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6-Bromo-2-methyl-1*H*-imidazo[4,5-*b*]pyridine

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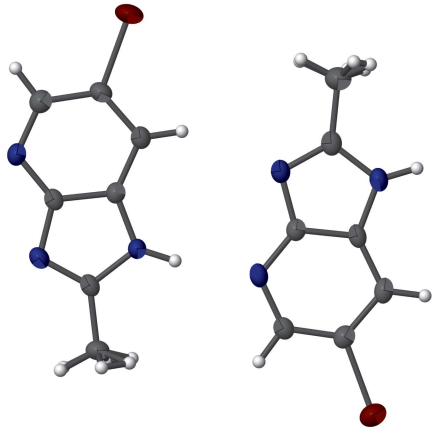
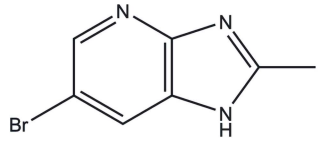
Structural data: full structural data are available from iucrdata.iucr.org

The title molecule, $C_7H_6BrN_3$, crystallizes with two molecules, *A* and *B*, in the asymmetric unit, with all non-hydrogen atoms lying on a crystallographic mirror plane. In the crystal, the molecules are linked into [100] chains of alternating *A* and *B* molecules by complementary N—H···N and C—H···N hydrogen bonds. The chains are associated through offset aromatic π–π stacking [shortest centroid–centroid separation = 3.6215 (9) Å] along the *b* axis.

3D view



Chemical scheme



Structure description

Heterocyclic ring systems having the imidazo[4,5-*b*]pyridine nucleus can be considered as structural analogues of purines and have shown diverse biological activities depending on the substituents of the heterocyclic ring. Their activities include anti-cancer (Lukasik *et al.*, 2012), antiviral (Cristalli, *et al.*, 1995) and antimitotic (Aridoss *et al.*, 2006) actions.

In this study, we have reacted 3-acetyl-4-hydroxy-6-methyl-3*H*-pyran-2-one (dehydroacetic acid) with 5-bromopyridine-2,3-diamine to furnish the title compound 6-bromo-2-methyl-1*H*-imidazo[4,5-*b*]pyridine·The asymmetric unit (Fig. 1) consists of two molecules, each lying on a crystallographic mirror plane.

In the crystal, complementary pairs of N2—H2···N4 and C3—H3···N5 as well as N6—H6···N1^{i} and C10—H10···N3^{i} [symmetry code: (i) $x-1, y, z$] hydrogen bonds (Table 1) form chains running parallel to the *a* axis. These ribbons form stacks in the *b*-axis direction which are associated through offset π-stacking with an average interplanar spacing of 3.236 (1) Å (Fig. 2).

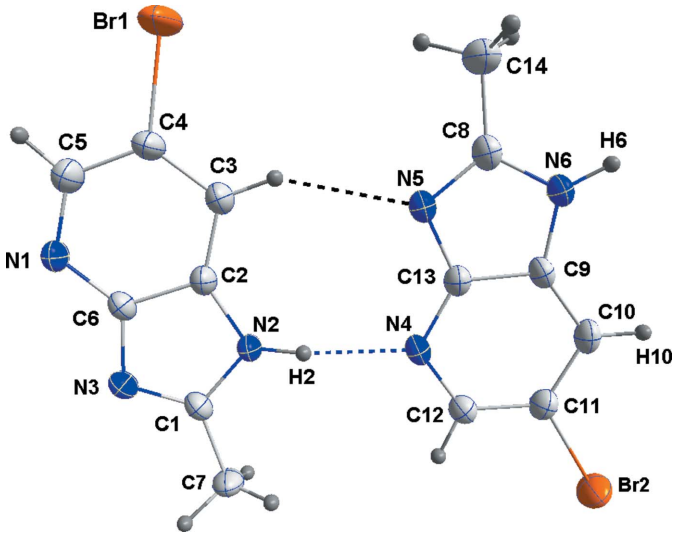


Figure 1
The asymmetric unit with 50% probability ellipsoids. Hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

Dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-3*H*-pyran-2-one) (0.27 g, 1.6 mmol) was added to a solution of 5-bromopyridine-2,3-diamine (0.3 g, 1.6 mmol) in ethanol (15 ml). The mixture was heated for 24 h. After the completion of reaction (as monitored by TLC), the mixture was filtered. The compound was recrystallized from ethanol–water (1:1) solution to afford colourless plates (yield = 68%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

JTM thanks Tulane University for support of the Tulane Crystallography Laboratory.

