Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Methoxyanilinium 3-carboxy-4-hydroxy-benzenesulfonate dihydrate

Graham Smith,[a]* Urs D. Wermuth[a] and Peter C. Healy[b]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and [b]School of Science, Griffith University, Nathan, Queensland 4111, Australia

Correspondence e-mail: g.smith@qut.edu.au

Received 8 May 2006
Accepted 9 May 2006

The 1:1 proton-transfer compound of *m*-anisidine with 5-sulfosalicylic acid, 3-methoxyanilinium 3-carboxy-4-hydroxy-benzenesulfonate dihydrate, $C_7H_{10}NO^+\cdot C_7H_5O_6S^-\cdot 2H_2O$, is a three-dimensional framework structure built from hydrogen-bonding interactions involving the aminium group of the cation, the two water molecules of solvation and the sulfonate, carboxylate and phenolic substituent groups of the anion.

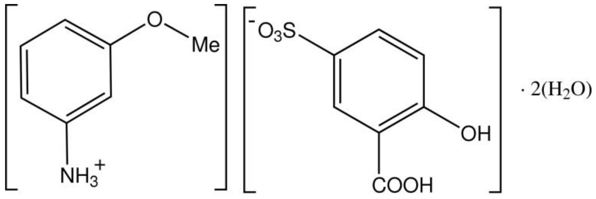
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.007 Å
R factor = 0.037
wR factor = 0.129
Data-to-parameter ratio = 8.6

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

Comment

A number of 1:1 proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) with aniline-type Lewis bases have been reported: with aniline (Bakasova *et al.*, 1991), the 4-X-substituted anilines (X = F, Cl, Br) (Smith *et al.*, 2005*a*), X = CO_2H (Smith *et al.*, 2005*b*), 3-aminobenzoic acid (Smith, 2005), and 1,4-phenylenediamine (Smith *et al.*, 2005). In the majority of these structures, 1:1 proton-transfer compounds are formed and are usually hydrates. The structure of the compound formed from the reaction of 5-SSA with 3-methoxyaniline (*m*-anisidine, MANIS) in 50% ethanol–water, *viz*. 3-methoxyanilinium 5-sulfosalicylate dihydrate, (I), reported here, also shows this common trend.



(I)

In (I), the MANIS cation, the 5-SSA anion and the two water molecules of solvation (Fig. 1) form a three-dimensional hydrogen-bonded framework structure (Fig. 2). The cation and anion pairs in the asymmetric unit have assembled with their benzene rings essentially parallel [ring centroid separation ($Cg\cdots Cg$) = 3.676 (3) Å and inter-plane dihedral angle α, = 4.9 (5)°], and their associative functional groups lying essentially parallel to the 2_1 screw axis of the unit cell. The two water molecules of solvation (O1*W* and O2*W*) lie in layers between these end groups and serve as donors for hydrogen-bonding associations with O-atom acceptors from three separate sulfonate groups, as well as one from a phenol group (Table 1). The water molecules also act as acceptors for an aminium H atom and the carboxylic acid H atom. The other aminium protons are also associated with either sulfonate O-atom acceptors or the carboxyl O-atom acceptor of the anion species, giving a three-dimensional framework structure.

doi:10.1107/S1600536806017090

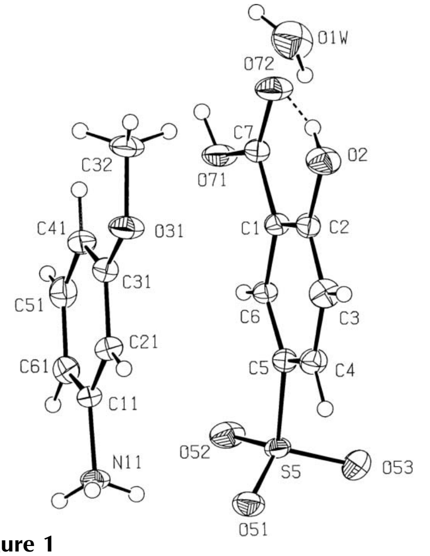


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 40% probability level. The intramolecular hydrogen bond is shown as a dashed line.

