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# 6-Chloro-$N^4$-methyl-$N^4$-phenylpyrimidine-4,5-diamine

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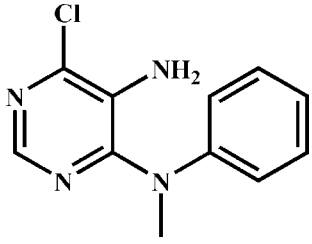
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.037; $wR$ factor = 0.105; data-to-parameter ratio = 17.7.

In the title compound, $C_{11}H_{11}ClN_4$, the dihedral angle between the aromatic rings is 66.47 (8)°. In the crystal, molecules are linked by N—H···N hydrogen bonds, generating $C(5)$ chains propagating in [010]. Slipped aromatic $\pi$–$\pi$ stacking between centrosymmetrically related pairs of pyrimidine rings also occurs [centroid–centroid separation = 3.7634 (12)Å and slippage = 1.715 Å].

## Related literature

For background to pyrimidines, see: Barillari *et al.* (2001); Gangjee *et al.* (2010). For slipped $\pi$–$\pi$ stacking interactions, see: Glówka *et al.* (1999).




## Experimental

### Crystal data

$C_{11}H_{11}ClN_4$
$M_r$ = 234.69
Monoclinic, $P2_1/c$
$a$ = 9.5887 (19) Å
$b$ = 9.948 (2) Å
$c$ = 12.671 (3) Å
$\beta$ = 109.63 (3)°
$V$ = 1138.4 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.31 mm$^{-1}$
$T$ = 293 K
0.45 × 0.36 × 0.33 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.872, $T_{max}$ = 0.905
10835 measured reflections
2588 independent reflections
1983 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
$S$ = 1.07
2588 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4$A$···N1$^{i}$ | 0.86 | 2.28 | 3.0993 (18) | 159 |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5937).

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# supporting information

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## 6-Chloro-$N^4$-methyl-$N^4$-phenylpyrimidine-4,5-diamine

**Fuqiang Shi, Li-Hong Zhu, Long Zhang and Ya-Feng Li**

### S1. Comment

Pyrimidine diamines exhibit a wide range of biological activities (Barillari, *et al.*, 2001; Gangjee *et al.*,2010). Here, the crystal structure of the title compound, (I), is determined by X-ray single crystal diffraction.

In the structure of (I) (Fig. 1), *N*-methyl group links pyrimidyl and phenyl rings of which the dihedral angle is 66.62 (5)°. Two chloropyrimidyl rings of two adjacent molecules point to the opposite directions with $\pi$-$\pi$ conjugation, in which stacking *h* (center-plane) is in 3.3411 Å, *d*(center-center) in 3.7633 Å and shift *r* (displacement of two centers) in 1.7319 Å (Glówka, *et al.*, 1999). The H-bond betwen amino group of pyrimidyl ring and the nitrogen of the adjacent pyrimidyl ring (N4—H4A···N1$^{i}$) results in the formation of infinite chain (Fig. 2).

### S2. Experimental

4,6-Dichloro-5-nitro-pyrimidine (5.20 g, 27 mmol), *N*-methylbenzenamine (3.2 mL, 32 mmol) and triethylamine (7.6 mL, 54 mmol) were dissolved in anhydrous THF (20 mL). The reaction mixture was stirred at room temperature overnight, concentrated *in vacuo*, diluted with water, and extracted with EtOAc. The organic phase was washed with 1mol/L HCl and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give rise to the solid crude product. The recrystallization of crude product from methanol provided the desired pure product of 6-chloro-*N*-methyl-5-nitro-*N*-phenylpyrimidin-4-amine (yellow solid, 5.7g, 80% yield, m.p. 133.5-135.5 °C). 6-Chloro-*N*-methyl-5-nitro-*N*-phenyl-pyrimidin-4-amine (4.36g, 16.5 mmol) was dissolved in a mixture of ethanol (59.0 mL) and water (17.0 mL). Iron powder (2.8 g, 50mmol) and $NH_4Cl$ (0.56 g, 10.0 mmol) were added to it. The mixture was then stirred in reflux for 5 h, cooled to room temperature, and filtered through a pad of celite. The filtrate was concentrated *in vacuo*. The residue was extracted with EtOAc. The organic extract was washed with saturated $NaHCO_3$, water, and brine and dried over anhydrous $MgSO_4$. It was then filtered and concentrated *in vacuo* to the crude product which was purified by flash chromatography (elution with 9% EtOAc in petroleum ether followed by 20% EtOAc in petroleum ether) to give 6-chloro-$N^4$-methyl-$N^4$-phenylpyrimidine-4,5-diamine (white solid, 3.1g, 80% yield, m.p. 81.0-83.0 °C).

