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Crystal structure and Hirshfeld surface analysis of 4-allyl-6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine

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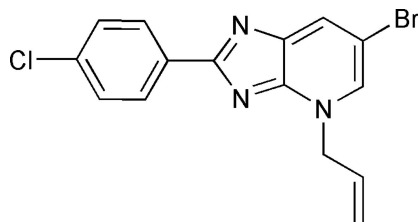
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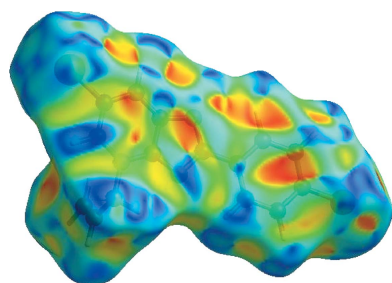
The title compound, C₁₅H₁₁BrClN₃, is built up from a planar imidazo[4,5-*b*]pyridine unit linked to phenyl and allyl substituents. The allyl substituent is rotated significantly out of the imidazo[4,5-*b*]pyridine plane, while the benzene ring is inclined by 3.84 (6)° to the ring system. In the crystal, molecules are linked *via* a pair of weak intermolecular C—H···N hydrogen bonds, forming an inversion dimer with an *R*₂²(20) ring motif. The dimers are further connected by π – π stacking interactions between the imidazo[4,5-*b*]pyridine ring systems [centroid–centroid distances = 3.7161 (13) and 3.8478 (13) Å]. The important contributions to the Hirshfeld surface are H···H (35.9%), H···Cl/Cl···H (15.0%), H···C/C···H (12.4%), H···Br/Br···H (10.8%), H···N/N···H (7.5%), C···Br/Br···C (5.9%), C···C (5.5%) and C···N/N···C (4.0%) contacts.

1. Chemical context

Heterocyclic ring systems having an imidazo[4,5-*b*]pyridine unit can be considered as structural analogues of purines and have shown diverse biological activity depending on the substituents of the heterocyclic ring. Their activities include anticancer (Zhiqiang *et al.*, 2005), tuberculostatic (Bukowski & Janowiec, 1989) and antimetabolic (Parthiban *et al.*, 2006) actions. Some imidazo[4,5-*b*]pyridine derivatives have also been reported as corrosion inhibitors for steel in acidic medium (Bouayad *et al.*, 2018; Sikine *et al.*, 2016), and some of them can be used to treat peptic ulcers, diabetes and mental illness (Scribner *et al.*, 2007; Liang *et al.*, 2007).



As a continuation of our research work devoted to the development of substituted imidazo[4,5-*b*]pyridine derivatives (Bourichi *et al.*, 2016; Ouzidan *et al.*, 2010*a,b,c*), we report herein the synthesis, the molecular and crystal structures along with the Hirshfeld surface analysis of the title compound, a new imidazo[4,5-*b*]pyridine derivative, which was obtained by the reaction of allyl bromide with 6-bromo-2-(4-chlorophen-



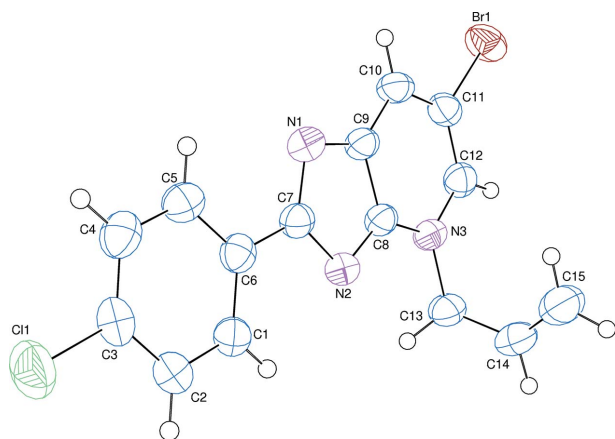


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

yl)-4*H*-imidazo[4,5-*b*]pyridine in the presence of a catalytic quantity of tetra-*n*-butylammonium bromide under mild conditions.

2. Structural commentary

The title compound is built up from an imidazo[4,5-*b*]pyridine unit linked to phenyl and allyl substituents (Fig. 1). The imidazo[4,5-*b*]pyridine ring system is planar, with a maximum deviation of 0.016 (2) Å for atom C12. The ring system is inclined by 3.84 (6)° to the benzene C1–C6 ring, with the N2–C7–C6–C1 torsion angle being 3.3 (3)°. The allyl substituent is nearly perpendicular to the imidazo[4,5-*b*]pyridine plane, as indicated by the C8–N3–C13–C14 torsion angle of –97.3 (2)°. Atoms C6 and C13 are 0.038 (2) and 0.014 (2) Å, respectively, away from the imidazo[4,5-*b*]pyridine plane.

