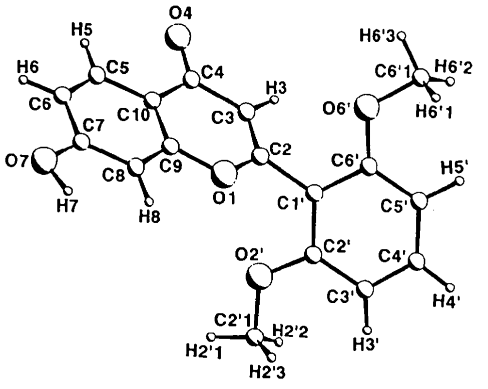

Fig. 1. Perspective view of the molecule with atom numbering.

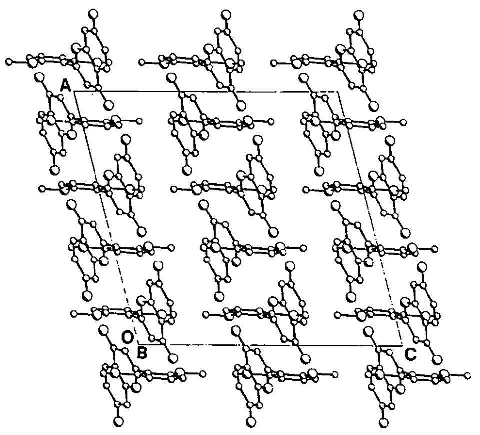

Fig. 2. Crystal packing.

Table 3. *Intra- and intermolecular short-contact distances* (Å) *and angles* (°)

	C—H	H···O	C···O	C—H···O
C5—H5···O4^{i}	1·008	2·545	2·870	98·3
C6—H6···O7^{ii}	0·966	2·893	3·365	134·4
C8—H8···O4^{iv}	0·951	2·604	3·210	122·0
C6′1—H6′1···O7^{iii}	1·066	3·180	3·430	94·4
C6′1—H6′3···O7^{iii}	1·029	3·140	3·430	97·5
	O—H	H···O	O···O	O—H···O
O7—H7···O4^{iv}	0·974	1·655	2·612	165·5

Symmetry code: (i) x, y, z; (ii) $1{\cdot}5-x$, $-0{\cdot}5-y$, $0{\cdot}5-z$; (iii) $1{\cdot}5-x$, $0{\cdot}5-y$, $0{\cdot}5-z$; (iv) $x-0{\cdot}5$, $-y$, z.

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O···H—C(CCl_3) Hydrogen Bonding in the Structure of Methyl 6-Methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylate

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Abstract. 6-Methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylic acid and its methyl and ethyl esters have been prepared. For the methyl ester $C_{13}H_{10}Cl_6O_4$, $M_r = 442{\cdot}94$, triclinic, $P\bar{1}$, $a = 9{\cdot}225\,(2)$, $b = 9{\cdot}401\,(1)$, $c = 10{\cdot}748\,(1)$ Å, $\alpha = 76{\cdot}746\,(9)$, $\beta = 72{\cdot}20\,(1)$, $\gamma = 82{\cdot}68\,(1)°$, $V = 862{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}71$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}2$ cm^{-1}, $F(000) = 444$, room temperature, final $R = 0{\cdot}031$ for 2385 unique counter reflections with $F_o > 4\sigma(F_o)$. The compound forms hydrogen-bonded dimers involving the carbonyl oxygen atom and the axial hydrogen atom bonded to C(2). In addition four carbon atoms in the aromatic ring and the non-hydrogen atoms of the methoxy-

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carbonyl group of centrosymmetrically related molecules overlap almost perfectly.

Introduction. From the condensation of *p*-cresotic acid and chloral hydrate in concentrated sulfuric acid, Alimchandani & Meldrum (1921) obtained a substance m.p. 558–559 K (decomposition) which they described as 6-methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylic acid solely on the basis of a chlorine analysis (found: Cl, 49·7%; $C_{12}H_8O_4Cl_6$ requires Cl, 49·6%). Chattaway & Calvet (1928) later commented that, in their experience, phenols 'in which one position *ortho* to the hydroxy group is occupied, did not condense with chloral in the presence of concentrated sulfuric acid', citing 5-nitrosalicylic acid, *p*-nitro-*o*-cresol and 2,4-dinitrophenol as examples. The apparently anomalous reactivity of a compound with a carboxy group *ortho* to a phenolic hydroxy group merited reinvestigation.

