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4-Bromo-3-methylanilinium hydrogen sulfate

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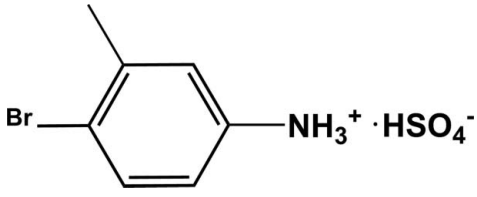
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.049; wR factor = 0.115; data-to-parameter ratio = 18.0.

In the cation of the title compound, $C_7H_9BrN^+\cdot HSO_4^-$, the amino N atom is protonated. In the crystal, intermolecular O—H···O and N—H···O hydrogen bonds generate an infinite two-dimensional network parallel to (001).

Related literature

For the structures of amino derivatives, see: Fu *et al.* (2007, 2008); Fu & Xiong (2008). Amino derivatives are used in the construction of metal-organic frameworks. For applications of metal-organic coordination compounds, see: Chen *et al.* (2001); Xiong *et al.* (1999); Xie *et al.* (2002); Zhao *et al.* (2004); Wang *et al.* (2002).



Experimental

Crystal data

$C_7H_9BrN^+\cdot HSO_4^-$
M_r = 284.13
Triclinic, $P\overline{1}$
a = 4.9448 (10) Å
b = 6.4084 (13) Å
c = 16.674 (3) Å
α = 98.92 (3)°
β = 96.22 (3)°
γ = 100.01 (3)°
V = 509.04 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 4.23 mm^{-1}
T = 298 K
0.40 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 1.000
5279 measured reflections
2323 independent reflections
1804 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.115
S = 1.07
2323 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.89	1.90	2.767 (3)	166
N1—H1B···O2^{ii}	0.89	1.91	2.797 (4)	173
O1—H1···O4^{iii}	0.82	1.84	2.650 (3)	168
N1—H1C···O4	0.89	2.09	2.829 (4)	140

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by a start-up grant from Southeast University to Professor Ren-Gen Xiong.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2203).

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supporting information

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4-Bromo-3-methylanilinium hydrogen sulfate

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S1. Comment

The construction of metal-organic coordination compounds has attracted much attention owing to potential functions, such as permittivity, fluorescence, magnetism and optical properties (Wang *et al.* 2002; Fu *et al.*, 2008; Chen *et al.*, 2001; Xie *et al.*, 2002; Zhao *et al.*,2004; Xiong *et al.*, 1999). Amino derivatives are a class of excellent ligands for the construction of novel metal-organic frameworks. (Fu *et al.*, 2007; Fu & Xiong 2008). We report here the crystal structure of the title compound, 4-bromo-3-methylanilinium bisulfate.

In the title compound (Fig.1), The amino N atoms are protonated. In the crystal structure, all the amine group H atoms and HSO_4^- H atoms are involved in N—H···O and O—H···O hydrogen bonds (Table 1) with O atoms of HSO_4^- anion. These hydrogen bonds link the ionic units into a two-dimensional network (Fig. 2).

S2. Experimental

The commercial 4-bromo-3-methylaniline (3 mmol) and H_2SO_4 (0.5 ml) were dissolved in ethanol (20 ml). Colourless block-shaped crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation at room temperature.

S3. Refinement

All H atoms attached to C, O and N atoms were fixed geometrically and treated as riding with C–H = 0.93 Å (aromatic), C–H = 0.96 Å (methyl), O–H = 0.82 Å and N–H = 0.89 Å with U_{iso}(H) =1.2U_{eq}(C) and U_{iso}(H) =1.5U_{eq}(O or N).

