

Methyl β -*N*-phenylmethylenedithiocarbazateShang Shan,^{a*} Yan-Ling Zhang^a
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Key indicators

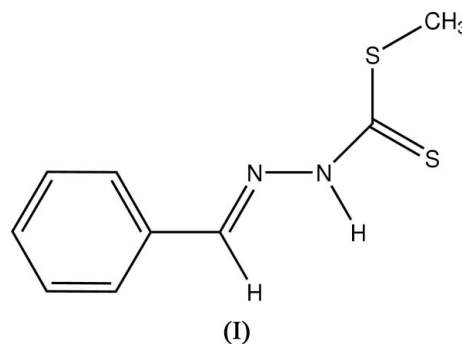
Single-crystal X-ray study
T = 295 K
Mean σ (C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.115
Data-to-parameter ratio = 19.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title compound, C₉H₁₀N₂S₂, were obtained from a condensation reaction of methyl dithiocarbazate and benzaldehyde. The planar dithiocarbazate unit is tilted with respect to the phenyl plane with a dihedral angle of 10.96 (12)°. Intermolecular N–H···S hydrogen bonding stabilizes the crystal structure. A C–H··· π interaction is also observed in the crystal structure.

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Comment

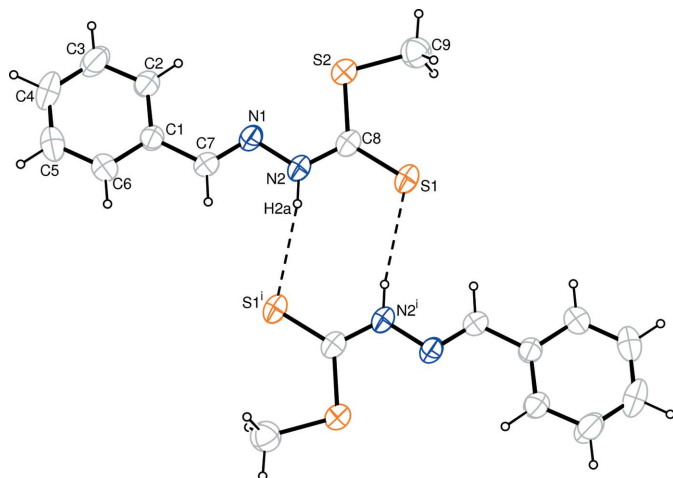
Hydrazine and its derivatives have attracted much attention as they show potential application in the biological field (Okabe *et al.*, 1993; Hu *et al.*, 2001). As part of an ongoing investigation on anticancer compounds, the title compound, (I), has been prepared in our laboratory and its structure is presented here.



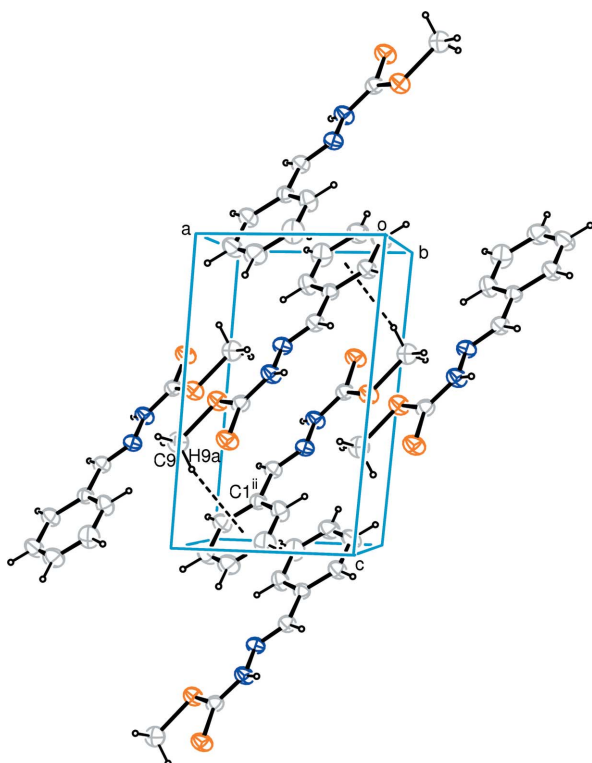
The molecular structure of (I) is shown in Fig. 1. The molecule assumes an *E* configuration; the phenyl ring and dithiocarbazate unit are located on opposite sides of the N1=C7 bond. The dithiocarbazate unit has a planar configuration and is tilted with respect to the phenyl mean plane, forming a dihedral angle of 10.96 (12)°, which agrees well with that of 10.54 (8)° found in a related compound, methyl β -*N*-(3-nitrophenylmethylene)dithiocarbazate (Zhang *et al.*, 2005). The C7–N1–N2–C8 torsion angle of 171.69 (16)° shows the relatively poor coplanarity of the whole molecule.

