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## Structure Reports

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# *N,N'*-Bis(5-bromopyridin-2-yl)methane-diamine

 Gary S. Nichol,<sup>a\*</sup> Anuj Sharma<sup>b</sup> and Hong-Yu Li<sup>b</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, 1306 E University Boulevard, The University of Arizona, Tucson, AZ 85721, USA, and <sup>b</sup>Southwest Center for Drug Discovery, College of Pharmacy, The University of Arizona, Tucson, AZ 85737, USA  
Correspondence e-mail: gsnichol@email.arizona.edu

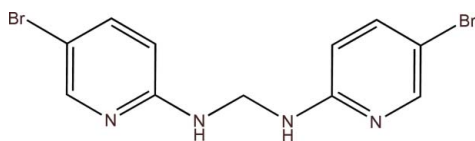
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.051; data-to-parameter ratio = 19.4.

The V-shaped title compound,  $\text{C}_{11}\text{H}_{10}\text{Br}_2\text{N}_4$ , lies on a crystallographic twofold rotation axis which passes through the central C atom. In the crystal, an infinite tape motif, which propagates in the  $a$ -axis direction, is formed by inversion-related  $\text{N}-\text{H}\cdots\text{N}$  hydrogen-bonding interactions. The structure confirmed the identity of the compound as a reaction side product.

## Related literature

For background information on the Groebke–Blackburn synthesis, see: Bienaymé & Bouzid (1998); Blackburn *et al.* (1998); Groebke *et al.* (1998); Mandair *et al.* (2002); Parchinsky *et al.* (2006). For the crystal structure of a similar compound, see: Wu *et al.* (2004). For information on graph-set notation to describe hydrogen-bonding motifs, see: Bernstein *et al.* (1995).



## Experimental

### Crystal data

$\text{C}_{11}\text{H}_{10}\text{Br}_2\text{N}_4$	$c = 25.8065$ (15) Å
$M_r = 358.05$	$\beta = 98.326$ (3)°
Monoclinic, $I2/a$	$V = 1232.11$ (11) Å <sup>3</sup>
$a = 11.9075$ (6) Å	$Z = 4$
$b = 4.0523$ (2) Å	Mo $K\alpha$ radiation

$\mu = 6.56$  mm<sup>-1</sup>  
 $T = 100$  K

$0.24 \times 0.08 \times 0.07$  mm

### Data collection

Bruker Kappa APEXII DUO CCD diffractometer	11800 measured reflections
Absorption correction: numerical (SADABS; Sheldrick, 1996)	1903 independent reflections
$T_{\min} = 0.297$ , $T_{\max} = 0.675$	1674 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.051$	$\Delta\rho_{\text{max}} = 0.70$ e Å <sup>-3</sup>
$S = 1.03$	$\Delta\rho_{\text{min}} = -0.47$ e Å <sup>-3</sup>
1903 reflections	
98 parameters	
1 restraint	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2N}\cdots\text{N1}^i$	0.87 (1)	2.11 (1)	2.9645 (18)	168 (2)

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL, publCIF (Westrip, 2010) and local programs.

The diffractometer was purchased with funding from NSF grant CHE-0741837.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5123).

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## supporting information

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***N,N'*-Bis(5-bromopyridin-2-yl)methanediamine**

Gary S. Nichol, Anuj Sharma and Hong-Yu Li

**S1. Comment**

The Groebke-Blackburn reaction is the most popular way to prepare imidazo-azines from 2-aminoazines in a single-step. (Groebke *et al.*, 1998; Bienaymé & Bouzid, 1998; Blackburn *et al.*, 1998). The reaction involves addition of 2-aminoazine **1** to the aldehyde in the presence of catalytic amounts of acid to generate the respective Schiff base which undergoes a non-concerted [4 + 1] cycloaddition with an isocyanide to form the imidazoazine **2** (Pathway A, Figure 1). Though imidazoazine **2** remained the major product, it was later found that the reaction also produced the isomeric imidazo[1,2-*a*]pyrimidine product **3** through an alternative iminium intermediate involving the ring nitrogen of **1** (Pathway B, Figure 1; Parchinsky *et al.*, 2006). Similarly, nucleophilic solvents (for example, methanol) were found to promote interaction of the primary imine intermediate with the second molecule of 2-aminoazine or the solvent itself to give side-products like **4** (Pathway C, Figure 1; Mandair *et al.*, 2002).

