

Crystal structure of *N*-ethyl-2-(1,2,3,4-tetrahydro- naphthalen-1-ylidene)hydrazinecarbothioamide

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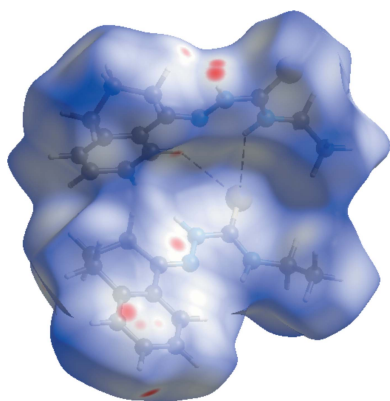
There are two crystallographically independent molecules in the asymmetric unit of the title compound, C₁₃H₁₇N₃S, one of them being disordered over the methyl group [site-occupancy ratio = 0.705 (5):0.295 (5)]. The maximum r.m.s. deviations from the mean plane of the non-H atoms for the tetralone fragments amount to 0.4572 (17) and 0.4558 (15) Å. The N–N–C–N fragments are not planar and torsion angles are –9.4 (2) and 8.3 (2)°. In the crystal, the molecules are linked by weak N–H···S interactions into chains along [100] with graph-set motif C(4) and connected by weak N–H···S and C–H···S interactions, forming R₂¹(10) rings. The Hirshfeld surface analysis indicates that the most important contributions for the crystal packing are the H···H (64.20%), H···S (12.60%) and H···C (12.00%) interactions. The crystal packing resembles a herringbone arrangement when viewed along [001].

1. Chemical context

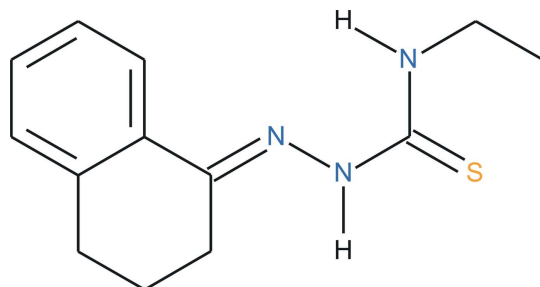
The synthesis of thiosemicarbazone derivatives can be traced back to the early 1900's (Freund & Schander, 1902). Initially, the chemically selective nucleophilic reaction with thiosemicarbazide, H₂N–N(H)C(=S)NH₂, was employed for the identification and characterization of aldehydes and ketones, yielding the respective thiosemicarbazone. In the 1940s it was reported that in *in vitro* assays, the thiosemicarbazone turned out to be very effective against tuberculosis. In contrast, the related oxygen-containing semicarbazones did not show biological activity in the same assays, so that the sulfur atom in the molecular structure is essential for *Mycobacterium tuberculosis* growth inhibition, a true milestone in the thiosemicarbazone pharmacological research (Domagk *et al.*, 1946). Today, thiosemicarbazone chemistry is present across a wide range of scientific disciplines, especially inorganic coordination chemistry (Lobana *et al.*, 2009) and medicinal chemistry. For example, the synthesis, the molecular docking calculation and the *in vitro* inhibition of Chikungunya virus replication by a thiosemicarbazone derivative was published in the past year (Mishra *et al.*, 2016). Thus, the crystal structure determination of thiosemicarbazone derivatives is an intensive research field, especially for biological chemistry.

2. Structural commentary

The asymmetric unit shows two crystallographically independent molecules, one of them being disordered over the terminal methyl group. For the disordered molecule, the C25 atom



was fixed with restraints and had to be split over two positions with an occupancy ratio of 0.705 (5):0.295 (5) with *A* and *B* labels. As the orientations for this sp^3 -hybridized C atom are different, two possibilities for the disordered C26-atom locations are generated (Fig. 1).



For the first molecule, the C1/C2/C5/C10 atoms are essentially planar and atoms C3 and C4 deviate by 0.564 (2) and -0.142 (2) Å, respectively, from this plane. For the second, the C14/C15/C18/C23 atoms are essentially planar while atoms C16 and C17 deviate from the plane by -0.534 (2) and 0.201 (2) Å, respectively.

In addition, the N1–N2–C11–N3 and N4–N5–C24–N6 torsion angles are 9.4 (2)° and 8.3 (2)°. The dihedral angle between the tetralone fragments of the two molecules within the asymmetric unit is 85.51 (02)°.

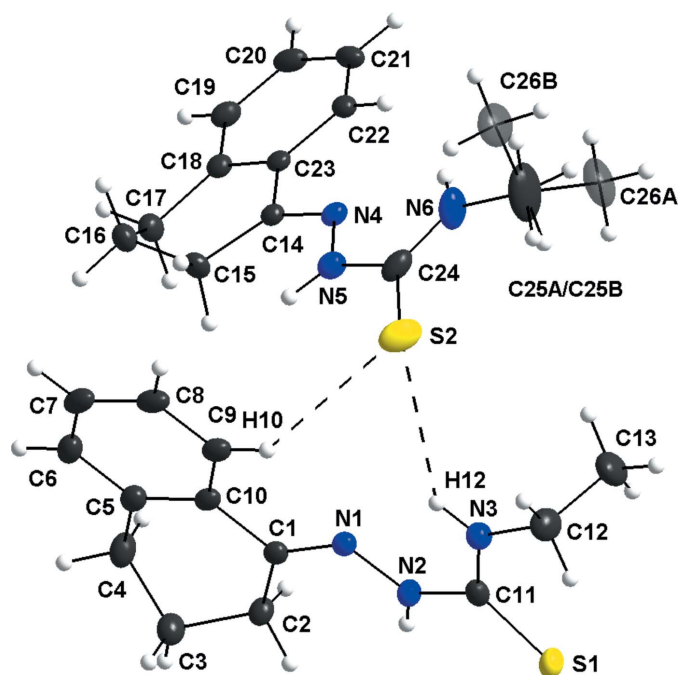


Figure 1

The molecular structure of the title compound, with labeling and displacement ellipsoids drawn at the 40% probability level. The N3–H12...S2 and C9–H10...S2 interactions are drawn as dashed lines. Disordered atoms are shown with 30% transparency. The C25A/B atom is itself not disordered, but it was split using the same occupancy ratio as C26A and C26B.

