Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-Methyl-2-(1-methyl-3-phenylprop-2-en-1-ylidene)hydrazinecarbothioamide

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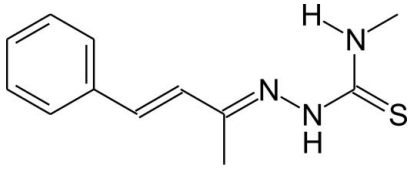
Received 30 May 2014; accepted 13 June 2014

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.080; data-to-parameter ratio = 13.6.

In the title compound, $C_{12}H_{15}N_3S$, the molecule deviates slightly from planarity, with a maximum deviation from the mean plane of the non-H atoms of 0.2756 (6) Å for the S atom and a torsion angle for the N—N—C—N fragment of −7.04 (16)°. In the crystal, molecules are linked by N—H···S hydrogen-bond interactions, forming centrosymmetric dimers. Additionally, one weak intramolecular N—H···N hydrogen-bond interaction is observed. The crystal packing shows a herringbone arrangement viewed along the *c* axis.

Related literature

For one of the first reports of the synthesis of thiosemicarbazone derivatives, see: Freund & Schander (1902). For a report of the antifungal activity of the title compound, see: Nishimura *et al.* (1979).



Experimental

Crystal data

$C_{12}H_{15}N_3S$ M_r = 233.33
Orthorhombic, *Pbca*
a = 10.5832 (2) Å
b = 7.9509 (2) Å
c = 28.9259 (5) Å
V = 2434.00 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 123 K
0.44 × 0.31 × 0.27 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.904, T_{max} = 0.955
26770 measured reflections
2783 independent reflections
2414 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.080
S = 1.05
2783 reflections
205 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H*N3*···N1	0.879 (17)	2.143 (16)	2.5877 (15)	110.7 (13)
N2—H*N2*···S1^{i}	0.862 (18)	2.663 (18)	3.4296 (12)	148.7 (15)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; 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 German Research Foundation (DFG) through the Collaborative Research Center SFB 813, Chemistry at Spin Centers and by FAPITEC/SE/FUNTEC/CNPq through the PPP Program 04/2011. FVR acknowledges FAPESP for the Post-Doctoral scholarship, Proc. No. 2013/20156–5.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BX2460).

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supporting information

Acta Cryst. (2014). E**70**, o800 [doi:10.1107/S1600536814013889]

N-Methyl-2-(1-methyl-3-phenylprop-2-en-1-ylidene)hydrazinecarbothioamide

Fillipe Vieira Rocha, Adelino Vieira de Godoy Netto, Johannes Beck, Jörg Daniels and Adriano Bof de Oliveira

1. Comment

Thiosemicarbazone derivatives have a wide range of biological properties. For example, some thiosemicarbazones similar to the title compound show antifungal activity (Nishimura *et al.*, 1979). As part of our study on synthesis and structural chemistry of thiosemicarbazone derivatives from natural products, we report herein the crystal structure of a derivative of the essential oil of cinnamon bark (benzylideneacetone, a methyl derivative of the cinnamaldehyde).

In the crystal structure of the title compound the central N–N–C–N unit is not planar with an torsion angle along N1–N2–C10–N3 of -7.04 (16)° and the maximum deviation from the mean plane of the non-H atoms amounting to 0.2756 (6) Å for S1. The molecule, shows a *trans* conformation at the C7—C8 and N1—N2 bonds (Fig. 1).

In the crystal the molecules are linked by N—H···S hydrogen bonds interactions forming centrosymmetric dimers. Additionally, one weak N—H···N intramolecular H-interaction is observed.The crystal packing shows a herringbone arrangement viewed along the *c*-axis.(Fig. 3).

2. Experimental

Starting materials were commercially available and were used without further purification. The title compound synthesis was adapted to a procedure reported previously (Freund & Schander, 1902). The hydrochloric acid catalyzed reaction, a mixture of benzylideneacetone (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. Crystals suitable for X-ray diffraction were obtained in ethanol by the slow evaporation of solvent.

3. Refinement

All hydrogen atoms were localized in a difference density Fourier map. Their positions and isotropic displacement parameters were refined.

