# Crystal and Molecular Structure of Perfluorobenzo[1,2:3,4:5,6]tricyclobutene

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Abstract: The structural parameters of perfluorobenzo[1,2:3,4:5,6]tricyclobutene have been determined by single-crystal x-ray analysis. The bond lengths and bond angles in the central ring have been found to be essentially identical with those of benzene itself. This lack of any observable bond alternation argues against current theories which predict that both the σ and π frameworks should show more double-bond character exocyclic to the small fused rings.

A recent report on the preparation of 1,5,9-cyclododecatriyne (**1**) has set forth the interesting postulate that acetylenic

1

2, R = H
3, R = F
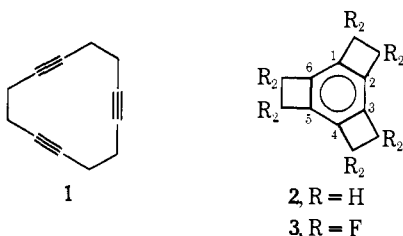
p orbitals might participate in σ overlap or π overlap to lend additional stabilization to such a molecule.[4] The possibility that the cyclic triyne might in fact exist as an extreme canonical form of the highly strained benzo[1,2:3,4:5,6]tricyclobutene (**2**) represents a unique situation where the relief of excessive ring strain could partially compensate for the stabilizing influence of aromatic delocalization. Although calculations show the triyne to be substantially less stable than its aromatic tetracyclic counterpart, attempts to isolate **2** have thus far been fruitless, although a trapping experiment invokes **2** as well as the corresponding 6-radialene as possible thermolysis products of **1**.[4]

Perfluorobenzo[1,2:3,4:5,6]tricyclobutene (**3**) was first prepared in 1971 by Camaggi via the copper–bronze coupling of 1,2-diiodoperfluorocyclobutene.[5] Two years later Soulen, Park, and Choi published an improved procedure for this reaction which also provided 34% of the corresponding tetramer.[6] Examination of the ^{19}F NMR, IR, and UV spectra for **3** revealed properties consistent with a symmetrically substituted aromatic structure. Compound **3** also shows remarkable stability. It melts sharply at 135–136 °C and showed little decomposition after room temperature storage for over 1 year. The material sublimes readily, giving high quality transparent crystals. In the light of observations made regarding the potentially interesting structural features of the elusive hydrocarbon **2**, we undertook a single-crystal x-ray analysis of **3** to determine its exact structural parameters.

Table I. Summary of Crystal Data

Molecular formula: $C_{12}F_{12}$
Molecular weight: 372.1
Space group: $P6_3/m$, hexagonal
Cell constants: $a = 8.966$ (1), $c = 8.671$ (1) Å
Cell volume: 603.6 Å^3
Molecules/cell: $Z = 2$ (the center of mass of each molecule occupies a $3/m$ symmetry site)
Density: $\rho = 2.05$ g/cm^3
Linear abs coeff: $\mu = 2.76$ cm^{-1} (Mo Kα)

Experimental Section

An approximately cylindrical crystal of dimensions 0.44 × 0.44 × 0.70 mm was mounted on a glass fiber with [001] nearly parallel to the Φ axis of the diffractometer, a Syntex P2$_1$ equipped with an ethanol-cooled nitrogen low temperature device. Since the crystal was found to sublime rapidly at room temperature, all measurements were carried out at −35 °C. Crystal data are shown in Table I. Data were collected from 4 to 60° 2θ using the ω scan technique. The radiation used was Mo Kα, monochromatized by a graphite crystal assumed to be 50% mosaic in character. Scan rates varied from 1.5 to 5.0° min^{-1} depending directly on the intensity of each reflection. A total of 630 independent reflections were collected, comprising the octant of reciprocal space where each of h, k, and l is nonnegative. Of these, 587 were considered observed, having $I > 3\sigma(I)$. The 10 most intense reflections had to be collected at a lower milliampere setting than the majority of the data. Intensities were corrected for Lorentz and polarization factors, but not for absorption. Monitoring of three standard intensities throughout the data collection did not warrant inclusion of a decay correction.

The structure was solved via program MULTAN.[7] Centric statistics, as well as the atomic positions in the initial E map, led to the conclusion that the space group was $P6_3/m$ and not $P6_3$. Anisotropic full-matrix least-squares refinement of the six atoms comprising the asymmetric unit (four carbons and two fluorines) converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.035$ and $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2 = 0.041$, where $w = \sigma(|F_o|)^{-2}$. The carbon atoms are restricted to lie in the mirror plane at $z = \frac{1}{4}$, with a perpendicular 3-fold rotation axis intersecting the center of the benzyl moiety. A total of 45 parameters were varied, including two separate scale factors and a primary extinction factor (3.15 × 10^{-3}). In the final cycle of refinement, scale factor 2 for the 10 most intense reflections was held constant while the extinction parameter was varied. The error of fit was 3.92. Final positional and thermal parameters are presented in Table II, based on the numbering scheme given in Figure 1. The scattering factors used were computed from numerical Hartree–Fock wave functions.[8] A complete listing of observed and calculated structure factors is available as supplementary material according to instructions given in a paragraph at the end of this article.

