

Received 23 October 2018

Accepted 22 November 2018

Edited by H. Stoeckli-Evans, University of  
Neuchâtel, Switzerland

**Keywords:** crystal structure; imidazole;  
imidazo[1,2-*a*]pyridine derivatives; N—H···N  
hydrogen bonding; C—H··· $\pi$  interactions; offset  
 $\pi$ – $\pi$  interactions; Hirshfeld surface analysis;  
fingerprint plots.

**CCDC references:** 1838744; 1858376

**Supporting information:** this article has  
supporting information at journals.iucr.org/e

# Crystal structure and Hirshfeld surface analysis of two imidazo[1,2-*a*]pyridine derivatives: *N*-*tert*-butyl-2-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridin-3-amine and *N*-*tert*-butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-*a*]pyridin-3-amine

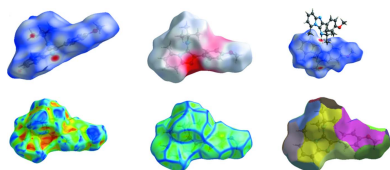
G. Dhanalakshmi,<sup>a</sup> Mala Ramanjaneyulu,<sup>b</sup> Sathiah Thennarasu<sup>b</sup> and  
S. Aravindhan<sup>c\*</sup>

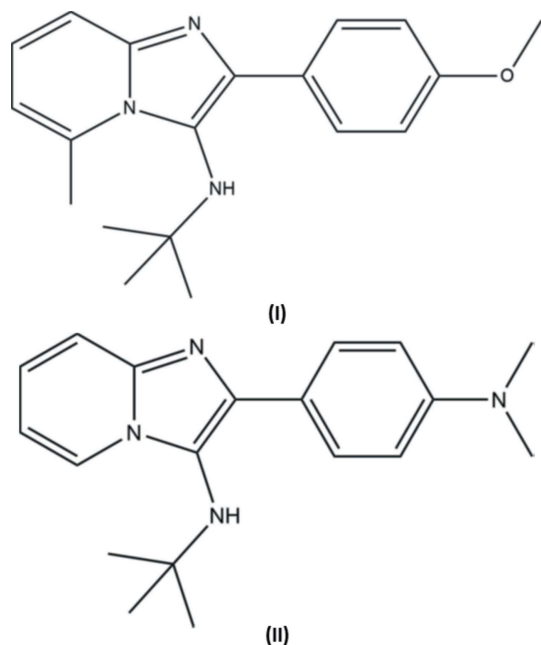
<sup>a</sup>Department of Physics, Misrimal Navajee Munoth Jain Engineering College, Chennai 600 097, India, <sup>b</sup>Organic & Bio-organic Chemistry Laboratory, Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Leather Research Institute Adyar, Chennai 600 020, India, and <sup>c</sup>Department of Physics, Presidency College (Autonomous), Chennai 600 005, India. \*Correspondence e-mail: aravindhanpresidency@gmail.com

In the title imidazo[1,2-*a*]pyridine derivatives, *N*-*tert*-butyl-2-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridin-3-amine, C<sub>19</sub>H<sub>23</sub>N<sub>3</sub>O, (I), and *N*-*tert*-butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-*a*]pyridin-3-amine, C<sub>19</sub>H<sub>24</sub>N<sub>4</sub>, (II), the 4-methoxyphenyl ring in (I) and the 4-(dimethylamino)phenyl ring in (II) are inclined to the respective imidazole rings by 26.69 (9) and 31.35 (10)°. In the crystal of (I), molecules are linked by N—H···N hydrogen bonds, forming chains propagating along the [001] direction. The chains are linked by C—H··· $\pi$  interactions, forming layers parallel to the (010) plane. In (II), the crystal packing also features N—H···N hydrogen bonds, which together with C—H···N hydrogen bonds link molecules to form chains propagating along the *c*-axis direction. The chains are linked by C—H··· $\pi$  interactions to form layers parallel to the (100) plane. Inversion-related layers are linked by offset  $\pi$ – $\pi$  interactions [intercentroid distance = 3.577 (1) Å]. The intermolecular interactions of both compounds were analyzed using Hirshfeld surface analysis and two-dimensional fingerprint plots.

## 1. Chemical context

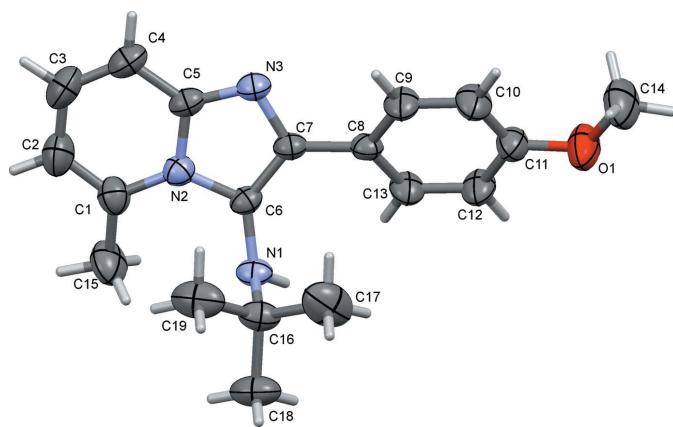
Imidazoles are heterocyclic compounds which show important pharmacological and biochemical properties. They exhibit anti-fungal (Banfi *et al.*, 2006), anti-bacterial (Jackson *et al.*, 2000), anti-tumour (Dooley *et al.*, 1992; Cui *et al.*, 2003), anti-protozoal (Biftu *et al.*, 2006), anti-herpes (Gudmundsson & Johns, 2007), anti-inflammatory (Rupert *et al.*, 2003), anti-ulcerative, anti-hypertensive, anti-histaminic and anti-helminthic properties (Spasov *et al.*, 1999). They also exhibit different therapeutic (Silvestre *et al.*, 1998; Lhassani *et al.*, 1999; Ertl *et al.*, 2000) and fluorescence properties (Kawai *et al.*, 2001; Abdullah, 2005). Imidazo[1,2-*a*]pyridines have been shown to be highly active against human cytomegalovirus and varicella-zoster virus (Gueffier *et al.*, 1998; Mavel *et al.*, 2002). In the present study, we report the synthesis, the single crystal X-ray diffraction studies, and Hirshfeld surface analysis of two new novel imidazole derivatives, *N*-*tert*-butyl-2-(4-methoxyphenyl)-5-methylimidazo[1,2-*a*]pyridin-3-amine, (I), and *N*-*tert*-butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-*a*]pyridin-3-amine, (II).



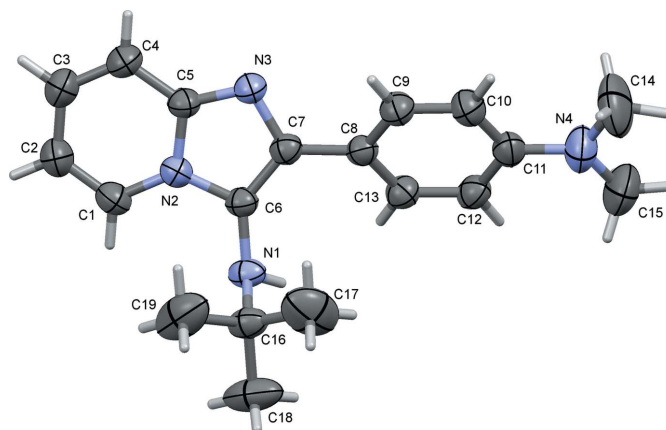


## 2. Structural commentary

The molecular structure of compound (I) is shown in Fig. 1, and that of compound (II) in Fig. 2. The overall conformation of the two molecules is similar, as shown in the structural overlap drawing, Fig. 3. In compound (I), the imidazole ring system is planar with an r.m.s deviation of 0.062 Å and a maximum deviation of 0.071 (2) Å for atom C1. In compound (II), the imidazole ring system is planar with an r.m.s deviation of 0.029 Å and a maximum deviation of 0.031 (2) Å for atom N2. In (I) the pyridine ring (N2/C1–C5) of the imidazole ring system makes a dihedral angle of 4.91 (11)° with the five-membered ring (N2/N3/C5–C7), while the corresponding angle in (II) is 2.90 (13)°. In both compounds, the difference in endocyclic angles [129.27 (19)° for bond angle C4–C5–N3 and 132.33 (17)° for bond angle C1–N2–C6 in compound



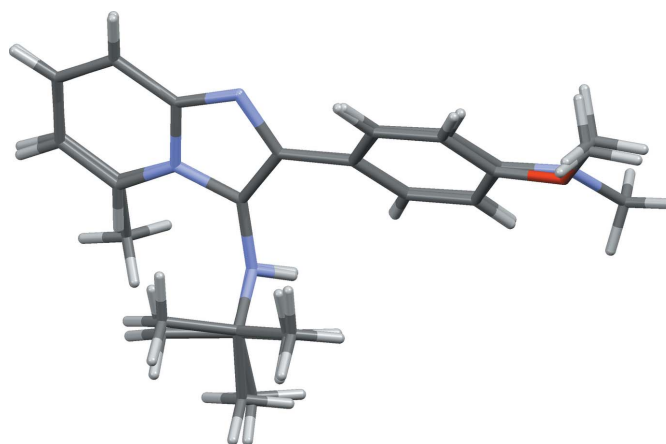
**Figure 1**  
The molecular structure of compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The molecular structure of compound (II), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

(I), and 131.1 (2) and 130.4 (2)°, respectively, in compound (II)] of the imidazole ring systems are due to the merging of five- and six-membered rings and the strain is taken up by angular distortion rather than by bond length distortion.

