# 6-Bromo-2-(4-chlorophenyl)-3-methyl-3*H*-imidazo[4,5-*b*]pyridine

Selma Bourichi,[a] Youssef Kandri Rodi,[a]* Younes Ouzidan,[a] Joel T. Mague,[b] El Mokhtar Essassi[c] and Hafid Zouihri[d]

[a]Laboratoire de Chimie Organique Appliquée, Université Sidi Mohamed Ben Abdallah, Faculté des Sciences et Techniques, Route d'Iimmouzzer, BP 2202, Fez, Morocco, [b]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA, [c]Laboratoire de Chimie Organique Hétérocyclique, Pôle de Compétences Pharmacochimie, Mohammed V University in Rabat, BP 1014, Avenue Ibn Batouta, Rabat, Morocco, and [d]Laboratoire d'Ingénierie des Matériaux et d'Environnement: Modélisation et Application (LIMEMA), Ibn Tofail University, Kénitra, Morocco. *Correspondence e-mail: youssef_kandri_rodi@yahoo.fr

In the title compound, $C_{13}H_9BrClN_3$, the imidazopyridine fused-ring system is almost planar, with r.m.s. deviation of 0.006 (19) Å, and makes a dihedral angle of 29.32 (8)° with the mean plane of the 4-chlorophenyl group. In the crystal, C—H⋯N hydrogen bonds link the molecules into chains propagating in the [100] direction. Weak intermolecular π–π interactions between the five- and six-membered rings of the 3*H*-imidazo[4,5-*b*]pyridine moieties of neighbouring molecules [centroid–centroid distance = 3.8648 (12) Å] further consolidate the packing into layers parallel to the *ab* plane.

3D view
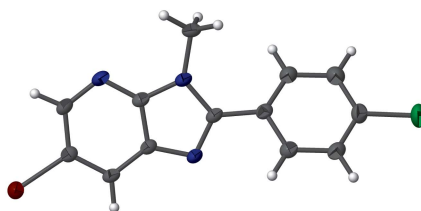
Chemical scheme
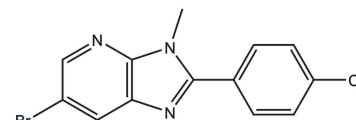
Structure description

