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4-Ammonio-5-methoxy-2-methylbenzenesulfonate

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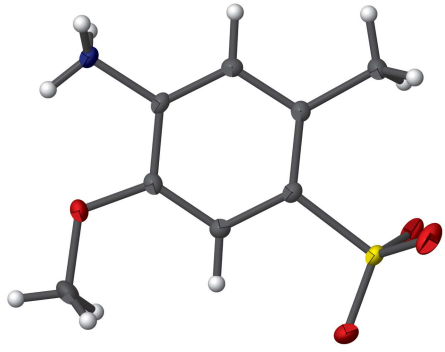
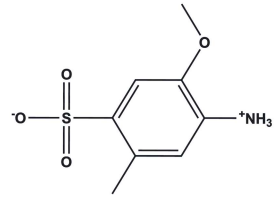
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_8H_{11}NO_4S$, crystallizes as a zwitterion, with the negatively charged benzenesulfonate group and the positively charged NH_3^+ group in mutually *para* positions. All the non-H atoms, except for one O atom of the sulfonate group, lie on a crystallographic mirror plane (Z' = 1/2). In the crystal, the hydrogen-bonding structure is two-dimensional, propagating in the *c*-axis direction through a bifurcated hydrogen bond between the NH_3^+ and the SO_3^- groups, and in the *b*-axis direction through an $R_2^2(16)$ ring motif involving the same functional groups. This latter hydrogen bonding is supported by offset π–π interactions [intercentroid distance = 3.8114 (4) Å].

3D view



Chemical scheme



Structure description

Amino-benzenesulfonic acids are used extensively in the preparation of azo dyes and pigments (Christie, 2015). Their crystal structures tend to be zwitterionic with a negatively charged sulfonate and protonation of the amine to give NH_3^+ (Smith *et al.*, 2006; Butcher & Deschamps, 2006; Śledź *et al.*, 2010).

The title compound, crystallizes as a zwitterion, as shown in Fig. 1. The body of the molecule lies on the crystallographic mirror plane ($Z' = \frac{1}{2}$) with only atom O3 of the sulfonate group and H atoms of the methyl and NH_3^+ groups out of plane. Close examination of the displacement ellipsoids of the methoxy group indicate that these are a little larger than those for the other atoms – thus there may be minor (unmodelled) out of plane disorder present.

In the crystal, hydrogen bonding involves the NH_3^+ group as an H-donor and the O atoms of the SO_3^- group as the acceptors (Table 1). This gives a two-dimensional hydrogen-bonding network (Fig. 2), with bifurcated bonds from H atom H2*N* to O3^{ii} and O3^{iii} (see Table 1), forming sheets parallel to the *ab* plane, and the remaining donor and acceptor atoms forming an $R_2^2(16)$ ring motif that supports offset π–π stacking parallel to the *b*-axis direction (Table 1 and Fig. 3); intercentroid distances $Cg\cdots Cg^{a,b,c}$ =

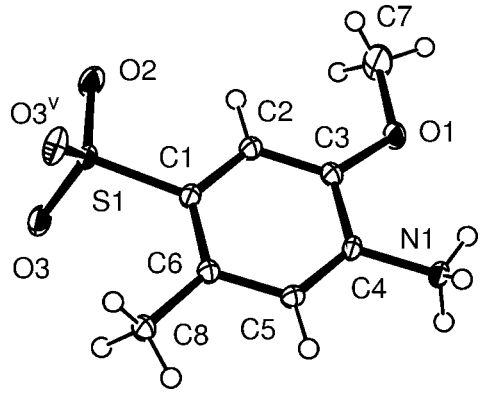


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level [symmetry code: (v) $x, -y+\frac{1}{2}, z$].

