

The Crystal Structure of 1,5-Endomethylenequinolizidinium *p*-Toluenesulphonate

BY CAROL SAUNDERSON HUBER

Division of Pure Chemistry, National Research Council of Canada, Ottawa 7, Canada

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The tosyl ester of the alkaloid lupinine cyclizes when heated, and the rearrangement product has been shown by a three-dimensional structure analysis to be 1,5-endomethylenequinolizidinium *p*-toluenesulphonate, $(C_{10}H_{18}N)^+(C_7H_7SO_3)^-$. The crystals are orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions $a = 12.88$, $b = 13.68$, $c = 9.19$ Å. The heavy-atom method was used to solve the structure, and refinement by block-diagonal least-squares techniques led to a final residual of 0.067 for 1793 observed reflexions. The two *trans*-fused six-membered rings comprising the quinolizidine ring system are in distorted chair forms, and the four-membered ring is puckered. The ions are arranged in pleated sheets, each positively charged region in one sheet facing a negatively charged region in an adjacent sheet.

Introduction

The tosyl ester of the alkaloid lupinine undergoes a cyclization reaction when heated to form a quaternary nitrogen salt (Galimovsky & Nesvadba, 1954). Two possible structures for the rearrangement product were suggested (Galimovsky & Nesvadba, 1954; Leonard, 1960); one structure incorporated a monomeric cation containing a four-membered ring [Fig. 1(a)], and the other a dimeric cation with an eight-membered ring [Fig. 1(b)]. This X-ray investigation was undertaken in order to distinguish between the two possibilities, and shows that the monomeric cation formulation, shown in Fig. 1(a), is correct. During the course of this analysis, osmometric determination of the apparent molecular weight of this compound, combined with infrared and nuclear magnetic resonance spectral evidence (Edwards, Fodor & Marion, 1966), have confirmed that the cation is monomeric and contains a four-membered ring.

Experimental

Crystal data

1,5-Endomethylenequinolizidinium *p*-toluenesulphonate, $(C_{10}H_{18}N)^+(C_7H_7SO_3)^-$.

$a = 12.88 \pm 0.01$, $b = 13.68 \pm 0.01$, $c = 9.19 \pm 0.01$ Å.

$U = 1620$ Å³, $F.W. = 323.45$.

$D_m = 1.32 \pm 0.01$ g.cm⁻³, $Z = 4$, $D_x = 1.326$ g.cm⁻³.

Space group: $P2_12_12_1$.

Crystal habit: colourless orthorhombic prisms.

Linear absorption coefficient: $\mu = 18.3$ cm⁻¹ (Cu $K\alpha$, $\lambda = 1.5418$ Å).

Specimens of the rearrangement product, crystallized from acetone solution, were kindly provided for this X-ray study by Professor G. Fodor.

The unit-cell dimensions were determined from precession photographs. The space group was determined from precession and Weissenberg photographs. Systematic absences are the $h00$ when h is odd, $0k0$ when k is odd, and $00l$ when l is odd.

Intensity data

Equi-inclination multiple-film Weissenberg photographs were taken with Cu $K\alpha$ radiation for the 0–8 layers about c and the 0–2 layers about a . The intensities were estimated by visual comparison with a calibrated intensity scale, and corrected for Lorentz and polarization factors, but not for absorption or extinction. The crystals used for data collection were block-shaped, with dimensions about $0.20 \times 0.25 \times 0.30$ mm, and were mounted with the longest dimension parallel to the rotation axis.

Data from the various layers were put on a common relative scale by comparing the F^2 values of reflexions common to each pair of intersecting layers. The absolute scale was established later by comparing observed and calculated structure amplitudes.

There were 1793 observed independent reflexions, about 86% of the total number theoretically accessible with Cu $K\alpha$ radiation. There were in addition 122 reflexions whose intensities were recorded as too weak to be measured. These were excluded from the structure determination and refinement, but were included in the final structure-factor calculation.

Structure determination and refinement

The coordinates of the sulphur atom were deduced from a sharpened ('point atoms at rest') three-dimen-

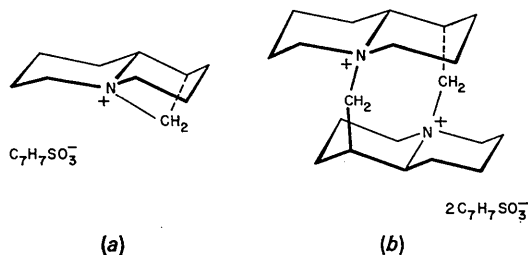


Fig. 1. Proposed structures for the rearrangement product.

sional Patterson synthesis. The positions of the other non-hydrogen atoms were obtained from one three-dimensional electron-density map, which was phased on the sulphur-atom contribution to the structure factors, and from a subsequent difference map.

The structure was refined by block-diagonal least-squares calculations, with two very similar programs. The one used initially was written by Dr G.A. Mair (Shoemaker, 1966) for the IBM 1620 computer. At a later stage the computations were transferred to an IBM system 360 computer, and a program written by Dr F.R. Ahmed (Shoemaker, 1966) was then used. Both programs minimize $\sum w(K|F_o| - |F_c|)^2$, and offer the possibility of refining some atoms anisotropically, using 3×3 and 6×6 matrices for each atom's positional and thermal parameters respectively, and other atoms isotropically. Schomaker's corrections (Hodgson & Rollett, 1963) are applied in both programs to the thermal vibration shifts.

