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Pyramidalization in a Hexachloronorborene Derivative

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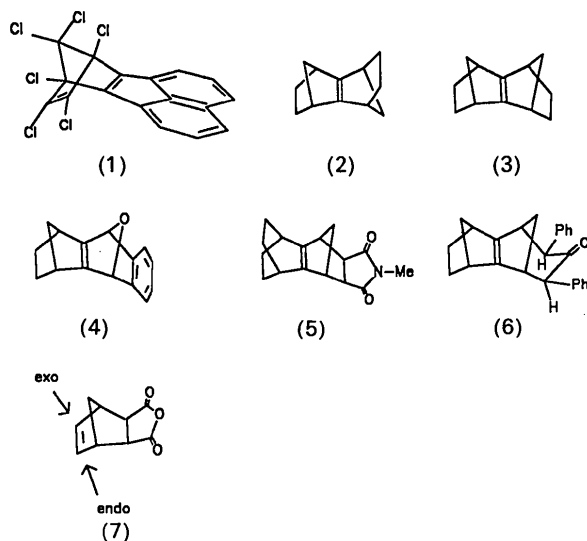
Abstract. 7,8,9,10,11,11-Hexachloro-7,10-dihydro-7,10-methanofluoranthene, (1), $C_{17}H_6Cl_6$, $M_r = 422.95$, monoclinic, $P2_1/c$, $a = 14.814$ (8), $b = 8.623$ (2), $c = 14.206$ (4) Å, $\beta = 111.22$ (3)°, $V = 1691.6$ (9) Å³, $Z = 4$, $D_x = 1.660$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 10.16$ cm⁻¹, $F(000) = 840$, $T = 295$ K, $R = 0.0488$ for 3186 reflections. The molecule is composed of a naphthalene ring system joined to a hexachloronorborene molecule forming an acenaphthylene moiety. The acenaphthylene system is planar (0.005 Å r.m.s. deviation); however, the $C(sp^2)$ atoms of the two double bonds in norbornene are pyramidalized with substituents bent away from the methano bridge in the *endo* direction. The $C(sp^2)$ atoms associated with the naphthalene ring fusion exhibit pyramidalization angles of 5.1 (3)° while the $C(sp^2)$ atoms substituted by Cl have pyramidalization angles of 2.4 (4)°.

Introduction. Most derivatives of *anti*-sesquinorborene (2) exhibit planar geometries around the olefinic C atoms (Watson, Galloy, Bartlett & Roof, 1981; Paquette, Hayes, Charumilind, Bohm, Gleiter & Blount, 1983; Gajhede, Jorgensen, Kopecky, Watson & Kashyap, 1985); however, the *exo*-4-nitrophenylmaleimide derivative (Ermer & Bodecker, 1983) exhibits a pyramidalization of 13.2 (3)° indicating a rather low barrier to the bending mode. In these papers the pyramidalization is reported either as the deviation of the interplanar angle from 180° or

as χ , the deviation from planarity of the dihedral angles about the sp^2 C atoms (Ermer & Mason, 1982). The olefinic C atoms of *syn*-sesquinorborene (3) and derivatives are considerably pyramidalized and exhibit deformation angles of 16–18° (Watson, Galloy, Bartlett & Roof, 1981; Hagenbuch, Vogel, Pinkerton & Schwarzenbach, 1981). Derivatives containing additional saturation at the ethano bridge exhibit slightly larger angles (Paquette, Green, Gleiter, Schaefer & Gallucci, 1984) with derivative (4) exhibiting a deformation angle of 22.1 (2)° (Watson, Galloy, Grossie, Bartlett & Combs, 1984). Recently, a *syn*-sesquinorborene with *spiro* fusion at the two methano C atoms was shown to have a deformation angle of 32.4° (Paquette & Shen, 1990). This deformation is enhanced by steric interactions of the spiro groups and the strained double bond is sterically shielded from reactants. Relief of angle strain about the central double bond is thought to be a major driving force in the pyramidalization; however, derivatives with bicyclo[2.2.1] (Paquette, Carr, Charumilind & Blount, 1980) (5) and bicyclo[3.2.1] (Paquette, Hsu, Gallucci, Korp, Bernal, Kravetz & Hathaway, 1984) (6) frameworks were found to have distortion angles of 9.3–11.8°. Recently, a neutron diffraction study of (7) (Ermer, Bell & Mason, 1989) found a 7.4 (2)° pyramidalization for the π bond which is larger than predicted by theory (Burkert, 1981; Spanget-Larsen & Gleiter, 1982; Ermer, Bodecker & Preut, 1984; Wipff & Morokuma, 1980; Rondan, Paddon-Row, Caramella & Houk, 1981). When the π bond in norbornene results from fusion

