

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(5Z)-5-(2-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol hemisolvateDurre Shahwar,^a M. Nawaz Tahir,^{b*} Muhammad Asam Raza,^a Bushra Iqbal^a and Sana Naz^a^aDepartment of Chemistry, Government College University, Lahore, Pakistan, and^bDepartment of Physics, University of Sargodha, Sargodha, Pakistan

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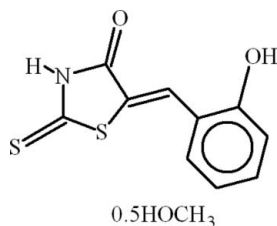
Received 22 September 2009; accepted 29 September 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in solvent or counterion; R factor = 0.044; wR factor = 0.101; data-to-parameter ratio = 15.8.

In the title compound, $\text{C}_{10}\text{H}_7\text{NO}_2\text{S}_2 \cdot 0.5\text{CH}_3\text{OH}$, the dihedral angle between the aromatic rings is 11.43 (11)° and a short intramolecular $\text{C}-\text{H} \cdots \text{S}$ contact occurs. The methanol solvent molecule is equally disordered over two sets of sites. In the crystal, inversion dimers linked by pairs of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds occur. The methanol solvent molecule connects the dimers through $\text{O}-\text{H} \cdots \text{S}$ and $\text{O}-\text{H} \cdots \text{O}$ intermolecular hydrogen bonds. Further stability is afforded by $\text{C}-\text{H} \cdots \pi$ and $\pi-\pi$ interactions [centroid-centroid separation = 3.5948 (13) Å].

Related literature

For related structures, see: Barreiro *et al.* (2007); Delgado *et al.* (2006). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_7\text{NO}_2\text{S}_2 \cdot 0.5\text{CH}_4\text{O}$ $M_r = 253.33$ Monoclinic, $C2/c$ $a = 20.4859$ (16) Å $b = 6.4422$ (4) Å $c = 18.4377$ (15) Å $\beta = 108.724$ (4)° $V = 2304.5$ (3) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.45$ mm⁻¹
 $T = 296$ K $0.28 \times 0.15 \times 0.12$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.925$, $T_{\max} = 0.947$

11803 measured reflections

2636 independent reflections

1562 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.101$ $S = 1.03$

2636 reflections

167 parameters

8 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1N} \cdots \text{O2}^i$	0.86	1.95	2.811 (2)	173
$\text{O1}-\text{H1O} \cdots \text{O11}^{ii}$	0.82	1.95	2.735 (7)	159
$\text{O1}-\text{H1O} \cdots \text{O11}^{iii}$	0.82	2.06	2.871 (7)	169
$\text{O11}-\text{H11} \cdots \text{S2}^i$	0.84 (3)	2.80 (5)	3.317 (8)	122 (4)
$\text{C6}-\text{H6} \cdots \text{S1}$	0.93	2.57	3.264 (3)	132
$\text{C4}-\text{H4} \cdots \text{Cg2}^{iv}$	0.93	2.81	3.599 (3)	143

Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $x, y - 1, z$; (iii) $-x, y - 1, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$. Cg2 is centroid of the C1–C6 benzene ring.

Data collection: APEX2 (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: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

MAR gratefully acknowledges the Higher Education Commission, Islamabad, Pakistan, for providing him with a Scholaship under the Indigenous PhD Program (PIN 042–111212-PS2–200).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5115).

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supplementary materials

Acta Cryst. (2009). E65, o2637 [doi:10.1107/S1600536809039555]

(5Z)-5-(2-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol hemisolvate

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Comment

The title compound (I, Fig. 1) has been prepared owing to medicinal properties of rhodanine derivatives.

The crystal structure of (II) (Z)-5-(2-Fluorobenzylidene)-2-thioxothiazolidin-4-one (Delgado *et al.*, 2006) and (III) 5-(2-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one dimethylsulfoxide solvate (Barreiro, *et al.*, 2007) have been published. The title compound (I) differs from (III) due to solvate i.e methanol instead of dimethylsulfoxide.

