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THE CRYSTAL AND MOLECULAR STRUCTURE OF OCTAFLUOROBIPHENYLENE, $C_{12}F_8$

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SUMMARY

Octafluorobiphenylene was made by heating 1,2-diiodotetrafluorobenzene in a sealed, evacuated tube with either copper, lead or bismuth. The crystal used for the diffraction studies was grown from hexane.
Crystal data: $C_{12}F_8$, M_r = 296.116, monoclinic, A2/a, a = 21.140(2), b = 6.430(6), c = 36.340(3) Å, β = 123.76(3)°, U = 4106.73 Å^3, Z = 16, D_m = 1.884 g cm^{-3}, D_x = 1.907 g cm^{-3}, λ(CuKα) = 1.5418 Å, μ = 1.810 mm^{-1}, F(000) = 2304, measurement temperature = 293K, R = 0.059 for 2230 reflections with I > 3σ(I).

INTRODUCTION

Biphenylene (I) was first prepared by Lothrop in 1941 by heating 2,2'-biphenyleneiodonium iodide with copper(I) oxide [1]. Many chemists at the time considered that the four-membered ring in such a molecule would be highly unstable and that the hydrocarbon must have some other, less strained structure. However, the problem was soon resolved by both electron [2] and X-ray [3] diffraction studies which confirm structure

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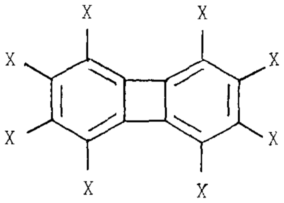
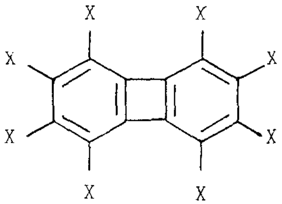
(II;X = H) but the data were too imprecise to allow fine detail of the molecular parameters to show up. Trotter and his co-workers [4] have refined the structure and shown that the molecule should be considered



(I) X = H;F



(II)

as a cyclobutane system with the predominant Kekulé structure shown in (I;X = H). The yield of biphenylene has since been considerably improved over that obtained by Lothrop and its chemistry may be interpreted in terms of structure (I) rather than the cyclobutadiene system (II) [5].

Octafluorobiphenylene was first obtained in low yield by heating 2,2'-diiodooctafluorobiphenyl in a sealed tube with dry copper powder. Being volatile at room temperature, it could readily be separated from the other product, hexadecafluorotetraphenylene, by fractional sublimation [6] Presently the best synthetic method, giving about a 20% yield, is to pyrolyse tetrafluorophthalic anhydride at 750° under low pressure [7]. During experiments attempting the direct synthesis of fluoroaromatic derivatives of a range of metals, it was found that mixtures of perfluoropolyphenylenes were formed by heating 1,2-diiodotetrafluorobenzene with copper, lead or granular bismuth. Perfluorobiphenylene was separated from the other phenylenes by fractional sublimation; the crystals used in the X-ray work described here were obtained from the copper reaction. Octafluorobiphenylene has high thermal stability and, unlike biphenylene, does not undergo insertion of selenium on heating to give the corresponding dibenzoselenophen.

