

Chemistry of the S=O Bond. 13. Structures of Isomers 1 (I) and 2 (II) of 4-Methyl-1,3,2-dioxathiane 2-Oxide and 1,3,2-Dioxathiepane 2-Oxide (III) at 256, 240 and 228 K

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Abstract

The structures of the two isomers of 4-methyl-1,3,2-dioxathiane 2-oxide, C₄H₈SO₃ (I, II), and 1,3,2-dioxathiepane 2-oxide, C₄H₈SO₃ (III), have been determined by X-ray diffraction methods for single crystals that were grown in this case at low temperatures from the normally liquid compounds. Compound (I): orthorhombic, *P*₂₁₂₁₂₁, *M*_r = 136.17, *a* = 7.204 (6), *b* = 13.670 (11), *c* = 6.041 (6) Å, *V* = 594.91 Å³, *Z* = 4, *D*_x = 1.520 Mg m⁻³, Mo *K*α (λ = 0.71068 Å), μ = 4.49 cm⁻¹, *F*(000) = 288, *T* = 256 K, *R* = 0.042 for 778 unique reflections. Compound (II): orthorhombic, *P*₂₁₂₁₂₁, *M*_r = 136.17, *a* = 18.238 (6), *b* = 10.265 (3), *c* = 6.616 (2) Å, *V* = 1238.60 Å³, *Z* = 8, *D*_x = 1.460 Mg m⁻³, Mo *K*α (λ = 0.71068 Å), μ = 4.31 cm⁻¹, *F*(000) = 576, *T* = 240 K, *R* = 0.032 for 1597 unique reflections. Compound (III): monoclinic, *P*₂₁/*n*, *M*_r = 136.17, *a* = 6.060 (3), *b* = 11.185 (8), *c* = 9.186 (4) Å, β = 101.32 (4)°, *V* = 610.52 Å³, *Z* = 4, *D*_x = 1.481 Mg m⁻³, Mo *K*α (λ = 0.71068 Å), μ = 4.38 cm⁻¹, *F*(000) = 288, *T* = 228 K, *R* = 0.037 for 1161 unique reflections. Compound (I) adopts a chair structure, which has a methyl group in an equatorial position and an axially oriented S=O group. Compound (II) is similar, except that the S=O group is equatorially oriented. Compound (III) adopts a twist-chair conformation with a local approximate endocyclic twofold axis passing through S(1) and the middle of the opposite bond, C(4)—C(5).

1. Experimental

1.1. Materials and measurements

Compounds (I), (II) and (III) were prepared as described earlier (Hellier, 1986, Part 12; Hellier & Liddy, 1989). Since all three compounds are liquid at room temperature, low-temperature crystallization directly on the diffractometer was necessary. This was made following a procedure described elsewhere (Luger & Buschmann, 1984). A thin-walled closed glass capillary containing a column of sample fluid at the tip and 3–4 mm long was cooled in the nitrogen

gas stream of a low-temperature device, built in-house (Dietrich & Dierks, 1970), yielding a polycrystalline material far below the melting point. Single-crystal growth was then attempted by partial melting (85%) of the polycrystalline substance in the direction against the gas stream with a heating coil at a temperature just a few degrees below the melting point and by subsequent, very slow, electronically controlled reduction of heat output from the coil. This process was repeated several times for each compound. However, in no case was one single crystal present in the capillary as the inspection of oscillation photographs and reflection searches indicated. In the most favourable attempts, only a few specimens were grown. In each of the three cases, it was then possible, by a detailed inspection of the reflection distribution on a graphic screen, to identify a small number of reflections from one single crystal, which were then used to describe the unit cell and in a further step to centre sufficient high-order reflections of this specimen for a precise orientation matrix and lattice constant determination. Intensity data collection was then executed almost routinely, except the reflection profiles were also recorded to allow a later recognition of possibly occurring reflection overlap of different sample crystals.

1.2. Structure determination and refinement

The reflection intensities were Lp-corrected, scaled according to the changes of standard reflections (which were below the statistical errors in all cases) and corrected for the changing crystal volume bathed by the X-ray beam (Luger, 1984) and for anomalous dispersion. No absorption correction was applied.

