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## Structure Reports

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# N-Phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide

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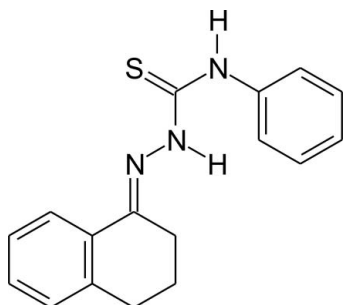
Received 21 January 2014; accepted 22 January 2014

Key indicators: single-crystal X-ray study;  $T = 200$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.089; data-to-parameter ratio = 18.5.

The conformation of the title molecule,  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{S}$ , is stabilized by an intramolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bond involving the azometinic group. The dihedral angle between the two aromatic rings is  $36.49$  (06)°. The non-aromatic ring of the tetralone substituent adopts a sofa conformation. In the crystal, molecules are linked by pairs of  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds related *via* centres of symmetry, forming dimers.

## Related literature

For the synthesis and pharmacological activity of ketone-thiosemicarbazones, see: Thanigaimalai *et al.* (2011). For one of the first reports of the synthesis of thiosemicarbazone derivatives, see: Freund & Schander (1902). For the synthesis and crystal structure of 2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide, see: de Oliveira *et al.* (2012).



## Experimental

### Crystal data

$\text{C}_{17}\text{H}_{17}\text{N}_3\text{S}$   
 $M_r = 295.40$   
 Monoclinic,  $P2_1/n$   
 $a = 8.4415$  (3) Å  
 $b = 18.0256$  (7) Å  
 $c = 10.0260$  (3) Å  
 $\beta = 107.495$  (2)°  
 $V = 1455.02$  (9) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.22$  mm<sup>-1</sup>  
 $T = 200$  K  
 $0.3 \times 0.3 \times 0.2$  mm

### Data collection

Stoe IPDS-1 diffractometer  
 23139 measured reflections  
 3520 independent reflections  
 3045 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.069$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.089$   
 $S = 1.05$   
 3520 reflections  
 190 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.24$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{S1}^i$	0.88	2.70	3.5793 (11)	176
$\text{N3}-\text{H2N}\cdots\text{N2}$	0.88	2.12	2.5630 (15)	111

Symmetry code: (i)  $-x + 1, -y, -z + 1$ .

Data collection: *X-Area* (Stoe & Cie, 2008); cell refinement: *X-Area*; data reduction: *X-Red32* (Stoe & Cie, 2008); 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).

We gratefully acknowledge financial support by the State of Schleswig-Holstein, Germany. We thank Professor Dr Wolfgang Bensch for access to his experimental facilities. BRSF thanks CNPq/UFS for the award of a PIBIC scholarship and ABO acknowledges financial support through the FAPITEC/SE/FUNTEC/CNPq PPP 04/2011 program.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BT6959).

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## supporting information

*Acta Cryst.* (2014). E70, o205 [doi:10.1107/S1600536814001585]

**N-Phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide****Adriano Bof de Oliveira, Bárbara Regina Santos Feitosa, Christian Näther and Inke Jess****S1. Comment**

Thiosemicarbazone derivatives have a wide range of pharmacological properties. For example, ketonethiosemicarbazones show pharmacological activity against melanogenesis in melanoma B16 cells (Thanigaimalai *et al.*, 2011). As part of our study on synthesis of thiosemicarbazone compounds, we report herein the crystal structure of a derivative of 2-(1,2,3,4-Tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide (Oliveira *et al.*, 2012). The title compound (Figure 1), in which the molecular structure matches the asymmetric unit, is not planar and the dihedral angle between the two aromatic rings is 36.49 (06)°. The maximum deviation from the mean plane of the non-H atoms for the non-aromatic ring of the tetralone substituent amount to 0.5003 (12) Å for C4, which corresponds to a sofa conformation. The molecule shows a *trans* conformation for the atoms about the N2–N1 bond. Due to an intramolecular hydrogen bond involving the N—H···N atoms (Figure 1), a *cis* conformation about the N1–C1 bond is observed. The planarity, atoms distances and angles of the thiosemicarbazone fragment are in agreement with literature data (de Oliveira *et al.*, 2012). The molecules are connected *via* centrosymmetric pairs of N—H···S, forming dimers (Figure 1, Figure 2 and Table 1).