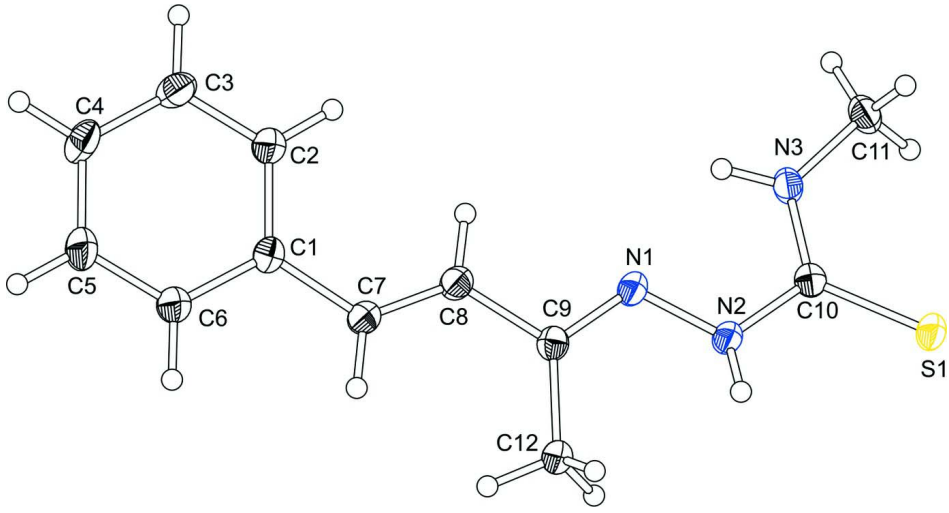

Figure 1

The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level.

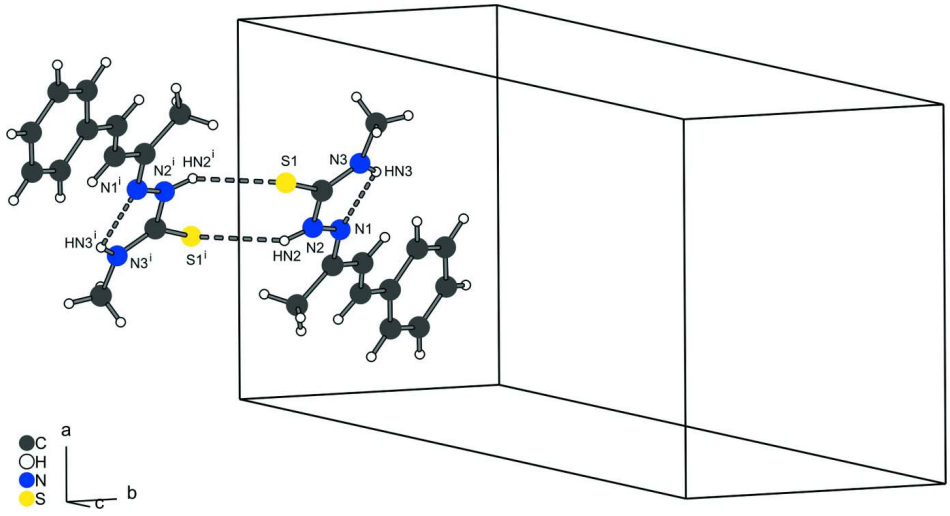

Figure 2

Part of the crystal structure of the title compound showing the inter- and intramolecular hydrogen bonding as dashed lines. Symmetry code: (i) -*x* + 1, -*y*, -*z*.