We have repeated the preparation of Alimchandani & Meldrum's compound and confirmed its composition. Since low solubility prevented nuclear magnetic resonance being used to establish its structure we prepared the more soluble ethyl and methyl esters and the latter compound methyl 6-methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylate was also studied by single-crystal X-ray methods.

Experimental. 6-Methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylic acid prepared following Alimchandani & Meldrum (1921), crystallized from boiling acetone in which it was sparingly soluble as felted needles m.p. 556–557·5 K (lit. 558–559 K). Found: C, 33·5; H, 1·85%. Calculated for $C_{12}H_8O_4Cl_6$: C, 33·60; H, 1·88%.

The acid chloride (m.p. 426–428 K) prepared from the above and thionyl chloride was treated with boiling methanol to give the title compound methyl 6-methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylate which formed colourless prisms from methanol m.p. 426·5–427·5 K. Found: C, 35·3; H, 2·25%; $C_{13}H_{10}O_4Cl_6$ requires C, 35·25; H, 2·28%. The proton NMR spectrum (90 MHz in $CDCl_3$) gave $\delta(^1H)$ 2·38 [3H, *s*, OCH_3]; 3·88 [3H, *s*, $6CH_3$]; 5·23 [1H, *s*, H(4)]; 5·63 [1H, *s*, H(2)]; 7·61 [1H, *d*, H(5)]; 7·81 [1H, *d*, H(7)]; $J = 2$ Hz. The corresponding ethyl ester prepared similarly gave colourless crystals from boiling ethanol, m.p. 404–406 K. Found: C, 36·7; H, 2·55%; $C_{14}H_{12}O_4Cl_6$ requires C, 36·79; H, 2·64%.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses for the title compound*

Equivalent isotropic U calculated from anisotropic U:

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

	x	y	z	U_{eq} ($Å^2$)
O(1)	4769 (2)	3899 (2)	2556 (2)	37 (1)
C(2)	5514 (3)	2508 (2)	2526 (2)	34 (1)
O(3)	4577 (2)	1481 (2)	2462 (2)	40 (1)
C(4)	3092 (3)	1435 (3)	3391 (2)	36 (1)
C(5)	1656 (3)	2479 (3)	5419 (3)	44 (1)
C(6)	1253 (3)	3608 (3)	6109 (3)	45 (1)
C(7)	2022 (3)	4880 (3)	5546 (3)	43 (1)
C(8)	3192 (3)	5044 (3)	4356 (2)	37 (1)
C(9)	3564 (3)	3869 (2)	3697 (2)	33 (1)
C(10)	2755 (3)	2611 (3)	4199 (2)	36 (1)
C(21)	6854 (3)	2647 (3)	1254 (2)	38 (1)
Cl(2*A*)	7913 (1)	941 (1)	1244 (1)	55 (1)
Cl(2*B*)	8047 (1)	3963 (1)	1269 (1)	49 (1)
Cl(2*C*)	6224 (1)	3171 (1)	− 179 (1)	49 (1)
C(41)	1979 (3)	1561 (3)	2537 (3)	41 (1)
Cl(4*A*)	2103 (1)	3217 (1)	1368 (1)	50 (1)
Cl(4*B*)	2407 (1)	98 (1)	1674 (1)	65 (1)
Cl(4*C*)	69 (1)	1436 (1)	3582 (1)	55 (1)
C(61)	27 (4)	3448 (5)	7421 (4)	67 (2)
C(81)	3956 (3)	6449 (3)	3913 (3)	40 (1)
O(811)	3680 (3)	7382 (2)	4566 (2)	68 (1)
O(812)	4961 (2)	6580 (2)	2724 (2)	50 (1)
C(813)	5822 (4)	7865 (4)	2245 (4)	56 (1)

