

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(Z)-1-(2,5-Dichloro-3-thienyl)ethanone semicarbazoneHoong-Kun Fun,^{a,*} Ching Kheng Quah,^{a,§} A. M. Vijesh,^{b,¶} Chitrakar Hegde^c and Arun M. Isloor^d

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, ^bSeQuent Scientific Limited, No. 120 A&B, Industrial Area, Baikampady, New Mangalore, Karnataka 575 011, India, ^cDepartment of Chemistry, NITTE Institute of Technology, Yelahanka, Bangalore 560 064, India, and ^dDepartment of Chemistry, National Institute of Technology-Karnataka, Surathkal, Mangalore 575 025, India

Correspondence e-mail: hkfun@usm.my

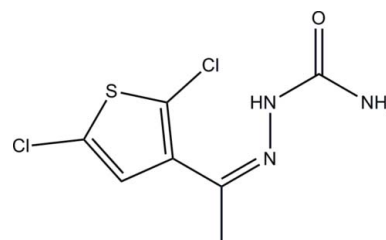
Received 7 July 2009; accepted 8 July 2009

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.100; data-to-parameter ratio = 26.7.

The title molecule, $\text{C}_7\text{H}_7\text{Cl}_2\text{N}_3\text{OS}$, is approximately planar [maximum deviation = 0.062 (1) Å]. Short intermolecular distances between the centroids of the five-membered rings [3.5340 (8) Å] indicate the existence of π - π interactions. An interesting feature of the crystal structure is the presence of short intramolecular $\text{Cl}\cdots\text{N}$ interactions [3.0015 (11) Å]. Molecules are linked *via* pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, generating $R_2^2(8)$ ring motifs. Furthermore, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds form $R_2^1(7)$ ring motifs with $\text{C}-\text{H}\cdots\text{O}$ contacts, further consolidating the crystal structure. In the crystal, molecules are linked by these intermolecular interactions, forming chains along [001].

Related literature

For the synthetic utility and applications of semicarbazone derivatives, see: Warren *et al.* (1977); Chandra & Gupta (2005); Jain *et al.* (2002); Pilgram (1978); Yogeewari *et al.* (2004). For related structures, see: Fun *et al.* (2009a,b). For the preparation, see: Furniss *et al.* (1978). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{Cl}_2\text{N}_3\text{OS}$
 $M_r = 252.12$
 Monoclinic, $C2/c$
 $a = 13.0796$ (2) Å
 $b = 10.4316$ (2) Å
 $c = 14.4352$ (2) Å
 $\beta = 94.599$ (1)°
 $V = 1963.21$ (6) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.84$ mm⁻¹
 $T = 100$ K
 $0.49 \times 0.22 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.683$, $T_{\max} = 0.934$
 16375 measured reflections
 3742 independent reflections
 3060 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.100$
 $S = 1.13$
 3742 reflections
 140 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Selected interatomic distance (Å).

$\text{Cg1}\cdots\text{Cg1}^i$	3.7188 (6)
--------------------------------	------------

Symmetry code: (i) $x + \frac{5}{2}, y + \frac{1}{2}, z + 1$. Cg1 is the centroid of the S1/C3-C6 five-membered ring.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N1}\cdots\text{O1}^{\text{ii}}$	0.86 (2)	2.02 (2)	2.8766 (15)	177.3 (19)
$\text{N2}-\text{H1N2}\cdots\text{O1}^{\text{iii}}$	0.863 (19)	2.035 (19)	2.8949 (14)	174.2 (17)
$\text{C7}-\text{H7A}\cdots\text{O1}^{\text{iii}}$	0.96	2.38	3.3370 (17)	176

Symmetry codes: (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

HKF and CKQ thank Universiti Sains Malaysia (USM) for the Research University Golden Goose Grant (No. 1001/

* Thomson Reuters ResearcherID: A-3561-2009.

§ Thomson Reuters ResearcherID: A-5525-2009.

¶ Current address: Department of Chemistry, National Institute of Technology-Karnataka, Surathkal, Mangalore 575 025, India.

PFIZIK/811012). CKQ thanks USM for a Research Fellowship. AMI is grateful to the Head of the Department of Chemistry and the Director, NITK, Surathkal, India, for providing research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2498).

