



Crystal structure, Hirshfeld surface analysis and DFT study of 6-bromo-3-(5-bromohexyl)-2-[4-(dimethylamino)phenyl]-3*H*-imidazo[4,5-*b*]pyridine

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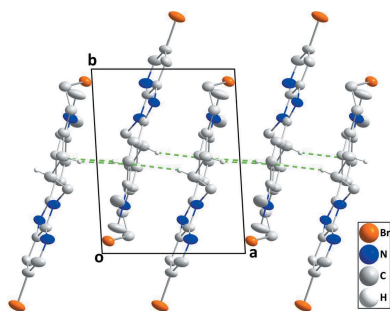
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In the title molecule, C₂₀H₂₄Br₂N₄, the imidazopyridine moiety is not planar as indicated by the dihedral angle of 2.0 (2)° between the constituent rings; the 4-dimethylaminophenyl ring is inclined to the mean plane of the imidazole ring by 27.4 (1)°. In the crystal, two sets of C—H... π (ring) interactions form stacks of molecules extending parallel to the *a*-axis direction. Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H...H (42.2%), H...C/C...H (23.1%) and H...Br/Br...H (22.3%) interactions. The optimized structure calculated using density functional theory (DFT) at the B3LYP/6-311 G(d,p) level is compared with the experimentally determined structure in the solid state. The calculated HOMO–LUMO energy gap is 2.3591 eV.

1. Chemical context

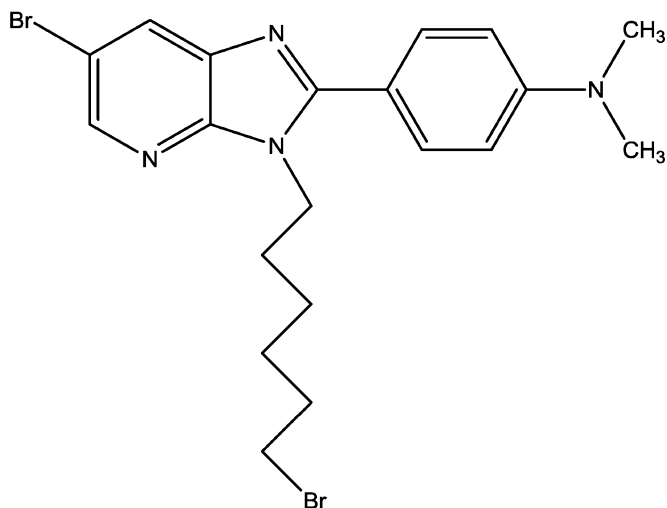
The family of nitrogenous drugs, particularly those containing the imidazopyridine moiety, is important in medicinal chemistry because of their wide range of pharmacological activities such as anticancer, anti-inflammatory, antibacterial, anti-tuberculosis, anti-glycation anti-analgesic and antifungal properties, and their antioxidant potential. In particular, imadazo[4,5-*b*]pyridine derivatives inhibit the P-glycoprotein, which could reverse the multidrug resistance of cancer cells (Bourichi *et al.*, 2018). They are also inhibitors of type 2 diabetes because of their ability to inhibit the Baker's yeast α -glucosidase enzyme, and are inhibitors of one or more proteins in the treatment of disorders characterized by the activation of Wnt pathway signalling (for example: cancer, abnormal cellular proliferation, angiogenesis, fibrotic disorders, bone or cartilage diseases and osteoarthritis), and of genetic and neurological diseases such as PAK4 kinase 4 inhibitor activated by p21 and aurora kinase inhibitors. Imadazo[4,5-*b*]pyridine derivatives are also therapeutic agents for dysferlinopathies through phenotypic screening on patient-induced pluripotent stem cells (Takada *et al.*, 2019).

Given the wide range of therapeutic applications for such compounds, we have already reported a route for the preparation of imidazo[4,5-*b*]pyridine derivatives using *N*-alkylation reactions carried out with di-halogenated carbon



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chains (Jabri *et al.*, 2020); a similar approach yielded the title compound, $C_{20}H_{24}Br_2N_4$ (I). Besides the synthesis, we also report the molecular and crystal structures along with a Hirshfeld surface analysis and a density functional theory (DFT) computational calculation carried out at the B3LYP/6-311 G(d,p) level.



2. Structural commentary

The molecular structure of (I) is depicted in Fig. 1. The imidazopyridine moiety is not planar, as indicated by the dihedral angle of $2.0(3)^\circ$ between the constituent rings. The ring of the 4-dimethylaminophenyl moiety is inclined to the mean plane of the imidazole ring by $27.4(1)^\circ$. The 5-bromopentyl chain is oriented in an arc-like form around the periphery of the 4-dimethylaminophenyl moiety so that the terminal Br2 atom of the chain is only $4.36(6)$ Å from one of the methyl C atoms (C20; Fig. 1).

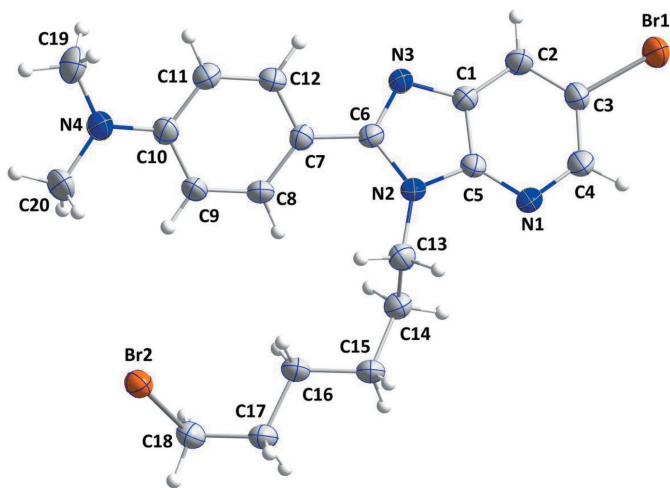


Figure 1

The asymmetric unit of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1

Hydrogen-bond geometry (Å, °).

