-39
11	1	1	23	10 *
11	2	1	58	47

h	k	l	F_o	F_c
11	3	1	24	-17 *
11	4	1	119	-138
11	5	1	25	28 *
11	6	1	116	113
11	7	1	26	43 *
12	0	1	60	67
12	1	1	52	-48
12	2	1	25	-36 *
12	3	1	68	-53
12	4	1	25	36 *
12	5	1	117	116
12	7	1	63	-60
13	0	1	132	107
13	1	1	76	66
13	2	1	26	-28 *
13	3	1	26	-32 *
13	4	1	55	-33
14	1	1	78	-75
15	1	1	54	-42
0	2	2	67	52
0	4	2	100	-80
0	6	2	80	78
0	8	2	26	-41 *
0	10	2	72	-58
1	0	2	1289	-1279
1	1	2	1815	-1913
1	2	2	81	119
1	3	2	138	-148
1	4	2	175	171
1	5	2	135	134
1	6	2	190	-197
1	7	2	276	-285
1	8	2	89	93
1	9	2	96	-105
1	10	2	125	134
1	11	2	92	108
2	0	2	787	-733
2	1	2	650	-635
2	2	2	226	236
2	3	2	16	-23 *
2	4	2	118	113
2	5	2	58	62
2	6	2	58	-57 *
2	7	2	27	17 *
2	9	2	29	-41 *
2	10	2	31	47 *
2	11	2	32	18 *
3	0	2	228	-265
3	1	2	130	134
3	2	2	256	-248
3	3	2	35	71
3	4	2	19	14 *
3	5	2	49	-77
3	6	2	167	-152
3	7	2	25	47 *
3	8	2	121	133
3	9	2	29	34 *
3	10	2	73	73
3	11	2	32	11 *
4	0	2	16	17 *
4	1	2	101	100
4	2	2	17	-17 *
4	3	2	49	39
4	4	2	89	-95
4	5	2	22	23 *
4	6	2	24	56 *
4	7	2	26	41 *
4	8	2	28	10 *
4	9	2	30	-0 *
4	10	2	31	-22 *
5	0	2	37	42
5	1	2	135	-109
5	2	2	208	-206
5	3	2	121	156
5	4	2	168	159
5	5	2	116	-151
5	6	2	103	-107
5	7	2	101	81
5	8	2	29	37 *
5	9	2	30	29 *
5	10	2	106	94
6	0	2	209	198
6	1	2	67	-55
6	2	2	49	-49
6	3	2	121	-115
6	4	2	23	-19 *
6	5	2	51	40
6	6	2	26	-23 *
6	7	2	28	21 *
6	8	2	29	8 *
6	9	2	31	-33 *
6	10	2	32	-20 *
7	0	2	352	-397
7	1	2	22	8 *
7	2	2	93	74
7	3	2	371	399
7	4	2	25	-22 *
7	5	2	136	-136

h	k	l	F_o	F_c
7	6	2	27	27 *
7	7	2	29	10 *
7	8	2	30	25 *
7	9	2	119	114
8	0	2	24	-17 *
8	1	2	130	123
8	2	2	24	-15 *
8	3	2	25	39 *
8	4	2	77	-64
8	5	2	92	-88
8	6	2	68	68
8	7	2	30	26 *
8	8	2	31	-10 *
8	9	2	32	15 *
9	1	2	130	-122
9	2	2	101	153
9	3	2	143	153
9	4	2	81	77
9	5	2	29	47 *
9	6	2	101	-121
9	7	2	31	19 *
9	8	2	32	59 *
10	0	2	66	-55
10	1	2	28	14 *
10	2	2	82	92
10	3	2	29	28 *
10	4	2	61	-45
10	5	2	63	47
10	6	2	31	-18 *
10	7	2	32	-30 *
11	0	2	70	64
11	1	2	30	-6 *
11	2	2	30	-44 *
11	3	2	63	64
11	4	2	73	86
11	5	2	160	-162
11	6	2	32	-18 *
11	7	2	76	103
12	0	2	64	-76
12	1	2	31	-15 *
12	2	2	31	40 *
12	3	2	31	25 *
12	4	2	32	36 *
12	5	2	67	-62
13	0	2	142	161
13	1	2	32	-45 *
13	2	2	76	-82
13	4	2	67	-69
13	6	2	66	89
0	1	3	101	-108
0	3	3	89	-91
0	5	3	145	140
0	7	3	128	-116
0	9	3	25	-49 *
0	11	3	99	-94
1	0	3	305	-361
1	1	3	118	-118
1	2	3	104	-86
1	3	3	27	-7
1	4	3	119	102
1	5	3	201	172
1	6	3	45	-36
1	7	3	21	-25 *
1	8	3	85	89
1	9	3	25	-20 *
1	10	3	26	-24 *
2	0	3	91	-70
2	1	3	108	102
2	2	3	12	-19 *
2	3	3	77	-83
2	4	3	16	14 *
2	5	3	320	-298
2	6	3	46	-57
2	7	3	22	5 *
2	8	3	23	19 *
2	9	3	25	19 *
2	10	3	61	-72
2	12	3	69	58
3	0	3	128	-114
3	1	3	103	-89
3	2	3	39	19
3	3	3	56	-31
3	4	3	78	-39
3	5	3	101	183
3	6	3	41	14
3	7	3	22	35 *
3	8	3	24	29 *
3	10	3	26	-12 *
4	0	3	181	-171
4	1	3	88	-83
4	2	3	213	-207
4	3	3	98	-97
4	4	3	93	-151
4	5	3	194	178
4	6	3	101	159
4	7	3	53	-92

