(1RS,3RS)-2-Methoxymethyl-1,3-dithiolane 1,3-dioxide

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.044
wR factor = 0.129
Data-to-parameter ratio = 10.4

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

The title compound, $C_5H_{10}O_3S_2$, consists of a five-membered dithiolane ring with one O atom bonded to each S atom and a methoxymethyl group at the 2-position. Some interatomic close contacts appear to influence the geometry of the dithiolane ring.

Comment

Sulfur-containing chiral dienophiles are extremely useful and important in organic synthesis (Aggarwal *et al.*, 1999; Posner, 1988). The reason for the use of sulfur functionalities lies in the fact that the reactivity may be modulated towards certain substrates by changing the oxidation state of the S atom. For example, while a vinyl sulfide is an electron-rich dienophile reacting best with electron-poor dienes, sulfoxides and sulfones impart electrophilicity which causes the olefin to react best with standard or electron-rich dienes.

A range of sulfur-containing dienophiles which act as chiral ketene equivalents has been reported (Maignan & Raphael, 1983; Arai *et al.*, 1986; Lopez & Carretero, 1991; Fallis *et al.*, 1993). Ketene equivalents have found widespread use as partners in Diels–Alder reactions for the construction of cyclic, fused and bridged unsaturated ketones (Ranganathan *et al.*, 1977; Aggarwal *et al.*, 1999).

The racemic and enantiomerically pure C_2-symmetric ketene equivalent (1RS,3RS)-2-methylene-1,3-dithiolane-1,3-dioxide has been developed and found to be highly reactive and highly diastereoselective (>97:3) in Diels–Alder reactions (Aggarwal *et al.*, 1995). 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).

Several methods have been applied for the synthesis of the racemic C_2-symmetric ketene equivalent (1RS,3RS)-2-methylene-1,3-dithiolane-1,3-dioxide (Aggarwal & Light-owler, 1993). This method suffers several problems on account of the water-sensitive chiral ketene equivalent.

Mannich conditions have been applied for the synthesis of the chiral ketene equivalent but gave a moderate yield of the Mannich base (45%) (Aggarwal, Grainger *et al.*, 1998). The best method found used the ether derivative of 1,3-dithiolane-1,3-dioxide (Aggarwal, Gültekin *et al.*, 1998), which was easily converted to the dimethylamino derivative in good yield (85%), and finally Hofmann elimination gave an excellent yield of the chiral ketene equivalent (1RS,3RS)-2-methylene-1,3-dithiolane-1,3-dioxide.

We have undertaken the racemic synthesis of 2-methoxy-methyl-1,3-dithiolane-1,3-dioxide, (I). This compound is a useful starting material for the racemic synthesis of the C_2-symmetric chiral ketene equivalent [(1RS,3RS)-2-methylene-1,3-dithiolane-1,3-dioxide] (Aggarwal, Gültekin *et al.*, 1998).

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The structure determination of the title compound, (I), was undertaken in order to understand the effects of the methoxymethyl group and the O atoms on the geometry of the five-membered dithiolane ring, and to compare the results with those found in 2-methoxymethyl-1,3-dithiolane 1,1,3,3-tetraoxide, (II) (Özcan *et al.*, 2003), *N*-(2-methoxyethyl)-*N*-{2,3,4,9-tetrahydrospiro-[1*H*-carbazole-1,2-[1,3]dithiolane]-4-yl}benzenesulfonamide, (III) (Patır *et al.*, 1997), spiro{carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one, (IV) (Hökelek *et al.*, 1998), 9-acetonyl-3-ethyldiene-1,2,3,4-tetrahydrospiro-[carbazole-1,2′-[1,3]dithiolan]-4-one, (V) (Hökelek *et al.*, 1999) and (1*RS*,3*RS*,α*SR*)-1,3-dioxo-α-phenyl-1,3-dithiolane-2-methanol, (VI) (Aggarwal *et al.*, 1997).

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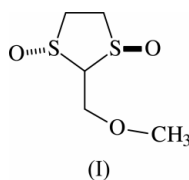
The title compound, (I) (Fig. 1), consists of a five-membered dithiolane ring with one O atom bonded to each S atom and a methoxymethyl group attached at the 2-position. The S atoms of the dithiolane ring have electron-releasing properties, but the O atoms bonded to S have electron-withdrawing properties,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

Some significant changes in the geometry of the dithiolane ring are evident when certain bond angles are compared with the values found in the compounds (II)–(VI) (Table 2).

