

2-Amino-6-bromopyridinium bromide

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Key indicators

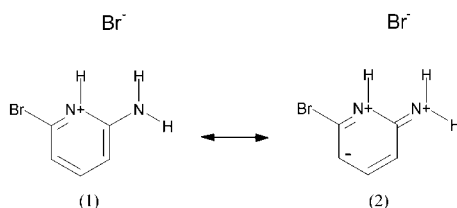
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$
 R factor = 0.040
 wR factor = 0.116
Data-to-parameter ratio = 13.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_5\text{H}_6\text{BrN}_2^+\cdot\text{Br}^-$, crystallizes in the centrosymmetric space group $Cmca$ with all atoms lying on a crystallographic mirror plane at $(0, y, z)$. The ion pairs pack as ribbons through $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds and $\text{Br}\cdots\text{Br}$ halogen interactions. The ribbons are linked through weak $\text{C}-\text{H}\cdots\text{Br}$ interactions to form layers which stack perpendicular to the a axis.

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Comment

The title compound, 2-amino-6-bromopyridinium bromide, (1), a precursor for 2-bromo-6-iodopyridine (Holmes *et al.*, 2002), was also of interest to us for comparison of weak $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonding with $\text{Br}^-\cdots\text{Br}-\text{C}$ halogen interactions. The conversion of commercially and synthetically abundant amino derivatives to halogens has traditionally been accomplished using Sandmeyer-type conditions and is very useful in organic synthesis (Lavastre *et al.*, 1997; Smith & Ho, 1990). The salt crystallizes in space group $Cmca$ with all non-H atoms lying on a crystallographic mirror plane at $(0, y, z)$ (Fig. 1). The geometric parameters for (1) are generally comparable to those found in related derivatives, such as 2-bromopyridinium bromide (Freytag & Jones, 2001), 2-chloro-6-dimethylamino-3,5-pyridinedicarbaldehyde (Lai *et al.*, 1995), 7-amino-5-bromo-4-methyl-2-oxo-1,2,3,4-tetrahydro-1,6-naphthyridine-8-carbonitrile monohydrate (Gómez de Anderez *et al.*, 1992), and 6-bromo-3,5-difluoro-2-piperidyl-4-(1,2,2,2-tetrafluoro-1-trifluoromethylethyl)pyridine (Chambers *et al.*, 2001), with the expected changes upon protonation at the pyridine N atom. The short $\text{C}-\text{NH}_2$ bond length and distortions exhibited in the ring bond distances indicate a substantial delocalization of the lone pair on the amine nitrogen into the π -system of the pyridine ring.



Ion-pairs of (1) form $\text{N}-\text{H}\cdots\text{Br}$ hydrogen-bonded ribbons with adjacent pairs related by a b -glide operation. There is also a $\text{Br}\cdots\text{Br}$ interaction within the ribbon structure between the bromide anion and the bromine substituent [$\text{Br}1\cdots\text{Br}2^i = 3.5484(13)\text{ \AA}$ and $\text{C}-\text{Br}1\cdots\text{Br}2^i = 179.43(19)^\circ$, where $\text{Br}2^i$ is related to $\text{Br}2$ by $(x, \frac{1}{2} + y, \frac{1}{2} - z)$]. Weak $\text{C}-\text{H}\cdots\text{Br}$ interactions link the ribbons in the c direction (Fig. 2). These layers

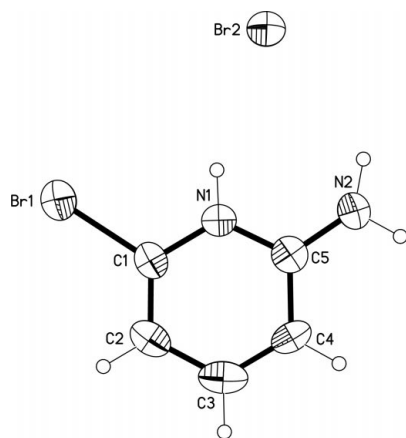


Figure 1
The molecular structure of (1). Displacement ellipsoids are shown at the 50% probability level and H atoms are of arbitrary radii.