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to a benzene ring such as in (4), the pyramidalization at the ethano bridge is decreased to $2-3^\circ$ (Ermer, Bell & Mason, 1989; Watson, Galloy, Grossie, Bartlett & Combs, 1984). There has been active discussion concerning the nature of the driving force for the distortion from planarity (Watson, 1983). Steric interactions involving the methano bridge were eliminated as primary causative factors and reduction of torsional strain around the $C(sp^2)-C(sp^3)$ bonds and σ - and π -bond interactions are the major considerations (Houk, Rondan, Brown, Jorgensen, Madura & Spellmeyer, 1983; Gleiter & Spanget-Larsen, 1982; Spanget-Larsen & Gleiter, 1982; Inagaki, Fukimoto & Fukui, 1976; Carrupt & Vogel, 1985). Compound (1) (Plummer, Chihal, D'Orsogna & Blenkarn, 1977) should provide additional insight into π -bond pyramidalization.



Experimental. An orange crystal (Plummer, Chihal, D'Orsogna & Blenkarn, 1977) of dimensions $0.53 \times 0.50 \times 0.30$ was mounted on a Nicolet R3m/ μ update of a P2, diffractometer; data collected in the ω mode ($3 \leq 2\theta \leq 55^\circ$), variable scan rate of 2 to $29.3^\circ \text{ min}^{-1}$ using graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from a least-squares refinement of 25 reflections ($23.14 \leq 2\theta \leq 28.99^\circ$), systematic extinctions ($h0l, l = 2n + 1; 0k0, k = 2n + 1$) consistent with space group $P2_1/n$; monitored reflections 502 and $8\bar{1}4$ showed variations in intensity of less than 2%; 5304 reflections measured ($-3 \leq h \leq 19, 0 \leq k \leq 11, -18 \leq l \leq 18$), 3905 unique reflections ($R_{\text{int}} = 0.008$) and $3186 \geq 3\sigma(I)$; Lorentz-polarization corrections and ψ -scan empirical absorption correction (transmission factors 0.631 to 0.590) applied; structure solved by direct methods and refined by a block-cascade least-squares technique, H atoms located in a difference map and refined with isotropic thermal parameters; $R = 0.0488$ ($R_{\text{all}} =$

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	8137 (2)	1431 (3)	1991 (2)	40 (1)
Cl(1)	8634 (1)	2932 (1)	1514 (1)	59 (1)
C(2)	8416 (2)	-233 (3)	1816 (2)	46 (1)
Cl(2)	8835 (1)	-699 (1)	891 (1)	71 (1)
C(3)	8239 (2)	-1144 (3)	2473 (2)	49 (1)
Cl(3)	8362 (1)	-3100 (1)	2593 (1)	83 (1)
C(4)	7832 (2)	-131 (3)	3122 (2)	43 (1)
Cl(4)	7879 (1)	-904 (1)	4278 (1)	63 (1)
C(5)	6872 (2)	493 (3)	2414 (2)	41 (1)
C(6)	7056 (2)	1418 (3)	1740 (2)	40 (1)
C(7)	6135 (2)	1927 (3)	973 (2)	39 (1)
C(8)	5839 (2)	2818 (3)	115 (2)	49 (1)
C(9)	4822 (3)	2957 (4)	-424 (2)	60 (1)
C(10)	4134 (2)	2272 (3)	-137 (2)	54 (1)
C(11)	3833 (2)	551 (4)	1177 (2)	55 (1)
C(12)	4236 (2)	-296 (4)	2050 (2)	55 (1)
C(13)	5235 (2)	-420 (3)	2560 (2)	50 (1)
C(14)	5837 (2)	325 (3)	2174 (2)	40 (1)
C(15)	5418 (2)	1223 (3)	1278 (2)	39 (1)
C(16)	4431 (2)	1351 (3)	757 (2)	44 (1)
C(17)	8472 (2)	1341 (3)	3178 (2)	41 (1)
Cl(5)	9721 (1)	1005 (1)	3804 (1)	62 (1)
Cl(6)	8163 (1)	2975 (1)	3740 (1)	62 (1)

