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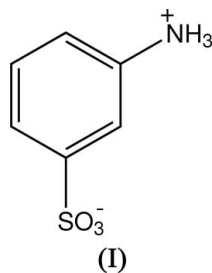
Key indicators

Single-crystal X-ray study
 $T = 130$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.041
 wR factor = 0.066
Data-to-parameter ratio = 13.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The second orthorhombic polymorph of zwitterionic
metanilic acid at 130 KReceived 27 January 2006
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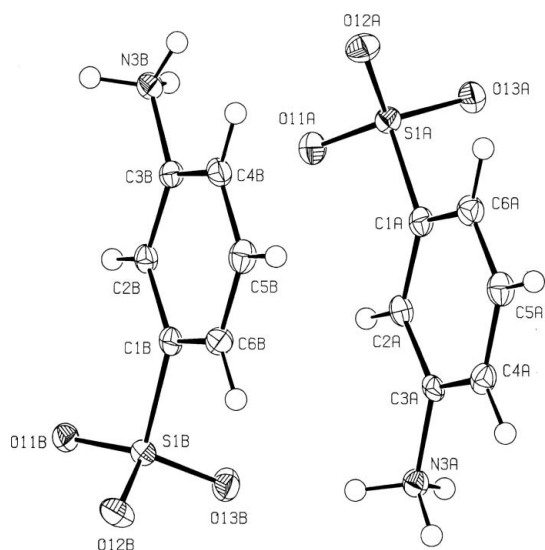
The low-temperature (130 K) crystal structure of the second orthorhombic polymorph of metanilic acid (3-aminobenzenesulfonic acid), $\text{C}_6\text{H}_7\text{NO}_3\text{S}$, shows the presence of two independent and conformationally similar molecules of the zwitterionic acid (3-ammoniobenzenesulfonate) in the asymmetric unit; these interact through hydrogen bonding to give a cyclic $R_2^2(14)$ association. Peripheral hydrogen bonding gives a three-dimensional framework polymer, such as was found in the earlier polymorph [Hall & Maslen (1965), *Acta Cryst.* **18**, 301–306], but the overall structural make-up is significantly different.

Comment

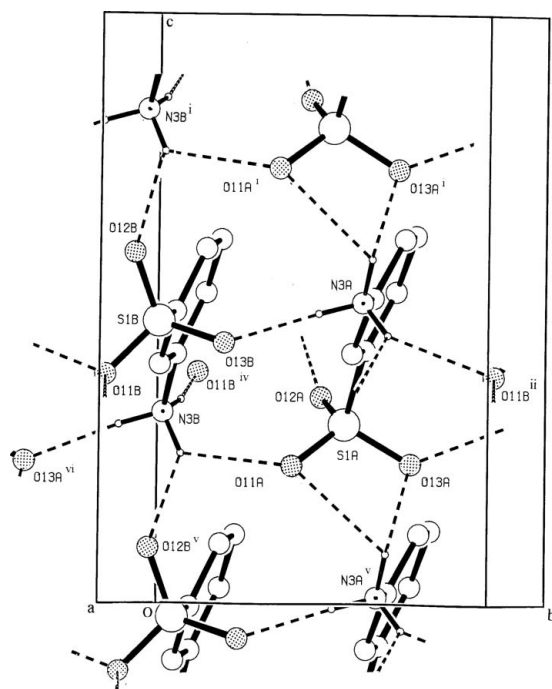
The crystal structures of the *ortho*- and *meta*-substituted monoaminobenzenesulfonic acids, orthanilic acid (Hall & Maslen, 1967) and metanilic acid (Hall & Maslen, 1965), show zwitterionic species, with the sulfonic acid H atom located on the amine group. With the metanilic acid structure (hereafter referred to as polymorph 1), the acid molecule is confined to a crystallographic mirror plane (space group *Pnam*), with two sulfonate O atoms and two aminium H atoms mirrored across the plane. Following the preparation and structure determination of a 1:1 complex between strychnine and 1,7-Cleves acid (8-aminonaphthalene-2-sulfonic acid) (Smith *et al.*, 2006), in which the acid species exists as a zwitterion rather than giving a proton-transfer compound, we attempted the synthesis of similar complexes of both strychnine and brucine with other amino-substituted aromatic sulfonic acids. Generally, there was little success in obtaining crystalline products. However, with metanilic acid, a small number of quality crystals were obtained and these were examined crystallographically at low temperature (130 K) using a CCD-equipped diffractometer. The compound was found to be a different orthorhombic polymorph of metanilic acid, $\text{C}_6\text{H}_7\text{NO}_3\text{S}$, (I) (polymorph 2), which is reported here.