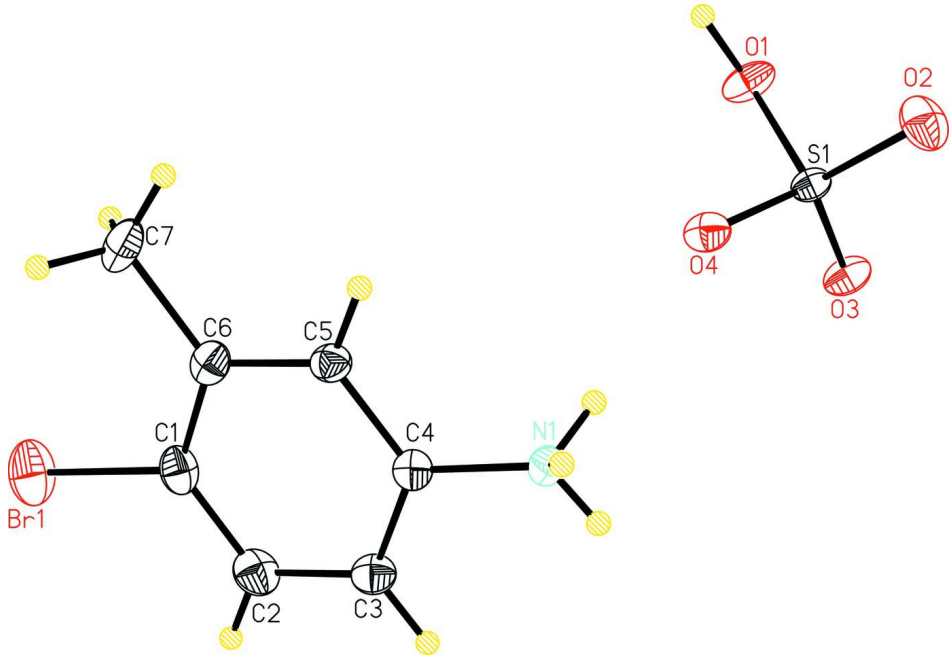

Figure 1

A view of the title compound with the atomic numbering scheme. Displacement ellipsoids have been drawn at the 30% probability level.

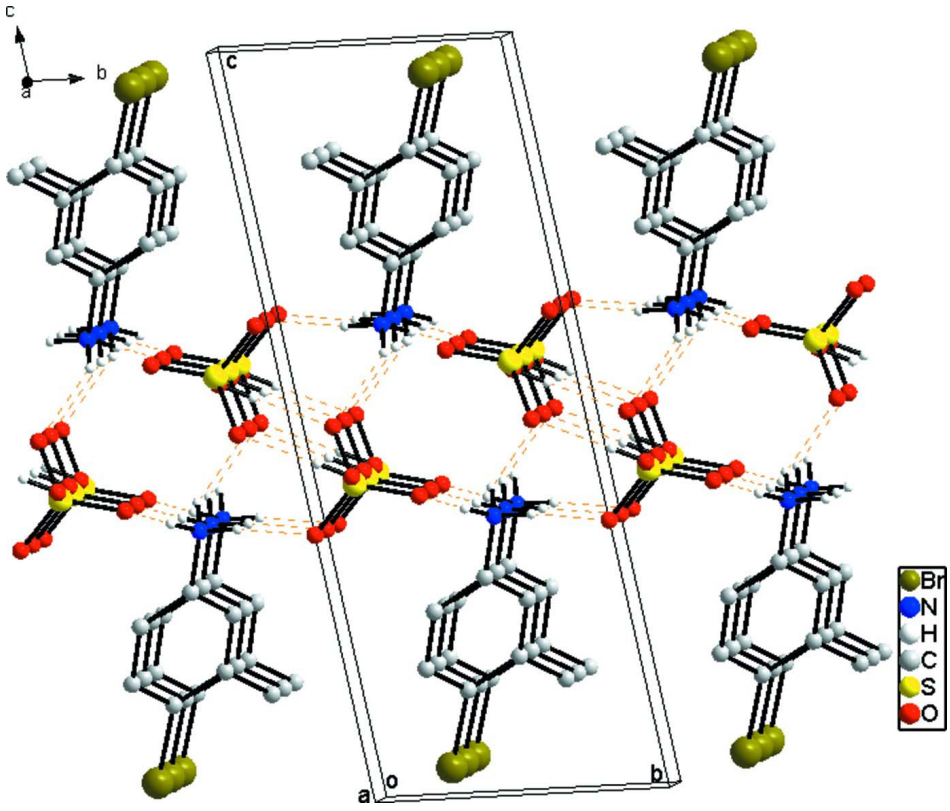

Figure 2

The crystal packing of the title compound, viewed along the *a* axis showing hydrogen bonding (dotted line); H atoms not involved in hydrogen bonding have been omitted for clarity.

