

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

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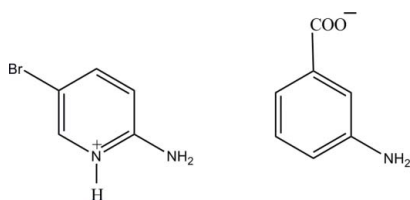
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.037; wR factor = 0.137; data-to-parameter ratio = 21.9.

In the title salt, $\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_7\text{H}_6\text{NO}_2^-$, 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 $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming an $R_2^2(8)$ ring motif. Two inversion-related 3-aminobenzoate anions are linked through $\text{N}-\text{H} \cdots \text{O}$ hydrogen-bonds, forming an $R_2^2(14)$ ring motif. The crystal structure is further stabilized by $\pi \cdots \pi$ 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

 $\text{C}_5\text{H}_6\text{BrN}_2^+ \cdot \text{C}_7\text{H}_6\text{NO}_2^-$
 $M_r = 309.15$

 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) Å³
 $Z = 4$
 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

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, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{O1}^{\text{i}}$	0.98	1.65	2.626 (3)	176
$\text{N2}-\text{H2A} \cdots \text{O2}^{\text{i}}$	0.86	1.99	2.826 (3)	165
$\text{N2}-\text{H2B} \cdots \text{O1}^{\text{ii}}$	0.86	2.06	2.909 (3)	170
$\text{N3}-\text{H3B} \cdots \text{O2}^{\text{iii}}$	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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2628).

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supplementary materials

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2-Amino-5-bromopyridinium 3-aminobenzoate

M. Hemamalini and H.-K. Fun

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-bromopyridinium 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 subtended 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 π ··· π 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].

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.

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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

Figures

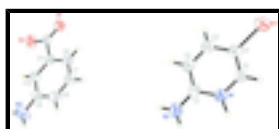


Fig. 1. The asymmetric unit of (I) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

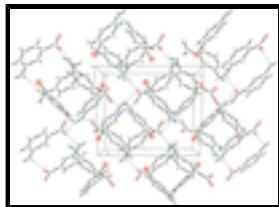
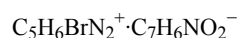


Fig. 2. The crystal packing of (I), showing hydrogen-bonded (dashed lines) networks.

2-Amino-5-bromopyridinium 3-aminobenzoate

Crystal data



$$M_r = 309.15$$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$$a = 10.1650 (7) \text{ \AA}$$

$$b = 11.0431 (7) \text{ \AA}$$

$$c = 11.9550 (9) \text{ \AA}$$

$$\beta = 113.710 (2)^\circ$$

$$V = 1228.71 (15) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 620$$

$$D_x = 1.671 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4215 reflections

$$\theta = 2.6\text{--}26.8^\circ$$

$$\mu = 3.34 \text{ mm}^{-1}$$

$$T = 296 \text{ K}$$

Block, brown

$$0.42 \times 0.39 \times 0.11 \text{ mm}$$

Data collection

Bruker APEX DUO CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2009)

$$T_{\min} = 0.332, T_{\max} = 0.708$$

15251 measured reflections

3565 independent reflections

2650 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.034$$

$$\theta_{\max} = 30.0^\circ, \theta_{\min} = 2.2^\circ$$

$$h = -14 \rightarrow 14$$

$$k = -15 \rightarrow 14$$

$$l = -16 \rightarrow 16$$

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.037$$

$$wR(F^2) = 0.137$$

$$S = 1.06$$

3565 reflections

163 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.125P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.51 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.54 \text{ e \AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

supplementary materials

Atomic displacement parameters (\AA^2)

	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 (\AA , $^\circ$)

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, °)

<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>
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) $x, -y+3/2, z-1/2$; (iii) $-x, -y+2, -z+2$.

Fig. 1

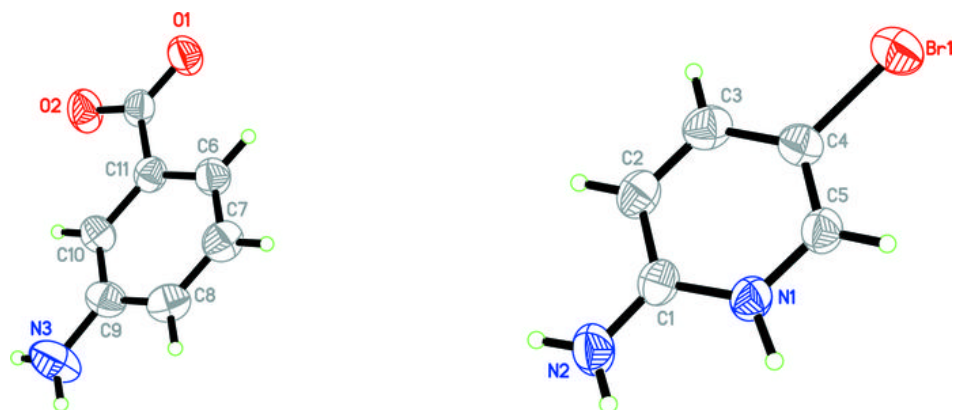


Fig. 2

