Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anhydrous and Hydrated 4-Aminotoluene-3-sulfonic Acid

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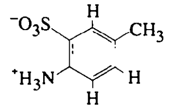
Abstract

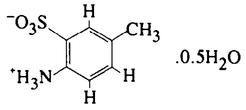
The crystal structures of 4-aminotoluene-3-sulfonic acid, $C_7H_9NO_3S$, (I), and its hemihydrate, $C_7H_9NO_3S.0.5H_2O$, (II), are reported. The acid molecules in both crystals exist as zwitterions (ammoniotoluenesulfonate) and pack in layers in which the phenyl rings are nearly parallel. In (I), the ammonium and sulfonate groups are arranged so that a two-dimensional network of intra- and intermolecular N—H···O hydrogen bonds exists on the faces of each layer. Each ammonium H atom is involved in a single hydrogen bond and there are no strong interactions between the layers. In the hydrate (II), the two crystallographically independent molecules adopt a more complicated double-layer structure in which the polar groups and water molecules are located between every other layer. An extensive two-dimensional network of N—H···O and O—H···O hydrogen bonds holds these double layers together, while only weak interactions involving the methyl and phenyl H atoms occur between these slabs. This two-dimensional nature of the intermolecular hydrogen bonding contrasts with that observed in similar sulfonic acids.

Comment

We have recently examined the crystal structures of several amine-substituted arenesulfonic acids (Shubnell & Squattrito, 1994; Gunderman & Squattrito, 1996) in order to compare the stacking patterns in these layered compounds. The present acid, 4-aminotoluene-3-sulfonic acid, is the third isomer of this compound that we have studied and the first for which both anhydrous, (I), and hydrated, (II), forms have been found. All of the compounds exist in the solid state as zwitterions, with the acidic proton on the amine N atom, and all have N—H···$O_{\text{sulfonate}}$ hydrogen bonds as a primary intermolecular interaction. Nonetheless, each compound displays a distinct packing pattern as a consequence of the different arrangement of the hydrogen-bonding groups on the molecule and, in some cases, the differing water content of the crystals. The 4-aminotoluene-3-sulfonic acid molecule is the first isomer in this series to form anhydrous crystals, (I), in water.



(I)



(II)

The structure of the acid molecule, (I), is shown in Fig. 1. The SO_3^- group is staggered with respect to the ring [torsion angle O3—S1—C3—C4 −36.7 (2)°] and there is a strong intramolecular hydrogen bond between H9 and O3 [1.92 (3) Å]. As the packing diagram (Fig. 2) reveals, the molecules are arranged in layers in the *ac* plane that stack in the **b** direction. The phenyl rings are approximately perpendicular to the plane of the layer, while the SO_3^- and NH_3^+ groups are directed towards the faces of the layer, with pairs of molecules in alternating up/down orientations. There are two intermolecular hydrogen bonds linking neighboring mol-

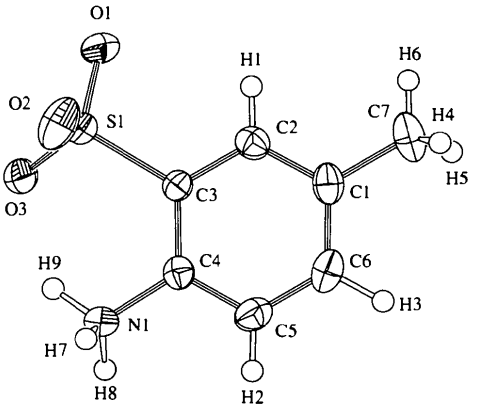


Fig. 1. Molecular diagram of (I) showing the atom-labeling scheme. The displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.

