

2-Amino-1-(4-nitrobenzyl)pyridinium bromide

T. V. Sundar,^a V. Parthasarathi,^{a*}
B. Sridhar,^b P. Venkatesan^c and
M. Nallu^c^aSchool of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, ^bLaboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and ^cSchool of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India

Correspondence e-mail: vpsarati@yahoo.com

Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.032
 wR factor = 0.085
Data-to-parameter ratio = 13.4For 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 pyridine and benzene rings make a dihedral angle of $85.0(1)^\circ$. In the solid state, $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonds link two cations and two anions into a centrosymmetric cluster.

Comment

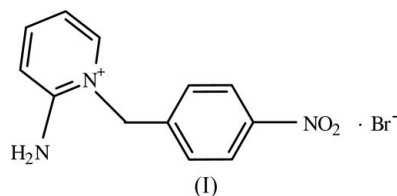
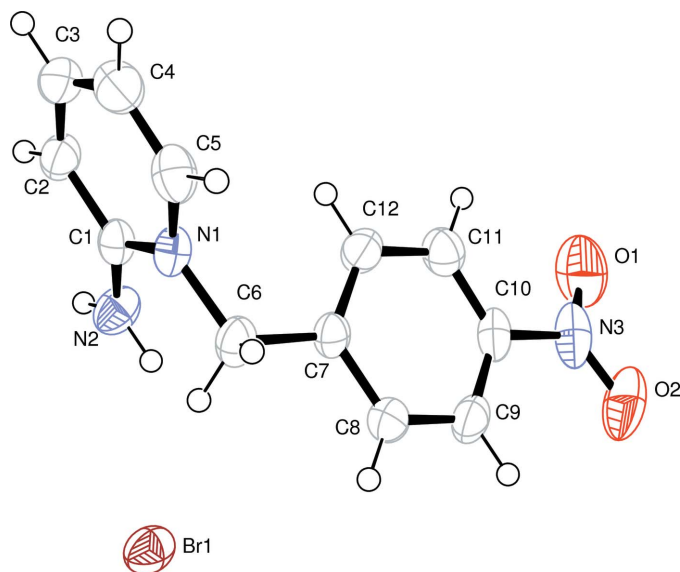
Pyridinium compounds show biological activities, such as antibacterial and antifungal (Akkurt *et al.*, 2005) properties. In continuation of our work on the study of pyridinium derivatives, the structure determination of the title compound, (I), has been undertaken.A view of the cation and anion of (I), with the atom-labelling scheme, is shown in Fig. 1. The bond lengths and angles in the pyridinium ring are normal (Allen *et al.*, 1987) and comparable with those reported for related structures (Sundar *et al.*, 2004*a,b*; 2005). The C1–N2 bond length [$1.330(3)$ Å] is intermediate between typical C–N single- and

Figure 1

A view of the cation and anion of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown by circles of arbitrary radii.

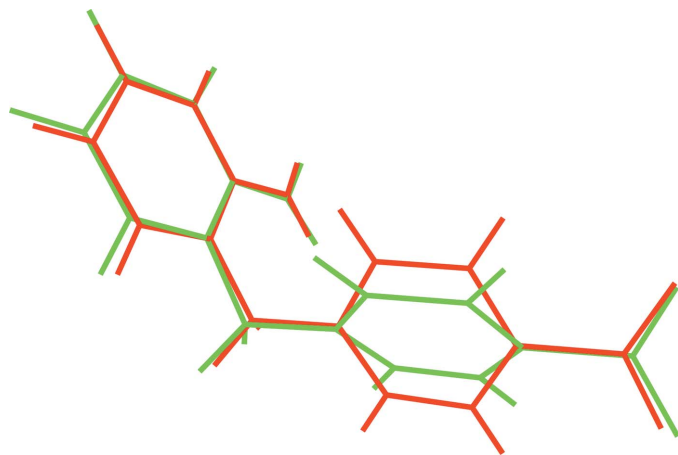


Figure 2
Superimposed fit of the cation of (I) (red) and its energy-minimized counterpart (green).

double-bond distances, indicating significant electron delocalization. The dihedral angle between the pyridine rings of two adjacent molecules related by the symmetry operator $(1 - x, y, \frac{1}{2} - z)$ is $7.31(2)^\circ$, with a separation distance of $3.803(2) \text{ \AA}$. This indicates the presence of some π - π stacking interaction. The sum of the bond angles around atom N3 is close to 360° (Table 1), indicating the absence of an sp^3 lone pair. The dihedral angle between the least-squares planes of the pyridine and benzene rings is $85.0(1)^\circ$. The NO_2 group is slightly twisted from the plane of the benzene ring by $12.1(4)^\circ$. This may be due to the intramolecular short contact between atoms O1 and H11 (2.45 \AA), which is less than the sum of their van der Waals radii (2.72 \AA ; Bondi, 1964).

