Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Amino-5-bromopyridine–benzoic acid (1/1)

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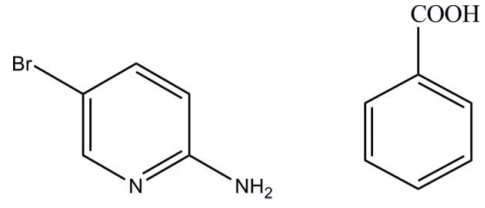
Received 9 February 2010; accepted 14 February 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.123; data-to-parameter ratio = 35.5.

In the title adduct, $C_5H_5BrN_2\cdot C_7H_6O_2$, the carboxyl group of the benzoic acid molecule is twisted away from the attached ring by 12.97 (11)°. The 2-amino-5-bromopyridine molecules interact with the carboxylic group of neighbouring benzoic acid molecules through N—H···O and O—H···N hydrogen bonds, forming cyclic $R_2^2(8)$ hydrogen-bonded motifs and linking the molecules into a two-dimensional network lying parallel to (100). The crystal structure is further stabilized by weak C—H···O hydrogen bonds.

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 details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_5H_5BrN_2\cdot C_7H_6O_2$
M_r = 295.14
Monoclinic, $P2_1/c$
a = 18.5614 (16) Å
b = 5.1769 (5) Å
c = 12.3613 (11) Å
β = 97.016 (2)°
V = 1178.91 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.48 mm^{-1}
T = 100 K
0.61 × 0.21 × 0.07 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.228, T_{max} = 0.788
19825 measured reflections
5495 independent reflections
3709 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.123
S = 1.01
5495 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1^{i}	0.82	1.83	2.626 (2)	162
N2—H2A···O2^{ii}	0.86	2.02	2.866 (3)	167
N2—H2B···O1^{iii}	0.86	2.25	3.105 (2)	171
C7—H7···O2^{iv}	0.93	2.51	3.064 (2)	118

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *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).

MH and HKF thank the Malaysian Government and Universiti Sains Malaysia for the Research University Golden Goose grant No. 1001/PFIZIK/811012. MH thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2420).

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‡ Thomson Reuters ResearcherID: A-3561-2009.

supporting information

Acta Cryst. (2010). E**66**, o663 [doi:10.1107/S1600536810005969]

2-Amino-5-bromopyridine–benzoic acid (1/1)

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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). 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 the literature. In the present study, the hydrogen-bonding patterns in the 2-amino-5-bromopyridine benzoic acid (1/1) cocrystal are investigated.

The asymmetric unit (Fig 1), contains one 2-amino-5-bromopyridine molecule and one benzoic acid molecule. The 2-amino-5-bromopyridine molecule is planar, with a maximum deviation of 0.024 (2)Å for atom N2. The carboxyl group of the benzoic acid molecule is twisted away from the attached ring by 12.97 (11)° . The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the 2-amino-5-bromopyridine molecules interact with the carboxylic group of the respective benzoic acid molecules through N2—H2A···O2 and O1—H1···N1 hydrogen bonds, forming a cyclic hydrogen-bonded motif $R_2^2(8)$ (Bernstein *et al.*, 1995), and linking the molecules into 2-dimensional networks parallel to the (100) plane. The crystal structure is further stabilized by strong N2—H2B···O1 and weak C7—H7···O2 (Table 1) hydrogen bonds.

S2. Experimental

A hot methanol solution (20 ml) of 2-amino-5-bromopyridine (87 mg, Aldrich) and benzoic acid (61 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 the title compound appeared after a few days.

S3. Refinement

All hydrogen atoms were positioned geometrically [C–H = 0.93 Å, N–H = 0.86 Å and O–H = 0.82 Å] and were refined using a riding model, with U_{iso}(H) = 1.2 U_{eq}(C, N) or 1.5 U_{eq}(O).