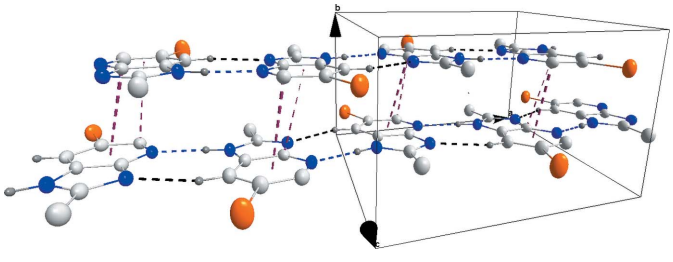


Figure 2
Packing showing portions of two ribbons with the N—H···N interactions shown as blue dotted lines, the C—H···N interactions as black dotted lines and the offset π-stacking as purple dotted lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N4	0.91	1.94	2.845 (4)	172
C3—H3···N5	0.95	2.43	3.286 (4)	150
N6—H6···N1^{i}	0.91	1.97	2.876 (4)	180
C10—H10···N3^{i}	0.95	2.48	3.312 (4)	146

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_6BrN_3$
M_r	212.06
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	150
a, b, c (Å)	11.0395 (12), 6.4734 (7), 11.1397 (12)
β (°)	98.889 (1)
V (Å^3)	786.52 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.16
Crystal size (mm)	0.18 × 0.17 × 0.06
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.39, 0.73
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14675, 2117, 1578
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.090, 0.99
No. of reflections	2117
No. of parameters	135
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, −0.37

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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full crystallographic data

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Crystal data

$C_7H_6BrN_3$
M_r = 212.06
Monoclinic, $P2_1/m$
a = 11.0395 (12) Å
b = 6.4734 (7) Å
c = 11.1397 (12) Å
β = 98.889 (1)°
V = 786.52 (15) Å^3
Z = 4
$F(000)$ = 416
D_x = 1.791 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3918 reflections
θ = 2.8–26.6°
μ = 5.16 mm^{-1}
T = 150 K
Plate, colourless
0.18 × 0.17 × 0.06 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2016)
T_{min} = 0.39, T_{max} = 0.73
14675 measured reflections
2117 independent reflections
1578 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 28.3°, θ_{min} = 1.9°
h = −14→14
k = −8→8
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.090
S = 0.99
2117 reflections
135 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 25 sec/frame.