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chandra, S. & Gupta, L. K. (2005). *Spectrochim. Acta Part A*, **62**, 1089–1094.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Fun, H.-K., Quah, C. K., Padaki, M., Malladi, S. & Isloor, A. M. (2009a). *Acta Cryst.* **E65**, o1634–o1635.
- Fun, H.-K., Yeap, C. S., Padaki, M., Malladi, S. & Isloor, A. M. (2009b). *Acta Cryst.* **E65**, o1619–o1620.
- Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. & Tatchell, A. R. (1978). *Vogel's Textbook of Practical Organic Chemistry*, 4th ed. p. 1112. London: ELBS.
- Jain, V. K., Handa, A., Pandya, R., Shrivastav, P. & Agrawal, Y. K. (2002). *React. Funct. Polym.* **51**, 101–110.
- Pilgram, K. H. G. (1978). US Patent No. 4 108 399.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Warren, J. D., Woodward, D. L. & Hargreaves, R. T. (1977). *J. Med. Chem.* **20**, 1520–1521.
- Yogeeswari, P., Sriram, D., Pandeya, S. N. & Stables, J. P. (2004). *Farmaco*, **59**, 609–613.

supporting information

Acta Cryst. (2009). E65, o1852–o1853 [doi:10.1107/S1600536809026567]

(Z)-1-(2,5-Dichloro-3-thienyl)ethanone semicarbazone

Hoong-Kun Fun, Ching Kheng Quah, A. M. Vijesh, Chitrakar Hegde and Arun M. Isloor

S1. Comment

Semicarbazones find immense applications in the field of synthetic chemistry, such as medicinal chemistry (Warren *et al.*, 1977), organometallics (Chandra & Gupta, 2005), polymers (Jain *et al.*, 2002) and herbicides (Pilgram, 1978). Further, 4-sulphamoylphenyl semicarbazones were found to possess anti-convulsant activity (Yogeeswari *et al.*, 2004). Herein, we report the crystal structure of the title semicarbazone (I).

The bond lengths and angles in (I), Fig. 1, are comparable to those observed in two closely related structures (Fun *et al.*, 2009*a*, *b*). The molecule is approximately planar, with an r.m.s. deviation of 0.062 (1) Å for atom O1. The short intramolecular distances between the centroids of five-membered rings [3.5340 (8) Å] prove existence of π - π interactions (Table 1). The interesting feature of the crystal structure is the short intermolecular Cl \cdots N interactions [3.0015 (11) Å].

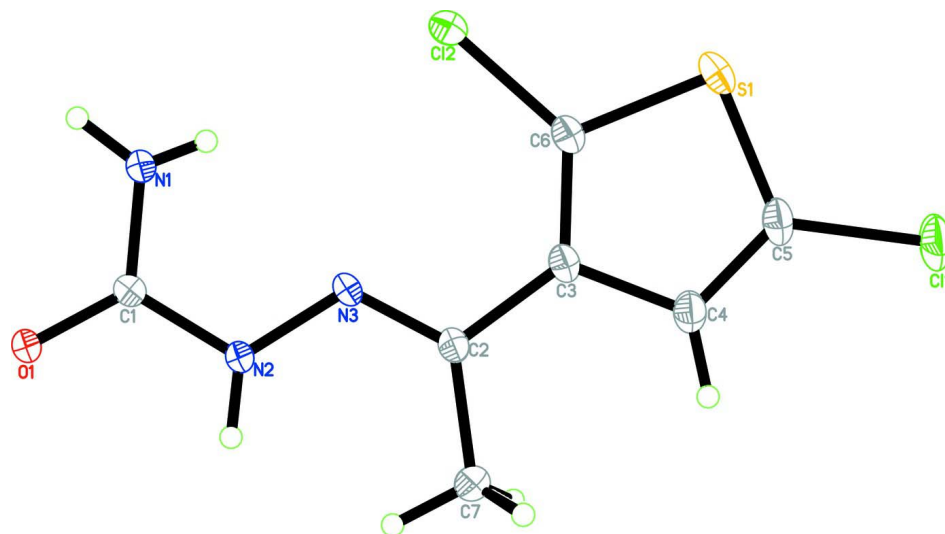
The molecules are linked *via* pairs of intermolecular N1—H1N1 \cdots O1 and N2—H1N2 \cdots O1 (Table 2) hydrogen bonds to generate $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995) (Fig. 2). Furthermore, N2—H1N2 \cdots O1 hydrogen bonds form $R_2^1(7)$ ring motifs with C7—H7A \cdots O1 contacts to further consolidate the crystal structure. The molecules are linked by these intermolecular interactions to form 1-D chains along the [0 0 1] direction.

