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

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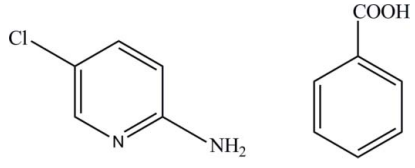
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.111; data-to-parameter ratio = 16.8.

In the title compound, $C_5H_5ClN_2\cdot C_7H_6O_2$, the carboxyl group of the benzoic acid molecule is twisted away from the attached ring by 14.22 (7)°. In the crystal, the 2-amino-5-chloropyridine molecules interact with the carboxyl groups of 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 chains parallel to the [001] direction. Neighbouring 2-amino-5-chloropyridine molecules are also centrosymmetrically paired through C—H···Cl hydrogen bonds, forming another $R_2^2(8)$ motif. 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 details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Lynch & Jones (2004). For reference 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

$C_5H_5ClN_2\cdot C_7H_6O_2$
M_r = 250.68
Monoclinic, $P2_1/c$
a = 17.6114 (19) Å
b = 5.3442 (6) Å
c = 12.4774 (13) Å
β = 100.161 (2)°
V = 1155.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 100 K
0.55 × 0.25 × 0.07 mm

Data collection

Bruker SMART APEX DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.844, T_{max} = 0.979
11852 measured reflections
3331 independent reflections
2802 reflections with $> 2(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.111
S = 1.12
3331 reflections
198 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1*O2*···N1^{i}	0.98 (2)	1.65 (2)	2.629 (1)	175 (2)
N2—H1*N2*···O1^{ii}	0.88 (2)	2.04 (2)	2.898 (2)	165.4 (18)
N2—H2*N2*···O2^{iii}	0.88 (2)	2.37 (2)	3.231 (2)	165.8 (17)
C3—H3···Cl1^{iv}	0.99 (2)	2.82 (2)	3.780 (2)	163.4 (16)
C6—H6···O1^{v}	0.91 (2)	2.58 (2)	3.095 (2)	116.3 (15)

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2376).

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supporting information

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2-Amino-5-chloropyridine–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). Pyridine and its substituted derivatives are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). The adducts of carboxylic acids with the 2-aminoheterocylic ring system form a graph-set motif $R_2^2(8)$ (Lynch & Jones, 2004). In the present study, the hydrogen-bonding patterns in the 2-amino-5-chloropyridine benzoic acid (1/1) cocrystal, are investigated.

The asymmetric unit (Fig. 1), contains one 2-amino-5-chloropyridine molecule and one benzoic acid molecule. The 2-amino-5-chloropyridine molecule is planar, with a maximum deviation of 0.002 (1) Å for atom N1. The carboxyl group of the benzoic acid molecule is twisted away from the attached ring by 14.22 (7)° . The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the 2-amino-5-chloropyridine molecules interact with the carboxyl group of benzoic acid molecules through N—H···O and O—H···N hydrogen bonds, forming a cyclic hydrogen-bonded motif $R_2^2(8)$ (Bernstein *et al.*, 1995), and linking the molecules into chains parallel to the [001] direction. Neighbouring 2-amino-5-chloropyridine molecules are also centrosymmetrically paired through C—H···Cl hydrogen bonds, forming another $R_2^2(8)$ motif. The crystal structure is further stabilized by weak C6—H6···O1 (Table 1) hydrogen bonds.

S2. Experimental

A hot methanol solution (20 ml) of 2-amino-5-chloropyridine (65 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 the H atoms were located in a difference Fourier map and allowed to refine freely [N—H = 0.88 (2) Å, O—H = 0.98 (2) Å, C—H = 0.91 (2) - 1.02 (2) Å].