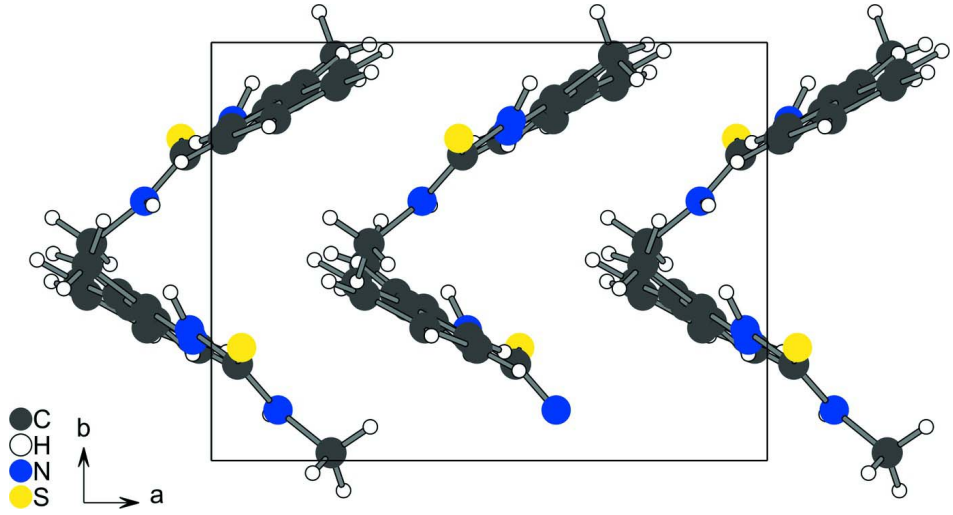

Figure 3

Crystal structure of the title compound viewed along the *c*-axis. The herringbone pattern of the crystal packing along the *a*-axis is observed.