Table 1

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>
N3–H12...S2	0.88	3.02	3.7172 (16)	138
C9–H10...S2	0.95	3.09	3.8835 (19)	142
N6–H29...S1 ⁱ	0.88	3.31	4.002 (2)	138
C22–H27...S1 ⁱ	0.95	2.98	3.7828 (17)	143

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

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the molecules are connected by weak N3–H12...S2 and N6–H29...S1ⁱ interactions into chains along [100]. The S1–C11–N3–H12 and S2–C24–N6–H29 fragments are the subunits of the periodic arrangement, with graph-set motif $C(4)$. In addition, the molecules are linked by C9–H10...S2 and C22–H27...S1ⁱ interactions building rings with graph-set motif $R_2^1(10)$. The sulfur atoms are hydrogen-bond acceptors and bridge two *D*–H...*S* interactions (Fig. 2, Table 1).

The Hirshfeld surface analysis (Hirshfeld, 1977) of the crystal structure suggests that the contribution of the H...H intermolecular interactions to the crystal packing amounts to 64.20%, the H...S interactions amount to 12.60% and the H...C interactions amount to 12.00%. Other important intermolecular contacts for the cohesion of the structure are (values given in %) are: H...N = 5.50, C...N = 3.60 and C...C = 2.20. For the Hirshfeld surface analysis, the disorder over the molecule was not considered and the calculations were performed using the major occupancy component atoms. The graphical representation of the Hirshfeld surface (Fig. 3,

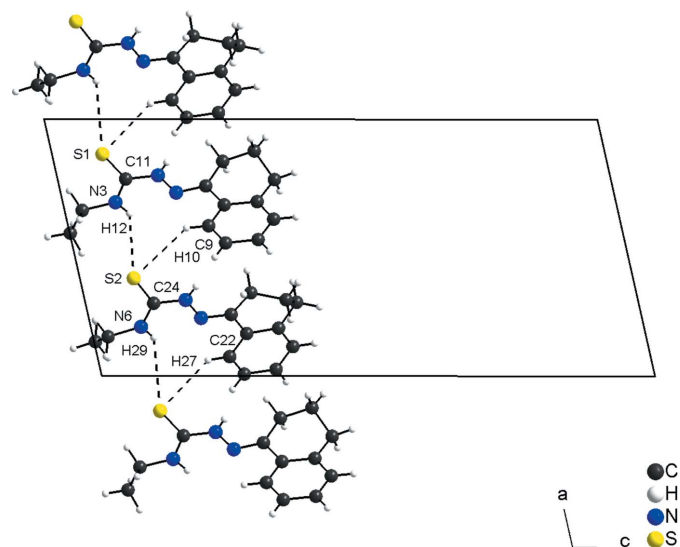


Figure 2

Section of the crystal structure of the title compound, showing the N–H...S and C–H...S interactions. The graph-set motifs for the hydrogen-bonding interactions in the crystal packing are $C(4)$ and $R_2^1(10)$. The H...S interactions are shown as dashed lines and connect the molecules into a chain along [100].

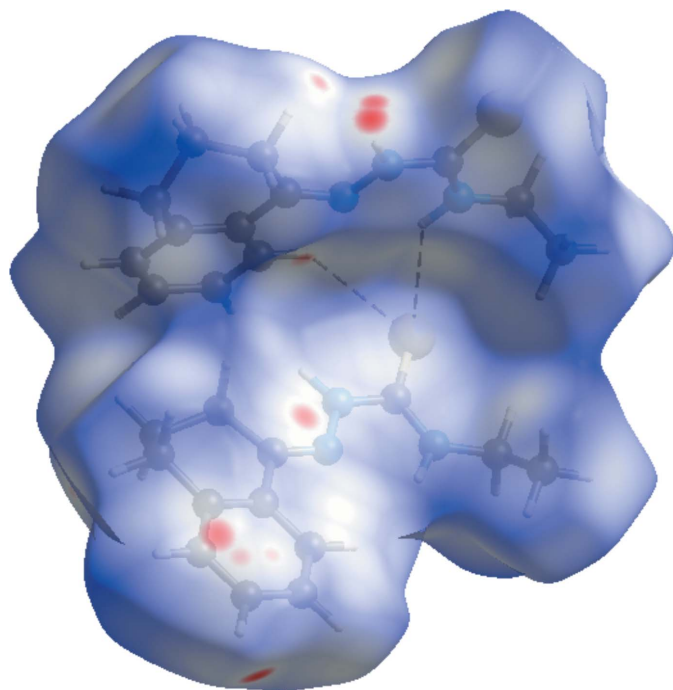


Figure 3

The Hirshfeld surface graphical representation (d_{norm}) for the asymmetric unit of the title compound. The surface regions with the strongest intermolecular interactions are shown in magenta. The disorder is not shown and the figure is simplified for clarity.

represented in magenta) suggests the locations of the strongest intermolecular contacts. The $\text{H}\cdots\text{H}$ contribution for the crystal packing is shown as a Hirshfeld surface two-dimensional fingerprint plot with cyan dots (Wolff *et al.*, 2012). The d_e (y axis) and d_i (x axis) values are the closest external and internal distances (in Å) from given points on the Hirshfeld surface contacts (Fig. 4). As the most important contribution for the crystal packing is from the $\text{H}\cdots\text{H}$ interactions, all other intermolecular interactions are relatively weak. As a consequence, the lengths of the $\text{H}\cdots\text{S}$ contacts are close to or slightly above the sum of the van der Waals radii for H and S atoms (Bondi, 1964; Rowland & Taylor, 1996). Finally, the molecular packing shows a herringbone motif when viewed along [001] (Fig. 5).