EXPERIMENTAL

Preparation of octafluorobiphenylene using copper

1,2-Diiodotetrafluorobenzene (1 g) and dry copper powder (1 g) were heated in a sealed, evacuated tube at 200° for three days. After cooling, the tube was cut open and the products extracted with diethyl ether; the solvent was removed under vacuum at 0° and the yellowish solid remaining subjected to fractional sublimation under vacuum (ca. 10^{-4} mm) to yield 30 mg (2%) of completely colourless octafluorobiphenylene, m.pt. 99-100°, when the sample was held at room temperature and the inner probe cooled by liquid nitrogen. The mass spectrum showed a mass cut-off at the parent ion ($^m/e = 296$); the base peak corresponded to $C_{12}F_8^+$, the next highest intensity peak, at 22% relative intensity, was due to $C_{11}F_6^+$. Three C_{11} fragments giving relatively strong peaks represented loss of CF, CF_2 and CF_3 from the parent ion; the ions $C_{10}F_4^+$ and $C_{10}F_3^+$ made up the remaining important features of the spectrum except for a peak at mass 148 (ca. 14%) due to P^{++} and/or $C_6F_4^+$. [Found: C, 48.7, 48.6; H, 0.0, 0.1; F, 51.2, 51.4%; $C_{12}F_8$ calcd.: C, 48.7; H, 0.0; F, 51.3%]. Infrared spectrum (cm^{-1}): 1661 w, 1656 w sh, 1634 w, 1490 s, 1466 s, 1456 s sh, 1439 m sh, 1385 w, 1379 w, 1333 w, 1321 m sh, 1305 s, 1101 s, 1083 s, 1076 s, 861 m, 685 m, 667 m.

Reaction of 1,2-diiodotetrafluorobenzene with lead and bismuth

Powdered lead (0.8 g) and 1,2-diiodotetrafluorobenzene (1.0 g) were heated for three days at 300° in a sealed, evacuated tube after which time the contents were extracted with diethyl ether. Removal of the solvent at 0° left a light brown solid which, on vacuum sublimation at room temperature afforded octafluorobiphenylene in 3% yield (m.pt. 98-99°; mol.wt. by mass spectrum, 296). Increasing the sublimation temperature to 80° gave colourless dodecafluorotriphenylene in 13% yield (m.pt. 104-106°; lit. [8] 102-104°; mol.wt. from mass spectrum, 444). Finally, at 150°, hexadecafluorotetraphenylene sublimed in 5% yield as a white solid, m.pt. 250-251° (lit. [6] 249-251°; mol. wt. from mass spectrum, 592).

Similar yields of the three perfluoropolyphenylenes were obtained when bismuth granules and 1,2-diiodotetrafluorobenzene were heated to 250° for three days. Powdered bismuth and $C_6F_4I_2$, when heated overnight at 250°, give perfluoro-1,6-dibismuth-triptycene, $Bi_2(C_6F_4)_3$, m.pt. 318° (20-30%).

Attempted reaction of octafluorobiphenylene with selenium and mercury

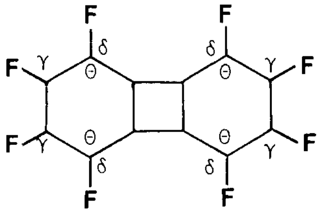
No selenium or mercury derivatives could be detected when either of the elements was heated in a sealed tube at 300° with octafluorobiphenylene (at temperatures above about 320° the $C_{12}F_8$ appeared to char slowly).

