IUCrData

4-Phenyl-1-[(1*R*,4*R*)-1,7,7-trimethyl-2-oxobicyclo-[2.2.1]heptan-3-ylidene]hydrazinecarbothioamide

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In the title compound, $C_{17}H_{21}N_3OS$ [common nomenclature: (*R*)-camphor 4-phenylthiosemicarbazone], the N—N—C—(S)—N fragment deviates slightly from planarity, with a maximum deviation of 0.0259 (12) Å for the hydrazinic N atom, and makes an angle of 29.55 (0)° with the aromatic ring. The molecular structure is stabilized by an intramolecular N—H···O hydrogen bond and a short N—H···N interaction with graph-set motifs *S*(6) and *S*(5), respectively. In the crystal, the centrosymmetric arrangement of the molecules resembles a herringbone packing motif along [001]. As a result of the steric effects of the camphor entity, an apolar organic periphery and the intramolecular nature of the hydrogen bonds, neither strong nor relevant intermolecular interactions are observed.

3D view
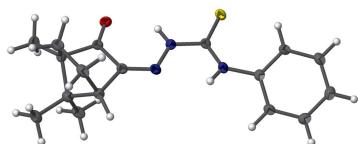
Chemical scheme
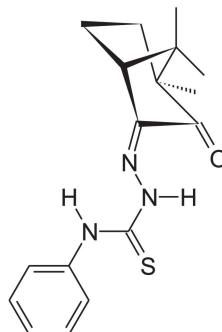
Structure description

As part of our study of the structural chemistry of camphor-thiosemicarbazone derivatives (Nogueira *et al.* 2015), we report herein the crystal structure of *R*-camphor-4-phenylthiosemicarbazone (Fig. 1). The molecule is not planar due to the camphor entity. The N1—N2—C11(=S1)—N3 fragment is almost planar with the maximum deviation being 0.0259 (12) Å for N2, and makes a dihedral angle of 29.55 (8)° with the aromatic ring. Two intramolecular interactions N3—H22···N1 with graph-set motif *S*(5), and N22–H21···O1 with graph-set motif *S*(6) rings] are the outstanding features of the structure (Fig. 1 and Table 1). The *R*-camphor entity contributes two chiral centres to the molecule
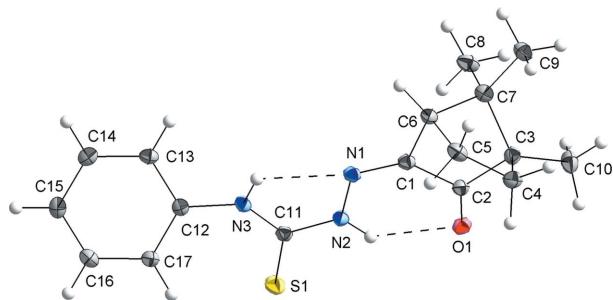
Figure 1
The molecular structure of the title compound, showing the labelling and displacement ellipsoids drawn at the 40% probability level.

at C3 and C6, but since the space group is centrosymmetric no effect on cell anisotropy should be expected due to molecular chirality.

In the crystal, the molecules show neither strong nor relevant intermolecular interactions of any kind (*e.g.* no intermolecular hydrogen-bonding or π–π interactions), probably due to the steric effect of the camphor entity with a substantial apolar organic periphery for such a small molecule and to the intramolecular nature of the hydrogen bonding. The structure shows a centrosymmetric herringbone packing motif, Fig. 2.

Synthesis and crystallization

Starting materials were commercially available and were used without further purification. *R*-camphor was oxidized with SeO₂ to the respective 1,2-diketone (Młochowski & Wójtowicz-Młochowska, 2015). The synthesis of the *R*-camphor-4-phenylthiosemicarbazone derivative was adapted from a procedure reported previously (Freund & Schander, 1902).
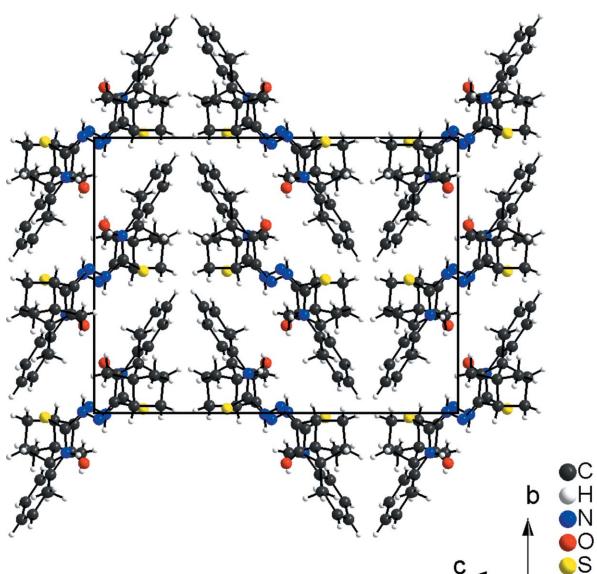