The phase problem was solved with the direct methods program *SHELXS86* (Sheldrick, 1990). The refinements with least-squares techniques were executed with the corresponding programs of the *Xtal2.2* program system (Hall & Stewart, 1987) using anisotropic displacement parameters for the S, C and O atoms. All the H atoms were located from difference-Fourier syntheses. They were included in the refinement with isotropic displacement parameters.

Table 1. *Experimental details*

	(I)	(II)	(III)
Crystal data			
Chemical formula	C ₄ H ₈ O ₃ S	C ₄ H ₈ O ₃ S	C ₄ H ₈ O ₃ S
Chemical formula weight	136.17	136.17	136.17
Cell setting	Orthorhombic	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n
<i>a</i> (Å)	7.204 (6)	18.238 (6)	6.060 (3)
<i>b</i> (Å)	13.670 (11)	10.265 (3)	11.185 (8)
<i>c</i> (Å)	6.041 (6)	6.616 (2)	9.186 (4)
β (°)	90	90	101.32 (4)
<i>V</i> (Å ³)	594.91	1238.60	610.52
<i>Z</i>	4	8	4
<i>D_s</i> (Mg m ⁻³)	1.52	1.46	1.48
Radiation type	Mo <i>K</i> α, Nb filter	Mo <i>K</i> α, Nb filter	Mo <i>K</i> α, Nb filter
Wavelength (Å)	0.71068	0.71068	0.71068
No. of reflections for cell parameters	32	32	47
θ range (°)	5–12.5	10–22.5	7–18.5
μ (mm ⁻¹)	0.449	0.431	0.438
Temperature of crystallization (K)	268	260	245
Temperature (K)	256	240	228
Crystal form	Cylinder	Cylinder	Cylinder
Crystal radius (mm)	0.15	0.25	0.25
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Siemens four-circle	Siemens four-circle	Siemens four-circle
Data collection method	ω -2 θ	ω -2 θ	ω -2 θ
Scan width, $\Delta\omega$ (°)	0.78 + 0.52tan ω	1.24 + 0.52tan ω	0.82 + 0.52tan ω
Time per step (s) to reach $I/\sigma(I) > 50$ within time limit	0.3–2.1	0.5–1.5	0.3–1.8
Interval in 2 θ (°)	4–54	4–57	4–54
Absorption correction	None	None	None
No. of measured reflections	797	1624	2544
No. of independent reflections	778	1597	1161
No. of observed reflections	600	1505	995
Criterion for observed reflections	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
Function minimized in parameter refinement	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
R_{int}	—	—	0.042
θ_{max} (°)	27	28.5	27
Range of <i>h, k, l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 17 0 → <i>l</i> → 7	0 → <i>h</i> → 24 0 → <i>k</i> → 13 0 → <i>l</i> → 6	0 → <i>h</i> → 7 -13 → <i>k</i> → 13 -11 → <i>l</i> → 11
No. of standard reflections	2	5	3
Frequency of standard reflections (min)	60	60	90
Refinement			
Refinement on	<i>F</i>	<i>F</i>	<i>F</i>
<i>R</i>	0.042	0.032	0.037
<i>wR</i>	0.049	0.023	0.031
<i>S</i>	—	4.27 (8)	2.48 (6)
No. of reflections used in refinement	600	1505	995
No. of parameters used	105	209	105
H-atom treatment	Isotropic	Isotropic	Isotropic
Weighting scheme	Unit weights used	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$	0.82	0.36	0.09
$\Delta\rho_{max}$ (e Å ⁻³)	0.49	0.21	0.27
$\Delta\rho_{min}$ (e Å ⁻³)	—	—	—
Extinction method	None	None	None
Source of atomic scattering factors	Xtal2.2 (Hall & Stewart, 1987)	Xtal2.2 (Hall & Stewart, 1987)	Xtal2.2 (Hall & Stewart, 1987)

2. Results and discussion

Details of the data collection and structure refinements are given in Table 1 and atomic coordinates are listed in Tables 2–4.* Selected bond lengths, bond angles and

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: HU0421). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

torsion angles are given in Tables 5 and 6. The atomic nomenclature is defined in Figs. 1(a)–(c), which were drawn using ORTEPII (Johnson, 1971).

