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Ethyl 3-methyl-1-oxo-4*H*-1,4-benzothiazine-2-carboxylate monohydrate

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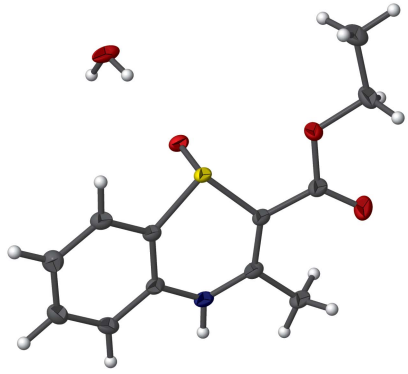
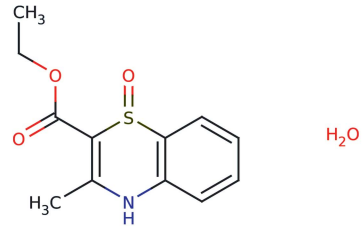
Structural data: full structural data are available from iucrdata.iucr.org

The organic molecule in the title hydrate, $C_{12}H_{13}NO_3S\cdot H_2O$, is folded across the S···N vector. Chains two molecules thick extending along the *a*-axis direction are formed by N—H···O and O—H···O hydrogen bonds. These interactions are reinforced by C—H···S hydrogen bonds and offset π-stacking interactions between centrosymmetrically related benzene rings. The chains are associated through C—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

1,4-Benzothiazine derivatives constitute an important class of natural products possessing a wide range of biological and pharmaceutical activity due to the presence of the nitrogen–sulfur axis, which is considered to be one of the structural features important for their activities (Nitin *et al.*, 2013; Gupta & Gupta, 2011). The 1,4-benzothiazine moiety is the pharmacophore of phenothiazines, which are well established anti-psychotic drugs (Barker & Miller, 1969), and is also known as the basic unit for their utility as dyestuffs (Bhikan & Bhata, 2015), photographic developers (Dabholkar & Gavande, 2016), ultraviolet light absorbers and antioxidants (Dabholkar & Gavande, 2010).

The overall shape of the title molecule (Fig. 1) may be described as an 'open butterfly' hinged about the S1···N1 vector. A puckering analysis of the heterocyclic ring gave the parameters Q = 0.301 (1) Å, θ = 65.7 (2)° and φ = 1.7 (3)°.

In the crystal, N1—H1···O4, O4—H4*A*···O1 and O4—H4*B*···O1 hydrogen bonds (Table 1) generate generate chains two molecules thick extending along the *a*-axis

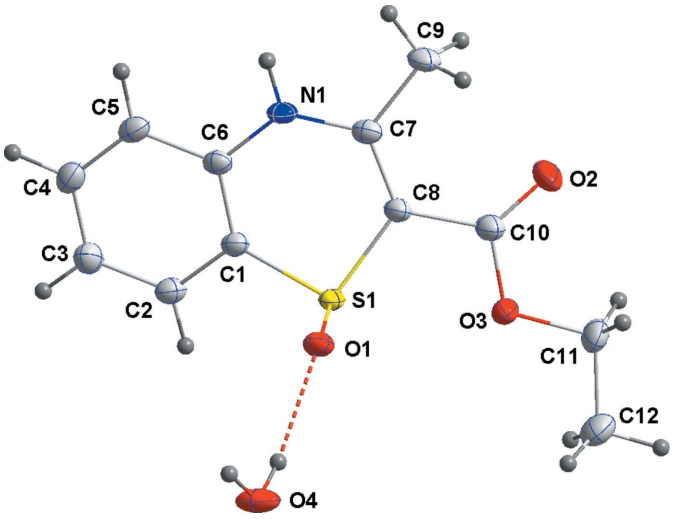


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids. The O—H···O hydrogen bond is shown as a dashed line.

direction and inclined at approximately 56° to [001] (Fig. 2). Reinforcing the above interactions are C2—H2···S1 hydrogen bonds (Table 1) and offset π-stacking interactions between benzene rings across centers of symmetry with centroid–centroid distances of 3.8263 (8) Å and interplanar spacings of 3.4260 (6) Å (Fig. 2). Finally, the chains are tied together *via* C4—H4···O2 hydrogen bonds (Table 2 and Fig. 3).

