

# Crystal structure of a new 2,6-bis(imino)pyridine derivative: (1*E*,1'*E*)-1,1'-(pyridine-2,6-diyl)bis[*N*-(4-chlorophenyl)ethan-1-imine]

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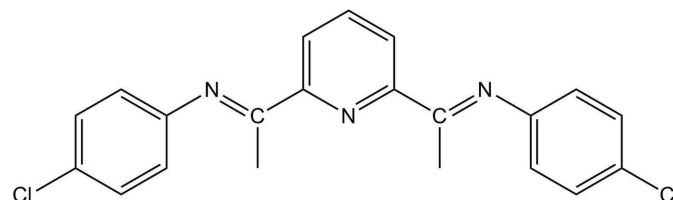
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The asymmetric unit of the title compound, C<sub>21</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>, contains two crystallographically independent molecules (*A* and *B*). Both molecules have *E* configurations for both imine double bonds with regard to the aryl and pyridine groups. The conformations of the two molecules differ with the 4-chlorophenyl rings being inclined to the central pyridine ring by 77.64 (6) and 86.18 (6)° in molecule *A*, and 80.02 (5) and 43.41 (6)° in molecule *B*. In the crystal, molecules are linked by a number of C—H... $\pi$  interactions, forming layers parallel to the *bc* plane.

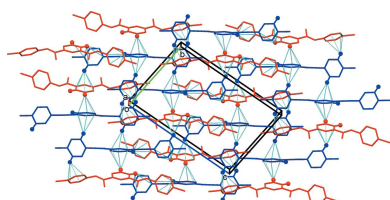
## 1. Chemical context

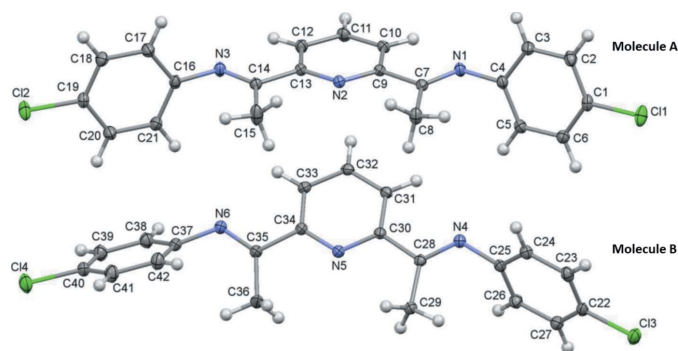
2,6-Bis(imino)pyridines have acquired widespread interest because of their potential application as ligands in olefin polymerization reactions: see, for example, the work of Antonov *et al.* (2012) or Kawakami *et al.* (2015). Metal complexes of such ligands have been applied to aryl C—H activation (Dayan *et al.*, 2010; Sigen *et al.*, 2013) and transfer hydrogenation reactions (Dayan & Çetinkaya, 2007). As a result of the redox activity of the ligand (Noss *et al.*, 2018), electrochemical and luminescent properties of its complexes have been reported (Fan *et al.*, 2004). Recently, the biomimetic reactivity of Zn-alkyl complexes has also been revealed (Sandoval *et al.*, 2018). We report herein on the crystal structure of a new 2,6-bis(imino)pyridine derivative with terminal 4-chlorophenyl rings.



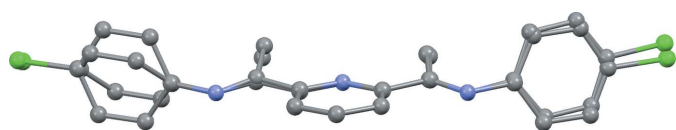
## 2. Structural commentary

The asymmetric unit of the title compound contains two crystallographically independent molecules (*A* and *B*), illustrated in Fig. 1. Both molecules have *E*-configurations for both imine double bonds with regard to the aryl and pyridine groups. The C=N bond lengths of the imine groups are in a narrow range, 1.2675 (15) to 1.2808 (14) Å (Table 1). These values are similar to the C=N bond lengths found in the





**Figure 1**  
Molecular structure of the title compound showing the two crystallographically independent molecules (*A* and *B*), with the atom labelling. Displacement ellipsoids drawn at the 30% probability level.



**Figure 2**  
View of the molecular overlay of the two independent molecules.

crystal structures of other 2,6-bis(imino)pyridyl ligands; for example 1.266 (4) Å in the 'parent' compound 2,6-bis[1-(phenylimino)ethyl]pyridine (Mentes *et al.*, 2001).

In molecule *A*, the 4-chlorophenyl rings (C1–C6 and C16–C21) are inclined to the central pyridine ring (N2/C9–C13) by 77.64 (6) and 86.18 (6)°, respectively. In molecule *B*, the dihedral angles between the 4-chlorophenyl rings (C22–C27 and C37–C42) and the central pyridine ring (N5/C30–C34) are 80.02 (5) and 43.41 (6)°, respectively. The terminal ring (C37–

**Table 1**  
Selected bond lengths (Å).

|        |             |        |             |
|--------|-------------|--------|-------------|
| C7–N1  | 1.2772 (14) | C28–N4 | 1.2808 (14) |
| C14–N3 | 1.2696 (14) | C35–N6 | 1.2675 (15) |

**Table 2**  
Hydrogen-bond geometry (Å, °).

Cg1, Cg2, Cg4, Cg5 and Cg6 are the centroids of rings N2/C9–C13, C1–C6, N5/C30–C34, C22–C27 and C37–C42, respectively.

