

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## (2E)-N-Methyl-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinecarbothioamide

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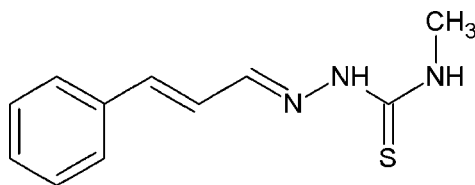
Received 8 August 2012; accepted 30 August 2012

Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.059;  $wR$  factor = 0.174; data-to-parameter ratio = 16.1.

The title compound,  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{S}$ , is close to being planar, with a dihedral angle of  $9.64(3)^\circ$  between the benzene ring and the thiosemicarbazone mean plane, maintained by the presence of  $\pi$ -conjugation in the chain linking the two systems. In the crystal,  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds form centrosymmetric dimers through a cyclic association [graph-set  $R_2^2(8)$ ].

## Related literature

For the biological activity and pharmaceutical properties of thiosemicarbazones and their derivatives, see: Casas *et al.* (2000); Ferrari *et al.* (2000); Murali Krishna *et al.* (2008); Murali Krishna & Hussain Reddy (2009). For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related compounds, see: Chumakov *et al.* (2006).



## Experimental

## Crystal data

$\text{C}_{11}\text{H}_{13}\text{N}_3\text{S}$   
 $M_r = 219.31$   
 Monoclinic,  $P2_1/n$   
 $a = 5.5265(11)$  Å

$b = 9.4670(19)$  Å  
 $c = 22.534(5)$  Å  
 $\beta = 91.206(3)^\circ$   
 $V = 1178.7(4)$  Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>

$T = 291$  K  
 $0.45 \times 0.26 \times 0.24$  mm

## Data collection

Bruker SMART CCD area-detector  
 diffractometer  
 8363 measured reflections

2201 independent reflections  
 1564 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.174$   
 $S = 1.06$   
 2201 reflections

137 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{S1}^i$	0.86	2.67	3.368 (3)	139

Symmetry code: (i)  $-x, -y, -z + 2$ .

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

We thank Professor T. N. Guru Row, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, for the data collection at the CCD facility.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2229).

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## supporting information

*Acta Cryst.* (2012). E68, o2842 [https://doi.org/10.1107/S1600536812037397]

**(2E)-N-Methyl-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinecarbothioamide**

**P. Murali Krishna, G. N. Anilkumar, K. Hussain Reddy and M. K. Kokila**

**S1. Comment**

Thiosemicarbazones, the derivatives of carbonyl compounds with thiosemicarbazides have been given a special place among sulfur containing compounds due to their propensity to react with a wide range of metals (Casas *et al.*, 2000) and possess a wide spectrum of medicinal properties (Ferrari *et al.*, 2000). It was advocated that their bioactivity arises because of the presence of the imino group ( $-\text{N}=\text{CH}-$ ) in addition to thioamino moieties present in the skeleton of the molecule. The title thiosemicarbazone derivative,  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{S}$  was synthesized and its crystal structure is reported here. It is possible that this compound may have biomedical properties similar to other nitrogen-sulfur donor ligands studied by our group.

In the title compound (Fig. 1), the aromatic ring and the thiosemicarbazone moiety are *anti*-related about the  $\text{C7}=\text{C8}$  bond and the molecule is almost planar, with maximum deviations from the l.s. plane of  $-0.127(3)$  Å (N2) and  $0.135(5)$  Å (N3). The dihedral angle between the benzene ring and the thiosemicarbazone plane is  $9.64(2)^\circ$ . The result is the presence of  $\pi$ -conjugation between the aromatic system and the thiosemicarbazide fragment of the molecule. All bond lengths and angles are normal (Allen *et al.*, 1987). A comparison of the interatomic distances of  $\text{C10}-\text{S1}$ ,  $\text{C2}-\text{N2}$  and  $\text{N2}-\text{N1}$  and the variations in bond angles  $\text{N2}-\text{C10}-\text{N3}$  [ $115.8(2)^\circ$ ],  $\text{N2}-\text{C10}-\text{S1}$  [ $119.7(2)^\circ$ ] and  $\text{N3}-\text{C10}-\text{S1}$  [ $124.5(2)^\circ$ ] in the ligand, indicate that in the TSC moiety of this substituted thiosemicarbazone there is extensive electron lone pair delocalization. The molecular conformation of this group is stabilized by intramolecular  $\text{N3}-\text{H}\cdots\text{N1}$  and  $\text{C11}-\text{H}\cdots\text{S1}$  interactions giving *S*(5) motifs (Bernstein *et al.*, 1995). Intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds (Table 1) give centrosymmetric dimers through a cyclic association [graph set  $R^2_2(8)$ ] (Fig. 2).