The title molecule basically consists of dimers due to intermolecular H-bondings of N—H \cdots O type with $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995). There exist a strong intermolecular H-bonding of C—H \cdots S type and two weak intramolecular H-bondings of C—H \cdots O (Table 1, Fig. 2) forming a twisted S(6) and two planar S(5) ring motifs. In (I), the 2-Hydroxybenzylidene moiety A (C1—C7/O1) and the rhodanine moiety B (C8/C9/N1/C10/S1/S2/O2) are planar with maximum r.m.s. deviations of 0.0042 and 0.0044 Å, respectively from their mean square planes. The dihedral angle between A/B is 11.35 (10)°. The methanol solvent of crystallization connects the dimers through O—H \cdots S and O—H \cdots O intermolecular H-bondings and form another ring motif $R_3^3(10)$ (Fig. 2). The molecules are stabilized in the form of two dimensional polymeric networks due to C—H \cdots π interaction (Table 1) and π — π interactions between the centroids of heterocyclic ring Cg1 (C8/C9/N1/C10/S1) and the benzene ring Cg2 (C1—C6). The distance between Cg1 \cdots Cg2ⁱ [symmetry code i = x, 1 + y, z] and Cg2—Cg1ⁱⁱ [symmetry code ii = x, -1 + y, z] is 3.5948 (13) Å.

Experimental

Rhodanine (0.266 g, 0.2 mol), salicylaldehyde (0.244 g, 0.2 mol) and K₂CO₃ (0.553 g, 0.4 mol) were dissolved in 10 ml distilled water at room temperature. The stirring was continued for 24 h and reaction was monitored by TLC. The precipitates were formed during neutralization of the reaction mixture with 5% HCl. The precipitates were filtered off and washed with saturated solution of NaCl. The crude material obtained was recrystallized in methanol to afford light red needles of (I).

Refinement

The multiplicity factor of C and O atom of methanol was initially refined and later it was fixed to 0.5.

The coordinates of H-atom of hydroxy group were refined. The coordinates of H-atoms of methanol were also refined with constraints. The H-atoms were positioned geometrically with N—H = 0.86, C—H = 0.93 Å for aromatic like H atoms and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C, N, O)$, where $x = 1.5$ for methyl H-atoms and $x = 1.2$ for all other H atoms.

Figures

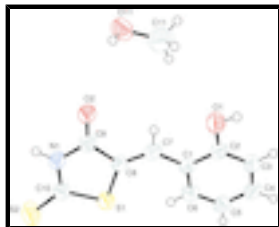


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radius.

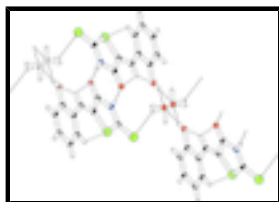


Fig. 2. The partial packing of (I), which shows that molecules form dimers and dimers are connected to each other with the help of methanol by intermolecular H-bondings. The double dotted lines represent intramolecular H-bondings.

(5*Z*)-5-(2-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol hemisolvate

Crystal data

$C_{10}H_7NO_2S_2 \cdot 0.5CH_4O$

$M_r = 253.33$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 20.4859\ (16)\ \text{\AA}$

$b = 6.4422\ (4)\ \text{\AA}$

$c = 18.4377\ (15)\ \text{\AA}$

$\beta = 108.724\ (4)^\circ$

$V = 2304.5\ (3)\ \text{\AA}^3$

$Z = 8$

$F_{000} = 1048$

$D_x = 1.460\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2636 reflections

$\theta = 2.1\text{--}27.5^\circ$

$\mu = 0.45\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Cut needle, light red

$0.28 \times 0.15 \times 0.12\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $7.50\ \text{pixels mm}^{-1}$

$T = 296\ \text{K}$

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2005)

$T_{\min} = 0.925$, $T_{\max} = 0.947$

11803 measured reflections

2636 independent reflections

1562 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -22 \rightarrow 26$

$k = -5 \rightarrow 8$

$l = -23 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 1.2743P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2636 reflections	$(\Delta/\sigma)_{\max} < 0.001$
167 parameters	$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
8 restraints	$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: ?

