4-Benzyl-6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine

Selma Bourichi,[a]* Youssef Kandri Rodi,[a] Jerry P. Jasinski,[b] Manpreet Kaur,[b] Younes Ouzidan[a] and El Mokhtar Essassi[c]

[a]Laboratoire de Chimie Organique Appliquée, Faculté des Sciences et Techniques, Université Sidi Mohammed Ben Abdellah, Fès, Morocco, [b]Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA, and [c]Laboratoire de Chimie Organique Hétérocyclique URAC 21, Pôle de Compétence Pharmacochimie, Av. Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco. *Correspondence e-mail: bourichiselma@hotmail.com

In the title compound, $C_{19}H_{13}BrClN_3$, the chlorophenyl ring occupies an equatorial position with respect to the mean plane of the imidazopyridine unit, while the other phenyl ring is twisted by 4.1 (2)° with respect to the mean plane of the imidazopyridine unit. In the crystal, pairwise C—H···Br interactions link the molecules into dimers, forming an $R_2^2(16)$ ring motif. In addition, weak π–π stacking interactions stabilize the crystal packing.

3D view
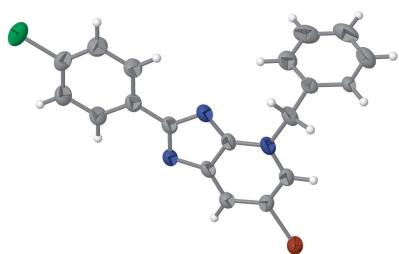
Chemical scheme
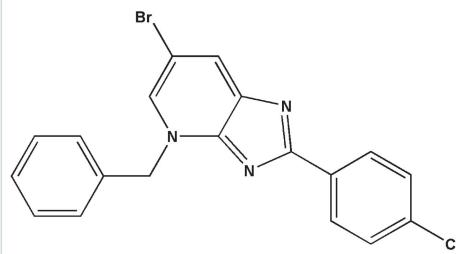
Structure description

Imidazopyridine derivatives display anticancer (Lukasik *et al.*, 2012), tuberculostatic (Bukowski & Janowiec, 1989) and antimitotic activities (Aridoss *et al.*, 2006). This study is a continuation of our work (Bourichi *et al.*, 2016; Ouzidan *et al.*, 2010) on the syntheses and structures of new imidazopyridine derivatives.

The title compound, $C_{19}H_{13}BrClN_3$, crystallizes with one molecule in the asymmetric unit (Fig. 1). The imidazo[4,5-*b*]pyridine unit is essentially planar (r.m.s. deviation = 0.010 Å). The chlorophenyl ring occupies an equatorial position with respect to the mean plane of the imidazopyridine unit, with a dihedral angle of 4.1 (2)°. The other phenyl ring is twisted with respect to the mean plane of the imidazopyridine unit by 72.2 (3)°.

In the crystal, pairwise C19—H19···Br1 interactions link the molecules into inversion dimers, forming an $R_2^2(16)$ ring motif (Table 1 and Fig. 2). In addition, weak π–π stacking interactions stabilize the crystal packing [$Cg1···Cg2^i$ = 3.858 (2) Å; symmetry code: (i) $-x + 1, -y + 1, -z + 1$; $Cg1$ is the centroid of ring N2/C4/C6/N3/C5 and $Cg2$ of ring N1/C1/C2/C3/C4/C6].
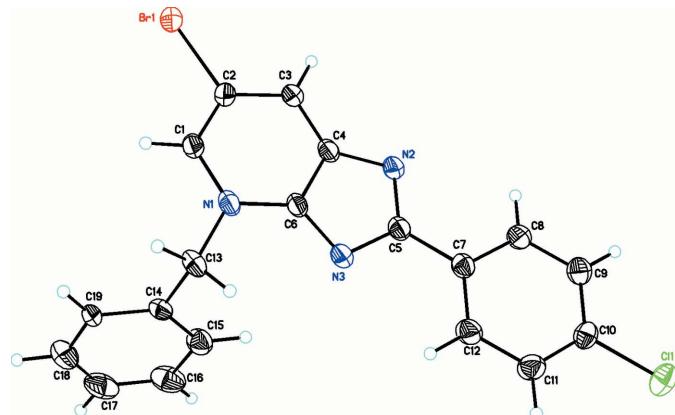
Figure 1
The structure of the title compound, showing the atom-numbering scheme and 30% probability displacement ellipsoids for the non-H atoms.

