$S = 1.49$
1470 reflections
145 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
I(1)	0.38538 (5)	0.98241 (2)	0.25723 (5)	3.49 (2)
O(1)	0.5386 (5)	0.9036 (2)	−0.0669 (5)	2.7 (2)
O(2)	0.9075 (5)	1.1609 (2)	0.1310 (5)	2.9 (2)
O(3)	0.6869 (5)	1.2254 (2)	0.1872 (5)	3.1 (2)
O(4)	0.3455 (6)	0.2508 (3)	0.5069 (6)	3.9 (2)
N(1)	0.9142 (5)	1.1873 (2)	−0.2040 (5)	2.6 (2)
C(1)	0.5853 (6)	1.1082 (3)	−0.1504 (6)	2.2 (2)
C(2)	0.5181 (6)	1.0826 (3)	0.0035 (6)	2.2 (2)
C(3)	0.5002 (6)	1.0150 (3)	0.0276 (6)	2.2 (2)
C(4)	0.5537 (6)	0.9696 (3)	−0.0970 (6)	2.2 (2)
C(5)	0.6169 (6)	0.9953 (2)	−0.2492 (8)	2.8 (2)
C(6)	0.6322 (6)	1.0642 (3)	−0.2766 (6)	2.6 (2)
C(7)	0.6036 (7)	1.1833 (3)	−0.1757 (6)	2.4 (2)
C(8)	0.7676 (6)	1.2130 (2)	−0.1043 (6)	2.1 (2)
C(9)	0.7899 (6)	1.1985 (2)	0.0889 (6)	2.1 (2)
C(10)	0.313 (1)	0.1826 (4)	0.4760 (9)	4.7 (3)

Table 2. *Selected geometric parameters* (Å, °)

I(1)—C(3)	2.103 (5)	C(1)—C(7)	1.527 (7)
O(1)—C(4)	1.350 (6)	C(2)—C(3)	1.378 (7)
O(2)—C(9)	1.249 (6)	C(3)—C(4)	1.394 (7)
O(3)—C(9)	1.244 (6)	C(4)—C(5)	1.381 (7)
O(4)—C(10)	1.414 (9)	C(5)—C(6)	1.405 (7)
N(1)—C(8)	1.496 (7)	C(7)—C(8)	1.543 (7)
C(1)—C(2)	1.403 (7)	C(8)—C(9)	1.532 (7)
C(1)—C(6)	1.370 (7)		
C(2)—C(1)—C(6)	118.2 (5)	C(4)—C(5)—C(6)	121.9 (5)
C(2)—C(1)—C(7)	120.5 (5)	C(1)—C(6)—C(5)	120.3 (5)
C(6)—C(1)—C(7)	121.3 (4)	C(1)—C(7)—C(8)	114.7 (4)
C(1)—C(2)—C(3)	121.1 (5)	N(1)—C(8)—C(7)	110.3 (4)
I(1)—C(3)—C(2)	117.8 (4)	N(1)—C(8)—C(9)	110.2 (4)
I(1)—C(3)—C(4)	121.0 (4)	C(7)—C(8)—C(9)	112.0 (4)
C(2)—C(3)—C(4)	121.3 (5)	O(2)—C(9)—O(3)	127.0 (5)
O(1)—C(4)—C(3)	119.7 (5)	O(2)—C(9)—C(8)	117.2 (5)
O(1)—C(4)—C(5)	123.1 (4)	O(3)—C(9)—C(8)	115.8 (5)
C(3)—C(4)—C(5)	117.2 (5)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-*tert*-Butyl-5-methyl-1,3,2-dioxathiane 2,2-Dioxide

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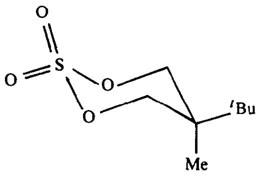
Abstract

The six-membered sulfate ring of the title compound, $C_8H_{16}O_4S$, has a chair form with the *tert*-butyl group in an equatorial position. Although most of the bond lengths and angles are as predicted, one C—C bond is considerably longer than the others. The structure determined confirms the interpretation of IR and NMR spectra.