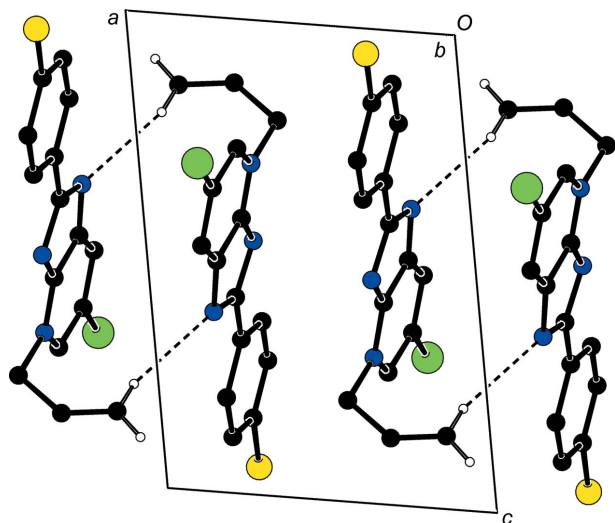


Figure 2
A part of the packing diagram of the title compound, viewed down [010]. The weak intermolecular C–H...N hydrogen bonds are shown as dashed lines. H atoms not involved in the hydrogen bonding have been omitted for clarity.

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C15–H15A...N1 ⁱ	0.93	2.59	3.454 (4)	155

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

3. Supramolecular features

In the crystal, molecules are linked *via* a pair of weak intermolecular C–H...N hydrogen bonds [C15–H15A...N1ⁱ; symmetry code: (i) $-x, -y + 1, -z + 1$; Table 1], forming an inversion dimer with an $R_2^2(20)$ ring motif (Fig. 2). The dimers are further connected by π – π stacking interactions between the imidazo[4,5-*b*]pyridine ring systems. The centroid–centroid distances, Cg1...Cg1ⁱⁱ and Cg1...Cg2ⁱ [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$], are 3.7161 (13) and 3.8478 (13) Å, respectively, where Cg1 and Cg2 are the centroids of the N1/N2/C7–C9 and N3/C8–C12 rings, respectively.

4. Database survey

A non-*para*-substituted analogue, namely 4-allyl-6-bromo-2-phenyl-4*H*-imidazo[4,5-*b*]pyridine monohydrate, has been reported (Ouzidan *et al.*, 2010c), and three similar structures,

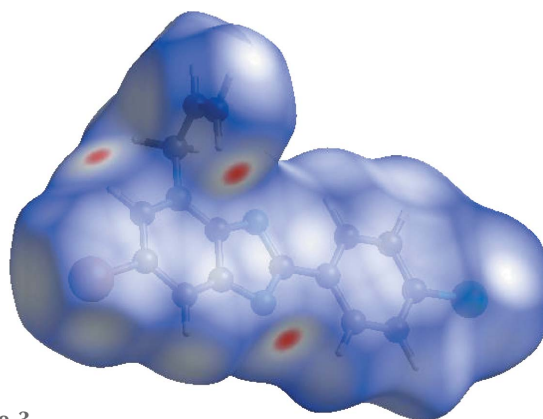


Figure 3
View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range –0.1373 to 1.1294 a.u.

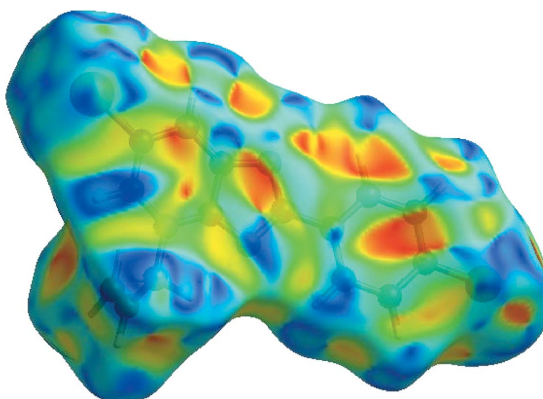


Figure 4
Hirshfeld surface of the title compound plotted over shape index.

4-benzyl-6-bromo-2-phenyl-4*H*-imidazo[4,5-*b*]pyridine (Ouzidan *et al.*, 2010*b*), 4-benzyl-6-bromo-2-methoxyphenyl-4*H*-imidazo[4,5-*b*]pyridine monohydrate (Ouzidan *et al.*, 2010*a*) and 4-benzyl-6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine (Bourichi *et al.*, 2017), have been also reported.

5. Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the crystal of the title compound, a Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) was carried out using

CrystalExplorer17.5 (Turner *et al.*, 2017). In the HS plotted over d_{norm} (Fig. 3), the white surface indicates contacts with distances equal to the sum of the van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the sum of the van der Waals radii, respectively (Venkatesan *et al.*, 2016). The bright-red spots appearing near atoms N1 and H15A indicate their roles as the respective donors and/or acceptors in the dominant C—H \cdots N hydrogen bond (Table 1). The shape index (Fig. 4) clearly suggests that there are π – π interactions, which are shown as adjacent red and blue triangles. The

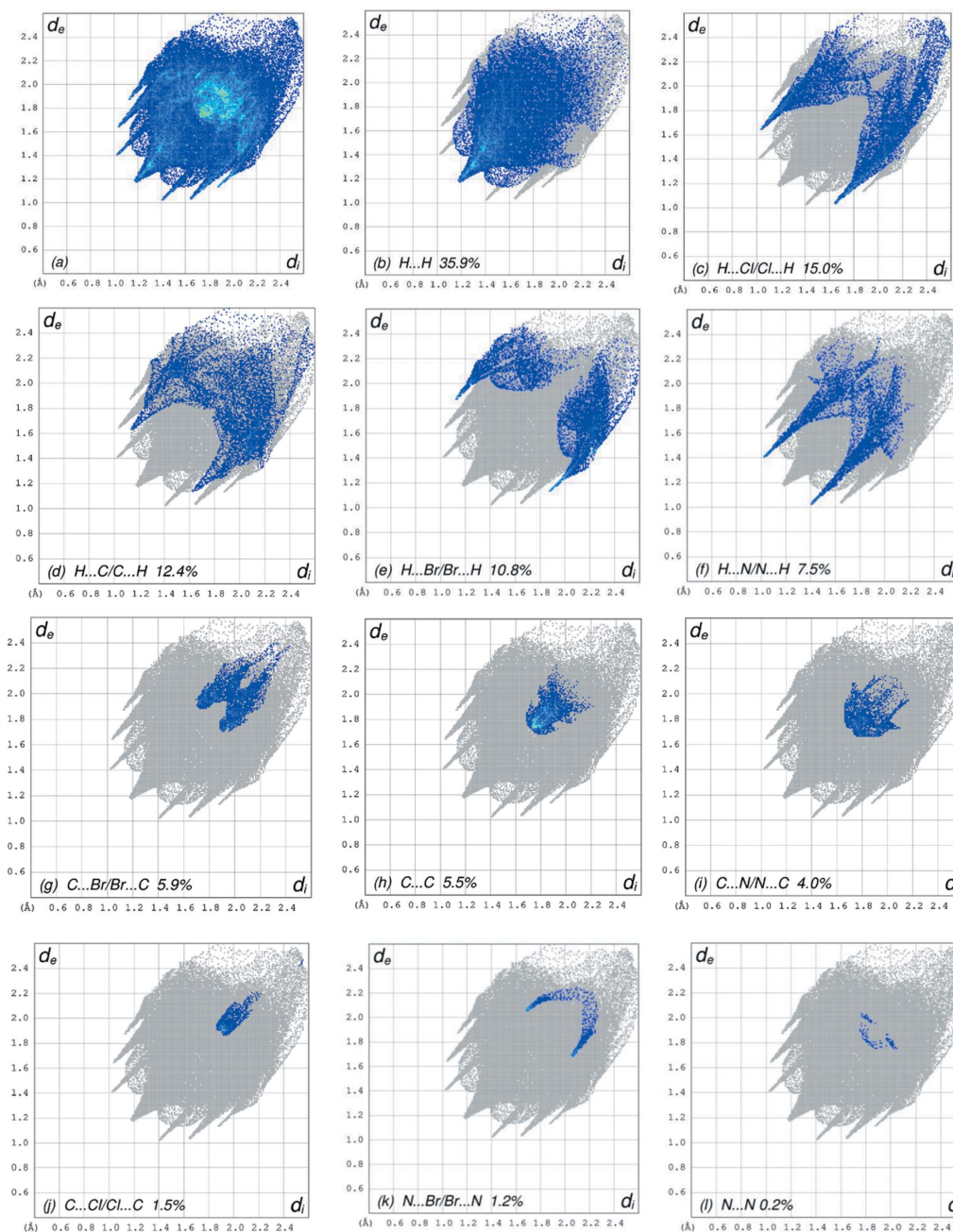


Figure 5

The full two-dimensional fingerprint plots for the title compound, showing (a) all contacts, and delineated into (b) H \cdots H, (c) H \cdots Cl/Cl \cdots H, (d) H \cdots C/C \cdots H, (e) H \cdots Br/Br \cdots H, (f) H \cdots N/N \cdots H, (g) C \cdots Br/Br \cdots C, (h) C \cdots C, (i) C \cdots N/N \cdots C, (j) C \cdots Cl/Cl \cdots C, (k) N \cdots Br/Br \cdots N and (l) N \cdots N contacts. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

