References

CHMIELEWSKA, B. (1983). *Pharmazie*, **38**, 872–873.
CHMIELEWSKA, B. (1984). *Pharmazie*, **39**, 259–262.
KWIATKOWSKI, W., KAROLAK-WOJCIECHOWSKA, J., OBNISKA, J. & ZEJC, A. (1990). *Acta Cryst.* C**46**, 108–112.
LANGE, J., RUMP, S., GAŁECKA, E., ILCZUK, I., LECHOWSKA-POSTEK, M., RABSZTYN, T., SZYMAŃSKA, T. & WALCZYNA, K. (1977). *Pharmazie*, **32**, 82–84.
LANGE, J., RUMP, S., ILCZUK, I., ŁAPISZEWICZ, J., RABSZTYN, T., & WALCZYNA, K. (1977). *Pharmazie*, **32**, 579–581.
ŁAPISZEWICZ, J., LANGE, J., RUMP, S. & WALCZYNA, T. (1978). *Eur. J. Med. Chem. Chim. Ther.* **13**, 465–468.
ŁUCKA-SOBSTEL, B., ZEJC, A. & OBNISKA, J. (1977). *Arch. Inmmunol. Ther. Exp.* **25**, 285–289.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
VICKOVIĆ, I. (1988). *Crystal Structure Utility*. Univ. of Zagreb, Yugoslavia.
ZEJC, A. & OBNISKA, J. (1984). *Acta Pol. Pharm.* **5**, 529–533.
ZEJC, A., OBNISKA, J., CHOJNACKA-WÓJCIK, E., TATARCZYŃSKA, E. & WICZYŃSKA, B. (1987). *Pol. J. Pharmacol. Pharm.* **39**, 91–95.

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Room-Temperature Structure of α–β Ethylenic Sulfoxide $C_{15}H_{18}OS$: (−)-4,5-Dimethyl-1-*p*-tolylsulfinyl-1,4-cyclohexadiene

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Abstract. $C_{15}H_{18}OS$, M_r = 246·37, orthorhombic, $P2_12_12_1$, a = 6·263 (2), b = 7·965 (2), c = 26·51 (1) Å, V = 1323 (1) $Å^3$, Z = 4, D_x = 1·24 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 0·18 mm^{-1}, $F(000)$ = 528, room temperature, R = 0·048, 701 unique reflections, crystal growth from toluene solution. The structure determination shows that the ground-state conformation of the molecule is S-*trans*.

Experimental. Crystal specimens were obtained from toluene solution by slow evaporation of the solvent giving rise to a prismatic 0·20 × 0·10 × 0·10 mm crystal.

Data were collected on a Siemens AED2 four-circle diffractometer, ω–θ step-scan mode in N steps of 0·035°, $37 \leq N \leq 41$, time per step: 4 s. Aperture D = 3·5 mm. Lattice constants were based on 36 reflections measured in double step scan mode at $\pm(2\theta \simeq 28°)$; no correction for absorption. Intensity measurement to $2\theta \leq 50°$ within range $0 \leq h \leq 7$, $0 \leq k \leq 8$, $0 \leq l \leq 30$. Standard reflections $1\bar{1}1$, $00\bar{8}$, 111, intensity variation 0·8%; 1419 independent reflections measured, 701 reflections used for refinements $[|F| > 6\sigma(|F|)]$.

Structure was solved from direct methods with the *TANG* option of the *SHELX76* program (Sheldrick, 1976). F magnitudes were used in least-squares refinements: 186 parameters refined; mean Δ/σ = 0·034, max. Δ/σ = 0·21; secondary-extinction factor: $x = 4·0 \times 10^{-8}$; atomic scattering factors for O, C, H and S were from *International Tables for X-ray Crystallography* (1974); calculations were with the *SHELX76* program (Sheldrick, 1976).

The multisolution tangent direct method of *SHELX76* gives a solution with all non-hydrogen atoms. Successive refinements and Fourier maps were allowed to distinguish oxygen from carbon atoms. Hydrogen atoms were then found from difference Fourier maps and geometric constraints were applied to CH_3, CH_2 or CH groups ($d_{C—H}$ = 1·08 Å). A unique isotropic thermal parameter was refined for all hydrogen atoms. The residuals decreased to R = 0·048, wR = 0·041; $w = 1·84/[\sigma^2(|F_o|) + 0·00007F_o^2]$. Max. and min. heights in final difference Fourier map: +0·24 and −0·28 e $Å^{-3}$. The absolute configuration of the molecule was not determined.

