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(2*E*)-*N*-Methyl-2-[1-(4-methylcyclohex-3-en-1-yl)-ethylidene]hydrazinecarbothioamide

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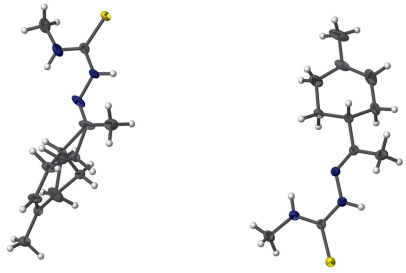
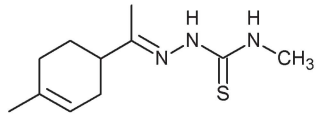
There are two independent molecules (*A* and *B*) in the asymmetric unit of the title compound, $C_{11}H_{19}N_3S$. In molecule *B*, two C atoms and the associated H atoms of the cyclohexene ring are disordered over two sets of sites with a site occupancy ratio of 0.649 (7):0.351 (7). The N—N—C—N fragments of the hydrazinecarbothioamide segments of both molecules are not planar, with a torsion angle of −5.8 (3)° for *A* and 11.6 (3)° for *B*. The stability of the conformations of both molecules is aided by the formation of intramolecular N—H···N hydrogen bonds. In the crystal, N—H···S hydrogen bonds link like molecules into $R_2^2(8)$ *A* + *B* dimers. These dimers are interconnected by additional N—H···S contacts, forming chains along the *c*-axis direction. The structure was refined as a two-component inversion twin.

3D view



Chemical scheme



Structure description

Thiosemicarbazones are a class of molecules that have been investigated over the last 50 years as antiviral (Pirrung *et al.* 2005) and antitumor agents (Hu *et al.* 2006). In addition, they show antiparasitic and antibacterial action against *Trypanasoma cruzi* (Du *et al.* 2002) and *Toxoplasma gondii* and against several other bacterial strains (de Aquino *et al.* 2008). To further our work on new thiosemicarbazone derivatives, we have prepared the title compound by the reaction of 4-acetyl-1-methylcyclohexene, a natural product extracted from the essential oil of *Cedrus atlanica* (Grimal, 1902), with 4-methyl-3-thiosemicarbazide in ethanol.

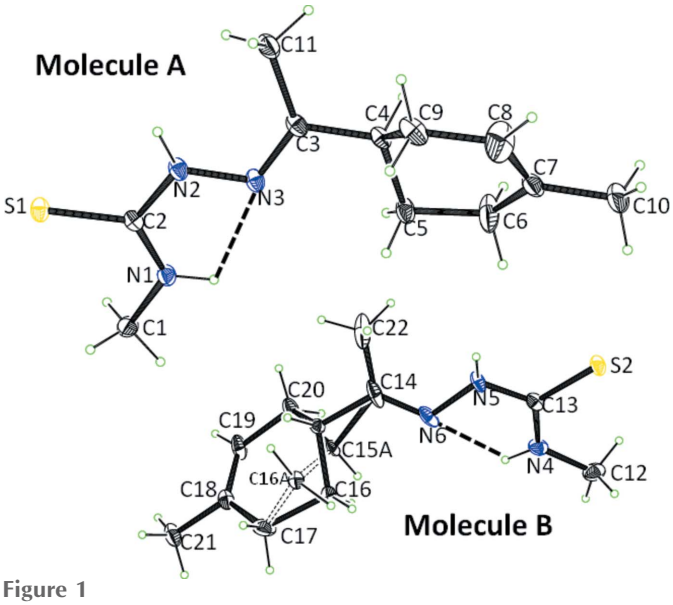


Figure 1
View of the pairs of molecules *A* and *B* of the title compound, showing the atom labeling and displacement ellipsoids drawn at the 30% probability level. The short intramolecular N—H···N contacts (see Table 1) are shown as dashed lines. Atoms of the minor disorder component are linked by double-dashed lines.

The title compound, crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit (Fig. 1). The N3—N2—C2—N1 and N6—N5—C13 fragments are not planar with torsion angles −5.8 (3) and 11.6 (3), respectively in molecules *A* and *B*. In each hydrazinecarbothioamide unit (=N—NH—C(=S)—NH–), the N—H hydrogen atoms are *anti*, and the terminal N—H hydrogen atoms form intramolecular N1—H1*N*···N3 and N4—H4*N*···N6 hydrogen bonds with *S*(5) ring motifs (Fig. 1 and Table 1). The bond lengths and angles of the title compound are normal and agree with those values reported in other methyl-hydrazinecarbothioamide structures (Gangadharan *et al.*, 2015; de Oliveira *et al.*, 2017; Tayamon *et al.*, 2012). In both molecules, the thiosemicarbazone groups adopts an extended conformation, as shown by the torsion angles S1—C2—N2—N3 [175.83 (14)°, molecule *A*] and S2—C13—N5—N6 [−171.21 (15)°, molecule *B*].

