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5-Bromo-N^3-[(*E*)-(6-bromopyridin-2-yl)-methylidene]pyridine-3,4-diamine

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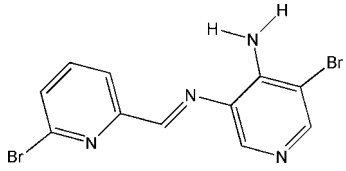
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.009 Å; R factor = 0.029; wR factor = 0.055; data-to-parameter ratio = 19.3.

The title compound, $C_{11}H_8Br_2N_4$, is a Schiff base obtained from 6-bromopicolinaldehyde and 5-bromopyridine-3,4-diamine. The molecule has an *E* configuration about the C=N bond and the dihedral angle between the two pyridine rings is 14.02 (1)°. The observed conformation is stabilised by an intramolecular N—H···N hydrogen bond. In the crystal, molecules are stacked along the *b* axis and are linked through N—H···N hydrogen bonds into chains along the *c* axis.

Related literature

For the use of Schiff bases in coordination, see: Burkhardt & Plass (2008); Keypour *et al.* (2011); Tarafder *et al.* (2002). For their properties, see: Kocyigit *et al.* (2010).



Experimental

Crystal data

$C_{11}H_8Br_2N_4$
M_r = 356.03
Monoclinic, *Cc*
a = 24.941 (2) Å
b = 3.8306 (6) Å
c = 15.0868 (14) Å
β = 126.116 (14)°
V = 1164.4 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.94 mm^{-1}
T = 113 K
0.20 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn 724CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
T_{min} = 0.337, T_{max} = 0.490
5047 measured reflections
2282 independent reflections
2070 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.055
S = 0.89
2282 reflections
118 parameters
38 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}
Absolute structure: Flack (1983), 1093 Friedel pairs
Flack parameter: 0.002 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···N2	0.88	2.33	2.686 (6)	104
N4—H4A···N1^{i}	0.88	2.44	3.043 (5)	126

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

Data collection: *CrystalClear* (Rigaku/MSC, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2009); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2006).

The authors thank Professor Wang, Department of Chemistry, Nankai University, for providing experimental facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LD2030).

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supporting information

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5-Bromo-N^3-[(*E*)-(6-bromopyridin-2-yl)methylidene]pyridine-3,4-diamine

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S1. Comment

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals (Burkhardt & Plass, 2008; Keypour, *et al.*, 2011; Tarafder, *et al.*, 2002). They possess important properties, such as an ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins, transfer of an amino group, photochromic properties and complexing ability towards toxic metals (Kocyigit *et al.*, 2010). In this paper, a new Schiff base compound derived from condensation of 6-bromopicolinaldehyde with 5-bromo-pyridine-3,4-diamine is reported. The molecule of the title compound has an E configuration about the C6=N2 bond (Fig.1). The dihedral angle between the two pyridyl rings is 14.02 (1)°. An intramolecular N—H···N hydrogen bond forms five-membered ring. The five-membered ring and two pyridyl ring form dihedral angles of 3.60 (1)° and 4.02 (1)°. In the crystal, molecules are stacked along *y* axis and are linked through intermolecular N—H···N hydrogen bonds into chains propagating along *z* axis (Fig.2).

S2. Experimental

A solution of 6-bromopicolinaldehyde and 5-bromopyridine-3,4-diamine in methanol was refluxed for 30 min, and then the crude product was filtered and recrystallized from methanol to yield yellowish title compound. A small amount of the product was dissolved in methanol and the solution was kept for 5 days at ambient temperature to produce yellowish acicular crystals on slow evaporation of the solvent.

S3. Refinement

Amino H atoms were located in a difference fourier map and were put in ideal positions with N—H=0.88 Å. The remaining H atoms were positioned geometrically, with C—H=0.95 Å, and constrained to ride on their parent atoms, with U_{iso}(H)=1.2U_{eq}(C/N).

