Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

T. V. Sundar,[a] V. Parthasarathi,[a]* B. Sridhar,[b] P. Venkatesan[c] and M. Nallu[c]

[a]School of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, [b]Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and [c]School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India

Correspondence e-mail: vpsarati@yahoo.com

Received 5 December 2005
Accepted 3 January 2006
Online 7 January 2006

Key indicators

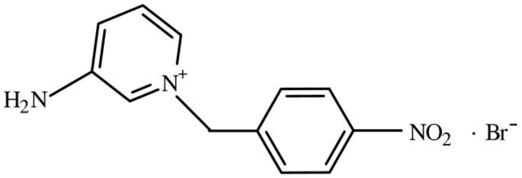
Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.076
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the cation of the title compound, $C_{12}H_{12}N_3O_2^+\cdot Br^-$, the pyridine and benzene rings are almost orthogonal. The amino N atom is displaced slightly from the plane of the pyridine ring. In the crystal structure, N—H···Br hydrogen bonds link two cations and two anions into centrosymmetric clusters. The crystal packing is further stabilized by weak intermolecular C—H···O interactions.

Comment

Pyridinium compounds exhibit biological activities such as antibacterial and antifungal (Akkurt *et al.*, 2005). In continuation of the structural analysis of amino pyridinium derivatives, the structure determination of the title compound, (I), was undertaken.



(I)

A view of the cation and anion of (I) with the atom-labelling scheme is shown in Fig. 1. The bond lengths and angles of the pyridinium ring in (I) are comparable to those reported for the related structures 2-amino-1-(4-nitrobenzyl)pyridinium bromide, (II) (Sundar *et al.*, 2006, and references therein), and 3-aminopyridine, (III) (Chao *et al.*, 1975). The C2—N2 bond

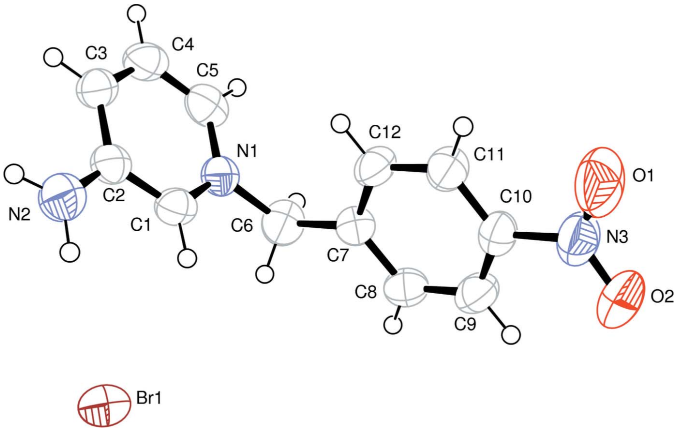


Figure 1
A view of the cation and anion of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown by circles of arbitrary radii.

doi:10.1107/S1600536806000079

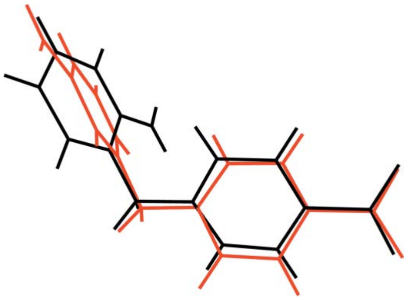


Figure 2
A superimposed fit of the cations of (I) (red) and (II) (black).

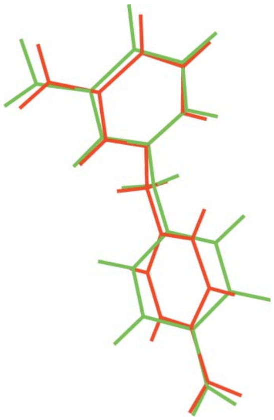


Figure 3
A superimposed fit of the cation of (I) (red) and its energy minimized counterpart (green).

length [1.346 (4) Å] is intermediate between the typical C—N single- and double-bond distances. In the pyridinium ring of (I), the bond lengths and ring planarity [within 0.004 (1) Å] correspond to a π-conjugated system (Allen *et al.*, 1987). Pyridine rings of adjacent molecules related by the symmetry element ($2 - x$, $1 - y$, $-z$) are exactly parallel by symmetry, with a separation distance between their centroids of 3.575 (1) Å, indicating a possible π–π interaction.

In (I), the amino N2 atom is displaced slightly from the plane of the pyridine ring by 0.016 (1) Å. The NH_2 group is twisted 17.7 (7)° from the plane of the pyridine ring. A similar situation was observed in (III). The pyridine and benzene rings are almost orthogonal, with a dihedral angle of 88.7 (1)°. The sum of the bond angles around N3 is 360° (Table 1), indicating the absence of an sp^3 lone pair. The NO_2 group is slightly twisted from the plane of the benzene ring by 3.6 (3)°. This may be due to the intramolecular short contact between atoms O1 and H11 (2.42 Å), which is less than the sum of their van der Waals radii (2.72 Å; Bondi, 1964). The same short contact was observed in (II). However, a superimposed fit of the cations (I) and (II) gives an r.m.s. deviation of 1.844 Å, indicating different conformations of the cations (Fig. 2).