In (I), the crystallographic asymmetric unit comprises two zwitterionic molecules of the acid, *A* and *B* (Fig. 1), which are

**Figure 1**

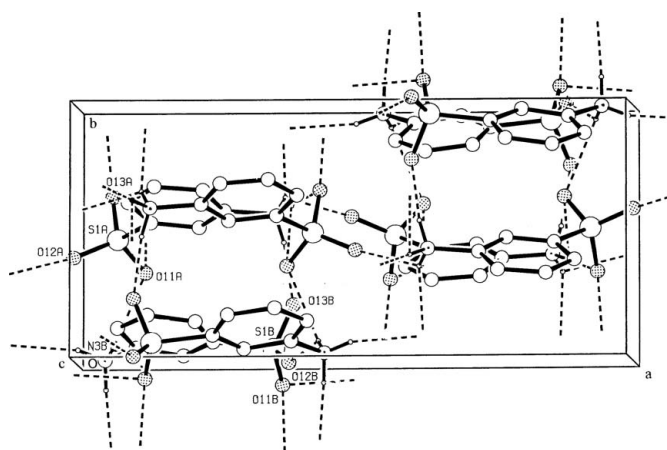
The molecular configuration and atom-labelling scheme for the two independent zwitterionic metanilic species (*A* and *B*) in (I). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

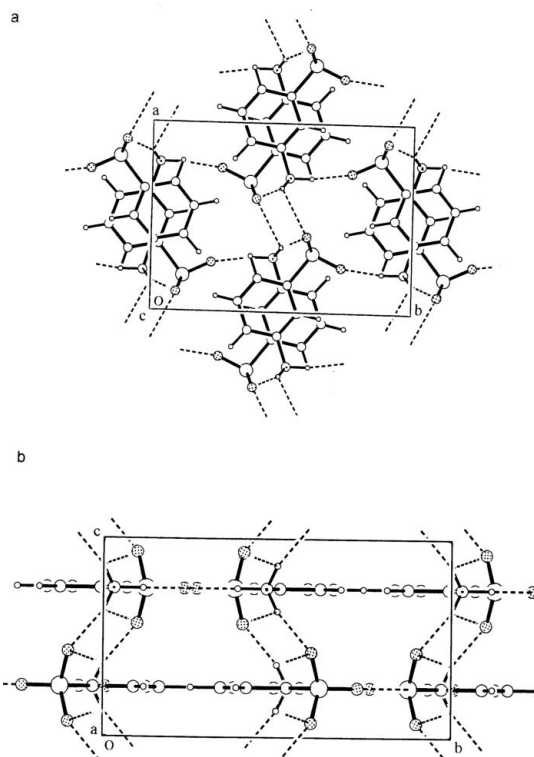
Hydrogen-bonding associations between molecules *A* and *B* of (I), and peripheral extensions in the unit cell, viewed approximately down the *a* axis. Hydrogen bonds are shown as broken lines. For symmetry codes, see Table 2.

conformationally similar; comparative torsion angles about the sulfonate group are given in Table 1. Atoms O11A and O11B lie out of the plane of the benzene ring [C2—C1—S1—O11 = 22.8 (2)° in molecule *A* and −22.2 (2)° in molecule *B*; Fig. 1], differing from what was found in polymorph 1 (0°; Hall & Maslen, 1965).

Molecules *A* and *B* lie anti-parallel and interact through $N^+ - H \cdots O^-_{\text{sulfonate}}$ hydrogen bonds [$N3A - H31A \cdots O13B =$

**Figure 3**

The three-dimensional polymer structure in the unit cell, viewed approximately down the *c* axis. Dashed lines indicate hydrogen bonds.