A weighting scheme of the form

$$w = 1 / \left[1 + \left\{ \frac{K|F_o| - g}{f} \right\}^2 \right]$$

was used throughout the refinement. The parameters f and g were re-evaluated several times during the refinement so as to give approximately constant averages of $w(K|F_o| - |F_c|)^2$ for ranges of $|F_o|$, and their final values were $f = 8.0$ and $g = -2.0$ electrons.

Atomic scattering factor values were taken from *International Tables for X-ray Crystallography* (1962).

Four cycles of refinement using isotropic temperature factors reduced the R value

$$\left(= \frac{\sum |K|F_o| - |F_c||}{\sum K|F_o|} \right)$$

from 0.35 to 0.117.

Positions of the hydrogen atoms were then calculated where possible, assuming a carbon-hydrogen bond length of 0.95 Å. A difference map obtained at this stage confirmed the hydrogen positions which had been

calculated and revealed the positions of the three hydrogen atoms in the methyl group. It also indicated that the sulphur atom, one carbon atom [C(18)], and the oxygen atoms were vibrating anisotropically. Fig. 2 is a composite projection of this synthesis, showing the hydrogen atoms with peak heights between 0.6 and 1.0 e. Å⁻³. Their final calculated positions are indicated for comparison.

Three additional cycles of refinement with the use of anisotropic temperature factors for the five atoms mentioned above and isotropic temperature factors for the remaining atoms reduced the R value to 0.083. For these three cycles the hydrogen atoms were included in the structure factor calculations with isotropic temperature factors 1.0 Å² higher than those of the carbon atoms to which they were respectively bonded. After these three cycles, positions were recalculated for all hydrogen atoms except those in the methyl group.

Six more least-squares cycles completed the refinement. For these last six cycles anisotropic temperature factors were used for all non-hydrogen atoms. The isotropic temperature factors which were assigned to the hydrogen atoms were calculated as a function of the average of the U_{ii} coefficients in Å² of the corresponding carbon atoms with the use of the graph given by Jensen & Sundaralingam (1964). Only the three hydrogen atoms of the methyl group were included in the refinement.

Five of the strongest reflexions were excluded from the least-squares calculations during the last four refinement cycles because they appeared to be affected by extinction. The final residual for all 1793 observed reflexions is 0.067; without these five reflexions it is 0.063.

The shifts in both positional and vibrational parameters from the final least-squares cycle were, in general, less than one-tenth of their respective estimated standard deviations. The maximum shift indicated for

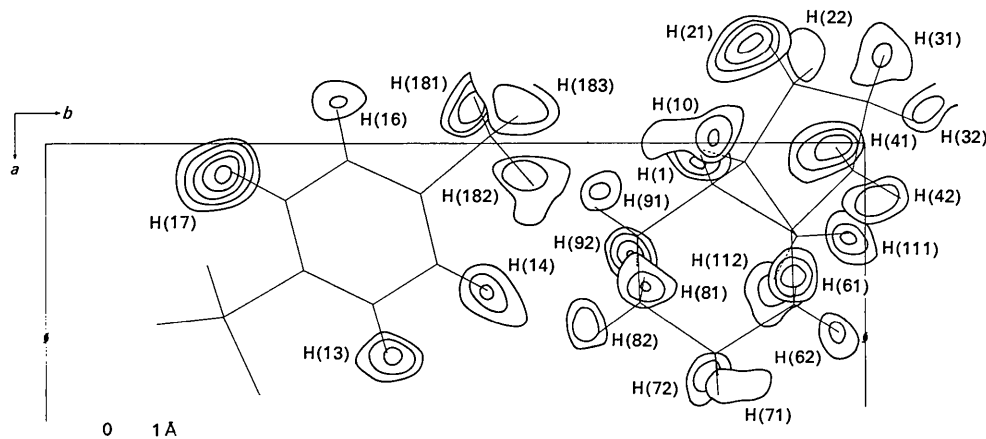


Fig. 2. Composite drawing of the second difference map, showing the hydrogen atoms, with contour lines at intervals of 0.1 e. Å⁻³, starting at 0.6 e. Å⁻³. Final calculated positions of the atoms are indicated.

any non-hydrogen parameter was 0.3σ , while among the hydrogen-atom parameters no shift exceeded 0.8σ .

Estimated standard deviations of the atomic parameters were calculated from the diagonal elements of the inverse to the normal equations matrix.

Results and discussion

Positional parameters and their associated estimated standard deviations obtained from the final least-squares cycle are given for the non-hydrogen atoms in Table 1. Final coordinates and isotropic temperature factors for the hydrogen atoms are given, with e.s.d.'s for the parameters which were refined, in Table 2. The anisotropic thermal parameters and corresponding e.s.d.'s of the non-hydrogen atoms are given in Table 3. Observed and calculated structure factors, based on the parameters in Tables 1 to 3, are listed in Table 4. Included in this listing are the calculated structure factors for the unobserved reflexions. The values given in the F_o column for these reflexions are the mean expected values described by Hamilton (1955), and are approximately two thirds of the minimum observable amplitudes.

