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6-Amino-2-ammoniotoluene-4-sulfonate

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2,6-Diaminotoluene-4-sulfonic acid exists in the zwitterionic form as 2-amino-6-ammoniotoluene-4-sulfonate, $C_7H_{10}N_2O_3S$; the molecule features a C—N_{amino} bond [1.372 (3) Å] which is significantly shorter than the C—$N_{ammonio}$ bond [1.473 (3) Å]. Neighbouring molecules are linked by extensive hydrogen bonds into a three-dimensional network structure.

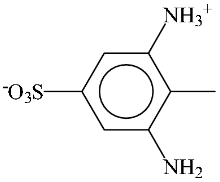
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.115
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

2-Aminotoluene-4-sulfonic acid crystallizes as a monohydrate in the zwitterionic form, and adjacent zwitterions are linked into layers by hydrogen bonds that also involve the water molecule (Shubnell & Squattrito, 1994). The addition of another amino substituent to the molecule gives rise to the title compound (Fig. 1), which now features a C—N_{amino} bond [1.372 (3) Å] as well as the C—$N_{ammonio}$ bond [1.473 (3) Å]. The latter bond distance is similar to that [1.467 (4) Å] in 2-aminotoluene-4-sulfonic acid, as well as that in 3-anilinesulfonic acid [1.44 (2) Å; Hall & Maslen, 1965]. On the other hand, the C—N_{amino} distance is somewhat shorter than those [1.386 (6) and 1.398 (8) Å] in the two independent molecules of aniline (Fukuyo *et al.*, 1982), the N atom of which is pyramidal. The crystal structure of (I) shows some pyramidalization of the amine N atom; however, the degree of pyramidalization is small, and this feature is interpreted in terms of the delocalization of the lone pair over the aromatic system; delocalization would lead to a shortening of the C—N_{amino} bond. If the lone pair is not delocalized, the distance would be similar to the C—$N_{ammonio}$ distance. The distance that is found from geometry-optimization calculations at the *PM*3 level, for which the amine N atom has an idealized pyramidal geometry, is 1.431 Å.



(I)

The molecules are linked by extensive hydrogen bonds (Table 2) into a three-dimensional network structure.

Experimental

The title compound was the unexpected product that resulted from the reaction of copper diacetate dihydrate (2.00 g, 10 mmol) and 3,5-diamino-4-methyl-sulfonic acid (2.02 g, 10 mmol) in ethanol solution. Colourless crystals separated from the solution after several days.

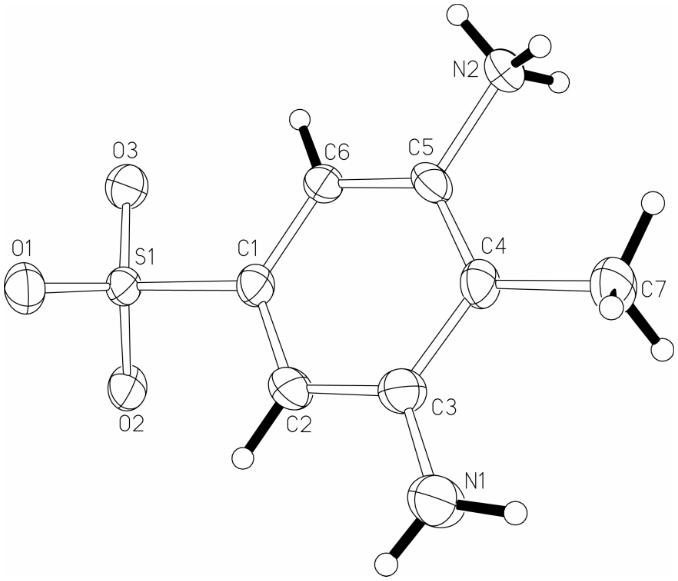


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Analysis calculated for $C_7H_{10}N_2O_3S$: C 41.58, H 4.98, N 13.85%; found: C 41.71, H 4.93, N 13.89%.

For the geometry-optimization calculations with *HYPERCHEM* (Hypercube, 2000), the starting structure was taken from the crystal structure, and this was optimized at the *PM*3 level.

Crystal data

$C_7H_{10}N_2O_3S$
$M_r = 202.23$
Monoclinic, $P2_1/c$
$a = 8.420$ (2) Å
$b = 13.087$ (3) Å
$c = 8.938$ (2) Å
$\beta = 116.45$ (3)°
$V = 881.7$ (3) Å^3
$Z = 4$
$D_x = 1.523$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7571 reflections
$\theta = 3.1$–27.5°
$\mu = 0.34$ mm^{-1}
$T = 295$ (2) K
Block, colourless
0.38 × 0.24 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scan
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.790$, $T_{\max} = 0.967$
8538 measured reflections
2010 independent reflections
1459 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.115$
$S = 1.04$
2010 reflections
158 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.3519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.447 (2)	C1—C6	1.383 (3)
S1—O2	1.462 (2)	C2—C3	1.397 (3)
S1—O3	1.451 (2)	C3—C4	1.410 (3)
S1—C1	1.767 (2)	C4—C5	1.387 (3)
N1—C3	1.372 (3)	C4—C7	1.503 (3)
N2—C5	1.473 (3)	C5—C6	1.382 (3)
C1—C2	1.381 (3)		
O1—S1—O2	111.3 (1)	N1—C3—C2	118.9 (2)
O1—S1—O3	113.3 (1)	N1—C3—C4	120.7 (2)
O2—S1—O3	112.9 (1)	C2—C3—C4	120.3 (2)
O1—S1—C1	106.6 (1)	C3—C4—C5	116.6 (2)
O2—S1—C1	106.0 (1)	C3—C4—C7	119.9 (2)
O3—S1—C1	106.2 (1)	C5—C4—C7	123.5 (2)
C2—C1—C6	121.3 (2)	C4—C5—C6	124.2 (2)
C2—C1—S1	118.9 (2)	C4—C5—N2	118.9 (2)
C6—C1—S1	119.8 (2)	C6—C5—N2	116.8 (2)
C1—C2—C3	120.0 (2)	C1—C6—C5	117.4 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O1$^{\rm i}$	0.85 (1)	2.13 (1)	2.950 (3)	164 (3)
N1—H1N2···O1$^{\rm ii}$	0.85 (1)	2.17 (2)	2.936 (3)	150 (2)
N2—H2N1···O2$^{\rm iii}$	0.85 (1)	2.25 (3)	2.854 (3)	128 (3)
N2—H2N2···O3$^{\rm iv}$	0.86 (1)	1.94 (1)	2.788 (3)	173 (3)
N2—H2N3···O2$^{\rm v}$	0.86 (1)	1.96 (1)	2.806 (3)	168 (3)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y, z-1$; (iv) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $-x, -y+1, -z+1$.

The C—H distances were restrained to 0.95 (1) Å and the N—H distances to 0.85 (1) Å.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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