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# 2-Chloro-6,6-dimethyl-5,6-dihydroindazolo[2,3-*c*]quinazoline

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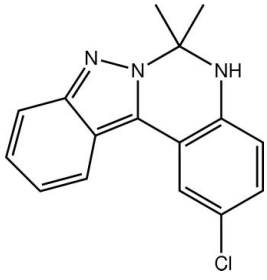
Key indicators: single-crystal X-ray study; $T$ = 120 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.036; $wR$ factor = 0.094; data-to-parameter ratio = 16.4.

Two independent but virtually identical molecules comprise the asymmetric unit of the title compound, $C_{16}H_{14}ClN_3$. The molecules have a slightly curved shape owing to puckering in the six-membered $C_4N_2$ ring; the respective dihedral angles formed between the benzene rings are 12.64 (7) and 11.72 (7)°. In the crystal, layers sustained by a combination of N—H···N hydrogen bonding as well as C—H···N and C—H···$\pi$ contacts are formed; these stack along [011] and are connected by further C—H···$\pi$ contacts.

## Related literature

For background to the synthesis and biological activity of the title compound, see: Rousselet *et al.* (1993); Ferreira *et al.* (2007). For additional geometric analysis, see Cremer & Pople (1975).




## Experimental

### *Crystal data*

$C_{16}H_{14}ClN_3$
$M_r$ = 283.75
Triclinic, $P\overline{1}$
$a$ = 9.8636 (2) Å
$b$ = 10.7971 (2) Å
$c$ = 13.2387 (3) Å
$\alpha$ = 93.483 (1)°
$\beta$ = 100.391 (1)°
$\gamma$ = 104.419 (1)°
$V$ = 1334.81 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.28 mm$^{-1}$
$T$ = 120 K
0.55 × 0.25 × 0.15 mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min}$ = 0.885, $T_{max}$ = 1.000
27218 measured reflections
6102 independent reflections
5108 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.094
$S$ = 1.02
6102 reflections
371 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.37 e Å$^{-3}$

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

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the N2,N3,C10,C11,C16, N5,N6,C26,C27,C32, C1–C6 and C17–C22 rings, respectively.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1n···N6 | 0.90 (2) | 2.32 (2) | 3.2090 (17) | 173 (2) |
| N4—H4n···N3$^{i}$ | 0.86 (2) | 2.39 (2) | 3.2384 (17) | 168 (2) |
| C9—H9b···N4$^{ii}$ | 0.98 | 2.58 | 3.537 (2) | 164 |
| C25—H25b···N1 | 0.98 | 2.61 | 3.545 (2) | 160 |
| C24—H24c···*Cg*1$^{i}$ | 0.98 | 2.90 | 3.8431 (17) | 162 |
| C8—H8c···*Cg*2 | 0.98 | 2.97 | 3.8929 (17) | 157 |
| C18—H18···*Cg*3$^{iii}$ | 0.95 | 2.92 | 3.6630 (15) | 135 |
| C14—H14···*Cg*4$^{iv}$ | 0.95 | 2.95 | 3.8062 (16) | 151 |

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5323).

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Westrip, S. P. (2010). *publCIF*. In preparation.

# supporting information

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## 2-Chloro-6,6-dimethyl-5,6-dihydroindazolo[2,3-*c*]quinazoline

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### S1. Comment

Referring to Fig. 1, amidines, 2 (e.g., X = Y = H; X = H, Y = 4-Cl, 4-Br, 4-F, 4-$NO_2$, 4-$CF_3$, 4-CN, 4-$CH_3$, 4-OMe, 2-Me, 3-$OCF_3$; X, Y = 2,6-F) can be formed from reaction of anilines, 1, with acetonitrile and gaseous hydrogen chloride (Rousselet *et al.*, 1993; Ferreira *et al.*, 2007). From, the *N*-aryl-amidines, 2, on successively reactions with 2-bromo-malonaldehyde and *N*,*N*-diethylaminosulfur trifluoride (DAST), can be formed 1-(substituted-phenyl)-5-(difluoro-methyl)-2-methyl-1*H*-imidazoles, potential anti-leishmanial agents (Ferreira *et al.*, 2007). Unexpectedly, the reaction of aniline 3 with acetonitrile and gaseous hydrogen chloride, followed by a workup using $Me_2CO$, not only produced the amidine, 4, but also the title compound, (5 in Fig. 1 but hereafter, I). Compound (I) had been formed by a condensation reaction between the acetone and the starting material 3. The molecular and crystal structures of (I) are now reported.

Two independent but similar molecules, molecule *a* (Fig. 1) and molecule *b* (Fig. 2), comprise the crystallographic asymmetric unit in (I). The r.m.s. values for bond distances and angles are 0.0028 Å and 0.325 °, respectively. The six-membered $C_4N_2$ ring is puckered as seen in the values of the puckering amplitude Q = 0.3609 (14) Å, $\theta$ = 63.3 (2) °, and $\varphi$ = 324.4 (3) ° (Cremer & Pople, 1975); the respective values for the equivalent ring in molecule *b* are 0.3841 (14) Å, 63.2 (2) °, and 323.6 (2) °. This puckering results in a slightly folded conformation for the molecule, as indicated by the dihedral angle formed between the peripheral benzene rings of 12.64 (7) ° [11.72 (7) ° for molecule *b*].

Supramolecular arrays are found in the crystal structure of (I) mediated by N–H···N hydrogen bonding and sustained by C–H···N as well as C–H···$\pi$ contacts, the latter involving hydrogen atoms from the methyl-C8 and -C24 groups and the ring centroids of the five-membered rings, Table 1 and Fig. 3. Layers stack along [0 1 1] as illustrated in Fig. 4, being associated via C–H···$\pi$ contacts involving aromatic-H atoms and benzene rings.

### S2. Experimental

Referring to Fig. 1, to a stirred solution of amine, 3, (10.75 mmol) in acetonitrile (43 ml) was bubbled hydrogen chloride gas. A precipitate was formed immediately. The resulting suspension was refluxed for 14 hours until homogeneous. The reaction mixture was evaporated at reduced pressure and the residue partitioned between $CH_2Cl_2$ and saturated aq. $NaHCO_3$. The aqueous layer was washed with $CH_2Cl_2$, and the combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. To the solid residue, a mixture of amidine 4 and the starting aniline, 3, was added acetone (50 ml) and the mixture stirred for 30 min. and filtered. The filtrate was evaporated under reduced pressure to give 4 in 70% yield. Recrystallization from acetone of the insoluble residue from the filtration gave pale yellow blocks of (I); 5 in Fig. 1, in 15% yield. M. pt. 483-485 K.