A difference map was computed using the final set of structure factors, omitting those reflexions which had been excluded from the last least-squares cycles. The only significant features of the map were a group of depressions of about $-0.40 \text{ e. \AA}^{-3}$ at a distance of approximately 1 \AA from the sulphur atom, and a further scattering of peaks and depressions, whose absolute magnitudes were about 0.25 e. \AA^{-3} , located about 2 \AA from the sulphur atom. A portion of the map in the plane of the aromatic ring is shown in Fig. 3. The ab-

Table 1. *Coordinates and (in parentheses) standard deviations of non-hydrogen atoms*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S	0.22750 (8)	0.21807 (7)	0.18479 (12)
O(1)	0.15890 (29)	0.19772 (26)	0.30582 (39)
O(2)	0.23552 (33)	0.13530 (22)	0.08792 (39)
O(3)	0.32664 (27)	0.25785 (27)	0.22762 (50)
C(1)	0.02155 (33)	0.85448 (31)	-0.02348 (49)
C(2)	-0.07443 (35)	0.91690 (36)	-0.00469 (59)
C(3)	-0.04944 (38)	1.00446 (37)	0.09086 (58)
C(4)	0.03638 (36)	0.98516 (31)	0.20210 (53)
N(5)	0.11270 (25)	0.90976 (23)	0.14825 (34)
C(6)	0.20753 (34)	0.91141 (33)	0.23944 (54)
C(7)	0.27307 (36)	0.82066 (35)	0.21909 (61)
C(8)	0.20647 (37)	0.72891 (33)	0.23893 (60)
C(9)	0.12435 (37)	0.72576 (31)	0.12241 (55)
C(10)	0.05399 (30)	0.81425 (27)	0.12590 (47)
C(11)	0.12093 (31)	0.91709 (31)	-0.01614 (45)
C(12)	0.16556 (29)	0.31183 (27)	0.08332 (43)
C(13)	0.20875 (30)	0.40337 (29)	0.07157 (52)
C(14)	0.15962 (33)	0.47603 (28)	-0.00538 (53)
C(15)	0.06455 (32)	0.45951 (31)	-0.07108 (48)
C(16)	0.02243 (32)	0.36658 (36)	-0.06138 (52)
C(17)	0.07232 (30)	0.29401 (29)	0.01356 (47)
C(18)	0.00779 (47)	0.54246 (42)	-0.14504 (58)

sence between the atom sites, and above and below the plane of the ring, of any significant residual density peaks similar to those discussed by O'Connell, Rae & Maslen (1966) and by many other authors, is not really surprising. The standard deviation of the electron density in the difference map, calculated as $0.083 \text{ e. \AA}^{-3}$, is not much higher in this case than in many structures where such features have been observed. Of more importance, however, is the fact that the calculation of the standard deviation (Cruickshank, 1959) assumes correct phase angles, and the lack of a centre of sym-

Table 2. *Hydrogen atom parameters*

(Standard deviations are given in parentheses for parameters which were refined.)

	Bonded to	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (\AA^2)
H(1)	C(1)	0.007	0.801	-0.088	2.0
H(21)	C(2)	-0.128	0.879	0.040	3.4
H(22)	C(2)	-0.098	0.939	-0.098	3.4
H(31)	C(3)	-0.111	1.023	0.141	3.9
H(32)	C(3)	-0.028	1.056	0.029	3.9
H(41)	C(4)	0.005	0.962	0.290	2.9
H(42)	C(4)	0.072	1.044	0.222	2.9
H(61)	C(6)	0.187	0.916	0.339	2.8
H(62)	C(6)	0.247	0.968	0.215	2.8
H(71)	C(7)	0.328	0.820	0.288	3.9
H(72)	C(7)	0.302	0.820	0.123	3.9
H(81)	C(8)	0.174	0.731	0.332	3.9
H(82)	C(8)	0.249	0.673	0.232	3.9
H(91)	C(9)	0.083	0.669	0.136	3.1
H(92)	C(9)	0.157	0.723	0.030	3.1
H(10)	C(10)	-0.008	0.797	0.178	1.1
H(111)	C(11)	0.114	0.982	-0.054	1.5
H(112)	C(11)	0.181	0.888	-0.057	1.5
H(13)	C(13)	0.273	0.416	0.117	1.6
H(14)	C(14)	0.192	0.538	-0.014	1.9
H(16)	C(16)	-0.042	0.353	-0.108	2.4
H(17)	C(17)	0.042	0.230	0.018	1.4
H(181)	C(18)	-0.058 (0.006)	0.524 (0.005)	-0.214 (0.008)	6.0 (1.9)
H(182)	C(18)	0.058 (0.007)	0.593 (0.007)	-0.191 (0.010)	6.2 (2.4)
H(183)	C(18)	-0.033 (0.005)	0.575 (0.006)	-0.071 (0.008)	4.6 (1.9)

metry in this crystal structure means that the possibility of phase errors is greatly increased with respect to the mainly centrosymmetric structures which have been discussed.