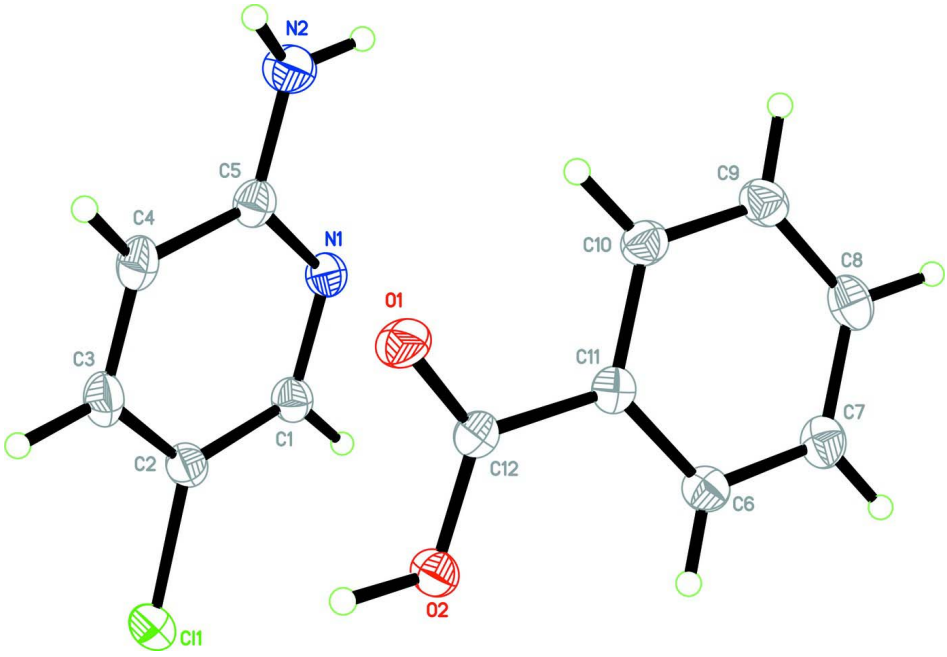

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

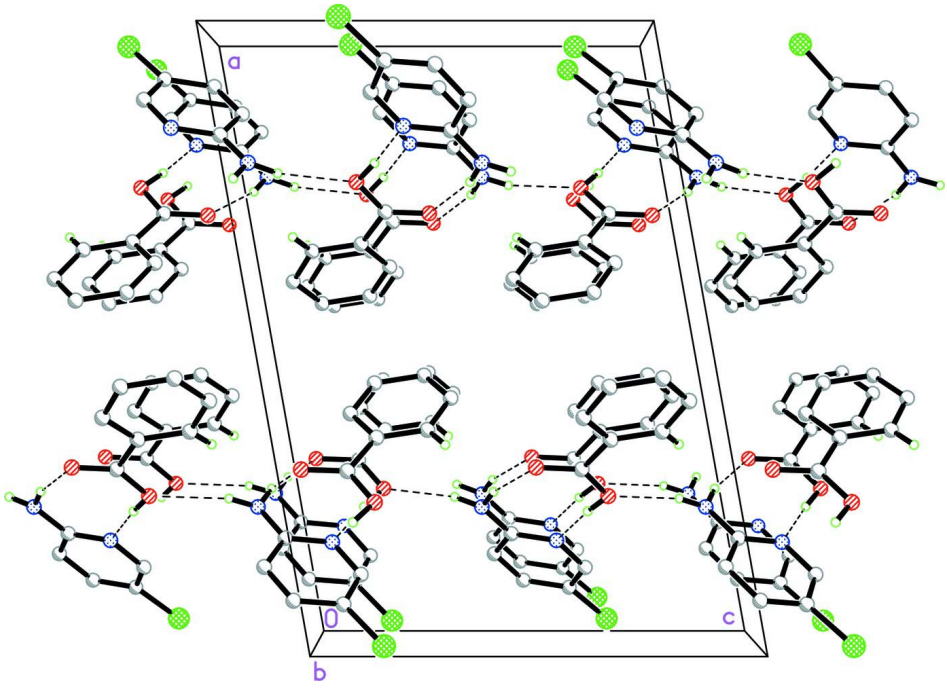

Figure 2

The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) networks. Hydrogen atoms not involved in hydrogen bonding have been omitted.

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

Crystal data

$C_5H_5ClN_2·C_7H_6O_2$
$M_r = 250.68$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 17.6114$ (19) Å
$b = 5.3442$ (6) Å
$c = 12.4774$ (13) Å
$\beta = 100.161$ (2)°
$V = 1155.9$ (2) Å^3
$Z = 4$
$F(000) = 520$
$D_x = 1.440$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5100 reflections
$\theta = 2.4$–30.0°
$\mu = 0.32$ mm^{-1}
$T = 100$ K
Plate, colourless
0.55 × 0.25 × 0.07 mm

Data collection

Bruker SMART 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)
$T_{min} = 0.844$, $T_{max} = 0.979$
11852 measured reflections
3331 independent reflections
2802 reflections with > 2(*I*)
$R_{int} = 0.025$
$\theta_{max} = 30.0°$, $\theta_{min} = 1.2°$
$h = -24\rightarrow24$
$k = -7\rightarrow7$
$l = -17\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.111$
$S = 1.12$
3331 reflections
198 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.2767P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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 esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
Cl1	0.029115 (18)	0.29660 (7)	0.17435 (3)	0.02611 (11)
N1	0.17431 (6)	−0.2004 (2)	0.08617 (9)	0.0197 (2)

