organic compounds

4-Bromo-3-methylanilinium perchlorate

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In the title compound, $C_7H_9BrN^+ \cdot ClO_4^-$, the cations and anions are linked by intermolecular N—H⋯O hydrogen bonds, forming a two-dimensional network parallel to the *ab* plane.

Related literature

For the use of amine derivatives in the construction of metal-organic frameworks, see: Fu *et al.* (2007, 2008); Fu & Xiong (2008); Wang *et al.* (2002). For applications of metal-organic coordination compounds, see: Chen *et al.* (2001); Xiong *et al.* (1999); Xie *et al.* (2003); Zhao *et al.* (2004).
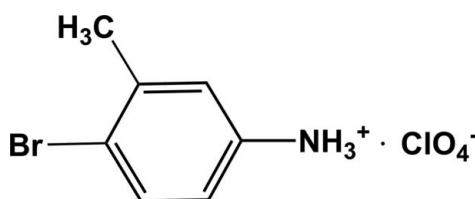
Experimental

Crystal data

$C_7H_9BrN^+ \cdot ClO_4^-$
$M_r = 286.51$
Triclinic, $P\bar{1}$
$a = 4.9455$ (10) Å
$b = 6.9647$ (14) Å
$c = 15.714$ (3) Å
$\alpha = 95.78$ (3)°
$\beta = 94.40$ (3)°

$\gamma = 102.62$ (3)°
$V = 522.8$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 4.18$ mm^{-1}
$T = 298$ K
$0.40 \times 0.05 \times 0.05$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan
  (*CrystalClear*; Rigaku, 2005)
  $T_{min} = 0.910$, $T_{max} = 1.000$

5411 measured reflections
2382 independent reflections
1584 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.127$
$S = 1.03$
2382 reflections

129 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O2^i	0.89	2.04	2.909 (4)	166
N1—H1B⋯O1^{ii}	0.89	2.03	2.875 (4)	159
N1—H1C⋯O3	0.89	2.02	2.857 (4)	156

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

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*.

References

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supporting information

4-Bromo-3-methylanilinium perchlorate

Li Zhang

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 (Chen *et al.*, 2001; Xie *et al.*, 2003; Zhao *et al.*, 2004; Xiong *et al.*, 1999). Amine derivatives are a class of excellent ligands for the construction of novel metal-organic frameworks (Fu *et al.*, 2007, 2008; Wang *et al.* 2002; Fu & Xiong 2008). We report here the crystal structure of the title compound, 4-bromo-3-methylanilinium perchlorate.

  In the title compound (Fig.1), the amino N atom is protonated. In the crystal structure, all the amine group H atoms are involved in N—H···O hydrogen bonding (Table 1) with O atoms of ClO_4^- anion. These hydrogen bonds link the ionic units into a two-dimensional network parallel to the *ab* plane (Fig. 2).

S2. Experimental

The commercial 4-bromo-3-methylbenzenamine (3 mmol, 0.75 g) and $HClO_4$ (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

