

2-Methoxymethyl-1,3-dithiolane 1,1,3,3-tetraoxide

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.037

wR factor = 0.103

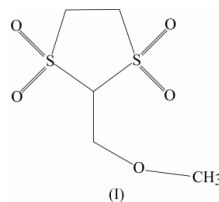
Data-to-parameter ratio = 17.2

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

The title compound, $\text{C}_5\text{H}_{10}\text{O}_5\text{S}_2$, consists of a five-membered dithiolane ring with two O atoms bonded to each S atom and a methoxymethyl group at the 2-position. The asymmetric unit contains two molecules. A few interatomic close contacts seem to influence the geometry of the dithiolane ring.

Comment

Simple vinyl (Maignan & Raphael, 1983) or acetylenic (Maignan & Belkasmoui, 1988; Lee *et al.*, 1988) sulfoxides are poor dienophiles, and show low levels of diastereocontrol, thereby limiting their synthetic use. The alkylation of a simple vinyl sulfoxide, however, gives rise to a much more reactive dienophile (Kagan & Ronan, 1991, 1992). Simple vinyl sulfoxides can also be made more reactive by the introduction of an additional electron-withdrawing group. 1,1-Bis(*p*-tolylsulfonyl)ethene (Arai *et al.*, 1986) facilitates a highly stereoselective reaction with cyclopentadiene under Lewis acid catalysis in a Diels–Alder reaction.



In recent years, compounds having two geminal sulfones have been shown to be good dienophiles, and their Diels–Alder reactions have attracted considerable attention (Lucchi *et al.*, 1992). 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).

C_2 -symmetric cyclic alkenyl sulfoxides (Aggarwal *et al.*, 1995) show high selectivity in Diels–Alder reactions. The Diels–Alder adducts may also be converted into bridged unsaturated ketones, *e.g.*, norbornenone, which is a useful intermediate for the synthesis of biologically important compounds.

Racemic 2-methoxymethyl-1,3-dithiolane 1,3-dioxide has been shown to be a useful starting material for the preparation of C_2 -symmetric ketene equivalents (Aggarwal *et al.*, 1998). The title compound, (I), may also be a useful starting material for the preparation of a new sulfone-containing dienophile.

The structure determination of (I) was undertaken in order to understand the effects of the methoxymethyl group and the

Received 22 April 2003

Accepted 28 April 2003

Online 9 May 2003

O atoms on the geometry of the five-membered dithiolane ring, and to compare the results with those found in 1,2,3,4-tetrahydrocarbazole-1-spiro-2'-[1,3]dithiolane, (II) (Hökelek *et al.*, 1994), *N*-(2-methoxyethyl)-*N*-[2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-[1,3]dithiolane]-4-yl]benzenesulfonamide, (III) (Patr *et al.*, 1997), spiro[carbazole-1(2*H*),2'-[1,3]dithiolane]-4(3*H*)-one, (IV) (Hökelek *et al.*, 1998), 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2'-[1,3]dithiolane]-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).

The title compound, (I) (Fig. 1), consists of a five-membered dithiolane ring with two O atoms bonded to each S atom and a methoxymethyl group attached at the 2-position. The asymmetric unit consists of two molecules. The S atoms of the dithiolane ring have electron-releasing properties, but the O atoms bonded to S have electron-withdrawing properties, thereby influencing bond lengths and angles of the dithiolane ring (Table 1). It should be stressed, however, that the values are almost identical in both molecules.

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

The dithiolane rings are, of course, not planar. In each of the two molecules of the asymmetric unit, the conformation is half-chair. In one molecule, considering only the ring atoms and atoms O1–O4, there is a local twofold rotation axis passing through C1 and the mid-point of C2–C3.

The structure reveals a number of short contacts (\AA): O2ⁱ...H11(C1) 2.24 (2), O1ⁱⁱ...H21(C2) 2.28 (3), O1ⁱⁱⁱ...H31(C3) 2.45 (3), O1ⁱⁱⁱ...H32(C3) 2.46 (3), O4^{iv}...H22'(C2') 2.47 (3), O2^v...H11'(C1') 2.51 (3) and O2^{vi}...H31'(C3') 2.54 (3) [symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y + 1, -z + 1$; (iv) $-x - 2, -y, -z + 2$; (v) $-x - 1, -y, -z + 2$; (vi) $-x - 1, -y + 1, -z + 1$]. These interactions play a role in determining the molecular conformation (the bond lengths and angles, and also the shape) of each molecule.

Experimental

The title compound, (I), was prepared, according to a literature method (Aggarwal *et al.*, 1998), from racemic 2-methoxymethyl-1,3-dithiolane 1,3-dioxide (2.7 g, 14.8 mmol) in dry acetonitrile (10 ml) and purified *m*-CPBA (*m*-chloroperoxybenzoic acid; 5.6 g, 32.6 mmol) in ether (50 ml), the mixture being stirred for 3 d at room temperature. Subsequently, a white solid was collected by filtration and crystallized from EtOAc (yield 2.3 g, 73%), m.p. 390 K.

