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2-Methoxymethyl-1,3-dithiepane 1,1,3,3-tetraoxide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.068
Data-to-parameter ratio = 10.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

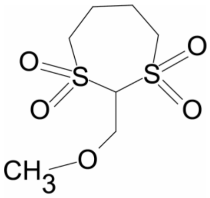
The title compound, $C_7H_{14}O_5S_2$, consists of a seven-membered dithiepane ring with two O atoms bonded to each S atom and a methoxymethyl group at the 2-position. A few close contacts seem to influence the geometry of the dithiepane ring.

Comment

During the last decade, compounds having two geminal sulfones have been shown to be useful dienophiles, and they have received considerable attention. A number of aryl-substituted ketenedithioacetal tetraoxides have been shown to be good dienophiles (De Lucchi *et al.*, 1992) in Diels–Alder reactions. The cycloadducts desulfonylate to the corresponding norbornenes.

Similarly, bis(phenylsulfonyl)ethene has been reported (De Lucchi *et al.*, 1991) and the bis-sulfone undergoes highly diastereoselective cycloadditions with unsymmetrical dienes. The bis-sulfone has been shown to be a useful acetylene equivalent in cycloaddition reactions (De Lucchi *et al.*, 1991).

Recently, a sulfone-containing dienophile, benzenesulfonylallene, has been reported (Trudell & Pavri, 1997), and found to undergo a Diels–Alder reaction with *N*-Boc-pyrrole. The cycloadduct transformed into the epibatidine precursor in three steps. The sulfonyl group has versatile functionality in organic synthesis and can be conveniently eliminated, resulting in an alkene (Little & Myong, 1980; Lopez & Carretero, 1991). Moreover, the sulfonyl group may undergo desulfonylation and oxidative desulfonylation with the formation of the corresponding ketones (Leon & Carretero, 1991).



(I)

Racemic 2-methoxymethyl-1,3-dithiolane 1,3-dioxide has been shown to be a useful starting material for the preparation of (1*R*,3*R*)-2-methylene-1,3-dithiolane 1,3-dioxide (Aggarwal *et al.*, 1998). The crystal structure of the five-membered ring analogue of the title compound, (I), *viz.* 2-methoxymethyl-1,3-dithiolane 1,1,3,3-tetraoxide has been reported previously (Özcan *et al.*, 2003). Compound (I) may also prove to be a useful starting material for the preparation of a new sulfone-containing dienophile.

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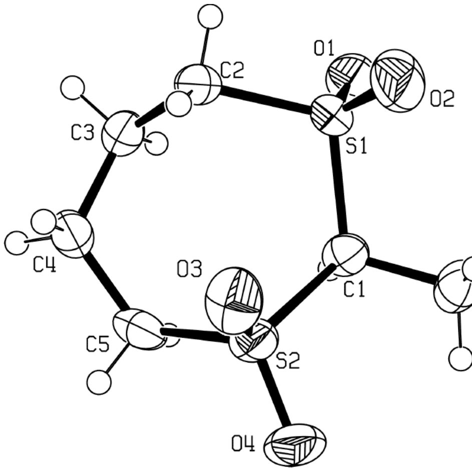

Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The title compound, (I) (Fig. 1), consists of a seven-membered dithiepane ring with two O atoms bonded to each S atom and a methoxymethyl group attached at the 2-position. The S atoms of the dithiepane ring have electron-releasing properties, but the O atoms bonded to the S atoms have electron-withdrawing properties, thereby influencing the bond lengths and angles of the dithiepane ring (Table 1). The dithiepane ring is, of course, not planar.

The structure reveals a number of short contacts: O1···H22(C2) = 2.51 (2), O2···H62(C6) = 2.50 (3), O3···H21(C2) = 2.58 (3), O4···H61(C6) = 2.45 (3), $O1^{i}$···H11(C1) = 2.59 (2), $O2^{ii}$...H42(C4) = 2.52 (3), $O3^{iii}$···H22(C2) = 2.59 (2), $O4^{iv}$···H31(C3) = 2.63 (3) and $O5^{i}$···H32(C3) = 2.68 (3) Å [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, y, z$; (iii) $x+\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}\ z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$]. These interactions may have an influence on the bond lengths and angles and also the shape of the molecule.