**S2. Experimental**

To a hot ethanolic (25 ml) solution of (2E)-3-phenylprop-2-enal (4.9 g, 0.03 mol) was added 50 ml of *N*-methylhydrazinecarbothioamide (0.03 mol) in 5% aqueous acetic acid (50 ml) and the reaction mixture was refluxed for 30–45 min. The crystalline solid product formed was collected by filtration, washed 5–6 times with 10 ml of hot water and then dried under vacuum and re-crystallized from methanol (20 ml). Good diffraction-quality pale yellow crystals of the title compound were obtained in a 1:1 mixture of ethanol and *n*-hexane.

**S3. Refinement**

All H atoms were fixed geometrically and treated as riding with  $\text{N}-\text{H} = 0.86$  Å,  $\text{C}-\text{H} = 0.93$  Å (aromatic) or  $0.96$  Å (methyl) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{C}_{\text{aromatic}})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ .

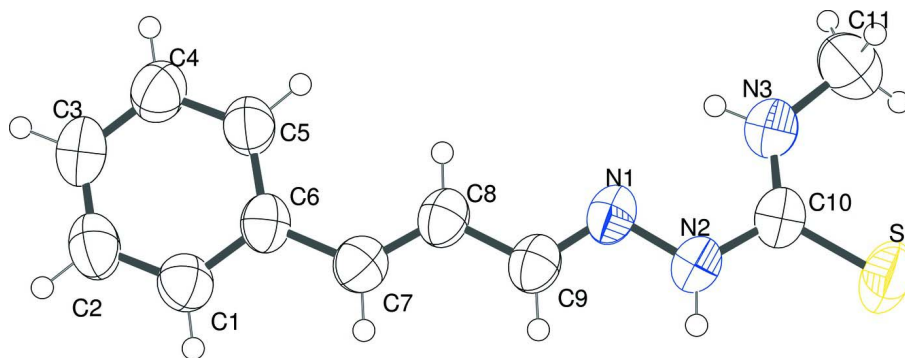


Figure 1

The structure of the title compound showing atom numbering, with probability ellipsoids drawn at the 50% level.

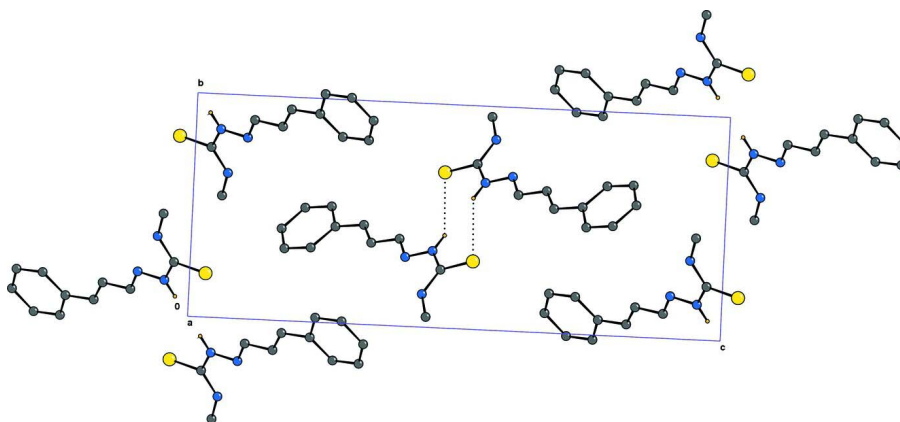


Figure 2

The packing diagram showing the molecular dimers with N—H...S interactions shown as dashed lines. H-atoms not involved in H-bonding are omitted.