The dihedral angle between the pyridine (N2/C1–C5) and the benzene (C8–C13) rings is 25.04 (10)° in (I) and 31.11 (12)° in (II). In (I) the methoxy group (C11/O1/C14) lies in the plane of the benzene ring (C8–C13) to which it is attached, with a dihedral angle of 0.6 (2)°. In (II) the dimethylamino group (N4/C14/C15) also lies close to the plane of the benzene ring (C8–C13) with a dihedral angle of 1.42 (19)°. The dihedral angle between atoms N1/C16/C18 and the imidazole ring mean plane is 80.28 (19)° in (I) and 84.6 (2)° in (II). The sum of the bond angles around atom N2 is 359.87° in (I), and the sums around atoms N2 and N4 in (II) are 359.85 and 360.0°, respectively, indicating  $sp^2$  hybridization. In compound (I) the torsion angles C10–C9–C8–C7 and C18–C16–N1–C6 are –178.9 (2) and 170.52 (18)°, respectively, while the corresponding torsion angles in compound (II) are –177.9 (2) and 179.4 (2)°, respectively. This shows that for both compounds the imidazole ring is (–) antiperiplanar with the



**Figure 3**  
A structural overlap view of molecules (I) and (II).

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

Cg4 is the centroid of the imidazole ring system N2/N3/C1–C7.

<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>
N1–H1A...N3 <sup>i</sup>	0.84 (2)	2.41 (2)	3.226 (2)	163.6 (19)
C14–H14A...Cg4 <sup>ii</sup>	0.96	2.93	3.862 (3)	165

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

**Table 2**

Hydrogen-bond geometry (Å, °) for (II).

Cg3 is the centroid of benzene ring C8–C13.

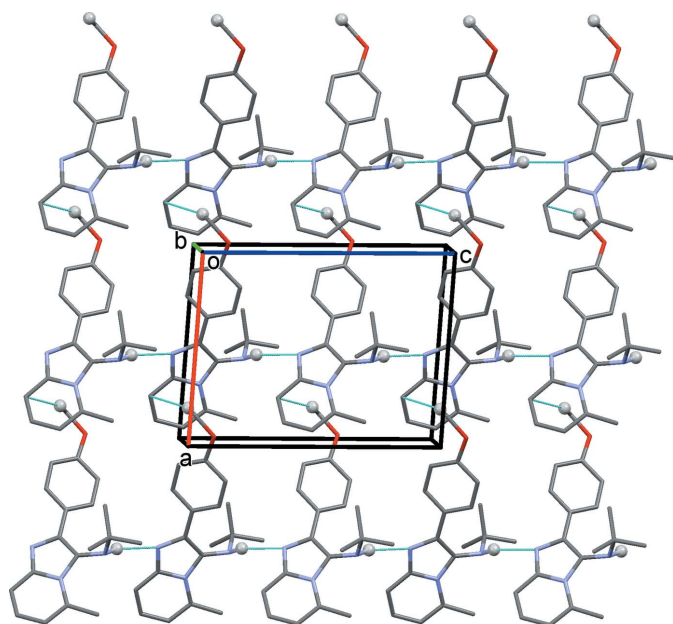
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1A...N3 <sup>i</sup>	0.86 (3)	2.56 (3)	3.412 (3)	167 (2)
C13–H13...N3 <sup>i</sup>	0.93	2.57	3.467 (3)	161
C19–H19B...Cg3 <sup>ii</sup>	0.96	2.87	3.829 (4)	174

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

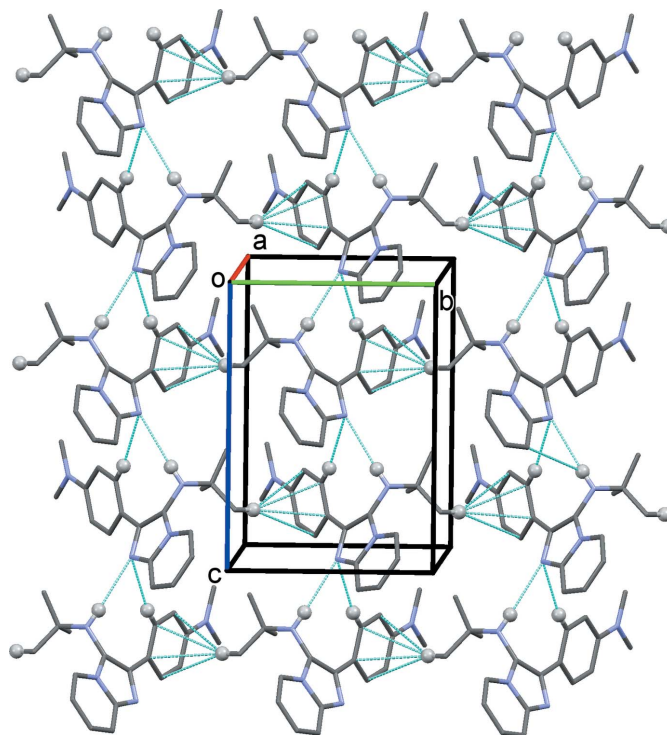
benzene ring and (+) antiperiplanar with the side-chain atoms N1, C16 and C18.

### 3. Supramolecular features

In the crystal of (I), molecules are linked by N1–H1A...N3<sup>i</sup> hydrogen bonds (Table 1), forming *C*(8) chains propagating along the *c*-axis direction, as shown in Fig. 4. The chains are linked by C–H... $\pi$  interactions, forming layers lying parallel to the *ac* plane (Fig. 4, Table 1).


**Figure 4**

The crystal packing of compound (I) viewed along the *b* axis, showing the intermolecular N–H...N hydrogen bonds as dashed lines (Table 1). The C–H... $\pi$  interactions are also represented by cyan dashed lines (Table 1).

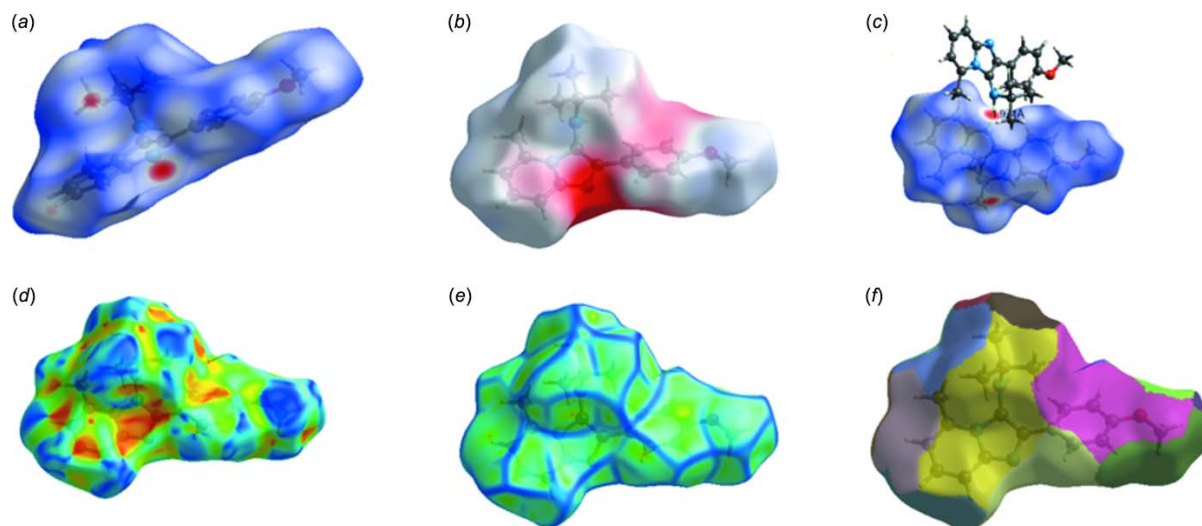

**Figure 5**

The crystal packing of compound (II) viewed along the *a* axis, showing the intermolecular N–H...N and C–H...N hydrogen bonds and C–H... $\pi$  interactions as dashed lines (Table 2).