## S3. Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H atoms were located from a difference map and refined with $U_{iso}(H) = 1.2U_{eq}(N)$.

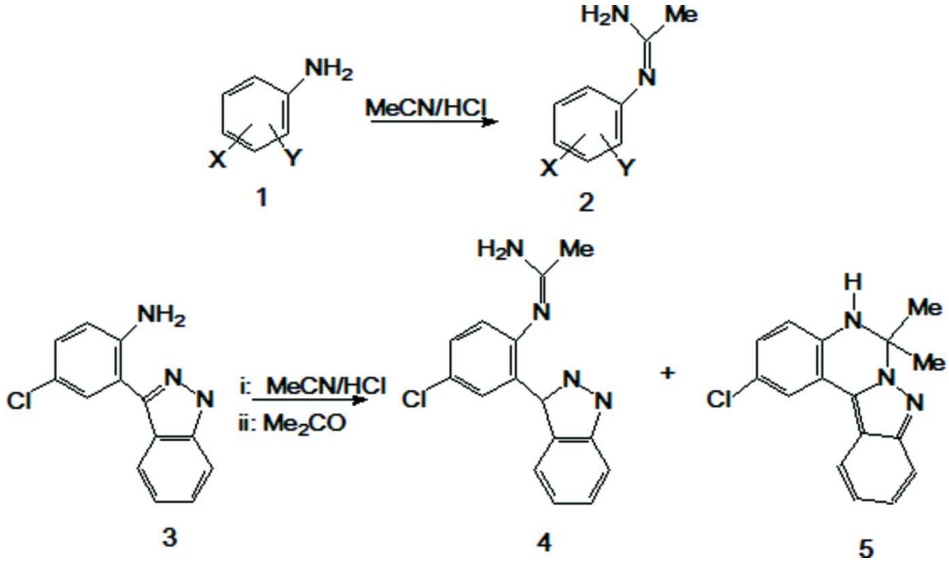


**Figure 1**

Reaction scheme for the synthesis of (I).

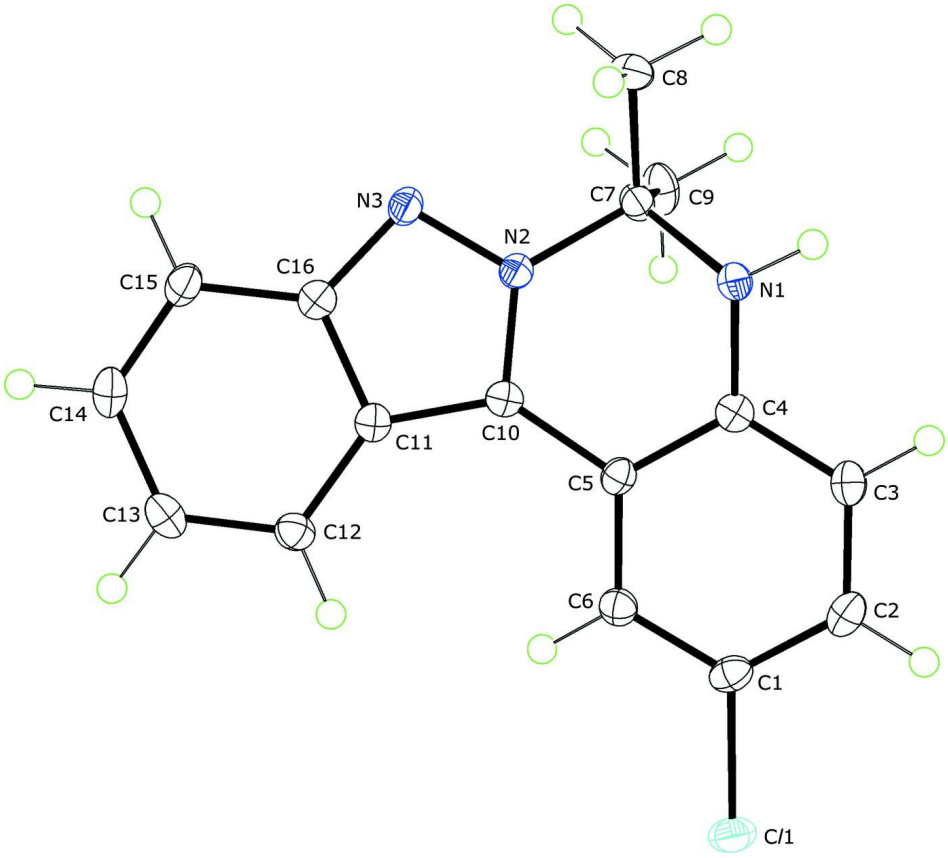


**Figure 2**

The molecular structure of the first independent molecule in (I) showing displacement ellipsoids at the 50% probability level.

