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7-(2,4-Dichlorophenyl)-2-methylsulfanyl-pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

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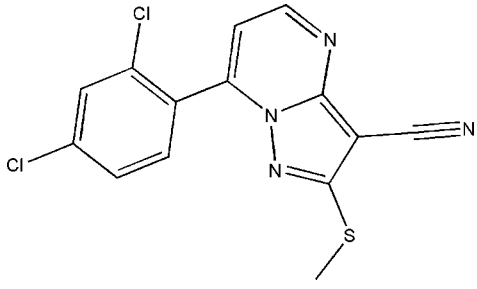
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.095; data-to-parameter ratio = 15.5.

In the molecule of the title compound, $C_{14}H_8Cl_2N_4S$, all the ring atoms in the pyrazolopyrimidine system are almost coplanar, the largest deviation from the mean plane being 0.027 (2) Å for a C atom. The conformation of the methylsulfanyl group is antiperiplanar, with a torsion angle of −176.7 (2)°. A weak intermolecular C—H···N hydrogen bond and a Cl···N halogen bond [Cl···N = 3.196 (5) Å] with a nearly linear N···Cl—C angle [174.2 (1)°] link the molecules into a two-dimensional assembly. Face-to-face π–π stacking, with a centroid–centroid separation of 3.557 (2) Å and an angle of 7.1 (1)° between the two planes, completes the intermolecular interactions in the solid state.

Related literature

For the biological activity of pyrazolo[1,5-*a*]pyrimidine derivatives, see: Li *et al.* (1995). For applications of enaminones, see: El-Taweei *et al.* (2001); Hernandez *et al.* (2003); Olivera *et al.* (2000). For bond-length data, see: Allen *et al.* (1987). For Cl···N halogen bonds, see: Chu, *et al.* (2001); Lommerse *et al.* (1996); Ramasubbu *et al.* (1986).



Experimental

Crystal data

$C_{14}H_8Cl_2N_4S$
M_r = 335.20
Monoclinic, $P2_1/n$
a = 8.230 (2) Å
b = 14.656 (4) Å
c = 12.667 (4) Å
β = 108.460 (5)°
V = 1449.3 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 293 K
0.32 × 0.26 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.814, T_{max} = 0.879
8252 measured reflections
2965 independent reflections
2181 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.095
S = 1.04
2965 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···N4^{i}	0.93	2.61	3.474 (3)	154

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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: ZL2192).

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7-(2,4-Dichlorophenyl)-2-methylsulfanylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

Li-rong Wen, Huai-yuan Xie and Shu-wen Wang

S1. Comment

Pyrazolo[1,5-*a*]pyrimidine derivatives have been reported to show various biological activities such as antibacterial, insulin releasing, anti-inflammatory activities (Li *et al.*, 1995). Enaminones have been widely used as building blocks in the synthesis of pyrazolo[1,5-*a*]pyrimidine derivatives (El-Taweei *et al.*, 2001; Hernandez *et al.*, 2003; Olivera *et al.*, 2000). We report here the crystal structure of title compound (Fig.1), which was synthesized by reaction of 1-(2,4-dichlorophenyl)-3-dimethylamino-2-en-1-one and 3-methylsulfanyl-4-cyano-5-amino-1*H*-pyrazole in the presence of acetic acid.

The bond lengths and angles in this compound are within normal ranges (Allen, 2002). All the ring atoms in the pyrazolopyrimidine moiety are almost coplanar, the largest deviation from the mean plane being 0.027 (2)Å for atom C10. The dihedral angle between the pyrazolopyrimidine moiety and the benzene ring is 54.9 (5)°. The conformation of the methylsulfanyl moiety is antiperiplanar with a torsion angle C11—C12—S1—C13 of -176.7 (2)°.

