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(5S,SS)-7-Methyl-8-p-toluenesulfinyl-1,6-dioxaspiro[4.5]dec-7-ene

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Abstract

The structure determination of $C_{16}H_{20}O_3S$ based on X-ray single-crystal diffraction confirms the S absolute configuration of the spiroketalic C atom.

Comment

The intermolecular hetero-Diels–Alder reaction between α,β-unsaturated carbonyl compounds and vinyl ethers has been applied extensively to the synthesis of natural products (Boger & Weinzed, 1987). In connection with our interest in using chiral sulfoxides in asymmetric syntheses, we sought new strategies for constructing spiroketal skeletons by heterocycloaddition using an enantiopure sulfinyl-hetero diene. (+)-(S)-3-p-Toluenesulfinyl-3-buten-2-one (Bonfand, Gosselin & Maignan, 1992) reacted smoothly with sensitive 2-methylene tetrahydrofuran yielding 1:1 diastereomeric dioxaspiro adducts. These spiroketals were completely separated by liquid chromatography on silica gel. In order to obtain information on the absolute configuration of the spirokelatic C atom, we obtained single crystals of one diastereomer, (I), with a view to determining its structure by X-ray diffraction.

(I)
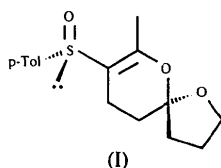
The perspective view of the structure of (5S,SS)-7-methyl-8-p-toluenesulfinyl-1,6-dioxaspiro[4.5]dec-7-ene reveals the S absolute configuration of the spirokelatic atom, C11.
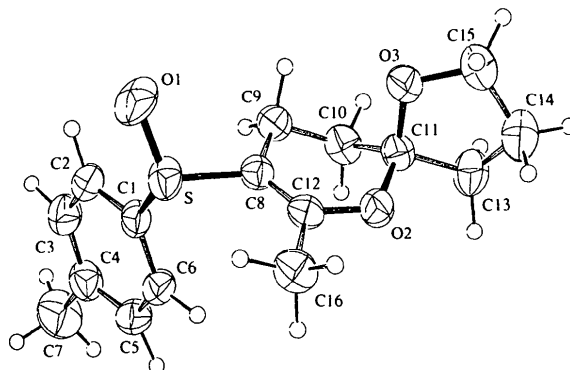

Fig. 1. *ORTEP* plot of $C_{16}H_{20}O_3S$. For the sake of clarity the displacement parameters of the H atoms have been divided by ten. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Recrystallization of the title compound from ether after liquid chromatography gave small colourless platelets. Suitable crystals for X-ray analysis were very difficult to find. Firelly, a parallelepipedic crystal was chosen and its quality was tested using Laue photographs.

Crystal data

$C_{16}H_{20}O_3S$	Mo $K\alpha$ radiation
$M_r = 292.37$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 32
$P2_12_12_1$	reflections
$a = 7.9680\ (14)$ Å	$\theta = 12.6–15.9°$
$b = 8.1104\ (11)$ Å	$\mu = 0.205$ mm^{-1}
$c = 23.761\ (3)$ Å	$T = 293\ (2)$ K
$V = 1535.5\ (4)$ Å^3	Plate
$Z = 4$	$0.741 \times 0.471 \times 0.201$ mm
$D_x = 1.265$ Mg m^{-3}	Colourless

Data collection

Stoe Siemens AED-2 diffractometer	$R_{int} = 0.0602$
	$\theta_{max} = 25°$
ω–2θ scans	$h = -9 \rightarrow 9$
Absorption correction:	$k = -9 \rightarrow 9$
none	$l = -28 \rightarrow 28$
3115 measured reflections	3 standard reflections
2626 independent reflections	frequency: 60 min
2268 observed reflections	intensity variation: 8%
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.0514$	*SHELXL93* (Sheldrick,
$wR(F^2) = 0.1337$	1993)
$S = 1.046$	Extinction coefficient:
2619 reflections	0.0069 (39)

216 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1214P)^2 + 0.0307P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.094$
$\Delta\rho_{max} = 0.290$ e Å^{-3}
$\Delta\rho_{min} = -0.237$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

gram(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) option *TREF*. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP* (Johnson, 1965).

