

### 3,4-Dibromo-2,3,4,5-tetrahydro-1,6-benzodioxocin

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**Abstract.**  $C_{10}H_{10}Br_2O_2$ ,  $M_r = 321.98$ , monoclinic,  $C2/c$ ,  $a = 21.43$  (4),  $b = 6.30$  (2),  $c = 16.65$  (4) Å,  $\beta = 101.87$  (5)°,  $V = 2199.83$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.95$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 8.59$  mm<sup>-1</sup>,  $F(000) = 1248$ ,  $T = 293$  K,  $R = 0.071$  for 815 reflexions. The crystal contains the racemate of the *R,R* isomer. The molecule has approximate  $C_2$  symmetry with the Br atoms in 'adjacent *trans*' positions and the Br–C–C–Br torsion angle 72.6 (5)°.

**Introduction.** The title compound was produced from 2,5-dihydro-1,6-benzodioxocin as an intermediate in an unsuccessful route to 1,6-benzodioxocin (Schroth & Werner, 1967). The detailed conformation of the molecule was of interest to clarify the mechanism of the formation of 1-(*o*-hydroxyphenoxy)-2-butyn-1-one instead of the desired product.

**Experimental.** White plates were available from previous work. After preliminary photographs, data were collected from crystals  $0.16 \times 0.47 \times 0.20$  mm by equi-inclination Weissenberg photography on layers  $h0-5l$  and  $hk0-2$ . The SERC Microdensitometer Service, Daresbury Laboratory, Warrington, England, measured 2289 reflexions which reduced to 815 unique data. After absorption correction  $R_{int} = 0.092$ . Index limits  $|h| \leq 24$ ,  $|k| \leq 7$ ,  $|l| \leq 19$ . Cell dimensions refined as part of intensity measurements routine. Max.  $2\theta$  124°.

Before attempting a direct-methods solution, the data were enhanced by the addition of visual estimates for 20 over-intense or streaky reflexions and 1588 reflexions which were below the film background were assigned  $F_o = 0.5F_{min}$ . Under-representation of the *ggu* and *uug* symmetry classes in the *E* list gave pseudo *F* centring. This was overcome by choosing the starting set for the direct-methods routine *EEES* largely from these reflexions. The best *E* map showed the two Br atoms. These were used to phase a difference synthesis which revealed all remaining non-H atoms. Conventional refinement gave  $R = 0.071$  with all non-H atoms

anisotropic and isotropic H atoms included on calculated positions.

Final refinement (minimizing  $\sum w|F_o - |F_c||^2$ ): 131 refined parameters,  $R = 0.071$ ,  $wR = 0.096$ ,  $w = 22.1422/(1 + 0.000273F^2)$ ; mean shift/e.s.d. = 0.004, max. shift/e.s.d. = 0.022; on difference map, max. positive peak = 1.27 e Å<sup>-3</sup> (near Br), max. negative peak = 1.11 e Å<sup>-3</sup>.

Programs used: *SHELX76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975). Atomic scattering factors from *SHELX76*.

**Discussion.** Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.† The molecule is shown in Fig. 1. The numbering scheme has been chosen to aid comparison with the recently determined structure of the isomer 2-(1,2-dibromoethyl)-1,4-benzodioxan (Barnes & Schroth, 1988) which was obtained from a second product of the reaction leading to the 2,5-dihydro-1,6-benzodioxocin (Schroth, Reinhardt, Kranke & Streichenbach, 1963; Schroth & Werner, 1967).

The crystal contains the racemate of the *R,R* isomer. The torsion angle Br12–C11–C13–Br14 is 72.6 (5)°, indicating that the Br atoms occupy 'adjacent *trans*' positions with H111 and H131 in the 'remote *trans*' positions with the H–C–C–H torsion angle *ca* 167°. The molecule has an approximate  $C_2$  axis through the midpoints of C6–C7 and C11–C13. Deviations from the mean plane of the benzene ring are 0.916 (1) (C2), –1.068 (1) (C3), 0.095 (1) (C11) and –0.346 (1) Å (C13). The bond C11–C13 makes an angle of 73.6 (5)° with the normal to this plane. Rotation about C11–C13 in a model of the title compound reveals an alternative low-energy conformation with the corresponding angle *ca* 35° with minimal movement of C2

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44519 (8 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. 3,4-Dibromo-2,3,4,5-tetrahydro-1,6-benzodioxocin coordinates ( $\times 10^4$ ) for non-H atoms and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

