

Naphtho[2,3:6,7]dicyclobutene[1,8:4,5]dicyclopentene

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Abstract. $C_{18}H_{16}$, $M_r = 232.3$, triclinic, $P\bar{1}$, $a = 6.603$ (2), $b = 8.545$ (2), $c = 5.238$ (2) Å, $\alpha = 95.10$ (2), $\beta = 94.72$ (3), $\gamma = 84.80$ (2) $^\circ$ (292 K), $Z = 1$, $D_x = 1.320$ Mg m $^{-3}$. The material was synthesized by pyrolysis of 1,4,5,8-tetrakis(chloromethyl)-2,3,6,7-tetramethylnaphthalene and was recrystallized from benzene. Identical material was synthesized by pyrolysis of 2,3,6,7-tetrakis(chloromethyl)-1,4,5,8-tetramethylnaphthalene; the crystallographic problem was one of overcoming spectral ambiguities and determining whether the material was the expected naphtho[1,2:3,4:5,6:7,8]tetracyclobutene or the title compound. The final refinement (using 442 'observed' of 765 unique data) led to $R = 0.046$ and R (weighted) = 0.035.

Introduction. Pyrolysis of either 1,4,5,8-tetrakis(chloromethyl)-2,3,6,7-tetramethylnaphthalene or 2,3,6,7-tetrakis(chloromethyl)-1,4,5,8-tetramethylnaphthalene gave a multi-cyclic product which was expected to be naphtho[1,2:3,4:5,6:7,8]tetracyclobutene; high-resolution mass spectra, proton NMR spectra, ^{13}C NMR spectra, UV spectra, IR spectra, the UV fluorescence properties, and the synthesis of this one product from two different starting materials are all consistent with the expected molecular structure and with the title compound (Hart, Jeffares, Teuerstein & Ward, 1978). The single-crystal X-ray structure determination was undertaken to overcome the spectral ambiguities and establish the molecular structure.

A single crystal of approximate dimensions 0.08 × 0.12 × 0.13 mm (μ for Mo $K\alpha = 0.0368$ mm $^{-1}$) was sealed in a capillary tube to minimize decomposition in air. Diffraction data were measured at 292 K with a Picker FACS-I automatic diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings of 17 reflections in the range $35^\circ < 2\theta < 40^\circ$ for which the α_1, α_2 doublet was resolved (λ for Mo $K\alpha_1 = 0.70926$ Å). The 765 unique data in the $+h \pm k \pm l$ hemisphere were collected for $2\theta < 45^\circ$ using the θ - 2θ scan method [scan speed 1° (2θ) min $^{-1}$; 20 s backgrounds; scan range of 1.8° (2θ) plus the $\alpha_1 - \alpha_2$ divergence; and three standard reflections measured after every 100 data were used to scale the data]. The

data were reduced and standard deviations were calculated as reported previously (Wei & Ward, 1976); the least-squares refinement weights were calculated from the standard deviation of the structure factor by $w = 1/(\sigma^2 + 0.02F^2)$; absorption corrections were applied to the data (Templeton & Templeton, 1973); extinction corrections were not applied to the data.

The structure was solved using the program ORTRAN (Busing & Thiessen, 1974) in which the molecular model (see Fig. 1) consisted of all 18 C atoms, *mmm* symmetry, C–C(aromatic) bond lengths 1.40 Å, and C–C(aliphatic) bond lengths 1.55 Å; the normalized structure factors (E 's) were calculated using the program NORMAL (Main, Woolfson, Lessinger, Germain & Declercq, 1974) in which the molecular fragment consisted of the same 18 C atoms. The structure was refined isotropically by full-matrix least squares in successive stages with data of increasing resolution (Parthasarathy, 1978); three cycles were performed each with $\sin \theta/\lambda$ less than 0.25, 0.30, 0.35, 0.40, 0.50 and 0.538 Å $^{-1}$. The scattering factors of Doyle & Turner (1968) and the anomalous-scattering factors of Cromer & Liberman (1970) were used for C and the scattering factors of Stewart, Davidson & Simpson (1965) were used for H. After anisotropic refinement had converged, H atoms were placed initially at calculated coordinates and further refinement [765 total data, 442 of which with $I > 2\sigma(I)$ were given non-zero weights and included in the refinement] led to $R_1 = \sum |F_o - F_c| / \sum |F_o| = 0.046$, $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2} = 0.035$, R_1 [including 323 data for which $I < 2\sigma(I)$] = 0.104, and the standard deviation of an observation of unit weight = 1.277; the atomic positional parameters are listed in Table 1.* During the final cycle of refinement, the maximum and average shift-to-error ratios were 0.020 and 0.006 for non-hydrogen and 0.040 and 0.008 for H atom parameters. The final difference map showed densities ranging from 0.31 to -0.27 e Å $^{-3}$ with no indication of missing or misplaced atoms. The com-

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34840 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

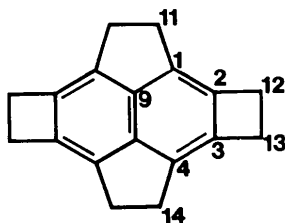


Fig. 1. The molecular structure indicating the numbering of the atoms.