Figure 2
Part of the crystal structure of the title compound, viewed along [100]. The centrosymmetric arrangement of the molecules resembles a herringbone packing motif.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H21$\cdots$O1	0.88	2.08	2.769 (2)	135
N3—H22$\cdots$N1	0.88	2.16	2.607 (2)	111

Table 2
Experimental details.

Crystal data	
Chemical formula	C₁₇H₂₁N₃OS
M_r	315.43
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	100
a, b, c (Å)	11.7947 (9), 14.2221 (11), 18.7864 (15)
V (Å³)	3151.3 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.21
Crystal size (mm)	0.22 × 0.20 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.956, 0.972
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	94152, 3933, 2879
R_{int}	0.105
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.108, 1.08
No. of reflections	3933
No. of parameters	202
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.37, −0.27

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

The glacial acetic acid-catalysed reaction of the 1,2-diketone (3 mmol) and 4-phenylthiosemicarbazide (3 mmol) in ethanol (50 ml) was stirred and refluxed for 6 h. Single crystals suitable for X-ray diffraction were obtained from an ethanol solution by solvent evaporation. The assignment of the correct absolute configuration was assured by the use of enantiopure reagent. The C3 and C6 chiral centres of the *R*-camphor remain unchanged during the synthesis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

4-Phenyl-1-[(1*R*,4*R*)-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptan-3-yl-idene]hydrazinecarbothioamide

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4-Phenyl-1-[(1*R*,4*R*)-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptan-3-ylidene]hydrazinecarbothioamide

Crystal data

$C_{17}H_{21}N_3OS$	$F(000) = 1344$
$M_r = 315.43$	$D_x = 1.330$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 9840 reflections
$a = 11.7947$ (9) Å	$\theta = 2.5$–27.4°
$b = 14.2221$ (11) Å	$\mu = 0.21$ mm^{-1}
$c = 18.7864$ (15) Å	$T = 100$ K
$V = 3151.3$ (4) Å^3	Block, yellow
$Z = 8$	$0.22 \times 0.20 \times 0.13$ mm