Table 1. Continued.

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.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
F1	− 849	3531	1729	126	319	602	166	85	− 63
	6	9	14	6	13	35	15	21	32
F2	659	4493	1212	184	140	715	96	− 92	− 60
	6	7	14	8	8	40	13	25	25
F3	2145	3482	694	106	151	588	− 77	− 52	87
	5	6	12	5	7	33	10	17	21
C1	− 81	2968	1460	78	194	257	75	8	− 114
	9	9	16	6	15	40	15	23	29
C2	703	3491	1204	100	105	464	66	32	− 108
	10	10	19	10	11	50	18	31	34
C3	1399	3011	941	79	90	351	− 12	16	82
	9	8	17	6	7	42	12	25	24
C4	13	2500	6329	50	113	407	0	− 3	0
	9	0	24	8	14	60	0	32	0
C5	446	3388	6296	74	102	197	52	− 47	8
	7	8	14	6	8	36	13	21	23
C6	1336	3426	5967	55	100	323	7	− 46	− 32
	6	7	15	5	7	37	11	20	24
C7	1765	2500	5879	46	117	175	0	− 19	0
	8	0	20	7	13	47	0	25	0
C8	− 990	2500	6722	53	235	386	0	33	0
	9	0	26	8	22	63	0	33	0
C9	1823	4422	5784	122	112	492	− 61	− 80	82
	9	9	20	9	10	51	16	32	34

of mesitylene, in the first two cycles only for those belonging to the methyl groups and in the next three cycles for all the carbon atoms. This refinement, where 100 parameters were varied simultaneously in the last cycles, led to an R-value of 10.4 %. Finally, one refinement cycle was carried out in which also 162 non-observed reflexions having low θ-values were included. They were given weight factors of 1/3 Al. The final R-value was 13.4 % for all reflexions, and 10.6 % for the observed reflexions. The structure factors are listed in Table 1, and the corresponding positional and thermal parameters in Table 2.

Difference syntheses calculated after each refinement series gave no indications, neither of statistical disorder nor of positions of the methyl hydrogen atoms. These hydrogen atoms are therefore not included in the structure factor calculations. The effect of secondary extinction did not seem to be great enough to be corrected for.

Refinements based on the non-centrosymmetrical space group $Pna2_1$ were also carried out, but none of the results seemed to confirm the correctness of this.

<div align="center">RESULTS</div>

Interatomic distances and angles are given in Table 3, principal axes of the vibration ellipsoids in Table 4. Fig. 1 shows sections of a three-dimensional Fourier-map through peaks having nearly the same z-coordinates. The orienta-

Table 3. Interatomic distances (Å) and angles (°). Estimated standard deviations are from 0.01 to 0.02 Å for the distances, and approximately 1° for the angles.

