The Structure of Perfluorotris(dihydrocyclopenta)benzene*

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Abstract. $C_{15}F_{18}$, $M_r = 522 \cdot 14$, orthorhombic, *Pbcn*, $a = 17 \cdot 845$ (4), $b = 17 \cdot 998$ (7), $c = 10 \cdot 143$ (4) Å, $V = 3257 \cdot 67$ Å^3, $Z = 8$, $D_c = 2 \cdot 129$, $D_o = 2 \cdot 10$ Mg m^{-3}. 1568 observed reflections collected at 173 K have been used to determine a model ($R = 0 \cdot 065$) in which an aromatic ring is attached to three nonplanar perfluorocyclopentane rings each of which exhibits a partly opened envelope conformation. The bond lengths within the six-membered ring are equal (within errors) and have an average value of $1 \cdot 39$ (1) Å.

Introduction. Precession and Weissenberg photography was used to determine the room-temperature cell dimensions and space group. A suitable crystal for data collection ($0 \cdot 46 \times 0 \cdot 30 \times 0 \cdot 25$ mm) was sealed in a Lindemann-glass capillary and mounted on the copper tip of a cryogenic goniometer head (the AC-1-101 A Cryo-tip refrigerator, Air Products and Chemical Inc.) so as to allow maximum transfer of heat between cold head and crystal. Accurate cell dimensions at 173 K were determined by least-squares refinement of 18 accurately measured reflections ($2\theta = 24 \cdot 7–31 \cdot 1°$, Mo $K\alpha_1$ radiation, $\lambda = 0 \cdot 70926$ Å). Data were collected on a Picker FACS-I automatic four-circle diffractometer using a graphite monochromator and a scintillation counter with pulse-height discrimination. Symmetrical θ–2θ scans ($2°$ min^{-1}) were used, whilst stationary-crystal–stationary-counter background counts were taken for 40% of the scan time at each scan limit. Intensities were measured for 2152 independent reflections ($2\theta \leq 45°$) of which 1568 were classed observed $[I \geq 2 \cdot 3\sigma(I)]$. During data collection there was a 13% drop in intensity. The intensity data were appropriately corrected. Lorentz and polarization factors were applied, but no absorption correction was made ($\mu = 0 \cdot 297$ mm^{-1}).

The structure was solved using *MULTAN*. The best solution revealed most of the atoms, the remaining atoms being located in difference Fourier syntheses. After assignment of electron density to what was thought to be all the atoms of the molecule, the

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Table 1. *Final fractional positional parameters* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = |\tfrac{1}{3}(U_{11}^2 + U_{22}^2 + U_{33}^2)|^{1/2}.$$