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Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.92832 (10)	0.51629 (9)	0.86263 (3)	0.0538 (3)
O1	0.8354 (5)	0.6597 (3)	0.88601 (11)	0.0825 (9)
O2	0.8600 (2)	0.3954 (3)	0.70150 (8)	0.0474 (5)
O3	0.6470 (3)	0.5830 (3)	0.68440 (9)	0.0577 (6)
C1	0.8600 (4)	0.3407 (4)	0.90273 (12)	0.0455 (6)
C2	0.7631 (4)	0.3635 (4)	0.95041 (13)	0.0546 (7)
C3	0.7202 (5)	0.2284 (5)	0.98276 (13)	0.0588 (8)
C4	0.7738 (4)	0.0711 (4)	0.96915 (13)	0.0565 (8)
C5	0.8691 (5)	0.0501 (4)	0.92021 (14)	0.0548 (7)
C6	0.9125 (4)	0.1838 (4)	0.88756 (12)	0.0494 (7)
C7	0.7331 (7)	-0.0760 (6)	1.00576 (2)	0.0862 (13)
C8	0.8320 (3)	0.4630 (3)	0.79788 (11)	0.0420 (6)
C9	0.6446 (4)	0.4595 (4)	0.79664 (12)	0.0508 (7)
C10	0.5887 (4)	0.3595 (4)	0.74638 (14)	0.0522 (7)
C11	0.6811 (4)	0.4146 (4)	0.69368 (12)	0.0449 (6)
C12	0.9264 (3)	0.4328 (3)	0.75319 (11)	0.0407 (6)
C13	0.6377 (5)	0.3249 (4)	0.6392 (2)	0.0625 (8)
C14	0.6653 (6)	0.4585 (7)	0.5951 (2)	0.0785 (11)
C15	0.6204 (6)	0.6126 (5)	0.6258 (2)	0.0750 (11)
C16	1.11562 (4)	0.4248 (4)	0.74984 (15)	0.0585 (8)

Table 2. *Selected geometric parameters* (Å, °)

S—O1	1.486 (3)	C8—C9	1.493 (4)
S—C8	1.773 (3)	C9—C10	1.511 (5)
S—C1	1.798 (3)	C10—C11	1.520 (4)
C1—C2	1.383 (5)	C11—O3	1.410 (4)
C1—C6	1.387 (4)	C11—O2	1.446 (4)
C2—C3	1.382 (5)	C11—C13	1.525 (5)
C3—C4	1.383 (5)	O2—C12	1.371 (3)
C4—C5	1.399 (5)	C12—C16	1.512 (4)
C4—C7	1.512 (5)	C13—C14	1.524 (6)
C5—C6	1.378 (4)	C14—C15	1.490 (6)
C8—C12	1.324 (4)	C15—O3	1.429 (4)
O1—S—C8	107.4 (2)	C8—C9—C10	108.7 (2)
O1—S—C1	105.7 (2)	C9—C10—C11	110.5 (2)
C8—S—C1	97.79 (12)	O3—C11—O2	108.3 (2)
C2—C1—C6	120.3 (3)	O3—C11—C10	108.7 (3)
C2—C1—S	119.8 (2)	O2—C11—C10	109.9 (2)
C6—C1—S	119.8 (2)	O3—C11—C13	106.6 (2)
C3—C2—C1	119.2 (3)	O2—C11—C13	106.3 (3)
C2—C3—C4	121.7 (3)	C10—C11—C13	116.7 (3)
C3—C4—C5	118.3 (3)	C12—O2—C11	118.1 (2)
C3—C4—C7	121.8 (3)	C8—C12—O2	122.7 (2)
C5—C4—C7	119.9 (3)	C8—C12—C16	128.1 (3)
C6—C5—C4	120.5 (3)	O2—C12—C16	109.2 (2)
C5—C6—C1	120.0 (3)	C14—C13—C11	102.2 (3)
C12—C8—C9	123.3 (3)	C15—C14—C13	103.0 (3)
C12—C8—S	119.7 (2)	O3—C15—C14	107.5 (3)
C9—C8—S	117.0 (2)	C11—O3—C15	110.1 (3)

The determination of the absolute configuration was possible from the known S configuration of the sulfoxide group in the starting heterodiene; using the method described by Flack (1983), the absolute configuration was confirmed by the calculations (*SHELXL*93; Sheldrick, 1993). H atoms were refined as rigid groups using the *AFIX* card of the *SHELXL*93 program.

Data collection: *DIF*4 (Stoe & Cie, 1988a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988b). Pro-

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The Diels–Alder Adduct of an Enantiopure 2-Sulfinyldiene and Maleimide: (1S,2R,3S,SR)-3-Methyl-5-p-toluenesulfinylcyclohex-4-en-1,2-dicarboximide

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Abstract

The title compound, $C_{16}H_{17}NO_3S$, is the single adduct obtained by cycloaddition of (E)-$(+)$-(R)-2-p-toluenesulfinyl-1,3-pentadiene with maleimide. The ab-