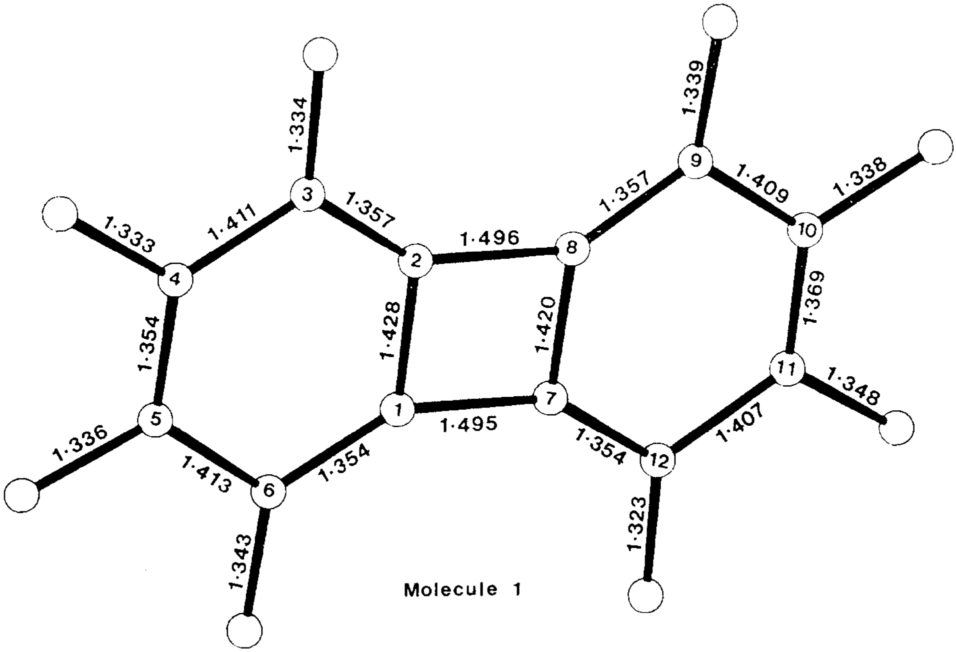
Crystal studies

Octafluorobiphenylene is volatile at room temperature, so the chosen crystal was sealed into a Lindemann capillary tube. Preliminary cell dimensions were determined from rotation and Weissenberg photographs taken from the crystal mounted about the $\mathfrak{b}$ axis. Refined cell dimensions were obtained from a Stadi-2 two-circle diffractometer which was used for data collection. The intensities of 3199 reflections were measured out to a maximum 2Θ of 135° using Cu Kα radiation; 2230 had $I > 3\sigma(I)$ and were classed as observed. A standard check reflection was measured for each layer and no significant anomalies were noted. Corrections were applied for Lp but not for absorption or extinction. The structure was solved by direct methods using SHELX-76 and refined by accelerated full matrix least-squares, minimizing $\Sigma\ w(\Delta F)^2$ and allowing anisotropic motion for all atoms. In the final cycle of refinement $w = 1/(\sigma^2(F) + 0.0296F^2)$, $\Delta/\sigma < 0.11$, $\Delta\rho$ excursions = +0.25 to -0.34 eÅ^{-3} and R = 0.059. Scattering factors used were those of Cromer & Mann [9]. A copy of the list of structure factors and anisotropic temperature factors is available on request from J.BJ.

