

1,5-Bis(4-methoxybenzylidene)thiocarbohydrazide methanol monosolvate

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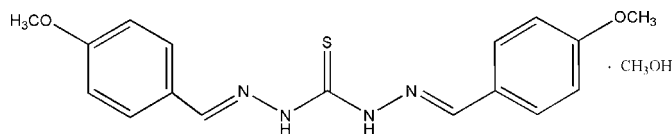
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.047; wR factor = 0.137; data-to-parameter ratio = 13.8.

In the title compound, $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S}\cdot\text{CH}_3\text{OH}$, the two benzene rings in the thiocarbohydrazide molecule form a dihedral angle of 22.42 (18)°. Pairs of $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds link thiocarbohydrazide molecules into centrosymmetric dimers. Methanol solvent molecules serve as donors ($\text{O}-\text{H}\cdots\text{S}$ and $\text{O}-\text{H}\cdots\text{N}$) and acceptors ($\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$) of weak intermolecular hydrogen bonds, which link further these dimers into double ribbons along the b axis.

Related literature

For related Schiff base derivatives of thiocarbohydrazide, see: Loncle *et al.* (2004); Camp *et al.* (2010); Opstal & Verpoort (2003). For a related structure, see: Affan *et al.* (2010).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_2\text{S}\cdot\text{CH}_4\text{O}$
 $M_r = 374.46$
 Triclinic, $P\bar{1}$
 $a = 8.8021$ (6) Å
 $b = 9.9949$ (10) Å
 $c = 11.5902$ (13) Å

$\alpha = 83.132$ (1)°
 $\beta = 84.179$ (2)°
 $\gamma = 70.505$ (1)°
 $V = 952.24$ (16) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.20$ mm⁻¹
 $T = 298$ K

$0.42 \times 0.39 \times 0.32$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.923$, $T_{\max} = 0.940$
 4936 measured reflections
 3302 independent reflections
 1934 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.137$
 $S = 1.01$
 3302 reflections
 239 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3A}\cdots\text{N1}$	0.82	2.55	3.171 (3)	134
$\text{O3}-\text{H3A}\cdots\text{S1}$	0.82	2.58	3.346 (3)	156
$\text{N2}-\text{H2}\cdots\text{O3}^{\text{i}}$	0.86	2.45	3.174 (3)	142
$\text{N3}-\text{H3}\cdots\text{S1}^{\text{ii}}$	0.86	2.61	3.446 (3)	165
$\text{C2}-\text{H2A}\cdots\text{O3}^{\text{i}}$	0.93	2.51	3.300 (4)	143

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5128).

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supplementary materials

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Comment

In recent years, there has been considerable interest in the chemistry of thiocarbohydrazide Schiff base derivatives (Loncle *et al.*, 2004; Camp *et al.*, 2010), because these derivatives offer opportunities for tuning the metal centred electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts (Opstal *et al.*, 2003). Herein we present the title compound, (I).

In (I) (Fig. 1), the bond lengths and angles are normal and correspond to those observed in 1,5-bis[(*E*)-1-(2-hydroxyphenyl)ethylidene] thiocarbohydrazide monohydrate (Affan *et al.*, 2010). Four N atoms and the C=S are almost coplanar, the N1/N2/C2 plane and the benzene ring C3–C8 form a dihedral angle of 12.32 (3)°. The benzene rings C3–C8 and C11–C16 form a dihedral angle of 22.42 (18)°.

In the crystal structure, intermolecular N—H···S hydrogen bonds (Table 1) link the molecules into centrosymmetric dimers. Solvent molecules serve as donors [O—H···S and O—H···N] and acceptors [N—H···O and C—H···O] of the weak intermolecular hydrogen bonds (Table 1), which link further these dimers into doubled ribbons along axis *b*.

Experimental

4-Methoxybenzaldehyde (10.0 mmol), 30 ml ethanol and thiocarbohydrazide (5.0 mmol) were mixed in 50 ml flask. After stirring 3 h at 373 K, the resulting mixture was cooled to room temperature, and recrystallized from ethanol, and afforded the title compound as a crystalline solid.

Refinement

All H atoms were placed in geometrically idealized positions (N—H 0.86; O—H 0.82 and C—H 0.93–0.96 Å) and treated as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}$ of the parent atom.

Figures

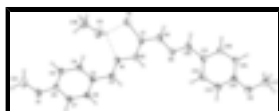


Fig. 1. View of (I) showing the atomic numbering and 30% probability displacement ellipsoids. Dashed lines denote hydrogen bonds.

