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## Structure Reports

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## 2,4-Dichloro-6-(3-methylpiperidin-1-yl)-1,3,5-triazine

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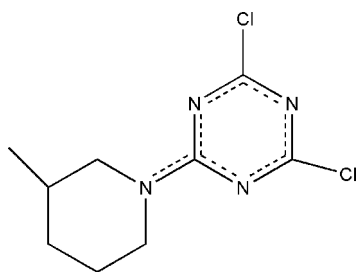
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.059;  $wR$  factor = 0.190; data-to-parameter ratio = 20.3.

In the title compound,  $\text{C}_9\text{H}_{12}\text{Cl}_2\text{N}_4$ , the piperidine ring adopts a chair conformation. The electron delocalization of the molecule is indicated by the similar  $\text{C}\cdots\text{N}$  distances within the triazine ring and by the double-bond character of the  $\text{C}=\text{N}$  triazine–piperidine connectivity. Weak intramolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds link the two rings within the molecule, which exhibits a pseudo-mirror plane if the methyl group is ignored.  $\pi-\pi$  Interactions between pairs of triazine rings with stacking distances of  $3.521(7)$  Å are observed in the crystal structure, generated *via* crystallographic inversion centers.

## Related literature

For general background and the experimental method, see: Sandford (2003); Masllorens *et al.* (2004); Ciunik (1997); Hunter & Sanders (1990); Taylor & Kennard (1982); Thalladi *et al.* (1998).



## Experimental

## Crystal data

$\text{C}_9\text{H}_{12}\text{Cl}_2\text{N}_4$	$V = 1164(4)$ Å <sup>3</sup>
$M_r = 247.13$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.086(16)$ Å	$\mu = 0.53$ mm <sup>-1</sup>
$b = 19.19(3)$ Å	$T = 293(2)$ K
$c = 7.813(15)$ Å	$0.40 \times 0.20 \times 0.15$ mm
$\beta = 106.18(3)^\circ$	

## Data collection

Rigaku Mercury2 diffractometer	11851 measured reflections
Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2005)	2765 independent reflections
$T_{\min} = 0.750$ , $T_{\max} = 1.000$	1118 reflections with $I > 2\sigma(I)$
(expected range = 0.692–0.923)	$R_{\text{int}} = 0.068$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	136 parameters
$wR(F^2) = 0.189$	H-atom parameters constrained
$S = 0.86$	$\Delta\rho_{\max} = 0.35$ e Å <sup>-3</sup>
2765 reflections	$\Delta\rho_{\min} = -0.27$ e Å <sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5B}\cdots\text{N4}$	0.97	2.34	2.787(6)	108
$\text{C9}-\text{H9B}\cdots\text{N2}$	0.97	2.35	2.794(6)	107

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2085).

## References

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## supporting information

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## 2,4-Dichloro-6-(3-methylpiperidin-1-yl)-1,3,5-triazine

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### S1. Comment

2,4,6-Trichloro-1,3,5-triazine is an interesting building block since it shows an unusual ability of replacement of the chlorine atoms by nucleophiles. It is often used for the construction of an array of novel complex derivatives and of a variety of structurally diverse macrocycles by sequential nucleophilic aromatic substitution processes (Sandford, 2003; Masllorens *et al.*, 2004). Besides, it can also be used to construct a target supramolecular network. A series of substituted triazine compounds stabilized by weak intermolecular interactions such as C—H $\cdots$ N hydrogen bonding and  $\pi\cdots\pi$  interaction were reported before (Thalladi *et al.*, 1998). Crystallographic evidence for the existence of C—H $\cdots$ N hydrogen bonds with H $\cdots$ N ranges between 2.52 and 2.72 Å was communicated by Taylor & Kennard (1982).

In the title compound, C<sub>9</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub>, the methylpiperidine group adopts a chair conformation and the chiral C6 atom is in S\* configuration (Figure 1). If the methyl group at the piperidine group is replaced by a hydrogen atom, the molecule is nearly mirror symmetrical. The crystal data shows that the N—C bond lengths of N1—C7, N3—C4 and N3—C8 are 1.330 (5), 1.344 (5) and 1.340 (5) Å respectively. These relative homogeneous bond distances indicate the inflexibility of the molecule. Though no classic hydrogen bond is found, there is evidence of weak C—H $\cdots$ N interactions in the molecule (Table 1). In contrast to these inflexible intramolecular C—H $\cdots$ N hydrogen bonds, an example of intramolecular C—H $\cdots$ N hydrogen bond interactions showed a stabilizing effect in the conformation of flexible pyranoid rings (Ciunik, 1997).