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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å) while those attached to nitrogen were placed in locations derived from a difference map and their coordinates adjusted to give N—H = 0.91 %A. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.64714 (4)	0.2500	0.95946 (3)	0.05475 (17)	
N1	0.8413 (2)	0.2500	0.6732 (2)	0.0256 (6)	
N2	0.5647 (2)	0.2500	0.4725 (2)	0.0244 (6)	
H2	0.4825	0.2500	0.4458	0.037*	
N3	0.7651 (2)	0.2500	0.4578 (2)	0.0258 (6)	
C1	0.6526 (3)	0.2500	0.3988 (3)	0.0250 (7)	
C2	0.6247 (3)	0.2500	0.5894 (3)	0.0236 (7)	
C3	0.5883 (3)	0.2500	0.7027 (3)	0.0273 (7)	
H3	0.5046	0.2500	0.7137	0.033*	
C4	0.6838 (3)	0.2500	0.7984 (3)	0.0301 (7)	
C5	0.8062 (3)	0.2500	0.7818 (3)	0.0309 (8)	
H5	0.8676	0.2500	0.8517	0.037*	
C6	0.7515 (3)	0.2500	0.5782 (3)	0.0223 (6)	
C7	0.6185 (3)	0.2500	0.2642 (3)	0.0316 (8)	
H7A	0.6869	0.3042	0.2271	0.047*	0.5
H7B	0.5461	0.3372	0.2411	0.047*	0.5
H7C	0.6001	0.1085	0.2358	0.047*	0.5
Br2	0.02840 (4)	0.2500	0.11797 (3)	0.04217 (15)	
N4	0.3046 (2)	0.2500	0.4123 (2)	0.0254 (6)	
N5	0.2886 (2)	0.2500	0.6267 (2)	0.0263 (6)	
N6	0.0824 (2)	0.2500	0.6055 (2)	0.0270 (6)	
H6	0.0062	0.2500	0.6272	0.040*	
C8	0.1909 (3)	0.2500	0.6830 (3)	0.0281 (7)	
C9	0.1110 (3)	0.2500	0.4897 (3)	0.0240 (7)	
C10	0.0408 (3)	0.2500	0.3754 (3)	0.0268 (7)	
H10	−0.0463	0.2500	0.3627	0.032*	
C11	0.1099 (3)	0.2500	0.2813 (3)	0.0271 (7)	
C12	0.2380 (3)	0.2500	0.3016 (3)	0.0253 (7)	
H12	0.2798	0.2500	0.2332	0.030*	
C13	0.2401 (3)	0.2500	0.5052 (3)	0.0239 (7)	
C14	0.1952 (3)	0.2500	0.8164 (3)	0.0385 (9)	
H14A	0.1729	0.3872	0.8430	0.058*	0.5
H14B	0.2783	0.2155	0.8559	0.058*	0.5
H14C	0.1374	0.1473	0.8387	0.058*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0464 (3)	0.0974 (4)	0.0221 (2)	0.000	0.01081 (17)	0.000
N1	0.0195 (13)	0.0290 (15)	0.0279 (14)	0.000	0.0027 (11)	0.000
N2	0.0184 (13)	0.0324 (15)	0.0224 (13)	0.000	0.0034 (10)	0.000
N3	0.0242 (14)	0.0291 (15)	0.0257 (13)	0.000	0.0088 (11)	0.000
C1	0.0231 (16)	0.0255 (17)	0.0279 (17)	0.000	0.0091 (13)	0.000
C2	0.0205 (16)	0.0252 (17)	0.0249 (16)	0.000	0.0031 (13)	0.000
C3	0.0225 (16)	0.0320 (19)	0.0280 (17)	0.000	0.0053 (13)	0.000
C4	0.0294 (18)	0.039 (2)	0.0229 (16)	0.000	0.0077 (14)	0.000
C5	0.0282 (18)	0.034 (2)	0.0300 (17)	0.000	0.0025 (14)	0.000
C6	0.0217 (15)	0.0204 (16)	0.0260 (15)	0.000	0.0072 (12)	0.000
C7	0.0313 (18)	0.042 (2)	0.0211 (16)	0.000	0.0040 (13)	0.000
Br2	0.0371 (2)	0.0574 (3)	0.0297 (2)	0.000	−0.00230 (15)	0.000
N4	0.0199 (13)	0.0258 (14)	0.0317 (15)	0.000	0.0077 (11)	0.000
N5	0.0211 (14)	0.0285 (15)	0.0298 (14)	0.000	0.0054 (11)	0.000
N6	0.0201 (14)	0.0311 (16)	0.0306 (15)	0.000	0.0069 (11)	0.000
C8	0.0241 (17)	0.0274 (18)	0.0334 (18)	0.000	0.0058 (14)	0.000
C9	0.0193 (15)	0.0234 (17)	0.0308 (16)	0.000	0.0080 (13)	0.000
C10	0.0200 (15)	0.0236 (17)	0.0364 (19)	0.000	0.0028 (14)	0.000
C11	0.0252 (16)	0.0258 (18)	0.0294 (17)	0.000	0.0014 (13)	0.000
C12	0.0249 (16)	0.0243 (17)	0.0277 (16)	0.000	0.0070 (13)	0.000
C13	0.0212 (15)	0.0230 (17)	0.0274 (16)	0.000	0.0033 (13)	0.000
C14	0.039 (2)	0.047 (2)	0.0298 (18)	0.000	0.0057 (16)	0.000

Geometric parameters (Å, º)

Br1—C4	1.899 (3)	Br2—C11	1.901 (3)
N1—C5	1.326 (4)	N4—C12	1.335 (4)
N1—C6	1.333 (4)	N4—C13	1.344 (4)
N2—C1	1.365 (4)	N5—C8	1.329 (4)
N2—C2	1.367 (4)	N5—C13	1.376 (4)
N2—H2	0.9100	N6—C8	1.363 (4)
N3—C1	1.313 (4)	N6—C9	1.375 (4)
N3—C6	1.372 (4)	N6—H6	0.9100
C1—C7	1.488 (4)	C8—C14	1.480 (5)
C2—C3	1.383 (4)	C9—C10	1.384 (4)
C2—C6	1.425 (4)	C9—C13	1.409 (4)
C3—C4	1.378 (5)	C10—C11	1.389 (4)
C3—H3	0.9500	C10—H10	0.9500
C4—C5	1.392 (4)	C11—C12	1.397 (4)
C5—H5	0.9500	C12—H12	0.9500
C7—H7A	0.9800	C14—H14A	0.9800
C7—H7B	0.9800	C14—H14B	0.9800
C7—H7C	0.9800	C14—H14C	0.9800
C5—N1—C6	116.0 (3)	C12—N4—C13	115.4 (3)