	x	y	z	U_{eq} or U^*
F(21)	2688 (3)	1854 (3)	998 (7)	139 (5)
F(22)	2576 (4)	2475 (3)	2713 (5)	182 (6)
F(31)	1242 (3)	1672 (3)	1887 (5)	99 (4)
F(32a)	1649 (6)	1655 (6)	88 (11)	79 (8)
F(32b)	1327 (4)	2652 (4)	2886 (6)	84 (5)
F(41)	850 (3)	2436 (4)	−404 (4)	151 (5)
F(42)	562 (3)	3088 (4)	1216 (6)	117 (4)
F(71)	872 (2)	3894 (2)	−2403 (4)	67 (3)
F(72)	392 (2)	4300 (2)	−578 (4)	66 (3)
F(81)	978 (2)	5323 (3)	−2780 (5)	92 (3)
F(82)	1104 (2)	5537 (2)	−692 (5)	81 (3)
F(91)	2344 (2)	4857 (2)	−2990 (3)	68 (3)
F(92)	2471 (2)	5648 (2)	−1404 (4)	73 (3)
F(121)	3926 (2)	4741 (2)	−1625 (3)	50 (2)
F(122)	3755 (2)	5172 (2)	355 (4)	62 (3)
F(131)	4651 (2)	3624 (3)	−798 (4)	84 (3)
F(132)	4838 (2)	4302 (3)	931 (4)	90 (3)
F(141)	4080 (2)	2737 (2)	846 (5)	93 (3)
F(142)	3881 (2)	3595 (2)	2276 (4)	72 (3)
C(1)	2411 (3)	3115 (3)	735 (5)	33 (1)
C(2)	2324 (4)	2417 (4)	1521 (7)	53 (5)
C(3a)	1558 (10)	2119 (11)	1098 (21)	47 (5)
C(3b)	1494 (6)	2333 (6)	1770 (13)	44 (3)
C(4)	1129 (4)	2783 (4)	612 (6)	46 (4)
C(5)	1731 (3)	3332 (3)	218 (6)	31 (1)
C(6)	1682 (3)	3956 (3)	−581 (5)	29 (1)
C(7)	1020 (3)	4275 (3)	−1293 (6)	42 (2)
C(8)	1280 (4)	5063 (4)	−1677 (7)	55 (2)
C(9)	2139 (4)	5013 (4)	−1736 (7)	45 (2)
C(10)	2320 (3)	4369 (3)	−846 (5)	31 (1)
C(11)	3009 (3)	4165 (3)	−284 (5)	30 (1)
C(12)	3758 (3)	4547 (3)	−384 (6)	38 (2)
C(13)	4314 (4)	3984 (4)	198 (6)	45 (2)
C(14)	3835 (4)	3428 (4)	985 (6)	43 (2)
C(15)	3058 (3)	3540 (3)	485 (5)	29 (1)

* All F atoms and C(2) and C(4) have been refined anisotropically; all other C atoms have been refined isotropically.

subsequent difference Fourier map revealed a number of strong residual peaks around the perfluorocyclopentyl ring C(1)–C(5). We were able to account for these peaks in terms of a disordered model involving C(3), F(31) and F(32). Two arrangements were found

in which atoms C(3), F(31) and F(32) were flipped either upwards or downwards with respect to the C(1), C(2), C(4), C(5) plane. After refinement, the ratio of occupancies for C(3a):C(3b) and F(32a):F(32b) showed very good agreement and a fixed average ratio of 0·3955:0·6045 was used in final refinement cycles. Although F(31) is also disordered, the mode of disorder is such that F(31a) and F(31b) would have very similar coordinates. A difference synthesis showed spurious peaks about C(2) and C(4) of the disordered cyclopentyl ring. This observation and the relatively high isotropic temperature factors of these atoms indicate that they are probably also disordered. Since two positions could not be resolved (nor expected to be), the best approximation was considered to be the refinement of anisotropic temperature factors of these atoms.

The major features in the final difference map were a few peaks and troughs adjacent to the disordered cyclopentyl ring, which were up to five times the estimated standard error (0·09 e $Å^{-3}$).

All F atoms were refined anisotropically, as were C(2) and C(4). The remaining C atoms were refined isotropically. The agreement factors settled at $R = 0·065$ $(R = \sum ||F_o| - |F_c||/\sum |F_o|)$ and $R_w = 0·072$ $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ for 246 variables. Weights were assigned to the F_o's on the basis of their standard deviations $[w = 1/\sigma(F^2)]$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The computer programs have been cited elsewhere (Einstein & Jones, 1972).

Final positional parameters are listed in Table 1.*

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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 36250 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
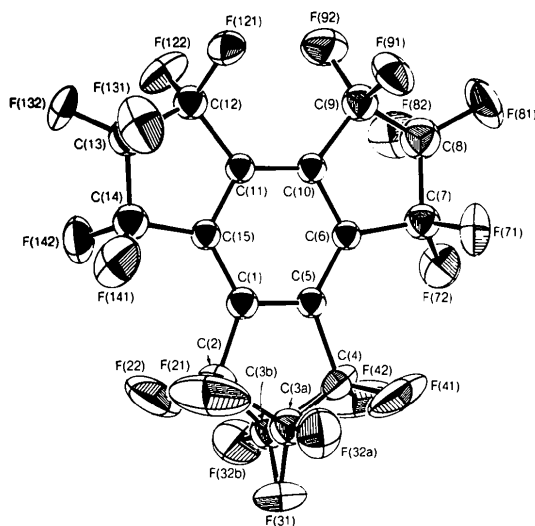

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule. The thermal ellipsoids are shown with 50% probability.