### S3. Refinement

All H atoms were located from difference Fourier maps. H atoms attached to C atoms were treated as riding [C-H = 0.93-0.96 Å and Uiso(H) = 1.5Ueq(C) (methyl groups) or 1.2Ueq(C) (other H atoms)]. N-atom of amino group of pyrimidyl ring was treated as $sp^2$ hybridization, and therefore H atoms of amino group were positioned as riding [N-H = 0.86 Å and Uiso(H) = 1.2Ueq(N)].

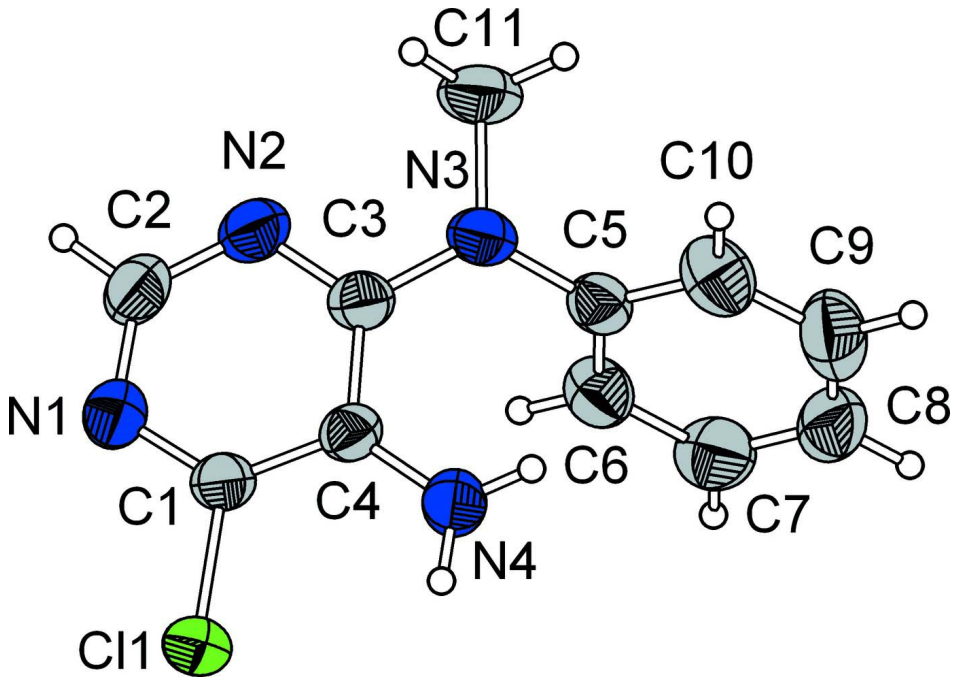


**Figure 1**

The title compound with displacement ellipsoids shown at the 50% probability level.