**Figure 4**

Comparative packing of the molecules in polymorph 1 (Hall & Maslen, 1965), viewed (*a*) perpendicular to the mirror planes and (*b*) parallel to the crystallographic mirror planes.

2.780 (3) Å and $N3B - H32B \cdots O11A = 2.971 (3) \text{ Å}$], completing a cyclic $R_2^2(14)$ association (Figs. 2 and 3). Other hydrogen-bonding associations involving all available aminium-H donors and sulfonate-O acceptors (Table 2), including an $R_3^3(8)$ extension along the *c* axis direction, gives a three-dimensional cage polymer structure. The three-dimensional structure of polymorph 1 is significantly different from (I), being based on inter-associated hydrogen-bonded layers of the acids which are confined to the crystallographic mirror planes (Fig. 4).

Experimental

The title compound was obtained from the attempted synthesis of a strychnine complex with 3-aminobenzenesulfonic acid (metanilic acid), by heating together 1 mmol quantities of the acid and strychnine in 80% ethanol–water (50 ml) for 10 min under reflux. After concentration to ca 30 ml, partial room-temperature evaporation of the hot-filtered solution gave a small quantity of pale-brown crystals of (I) [literature indicates decomposition without melting (O’Neil, 2001)].

Crystal data

C₆H₇NO₃S
M_r = 173.20
 Orthorhombic, *Pca*2₁
a = 15.9489 (15) Å
b = 7.4448 (7) Å
c = 11.1716 (11) Å
V = 1326.5 (2) Å³
Z = 8
D_x = 1.734 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 2303 reflections
 θ = 3.0–27.3°
 μ = 0.44 mm⁻¹
T = 130 (2) K
 Plate, pale brown
 0.45 × 0.35 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.83, *T_{max}* = 0.96
 7877 measured reflections

2995 independent reflections
 2682 reflections with *I* > 2σ(*I*)
R_{int} = 0.043
 θ_{\max} = 27.5°
h = -20 → 17
k = -9 → 9
l = -14 → 14

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.041
wR (*F*²) = 0.066
S = 0.94
 2995 reflections
 223 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1985), with 200 Friedel pairs
 Flack parameter: -0.03 (6)

Table 1

Selected torsion angles (°).

O11A–S1A–C1A–C2A	22.8 (2)	O12B–S1B–C1B–C2B	-141.6 (2)
O12A–S1A–C1A–C2A	145.46 (18)	O13B–S1B–C1B–C2B	97.1 (2)
O13A–S1A–C1A–C2A	-94.40 (19)	O11B–S1B–C1B–C6B	159.05 (17)
O11A–S1A–C1A–C6A	-160.2 (2)	O12B–S1B–C1B–C6B	39.7 (2)
O12A–S1A–C1A–C6A	-37.6 (2)	O13B–S1B–C1B–C6B	-81.6 (2)
O13A–S1A–C1A–C6A	82.6 (2)	O11B–S1B–C1B–C2B	-22.2 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N3A–H31A···O11A ⁱ	0.98 (3)	2.46 (3)	2.979 (3)	113 (2)
N3A–H31A···O13A ⁱ	0.98 (3)	1.95 (3)	2.935 (3)	177 (3)
N3A–H32A···O13B	0.88 (3)	1.91 (3)	2.780 (3)	171 (3)
N3A–H33A···O11B ⁱⁱ	0.83 (3)	2.19 (3)	2.894 (3)	143 (3)
N3A–H33A···O12A ⁱⁱⁱ	0.83 (3)	2.26 (3)	2.808 (3)	124 (2)
N3B–H31B···O11B ^{iv}	0.85 (3)	2.15 (3)	2.985 (3)	169 (3)
N3B–H32B···O11A	0.88 (3)	2.40 (3)	2.971 (3)	123 (2)
N3B–H32B···O12B ^v	0.88 (3)	2.06 (3)	2.781 (3)	138 (2)
N3B–H33B···O13A ^{vi}	0.96 (3)	1.88 (3)	2.837 (3)	178 (3)

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

H atoms potentially involved in hydrogen-bonding interactions [H31A–H33A and H31B–H33B] were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions, with C–H = 0.95 Å, and treated as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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