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cis-(1*RS*,3*RS*)-2-Methoxymethyl-1,3-dithiane 1,3-dioxide

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The title compound, $C_6H_{12}O_3S_2$, consists of a six-membered dithiane ring with one O atom bonded to each S atom and a methoxymethyl group at the 2-position. Crystal packing is stabilized by van der Waals interactions and short intermolecular C—H···O contacts.

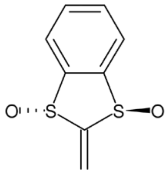
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.107
Data-to-parameter ratio = 17.1

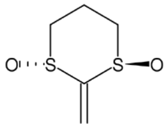
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

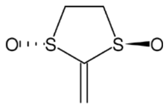
C_2-symmetric chiral molecules are particularly suitable for use as chiral acyl anion equivalents (Aggarwal *et al.*, 1991). They are also finding increasing attention in asymmetric synthesis as a result of the generally high selectivities that are obtained with them (Whitesell, 1989). Sulfur-containing chiral dienophiles are extremely useful synthons in asymmetric synthesis (Aggarwal *et al.*, 1995, 1999). A range of sulfur-containing dienophiles has been reported which act as chiral ketene equivalents (Maignan & Raphael, 1983; Fallis *et al.*, 1993; Lopez & Carretero, 1991; Arai *et al.*, 1986). Ketene equivalents have found wide use in synthesis because they readily undergo [4 + 2]-cycloadditions with dienes, whereas ketene itself gives [2 + 2]-cycloadducts (Ranganathan *et al.*, 1977; Aggarwal *et al.*, 1995).



(1)



(2)

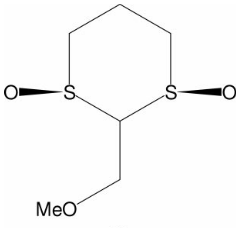


(3)

Cyclic alkenyl sulfoxide C_2-symmetric ketene equivalents (1), (2) and (3) have been developed by Aggarwal and found to be highly effective dienophiles in Diels–Alder reactions with a range of dienes (Aggarwal *et al.*, 1992; Aggarwal & Lightowler, 1992; Aggarwal *et al.*, 1995, 1998). *trans*-[(1*RS*,3*RS*)-3-Methylene-1,3-dithiolane 1,3-dioxide], (3), has been shown to have superior reactivity and selectivity to both (1) and (2). The advantage of this chiral ketene equivalent is that it requires only two steps for removal of the chiral auxiliary from the cycloadduct (Aggarwal *et al.*, 1995).

One method has been applied for the synthesis of the racemic C_2-symmetric ketene equivalent *trans*-[(1*RS*,3*RS*)-2-methylene-1,3-dithiane-1,3-dioxide], (2) (Aggarwal & Lightowler, 1992). The ether derivative of 1,3-dithiolane 1,3-dioxide has been applied for the preparation of [(1*RS*,3*RS*)-2-methylene 1,3-dioxide] (Aggarwal *et al.*, 1998). The ether derivative of 1,3-dithiolane 1,3-dioxide easily converted to the dimethylamino derivative in good yield (85%) and finally

Hofmann elimination gave an excellent yield of the chiral ketene equivalent (1*RS*,3*RS*)-2-methylene-1,3-dithiolane 1,3-dioxide (Aggarwal *et al.*, 1998).



(I)

The title compound, (I), may be a useful starting material for the racemic synthesis of the C_2-symmetric chiral ketene equivalent *cis*-(1*RS*,3*RS*)-2-methylene-1,3-dithiane 1,3-dioxide.

Compound (I) (Fig. 1) consists of a six-membered dithiane ring with one O atom bonded to each S atom and a methoxymethyl group attached at the 2-position. The S atoms of the dithiane ring have electron-releasing properties, but the O atoms bonded to S have electron-withdrawing properties, thereby influencing bond lengths and angles of the dithiane ring (Table 1).

The dithiane ring is, of course, not planar and it has a local mirror plane passing through atoms C1 and C3, as can be deduced from the torsion angles (Table 1). It adopts a distorted chair conformation with puckering parameters (Cremer & Pople, 1975) $Q_T = 1.735\ (4)$ Å, $\varphi = 41.33\ (14)^\circ$ and $\theta = 117.86\ (8)^\circ$ (Fig. 2).

The crystal packing (Fig. 3) is stabilized by van der Waals interactions and short intermolecular C—H···O contacts (Table 2).

Experimental

The title compound was prepared according to a literature method (Aggarwal *et al.*, 1998). 2-Methoxymethyl-1,3-dithiane (4.4 g, 24.4 mmol) was dissolved in dry ether (100 ml) at 273 K. Purified *m*-CPBA (*m*-chloroperoxybenzoic acid; 9.3 g, 53.7 mmol) in dry ether (150 ml) was added *via* a dropping funnel over 20 min. The reaction mixture was stirred for 2 h at 273 K, after which the resulting white solid was collected by filtration and washed with more ether, to give *cis* and *trans* products in 81% yield. Column chromatography of the residue, eluting with EtOAc–MeOH (50:50), gave the title compound as a white crystalline solid. It was recrystallized from MeOH (m.p. 395–398 K).

