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1,5-Bis[(1*E*)-(2-methoxyphenyl)methylene]-thiocarbonohydrazide ethanol solvate

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Key indicators

Single-crystal X-ray study
$T = 296$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.162
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{17}H_{18}N_4O_2S \cdot C_2H_5OH$, has been synthesized by the reaction of thiocarbohydrazide with 2-methoxy-benzaldehyde in ethanol. The two aromatic rings are not coplanar, making an angle of 34.8 (2)°. Strong intermolecular (N—H⋯O and O—H⋯N) and weak intermolecular hydrogen bonds (N—H⋯S and C—H⋯O) are found in the crystal structure. These hydrogen bonds link the molecules of the Schiff base and ethanol molecules into an infinite chain. Aromatic stacking interactions are also found in the crystal structure.

Comment

1,5-Bis-Schiff bases of thiocarbohydrazide (TCH) and their metal complexes are of wide interest and have been investigated over recent years. Some of them have biological activities (Liang, 2003; Bacchi *et al.*, 2005), and can be used for the analysis of metals in biological samples to determine trace heavy metals (Vereda-Alonso *et al.*, 1996; Sánchez-Rojas *et al.*, 2004). A few crystal structures of this type of Schiff base have been previously reported (Huang & Yao, 1996; Zhang *et al.*, 2003). We report here the synthesis and the X-ray crystal structure of the title compound, (I).
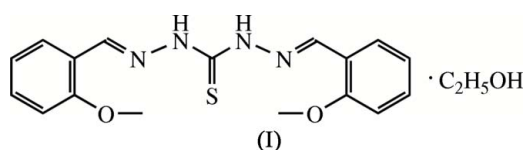
The title compound, (I) (Fig. 1), crystallizes in the space group $P\bar{1}$ with one molecule of ethanol solvent also in the asymmetric unit. Some important bond lengths and angles are given in Table 1. These are comparable to those reported for similar systems (Zhang *et al.*, 2003). The four N atoms and atoms S1 and C9 are nearly coplanar, with a mean deviation of 0.020 (2) Å; this plane makes a dihedral angle of 5.4 (1)° with the C11–C16 benzene ring. The existence of the solvent ethanol molecule forces the C2–C7 benzene ring to twist away from this plane by an angle of 34.8 (2)°. It also forces the N1—N2 bond to change its orientation, forming an s-*cis* S1—C9—N1—N2 configuration rather than the s-*trans* S1—C9—N3—N4 configuration.

The hydrogen-bonding parameters are given in Table 2 and Fig. 2. Both strong intermolecular (N—H⋯O and O—H⋯N) and weak intermolecular hydrogen bonds (N—H⋯S and C—H⋯O) exist in the crystal structure (as shown in Fig. 3). These hydrogen bonds and aromatic stacking interactions link the molecules of the Schiff base and ethanol molecules into an infinite chain.
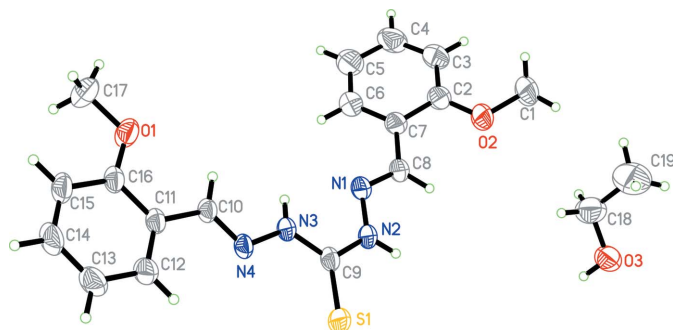
Figure 1
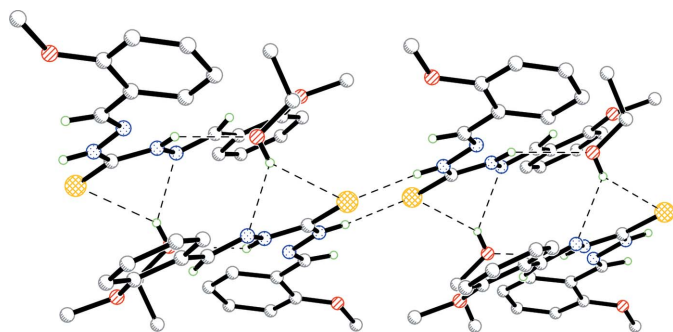The asymmetric unit of (I), showing 30% probability displacement ellipsoids.

