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(5*E*)-5-(4-Hydroxy-3-methoxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol monosolvate

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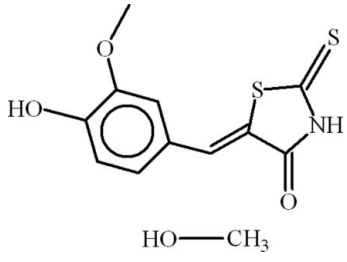
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; disorder in solvent or counterion; R factor = 0.039; wR factor = 0.070; data-to-parameter ratio = 13.4.

In the title compound, $C_{11}H_9NO_3S_2\cdot CH_4O$, the dihedral angle between the aromatic rings is 3.57 (16)° and intramolecular O—H···O and C—H···S interactions occur. In the crystal, the thiazolidin-4-one molecules are linked by N—H···O hydrogen bonds, forming chains. The hydrogen-bond motifs lead to $S(5)$, $S(6)$ and $R_3^3(8)$ ring motifs. There exist C=O···π interactions between the heterocyclic rings and π–π interactions between the heterocyclic and benzene rings at distances of 3.455 (2) and 3.602 (2) Å, respectively. The methanol solvent molecule is disordered over two sets of sites in a 0.542 (9):0.458 (9) ratio.

Related literature

For related structures, see: Barreiro *et al.* (2007); Shahwar *et al.* (2009). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{11}H_9NO_3S_2\cdot CH_4O$
M_r = 299.35
Orthorhombic, $Pna2_1$
a = 17.731 (2) Å
b = 11.7528 (14) Å
c = 6.5715 (6) Å
V = 1369.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 296 K
0.26 × 0.13 × 0.12 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.942, T_{max} = 0.955
7574 measured reflections
2472 independent reflections
1807 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.070
S = 1.02
2472 reflections
185 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 829 Friedal Pairs
Flack parameter: 0.01 (8)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.88 (3)	2.21 (3)	2.641 (3)	109 (3)
C2—H2···S1	0.93	2.66	3.349 (3)	132
O1—H1···O4A^{i}	0.88 (3)	1.85 (3)	2.622 (7)	145 (3)
N1—H1N···O1^{ii}	0.86	2.05	2.899 (3)	169
O4A—H4A···O3^{iii}	0.96 (8)	1.79 (8)	2.744 (7)	173 (7)
C12A—H12A···O3^{iv}	0.96	2.37	3.150 (5)	139

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{3}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z$. *Cg*2 is the 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5118).

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supplementary materials

Acta Cryst. (2009). E**65**, o2638 [**doi:10.1107/S1600536809039567**]

(5*E*)-5-(4-Hydroxy-3-methoxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol monosolvate

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Comment

We have recently reported the crystal structure of (5*Z*)-5-(2-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one - methanol (1:0.5) (Shahwar *et al.*, 2009). In continuation of synthesizing various derivatives of rhodanine, the title compound (I, Fig. 1), is being reported.

The crystal structure of (II) 5-(4-Hydroxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one dimethylsulfoxide solvate (Barreiro, *et al.*, 2007) has been published. The title compound (I) differs from (II) due to attachment of methoxy group adjacent to the hydroxy group and due to solvate i.e methanol instead of dimethylsulfoxide.

In the title molecule there exist interamolecular H-bondings of O—H···O, C—H···O and S—H···O types (Table 1, Fig. 1) forming two S(5) and one S(6) ring motif (Bernstein *et al.*, 1995). The role of disordered methanol solvate is to interlink the molecules through O—H···O type of H-bondings forming $R_3^3(8)$ ring motifs (Fig. 2). The molecules are stabilized in the form of infinite one dimensional polymeric chains. There exist π–π interactions between the centroids of heterocyclic ring *Cg*1 (C8/C9/N1/C10/S1) and the benzene ring *Cg*2 (C1—C6). The distance between the centroids *Cg*1 → *Cg*2 is 3.455 (2) Å due to symmetry (*x*, *y*, ∓1 + *z*) and for *Cg*2 → *Cg*1 is 3.602 (2) Å due to symmetry (1/2 - *x*, ∓1/2 + *y*, ∓1/2 + *z*), respectively. The molecules may also be stabilized due C==O···π interaction (Table 1). The methanol molecule is disordered over two sites with an occupancy ratio of 0.542 (9):0.458 (9).

Experimental

Rhodanine (0.266 g, 0.2 mol), 4-hydroxy-3-methoxybenzaldehyde (0.304 g, 0.2 mol) and K_2CO_3 (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 neutalization of the reaction mixture with 5% HCl. The precipitates were filtered off and washed with saturated solution of NaCl. The crude material obtained was recrystalized in methanol to affoard dark brown needles of (I).

