

in the crystal between the two C atoms which become bonded on cyclization is 3.369 Å (Brown & Levy, 1979) and the reaction occurs only under oxidative conditions (Sato, Goto & Hata, 1967), and on 6,6-dichloro-1-methyl-3,4,5-triphenylbicyclo-[3.1.0]hex-3-en-2-one (IV) (Barnes, Horspool & Mackie, 1990) where C12...C14 is 3.560 (5) Å and no cyclization is observed. [The last-named compound has been numbered like (I) up to C25.] In every calculation each phenyl group in turn has been rotated about its bond to ring A. The effect of these rotations on the lattice energy of the crystal (neglecting dipole terms) and on the interaction packing energy between the chosen phenyl group and the rest of the molecule have been evaluated.

The lattice-energy calculation showed that in every case the observed structure had the minimum energy and that rotation of any phenyl group by  $\pm 15^\circ$  increased the energy by 5–10 kJ mol<sup>-1</sup>. However the local-energy calculation showed that the energy minima usually occurred with the phenyl group rotated 15–30° further away from coplanarity with ring A than the observed structure. For (I) this minimum energy was in the range 4–10 kJ mol<sup>-1</sup> lower than the observed energy. Twisting a phenyl group towards coplanarity with ring A gives a rapid increase in local energy for rings B and C ranging from 49 kJ mol<sup>-1</sup> [ring B, (IV)] to 226 kJ mol<sup>-1</sup> [ring C, (I)] for a 45° rotation. Rotation of ring B of *o*-diphenylbenzene shows an unusually steep well of 35 kJ mol<sup>-1</sup> at 45° and 90 kJ mol<sup>-1</sup> at 30°. The photocyclization process must involve simultaneous rotation of phenyl groups B and C with distortion of ring A to allow the formation of the new C—C bond. These rotations are too complex to be examined with the present program.

The disordered toluene molecule in (IIIa) has been studied by comparing the site of approximately 8.8 × 5.3 × 4.4 Å revealed by a packing calculation (Gavezzotti, 1987) with the observed interatomic

distances, thermal parameters and the final difference map. The only symmetry constraint is that equal numbers of methyl groups must point in opposite directions to satisfy the centre of inversion. There is no requirement for each benzene ring to be symmetrical about the centre of inversion or for all the benzene rings to be coplanar (Jewess, 1982).

This study suggests an 'average molecule' in which the methyl group C54 is displaced towards the centre of inversion and the molecule tilted about C52...C52' to optimize the fit to the cavity. The displacements from the centrosymmetric positions used in the refinement are of the order of 0.2 Å. There are no channels by which the molecule could enter or leave the site so that the toluene must have been included during crystal growth.

#### References

- ALLEN, C. F. & VAN ALLAN, J. A. (1950). *J. Am. Chem. Soc.* **72**, 5166–5171.  
 BARNES, J. C., HORSPOOL, W. M. & MACKIE, F. L. (1990). In preparation.  
 BROWN, G. M. & LEVY, H. A. (1979). *Acta Cryst.* **B35**, 785–788.  
 DELAUNAY, J., SIMONET, J. & TOUPET, L. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1093–1094.  
 GAVEZZOTTI, A. (1985). *J. Am. Chem. Soc.* **105**, 5220–5235.  
 GAVEZZOTTI, A. (1987). *Tetrahedron*, **47**, 1241–1251.  
 HORSPOOL, W. M. (1969). *J. Chem. Soc. Chem. Commun.* p. 467.  
 HORSPOOL, W. M. (1971). *J. Chem. Soc. C*, pp. 400–404.  
 JEWESS, M. (1982). *Acta Cryst.* **B38**, 1418–1422.  
 MORITANI, I., TOSHIMA, N., NAKAGAWA, S. & YAKUSHIJI, M. (1967). *Bull. Chem. Soc. Jpn.* **40**, 2129–2133.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.  
 SATO, T., GOTO, Y. & HATA, K. (1967). *Bull. Chem. Soc. Jpn.* **40**, 1994–2001.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 TOSHIMA, N. & MORITANI, I. (1967). *Bull. Chem. Soc. Jpn.* **40**, 1495–1500.