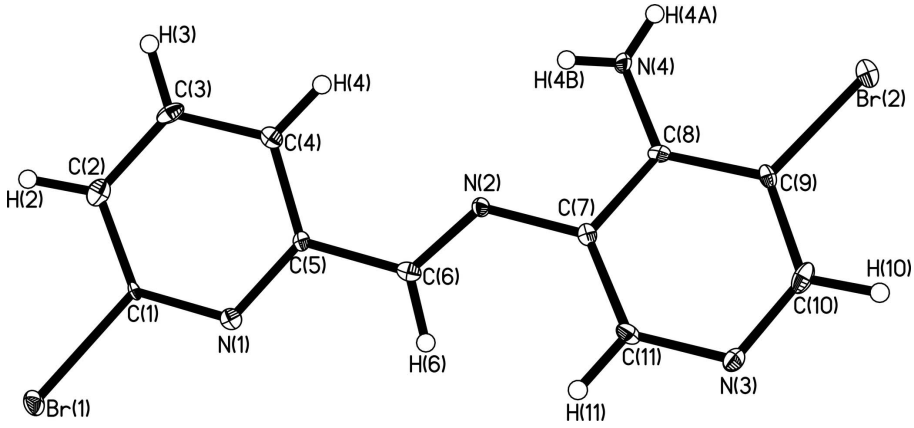

Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

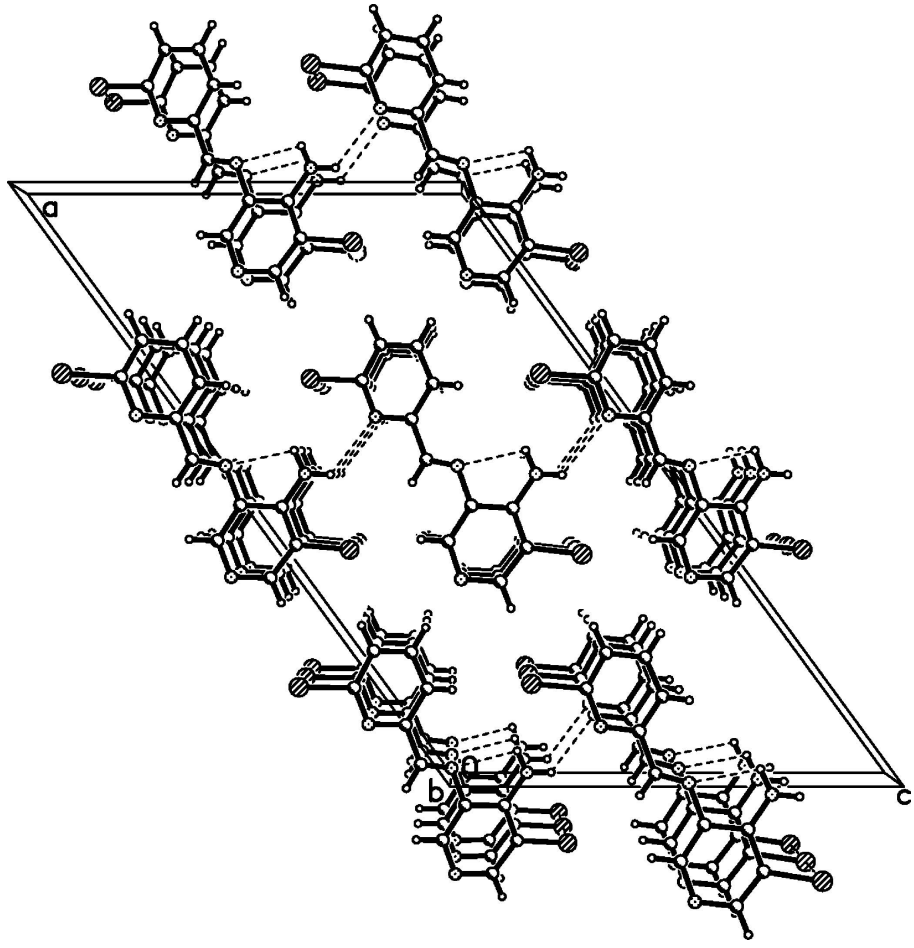

Figure 2

Molecular packing of the title compound with hydrogen bonding shown as dashed lines

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Crystal data

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b = 3.8306 (6) Å
c = 15.0868 (14) Å
β = 126.116 (14)°
V = 1164.4 (2) Å^3
Z = 4
F(000) = 688
D_x = 2.031 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2086 reflections
θ = 1.7–27.9°
μ = 6.94 mm^{-1}
T = 113 K
Prism, colorless
0.20 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn 724CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
T_{min} = 0.337, T_{max} = 0.490
5047 measured reflections
2282 independent reflections
2070 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 26.4°, θ_{min} = 2.0°
h = −30→29
k = −4→4
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.055
S = 0.89
2282 reflections
118 parameters
38 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
$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00177 (14)
Absolute structure: Flack (1983), **1093 Friedel pairs**
Absolute structure parameter: 0.002 (12)