C1 – C1′	1.26	∠C1′ – C1 – C2	119.7
C1 – C2	1.42	∠C1 – C2 – C3	119.8
C2 – C3	1.27	∠C2 – C3 – C3′	120.5
C3 – C3′	1.37	∠C1′ – C1 – F1	122.0
C1 – F1	1.42	∠F1 – C1 – C2	118.3
C2 – F2	1.35	∠C1 – C2 – F2	116.8
C3 – F3	1.33	∠F2 – C2 – C3	123.4
C4 – C5	1.37	∠C2 – C3 – F3	121.1
C5 – C6	1.40	∠F3 – C3 – C3′	118.4
C6 – C7	1.41	∠C5′ – C4 – C5	121.2
C4 – C8	1.58	∠C4 – C5 – C6	121.2
C6 – C9	1.54	∠C5 – C6 – C7	116.1
C9″ – F3	3.24	∠C6 – C7 – C6′	123.6
		∠C8 – C4 – C5	119.1
		∠C5 – C6 – C9	121.8
		∠C9 – C6 – C7	122.1
		∠C6″ – C9″ – F3	176.1

tion and packing of the molecules is shown in Fig. 2. Strong anisotropic thermal vibrations are in agreement with the results from the NMR investigations,[7] but the extremely great values given in Table 4 may also partly be due to statistical disorder. Attempts of rigid body analysis of the movements did not

Table 4. Principal axes of the thermal vibration ellipsoids.

r.m.s. amplitudes Å		B-values Å²	Direction cosines relative to the a-, b-, and c-axis		
			cos a	cos b	cos c
F1	0.579	26.4	0.433	0.901	− 0.019
	0.414	13.5	0.392	− 0.169	0.904
	0.313	7.7	0.812	− 0.399	− 0.426
F2	0.508	20.4	0.843	0.372	− 0.388
	0.419	13.8	0.374	0.113	0.921
	0.325	8.3	0.387	− 0.921	− 0.044
F3	0.438	15.2	0.541	− 0.626	− 0.562
	0.370	10.8	0.424	− 0.373	0.825
	0.305	7.3	0.726	0.685	− 0.064
C1	0.445	15.6	0.348	0.918	− 0.190
	0.293	6.8	0.856	− 0.228	0.465
	0.237	4.4	0.383	− 0.324	− 0.865
C2	0.386	11.8	0.671	0.632	− 0.389
	0.361	10.3	0.552	− 0.075	− 0.830
	0.244	4.7	0.496	− 0.771	− 0.399
C3	0.328	8.5	0.041	− 0.622	− 0.782
	0.313	7.7	0.971	− 0.161	0.179
	0.254	5.1	0.237	0.767	− 0.597
C4	0.327	8.4	0.017	0	− 1.000
	0.322	8.2	0	1	0
	0.248	4.9	1.000	0	0.017
C5	0.346	9.5	0.697	0.707	− 0.118
	0.265	5.5	0.581	− 0.654	− 0.485
	0.211	3.5	0.420	− 0.270	0.867
C6	0.316	7.9	0.323	0.699	− 0.638
	0.288	6.5	0.342	− 0.715	− 0.610
	0.245	4.8	0.883	0.021	0.470
C7	0.327	8.4	0	− 1	0
	0.242	4.6	0.917	0	− 0.400
	0.209	3.5	0.400	0	0.917
C8	0.463	17.0	0	1	0
	0.322	8.2	0.233	0	0.973
	0.249	4.9	0.973	0	− 0.233
C9	0.426	14.3	0.756	− 0.432	− 0.492
	0.338	9.0	0.534	− 0.026	0.845
	0.290	6.7	0.378	0.901	− 0.211

give satisfactory results, and corrections for such effects have not been carried out. It must therefore be assumed, in general, that the intramolecular distances given in Table 3 are too short. For these reasons it is difficult to draw definitive conclusions about the details of the structure. The alternately short and long C−C distances in hexafluorobenzene are conspicuous, but one should be careful to believe that this is due to differences in bond orders.

