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2-Amino-5-bromopyridinium hydrogen succinate

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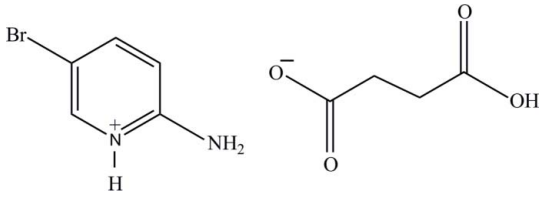
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.057; data-to-parameter ratio = 16.5.

In the title compound, $C_5H_6BrN_2^+\cdot C_4H_5O_4^-$, the pyridine N atom of the 2-amino-5-bromopyridine molecule is protonated. The protonated N atom and the amino group are linked *via* N—H···O hydrogen bonds to the carboxylate O atoms of the singly deprotonated succinate anion. The hydrogen succinate anions are linked *via* O—H···O hydrogen bonds. A weak intermolecular C—H···O hydrogen bond is also observed.

Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For related structures, see: Goubitz *et al.* (2001); Vaday & Foxman (1999). For applications of succinic acid, see: Sauer *et al.* (2008). For bond-length data, see: Allen *et al.* (1987). 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

$C_5H_6N_2Br^+\cdot C_4H_5O_4^-$
M_r = 291.11
Orthorhombic, $P2_12_12_1$
a = 5.3275 (2) Å
b = 13.6226 (5) Å
c = 15.1687 (5) Å
V = 1100.86 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.74 mm^{-1}
T = 296 K
0.80 × 0.15 × 0.13 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.155, T_{max} = 0.650
10042 measured reflections
2472 independent reflections
2138 reflections with $I > 2s(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.057
S = 0.99
2472 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 995 Friedel pairs
Flack parameter: 0.013 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···O2	0.85 (3)	1.88 (3)	2.720 (3)	171 (3)
N2—H2*A*···O1	0.86	1.92	2.782 (3)	178
N2—H2*B*···O1^{i}	0.86	2.01	2.805 (3)	154
O4—H4···O2^{ii}	0.82	1.85	2.609 (2)	154
C1—H1···O3^{iii}	0.93	2.43	3.280 (3)	152

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: IS2526).

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supporting information

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2-Amino-5-bromopyridinium hydrogen succinate

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-bonding interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). Succinic acid derivatives are mostly used in chemicals, food and pharmaceuticals (Sauer *et al.*, 2008). The crystal structures of 2-amino-5-bromopyridine (Goubitz *et al.*, 2001) and 2-amino-5-bromopyridinium propynoate (Vaday & Foxman, 1999) have been reported. In this paper, we present the X-ray single-crystal structure of 2-amino-5-bromopyridinium hydrogen succinate (I).

The asymmetric unit of (I) (Fig. 1) contains a 2-amino-5-bromopyridinium cation and a hydrogen succinate anion, indicating that proton transfer has occurred during the co-crystallization experiment. In the 2-amino-5-bromopyridinium cation, a wider than normal angle [122.9 (2)°] is subtended at the protonated N1 atom. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the protonated N1 atom and the 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) *via* a pair of N—H···O hydrogen bonds, forming a $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). The hydrogen succinate anions self-assemble *via* O4—H4···O2 (Table 1) hydrogen bonds. Furthermore, the crystal structure is stabilized by weak C—H···O hydrogen bonds, forming a 3D-network.

S2. Experimental

A hot methanol solution (10 ml) of 2-amino-5-bromopyridine (87 mg, Aldrich) and a hot aqueous solution (10 ml) of succinic acid (59 mg, Merck) were mixed and warmed over a water bath for 10 minutes. The resulting solution was allowed to cool slowly at room temperature. Single crystals of the title compound appeared from the mother liquor after a few days.

S3. Refinement

Atom H1N1 was located in a difference Fourier map and refined freely. The remaining H atoms were positioned geometrically [C–H = 0.93 or 0.97 Å, O—H = 0.82 Å and N—H = 0.86 Å] and were refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). 995 Friedel pairs were used to determine the absolute configuration.