Imidazopyridine derivatives are a very important class of nitrogen-containing fused heterocyclic compounds. Many imidazopyridines have a significant inhibitory effect on many target enzymes (Palmer *et al.* 2007; Katritzky *et al.* 2003), as well as anti-viral, anti-bacterial, anti-microbial and anti-cytokinin activity. Some of them can be used to treat peptic ulcers, diabetes and mental illness (Scribner *et al.* 2007, Liang *et al.* 2007). Hence, the synthesis of imidazo[4,5-*b*]pyridine derivatives is currently of great interest. Many synthetic strategies have been developed to obtain a variety of substituted structures of this class. The most popular synthetic approach generally involves the cyclocondensation of 2,3-pyridinediamine with carboxylic acid derivatives or with aldehydes (Dubey *et al.* 2004). In this work we report the synthesis of 6-bromo-2-(4-chlorophenyl)-3-methyl-3*H*-
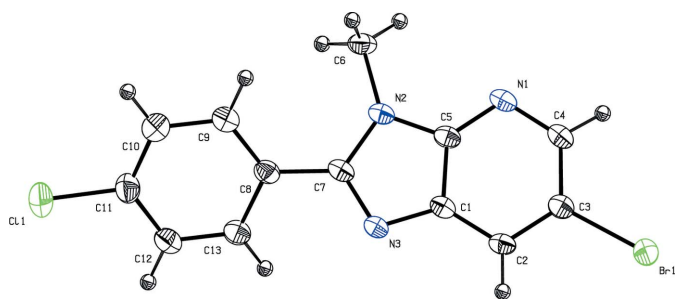
Figure 1
The molecular structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.
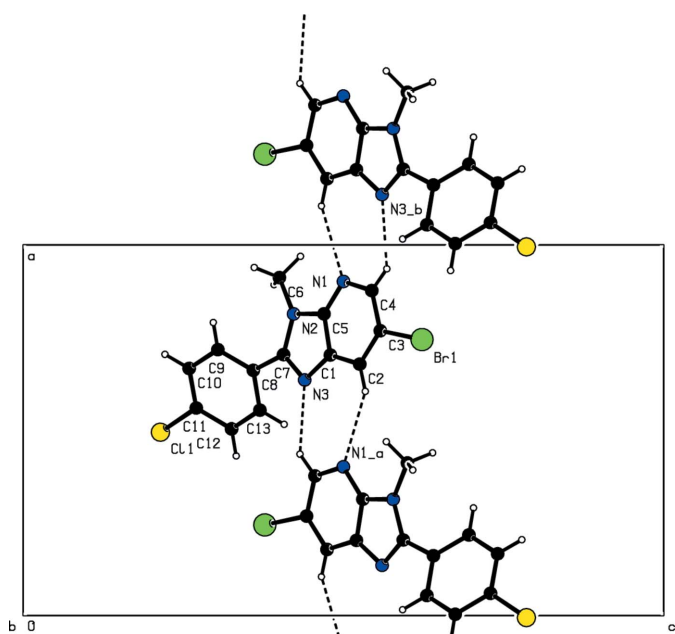
Figure 2
The packing viewed down the *b* axis. C—H···N interactions are shown as dotted lines.
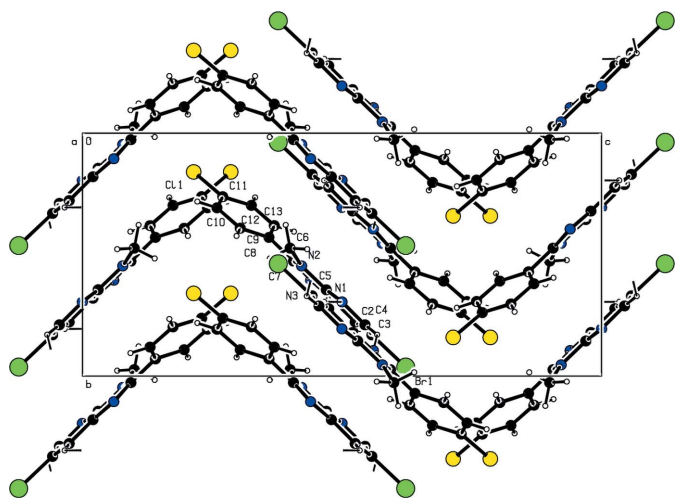
Figure 3
The packing viewed down the *a* axis. C—H···N interactions are shown as dotted lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N3^i	0.95	2.51	3.321 (3)	143
C2—H2···N1^{ii}	0.95	2.57	3.411 (3)	148

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_9BrClN_3$
M_r	322.59
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	150
a, b, c (Å)	12.1163 (2), 9.7911 (2), 20.9428 (4)
V (Å^3)	2484.48 (8)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.35
Crystal size (mm)	$0.28 \times 0.18 \times 0.12$
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Numerical (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.37, 0.52
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17929, 2433, 2111
R_{int}	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.619
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.069, 1.03
No. of reflections	2433
No. of parameters	165
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.38, −0.44

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

imidazo[4,5-*b*]pyridine according to the method employed for 4-benzyl-6-bromo-2-phenyl-4*H*-imidazo[4,5-*b*]pyridine (Ouzidan *et al.* 2010).

In the title compound (Fig. 1), the imidazopyridine fused ring system is quasiplanar, with a maximum deviation of 0.006 (19) Å, and forms a dihedral angle of 29.32 (8)° with the mean plane of the 4-chlorophenyl group. In the crystal, C—H···N hydrogen bonds (Table 1) link the molecules into chains propagating in [100]. The chains are further linked by π–π interactions between the five- and six-membered rings of the 3*H*-imidazo[4,5-*b*]pyridine moieties of neighbouring molecules [centroid–centroid distance = 3.8648 (12) Å], forming layers parallel to the *ab* plane (Figs. 2 and 3).