**S2. Experimental**

Starting materials were commercially available and were used without further purification. The tetralone-thiosemicarbazone derivative synthesis was adapted from a procedure reported previously (Freund & Schander, 1902). The hydrochloric acid catalyzed reaction of tetralone (8,83 mmol) and 4-phenylthiosemicarbazide (8,83 mmol) in ethanol (50 ml) was refluxed for 6 h. After cooling and filtering, the title compound was obtained. Crystals suitable for X-ray diffraction of the title compound were obtained in tetrahydrofuran by the slow evaporation of solvent.

**S3. Refinement**

All H atoms were located in difference map but were positioned with idealized geometry and were refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C and N})$  with C—H = 0.95 Å for aromatic, C—H = 0.99 Å for methylene and N—H = 0.88 Å for N—H H atoms.

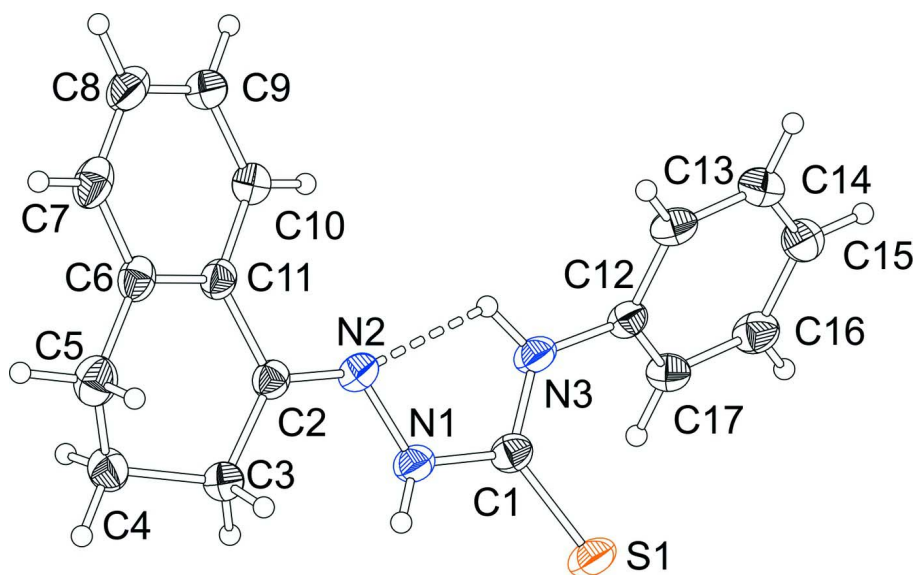


Figure 1

The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level, with intramolecular hydrogen bonding shown as dashed line.

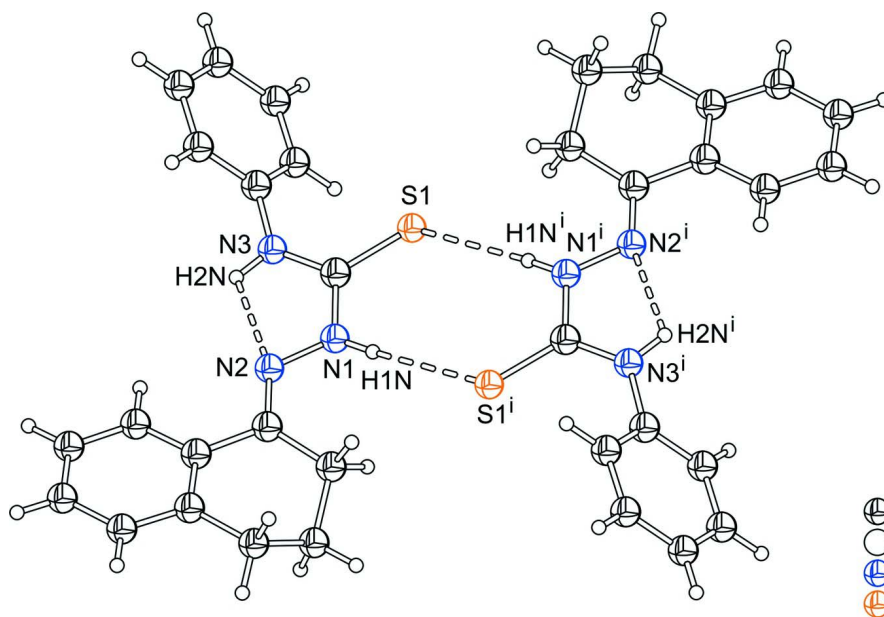


Figure 2

Crystal structure of the title compound with inter- and intramolecular hydrogen bonding shown as dashed lines. Symmetry code: (i)  $-x + 1, -y, -z + 1$ .