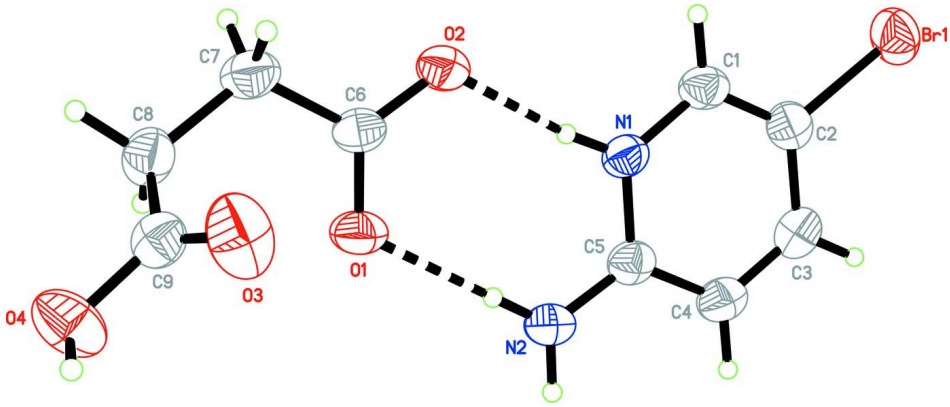

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

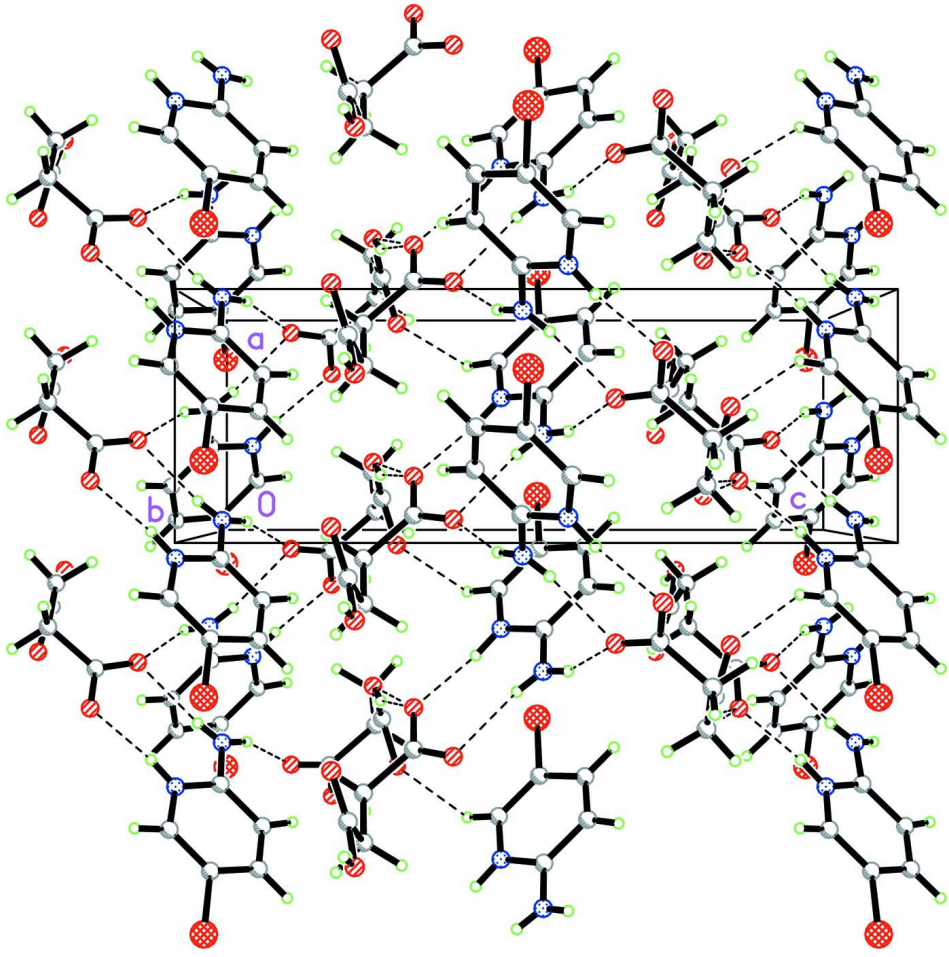

Figure 2

The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) networks.

