

Irving, 1986c) and 1.353 (4) Å in 6,8-dinitro-2-trichloromethyl-4-dichloromethylene-1,3-benzodioxin (VI) (Irving & Irving, 1987b). The endocyclic angles at O(1), C(2), O(3), C(4) are in excellent agreement with those reported for (III): the difference at O(1) and O(3) from the corresponding values in (I) and (II) has been discussed for (III).

Torsion angles between the nitro groups and the aromatic ring show that these groups are twisted by 16° for 6-NO₂ and 44° for 8-NO₂. Corresponding values for (V) are 16 and 11°, and for (VI) are 4 and 27°. A packing diagram is given in Fig. 2. There are no unusually short intermolecular distances, and packing is effected by normal van der Waals forces.

We thank Dr M. L. Niven for the data collection and the UCT Research Committee for financial support.

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Acta Cryst. (1988). **C44**, 1230–1233

5,7-Dichloro-6-methoxy-2,4-bis(trichloromethyl)-1,3-benzodioxin

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(Received 12 October 1987; accepted 1 March 1988)

Abstract. C₁₁H₆Cl₈O₃, *M_r* = 469.79, monoclinic, *P*2₁/*n*, *a* = 10.438 (2), *b* = 15.113 (6), *c* = 10.885 (2) Å, β = 98.40 (2)°, *V* = 1698.7 (8) Å³, *Z* = 4, *D_x* = 1.84 Mg m⁻³, *F*(000) = 928, λ(Mo *K*α) = 0.71069 Å, μ = 1.34 mm⁻¹, room temperature, final *R* = 0.034 for 2521 unique counter reflections with *F_o* > 4σ(*F_o*). The distorted screw-boat heterocyclic ring is substituted pseudoequatorially at the 2-position and pseudoaxially at the 4-position, C–C_{eq} 1.534 (4) and C–C_{ax} 1.555 (4) Å. Endocyclic parameters in the heterocyclic ring are C_{Ar}–O 1.387 (3), (C_{Ar})O–C 1.408 (4), (C_{Ar})O–C–O 1.402 (4), O–C(C_{Ar}) 1.430 (3) Å; C_{Ar}–O–C 108.8 (2), (C_{Ar})O–C–O 112.5 (3), (C_{Ar})O–C–O–C 116.7 (2), O–C–C_{Ar} 112.5°. The methoxy group is perpendicular to the aromatic ring, C_{Ar}–C_{Ar}–O 120.3 (3), 120.9 (2)°, C_{Ar}–O–C 113.2 (3)°.

Introduction. The structure of the title compound has been determined as part of a program of work (Irving & Irving, 1986a, 1987a) undertaken in order to study the effect of changing the substituents, both in the heterocyclic ring and in the aromatic ring, on the molecular parameters and conformation of 1,3-benzodioxins.

Experimental. The condensation product of chloral hydrate with 2,6-dichloroquinol in concentrated sulfuric acid (Chattaway & Calvet, 1928, 1929) was methylated by the cautious addition of aqueous potassium hydroxide to its solution in dimethyl sulfate. The resulting 5,7-dichloro-6-methoxy-2,4-bis(trichloromethyl)-1,3-benzodioxin was recrystallized repeatedly from hot glacial acetic acid in which it was sparingly soluble and gave colourless compact tablets, m.p. 467.7–468.7 K. Found: C, 28.1; H, 1.25%. C₁₁H₆Cl₈O₃ requires C, 28.12; H, 1.29%. The NMR