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_{iso}*/U_{eq}
Br1	−0.32411 (2)	−1.16292 (13)	−0.65216 (3)	0.01513 (13)

Br2	−0.60799 (2)	0.03838 (13)	−0.34064 (3)	0.01849 (14)
C6	−0.4590 (3)	−0.6690 (12)	−0.5248 (4)	0.0102 (6)
H6	−0.4959	−0.7657	−0.5913	0.012*
C1	−0.3284 (3)	−0.9595 (12)	−0.5398 (4)	0.0102 (7)
C9	−0.5986 (3)	−0.1427 (11)	−0.4469 (4)	0.0102 (6)
N2	−0.4692 (2)	−0.4839 (10)	−0.4673 (3)	0.0102 (6)
C4	−0.3354 (3)	−0.6323 (13)	−0.3902 (4)	0.0117 (12)
H4	−0.3393	−0.5114	−0.3393	0.014*
C5	−0.3928 (3)	−0.7397 (13)	−0.4927 (4)	0.0102 (7)
C8	−0.5367 (3)	−0.2611 (13)	−0.4152 (4)	0.0102 (6)
N1	−0.3883 (2)	−0.9064 (10)	−0.5679 (3)	0.0102 (10)
N3	−0.6504 (2)	−0.2897 (11)	−0.6358 (3)	0.0160 (11)
C2	−0.2699 (3)	−0.8765 (12)	−0.4417 (4)	0.0102 (7)
H2	−0.2282	−0.9341	−0.4266	0.012*
C10	−0.6531 (3)	−0.1634 (12)	−0.5552 (4)	0.0102 (6)
H10	−0.6947	−0.0846	−0.5738	0.012*
N4	−0.4818 (2)	−0.2585 (10)	−0.3118 (3)	0.0156 (10)
H4A	−0.4834	−0.1785	−0.2587	0.019*
H4B	−0.4441	−0.3367	−0.2969	0.019*
C3	−0.2743 (3)	−0.7040 (13)	−0.3652 (4)	0.0136 (12)
H3	−0.2353	−0.6368	−0.2963	0.016*
C11	−0.5907 (3)	−0.3985 (12)	−0.6050 (4)	0.0127 (13)
H11	−0.5878	−0.4893	−0.6606	0.015*
C7	−0.5329 (3)	−0.3906 (12)	−0.4994 (4)	0.0102 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0168 (3)	0.0139 (3)	0.0191 (3)	0.0022 (2)	0.0129 (2)	−0.0024 (2)
Br2	0.0207 (3)	0.0179 (3)	0.0219 (3)	0.0026 (3)	0.0153 (3)	−0.0004 (3)
C6	0.0118 (15)	0.0111 (14)	0.0086 (13)	−0.0005 (15)	0.0064 (12)	0.0002 (13)
C1	0.0100 (17)	0.0077 (15)	0.0135 (17)	−0.0007 (12)	0.0073 (14)	0.0026 (12)
C9	0.0122 (15)	0.0052 (13)	0.0154 (14)	−0.0006 (10)	0.0094 (12)	0.0015 (10)
N2	0.0118 (15)	0.0111 (14)	0.0086 (13)	−0.0005 (15)	0.0064 (12)	0.0002 (13)
C4	0.018 (3)	0.010 (3)	0.010 (3)	0.001 (2)	0.010 (3)	0.002 (2)
C5	0.0100 (17)	0.0077 (15)	0.0135 (17)	−0.0007 (12)	0.0073 (14)	0.0026 (12)
C8	0.0122 (15)	0.0052 (13)	0.0154 (14)	−0.0006 (10)	0.0094 (12)	0.0015 (10)
N1	0.013 (3)	0.008 (2)	0.008 (2)	−0.0011 (18)	0.006 (2)	0.0017 (17)
N3	0.009 (3)	0.023 (3)	0.012 (2)	0.003 (2)	0.004 (2)	0.0014 (19)
C2	0.0100 (17)	0.0077 (15)	0.0135 (17)	−0.0007 (12)	0.0073 (14)	0.0026 (12)
C10	0.0122 (15)	0.0052 (13)	0.0154 (14)	−0.0006 (10)	0.0094 (12)	0.0015 (10)
N4	0.005 (2)	0.031 (3)	0.010 (2)	0.0035 (19)	0.004 (2)	−0.0036 (18)
C3	0.008 (3)	0.017 (3)	0.008 (3)	−0.003 (2)	0.000 (2)	0.004 (2)
C11	0.016 (3)	0.011 (3)	0.012 (3)	0.002 (2)	0.009 (3)	0.000 (2)
C7	0.0122 (15)	0.0052 (13)	0.0154 (14)	−0.0006 (10)	0.0094 (12)	0.0015 (10)