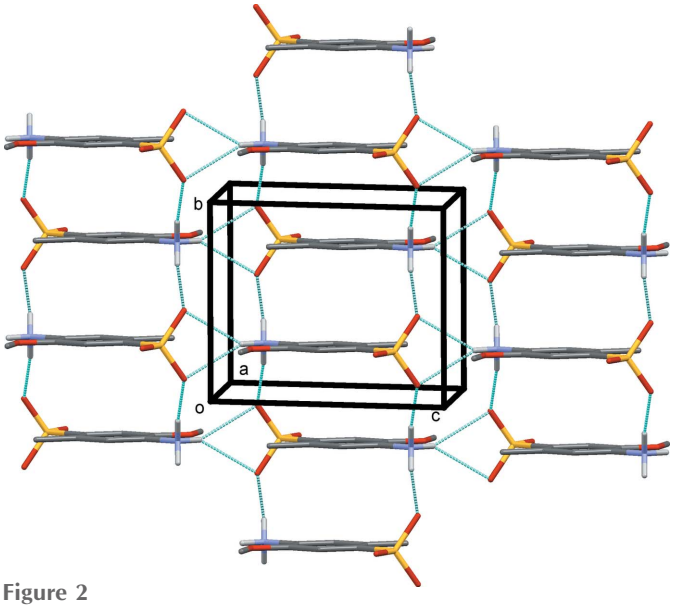


Figure 2
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds are drawn as dashed lines (see Table 1) and only the ammonium H atoms have been included.

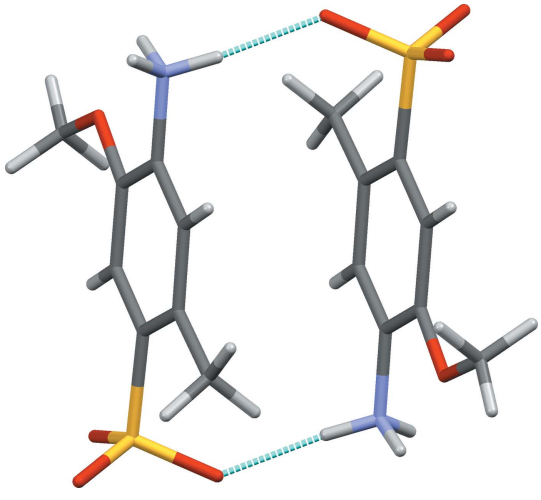


Figure 3
The $R_2^2(16)$ ring motif, with hydrogen bonds drawn as dashed lines (see Table 1), that supports π–π stacking parallel to the *b*-axis direction.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O3^{i}	0.89 (2)	1.83 (2)	2.7100 (13)	171.9 (16)
N1—H2*N*···O3^{ii}	0.89 (3)	2.35 (3)	3.0909 (18)	141 (1)
N1—H2*N*···O3^{iii}	0.89 (3)	2.35 (3)	3.0909 (18)	141 (1)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$NH_4^+ \cdot C_8H_7O_4S^-$
M_r	217.24
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	123
a, b, c (Å)	8.0644 (3), 6.9410 (2), 8.6192 (3)
β (°)	105.039 (4)
V (Å^3)	465.94 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.34
Crystal size (mm)	0.34 × 0.19 × 0.08
Data collection	
Diffractometer	Oxford Diffraction Xcalibur E
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.960, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4897, 1187, 1101
R_{int}	0.017
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.680
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.081, 1.10
No. of reflections	1187
No. of parameters	103
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.46

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

3.8114 (4) Å, *Cg* is the centroid of the benzene ring C1–C6, interplanar distances = 3.4705 Å, slippages = 1.575 Å, symmetry codes: (*a*) $-x+1, -y, -z+1$, (*b*) $-x+1, y-\frac{1}{2}, -z+1$, (*c*) $-x+1, y+\frac{1}{2}, -z+1$.

Synthesis and crystallization

The crystallization of 4-azaniumyl-5-methoxy-2-methylbenzene-1-sulfonate occurred during an attempt to synthesize a salt form of *rac*-methylephedrine by reaction with 4-amino-5-methoxy-2-methylbenzenesulfonic acid (Kennedy *et al.*, 2011). Synthesis was by adding 1.10 mmol of the acid to 1.00 mmol of the base, both previously partially dissolved in approximately 5 ml of deionized water. The resulting solution was stirred for 30 min at 323 K, filtered into a test tube and left to slowly evaporate. The title compound crystallized as colourless plates on the walls of the test tube.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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4-Ammonio-5-methoxy-2-methylbenzenesulfonate

