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ISSN 2414-3146

(*Z*)-2-Benzylidene-3-*n*-butoxy-2*H*-1,4-benzothiazine

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Received 10 June 2017
Accepted 14 June 2017

Edited by J. Simpson, University of Otago, New Zealand

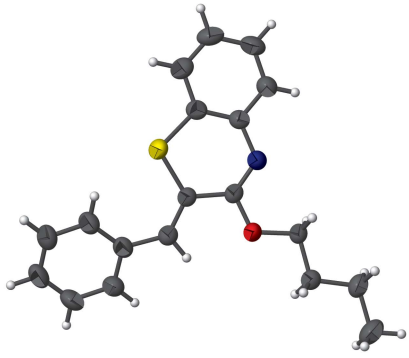
Keywords: crystal structure; benzothiazine; hydrogen bonds; π-stacking.

CCDC reference: 1556121

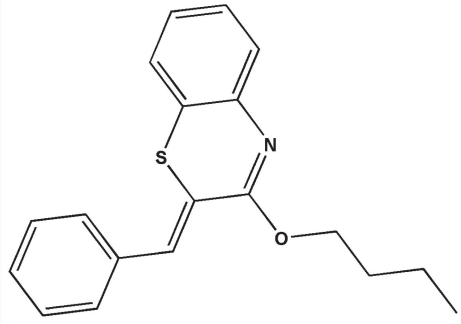
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{19}H_{19}NOS$, the thiazin-3-one ring of the 1,4-thiazin-3-one moiety adopts a screw-boat conformation. The dihedral angle between the benzene rings is 31.0 (5)°. An intramolecular C—H···S hydrogen bond forms an $S(6)$ ring motif. In the crystal, C—H···π(ring) contacts form inversion dimers and weak π–π stacking interactions, with a centroid-to-centroid distance of 3.8766 (2) Å, also occur.

3D view



Chemical scheme



Structure description

1,4-Benzothiazines and their analogues have been studied extensively in different areas of chemistry particularly as pharmaceuticals (Sebbar *et al.*, 2016*a*; Ellouz *et al.*,2017*a*; Malagu *et al.*,1998). With respect to their biological applications, they have been found to have potent anti-inflammatory, (Trapani *et al.*,1985); analgesic (Wammack *et al.*, 2002) and anti-oxidant properties (Zia-ur-Rehman *et al.*, 2009). Slight changes in the substitution pattern in the benzothiazine nucleus can cause a distinguishable difference in their biological properties (Niewiadomy *et al.*, 2011; Gautam *et al.*,2012). As a continuation of our research into the development of new 1,4-benzothiazine derivatives with potential pharmacological applications, we have studied the reaction of 1-bromobutane with (*Z*)-2-benzylidene-2*H*-1,4-benzothiazin-3(4*H*)-one under phase-transfer catalysis conditions using tetra-*n*-butyl ammonium bromide as a catalyst and potassium carbonate as the base (Sebbar *et al.*, 2016*b*; Ellouz *et al.*,2017*b*) to give the title compound (Fig. 1).

The thiazine-3-one ring of the [1,4]thiazin-3-one moiety adopts a screw-boat conformation (puckering parameters: Q = 0.176 (8) Å, θ = 66.8 (6)° and φ = 26.989 (1)°. The

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

*Cg*2 is the centroid of the C3–C8 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···S1	0.93	2.51	3.155 (2)	127
C17—H17*A*···*Cg*2^{i}	0.97	2.82	3.665 (3)	146

Symmetry code: (i) $-x, -y+1, -z+1$.

dihedral angle between the benzene rings is 31.0 (5)°. The intramolecular C11—H11···S1 hydrogen bond affects the overall conformation of the molecule.

In the crystal C17—H17*A*···*Cg*2 contacts, Table 1, form inversion dimers and link adjacent molecules in a head-to-tail fashion. In addition, π–π stacking interactions, [*Cg*3···*Cg*3^{iii} = 3.8766 (2) Å; *Cg*3 is the centroid of the C10–C15 phenyl ring; symmetry code: (iii) $1-x, -y, -z$] are observed, Fig. 2.

Synthesis and crystallization

To a solution of (*Z*)-2-benzylidene-3,4-dihydro-2*H*-1,4-benzothiazin-3(4*H*)-one (1.4 mmol), potassium carbonate (2.8 mmol) and tetra-*n*-butyl ammonium bromide (0.14 mmol) in DMF (15 ml) was added 1-bromobutane (2.8 mmol). Stirring was continued at room temperature for 24 h. The mixture was filtered and the solvent removed. The residue obtained was washed with water. The organic compound was chromatographed on a column of silica gel with ethyl acetate–hexane (9/1) as eluent. Colorless crystals were isolated when the solvent was allowed to evaporate (yield = 21%).