The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Selected bond lengths and angles are listed in Table

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52466 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates and equivalent isotropic temperature factors* (Å^2) *in* $C_{15}H_{18}OS$ (*e.s.d.'s in parentheses*)

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959).

	x	y	z	B_{eq}
S	0·2651 (5)	0·0449 (3)	0·1058 (1)	4·90 (8)
O	0·3962 (9)	−0·1103 (6)	0·1045 (2)	6·8 (2)
C(1)	0·226 (1)	0·1061 (7)	0·1702 (2)	4·2 (2)
C(2)	0·047 (1)	0·1853 (8)	0·1834 (3)	4·6 (2)
C(3)	0·014 (2)	0·2296 (8)	0·2364 (3)	5·4 (2)
C(4)	0·170 (1)	0·1743 (8)	0·2725 (3)	3·9 (2)
C(5)	0·351 (1)	0·0945 (7)	0·2587 (3)	4·0 (2)
C(6)	0·393 (1)	0·0589 (9)	0·2052 (3)	4·4 (2)
C(7)	0·439 (1)	0·2141 (9)	0·0850 (2)	3·8 (2)
C(8)	0·639 (1)	0·1784 (9)	0·0678 (2)	5·2 (2)
C(9)	0·766 (2)	0·3051 (9)	0·0491 (2)	4·8 (2)
C(10)	0·694 (1)	0·4721 (9)	0·0479 (2)	4·9 (2)
C(11)	0·490 (2)	0·5028 (8)	0·0655 (2)	4·7 (2)
C(12)	0·355 (1)	0·3782 (8)	0·0843 (2)	4·2 (2)
C(13)	0·120 (1)	0·2076 (9)	0·3288 (2)	5·6 (2)
C(14)	0·512 (1)	0·0336 (9)	0·2969 (3)	5·9 (2)
C(15)	0·832 (2)	0·6131 (8)	0·0297 (3)	7·0 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* $C_{15}H_{18}OS$ (*e.s.d.'s in parentheses*)

O—S	1·484 (5)	C(1)—S	1·791 (6)
C(7)—S	1·817 (7)	C(2)—C(1)	1·334 (8)
C(6)—C(1)	1·447 (8)	C(3)—C(2)	1·464 (8)
C(4)—C(3)	1·436 (9)	C(5)—C(4)	1·354 (8)
C(13)—C(4)	1·548 (9)	C(6)—C(5)	1·468 (9)
C(14)—C(5)	1·511 (8)	C(8)—C(7)	1·366 (9)
C(12)—C(7)	1·407 (8)	C(9)—C(8)	1·379 (9)
C(10)—C(9)	1·406 (9)	C(11)—C(10)	1·380 (9)
C(15)—C(10)	1·500 (8)	C(12)—C(11)	1·394 (8)
C(1)—S—O	108·9 (3)	C(7)—S—O	106·3 (3)
C(7)—S—C(1)	99·7 (3)	C(2)—C(1)—S	119·6 (6)
C(6)—C(1)—S	116·3 (5)	C(6)—C(1)—C(2)	124·0 (6)
C(3)—C(2)—C(1)	119·2 (7)	C(4)—C(3)—C(2)	117·9 (6)
C(5)—C(4)—C(3)	122·3 (7)	C(13)—C(4)—C(3)	116·9 (6)
C(13)—C(4)—C(5)	120·8 (7)	C(6)—C(5)—C(4)	120·1 (7)
C(14)—C(5)—C(4)	122·0 (7)	C(14)—C(5)—C(6)	117·9 (6)
C(5)—C(6)—C(1)	116·2 (6)	C(8)—C(7)—S	119·8 (6)
C(12)—C(7)—S	118·1 (6)	C(12)—C(7)—C(8)	122·0 (7)
C(9)—C(8)—C(7)	120·0 (7)	C(10)—C(9)—C(8)	120·9 (7)
C(11)—C(10)—C(9)	117·4 (7)	C(15)—C(10)—C(9)	121·8 (6)
C(15)—C(10)—C(11)	120·8 (6)	C(12)—C(11)—C(10)	123·6 (7)
C(11)—C(12)—C(7)	116·2 (7)		

2. The *ORTEP* plot (Johnson, 1965) of the molecule is represented in Fig. 1.

Related literature. Alkenyl *p*-tolyl sulfoxides with an optically active center at the sulfur atom were used successfully in various asymmetric syntheses. In particular, extremely high asymmetric induction was accomplished during asymmetric Michael additions (Posner, Weitzberg, Hamill & Asirvatham, 1986) and high diastereofacial selectivity was observed in Diels–Alder cycloaddition (Koizumi, Arai & Takayama, 1987) starting from enantiomerically pure vinylic sulfoxides.

