Perfluorotetracyclobutacyclo-octatetraene; a Planar Eight-membered Ring System; X-Ray Crystal Structure

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Summary The title compound is planar, with a variation of only ± 0·036 Å in the bond lengths of the eight-membered ring, and gives an enhanced diamagnetism which suggests that there is some double-bond delocalization around the inner ring.

The crystal structures of perfluorotricyclobutabenzene (1)[1,2] and perfluorotetracyclopentaoctatetraene (2)[3] are known.

In compound (1), the C–C bond lengths around the inner ring are equal, within experimental error, [3 × 1·386(2) and 3 × 1·392(2) Å],[2] the C-atoms are coplanar, and, as in benzene, the double bonds are delocalized around the ring. This planarity is also observed for the related molecules cyclobutadicyclopentabenzene (3)[4] and tricyclopentabenzene (4).[5]

Compound (2), however, resembles cyclo-octatetraene and

its derivatives.[6] The C-atoms of the eight-membered ring assume a boat conformation and the average lengths for the C–C bonds endocyclic and exocyclic to the cyclopentene rings are 1·324(7) and 1·465(9) Å, respectively.

(1)

(2)

(3)

(4)
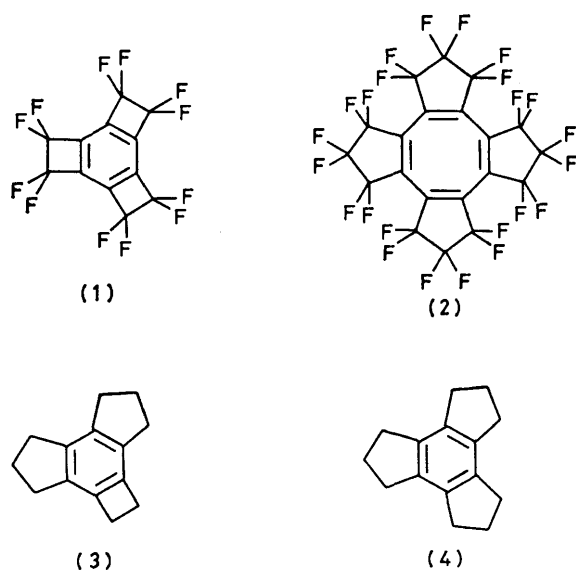
Perfluorotetracyclobutacyclo-octatetraene (5) was synthesized by coupling tetrafluoro-1,2-di-iodocyclobutene with Cu powder in the presence of dimethylformamide[7] and is a red solid which gives a single ^{19}F n.m.r. resonance at δ_F 118·5 p.p.m. from the internal $CFCl_3$ resonance. As it has eight π-electrons, it was thought that the structure of this compound would closely resemble that of compound (2); i.e., non-planar with alternating short and long bonds. The former prediction proved to be incorrect, the latter to be correct.

(5)
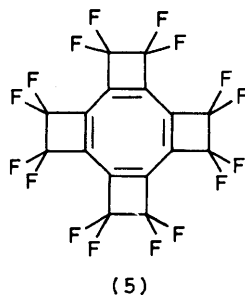
Crystal data: $C_{16}F_{16}$, M = 496·15, monoclinic, space group $C2/c$, a = 18·946(7), b = 8·311(5), c = 10·739(5) Å, β = 101·96(4)°, U = 1654·3 Å^3, Z = 4, D_c = 1·99 g cm^{-3}, μ = 2·2 cm^{-1} for Mo-$K_{\alpha 1}$ radiation (λ = 0·70926 Å). The intensities of 770 independent reflections ($3° \leqslant 2\theta \leqslant 40°$) were measured at room temperature on a four-circle Picker FACS-I diffractometer using a crystal of dimensions 0·28 ×

