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Structure of *cis*-3,3-Dimethyl-2,4-dioxa-7-thiabicyclo[3.3.0]octane 7-Oxide Monohydrate

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Abstract. C₇H₁₂O₃S.H₂O, monoclinic, space group *A2/m*, *a* = 6.484 (1), *b* = 8.995 (3), *c* = 15.899 (3) Å, β = 92.37 (1)°, *V* = 926.5 Å³, *Z* = 4, *M_r* = 194, *F*(000) = 416, μ = 29.9 cm⁻¹. The structure was solved by the heavy-atom method and refined by full-matrix least-squares computations to *R* = 0.064 for 819 observed reflections. The dihedral angle between atoms H2(C1) and H(C2) (respectively in equatorial and axial positions on the S heterocycle), through the C(1)–C(2) bond, is close to 90°, as had been predicted by Lett & Marquet [*Tetrahedron Lett.* (1974). **30**, 3365–3377] from NMR measurements.

Introduction. This crystal structure is the last of a series of X-ray studies of some bicyclic sulfoxides (Stora & Marquet, 1973; Stora, 1974; Lefebvre & Robert, 1974) which have structural analogies with biotin (Lett & Marquet, 1974). It has been undertaken to study the respective positions of the S heterocycle H atoms which are not substituted in this new molecule.

The space group (systematic absences: *k* + *l* = 2*n*) is *A2/m*. The unit-cell dimensions were refined from 35 reflections (θ up to 54°), manually set on a CAD-3 diffractometer with Cu *K* α radiation (λ = 1.5418 Å), 19 of them having θ *ca* \pm 15°. The density was

determined by flotation in CHCl₃/C₆H₆. The measured value, 1.40 g cm⁻³, was greater than that calculated, 1.261 g cm⁻³, before a water molecule was discovered. The calculated density was then 1.392 g cm⁻³, in agreement with only half a molecule in the asymmetric unit, *i.e.* *Z* = 4 in the cell instead of 8. We concluded that the molecule itself has a mirror plane. The crystal used for data collection was 0.30 × 0.20 × 0.50 mm. 893 intensities were measured, of which 819 with *I* > 2 σ (*I*) were considered as observed. They were collected at 295 K in the range 3° ≤ 2 θ ≤ 66.8° ($\theta/2\theta$ scan mode), at a rate of 10° min⁻¹ (scan width = 1.1° + 0.35° tan θ). Two standard reflections were monitored every 40 reflections and they remained constant within \pm 3%.

The S-atom position was given by Harker and Patterson maps. All the non-H atoms with one exception, O(*W*), appeared in the first Fourier synthesis. Full-matrix least-squares isotropic refinement led to *R* (= $\sum ||F_o| - |F_c|| / \sum |F_o|$) = 0.28, which only fell to 0.24 by anisotropic refinement, suggesting one or more water molecules were present. A difference synthesis then showed a strong peak on the twofold axis; this was assigned as an O atom, O(*W*). A new isotropic refinement of all non-H atoms led to *R* = 0.19 which fell to 0.095 by anisotropic refinements and a difference synthesis gave all the H atoms in their expected positions, except those of the water molecule.

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Since a short distance of 2.776 Å (hydrogen bonding) exists between the O(W) atom of the water molecule and the O(S) and O(S^{iv}) atoms of two centrosymmetric sulfoxide molecules, it suggests that the H atom lies along the line between O(W) and O(S). Since the angle O(S)—O(W)—O(S^{iv}) is equal to about 104°, this assignment puts the second H atom in the normal position for a water molecule. Thus, the H atom of the water molecule was introduced at the normal distance of 1.0 Å from the O(W) atom, on the O(W)⋯O(S) line and was kept fixed. Full-matrix least-squares anisotropic refinements of all non-H atoms and isotropic refinement of H atoms (isotropic thermal parameters of the atoms to which they are bound), led to a final *R* of 0.064 and *R*_w = (∑ w|F_o - |F_c||²/∑ w|F_o|²)^{1/2} of 0.091. All calculations were performed on an IBM 70-168 computer. Scattering factors were those of Cromer & Waber (1965) for C and O and of Stewart, Davidson & Simpson (1965) for H.

