organic compounds

2-Amino-5-bromopyridinium 3-amino-benzoate

Madhukar Hemamalini and Hoong-Kun Fun*‡

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

In the title salt, $C_5H_6BrN_2^+ \cdot C_7H_6NO_2^-$, the pyridine N atom of the 2-amino-5-bromopyridine molecule is protonated. In the crystal, the protonated N atom and the 2-amino group are hydrogen-bonded to the carboxylate O atoms *via* a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. Two inversion-related 3-aminobenzoate anions are linked through N—H···O hydrogen-bonds, forming an $R_2^2(14)$ ring motif. The crystal structure is further stabilized by π···π interactions involving the benzene and pyridinium rings with a centroid–centroid distance of 3.7743 (15) Å.

Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). Balasubramani & Fun (2009). For related structures, see: Goubitz *et al.* (2001); Vaday & Foxman (1999). For details of 3-aminobenzoic acid, see: Windholz (1976); Voogd *et al.* (1980). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).
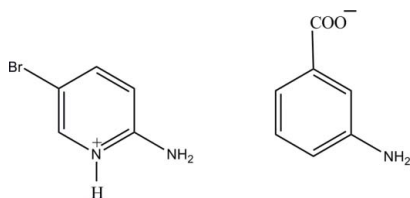
Experimental

Crystal data

$C_5H_6BrN_2^+ \cdot C_7H_6NO_2^-$
$M_r = 309.15$
Monoclinic, $P2_1/c$
$a = 10.1650\ (7)$ Å

$b = 11.0431\ (7)$ Å
$c = 11.9550\ (9)$ Å
$\beta = 113.710\ (2)°$
$V = 1228.71\ (15)$ Å^3

$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.34$ mm^{-1}

$T = 296$ K
$0.42 \times 0.39 \times 0.11$ mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.332$, $T_{max} = 0.708$

15251 measured reflections
3565 independent reflections
2650 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.137$
$S = 1.06$
3565 reflections

163 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.98	1.65	2.626 (3)	176
N2—H2A···O2^i	0.86	1.99	2.826 (3)	165
N2—H2B···O1^{ii}	0.86	2.06	2.909 (3)	170
N3—H3B···O2^{iii}	0.86	2.26	3.028 (4)	148

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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‡ Thomson Reuters ResearcherID: A-3561-2009.

supporting information

2-Amino-5-bromopyridinium 3-aminobenzoate

Madhukar Hemamalini and Hoong-Kun Fun

S1. Comment

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). They are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). 3-Aminobenzoic acid is used as an intermediate for dyes and pesticides (Windholz, 1976). The crystal structures of 3-aminobenzoic acid (Voogd *et al.*, 1980), 2-amino-5-bromopyridine (Goubitz *et al.*, 2001) and 2-amino-5-bromo-pyridinium propynoate (Vaday & Foxman, 1999) have been reported in the literature. In order to study some interesting hydrogen bonding interactions, the synthesis and structure of the title salt, (I), is presented here.

The asymmetric unit of (I) (Fig. 1) contains a 2-amino-5-bromopyridinium cation and a 3-aminobenzoate anion, indicating that proton transfer has occurred during the co-crystallisation experiment. In the 2-amino-5-bromopyridinium cation, a wider than normal angle (C5—N1—C1 = 122.5 (2)°) is subtented at the protonated N1 atom. The 2-amino-5-methylpyridinium cation is essentially planar, with a maximum deviation of 0.020 (2)Å for atom N1.

In the crystal packing (Fig. 2), the protonated N1 atom and 2-amino group (N2) are hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) via a pair of N—H···O hydrogen bonds forming a ring motif $R_2^2(8)$ (Bernstein *et al.*, 1995). Two inversion-related 3-aminobenzoate anions are linked through N3—H3B···O2 hydrogen-bonding to form a $R_2^2(14)$ ring motif (Table 1). This motif is also observed in the crystal structure of 2,3-diaminopyridinium 3-amino benzoate (Balasubramani & Fun, 2009). The crystal structure is further stabilized by a $\pi\cdots\pi$ stacking interaction between the pyridine rings (C1–C5/N1) and benzene ring (C6–C11) with a centroid- to-centroid distance of 3.7743 (15)Å [symmetry codes: 1-x, 1-y, 1-z].

S2. Experimental

A hot methanol solution (20 ml) of 2-amino-5-bromopyridine (87 mg, Aldrich) and 3-aminobenzoic acid (68 mg, Merck) were mixed and warmed over a heating magnetic stirrer for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of (I) appeared after a few days.