N-Methyl-2-(1-methyl-3-phenylprop-2-en-1-ylidene)hydrazinecarbothioamide

Crystal data

$C_{12}H_{15}N_3S$
$M_r = 233.33$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 10.5832\ (2)$ Å
$b = 7.9509\ (2)$ Å
$c = 28.9259\ (5)$ Å
$V = 2434.00\ (9)$ Å^3
$Z = 8$
$F(000) = 992$
$D_x = 1.273$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 31577 reflections
$\theta = 2.9–27.5°$
$\mu = 0.24$ mm^{-1}
$T = 123$ K
Fragment, yellow
0.44 × 0.31 × 0.27 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube, Nonius KappaCCD
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images, thick slices scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.904$, $T_{max} = 0.955$
26770 measured reflections
2783 independent reflections
2414 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
$h = -13\rightarrow13$
$k = -10\rightarrow10$
$l = -37\rightarrow37$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.05$
2783 reflections
205 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
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 1.1303P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.55474 (3)	0.22917 (4)	−0.026590 (10)	0.02121 (10)
N1	0.46643 (10)	0.21163 (13)	0.10454 (3)	0.0194 (2)
N2	0.46052 (10)	0.18678 (14)	0.05748 (4)	0.0197 (2)
N3	0.62048 (10)	0.37903 (13)	0.05248 (4)	0.0209 (2)
C1	0.35320 (12)	0.12835 (15)	0.26361 (4)	0.0198 (3)
C2	0.46266 (13)	0.20581 (18)	0.28079 (5)	0.0238 (3)
C3	0.47782 (14)	0.23114 (18)	0.32807 (5)	0.0265 (3)
C4	0.38429 (14)	0.18207 (18)	0.35891 (5)	0.0283 (3)
C5	0.27620 (14)	0.10384 (19)	0.34236 (5)	0.0292 (3)
C6	0.26153 (13)	0.07566 (18)	0.29525 (4)	0.0248 (3)
C7	0.33153 (12)	0.10103 (16)	0.21392 (4)	0.0203 (3)
C8	0.39960 (12)	0.16857 (16)	0.17955 (4)	0.0203 (3)
C9	0.38228 (11)	0.13760 (15)	0.13014 (4)	0.0183 (2)
C10	0.54759 (11)	0.26906 (15)	0.03065 (4)	0.0174 (2)
C11	0.71582 (13)	0.48111 (18)	0.02979 (5)	0.0252 (3)
C12	0.27638 (12)	0.03234 (18)	0.11160 (4)	0.0213 (3)
HN2	0.4267 (16)	0.097 (2)	0.0461 (6)	0.035 (5)*
HN3	0.6058 (15)	0.390 (2)	0.0823 (6)	0.031 (4)*
H2	0.5277 (16)	0.240 (2)	0.2603 (6)	0.034 (4)*
H3	0.5538 (15)	0.286 (2)	0.3389 (6)	0.033 (4)*
H4	0.3962 (15)	0.201 (2)	0.3915 (6)	0.032 (4)*
H5	0.2119 (16)	0.071 (2)	0.3634 (6)	0.040 (5)*
H6	0.1862 (15)	0.020 (2)	0.2843 (5)	0.034 (4)*
H7	0.2640 (15)	0.026 (2)	0.2072 (5)	0.026 (4)*
H8	0.4663 (14)	0.245 (2)	0.1856 (6)	0.026 (4)*
H11A	0.6826 (18)	0.530 (3)	0.0021 (7)	0.059 (6)*
H11B	0.7862 (19)	0.419 (3)	0.0221 (7)	0.052 (6)*
H11C	0.738 (2)	0.572 (3)	0.0489 (7)	0.061 (6)*
H12A	0.2344 (17)	0.088 (2)	0.0863 (6)	0.038 (5)*
H12B	0.3056 (16)	−0.073 (2)	0.0991 (6)	0.036 (5)*
H12C	0.2155 (15)	0.005 (2)	0.1358 (6)	0.033 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02483 (17)	0.02489 (17)	0.01390 (16)	−0.00102 (12)	0.00080 (11)	0.00161 (11)
N1	0.0220 (5)	0.0225 (5)	0.0138 (5)	−0.0007 (4)	−0.0006 (4)	0.0000 (4)
N2	0.0226 (5)	0.0224 (5)	0.0140 (5)	−0.0047 (4)	−0.0002 (4)	0.0002 (4)
N3	0.0236 (5)	0.0208 (5)	0.0183 (5)	−0.0042 (4)	0.0058 (4)	−0.0026 (4)
C1	0.0228 (6)	0.0204 (6)	0.0163 (6)	0.0009 (5)	0.0004 (5)	0.0005 (5)
C2	0.0241 (6)	0.0282 (7)	0.0191 (6)	−0.0035 (5)	0.0001 (5)	0.0012 (5)
C3	0.0304 (7)	0.0275 (7)	0.0217 (7)	−0.0049 (6)	−0.0065 (5)	0.0002 (5)
C4	0.0407 (8)	0.0288 (7)	0.0154 (6)	−0.0017 (6)	−0.0031 (5)	0.0007 (5)
C5	0.0336 (8)	0.0356 (8)	0.0185 (6)	−0.0045 (6)	0.0046 (5)	0.0030 (6)
C6	0.0253 (6)	0.0292 (7)	0.0201 (6)	−0.0052 (5)	0.0005 (5)	0.0011 (5)
C7	0.0214 (6)	0.0216 (6)	0.0179 (6)	−0.0013 (5)	−0.0012 (5)	−0.0014 (5)
C8	0.0217 (6)	0.0212 (6)	0.0180 (6)	−0.0009 (5)	−0.0009 (5)	−0.0013 (5)
C9	0.0197 (6)	0.0183 (6)	0.0170 (6)	0.0019 (5)	0.0002 (4)	0.0010 (5)
C10	0.0168 (5)	0.0176 (5)	0.0177 (6)	0.0035 (4)	0.0001 (4)	0.0019 (4)
C11	0.0245 (6)	0.0258 (7)	0.0252 (7)	−0.0062 (5)	0.0086 (5)	−0.0030 (6)
C12	0.0212 (6)	0.0267 (7)	0.0161 (6)	−0.0029 (5)	0.0004 (5)	0.0000 (5)

Geometric parameters (Å, º)