In order to understand the packing effect on its structure, an energy minimization of the cation of (I) was carried out using the program *WINMOPAC* (Shchepin & Litvinov, 1998). A least-squares fit of the cation of (I) with its energy-minimized counterpart gives an r.m.s. deviation of 0.45 \AA (Fig. 2). The conformations of the cation in the crystal structure and the isolated cation are significantly different only in the orientation of the benzene ring. This is evident from the increase of the non-bonded distance of $\text{O1} \cdots \text{H11}$ from 2.45 \AA (the cation in the crystal structure) to 3.22 \AA (energy-minimized cation). In the energy-minimized cation, the rotation about the $\text{N3}-\text{C10}$ bond has obviously reduced the strain that is observed in the cation in the crystal structure.

In the solid state, the crystal packing is stabilized by $\text{N}-\text{H} \cdots \text{Br}$ hydrogen bonds (Table 2), which link two cations and two anions into a centrosymmetric cluster (Fig. 3).

Experimental

A solution of 2-aminopyridine (1.15 g, 0.5 mol) and *p*-nitrobenzyl bromide (2.7 g, 0.5 mol) in dry acetone was refluxed for 2 h. After cooling to room temperature (303 K), the solid which separated was filtered off and washed with dry acetone to give the stable salt, (I) (yield 2.35 g, 61%; m.p. 517–519 K), which was recrystallized from ethanol–water (9:1 v/v).

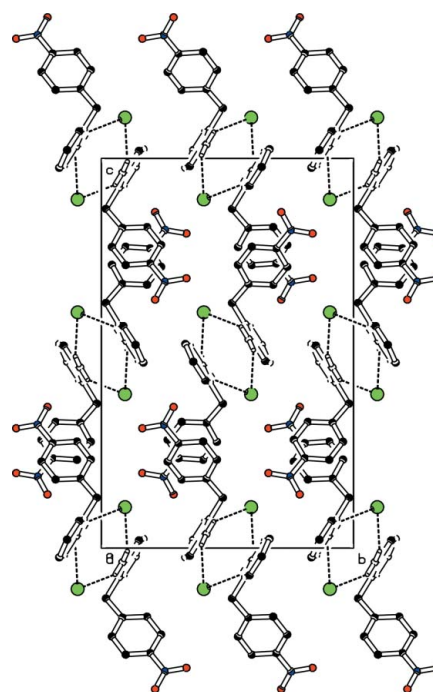


Figure 3
The crystal packing, viewed along the *a* axis and showing $\text{N}-\text{H} \cdots \text{Br}$ hydrogen-bonded (dashed lines) clusters.

Crystal data

$\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_3^+\cdot\text{Br}^-$
 $M_r = 310.16$
Orthorhombic, *Pbcn*
 $a = 8.0505(6) \text{ \AA}$
 $b = 14.0971(10) \text{ \AA}$
 $c = 21.8990(15) \text{ \AA}$
 $V = 2485.3(3) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.658 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 6556 reflections
 $\theta = 2.7\text{--}26.6^\circ$
 $\mu = 3.31 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
Block, colourless
 $0.10 \times 0.10 \times 0.09 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
Absorption correction: none
16442 measured reflections
2203 independent reflections

1899 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.07$
2203 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 2.4183P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0062 (5)

Table 1

Selected geometric parameters ($^\circ$).

O1–N3–O2	123.8 (3)	O2–N3–C10	117.6 (3)
O1–N3–C10	118.6 (3)		
N1–C6–C7–C12	9.9 (4)	N1–C6–C7–C8	–170.4 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots Br1$	0.86	2.64	3.382 (2)	145
$N2-H2B\cdots Br1^i$	0.86	2.65	3.416 (2)	150

Symmetry code: (i) $-x + 2, -y, -z$.

All H atoms were placed in geometrically calculated positions and refined as riding, with $C-H = 0.93-0.98$ Å and $N-H = 0.86$ Å, and with $U_{iso}(H) = 1.2U_{eq}$ of the parent atom.

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: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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