Specimen with dimensions 0·45 × 0·40 × 0·20 mm used for X-ray work. Lattice parameters determined by least-squares fitting of setting angles of 24 reflections $16 < \theta < 17°$, automatically centred on a CAD-4 diffractometer. Intensities collected with graphite-monochromated Mo $K\alpha$ radiation, λ = 0·71069 Å. $\omega/2\theta$-scan mode, variable scan rate, scan width $(0{\cdot}85 + 0{\cdot}35\tan\theta)°$, aperture setting 4 mm, range of reflections $1 < \theta < 25°$, 3194 reflections measured, 2730 unique, $R_{int} = 0{\cdot}011$, 2385 $[F_o > 4\sigma(F_o)]$ used in refinement, index range h −10/10, k −11/11, l 0/12. Three intensity control reflections (374, 547, 438) showed no significant decline in intensity. Data corrected for background, scan speed, Lorentz and polarization factors; empirical absorption correction applied (North, Phillips & Mathews, 1968), transmission factors 0·88 to 0·99. Structure solved by direct methods.

Least-squares anisotropic refinement (based on F) for positions of non-hydrogen atoms and free isotropic refinement of hydrogen-atom positions gave final $R = 0{\cdot}031$, $wR = 0{\cdot}037$, $w = 1/[\sigma^2(F_o) + 0{\cdot}000825(F_o)^2]$, $S = 1{\cdot}17$, $\Delta/\sigma(\max) < 0{\cdot}01$, residual electron density $-0{\cdot}30 < \Delta\rho < 0{\cdot}42$ e Å^{-3}. Complex neutral-atom scattering factors from Stewart, Davidson & Simpson (1965) for hydrogen atoms, 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: *SHELX*76 (Sheldrick, 1978), *SHELXS*86 (Sheldrick, 1985), *PLUTO*89 (Galloy & Macrae, 1989), and *PARST* (Nardelli, 1983). All calculations performed at the University of Cape Town on a VAX 8550 computer.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54319 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A perspective view of a molecule of the title compound is given in Fig. 1. Selected molecular parameters are reported in Table 2. The results of several structure determinations of other 2,4-bis(trichloromethyl)-1,3-benzodioxin derivatives have been reported [lead reference is Irving & Irving (1989*a*)]. In the title compound, as in all these previously reported structures, the fused heterocyclic ring has a distorted envelope conformation with C(2) at the tip of a well developed flap (see torsion angles in Table 2). One trichloromethyl group occupies a pseudoequatorial position at C(2); for reasons discussed previously (Irving & Irving, 1988*a*) the other trichloromethyl group is *cis* to this and situated pseudoaxially on C(4).

In the title compound the bond lengths O(1)—C(2) and C(2)—O(3) are the same but this equality is not always found in analogous compounds; *e.g.* in 6,8-dinitro-2,4-bis(trichloromethyl)1-1,3-benzodioxin where O(1)—C(2) is 1·414 (3) Å and is significantly larger than C(2)—O(3) 1·361 (3) Å (Irving & Irving, 1986).

Fig. 2 shows that the methoxycarbonyl group of one molecule is aligned nearly parallel to and overlaps with the aromatic ring of another molecule [at 1 − *x*, 1 − *y*, 1 − *z* (i)] forming a dimer. In each dimer the molecules form hydrogen bonds between the pseudoequatorial H(2) of the >CH(CCl_3) group of one molecule and the carbonyl oxygen atom, O(811), of the methoxycarbonyl group of the second molecule; H···O is 2·57 (3) Å, and the C—H···O angle is 155 (2)°. The dimer thus exists because of the two hydrogen bonds and the favourable overlap of the aromatic ring and the planar 8-methoxycarbonyl system. The angle between the mean plane of the aromatic ring and the mean plane through the atoms O(811^{i}), O(812^{i}), C(81^{i}) and C(813^{i}) is 5·8 (2)°. Perpendicular distances of these atoms from the aromatic plane are 3·542 (3), 3·733 (2), 3·636 (3) and 3·634 (4) Å.