4. Comparison with related structures

$\text{H}\cdots\text{H}$ connections are the most important contribution for the crystal packing of 1-tetralone thiosemicarbazone derivatives; however, the $\text{H}\cdots\text{S}$ contacts are relevant intermolecular interactions because of the possibility of forming hydrogen bonds. Therefore, $D\text{—H}\cdots\text{S}$ hydrogen bonding is considered in the comparison of the title compound with related structures. In the crystal structure of 2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide, the molecules are linked into chains by $\text{N—H}\cdots\text{S}$ hydrogen bonds ($\text{H}\cdots\text{S}$ distances = 2.45 and 2.71 Å) and the $\text{H}\cdots\text{S}$ contribution for the cohesion of the structure amounts to 19.20% (Fig. 6a and

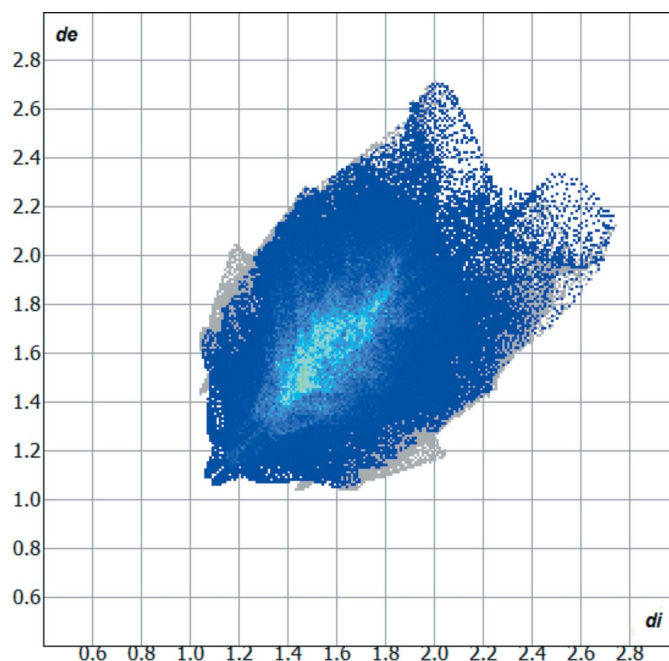


Figure 4

Hirshfeld surface two-dimensional fingerprint plot for the title compound showing the $\text{H}\cdots\text{H}$ contacts in detail (cyan dots). The contribution of the $\text{H}\cdots\text{H}$ interactions to the crystal packing amounts to 64.20%. The d_e (y axis) and d_i (x axis) values are the closest external and internal distances (in Å) from given points on the Hirshfeld surface contacts. The disorder was not considered.

7a). This kind of arrangement, the one-dimensional hydrogen-bonded polymer, is possible due to the unsubstituted amine, which increases the possibilities for intermolecular hydrogen

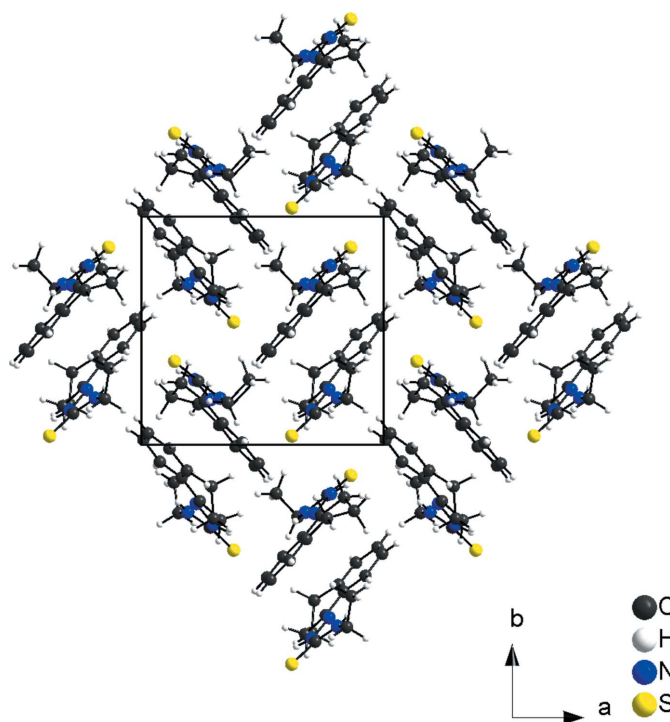


Figure 5

Section of the crystal structure of the title compound, in a view along the [001], showing the herringbone motif.

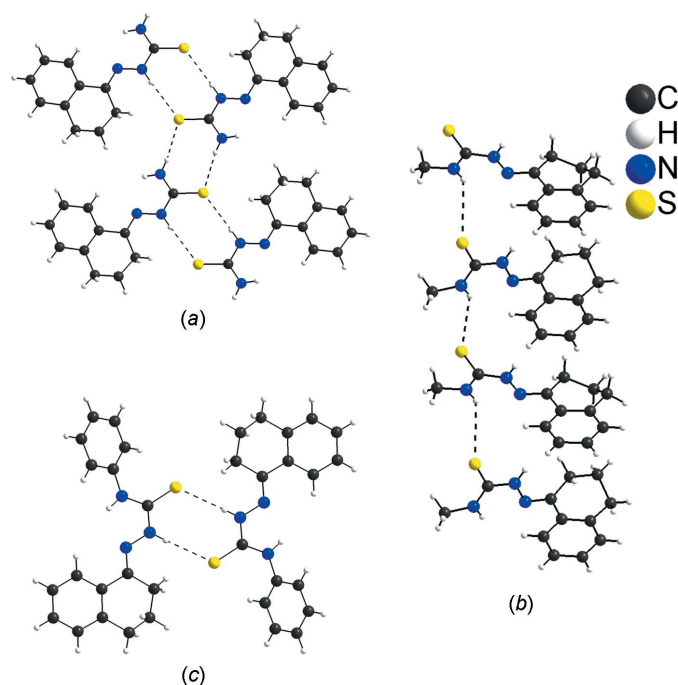


Figure 6
Sections of the crystal structures of 1-tetralone thiosemicarbazone derivatives: (a) 1-tetralone thiosemicarbazone, (b) 1-tetralone 4-methylthiosemicarbazone and (c) 1-tetralone 4-phenylthiosemicarbazone. The H...S intermolecular interactions are shown as dashed lines. The disorder of the 1-tetralone 4-methylthiosemicarbazone molecule is not shown and the figures are simplified for clarity.