Thermal parameters

Table 5(a) lists the magnitudes of the principal axes of the individual vibration ellipsoids and the direction

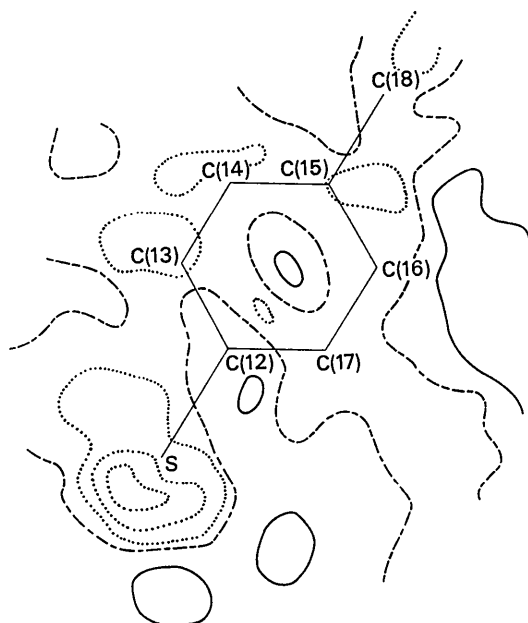


Fig. 3. A portion of the final difference map in the mean plane of the aromatic ring. Contour lines are at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$, with the zero contour chain dotted, negative contours dotted and positive contours unbroken.

cosines of these axes to the unit cell axes a , b , and c . The general increase in magnitude of the vibration parameters of individual atoms within each ion with increasing distance from the centre of gravity suggested that the tosylate and quinolizidinium moieties comprising the asymmetric unit might each be executing rigid-body librations. The translational and rotational vibration tensors, T_{ij} and ω_{ij} , for each of the ions were therefore calculated using Cruickshank's (1956a) formulae. For these calculations, the results of which are given in Table 5(b), molecular axis directions for the tosylate group were defined as follows. Axis (3) was normal to the mean plane of the benzene ring, axis (2) was in the plane of the ring, approximately parallel to the line connecting C(12) and C(15), and axis (1) was orthogonal to axes (2) and (3). A parallel axial system was used for the cation. For the particular equivalent position used for the cation this meant that axis (1) was roughly parallel to the line connecting C(7) and a point midway between C(8) and C(9), axis (2) was approximately parallel to a line joining C(1) and C(9), and axis (3) was approximately parallel to a line joining C(4) and C(11). The respective centres of gravity were used as origin for the two groups.

These calculations show that, for the tosylate ion, rigid-body translational motion is greater in the plane of the benzene-ring than normal to it. For some of the atoms in this group, however, substantial components of vibration normal to the plane result from the libration of the tosylate ion about axis (2). The value obtained for ω_{22} represents rotational oscillation about this axis, as defined above, with a root mean square amplitude of 8.6° .

The tensor element ω_{22} for the cation is also relatively large, representing an r.m.s. amplitude of 5.8° . It

Table 3. Non-hydrogen atom vibration tensor components (\AA^2) and (in parentheses, $\times 10^4$) their standard deviations. The vibration tensor components are defined by the expression

$$T = \exp [-2\pi^2(U_{11}a^2h^2 + \dots + 2U_{23}b^*c^*kl + \dots)].$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S	0.0416 (4)	0.0359 (4)	0.0417 (5)	0.0056 (8)	0.0068 (9)	0.0220 (8)
O(1)	0.0697 (20)	0.0647 (19)	0.0449 (18)	0.0273 (35)	0.0401 (38)	0.0420 (35)
O(2)	0.0893 (25)	0.0387 (14)	0.0546 (20)	-0.0008 (29)	0.0314 (41)	0.0401 (34)
O(3)	0.0477 (17)	0.0631 (20)	0.0972 (30)	0.0206 (44)	-0.0608 (41)	0.0128 (33)
C(1)	0.0450 (21)	0.0442 (21)	0.0414 (22)	0.0002 (36)	-0.0067 (40)	-0.0050 (36)
C(2)	0.0404 (20)	0.0576 (25)	0.0577 (29)	0.0139 (49)	-0.0116 (43)	-0.0012 (39)
C(3)	0.0519 (24)	0.0533 (24)	0.0590 (29)	0.0002 (47)	0.0028 (46)	0.0281 (43)
C(4)	0.0551 (24)	0.0422 (20)	0.0475 (24)	-0.0152 (40)	0.0159 (43)	0.0115 (37)
N(5)	0.0365 (14)	0.0331 (13)	0.0315 (17)	0.0056 (26)	0.0059 (27)	-0.0083 (25)
C(6)	0.0445 (21)	0.0470 (20)	0.0512 (25)	0.0127 (40)	-0.0239 (41)	-0.0212 (37)
C(7)	0.0437 (21)	0.0548 (23)	0.0662 (33)	0.0274 (46)	-0.0124 (47)	-0.0025 (40)
C(8)	0.0525 (24)	0.0472 (22)	0.0632 (29)	0.0283 (45)	-0.0064 (47)	0.0122 (40)
C(9)	0.0565 (24)	0.0374 (19)	0.0563 (26)	-0.0028 (40)	-0.0002 (46)	0.0154 (38)
C(10)	0.0390 (18)	0.0324 (16)	0.0432 (21)	0.0008 (32)	0.0026 (35)	-0.0055 (30)
C(11)	0.0420 (19)	0.0473 (20)	0.0314 (19)	0.0147 (36)	0.0102 (34)	0.0024 (34)
C(12)	0.0331 (16)	0.0373 (16)	0.0344 (20)	-0.0018 (31)	0.0091 (31)	0.0064 (29)
C(13)	0.0340 (18)	0.0380 (18)	0.0519 (24)	-0.0038 (36)	-0.0127 (37)	-0.0015 (30)
C(14)	0.0393 (19)	0.0375 (19)	0.0513 (24)	-0.0036 (37)	0.0067 (38)	-0.0009 (32)
C(15)	0.0393 (18)	0.0458 (20)	0.0380 (21)	-0.0025 (34)	-0.0035 (36)	0.0262 (33)
C(16)	0.0382 (19)	0.0586 (25)	0.0416 (21)	-0.0180 (41)	-0.0095 (39)	0.0042 (38)
C(17)	0.0372 (17)	0.0423 (19)	0.0389 (20)	-0.0109 (34)	0.0080 (34)	-0.0106 (31)
C(18)	0.0725 (32)	0.0658 (29)	0.0515 (29)	0.0049 (48)	-0.0339 (53)	0.0578 (53)