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.87 (3)	2.28 (3)	2.645 (3)	105 (2)
N4—H4*N*···N6	0.87 (3)	2.24 (3)	2.637 (3)	107 (2)
N2—H2*N*···S2^{i}	0.89 (3)	2.54 (3)	3.4284 (19)	172 (2)
N4—H4*N*···S1^{ii}	0.87 (3)	2.60 (3)	3.337 (2)	143 (2)
N5—H5*N*···S1^{iii}	0.86 (3)	2.72 (3)	3.547 (2)	161 (2)

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

In the crystal, the two independent molecules are linked by a pair of (N2, N5)—H···S hydrogen bonds, Table 1, forming *A*–*B* dimers with $R_2^2(8)$ ring motifs. These dimers are linked by N4—H···S hydrogen bonds, forming chains along the *c*-axis direction. Adjacent chains form sheets parallel to (001), Figs. 2 and 3.

Synthesis and crystallization

To a solution of 4-methyl-3-thiosemicarbazide (1.43 g, 13.61 mmol) in ethanol (72 ml) was added 4-acetyl-1-methylcyclohexene (2 g, 14.29 mmol) and acetic acid (0.50 ml). The mixture was stirred at 85°C for 3 h. After cooling, the mixture

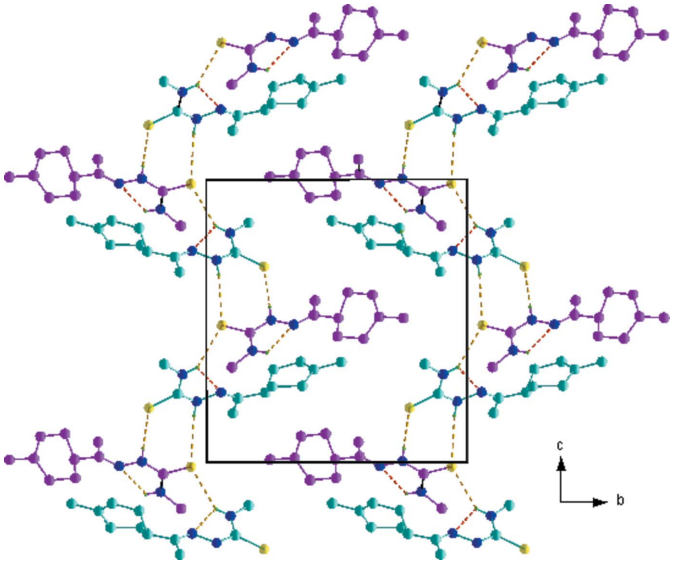


Figure 2
A partial view along the *a* axis of the crystal packing of the title compound (molecule *A* purple and molecule *B* green), showing the N—H···S hydrogen bonds (dashed lines; see Table 1), which result in the formation of $R_2^2(8)$ ring motifs. H atoms not involved in hydrogen bonding have been omitted for clarity.

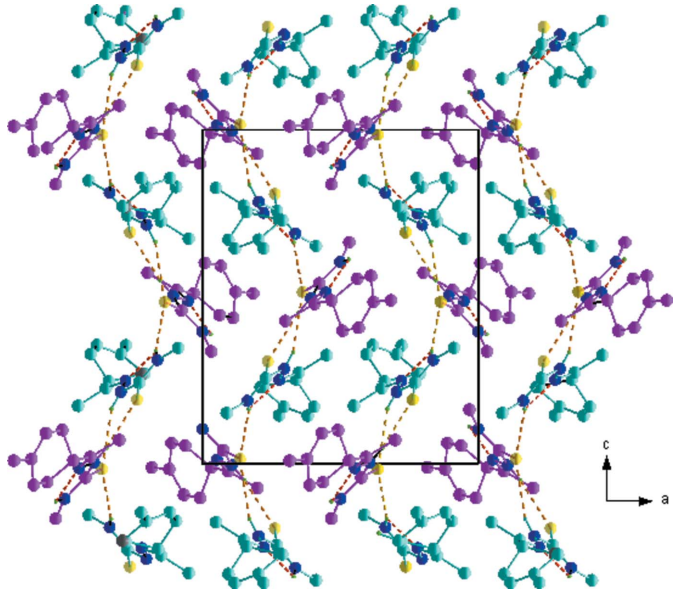


Figure 3
Crystal packing of the title compound (molecule *A* purple and molecule *B* green), viewed along the *b* axis, showing the hydrogen bonds as dashed lines (see Table 1).

