

(–)-Tosyloxylupinane *p*-Toluenesulfonate,* C₁₇H₂₆NO₃S⁺·C₇H₇O₃S[–]

BY ANNA E. KOZIOL

*Department of Crystallography, Institute of Chemistry, M. Curie-Skłodowska University, pl. M.C. Skłodowskiej 3,
20-031 Lublin, Poland*

AND HALINA PODKOWIŃSKA

Department of Chemistry, Academy of Economics, ul. Marchlewskiego 146, 60-967 Poznań, Poland

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Abstract. $M_r = 495.7$, monoclinic, $P2_1$, $a = 8.226$ (1), $b = 13.857$ (3), $c = 11.300$ (3) Å, $\beta = 99.90$ (2)°, $V = 1268.8$ (5) Å³, $Z = 2$, $D_m = 1.28$ (floatation in xylene/CCl₄), $D_x = 1.30$ Mg m^{–3}, $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 2.16$ mm^{–1}, $F(000) = 528$, room temperature. The final R value is 0.049 for 1569 independent reflexions and 297 parameters. The tosyloxylupinanium cation has the *trans*-quinolizidine system with the –CH₂OTs group axially oriented. The interionic N–H···O hydrogen bond forms a cation–anion pair which is the structural element in the crystal.

Introduction. The tosyl group is an excellent leaving group so tosyl esters are commonly used in *trans*-esterification and interchange reactions.

Galinovskiy & Nesvadba (1954) have reported that 1,5-*endo*-methylenequinolizidinium *p*-toluenesulfonate was obtained when the tosyl ester of lupinine (tosyloxylupinane) was heated under reduced pressure. There is considerable stress in the azetidene ring of the 1,5-*endo*-methylenequinolizidinium cation (Huber, 1969) but nevertheless the cyclization reaction is almost completely quantitative.

This X-ray study was carried out to investigate the conformation of the tosyloxylupinanium cation.

Experimental. Tosyloxylupinane was obtained during the esterification of lupinine with tosyl chloride in anhydrous acetone (Edwards, Fodor & Marion, 1966; Podkowińska & Wiewiórowski, 1967). This compound was then treated with a solution of *p*-toluenesulfonic acid and evaporated to dryness. Tosyloxylupinane *p*-toluenesulfonate (m.p. 432 K) was recrystallized from anhydrous chloroform.

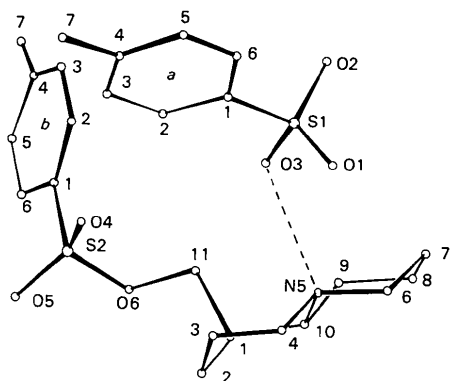
Crystal 0.15 × 0.3 × 0.4 mm, Syntex P2₁ diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters by least squares from 2θ values of 14 reflexions centered on the diffractometer; θ – 2θ scan,

$2\theta_{\text{max}} = 115^\circ$, hkl range: h 0–8, k 0–15, l –12–12. Scan rate dependent on the intensity of reflexion and varied from 1.95 to 29.3° min^{–1}, no stationary background measurements made; background and integrated intensity for each reflexion calculated by the Lehmann & Larsen (1974) profile-analysis method using PRAN (Jaskolski, 1979); two standard reflexions (102, 040) monitored every 100 showed intensity variation <3.5%. 1925 reflexions recorded, 1575 considered observed [$F/\sigma(F) \geq 4.0$], $R_1(F) = R_2(F) = 0.010$ (Syntex XTL). Direct methods (Germain, Main & Woolfson, 1971); E map based on the set with highest combined figure of merit yielded positions of the cation S atom and the SO₃ group of the anion, remaining non-hydrogen atoms located on subsequent Fourier maps, H atoms positioned geometrically; full-matrix least-squares refinement [minimizing $\sum w(\Delta F)^2$], anisotropic thermal parameters for the non-hydrogen atoms, $B_{\text{iso}} = 6.0$ Å² for H atoms at fixed positions). Atomic scattering factors, with anomalous-dispersion correction terms for S, N and O, from *International Tables for X-ray Crystallography* (1974); final $R = 0.049$, $R_w = 0.055$ and $S = 5.62$ [$w = 1/\sigma^2(F)$] for 1569 reflexions [six reflexions with $\Delta(F)/\sigma(F) > 30$ omitted in late stages of the refinement], maximum shift/e.s.d. = 0.15, maximum electron density peak in final difference Fourier map = 0.25 e Å^{–3}. Syntex XTL (1973) structure determination system.