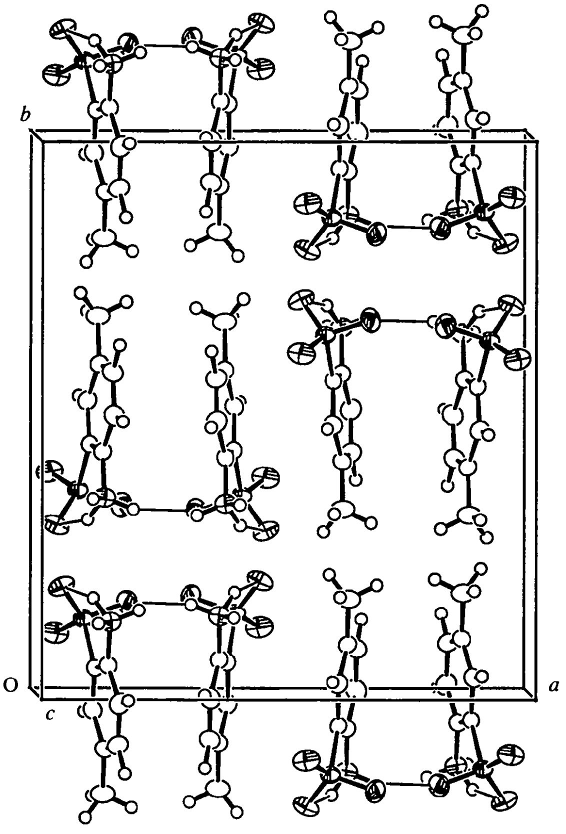


Fig. 2. Packing diagram of (I) showing the outline of the unit cell. The S, O and N atoms are shown with octant shading and hydrogen bonds are indicated by narrow lines. Only one of the intermolecular hydrogen bonds is shown in this view. The displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.

ecules within the layer [H8···O1 1.96 (3) and H7···O2 1.90 (3) Å] so that each amino H atom is involved in a single N—H···O interaction (Table 2). There are no other H···O contacts shorter than 2.5 Å involving either the amino or carbon H atoms.

The hydrogen-bond network is two dimensional, with molecules linked within the layer in the **a** (H7···O2; Fig. 2) and **c** (H8···O1) directions, but not between the layers along **b**. The distances and angles for the N—H···O bonds in (I) and (II) are within the ranges reported for a literature study of 320 such interactions (Pirard, Baudoux & Durant, 1995). This compound also crystallized from the same solution as a hemihydrate (II) with two independent acid molecules and one water molecule in the asymmetric unit (Fig. 3). Both molecules exist as ammonium sulfonate zwitterions, however, in contrast to the case in (I), there are no short intramolecular N—H···O hydrogen bonds. The only such contact under 2.5 Å [H8···O2 2.34 (3) Å] is part of a bifurcated hydrogen bond to another molecule. The SO_3^- groups are rotated differently from each other and from (I) with respect to the C-atom ring [torsion angles O1—S1—C3—C2 −5.2 (4) and O4—S2—C10—C9 −22.3 (3)°]. The hydrate also adopts quite a different packing pattern, as shown in Fig. 4. The acid molecules form double layers in the *bc* plane in which the SO_3^- and NH_3^+ groups are directed towards the interior of the slab where the water molecules also reside. A series of strong intermolecular N—H···O and O—H···O hydrogen bonds (Table 4) links the molecules together in the *bc* plane. In each ammonium group, two H atoms have short (<2.1 Å) hydrogen bonds, while the remaining H atom participates only in substantially longer interactions. The methyl groups of both acid molecules are directed towards the outer surfaces of the double layer, so that no significant hydrogen bonding occurs between double layers.

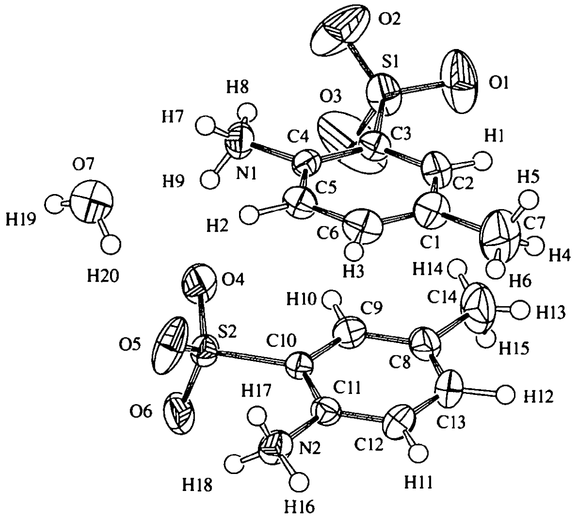


Fig. 3. Molecular diagram of the asymmetric unit of (II) showing the atom-labeling scheme. The displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.

