

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-(5-Iodo-2-oxoindolin-3-ylidene)-hydrazinecarbothioamide including an unknown solvate

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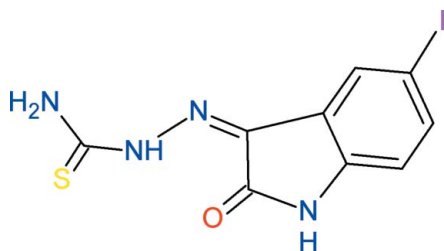
Received 2 May 2014; accepted 11 May 2014

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.028; wR factor = 0.062; data-to-parameter ratio = 18.0.

The molecule of the title compound, $\text{C}_9\text{H}_7\text{IN}_4\text{OS}$, is almost planar (r.m.s. deviation = 0.0373 Å). In the molecule, $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds generate, respectively, $S(5)$ and $S(6)$ ring motifs. In the crystal, molecules are linked via $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming chains propagating along [010]. These chains are linked via $\text{S}\cdots\text{I}$ contacts [3.4915 (16) Å], forming sheets lying parallel to (100). A region of disordered electron density, probably a disordered tetrahydrofuran solvent molecule, was treated using the SQUEEZE routine in PLATON [Spek (2009)]. *Acta Cryst.* **D65**, 148–155]. The formula mass and unit-cell characteristics were not taken into account during refinement.

Related literature

For the synthesis, see: Chiyanzu *et al.* (2003). For applications, see: Silva *et al.* (2001); Chiyanzu *et al.* (2003). For similar structures, see: de Bittencourt *et al.* (2014); Bandeira *et al.* (2013); de Oliveira *et al.* (2012). For $\text{S}\cdots\text{I}$ interactions, see: Auffinger *et al.* (2004).



Experimental

Crystal data

$\text{C}_9\text{H}_7\text{IN}_4\text{OS}$
 $M_r = 346.15$
 Monoclinic, $C2/c$
 $a = 33.765$ (5) Å
 $b = 4.4569$ (5) Å
 $c = 19.977$ (3) Å
 $\beta = 123.100$ (4)°
 $V = 2518.4$ (6) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 2.69$ mm⁻¹
 $T = 100$ K
 $1.15 \times 0.10 \times 0.09$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: numerical (SADABS; Bruker, 2009)
 $T_{\min} = 0.701$, $T_{\max} = 0.777$
 18679 measured reflections
 2892 independent reflections
 2577 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.062$
 $S = 1.05$
 2892 reflections
 161 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.52$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H12}\cdots\text{N3}$	0.85 (4)	2.28 (4)	2.633 (3)	105 (3)
$\text{N2}-\text{H21}\cdots\text{O1}$	0.83 (4)	2.07 (4)	2.725 (3)	135 (3)
$\text{N4}-\text{H41}\cdots\text{O1}^i$	0.77 (3)	2.04 (4)	2.809 (3)	178 (3)
$\text{N1}-\text{H11}\cdots\text{S1}^{ii}$	0.79 (3)	2.66 (4)	3.448 (3)	170 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 4, -z + 1$.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010) and PLATON (Spek, 2009).

We gratefully acknowledge Professor Dr Manfredo Hörner (Federal University of Santa Maria, Brazil) for his help and support with the X-ray measurements. We also acknowledge financial support through the DECIT/SCTIE-MS-CNPq-FAPERGS-Pronem-# 11/2029-1 and PRONEX-CNPq-FAPERGS projects.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BG2528).