Table 5(a). Magnitudes *B* and direction cosines relative to *a*, *b*, and *c* of the principal axes of the thermal ellipsoids

	<i>B</i> ₁	<i>B</i> ₂	<i>B</i> ₃	<i>D</i> _{1a}	<i>D</i> _{1b}	<i>D</i> _{1c}	<i>D</i> _{2a}	<i>D</i> _{2b}	<i>D</i> _{2c}	<i>D</i> _{3a}	<i>D</i> _{3b}	<i>D</i> _{3c}
S	3.15	4.11	2.16	0.316	0.232	-0.920	0.726	0.565	0.392	-0.611	0.791	-0.010
O(1)	3.68	7.82	2.65	0.563	-0.803	0.194	0.699	0.588	0.407	-0.441	-0.094	0.892
O(2)	7.97	4.06	2.39	0.907	0.290	0.304	0.198	0.343	-0.918	-0.371	0.893	0.254
O(3)	8.88	5.17	2.37	-0.410	0.136	0.902	-0.328	-0.945	-0.007	0.851	-0.298	0.431
C(1)	3.41	3.81	3.09	-0.285	-0.830	0.480	-0.774	0.498	0.391	0.558	0.259	0.789
C(2)	3.04	5.17	4.08	0.945	-0.084	0.316	-0.184	0.660	0.728	-0.270	-0.747	0.608
C(3)	4.65	5.28	3.04	0.057	0.125	-0.990	0.687	0.715	0.130	-0.723	0.689	0.046
C(4)	4.09	4.75	2.59	-0.321	-0.699	0.639	0.862	0.065	0.502	-0.393	0.712	0.582
N(5)	2.75	3.11	2.12	-0.242	-0.627	-0.740	0.854	-0.500	0.142	0.459	0.598	-0.657
C(6)	3.36	5.30	2.61	-0.085	0.739	-0.668	-0.578	0.508	0.638	0.811	0.445	0.380
C(7)	3.27	6.03	3.71	0.863	-0.318	0.391	-0.177	0.535	0.826	-0.471	-0.783	0.405
C(8)	4.37	5.64	2.85	-0.922	-0.323	0.212	0.020	0.508	0.861	0.386	-0.799	0.462
C(9)	4.45	4.68	2.73	0.133	-0.019	-0.991	0.933	0.337	0.124	-0.332	0.941	-0.062
C(10)	3.13	3.44	2.48	-0.889	0.360	0.284	0.299	-0.038	0.953	0.350	0.934	-0.072
C(11)	3.34	4.05	2.15	-0.898	0.418	-0.140	0.335	0.852	0.402	-0.287	-0.314	0.905
C(12)	2.92	3.13	2.22	-0.250	0.678	-0.691	0.616	0.666	0.420	-0.745	0.321	0.585
C(13)	2.51	4.27	3.01	0.928	0.205	0.312	-0.297	-0.097	0.950	0.226	-0.974	-0.029
C(14)	3.04	4.14	2.94	-0.968	0.011	0.250	0.249	-0.122	0.961	0.010	0.992	0.122
C(15)	2.98	4.44	2.29	-0.013	-0.133	-0.991	0.615	0.781	-0.112	0.789	-0.611	0.071
C(16)	3.25	4.98	2.70	0.692	-0.395	-0.605	0.154	0.899	-0.411	0.707	0.191	0.681
C(17)	2.76	3.93	2.66	-0.044	-0.614	-0.788	0.465	-0.711	0.528	0.884	0.341	-0.321
C(18)	4.58	7.96	2.44	0.221	-0.574	-0.788	0.759	0.609	-0.231	0.613	-0.547	0.570

Table 5(b). Molecular vibration tensors, *T*_{*ij*} and ω_{*ij*}Standard deviations (× 10⁴) are given in parentheses. *T*_{*ij*} values are in Å². ω_{*ij*} values are in rad².

Tosylate group					
<i>T</i> ₁₁	<i>T</i> ₂₂	<i>T</i> ₃₃	<i>T</i> ₁₂	<i>T</i> ₁₃	<i>T</i> ₂₃
0.0354 (35)	0.0383 (25)	0.0174 (44)	-0.0025 (25)	0.0022 (33)	0.0043 (25)
ω ₁₁	ω ₂₂	ω ₃₃	ω ₁₂	ω ₁₃	ω ₂₃
0.0028 (5)	0.0226 (27)	0.0033 (5)	-0.0023 (7)	0.0007 (5)	0.0001 (9)
1,5-Endomethylenequinolizidium group					
<i>T</i> ₁₁	<i>T</i> ₂₂	<i>T</i> ₃₃	<i>T</i> ₁₂	<i>T</i> ₁₃	<i>T</i> ₂₃
0.0336 (13)	0.0361 (10)	0.0299 (15)	0.0029 (9)	0.0027 (12)	-0.0019 (10)
ω ₁₁	ω ₂₂	ω ₃₃	ω ₁₂	ω ₁₃	ω ₂₃
0.0049 (4)	0.0102 (9)	0.0033 (4)	0.0008 (4)	-0.0003 (3)	0.0003 (4)

and ammonium acid *o*-carboxybenzenesulphonate (Okaya, 1967)] is very good when allowance is made for the fact that Okaya's values have not been corrected for rotational oscillation. The S-C and average S-O bond lengths are respectively, 1.780 ± 0.004 and 1.457 ± 0.003 (this analysis), 1.774 ± 0.003 and 1.454 ± 0.005 (Hall & Maslen, 1967), and 1.775 ± 0.004 and 1.444 ± 0.003 Å (Okaya, 1967).

