

# {[(*E*)-(1,3-Benzodioxol-5-yl)methylidene]amino}-thiourea

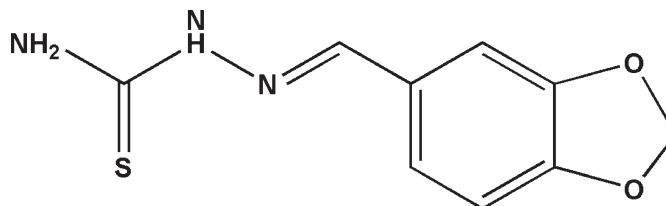
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The synthesis and crystallographic analysis of the title compound, C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>S, are reported. The compound crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*, revealing characteristic bond lengths and angles typical of thiosemicarbazone groups. The supramolecular organization primarily arises from hydrogen bonding and  $\pi$ - $\pi$  stacking interactions, leading to distinctive dimeric formations.

## 1. Chemical context

The group of thiosemicarbazone Schiff bases, capable of coordinating with metal centers through nitrogen and sulfur atoms, has garnered significant recent attention (Cortés *et al.*, 2011; Singh *et al.*, 2016) due to the exhibited biological and pharmacological properties, such as antibacterial and antiviral activities (Hu *et al.*, 2006). This study focuses on describing the synthesis and the analysis of the crystal structure of the title molecule.

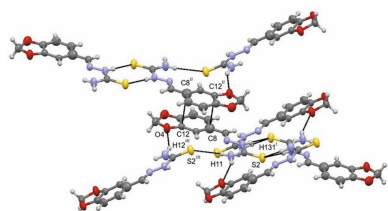


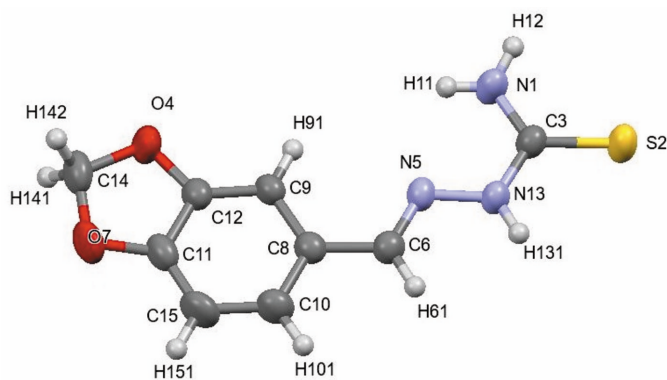
## 2. Structural commentary

The target compound (**I**) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with one molecule in the asymmetric unit (*Z* = 4). A view of the molecule is shown in Fig. 1. Selected bond lengths and angles for the product are listed in Table 1. All bond lengths exhibit typical values (Dias *et al.*, 2017).

## 3. Supramolecular features

The supramolecular arrangements of **I** primarily result from classical and non-classical hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. These contacts were recognized by *Mercury 2022* (Macrae *et al.*, 2020; sum of van der Waals radii plus 0.1 Å). The hydrogen-bonding geometry is listed in Table 2, and the packing of molecules viewed down along the *c* axis is shown in Fig. 2. Together, the hydrogen-bonding interactions lead to the formation of a two-dimensional network parallel to (100). The molecules at (*x*, *y*, *z*) and (2 - *x*, -*y*, 1 - *z*) are components of dimers centered at (1, 0,  $\frac{1}{2}$ ), while the separation between the



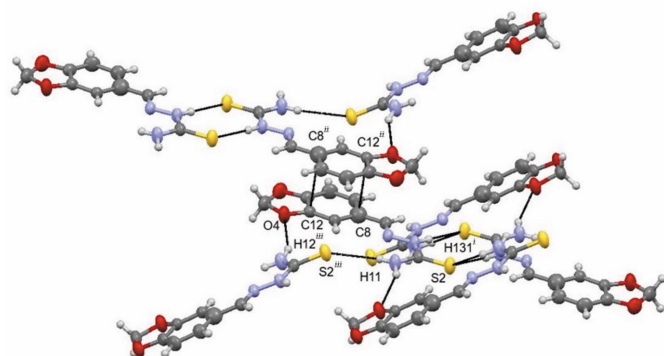


**Figure 1**  
Labelling scheme and structure of **I**. Displacement ellipsoids are drawn at the 50% probability level.

aryl ring centroids is 3.778 (2) Å, indicating  $\pi$ - $\pi$  stacking interactions between the aromatic ring systems.

