

6-Bromo-3-methyl-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine

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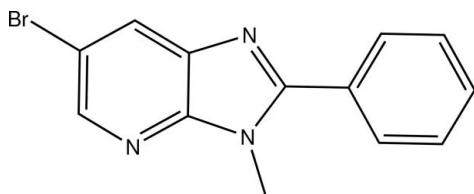
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.090; data-to-parameter ratio = 15.3.

The two fused five- and six-membered rings building the molecule of the title compound, $\text{C}_{13}\text{H}_{10}\text{BrN}_3$, are approximately planar, the largest deviation from the mean plane being 0.004 (2) Å. The dihedral angle between the imidazo[4,5-*b*]pyridine mean plane and that of the phenyl ring is 41.84 (11)°. The structure is held together by slipped π - π stacking between symmetry-related molecules, with an interplanar distance of 3.583 (1) Å and a centroid-centroid vector of 3.670 (2) Å.

Related literature

For background regarding biological activity of imidazo[4,5-*b*]pyridines, see: Cristalli *et al.* (1995); Bukowski & Kaliszan (1991); Aridoss *et al.* (2006); Bavetsias *et al.* (2007). For background to their pharmacological activity, see: Chen & Dost (1992); Weier *et al.* (1993).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{10}\text{BrN}_3$	$V = 2329.68$ (12) Å ³
$M_r = 288.15$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 13.7138$ (4) Å	$\mu = 3.51$ mm ⁻¹
$b = 6.7088$ (2) Å	$T = 298$ K
$c = 25.3217$ (7) Å	$0.60 \times 0.30 \times 0.06$ mm

Data collection

Bruker SMART CCD three-circle diffractometer	13535 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1997)	2378 independent reflections
$T_{\min} = 0.227$, $T_{\max} = 0.825$	1804 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	155 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.37$ e Å ⁻³
2378 reflections	$\Delta\rho_{\text{min}} = -0.40$ e Å ⁻³

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2697).

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supplementary materials

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6-Bromo-3-methyl-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine

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Comment

Heterocyclic ring systems having imidazo[4,5-*b*]pyridine nucleus can be considered as structural analogues of purines and have shown a diverse biological activity depending on the substituents of the heterocyclic ring. Their activity includes antiviral (Cristalli *et al.*, 1995), anticancer (Bavetsias *et al.*, 2007), tuberculostatic (Bukowski & Kaliszan, 1991) and antimetabolic (Aridoss *et al.*, 2006) actions. They have also been evaluated as antagonists of various biological receptors including angiotensin-II (Chen & Dost, 1992) and platelet activating factor (PAF) (Weier *et al.*, 1993). Hence, the synthesis of imidazo[4,5-*b*]pyridine derivatives represents nowadays an important topic in organic synthesis.

The two fused five and six-membered rings are nearly planar with the maximum deviation of 0.004 (2) Å from N1. The dihedral angle between the imidazo[4,5-*b*]pyridine system and the phenyl ring is 41.84 (11)° (Fig. 1). The structure is held together by slipped π - π stacking between symmetry related molecules with interplanar distance of 3.583 (1) Å and centroid to centroid vector of 3.670 (2) Å resulting in a slippage of 0.79 Å.

Experimental

To a solution of the 6-bromo-2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (0.3 g, 1.09 mmol), potassium carbonate (0.2 g, 1.42 mmol) and tetra-*n*-butylammonium bromide (0.04 g, 0.1 mmol) in DMF (15 ml) was added methyl iodide (0.08 ml, 1.31 mmol). Stirring was continued at room temperature for 12 h. The salt was removed by filtration and the filtrate concentrated under reduced pressure. The residue was separated by chromatography on a column of silica gel with ethyl acetate/hexane (1/2) as eluent. The compound was recrystallized from ethanol.

Refinement

H atoms were located in a difference map and treated as riding with C—H = 0.93 Å, and 0.96 Å for aromatic and methyl respectively and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{aromatic})$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{methyl})$.

Figures

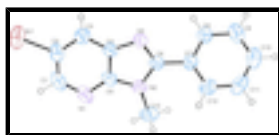


Fig. 1. : Molecular view of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles of arbitrary radii.