2-Amino-5-bromopyridinium hydrogen succinate

Crystal data

$C_5H_6N_2Br^+·C_4H_5O_4^-$
M_r = 291.11
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 5.3275 (2) Å
b = 13.6226 (5) Å
c = 15.1687 (5) Å
V = 1100.86 (7) Å^3
Z = 4
$F(000)$ = 584
D_x = 1.756 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4688 reflections
θ = 3.0–26.7°
μ = 3.74 mm^{-1}
T = 296 K
Needle, yellow
0.80 × 0.15 × 0.13 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.155, T_{max} = 0.650
10042 measured reflections
2472 independent reflections
2138 reflections with $I > 2s(I)$
R_{int} = 0.029
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −6→6
k = −17→16
l = −19→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.057
S = 0.99
2472 reflections
150 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 995 Friedel pairs
Absolute structure parameter: 0.013 (8)

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}
O1	0.0791 (3)	0.66915 (12)	0.38303 (10)	0.0490 (4)
O2	0.2588 (3)	0.53970 (10)	0.32236 (11)	0.0441 (4)
O3	0.0528 (4)	0.80559 (14)	0.20813 (14)	0.0633 (6)

O4	−0.3210 (4)	0.86482 (12)	0.24424 (12)	0.0561 (5)
H4	−0.2572	0.9169	0.2290	0.084*
C6	0.0954 (4)	0.60694 (15)	0.32351 (14)	0.0341 (5)
C7	−0.0907 (5)	0.61018 (17)	0.24855 (15)	0.0450 (6)
H7A	−0.1850	0.5493	0.2485	0.054*
H7B	0.0017	0.6134	0.1935	0.054*
C8	−0.2747 (5)	0.69486 (17)	0.25115 (16)	0.0437 (6)
H8A	−0.4068	0.6826	0.2085	0.052*
H8B	−0.3515	0.6971	0.3091	0.052*
C9	−0.1593 (5)	0.79274 (16)	0.23193 (13)	0.0377 (5)
Br1	1.17196 (5)	0.336238 (18)	0.513704 (18)	0.05230 (10)
N1	0.6002 (4)	0.52635 (13)	0.45518 (13)	0.0345 (4)
N2	0.4388 (4)	0.66737 (14)	0.51595 (13)	0.0459 (5)
H2A	0.3300	0.6690	0.4741	0.055*
H2B	0.4388	0.7123	0.5558	0.055*
C1	0.7639 (4)	0.45042 (15)	0.45213 (15)	0.0377 (5)
H1	0.7547	0.4047	0.4067	0.045*
C2	0.9404 (4)	0.44144 (16)	0.51537 (15)	0.0380 (5)
C3	0.9540 (5)	0.51139 (18)	0.58345 (16)	0.0414 (6)
H3	1.0756	0.5056	0.6271	0.050*
C4	0.7899 (5)	0.58693 (16)	0.58521 (14)	0.0405 (5)
H4A	0.7984	0.6332	0.6302	0.049*
C5	0.6060 (4)	0.59588 (15)	0.51909 (14)	0.0343 (5)
H1N1	0.482 (5)	0.5320 (17)	0.4180 (16)	0.047 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0616 (11)	0.0425 (9)	0.0428 (8)	0.0111 (9)	−0.0104 (8)	−0.0157 (8)
O2	0.0495 (10)	0.0309 (8)	0.0520 (9)	0.0067 (7)	−0.0090 (8)	−0.0090 (7)
O3	0.0470 (12)	0.0576 (12)	0.0852 (14)	−0.0024 (9)	0.0118 (11)	0.0229 (10)
O4	0.0603 (11)	0.0347 (9)	0.0733 (12)	0.0024 (10)	0.0199 (11)	0.0111 (8)
C6	0.0412 (13)	0.0265 (10)	0.0347 (11)	−0.0057 (9)	0.0013 (9)	−0.0001 (9)
C7	0.0572 (17)	0.0345 (12)	0.0432 (13)	−0.0017 (11)	−0.0075 (12)	−0.0049 (10)
C8	0.0426 (15)	0.0392 (12)	0.0493 (13)	−0.0033 (10)	−0.0088 (11)	0.0050 (10)
C9	0.0418 (13)	0.0385 (12)	0.0330 (10)	−0.0026 (12)	−0.0029 (12)	0.0039 (9)
Br1	0.04413 (14)	0.04024 (13)	0.07255 (17)	0.00556 (11)	−0.00191 (13)	0.00411 (12)
N1	0.0360 (11)	0.0308 (10)	0.0367 (10)	−0.0035 (8)	−0.0032 (9)	−0.0029 (8)
N2	0.0480 (11)	0.0377 (10)	0.0520 (10)	0.0049 (9)	−0.0099 (10)	−0.0151 (10)
C1	0.0415 (13)	0.0291 (11)	0.0426 (11)	−0.0051 (10)	0.0030 (10)	−0.0034 (9)
C2	0.0364 (12)	0.0334 (11)	0.0442 (11)	−0.0016 (9)	0.0024 (11)	0.0036 (10)
C3	0.0397 (13)	0.0436 (13)	0.0410 (12)	−0.0064 (12)	−0.0046 (11)	0.0035 (11)
C4	0.0443 (14)	0.0411 (12)	0.0362 (11)	−0.0048 (12)	−0.0015 (11)	−0.0057 (10)
C5	0.0355 (11)	0.0303 (10)	0.0370 (10)	−0.0069 (9)	0.0046 (10)	−0.0002 (9)

