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

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Abstract: The asymmetric unit of the title compound, C21H17Cl2N3, 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 interactions, forming layers parallel to the bc plane.

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The asymmetric unit of the title compound, \(\text{C}_{21}\text{H}_{17}\text{Cl}_{2}\text{N}_{3}\), 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 \(C-H\cdots\pi\) 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 & Ç etinkaya, 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 \(C\equiv N\) 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 \(C\equiv N\) bond lengths found in the
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)°/C14, 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–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•••π 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.

| Table 1
| Selected bond lengths (Å). |
| C7—N1 | 1.2772 (14) |
| C14—N3 | 1.2696 (14) |
| C28—N4 | 1.2808 (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. |
| D—H—A | D—H | H•••A | D•••A | D—H•••A |
| 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 | 0.95 | 2.67 | 3.4012 (13) | 134 |
| C10—H10—Cg5 | 0.95 | 2.81 | 3.6446 (13) | 147 |
| C17—H17—Cg1 | 0.95 | 2.70 | 3.5850 (14) | 155 |
| C31—H31—Cg2 | 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.
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-diy)bis(N-phenylethyl-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; Mentes et al., 2001). The first crystal structure with that molecule used a tridentate ligand for a transition metal (M = 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 = Cl, 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 H···N and H·Br/Ci intermolecular distances all exceed the sum of their van der Waals radii.

5. Synthesis and crystallization

To a solution of 2,6-diacytlypyridine (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).

The spectroscopic data: IR (ATR, cm⁻¹): 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); ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (75 MHz, CDCl₃): 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(eq)(H) = 1.5U(eq)(C-methyl) and 1.2U(eq)(C) for other H atoms.

| Table 3 | Experimental details. |
|---------|------------------------|
| Crystal data | C₁₂H₁₇Cl₂N₃ |
| Chemical formula | 382.27 |
| M, | Triclinic, P | |
| Crystal system, space group | |
| Temperature (K) | 160 |
| a, b, c (Å) | 10.5375 (2), 10.8479 (2), 16.8936 (3) |
| α, β, γ (°) | 82.261 (2), 88.543 (1), 84.930 (2) |
| V (Å³) | 1905.85 (6) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.35 |
| Crystal size (mm) | 0.36 x 0.28 x 0.20 |
| Data collection | XtaLAB Synergy, Dualflex, Pilatus 200K |
| Diffractometer | Analytical (CrysAlis PRO; Rigaku OD, 2018) |
| Absorption correction | X-ray Absorption Correction, CrysAlis PRO (Sheldrick, 2015) |
| No. of measured, independent and observed [F > 2σ(F)] reflections | 54775, 11604, 9934 |
| L | 0.027 |
| sin θ/λ max (Å⁻¹) | 0.714 |
| Refinement | R[F² > 2σ(F²)] | |
| R | 0.039, 0.111, 1.06 |
| No. of reflections | 11604 |
| No. of parameters | 473 |
| H-atom treatment | H-atom parameters constrained |
| Δρ max, Δρ min (e Å⁻³) | 0.47, −0.67 |

Computer programs: CrysAlis PRO (Rigaku OD, 2018), SHELXT (Sheldrick, 2015a) SHELXTL2018 (Sheldrick, 2015b); OLEX2 (Dolomanov et al., 2009) and Mercury (Macrae et al., 2008).
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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).

Crystal data
C21H17Cl2N3
Mr = 382.27
Triclinic, P1
a = 10.5375 (2) Å
b = 10.8479 (2) Å
c = 16.8936 (3) Å
α = 82.261 (2)°
β = 88.543 (1)°
γ = 84.930 (2)°
V = 1905.85 (6) Å³
Z = 4
F(000) = 792
Dc = 1.332 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 27060 reflections
θ = 2.3–33.2°
µ = 0.35 mm⁻¹
T = 160 K
Block, pale yellow
0.36 × 0.28 × 0.20 mm

Data collection
XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
ω scans
Absorption correction: analytical
(CrysAlis PRO; Rigaku OD, 2018)
Tmin = 0.919, Tmax = 0.941

54775 measured reflections
11604 independent reflections
9934 reflections with I > 2σ(I)
Rint = 0.027
θmax = 30.5°, θmin = 2.1°
h = −14→15
k = −15→15
l = −24→24

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.039
wR(F²) = 0.111
S = 1.06
11604 reflections
473 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/[σ²(Fo)² + (0.0577P)² + 0.5294P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.47 e Å\(^{-3}\)