2.1. Six-membered ring compounds (I) and (II)

For (I) and (II), the six-membered rings have almost undistorted chair conformations as the ring torsion angles and the Cremer & Pople (1975) puckering angles θ show (close to 180° for both compounds).

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(1)	0.2987 (2)	0.7996 (1)	0.0616 (3)	0.0364 (4)
O(1)	0.4551 (6)	0.8577 (4)	0.1296 (8)	0.049 (2)
O(2)	0.1294 (6)	0.8730 (3)	0.0103 (7)	0.035 (1)
C(3)	0.0767 (9)	0.9407 (4)	0.190 (1)	0.032 (2)
C(4)	0.0226 (9)	0.8832 (5)	0.391 (1)	0.039 (2)
C(5)	0.169 (1)	0.8106 (5)	0.463 (1)	0.041 (2)
O(6)	0.2175 (7)	0.7463 (3)	0.2760 (7)	0.042 (1)
C(6)	-0.080 (1)	1.0014 (5)	0.098 (2)	0.047 (2)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(11)	0.33543 (3)	0.26134 (6)	0.1576 (1)	0.0450 (2)
O(11)	0.4051 (1)	0.2544 (2)	0.0559 (2)	0.0615 (7)
O(12)	0.34567 (9)	0.1696 (1)	0.3544 (3)	0.0430 (6)
C(13)	0.2844 (1)	0.1812 (2)	0.4993 (4)	0.0380 (9)
C(14)	0.2845 (2)	0.3171 (3)	0.5818 (5)	0.0409 (9)
C(15)	0.2778 (2)	0.4166 (3)	0.4156 (5)	0.046 (1)
O(16)	0.3377 (1)	0.4009 (2)	0.2704 (3)	0.0491 (6)
C(16)	0.2959 (2)	0.0768 (3)	0.6541 (7)	0.061 (1)
S(21)	0.58278 (4)	0.21231 (6)	0.8848 (1)	0.0445 (2)
O(21)	0.6510 (1)	0.2217 (2)	0.9925 (3)	0.0577 (6)
O(22)	0.59417 (9)	0.3073 (1)	0.6934 (2)	0.0418 (5)
C(23)	0.5362 (2)	0.2954 (3)	0.5379 (5)	0.0425 (9)
C(24)	0.5395 (2)	0.1591 (3)	0.4524 (5)	0.044 (1)
C(25)	0.5312 (2)	0.0583 (3)	0.6132 (6)	0.055 (1)
O(26)	0.5882 (1)	0.0747 (2)	0.7684 (3)	0.0482 (6)
C(26)	0.5505 (2)	0.4011 (3)	0.3862 (6)	0.063 (1)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (III)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(1)	0.0273 (1)	0.93114 (6)	0.30896 (7)	0.0485 (2)
O(1)	-0.0741 (3)	1.0438 (2)	0.2592 (2)	0.0634 (7)
O(2)	0.2782 (2)	0.9250 (1)	0.2832 (2)	0.0422 (5)
C(3)	0.3267 (4)	0.9350 (2)	0.1340 (3)	0.0407 (8)
C(4)	0.3512 (4)	0.8134 (2)	0.0720 (3)	0.0453 (9)
C(5)	0.1387 (5)	0.7408 (2)	0.0342 (3)	0.0433 (9)
C(6)	0.0096 (5)	0.7294 (2)	0.1567 (3)	0.0480 (9)
O(7)	-0.0957 (3)	0.8436 (2)	0.1777 (2)	0.0513 (6)

The complete puckering parameter sets (Luger & Bülow, 1983) are $Q = 0.58 (6) \text{\AA}$, $\theta = 174.3 (6)^\circ$, $\Phi = 175 (6)^\circ$ for (I); $Q = 0.647 (2)/0.6348 (3) \text{\AA}$, $\theta = 172.5 (2)/173.1 (2)^\circ$, $\Phi = 190 (2)/188 (2)^\circ$ for (II).