Synthesis and crystallization

A mixture of 2,2-disulfanediyldianiline (0.5 g, 2 mmol) and ethyl acetoacetate (0.5 ml, 4 mmol) was refluxed at 453 K for 3 h in xylene. After cooling and filtration, the solution was then concentrated to dryness under reduced pressure. The residue obtained was chromatographed on silica gel using dichloromethane/ether (9/1) as eluent. The title compound was isolated in 36% yield and recrystallized from ethanol solution to give colorless crystals.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^{i}	0.88 (2)	1.98 (2)	2.8504 (16)	170.7 (19)
C2—H2···S1^{ii}	0.964 (19)	2.898 (19)	3.6729 (15)	138.2 (14)
O4—H4*A*···O1	0.82 (2)	2.05 (2)	2.8458 (15)	164 (2)
O4—H4*B*···O1^{iii}	0.89 (2)	1.90 (2)	2.7841 (15)	175 (2)
C4—H4···O2^{iv}	0.985 (19)	2.283 (17)	3.0694 (15)	136.1 (13)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{13}NO_3S\cdot H_2O$
M_r	269.31
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.8340 (3), 18.6849 (6), 7.6927 (3)
β (°)	91.478 (1)
V (Å^3)	1269.35 (8)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.35
Crystal size (mm)	0.31 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.74, 0.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9610, 2466, 2332
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.078, 1.09
No. of reflections	2466
No. of parameters	223
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.42

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

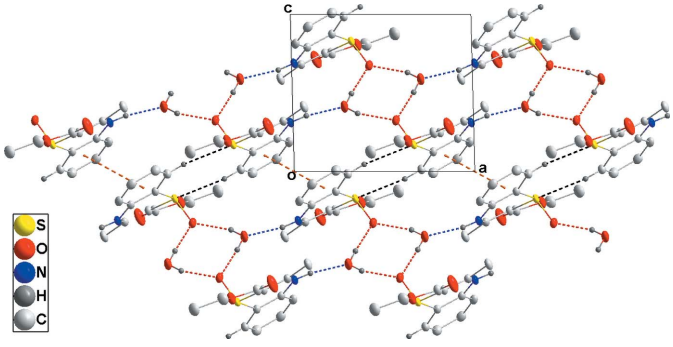


Figure 2
A portion of one chain viewed along the *b*-axis direction. O—H···O, N—H···O and C—H···S hydrogen bonds are depicted, respectively, as red, dark-blue and black dashed lines. The offset π-stacking interactions are shown as orange dashed lines.

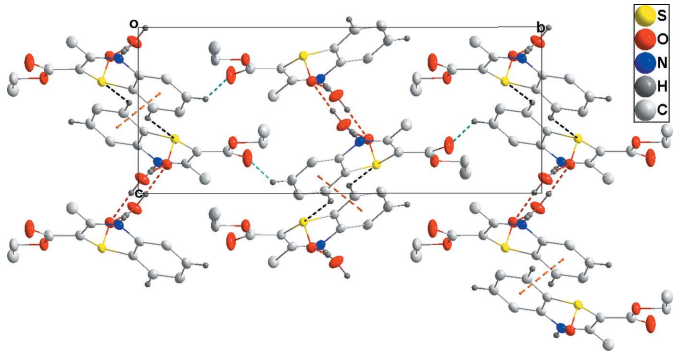


Figure 3
Packing viewed along the *a*-axis direction with intermolecular interactions depicted as in Fig. 2 with the addition of light-blue dashed lines for the C—H···O hydrogen bonds.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

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Ethyl 3-methyl-1-oxo-4*H*-1λ^4,4-benzothiazine-2-carboxylate monohydrate