In the crystal structure of the title compound, there are a weak intermolecular hydrogen bond of one phenyl hydrogen atom towards the nitrile N atom (C8—H8···N4, Table 1) and a nitrogen-chlorine donor-acceptor interaction (Chu, *et al.*, 2001; Lommerse *et al.*, 1996; Ramasubbu, *et al.*, 1986) between the pyrimidinyl N atom and one of the chlorine atoms. The distance between Cl2 and N3 is 3.196 (5) Å which is definitively shorter than the sum of the corresponding van der Waals radii of Cl (1.75 Å) and N (1.55 Å). Moreover, this contact of N3 with Cl2 is nearly "head on" with N approaching Cl along the backside of C3—Cl2 with the N3···Cl2—C3 angle approximately linear 174.2 (1)° [symmetry code: -3/2 + *x*, 1/2 - *y*, -1/2 + *z*] (Fig. 2). These interactions loosly link the molecules into a two-dimensional assembly (Fig. 3). Face-to-face π-π stacking between the phenyl ring (C1—C6) and the pyrazol ring (C10—C12/N1/N2) in another molecule at 1/2+x, 3/2-y, 1/2+z complete the intermolecular interactions in the solid state. The centroid to centroid separation is 3.557 (2) Å and the angle between the two planes is 7.1 (1)°.

S2. Experimental

A mixture of 1-(2,4-dichlorophenyl)-3-dimethylamino-2-en-1-one (2 mmol) and 3-methylsulfanyl-4-cyano-5-amino-1*H*-pyrazole (2 mmol) in glacial acetic acid (15 ml) was stirred for 12 h at room temperature. Then the mixture was evaporated by rotary evaporation to remove the acetic acid, and recrystallized from a mixture of EtOH and DMF. Yield: 77%. (m.p. 475 K).

S3. Refinement

All H atoms were placed in calculated positions, with C—H = 0.93 or 0.96 Å, and included in the final cycles of the refinement using a riding model, with U_{iso}(H) set to 1.2 U_{eq}(C) for CH, and 1.5 U_{eq}(C) for CH_3.