S3. Refinement

All hydrogen atoms were positioned geometrically [C–H = 0.93Å and N–H = 0.86–0.98Å] and were refined using a riding model, with $U_{iso}(H) = 1.2\ U_{eq}(C, N)$.
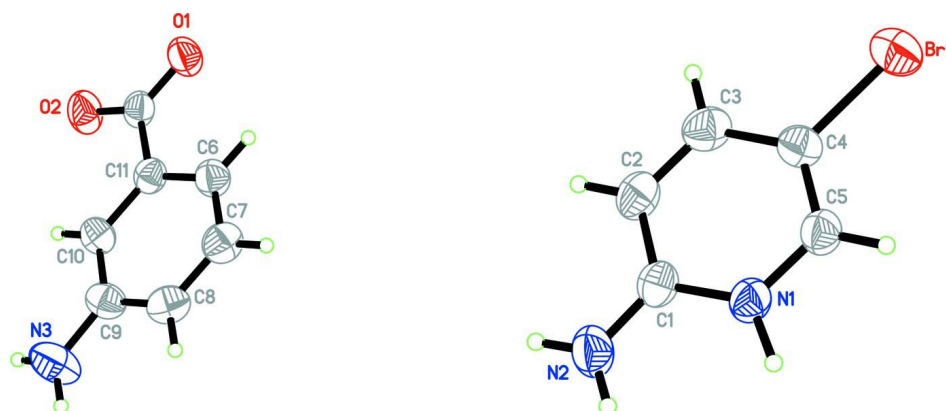
Figure 1

The asymmetric unit of (I) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
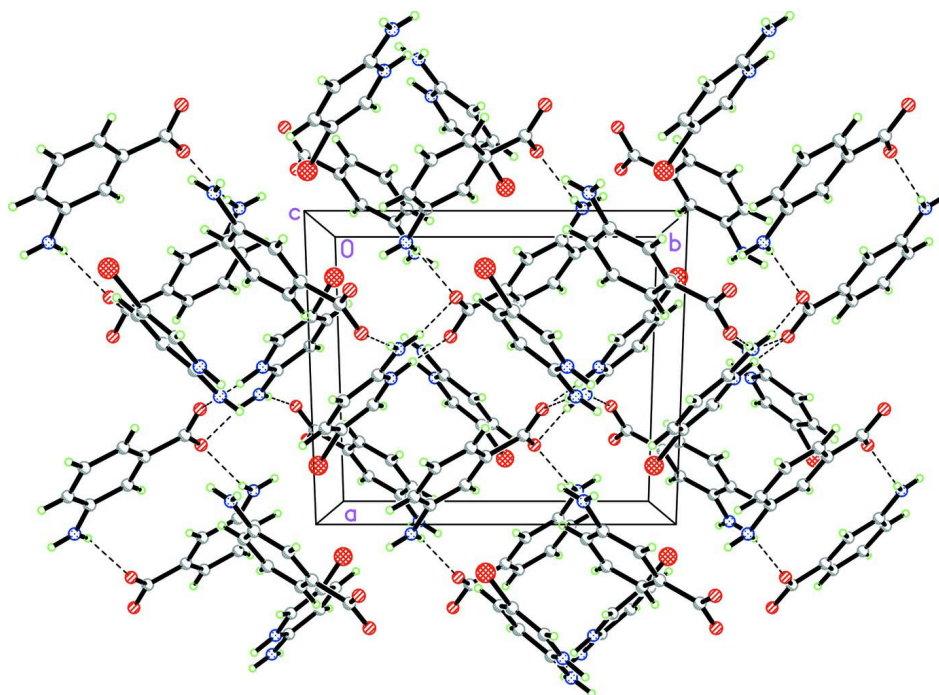
Figure 2

The crystal packing of (I), showing hydrogen-bonded (dashed lines) networks.

2-Amino-5-bromopyridinium 3-aminobenzoate

Crystal data

$C_5H_6BrN_2^+ \cdot C_7H_6NO_2^-$	$V = 1228.71 (15)$ Å^3
$M_r = 309.15$	$Z = 4$
Monoclinic, $P2_1/c$	$F(000) = 620$
Hall symbol: -P 2ybc	$D_x = 1.671$ Mg m^{-3}
$a = 10.1650 (7)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.0431 (7)$ Å	Cell parameters from 4215 reflections
$c = 11.9550 (9)$ Å	$\theta = 2.6–26.8°$
$\beta = 113.710 (2)°$	$\mu = 3.34$ mm^{-1}

