

respectively, indicating the absence of rotation about the C(1)—C(4) bond.

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#### References

BECKER, P. J. & COPPENS, P. (1974a). *Acta Cryst. A* **30**, 129–147.  
 BECKER, P. J. & COPPENS, P. (1974b). *Acta Cryst. A* **30**, 148–153.  
 BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst. A* **31**, 417–425.  
 BURGESS, E. M. & LIOTTA, C. L. (1981). *J. Org. Chem.* **46**, 1703–1708.  
 HOWARD, J. A. K., JOHNSON, O., SCHULTZ, A. J. & STRINGER, A. M. (1987). *J. Appl. Cryst.* **20**, 120–122.  
 JACOBSON, R. A. (1986). *J. Appl. Cryst.* **19**, 283–286.  
 JAUCH, W., SCHULTZ, A. J. & SCHNEIDER, J. R. (1988). *J. Appl. Cryst.* **21**, 975–979.  
 SCHULTZ, A. J. (1987). *Trans. Am. Crystallogr. Assoc.* **23**, 61–69.  
 SEARS, V. F. (1986). *Methods of Experimental Physics*, edited by K. SKÖLD & D. L. PRICE, Vol. 23, Part A, pp. 521–550. Orlando: Academic Press.  
 SKANCKE, A., SCHAAD, L. J. & HESS, B. A. JR (1988). *J. Am. Chem. Soc.* **110**, 5315–5316.  
 VAN DERVEER, D. G., BALDWIN, J. E. & PARKER, D. W. (1987). *J. Org. Chem.* **52**, 1173–1174.

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## (Z)-Methyl 2-Phenyl-2-(pyrid-4-yl)vinyl Sulfoxide

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**Abstract.**  $C_{14}H_{13}NOS$ ,  $M_r = 243.33$ , triclinic,  $P\bar{1}$ ,  $a = 5.455$  (6),  $b = 10.064$  (3),  $c = 12.831$  (1) Å,  $\alpha = 71.59$  (3),  $\beta = 79.60$  (7),  $\gamma = 75.79$  (5)°,  $V = 643.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.27$ ,  $D_x = 1.26$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 2.3$  cm<sup>-1</sup>,  $T = 293$  K, final  $R = 0.047$  for 2369 observed reflections (of 8164 unique data). For the title compound the unambiguous identification of the *Z* configuration by X-ray diffraction confirms a previous tentative assignment based on NMR. The two planar rings (phenyl and pyridyl) are at an angle of about 87°. Crystal cohesion is ensured by a dense network of van der Waals contacts.

**Introduction.** Certain unsaturated sulfoxides and particularly vinyl sulfoxides have been found to have a significant antianoxia activity (Madesclaire, Roche, Carpy & Boucherle, 1982).

Knowledge of the exact configuration of the *Z* and *E* diastereoisomers was required in order to perform a pharmacological study and to establish any structure–activity relationships. The stereoisomers were prepared by oxidation of sulfides with *m*-chloroperbenzoic acid (*m*-CPBA) (Madesclaire,

1986). The vinyl sulfides were synthesized by the Horner–Wittig reaction and separated by flash chromatography (Roche, Madesclaire, Veschambre & Fauve, 1988).

**Experimental.** Plate-like crystals of the title compound were grown by slow evaporation (a few weeks) of an ether solution at 277 K.  $D_m$  by flotation; white crystal, dimensions 0.75 × 0.55 × 0.07 mm; unit-cell parameters using 24 reflections with  $\theta$  values of about 10° and refining by the least-squares method; data collection on Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\theta$ – $2\theta$  scan mode,  $\theta$  scan width (1.0 + 0.35tan  $\theta$ )°, aperture width (2.0 + 1.0tan  $\theta$ ) mm; data having  $2\theta_{\max} \leq 80$ °,  $-9 \leq h \leq 9$ ,  $-18 \leq k \leq 18$ ,  $0 \leq l \leq 23$  measured; intensities of three standard reflections monitored after every 3600 s of exposure; variation in intensity  $\leq 2\%$  during complete data collection; orientation matrix checked every 100 reflections, no significant systematic fluctuation; 8164 reflections registered and reduced to 2369 with  $I \geq 3\sigma(I)$ ; intensities corrected for Lorentz and polarization effects but not for absorption; structure solved using *MULTAN11/82*

