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A second crystalline modification of 2-{3-methyl-2-[(2Z)-pent-2-en-1-yl]cyclopent-2-en-1-ylidene}-hydrazinecarbothioamide

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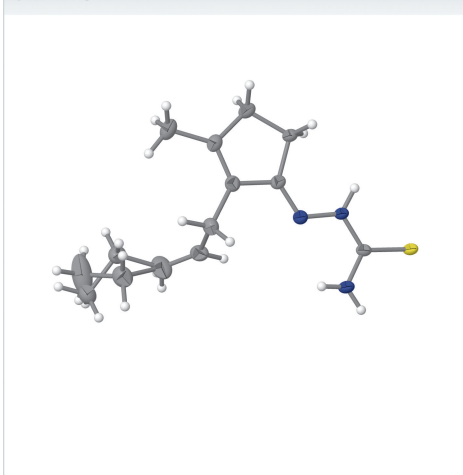
CCDC reference: 2310189

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

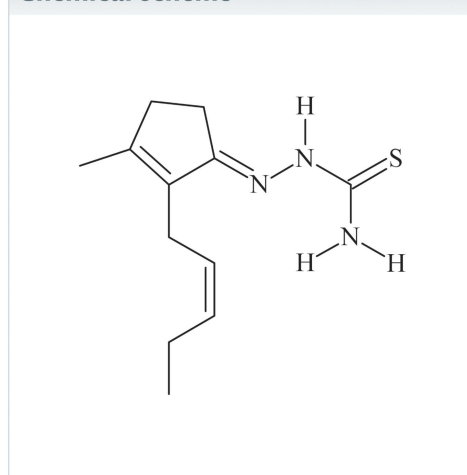
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A second crystalline modification of the title compound, C₁₂H₁₉N₃S [common name: *cis*-jasmone thiosemicarbazone] was crystallized from tetrahydrofuran at room temperature. There is one crystallographic independent molecule in the asymmetric unit, showing disorder in the *cis*-jasmone chain [site-occupancy ratio = 0.590 (14):0.410 (14)]. The thiosemicarbazone entity is approximately planar, with the maximum deviation from the mean plane through the N/N/C/S/N atoms being 0.0463 (14) Å [r.m.s.d. = 0.0324 Å], while for the five-membered ring of the jasmone fragment, the maximum deviation from the mean plane through the carbon atoms amounts to 0.0465 (15) Å [r.m.s.d. = 0.0338 Å]. The molecule is not planar due to the dihedral angle between these two fragments, which is 8.93 (1)°, and due to the *sp*³-hybridized carbon atoms in the jasmone fragment chain. In the crystal, the molecules are connected by N—H···S and C—H···S interactions, with graph-set motifs *R*₂²(8) and *R*₂¹(7), building mono-periodic hydrogen-bonded ribbons along [010]. A Hirshfeld surface analysis indicates that the major contributions for the crystal cohesion are H···H (67.8%), H···S/S···H (15.0%), H···C/C···H (8.5%) and H···N/N···H (5.6%) [only non-disordered atoms and those with the highest s.o.f. were considered]. This work reports the second crystalline modification of the *cis*-jasmone thiosemicarbazone structure, the first one being published recently [Orsoni *et al.* (2020). *Int. J. Mol. Sci.* **21**, 8681–8697] with the crystals obtained in ethanol at 273 K.

3D view



Chemical scheme



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Structure description

The first references to the synthesis of thiosemicarbazone derivatives [$R_1R_2N-N(H)-C(=S)-NR_3R_4$] can be traced back to the beginning of the 1900s (Freund & Schander, 1902) and since the report of Domagk *et al.* (1946) on the tuberculostatic effect of some compounds with this functional group, the biological activity of these molecules has been intensively studied, being one of the major approaches for this chemistry (for some examples, see: Acharya *et al.*, 2021; Bajaj *et al.*, 2021; Kanso *et al.*, 2021; Siqueira *et al.*, 2019). Concerning the *cis*-jasmine thiosemicarbazone, it has been pointed out that this compound has antifungal activity (Orsoni *et al.*, 2020; Jamiołkowska *et al.*, 2022). As part of our studies on the thiosemicarbazone derivatives of natural products, the crystal structure and the Hirshfeld analysis of a new crystalline modification of the *cis*-jasmine thiosemicarbazone is reported herein.

The first crystalline modification of *cis*-jasmine thiosemicarbazone (Orsoni *et al.*, 2020) [triclinic, $P\bar{1}$, $a = 8.164$ (5), $b = 15.645$ (9), $c = 16.434$ (9) Å, $\alpha = 84.723$ (1), $\beta = 82.036$ (1), $\gamma = 84.632$ (1)°] will be designated from now on as the α -modification and α -JATSC. α -JATSC(A), α -JATSC(B) and α -JATSC(C) abbreviations will be used for the three crystallographically independent molecules in the asymmetric unit of the structure. The present work reports the second crystalline modification of the molecule, which will be designated from now on as the β -modification, or β -JATSC.