The major difference between the molecular structures of (I) and (II) in the crystal is the position of the exocyclic O(1), being axial for (I) but equatorial for (II) (see Figs. 1*a* and *b*). The methyl group at C(3) is in an equatorial position in both cases. The opposite substitution on S(1) causes small differences in the bond lengths and angles around this atom. Table 5 shows some averaged and individual bonding data for the two sulfites. First, it can be seen that C—C, C—O

Table 5. Summary of bond lengths (\AA) and angles ($^\circ$), averages calculated where possible; number of averaged data in square brackets if more than one contribution*

	(I)	(II)	(III)
C—C	1.507 (6) [3]	1.501 (7) [6]	1.498 (6) [3]
C—O	1.474 (4) [2]	1.473 (7) [4]	1.459 (6) [2]
S—O	1.603 (8) [2]	1.615 (3) [4]	1.586 (2), 1.617 (2),
S=O	1.438 (5)	1.438 (2) [2]	1.436 (2)
O—S—O(en)	99.4 (3)	98.3 (2) [2]	100.20 (9)
O—S—O(ex)	107.6 (4) [2]	103.9 (2) [4]	110.7 (1), 100.8 (1),
S—O—C	116.1 (4) [2]	113.0 (6) [4]	120.8 (1), 118.6 (1),
O—C—C(en)	109.7 (2) [2]	109.1 (12) [4]	109.7 (4) [2]
C—C—C(en)	113.1 (6)	111.6 (3)	115.4 (6) [2]

(en)=endocyclic, (ex)=exocyclic, *g* = gauche, *t* = trans fragments. * Note that (II) has two molecules in the asymmetric unit so that the number of data available for this structure is double.

Table 6. Endocyclic torsion angles for 1,3,2-dioxathiane 2-oxide (III) and theoretical values for TC* form of cycloheptane after Hendrickson (1967)

	(III)	TC-cycloheptane
O(7)—S(1)—O(2)—C(3)	45.2 (2)	39.1
S(1)—O(2)—C(3)—C(4)	-96.5 (2)	-88.1
O(2)—C(3)—C(4)—C(5)	69.7 (3)	72.3
C(3)—C(4)—C(5)—C(6)	-52.3 (3)	-54.3
C(4)—C(5)—C(6)—O(7)	71.8 (3)	72.3
C(5)—C(6)—O(7)—S(1)	-98.2 (2)	-88.1
C(6)—O(7)—S(1)—O(2)	46.0 (2)	39.1

* TC = twist-chair.

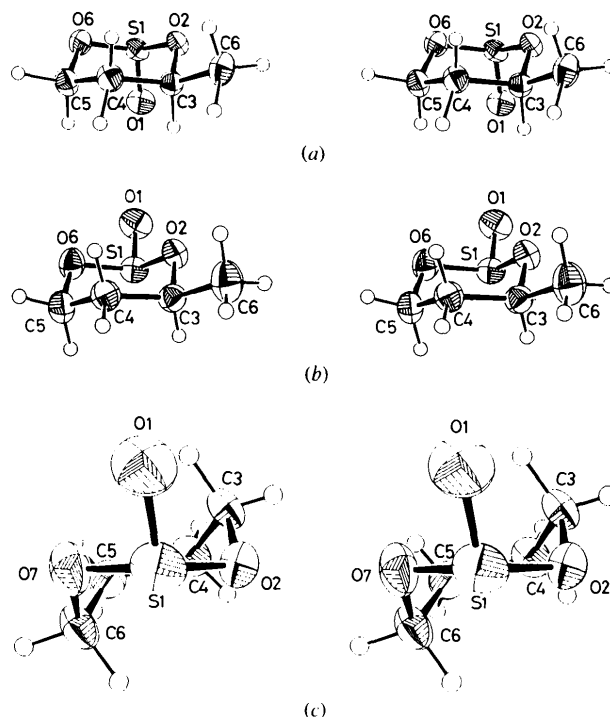


Fig. 1. Atomic numbering and thermal ellipsoid plots at 50% probability. All figures are stereo representations: (a) 4-methyl-1,3,2-dioxathiane 2-oxide, isomer 1 (I); (b) 4-methyl-1,3,2-dioxathiane 2-oxide, isomer 2 (II); (c) 1,3,2-dioxathiane 2-oxide (III).

and S=O compare well for (I) and (II), but S—O is somewhat shorter for (I). However, the difference between (I) and (II) for this bond is only two standard deviations and hence probably insignificant.

