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# 2-[(*E*)-(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-*N*-methylhydrazine-1-carbothioamide

**Adriano Bof de Oliveira,[a]* Johannes Beck,[b] Jörg Daniels[b] and Renan Lira de Farias[c]**

[a]Departamento de Química, Universidade Federal de Sergipe, Av. Marechal Rondon s/n, 49100-000 São Cristóvão-SE, Brazil, [b]Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany, and [c]Instituto de Química, Universidade Estadual Paulista, Rua Francisco Degni s/n, 14801-970 Araraquara-SP, Brazil. *Correspondence e-mail: adriano@daad-alumni.de

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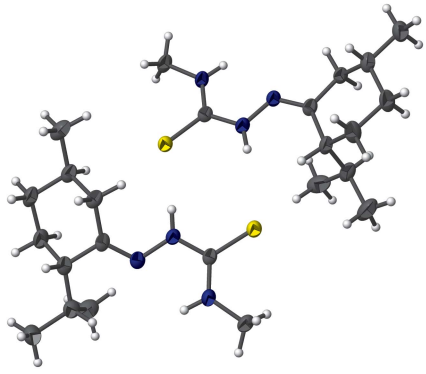
**CCDC reference**: 1469055

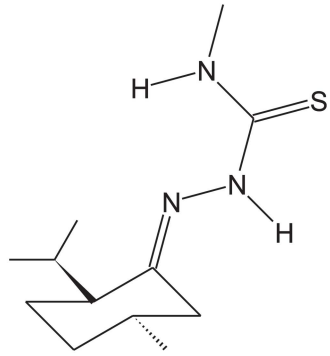
**Structural data**: full structural data are available from iucrdata.iucr.org

There are two molecules in the asymmetric unit of the title compound, $C_{12}H_{23}N_3S$, which are linked by two strong N—H···S hydrogen bonds, building a non-centrosymmetric dimer with graph-set motif $R_2^2(8)$. The molecules are further connected by N—H···S interactions into a two-dimensional hydrogen-bonded polymeric structure along the [001] direction. The absolute structure is based on the refinement of the Flack parameter.

**3D view**



**Chemical scheme**




## Structure description

As part of our ongoing research on the synthesis and chemical structure of thiosemicarbazone derivatives from natural products, we report herein the crystal structure of a (−)-menthone-thiosemicarbazone compound.

In the crystal structure of the title compound, there are two discrete molecules in general positions in the asymmetric unit. As enantiopure (−)-menthone was used in the chemical reaction, both of the crystallographically independent molecules have the same chirality. The atoms C3, C6, C15 and C18 are chiral centres and maintain the chirality of the employed reagent and the obtained product emerges as enantiopure crystals in the non-centrosymmetric space group $P2_1$. The molecules are connected by mutual N—H···S interactions, building a non-centrosymmetric dimer with an $R_2^2(8)$ ring. The thiosemicarbazone entities are not planar and the torsion angles N1—N2—C11—N3 and N4—N5—C23—N6 are 2.4 (3) and 12.5 (3)°, respectively. For the N1—N2 and N4—N5 bonds, the *E* conformation is observed. The cyclohexane rings of the menthone units are in a chair conformation (Fig. 1). Both of these conformations are also observed for the (−)-menthone-3-thiosemicarbazone derivative (Oliveira *et al.*, 2014).

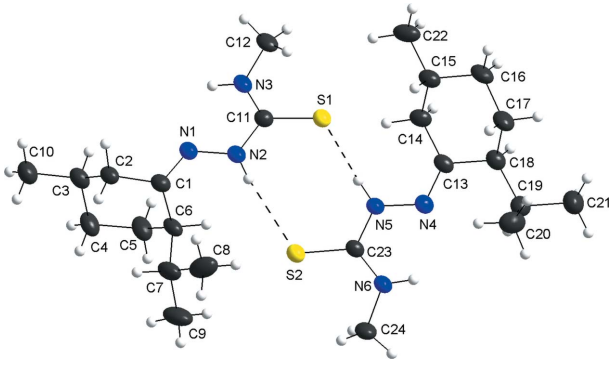



**Figure 1**
The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines; see Table 1 for details.

In the crystal, the molecules are also connected by symmetry-generated N—H···S hydrogen bonds into a one-dimensional polymer along the *b*-axis (Fig. 2 and Table 1). In addition, other hydrogen bonds of the same type, with bridging sulfur atoms, connect the molecules into a two-dimensional polymeric chain along [001].