*Acta Cryst.* (1991). **C47**, 168–170

### Structure of Ammonium *p*-Toluenesulfonate

BY ROBIN D. ROGERS,\* ANDREW H. BOND AND RODGER F. HENRY

*Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA*

(Received 21 March 1990; accepted 5 June 1990)

**Abstract.** NH<sub>4</sub><sup>+</sup>·C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S<sup>-</sup>, *M*<sub>r</sub> = 189.24, orthorhombic, *Pn*2<sub>1</sub>*a* (an alternate setting of *Pna*2<sub>1</sub>, No.

33), *a* = 20.411 (4), *b* = 7.066 (2), *c* = 6.272 (4) Å, *V* = 904.6 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.39 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 3.22 cm<sup>-1</sup>, *F*(000) = 400, *T* = 293 K, final *R* = 0.045 for 596 observed [*F*<sub>o</sub> ≥ 5σ(*F*<sub>o</sub>)] reflex-

\* Author to whom correspondence should be addressed.

tions. The published structure of the orthorhombic form of oxonium *p*-toluenesulfonic acid [Dexter (1971). *Z. Kristallogr.* **134**, 350–359] has been shown to be the ammonium salt. The ammonium cation is hydrogen bonded to four symmetry-related tosylate anions. The H(N)⋯O distances range from 1.87 to 2.21 Å. The longest distances are to O(3) which participates in two hydrogen bonds.

**Introduction.** *p*-Toluenesulfonate salts have been extensively utilized as leaving groups in organic syntheses and as anions in many inorganic reactions (Ohki, Suzuki, Takeuchi & Ouchi, 1988; Bernhard, Burgi, Hauser, Lehmann & Ludi, 1982). The isolation of the title complex was a result of our efforts directed to the synthesis and modification of crown ethers with improved heavy-metal extraction properties. Elemental analysis indicated the ammonium salt of *p*-toluenesulfonic acid; however, the cell parameters, crystal system and space group were identical to those reported for an orthorhombic form of the oxonium salt (Dexter, 1971).

Dexter's report indicated that the compound was crystallized from a solution also containing a tetrahydrate which we feel could easily have contained ammonium ions. In addition, three reports on the oxonium salt (X-ray and neutron diffraction data) revealed a 'monoclinic form' (Arora & Sundaralingam, 1971; Lundgren & Williams, 1973; Finholt & Williams, 1973). We therefore decided to continue the investigation of our compound which we knew to be the ammonium salt.

**Experimental.** The crystals were isolated as a by-product in a reaction mixture consisting of triethylene glycol ditosylate, 1-hydroxy-1-hydroxymethyl-16-crown-5, and ammonium iodide in a 3:1 solution of acetonitrile and methanol. Elemental analysis: Calc. % C 44.43, H 5.86, N 7.40; Found C 43.73, H 5.97, N 7.05.  $D_m$  not determined. Crystal 0.20 × 0.35 × 0.50 mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. Cell constants from setting angles of 25 reflections ( $\theta > 20^\circ$ ).  $\omega$ - $2\theta$  scans. Correction for Lorentz-polarization effects. No absorption correction.  $\theta_{\max} = 50^\circ$ ;  $h$  0 to 24,  $k$  0 to 8,  $l$  0 to 7. Standard reflections observed every 3600 s of data-collection time (12.0, 0; 040; 004), variation =  $\pm 2.6\%$ . 978 reflections measured, 596 independent observed reflections [ $F_o \geq 5\sigma(F_o)$ ]. Structure solved utilizing *SHELXS* (Sheldrick, 1985) direct-methods program. The geometrically constrained H atoms were placed in calculated positions 0.95 Å from the bonded C atom and allowed to ride on that atom with  $B$  fixed at 5.5 Å<sup>2</sup>. The methyl H atoms were included as a rigid group with rotational freedom at the bonded C atom (C—H = 0.95 Å,  $B = 5.5$  Å<sup>2</sup>).