Characteristic bond-angle differences are seen around S(1). The exocyclic O—S—O and endocyclic S—O—C angles are remarkably larger for (I) than for (II), which is in accordance with the corresponding values at the S atom of (III).

The X-ray diffraction results confirm that, as crystals, both sulfites have single chair forms. Additionally, solution-based studies also predict a single chair form for (I) with the S=O group axial. In contrast, (II) has only one form when crystalline, but possibly chair–chair and/or twist–chair forms in solution – a conclusion based primarily on IR and NMR studies (Hellier & Phillips, 1982; Cazaux, Bastide, Chaissang & Maroni, 1979; Pihlaja, Rossi & Nikander, 1985). From our study there is no evidence for the existence of twist–chair or chair–chair forms for isomer 2 (II) in the crystal.

2.2. The seven-membered ring compound (III)

Compared with six-membered rings, 1,3,2-dioxathiane 2-oxides, there have been few reports on the conformational analysis of 1,3,2-dioxathiepane 2-oxides (Hellier & Liddy, 1989; Guimaraes, de Almeida, Baltas & Cazaux, 1983). Nevertheless, an understanding of possible ring conformations has been obtained by studies of other saturated seven-membered ring compounds. Theoretical calculations on cycloheptane (Hendrickson, 1967) and on oxepane and 1,3-dioxepane (Bocian & Strauss, 1977) have suggested that the twist–chair form is energetically favoured. If only the molecular structure of (III) is considered, it seems clear from Fig. 1(c) and the table of ring torsion angles (Table 5) that a local C_2 symmetry is well realised in this ring by adopting a twist–chair conformation. The local twofold axis passes through the S atom and the middle of the opposite bond, C(4)—C(5). The endocyclic torsion angles in the title compound (III) compare well with the theoretical values for the twist–chair form of cycloheptane (Hendrickson, 1967). Moreover, with respect to the torsion angle along C(4)—C(5), a twofold axis of symmetry for the endocyclic torsion angle sequence is satisfied within 2° (see Table 6).

Although the chemical structure suggests that the entire molecule should have a twofold symmetry, the endocyclic S—O bond lengths show already significant deviations from this symmetry. The difference between S(1)—O(2) [1.586(2) Å] and S(1)—O(7) [1.617(2) Å] of 0.031 Å, being greater than 15σ , is accompanied by a difference of the bond angles O(1)—S(1)—O(7) [100.8(1)°] and O(1)—S(1)—O(2)

[110.7(1)°] of almost 10° . These most surprising findings are understood if the linkage of O(1) to the ring is considered, which is totally asymmetric. The two exocyclic torsion angles O(1)—S(1)—O(2)—C(3) $-60.6(2)^\circ$ and O(1)—S(1)—O(7)—C(6) $159.5(2)^\circ$ show a *gauche* arrangement of O(1) with respect to C(3) and a *trans* position to C(6).

Both the difference between the two O—S—O angles and the S—O(2) distance being shorter than the S—O(7) distance can be attributed to the anomeric effect (Petit, van Nuffel, van Alsenoy, Lenstra & Geise, 1984). Thus, in this molecule different local conformations are realized along the endocyclic S—O bonds. Similar observations can be made for 1,3,2-dioxathiane 2-oxides with twist–chair structures, e.g. *trans*,5-chloro-*cis*,*trans*-4,6-di-*tert*-butyl-1,3,2-dioxathiane 2-oxide (Carbonelle, Jeannin & Robert, 1978) and 5,5-dimethyl-*cis*-4,*trans*-6-di-*tert*-butyl-1,3,2-dioxathiane 2-oxide (Hellier, Motevalli, Hursthouse & Liddy, 1990).

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