In the crystal of (II), molecules are linked by N1–H1A...N3<sup>i</sup> and C13–H13...N3<sup>i</sup> hydrogen bonds (Table 2), forming chains propagating along the [001] direction, as shown in Fig. 5. The chains are also linked by C–H... $\pi$  interactions, forming layers lying parallel to the *bc* plane (Fig. 5, Table 2). Inversion-related layers are linked by offset  $\pi$ – $\pi$  interactions involving the pyridine ring of the imidazole ring system: Cg2...Cg2<sup>iii</sup> = 3.577 (1) Å, Cg2 is the centroid of the pyridine ring (N2/C1–C5),  $\alpha = 0.0$  (1)°,  $\beta = 22.3$ °, interplanar distance = 3.309 (1) Å, offset = 1.357 Å; symmetry code (iii)  $-x + 1, -y + 1, -z + 1$ .

### 4. Hirshfeld Surface Analysis

Hirshfeld surface analysis was used to quantify the intermolecular contacts of the title compounds, using the software *CrystalExplorer17.5* (Turner *et al.*, 2017). The bright-red spots on the Hirshfeld surface mapped over  $d_{\text{norm}}$  [Fig. 6(a) and 7(a)], show the presence of N–H...N and C–H...N interactions with neighbouring molecules. The surfaces mapped over the electrostatic potential are illustrated in Fig. 6(b) and 7(b), while Fig. 6(c) and 7(c) show the intermolecular contacts. The presence of red and blue triangles on the shape index map [Fig. 7(d)], indicates the presence of  $\pi$ – $\pi$  stacking interactions in compound (II), and their absence in Fig. 6(d) shows that such interactions are absent in compound (I). The large flat region in Fig. 7(e), shown on the curvature map, confirms the presence of C–H... $\pi$  interactions in compound (II). The



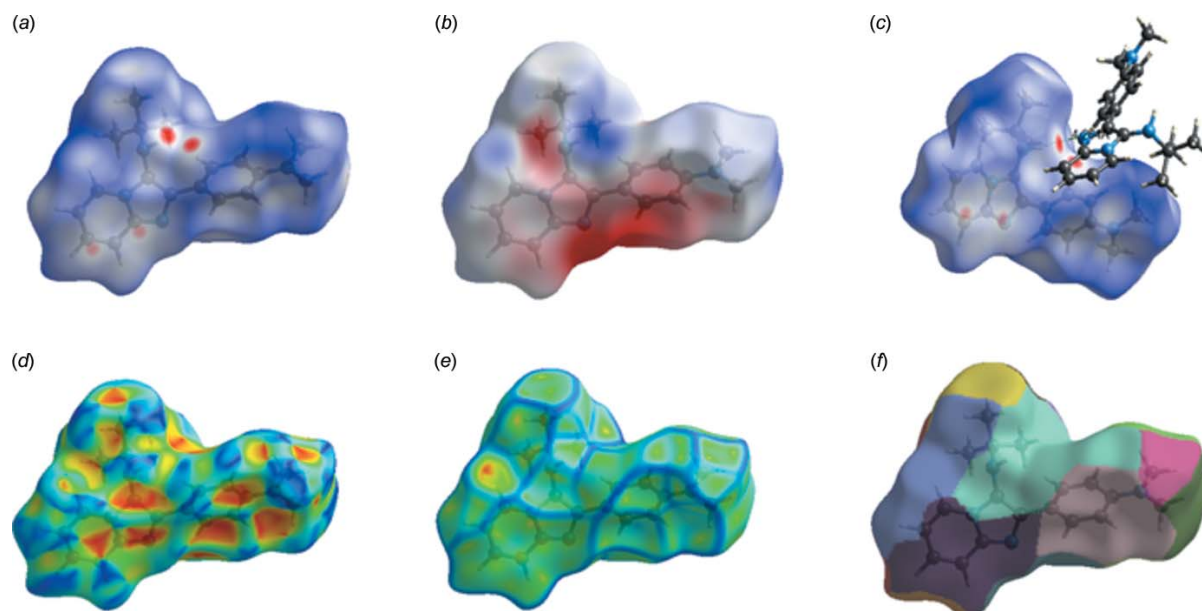
**Figure 6**  
View of the Hirshfeld surface for compound (I), mapped over: (a)  $d_{\text{norm}}$ ; (b) electrostatic potential; (c) intermolecular contacts; (d) shape index; (e) curvature; (f) fragment patches.

fragment patches on the Hirshfeld surface [Figs. 6(f) and 7(f)] show the coordination environments of the molecules. The complete two-dimensional fingerprint plots are shown in Fig. 8(a) and 9(a). The  $\text{H}\cdots\text{H}$ ,  $\text{C}\cdots\text{H}$ ,  $\text{N}\cdots\text{H}$ ,  $\text{C}\cdots\text{N}$ ,  $\text{H}\cdots\text{O}$  and  $\text{C}\cdots\text{C}$  interactions are illustrated in Fig. 8(b)–8(e) for (I) and Fig. 9(b)–9(e) for (II). The  $\text{H}\cdots\text{H}$  interactions make the largest contributions [Fig. 8(b) and 9(b)] to the overall Hirshfeld surfaces [68.3% for compound (I) and 71.6% for compound (II)]. The  $\text{C}\cdots\text{H}$  interactions appear as two wings in the fingerprint plot [Fig. 8(c) and 9(c)], showing a contribution of 18.2% for compound (I) and 17.7% for compound (II) of the Hirshfeld surfaces. The contribution from the  $\text{N}\cdots\text{H}$  contacts, corresponding to  $\text{C}-\text{H}\cdots\text{N}$  interactions, is represented by a pair of sharp spikes with a contribution of

7.1% for compound (I) and 8.2% for compound (II) of the Hirshfeld surfaces [Fig. 8(d) and 9(d)]. The  $\text{H}\cdots\text{O}$  contacts have a contribution of 5.4% of the Hirshfeld surface for compound (I). The  $\text{C}\cdots\text{C}$  contacts, which refers to  $\pi-\pi$  interactions, contribute 1.8% of the Hirshfeld surfaces for compound (II). This can be seen in the shape of a butterfly at  $d_e = d_i$  1.7 Å [Fig. 9(e)].

## 5. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39, last update August 2018; Groom *et al.*, 2016) revealed 29 hits for substructure imidazo[1,2-*a*]pyridin-3-amine and 16 hits for 5-methyl imidazo[1,2-*a*]pyridin-3-amine. Two compounds,



**Figure 7**  
View of the Hirshfeld surface for compound (II), mapped over: (a)  $d_{\text{norm}}$ ; (b) electrostatic potential; (c) intermolecular contacts; (d) shape index; (e) curvature; (f) fragment patches.

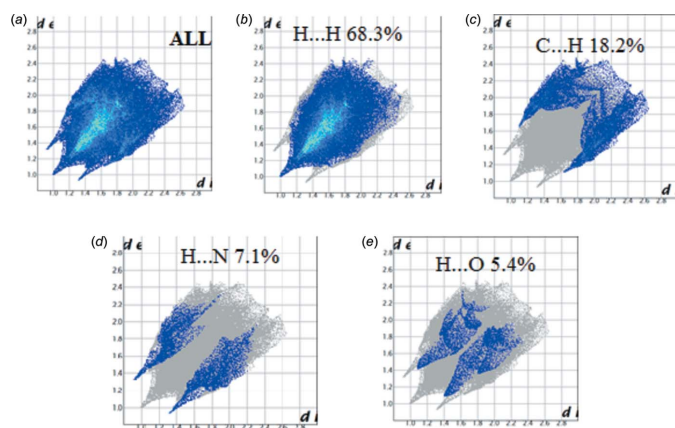


Figure 8

Two-dimensional fingerprint plots for compound (I): (a) all intermolecular interactions; (b) H...H contacts; (c) C...H contacts; (d) H...N contacts; (e) H...O contacts.

(5-methylimidazo[1,2-*a*]pyridin-2-yl)methanol (CSD refcode PONVUL; Elaataoui *et al.*, 2014), and ethyl 5-methylimidazo[1,2-*a*]pyridine-2-carboxylate (DUSWOE; Yao *et al.*, 2010) are close analogues of compound (I). A third compound, (*E*)-2-phenyl-*N*-(thiophen-2-ylmethylidene)imidazo[1,2-*a*]pyridin-3-amine (OLEBOY; Elaataoui *et al.*, 2016), is a close analogue of compound (II). The crystal packing of compounds (I) and (II) are stabilized by N—H...N, C—H...N and C—H... $\pi$  interactions, but the above mentioned crystal structures exhibit in general C—H...O, O—H...N and  $\pi$ – $\pi$  interactions.