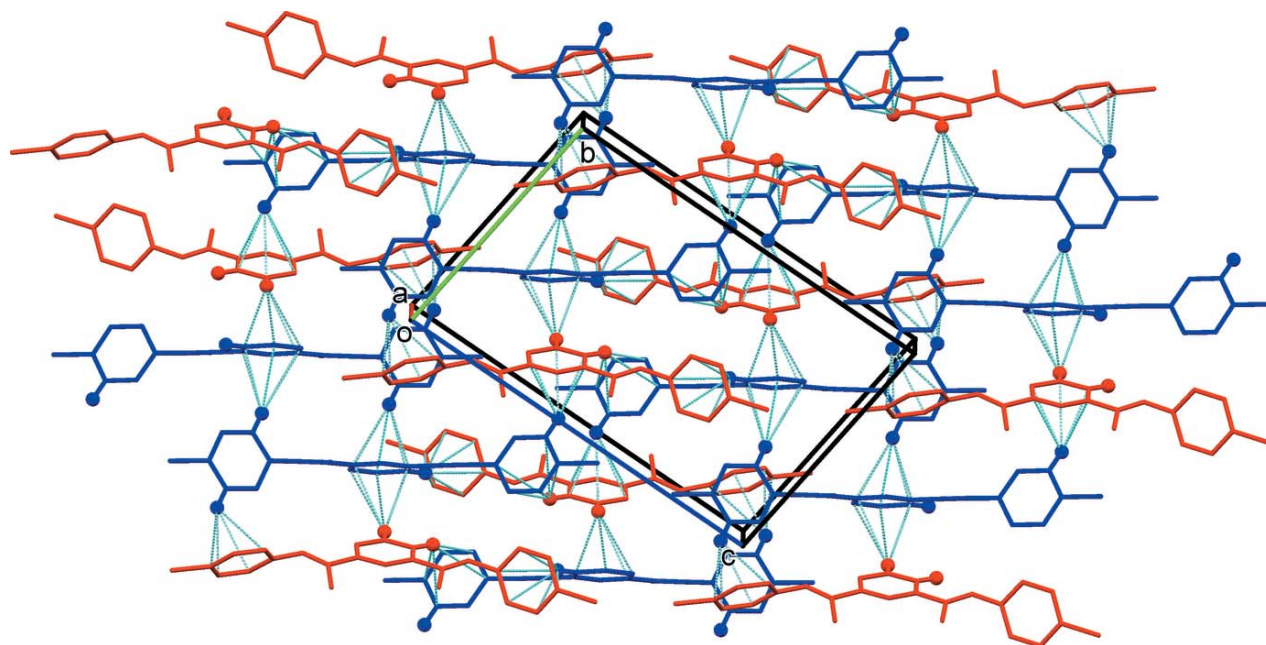
| <i>D</i> –H... <i>A</i>      | <i>D</i> –H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> –H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C20–H20...Cg6                | 0.95        | 2.94          | 3.6735 (14)           | 135                     |
| C32–H32...Cg1                | 0.95        | 2.73          | 3.3273 (12)           | 121                     |
| C2–H2...Cg4 <sup>i</sup>     | 0.95        | 2.67          | 3.4012 (13)           | 134                     |
| C10–H10...Cg5 <sup>ii</sup>  | 0.95        | 2.81          | 3.6446 (13)           | 147                     |
| C17–H17...Cg1 <sup>iii</sup> | 0.95        | 2.70          | 3.5850 (14)           | 155                     |
| C31–H31...Cg2 <sup>ii</sup>  | 0.95        | 2.93          | 3.5795 (12)           | 127                     |

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

C42) in molecule *B* adopts a significantly different conformation from the other benzene rings, as shown in Fig. 2, a molecular overlay figure calculated with *Mercury* (Macrae *et al.*, 2008).

### 3. Supramolecular features

In the crystal, molecules are linked by a series of C–H... $\pi$  interactions, forming layers lying parallel to the *bc* plane (Table 2 and Fig. 3). There are no other significant intermolecular interactions present in the crystal structure. All H...N and H...Cl intermolecular distances exceed the sum of their van der Waals radii.



**Figure 3**  
A view along the *a* axis of the crystal packing of the title compound, showing the C–H... $\pi$  interactions as dashed lines (Table 2; colour code: molecule *A* blue, molecule *B* red). Only the H atoms (blue and red balls) involved in these interactions have been included.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, V5.39, last update August 2018; Groom *et al.*, 2016) confirmed that 2,6-bis(imino)pyridine derivatives are widely used as tridentate chelating ligands for transition metals (more than 600 hits). A search for the substructure 1,1'-(pyridine-2,6-diyl)bis(*N*-(phenyl)ethan-1-imine) gave 25 hits. The crystal structure of the 2,6-bis[1-(phenylimino)ethyl]pyridine molecule was reported in 2001 (CSD refcode QOQROD; Mentis *et al.*, 2001). The first crystal structure with that molecule used a tridentate ligand for a transition metal ( $M = \text{Ni}$ ) was reported earlier in 1975 (PIEPNI10; Alyea *et al.*, 1975). The crystal structure of the bis(4-methoxyphenyl) derivative has also been reported (REMSEH; Meehan *et al.*, 1997). In the 25 structures deposited in the CSD, the C=N bond lengths range from *ca* 1.262–1.294 Å and the dihedral angles involving the outer benzene rings with respect to the central pyridine ring range from *ca* 52.75 to 88.76°. In QOQROD and REMSEH, which both possess mirror symmetry, the C=N bond lengths are 1.266 (4) and 1.274 (5) Å, respectively, while the benzene rings are inclined to the central pyridine ring by 60.2 (2) and 55.2 (2)°, respectively. While the conformation of molecule *A* conforms to the overall limits, that of molecule *B* does not, with the terminal ring (C37–C42) being inclined to the pyridine ring by only 43.41 (6)°.

The crystal structures of two 2,6-dihalogeno ( $X = \text{Cl}, \text{Br}$ ) derivatives have also been reported, *viz.* 2,6-bis[1-(2,6-dibromophenylimino)ethyl]pyridine (EMEJIP; Chen *et al.*, 2003) and 2,6-bis[1-(2,6-dichlorophenylimino)ethyl]pyridine (EYACUD; Sieh *et al.*, 2011). Both compounds have *E* configurations around both C=N imine bonds. Owing to steric hindrance, the 2,6-dihalophenyl rings are inclined to the central pyridine ring by 85.7 (3) and 88.0 (3)° in EMEJIP and 81.13 (6) and 74.22 (7)° in EYACUD. In the crystals of these two compounds, as in the crystal of the title compound, the  $\text{H} \cdots \text{N}$  and  $\text{H} \cdots \text{Br/Cl}$  intermolecular distances all exceed the sum of their van der Waals radii.