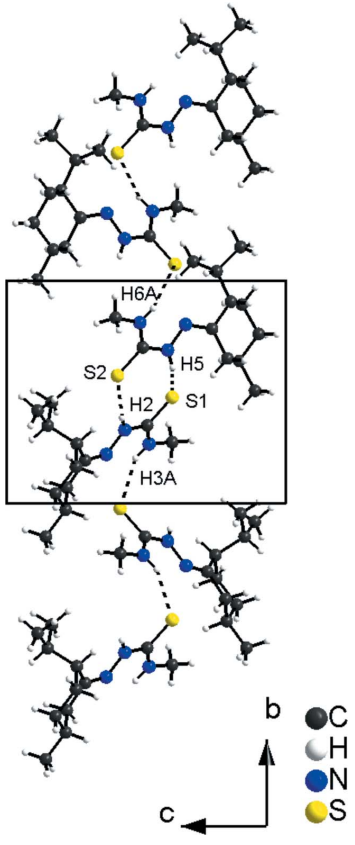



**Figure 2**
Partial view of the of the crystal structure of the title compound along the *a* axis, showing the non non-centrosymmetric dimer and the extended N—H···S interactions along the *b* axis. The complete two-dimensional hydrogen-bonded polymeric structure is not shown for clarity. Hydrogen bonds are shown as dashed lines; see Table 1 for details.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···S2 | 0.88 | 2.79 | 3.671 (2) | 174 |
| N3—H3*A*···S1$^{i}$ | 0.88 | 2.61 | 3.378 (2) | 147 |
| N5—H5···S1 | 0.88 | 2.61 | 3.356 (2) | 143 |
| N6—H6*A*···S2$^{ii}$ | 0.88 | 2.79 | 3.445 (2) | 132 |

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

## Synthesis and crystallization

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 (−)-menthone (10 mmol) and 4-methyl-3-thiosemicarbazide (10 mmol) in ethanol (80 mL) was refluxed for 5 h. After cooling and filtering, the title compound was obtained. Colourless plates were obtained by slow evaporation of a solution in the solvent DMSO.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The correct assignment of the

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{12}H_{23}N_3S$ |
| $M_r$ | 241.39 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 123 |
| *a*, *b*, *c* (Å) | 11.5579 (5), 9.9279 (4), 12.5271 (5) |
| $\beta$ (°) | 95.030 (2) |
| *V* (Å$^3$) | 1431.90 (10) |
| *Z* | 4 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.21 |
| Crystal size (mm) | 0.77 × 0.30 × 0.08 |
| | |
| Data collection | |
| Diffractometer | Nonius KappaCCD |
| Absorption correction | Analytical (Alcock, 1970) |
| $T_{min}$, $T_{max}$ | 0.857, 0.984 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 23116, 6380, 5069 |
| $R_{int}$ | 0.075 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.649 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.044, 0.104, 1.06 |
| No. of reflections | 6380 |
| No. of parameters | 297 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.24, −0.37 |
| Absolute structure | Flack *x* determined using 1954 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | 0.00 (7) |

Computer programs: *COLLECT* (Nonius, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

absolute configuration was assured by the Flack parameter of 0.00 (7).

## Acknowledgements

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## References

Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Freund, M. & Schander, A. (1902). *Chem. Ber.* **35**, 2602–2606.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Oliveira, A. B. de, Beck, J., Daniels, J., de Farias, R. L. & de Godoy Netto, A. V. (2014). *Acta Cryst.* E**70**, o903–o904.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press, United States.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

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

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

# full crystallographic data

*IUCrData* (2016). **1**, x160459 [doi:10.1107/S2414314616004594]

## 2-[(*E*)-(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-*N*-methylhydrazine-1-carbothioamide

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**2-[(*E*)-(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-*N*-methylhydrazine-1-carbothioamide**