$Cg3$ is the centroid of the C7–C12 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C14-H14B\cdots Cg3^{vi}$	0.99	2.60	3.502 (4)	151
$C15-H15A\cdots Cg3^{ii}$	0.99	2.94	3.904 (4)	165

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

3. Supramolecular features

In the crystal, stacks of molecules extending along the a -axis direction are formed by inversion-related $C14-H14B\cdots Cg3^i$ and $C15-H15A\cdots Cg3^{ii}$ interactions [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$] where $Cg3$ is the centroid of the C7–C12 phenyl ring (Fig. 2, Table 1).

4. Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the crystal of the title compound, a Hirshfeld surface (HS) analysis (Hirshfeld, 1977) was carried out by using *Crystal Explorer 17.5* (Turner *et al.*, 2017). A view of the three-dimensional Hirshfeld surface of (I), plotted over d_{norm} and electrostatic potential are shown in Fig. 3a and 3b. The shape-index of the HS reveals that there are no significant $\pi-\pi$ interactions in (I), as shown in Fig. 4. The overall two-dimensional fingerprint plot (McKinnon *et al.*, 2007) is shown in Fig. 5a, while those delineated into $H\cdots H$, $H\cdots C/C\cdots H$, $H\cdots Br/Br\cdots H$, $H\cdots N/N\cdots H$, $C\cdots Br/Br\cdots C$, $N\cdots Br/Br\cdots N$ and $N\cdots C/C\cdots N$ contacts are illustrated in Fig. 5b–h, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is $H\cdots H$, contributing 42.2% to the overall crystal packing, which is reflected in Fig. 5b as widely scattered points of high density due to the large hydrogen content of the molecule, with the tip

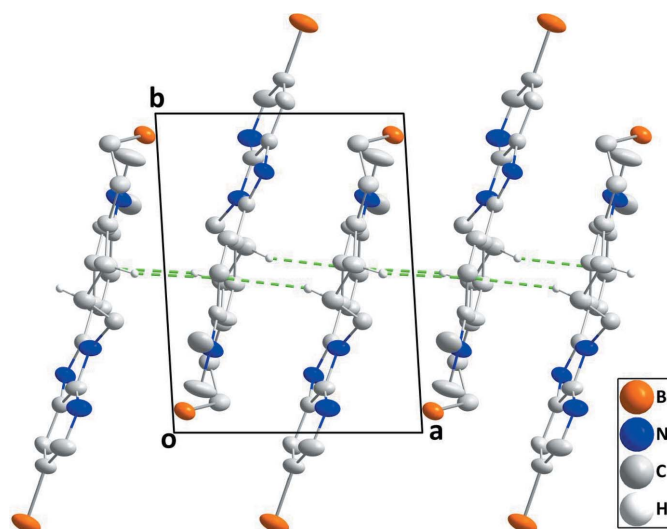


Figure 2

A portion of one stack of molecules viewed along the c -axis direction with the $C-H\cdots\pi(\text{ring})$ interactions depicted by green dashed lines.

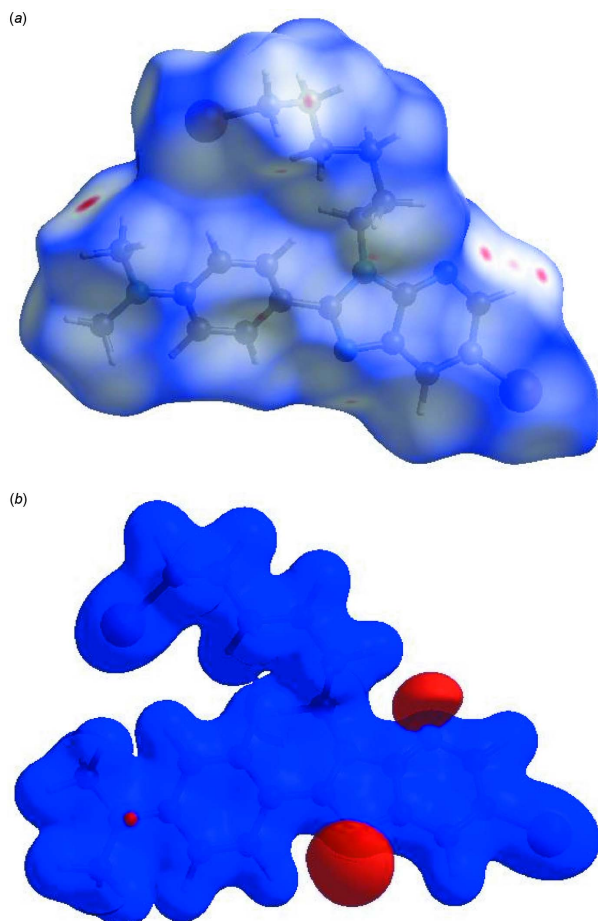


Figure 3
 (a) View of the three-dimensional Hirshfeld surface of the title compound, plotted over d_{norm} in the range of -0.0709 to 1.1781 a.u. (b) View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range -0.0500 to 0.0500 a.u. using the STO-3 G basis set at the Hartree-Fock level of theory.

at $d_e = d_i = 1.18$ Å. In the presence of $C-H \cdots \pi$ interactions, the pair of characteristic wings in the fingerprint plot delineated into $H \cdots C/C \cdots H$ contacts (23.1% contribution to the HS), Fig. 5c, has the tips at $d_e + d_i = 2.76$ Å. The pair of scattered points of spikes in the fingerprint plot delineated into $H \cdots Br/Br \cdots H$, Fig. 5d (22.3%), have the tips at $d_e + d_i = 2.95$ Å. The $H \cdots N/N \cdots H$ contacts, Fig. 5e (10.1%), have the tips at $d_e + d_i = 2.56$ Å. The $C \cdots Br/Br \cdots C$ contacts, Fig. 5f, contribute 1.2% to the HS and appear as a pair of scattered points of spikes with the tips at $d_e + d_i = 3.50$ Å. The $N \cdots Br/Br \cdots N$ contacts, Fig. 5g, contribute 1.1% to the HS appearing as pair of scattered points of spikes with the tips at $d_e + d_i = 3.59$ Å. Finally, the $N \cdots C/C \cdots N$ contacts, Fig. 5h, make only 0.1% contribution to the HS and have a low-density distribution of points.