#### 5. Synthesis and crystallization

To a solution of 2,6-diacetylpyridine (0.5 g, 3.06 mmol) and *p*-chloroaniline (0.977 g, 7.66 mmol) in 20 ml of toluene was added 20 mg of *p*-toluenesulfonic acid (Görl *et al.*, 2011). The reaction mixture was refluxed for 24 h using a Dean–Stark trap, then cooled to room temperature and 50 ml of saturated sodium bicarbonate solution was added. The organic layer was separated and filtered over sodium sulfate. The solvent was removed in a rotary evaporator giving a light-brown-coloured mass. Ethanol (*ca* 25 ml) was added to this solid mass followed by the addition of hexane (*ca* 10 ml). The solution was then kept in the deep-freezer at 253 K. The title compound was obtained as a yellow solid in 31% yield (0.363 g, 0.95 mmol). A very dilute solution of the compound was prepared in a 1:1 mixture of ethanol and hexane. On slow evaporation of the solvents at room temperature, pale-yellow crystals were obtained over a period of two weeks.

Table 3

Experimental details.

|                                                                            |                                                   |
|----------------------------------------------------------------------------|---------------------------------------------------|
| Crystal data                                                               |                                                   |
| Chemical formula                                                           | $\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{N}_3$ |
| $M_r$                                                                      | 382.27                                            |
| Crystal system, space group                                                | Triclinic, $P\bar{1}$                             |
| Temperature (K)                                                            | 160                                               |
| $a, b, c$ (Å)                                                              | 10.5375 (2), 10.8479 (2), 16.8936 (3)             |
| $\alpha, \beta, \gamma$ (°)                                                | 82.261 (2), 88.543 (1), 84.930 (2)                |
| $V$ (Å <sup>3</sup> )                                                      | 1905.85 (6)                                       |
| $Z$                                                                        | 4                                                 |
| Radiation type                                                             | Mo $K\alpha$                                      |
| $\mu$ (mm <sup>−1</sup> )                                                  | 0.35                                              |
| Crystal size (mm)                                                          | 0.36 × 0.28 × 0.20                                |
| Data collection                                                            |                                                   |
| Diffraction                                                                | XtaLAB Synergy, Dualflex, Pilatus 200K            |
| Absorption correction                                                      | Analytical (CrysAlis PRO; Rigaku OD, 2018)        |
| $T_{\min}, T_{\max}$                                                       | 0.919, 0.941                                      |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 54775, 11604, 9934                                |
| $R_{\text{int}}$                                                           | 0.027                                             |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>−1</sup> )                    | 0.714                                             |
| Refinement                                                                 |                                                   |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$                                        | 0.039, 0.111, 1.06                                |
| No. of reflections                                                         | 11604                                             |
| No. of parameters                                                          | 473                                               |
| H-atom treatment                                                           | H-atom parameters constrained                     |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>−3</sup> )    | 0.47, −0.67                                       |

Computer programs: CrysAlis PRO (Rigaku OD, 2018), SHELXT (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009) and Mercury (Macrae *et al.*, 2008).

An alternate method for the synthesis is as follows: To a solution of 2,6-diacetylpyridine (0.5 g, 3.06 mmol) and *p*-chloroaniline (0.782 g, 6.13 mmol) in 5 mL of absolute ethanol was added three drops of acetic acid. The reaction mixture was refluxed for 24 h, cooled to room temperature and then approximately 15 mL of hexane were added. The mixture was heated on a water bath and filtered hot using filter paper. The solution was kept in a deep freezer at 253 K. The title compound was obtained as a yellow solid in 26% yield (0.305 g, 0.80 mmol).

**Spectroscopic data:** IR (ATR, cm<sup>−1</sup>): 3072 (*w*), 1638 (*s*), 1567 (*w*), 1482 (*s*), 1450 (*w*), 1362 (*s*), 1322 (*w*), 1297 (*m*), 1216 (*s*), 1171 (*w*), 1148 (*w*), 1119 (*m*), 1091 (*m*), 1010 (*w*), 994 (*w*), 955 (*w*), 842 (*s*), 787 (*s*), 743 (*w*), 723 (*m*), 672 (*m*), 635 (*w*), 597 (*m*), 532 (*w*), 517 (*m*); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.40 (*s*, 6H), 6.79 (*d*,  $J = 8.5$  Hz, 4H), 7.35 (*d*,  $J = 8.5$  Hz, 4H), 7.88 (*t*,  $J = 7.8$  Hz, 1H), 8.32 (*d*,  $J = 7.8$  Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 16.6, 121.0, 122.9, 129.4, 129.5, 137.3, 150.0, 155.6, 168.3.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were placed in calculated positions and refined as riding atoms: C—H = 0.95–0.98 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.

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## supporting information

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## Crystal structure of a new 2,6-bis(imino)pyridine derivative: (1*E*,1'*E*)-1,1'-(pyridine-2,6-diyl)bis[*N*-(4-chlorophenyl)ethan-1-imine]

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### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### (1*E*,1'*E*)-1,1'-(Pyridine-2,6-diyl)bis[*N*-(4-chlorophenyl)ethan-1-imine]

#### Crystal data

|                                 |                                                         |
|---------------------------------|---------------------------------------------------------|
| $C_{21}H_{17}Cl_2N_3$           | $Z = 4$                                                 |
| $M_r = 382.27$                  | $F(000) = 792$                                          |
| Triclinic, $P\bar{1}$           | $D_x = 1.332 \text{ Mg m}^{-3}$                         |
| $a = 10.5375 (2) \text{ \AA}$   | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $b = 10.8479 (2) \text{ \AA}$   | Cell parameters from 27060 reflections                  |
| $c = 16.8936 (3) \text{ \AA}$   | $\theta = 2.3\text{--}33.2^\circ$                       |
| $\alpha = 82.261 (2)^\circ$     | $\mu = 0.35 \text{ mm}^{-1}$                            |
| $\beta = 88.543 (1)^\circ$      | $T = 160 \text{ K}$                                     |
| $\gamma = 84.930 (2)^\circ$     | Block, pale yellow                                      |
| $V = 1905.85 (6) \text{ \AA}^3$ | $0.36 \times 0.28 \times 0.20 \text{ mm}$               |

#### Data collection

|                                                                              |                                                                        |
|------------------------------------------------------------------------------|------------------------------------------------------------------------|
| XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer                        | 54775 measured reflections                                             |
| Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source | 11604 independent reflections                                          |
| Mirror monochromator                                                         | 9934 reflections with $I > 2\sigma(I)$                                 |
| $\omega$ scans                                                               | $R_{\text{int}} = 0.027$                                               |
| Absorption correction: analytical (CrysAlis PRO; Rigaku OD, 2018)            | $\theta_{\text{max}} = 30.5^\circ$ , $\theta_{\text{min}} = 2.1^\circ$ |
| $T_{\text{min}} = 0.919$ , $T_{\text{max}} = 0.941$                          | $h = -14 \rightarrow 15$                                               |
|                                                                              | $k = -15 \rightarrow 15$                                               |
|                                                                              | $l = -24 \rightarrow 24$                                               |