4-Bromo-3-methylanilinium hydrogen sulfate

Crystal data

$C_7H_9BrN^+\cdot HSO_4^-$
$M_r = 284.13$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 4.9448\ (10)$ Å
$b = 6.4084\ (13)$ Å
$c = 16.674\ (3)$ Å
$\alpha = 98.92\ (3)°$
$\beta = 96.22\ (3)°$
$\gamma = 100.01\ (3)°$
$V = 509.04\ (17)$ Å^3
$Z = 2$
$F(000) = 284$
$D_x = 1.854$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1804 reflections
$\theta = 3.3–27.5°$
$\mu = 4.23$ mm^{-1}
$T = 298$ K
Block, colorless
0.40 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
CCD profile fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.910$, $T_{max} = 1.000$
5279 measured reflections
2323 independent reflections
1804 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

θ_{max} = 27.5°, θ_{min} = 3.3°
h = −6→6
k = −8→8
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.115
S = 1.07
2323 reflections
129 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.1536P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.74330 (10)	0.74731 (8)	0.96412 (3)	0.0635 (2)
N1	0.0682 (6)	0.3866 (4)	0.63055 (17)	0.0278 (6)
H1A	−0.0452	0.4741	0.6182	0.042*
H1B	−0.0308	0.2561	0.6299	0.042*
H1C	0.1857	0.3782	0.5939	0.042*
C1	0.5271 (7)	0.6260 (6)	0.8613 (2)	0.0355 (8)
C4	0.2233 (7)	0.4704 (5)	0.7120 (2)	0.0273 (7)
C5	0.4016 (7)	0.3520 (5)	0.7448 (2)	0.0290 (7)
H5	0.4154	0.2193	0.7156	0.035*
C3	0.1915 (7)	0.6643 (5)	0.7535 (2)	0.0329 (8)
H3	0.0696	0.7418	0.7309	0.039*
C6	0.5593 (7)	0.4282 (6)	0.8206 (2)	0.0309 (8)
C2	0.3444 (8)	0.7420 (6)	0.8295 (2)	0.0404 (9)
H2	0.3247	0.8723	0.8594	0.049*
C7	0.7547 (8)	0.2971 (7)	0.8549 (3)	0.0458 (10)
H7A	0.9411	0.3782	0.8635	0.069*
H7B	0.7431	0.1659	0.8169	0.069*
H7C	0.7043	0.2638	0.9061	0.069*
S1	0.37322 (15)	0.18764 (12)	0.42345 (5)	0.0231 (2)
O1	0.6927 (5)	0.1969 (4)	0.43590 (16)	0.0379 (6)
H1	0.7257	0.0932	0.4558	0.057*
O2	0.2512 (6)	0.0108 (4)	0.35840 (16)	0.0433 (7)
O3	0.3537 (5)	0.3945 (3)	0.40391 (16)	0.0328 (6)