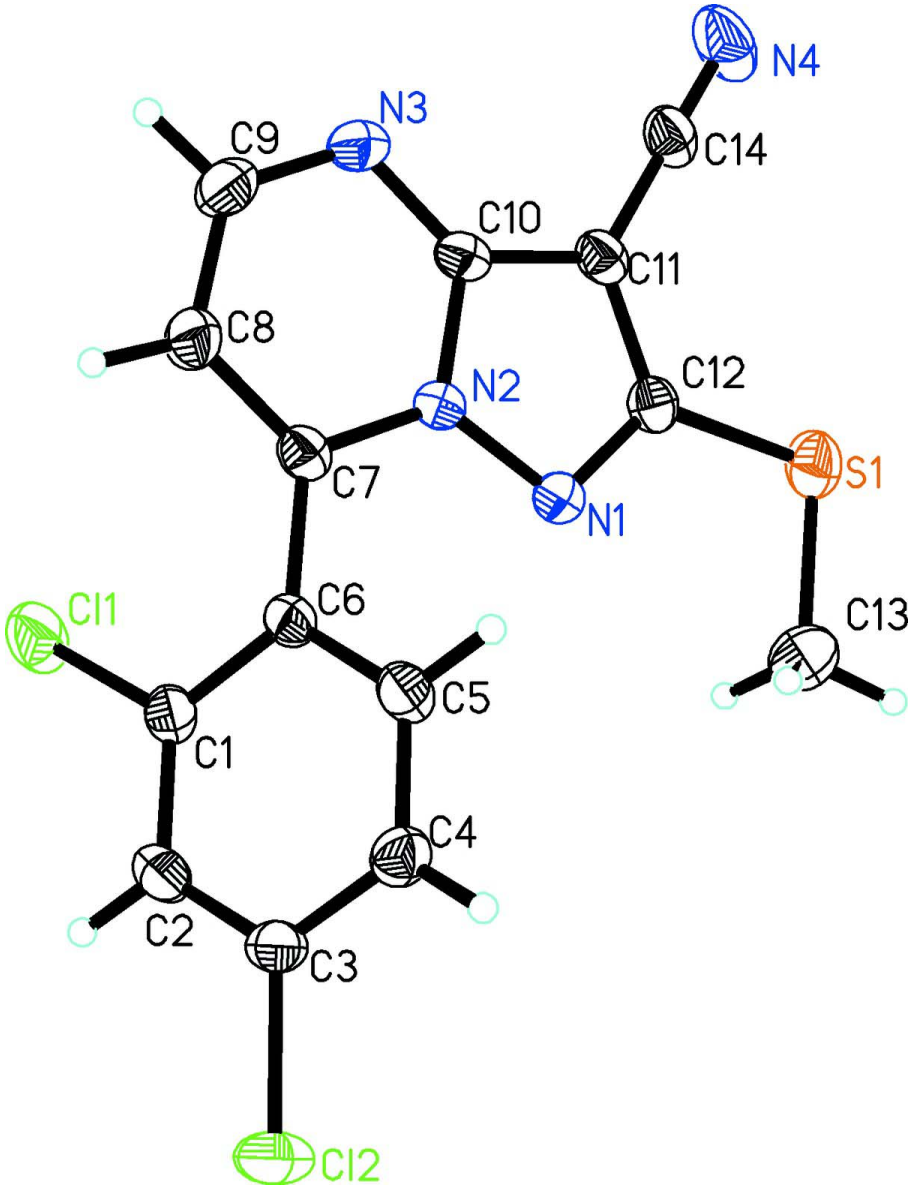

Figure 1

View of the title compound with 35% probability ellipsoids.

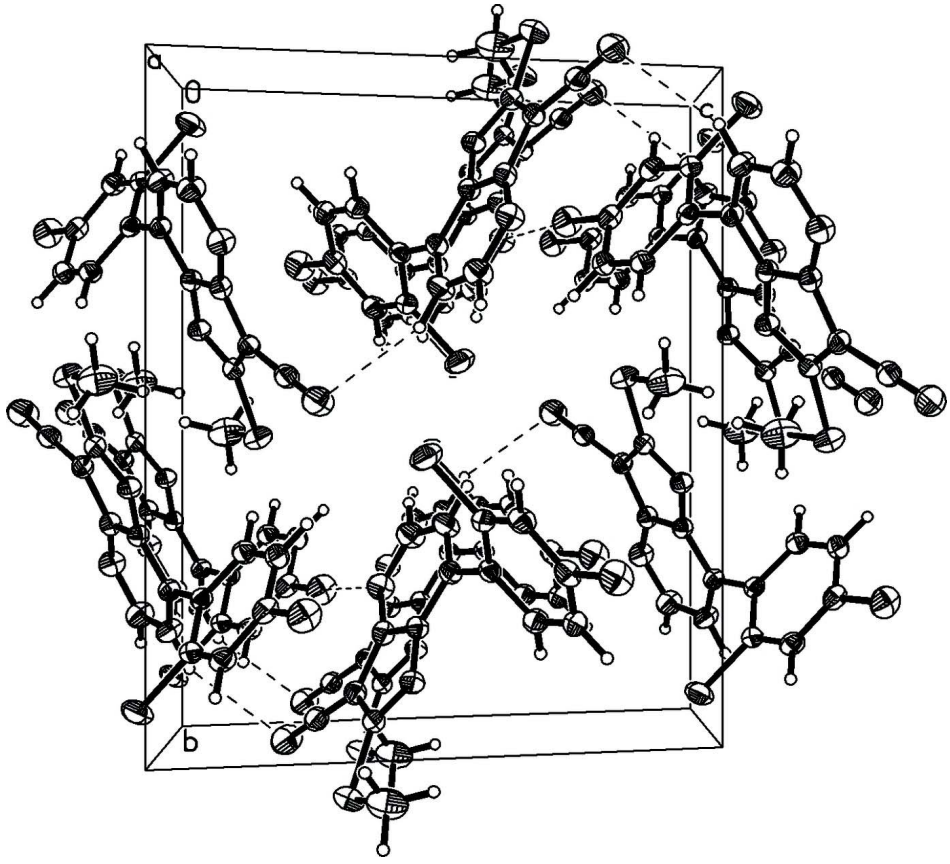

Figure 2

The molecular packing of the title compound viewed along the *a* axis. Dashed lines indicate the hydrogen bonds and N···Cl short contacts.