#### Refinement

|                                 |                                                          |
|---------------------------------|----------------------------------------------------------|
| Refinement on $F^2$             | Primary atom site location: dual                         |
| Least-squares matrix: full      | Secondary atom site location: difference Fourier map     |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.111$               | H-atom parameters constrained                            |
| $S = 1.06$                      | $w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.5294P]$        |
| 11604 reflections               | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 473 parameters                  |                                                          |
| 0 restraints                    |                                                          |

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

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$$

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

|      | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| C1   | 0.33253 (11) | 0.84351 (11) | 0.52377 (7)  | 0.0277 (2)                       |
| C2   | 0.39558 (13) | 0.89874 (11) | 0.45751 (7)  | 0.0319 (2)                       |
| H2   | 0.403602     | 0.986096     | 0.450265     | 0.038*                           |
| C3   | 0.44713 (13) | 0.82499 (11) | 0.40155 (7)  | 0.0310 (2)                       |
| H3   | 0.492617     | 0.861820     | 0.356481     | 0.037*                           |
| C4   | 0.43261 (11) | 0.69734 (10) | 0.41106 (7)  | 0.0254 (2)                       |
| C5   | 0.37049 (12) | 0.64286 (11) | 0.47914 (7)  | 0.0282 (2)                       |
| H5   | 0.362343     | 0.555521     | 0.486755     | 0.034*                           |
| C6   | 0.32057 (11) | 0.71611 (11) | 0.53576 (7)  | 0.0285 (2)                       |
| H6   | 0.278606     | 0.679231     | 0.582298     | 0.034*                           |
| C7   | 0.42305 (10) | 0.57357 (10) | 0.30817 (6)  | 0.02233 (19)                     |
| C8   | 0.27998 (11) | 0.58318 (13) | 0.30540 (8)  | 0.0320 (2)                       |
| H8A  | 0.248873     | 0.504655     | 0.330749     | 0.048*                           |
| H8B  | 0.252739     | 0.599462     | 0.249660     | 0.048*                           |
| H8C  | 0.245071     | 0.651695     | 0.333999     | 0.048*                           |
| C9   | 0.49567 (10) | 0.49648 (9)  | 0.25206 (6)  | 0.02101 (19)                     |
| C10  | 0.62744 (11) | 0.47078 (10) | 0.25912 (7)  | 0.0249 (2)                       |
| H10  | 0.672537     | 0.503405     | 0.298482     | 0.030*                           |
| C11  | 0.69096 (11) | 0.39668 (12) | 0.20746 (7)  | 0.0291 (2)                       |
| H11  | 0.780494     | 0.377219     | 0.211023     | 0.035*                           |
| C12  | 0.62190 (11) | 0.35128 (11) | 0.15043 (7)  | 0.0271 (2)                       |
| H12  | 0.663229     | 0.300253     | 0.114345     | 0.032*                           |
| C13  | 0.49066 (10) | 0.38206 (10) | 0.14718 (6)  | 0.02198 (19)                     |
| C14  | 0.41233 (10) | 0.33185 (10) | 0.08780 (6)  | 0.0232 (2)                       |
| C15  | 0.27004 (12) | 0.35106 (16) | 0.09431 (10) | 0.0425 (3)                       |
| H15A | 0.231832     | 0.322186     | 0.048576     | 0.064*                           |
| H15B | 0.244269     | 0.440024     | 0.094688     | 0.064*                           |
| H15C | 0.240977     | 0.303534     | 0.143916     | 0.064*                           |
| C16  | 0.41268 (10) | 0.21412 (11) | −0.01944 (7) | 0.0252 (2)                       |
| C17  | 0.41070 (12) | 0.26750 (12) | −0.09902 (7) | 0.0306 (2)                       |
| H17  | 0.438136     | 0.348713     | −0.113385    | 0.037*                           |
| C18  | 0.36890 (12) | 0.20299 (12) | −0.15767 (7) | 0.0304 (2)                       |
| H18  | 0.367791     | 0.239417     | −0.212058    | 0.036*                           |
| C19  | 0.32891 (11) | 0.08498 (11) | −0.13579 (7) | 0.0267 (2)                       |
| C20  | 0.32610 (13) | 0.03190 (12) | −0.05683 (7) | 0.0320 (2)                       |
| H20  | 0.295806     | −0.048126    | −0.042522    | 0.038*                           |