O4	0.2770 (5)	0.1540 (4)	0.50052 (14)	0.0305 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0640 (3)	0.0704 (4)	0.0396 (3)	−0.0081 (2)	−0.0124 (2)	−0.0034 (2)
N1	0.0312 (15)	0.0272 (15)	0.0268 (14)	0.0091 (11)	0.0038 (11)	0.0062 (12)
C1	0.0342 (19)	0.038 (2)	0.0290 (18)	−0.0039 (15)	0.0024 (15)	0.0041 (16)
C4	0.0278 (17)	0.0235 (17)	0.0296 (18)	0.0015 (13)	0.0040 (13)	0.0058 (14)
C5	0.0307 (17)	0.0267 (17)	0.0319 (18)	0.0076 (14)	0.0071 (14)	0.0080 (15)
C3	0.0350 (19)	0.0261 (18)	0.038 (2)	0.0064 (14)	0.0067 (15)	0.0066 (16)
C6	0.0254 (17)	0.0352 (19)	0.0342 (19)	0.0017 (14)	0.0067 (14)	0.0156 (16)
C2	0.050 (2)	0.0265 (19)	0.041 (2)	0.0040 (16)	0.0063 (18)	−0.0014 (17)
C7	0.044 (2)	0.055 (3)	0.043 (2)	0.0132 (18)	−0.0031 (18)	0.023 (2)
S1	0.0207 (4)	0.0192 (4)	0.0313 (4)	0.0042 (3)	0.0043 (3)	0.0091 (3)
O1	0.0225 (12)	0.0427 (15)	0.0590 (17)	0.0108 (10)	0.0136 (11)	0.0304 (13)
O2	0.0570 (17)	0.0272 (13)	0.0392 (15)	−0.0020 (11)	0.0044 (13)	−0.0009 (12)
O3	0.0303 (13)	0.0235 (12)	0.0486 (15)	0.0056 (10)	0.0055 (11)	0.0181 (11)
O4	0.0318 (13)	0.0285 (13)	0.0369 (14)	0.0092 (10)	0.0122 (10)	0.0145 (11)

Geometric parameters (Å, º)

Br1—C1	1.894 (4)	C3—H3	0.9300
N1—C4	1.458 (4)	C6—C7	1.509 (5)
N1—H1A	0.8900	C2—H2	0.9300
N1—H1B	0.8900	C7—H7A	0.9600
N1—H1C	0.8900	C7—H7B	0.9600
C1—C2	1.379 (6)	C7—H7C	0.9600
C1—C6	1.386 (5)	S1—O3	1.430 (2)
C4—C3	1.369 (5)	S1—O2	1.437 (3)
C4—C5	1.382 (5)	S1—O4	1.452 (2)
C5—C6	1.380 (5)	S1—O1	1.560 (2)
C5—H5	0.9300	O1—H1	0.8200
C3—C2	1.376 (5)		
C4—N1—H1A	109.5	C5—C6—C7	119.9 (3)
C4—N1—H1B	109.5	C1—C6—C7	123.4 (3)
H1A—N1—H1B	109.5	C3—C2—C1	119.8 (3)
C4—N1—H1C	109.5	C3—C2—H2	120.1
H1A—N1—H1C	109.5	C1—C2—H2	120.1
H1B—N1—H1C	109.5	C6—C7—H7A	109.5
C2—C1—C6	122.6 (3)	C6—C7—H7B	109.5
C2—C1—Br1	117.8 (3)	H7A—C7—H7B	109.5
C6—C1—Br1	119.6 (3)	C6—C7—H7C	109.5
C3—C4—C5	121.7 (3)	H7A—C7—H7C	109.5
C3—C4—N1	119.5 (3)	H7B—C7—H7C	109.5
C5—C4—N1	118.8 (3)	O3—S1—O2	114.06 (16)
C6—C5—C4	120.8 (3)	O3—S1—O4	113.59 (14)

C6—C5—H5	119.6	O2—S1—O4	111.41 (15)
C4—C5—H5	119.6	O3—S1—O1	102.60 (13)
C4—C3—C2	118.4 (3)	O2—S1—O1	107.73 (16)
C4—C3—H3	120.8	O4—S1—O1	106.61 (14)
C2—C3—H3	120.8	S1—O1—H1	109.5
C5—C6—C1	116.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3^{i}	0.89	1.90	2.767 (3)	166
N1—H1*B*···O2^{ii}	0.89	1.91	2.797 (4)	173
O1—H1···O4^{iii}	0.82	1.84	2.650 (3)	168
N1—H1*C*···O4	0.89	2.09	2.829 (4)	140

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