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Table 1. Fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

	$x$	$y$	$z$	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
C(1)	6763 (5)	5385 (3)	2084 (2)	3.28
C(2)	7331 (6)	6703 (3)	1937 (3)	4.63
C(3)	6193 (8)	7909 (3)	1189 (3)	5.54
C(4)	4475 (8)	7831 (4)	574 (3)	5.27
C(5)	3887 (7)	6548 (4)	698 (3)	5.51
C(6)	5019 (6)	5330 (3)	1440 (3)	4.66
C(7)	8157 (5)	2688 (3)	2699 (2)	3.36
C(8)	9914 (6)	2322 (3)	1867 (3)	4.74
C(9)	143 (7)	1029 (4)	1686 (3)	5.83
N(10)	8733 (6)	86 (3)	2249 (3)	6.28
C(11)	7035 (7)	449 (4)	3033 (4)	6.00
C(12)	6693 (6)	1715 (3)	3300 (3)	4.70
C(13)	7857 (4)	4087 (3)	2925 (2)	3.23
C(14)	8468 (5)	4176 (3)	3856 (2)	3.67
S(15)	9893 (1)	2696 (1)	4881 (1)	3.80
O(16)	2191 (3)	3108 (2)	5080 (7)	4.60
C(17)	7544 (6)	2951 (4)	5996 (3)	4.61

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses, and selected torsion angles ( $^\circ$ )

C(1)—C(2)	1.383 (5)	C(7)—C(13)	1.490 (5)
C(1)—C(6)	1.389 (5)	C(8)—C(9)	1.365 (6)
C(1)—C(13)	1.479 (3)	C(9)—N(10)	1.319 (5)
C(2)—C(3)	1.375 (4)	N(10)—C(11)	1.316 (6)
C(3)—C(4)	1.360 (7)	C(11)—C(12)	1.383 (6)
C(4)—C(5)	1.360 (6)	C(13)—C(14)	1.331 (4)
C(5)—C(6)	1.376 (4)	C(14)—S(15)	1.765 (2)
C(7)—C(8)	1.378 (4)	S(15)—O(16)	1.499 (2)
C(7)—C(12)	1.370 (4)	S(15)—C(17)	1.778 (4)
C(2)—C(1)—C(6)	117.4 (2)	C(8)—C(9)—N(10)	124.1 (3)
C(2)—C(1)—C(13)	122.1 (3)	C(9)—N(10)—C(11)	116.0 (4)
C(6)—C(1)—C(13)	120.5 (3)	N(10)—C(11)—C(12)	124.5 (4)
C(1)—C(2)—C(3)	121.1 (4)	C(11)—C(12)—C(7)	118.7 (3)
C(2)—C(3)—C(4)	120.5 (3)	C(1)—C(13)—C(7)	117.2 (2)
C(3)—C(4)—C(5)	119.7 (3)	C(1)—C(13)—C(14)	120.8 (3)
C(4)—C(5)—C(6)	120.5 (4)	C(7)—C(13)—C(14)	122.0 (2)
C(5)—C(6)—C(1)	120.9 (3)	C(13)—C(14)—S(15)	124.0 (2)
C(8)—C(7)—C(12)	117.0 (3)	C(14)—S(15)—O(16)	105.3 (1)
C(8)—C(7)—C(13)	121.3 (2)	C(14)—S(15)—C(17)	96.4 (1)
C(12)—C(7)—C(13)	121.7 (2)	O(16)—S(15)—C(17)	105.5 (2)
C(7)—C(8)—C(9)	119.7 (3)		
C(2)—C(1)—C(13)—C(14)	29.7	C(13)—C(14)—S(15)—O(16)	78.1
C(8)—C(7)—C(13)—C(14)	69.9	C(13)—C(14)—S(15)—C(17)	58.9