was extracted with dichloromethane (3× 20 ml). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure. The residue was chromatographed on a silica gel column using hexane/ethyl acetate (92/8) as eluent, to give the title compound (2.286 g) in 88% yield. Colourless plate-like crystals were obtained from a petroleum ether solution, by slow evaporation of the solvent at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a two-component inversion twin. The C15 and C16 atoms of the cyclohexene ring in molecule *B* and their associated hydrogen atoms are disordered over two sets of sites with refined site occupancies of 0.649 (7) and 0.351 (7). This disorder inverts the configuration at C15 (*R* for C15 and *S* for C15*A*). The configuration at C4 in molecule *A* is *R*.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{19}N_3S$
M_r	225.35
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	12.2974 (4), 13.7295 (4), 14.8952 (5)
V (Å^3)	2514.86 (14)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.07
Crystal size (mm)	0.44 × 0.31 × 0.22
Data collection	
Diffractometer	Bruker D8 venture CMOS area-detector
Absorption correction	Numerical (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.707, 0.858
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48702, 5139, 5028
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.070, 1.04
No. of reflections	5139
No. of parameters	319
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.31
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.065 (15)

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg *et al.*, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

References

Aquino, T. M. de, Liesen, A. P., da Silva, R. E., Lima, V. T., Carvalho, C. S., de Faria, A. R., de Araújo, J. M., de Lima, J. G., Alves, A. J., de Melo, E. J. & Góes, A. J. (2008). *Bioorg. Med. Chem.* **16**, 446–456.

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Du, X., Guo, C., Hansell, E., Doyle, P. S., Caffrey, C. R., Holler, T. P., McKerrow, J. H. & Cohen, E. (2002). *J. Med. Chem.* **45**, 2695–2707.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gangadharan, R., Haribabu, J., Karvembu, R. & Sethusankar, K. (2015). *Acta Cryst.* E**71**, 305–308.

Grimal, E. (1902). *C. R. Acad. Sci.* **135**, 582–583.

Hu, W.-X., Zhou, W., Xia, C. N. & Wen, X. (2006). *Bioorg. Med. Chem. Lett.* **16**, 2213–2218.

Oliveira, A. B. de, Beck, J., Landvogt, C., de Farias, R. L. & Feitoza, B. R. S. (2017). *Acta Cryst.* E**73**, 291–295.

Pirrung, M. C., Pansare, S. V., Das Sarma, K., Keith, K. A. & Kern, E. R. (2005). *J. Med. Chem.* **48**, 3045–3050.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Tayamon, S., Mazlan, N. A., Ravoof, T. B. S. A., Mohamed Tahir, M. I. & Crouse, K. A. (2012). *Acta Cryst.* E**68**, o3104–o3105.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). **2**, x170513 [https://doi.org/10.1107/S2414314617005132]

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Crystal data

$C_{11}H_{19}N_3S$
M_r = 225.35
Orthorhombic, $P2_12_12_1$
a = 12.2974 (4) Å
b = 13.7295 (4) Å
c = 14.8952 (5) Å
V = 2514.86 (14) Å^3
Z = 8
$F(000)$ = 976
D_x = 1.190 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 5139 reflections
θ = 4.4–74.6°
μ = 2.07 mm^{-1}
T = 100 K
Plate, colourless
0.44 × 0.31 × 0.22 mm

Data collection

Bruker D8 venture CMOS area-detector diffractometer
Radiation source: microsource
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2012)
T_{min} = 0.707, T_{max} = 0.858
48702 measured reflections
5139 independent reflections
5028 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 74.6°, θ_{min} = 4.4°
h = −15→15
k = −17→17
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.070
S = 1.04
5139 reflections
319 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.9302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.065 (15)