Table 6(a). Bond lengths (Å)

	Length	Corrected length	σ
S—O(1)	1.448	1.461	0.004
S—O(2)	1.444	1.456	0.003
S—O(3)	1.443	1.455	0.004
S—C(12)	1.775	1.780	0.004
C(1)—C(2)	1.512	1.519	0.006
C(1)—C(10)	1.537	1.543	0.006
C(1)—C(11)	1.542	1.551	0.006
C(2)—C(3)	1.520	1.528	0.007
C(3)—C(4)	1.529	1.534	0.007
C(4)—N(5)	1.508	1.516	0.006
N(5)—C(6)	1.481	1.487	0.006

Table 6(a) (cont.)

N(5)—C(10)	1.524	1.533	0.005
N(5)—C(11)	1.518	1.527	0.005
C(6)—C(7)	1.513	1.520	0.007
C(7)—C(8)	1.531	1.539	0.007
C(8)—C(9)	1.506	1.512	0.007
C(9)—C(10)	1.513	1.519	0.006
C(12)—C(13)	1.375	1.385	0.005
C(12)—C(17)	1.383	1.395	0.006
C(13)—C(14)	1.374	1.378	0.006
C(14)—C(15)	1.384	1.396	0.006
C(15)—C(16)	1.385	1.394	0.006
C(15)—C(18)	1.511	1.513	0.007
C(16)—C(17)	1.368	1.371	0.006
C(18)—H(181)	1.08		0.08
C(18)—H(182)	1.04		0.09
C(18)—H(183)	0.97		0.07

Table 6(b). Bond angles (°)

	Uncorrected	Corrected	σ
O(1)—S—O(2)	111.5	111.6	0.2
O(1)—S—O(3)	113.8	113.9	0.2
O(2)—S—O(3)	113.6	113.7	0.2
O(1)—S—C(12)	105.6	105.4	0.2

Table 6(b) (cont.)

O(2)—S—C(12)	106.0	105.7	0.2
O(3)—S—C(12)	105.6	105.5	0.2
C(2)—C(1)—C(10)	108.8	108.6	0.4
C(2)—C(1)—C(11)	111.1	111.1	0.4
C(10)—C(1)—C(11)	86.2	86.3	0.3
C(1)—C(2)—C(3)	109.8	109.8	0.4
C(2)—C(3)—C(4)	113.8	113.9	0.4
C(3)—C(4)—N(5)	111.7	111.6	0.4
C(4)—N(5)—C(6)	110.0	109.9	0.3
C(4)—N(5)—C(10)	107.9	107.9	0.3
C(4)—N(5)—C(11)	109.1	109.2	0.3
C(6)—N(5)—C(10)	119.9	120.0	0.3
C(6)—N(5)—C(11)	120.3	120.0	0.3
C(10)—N(5)—C(11)	87.5	87.5	0.3
N(5)—C(6)—C(7)	112.2	112.1	0.4
C(6)—C(7)—C(8)	110.2	110.2	0.4
C(7)—C(8)—C(9)	109.4	109.5	0.4
C(8)—C(9)—C(10)	112.5	112.4	0.4
C(1)—C(10)—N(5)	87.0	87.1	0.3
C(1)—C(10)—C(9)	115.5	115.4	0.3
N(5)—C(10)—C(9)	113.1	113.0	0.3
C(1)—C(11)—N(5)	87.1	87.1	0.3
S—C(12)—C(13)	121.2	120.9	0.3
S—C(12)—C(17)	120.4	120.3	0.3
C(13)—C(12)—C(17)	118.4	118.8	0.4
C(12)—C(13)—C(14)	120.9	120.6	0.4
C(13)—C(14)—C(15)	120.9	120.8	0.4
C(14)—C(15)—C(16)	117.9	118.3	0.4

Table 6(b) (cont.)

C(14)—C(15)—C(18)	120.1	120.0	0.4
C(16)—C(15)—C(18)	121.9	121.7	0.4
C(15)—C(16)—C(17)	121.0	120.8	0.4
C(12)—C(17)—C(16)	120.9	120.7	0.4
C(15)—C(18)—H(181)	117.5		4.0
C(15)—C(18)—H(182)	112.6		5.0
C(15)—C(18)—H(183)	106.9		4.4
H(181)—C(18)—H(182)	113.8		6.4
H(181)—C(18)—H(183)	95.4		5.9
H(182)—C(18)—H(183)	108.7		6.6

The frequently observed flattening of the SO_3^- group is evident in this crystal structure also. The average O—S—O bond angle (113.1°) is significantly larger than the tetrahedral value and the average O—S—C bond angle (105.5°) is significantly smaller.

