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## Structure of (+)-[S-(E)]-N-( $\alpha$ -Methylbenzylidene)-*p*-toluenesulfinamide

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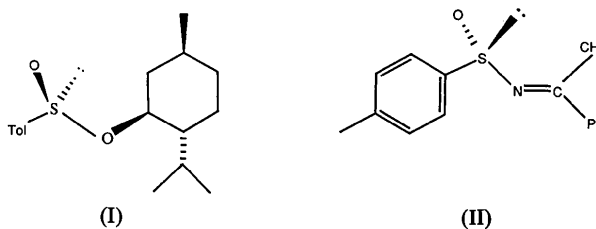
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**Abstract.** C<sub>15</sub>H<sub>15</sub>NOS, *M<sub>r</sub>* = 257.35, monoclinic, *P*2<sub>1</sub>, *a* = 7.710 (2), *b* = 5.903 (5), *c* = 14.700 (3) Å,  $\beta$  = 91.48 (2)°, *V* = 668.8 (6) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.278 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 2.18 cm<sup>-1</sup>, *F*(000) = 272, *T* = 296 K, *R* = 0.043, 944 unique observed reflections. This is the first structure determination of an *N*-alkylidenesulfinamide. The C=N bond is distorted and lengthened presumably because of the steric interaction and electron-withdrawing effect of the sulfinyl group. The non-planar conformation is also a result of repulsive steric interaction. The configuration at C=N is *trans*. The title compound was obtained from the displacement reaction of (–)-1-menthyl (*S*)-*p*-toluenesulfinate with methyllithium.

**Introduction.** We have recently studied some asymmetric reactions of chiral *N*-alkylidenesulfinamides. Their preparation as reported (Cinquini & Cozzi, 1977*a*) involved the reaction of an alkyl or aryl Grignard reagent with benzonitrile and subsequent reaction with (–)-1-menthyl (*S*)-*p*-toluenesulfinate (I). However, the yields were low and the stereochemistry at C=N of the *N*-alkylidenesulfinamides was not reported. We found that treatment of methylmagnesium bromide with benzonitrile followed by sulfinate (I) gave only 12% yield of (+)-[S-(E)]-N-( $\alpha$ -methylbenzylidene)-*p*-toluenesulfinamide (II). The use of methyllithium instead of methylmagnesium

bromide increased the yield to 50%. The relative stereochemistry at the S site and C=N of (II) was determined by this X-ray study. The absolute configuration at the S site is assigned the *S* configuration based on studies by Cinquini & Cozzi (1977*a*). This determination of the stereochemistry at C=N in turn provides explanations for the stereochemical course followed in the asymmetric transformations of chiral *N*-alkylidenesulfinamides (Cinquini & Cozzi, 1977*b*; Hua, Miao, Chen & Saha, 1990). Chelation of the O atom with metal hydride directs the attack from the pre-*S* face of the C=N.



**Experimental.** Compound (II) displayed satisfactory <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz), UV, IR and low-resolution mass spectra (both EI and CI) and satisfactory elemental analysis. Title compound, (+)-[S-(E)]-N-( $\alpha$ -methylbenzylidene)-*p*-toluenesulfinamide (II), was prepared as follows. To a cold (273 K) solution of 1.75 g (17 mmol) benzonitrile in 20 ml ether under argon was added a solution of 11.8 ml (17 mmol) methyllithium (1.5 M in ether). Solution stirred at 173 K for 1 h, cold (273 K) solution of (I) (2.5 g, 8.5 mmol) added. After stirring at

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Table 1. Positional and equivalent isotropic thermal parameters for the non-H atoms and their *e.s.d.*'s
$$B_{\text{eq}} = (8\pi^2/3)[U_{22} + (1/\sin^2\beta)(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	0.8011 (6)	0.5846	0.3841 (3)	3.5 (2)
C(2)	0.8544 (8)	0.352 (1)	0.3573 (4)	5.8 (3)
N(3)	0.7847 (5)	0.751 (1)	0.3287 (3)	4.2 (2)
C(4)	0.7585 (6)	0.628 (1)	0.4804 (3)	3.2 (2)
C(5)	0.6789 (6)	0.831 (1)	0.5045 (3)	4.0 (3)
C(6)	0.6401 (7)	0.875 (1)	0.5942 (4)	4.8 (3)
C(7)	0.6807 (7)	0.718 (2)	0.6607 (3)	5.4 (3)
C(8)	0.7581 (8)	0.516 (2)	0.6389 (4)	5.3 (3)
C(9)	0.7971 (6)	0.471 (1)	0.5481 (4)	4.5 (3)
S(10)	0.8480 (2)	0.721 (1)	0.21846 (8)	4.52 (7)
O(11)	0.8773 (5)	0.958 (1)	0.1884 (2)	5.9 (2)
C(12)	0.6429 (7)	0.632 (1)	0.1717 (3)	3.8 (2)
C(13)	0.6322 (7)	0.424 (1)	0.1289 (3)	4.2 (3)
C(14)	0.4744 (7)	0.355 (1)	0.0905 (3)	4.4 (3)
C(15)	0.3282 (7)	0.490 (1)	0.0951 (3)	4.4 (3)
C(16)	0.3441 (7)	0.698 (1)	0.1373 (3)	5.0 (3)
C(17)	0.4993 (7)	0.769 (1)	0.1755 (3)	4.6 (3)
C(18)	0.1577 (7)	0.408 (2)	0.0552 (4)	6.8 (4)