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. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.36364 (4)	0.94045 (4)	0.01514 (3)	0.02417 (12)	
N1	0.49945 (15)	0.82337 (14)	0.10431 (12)	0.0243 (4)	
H1N	0.530 (2)	0.767 (2)	0.1124 (19)	0.033 (7)*	
N2	0.39334 (15)	0.75188 (13)	−0.00369 (12)	0.0240 (4)	
H2N	0.347 (2)	0.757 (2)	−0.0494 (19)	0.033 (7)*	
N3	0.44757 (15)	0.66492 (12)	0.01283 (12)	0.0222 (3)	
C1	0.53214 (19)	0.90195 (17)	0.16325 (16)	0.0295 (5)	
H1A	0.5535	0.9573	0.1280	0.044*	
H1B	0.5923	0.8811	0.1996	0.044*	
H1C	0.4723	0.9196	0.2013	0.044*	
C2	0.42426 (17)	0.83324 (15)	0.04084 (13)	0.0204 (4)	
C3	0.40645 (18)	0.58777 (15)	−0.02091 (14)	0.0247 (4)	
C4	0.46798 (17)	0.49360 (14)	−0.01048 (14)	0.0223 (4)	
H4	0.4165	0.4450	0.0123	0.027*	
C5	0.5621 (2)	0.49720 (16)	0.05467 (16)	0.0305 (5)	
H5A	0.6164	0.5430	0.0334	0.037*	
H5B	0.5367	0.5190	0.1130	0.037*	
C6	0.6116 (3)	0.3972 (2)	0.0628 (2)	0.0671 (12)	
H6A	0.6843	0.4050	0.0872	0.081*	
H6B	0.5697	0.3614	0.1070	0.081*	
C7	0.62018 (19)	0.33763 (16)	−0.01496 (19)	0.0346 (5)	
C8	0.5671 (3)	0.3628 (2)	−0.0924 (2)	0.0592 (9)	
H8	0.5676	0.3198	−0.1406	0.071*	
C9	0.5082 (2)	0.45746 (18)	−0.10149 (15)	0.0343 (5)	
H9A	0.4468	0.4493	−0.1416	0.041*	
H9B	0.5565	0.5056	−0.1276	0.041*	
C10	0.6836 (2)	0.24421 (19)	−0.0102 (3)	0.0538 (8)	
H10A	0.6423	0.1964	0.0223	0.081*	
H10B	0.7513	0.2556	0.0201	0.081*	
H10C	0.6975	0.2209	−0.0698	0.081*	
C11	0.3008 (2)	0.58335 (17)	−0.07200 (18)	0.0373 (6)	
H11A	0.2498	0.6280	−0.0459	0.056*	
H11B	0.2720	0.5184	−0.0691	0.056*	
H11C	0.3134	0.6008	−0.1335	0.056*	
S2	0.76273 (5)	0.27916 (4)	0.69275 (3)	0.02686 (13)	
N4	0.83663 (15)	0.40843 (15)	0.81084 (14)	0.0285 (4)	
H4N	0.830 (2)	0.465 (2)	0.836 (2)	0.036 (8)*	
N5	0.70352 (17)	0.46203 (13)	0.71559 (12)	0.0259 (4)	
H5N	0.671 (2)	0.453 (2)	0.665 (2)	0.033 (7)*	
N6	0.72110 (17)	0.55541 (14)	0.74845 (13)	0.0316 (4)	
C12	0.9124 (2)	0.3382 (2)	0.84744 (17)	0.0358 (6)	
H12A	0.8746	0.2788	0.8610	0.054*	
H12B	0.9442	0.3638	0.9013	0.054*	
H12C	0.9686	0.3253	0.8043	0.054*	
C13	0.77058 (18)	0.38938 (15)	0.74270 (13)	0.0239 (4)	