### *N*-Phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide

#### Crystal data

$C_{17}H_{17}N_3S$

$M_r = 295.40$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P 2_1n$

$a = 8.4415 (3) \text{ \AA}$

$b = 18.0256 (7) \text{ \AA}$

$c = 10.0260 (3) \text{ \AA}$   
 $\beta = 107.495 (2)^\circ$   
 $V = 1455.02 (9) \text{ \AA}^3$   
 $Z = 4$   
 $F(000) = 624$   
 $D_x = 1.348 \text{ Mg m}^{-3}$   
 Melting point: 452 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 26099 reflections  
 $\theta = 2.3\text{--}28.1^\circ$   
 $\mu = 0.22 \text{ mm}^{-1}$   
 $T = 200 \text{ K}$   
 Cubic, yellow  
 $0.3 \times 0.3 \times 0.2 \text{ mm}$

*Data collection*

Stoe IPDS-1  
 diffractometer  
 Radiation source: fine-focus sealed tube, Stoe  
 IPDS-1  
 Graphite monochromator  
 $\varphi$  scans  
 23139 measured reflections

3520 independent reflections  
 3045 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.069$   
 $\theta_{\text{max}} = 28.1^\circ$ ,  $\theta_{\text{min}} = 2.3^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -23 \rightarrow 23$   
 $l = -13 \rightarrow 12$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.089$   
 $S = 1.05$   
 3520 reflections  
 190 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.419P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.37784 (5)	0.09351 (2)	0.54195 (3)	0.03751 (11)
C1	0.47689 (15)	0.07366 (7)	0.70981 (13)	0.0270 (3)
N1	0.55649 (13)	0.00734 (6)	0.74440 (11)	0.0284 (2)
H1N	0.5703	-0.0195	0.6754	0.034*
N2	0.65846 (13)	-0.00109 (6)	0.88038 (11)	0.0278 (2)
C2	0.74837 (15)	-0.06010 (7)	0.91151 (12)	0.0250 (2)
C3	0.74732 (17)	-0.12214 (7)	0.81071 (13)	0.0291 (3)
H3A	0.8085	-0.1061	0.7455	0.035*
H3B	0.6312	-0.1327	0.7549	0.035*
C4	0.82614 (18)	-0.19283 (7)	0.88489 (14)	0.0328 (3)

H4A	0.7561	-0.2134	0.9394	0.039*
H4B	0.8337	-0.2303	0.8149	0.039*
C5	0.99852 (18)	-0.17606 (8)	0.98201 (15)	0.0363 (3)
H5A	1.0483	-0.2220	1.0311	0.044*
H5B	1.0702	-0.1583	0.9265	0.044*
C6	0.99093 (16)	-0.11786 (7)	1.08793 (14)	0.0286 (3)
C7	1.10660 (17)	-0.11733 (8)	1.22097 (15)	0.0351 (3)
H7	1.1929	-0.1532	1.2435	0.042*
C8	1.09825 (18)	-0.06577 (8)	1.32042 (15)	0.0383 (3)
H8	1.1796	-0.0657	1.4097	0.046*
C9	0.9709 (2)	-0.01430 (8)	1.28947 (14)	0.0382 (3)
H9	0.9627	0.0203	1.3585	0.046*
C10	0.85514 (18)	-0.01313 (7)	1.15781 (14)	0.0332 (3)
H10	0.7684	0.0226	1.1370	0.040*
C11	0.86494 (15)	-0.06406 (7)	1.05523 (12)	0.0262 (3)
N3	0.48970 (14)	0.11902 (6)	0.81878 (11)	0.0290 (2)
H2N	0.5513	0.1028	0.9008	0.035*
C12	0.41601 (15)	0.18985 (7)	0.81780 (12)	0.0255 (2)
C13	0.51258 (16)	0.24662 (8)	0.89485 (13)	0.0303 (3)
H13	0.6266	0.2382	0.9427	0.036*
C14	0.44270 (18)	0.31549 (8)	0.90199 (14)	0.0341 (3)
H14	0.5089	0.3542	0.9551	0.041*
C15	0.27640 (18)	0.32813 (8)	0.83178 (14)	0.0339 (3)
H15	0.2284	0.3754	0.8362	0.041*
C16	0.18101 (16)	0.27136 (8)	0.75537 (14)	0.0323 (3)
H16	0.0671	0.2799	0.7071	0.039*
C17	0.24953 (16)	0.20221 (7)	0.74832 (13)	0.0286 (3)
H17	0.1828	0.1634	0.6961	0.034*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0426 (2)	0.0436 (2)	0.02103 (15)	0.01742 (15)	0.00155 (13)	-0.00099 (13)
C1	0.0239 (6)	0.0313 (6)	0.0248 (6)	0.0019 (5)	0.0060 (5)	0.0000 (5)
N1	0.0290 (5)	0.0306 (6)	0.0223 (5)	0.0048 (4)	0.0029 (4)	-0.0006 (4)
N2	0.0277 (5)	0.0311 (6)	0.0223 (5)	0.0017 (4)	0.0040 (4)	0.0024 (4)
C2	0.0243 (6)	0.0258 (6)	0.0246 (6)	-0.0015 (5)	0.0070 (5)	0.0022 (4)
C3	0.0313 (6)	0.0284 (6)	0.0261 (6)	-0.0019 (5)	0.0066 (5)	-0.0003 (5)
C4	0.0397 (7)	0.0266 (6)	0.0331 (7)	0.0021 (5)	0.0125 (6)	-0.0002 (5)
C5	0.0343 (7)	0.0360 (7)	0.0395 (7)	0.0090 (6)	0.0127 (6)	0.0045 (6)
C6	0.0252 (6)	0.0289 (6)	0.0315 (6)	-0.0017 (5)	0.0082 (5)	0.0069 (5)
C7	0.0254 (6)	0.0386 (7)	0.0377 (7)	-0.0014 (5)	0.0038 (5)	0.0131 (6)
C8	0.0364 (7)	0.0414 (8)	0.0292 (6)	-0.0121 (6)	-0.0020 (5)	0.0101 (6)
C9	0.0509 (9)	0.0318 (7)	0.0266 (6)	-0.0076 (6)	0.0037 (6)	0.0003 (5)
C10	0.0405 (7)	0.0268 (7)	0.0288 (6)	0.0009 (5)	0.0050 (5)	0.0019 (5)
C11	0.0263 (6)	0.0255 (6)	0.0254 (6)	-0.0027 (5)	0.0058 (5)	0.0044 (4)
N3	0.0294 (5)	0.0337 (6)	0.0202 (5)	0.0072 (4)	0.0019 (4)	0.0002 (4)
C12	0.0263 (6)	0.0297 (6)	0.0205 (5)	0.0030 (5)	0.0069 (4)	0.0008 (4)