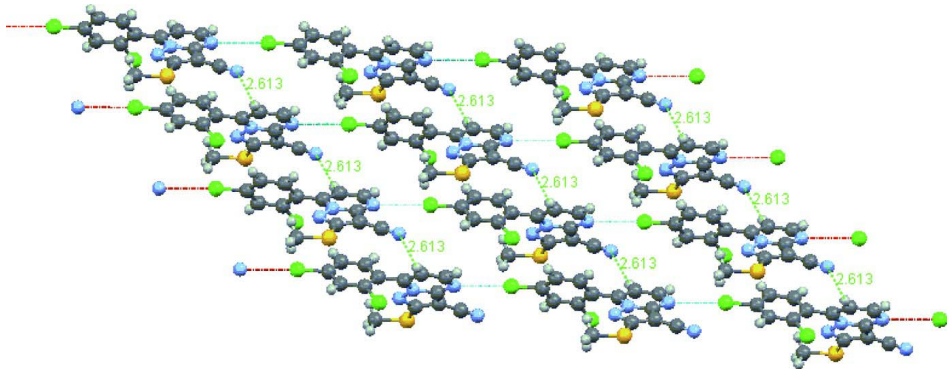

Figure 3

Diagram of two-dimensional structure linked by the hydrogen bonds and N···Cl short contacts.

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c = 12.667 (4) Å
β = 108.460 (5)°
V = 1449.3 (7) Å^3
Z = 4
F(000) = 680
D_x = 1.536 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 970 reflections
θ = 2.8–26.3°
μ = 0.59 mm^{-1}
T = 293 K
Prism, colorless
0.32 × 0.26 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.814, T_{max} = 0.879

8252 measured reflections
2965 independent reflections
2181 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.4°, θ_{min} = 2.6°
h = −6→10
k = −16→18
l = −15→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.095
S = 1.04
2965 reflections
191 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
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.5056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 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}
S1	0.07522 (9)	1.04589 (4)	0.33961 (6)	0.0515 (2)
Cl1	0.27654 (9)	0.56767 (4)	0.47097 (6)	0.0587 (2)
Cl2	0.81796 (7)	0.72025 (5)	0.77238 (6)	0.0570 (2)
N1	0.1176 (2)	0.88388 (12)	0.44665 (15)	0.0337 (4)
N2	0.0148 (2)	0.81205 (12)	0.45471 (14)	0.0304 (4)
N4	−0.4254 (3)	0.99138 (17)	0.2170 (2)	0.0694 (8)
C1	0.3585 (3)	0.65420 (15)	0.56647 (18)	0.0351 (5)
C2	0.5304 (3)	0.65097 (16)	0.62770 (19)	0.0399 (6)
H2	0.5982	0.6025	0.6193	0.048*
C3	0.6000 (3)	0.72040 (16)	0.70121 (19)	0.0373 (5)