Data collection

Bruker APEXII CCD diffractometer	94152 measured reflections
Radiation source: fine-focus sealed tube, Bruker APEXII	3933 independent reflections
Graphite monochromator	2879 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.105$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$\theta_{max} = 28.4°$, $\theta_{min} = 2.5°$
$T_{min} = 0.956$, $T_{max} = 0.972$	$h = -15 \rightarrow 13$
	$k = -19 \rightarrow 18$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 3.2431P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	
3933 reflections	$(\Delta/\sigma)_{max} < 0.001$
202 parameters	$\Delta\rho_{max} = 0.37$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.71911 (16)	−0.04008 (13)	0.44422 (10)	0.0189 (4)
C2	0.75320 (16)	−0.14112 (13)	0.43709 (10)	0.0186 (4)
C3	0.67901 (17)	−0.18022 (14)	0.37840 (10)	0.0218 (4)
C4	0.72486 (17)	−0.13055 (15)	0.30938 (10)	0.0245 (4)
H1	0.8085	−0.1355	0.3066	0.029*
H2	0.6915	−0.1592	0.2662	0.029*
C5	0.68791 (17)	−0.02744 (15)	0.31681 (10)	0.0233 (4)
H3	0.6356	−0.0091	0.2780	0.028*
H4	0.7542	0.0152	0.3165	0.028*
C6	0.62677 (16)	−0.02577 (14)	0.39040 (10)	0.0210 (4)
H5	0.5761	0.0295	0.3990	0.025*
C7	0.56806 (16)	−0.12318 (14)	0.39241 (10)	0.0212 (4)
C8	0.51481 (18)	−0.14473 (16)	0.46468 (10)	0.0271 (5)
H6	0.4498	−0.1030	0.4725	0.041*
H7	0.5711	−0.1347	0.5023	0.041*
H8	0.4894	−0.2103	0.4656	0.041*
C9	0.47884 (17)	−0.13701 (15)	0.33435 (11)	0.0262 (4)
H9	0.4566	−0.2034	0.3325	0.039*
H10	0.5105	−0.1182	0.2883	0.039*
H11	0.4122	−0.0983	0.3451	0.039*
C10	0.67500 (19)	−0.28552 (14)	0.37539 (11)	0.0286 (5)
H12	0.7522	−0.3103	0.3708	0.043*
H13	0.6297	−0.3053	0.3343	0.043*
H14	0.6405	−0.3098	0.4191	0.043*
C11	0.88749 (15)	0.05697 (13)	0.57968 (10)	0.0181 (4)
C12	0.86509 (16)	0.22342 (13)	0.61970 (9)	0.0182 (4)
C13	0.77715 (16)	0.28713 (14)	0.62938 (10)	0.0204 (4)
H15	0.7051	0.2750	0.6088	0.025*
C14	0.79379 (17)	0.36801 (14)	0.66875 (10)	0.0236 (4)
H17	0.7334	0.4114	0.6750	0.028*
C15	0.89868 (18)	0.38574 (14)	0.69908 (10)	0.0240 (4)
H18	0.9103	0.4408	0.7268	0.029*
C16	0.98636 (17)	0.32276 (14)	0.68867 (10)	0.0237 (4)
H19	1.0583	0.3349	0.7095	0.028*
C17	0.97111 (16)	0.24224 (14)	0.64831 (10)	0.0210 (4)

H20	1.0326	0.2004	0.6403	0.025*
N1	0.75715 (13)	0.02268 (11)	0.48709 (8)	0.0193 (3)
N2	0.84297 (13)	−0.00435 (11)	0.53138 (8)	0.0193 (3)
H21	0.8698	−0.0620	0.5287	0.023*
N3	0.84240 (13)	0.14351 (11)	0.57670 (8)	0.0200 (3)
H22	0.7913	0.1520	0.5432	0.024*
O1	0.82511 (11)	−0.18192 (9)	0.47199 (7)	0.0223 (3)
S1	0.98673 (4)	0.01558 (4)	0.63485 (3)	0.02212 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0174 (9)	0.0210 (10)	0.0183 (9)	0.0009 (7)	−0.0013 (7)	0.0005 (7)
C2	0.0167 (9)	0.0216 (10)	0.0176 (9)	0.0007 (8)	0.0002 (8)	−0.0005 (7)
C3	0.0229 (10)	0.0205 (10)	0.0221 (10)	0.0016 (8)	−0.0038 (8)	−0.0036 (8)
C4	0.0201 (10)	0.0347 (12)	0.0187 (9)	0.0003 (9)	0.0001 (8)	−0.0026 (8)
C5	0.0205 (10)	0.0294 (11)	0.0201 (9)	−0.0058 (8)	−0.0017 (8)	0.0031 (8)
C6	0.0186 (9)	0.0221 (10)	0.0224 (9)	0.0017 (8)	−0.0037 (8)	−0.0026 (8)
C7	0.0198 (10)	0.0225 (10)	0.0214 (10)	−0.0012 (8)	−0.0010 (8)	0.0012 (8)
C8	0.0198 (10)	0.0387 (12)	0.0228 (10)	−0.0044 (9)	0.0017 (8)	0.0022 (9)
C9	0.0218 (10)	0.0276 (11)	0.0292 (11)	−0.0031 (9)	−0.0056 (9)	0.0003 (8)
C10	0.0357 (12)	0.0196 (10)	0.0305 (11)	0.0002 (9)	−0.0083 (9)	−0.0022 (9)
C11	0.0158 (9)	0.0219 (10)	0.0167 (9)	−0.0024 (7)	0.0021 (7)	−0.0011 (7)
C12	0.0199 (9)	0.0185 (9)	0.0161 (9)	−0.0016 (7)	0.0007 (7)	0.0008 (7)
C13	0.0170 (10)	0.0247 (10)	0.0196 (9)	0.0000 (7)	−0.0015 (7)	0.0018 (8)
C14	0.0237 (10)	0.0234 (10)	0.0238 (10)	0.0034 (8)	0.0016 (8)	0.0007 (8)
C15	0.0306 (11)	0.0203 (10)	0.0209 (10)	−0.0029 (8)	0.0011 (8)	−0.0015 (8)
C16	0.0202 (10)	0.0260 (11)	0.0249 (10)	−0.0049 (8)	−0.0027 (8)	0.0002 (8)
C17	0.0163 (9)	0.0227 (10)	0.0241 (10)	−0.0003 (8)	0.0003 (7)	−0.0003 (8)
N1	0.0161 (8)	0.0226 (9)	0.0193 (8)	0.0005 (7)	−0.0031 (6)	−0.0002 (7)
N2	0.0186 (8)	0.0195 (8)	0.0200 (8)	0.0026 (6)	−0.0041 (6)	−0.0021 (6)
N3	0.0187 (8)	0.0211 (8)	0.0204 (8)	0.0006 (7)	−0.0057 (6)	−0.0027 (6)
O1	0.0217 (7)	0.0240 (7)	0.0211 (7)	0.0056 (6)	−0.0030 (6)	0.0000 (6)
S1	0.0192 (2)	0.0241 (2)	0.0230 (2)	0.0002 (2)	−0.00591 (19)	0.00026 (19)