Synthesis and crystallization

A mixture of 0.2 g (0.65 mmol) of 6-bromo-2-(4-chlorophenyl)-3*H*-imidazo[4,5-*b*]pyridine, dissolved in 25 ml of DMF, and 0.13 g (0.92 mmol) of potassium carbonate was stirred magnetically for 5 min and then 0.032 g (0.1 mmol) of tetra-*n*-butylammonium bromide (TBAB) and 0.094 g (0.78 mmol) of benzyl bromide were added. Stirring was continued at room temperature for 24 h. After removing the salts by filtration,
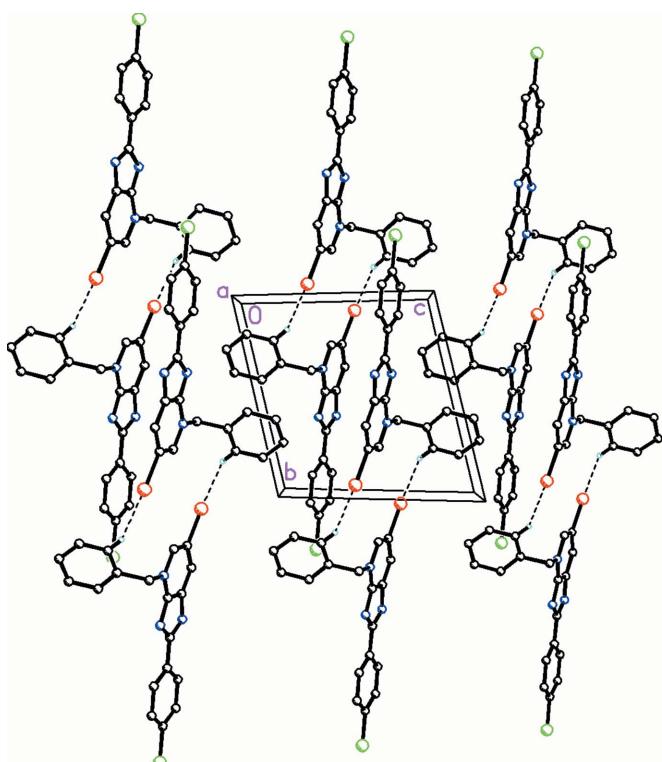

Figure 2
The molecular packing of the title compound, viewed along the *a* axis. Dashed lines indicate weak C—H···Br intermolecular interactions linking the molecules into dimers. H atoms not involved in the packing have been omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19···Br1[i]	0.93	2.54	3.202 (3)	128

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{13}BrClN_3$
M_r	398.68
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	8.7749 (7), 9.9403 (7), 10.4475 (8)
α, β, γ (°)	76.030 (6), 66.511 (7), 85.843 (6)
V (Å^3)	810.76 (12)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	5.00
Crystal size (mm)	$0.14 \times 0.12 \times 0.06$
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
T_{min}, T_{max}	0.393, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5047, 3076, 2637
R_{int}	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.614
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.124, 1.04
No. of reflections	3076
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.64, −0.60

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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 was chromatographed on a silica-gel column (eluent: ethyl acetate–hexane, 1:3 *v*/*v*). Yellow crystals were isolated when the solvent was allowed to evaporate (yield 65%; m.p. 464–465 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in calculated positions and refined using the riding model, with C—H bond lengths of 0.93 (CH) or 0.97 Å (CH$_2$). Isotropic displacement parameters for these atoms were set at 1.2 times U_{eq} of the parent atom.