These results were rationalized in terms of diastereoselective addition of the reactants to energetically favoured S-*trans* or S-*cis* conformers of vinyl sulfoxides.

Single-crystal X-ray analyses of *β*-carbonyl sulfoxides (Posner, Weitzberg, Hamill & Asirvatham, 1986) and *β*-ester sulfoxides (Koizumi, Arai & Takayama, 1987) have already established that in the ground-state conformation the carbon—oxygen and sulfur—oxygen bond dipoles of these compounds are oriented in opposite directions to minimize dipole–dipole interactions.

The ground-state conformation of a vinyl sulfoxide without sulfoxide–carbonyl interaction is described here for the first time: (−)-4,5-dimethyl-1-*p*-tolylsulfinyl-1,4-cyclohexadiene (Fig. 2) was obtained through cycloaddition of (*R*)-ethynyl *p*-tolyl sulfoxide and 2,3-dimethylbutadiene (Maignan & Belkasmioui, 1989). The perspective view (Fig. 1) reveals the S-*trans* conformation of this compound; the dihedral angle between O—S—C(1) and S—C(1)—C(2) is 149·0 (9)°.

This determination shows that vinyl sulfoxide probably reacts in this S-*trans* conformation with dienes to yield Diels–Alder adducts (Maignan & Raphael, 1983; Maignan, Guessous & Rouessac, 1984), and not in an S-*cis* conformation (Kahn & Hehre, 1986).

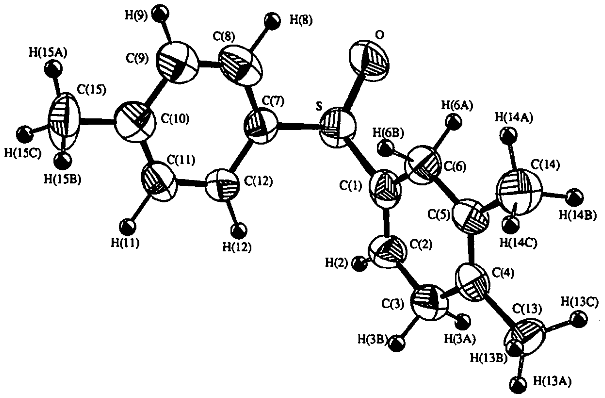

Fig. 1. *ORTEP* plot of the molecule of $C_{15}H_{18}OS$. For the sake of clarity, the thermal parameters of the hydrogen atoms were divided by ten.

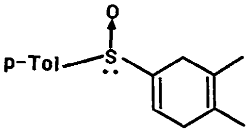

Fig. 2. Simplified representation of the molecule of $C_{15}H_{18}OS$.

References

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
KAHN, S. D. & HEHRE, W. T. (1986). *Tetrahedron Lett.* **27**, 6041–6044.
KOIZUMI, T., ARAI, Y. & TAKAYAMA, M. (1987). *Tetrahedron Lett.* **28**, 3692–3695.
MAIGNAN, C. & BELKASMIOUI, F. (1989). *Bull. Soc. Chim Fr.* pp. 695–698.
MAIGNAN, C., GUESSOUS, A. & ROUESSAC, F. (1984). *Tetrahedron Lett.* **25**, 1727–1729.
MAIGNAN, C. & RAPHAEL, R. A. (1983). *Tetrahedron*, **39**, 3245–3249.
POSNER, G. H., WEITZBERG, M., HAMILL, G. & ASIRVATHAM, E. (1986). *Tetrahedron*, **42**, 2919–2929.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of Triphenylstibine

