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2-(p-Toluenesulfonyl)-3-(m-nitrophenyl)oxaziridine

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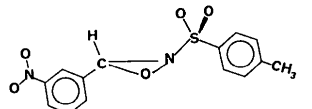
Abstract. $C_{14}H_{12}N_2O_5S$, FW 320·33, monoclinic, $P2_1/n$, $a = 10·591$ (4), $b = 10·462$ (4), $c = 13·604$ (4) Å, $\beta = 105·67$ (3)°, $V = 1451·3$ (8) Å^3, $Z = 4$, $d_c = 1·465$ g cm^{-3}. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1983 reflexions led to a final R of 0·069. The p-toluenesulfonyl and m-nitrophenyl groups are *trans* with respect to the oxaziridine ring.

Introduction. Oxaziridines are of considerable interest because of the unusual heterocyclic ring system; however, thermal rearrangement to amides and nitrones has hindered their investigation. Stable oxaziridines have been restricted to those compounds with C directly attached to the ring N atom (Schmitz, 1963; Emmons, 1976; Spence, Taylor & Buchardt, 1970; Ono, Splitter & Calvin, 1973). Procedures have been developed for the assignment of configuration of oxaziridines utilizing proton and ^{13}C NMR data (Jerina, Boyd, Paolillo & Becker, 1970; Jennings, Boyd, Watson, Becker, Bradley & Jerina, 1972; Cannon, Daly, Silverton, Boyd & Jerina, 1972). Recently, the synthesis of a new class of thermally-stable N-sulfonyloxaziridines has been reported (Davis, Nadir & Kluger, 1977; Davis & Nadir, 1977). Proton and ^{13}C NMR data suggest these compounds should have the Z configuration; however, it can be argued that the interpretation of these data may be complicated by the electron-attracting N-sulfonyl group. We report that the title compound (I) has the E configuration in the solid state.



(I)

A crystal of dimensions 0·34 × 0·34 × 0·16 mm was used to collect intensity data on a Syntex $P2_1$ diffractometer system by the $\theta/2\theta$ scanning technique using a variable scan speed with Cu $K\alpha$ radiation ($\lambda = 1·54178$ Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group $P2_1/n$. 1983 independent reflexions were measured, and Lorentz and polarization

Table 1. *Positional parameters* (× 10^4, *for* H × 10^3)

	x	y	z
S(1)	1425 (1)	9614 (1)	6902 (1)
O(1)	445 (3)	10601 (4)	6672 (3)
O(2)	1085 (4)	8362 (4)	6500 (3)
O(3)	3604 (4)	9292 (3)	6328 (3)
O(4)	2420 (4)	12763 (4)	1645 (3)
O(5)	1276 (4)	11107 (4)	1792 (3)
N(1)	2651 (4)	10282 (4)	6450 (3)
N(2)	2140 (4)	11887 (4)	2155 (3)
C(1)	2701 (5)	9818 (5)	5462 (4)
C(2)	3180 (4)	10744 (4)	4818 (4)
C(3)	2515 (4)	10829 (4)	3811 (4)
C(4)	2892 (4)	11762 (5)	3226 (3)
C(5)	3905 (5)	12618 (5)	3629 (4)
C(6)	4558 (5)	12489 (5)	4634 (4)
C(7)	4201 (5)	11572 (5)	5240 (4)
C(8)	2191 (4)	9566 (4)	8194 (4)
C(9)	2870 (5)	8476 (5)	8639 (4)
C(10)	3532 (5)	8467 (5)	9656 (4)
C(11)	3533 (5)	9529 (5)	10271 (4)
C(12)	2870 (5)	10620 (5)	9807 (4)
C(13)	2207 (5)	10655 (5)	8791 (4)
C(14)	4230 (5)	9510 (6)	11370 (4)
H(1)	192 (5)	932 (5)	508 (4)
H(3)	170 (4)	1034 (5)	352 (3)
H(5)	432 (5)	1314 (5)	311 (4)
H(6)	522 (4)	1299 (5)	492 (4)
H(7)	467 (4)	1146 (4)	588 (3)
H(9)	292 (6)	788 (6)	815 (5)
H(10)	418 (6)	780 (6)	1002 (5)
H(12)	296 (5)	1133 (6)	1032 (4)
H(13)	152 (7)	1127 (7)	834 (5)
H(14*a*)	385 (5)	944 (5)	1186 (4)
H(14*b*)	474 (6)	884 (7)	1159 (5)
H(14*c*)	471 (6)	1016 (6)	1162 (5)

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Table 2. *Interatomic distances* (Å) *and angles* (°)

