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A Statistical Comparison of Two Determinations of the Crystal Structure of 2,3,4,5,6-Pentafluorobiphenyl, a Molecule Forming Mixed Stacks in the Solid State*

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Two independent determinations of the structure of 2,3,4,5,6-pentafluorobiphenyl have been made using X-ray counter data. Molecules of $C_{12}H_5F_5$ crystallize in the orthorhombic space group $C222_1$ with average cell constants $a = 21.066$ (11), $b = 5.876$ (1), and $c = 7.853$ (2) Å. The molecules, which possess crystallographic C_2 symmetry, have a central C—C bond length of 1·493 (3) Å and an inter-ring angle of 52·9°. The C_6H_5 and C_6F_5 rings of pentafluorobiphenyl form mixed stacks in the solid state, and are inclined by 23·7 and 29·2° respectively to the stack axis. The mean distance between the C_6H_5 group and the C_6F_5 plane is 3·43 Å. Interactions along the stack may account for the morphology and high melting point of these crystals. A statistical comparison between the two sets of derived parameters shows generally good agreement between the atomic positions but suggests that one of the H-atom positions is in error. This treatment also reveals systematic discrepancies between the two sets of thermal parameters even though rigid-body analyses for the two determinations give the same general picture of thermal motion.

Introduction

Crystals of 2,3,4,5,6-pentafluorobiphenyl, $C_{12}H_5F_5$, have an unexpectedly high melting point (110–112 °C) relative to those of biphenyl ($C_{12}H_{10}$, 70–71 °C) and perfluorobiphenyl ($C_{12}F_{10}$, 67–68 °C). Their structures have been studied in order to investigate the interactions responsible for this elevated melting point. We suspected that this compound forms mixed stacks of C_6H_5 and C_6F_5 groups in the solid state similar to those found in complexes of hexafluorobenzene with *p*-xylene, mesitylene, durene, and hexamethylbenzene (Dahl, 1971, 1972, 1973, 1975*a*,*b*).

A second reason for studying this structure was to compare its molecular dimensions with those found for other biphenyls. Of particular interest are the effect of F substitution on the C—C bond lengths and the possibility of a correlation between the inter-ring dihedral angle and the length of the central C—C bond.

The two groups collaborating on this paper were unaware of each other's work until after nearly simultaneous submission of manuscripts. We then agreed to a joint publication with the thought that a statistical comparison of our results, derived from data taken on diffractometers of quite different design, would be of interest.

Experimental

Colorless crystals of $C_{12}H_5F_5$ were prepared in both laboratories by the method of Chaudhry & Stephens (1963) and were mounted in capillaries to prevent sublimation. Photographs showed systematic absences *hkl* for $h + k$ odd and 00*l* for *l* odd indicative of the space group $C222_1$. The calculated density for $Z = 4$ is 1·67 g cm^{-3} while the value measured by flotation in aqueous ZnI_2 is 1·63 (2) g cm^{-3}.

The crystal used by Brock & Naae (hereafter referred to as B & N) was grown from ethanol and cut perpendicular to the greatly elongated *c* direction; its final dimensions were 0·11 × 0·25 × 0·45 mm. The cell constants [$a = 21.0679$ (20), $b = 5.8763$ (3), $c = 7.8528$ (10) Å] were refined by a least-squares procedure from the setting angles of 25 reflections centered with Cu $K\alpha$ radiation on a Nonius CAD-4 computer-controlled four-circle diffractometer. Intensities of the 838 unique reflections contained in an octant of reciprocal space and having $2\theta \leq 60°$ were measured with a variable θ–2θ scan rate, a 2:1 ratio of peak and background counting times, and graphite-monochromated Mo $K\alpha$ radiation.† Of these, 538 had $I \geq 3\sigma(I)$ where *p* was taken as 0·05 in the usual expression for the standard deviation (Brock &

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* Part III of the series 'Structures of Polyfluoroaromatic Compounds'. Part II: Goodhand & Hamor (1978).

† Data were collected at the Molecular Structure Corporation, College Station, Texas.

Webster, 1976). No correction was made for absorption. Intensities of three standard reflections were essentially constant over the length of the experiment.