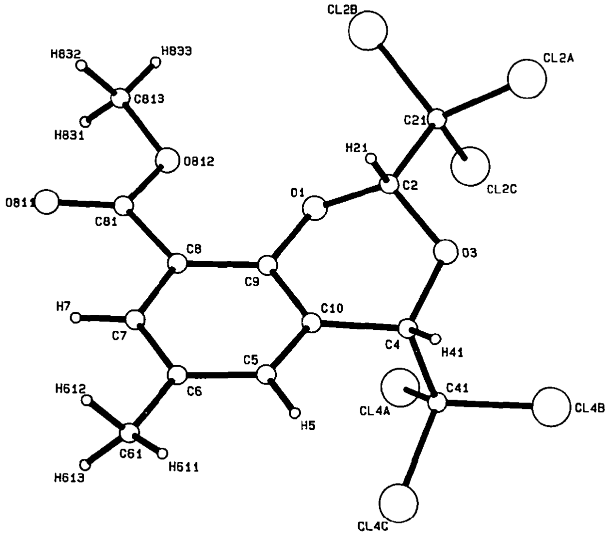

Fig. 1. Perspective view of a molecule of the title compound showing the numbering scheme used.

Table 2. *Selected bond lengths* (Å), *angles* (°) *and torsion angles* (°) *for the title compound*

O(1)—C(2)	1·400 (3)	C(8)—C(9)	1·398 (4)
O(1)—C(9)	1·378 (3)	C(8)—C(81)	1·486 (4)
C(2)—O(3)	1·401 (3)	C(9)—C(10)	1·390 (4)
C(2)—C(21)	1·530 (3)	C(21)—Cl(2*A*)	1·769 (3)
O(3)—C(4)	1·426 (3)	C(21)—Cl(2*B*)	1·764 (3)
C(4)—C(10)	1·504 (4)	C(21)—Cl(2*C*)	1·756 (3)
C(4)—C(41)	1·551 (5)	C(41)—Cl(4*A*)	1·754 (3)
C(5)—C(6)	1·381 (5)	C(41)—Cl(4*B*)	1·769 (3)
C(5)—C(10)	1·382 (3)	C(41)—Cl(4*C*)	1·778 (3)
C(6)—C(7)	1·386 (4)	C(81)—O(811)	1·201 (4)
C(6)—C(61)	1·503 (4)	C(81)—O(812)	1·319 (3)
C(7)—C(8)	1·390 (3)	O(812)—C(813)	1·437 (4)
C(2)—O(1)—C(9)	110·7 (2)	C(7)—C(8)—C(81)	116·9 (2)
O(1)—C(2)—C(21)	107·3 (2)	C(7)—C(8)—C(9)	117·3 (2)
O(1)—C(2)—O(3)	112·5 (2)	C(9)—C(8)—C(81)	125·9 (2)
O(3)—C(2)—C(21)	107·1 (2)	O(1)—C(9)—C(8)	121·3 (2)
C(2)—O(3)—C(4)	116·0 (2)	C(8)—C(9)—C(10)	120·8 (2)
O(3)—C(4)—C(41)	105·1 (2)	O(1)—C(9)—C(10)	117·9 (2)
O(3)—C(4)—C(10)	113·0 (2)	C(5)—C(10)—C(9)	119·3 (2)
C(10)—C(4)—C(41)	112·5 (2)	C(4)—C(10)—C(9)	119·0 (2)
C(6)—C(5)—C(10)	121·8 (3)	C(4)—C(10)—C(5)	121·7 (3)
C(5)—C(6)—C(61)	120·8 (3)	C(8)—C(81)—O(812)	113·5 (2)
C(5)—C(6)—C(7)	117·4 (3)	C(8)—C(81)—O(811)	123·5 (3)
C(7)—C(6)—C(61)	121·8 (3)	O(811)—C(81)—O(812)	123·0 (3)
C(6)—C(7)—C(8)	123·2 (3)	C(81)—O(812)—C(813)	117·4 (3)
C(2)—O(1)—C(9)—C(10)	−34·4 (3)	C(41)—C(4)—C(10)—C(5)	83·5 (3)
C(2)—O(1)—C(9)—C(8)	143·6 (2)	C(41)—C(4)—C(10)—C(9)	−95·8 (3)
C(9)—O(1)—C(2)—C(21)	−178·5 (2)	C(7)—C(8)—C(81)—O(811)	5·0 (4)
C(9)—O(1)—C(2)—O(3)	63·9 (3)	C(7)—C(8)—C(81)—O(812)	−174·5 (3)
O(1)—C(2)—O(3)—C(4)	−48·3 (3)	C(9)—C(8)—C(81)—O(811)	−173·7 (3)
C(2)—O(3)—C(4)—C(10)	5·2 (3)	C(9)—C(8)—C(81)—O(812)	6·8 (4)
O(3)—C(4)—C(10)—C(5)	−157·6 (3)	C(8)—C(81)—O(812)—C(813)	−176·5 (3)
O(3)—C(4)—C(10)—C(9)	23·0 (3)	O(811)—C(81)—O(812)—C(813)	4·1 (4)