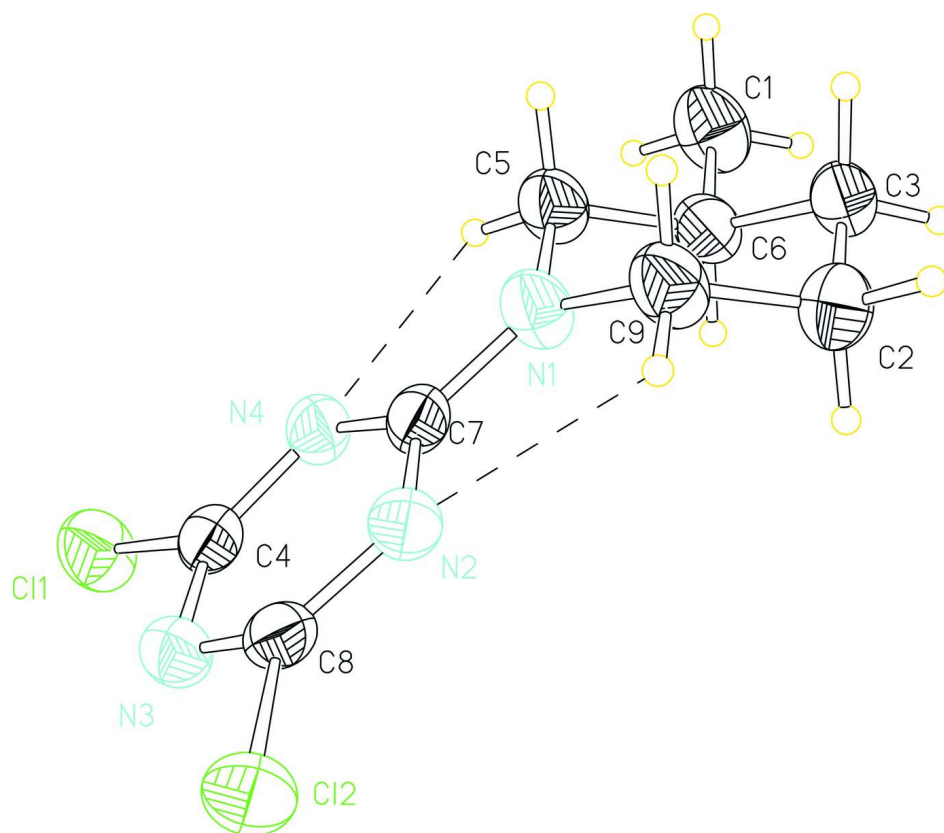
Fig. 2 shows the packing diagram and the stacking between pairs of pyrazine rings. The stacking distance between the ring centroids  $Cg\cdots Cg^i$  is 3.521 (7) Å, indicating quite strong  $\pi\cdots\pi$  interactions between the symmetry-related molecules (symmetry code:  $-x, 1 - y, 1 - z$ ). This face to face  $\pi\cdots\pi$  interaction plays a very important function in stabilizing the crystal structure (Hunter & Sanders, 1990).

### S2. Experimental

2,4,6-Trichloro-1,3,5-triazine (1.84 g, 10 mmol) and 3-methylpiperidine (0.99 g, 10 mmol) were dissolved in the mixture of acetone (25 ml) and H<sub>2</sub>O (5 ml) in the presence of KOH (0.56 g, 10 mmol) and refluxed for 24 h. The conversion of reaction was monitored by TLC. After the mixture was cooled to room temperature, the solution was filtered and rotated in vacuum. A white solid was obtained after purification by column chromatography on silica gel (n-18 hexane). Colorless crystals suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of a solution in ethanol at room temperature over several days.