Refinement

The coordinates of H1 and H4A attached with O1 and O4A respectively, were refined.

The H-atoms were positioned geometrically with O–H = 0.82, N–H = 0.86, C–H = 0.93 and 0.96 Å for aromatic like and methyl H atoms and constrained to ride on their parent atoms, with U_{iso}(H) = xUeq(C, N, O), where *x* = 1.5 for methyl and *x* = 1.2 for all other H atoms.

Figures

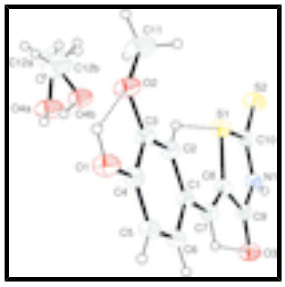

Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radius. The dotted line represent the intramolecular H-bond.

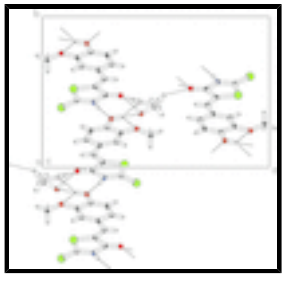

Fig. 2. The partial packing of (I), which shows that molecules form polymeric chains.

(5*E*)-5-(4-Hydroxy-3-methoxybenzylidene)-2-thioxo-1,3-thiazolidin-4-one methanol monosolvate

Crystal data

$C_{11}H_9NO_3S_2 \cdot CH_4O$	$F_{000} = 624$
$M_r = 299.35$	$D_x = 1.452$ Mg m^{-3}
Orthorhombic, *Pna*2$_1$	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: P 2c -2n	Cell parameters from 2472 reflections
a = 17.731 (2) Å	θ = 2.9–27.1°
b = 11.7528 (14) Å	μ = 0.40 mm^{-1}
c = 6.5715 (6) Å	*T* = 296 K
V = 1369.4 (3) Å^3	Cut needle, dark brown
Z = 4	0.26 × 0.13 × 0.12 mm

Data collection

Bruker Kappa APEXII CCD diffractometer	2472 independent reflections
Radiation source: fine-focus sealed tube	1807 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.045$
Detector resolution: 7.50 pixels mm^{-1}	$\theta_{max} = 27.1°$
T = 296 K	$\theta_{min} = 2.9°$
ω scans	*h* = −22→22
Absorption correction: multi-scan (SADABS; Bruker, 2007)	*k* = −13→15
$T_{min} = 0.942$, $T_{max} = 0.955$	*l* = −5→8
7574 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 0.2762P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
2472 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
185 parameters	Extinction coefficient: ?
1 restraint	Absolute structure: Flack (1983), 829 Friedal Pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.01 (8)
Secondary atom site location: difference Fourier map	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.36194 (4)	0.02090 (7)	0.57918 (14)	0.0440 (3)	
S2	0.41466 (5)	−0.10304 (9)	0.20833 (15)	0.0609 (4)	
O1	0.30380 (12)	0.3234 (2)	1.4811 (3)	0.0514 (9)	
O2	0.41511 (11)	0.2575 (2)	1.2416 (3)	0.0540 (9)	
O3	0.15476 (12)	−0.0232 (2)	0.4387 (3)	0.0531 (9)	
N1	0.27209 (14)	−0.0654 (2)	0.3174 (4)	0.0403 (9)	
C1	0.25139 (18)	0.1479 (3)	0.9536 (4)	0.0352 (10)	
C2	0.32661 (18)	0.1714 (3)	1.0013 (5)	0.0383 (11)	
C3	0.34462 (16)	0.2296 (3)	1.1767 (5)	0.0377 (11)	
C4	0.28684 (17)	0.2662 (3)	1.3082 (4)	0.0373 (11)	
C5	0.21274 (17)	0.2455 (3)	1.2609 (5)	0.0412 (11)	
C6	0.19503 (16)	0.1858 (3)	1.0864 (5)	0.0411 (11)	
C7	0.22722 (18)	0.0873 (3)	0.7745 (5)	0.0410 (11)	
C8	0.26494 (16)	0.0363 (3)	0.6206 (4)	0.0376 (11)	
C9	0.22317 (17)	−0.0188 (3)	0.4558 (5)	0.0405 (11)	
C10	0.34766 (17)	−0.0547 (3)	0.3526 (5)	0.0392 (11)	