For the title compound, the β -crystalline modification of the *cis*-jasmine thiosemicarbazone, there is one molecule with all atoms in general positions in the asymmetric unit, which shows disorder in the *cis*-jasmine chain [s.o.f. = 0.590 (14): 0.410 (14)]. The atoms with the higher s.o.f. are *A*-labelled and

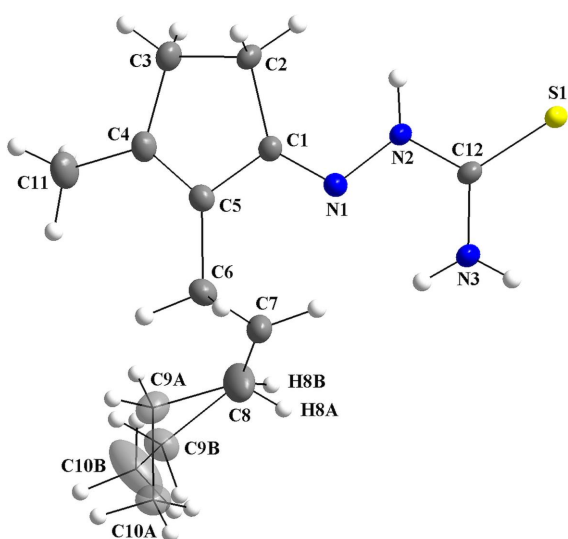


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 40% probability level. Disordered atoms are drawn with 30% transparency and labelled H8A, C9A and C10A [s.o.f. = 0.590 (14)] and H8B, C9B and C10B [s.o.f. = 0.410 (14)]. All H atoms are drawn in ball and stick mode.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H1\cdots S1^i$	0.90 (3)	2.53 (3)	3.4142 (19)	166 (2)
$N3-H3\cdots S1^{ii}$	0.85 (3)	2.48 (3)	3.325 (2)	173 (3)
$C2-H2B\cdots S1^i$	1.00 (2)	2.93 (2)	3.436 (2)	112.2 (16)

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

those with the lower, *B*-labelled (Fig. 1). The thiosemicarbazone (**TSC**) entity is approximately planar, with the maximum deviation from the mean plane through the N1/N2/C12/S1/N3 atoms being 0.0463 (14) Å for N2 (r.m.s.d. = 0.0324 Å). The **TSC** entity is attached to the C1–C5 five-membered ring of the jasmine fragment, which is also almost planar, with the maximum deviation from the mean plane through the C atoms being 0.0465 (15) Å for C2 (r.m.s.d. = 0.0338 Å). The molecule is not planar due the dihedral angle between these two entities, 8.93 (1)°, and due to the sp^3 -hybridized carbon atoms in the jasmine fragment. In addition, the torsion angles for the N1/N2/C12/S1 and N1/N2/C12/N3 chains are 174.04 (15) and -4.8 (3)°, respectively.

In the crystal, the molecules are connected by pairs of $N-H\cdots S$ interactions, forming rings with $R_2^2(8)$ graph-set motif, and by pairs of $N-H\cdots S/C-H\cdots S$ interactions, where rings of graph-set motif $R_1^2(7)$ are observed (Fig. 2, Table 1). The N1, N3 and C2 atoms act as hydrogen-bond donors and the S1 atoms act as hydrogen-bond acceptors, connecting the molecules into mono-periodic hydrogen-bonded ribbons along [010] (Fig. 3). No other strong intermolecular interactions are observed for the title compound, possibly due to the non-polar organic periphery of the *cis*-jasmine fragment, and only weak interactions, *i.e.*, London dispersion forces can be suggested.

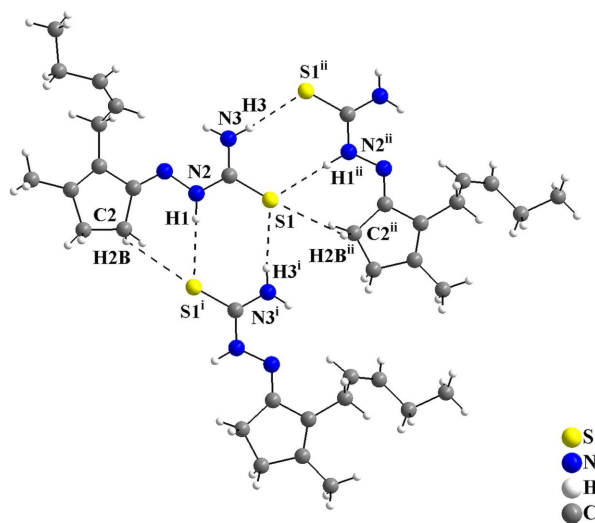


Figure 2
The molecular structure of the β -crystalline modification of the *cis*-jasmine thiosemicarbazone showing the intermolecular hydrogen-bonding interactions as dashed lines. The molecules are linked *via* pairs of $N-H\cdots S$ and $C-H\cdots S$ interactions, forming graph-set motifs of $R_2^2(8)$ and $R_1^2(7)$. Disorder is not shown for clarity. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$]