5. DFT calculations

The optimized structure of (I) in the gas phase was calculated by density functional theory (DFT) using a standard B3LYP

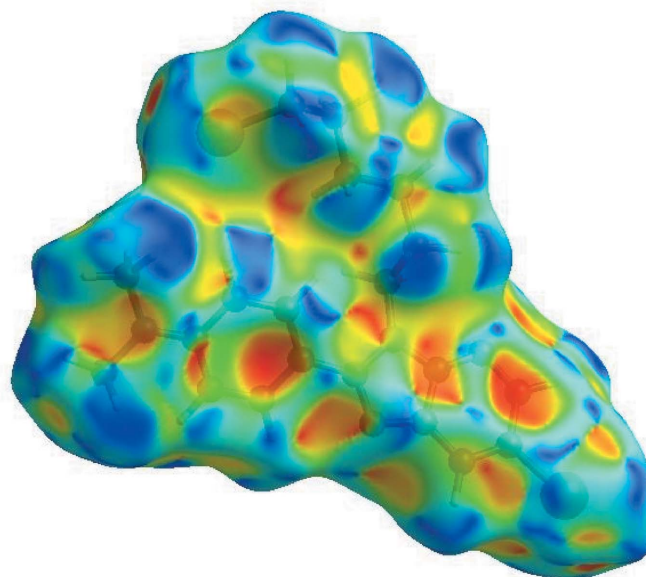


Figure 4
 Hirshfeld surface of the title compound plotted over shape-index.

functional and the 6-311 G(d,p) basis-set (Becke, 1993) as implemented in GAUSSIAN 09 (Frisch *et al.*, 2009). The theoretical and experimental results related to bond lengths and angles are in good agreement (Table 2). Calculated numerical values for (I) including electronegativity (χ),

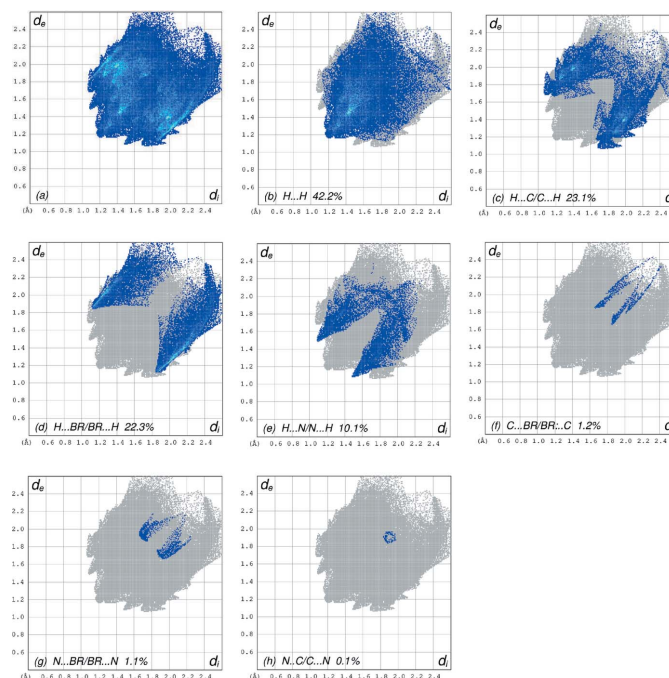


Figure 5
 The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) $H \cdots H$, (c) $H \cdots C/C \cdots H$, (d) $H \cdots Br/Br \cdots H$, (e) $H \cdots N/N \cdots H$, (f) $C \cdots Br/Br \cdots C$, (g) $N \cdots Br/Br \cdots N$ and (h) $N \cdots C/C \cdots N$ interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

Table 2

Comparison of selected (X-ray and DFT) bond length and angles (Å, °).

	X-ray	B3LYP/6-311G(d,p)
Br1—C3	1.905 (3)	1.95402
Br2—C18	1.993 (4)	2.02785
N1—C5	1.346 (4)	1.33429
N1—C4	1.347 (4)	1.37682
N2—C5	1.373 (4)	1.39261
N2—C6	1.387 (4)	1.39443
N2—C13	1.497 (4)	1.47275
N3—C6	1.321 (4)	1.33277
N3—C1	1.381 (4)	1.38362
N4—C10	1.373 (4)	1.39418
N4—C20	1.449 (5)	1.46048
N4—C19	1.464 (5)	1.46022
C5—N1—C4	112.1 (3)	114.50142
C5—N2—C6	105.4 (2)	108.33854
C5—N2—C13	124.1 (2)	118.46297
C6—N2—C13	129.9 (3)	128.08505
C6—N3—C1	105.2 (2)	107.12596
C10—N4—C20	119.7 (3)	120.14593
C10—N4—C19	120.1 (3)	120.10245
C20—N4—C19	117.7 (3)	119.74504
N3—C1—C2	131.6 (3)	134.19166
N3—C1—C5	109.6 (3)	106.29375

hardness (η), potential (μ), electrophilicity (ω) and softness (σ) are collated in Table 3. The electron transition from the HOMO to the LUMO energy level is shown in Fig. 6. The HOMO and LUMO are localized in the plane extending over