The $0{\cdot}1 \times 0{\cdot}4 \times 0{\cdot}5$ mm data crystal used by Goodhand & Hamor (hereafter G & H) was obtained by sublimation at reduced pressure. Unit-cell dimensions [$a = 21{\cdot}01\,(1)$, $b = 5{\cdot}87\,(1)$, $c = 7{\cdot}83\,(1)$ Å] and intensities were measured with a Stoe computer-controlled two-circle diffractometer and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) by the ω scan technique. The scan rate was 0·6° min^{-1} and 30 s background counts were taken at the beginning and end of each scan. Four reflections from the zero layer were re-measured after each layer of data collection to monitor the stability of the system. Their intensities showed no significant variation with time. Of 815 unique reflections measured in the range $0{\cdot}1 < \sin\theta/\lambda < 0{\cdot}65$ Å^{-1}, 465 for which $I > 2{\cdot}5\sigma(I)$ were considered to be observed and were used in the analysis.

Structure solution and refinement

Inspection of the relative dimensions of the cell and molecule and of the coordinates of the fourfold positions in $C222_1$ showed that the molecular twofold axis must lie parallel to a at $y = z = 0$. The structure could then be solved either from the Patterson function (B & N) or with Germain, Main & Woolfson's (1971) direct-methods program *MULTAN* (G & H). Least-squares minimizations of the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, proceeded smoothly. In the case of B & N all calculations were performed as described previously (Brock & Webster, 1976); scattering factors were taken from the usual tabulation (Cromer & Waber, 1974). H atom positions were clearly revealed in difference Fourier maps and were subsequently included in the refinement. Final agreement indices are $R_1 = \sum ||F_o - F_c|| / \sum |F_o| = 0{\cdot}032$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o^2|]^{1/2} = 0{\cdot}046$ for 538 data and 90 variables; the final value of R_1 based on all 838 data is 0·082 and the error in an observation of unit weight is 1·45. The largest peak in a final difference map has a height of 0·23 e Å^{-3}. No correction for extinction appeared to be necessary. The atom positions found by G & H were refined with *SHELX* (Sheldrick, 1975). Full-matrix least-squares calculations varying the coordinates and isotropic temperature factors of the C and F atoms reduced R to 10·3%. With the introduction of anisotropic temperature factors R was reduced to 6%. At this stage the H atoms were located from a difference synthesis and their positional and isotropic thermal parameters included in the least-squares refinement.

The calculations were terminated when all shifts were $<0{\cdot}01\sigma$; the weighting scheme used was $1/\sigma^2(F_o)$. Final agreement indices are $R_1 = 0{\cdot}042$ and $R_2 = 0{\cdot}048$ for 465 data and 90 variables and the error in an observation of unit weight is 1·61. Comparison of observed and calculated structure amplitudes revealed no significant extinction effects. The atomic scattering factors for C and F were obtained from the analytical expression and coefficients given by Cromer & Mann (1968) and those for H were obtained from the analytic fit to the scattering factors of Stewart, Davidson & Simpson (1965). Final atomic coordinates for both determinations are given in Table 1.*

The results of the two determinations were compared by the use of normal probability plots (Abrahams & Keve, 1971; Abrahams, 1972; Hamilton, 1974). For the most part the agreement between the positional parameters (Fig. 1) is excellent; a least-squares line

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for* $C_{12}H_5F_5$ *with estimated standard deviations in parentheses*

	B & N			G & H		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	5538·0 (13)	0	0	5538 (2)	0	0
C(2)	5889·3 (11)	1755 (4)	−730 (3)	5890 (2)	1752 (7)	−734 (4)
C(3)	6544·8 (11)	1759 (5)	−737 (3)	6542 (2)	1764 (9)	−735 (5)
C(4)	6870·5 (17)	0	0	6867 (2)	0	0
C(5)	4829·6 (13)	0	0	4829 (2)	0	0
C(6)	4497·0 (11)	1873 (4)	611 (3)	4494 (2)	1852 (7)	604 (5)
C(7)	3836·7 (12)	1845 (5)	612 (4)	3838 (2)	1849 (8)	608 (6)
C(8)	3515·0 (17)	0	0	3513 (3)	0	0
F(2)	5593·0 (7)	3490 (3)	−1496 (2)	5592 (1)	3489 (4)	−1496 (3)
F(3)	6859·5 (8)	3469 (3)	−1499 (2)	6859 (1)	3466 (5)	−1507 (3)
F(4)	7505·2 (9)	0	0	7504 (1)	0	0
H(6)	4718 (12)	3146 (51)	970 (32)	4675 (16)	2739 (65)	1037 (43)
H(7)	3630 (16)	3184 (67)	1013 (49)	3612 (15)	3190 (71)	1058 (42)
H(8)	3117 (22)	0	0	3126 (26)	0	0