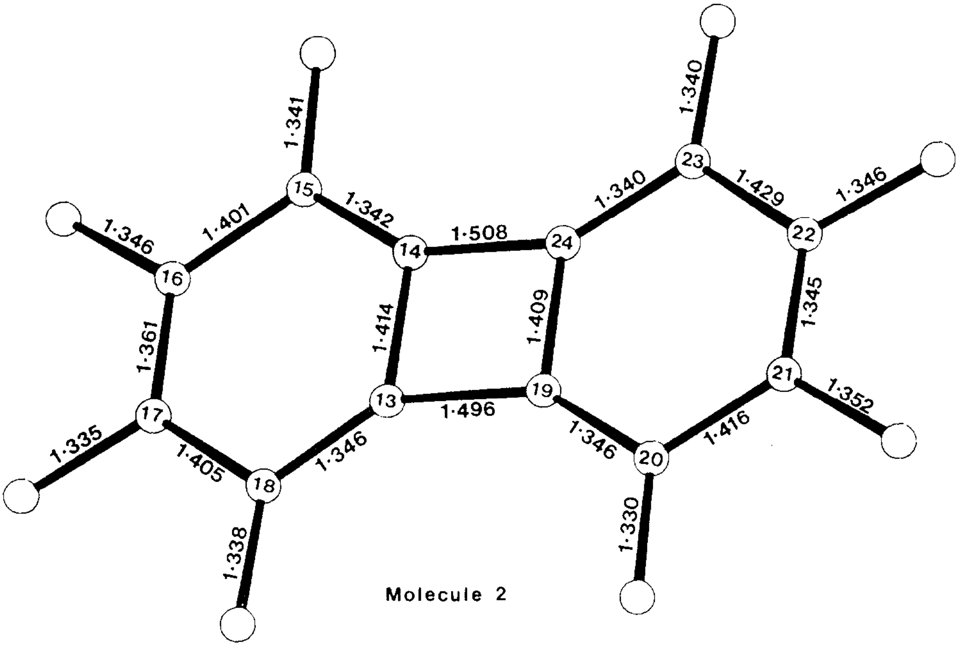
DISCUSSION

The bond lengths and angles in the two molecules comprising the asymmetric unit are shown in Figs. 1 and 2, while the atomic co-ordinates are given in Table 1. A notable geometrical feature is the small value of the angles, Θ (mean = 116.1°); the corresponding average value for biphenylene is 115.2°. The rectangular C_4 ring doubtless causes Θ to be significantly less than 120° in both compounds which, in turn, is responsible for the FCC angles δ being greater than 120° (average value 124.7°). The four fluorine atoms on each ring are close to the expected F---F van der Waals distance of 2.7 Å from their immediate





Molecule 1



Molecule 2

Fig. 1. ORTEP drawing showing the bond lengths, Å, and the numbering scheme for the two molecules in the asymmetric unit; e.s.d. is 0.005 Å.