Geometric parameters (Å, º)

Br1—C1	1.925 (5)	C5—N1	1.363 (6)
Br2—C9	1.884 (5)	C8—N4	1.337 (6)
C6—N2	1.256 (5)	C8—C7	1.418 (7)
C6—C5	1.447 (7)	N3—C11	1.339 (6)
C6—H6	0.9500	N3—C10	1.347 (5)
C1—N1	1.305 (7)	C2—C3	1.389 (7)
C1—C2	1.370 (7)	C2—H2	0.9500
C9—C10	1.380 (6)	C10—H10	0.9500
C9—C8	1.397 (7)	N4—H4A	0.8800
N2—C7	1.407 (7)	N4—H4B	0.8800
C4—C3	1.363 (7)	C3—H3	0.9500
C4—C5	1.414 (7)	C11—C7	1.382 (7)
C4—H4	0.9500	C11—H11	0.9500
N2—C6—C5	122.0 (4)	C11—N3—C10	115.9 (5)
N2—C6—H6	119.0	C1—C2—C3	116.9 (5)
C5—C6—H6	119.0	C1—C2—H2	121.6
N1—C1—C2	127.0 (5)	C3—C2—H2	121.6
N1—C1—Br1	115.1 (4)	N3—C10—C9	123.4 (5)
C2—C1—Br1	117.9 (4)	N3—C10—H10	118.3
C10—C9—C8	120.4 (5)	C9—C10—H10	118.3
C10—C9—Br2	119.9 (4)	C8—N4—H4A	120.0
C8—C9—Br2	119.6 (4)	C8—N4—H4B	120.0
C6—N2—C7	123.5 (4)	H4A—N4—H4B	120.0
C3—C4—C5	119.4 (5)	C4—C3—C2	119.2 (5)
C3—C4—H4	120.3	C4—C3—H3	120.4
C5—C4—H4	120.3	C2—C3—H3	120.4
N1—C5—C4	121.3 (5)	N3—C11—C7	125.8 (5)
N1—C5—C6	116.6 (5)	N3—C11—H11	117.1
C4—C5—C6	122.1 (5)	C7—C11—H11	117.1
N4—C8—C9	124.2 (5)	C11—C7—N2	126.2 (5)
N4—C8—C7	119.0 (5)	C11—C7—C8	117.7 (5)
C9—C8—C7	116.8 (5)	N2—C7—C8	116.0 (5)
C1—N1—C5	116.2 (4)		
C5—C6—N2—C7	175.6 (5)	C11—N3—C10—C9	0.3 (7)
C3—C4—C5—N1	−1.5 (7)	C8—C9—C10—N3	−1.1 (7)
C3—C4—C5—C6	−179.4 (4)	Br2—C9—C10—N3	−180.0 (4)
N2—C6—C5—N1	−172.0 (4)	C5—C4—C3—C2	1.0 (7)
N2—C6—C5—C4	6.0 (7)	C1—C2—C3—C4	1.0 (7)
C10—C9—C8—N4	−178.3 (4)	C10—N3—C11—C7	−0.2 (8)
Br2—C9—C8—N4	0.6 (7)	N3—C11—C7—N2	−175.7 (5)
C10—C9—C8—C7	1.8 (7)	N3—C11—C7—C8	1.0 (8)
Br2—C9—C8—C7	−179.3 (3)	C6—N2—C7—C11	−19.0 (8)
C2—C1—N1—C5	2.4 (7)	C6—N2—C7—C8	164.2 (4)
Br1—C1—N1—C5	−175.4 (3)	N4—C8—C7—C11	178.4 (4)

C4—C5—N1—C1	−0.1 (7)	C9—C8—C7—C11	−1.7 (7)
C6—C5—N1—C1	177.9 (4)	N4—C8—C7—N2	−4.5 (7)
N1—C1—C2—C3	−2.9 (7)	C9—C8—C7—N2	175.4 (4)
Br1—C1—C2—C3	174.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*B*···N2	0.88	2.33	2.686 (6)	104
N4—H4*A*···N1^{i}	0.88	2.44	3.043 (5)	126

Symmetry code: (i) *x*, −*y*−1, *z*+1/2.