*Crystal data*

$C_{12}H_{23}N_3S$
$M_r$ = 241.39
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a$ = 11.5579 (5) Å
$b$ = 9.9279 (4) Å
$c$ = 12.5271 (5) Å
$\beta$ = 95.030 (2)°
$V$ = 1431.90 (10) Å$^3$
$Z$ = 4
$F(000)$ = 528
$D_x$ = 1.120 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 80422 reflections
$\theta$ = 2.9–27.5°
$\mu$ = 0.21 mm$^{-1}$
$T$ = 123 K
Plate, colourless
0.77 × 0.30 × 0.08 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube, Nonius KappaCCD
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm$^{-1}$
CCD scans
Absorption correction: analytical (Alcock, 1970)
$T_{min}$ = 0.857, $T_{max}$ = 0.984
23116 measured reflections
6380 independent reflections
5069 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.075
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 3.1°
$h$ = −15→14
$k$ = −12→12
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.104
$S$ = 1.06
6380 reflections
297 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.1712P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.36 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 1954 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.00 (7)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.73525 (19) | 0.1924 (3) | 0.71879 (19) | 0.0293 (5) |
| C2 | 0.71388 (19) | 0.0693 (3) | 0.78399 (18) | 0.0302 (5) |
| H2A | 0.6428 | 0.0234 | 0.7526 | 0.036* |
| H2B | 0.7005 | 0.0970 | 0.8578 | 0.036* |
| C3 | 0.81593 (19) | −0.0294 (3) | 0.78822 (19) | 0.0365 (5) |
| H3 | 0.8226 | −0.0636 | 0.7139 | 0.044* |
| C4 | 0.9285 (2) | 0.0439 (3) | 0.8247 (2) | 0.0420 (7) |
| H4A | 0.9947 | −0.0193 | 0.8238 | 0.050* |
| H4B | 0.9251 | 0.0763 | 0.8991 | 0.050* |
| C5 | 0.9473 (2) | 0.1634 (3) | 0.7512 (2) | 0.0424 (7) |
| H5A | 0.9547 | 0.1297 | 0.6778 | 0.051* |
| H5B | 1.0210 | 0.2087 | 0.7763 | 0.051* |
| C6 | 0.84778 (19) | 0.2668 (3) | 0.74798 (19) | 0.0330 (5) |
| H6 | 0.8592 | 0.3319 | 0.6889 | 0.040* |
| C7 | 0.8407 (2) | 0.3491 (3) | 0.8524 (2) | 0.0451 (7) |
| H7 | 0.8211 | 0.2855 | 0.9101 | 0.054* |
| C8 | 0.7447 (3) | 0.4539 (3) | 0.8378 (2) | 0.0536 (8) |
| H8A | 0.7419 | 0.5055 | 0.9042 | 0.080* |
| H8B | 0.6700 | 0.4087 | 0.8205 | 0.080* |
| H8C | 0.7602 | 0.5149 | 0.7793 | 0.080* |
| C9 | 0.9558 (3) | 0.4164 (4) | 0.8886 (3) | 0.0687 (10) |
| H9A | 0.9843 | 0.4656 | 0.8284 | 0.103* |
| H9B | 1.0126 | 0.3476 | 0.9137 | 0.103* |
| H9C | 0.9446 | 0.4793 | 0.9471 | 0.103* |
| C10 | 0.7951 (2) | −0.1501 (3) | 0.8595 (2) | 0.0463 (7) |
| H10A | 0.8580 | −0.2155 | 0.8555 | 0.069* |
| H10B | 0.7208 | −0.1925 | 0.8351 | 0.069* |
| H10C | 0.7929 | −0.1198 | 0.9338 | 0.069* |
| C11 | 0.58527 (19) | 0.3497 (2) | 0.49598 (19) | 0.0272 (5) |
| C12 | 0.3993 (2) | 0.2741 (3) | 0.4070 (2) | 0.0376 (6) |
| H12A | 0.3523 | 0.3538 | 0.4193 | 0.056* |
| H12B | 0.3512 | 0.1931 | 0.4095 | 0.056* |
| H12C | 0.4296 | 0.2808 | 0.3366 | 0.056* |
| N1 | 0.65657 (16) | 0.2190 (2) | 0.64304 (16) | 0.0293 (5) |
| N2 | 0.66934 (17) | 0.3292 (2) | 0.57647 (17) | 0.0309 (5) |