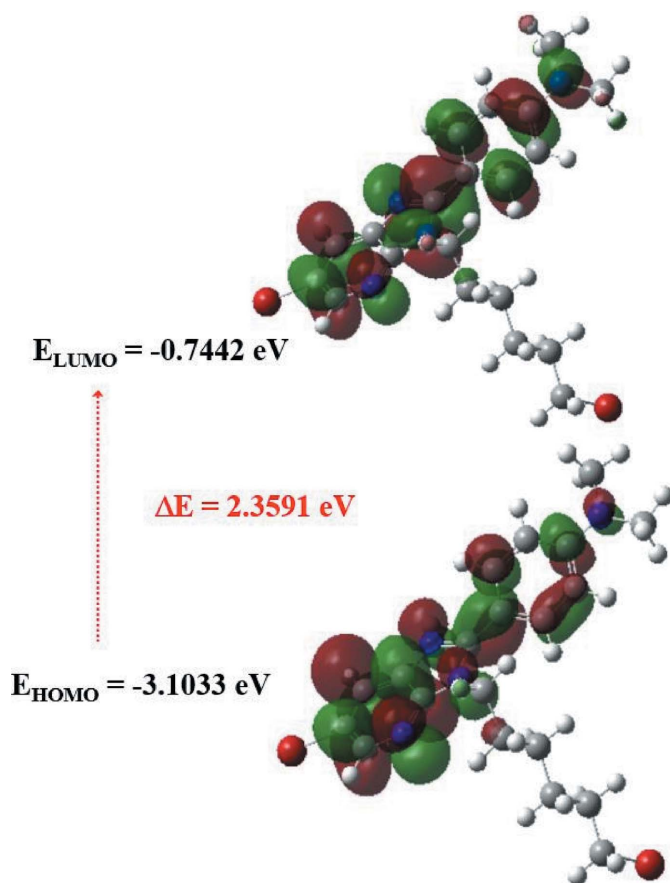


Figure 6
The energy band gap of (I).

Table 3

Calculated energies.

Molecular Energy	Compound (I)
Total Energy TE (eV)	-167186.456
E_{HOMO} (eV)	-3.1033
E_{LUMO} (eV)	-0.7442
Gap, ΔE (eV)	2.3591
Dipole moment, μ (Debye)	6.1953
Ionization potential, I (eV)	3.1033
Electron affinity, A	0.7442
Electronegativity, χ	1.9237
Hardness, η	1.1796
Electrophilicity, index ω	1.5687
Softness, σ	0.8478
Fraction of electron transferred, ΔN	2.1518

the whole 6-bromo-3-(5-bromopentyl)-2-[4-(dimethylamino)-phenyl]-3-*H*-imidazo[4,5-*b*]pyridine system. The energy band gap [$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$] of the molecule is 2.3591 eV, and the frontier molecular orbital energies, E_{HOMO} and E_{LUMO} , are -3.1033 and -0.7442 eV, respectively.

6. Database survey

A search of the Cambridge Structural Database (CSD version 5.40, updated to March 2020; Groom *et al.*, 2016) with fragment (II) (Fig. 7) and excluding metal complexes gave seven matches. Of these, two had a $-\text{CH}_2\text{CH}_2\text{X}-$ ($X = \text{O}, \text{NH}$) chain connecting a saturated nitrogen atom [corresponding to N2 in (I)] to an *ortho* position of the phenyl ring and so were considered less comparable to (I) than the remainder, which can be represented by the general structure (III) (Fig. 7). For $R = \text{Ph}$ and $R' = \text{Br}$, examples are UCOXES ($R' = \text{CH}_2\text{COOC}_2\text{H}_5$; Hjouji *et al.*, 2016), UNUWIK [$R' = (1\text{-benzyl-}1H\text{-}1,2,3\text{-triazol-}5\text{-yl)methyl}$; Ouzidan *et al.*, 2011a] and URAQOU [$R' = (2\text{-oxooxazolidin-}3\text{-yl)ethyl}$; Ouzidan *et al.*, 2011b]. For $R = 4\text{-ClC}_6\text{H}_4$ and $R' = \text{Br}$ there are two reports of the compound with $R' = 1\text{-octyl-}1H\text{-}1,2,3\text{-triazol-}4\text{-yl)methyl}$ [XITLUK (Bourichi *et al.*, 2019a) and XITLUK01 (Bourichi *et al.*, 2019b)]. The dihedral angle between the plane of the 4-dimethylaminophenyl group and the mean plane of the imidazopyridine unit is *ca* 19° in XITLUK and *ca* 49° in UCOXES. Of all of these related structures, (I) is the only one with the substituent on nitrogen approximately coplanar with the imidazopyridine unit. In UCOXES, this substituent is directed outward and away from the phenyl group while in all the others, it is bent back over the phenyl group. In fact, in UNUWIK there is an $\text{H}\cdots\text{H}$ contact of 2.4 Å between the phenyl ring of the benzyl group and that attached to the imidazole ring.

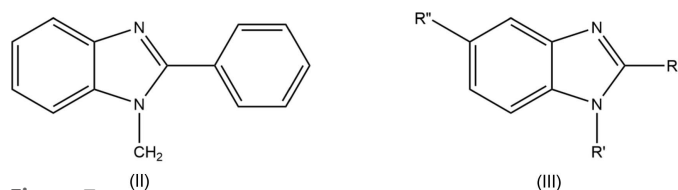


Figure 7
Structural fragments (II) and (III) used in the database search.

7. Synthesis and crystallization

To a solution of 4-(6-bromo-3*H*-imidazo[4,5-*b*]pyridin-2-yl)-*N,N*-dimethylaniline (0.4 g, 1.25 mmol), 2.2 equivalents of potassium carbonate (0.38 g, 2.75 mmol) and 0.2 equivalents of tetra-*n*-butyl ammonium bromide (BTBA) (0.061 g, 0.187 mmol) in 40 ml of DMF were added in small portions to 1.5 equivalent of the 1,6-dibromododecanedihalogenated reagent, and the mixture was stirred magnetically at room temperature for 48 h. After removal of the salts and evaporation of DMF under reduced pressure, the product was subjected to separation by chromatography on a column of silica gel using a mixture of hexane/dichloromethane = 1/4 (*v/v*) as the mobile phase. Brown single crystals suitable for X-ray diffraction were obtained by evaporation of a dichloromethane/hexane solution (1:4 *v/v*).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atoms were included as riding contributions in idealized positions (C–H = 0.95–0.99 Å) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C-methyl})$.