273 K for 2.5 h, solution diluted with 50 ml of  $\text{H}_2\text{O}$ , extracted with  $\text{CH}_2\text{Cl}_2$  three times (100 ml each). Combined extracts washed with brine, dried ( $\text{MgSO}_4$ ), concentrated and column chromatographed on silica gel using mixtures of hexane, ether and  $\text{CH}_2\text{Cl}_2$  as eluant to give 1.09 g (50% yield) of (II)  $\{[\alpha]_D^{22^\circ}\text{C} + 98^\circ$  (*c* 1,  $\text{CHCl}_3$ ); lit.  $[\alpha]_D^{25^\circ}\text{C} + 98^\circ$  (*c* 1,  $\text{CHCl}_3$ ) (Cinquini & Cozzi, 1977a)} and 0.25 g (10% recovery) of sulfinate (I). Recrystallization of solid (II) by cooling in ether yielded single crystals suitable for X-ray study; m.p. 372.7–373.2 K.

Crystal used for data collection  $0.35 \times 0.16 \times 0.08$  mm, colorless transparent fragment cut from larger crystal. Rigaku AFC5S diffractometer, graphite-monochromated  $\text{Mo } K\alpha$  radiation,  $\omega$ – $2\theta$  scans, scan speed  $4^\circ \text{ min}^{-1}$  (in  $\omega$ ), weak reflections [ $I < 10.0\sigma(I)$ ] rescanned (maximum of two rescans) and the counts accumulated to ensure good counting statistics. Lattice parameters from least-squares fit of 25 strong reflections in  $2\theta$  range 25–35°. A total of 1296 reflections measured ( $h$  0 to 13,  $k$  0 to 7,  $l$  –17 to 17), 352 reflections considered unobserved with [ $I < 2\sigma(I)$ ], data set comprised of 944 unique reflections,  $(\sin\theta/\lambda)_{\text{max}} = 0.60 \text{ \AA}^{-1}$ . Three standard reflections ( $20\bar{1}$ ,  $\bar{1}10$ ,  $\bar{1}11$ ) changed by 1.1, 0.6 and –0.2%, respectively; no decay correction applied. Data corrected for Lorentz and polarization, no absorption correction. Direct-method programs *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984) provided the locations of all non-H atomic positions. Full-matrix least-squares refinement was performed to minimize  $\sum w(|F_o| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$  and  $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$  ( $S$  = scan rate,  $C$  = total integrated peak count,  $R$  = ratio of scan time to background counting time,  $B$  = total background count,  $Lp$  = Lorentz–polarization factor and  $p = 0.03$ ). After convergence methyl and phenyl H atoms placed at assumed positions ( $\text{C}–\text{H} =$

0.95 Å), methyl-group orientations determined on the basis of H positions obtained from difference Fourier synthesis, H positions not refined. Final stages of refinement performed with 163 variables including all non-H positional and anisotropic thermal parameters, one scale factor and a secondary-extinction coefficient ( $0.62795 \times 10^{-7}$ ). Convergence yielded  $R = 0.043$ ,  $wR = 0.044$ ,  $S = 1.42$  and  $(\Delta/\sigma)_{\text{max}} = 0.01$ . Final difference synthesis produced  $(\Delta\rho)_{\text{max}} = 0.18$  and  $(\Delta\rho)_{\text{min}} = -0.16 \text{ e \AA}^{-3}$ . The absolute molecular configuration could not be conclusively determined from the S anomalous signal. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148). All computer programs from the *TEXSAN* crystal-structure analysis package (Molecular Structure Corporation, 1985).

**Discussion.** Final atomic coordinates with equivalent isotropic temperature factors are given in Table 1.\* As far as we know, this is the first reported structure of this class of *N*-alkylidenesulfinamides (Fig. 1).