0.0605), $wR = 0.0575$ ($wR_{\text{all}} = 0.0586$), for 232 parameters and 3186 reflections, $S = 2.073$, $(\Delta/\sigma)_{\text{max}} = 0.027$; largest peaks in the final difference map of -0.40 and 0.61 e \AA^{-3} ; $\sum w(|F_o| - |F_c|)^2$ refined with $w = [\sigma^2(F_o) + 0.00022F_o^2]^{-1}$. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microclipse and Nova 4/C configuration; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 lists the atomic positional parameters while Table 2 gives bond lengths and bond angles.*

Discussion. Fig. 1 is a drawing of compound (1). The molecule is composed of a norbornadiene moiety fused to a acenaphthylene system. All H atoms in the norbornadiene moiety are replaced with Cl atoms. The molecule contains an approximate non-crystallographic mirror plane with all chemically equivalent bonds statistically equivalent except for the pairs C(5)—C(14), C(6)—C(7) [1.453 (4) and 1.471 (3) \AA] and C(8)—C(9), C(12)—C(13) [1.427 (4) and 1.396 (4) \AA]. The chemically equivalent C—Cl bonds are statistically equivalent, but the pairs differ significantly in length; C(2)—Cl(2)_{av} = 1.695 (3), C(1)—Cl(1)_{av} = 1.748 (4) and C(17)—Cl(15)_{av} = 1.762 (2) \AA . The $C(sp^2)-Cl$ bond is the shortest as expected.

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53302 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and bond angles (°)