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33835 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

through the first 26 of the 30 points has a slope of 1·00 (3) and an intercept of −0·02 (2). The sharp curvature at the upper part of the plot suggests the presence of significant systematic error in one or both of the determinations involving the C(6) and H(6) atoms. Were this error removed, the deviation of Δ/σ for F(3)z from the line would be greatly reduced.

The coordinates of B & N lead to a length of 0·93 Å for the C(6)—H(6) bond, whereas those of G & H lead to a length of 0·73 Å. The latter distance is unusually short, and in 2,3,5,6-tetrafluorobiphenyl (Goodhand & Hamor, 1978) which would be expected to have similar dimensions, the *ortho* C—H lengths are 0·91 and 0·87 Å in good agreement with B & N's value for the C(6)—H(6) bond. It therefore seems likely that the large Δ/σ values for H(6)x and H(6)y are due mainly to errors in the parameters of G & H. Since there is no other inconsistency in the atomic positions, the distances and angles cited below and the associated standard deviations were calculated from the weighted averages of the two sets of positional parameters and corresponding sets of experimental standard deviations. An exception to this procedure was made for H(6), for which the B & N coordinates were used.

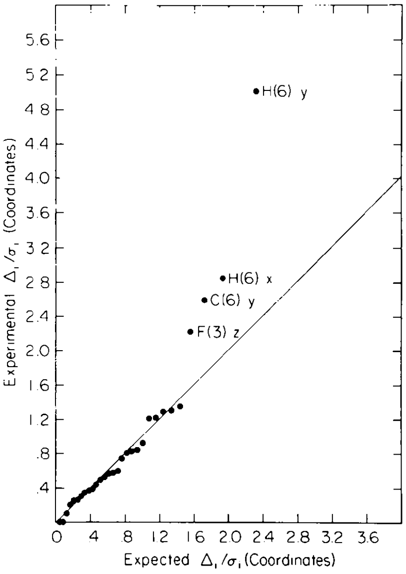

Fig. 1. Half-normal probability plot of Δ_i/σ_i for the 30 positional parameters refined by B & N and G & H. The line is that obtained by a least-squares fit to the first 26 points.

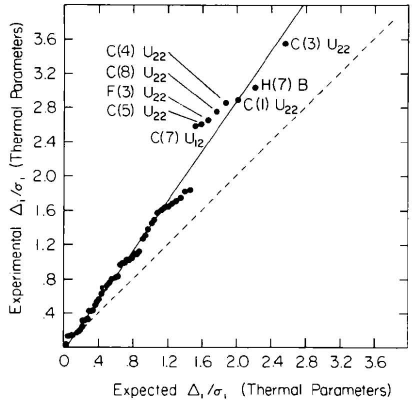

Fig. 2. Half-normal probability plot of Δ_i/σ_i for the 59 thermal parameters. The dashed line would be expected for normal populations with zero variance and zero mean; the full line is that obtained by a least-squares fit to all the points.

The slope and intercept of the half-normal probability plot for the thermal parameters (Fig. 2) are 1·45 (3) and −0·02 (3) respectively. The large departure from unit slope indicates that the standard deviations are significantly underestimated. Furthermore, the presence of noticeable structure in the curve and the clustering of the U_{22} points near the extremity of the plot are suggestive of systematic error. Therefore a full-normal probability plot for the 33 U_{ii} values was constructed. The central region of this plot is relatively straight and has a slope not far from unity, but the curve has an intercept of −0·4 and is clearly non-linear at either end. In order to locate the area of disagreement more precisely, a similar analysis was performed for each of the three sets of U_{ii}'s, $i = 1, 3$. These plots (Fig. 3) confirm that the U_{22}'s are the major contributors to the discrepancies between the two sets of thermal parameters and that the variance therefore contains an anisotropic component. The shape of the U_{22} curve also reveals that the Δ/σ for this type of parameter are nearly normally distributed. The failure of either B & N or G & H to make an absorption