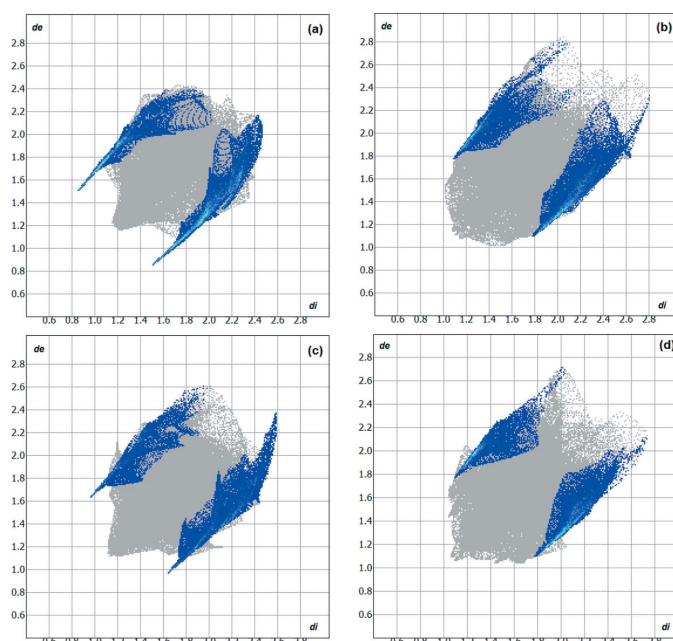


Figure 7
Hirshfeld surface two-dimensional fingerprint plots for the crystal structures of (a) 1-tetralone thiosemicarbazone, (b) 1-tetralone 4-methylthiosemicarbazone, (c) 1-tetralone 4-phenylthiosemicarbazone and (d) 1-tetralone 4-ethylthiosemicarbazone showing the H...S contacts in detail (cyan dots). The H...S interactions contributions to the molecular cohesion on the crystal structures amount to 19.20, 15.80, 13.00 and 12.60%, respectively.

bonding (Oliveira *et al.*, 2012). For the crystal structure of *N*-methyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide, one H atom of the amine group is substituted by one methyl group. The N—H...S hydrogen bonds are weaker in comparison with the first structure (H...S distances = 3.03 and 3.29 Å), the H...S contribution for the cohesion of the structure amounts to 15.80% and the dimensionality of the structure is preserved with molecules linked into chains (Fig. 6b and 7b). The disorder over the molecules in the asymmetric unit was not considered and the calculations were performed using atoms of the major occupancy component (Oliveira *et al.*, 2014a). Finally, for *N*-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide, the molecules are also linked by N—H...S hydrogen bonds, but not into hydrogen-bonded polymers (H...S distance = 2.70 Å). The phenyl rings linked to the amino groups change the molecular arrangement due to steric effects: the molecules build dimers and the H...S contribution to the crystal packing amounts to 13.00% (Fig. 6c and 7c) (Oliveira *et al.*, 2014b). For the 1-tetralone 4-ethylthiosemicarbazone reported here, the H...S contribution for the molecular cohesion on the crystal structure amounts to 12.60% (Fig. 7d). Thus, there is a relationship between the molecular assembly, the geometry of the H...S interactions and their contribution to the crystal structures (Hirshfeld, 1977 and Wolff *et al.*, 2012).

5. Synthesis and crystallization

The starting materials are commercially available and were used without further purification. The synthesis of the title compound was adapted from a previously reported procedure (Freund & Schander, 1902). In a hydrochloric acid catalysed reaction, a mixture of 1-tetralone (10 mmol) and 4-ethyl-3-thiosemicarbazide (10 mmol) in ethanol (80 mL) was stirred and refluxed for 4 h. After cooling and filtering, a pale-yellow solid was obtained. Colourless crystals were grown in tetrahydrofuran by slow evaporation of the solvent.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. One of the two independent molecules exhibits disorder of the methyl group. Although the secondary C atom of the ethyl substituent is not itself disordered, it was split using the same occupancy ratio as the terminal C atom to account for the different orientations of the two hydrogen atoms for the two disordered parts. The C25A and C25B atoms share the same site (EXYZ and EADP commands) and two positions will be possible for the terminal CH₃-group. The C25 and C26 atoms were fixed with restraints (SADI command) and had to be split over two positions. The occupancy factor for C25A and C26A is 0.705 (5) and for C25B and C26B it is 0.295 (5). H atoms were located in difference maps but were positioned with idealized geometry and were refined with isotropic displacement parameters using a riding model (HFIX command) with $U_{\text{iso}}(\text{H}) =$

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₇ N ₃ S
<i>M_r</i>	247.36
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.1342 (2), 10.2330 (2), 23.3990 (5)
β (°)	102.724 (1)
<i>V</i> (Å ³)	2600.52 (9)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.23
Crystal size (mm)	0.35 × 0.15 × 0.05
Data collection	
Diffractometer	Nonius KappaCCD area detector
Absorption correction	Multi-scan (Blessing, 1995)
<i>T_{min}</i> , <i>T_{max}</i>	0.902, 0.987
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	39942, 5952, 4615
<i>R_{int}</i>	0.050
(sin θ/λ) _{max} (Å ⁻¹)	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.116, 1.02
No. of reflections	5952
No. of parameters	318
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.48, -0.41

Computer programs: *COLLECT* (Nonius, 1998), *HKL*, *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SUPERFLIP* (Palatinus & Chapuis, 2007), *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006), *Crystal Explorer* (Wolff *et al.*, 2012), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

1.2 *U*_{eq}(secondary C atoms) (C–H = 0.99 Å for aliphatic and C–H = 0.95 Å for aromatic atoms), *U*_{iso}(H) = 1.5 *U*_{eq}(terminal C atoms) (C–H = 0.98 Å) and *U*_{iso}(H) = 1.2 *U*_{eq}(N) (N–H = 0.88 Å).

