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3-Amino-5-bromo-2-iodopyridine

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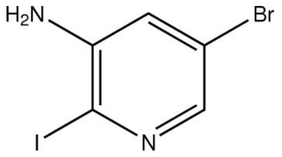
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.009 Å; R factor = 0.032; wR factor = 0.082; data-to-parameter ratio = 15.3.

The reaction of 3-amino-5-bromopyridine with *N*-iodosuccinimide in the presence of acetic acid produces the title compound, C_5H_4BrIN, with an iodo substituent in position 2 of the pyridine ring. The crystal structure features rather weak intermolecular N—H⋯N hydrogen bonds linking the molecules into chains along the z axis of the crystal.

Related literature

For structures of *ortho*-iodoanilines, see: McWilliam *et al.* (2001); Sandor & Foxman (2000); Parkin *et al.* (2005).



Experimental

Crystal data

$C_5H_4BrIN_2$
M_r = 298.90
Monoclinic, $P2_1/c$
a = 4.0983 (12) Å
b = 15.172 (4) Å
c = 12.038 (3) Å
β = 90.152 (5)°
V = 748.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 9.53 mm^{-1}
T = 100 (2) K
0.40 × 0.33 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min}$ = 0.234, $T_{\max}$ = 0.557
3783 measured reflections
1251 independent reflections
1086 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.082
S = 1.05
1251 reflections
82 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.33 e Å^{-3}
$\Delta\rho_{\min}$ = −0.92 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2A⋯N1$^{\rm i}$	0.88	2.16	3.025 (8)	166
N2—H2B⋯I1	0.88	2.79	3.259 (5)	115

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2275).

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supplementary materials

Acta Cryst. (2009). E**65**, o28   [**doi:10.1107/S1600536808040452**]

3-Amino-5-bromo-2-iodopyridine

K. D. Bunker, N. W. Sach, S. Nukui, A. L. Rheingold and **A. Yanovsky**

Comment

The reaction of 5-bromo-3-aminopyridine with *N*-iodosuccinimide in the presence of acetic acid leads to iodo-substitution at position 2 of the pyridine ring, as shown by the X-ray study of the title compound (Fig. 1). To the best of our knowledge, this is the first structure of *ortho*-iodoaminopyridine derivative. The N2···I1 distance 3.259 (5) Å is typical for *ortho*-iodoanilines (McWilliam *et al.*, 2001; Sandor & Foxman, 2000; Parkin *et al.*, 2005) and may suggest involvement of the H2B atom in weak intramolecular N2—H2B···I1 interaction (Table 1).

The second `active' H-atom, H2A, participates in the intermolecular H-bond N2—H2A···N1^{i} (symmetry code (i): *x*, 1/2 - *y*, *z* - 1/2; Table 1), which links the molecules into the chains along the *z*-axis of the crystal (Fig. 2). There are no strong halogen···halogen interactions in the structure; the shortest intermolecular I···I distances are 4.091 (1) Å and 4.098 (1) Å.

Experimental

To a solution of 3-amino-5-bromopyridine (100 mg, 0.56 mmol) in acetic acid (0.1 *M*, 5.61 ml) was added *N*-iodosuccinimide (133 mg, 0.56 mmol) at rt. After 3 h, the reaction was quenched with sat. sodium bicarbonate and extracted 3 times with EtOAc. The organic layers were combined, dried, filtered, and concentrated. The crude residue was subjected to flash chromatography (silica gel, 0–50% EtOAc/heptane). Isolated 93 mg (55%) of 3-amino-5-bromo-2-iodopyridine, as a brown solid. X-ray quality crystals were obtained by slow evaporation of a concentrated chromatography fraction (approx. 30% EtOAc/heptane). ^{1}H NMR (400 MHz, DMSO-d_6) (δ p.p.m.) 5.65 (s, 2 H), 7.16 (d, J = 2.27 Hz, 1 H), 7.67 (d, J = 2.01 Hz, 1 H). ^{13}C NMR (101 MHz, DMSO-d_6) (δ p.p.m.) 106.10, 120.01, 120.92, 137.97, 147.68.