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supporting information

Acta Cryst. (2014). E70, o666–o667 [doi:10.1107/S1600536814010782]

2-(5-Iodo-2-oxindolin-3-ylidene)hydrazinecarbothioamide including an unknown solvate

Viviane Conceição Duarte de Bittencourt, Vanessa Carratu Gervini, Juliano Rosa de Menezes Vicenti, Jecika Maciel Velasques and Priscilla Jussiane Zambiasi

S1. Comment

Isatins and their derivatives are described as compounds with technological applications, such as organic analytical chemistry and pigments and dyes (Silva *et al.*, 2001). Particularly, halogen substituted isatins containing thio-semicarbazone fragment demonstrated biological activity against some trypanosomes (cruzain and rhodesain) and malaria (falcipain-2) parasites (Chiyanzu *et al.*, 2003). In this paper, we describe the crystal structure of 2-(5-Iodo-2-oxindolin-3-ylidene)-hydrazinecarbothioamide, C₉H₇ON₄SI. There is one molecule in the asymmetric unit (Figure 1), and it is very similar to that of the Cl analogue previously published by us (de Bittencourt *et al.*, 2014). The molecule is almost planar (Bandeira *et al.*, 2013; de Oliveira *et al.*, 2012), displaying a r.m.s. deviation of 0.0373 Å for all fitted non-hydrogenoid atoms (with maximum deviation of 0.1057 (12) observed for S1 atom). Although the same intramolecular S(5) and S(6) ring motifs are verified (Table 1), the crystal packing differs totally when compared with the chloro substituted analog. In the present case, co-operative dimmers are formed through N1—H11ⁱ⋯S1ⁱ interactions displaying distances of 2.67 (4) Å. The crystal structure is expanded along the [010] crystallographic direction through N4—H41ⁱⁱ⋯O1ⁱⁱ interactions with distances of 2.08 (4) Å, generating a *one-dimensional polymer-like* motif. One of the most interesting features are the Sⁱⁱⁱ⋯Iⁱⁱⁱ contacts which further connects the molecules along the [001] crystallographic direction, presenting distances of 3.4915 (16) Å (Figure 2, symmetry codes: (i) $-x, 2-y, -z$; (ii) $1/2-x, -1/2+y, 1/2-z$; (iii) $x, -y, 1/2+z$). Such Sⁱⁱⁱ⋯I short interactions are related to be present in sulfur-containing proteins like cysteine and methionine (Auffinger *et al.*, 2004), being mentioned to play an important role in biological systems. As a second interesting feature, it was noted disordered solvent molecules occupying accessible voids of 83 Å³, suggestive of tetrahydrofuran, which was indeed used for crystallization. Due to this, collected data was treated using the *SQUEEZE* routine of the *PLATON* software (Spek, 2009) in order to remove solvent electronic density. The new *HKP* file generated was then used for further refinement of the final solvent free crystal structure. For solvent-voids position assignment in the unit cell, a solvent plot calculated by *PLATON* is shown in Figure 3.

S2. Experimental

To 20 ml of ethanol it was mixed 500 mg (1.83 mmol s) of 5-iodo-isatine with 170 mg (1.83 mmol s) of thio-semicarbazide. Then, it was added ten drops of glacial acetic acid and the system was kept under reflux for four hours. After this time, the reaction mixture was cooled and an orange precipitated was filtered off under vacuum and dried at room temperature. m.p. 249–253 °C. Yield: 98%. Crystallization: needle single crystals of the title compound suitable for X-ray diffraction were obtained by slow evaporating a solution containing 30 mg of the product dissolved in 5 ml of tetrahydrofuran.

S3. Refinement

All H atoms attached to C atoms were positioned with idealized geometry and were refined isotropic with $U_{\text{eq}}(\text{H})$ set to 1.2 times of the $U_{\text{eq}}(\text{C})$. It was used a riding model with aromatic C—H = 0.93 Å. Reflection 200 was omitted due to the large difference observed between F_o^2 and F_c^2 .

The needle-like single crystals were very weakly diffracting for what an unusually large crystal (1.152mm, with a 0.6 mm collimator) was used.