Acknowledgements

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supporting information

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Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL*, *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *Crystal Explorer* (Wolff *et al.*, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

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

Crystal data

$C_{13}H_{17}N_3S$	$F(000) = 1056$
$M_r = 247.36$	$D_x = 1.264 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P 2_1/c$	Cell parameters from 42401 reflections
$a = 11.1342 (2) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 10.2330 (2) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$c = 23.3990 (5) \text{ \AA}$	$T = 123 \text{ K}$
$\beta = 102.724 (1)^\circ$	Block, colourless
$V = 2600.52 (9) \text{ \AA}^3$	$0.35 \times 0.15 \times 0.05 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD area detector diffractometer	$T_{\min} = 0.902$, $T_{\max} = 0.987$
Radiation source: fine-focus sealed tube, Nonius Kappa CCD	39942 measured reflections
Graphite monochromator	5952 independent reflections
Detector resolution: 9 pixels mm^{-1}	4615 reflections with $I > 2\sigma(I)$
CCD rotation images, thick slices scans	$R_{\text{int}} = 0.050$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
	$h = -14 \rightarrow 14$
	$k = -13 \rightarrow 13$
	$l = -30 \rightarrow 28$

Refinement

Refinement on F^2	5952 reflections
Least-squares matrix: full	318 parameters
$R[F^2 > 2\sigma(F^2)] = 0.044$	1 restraint
$wR(F^2) = 0.116$	Primary atom site location: structure-invariant direct methods
$S = 1.02$	

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 1.4032P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.74029 (14)	0.81156 (15)	0.26519 (7)	0.0204 (3)	
C2	0.83649 (16)	0.73161 (17)	0.30579 (7)	0.0259 (4)	
H1	0.9095	0.7229	0.2884	0.031*	
H2	0.8034	0.6429	0.3092	0.031*	
C3	0.87661 (18)	0.7906 (2)	0.36697 (8)	0.0338 (4)	
H3	0.9301	0.7279	0.3931	0.041*	
H4	0.9248	0.8711	0.3650	0.041*	
C4	0.76544 (19)	0.8229 (2)	0.39190 (8)	0.0356 (4)	
H5	0.7211	0.7413	0.3970	0.043*	
H6	0.7930	0.8641	0.4309	0.043*	
C5	0.67946 (16)	0.91465 (17)	0.35168 (8)	0.0271 (4)	
C6	0.61121 (17)	1.00840 (19)	0.37437 (9)	0.0331 (4)	
H7	0.6197	1.0146	0.4156	0.040*	
C7	0.53164 (17)	1.09221 (18)	0.33808 (9)	0.0338 (4)	
H8	0.4864	1.1556	0.3543	0.041*	
C8	0.51821 (16)	1.08314 (17)	0.27784 (9)	0.0302 (4)	
H9	0.4627	1.1397	0.2527	0.036*	
C9	0.58507 (15)	0.99229 (16)	0.25425 (8)	0.0255 (4)	
H10	0.5758	0.9872	0.2130	0.031*	
C10	0.66681 (15)	0.90726 (16)	0.29086 (7)	0.0223 (3)	
C11	0.76692 (15)	0.72188 (16)	0.12327 (7)	0.0233 (3)	
C12	0.64454 (19)	0.8165 (2)	0.03189 (8)	0.0359 (4)	
H13	0.7207	0.8130	0.0166	0.043*	
H14	0.6077	0.9042	0.0231	0.043*	
C13	0.5557 (2)	0.7151 (3)	0.00106 (9)	0.0498 (6)	
H15	0.5906	0.6278	0.0106	0.075*	
H16	0.5407	0.7290	-0.0414	0.075*	
H17	0.4779	0.7224	0.0138	0.075*	
C14	0.23948 (14)	0.74836 (15)	0.25873 (7)	0.0195 (3)	
C15	0.32438 (16)	0.83155 (17)	0.30316 (7)	0.0261 (4)	