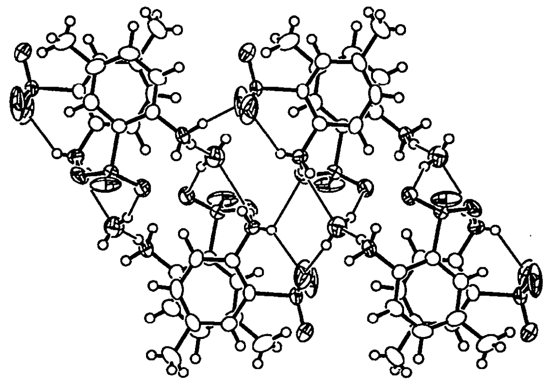


Fig. 4. Packing diagram of (II) showing part of the double layer. The view is along **b** while the *c* axis is horizontal. The S, O and N atoms are shown with octant shading and hydrogen bonds are indicated by narrow lines. The double layers stack vertically with the methyl groups of adjacent slabs in contact. The displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.

This structure differs substantially from those of 2-aminotoluene-4-sulfonic acid and 4-aminotoluene-2-sulfonic acid (Shubnell & Squattrito, 1994), both of which crystallize as monohydrates with water molecules between each layer of acid molecules. A hemihydrate of 3-amino-4-hydroxybenzenesulfonic acid (Gunderman & Squattrito, 1996) also has the water molecules between every layer of acid molecules and a strong three-dimensional hydrogen-bond network, the difference with (II) presumably being due to the presence of the hydroxyl group in place of the methyl group. Despite the lower dimensionality of the hydrogen-bonding network and the reduced water content of (II), its density ($1.494\ \mathrm{Mg\ m^{-3}}$) is essentially the same as those of the other aminotoluenesulfonic acid isomers, while the anhydrous material (I) is denser still ($1.557\ \mathrm{Mg\ m^{-3}}$). It appears that (II) is the more thermodynamically stable phase, as it preferentially crystallizes from either water or aqueous ethanol under a variety of conditions. Indeed, we have not been able to duplicate the growth of single crystals of (I) from aqueous solutions. The anhydrous material can be readily obtained in powder form by dehydration of (II).

Experimental

Light-brown rod-shaped crystals of (I) grew on cooling and evaporating a warm aqueous solution. For (II), yellow needle-shaped crystals grew upon evaporation of solvent from the same aqueous solution that produced (I). Subsequent attempts to duplicate the crystallization of both phases from the same solution have produced only single crystals of the hydrate (II).

Compound (I)

Crystal data

$C_7H_9NO_3S$
$M_r = 187.21$
Orthorhombic
Pccn
$a = 14.637 (3)$ Å
$b = 16.460 (2)$ Å
$c = 6.629 (2)$ Å
$V = 1597.1 (6)$ Å^3
$Z = 8$
$D_x = 1.557$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 17 reflections
$\theta = 13.7–19.1°$
$\mu = 0.352$ mm^{-1}
$T = 296$ K
Rod
$0.25 \times 0.20 \times 0.20$ mm
Brown

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: none
1646 measured reflections
1646 independent reflections
1386 reflections with $I > 0$

$\theta_{max} = 25°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: -0.10%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.038$
$S = 2.18$
1386 reflections
136 parameters
H-atom coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.25$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

S1—O1	1.443 (2)	S1—C3	1.786 (3)
S1—O2	1.456 (2)	N1—C4	1.463 (3)
S1—O3	1.448 (2)		
O1—S1—O2	111.3 (1)	O3—S1—C3	106.4 (1)
O1—S1—O3	114.4 (1)	S1—C3—C2	119.1 (2)
O1—S1—C3	106.7 (1)	S1—C3—C4	122.0 (2)
O2—S1—O3	111.6 (1)	N1—C4—C3	121.4 (2)
O2—S1—C3	105.8 (1)	N1—C4—C5	118.6 (2)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H7···O2^{i}	0.92 (3)	1.90 (3)	2.766 (3)	157 (2)
N1—H8···O1^{ii}	0.96 (3)	1.96 (3)	2.893 (3)	162 (2)
N1—H9···O3	0.98 (3)	1.92 (3)	2.754 (3)	142 (2)

Symmetry codes: (i) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (ii) $x, y, 1 + z$.

Compound (II)

Crystal data

$C_7H_9NO_3S.0.5H_2O$
$M_r = 196.22$
Monoclinic
$P2_1/c$
$a = 15.908 (2)$ Å
$b = 7.337 (5)$ Å
$c = 16.798 (2)$ Å
$\beta = 117.145 (6)°$
$V = 1744 (1)$ Å^3
$Z = 8$
$D_x = 1.494$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 16.5–18.8°$
$\mu = 0.329$ mm^{-1}
$T = 296$ K
Needle
$0.25 \times 0.20 \times 0.10$ mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: none
3438 measured reflections
3314 independent reflections
3046 reflections with $I > 0$