|      |              |               |              |              |
|------|--------------|---------------|--------------|--------------|
| C21  | 0.36821 (13) | 0.09712 (12)  | 0.00144 (7)  | 0.0322 (2)   |
| H21  | 0.366580     | 0.061451      | 0.055952     | 0.039*       |
| Cl1  | 0.26945 (4)  | 0.93500 (3)   | 0.59507 (2)  | 0.04153 (9)  |
| Cl2  | 0.28305 (4)  | 0.00035 (3)   | −0.20954 (2) | 0.04044 (9)  |
| N1   | 0.49029 (10) | 0.62550 (10)  | 0.35388 (6)  | 0.0281 (2)   |
| N2   | 0.42787 (9)  | 0.45348 (8)   | 0.19705 (5)  | 0.02178 (17) |
| N3   | 0.47403 (10) | 0.27235 (10)  | 0.03734 (6)  | 0.0296 (2)   |
| C22  | 0.04883 (11) | 0.44751 (12)  | 0.72766 (7)  | 0.0278 (2)   |
| C23  | 0.04388 (11) | 0.53195 (11)  | 0.65837 (8)  | 0.0293 (2)   |
| H23  | 0.005799     | 0.614549      | 0.658940     | 0.035*       |
| C24  | 0.09527 (11) | 0.49444 (11)  | 0.58799 (7)  | 0.0267 (2)   |
| H24  | 0.093327     | 0.552097      | 0.540346     | 0.032*       |
| C25  | 0.14964 (10) | 0.37279 (10)  | 0.58684 (7)  | 0.0238 (2)   |
| C26  | 0.15381 (12) | 0.28959 (11)  | 0.65750 (7)  | 0.0298 (2)   |
| H26  | 0.191543     | 0.206783      | 0.657329     | 0.036*       |
| C27  | 0.10335 (12) | 0.32680 (12)  | 0.72790 (7)  | 0.0305 (2)   |
| H27  | 0.106202     | 0.269881      | 0.775889     | 0.037*       |
| C28  | 0.16246 (10) | 0.25644 (10)  | 0.47943 (6)  | 0.02186 (19) |
| C29  | 0.04079 (11) | 0.19559 (11)  | 0.50021 (7)  | 0.0266 (2)   |
| H29A | 0.060896     | 0.106970      | 0.519780     | 0.040*       |
| H29B | −0.011964    | 0.203652      | 0.452537     | 0.040*       |
| H29C | −0.005754    | 0.236549      | 0.541826     | 0.040*       |
| C30  | 0.23750 (10) | 0.21730 (10)  | 0.40933 (6)  | 0.02175 (19) |
| C31  | 0.36130 (10) | 0.25147 (10)  | 0.39370 (7)  | 0.0236 (2)   |
| H31  | 0.399260     | 0.302265      | 0.426474     | 0.028*       |
| C32  | 0.42741 (11) | 0.20937 (10)  | 0.32913 (7)  | 0.0250 (2)   |
| H32  | 0.511683     | 0.231219      | 0.316838     | 0.030*       |
| C33  | 0.36935 (11) | 0.13513 (10)  | 0.28271 (7)  | 0.0253 (2)   |
| H33  | 0.412512     | 0.106145      | 0.237813     | 0.030*       |
| C34  | 0.24608 (11) | 0.10387 (10)  | 0.30336 (6)  | 0.0244 (2)   |
| C35  | 0.18171 (12) | 0.01753 (12)  | 0.25878 (7)  | 0.0290 (2)   |
| C36  | 0.0712 (2)   | −0.0429 (2)   | 0.29993 (11) | 0.0687 (7)   |
| H36A | −0.003006    | 0.018417      | 0.298850     | 0.103*       |
| H36B | 0.093131     | −0.074184     | 0.355476     | 0.103*       |
| H36C | 0.051163     | −0.112627     | 0.272397     | 0.103*       |
| C37  | 0.18205 (12) | −0.08525 (11) | 0.14453 (7)  | 0.0274 (2)   |
| C38  | 0.26630 (12) | −0.18181 (13) | 0.12313 (8)  | 0.0332 (3)   |
| H38  | 0.349787     | −0.193775     | 0.144341     | 0.040*       |
| C39  | 0.23006 (13) | −0.26095 (13) | 0.07117 (8)  | 0.0351 (3)   |
| H39  | 0.287777     | −0.327254     | 0.057339     | 0.042*       |
| C40  | 0.10945 (13) | −0.24197 (12) | 0.04003 (7)  | 0.0321 (2)   |
| C41  | 0.02384 (13) | −0.14670 (14) | 0.06006 (8)  | 0.0377 (3)   |
| H41  | −0.059284    | −0.135010     | 0.038303     | 0.045*       |
| C42  | 0.06052 (13) | −0.06793 (13) | 0.11246 (8)  | 0.0355 (3)   |
| H42  | 0.002237     | −0.002089     | 0.126326     | 0.043*       |
| Cl3  | −0.01235 (3) | 0.49452 (4)   | 0.81635 (2)  | 0.04202 (9)  |
| Cl4  | 0.06545 (4)  | −0.33813 (4)  | −0.02725 (2) | 0.04994 (10) |
| N4   | 0.20804 (9)  | 0.33848 (9)   | 0.51589 (6)  | 0.02557 (18) |

