

N(8)—C(3)—C(2)—N(1) angle  $-37.5(2)^\circ$  differs from that observed in other phenyl 2-pyridyl ketone oximes (Taga & Miyasaka, 1987; Taga, Uchiyama, Machida & Miyasaka, 1988), in which the pyridine N atom locates near the phenyl ring. From the viewpoint of non-bonding interactions between the aromatic rings, the orientation of the present pyridine ring is unfavorable, because the C(14)H $\cdots$ HC(4) repulsions between the rings may be larger than C(14)H $\cdots$ N repulsions. However, this orientation brings the pyridine N atom to a favorable position for the formation of the OH $\cdots$ N(pyridine) hydrogen bond.

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## Structure of *o*-Toluenesulfonic Acid Dihydrate

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**Abstract.**  $C_7H_7SO_3^- \cdot H_5O_2^+$ ,  $M_r = 208.2$ , orthorhombic,  $Pca2_1$  (No. 29),  $a = 9.565(1)$ ,  $b = 8.694(1)$ ,  $c = 11.866(2)$  Å,  $V = 986.8(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.401$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 3.03$  cm<sup>-1</sup>,  $F(000) = 440$ ,  $T = 296$  K,  $R = 0.037$  for 1436 reflections. The benzene ring is distorted by the *ortho* substituent, and the sulfonate group has a usual orientation to the ring. Two water molecules form an  $H_5O_2^+$  cation with a short hydrogen bond [2.425(3) Å], and the cation looks like an aqua-oxonium ion with the pyramidal  $H_3O^+$  ion bonded to the normal  $H_2O$  molecule.

**Introduction.** Several types of hydrogen bonding around a hydronium ion have been reported so far (Lundgren & Olovsson, 1976). The  $H_5O_2^+$  cation in picrylsulfonic acid tetrahydrate has a *gauche* type (Lundgren & Tellgren, 1974), while that in *o*-sulfobenzoic acid trihydrate has a *cis* type (Attig & Mootz, 1976). In the present work, the hydrogen

bonding in the title crystal as a hydrated proton complex of the strong sulfonic acid has been determined.

**Experimental.** A prismatic translucent crystal obtained from aqueous solution was mounted on a Rigaku AFC-5RU diffractometer; dimensions were 0.4 × 0.4 × 0.5 mm. Cell dimensions were determined by a least-squares method from the setting angles of 20 reflections having  $16 < \theta < 20^\circ$ . Intensity data of 1470 reflections ( $0 \leq h \leq 12$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 16$ ) were collected within  $2\theta < 60^\circ$ , using graphite-monochromated  $Mo K\alpha$  radiation;  $2\theta-\omega$  scans at speeds of  $4^\circ \text{ min}^{-1}$  were made over a range of  $(0.7 + 0.45 \tan \theta)^\circ$ . Three check reflections showed no significant fluctuation during data collection. Data were corrected for Lorentz and polarization factors, but not for absorption. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by full-

matrix least squares based upon  $F$  with  $w = [\sigma^2(F) + (0.023F)^2]^{-1}$ . Non-H atoms were refined anisotropically. H atoms were located by difference Fourier synthesis, and refined isotropically; the peak of the H atom between the two water molecules was broad, but it was included in the refinement. The final  $R$  value was 0.037 ( $wR = 0.053$ ,  $S = 1.1$ ) for 1436 unique reflections with  $F > 3\sigma(F_o)$ ; parameter shifts were less than  $0.3\sigma$ , and maximum residual density was  $0.25 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a FACOM M780 in the Data Processing Center of Kyoto University, using the program *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

The *o*-toluenesulfonate anion with the labelling scheme, and the hydrogen-bonding diagram around the  $\text{H}_5\text{O}_2^+$  cation are illustrated in Figs. 1(a) and 1(b), respectively. The crystal structure projected along the  $b$  axis is shown in Fig. 2. The atomic parameters are listed in Table 1. Bond distances and angles for the anion are listed in Table 2.\*