We, in one case, decided to synthesize *N*-benzyl-6-bromoindolizin-3-amine, **3a**. Interestingly, the reaction did not yield the expected product **2a** or the regioisomer **3a**. However, the product which crystallized from a solution of dichloromethane turned out to be *N,N'*-bis(5-bromopyridin-2-yl)methanediamine, **4a** in 20% yield (Figure 2).

The V-shaped structure of **4a** is shown in Figure 3. The compound has crystallized with atom C6 on a twofold rotation axis, and has been set in space group *I2/a*. Molecular dimensions are unexceptional. In the crystal, inversion-related N—H···N hydrogen bonding interactions form an  $R^2_2(8)$  graph set motif (Bernstein *et al.*, 1995). As a result, the crystal forms an infinite hydrogen bonded tape of V-shaped molecules, which propagates in the *a*-axis direction. The tapes are stacked in the *b*-axis direction, and the separation between each tape is approximately 3.6 Å. The structure of the related compound *N,N'*-Di-2-pyridylmethylenediamine exhibits the same V-shaped structure, but with a different crystal packing arrangement (Wu *et al.*, 2004).

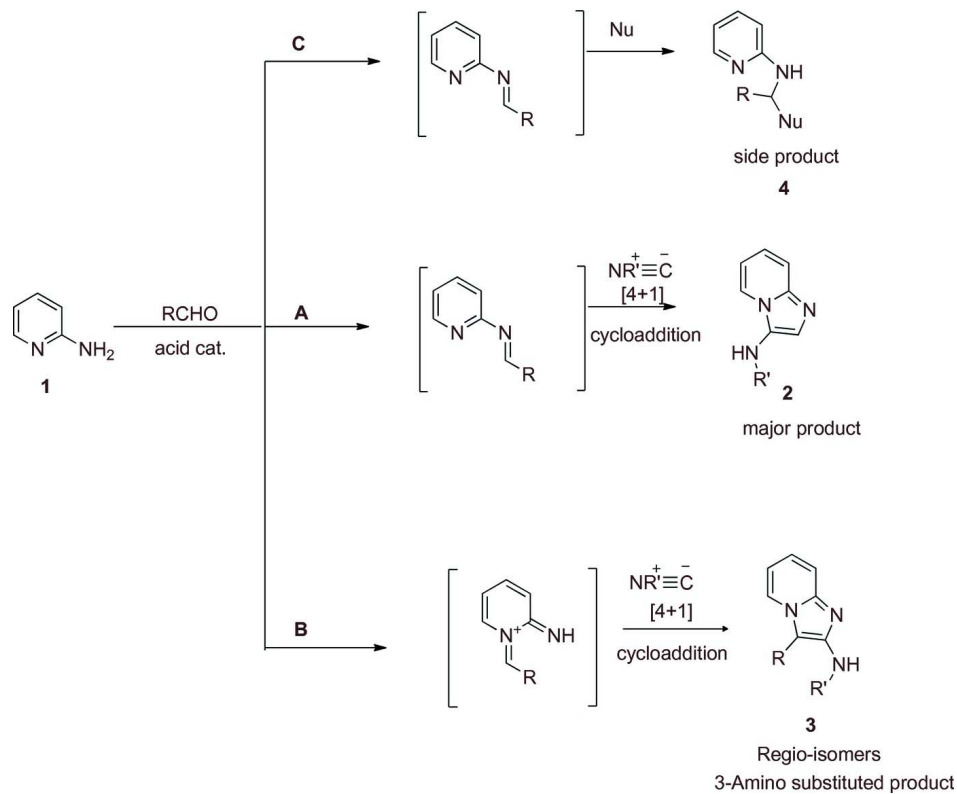
**S2. Experimental**

To a solution of 5-bromopyridin-2-amine **1a** (0.58 mmol, 100 mg) in dichloromethane (DCM) (1.5 ml), was added aq. 37% solution of formaldehyde (140  $\mu$ l, 1.78 mmol) followed by (isocyanomethyl)benzene (75.4  $\mu$ l, 0.58 mmol) and the solution was stirred for 10 min. DCM was evaporated and the resulting solid was irradiated under microwave at 100° C for 10 min. The crude product was purified through silica gel chromatography to provide 41 mg of **4a** in (20% yield). The product was recrystallized from a DCM solution.

