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6,8-Dichloro-1,3-benzodioxin

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Abstract. $C_8H_6Cl_2O_2$, $M_r = 205.04$, monoclinic, $P2_1/c$, $a = 13.895$ (6), $b = 4.0356$ (9), $c = 15.788$ (3) Å, $\beta = 109.51$ (2)°, $V = 834.5$ (5) Å³, $Z = 4$, $D_x = 1.63$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.73$ mm⁻¹, $F(000) = 416$, room temperature, final $R = 0.059$ for 1175 unique reflections with $F_o > 4\sigma(F_o)$. Endocyclic parameters in the heterocyclic ring are $C_{Ar}-O$ 1.365 (4), $(C_{Ar})O-C$ 1.433 (6), $(C_{Ar}O)C-O$ 1.401 (6), $O-C(C_{Ar})$ 1.422 (4) Å; $C_{Ar}-O-C$ 112.7 (3), $(C_{Ar})O-C-O$ 110.5 (4), $(C_{Ar}O)C-O-C$ 110.1 (3), $O-C-C_{Ar}$ 111.0 (3)°; $(C_{Ar})O-C-O-C(C_{Ar})-70.0$ (4)°.

Introduction. This paper continues the reports of a series of investigations into the effect of substituent groups, both in the heterocyclic ring and in the aromatic ring of 1,3-benzodioxins, on the conformation and molecular parameters of these compounds. Details of the background to these studies can be found in Irving & Irving (1988a,b,c, and references therein).

Experimental. 6,8-Dichloro-1,3-benzodioxin was prepared by the condensation of 2,4-dichlorophenol with formaldehyde in a mixture of concentrated hydrochloric and sulfuric acids following Buehler, Brown, Holbert, Fulmer & Parker (1941). The solid reaction product was collected, purified by steam distillation and recrystallized from boiling methanol, in which it is readily soluble, as colourless flat needles, m.p. 381.5 K (lit. 382–382.5 K). Better-formed and stouter needles

were obtained by slow growth from chloroform. Found: C, 46.9; H, 3.00%. $C_8H_6Cl_2O_2$ requires C, 46.86; H, 2.95%. The NMR spectrum (90 MHz in $CDCl_3$) gave $\delta(^1H)$ 4.84 [2H, t, H (4)], $J_{4,5}$ 8.6 Hz; 5.30 [2H, s, H (2)]; 6.85 [1H, td, H (5)]; 7.22 [1H, td, H (7)]. Specimen with dimensions 0.44 × 0.44 × 0.47 mm used for X-ray work. Lattice parameters determined by least-squares fitting of setting angles of 24 reflections $16 < \theta < 17^\circ$ automatically centred on CAD-4 diffractometer. Intensities collected with graphite-monochromated $Mo K\alpha$ radiation, $\lambda = 0.71069$ Å. $\omega/2\theta$ scan mode, variable scan rate, scan width $(1.73 + 0.35\tan\theta)^\circ$, aperture setting 4 mm, range of reflections $1 < \theta < 25^\circ$, 1761 reflections measured, 1325 unique, $R_{int} = 0.036$, 1175 [$F_o > 4\sigma(F_o)$] used in refinement, index range $h-16/16$, $k 0/4$, $l 0/18$. Three intensity-control reflections ($\bar{3}, 2, 10$, $\bar{8}27$, $\bar{2}35$) monitored after every hour of data collection, showed an average decline in intensity of 1.5%. Data corrected for background, scan-speed, Lorentz and polarization factors; empirical absorption correction applied (North, Phillips & Mathews, 1968), transmission factors 0.859 to 0.998. Structure solved by direct methods. Least-squares anisotropic refinement (based on F) of positions of non-H atoms and free isotropic refinement of H-atom positions gave final $R = 0.059$, $wR = 0.054$, $w = 1/[\sigma^2(F_o) + 0.000723F_o^2]$, $S = 7.8$, $\Delta/\sigma(\max.) < 0.001$, residual electron density $-0.72 \leq \Delta\rho \leq +0.49$ e Å⁻³. Complex neutral-atom scattering factors from Stewart, Davidson & Simpson (1965) for hydrogen and from Cromer & Mann (1968) for all other atom types; dispersion corrections from Cromer & Liberman (1970). Final atomic parameters are listed in