N2	0.22948 (8)	−0.2526 (3)	−0.06737 (10)	0.0270 (3)
C1	0.12668 (7)	−0.0733 (2)	0.14079 (10)	0.0202 (2)
C2	0.08720 (7)	0.1356 (2)	0.09858 (10)	0.0203 (2)
C3	0.09605 (8)	0.2235 (3)	−0.00426 (11)	0.0232 (3)
C4	0.14399 (8)	0.0960 (3)	−0.06017 (11)	0.0229 (3)
C5	0.18308 (7)	−0.1193 (2)	−0.01300 (10)	0.0199 (2)
O1	0.30023 (6)	0.33873 (19)	0.06701 (7)	0.0235 (2)
O2	0.25316 (5)	0.46305 (18)	0.21358 (7)	0.0202 (2)
C6	0.35843 (7)	0.1449 (3)	0.34708 (10)	0.0194 (2)
C7	0.40642 (7)	−0.0304 (3)	0.40807 (10)	0.0226 (3)
C8	0.44122 (8)	−0.2180 (3)	0.35634 (12)	0.0232 (3)
C9	0.42870 (8)	−0.2295 (3)	0.24289 (12)	0.0227 (3)
C10	0.38163 (7)	−0.0544 (2)	0.18193 (10)	0.0202 (2)
C11	0.34623 (7)	0.1339 (2)	0.23375 (10)	0.0170 (2)
C12	0.29775 (7)	0.3214 (2)	0.16423 (10)	0.0173 (2)
H1	0.1213 (10)	−0.132 (3)	0.2126 (14)	0.028 (4)*
H3	0.0695 (11)	0.375 (4)	−0.0377 (16)	0.040 (5)*
H4	0.1539 (10)	0.154 (4)	−0.1271 (15)	0.032 (5)*
H6	0.3370 (10)	0.270 (4)	0.3810 (14)	0.026 (4)*
H7	0.4150 (10)	−0.018 (4)	0.4848 (14)	0.032 (5)*
H8	0.4762 (10)	−0.344 (3)	0.4016 (14)	0.026 (4)*
H9	0.4506 (10)	−0.362 (3)	0.2061 (14)	0.029 (4)*
H10	0.3722 (9)	−0.058 (3)	0.1028 (13)	0.024 (4)*
H1O2	0.2262 (13)	0.590 (5)	0.1647 (19)	0.061 (7)*
H1N2	0.2563 (11)	−0.378 (4)	−0.0353 (16)	0.039 (5)*
H2N2	0.2443 (11)	−0.186 (4)	−0.1250 (16)	0.033 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02624 (17)	0.02425 (18)	0.02760 (18)	0.00709 (12)	0.00407 (12)	0.00036 (12)
N1	0.0220 (5)	0.0181 (5)	0.0187 (5)	0.0018 (4)	0.0026 (4)	0.0026 (4)
N2	0.0345 (6)	0.0266 (6)	0.0217 (5)	0.0075 (5)	0.0096 (5)	0.0059 (5)
C1	0.0208 (5)	0.0187 (6)	0.0208 (6)	0.0005 (5)	0.0025 (4)	0.0021 (5)
C2	0.0185 (5)	0.0186 (6)	0.0228 (6)	0.0008 (5)	0.0011 (4)	−0.0009 (5)
C3	0.0232 (6)	0.0200 (6)	0.0240 (6)	0.0016 (5)	−0.0028 (5)	0.0040 (5)
C4	0.0249 (6)	0.0229 (6)	0.0193 (6)	0.0005 (5)	−0.0006 (5)	0.0049 (5)
C5	0.0208 (5)	0.0189 (6)	0.0193 (5)	−0.0018 (5)	0.0012 (4)	0.0010 (5)
O1	0.0320 (5)	0.0243 (5)	0.0148 (4)	0.0045 (4)	0.0059 (3)	0.0020 (4)
O2	0.0225 (4)	0.0211 (4)	0.0178 (4)	0.0043 (4)	0.0055 (3)	0.0031 (4)
C6	0.0207 (5)	0.0203 (6)	0.0182 (5)	0.0006 (5)	0.0063 (4)	0.0022 (5)
C7	0.0219 (6)	0.0267 (7)	0.0191 (6)	0.0010 (5)	0.0037 (4)	0.0056 (5)
C8	0.0197 (6)	0.0206 (6)	0.0291 (7)	0.0010 (5)	0.0034 (5)	0.0065 (5)
C9	0.0210 (6)	0.0182 (6)	0.0289 (7)	0.0010 (5)	0.0044 (5)	−0.0018 (5)
C10	0.0210 (5)	0.0195 (6)	0.0200 (5)	−0.0013 (5)	0.0033 (4)	−0.0026 (5)
C11	0.0165 (5)	0.0158 (5)	0.0187 (5)	−0.0029 (4)	0.0030 (4)	0.0015 (4)
C12	0.0179 (5)	0.0167 (6)	0.0172 (5)	−0.0025 (4)	0.0027 (4)	0.0001 (4)

