

Terephthalaldehyde bis(thiosemicarbazone) bis(dimethylformamide) solvate

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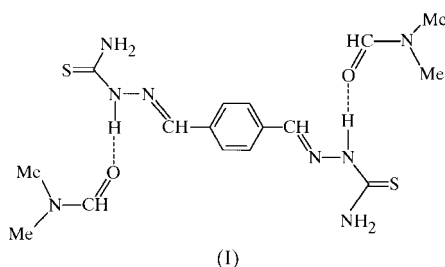
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The thiosemicarbazone molecule in $C_{10}H_{12}N_6S_2 \cdot 2C_3H_7NO$ has $\bar{1}$ symmetry. The thiosemicarbazone moiety and the benzene ring are essentially coplanar, with mean and maximum deviations of 0.03 and 0.11 Å, respectively. The dimethylformamide molecules bridge the thiosemicarbazone moieties, forming two-dimensional sheets through N—H...O hydrogen bonds.

Comment

Recently, there has been considerable interest in the coordination chemistry of thiosemicarbazones because of their biological and carcinostatic activities (Liu *et al.*, 1995; Lukevics *et al.*, 1996) and their non-linear optical properties (Tian *et al.*, 1997; Liu *et al.*, 1999). It has been postulated that extensive electron delocalization in the thiosemicarbazone moiety helps the free thiosemicarbazone ligands and their metal complexes to exhibit SHG (second harmonic generation) efficiency (Tian *et al.*, 1997; Liu *et al.*, 1999). As part of research on non-linear optical materials, specifically thiosemicarbazones and their metal complexes, we report here the crystal structure of a new Schiff base compound derived from thiosemicarbazide and terephthalaldehyde which crystallizes as the dimethylformamide solvate, (I).



The structure of (I) consists of crystallographically imposed $\bar{1}$ symmetry with the thiosemicarbazone and dimethylform-

amide molecules in general positions (Fig. 1). The thiosemicarbazone moiety commonly shows an *E* configuration about both the C1—N2 and C2—N3 bonds. The C—S bond distance of 1.674 (2) Å agrees well with similar bonds in related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (Sutton, 1965). The corresponding C1—N2 bond distance of

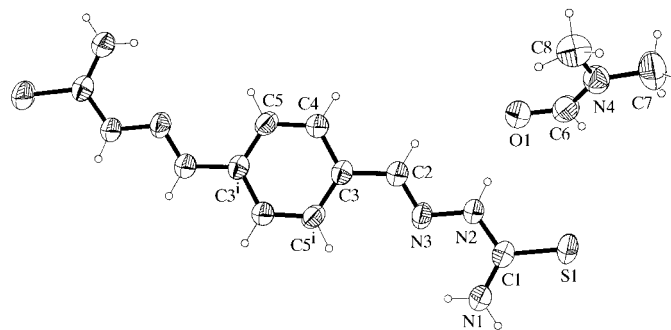


Figure 1

The title compound with the atomic numbering scheme and 50% probability displacement ellipsoids [symmetry code: (i) $1 - x, 2 - y, 1 - z$].

1.352 (3) Å is indicative of some double-bond character, suggesting extensive electron delocalization in the whole molecule. It has been reported (Tian *et al.*, 1997; Liu *et al.*, 1999) that this type of structure helps thiosemicarbazone complexes to exhibit SHG efficiency, however, in this case, the centrosymmetry of both molecules of the title compound and of the space group do not allow the compound to exhibit any SHG efficiency. The C1—N1 bond distance of 1.319 (3) Å is also indicative of some double-bond character, the peak at 8.04 p.p.m. for the amino H atom in the 1H NMR spectrum

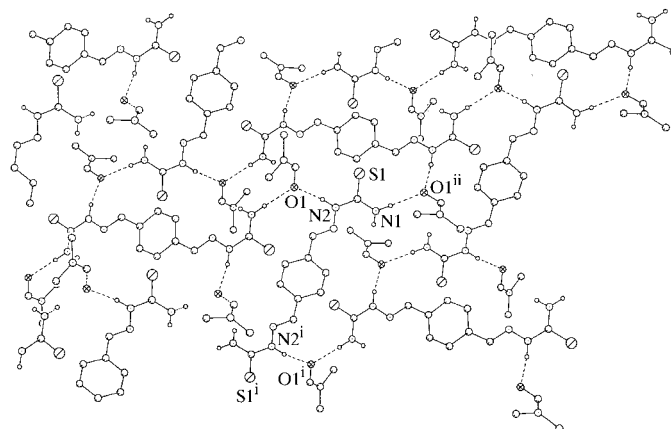


Figure 2

View of the two-dimensional hydrogen-bonded sheets [symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $x, 1 - y, -\frac{1}{2} + z$].

clearly indicates the presence of a resonance form, such as $S^-=C(R)=NH_2^+$. Similar chemical shifts are also observed in other thiosemicarbazones (Tian *et al.*, 1997).