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.15938 (4)	0.58242 (10)	-0.00444 (4)	0.0600 (2)	
S2	0.14589 (4)	0.94002 (13)	-0.11023 (5)	0.0802 (3)	
O1	0.06021 (9)	0.1385 (3)	0.18770 (11)	0.0619 (7)	
O2	0.01091 (8)	0.7729 (2)	0.06117 (9)	0.0516 (6)	
N1	0.06936 (9)	0.8655 (3)	-0.02055 (10)	0.0467 (7)	
C1	0.14189 (11)	0.2372 (3)	0.12922 (12)	0.0389 (7)	
C2	0.12016 (12)	0.0955 (3)	0.17442 (12)	0.0428 (8)	
C3	0.15870 (12)	-0.0790 (4)	0.20299 (13)	0.0485 (8)	
C4	0.21827 (13)	-0.1171 (4)	0.18715 (13)	0.0531 (9)	
C5	0.24140 (13)	0.0198 (4)	0.14359 (14)	0.0566 (9)	
C6	0.20350 (13)	0.1944 (4)	0.11522 (13)	0.0512 (9)	
C7	0.10043 (11)	0.4192 (3)	0.10120 (12)	0.0422 (8)	
C8	0.10408 (11)	0.5631 (3)	0.05020 (12)	0.0396 (7)	
C9	0.05620 (11)	0.7391 (3)	0.03308 (12)	0.0405 (8)	
C10	0.12115 (12)	0.8120 (4)	-0.04789 (13)	0.0502 (8)	
O11	-0.0100 (5)	0.8280 (6)	0.2318 (3)	0.066 (3)	0.500
C11	0.014 (2)	0.6235 (11)	0.262 (3)	0.112 (14)	0.500

supplementary materials

H1N	0.04538	0.97578	-0.03643	0.0561*	
H1O	0.04906	0.03909	0.20888	0.0743*	
H3	0.14403	-0.17151	0.23327	0.0582*	
H4	0.24344	-0.23670	0.20598	0.0637*	
H5	0.28232	-0.00571	0.13348	0.0680*	
H6	0.21932	0.28673	0.08585	0.0614*	
H7	0.06521	0.44009	0.12207	0.0507*	
H11	-0.035 (3)	0.804 (7)	0.1868 (16)	0.0792*	0.500
H11A	-0.012 (4)	0.500 (7)	0.244 (5)	0.1677*	0.500
H11B	0.019 (4)	0.608 (13)	0.316 (4)	0.1677*	0.500
H11C	0.058 (3)	0.572 (11)	0.265 (5)	0.1677*	0.500

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0676 (4)	0.0634 (4)	0.0594 (4)	0.0280 (4)	0.0349 (4)	0.0186 (3)
S2	0.0750 (5)	0.0963 (6)	0.0837 (6)	0.0304 (4)	0.0457 (4)	0.0451 (5)
O1	0.0609 (11)	0.0550 (11)	0.0805 (13)	0.0130 (9)	0.0376 (10)	0.0213 (9)
O2	0.0495 (10)	0.0516 (10)	0.0591 (11)	0.0152 (8)	0.0249 (9)	0.0124 (8)
N1	0.0446 (12)	0.0464 (11)	0.0511 (12)	0.0133 (9)	0.0180 (10)	0.0116 (10)
C1	0.0446 (13)	0.0359 (12)	0.0364 (13)	0.0055 (10)	0.0131 (10)	-0.0019 (10)
C2	0.0448 (13)	0.0401 (13)	0.0433 (13)	0.0031 (11)	0.0137 (11)	-0.0050 (11)
C3	0.0596 (16)	0.0406 (13)	0.0448 (14)	0.0038 (12)	0.0162 (12)	0.0050 (11)
C4	0.0631 (17)	0.0431 (14)	0.0490 (15)	0.0180 (12)	0.0124 (13)	0.0002 (12)
C5	0.0598 (16)	0.0600 (16)	0.0560 (16)	0.0212 (13)	0.0269 (13)	0.0061 (13)
C6	0.0589 (16)	0.0516 (15)	0.0481 (15)	0.0113 (13)	0.0243 (12)	0.0067 (12)
C7	0.0425 (13)	0.0409 (13)	0.0439 (13)	0.0037 (10)	0.0148 (11)	-0.0049 (11)
C8	0.0422 (13)	0.0374 (12)	0.0387 (12)	0.0049 (10)	0.0123 (10)	-0.0002 (11)
C9	0.0385 (13)	0.0410 (13)	0.0394 (13)	0.0029 (11)	0.0087 (11)	-0.0007 (11)
C10	0.0483 (14)	0.0550 (15)	0.0468 (15)	0.0131 (12)	0.0146 (12)	0.0081 (12)
O11	0.082 (7)	0.067 (2)	0.049 (5)	-0.007 (2)	0.022 (5)	-0.0010 (19)
C11	0.16 (3)	0.063 (3)	0.15 (3)	-0.004 (7)	0.10 (2)	0.002 (8)