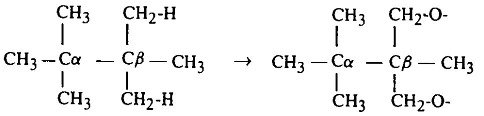
Comment

The conformational analysis of cyclic sulfates using ^{13}C and ^{17}O NMR spectroscopy has been reported (Hellier & Liddy, 1988); all of these sulfates (which have five- and six-membered rings) have flexible conformations in solution, and ^1H NMR studies at ambient-to-low temperatures suggest that the barrier to pseudorotation or inversion is quite low. The title compound, (1), was studied initially by ^1H NMR spectroscopy (Hellier & Webb, 1977), which showed it to be exceptional in having a rigid chair form in solution. Following a report on the X-ray structures of two flexible-six-membered-ring sulfates (Lowe, Thatcher, Turner, Waller & Watkin, 1988), we determined the solid-state structure of (1) (Fig. 1) in order to compare it with that of the flexible sulfate 1,3,2-dioxathiane 2,2-dioxide, (2), and thus determine the geometrical differences arising from the change in substitution at C(2) from protons in (2) to methyl and *tert*-butyl groups in (1).



(1)

A selection of geometrical parameters are compared in Table 3. This shows that bond lengths and angles are quite similar in the two compounds. However, the Cα—Cβ bond in (1) is longer than normal (~1.58 *cf.* 1.51 Å). This is easily explained if the carbon skeleton is considered as a substituted hexamethylethane (2,2,3,3-tetramethylbutane), (3):



$$\begin{array}{ccccccc} & CH_3 & & CH_2\text{-}H & & & CH_3 & & CH_2\text{-}O\text{-} \\ & | & & | & & & | & & | \\ CH_3- & C\alpha & - & C\beta-CH_3 & \rightarrow & CH_3- & C\alpha & - & C\beta-CH_3 \\ & | & & | & & & | & & | \\ & CH_3 & & CH_2\text{-}H & & & CH_3 & & CH_2\text{-}O\text{-} \end{array}$$

(3) (1)

Compound (3) is difficult to crystallize but an electron diffraction study (Bauer & Beach, 1942) suggested a value of 1.58 Å for the Cα—Cβ bond, which is identical to that in (1). A sulfite with a related structure, *cis*-5-*tert*-butyl-1,3,2-dioxathiane 2-oxide (Van Nuffel, Petit, Geise & Lenstra, 1980), gave an intermediate value of 1.55 Å for this bond. The stretching of the Cα—Cβ bond in (1) is apparently the result of steric repulsion between the *tert*-butyl and the ring protons.

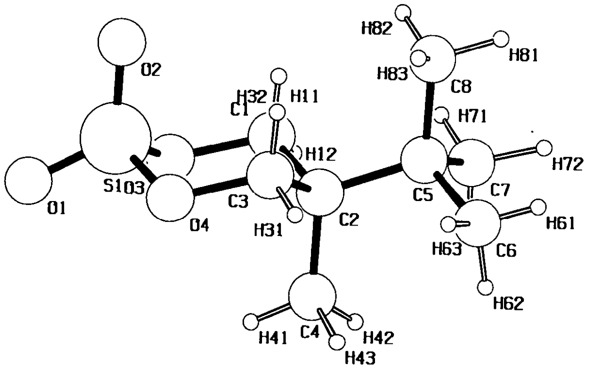


Fig. 1. A *PLUTON* (Spek, 1993) drawing of (1) showing the atom-numbering scheme.

Experimental

Single crystals were grown by recrystallization from ether at 263 K; m.p. 405 K. The crystal density D_m was measured by flotation.

Crystal data

$C_8H_{16}O_4S$
$M_r = 208.27$
Orthorhombic
$P2_12_12_1$
$a = 11.6790\,(10)$ Å
$b = 11.3100\,(10)$ Å
$c = 7.8470\,(10)$ Å
$V = 1036.5\,(2)$ Å^3
$Z = 4$
$D_x = 1.335$ Mg m^{-3}
$D_m = 1.34$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11–17°$
$\mu = 0.295$ mm^{-1}
$T = 238\,(5)$ K
Rhombic
0.3 × 0.2 × 0.12 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.967$, $T_{max} = 0.978$
1231 measured reflections
1231 independent reflections

896 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 24.92°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0248$
$wR(F^2) = 0.0570$
$S = 1.017$
896 reflections
182 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.4095P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.158$
$\Delta\rho_{max} = 0.096$ e Å^{-3}
$\Delta\rho_{min} = -0.129$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
S1	0.28028 (7)	0.82634 (7)	0.94821 (11)	0.0482 (2)
O1	0.2139 (2)	0.7629 (2)	0.8292 (3)	0.0702 (7)
O2	0.2611 (2)	0.8107 (2)	1.1246 (3)	0.0663 (7)
O3	0.2699 (2)	0.9589 (2)	0.9007 (3)	0.0492 (5)
O4	0.4073 (2)	0.8002 (2)	0.9056 (3)	0.0511 (6)
C1	0.3514 (3)	1.0397 (3)	0.9876 (5)	0.0448 (8)
C2	0.4746 (2)	1.0054 (2)	0.9486 (4)	0.0397 (6)
C3	0.4907 (3)	0.8761 (3)	0.9957 (5)	0.0506 (9)
C4	0.4962 (4)	1.0191 (4)	0.7568 (5)	0.0661 (10)
C5	0.5582 (2)	1.0840 (3)	1.0594 (5)	0.0485 (7)
C6	0.6827 (3)	1.0620 (5)	1.0059 (7)	0.0754 (13)
C7	0.5314 (4)	1.2154 (3)	1.0334 (6)	0.0632 (10)
C8	0.5481 (4)	1.0572 (4)	1.2508 (5)	0.0644 (10)