H18	0.3173	0.9235	0.2897	0.031*	
H19	0.4103	0.8032	0.3055	0.031*	
C16	0.29737 (17)	0.82471 (18)	0.36413 (8)	0.0294 (4)	
H20	0.3641	0.8686	0.3926	0.035*	
H21	0.2193	0.8709	0.3643	0.035*	
C17	0.28738 (16)	0.68370 (18)	0.38210 (7)	0.0280 (4)	
H22	0.3667	0.6387	0.3837	0.034*	
H23	0.2694	0.6804	0.4217	0.034*	
C18	0.18651 (15)	0.61472 (16)	0.33905 (7)	0.0221 (3)	
C19	0.11481 (16)	0.51819 (17)	0.35743 (8)	0.0269 (4)	
H24	0.1274	0.4984	0.3980	0.032*	
C20	0.02604 (16)	0.45102 (17)	0.31785 (8)	0.0285 (4)	
H25	-0.0221	0.3858	0.3311	0.034*	
C21	0.00738 (15)	0.47942 (17)	0.25843 (8)	0.0265 (4)	
H26	-0.0525	0.4322	0.2310	0.032*	
C22	0.07550 (15)	0.57592 (16)	0.23918 (7)	0.0227 (3)	
H27	0.0615	0.5955	0.1986	0.027*	
C23	0.16531 (14)	0.64538 (15)	0.27924 (7)	0.0192 (3)	
C24	0.28275 (18)	0.86401 (18)	0.12330 (8)	0.0309 (4)	
C25A	0.1525 (3)	0.8000 (3)	0.02723 (10)	0.0733 (9)	0.705 (5)
H30	0.2162	0.8448	0.0108	0.088*	0.705 (5)
H31	0.0751	0.8504	0.0157	0.088*	0.705 (5)
C26A	0.1331 (4)	0.6658 (4)	0.00242 (14)	0.0625 (12)	0.705 (5)
H34	0.1060	0.6709	-0.0403	0.094*	0.705 (5)
H35	0.0700	0.6213	0.0186	0.094*	0.705 (5)
H36	0.2104	0.6166	0.0127	0.094*	0.705 (5)
C25B	0.1525 (3)	0.8000 (3)	0.02723 (10)	0.0733 (9)	0.295 (5)
H32	0.1167	0.7150	0.0120	0.088*	0.295 (5)
H33	0.2232	0.8199	0.0093	0.088*	0.295 (5)
C26B	0.0497 (8)	0.9155 (8)	0.0132 (3)	0.053 (3)	0.295 (5)
H37	0.0185	0.9224	-0.0292	0.080*	0.295 (5)
H38	0.0871	0.9987	0.0285	0.080*	0.295 (5)
H39	-0.0185	0.8948	0.0320	0.080*	0.295 (5)
N1	0.71417 (12)	0.80254 (13)	0.20897 (6)	0.0214 (3)	
N2	0.78106 (13)	0.71646 (13)	0.18298 (6)	0.0231 (3)	
H11	0.8314	0.6596	0.2041	0.028*	
N3	0.67615 (13)	0.79765 (14)	0.09517 (6)	0.0260 (3)	
H12	0.6320	0.8394	0.1162	0.031*	
N4	0.22574 (12)	0.75948 (13)	0.20292 (6)	0.0217 (3)	
N5	0.29620 (13)	0.85150 (14)	0.18236 (6)	0.0262 (3)	
H28	0.3485	0.9009	0.2067	0.031*	
N6	0.19103 (18)	0.79705 (17)	0.09097 (7)	0.0409 (4)	
H29	0.1492	0.7457	0.1097	0.049*	
S1	0.86369 (4)	0.63602 (5)	0.091362 (19)	0.03122 (13)	
S2	0.38000 (5)	0.96310 (6)	0.09740 (2)	0.04411 (16)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0202 (8)	0.0188 (8)	0.0229 (8)	-0.0027 (6)	0.0061 (6)	0.0006 (6)
C2	0.0298 (9)	0.0260 (9)	0.0223 (8)	0.0062 (7)	0.0067 (7)	0.0012 (7)
C3	0.0368 (11)	0.0373 (11)	0.0252 (9)	0.0077 (8)	0.0022 (8)	0.0006 (8)
C4	0.0457 (12)	0.0378 (11)	0.0242 (9)	0.0063 (9)	0.0094 (8)	-0.0017 (8)
C5	0.0264 (9)	0.0261 (9)	0.0302 (9)	-0.0026 (7)	0.0089 (7)	-0.0033 (7)
C6	0.0333 (10)	0.0349 (10)	0.0341 (10)	-0.0053 (8)	0.0134 (8)	-0.0111 (8)
C7	0.0260 (9)	0.0250 (9)	0.0541 (12)	-0.0028 (7)	0.0169 (9)	-0.0104 (9)
C8	0.0209 (8)	0.0221 (9)	0.0487 (11)	-0.0008 (7)	0.0099 (8)	0.0002 (8)
C9	0.0212 (8)	0.0221 (8)	0.0344 (9)	-0.0026 (7)	0.0087 (7)	0.0014 (7)
C10	0.0199 (8)	0.0199 (8)	0.0287 (9)	-0.0030 (6)	0.0089 (7)	-0.0007 (7)
C11	0.0260 (9)	0.0228 (8)	0.0206 (8)	-0.0047 (7)	0.0044 (7)	-0.0001 (6)
C12	0.0400 (11)	0.0446 (12)	0.0222 (9)	0.0059 (9)	0.0048 (8)	0.0087 (8)
C13	0.0402 (12)	0.0742 (17)	0.0295 (11)	-0.0016 (11)	-0.0039 (9)	-0.0083 (11)
C14	0.0180 (7)	0.0202 (8)	0.0210 (8)	0.0027 (6)	0.0057 (6)	0.0000 (6)
C15	0.0244 (9)	0.0262 (9)	0.0270 (9)	-0.0068 (7)	0.0041 (7)	-0.0011 (7)
C16	0.0291 (9)	0.0308 (9)	0.0267 (9)	-0.0023 (7)	0.0025 (7)	-0.0054 (7)
C17	0.0293 (9)	0.0330 (10)	0.0209 (8)	-0.0013 (7)	0.0038 (7)	-0.0001 (7)
C18	0.0210 (8)	0.0231 (8)	0.0230 (8)	0.0035 (6)	0.0064 (6)	0.0012 (6)
C19	0.0263 (9)	0.0283 (9)	0.0285 (9)	0.0049 (7)	0.0108 (7)	0.0071 (7)
C20	0.0224 (9)	0.0221 (8)	0.0433 (11)	0.0013 (7)	0.0123 (8)	0.0068 (7)
C21	0.0186 (8)	0.0215 (8)	0.0386 (10)	-0.0012 (6)	0.0045 (7)	-0.0034 (7)
C22	0.0187 (8)	0.0239 (8)	0.0252 (8)	0.0030 (6)	0.0040 (6)	-0.0021 (7)
C23	0.0169 (7)	0.0185 (8)	0.0230 (8)	0.0034 (6)	0.0060 (6)	0.0000 (6)
C24	0.0393 (11)	0.0284 (9)	0.0293 (9)	0.0125 (8)	0.0172 (8)	0.0089 (8)
C25A	0.126 (3)	0.0721 (19)	0.0224 (11)	-0.0116 (18)	0.0169 (14)	0.0022 (11)
C26A	0.082 (3)	0.063 (2)	0.0323 (17)	-0.003 (2)	-0.0089 (17)	-0.0075 (16)
C25B	0.126 (3)	0.0721 (19)	0.0224 (11)	-0.0116 (18)	0.0169 (14)	0.0022 (11)
C26B	0.066 (6)	0.064 (6)	0.025 (4)	0.011 (4)	-0.001 (3)	0.008 (3)
N1	0.0218 (7)	0.0190 (7)	0.0239 (7)	-0.0011 (5)	0.0062 (5)	-0.0004 (5)
N2	0.0270 (7)	0.0211 (7)	0.0208 (7)	0.0036 (6)	0.0045 (6)	0.0009 (5)
N3	0.0275 (8)	0.0282 (8)	0.0217 (7)	0.0006 (6)	0.0044 (6)	0.0013 (6)
N4	0.0222 (7)	0.0209 (7)	0.0238 (7)	0.0027 (5)	0.0091 (6)	0.0033 (5)
N5	0.0284 (8)	0.0263 (8)	0.0257 (7)	0.0002 (6)	0.0099 (6)	0.0053 (6)
N6	0.0652 (12)	0.0371 (9)	0.0223 (8)	-0.0036 (9)	0.0137 (8)	0.0017 (7)
S1	0.0346 (3)	0.0357 (3)	0.0240 (2)	0.0030 (2)	0.00759 (18)	-0.00517 (18)
S2	0.0437 (3)	0.0503 (3)	0.0441 (3)	0.0090 (2)	0.0224 (2)	0.0260 (2)