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

S1—C8	1.745 (2)	C2—C3	1.378 (3)
S1—C10	1.744 (3)	C3—C4	1.365 (4)
S2—C10	1.622 (3)	C4—C5	1.375 (4)
O1—C2	1.356 (3)	C5—C6	1.372 (4)
O2—C9	1.219 (3)	C7—C8	1.340 (3)
O1—H1O	0.8200	C8—C9	1.466 (3)
O11—C11	1.45 (2)	C3—H3	0.9300
O11—H11	0.84 (3)	C4—H4	0.9300
N1—C9	1.373 (3)	C5—H5	0.9300
N1—C10	1.357 (3)	C6—H6	0.9300
N1—H1N	0.8600	C7—H7	0.9300
C1—C7	1.443 (3)	C11—H11A	0.96 (6)
C1—C2	1.402 (3)	C11—H11B	0.97 (9)
C1—C6	1.395 (4)	C11—H11C	0.95 (8)

C8—S1—C10	92.67 (11)	O2—C9—C8	126.50 (19)
C2—O1—H1O	109.00	O2—C9—N1	123.54 (19)
C11—O11—H11	104 (4)	S1—C10—S2	124.08 (16)
C9—N1—C10	118.3 (2)	S2—C10—N1	126.4 (2)
C10—N1—H1N	121.00	S1—C10—N1	109.52 (17)
C9—N1—H1N	121.00	C4—C3—H3	120.00
C2—C1—C7	118.7 (2)	C2—C3—H3	120.00
C2—C1—C6	117.4 (2)	C3—C4—H4	120.00
C6—C1—C7	123.9 (2)	C5—C4—H4	120.00
O1—C2—C3	122.6 (2)	C6—C5—H5	120.00
O1—C2—C1	116.96 (19)	C4—C5—H5	120.00
C1—C2—C3	120.4 (2)	C1—C6—H6	119.00
C2—C3—C4	120.5 (2)	C5—C6—H6	119.00
C3—C4—C5	120.6 (2)	C1—C7—H7	115.00
C4—C5—C6	119.3 (3)	C8—C7—H7	115.00
C1—C6—C5	121.8 (2)	O11—C11—H11A	123 (6)
C1—C7—C8	130.9 (2)	O11—C11—H11B	113 (6)
S1—C8—C9	109.51 (15)	O11—C11—H11C	123 (6)
C7—C8—C9	120.2 (2)	H11A—C11—H11B	98 (8)
S1—C8—C7	130.34 (18)	H11A—C11—H11C	98 (7)
N1—C9—C8	109.96 (19)	H11B—C11—H11C	97 (8)
C10—S1—C8—C7	179.8 (2)	C2—C1—C7—C8	-170.5 (2)
C10—S1—C8—C9	0.0 (2)	C6—C1—C7—C8	10.7 (4)
C8—S1—C10—S2	179.12 (17)	O1—C2—C3—C4	179.1 (2)
C8—S1—C10—N1	0.05 (18)	C1—C2—C3—C4	-0.5 (3)
C10—N1—C9—O2	-179.9 (2)	C2—C3—C4—C5	1.2 (4)
C10—N1—C9—C8	0.1 (3)	C3—C4—C5—C6	-0.8 (4)
C9—N1—C10—S1	-0.1 (3)	C4—C5—C6—C1	-0.1 (4)
C9—N1—C10—S2	-179.14 (18)	C1—C7—C8—S1	2.0 (4)
C6—C1—C2—O1	180.0 (2)	C1—C7—C8—C9	-178.2 (2)
C6—C1—C2—C3	-0.4 (3)	S1—C8—C9—O2	179.96 (19)
C7—C1—C2—O1	1.1 (3)	S1—C8—C9—N1	-0.1 (2)
C7—C1—C2—C3	-179.3 (2)	C7—C8—C9—O2	0.1 (3)
C2—C1—C6—C5	0.7 (3)	C7—C8—C9—N1	-179.90 (19)
C7—C1—C6—C5	179.5 (2)		

