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anti-8,16-Difluorometacyclophane-1,9-diene

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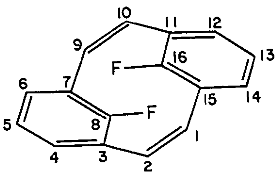
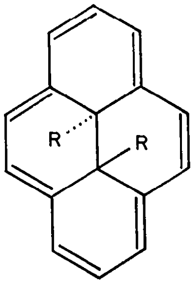
Abstract. $C_{16}H_{10}F_2$, monoclinic, $P2_1/c$; $a=14{\cdot}22$ (1), $b=7{\cdot}072$ (5), $c=12{\cdot}05$ (1) Å, $\beta=114{\cdot}0$ (1)° (20°C); F.W. 240·2, $D_m=1{\cdot}43$ g cm^{-3}, $Z=4$, $D_x=1{\cdot}44$ g cm^{-3}. Molecular symmetry centre for each of two independent molecules.

Introduction. As this compound (I) was initially assigned the *syn* conformation (Boekelheide & Anderson, 1973), it is evident that the most important result of the present analysis is implicit in the title.



(I)



(II)

The crystals were deep green, opaque, and of reasonably compact habit. Although the space group was determined (from single-crystal photographs) unequivocally, the diffraction pattern was characterized by a remarkable pseudosymmetry, with the following properties. Reflexions with l even, and with indices related by the transformation hkl: $\bar{h}+l,k,l$ are of nearly equal intensity. The plane containing reflexions $\bar{h}k2h$ (invariant under this transformation) is inclined at 88·9° (and thus, nearly perpendicular) to **a***. The transformation is very nearly equivalent to reflexion in this plane. In addition, reflexions $hk0$ are very weak when h is odd, as are reflexions $\bar{h}k2h$ when $h+k$ is odd. As a result, the ($h0l$) zone of reflexions has the symmetry and absences characteristic of the plane group *Pgg*. This pseudosymmetry has venerable antecedents, having been reported by Robertson, Prasad & Woodward (1936) for crystals of stilbene, azobenzene and tolan. In these structures, as in that reported here, two centrosymmetrical molecules occupy crystallographically different centres of symmetry.

The specimen used for intensity measurements (0·2 × 0·3 × 0·2 mm) was mounted about **b**. The intensities of 1877 independent reflexions within the limiting sphere $2\theta=130°$ were measured on a Picker four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation and a scintillation counter. The θ–2θ scan mode was used, with scans of 2° for $2\theta<100°$ and 3° otherwise. Background intensities were not measured individually, but were estimated from an experimentally determined function of θ. 409 reflexions were considered to be unobserved, as their net intensities were less than either 100 counts or 10% of the corresponding background intensity. No correction was made for absorption ($\mu=10{\cdot}3$ cm^{-1}).

The structure was determined by the routine application of symbolic addition procedures, with all non-hydrogen atoms readily located in the E map. Refinement was by the block-diagonal least-squares method; the quantity minimized was $\sum w\Delta F^2$, where $w=w_1w_2$ with

$$\begin{aligned} w_1 &= F_o/12{\cdot}5 \text{ for } F_o<12{\cdot}5\\ &= 12{\cdot}5/F_o \text{ otherwise, and}\\ w_2 &= \sin^2\theta/0{\cdot}25 \text{ for } \sin^2\theta<0{\cdot}25\\ &= 1 \text{ otherwise.}\end{aligned}$$

This weighting scheme was found to be effective in removing systematic dependence of the weighted residual on F_o and θ. The H atoms were assigned physically reasonable positions and were included in the refinement. The final R (for observed reflexions only) was 0·054. The maximum final coordinate shift of a non-hydrogen atom was one quarter of the corresponding e.s.d. The final coordinates are given in Table 1.*

Although there can be no doubt of the essential correctness of the proposed structure, some anomalies in the final ΔF synthesis suggest the presence of small proportions of other chemical species. This point will be discussed further; meanwhile it must be emphasized that, as a result, the atomic parameters may suffer some systematic error.

The computer programs used were those of Ahmed, Hall, Pippy & Huber (1966). Scattering factors were taken from Stewart, Davidson & Simpson (1965) for H, and from Hanson, Herman, Lea & Skillman (1964).

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* A list of atomic thermal-motion parameters (anisotropic for the non-hydrogen atoms) and structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31051 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic positions* $\times 10^4$ *for the non-hydrogen atoms,* $\times 10^3$ *for the hydrogen atoms*

