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Structure of 2-(*p*-Bromophenoxy)-*N*-ethyl-2-phenyl-*N*-(*p*-tolyl)ethanesulfonamide, $C_{23}H_{24}BrNO_3S$

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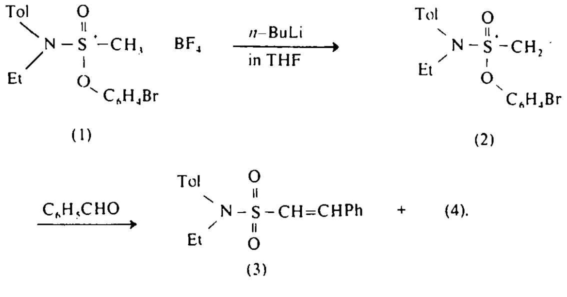
Abstract. $M_r = 473{\cdot}9$, triclinic, $P\bar{1}$, $a = 11{\cdot}560\,(2)$, $b = 10{\cdot}356\,(1)$, $c = 10{\cdot}549\,(1)$ Å, $\alpha = 90{\cdot}15\,(1)$, $\beta = 111{\cdot}94\,(1)$, $\gamma = 107{\cdot}92\,(1)°$, $V = 1104{\cdot}7$ Å^3, $Z = 2$, D_m(flotation in benzene/carbon tetrachloride) = $1{\cdot}42\,(1)$, $D_x = 1{\cdot}43$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo }K\alpha) = 4{\cdot}12$ mm^{-1}, $F(000) = 488$, $T = 296$ K, $R = 0{\cdot}0526$ for 2916 diffractometer-measured reflections (at 293 K). The compound is a racemate in which two enantiomers are related by a center of symmetry. The S—N(sp^2) and S—C(sp^3) bond lengths are 1·618 (5) and 1·779 (6) Å, respectively. This investigation suggests that the reaction of aminoaryl-oxyoxosulfonium ylide and benzaldehyde involves a four-membered-ring intermediate (C—C—S—O).

Introduction. After the original work by Corey & Chaykovsky (1965), several kinds of reactions of sulfur ylides have been reported. These ylides are now used as methylene transfer reagents (Chalkley, Snodin, Stevens & Whiting, 1970, 1978). However, no report has yet been published that sulfur ylides react with carbonyl compounds to give unsaturated sulfones *via* four-membered cyclic intermediates.

The authors have recently found that the reaction of aminoaryl-oxyoxosulfonium ylide (2) with benzaldehyde gave two compounds, α,β-unsaturated sulfonamide (3) and a compound (4) which could not be identified by spectroscopic methods (Okuma, Tanaka & Ohta, 1981) (Tol is *p*-tolyl).



To explain the reaction mechanism, the authors have undertaken the structure determination of (4) by X-ray crystallographic analysis.

Experimental. Colorless transparent needle crystals from EtOH solution by slow evaporation at room temperature; cell dimensions by least-squares refinement of the 2θ values of 176 reflections with $2\theta = 40$–$53°$; crystal $0{\cdot}4 \times 0{\cdot}5 \times 2{\cdot}1$ mm, Rigaku–Denki AFC-3 automated diffractometer, $2\theta_{\text{max}} = 59{\cdot}7°$, ω–2θ scan techniques; of 5864 unique reflections ($-11 \le h \le 11$, $0 \le k \le 14$, $-14 \le l \le 14$), 2916 had $|F_o| > 5\sigma(F_o)$; three reflections (300, 010, 002) monitored after every 50 reflections showed less than 0·9% intensity fluctuation throughout data collection; intensities corrected for Lorentz and polarization factors but not for absorption or extinction; structure solved by Patterson method; block-diagonal least squares (*HBLSVI*: Ashida, 1981), $\sum w(|F_o| - k|F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}0366|F_o| + 0{\cdot}00049|F_o|^2]^{-1}$; positions of H atoms except for those of the methyl and primary amino group were calculated assuming 1·09 Å for each C—H bond; their positional and isotropic thermal parameters (fixed to 3·0 Å^2) were not included in the refinement; final $R = 0{\cdot}053$ ($wR = 0{\cdot}060$) for 2916 reflections, $S = 0{\cdot}478$ for 263 (nine for each non-H atom and two overall scale and thermal parameters); mean and max. Δ/σ values in final refinement cycle 0·27 and 1·3 [z of C(21)]; max. and min. heights on final difference Fourier maps 0·14 and $-0{\cdot}15$ e Å^{-3}, no other significant feature observed; atomic scattering factors from *International Tables for X-ray Crystallography* (1962); HITAC-M200H computer at the computer room, the National Defense Academy.