C11	0.47733 (18)	0.2154 (4)	1.1321 (6)	0.0780 (18)	
O4A	0.4252 (3)	0.4356 (7)	0.5888 (10)	0.078 (3)	0.542 (9)
C12A	0.5055 (2)	0.4123 (5)	0.6066 (13)	0.096 (2)	0.542 (9)
O4B	0.4343 (2)	0.3568 (4)	0.6677 (9)	0.059 (3)	0.458 (9)
C12B	0.4913 (2)	0.4044 (4)	0.6141 (9)	0.096 (2)	0.458 (9)
H1	0.3525 (17)	0.334 (3)	1.499 (5)	0.0617*	
H1N	0.25564	−0.10029	0.21132	0.0483*	
H2	0.36478	0.14769	0.91393	0.0460*	
H5	0.17457	0.27152	1.34604	0.0495*	
H6	0.14477	0.17047	1.05653	0.0492*	
H7	0.17507	0.08219	0.76231	0.0494*	
H11A	0.47613	0.13375	1.13217	0.1166*	
H11B	0.52316	0.24114	1.19480	0.1166*	
H11C	0.47516	0.24266	0.99447	0.1166*	
H4A	0.401 (4)	0.449 (6)	0.717 (13)	0.0935*	0.542 (9)
H12C	0.51734	0.39385	0.74524	0.1441*	0.542 (9)
H12A	0.53358	0.47831	0.56588	0.1441*	0.542 (9)
H12B	0.51849	0.34937	0.52036	0.1441*	0.542 (9)
H4B	0.40848	0.40061	0.73547	0.0709*	0.458 (9)
H12D	0.50918	0.45230	0.72210	0.1441*	0.458 (9)
H12E	0.48086	0.44993	0.49615	0.1441*	0.458 (9)
H12F	0.52902	0.34877	0.58154	0.1441*	0.458 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0445 (4)	0.0523 (5)	0.0353 (4)	0.0038 (4)	−0.0056 (4)	−0.0094 (5)
S2	0.0552 (5)	0.0804 (8)	0.0472 (5)	0.0164 (5)	0.0008 (5)	−0.0137 (6)
O1	0.0444 (14)	0.0726 (19)	0.0372 (13)	0.0026 (13)	0.0019 (11)	−0.0231 (12)
O2	0.0383 (13)	0.0796 (17)	0.0442 (14)	−0.0046 (12)	0.0060 (11)	−0.0230 (13)
O3	0.0435 (13)	0.0691 (18)	0.0467 (14)	0.0004 (12)	−0.0084 (11)	−0.0146 (13)
N1	0.0527 (17)	0.0388 (18)	0.0293 (14)	0.0048 (14)	−0.0049 (12)	−0.0101 (13)
C1	0.0417 (17)	0.0343 (19)	0.0295 (17)	0.0022 (14)	0.0031 (14)	−0.0013 (14)
C2	0.0442 (19)	0.041 (2)	0.0297 (17)	0.0029 (16)	0.0060 (14)	−0.0062 (16)
C3	0.0389 (17)	0.040 (2)	0.0341 (19)	0.0002 (15)	0.0035 (15)	−0.0030 (17)
C4	0.047 (2)	0.037 (2)	0.0278 (18)	0.0023 (15)	0.0007 (15)	−0.0093 (16)
C5	0.0414 (19)	0.051 (2)	0.0313 (18)	0.0070 (17)	0.0024 (15)	−0.0069 (16)
C6	0.0372 (17)	0.045 (2)	0.0410 (18)	0.0037 (14)	−0.0008 (18)	−0.001 (2)
C7	0.0437 (18)	0.041 (2)	0.0383 (19)	0.0002 (16)	−0.0016 (15)	0.0005 (17)
C8	0.0464 (17)	0.039 (2)	0.0275 (19)	0.0024 (14)	−0.0081 (14)	−0.0034 (15)
C9	0.048 (2)	0.037 (2)	0.0364 (18)	0.0040 (17)	−0.0041 (16)	−0.0005 (16)
C10	0.047 (2)	0.038 (2)	0.0327 (18)	0.0049 (15)	−0.0088 (15)	−0.0018 (15)
C11	0.044 (2)	0.113 (4)	0.077 (3)	−0.005 (2)	0.0177 (18)	−0.026 (3)
O4A	0.048 (3)	0.119 (6)	0.067 (4)	0.004 (3)	0.005 (3)	−0.039 (5)
C12A	0.064 (3)	0.131 (5)	0.093 (4)	−0.008 (3)	0.011 (3)	−0.019 (4)
O4B	0.043 (3)	0.079 (6)	0.055 (4)	−0.001 (3)	0.006 (3)	−0.020 (4)
C12B	0.064 (3)	0.131 (5)	0.093 (4)	−0.008 (3)	0.011 (3)	−0.019 (4)