Discussion

Pertinent bond distances and angles for the asymmetric unit are presented in Table III according to the labels in Figure 1. Since the molecule has $3/m$ symmetry, these values are identical in the other two cyclobutene groups. Within the accuracy of the determination, there is no evidence for any bond alternation in the benzenoid fragment of the molecule. In fact, the bond lengths and angles of the central ring are essentially identical with those of benzene itself.

Significant contribution in the crystalline state from a triyne similar to **1** is ruled out by the observation of uniform benzene bond lengths. The lack of any such bond alternation also directly contradicts the much debated Mills–Nixon effect.[9] According to this theory, the double bonds in this molecule
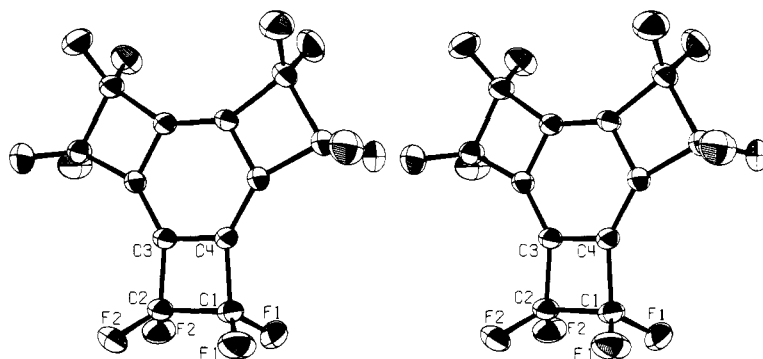
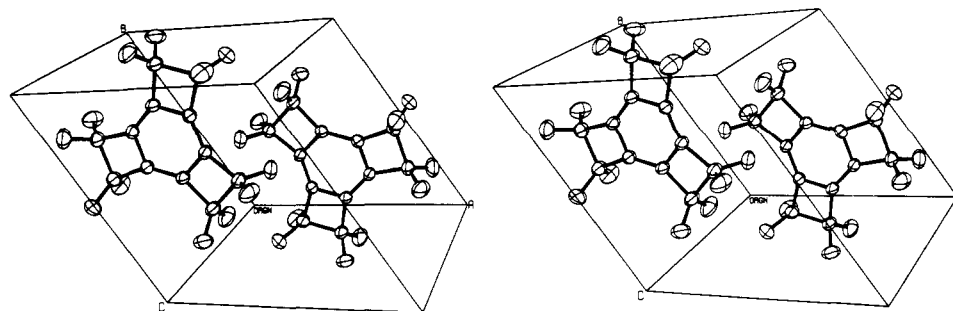**Figure 1.** Stereoscopic atom numbering scheme; 50% equiprobability ellipsoids.

Figure 2. Stereodiagram of the contents of the unit cell.

Table II. Positional and Thermal Parameters $(\times 10^4)^a$

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(1)	7440 (1)	7610 (1)	3748 (1)	418 (5)	346 (5)	843 (9)	205 (4)	−103 (4)	−229 (4)
F(2)	4050 (1)	5259 (1)	3740 (1)	375 (5)	395 (5)	818 (9)	237 (4)	165 (4)	− 24 (4)
C(1)	6900 (2)	6602 (2)	2500	276 (8)	221 (8)	582 (12)	141 (7)		
C(2)	4914 (2)	5216 (2)	2500	247 (8)	254 (8)	568 (12)	148 (6)		
C(3)	5459 (2)	3874 (2)	2500	221 (7)	223 (8)	425 (10)	126 (6)		
C(4)	7202 (2)	5079 (2)	2500	216 (7)	184 (7)	422 (10)	92 (5)		

^{a} The estimated standard deviation in the last place is given in parentheses.