Crystal data

C₅H₁₀O₅S₂
M_r = 214.25
 Triclinic, *P* $\bar{1}$
a = 6.7699 (10) \AA
b = 9.1736 (13) \AA
c = 14.5311 (19) \AA
 α = 77.910 (11) $^\circ$
 β = 85.013 (11) $^\circ$
 γ = 86.886 (12) $^\circ$

V = 878.5 (2) \AA^3
Z = 4
D_x = 1.620 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 10–15 $^\circ$
 μ = 0.59 mm⁻¹
T = 293 (2) K

Prism, colourless

0.35 × 0.25 × 0.20 mm

Data collection

Siemens *P4* diffractometer
 Non-profiled ω scans
 Absorption correction: none
 5527 measured reflections
 5125 independent reflections
 4609 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

θ_{max} = 30.0 $^\circ$
 $h = 0 \rightarrow 9$
 $k = -12 \rightarrow 12$
 $l = -20 \rightarrow 20$
 2 standard reflections every 50 reflections
 intensity decay: 1%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
S = 1.12
 5125 reflections
 298 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.3797P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.077 (4)

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1–O1	1.4342 (14)	S1'–O1'	1.4320 (15)
S1–O2	1.4363 (14)	S1'–C3'	1.7820 (19)
S1–C3	1.7671 (17)	S1'–C1'	1.8185 (17)
S1–C1	1.8199 (16)	S2–O4	1.4327 (15)
S2'–O3'	1.4347 (14)	S2–O3	1.4359 (16)
S2'–O4'	1.4361 (15)	S2–C2	1.7772 (19)
S2'–C2'	1.7714 (19)	S2–C1	1.8197 (17)
S2'–C1'	1.8125 (18)	C3–C2	1.517 (2)
S1'–O2'	1.4296 (15)	C2'–C3'	1.506 (3)
O1–S1–O2	118.48 (9)	O2'–S1'–C1'	108.25 (9)
O1–S1–C3	111.07 (8)	O1'–S1'–C1'	109.67 (10)
O2–S1–C3	108.80 (9)	C3'–S1'–C1'	99.81 (8)
O1–S1–C1	110.05 (8)	O4–S2–O3	118.90 (11)
O2–S1–C1	107.00 (8)	O4–S2–C2	110.46 (10)
C3–S1–C1	99.74 (8)	O3–S2–C2	108.94 (10)
O3'–S2'–O4'	119.33 (10)	O4–S2–C1	109.93 (9)
O3'–S2'–C2'	108.49 (10)	O3–S2–C1	108.07 (9)
O4'–S2'–C2'	110.67 (10)	C2–S2–C1	98.60 (8)
O3'–S2'–C1'	108.19 (9)	S2–C1–S1	105.83 (8)
O4'–S2'–C1'	110.18 (9)	C2–C3–S1	105.61 (12)
C2'–S2'–C1'	97.80 (9)	S2'–C1'–S1'	106.20 (9)
O2'–S1'–O1'	118.19 (11)	C3'–C2'–S2'	106.31 (13)
O2'–S1'–C3'	109.45 (10)	C2'–C3'–S1'	107.96 (13)
O1'–S1'–C3'	109.89 (10)	C3–C2–S2	106.13 (12)
C2–S2–C1–S1	14.61 (10)	C1'–S2'–C2'–C3'	–44.79 (15)
C3–S1–C1–S2	11.25 (10)	S2'–C2'–C3'–S1'	48.07 (17)
C1–S1–C3–C2	–38.87 (13)	C1'–S1'–C3'–C2'	–28.73 (16)
C2'–S2'–C1'–S1'	24.32 (11)	S1–C3–C2–S2	52.20 (14)
C3'–S1'–C1'–S2'	–0.80 (11)	C1–S2–C2–C3	–41.24 (14)

Table 2

Comparison of the bond angles ($^\circ$) in the dithiolane ring of (I) with the corresponding values in the related compounds (II), (III), (IV), (V) and (VI). Note that s.u. values are not available for (VI).

Angles	(I)	(II)	(III)	(IV)	(V)	(VI)
S1–C1–S2	105.83 (8)/106.20 (9)	105.8 (2)	106.6 (4)	106.93 (8)	107.37 (9)	112
C1–S2–C2	98.60 (8)/97.80 (9)	94.7 (2)	96.1 (5)	94.6 (1)	95.04 (9)	94
C1–S1–C3	99.74 (8)/99.81 (8)	99.0 (2)	97.9 (5)	98.4 (1)	97.89 (9)	92
S2–C2–C3	106.13 (12)/106.31 (13)	106.9 (3)	111.7 (5)	107.5 (2)	109.0 (2)	109
C2–C3–S1	105.61 (12)/107.96 (13)	108.3 (4)	111.4 (5)	109.7 (2)	107.2 (1)	106

The H-atom positions were located in a difference synthesis and refined isotropically [$C-H = 0.88$ (3)– 1.09 (3) \AA].

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (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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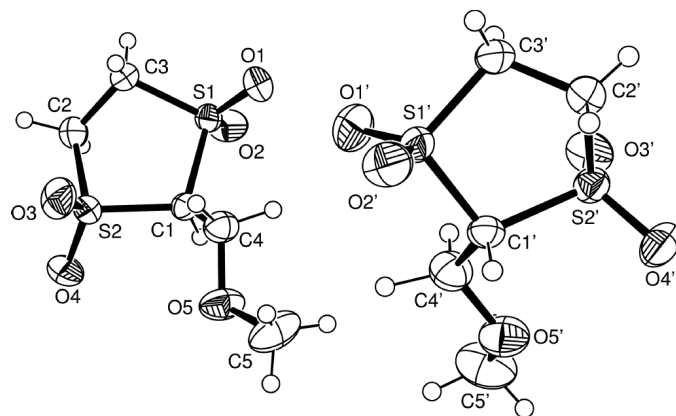


Figure 1

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

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