0·19 × 0·19 mm. The crystals were soft and the diffraction pattern showed a high overall temperature factor ($\overline{B}$ 4·2 Å^2 from the Wilson plot). The structure was solved by MULTAN and refined by full-matrix least-squares methods using 580 'observed' reflections [$I > 2 \cdot 3\sigma(I)$] to give a final R value of 0·072.† An ORTEP diagram of the molecule with average bond lengths and angles is presented in the Figure.
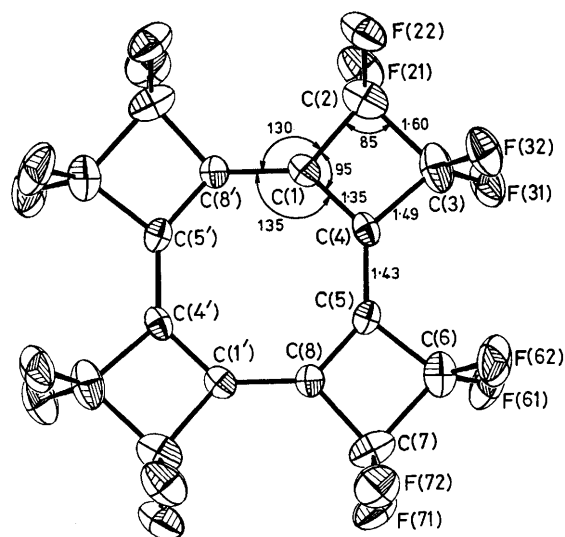

FIGURE. Projected view of compound (5) with selected average bond values of lengths (Å) and angles (°), assuming 4/mmm symmetry. E.s.d.s are 0·01—0·02 Å and 1—2°.

Molecules of compound (5) possess a crystallographic centre of symmetry with the eight atoms of the inner ring planar (see the Table). Around the ring, the bonds are alternately short [average 1·353(10) Å] and long [average 1·425(14) Å] with the shorter bonds endocyclic to the cyclobutene rings. These distances are, however, intermediate between those reported for compounds (1) and (2), suggesting that there is some degree of double-bond delocalization.

The internal angle of a regular octagon is 135°. In compound (5), angles of the type C(4)–C(1)–C(2) have an

TABLE. Deviations (Å) of atoms from the least-squares plane of the eight-membered ring in compound(5).[a,b] The equation of the plane refers to the orthogonal axes a, b', and c^*.

$0\cdot1906\,x - 0\cdot5845\,y - 0\cdot7887\,z + 4\cdot6666 = 0$ $\chi^2 = 7\cdot2$

Atoms in the plane

C(1)	−0·004(7)	C(5)	−0·009(7)
C(4)	0·009(7)	C(8)	0·004(7)

Other C atoms:

C(2)	0·109(10)	C(6)	0·039(10)
C(3)	0·031(9)	C(7)	0·031(9)

[a] Plane defined by C(1), C(4), C(5), C(8), C(1′), C(4′), C(5′), and C(8′). [b] Deviation for atom C(n′) = − [deviation for atom C(n)].

average value of 95°. As a result, the angle C(4)–C(1)–C(8') can be as high as 135° without causing additional angular strain at C(1). This is in contrast with compound (2) where the angle C(4)–C(1)–C(2) has an average value of 111°. If the eight-membered ring were planar in compound (2), the angle C(2)–C(1)–C(8') would have to be 114°, which would be prohibitive in a system not stabilized by *extensive* double-bond delocalization [such as in compound (1)]. As a consequence, the eight-membered ring of compound (2) is buckled and the average values of the angles C(4)–C(1)–C(8') and C(2)–C(1)–C(8') are 127 and 122°, respectively.

Magnetic studies at room temperature on compound (5) show that it is diamagnetic with X_m -389×10^{-6} in comparison with a calculated value of -199×10^{-6} derived from Pascal constants. Such an enhancement is consistent with increased delocalization. It could also indicate a Jahn–Teller distortion with spin-pairing of the otherwise degenerate orbitals. The relatively high overall thermal motion, precluding data collection beyond 2θ 40°, may also be accounted for by a 'dynamic' Jahn–Teller effect. We intend to repeat the crystal structure at reduced temperatures to obtain greater precision.

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