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(1)–C(5)	1·378 (7)		C(10)–C(11)	1·403 (7)
C(5)–C(6)	1·387 (8)		C(11)–C(15)	1·373 (8)
C(6)–C(10)	1·388 (7)		C(15)–C(1)	1·408 (8)
C(1)–C(2)	1·496 (8)		C(7)–C(8)	1·542 (9)
C(2)–C(3a)	1·529 (18)		C(8)–C(9)	1·539 (9)
C(2)–C(3b)	1·510 (13)		C(9)–C(10)	1·504 (8)
C(3a)–C(4)	1·501 (18)		C(11)–C(12)	1·507 (8)
C(3b)–C(4)	1·568 (13)		C(12)–C(13)	1·536 (8)
C(4)–C(5)	1·513 (8)		C(13)–C(14)	1·540 (9)
C(6)–C(7)	1·498 (8)		C(14)–C(15)	1·489 (8)
C(2)–F(21)	1·315 (8)		C(8)–F(82)	1·351 (8)
C(2)–F(22)	1·294 (8)		C(8)–F(81)	1·327 (8)
C(3a)–F(31)	1·268 (18)		C(9)–F(92)	1·331 (7)
C(3a)–F(32a)	1·332 (21)		C(9)–F(91)	1·352 (7)
C(3b)–F(31)	1·279 (11)		C(12)–F(121)	1·340 (6)
C(3b)–F(32b)	1·304 (14)		C(12)–F(122)	1·352 (6)
C(4)–F(42)	1·305 (7)		C(13)–F(131)	1·342 (7)
C(4)–F(41)	1·304 (7)		C(13)–F(132)	1·324 (7)
C(7)–F(71)	1·345 (7)		C(14)–F(142)	1·346 (7)
C(7)–F(72)	1·335 (7)		C(14)–F(141)	1·326 (7)
C(1)–C(5)–C(6)	120·5 (5)		C(2)–C(1)–C(5)	110·4 (5)
C(5)–C(6)–C(10)	119·6 (5)		C(1)–C(5)–C(4)	109·8 (5)
C(6)–C(10)–C(11)	120·0 (5)		C(7)–C(6)–C(10)	110·4 (5)
C(10)–C(11)–C(15)	120·1 (5)		C(6)–C(10)–C(9)	110·6 (5)
C(11)–C(15)–C(1)	119·6 (5)		C(12)–C(11)–C(15)	110·8 (5)
C(15)–C(1)–C(5)	120·0 (5)		C(11)–C(15)–C(14)	111·4 (5)
C(15)–C(1)–C(2)	129·5 (5)		C(10)–C(11)–C(12)	129·1 (5)
C(5)–C(6)–C(7)	129·9 (5)		C(14)–C(15)–C(1)	129·0 (5)
C(9)–C(10)–C(11)	129·3 (5)		C(4)–C(5)–C(6)	129·7 (5)
C(1)–C(2)–F(21)	112·4 (6)		C(7)–C(8)–F(82)	108·9 (6)
C(1)–C(2)–F(22)	113·2 (6)		C(7)–C(8)–F(81)	114·6 (6)
C(1)–C(2)–C(3a)	103·7 (8)		C(7)–C(8)–C(9)	104·8 (6)
C(1)–C(2)–C(3b)	105·9 (7)		C(9)–C(8)–F(82)	107·2 (6)