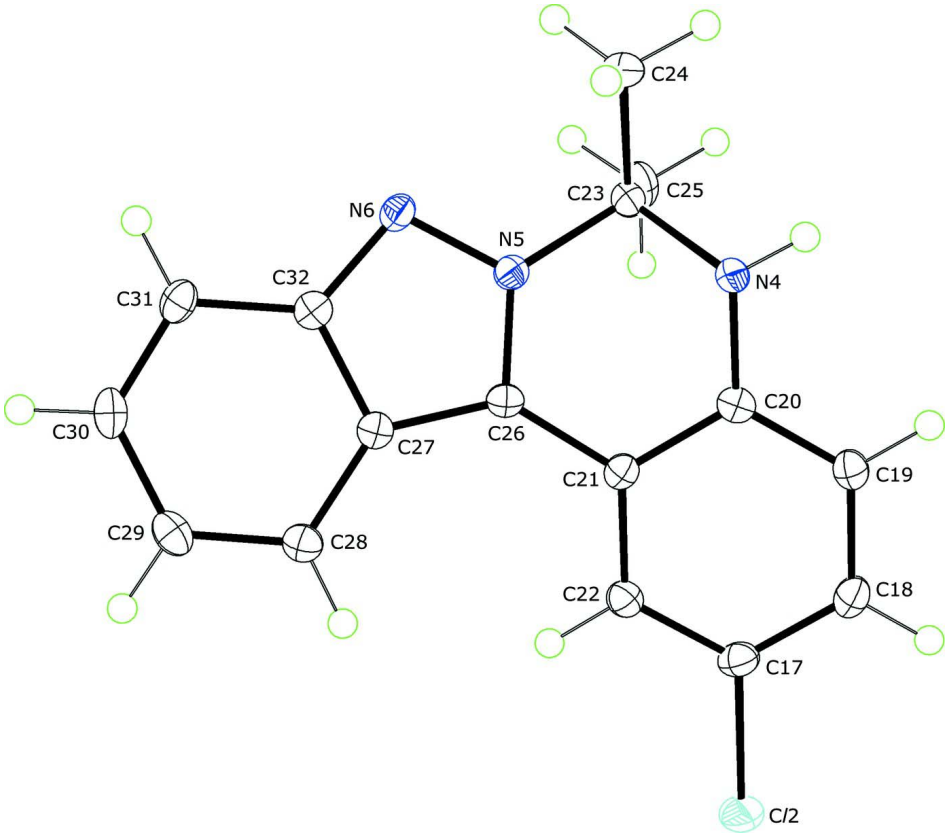


**Figure 3**

The molecular structure of the second independent molecule in (I) showing displacement ellipsoids at the 50% probability level.

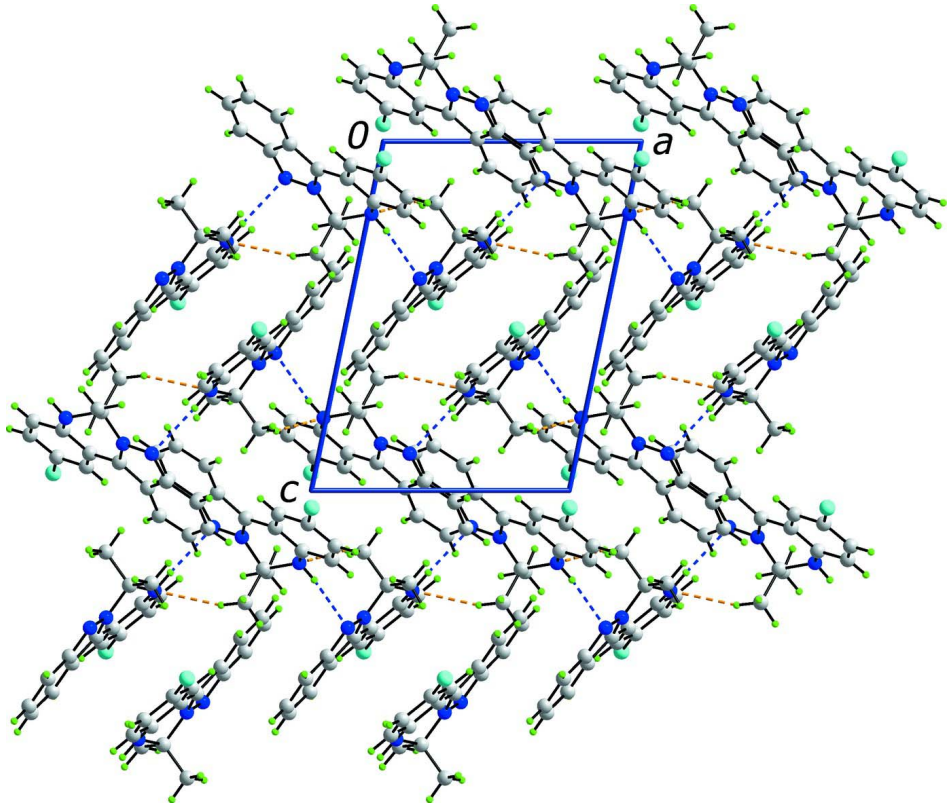


**Figure 4**

A view of the supramolecular array in (I) held together by N–H···N hydrogen bonds (blue dashed bonds), as well as C–H···N (orange dashed lines) and C–H···$\pi$ (not shown) interactions. Colour code: Cl, cyan; N, blue; C, grey; and H, green.

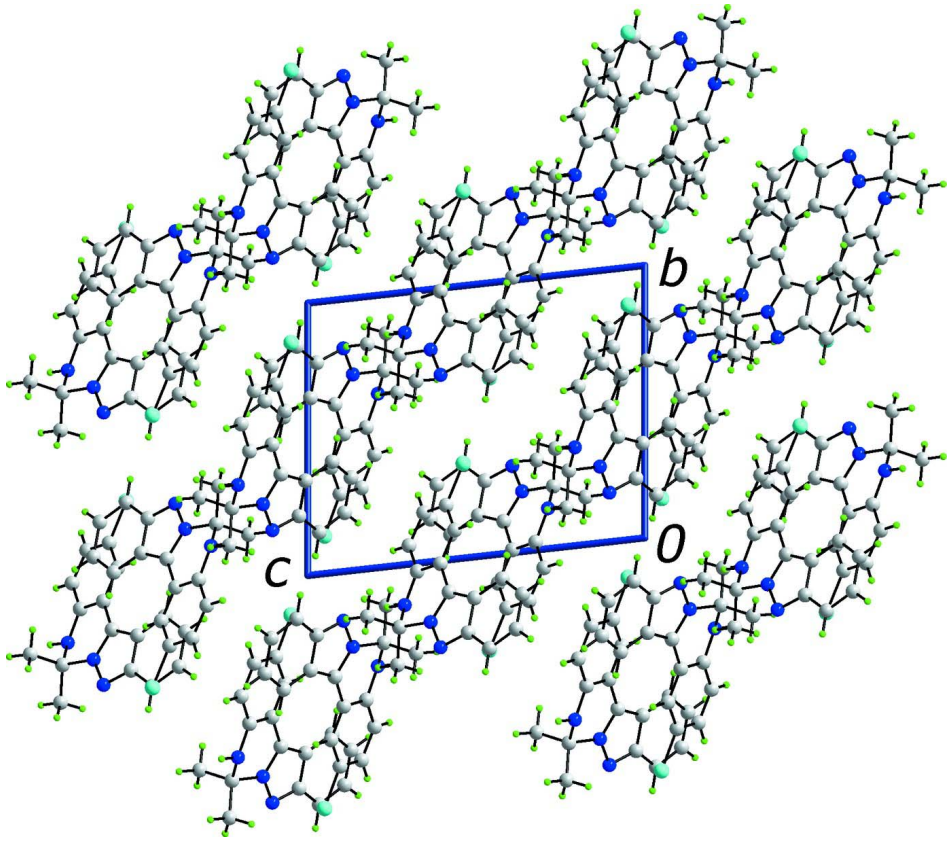


**Figure 5**

View of the stacking of layers in (I) in projection down the *a* axis. Colour code: Cl, cyan; N, blue; C, grey; and H, green.