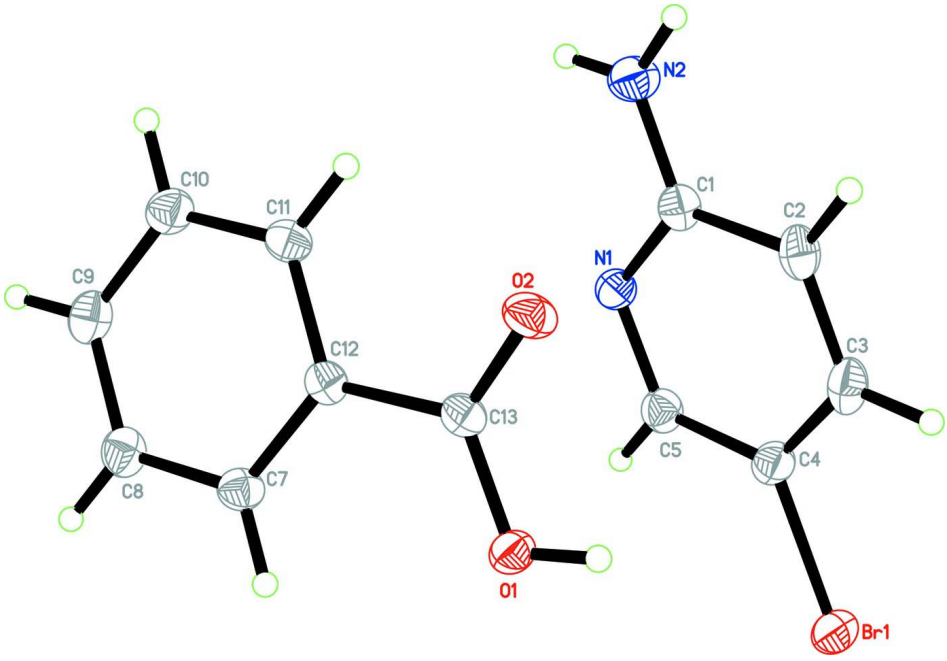

Figure 1

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

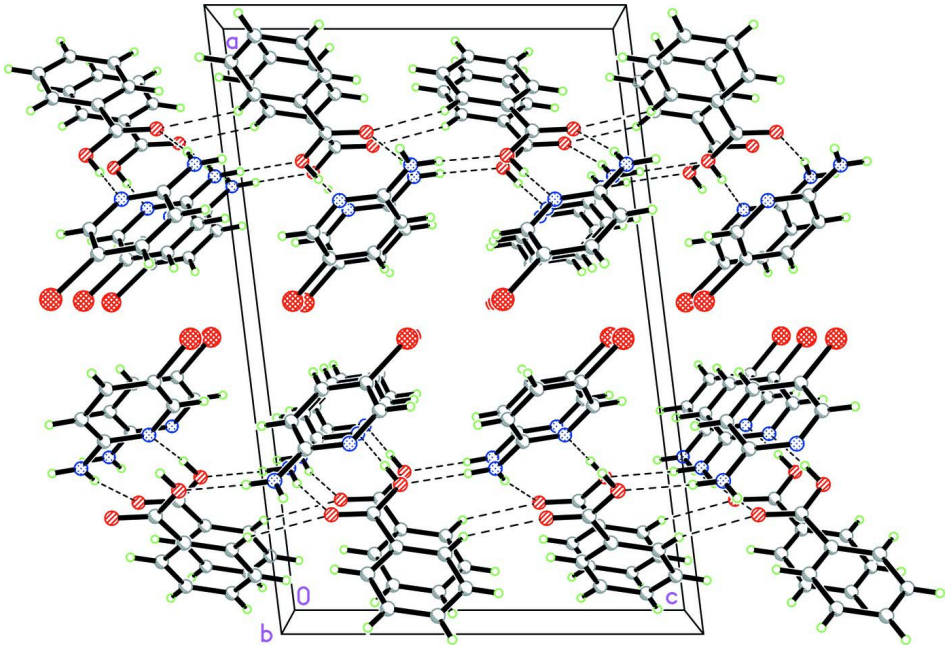

Figure 2

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

2-Amino-5-bromopyridine–benzoic acid (1/1)

Crystal data

$C_5H_5BrN_2 \cdot C_7H_6O_2$
$M_r = 295.14$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 18.5614$ (16) Å
$b = 5.1769$ (5) Å
$c = 12.3613$ (11) Å
$\beta = 97.016$ (2)°
$V = 1178.91$ (19) Å^3
$Z = 4$
$F(000) = 592$
$D_x = 1.663$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3648 reflections
$\theta = 3.8$–$32.0°$
$\mu = 3.48$ mm^{-1}
$T = 100$ K
Plate, colourless
0.61 × 0.21 × 0.07 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.228$, $T_{max} = 0.788$
19825 measured reflections
5495 independent reflections
3709 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 35.9°$, $\theta_{min} = 3.8°$
$h = -30 \rightarrow 30$
$k = -8 \rightarrow 8$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.123$
$S = 1.01$
5495 reflections
155 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
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) k.