Refinement

All H atoms were treated as riding with the C—H and N—H distances of 0.95 Å and 0.88 Å respectively; the U_{iso}(H) were set to 1.2U_{eq} of the carrying atom.

Figures

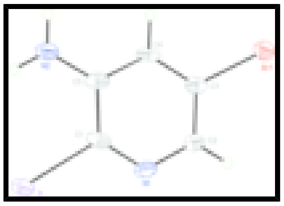

Fig. 1. Molecular structure of the title compound, showing 50% probability displacement ellipsoids and atom numbering scheme. H atoms are drawn as circles with arbitrary small radius.

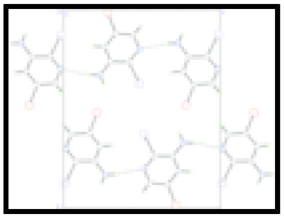

Fig. 2. The crystal packing diagram viewed down the *x*-axis.

3-Amino-5-bromo-2-iodopyridine

Crystal data

$C_5H_4BrIN_2$

M_r = 298.90

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 4.0983 (12) Å

b = 15.172 (4) Å

c = 12.038 (3) Å

β = 90.152 (5)°

V = 748.5 (3) Å^3

Z = 4

F_{000} = 544

D_x = 2.652 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 2536 reflections

θ = 2.7–25.3°

μ = 9.53 mm^{-1}

T = 100 (2) K

Plate, colourless

0.40 × 0.33 × 0.04 mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 100(2) K

φ and ω scans

Absorption correction: analytical
(SADABS; Bruker, 2001)

T_{min} = 0.234, T_{max} = 0.557

3783 measured reflections

1251 independent reflections

1086 reflections with $I > 2\sigma(I)$

R_{int} = 0.037

θ_{max} = 25.3°

θ_{min} = 2.2°

$h = -4 \rightarrow 1$

$k = -17 \rightarrow 18$

$l = -10 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.032

$wR(F^2)$ = 0.082

S = 1.05

1251 reflections

82 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 2.524P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.003

$\Delta\rho_{max}$ = 1.33 e Å^{-3}

$\Delta\rho_{min}$ = −0.92 e Å^{-3}

Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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	$U_{\rm iso}$*/$U_{\rm eq}$
I1	0.18405 (10)	0.37509 (3)	0.48761 (3)	0.02516 (17)
Br1	−0.56202 (16)	0.01782 (4)	0.28399 (5)	0.0266 (2)
N2	−0.0278 (15)	0.3306 (4)	0.2326 (4)	0.0298 (13)
H2A	−0.0808	0.3282	0.1617	0.036*
H2B	0.0760	0.3769	0.2589	0.036*
N1	−0.1133 (14)	0.1994 (4)	0.4858 (4)	0.0264 (13)
C2	−0.2684 (18)	0.1278 (4)	0.4470 (6)	0.0264 (15)
H2	−0.3243	0.0815	0.4965	0.032*
C1	−0.0390 (15)	0.2637 (5)	0.4165 (5)	0.0242 (14)
C5	−0.1071 (15)	0.2622 (5)	0.3019 (5)	0.0227 (14)
C3	−0.3480 (16)	0.1208 (4)	0.3350 (5)	0.0221 (14)
C4	−0.2713 (15)	0.1878 (4)	0.2636 (5)	0.0213 (14)
H4	−0.3303	0.1834	0.1874	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0244 (3)	0.0324 (3)	0.0187 (3)	−0.00094 (16)	−0.00522 (18)	−0.00340 (17)
Br1	0.0285 (4)	0.0274 (4)	0.0238 (4)	−0.0007 (3)	−0.0039 (3)	−0.0027 (3)
N2	0.044 (4)	0.029 (3)	0.016 (3)	−0.002 (3)	−0.008 (3)	−0.001 (2)
N1	0.035 (3)	0.030 (3)	0.015 (3)	0.002 (2)	−0.005 (2)	0.002 (2)
C2	0.035 (4)	0.024 (4)	0.020 (3)	0.000 (3)	−0.007 (3)	0.002 (3)
C1	0.017 (3)	0.036 (4)	0.020 (3)	0.004 (3)	−0.006 (3)	−0.008 (3)
C5	0.017 (3)	0.035 (4)	0.016 (3)	0.006 (3)	−0.001 (2)	−0.002 (3)
C3	0.021 (4)	0.027 (4)	0.018 (3)	0.005 (3)	−0.001 (3)	−0.001 (3)
C4	0.021 (3)	0.033 (4)	0.011 (3)	0.007 (3)	−0.005 (2)	−0.006 (3)

