organic compounds

(1R,2S,5R)-(−)-Menthyl (S)-2-(methoxycarbonyl)benzenesulfinate

Maria Altamura,[a] Antonio Guidi,[a] Loic Jierry,[b] Paola Paoli[c]* and Patrizia Rossi[c]

[a]Chemistry Department, Menarini Ricerche S.p.A., Via dei Sette Santi 3, I-50131 Firenze, Italy, [b]ICS, Université de Strasbourg, France, and [c]Dipartimento di Ingegneria Industriale, University of Firenze, Via S. Marta 3, I-50139 Firenze, Italy
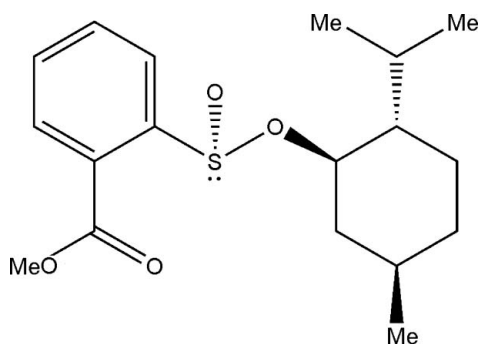Correspondence e-mail: paolapaoli@unifi.it

In the title chiral sulfinic acid ester, $C_{18}H_{26}O_4S$, the cyclohexane ring of the menthyl fragment adopts a chair conformation. The molecular shape is defined by the dihedral angle of 47.87 (8)° between the mean planes of the cyclohexane and benzene rings. In the crystal, molecules related by the screw axis are connected into chains along [010] by weak C_{ar}—H⋯O═S contacts.

Related literature

For the synthesis of the title compound, see: Klunder & Sharpless (1987) and of chiral sulfoxides, see: Drabowicz et al. (1982); Solladié et al. (1987). For applications of menthol in synthetic chemistry, see: Oertling et al. (2007). For structural studies of analogous chiral sulfinic acid esters, see: Mariz et al. (2010); Heinemann et al. (2007); Cherkaoui & Nicoud (1995).

Experimental

Crystal data

$C_{18}H_{26}O_4S$	$b = 9.3938$ (2) Å
$M_r = 338.45$	$c = 10.6998$ (2) Å
Monoclinic, $P2_1$	$\beta = 112.176$ (2)°
$a = 9.7918$ (2) Å	$V = 911.39$ (3) Å³

$Z = 2$	$T = 150$ K
Cu $K\alpha$ radiation	$0.26 \times 0.22 \times 0.08$ mm
$\mu = 1.72$ mm^{-1}	

Data collection

Oxford Diffraction Xcalibur PX diffractometer	4681 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	2354 independent reflections
	2115 reflections with $I > 2\sigma(I)$
$T_{min} = 0.660$, $T_{max} = 0.872$	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.078$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.22$ e Å^{-3}
2354 reflections	Absolute structure: Flack (1983),
209 parameters	767 Friedel pairs
1 restraint	Flack parameter: 0.038 (18)

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5⋯O4^i	0.95	2.42	3.337 (3)	161

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare et al., 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PARST* (Nardelli, 1995).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YK2089).

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supporting information

(1*R*,2*S*,5*R*)-(–)-Menthyl (*S*)-2-(methoxycarbonyl)benzenesulfinate

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S1. Comment

As a result of the trigonal pyramidal stereochemistry which characterizes the sulfur atom in organic sulfinic acid esters and sulfoxides bearing two different substituents, these species are chiral. Chiral sulfoxides are key intermediates for asymmetric synthesis and can be obtained from the reaction of an organometallic reagent (*e.g.* a Grignard reagent) with a diastereomerically pure sulfinate ester of menthol (Drabowicz *et al.*, 1982). On the other hand, menthyl sulfinates can be prepared by reaction of menthol (Oertling *et al.*, 2007) either with sodium sulfinates (Solladié *et al.*, 1987) or with a sulfonyl chloride in the presence of trimethylphosphite as *in situ* reducing agent (Klunder & Sharpless, 1987). We used the latter method to prepare the chiral sulfinic acid ester, (1*R*,2S,5*R*)-(-)-menthyl (*S*)-2-carbomethoxybenzenesulfinate, here reported. The overall molecular shape of the title compound depends on the dihedral angle formed between the mean plane defined by the ring atoms of the menthyl and of the phenyl groupings (132.13°(8)). Bond distances and angles about the sulfur atom, as well as the orientation of the isopropyl chain with respect to the menthyl ring are in keeping with those already reported for this molecular fragment (Heinemann *et al.*, 2007; Mariz *et al.*, 2010; Cherkaoui & Nicoud, 1995). In the crystal, molecules are connected *via* weak C_{ar}—H···O contacts involving the double bonded oxygen atom of the sulfinate group as acceptor. The resulting molecular chain propagates along the *b* axis direction around the screw axis.

