

(1*RS*,4*RS*)-1-Methoxyspiro[bicyclo[2.2.2]oct-5-ene-2,2'-[1',3']dithiolane]. Corrigendum

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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 R factor = 0.058
 wR factor = 0.144
 Data-to-parameter ratio = 14.9

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

In the paper by Gültekin, Adams & Hökelek [*Acta Cryst.* (2003), **E59**, o926–o928], the placement of H atoms bonded to C3, C4, C10 and C11 is wrong. C10=C11 is a double bond, but there are two H atoms on each C atom instead of one. On the other hand, C3–C4 is a single bond and there is one H atom on each C atom instead of two. The structure has now been re-refined with the correct assignment of H atoms and the structure is shown in Fig. 1.

Received 20 January 2006
 Accepted 25 January 2006

Experimental

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.144$
 $S = 1.02$
 1983 reflections
 133 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0805P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

S1–C7	1.802 (5)	C2–C1	1.558 (5)
S1–C2	1.823 (4)	C2–C6	1.566 (5)
S2–C8	1.774 (7)	C4–C3	1.511 (7)
S2–C2	1.844 (4)	C4–C5	1.529 (7)
O1–C1	1.416 (4)	C5–C6	1.536 (8)
O1–C9	1.420 (5)	C7–C8	1.467 (9)
C1–C10	1.506 (6)	C11–C10	1.332 (7)
C1–C3	1.516 (6)	C11–C5	1.502 (7)
C7–S1–C2	97.3 (2)	C1–C2–S2	110.7 (3)
C8–S2–C2	99.3 (2)	C6–C2–S2	110.4 (3)
C1–O1–C9	116.2 (3)	S1–C2–S2	106.1 (2)
O1–C1–C10	114.9 (3)	C4–C3–C1	112.1 (3)
O1–C1–C3	112.7 (3)	C4–C5–C6	106.0 (4)
O1–C1–C2	106.6 (3)	C8–C7–S1	109.5 (4)
C3–C1–C2	107.1 (3)	C7–C8–S2	114.0 (4)
C1–C2–S1	113.8 (2)	C11–C10–C1	114.7 (4)
C6–C2–S1	108.4 (3)	C10–C11–C5	114.0 (4)
C7–S1–C2–S2	30.0 (3)	C9–O1–C1–C3	–70.9 (5)
C2–S1–C7–C8	–37.9 (5)	S1–C2–C1–O1	56.8 (4)
C2–S2–C8–C7	–9.2 (5)	S2–C2–C1–O1	–62.5 (3)
C8–S2–C2–S1	–15.6 (3)	S1–C7–C8–S2	31.2 (6)

Atoms H10 and H11 were located in a difference map and refined isotropically [$\text{C}-\text{H} = 0.96(2)\text{--}0.99(2) \text{ \AA}$]. The other H atoms were positioned geometrically, with $\text{C}-\text{H} = 0.96, 0.97$ and 0.98 \AA for methyl, methylene and methine H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$, where $x = 1.5$ for methyl H atoms and $x = 1.2$ for all others.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 1997); program(s)

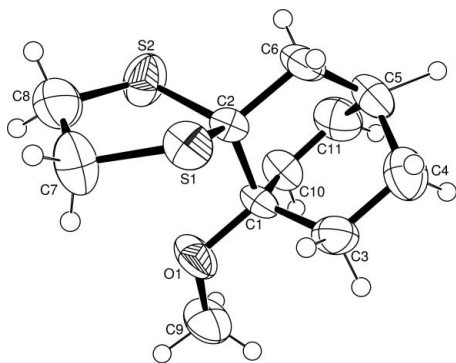


Figure 1

A view of the molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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* (Farrugia, 1999).

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.054

wR factor = 0.127

Data-to-parameter ratio = 13.5

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

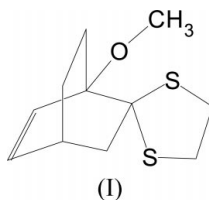
The title compound, $\text{C}_{11}\text{H}_{16}\text{OS}_2$, consists of a five-membered dithiolane ring with a methoxybicyclooctene spiro-fused at the 2-position. A few interatomic close contacts seem to influence the geometry of the dithiolane ring.