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*Crystal data*

$C_{16}H_{14}ClN_3$
$M_r = 283.75$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.8636\ (2)$ Å
$b = 10.7971\ (2)$ Å
$c = 13.2387\ (3)$ Å
$\alpha = 93.483\ (1)°$
$\beta = 100.391\ (1)°$
$\gamma = 104.419\ (1)°$
$V = 1334.81\ (5)$ Å$^3$
$Z = 4$
$F(000) = 592$
$D_x = 1.412$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5954 reflections
$\theta = 2.9–27.5°$
$\mu = 0.28$ mm$^{-1}$
$T = 120$ K
Block, pale-yellow
0.55 × 0.25 × 0.15 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Radiation source: Enraf Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.885$, $T_{max} = 1.000$
27218 measured reflections
6102 independent reflections
5108 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

$\theta_{max}$ = 27.5°, $\theta_{min}$ = 2.9°
$h$ = −12→12
$k$ = −14→14
$l$ = −17→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.094
$S$ = 1.02
6102 reflections
371 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.5871P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.37 e Å$^{-3}$

*Special details*

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

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor wR and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.33159 (4) | −0.34794 (3) | 0.46107 (3) | 0.02533 (10) |
| N1 | 0.47189 (12) | 0.14829 (11) | 0.28749 (9) | 0.0170 (2) |
| H1N | 0.5189 (18) | 0.1492 (16) | 0.2355 (13) | 0.020* |
| N2 | 0.30560 (12) | 0.22108 (10) | 0.36420 (8) | 0.0146 (2) |
| N3 | 0.25126 (12) | 0.31785 (11) | 0.39366 (9) | 0.0166 (2) |
| C1 | 0.37097 (15) | −0.20111 (13) | 0.41036 (10) | 0.0178 (3) |
| C2 | 0.46556 (15) | −0.18303 (13) | 0.34342 (11) | 0.0191 (3) |
| H2 | 0.5094 | −0.2488 | 0.3275 | 0.023* |
| C3 | 0.49562 (14) | −0.06863 (13) | 0.30000 (11) | 0.0180 (3) |
| H3 | 0.5592 | −0.0565 | 0.2532 | 0.022* |
| C4 | 0.43335 (14) | 0.02947 (13) | 0.32429 (10) | 0.0153 (3) |
| C5 | 0.33861 (14) | 0.01066 (13) | 0.39313 (10) | 0.0149 (3) |
| C6 | 0.30674 (14) | −0.10637 (13) | 0.43533 (10) | 0.0166 (3) |
| H6 | 0.2415 | −0.1207 | 0.4808 | 0.020* |
| C7 | 0.37046 (14) | 0.22740 (13) | 0.27162 (10) | 0.0160 (3) |
| C8 | 0.45339 (16) | 0.36485 (14) | 0.26594 (12) | 0.0215 (3) |
| H8A | 0.5234 | 0.3969 | 0.3306 | 0.032* |
| H8B | 0.3871 | 0.4193 | 0.2555 | 0.032* |
| H8C | 0.5032 | 0.3670 | 0.2081 | 0.032* |
| C9 | 0.25205 (16) | 0.17480 (15) | 0.17637 (11) | 0.0231 (3) |
| H9A | 0.2939 | 0.1762 | 0.1146 | 0.035* |
| H9B | 0.1845 | 0.2282 | 0.1703 | 0.035* |