Discussion. The final atomic parameters for non-hydrogen atoms are given in Table 1.† Fig. 1 shows the conformation of the title compound and atom-numbering scheme. Bond lengths are given in Table 2. Table 3 lists torsion angles of the tosyloxylupinanium cation.

† Tables of structure factors, final H-atom positions, anisotropic temperature factors and valence angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38536 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* 1-(Tosyloxymethyl)perhydroquinolizinium *p*-toluenesulfonate.

Fig. 1. The conformation of tosyloxylupinane *p*-toluenesulfonate.Table 3. Some torsion angles ($^{\circ}$) in the cation

O(6)–C(11)–C(1)–C(2)	–59.6 (7)	C(10)–C(1)–C(2)–C(3)	56.9 (7)
O(6)–C(11)–C(1)–C(10)	173.6 (6)	N(5)–C(6)–C(7)–C(8)	–56.0 (7)
C(1)–C(2)–C(3)–C(4)	–59.3 (7)	C(6)–C(7)–C(8)–C(9)	53.0 (8)
C(2)–C(3)–C(4)–N(5)	57.2 (9)	C(7)–C(8)–C(9)–C(10)	–55.2 (9)
C(3)–C(4)–N(5)–C(10)	–52.9 (7)	C(8)–C(9)–C(10)–N(5)	58.3 (6)
C(4)–N(5)–C(10)–C(1)	49.5 (6)	C(9)–C(10)–N(5)–C(6)	–58.8 (6)
N(5)–C(10)–C(1)–C(2)	–51.7 (7)	C(10)–N(5)–C(6)–C(7)	59.1 (8)

The cation consists of the *trans*-quinolizidine nucleus in the chair–chair conformation and the ester tosyl group axially oriented. The geometry of the quinolizidine resembles those found in lupinine.HCl (Kozioł, Gdaniec & Kosturkiewicz, 1980) and iodolupinane.HClO₄ (Kozioł & Kosturkiewicz, 1980). The conformation about the C(1)–C(11) bond is the same as in the iodolupinanium cation, the O(6) atom being *trans*–*gauche* (*ap*,–*sc*); thus no intramolecular hydrogen bond could be realized.

The bond lengths and angles for the tosyl residue and the *p*-toluenesulfonate anion are not significantly different from those found earlier (Altona & Sundaralingam, 1972; Wiczorek, 1980; Huber, 1969; Nakamura & Itaka, 1978). Both benzene rings are planar and no stacking between them is observed in the crystal [interplanar angle is 88.1 (8) $^{\circ}$].

The N(5)–H(N5)⋯O(3) hydrogen bond [N(5)⋯O(3) 2.808 (6) Å] links the cation and the anion to form the ionic pair. The other short interionic contact is N(5)⋯O(1) 3.193 (7) Å.