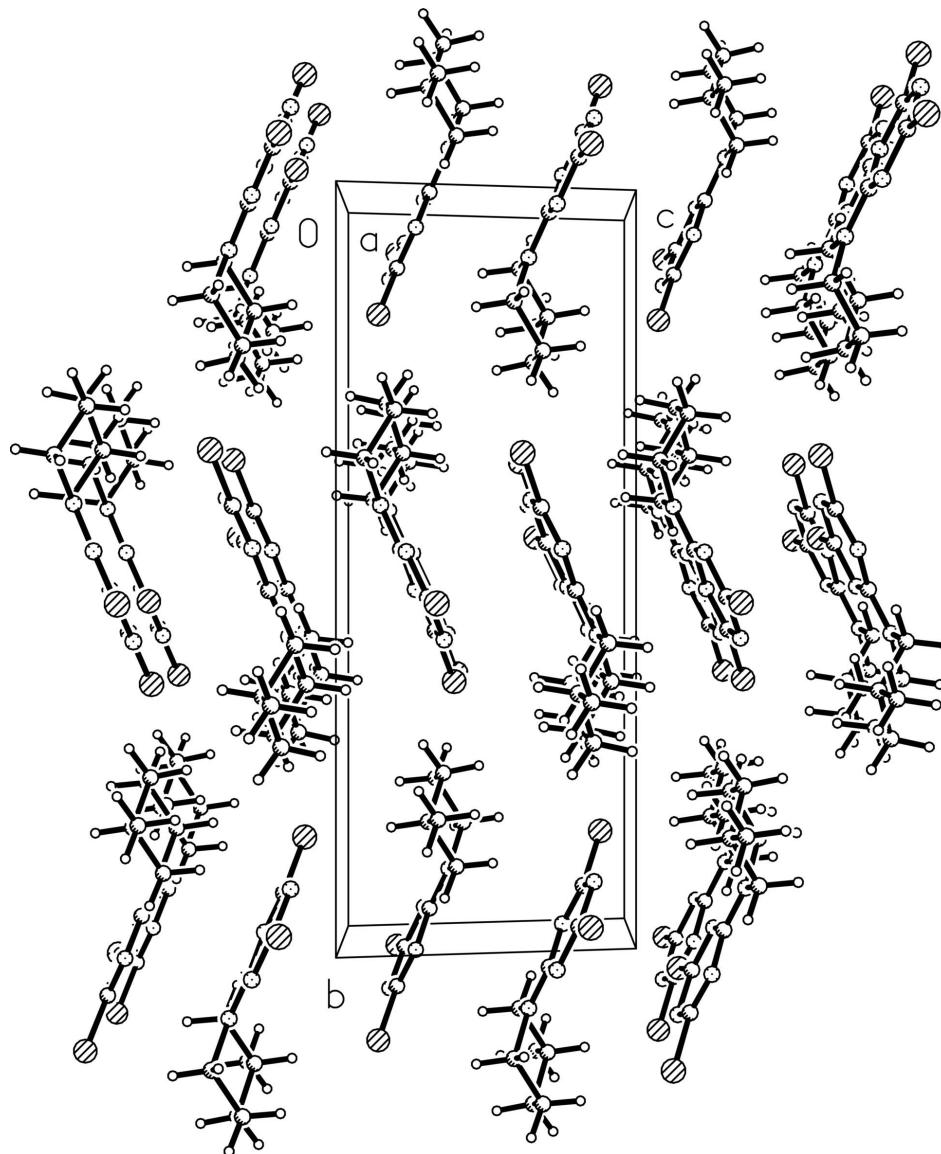
### S3. Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

View of the molecular structure of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.



**Figure 2**

The packing diagram of the title compound, viewed along the *a* axis.

### 2,4-Dichloro-6-(3-methylpiperidin-1-yl)-1,3,5-triazine

#### Crystal data

$C_9H_{12}Cl_2N_4$

$M_r = 247.13$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 8.086\ (16)\ \text{\AA}$

$b = 19.19\ (3)\ \text{\AA}$

$c = 7.813\ (15)\ \text{\AA}$

$\beta = 106.18\ (3)^\circ$

$V = 1164\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 512$

$D_x = 1.409\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2183 reflections

$\theta = 3.4\text{--}27.4^\circ$

$\mu = 0.53\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.40 \times 0.20 \times 0.15\ \text{mm}$

Data collection

Rigaku Mercury2 diffractometer	11851 measured reflections 2765 independent reflections
Radiation source: fine-focus sealed tube	1118 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.068$
Detector resolution: 13.6612 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 27.9^\circ$ , $\theta_{\text{min}} = 2.6^\circ$
CCD_Profile_fitting scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2005)	$k = -25 \rightarrow 25$
$T_{\text{min}} = 0.750$ , $T_{\text{max}} = 1.000$	$l = -10 \rightarrow 10$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.189$	$w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$
$S = 0.86$	where $P = (F_o^2 + 2F_c^2)/3$
2765 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
136 parameters	$\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

**Experimental.** The relative large standard uncertainties (s. u.) noted in Alert level B of PLATON may be explained by measurement at room temperature and weak diffraction power of the crystal.