**(2E)-N-Methyl-2-[(2E)-3-phenylprop-2-en-1-ylidene]hydrazinecarbothioamide**

*Crystal data*

$C_{11}H_{13}N_3S$

$M_r = 219.31$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P 2_1n$

$a = 5.5265$  (11) Å

$b = 9.4670$  (19) Å

$c = 22.534$  (5) Å

$\beta = 91.206$  (3)°

$V = 1178.7$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 464$

$D_x = 1.236$  Mg m<sup>-3</sup>

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

Cell parameters from 290 reflections

$\theta = 1.5$ – $26.8$ °

$\mu = 0.25$  mm<sup>-1</sup>

$T = 291$  K

Needle, pale yellow

$0.45 \times 0.26 \times 0.24$  mm

*Data collection*

Bruker SMART CCD area-detector

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\psi$  and  $\omega$  scans

8363 measured reflections

2201 independent reflections

1564 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.031$

$\theta_{max} = 25.5$ °,  $\theta_{min} = 1.8$ °

$h = -6 \rightarrow 6$   
 $k = -11 \rightarrow 11$

$l = -27 \rightarrow 27$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.174$   
 $S = 1.06$   
 2201 reflections  
 137 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  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0883P)^2 + 0.2979P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	-0.18251 (17)	0.19579 (9)	1.02989 (4)	0.0887 (4)
N1	0.2855 (4)	0.1898 (2)	0.90259 (9)	0.0638 (6)
N2	0.1638 (4)	0.1576 (3)	0.95336 (10)	0.0675 (6)
H2	0.2067	0.086	0.9746	0.081*
N3	-0.0653 (4)	0.3521 (3)	0.93696 (10)	0.0709 (7)
H3	0.0296	0.3671	0.9079	0.085*
C1	1.1293 (5)	-0.0205 (3)	0.76071 (12)	0.0668 (7)
H1	1.1667	-0.0888	0.7891	0.08*
C2	1.2696 (5)	-0.0095 (4)	0.71108 (13)	0.0764 (8)
H2A	1.4009	-0.0698	0.7066	0.092*
C3	1.2180 (5)	0.0884 (3)	0.66856 (14)	0.0753 (8)
H3A	1.3135	0.0957	0.6352	0.09*
C4	1.0231 (6)	0.1766 (3)	0.67547 (14)	0.0760 (8)
H4	0.9867	0.2435	0.6464	0.091*
C5	0.8811 (5)	0.1673 (3)	0.72468 (13)	0.0685 (7)
H5	0.7493	0.2275	0.7283	0.082*
C6	0.9323 (4)	0.0688 (3)	0.76925 (11)	0.0571 (6)
C7	0.7899 (4)	0.0553 (3)	0.82258 (11)	0.0616 (7)
H7	0.8363	-0.0157	0.849	0.074*
C8	0.6004 (5)	0.1334 (3)	0.83780 (12)	0.0626 (7)
H8	0.5532	0.2071	0.8128	0.075*
C9	0.4655 (5)	0.1101 (3)	0.89050 (11)	0.0627 (7)

H9	0.5088	0.0368	0.9161	0.075*
C10	-0.0242 (5)	0.2395 (3)	0.96975 (12)	0.0621 (7)
C11	-0.2592 (6)	0.4535 (4)	0.94608 (16)	0.0907 (10)
H11A	-0.4034	0.422	0.9256	0.136*
H11B	-0.2123	0.544	0.9309	0.136*
H11C	-0.2896	0.4613	0.9877	0.136*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.1036 (7)	0.0873 (6)	0.0769 (6)	-0.0033 (5)	0.0421 (5)	-0.0020 (4)
N1	0.0603 (13)	0.0759 (15)	0.0558 (13)	-0.0073 (11)	0.0119 (10)	-0.0001 (11)
N2	0.0673 (14)	0.0775 (15)	0.0582 (13)	0.0019 (12)	0.0148 (11)	0.0093 (11)
N3	0.0657 (14)	0.0768 (15)	0.0705 (14)	-0.0019 (12)	0.0103 (11)	0.0037 (12)
C1	0.0565 (15)	0.0770 (18)	0.0668 (17)	0.0015 (13)	-0.0017 (13)	-0.0026 (14)
C2	0.0565 (16)	0.095 (2)	0.077 (2)	0.0084 (15)	0.0084 (14)	-0.0134 (17)
C3	0.0700 (18)	0.085 (2)	0.0713 (18)	-0.0077 (16)	0.0201 (14)	-0.0150 (16)
C4	0.084 (2)	0.0718 (19)	0.0728 (19)	-0.0015 (16)	0.0184 (15)	0.0046 (14)
C5	0.0659 (16)	0.0680 (17)	0.0722 (18)	0.0046 (13)	0.0148 (13)	0.0011 (14)
C6	0.0461 (13)	0.0651 (15)	0.0601 (15)	-0.0095 (12)	0.0042 (11)	-0.0082 (12)
C7	0.0517 (14)	0.0700 (16)	0.0628 (15)	-0.0083 (12)	-0.0008 (12)	0.0007 (13)
C8	0.0555 (15)	0.0743 (17)	0.0581 (15)	-0.0084 (13)	0.0056 (12)	-0.0023 (13)
C9	0.0577 (15)	0.0745 (18)	0.0560 (15)	-0.0083 (14)	0.0034 (12)	-0.0030 (13)
C10	0.0608 (15)	0.0658 (16)	0.0601 (16)	-0.0071 (13)	0.0094 (12)	-0.0074 (13)
C11	0.076 (2)	0.081 (2)	0.115 (3)	0.0053 (16)	0.0029 (18)	0.0001 (19)

