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(*Z*)-(−)-(*R*)-β-Styryl *p*-Tolyl Sulfoxide

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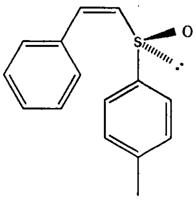
Abstract

The crystal structure determination of (*Z*)-(−)-(*R*)-β-styryl *p*-tolyl sulfoxide, $C_{15}H_{14}OS$, confirms its absolute configuration and establishes that the slightly twisted olefinic bond is not antiperiplanar to the S—O bond. It also provides a molecular basis for the theoretical study of cycloadditions between nitrones and vinylic sulfoxides.

Comment

The 1,3-dipolar cycloaddition of nitrones with alkenes constitutes a powerful method for the synthesis of alkaloids and related bases (Tufariello, 1984). In order to perform a theoretical study concerning the regiochemistry of cycloadditions between nitrones and vinylic sulfoxides, the molecular parameters of this latter type of compound were required. A search through the Cambridge Structural Database, version 5.06 (Allen *et al.*, 1991), revealed several X-ray crystallographic studies on sulfoxides (Hua, Badejo, McCann & Takusagawa, 1987; Swindell, Blase, Eggleston & Krause, 1990), but with the exception of one paper (Koizumi, Arai, Takayama, Kuriyama & Shiro, 1987), no information was found on (*Z*)-sulfinylethene derivatives. The title compound, (I), was synthesized by Andersen's method (House *et al.*, 1987); m.p. 330–331 K, $[\alpha]_{D22} = -738°$ ($CHCl_3$; $c = 1.0$) {literature: $[\alpha]_{D22} = -736°$ ($CHCl_3$; $c = 1.0$)}, NMR and MS spectra are all in agreement with the published data (Mikolajczyk, Midura, Grzejszczak, Zatorski & Chefczynska, 1978).



(I)

The complete structure was determined by a single-crystal X-ray diffraction study. The absolute configuration established by the X-ray analysis [Flack (1983) parameter = −0.02 (2)] confirms the previously determined stereochemistry (Mikolajczyk, Midura, Grzejszczak, Zatorski & Chefczynska, 1978); the S atom has an *R* configuration. The C1═C2 bond is slightly twisted owing to steric hindrance; the dihedral angle defined by C12—C1═C2—S3 is 11.9 (4)°. Noteworthy is the conformation of the vinyl sulfoxide moiety, where the S3—O4 and C1═C2 bonds are not *anti* coplanar (*s-trans*), as observed in benzyl (*Z*)-3-*p*-tolylsulfinylacrylate (Koizumi, Arai, Takayama, Kuriyama & Shiro, 1987), but have a dihedral angle of 121.9 (3)°, compared to 157° in the acrylate compound. The S-atom lone pair, therefore, lies more or less in the plane of the alkene; this observation corroborates the conformation assumed by Kimmelma (1993) for (*Z*)-vinylic sulfoxides on the basis of *ab initio* calculations. Indeed, in (*Z*)-vinylic sulfoxides steric strain between the sulfoxide group and the β-substituent precludes the *s-cis* conformation which would allow conjugation between the S—O and the olefinic bonds.

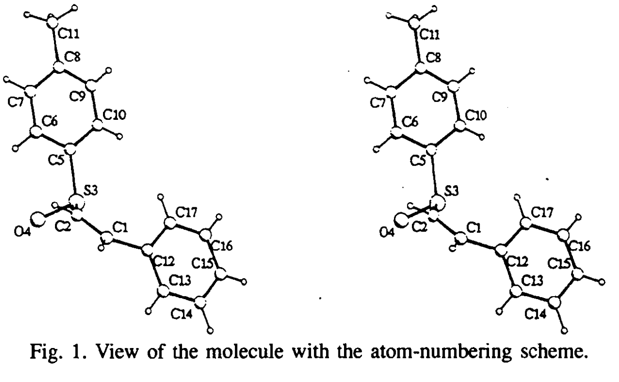


Fig. 1. View of the molecule with the atom-numbering scheme.