The distribution of $|E_h|$ suggested that the space group is $P1$ at the early stage of refinement, but the bond lengths and angles, and the form of the thermal ellipsoids showed $P\bar{1}$ symmetry. Accordingly $P\bar{1}$ was applied for this crystal.

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Discussion. The final atomic coordinates with their estimated standard deviations are given in Table 1.* The numbering scheme is presented in Fig. 1. The bond distances and angles are shown in Table 2.

The average C—C bond length observed in the benzene rings is 1·382 Å. The length of the S—N(sp^2) bond is 1·618 (5) Å, which lies within the range of values [1·581 (10)–1·623 (7) Å] previously reported (Cameron, Hair & Morris, 1973, 1974; Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Jordan, Smith, Lohr & Lipscomb, 1963). The S—C(sp^3) bond length [1·779 (6) Å] is in good agreement with the other experimental data [1·761 (10)–1·770 (7) Å] (Wheatley, 1954; Bullough & Wheatley, 1957; Truter, 1962).

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$), *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j B_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}
C(1)	5013 (5)	2419 (5)	4123 (6)	360 (17)
C(2)	5386 (5)	1338 (6)	3881 (5)	352 (17)
C(3)	4429 (5)	76 (5)	3294 (6)	324 (16)
C(4)	3104 (5)	−92 (5)	2936 (5)	288 (15)
C(5)	2738 (5)	1005 (6)	3203 (6)	394 (19)
C(6)	3704 (6)	2264 (6)	3807 (7)	468 (22)
C(7)	824 (5)	−1638 (5)	1808 (5)	284 (15)
C(8)	311 (5)	−1877 (5)	2935 (5)	305 (15)
C(9)	646 (6)	−2797 (6)	3865 (6)	426 (20)
C(10)	129 (7)	−3027 (7)	4858 (6)	494 (23)
C(11)	−734 (7)	−2413 (7)	4941 (6)	497 (23)
C(12)	−1051 (7)	−1496 (7)	4042 (7)	477 (23)
C(13)	−528 (6)	−1236 (5)	3048 (6)	370 (18)
C(14)	198 (5)	−2919 (5)	750 (5)	323 (17)
C(15)	2412 (5)	−3585 (5)	−396 (5)	304 (16)
C(16)	2347 (5)	−4339 (5)	−1520 (6)	349 (17)
C(17)	2842 (5)	−5425 (6)	−1310 (6)	387 (19)
C(18)	3384 (5)	−5760 (5)	−9 (6)	352 (17)
C(19)	3465 (6)	−4978 (6)	1108 (6)	409 (20)
C(20)	2984 (6)	−3887 (6)	916 (6)	366 (18)
C(21)	3866 (8)	−6999 (6)	209 (9)	575 (28)
C(22)	2856 (6)	−1046 (5)	−354 (6)	370 (18)
C(23)	3254 (7)	−720 (7)	−1545 (8)	530 (25)
Br	6343 (1)	4153 (1)	4897 (1)	650 (2)
S	384 (1)	−2709 (1)	−844 (1)	275 (3)
O(1)	2240 (3)	−1383 (3)	2316 (4)	337 (11)
O(2)	112 (4)	−1477 (4)	−1272 (4)	409 (14)
O(3)	−405 (4)	−3984 (4)	−1718 (4)	378 (12)
N	1903 (4)	−2458 (4)	−624 (5)	325 (14)

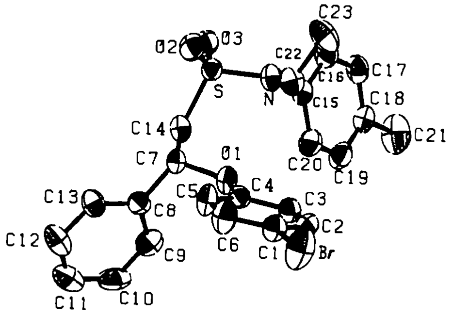

Fig. 1. Molecular structure of the title compound, with atom labeling. Thermal ellipsoids are at the 50% probability level (*ORTEP*II, Johnson, 1976).