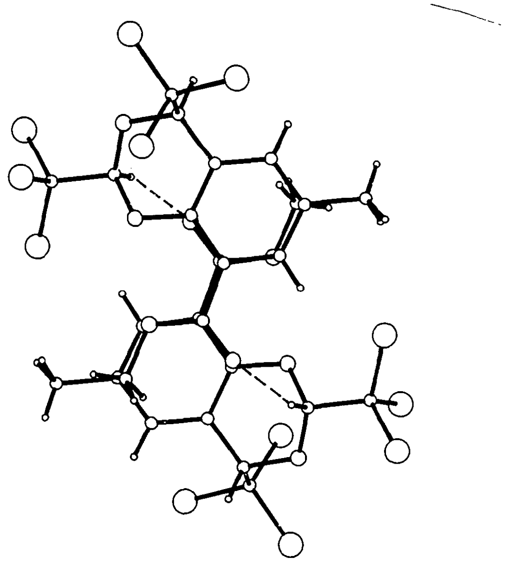

Fig. 2. View of a dimer from the direction perpendicular to the plane of the aromatic rings. Hydrogen bonds are indicated by dashed lines.

Hydrogen bonds of the type O···H—C(CCl_3) have been reported to give rise to dimers with (*A*) 5,7-dichloro-6-methyl- and (*B*) 6-methyl-8-*N*,*N*-diacetylamino- derivatives of 2,4-bis(trichloromethyl)-1,3-benzodioxin (Irving & Irving, 1988*b*, 1989*b*, respectively). In both these compounds, as in the title compound, the dimers are formed by two molecules related by a centre of symmetry. [*A* is $P2_1/n$, $Z = 4$; *B* is $P\bar{1}$, $Z = 2$.] In *A* where the hydrogen bond is described by C(2)—H(21)···O (from the 6-methoxy group) some overlap of the aromatic rings in the dimer occurs giving H···O 2·44 (3) Å and the C—H···O angle 151 (2)°. In *B* no overlap of the aromatic rings is possible due to the presence of the bulky 8-substituent. Here the dimers are formed by hydrogen bonds between one of the carbonyl oxygen atoms of one molecule and both the atoms H(21) and H(41) in the other [H(21)···O 2·49 (3) Å, C(2)—H(21)···O 131 (2)°, H(41)···O 2·47 (3) Å, C(4)—H(41)···O 122 (2)°]. The new data support the claim that C···O distances for very weakly acidic C—H groups extend well beyond the 'conventional' van der Waals limit based on a survey of C—H···O interactions in chloroalkyl compounds (Desiraju, 1989).

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Structure of the High-Temperature-Melting Polymorph of 2,2′-Dipyridylamine

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Abstract. $C_{10}H_9N_3$, $M_r = 171{\cdot}21$, triclinic, $P\bar{1}$, $a = 8{\cdot}229\,(2)$, $b = 10{\cdot}654\,(3)$, $c = 10{\cdot}668\,(2)$ Å, $\alpha = 92{\cdot}93\,(2)$, $\beta = 93{\cdot}01\,(2)$, $\gamma = 107{\cdot}5\,(2)°$, $V = 888{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 360$, $T = 296\,(1)$ K, $R = 0{\cdot}041$ for 1788 unique observed reflections. The structure consists of hydrogen-bonded dimeric molecules. The dihedral angles between the pyridyl rings in the two monomeric units are distinctly different [7·0 (5) and 28·8 (1)°].

Introduction. Dipyridylamine has received interest as a ligand due to the flexibility of the molecule at the amine N atom and its ability to stabilize five-coordinate copper(II) complexes without formation of a macrocycle (Johnson & Jacobson, 1973*a*; Jensen & Jacobson, 1981; Jacobson & Jensen, 1986). Much of the interesting chemistry of dipyridylamine is the

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