Table III. Bond Distances^a and Angles^{b,c}

C(1)-F(1)	1.335 (2)	F(1)-C(1)-F(1'')	108.2 (1)
C(2)-F(2)	1.337 (2)	F(1)-C(1)-C(4)	116.1 (1)
C(1)-C(2)	1.582 (2)	F(1)-C(1)-C(2)	114.6 (1)
C(2)-C(3)	1.508 (3)	F(2)-C(2)-F(2'')	107.1 (2)
C(3)-C(4)	1.386 (2)	F(2)-C(2)-C(3)	116.5 (1)
C(4)-C(1)	1.520 (3)	F(2)-C(2)-C(1)	114.7 (1)
C(3)-C(4')	1.392 (2)	C(1)-C(2)-C(3)	86.6 (2)
		C(2)-C(3)-C(4)	93.9 (1)
		C(3)-C(4)-C(1)	93.6 (2)
		C(4)-C(1)-C(2)	86.0 (1)
		C(3)-C(4)-C(3''')	120.1 (2)
		C(4)-C(3)-C(4')	119.9 (2)

^{a} Ångstroms. ^{b} Degrees. ^{c} The estimated standard deviation in the last place is given in parentheses. Symmetry relatives: $' = 1 - y, x - y, z$; $'' = x, y, \frac{1}{2} - z$; $''' = 1 - x + y, 1 - x, z$.

should prefer to orient themselves such that they would be exocyclic to the four-membered rings, favoring structure **4** over structure **5**. Furthermore, arguments based on rehybridization of strained bridgehead carbons[10] would demand alternation of the σ framework such that the bridging bonds (C(1)-C(2), C(3)-C(4), and C(5)-C(6)) would show increased p character

4   **5**
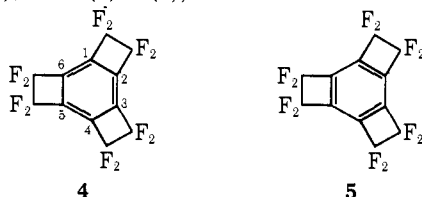
(bond lengthening) while the intervening bonds (C(2)-C(3), C(4)-C(5), and C(1)-C(6)) would show increased s character (bond shortening).[11] In view of the fact that all of these effects argue for bond alternation favoring structure **4**, it is quite surprising that no such irregularity is observed.

With regard to the perfluorocyclobutene portion of the molecule, good agreement is found with previous reports in the literature. The C-F parameters are typical for sp^3-hybridized carbons,[12,13] and the C-C distances and angles are similar to those found in other cyclobutene and perfluorocyclobutene structures.[11,14] The only possible anomaly noted is that in this determination the perfluorocyclobutene ring is perfectly planar, which does not seem to be the usual case.[14,15] Typically, the ring puckers so as to "stagger" effectively the fluorine-fluorine overlaps. In the present investigation, however, any fluorine-fluorine repulsion seems to be accommodated by a lengthening of the intervening F_2C-CF_2 bond.

There may be some question about the validity of comparing molecules such as **2** and **3**. Fluorine atoms are well known to exert a stabilizing influence on strained organic molecules, and such an effect could lead to less of an energy difference between resonance contributors **4** and **5**. The effect of electronegative fluorines on rehybridization of the σ framework might also be important. We are currently attempting to better evaluate the influence of fluorine on such strained molecules by a further investigation of the chemistry of **3** and related systems.

Figure 2 shows a stereoscopic view of the contents of the unit cell. No unusually short intermolecular contacts are noted.

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Supplementary Material Available: Listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) University of Houston.
(2) University of Texas at Austin.
(3) Southwestern University.
(4) A. J. Barkovich and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **98**, 2667 (1976).
(5) G. Camaggi, *J. Chem. Soc. C*, 2382 (1971).
(6) R. L. Soulen, S. K. Choi, and J. D. Park, *J. Fluorine Chem.*, **3**, 141 (1973/74).
(7) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sec. A,* **27**, 368 (1971).
(8) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A,* **24**, 321 (1968).
(9) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).
(10) (a) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965); (b) A. Streitweiser, Jr., G. R. Ziegler, P. C. Mowry, A. Lewls, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
(11) We have recently examined in detail the structure of dicyclopentenobenzocyclobutene. Although this molecule shows good evidence for rehybridization of its aromatic carbons, we again observe no bond alternation in the benzene ring: J. D. Korp, R. P. Thummel, and I. Bernal, *Tetrahedron,* in press.
(12) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.
(13) C. J. Marsden, *J. Mol. Struct.*, **21**, 168 (1974).
(14) F. W. B. Einstein and A. C. MacGregor, *J. Chem. Soc., Dalton Trans.*, 783 (1974).
(15) H. P. Lemaire and R. L. Livingston, *J. Am. Chem. Soc.*, **18**, 569 (1950).