|    |              |               |             |              |
|----|--------------|---------------|-------------|--------------|
| N5 | 0.18092 (9)  | 0.14407 (9)   | 0.36555 (6) | 0.02414 (18) |
| N6 | 0.23082 (10) | −0.00296 (10) | 0.19202 (6) | 0.0294 (2)   |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$      | $U^{23}$      |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C1  | 0.0296 (5)   | 0.0297 (5)   | 0.0252 (5)   | 0.0036 (4)    | −0.0053 (4)   | −0.0117 (4)   |
| C2  | 0.0443 (7)   | 0.0233 (5)   | 0.0289 (6)   | −0.0020 (5)   | −0.0045 (5)   | −0.0058 (4)   |
| C3  | 0.0413 (7)   | 0.0274 (5)   | 0.0253 (5)   | −0.0070 (5)   | 0.0014 (5)    | −0.0050 (4)   |
| C4  | 0.0256 (5)   | 0.0270 (5)   | 0.0259 (5)   | −0.0043 (4)   | −0.0019 (4)   | −0.0107 (4)   |
| C5  | 0.0313 (6)   | 0.0251 (5)   | 0.0301 (5)   | −0.0071 (4)   | 0.0012 (4)    | −0.0081 (4)   |
| C6  | 0.0292 (5)   | 0.0325 (6)   | 0.0251 (5)   | −0.0054 (4)   | 0.0014 (4)    | −0.0068 (4)   |
| C7  | 0.0262 (5)   | 0.0204 (4)   | 0.0209 (5)   | −0.0038 (4)   | 0.0006 (4)    | −0.0036 (4)   |
| C8  | 0.0251 (5)   | 0.0400 (6)   | 0.0336 (6)   | 0.0012 (5)    | −0.0030 (4)   | −0.0163 (5)   |
| C9  | 0.0240 (5)   | 0.0193 (4)   | 0.0203 (4)   | −0.0050 (4)   | 0.0009 (4)    | −0.0031 (3)   |
| C10 | 0.0239 (5)   | 0.0269 (5)   | 0.0256 (5)   | −0.0068 (4)   | −0.0011 (4)   | −0.0062 (4)   |
| C11 | 0.0206 (5)   | 0.0355 (6)   | 0.0337 (6)   | −0.0050 (4)   | 0.0003 (4)    | −0.0113 (5)   |
| C12 | 0.0232 (5)   | 0.0316 (5)   | 0.0284 (5)   | −0.0040 (4)   | 0.0028 (4)    | −0.0108 (4)   |
| C13 | 0.0238 (5)   | 0.0219 (4)   | 0.0213 (5)   | −0.0053 (4)   | 0.0013 (4)    | −0.0049 (4)   |
| C14 | 0.0229 (5)   | 0.0244 (5)   | 0.0231 (5)   | −0.0032 (4)   | −0.0008 (4)   | −0.0059 (4)   |
| C15 | 0.0246 (6)   | 0.0600 (9)   | 0.0490 (8)   | 0.0030 (6)    | −0.0048 (5)   | −0.0327 (7)   |
| C16 | 0.0210 (5)   | 0.0317 (5)   | 0.0251 (5)   | −0.0023 (4)   | 0.0021 (4)    | −0.0118 (4)   |
| C17 | 0.0344 (6)   | 0.0298 (5)   | 0.0289 (6)   | −0.0079 (5)   | −0.0029 (5)   | −0.0048 (4)   |
| C18 | 0.0337 (6)   | 0.0351 (6)   | 0.0228 (5)   | −0.0060 (5)   | −0.0031 (4)   | −0.0032 (4)   |
| C19 | 0.0287 (5)   | 0.0293 (5)   | 0.0237 (5)   | −0.0006 (4)   | −0.0033 (4)   | −0.0102 (4)   |
| C20 | 0.0405 (7)   | 0.0296 (6)   | 0.0275 (6)   | −0.0097 (5)   | −0.0028 (5)   | −0.0048 (4)   |
| C21 | 0.0381 (6)   | 0.0394 (6)   | 0.0214 (5)   | −0.0125 (5)   | 0.0014 (4)    | −0.0060 (4)   |
| Cl1 | 0.04879 (19) | 0.04263 (17) | 0.03431 (16) | 0.01175 (14)  | −0.00271 (13) | −0.01911 (13) |
| Cl2 | 0.0540 (2)   | 0.03864 (16) | 0.03227 (16) | −0.00355 (14) | −0.01178 (13) | −0.01599 (12) |
| N1  | 0.0285 (5)   | 0.0300 (5)   | 0.0288 (5)   | −0.0063 (4)   | 0.0019 (4)    | −0.0130 (4)   |
| N2  | 0.0237 (4)   | 0.0214 (4)   | 0.0212 (4)   | −0.0038 (3)   | 0.0001 (3)    | −0.0049 (3)   |
| N3  | 0.0253 (5)   | 0.0389 (5)   | 0.0282 (5)   | −0.0061 (4)   | 0.0019 (4)    | −0.0157 (4)   |
| C22 | 0.0203 (5)   | 0.0394 (6)   | 0.0273 (5)   | −0.0086 (4)   | 0.0029 (4)    | −0.0144 (4)   |
| C23 | 0.0247 (5)   | 0.0302 (5)   | 0.0349 (6)   | −0.0012 (4)   | −0.0006 (4)   | −0.0121 (5)   |
| C24 | 0.0276 (5)   | 0.0268 (5)   | 0.0264 (5)   | −0.0031 (4)   | −0.0023 (4)   | −0.0056 (4)   |
| C25 | 0.0232 (5)   | 0.0258 (5)   | 0.0242 (5)   | −0.0057 (4)   | 0.0000 (4)    | −0.0074 (4)   |
| C26 | 0.0363 (6)   | 0.0255 (5)   | 0.0277 (5)   | −0.0021 (4)   | 0.0000 (5)    | −0.0048 (4)   |
| C27 | 0.0336 (6)   | 0.0344 (6)   | 0.0246 (5)   | −0.0089 (5)   | 0.0003 (4)    | −0.0045 (4)   |
| C28 | 0.0237 (5)   | 0.0209 (4)   | 0.0208 (4)   | −0.0013 (4)   | −0.0001 (4)   | −0.0024 (3)   |
| C29 | 0.0263 (5)   | 0.0282 (5)   | 0.0267 (5)   | −0.0058 (4)   | 0.0039 (4)    | −0.0068 (4)   |
| C30 | 0.0246 (5)   | 0.0204 (4)   | 0.0204 (4)   | −0.0035 (4)   | 0.0006 (4)    | −0.0026 (3)   |
| C31 | 0.0251 (5)   | 0.0216 (4)   | 0.0246 (5)   | −0.0054 (4)   | −0.0011 (4)   | −0.0025 (4)   |
| C32 | 0.0241 (5)   | 0.0246 (5)   | 0.0261 (5)   | −0.0067 (4)   | 0.0021 (4)    | −0.0005 (4)   |
| C33 | 0.0280 (5)   | 0.0265 (5)   | 0.0217 (5)   | −0.0057 (4)   | 0.0047 (4)    | −0.0028 (4)   |
| C34 | 0.0289 (5)   | 0.0256 (5)   | 0.0200 (5)   | −0.0079 (4)   | 0.0025 (4)    | −0.0045 (4)   |
| C35 | 0.0331 (6)   | 0.0335 (6)   | 0.0233 (5)   | −0.0130 (5)   | 0.0051 (4)    | −0.0082 (4)   |
| C36 | 0.0795 (13)  | 0.1008 (15)  | 0.0441 (9)   | −0.0696 (12)  | 0.0337 (9)    | −0.0417 (9)   |
| C37 | 0.0318 (6)   | 0.0315 (5)   | 0.0207 (5)   | −0.0096 (4)   | 0.0043 (4)    | −0.0068 (4)   |

|     |              |            |              |               |               |               |
|-----|--------------|------------|--------------|---------------|---------------|---------------|
| C38 | 0.0297 (6)   | 0.0390 (6) | 0.0332 (6)   | −0.0049 (5)   | −0.0012 (5)   | −0.0119 (5)   |
| C39 | 0.0349 (6)   | 0.0355 (6) | 0.0375 (6)   | −0.0036 (5)   | 0.0025 (5)    | −0.0145 (5)   |
| C40 | 0.0371 (6)   | 0.0371 (6) | 0.0256 (5)   | −0.0127 (5)   | 0.0025 (5)    | −0.0113 (5)   |
| C41 | 0.0329 (6)   | 0.0483 (7) | 0.0345 (6)   | −0.0032 (5)   | −0.0057 (5)   | −0.0139 (6)   |
| C42 | 0.0337 (6)   | 0.0416 (7) | 0.0332 (6)   | 0.0003 (5)    | −0.0008 (5)   | −0.0140 (5)   |
| Cl3 | 0.03482 (16) | 0.0619 (2) | 0.03569 (16) | −0.01407 (14) | 0.01212 (12)  | −0.02555 (15) |
| Cl4 | 0.0486 (2)   | 0.0618 (2) | 0.0484 (2)   | −0.01678 (17) | −0.00091 (16) | −0.03205 (18) |
| N4  | 0.0283 (5)   | 0.0257 (4) | 0.0239 (4)   | −0.0049 (4)   | 0.0019 (4)    | −0.0067 (3)   |
| N5  | 0.0257 (4)   | 0.0267 (4) | 0.0212 (4)   | −0.0071 (3)   | 0.0022 (3)    | −0.0052 (3)   |
| N6  | 0.0327 (5)   | 0.0343 (5) | 0.0237 (4)   | −0.0107 (4)   | 0.0043 (4)    | −0.0092 (4)   |