| | | | | |
|---|---|---|---|---|
| H9C | 0.2017 | 0.0862 | 0.1831 | 0.035* |
| C10 | 0.28291 (14) | 0.11864 (13) | 0.41894 (10) | 0.0148 (3) |
| C11 | 0.20930 (14) | 0.15069 (13) | 0.49425 (10) | 0.0150 (3) |
| C12 | 0.15553 (15) | 0.09112 (13) | 0.57641 (10) | 0.0177 (3) |
| H12 | 0.1643 | 0.0077 | 0.5897 | 0.021* |
| C13 | 0.09056 (15) | 0.15635 (14) | 0.63631 (11) | 0.0211 (3) |
| H13 | 0.0535 | 0.1171 | 0.6915 | 0.025* |
| C14 | 0.07742 (16) | 0.28172 (14) | 0.61761 (11) | 0.0219 (3) |
| H14 | 0.0322 | 0.3245 | 0.6608 | 0.026* |
| C15 | 0.12848 (15) | 0.34197 (13) | 0.53880 (11) | 0.0194 (3) |
| H15 | 0.1199 | 0.4259 | 0.5271 | 0.023* |
| C16 | 0.19440 (14) | 0.27539 (13) | 0.47525 (10) | 0.0160 (3) |
| Cl2 | 1.01515 (4) | 0.86179 (3) | 0.04959 (3) | 0.02812 (11) |
| N4 | 1.01094 (12) | 0.36108 (11) | 0.20762 (9) | 0.0162 (2) |
| H4N | 1.0824 (18) | 0.3620 (16) | 0.2564 (13) | 0.019* |
| N5 | 0.76776 (12) | 0.28013 (10) | 0.13350 (8) | 0.0147 (2) |
| N6 | 0.64868 (12) | 0.18074 (11) | 0.10529 (9) | 0.0159 (2) |
| C17 | 1.01399 (15) | 0.71382 (13) | 0.09521 (11) | 0.0182 (3) |
| C18 | 1.13622 (15) | 0.69989 (13) | 0.15913 (11) | 0.0186 (3) |
| H18 | 1.2199 | 0.7697 | 0.1762 | 0.022* |
| C19 | 1.13493 (14) | 0.58330 (13) | 0.19782 (10) | 0.0171 (3) |
| H19 | 1.2183 | 0.5733 | 0.2415 | 0.020* |
| C20 | 1.01243 (14) | 0.48057 (13) | 0.17320 (10) | 0.0146 (3) |
| C21 | 0.88979 (14) | 0.49500 (12) | 0.10646 (10) | 0.0143 (3) |
| C22 | 0.89169 (15) | 0.61293 (13) | 0.06827 (10) | 0.0166 (3) |
| H22 | 0.8093 | 0.6239 | 0.0240 | 0.020* |
| C23 | 0.87707 (14) | 0.27850 (13) | 0.22571 (10) | 0.0157 (3) |
| C24 | 0.89323 (16) | 0.14258 (13) | 0.23258 (12) | 0.0209 (3) |
| H24A | 0.9129 | 0.1102 | 0.1675 | 0.031* |
| H24B | 0.8047 | 0.0865 | 0.2453 | 0.031* |
| H24C | 0.9725 | 0.1435 | 0.2894 | 0.031* |
| C25 | 0.83271 (15) | 0.33020 (15) | 0.32098 (11) | 0.0215 (3) |
| H25A | 0.9060 | 0.3329 | 0.3824 | 0.032* |
| H25B | 0.7414 | 0.2738 | 0.3288 | 0.032* |
| H25C | 0.8222 | 0.4172 | 0.3129 | 0.032* |
| C26 | 0.76750 (14) | 0.38327 (12) | 0.08024 (10) | 0.0142 (3) |
| C27 | 0.63765 (14) | 0.34888 (12) | 0.00739 (10) | 0.0146 (3) |
| C28 | 0.57034 (15) | 0.40825 (13) | −0.07201 (10) | 0.0174 (3) |
| H28 | 0.6155 | 0.4920 | −0.0863 | 0.021* |
| C29 | 0.43847 (15) | 0.34197 (14) | −0.12786 (11) | 0.0200 (3) |
| H29 | 0.3911 | 0.3813 | −0.1806 | 0.024* |
| C30 | 0.37114 (15) | 0.21577 (14) | −0.10858 (11) | 0.0201 (3) |
| H30 | 0.2795 | 0.1727 | −0.1486 | 0.024* |
| C31 | 0.43480 (15) | 0.15426 (13) | −0.03367 (10) | 0.0175 (3) |
| H31 | 0.3900 | 0.0690 | −0.0225 | 0.021* |
| C32 | 0.56925 (14) | 0.22232 (13) | 0.02623 (10) | 0.0155 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0402 (2) | 0.01712 (17) | 0.02142 (18) | 0.01136 (15) | 0.00696 (15) | 0.00566 (13) |
| N1 | 0.0154 (6) | 0.0180 (6) | 0.0202 (6) | 0.0058 (5) | 0.0075 (5) | 0.0043 (5) |
| N2 | 0.0157 (5) | 0.0143 (5) | 0.0144 (5) | 0.0050 (4) | 0.0034 (4) | 0.0015 (4) |
| N3 | 0.0191 (6) | 0.0153 (6) | 0.0165 (6) | 0.0068 (5) | 0.0041 (5) | 0.0004 (4) |
| C1 | 0.0207 (7) | 0.0149 (6) | 0.0161 (6) | 0.0053 (5) | −0.0011 (5) | 0.0010 (5) |
| C2 | 0.0188 (7) | 0.0192 (7) | 0.0193 (7) | 0.0090 (5) | −0.0001 (5) | −0.0019 (5) |
| C3 | 0.0149 (6) | 0.0208 (7) | 0.0183 (7) | 0.0049 (5) | 0.0041 (5) | −0.0006 (5) |
| C4 | 0.0130 (6) | 0.0163 (6) | 0.0150 (6) | 0.0027 (5) | 0.0007 (5) | 0.0008 (5) |
| C5 | 0.0143 (6) | 0.0156 (6) | 0.0146 (6) | 0.0053 (5) | 0.0012 (5) | 0.0005 (5) |
| C6 | 0.0172 (6) | 0.0181 (7) | 0.0145 (6) | 0.0050 (5) | 0.0022 (5) | 0.0020 (5) |
| C7 | 0.0161 (6) | 0.0191 (7) | 0.0146 (6) | 0.0060 (5) | 0.0049 (5) | 0.0036 (5) |
| C8 | 0.0244 (7) | 0.0202 (7) | 0.0233 (7) | 0.0074 (6) | 0.0093 (6) | 0.0092 (6) |
| C9 | 0.0197 (7) | 0.0350 (8) | 0.0152 (7) | 0.0100 (6) | 0.0023 (6) | −0.0010 (6) |
| C10 | 0.0132 (6) | 0.0155 (6) | 0.0150 (6) | 0.0031 (5) | 0.0016 (5) | 0.0022 (5) |
| C11 | 0.0129 (6) | 0.0169 (6) | 0.0144 (6) | 0.0042 (5) | 0.0009 (5) | 0.0006 (5) |
| C12 | 0.0176 (7) | 0.0190 (7) | 0.0168 (7) | 0.0052 (5) | 0.0032 (5) | 0.0040 (5) |
| C13 | 0.0199 (7) | 0.0276 (8) | 0.0161 (7) | 0.0052 (6) | 0.0055 (5) | 0.0038 (6) |
| C14 | 0.0223 (7) | 0.0258 (8) | 0.0189 (7) | 0.0093 (6) | 0.0054 (6) | −0.0033 (6) |
| C15 | 0.0229 (7) | 0.0175 (7) | 0.0186 (7) | 0.0085 (6) | 0.0030 (6) | −0.0015 (5) |
| C16 | 0.0148 (6) | 0.0170 (7) | 0.0149 (6) | 0.0040 (5) | 0.0002 (5) | 0.0005 (5) |
| Cl2 | 0.0325 (2) | 0.01460 (17) | 0.0300 (2) | −0.00067 (14) | −0.00427 (16) | 0.00690 (14) |
| N4 | 0.0123 (5) | 0.0167 (6) | 0.0195 (6) | 0.0039 (4) | 0.0018 (5) | 0.0055 (5) |
| N5 | 0.0147 (5) | 0.0141 (5) | 0.0146 (5) | 0.0028 (4) | 0.0029 (4) | 0.0019 (4) |
| N6 | 0.0158 (5) | 0.0138 (5) | 0.0163 (6) | 0.0007 (4) | 0.0030 (4) | 0.0004 (4) |
| C17 | 0.0221 (7) | 0.0139 (6) | 0.0180 (7) | 0.0032 (5) | 0.0044 (5) | 0.0026 (5) |
| C18 | 0.0163 (7) | 0.0179 (7) | 0.0190 (7) | 0.0001 (5) | 0.0033 (5) | −0.0002 (5) |
| C19 | 0.0146 (6) | 0.0196 (7) | 0.0169 (7) | 0.0049 (5) | 0.0026 (5) | 0.0016 (5) |
| C20 | 0.0167 (6) | 0.0157 (6) | 0.0132 (6) | 0.0063 (5) | 0.0049 (5) | 0.0014 (5) |
| C21 | 0.0145 (6) | 0.0143 (6) | 0.0137 (6) | 0.0026 (5) | 0.0038 (5) | 0.0007 (5) |
| C22 | 0.0174 (7) | 0.0173 (7) | 0.0149 (6) | 0.0045 (5) | 0.0023 (5) | 0.0022 (5) |
| C23 | 0.0143 (6) | 0.0167 (6) | 0.0153 (6) | 0.0034 (5) | 0.0017 (5) | 0.0034 (5) |
| C24 | 0.0209 (7) | 0.0175 (7) | 0.0244 (7) | 0.0050 (6) | 0.0030 (6) | 0.0080 (6) |
| C25 | 0.0176 (7) | 0.0295 (8) | 0.0157 (7) | 0.0046 (6) | 0.0020 (5) | 0.0004 (6) |
| C26 | 0.0159 (6) | 0.0143 (6) | 0.0138 (6) | 0.0051 (5) | 0.0049 (5) | 0.0024 (5) |
| C27 | 0.0146 (6) | 0.0157 (6) | 0.0141 (6) | 0.0043 (5) | 0.0044 (5) | 0.0010 (5) |
| C28 | 0.0193 (7) | 0.0176 (7) | 0.0163 (7) | 0.0060 (5) | 0.0042 (5) | 0.0021 (5) |
| C29 | 0.0211 (7) | 0.0247 (7) | 0.0150 (7) | 0.0096 (6) | 0.0014 (5) | 0.0004 (5) |
| C30 | 0.0148 (6) | 0.0242 (7) | 0.0182 (7) | 0.0034 (5) | −0.0001 (5) | −0.0046 (6) |
| C31 | 0.0179 (7) | 0.0158 (6) | 0.0167 (7) | 0.0012 (5) | 0.0047 (5) | −0.0033 (5) |
| C32 | 0.0169 (6) | 0.0160 (6) | 0.0143 (6) | 0.0045 (5) | 0.0052 (5) | 0.0005 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.7411 (14) | Cl2—C17 | 1.7401 (14) |
| N1—C4 | 1.3884 (17) | N4—C20 | 1.3917 (17) |