**S3. Refinement**

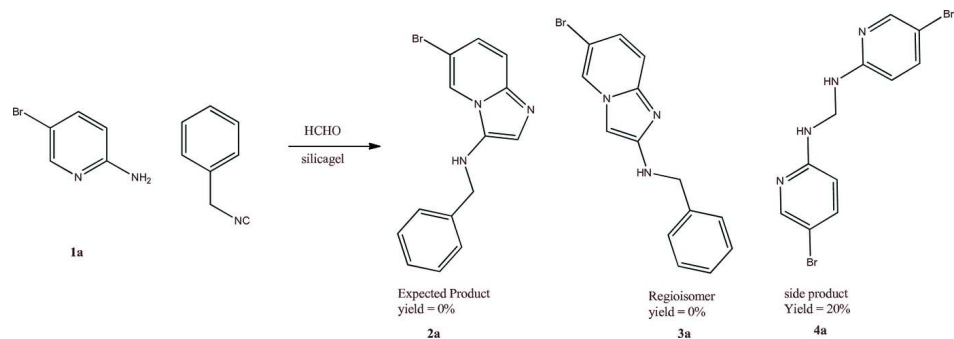
All H atoms were located in a difference map and are freely refined, with the exception of an N—H distance restraint of 0.88 (1) Å used on H2N. C—H distances lie in the range 0.92 (2) to 1.01 (2) Å.

The space group was set as *I2/a* since *I2/a* results in a smaller beta angle (and slightly shorter *c* axis).



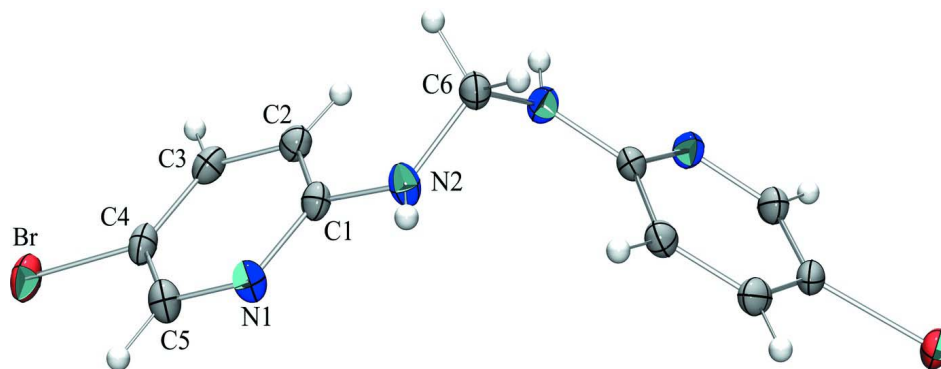
**Figure 1**

Three reaction pathways in the Groebke-Blackburn reaction.