| | | | | |
|---|---|---|---|---|
| H2 | 0.7296 | 0.3834 | 0.5863 | 0.037* |
| N3 | 0.49569 (16) | 0.2660 (2) | 0.48970 (16) | 0.0306 (5) |
| H3A | 0.4944 | 0.2019 | 0.5382 | 0.037* |
| S1 | 0.59813 (5) | 0.47563 (6) | 0.40686 (5) | 0.03005 (15) |
| C13 | 0.75271 (18) | 0.7836 (3) | 0.26402 (18) | 0.0284 (5) |
| C14 | 0.7259 (2) | 0.6502 (3) | 0.20902 (19) | 0.0322 (5) |
| H14A | 0.7458 | 0.5760 | 0.2602 | 0.039* |
| H14B | 0.7746 | 0.6403 | 0.1483 | 0.039* |
| C15 | 0.5962 (2) | 0.6393 (3) | 0.16702 (19) | 0.0333 (5) |
| H15 | 0.5489 | 0.6421 | 0.2301 | 0.040* |
| C16 | 0.5633 (2) | 0.7605 (3) | 0.0968 (2) | 0.0412 (6) |
| H16A | 0.4794 | 0.7564 | 0.0729 | 0.049* |
| H16B | 0.6070 | 0.7577 | 0.0323 | 0.049* |
| C17 | 0.5897 (2) | 0.8927 (3) | 0.1569 (2) | 0.0425 (6) |
| H17A | 0.5428 | 0.8975 | 0.2192 | 0.051* |
| H17B | 0.5670 | 0.9693 | 0.1089 | 0.051* |
| C18 | 0.7195 (2) | 0.9054 (3) | 0.1962 (2) | 0.0337 (5) |
| H18 | 0.7634 | 0.8985 | 0.1310 | 0.040* |
| C19 | 0.7520 (2) | 1.0418 (3) | 0.2477 (2) | 0.0380 (6) |
| H19 | 0.8317 | 1.0329 | 0.2850 | 0.046* |
| C20 | 0.6707 (2) | 1.0854 (3) | 0.3315 (2) | 0.0486 (7) |
| H20A | 0.5934 | 1.1043 | 0.2961 | 0.073* |
| H20B | 0.7015 | 1.1668 | 0.3681 | 0.073* |
| H20C | 0.6651 | 1.0131 | 0.3841 | 0.073* |
| C21 | 0.7570 (3) | 1.1512 (3) | 0.1618 (3) | 0.0549 (8) |
| H21A | 0.6799 | 1.1620 | 0.1234 | 0.082* |
| H21B | 0.8129 | 1.1249 | 0.1112 | 0.082* |
| H21C | 0.7813 | 1.2366 | 0.1960 | 0.082* |
| C22 | 0.5731 (2) | 0.5053 (3) | 0.1103 (2) | 0.0441 (7) |
| H22A | 0.4907 | 0.4990 | 0.0848 | 0.066* |
| H22B | 0.5936 | 0.4314 | 0.1602 | 0.066* |
| H22C | 0.6203 | 0.4992 | 0.0491 | 0.066* |
| C23 | 0.89897 (19) | 0.7001 (2) | 0.51244 (18) | 0.0264 (5) |
| C24 | 1.0523 (2) | 0.8330 (3) | 0.6096 (2) | 0.0418 (6) |
| H24A | 1.0229 | 0.8081 | 0.6779 | 0.063* |
| H24B | 1.0749 | 0.9282 | 0.6116 | 0.063* |
| H24C | 1.1200 | 0.7774 | 0.5976 | 0.063* |
| N4 | 0.80179 (16) | 0.8028 (2) | 0.35901 (16) | 0.0290 (4) |
| N5 | 0.82468 (16) | 0.6882 (2) | 0.42301 (16) | 0.0284 (4) |
| H5 | 0.7916 | 0.6106 | 0.4055 | 0.034* |
| N6 | 0.96169 (16) | 0.8114 (2) | 0.52266 (16) | 0.0326 (5) |
| H6A | 0.9481 | 0.8756 | 0.4747 | 0.039* |
| S2 | 0.90891 (5) | 0.57300 (6) | 0.60289 (5) | 0.03129 (15) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0226 (11) | 0.0391 (14) | 0.0259 (12) | −0.0002 (10) | 0.0012 (9) | 0.0003 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0238 (11) | 0.0398 (14) | 0.0267 (12) | −0.0056 (11) | −0.0003 (9) | 0.0046 (11) |
| C3 | 0.0321 (12) | 0.0480 (15) | 0.0286 (12) | 0.0019 (12) | −0.0014 (9) | 0.0066 (12) |
| C4 | 0.0287 (12) | 0.0542 (18) | 0.0420 (15) | 0.0028 (12) | −0.0027 (10) | 0.0173 (13) |
| C5 | 0.0241 (12) | 0.0587 (18) | 0.0440 (15) | −0.0019 (12) | 0.0000 (10) | 0.0178 (13) |
| C6 | 0.0253 (11) | 0.0475 (15) | 0.0251 (12) | −0.0060 (11) | −0.0038 (9) | 0.0073 (11) |
| C7 | 0.0456 (15) | 0.0631 (19) | 0.0257 (13) | −0.0186 (14) | −0.0022 (11) | 0.0035 (12) |
| C8 | 0.0587 (18) | 0.060 (2) | 0.0449 (17) | −0.0211 (16) | 0.0193 (14) | −0.0158 (14) |
| C9 | 0.064 (2) | 0.094 (3) | 0.0449 (19) | −0.034 (2) | −0.0157 (15) | −0.0006 (18) |
| C10 | 0.0439 (15) | 0.0507 (17) | 0.0425 (16) | −0.0014 (13) | −0.0061 (12) | 0.0131 (13) |
| C11 | 0.0218 (11) | 0.0333 (14) | 0.0264 (13) | 0.0006 (10) | 0.0023 (9) | −0.0010 (10) |
| C12 | 0.0234 (11) | 0.0545 (16) | 0.0332 (13) | −0.0072 (12) | −0.0067 (10) | 0.0055 (12) |
| N1 | 0.0257 (10) | 0.0340 (11) | 0.0276 (11) | −0.0025 (8) | −0.0012 (8) | 0.0034 (9) |
| N2 | 0.0253 (10) | 0.0367 (11) | 0.0296 (11) | −0.0056 (9) | −0.0042 (8) | 0.0044 (9) |
| N3 | 0.0228 (9) | 0.0401 (12) | 0.0280 (10) | −0.0045 (9) | −0.0028 (7) | 0.0062 (9) |
| S1 | 0.0250 (3) | 0.0327 (3) | 0.0315 (3) | −0.0010 (3) | −0.0026 (2) | 0.0036 (3) |
| C13 | 0.0190 (10) | 0.0412 (14) | 0.0249 (12) | 0.0031 (10) | 0.0016 (9) | 0.0014 (11) |
| C14 | 0.0268 (12) | 0.0423 (14) | 0.0275 (12) | 0.0002 (11) | 0.0021 (9) | −0.0057 (11) |
| C15 | 0.0255 (12) | 0.0468 (15) | 0.0273 (13) | −0.0028 (11) | 0.0002 (9) | −0.0012 (11) |
| C16 | 0.0312 (12) | 0.0596 (18) | 0.0309 (13) | −0.0061 (13) | −0.0078 (10) | 0.0042 (13) |
| C17 | 0.0320 (13) | 0.0521 (17) | 0.0407 (15) | −0.0039 (12) | −0.0116 (11) | 0.0084 (13) |
| C18 | 0.0292 (12) | 0.0405 (14) | 0.0310 (13) | 0.0028 (11) | −0.0004 (10) | 0.0033 (11) |
| C19 | 0.0314 (12) | 0.0396 (16) | 0.0416 (15) | 0.0002 (11) | −0.0048 (11) | 0.0042 (12) |
| C20 | 0.0408 (14) | 0.0474 (16) | 0.0566 (18) | 0.0070 (13) | −0.0018 (13) | −0.0115 (14) |
| C21 | 0.0588 (18) | 0.0495 (18) | 0.0535 (19) | −0.0042 (15) | −0.0122 (14) | 0.0127 (15) |
| C22 | 0.0342 (13) | 0.0651 (19) | 0.0330 (14) | −0.0115 (13) | 0.0023 (11) | −0.0111 (13) |
| C23 | 0.0221 (11) | 0.0331 (13) | 0.0239 (12) | 0.0025 (10) | 0.0011 (9) | −0.0002 (10) |
| C24 | 0.0366 (14) | 0.0486 (16) | 0.0377 (15) | −0.0136 (12) | −0.0115 (11) | 0.0039 (12) |
| N4 | 0.0238 (9) | 0.0333 (11) | 0.0295 (11) | 0.0037 (8) | 0.0005 (8) | 0.0013 (9) |
| N5 | 0.0252 (10) | 0.0320 (11) | 0.0270 (10) | −0.0022 (8) | −0.0026 (8) | 0.0016 (8) |
| N6 | 0.0321 (11) | 0.0357 (12) | 0.0283 (11) | −0.0025 (9) | −0.0065 (8) | 0.0040 (9) |
| S2 | 0.0281 (3) | 0.0348 (4) | 0.0302 (3) | −0.0015 (3) | −0.0020 (2) | 0.0035 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N1 | 1.283 (3) | C13—N4 | 1.287 (3) |
| C1—C2 | 1.502 (3) | C13—C18 | 1.508 (4) |
| C1—C6 | 1.513 (3) | C13—C14 | 1.512 (4) |
| C2—C3 | 1.531 (4) | C14—C15 | 1.549 (3) |
| C2—H2A | 0.9900 | C14—H14A | 0.9900 |
| C2—H2B | 0.9900 | C14—H14B | 0.9900 |
| C3—C4 | 1.525 (4) | C15—C16 | 1.519 (4) |
| C3—C10 | 1.526 (4) | C15—C22 | 1.520 (4) |
| C3—H3 | 1.0000 | C15—H15 | 1.0000 |
| C4—C5 | 1.529 (4) | C16—C17 | 1.531 (4) |
| C4—H4A | 0.9900 | C16—H16A | 0.9900 |
| C4—H4B | 0.9900 | C16—H16B | 0.9900 |
| C5—C6 | 1.539 (4) | C17—C18 | 1.543 (3) |
| C5—H5A | 0.9900 | C17—H17A | 0.9900 |

