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4-Methyl-2-phenylpent-2-enal thiosemicarbazone

L. Anitha,[a] S. R. Saritha,[a] S. R. Layana,[a] M. Sithambaresan[b]* and M. R. Sudarsanakumar[a]

[a]Department of Chemistry, Mahatma Gandhi College, University of Kerala, Thiruvananthapuram 695 004, Kerala, India, and [b]Department of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka. *Correspondence e-mail: msithambaresan@gmail.com

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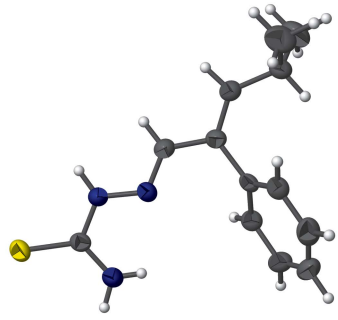
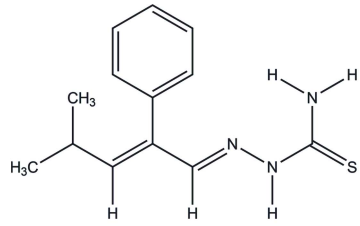
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{13}H_{17}N_3S$, the dihedral angle between the thiosemicarbazone moiety [maximum deviation = 0.055 (2) Å] and the phenyl ring is 53.15 (12)°. In the crystal, N—H···S hydrogen bonds generate (100) layers, with the S atom accepting two such bonds.

3D view



Chemical scheme



Structure description

Thiosemicarbazones are a family of nitrogen–sulfur donor ligands with a wide range of biological applications due in part to their ability to form terdentate chelates with transition metal ions (*e.g.* Scovill *et al.*, 1982; Joseph *et al.*, 2004). As part of our studies in this area, we now describe the synthesis and structure of the title compound (Fig. 1).

The C1═S1 [1.689 (3) Å], C2═N3 [1.270 (3) Å], N2—N3 [1.376 (3) Å] and C1—N2 [1.352 (3) Å] bond lengths show good agreement with the equivalent data for related structures (Palenik *et al.*, 1974; Nandi *et al.*, 1984). The title molecule exists in the *E* and *Z* configurations with respect to the C2═N2 and C3═C4 bonds, respectively. The thiosemicarbazone moiety is almost planar as a result of the extended conjugation along the moiety [maximum deviation = 0.055 (2) Å for N2] and subtends a dihedral angle of 53.15 (12)° with the pendant C8–C13 phenyl ring.

In the crystal, the molecules are linked by pairwise N1—H1*A*···S1 hydrogen bonds (Table 1), generating inversion dimers (Fig. 2). The dimers are linked into (100) sheets by N2—H2*A*···S1 bonds. There are no significant π–π interactions present in this crystal.

Synthesis and crystallization

A mixture of thiosemicarbazide (0.091 g; 1 mmol) and 4-methyl-2-phenyl-2-pentenal (0.18 g; 1 mmol) was refluxed in 30 ml methanol for 2–3 h. The resultant solution was

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S1^{i}	0.86 (2)	2.56 (2)	3.409 (3)	168 (3)
N2—H2A···S1^{ii}	0.88 (2)	2.59 (2)	3.456 (2)	167 (2)

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

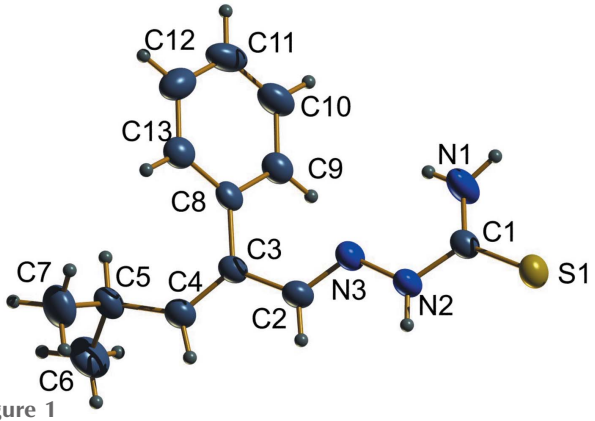


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

concentrated and cooled to room temperature. A precipitate formed with a yield of 56% and was filtered and washed with methanol. Brown block-shaped crystals were grown by slow evaporation using ethanol as the solvent, m.p. = 199–202°C. Analysis calculated for $C_{13}H_{17}N_3S$: C 63.07; H 6.87; N 16.97; S 12.94%; found: C 62.92; H 7.18; N 16.91; S 12.58%.