\* Lists of structure factors, H-atom parameters, anisotropic thermal parameter, bond distances involving the phenyl rings, intermolecular distances, selected least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53283 (15pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

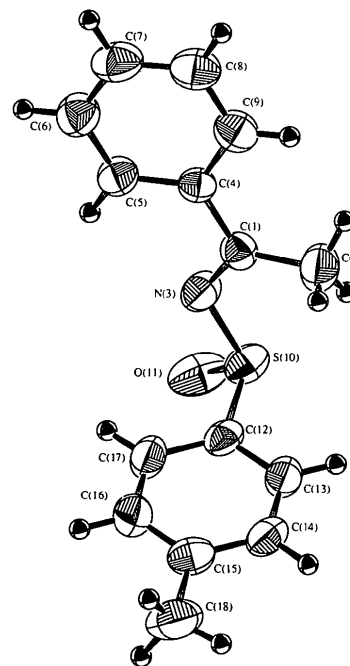


Fig. 1. Molecular configuration and atom-numbering scheme for the non-H atoms, thermal ellipsoids at the 50% probability level. H atoms shown as isotropic spheres with  $B$ 's of  $1.0 \text{ \AA}^2$ .

Table 2. Selected bond distances (Å) and bond angles (°) and their e.s.d.'s

C(1)—C(2)	1.486 (8)	S(10)—O(11)	1.484 (5)
C(1)—N(3)	1.282 (6)	S(10)—C(12)	1.787 (5)
C(1)—C(4)	1.484 (7)	C(15)—C(18)	1.504 (7)
N(3)—S(10)	1.714 (4)		
C(2)—C(1)—N(3)	124.3 (5)	N(3)—S(10)—C(12)	97.1 (2)
C(2)—C(1)—C(4)	118.9 (5)	O(11)—S(10)—C(12)	107.6 (2)
N(3)—C(1)—C(4)	116.8 (4)	S(10)—C(12)—C(13)	118.6 (4)
C(1)—N(3)—S(10)	119.6 (4)	S(10)—C(12)—C(17)	121.1 (4)
C(1)—C(4)—C(5)	120.2 (5)	C(14)—C(15)—C(18)	120.2 (6)
C(1)—C(4)—C(9)	121.2 (5)	C(16)—C(15)—C(18)	121.7 (6)
N(3)—S(10)—O(11)	103.4 (2)		

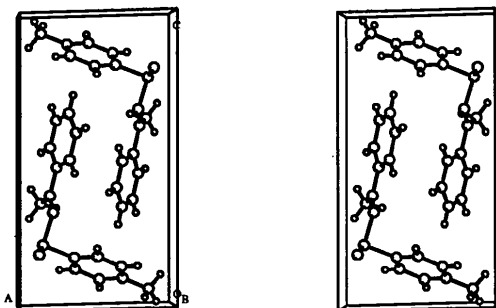


Fig. 2. Stereoscopic illustration of the molecular packing.

The bond angle N(3)—C(1)—C(4) of 116.8 (4)° is smaller than the 122.0° value for the imine (Bernstein & Schmidt, 1972), while C(2)—C(1)—N(3) of 124.3 (5)° is larger (Table 2). This wider angle at C(2)—C(1)—N(3) is presumably derived from avoiding steric interaction of the C(2) methyl and S(10) sulfinyl groups. According to Bürgi & Dunitz (1971), an electron-withdrawing group should lead to lengthening of the C=N bond. Indeed, the bond length C(1)—N(3) of 1.282 (6) Å is longer than the normal 1.262 Å of the imine (Bernstein & Schmidt, 1972). Least-squares-plane calculations show that all

three groups (phenyl ring, methyl and sulfinyl) are distorted from the central plane defined by C(4)—C(1)—N(3). The dihedral angles, with respect to the central plane, are 9.97° for the phenyl ring [C(4) to C(9)], 1.72° for the methyl group [C(2)—C(1)—C(4)] and 5.25° for the sulfinyl group [C(1)—N(3)—S(10)]. This non-planar conformation further relieves the repulsive interaction of the above three groups around C=N. The bond angle N(3)—S(10)—C(12) and bond lengths S(10)—C(12) and S(10)—O(11) are normal (Hua, Badejo, McCann & Takusagawa, 1987). The configuration at C=N is *trans* (the sulfinyl and phenyl groups are *trans*). The molecular packing is shown in Fig. 2.

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## Structure of a Charge-Transfer Complex, Dithieno[3,4-*b*:3',4'-*d*]thiophene–Tetracyanoquinodimethane (DTT1–TCNQ)

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**Abstract.** Dithieno[3,4-*b*:3',4'-*d*]thiophene–tetracyanoquinodimethane, C<sub>8</sub>H<sub>4</sub>S<sub>3</sub>.C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>, *M<sub>r</sub>* = 400.51, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.272 (3), *b* = 7.674 (3), *c* = 32.613 (9) Å,  $\beta$  = 93.6 (2)°, *V* = 1816 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.464 g cm<sup>-3</sup>, Cu *K* $\alpha$  radiation,  $\lambda$  = 1.54184 Å,  $\mu$  = 18.16 cm<sup>-1</sup>, *F*(000) = 816, *T* = 293 K, *R* = 0.085 based on 1843 reflections (*F<sub>o</sub>* > 4 $\sigma$ ). The low accuracy of this structural determination is due to the fact that only needle-shaped single crystals shorter than 70  $\mu$ m were obtainable by

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