C14	0.6501 (3)	0.62087 (16)	0.72682 (18)	0.0393 (7)	
C18	0.70439 (19)	0.91269 (15)	0.82868 (14)	0.0269 (5)	
C17	0.7888 (2)	0.8686 (2)	0.7702 (2)	0.0425 (6)	
H17A	0.866 (3)	0.875 (2)	0.798 (2)	0.051*	
H17B	0.801 (3)	0.899 (2)	0.706 (2)	0.051*	
C19	0.6175 (2)	0.86244 (16)	0.85558 (16)	0.0337 (6)	
H19	0.5679	0.8934	0.8930	0.040*	
C20	0.5949 (2)	0.75825 (16)	0.82896 (17)	0.0335 (5)	
H20A	0.5180	0.7512	0.8159	0.040*	
H20B	0.6122	0.7158	0.8790	0.040*	
C21	0.7221 (2)	1.01765 (16)	0.85489 (17)	0.0374 (6)	
H21A	0.7109	1.0587	0.8035	0.056*	
H21B	0.7951	1.0258	0.8765	0.056*	
H21C	0.6717	1.0352	0.9013	0.056*	
C22	0.5491 (3)	0.6021 (2)	0.6742 (2)	0.0578 (9)	
H22A	0.5153	0.5434	0.6954	0.087*	
H22B	0.5671	0.5950	0.6118	0.087*	
H22C	0.4998	0.6557	0.6815	0.087*	
C15	0.6606 (3)	0.7265 (3)	0.7470 (3)	0.0198 (8)	0.649 (7)
H15	0.6371	0.7642	0.6947	0.024*	0.649 (7)
C16	0.7785 (3)	0.7517 (2)	0.7685 (2)	0.0256 (10)	0.649 (7)
H16A	0.8265	0.7247	0.7232	0.031*	0.649 (7)
H16B	0.7988	0.7248	0.8264	0.031*	0.649 (7)
C16A	0.7427 (5)	0.7894 (4)	0.7130 (4)	0.0218 (17)	0.351 (7)
H′A	0.7982	0.7606	0.6751	0.026*	0.351 (7)
H′B	0.6840	0.8135	0.6756	0.026*	0.351 (7)
C15A	0.7013 (6)	0.7169 (5)	0.7815 (5)	0.0185 (15)	0.351 (7)
H15A	0.7575	0.6982	0.8249	0.022*	0.351 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0334 (3)	0.0203 (2)	0.0188 (2)	0.0051 (2)	−0.0011 (2)	−0.00187 (19)
N1	0.0287 (9)	0.0191 (8)	0.0252 (9)	0.0017 (8)	−0.0034 (7)	−0.0026 (7)
N2	0.0341 (9)	0.0185 (8)	0.0194 (8)	−0.0007 (7)	−0.0047 (7)	0.0009 (6)
N3	0.0318 (9)	0.0177 (8)	0.0170 (8)	0.0001 (7)	−0.0006 (7)	0.0012 (7)
C1	0.0286 (11)	0.0268 (11)	0.0330 (12)	0.0035 (9)	−0.0089 (9)	−0.0089 (9)
C2	0.0247 (10)	0.0200 (10)	0.0165 (9)	−0.0022 (8)	0.0036 (7)	0.0001 (7)
C3	0.0363 (11)	0.0202 (10)	0.0176 (9)	−0.0056 (8)	−0.0016 (9)	0.0028 (8)
C4	0.0313 (10)	0.0178 (9)	0.0179 (9)	−0.0047 (8)	0.0019 (8)	0.0000 (8)
C5	0.0447 (13)	0.0201 (11)	0.0266 (11)	0.0050 (10)	−0.0094 (10)	−0.0067 (9)
C6	0.101 (3)	0.0338 (15)	0.067 (2)	0.0305 (17)	−0.052 (2)	−0.0223 (15)
C7	0.0301 (11)	0.0220 (10)	0.0517 (14)	−0.0044 (9)	0.0095 (11)	−0.0124 (10)
C8	0.082 (2)	0.060 (2)	0.0355 (15)	0.0271 (18)	−0.0011 (15)	−0.0265 (14)
C9	0.0521 (15)	0.0318 (12)	0.0188 (10)	−0.0099 (11)	0.0037 (10)	−0.0058 (9)
C10	0.0443 (15)	0.0275 (12)	0.090 (2)	0.0040 (11)	0.0063 (16)	−0.0202 (15)
C11	0.0498 (15)	0.0215 (11)	0.0405 (13)	−0.0062 (10)	−0.0178 (12)	0.0050 (9)
S2	0.0371 (3)	0.0182 (2)	0.0252 (2)	0.0030 (2)	−0.0074 (2)	−0.00647 (19)