Acknowledgements

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full crystallographic data

4-Benzyl-6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine

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Crystal data

$C_{19}H_{13}BrClN_3$	$Z = 2$
$M_r = 398.68$	$F(000) = 400$
Triclinic, $P\bar{1}$	$D_x = 1.633$ Mg m^{-3}
$a = 8.7749$ (7) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 9.9403$ (7) Å	Cell parameters from 2096 reflections
$c = 10.4475$ (8) Å	$\theta = 4.6$–71.2°
$\alpha = 76.030$ (6)°	$\mu = 5.00$ mm^{-1}
$\beta = 66.511$ (7)°	$T = 293$ K
$\gamma = 85.843$ (6)°	Irregular, yellow
$V = 810.76$ (12) Å^3	$0.14 \times 0.12 \times 0.06$ mm

Data collection

Rigaku Oxford Diffraction diffractometer	$T_{min} = 0.393$, $T_{max} = 1.000$
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source	5047 measured reflections
	3076 independent reflections
Graphite monochromator	2637 reflections with $I > 2\sigma(I)$
Detector resolution: 16.0416 pixels mm^{-1}	$R_{int} = 0.037$
ω scans	$\theta_{max} = 71.3°$, $\theta_{min} = 4.6°$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku Oxford Diffraction, 2015)	$h = -6 \rightarrow 10$
	$k = -11 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.2037P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
3076 reflections	$\Delta\rho_{min} = -0.60$ e Å^{-3}
218 parameters	Extinction correction: SHELXT2014 (Sheldrick, 2015a), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	
Primary atom site location: dual	Extinction coefficient: 0.0012 (4)
Hydrogen site location: inferred from neighbouring sites	