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	0.470134 (11)	0.30630 (5)	0.886018 (18)	0.02683 (8)
N1	0.31375 (10)	−0.1799 (3)	0.73265 (14)	0.0191 (3)

N2	0.25884 (11)	−0.2217 (4)	0.55605 (15)	0.0252 (4)
H2A	0.2364	−0.3558	0.5758	0.030*
H2B	0.2519	−0.1704	0.4894	0.030*
C1	0.30452 (10)	−0.0928 (4)	0.62906 (16)	0.0188 (3)
C2	0.34283 (11)	0.1260 (4)	0.59759 (17)	0.0214 (4)
H2	0.3351	0.1861	0.5262	0.026*
C3	0.39160 (12)	0.2490 (4)	0.67336 (19)	0.0231 (4)
H3	0.4172	0.3930	0.6543	0.028*
C4	0.40175 (11)	0.1516 (4)	0.78013 (17)	0.0210 (4)
C5	0.36211 (11)	−0.0591 (4)	0.80675 (16)	0.0206 (4)
H5	0.3688	−0.1204	0.8780	0.025*
O1	0.23842 (7)	0.4732 (3)	0.82571 (10)	0.0188 (3)
H1	0.2668	0.5550	0.7929	0.028*
O2	0.19345 (9)	0.3546 (3)	0.65709 (11)	0.0217 (3)
C7	0.13808 (11)	0.1436 (4)	0.91317 (15)	0.0186 (4)
H7	0.1616	0.2660	0.9600	0.022*
C8	0.09178 (11)	−0.0370 (4)	0.95201 (16)	0.0215 (4)
H8	0.0842	−0.0341	1.0250	0.026*
C9	0.05710 (11)	−0.2199 (4)	0.88304 (18)	0.0215 (4)
H9	0.0265	−0.3401	0.9097	0.026*
C10	0.06795 (12)	−0.2244 (4)	0.77347 (18)	0.0217 (4)
H10	0.0446	−0.3477	0.7269	0.026*
C11	0.11352 (10)	−0.0450 (4)	0.73404 (15)	0.0191 (3)
H11	0.1205	−0.0473	0.6608	0.023*
C12	0.14884 (10)	0.1389 (4)	0.80347 (15)	0.0163 (3)
C13	0.19580 (10)	0.3321 (4)	0.75609 (15)	0.0163 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02372 (11)	0.02522 (13)	0.03212 (12)	−0.00568 (8)	0.00565 (8)	−0.00818 (9)
N1	0.0222 (7)	0.0160 (8)	0.0196 (7)	−0.0029 (6)	0.0045 (6)	−0.0009 (6)
N2	0.0331 (9)	0.0235 (9)	0.0182 (7)	−0.0074 (8)	0.0000 (7)	0.0037 (7)
C1	0.0201 (8)	0.0154 (8)	0.0212 (8)	0.0012 (7)	0.0041 (7)	0.0016 (7)
C2	0.0221 (8)	0.0194 (9)	0.0239 (8)	0.0008 (7)	0.0076 (7)	0.0056 (8)
C3	0.0208 (8)	0.0181 (9)	0.0320 (10)	−0.0006 (7)	0.0097 (8)	0.0032 (8)
C4	0.0191 (8)	0.0176 (9)	0.0268 (9)	−0.0005 (7)	0.0053 (7)	−0.0045 (7)
C5	0.0220 (8)	0.0194 (9)	0.0208 (8)	−0.0005 (8)	0.0043 (7)	0.0011 (7)
O1	0.0209 (6)	0.0193 (7)	0.0159 (6)	−0.0052 (6)	0.0013 (5)	0.0003 (5)
O2	0.0310 (7)	0.0199 (7)	0.0145 (5)	−0.0032 (6)	0.0043 (5)	0.0000 (5)
C7	0.0219 (8)	0.0183 (9)	0.0153 (7)	−0.0007 (7)	0.0010 (6)	0.0010 (7)
C8	0.0225 (8)	0.0226 (10)	0.0199 (8)	−0.0018 (8)	0.0041 (7)	0.0052 (8)
C9	0.0207 (8)	0.0165 (9)	0.0277 (9)	−0.0007 (7)	0.0043 (7)	0.0054 (8)
C10	0.0218 (8)	0.0168 (9)	0.0266 (9)	−0.0009 (7)	0.0027 (7)	−0.0033 (8)
C11	0.0214 (8)	0.0171 (9)	0.0190 (8)	0.0013 (7)	0.0033 (6)	−0.0029 (7)
C12	0.0176 (7)	0.0141 (8)	0.0173 (7)	0.0018 (6)	0.0031 (6)	0.0008 (6)
C13	0.0191 (8)	0.0143 (8)	0.0158 (7)	0.0022 (7)	0.0028 (6)	0.0002 (6)