N4	0.0272 (9)	0.0307 (10)	0.0276 (9)	−0.0047 (7)	0.0000 (8)	−0.0112 (8)
N5	0.0408 (11)	0.0149 (8)	0.0220 (9)	−0.0015 (7)	−0.0006 (8)	−0.0059 (7)
N6	0.0428 (11)	0.0209 (9)	0.0312 (10)	−0.0111 (8)	0.0174 (9)	−0.0126 (8)
C12	0.0275 (11)	0.0466 (15)	0.0332 (13)	−0.0005 (10)	−0.0069 (10)	−0.0100 (11)
C13	0.0294 (10)	0.0224 (10)	0.0199 (9)	−0.0048 (9)	0.0045 (8)	−0.0032 (8)
C14	0.0651 (18)	0.0145 (10)	0.0384 (13)	−0.0008 (11)	0.0292 (13)	−0.0041 (9)
C18	0.0380 (12)	0.0208 (10)	0.0218 (10)	0.0014 (9)	−0.0067 (9)	−0.0012 (8)
C17	0.0307 (13)	0.0388 (14)	0.0581 (17)	−0.0103 (10)	0.0025 (12)	−0.0212 (13)
C19	0.0527 (16)	0.0177 (10)	0.0308 (12)	0.0059 (10)	0.0164 (11)	−0.0023 (9)
C20	0.0442 (13)	0.0188 (10)	0.0376 (13)	−0.0006 (9)	0.0204 (11)	−0.0027 (9)
C21	0.0553 (16)	0.0204 (11)	0.0365 (13)	−0.0005 (11)	−0.0114 (12)	−0.0020 (9)
C22	0.101 (3)	0.0314 (14)	0.0406 (16)	0.0296 (16)	−0.0126 (16)	−0.0069 (12)
C15	0.0216 (19)	0.0175 (17)	0.0203 (19)	−0.0014 (14)	−0.0027 (15)	−0.0021 (14)
C16	0.0243 (18)	0.0187 (16)	0.034 (2)	0.0019 (13)	−0.0032 (15)	−0.0033 (14)
C16A	0.024 (3)	0.019 (3)	0.022 (3)	0.003 (2)	0.000 (2)	0.000 (2)
C15A	0.024 (4)	0.011 (3)	0.020 (3)	−0.002 (3)	0.001 (3)	−0.006 (2)

Geometric parameters (Å, º)

S1—C2	1.694 (2)	N5—C13	1.356 (3)
N1—C2	1.329 (3)	N5—N6	1.389 (2)
N1—C1	1.448 (3)	N5—H5N	0.86 (3)
N1—H1N	0.87 (3)	N6—C14	1.294 (4)
N2—C2	1.354 (3)	C12—H12A	0.9600
N2—N3	1.389 (2)	C12—H12B	0.9600
N2—H2N	0.89 (3)	C12—H12C	0.9600
N3—C3	1.277 (3)	C14—C15	1.487 (4)
C1—H1A	0.9600	C14—C22	1.492 (5)
C1—H1B	0.9600	C14—C15A	1.673 (7)
C1—H1C	0.9600	C18—C19	1.333 (4)
C3—C4	1.506 (3)	C18—C17	1.484 (4)
C3—C11	1.507 (3)	C18—C21	1.509 (3)
C4—C5	1.511 (3)	C17—C16A	1.494 (6)
C4—C9	1.526 (3)	C17—C16	1.610 (4)
C4—H4	0.9800	C17—H17A	1.04 (3)
C5—C6	1.507 (3)	C17—H17B	1.06 (3)
C5—H5A	0.9700	C19—C20	1.510 (3)
C5—H5B	0.9700	C19—H19	0.9300
C6—C7	1.422 (4)	C20—C15	1.527 (4)
C6—H6A	0.9700	C20—C15A	1.592 (7)
C6—H6B	0.9700	C20—H20A	0.9700
C7—C8	1.370 (4)	C20—H20B	0.9700
C7—C10	1.503 (3)	C21—H21A	0.9600
C8—C9	1.493 (4)	C21—H21B	0.9600
C8—H8	0.9300	C21—H21C	0.9600
C9—H9A	0.9700	C22—H22A	0.9600
C9—H9B	0.9700	C22—H22B	0.9600
C10—H10A	0.9600	C22—H22C	0.9600

C10—H10B	0.9600	C15—C16	1.524 (5)
C10—H10C	0.9600	C15—H15	0.9800
C11—H11A	0.9600	C16—H16A	0.9700
C11—H11B	0.9600	C16—H16B	0.9700
C11—H11C	0.9600	C16A—C15A	1.513 (9)
S2—C13	1.689 (2)	C16A—H′A	0.9700
N4—C13	1.326 (3)	C16A—H′B	0.9700
N4—C12	1.447 (3)	C15A—H15A	0.9800
N4—H4N	0.87 (3)		