Crystal data

$C_{12}H_{13}NO_3S·H_2O$
M_r = 269.31
Monoclinic, $P2_1/c$
a = 8.8340 (3) Å
b = 18.6849 (6) Å
c = 7.6927 (3) Å
β = 91.478 (1)°
V = 1269.35 (8) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.409 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 8322 reflections
θ = 5.0–72.3°
μ = 2.35 mm^{-1}
T = 100 K
Plate, colourless
0.31 × 0.15 × 0.05 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.74, T_{max} = 0.90
9610 measured reflections
2466 independent reflections
2332 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 72.3°, θ_{min} = 4.7°
h = −10→10
k = −21→23
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.09
2466 reflections
223 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.6004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.66513 (4)	0.40943 (2)	0.17180 (4)	0.01696 (11)
O1	0.57044 (11)	0.42958 (5)	0.32582 (13)	0.0221 (2)
O2	0.86274 (14)	0.22973 (6)	0.2877 (2)	0.0436 (3)
O3	0.63340 (11)	0.26569 (5)	0.19465 (14)	0.0253 (2)
N1	0.98546 (14)	0.45089 (6)	0.31178 (15)	0.0204 (3)
H1	1.074 (2)	0.4638 (11)	0.355 (3)	0.038 (5)*
C1	0.77255 (15)	0.48632 (7)	0.12616 (17)	0.0182 (3)
C2	0.70433 (17)	0.53641 (8)	0.01453 (18)	0.0224 (3)
H2	0.612 (2)	0.5229 (10)	−0.046 (2)	0.029 (5)*
C3	0.76857 (18)	0.60286 (8)	−0.0078 (2)	0.0259 (3)
H3	0.720 (2)	0.6385 (11)	−0.081 (2)	0.032 (5)*
C4	0.90414 (17)	0.61925 (8)	0.08057 (19)	0.0251 (3)
H4	0.952 (2)	0.6665 (10)	0.068 (2)	0.031 (5)*
C5	0.97550 (17)	0.56955 (8)	0.18726 (19)	0.0225 (3)
H5	1.073 (2)	0.5811 (9)	0.245 (2)	0.023 (4)*
C6	0.91021 (15)	0.50198 (7)	0.21074 (17)	0.0187 (3)
C7	0.94695 (15)	0.38111 (8)	0.32003 (17)	0.0197 (3)
C8	0.81306 (15)	0.35467 (7)	0.24803 (18)	0.0192 (3)
C9	1.06292 (17)	0.33497 (9)	0.4119 (2)	0.0266 (3)
H9A	1.015 (2)	0.3080 (11)	0.505 (3)	0.038 (5)*
H9B	1.103 (2)	0.2996 (11)	0.334 (3)	0.039 (5)*
H9C	1.142 (2)	0.3650 (12)	0.458 (3)	0.041 (5)*
C10	0.77751 (16)	0.27792 (8)	0.24753 (19)	0.0232 (3)
C11	0.58618 (19)	0.19092 (8)	0.1915 (2)	0.0301 (3)
H11A	0.596 (2)	0.1731 (11)	0.308 (3)	0.041 (5)*
H11B	0.656 (2)	0.1661 (11)	0.112 (3)	0.044 (6)*
C12	0.4257 (2)	0.18889 (10)	0.1244 (3)	0.0348 (4)
H12A	0.360 (3)	0.2185 (13)	0.195 (3)	0.051 (6)*
H12B	0.422 (3)	0.2062 (12)	0.006 (3)	0.049 (6)*
H12C	0.391 (2)	0.1366 (12)	0.124 (3)	0.046 (6)*
O4	0.28682 (12)	0.49043 (7)	0.41229 (16)	0.0331 (3)
H4A	0.359 (3)	0.4700 (12)	0.370 (3)	0.043 (6)*
H4B	0.327 (3)	0.5176 (12)	0.496 (3)	0.047 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01205 (18)	0.01823 (18)	0.02045 (18)	0.00045 (11)	−0.00286 (12)	−0.00170 (11)
O1	0.0151 (5)	0.0248 (5)	0.0265 (5)	0.0017 (4)	0.0029 (4)	−0.0026 (4)
O2	0.0310 (7)	0.0222 (6)	0.0762 (9)	0.0054 (5)	−0.0220 (6)	−0.0006 (6)