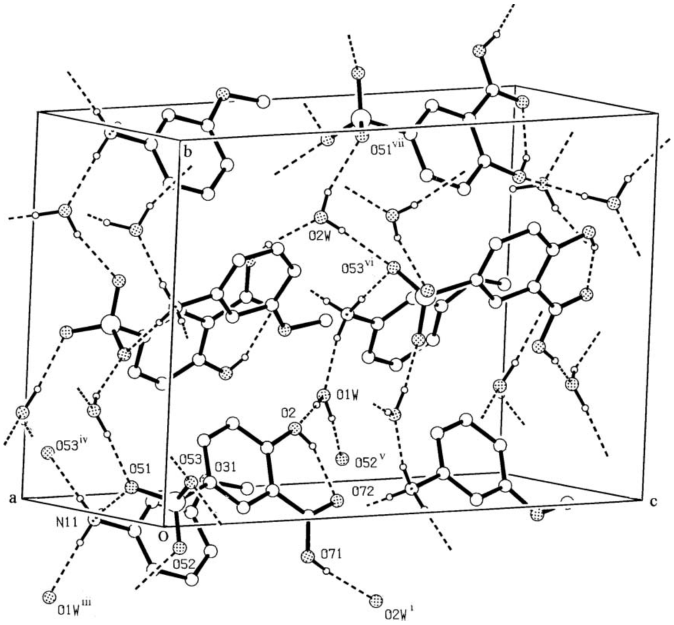


Figure 2
A perspective view of the packing of (I) in the unit cell, showing hydrogen-bonding associations as dashed lines. For symmetry codes see Table 1.

The 5-SSA anions have the usual intramolecular O—H(phenol)···O(carboxyl) hydrogen bond [2.593 (5) Å] with the carboxylic acid group lying essentially in the plane of the benzene ring [torsion angle C2—C1—C7—O71 = −171.6 (5)°]. The methoxy group of the MANIS cation is also essentially coplanar with the benzene ring [torsion angle C21—C31—O31—C32 = 177.7 (5)°].

Experimental

The title compound, (I), was synthesized by heating 1 mmol quantities of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) and 3-methoxyaniline (*m*-anisidine) in 50% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, total room-temperature evaporation of the hot-filtered solution gave pale-brown prisms of (I).

Crystal data

$C_7H_{10}NO^+\cdot C_7H_5O_6S^-\cdot 2H_2O$
$M_r = 377.37$
Orthorhombic, $Pna2_1$
$a = 7.1911$ (6) Å
$b = 12.1574$ (12) Å
$c = 18.7595$ (12) Å
$V = 1640.1$ (2) Å^3
$Z = 4$
$D_x = 1.528$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 297$ (2) K
Prism, pale brown
0.44 × 0.30 × 0.15 mm

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
$T_{min} = 0.899$, $T_{max} = 0.964$
2366 measured reflections
1943 independent reflections
1462 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.5°$
3 standard reflections
frequency: 150 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.129$
$S = 0.84$
1943 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.5948P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.13 (14)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O72	0.78 (7)	1.88 (7)	2.593 (5)	153 (8)
O71—H71···O2W^{i}	0.86 (6)	1.84 (6)	2.649 (7)	157 (6)
N11—H11A···O51	0.84 (7)	2.09 (8)	2.910 (6)	166 (7)
N11—H11A···O72^{ii}	0.84 (7)	2.52 (8)	2.791 (5)	100 (6)
N11—H11B···O1W^{iii}	0.86 (8)	1.95 (8)	2.797 (7)	170 (5)
N11—H11C···O53^{iv}	0.92 (8)	2.02 (8)	2.937 (6)	178 (10)
O1W—H11W···O2	0.93 (9)	2.12 (9)	3.048 (7)	174 (9)
O1W—H12W···O52^{v}	0.87 (9)	1.98 (9)	2.811 (6)	161 (7)
O2W—H21W···O53^{vi}	0.90 (8)	1.90 (8)	2.804 (7)	180 (10)
O2W—H22W···O51^{vii}	0.86 (9)	2.08 (8)	2.911 (6)	161 (7)

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

H atoms potentially involved in hydrogen-bonding interactions 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 (C—H = 0.95 Å), using a riding-model approximation, with U_{iso}(H) values fixed at $1.2U_{eq}$(C). The absolute structure was determined without any Friedel pairs.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The School of Science, Griffith University and the School of Physical and Chemical Sciences, Queensland University of Technology are thanked for financial assistance.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarno, C., Giacovazzo, A., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.

Bakasova, Z. B., Abdybaliev, D. A., Sharipov, Kh. T., Akbaev, A. A., Ibragimov, B. T., Talipov, S. A. & Ismankulov, A. I. (1991). *Uzb. Khim. Zh.* pp. 22–25.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN for Windows* (Version 1.06). MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Smith, G. (2005). *Acta Cryst.* E**61**, o3398–o3400.

Smith, G., Wermuth, U. D. & Healy, P. C. (2005). *Acta Cryst.* C**61**, o555–o558.

Smith, G., Wermuth, U. D. & White, J. M. (2005*a*). *Acta Cryst.* C**61**, o105–o109.

Smith, G., Wermuth, U. D. & White, J. M. (2005*b*). *Acta Cryst.* E**61**, o313–o316.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.