The value $1.513 \pm 0.007 \text{ \AA}$ for the C(15)—C(18) ($C_{sp^2}-C_{sp^3}$) bond length and the average value 1.387 \AA for the aromatic bond length do not differ significantly from the accepted values 1.501 ± 0.004 (Lide, 1962) and $1.394 \pm 0.005 \text{ \AA}$ (Sutton, 1965), for such bonds, and require no special comment. It is interesting, however, that the bonds C(13)—C(14) and C(16)—C(17), parallel to the long axis of the tosylate group, appear to be shorter

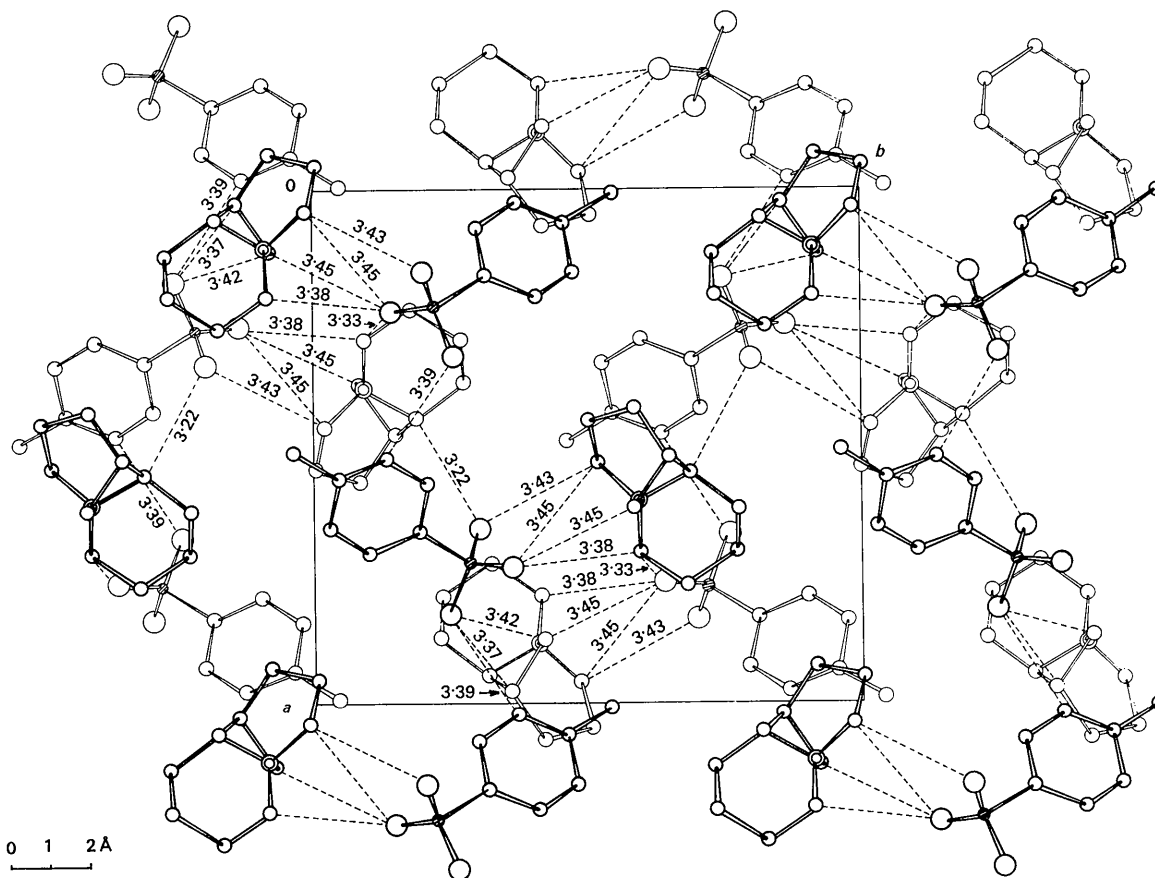


Fig. 5. Projection of the structure on the (001) plane, showing the packing of the ions. Large open circles, small open circles, double circles, and small hatched circles represent oxygen, carbon, nitrogen, and sulphur atoms respectively.

than the other four aromatic C–C bonds. The difference between the shortened bond lengths, whose average is 1.375 ± 0.004 Å, and the other four, whose average is 1.392 ± 0.003 Å, is significant at about the 0.1% level, using the *t* test. Similar shortening of the central C–C aromatic bonds has been observed in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961), in the α and β modifications of *p*-nitrophenol (Coppens & Schmidt, 1965*a* and *b*), in *p*-aminobenzoic acid (Lai & Marsh, 1967) and in β -sulphanilamide (O'Connell & Maslen, 1967). In the present structure, as in those quoted, it seems that the effect could be explained according to resonance theory by contributions of quinonoid valence-bond structures.

The $C_{sp^3} - C_{sp^3}$ bond lengths in the quinolizidinium part of the structure can be grouped in two categories, those which are found in the four-membered ring, and those which occur elsewhere. The average value of those in the four-membered ring is 1.547 ± 0.004 Å, which agrees closely with the value 1.548 ± 0.003 Å found in cyclobutane by electron diffraction (Almenningen, Bastiansen & Skancke, 1961). The average for the others is 1.524 Å, which does not differ significantly from the average 1.534 Å for $C_{sp^3} - C_{sp^3}$ bonds taken from Stoicheff's (1962) compilation of accurately determined carbon-carbon bond lengths.

The $C_{sp^3} - N_{sp^3}^+$ bond lengths also vary according to their environment. The two C–N bonds in the four-membered ring have an average length of 1.530 ± 0.004 Å, while the other two, C(4)–N(5) and C(6)–N(5), have values of 1.516 and 1.487 Å respectively, both e.s.d.'s being 0.006 Å. The difference between the C(4)–N(5) bond length and those in the four-membered ring may not be significant, but the difference between the C(6)–N(5) bond length and the others is too large not to be real.