The three H atoms attached to the N1 and N2 atoms have the potential to form donor hydrogen bonds. The intermolecular hydrogen bonds which link the molecules together in the solid state are shown in Fig. 2, and the structure features two-dimensional sheets consolidated by N1—H1B···O1(x , $1 - y$, $-\frac{1}{2} + z$) and N2—H2A···O1 hydrogen bonds, with N···O separations of 2.949 (2) and 2.837 (3) Å, respectively. The H1A···N3 distance of *ca* 2.30 Å is less than a normal van der Waals contact, suggesting a possible intramolecular hydrogen bond, however, the N—H···N angle of *ca* 105° does not support this hypothesis. The C8···S1C(x , $-y$, $\frac{1}{2} + z$) separation of 3.506 (5) Å and the C8—H8B···S1C angle of *ca* 146° also indicates a weak hydrogen bond.

Experimental

The title compound was synthesized by refluxing terephthalaldehyde (0.53 g, 4 mmol) and thiosemicarbazide (0.73 g, 8 mmol) in absolute methanol (50 ml) for 2 h. After cooling to room temperature, the yellow solid which formed was isolated and dried under vacuum (yield 0.96 g). Single crystals suitable for X-ray structure analysis were obtained by the slow evaporation of a dimethylformamide solution in air. ¹H NMR spectrum in *d*₆-dimethyl sulfoxide (p.p.m.): 11.49 [*br*, 2H, N(H)—C=S], 8.24 (*s*, 2H, —CH=N), 8.03 [*br*, 4H, —NH₂], 7.82 (*d*, 4H, Ar—H), 7.94 [*s*, 2H, —C(H)=O], 2.89 (*s*, 6H, N—CH₃), 2.73 (*s*, 6H, N—CH₃).

Crystal data

C ₁₀ H ₁₂ N ₆ S ₂ ·2C ₃ H ₇ NO	$D_x = 1.306 \text{ Mg m}^{-3}$
$M_r = 426.56$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 32 reflections
$a = 28.227 (6) \text{ \AA}$	$\theta = 5.18\text{--}11.74^\circ$
$b = 5.991 (3) \text{ \AA}$	$\mu = 0.274 \text{ mm}^{-1}$
$c = 12.873 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 94.753 (19)^\circ$	Block, yellow
$V = 2169.2 (14) \text{ \AA}^3$	$0.50 \times 0.40 \times 0.40 \text{ mm}$
$Z = 4$	

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.674 (2)	C1—N1	1.319 (3)
N2—C1	1.352 (2)	C2—C3	1.457 (3)
N2—N3	1.373 (2)	C3—C4	1.394 (3)
N3—C2	1.276 (2)	C4—C5	1.375 (3)
C1—N2—N3	119.96 (17)	N3—C2—C3	121.53 (19)
N1—C1—S1	123.34 (15)	C4—C3—C2	119.21 (18)
N2—C1—S1	119.20 (16)	C5—C4—C3	120.99 (19)

Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.028$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.01^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 33$
$T_{\text{min}} = 0.817$, $T_{\text{max}} = 0.938$	$k = -1 \rightarrow 7$
2412 measured reflections	$l = -15 \rightarrow 15$
1902 independent reflections	3 standard reflections
1578 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 9.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 1.5245P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.027$	$\Delta\rho_{\text{max}} = 0.175 \text{ e \AA}^{-3}$
1902 reflections	$\Delta\rho_{\text{min}} = -0.191 \text{ e \AA}^{-3}$
130 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.0036 (6)

H atoms were placed in calculated positions (N—H = 0.86 Å; C—H = 0.93 and 0.96 Å for C_{sp^2} and C_{sp^3} atoms, respectively), assigned fixed U_{iso} values [$U_{\text{iso}} = 1.2U_{\text{eq}}(C_{sp^2}/N)$ and $1.5U_{\text{eq}}(C_{sp^3})$] and allowed to ride.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1278). Services for accessing these data are described at the back of the journal.

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