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{17}N_3S$
M_r	247.35
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	296
a, b, c (Å)	30.3184 (13), 11.0972 (5), 8.0354 (3)
β (°)	93.127 (5)
V (Å^3)	2699.5 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.22
Crystal size (mm)	0.15 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEXIII CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.611, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15555, 2373, 1723
R_{int}	0.065
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.135, 1.06
No. of reflections	2373
No. of parameters	168
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.22

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014* (Sheldrick, 2015*a*), *DIAMOND* (Brandenburg, 2010), *SHELXL2014* (Sheldrick, 2015*b*) and *publCIF* (Westrip, 2010).

Acknowledgements

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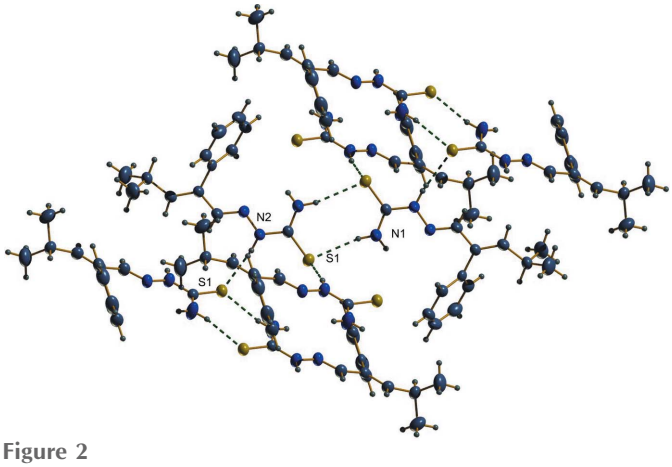

Figure 2
N—H···S hydrogen-bonding interactions (dashed lines) in the title compound.

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full crystallographic data

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4-Methyl-2-phenylpent-2-enal thiosemicarbazone

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4-Methyl-2-phenylpent-2-enal thiosemicarbazone

Crystal data

$C_{13}H_{17}N_3S$
M_r = 247.35
Monoclinic, *C*2/*c*
a = 30.3184 (13) Å
b = 11.0972 (5) Å
c = 8.0354 (3) Å
β = 93.127 (5)°
V = 2699.5 (2) Å^3
Z = 8
F(000) = 1056
D_x = 1.217 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 5545 reflections
θ = 3.2–27.9°
μ = 0.22 mm^{-1}
T = 296 K
Block, brown
0.15 × 0.15 × 0.10 mm

Data collection

Bruker Kappa APEXIII CMOS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.611, T_{max} = 0.746
15555 measured reflections
2373 independent reflections
1723 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 25.0°, θ_{min} = 3.2°
h = −36→36
k = −13→13
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.135
S = 1.06
2373 reflections
168 parameters
4 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 1.9983P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 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.