O3	0.0195 (5)	0.0185 (5)	0.0375 (6)	−0.0020 (4)	−0.0066 (4)	−0.0006 (4)
N1	0.0131 (6)	0.0242 (6)	0.0236 (6)	0.0004 (5)	−0.0038 (5)	−0.0044 (5)
C1	0.0145 (7)	0.0199 (7)	0.0203 (6)	0.0003 (5)	0.0002 (5)	−0.0025 (5)
C2	0.0170 (7)	0.0264 (7)	0.0236 (7)	−0.0011 (5)	−0.0007 (5)	0.0008 (6)
C3	0.0250 (8)	0.0247 (7)	0.0280 (7)	0.0005 (6)	0.0015 (6)	0.0042 (6)
C4	0.0251 (8)	0.0220 (7)	0.0284 (7)	−0.0042 (6)	0.0051 (6)	−0.0030 (6)
C5	0.0176 (7)	0.0249 (7)	0.0252 (7)	−0.0037 (5)	0.0021 (5)	−0.0067 (6)
C6	0.0154 (7)	0.0213 (7)	0.0195 (6)	0.0015 (5)	0.0011 (5)	−0.0044 (5)
C7	0.0157 (7)	0.0237 (7)	0.0198 (6)	0.0024 (5)	−0.0005 (5)	−0.0035 (5)
C8	0.0146 (7)	0.0198 (7)	0.0230 (7)	0.0017 (5)	−0.0017 (5)	−0.0016 (5)
C9	0.0171 (7)	0.0292 (8)	0.0332 (8)	0.0031 (6)	−0.0076 (6)	−0.0008 (6)
C10	0.0187 (7)	0.0224 (7)	0.0282 (7)	0.0016 (5)	−0.0040 (6)	−0.0029 (5)
C11	0.0319 (9)	0.0194 (7)	0.0384 (9)	−0.0055 (6)	−0.0066 (7)	−0.0007 (6)
C12	0.0293 (9)	0.0318 (9)	0.0429 (10)	−0.0094 (7)	−0.0049 (7)	−0.0019 (8)
O4	0.0149 (6)	0.0489 (7)	0.0355 (6)	0.0018 (5)	−0.0026 (5)	−0.0184 (5)

Geometric parameters (Å, º)

S1—O1	1.5154 (10)	C5—C6	1.402 (2)
S1—C8	1.7490 (14)	C5—H5	0.986 (19)
S1—C1	1.7621 (14)	C7—C8	1.3842 (19)
O2—C10	1.2088 (19)	C7—C9	1.5015 (19)
O3—C10	1.3460 (18)	C8—C10	1.468 (2)
O3—C11	1.4581 (18)	C9—H9A	0.98 (2)
N1—C7	1.3494 (19)	C9—H9B	0.96 (2)
N1—C6	1.3895 (18)	C9—H9C	0.96 (2)
N1—H1	0.88 (2)	C11—C12	1.497 (2)
C1—C6	1.3953 (19)	C11—H11A	0.96 (2)
C1—C2	1.396 (2)	C11—H11B	0.99 (2)
C2—C3	1.378 (2)	C12—H12A	0.97 (2)
C2—H2	0.964 (19)	C12—H12B	0.97 (2)
C3—C4	1.396 (2)	C12—H12C	1.02 (2)
C3—H3	0.97 (2)	O4—H4A	0.82 (2)
C4—C5	1.381 (2)	O4—H4B	0.89 (2)
C4—H4	0.985 (19)		
O1—S1—C8	107.82 (6)	C8—C7—C9	123.30 (13)
O1—S1—C1	105.32 (6)	C7—C8—C10	122.02 (13)
C8—S1—C1	98.18 (6)	C7—C8—S1	123.28 (11)
C10—O3—C11	115.82 (11)	C10—C8—S1	114.37 (10)
C7—N1—C6	124.93 (12)	C7—C9—H9A	109.8 (12)
C7—N1—H1	118.1 (14)	C7—C9—H9B	111.0 (12)
C6—N1—H1	115.6 (14)	H9A—C9—H9B	105.9 (17)
C6—C1—C2	120.22 (13)	C7—C9—H9C	108.7 (13)
C6—C1—S1	123.06 (11)	H9A—C9—H9C	110.5 (17)
C2—C1—S1	116.29 (10)	H9B—C9—H9C	110.8 (17)
C3—C2—C1	120.54 (14)	O2—C10—O3	121.94 (14)
C3—C2—H2	121.5 (11)	O2—C10—C8	126.52 (14)