S2. Experimental

For the synthesis of the title compound, see: Klunder & Sharpless (1987). Crystals of the title compound suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation from a diethyl ether solution of the sulfinate ester.

S3. Refinement

All the H atoms were positioned with idealized geometry using a riding model and refined with $U_{iso}(H)$ 1.2 times $U_{eq}(C)$ (1.5 for methyl H atoms).

Figure 1

Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level.

Figure 2

Crystal structure of the title compound with view along the c-axis. Intermolecular interactions are shown as dashed lines.

(1*R*,2*S*,5*R*)-(-)-Menthyl (*S*)-2-(methoxycarbonyl)benzenesulfinate

Crystal data

$C_{18}H_{26}O_4S$	$a = 9.7918$ (2) Å
$M_r = 338.45$	$b = 9.3938$ (2) Å
Monoclinic, $P2_1$	$c = 10.6998$ (2) Å

$\beta = 112.176\ (2)°$
$V = 911.39\ (3)\ \text{Å}^3$
$Z = 2$
$F(000) = 364$
$D_x = 1.233\ \text{Mg m}^{-3}$
Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å

Cell parameters from 3618 reflections
$\theta = 4.5–64.6°$
$\mu = 1.72\ \text{mm}^{-1}$
$T = 150$ K
Platelet, colourless
$0.26 \times 0.22 \times 0.08$ mm

Data collection

Oxford Diffraction Xcalibur PX
   diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 8.1241 pixels mm^{-1}
ω scans
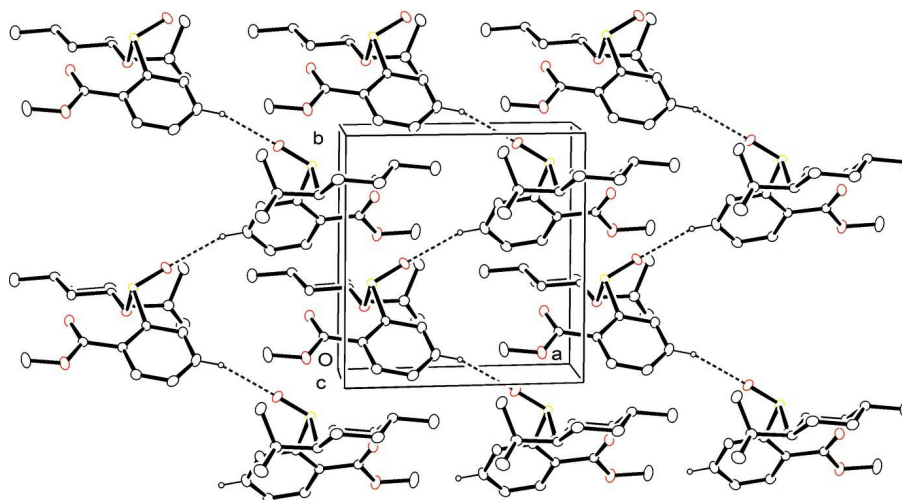Absorption correction: multi-scan
   (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.660$, $T_{max} = 0.872$

4681 measured reflections
2354 independent reflections
2115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 64.8°$, $\theta_{min} = 4.5°$
$h = -11 \rightarrow 10$
$k = -10 \rightarrow 8$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.07$
2354 reflections
209 parameters
1 restraint
Primary atom site location: structure-invariant
   direct methods
Secondary atom site location: difference Fourier
   map

Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 767 Friedel
   pairs
Absolute structure parameter: 0.038 (18)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.13357 (6)	0.36878 (7)	0.29567 (5)	0.02816 (16)
O1	−0.12928 (17)	0.2413 (2)	0.29271 (17)	0.0370 (5)
O2	−0.14622 (19)	0.0826 (2)	0.44178 (18)	0.0456 (5)
O3	0.10664 (16)	0.26365 (17)	0.16750 (14)	0.0276 (4)
O4	0.27015 (18)	0.4479 (2)	0.31899 (17)	0.0393 (5)
C1	0.1889 (2)	0.2232 (3)	0.4157 (2)	0.0276 (6)
C2	0.0910 (3)	0.1423 (3)	0.4543 (2)	0.0278 (5)
C3	0.1479 (3)	0.0401 (3)	0.5550 (2)	0.0351 (6)

H3	0.0830	−0.0130	0.5844	0.042*
C4	0.2987 (3)	0.0150 (3)	0.6128 (2)	0.0401 (7)
H4	0.3364	−0.0556	0.6808	0.048*
C5	0.3939 (3)	0.0927 (3)	0.5715 (2)	0.0417 (7)
H5	0.4969	0.0741	0.6096	0.050*
C6	0.3395 (3)	0.1976 (3)	0.4747 (2)	0.0350 (6)
H6	0.4056	0.2526	0.4484	0.042*
C7	−0.0714 (2)	0.1625 (3)	0.3865 (2)	0.0288 (5)
C8	−0.3054 (3)	0.0939 (4)	0.3802 (3)	0.0586 (9)
H8A	−0.3501	0.0279	0.4248	0.088*
H8B	−0.3386	0.0700	0.2842	0.088*
H8C	−0.3353	0.1915	0.3901	0.088*
C9	0.0431 (2)	0.3366 (2)	0.03670 (19)	0.0252 (5)
H9	0.0707	0.4396	0.0496	0.030*
C10	0.1105 (3)	0.2704 (3)	−0.0566 (2)	0.0322 (6)
H10	0.0819	0.1676	−0.0660	0.039*
C11	0.0369 (3)	0.3372 (3)	−0.1967 (2)	0.0404 (7)
H11A	0.0642	0.4391	−0.1920	0.048*
H11B	0.0742	0.2898	−0.2602	0.048*
C12	−0.1312 (3)	0.3239 (3)	−0.2505 (2)	0.0439 (7)
H12A	−0.1740	0.3709	−0.3397	0.053*
H12B	−0.1588	0.2220	−0.2628	0.053*
C13	−0.1943 (3)	0.3903 (3)	−0.1564 (2)	0.0377 (7)
H13	−0.1691	0.4939	−0.1486	0.045*
C14	−0.1233 (2)	0.3239 (3)	−0.0165 (2)	0.0333 (6)
H14A	−0.1609	0.3721	0.0464	0.040*
H14B	−0.1511	0.2222	−0.0210	0.040*
C15	−0.3628 (3)	0.3767 (5)	−0.2088 (3)	0.0574 (8)
H15A	−0.3992	0.4212	−0.1445	0.086*
H15B	−0.3903	0.2757	−0.2188	0.086*
H15C	−0.4067	0.4242	−0.2964	0.086*
C16	0.2812 (3)	0.2752 (3)	0.0022 (3)	0.0397 (7)
H16	0.3151	0.2284	0.0928	0.048*
C17	0.3439 (3)	0.4256 (3)	0.0237 (3)	0.0487 (8)
H17A	0.3020	0.4796	0.0791	0.073*
H17B	0.3188	0.4728	−0.0639	0.073*
H17C	0.4514	0.4214	0.0697	0.073*
C18	0.3433 (4)	0.1894 (4)	−0.0842 (3)	0.0599 (9)
H18A	0.3017	0.0932	−0.0970	0.090*
H18B	0.4509	0.1839	−0.0393	0.090*
H18C	0.3176	0.2358	−0.1722	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0300 (3)	0.0257 (3)	0.0306 (3)	−0.0036 (3)	0.0135 (2)	−0.0045 (3)
O1	0.0298 (9)	0.0443 (12)	0.0374 (9)	0.0010 (8)	0.0133 (8)	0.0100 (9)
O2	0.0312 (9)	0.0591 (14)	0.0451 (10)	−0.0078 (9)	0.0127 (9)	0.0180 (10)