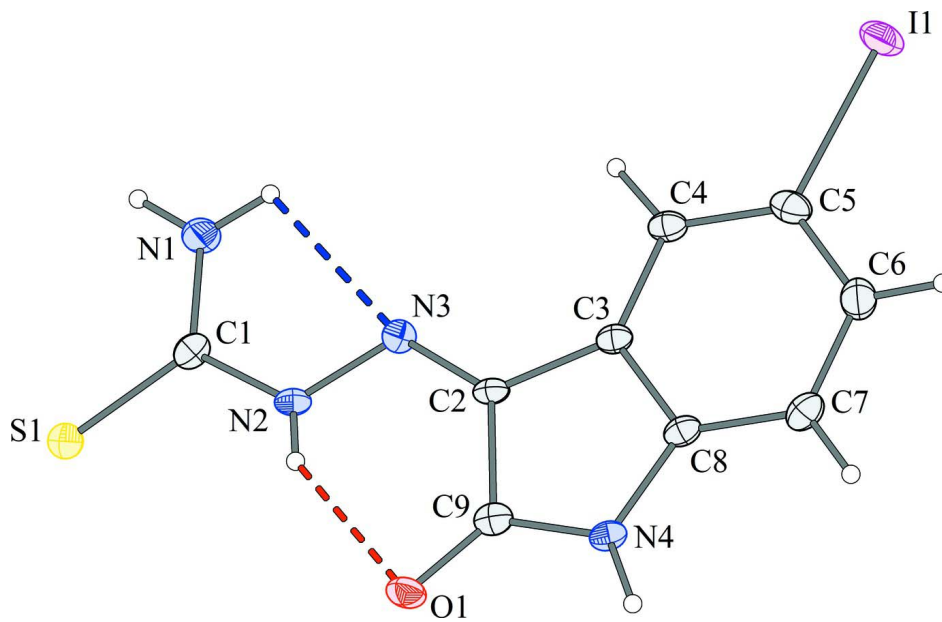


Figure 1

Asymmetric unit of the title compound showing intramolecular hydrogen bond interactions represented with dashed lines. Ellipsoid probability: 50%.

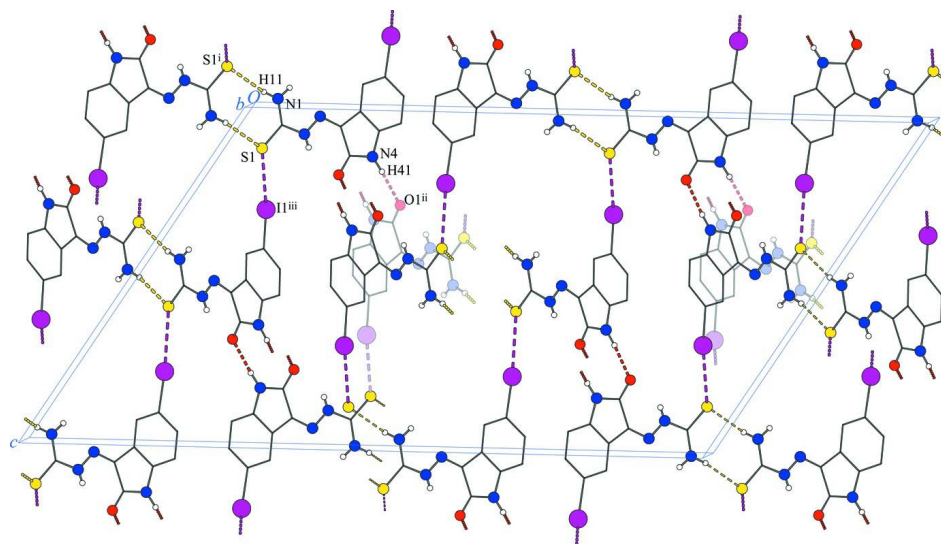


Figure 2

Packing diagram of the title compound showing hydrogen bond network generated through interactions represented as dashed lines. Some hydrogen atoms were omitted for clarity. Symmetry codes: (i) $-x, 2-y, -z$; (ii) $1/2-x, -1/2+y, 1/2-z$; (iii) $x, -y, 1/2+z$.