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4-Azaniumyl-5-methoxy-2-methylbenzenesulfonate

Crystal data

$NH_4^+ \cdot C_8H_7O_4S^-$
M_r = 217.24
Monoclinic, $P2_1/m$
a = 8.0644 (3) Å
b = 6.9410 (2) Å
c = 8.6192 (3) Å
β = 105.039 (4)°
V = 465.94 (3) Å^3
Z = 2
$F(000)$ = 228
D_x = 1.548 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3052 reflections
θ = 3.8–28.4°
μ = 0.34 mm^{-1}
T = 123 K
Plate, colourless
0.34 × 0.19 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur E diffractometer
Radiation source: sealed tube
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.960, T_{max} = 1.000
4897 measured reflections
1187 independent reflections
1101 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.9°, θ_{min} = 3.1°
h = −10→10
k = −9→8
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.081
S = 1.10
1187 reflections
103 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.2128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3390 (2)	0.2500	0.5975 (2)	0.0141 (3)
C2	0.2229 (2)	0.2500	0.4465 (2)	0.0153 (4)
H2	0.1029	0.2500	0.4370	0.018*
C3	0.2838 (2)	0.2500	0.3100 (2)	0.0145 (3)
C4	0.4604 (2)	0.2500	0.3286 (2)	0.0136 (3)
C5	0.5753 (2)	0.2500	0.4784 (2)	0.0143 (3)
H5	0.6951	0.2500	0.4868	0.017*
C6	0.5174 (2)	0.2500	0.6183 (2)	0.0139 (3)
C8	0.6490 (2)	0.2500	0.7788 (2)	0.0179 (4)
N1	0.5211 (2)	0.2500	0.18268 (18)	0.0160 (3)
O1	0.18687 (16)	0.2500	0.15613 (15)	0.0203 (3)
O2	0.06437 (18)	0.2500	0.70299 (17)	0.0283 (4)
O3	0.31405 (13)	0.07835 (14)	0.85950 (11)	0.0242 (3)
S1	0.24756 (5)	0.2500	0.76544 (5)	0.01480 (15)
C7	0.0052 (3)	0.2500	0.1290 (3)	0.0410 (7)
H1N	0.583 (2)	0.146 (2)	0.1771 (19)	0.023 (4)*
H2N	0.430 (4)	0.2500	0.097 (3)	0.037 (7)*
H8B	0.642 (2)	0.140 (3)	0.844 (2)	0.033 (5)*
H7B	−0.033 (3)	0.136 (3)	0.178 (3)	0.053 (6)*
H7A	−0.036 (4)	0.2500	0.022 (4)	0.056 (9)*
H8A	0.762 (4)	0.2500	0.763 (3)	0.043 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0145 (8)	0.0160 (8)	0.0127 (8)	0.000	0.0055 (6)	0.000
C2	0.0126 (8)	0.0195 (9)	0.0142 (8)	0.000	0.0041 (6)	0.000
C3	0.0145 (8)	0.0164 (8)	0.0116 (8)	0.000	0.0017 (6)	0.000
C4	0.0163 (8)	0.0146 (8)	0.0116 (8)	0.000	0.0066 (6)	0.000
C5	0.0118 (8)	0.0163 (8)	0.0149 (8)	0.000	0.0038 (6)	0.000
C6	0.0140 (8)	0.0153 (8)	0.0123 (8)	0.000	0.0033 (6)	0.000
C8	0.0142 (9)	0.0258 (10)	0.0127 (8)	0.000	0.0018 (6)	0.000
N1	0.0156 (8)	0.0219 (8)	0.0117 (7)	0.000	0.0059 (6)	0.000
O1	0.0149 (7)	0.0344 (8)	0.0105 (6)	0.000	0.0010 (5)	0.000
O2	0.0150 (7)	0.0522 (10)	0.0195 (7)	0.000	0.0077 (5)	0.000
O3	0.0332 (6)	0.0241 (5)	0.0201 (5)	0.0068 (4)	0.0156 (4)	0.0057 (4)
S1	0.0150 (2)	0.0192 (2)	0.0118 (2)	0.000	0.00628 (16)	0.000
C7	0.0151 (10)	0.088 (2)	0.0167 (10)	0.000	−0.0021 (8)	0.000