Geometric parameters (Å, °)

C1—N1	1.283 (2)	C9—H11	0.9800
C1—C2	1.498 (3)	C10—H12	0.9800
C1—C6	1.500 (3)	C10—H13	0.9800
C2—O1	1.219 (2)	C10—H14	0.9800
C2—C3	1.513 (3)	C11—N3	1.342 (2)
C3—C10	1.499 (3)	C11—N2	1.364 (2)
C3—C7	1.562 (3)	C11—S1	1.6705 (19)
C3—C4	1.572 (3)	C12—C17	1.387 (3)
C4—C5	1.536 (3)	C12—C13	1.389 (3)
C4—H1	0.9900	C12—N3	1.420 (2)
C4—H2	0.9900	C13—C14	1.382 (3)

C5—C6	1.559 (3)	C13—H15	0.9500
C5—H3	0.9900	C14—C15	1.385 (3)
C5—H4	0.9900	C14—H17	0.9500
C6—C7	1.549 (3)	C15—C16	1.382 (3)
C6—H5	1.0000	C15—H18	0.9500
C7—C8	1.527 (3)	C16—C17	1.385 (3)
C7—C9	1.528 (3)	C16—H19	0.9500
C8—H6	0.9800	C17—H20	0.9500
C8—H7	0.9800	N1—N2	1.366 (2)
C8—H8	0.9800	N2—H21	0.8800
C9—H9	0.9800	N3—H22	0.8800
C9—H10	0.9800		
N1—C1—C2	129.01 (17)	H7—C8—H8	109.5
N1—C1—C6	125.63 (17)	C7—C9—H9	109.5
C2—C1—C6	105.35 (16)	C7—C9—H10	109.5
O1—C2—C1	126.53 (17)	H9—C9—H10	109.5
O1—C2—C3	128.26 (18)	C7—C9—H11	109.5
C1—C2—C3	105.21 (15)	H9—C9—H11	109.5
C10—C3—C2	114.37 (17)	H10—C9—H11	109.5
C10—C3—C7	119.91 (18)	C3—C10—H12	109.5
C2—C3—C7	99.83 (15)	C3—C10—H13	109.5
C10—C3—C4	115.37 (17)	H12—C10—H13	109.5
C2—C3—C4	103.70 (15)	C3—C10—H14	109.5
C7—C3—C4	101.18 (15)	H12—C10—H14	109.5
C5—C4—C3	104.85 (15)	H13—C10—H14	109.5
C5—C4—H1	110.8	N3—C11—N2	113.96 (16)
C3—C4—H1	110.8	N3—C11—S1	128.81 (15)
C5—C4—H2	110.8	N2—C11—S1	117.21 (14)
C3—C4—H2	110.8	C17—C12—C13	119.77 (17)
H1—C4—H2	108.9	C17—C12—N3	123.02 (17)
C4—C5—C6	103.08 (15)	C13—C12—N3	117.11 (17)
C4—C5—H3	111.1	C14—C13—C12	120.47 (18)
C6—C5—H3	111.1	C14—C13—H15	119.8
C4—C5—H4	111.1	C12—C13—H15	119.8
C6—C5—H4	111.1	C13—C14—C15	119.91 (19)
H3—C5—H4	109.1	C13—C14—H17	120.0
C1—C6—C7	100.76 (15)	C15—C14—H17	120.0
C1—C6—C5	105.05 (15)	C16—C15—C14	119.48 (19)
C7—C6—C5	102.40 (15)	C16—C15—H18	120.3
C1—C6—H5	115.6	C14—C15—H18	120.3
C7—C6—H5	115.6	C15—C16—C17	121.07 (19)
C5—C6—H5	115.6	C15—C16—H19	119.5
C8—C7—C9	109.00 (16)	C17—C16—H19	119.5
C8—C7—C6	112.64 (16)	C16—C17—C12	119.26 (18)
C9—C7—C6	113.92 (16)	C16—C17—H20	120.4
C8—C7—C3	112.97 (16)	C12—C17—H20	120.4
C9—C7—C3	112.94 (16)	C1—N1—N2	116.47 (16)