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spectrum (90 MHz) in acetone- d_6 gave $\delta(^1\text{H})$ 3.82 (3H, s, CH₃); 5.0 [1H, s, H(4)]; 5.9 [1H, s, H(2)]; 7.19 [1H, s, H(8)]. Specimen with dimensions 0.31 × 0.44 × 0.50 mm used for X-ray work. Lattice parameters determined by least-squares fitting of setting angles of 24 reflections ($16 \leq \theta \leq 17^\circ$), automatically centred on CAD-4 diffractometer. Intensities collected with graphite-monochromated Mo K α radiation, $\lambda = 0.71069 \text{ \AA}$, $\omega/2\theta$ scan mode, variable scan rate, scan width $(0.95 + 0.35 \tan \theta)^\circ$, aperture setting 4 mm, range of reflections $\theta = 1\text{--}25^\circ$, 3287 reflections measured, 2807 unique reflections, $R_{\text{int}} = 0.018$, 2521 [$F_o > 4\sigma(F_o)$] used in refinement, index range $h\text{--}12/12$, $k\text{--}0/18$, $l\text{--}0/12$. Three intensity-control reflections ($\bar{3}, 11, 2, 3, 10, 3, 167$) monitored after every hour of data collection showed an average decline in intensity of 1.4%. Data corrected for background, scan-speed, Lorentz and polarization factors; empirical absorption correction applied (North, Phillips & Mathews, 1968), transmission factors 0.886 to 1.000. Structure solved by random-start multiresolution direct methods. Least-squares anisotropic refinement (based on F) of positions of non-hydrogen atoms and free isotropic refinement of H-atom positions gave final $R = 0.034$, $wR = 0.033$, $w = 1/\sigma^2(F_o)$, $S = 2.67$, $\Delta/\sigma(\text{max.}) = 0.009$, residual electron density $-0.58 \leq \Delta\rho \leq 0.68 \text{ e \AA}^{-3}$. Complex neutral-atom scattering factors from Stewart, Davidson & Simpson (1965) for H and from Cromer & Mann (1968) for all other atom types; dispersion corrections from Cromer & Liberman (1970). Final atomic parameters are listed in Table 1.* Computer programs used: *SHELX76* (Sheldrick, 1978); *SHELX84* (Sheldrick, 1983); *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. In the title compound (I), the 1,3-benzodioxin moiety consists of a heterocyclic ring which has a distorted screw-boat conformation (Boeyens, 1978) fused to a significantly non-planar aromatic ring. Cremer-Pople parameters (Cremer & Pople, 1975) for both rings are given in Table 2. The trichloromethyl group at the 2-position is pseudo-equatorial whereas that at the 4-position is pseudoaxial (see Fig. 1); this same situation has been found for all the 2,4-bis(trichloromethyl)-1,3-benzodioxins that have been reported. There derivatives are the 6-nitro (II) (Irving & Irving, 1986*b*; Hamada, Kiriya, Tsuji & Hashimoto, 1987), the 6-carboxylic acid (III) and the

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)	-1461 (2)	7122 (1)	-784 (2)	359 (6)
C(2)	-1657 (3)	7259 (2)	454 (3)	349 (9)
O(3)	-638 (2)	7728 (1)	1144 (2)	375 (6)
C(4)	646 (2)	7483 (2)	968 (3)	319 (9)
C(5)	1667 (2)	6078 (2)	179 (2)	316 (8)
C(6)	1655 (2)	5417 (2)	-709 (3)	330 (9)
C(7)	587 (3)	5346 (2)	-1624 (2)	338 (9)
C(8)	-463 (3)	5903 (2)	-1657 (3)	340 (9)
C(9)	-399 (2)	6572 (2)	-791 (2)	304 (9)
C(10)	664 (2)	6700 (2)	116 (2)	288 (9)
C(21)	-2883 (3)	7818 (2)	456 (3)	450 (10)
Cl(2A)	-3225 (1)	7838 (1)	1990 (1)	766 (4)
Cl(2B)	-4185 (1)	7297 (1)	-507 (1)	725 (4)
Cl(2C)	-2705 (1)	8896 (1)	-71 (1)	673 (4)
C(41)	1257 (3)	8332 (2)	493 (3)	386 (9)
Cl(4A)	483 (1)	8674 (1)	-974 (1)	569 (3)
Cl(4B)	2915 (1)	8149 (1)	382 (1)	571 (3)
Cl(4C)	1160 (1)	9191 (1)	1588 (1)	591 (3)
Cl(5)	2918 (1)	6084 (1)	1411 (1)	507 (3)
Cl(7)	549 (1)	4522 (1)	-2730 (1)	533 (3)
O(61)	2651 (2)	4818 (1)	-637 (2)	438 (6)
C(61)	3640 (4)	5067 (4)	-1368 (5)	662 (18)
H(2)	-1815 (23)	6693 (17)	817 (24)	341 (74)†
H(4)	1122 (22)	7375 (16)	1824 (23)	294 (69)†
H(8)	-1193 (24)	5817 (17)	-2257 (25)	399 (79)†
H(611)	4073 (42)	5542 (30)	-1059 (44)	1186 (202)†
H(612)	3305 (37)	5086 (28)	-2178 (40)	1053 (175)†
H(613)	4201 (40)	4565 (28)	-1266 (41)	1138 (164)†

* Equivalent isotropic U calculated from anisotropic U :

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

† Isotropic U .