S1—C10	1.6875 (12)	C4—H4	0.964 (17)
N1—C9	1.2994 (16)	C5—C6	1.3896 (19)
N1—N2	1.3769 (14)	C5—H5	0.950 (18)
N2—C10	1.3708 (15)	C6—H6	0.967 (17)
N2—HN2	0.862 (18)	C7—C8	1.3402 (18)
N3—C10	1.3261 (16)	C7—H7	0.950 (16)
N3—C11	1.4518 (16)	C8—C9	1.4616 (16)
N3—HN3	0.879 (17)	C8—H8	0.948 (16)
C1—C6	1.3980 (18)	C9—C12	1.4981 (17)
C1—C2	1.4029 (18)	C11—H11A	0.96 (2)
C1—C7	1.4716 (17)	C11—H11B	0.92 (2)
C2—C3	1.3917 (18)	C11—H11C	0.94 (2)
C2—H2	0.949 (18)	C12—H12A	0.965 (18)
C3—C4	1.388 (2)	C12—H12B	0.964 (18)
C3—H3	0.965 (17)	C12—H12C	0.977 (17)
C4—C5	1.387 (2)		
C9—N1—N2	117.87 (10)	C8—C7—C1	125.58 (12)
C10—N2—N1	117.43 (10)	C8—C7—H7	120.2 (9)
C10—N2—HN2	117.2 (11)	C1—C7—H7	114.3 (9)
N1—N2—HN2	121.0 (11)	C7—C8—C9	126.19 (12)
C10—N3—C11	123.89 (11)	C7—C8—H8	121.4 (10)
C10—N3—HN3	115.2 (11)	C9—C8—H8	112.4 (10)
C11—N3—HN3	120.8 (11)	N1—C9—C8	113.27 (11)
C6—C1—C2	118.21 (12)	N1—C9—C12	124.17 (11)
C6—C1—C7	119.15 (11)	C8—C9—C12	122.55 (11)

C2—C1—C7	122.64 (11)	N3—C10—N2	115.86 (11)
C3—C2—C1	120.46 (12)	N3—C10—S1	124.41 (9)
C3—C2—H2	119.3 (10)	N2—C10—S1	119.73 (9)
C1—C2—H2	120.3 (10)	N3—C11—H11A	110.6 (12)
C4—C3—C2	120.56 (13)	N3—C11—H11B	111.8 (13)
C4—C3—H3	120.8 (10)	H11A—C11—H11B	108.3 (17)
C2—C3—H3	118.7 (10)	N3—C11—H11C	109.8 (13)
C5—C4—C3	119.49 (12)	H11A—C11—H11C	105.7 (18)
C5—C4—H4	121.0 (10)	H11B—C11—H11C	110.4 (18)
C3—C4—H4	119.5 (10)	C9—C12—H12A	111.0 (10)
C4—C5—C6	120.18 (13)	C9—C12—H12B	112.4 (10)
C4—C5—H5	119.6 (11)	H12A—C12—H12B	105.3 (14)
C6—C5—H5	120.2 (11)	C9—C12—H12C	111.2 (10)
C5—C6—C1	121.07 (13)	H12A—C12—H12C	110.1 (14)
C5—C6—H6	119.2 (10)	H12B—C12—H12C	106.6 (14)
C1—C6—H6	119.7 (10)		

N1—N1—N2—C10	0.00 (9)	N2—N1—C9—N1	0 (100)
C9—N1—N2—C10	178.27 (11)	N1—N1—C9—C8	0.00 (7)
C9—N1—N2—N1	0 (100)	N2—N1—C9—C8	178.31 (10)
C6—C1—C2—C3	−0.9 (2)	N1—N1—C9—C12	0.000 (19)
C7—C1—C2—C3	178.99 (13)	N2—N1—C9—C12	−2.44 (18)
C1—C2—C3—C4	−0.8 (2)	C7—C8—C9—N1	−176.06 (12)
C2—C3—C4—C5	1.4 (2)	C7—C8—C9—N1	−176.06 (12)
C3—C4—C5—C6	−0.3 (2)	C7—C8—C9—C12	4.7 (2)
C4—C5—C6—C1	−1.4 (2)	C11—N3—C10—N2	−178.42 (12)
C2—C1—C6—C5	2.0 (2)	C11—N3—C10—S1	0.53 (18)
C7—C1—C6—C5	−177.89 (13)	N1—N2—C10—N3	−7.04 (16)
C6—C1—C7—C8	168.26 (13)	N1—N2—C10—N3	−7.04 (16)
C2—C1—C7—C8	−11.7 (2)	N1—N2—C10—S1	173.96 (9)
C1—C7—C8—C9	177.50 (12)	N1—N2—C10—S1	173.96 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H*N*3···N1	0.879 (17)	2.143 (16)	2.5877 (15)	110.7 (13)
N2—H*N*2···S1^{i}	0.862 (18)	2.663 (18)	3.4296 (12)	148.7 (15)

Symmetry code: (i) −*x*+1, −*y*, −*z*.