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

	x	y	z	$U_{eq}$
O1	4610 (5)	870 (18)	3521 (8)	50 (4)
C2	4229 (7)	1289 (28)	4112 (10)	41 (5)
C3	4419 (6)	5490 (30)	3312 (10)	44 (5)
O4	4955 (5)	5166 (18)	3983 (7)	50 (4)
C5	6042 (8)	4249 (29)	4023 (11)	53 (6)
C6	6508 (8)	2780 (33)	3927 (12)	61 (6)
C7	6344 (8)	794 (33)	3673 (12)	55 (6)
C8	5705 (7)	169 (32)	3574 (11)	52 (6)
C9	5235 (6)	1597 (27)	3679 (9)	36 (4)
C10	5394 (7)	3665 (28)	3875 (10)	44 (5)
C11	3639 (7)	2589 (27)	3670 (9)	38 (4)
Br12	2958 (1)	2229 (4)	4271 (1)	63 (1)
C13	3802 (6)	5002 (28)	3656 (10)	43 (5)
Br14	3093 (1)	6415 (4)	2892 (2)	74 (1)

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

C2—O1	1.427 (18)	C9—O1—C2	118.3 (12)
C9—O1	1.390 (17)	C11—C2—O1	107.1 (12)
C11—C2	1.559 (21)	C13—C3—O4	106.6 (12)
O4—C3	1.443 (17)	C10—O4—C3	117.0 (12)
C13—C3	1.576 (20)	C10—C5—C6	120.7 (17)
C10—O4	1.373 (19)	C7—C6—C5	120.4 (15)
C6—C5	1.394 (24)	C8—C7—C6	119.0 (17)
C10—C5	1.409 (21)	C9—C8—C7	121.3 (18)
C7—C6	1.344 (26)	C8—C9—O1	117.3 (15)
C8—C7	1.402 (21)	C10—C9—O1	122.8 (14)
C9—C8	1.387 (22)	C10—C9—C8	119.7 (14)
C10—C9	1.369 (23)	C5—C10—O4	118.4 (15)
Br12—C11	1.944 (13)	C9—C10—O4	122.9 (13)
C13—C11	1.561 (24)	C9—C10—C5	118.6 (16)
Br14—C13	1.980 (15)	Br12—C11—C2	108.5 (9)
		C13—C11—C2	110.9 (12)
		C13—C11—Br12	108.4 (11)
		C11—C13—C3	113.7 (13)
		Br14—C13—C3	105.6 (10)
		Br14—C13—C11	107.7 (10)

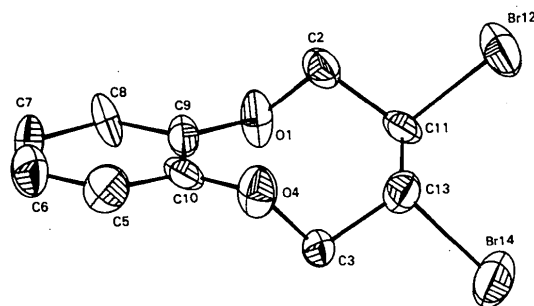


Fig. 1. 3,4-Dibromo-2,3,4,5-tetrahydro-1,6-benzodioxocin.

and C3 but at the expense of eclipsing the C—H bonds on C2 and C11 and on C3 and C13 which are staggered in the observed structure. This conformation is that found in 8,9-dimethyl-1,6-benzodithiocin (Barnes, Schroth & Moegel, 1978) where the corresponding deviations from the plane of the benzene ring are 0.808,  $-1.080$ , 0.368 and  $-0.837$   $\text{\AA}$ , making the angle between C11—C13 and the normal to the benzene ring plane  $33.8$  ( $4$ ) $^\circ$ .

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## The Structure of 11 $\alpha$ -Hydroxycon-1,4-dienine-3-one Monohydrate

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**Abstract.**  $C_{22}H_{31}NO_2 \cdot H_2O$ ,  $M_r = 359.5$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.032$  (1),  $b = 11.186$  (1),  $c = 17.980$  (1)  $\text{\AA}$ ,  $U = 2017.48$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.276$   $\text{Mg m}^{-3}$ ,  $\lambda(\text{Cu K}\alpha) = 1.5418$   $\text{\AA}$ ,  $\mu = 0.69$   $\text{mm}^{-1}$ ,  $F(000) = 784$ ,  $T = 293$  K. Final  $R = 0.05$  for 1972

unique reflections with  $I \geq 3\sigma(I)$ . Ring *A* is planar, and rings *B* and *C* adopt a chair conformation. Rings *D* and *E* are envelopes, with C(14) and C(20) displaced from their respective ring planes by 0.616 (2) and 0.648 (3)  $\text{\AA}$ . The *A/B* ring junction is quasi-*trans*,