#### 4. Database Survey

Six crystal structures, authored by different researchers and featuring the [(*E*)-1,3-benzodioxol-5-ylmethylideneamino]-thiourea fragment (piperonal, thiosemicarbazone), have been documented in the Cambridge Structural Database (CSD, WebCSD search December 2023; Groom *et al.*, 2016). The crystal structure here under discussion can be considered the parent compound among those reported in the CSD. These other structures show substitutions in the imine hydrogen with methyl (de Oliveira *et al.*, 2013, 2015*a,b*) or nitro group (Dias *et al.*, 2017), and in the amidic hydrogen with methyl (de Oliveira *et al.*, 2015*b*), ethyl (Dias *et al.* 2017; de Oliveira *et al.*, 2015*a*), and phenyl (Dias *et al.* 2017) radicals. Some of these structures crystallize in the triclinic space group  $P\bar{1}$ , while others in the monoclinic space group  $P2_1/c$ . Finally, Beckford *et al.* (2011), provide detailed information on the crystal structure of [( $\eta^6$ -*p*-cymene)Ru(*p*PhTSC)Cl]Cl, which crystallizes in the monoclinic space group  $P2_1/n$ . All of the structures reveal co-planar arrangements of the piperonal thio-



**Figure 2**  
The molecular dimers of molecule **I** (arbitrary view). Hydrogen bonds and  $\pi$ - $\pi$  stacking interactions are indicated by dotted lines. [Symmetry codes: (i) 1 - *x*, -*y*, 1 - *z*; (ii) 2 - *x*, -*y*, 1 - *z*; (iii) 1 - *x*,  $\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ .]

**Table 1**  
Selected geometric parameters (Å, °).

N1—C3	1.3281 (17)	N5—C6	1.2793 (17)
S2—C3	1.6899 (13)	N5—N13	1.3800 (15)
C3—N13	1.3414 (17)		
S2—C3—N1	122.87 (11)	N1—C3—N13	116.82 (12)
S2—C3—N13	120.31 (10)	C6—N5—N13	117.07 (11)

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H11···N5	0.85 (2)	2.23 (2)	2.6034 (17)	107 (1)
N1—H11···S2 <sup>i</sup>	0.85 (2)	2.84 (2)	3.4805 (14)	134 (1)
N1—H12···O4 <sup>ii</sup>	0.86 (1)	2.32 (2)	3.112 (2)	153 (2)
N13—H131···S2 <sup>iii</sup>	0.86 (1)	2.50 (1)	3.3550 (12)	172 (1)

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

semicarbazone portion along with  $\pi$ - $\pi$  and hydrogen-bonding interactions.

#### 5. Synthesis and crystallization

The synthesis of the Schiff base ligand (1,3-benzodioxol-5-ylformaldehyde) thiosemicarbazone was performed according to a previously published procedure (Casas *et al.*, 2015).

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> S
<i>M<sub>r</sub></i>	223.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.1189 (2), 10.9687 (2), 13.0678 (3)
$\beta$ (°)	100.426 (2)
<i>V</i> (Å <sup>3</sup> )	1003.55 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.31
Crystal size (mm)	0.58 × 0.34 × 0.17
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.88, 0.95
No. of measured, independent and observed [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )] reflections	19600, 3818, 2447
<i>R<sub>int</sub></i>	0.000
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.770
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.040, 0.104, 0.95
No. of reflections	3810
No. of parameters	148
No. of restraints	10
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.38, -0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003) and *Mercury* (Macrae *et al.*, 2020).

Piperonal (1.00 g, 6.66 mmol) and thiosemicarbazide (0.61 g, 6.66 mmol) were dissolved in ethanol and stirred under reflux for 2 h. Upon cooling, the solvent was removed and the remaining solid was recrystallized from ethanol/dichloromethane. Yellowish crystals suitable for X-ray diffraction were grown by slow evaporation after a couple of weeks, yield 78%; m.p. 409–411). FT-IR (ATR,  $\text{cm}^{-1}$ ): 3323  $\nu(\text{N-H})$ , 1585  $\nu(\text{C=N})$ , 1090  $\nu(\text{N-N})$ , 931  $\nu(\text{C=S})$ .

## 6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were all located in difference maps, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å, N–H = 0.86 Å, O–H = 0.82 Å) and  $U_{\text{iso}}(\text{H})$  (in the range 1.2–1.5 times  $U_{\text{eq}}$  of the parent atom), after which the positions were refined with riding constraints.