*Geometric parameters (Å, °)*

|          |             |          |             |
|----------|-------------|----------|-------------|
| C1—C2    | 1.3803 (18) | C22—C23  | 1.3849 (18) |
| C1—C6    | 1.3860 (17) | C22—C27  | 1.3823 (18) |
| C1—Cl1   | 1.7442 (11) | C22—Cl3  | 1.7376 (12) |
| C2—H2    | 0.9500      | C23—H23  | 0.9500      |
| C2—C3    | 1.3891 (17) | C23—C24  | 1.3895 (16) |
| C3—H3    | 0.9500      | C24—H24  | 0.9500      |
| C3—C4    | 1.3939 (16) | C24—C25  | 1.3939 (16) |
| C4—C5    | 1.3956 (17) | C25—C26  | 1.3953 (16) |
| C4—N1    | 1.4138 (14) | C25—N4   | 1.4128 (14) |
| C5—H5    | 0.9500      | C26—H26  | 0.9500      |
| C5—C6    | 1.3887 (16) | C26—C27  | 1.3854 (17) |
| C6—H6    | 0.9500      | C27—H27  | 0.9500      |
| C7—C8    | 1.5035 (16) | C28—C29  | 1.5057 (15) |
| C7—C9    | 1.4989 (15) | C28—C30  | 1.4955 (15) |
| C7—N1    | 1.2772 (14) | C28—N4   | 1.2808 (14) |
| C8—H8A   | 0.9800      | C29—H29A | 0.9800      |
| C8—H8B   | 0.9800      | C29—H29B | 0.9800      |
| C8—H8C   | 0.9800      | C29—H29C | 0.9800      |
| C9—C10   | 1.3968 (15) | C30—C31  | 1.3966 (15) |
| C9—N2    | 1.3420 (13) | C30—N5   | 1.3408 (13) |
| C10—H10  | 0.9500      | C31—H31  | 0.9500      |
| C10—C11  | 1.3856 (16) | C31—C32  | 1.3868 (16) |
| C11—H11  | 0.9500      | C32—H32  | 0.9500      |
| C11—C12  | 1.3882 (16) | C32—C33  | 1.3853 (15) |
| C12—H12  | 0.9500      | C33—H33  | 0.9500      |
| C12—C13  | 1.3945 (16) | C33—C34  | 1.3953 (15) |
| C13—C14  | 1.5009 (14) | C34—C35  | 1.4942 (15) |
| C13—N2   | 1.3433 (13) | C34—N5   | 1.3414 (14) |
| C14—C15  | 1.4987 (17) | C35—C36  | 1.4967 (18) |
| C14—N3   | 1.2696 (14) | C35—N6   | 1.2675 (15) |
| C15—H15A | 0.9800      | C36—H36A | 0.9800      |
| C15—H15B | 0.9800      | C36—H36B | 0.9800      |
| C15—H15C | 0.9800      | C36—H36C | 0.9800      |
| C16—C17  | 1.3902 (17) | C37—C38  | 1.3919 (18) |
| C16—C21  | 1.3895 (17) | C37—C42  | 1.3907 (18) |

|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C16—N3      | 1.4156 (14) | C37—N6        | 1.4141 (14) |
| C17—H17     | 0.9500      | C38—H38       | 0.9500      |
| C17—C18     | 1.3888 (16) | C38—C39       | 1.3898 (17) |
| C18—H18     | 0.9500      | C39—H39       | 0.9500      |
| C18—C19     | 1.3831 (17) | C39—C40       | 1.3758 (19) |
| C19—C20     | 1.3805 (17) | C40—C41       | 1.382 (2)   |
| C19—C12     | 1.7453 (11) | C40—C14       | 1.7397 (12) |
| C20—H20     | 0.9500      | C41—H41       | 0.9500      |
| C20—C21     | 1.3899 (16) | C41—C42       | 1.3938 (18) |
| C21—H21     | 0.9500      | C42—H42       | 0.9500      |
| C2—C1—C6    | 121.33 (11) | C23—C22—C13   | 119.53 (10) |
| C2—C1—C11   | 119.49 (9)  | C27—C22—C23   | 121.20 (11) |
| C6—C1—C11   | 119.17 (9)  | C27—C22—C13   | 119.25 (10) |
| C1—C2—H2    | 120.4       | C22—C23—H23   | 120.4       |
| C1—C2—C3    | 119.17 (11) | C22—C23—C24   | 119.22 (11) |
| C3—C2—H2    | 120.4       | C24—C23—H23   | 120.4       |
| C2—C3—H3    | 119.8       | C23—C24—H24   | 119.8       |
| C2—C3—C4    | 120.48 (11) | C23—C24—C25   | 120.45 (11) |
| C4—C3—H3    | 119.8       | C25—C24—H24   | 119.8       |
| C3—C4—C5    | 119.47 (10) | C24—C25—C26   | 119.23 (10) |
| C3—C4—N1    | 118.39 (11) | C24—C25—N4    | 119.60 (10) |
| C5—C4—N1    | 121.97 (10) | C26—C25—N4    | 120.99 (10) |
| C4—C5—H5    | 119.9       | C25—C26—H26   | 119.7       |
| C6—C5—C4    | 120.10 (10) | C27—C26—C25   | 120.52 (11) |
| C6—C5—H5    | 119.9       | C27—C26—H26   | 119.7       |
| C1—C6—C5    | 119.40 (11) | C22—C27—C26   | 119.38 (11) |
| C1—C6—H6    | 120.3       | C22—C27—H27   | 120.3       |
| C5—C6—H6    | 120.3       | C26—C27—H27   | 120.3       |
| C9—C7—C8    | 117.79 (9)  | C30—C28—C29   | 116.83 (9)  |
| N1—C7—C8    | 126.31 (10) | N4—C28—C29    | 126.40 (10) |
| N1—C7—C9    | 115.90 (10) | N4—C28—C30    | 116.77 (10) |
| C7—C8—H8A   | 109.5       | C28—C29—H29A  | 109.5       |
| C7—C8—H8B   | 109.5       | C28—C29—H29B  | 109.5       |
| C7—C8—H8C   | 109.5       | C28—C29—H29C  | 109.5       |
| H8A—C8—H8B  | 109.5       | H29A—C29—H29B | 109.5       |
| H8A—C8—H8C  | 109.5       | H29A—C29—H29C | 109.5       |
| H8B—C8—H8C  | 109.5       | H29B—C29—H29C | 109.5       |
| C10—C9—C7   | 120.17 (9)  | C31—C30—C28   | 120.98 (9)  |
| N2—C9—C7    | 116.86 (9)  | N5—C30—C28    | 116.05 (9)  |
| N2—C9—C10   | 122.96 (10) | N5—C30—C31    | 122.91 (10) |
| C9—C10—H10  | 120.7       | C30—C31—H31   | 120.8       |
| C11—C10—C9  | 118.57 (10) | C32—C31—C30   | 118.31 (10) |
| C11—C10—H10 | 120.7       | C32—C31—H31   | 120.8       |
| C10—C11—H11 | 120.5       | C31—C32—H32   | 120.3       |
| C10—C11—C12 | 119.05 (11) | C33—C32—C31   | 119.35 (10) |
| C12—C11—H11 | 120.5       | C33—C32—H32   | 120.3       |
| C11—C12—H12 | 120.7       | C32—C33—H33   | 120.7       |