Geometric parameters (Å, °)

I1—C1	2.102 (7)	C2—C3	1.390 (9)
Br1—C3	1.894 (7)	C2—H2	0.9500

N2—C5	1.371 (9)	C1—C5	1.407 (9)
N2—H2A	0.8800	C5—C4	1.393 (9)
N2—H2B	0.8800	C3—C4	1.368 (9)
N1—C1	1.320 (9)	C4—H4	0.9500
N1—C2	1.342 (9)		

C5—N2—H2A	120.0	N2—C5—C4	121.8 (5)
C5—N2—H2B	120.0	N2—C5—C1	122.6 (6)
H2A—N2—H2B	120.0	C4—C5—C1	115.6 (6)
C1—N1—C2	119.3 (5)	C4—C3—C2	119.9 (6)
N1—C2—C3	120.6 (6)	C4—C3—Br1	121.1 (5)
N1—C2—H2	119.7	C2—C3—Br1	119.0 (5)
C3—C2—H2	119.7	C3—C4—C5	120.4 (6)
N1—C1—C5	124.2 (6)	C3—C4—H4	119.8
N1—C1—I1	116.0 (4)	C5—C4—H4	119.8
C5—C1—I1	119.8 (5)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···N1^{i}	0.88	2.16	3.025 (8)	166
N2—H2B···I1	0.88	2.79	3.259 (5)	115

Symmetry codes: (i) x, $-y+1/2$, $z-1/2$.

Fig. 1

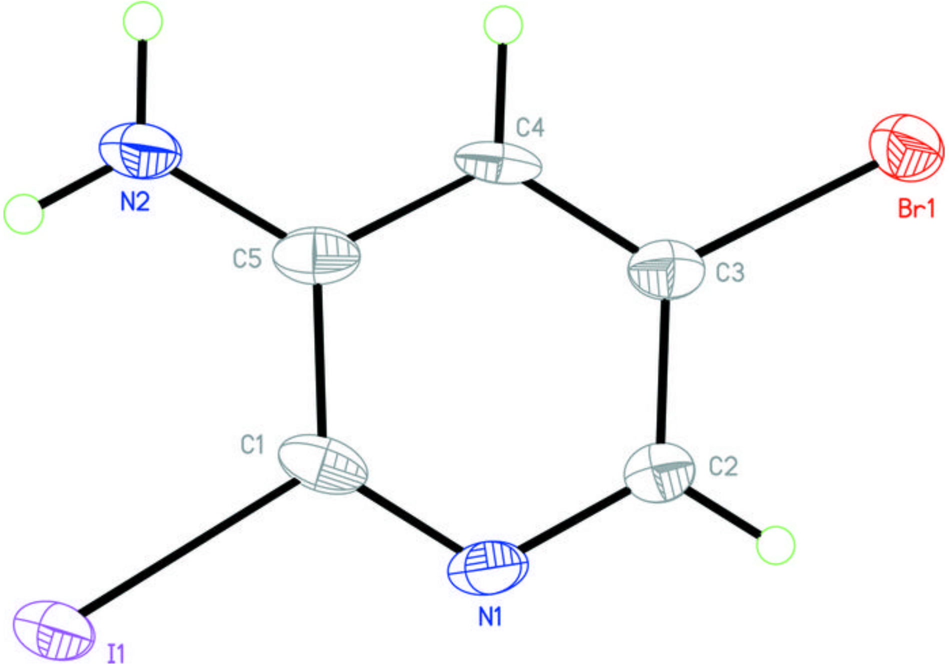

Fig. 2