Funding information

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References

Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
 Bourichi, S., Kandri Rodi, Y., Hökelek, T., Chakroune, S., Ouzidan, Y. & Capet, F. (2019*a*). *IUCrData*, **4**, x190053.
 Bourichi, S., Kandri Rodi, Y., Hökelek, T., Ouzidan, Y., Chahdi, F., Akhazzane, M. & Essassi, E. M. (2019*b*). *J. Maroc. Chem. Heterocycli.* **18**, 43–53.
 Bourichi, S., Misbahi, H., Rodi, Y. K., Chahdi, F. O., Essassi, E. M., Szabó, S., Szalontai, B., Gajdács, M., Molnár, J. & Spengler, G. (2018). *Anticancer Res.* **38**, 3999–4003.
 Brandenburg, K. & Putz, H. (2012). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.
 Bruker (2016). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr, Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J.,

Table 4
Experimental details.

Crystal data	
Chemical formula	C ₂₀ H ₂₄ Br ₂ N ₄
<i>M_r</i>	480.25
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.1488 (11), 11.2243 (15), 12.6378 (17)
α , β , γ (°)	64.049 (2), 74.184 (2), 86.067 (2)
<i>V</i> (Å ³)	998.3 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.07
Crystal size (mm)	0.35 × 0.21 × 0.20
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.41, 0.50
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	19397, 5325, 4168
<i>R</i> _{int}	0.025
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.046, 0.140, 1.12
No. of reflections	5325
No. of parameters	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	2.18, -0.81

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/1* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *publCIF* (Westrip, 2010).

Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & Fox, D. J. (2009). *GAUSSIAN09*. Gaussian Inc., Wallingford, CT, US.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Hirshfeld, H. L. (1977). *Theor. Chim. Acta*, **44**, 129–138.
 Hjouji, M. Y., Mague, J. T., Kandri Rodi, Y., Ouzidan, Y. & Essassi, E. M. (2016). *IUCrData* **1**, x161999.
 Jabri, Z., Jarmoni, K., Hökelek, T., Mague, J. T., Sabir, S., Kandri Rodi, Y. & Misbahi, K. (2020). *Acta Cryst.* **E76**, 677–682.
 Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
 Ouzidan, Y., Jasinski, J. P., Butcher, R. J., Golen, J. A., Essassi, E. M. & El Ammari, L. (2011*b*). *Acta Cryst.* **E67**, o1095.
 Ouzidan, Y., Kandri Rodi, Y., Fronczek, F. R., Venkatraman, R., Essassi, E. M. & El Ammari, L. (2011*a*). *Acta Cryst.* **E67**, o890–o891.
 Sheldrick, G. M. (2015*a*). *Acta Cryst. A*, **71**, 3–8.
 Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.
 Takada, H., Kaieda, A., Tawada, M., Nagino, T., Sasa, K., Oikawa, T., Oki, A., Sameshima, T., Miyamoto, K., Miyamoto, M., Kokubu, Y., Tozawa, R., Sakurai, H. & Saito, B. (2019). *J. Med. Chem.* **62**, 9175–9187.
 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.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

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Crystal structure, Hirshfeld surface analysis and DFT study of 6-bromo-3-(5-bromohexyl)-2-[4-(dimethylamino)phenyl]-3*H*-imidazo[4,5-*b*]pyridine

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018/1* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

6-Bromo-3-(5-bromohexyl)-2-[4-(dimethylamino)phenyl]-3*H*-imidazo[4,5-*b*]pyridine

Crystal data

$C_{20}H_{24}Br_2N_4$

$M_r = 480.25$

Triclinic, $P\bar{1}$

$a = 8.1488$ (11) Å

$b = 11.2243$ (15) Å

$c = 12.6378$ (17) Å

$\alpha = 64.049$ (2)°

$\beta = 74.184$ (2)°

$\gamma = 86.067$ (2)°

$V = 998.3$ (2) Å³

$Z = 2$

$F(000) = 484$

$D_x = 1.598$ Mg m⁻³

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

Cell parameters from 9203 reflections

$\theta = 2.6\text{--}29.1^\circ$

$\mu = 4.07$ mm⁻¹

$T = 150$ K

Block, brown

$0.35 \times 0.21 \times 0.20$ 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: multi-scan

(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.41$, $T_{\max} = 0.50$

19397 measured reflections

5325 independent reflections

4168 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 29.2^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 15$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.140$