An interesting pyrazine analogue of compound (II) has been reported, *i.e.* *N*-*tert*-butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-*a*]pyrazin-3-amine (WIGKOO; Fatima *et al.*, 2013). Here the pyrazine and benzene rings are inclined to each other by 16.96 (7)°, compared to the corresponding dihedral angle of 31.11 (12)° involving the pyridine and benzene rings in (II). In the crystal, molecules are linked *via* N—H...N hydrogen bonds, forming chains along [010], which in turn are linked by C—H...N hydrogen bonds forming layers parallel to the *ab* plane. This is very similar to the crystal-packing arrangement observed for compound (II).

## 6. Synthesis and crystallization

### Compound (I)

5-Methyl-2-aminopyridine (10 mmol) and 4-methoxybenzaldehyde (1 eq.) were solubilized in ethanol. To this solution, *tert*-butyl isocyanide (1 eq.) and iodine (0.5 mmol %) were added. The reaction mixture was stirred at room temperature overnight. The white precipitate that had formed was filtered off and purified further using silica-gel column chromatography to give a white solid in 60% yield.

### Compound (II)

2-Aminopyridine (10 mmol) and 4-(dimethylamino)benzaldehyde (1 eq.) were solubilized in ethanol. To this solution, *tert*-butyl isocyanide (1 eq.) and iodine (0.5 mmol %) were added. The reaction mixture was stirred at room

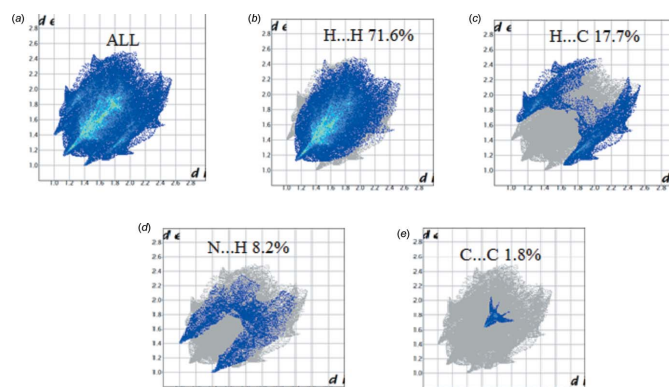


Figure 9

Two-dimensional fingerprint plots for compound (II): (a) all intermolecular interactions; (b) H...H contacts; (c) H...C contacts; (d) N...H contacts; (e) C...C contacts.

temperature overnight. The white precipitate that formed was filtered off and purified further using silica-gel column chromatography to give a yellow solid (yield 0.282 g, 91%).

**Spectroscopic data:** NMR spectra were recorded on a Bruker 400 MHz NMR spectrophotometer in CdCl<sub>3</sub> and chemical shifts were recorded in parts per million relative to tetramethylsilane (TMS), used as an internal standard.

### Compound (I)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.57 (*ddd*, *J* = 4.9, 1.8, 0.9, 1H), 8.14 (*dt*, *J* = 8.0, 1.0, 1H), 7.77 (*td*, *J* = 7.7, 1.8, 1H), 7.40 (*d*, *J* = 9.0, 1H), 7.16 (*ddd*, *J* = 7.5, 4.9, 1.2, 1H), 7.01 (*dd*, *J* = 9.0, 6.7, 1H), 6.46–6.41 (*m*, 1H), 4.99 (*s*, 1H), 2.96 (*s*, 3H), 0.93 (*s*, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.31, 148.37, 142.86, 138.16, 137.65, 137.35, 136.54, 130.34, 124.28, 121.80, 121.79, 115.58, 113.91, 105.48, 57.20, 28.97, 20.21.

### Compound (II)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  1.05 [*s*, 9H, –C(CH<sub>3</sub>)<sub>3</sub>], 2.97 [*s*, 6H, Ar–N(CH<sub>3</sub>)<sub>2</sub>], 6.69 (*t*, 1H, –Ar–H), 6.77 (*d*, 2H, *J* = 8.40 Hz, –Ar–H), 7.17 (*t*, 1H, –Ar–H, –Ar–H), 7.53 (*d*, 1H, *J* = 8.40 Hz, –Ar–H), 7.8 (*d*, 2H, *J* = 4.5 Hz, –Ar–H), 8.19 (*d*, 1H, *J* = 8.40 Hz, –Ar–H). ESI–MS: calculated for C<sub>19</sub>H<sub>24</sub>N<sub>4</sub> [*M* + *H*]<sup>+</sup> 308.2007; found: 308.27.

Crystals of compounds (I) and (II), suitable for X-ray diffraction analysis, were obtained by slow evaporation from ethyl alcohol (EtOH) solution at room temperature.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For both compounds the NH H atoms were located in difference-Fourier maps and freely refined. The C-bound H atoms were included in calculated positions and treated as riding: C—H = 0.93–0.96 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$  and  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

## Acknowledgements

The authors wish to acknowledge the SAIF, IIT, Madras for the data collection.

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C <sub>19</sub> H <sub>23</sub> N <sub>3</sub> O	C <sub>19</sub> H <sub>24</sub> N <sub>4</sub>
<i>M<sub>r</sub></i>	309.40	308.42
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Monoclinic, <i>C</i> <sub>2</sub> / <i>c</i>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.2357 (7), 15.6388 (12), 11.984 (1)	34.9185 (14), 8.4656 (5), 11.8361 (6)
β (°)	93.998 (3)	91.061 (5)
<i>V</i> (Å <sup>3</sup> )	1726.7 (2)	3498.2 (3)
<i>Z</i>	4	8
Radiation type	Mo Kα	Mo Kα
μ (mm <sup>-1</sup> )	0.08	0.07
Crystal size (mm)	0.15 × 0.15 × 0.10	0.15 × 0.10 × 0.10
Data collection		
Diffractometer	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.552, 0.746	0.697, 0.745
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	16458, 3208, 2109	32313, 3259, 1834
<i>R<sub>int</sub></i>	0.044	0.071
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.606	0.606
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.047, 0.119, 1.03	0.049, 0.159, 1.02
No. of reflections	3208	3259
No. of parameters	218	218
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.15, -0.13	0.22, -0.18

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae et al., 2008), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

## References

- Abdullah, Z. (2005). *Int. J. Chem. Sci.* **3**, 9–15.
- Banfi, E., Scialino, G., Zampieri, D., Mamolo, M. G., Vio, L., Ferrone, M., Fermeglia, M., Paneni, M. S. & Pricl, S. (2006). *J. Antimicrob. Chemother.* **58**, 76–84.
- Biftu, T., Feng, D., Fisher, M., Liang, G. B., Qian, X., Scribner, A., Dennis, R., Lee, S., Liberator, P. A., Brown, C., Gurnett, A., Leavitt, P. S., Thompson, D., Mathew, J., Misura, A., Samaras, S., Tamas, T., Sina, J. F., McNulty, K. A., McKnight, C. G., Schmatz, D. M. & Wyvrat, M. (2006). *Bioorg. Med. Chem. Lett.* **16**, 2479–2483.
- Bruker (2016). *APEX2*, *SAINT*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cui, B., Zheng, B. L., He, K. & Zheng, Q. Y. (2003). *J. Nat. Prod.* **66**, 1101–1103.
- Dooley, S. W., Jarvis, W. R., Martone, W. J. & Snider, D. E. Jr (1992). *Ann. Intern. Med.* **117**, 257–259.
- Elaatiaoui, A., Elkalai, F., Benchat, N., Saadi, M. & El Ammari, L. (2016). *IUCrData*, **1**, x160723.
- Elaatiaoui, A., Koudad, M., Saddik, R., Benchat, N. & El Ammari, L. (2014). *Acta Cryst.* **E70**, o1189–o1190.
- Ertl, P., Rohde, B. & Selzer, P. (2000). *J. Med. Chem.* **43**, 3714–3717.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Fatima, Z., Srinivasan, T., Koorathota, S., Thennarasu, S. & Velmurugan, D. (2013). *Acta Cryst.* **E69**, o612–o613.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Gudmundsson, K. S. & Johns, B. A. (2007). *Bioorg. Med. Chem. Lett.* **17**, 2735–2739.
- Gueiffier, A., Mavel, S., Lhassani, M., Elhakmaoui, A., Snoeck, R., Andrei, G., Chavignon, O., Teulade, J. C., Witvrouw, M., Balzarini, J., De Clercq, E. & Chapat, J. (1998). *J. Med. Chem.* **41**, 5108–5112.
- Jackson, C. J., Lamb, D. C., Kelly, D. E. & Kelly, S. L. (2000). *FEMS Microbiol. Lett.* **192**, 159–162.
- Kawai, M., Lee, M. J., Evans, K. O. & Nordlund, T. M. (2001). *J. Fluoresc.* **11**, 23–32.
- Lhassani, M., Chavignon, O., Chezal, J. M., Teulade, J. C., Chapat, J. P., Snoeck, R., Andrei, G., Balzarini, J., De Clercq, E. & Gueiffier, A. (1999). *Eur. J. Med. Chem.* **34**, 271–274.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Mavel, S., Renou, J. L., Galtier, C., Allouchi, H., Snoeck, R., Andrei, G., De Clercq, E., Balzarini, J. & Gueiffier, A. (2002). *Bioorg. Med. Chem.* **10**, 941–946.
- Rupert, K. C., Henry, J. R., Dodd, J. H., Wadsworth, S. A., Cavender, D. E., Olini, G. C., Fahmy, B. & Siekierka, J. J. (2003). *Bioorg. Med. Chem. Lett.* **13**, 347–350.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Silvestre, J., Leeson, P. A. & Castañer, J. (1998). *Drugs Fut.* **23**, 598–601.
- Spasov, A. A., Yozhitsa, I. N., Bugaeva, L. I. & Anisimova, V. A. (1999). *Pharm. Chem. J.* **33**, 232–243.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Turner, M. J., MacKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17.5*. University of Western Australia, Perth.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yao, J., Wang, L., Guo, B., An, K. & Guan, J. (2010). *Acta Cryst.* **E66**, o1999.