van der Waals contacts

S(15)—C(11 <sup>iv</sup> )	3.695 (4)	N(10)—C(7 <sup>iv</sup> )	3.577 (4)
O(16)—C(11 <sup>iv</sup> )	3.607 (4)	C(2)—C(5 <sup>ii</sup> )	3.629 (5)
O(16)—C(14 <sup>ii</sup> )	3.341 (4)	C(6)—C(5 <sup>ii</sup> )	3.686 (6)
O(16)—C(14 <sup>ii</sup> )	3.761 (3)	C(17)—C(1 <sup>i</sup> )	3.602 (5)
O(16)—C(17 <sup>i</sup> )	3.291 (4)	C(17)—C(2 <sup>i</sup> )	3.436 (5)
N(10)—C(3 <sup>ii</sup> )	3.553 (6)	C(17)—C(3 <sup>i</sup> )	3.766 (5)

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 + x, y, z$ ; (iii)  $1 - x, -y, 1 - z$ ; (iv)  $2 - x, -y, 1 - z$ ; (v)  $x, -1 + y, z$ .

(Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods; atomic scattering factors and anomalous-dispersion correction for the S atom were taken from *International Tables for X-ray Crystallography* (1974); refinement with anisotropic thermal factors for non-H atoms led to  $R = 0.089$ ; difference electron density maps revealed positions of H atoms; subsequent full-

matrix least-squares refinements performed with a modified version of the ORFLS refinement program (ORFLS; Busing, Martin & Levy, 1962) and use of anisotropic thermal parameters and weights assigned according to the counting statistics  $w = 1/\sigma^2(F)$ ,  $\sigma(I) = [I_t + 4(B_1 + B_2) + p^2 I_{\text{net}}^2]^{1/2}$ .  $I_{\text{net}} = I_{\text{tot}} - 2(B_1 + B_2)$ ,  $B_1$  and  $B_2$  are the background counts on the low and high  $2\theta$  side respectively,  $p$  is the fudge factor corresponding to the relative standard deviation ( $p = 0.02$ ); final cycles of refinement with anisotropic thermal parameters for non-H atoms, isotropic for H atoms led to  $R = 0.047$  for 2369 observed reflections only;  $wR = 0.050$ ; max.  $\Delta/\sigma = 0.50$  in final cycle, max. residual density  $0.20 \text{ e \AA}^{-3}$ .

**Discussion.** The final atomic parameters of the non-H atoms and equivalent isotropic  $B_{\text{eq}}$ 's are given in Table 1. Bond distances, angles and essential torsion angles are listed in Table 2.\* Figs. 1 and 2 show the molecular structure with the numbering scheme and the crystal structure projection on (010), respectively.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52264 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

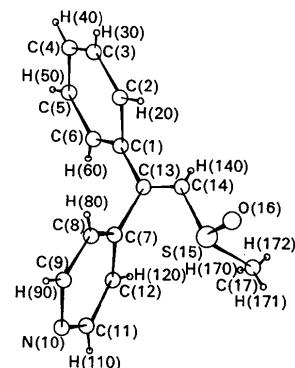


Fig. 1. Perspective view of the molecule with numbering scheme.

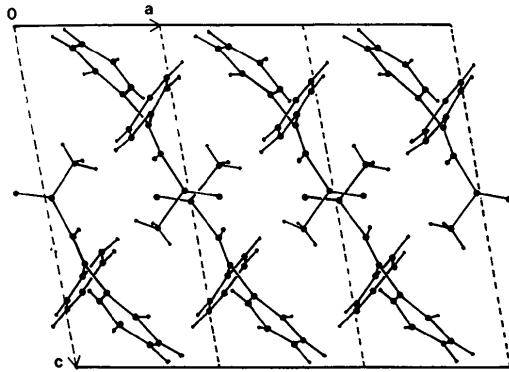


Fig. 2. Projection of the structure on (010).

The X-ray crystal diffraction study of the title compound confirmed the *Z* configuration for this diastereoisomer, as suggested by NMR spectroscopy. Similarly, the analysis of the crystal structure of this vinyl sulfoxide shows that it is a true racemate and not a conglomerate. The two molecules in the unit cell correspond to the two enantiomers *ZR* and *ZS*. The absolute configurations of the chiral sulfur are *R* and *S*.