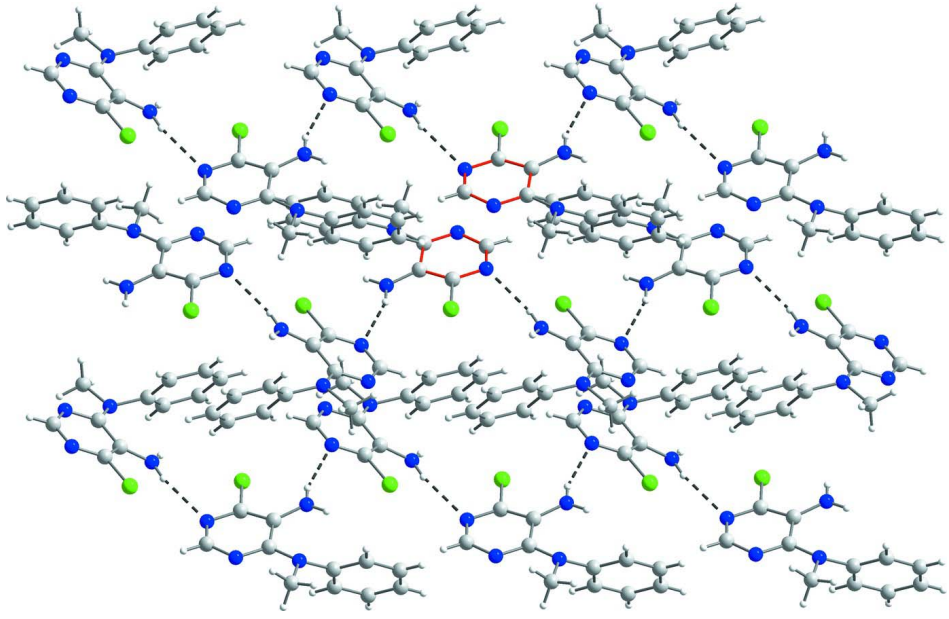

**Figure 2**

The hydrogen bond of amino group of pyrimidyl ring and the nitrogen of the adjacent pyrimidyl ring and $\pi$–$\pi$ stacking of adjacent pyrimidyl rings.

## 6-Chloro-*N*$^4$-methyl-*N*$^4$-phenylpyrimidine-4,5-diamine

*Crystal data*

$C_{11}H_{11}ClN_4$
$M_r = 234.69$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.5887$ (19) Å
$b = 9.948$ (2) Å
$c = 12.671$ (3) Å
$\beta = 109.63$ (3)°
$V = 1138.4$ (4) Å$^3$
$Z = 4$
$F(000) = 488$
$D_x = 1.369$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1000 reflections
$\theta = 3.1$–$27.5°$
$\mu = 0.31$ mm$^{-1}$
$T = 293$ K
Block, colorless
0.45 × 0.36 × 0.33 mm

*Data collection*

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.872$, $T_{max} = 0.905$
10835 measured reflections
2588 independent reflections
1983 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.105$
$S = 1.07$
2588 reflections
146 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.0777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 | 0.39218 (4) | 0.36966 (4) | 0.22870 (4) | 0.06006 (16) |
| N1 | 0.52906 (15) | 0.54876 (12) | 0.14917 (12) | 0.0536 (3) |
| N2 | 0.74328 (16) | 0.50645 (12) | 0.10019 (11) | 0.0533 (3) |
| N3 | 0.85704 (14) | 0.29788 (13) | 0.11914 (11) | 0.0515 (3) |