Discussion. Fig. 1 (*a* and *b*) shows a projection of the molecule (*ORTEP*, Johnson, 1965) on the *Oyz* and *xOz* planes (with thermal-vibration ellipsoids scaled to 35% probability for the non-H atoms) confirming its boat-chair conformation. Atomic parameters are listed in Table 1, bond lengths and angles in Table 2 and torsion angles in Table 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36501 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

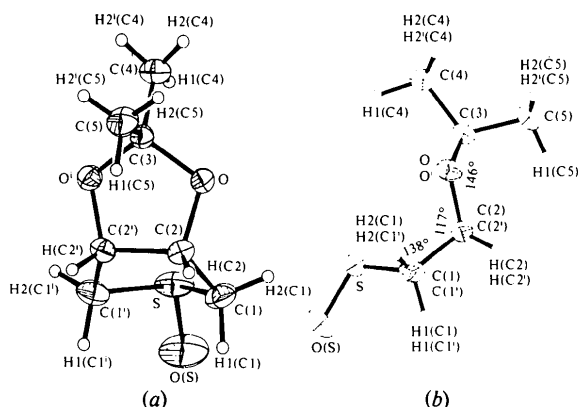


Fig. 1. The molecule viewed along (a) *a* and (b) *b* (e.s.d.'s for dihedral angles are ~2°).

The structure studied here is similar to that of its dimethyl derivative (Stora, 1974) and also to biotin (Traub, 1956; Bonnemere, Hamilton, Steinrauf &

Table 1. Fractional coordinates (×10⁴, for H ×10³) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O(S)	7101 (6)	0	4263 (3)	8.29
S	5798 (2)	0	3450.8 (0.6)	5.00
C(1)	3829 (4)	8590 (4)	3540 (2)	4.55
C(2)	2019 (4)	9133 (3)	2993 (2)	3.47
C(3)	1769 (6)	0	1623 (2)	3.30
C(4)	3083 (7)	0	858 (2)	4.61
C(5)	-527 (7)	0	1410 (3)	4.61
O	2343 (3)	8749 (2)	2137 (1)	3.79
O(W)	0	1920 (7)	5000	9.50
H1(C1)	348 (5)	855 (4)	416 (2)	
H2(C1)	435 (5)	763 (3)	331 (2)	
H(C2)	84 (4)	870 (3)	324 (2)	
H1(C4)	474 (7)	0	105 (3)	
H2(C4)	262 (5)	915 (4)	49 (2)	
H1(C5)	893 (7)	0	196 (3)	
H2(C5)	924 (5)	909 (4)	110 (2)	
H(OW)	896	120	474	

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

S—O(S)	1.513 (4)	O(S)—S—C(1)	107.7 (2)
S—C(1)	1.809 (3)	S—C(1)—C(2)	105.2 (2)
C(1)—C(2)	1.512 (4)	C(1)—S—C(1) ⁽ⁱ⁾	89.2 (2)
C(2)—C(2 ⁽ⁱ⁾)	1.560 (4)	C(1)—C(2)—O	109.2 (2)
C(2)—O	1.428 (3)	C(1)—C(2)—C(2 ⁽ⁱ⁾)	108.8 (2)
O—C(3)	1.431 (3)	O—C(2)—C(2 ⁽ⁱ⁾)	104.0 (2)
C(3)—C(4)	1.513 (6)	C(2)—O—C(3)	108.0 (2)
C(3)—C(5)	1.513 (6)	O—C(3)—O ⁽ⁱ⁾	103.9 (3)
O(W)—O(S)	2.776 (5)	O—C(3)—C(4)	108.5 (2)
O(W)—O(W ^{iv})	3.454 (8)	O—C(3)—C(5)	111.0 (2)
		C(4)—C(3)—C(5)	113.7 (3)
		S—O(S)—O(W)	134.8 (2)
		O(W)—O(S)—O(W ^{iv})	76.9 (1)
		O(S)—O(W)—O(S ^{iv})	103.1 (2)
H1(C1)—C(1)	1.01 (3)	H1(C1)—C(1)—S	107 (2)
H2(C1)—C(1)	1.00 (3)	H2(C1)—C(1)—S	109 (2)
H(C2)—C(2)	0.96 (3)	H1(C1)—C(1)—H2(C2)	115 (3)
H1(C4)—C(4)	1.10 (5)	H1(C1)—C(1)—C(2)	112 (2)
H2(C4)—C(4)	1.00 (3)	H2(C1)—C(1)—C(2)	109 (2)
H1(C5)—C(5)	0.96 (5)	H(C2)—C(2)—C(1)	104 (2)
H2(C5)—C(5)	0.96 (3)	H(C2)—C(2)—O	117 (2)
		H(C2)—C(2)—C(2 ⁽ⁱ⁾)	114 (2)

Equivalent positions

Superscript: none *x,y,z*; (i) *x,-y,z*; (ii) *x, ½ + y, ½ + z*; (iii) *x, ½ - y, ½ + z*; (iv) *-x,-y,-z*; (v) *-x,y,-z*; (vi) *-x, ½ - y, ½ - z*; (vii) *-x, ½ + y, ½ - z*.