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|   | x     | y     | z     | U_{eq}/*U_{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* |
| Atom | x | y | z | Uiso |
|------|---|---|---|------|
| C21  | 0.36821 (13) | 0.09712 (12) | 0.00144 (7) | 0.0322 (2) |
| H21  | 0.366580 | 0.061451 | 0.055952 | 0.039* |
| C11  | 0.26945 (4) | 0.93500 (3) | 0.59507 (2) | 0.04153 (9) |
| C12  | 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) |
| C27  | 0.10335 (12) | 0.32680 (12) | 0.72790 (7) | 0.0305 (2) |
| C28  | 0.106202 | 0.269881 | 0.775889 | 0.037* |
| C29  | 0.16246 (10) | 0.25644 (10) | 0.47943 (6) | 0.02186 (19) |
| 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* |
| C13  | −0.01235 (3) | 0.49452 (4) | 0.81635 (2) | 0.04202 (9) |
| C14  | 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) |
### Atomic displacement parameters (Å²)

|  | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{12}\)  | \(U^{13}\)  | \(U^{23}\)  |
|---|---|---|---|---|---|---|
| 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 | 0.18092 (9) | 0.14407 (9) | 0.36555 (6) | 0.02414 (18) |
| N5 | 0.23082 (10) | −0.00296 (10) | 0.19202 (6) | 0.0294 (2) |
| N6 | 0.23082 (10) | −0.00296 (10) | 0.19202 (6) | 0.0294 (2) |
| 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)  −0.0012 (5)  −0.0119 (5)
C42  0.0337 (6)  0.0416 (7)  0.0332 (6)  0.0003 (5)  −0.0057 (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)  −0.0057 (4)  −0.0113 (4)
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—C11 1.7442 (11)  C22—Cl3  1.7376 (12)  C2—H2  0.9500  C23—H23  0.9500
C2—H2  0.9500  C23—C24  1.3895 (16)  C2—C3  1.3891 (17)  C23—C24  1.3895 (16)
C2—C3  1.3939 (16)  C24—H24  0.9500  C3—H3  0.9500  C24—C25  1.3939 (16)
C3—C4  1.3956 (17)  C25—H25  0.9500  C4—C5  1.3956 (17)  C25—C26  1.3953 (16)
C4—C5  1.4138 (14)  C25—N4  1.4128 (14)  C5—H5  0.9500  C26—H26  0.9500
C5—H5  0.9500  C26—C27  1.3854 (17)  C7—C8  1.5035 (16)  C28—C29  1.5057 (15)
C7—C9  1.3989 (15)  C28—C30  1.4955 (15)  C7—N1  1.2772 (14)  C28—N4  1.2808 (14)
C7—N1  1.2772 (14)  C28—H29A  0.9800  C8—H8A  0.9800  C29—H29A  0.9800
C8—H8B  0.9800  C29—H29B  0.9800  C8—H8C  0.9800  C29—H29C  0.9800
C8—H8C  0.9800  C30—C31  1.3868 (16)  C9—C10  1.3968 (15)  C30—C31  1.3868 (16)
C9—C10  1.3968 (15)  C30—C31  1.3868 (16)  C9—N2  1.3420 (13)  C30—C31  1.3868 (16)
C10—H10 0.9500  C30—H31  0.9500  C10—C11  1.3856 (16)  C31—C32  1.3853 (15)
C10—C11  1.3856 (16)  C31—C32  1.3853 (15)  C11—H11  0.9500  C32—C33  1.3853 (15)
C11—H11  0.9500  C32—C33  1.3853 (15)  C11—C12  1.3882 (16)  C32—C33  1.3853 (15)
C11—C12  1.3882 (16)  C32—C33  1.3853 (15)  C12—H12  0.9500  C33—C34  1.3953 (15)
C12—H12  0.9500  C33—C34  1.3953 (15)  C12—C13  1.3945 (16)  C33—C34  1.3953 (15)
C12—C13  1.3945 (16)  C33—C34  1.3953 (15)  C13—H13  0.9500  C34—C35  1.4942 (15)
C13—H13  0.9500  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)
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—C17  1.3895 (17)  C37—C42  1.3907 (18)
C16—C21  1.3895 (17)  C37—C42  1.3907 (18)
| Bond          | Length (Å) | Bond         | Length (Å) | Bond        | Length (Å) |
|---------------|------------|--------------|------------|-------------|------------|
| 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—C41     | 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—C33—H33 120.7
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
C15—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—C37 120.5
C19—C18—C17 119.08 (11)  C38—C39—C37 119.09 (12)
C19—C18—H18 120.5  C38—C39—C37 120.5
C18—C19—C12 119.41 (9)  C39—C40—C41 121.24 (11)
C20—C19—C18 121.38 (10)  C39—C40—C41 119.16 (10)
C20—C19—C12 119.21 (9)  C41—C40—C41 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 122.82 (10)  C35—N6—C37 122.78 (10)

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H  | H···A | D···A       | D—H···A       |
|------------|------|-------|-------------|---------------|
| 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      | 0.95  | 2.67  | 3.4012 (13) | 134           |
| C10—H10···Cg5ii  | 0.95  | 2.81  | 3.6446 (13) | 147           |
| C17—H17···Cg1ii  | 0.95  | 2.70  | 3.5850 (14) | 155           |
| C31—H31···Cg2ii  | 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.