## supporting information

*Acta Cryst.* (2018). E74, 1913-1918 [https://doi.org/10.1107/S2056989018016651]

## Crystal structure and Hirshfeld surface analysis of two imidazo[1,2-a]pyridine derivatives: *N*-*tert*-butyl-2-(4-methoxyphenyl)-5-methylimidazo[1,2-a]pyridin-3-amine and *N*-*tert*-butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-a]pyridin-3-amine

G. Dhanalakshmi, Mala Ramanjaneyulu, Sathiah Thenarasu and S. Aravindhan

### Computing details

For both structures, data collection: *APEX2* (Bruker, 2016); cell refinement: *APEX2/SAINT* (Bruker, 2016); data reduction: *SAINT/XPREP* (Bruker, 2016); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008). Software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010) for (I); *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010). for (II).

### *N*-*tert*-Butyl-2-(4-methoxyphenyl)-5-methylimidazo[1,2-a]pyridin-3-amine (I)

#### Crystal data

$C_{19}H_{23}N_3O$	$F(000) = 664$
$M_r = 309.40$	$D_x = 1.190 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 9.2357 (7) \text{ \AA}$	Cell parameters from 3732 reflections
$b = 15.6388 (12) \text{ \AA}$	$\theta = 2.6\text{--}29.2^\circ$
$c = 11.984 (1) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 93.998 (3)^\circ$	$T = 296 \text{ K}$
$V = 1726.7 (2) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.15 \times 0.15 \times 0.10 \text{ mm}$

#### Data collection

Bruker Kappa APEXII CCD diffractometer	16458 measured reflections
Radiation source: fine-focus sealed tube	3208 independent reflections
Graphite monochromator	2109 reflections with $I > 2\sigma(I)$
$\omega$ and $\varphi$ scan	$R_{\text{int}} = 0.044$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$\theta_{\text{max}} = 25.5^\circ$ , $\theta_{\text{min}} = 2.2^\circ$
$T_{\text{min}} = 0.552$ , $T_{\text{max}} = 0.746$	$h = -11 \rightarrow 11$
	$k = -18 \rightarrow 18$
	$l = -14 \rightarrow 13$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$  $wR(F^2) = 0.119$  $S = 1.03$ 

3208 reflections

218 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.6929P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$ Extinction correction: SHELXL2018  
(Sheldrick, 2015b), $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.0063 (11)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.02423 (18)	0.88980 (13)	0.62308 (14)	0.0800 (6)
N1	0.58139 (18)	0.64812 (11)	0.72686 (14)	0.0385 (4)
H1A	0.560 (2)	0.6854 (13)	0.7736 (17)	0.045 (6)*
N2	0.71475 (16)	0.66024 (10)	0.55928 (13)	0.0381 (4)
N3	0.55442 (18)	0.72815 (11)	0.43982 (13)	0.0417 (4)
C1	0.8497 (2)	0.62484 (14)	0.59167 (19)	0.0480 (6)
C2	0.9389 (2)	0.60796 (16)	0.5092 (2)	0.0618 (7)
H2	1.028199	0.582474	0.528113	0.074*
C3	0.9016 (3)	0.62747 (17)	0.3962 (2)	0.0633 (7)
H3	0.963493	0.611842	0.341717	0.076*
C4	0.7768 (2)	0.66868 (14)	0.36672 (18)	0.0524 (6)
H4	0.754319	0.684394	0.292687	0.063*
C5	0.6809 (2)	0.68762 (13)	0.44948 (16)	0.0401 (5)
C6	0.5944 (2)	0.68161 (12)	0.61971 (15)	0.0345 (5)
C7	0.5016 (2)	0.72552 (12)	0.54407 (15)	0.0361 (5)
C8	0.3630 (2)	0.76695 (12)	0.56396 (15)	0.0367 (5)
C9	0.2546 (2)	0.77465 (15)	0.47894 (17)	0.0516 (6)
H9	0.270036	0.752223	0.408881	0.062*
C10	0.1244 (2)	0.81454 (16)	0.49472 (18)	0.0574 (6)
H10	0.053459	0.818460	0.435930	0.069*
C11	0.0997 (2)	0.84844 (15)	0.59730 (18)	0.0512 (6)
C12	0.2067 (2)	0.84190 (15)	0.68339 (18)	0.0540 (6)
H12	0.190965	0.864567	0.753249	0.065*
C13	0.3361 (2)	0.80227 (14)	0.66681 (17)	0.0463 (5)
H13	0.407187	0.799021	0.725600	0.056*
C14	-0.1377 (3)	0.8996 (2)	0.5385 (2)	0.0848 (9)
H14A	-0.170048	0.844251	0.512568	0.127*