Refinement. All H atoms bound to carbon atoms were placed in calculated positions with C—H = 0.93–0.96 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The N–H hydrogen atoms of the molecule were located from difference maps and N—H was restrained to 0.85 ±0.02 Å and the H···H distance to 1.38±0.02.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.73348 (9)	0.8377 (2)	0.2590 (3)	0.0333 (6)
C2	0.67138 (9)	0.8558 (2)	0.6111 (3)	0.0383 (7)
H2	0.6881	0.9141	0.6689	0.046*
C3	0.63249 (8)	0.8067 (2)	0.6863 (3)	0.0326 (6)
C4	0.62187 (9)	0.8526 (2)	0.8338 (3)	0.0386 (7)
H4	0.6408	0.9123	0.8769	0.046*
C5	0.58446 (9)	0.8221 (3)	0.9380 (3)	0.0412 (7)
H5	0.5688	0.7521	0.8896	0.049*
C6	0.60133 (12)	0.7917 (4)	1.1154 (4)	0.0690 (10)
H6A	0.6193	0.7204	1.1141	0.104*
H6B	0.5767	0.7779	1.1832	0.104*
H6C	0.6187	0.8575	1.1606	0.104*
C7	0.55250 (11)	0.9280 (3)	0.9420 (4)	0.0649 (10)
H7A	0.5680	0.9982	0.9836	0.097*
H7B	0.5291	0.9089	1.0135	0.097*
H7C	0.5403	0.9436	0.8314	0.097*
C8	0.60645 (8)	0.7130 (2)	0.5914 (3)	0.0318 (6)
C9	0.62684 (9)	0.6100 (2)	0.5307 (3)	0.0383 (7)
H9	0.6569	0.5981	0.5543	0.046*
C10	0.60319 (11)	0.5259 (3)	0.4366 (4)	0.0488 (8)
H10	0.6174	0.4584	0.3966	0.059*
C11	0.55885 (12)	0.5411 (3)	0.4016 (4)	0.0554 (9)
H11	0.5430	0.4845	0.3375	0.066*
C12	0.53782 (10)	0.6413 (3)	0.4624 (4)	0.0523 (8)
H12	0.5076	0.6514	0.4401	0.063*
C13	0.56145 (9)	0.7264 (3)	0.5560 (3)	0.0402 (7)
H13	0.5470	0.7936	0.5956	0.048*
N1	0.71567 (10)	0.7372 (3)	0.2016 (4)	0.0586 (8)
N2	0.71870 (8)	0.8787 (2)	0.4043 (3)	0.0389 (6)
N3	0.68323 (7)	0.8216 (2)	0.4694 (3)	0.0369 (6)
S1	0.77299 (2)	0.91402 (6)	0.16283 (9)	0.0398 (3)
H1A	0.7209 (9)	0.709 (3)	0.105 (3)	0.063 (10)*
H2A	0.7316 (8)	0.940 (2)	0.457 (3)	0.045 (8)*
H1B	0.6953 (8)	0.704 (3)	0.245 (3)	0.048 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0404 (15)	0.0315 (15)	0.0279 (15)	0.0029 (12)	0.0019 (12)	0.0007 (12)
C2	0.0447 (17)	0.0358 (15)	0.0343 (16)	−0.0075 (13)	0.0028 (13)	−0.0050 (13)
C3	0.0395 (15)	0.0304 (14)	0.0280 (14)	−0.0002 (12)	0.0014 (11)	−0.0011 (12)
C4	0.0446 (16)	0.0336 (15)	0.0379 (17)	−0.0035 (13)	0.0041 (13)	−0.0042 (13)
C5	0.0513 (18)	0.0384 (16)	0.0348 (16)	−0.0021 (13)	0.0101 (13)	−0.0056 (13)
C6	0.086 (3)	0.084 (3)	0.0379 (19)	−0.003 (2)	0.0090 (17)	0.0054 (18)
C7	0.065 (2)	0.063 (2)	0.068 (2)	0.0127 (17)	0.0193 (18)	−0.0117 (19)

C8	0.0422 (16)	0.0322 (15)	0.0217 (13)	−0.0010 (12)	0.0071 (11)	0.0030 (11)
C9	0.0476 (17)	0.0335 (15)	0.0342 (15)	−0.0005 (12)	0.0051 (13)	0.0016 (12)
C10	0.071 (2)	0.0356 (16)	0.0407 (17)	−0.0073 (15)	0.0081 (15)	−0.0059 (14)
C11	0.078 (2)	0.0484 (19)	0.0391 (18)	−0.0258 (18)	0.0012 (16)	−0.0064 (15)
C12	0.0470 (18)	0.065 (2)	0.0441 (18)	−0.0146 (16)	−0.0035 (14)	0.0077 (16)
C13	0.0466 (17)	0.0412 (16)	0.0331 (16)	−0.0027 (13)	0.0040 (13)	0.0036 (13)
N1	0.078 (2)	0.0532 (18)	0.0479 (18)	−0.0259 (15)	0.0292 (15)	−0.0187 (15)
N2	0.0449 (14)	0.0393 (14)	0.0333 (14)	−0.0106 (11)	0.0095 (11)	−0.0079 (11)
N3	0.0440 (14)	0.0381 (13)	0.0290 (13)	−0.0063 (11)	0.0068 (10)	−0.0008 (10)
S1	0.0449 (4)	0.0393 (4)	0.0361 (4)	−0.0001 (3)	0.0096 (3)	0.0032 (3)

Geometric parameters (Å, º)