| | | | |
|---|---|---|---|
| C5—H5B | 0.9900 | C17—H17B | 0.9900 |
| C6—C7 | 1.550 (4) | C18—C19 | 1.532 (4) |
| C6—H6 | 1.0000 | C18—H18 | 1.0000 |
| C7—C8 | 1.521 (4) | C19—C20 | 1.532 (4) |
| C7—C9 | 1.522 (4) | C19—C21 | 1.533 (4) |
| C7—H7 | 1.0000 | C19—H19 | 1.0000 |
| C8—H8A | 0.9800 | C20—H20A | 0.9800 |
| C8—H8B | 0.9800 | C20—H20B | 0.9800 |
| C8—H8C | 0.9800 | C20—H20C | 0.9800 |
| C9—H9A | 0.9800 | C21—H21A | 0.9800 |
| C9—H9B | 0.9800 | C21—H21B | 0.9800 |
| C9—H9C | 0.9800 | C21—H21C | 0.9800 |
| C10—H10A | 0.9800 | C22—H22A | 0.9800 |
| C10—H10B | 0.9800 | C22—H22B | 0.9800 |
| C10—H10C | 0.9800 | C22—H22C | 0.9800 |
| C11—N3 | 1.325 (3) | C23—N6 | 1.322 (3) |
| C11—N2 | 1.353 (3) | C23—N5 | 1.356 (3) |
| C11—S1 | 1.691 (2) | C23—S2 | 1.693 (2) |
| C12—N3 | 1.455 (3) | C24—N6 | 1.459 (3) |
| C12—H12A | 0.9800 | C24—H24A | 0.9800 |
| C12—H12B | 0.9800 | C24—H24B | 0.9800 |
| C12—H12C | 0.9800 | C24—H24C | 0.9800 |
| N1—N2 | 1.392 (3) | N4—N5 | 1.403 (3) |
| N2—H2 | 0.8800 | N5—H5 | 0.8800 |
| N3—H3A | 0.8800 | N6—H6A | 0.8800 |