The C8–N2 bond distance (Table 1) is much shorter than a typical single C–N bond and suggests electron delocalization between the imino and dithiocarboxyl groups.

N–H···S hydrogen bonding is observed between neighboring molecules related by an inversion center (Table 2 and Fig. 1). A C–H··· π interaction occurs in the crystal structure (Fig. 2): C9–H9A···C_g = 144°, H9A···C_g = 2.87 Å and C9···C_g = 3.696 (3) Å, where C_g is the centroid of the C1ⁱⁱ phenyl ring [symmetry code: (ii) 1 – *x*, 1 – *y*, 1 – *z*]. The shortest centroid-to-centroid separation between parallel benzene rings is 4.202 (2) Å, which indicates there is no π - π


Figure 1

The molecular structure of (I) and a hydrogen-bonded neighbor, with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate the hydrogen bonds [symmetry code: (i) $1 - x, -y, 1 - z$].


Figure 2

The packing, showing the C—H... π interactions (dashed lines) between neighboring molecules [symmetry code: (ii) $1 - x, 1 - y, 1 - z$].

stacking between neighboring molecules in the crystal structure of (I).

Experimental

Methyl dithiocarbazate was synthesized in the manner reported previously (Hu *et al.*, 2001). Methyl dithiocarbazate (1.24 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) were dissolved in ethanol (10 ml) and refluxed for 4 h. Fine colorless crystals appeared on

cooling. They were separated and washed with cold water three times. Single crystals of (I) were obtained by recrystallization from absolute ethanol.

Crystal data

$C_9H_{10}N_2S_2$
 $M_r = 210.31$
 Triclinic, $P\bar{1}$
 $a = 5.909$ (2) Å
 $b = 9.411$ (4) Å
 $c = 10.2423$ (18) Å
 $\alpha = 69.929$ (11)°
 $\beta = 80.34$ (2)°
 $\gamma = 78.829$ (15)°
 $V = 521.7$ (3) Å³

$Z = 2$
 $D_x = 1.339$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4400 reflections
 $\theta = 3.5$ – 27.0 °
 $\mu = 0.47$ mm⁻¹
 $T = 295$ (2) K
 Prism, colorless
 $0.43 \times 0.33 \times 0.30$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: none
 5121 measured reflections
 2365 independent reflections

1868 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 27.5$ °
 $h = -7 \rightarrow 6$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.115$
 $S = 1.08$
 2365 reflections
 119 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.23$ e Å⁻³
 $\Delta\rho_{min} = -0.33$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C8	1.6630 (16)	N1—C7	1.263 (2)
S2—C8	1.7442 (18)	N1—N2	1.3755 (18)
S2—C9	1.791 (2)	N2—C8	1.331 (2)
C8—S2—C9	102.05 (9)	N2—C8—S1	120.90 (13)
C7—N1—N2	115.44 (13)	N2—C8—S2	113.69 (11)
C8—N2—N1	120.56 (13)	S1—C8—S2	125.40 (11)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots S1 ⁱ	0.86	2.59	3.431 (2)	168

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and their torsion angles refined to fit the electron density, with $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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