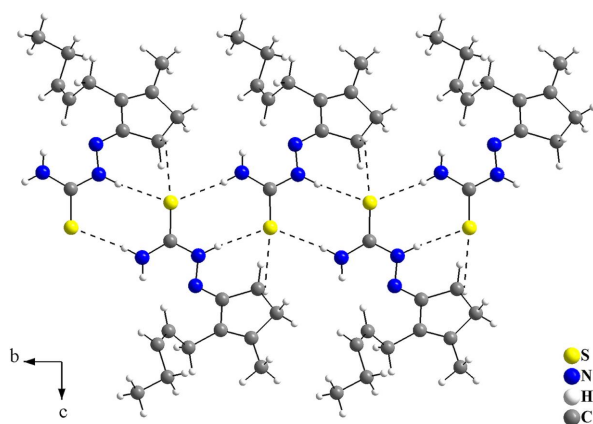


Figure 3
Graphical representation of the N–H...S and C–H...S intermolecular interactions in the title compound viewed along [100]. The interactions are drawn as dashed lines and connect the molecules along [010] with graph-set motifs of $R_2^2(8)$ and $R_2^1(7)$, forming a mono-periodic hydrogen-bonded ribbon. Disorder is not shown for clarity.

In the Hirshfeld surface analysis (Hirshfeld, 1977), the graphical representations and the two-dimensional Hirshfeld surface fingerprint (HSFP) were evaluated with *Crystal Explorer* (Wolff *et al.*, 2012). The Hirshfeld surface analysis of the title compound considering the *A*-labelled atoms [s.o.f. = 0.590 (14)] indicates that the most relevant intermolecular interactions for crystal cohesion are the following: H...H = 67.8%, (b) H...S/S...H = 15.0%, (c) H...C/C...H = 8.5% and

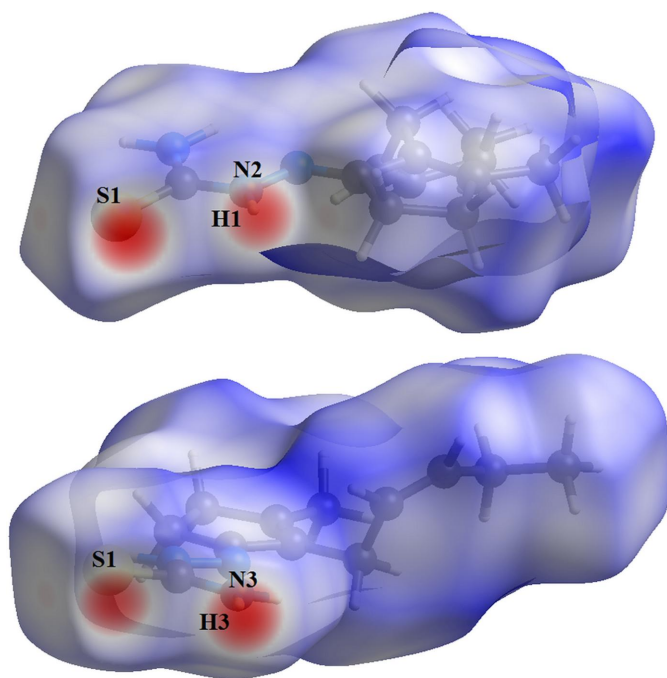


Figure 4
Two opposite side-views in separate figures of the Hirshfeld surface graphical representation (d_{norm}) for the title compound. The surface is drawn with transparency, the molecule is drawn in ball and stick mode and the disorder is not shown for clarity. The regions with strongest intermolecular interactions are shown in red. (d_{norm} range: -0.404 to 1.518 .)

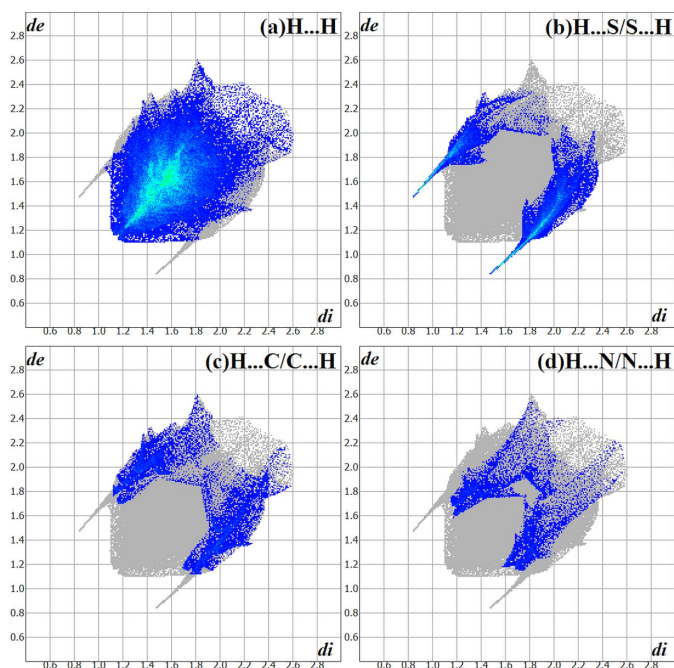


Figure 5
The Hirshfeld surface two-dimensional fingerprint plots for the title compound, showing the contacts in detail (cyan dots). The major contributions of the interactions to the crystal cohesion amount to (a) H...H = 67.8%, (b) H...S/S...H = 15.0%, (c) H...C/C...H = 8.5% and (d) H...N/N...H = 5.6%. The d_i (*x*-axis) and the d_e (*y*-axis) values are the closest internal and external distances from given points on the Hirshfeld surface (in Å). Regarding the disorder, only the atoms with the highest s.o.f. were considered.