| | | | | |
|---|---|---|---|---|
| N4 | 0.64945 (17) | 0.20317 (13) | 0.22608 (13) | 0.0607 (4) |
| H4A | 0.5861 | 0.1794 | 0.2571 | 0.073* |
| H4B | 0.7179 | 0.1483 | 0.2243 | 0.073* |
| C1 | 0.53371 (16) | 0.42063 (14) | 0.18003 (12) | 0.0439 (3) |
| C2 | 0.6380 (2) | 0.58510 (16) | 0.11281 (15) | 0.0590 (4) |
| H2 | 0.6410 | 0.6752 | 0.0941 | 0.071* |
| C3 | 0.74410 (16) | 0.37803 (13) | 0.12985 (12) | 0.0436 (3) |
| C4 | 0.64133 (15) | 0.32788 (13) | 0.17980 (11) | 0.0411 (3) |
| C5 | 0.83458 (16) | 0.15897 (14) | 0.08849 (12) | 0.0443 (3) |
| C6 | 0.70775 (18) | 0.11594 (16) | 0.00632 (14) | 0.0529 (4) |
| H6 | 0.6337 | 0.1773 | −0.0293 | 0.064* |
| C7 | 0.6902 (2) | −0.01899 (18) | −0.02337 (15) | 0.0645 (5) |
| H7 | 0.6035 | −0.0482 | −0.0777 | 0.077* |
| C8 | 0.8007 (2) | −0.10947 (17) | 0.02737 (17) | 0.0659 (5) |
| H8 | 0.7892 | −0.1997 | 0.0070 | 0.079* |
| C9 | 0.9276 (2) | −0.0667 (2) | 0.10786 (17) | 0.0731 (5) |
| H9 | 1.0029 | −0.1277 | 0.1416 | 0.088* |
| C10 | 0.9443 (2) | 0.06674 (19) | 0.13924 (15) | 0.0627 (4) |
| H10 | 1.0302 | 0.0948 | 0.1950 | 0.075* |
| C11 | 0.9716 (2) | 0.36428 (19) | 0.0848 (2) | 0.0854 (7) |
| H11A | 0.9328 | 0.3842 | 0.0061 | 0.128* |
| H11B | 1.0556 | 0.3058 | 0.0994 | 0.128* |
| H11C | 1.0013 | 0.4462 | 0.1263 | 0.128* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0518 (2) | 0.0508 (2) | 0.0909 (3) | −0.00514 (16) | 0.0415 (2) | −0.00430 (18) |
| N1 | 0.0596 (8) | 0.0419 (7) | 0.0655 (8) | 0.0004 (6) | 0.0290 (7) | −0.0013 (5) |
| N2 | 0.0625 (8) | 0.0450 (7) | 0.0612 (8) | −0.0097 (6) | 0.0322 (7) | −0.0021 (5) |
| N3 | 0.0441 (7) | 0.0521 (7) | 0.0666 (8) | −0.0087 (5) | 0.0294 (6) | −0.0103 (6) |
| N4 | 0.0722 (9) | 0.0451 (7) | 0.0856 (10) | 0.0066 (6) | 0.0541 (9) | 0.0102 (6) |
| C1 | 0.0441 (7) | 0.0418 (7) | 0.0507 (8) | −0.0071 (6) | 0.0225 (7) | −0.0064 (6) |
| C2 | 0.0754 (11) | 0.0386 (7) | 0.0744 (11) | −0.0032 (7) | 0.0400 (10) | 0.0019 (7) |
| C3 | 0.0439 (7) | 0.0441 (7) | 0.0461 (7) | −0.0073 (6) | 0.0195 (6) | −0.0064 (6) |
| C4 | 0.0426 (7) | 0.0372 (7) | 0.0457 (7) | −0.0068 (5) | 0.0180 (6) | −0.0057 (5) |
| C5 | 0.0432 (7) | 0.0482 (8) | 0.0464 (7) | 0.0000 (6) | 0.0215 (6) | −0.0025 (6) |
| C6 | 0.0468 (8) | 0.0577 (9) | 0.0529 (8) | 0.0021 (7) | 0.0148 (7) | −0.0053 (7) |
| C7 | 0.0640 (11) | 0.0676 (11) | 0.0659 (11) | −0.0135 (8) | 0.0272 (9) | −0.0210 (8) |
| C8 | 0.0855 (14) | 0.0476 (9) | 0.0830 (13) | −0.0023 (9) | 0.0525 (12) | −0.0074 (8) |
| C9 | 0.0815 (13) | 0.0634 (11) | 0.0800 (13) | 0.0262 (10) | 0.0348 (11) | 0.0136 (9) |
| C10 | 0.0518 (9) | 0.0723 (11) | 0.0595 (10) | 0.0099 (8) | 0.0126 (8) | 0.0002 (8) |
| C11 | 0.0773 (13) | 0.0696 (12) | 0.140 (2) | −0.0238 (10) | 0.0768 (15) | −0.0253 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.7440 (14) | C5—C6 | 1.377 (2) |
| N1—C2 | 1.326 (2) | C5—C10 | 1.381 (2) |

| | | | |
|---|---|---|---|
| N1—C1 | 1.3296 (19) | C6—C7 | 1.389 (2) |
| N2—C2 | 1.329 (2) | C6—H6 | 0.9300 |
| N2—C3 | 1.3309 (18) | C7—C8 | 1.374 (3) |
| N3—C3 | 1.3876 (18) | C7—H7 | 0.9300 |
| N3—C5 | 1.4320 (19) | C8—C9 | 1.367 (3) |
| N3—C11 | 1.467 (2) | C8—H8 | 0.9300 |
| N4—C4 | 1.3633 (18) | C9—C10 | 1.379 (3) |
| N4—H4A | 0.8600 | C9—H9 | 0.9300 |
| N4—H4B | 0.8600 | C10—H10 | 0.9300 |
| C1—C4 | 1.3850 (19) | C11—H11A | 0.9600 |
| C2—H2 | 0.9300 | C11—H11B | 0.9600 |
| C3—C4 | 1.4282 (18) | C11—H11C | 0.9600 |