C(1)—C(1)	1.744 (3)	C(1)—C(2)	1.539 (4)
C(1)—C(6)	1.508 (4)	C(1)—C(17)	1.578 (4)
C(2)—Cl(2)	1.692 (3)	C(2)—C(3)	1.317 (4)
C(3)—Cl(3)	1.698 (3)	C(3)—C(4)	1.542 (4)
C(4)—Cl(4)	1.751 (3)	C(4)—C(5)	1.512 (3)
C(4)—C(17)	1.569 (4)	C(5)—C(6)	1.348 (4)
C(5)—C(14)	1.453 (4)	C(6)—C(7)	1.471 (3)
C(7)—C(8)	1.373 (4)	C(7)—C(15)	1.421 (4)
C(8)—C(9)	1.427 (4)	C(9)—C(10)	1.363 (5)
C(10)—C(16)	1.425 (4)	C(11)—C(12)	1.375 (4)
C(11)—C(16)	1.415 (5)	C(12)—C(13)	1.396 (4)
C(13)—C(14)	1.365 (5)	C(14)—C(15)	1.426 (3)
C(15)—C(16)	1.384 (3)	C(17)—Cl(5)	1.763 (3)
C(17)—Cl(6)	1.760 (3)		
Cl(1)—C(1)—C(2)	116.9 (2)	Cl(1)—C(1)—C(6)	118.4 (2)
C(2)—C(1)—C(6)	106.2 (2)	Cl(1)—C(1)—C(17)	116.0 (2)
C(2)—C(1)—C(17)	97.3 (2)	C(6)—C(1)—C(17)	98.6 (2)
C(1)—C(2)—Cl(2)	122.9 (2)	C(1)—C(2)—C(3)	107.9 (3)
Cl(2)—C(2)—C(3)	129.2 (2)	C(2)—C(3)—Cl(3)	128.4 (3)
C(2)—C(3)—C(4)	107.9 (2)	Cl(3)—C(3)—C(4)	123.6 (2)
C(3)—C(4)—Cl(4)	117.0 (2)	C(3)—C(4)—C(5)	106.4 (2)
Cl(4)—C(4)—C(5)	117.9 (2)	C(3)—C(4)—C(17)	97.4 (2)
Cl(4)—C(4)—C(17)	116.2 (2)	C(5)—C(4)—C(17)	98.7 (2)
C(4)—C(5)—C(6)	107.4 (2)	C(4)—C(5)—C(14)	141.2 (3)
C(6)—C(5)—C(14)	111.1 (2)	C(1)—C(6)—C(5)	107.8 (2)
C(1)—C(6)—C(7)	142.5 (3)	C(5)—C(6)—C(7)	109.3 (2)
C(6)—C(7)—C(8)	137.5 (3)	C(6)—C(7)—C(15)	104.1 (2)
C(8)—C(7)—C(15)	118.4 (2)	C(7)—C(8)—C(9)	117.4 (3)
C(8)—C(9)—C(10)	124.2 (3)	C(9)—C(10)—C(16)	119.0 (3)
C(12)—C(11)—C(16)	120.3 (3)	C(11)—C(12)—C(13)	122.8 (3)
C(12)—C(13)—C(14)	118.6 (3)	C(5)—C(14)—C(13)	137.7 (2)
C(5)—C(14)—C(15)	103.7 (2)	C(13)—C(14)—C(15)	118.6 (2)
C(7)—C(15)—C(16)	111.8 (2)	C(7)—C(15)—C(16)	124.4 (2)
C(14)—C(15)—C(16)	123.7 (3)	C(10)—C(16)—C(11)	127.5 (2)
C(10)—C(16)—C(15)	116.5 (3)	C(11)—C(16)—C(15)	115.9 (2)
C(1)—C(17)—C(4)	92.0 (2)	C(1)—C(17)—Cl(5)	114.5 (2)
C(4)—C(17)—Cl(5)	113.4 (2)	C(1)—C(17)—Cl(6)	114.3 (2)
C(4)—C(17)—Cl(6)	114.8 (2)	Cl(6)—C(17)—Cl(6)	107.5 (1)

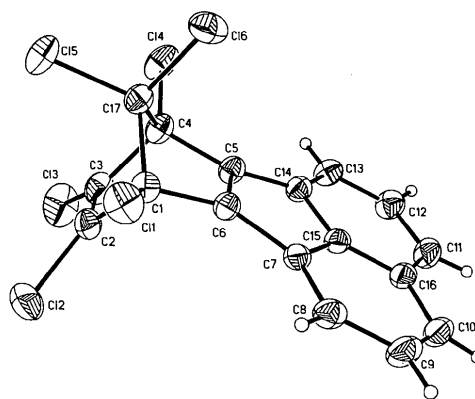


Fig. 1. Drawing of compound (1) with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

bond is $0.4(3)^\circ$ with $\chi_2 = 2.1(2)$, $\chi_3 = 2.8(2)^\circ$ and an average of $2.4(4)^\circ$. The atoms Cl(2), Cl(3), C(7) and C(14) are bent towards the *endo* face as is observed for all norbornene-type pyramidalizations.