The molecules are stacked alternately along the c-axis, and the separation between the molecular centers projected along this axis is only 0.36 Å. The rings are twisted 30° relative to each other about the plane normal. One C−C bond to a methyl group of mesitylene is pointing nearly directly towards a fluorine atom of hexafluorobenzene, and the corresponding C···F distance (dotted on Fig. 2) is 3.24 Å.
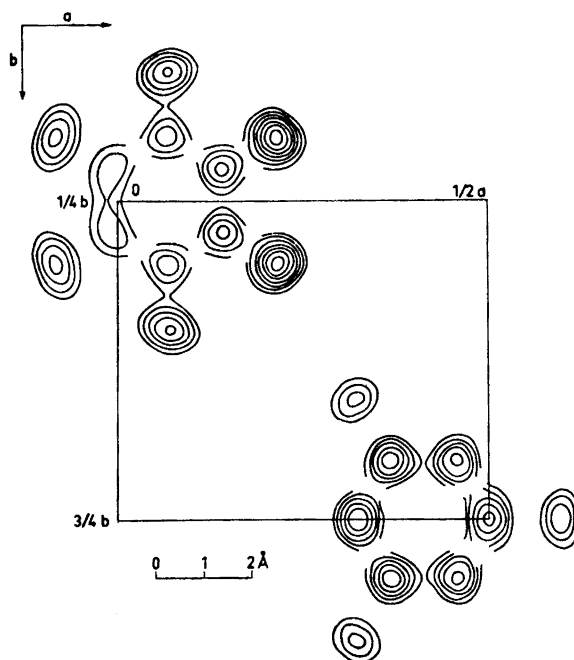
Fig. 1. Sections through a three-dimensional Fourier map showing peaks with nearly the same z-coordinates. Contour intervals of $1/2$ e/Å³, and lowest contour at 2 e/Å³.

Least squares planes through the molecules give the following fit:

Mesitylene		Hexafluorobenzene	
	Deviation (Å)		Deviation (Å)
C4	0.047	C1	0.003
C5	0.028	C2	0.008
C6	0.002	C3	0.008
C7	0.034	F1	0.001
C8	0.002	F2	0.003
C9	0.021	F3	0.000

None of the deviations are significant.

The angles between the molecular planes and the (001) plane, "the stacking angles", are 8.5° for mesitylene and 9.1° for hexafluorobenzene. The difference between these angles are probably significant, so that the molecular planes are not quite parallel. The mean separation between the planes is 3.56 Å.

The finding that the molecules are stacked alternately, with nearly parallel planes and only a small displacement of the ring centers normal to the stack axis is in good agreement with what has usually been found in complexes of the $\pi - \pi$ donor-acceptor type. However, the twisting of the rings relative
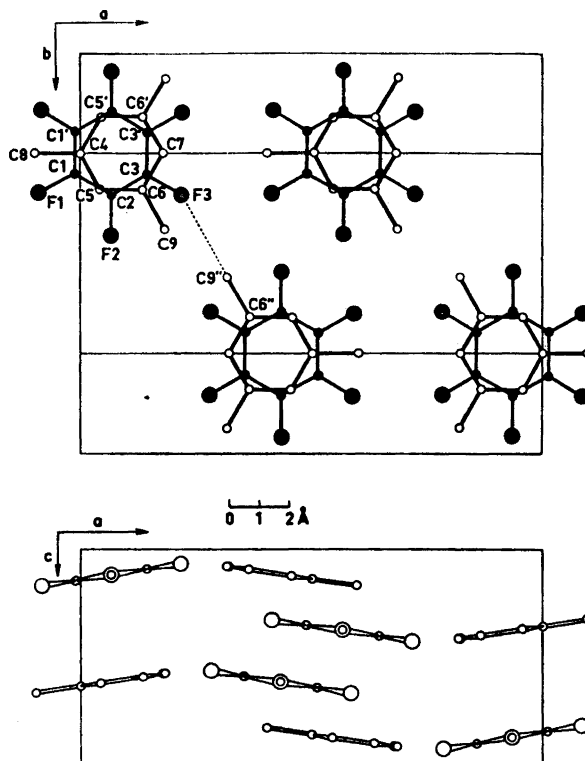
Fig. 2. The packing and the orientation of the molecules.

to each other and the great separation between the molecular planes is surprising. In complexes of this type, the separation is usually well below 3.50 Å, unless there is steric hindrance. Because of the small size of the fluorine atoms, it seems unsatisfactory to explain the great separation in this complex by such hindrance.

For these reasons it is natural to look for other, localized forces which may be responsible for the formation of the complex. No intermolecular $F-F$ separation shorter than 3.01 Å, and no intermolecular $C-C$ or $C-F$ separation shorter than 3.5 Å has been found, except the $C-F$ contact indicated in Fig. 2. If the van der Waals radius for a methyl group is assumed to be 2.0 Å in all directions, this $C-F$ distance of 3.24 Å is shorter than van der Waals separation. However, the distances from the fluorine atom to the carbon atom and the assumed hydrogen positions are greater than normal van der Waals separation for the individual atoms. Probably none of these ways of calculation are quite correct. However, the nearly linear arrangement $C-C\cdots F$ is conspicuous, and the existence of forces stronger than normal van der Waals interaction between the methyl group and the fluorine atom should not be regarded as impossible.

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