Table 2. Some bond lengths (\AA), bond angles ($^\circ$), torsion angles ($^\circ$), Cremer-Pople parameters and intramolecular distances (\AA) in the title compound

C(9)–O(1)	1.387 (3)	C(9)–O(1)–C(2)	108.8 (2)
O(1)–C(2)	1.408 (4)	O(1)–C(2)–O(3)	112.5 (3)
C(2)–O(3)	1.402 (4)	C(2)–O(3)–C(4)	116.7 (2)
O(3)–C(4)	1.430 (3)	O(3)–C(4)–C(10)	112.5 (2)
C(4)–C(10)	1.505 (4)	C(4)–C(10)–C(9)	117.9 (2)
C(10)–C(9)	1.387 (3)	C(10)–C(9)–O(1)	118.0 (2)
C(9)–C(8)	1.377 (4)	C(8)–C(9)–O(1)	119.0 (2)
C(8)–C(7)	1.378 (4)	C(5)–C(10)–C(4)	125.0 (2)
C(7)–C(6)	1.386 (4)	C(10)–C(5)–C(6)	121.2 (2)
C(6)–C(5)	1.389 (4)	C(5)–C(6)–C(7)	118.7 (3)
C(5)–C(10)	1.401 (4)	C(6)–C(7)–C(8)	121.6 (3)
C(2)–C(21)	1.534 (4)	C(7)–C(8)–C(9)	118.1 (3)
C(4)–C(41)	1.555 (4)	C(8)–C(9)–C(10)	122.9 (3)
C(6)–O(61)	1.372 (3)	C(9)–C(10)–C(5)	117.1 (2)
O(61)–C(61)	1.442 (6)	O(3)–C(4)–C(41)	105.6 (2)
C(9)–O(1)–C(2)–O(3)	65.6 (3)	C(10)–C(4)–C(41)	113.7 (2)
O(1)–C(2)–O(3)–C(4)	-42.5 (3)	C(10)–C(5)–Cl(5)	120.6 (2)
C(2)–O(3)–C(4)–C(10)	-4.2 (3)	C(6)–C(5)–Cl(5)	118.2 (2)
O(3)–C(4)–C(10)–C(9)	28.9 (3)	C(6)–C(7)–Cl(7)	119.4 (2)
C(4)–C(10)–C(9)–O(1)	-5.9 (4)	C(8)–C(7)–Cl(7)	119.0 (2)
C(10)–C(9)–O(1)–C(2)	-40.0 (3)	C(5)–C(6)–O(61)	120.3 (3)
C(9)–C(10)–C(4)–H(4)	148 (2)	C(7)–C(6)–O(61)	120.9 (3)
C(9)–C(10)–C(4)–C(41)	-91.1 (3)	C(6)–O(61)–C(61)	113.2 (3)
C(10)–C(5)–C(6)–O(61)	179.5 (2)		
C(5)–C(6)–O(61)–C(61)	-94.6 (4)		
C(7)–C(6)–O(6)–C(61)	89.1 (4)		

Cremer-Pople parameters

	φ ($^\circ$)	Q_T (\AA)	θ ($^\circ$)
Dioxin ring	-149.8 (3)	0.557 (3)	106.0 (3)
Aromatic ring	89 (3)	0.055 (3)	76 (3)
O(1)...Cl(4A)	3.128 (2)	O(3)...Cl(4A)	3.085 (3)
Cl(5)...Cl(4B)	3.316 (2)	O(3)...Cl(4C)	2.895 (2)

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44820 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

6-sulfonic methyl ester (IV) (Irving & Irving, 1987b) and the 6,8-dinitro (V) (Irving & Irving, 1986c). In (I), both C(2) and O(3) lie remote from the C(41)Cl₃ group on the same side of the mean plane through O(1), C(9), C(10), C(4), and are at 0.935 (3) and 0.535 (2) Å respectively from this plane (see Fig. 1). The detailed conformation of the heterocyclic ring is described by some torsion angles in Table 2 and is similar to that found in compounds (II)–(V). As in these cases it is strongly affected by the necessity of maintaining the bulky C(41)Cl₃ group at a reasonable distance from each of O(3) and O(1) and from the non-carbon atom bonded to C(5) (see Table 2). The lengthening of the C(4)–C(41) bond length relative to that of C(2)–C(21) has also been observed in all of compounds (II)–(V) and is consistent with the avoidance of the steric interactions referred to above. The bond lengths and angles in the heterocycle do not differ significantly from those in (II)–(IV) and differences from (V) in the bond lengths C(9)–O(1) and C(2)–O(3) can be attributed to electronic effects arising from the substituted aromatic ring.