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|---|---|---|---|
| N1—C7 | 1.4649 (17) | N4—C23 | 1.4662 (17) |
| N1—H1N | 0.896 (18) | N4—H4N | 0.863 (17) |
| N2—C10 | 1.3532 (17) | N5—C26 | 1.3540 (17) |
| N2—N3 | 1.3550 (15) | N5—N6 | 1.3551 (15) |
| N2—C7 | 1.4791 (17) | N5—C23 | 1.4800 (17) |
| N3—C16 | 1.3573 (18) | N6—C32 | 1.3591 (17) |
| C1—C6 | 1.3835 (19) | C17—C22 | 1.3828 (19) |
| C1—C2 | 1.387 (2) | C17—C18 | 1.389 (2) |
| C2—C3 | 1.382 (2) | C18—C19 | 1.3855 (19) |
| C2—H2 | 0.9500 | C18—H18 | 0.9500 |
| C3—C4 | 1.3987 (19) | C19—C20 | 1.3939 (19) |
| C3—H3 | 0.9500 | C19—H19 | 0.9500 |
| C4—C5 | 1.4072 (19) | C20—C21 | 1.4118 (18) |
| C5—C6 | 1.3995 (19) | C21—C22 | 1.3954 (18) |
| C5—C10 | 1.4548 (18) | C21—C26 | 1.4506 (18) |
| C6—H6 | 0.9500 | C22—H22 | 0.9500 |
| C7—C8 | 1.5194 (19) | C23—C24 | 1.5214 (18) |
| C7—C9 | 1.5258 (19) | C23—C25 | 1.5261 (19) |
| C8—H8A | 0.9800 | C24—H24A | 0.9800 |
| C8—H8B | 0.9800 | C24—H24B | 0.9800 |
| C8—H8C | 0.9800 | C24—H24C | 0.9800 |
| C9—H9A | 0.9800 | C25—H25A | 0.9800 |
| C9—H9B | 0.9800 | C25—H25B | 0.9800 |
| C9—H9C | 0.9800 | C25—H25C | 0.9800 |
| C10—C11 | 1.4090 (19) | C26—C27 | 1.4080 (18) |
| C11—C12 | 1.4147 (19) | C27—C28 | 1.4137 (19) |
| C11—C16 | 1.4227 (18) | C27—C32 | 1.4240 (18) |
| C12—C13 | 1.370 (2) | C28—C29 | 1.370 (2) |
| C12—H12 | 0.9500 | C28—H28 | 0.9500 |
| C13—C14 | 1.424 (2) | C29—C30 | 1.420 (2) |
| C13—H13 | 0.9500 | C29—H29 | 0.9500 |
| C14—C15 | 1.369 (2) | C30—C31 | 1.372 (2) |
| C14—H14 | 0.9500 | C30—H30 | 0.9500 |
| C15—C16 | 1.4156 (19) | C31—C32 | 1.4114 (19) |
| C15—H15 | 0.9500 | C31—H31 | 0.9500 |

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|---|---|---|---|
| C4—N1—C7 | 120.26 (11) | C20—N4—C23 | 119.47 (11) |
| C4—N1—H1N | 114.6 (11) | C20—N4—H4N | 114.1 (11) |
| C7—N1—H1N | 111.3 (11) | C23—N4—H4N | 111.7 (11) |
| C10—N2—N3 | 115.05 (11) | C26—N5—N6 | 114.95 (11) |
| C10—N2—C7 | 124.91 (11) | C26—N5—C23 | 124.25 (11) |
| N3—N2—C7 | 119.74 (11) | N6—N5—C23 | 120.24 (10) |
| N2—N3—C16 | 103.00 (11) | N5—N6—C32 | 103.14 (10) |
| C6—C1—C2 | 121.31 (13) | C22—C17—C18 | 121.23 (13) |
| C6—C1—Cl1 | 120.29 (11) | C22—C17—Cl2 | 119.69 (11) |
| C2—C1—Cl1 | 118.39 (10) | C18—C17—Cl2 | 119.08 (11) |
| C3—C2—C1 | 119.49 (13) | C19—C18—C17 | 119.40 (13) |
| C3—C2—H2 | 120.3 | C19—C18—H18 | 120.3 |

