The second orthorhombic polymorph of zwitterionic metanilic acid at 130 K
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Key indicators

Single-crystal X-ray study

\[ T = 130 \text{ K} \]

Mean \( \sigma(C-C) = 0.003 \text{ \AA} \)

\( R \) factor = 0.041

\( wR \) factor = 0.066

Data-to-parameter ratio = 13.4

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

Comment

The crystal structures of the \textit{ortho}- and \textit{meta}-substituted monoaminobenzenesulfonic acids, orthanilic acid (Hall & Maslen, 1967) and metanilic acid (Hall & Maslen, 1965), show zwitterionic species, with the sulfonic acid \( \text{H} \) 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 \textit{Pnam\textendash}), with two sulfonate \( \text{O} \) atoms and two aminium \( \text{H} \) 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 \textit{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, \textit{A} and \textit{B} (Fig. 1), which are...
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···O− sulfonate hydrogen bonds [N3A—H31A···O13B = 2.780 (3) Å and N3B—H32B···O11A = 2.971 (3) 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 (metanic 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, Pca₂̃

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

Data collection

Bruker SMART CCD area-detector diffractometer

w and o scans

Absorption correction: multi-scan (SADABS; Bruker, 1999)

T_max = 0.83, T_min = 0.96

2995 independent reflections

Refinement

Reefinement on F²

wR(F²) = 0.066

S = 0.94

2995 reflections

H atoms treated by a mixture of independent and constrained refinement

Table 1

Selected torsion angles (°).

<table>
<thead>
<tr>
<th>Torsion angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O11–C1–C1A–C2A</td>
<td>22.8 (2)</td>
</tr>
<tr>
<td>O12A–C1–C1A–C2A</td>
<td>145.46 (18)</td>
</tr>
<tr>
<td>O11A–C1–C1A–C6A</td>
<td>160.2 (2)</td>
</tr>
<tr>
<td>O13A–C1–C1A–C6A</td>
<td>82.6 (2)</td>
</tr>
</tbody>
</table>

Table 2

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>D–H...A</th>
<th>D–H</th>
<th>H–A</th>
<th>D–A</th>
<th>D–H...A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3A–H31A...O11A</td>
<td>0.98 (3)</td>
<td>2.46 (3)</td>
<td>2.979 (3)</td>
<td>113 (2)</td>
<td></td>
</tr>
<tr>
<td>N3A–H31A...O13A</td>
<td>0.98 (3)</td>
<td>1.95 (3)</td>
<td>2.935 (3)</td>
<td>177 (3)</td>
<td></td>
</tr>
<tr>
<td>N3A–H32A...O13B</td>
<td>0.83 (3)</td>
<td>1.91 (3)</td>
<td>2.780 (3)</td>
<td>171 (3)</td>
<td></td>
</tr>
<tr>
<td>N3A–H33A...O11Bᵦ</td>
<td>0.83 (3)</td>
<td>2.19 (3)</td>
<td>2.894 (3)</td>
<td>143 (3)</td>
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</tr>
<tr>
<td>N3A–H33A...O12Aᵦ</td>
<td>0.83 (3)</td>
<td>2.26 (3)</td>
<td>2.808 (3)</td>
<td>124 (2)</td>
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</tr>
<tr>
<td>N3B–H31B...O11Bᵦ</td>
<td>0.85 (3)</td>
<td>2.15 (3)</td>
<td>2.985 (3)</td>
<td>169 (3)</td>
<td></td>
</tr>
<tr>
<td>N3B–H32B...O12Bᵦ</td>
<td>0.88 (3)</td>
<td>2.40 (3)</td>
<td>2.971 (3)</td>
<td>123 (2)</td>
<td></td>
</tr>
<tr>
<td>N3B–H33B...O13Aᵦ</td>
<td>0.96 (3)</td>
<td>1.83 (3)</td>
<td>2.837 (3)</td>
<td>178 (3)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x+1/2, y, z+1/2; (ii) x, y+1, z; (iii) x+1/2, y, z−1/2; (iv) −x+1/2, y, z−1/2.

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 Uiso(H) = 1.2Ueq(C).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; 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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References


