

& Coulson, 1975). The average C—C bond length in the benzene ring is 1.38 Å and the average C—H length is 0.94 Å. The C(7)—C(8) bond is 1.48 Å, which is shorter than the 1.517 Å reported for the 2,4-di- and 2,4,5-trichlorophenoxyacetic acids (Smith *et al.*, 1976*a*, *b*), but a similar shortening of the C(7)—C(8) bond has been observed in 2-chlorophenoxyacetic acid (Chandrasekhar & Pattabhi, 1977). The nearly equal lengths of the two C—O bonds [1.271 (12) and 1.250 (6) Å] and the smaller difference in the C—C—O angles [115.5 (1.1) and 119.6 (1.0)°] in the carboxyl group

may be attributed to the disorder of the carboxyl group. Similar disorder has been observed in the carboxyl group of β -chloro-*cis*-cinnamic acid (Filippakis, Leiserowitz, Rabinovich & Schmidt, 1972).

The equations of the least-squares planes (1) through O(1), O(2) and N(1), (2) through C(1) to C(6), and (3) through C(7), C(8), O(4) and O(5), are

- (1) $0.5032X - 0.8612Y - 0.0718Z = 0.1779$,
- (2) $0.4457X - 0.8944Y - 0.0370Z = 0.1785$,
- (3) $-0.4641X + 0.8840Y - 0.0563Z = 0.6450$.

The N(1) atom is in the plane of the benzene ring and the unsymmetrical nitro group is strictly planar; the dihedral angle between these two planes is 4.3°. The planar acetic acid group makes an angle of 5.5° with the ring plane, which is very similar to those of many substituted phenoxyacetic acids (Smith *et al.*, 1976*b*). The packing of these dimeric molecules is shown in Fig. 2, along with principal intermolecular distances.

We thank the Department of Science and Technology, India, for financial support enabling us to carry out this work.

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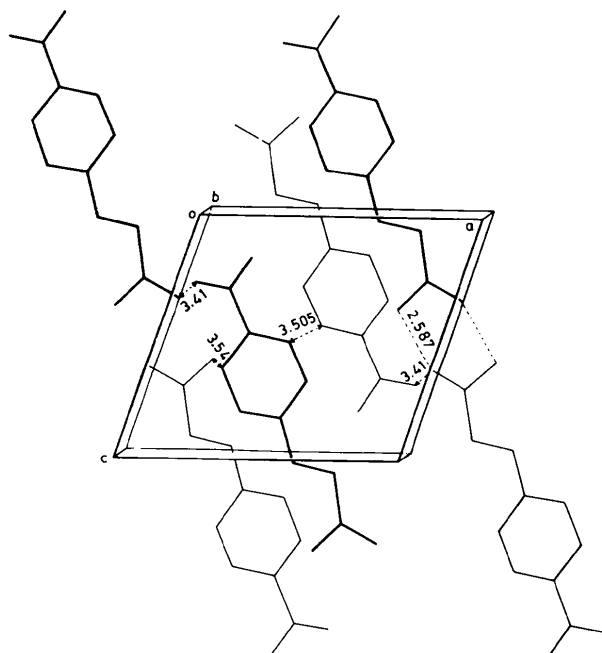


Fig. 2. Packing of the molecules in the unit cell viewed perpendicular to the *ac* plane, showing some intermolecular distances (Å). E.s.d.'s in the distances are 0.01 Å.

Acta Cryst. (1980). **B36**, 1220–1222

cis-5-*tert*-Butyl-1,3,2-dioxathiane 2-Oxide

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(Received 2 December 1979; accepted 25 February 1980)

Abstract. $C_7H_{14}O_3S$, monoclinic, $P2_1/b$, $Z = 4$, $a = 6.106$ (4), $b = 7.743$ (4), $c = 18.968$ (7) Å, $\gamma = 99.46$ (5)°, $D_c = 1.338$ Mg m⁻³ at 123 K. The sulfite ring adopts a chair conformation with the *tert*-butyl group in equatorial and the S=O group in axial

position. The conformation confirms the interpretation of IR and NMR spectra.

Introduction. Substituted cyclic sulfites are very well suited for the study of the influence of the anomeric

0567-7408/80/051220-03\$01.00

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effect on the geometry of molecules, and a number of structure determinations are available: trimethylene sulfite (Altona, Geise & Romers, 1966); 2,2'-dichlorotrimethylene sulfite (Van Oyen, Hasekamp, Verschoor & Romers, 1968); dihydrofukinolidol sulfite, isomers (I) and (II) (Furusaki & Watanabe, 1972); 17 β -acetoxy-2,4-dioxo-3-thia-5 α -androstan-3-one (Duax, Griffin & Wolff, 1976); *trans*-5-chloro-*cis*-4,*trans*-6-di-*tert*-butyl-1,3,2-dioxathiane 2-oxide (Carbonelle, Jeannin & Robert, 1978); *cis,cis*-4,6-dimethyl-1,3,2-dioxathiane 2-oxide (Petit, Lenstra & Geise, 1978); *cis*-1,1,3-trimethyltrimethylene sulfite (Petit, Lenstra, Van de Mieroop, Geise & Hellier, 1978); 2-methyl-2-nitrotrimethylene sulfite (Petit, Lenstra, Geise & Swepston, 1980); and 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxathiane 2-oxide (Petit, Lenstra & Geise, 1980).