	x	y	z
Molecule *A*			
C(1)	138 (2)	7269 (4)	1649 (3)
C(2)	1034 (2)	6358 (5)	2048 (3)
C(3)	1292 (2)	4753 (4)	1442 (2)
C(4)	1708 (2)	3098 (4)	2089 (3)
C(5)	1682 (2)	1430 (4)	1494 (3)
C(6)	1132 (2)	1309 (3)	258 (3)
C(7)	704 (2)	2928 (4)	−430 (3)
C(8)	967 (2)	4639 (4)	189 (3)
F	774 (1)	6269 (2)	−462 (1)
H(1)	6 (2)	832 (5)	215 (3)
H(2)	152 (2)	659 (5)	284 (3)
H(4)	197 (2)	313 (4)	297 (3)
H(5)	198 (2)	28 (5)	196 (3)
H(6)	107 (2)	8 (4)	−14 (2)
Molecule *B*			
C(1)	5187 (2)	−2155 (5)	3462 (3)
C(2)	6072 (2)	−1216 (5)	3953 (3)
C(3)	6301 (2)	354 (4)	4825 (3)
C(4)	6679 (2)	2070 (5)	4592 (3)
C(5)	6606 (2)	3697 (5)	5155 (3)
C(6)	6057 (2)	3729 (4)	5873 (3)
C(7)	5662 (2)	2063 (4)	6136 (2)
C(8)	5959 (2)	400 (4)	5754 (2)
F	5788 (2)	−1279 (2)	6196 (1)
H(1)	510 (2)	−307 (5)	289 (3)
H(2)	657 (2)	−146 (4)	363 (3)
H(4)	696 (2)	208 (4)	397 (3)
H(5)	683 (3)	481 (5)	497 (3)
H(6)	593 (2)	500 (4)	615 (3)

Discussion. The molecule is found to have the *anti* conformation and dimensions similar to the parent hydrocarbon (Hanson & Röhrl, 1972). Each molecule has a non-crystallographic mirror plane, and a crystallographic centre of symmetry. Bond lengths and angles are summarized in Table 2; ideal $2/m$ symmetry is implied in the averaging. Each F atom is displaced about 0·18 Å from a position of coplanarity with the three nearest C atoms, the displacement being towards the opposing phenyl ring (Fig. 1; Table 3). A similar displacement was observed for the corresponding H atom of the parent hydrocarbon, and was presented as evidence of resistance to twisting of the aromatic bonds. It is reassuring to find the phenomenon confirmed for the more precisely locatable F atoms.

Table 2. *Summary of bond lengths* (Å) *and angles* (°) (*averaged assuming* $2/m$ *symmetry*)

	Mean	Range
C(1)–C(2)	1·330 (5)	1·330–1·331
C(2)–C(3)	1·474 (4)	1·471–1·477
C(3)–C(4)	1·398 (5)	1·396–1·401
C(4)–C(5)	1·372 (5)	1·360–1·382
C(3)–C(8)	1·390 (4)	1·389–1·391
C(8)–F	1·360 (3)	1·358–1·363
C—H	0·96 (3)	0·91–1·00
C(1)–C(2)–C(3)	125·9 (3)	125·7–126·1
C(2)–C(3)–C(4)	119·9 (3)	119·6–120·2
C(2)–C(3)–C(8)	123·0 (3)	122·8–123·2
C(4)–C(3)–C(8)	115·7 (3)	115·4–115·9
C(3)–C(4)–C(5)	120·9 (3)	120·7–121·3
C(4)–C(5)–C(6)	120·1 (3)	120·1–120·2
C(3)–C(8)–C(7)	122·3 (3)	122·1–122·6
C(3)–C(8)–F	118·6 (3)	118·0–118·8

Table 3. *Distances* ($\text{Å} \times 10^3$) *of some atoms from certain planes*

Atoms specified in bold type define the plane. Two distances are given, the first for molecule *A*, the second for *B*.

C(1′) 510, 512; C(2) 494, 509; **C(3)** 0, 0; **C(4)** 0, 0; C(5) −85, −69; **C(6)** 0, 0; **C(7)** 0, 0; C(8) −239, −227.

C(4) 0, 0; **C(5)** 0, 0; **C(6)** 0, 0; F 181, 177.

In the final ΔF synthesis there is a well formed peak, of height about 0·4 e Å^{-3}, near the centre of each molecule. Each peak lies on the plane of symmetry of the molecule and is otherwise in the same relative position (Fig. 1). A peak of similar height and position was observed in the structure of the parent hydrocarbon, and was attributed to the presence of 15,16-

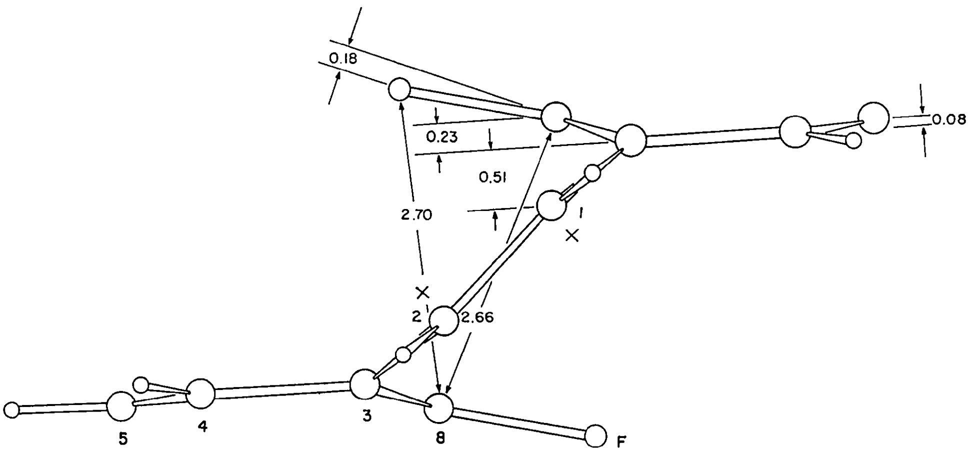

Fig. 1. Idealized average molecule viewed normal to the plane of symmetry. One hydrogen atom has been omitted. Distances are given in Å. The crosses indicate the positions of anomalous peaks in the difference map.

