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Perfluoro-1,2-3,4-5,6-triethanobenzene

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Abstract. $C_{12}F_{12}$, $M=372{\cdot}13$, hexagonal, space group $P6_3/m$; $a=8{\cdot}977$ (3), $c=8{\cdot}757$ (4) Å, $V=611{\cdot}1$ Å^3; $Z=2$, $D_c=2{\cdot}022$, $D_o=2{\cdot}00$ g cm^{-3}. The structure was solved by Patterson methods from Mo $K\alpha$ X-ray diffractometer intensities and refined by full-matrix least squares to a final R of 0·079 for 295 observed reflexions. A model in which the molecule has $\bar{6}$ symmetry with the C atoms lying in a crystallographic mirror plane provides satisfactory agreement.

Introduction. Crystals sublimed at room temperature and were sealed in Lindemann glass capillaries. Photographs taken with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) showed the crystals to have Laue symmetry $6/m$ and systematic absences $00l$, $l=2n+1$ indicated space groups $P6_3$ or $P6_3/m$.

A crystal $0{\cdot}3\times0{\cdot}3\times0{\cdot}3$ mm was used in the measurement of cell dimensions and for the collection of intensities on a Picker FACS-I diffractometer with Mo $K\alpha$ radiation [$\lambda(K\alpha_1)=0{\cdot}70926$ Å]. Cell dimensions were obtained by a least-squares fit of 2θ values of six reflexions with $2\theta>30°$. Intensities were collected with Nb-filtered Mo $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The reflexions were scanned by the θ–2θ method with a scan width of 1·4° (increased for dispersion) and a scan speed of 2° min^{-1}. The take-off angle was 3·5°. At each scan limit the background was measured for 20 s. The scan intensities were corrected for background (normalized to the scan time) and for Lorentz and polarization effects but not for absorption [μ(Mo $K\alpha$) = 2·72 cm^{-1}]. Intensities of 400 reflexions with $2\theta\leq50°$ were measured, of which 105 were regarded as unobservable ($I\leq2{\cdot}3\sigma I$, where σI is the standard deviation).

The intensity statistics indicated a centrosymmetric structure and the space group was initially assumed to be $P6_3/m$. For an ordered structure with $Z=2$ this requires the molecule to have $\bar{6}$ symmetry. This was considered reasonable and the unsharpened Patterson function was used to obtain the orientation of a trial model. Least-squares refinement with anisotropic temperature parameters gave a final $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}079$ with a maximum shift to error ratio of 0·02 on the last cycle.

In view of the large amplitudes of vibration of the F atoms in the **c** direction, attempts were made to refine a model in space group $P6_3$. This model was obtained by puckering the outer atoms (F and C) a small amount to destroy the mirror symmetry. No

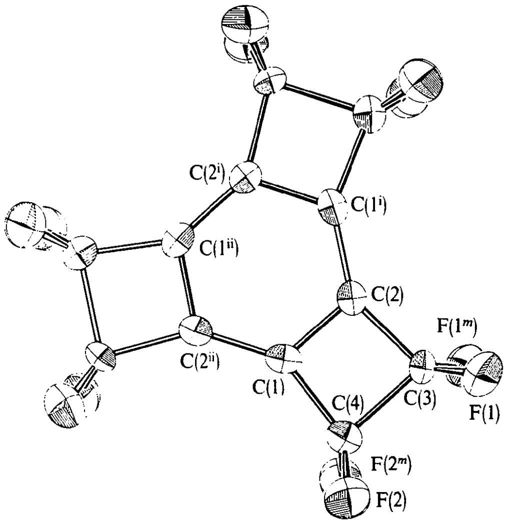

Fig. 1. Perspective view of perfluoro-1,2-3,4-5,6-triethanobenzene, parallel to the c axis, drawn by *ORTEP* (Johnson, 1965). The thermal ellipsoids are shown with 50% probability.

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Table 1. *Final atomic parameters*

The values of the atomic fractional coordinates and their estimated standard deviations (in parentheses) are multiplied by 10^4. The thermal parameters are anisotropic U_{ij} values (Å$^2\times10^4$) in the form

$$\exp\,[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	5069 (9)	7861 (10)	2500	192 (41)	290 (44)	495 (59)	113 (34)	0	0
C(2)	3885 (10)	8419 (10)	2500	258 (43)	236 (42)	531 (59)	133 (34)	0	0
C(3)	5225 (10)	10291 (10)	2500	274 (45)	181 (41)	726 (71)	124 (35)	0	0
C(4)	6593 (11)	9652 (10)	2500	250 (45)	307 (48)	749 (78)	150 (39)	0	0
F(1)	5273 (4)	11193 (4)	3731 (5)	447 (23)	338 (20)	1009 (35)	148 (18)	−20 (21)	−201 (20)
F(2)	7599 (4)	10153 (5)	3736 (5)	453 (22)	445 (23)	1073 (37)	216 (18)	−294 (25)	−186 (25)

significant improvement in agreement was achieved and we attribute this to the extensive correlation between parameters of pseudo-symmetrically related atoms. It may also be noted that the carbon skeleton in perfluorocyclobutene (Chang, Porter & Bauer, 1971) was found to be planar.

Only the results from the $P6_3/m$ refinement are reported here. No significant peaks were found on the final difference map. Scattering factors were taken from Cromer & Waber (1965) and in the final cycles of refinement the weighting scheme was $w=1/\sigma(F)^2$ where $\sigma(F)$ is the standard deviation in F. The programs used in the structure determination and refinement have been described elsewhere (Einstein & Jones, 1972).