C1—N2—C2	106.8 (3)	C8—N5—C13	104.1 (3)
C1—N2—H2	124.6	C8—N6—C9	106.7 (3)
C2—N2—H2	128.6	C8—N6—H6	126.1
C1—N3—C6	104.6 (2)	C9—N6—H6	127.2
N3—C1—N2	113.8 (3)	N5—C8—N6	113.5 (3)
N3—C1—C7	125.2 (3)	N5—C8—C14	124.8 (3)
N2—C1—C7	120.9 (3)	N6—C8—C14	121.6 (3)
N2—C2—C3	134.7 (3)	N6—C9—C10	133.3 (3)
N2—C2—C6	104.8 (3)	N6—C9—C13	105.0 (3)
C3—C2—C6	120.5 (3)	C10—C9—C13	121.7 (3)
C4—C3—C2	114.2 (3)	C9—C10—C11	113.6 (3)
C4—C3—H3	122.9	C9—C10—H10	123.2
C2—C3—H3	122.9	C11—C10—H10	123.2
C3—C4—C5	122.7 (3)	C10—C11—C12	122.5 (3)
C3—C4—Br1	118.8 (2)	C10—C11—Br2	119.3 (2)
C5—C4—Br1	118.6 (2)	C12—C11—Br2	118.2 (2)
N1—C5—C4	123.2 (3)	N4—C12—C11	123.3 (3)
N1—C5—H5	118.4	N4—C12—H12	118.3
C4—C5—H5	118.4	C11—C12—H12	118.3
N1—C6—N3	126.6 (3)	N4—C13—N5	125.8 (3)
N1—C6—C2	123.4 (3)	N4—C13—C9	123.5 (3)
N3—C6—C2	110.0 (3)	N5—C13—C9	110.7 (3)
C1—C7—H7A	109.5	C8—C14—H14A	109.5
C1—C7—H7B	109.5	C8—C14—H14B	109.5
H7A—C7—H7B	109.5	H14A—C14—H14B	109.5
C1—C7—H7C	109.5	C8—C14—H14C	109.5
H7A—C7—H7C	109.5	H14A—C14—H14C	109.5
H7B—C7—H7C	109.5	H14B—C14—H14C	109.5

C6—N3—C1—N2	0.000 (1)	C13—N5—C8—N6	0.000 (1)
C6—N3—C1—C7	180.000 (1)	C13—N5—C8—C14	180.000 (1)
C2—N2—C1—N3	0.000 (1)	C9—N6—C8—N5	0.000 (1)
C2—N2—C1—C7	180.000 (1)	C9—N6—C8—C14	180.000 (1)
C1—N2—C2—C3	180.000 (1)	C8—N6—C9—C10	180.000 (1)
C1—N2—C2—C6	0.000 (1)	C8—N6—C9—C13	0.000 (1)
N2—C2—C3—C4	180.000 (1)	N6—C9—C10—C11	180.000 (1)
C6—C2—C3—C4	0.000 (1)	C13—C9—C10—C11	0.000 (1)
C2—C3—C4—C5	0.000 (1)	C9—C10—C11—C12	0.000 (1)
C2—C3—C4—Br1	180.000 (1)	C9—C10—C11—Br2	180.000 (1)
C6—N1—C5—C4	0.000 (1)	C13—N4—C12—C11	0.000 (1)
C3—C4—C5—N1	0.000 (1)	C10—C11—C12—N4	0.000 (1)
Br1—C4—C5—N1	180.000 (1)	Br2—C11—C12—N4	180.000 (1)
C5—N1—C6—N3	180.000 (1)	C12—N4—C13—N5	180.000 (1)
C5—N1—C6—C2	0.000 (1)	C12—N4—C13—C9	0.000 (1)
C1—N3—C6—N1	180.000 (1)	C8—N5—C13—N4	180.000 (1)
C1—N3—C6—C2	0.000 (1)	C8—N5—C13—C9	0.000 (1)
N2—C2—C6—N1	180.000 (1)	N6—C9—C13—N4	180.000 (1)
C3—C2—C6—N1	0.000 (1)	C10—C9—C13—N4	0.000 (1)

N2—C2—C6—N3	0.000 (1)	N6—C9—C13—N5	0.000 (1)
C3—C2—C6—N3	180.000 (1)	C10—C9—C13—N5	180.000 (1)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N4	0.91	1.94	2.845 (4)	172
C3—H3···N5	0.95	2.43	3.286 (4)	150
N6—H6···N1^{i}	0.91	1.97	2.876 (4)	180
C10—H10···N3^{i}	0.95	2.48	3.312 (4)	146

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