$T = 296$ K	$0.42 \times 0.39 \times 0.11$ mm
Blcok, brown	

Data collection

Bruker APEX DUO CCD area-detector diffractometer	15251 measured reflections
Radiation source: fine-focus sealed tube	3565 independent reflections
Graphite monochromator	2650 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.034$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$\theta_{max} = 30.0°$, $\theta_{min} = 2.2°$
	$h = -14 \rightarrow 14$
	$k = -15 \rightarrow 14$
$T_{min} = 0.332$, $T_{max} = 0.708$	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.137$	
$S = 1.06$	H-atom parameters constrained
3565 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.125P]$
163 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.51$ e Å^{-3}
	$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.82844 (3)	0.52926 (3)	0.04268 (3)	0.05749 (15)
N1	0.5198 (2)	0.30649 (19)	0.06832 (17)	0.0383 (4)
N2	0.4208 (3)	0.2756 (2)	0.2082 (2)	0.0499 (5)
H2A	0.3715	0.2168	0.1638	0.060*
H2B	0.4125	0.2940	0.2749	0.060*
C1	0.5087 (2)	0.3373 (2)	0.1739 (2)	0.0378 (5)
C2	0.5959 (3)	0.4328 (3)	0.2429 (2)	0.0442 (5)
H2	0.5897	0.4569	0.3151	0.053*
C3	0.6892 (3)	0.4899 (2)	0.2043 (3)	0.0448 (5)
H3	0.7469	0.5525	0.2502	0.054*
C4	0.6971 (2)	0.4537 (2)	0.0954 (2)	0.0387 (5)
C5	0.6125 (2)	0.3619 (2)	0.0294 (2)	0.0387 (5)
H5	0.6183	0.3370	−0.0428	0.046*
O1	0.3733 (2)	1.13481 (18)	0.91776 (17)	0.0528 (5)

O2	0.2423 (2)	1.11501 (19)	1.02651 (17)	0.0549 (5)
N3	−0.0679 (3)	0.7483 (2)	0.8606 (3)	0.0677 (7)
H3A	−0.1118	0.6865	0.8182	0.081*
H3B	−0.0901	0.7746	0.9185	0.081*
C6	0.2439 (3)	0.9284 (2)	0.7774 (2)	0.0426 (5)
H6	0.3115	0.9693	0.7576	0.051*
C7	0.1775 (3)	0.8250 (3)	0.7134 (2)	0.0477 (6)
H7	0.2012	0.7963	0.6508	0.057*
C8	0.0755 (3)	0.7644 (2)	0.7426 (2)	0.0461 (6)
H8	0.0315	0.6954	0.6992	0.055*
C9	0.0388 (3)	0.8058 (2)	0.8355 (2)	0.0445 (5)
C10	0.1058 (3)	0.9094 (2)	0.9004 (2)	0.0412 (5)
H10	0.0820	0.9380	0.9630	0.049*
C11	0.2085 (3)	0.9701 (2)	0.8712 (2)	0.0375 (5)
C12	0.2807 (3)	1.0815 (2)	0.9441 (2)	0.0399 (5)
H1	0.4617	0.2439	0.0129	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0532 (2)	0.0605 (2)	0.0637 (2)	−0.01495 (12)	0.02867 (15)	−0.00314 (12)
N1	0.0453 (10)	0.0357 (10)	0.0354 (9)	−0.0041 (8)	0.0179 (8)	−0.0056 (8)
N2	0.0630 (14)	0.0513 (13)	0.0451 (11)	−0.0075 (10)	0.0320 (10)	−0.0064 (10)
C1	0.0432 (11)	0.0364 (12)	0.0346 (10)	0.0035 (9)	0.0165 (8)	−0.0018 (9)
C2	0.0519 (13)	0.0432 (13)	0.0391 (12)	0.0008 (11)	0.0200 (10)	−0.0102 (10)
C3	0.0454 (13)	0.0388 (12)	0.0480 (13)	−0.0018 (10)	0.0167 (10)	−0.0113 (10)
C4	0.0357 (11)	0.0374 (12)	0.0438 (12)	−0.0006 (8)	0.0168 (9)	−0.0014 (9)
C5	0.0427 (11)	0.0401 (13)	0.0356 (11)	−0.0004 (9)	0.0183 (9)	−0.0031 (9)
O1	0.0679 (12)	0.0533 (12)	0.0469 (10)	−0.0214 (9)	0.0332 (9)	−0.0119 (8)
O2	0.0784 (13)	0.0500 (11)	0.0479 (10)	−0.0120 (9)	0.0376 (10)	−0.0104 (8)
N3	0.0686 (16)	0.0571 (16)	0.094 (2)	−0.0195 (13)	0.0496 (15)	−0.0166 (15)
C6	0.0455 (12)	0.0433 (13)	0.0412 (12)	−0.0013 (10)	0.0196 (9)	−0.0006 (10)
C7	0.0490 (13)	0.0480 (15)	0.0467 (13)	0.0038 (11)	0.0198 (10)	−0.0063 (11)
C8	0.0443 (13)	0.0380 (13)	0.0508 (14)	0.0026 (10)	0.0137 (10)	−0.0052 (11)
C9	0.0384 (11)	0.0407 (13)	0.0546 (14)	0.0005 (9)	0.0191 (10)	0.0024 (11)
C10	0.0430 (12)	0.0389 (13)	0.0457 (12)	0.0005 (9)	0.0221 (10)	0.0008 (10)
C11	0.0422 (11)	0.0334 (12)	0.0353 (11)	0.0024 (8)	0.0139 (9)	0.0034 (9)
C12	0.0493 (13)	0.0365 (12)	0.0336 (10)	−0.0017 (9)	0.0163 (9)	0.0021 (9)