**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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl2	0.33512 (12)	0.54293 (6)	0.33576 (14)	0.0794 (4)
Cl1	-0.24201 (14)	0.64892 (6)	0.38583 (16)	0.0890 (4)
N4	-0.2234 (3)	0.52641 (15)	0.2549 (4)	0.0597 (8)
N3	0.0402 (4)	0.59106 (15)	0.3557 (4)	0.0641 (8)
N2	0.0437 (4)	0.47725 (15)	0.2313 (4)	0.0615 (8)
C9	-0.1242 (5)	0.35428 (19)	0.0892 (6)	0.0774 (12)
H9A	-0.1644	0.3467	-0.0385	0.093*
H9B	-0.0010	0.3627	0.1210	0.093*
C8	0.1142 (4)	0.53582 (19)	0.3024 (4)	0.0598 (9)
N1	-0.2137 (4)	0.41552 (15)	0.1395 (4)	0.0682 (9)
C7	-0.1306 (4)	0.47334 (18)	0.2081 (5)	0.0574 (9)
C6	-0.4391 (5)	0.34335 (18)	0.2078 (5)	0.0681 (10)
H6A	-0.3900	0.3513	0.3359	0.082*
C5	-0.4023 (4)	0.4065 (2)	0.1093 (6)	0.0711 (11)

H5A	-0.4575	0.4012	-0.0172	0.085*
H5B	-0.4496	0.4477	0.1502	0.085*
C4	-0.1300 (5)	0.58034 (19)	0.3233 (5)	0.0600 (9)
C3	-0.3548 (5)	0.27924 (19)	0.1560 (5)	0.0720 (11)
H3A	-0.3735	0.2397	0.2257	0.086*
H3B	-0.4074	0.2688	0.0312	0.086*
C2	-0.1620 (5)	0.2904 (2)	0.1872 (6)	0.0826 (12)
H2A	-0.1078	0.2958	0.3139	0.099*
H2B	-0.1127	0.2496	0.1470	0.099*
C1	-0.6342 (6)	0.3354 (2)	0.1702 (7)	0.0919 (14)
H1A	-0.6814	0.3769	0.2065	0.138*
H1B	-0.6590	0.2962	0.2356	0.138*
H1C	-0.6846	0.3279	0.0450	0.138*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl2	0.0528 (6)	0.0896 (8)	0.0908 (8)	-0.0078 (5)	0.0118 (5)	0.0008 (6)
Cl1	0.0794 (8)	0.0676 (7)	0.1162 (10)	0.0117 (5)	0.0206 (7)	-0.0158 (6)
N4	0.0487 (16)	0.0527 (17)	0.075 (2)	0.0032 (14)	0.0119 (15)	0.0052 (15)
N3	0.0560 (19)	0.0611 (19)	0.072 (2)	-0.0043 (15)	0.0119 (15)	-0.0010 (15)
N2	0.0494 (16)	0.0615 (18)	0.0692 (19)	-0.0032 (14)	0.0092 (14)	0.0042 (15)
C9	0.064 (2)	0.063 (2)	0.102 (3)	0.004 (2)	0.018 (2)	-0.014 (2)
C8	0.0500 (19)	0.067 (2)	0.056 (2)	-0.0029 (18)	0.0052 (17)	0.0127 (18)
N1	0.0432 (16)	0.0593 (19)	0.100 (2)	-0.0032 (14)	0.0157 (16)	-0.0056 (17)
C7	0.0513 (19)	0.053 (2)	0.064 (2)	0.0009 (17)	0.0095 (17)	0.0117 (17)
C6	0.074 (3)	0.060 (2)	0.070 (2)	-0.0073 (19)	0.018 (2)	-0.0074 (19)
C5	0.052 (2)	0.062 (2)	0.094 (3)	-0.0047 (18)	0.012 (2)	-0.002 (2)
C4	0.062 (2)	0.056 (2)	0.059 (2)	0.0055 (18)	0.0129 (18)	0.0089 (17)
C3	0.090 (3)	0.054 (2)	0.070 (3)	-0.002 (2)	0.019 (2)	-0.0021 (18)
C2	0.085 (3)	0.066 (3)	0.092 (3)	0.015 (2)	0.018 (2)	-0.001 (2)
C1	0.077 (3)	0.081 (3)	0.125 (4)	-0.012 (2)	0.041 (3)	-0.010 (3)