Geometric parameters (Å, °)

S1—C8	1.751 (3)	C3—C4	1.408 (4)
S1—C10	1.752 (3)	C4—C5	1.372 (4)
S2—C10	1.623 (3)	C5—C6	1.381 (5)
O1—C4	1.354 (4)	C7—C8	1.353 (4)
O2—C3	1.361 (4)	C8—C9	1.463 (4)
O2—C11	1.407 (4)	C2—H2	0.9300
O3—C9	1.219 (4)	C5—H5	0.9300
O1—H1	0.88 (3)	C6—H6	0.9300
O4A—C12A	1.455 (7)	C7—H7	0.9300
O4B—C12B	1.208 (6)	C11—H11A	0.9600
O4A—H4A	0.96 (8)	C11—H11B	0.9600
O4B—H4B	0.8200	C11—H11C	0.9600
N1—C10	1.366 (4)	C12A—H12B	0.9600
N1—C9	1.371 (4)	C12A—H12C	0.9600
N1—H1N	0.8600	C12A—H12A	0.9600
C1—C2	1.398 (5)	C12B—H12D	0.9600
C1—C7	1.441 (4)	C12B—H12E	0.9600
C1—C6	1.400 (4)	C12B—H12F	0.9600
C2—C3	1.378 (5)		
C8—S1—C10	92.44 (14)	S2—C10—N1	126.0 (3)
C3—O2—C11	118.4 (3)	S1—C10—S2	124.63 (19)
C4—O1—H1	114 (2)	C3—C2—H2	120.00
C12A—O4A—H4A	114 (4)	C1—C2—H2	120.00
C12B—O4B—H4B	110.00	C4—C5—H5	120.00
C9—N1—C10	118.1 (3)	C6—C5—H5	120.00
C10—N1—H1N	121.00	C5—C6—H6	119.00
C9—N1—H1N	121.00	C1—C6—H6	119.00
C2—C1—C7	124.4 (3)	C8—C7—H7	113.00
C2—C1—C6	118.6 (3)	C1—C7—H7	113.00
C6—C1—C7	117.0 (3)	O2—C11—H11C	109.00
C1—C2—C3	120.5 (3)	O2—C11—H11A	110.00
O2—C3—C4	113.7 (3)	O2—C11—H11B	109.00
O2—C3—C2	126.5 (3)	H11B—C11—H11C	109.00
C2—C3—C4	119.8 (3)	H11A—C11—H11B	109.00
O1—C4—C5	119.4 (3)	H11A—C11—H11C	109.00
C3—C4—C5	120.3 (3)	O4A—C12A—H12B	109.00
O1—C4—C3	120.4 (3)	O4A—C12A—H12C	109.00
C4—C5—C6	119.8 (3)	O4A—C12A—H12A	109.00
C1—C6—C5	121.2 (3)	H12A—C12A—H12C	109.00
C1—C7—C8	133.1 (3)	H12B—C12A—H12C	110.00
S1—C8—C9	109.7 (2)	H12A—C12A—H12B	109.00
S1—C8—C7	130.4 (2)	O4B—C12B—H12D	109.00
C7—C8—C9	120.0 (3)	O4B—C12B—H12E	109.00
O3—C9—C8	126.2 (3)	O4B—C12B—H12F	109.00
N1—C9—C8	110.3 (3)	H12D—C12B—H12E	110.00
O3—C9—N1	123.5 (3)	H12D—C12B—H12F	110.00