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Crystal data

C₁₇H₁₈N₄O₂S·CH₄O

Z = 2

supplementary materials

$M_r = 374.46$	$F(000) = 396$
Triclinic, $P\bar{1}$	$D_x = 1.306 \text{ Mg m}^{-3}$
$a = 8.8021 (6) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 9.9949 (10) \text{ \AA}$	Cell parameters from 1379 reflections
$c = 11.5902 (13) \text{ \AA}$	$\theta = 2.7\text{--}25.2^\circ$
$\alpha = 83.132 (1)^\circ$	$\mu = 0.20 \text{ mm}^{-1}$
$\beta = 84.179 (2)^\circ$	$T = 298 \text{ K}$
$\gamma = 70.505 (1)^\circ$	Block, red
$V = 952.24 (16) \text{ \AA}^3$	$0.42 \times 0.39 \times 0.32 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3302 independent reflections
Radiation source: fine-focus sealed tube graphite	1934 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.7^\circ$
$T_{\text{min}} = 0.923$, $T_{\text{max}} = 0.940$	$h = -7 \rightarrow 10$
4936 measured reflections	$k = -11 \rightarrow 11$
	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.137$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.1975P]$
3302 reflections	where $P = (F_o^2 + 2F_c^2)/3$
239 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.63183 (11)	0.63686 (9)	-0.08592 (7)	0.0604 (3)
N1	0.6991 (3)	0.8790 (2)	-0.00620 (19)	0.0435 (6)
N2	0.6220 (3)	0.8089 (2)	0.07669 (19)	0.0445 (6)
H2	0.5951	0.8368	0.1454	0.053*
N3	0.5206 (3)	0.6273 (2)	0.1308 (2)	0.0487 (7)
H3	0.5021	0.5523	0.1154	0.058*
N4	0.4772 (3)	0.6718 (2)	0.2409 (2)	0.0458 (6)
O1	1.0808 (3)	1.2665 (2)	-0.28491 (19)	0.0653 (7)
O2	0.1682 (3)	0.6793 (2)	0.76724 (19)	0.0688 (7)
C1	0.5902 (3)	0.6955 (3)	0.0468 (2)	0.0424 (7)
C2	0.7256 (3)	0.9876 (3)	0.0215 (2)	0.0412 (7)
H2A	0.6890	1.0203	0.0944	0.049*
C3	0.8135 (3)	1.0612 (3)	-0.0612 (2)	0.0388 (7)
C4	0.8918 (4)	1.0014 (3)	-0.1615 (2)	0.0471 (8)
H4A	0.8839	0.9150	-0.1773	0.057*
C5	0.9813 (4)	1.0662 (3)	-0.2389 (3)	0.0522 (8)
H5	1.0332	1.0239	-0.3057	0.063*
C6	0.9927 (4)	1.1946 (3)	-0.2158 (3)	0.0463 (8)
C7	0.9135 (3)	1.2564 (3)	-0.1173 (3)	0.0473 (8)
H7	0.9189	1.3442	-0.1029	0.057*
C8	0.8264 (3)	1.1902 (3)	-0.0399 (2)	0.0439 (7)
H8	0.7757	1.2323	0.0272	0.053*
C9	1.1754 (5)	1.1998 (4)	-0.3814 (3)	0.0838 (12)
H9A	1.1057	1.1927	-0.4373	0.126*
H9B	1.2437	1.1062	-0.3555	0.126*
H9C	1.2410	1.2554	-0.4168	0.126*
C10	0.3907 (4)	0.6071 (3)	0.3027 (3)	0.0501 (8)
H10	0.3638	0.5391	0.2686	0.060*
C11	0.3309 (4)	0.6312 (3)	0.4222 (2)	0.0458 (8)
C12	0.3712 (4)	0.7200 (3)	0.4869 (3)	0.0589 (9)
H12	0.4377	0.7710	0.4525	0.071*
C13	0.3152 (4)	0.7345 (3)	0.6009 (3)	0.0639 (10)
H13	0.3445	0.7943	0.6433	0.077*
C14	0.2149 (4)	0.6601 (3)	0.6531 (3)	0.0498 (8)
C15	0.1720 (4)	0.5731 (3)	0.5907 (3)	0.0540 (8)
H15	0.1037	0.5236	0.6248	0.065*
C16	0.2307 (4)	0.5589 (3)	0.4766 (3)	0.0573 (9)
H16	0.2017	0.4984	0.4347	0.069*
C17	0.0688 (5)	0.6007 (4)	0.8248 (3)	0.0738 (11)
H17A	0.1258	0.5005	0.8237	0.111*
H17B	-0.0289	0.6249	0.7854	0.111*
H17C	0.0429	0.6239	0.9040	0.111*
O3	0.5382 (3)	0.9498 (3)	-0.2485 (2)	0.0849 (8)
H3A	0.5673	0.8888	-0.1940	0.127*
C18	0.6365 (5)	0.9076 (5)	-0.3470 (3)	0.0884 (13)