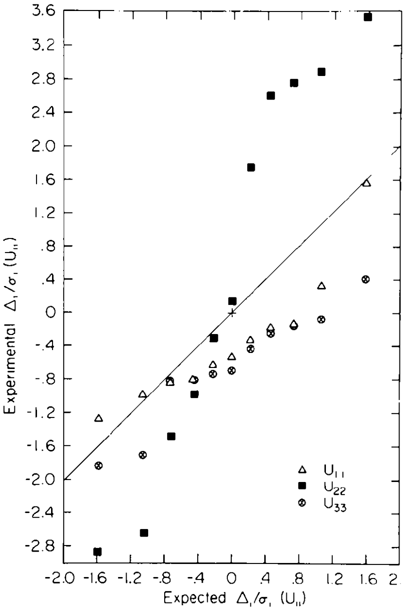

Fig. 3. Normal probability plots of Δ_i/σ_i for the 11 U_{ii} values, $i = 1, 3$. In all cases $\Delta_i = U_{ii}$ (G & H) − U_{ii} (B & N). The line is that expected for normal populations with zero variance and zero mean.

correction ($\mu = 1{\cdot}6$ cm^{-1}) may have contributed to these discrepancies, as might an anisotropic difference in the perfection of the two data crystals. It may also be noteworthy that G & H's data were collected on a Weissenberg geometry diffractometer with the crystal oriented about *b*. The curves for the U_{11}'s and U_{33}'s are more linear than the U_{22} curve and have slopes closer to the ideal value. They do show, however, that the thermal parameters of G & H are generally smaller than those of B & N. This disparity is perhaps also reflected in the slightly smaller size of the G & H unit cell and may be related to temperature (the determinations were carried out at 23 and 18 °C) or crystal perfection. The use of slightly different scattering factors may also have been a contributing factor.

Discussion

The conformation of the molecule and its dimensions are shown in Fig. 4. The thermal parameters for the C and F atoms of the fluorinated phenyl ring and those of the C atoms of the hydrocarbon ring were analyzed for rigid-body thermal motion (Schomaker & Trueblood, 1968). Reasonable agreement between observed and calculated U_{ij} values was obtained when the two ring systems were treated as independent units (Table 2). Both sets of thermal parameters lead to essentially the same picture of rigid-body motion. Bond lengths corrected for rigid-body motion (Cruickshank, 1956) are shown in square brackets on Fig. 4. The only

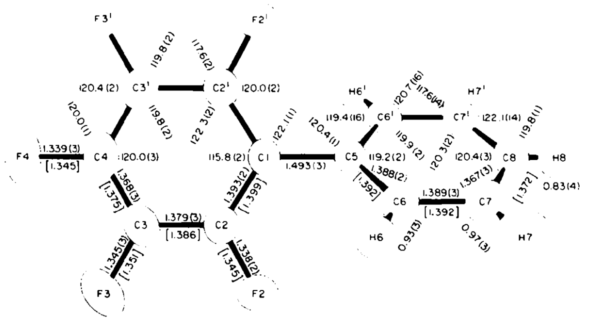

Fig. 4. A drawing of the $C_{12}H_5F_5$ molecule; the shapes of the atoms correspond to 50% contours of thermal motion as determined by B & N. The bond lengths enclosed in brackets have been corrected for thermal motion (see text). The other molecular dimensions have been calculated from the averaged parameters. Standard deviations for the individual determinations were *ca* 2–6 × 10^{-3} Å and 0·2–0·6° for dimensions not involving H atoms.

Table 2. *Results of rigid-body-motion analysis*

The eigenvectors of the libration tensor **L** and translation tensor **T** are referred, in terms of the corresponding direction cosines, to the orthogonal molecular system defined by the eigenvectors of the molecular tensor of inertia **I**. The eigenvectors of **I** are referred to the unit-cell axes.