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| N1—C1—C2 | 115.5 (2) | N4—C13—C18 | 118.2 (2) |
| N1—C1—C6 | 128.1 (2) | N4—C13—C14 | 127.4 (2) |
| C2—C1—C6 | 116.4 (2) | C18—C13—C14 | 114.43 (19) |
| C1—C2—C3 | 112.13 (19) | C13—C14—C15 | 111.7 (2) |
| C1—C2—H2A | 109.2 | C13—C14—H14A | 109.3 |
| C3—C2—H2A | 109.2 | C15—C14—H14A | 109.3 |
| C1—C2—H2B | 109.2 | C13—C14—H14B | 109.3 |
| C3—C2—H2B | 109.2 | C15—C14—H14B | 109.3 |
| H2A—C2—H2B | 107.9 | H14A—C14—H14B | 107.9 |
| C4—C3—C10 | 111.9 (2) | C16—C15—C22 | 113.4 (2) |
| C4—C3—C2 | 109.8 (2) | C16—C15—C14 | 109.1 (2) |
| C10—C3—C2 | 111.2 (2) | C22—C15—C14 | 110.2 (2) |
| C4—C3—H3 | 107.9 | C16—C15—H15 | 108.0 |
| C10—C3—H3 | 107.9 | C22—C15—H15 | 108.0 |
| C2—C3—H3 | 107.9 | C14—C15—H15 | 108.0 |
| C3—C4—C5 | 110.6 (2) | C15—C16—C17 | 111.4 (2) |
| C3—C4—H4A | 109.5 | C15—C16—H16A | 109.3 |
| C5—C4—H4A | 109.5 | C17—C16—H16A | 109.3 |
| C3—C4—H4B | 109.5 | C15—C16—H16B | 109.3 |
| C5—C4—H4B | 109.5 | C17—C16—H16B | 109.3 |
| H4A—C4—H4B | 108.1 | H16A—C16—H16B | 108.0 |
| C4—C5—C6 | 112.8 (2) | C16—C17—C18 | 111.9 (2) |