6-Bromo-3-methyl-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine

Crystal data

C₁₃H₁₀BrN₃

$F(000) = 1152$

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$M_r = 288.15$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 13.7138$ (4) Å

$b = 6.7088$ (2) Å

$c = 25.3217$ (7) Å

$V = 2329.68$ (12) Å³

$Z = 8$

$D_x = 1.643$ Mg m⁻³

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

Cell parameters from 5157 reflections

$\theta = 3.0$ – 29.6°

$\mu = 3.51$ mm⁻¹

$T = 298$ K

Platelet, colourless

$0.60 \times 0.30 \times 0.06$ mm

Data collection

Bruker CCD three-circle diffractometer

Radiation source: fine-focus sealed tube graphite

ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 1997)

$T_{\min} = 0.227$, $T_{\max} = 0.825$

13535 measured reflections

2378 independent reflections

1804 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.2^\circ$

$h = 0$ → 17

$k = 0$ → 8

$l = 0$ → 31

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.090$

$S = 1.04$

2378 reflections

155 parameters

0 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

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 1.2509P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.40$ e Å⁻³

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.65259 (2)	1.16657 (6)	0.626463 (10)	0.06788 (15)
N1	0.60483 (17)	0.7251 (3)	0.51723 (8)	0.0509 (6)
N2	0.60942 (14)	0.7570 (3)	0.42245 (7)	0.0396 (4)
N3	0.64274 (15)	1.0833 (3)	0.41558 (8)	0.0425 (5)
C1	0.6160 (2)	0.8347 (4)	0.56091 (10)	0.0528 (7)
H1	0.6093	0.7719	0.5934	0.063*
C2	0.63682 (17)	1.0361 (4)	0.56042 (9)	0.0477 (6)
C3	0.64811 (18)	1.1434 (4)	0.51422 (10)	0.0464 (6)
H3	0.6620	1.2790	0.5138	0.056*
C4	0.63692 (16)	1.0313 (4)	0.46819 (9)	0.0385 (5)
C5	0.61634 (17)	0.8291 (3)	0.47310 (9)	0.0386 (5)
C6	0.62568 (16)	0.9162 (4)	0.38966 (9)	0.0369 (5)
C7	0.62409 (16)	0.9055 (4)	0.33165 (9)	0.0378 (5)
C8	0.58108 (18)	1.0590 (4)	0.30370 (9)	0.0463 (6)
H8	0.5525	1.1644	0.3218	0.056*
C9	0.5801 (2)	1.0574 (5)	0.24902 (10)	0.0561 (7)
H9	0.5506	1.1610	0.2306	0.067*
C10	0.6226 (2)	0.9037 (5)	0.22203 (11)	0.0590 (8)
H10	0.6217	0.9025	0.1853	0.071*
C11	0.6665 (2)	0.7515 (6)	0.24919 (12)	0.0641 (8)
H11	0.6957	0.6476	0.2307	0.077*
C12	0.66776 (19)	0.7512 (5)	0.30402 (11)	0.0531 (7)
H12	0.6978	0.6475	0.3222	0.064*
C13	0.5829 (2)	0.5528 (4)	0.40922 (12)	0.0607 (8)
H13A	0.5461	0.5518	0.3770	0.091*
H13B	0.5441	0.4973	0.4372	0.091*
H13C	0.6409	0.4746	0.4048	0.091*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0669 (2)	0.0970 (3)	0.03975 (18)	-0.00449 (16)	-0.00264 (12)	-0.01196 (14)
N1	0.0583 (14)	0.0484 (13)	0.0460 (12)	-0.0094 (11)	-0.0071 (10)	0.0159 (10)
N2	0.0467 (11)	0.0275 (10)	0.0445 (11)	-0.0009 (9)	-0.0056 (9)	0.0035 (9)
N3	0.0584 (13)	0.0312 (10)	0.0379 (10)	-0.0030 (9)	0.0000 (9)	0.0023 (9)
C1	0.0529 (15)	0.0641 (19)	0.0414 (14)	-0.0091 (14)	-0.0064 (11)	0.0176 (13)
C2	0.0411 (13)	0.0662 (19)	0.0358 (12)	-0.0012 (12)	-0.0042 (10)	0.0006 (12)
C3	0.0526 (15)	0.0436 (15)	0.0430 (13)	-0.0035 (11)	-0.0023 (11)	-0.0017 (11)
C4	0.0427 (13)	0.0344 (13)	0.0385 (12)	-0.0008 (10)	-0.0019 (9)	0.0043 (10)
C5	0.0385 (12)	0.0347 (12)	0.0426 (12)	-0.0022 (10)	-0.0061 (10)	0.0066 (10)
C6	0.0381 (12)	0.0316 (12)	0.0410 (12)	0.0030 (10)	-0.0028 (10)	0.0016 (10)
C7	0.0362 (11)	0.0391 (13)	0.0380 (12)	-0.0019 (10)	0.0003 (9)	-0.0014 (10)
C8	0.0522 (14)	0.0459 (15)	0.0408 (13)	0.0073 (12)	0.0051 (11)	0.0026 (11)
C9	0.0575 (16)	0.071 (2)	0.0402 (14)	0.0032 (14)	0.0022 (12)	0.0109 (13)