(d) H...N/N...H = 5.6%. For comparison, the contributions for the structure with the *B*-labelled atoms [s.o.f. = 0.410 (14)] amount to (a) H...H = 68.3%, (b) H...S/S...H = 15.0%, (c) H...C/C...H = 8.2% and (d) H...N/N...H = 5.5%. Since no considerable differences between the values were observed, the evaluations and graphics were performed for the structure with the *A*-labelled atoms only. The graphical representation of the Hirshfeld surface (d_{norm}) is drawn in a figure with two separate opposite side-views of the molecule with transparency and using a ball-and-stick model. The locations of the strongest intermolecular contacts, *i.e.*, the regions around the H1, H3 and S1 atoms (Fig. 4) are indicated in red. These atoms are those involved in the H...S interactions shown in the previous figures (Figs. 2 and 3). The contributions to the crystal packing are shown as two-dimensional Hirshfeld surface fingerprint plots (HSFP) with cyan dots (Fig. 5). The d_i (*x*-axis) and the d_e (*y*-axis) values are the closest internal and external distances from given points on the Hirshfeld surface (in Å).

The crystal structure of the α -crystalline modification of the *cis*-jasmonone thiosemicarbazone was reported recently (Orsoni *et al.*, 2020). As already mentioned above, the α -modification has three crystallographically independent molecules in the asymmetric unit, namely α -JATSC(A), α -JATSC(B) and α -JATSC(C). In the crystal, the molecules are connected by pairs of N–H...S interactions, with graph-set motif $R_2^2(8)$, into mono-periodic hydrogen-bonded ribbons along [100]

Table 2

Selected geometric parameters (Å, °) of the TSC entities for the α - and β -crystalline modifications of the *cis*-jasmine thiosemicarbazone.

α -JATSC(A), α -JATSC(B) and α -JATSC(C) refer to the three crystallographically independent molecules in the α -crystalline modification of *cis*-jasmine thiosemicarbazone (Orsoni *et al.*, 2020) (Fig. 6). β -JATSC refers to the β -crystalline modification of *cis*-jasmine thiosemicarbazone reported in this work (Fig. 1).

Compound	Bond length	N=N	N-C	C=S
α -JATSC(A)		1.383 (5)	1.305 (5)	1.695 (5)
α -JATSC(B)		1.384 (5)	1.349 (5)	1.701 (5)
α -JATSC(C)		1.400 (5)	1.341 (5)	1.689 (5)
β -JATSC		1.388 (2)	1.345 (3)	1.698 (2)
	Atom chain 1	Torsion angle	Atom chain 2	Torsion angle
α -JATSC(A)	N3A–N2A–C1A–S1A	–179.4 (3)	N3A–N2A–C1A–N1A	0.0 (6)
α -JATSC(B)	N3B–N2B–C1B–S1B	180.0 (3)	N3B–N2B–C1B–N1B	0.2 (6)
α -JATSC(C)	N3C–N2C–C1C–S1C	177.4 (3)	N3C–N2C–C1C–N1C	–1.8 (6)
β -JATSC	N1–N2–C12–S1	174.04 (15)	N1–N2–C12–N3	–4.8 (3)

(Fig. 6). The α -modification contains two crystallographically different strands. Within one of the strands, inversion centres are located at the centroids of every eight-membered $C_2H_2N_2S_2$ ring, while the other strand has no internal symmetry. The β -modification has only one independent strand that has no internal symmetry. For a comparison of selected geometric parameters of the α - and β -modifications of *cis*-jasmine thiosemicarbazone, see Table 2. The crystal structures of non-substituted thiosemicarbazones attached to non-polar organic groups have been studied by our group, such as the structures of the (–)-menthone (Oliveira *et al.*, 2014) and the tetralone thiosemicarbazone derivatives (Oliveira *et al.*, 2012, 2017). In the structure of the (–)-menthone thiosemicarbazone, the molecules are linked by N–H...S intermolecular interactions, forming rings with graph-set motif $R_2^2(8)$, into mono-periodic hydrogen-bonded ribbons along [100]. For the structure of the tetralone thiosemicarbazone, the molecules are connected by N–H...S

and C–H...S intermolecular interactions along $[1\bar{1}0]$, where rings of graph-set motifs $R_2^2(8)$ and $R_2^1(7)$ are observed. The same supramolecular arrangement was observed for both structures, forming a structural pattern for these entities (Fig. 7). This packing pattern is common for non-substituted thiosemicarbazones attached to non-polar organic entities, as observed in this work (Fig. 3).