C4	0.4996 (3)	0.79158 (16)	0.71666 (19)	0.0385 (5)
H4	0.5468	0.8373	0.7681	0.046*
C5	0.3289 (3)	0.79383 (16)	0.65490 (19)	0.0383 (5)
H5	0.2616	0.8420	0.6648	0.046*
C6	0.2541 (3)	0.72596 (14)	0.57789 (18)	0.0317 (5)
C7	0.0708 (3)	0.73292 (15)	0.51216 (18)	0.0335 (5)
C8	−0.0531 (3)	0.66876 (16)	0.5045 (2)	0.0437 (6)
H8	−0.0243	0.6132	0.5411	0.052*
C9	−0.2230 (3)	0.68669 (18)	0.4416 (2)	0.0479 (6)
H9	−0.3036	0.6412	0.4376	0.057*
N3	−0.2771 (2)	0.76324 (14)	0.38782 (17)	0.0427 (5)
C10	−0.1555 (3)	0.82588 (15)	0.39444 (18)	0.0336 (5)
C11	−0.1611 (3)	0.91130 (15)	0.34518 (18)	0.0352 (5)
C12	0.0087 (3)	0.94280 (15)	0.38006 (18)	0.0342 (5)
C13	0.3024 (4)	1.0381 (2)	0.4068 (3)	0.0697 (9)
H13A	0.3249	1.0229	0.4838	0.105*
H13B	0.3547	1.0957	0.4012	0.105*
H13C	0.3489	0.9916	0.3714	0.105*
C14	−0.3084 (3)	0.95536 (16)	0.2741 (2)	0.0429 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0594 (4)	0.0374 (4)	0.0588 (4)	0.0004 (3)	0.0206 (3)	0.0114 (3)
Cl1	0.0602 (4)	0.0408 (4)	0.0615 (4)	0.0086 (3)	−0.0002 (3)	−0.0164 (3)
Cl2	0.0290 (3)	0.0678 (5)	0.0654 (5)	0.0002 (3)	0.0025 (3)	0.0056 (4)
N1	0.0313 (10)	0.0320 (10)	0.0379 (11)	0.0008 (8)	0.0110 (8)	0.0017 (8)
N2	0.0266 (9)	0.0312 (10)	0.0319 (10)	0.0020 (7)	0.0069 (7)	0.0012 (8)
N4	0.0641 (15)	0.0544 (15)	0.0648 (16)	0.0238 (12)	−0.0150 (13)	−0.0040 (12)
C1	0.0396 (13)	0.0294 (11)	0.0335 (12)	0.0021 (10)	0.0075 (10)	0.0003 (10)
C2	0.0361 (13)	0.0379 (13)	0.0445 (14)	0.0101 (10)	0.0113 (11)	0.0052 (11)
C3	0.0276 (11)	0.0421 (13)	0.0400 (13)	−0.0003 (10)	0.0075 (10)	0.0083 (11)
C4	0.0385 (13)	0.0377 (13)	0.0347 (12)	−0.0040 (10)	0.0049 (10)	−0.0013 (10)
C5	0.0391 (13)	0.0346 (13)	0.0388 (13)	0.0072 (10)	0.0089 (10)	−0.0002 (10)
C6	0.0309 (11)	0.0302 (11)	0.0312 (11)	0.0028 (9)	0.0056 (9)	0.0034 (9)
C7	0.0338 (12)	0.0325 (12)	0.0323 (12)	0.0048 (9)	0.0079 (10)	0.0029 (9)
C8	0.0417 (14)	0.0374 (14)	0.0475 (15)	−0.0015 (11)	0.0075 (11)	0.0110 (11)
C9	0.0385 (14)	0.0461 (15)	0.0550 (16)	−0.0102 (11)	0.0089 (12)	0.0053 (12)
N3	0.0289 (10)	0.0456 (12)	0.0497 (12)	−0.0016 (9)	0.0070 (9)	0.0027 (10)
C10	0.0280 (11)	0.0383 (13)	0.0327 (12)	0.0045 (10)	0.0069 (9)	−0.0005 (10)
C11	0.0353 (12)	0.0347 (12)	0.0319 (12)	0.0072 (10)	0.0054 (9)	0.0002 (10)
C12	0.0391 (12)	0.0320 (12)	0.0319 (12)	0.0021 (10)	0.0117 (10)	0.0001 (10)
C13	0.0535 (17)	0.0595 (19)	0.104 (3)	−0.0107 (14)	0.0367 (17)	0.0076 (18)
C14	0.0450 (14)	0.0362 (13)	0.0393 (13)	0.0077 (11)	0.0016 (11)	−0.0040 (11)

Geometric parameters (Å, º)