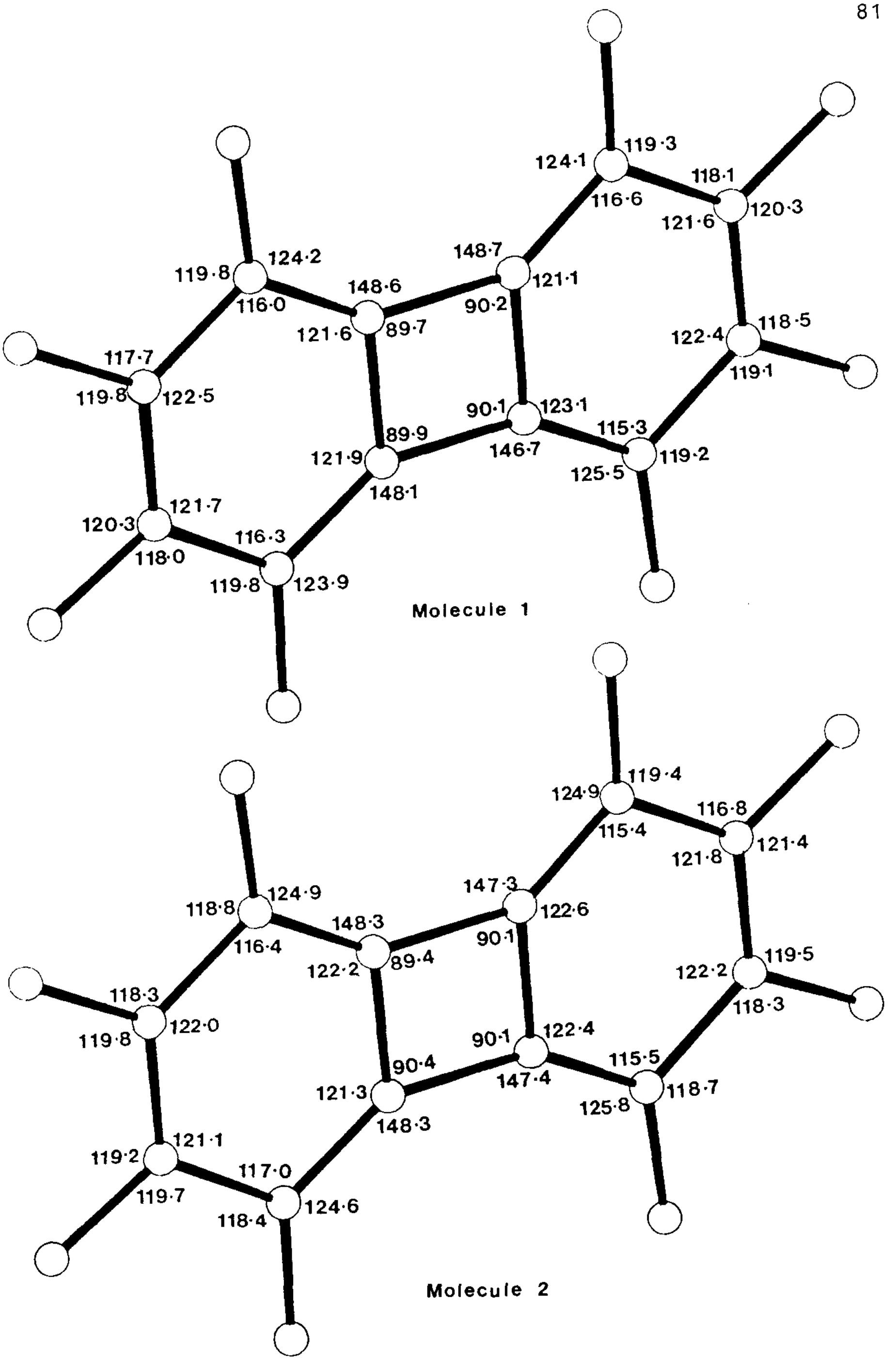


Fig. 2. The bond angles, in degrees, for the two molecules in the asymmetric unit; e.s.d. s are in the range 0.3° to 0.4°.

TABLE 1

Atomic coordinates (x 10^4) and equivalent isotropic thermal parameters

$B_{eq} = {}^1/_3 \Sigma_i B_{ii}$

	x	y	z	B_{eq}(Å^2)
C(1)	120(2)	6490(6)	666(1)	4.6(2)
C(2)	392(2)	4522(6)	628(1)	4.3(1)
C(3)	1147(2)	4078(6)	861(1)	4.7(2)
C(4)	1639(2)	5653(7)	1148(1)	4.9(2)
C(5)	1382(2)	7503(7)	1192(1)	5.1(2)
C(6)	598(2)	7992(6)	942(1)	5.1(2)
C(7)	-677(2)	5839(6)	322(1)	4.5(2)
C(8)	-407(2)	3884(6)	284(1)	4.3(2)
C(9)	-893(2)	2421(6)	-4(1)	4.7(2)
C(10)	-1669(2)	2972(6)	-268(1)	5.0(2)
C(11)	-1918(2)	4875(6)	-230(1)	4.9(2)
C(12)	-1420(2)	6388(7)	74(1)	5.1(2)
F(3)	1435(1)	2303(4)	824(1)	5.9(1)
F(4)	2385(1)	5279(4)	1379(1)	6.4(1)
F(5)	1871(1)	8951(4)	1467(1)	6.2(1)
F(6)	366(2)	9854(4)	992(1)	6.6(1)
F(9)	-676(1)	555(4)	-57(1)	6.0(1)
F(10)	-2161(1)	1590(4)	-565(1)	6.1(1)

TABLE 1 (cont.)

	x	y	z	B_{eq} ($\mathring{A}^2$)
F(11)	-2667(1)	5305(4)	-494(1)	6.4(1)
F(12)	-1700(1)	8188(4)	97(1)	6.7(1)
C(13)	1057(2)	2229(6)	2642(1)	4.6(2)
C(14)	1345(2)	4176(6)	2850(1)	4.7(2)
C(15)	1620(2)	5580(6)	2700(1)	4.8(2)
C(16)	1607(2)	5017(7)	2323(1)	5.6(2)
C(17)	1325(2)	3155(7)	2117(1)	5.5(2)
C(18)	1042(2)	1693(6)	2279(1)	4.9(2)
C(19)	896(2)	1651(7)	2981(1)	5.0(2)
C(20)	643(2)	198(8)	3135(1)	5.9(2)
C(21)	680(3)	745(11)	3525(2)	7.9(3)
C(22)	954(3)	2590(11)	3727(1)	7.9(3)
C(23)	1237(3)	4102(9)	3565(1)	6.7(3)
C(24)	1192(2)	3574(7)	3194(1)	5.5(2)
F(15)	1910(2)	7436(5)	2887(1)	7.0(1)
F(16)	1882(2)	6376(5)	2164(1)	8.2(2)
F(17)	1318(2)	2718(5)	1756(1)	8.4(2)
F(18)	763(2)	-99(4)	2059(1)	6.8(1)
F(20)	365(2)	-1656(5)	2955(1)	7.9(2)
F(21)	420(2)	-634(6)	3691(1)	10.7(2)
F(22)	999(2)	3068(7)	4102(1)	11.3(2)
F(23)	1517(2)	5904(5)	3782(1)	8.4(2)