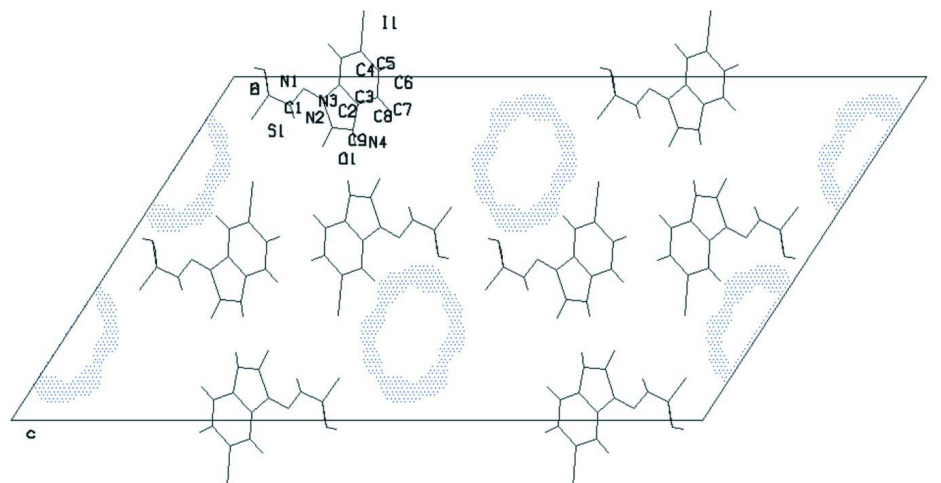


Figure 3

Plot generated by *PLATON* showing solvent accessible voids positions in the unit cell as dashed delimited circles.

2-(5-Iodo-2-oxoindolin-3-ylidene)hydrazinecarbothioamide

Crystal data

$C_9H_7IN_4OS$

$M_r = 346.15$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 33.765 (5) \text{ \AA}$

$b = 4.4569 (5) \text{ \AA}$

$c = 19.977 (3) \text{ \AA}$

$\beta = 123.100 (4)^\circ$

$V = 2518.4 (6) \text{ \AA}^3$

$Z = 8$

$F(000) = 1328$

$D_x = 1.826 \text{ Mg m}^{-3}$

Melting point: 522 K

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

Cell parameters from 9997 reflections

$\theta = 2.4\text{--}28.3^\circ$

$\mu = 2.69 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Needle, yellow
 $1.15 \times 0.10 \times 0.09 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: numerical
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.701$, $T_{\max} = 0.777$

18679 measured reflections
 2892 independent reflections
 2577 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -44 \rightarrow 44$
 $k = -3 \rightarrow 5$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.062$
 $S = 1.05$
 2892 reflections
 161 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
 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 10.8261P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.52 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C6	0.20209 (11)	0.5198 (5)	0.48073 (18)	0.0190 (6)
H6	0.2160	0.3772	0.4658	0.023*
C7	0.22592 (10)	0.6149 (6)	0.55978 (17)	0.0168 (5)
H7	0.2555	0.5382	0.5981	0.020*
C5	0.15782 (10)	0.6347 (6)	0.42365 (16)	0.0170 (6)
H41	0.2442 (12)	0.924 (7)	0.693 (2)	0.016 (8)*
H21	0.1270 (13)	1.502 (7)	0.631 (2)	0.023 (9)*
H11	0.0129 (12)	1.770 (7)	0.4600 (19)	0.019 (8)*
H12	0.0403 (15)	1.560 (9)	0.449 (3)	0.043 (12)*
I1	0.125098 (8)	0.47387 (4)	0.306159 (11)	0.02521 (7)
S1	0.06378 (3)	1.88628 (14)	0.62093 (4)	0.01889 (15)
O1	0.19376 (7)	1.3146 (4)	0.70372 (11)	0.0168 (4)
N4	0.22091 (9)	0.9605 (5)	0.65344 (15)	0.0145 (5)