H14B	-0.102994	0.931447	0.477349	0.127*
H14C	-0.217011	0.929636	0.568295	0.127*
C15	0.8957 (3)	0.61354 (19)	0.7129 (2)	0.0712 (8)
H15A	0.992141	0.590353	0.720247	0.107*
H15B	0.830116	0.575101	0.746182	0.107*
H15C	0.894405	0.667913	0.749953	0.107*
C16	0.4969 (2)	0.56772 (13)	0.73775 (17)	0.0478 (5)
C17	0.3348 (3)	0.58040 (18)	0.7103 (3)	0.0830 (9)
H17A	0.318020	0.596991	0.633344	0.124*
H17B	0.299696	0.624313	0.757429	0.124*
H17C	0.284589	0.527895	0.722769	0.124*
C18	0.5237 (3)	0.53949 (16)	0.85894 (19)	0.0676 (7)
H18A	0.491235	0.583342	0.907398	0.101*
H18B	0.625574	0.529685	0.875337	0.101*
H18C	0.471174	0.487645	0.870558	0.101*
C19	0.5532 (3)	0.50019 (15)	0.6600 (2)	0.0712 (8)
H19A	0.654518	0.490342	0.679215	0.107*
H19B	0.540247	0.519762	0.584077	0.107*
H19C	0.500409	0.447913	0.667862	0.107*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0547 (10)	0.1337 (17)	0.0507 (11)	0.0372 (11)	-0.0036 (8)	-0.0104 (11)
N1	0.0478 (10)	0.0425 (10)	0.0246 (9)	-0.0031 (8)	-0.0024 (7)	-0.0012 (8)
N2	0.0392 (9)	0.0403 (9)	0.0346 (10)	-0.0010 (7)	0.0019 (7)	-0.0022 (7)
N3	0.0473 (10)	0.0488 (10)	0.0290 (9)	0.0023 (8)	0.0035 (7)	0.0027 (8)
C1	0.0412 (12)	0.0509 (13)	0.0513 (14)	0.0026 (10)	-0.0018 (10)	-0.0050 (11)
C2	0.0425 (13)	0.0714 (17)	0.0720 (18)	0.0081 (12)	0.0084 (12)	-0.0068 (14)
C3	0.0550 (15)	0.0765 (17)	0.0612 (17)	0.0001 (13)	0.0240 (13)	-0.0099 (14)
C4	0.0582 (15)	0.0613 (15)	0.0392 (13)	-0.0063 (12)	0.0147 (11)	-0.0027 (11)
C5	0.0472 (12)	0.0430 (11)	0.0307 (11)	-0.0073 (10)	0.0058 (9)	-0.0019 (9)
C6	0.0374 (10)	0.0398 (11)	0.0263 (10)	-0.0045 (9)	0.0019 (8)	-0.0040 (8)
C7	0.0416 (11)	0.0407 (11)	0.0257 (10)	-0.0025 (9)	-0.0001 (8)	0.0006 (9)
C8	0.0400 (11)	0.0428 (11)	0.0267 (10)	-0.0002 (9)	-0.0013 (8)	0.0032 (9)
C9	0.0536 (13)	0.0747 (16)	0.0256 (11)	0.0113 (12)	-0.0037 (10)	-0.0055 (11)
C10	0.0494 (13)	0.0846 (17)	0.0363 (13)	0.0130 (12)	-0.0114 (10)	-0.0019 (12)
C11	0.0428 (12)	0.0695 (15)	0.0410 (13)	0.0112 (11)	0.0000 (10)	0.0011 (11)
C12	0.0516 (13)	0.0801 (16)	0.0300 (12)	0.0137 (12)	0.0002 (10)	-0.0098 (11)
C13	0.0457 (12)	0.0609 (14)	0.0307 (12)	0.0066 (10)	-0.0090 (9)	-0.0043 (10)
C14	0.0514 (15)	0.127 (3)	0.074 (2)	0.0277 (16)	-0.0128 (14)	-0.0110 (18)
C15	0.0511 (14)	0.097 (2)	0.0626 (17)	0.0198 (14)	-0.0146 (12)	-0.0050 (15)
C16	0.0568 (13)	0.0468 (12)	0.0386 (12)	-0.0101 (11)	-0.0062 (10)	0.0059 (10)
C17	0.0623 (17)	0.0747 (18)	0.109 (2)	-0.0249 (14)	-0.0135 (16)	0.0225 (17)
C18	0.097 (2)	0.0635 (16)	0.0422 (14)	-0.0124 (14)	0.0028 (13)	0.0133 (12)
C19	0.112 (2)	0.0494 (14)	0.0506 (15)	-0.0149 (15)	-0.0056 (14)	-0.0033 (12)

*Geometric parameters (Å, °)*

O1—C11	1.368 (3)	C10—C11	1.372 (3)
O1—C14	1.414 (3)	C10—H10	0.9300
N1—C6	1.400 (2)	C11—C12	1.382 (3)
N1—C16	1.490 (3)	C12—C13	1.373 (3)
N1—H1A	0.84 (2)	C12—H12	0.9300
N2—C1	1.394 (3)	C13—H13	0.9300
N2—C5	1.398 (2)	C14—H14A	0.9600
N2—C6	1.409 (2)	C14—H14B	0.9600
N3—C5	1.327 (2)	C14—H14C	0.9600
N3—C7	1.373 (2)	C15—H15A	0.9600
C1—C2	1.355 (3)	C15—H15B	0.9600
C1—C15	1.495 (3)	C15—H15C	0.9600
C2—C3	1.407 (3)	C16—C18	1.522 (3)
C2—H2	0.9300	C16—C19	1.523 (3)
C3—C4	1.346 (3)	C16—C17	1.523 (3)
C3—H3	0.9300	C17—H17A	0.9600
C4—C5	1.407 (3)	C17—H17B	0.9600
C4—H4	0.9300	C17—H17C	0.9600
C6—C7	1.385 (3)	C18—H18A	0.9600
C7—C8	1.469 (3)	C18—H18B	0.9600
C8—C9	1.383 (3)	C18—H18C	0.9600
C8—C13	1.389 (3)	C19—H19A	0.9600
C9—C10	1.380 (3)	C19—H19B	0.9600
C9—H9	0.9300	C19—H19C	0.9600
C11—O1—C14	118.61 (19)	C13—C12—H12	119.7
C6—N1—C16	118.36 (16)	C11—C12—H12	119.7
C6—N1—H1A	112.9 (14)	C12—C13—C8	121.27 (19)
C16—N1—H1A	112.4 (14)	C12—C13—H13	119.4
C1—N2—C5	121.38 (17)	C8—C13—H13	119.4
C1—N2—C6	132.33 (17)	O1—C14—H14A	109.5
C5—N2—C6	106.16 (15)	O1—C14—H14B	109.5
C5—N3—C7	105.83 (16)	H14A—C14—H14B	109.5
C2—C1—N2	116.8 (2)	O1—C14—H14C	109.5
C2—C1—C15	122.6 (2)	H14A—C14—H14C	109.5
N2—C1—C15	120.36 (19)	H14B—C14—H14C	109.5
C1—C2—C3	122.6 (2)	C1—C15—H15A	109.5
C1—C2—H2	118.7	C1—C15—H15B	109.5
C3—C2—H2	118.7	H15A—C15—H15B	109.5
C4—C3—C2	120.3 (2)	C1—C15—H15C	109.5
C4—C3—H3	119.9	H15A—C15—H15C	109.5
C2—C3—H3	119.9	H15B—C15—H15C	109.5
C3—C4—C5	119.0 (2)	N1—C16—C18	106.10 (17)
C3—C4—H4	120.5	N1—C16—C19	109.17 (18)
C5—C4—H4	120.5	C18—C16—C19	110.05 (19)
N3—C5—N2	111.49 (16)	N1—C16—C17	112.57 (18)

N3—C5—C4	129.27 (19)	C18—C16—C17	109.6 (2)
N2—C5—C4	119.23 (19)	C19—C16—C17	109.3 (2)
C7—C6—N1	134.20 (17)	C16—C17—H17A	109.5
C7—C6—N2	104.80 (15)	C16—C17—H17B	109.5
N1—C6—N2	120.27 (17)	H17A—C17—H17B	109.5
N3—C7—C6	111.55 (17)	C16—C17—H17C	109.5
N3—C7—C8	120.23 (17)	H17A—C17—H17C	109.5
C6—C7—C8	128.23 (17)	H17B—C17—H17C	109.5
C9—C8—C13	117.03 (18)	C16—C18—H18A	109.5
C9—C8—C7	120.86 (17)	C16—C18—H18B	109.5
C13—C8—C7	122.08 (18)	H18A—C18—H18B	109.5
C10—C9—C8	122.11 (19)	C16—C18—H18C	109.5
C10—C9—H9	118.9	H18A—C18—H18C	109.5
C8—C9—H9	118.9	H18B—C18—H18C	109.5
C11—C10—C9	119.9 (2)	C16—C19—H19A	109.5
C11—C10—H10	120.0	C16—C19—H19B	109.5
C9—C10—H10	120.0	H19A—C19—H19B	109.5
O1—C11—C10	125.4 (2)	C16—C19—H19C	109.5
O1—C11—C12	115.63 (19)	H19A—C19—H19C	109.5
C10—C11—C12	119.0 (2)	H19B—C19—H19C	109.5
C13—C12—C11	120.7 (2)		
C5—N2—C1—C2	-8.4 (3)	N1—C6—C7—N3	-166.5 (2)
C6—N2—C1—C2	176.4 (2)	N2—C6—C7—N3	3.3 (2)
C5—N2—C1—C15	166.7 (2)	N1—C6—C7—C8	14.0 (4)
C6—N2—C1—C15	-8.5 (3)	N2—C6—C7—C8	-176.20 (18)
N2—C1—C2—C3	2.2 (3)	N3—C7—C8—C9	29.4 (3)
C15—C1—C2—C3	-172.7 (2)	C6—C7—C8—C9	-151.2 (2)
C1—C2—C3—C4	3.7 (4)	N3—C7—C8—C13	-148.62 (19)
C2—C3—C4—C5	-3.5 (4)	C6—C7—C8—C13	30.8 (3)
C7—N3—C5—N2	-1.7 (2)	C13—C8—C9—C10	-0.8 (3)
C7—N3—C5—C4	176.8 (2)	C7—C8—C9—C10	-178.9 (2)
C1—N2—C5—N3	-172.63 (17)	C8—C9—C10—C11	0.3 (4)
C6—N2—C5—N3	3.7 (2)	C14—O1—C11—C10	-0.2 (4)
C1—N2—C5—C4	8.7 (3)	C14—O1—C11—C12	179.3 (2)
C6—N2—C5—C4	-174.96 (18)	C9—C10—C11—O1	179.6 (2)
C3—C4—C5—N3	179.1 (2)	C9—C10—C11—C12	0.0 (4)
C3—C4—C5—N2	-2.5 (3)	O1—C11—C12—C13	-179.5 (2)
C16—N1—C6—C7	75.4 (3)	C10—C11—C12—C13	0.1 (4)
C16—N1—C6—N2	-93.2 (2)	C11—C12—C13—C8	-0.6 (4)
C1—N2—C6—C7	171.71 (19)	C9—C8—C13—C12	0.9 (3)
C5—N2—C6—C7	-4.1 (2)	C7—C8—C13—C12	179.0 (2)
C1—N2—C6—N1	-16.7 (3)	C6—N1—C16—C18	170.52 (18)
C5—N2—C6—N1	167.46 (17)	C6—N1—C16—C19	52.0 (2)
C5—N3—C7—C6	-1.1 (2)	C6—N1—C16—C17	-69.6 (3)
C5—N3—C7—C8	178.47 (17)		

*Hydrogen-bond geometry* (Å, °)

Cg4 is the centroid of the imidazole ring system N2/N3/C1–C7.