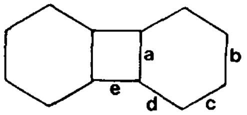
neighbours and hence contribute little or no distortion to the octafluorobiphenylene molecule. Thus, the fact that the angles γ are slightly less than 120° (average 118.2°) is probably a continuation of the distortion in the ring caused by the small Θ angles rather than being due to F---F steric repulsion effects.

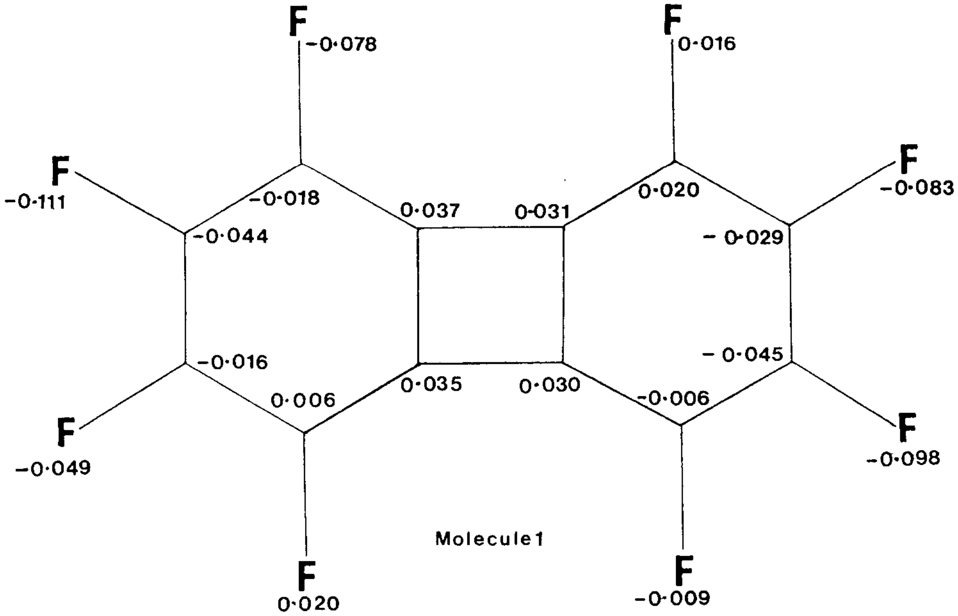
Using simple Hückel molecular orbital theory, Ali and Coulson [10] have calculated the π-bond order in the rings of $C_{12}H_8$ and deduced the bond lengths using the equation l (bond length) = $(1.50-0.15\,p)$ Å where p is the π-bond order (the C-C single bond distance of 1.54 Å derived from diamond was reduced to 1.50 Å to allow for the change from sp^3 to sp^2 hybridization in aromatic molecules); see Table 2. The calculated bond lengths hold at least as well for octafluorobiphenylene as for biphenylene; however, the somewhat short bond lengths for b and d suggest certain canonical forms contribute more than others in $C_{12}F_8$ (I;X = F) than in biphenylene. The value of e (1.499 Å) in $C_{12}F_8$ may be indicative of even less π-bonding across the central C_4 ring than the minimal π-bond order of 0.219 calculated for $C_{12}H_8$, apparently in agreement with the suggestion of Burdon and Parsons [11] that conjugation across the C_4 ring is best ignored in octafluorobiphenylene. Clearly, if this is the case, e should be about 1.50 Å (i.e. with p close to zero) as found. In biphenylene e is even longer at 1.514 Å, showing that the two molecules can be mainly represented by the canonical structure (I) involving two minimally interacting benzene rings. The molecules, however, do not contain anything approaching a cyclobutane-like central C_4 ring, since this ring is completely planar within experimental error and is actually rectangular in shape rather than square, which suggests that any discussion about the cyclobutane nature of the C_4 ring in the biphenylene skeleton is perhaps rather academic - this type of C_4 ring flanked by aromatic systems is probably best considered as being a unique system in its own right.