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|---|---|---|---|
| C4—C5—H5A | 109.0 | C16—C17—H17A | 109.2 |
| C6—C5—H5A | 109.0 | C18—C17—H17A | 109.2 |
| C4—C5—H5B | 109.0 | C16—C17—H17B | 109.2 |
| C6—C5—H5B | 109.0 | C18—C17—H17B | 109.2 |
| H5A—C5—H5B | 107.8 | H17A—C17—H17B | 107.9 |
| C1—C6—C5 | 107.8 (2) | C13—C18—C19 | 115.48 (19) |
| C1—C6—C7 | 110.70 (19) | C13—C18—C17 | 107.8 (2) |
| C5—C6—C7 | 115.1 (2) | C19—C18—C17 | 113.7 (2) |
| C1—C6—H6 | 107.7 | C13—C18—H18 | 106.4 |
| C5—C6—H6 | 107.7 | C19—C18—H18 | 106.4 |
| C7—C6—H6 | 107.7 | C17—C18—H18 | 106.4 |
| C8—C7—C9 | 110.2 (3) | C20—C19—C18 | 113.4 (2) |
| C8—C7—C6 | 110.5 (2) | C20—C19—C21 | 110.1 (2) |
| C9—C7—C6 | 111.9 (2) | C18—C19—C21 | 110.7 (2) |
| C8—C7—H7 | 108.0 | C20—C19—H19 | 107.5 |
| C9—C7—H7 | 108.0 | C18—C19—H19 | 107.5 |
| C6—C7—H7 | 108.0 | C21—C19—H19 | 107.5 |
| C7—C8—H8A | 109.5 | C19—C20—H20A | 109.5 |
| C7—C8—H8B | 109.5 | C19—C20—H20B | 109.5 |
| H8A—C8—H8B | 109.5 | H20A—C20—H20B | 109.5 |
| C7—C8—H8C | 109.5 | C19—C20—H20C | 109.5 |
| H8A—C8—H8C | 109.5 | H20A—C20—H20C | 109.5 |
| H8B—C8—H8C | 109.5 | H20B—C20—H20C | 109.5 |
| C7—C9—H9A | 109.5 | C19—C21—H21A | 109.5 |
| C7—C9—H9B | 109.5 | C19—C21—H21B | 109.5 |
| H9A—C9—H9B | 109.5 | H21A—C21—H21B | 109.5 |
| C7—C9—H9C | 109.5 | C19—C21—H21C | 109.5 |
| H9A—C9—H9C | 109.5 | H21A—C21—H21C | 109.5 |
| H9B—C9—H9C | 109.5 | H21B—C21—H21C | 109.5 |
| C3—C10—H10A | 109.5 | C15—C22—H22A | 109.5 |
| C3—C10—H10B | 109.5 | C15—C22—H22B | 109.5 |
| H10A—C10—H10B | 109.5 | H22A—C22—H22B | 109.5 |
| C3—C10—H10C | 109.5 | C15—C22—H22C | 109.5 |
| H10A—C10—H10C | 109.5 | H22A—C22—H22C | 109.5 |
| H10B—C10—H10C | 109.5 | H22B—C22—H22C | 109.5 |
| N3—C11—N2 | 117.1 (2) | N6—C23—N5 | 117.0 (2) |
| N3—C11—S1 | 122.56 (18) | N6—C23—S2 | 123.64 (17) |
| N2—C11—S1 | 120.29 (18) | N5—C23—S2 | 119.31 (18) |
| N3—C12—H12A | 109.5 | N6—C24—H24A | 109.5 |
| N3—C12—H12B | 109.5 | N6—C24—H24B | 109.5 |
| H12A—C12—H12B | 109.5 | H24A—C24—H24B | 109.5 |
| N3—C12—H12C | 109.5 | N6—C24—H24C | 109.5 |
| H12A—C12—H12C | 109.5 | H24A—C24—H24C | 109.5 |
| H12B—C12—H12C | 109.5 | H24B—C24—H24C | 109.5 |
| C1—N1—N2 | 119.97 (19) | C13—N4—N5 | 117.0 (2) |
| C11—N2—N1 | 117.26 (19) | C23—N5—N4 | 118.4 (2) |
| C11—N2—H2 | 121.4 | C23—N5—H5 | 120.8 |
| N1—N2—H2 | 121.4 | N4—N5—H5 | 120.8 |