C13	0.0248 (6)	0.0391 (7)	0.0242 (6)	-0.0001 (5)	0.0033 (5)	-0.0019 (5)
C14	0.0360 (7)	0.0323 (7)	0.0310 (6)	-0.0038 (5)	0.0057 (5)	-0.0058 (5)
C15	0.0383 (7)	0.0303 (7)	0.0318 (7)	0.0055 (5)	0.0086 (6)	-0.0012 (5)
C16	0.0263 (6)	0.0388 (7)	0.0292 (6)	0.0054 (5)	0.0044 (5)	-0.0012 (5)
C17	0.0255 (6)	0.0323 (7)	0.0266 (6)	-0.0014 (5)	0.0058 (5)	-0.0036 (5)

*Geometric parameters (Å, °)*

S1—C1	1.6773 (13)	C7—H7	0.9500
C1—N3	1.3427 (16)	C8—C9	1.383 (2)
C1—N1	1.3642 (16)	C8—H8	0.9500
N1—N2	1.3846 (14)	C9—C10	1.3864 (19)
N1—H1N	0.8800	C9—H9	0.9500
N2—C2	1.2894 (16)	C10—C11	1.3995 (18)
C2—C11	1.4823 (16)	C10—H10	0.9500
C2—C3	1.5055 (18)	N3—C12	1.4190 (16)
C3—C4	1.5238 (18)	N3—H2N	0.8800
C3—H3A	0.9900	C12—C17	1.3861 (18)
C3—H3B	0.9900	C12—C13	1.3892 (18)
C4—C5	1.518 (2)	C13—C14	1.3854 (19)
C4—H4A	0.9900	C13—H13	0.9500
C4—H4B	0.9900	C14—C15	1.387 (2)
C5—C6	1.508 (2)	C14—H14	0.9500
C5—H5A	0.9900	C15—C16	1.3826 (19)
C5—H5B	0.9900	C15—H15	0.9500
C6—C7	1.3963 (18)	C16—C17	1.3849 (19)
C6—C11	1.4033 (18)	C16—H16	0.9500
C7—C8	1.380 (2)	C17—H17	0.9500
N3—C1—N1	114.44 (11)	C7—C8—C9	119.65 (13)
N3—C1—S1	125.48 (10)	C7—C8—H8	120.2
N1—C1—S1	120.06 (9)	C9—C8—H8	120.2
C1—N1—N2	117.35 (10)	C8—C9—C10	120.11 (14)
C1—N1—H1N	116.9	C8—C9—H9	119.9
N2—N1—H1N	121.6	C10—C9—H9	119.9
C2—N2—N1	118.38 (11)	C9—C10—C11	120.61 (13)
N2—C2—C11	116.45 (11)	C9—C10—H10	119.7
N2—C2—C3	124.48 (11)	C11—C10—H10	119.7
C11—C2—C3	119.01 (11)	C10—C11—C6	119.32 (12)
C2—C3—C4	112.33 (10)	C10—C11—C2	120.94 (11)
C2—C3—H3A	109.1	C6—C11—C2	119.70 (11)
C4—C3—H3A	109.1	C1—N3—C12	127.91 (11)
C2—C3—H3B	109.1	C1—N3—H2N	116.0
C4—C3—H3B	109.1	C12—N3—H2N	116.0
H3A—C3—H3B	107.9	C17—C12—C13	119.87 (12)
C5—C4—C3	109.89 (11)	C17—C12—N3	121.61 (11)
C5—C4—H4A	109.7	C13—C12—N3	118.44 (11)
C3—C4—H4A	109.7	C14—C13—C12	120.06 (12)