The lengthening of the bonds, both C–N and C–C, in the four-membered ring obviously helps to increase the distance, and thereby reduce the repulsion, between diagonally opposite atoms. Even with the increased bond lengths, however, the C(1)–N(5) and C(10)–C(11) non-bonded distances are only 2.12 Å; a normal value would be about 2.5 Å. No particularly short non-bonded distances affect the N(5)–C(6) bond length, the relevant distances being C(6)···C(10) (2.61 Å), C(6)···C(11) (2.62 Å), C(6)···C(4) (2.46 Å) and N(5)···C(7) (2.49 Å). Its length, 1.487 Å, should, therefore, be capable of comparison with standard values for the $C_{sp^3} - N_{sp^3}^+$ bond.

In fact, it agrees fortuitously well with what appears to be the most accurate value in the literature for the $C_{sp^3} - N_{sp^3}^+$ bond, 1.487 Å. This is an average derived by Marsh & Donohue (1967) from a large number of three-dimensional structure analyses of amino acids. Its standard deviation, not quoted by the authors, is very low; the individual e.s.d.'s of bond lengths upon which the average is based are as low as 0.002 Å. According to Bartell's (1962) discussion of non-bonded repulsions, the repulsions associated with three hydro-

gen atoms arranged tetrahedrally with a fourth substituent would not be appreciably different from the repulsions of similarly arranged carbon atoms, because the weaker C···H and H···H repulsions would be acting over shorter distances. On this basis one should expect the length of the C–N bond to be the same, other factors being equal, whether the atoms coordinating nitrogen were carbon or hydrogen.

The strain in the cation is indicated by the abnormal values of some of the bond angles as well as by the abnormal bond lengths already discussed. The ring formed by C(1)···C(4), N(5) and C(10) is in a distorted chair form. Because of the formation of the four-membered ring, the angle C(1)–C(10)–N(5) is greatly reduced from the tetrahedral value to 87.1° . Also, C(3) is forced close to the approximate plane formed by C(1), C(2), C(4) and N(5) because of repulsion between C(3) and C(11). This effect seems to be mainly reflected in the C(2)–C(3)–C(4) angle, which is 113.9° , with the C(3)–C(4)–N(5) angle showing a smaller increase from the expected tetrahedral value to 111.6° . The other six-membered ring, formed by atoms N(5), C(6)···C(10), is also in a distorted chair form, and the fusion of these two rings is *trans*, as required by the derivation of this compound from lupinine. The angles at N(5) and C(10) for this second ring are enlarged with respect to the tetrahedral value, as are the angles at C(6) and C(9), giving a somewhat flattened shape to the ring.

Planarity of rings

The benzene ring shows small but significant distortions from planarity and has a slight boat shape. The equation of the least-squares plane, calculated according to Blow's (1960) procedure, is $0.4808X - 0.2754Y - 0.8325Z + 0.7742 = 0$. (The coefficients are the direction cosines of the normal to the plane relative to the unit-cell axes.) C(12) and C(15) both deviate in the same direction from the plane by about 0.012 Å, carrying the sulphur atom 0.05 Å and C(18) 0.11 Å out of the plane. The last two atoms were not used in defining the least-squares plane, and hydrogen atoms were excluded from the calculations.

The four-membered ring is markedly non-planar, as implied by the 87.0° average of the four angles in the ring. The average deviation from the mean plane is 0.177 Å. Non-planarity of this ring had also been suggested by the nuclear magnetic resonance spectra (Edwards, Fodor & Marion, 1966).

Packing arrangement

A projection of the structure down the *c* axis is shown in Fig. 5. The ions are arranged in pleated sheets which are approximately perpendicular to the *b* axis, and contact distances between ions in the same sheet tend to be slightly shorter than contact distances between ions in adjacent sheets. Interionic distances under 3.5 Å, not involving hydrogen atoms, are indicated, with the exception of C(7)–O(2ⁱⁱⁱ), in the Figure

by dashed lines, and are listed in Table 7. The positively charged nitrogen atom is not itself involved in any of these close contacts because, being tetravalent, it is rather inaccessible. However, most of the short interionic distances are between an oxygen atom, bearing a partial negative charge, and an atom adjacent to the nitrogen. This fact, together with the arrangement of the interionic bonds, indicates that the packing is governed partially by Coulomb forces. The contact distances are all, however, above the lower limit for van der Waals interaction.

Table 7. *Interionic distances less than 3.5 Å*

C(4)—O(1 ⁱ)	3.43 Å
C(10)—O(1 ⁱⁱ)	3.22
C(11)—O(2 ⁱ)	3.45
C(4)—O(2 ⁱ)	3.45
C(6)—O(2 ⁱ)	3.38
C(6)—O(2 ⁱⁱⁱ)	3.33
C(7)—O(2 ⁱⁱⁱ)	3.44
C(1)—O(3 ^{iv})	3.37
C(11)—O(3 ^{iv})	3.42
C(16)—O(3 ^v)	3.39

The following superscripts are used for this table.

i	$x, y+1, z$
ii	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
iii	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
iv	$\frac{1}{2}-x, 1-y, z-\frac{1}{2}$
v	$x-\frac{1}{2}, \frac{1}{2}-y, -z$

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