Experimental

The title compound, (I), was prepared according to a literature method (Aggarwal *et al.*, 1998) from 2-methoxymethyl-1,3-dithiepane (3.3 g, 18.5 mmol) in dry ether (40 ml) and purified *m*-CPBA (*m*-chloroperoxybenzoic acid; 7.03 g, 40.7 mmol) in diethyl ether (70 ml). The reaction was stirred for 4 h at 273 K, after which the white solid was collected by filtration and purified by column chromatography. Eluting with EtOAc gave racemic (1*RS*,3*RS*)-2-methoxymethyl-1,3-dithiepane 1,3-dioxide (yield 0.5 g, 45%) and 2-methoxymethyl-1,3-dithiepane 1,1,3,3-tetraoxide (yield 0.5 g, 13%); the latter was crystallized from EtOAc (m.p. 361 K).

Crystal data

$C_7H_{14}O_5S_2$
M_r = 242.30
Monoclinic, $P2_1/n$
a = 7.8972 (9) Å
b = 14.627 (2) Å
c = 9.5192 (10) Å
β = 108.739 (8)°
V = 1041.3 (2) Å^3
Z = 4
D_x = 1.546 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–22°
μ = 0.51 mm^{-1}
T = 293 (2) K
Prism, yellow
0.35 × 0.20 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
Non-profiled ω scans
Absorption correction: none
1933 measured reflections
1800 independent reflections
1255 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.052
$\theta_{\rm max}$ = 26.0°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = -11 \rightarrow 11$
2 standard reflections every 50 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.068$
S = 0.99
1800 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4259 (19)	S2—C1	1.810 (2)
S1—O1	1.439 (2)	O5—C6	1.398 (3)
S1—C2	1.776 (3)	O5—C7	1.423 (3)
S1—C1	1.816 (3)	C5—C4	1.515 (4)
S2—O4	1.429 (2)	C3—C2	1.518 (4)
S2—O3	1.4308 (19)	C3—C4	1.520 (4)
S2—C5	1.762 (3)	C1—C6	1.521 (4)
O2—S1—O1	119.86 (13)	C5—S2—C1	104.78 (13)
O2—S1—C2	107.49 (13)	C6—O5—C7	111.8 (2)
O1—S1—C2	107.99 (13)	C4—C5—S2	117.6 (2)
O2—S1—C1	107.47 (13)	C2—C3—C4	114.5 (2)
O1—S1—C1	104.47 (12)	C5—C4—C3	116.1 (2)
C2—S1—C1	109.24 (12)	C3—C2—S1	115.0 (2)
O4—S2—O3	118.63 (12)	C6—C1—S2	109.78 (17)
O4—S2—C5	107.94 (14)	C6—C1—S1	108.92 (19)
O3—S2—C5	110.34 (13)	S2—C1—S1	116.44 (14)
O4—S2—C1	105.41 (11)	O5—C6—C1	107.2 (2)
O3—S2—C1	108.78 (12)		
C1—S2—C5—C4	−78.5 (2)	C1—S1—C2—C3	−52.1 (2)
S2—C5—C4—C3	64.1 (3)	C5—S2—C1—S1	77.89 (18)
C2—C3—C4—C5	−76.7 (3)	C2—S1—C1—S2	−27.0 (2)
C4—C3—C2—S1	97.1 (3)		

Atoms H7*A*, H7*B* and H7*C* were positioned geometrically at a distance of 0.96 Å from C7, and a riding model was used during the refinement process. The $U_{\rm iso}$ value was set equal to $1.5U_{\rm eq}$(C7). The remaining H atoms were located in a difference synthesis and refined isotropically [C—H = 0.89 (2)–1.01 (3) Å].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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