In continuation of this research the crystal structure of the title compound (abbreviated as BDO) has been undertaken. BDO (m.p. 320 K) was synthesized by Phillips (1978) and D. G. Hellier. Suitable single crystals were obtained by slow evaporation of an ether-petroleum ether (50/50) solution at 248 K.

Reflections were measured on an Enraf-Nonius CAD-4 diffractometer using Mo $K\alpha$ radiation. A total of 2133 independent reflections, up to $\theta = 28^\circ$, were

Table 1. Positional parameters of BDO in fractions of the cell edges

The e.s.d.'s (given in parentheses) refer to the last significant digit. Isotropic temperature factors (\AA^2) are calculated from anisotropic temperature parameters, equal volume of the 50% probability region being assumed. All anisotropic thermal ellipsoids were physically acceptable. Hydrogen atom H(*xj*) (*j* = 1, 2, 3) is attached to atom *x*.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
O(1)	0.1195 (2)	0.3391 (2)	0.42748 (8)	1.77
S(2)	-0.07360 (8)	0.28886 (6)	0.37080 (3)	1.78
O(3)	0.0498 (2)	0.3805 (2)	0.30222 (8)	1.78
C(4)	0.1356 (3)	0.5685 (2)	0.3090 (1)	1.61
C(5)	0.3103 (3)	0.5980 (2)	0.3661 (1)	1.30
C(6)	0.2083 (3)	0.5266 (2)	0.4349 (1)	1.64
C(7)	0.4249 (3)	0.7922 (2)	0.3720 (1)	1.43
C(8)	0.5477 (3)	0.8434 (3)	0.3028 (1)	2.05
C(9)	0.2574 (3)	0.9159 (3)	0.3856 (1)	2.03
C(10)	0.5949 (3)	0.8098 (3)	0.4318 (1)	1.97
O(11)	-0.2518 (2)	0.3827 (2)	0.38843 (8)	2.28
H(41)	0.188 (3)	0.602 (3)	0.261 (1)	3.00
H(42)	0.012 (3)	0.626 (3)	0.317 (1)	3.00
H(51)	0.426 (3)	0.528 (3)	0.353 (1)	3.00
H(61)	0.085 (3)	0.586 (3)	0.448 (1)	3.00
H(62)	0.310 (3)	0.529 (3)	0.471 (1)	3.00
H(81)	0.441 (3)	0.839 (3)	0.259 (1)	3.00
H(82)	0.654 (3)	0.759 (3)	0.290 (1)	3.00
H(83)	0.629 (3)	0.956 (3)	0.303 (1)	3.00
H(91)	0.177 (3)	0.886 (3)	0.429 (1)	3.00
H(92)	0.147 (3)	0.912 (3)	0.346 (1)	3.00
H(93)	0.337 (3)	1.039 (3)	0.389 (1)	3.00
H(101)	0.694 (3)	0.722 (3)	0.426 (1)	3.00
H(102)	0.693 (3)	0.931 (3)	0.429 (1)	3.00
H(103)	0.535 (4)	0.792 (3)	0.479 (1)	3.00

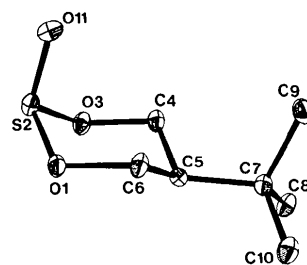


Fig. 1. Numbering of atoms and conformation of the molecule. The direction of view is perpendicular to a plane through S(2), C(5), C(7).

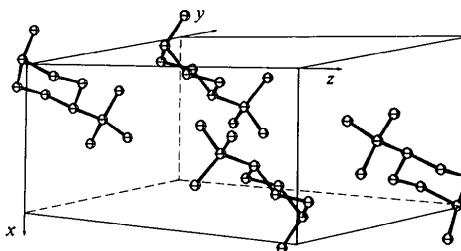


Fig. 2. The packing of BDO.

collected in an $\omega/2\theta$ scan mode. Since the crystals rapidly sublime at room temperature the measurements were performed at 123 K. In view of the small size of the crystal ($0.1 \times 0.1 \times 0.12$ mm) and the low absorption coefficient ($\mu = 0.321 \text{ mm}^{-1}$ for Mo $K\alpha$) no absorption correction was applied.

A set of 1820 reflections with $I > 2\sigma(I)$ was used in the analysis. The structure was solved by conventional Patterson and (difference) Fourier techniques. The isotropic temperature parameters of the H atoms were fixed at $B_{\text{iso}} = 3.0 \text{ \AA}^2$ during the least-squares refinement. A weighting scheme based on counting statistics was used. No extinction correction was applied. The weighted *R* value converged to 0.042 for observed reflections.† The positional parameters are presented in Table 1, the numbering of the atoms is given in Fig. 1, and Fig. 2 shows the contents of the unit cell.