(i) C_6F_5 ring (11 atoms)

	Eigenvalues		Eigenvectors					
	B & N	G & H	B & N			G & H		
I	329 (at. wt Å^2)	327	0	0·8677	−0·4970	0	0·8676	−0·4972
	490	489	1·0	0	0	1·0	0	0
	819	815	0	−0·4970	−0·8677	0	−0·4972	−0·8676
L	78 × 10^{-4} rad^2	74	0·9923	0	0·1236	1·0	0	−0·0051
	51	52	0	−1·0	0	0	−1·0	0
	39	40	0·1236	0	−0·9923	−0·0051	0	−1·0000
T	436 × 10^{-4} Å^2	468	0·9958	0	0·0918	0·9916	0	−0·1296
	349	338	0	1·0	0	0	1·0	0
	315	304	−0·0918	0	0·9958	0·1296	0	0·9916
$\langle \Delta U^2 \rangle^{1/2}$	0·0021 Å^2	0·0032	(r.m.s. discrepancy)					

(ii) C_6H_5 ring (6 carbon atoms only)

	Eigenvalues		Eigenvectors					
	B & N	G & H	B & N			G & H		
I	68 (at. wt Å^2)	67	1·0	0	0	1·0	0	0
	77	69	0	0·9155	0·4024	0	0·9165	0·4001
	146	136	0	−0·4024	0·9155	0	−0·4001	0·9165
L	45 × 10^{-4} rad^2	81	0	−0·1893	0·9836	0	−0·0611	0·9981
	35	36	1·0	0	0	1·0	0	0
	14	25	0	0·9836	0·1803	0	0·9981	0·0611
T	414 × 10^{-4} Å^2	451	0	0·9354	0·3535	0	0·9990	0·0445
	363	350	1·0	0	0	0	−0·0445	0·9990
	336	339	0	0·3535	−0·9354	1·0	0	0
$\langle \Delta U^2 \rangle^{1/2}$	0·0021 Å^2	0·0044	(r.m.s. discrepancy)					

unusual dimensions are the C(2)–C(1)–C(2′) and C(1)–C(2)–C(3) angles which are compressed and enlarged respectively by 4·2 (2) and 2·3 (2)° from the benzene value of 120°. Similar perturbations have been noted by Domenicano, Vaciago & Coulson (1975) in three other pentafluorophenyl rings. Least-squares planes through the six C atoms of the C_6H_5 and C_6F_5 groups give r.m.s. deviations of 0·003 and 0·001 Å respectively, averaged over the two determinations. Inclusion of the H and F atoms in the planes raises the average deviations by a factor of about three; an inspection of the individual values suggests that the H and F atoms deviate systematically from the C-atom planes (see below). The dihedral angle between the rings is 52·9°, somewhat smaller than the angles of 59·6, 59·5 and 57·9° in the crystal structures of perfluorobiphenyl (Gleason & Britton, 1976), 2*H*-nonafluorobiphenyl (Hamor & Hamor, 1978) and 2,3,5,6-tetrafluorobiphenyl. The most closely related compound for which a gas-phase value is available is 2-fluorobiphenyl which has a corresponding angle of 49 (5)° (Bastiansen & Smedvik, 1954). The inter-ring bond has a length of 1·493 Å (uncorrected for thermal motion), very similar to the corresponding lengths in perfluorobiphenyl and 2*H*-nonafluorobiphenyl (both 1·486 Å), in tetrafluorobiphenyl (1·492 Å) and in the near-planar parent hydrocarbon where its length is 1·494 Å (Robertson, 1961). There does not, therefore, appear to be any correlation between the inter-ring angle and the inter-ring bond length.

The aromatic C—C bonds range from 1·372 to 1·399 Å, mean 1·386 Å (corrected for thermal motion). This compares with means of 1·381 Å in perfluorobiphenyl, 1·385 Å in 2*H*-nonafluorobiphenyl, 1·384 Å in tetrafluorobiphenyl and 1·390 Å in biphenyl (Robertson, 1961; Charbonneau & Delugeard, 1976, 1977). Thus, as has been noted previously [Hamor & Hamor, 1976 (and references therein)] the C—C bonds in the fluorinated systems are slightly shorter than in the parent hydrocarbon. However, considering the two rings separately, this effect is not apparent. The mean C—C length is virtually the same for both the fluorinated and the hydrocarbon ring.

The C—F bond lengths range from 1·345 to 1·351 Å, mean 1·347 Å (corrected), similar to the means in perfluorobiphenyl (1·344 Å) and 2*H*-nonafluorobiphenyl (1·351 Å), but somewhat shorter than in tetrafluorobiphenyl where the mean is 1·360 Å.