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·373 (8)	C(1)—C(6)	1·378 (10)
C(1)—Br	1·900 (6)	C(2)—C(3)	1·382 (8)
C(3)—C(4)	1·387 (8)	C(4)—C(5)	1·391 (9)
C(4)—O(1)	1·377 (7)	C(5)—C(6)	1·386 (10)
C(7)—C(8)	1·505 (8)	C(7)—C(14)	1·526 (8)
C(7)—O(1)	1·454 (7)	C(8)—C(9)	1·403 (9)
C(8)—C(13)	1·371 (9)	C(9)—C(10)	1·375 (10)
C(10)—C(11)	1·367 (11)	C(11)—C(12)	1·375 (11)
C(12)—C(13)	1·383 (10)	C(14)—S	1·779 (6)
C(15)—C(16)	1·384 (8)	C(15)—C(20)	1·378 (8)
C(15)—N	1·444 (7)	C(16)—C(17)	1·394 (9)
C(17)—C(18)	1·375 (9)	C(18)—C(19)	1·386 (9)
C(18)—C(21)	1·535 (11)	C(19)—C(20)	1·389 (9)
C(22)—C(23)	1·497 (10)	C(22)—N	1·485 (8)
S—O(2)	1·440 (5)	S—O(3)	1·432 (4)
S—N	1·618 (5)		
C(2)—C(1)—C(6)	121·2 (6)	C(2)—C(1)—Br	118·5 (5)
C(6)—C(1)—Br	120·3 (5)	C(1)—C(2)—C(3)	119·3 (6)
C(2)—C(3)—C(4)	120·4 (5)	C(3)—C(4)—C(5)	119·8 (5)
C(3)—C(4)—O(1)	115·1 (5)	C(5)—C(4)—O(1)	125·1 (5)
C(4)—C(5)—C(6)	119·5 (6)	C(1)—C(6)—C(5)	119·8 (7)
C(8)—C(7)—C(14)	110·1 (5)	C(8)—C(7)—O(1)	112·5 (4)
C(14)—C(7)—O(1)	105·1 (4)	C(7)—C(8)—C(9)	120·6 (5)
C(7)—C(8)—C(13)	120·8 (5)	C(9)—C(8)—C(13)	118·6 (6)
C(8)—C(9)—C(10)	119·3 (6)	C(9)—C(10)—C(11)	121·8 (7)
C(10)—C(11)—C(12)	118·9 (8)	C(11)—C(12)—C(13)	120·2 (7)
C(8)—C(13)—C(12)	121·1 (6)	C(7)—C(14)—S	116·2 (4)
C(16)—C(15)—C(20)	120·3 (5)	C(16)—C(15)—N	118·8 (5)
C(20)—C(15)—N	120·9 (5)	C(15)—C(16)—C(17)	119·2 (6)
C(16)—C(17)—C(18)	121·1 (6)	C(17)—C(18)—C(19)	119·0 (6)
C(17)—C(18)—C(21)	120·9 (6)	C(19)—C(18)—C(21)	120·1 (6)
C(18)—C(19)—C(20)	120·6 (6)	C(15)—C(20)—C(19)	119·8 (6)
C(23)—C(22)—N	111·0 (5)	C(14)—S—O(2)	107·1 (3)
C(14)—S—O(3)	106·2 (3)	C(14)—S—N	110·2 (3)
O(2)—S—O(3)	119·4 (3)	O(2)—S—N	106·6 (3)
O(3)—S—N	107·3 (3)	C(4)—O(1)—C(7)	119·4 (4)
C(15)—N—C(22)	118·5 (5)	C(15)—N—S	119·8 (4)
C(22)—N—S	120·5 (4)		