Synthesis and crystallization

The a solution of 0.2 g (0.64 mmol) of 6-bromo-2-(4-chlorophenyl)-3*H*-imidazo[4,5-*b*]pyridine dissolved in 25 ml of DMF, was added potassium carbonate (K_2CO_3; 0.11 g, 0.84 mmol). The mixture was stirred magnetically for 5 minutes and then 0.02 g (0.07 mmol) of tetra-*n*-butylammonium bromide

(TBAB) and 0.05 ml (0.77 mmol) of methyl iodide was added. Stirring was continued at room temperature for 6 h. After removing salts by filtration, the DMF was evaporated under reduced pressure and the residue obtained was dissolved in dichloromethane. The remaining salts were extracted with distilled water and the resulting mixture is chromatographed on silica gel column (eluent: ethyl acetate/hexane,1:3). Yellow crystals were isolated when the solvent was allowed to evaporate, yield = 72%

Refinement

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

Acknowledgements

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full crystallographic data

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Crystal data

$C_{13}H_9BrClN_3$	$D_x = 1.725$ Mg m^{-3}
$M_r = 322.59$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Orthorhombic, *Pbca*	Cell parameters from 9992 reflections
$a = 12.1163$ (2) Å	$\theta = 4.2–72.4°$
$b = 9.7911$ (2) Å	$\mu = 6.35$ mm^{-1}
$c = 20.9428$ (4) Å	$T = 150$ K
$V = 2484.48$ (8) Å^3	Thick plate, light yellow
$Z = 8$	$0.28 \times 0.18 \times 0.12$ mm
$F(000) = 1280$	

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer	$T_{min} = 0.37$, $T_{max} = 0.52$
Radiation source: INCOATEC IμS micro–focus source	17929 measured reflections
Mirror monochromator	2433 independent reflections
Detector resolution: 10.4167 pixels mm^{-1}	2111 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.042$
Absorption correction: numerical (*SADABS*; Bruker, 2015)	$\theta_{max} = 72.5°$, $\theta_{min} = 4.2°$
	$h = -14\rightarrow12$
	$k = -12\rightarrow10$
	$l = -24\rightarrow25$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 1.6642P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.002$
2433 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
165 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL2014* (Sheldrick, 2015b), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00050 (5)
Secondary atom site location: difference Fourier map	

Special details

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. H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached carbon atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Br1	0.74454 (2)	0.96264 (2)	0.62272 (2)	0.02958 (10)
Cl1	0.49454 (6)	0.15942 (7)	0.21428 (3)	0.05102 (19)
N1	0.90119 (14)	0.69452 (18)	0.50012 (8)	0.0259 (4)
N2	0.81367 (14)	0.54647 (17)	0.42228 (8)	0.0233 (4)
N3	0.63564 (13)	0.60528 (18)	0.43957 (8)	0.0255 (4)
C1	0.70284 (17)	0.6795 (2)	0.47964 (10)	0.0235 (4)
C2	0.67830 (17)	0.7774 (2)	0.52549 (10)	0.0244 (4)
H2	0.6049	0.8058	0.5342	0.029*
C3	0.76839 (16)	0.8304 (2)	0.55755 (10)	0.0246 (4)
C4	0.87671 (17)	0.7888 (2)	0.54435 (10)	0.0265 (4)
H4	0.9354	0.8293	0.5678	0.032*
C5	0.81385 (16)	0.6445 (2)	0.46971 (9)	0.0232 (4)
C6	0.91170 (17)	0.4733 (2)	0.40010 (11)	0.0283 (4)
H6A	0.9390	0.5157	0.3608	0.042*
H6B	0.8926	0.3777	0.3917	0.042*
H6C	0.9691	0.4774	0.4330	0.042*
C7	0.70395 (17)	0.5267 (2)	0.40658 (10)	0.0244 (4)
C8	0.66153 (17)	0.4291 (2)	0.35938 (10)	0.0248 (4)
C9	0.71738 (19)	0.3912 (2)	0.30403 (11)	0.0321 (5)
H9	0.7905	0.4228	0.2969	0.039*
C10	0.6667 (2)	0.3072 (2)	0.25921 (12)	0.0376 (5)
H10	0.7047	0.2815	0.2214	0.045*
C11	0.55998 (19)	0.2614 (2)	0.27032 (11)	0.0335 (5)
C12	0.50354 (18)	0.2972 (2)	0.32544 (11)	0.0293 (5)
H12	0.4307	0.2647	0.3326	0.035*
C13	0.55415 (17)	0.3804 (2)	0.36966 (10)	0.0264 (4)
H13	0.5159	0.4051	0.4075	0.032*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02748 (16)	0.02992 (15)	0.03136 (15)	−0.00062 (8)	−0.00260 (8)	−0.00404 (9)
Cl1	0.0467 (4)	0.0564 (4)	0.0499 (4)	−0.0141 (3)	−0.0010 (3)	−0.0251 (3)
N1	0.0163 (8)	0.0318 (9)	0.0297 (9)	−0.0019 (6)	−0.0011 (7)	0.0026 (7)