N3	0.11031 (8)	1.3194 (4)	0.53273 (13)	0.0130 (4)
C9	0.18938 (9)	1.1590 (5)	0.64912 (16)	0.0137 (5)
C1	0.06744 (9)	1.6773 (5)	0.55453 (16)	0.0140 (5)
N1	0.03597 (10)	1.6699 (6)	0.47747 (15)	0.0209 (5)
C3	0.15944 (9)	0.9428 (5)	0.52186 (16)	0.0127 (5)
N2	0.10679 (9)	1.5041 (4)	0.58282 (15)	0.0145 (5)
C8	0.20411 (9)	0.8269 (5)	0.57920 (15)	0.0133 (5)
C2	0.14815 (9)	1.1580 (5)	0.56399 (15)	0.0127 (5)
C4	0.13579 (10)	0.8471 (5)	0.44356 (16)	0.0143 (5)
H4	0.1061	0.9222	0.4053	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C6	0.0251 (17)	0.0160 (11)	0.0226 (17)	0.0021 (10)	0.0173 (14)	0.0005 (9)
C7	0.0115 (15)	0.0176 (11)	0.0198 (15)	0.0015 (9)	0.0076 (12)	0.0034 (9)
C5	0.0212 (16)	0.0181 (11)	0.0129 (15)	-0.0041 (10)	0.0101 (13)	-0.0011 (9)
I1	0.04097 (15)	0.02153 (9)	0.01480 (12)	-0.00098 (7)	0.01630 (11)	-0.00167 (6)
S1	0.0206 (4)	0.0199 (3)	0.0160 (4)	0.0050 (2)	0.0099 (3)	0.0011 (2)
O1	0.0125 (10)	0.0216 (9)	0.0106 (10)	-0.0011 (7)	0.0026 (8)	-0.0027 (7)
N4	0.0091 (13)	0.0177 (10)	0.0095 (13)	0.0006 (8)	0.0005 (11)	0.0010 (8)
N3	0.0119 (12)	0.0143 (9)	0.0125 (12)	-0.0011 (8)	0.0065 (10)	-0.0002 (7)
C9	0.0106 (14)	0.0153 (11)	0.0124 (14)	-0.0029 (9)	0.0044 (12)	0.0013 (9)
C1	0.0101 (14)	0.0154 (11)	0.0160 (15)	-0.0001 (9)	0.0068 (12)	0.0019 (9)
N1	0.0137 (14)	0.0276 (12)	0.0147 (14)	0.0078 (10)	0.0034 (11)	-0.0008 (9)
C3	0.0110 (14)	0.0139 (10)	0.0123 (14)	-0.0017 (9)	0.0057 (12)	0.0019 (8)
N2	0.0130 (13)	0.0168 (10)	0.0091 (13)	0.0007 (8)	0.0030 (10)	-0.0001 (8)
C8	0.0117 (14)	0.0144 (10)	0.0111 (14)	-0.0011 (9)	0.0044 (11)	0.0020 (9)
C2	0.0131 (14)	0.0135 (10)	0.0090 (13)	-0.0025 (9)	0.0043 (11)	0.0008 (8)
C4	0.0119 (14)	0.0159 (11)	0.0110 (14)	-0.0025 (9)	0.0036 (11)	0.0010 (9)

Geometric parameters (Å, °)

C6—C7	1.390 (4)	N3—C2	1.292 (3)
C6—C5	1.391 (4)	N3—N2	1.350 (3)
C6—H6	0.9300	C9—C2	1.498 (4)
C7—C8	1.378 (4)	C1—N1	1.309 (4)
C7—H7	0.9300	C1—N2	1.364 (3)
C5—C4	1.389 (4)	N1—H11	0.79 (3)
C5—I1	2.100 (3)	N1—H12	0.82 (4)
S1—C1	1.680 (3)	C3—C4	1.379 (4)
O1—C9	1.232 (3)	C3—C8	1.402 (4)
N4—C9	1.350 (3)	C3—C2	1.457 (3)
N4—C8	1.399 (3)	N2—H21	0.83 (4)
N4—H41	0.77 (3)	C4—H4	0.9300
C7—C6—C5	121.0 (2)	C1—N1—H11	118 (2)
C7—C6—H6	119.5	C1—N1—H12	119 (3)