TABLE 2.

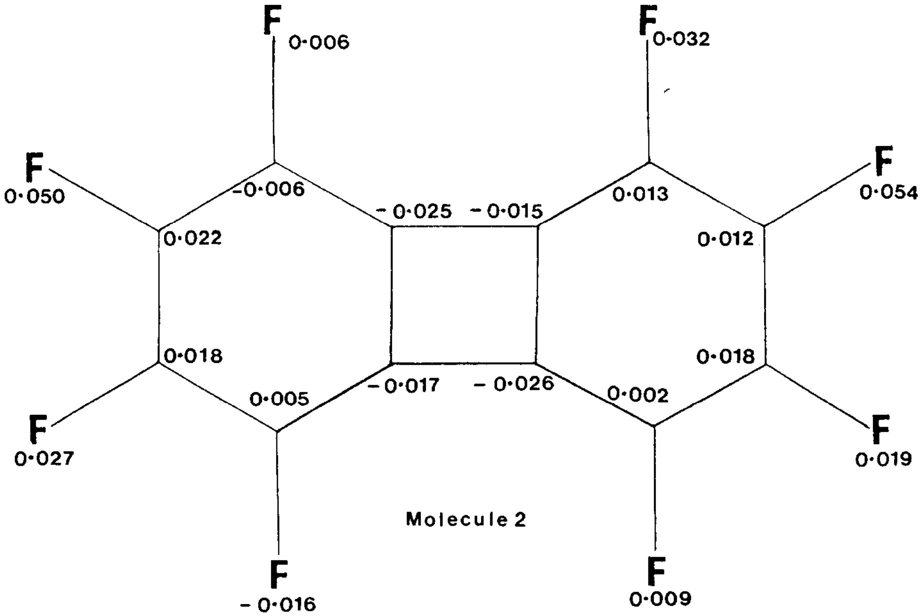
Comparison of calculated bond lengths (Å) in $C_{12}H_8$ with those obtained by X-ray diffraction for $C_{12}H_8$ and $C_{12}F_8$[10]

Bond	π bond order	Calculated bond length	Bond lengths[4] in $C_{12}H_8$	Difference	Bond lengths in $C_{12}F_8$	Difference
a	0.572	1.414	1.426	-0.012	1.413	+0.001
b	0.702	1.394	1.385	+0.009	1.357	+0.037
c	0.612	1.408	1.423	-0.015	1.411	-0.003
d	0.701	1.395	1.372	+0.023	1.349	+0.046
e	0.219	1.467	1.514	-0.047	1.499	-0.032





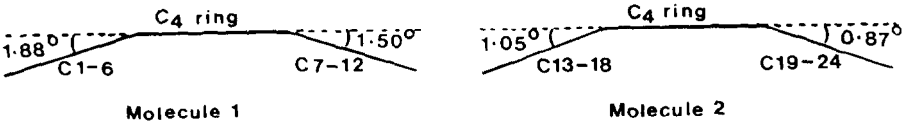
Molecule 1



Molecule 2

Fig. 3. Deviations, in Å, of atoms from the least-squares plane through each molecule in the asymmetric unit.

There were no abnormal inter-molecular contacts within the unit cell. The two molecules in the asymmetric unit are, as expected, almost completely planar (Fig. 3); in both, the benzene rings are slightly cis relative to the C_4 central ring, the angles between the benzene planes being 3.38° and 1.92° for molecules 1 and 2, respectively.



