

6,8-Dinitro-1,3-benzodioxin-4-one

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(Received 15 September 1987; accepted 1 March 1988)

Abstract. $C_8H_4N_2O_7$, $M_r = 240.13$, orthorhombic, *Pbca*, $a = 10.601$ (3), $b = 11.409$ (1), $c = 14.896$ (2) Å, $V = 1801.6$ (6) Å³, $Z = 8$, $D_x = 1.771$ Mg m⁻³, $F(000) = 976$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.15$ mm⁻¹, room temperature, final $R = 0.034$ for 1228 unique counter reflections with $F_o > 4\sigma(F_o)$. The (C_{Ar})O–C–O–C(C_{Ar}) torsion angle is 54.4 (3)°. Endocyclic bond lengths and angles in the heterocyclic ring are C_{Ar}–O 1.346 (2), (C_{Ar})O–C 1.419 (3), (C_{Ar})O–C–O 1.432 (3), O–C(C_{Ar}) 1.360 (3), C–C_{Ar} 1.474 (3) Å; C_{Ar}–O–C 111.4 (2), O–C–O 111.3 (2), C–O–C(C_{Ar}) 115.9 (2), O–C–C_{Ar} 115.0 (2)°. The nitro groups are twisted with respect to the aromatic ring by 16° for 6-NO₂ and 44° for 8-NO₂.

Introduction. This paper continues a series of investigations into the effect of substituent groups, both in the heterocyclic 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 (1986*a*, 1987*a*). Other compounds studied in this series are referred to in the text.

So far as we are aware the structures of only three derivatives of 1,3-benzodioxin-4-one have been reported, *viz* 2-methyl-2-(2-naphthoxy)-4*H*-1,3-benzodioxin-4-one (Jørgensen & Hansen, 1982) (I), 2-(2-methoxyphenoxy)-2-methyl-4-oxo-1,3-benzodioxane (Destro & Saccarello, 1983) (II), and 6-nitro-2-trichloromethyl-1,3-benzodioxin-4-one (Irving & Irving, 1986*b*) (III). In (I) and (II) the aromatic ring is unsubstituted and a bulky group occupies a pseudo-axial position at the 2-position, whereas (III) contains a 6-nitro group in the aromatic ring and the 2-position contains a pseudo-equatorial –CCl₃ group. In the present work we report the structure of 6,8-dinitro-1,3-benzodioxin-4-one, (IV), in which the 2-position is unsubstituted.

Experimental. Title compound prepared according to the literature method (Chattaway & Irving, 1931). Fine colourless prisms grown from glacial acetic acid, m.p. 469.2–469.7 K (lit. 469.7–470.7 K). Found: C, 40.1; H, 1.75; N, 11.7%. Calc. for $C_8H_4N_2O_7$: C, 40.01;

H, 1.67; N, 11.67%. NMR spectrum (200 MHz) gave $\delta(\text{H})$ 5.92 [s, 2H, H(2)]; 9.14, 9.16 [q, H(5) and H(7)], $J_{5,7} = 3$ Hz. Specimen with dimensions 0.19 × 0.25 × 0.44 mm used for X-ray work. Lattice parameters determined by least-squares fitting of setting angles of 24 reflections ($16 \leq \theta \leq 17$)° automatically centred on CAD-4 diffractometer. Intensities collected with graphite-monochromated Mo *K*α radiation, $\lambda = 0.71069$ Å. $\omega/2\theta$ scan mode, variable scan speed, scan width (0.84 + 0.35 tan θ)°, aperture setting 4 mm, range of reflections $\theta = 1$ –25°, 1848 reflections measured, 1433 unique, $R_{\text{int}} < 0.0001$, 1228 [$F_o > 4\sigma(F_o)$] used in refinement, index range h 0/12, k 0/13, l 0/17. Three intensity-control reflections (4,3,10, 548, 751) monitored after every hour of data collection showed an average decline in intensity of 1.0%. Data corrected for background, scan-speed, Lorentz and polarization factors; empirical absorption correction applied (North, Phillips & Mathews, 1968), transmission factors 0.97 to 1.00. Structure solved by random-start multiscan 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 $R = 0.034$, $wR = 0.035$, $w = 1/\sigma^2(F_o)$, $S = 1.03$, $\Delta/\sigma(\text{max.}) = 0.009$, residual electron density $-0.17 \leq \Delta\rho \leq 0.16$ 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 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. Structural formulae for the three derivatives of 1,3-benzodioxin-4-one whose X-ray structures