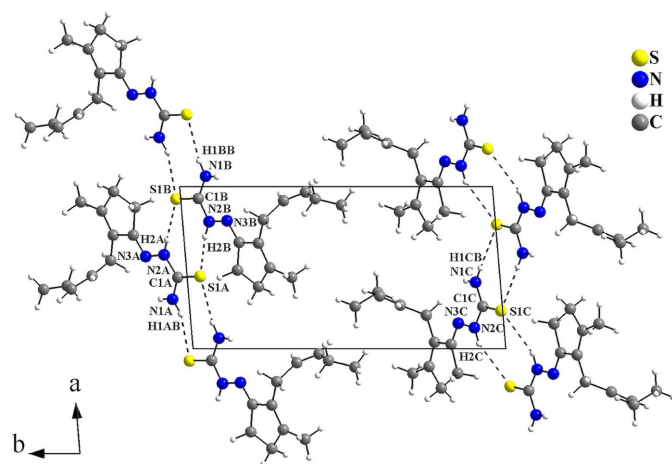


Figure 6

Crystal structure section of the α -*cis*-jasmine thiosemicarbazone (Orsoni *et al.*, 2020) viewed along [001]. Selected atoms of the TSC entities are labelled to indicate the three crystallographically independent molecules [α -JATSC(A); α -JATSC(B); α -JATSC(C)]. The N–H...S intermolecular interactions, forming rings with graph-set motif $R_2^2(8)$, are drawn as dashed lines and connect the molecules into mono-periodic H-bonded ribbons along [100].

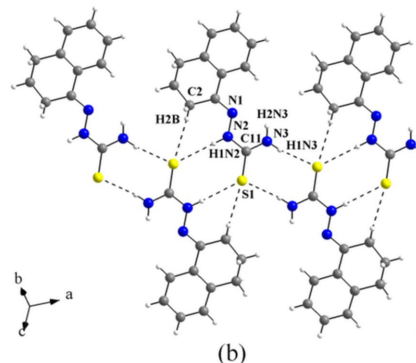
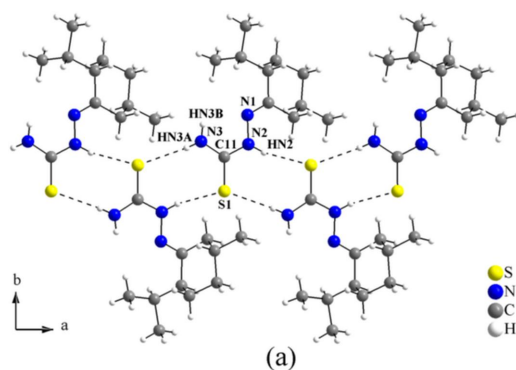


Figure 7

(a) (–)-Menthone thiosemicarbazone (Oliveira *et al.*, 2014) and (b) tetralone thiosemicarbazone (Oliveira *et al.*, 2012) graphical representations of the mono-periodic hydrogen-bonded ribbons structures along [100] and $[1\bar{1}0]$, respectively. The molecules are connected by H...S intermolecular interactions drawn as dashed lines. The atoms of the TSC entities and one C–H donor in general positions are labelled. This packing pattern is common for non-substituted thiosemicarbazones attached to non-polar organic entities.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₉ N ₃ S
<i>M_r</i>	237.36
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)	15.0159 (7), 8.0595 (3), 10.8243 (5)
β (°)	94.372 (3)
<i>V</i> (Å ³)	1306.15 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.23
Crystal size (mm)	0.17 × 0.14 × 0.05
Data collection	
Diffractometer	Enraf–Nonius FR590 Kappa CCD
Absorption correction	Multi-scan (Blessing, 1995)
<i>T</i> _{min} , <i>T</i> _{max}	0.922, 0.998
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	24176, 3002, 2241
<i>R</i> _{int}	0.083
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.651
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.054, 0.143, 1.09
No. of reflections	3002
No. of parameters	212
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.59, -0.45

Computer programs: *COLLECT* (Nonius, 1998), *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SIR92* (Altomare *et al.*, 1994), *SHELXL2018/3* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006), *CrystalExplorer* (Wolff *et al.*, 2012), *WinGX* (Farrugia, 2012), *pubCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

Synthesis and crystallization

The starting materials are commercially available and were used without further purification. The synthesis of *cis*-jasmone thiosemicarbazone was adapted from previously reported procedures (Freund & Schander, 1902; Oliveira *et al.*, 2017; Orsoni *et al.*, 2020). The mixture of ethanolic solutions of *cis*-jasmone (8 mmol in 50 ml) and thiosemicarbazide (8 mmol in 50 ml), was catalysed with HCl and refluxed for 8 h. After cooling, the precipitated product was filtered off and washed with cold ethanol. Colourless single crystals suitable for X-ray diffraction were obtained from tetrahydrofuran solution by slow evaporation of the solvent at room temperature. The template effect of the crystallization solvent and the temperature can be suggested as factors for the formation of the new crystalline modification of the *cis*-jasmone thiosemicarbazone, since the α -crystalline modification was crystallized from ethanol solution at 273 K (Orsoni *et al.*, 2020).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The molecule of title compound shows disorder over the chain of the *cis*-jasmone fragment, namely the H8, C9 and C10 atoms (Fig. 1), which are *A*-labelled for the atoms with the higher s.o.f. value and *B*-labelled for the lower [site-occupancy ratio = 0.590 (14):0.410 (14)]. H atoms attached to the C2, C3, C6, C7,

C11, N2 and N3 atoms were located in the difference Fourier map. The one bonded to N2 was refined freely, and those bonded to C2, C3, C6, C7, C11, and N3 were refined freely using the same isotropic displacement parameter for the atoms bonded to the same parent atom. The remaining hydrogen atoms were located in a difference-Fourier map, but were positioned with idealized geometry and refined isotropically using a riding model (HFIX command). Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Thus, for the C10AH₃ and C10BH₃ fragments, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$, the C–H bond lengths were set to 0.96 Å. For the H atoms attached to the C8 atom and to the C9A and C9B atoms, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$, the C–H bond lengths were set to 0.93 and 0.97 Å, respectively.