Crystal and Molecular Structure of 2,3-Dihydro-α,β,γ,δ-tetraphenylporphyrinatopyridinezinc(II)–Benzene Solvate[1]

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Abstract: The structure of 2,3-dihydro-α,β,γ,δ-tetraphenylporphyrinatopyridinezinc(II)–benzene solvate, ZnTPC(Py)·C$_6$H$_6$, has been determined from three-dimensional x-ray diffraction. The compound crystallizes with one molecule of benzene and one ZnTPC(Py) per asymmetric unit in the triclinic space group $P\bar{1}$ with a = 11.414 (2) Å, b = 13.334 (2) Å, c = 14.809 (1) Å, α = 99.18 (1)°, β = 94.14 (1)°, and γ = 105.08 (1)°. The structure has been refined by block-diagonal least-squares to R = 0.046 based on 8792 measured intensities with a 13:1 parameter-to-variable ratio. Agreement of chemically similar bond distances and angles is excellent. The reduced pyrrole ring is clearly distinct with a C$_\beta$–C$_\beta$ distance of 1.478 (3) Å and C$_\alpha$–C$_\beta$ distance of 1.495 (2) Å. Comparison of ZnTPC(Py) with analogous porphyrins shows the effect of reduction on the porphyrin macrocycle and on the zinc coordination. Differences in the orientations of the reduced pyrrole ring hydrogen atoms in chlorophylls and ZnTPC(Py), previously predicted by ESR experiments, are confirmed.

Metallotetraphenylporphyrins, MTPP, Figure 1a, have been widely studied by x-ray diffraction as models of naturally occurring porphyrins.[3] The dihydrotetraphenylporphyrins (tetraphenylchlorins), Figure 1b, have been used to model chlorophyll;[4] however, no structure of a metallotetraphenylchlorin has been determined to date. Such a structure would illustrate the effect of reducing the porphyrin conjugated π-electron system, and allow direct comparison with the recently determined structures of ethylchlorophyllides a[5] and b.[6] We present here the structural determination of 2,3-dihydrotetraphenylporphyrinatopyridinezinc(II)–benzene solvate.

Experimental Section

Tetraphenylchlorin (TPCH$_2$) was prepared by standard methods[7] and reacted with zinc acetate in pyridine to form 2,3-dihydro-α,β,γ,δ-tetraphenylporphyrinatopyridinezinc(II), ZnTPC(Py).[8] The reaction mixture was partitioned between benzene and water, and the organic layer washed with water. The product was crystallized from benzene and dried in vacuum at room temperature. A combination of diffusion and evaporation at room temperature using Fisher Certified hexanes and dichloromethane, distilled from calcium hydride, as solvents yielded crystals suitable for diffraction studies.

A purple prism (0.3 × 0.7 × 0.4 mm) was mounted along its long axis and the crystallographic properties were examined on a precession camera. Good quality diffraction patterns, exhibiting only inversion symmetry, were obtained. After approximate cell dimensions were measured, the crystal was mounted on an Enraf–Nonius CAD4 diffractometer. Some crystallographic details are given in Table I. During the 2 weeks of data collection, three reflections were monitored periodically. The intensities of these reflections showed no significant trends or fluctuations; therefore no time-dependent correction for experimental instability was made.

Solution and Refinement. The position of the zinc atom was determined from a vector map, and electron-density and difference-electron-density syntheses were used to obtain positions for all other nonhydrogen atoms. This model was refined by block-diagonal least-squares against the 7760 data with $|F_o| > 12\sigma|F_o|$. A further difference map indicated positions for all hydrogen atoms except those of the benzene molecule of solvation. Refinement was continued against all the unique intensity data (Is), except 3·$\bar{4}$·4 which was omitted because of an unusually large weighted discrepancy. All nonhydrogen atoms were permitted anisotropic expression of their thermal motion, but each hydrogen atom was restricted to a single isotropic vibration parameter. Hydrogen atoms of the benzene solvate were placed in their calculated positions and periodically updated. Because of the apparently very high thermal motion of the benzene ring, refinement of the occupancy factors for its atoms was attempted. Values near unity resulted, and so full occupancy was assumed.

Refinement was terminated when the parameter shifts for all nonhydrogen atoms, except those for the benzene solvate, were reduced to less than their nominal standard deviations. The largest positional shift in the final cycle was 1.08 σ for two hydrogen atoms, and the largest change in a vibrational parameter was 1.9 σ for U_{23} of C(55). A final difference synthesis revealed a peak of height ~0.6 $e/\text{Å}^3$ near the benzene ring as its most prominent feature. The region near the reduced pyrrole ring was carefully examined for evidence of conformational or rotational disorder, but no evidence for these phenomena was found. Final residuals are given in Table I.

The structure and numbering system are shown in Figure 2 and the atomic positions are given in Tables II and III. The bond distances