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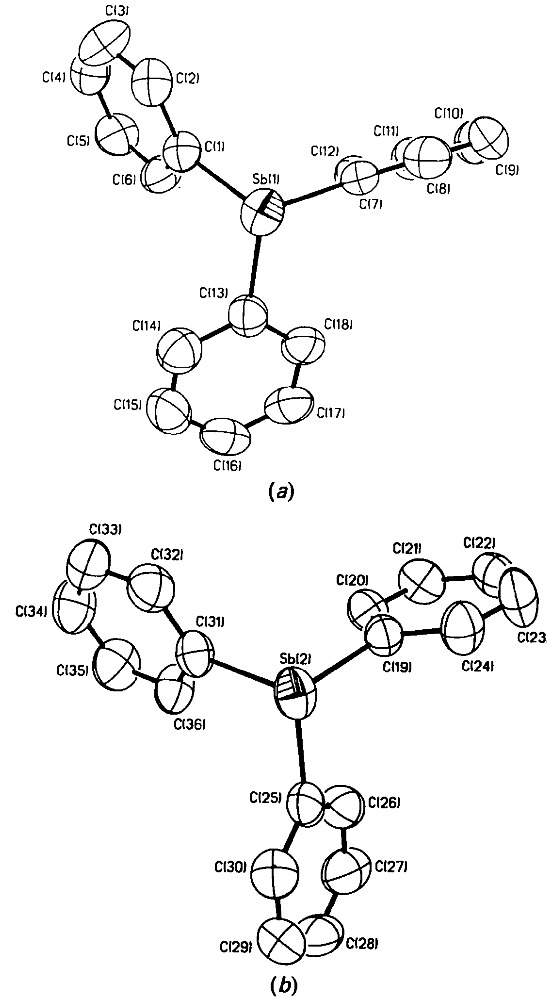
Abstract. $C_{18}H_{15}Sb$, $M_r = 353{\cdot}08$, triclinic, $P\bar{1}$, $a = 10{\cdot}909\,(7)$, $b = 11{\cdot}728\,(6)$, $c = 13{\cdot}737\,(6)$ Å, $\alpha = 102{\cdot}61\,(4)$, $\beta = 104{\cdot}42\,(4)$, $\gamma = 107{\cdot}94\,(4)°$, $V = 1534\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}53$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 17{\cdot}92$ cm^{-1}, $F(000) = 696$, $T = 294$ K, $R = 0{\cdot}0373$ for 2421 observed reflections. The two independent molecules in the asymmetric unit differ in phenyl ring conformation; dihedral angles between phenyl ring planes C(1)–C(6), C(7)–C(12) and C(13)–C(18) and the basal plane defined by atoms C(1), C(7) and C(13) for molecule (1) are 65·1, 93·2 and 37·2°, respectively; corresponding values for molecule (2) [phenyl rings: C(19)–C(24), C(25)–C(30) and C(31)–C(36)] with the basal plane defined by atoms C(19), C(25) and C(31) are 64·9, 118·4 and 58·7°, respectively. Average Sb—C distance is 2·155 (9) Å, C—Sb—C angles range from 95·1 (3) to 98·0 (3)°.

Experimental. Colorless parallelepiped crystal (m.p. 326·5 K), obtained by slow evaporation of an acetone/water solution, dimensions 0·20 × 0·30 × 0·45 mm. Data collected at room temperature, graphite-monochromated Mo $K\alpha$ radiation, Nicolet $R3m$/V diffractometer, $\omega/2\theta$ scans of 2–15°min^{-1}, $2\theta_{\max} = 45°$, $h = 0$ to 11, $k = -12$ to 12, $l = -14$ to 14, 4299 measurements, 4042 unique ($R_{\rm int} = 0{\cdot}030$), 2421 observed [$I > 3\sigma(I)$]. Unit-cell dimensions determined by least-squares fit to settings for 29 reflections ($15 < 2\theta < 30°$). Empirical absorption correction ($\mu = 17{\cdot}92$ cm^{-1}), transmission factors 0·78–1·00; three standards monitored (± 1%), 40·2 h of X-ray exposure.

Solved by direct methods; full-matrix least-squares refinement on F, $R = 0{\cdot}0373$, $wR = 0{\cdot}0432$, $S = 0{\cdot}95$,



(*a*)

(*b*)

Fig. 1. Thermal-ellipsoid plots (50% probability); H atoms omitted. Molecules are viewed normal to their basal planes. (*a*) Molecule (1). (*b*) Molecule (2).

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