<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>
N1—H1A···N3 <sup>i</sup>	0.84 (2)	2.41 (2)	3.226 (2)	163.6 (19)
C14—H14A···Cg4 <sup>ii</sup>	0.96	2.93	3.862 (3)	165

Symmetry codes: (i)  $x, -y+3/2, z+1/2$ ; (ii)  $x-1, y, z$ .*N-tert-Butyl-2-[4-(dimethylamino)phenyl]imidazo[1,2-a]pyridin-3-amine* (II)*Crystal data*C<sub>19</sub>H<sub>24</sub>N<sub>4</sub> $M_r = 308.42$ Monoclinic, *C*2/*c* $a = 34.9185$  (14) Å $b = 8.4656$  (5) Å $c = 11.8361$  (6) Å $\beta = 91.061$  (5)° $V = 3498.2$  (3) Å<sup>3</sup> $Z = 8$  $F(000) = 1328$  $D_x = 1.171$  Mg m<sup>-3</sup>Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4941 reflections

 $\theta = 2.3$ – $21.5$ ° $\mu = 0.07$  mm<sup>-1</sup> $T = 296$  K

Block, brown

 $0.15 \times 0.10 \times 0.10$  mm*Data collection*Bruker Kappa APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\omega$  and  $\varphi$  scanAbsorption correction: multi-scan  
(SADABS; Bruker, 2016) $T_{\min} = 0.697$ ,  $T_{\max} = 0.745$ 

32313 measured reflections

3259 independent reflections

1834 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.071$  $\theta_{\max} = 25.5$ °,  $\theta_{\min} = 2.3$ ° $h = -42 \rightarrow 42$  $k = -10 \rightarrow 10$  $l = -14 \rightarrow 14$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.049$  $wR(F^2) = 0.159$  $S = 1.01$ 

3259 reflections

218 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 2.4598P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.22$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.0021 (4)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.58246 (6)	0.2712 (2)	0.25418 (17)	0.0442 (6)
H1A	0.5872 (7)	0.328 (3)	0.196 (2)	0.059 (8)*
N2	0.55040 (5)	0.3250 (2)	0.42684 (15)	0.0409 (5)
N3	0.58530 (6)	0.5154 (2)	0.50989 (15)	0.0438 (5)
N4	0.72538 (7)	0.8380 (3)	0.2431 (2)	0.0757 (8)
C1	0.52002 (7)	0.2237 (3)	0.4153 (2)	0.0508 (7)
H1	0.517019	0.162595	0.350459	0.061*
C2	0.49463 (8)	0.2134 (3)	0.4987 (2)	0.0571 (7)
H2	0.473839	0.145323	0.491098	0.068*
C3	0.49907 (8)	0.3043 (3)	0.5975 (2)	0.0582 (7)
H3	0.481526	0.294650	0.655271	0.070*
C4	0.52893 (7)	0.4063 (3)	0.6088 (2)	0.0534 (7)
H4	0.531869	0.466408	0.674089	0.064*
C5	0.55533 (7)	0.4205 (3)	0.52145 (18)	0.0421 (6)
C6	0.57963 (7)	0.3602 (3)	0.35289 (18)	0.0393 (6)
C7	0.60021 (6)	0.4794 (3)	0.40559 (18)	0.0401 (6)
C8	0.63292 (7)	0.5687 (3)	0.36299 (18)	0.0402 (6)
C9	0.66073 (7)	0.6297 (3)	0.4354 (2)	0.0497 (7)
H9	0.658973	0.610551	0.512451	0.060*
C10	0.69081 (8)	0.7177 (3)	0.3970 (2)	0.0553 (7)
H10	0.708854	0.756665	0.448615	0.066*
C11	0.69492 (7)	0.7499 (3)	0.2825 (2)	0.0508 (7)
C12	0.66718 (7)	0.6877 (3)	0.2090 (2)	0.0508 (7)
H12	0.669089	0.705457	0.131802	0.061*
C13	0.63701 (7)	0.6006 (3)	0.24861 (19)	0.0462 (6)
H13	0.618807	0.561903	0.197371	0.055*
C14	0.75347 (10)	0.8995 (5)	0.3193 (3)	0.1142 (15)
H14A	0.741602	0.971727	0.370444	0.171*
H14B	0.772753	0.954037	0.277596	0.171*
H14C	0.765061	0.814507	0.361250	0.171*
C15	0.72835 (11)	0.8749 (5)	0.1261 (3)	0.1039 (13)
H15A	0.727624	0.779098	0.082673	0.156*
H15B	0.752067	0.928862	0.113508	0.156*
H15C	0.707347	0.941516	0.103264	0.156*
C16	0.60865 (8)	0.1322 (3)	0.25466 (19)	0.0507 (7)
C17	0.64993 (10)	0.1807 (4)	0.2766 (4)	0.1032 (13)
H17A	0.657379	0.256783	0.220981	0.155*
H17B	0.666177	0.089525	0.272039	0.155*
H17C	0.652367	0.226531	0.350538	0.155*
C18	0.60542 (11)	0.0597 (4)	0.1387 (2)	0.0899 (12)
H18A	0.579787	0.021809	0.125922	0.135*
H18B	0.623086	-0.026745	0.133299	0.135*
H18C	0.611317	0.137832	0.082842	0.135*
C19	0.59690 (11)	0.0154 (4)	0.3429 (3)	0.0996 (13)
H19A	0.597112	0.065823	0.415539	0.149*

H19B	0.614509	-0.071669	0.344110	0.149*
H19C	0.571574	-0.022513	0.325394	0.149*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0602 (14)	0.0398 (12)	0.0327 (12)	0.0071 (10)	0.0018 (10)	-0.0009 (9)
N2	0.0434 (12)	0.0376 (11)	0.0417 (11)	-0.0020 (10)	0.0017 (9)	-0.0031 (9)
N3	0.0492 (12)	0.0451 (12)	0.0372 (11)	-0.0053 (10)	0.0044 (9)	-0.0036 (9)
N4	0.0694 (17)	0.0800 (19)	0.0784 (18)	-0.0236 (15)	0.0188 (14)	0.0092 (14)
C1	0.0549 (16)	0.0452 (15)	0.0524 (16)	-0.0078 (13)	-0.0015 (13)	-0.0073 (12)
C2	0.0529 (17)	0.0563 (17)	0.0623 (17)	-0.0120 (14)	0.0069 (14)	-0.0029 (14)
C3	0.0564 (17)	0.0631 (18)	0.0556 (17)	-0.0070 (15)	0.0144 (13)	0.0000 (14)
C4	0.0596 (17)	0.0574 (17)	0.0434 (14)	-0.0049 (15)	0.0107 (12)	-0.0057 (13)
C5	0.0490 (15)	0.0422 (14)	0.0350 (13)	-0.0032 (12)	0.0017 (11)	-0.0043 (11)
C6	0.0462 (14)	0.0375 (13)	0.0343 (12)	0.0014 (11)	0.0017 (11)	-0.0019 (10)
C7	0.0438 (14)	0.0400 (13)	0.0365 (13)	0.0026 (11)	0.0020 (10)	0.0013 (11)
C8	0.0437 (14)	0.0388 (13)	0.0384 (13)	0.0017 (12)	0.0037 (10)	-0.0016 (11)
C9	0.0542 (16)	0.0538 (16)	0.0411 (14)	-0.0058 (14)	0.0017 (12)	-0.0010 (12)
C10	0.0514 (16)	0.0569 (17)	0.0575 (17)	-0.0098 (14)	0.0015 (13)	-0.0036 (13)
C11	0.0501 (16)	0.0431 (15)	0.0596 (17)	-0.0023 (13)	0.0114 (13)	-0.0004 (13)
C12	0.0621 (17)	0.0482 (15)	0.0426 (14)	0.0011 (14)	0.0128 (13)	0.0041 (12)
C13	0.0516 (16)	0.0464 (15)	0.0407 (14)	-0.0017 (13)	0.0015 (11)	0.0005 (11)
C14	0.082 (3)	0.131 (4)	0.129 (3)	-0.059 (3)	-0.003 (2)	0.019 (3)
C15	0.107 (3)	0.115 (3)	0.092 (3)	-0.034 (2)	0.043 (2)	0.006 (2)
C16	0.0687 (18)	0.0412 (14)	0.0422 (14)	0.0131 (13)	0.0054 (12)	-0.0005 (11)
C17	0.074 (2)	0.082 (3)	0.154 (4)	0.029 (2)	-0.012 (2)	-0.021 (2)
C18	0.145 (3)	0.071 (2)	0.0538 (18)	0.040 (2)	0.0069 (19)	-0.0116 (16)
C19	0.150 (3)	0.066 (2)	0.084 (2)	0.046 (2)	0.043 (2)	0.0315 (19)