C1—C2—H2	118.0 (11)	O3—C10—C8	111.54 (12)
C2—C3—C4	119.21 (14)	O3—C11—C12	107.35 (13)
C2—C3—H3	121.1 (11)	O3—C11—H11A	107.3 (12)
C4—C3—H3	119.7 (11)	C12—C11—H11A	112.3 (13)
C5—C4—C3	120.98 (14)	O3—C11—H11B	106.1 (12)
C5—C4—H4	118.0 (11)	C12—C11—H11B	111.9 (12)
C3—C4—H4	121.0 (11)	H11A—C11—H11B	111.5 (17)
C4—C5—C6	119.95 (13)	C11—C12—H12A	111.5 (14)
C4—C5—H5	120.2 (10)	C11—C12—H12B	109.2 (14)
C6—C5—H5	119.8 (10)	H12A—C12—H12B	108.9 (19)
N1—C6—C1	121.02 (12)	C11—C12—H12C	107.8 (12)
N1—C6—C5	119.89 (13)	H12A—C12—H12C	111.0 (18)
C1—C6—C5	119.04 (13)	H12B—C12—H12C	108.4 (17)
N1—C7—C8	122.67 (13)	H4A—O4—H4B	104 (2)
N1—C7—C9	114.02 (12)		

O1—S1—C1—C6	85.12 (12)	C6—N1—C7—C8	−10.1 (2)
C8—S1—C1—C6	−25.97 (13)	C6—N1—C7—C9	169.10 (13)
O1—S1—C1—C2	−87.29 (11)	N1—C7—C8—C10	175.71 (13)
C8—S1—C1—C2	161.62 (11)	C9—C7—C8—C10	−3.5 (2)
C6—C1—C2—C3	−2.8 (2)	N1—C7—C8—S1	−11.2 (2)
S1—C1—C2—C3	169.89 (11)	C9—C7—C8—S1	169.57 (11)
C1—C2—C3—C4	1.0 (2)	O1—S1—C8—C7	−83.78 (13)
C2—C3—C4—C5	1.1 (2)	C1—S1—C8—C7	25.27 (13)
C3—C4—C5—C6	−1.3 (2)	O1—S1—C8—C10	89.75 (11)
C7—N1—C6—C1	9.2 (2)	C1—S1—C8—C10	−161.20 (11)
C7—N1—C6—C5	−168.34 (13)	C11—O3—C10—O2	0.9 (2)
C2—C1—C6—N1	−175.06 (12)	C11—O3—C10—C8	−179.32 (12)
S1—C1—C6—N1	12.82 (18)	C7—C8—C10—O2	−9.4 (2)
C2—C1—C6—C5	2.5 (2)	S1—C8—C10—O2	177.01 (15)
S1—C1—C6—C5	−169.63 (10)	C7—C8—C10—O3	170.85 (12)
C4—C5—C6—N1	177.08 (13)	S1—C8—C10—O3	−2.77 (16)
C4—C5—C6—C1	−0.5 (2)	C10—O3—C11—C12	−178.26 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88 (2)	1.98 (2)	2.8504 (16)	170.7 (19)
C2—H2···S1^{ii}	0.964 (19)	2.898 (19)	3.6729 (15)	138.2 (14)
O4—H4*A*···O1	0.82 (2)	2.05 (2)	2.8458 (15)	164 (2)
O4—H4*B*···O1^{iii}	0.89 (2)	1.90 (2)	2.7841 (15)	175 (2)
C4—H4···O2^{iv}	0.985 (19)	2.283 (17)	3.0694 (15)	136.1 (13)

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