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.20904 (4)	0.05758 (4)	0.60405 (4)	0.04964 (18)
Cl1	0.40328 (14)	1.29736 (10)	0.10620 (12)	0.0608 (3)
N1	0.5634 (3)	0.3647 (3)	0.3684 (3)	0.0384 (6)
N2	0.2447 (3)	0.6063 (3)	0.3757 (3)	0.0384 (6)
N3	0.5333 (3)	0.6100 (3)	0.2869 (3)	0.0391 (6)
C1	0.4801 (4)	0.2417 (3)	0.4415 (3)	0.0393 (7)
H1	0.5392	0.1616	0.4542	0.047*
C2	0.3102 (4)	0.2344 (3)	0.4964 (4)	0.0401 (7)
C3	0.2119 (4)	0.3497 (3)	0.4823 (4)	0.0393 (7)
H3	0.0964	0.3427	0.5206	0.047*
C4	0.2966 (4)	0.4739 (4)	0.4081 (3)	0.0373 (7)
C5	0.3881 (4)	0.6806 (3)	0.3058 (3)	0.0373 (7)
C6	0.4742 (4)	0.4804 (3)	0.3519 (3)	0.0357 (6)
C7	0.3929 (4)	0.8314 (4)	0.2557 (4)	0.0385 (7)
C8	0.2453 (4)	0.9043 (4)	0.2807 (4)	0.0486 (8)
H8	0.1438	0.8561	0.3283	0.058*
C9	0.2486 (5)	1.0471 (4)	0.2356 (4)	0.0511 (9)
H9	0.1500	1.0950	0.2533	0.061*
C10	0.3991 (5)	1.1173 (3)	0.1645 (4)	0.0425 (7)
C11	0.5467 (4)	1.0485 (4)	0.1389 (4)	0.0497 (9)
H11	0.6477	1.0977	0.0919	0.060*
C12	0.5431 (4)	0.9057 (4)	0.1838 (4)	0.0470 (8)
H12	0.6424	0.8588	0.1657	0.056*
C13	0.7474 (4)	0.3741 (4)	0.3102 (4)	0.0416 (7)
H13A	0.7865	0.3112	0.3768	0.050*
H13B	0.7822	0.4675	0.3013	0.050*
C14	0.8254 (3)	0.3382 (3)	0.1653 (4)	0.0362 (7)
C15	0.8029 (4)	0.4197 (4)	0.0478 (4)	0.0500 (8)
H15	0.7384	0.4981	0.0560	0.060*
C16	0.8781 (5)	0.3832 (6)	−0.0831 (4)	0.0649 (12)
H16	0.8628	0.4348	−0.1639	0.078*
C17	0.9753 (6)	0.2690 (6)	−0.0899 (5)	0.0676 (12)
H17	1.0290	0.2421	−0.1762	0.081*
C18	0.9923 (5)	0.1951 (5)	0.0320 (5)	0.0649 (12)
H18	1.0594	0.1181	0.0258	0.078*
C19	0.9186 (4)	0.2268 (3)	0.1588 (3)	0.0369 (7)
H19	0.9319	0.1732	0.2398	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0423 (2)	0.0371 (2)	0.0573 (3)	0.00609 (15)	−0.01030 (17)	−0.00689 (16)
Cl1	0.0740 (6)	0.0384 (5)	0.0712 (7)	0.0027 (4)	−0.0354 (5)	−0.0031 (4)
N1	0.0338 (13)	0.0426 (15)	0.0375 (14)	0.0121 (11)	−0.0121 (11)	−0.0132 (12)
N2	0.0331 (12)	0.0376 (14)	0.0392 (14)	0.0080 (11)	−0.0108 (11)	−0.0075 (11)
N3	0.0323 (13)	0.0410 (15)	0.0403 (15)	0.0071 (11)	−0.0104 (11)	−0.0111 (12)
C1	0.0416 (16)	0.0368 (16)	0.0355 (16)	0.0104 (13)	−0.0116 (14)	−0.0101 (13)
C2	0.0442 (17)	0.0325 (15)	0.0380 (17)	0.0062 (13)	−0.0114 (14)	−0.0078 (13)
C3	0.0321 (14)	0.0392 (17)	0.0393 (17)	0.0061 (12)	−0.0083 (13)	−0.0074 (13)
C4	0.0335 (15)	0.0411 (17)	0.0335 (16)	0.0107 (13)	−0.0097 (13)	−0.0109 (13)
C5	0.0354 (15)	0.0400 (17)	0.0349 (16)	0.0080 (13)	−0.0127 (13)	−0.0097 (13)
C6	0.0352 (15)	0.0372 (16)	0.0322 (15)	0.0109 (12)	−0.0107 (13)	−0.0113 (12)
C7	0.0367 (15)	0.0403 (17)	0.0389 (17)	0.0064 (13)	−0.0156 (13)	−0.0101 (13)
C8	0.0329 (15)	0.0441 (19)	0.059 (2)	0.0048 (14)	−0.0119 (15)	−0.0061 (16)
C9	0.0436 (18)	0.047 (2)	0.058 (2)	0.0119 (15)	−0.0194 (17)	−0.0081 (17)
C10	0.0523 (19)	0.0358 (17)	0.0424 (18)	0.0033 (14)	−0.0244 (16)	−0.0051 (14)
C11	0.0402 (17)	0.047 (2)	0.057 (2)	−0.0028 (15)	−0.0185 (16)	−0.0052 (17)
C12	0.0346 (16)	0.050 (2)	0.051 (2)	0.0062 (14)	−0.0153 (15)	−0.0060 (16)
C13	0.0309 (15)	0.052 (2)	0.0420 (18)	0.0125 (14)	−0.0123 (14)	−0.0186 (15)
C14	0.0241 (12)	0.0405 (17)	0.0393 (17)	0.0001 (12)	−0.0074 (12)	−0.0094 (13)
C15	0.0413 (17)	0.058 (2)	0.048 (2)	0.0093 (16)	−0.0183 (16)	−0.0084 (17)
C16	0.052 (2)	0.098 (3)	0.039 (2)	−0.002 (2)	−0.0152 (17)	−0.009 (2)
C17	0.056 (2)	0.090 (3)	0.045 (2)	−0.005 (2)	0.0007 (19)	−0.029 (2)
C18	0.052 (2)	0.065 (3)	0.064 (3)	0.013 (2)	−0.004 (2)	−0.025 (2)
C19	0.0307 (13)	0.0339 (15)	0.0349 (16)	0.0091 (12)	−0.0038 (12)	−0.0061 (12)