Table 3. Torsion angles (°) in the two rings with their e.s.d.'s in parentheses

O(S)—S—C(1)—C(2)	-150.9 (3)	H1(C1)—C(1)—C(2)—C(2 ⁽ⁱ⁾)	-84.0 (1.8)	C(1)—C(2)—O—C(3)	137.1 (3)
C(1 ⁽ⁱ⁾)—S—C(1)—C(2)	-42.6 (3)	H1(C1)—C(1)—C(2)—H(C2)	38.0 (2.0)	C(2)—C(2)—O—C(3)	21.1 (3)
S—C(1)—C(2)—O	-82.2 (3)	H2(C1)—C(1)—C(2)—O	35.0 (1.6)	C(2)—O—C(3)—C(4)	-149.6 (3)
S—C(1)—C(2)—C(2 ⁽ⁱ⁾)	30.7 (3)	H2(C1)—C(1)—C(2)—C(2 ⁽ⁱ⁾)	147.0 (2.0)	C(2)—O—C(3)—C(5)	84.9 (3)
S—C(1)—C(2)—H(C2)	153.0 (1.9)	H2(C1)—C(1)—C(2)—H(C2)	-91.0 (2.5)	C(2)—O—C(3)—O ⁽ⁱ⁾	-34.4 (2)
H1(C1)—C(1)—C(2)—O	163.0 (1.8)				

Knappe, 1965). It is, however, perfectly symmetrical, because of the molecular mirror plane which passes through the five atoms O(S), S, C(3), C(4), C(5) [only the three atoms C(1), C(2) and O are in general positions in the asymmetric unit]. In the S heterocycle the bonds S—C(1) [1.809 (3)] and C(1)—C(2) [1.512 (4) Å] are significantly shorter than the corresponding bonds in the dimethyl derivative [1.822 (7), 1.842 (7) and 1.551 (9), 1.530 (10) Å]. The angles are nearly the same in both compounds. On the other hand, in the dioxolane ring the bonds C(2)—O [1.428 (3)] and O—C(3) [1.431 (3) Å] are significantly longer than the corresponding bonds of the dimethyl derivative [1.419 (9), 1.409 (8) and 1.413 (9), 1.407 (9) Å] but here also the angles remain nearly the same for both molecules. The angles between the different planes (Fig. 1b) of the two rings, *i.e.* C(1)—S—C(1'), C(1)—C(2)—C(2')—C(1'), C(2)—O—O'—C(2') and O—C(3)—O' are sequentially 138, 117 and 146°. When these dihedral angles are compared to those of the dimethyl sulfoxide (132, 119, and 147° respectively) and of biotin (142, 118°, the third not cited), we note a close similarity, except for the first dihedral angle which differs significantly between the three compounds. Of particular interest is the value of 91° (Table 3) found for the dihedral angle between the atoms H2(C1) and

H(C2) through the C(1)—C(2) bond, close to that which had been predicted (90°) from NMR measurements (Lett & Marquet, 1974). The packing is governed by hydrogen bonds [2.776 (5) Å] between the two centrosymmetric water molecules [O(W)H₂ and O(W'^{iv})H₂] on the twofold axis and the O(S) and O(S'^{iv}) atoms of the two centrosymmetric sulfoxide molecules.

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Structure of the 1 : 1 Adduct of Orthoperiodic Acid and Urea

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Abstract. H₅IO₆·CH₄N₂O, monoclinic, *P*2₁/*c*, *a* = 5.175 (1), *b* = 6.870 (2), *c* = 20.480 (5) Å, β = 90.96 (2)° at 293 K, *Z* = 4, *D*_{pyc} = 2.60 (1) at 298 K, *D*_c = 2.627 Mg m⁻³, *R* = 0.054, *R*_w = 0.081 for 1254 reflexions. The structure consists of orthoperiodic acid and urea molecules, connected by relatively strong hydrogen bonds, forming a three-dimensional network.

Introduction. The title compound IO(OH)₅·CO(NH₂)₂ was studied as an analogue of the adduct of ortho-

telluric acid and urea, Te(OH)₆·2CO(NH₂)₂ (Loub, Haase & Mergehenn, 1979). The adduct was prepared by crystallization from a concentrated aqueous solution of orthoperiodic acid and urea with a molar ratio of 1 : 2 at 298 K. With increasing temperature and time of crystallization, ammonium periodate, NH₄IO₄, is gradually formed. Clear crystals were obtained as multiface prisms with well developed (001) faces. The cell dimensions were determined from the setting angles of 15 reflexions measured on an automatic Syntex *P*2₁ four-circle diffractometer with graphite-monochromated Mo *K*α radiation. 1290 independent inten-

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