S2. Experimental

Semicarbazide hydrochloride (1.84 g, 16.5 mmol) and freshly recrystallized sodium acetate (1.64 g, 20.0 mmol) was dissolved in water (15 ml) according to a literature procedure (Furniss *et al.*, 1978). The reaction mixture was stirred at room temperature for 10 minutes. To this, 2,5-dichloro-3-acetylthiophene (3.0 g, 15.4 mmol) in ethanol (15 ml) was added and stirred well for 6 h. The separated semicarbazone was filtered, washed with chilled water and recrystallized from an ethanol/dimethylformamide mixture. Yield: 3.19 g, 82.22%. *M.p.* 491–493 K.

S3. Refinement

N-bound H atoms were located in a difference Fourier map and were allowed to refine freely, see Table 2 for distances. All the other H atoms were placed in calculated positions, with C—H = 0.93 or 0.96 Å, and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C})$. A rotating-group model was applied for the methyl group.

**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

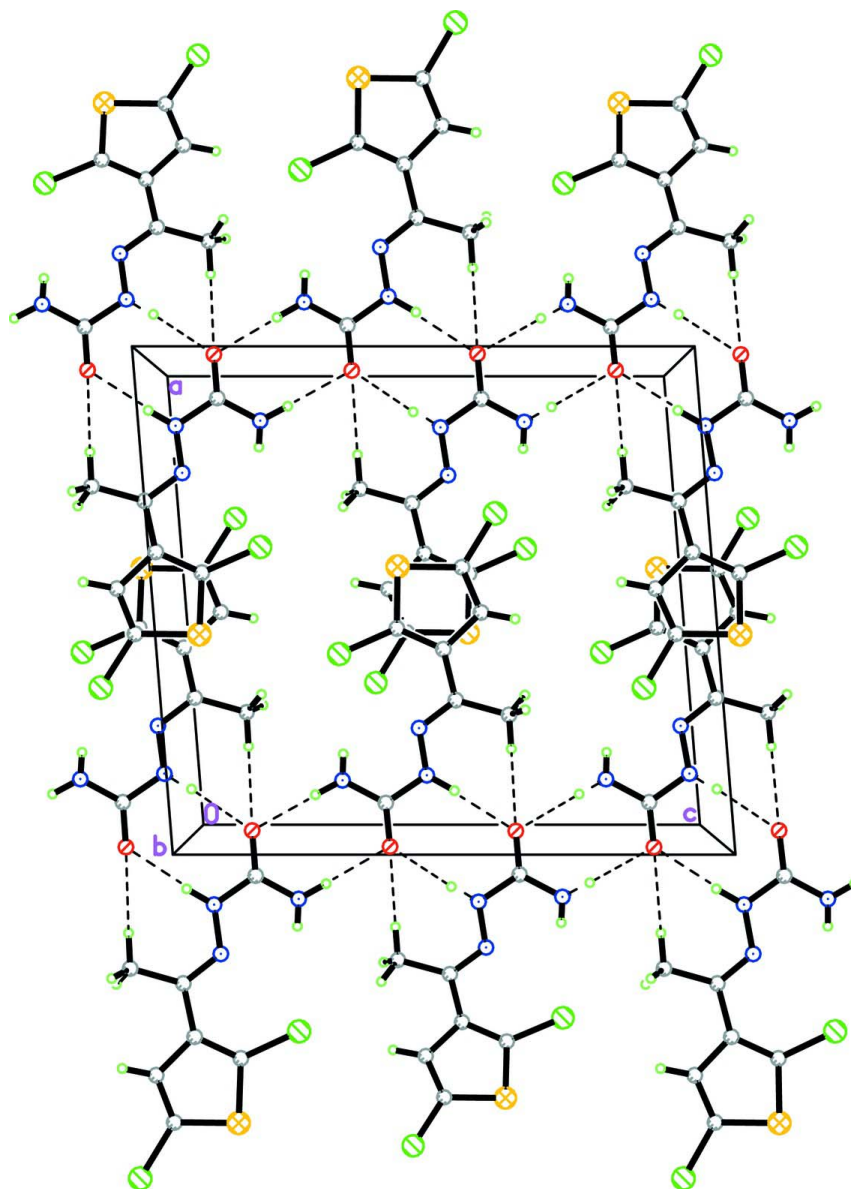


Figure 2

The crystal packing in (I), viewed along the *b* axis. The dashed lines indicate hydrogen bonds and C-H...O contacts.