Geometric parameters (Å, º)

Br1—C2	1.902 (3)	C9—H9	0.9300
Cl1—C10	1.744 (3)	C9—C10	1.373 (5)
N1—C1	1.359 (4)	C10—C11	1.379 (5)
N1—C6	1.359 (4)	C11—H11	0.9300
N1—C13	1.482 (4)	C11—C12	1.382 (5)
N2—C4	1.370 (4)	C12—H12	0.9300
N2—C5	1.343 (4)	C13—H13A	0.9700
N3—C5	1.376 (4)	C13—H13B	0.9700
N3—C6	1.336 (4)	C13—C14	1.512 (4)
C1—H1	0.9300	C14—C15	1.376 (5)
C1—C2	1.367 (5)	C14—C19	1.326 (4)
C2—C3	1.399 (4)	C15—H15	0.9300
C3—H3	0.9300	C15—C16	1.387 (6)
C3—C4	1.375 (5)	C16—H16	0.9300
C4—C6	1.429 (4)	C16—C17	1.367 (7)
C5—C7	1.461 (5)	C17—H17	0.9300
C7—C8	1.398 (4)	C17—C18	1.367 (7)
C7—C12	1.390 (5)	C18—H18	0.9300

C8—H8	0.9300	C18—C19	1.328 (5)
C8—C9	1.382 (5)	C19—H19	0.9300
C1—N1—C13	121.2 (3)	C9—C10—C11	121.4 (3)
C6—N1—C1	118.5 (3)	C11—C10—Cl1	119.4 (3)
C6—N1—C13	120.3 (3)	C10—C11—H11	120.4
C5—N2—C4	103.0 (3)	C10—C11—C12	119.3 (3)
C6—N3—C5	100.9 (3)	C12—C11—H11	120.4
N1—C1—H1	119.6	C7—C12—H12	119.6
N1—C1—C2	120.7 (3)	C11—C12—C7	120.8 (3)
C2—C1—H1	119.6	C11—C12—H12	119.6
C1—C2—Br1	116.4 (3)	N1—C13—H13A	109.3
C1—C2—C3	123.3 (3)	N1—C13—H13B	109.3
C3—C2—Br1	120.2 (3)	N1—C13—C14	111.8 (3)
C2—C3—H3	122.1	H13A—C13—H13B	107.9
C4—C3—C2	115.8 (3)	C14—C13—H13A	109.3
C4—C3—H3	122.1	C14—C13—H13B	109.3
N2—C4—C3	132.5 (3)	C15—C14—C13	121.1 (3)
N2—C4—C6	107.1 (3)	C19—C14—C13	116.0 (3)
C3—C4—C6	120.4 (3)	C19—C14—C15	122.9 (3)
N2—C5—N3	117.5 (3)	C14—C15—H15	120.5
N2—C5—C7	122.3 (3)	C14—C15—C16	118.9 (4)
N3—C5—C7	120.2 (3)	C16—C15—H15	120.5
N1—C6—C4	121.3 (3)	C15—C16—H16	121.0
N3—C6—N1	127.2 (3)	C17—C16—C15	118.1 (4)
N3—C6—C4	111.5 (3)	C17—C16—H16	121.0
C8—C7—C5	120.4 (3)	C16—C17—H17	120.5
C12—C7—C5	121.1 (3)	C18—C17—C16	119.0 (4)
C12—C7—C8	118.5 (3)	C18—C17—H17	120.5
C7—C8—H8	119.6	C17—C18—H18	118.1
C9—C8—C7	120.8 (3)	C19—C18—C17	123.8 (4)
C9—C8—H8	119.6	C19—C18—H18	118.1
C8—C9—H9	120.4	C14—C19—C18	117.3 (4)
C10—C9—C8	119.2 (3)	C14—C19—H19	121.4
C10—C9—H9	120.4	C18—C19—H19	121.4
C9—C10—Cl1	119.2 (3)		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C19—H19⋯Br1[i]	0.93	2.54	3.202 (3)	128

Symmetry code: (i) −x+1, −y, −z+1.