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|---|---|---|---|
| C1—C2—H2 | 120.3 | C17—C18—H18 | 120.3 |
| C2—C3—C4 | 120.61 (13) | C18—C19—C20 | 120.59 (13) |
| C2—C3—H3 | 119.7 | C18—C19—H19 | 119.7 |
| C4—C3—H3 | 119.7 | C20—C19—H19 | 119.7 |
| N1—C4—C3 | 120.82 (12) | N4—C20—C19 | 121.43 (12) |
| N1—C4—C5 | 119.55 (12) | N4—C20—C21 | 118.93 (12) |
| C3—C4—C5 | 119.45 (12) | C19—C20—C21 | 119.51 (12) |
| C6—C5—C4 | 119.58 (12) | C22—C21—C20 | 119.53 (12) |
| C6—C5—C10 | 123.71 (12) | C22—C21—C26 | 123.40 (12) |
| C4—C5—C10 | 116.68 (12) | C20—C21—C26 | 117.06 (12) |
| C1—C6—C5 | 119.54 (13) | C17—C22—C21 | 119.71 (13) |
| C1—C6—H6 | 120.2 | C17—C22—H22 | 120.1 |
| C5—C6—H6 | 120.2 | C21—C22—H22 | 120.1 |
| N1—C7—N2 | 105.41 (10) | N4—C23—N5 | 105.27 (10) |
| N1—C7—C8 | 108.36 (11) | N4—C23—C24 | 108.66 (11) |
| N2—C7—C8 | 109.95 (11) | N5—C23—C24 | 109.72 (11) |
| N1—C7—C9 | 112.12 (11) | N4—C23—C25 | 112.27 (11) |
| N2—C7—C9 | 108.61 (11) | N5—C23—C25 | 108.52 (11) |
| C8—C7—C9 | 112.17 (12) | C24—C23—C25 | 112.16 (12) |
| C7—C8—H8A | 109.5 | C23—C24—H24A | 109.5 |
| C7—C8—H8B | 109.5 | C23—C24—H24B | 109.5 |
| H8A—C8—H8B | 109.5 | H24A—C24—H24B | 109.5 |
| C7—C8—H8C | 109.5 | C23—C24—H24C | 109.5 |
| H8A—C8—H8C | 109.5 | H24A—C24—H24C | 109.5 |
| H8B—C8—H8C | 109.5 | H24B—C24—H24C | 109.5 |
| C7—C9—H9A | 109.5 | C23—C25—H25A | 109.5 |
| C7—C9—H9B | 109.5 | C23—C25—H25B | 109.5 |
| H9A—C9—H9B | 109.5 | H25A—C25—H25B | 109.5 |
| C7—C9—H9C | 109.5 | C23—C25—H25C | 109.5 |
| H9A—C9—H9C | 109.5 | H25A—C25—H25C | 109.5 |
| H9B—C9—H9C | 109.5 | H25B—C25—H25C | 109.5 |
| N2—C10—C11 | 105.47 (11) | N5—C26—C27 | 105.54 (11) |
| N2—C10—C5 | 118.79 (12) | N5—C26—C21 | 118.71 (12) |
| C11—C10—C5 | 135.69 (13) | C27—C26—C21 | 135.74 (12) |
| C10—C11—C12 | 135.86 (13) | C26—C27—C28 | 135.70 (13) |
| C10—C11—C16 | 104.30 (12) | C26—C27—C32 | 104.40 (11) |
| C12—C11—C16 | 119.84 (12) | C28—C27—C32 | 119.90 (12) |
| C13—C12—C11 | 118.54 (13) | C29—C28—C27 | 118.35 (13) |
| C13—C12—H12 | 120.7 | C29—C28—H28 | 120.8 |
| C11—C12—H12 | 120.7 | C27—C28—H28 | 120.8 |
| C12—C13—C14 | 121.35 (13) | C28—C29—C30 | 121.35 (13) |
| C12—C13—H13 | 119.3 | C28—C29—H29 | 119.3 |
| C14—C13—H13 | 119.3 | C30—C29—H29 | 119.3 |
| C15—C14—C13 | 121.50 (13) | C31—C30—C29 | 121.81 (13) |
| C15—C14—H14 | 119.3 | C31—C30—H30 | 119.1 |
| C13—C14—H14 | 119.3 | C29—C30—H30 | 119.1 |
| C14—C15—C16 | 117.97 (13) | C30—C31—C32 | 117.58 (13) |
| C14—C15—H15 | 121.0 | C30—C31—H31 | 121.2 |