| | | | |
|---|---|---|---|
| C2—N1—C1 | 114.28 (13) | C10—C5—N3 | 119.55 (15) |
| C2—N2—C3 | 117.64 (12) | C5—C6—C7 | 120.07 (16) |
| C3—N3—C5 | 121.99 (11) | C5—C6—H6 | 120.0 |
| C3—N3—C11 | 117.18 (13) | C7—C6—H6 | 120.0 |
| C5—N3—C11 | 114.41 (12) | C8—C7—C6 | 120.14 (17) |
| C4—N4—H4A | 120.0 | C8—C7—H7 | 119.9 |
| C4—N4—H4B | 120.0 | C6—C7—H7 | 119.9 |
| H4A—N4—H4B | 120.0 | C9—C8—C7 | 119.88 (16) |
| N1—C1—C4 | 126.12 (12) | C9—C8—H8 | 120.1 |
| N1—C1—Cl1 | 115.43 (10) | C7—C8—H8 | 120.1 |
| C4—C1—Cl1 | 118.42 (11) | C8—C9—C10 | 120.19 (17) |
| N1—C2—N2 | 126.91 (14) | C8—C9—H9 | 119.9 |
| N1—C2—H2 | 116.5 | C10—C9—H9 | 119.9 |
| N2—C2—H2 | 116.5 | C9—C10—C5 | 120.57 (18) |
| N2—C3—N3 | 117.05 (12) | C9—C10—H10 | 119.7 |
| N2—C3—C4 | 121.39 (13) | C5—C10—H10 | 119.7 |
| N3—C3—C4 | 121.33 (12) | N3—C11—H11A | 109.5 |
| N4—C4—C1 | 122.70 (12) | N3—C11—H11B | 109.5 |
| N4—C4—C3 | 124.08 (13) | H11A—C11—H11B | 109.5 |
| C1—C4—C3 | 113.19 (12) | N3—C11—H11C | 109.5 |
| C6—C5—C10 | 119.13 (15) | H11A—C11—H11C | 109.5 |
| C6—C5—N3 | 121.28 (14) | H11B—C11—H11C | 109.5 |

| | | | |
|---|---|---|---|
| C2—N1—C1—C4 | 1.8 (2) | N3—C3—C4—N4 | 3.9 (2) |
| C2—N1—C1—Cl1 | 179.82 (12) | N2—C3—C4—C1 | 7.6 (2) |
| C1—N1—C2—N2 | 3.2 (3) | N3—C3—C4—C1 | −178.05 (13) |
| C3—N2—C2—N1 | −2.2 (3) | C3—N3—C5—C6 | 41.5 (2) |
| C2—N2—C3—N3 | −178.27 (15) | C11—N3—C5—C6 | −109.51 (18) |
| C2—N2—C3—C4 | −3.7 (2) | C3—N3—C5—C10 | −140.87 (15) |
| C5—N3—C3—N2 | −145.53 (14) | C11—N3—C5—C10 | 68.1 (2) |
| C11—N3—C3—N2 | 4.8 (2) | C10—C5—C6—C7 | 1.0 (2) |
| C5—N3—C3—C4 | 39.9 (2) | N3—C5—C6—C7 | 178.65 (13) |
| C11—N3—C3—C4 | −169.80 (17) | C5—C6—C7—C8 | −1.5 (2) |
| N1—C1—C4—N4 | 171.27 (15) | C6—C7—C8—C9 | 0.5 (3) |
| Cl1—C1—C4—N4 | −6.7 (2) | C7—C8—C9—C10 | 0.8 (3) |

| | | | |
|---|---|---|---|
| N1—C1—C4—C3 | −6.8 (2) | C8—C9—C10—C5 | −1.2 (3) |
| Cl1—C1—C4—C3 | 175.23 (10) | C6—C5—C10—C9 | 0.3 (2) |
| N2—C3—C4—N4 | −170.43 (14) | N3—C5—C10—C9 | −177.38 (14) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*A*···N1$^{i}$ | 0.86 | 2.28 | 3.0993 (18) | 159 |

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+1/2.