Table 1. Final fractional coordinates for  $\text{NH}_4^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$

$$B_{\text{eq}} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
S	0.84890 (6)	0.2117	0.1153 (2)	2.51
O(1)	0.8476 (2)	0.220 (3)	-0.1120 (7)	5.80
O(2)	0.8216 (4)	0.042 (1)	0.204 (2)	4.97
O(3)	0.8180 (4)	0.373 (1)	0.219 (2)	4.26
N	0.7467 (2)	0.215 (3)	-0.3975 (8)	2.95
C(1)	0.9321 (2)	0.217 (2)	0.1896 (9)	2.10
C(2)	0.9798 (3)	0.155 (1)	0.049 (1)	2.71
C(3)	1.0449 (3)	0.159 (1)	0.111 (1)	2.80
C(4)	1.0636 (3)	0.223 (2)	0.310 (1)	2.63
C(5)	1.0152 (4)	0.284 (1)	0.445 (1)	2.88
C(6)	0.9494 (3)	0.280 (1)	0.390 (1)	2.59
C(7)	1.1341 (3)	0.243 (2)	0.372 (1)	3.40

Table 2. Bond distances (Å) and angles (°) for  $\text{NH}_4^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$

S—O(1)	1.427 (5)	S—O(2)	1.433 (8)
S—O(3)	1.455 (9)	S—C(1)	1.762 (5)
C(1)—C(2)	1.387 (9)	C(1)—C(6)	1.38 (1)
C(2)—C(3)	1.387 (9)	C(3)—C(4)	1.38 (1)
C(4)—C(5)	1.37 (1)	C(4)—C(7)	1.500 (9)
C(5)—C(6)	1.387 (9)		
O(1)—S—O(2)	114.5 (8)	O(1)—S—O(3)	114.1 (8)
O(2)—S—O(3)	108.0 (4)	O(1)—S—C(1)	106.3 (3)
O(2)—S—C(1)	106.9 (6)	O(3)—S—C(1)	106.4 (6)
S—C(1)—C(2)	120.1 (6)	S—C(1)—C(6)	119.6 (5)
C(2)—C(1)—C(6)	120.3 (5)	C(1)—C(2)—C(3)	119.0 (7)
C(2)—C(3)—C(4)	121.9 (7)	C(3)—C(4)—C(5)	117.7 (6)
C(3)—C(4)—C(7)	122.0 (7)	C(5)—C(4)—C(7)	120.1 (8)
C(4)—C(5)—C(6)	122.4 (7)	C(1)—C(6)—C(5)	118.7 (6)

Table 3. Hydrogen-bonding contact geometries (Å, °) for  $\text{NH}_4^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$

H(1)N—N	0.92	H(1)N—O(2) <sup>a</sup>	1.87
H(2)N—N	0.90	H(2)N—O(3) <sup>a</sup>	2.00
H(3)N—N	0.82	H(3)N—O(1)	1.92
H(4)N—N	0.83	H(4)N—O(3) <sup>a</sup>	2.21
N—H(1)N—O(2) <sup>a</sup>	168.2	N—H(2)N—O(3) <sup>a</sup>	159.6
N—H(3)N—O(1)	169.9	N—H(4)N—O(3) <sup>a</sup>	166.2

Atoms related to those in Table 1 by: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x, y, z - 1$ .

The ammonium H atoms were located from a difference Fourier map and included with fixed contributions ( $B = 5.5$  Å<sup>2</sup>). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72, 99, 149); structure refined with *SHELX76* (Sheldrick, 1976).  $\sum w(|F_o| - |F_c|)^2$  minimized, weights =  $[\sigma(F_o)^2 + 0.0005F_o^2]^{-1}$ , 111 parameters varied,  $R = 0.045$ ,  $wR = 0.059$ ,  $S = 1.42$ ,  $R$  inverse = 0.048.  $\Delta/\sigma$  in final least-squares refinement cycle  $< 0.01$ ,  $\Delta\rho < 0.3$  e Å<sup>-3</sup> in final difference map.

**Discussion.** Fractional coordinates and  $B_{eq}$  values are given in Table 1,\* bond distances and angles in Table 2, hydrogen-bonding contact geometries in Table 3, and ORTEP (Johnson, 1976) illustrations of the cation environment and cell packing in Figs. 1 and 2.