C5—C6—H6	119.5	H11—N1—H12	122 (4)
C6—C7—C8	117.5 (3)	C4—C3—C8	120.7 (2)
C6—C7—H7	121.2	C4—C3—C2	133.3 (3)
C8—C7—H7	121.2	C8—C3—C2	105.9 (2)
C6—C5—C4	121.3 (2)	N3—N2—C1	119.9 (2)
C6—C5—I1	117.67 (19)	N3—N2—H21	121 (2)
C4—C5—I1	121.0 (2)	C1—N2—H21	119 (2)
C9—N4—C8	111.2 (2)	C7—C8—N4	128.4 (3)
C9—N4—H41	122 (2)	C7—C8—C3	121.6 (2)
C8—N4—H41	127 (2)	N4—C8—C3	110.0 (2)
C2—N3—N2	116.5 (2)	N3—C2—C3	126.1 (2)
O1—C9—N4	127.1 (3)	N3—C2—C9	127.4 (2)
O1—C9—C2	126.5 (2)	C3—C2—C9	106.5 (2)
N4—C9—C2	106.4 (2)	C3—C4—C5	117.8 (2)
N1—C1—N2	117.0 (2)	C3—C4—H4	121.1
N1—C1—S1	125.4 (2)	C5—C4—H4	121.1
N2—C1—S1	117.5 (2)		
C5—C6—C7—C8	-0.1 (4)	C2—C3—C8—N4	-0.6 (3)
C7—C6—C5—C4	-0.3 (4)	N2—N3—C2—C3	179.7 (2)
C7—C6—C5—I1	-179.88 (19)	N2—N3—C2—C9	-2.1 (4)
C8—N4—C9—O1	-179.3 (2)	C4—C3—C2—N3	-1.1 (5)
C8—N4—C9—C2	-0.5 (3)	C8—C3—C2—N3	178.9 (2)
C2—N3—N2—C1	-178.7 (2)	C4—C3—C2—C9	-179.7 (3)
N1—C1—N2—N3	-4.7 (3)	C8—C3—C2—C9	0.3 (3)
S1—C1—N2—N3	176.33 (18)	O1—C9—C2—N3	0.4 (4)
C6—C7—C8—N4	-178.9 (2)	N4—C9—C2—N3	-178.4 (2)
C6—C7—C8—C3	0.3 (4)	O1—C9—C2—C3	179.0 (2)
C9—N4—C8—C7	-180.0 (2)	N4—C9—C2—C3	0.1 (3)
C9—N4—C8—C3	0.7 (3)	C8—C3—C4—C5	-0.4 (4)
C4—C3—C8—C7	0.0 (4)	C2—C3—C4—C5	179.5 (3)
C2—C3—C8—C7	-180.0 (2)	C6—C5—C4—C3	0.5 (4)
C4—C3—C8—N4	179.4 (2)	I1—C5—C4—C3	-179.85 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H12...N3	0.85 (4)	2.28 (4)	2.633 (3)	105 (3)
N2—H21...O1	0.83 (4)	2.07 (4)	2.725 (3)	135 (3)
N4—H41...O1 ⁱ	0.77 (3)	2.04 (4)	2.809 (3)	178 (3)
N1—H11...S1 ⁱⁱ	0.79 (3)	2.66 (4)	3.448 (3)	170 (3)

Symmetry codes: (i) $-x+1/2, y-1/2, -z+3/2$; (ii) $-x, -y+4, -z+1$.