*Geometric parameters (Å, °)*

S1—C10	1.680 (3)	C3—H3A	0.93
N1—C9	1.282 (3)	C4—C5	1.375 (4)
N1—N2	1.373 (3)	C4—H4	0.93
N2—C10	1.354 (3)	C5—C6	1.395 (4)
N2—H2	0.86	C5—H5	0.93
N3—C10	1.314 (4)	C6—C7	1.456 (3)
N3—C11	1.456 (4)	C7—C8	1.333 (4)
N3—H3	0.86	C7—H7	0.93
C1—C2	1.378 (4)	C8—C9	1.432 (4)
C1—C6	1.394 (4)	C8—H8	0.93
C1—H1	0.93	C9—H9	0.93
C2—C3	1.359 (4)	C11—H11A	0.96
C2—H2A	0.93	C11—H11B	0.96
C3—C4	1.374 (4)	C11—H11C	0.96
C9—N1—N2	116.3 (2)	C1—C6—C5	116.9 (2)
C10—N2—N1	119.5 (2)	C1—C6—C7	119.8 (2)
C10—N2—H2	120.2	C5—C6—C7	123.2 (2)
N1—N2—H2	120.2	C8—C7—C6	127.2 (3)
C10—N3—C11	125.0 (3)	C8—C7—H7	116.4

C10—N3—H3	117.5	C6—C7—H7	116.4
C11—N3—H3	117.5	C7—C8—C9	123.6 (3)
C2—C1—C6	121.4 (3)	C7—C8—H8	118.2
C2—C1—H1	119.3	C9—C8—H8	118.2
C6—C1—H1	119.3	N1—C9—C8	120.3 (3)
C3—C2—C1	120.7 (3)	N1—C9—H9	119.8
C3—C2—H2A	119.7	C8—C9—H9	119.8
C1—C2—H2A	119.7	N3—C10—N2	115.8 (2)
C2—C3—C4	119.2 (3)	N3—C10—S1	124.5 (2)
C2—C3—H3A	120.4	N2—C10—S1	119.7 (2)
C4—C3—H3A	120.4	N3—C11—H11A	109.5
C5—C4—C3	121.0 (3)	N3—C11—H11B	109.5
C5—C4—H4	119.5	H11A—C11—H11B	109.5
C3—C4—H4	119.5	N3—C11—H11C	109.5
C4—C5—C6	120.9 (3)	H11A—C11—H11C	109.5
C4—C5—H5	119.6	H11B—C11—H11C	109.5
C6—C5—H5	119.6		
C9—N1—N2—C10	178.3 (2)	C1—C6—C7—C8	178.7 (2)
C6—C1—C2—C3	-0.6 (4)	C5—C6—C7—C8	-1.9 (4)
C1—C2—C3—C4	-0.2 (4)	C6—C7—C8—C9	178.0 (2)
C2—C3—C4—C5	0.3 (5)	N2—N1—C9—C8	178.6 (2)
C3—C4—C5—C6	0.5 (5)	C7—C8—C9—N1	179.7 (2)
C2—C1—C6—C5	1.4 (4)	C11—N3—C10—N2	179.2 (3)
C2—C1—C6—C7	-179.2 (2)	C11—N3—C10—S1	-2.5 (4)
C4—C5—C6—C1	-1.3 (4)	N1—N2—C10—N3	-4.7 (4)
C4—C5—C6—C7	179.3 (3)	N1—N2—C10—S1	176.89 (18)

*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—H2...S1 <sup>i</sup>	0.86	2.67	3.368 (3)	139
N3—H3...N1	0.86	2.20	2.604 (6)	109
C11—H11C...S1	0.96	2.75	3.108 (6)	103

Symmetry code: (i)  $-x, -y, -z+2$ .