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full crystallographic data

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A second crystalline modification of 2-{3-methyl-2-[(2*Z*)-pent-2-en-1-yl]cyclopent-2-en-1-ylidene}hydrazinecarbothioamide

Adriano Bof de Oliveira, Leandro Bresolin, Vanessa Carratu Gervini, Johannes Beck and Jörg Daniels

2-{3-Methyl-2-[(2*Z*)-pent-2-en-1-yl]cyclopent-2-en-1-ylidene}hydrazinecarbothioamide

Crystal data

$C_{12}H_{19}N_3S$

$M_r = 237.36$

Monoclinic, $P2_1/c$

$a = 15.0159$ (7) Å

$b = 8.0595$ (3) Å

$c = 10.8243$ (5) Å

$\beta = 94.372$ (3)°

$V = 1306.15$ (10) Å³

$Z = 4$

$F(000) = 512$

$D_x = 1.207$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 60208 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.23$ mm⁻¹

$T = 123$ K

Plate, colourless

$0.17 \times 0.14 \times 0.05$ mm

Data collection

Enraf–Nonius FR590 Kappa CCD
diffractometer

Radiation source: sealed X-ray tube, Enraf
Nonius FR590

Horizontally mounted graphite crystal
monochromator

Detector resolution: 9 pixels mm⁻¹

CCD rotation images, thick slices, κ -goniostat
scans

Absorption correction: multi-scan
(Blessing, 1995)

$T_{\min} = 0.922$, $T_{\max} = 0.998$

24176 measured reflections

3002 independent reflections

2241 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.083$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 3.2$ °

$h = -19 \rightarrow 19$

$k = -10 \rightarrow 10$

$l = -13 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.143$

$S = 1.09$

3002 reflections

212 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.069P)^2 + 0.7307P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.59$ e Å⁻³

$\Delta\rho_{\min} = -0.45$ e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.49279 (4)	-0.38063 (6)	0.29692 (5)	0.02576 (19)	
N1	0.35988 (12)	-0.5052 (2)	-0.01509 (16)	0.0239 (4)	
N2	0.40985 (12)	-0.5194 (2)	0.09773 (17)	0.0235 (4)	
H1	0.4271 (17)	-0.617 (3)	0.133 (2)	0.030 (7)*	
N3	0.42480 (14)	-0.2376 (2)	0.09074 (19)	0.0275 (5)	
H2	0.3988 (18)	-0.242 (4)	0.016 (3)	0.039 (5)*	
H3	0.4455 (19)	-0.149 (4)	0.126 (3)	0.039 (5)*	
C1	0.32864 (14)	-0.6392 (3)	-0.0662 (2)	0.0224 (5)	
C2	0.33976 (16)	-0.8181 (3)	-0.0266 (2)	0.0251 (5)	
H2A	0.3276 (15)	-0.833 (3)	0.065 (2)	0.024 (4)*	
H2B	0.4031 (17)	-0.853 (3)	-0.036 (2)	0.024 (4)*	
C3	0.27458 (17)	-0.9129 (3)	-0.1170 (2)	0.0295 (5)	
H3A	0.3041 (16)	-1.002 (4)	-0.156 (2)	0.035 (5)*	
H3B	0.2234 (17)	-0.961 (3)	-0.074 (2)	0.035 (5)*	
C4	0.24066 (15)	-0.7858 (3)	-0.2109 (2)	0.0269 (5)	
C5	0.27121 (15)	-0.6322 (3)	-0.1810 (2)	0.0253 (5)	
C6	0.25021 (17)	-0.4704 (3)	-0.2465 (2)	0.0299 (5)	
H6A	0.3013 (19)	-0.413 (4)	-0.246 (3)	0.039 (5)*	
H6B	0.2284 (17)	-0.490 (3)	-0.337 (3)	0.039 (5)*	
C7	0.18173 (18)	-0.3701 (3)	-0.1851 (2)	0.0349 (6)	
H7	0.1977 (18)	-0.347 (3)	-0.097 (3)	0.041 (8)*	
C8	0.1055 (2)	-0.3144 (4)	-0.2354 (3)	0.0520 (8)	
H8A	0.077777	-0.233393	-0.190673	0.062*	0.590 (14)
H8B	0.059808	-0.292155	-0.184493	0.062*	0.410 (14)
C9A	0.0569 (4)	-0.3651 (9)	-0.3570 (6)	0.0381 (17)	0.590 (14)
H9A1	0.014033	-0.451696	-0.342863	0.046*	0.590 (14)
H9A2	0.099214	-0.408217	-0.412357	0.046*	0.590 (14)
C10A	0.0088 (6)	-0.2146 (8)	-0.4159 (9)	0.0420 (18)	0.590 (14)
H10A	-0.034413	-0.174691	-0.362002	0.063*	0.590 (14)
H10B	-0.020921	-0.245795	-0.494084	0.063*	0.590 (14)
H10C	0.051400	-0.128624	-0.428493	0.063*	0.590 (14)
C11	0.17972 (19)	-0.8356 (4)	-0.3194 (3)	0.0371 (6)	
H11A	0.161 (2)	-0.743 (4)	-0.376 (3)	0.051 (5)*	
H11B	0.125 (2)	-0.877 (4)	-0.291 (3)	0.051 (5)*	
H11C	0.206 (2)	-0.916 (4)	-0.370 (3)	0.051 (5)*	
C12	0.43977 (14)	-0.3783 (2)	0.1527 (2)	0.0221 (4)	
C9B	0.0882 (7)	-0.2831 (15)	-0.3810 (7)	0.043 (3)	0.410 (14)
H9B1	0.108084	-0.172234	-0.400126	0.052*	0.410 (14)
H9B2	0.120614	-0.362544	-0.427766	0.052*	0.410 (14)