C2—N1—C1	123.25 (19)	H12A—C12—H12B	109.5
C2—N1—H1N	119.5 (19)	N4—C12—H12C	109.5
C1—N1—H1N	117.3 (19)	H12A—C12—H12C	109.5
C2—N2—N3	119.18 (18)	H12B—C12—H12C	109.5
C2—N2—H2N	119.0 (18)	N4—C13—N5	117.09 (19)
N3—N2—H2N	121.0 (18)	N4—C13—S2	123.30 (18)
C3—N3—N2	116.94 (18)	N5—C13—S2	119.55 (16)
N1—C1—H1A	109.5	N6—C14—C15	124.7 (3)
N1—C1—H1B	109.5	N6—C14—C22	124.9 (2)
H1A—C1—H1B	109.5	C15—C14—C22	110.3 (3)
N1—C1—H1C	109.5	N6—C14—C15A	99.9 (4)
H1A—C1—H1C	109.5	C22—C14—C15A	134.9 (4)
H1B—C1—H1C	109.5	C19—C18—C17	121.7 (2)
N1—C2—N2	117.37 (19)	C19—C18—C21	122.2 (2)
N1—C2—S1	123.74 (16)	C17—C18—C21	116.1 (2)
N2—C2—S1	118.87 (16)	C18—C17—C16A	111.5 (3)
N3—C3—C4	118.21 (19)	C18—C17—C16	111.2 (2)
N3—C3—C11	125.0 (2)	C18—C17—H17A	111.6 (18)
C4—C3—C11	116.79 (18)	C16A—C17—H17A	129.7 (18)
C3—C4—C5	115.02 (17)	C16—C17—H17A	99.6 (18)
C3—C4—C9	110.51 (18)	C18—C17—H17B	118.1 (18)
C5—C4—C9	109.44 (19)	C16A—C17—H17B	80.1 (18)
C3—C4—H4	107.2	C16—C17—H17B	113.2 (18)
C5—C4—H4	107.2	H17A—C17—H17B	101 (3)
C9—C4—H4	107.2	C18—C19—C20	124.0 (2)
C6—C5—C4	109.36 (19)	C18—C19—H19	118.0
C6—C5—H5A	109.8	C20—C19—H19	118.0
C4—C5—H5A	109.8	C19—C20—C15	112.5 (2)
C6—C5—H5B	109.8	C19—C20—C15A	107.6 (3)
C4—C5—H5B	109.8	C19—C20—H20A	109.1
H5A—C5—H5B	108.3	C15—C20—H20A	109.1
C7—C6—C5	119.2 (3)	C19—C20—H20B	109.1
C7—C6—H6A	107.5	C15—C20—H20B	109.1
C5—C6—H6A	107.5	H20A—C20—H20B	107.8
C7—C6—H6B	107.5	C18—C21—H21A	109.5
C5—C6—H6B	107.5	C18—C21—H21B	109.5
H6A—C6—H6B	107.0	H21A—C21—H21B	109.5
C8—C7—C6	120.4 (2)	C18—C21—H21C	109.5

C8—C7—C10	120.2 (3)	H21A—C21—H21C	109.5
C6—C7—C10	119.4 (3)	H21B—C21—H21C	109.5
C7—C8—C9	121.8 (2)	C14—C22—H22A	109.5
C7—C8—H8	119.1	C14—C22—H22B	109.5
C9—C8—H8	119.1	H22A—C22—H22B	109.5
C8—C9—C4	111.0 (2)	C14—C22—H22C	109.5
C8—C9—H9A	109.4	H22A—C22—H22C	109.5
C4—C9—H9A	109.4	H22B—C22—H22C	109.5
C8—C9—H9B	109.4	C14—C15—C16	110.3 (3)
C4—C9—H9B	109.4	C14—C15—C20	113.2 (3)
H9A—C9—H9B	108.0	C16—C15—C20	105.7 (3)
C7—C10—H10A	109.5	C14—C15—H15	109.2
C7—C10—H10B	109.5	C16—C15—H15	109.2
H10A—C10—H10B	109.5	C20—C15—H15	109.2
C7—C10—H10C	109.5	C15—C16—C17	107.7 (3)
H10A—C10—H10C	109.5	C15—C16—H16A	110.2
H10B—C10—H10C	109.5	C17—C16—H16A	110.2
C3—C11—H11A	109.5	C15—C16—H16B	110.2
C3—C11—H11B	109.5	C17—C16—H16B	110.2
H11A—C11—H11B	109.5	H16A—C16—H16B	108.5
C3—C11—H11C	109.5	C17—C16A—C15A	102.8 (5)
H11A—C11—H11C	109.5	C17—C16A—H′A	111.2
H11B—C11—H11C	109.5	C15A—C16A—H′A	111.2
C13—N4—C12	123.4 (2)	C17—C16A—H′B	111.2
C13—N4—H4N	116.9 (19)	C15A—C16A—H′B	111.2
C12—N4—H4N	120 (2)	H′A—C16A—H′B	109.1
C13—N5—N6	118.65 (19)	C16A—C15A—C20	109.9 (5)
C13—N5—H5N	115.8 (19)	C16A—C15A—C14	108.5 (5)
N6—N5—H5N	121.0 (19)	C20—C15A—C14	100.8 (4)
C14—N6—N5	116.6 (2)	C16A—C15A—H15A	112.3
N4—C12—H12A	109.5	C20—C15A—H15A	112.3
N4—C12—H12B	109.5	C14—C15A—H15A	112.3