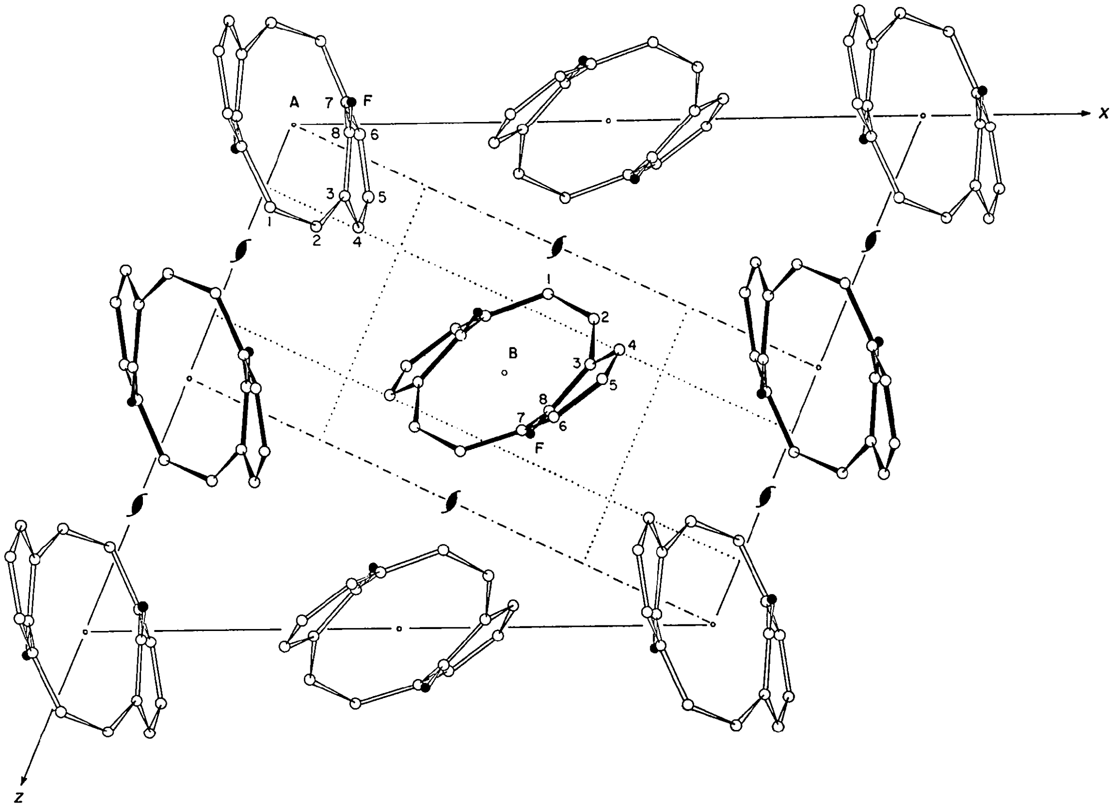

Fig. 2. The structure viewed along **b**. Molecules shown with solid bonds are centred at $y=0$, and the others at $y=\frac{1}{2}$. The chain lines are boundaries of the *pseudo* cell with plane group symmetry *Pgg*, while the dotted lines indicate the *pseudo* glide planes.

dihydropyrene (II, R=H) as a minor contaminant. The explanation is equally plausible here; if a dihydropyrene molecule were to occupy roughly the same space as (I), most atoms would overlap to some degree. However, the terminal atoms of the central bond would be resolved, and would lie roughly in the positions observed. [Logically, the contaminant to be expected would be the 15,16-difluoro derivative of (II, R=F). However, the presence of low-occupancy F sites is not demonstrable.]

In addition to the anomalous peaks discussed, there are in the ΔF synthesis extended regions of negative density (maximum $-0{\cdot}25$ e Å^{-3}) containing the F atoms. These troughs suggest partial occupancy of the F sites, as would be the case if some of the molecules had lost one or both of their substituent atoms. In summary, it seems probable that the specimen material is a solid solution of chemical species of which (I) is predominant.

The structural basis of the pseudosymmetry is illustrated in Fig. 2. Formally the structure can be considered to consist of layers [parallel to (100)] of *A*-type molecules, interleaved by layers of *B*-type molecules. One layer can (very nearly) be transformed into an adjacent layer by a rotation of 180° in its own plane and a translation of $\frac{1}{2}\mathbf{a}$. [For the coordinates of Table 1, the transformation of *A* to *B* is $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+x-z)$; the greatest discrepancy for any non-hydrogen atom is 0·134 Å.]

The author is grateful to Professor Boekelheide for suggesting the problem, and for supplying the specimen material.

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