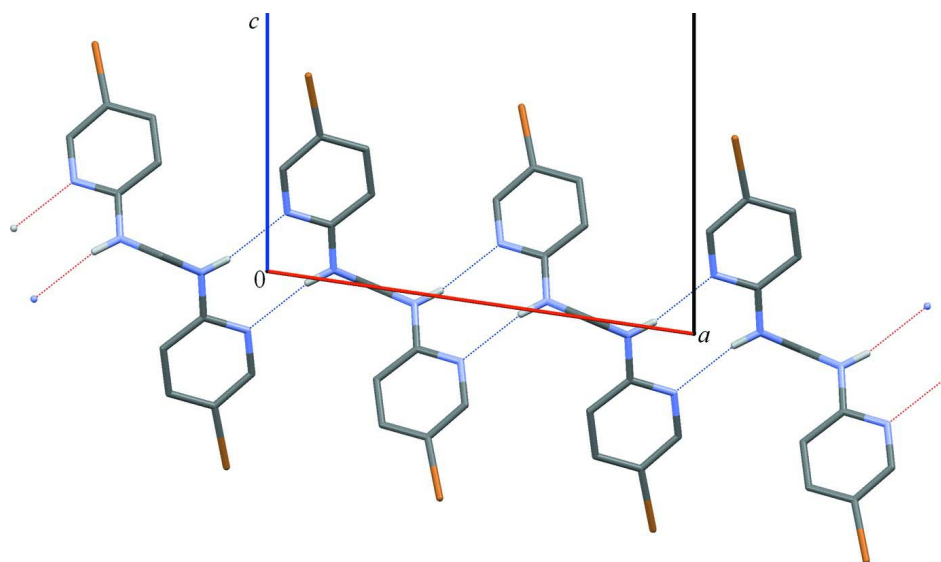


**Figure 2**

Three possible products in the reaction described herein.

**Figure 3**

The molecular structure of **4a**, with displacement ellipsoids at the 50% probability level. Unlabelled atoms are related to labelled atoms by a twofold rotation (symmetry operator:  $-x + 3/2, y, -z$ ).

**Figure 4**

Hydrogen bonding interactions (blue dotted lines; red dotted lines indicate continuation) in the crystal structure of **4a**. The long  $c$  axis has been truncated.

### 5-bromo-*N*-{[(5-bromopyridin-2-yl)amino]methyl}pyridin-2-amine

#### Crystal data

$C_{11}H_{10}Br_2N_4$

$M_r = 358.05$

Monoclinic,  $I2/a$

Hall symbol:  $-I 2/a$

$a = 11.9075$  (6) Å

$b = 4.0523$  (2) Å

$c = 25.8065$  (15) Å

$\beta = 98.326$  (3)°

$V = 1232.11$  (11) Å<sup>3</sup>

$Z = 4$

$F(000) = 696$

$D_x = 1.930$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6689 reflections

$\theta = 3.2\text{--}30.6^\circ$

$\mu = 6.56$  mm<sup>-1</sup>

$T = 100$  K

Rod, colourless

$0.24 \times 0.08 \times 0.07$  mm

*Data collection*

Bruker Kappa APEXII DUO CCD  
diffractometer

Radiation source: fine-focus sealed tube with  
Miracol optics

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: numerical  
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.297$ ,  $T_{\max} = 0.675$

11800 measured reflections

1903 independent reflections

1674 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 30.7^\circ$ ,  $\theta_{\min} = 1.6^\circ$

$h = -16 \rightarrow 17$

$k = -5 \rightarrow 5$

$l = -36 \rightarrow 37$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.051$