| | | | |
|---|---|---|---|
| C11—N3—C12 | 123.6 (2) | C23—N6—C24 | 123.2 (2) |
| C11—N3—H3A | 118.2 | C23—N6—H6A | 118.4 |
| C12—N3—H3A | 118.2 | C24—N6—H6A | 118.4 |
| | | | |
| N1—C1—C2—C3 | 125.8 (2) | N4—C13—C14—C15 | 126.1 (2) |
| C6—C1—C2—C3 | −52.4 (3) | C18—C13—C14—C15 | −55.5 (3) |
| C1—C2—C3—C4 | 52.6 (3) | C13—C14—C15—C16 | 53.7 (3) |
| C1—C2—C3—C10 | 177.1 (2) | C13—C14—C15—C22 | 178.8 (2) |
| C10—C3—C4—C5 | 179.6 (2) | C22—C15—C16—C17 | −179.2 (2) |
| C2—C3—C4—C5 | −56.4 (3) | C14—C15—C16—C17 | −56.0 (3) |
| C3—C4—C5—C6 | 59.1 (3) | C15—C16—C17—C18 | 59.1 (3) |
| N1—C1—C6—C5 | −126.7 (3) | N4—C13—C18—C19 | 1.8 (3) |
| C2—C1—C6—C5 | 51.2 (3) | C14—C13—C18—C19 | −176.7 (2) |
| N1—C1—C6—C7 | 106.7 (3) | N4—C13—C18—C17 | −126.6 (2) |
| C2—C1—C6—C7 | −75.4 (3) | C14—C13—C18—C17 | 54.9 (3) |
| C4—C5—C6—C1 | −53.9 (3) | C16—C17—C18—C13 | −55.9 (3) |
| C4—C5—C6—C7 | 70.1 (3) | C16—C17—C18—C19 | 174.7 (2) |
| C1—C6—C7—C8 | −61.2 (3) | C13—C18—C19—C20 | −76.8 (3) |
| C5—C6—C7—C8 | 176.3 (2) | C17—C18—C19—C20 | 48.6 (3) |
| C1—C6—C7—C9 | 175.6 (2) | C13—C18—C19—C21 | 158.9 (2) |
| C5—C6—C7—C9 | 53.1 (3) | C17—C18—C19—C21 | −75.6 (3) |
| C2—C1—N1—N2 | −178.62 (19) | C18—C13—N4—N5 | 175.85 (18) |
| C6—C1—N1—N2 | −0.7 (4) | C14—C13—N4—N5 | −5.9 (3) |
| N3—C11—N2—N1 | 2.4 (3) | N6—C23—N5—N4 | −12.5 (3) |
| S1—C11—N2—N1 | −176.24 (16) | S2—C23—N5—N4 | 168.60 (15) |
| C1—N1—N2—C11 | 178.0 (2) | C13—N4—N5—C23 | 165.0 (2) |
| N2—C11—N3—C12 | −179.2 (2) | N5—C23—N6—C24 | −174.4 (2) |
| S1—C11—N3—C12 | −0.6 (3) | S2—C23—N6—C24 | 4.4 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···S2 | 0.88 | 2.79 | 3.671 (2) | 174 |
| N3—H3*A*···S1$^{i}$ | 0.88 | 2.61 | 3.378 (2) | 147 |
| N5—H5···S1 | 0.88 | 2.61 | 3.356 (2) | 143 |
| N6—H6*A*···S2$^{ii}$ | 0.88 | 2.79 | 3.445 (2) | 132 |

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