In order to understand the influence of the packing on the molecular conformation, energy minimization was carried out on the isolated cation using *WinMopac7.21* (Shchepin & Litvinov, 1998). A least-squares fit of the cation of (I) with its energy minimized counterpart gives an r.m.s. deviation of 0.51 Å (Fig. 3). The conformations of the cation in the crystal structure and the free cation are significantly different only in the orientation of the benzene ring. This is evident from the increase of the O1···H11 distance from 2.42 Å in (I) to 2.87 Å in the energy minimized cation. In the energy minimized cation, the rotation about the N3—C10 bond has obviously reduced the strain observed in (I).

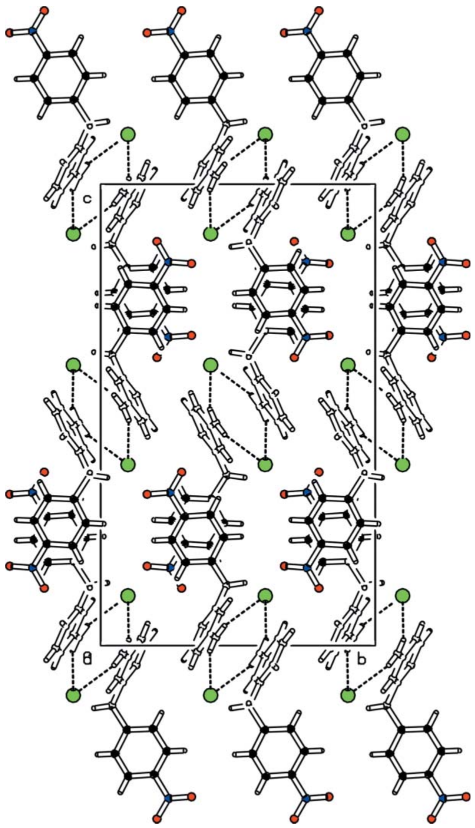


Figure 4
The crystal packing viewed along the *a* axis and showing the N—H···Br hydrogen-bonded (dashed lines) clusters.

In the crystal structure, N—H···Br hydrogen bonds (Table 2) link two cations and two anions into centrosymmetric clusters. Weak intermolecular C—H···O interactions (Table 2) stabilize further the crystal packing (Fig. 4).

Experimental

A solution of 3-aminopyridine (1.15 g, 0.5 mol) and *p*-nitrobenzyl bromide (2.7 g, 0.5 mol) in dry acetone was stirred for 2 h at room temperature (303 K). A separated solid was filtered off and washed with dry acetone to give the stable salt (I) (yield 3 g, 78%; m.p. 476–478 K), which was recrystallized from ethanol/water (9:1 *v*/*v*) solution.

Crystal data

$C_{12}H_{12}O_2N_3^+\cdot Br^-$
$M_r = 310.16$
Orthorhombic, *Pbca*
$a = 7.6440$ (5) Å
$b = 14.1397$ (10) Å
$c = 23.7588$ (16) Å
$V = 2567.9$ (3) Å^3
$Z = 8$
$D_x = 1.604$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5116 reflections
$\theta = 2.7$–25.4°
$\mu = 3.20$ mm^{-1}
$T = 273$ (2) K
Block, colourless
0.12 × 0.10 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
17077 measured reflections
2254 independent reflections
1852 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.076$
$S = 1.05$
2254 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 1.4922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (°).

O1—N3—O2	123.3 (3)	O2—N3—C10	118.1 (3)
O1—N3—C10	118.6 (3)		
N1—C6—C7—C12	−25.5 (4)	C3—C2—N2—H2*B*	10 (2)
N1—C6—C7—C8	156.7 (2)	C1—C2—N2—H2*A*	−11 (3)
C3—C2—N2—H2*A*	169 (3)	C1—C2—N2—H2*B*	−170 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···Br1	0.902 (18)	2.55 (2)	3.422 (3)	163 (3)
N2—H2*B*···Br1$^{\rm i}$	0.876 (18)	2.531 (19)	3.398 (3)	170 (3)
C6—H6*B*···O1$^{\rm ii}$	0.97	2.41	3.354 (4)	165

Symmetry code: (i) $-x+3, -y+1, -z$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$.

All H atoms, except the amino H atoms, were placed at geometrically calculated positions and a riding model was used for their refinement, with C—H = 0.93 and 0.97 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). The amino H atoms were located in a difference map and refined isotropically, with N—H = 0.89 (2) Å bond length restraints.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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).

TVS thanks Dr K. Ravikumar of the Indian Institute of Chemical Technology, Hyderabad, for the use of the facilities in his laboratory and fruitful discussion.

References

Akkurt, M., Karaca, S., Jarrahpour, A. A., Zarei, M. & Buyukgungor, O. (2005). *Acta Cryst.* E**61**, o776–o778.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Beurskens, P. T., Beurskens, G., de Gelder, R., Garcia-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1999). The *DIRDIF99* Program System. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–452.
Bruker (2001). *SAINT* (Version 6.28a) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
Chao, M., Schempp, E. & Rosenstein, R. D. (1975). *Acta Cryst.* B**31**, 2924–2926.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gans, J. & Shalloway, D. (2001). *J. Mol. Graphics Model.* **19**, 557–559.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Shchepin, R. & Litvinov, D. (1998). *WinMopac7.21*. Perm State University, Perm, Russia. http://www.psu.ru/science/soft/winmopac/index_e.html.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Sundar, T. V., Parthasarathi, V., Sridhar, B., Venkatesan, P. & Nallu, M. (2006). *Acta Cryst.* E**62**, o74–o76.