$S = 1.12$

5325 reflections

237 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 0.5344P]$$

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

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 2.18 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.80 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00, 90.00$ and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00$ and 210.00° . The scan time was 20 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 - 0.99 Å). 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.38201 (6)	-0.28330 (4)	0.92693 (3)	0.05798 (15)
Br2	0.95197 (4)	0.93260 (3)	0.34919 (3)	0.04034 (12)
N1	0.6232 (4)	0.0771 (3)	0.8277 (2)	0.0434 (7)
N2	0.6823 (4)	0.2652 (3)	0.6288 (2)	0.0367 (6)
N3	0.5754 (3)	0.1802 (3)	0.5275 (2)	0.0348 (6)
N4	0.8327 (4)	0.7359 (3)	0.0600 (3)	0.0487 (7)
C1	0.5486 (4)	0.0877 (3)	0.6478 (3)	0.0305 (6)
C2	0.4742 (4)	-0.0402 (3)	0.7100 (3)	0.0375 (7)
H2	0.426342	-0.080259	0.671849	0.045*
C3	0.4747 (4)	-0.1051 (3)	0.8308 (3)	0.0382 (7)
C4	0.5490 (5)	-0.0466 (3)	0.8856 (3)	0.0457 (8)
H4	0.547009	-0.097433	0.969032	0.055*
C5	0.6152 (4)	0.1393 (3)	0.7109 (3)	0.0348 (6)
C6	0.6541 (4)	0.2842 (3)	0.5191 (3)	0.0287 (6)
C7	0.7070 (4)	0.4037 (3)	0.4039 (3)	0.0298 (6)
C8	0.7208 (4)	0.5323 (3)	0.3942 (3)	0.0356 (6)
H8	0.698994	0.544398	0.466483	0.043*
C9	0.7655 (4)	0.6417 (3)	0.2817 (3)	0.0391 (7)
H9	0.775946	0.727231	0.278106	0.047*
C10	0.7958 (4)	0.6281 (3)	0.1725 (3)	0.0355 (6)
C11	0.7797 (4)	0.4999 (3)	0.1826 (3)	0.0371 (7)
H11	0.799081	0.487401	0.110577	0.044*
C12	0.7362 (4)	0.3916 (3)	0.2950 (3)	0.0357 (7)
H12	0.725654	0.306081	0.298581	0.043*
C13	0.7850 (4)	0.3494 (3)	0.6551 (3)	0.0370 (7)
H13A	0.855360	0.417953	0.577241	0.044*

H13B	0.863039	0.293447	0.702436	0.044*
C14	0.6702 (5)	0.4158 (3)	0.7268 (3)	0.0401 (7)
H14A	0.621256	0.348586	0.811797	0.048*
H14B	0.574420	0.452669	0.690150	0.048*
C15	0.7645 (5)	0.5269 (3)	0.7290 (3)	0.0410 (7)
H15A	0.879431	0.499333	0.739215	0.049*
H15B	0.701343	0.543649	0.799681	0.049*
C16	0.7824 (4)	0.6547 (3)	0.6111 (3)	0.0374 (7)
H16A	0.865311	0.642510	0.543472	0.045*
H16B	0.670741	0.670141	0.591780	0.045*
C17	0.8412 (5)	0.7779 (3)	0.6165 (3)	0.0386 (7)
H17A	0.779730	0.776918	0.696102	0.046*
H17B	0.964794	0.775162	0.610989	0.046*
C18	0.8093 (5)	0.9053 (3)	0.5144 (3)	0.0406 (7)
H18A	0.832848	0.981153	0.529282	0.049*
H18B	0.687247	0.904205	0.516041	0.049*
C19	0.8714 (6)	0.7165 (4)	-0.0514 (3)	0.0552 (10)
H19A	0.972594	0.664450	-0.055484	0.083*
H19B	0.893616	0.802985	-0.123010	0.083*
H19C	0.773928	0.668979	-0.050252	0.083*
C20	0.8846 (7)	0.8629 (4)	0.0483 (4)	0.0683 (13)
H20A	0.793094	0.891955	0.098904	0.103*
H20B	0.907455	0.928588	-0.037358	0.103*
H20C	0.988418	0.854195	0.075477	0.103*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0870 (3)	0.0396 (2)	0.0379 (2)	-0.02465 (19)	-0.01769 (19)	-0.00405 (15)
Br2	0.0480 (2)	0.03483 (19)	0.03595 (19)	-0.00702 (14)	-0.00713 (14)	-0.01459 (14)
N1	0.070 (2)	0.0335 (14)	0.0294 (13)	-0.0024 (13)	-0.0171 (13)	-0.0132 (11)
N2	0.0564 (17)	0.0280 (13)	0.0286 (12)	-0.0006 (11)	-0.0137 (11)	-0.0133 (10)
N3	0.0453 (15)	0.0297 (13)	0.0298 (12)	-0.0058 (11)	-0.0160 (11)	-0.0087 (10)
N4	0.068 (2)	0.0363 (15)	0.0358 (15)	-0.0161 (14)	-0.0163 (14)	-0.0067 (12)
C1	0.0333 (14)	0.0294 (14)	0.0289 (14)	0.0005 (11)	-0.0102 (11)	-0.0118 (11)
C2	0.0408 (17)	0.0364 (16)	0.0351 (16)	-0.0080 (13)	-0.0134 (13)	-0.0122 (13)
C3	0.0507 (19)	0.0274 (14)	0.0321 (15)	-0.0053 (13)	-0.0081 (13)	-0.0096 (12)
C4	0.074 (2)	0.0338 (17)	0.0284 (15)	-0.0023 (16)	-0.0110 (15)	-0.0141 (13)
C5	0.0517 (18)	0.0257 (14)	0.0290 (14)	0.0020 (13)	-0.0107 (13)	-0.0137 (11)
C6	0.0329 (14)	0.0303 (14)	0.0266 (13)	0.0023 (11)	-0.0100 (11)	-0.0144 (11)
C7	0.0328 (14)	0.0272 (14)	0.0293 (14)	0.0023 (11)	-0.0127 (11)	-0.0099 (11)
C8	0.0484 (18)	0.0303 (15)	0.0341 (15)	-0.0027 (13)	-0.0182 (13)	-0.0147 (12)
C9	0.056 (2)	0.0262 (14)	0.0380 (16)	-0.0069 (13)	-0.0218 (15)	-0.0100 (12)
C10	0.0364 (16)	0.0331 (15)	0.0337 (15)	-0.0062 (12)	-0.0127 (12)	-0.0087 (12)
C11	0.0449 (18)	0.0364 (16)	0.0317 (15)	0.0008 (13)	-0.0106 (13)	-0.0161 (13)
C12	0.0485 (18)	0.0290 (15)	0.0337 (16)	0.0006 (13)	-0.0121 (13)	-0.0166 (13)
C13	0.0416 (17)	0.0328 (15)	0.0387 (16)	0.0016 (13)	-0.0165 (13)	-0.0140 (13)
C14	0.0522 (19)	0.0370 (17)	0.0324 (16)	-0.0025 (14)	-0.0114 (14)	-0.0157 (13)