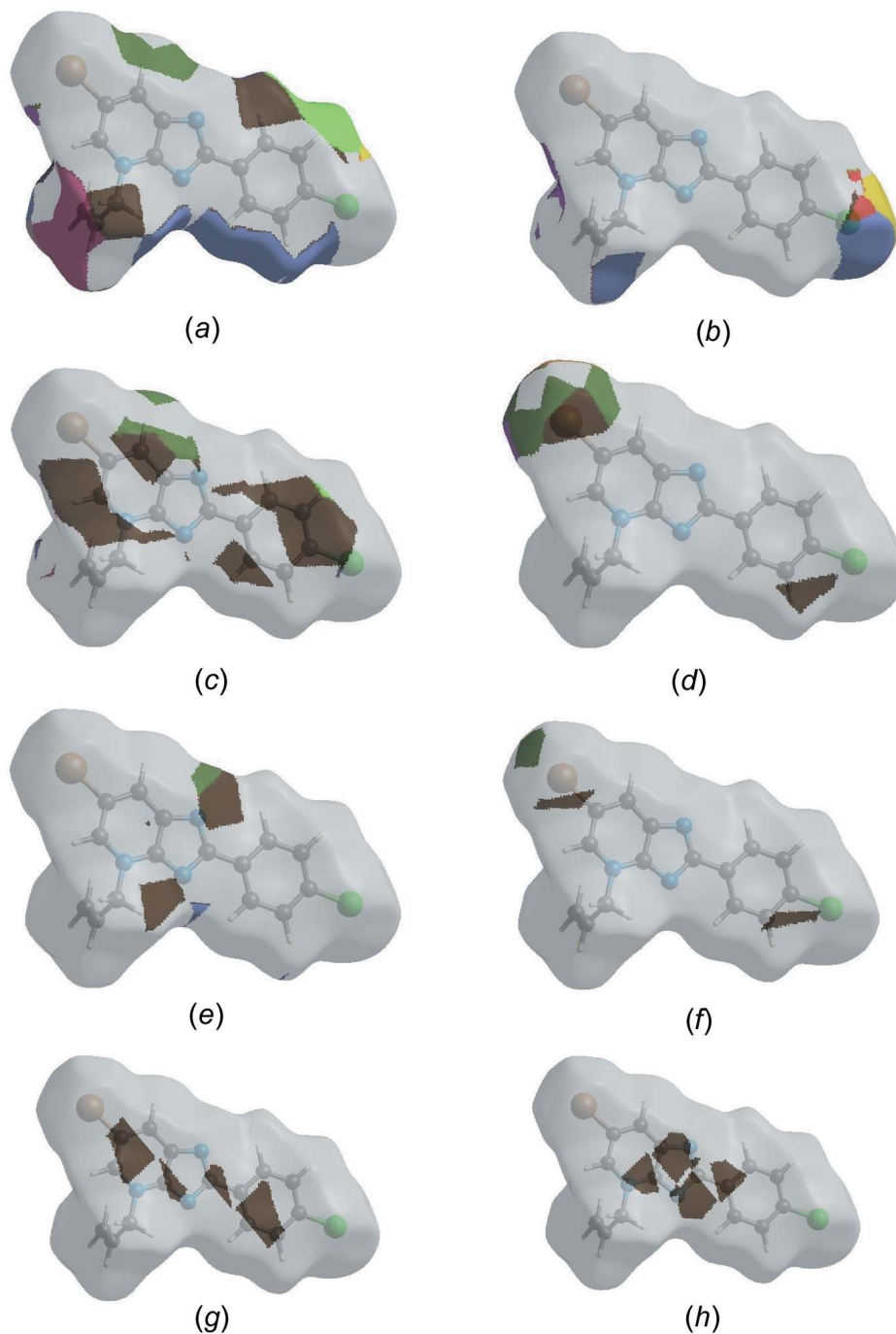


Figure 6
 The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for (a) H...H, (b) H...Cl/Cl...H, (c) H...C/C...H, (d) H...Br/Br...H, (e) H...N/N...H, (f) C...Br/Br...C, (g) C...C and (h) C...N/N...C contacts.

overall two-dimensional fingerprint plot and those delineated into H...H, H...Cl/Cl...H, H...C/C...H, H...Br/Br...H, H...N/N...H, C...Br/Br...C, C...C, C...N/N...C, C...Cl/Cl...C, N...Br/Br...N and N...N contacts (McKinnon *et al.*, 2007) are illustrated in Figs. 5(a)–(l), together with their relative contributions to the Hirshfeld surface. The contributions are 35.9, 15.0, 12.4, 10.8, 7.5, 5.9, 5.5, 4.0, 1.5, 1.2 and 0.2%, respectively, for H...H, H...Cl/Cl...H, H...C/C...H, H...Br/Br...H, H...N/N...H, C...Br/Br...C, C...C, C...N/N...