N2	0.0162 (8)	0.0270 (9)	0.0268 (8)	0.0017 (6)	−0.0011 (6)	0.0019 (7)
N3	0.0166 (8)	0.0309 (9)	0.0291 (9)	0.0009 (7)	−0.0031 (7)	−0.0038 (7)
C1	0.0176 (10)	0.0262 (10)	0.0268 (10)	−0.0005 (8)	−0.0020 (8)	0.0022 (8)
C2	0.0167 (10)	0.0295 (11)	0.0271 (10)	0.0023 (8)	−0.0005 (8)	0.0025 (8)
C3	0.0218 (10)	0.0257 (10)	0.0262 (10)	−0.0002 (8)	−0.0013 (8)	0.0028 (8)
C4	0.0189 (10)	0.0310 (11)	0.0295 (10)	−0.0033 (8)	−0.0037 (8)	0.0014 (8)
C5	0.0183 (10)	0.0254 (10)	0.0260 (9)	0.0015 (8)	−0.0013 (7)	0.0048 (8)
C6	0.0189 (10)	0.0306 (11)	0.0354 (11)	0.0034 (8)	0.0028 (8)	0.0002 (9)
C7	0.0168 (10)	0.0283 (10)	0.0280 (10)	−0.0009 (8)	−0.0022 (8)	0.0027 (8)
C8	0.0202 (10)	0.0259 (10)	0.0281 (10)	0.0024 (8)	−0.0037 (8)	0.0019 (8)
C9	0.0248 (11)	0.0366 (12)	0.0350 (12)	−0.0018 (9)	0.0006 (9)	−0.0042 (10)
C10	0.0339 (13)	0.0427 (13)	0.0362 (12)	−0.0008 (10)	0.0026 (10)	−0.0083 (10)
C11	0.0338 (13)	0.0290 (11)	0.0376 (12)	−0.0023 (9)	−0.0040 (10)	−0.0074 (9)
C12	0.0231 (11)	0.0299 (11)	0.0348 (11)	−0.0032 (8)	−0.0014 (9)	0.0014 (9)
C13	0.0237 (11)	0.0275 (10)	0.0281 (10)	0.0004 (8)	−0.0009 (8)	0.0031 (8)

Geometric parameters (Å, °)