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H18A	0.5743	0.9401	-0.4144	0.133*
H18B	0.6812	0.8055	-0.3413	0.133*
H18C	0.7224	0.9477	-0.3540	0.133*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0755 (7)	0.0533 (5)	0.0593 (5)	-0.0349 (5)	0.0242 (5)	-0.0148 (4)
N1	0.0458 (15)	0.0437 (14)	0.0427 (14)	-0.0205 (12)	0.0033 (12)	0.0020 (11)
N2	0.0531 (16)	0.0473 (14)	0.0359 (13)	-0.0236 (13)	0.0047 (12)	-0.0001 (11)
N3	0.0550 (16)	0.0413 (14)	0.0514 (15)	-0.0228 (13)	0.0114 (13)	-0.0019 (12)
N4	0.0468 (16)	0.0451 (14)	0.0437 (15)	-0.0162 (13)	0.0036 (12)	0.0016 (12)
O1	0.0743 (16)	0.0593 (14)	0.0680 (15)	-0.0371 (13)	0.0204 (13)	-0.0045 (12)
O2	0.0862 (18)	0.0785 (16)	0.0553 (14)	-0.0468 (14)	0.0218 (13)	-0.0227 (12)
C1	0.0329 (17)	0.0382 (16)	0.0516 (18)	-0.0106 (14)	0.0059 (14)	0.0037 (14)
C2	0.0401 (18)	0.0455 (17)	0.0389 (16)	-0.0152 (14)	-0.0007 (14)	-0.0048 (13)
C3	0.0348 (16)	0.0412 (16)	0.0418 (16)	-0.0138 (13)	-0.0008 (13)	-0.0056 (13)
C4	0.0506 (19)	0.0429 (17)	0.0529 (19)	-0.0220 (15)	0.0043 (16)	-0.0104 (15)
C5	0.059 (2)	0.0518 (19)	0.0490 (18)	-0.0235 (17)	0.0127 (16)	-0.0134 (15)
C6	0.0450 (19)	0.0436 (18)	0.0522 (19)	-0.0202 (15)	-0.0008 (15)	0.0028 (15)
C7	0.0495 (19)	0.0382 (17)	0.0580 (19)	-0.0193 (15)	0.0007 (16)	-0.0082 (15)
C8	0.0434 (18)	0.0430 (17)	0.0474 (18)	-0.0158 (15)	0.0011 (15)	-0.0109 (14)
C9	0.087 (3)	0.075 (3)	0.084 (3)	-0.033 (2)	0.040 (2)	-0.004 (2)
C10	0.056 (2)	0.0481 (18)	0.0496 (19)	-0.0248 (16)	-0.0010 (16)	0.0049 (15)
C11	0.0470 (19)	0.0447 (17)	0.0461 (18)	-0.0194 (15)	0.0039 (15)	0.0011 (14)
C12	0.067 (2)	0.054 (2)	0.065 (2)	-0.0360 (18)	0.0159 (19)	-0.0095 (17)
C13	0.077 (3)	0.060 (2)	0.068 (2)	-0.041 (2)	0.014 (2)	-0.0211 (17)
C14	0.053 (2)	0.0495 (18)	0.0498 (19)	-0.0210 (16)	0.0049 (16)	-0.0088 (15)
C15	0.060 (2)	0.063 (2)	0.0486 (19)	-0.0372 (18)	0.0078 (16)	-0.0024 (16)
C16	0.074 (2)	0.063 (2)	0.049 (2)	-0.0430 (19)	0.0036 (18)	-0.0061 (16)
C17	0.089 (3)	0.092 (3)	0.052 (2)	-0.049 (2)	0.019 (2)	-0.0131 (19)
O3	0.095 (2)	0.0784 (18)	0.0610 (16)	-0.0093 (15)	0.0104 (15)	0.0029 (13)
C18	0.091 (3)	0.115 (3)	0.062 (2)	-0.040 (3)	0.002 (2)	-0.003 (2)

Geometric parameters (\AA , $^\circ$)