H atoms were positioned geometrically and treated as riding [C-H = 0.93 Å (aromatic), 0.96 Å (methyl) and N-H = 0.89 Å (N)], with $U_{iso}(H) = 1.2U_{eq}$ (aromatic C) and $1.5U_{eq}$(methyl C or N). A rotating-group model was used for the methyl and -NH$_3$ groups.
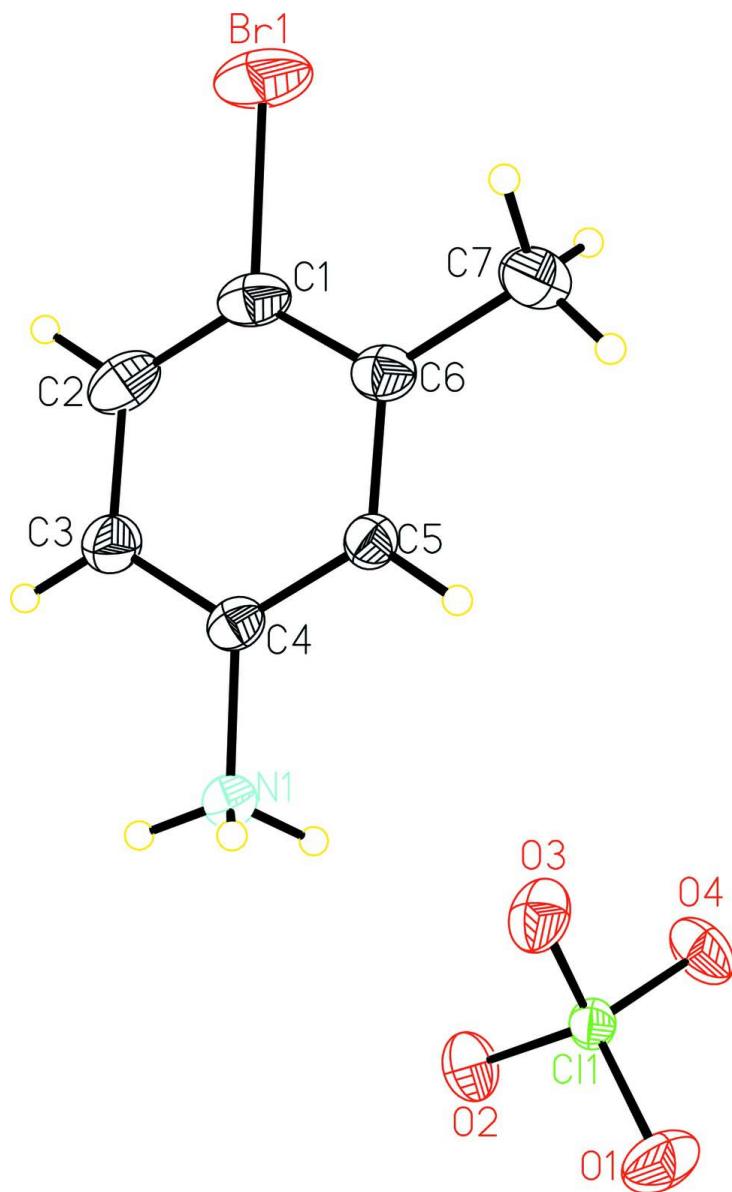
Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.
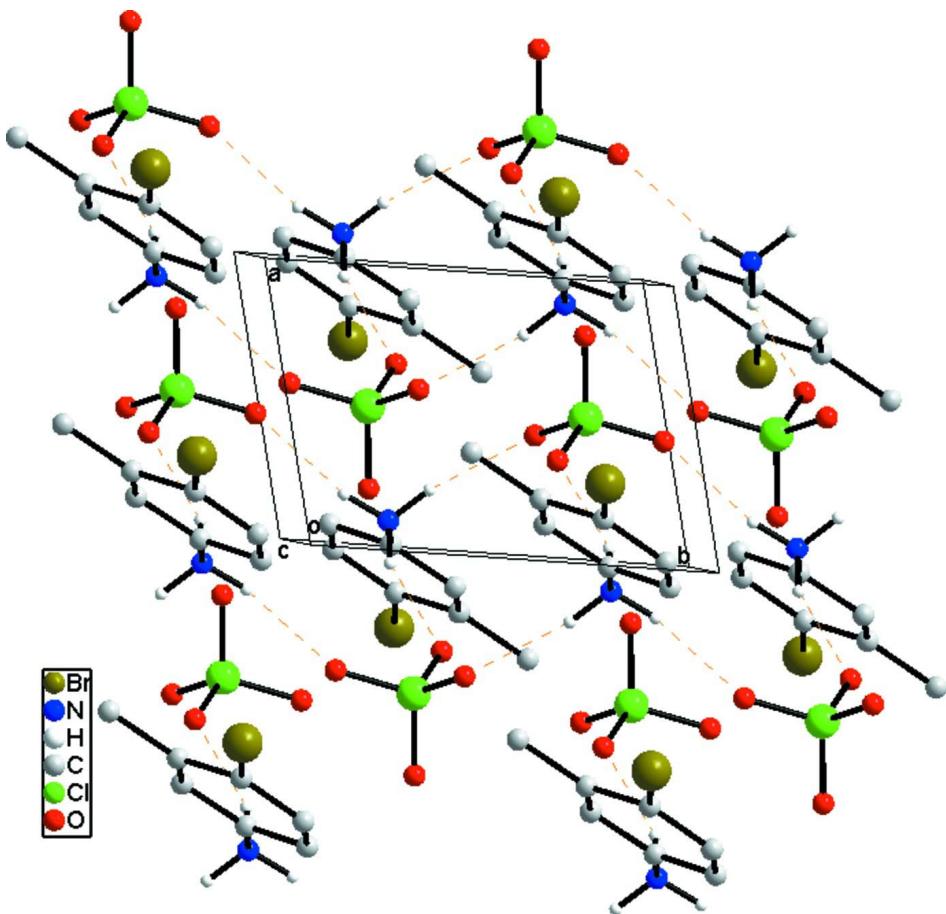
Figure 2