Br1—C3	1.903 (2)	C6—H6A	0.9800
Cl1—C11	1.733 (2)	C6—H6B	0.9800
N1—C5	1.329 (3)	C6—H6C	0.9800
N1—C4	1.341 (3)	C7—C8	1.468 (3)
N2—C5	1.381 (3)	C8—C9	1.393 (3)
N2—C7	1.383 (3)	C8—C13	1.402 (3)
N2—C6	1.463 (3)	C9—C10	1.391 (3)
N3—C7	1.325 (3)	C9—H9	0.9500
N3—C1	1.377 (3)	C10—C11	1.388 (3)
C1—C2	1.389 (3)	C10—H10	0.9500
C1—C5	1.404 (3)	C11—C12	1.387 (3)
C2—C3	1.383 (3)	C12—C13	1.378 (3)
C2—H2	0.9500	C12—H12	0.9500
C3—C4	1.402 (3)	C13—H13	0.9500
C4—H4	0.9500		
C5—N1—C4	114.13 (18)	H6A—C6—H6C	109.5
C5—N2—C7	105.66 (16)	H6B—C6—H6C	109.5
C5—N2—C6	124.56 (17)	N3—C7—N2	113.28 (18)
C7—N2—C6	129.52 (18)	N3—C7—C8	120.71 (18)
C7—N3—C1	104.77 (16)	N2—C7—C8	126.01 (19)
N3—C1—C2	131.22 (19)	C9—C8—C13	119.2 (2)
N3—C1—C5	110.34 (18)	C9—C8—C7	124.34 (19)
C2—C1—C5	118.44 (19)	C13—C8—C7	116.28 (19)
C3—C2—C1	115.20 (19)	C10—C9—C8	120.3 (2)
C3—C2—H2	122.4	C10—C9—H9	119.8
C1—C2—H2	122.4	C8—C9—H9	119.8
C2—C3—C4	122.31 (19)	C11—C10—C9	119.3 (2)
C2—C3—Br1	118.93 (15)	C11—C10—H10	120.4
C4—C3—Br1	118.75 (15)	C9—C10—H10	120.4

N1—C4—C3	122.90 (19)	C12—C11—C10	121.1 (2)
N1—C4—H4	118.6	C12—C11—Cl1	118.94 (17)
C3—C4—H4	118.6	C10—C11—Cl1	119.92 (19)
N1—C5—N2	127.03 (18)	C13—C12—C11	119.3 (2)
N1—C5—C1	127.02 (19)	C13—C12—H12	120.3
N2—C5—C1	105.94 (17)	C11—C12—H12	120.3
N2—C6—H6A	109.5	C12—C13—C8	120.7 (2)
N2—C6—H6B	109.5	C12—C13—H13	119.6
H6A—C6—H6B	109.5	C8—C13—H13	119.6
N2—C6—H6C	109.5		
C7—N3—C1—C2	−179.5 (2)	C1—N3—C7—C8	178.44 (19)
C7—N3—C1—C5	0.4 (2)	C5—N2—C7—N3	0.8 (2)
N3—C1—C2—C3	179.4 (2)	C6—N2—C7—N3	175.10 (19)
C5—C1—C2—C3	−0.5 (3)	C5—N2—C7—C8	−178.35 (19)
C1—C2—C3—C4	0.4 (3)	C6—N2—C7—C8	−4.1 (3)
C1—C2—C3—Br1	−178.73 (15)	N3—C7—C8—C9	148.4 (2)
C5—N1—C4—C3	0.3 (3)	N2—C7—C8—C9	−32.5 (3)
C2—C3—C4—N1	−0.4 (3)	N3—C7—C8—C13	−26.8 (3)
Br1—C3—C4—N1	178.78 (16)	N2—C7—C8—C13	152.37 (19)
C4—N1—C5—N2	−179.77 (19)	C13—C8—C9—C10	0.7 (3)
C4—N1—C5—C1	−0.4 (3)	C7—C8—C9—C10	−174.3 (2)
C7—N2—C5—N1	178.96 (19)	C8—C9—C10—C11	−0.2 (4)
C6—N2—C5—N1	4.3 (3)	C9—C10—C11—C12	−0.4 (4)
C7—N2—C5—C1	−0.5 (2)	C9—C10—C11—Cl1	178.75 (19)
C6—N2—C5—C1	−175.13 (18)	C10—C11—C12—C13	0.4 (4)
N3—C1—C5—N1	−179.42 (19)	Cl1—C11—C12—C13	−178.75 (17)
C2—C1—C5—N1	0.5 (3)	C11—C12—C13—C8	0.1 (3)
N3—C1—C5—N2	0.1 (2)	C9—C8—C13—C12	−0.7 (3)
C2—C1—C5—N2	179.97 (18)	C7—C8—C13—C12	174.72 (19)
C1—N3—C7—N2	−0.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N3[i]	0.95	2.51	3.321 (3)	143
C2—H2···N1[ii]	0.95	2.57	3.411 (3)	148

Symmetry codes: (i) $x+1/2, -y+3/2, -z+1$; (ii) $x-1/2, -y+3/2, -z+1$.