† Lists of structure factors, anisotropic thermal parameters and least-squares-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44819 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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)	2147 (1)	1165 (1)	1307 (1)	363 (5)
C(2)	2603 (3)	1259 (2)	414 (2)	429 (8)
O(3)	2922 (2)	134 (2)	54 (1)	458 (6)
C(4)	3746 (2)	-515 (2)	547 (2)	384 (8)
C(10)	3846 (2)	-176 (2)	1499 (1)	313 (7)
C(9)	2994 (2)	639 (2)	1846 (1)	291 (6)
C(8)	3029 (2)	889 (2)	2767 (1)	294 (6)
C(7)	3863 (2)	336 (2)	3332 (1)	318 (7)
C(6)	4661 (2)	-495 (2)	2968 (1)	313 (8)
C(5)	4682 (2)	-754 (2)	2060 (2)	341 (8)
N(6)	5506 (2)	-1127 (2)	3573 (1)	386 (7)
O(6A)	6388 (2)	-1662 (2)	3243 (1)	525 (7)
O(6B)	5291 (2)	-1079 (2)	4376 (1)	538 (7)
N(8)	2195 (2)	1789 (2)	3146 (1)	369 (7)
O(8A)	2668 (2)	2481 (2)	3669 (1)	554 (7)
O(8B)	1095 (2)	1795 (2)	2911 (1)	507 (6)
O(41)	4277 (2)	-1329 (2)	210 (1)	556 (7)
H(5)	5295 (21)	-1326 (20)	1769 (14)	463 (70)†
H(7)	3877 (18)	546 (18)	3951 (14)	295 (58)†
H(21)	3414 (22)	1785 (21)	475 (14)	466 (70)†
H(22)	1865 (22)	1577 (21)	95 (16)	521 (77)†

* Equivalent isotropic U calculated from anisotropic U :

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

† Isotropic U .

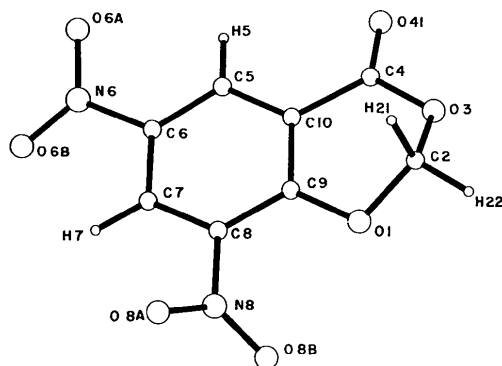


Fig. 1. A perspective view of a molecule of the title compound.

have been reported are given in Fig. 1 of Irving & Irving (1986*b*) and their molecular parameters can be found in Table 2 of that paper. Fig. 1 is a perspective view of a molecule of the title compound which comprises a heterocyclic ring in a distorted 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 heterocyclic ring in (IV) is very similar to that in (I) and (III) and has been discussed previously. In (IV) the atoms C(2) and O(3) deviate from the mean plane through O(1), C(9), C(10), C(4) in the same direction by 0.697 (3) and 0.115 (2) \AA respectively, other deviations being less than 0.020 (2) \AA . The only significant difference in the bond lengths in the heterocyclic ring between (III) and (IV) is a shortening of 0.028 \AA in C(9)-O(1) in (IV)

Table 2. Bond lengths (\AA), bond angles ($^\circ$), torsion angles ($^\circ$) and Cremer-Pople parameters