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}^*
O(1)	1195 (2)	3230 (6)	528 (2)	441 (9)
C(2)	1241 (3)	5049 (12)	-237 (3)	505 (15)
H(21)	1122 (30)	7582 (103)	-235 (25)	512 (107)†
H(22)	769 (33)	3981 (86)	-771 (28)	487 (108)†
O(3)	2201 (2)	4681 (7)	-334 (2)	510 (10)
C(4)	2955 (3)	6384 (10)	368 (2)	417 (13)
H(41)	3567 (32)	5671 (94)	359 (25)	487 (109)†
H(42)	2892 (32)	8863 (102)	256 (27)	578 (120)†
C(5)	3634 (3)	6249 (9)	2062 (2)	374 (13)
H(5)	4179 (34)	7379 (96)	2024 (26)	502 (105)†
C(6)	3531 (2)	5365 (9)	2871 (2)	368 (12)
C(7)	2672 (3)	3757 (9)	2907 (2)	375 (12)
H(7)	2585 (27)	3200 (84)	3428 (24)	386 (94)†
C(8)	1908 (2)	3049 (8)	2116 (2)	335 (11)
C(9)	1985 (2)	3959 (8)	1292 (2)	323 (12)
C(10)	2871 (2)	5538 (8)	1270 (2)	330 (12)
Cl(6)	4495 (1)	6333 (3)	3872 (1)	575 (4)
Cl(8)	817 (1)	1042 (2)	2145 (1)	501 (4)

* Equivalent isotropic U calculated from anisotropic U :

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

† Isotropic U .

Table 1.* Computer programs used: *SHELX76* (Sheldrick, 1978); *SHELX86* (Sheldrick, 1985); *PLUTO* (Motherwell, 1974); *PARST* (Nardelli, 1983). All calculations performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer.

Discussion. Fig. 1 is a perspective view of a molecule of the title compound, (I), which comprises a heterocyclic ring in a half-boat conformation fused to a significantly non-planar aromatic ring. Molecular parameters and Cremer–Pople parameters (Cremer & Pople, 1975) are given in Table 2. The conformation of the molecule is such that the atoms C(4), C(10), C(9), O(1) are coplanar: C(2) is 0.407 (5) Å distant from this plane and O(3) is 0.352 (3) Å distant on the opposite side. The distance of 2.38 (6) Å between the two pseudoaxial H atoms, H(21)···H(42), is similar to the corresponding distances of 2.52 (5) Å in 6-nitro-1,3-benzodioxin, (II) (Irving & Irving, 1988c), and 2.56 (4) Å in 6-nitro-2,4-bis(dichloromethyl)-1,3-benzodioxin, (III) (Irving & Irving, 1987). The conformation of (I) is very similar to that of (II) and (III) and it seems likely that it is this H···H distance that mainly determines the torsion angle O(1)–C(2)–O(3)–C(4).

The only X-ray structure so far reported of a 1,3-benzodioxin which is unsubstituted in the heterocyclic ring is that of (II). Molecular parameters in the 1,3-dioxin ring are in agreement with those for (II)

* Lists of structure factors and anisotropic thermal parameters and weighted least-squares plane equation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51602 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å), angles (°), intramolecular distance (Å) and torsion angles (°) in the title compound and Cremer–Pople parameters

C(9)–O(1)	1.365 (4)	C(9)–O(1)–C(2)	112.7 (3)
O(1)–C(2)	1.433 (6)	O(1)–C(2)–O(3)	110.5 (4)
C(2)–O(3)	1.401 (6)	C(2)–O(3)–C(4)	110.1 (3)
O(3)–C(4)	1.422 (4)	O(3)–C(4)–C(10)	111.0 (3)
C(4)–C(10)	1.506 (5)	C(4)–C(10)–C(9)	118.3 (3)
C(10)–C(9)	1.397 (4)	C(10)–C(9)–O(1)	122.1 (3)
C(9)–C(8)	1.390 (5)	C(8)–C(9)–O(1)	118.7 (3)
C(8)–C(7)	1.372 (4)	C(5)–C(10)–C(4)	122.3 (3)
C(7)–C(6)	1.376 (5)	C(10)–C(5)–C(6)	120.1 (3)
C(6)–C(5)	1.379 (5)	C(5)–C(6)–C(7)	121.3 (3)
C(5)–C(10)	1.373 (4)	C(6)–C(7)–C(8)	118.6 (3)
C(6)–Cl(6)	1.741 (3)	C(7)–C(8)–C(9)	121.3 (3)
C(8)–Cl(8)	1.733 (3)	C(8)–C(9)–C(10)	119.2 (3)
C(2)–H(21)	1.04 (4)	C(9)–C(10)–C(5)	119.5 (3)
C(2)–H(22)	0.98 (4)	C(5)–C(6)–Cl(6)	119.8 (3)
C(4)–H(41)	0.90 (5)	C(7)–C(6)–Cl(6)	118.9 (2)
C(4)–H(42)	1.01 (4)	C(7)–C(8)–Cl(8)	119.4 (3)
C(9)–C(8)–Cl(8)	119.3 (2)		
H(21)···H(42)	2.38 (6)		
C(9)–O(1)–C(2)–O(3)	52.2 (4)	O(3)–C(4)–C(10)–C(9)	-14.4 (4)
O(1)–C(2)–O(3)–C(4)	-70.0 (4)	C(4)–C(10)–C(9)–O(1)	-1.3 (5)
C(2)–O(3)–C(4)–C(10)	48.6 (4)	C(10)–C(9)–O(1)–C(2)	-17.0 (5)