S1—C12	1.739 (2)	C5—C6	1.393 (3)
S1—C13	1.796 (3)	C5—H5	0.9300
Cl1—C1	1.735 (2)	C6—C7	1.478 (3)
Cl2—C3	1.734 (2)	C7—C8	1.368 (3)
N1—C12	1.335 (3)	C8—C9	1.398 (3)
N1—N2	1.375 (2)	C8—H8	0.9300
N2—C7	1.369 (3)	C9—N3	1.315 (3)
N2—C10	1.383 (3)	C9—H9	0.9300
N4—C14	1.135 (3)	N3—C10	1.341 (3)
C1—C2	1.382 (3)	C10—C11	1.393 (3)
C1—C6	1.394 (3)	C11—C12	1.404 (3)
C2—C3	1.376 (3)	C11—C14	1.416 (3)
C2—H2	0.9300	C13—H13A	0.9600
C3—C4	1.383 (3)	C13—H13B	0.9600
C4—C5	1.375 (3)	C13—H13C	0.9600
C4—H4	0.9300		
C12—S1—C13	100.53 (12)	N2—C7—C6	118.02 (18)
C12—N1—N2	103.65 (17)	C7—C8—C9	120.0 (2)
C7—N2—N1	125.20 (17)	C7—C8—H8	120.0
C7—N2—C10	121.97 (18)	C9—C8—H8	120.0
N1—N2—C10	112.79 (17)	N3—C9—C8	124.7 (2)
C2—C1—C6	121.5 (2)	N3—C9—H9	117.6
C2—C1—Cl1	117.98 (17)	C8—C9—H9	117.6
C6—C1—Cl1	120.48 (17)	C9—N3—C10	115.34 (19)
C3—C2—C1	119.2 (2)	N3—C10—N2	122.7 (2)
C3—C2—H2	120.4	N3—C10—C11	132.0 (2)
C1—C2—H2	120.4	N2—C10—C11	105.25 (18)
C2—C3—C4	120.9 (2)	C10—C11—C12	105.43 (18)
C2—C3—Cl2	119.44 (18)	C10—C11—C14	126.5 (2)
C4—C3—Cl2	119.59 (18)	C12—C11—C14	128.1 (2)
C5—C4—C3	119.1 (2)	N1—C12—C11	112.9 (2)
C5—C4—H4	120.4	N1—C12—S1	122.49 (17)
C3—C4—H4	120.4	C11—C12—S1	124.61 (17)
C4—C5—C6	121.8 (2)	S1—C13—H13A	109.5
C4—C5—H5	119.1	S1—C13—H13B	109.5
C6—C5—H5	119.1	H13A—C13—H13B	109.5
C5—C6—C1	117.5 (2)	S1—C13—H13C	109.5
C5—C6—C7	119.43 (19)	H13A—C13—H13C	109.5
C1—C6—C7	123.12 (19)	H13B—C13—H13C	109.5
C8—C7—N2	115.24 (19)	N4—C14—C11	179.3 (3)
C8—C7—C6	126.7 (2)		
C12—N1—N2—C7	177.7 (2)	N2—C7—C8—C9	−0.3 (3)
C12—N1—N2—C10	−0.1 (2)	C6—C7—C8—C9	177.8 (2)
C6—C1—C2—C3	−0.3 (3)	C7—C8—C9—N3	−0.8 (4)

Cl1—C1—C2—C3	177.75 (18)	C8—C9—N3—C10	1.3 (4)
C1—C2—C3—C4	1.8 (4)	C9—N3—C10—N2	−0.9 (3)
C1—C2—C3—Cl2	−176.31 (18)	C9—N3—C10—C11	176.2 (2)
C2—C3—C4—C5	−1.9 (4)	C7—N2—C10—N3	−0.1 (3)
Cl2—C3—C4—C5	176.16 (18)	N1—N2—C10—N3	177.8 (2)
C3—C4—C5—C6	0.6 (4)	C7—N2—C10—C11	−177.85 (19)
C4—C5—C6—C1	0.9 (3)	N1—N2—C10—C11	0.1 (2)
C4—C5—C6—C7	−178.7 (2)	N3—C10—C11—C12	−177.4 (2)
C2—C1—C6—C5	−1.0 (3)	N2—C10—C11—C12	0.0 (2)
Cl1—C1—C6—C5	−179.02 (18)	N3—C10—C11—C14	1.9 (4)
C2—C1—C6—C7	178.6 (2)	N2—C10—C11—C14	179.4 (2)
Cl1—C1—C6—C7	0.6 (3)	N2—N1—C12—C11	0.1 (2)
N1—N2—C7—C8	−177.0 (2)	N2—N1—C12—S1	−178.37 (15)
C10—N2—C7—C8	0.7 (3)	C10—C11—C12—N1	−0.1 (3)
N1—N2—C7—C6	4.8 (3)	C14—C11—C12—N1	−179.5 (2)
C10—N2—C7—C6	−177.55 (19)	C10—C11—C12—S1	178.38 (17)
C5—C6—C7—C8	−125.1 (3)	C14—C11—C12—S1	−1.0 (3)
C1—C6—C7—C8	55.3 (3)	C13—S1—C12—N1	1.7 (2)
C5—C6—C7—N2	52.9 (3)	C13—S1—C12—C11	−176.7 (2)
C1—C6—C7—N2	−126.7 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···N4^{i}	0.93	2.61	3.474 (3)	154

Symmetry code: (i) *x*+1/2, −*y*+3/2, *z*+1/2.