C10B	-0.0104 (10)	-0.290 (3)	-0.4108 (15)	0.090 (6)	0.410 (14)
H10D	-0.034871	-0.381309	-0.367063	0.135*	0.410 (14)
H10E	-0.022841	-0.306245	-0.498360	0.135*	0.410 (14)
H10F	-0.037061	-0.188515	-0.386266	0.135*	0.410 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0399 (4)	0.0149 (3)	0.0215 (3)	-0.0017 (2)	-0.0048 (2)	-0.0004 (2)
N1	0.0299 (10)	0.0203 (9)	0.0208 (9)	-0.0005 (8)	-0.0020 (7)	0.0003 (7)
N2	0.0330 (10)	0.0148 (9)	0.0215 (9)	-0.0010 (7)	-0.0045 (8)	-0.0010 (7)
N3	0.0414 (12)	0.0160 (9)	0.0241 (11)	-0.0025 (8)	-0.0047 (9)	-0.0005 (8)
C1	0.0252 (11)	0.0207 (11)	0.0215 (11)	-0.0015 (8)	0.0023 (8)	-0.0016 (9)
C2	0.0298 (12)	0.0174 (10)	0.0275 (12)	-0.0013 (9)	-0.0023 (9)	-0.0026 (9)
C3	0.0343 (13)	0.0249 (12)	0.0289 (12)	-0.0053 (10)	-0.0004 (10)	-0.0040 (10)
C4	0.0252 (11)	0.0303 (12)	0.0250 (11)	-0.0026 (9)	0.0014 (9)	-0.0039 (10)
C5	0.0265 (11)	0.0266 (11)	0.0226 (11)	0.0005 (9)	0.0009 (9)	-0.0002 (9)
C6	0.0339 (13)	0.0299 (12)	0.0253 (12)	0.0003 (10)	-0.0026 (10)	0.0028 (10)
C7	0.0506 (16)	0.0272 (13)	0.0261 (13)	0.0051 (11)	-0.0020 (11)	-0.0040 (10)
C8	0.0579 (19)	0.0569 (18)	0.0405 (16)	0.0247 (15)	-0.0007 (14)	-0.0123 (15)
C9A	0.032 (3)	0.033 (3)	0.048 (3)	0.003 (2)	-0.003 (2)	-0.004 (3)
C10A	0.041 (4)	0.038 (3)	0.046 (4)	0.006 (2)	-0.007 (3)	0.003 (3)
C11	0.0353 (15)	0.0436 (15)	0.0316 (14)	-0.0105 (12)	-0.0024 (11)	-0.0053 (12)
C12	0.0258 (11)	0.0156 (10)	0.0249 (11)	0.0009 (8)	0.0019 (9)	-0.0006 (9)
C9B	0.047 (5)	0.046 (5)	0.037 (4)	0.004 (4)	0.003 (3)	0.005 (3)
C10B	0.047 (7)	0.173 (19)	0.050 (6)	0.012 (10)	0.001 (5)	0.021 (11)

Geometric parameters (Å, °)

S1—C12	1.698 (2)	C7—C8	1.308 (4)
N1—C1	1.285 (3)	C7—H7	0.98 (3)
N1—N2	1.388 (2)	C8—C9A	1.512 (6)
N2—C12	1.345 (3)	C8—C9B	1.598 (8)
N2—H1	0.90 (3)	C8—H8A	0.9300
N3—C12	1.328 (3)	C8—H8B	0.9300
N3—H2	0.87 (3)	C9A—C10A	1.526 (10)
N3—H3	0.85 (3)	C9A—H9A1	0.9700
C1—C5	1.458 (3)	C9A—H9A2	0.9700
C1—C2	1.510 (3)	C10A—H10A	0.9600
C2—C3	1.534 (3)	C10A—H10B	0.9600
C2—H2A	1.03 (2)	C10A—H10C	0.9600
C2—H2B	1.00 (2)	C11—H11A	1.00 (3)
C3—C4	1.504 (3)	C11—H11B	0.96 (3)
C3—H3A	0.96 (3)	C11—H11C	0.95 (3)
C3—H3B	1.00 (3)	C9B—C10B	1.49 (2)
C4—C5	1.351 (3)	C9B—H9B1	0.9700
C4—C11	1.489 (3)	C9B—H9B2	0.9700
C5—C6	1.506 (3)	C10B—H10D	0.9600