Geometric parameters (Å, º)

Br1—C4	1.887 (2)	O1—H1	0.8200
N1—C1	1.349 (3)	O2—C13	1.225 (2)
N1—C5	1.355 (3)	C7—C8	1.394 (3)
N2—C1	1.339 (3)	C7—C12	1.395 (2)
N2—H2A	0.8600	C7—H7	0.9300
N2—H2B	0.8600	C8—C9	1.380 (3)
C1—C2	1.417 (3)	C8—H8	0.9300
C2—C3	1.377 (3)	C9—C10	1.394 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—C4	1.404 (3)	C10—C11	1.384 (3)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.378 (3)	C11—C12	1.391 (3)
C5—H5	0.9300	C11—H11	0.9300
O1—C13	1.317 (2)	C12—C13	1.493 (3)
C1—N1—C5	118.98 (18)	C8—C7—H7	120.3
C1—N2—H2A	120.0	C12—C7—H7	120.3
C1—N2—H2B	120.0	C9—C8—C7	120.53 (18)
H2A—N2—H2B	120.0	C9—C8—H8	119.7
N2—C1—N1	118.04 (19)	C7—C8—H8	119.7
N2—C1—C2	120.74 (19)	C8—C9—C10	120.01 (19)
N1—C1—C2	121.21 (19)	C8—C9—H9	120.0
C3—C2—C1	119.56 (19)	C10—C9—H9	120.0
C3—C2—H2	120.2	C11—C10—C9	119.9 (2)
C1—C2—H2	120.2	C11—C10—H10	120.1
C2—C3—C4	118.38 (19)	C9—C10—H10	120.1
C2—C3—H3	120.8	C10—C11—C12	120.26 (18)
C4—C3—H3	120.8	C10—C11—H11	119.9
C5—C4—C3	119.6 (2)	C12—C11—H11	119.9
C5—C4—Br1	120.26 (16)	C11—C12—C7	119.95 (18)
C3—C4—Br1	120.10 (16)	C11—C12—C13	118.04 (16)
N1—C5—C4	122.22 (19)	C7—C12—C13	121.98 (18)
N1—C5—H5	118.9	O2—C13—O1	123.04 (18)
C4—C5—H5	118.9	O2—C13—C12	120.31 (18)
C13—O1—H1	109.5	O1—C13—C12	116.65 (16)
C8—C7—C12	119.37 (19)		
C5—N1—C1—N2	177.14 (19)	C7—C8—C9—C10	−0.3 (3)
C5—N1—C1—C2	−1.8 (3)	C8—C9—C10—C11	−0.1 (3)
N2—C1—C2—C3	−177.5 (2)	C9—C10—C11—C12	0.4 (3)
N1—C1—C2—C3	1.4 (3)	C10—C11—C12—C7	−0.3 (3)
C1—C2—C3—C4	0.1 (3)	C10—C11—C12—C13	−178.42 (19)
C2—C3—C4—C5	−1.2 (3)	C8—C7—C12—C11	0.0 (3)
C2—C3—C4—Br1	178.02 (16)	C8—C7—C12—C13	177.99 (19)
C1—N1—C5—C4	0.6 (3)	C11—C12—C13—O2	12.0 (3)
C3—C4—C5—N1	0.9 (3)	C7—C12—C13—O2	−166.00 (19)

Br1—C4—C5—N1	−178.36 (15)	C11—C12—C13—O1	−168.26 (18)
C12—C7—C8—C9	0.3 (3)	C7—C12—C13—O1	13.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1^{i}	0.82	1.83	2.626 (2)	162
N2—H2*A*···O2^{ii}	0.86	2.02	2.866 (3)	167
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Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) *x*, −*y*+1/2, *z*+1/2.