Figure 2
The hydrogen bonds (dashed lines) in the packing of (I). H atoms not involved in hydrogen bonds have been omitted for clarity.
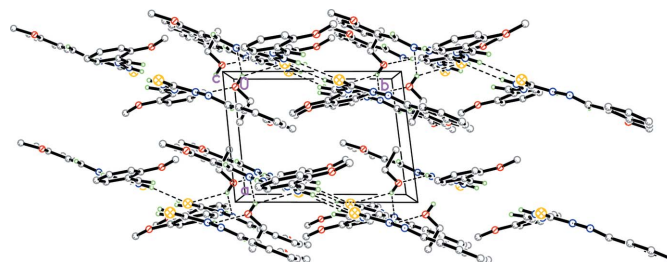

Figure 3
A packing diagram of (I), viewed along the c axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

Experimental

2-Methoxybenzaldehyde (0.545 g, 4 mmol) and thiocarbohydrazide oxide (0.212 g, 2 mmol) were dissolved in ethanol (30 ml) and heated for 5 h under reflux. The solvent was removed using a rotatory evaporator and the residue was recrystallized from ethanol (0.577 g, yield: 81.3%; m.p. 447.5 K). A yellow product was obtained. Single crystals suitable for X-ray diffraction analysis precipitated after several days from the ethanol solution. Analysis calculated for $C_{17}H_{18}N_4O_2S$: C 59.63, H 5.30, N 16.36, S 9.36%; found: C 59.56, H 5.51, N 16.79, S 9.35%. IR (KBr, cm^{-1}): 3440 ν(NH), 1600 ν(C=N), 1533 ν(CS—NH), 1254 ν(C=S).

Crystal data

$C_{17}H_{18}N_4O_2S \cdot C_2H_6O$	$Z = 2$
$M_r = 388.48$	$D_x = 1.282$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.8197$ (8) Å	Cell parameters from 1377
$b = 10.387$ (1) Å	reflections
$c = 12.940$ (1) Å	$\theta = 2.6–21.9°$
$\alpha = 87.547$ (2)°	$\mu = 0.19$ mm^{-1}
$\beta = 74.645$ (2)°	$T = 296$ (2) K
$\gamma = 83.177$ (2)°	Block, yellow
$V = 1006.3$ (2) Å^3	$0.47 \times 0.22 \times 0.11$ mm

Data collection

Bruker APEX-II area-detector diffractometer	3909 independent reflections
φ and ω scans	2509 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.028$
	$\theta_{max} = 26.0°$
$T_{min} = 0.908$, $T_{max} = 0.979$	$h = -9 \rightarrow 9$
7920 measured reflections	$k = -12 \rightarrow 12$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.2726P]$
$wR(F^2) = 0.162$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
3909 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
248 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C16	1.349 (3)	N1—C8	1.277 (3)
O1—C17	1.428 (3)	N1—N2	1.372 (3)
O2—C2	1.350 (4)	N4—C10	1.262 (3)
O2—C1	1.426 (3)	N4—N3	1.385 (2)
O3—C18	1.376 (4)	C9—N3	1.339 (3)
S1—C9	1.670 (3)	C9—N2	1.354 (3)
N1—C8—C7	121.2 (2)	C8—N1—N2	115.8 (2)
N2—C9—S1	120.3 (2)	C9—N2—N1	120.9 (2)
N3—C9—N2	114.3 (2)	C9—N3—N4	120.2 (2)
N3—C9—S1	125.4 (2)	C10—N4—N3	114.3 (2)
N4—C10—C11	122.1 (2)	C16—O1—C17	118.5 (2)
C2—O2—C1	117.2 (3)		

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

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
N2—H2$\cdots$S1^i	0.86	2.59	3.435 (2)	168
O3—H3$\cdots$N4^i	0.82	2.35	3.013 (3)	139
N3—H3B$\cdots$O3^{ii}	0.86	2.47	3.220 (3)	146
C10—H10$\cdots$O3^{ii}	0.93	2.58	3.319 (3)	137

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

H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances of 0.97 (methylene) and 0.96 Å (methyl), and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms. The ethanol solvent molecule may have unresolved disorder and one restraint (DFIX 1.54 0.005) was applied for the distance C18—C19.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *APEX2*; program(s) used to refine structure: *APEX2*; molecular graphics: *APEX2*; software used to prepare material for publication: *APEX2*.

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