Discussion. The sulfite ring is in the chair form with the *tert*-butyl group in equatorial and the S=O in axial position. This conformation was predicted on the basis of IR and ^1H NMR spectra.

The stabilization of an axial S=O group is due to the anomeric effect, and can be explained as a 'back donation' from O lone-pair electrons into an anti-bonding σ^* or π^* level (Jeffrey, Pople & Radom, 1972). Spatial requirements for the interaction are such that

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35157 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the conformer with the largest number of lone pairs in antiperiplanar position to electronegative groups is the most stable (Fig. 3). A *tert*-butyl group tends to be in an equatorial position and therefore cooperates to obtain the conformation of Fig. 3(a).

Bond lengths and angles are presented in Tables 2 and 3 respectively.

Their values are normal compared with those of other cyclic sulfites (Petit, Lenstra & Geise, 1978). One should note that the C—O bonds are significantly longer (1.47 ± 0.01 Å) than those normally found in ethers and alcohols (1.43–1.44 Å). Such elongations are to be expected as a result of anomeric delocalization (Jeffrey, Pople, Binkley & Vishveshwara, 1978).

Ring torsion angles are listed in Table 4. Clearly, the most puckered side of the ring occurs near C(5), which

Table 2. Bond lengths (Å) with *e.s.d.*'s in parentheses

S(2)—O(1)	1.596 (3)	S(2)—O(3)	1.609 (3)	S(2)—O(11)	1.443 (3)
O(1)—C(6)	1.471 (3)	O(3)—C(4)	1.469 (3)	C(5)—C(7)	1.554 (3)
C(4)—C(5)	1.511 (3)	C(6)—C(5)	1.512 (3)	C(7)—C(10)	1.528 (3)
C(7)—C(8)	1.532 (3)	C(7)—C(9)	1.534 (3)	C(5)—H(51)	0.99 (3)
C(4)—H(41)	0.99 (3)	C(4)—H(42)	0.95 (3)	C(8)—H(83)	0.93 (3)
C(6)—H(61)	0.97 (3)	C(6)—H(62)	0.93 (3)	C(9)—H(93)	1.00 (3)
C(8)—H(81)	1.06 (3)	C(8)—H(82)	1.02 (3)	C(10)—H(103)	0.97 (3)
C(9)—H(91)	0.97 (3)	C(9)—H(92)	1.00 (3)		
C(10)—H(101)	0.99 (3)	C(10)—H(102)	1.03 (3)		

Table 3. Bond angles (°) with *e.s.d.*'s in parentheses

S(2)—O(1)—C(6)	116.3 (2)	C(6)—C(5)—C(7)	112.6 (2)
O(1)—S(2)—O(3)	99.4 (1)	O(1)—C(6)—C(5)	110.0 (2)
O(1)—S(2)—O(11)	108.0 (1)	C(5)—C(7)—C(8)	108.1 (2)
O(3)—S(2)—O(11)	107.6 (1)	C(5)—C(7)—C(9)	112.1 (2)
S(2)—O(3)—C(4)	115.6 (2)	C(5)—C(7)—C(10)	109.4 (2)
O(3)—C(4)—C(5)	109.9 (2)	C(8)—C(7)—C(9)	109.3 (2)
C(4)—C(5)—C(6)	109.0 (2)	C(8)—C(7)—C(10)	108.4 (2)
C(4)—C(5)—C(7)	113.1 (2)	C(9)—C(7)—C(10)	109.5 (2)

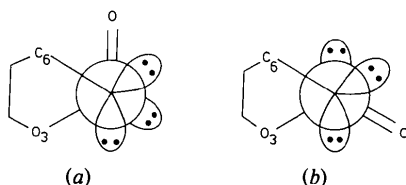


Fig. 3. Newman projections along O(1)—S(2) for a sulfite with S=O in (a) axial and (b) equatorial positions.

Table 4. Ring torsion angles (°) with *e.s.d.*'s in parentheses

O(1)—S(2)—O(3)—O(4)	−55.9 (5)
S(2)—O(3)—C(4)—C(5)	62.5 (5)
O(3)—C(4)—C(5)—C(6)	−59.1 (5)
C(4)—C(5)—C(6)—O(1)	58.4 (5)
C(5)—C(6)—O(1)—S(2)	−61.6 (5)
C(6)—O(1)—S(2)—O(3)	55.5 (5)

is the normal situation for cyclic sulfites with an axial S=O group (Petit, Lenstra & Geise, 1978).

We thank Professor D. G. Hellier (Westfield College, University of London, England) for supplying the necessary crystals. One of us (GHP) is grateful to the Belgian organization 'Instituut voor Wetenschappelijk Onderzoek in Nijverheid en Landbouw (IWONL)' for a predoctoral grant. This research was carried out with support from NATO grant 1583.

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