*Geometric parameters (Å, °)*

Cl2—C8	1.737 (5)	C6—C5	1.510 (5)
Cl1—C4	1.743 (4)	C6—C1	1.529 (6)
N4—C4	1.305 (5)	C6—C3	1.516 (5)
N4—C7	1.373 (4)	C6—H6A	0.9800
N3—C8	1.340 (5)	C5—H5A	0.9700
N3—C4	1.344 (5)	C5—H5B	0.9700
N2—C8	1.312 (5)	C3—C2	1.524 (6)
N2—C7	1.372 (5)	C3—H3A	0.9700
C9—C2	1.521 (6)	C3—H3B	0.9700
C9—N1	1.489 (5)	C2—H2A	0.9700
C9—H9A	0.9700	C2—H2B	0.9700
C9—H9B	0.9700	C1—H1A	0.9600
N1—C7	1.330 (5)	C1—H1B	0.9600

N1—C5	1.487 (5)	C1—H1C	0.9600
C4—N4—C7	113.6 (3)	C6—C5—H5A	109.5
C8—N3—C4	110.1 (3)	N1—C5—H5B	109.5
C8—N2—C7	114.3 (3)	C6—C5—H5B	109.5
C2—C9—N1	108.8 (3)	H5A—C5—H5B	108.1
C2—C9—H9A	109.9	N4—C4—N3	130.1 (3)
N1—C9—H9A	109.9	N4—C4—C11	115.3 (3)
C2—C9—H9B	109.9	N3—C4—C11	114.6 (3)
N1—C9—H9B	109.9	C2—C3—C6	111.1 (3)
H9A—C9—H9B	108.3	C2—C3—H3A	109.4
N2—C8—N3	129.1 (3)	C6—C3—H3A	109.4
N2—C8—C12	116.0 (3)	C2—C3—H3B	109.4
N3—C8—C12	114.9 (3)	C6—C3—H3B	109.4
C7—N1—C5	122.8 (3)	H3A—C3—H3B	108.0
C7—N1—C9	122.5 (3)	C9—C2—C3	111.9 (3)
C5—N1—C9	114.8 (3)	C9—C2—H2A	109.2
N1—C7—N2	118.9 (3)	C3—C2—H2A	109.2
N1—C7—N4	118.3 (3)	C9—C2—H2B	109.2
N2—C7—N4	122.8 (3)	C3—C2—H2B	109.2
C5—C6—C1	108.8 (3)	H2A—C2—H2B	107.9
C5—C6—C3	110.4 (3)	C6—C1—H1A	109.5
C1—C6—C3	112.6 (3)	C6—C1—H1B	109.5
C5—C6—H6A	108.3	H1A—C1—H1B	109.5
C1—C6—H6A	108.3	C6—C1—H1C	109.5
C3—C6—H6A	108.3	H1A—C1—H1C	109.5
N1—C5—C6	110.6 (3)	H1B—C1—H1C	109.5
N1—C5—H5A	109.5		
C7—N2—C8—N3	0.6 (5)	C4—N4—C7—N2	-0.1 (5)
C7—N2—C8—C12	179.6 (2)	C7—N1—C5—C6	-122.5 (4)
C4—N3—C8—N2	-1.3 (5)	C9—N1—C5—C6	56.7 (4)
C4—N3—C8—C12	179.7 (2)	C1—C6—C5—N1	-178.9 (3)
C2—C9—N1—C7	124.0 (4)	C3—C6—C5—N1	-54.9 (4)
C2—C9—N1—C5	-55.2 (4)	C7—N4—C4—N3	-0.8 (5)
C5—N1—C7—N2	-179.9 (3)	C7—N4—C4—C11	-179.7 (2)
C9—N1—C7—N2	0.9 (5)	C8—N3—C4—N4	1.4 (5)
C5—N1—C7—N4	0.8 (5)	C8—N3—C4—C11	-179.7 (2)
C9—N1—C7—N4	-178.3 (3)	C5—C6—C3—C2	55.6 (4)
C8—N2—C7—N1	-179.0 (3)	C1—C6—C3—C2	177.3 (3)
C8—N2—C7—N4	0.2 (5)	N1—C9—C2—C3	53.9 (4)
C4—N4—C7—N1	179.0 (3)	C6—C3—C2—C9	-55.9 (5)

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C5—H5B $\cdots$ N4	0.97	2.34	2.787 (6)	108
C9—H9B $\cdots$ N2	0.97	2.35	2.794 (6)	107