The structure reveals a number of close contacts (Å): O1···H41(C4) 2.55 (5), O2···H1(C1) 2.52 (3), O1^i···H21(C2) 2.47 (4), O2^{ii}···H22(C2) 2.35 (4), O2^{iii}···H3*A*(C3) 2.434 (2) and O3^{iv}···H5*B*(C5) 2.555 (3) [symmetry codes: (i) x, $\frac{1}{2} - y$, $z - \frac{1}{2}$; (ii) x, $\frac{1}{2} - y$, $z + \frac{1}{2}$; (iii) $-x$, $-y$, $-z$; (iv) $1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$]. These interactions play a role in determining the molecular conformation (the bond lengths and angles, and also the shape) of the molecule.

Experimental

2-Methoxymethyl-1,3-dithiolane (8.3 g, 55.7 mmol) was dissolved in dry ether (100 cm³) at 273 K. Purified *m*-CPBA (*m*-chloroperoxybenzoic acid; 21.0 g, 121.8 mmol) in ether (200 cm³) was added using
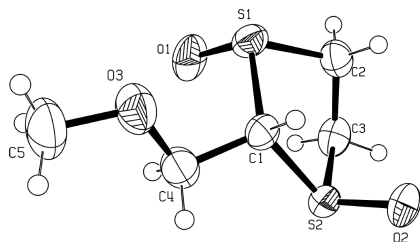
a dropping funnel over 20 minutes. The mixture was stirred for 2 h at 273 K, after which the white solid that had formed was collected by filtration and crystallized from EtOAc (yield 4.6 g, 45%), m.p. 397–398 K.

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.499 (2)	S2—C1	1.839 (3)
S1—C2	1.798 (3)	O3—C4	1.409 (4)
S1—C1	1.828 (3)	O3—C5	1.421 (5)
S2—O2	1.498 (2)	C2—C3	1.494 (5)
S2—C3	1.799 (3)	C4—C1	1.502 (5)
O1—S1—C2	106.04 (15)	C3—C2—S1	107.0 (2)
O1—S1—C1	106.54 (14)	C2—C3—S2	108.4 (2)
C2—S1—C1	91.29 (15)	O3—C4—C1	106.6 (3)
O2—S2—C3	107.00 (15)	C4—C1—S1	110.2 (2)
O2—S2—C1	104.96 (14)	C4—C1—S2	112.7 (2)
C3—S2—C1	93.57 (14)	S1—C1—S2	112.51 (16)
C4—O3—C5	113.2 (3)		
C1—S1—C2—C3	47.4 (2)	C2—S1—C1—S2	−24.30 (19)
S1—C2—C3—S2	−56.1 (3)	C3—S2—C1—S1	−0.96 (19)
C1—S2—C3—C2	33.3 (2)		

Table 2
Comparison of the bond angles (°) in the dithiolane ring of (I) with those in the related compounds (II), (III), (IV), (V) and (VI).

	S1—C1—S2	C1—S1—C2	C1—S2—C3	S1—C2—C3	C2—C3—S2
(I)	112.51 (16)	91.29 (15)	93.57 (14)	107.0 (2)	108.4 (2)
(II)	105.83 (8)	98.60 (8)	99.74 (8)	106.13 (12)	105.61 (12)
	106.20 (9)	97.80 (9)	99.81 (9)	106.31 (13)	107.96 (13)
(III)	106.6 (4)	96.1 (5)	97.9 (5)	111.7 (5)	111.4 (5)
(IV)	106.93 (8)	94.6 (1)	98.4 (1)	107.5 (2)	109.7 (2)
(V)	107.37 (9)	95.04 (9)	97.89 (9)	109.0 (2)	107.2 (1)
(VI)	112	94	92	109	106

Note: the s.u. values are not available for (VI).

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.

Most of the reflections were weak, probably due to the crystal quality. Atoms H1, H21, H22, H41 and H42 were located in a difference synthesis and refined isotropically [C—H = 0.92 (4)–1.04 (3) Å]. The remaining H atoms were positioned geometrically at distances of 0.97 Å (CH$_2$) and 0.96 Å (CH$_3$) from the parent C atoms; a riding model was used during the refinement process. The U_{iso} values were set equal to $1.2U_{eq}$(C3) and $1.5U_{eq}$(C5).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL*97 (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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