C(3a)–C(2)–F(21)	93·4 (9)		C(9)–C(8)–F(81)	113·1 (6)
C(3a)–C(2)–F(22)	126·9 (10)		F(82)–C(8)–F(81)	107·9 (6)
C(3b)–C(2)–F(21)	118·4 (7)			
C(3b)–C(2)–F(22)	101·1 (8)			
F(21)–C(2)–F(22)	105·5 (7)		C(8)–C(9)–F(92)	112·6 (6)
			C(8)–C(9)–F(91)	108·6 (5)
C(2)–C(3a)–F(31)	116·3 (14)		C(8)–C(9)–C(10)	103·6 (5)
C(2)–C(3a)–F(32a)	109·1 (14)		C(10)–C(9)–F(92)	114·4 (5)
C(2)–C(3a)–C(4)	105·6 (12)		C(10)–C(9)–F(91)	110·3 (5)
C(4)–C(3a)–F(31)	119·1 (14)		F(92)–C(9)–F(91)	107·2 (5)
C(4)–C(3a)–F(32a)	108·0 (14)			
F(31)–C(3a)–F(32a)	98·1 (14)			
			C(11)–C(12)–F(121)	112·3 (5)
C(2)–C(3b)–F(31)	117·0 (9)		C(11)–C(12)–F(122)	109·8 (5)
C(2)–C(3b)–F(32b)	109·0 (10)		C(11)–C(12)–C(13)	104·3 (5)
C(2)–C(3b)–C(4)	103·3 (8)		C(13)–C(12)–F(121)	112·9 (5)
C(4)–C(3b)–F(31)	113·9 (9)		C(13)–C(12)–F(122)	109·8 (5)
C(4)–C(3b)–F(32b)	109·2 (9)		F(121)–C(12)–F(122)	107·8 (5)
F(31)–C(3b)–F(32b)	104·4 (10)			
			C(12)–C(13)–F(131)	108·6 (5)
C(5)–C(4)–F(42)	113·6 (5)		C(12)–C(13)–F(132)	112·8 (5)
C(5)–C(4)–F(41)	112·1 (5)		C(12)–C(13)–C(14)	105·6 (5)
C(5)–C(4)–C(3a)	104·2 (8)		C(14)–C(13)–F(131)	109·0 (5)
C(5)–C(4)–C(3b)	103·9 (6)		C(14)–C(13)–F(132)	112·4 (5)
C(3a)–C(4)–F(42)	125·1 (10)		F(131)–C(13)–F(132)	108·4 (5)
C(3a)–C(4)–F(41)	94·2 (10)			
C(3b)–C(4)–F(42)	100·8 (7)		C(13)–C(14)–F(142)	109·0 (5)
C(3b)–C(4)–F(41)	120·2 (7)		C(13)–C(14)–F(141)	111·8 (5)
F(42)–C(4)–F(41)	106·1 (6)		C(13)–C(14)–C(15)	104·6 (5)
			C(15)–C(14)–F(142)	111·0 (5)
C(6)–C(7)–F(71)	111·3 (5)		C(15)–C(14)–F(141)	113·4 (5)
C(6)–C(7)–F(72)	114·4 (5)		F(142)–C(14)–F(141)	107·0 (6)
C(6)–C(7)–C(8)	103·8 (5)			
C(8)–C(7)–F(71)	108·4 (5)			
C(8)–C(7)–F(72)	111·0 (5)			
F(71)–C(7)–F(72)	107·9 (5)			