C15	0.060 (2)	0.0330 (16)	0.0379 (17)	-0.0038 (14)	-0.0218 (15)	-0.0167 (13)
C16	0.0467 (18)	0.0334 (16)	0.0367 (16)	-0.0051 (13)	-0.0157 (13)	-0.0157 (13)
C17	0.0475 (18)	0.0349 (16)	0.0422 (18)	0.0015 (14)	-0.0184 (14)	-0.0210 (14)
C18	0.0502 (19)	0.0333 (16)	0.0441 (18)	0.0022 (14)	-0.0165 (15)	-0.0199 (14)
C19	0.071 (3)	0.049 (2)	0.0316 (17)	-0.0067 (19)	-0.0104 (17)	-0.0059 (15)
C20	0.112 (4)	0.0352 (19)	0.051 (2)	-0.026 (2)	-0.031 (2)	-0.0034 (17)

Geometric parameters (Å, °)

Br1—C3	1.905 (3)	C11—C12	1.376 (4)
Br2—C18	1.993 (4)	C11—H11	0.9500
N1—C5	1.346 (4)	C12—H12	0.9500
N1—C4	1.347 (4)	C13—C14	1.512 (5)
N2—C5	1.373 (4)	C13—H13A	0.9900
N2—C6	1.387 (4)	C13—H13B	0.9900
N2—C13	1.497 (4)	C14—C15	1.523 (4)
N3—C6	1.321 (4)	C14—H14A	0.9900
N3—C1	1.381 (4)	C14—H14B	0.9900
N4—C10	1.373 (4)	C15—C16	1.530 (5)
N4—C20	1.449 (5)	C15—H15A	0.9900
N4—C19	1.464 (5)	C15—H15B	0.9900
C1—C2	1.385 (4)	C16—C17	1.528 (4)
C1—C5	1.396 (4)	C16—H16A	0.9900
C2—C3	1.376 (4)	C16—H16B	0.9900
C2—H2	0.9500	C17—C18	1.514 (5)
C3—C4	1.399 (5)	C17—H17A	0.9900
C4—H4	0.9500	C17—H17B	0.9900
C6—C7	1.461 (4)	C18—H18A	0.9900
C7—C12	1.396 (4)	C18—H18B	0.9900
C7—C8	1.404 (4)	C19—H19A	0.9800
C8—C9	1.383 (4)	C19—H19B	0.9800
C8—H8	0.9500	C19—H19C	0.9800
C9—C10	1.408 (4)	C20—H20A	0.9800
C9—H9	0.9500	C20—H20B	0.9800
C10—C11	1.401 (4)	C20—H20C	0.9800
Br1...C11 ⁱ	3.734 (4)	C9...H20A	2.72
Br2...N1 ⁱⁱ	3.597 (3)	C9...H14B ^{vi}	2.91
Br2...N2 ⁱⁱ	3.591 (3)	C9...H20C	2.89
Br2...C5 ⁱⁱ	3.515 (4)	C11...H19C	2.73
Br2...C13 ⁱⁱ	3.711 (4)	C11...H19A	2.81
Br1...H14A ⁱⁱⁱ	3.05	C12...H14B ^{vi}	2.99
Br1...H11 ⁱ	3.07	C13...H8	2.66
Br2...H16A	3.08	C14...H8	2.90
Br2...H13B ⁱⁱ	3.09	C16...H8	2.85
Br2...H18A ^{iv}	3.06	C16...H13A	2.87
Br2...H19B ^v	3.11	C19...H11	2.47
N1...C4 ⁱⁱⁱ	3.380 (5)	C20...H9	2.54

N1...H13B	2.80	C20...H20B ^v	2.92
N1...H4 ⁱⁱⁱ	2.67	C20...H20C ^v	2.97
N2...H8	2.89	H2...H18B ^{vii}	2.53
N3...H12	2.57	H8...H13A	2.14
N3...H16B ^{vi}	2.84	H8...H14B	2.47
N3...H18B ^{vii}	2.68	H8...H16A	2.42
C1...C18 ^{vii}	3.467 (5)	H8...H16B	2.50
C2...C18 ^{vii}	3.370 (5)	H9...H20A	2.18
C4...C19 ^{viii}	3.597 (6)	H9...H20C	2.51
C4...C4 ⁱⁱⁱ	3.372 (5)	H11...C19	2.47
C8...C13	3.198 (5)	H11...H19C	2.21
C20...C20 ^v	3.279 (7)	H13A...H16A	2.37
C1...H18A ^{vii}	2.89	H13B...H15A	2.57
C2...H18B ^{vii}	2.88	H14B...H16B	2.28
C4...H4 ⁱⁱⁱ	2.87	H15B...H17A	2.40
C7...H14B ^{vi}	2.93	H16B...H18B	2.37
C7...H13A	2.84	H19B...H20B	2.14
C8...H13A	2.61	H20B...H20C ^v	2.43
C8...H14B ^{vi}	2.85		
C5—N1—C4	112.1 (3)	C14—C13—H13A	109.4
C5—N2—C6	105.4 (2)	N2—C13—H13B	109.4
C5—N2—C13	124.1 (2)	C14—C13—H13B	109.4
C6—N2—C13	129.9 (3)	H13A—C13—H13B	108.0
C6—N3—C1	105.2 (2)	C13—C14—C15	112.5 (3)
C10—N4—C20	119.7 (3)	C13—C14—H14A	109.1
C10—N4—C19	120.1 (3)	C15—C14—H14A	109.1
C20—N4—C19	117.7 (3)	C13—C14—H14B	109.1
N3—C1—C2	131.6 (3)	C15—C14—H14B	109.1
N3—C1—C5	109.6 (3)	H14A—C14—H14B	107.8
C2—C1—C5	118.7 (3)	C14—C15—C16	111.1 (3)
C3—C2—C1	115.2 (3)	C14—C15—H15A	109.4
C3—C2—H2	122.4	C16—C15—H15A	109.4
C1—C2—H2	122.4	C14—C15—H15B	109.4
C2—C3—C4	122.1 (3)	C16—C15—H15B	109.4
C2—C3—Br1	120.0 (2)	H15A—C15—H15B	108.0
C4—C3—Br1	117.9 (2)	C17—C16—C15	114.3 (3)
N1—C4—C3	124.2 (3)	C17—C16—H16A	108.7
N1—C4—H4	117.9	C15—C16—H16A	108.7
C3—C4—H4	117.9	C17—C16—H16B	108.7
N1—C5—N2	125.4 (3)	C15—C16—H16B	108.7
N1—C5—C1	127.6 (3)	H16A—C16—H16B	107.6
N2—C5—C1	106.8 (3)	C18—C17—C16	112.2 (3)
N3—C6—N2	113.0 (3)	C18—C17—H17A	109.2
N3—C6—C7	121.8 (2)	C16—C17—H17A	109.2
N2—C6—C7	125.3 (3)	C18—C17—H17B	109.2
C12—C7—C8	117.0 (3)	C16—C17—H17B	109.2
C12—C7—C6	118.3 (3)	H17A—C17—H17B	107.9