The structural features of the title compound and those reported by Dexter (1971) for an orthorhombic form of oxonium *p*-toluenesulfonic acid are nearly identical. Support for the formulation of this com-

\* Lists of H-atom coordinates, thermal parameters, least-squares-planes results and observed and calculated structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53267 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

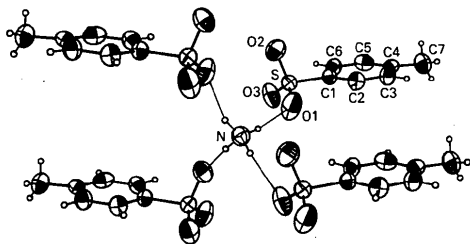


Fig. 1. ORTEP (Johnson, 1976) illustration of the title compound with 50% probability thermal ellipsoids. Symmetry relationships of the molecules depicted are given in the footnote to Table 3.

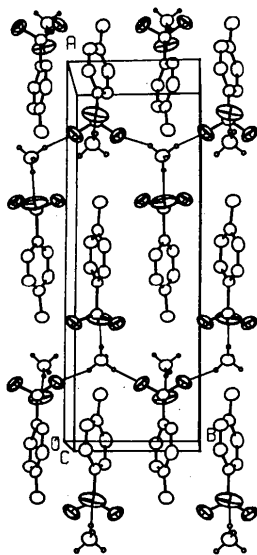


Fig. 2. Cell packing diagram.

pound as the ammonium salt comes not only from the crystallography discussed below, but also from our elemental analysis taken on the crystals used in this study.

The ammonium ion clearly sits in a tetrahedral hole formed by O atoms on four different anion molecules. The  $N\cdots O$  separations range from 2.730 (6) [O(1)] to 3.02 (1) Å [O(3)] and are nearly identical to the  $H_3O^+\cdots O$  separations calculated from the data reported by Dexter (1971). The H atoms were located and indicate hydrogen bonding to O(1) (one interaction), O(2) (one interaction) and O(3) (two interactions). The two largest  $N\cdots O$  distances and  $N-H\cdots O$  separations are found for O(3), the only O atom with two hydrogen bonds. The  $S-O(3)$  bond length [1.455 (9) Å] is also slightly larger than the  $S-O(1)$  and  $S-O(2)$  separations of 1.427 (5) and 1.433 (8) Å, respectively.

The average bonding parameters in the anion include  $S-C(1) = 1.762$  (5),  $C(4)-C(7) = 1.500$  (9),  $C-C = 1.382$  (6) Å,  $C-C-C$  (internal) = 120 (2),  $C(1)-S-O = 106.5$  (3),  $O(1)-S-O = 114.3$  (2),  $O(2)-S-O(3) = 108.0$  (4)°. These results compare favourably with earlier reports of oxonium *p*-toluenesulfonic acid (Arora & Sundaralingam, 1971; Lundgren & Williams, 1973; Finholt & Williams, 1973) and more recent reports such as that of 5-*tert*-butylhexahydro-2*H*-azepin-2-onium *p*-toluenesulfonate monohydrate (Edwards, Holden, Kirby & Raithby, 1986).

The authors wish to thank the National Science Foundation Chemical Instrumentation Program for the funds used to purchase the diffractometer.

#### References

- ARORA, S. K. & SUNDARALINGAM, M. (1971). *Acta Cryst.* **B27**, 1293-1298.
- BERNHARD, P., BURGI, H.-B., HAUSER, J., LEHMANN, H. & LUDI, A. (1982). *Inorg. Chem.* **21**, 3936-3941.
- DEXTER, D. (1971). *Z. Kristallogr.* **134**, 350-359.
- EDWARDS, M. R., HOLDEN, H. D., KIRBY, A. J. & RAITHY, P. R. (1986). *Acta Cryst.* **C42**, 1225-1227.
- FINHOLT, J. E. & WILLIAMS, J. M. (1973). *J. Chem. Phys.* **59**, 5114-5121.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LUNDGREN, J.-O. & WILLIAMS, J. M. (1973). *J. Chem. Phys.* **59**, 788-796.
- OHKI, Y., SUZUKI, Y., TAKEUCHI, T. & OUCHI, A. (1988). *Bull. Chem. Soc. Jpn.* **61**, 393-405.
- SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1985). SHELXS86. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175-189. Oxford Univ. Press.