Experimental

Crystal data

$C_{15}H_{14}OS$
$M_r = 242.32$

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å

Orthorhombic
$P2_12_12_1$
$a = 6.061$ (1) Å
$b = 11.439$ (1) Å
$c = 18.858$ (2) Å
$V = 1307.5$ (2) Å^3
$Z = 4$
$D_x = 1.231$ Mg m^{-3}

Cell parameters from 14 reflections
$\theta = 17\text{–}49°$
$\mu = 2.029$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
$0.50 \times 0.18 \times 0.03$ mm
Colourless

Data collection

Huber four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2364 measured reflections
2364 independent reflections
2091 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 67.46°$
$h = -5 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 22$
1 standard reflection monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0432$
$wR(F^2) = 0.1164$
$S = 1.083$
2364 reflections
155 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.0848P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.473$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.1273 (5)	0.8016 (2)	0.58792 (15)	0.0690 (7)
C2	0.0548 (4)	0.7015 (3)	0.56282 (15)	0.0675 (7)
S3	0.10574 (12)	0.56359 (6)	0.60339 (3)	0.0672 (2)
O4	−0.1215 (4)	0.5191 (2)	0.61637 (14)	0.0963 (7)
C5	0.2118 (4)	0.4861 (2)	0.52862 (14)	0.0606 (6)
C6	0.0865 (5)	0.4701 (3)	0.4684 (2)	0.0755 (8)
C7	0.1675 (6)	0.4061 (3)	0.4130 (2)	0.0853 (9)
C8	0.3748 (6)	0.3558 (2)	0.4161 (2)	0.0793 (8)
C9	0.4950 (6)	0.3707 (3)	0.4766 (2)	0.0836 (9)
C10	0.4192 (5)	0.4361 (3)	0.5332 (2)	0.0745 (7)
C11	0.4611 (9)	0.2842 (3)	0.3548 (2)	0.118 (2)
C12	0.2892 (5)	0.8233 (2)	0.64342 (13)	0.0604 (6)
C13	0.2562 (5)	0.9143 (2)	0.6913 (2)	0.0775 (8)
C14	0.4098 (7)	0.9374 (3)	0.7440 (2)	0.0912 (10)
C15	0.5967 (7)	0.8718 (3)	0.7491 (2)	0.0901 (10)
C16	0.6324 (6)	0.7814 (3)	0.7019 (2)	0.0818 (8)
C17	0.4803 (5)	0.7580 (2)	0.64969 (14)	0.0652 (7)

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

C1—C2	1.315 (4)	C8—C9	1.364 (5)
C1—C12	1.456 (4)	C8—C11	1.511 (5)
C2—S3	1.780 (3)	C9—C10	1.382 (5)
S3—O4	1.489 (2)	C12—C17	1.383 (4)
S3—C5	1.785 (3)	C12—C13	1.393 (4)
C5—C6	1.378 (4)	C13—C14	1.387 (5)
C5—C10	1.384 (4)	C14—C15	1.362 (5)
C6—C7	1.366 (5)	C15—C16	1.382 (5)
C7—C8	1.383 (5)	C16—C17	1.375 (4)
C2—C1—C12	129.2 (2)	C7—C8—C11	120.5 (4)
C1—C2—S3	124.0 (2)	C8—C9—C10	122.4 (3)
O4—S3—C2	102.3 (1)	C5—C10—C9	118.5 (3)
O4—S3—C5	107.1 (1)	C17—C12—C13	117.9 (3)
C2—S3—C5	99.4 (1)	C17—C12—C1	122.3 (2)
C6—C5—C10	119.8 (3)	C13—C12—C1	119.8 (3)
C6—C5—S3	121.2 (2)	C14—C13—C12	120.7 (3)
C10—C5—S3	118.9 (2)	C15—C14—C13	120.3 (3)
C7—C6—C5	120.2 (3)	C14—C15—C16	119.8 (3)
C6—C7—C8	121.1 (3)	C17—C16—C15	120.1 (3)
C9—C8—C7	117.9 (3)	C16—C17—C12	121.2 (3)
C9—C8—C11	121.5 (4)		

Data collection, cell refinement and data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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