The crystal packing of the title compound, viewed along the *c* axis, showing the N—H⋯O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

4-Bromo-3-methylanilinium perchlorate

Crystal data

$C_7H_9BrN^+ \cdot ClO_4^-$	$Z = 2$
$M_r = 286.51$	$F(000) = 284$
Triclinic, $P\bar{1}$	$D_x = 1.820$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.9455$ (10) Å	Cell parameters from 1584 reflections
$b = 6.9647$ (14) Å	$\theta = 3.0$–27.5°
$c = 15.714$ (3) Å	$\mu = 4.18$ mm^{-1}
$\alpha = 95.78$ (3)°	$T = 298$ K
$\beta = 94.40$ (3)°	Needle, colourless
$\gamma = 102.62$ (3)°	$0.40 \times 0.05 \times 0.05$ mm
$V = 522.8$ (2) Å^3	

Data collection

Rigaku Mercury2 diffractometer	Detector resolution: 13.6612 pixels mm^{-1}
Radiation source: fine-focus sealed tube	CCD profile fitting scans
Graphite monochromator	Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)

$T_{min} = 0.910$, $T_{max} = 1.000$

5411 measured reflections

2382 independent reflections

1584 reflections with $I > 2\sigma(I)$

$R_{int} = 0.053$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.127$

$S = 1.03$

2382 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

$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.0338P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.44$ e Å^{-3}

$\Delta\rho_{min} = -0.57$ 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.

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 > 2sigma(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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.71423 (12)	0.24442 (9)	0.97211 (3)	0.0819 (3)
N1	1.0957 (6)	0.2471 (5)	0.6136 (2)	0.0392 (7)
H1A	1.1784	0.1471	0.6028	0.059*
H1B	1.2142	0.3609	0.6090	0.059*
H1C	0.9465	0.2317	0.5759	0.059*
C1	0.8397 (8)	0.2542 (6)	0.8609 (3)	0.0470 (10)
C2	0.9780 (10)	0.1151 (6)	0.8326 (3)	0.0548 (12)
H2	1.0127	0.0226	0.8682	0.066*
C3	1.0671 (9)	0.1102 (6)	0.7516 (3)	0.0461 (10)
H3	1.1623	0.0160	0.7319	0.055*
C4	1.0104 (8)	0.2496 (5)	0.7008 (2)	0.0351 (8)
C5	0.8762 (7)	0.3934 (5)	0.7301 (2)	0.0357 (8)
H5	0.8456	0.4876	0.6948	0.043*
C6	0.7862 (8)	0.3996 (6)	0.8114 (3)	0.0412 (9)
C7	0.6377 (9)	0.5534 (7)	0.8433 (3)	0.0582 (12)
H7A	0.6417	0.6485	0.8029	0.087*
H7B	0.7280	0.6191	0.8980	0.087*
H7C	0.4479	0.4913	0.8493	0.087*
Cl1	0.49638 (17)	0.22738 (12)	0.42344 (6)	0.0330 (2)
O1	0.5691 (7)	0.3547 (4)	0.3590 (2)	0.0653 (9)