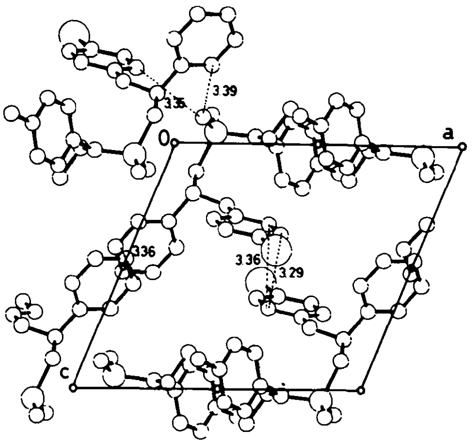

Fig. 2. Crystal structure projected along **b** (distances in Å; e.s.d.'s ~0·01 Å).

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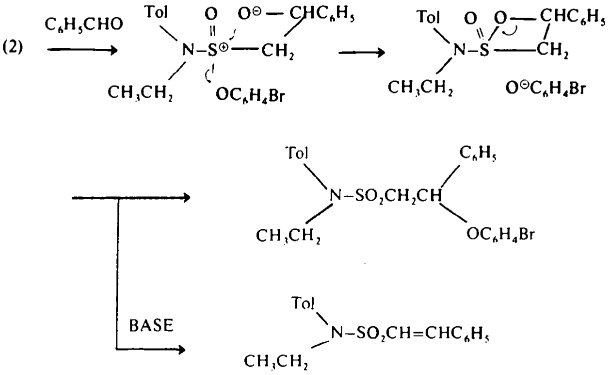
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39889 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The O(2)—S—O(3) bond angle is 119·4 (3)° in agreement with that in related compounds (Kálmán, 1967; Kálmán *et al.*, 1971; Cameron *et al.*, 1973, 1974).

The molecular packing is shown in Fig. 2. The molecule is a racemate and two enantiomers are related by a center of symmetry. The shortest intermolecular contact of 3·29 Å is seen between C(2) and C(3). The molecules are held together by van der Waals forces in the crystal.

Compound (4) is identified as the title compound. Thus the reaction mechanism can be deduced as follows.



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Structure of 2-[5'-Aminocyclohexanespiro-4'-(4'*H*-imidazol)-2'-yl]-1-methylpyridinium Iodide, $C_{14}H_{19}N_4^+.I^-$

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Abstract. $M_r = 370·235$, tetragonal, $I4_1/a$, $a = 31·475$ (6), $c = 6·446$ (1) Å, $V = 6385·64$ (5) Å^3, $Z = 16$, $D_x = 1·5404$ (3) g cm^{-3}, $F(000) = 2944$, Mo $K\alpha$, $\mu = 19·765$ cm^{-1}, $\lambda = 0·7107$ Å, room temperature, $R = 0·024$ for 1643 unique observed reflections. The reaction of 5'-amino-2'-(2-pyridyl)cyclohexanespiro-4'-4'*H*-imidazole with methyl iodide takes place at the pyridine N atom giving the pyridinium salt. The pyridine ring is planar, the five-membered ring is near planar and the cyclohexane ring adopts a slightly flattened chair conformation. The molecules are held together by van der Waals contacts and N—H···N hydrogen bonds.

Introduction. The reaction of 5'-amino-2'-(2-pyridyl)-cyclohexanespiro-4'-4'*H*-imidazole, previously studied by X-ray diffraction (Avendaño, Ramos, Bellanato, Smith-Verdier, Florencio & García-Blanco, 1984), with methyl iodide in acetonitrile (Avendaño & Ramos, 1984) afforded crystals of the title compound. Among all possible alkylated products on any of the four N atoms which are present, this study shows that the reaction takes place at the pyridine N atom giving the pyridinium salt.

Experimental. Crystal 0·10 × 0·20 × 0·25 mm. D_m not determined. Unit-cell parameters determined by least-

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