	ψ (°)	Q_T (Å)	θ (°)
Dioxin ring	-92.2 (5)	0.502 (4)	128.3 (4)
Aromatic ring	4 (15)	0.015 (3)	60 (14)

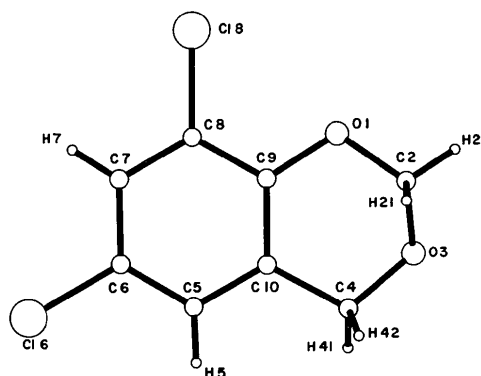
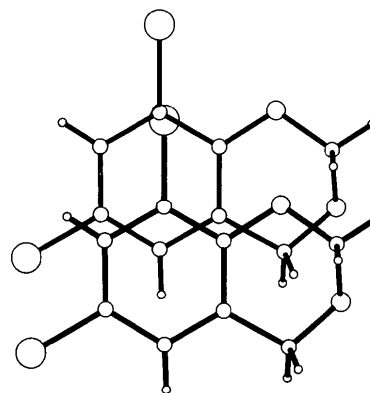


Fig. 1. A perspective view of a molecule of the title compound.

Fig. 2. View perpendicular to C(5), C(6), C(7) in the molecule at (x, y, z) of the molecules at (x, y, z) and $(x, 1+y, z)$.

where C(9)–O(1) is 1.362 (3) Å and O(3)–C(4) is 1.431 (5) Å, although the difference between the bond lengths O(1)–C(2) 1.434 (5) Å, and C(2)–O(3) 1.377 (5) Å in (II) is much more pronounced than the corresponding marginal difference in the title compound in which the torsion angle O(1)–C(2)–O(3)–C(4) of 69.1 (4)° in (II) is not different from that in (I). The aromatic rings of molecules at (x, y, z) and $(x, 1+y, z)$ form stacks, the overlap between molecules in these stacks being illustrated in Fig. 2. The average perpendicular distance between the C atoms in the aromatic ring and the plane through these related atoms in adjacent molecules is 3.566 (7) Å, which is close to the corresponding distances of 3.472 (96) and 3.503 (96) Å found in (II).

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The Tri-*ortho*-thymotide–3-Buten-2-ol (2/1) Clathrate at 153 K. Lattice Energy and Chiral Discrimination

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Abstract. 1,7,13-Trimethyl-4,10,16-tris(1-methylethyl)-6*H*,12*H*,18*H*-tribenzo[*b,f,j*][1,5,9]trioxacyclododecin-6,12,18-trione–3-buten-2-ol (2/1), C₃₃H₃₆O₆·½C₄H₈O, *M_r* = 564.70, trigonal, *P*3₁21, *a* = 13.444 (3), *c* = 30.217 (9) Å, *V* = 4730 (1) Å³, *Z* = 6, *D_x* = 1.190 g cm^{−3}, λ(Mo *K*α) = 0.71069 Å, μ = 0.875 cm^{−1}, *F*(000) = 1812, *T* = 153 K, *R* = 0.068 for 1657 observed reflections at the |*F_o*| > 3σ(*F_o*) level. The host structure was refined starting from previously determined coordinates in an isomorphous tri-*ortho*-thymotide (TOT) clathrate. A strained conformation of the guest, derived from a calculated two-dimensional energy map, was favourably used as rigid component in the X-ray model. Evidence for low chiral discrimination of the guest was quantitatively demonstrated.

Correlation of configuration between TOT in a single crystal and the major included enantiomer was shown to obey previously established structural rules. Lattice-energy calculations corroborate the experimental observations.

Introduction. Strongly basic reagents are required to promote the ring-opening of epoxides involving a rearrangement to allylic alcohols (e.g. Price & Carmelite, 1966). Pseudo-enzymatic activity of TOT clathrate cages was demonstrated by the occurrence of the analogous chemical transformation of simple enclathrated epoxides, but under acidic conditions (Gerdil & Barchietto, 1987). A noteworthy result is the acid-catalysed rearrangement of included *cis*-2,3-dimethyloxirane (1) to form quantitatively 3-buten-2-ol (2) in slight enantiomeric excess, when clathrate crystals of TOT/(1) are submitted to a flow of gaseous HCl or HBr. The present structure analysis is part of a

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