C5—C4—H4B	109.7	C14—C13—H13	120.0
C3—C4—H4B	109.7	C12—C13—H13	120.0
H4A—C4—H4B	108.2	C13—C14—C15	120.17 (13)
C6—C5—C4	110.78 (11)	C13—C14—H14	119.9
C6—C5—H5A	109.5	C15—C14—H14	119.9
C4—C5—H5A	109.5	C16—C15—C14	119.45 (13)
C6—C5—H5B	109.5	C16—C15—H15	120.3
C4—C5—H5B	109.5	C14—C15—H15	120.3
H5A—C5—H5B	108.1	C15—C16—C17	120.79 (12)
C7—C6—C11	118.80 (13)	C15—C16—H16	119.6
C7—C6—C5	120.80 (12)	C17—C16—H16	119.6
C11—C6—C5	120.40 (12)	C16—C17—C12	119.66 (12)
C8—C7—C6	121.45 (13)	C16—C17—H17	120.2
C8—C7—H7	119.3	C12—C17—H17	120.2
C6—C7—H7	119.3		
N3—C1—N1—N2	-9.03 (16)	C5—C6—C11—C10	176.54 (12)
S1—C1—N1—N2	169.57 (9)	C7—C6—C11—C2	175.51 (11)
C1—N1—N2—C2	-172.78 (11)	C5—C6—C11—C2	-5.79 (18)
N1—N2—C2—C11	175.47 (10)	N2—C2—C11—C10	11.35 (18)
N1—N2—C2—C3	-1.69 (18)	C3—C2—C11—C10	-171.33 (12)
N2—C2—C3—C4	-163.68 (12)	N2—C2—C11—C6	-166.29 (11)
C11—C2—C3—C4	19.23 (16)	C3—C2—C11—C6	11.04 (17)
C2—C3—C4—C5	-53.39 (15)	N1—C1—N3—C12	-177.29 (12)
C3—C4—C5—C6	58.18 (15)	S1—C1—N3—C12	4.2 (2)
C4—C5—C6—C7	149.58 (12)	C1—N3—C12—C17	47.42 (19)
C4—C5—C6—C11	-29.09 (17)	C1—N3—C12—C13	-135.95 (14)
C11—C6—C7—C8	0.67 (19)	C17—C12—C13—C14	-0.13 (19)
C5—C6—C7—C8	-178.02 (13)	N3—C12—C13—C14	-176.81 (12)
C6—C7—C8—C9	1.4 (2)	C12—C13—C14—C15	-0.3 (2)
C7—C8—C9—C10	-1.9 (2)	C13—C14—C15—C16	0.3 (2)
C8—C9—C10—C11	0.4 (2)	C14—C15—C16—C17	0.1 (2)
C9—C10—C11—C6	1.6 (2)	C15—C16—C17—C12	-0.5 (2)
C9—C10—C11—C2	-175.99 (12)	C13—C12—C17—C16	0.51 (19)
C7—C6—C11—C10	-2.16 (18)	N3—C12—C17—C16	177.09 (11)

*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—H1N...S1 <sup>i</sup>	0.88	2.70	3.5793 (11)	176
N3—H2N...N2	0.88	2.12	2.5630 (15)	111

Symmetry code: (i)  $-x+1, -y, -z+1$ .