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C10	0.0541 (15)	0.084 (2)	0.0389 (14)	-0.0069 (16)	0.0070 (12)	-0.0068 (14)
C11	0.0615 (19)	0.071 (2)	0.0594 (18)	0.0084 (16)	0.0145 (14)	-0.0249 (17)
C12	0.0514 (16)	0.0528 (16)	0.0551 (16)	0.0114 (13)	0.0018 (12)	-0.0064 (14)
C13	0.087 (2)	0.0329 (14)	0.0622 (17)	-0.0136 (14)	-0.0098 (15)	-0.0003 (13)

Geometric parameters (Å, °)

Br1—C2	1.900 (3)	C7—C8	1.382 (3)
N1—C5	1.327 (3)	C7—C12	1.386 (4)
N1—C1	1.337 (3)	C8—C9	1.385 (3)
N2—C6	1.371 (3)	C8—H8	0.9300
N2—C5	1.374 (3)	C9—C10	1.367 (4)
N2—C13	1.456 (3)	C9—H9	0.9300
N3—C6	1.320 (3)	C10—C11	1.371 (5)
N3—C4	1.380 (3)	C10—H10	0.9300
C1—C2	1.381 (4)	C11—C12	1.388 (4)
C1—H1	0.9300	C11—H11	0.9300
C2—C3	1.382 (4)	C12—H12	0.9300
C3—C4	1.395 (3)	C13—H13A	0.9600
C3—H3	0.9300	C13—H13B	0.9600
C4—C5	1.391 (3)	C13—H13C	0.9600
C6—C7	1.471 (3)		
C5—N1—C1	113.2 (2)	C8—C7—C6	118.8 (2)
C6—N2—C5	106.23 (19)	C12—C7—C6	122.3 (2)
C6—N2—C13	129.4 (2)	C7—C8—C9	120.7 (3)
C5—N2—C13	124.3 (2)	C7—C8—H8	119.7
C6—N3—C4	104.8 (2)	C9—C8—H8	119.7
N1—C1—C2	123.7 (2)	C10—C9—C8	120.1 (3)
N1—C1—H1	118.2	C10—C9—H9	119.9
C2—C1—H1	118.2	C8—C9—H9	119.9
C1—C2—C3	122.7 (2)	C9—C10—C11	119.9 (3)
C1—C2—Br1	117.80 (19)	C9—C10—H10	120.1
C3—C2—Br1	119.5 (2)	C11—C10—H10	120.1
C2—C3—C4	114.5 (2)	C10—C11—C12	120.6 (3)
C2—C3—H3	122.8	C10—C11—H11	119.7
C4—C3—H3	122.8	C12—C11—H11	119.7
N3—C4—C5	110.2 (2)	C7—C12—C11	119.9 (3)
N3—C4—C3	131.6 (2)	C7—C12—H12	120.1
C5—C4—C3	118.2 (2)	C11—C12—H12	120.1
N1—C5—N2	126.4 (2)	N2—C13—H13A	109.5
N1—C5—C4	127.7 (2)	N2—C13—H13B	109.5
N2—C5—C4	105.9 (2)	H13A—C13—H13B	109.5
N3—C6—N2	112.9 (2)	N2—C13—H13C	109.5
N3—C6—C7	122.7 (2)	H13A—C13—H13C	109.5
N2—C6—C7	124.3 (2)	H13B—C13—H13C	109.5
C8—C7—C12	118.9 (2)		

Fig. 1