Comment

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 C_2 -symmetric ketene equivalent has been prepared in racemic and enantiomerically pure forms in four steps, 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 to remove the chiral auxiliary from the cycloadduct (Aggarwal *et al.*, 1995).

Ketene equivalents have also been used in the synthesis of terpenes (Subba Rao & Kalliappan, 1996; Mirrington & Gregson, 1973; Monti & Yang, 1979). 1-Methoxycyclohexa-1,3-diene has been used as a diene in the Diels–Alder reaction (Evans *et al.*, 1972) and it is also a useful diene in the synthesis of terpenoids (Subba Rao & Kalliappan, 1996; Monti & Yang, 1979).

The C_2 symmetric ketene equivalent (Aggarwal *et al.*, 1995) has been investigated with 1-methoxycyclohexa-1,3-diene, under a range of conditions (Aggarwal *et al.*, 1998), giving >97:3 diastereoselectivity in 95% yield.



The title compound, (I), was obtained by reduction of the cycloadduct, according to a literature method (Oea & Drabowicz, 1977). It is a useful starting material for the synthesis of terpenes. The structure determination of (I) was undertaken to understand the effects of the methoxybicyclooctene system 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), spiro[carbazole-1(2*H*),2'-[1,3]dithiolan]-4(3*H*)-one, (III) (Hökelek *et al.*, 1998) and 9-acetyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2'-[1,3]dithiolan]-4-one, (IV) (Hökelek *et al.*, 1999).

Received 16 May 2003

Accepted 2 June 2003

Online 17 June 2003

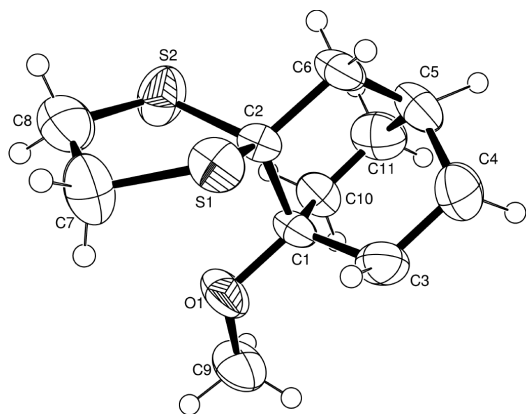


Figure 1

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 five-membered dithiolane ring with a methoxybicyclooctene spiro-fused at the 2-position; the dithiolane ring adopts a twist conformation. The S atoms of the dithiolane ring have electron-releasing properties, but the O atom of the methoxy group is electron-withdrawing, thereby influencing the bond lengths and angles of the dithiolane ring (Table 1). 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)–(IV) (Table 2).

The structure reveals a number of close contacts: S1 \cdots H31(C3) 2.562 (38), O1 \cdots H31(C3) 2.403 (31), S2 \cdots H61(C6) 2.621 (28), S1 \cdots H62(C6) 2.602 (48), O1 \cdots H7A(C7) 2.639 (3), S2 \cdots H10B(C10) 2.556 (2), O1 \cdots H11A(C11) 2.813 (3) and O \cdots H9A(C9) 2.869 (3) Å [symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 2 - y, 1 - z$]. 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 (Oea & Drabowicz, 1977), from (1*S*,1'*R*,3'*R*)-1-methoxybicyclo[2.2.2]oct-2-ene-6,2'-(1,3-dithiolane)]-1',3'-dioxide (compound 29a in Aggarwal *et al.*, 1998) (0.127 g, 0.49 mmol) in acetone (3 cm³), sodium iodide (0.366 g, 2.44 mmol) and TFAA (trifluoroacetic anhydride; 0.4 cm³, 2.94 mmol) at 195 K for 7 h. The crude sulfide was subjected to flash chromatography, eluting with acetone/petrol (50:50) and yielded the title compound, (I), as a white solid. It was crystallized from petrol ether (yield 0.035 g, 32%), m.p. 331 K.