An examination of packing diagrams reveals the presence of stacks of molecules along *c* in which the C_6H_5 and C_5F_5 groups alternate and are nearly parallel. The 2_1 symmetry axes pass through the C(1)—C(5) bonds, and the two types of rings are rotated in opposite directions by similar amounts. The displacement along *a* of the ring centers within the stack is 0·79 Å. The molecular overlap diagrams in Figs. 5 and 6 show that each C_6H_5 ring interacts more strongly with one half of the adjoining C_6F_5 rings than with the other. The angle between the two types of planes is 5·5°; consequently, the interacting parts of the rings are closer than they would be if strictly parallel. The deviations of both the F (0·026 and 0·036 Å) and H (0·046 and 0·006 Å) atoms from their respective C-atom planes are also in the direction of the nearer member of the stack. The perpendicular distance from the center of the phenyl ring to the plane of the fluorinated ring is 3·43 Å; some individual interatomic distances are given in Table 3. No important interactions between stacks are apparent, all intermolecular contact distances being greater than the sum of the van der Waals radii of the atoms concerned.

The question remains as to the nature of the intermolecular interactions in these crystals. Their unexpec-

Table 3. *Interatomic contacts* (Å) *less than* 3·65 Å *between rings in the stack*

F(2)···C(6)	3·373 (3)	F(2)···H(6)	3·58 (3)
F(3)···H(8)	3·421 (2)	C(3)···H(8)	3·575 (7)
C(3)···C(8)	3·506 (2)	F(2)···C(7)	3·580 (3)
F(3)···C(8)	3·510 (2)	C(2)···C(7)	3·614 (3)
F(2)···C(5)	3·545 (2)	C(1)···C(6)	3·619 (2)

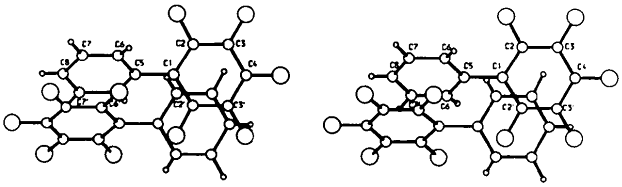

Fig. 5. A stereoscopic view showing the overlap of two $C_{12}H_5F_5$ molecules.

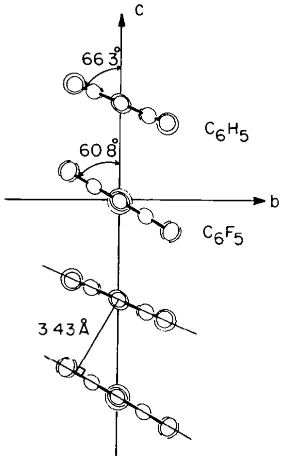

Fig. 6. Projection of a stack of C_6H_5 and C_6F_5 rings onto the *bc* plane.

tedly high melting point is evidence for the existence of stronger forces than are often found in molecular crystals; their rapid growth along the stack axis *c* suggests that these forces are directional. It is possible that the π orbitals of the C_6H_5 and C_6F_5 rings interact since the crystalline arrangement meets Herbstein's (1971) structural criteria for a donor–acceptor complex. These requirements include the presence of mixed stacks of potential donors and acceptors in which the essentially planar components are inclined between 20 and 30° to the stack axis and are separated by a perpendicular distance of 3·2 to 3·5 Å.

Compared with the addition compounds studied by Dahl (1971, 1973, 1975*a*,*b*), the stack angles in $C_{12}H_5F_5$ are 5 to 10° larger, and the interplanar separation is smaller than in the four complexes of C_6F_6 with various methyl-substituted benzenes. Only in the hexamethylbenzene complex (Dahl, 1973), which was studied at −40°C, is the mean interplanar distance (3·43 Å) less than 3·5 Å. In spite of the covalent linkage between the two types of aromatic rings, the solid-state interactions in $C_{12}H_5F_5$ appear to be at least as strong as those in the hexafluorobenzene addition compounds. Still, the fact remains that except in unusual circumstances (Filler & Choe, 1969) no charge-transfer band of the type normally associated with π complexes has ever been seen when the potential acceptor is a polyfluorinated aromatic hydrocarbon. Therefore the interactions in this crystal are probably not of the conventional π-donor/π-acceptor type. The data do indicate, however, the presence of important directional intermolecular forces. Their origin is not yet clear; possibilities include London dispersion forces and attractions between the permanent dipoles of the C—H and C—F bonds.

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