C(9)-O(1)	1.346 (2)	C(9)-O(1)-C(2)	111.4 (2)
O(1)-C(2)	1.419 (3)	O(1)-C(2)-O(3)	111.3 (2)
C(2)-O(3)	1.432 (3)	C(2)-O(3)-C(4)	115.9 (2)
O(3)-C(4)	1.360 (3)	O(3)-C(4)-C(10)	115.0 (2)
C(4)-C(10)	1.474 (3)	C(4)-C(10)-C(9)	119.0 (2)
C(9)-C(10)	1.396 (3)	C(10)-C(9)-O(1)	120.5 (1)
C(4)-O(41)	1.196 (3)	C(10)-C(4)-O(41)	125.0 (2)
C(10)-C(5)	1.385 (3)	O(3)-C(4)-O(41)	119.9 (2)
C(5)-C(6)	1.385 (3)	C(10)-C(5)-C(6)	118.5 (2)
C(6)-C(7)	1.382 (3)	C(5)-C(6)-C(7)	122.7 (2)
C(7)-C(8)	1.374 (3)	C(6)-C(7)-C(8)	118.0 (2)
C(8)-C(9)	1.402 (2)	C(7)-C(8)-C(9)	121.5 (2)
C(6)-N(6)	1.461 (3)	C(8)-C(9)-C(10)	118.8 (2)
N(6)-O(6A)	1.220 (3)	C(9)-C(10)-C(5)	120.5 (2)
N(6)-O(6B)	1.219 (2)	C(8)-C(9)-O(1)	120.7 (2)
C(8)-N(8)	1.468 (3)	C(4)-C(10)-C(5)	120.1 (2)
N(8)-O(8A)	1.217 (3)	C(5)-C(6)-N(6)	119.2 (2)
N(8)-O(8B)	1.218 (3)	C(7)-C(6)-N(6)	118.2 (2)
C(9)-O(1)-C(2)-O(3)	-57.4 (3)	C(6)-N(6)-O(6A)	117.9 (2)
O(1)-C(2)-O(3)-C(4)	54.4 (3)	C(6)-N(6)-O(6B)	117.9 (2)
C(2)-O(3)-C(4)-C(10)	-20.4 (3)	O(6A)-N(6)-O(6B)	124.1 (2)
O(3)-C(4)-C(10)-C(9)	-8.8 (3)	C(7)-C(8)-N(8)	118.2 (1)
C(4)-C(10)-C(9)-O(1)	4.3 (3)	C(9)-C(8)-N(8)	120.2 (2)
C(10)-C(9)-O(1)-C(2)	28.8 (3)	C(8)-N(8)-O(8A)	116.9 (2)
C(7)-C(8)-C(9)-O(1)	178.1 (2)	C(8)-N(8)-O(8B)	118.1 (2)
C(6)-C(5)-C(10)-C(4)	173.6 (2)	O(8A)-N(8)-O(8B)	125.1 (2)
C(9)-C(10)-C(4)-O(41)	167.4 (2)		
C(5)-C(10)-C(4)-O(41)	-5.6 (4)		

Cremer-Pople parameters

	φ ($^\circ$)	Q_T (\AA)	θ ($^\circ$)
Dioxin ring	-127.1 (3)	0.467 (2)	118.3 (3)
Aromatic ring	-158 (5)	0.024 (2)	86 (5)

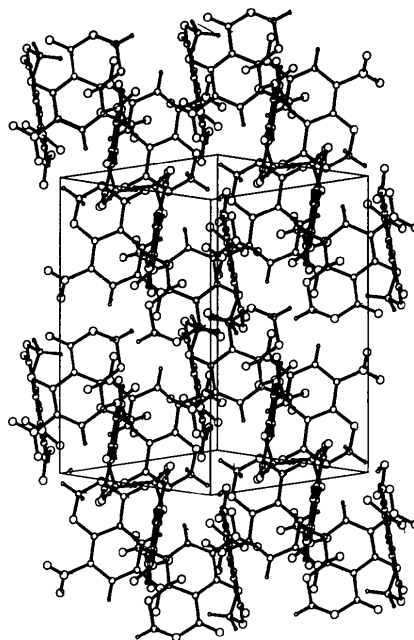


Fig. 2. Packing diagram viewed perpendicular to the plane through C(5), C(6), C(7) of the molecule whose coordinates are given.

relative to (III), the value of which agrees with the corresponding values of 1.352 (3) \AA in 6,8-dinitro-2,4-bis(trichloromethyl)-1,3-benzodioxin (V) (Irving &

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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