The angle at O(1) is of interest. Data are presented in Table 3 which suggest that there is almost a linear relationship between the endocyclic angle at O(1) and the C(10)–C(9)–O(1)–C(2) torsion angle in 2,4-bis(trichloromethyl)-1,3-benzodioxins: interestingly the corresponding data for 2,4-bis(dichloromethyl)-1,3-benzodioxin (VI) (Irving & Irving, 1987a) appear to be part of this same pattern. Work on further compounds in these and other related series of 1,3-benzodioxins with various substituents in the aromatic ring is in progress.

Molecules at (x, y, z) and $(-x, 1-y, -z)$, (i), form hydrogen-bonded dimers between H(2) and the methoxy oxygen atom; H(2)···O(61) is 2.44 (3) Å and the angle C(2)–H(2)···O(61) is 151 (2)°; see Fig. 2. The methoxy group is perpendicular to the aromatic ring; C(7)–C(6)–O(61)–C(61) is 89.1 (4)°. C–C–O angles are in agreement with those for a perpendicular methoxy group of 119.5 (7)° (for two unhindered *o*-dimethoxy derivatives in each of which there is a planar and a perpendicular methoxy group) (Anderson,

Table 3. *The relationship between the endocyclic angle (°) at O(1) and the torsion angle (°) C(10)–C(9)–O(1)–C(2)*

Compound	O(1)	τ
(I)	108.8 (2)	40.0 (3)
X*	110.1 (7)	32.3 (2)
(V)	112.2 (2)	26.3 (3)
(VI)	113.3 (2)	20.5 (4)

* Values for X are the mean of those for compounds (II), (III) and (IV).

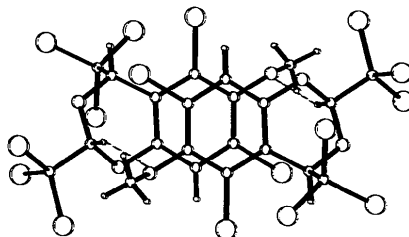


Fig. 2. View perpendicular to C(5), C(6), C(7) of the hydrogen-bonded dimer showing the overlap of the aromatic rings. Hydrogen bonds are indicated by broken lines.

Kollman, Domelsmith & Houk, 1979). The angle C(6)–O(61)–C(61) is intermediate in value between calculated and measured values of 110 and 115° for this parameter (Anderson *et al.*, 1979) and has the same value as in one of the non-planar methoxy groups in 7,8-dimethoxybenzo[*j*]fluoranthene (Briant & Jones, 1987). C–C–O and C–O–C angles associated with the methoxy group do not agree with either calculated or experimental data reported for unhindered coplanar methoxyphenyl groups (Nyburg, Faerman, Prasad, Palleros & Nudelman, 1987).

Atoms C(5) to C(10) in molecule (i) are at an average distance of 3.60 (2) Å from the mean plane through these atoms in the molecule at (x, y, z) . Fig. 2 shows the partial overlap of the aromatic rings in the hydrogen-bonded dimers.

We thank Dr M. L. Niven for the data collection and the UCT Research Committee for financial support for this work.

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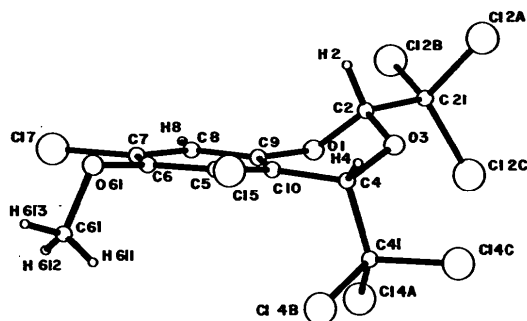


Fig. 1. A perspective view of a molecule of the title compound.