Final positional and thermal parameters are shown in Table 1* and bond lengths and angles in Table 2. A perspective view of the molecule and the atom labelling are shown in Fig. 1.

Discussion. The choice of $P6_3/m$ required the molecule to have $\bar{6}$ symmetry with the C atoms lying in a crystallographic mirror plane. Bond lengths were corrected for thermal motion by analysis of the vibrational parameters in terms of rigid-body motion. The molecule has site symmetry $\bar{6}$ and the screw tensor is zero (Schomaker & Trueblood, 1968). Comparison of the 'observed' U_{ij} values with those calculated from the **T** and **L** tensors showed the F atoms to have independent motion (r.m.s. ΔU_{ij} of 0·0059 compared with an average σU_{ij} of 0·0037 Å^2). Inclusion of only the C atoms in the rigid-body model gave satisfactory agreement between the 'observed' and calculated U_{ij} values (r.m.s.ΔU_{ij} of 0·0037 compared with an average σU_{ij} of 0·0047 Å^2). The bond distances and angles were corrected for thermal motion by assuming rigid-body motion for the C and 'riding' motion for the F atoms. Corrected bond lengths are shown in Table 2.

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

Values for perfluorocyclobutene (Chang *et al.*, 1971) are included for comparison.

	Uncorrected	Corrected for libration	Perfluoro-cyclobutene
C(1)–C(2)	1·383 (9)	1·386	1·342 (2)
C(1)–C(2^{ii})	1·391 (9)	1·393	–
C(1)–C(4)	1·502 (9)	1·504	1·508 (1)
C(2)–C(3)	1·500 (10)	1·502	1·508 (1)
C(3)–C(4)	1·594 (9)	1·597	(1·595)
C(3)–F(1)	1·335 (5)	1·359	1·336 (2)
C(4)–F(2)	1·335 (5)	1·361	1·336 (2)

	Uncorrected	Perfluoro-cyclobutene
C(2)—C(1)–C(2^{ii})	120·8 (7)	–
C(2)—C(1)–C(4)	93·8 (6)	94·8 (1)
C(2^{ii})–C(1)–C(4)	145·4 (6)	–
C(1)—C(2)–C(1^{i})	119·2 (7)	–
C(1)—C(2)–C(3)	94·3 (5)	94·8 (1)
C(1^{i})–C(2)–C(3)	146·5 (6)	–
C(2)—C(3)–F(1)	116·4 (4)	115·9 (2)
F(1)—C(3)–C(4)	114·9 (4)	(114·5)
C(2)—C(3)–C(4)	85·8 (5)	(85·2)
C(1)—C(4)–F(2)	117·5 (4)	115·9 (2)
C(1)—C(4)–C(3)	86·1 (5)	(85·2)
C(3)—C(4)–F(2)	113·1 (5)	(114·5)
F(1)—C(3)–F(1^{m})	107·6 (5)	(109·2)
F(2)—C(4)–F(2^{m})	108·3 (6)	(109·2)

Electron and X-ray diffraction studies of a number of cyclobutane and cyclobutene derivatives have shown long C–C lengths in the range 1·55–1·60 compared with the usually accepted value of 1·54 Å. An early electron diffraction study of cyclobutane (Dunitz & Schomaker, 1952) gave a C–C$_{av}$ length of 1·56$_8$ ± 0·02 Å but a more recent investigation (Almenningen, Bastiansen & Skancke, 1961) gave 1·548 (3) Å. An electron diffraction study of cyclobutene (Goldish, Hedberg & Schomaker, 1956) gave a C–C$_{av}$ length of 1·537 ± 0·010 Å and it was deduced that the two types of single bonds (=C–C– and –C–C–) probably did not differ by more than 0·06 Å. A more precise microwave determination (Bak, Led, Nygaard, Rastrup-Andersen & Sørensen, 1969) gave distances of 1·517 (3) and 1·566 (3) Å for the two types of single bonds. Electron diffraction studies of perfluorocyclobutane and perfluorocyclobutene (Chang, Porter & Bauer, 1971) indicated that F substitution shortens the =C–C– bond by approximately 0·01 and increases the –C–C– bond by about 0·03 Å in the cyclobutene ring but did not have such a large effect on the cyclobutane ring. Bond lengths and angles in perfluoro-1,2-3,4-5,6-triethanobenzene are very similar to the comparable ones in perfluorocyclobutene which are shown for comparison in Table 2. There are no short intermolecular contacts in the structure.

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References

ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1961). *Acta Chem. Scand.* **15**, 711–712.

BAK, B., LED, J. J., NYGAARD, L., RASTRUP-ANDERSEN, J. & SØRENSEN, G. O. (1969). *J. Mol. Struct.* **3**, 369–378.

CHANG, C. H., PORTER, R. F. & BAUER, S. N. (1971). *J. Mol. Struct.* **7**, 89–99.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DUNITZ, J. D. & SCHOMAKER, V. (1952). *J. Chem. Phys.* **20**, 1703–1707.

EINSTEIN, F. W. B. & JONES, R. D. G. (1972). *Inorg. Chem.* **11**, 395–400.

GOLDISH, E., HEDBERG, K. & SCHOMAKER, V. (1956). *J. Amer. Chem. Soc.* **78**, 2714–2716.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31706 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.