**Discussion.** The benzene ring is planar within  $0.02 \text{ \AA}$ , but it is slightly distorted from the regular hexagon. The short C(4)—C(5) bond opposite to the bond between the *ortho* substituents agrees with the usual trend observed in the *ortho*-substituted benzene rings, and deviations of the internal angles of the benzene ring at C(1) and C(2) are consistent with the data reported for the same kinds of substituents (Domenicano & Murray-Rust, 1979). The exocyclic C(1)—C(2)—C(7) and C(2)—C(1)—S(1) angles are large mainly owing to repulsion between the sulfonate and methyl groups as observed in *o*-carboxybenzenesulfonates (Okaya, 1967; Attig & Mootz, 1976). The sulfonate group, with an average C—S—O angle of  $107.0^\circ$  and an average O—S—O angle of  $111.8^\circ$ , has a usual orientation to the benzene ring with C(2)—C(1)—S(1)—O torsion angles of  $57.5(2)$ ,  $-61.2(2)$  and  $174.6(2)^\circ$  (Fig. 1a), as observed e.g. in orthanilic acid (Hall & Maslen, 1967). Although the S(1)—O(1) distance is slightly longer than the other two bonds, the almost equivalent S—O bonds with an average distance of  $1.456(12) \text{ \AA}$  show that the group is deprotonated. As shown in Fig. 1(b), two water molecules form an  $\text{H}_5\text{O}_2^+$  cation with a very short hydrogen-bond distance  $2.425(3) \text{ \AA}$ . Each water molecule is hydrogen bonded to the O atoms in a pyramidal arrangement. The hydrogen bonds around O(W1)—O(W2) are

staggered; O(1)—O(W1)—O(W2)—O(3<sup>iii</sup>) [O(2)—O(W1)—O(W2)—O(1<sup>i</sup>)] is  $64.4(2)^\circ$  [ $-56.1(2)^\circ$ ], whereas O(1)—O(W1)—O(W2)—O(1<sup>i</sup>) [O(2<sup>ii</sup>)—O(W1)—O(W2)—O(3<sup>iii</sup>)] is  $-179.6(2)^\circ$  [ $-172.0(2)^\circ$ ]. This hydrogen-bonding scheme resembles that of the centrosymmetric  $\text{H}_5\text{O}_2^+$  cation observed in  $\text{H}_5\text{O}_2^+\text{ClO}_4^-$  (Olovsson, 1968). However, the present  $\text{H}_5\text{O}_2^+$  cation has no crystallographic center of symmetry, and has a non-equivalent environment about the two water molecules (Fig. 2). the —O(1)—O(W1)—O(W2)—O(1<sup>i</sup>)— hydrogen-

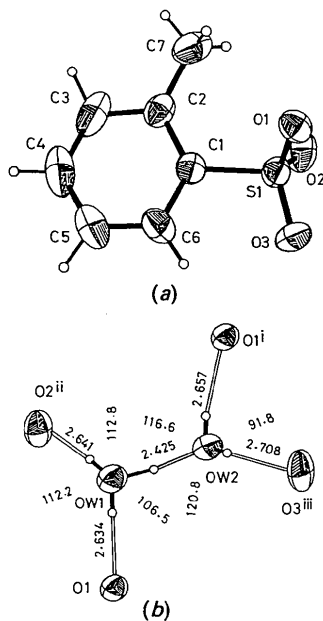


Fig. 1. (a) A view of the anion with the atomic numbering and thermal ellipsoids drawn at the 50% probability level. (b) The hydrogen bonding around the  $\text{H}_5\text{O}_2^+$  cation, showing the O—O distances ( $\text{\AA}$ ) and angles ( $^\circ$ ). The e.s.d.'s for the distances and angles are less than  $0.03 \text{ \AA}$  and  $0.1^\circ$ , respectively. Symmetry code: (i)  $1 - x, 2 - y, -\frac{1}{2} + z$ ; (ii)  $-\frac{1}{2} + x, 2 - y, z$ ; (iii)  $\frac{3}{2} - x, y, -\frac{1}{2} + z$ .

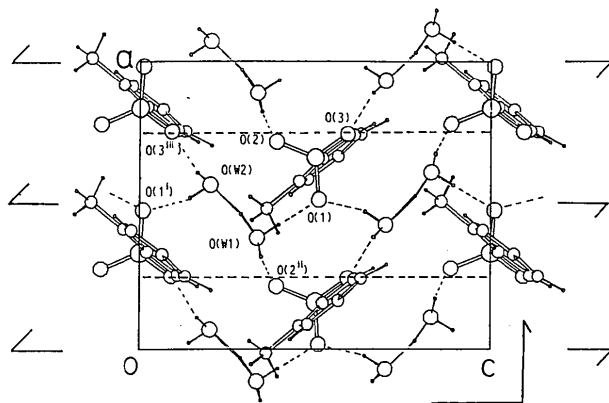


Fig. 2. The crystal structure projected along the  $b$  axis.

\* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53116 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors

	x	y	z	$B_{eq}(\text{\AA}^2)^*$
S(1)	0.6641 (1)	0.7876 (1)	0.50000	3.19 (4)
C(1)	0.6608 (2)	0.5859 (2)	0.5209 (2)	3.16 (8)
C(2)	0.5812 (3)	0.4904 (2)	0.4531 (3)	3.80 (9)
C(3)	0.5874 (3)	0.3332 (3)	0.4767 (4)	5.72 (14)
C(4)	0.6690 (4)	0.2751 (4)	0.5645 (5)	6.38 (18)
C(5)	0.7457 (3)	0.3721 (4)	0.6297 (3)	5.80 (15)
C(6)	0.7426 (3)	0.5292 (3)	0.6088 (3)	4.54 (10)
C(7)	0.4880 (4)	0.5467 (3)	0.3602 (3)	5.16 (12)
O(1)	0.5180 (2)	0.8399 (2)	0.5090 (2)	3.62 (6)
O(2)	0.7188 (2)	0.8164 (2)	0.3883 (2)	4.72 (9)
O(3)	0.7456 (2)	0.8530 (3)	0.5910 (2)	5.57 (9)
O(W1)	0.3881 (2)	0.9559 (2)	0.3327 (2)	4.40 (8)
O(W2)	0.5682 (2)	1.0337 (2)	0.2007 (2)	4.66 (8)

$$*B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

S(1)—C(1)	1.771 (2)	S(1)—O(1)	1.473 (2)
S(1)—O(2)	1.447 (2)	S(1)—O(3)	1.448 (2)
C(1)—C(2)	1.384 (3)	C(1)—C(6)	1.394 (4)
C(2)—C(3)	1.396 (3)	C(2)—C(7)	1.500 (5)
C(3)—C(4)	1.396 (6)	C(4)—C(5)	1.359 (6)
C(5)—C(6)	1.388 (4)		
C(1)—S(1)—O(1)	106.2 (1)	C(1)—S(1)—O(2)	107.8 (1)
C(1)—S(1)—O(3)	107.1 (1)	O(1)—S(1)—O(2)	110.9 (1)
O(1)—S(1)—O(3)	109.6 (1)	O(2)—S(1)—O(3)	114.9 (1)
S(1)—C(1)—C(2)	121.5 (2)	S(1)—C(1)—C(6)	116.4 (2)
C(2)—C(1)—C(6)	122.1 (2)	C(1)—C(2)—C(3)	116.6 (3)
C(1)—C(2)—C(7)	123.9 (2)	C(3)—C(2)—C(7)	119.5 (3)
C(2)—C(3)—C(4)	121.8 (3)	C(3)—C(4)—C(5)	120.1 (3)
C(4)—C(5)—C(6)	119.8 (3)	C(1)—C(6)—C(5)	119.6 (3)

bonding linkage runs through the crystal along the *c* axis. The sulfonate O(1) atom accepts two hydrogen bonds from the water molecules in contrast to the O(2) and O(3) atoms accepting one hydrogen bond.

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## Structure of 1,3,3,5-Tetramethylcyclohexanol

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**Abstract.**  $C_{10}H_{20}O$ ,  $M_r = 156.27$ , tetragonal,  $I\bar{4}$ ,  $a = b = 16.600$  (12),  $c = 7.337$  (3)  $\text{\AA}$ ,  $V = 2022$  (2)  $\text{\AA}^3$ ,  $Z = 8$ ,  $D_m$  (floatation) = 0.96 (2),  $D_x = 1.03$   $\text{g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha_1) = 0.7107$   $\text{\AA}$ ,  $\mu = 0.34$   $\text{cm}^{-1}$ ,  $F(000) = 704$ ,  $T = 184$  K,  $R(F) = 0.062$  for 1288 independent

The lone pair on the sulfonate O(1) atom almost coincides with the hydrogen-bond direction with S—O(1)⋯O angles of 118.9 (2) and 120.5 (2)°. On the other hand, the O(W1)H⋯O(2) hydrogen bond with an S—O(2)⋯O angle of 125.3 (2)° is also satisfactory for the O(2) lone pair, but the O(W2)⋯O(3) hydrogen bond with an S—O(3)⋯O angle of 160.0 (2)° largely deviates from the lone-pair direction of the O(3) atom. Thus the O(W2)H⋯O(3) hydrogen bond is weaker than the others. From such asymmetry, the  $H_5O_2^+$  cation can be assumed to be an aquaoxonium ion with the  $H_3O(W1)^+$  ion bonded to the normal  $H_2O(W2)$  molecule, because the O⋯O distances around O(W1) are shorter than those around O(W2) (Fig. 1b), and the refined H atom between the two water molecules is closer to O(W1).

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