Geometric parameters (Å, º)

O1—C6	1.241 (2)	N1—C1	1.354 (3)
O2—C6	1.264 (3)	N1—C5	1.356 (3)
O3—C9	1.199 (3)	N1—H1N1	0.85 (3)
O4—C9	1.319 (3)	N2—C5	1.321 (3)
O4—H4	0.8200	N2—H2A	0.8600
C6—C7	1.509 (3)	N2—H2B	0.8600
C7—C8	1.514 (3)	C1—C2	1.349 (3)
C7—H7A	0.9700	C1—H1	0.9300
C7—H7B	0.9700	C2—C3	1.407 (3)
C8—C9	1.497 (3)	C3—C4	1.351 (3)
C8—H8A	0.9700	C3—H3	0.9300
C8—H8B	0.9700	C4—C5	1.407 (3)
Br1—C2	1.891 (2)	C4—H4A	0.9300
C9—O4—H4	109.5	C1—N1—H1N1	121.6 (17)
O1—C6—O2	123.6 (2)	C5—N1—H1N1	115.4 (17)
O1—C6—C7	118.8 (2)	C5—N2—H2A	120.0
O2—C6—C7	117.60 (18)	C5—N2—H2B	120.0
C6—C7—C8	115.32 (18)	H2A—N2—H2B	120.0
C6—C7—H7A	108.4	C2—C1—N1	119.6 (2)
C8—C7—H7A	108.4	C2—C1—H1	120.2
C6—C7—H7B	108.4	N1—C1—H1	120.2
C8—C7—H7B	108.4	C1—C2—C3	119.8 (2)
H7A—C7—H7B	107.5	C1—C2—Br1	120.93 (17)
C9—C8—C7	114.1 (2)	C3—C2—Br1	119.31 (18)
C9—C8—H8A	108.7	C4—C3—C2	119.8 (2)
C7—C8—H8A	108.7	C4—C3—H3	120.1
C9—C8—H8B	108.7	C2—C3—H3	120.1
C7—C8—H8B	108.7	C3—C4—C5	120.2 (2)
H8A—C8—H8B	107.6	C3—C4—H4A	119.9
O3—C9—O4	123.3 (2)	C5—C4—H4A	119.9
O3—C9—C8	125.1 (2)	N2—C5—N1	118.3 (2)
O4—C9—C8	111.5 (2)	N2—C5—C4	123.99 (19)
C1—N1—C5	122.9 (2)	N1—C5—C4	117.7 (2)
O1—C6—C7—C8	3.3 (3)	C1—C2—C3—C4	0.2 (3)
O2—C6—C7—C8	−177.4 (2)	Br1—C2—C3—C4	179.88 (18)
C6—C7—C8—C9	70.8 (3)	C2—C3—C4—C5	−0.1 (3)
C7—C8—C9—O3	6.8 (3)	C1—N1—C5—N2	179.6 (2)
C7—C8—C9—O4	−173.26 (18)	C1—N1—C5—C4	−0.7 (3)
C5—N1—C1—C2	0.8 (3)	C3—C4—C5—N2	−180.0 (2)
N1—C1—C2—C3	−0.5 (3)	C3—C4—C5—N1	0.4 (3)
N1—C1—C2—Br1	179.82 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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