C6—C7	1.502 (4)	C10B—H10E	0.9600
C6—H6A	0.90 (3)	C10B—H10F	0.9600
C6—H6B	1.02 (3)		
C1—N1—N2	117.67 (18)	C7—C8—C9B	122.4 (4)
C12—N2—N1	117.32 (18)	C7—C8—H8A	115.9
C12—N2—H1	118.2 (16)	C9A—C8—H8A	115.9
N1—N2—H1	124.3 (16)	C7—C8—H8B	118.8
C12—N3—H2	118.8 (19)	C9B—C8—H8B	118.8
C12—N3—H3	116.3 (19)	C8—C9A—C10A	109.3 (5)
H2—N3—H3	125 (3)	C8—C9A—H9A1	109.8
N1—C1—C5	120.47 (19)	C10A—C9A—H9A1	109.8
N1—C1—C2	130.6 (2)	C8—C9A—H9A2	109.8
C5—C1—C2	108.90 (18)	C10A—C9A—H9A2	109.8
C1—C2—C3	104.07 (18)	H9A1—C9A—H9A2	108.3
C1—C2—H2A	111.4 (14)	C9A—C10A—H10A	109.5
C3—C2—H2A	113.8 (13)	C9A—C10A—H10B	109.5
C1—C2—H2B	108.9 (13)	H10A—C10A—H10B	109.5
C3—C2—H2B	111.0 (13)	C9A—C10A—H10C	109.5
H2A—C2—H2B	107.6 (19)	H10A—C10A—H10C	109.5
C4—C3—C2	105.00 (19)	H10B—C10A—H10C	109.5
C4—C3—H3A	110.8 (15)	C4—C11—H11A	114.3 (18)
C2—C3—H3A	111.1 (15)	C4—C11—H11B	109.3 (18)
C4—C3—H3B	110.1 (15)	H11A—C11—H11B	104 (2)
C2—C3—H3B	111.7 (14)	C4—C11—H11C	112.3 (18)
H3A—C3—H3B	108 (2)	H11A—C11—H11C	105 (3)
C5—C4—C11	127.8 (2)	H11B—C11—H11C	111 (3)
C5—C4—C3	111.8 (2)	N3—C12—N2	117.47 (19)
C11—C4—C3	120.4 (2)	N3—C12—S1	121.54 (17)
C4—C5—C1	109.67 (19)	N2—C12—S1	120.98 (16)
C4—C5—C6	128.7 (2)	C10B—C9B—C8	107.0 (10)
C1—C5—C6	121.56 (19)	C10B—C9B—H9B1	107.9
C7—C6—C5	112.6 (2)	C8—C9B—H9B1	109.0
C7—C6—H6A	109.3 (18)	C10B—C9B—H9B2	113.0
C5—C6—H6A	107.2 (18)	C8—C9B—H9B2	111.1
C7—C6—H6B	109.0 (15)	H9B1—C9B—H9B2	108.7
C5—C6—H6B	111.1 (16)	C9B—C10B—H10D	109.5
H6A—C6—H6B	108 (2)	C9B—C10B—H10E	109.5
C8—C7—C6	127.4 (2)	H10D—C10B—H10E	109.5
C8—C7—H7	118.7 (16)	C9B—C10B—H10F	109.5
C6—C7—H7	113.9 (16)	H10D—C10B—H10F	109.5
C7—C8—C9A	128.2 (3)	H10E—C10B—H10F	109.5
C1—N1—N2—C12	-177.82 (19)	C2—C1—C5—C4	4.5 (3)
N2—N1—C1—C5	176.34 (19)	N1—C1—C5—C6	3.0 (3)
N2—N1—C1—C2	-2.8 (4)	C2—C1—C5—C6	-177.7 (2)
N1—C1—C2—C3	171.8 (2)	C4—C5—C6—C7	100.2 (3)
C5—C1—C2—C3	-7.4 (2)	C1—C5—C6—C7	-77.0 (3)

C1—C2—C3—C4	7.3 (3)	C5—C6—C7—C8	-123.5 (3)
C2—C3—C4—C5	-5.1 (3)	C6—C7—C8—C9A	14.5 (7)
C2—C3—C4—C11	175.9 (2)	C6—C7—C8—C9B	-24.3 (7)
C11—C4—C5—C1	179.4 (2)	C7—C8—C9A—C10A	-145.8 (5)
C3—C4—C5—C1	0.5 (3)	N1—N2—C12—N3	-4.8 (3)
C11—C4—C5—C6	1.9 (4)	N1—N2—C12—S1	174.04 (15)
C3—C4—C5—C6	-177.1 (2)	C7—C8—C9B—C10B	156.7 (12)
N1—C1—C5—C4	-174.7 (2)		

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>
N2—H1...S1 ⁱ	0.90 (3)	2.53 (3)	3.4142 (19)	166 (2)
N3—H3...S1 ⁱⁱ	0.85 (3)	2.48 (3)	3.325 (2)	173 (3)
C2—H2B...S1 ⁱ	1.00 (2)	2.93 (2)	3.436 (2)	112.2 (16)

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