

Cyclic Sulfito of 1,1'-Dicyclohexyl-1,1'-diol

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Abstract. Dispiro[1,3,2-dioxathiolane-4,5-bis(cyclohexane)] 2-oxide, $C_{12}H_{20}O_3S$, $M_r = 244.348$, monoclinic, $P2_1/c$, $a = 9.543$ (2), $b = 11.360$ (1), $c = 11.681$ (2) Å, $\beta = 98.42$ (3)°, $V = 1252.7$ (4) Å³, $Z = 4$, $D_x = 1.29$, $D_m = 1.3$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.37$ cm⁻¹, $F(000) = 528$, $T = 298$ K, $R = 0.0436$ for 1414 unique reflections. The structure consists of a 1,3,2-dioxathiolane 2-oxide ring fused to two cyclohexyl rings. The five-membered ring adopts a half-chair conformation with the S=O group and the cyclohexyl groups in pseudo-axial and pseudo-equatorial positions, respectively. The title compound is the first spiro sulfite of this type to be studied by X-ray analysis. Nevertheless, bond lengths and bond angles are similar to those in related compounds.

Introduction. The conformations of simple 1,3,2-dioxathiolane 2-oxides have been studied by many physical methods (Green & Hellier, 1973, 1975; Buchanan & Hellier, 1976) including X-ray analysis (Jones, Lowe & Salamone, 1984). From these studies it was considered that the sulfite ring adopts a half-chair conformation. We continue our interest in the stereochemistry of cyclic sulfites by preparation and isolation of the title spiro sulfite *via* HPLC, following a previously described procedure (Liddy, 1988).

Experimental. Single crystals were grown by recrystallization from ether at 263 K, m.p. 301 K. Density measured by flotation. The X-ray measurements were made using an Enraf-Nonius CAD-4 diffractometer, operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The lattice parameters were determined by least-squares refinement using setting angles for 25 reflections ($9 < \theta < 15^\circ$). Intensities were collected for $1.5 < \theta < 25^\circ$, the index range was $h - 11/11$, $k/13$, $l 0/13$, with scan rate $1.3-5.9^\circ \text{ min}^{-1}$, ω -scan width $0.85^\circ + 0.35^\circ \tan\theta$ and aperture setting 4 mm. Three intensity-control reflections were monitored every hour. They showed ~12% decay which was corrected for during the data processing. 2541 reflections were measured. The data were corrected for absorption by the method of North, Phillips & Mathews (1968), with transmission factors in the

range 0.986–0.965. The data were averaged to 2208 unique reflections, $R_{\text{int}} = 0.0132$, of which 1414 [$I_o > 3\sigma(I_o)$] were used in refinement. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). All non-H atoms were located in the best E map. A subsequent difference map revealed the H-atom positions. Least-squares anisotropic refinement on F of non-H atoms and isotropic refinement of H atoms gave final $R = 0.0436$, $wR = 0.0419$ and $S = 1.5$, with $w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$, giving acceptable agreement analyses; maximum and minimum $\Delta\rho = +0.22$ and -0.36 e Å⁻³. Maximum shift/e.s.d. = 0.23 (*SHELX76*, Sheldrick, 1976). The computations were made on a VAX 11/750 computer. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The refined atomic coordinates and isotropic temperature factors are presented in Table 1.* Bond distances and bond angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53008 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² $\times 10^3$)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S(1)	2453.5 (9)	151.0 (7)	7207.0 (10)	76.5 (4)
O(1)	1109 (2)	368 (1)	7875 (2)	53.6 (7)
O(2)	3190 (2)	1396 (2)	7600 (2)	54.2 (7)
O(3)	2016 (3)	234 (3)	5982 (3)	112 (1)
C(1)	935 (3)	1624 (2)	8168 (2)	35.1 (8)
C(2)	74 (3)	1625 (3)	9155 (2)	43 (1)
C(3)	-1415 (3)	1130 (3)	8805 (3)	53 (1)
C(4)	-2196 (3)	1742 (3)	7756 (3)	63 (1)
C(5)	-1338 (4)	1726 (4)	6763 (3)	68 (2)
C(6)	132 (3)	2246 (3)	7128 (3)	49 (1)
C(7)	2500 (2)	2018 (2)	8472 (2)	36.6 (8)
C(8)	2765 (3)	3322 (2)	8296 (3)	47 (1)
C(9)	4333 (3)	3642 (3)	8534 (3)	62 (1)
C(10)	5008 (4)	3247 (4)	9717 (3)	75 (2)
C(11)	4786 (3)	1948 (4)	9873 (4)	72 (2)
C(12)	3214 (3)	1635 (3)	9668 (3)	56 (1)

Table 2. Selected bond lengths (Å) and bond angles (°)