$S = 1.03$

1903 reflections

98 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 1.5219P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.596053 (15)	1.07921 (4)	0.214841 (6)	0.02877 (6)
N1	0.54707 (10)	0.7010 (3)	0.06616 (5)	0.0220 (2)
N2	0.65505 (10)	0.4435 (3)	0.01189 (5)	0.0213 (2)
H2N	0.5900 (11)	0.412 (5)	-0.0074 (7)	0.026 (5)*
C1	0.64953 (12)	0.5832 (4)	0.05935 (6)	0.0189 (3)
C2	0.74416 (12)	0.6124 (4)	0.09880 (6)	0.0205 (3)
H2	0.8137 (17)	0.536 (5)	0.0930 (8)	0.025 (5)*
C3	0.73085 (13)	0.7578 (4)	0.14580 (6)	0.0224 (3)
H3	0.7917 (16)	0.776 (5)	0.1733 (8)	0.026 (5)*
C4	0.62425 (13)	0.8776 (4)	0.15222 (6)	0.0218 (3)
C5	0.53646 (13)	0.8461 (4)	0.11167 (6)	0.0231 (3)
H5	0.4625 (18)	0.923 (5)	0.1152 (9)	0.030 (6)*
C6	0.7500	0.2511 (5)	0.0000	0.0207 (4)
H6	0.7804 (16)	0.108 (5)	0.0309 (8)	0.024 (5)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br	0.04319 (11)	0.02711 (9)	0.01784 (8)	-0.00538 (7)	0.01056 (6)	-0.00376 (6)
N1	0.0194 (5)	0.0262 (6)	0.0208 (6)	-0.0010 (5)	0.0045 (4)	-0.0038 (5)
N2	0.0166 (5)	0.0286 (6)	0.0188 (6)	-0.0013 (5)	0.0033 (4)	-0.0050 (5)
C1	0.0201 (6)	0.0198 (6)	0.0175 (6)	-0.0032 (5)	0.0052 (5)	0.0006 (5)
C2	0.0192 (6)	0.0231 (7)	0.0192 (6)	-0.0013 (5)	0.0030 (5)	0.0023 (5)
C3	0.0258 (7)	0.0232 (7)	0.0176 (6)	-0.0029 (6)	0.0010 (5)	0.0026 (6)
C4	0.0294 (7)	0.0214 (6)	0.0159 (6)	-0.0049 (5)	0.0074 (5)	-0.0013 (5)
C5	0.0224 (7)	0.0260 (7)	0.0219 (7)	-0.0020 (6)	0.0071 (5)	-0.0032 (6)
C6	0.0227 (9)	0.0204 (9)	0.0199 (9)	0.000	0.0067 (7)	0.000

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br—C4	1.8838 (15)	C2—C3	1.378 (2)
N1—C1	1.3452 (19)	C3—H3	0.94 (2)
N1—C5	1.3356 (19)	C3—C4	1.391 (2)
N2—H2N	0.868 (9)	C4—C5	1.374 (2)
N2—C1	1.3596 (18)	C5—H5	0.95 (2)
N2—C6	1.4425 (17)	C6—N2 <sup>i</sup>	1.4425 (17)
C1—C2	1.410 (2)	C6—H6	1.01 (2)
C2—H2	0.92 (2)		
C1—N1—C5	118.31 (13)	C2—C3—C4	118.51 (14)
H2N—N2—C1	115.0 (14)	H3—C3—C4	119.9 (13)
H2N—N2—C6	117.5 (14)	Br—C4—C3	122.18 (11)
C1—N2—C6	123.94 (11)	Br—C4—C5	118.90 (12)
N1—C1—N2	115.37 (13)	C3—C4—C5	118.92 (14)
N1—C1—C2	121.41 (13)	N1—C5—C4	123.52 (14)
N2—C1—C2	123.20 (13)	N1—C5—H5	115.8 (13)
C1—C2—H2	120.1 (13)	C4—C5—H5	120.6 (13)
C1—C2—C3	119.31 (14)	N2—C6—N2 <sup>i</sup>	114.56 (18)
H2—C2—C3	120.6 (13)	N2—C6—H6	110.2 (11)
C2—C3—H3	121.6 (13)	N2 <sup>i</sup> —C6—H6	106.1 (11)
C5—N1—C1—N2	-178.95 (14)	C2—C3—C4—Br	179.74 (11)
C5—N1—C1—C2	-0.4 (2)	C2—C3—C4—C5	0.1 (2)
C6—N2—C1—N1	-168.30 (15)	C1—N1—C5—C4	-0.9 (2)
C6—N2—C1—C2	13.2 (2)	Br—C4—C5—N1	-178.55 (12)
N1—C1—C2—C3	1.6 (2)	C3—C4—C5—N1	1.1 (2)
N2—C1—C2—C3	179.98 (14)	C1—N2—C6—N2 <sup>i</sup>	-80.54 (14)
C1—C2—C3—C4	-1.4 (2)		

Symmetry code: (i)  $-x+3/2, y, -z$ .

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2N $\cdots$ N1 <sup>ii</sup>	0.87 (1)	2.11 (1)	2.9645 (18)	168 (2)

Symmetry code: (ii)  $-x+1, -y+1, -z$ .