Table 1. *Positional parameters*

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.0110 (6)	-0.1950 (5)	-0.1952 (8)
C(2)	-0.1475 (7)	-0.2529 (5)	-0.0915 (9)
C(3)	-0.2593 (6)	-0.1651 (5)	0.1029 (8)
C(4)	-0.2186 (7)	-0.0175 (4)	0.2012 (8)
C(9)	0.0543 (7)	-0.0421 (5)	-0.0958 (9)
C(11)	0.1614 (8)	-0.2500 (6)	-0.4007 (10)
C(12)	-0.2735 (9)	-0.3947 (6)	-0.0972 (10)
C(13)	-0.3951 (9)	-0.2986 (6)	0.1226 (11)
C(14)	-0.2981 (8)	0.1086 (6)	0.4014 (10)
H(111)	0.081 (6)	-0.285 (4)	-0.578 (8)
H(112)	0.233 (5)	-0.353 (4)	-0.370 (7)
H(121)	-0.188 (6)	-0.504 (4)	-0.046 (7)
H(122)	-0.362 (6)	-0.421 (5)	-0.269 (8)
H(131)	-0.537 (7)	-0.272 (5)	0.082 (9)
H(132)	-0.374 (6)	-0.346 (5)	0.292 (9)
H(141)	-0.286 (6)	0.065 (4)	0.569 (7)
H(142)	-0.447 (6)	0.142 (4)	0.353 (7)

puter programs used also include Zalkin's (1974) system; a CDC 6500 computer was used.

Discussion. An interesting feature of the molecular structure is that it is *not* the structural isomer originally expected from the synthesis; however, the determined structure is equally consistent with the spectral data and a reasonable mechanism for its synthesis has been presented (Hart, Jeffares, Teuerstein & Ward, 1978).

The two equivalent halves of the molecule are related by a center of symmetry and the interatomic distances and angles, listed in Table 2, show good agreement between chemically equivalent atoms in the molecule; only one pair of chemically equivalent bond lengths [C(1)–C(11) 1.539 (6), C(4)–C(14) 1.524 (6) Å] and three pairs of bond angles [C(1)–C(11)–C(14') 104.3 (3), C(4)–C(14)–C(11') 106.1 (4); C(2)–C(1)–C(11) 137.5 (4), C(3)–C(4)–C(14) 138.7 (4); and C(1)–C(2)–C(3) 122.4 (4), C(2)–C(3)–C(4) 123.4 (4)°] differ from their averages by more than one standard deviation. The least-squares plane calculation, listed in Table 3, shows the C atoms of the molecule to be planar to within ±0.020 Å.

The crystal structures have been determined for several naphthalene derivatives containing the four-membered (Crawford & Marsh, 1973; Thummel &

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

A prime indicates an atom at $-x, -y, -z$.

C(1)–C(2)	1.368 (5)	C(3)–C(4)	1.361 (5)
C(2)–C(3)	1.426 (6)		
C(1)–C(9)	1.407 (4)	C(4)–C(9')	1.411 (5)
C(1)–C(11)	1.539 (6)	C(4)–C(14)	1.524 (6)
C(2)–C(12)	1.527 (6)	C(3)–C(13)	1.529 (6)
C(9)–C(9')	1.391 (8)		
C(11)–C(14')	1.573 (6)		
C(12)–C(13)	1.584 (7)		
C(11)–H(111)	1.07 (4)	C(14)–H(141)	0.98 (4)
C(11)–H(112)	0.98 (3)	C(14)–H(142)	1.02 (4)
C(12)–H(121)	1.09 (4)	C(13)–H(131)	0.96 (4)
C(12)–H(122)	1.05 (4)	C(13)–H(132)	1.00 (5)
C(2)–C(1)–C(9)	114.8 (4)	C(3)–C(4)–C(9')	114.3 (4)
C(2)–C(1)–C(11)	137.5 (4)	C(3)–C(4)–C(14)	138.7 (4)
C(9)–C(1)–C(11)	107.7 (4)	C(9')–C(4)–C(14)	107.0 (4)
C(1)–C(2)–C(3)	122.4 (4)	C(2)–C(3)–C(4)	123.4 (4)
C(1)–C(2)–C(12)	144.4 (4)	C(4)–C(3)–C(13)	143.9 (4)
C(3)–C(2)–C(12)	93.2 (4)	C(2)–C(3)–C(13)	92.7 (4)
C(1)–C(9)–C(4')	114.9 (4)		
C(1)–C(9)–C(9')	122.4 (6)	C(4')–C(9)–C(9')	122.6 (5)
C(1)–C(11)–C(14')	104.3 (3)	C(4)–C(14)–C(11')	106.1 (4)
C(2)–C(12)–C(13)	86.9 (3)	C(3)–C(13)–C(12)	87.2 (3)

