

2,6-Diaminopyridinium bromide monohydrate

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Key indicators

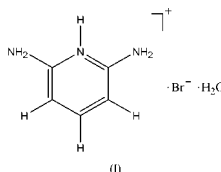
Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.038
wR factor = 0.100
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $[\text{C}_5\text{H}_6\text{N}_3]^+\text{Br}^-\cdot\text{H}_2\text{O}$, the 2,6-diaminopyridine is protonated on the ring N atom. The cation is planar. The moieties are held together by extensive hydrogen bonding and by π - π interactions. The bromide ion is hydrogen bonded, as acceptor, to two H_2O molecules, with an average $\text{Br}\cdots\text{H}-\text{O}(\text{H}_2\text{O})$ distance of $3.322(11) \text{ \AA}$, to the ring N atom $\text{Br}\cdots\text{N}-\text{H}(\text{NH})$ $3.353(3) \text{ \AA}$, and to four amino N atoms, with an average $\text{Br}\cdots\text{H}-\text{N}(\text{NH}_2)$ $3.63(14) \text{ \AA}$. The water molecule bonds, as acceptor, to the pyridine N atom $\text{O}\cdots\text{H}-\text{N}(\text{NH}_2)$ $2.583(5) \text{ \AA}$. The closest π - π interaction is between pyridine ring planes, with an interplanar spacing 3.358 \AA apart.

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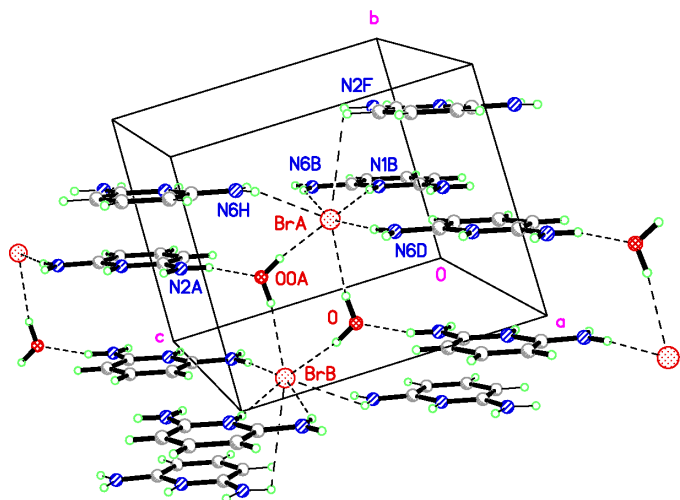
Comment

As part of our studies of the role of weak intermolecular interactions in the determination of crystal-structure hydrogen bonding involving halide ions, halogen-halide interactions, as well as π - π stacking effects, are found to play a role in the organization of structural units (Desiraju, 2001; Haddad & Willett, 2001; Willett *et al.*, 2003). The determination of the title structure, (I), was undertaken to investigate the structural synthetic effects in the absence of aryl-halogen and halometalate anions.



The cations in the title compound are planar, with a mean deviation from planarity of 0.0034 \AA . The closest $\text{O}(\text{H}_2\text{O})$ to the plane is at a distance of 0.4460 \AA , while the closest Br^- is only 0.042 \AA from the plane (Fig. 1). Each Br^- forms a total of seven hydrogen bonds with NH , NH_2 and H_2O donors. H_2O hydrogen bonds as an acceptor to amino N. In this manner, an extended three-dimensional network is formed. Fig. 2 shows the cation disposition. One of the H atoms, H6A, exhibits bifurcated hydrogen bonding.

The cations form stacks running parallel to the *b* axis. The closest π - π stacking interaction is between two inversion-related cations (Fig. 1). The interplanar separation is $3.358(5) \text{ \AA}$, while the distance between the two centroids of the six-membered rings is $3.492(5) \text{ \AA}$. The angle between the vector joining the centroids and the vector perpendicular to the molecular plane is $15.9(4)^\circ$. The antiparallel disposition of the cations is expected from the dipole-dipole interaction. The

**Figure 1**

Hydrogen bonding of bromide and of water; π - π contacts are also shown. Labeled atoms in the figure are defined by the following transformations: O ($1-x, 2-y, 1-z$), OOA ($x-1, y, z$), N1B ($x-1, y, z-1$), N6B ($x-1, y, z-1$), N6H ($1-x, -1-y, -z$), N6D ($x, y, z-1$), N2F ($1-x, 1-y, 1-z$), N2A (x, y, z)

rather close stacking implies significant π - π interaction. (Haddad *et al.*, 2003).