C1—N1	1.312 (4)	C7—H7B	0.9600
C1—N2	1.352 (3)	C7—H7C	0.9600
C1—S1	1.689 (3)	C8—C13	1.386 (4)
C2—N3	1.270 (3)	C8—C9	1.401 (4)
C2—C3	1.459 (4)	C9—C10	1.377 (4)
C2—H2	0.9300	C9—H9	0.9300
C3—C4	1.345 (4)	C10—C11	1.369 (4)
C3—C8	1.490 (3)	C10—H10	0.9300
C4—C5	1.485 (4)	C11—C12	1.384 (5)
C4—H4	0.9300	C11—H11	0.9300
C5—C7	1.524 (4)	C12—C13	1.383 (4)
C5—C6	1.526 (4)	C12—H12	0.9300
C5—H5	0.9800	C13—H13	0.9300
C6—H6A	0.9600	N1—H1A	0.859 (17)
C6—H6B	0.9600	N1—H1B	0.816 (16)
C6—H6C	0.9600	N2—N3	1.376 (3)
C7—H7A	0.9600	N2—H2A	0.881 (17)
N1—C1—N2	116.1 (3)	H7A—C7—H7C	109.5
N1—C1—S1	123.6 (2)	H7B—C7—H7C	109.5
N2—C1—S1	120.2 (2)	C13—C8—C9	117.6 (2)
N3—C2—C3	122.3 (2)	C13—C8—C3	121.2 (2)
N3—C2—H2	118.9	C9—C8—C3	121.1 (2)
C3—C2—H2	118.9	C10—C9—C8	121.2 (3)
C4—C3—C2	117.5 (2)	C10—C9—H9	119.4
C4—C3—C8	124.7 (2)	C8—C9—H9	119.4
C2—C3—C8	117.8 (2)	C11—C10—C9	120.3 (3)
C3—C4—C5	129.6 (3)	C11—C10—H10	119.8
C3—C4—H4	115.2	C9—C10—H10	119.8
C5—C4—H4	115.2	C10—C11—C12	119.5 (3)
C4—C5—C7	110.0 (2)	C10—C11—H11	120.2
C4—C5—C6	110.5 (2)	C12—C11—H11	120.2
C7—C5—C6	109.4 (3)	C13—C12—C11	120.4 (3)
C4—C5—H5	109.0	C13—C12—H12	119.8
C7—C5—H5	109.0	C11—C12—H12	119.8

C6—C5—H5	109.0	C12—C13—C8	120.9 (3)
C5—C6—H6A	109.5	C12—C13—H13	119.6
C5—C6—H6B	109.5	C8—C13—H13	119.6
H6A—C6—H6B	109.5	C1—N1—H1A	122 (2)
C5—C6—H6C	109.5	C1—N1—H1B	123 (2)
H6A—C6—H6C	109.5	H1A—N1—H1B	114 (2)
H6B—C6—H6C	109.5	C1—N2—N3	118.4 (2)
C5—C7—H7A	109.5	C1—N2—H2A	120.8 (19)
C5—C7—H7B	109.5	N3—N2—H2A	120.7 (19)
H7A—C7—H7B	109.5	C2—N3—N2	117.9 (2)
C5—C7—H7C	109.5		

N3—C2—C3—C4	−177.4 (3)	C3—C8—C9—C10	−177.1 (2)
N3—C2—C3—C8	0.3 (4)	C8—C9—C10—C11	−0.6 (4)
C2—C3—C4—C5	179.3 (3)	C9—C10—C11—C12	−0.4 (4)
C8—C3—C4—C5	1.8 (5)	C10—C11—C12—C13	0.8 (5)
C3—C4—C5—C7	−112.3 (3)	C11—C12—C13—C8	−0.3 (4)
C3—C4—C5—C6	126.8 (3)	C9—C8—C13—C12	−0.6 (4)
C4—C3—C8—C13	51.8 (4)	C3—C8—C13—C12	177.5 (2)
C2—C3—C8—C13	−125.7 (3)	N1—C1—N2—N3	−7.6 (4)
C4—C3—C8—C9	−130.1 (3)	S1—C1—N2—N3	172.97 (18)
C2—C3—C8—C9	52.4 (3)	C3—C2—N3—N2	175.9 (2)
C13—C8—C9—C10	1.1 (4)	C1—N2—N3—C2	175.6 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···S1^{i}	0.86 (2)	2.56 (2)	3.409 (3)	168 (3)
N2—H2*A*···S1^{ii}	0.88 (2)	2.59 (2)	3.456 (2)	167 (2)

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