O(1)—S(1)	1.615 (4)	O(2)—S(1)	1.616 (4)
O(3)—S(1)	1.434 (4)	C(1)—O(1)	1.483 (4)
C(7)—O(2)	1.473 (4)	C(2)—C(1)	1.511 (5)
C(6)—C(1)	1.514 (6)	C(7)—C(1)	1.549 (5)
C(3)—C(2)	1.527 (6)	C(4)—C(3)	1.507 (6)
C(5)—C(4)	1.514 (7)	C(6)—C(5)	1.524 (6)
C(8)—C(7)	1.522 (5)	C(12)—C(7)	1.525 (6)
C(9)—C(8)	1.525 (6)	C(10)—C(9)	1.505 (7)
C(11)—C(10)	1.506 (7)	C(12)—C(11)	1.526 (6)
O(2)—S(1)—O(1)	94.2 (2)	O(3)—S(1)—O(1)	109.7 (2)
O(3)—S(1)—O(2)	106.1 (2)	C(1)—O(1)—S(1)	112.5 (2)
C(7)—O(2)—S(1)	113.4 (2)	C(2)—C(1)—O(1)	105.6 (3)
C(6)—C(1)—O(1)	109.0 (3)	C(6)—C(1)—C(2)	110.1 (3)
C(7)—C(1)—O(1)	101.2 (3)	C(7)—C(1)—C(2)	116.0 (3)
C(7)—C(1)—C(6)	114.0 (3)	C(3)—C(2)—C(1)	112.6 (3)
C(4)—C(3)—C(2)	112.2 (4)	C(5)—C(4)—C(3)	111.0 (4)
C(6)—C(5)—C(4)	111.1 (4)	C(5)—C(6)—C(1)	112.3 (3)
C(1)—C(7)—O(2)	102.5 (3)	C(8)—C(7)—O(2)	105.9 (3)
C(8)—C(7)—C(1)	115.1 (3)	C(12)—C(7)—O(2)	108.1 (3)
C(12)—C(7)—C(1)	114.5 (3)	C(12)—C(7)—C(8)	109.9 (3)
C(9)—C(8)—C(7)	112.6 (3)	C(10)—C(9)—C(8)	111.9 (4)
C(11)—C(10)—C(9)	110.7 (4)	C(12)—C(11)—C(10)	111.2 (4)
C(11)—C(12)—C(7)	112.0 (4)		

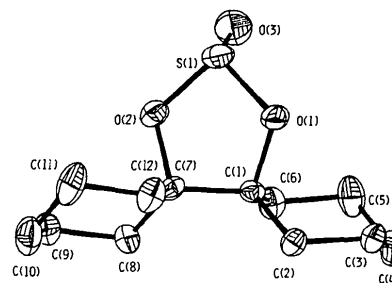


Fig. 1. Numbering of atoms and conformation of the molecule.

those found for 4-phenyl-1,3,2-dioxathiolane 2-oxide (25°) and *meso*-4,5-diphenyl-1,3,2-dioxathiolane 2-oxide (35°).

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A *SNOOPI* (Davies, 1983) drawing of the molecular structure and the numbering of atoms are shown in Fig. 1. The five-membered ring has a half-chair form and the six-membered rings have chair forms. Bond lengths and bond angles are close to normal values for other five-membered-ring cyclic sulfites (Jones, Lowe & Salamone, 1984): C(1)—C(7) 1.549 (5), C(7)—O(2) 1.473 (4), C(1)—O(1) 1.483 (4), S(1)—O(1) 1.615 (4), S(1)—O(2) 1.616 (4), S(1)—O(1) (S=O) 1.434 (4) Å, and O(2)—S(1)—O(1) 94.2 (2), O(2)—S(1)—O(3) 106.1 (2), O(3)—S(1)—O(1) 109.7 (2), S(1)—O(2)—C(7) 113.4 (2) and S(1)—O(1)—C(1) 112.5 (2)°. The stereochemical constraint in this spiro sulfite is shown by the high value (39.4°) of the O—C—C—O dihedral angle compared with

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Structure of *cis*-4,*trans*-6-Di-*tert*-butyl-5,5-dimethyl-1,3,2-dioxathiane 2-Oxide

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Abstract. C₁₃H₂₆O₃S, *M_r* = 262.407, monoclinic, *P*₂₁/*c*, *a* = 8.559 (3), *b* = 12.562 (3), *c* = 14.116 (6) Å, β = 102.18 (3)°, *V* = 1483.56 (4) Å³, *Z* = 4, *D_x* = 1.17, *D_m* = 1.2 g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 2.05 cm⁻¹, *F*(000) = 576, *T* = 298 K, *R* = 0.0506 for 2601 unique reflections. The six-membered sulfite ring has an unusual twist conformation with the

exocyclic S=O group in an isoclinal position and the *tert*-butyl groups in pseudo-equatorial positions. Although most of the bond lengths and bond angles are as predicted, the S=O bond length of 1.392 (5) Å is considerably shorter than expected. The structure determined confirms the interpretations of IR and NMR spectra.