There has been considerable controversy concerning the driving force for pyramidalization in these systems (Watson, 1983). Steric interactions with methano substituents were eliminated as a major causative factor in *endo* bending. Major arguments involve either the relief of torsional interactions around the π bond or asymmetric interactions between σ - and π -bonding components (Houk, Rondan, Brown, Jorgensen, Madura & Spellmeyer, 1983; Gleiter & Spanget-Larsen, 1982). The pyramidalization of C(5) and C(6) is larger than that expected for benzonorbornenes but is in the expected range for norbornenes. It is interesting to note that conjugation of the π bond at C(5) and C(6) with the *peri*-fused naphthalene ring does not reduce the pyramidalization from that found for other norbornenes. The pyramidalization at C(2) and C(3) is at the low end of the deviation range and close to that observed for benzonorbornenes. This may result from polarization of the electron density toward the Cl atoms and may provide some support for the σ -bond- π -bond interaction theory; however, no detailed calculations have been made on this system.

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The acenaphthylene ring system is planar (0.005 \AA r.m.s. deviation). The $C(sp^2)$ atoms C(5) and C(6) are pyramidalized with the two C atoms lying out of the planes of the three contiguous atoms by $0.042(4)$ and $0.048(4) \text{ \AA}$, respectively. The planes C(4)C(5)C(6)C(1) (0.002 \AA r.m.s. deviation) and C(7)C(6)C(5)C(14) (0.004 \AA r.m.s. deviation) deviate from coplanarity by $5.1(3)^\circ$. Two geometrical parameters were used to describe the double-bond deformation in (7) (Ermer, Bell & Mason, 1989). A twist angle Φ_o which is the arithmetic mean of the two double-bond torsion angles [C(4)—C(5)—C(6)—C(1) and C(7)—C(6)—C(5)—C(14)] and a bending (pyramidalization) angle χ [χ_s , the deviation from planarity of the dihedral angles C(4)C(5)C(6)/C(14)C(5)C(6), is equal to the improper torsion angle C(4)—C(5)—C(6)—C(14)]. Φ_o for the C(5)—C(6) bond is $0.6(3)^\circ$ indicating negligible twist with $\chi_5 = 4.8(2)$, $\chi_6 = 5.4(2)^\circ$ and an average of $5.1(3)^\circ$. Atoms C(2) and C(3) are pyramidalized to a smaller extent and lie out of the planes of the three attached atoms by $0.016(5)$ and $0.023(5) \text{ \AA}$, respectively. The planes C(1)C(2)C(3)C(4) (0.008 \AA r.m.s. deviation) and Cl(2)C(2)C(3)Cl(3) (0.003 \AA r.m.s. deviation) deviate from coplanarity by $2.6(3)^\circ$. Φ_o for the π

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Strained Heterocyclic Systems. 18.* Structure of 1,2,3-Methyldiyne-2,3-dihydro-1H-cyclopenta[b]quinoxaline

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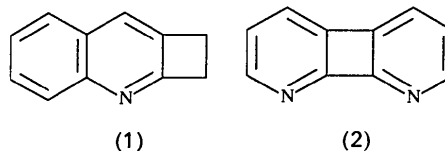
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Abstract. $C_{12}H_8N_2$, $M_r = 180.211$, monoclinic, $P2_1/n$, $a = 8.6126$ (8), $b = 12.5147$ (13), $c = 8.5484$ (7) Å, $\beta = 99.663$ (7)°, $V = 908.31$ (15) Å³, $Z = 4$, $D_x = 1.32$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 5.93$ cm⁻¹, $F(000) = 376$, $T = 291$ K, final $R = 0.063$ for 1645 unique reflections. This study demonstrates that a fused strained ring system adjacent to the N atom of an azaarene results in an abnormally small C—N—C bond angle.

Introduction. In previous papers (Deroski, Markgraf & Ricci, 1983; Deroski, Ricci, MacBride & Mark-

graf, 1984) we reported that 1,2-dihydrocyclobuta[b]quinoline (1) and 1,8-diazabiphenylene (2) contained C—N—C bond angles of 112.5 and 112.9°, respectively.



Such abnormally small angles resulting from the fusion of a strained ring adjacent to the N atom cause an increase in the s character of the non-bonding orbital (Moomaw, Kleier, Markgraf,

* Part 17: Markgraf, Mueller & Myers (1989).

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