(Z)-1-(2,5-Dichloro-3-thienyl)ethanone semicarbazone

Crystal data

$C_7H_7Cl_2N_3OS$

$M_r = 252.12$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 13.0796 (2) \text{ \AA}$

$b = 10.4316 (2) \text{ \AA}$

$c = 14.4352 (2) \text{ \AA}$

$\beta = 94.599 (1)^\circ$

$V = 1963.21 (6) \text{ \AA}^3$

$Z = 8$

$F(000) = 1024$

$D_x = 1.706 \text{ Mg m}^{-3}$

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

Cell parameters from 6313 reflections

$\theta = 2.5\text{--}33.2^\circ$

$\mu = 0.84 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Plate, colourless

$0.49 \times 0.22 \times 0.08 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2005)
 $T_{\min} = 0.683$, $T_{\max} = 0.934$

16375 measured reflections
3742 independent reflections
3060 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 33.2^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -20 \rightarrow 19$
 $k = -16 \rightarrow 15$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.100$
 $S = 1.13$
3742 reflections
140 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
 $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.6332P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	1.17736 (3)	0.23231 (4)	0.62567 (3)	0.02794 (10)
C12	0.88955 (3)	0.12728 (4)	0.31571 (2)	0.02421 (10)
S1	1.06944 (2)	0.19596 (3)	0.43833 (3)	0.01940 (9)
O1	0.48318 (7)	-0.00827 (9)	0.37962 (6)	0.01622 (18)
N1	0.62401 (10)	0.02718 (15)	0.30045 (8)	0.0247 (3)
N2	0.63508 (8)	0.03704 (11)	0.46052 (7)	0.0150 (2)
N3	0.73470 (8)	0.07286 (10)	0.45321 (7)	0.0146 (2)
C1	0.57608 (9)	0.01731 (12)	0.37865 (8)	0.0147 (2)
C2	0.79348 (9)	0.09889 (12)	0.52643 (9)	0.0141 (2)
C3	0.89959 (10)	0.13686 (12)	0.51073 (9)	0.0150 (2)
C4	0.97547 (10)	0.16495 (13)	0.58619 (9)	0.0183 (2)
H4A	0.9621	0.1617	0.6485	0.022*
C5	1.06803 (10)	0.19643 (13)	0.55714 (10)	0.0194 (3)
C6	0.94260 (10)	0.15031 (13)	0.42725 (9)	0.0167 (2)

C7	0.76299 (11)	0.09363 (16)	0.62397 (9)	0.0232 (3)
H7A	0.6913	0.0734	0.6234	0.035*
H7B	0.7757	0.1753	0.6533	0.035*
H7C	0.8024	0.0288	0.6579	0.035*
H1N1	0.5931 (16)	0.0142 (19)	0.2466 (16)	0.036 (5)*
H2N1	0.6797 (17)	0.0442 (19)	0.3063 (14)	0.030 (5)*
H1N2	0.6027 (14)	0.0324 (17)	0.5102 (13)	0.022 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01347 (16)	0.0327 (2)	0.0365 (2)	-0.00378 (13)	-0.00478 (14)	-0.00720 (15)
Cl2	0.01543 (15)	0.0411 (2)	0.01659 (15)	-0.00354 (13)	0.00432 (11)	0.00003 (12)
S1	0.01115 (15)	0.02034 (16)	0.02707 (17)	-0.00210 (11)	0.00391 (12)	0.00104 (12)
O1	0.0101 (4)	0.0251 (5)	0.0135 (4)	-0.0015 (4)	0.0005 (3)	0.0007 (3)
N1	0.0116 (5)	0.0502 (8)	0.0124 (5)	-0.0061 (5)	0.0008 (4)	-0.0013 (5)
N2	0.0102 (4)	0.0224 (5)	0.0122 (4)	-0.0034 (4)	0.0008 (4)	-0.0002 (4)
N3	0.0095 (4)	0.0199 (5)	0.0148 (4)	-0.0027 (4)	0.0018 (4)	-0.0003 (4)
C1	0.0121 (5)	0.0185 (6)	0.0136 (5)	-0.0006 (4)	0.0020 (4)	-0.0001 (4)
C2	0.0113 (5)	0.0156 (5)	0.0152 (5)	-0.0010 (4)	0.0010 (4)	-0.0004 (4)
C3	0.0113 (5)	0.0154 (5)	0.0182 (5)	-0.0006 (4)	0.0006 (4)	-0.0008 (4)
C4	0.0137 (6)	0.0199 (6)	0.0208 (6)	-0.0011 (5)	-0.0010 (5)	-0.0029 (5)
C5	0.0121 (5)	0.0195 (6)	0.0261 (6)	-0.0011 (5)	-0.0020 (5)	-0.0041 (5)
C6	0.0117 (5)	0.0192 (6)	0.0192 (6)	-0.0010 (5)	0.0016 (4)	0.0000 (4)
C7	0.0164 (6)	0.0390 (8)	0.0140 (5)	-0.0029 (6)	0.0005 (5)	-0.0002 (5)