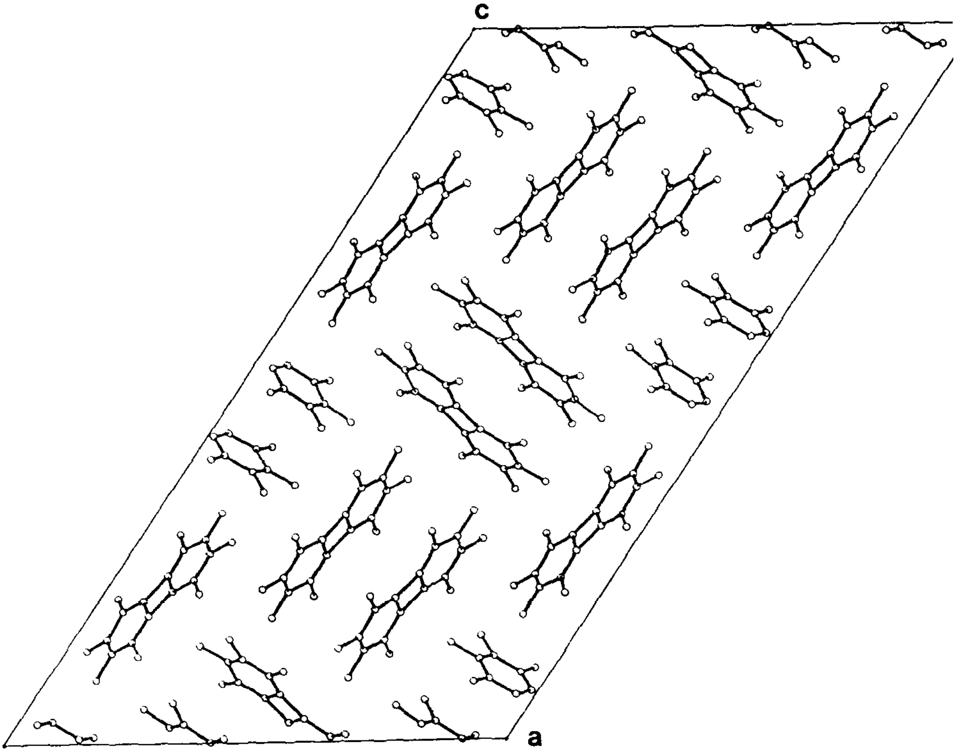


Fig. 4. **b**-axial projection of the cell contents.

REFERENCES

1 W. C. Lothrop, J. Am. Chem. Soc., 63 (1941) 1187.

2 J. Waser and V. Schomaker, J. Am. Chem. Soc., 65 (1943) 1451.

3 J. Waser and C-S. Lu, J. Am. Chem. Soc., 66 (1944) 2035.

4 T. C. W. Mak and J. Trotter, J. Chem. Soc., (1962) 1; J. K. Fawcett and J. Trotter, Acta Cryst., 20 (1966) 87.

5 W. Baker, M. P. V. Boarland and J. F. W. McOmie, J. Chem. Soc., (1954) 1476.

6 S. C. Cohen and A. G. Massey, J. Organometal. Chem., 10 (1967) 471.

7 D. V. Gardner, J. F. W. McOmie, P. Albriktsen and R. K. Harris, J. Chem. Soc., (1969C) 1994; see also P. Sartori and A. Golloch, Ber., 101 (1968) 2004.

8 V. B. Smith and A. G. Massey, Tetrahedron, 25 (1969) 5495.

9 D. T. Cromer and J. B. Mann, Acta Cryst., A24 (1968) 321.

10 M. A. Ali and C. A. Coulson, Tetrahedron, 10 (1960) 41.

11 J. Burdon and I. W. Parsons, J. Am. Chem. Soc., 99 (1977) 7445.