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## supporting information

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## {[(E)-(1,3-Benzodioxol-5-yl)methylidene]amino}thiourea

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### Computing details

#### {[(E)-(1,3-Benzodioxol-5-yl)methylidene]amino}thiourea

##### Crystal data

$C_9H_9N_3O_2S$	$F(000) = 464$
$M_r = 223.26$	$D_x = 1.478 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ybc	Cell parameters from 3399 reflections
$a = 7.1189 (2) \text{ \AA}$	$\theta = 3.2\text{--}27.6^\circ$
$b = 10.9687 (2) \text{ \AA}$	$\mu = 0.31 \text{ mm}^{-1}$
$c = 13.0678 (3) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 100.426 (2)^\circ$	Tabular, colourless
$V = 1003.55 (4) \text{ \AA}^3$	$0.58 \times 0.34 \times 0.17 \text{ mm}$
$Z = 4$	

##### Data collection

Bruker APEXII diffractometer	3818 independent reflections
Graphite monochromator	2447 reflections with $I > 2.0\sigma(I)$
$\varphi$ & $\omega$ scans	$R_{\text{int}} = 0.000$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 33.2^\circ$ , $\theta_{\text{min}} = 3.2^\circ$
$T_{\text{min}} = 0.88$ , $T_{\text{max}} = 0.95$	$h = -10 \rightarrow 10$
19600 measured reflections	$k = -16 \rightarrow 16$
	$l = -20 \rightarrow 20$

##### Refinement

Refinement on $F^2$	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.31P]$ ,
$wR(F^2) = 0.104$	where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3810 reflections	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
148 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
10 restraints	
Primary atom site location: other	

##### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4666 (2)	0.28730 (12)	0.27357 (10)	0.0521
S2	0.41135 (7)	0.51407 (3)	0.33300 (3)	0.0508
C3	0.4856 (2)	0.36798 (11)	0.35054 (10)	0.0378

O4	0.82417 (18)	-0.24246 (9)	0.43350 (9)	0.0596
N5	0.62732 (16)	0.20875 (9)	0.45653 (9)	0.0383
C6	0.70095 (19)	0.17336 (12)	0.54832 (10)	0.0392
O7	0.96272 (18)	-0.30444 (10)	0.59886 (10)	0.0619
C8	0.76809 (19)	0.04823 (12)	0.56576 (10)	0.0370
C9	0.75307 (19)	-0.03330 (11)	0.48105 (10)	0.0375
C10	0.8517 (2)	0.01062 (15)	0.66540 (11)	0.0497
C11	0.9050 (2)	-0.18475 (13)	0.60146 (12)	0.0451
C12	0.82203 (19)	-0.14781 (12)	0.50257 (11)	0.0389
N13	0.56921 (18)	0.32877 (10)	0.44507 (9)	0.0405
C14	0.9020 (3)	-0.34471 (13)	0.49501 (14)	0.0556
C15	0.9220 (3)	-0.10782 (16)	0.68462 (12)	0.0560
H61	0.7130	0.2267	0.6055	0.0484*
H91	0.6977	-0.0091	0.4133	0.0462*
H101	0.8592	0.0663	0.7228	0.0604*
H141	1.0143	-0.3736	0.4670	0.0677*
H142	0.8011	-0.4081	0.4918	0.0665*
H151	0.9779	-0.1327	0.7520	0.0688*
H12	0.395 (3)	0.3055 (15)	0.2155 (12)	0.0633 (19)*
H131	0.577 (2)	0.3758 (12)	0.4987 (10)	0.0488 (18)*
H11	0.498 (3)	0.2137 (13)	0.2878 (12)	0.0632 (19)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0787 (10)	0.0371 (6)	0.0379 (6)	0.0057 (6)	0.0032 (6)	-0.0042 (5)
S2	0.0777 (3)	0.03268 (16)	0.04106 (19)	0.00766 (16)	0.00842 (17)	0.00264 (13)
C3	0.0442 (7)	0.0321 (6)	0.0381 (6)	-0.0018 (5)	0.0103 (5)	-0.0016 (5)
O4	0.0838 (9)	0.0308 (5)	0.0576 (7)	0.0074 (5)	-0.0046 (6)	0.0013 (4)
N5	0.0428 (6)	0.0299 (5)	0.0426 (6)	0.0028 (4)	0.0086 (5)	-0.0001 (4)
C6	0.0410 (7)	0.0381 (6)	0.0392 (7)	0.0004 (5)	0.0090 (5)	-0.0018 (5)
O7	0.0703 (8)	0.0422 (6)	0.0685 (8)	0.0094 (5)	-0.0002 (6)	0.0207 (5)
C8	0.0353 (6)	0.0380 (6)	0.0376 (6)	-0.0017 (5)	0.0067 (5)	0.0040 (5)
C9	0.0385 (7)	0.0346 (6)	0.0374 (6)	-0.0010 (5)	0.0009 (5)	0.0055 (5)
C10	0.0577 (9)	0.0547 (8)	0.0353 (7)	0.0021 (7)	0.0048 (6)	0.0027 (6)
C11	0.0417 (7)	0.0405 (7)	0.0517 (8)	0.0005 (6)	0.0045 (6)	0.0161 (6)
C12	0.0386 (7)	0.0334 (6)	0.0430 (7)	-0.0029 (5)	0.0027 (5)	0.0046 (5)
N13	0.0534 (7)	0.0310 (5)	0.0362 (6)	0.0055 (5)	0.0060 (5)	-0.0031 (4)
C14	0.0565 (9)	0.0339 (7)	0.0760 (11)	0.0052 (6)	0.0107 (8)	0.0129 (7)
C15	0.0631 (10)	0.0617 (10)	0.0390 (7)	0.0037 (8)	-0.0016 (7)	0.0164 (7)