The lengths of the S(15)—C(14) and S(15)—C(17) bonds [1.765 (2) and 1.778 (4) Å respectively] are practically the same, and comparable to those given in the literature for other vinyl sulfoxides (Tranqui & Fillion, 1972; Madesclaire, Roche & Carpy, 1988). The S(15)—O(16) distance [1.499 (2) Å] suggests that this bond is closer to a double bond than to a single bond. In addition, the angle between the planes containing the vinyl [C(1), C(7), C(13), C(14), S(15)] and sulfoxide [C(14), S(15), O(16)] groups is 78 (2)°, which rules out any delocalization of the  $\pi$  electrons of the S(15)—O(16) and C(13)—C(14) bonds.

The S(15) atom is placed at the 'center' of an irregular tetrahedron the base of which is formed by C(14), O(16) and C(17) and the fourth apex of which is the lone pair of the S atom.

The angle between the phenyl and pyridyl rings is 87 (2)°. The plane containing the vinyl group, *i.e.* C(1), C(7), C(13), C(14), S(15), is at an angle of 30 (2)° to the plane of the phenyl ring and at an angle of 70 (2)° to the plane of the pyridyl ring, which prevents conjugation.

Crystal cohesion is ensured by a dense three-dimensional network of van der Waals interactions, listed in Table 2.

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### References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
MADESCLAIRE, M. (1986). *Tetrahedron*, **42**, 5459–5495.  
MADESCLAIRE, M., ROCHE, D. & CARPY, A. (1988). *C. R. Acad. Sci. Sér. B*, **306**, 891–896.  
MADESCLAIRE, M., ROCHE, D., CARPY, A. & BOUCHERLE, A. (1982). *Arch. Pharm. (Weinheim, Ger.)*, **315**, 741–748.  
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). MULTAN11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
ROCHE, D., MADESCLAIRE, M., VESCHAMBRE, H. & FAUVE, A. (1988). *Synthesis*. Accepted.  
TRANQUI, D. S. & FILLION, H. (1972). *Acta Cryst. B*, **28**, 3306–3315.

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## Structures of Benzylammonium Hydrogen Malonate (I) and 4-Picolinium Hydrogen Malonate (II)

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**Abstract.** (I):  $C_7H_{10}N^+ \cdot C_3H_3O_4^-$ ,  $M_r = 211.22$ , triclinic,  $P\bar{1}$ ,  $a = 5.455$  (1),  $b = 8.788$  (2),  $c = 11.060$  (4) Å,  $\alpha = 83.67$  (2),  $\beta = 86.18$  (3),  $\gamma = 78.07$  (2)°,  $V = 515.0$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.362$ ,  $D_m = 1.36$  (4) g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 0.948$  cm<sup>-1</sup>,  $F(000) = 224$ ,  $T = 293$  (2) K, final  $R = 0.039$  and  $wR = 0.040$  for 848 observed reflections. (II):  $C_6H_8N^+ \cdot C_3H_3O_4^-$ ,  $M_r = 197.19$ , monoclinic,  $P2_1/n$ ,  $a = 3.955$  (1),  $b = 21.663$  (5),  $c = 11.259$  (3) Å,  $\beta = 99.33$  (2)°,  $V = 951.9$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.376$ ,  $D_m = 1.35$  (2) g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,

$\lambda = 0.71069$  Å,  $\mu = 1.022$  cm<sup>-1</sup>,  $F(000) = 416$ ,  $T = 293$  (2) K, final  $R = 0.039$  and  $wR = 0.040$  for 1328 observed reflections. Short asymmetrical intramolecular hydrogen bonds [2.430 (2) and 2.493 (3) Å for (I) and (II) respectively] stabilize the planar hydrogen malonate ions. Benzylammonium groups are linked to hydrogen malonate ions by three intermolecular hydrogen bonds of 2.912 (2), 2.874 (2) and 2.969 (2) Å while 4-picolinium ions are hydrogen bonded to hydrogen malonate moieties by only one short hydrogen bond [2.639 (3) Å].