S1—C10—N1	109.4 (2)	H12E—C12B—H12F	110.00
C10—S1—C8—C7	179.4 (4)	C1—C2—C3—O2	179.7 (3)
C10—S1—C8—C9	0.3 (3)	C1—C2—C3—C4	−0.4 (5)
C8—S1—C10—S2	179.6 (3)	O2—C3—C4—O1	−0.1 (5)
C8—S1—C10—N1	−0.1 (3)	O2—C3—C4—C5	179.1 (3)
C11—O2—C3—C2	−6.2 (5)	C2—C3—C4—O1	180.0 (3)
C11—O2—C3—C4	173.9 (3)	C2—C3—C4—C5	−0.9 (5)
C10—N1—C9—O3	179.8 (3)	O1—C4—C5—C6	−179.1 (3)
C10—N1—C9—C8	0.4 (4)	C3—C4—C5—C6	1.8 (5)
C9—N1—C10—S1	−0.2 (4)	C4—C5—C6—C1	−1.4 (5)
C9—N1—C10—S2	−179.8 (3)	C1—C7—C8—S1	1.4 (6)
C6—C1—C2—C3	0.7 (5)	C1—C7—C8—C9	−179.5 (4)
C7—C1—C2—C3	−179.7 (3)	S1—C8—C9—O3	−179.8 (3)
C2—C1—C6—C5	0.2 (5)	S1—C8—C9—N1	−0.4 (3)
C7—C1—C6—C5	−179.4 (3)	C7—C8—C9—O3	1.0 (5)
C2—C1—C7—C8	3.1 (6)	C7—C8—C9—N1	−179.6 (3)
C6—C1—C7—C8	−177.4 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.88 (3)	2.21 (3)	2.641 (3)	109 (3)
C2—H2···S1	0.93	2.66	3.349 (3)	132
O1—H1···O4A^{i}	0.88 (3)	1.85 (3)	2.622 (7)	145 (3)
N1—H1N···O1^{ii}	0.86	2.05	2.899 (3)	169
O4A—H4A···O3^{iii}	0.96 (8)	1.79 (8)	2.744 (7)	173 (7)
C12A—H12A···O3^{iv}	0.96	2.37	3.150 (5)	139

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1/2, *y*−1/2, *z*−3/2; (iii) −*x*+1/2, *y*+1/2, *z*+1/2; (iv) *x*+1/2, −*y*+1/2, *z*.

Fig. 1

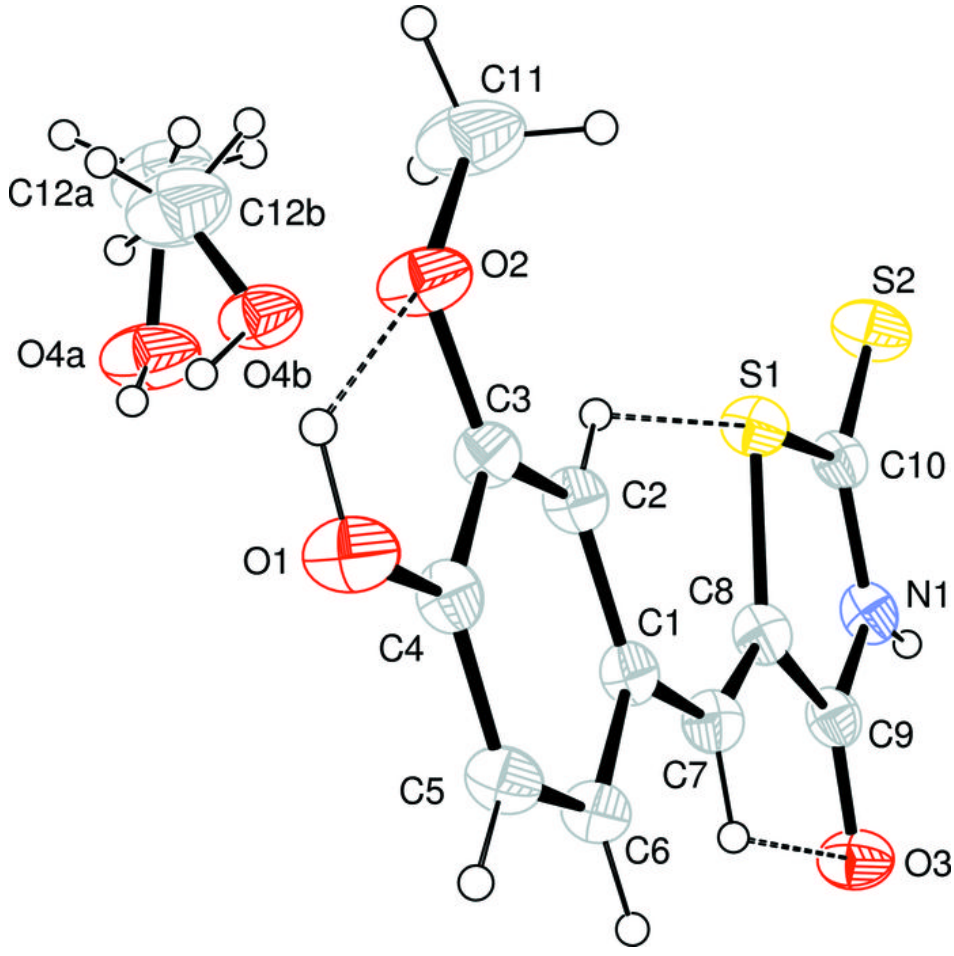
C11
C12a
C12b
O2
S2
O4a
O4b
S1
C3
C10
C2
O1
C8
N1
C1
C4
C9
C7
C5
C6
O3

Fig. 2