S1—C1	1.673 (3)	C8—H8	0.9300
N1—C2	1.267 (3)	C9—H9A	0.9600
N1—N2	1.377 (3)	C9—H9B	0.9600
N2—C1	1.346 (3)	C9—H9C	0.9600
N2—H2	0.8600	C10—C11	1.449 (4)
N3—C1	1.337 (3)	C10—H10	0.9300
N3—N4	1.377 (3)	C11—C12	1.378 (4)
N3—H3	0.8600	C11—C16	1.379 (4)
N4—C10	1.272 (3)	C12—C13	1.369 (4)
O1—C6	1.367 (3)	C12—H12	0.9300
O1—C9	1.417 (4)	C13—C14	1.385 (4)
O2—C14	1.362 (3)	C13—H13	0.9300
O2—C17	1.429 (4)	C14—C15	1.359 (4)

C2—C3	1.455 (4)	C15—C16	1.376 (4)
C2—H2A	0.9300	C15—H15	0.9300
C3—C4	1.383 (4)	C16—H16	0.9300
C3—C8	1.384 (4)	C17—H17A	0.9600
C4—C5	1.379 (4)	C17—H17B	0.9600
C4—H4A	0.9300	C17—H17C	0.9600
C5—C6	1.379 (4)	O3—C18	1.380 (4)
C5—H5	0.9300	O3—H3A	0.8200
C6—C7	1.375 (4)	C18—H18A	0.9600
C7—C8	1.374 (4)	C18—H18B	0.9600
C7—H7	0.9300	C18—H18C	0.9600
C2—N1—N2	117.7 (2)	O1—C9—H9C	109.5
C1—N2—N1	117.9 (2)	H9A—C9—H9C	109.5
C1—N2—H2	121.0	H9B—C9—H9C	109.5
N1—N2—H2	121.0	N4—C10—C11	125.0 (3)
C1—N3—N4	122.9 (2)	N4—C10—H10	117.5
C1—N3—H3	118.5	C11—C10—H10	117.5
N4—N3—H3	118.5	C12—C11—C16	117.2 (3)
C10—N4—N3	113.5 (3)	C12—C11—C10	124.0 (3)
C6—O1—C9	117.8 (2)	C16—C11—C10	118.7 (3)
C14—O2—C17	117.2 (2)	C13—C12—C11	121.2 (3)
N3—C1—N2	116.1 (3)	C13—C12—H12	119.4
N3—C1—S1	119.4 (2)	C11—C12—H12	119.4
N2—C1—S1	124.5 (2)	C12—C13—C14	120.1 (3)
N1—C2—C3	119.8 (3)	C12—C13—H13	120.0
N1—C2—H2A	120.1	C14—C13—H13	120.0
C3—C2—H2A	120.1	C15—C14—O2	124.4 (3)
C4—C3—C8	118.0 (3)	C15—C14—C13	119.8 (3)
C4—C3—C2	120.8 (3)	O2—C14—C13	115.7 (3)
C8—C3—C2	121.2 (3)	C14—C15—C16	119.2 (3)
C5—C4—C3	121.9 (3)	C14—C15—H15	120.4
C5—C4—H4A	119.0	C16—C15—H15	120.4
C3—C4—H4A	119.0	C15—C16—C11	122.4 (3)
C6—C5—C4	119.1 (3)	C15—C16—H16	118.8
C6—C5—H5	120.4	C11—C16—H16	118.8
C4—C5—H5	120.4	O2—C17—H17A	109.5
O1—C6—C7	116.3 (3)	O2—C17—H17B	109.5
O1—C6—C5	124.1 (3)	H17A—C17—H17B	109.5
C7—C6—C5	119.6 (3)	O2—C17—H17C	109.5
C8—C7—C6	120.9 (3)	H17A—C17—H17C	109.5
C8—C7—H7	119.6	H17B—C17—H17C	109.5
C6—C7—H7	119.6	C18—O3—H3A	109.5
C7—C8—C3	120.5 (3)	O3—C18—H18A	109.5
C7—C8—H8	119.8	O3—C18—H18B	109.5
C3—C8—H8	119.8	H18A—C18—H18B	109.5
O1—C9—H9A	109.5	O3—C18—H18C	109.5
O1—C9—H9B	109.5	H18A—C18—H18C	109.5
H9A—C9—H9B	109.5	H18B—C18—H18C	109.5

supplementary materials

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>
O3—H3A···N1	0.82	2.55	3.171 (3)	134.
O3—H3A···S1	0.82	2.58	3.346 (3)	156.
N2—H2···O3 ⁱ	0.86	2.45	3.174 (3)	142.
N3—H3···S1 ⁱⁱ	0.86	2.61	3.446 (3)	165.
C2—H2A···O3 ⁱ	0.93	2.51	3.300 (4)	143.

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

Fig. 1