O3	0.0333 (8)	0.0240 (9)	0.0245 (8)	0.0019 (7)	0.0099 (7)	−0.0007 (7)
O4	0.0361 (9)	0.0407 (11)	0.0410 (9)	−0.0146 (9)	0.0144 (8)	−0.0045 (9)
C1	0.0289 (12)	0.0302 (15)	0.0209 (11)	−0.0024 (11)	0.0065 (10)	−0.0045 (10)
C2	0.0302 (12)	0.0306 (15)	0.0225 (11)	0.0002 (11)	0.0097 (9)	−0.0035 (10)
C3	0.0395 (14)	0.0363 (16)	0.0276 (12)	−0.0029 (12)	0.0104 (12)	−0.0004 (12)
C4	0.0456 (16)	0.0387 (18)	0.0291 (13)	0.0101 (13)	0.0062 (13)	0.0005 (12)
C5	0.0318 (14)	0.0530 (19)	0.0331 (13)	0.0105 (13)	0.0040 (12)	−0.0082 (14)
C6	0.0303 (13)	0.0414 (17)	0.0332 (13)	0.0015 (12)	0.0119 (11)	−0.0065 (12)
C7	0.0310 (13)	0.0292 (15)	0.0279 (12)	−0.0023 (11)	0.0131 (11)	−0.0033 (12)
C8	0.0299 (14)	0.083 (3)	0.0579 (18)	−0.0111 (16)	0.0109 (14)	0.0230 (18)
C9	0.0300 (11)	0.0190 (15)	0.0264 (11)	−0.0018 (10)	0.0102 (9)	0.0021 (10)
C10	0.0383 (13)	0.0275 (15)	0.0333 (12)	−0.0012 (12)	0.0163 (11)	0.0009 (11)
C11	0.0554 (16)	0.038 (2)	0.0332 (12)	−0.0040 (13)	0.0226 (12)	0.0031 (12)
C12	0.0538 (16)	0.0390 (18)	0.0301 (12)	−0.0056 (13)	0.0058 (11)	0.0043 (12)
C13	0.0370 (13)	0.0301 (18)	0.0368 (12)	−0.0022 (12)	0.0034 (11)	0.0035 (13)
C14	0.0284 (12)	0.0338 (17)	0.0352 (12)	−0.0003 (11)	0.0092 (10)	0.0000 (11)
C15	0.0369 (13)	0.068 (2)	0.0492 (15)	−0.0022 (17)	−0.0037 (12)	0.0096 (18)
C16	0.0421 (15)	0.0395 (18)	0.0469 (15)	0.0020 (13)	0.0275 (12)	0.0043 (14)
C17	0.0396 (15)	0.053 (2)	0.0575 (18)	−0.0113 (14)	0.0229 (14)	−0.0056 (15)
C18	0.065 (2)	0.056 (2)	0.076 (2)	0.0083 (18)	0.0462 (17)	−0.0065 (19)

Geometric parameters (Å, º)

S1—O4	1.4669 (17)	C10—C16	1.548 (3)
S1—O3	1.6287 (16)	C10—H10	1.0000
S1—C1	1.813 (2)	C11—C12	1.530 (3)
O1—C7	1.203 (3)	C11—H11A	0.9900
O2—C7	1.333 (3)	C11—H11B	0.9900
O2—C8	1.449 (3)	C12—C13	1.501 (4)
O3—C9	1.469 (2)	C12—H12A	0.9900
C1—C6	1.388 (3)	C12—H12B	0.9900
C1—C2	1.403 (3)	C13—C14	1.525 (3)
C2—C3	1.392 (4)	C13—C15	1.535 (3)
C2—C7	1.490 (3)	C13—H13	1.0000
C3—C4	1.389 (4)	C14—H14A	0.9900
C3—H3	0.9500	C14—H14B	0.9900
C4—C5	1.382 (4)	C15—H15A	0.9800
C4—H4	0.9500	C15—H15B	0.9800
C5—C6	1.382 (4)	C15—H15C	0.9800
C5—H5	0.9500	C16—C18	1.517 (4)
C6—H6	0.9500	C16—C17	1.524 (4)
C8—H8A	0.9800	C16—H16	1.0000
C8—H8B	0.9800	C17—H17A	0.9800
C8—H8C	0.9800	C17—H17B	0.9800
C9—C14	1.514 (3)	C17—H17C	0.9800
C9—C10	1.522 (3)	C18—H18A	0.9800
C9—H9	1.0000	C18—H18B	0.9800
C10—C11	1.532 (3)	C18—H18C	0.9800