*Geometric parameters (Å, °)*

N1—C3	1.3281 (17)	C8—C9	1.4120 (18)
N1—H12	0.858 (14)	C8—C10	1.3926 (19)
N1—H11	0.849 (14)	C9—C12	1.3592 (17)
S2—C3	1.6899 (13)	C9—H91	0.941
C3—N13	1.3414 (17)	C10—C15	1.399 (2)

O4—C12	1.3776 (17)	C10—H101	0.961
O4—C14	1.4318 (17)	C11—C12	1.3809 (19)
N5—C6	1.2793 (17)	C11—C15	1.364 (2)
N5—N13	1.3800 (15)	N13—H131	0.864 (13)
C6—C8	1.4576 (18)	C14—H141	0.990
C6—H61	0.941	C14—H142	0.995
O7—C11	1.3779 (18)	C15—H151	0.939
O7—C14	1.418 (2)		
C3—N1—H12	118.5 (11)	C15—C10—H101	118.8
C3—N1—H11	118.8 (11)	O7—C11—C12	109.60 (14)
H12—N1—H11	120.3 (15)	O7—C11—C15	128.71 (13)
S2—C3—N1	122.87 (11)	C12—C11—C15	121.69 (13)
S2—C3—N13	120.31 (10)	C11—C12—O4	109.78 (12)
N1—C3—N13	116.82 (12)	C11—C12—C9	122.83 (13)
C12—O4—C14	105.76 (11)	O4—C12—C9	127.39 (12)
C6—N5—N13	117.07 (11)	N5—N13—C3	118.70 (11)
N5—C6—C8	119.96 (12)	N5—N13—H131	120.5 (9)
N5—C6—H61	121.3	C3—N13—H131	120.5 (9)
C8—C6—H61	118.7	O4—C14—O7	108.25 (12)
C11—O7—C14	106.25 (11)	O4—C14—H141	107.4
C6—C8—C9	119.84 (12)	O7—C14—H141	109.1
C6—C8—C10	119.85 (13)	O4—C14—H142	108.7
C9—C8—C10	120.28 (13)	O7—C14—H142	110.5
C8—C9—C12	116.73 (12)	H141—C14—H142	112.7
C8—C9—H91	121.3	C10—C15—C11	117.03 (13)
C12—C9—H91	122.0	C10—C15—H151	121.0
C8—C10—C15	121.44 (14)	C11—C15—H151	121.9
C8—C10—H101	119.7		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H11 $\cdots$ N5	0.85 (2)	2.23 (2)	2.6034 (17)	107 (1)
N1—H11 $\cdots$ S2 <sup>i</sup>	0.85 (2)	2.84 (2)	3.4805 (14)	134 (1)
N1—H12 $\cdots$ O4 <sup>ii</sup>	0.86 (1)	2.32 (2)	3.112 (2)	153 (2)
N13—H131 $\cdots$ S2 <sup>iii</sup>	0.86 (1)	2.50 (1)	3.3550 (12)	172 (1)

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