N...C, C...Cl/Cl...C, N...Br/Br...N and N...N contacts. The most important interaction is H...H (35.9%), which is reflected as widely scattered points of high density due to the large hydrogen content of the molecule [Fig. 5(b)]. The spike with the tip at $d_e = d_i = 1.16$ Å is due to the short interatomic H...H contacts. The H...Cl/Cl...H contacts (15.0%) have a nearly symmetrical distribution of points and a pair of spikes with tips at $d_e + d_i = 2.67$ Å [Fig. 5(c)]. In the absence of C—H... π interactions, the H...C/C...H contacts (12.4%) also

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₅ H ₁₁ BrClN ₃
<i>M_r</i>	348.63
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6218 (5), 8.5238 (5), 11.1093 (7)
α , β , γ (°)	95.739 (3), 98.880 (3), 94.979 (3)
<i>V</i> (Å ³)	705.66 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.09
Crystal size (mm)	0.3 × 0.23 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.591, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	31084, 4288, 3226
<i>R_{int}</i>	0.033
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.089, 1.03
No. of reflections	4288
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.57, -0.47

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2015).

have a nearly symmetrical distribution of points with tips at $d_e + d_i = 2.79$ Å [Fig. 5(*d*)]. The H \cdots Br/Br \cdots H contacts (10.8%) have a symmetrical distribution of points and a pair of spikes with tips at $d_e + d_i = 3.00$ Å [Fig. 5(*e*)]. A pair of spikes with tips at $d_e + d_i = 2.42$ Å (Fig. 5*f*) in the H \cdots N/N \cdots H contacts (7.5%) arises from the C–H \cdots N hydrogen bond (Table 1). The C \cdots Br/Br \cdots C contacts (5.9%) have a pair of wings with tips at $d_e + d_i \sim 3.62$ Å [Fig. 5(*g*)]. The C \cdots C contacts (5.5%) have an arrow-shaped distribution of points with the tip at $d_e = d_i = 1.75$ Å [Fig. 5(*h*)]. The C \cdots N/N \cdots C contacts (4.0%) have wide spikes with tips at $d_e + d_i = 3.44$ Å [Fig. 5(*i*)]. The HS representations with the function d_{norm} plotted onto the surface are shown for the H \cdots H, H \cdots Cl/Cl \cdots H, H \cdots C/C \cdots H, H \cdots Br/Br \cdots H, H \cdots N/N \cdots H, C \cdots Br/Br \cdots C, C \cdots C and C \cdots N/N \cdots C contacts [Figs. 6(*a*)–(*h*)].

5. Synthesis and crystallization

A mixture of 6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine (0.2 g, 0.65 mmol) dissolved in 25 ml of *N,N*-dimethylformamide (DMF) and potassium carbonate (0.13 g, 0.92 mmol) was stirred for 5 min, and then to a mixture of tetra-*n*-butylammonium bromide (0.032 g, 0.1 mmol) and allyl bromide (0.094 g, 0.77 mmol) was added. Stirring was continued for 6 h at room temperature. After removing the salts by filtration, DMF was evaporated under reduced pressure, and the solid obtained was dissolved in dichloromethane. The residue was extracted with distilled water and the

resulting mixture was chromatographed on a silica-gel column (eluent = ethyl acetate–hexane, 1:3 *v/v*). Brown single crystals suitable for X-ray diffraction were obtained by evaporation of an ethyl acetate–hexane (1:3 *v/v*) solution.

6. Refinement

Crystal data, data collection and refinement details are summarized in Table 2. All H atoms were positioned geometrically, with C–H = 0.93 or 0.97 Å, and constrained to ride on their parent C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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References

- Bouayad, K., Kandri Rodi, Y., Elmsellem, H., El Ghadraoui, E. H., Ouzidan, Y., Abdel-Rahman, I., Kusuma, H. S., Warad, I., Mague, J. T., Essassi, E. M., Hammouti, B. & Chetouani, A. (2018). *Mor. J. Chem.* **6**, 22–34.
- Bourichi, S., Kandri Rodi, Y., Jasinski, J. P., Kaur, M., Ouzidan, Y. & Essassi, E. M. (2017). *IUCrData*, **2**, x170899.
- Bourichi, S., Kandri Rodi, Y., Ouzidan, Y., Mague, J. T., Essassi, E. M. & Zouihri, H. (2016). *IUCrData*, **1**, x160763.
- Bruker (2014). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2015). *APEX2*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bukowski, L. & Janowiec, M. (1989). *Pharmazie*, **44**, 267–269.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Liang, G. B., Qian, X., Feng, D., Fisher, M., Brown, C. M., Gurnett, A., Leavitt, P. S., Liberator, P. A., Misura, A. S., Tamas, T., Schmatz, D. M., Wyvratt, M. & Biftu, T. (2007). *Bioorg. Med. Chem. Lett.* **17**, 3558–3561.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Ouzidan, Y., Kandri Rodi, Y., Obbade, S., Essassi, E. M. & Ng, S. W. (2010a). *Acta Cryst.* **E66**, o947.
- Ouzidan, Y., Obbade, S., Capet, F., Essassi, E. M. & Ng, S. W. (2010b). *Acta Cryst.* **E66**, o946.
- Ouzidan, Y., Rodi, Y. K., Zouihri, H., Essassi, E. M. & Ng, S. W. (2010c). *Acta Cryst.* **E66**, o1903.
- Parthiban, S., Kabilan, G. & Aridoss, S. (2006). *Eur. J. Med. Chem.* **41**, 268–275.
- Scribner, A., Dennis, R., Hong, J., Lee, S., McIntyre, D., Perrey, D., Feng, D., Fisher, M., Wyvratt, M., Leavitt, P., Liberator, P., Gurnett, A., Brown, C., Mathew, J., Thompson, D., Schmatz, D. & Biftu, T. (2007). *Eur. J. Med. Chem.* **42**, 1334–1357.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Sikine, M., Elmsellem, H., Kandri Rodi, Y., Steli, H., Aouniti, A., Hammouti, B., Ouzidan, Y., Ouazzani Chahdi, F., Bourass, M. & Essassi, E. M. (2016). *J. Mater. Environ. Sci.* **7**, 4620–4632.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2015). *Acta Cryst.* **C71**, 9–18.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.