Discussion. The molecular structure and bond parameters are shown in Fig. 1 and Table 2 respectively. The perfluorocyclopentyl rings are nonplanar and have a partially opened envelope conformation as found in $C_{20}F_{24}$, perfluorotetrakis(dihydrocyclopenta)cyclooctene (Cobbledick & Einstein, 1977). Mean-plane calculations are shown in Table 3. The flap angles (18–26°) are similar to the values of 19 and 26° in $C_{20}F_{24}$, 20·5° in perfluorocyclopentene* (Chang & Bauer, 1971) and 29 (1)° in cyclopentene* (Davis & Muecke, 1970).

The geometry and planarity of the six-membered carbon core of the molecule are consistent with complete electron delocalization in the ring, similar to that observed in the non-fluorinated analogue $C_{15}H_{18}$, tris(cyclopenta)benzene (Boyko & Vaughan, 1964), and

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* These values were determined by gas-phase electron diffraction.

Table 3. *Mean-plane calculations*

(i) Deviations of atoms (Å) from least-squares planes

(The equations of the planes are referred to orthogonal axes *a*, *b'* and *c**.)

(*a*) Plane through C(1), C(2), C(4), C(5)

$0·1868x - 0·5395y - 0·8210z + 2·8365 = 0; \chi^2 = 0·78$

C(1)	0·003 (6)	C(5)	−0·003 (6)
C(2)	−0·002 (7)	C(3a)†	0·38 (2)
C(4)	0·002 (6)	C(3b)†	−0·40 (1)

(*b*) Plane through C(6), C(7), C(9), C(10)

$0·1983x - 0·5734y - 0·7949z + 3·0124 = 0; \chi^2 = 3·34$

C(6)	−0·006 (5)	C(10)	0·006 (6)
C(7)	0·004 (6)	C(8)†	−0·407 (7)
C(9)	−0·004 (7)		

(*c*) Plane through C(11), C(12), C(14), C(15)

$0·2180x - 0·5441y - 0·8102z + 2·6751 = 0; \chi^2 = 0·01$

C(11)	0·000 (5)	C(15)	0·000 (5)
C(12)	0·000 (6)	C(13)	0·289 (6)
C(14)	0·000 (6)		

(*d*) Plane through C(1), C(5), C(6), C(10), C(11), C(15)

$0·1862x - 0·5594y - 0·8077z + 2·9472 = 0; \chi^2 = 17·84$

C(1)	0·010 (6)	C(10)	0·012 (6)
C(5)	−0·011 (6)	C(11)	−0·013 (5)
C(6)	−0·000 (5)	C(15)	0·002 (5)

(ii) Flap angles (°) for perfluorocyclopentyl rings

Out-of-plane atom	Flap angle
C(3a)	25
C(3b)	−25
C(8)	−26
C(13)	18

† These atoms have not been included in the mean-plane calculations.

Table 4. *Comparison of bond distances (Å) in perfluorocyclopentyl rings*

Bond type	$C_{15}F_{18}$	$C_{20}F_{24}$	C_5F_8
av. C−F	1·34 (1)	1·33 (1)	–
av. −C−C−	1·539 (9)	1·524 (4)	1·539 (13)
av. =C−C−	–	1·497 (4)	1·510 (9)
av. ≃C−C−	1·500 (8)	–	–
av. −C=C−	–	1·326 (5)	1·342
av. −C≃C−	1·38 (1)	–	–

$C_{12}F_{12}$, perfluorotris(dihydrocyclobuta)benzene (Cobbledick & Einstein, 1976; Thummel, Korp, Bernal, Harlow & Soulen, 1977). The average C−C distance and internal C−C−C angle for the ring are 1·390 (14) Å and 119·9 (5)° respectively [*cf.* 1·387 (9) Å and 120·0 (7)° in $C_{12}F_{12}$ and 1·38 (2) Å and 120 (2)° in $C_{15}H_{18}$].

The average C−C and C−F bond lengths associated with the two ordered perfluorocyclopentyl rings in the present delocalized system show good agreement with those found in the localized $C_{20}F_{24}$ (Cobbledick & Einstein, 1977) and perfluorocyclopentene (Chang & Bauer, 1971) systems (Table 4).

Not surprisingly the geometry of the disordered perfluorocyclopentyl ring is not totally consistent with those of the two ordered rings. There are no short intermolecular interactions.

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