

4-Amino-1-(4-nitrobenzyl)pyridinium  
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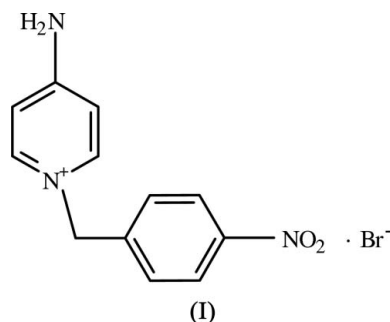
## Key indicators

Single-crystal X-ray study  
 $T = 273$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.024  
 $wR$  factor = 0.068  
Data-to-parameter ratio = 10.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title compound,  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2^+\cdot\text{Br}^-$ , the bromide anion and most atoms of the cation lie on a mirror plane. In the cation, the pyridine and benzene rings are almost orthogonal to each other, forming a dihedral angle of  $89.2(1)^\circ$ . The crystal packing is stabilized by weak  $\text{N}-\text{H}\cdots\text{Br}$  and  $\text{C}-\text{H}\cdots\text{O}$  intermolecular hydrogen bonds.

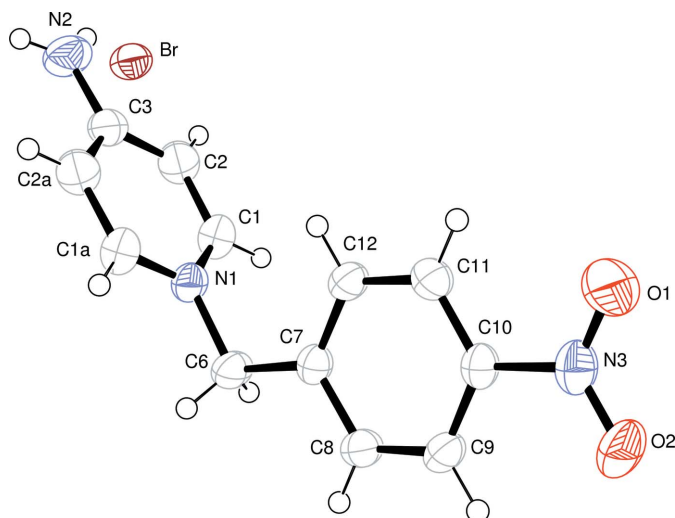
## Comment

Derivatives of pyridinium compounds often exhibit antibacterial and antifungal activities (Akkurt *et al.*, 2005). It has recently been demonstrated in human peripheral mononuclear cells isolated from healthy volunteers that 4-aminopyridine (4AP), a drug affecting potassium permeability and capable of provoking membrane depolarization (Grissmer *et al.*, 1992), is also able to induce an increase in intracellular calcium influx through modulation of the activity of purinergic cationic channels (Lajdova *et al.*, 2004). This drug is also used in the treatment of neurological ailments, such as multiple sclerosis (MS), with tests showing that 4AP improves motor function in MS patients (Anderson *et al.*, 2005). In the light of the aforementioned significant importance of pyridinium compounds and as a continuation of our work on the study of pyridinium derivatives, an X-ray structure determination of the title compound, (I), was undertaken and the results are presented here.



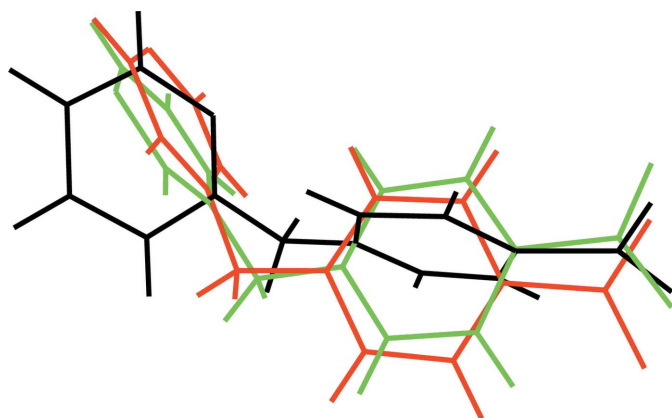
The title compound, (I), crystallizes in the orthorhombic space group  $Cmca$  with eight formula units in the unit cell. The bromine anion and most atoms of the cation, except atoms C1, C2, H1, H2, H6 and H2N, lie on a mirror plane (Fig. 1). The bond lengths and angles of the pyridine ring in (I) are normal and are comparable to those in five related structures, namely 2-amino-1-(4-nitrobenzyl)pyridinium bromide, (II) (Sundar *et al.*, 2006a), 3-amino-1-(4-nitrobenzyl)pyridinium bromide, (III) (Sundar *et al.*, 2006b), 2-aminopyridine, (IV) (Chao *et al.*, 1975a), 3-aminopyridine, (V) (Chao *et al.*, 1975b), and 4-aminopyridine, (VI) (Chao & Schempp, 1977).

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**Figure 1**

A view of the cation and anion of (I) with the atom-labelling scheme. Atoms C1a and C2a are related to atoms C1 and C2 by  $(-x, y, z)$ . Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown by circles of arbitrary radii.

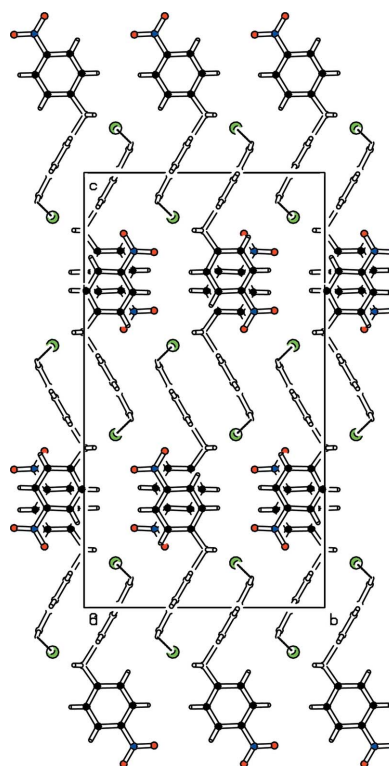


**Figure 2**

Superimposed fit of the cations of (I) (red), (II) (green) and (III) (black), excluding the amino group substituents.