$R_{int} = 0.028$
$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 8$
$l = -19 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: -0.10%

Refinement

Refinement on F
$R = 0.087$
$wR = 0.045$
$S = 1.95$
3046 reflections
286 parameters
H-atom coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.27$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (II)*

S1—O1	1.402 (2)	S2—O5	1.446 (2)
S1—O2	1.424 (3)	S2—O6	1.431 (3)
S1—O3	1.439 (3)	S2—C10	1.773 (3)
S1—C3	1.783 (3)	N1—C4	1.465 (4)
S2—O4	1.438 (2)	N2—C11	1.461 (4)
O1—S1—O2	115.4 (2)	O5—S2—C10	107.0 (1)
O1—S1—O3	112.8 (2)	O6—S2—C10	106.0 (2)
O1—S1—C3	108.1 (1)	S1—C3—C2	120.1 (2)
O2—S1—O3	110.9 (2)	S1—C3—C4	121.4 (2)
O2—S1—C3	105.1 (2)	N1—C4—C3	120.8 (3)
O3—S1—C3	103.4 (2)	N1—C4—C5	118.3 (3)
O4—S2—O5	112.6 (2)	S2—C10—C9	118.5 (2)
O4—S2—O6	112.9 (2)	S2—C10—C11	123.1 (2)
O4—S2—C10	106.4 (1)	N2—C11—C10	120.3 (3)
O5—S2—O6	111.5 (2)	N2—C11—C12	118.8 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H7···O6^{i}	0.86 (3)	2.09 (3)	2.821 (5)	143 (3)
N1—H8···O2	0.77 (3)	2.34 (3)	2.947 (4)	137 (3)
N1—H8···O4^{ii}	0.77 (3)	2.44 (3)	2.847 (4)	114 (3)
N1—H9···O4	0.92 (3)	2.08 (3)	2.907 (5)	149 (3)
N2—H16···O3^{iii}	0.95 (3)	1.75 (3)	2.696 (4)	175 (3)
N2—H17···O7^{iv}	0.87 (3)	1.92 (4)	2.779 (5)	169 (3)
N2—H18···O6^{v}	0.92 (3)	2.41 (3)	2.900 (4)	114 (2)
O7—H19···O2^{vi}	0.83 (4)	2.00 (4)	2.762 (4)	151 (4)
O7—H20···O5	0.89 (4)	2.15 (4)	2.996 (4)	160 (4)

Symmetry codes: (i) $x, 1+y, z$; (ii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (iv) $2-x, -y, -z$; (v) $2-x, -1-y, -z$; (vi) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Phenyl C—C bond distances: (I), 1.379 (4)–1.393 (4), mean 1.386 (4) Å; (II), 1.363 (4)–1.396 (4), mean 1.385 (4) Å. All H atoms were located on difference electron-density maps and refined with fixed isotropic *B* values equal to 1.2 times those of the attached atoms at the time of their inclusion. Bond distance ranges: (I), C—H 0.91 (3)–1.02 (3) and N—H 0.92 (3)–0.98 (3) Å; (II), C—H 0.80 (3)–1.04 (3), N—H 0.77 (3)–0.95 (3) and O—H 0.83 (4)–0.89 (4) Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C53, 651–654

3-Acetamido-4-(cyclooctylamino)nitrobenzene

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Abstract

The crystal and molecular structure of the title compound, *N*-(2-cyclooctylamino-4-nitrophenyl)acetamide, $C_{16}H_{23}N_3O_3$, has been determined as part of an investigation into substituted benzene derivatives having non-linear optical properties. There are two similar independent molecules in the asymmetric unit. The eight-membered rings have very distorted conformations. The molecules are linked by N—H···O hydrogen bonds, with N···O distances in the range 2.889 (5)–3.071 (6) Å.

Comment

There is currently extensive interest in substituted benzene derivatives because of their exceptional non-linear optical properties (Williams, 1983, 1984). Many of these compounds, such as *p*-nitroaniline, exhibit extremely large microscopic second-order non-linear susceptibilities, which are the result of a highly asymmetric charge correlated with the excited states of the π-electronic structure of the molecule, as shown by theoretical calculations (Lalama & Garito, 1979). However, most substituted benzene molecular crystals, for example *p*-nitroaniline, have a centrosymmetric crystal structure which forbids any macroscopic second-order non-linear optical effects (Lalama & Garito, 1979; Oudar & Chemla, 1971; Southgate & Hall, 1971; Carenco, Jerphagnon & Periquard, 1977).

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