S(1)—O(1)	1·438 (4)	C(6)—C(7)	1·382 (8)
S(1)—O(2)	1·428 (4)	C(7)—C(2)	1·383 (7)
S(1)—N(1)	1·728 (4)	C(4)—N(2)	1·465 (5)
S(1)—C(8)	1·726 (5)	N(2)—O(4)	1·233 (6)
N(1)—O(3)	1·487 (6)	N(2)—O(5)	1·226 (6)
N(1)—C(1)	1·443 (6)	C(8)—C(9)	1·396 (7)
C(1)—O(3)	1·414 (5)	C(9)—C(10)	1·372 (7)
C(1)—C(2)	1·486 (7)	C(10)—C(11)	1·390 (8)
C(2)—C(3)	1·363 (6)	C(11)—C(12)	1·399 (7)
C(3)—C(4)	1·384 (7)	C(12)—C(13)	1·371 (7)
C(4)—C(5)	1·391 (6)	C(13)—C(8)	1·397 (7)
C(5)—C(6)	1·363 (7)	C(11)—C(14)	1·479 (7)
C(1)—H(1)	1·00 (4)	C(10)—H(10)	1·01 (6)
C(3)—H(3)	0·99 (4)	C(12)—H(12)	1·01 (6)
C(5)—H(5)	1·07 (6)	C(13)—H(13)	1·04 (7)
C(6)—H(6)	0·88 (4)	C(14)—H(14*a*)	0·87 (6)
C(7)—H(7)	0·88 (4)	C(14)—H(14*b*)	0·89 (7)
C(9)—H(9)	0·92 (7)	C(14)—H(14*c*)	0·86 (6)

O(1)S(1)O(2)	118·9 (3)	C(3)C(4)N(2)	118·1 (3)
O(1)S(1)N(1)	101·5 (3)	C(5)C(4)N(2)	119·2 (4)
O(2)S(1)C(8)	111·4 (3)	C(4)N(2)O(4)	118·5 (4)
N(1)S(1)C(8)	100·5 (3)	C(4)N(2)O(5)	119·2 (4)
S(1)N(1)O(3)	110·8 (3)	O(5)N(2)O(4)	122·3 (4)
N(1)O(3)C(1)	59·6 (3)	C(7)C(2)C(1)	121·1 (4)
O(3)C(1)N(1)	62·7 (3)	S(1)C(8)C(9)	120·7 (4)
C(1)N(1)O(3)	57·7 (3)	S(1)C(8)C(13)	119·8 (4)
N(1)C(1)C(2)	115·7 (4)	C(8)C(9)C(10)	120·4 (5)
C(1)C(2)C(3)	118·0 (4)	C(9)C(10)C(11)	121·2 (5)
C(2)C(3)C(4)	118·2 (4)	C(10)C(11)C(12)	117·6 (5)
C(3)C(4)C(5)	122·6 (4)	C(11)C(12)C(13)	122·3 (5)
C(4)C(5)C(6)	117·4 (4)	C(12)C(13)C(8)	119·1 (5)
C(5)C(6)C(7)	121·4 (5)	C(13)C(8)C(9)	119·4 (4)
C(6)C(7)C(2)	119·7 (4)	C(10)C(11)C(14)	121·1 (5)
C(7)C(2)C(3)	120·7 (4)	C(12)C(11)C(14)	121·3 (5)
O(1)S(1)C(8)	110·8 (3)	S(1)N(1)C(1)	114·6 (3)
O(2)S(1)N(1)	111·8 (3)		

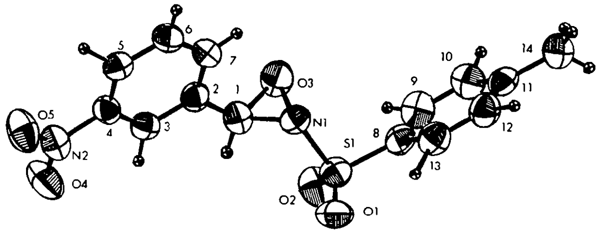

Fig. 1. *ORTEP* drawing of the title compound. Thermal ellipsoids are presented at the 50% probability level while H atoms are represented by spheres of arbitrary radius.

corrections were applied. Reflexions with negative measured intensities were assigned the value zero while others with $I < 2\sigma(I)$ were assigned the value $\sigma(I)$. No absorption corrections were made. The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 400 $|E|$ values greater than 1·30. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of a 14-atom fragment. Alternate least-squares refinements and difference Fourier calculations yielded the coordinates of the missing six C and 12 H atoms. Least-squares refinement yielded a final R of 0·069 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the least-squares refinement was $w(|F_o| - |F_c|)^2$ where $w = [1/\sigma(F_o)]^2$ was determined from counting statistics. H atom thermal parameters were refined isotropically.