The dihedral angle between the pyridine rings of two adjacent molecules, related by the symmetry code  $(x, 1 - y, -z)$ , is almost zero  $[0.02 (1)^\circ]$ . The short separation of  $3.475 (1) \text{ \AA}$  between those pyridine rings indicates the presence of  $\pi$ - $\pi$  stacking interactions. The dihedral angle between the least-squares planes of the pyridine and benzene rings is  $89.2 (1)^\circ$ . The  $\text{NO}_2$  group and benzene ring lie on a mirror plane and, therefore, make a dihedral angle exactly equal to zero, in contrast to non-zero dihedral angles observed in (II)  $[12.1 (4)^\circ]$  and (III)  $[3.6 (3)^\circ]$ , respectively. A short intramolecular contact is observed between atoms O1 and H11 ( $2.44 \text{ \AA}$ ), which is less than the sum of their van der Waals radii ( $2.72 \text{ \AA}$ ; Bondi, 1964).

In order to understand the influence of the packing on the molecular conformation, energy minimization was carried out on the isolated cation using the *WinMopac 7.21* program (Shchepin & Litvinov, 1998). A superimposed fit of the cation of (I) with its energy-minimized free cation counterpart gives an r.m.s. deviation of  $0.739 \text{ \AA}$ . The conformation of the cation



**Figure 3**

The crystal packing, viewed along the  $a$  axis, showing the  $\text{N-H}\cdots\text{Br}$  hydrogen-bonded (dashed lines) chains.

in the crystal structure and that observed in the free cation differ mostly in the orientation of the nitrobenzyl ring with respect to the plane of the pyridine ring. This is evident from the increase of the  $\text{O1}\cdots\text{H11}$  distance from  $2.44 \text{ \AA}$  in (I) to  $3.17 \text{ \AA}$  in the free cation. In the energy-minimized cation, the rotation about the  $\text{C10-N3}$  bond has obviously reduced the strain observed in (I). This may be evident from the r.m.s. deviations calculated by the superimposed fits of the non-amino atoms between the cations of (I) and (II) of  $2.598 \text{ \AA}$ , and (I) and (III) of  $2.672 \text{ \AA}$ , respectively (Fig. 2). The presence of the amino group at different positions *viz.* 2-, 3- and 4- in the pyridine ring might have been the reason for the changes observed in the conformation of the cation.

In the crystal structure (Fig. 3), weak  $\text{N-H}\cdots\text{Br}$  interactions (Table 1) link the cations and anions into an extended chain running parallel to the  $a$  axis, with a graph-set motif  $C(4)$  (Bernstein *et al.*, 1995). Weak intermolecular  $\text{C-H}\cdots\text{O}$  hydrogen bonds (Table 1) link the cations into a continuous chain running parallel to the  $c$  axis, which can be described by graph-set motif  $C(6)$ .

## Experimental

A solution of 4-aminopyridine (1.15 g, 0.5 mol) and *p*-nitrobenzyl bromide (2.7 g, 0.5 mol) in dry acetone (25 ml) was stirred for 1–2 h at room temperature (303 K). A solid separated, which was filtered off, washed with dry acetone to give the stable salt (I) (yield 3.25 g, 85%; m.p. 561–563 K), which was recrystallized from an ethanol–water (9:1 *v/v*) solution.

Crystal data

C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>·Br<sup>-</sup>  
*M<sub>r</sub>* = 310.16  
 Orthorhombic, *Cmca*  
*a* = 6.7257 (4) Å  
*b* = 14.3806 (8) Å  
*c* = 26.0364 (15) Å  
*V* = 2518.2 (3) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.636 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 6556 reflections  
 $\theta$  = 5.4–53.1°  
 $\mu$  = 3.26 mm<sup>-1</sup>  
*T* = 273 (2) K  
 Prism, colourless  
 0.10 × 0.10 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 11396 measured reflections  
 1205 independent reflections

1134 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.032  
 $\theta_{\max}$  = 25.0°  
*h* = -7 → 7  
*k* = -16 → 16  
*l* = -30 → 30

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.024  
*wR*(*F*<sup>2</sup>) = 0.068  
*S* = 1.06  
 1205 reflections  
 111 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 2.5916P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<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—H2N...Br <sup>i</sup>	0.881 (16)	2.888 (19)	3.6912 (11)	152 (2)
C8—H8...O1 <sup>ii</sup>	0.93	2.52	3.363 (4)	150

Symmetry codes: (i) *x* - ½, -*y* + 1, *z* - ½; (ii) *x*, *y* + ½, -*z* + ½.

All H atoms, except H2N and H6 attached to atoms N2 and C6, respectively, were placed in geometrically calculated positions and refined as riding, with C—H = 0.93–0.97 Å and *U*<sub>iso</sub>(H) = 1.2 *U*<sub>eq</sub>(C). Atoms H2N and H6 were located in a difference Fourier map and refined isotropically with bond-length restraints (N—H = 0.92 Å and C—H = 0.95 Å, using the DFIX command of *SHELXL97*).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997), *PLATON* (Spek, 2003) and *Qmol* (Gans & Shalloway, 2001); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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