Geometric parameters (Å, °)

C1—N1	1.287 (2)	C15—H19	0.9900
C1—C10	1.485 (2)	C16—C17	1.514 (3)
C1—C2	1.507 (2)	C16—H20	0.9900
C2—C3	1.527 (2)	C16—H21	0.9900
C2—H1	0.9900	C17—C18	1.509 (2)
C2—H2	0.9900	C17—H22	0.9900

C3—C4	1.516 (3)	C17—H23	0.9900
C3—H3	0.9900	C18—C19	1.396 (2)
C3—H4	0.9900	C18—C23	1.403 (2)
C4—C5	1.513 (3)	C19—C20	1.380 (3)
C4—H5	0.9900	C19—H24	0.9500
C4—H6	0.9900	C20—C21	1.391 (3)
C5—C6	1.399 (2)	C20—H25	0.9500
C5—C10	1.401 (2)	C21—C22	1.380 (2)
C6—C7	1.382 (3)	C21—H26	0.9500
C6—H7	0.9500	C22—C23	1.404 (2)
C7—C8	1.387 (3)	C22—H27	0.9500
C7—H8	0.9500	C24—N6	1.321 (3)
C8—C9	1.380 (2)	C24—N5	1.363 (2)
C8—H9	0.9500	C24—S2	1.6904 (19)
C9—C10	1.406 (2)	C25A—N6	1.458 (3)
C9—H10	0.9500	C25A—C26A	1.489 (4)
C11—N3	1.327 (2)	C25A—H30	0.9900
C11—N2	1.372 (2)	C25A—H31	0.9900
C11—S1	1.6866 (17)	C26A—H34	0.9800
C12—N3	1.457 (2)	C26A—H35	0.9800
C12—C13	1.503 (3)	C26A—H36	0.9800
C12—H13	0.9900	C26B—H37	0.9800
C12—H14	0.9900	C26B—H38	0.9800
C13—H15	0.9800	C26B—H39	0.9800
C13—H16	0.9800	N1—N2	1.3785 (18)
C13—H17	0.9800	N2—H11	0.8800
C14—N4	1.286 (2)	N3—H12	0.8800
C14—C23	1.482 (2)	N4—N5	1.3785 (19)
C14—C15	1.505 (2)	N5—H28	0.8800
C15—C16	1.523 (2)	N6—H29	0.8800
C15—H18	0.9900		
N1—C1—C10	116.11 (14)	C17—C16—C15	110.22 (15)
N1—C1—C2	125.09 (14)	C17—C16—H20	109.6
C10—C1—C2	118.78 (14)	C15—C16—H20	109.6
C1—C2—C3	113.38 (14)	C17—C16—H21	109.6
C1—C2—H1	108.9	C15—C16—H21	109.6
C3—C2—H1	108.9	H20—C16—H21	108.1
C1—C2—H2	108.9	C18—C17—C16	110.49 (14)
C3—C2—H2	108.9	C18—C17—H22	109.6
H1—C2—H2	107.7	C16—C17—H22	109.6
C4—C3—C2	110.59 (16)	C18—C17—H23	109.6
C4—C3—H3	109.5	C16—C17—H23	109.6
C2—C3—H3	109.5	H22—C17—H23	108.1
C4—C3—H4	109.5	C19—C18—C23	118.92 (15)
C2—C3—H4	109.5	C19—C18—C17	121.17 (15)
H3—C3—H4	108.1	C23—C18—C17	119.90 (15)
C5—C4—C3	110.73 (15)	C20—C19—C18	121.30 (16)