Geometric parameters (Å, º)

Cl1—C2	1.7382 (13)	O2—C12	1.3190 (15)
N1—C5	1.3454 (16)	O2—H1O2	0.98 (2)
N1—C1	1.3532 (17)	C6—C11	1.3936 (17)
N2—C5	1.3530 (18)	C6—C7	1.3946 (18)
N2—H1N2	0.88 (2)	C6—H6	0.907 (18)
N2—H2N2	0.881 (19)	C7—C8	1.392 (2)
C1—C2	1.3705 (18)	C7—H7	0.945 (17)
C1—H1	0.970 (18)	C8—C9	1.395 (2)
C2—C3	1.4006 (19)	C8—H8	1.015 (18)
C3—C4	1.368 (2)	C9—C10	1.3854 (19)
C3—H3	0.99 (2)	C9—H9	0.962 (18)
C4—C5	1.4149 (18)	C10—C11	1.4005 (18)
C4—H4	0.936 (18)	C10—H10	0.972 (16)
O1—C12	1.2250 (15)	C11—C12	1.4913 (17)
C5—N1—C1	118.92 (11)	C11—C6—H6	120.1 (11)
C5—N2—H1N2	120.0 (13)	C7—C6—H6	120.1 (11)
C5—N2—H2N2	119.3 (13)	C8—C7—C6	120.33 (12)
H1N2—N2—H2N2	117.8 (18)	C8—C7—H7	120.9 (11)
N1—C1—C2	122.21 (12)	C6—C7—H7	118.7 (11)
N1—C1—H1	118.2 (11)	C7—C8—C9	119.92 (12)
C2—C1—H1	119.5 (11)	C7—C8—H8	119.6 (10)
C1—C2—C3	119.61 (12)	C9—C8—H8	120.5 (10)
C1—C2—Cl1	120.10 (10)	C10—C9—C8	119.96 (12)
C3—C2—Cl1	120.25 (10)	C10—C9—H9	119.2 (11)
C4—C3—C2	118.61 (12)	C8—C9—H9	120.8 (11)
C4—C3—H3	118.7 (11)	C9—C10—C11	120.26 (12)
C2—C3—H3	122.6 (11)	C9—C10—H10	121.5 (10)
C3—C4—C5	119.45 (12)	C11—C10—H10	118.3 (10)
C3—C4—H4	121.2 (11)	C6—C11—C10	119.82 (12)
C5—C4—H4	119.3 (11)	C6—C11—C12	122.12 (11)
N1—C5—N2	117.98 (12)	C10—C11—C12	118.04 (11)
N1—C5—C4	121.20 (12)	O1—C12—O2	123.17 (11)
N2—C5—C4	120.81 (12)	O1—C12—C11	120.66 (11)
C12—O2—H1O2	111.7 (14)	O2—C12—C11	116.17 (10)
C11—C6—C7	119.69 (12)		
C5—N1—C1—C2	−0.16 (19)	C6—C7—C8—C9	0.6 (2)
N1—C1—C2—C3	−0.2 (2)	C7—C8—C9—C10	0.0 (2)
N1—C1—C2—Cl1	−178.03 (10)	C8—C9—C10—C11	−0.3 (2)
C1—C2—C3—C4	0.34 (19)	C7—C6—C11—C10	0.60 (19)
Cl1—C2—C3—C4	178.12 (10)	C7—C6—C11—C12	−177.84 (11)
C2—C3—C4—C5	−0.04 (19)	C9—C10—C11—C6	−0.01 (19)
C1—N1—C5—N2	−178.39 (12)	C9—C10—C11—C12	178.49 (11)
C1—N1—C5—C4	0.47 (19)	C6—C11—C12—O1	165.21 (12)
C3—C4—C5—N1	−0.37 (19)	C10—C11—C12—O1	−13.25 (18)

C3—C4—C5—N2	178.46 (13)	C6—C11—C12—O2	−14.87 (17)
C11—C6—C7—C8	−0.9 (2)	C10—C11—C12—O2	166.67 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*O*2···N1^{i}	0.98 (2)	1.65 (2)	2.629 (1)	175 (2)
N2—H1*N*2···O1^{ii}	0.88 (2)	2.04 (2)	2.898 (2)	165.4 (18)
N2—H2*N*2···O2^{iii}	0.88 (2)	2.37 (2)	3.231 (2)	165.8 (17)
C3—H3···Cl1^{iv}	0.99 (2)	2.82 (2)	3.780 (2)	163.4 (16)
C6—H6···O1^{v}	0.91 (2)	2.58 (2)	3.095 (2)	116.3 (15)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) −*x*, −*y*+1, −*z*; (v) *x*, −*y*+1/2, *z*+1/2.