Data collection: *MARxds* (Kabsch, 1988). Cell refinement: *MARxds*. Data reduction: *CRYSTALS* (Watkin *et al.*, 1985). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTALS* and local software.

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A Cyclic Sulfate with a Seven-Membered Ring: 1,3,2-Dioxathiepane 2,2-Dioxide

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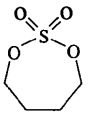
Abstract

We report the first structure of a seven-membered cyclic organosulfate, $C_4H_8O_4S$. The molecule has almost a local C_2 symmetry (r.m.s. deviation within molecule 1 is 0.018 Å). The two molecules in the asymmetric unit show the same conformation [r.m.s. deviation of all non-H atoms is 0.017 (7) Å]. Although the seven-membered ring is flexible in solution, the conformations of the two independent molecules are apparently not influenced by crystal-packing effects.

Comment

Epoxides play a unique role in organic synthesis. They simultaneously activate and protect adjacent functionalized C atoms for nucleophilic attack (Gao & Sharpless, 1988). The same favorable properties are shared by cyclic sulfates, which have recently found useful applications as ring-closing reagents for the synthesis of saturated phosphorous-containing heterocycles (Field & Thomas, 1996) and as substrates for selective substitution reactions involving fluoride or phenoxide ions as nucleophiles (Berridge *et al.*, 1990). The title compound, (I), was prepared in a two-step synthesis according to the method described by Sharpless (Gao & Sharpless, 1988).



(I)

Compound (I) crystallizes in space group $P\bar{1}$ with two molecules in the asymmetric unit. Both molecules have a local C_2 symmetry (r.m.s. deviation within molecule 1 is 0.018 Å), which does not coincide with any crystallographic symmetry element. The S—O and O—C bond lengths are as expected from other cyclic sulfates. In both independent molecules, the α-C—C (*e.g.* C1—C2) bond lengths (average 1.488 Å) are shorter than the β-C—C (*e.g.* C2—C3) bond lengths (average 1.504 Å), but agree within both molecules in spite of their different environments [r.m.s. deviation of all non-H atoms is 0.017 (7) Å]. The relatively short C_{sp^3}—C_{sp^3} bonds lengths and the correspondingly large

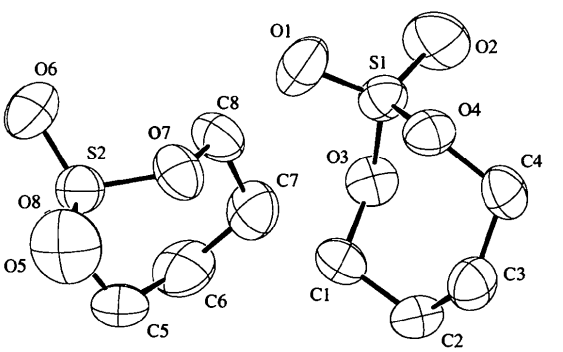


Fig. 1. View of the two molecules in the asymmetric unit of (I) showing the labeling of the non-H atoms. Atomic displacement ellipsoids are shown at the 50% probability level.

C—C—C bond angles (average 115.4°) may be due to slight disorder. The means of the S—O bonds for the neutral tetrahedra (1.477 and 1.470 Å) substantiate Kálmán's early findings on tetrahedral oxy anions (Kálmán, 1971). The O3—S1—O4 (O7—S1—O8 in molecule 2) bond angle [103.45 (10) and 103.92 (10)°, respectively] is in the upper range of corresponding O—S—O angles in cyclic sulfates. Interestingly, this angle becomes much smaller in an eight-membered ring such as benzophenone-2,2′-sulfate (99.59°; Litvinov *et al.*, 1982).