Table 2. *Selected geometric parameters* (Å, °)

S1—O1	1.410 (3)	C2—C3	1.521 (4)
S1—O2	1.413 (2)	C2—C4	1.534 (5)
S1—O3	1.549 (2)	C2—C5	1.580 (4)
S1—O4	1.549 (2)	C5—C6	1.534 (5)
O3—C1	1.486 (4)	C5—C7	1.533 (5)
O4—C3	1.478 (4)	C5—C8	1.537 (5)
C1—C2	1.521 (4)		
O1—S1—O2	119.9 (2)	C1—C2—C4	109.1 (3)
O1—S1—O3	106.85 (14)	C3—C2—C5	109.3 (2)
O2—S1—O3	110.14 (14)	C1—C2—C5	109.3 (2)
O1—S1—O4	106.66 (15)	C4—C2—C5	112.4 (3)
O2—S1—O4	109.82 (14)	O4—C3—C2	111.1 (2)
O3—S1—O4	101.97 (11)	C6—C5—C7	108.3 (3)
C1—O3—S1	115.8 (2)	C6—C5—C8	108.0 (3)
C3—O4—S1	114.7 (2)	C7—C5—C8	107.8 (4)
O3—C1—C2	110.9 (3)	C6—C5—C2	110.1 (3)
C3—C2—C1	108.3 (3)	C7—C5—C2	110.2 (3)
C3—C2—C4	108.4 (3)	C8—C5—C2	112.3 (3)

Table 3. *Comparison of selected geometric parameters* (Å, °) *for* (1) *and* (2)

	(1)	(2)
S1—O1	1.409	1.412
S1—O2	1.409	1.415
S1—O3	1.548	1.552
S1—O4	1.549	1.551
C3—O4	1.473	1.481
C1—O3	1.485	1.482
C2—C3	1.523	1.494
C1—C2	1.527	1.513
C2—C5 (Cα—Cβ)	1.575	-
O1—S1—O2	120.1	119.50
O3—S1—O4	101.9	102.60
O4—C3—C2	111.3	109.40
O3—C1—C2	110.7	109.00
O1—S1—O3	106.8	107.10
O2—S1—O4	109.7	109.50

The data were collected with scan rate of 1.3–5.9 $\min^{-1}$, ω scan width of $(0.85 + 0.35\tan\theta)^\circ$ and aperture setting of 4 mm. The structure was solved by direct methods. All non-H atoms were located in the best *E* map. A subsequent difference map revealed the H-atom positions. Refinement was by least squares, with non-H atoms anisotropic and H atoms isotropic. The calculations were performed on a PC (IBM, AT-compatible).

Data collection: CAD-4/PC diffractometer software. Cell refinement: CAD-4/PC diffractometer software. Data reduction: CAD-4/PC diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1993). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Scalaradial, a Sesterterpenoid Metabolite from the Marine Sponge *Cacospongia mollior*

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Abstract

The X-ray study of scalaradial [Cimino, De Stefano & Minale (1974). *Experientia*, **30**, 846–847], the major secondary metabolite from the marine sponge *Cacospongia mollior*, is reported. In the crystal of 12-(acetyloxy)-4,4,8-trimethyl-D-homoandrost-16-ene-17,17a-dicarboxaldehyde, $C_{27}H_{40}O_4$, the asymmetric unit comprises two molecules which display high geometrical and conformational similarity. All the saturated rings are in chair conformations, whereas the cyclohexene ring adopts a half-chair form. The molecule is highly bent in a direction normal to the average skeletal plane, with rings *A* and *C* forming an angle of about 30°. The four axial iso-oriented methyl groups in the tetracyclic system produce distortions of the skeletal geometry similar to those observed in other molecules with analogous sequences of axial substituents, and are probably responsible for the remarkable bend of the skeleton.

Comment

Among marine organisms, sponges are a particularly rich source of sesterterpenoids (Faulkner, 1994, and references therein). These substances often display multi-