C8—C7—C6	124.6 (3)	C17—C18—Br2	113.4 (2)
C9—C8—C7	121.5 (3)	C17—C18—H18A	108.9
C9—C8—H8	119.3	Br2—C18—H18A	108.9
C7—C8—H8	119.3	C17—C18—H18B	108.9
C8—C9—C10	121.0 (3)	Br2—C18—H18B	108.9
C8—C9—H9	119.5	H18A—C18—H18B	107.7
C10—C9—H9	119.5	N4—C19—H19A	109.5
N4—C10—C11	120.6 (3)	N4—C19—H19B	109.5
N4—C10—C9	122.0 (3)	H19A—C19—H19B	109.5
C11—C10—C9	117.3 (3)	N4—C19—H19C	109.5
C12—C11—C10	121.2 (3)	H19A—C19—H19C	109.5
C12—C11—H11	119.4	H19B—C19—H19C	109.5
C10—C11—H11	119.4	N4—C20—H20A	109.5
C11—C12—C7	122.0 (3)	N4—C20—H20B	109.5
C11—C12—H12	119.0	H20A—C20—H20B	109.5
C7—C12—H12	119.0	N4—C20—H20C	109.5
N2—C13—C14	111.0 (3)	H20A—C20—H20C	109.5
N2—C13—H13A	109.4	H20B—C20—H20C	109.5
C6—N3—C1—C2	-179.0 (3)	N3—C6—C7—C12	-24.9 (4)
C6—N3—C1—C5	-0.6 (3)	N2—C6—C7—C12	153.7 (3)
N3—C1—C2—C3	178.0 (3)	N3—C6—C7—C8	151.0 (3)
C5—C1—C2—C3	-0.3 (4)	N2—C6—C7—C8	-30.4 (5)
C1—C2—C3—C4	-1.5 (5)	C12—C7—C8—C9	-1.6 (5)
C1—C2—C3—Br1	-178.4 (2)	C6—C7—C8—C9	-177.5 (3)
C5—N1—C4—C3	1.0 (5)	C7—C8—C9—C10	1.2 (5)
C2—C3—C4—N1	1.2 (6)	C20—N4—C10—C11	-166.9 (4)
Br1—C3—C4—N1	178.2 (3)	C19—N4—C10—C11	-5.7 (5)
C4—N1—C5—N2	-178.8 (3)	C20—N4—C10—C9	15.9 (6)
C4—N1—C5—C1	-3.1 (5)	C19—N4—C10—C9	177.1 (3)
C6—N2—C5—N1	176.1 (3)	C8—C9—C10—N4	177.0 (3)
C13—N2—C5—N1	4.1 (5)	C8—C9—C10—C11	-0.3 (5)
C6—N2—C5—C1	-0.3 (3)	N4—C10—C11—C12	-177.4 (3)
C13—N2—C5—C1	-172.3 (3)	C9—C10—C11—C12	-0.1 (5)
N3—C1—C5—N1	-175.8 (3)	C10—C11—C12—C7	-0.3 (5)
C2—C1—C5—N1	2.9 (5)	C8—C7—C12—C11	1.2 (5)
N3—C1—C5—N2	0.5 (4)	C6—C7—C12—C11	177.4 (3)
C2—C1—C5—N2	179.2 (3)	C5—N2—C13—C14	-80.8 (4)
C1—N3—C6—N2	0.4 (3)	C6—N2—C13—C14	109.3 (4)
C1—N3—C6—C7	179.1 (3)	N2—C13—C14—C15	-166.1 (3)
C5—N2—C6—N3	0.0 (3)	C13—C14—C15—C16	80.7 (4)
C13—N2—C6—N3	171.4 (3)	C14—C15—C16—C17	167.7 (3)
C5—N2—C6—C7	-178.8 (3)	C15—C16—C17—C18	-163.7 (3)
C13—N2—C6—C7	-7.4 (5)	C16—C17—C18—Br2	-67.2 (3)

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

Hydrogen-bond geometry (Å, °)

Cg3 is the centroid of the C7–C12 phenyl ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C14—H14 <i>B</i> \cdots <i>Cg3</i> ^{vi}	0.99	2.60	3.502 (4)	151
C15—H15 <i>A</i> \cdots <i>Cg3</i> ⁱⁱ	0.99	2.94	3.904 (4)	165

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