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Table 1. Coordinates for non-hydrogen atoms ($\times 10^4$) and isotropic *B* values ($B_{\text{iso}} = \frac{1}{3} \sum B_{ii}$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
S(1)	3427 (2)	2950	5579 (2)	4.7 (1)
S(2)	–170 (3)	943 (2)	1198 (2)	6.7 (2)
O(1)	2468 (6)	3570 (4)	6251 (4)	6.3 (5)
O(2)	4987 (5)	2634 (4)	6285 (4)	5.5 (4)
O(3)	2423 (5)	2146 (3)	4994 (4)	5.2 (4)
O(4)	523 (7)	1889 (4)	1506 (5)	7.7 (6)
O(5)	–1388 (7)	838 (7)	153 (4)	10.4 (8)
O(6)	–988 (6)	543 (4)	2262 (4)	7.0 (5)
C(1) <i>a</i>	3919 (7)	3674 (4)	4385 (6)	3.8 (5)
C(2) <i>a</i>	3335 (8)	3472 (5)	3210 (6)	4.7 (6)
C(3) <i>a</i>	3717 (8)	4058 (6)	2324 (6)	5.3 (6)
C(4) <i>a</i>	4709 (8)	4883 (5)	2616 (6)	5.2 (6)
C(5) <i>a</i>	5262 (8)	5074 (5)	3809 (6)	4.7 (6)
C(6) <i>a</i>	4894 (7)	4491 (5)	4695 (6)	4.1 (5)
C(7) <i>a</i>	5059 (11)	5521 (7)	1619 (7)	7.8 (9)
C(1)	–1867 (7)	1052 (5)	4046 (5)	4.2 (5)
C(2)	–2864 (8)	1891 (6)	3410 (7)	5.6 (7)
C(3)	–1947 (9)	2846 (6)	3673 (7)	5.7 (7)
C(4)	–1636 (8)	3026 (6)	4993 (7)	5.6 (6)
N(5)	–682 (5)	2228 (4)	5703 (4)	4.1 (4)
C(6)	–507 (8)	2420 (6)	7015 (6)	5.7 (7)
C(7)	502 (10)	1698 (6)	7732 (6)	6.3 (8)
C(8)	–158 (9)	678 (6)	7460 (6)	6.3 (7)
C(9)	–381 (8)	488 (5)	6119 (6)	4.9 (6)
C(10)	–1470 (7)	1239 (5)	5405 (5)	4.1 (5)
C(11)	–358 (8)	797 (6)	3484 (5)	4.7 (6)
C(1) <i>b</i>	1433 (8)	128 (6)	1100 (6)	5.1 (6)
C(2) <i>b</i>	3007 (10)	348 (6)	1642 (7)	6.5 (8)
C(3) <i>b</i>	4279 (10)	–296 (8)	1553 (8)	7.7 (9)
C(4) <i>b</i>	3989 (12)	–1116 (6)	920 (7)	8.0 (9)
C(5) <i>b</i>	2425 (13)	–1349 (7)	411 (8)	8.6 (10)
C(6) <i>b</i>	1105 (11)	–719 (7)	477 (7)	7.4 (9)
C(7) <i>b</i>	5548 (19)	–1761 (10)	819 (9)	13.9 (16)

Table 2. Bond lengths (Å)

Cation			
C(1)–C(2)	1.529 (10)	C(11)–O(6)	1.432 (7)
C(2)–C(3)	1.527 (11)	O(6)–S(2)	1.577 (5)
C(3)–C(4)	1.490 (11)	S(2)–O(5)	1.418 (5)
C(4)–N(5)	1.504 (9)	S(2)–O(4)	1.447 (6)
N(5)–C(6)	1.489 (8)	S(2)–C(1) <i>b</i>	1.755 (8)
N(5)–C(10)	1.529 (8)	C(1) <i>b</i> –C(2) <i>b</i>	1.368 (11)
C(6)–C(7)	1.454 (11)	C(2) <i>b</i> –C(3) <i>b</i>	1.392 (13)
C(7)–C(8)	1.526 (12)	C(3) <i>b</i> –C(4) <i>b</i>	1.342 (13)
C(8)–C(9)	1.518 (9)	C(4) <i>b</i> –C(7) <i>b</i>	1.584 (18)
C(9)–C(10)	1.511 (9)	C(4) <i>b</i> –C(5) <i>b</i>	1.354 (14)
C(10)–C(1)	1.536 (8)	C(5) <i>b</i> –C(6) <i>b</i>	1.405 (14)
C(1)–C(11)	1.530 (9)	C(6) <i>b</i> –C(1) <i>b</i>	1.370 (12)
Anion			
S(1)–O(1)	1.465 (5)	C(3) <i>a</i> –C(4) <i>a</i>	1.410 (10)
S(1)–O(2)	1.457 (5)	C(4) <i>a</i> –C(7) <i>a</i>	1.498 (11)
S(1)–O(3)	1.474 (5)	C(4) <i>a</i> –C(5) <i>a</i>	1.372 (10)
S(1)–C(1) <i>a</i>	1.783 (6)	C(5) <i>a</i> –C(6) <i>a</i>	1.361 (9)
C(1) <i>a</i> –C(2) <i>a</i>	1.362 (9)	C(6) <i>a</i> –C(1) <i>a</i>	1.396 (9)
C(2) <i>a</i> –C(3) <i>a</i>	1.367 (10)		