C6—C7—C3	94.92 (15)	C11—N2—N1	120.72 (15)
C7—C8—H6	109.5	C11—N2—H21	119.6
C7—C8—H7	109.5	N1—N2—H21	119.6
H6—C8—H7	109.5	C11—N3—C12	129.47 (16)
C7—C8—H8	109.5	C11—N3—H22	115.3
H6—C8—H8	109.5	C12—N3—H22	115.3
N1—C1—C2—O1	0.0 (3)	C10—C3—C7—C8	62.0 (2)
C6—C1—C2—O1	−178.98 (18)	C2—C3—C7—C8	−63.6 (2)
N1—C1—C2—C3	179.61 (19)	C4—C3—C7—C8	−169.85 (16)
C6—C1—C2—C3	0.60 (19)	C10—C3—C7—C9	−62.3 (2)
O1—C2—C3—C10	15.6 (3)	C2—C3—C7—C9	172.08 (16)
C1—C2—C3—C10	−163.93 (17)	C4—C3—C7—C9	65.87 (19)
O1—C2—C3—C7	145.0 (2)	C10—C3—C7—C6	179.16 (17)
C1—C2—C3—C7	−34.58 (18)	C2—C3—C7—C6	53.51 (16)
O1—C2—C3—C4	−110.8 (2)	C4—C3—C7—C6	−52.71 (16)
C1—C2—C3—C4	69.58 (18)	C17—C12—C13—C14	−1.6 (3)
C10—C3—C4—C5	163.66 (17)	N3—C12—C13—C14	−178.03 (17)
C2—C3—C4—C5	−70.49 (18)	C12—C13—C14—C15	−0.2 (3)
C7—C3—C4—C5	32.65 (18)	C13—C14—C15—C16	1.0 (3)
C3—C4—C5—C6	1.47 (19)	C14—C15—C16—C17	0.1 (3)
N1—C1—C6—C7	−145.01 (19)	C15—C16—C17—C12	−1.9 (3)
C2—C1—C6—C7	34.04 (18)	C13—C12—C17—C16	2.6 (3)
N1—C1—C6—C5	108.9 (2)	N3—C12—C17—C16	178.86 (17)
C2—C1—C6—C5	−72.07 (18)	C2—C1—N1—N2	2.1 (3)
C4—C5—C6—C1	69.27 (18)	C6—C1—N1—N2	−179.05 (17)
C4—C5—C6—C7	−35.63 (18)	N3—C11—N2—N1	−2.4 (2)
C1—C6—C7—C8	63.84 (19)	S1—C11—N2—N1	176.39 (13)
C5—C6—C7—C8	172.04 (16)	C1—N1—N2—C11	−178.80 (17)
C1—C6—C7—C9	−171.36 (16)	N2—C11—N3—C12	177.82 (17)
C5—C6—C7—C9	−63.2 (2)	S1—C11—N3—C12	−0.8 (3)
C1—C6—C7—C3	−53.57 (16)	C17—C12—N3—C11	33.0 (3)
C5—C6—C7—C3	54.63 (16)	C13—C12—N3—C11	−150.65 (19)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H21⋯O1	0.88	2.08	2.769 (2)	135
N3—H22⋯N1	0.88	2.16	2.607 (2)	111