O2	0.5586 (6)	0.0410 (4)	0.3998 (2)	0.0556 (8)
O3	0.6498 (6)	0.3195 (4)	0.50396 (19)	0.0547 (8)
O4	0.2066 (5)	0.1974 (4)	0.4320 (2)	0.0575 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0920 (5)	0.1064 (5)	0.0435 (4)	0.0025 (4)	0.0248 (3)	0.0218 (3)
N1	0.0411 (17)	0.0467 (18)	0.0321 (18)	0.0158 (15)	0.0029 (14)	0.0044 (15)
C1	0.046 (2)	0.055 (2)	0.034 (2)	−0.002 (2)	0.0072 (18)	0.006 (2)
C2	0.068 (3)	0.051 (2)	0.044 (3)	0.006 (2)	0.003 (2)	0.023 (2)
C3	0.056 (3)	0.044 (2)	0.041 (3)	0.018 (2)	0.004 (2)	0.0060 (19)
C4	0.0342 (18)	0.0356 (19)	0.032 (2)	0.0021 (16)	−0.0007 (16)	0.0044 (16)
C5	0.0339 (19)	0.039 (2)	0.036 (2)	0.0094 (16)	0.0042 (16)	0.0087 (17)
C6	0.038 (2)	0.045 (2)	0.036 (2)	0.0029 (18)	0.0026 (18)	0.0000 (18)
C7	0.059 (3)	0.071 (3)	0.048 (3)	0.022 (2)	0.011 (2)	−0.002 (2)
Cl1	0.0322 (4)	0.0332 (4)	0.0357 (5)	0.0104 (4)	0.0041 (4)	0.0074 (4)
O1	0.087 (2)	0.0574 (18)	0.055 (2)	0.0112 (18)	0.0140 (18)	0.0289 (16)
O2	0.0624 (19)	0.0415 (15)	0.068 (2)	0.0236 (15)	0.0084 (16)	0.0015 (14)
O3	0.0547 (18)	0.0522 (17)	0.0515 (19)	0.0132 (14)	−0.0179 (14)	−0.0049 (14)
O4	0.0305 (14)	0.072 (2)	0.068 (2)	0.0109 (14)	0.0101 (14)	−0.0056 (17)

Geometric parameters (Å, º)

Br1—C1	1.902 (4)	C4—C5	1.379 (5)
N1—C4	1.464 (5)	C5—C6	1.384 (5)
N1—H1A	0.89	C5—H5	0.93
N1—H1B	0.89	C6—C7	1.493 (6)
N1—H1C	0.89	C7—H7A	0.96
C1—C2	1.362 (6)	C7—H7B	0.96
C1—C6	1.394 (6)	C7—H7C	0.96
C2—C3	1.377 (6)	Cl1—O2	1.419 (3)
C2—H2	0.93	Cl1—O4	1.421 (3)
C3—C4	1.378 (5)	Cl1—O1	1.428 (3)
C3—H3	0.93	Cl1—O3	1.437 (3)
C4—N1—H1A	109.5	C4—C5—C6	120.9 (4)
C4—N1—H1B	109.5	C4—C5—H5	119.5
H1A—N1—H1B	109.5	C6—C5—H5	119.5
C4—N1—H1C	109.5	C5—C6—C1	116.4 (4)
H1A—N1—H1C	109.5	C5—C6—C7	121.3 (4)
H1B—N1—H1C	109.5	C1—C6—C7	122.3 (4)
C2—C1—C6	122.6 (4)	C6—C7—H7A	109.5
C2—C1—Br1	117.7 (3)	C6—C7—H7B	109.5
C6—C1—Br1	119.7 (3)	H7A—C7—H7B	109.5
C1—C2—C3	120.6 (4)	C6—C7—H7C	109.5
C1—C2—H2	119.7	H7A—C7—H7C	109.5
C3—C2—H2	119.7	H7B—C7—H7C	109.5

C2—C3—C4	117.8 (4)	O2—Cl1—O4	108.72 (18)
C2—C3—H3	121.1	O2—Cl1—O1	109.8 (2)
C4—C3—H3	121.1	O4—Cl1—O1	109.9 (2)
C3—C4—C5	121.6 (4)	O2—Cl1—O3	110.55 (17)
C3—C4—N1	119.6 (3)	O4—Cl1—O3	109.01 (19)
C5—C4—N1	118.7 (3)	O1—Cl1—O3	108.79 (18)
C6—C1—C2—C3	−1.4 (7)	C4—C5—C6—C1	0.2 (5)
Br1—C1—C2—C3	178.0 (3)	C4—C5—C6—C7	−179.3 (4)
C1—C2—C3—C4	−0.2 (6)	C2—C1—C6—C5	1.4 (6)
C2—C3—C4—C5	1.8 (6)	Br1—C1—C6—C5	−178.0 (3)
C2—C3—C4—N1	−178.6 (3)	C2—C1—C6—C7	−179.2 (4)
C3—C4—C5—C6	−1.8 (6)	Br1—C1—C6—C7	1.4 (5)
N1—C4—C5—C6	178.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O2[i]	0.89	2.04	2.909 (4)	166
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