A final difference map showed no peak larger than 0·4 e Å^{-3}, except for a peak of 0·66 e Å^{-3} near the S atom. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1 while interatomic distances and angles are presented in Table 2.*

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of the title compound. The *p*-toluenesulfonyl and *m*-nitrophenyl groups are *trans* with respect to the oxaziridine ring. The two sulfonyl O atoms and N(1) are symmetrically oriented with respect to the toluene ring, as indicated by the torsion angles O(2)S(1)-C(8)C(9) = 26°, O(1)S(1)C(8)C(13) = −24°, N(1)S(1)C(8)C(13) = 93° and N(1)S(1)C(8)C(9) = −93°. The nitrogen lone pair and the bisector of the two sulfonyl O atoms are rotated approximately 120° with respect to each other about the N—S bond. In *N*,*N*,*N'*,*N'*-tetramethylsulfamide (Jordan, Smith, Lohr & Lipscomb, 1963), *p*-methoxybenzenesulfonyl-*p*-anisidine (Pokrywiecki, Weeks & Duax, 1973*a*) and *p*-methoxybenzenesulfonyl-*N*-isopropyl-*p*-anisidine (Pokrywiecki, Weeks & Duax, 1973*b*) the lone pairs of the N atoms lie between the two sulfonyl O atoms. The flattening of the N geometry and the shortening of the S—N bond to an average distance of 1·628 (4) Å can be interpreted as arising from lone-pair–*d*-orbital interactions. This observation has been used to rationalize the retention of configuration in α-sulfonyl carbanions (Cram, 1965); however, the question of a planar or pyramidal transition state in the carbanion system has not been resolved conclusively (Oae, 1977). The N—S distance of 1·728 (4) Å and other distances and angles associated with the S atom in the oxaziridine compound more closely resemble parameters reported for sulfones. The C(1)N(1)O(3) angle of 57·7° makes it energetically unfavorable for the N atom to achieve a pseudoplanar conformation which would favor lone-pair–*d*-orbital interactions. Electron-repulsion interactions are more significant in the determination of the conformation about the S—N bond.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33537 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl 3-Cyano-6-methyl-2-oxo-4-(3-pyridyl)-3,4-dihydro-5-pyridinecarboxylate

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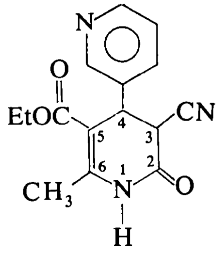
Abstract. $C_{15}H_{15}N_3O_3$, monoclinic, $P2_1/n$, a = 9·789 (2), b = 8·425 (2), c = 18·386 (3) Å, β = 103·70 (2)°, V = 1473·4 Å^3, Z = 4, D_c = 1·28 g cm^{-3}, μ(Cu $K\alpha$) = 7·7 cm^{-1}. The structure was solved by direct methods and refined to an R value of 0·058 for 1808 unique reflections. The investigated molecule exists in the keto form in the solid state. An intermolecular hydrogen bond, N(1)—H(1)···N(2*) = 2·866 (4) Å, is present.

Introduction. The structure of the title compound has been determined as a part of a study of potentially cytostatic compounds (Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1977*a*,*b*) prepared by Nantka-Namirski & Balicki (1978).



The crystals were obtained by the action of ethyl acetoacetate on 2-cyano-3-(3-pyridyl)acrylamide (Nantka-Namirski & Balicki, 1972), and crystallized from ethyl alcohol.

A crystal of dimensions 0·3 × 0·25 × 0·28 mm was used for the collection of the data on a four-circle automated CAD-4 diffractometer (SLAF & BS, Kraków, Poland). Intensities were measured by the $\omega/2\theta$ scan technique up to $2\theta_{\max}$ = 120°, with graphite-monochromated Cu $K\alpha$ radiation.

1808 reflections with intensities $I > 2\sigma(I)$ were used for the structure determination and refinement. The structure was solved by direct methods using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and refined by the full-matrix least-squares method with anisotropic thermal parameters to an R value of 0·058 (unit weights). Fractional coordinates for the non-hydrogen atoms are given in Table 1. The hydrogen atom coordinates were located from Fourier difference syntheses. Hydrogen atoms for the methyl and ethoxy groups were calculated. All hydrogen atoms were refined with a damping factor of 0·1. The refinement process was terminated when the maximum shift/error