C2—N2—N3—C3	170.57 (19)	N5—N6—C14—C15A	178.7 (3)
C1—N1—C2—N2	−173.5 (2)	C19—C18—C17—C16A	27.5 (4)
C1—N1—C2—S1	4.8 (3)	C21—C18—C17—C16A	−151.8 (3)
N3—N2—C2—N1	−5.8 (3)	C19—C18—C17—C16	−15.7 (4)
N3—N2—C2—S1	175.83 (14)	C21—C18—C17—C16	164.9 (2)
N2—N3—C3—C4	175.21 (17)	C17—C18—C19—C20	−1.1 (4)
N2—N3—C3—C11	−3.9 (3)	C21—C18—C19—C20	178.3 (2)
N3—C3—C4—C5	11.3 (3)	C18—C19—C20—C15	−17.6 (4)
C11—C3—C4—C5	−169.5 (2)	C18—C19—C20—C15A	10.6 (5)
N3—C3—C4—C9	−113.2 (2)	N6—C14—C15—C16	18.1 (4)
C11—C3—C4—C9	66.0 (3)	C22—C14—C15—C16	−159.0 (3)
C3—C4—C5—C6	176.5 (3)	N6—C14—C15—C20	−100.1 (4)
C9—C4—C5—C6	−58.4 (3)	C22—C14—C15—C20	82.8 (4)
C4—C5—C6—C7	38.2 (4)	C19—C20—C15—C14	172.7 (3)
C5—C6—C7—C8	−11.7 (5)	C19—C20—C15—C16	51.9 (4)

C5—C6—C7—C10	171.3 (3)	C14—C15—C16—C17	168.9 (3)
C6—C7—C8—C9	6.3 (5)	C20—C15—C16—C17	−68.4 (4)
C10—C7—C8—C9	−176.6 (3)	C18—C17—C16—C15	51.0 (4)
C7—C8—C9—C4	−27.9 (4)	C18—C17—C16A—C15A	−60.7 (5)
C3—C4—C9—C8	−178.6 (2)	C17—C16A—C15A—C20	72.4 (6)
C5—C4—C9—C8	53.7 (3)	C17—C16A—C15A—C14	−178.2 (4)
C13—N5—N6—C14	−174.5 (2)	C19—C20—C15A—C16A	−47.0 (6)
C12—N4—C13—N5	179.7 (2)	C19—C20—C15A—C14	−161.3 (3)
C12—N4—C13—S2	2.7 (3)	N6—C14—C15A—C16A	111.6 (5)
N6—N5—C13—N4	11.6 (3)	C22—C14—C15A—C16A	−74.1 (6)
N6—N5—C13—S2	−171.21 (15)	N6—C14—C15A—C20	−133.0 (4)
N5—N6—C14—C15	−173.2 (2)	C22—C14—C15A—C20	41.4 (7)
N5—N6—C14—C22	3.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N3	0.87 (3)	2.28 (3)	2.645 (3)	105 (2)
N4—H4*N*···N6	0.87 (3)	2.24 (3)	2.637 (3)	107 (2)
N2—H2*N*···S2^{i}	0.89 (3)	2.54 (3)	3.4284 (19)	172 (2)
N4—H4*N*···S1^{ii}	0.87 (3)	2.60 (3)	3.337 (2)	143 (2)
N5—H5*N*···S1^{iii}	0.86 (3)	2.72 (3)	3.547 (2)	161 (2)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*+1/2, −*y*+3/2, −*z*+1; (iii) −*x*+1, *y*−1/2, −*z*+1/2.