Geometric parameters (Å, °)

Cl1—C5	1.7137 (14)	N3—C2	1.2851 (16)
Cl2—C6	1.7182 (13)	C2—C3	1.4782 (18)
S1—C5	1.7167 (15)	C2—C7	1.4949 (18)
S1—C6	1.7211 (13)	C3—C6	1.3773 (19)
O1—C1	1.2452 (15)	C3—C4	1.4436 (18)
N1—C1	1.3384 (17)	C4—C5	1.3530 (19)
N1—H1N1	0.86 (2)	C4—H4A	0.9300
N1—H2N1	0.75 (2)	C7—H7A	0.9600
N2—N3	1.3677 (15)	C7—H7B	0.9600
N2—C1	1.3741 (16)	C7—H7C	0.9600
N2—H1N2	0.863 (19)		
Cg1...Cg1 ⁱ	3.7188 (6)	Cl2...N3	3.0015 (11)
C5—S1—C6	90.35 (6)	C4—C3—C2	122.41 (12)
C1—N1—H1N1	122.3 (14)	C5—C4—C3	113.17 (13)
C1—N1—H2N1	116.2 (16)	C5—C4—H4A	123.4
H1N1—N1—H2N1	122 (2)	C3—C4—H4A	123.4
N3—N2—C1	116.57 (10)	C4—C5—Cl1	126.87 (12)
N3—N2—H1N2	127.8 (12)	C4—C5—S1	112.98 (10)

C1—N2—H1N2	115.3 (12)	C11—C5—S1	120.14 (8)
C2—N3—N2	120.34 (11)	C3—C6—C12	130.02 (10)
O1—C1—N1	123.33 (12)	C3—C6—S1	113.90 (10)
O1—C1—N2	120.24 (11)	C12—C6—S1	116.08 (8)
N1—C1—N2	116.44 (11)	C2—C7—H7A	109.5
N3—C2—C3	115.96 (11)	C2—C7—H7B	109.5
N3—C2—C7	125.43 (11)	H7A—C7—H7B	109.5
C3—C2—C7	118.61 (11)	C2—C7—H7C	109.5
C6—C3—C4	109.59 (11)	H7A—C7—H7C	109.5
C6—C3—C2	128.00 (12)	H7B—C7—H7C	109.5
C1—N2—N3—C2	176.77 (12)	C3—C4—C5—C11	-178.46 (10)
N3—N2—C1—O1	-175.87 (11)	C3—C4—C5—S1	0.65 (16)
N3—N2—C1—N1	4.15 (18)	C6—S1—C5—C4	-0.70 (11)
N2—N3—C2—C3	-179.86 (11)	C6—S1—C5—C11	178.47 (9)
N2—N3—C2—C7	0.1 (2)	C4—C3—C6—C12	179.02 (11)
N3—C2—C3—C6	1.5 (2)	C2—C3—C6—C12	-0.5 (2)
C7—C2—C3—C6	-178.55 (13)	C4—C3—C6—S1	-0.35 (15)
N3—C2—C3—C4	-177.95 (12)	C2—C3—C6—S1	-179.82 (10)
C7—C2—C3—C4	2.03 (19)	C5—S1—C6—C3	0.60 (11)
C6—C3—C4—C5	-0.19 (17)	C5—S1—C6—C12	-178.86 (9)
C2—C3—C4—C5	179.32 (12)		

Symmetry code: (i) $x+5/2, y+1/2, z+1$.

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>
N1—H1N1 \cdots O1 ⁱⁱ	0.86 (2)	2.02 (2)	2.8766 (15)	177.3 (19)
N2—H1N2 \cdots O1 ⁱⁱⁱ	0.863 (19)	2.035 (19)	2.8949 (14)	174.2 (17)
C7—H7A \cdots O1 ⁱⁱⁱ	0.96	2.38	3.3370 (17)	176

Symmetry codes: (ii) $-x+1, y, -z+1/2$; (iii) $-x+1, -y, -z+1$.