Table 3. *Least-squares plane*

The equation of the plane through 18 carbon atoms, referred to triclinic fractional coordinates, is

$$3.6421X - 3.4042Y + 3.6074Z = 0.$$

Distances of atoms from plane (Å)

C(1)	-0.000	C(11)	-0.006
C(2)	-0.006	C(12)	-0.003
C(3)	-0.011	C(13)	0.020
C(4)	-0.011	C(14)	-0.008
C(9)	-0.005		

Nutakul, 1978) or the five-membered (Ehrlich, 1957; Simmons & Lingafelter, 1961; Rodesiler & Amma, 1972; Tickle & Prout, 1973*a,b*) rings as in the title compound. A comparison of the bond distances and angles in the four-membered rings and the adjacent portion of the naphthalene rings with those determined for naphtho[*b*]cyclobutene (Crawford & Marsh, 1973) and for naphtho[*b,e*]dicyclobutene (Thummel & Nutakul, 1978) shows fairly good agreement between the three structures; the C–C lengths are all longer in the present compound by an average of 0.013 (four-membered rings) and 0.004 Å (adjacent portion of naphthalene) and the C–C–C angles differ by an average of only 0.3°.

A comparison of the weighted (by $1/\sigma$) average bond distances in naphtho[1,8]cyclopentene (Ehrlich, 1957; Rodesiler & Amma, 1972; Tickle & Prout, 1973*a,b*) with those in the present compound shows generally good agreement; however, the C(3)–C(4) bond is

0.007 Å (1.4σ) shorter and C(1)–C(11) and C(11)–C(14') are longer by 0.020 Å (3.3σ) and 0.029 Å (4.8σ), respectively, in the present compound. The bond lengths in the present compound agree with those in naphtho[1,8:4,5]dicyclopentene (Simmons & Lingafelter, 1961) within the precision of the earlier work.

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Structure of Halopemide, an Antipsychotic Benzamide Derivative

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Abstract. C₂₁H₂₂ClFN₄O₂; *N*-{2-[4-(5-chloro-2-oxo-1-benzimidazoliny)]piperidino}ethyl-*p*-fluorobenzamide; triclinic, *P*1̄; *a* = 14.322 (5), *b* = 15.057 (5), *c* = 10.271 (5) Å, *α* = 103.94 (5), *β* = 110.86 (5), *γ* = 92.67 (5)°; *D_m* = 1.38 (2), *D_c* = 1.39 Mg m⁻³, *Z* = 4, *T* = 294 K. The molecules form dimers linked through the endocyclic amide groups (imidazolinone group); moreover, each molecule is hydrogen bonded to two neighbours through the exocyclic amide group (benzamide group).

Introduction. Halopemide is an anti-autistic benzamide derivative related to the class of butyrophenones. The space group was determined from photographs. The final cell dimensions and intensities were measured on a Nonius CAD-4 four-circle computer-controlled diffractometer. The instrumental settings are given in Table 1. No corrections were made for absorption.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Three fragments containing 48 atoms were found in the most probable *E* map. Three successive Fourier maps revealed the two molecules of the asymmetric unit, H atoms excepted. Full-matrix least-squares refinement was performed with *XRAY 72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) minimizing $\sum w(F_o - F_c)^2$; the weight *w*

Table 1. *Instrumental settings for the data collection*

Crystal size: 0.5 × 0.4 × 0.2 mm
 Source: Cu Kα; λ = 1.54178 Å
 Graphite monochromator
 2 ≤ θ ≤ 65°
 Δ2θ = 0.75 + 0.14 tg θ (°)
 Aperture = 2.5 + 0.5 tg θ (mm)
 Confidence level: 2.5σ, where σ² = *S* + *B* + (0.03*S*)², *S* being the scan and *B* the background count
 Total number of independent reflexions: 5361
 Total observed: 2535

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