|               |             |               |             |
|---------------|-------------|---------------|-------------|
| C11—C12—C13   | 118.68 (10) | C32—C33—C34   | 118.54 (10) |
| C13—C12—H12   | 120.7       | C34—C33—H33   | 120.7       |
| C12—C13—C14   | 120.18 (10) | C33—C34—C35   | 120.98 (10) |
| N2—C13—C12    | 122.87 (10) | N5—C34—C33    | 122.76 (10) |
| N2—C13—C14    | 116.92 (9)  | N5—C34—C35    | 116.20 (10) |
| C15—C14—C13   | 118.42 (10) | C34—C35—C36   | 116.71 (10) |
| N3—C14—C13    | 116.05 (10) | N6—C35—C34    | 116.71 (10) |
| N3—C14—C15    | 125.49 (10) | N6—C35—C36    | 126.43 (11) |
| C14—C15—H15A  | 109.5       | C35—C36—H36A  | 109.5       |
| C14—C15—H15B  | 109.5       | C35—C36—H36B  | 109.5       |
| C14—C15—H15C  | 109.5       | C35—C36—H36C  | 109.5       |
| H15A—C15—H15B | 109.5       | H36A—C36—H36B | 109.5       |
| H15A—C15—H15C | 109.5       | H36A—C36—H36C | 109.5       |
| H15B—C15—H15C | 109.5       | H36B—C36—H36C | 109.5       |
| C17—C16—N3    | 119.44 (10) | C38—C37—N6    | 116.87 (11) |
| C21—C16—C17   | 119.39 (10) | C42—C37—C38   | 118.98 (11) |
| C21—C16—N3    | 120.71 (11) | C42—C37—N6    | 123.86 (11) |
| C16—C17—H17   | 119.8       | C37—C38—H38   | 119.5       |
| C18—C17—C16   | 120.49 (11) | C39—C38—C37   | 120.95 (12) |
| C18—C17—H17   | 119.8       | C39—C38—H38   | 119.5       |
| C17—C18—H18   | 120.5       | C38—C39—H39   | 120.5       |
| C19—C18—C17   | 119.08 (11) | C40—C39—C38   | 119.09 (12) |
| C19—C18—H18   | 120.5       | C40—C39—H39   | 120.5       |
| C18—C19—C12   | 119.41 (9)  | C39—C40—C41   | 121.24 (11) |
| C20—C19—C18   | 121.38 (10) | C39—C40—C14   | 119.16 (10) |
| C20—C19—C12   | 119.21 (9)  | C41—C40—C14   | 119.58 (10) |
| C19—C20—H20   | 120.5       | C40—C41—H41   | 120.3       |
| C19—C20—C21   | 119.10 (11) | C40—C41—C42   | 119.41 (12) |
| C21—C20—H20   | 120.5       | C42—C41—H41   | 120.3       |
| C16—C21—C20   | 120.49 (11) | C37—C42—C41   | 120.32 (12) |
| C16—C21—H21   | 119.8       | C37—C42—H42   | 119.8       |
| C20—C21—H21   | 119.8       | C41—C42—H42   | 119.8       |
| C7—N1—C4      | 121.10 (10) | C28—N4—C25    | 120.59 (9)  |
| C9—N2—C13     | 117.87 (9)  | C30—N5—C34    | 118.12 (9)  |
| C14—N3—C16    | 122.28 (10) | C35—N6—C37    | 122.78 (10) |

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

Cg1, Cg2, Cg4, Cg5 and Cg6 are the centroids of rings N2/C9—C13, C1—C6, N5/C30—C34, C22—C27 and C37—C42, respectively.

| $D-H\cdots A$                       | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| C20—H20 $\cdots$ Cg6                | 0.95  | 2.94        | 3.6735 (14) | 135           |
| C32—H32 $\cdots$ Cg1                | 0.95  | 2.73        | 3.3273 (12) | 121           |
| C2—H2 $\cdots$ Cg4 <sup>i</sup>     | 0.95  | 2.67        | 3.4012 (13) | 134           |
| C10—H10 $\cdots$ Cg5 <sup>ii</sup>  | 0.95  | 2.81        | 3.6446 (13) | 147           |
| C17—H17 $\cdots$ Cg1 <sup>iii</sup> | 0.95  | 2.70        | 3.5850 (14) | 155           |
| C31—H31 $\cdots$ Cg2 <sup>ii</sup>  | 0.95  | 2.93        | 3.5795 (12) | 127           |

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