O4—S1—O3	107.34 (9)	C10—C11—H11A	109.2
O4—S1—C1	104.61 (10)	C12—C11—H11B	109.2
O3—S1—C1	92.81 (9)	C10—C11—H11B	109.2
C7—O2—C8	115.7 (2)	H11A—C11—H11B	107.9
C9—O3—S1	113.26 (13)	C13—C12—C11	111.8 (2)
C6—C1—C2	119.9 (2)	C13—C12—H12A	109.3
C6—C1—S1	115.80 (19)	C11—C12—H12A	109.3
C2—C1—S1	124.25 (17)	C13—C12—H12B	109.3
C3—C2—C1	118.9 (2)	C11—C12—H12B	109.3
C3—C2—C7	120.4 (2)	H12A—C12—H12B	107.9
C1—C2—C7	120.7 (2)	C12—C13—C14	109.7 (2)
C4—C3—C2	120.6 (2)	C12—C13—C15	112.2 (2)
C4—C3—H3	119.7	C14—C13—C15	110.7 (2)
C2—C3—H3	119.7	C12—C13—H13	108.0
C5—C4—C3	120.0 (3)	C14—C13—H13	108.0
C5—C4—H4	120.0	C15—C13—H13	108.0
C3—C4—H4	120.0	C9—C14—C13	111.34 (19)
C4—C5—C6	120.0 (2)	C9—C14—H14A	109.4
C4—C5—H5	120.0	C13—C14—H14A	109.4
C6—C5—H5	120.0	C9—C14—H14B	109.4
C5—C6—C1	120.5 (2)	C13—C14—H14B	109.4
C5—C6—H6	119.8	H14A—C14—H14B	108.0
C1—C6—H6	119.8	C13—C15—H15A	109.5
O1—C7—O2	123.5 (2)	C13—C15—H15B	109.5
O1—C7—C2	124.4 (2)	H15A—C15—H15B	109.5
O2—C7—C2	112.1 (2)	C13—C15—H15C	109.5
O2—C8—H8A	109.5	H15A—C15—H15C	109.5
O2—C8—H8B	109.5	H15B—C15—H15C	109.5
H8A—C8—H8B	109.5	C18—C16—C17	110.6 (2)
O2—C8—H8C	109.5	C18—C16—C10	110.9 (2)
H8A—C8—H8C	109.5	C17—C16—C10	113.6 (2)
H8B—C8—H8C	109.5	C18—C16—H16	107.1
O3—C9—C14	109.29 (17)	C17—C16—H16	107.1
O3—C9—C10	107.54 (18)	C10—C16—H16	107.1
C14—C9—C10	113.12 (18)	C16—C17—H17A	109.5
O3—C9—H9	108.9	C16—C17—H17B	109.5
C14—C9—H9	108.9	H17A—C17—H17B	109.5
C10—C9—H9	108.9	C16—C17—H17C	109.5
C9—C10—C11	108.34 (19)	H17A—C17—H17C	109.5
C9—C10—C16	112.98 (19)	H17B—C17—H17C	109.5
C11—C10—C16	115.0 (2)	C16—C18—H18A	109.5
C9—C10—H10	106.7	C16—C18—H18B	109.5
C11—C10—H10	106.7	H18A—C18—H18B	109.5
C16—C10—H10	106.7	C16—C18—H18C	109.5
C12—C11—C10	112.09 (19)	H18A—C18—H18C	109.5
C12—C11—H11A	109.2	H18B—C18—H18C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O4[i]	0.95	2.42	3.337 (3)	161

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1.