*Geometric parameters (Å, °)*

N1—C6	1.395 (3)	C10—C11	1.393 (3)
N1—C16	1.491 (3)	C10—H10	0.9300
N1—H1A	0.86 (3)	C11—C12	1.393 (4)
N2—C1	1.369 (3)	C12—C13	1.375 (3)
N2—C6	1.389 (3)	C12—H12	0.9300
N2—C5	1.389 (3)	C13—H13	0.9300
N3—C5	1.329 (3)	C14—H14A	0.9600
N3—C7	1.383 (3)	C14—H14B	0.9600
N4—C11	1.387 (3)	C14—H14C	0.9600
N4—C14	1.419 (4)	C15—H15A	0.9600
N4—C15	1.425 (4)	C15—H15B	0.9600
C1—C2	1.342 (4)	C15—H15C	0.9600
C1—H1	0.9300	C16—C19	1.500 (4)
C2—C3	1.406 (4)	C16—C18	1.506 (4)
C2—H2	0.9300	C16—C17	1.516 (4)
C3—C4	1.358 (4)	C17—H17A	0.9600

C3—H3	0.9300	C17—H17B	0.9600
C4—C5	1.403 (3)	C17—H17C	0.9600
C4—H4	0.9300	C18—H18A	0.9600
C6—C7	1.381 (3)	C18—H18B	0.9600
C7—C8	1.467 (3)	C18—H18C	0.9600
C8—C9	1.383 (3)	C19—H19A	0.9600
C8—C13	1.390 (3)	C19—H19B	0.9600
C9—C10	1.372 (3)	C19—H19C	0.9600
C9—H9	0.9300		
C6—N1—C16	118.45 (19)	C13—C12—C11	121.2 (2)
C6—N1—H1A	112.8 (17)	C13—C12—H12	119.4
C16—N1—H1A	108.6 (17)	C11—C12—H12	119.4
C1—N2—C6	130.4 (2)	C12—C13—C8	121.9 (2)
C1—N2—C5	121.9 (2)	C12—C13—H13	119.0
C6—N2—C5	107.55 (18)	C8—C13—H13	119.0
C5—N3—C7	105.59 (18)	N4—C14—H14A	109.5
C11—N4—C14	120.6 (3)	N4—C14—H14B	109.5
C11—N4—C15	121.0 (3)	H14A—C14—H14B	109.5
C14—N4—C15	118.4 (3)	N4—C14—H14C	109.5
C2—C1—N2	119.2 (2)	H14A—C14—H14C	109.5
C2—C1—H1	120.4	H14B—C14—H14C	109.5
N2—C1—H1	120.4	N4—C15—H15A	109.5
C1—C2—C3	120.8 (3)	N4—C15—H15B	109.5
C1—C2—H2	119.6	H15A—C15—H15B	109.5
C3—C2—H2	119.6	N4—C15—H15C	109.5
C4—C3—C2	120.1 (2)	H15A—C15—H15C	109.5
C4—C3—H3	119.9	H15B—C15—H15C	109.5
C2—C3—H3	119.9	N1—C16—C19	110.3 (2)
C3—C4—C5	119.7 (2)	N1—C16—C18	106.4 (2)
C3—C4—H4	120.1	C19—C16—C18	110.4 (3)
C5—C4—H4	120.1	N1—C16—C17	111.6 (2)
N3—C5—N2	110.80 (19)	C19—C16—C17	109.3 (3)
N3—C5—C4	131.1 (2)	C18—C16—C17	108.7 (3)
N2—C5—C4	118.1 (2)	C16—C17—H17A	109.5
C7—C6—N2	104.74 (19)	C16—C17—H17B	109.5
C7—C6—N1	136.7 (2)	H17A—C17—H17B	109.5
N2—C6—N1	118.4 (2)	C16—C17—H17C	109.5
C6—C7—N3	111.3 (2)	H17A—C17—H17C	109.5
C6—C7—C8	128.5 (2)	H17B—C17—H17C	109.5
N3—C7—C8	120.1 (2)	C16—C18—H18A	109.5
C9—C8—C13	116.5 (2)	C16—C18—H18B	109.5
C9—C8—C7	121.5 (2)	H18A—C18—H18B	109.5
C13—C8—C7	122.0 (2)	C16—C18—H18C	109.5
C10—C9—C8	122.1 (2)	H18A—C18—H18C	109.5
C10—C9—H9	119.0	H18B—C18—H18C	109.5
C8—C9—H9	119.0	C16—C19—H19A	109.5
C9—C10—C11	121.5 (2)	C16—C19—H19B	109.5

C9—C10—H10	119.3	H19A—C19—H19B	109.5
C11—C10—H10	119.3	C16—C19—H19C	109.5
N4—C11—C10	121.7 (2)	H19A—C19—H19C	109.5
N4—C11—C12	121.5 (2)	H19B—C19—H19C	109.5
C10—C11—C12	116.8 (2)		
C6—N2—C1—C2	-178.1 (2)	C5—N3—C7—C6	-0.7 (3)
C5—N2—C1—C2	-1.4 (4)	C5—N3—C7—C8	177.1 (2)
N2—C1—C2—C3	-0.5 (4)	C6—C7—C8—C9	-150.6 (2)
C1—C2—C3—C4	1.2 (4)	N3—C7—C8—C9	32.0 (3)
C2—C3—C4—C5	0.0 (4)	C6—C7—C8—C13	31.5 (4)
C7—N3—C5—N2	-0.4 (2)	N3—C7—C8—C13	-145.9 (2)
C7—N3—C5—C4	-178.6 (3)	C13—C8—C9—C10	0.2 (4)
C1—N2—C5—N3	-175.9 (2)	C7—C8—C9—C10	-177.9 (2)
C6—N2—C5—N3	1.4 (3)	C8—C9—C10—C11	-0.1 (4)
C1—N2—C5—C4	2.5 (3)	C14—N4—C11—C10	-0.4 (4)
C6—N2—C5—C4	179.9 (2)	C15—N4—C11—C10	-177.6 (3)
C3—C4—C5—N3	176.3 (3)	C14—N4—C11—C12	-179.6 (3)
C3—C4—C5—N2	-1.8 (4)	C15—N4—C11—C12	3.2 (4)
C1—N2—C6—C7	175.3 (2)	C9—C10—C11—N4	-179.6 (3)
C5—N2—C6—C7	-1.7 (2)	C9—C10—C11—C12	-0.4 (4)
C1—N2—C6—N1	-7.4 (4)	N4—C11—C12—C13	-179.9 (2)
C5—N2—C6—N1	175.56 (19)	C10—C11—C12—C13	0.8 (4)
C16—N1—C6—C7	81.8 (4)	C11—C12—C13—C8	-0.8 (4)
C16—N1—C6—N2	-94.4 (3)	C9—C8—C13—C12	0.3 (4)
N2—C6—C7—N3	1.6 (3)	C7—C8—C13—C12	178.3 (2)
N1—C6—C7—N3	-175.0 (2)	C6—N1—C16—C19	59.6 (3)
N2—C6—C7—C8	-176.1 (2)	C6—N1—C16—C18	179.4 (2)
N1—C6—C7—C8	7.4 (4)	C6—N1—C16—C17	-62.1 (3)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg3 is the centroid of benzene ring C8–C13.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ N3 <sup>i</sup>	0.86 (3)	2.56 (3)	3.412 (3)	167 (2)
C13—H13 $\cdots$ N3 <sup>i</sup>	0.93	2.57	3.467 (3)	161
C19—H19B $\cdots$ Cg3 <sup>ii</sup>	0.96	2.87	3.829 (4)	174

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