Venkatesan, P., Thamocharan, S., Ilangovan, A., Liang, H. & Sundius, T. (2016). *Spectrochim. Acta Part A*, **153**, 625–636.

Zhiqiang, G., John Tellew, E., Raymond Gross, S., Brian, D., Jonathan, G., Haddach, M., Kiankarimi, M., Lanier, M. & Bin-Feng, L. (2005). *J. Med. Chem.* **48**, 5104–5107.

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Crystal structure and Hirshfeld surface analysis of 4-allyl-6-bromo-2-(4-chlorophenyl)-4*H*-imidazo[4,5-*b*]pyridine

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Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *APEX2* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015*b*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2015).

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

Crystal data

$C_{15}H_{11}BrClN_3$

$M_r = 348.63$

Triclinic, $P\bar{1}$

$a = 7.6218$ (5) Å

$b = 8.5238$ (5) Å

$c = 11.1093$ (7) Å

$\alpha = 95.739$ (3)°

$\beta = 98.880$ (3)°

$\gamma = 94.979$ (3)°

$V = 705.66$ (8) Å³

$Z = 2$

$F(000) = 348$

$D_x = 1.641$ Mg m⁻³

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

Cell parameters from 9961 reflections

$\theta = 2.4$ – 25.8 °

$\mu = 3.09$ mm⁻¹

$T = 296$ K

Plate, colourless

$0.3 \times 0.23 \times 0.06$ mm

Data collection

Bruker APEX-II CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

$T_{\min} = 0.591$, $T_{\max} = 0.746$

31084 measured reflections

4288 independent reflections

3226 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 30.5$ °, $\theta_{\min} = 1.9$ °

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.089$

$S = 1.02$

4288 reflections

181 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.2342P]$

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

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

$\Delta\rho_{\max} = 0.57$ e Å⁻³

$\Delta\rho_{\min} = -0.47$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.17874 (3)	1.01452 (2)	0.68946 (2)	0.05997 (10)
Cl1	0.27559 (10)	-0.20635 (8)	0.05226 (6)	0.07320 (19)
N1	0.1843 (2)	0.4932 (2)	0.37610 (15)	0.0451 (4)
N2	0.3231 (2)	0.36057 (19)	0.53108 (14)	0.0408 (3)
N3	0.3389 (2)	0.57048 (19)	0.69517 (14)	0.0416 (3)
C1	0.3258 (3)	0.0867 (2)	0.36107 (18)	0.0460 (4)
H1	0.3669	0.0842	0.4441	0.055*
C2	0.3317 (3)	-0.0449 (3)	0.27905 (19)	0.0502 (5)
H2	0.3753	-0.1360	0.3063	0.060*
C3	0.2715 (3)	-0.0391 (3)	0.15560 (19)	0.0506 (5)
C4	0.2054 (3)	0.0941 (3)	0.11321 (19)	0.0538 (5)
H4	0.1664	0.0962	0.0299	0.065*
C5	0.1979 (3)	0.2241 (3)	0.19575 (19)	0.0493 (5)
H5	0.1515	0.3137	0.1678	0.059*
C6	0.2590 (3)	0.2232 (2)	0.32120 (17)	0.0420 (4)
C7	0.2538 (2)	0.3616 (2)	0.40937 (17)	0.0400 (4)
C8	0.2942 (2)	0.5038 (2)	0.57750 (16)	0.0390 (4)
C9	0.2078 (3)	0.5896 (2)	0.48503 (17)	0.0408 (4)
C10	0.1670 (3)	0.7408 (2)	0.51508 (19)	0.0453 (4)
H10	0.1095	0.7982	0.4567	0.054*
C11	0.2162 (3)	0.8041 (2)	0.63802 (19)	0.0444 (4)
C12	0.3010 (3)	0.7204 (2)	0.72501 (18)	0.0452 (4)
H12	0.3328	0.7673	0.8056	0.054*
C13	0.4300 (3)	0.4809 (3)	0.78916 (18)	0.0489 (5)
H13A	0.5192	0.5528	0.8446	0.059*
H13B	0.4916	0.4010	0.7491	0.059*
C14	0.3080 (3)	0.4023 (3)	0.8615 (2)	0.0550 (5)
H14	0.3600	0.3461	0.9228	0.066*
C15	0.1374 (4)	0.4035 (3)	0.8484 (3)	0.0709 (7)
H15A	0.0789	0.4579	0.7884	0.085*
H15B	0.0727	0.3499	0.8990	0.085*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05960 (16)	0.03754 (12)	0.08491 (19)	0.00970 (9)	0.01673 (12)	0.00593 (10)
Cl1	0.0863 (5)	0.0732 (4)	0.0594 (3)	0.0184 (3)	0.0175 (3)	-0.0136 (3)
N1	0.0482 (9)	0.0466 (9)	0.0414 (8)	0.0074 (7)	0.0058 (7)	0.0105 (7)
N2	0.0446 (9)	0.0398 (8)	0.0399 (8)	0.0079 (7)	0.0079 (7)	0.0090 (6)