C5—C4—H5	109.5	C20—C19—H24	119.4
C3—C4—H5	109.5	C18—C19—H24	119.4
C5—C4—H6	109.5	C19—C20—C21	119.62 (16)
C3—C4—H6	109.5	C19—C20—H25	120.2
H5—C4—H6	108.1	C21—C20—H25	120.2
C6—C5—C10	118.75 (17)	C22—C21—C20	120.27 (16)
C6—C5—C4	120.79 (16)	C22—C21—H26	119.9
C10—C5—C4	120.46 (15)	C20—C21—H26	119.9
C7—C6—C5	121.38 (18)	C21—C22—C23	120.42 (16)
C7—C6—H7	119.3	C21—C22—H27	119.8
C5—C6—H7	119.3	C23—C22—H27	119.8
C6—C7—C8	119.59 (17)	C18—C23—C22	119.44 (15)
C6—C7—H8	120.2	C18—C23—C14	119.92 (14)
C8—C7—H8	120.2	C22—C23—C14	120.63 (14)
C9—C8—C7	120.30 (18)	N6—C24—N5	115.50 (16)
C9—C8—H9	119.8	N6—C24—S2	125.54 (14)
C7—C8—H9	119.8	N5—C24—S2	118.95 (15)
C8—C9—C10	120.47 (17)	N6—C25A—C26A	111.4 (2)
C8—C9—H10	119.8	N6—C25A—H30	109.4
C10—C9—H10	119.8	C26A—C25A—H30	109.4
C5—C10—C9	119.51 (15)	N6—C25A—H31	109.4
C5—C10—C1	120.35 (15)	C26A—C25A—H31	109.4
C9—C10—C1	120.14 (15)	H30—C25A—H31	108.0
N3—C11—N2	115.60 (15)	C25A—C26A—H34	109.5
N3—C11—S1	125.16 (13)	C25A—C26A—H35	109.5
N2—C11—S1	119.24 (13)	H34—C26A—H35	109.5
N3—C12—C13	112.49 (17)	C25A—C26A—H36	109.5
N3—C12—H13	109.1	H34—C26A—H36	109.5
C13—C12—H13	109.1	H35—C26A—H36	109.5
N3—C12—H14	109.1	H37—C26B—H38	109.5
C13—C12—H14	109.1	H37—C26B—H39	109.5
H13—C12—H14	107.8	H38—C26B—H39	109.5
C12—C13—H15	109.5	C1—N1—N2	118.32 (14)
C12—C13—H16	109.5	C11—N2—N1	118.12 (14)
H15—C13—H16	109.5	C11—N2—H11	120.9
C12—C13—H17	109.5	N1—N2—H11	120.9
H15—C13—H17	109.5	C11—N3—C12	124.58 (15)
H16—C13—H17	109.5	C11—N3—H12	117.7
N4—C14—C23	116.20 (14)	C12—N3—H12	117.7
N4—C14—C15	124.57 (15)	C14—N4—N5	117.74 (14)
C23—C14—C15	119.23 (14)	C24—N5—N4	118.31 (15)
C14—C15—C16	113.42 (14)	C24—N5—H28	120.8
C14—C15—H18	108.9	N4—N5—H28	120.8
C16—C15—H18	108.9	C24—N6—C25A	126.23 (19)
C14—C15—H19	108.9	C24—N6—H29	116.9
C16—C15—H19	108.9	C25A—N6—H29	116.9
H18—C15—H19	107.7		

N1—C1—C2—C3	161.54 (16)	C18—C19—C20—C21	0.1 (3)
C10—C1—C2—C3	-19.7 (2)	C19—C20—C21—C22	-1.2 (3)
C1—C2—C3—C4	50.9 (2)	C20—C21—C22—C23	0.8 (2)
C2—C3—C4—C5	-57.0 (2)	C19—C18—C23—C22	-1.9 (2)
C3—C4—C5—C6	-146.70 (17)	C17—C18—C23—C22	176.74 (15)
C3—C4—C5—C10	33.3 (2)	C19—C18—C23—C14	179.44 (14)
C10—C5—C6—C7	0.5 (3)	C17—C18—C23—C14	-1.9 (2)
C4—C5—C6—C7	-179.51 (18)	C21—C22—C23—C18	0.8 (2)
C5—C6—C7—C8	0.4 (3)	C21—C22—C23—C14	179.48 (14)
C6—C7—C8—C9	-0.9 (3)	N4—C14—C23—C18	171.47 (14)
C7—C8—C9—C10	0.5 (3)	C15—C14—C23—C18	-8.4 (2)
C6—C5—C10—C9	-0.9 (2)	N4—C14—C23—C22	-7.2 (2)
C4—C5—C10—C9	179.10 (16)	C15—C14—C23—C22	172.93 (15)
C6—C5—C10—C1	178.29 (15)	C10—C1—N1—N2	179.05 (13)
C4—C5—C10—C1	-1.7 (2)	C2—C1—N1—N2	-2.1 (2)
C8—C9—C10—C5	0.4 (2)	N3—C11—N2—N1	-9.4 (2)
C8—C9—C10—C1	-178.77 (15)	S1—C11—N2—N1	170.01 (11)
N1—C1—C10—C5	173.40 (15)	C1—N1—N2—C11	-169.76 (14)
C2—C1—C10—C5	-5.5 (2)	N2—C11—N3—C12	-179.47 (16)
N1—C1—C10—C9	-7.4 (2)	S1—C11—N3—C12	1.2 (3)
C2—C1—C10—C9	173.72 (15)	C13—C12—N3—C11	87.5 (2)
N4—C14—C15—C16	163.89 (16)	C23—C14—N4—N5	-177.99 (13)
C23—C14—C15—C16	-16.2 (2)	C15—C14—N4—N5	1.9 (2)
C14—C15—C16—C17	49.6 (2)	N6—C24—N5—N4	8.3 (2)
C15—C16—C17—C18	-58.95 (19)	S2—C24—N5—N4	-172.76 (11)
C16—C17—C18—C19	-145.52 (16)	C14—N4—N5—C24	179.83 (15)
C16—C17—C18—C23	35.9 (2)	N5—C24—N6—C25A	175.9 (2)
C23—C18—C19—C20	1.4 (2)	S2—C24—N6—C25A	-3.0 (3)
C17—C18—C19—C20	-177.19 (16)	C26A—C25A—N6—C24	133.2 (3)

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>
N3—H12...S2	0.88	3.02	3.7172 (16)	138
C9—H10...S2	0.95	3.09	3.8835 (19)	142
N6—H29...S1 ⁱ	0.88	3.31	4.002 (2)	138
C22—H27...S1 ⁱ	0.95	2.98	3.7828 (17)	143

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