There are no significant Br \cdots Br interactions, the closest contact being 4.264 (4) Å.

Experimental

1 mmol 2,6-diaminopyridine (98%) was dissolved in 20 ml of 95% ethyl alcohol. While stirring, 48% hydrobromic acid was added dropwise until the pH reached 3. The solution was then brought to boiling for ten minutes. The beaker was left uncovered at room temperature. Parallelepiped-shaped crystals developed next morning, colored, surprisingly, pink.

Crystal data

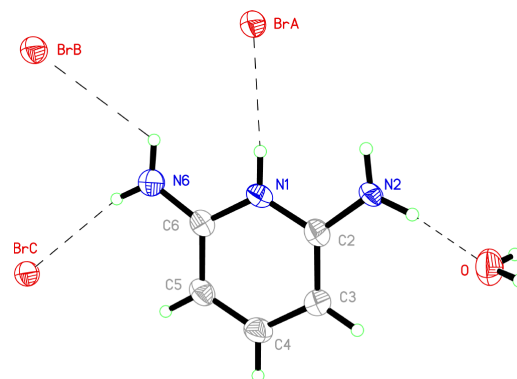
$C_5H_8N_3^+ \cdot Br^- \cdot H_2O$
 $M_r = 208.07$
 Triclinic, $P\bar{1}$
 $a = 7.1225$ (12) Å
 $b = 7.2333$ (8) Å
 $c = 8.7082$ (13) Å
 $\alpha = 91.557$ (11)°
 $\beta = 102.518$ (17)°
 $\gamma = 112.627$ (11)°
 $V = 401.21$ (10) Å³

$Z = 2$
 $D_x = 1.722$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 28 reflections
 $\theta = 5.9$ -18.1°
 $\mu = 5.06$ mm⁻¹
 $T = 295$ (2) K
 Parallelepiped, pink
 $0.40 \times 0.35 \times 0.28$ mm

Data collection

Siemens P_2 diffractometer upgraded to P_4
 ω scans
 Absorption correction: ψ scan (XPREP in SHELXTL; Bruker, 1996)
 $T_{\min} = 0.146$, $T_{\max} = 0.242$
 1781 measured reflections
 1412 independent reflections

1292 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 25.0$ °
 $h = -8 \rightarrow 1$
 $k = -8 \rightarrow 8$
 $l = -10 \rightarrow 10$
 3 standard reflections every 97 reflections
 intensity decay: <0.01%

**Figure 2**

Cation disposition, showing hydrogen bonding with pyridine and amino N atoms. Displacement ellipsoids are drawn at the 30% probability level.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.100$
 $S = 1.09$
 1412 reflections
 99 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.2936P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.63$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
N2—H2B \cdots O	0.86	1.76	2.583 (5)	161
N1—H1A \cdots Br ⁱ	0.86	2.52	3.353 (3)	162
N6—H6A \cdots Br ⁱⁱ	0.86	2.91	3.464 (4)	124
N6—H6A \cdots Br ⁱⁱⁱ	0.86	3.01	3.735 (4)	144
N6—H6B \cdots Br ⁱⁱⁱ	0.86	2.71	3.553 (4)	167
O—H1 \cdots Br ^{iv}	0.882 (19)	2.46 (2)	3.329 (4)	169 (5)
O—H2 \cdots Br ^v	0.881 (19)	2.47 (3)	3.314 (4)	161 (5)
N2—H2B \cdots Br ^{vi}	0.86	3.51	3.752 (3)	100

Symmetry codes: (i) $x-1, y, z-1$; (ii) $1-x, 1-y, -z$; (iii) $x, y, z-1$; (iv) $1-x, 2-y, 1-z$; (v) $x-1, y, z$; (vi) $1-x, 1-y, 1-z$.

H atoms attached to water O atoms were located in a difference map and refined with loose restraints. Other H atoms were placed geometrically (C—H = 0.86–0.93 Å), with U_{iso} constrained to be $1.2U_{\text{eq}}$ of the carrier atom. The largest residual electron density peak is 0.437 e Å⁻³ and lies 1.482 Å from the Br atom.

Data collection: XSCANS (Bruker, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: XS in SHELXTL (Bruker, 1996); program(s) used to refine structure: XL in SHELXTL; molecular graphics: XP in SHELXTL; software used to prepare material for publication: XCIF in SHELXTL.

References

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