N3	0.0486 (9)	0.0397 (8)	0.0383 (8)	0.0076 (7)	0.0078 (7)	0.0100 (6)
C1	0.0462 (11)	0.0510 (11)	0.0425 (10)	0.0094 (9)	0.0090 (8)	0.0066 (8)
C2	0.0508 (12)	0.0515 (12)	0.0511 (11)	0.0131 (9)	0.0133 (9)	0.0050 (9)
C3	0.0479 (11)	0.0554 (12)	0.0489 (11)	0.0053 (9)	0.0158 (9)	-0.0042 (9)
C4	0.0542 (12)	0.0648 (14)	0.0407 (10)	0.0030 (10)	0.0055 (9)	0.0041 (9)
C5	0.0487 (11)	0.0521 (12)	0.0464 (10)	0.0054 (9)	0.0033 (9)	0.0092 (9)
C6	0.0370 (9)	0.0468 (11)	0.0426 (9)	0.0016 (8)	0.0086 (8)	0.0058 (8)
C7	0.0369 (9)	0.0427 (10)	0.0419 (9)	0.0040 (8)	0.0082 (7)	0.0094 (8)
C8	0.0390 (9)	0.0395 (9)	0.0410 (9)	0.0042 (7)	0.0095 (7)	0.0117 (7)
C9	0.0394 (10)	0.0421 (10)	0.0441 (9)	0.0056 (8)	0.0096 (8)	0.0145 (8)
C10	0.0441 (10)	0.0407 (10)	0.0546 (11)	0.0079 (8)	0.0094 (9)	0.0182 (9)
C11	0.0436 (10)	0.0347 (9)	0.0584 (11)	0.0048 (8)	0.0161 (9)	0.0094 (8)
C12	0.0508 (11)	0.0403 (10)	0.0458 (10)	0.0038 (8)	0.0130 (9)	0.0054 (8)
C13	0.0532 (12)	0.0523 (12)	0.0416 (10)	0.0121 (9)	0.0019 (9)	0.0107 (9)
C14	0.0662 (15)	0.0521 (12)	0.0472 (11)	0.0093 (10)	0.0024 (10)	0.0170 (9)
C15	0.0673 (17)	0.0755 (18)	0.0765 (17)	0.0097 (13)	0.0144 (13)	0.0348 (14)

Geometric parameters (Å, °)

Br1—C11	1.886 (2)	C6—C1	1.395 (3)
C11—C3	1.744 (2)	C6—C5	1.401 (3)
N1—C7	1.342 (3)	C7—C6	1.464 (3)
N1—C9	1.371 (3)	C8—C9	1.431 (3)
N2—C7	1.375 (2)	C9—C10	1.373 (3)
N2—C8	1.327 (2)	C10—H10	0.9300
N3—C8	1.352 (2)	C11—C10	1.399 (3)
N3—C12	1.355 (3)	C11—C12	1.373 (3)
N3—C13	1.477 (2)	C12—H12	0.9300
C1—H1	0.9300	C13—H13A	0.9700
C1—C2	1.381 (3)	C13—H13B	0.9700
C2—H2	0.9300	C13—C14	1.480 (3)
C2—C3	1.384 (3)	C14—H14	0.9300
C4—H4	0.9300	C14—C15	1.287 (4)
C4—C3	1.378 (3)	C15—H15A	0.9300
C5—H5	0.9300	C15—H15B	0.9300
C5—C4	1.377 (3)		
Br1...C14 ⁱ	3.624 (2)	N3...H15A	2.5350
Br1...C15 ⁱ	3.660 (3)	C1...C11 ⁱⁱ	3.532 (3)
Br1...C2 ⁱⁱ	3.677 (2)	C1...C12 ⁱⁱ	3.472 (3)
Br1...C6 ⁱⁱⁱ	3.729 (2)	C5...C13 ⁱⁱ	3.595 (3)
Br1...H10 ^{iv}	3.1682	C6...C12 ⁱⁱ	3.470 (3)
C11...H12 ^v	2.8304	C7...C8 ⁱⁱ	3.512 (3)
C11...H14 ^{vi}	3.1002	C7...C10 ⁱⁱⁱ	3.499 (3)
C11...H15B ^{vii}	2.9750	C8...C15	3.559 (4)
N3...C6 ⁱⁱ	3.437 (3)	C9...C9 ⁱⁱⁱ	3.473 (3)
N1...H5	2.6087	C12...C15	3.378 (3)
N1...H15A ⁱⁱⁱ	2.5889	C5...H13A ⁱⁱ	2.8677