Geometric parameters (Å, º)

C1—C2	1.392 (2)	C6—C8	1.510 (2)
C1—C6	1.403 (2)	C8—H8B	0.960 (18)
C1—S1	1.7869 (17)	C8—H8A	0.96 (3)
C2—C3	1.388 (2)	N1—H1N	0.886 (18)

C2—H2	0.9500	N1—H2N	0.89 (3)
C3—O1	1.354 (2)	O1—C7	1.422 (3)
C3—C4	1.391 (2)	O2—S1	1.4351 (14)
C4—C5	1.380 (2)	O3—S1	1.4625 (10)
C4—N1	1.464 (2)	S1—O3^{i}	1.4624 (10)
C5—C6	1.401 (2)	C7—H7B	0.99 (2)
C5—H5	0.9500	C7—H7A	0.90 (4)
C2—C1—C6	122.56 (15)	C1—C6—C8	124.83 (15)
C2—C1—S1	116.02 (13)	C6—C8—H8B	113.8 (11)
C6—C1—S1	121.42 (13)	C6—C8—H8A	109.9 (17)
C3—C2—C1	119.50 (16)	H8B—C8—H8A	106.4 (14)
C3—C2—H2	120.2	C4—N1—H1N	111.3 (11)
C1—C2—H2	120.2	C4—N1—H2N	108.6 (18)
O1—C3—C2	126.10 (16)	H1N—N1—H2N	108.0 (14)
O1—C3—C4	115.26 (15)	C3—O1—C7	118.00 (15)
C2—C3—C4	118.64 (16)	O2—S1—O3^{i}	113.68 (5)
C5—C4—C3	121.77 (15)	O2—S1—O3	113.68 (5)
C5—C4—N1	120.73 (15)	O3^{i}—S1—O3	109.11 (8)
C3—C4—N1	117.49 (15)	O2—S1—C1	107.28 (8)
C4—C5—C6	120.80 (16)	O3^{i}—S1—C1	106.27 (5)
C4—C5—H5	119.6	O3—S1—C1	106.27 (5)
C6—C5—H5	119.6	O1—C7—H7B	110.8 (13)
C5—C6—C1	116.72 (15)	O1—C7—H7A	105 (2)
C5—C6—C8	118.44 (15)	H7B—C7—H7A	111.6 (17)
C6—C1—C2—C3	0.000 (1)	C2—C1—C6—C5	0.000 (1)
S1—C1—C2—C3	180.000 (1)	S1—C1—C6—C5	180.000 (1)
C1—C2—C3—O1	180.000 (1)	C2—C1—C6—C8	180.000 (1)
C1—C2—C3—C4	0.000 (1)	S1—C1—C6—C8	0.000 (1)
O1—C3—C4—C5	180.000 (1)	C2—C3—O1—C7	0.000 (1)
C2—C3—C4—C5	0.000 (1)	C4—C3—O1—C7	180.000 (1)
O1—C3—C4—N1	0.000 (1)	C2—C1—S1—O2	0.000 (1)
C2—C3—C4—N1	180.000 (1)	C6—C1—S1—O2	180.000 (1)
C3—C4—C5—C6	0.000 (1)	C2—C1—S1—O3^{i}	−121.93 (5)
N1—C4—C5—C6	180.000 (1)	C6—C1—S1—O3^{i}	58.07 (5)
C4—C5—C6—C1	0.000 (1)	C2—C1—S1—O3	121.93 (5)
C4—C5—C6—C8	180.000 (1)	C6—C1—S1—O3	−58.07 (5)

Symmetry code: (i) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O3^{ii}	0.89 (2)	1.83 (2)	2.7100 (13)	171.9 (16)
N1—H2*N*···O3^{iii}	0.89 (3)	2.35 (3)	3.0909 (18)	141 (1)
N1—H2*N*···O3^{iv}	0.89 (3)	2.35 (3)	3.0909 (18)	141 (1)

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