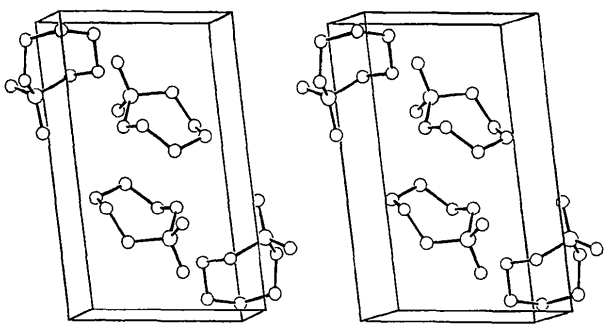


Fig. 2. Stereoview of the unit cell.

Experimental

The title compound, (I), was prepared in a two-step synthesis according to the method described by Sharpless (Gao & Sharpless, 1988). Crystals were isolated from the reaction mixture.

Crystal data

$C_4H_8O_4S$
M_r = 152.16
Triclinic
$P\bar{1}$
a = 6.4376 (8) Å
b = 9.7440 (9) Å
c = 10.8177 (10) Å
α = 92.328 (8)°
β = 96.772 (11)°
γ = 99.011 (11)°
V = 664.31 (12) Å^3
Z = 4
D_x = 1.521 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 2.0–26.3°
μ = 0.429 mm^{-1}
T = 293 K
Plate
0.46 × 0.25 × 0.25 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2940 measured reflections
2690 independent reflections
1823 reflections with $I > 2\sigma(I)$

R_{int} = 0.094
θ_{max} = 26.29°
h = −8 → 0
k = −11 → 12
l = −13 → 13
3 standard reflections
frequency: 30 min
intensity decay: 9.1%

Refinement

Refinement on F^2
$R(F)$ = 0.042
$wR(F^2)$ = 0.096
S = 1.047
2690 reflections
227 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 0.1871P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.231 e Å^{-3}
$\Delta\rho_{min}$ = −0.378 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O3	1.471 (3)	C5—O8	1.486 (4)
C1—C2	1.485 (4)	C5—C6	1.474 (5)
C2—C3	1.500 (5)	C6—C7	1.508 (6)
C3—C4	1.488 (4)	C7—C8	1.492 (4)
C4—O4	1.478 (3)	C8—O7	1.471 (4)
O1—S1	1.412 (2)	O5—S2	1.401 (2)
O2—S1	1.404 (2)	O6—S2	1.411 (2)
O3—S1	1.546 (2)	O7—S2	1.532 (2)
O4—S1	1.545 (2)	O8—S2	1.535 (2)
O3—C1—C2	109.6 (3)	C6—C5—O8	108.6 (3)
C1—C2—C3	116.0 (3)	C5—C6—C7	115.2 (3)
C4—C3—C2	115.5 (3)	C8—C7—C6	114.9 (3)
O4—C4—C3	108.5 (2)	O7—C8—C7	109.3 (3)
C1—O3—S1	118.4 (2)	C8—O7—S2	119.5 (2)
C4—O4—S1	119.2 (2)	C5—O8—S2	117.8 (2)
O2—S1—O1	118.79 (14)	O5—S2—O6	118.7 (2)
O2—S1—O4	112.14 (14)	O5—S2—O7	106.3 (2)
O1—S1—O4	104.14 (12)	O6—S2—O7	111.46 (14)
O2—S1—O3	105.67 (13)	O5—S2—O8	110.7 (2)
O1—S1—O3	111.71 (13)	O6—S2—O8	104.9 (2)
O4—S1—O3	103.45 (10)	O7—S2—O8	103.92 (10)

The title structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990) and refined by full-matrix least squares, where the quantity minimized was $[\Sigma\omega(F_o^2 - F_c^2)^2]$ (*SHELXL*-93; Sheldrick, 1993). Non-H atoms were refined anisotropically and H atoms were included in the refinement using a riding model.

Data collection: *CAD-4 Express Software* (Enraf–Nonius, 1995). Data reduction: *DATAP* (Coppens *et al.*, 1965). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1250). Services for accessing these data are described at the back of the journal.

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