N2...H13B	2.5360	C12...H15A	2.8971
N2...H1	2.5251	H12...H13A	2.4427
C7—N1—C9	102.65 (16)	N2—C8—C9	111.53 (16)
C8—N2—C7	101.17 (15)	N3—C8—C9	120.81 (17)
C8—N3—C12	119.16 (16)	N1—C9—C8	107.12 (17)
C8—N3—C13	120.08 (16)	N1—C9—C10	132.60 (18)
C12—N3—C13	120.76 (16)	C10—C9—C8	120.27 (18)
C6—C1—H1	119.5	C9—C10—C11	116.59 (18)
C2—C1—C6	120.95 (19)	C9—C10—H10	121.7
C2—C1—H1	119.5	C11—C10—H10	121.7
C1—C2—H2	120.5	C10—C11—Br1	120.71 (15)
C1—C2—C3	118.9 (2)	C12—C11—Br1	117.03 (16)
C3—C2—H2	120.5	C12—C11—C10	122.18 (18)
C4—C3—C11	119.49 (17)	N3—C12—C11	120.99 (18)
C4—C3—C2	121.6 (2)	N3—C12—H12	119.5
C2—C3—C11	118.93 (18)	C11—C12—H12	119.5
C5—C4—H4	120.4	N3—C13—H13A	108.8
C5—C4—C3	119.2 (2)	N3—C13—H13B	108.8
C3—C4—H4	120.4	N3—C13—C14	113.74 (18)
C6—C5—H5	119.5	H13A—C13—H13B	107.7
C4—C5—C6	120.9 (2)	C14—C13—H13A	108.8
C4—C5—H5	119.5	C14—C13—H13B	108.8
C1—C6—C7	120.23 (17)	C13—C14—H14	116.6
C1—C6—C5	118.48 (19)	C15—C14—C13	126.8 (2)
C5—C6—C7	121.28 (18)	C15—C14—H14	116.6
N2—C7—C6	120.09 (17)	C14—C15—H15A	120.0
N1—C7—N2	117.53 (17)	C14—C15—H15B	120.0
N1—C7—C6	122.39 (17)	H15A—C15—H15B	120.0
N2—C8—N3	127.66 (17)		
C9—N1—C7—N2	-0.3 (2)	C6—C5—C4—C3	1.1 (3)
C9—N1—C7—C6	-179.75 (17)	C5—C6—C1—C2	0.0 (3)
C7—N1—C9—C8	0.5 (2)	C7—C6—C1—C2	-179.96 (19)
C7—N1—C9—C10	179.6 (2)	C1—C6—C5—C4	-0.8 (3)
C8—N2—C7—N1	0.0 (2)	C7—C6—C5—C4	179.11 (19)
C8—N2—C7—C6	179.45 (17)	N1—C7—C6—C1	-177.28 (18)
C7—N2—C8—N3	-178.58 (19)	N1—C7—C6—C5	2.8 (3)
C7—N2—C8—C9	0.3 (2)	N2—C7—C6—C1	3.3 (3)
C12—N3—C8—N2	178.81 (19)	N2—C7—C6—C5	-176.66 (18)
C12—N3—C8—C9	0.0 (3)	N2—C8—C9—N1	-0.5 (2)
C13—N3—C8—N2	-0.5 (3)	N2—C8—C9—C10	-179.82 (17)
C13—N3—C8—C9	-179.29 (18)	N3—C8—C9—N1	178.47 (17)
C8—N3—C12—C11	0.8 (3)	N3—C8—C9—C10	-0.8 (3)
C13—N3—C12—C11	-179.93 (19)	N1—C9—C10—C11	-178.3 (2)
C8—N3—C13—C14	-97.3 (2)	C8—C9—C10—C11	0.8 (3)
C12—N3—C13—C14	83.4 (2)	C12—C11—C10—C9	0.0 (3)
C6—C1—C2—C3	0.6 (3)	Br1—C11—C10—C9	176.73 (14)

C1—C2—C3—C11	-178.98 (17)	Br1—C11—C12—N3	-177.67 (15)
C1—C2—C3—C4	-0.4 (3)	C10—C11—C12—N3	-0.8 (3)
C5—C4—C3—C11	178.14 (17)	N3—C13—C14—C15	1.2 (4)
C5—C4—C3—C2	-0.5 (3)		

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $-x, -y+2, -z+1$; (v) $x, y-1, z-1$; (vi) $-x+1, -y, -z+1$; (vii) $-x, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15A \cdots N1 ⁱⁱⁱ	0.93	2.59	3.454 (4)	155

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