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Acta Cryst. (1988). **C44**, 1233–1235

Pyridiniumpentaiodid

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(Eingegangen am 16. August 1987; angenommen am 14. März 1988)

Abstract. $C_5NH_6[I_3I_2]$, $M_r = 714.6$, monoclinic, $P2_1/m$, $a = 6.026$ (1), $b = 12.928$ (2), $c = 9.213$ (1) Å, $\beta = 103.63$ (2)°, $V = 697.7$ Å³, $Z = 2$, $D_x = 3.40$ g cm⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 110.0$ cm⁻¹, $F(000) = 616$, $T = 296$ K, $R = 0.058$ for 1481 unique observed reflexions. The compound consists of pyridinium ions which are positionally disordered about inversion centres and of polymeric I_5^- ions. The I_5^- ions form zigzag chains running in the **b** direction. The chains can be regarded as an association of alternating I_2 molecules and I_3^- ions. Only one of the terminal I atoms of an I_3^- ion is involved in this association. The pyridinium ions are inserted between iodine atoms of two I_3^- ions of different chains.

Einleitung. Polyiodide zeichnen sich durch eine Vielfalt von Varianten aus, die sich oft als Assoziante von Iodmolekülen mit Iodid-Ionen deuten lassen. Dabei treten interatomare Abstände im Bereich von der Bindungslänge im Iod-Molekül (2,66 Å) bis zum van der Waals-Abstand (4,30 Å) auf (Tebbe, 1977). Neben inselartigen Anionen wie I_3^- oder I_4^{2-} sind auch kettenförmige Ionen bekannt, zum Beispiel Ketten $\cdots I \cdots I \cdots$ im $Cd(NH_3)_4I_6$ (Tebbe & Plewa, 1982) oder Ketten aus Triiodid-Ionen $\cdots I - I - I \cdots$ in Cyclam-Komplexen (Heinlein & Tebbe, 1981) oder im $N(C_4H_9)_4I_3$ (Herbstein, Kaftory, Kapon & Saenger, 1981); Zitate für weitere Beispiele siehe bei Tebbe & Plewa (1982) und bei Coppens (1982). Die kettenförmigen Polyiodide sind wegen ihrer elektrischen Eigenschaften in neuerer Zeit Gegenstand von Unter-

suchungen geworden (Coppens, 1982). In vielen Fällen treten bei diesen Polyiodiden Fehlordnungen auf. Im allgemeinen sind die Polyiodidketten weitgehend gestreckt, mit Bindungswinkeln zwischen 140 und 180°. Dies gilt auch für die fehlgeordneten, kettenförmigen Pentaiodide (α -Cyclodextrin)₂LiI₃I₂·8H₂O (Noltemeyer & Saenger, 1980) und (Benzophenon)₉K₂I₂ (Coppens, Leung, Ortega, Young & Laporta, 1983). Zickzackförmige Ketten von I_5^- -Ionen wurden dagegen beim (Benzophenon)₄LiI₅ gefunden (Leung, Boehme & Coppens, 1981); beim $N(CH_3)_4I_5$ sind die I_5^- -Ionen zu Schichten assoziiert (Broekema, Havinga & Wiebenga, 1957; Hach & Rundle, 1951). Wir berichten über ein geordnet kristallisierendes Pentaiodid mit zickzackförmigen Ketten.

Experimentelles. $PyH^+[I_3I_2]^-$ entstand als Begleitprodukt bei der Umsetzung von $VCl(N_3S_2)Py_2 \cdot CH_2Cl_2$ (Py = Pyridin) (Christophersen, Willing, Müller & Dehnicke, 1986) mit überschüssigem Trimethylsilylan innerhalb von 3 h bei 343 K. Der entstandene Niederschlag wurde in CH_2Cl_2 gelöst. Nach Übersichten der Lösung mit *n*-Hexan entstanden im Laufe von zwei Tagen nadelförmige, in der Durchsicht rotbraune, in der Aufsicht schwarze, sehr feuchtigkeitsempfindliche Kristalle, die abgefrittet und im Vakuum getrocknet wurden (Christophersen, 1987).

Unregelmäßig geformter, nadelförmiger Kristall mit schlecht ausgebildeten Begrenzungsflächen in Quarzkapillare, 0,47 mm lang, 0,15 bis 0,175 mm dick.