| | | | |
|---|---|---|---|
| C16—C15—H15 | 121.0 | C32—C31—H31 | 121.2 |
| N3—C16—C15 | 127.06 (13) | N6—C32—C31 | 127.08 (12) |
| N3—C16—C11 | 112.13 (12) | N6—C32—C27 | 111.93 (12) |
| C15—C16—C11 | 120.80 (13) | C31—C32—C27 | 120.99 (12) |
| | | | |
| C10—N2—N3—C16 | 2.18 (14) | C26—N5—N6—C32 | 2.02 (14) |
| C7—N2—N3—C16 | 176.26 (11) | C23—N5—N6—C32 | 173.79 (11) |
| C6—C1—C2—C3 | −0.5 (2) | C22—C17—C18—C19 | −0.9 (2) |
| Cl1—C1—C2—C3 | 178.29 (10) | Cl2—C17—C18—C19 | 178.41 (10) |
| C1—C2—C3—C4 | 1.0 (2) | C17—C18—C19—C20 | 0.0 (2) |
| C7—N1—C4—C3 | 152.54 (13) | C23—N4—C20—C19 | 150.56 (13) |
| C7—N1—C4—C5 | −32.29 (18) | C23—N4—C20—C21 | −33.59 (17) |
| C2—C3—C4—N1 | 174.78 (12) | C18—C19—C20—N4 | 177.17 (12) |
| C2—C3—C4—C5 | −0.4 (2) | C18—C19—C20—C21 | 1.4 (2) |
| N1—C4—C5—C6 | −175.99 (12) | N4—C20—C21—C22 | −177.61 (12) |
| C3—C4—C5—C6 | −0.75 (19) | C19—C20—C21—C22 | −1.68 (19) |
| N1—C4—C5—C10 | 1.91 (18) | N4—C20—C21—C26 | 1.62 (18) |
| C3—C4—C5—C10 | 177.16 (12) | C19—C20—C21—C26 | 177.55 (12) |
| C2—C1—C6—C5 | −0.6 (2) | C18—C17—C22—C21 | 0.6 (2) |
| Cl1—C1—C6—C5 | −179.41 (10) | Cl2—C17—C22—C21 | −178.75 (10) |
| C4—C5—C6—C1 | 1.3 (2) | C20—C21—C22—C17 | 0.7 (2) |
| C10—C5—C6—C1 | −176.50 (12) | C26—C21—C22—C17 | −178.46 (13) |
| C4—N1—C7—N2 | 44.02 (15) | C20—N4—C23—N5 | 46.66 (15) |
| C4—N1—C7—C8 | 161.69 (12) | C20—N4—C23—C24 | 164.13 (12) |
| C4—N1—C7—C9 | −73.97 (16) | C20—N4—C23—C25 | −71.22 (15) |
| C10—N2—C7—N1 | −31.81 (16) | C26—N5—C23—N4 | −34.21 (16) |
| N3—N2—C7—N1 | 154.73 (11) | N6—N5—C23—N4 | 154.83 (11) |
| C10—N2—C7—C8 | −148.40 (13) | C26—N5—C23—C24 | −150.96 (12) |
| N3—N2—C7—C8 | 38.14 (16) | N6—N5—C23—C24 | 38.07 (16) |
| C10—N2—C7—C9 | 88.52 (15) | C26—N5—C23—C25 | 86.17 (15) |
| N3—N2—C7—C9 | −84.94 (14) | N6—N5—C23—C25 | −84.79 (14) |
| N3—N2—C10—C11 | −1.57 (15) | N6—N5—C26—C27 | −1.68 (15) |
| C7—N2—C10—C11 | −175.31 (11) | C23—N5—C26—C27 | −173.07 (11) |
| N3—N2—C10—C5 | −179.50 (11) | N6—N5—C26—C21 | 179.01 (11) |
| C7—N2—C10—C5 | 6.77 (19) | C23—N5—C26—C21 | 7.62 (19) |
| C6—C5—C10—N2 | −171.72 (12) | C22—C21—C26—N5 | −169.74 (12) |
| C4—C5—C10—N2 | 10.47 (18) | C20—C21—C26—N5 | 11.07 (18) |
| C6—C5—C10—C11 | 11.1 (2) | C22—C21—C26—C27 | 11.2 (2) |
| C4—C5—C10—C11 | −166.67 (14) | C20—C21—C26—C27 | −167.98 (14) |
| N2—C10—C11—C12 | −178.65 (15) | N5—C26—C27—C28 | −178.92 (15) |
| C5—C10—C11—C12 | −1.3 (3) | C21—C26—C27—C28 | 0.2 (3) |
| N2—C10—C11—C16 | 0.26 (14) | N5—C26—C27—C32 | 0.58 (14) |
| C5—C10—C11—C16 | 177.66 (14) | C21—C26—C27—C32 | 179.71 (14) |
| C10—C11—C12—C13 | 178.45 (15) | C26—C27—C28—C29 | −179.44 (14) |
| C16—C11—C12—C13 | −0.33 (19) | C32—C27—C28—C29 | 1.13 (19) |
| C11—C12—C13—C14 | −0.4 (2) | C27—C28—C29—C30 | −1.2 (2) |
| C12—C13—C14—C15 | 0.3 (2) | C28—C29—C30—C31 | −0.2 (2) |
| C13—C14—C15—C16 | 0.5 (2) | C29—C30—C31—C32 | 1.6 (2) |

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|---|---|---|---|
| N2—N3—C16—C15 | 177.09 (13) | N5—N6—C32—C31 | 178.35 (13) |
| N2—N3—C16—C11 | −1.92 (14) | N5—N6—C32—C27 | −1.56 (14) |
| C14—C15—C16—N3 | 179.89 (13) | C30—C31—C32—N6 | 178.42 (13) |
| C14—C15—C16—C11 | −1.2 (2) | C30—C31—C32—C27 | −1.69 (19) |
| C10—C11—C16—N3 | 1.08 (15) | C26—C27—C32—N6 | 0.64 (15) |
| C12—C11—C16—N3 | −179.79 (12) | C28—C27—C32—N6 | −179.77 (12) |
| C10—C11—C16—C15 | −178.01 (12) | C26—C27—C32—C31 | −179.27 (12) |
| C12—C11—C16—C15 | 1.12 (19) | C28—C27—C32—C31 | 0.32 (19) |

*Hydrogen-bond geometry (Å, º)*

Cg1, Cg2, Cg3 and Cg4 are the centroids of the N2,N3,C10,C11,C16, N5,N6,C26,C27,C32, C1–C6 and C17–C22 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1n···N6 | 0.90 (2) | 2.32 (2) | 3.2090 (17) | 173 (2) |
| N4—H4n···N3$^{i}$ | 0.86 (2) | 2.39 (2) | 3.2384 (17) | 168 (2) |
| C9—H9b···N4$^{ii}$ | 0.98 | 2.58 | 3.537 (2) | 164 |
| C25—H25b···N1 | 0.98 | 2.61 | 3.545 (2) | 160 |
| C24—H24c···*Cg*1$^{i}$ | 0.98 | 2.90 | 3.8431 (17) | 162 |
| C8—H8c···*Cg*2 | 0.98 | 2.97 | 3.8929 (17) | 157 |
| C18—H18···*Cg*3$^{iii}$ | 0.95 | 2.92 | 3.6630 (15) | 135 |
| C14—H14···*Cg*4$^{iv}$ | 0.95 | 2.95 | 3.8062 (16) | 151 |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*+1, *z*; (iv) −*x*+1, −*y*+1, −*z*+1.