Geometric parameters (Å, º)

Br1—C4	1.885 (2)	O2—C12	1.252 (3)
N1—C5	1.353 (3)	N3—C9	1.390 (3)
N1—C1	1.355 (3)	N3—H3A	0.8600
N1—H1	0.9745	N3—H3B	0.8600
N2—C1	1.313 (3)	C6—C11	1.387 (3)
N2—H2A	0.8600	C6—C7	1.389 (4)
N2—H2B	0.8600	C6—H6	0.9300

C1—C2	1.410 (4)	C7—C8	1.391 (4)
C2—C3	1.365 (4)	C7—H7	0.9300
C2—H2	0.9300	C8—C9	1.384 (4)
C3—C4	1.395 (4)	C8—H8	0.9300
C3—H3	0.9300	C9—C10	1.396 (4)
C4—C5	1.358 (3)	C10—C11	1.398 (3)
C5—H5	0.9300	C10—H10	0.9300
O1—C12	1.254 (3)	C11—C12	1.515 (3)
C5—N1—C1	122.5 (2)	H3A—N3—H3B	120.0
C5—N1—H1	113.7	C11—C6—C7	119.5 (2)
C1—N1—H1	123.8	C11—C6—H6	120.3
C1—N2—H2A	120.0	C7—C6—H6	120.3
C1—N2—H2B	120.0	C6—C7—C8	120.2 (2)
H2A—N2—H2B	120.0	C6—C7—H7	119.9
N2—C1—N1	118.8 (2)	C8—C7—H7	119.9
N2—C1—C2	123.5 (2)	C9—C8—C7	120.8 (2)
N1—C1—C2	117.7 (2)	C9—C8—H8	119.6
C3—C2—C1	120.4 (2)	C7—C8—H8	119.6
C3—C2—H2	119.8	C8—C9—N3	120.6 (2)
C1—C2—H2	119.8	C8—C9—C10	119.2 (2)
C2—C3—C4	119.5 (2)	N3—C9—C10	120.2 (2)
C2—C3—H3	120.3	C9—C10—C11	120.1 (2)
C4—C3—H3	120.3	C9—C10—H10	120.0
C5—C4—C3	119.7 (2)	C11—C10—H10	120.0
C5—C4—Br1	120.33 (18)	C6—C11—C10	120.3 (2)
C3—C4—Br1	119.97 (19)	C6—C11—C12	120.8 (2)
N1—C5—C4	120.3 (2)	C10—C11—C12	118.9 (2)
N1—C5—H5	119.9	O2—C12—O1	124.2 (2)
C4—C5—H5	119.9	O2—C12—C11	117.4 (2)
C9—N3—H3A	120.0	O1—C12—C11	118.4 (2)
C9—N3—H3B	120.0		
C5—N1—C1—N2	−177.0 (2)	C7—C8—C9—N3	176.9 (3)
C5—N1—C1—C2	1.5 (3)	C7—C8—C9—C10	−0.2 (4)
N2—C1—C2—C3	177.4 (3)	C8—C9—C10—C11	0.0 (4)
N1—C1—C2—C3	−1.0 (4)	N3—C9—C10—C11	−177.1 (3)
C1—C2—C3—C4	0.4 (4)	C7—C6—C11—C10	−0.7 (4)
C2—C3—C4—C5	−0.2 (4)	C7—C6—C11—C12	179.1 (2)
C2—C3—C4—Br1	−178.6 (2)	C9—C10—C11—C6	0.4 (4)
C1—N1—C5—C4	−1.3 (4)	C9—C10—C11—C12	−179.3 (2)
C3—C4—C5—N1	0.7 (4)	C6—C11—C12—O2	179.1 (2)
Br1—C4—C5—N1	178.99 (18)	C10—C11—C12—O2	−1.2 (3)
C11—C6—C7—C8	0.5 (4)	C6—C11—C12—O1	−0.2 (4)
C6—C7—C8—C9	−0.1 (4)	C10—C11—C12—O1	179.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1[i]	0.98	1.65	2.626 (3)	176
N2—H2A···O2[i]	0.86	1.99	2.826 (3)	165
N2—H2B···O1[ii]	0.86	2.06	2.909 (3)	170
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Symmetry codes: (i) x, y−1, z−1; (ii) x, −y+3/2, z−1/2; (iii) −x, −y+2, −z+2.