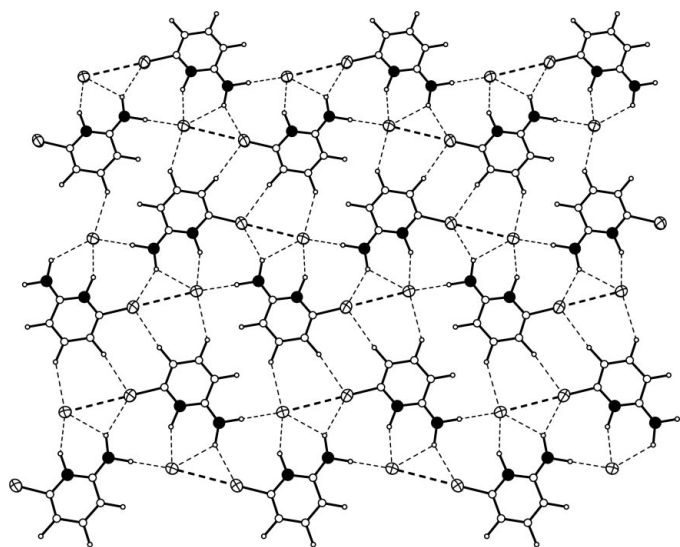


Figure 2
Hydrogen-bonded layer of (1). Dashed lines represent N—H...Br and C—H...Br hydrogen-bonds. Filled dashed lines represent Br...Br interactions.

stack to complete the structure, with neighboring layers related by *C*-centering. The packing of (1) is quite similar to that of 2-bromopyridinium bromide (Freitag & Jones, 2001), with the only significant difference being the alternation of direction of the ribbons in (1) as opposed to the polar nature of the ribbon packing in the simpler analog.

Experimental

2-Amino-6-bromopyridinium bromide was synthesized using a literature method (Johnson *et al.*, 1962), by slowly dissolving 3-hydroxypentanedinitrile in a 33 wt% solution of hydrogen bromide in glacial acetic acid with cooling and stirring. The resultant dark yellow precipitate was removed by filtration and allowed to air dry, affording a quantitative yield of the desired product. Diffraction quality crystals of 2-amino-6-bromopyridinium bromide were

obtained by slow evaporation of an ethanol solution at room temperature.

Crystal data

$C_5H_6BrN_2^+ \cdot Br^-$
 $M_r = 253.94$
 Orthorhombic, *Cmca*
 $a = 6.9230(10) \text{ \AA}$
 $b = 11.616(2) \text{ \AA}$
 $c = 19.413(4) \text{ \AA}$
 $V = 1561.1(5) \text{ \AA}^3$
 $Z = 8$
 $D_x = 2.161 \text{ Mg m}^{-3}$

Mo *K* α radiation
 Cell parameters from 25 reflections
 $\theta = 2.5\text{--}25.0^\circ$
 $\mu = 10.30 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, brown
 $0.24 \times 0.21 \times 0.12 \text{ mm}$

Data collection

Rigaku AFC-7 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (TEXSAN; Molecular Structure Corporation/Rigaku, 1997)
 $T_{\min} = 0.082$, $T_{\max} = 0.291$
 750 measured reflections
 750 independent reflections

580 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 25.0^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 23$
 3 standard reflections every 100 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.116$
 $S = 1.03$
 750 reflections
 56 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 0.9155P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.80 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.81 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0020 (4)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Br1—C1	1.876 (8)	C2—C3	1.402 (12)
N1—C5	1.336 (10)	C3—C4	1.346 (11)
N1—C1	1.341 (8)	C4—C5	1.406 (9)
N2—C5	1.320 (9)	Br1—Br2 ⁱ	3.5484 (13)
C1—C2	1.331 (10)		
C5—N1—C1	123.5 (6)	C3—C4—C5	119.7 (8)
C2—C1—N1	121.1 (7)	N2—C5—N1	119.9 (6)
C2—C1—Br1	122.7 (6)	N2—C5—C4	123.2 (7)
N1—C1—Br1	116.2 (5)	N1—C5—C4	116.9 (7)
C1—C2—C3	117.6 (7)	C1—Br1—Br2 ⁱ	179.43 (19)
C4—C3—C2	121.1 (7)		

Symmetry code: (i) $x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H3...Br1 ⁱⁱ	0.90	2.70	3.486 (7)	146
N2—H2...Br2 ⁱⁱ	0.90	2.53	3.431 (7)	180
N1—H1...Br2	0.86	2.55	3.360 (5)	158
C2—H2A...Br1 ⁱⁱⁱ	0.93	3.00	3.923 (8)	174
C3—H3A...Br2 ^{iv}	0.93	3.04	3.864 (7)	149

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

Data collection: *AFC-7 Diffractometer Control Software* (Molecular Structure Corporation/Rigaku, 1997); cell refinement: *AFC-7 Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation/Rigaku, 1997); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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