Crystal data

C₁₁H₁₆OS₂
M_r = 228.36
 Triclinic, *P*1
a = 6.748 (4) Å
b = 7.870 (4) Å
c = 11.474 (7) Å
 α = 99.23 (4)°
 β = 103.00 (5)°
 γ = 102.69 (3)°
V = 564.9 (6) Å³

Z = 2
D_x = 1.342 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 12–20°
 μ = 0.44 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.55 × 0.34 × 0.28 mm

Data collection

Siemens P4 diffractometer
 Non-profiled ω scans
 2493 measured reflections
 1983 independent reflections
 1040 reflections with $I > 2\sigma(I)$
 R_{int} = 0.037
 θ_{max} = 25.0°

$h = -1 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -13 \rightarrow 13$
 3 standard reflections
 every 100 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.055
 $wR(F^2)$ = 0.127
 S = 1.00
 1983 reflections
 147 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.002
 $\Delta\rho_{\text{max}}$ = 0.30 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.17 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C7	1.811 (4)	C1–C10	1.507 (4)
S1–C2	1.826 (3)	C1–C3	1.526 (4)
S2–C8	1.782 (5)	C4–C3	1.521 (5)
S2–C2	1.852 (3)	C4–C5	1.532 (5)
O1–C1	1.412 (3)	C11–C10	1.319 (4)
O1–C9	1.421 (4)	C11–C5	1.488 (5)
C2–C1	1.554 (4)	C5–C6	1.547 (6)
C2–C6	1.560 (4)	C7–C8	1.462 (6)
C7–S1–C2	97.42 (16)	O1–C1–C3	112.3 (2)
C8–S2–C2	99.37 (16)	O1–C1–C2	106.8 (2)
C1–O1–C9	116.0 (2)	C3–C1–C2	107.1 (2)
C1–C2–S1	113.79 (18)	C10–C11–C5	114.9 (3)
C6–C2–S1	108.1 (2)	C4–C3–C1	111.7 (3)
C1–C2–S2	110.58 (17)	C4–C5–C6	105.3 (3)
C6–C2–S2	110.6 (2)	C8–C7–S1	109.3 (3)
S1–C2–S2	105.72 (15)	C7–C8–S2	113.9 (3)
O1–C1–C10	115.5 (2)	C11–C10–C1	114.6 (3)
C7–S1–C2–S2	30.1 (2)	S2–C2–C1–O1	–62.4 (2)
C8–S2–C2–S1	–15.3 (2)	C2–S1–C7–C8	–38.6 (4)
C9–O1–C1–C3	–71.4 (3)	S1–C7–C8–S2	32.1 (4)
S1–C2–C1–O1	56.4 (2)	C2–S2–C8–C7	–10.1 (4)

Table 2

Comparison of the bond angles (°) in the dithiolane ring of (I) with the corresponding values in the related compounds (II), (III) and (IV).

Angles	(I)	(II)	(III)	(IV)
S1–C2–S2	105.72 (15)	105.8 (2)	106.93 (8)	107.37 (9)
C2–S1–C7	97.42 (16)	94.7 (2)	94.6 (1)	95.04 (9)
C2–S2–C8	99.37 (16)	99.0 (2)	98.4 (1)	97.89 (9)
S2–C8–C7	113.9 (3)	108.3 (4)	109.7 (2)	109.0 (2)
S1–C7–C8	109.3 (3)	106.9 (3)	107.5 (2)	107.2 (1)

Atoms H31, H41, H51, H61 and H62 were located in a difference synthesis and refined isotropically [$C-H = 0.87$ (4)– 1.09 (7) Å]. The remaining H atoms were positioned geometrically at distances of 0.97 Å (CH₂) and 0.96 Å (CH₃) from the parent C atoms; a riding model was used during the refinement process.

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).

This work was carried out at the University of Sheffield, UK. We thank Professor Varinder K. Aggarwal of the University of Bristol, UK, for his advice.

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