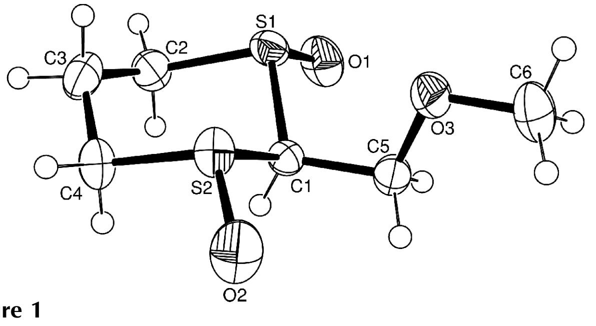


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

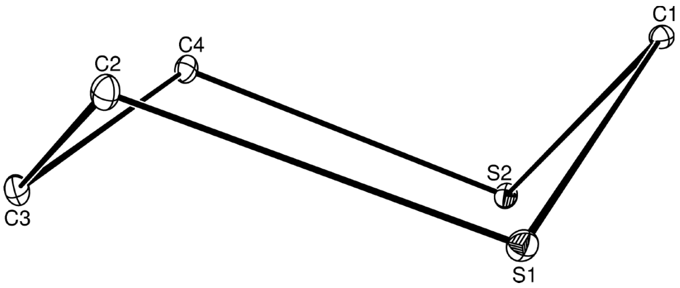


Figure 2
The conformation of the dithiane ring.

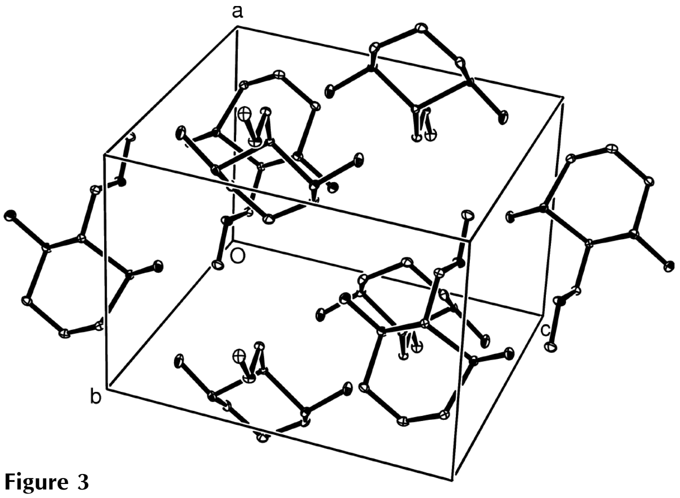


Figure 3
Packing diagram of (I). H atoms have been deleted.

Crystal data

$C_6H_{12}O_3S_2$
$M_r = 196.28$
Monoclinic, $P2_1/n$
$a = 7.8086\ (12)$ Å
$b = 10.3018\ (18)$ Å
$c = 10.8659\ (12)$ Å
$\beta = 92.528\ (10)^\circ$
$V = 873.2\ (2)$ Å^3
$Z = 4$

$D_x = 1.493$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.57$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
Non-profiled ω scans
Absorption correction: none
2696 measured reflections
2531 independent reflections
2039 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$

$\theta_{\rm max} = 30.0^\circ$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections every 50 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.107$
$S = 1.12$
2531 reflections
148 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.3189P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

C6—O3	1.423 (3)	S2—C1	1.8344 (19)
S1—O1	1.5026 (19)	C1—C5	1.515 (3)
S1—C2	1.806 (2)	O3—C5	1.407 (3)
S1—C1	1.8270 (19)	C2—C3	1.526 (4)
S2—O2	1.4930 (19)	C4—C3	1.522 (3)
S2—C4	1.805 (2)		
O1—S1—C2	106.96 (11)	C5—C1—S2	109.35 (13)
O1—S1—C1	106.05 (10)	S1—C1—S2	108.42 (10)
C2—S1—C1	95.46 (10)	C5—O3—C6	111.4 (2)
O2—S2—C4	108.70 (12)	C3—C2—S1	112.32 (17)
O2—S2—C1	105.69 (10)	C3—C4—S2	109.85 (17)
C4—S2—C1	95.17 (9)	O3—C5—C1	108.81 (17)
C5—C1—S1	111.03 (14)	C4—C3—C2	114.88 (19)
C2—S1—C1—S2	−70.02 (12)	C1—S2—C4—C3	−65.88 (17)
C4—S2—C1—S1	72.62 (12)	S2—C4—C3—C2	68.3 (2)
C1—S1—C2—C3	61.87 (18)	S1—C2—C3—C4	−66.6 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H11···O1^{i}	0.95 (2)	2.59 (3)	3.478 (3)	157.1 (18)
C2—H21···O1^{i}	1.00 (3)	2.53 (3)	3.481 (3)	157 (2)
C2—H22···O2^{ii}	0.94 (3)	2.66 (3)	3.275 (3)	124 (2)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

All H atoms were located in a difference synthesis and refined isotropically [C—H = 0.92 (3)–1.02 (3) Å].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 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* publication routines (Farrugia, 1999).

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