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>
N1—H1N...O2 ⁱ	0.86	1.95	2.811 (2)	173
O1—H1O...O11 ⁱⁱ	0.82	1.95	2.735 (7)	159
O1—H1O...O11 ⁱⁱⁱ	0.82	2.06	2.871 (7)	169
O11—H11...S2 ⁱ	0.84 (3)	2.80 (5)	3.317 (8)	122 (4)
C6—H6...S1	0.93	2.57	3.264 (3)	132
C4—H4...Cg2 ^{iv}	0.93	2.81	3.599 (3)	143

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

Fig. 1

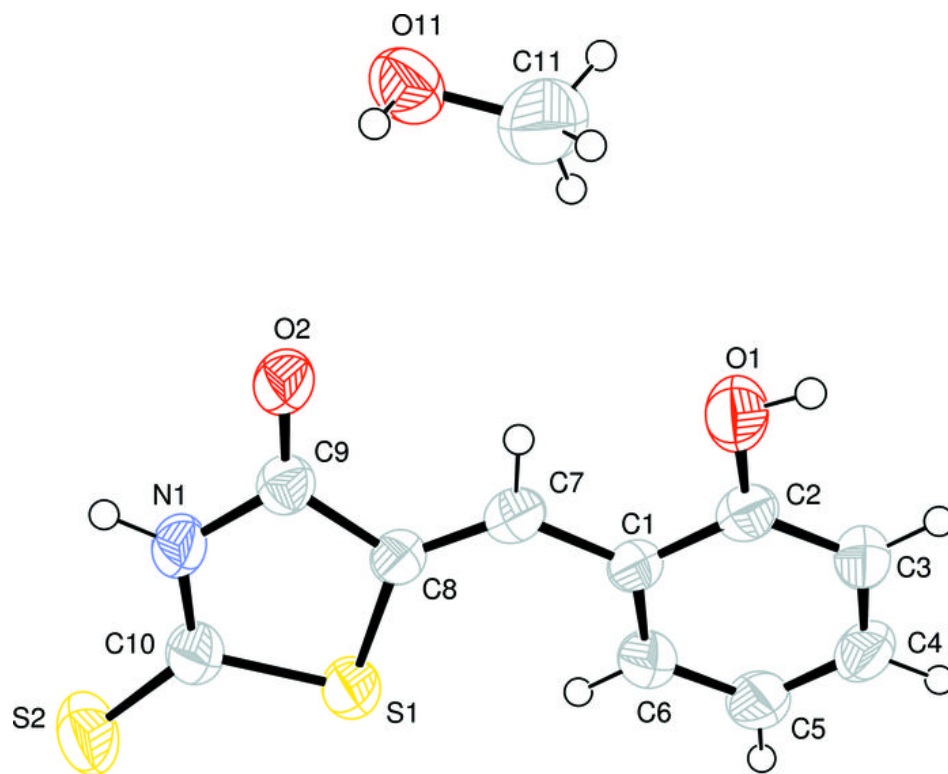


Fig. 2