Refinement

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

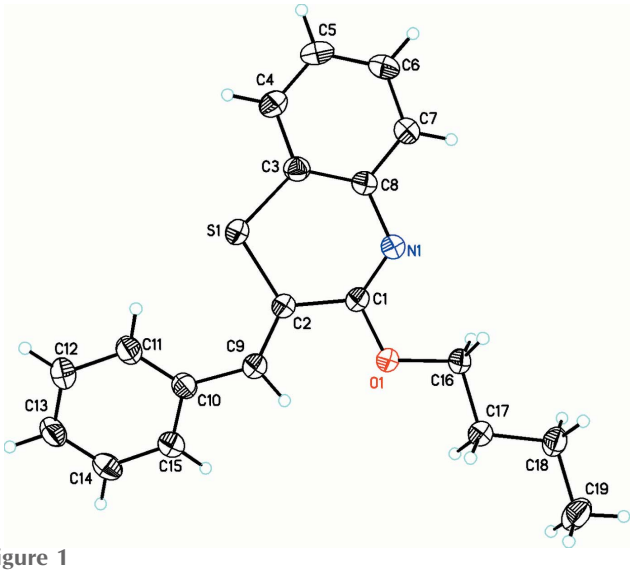


Figure 1
The structure of the title compound, showing the atom-numbering scheme, with ellipsoids drawn at the 30% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{19}NOS$
M_r	309.41
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, *b*, *c* (Å)	7.7711 (6), 10.9897 (11), 11.4090 (11)
α, β, γ (°)	112.013 (9), 109.259 (8), 98.120 (7)
V (Å^3)	812.78 (14)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	1.76
Crystal size (mm)	0.38 × 0.18 × 0.08
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
T_{min}, T_{max}	0.611, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5063, 3070, 2492
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.614
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.140, 1.05
No. of reflections	3070
No. of parameters	200
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.22

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2015* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Acknowledgements

JPJ acknowledges the NSF–MRI program (grant No. CHE-1039027) for funds to purchase the X-ray diffractometer.

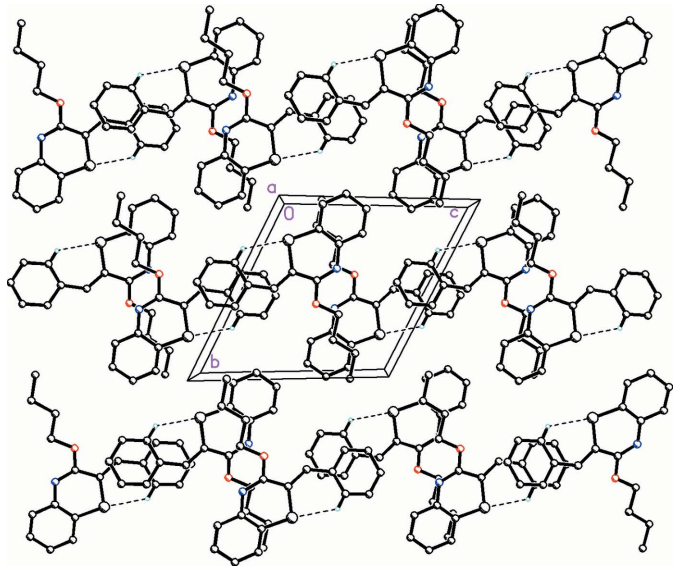


Figure 2
The packing of the title compound, viewed along the *a* axis. Dashed lines indicate weak intramolecular hydrogen bonds. The C—H···π contact is not shown.

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full crystallographic data

IUCrData (2017). **2**, x170890 [https://doi.org/10.1107/S2414314617008902]

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Crystal data

$C_{19}H_{19}NOS$
M_r = 309.41
Triclinic, $P\overline{1}$
a = 7.7711 (6) Å
b = 10.9897 (11) Å
c = 11.4090 (11) Å
α = 112.013 (9)°
β = 109.259 (8)°
γ = 98.120 (7)°
V = 812.78 (14) Å^3
Z = 2
$F(000)$ = 328
D_x = 1.264 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 1693 reflections
θ = 7.7–71.5°
μ = 1.76 mm^{-1}
T = 293 K
Irregular fragment, colourless
0.38 × 0.18 × 0.08 mm

Data collection

Rigaku Oxford Diffraction diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku Oxford Diffraction, 2015)
T_{min} = 0.611, T_{max} = 1.000
5063 measured reflections
3070 independent reflections
2492 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 71.3°, θ_{min} = 4.6°
h = −7→9
k = −13→12
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.140
S = 1.05
3070 reflections
200 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.0842P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.32522 (9)	0.77222 (5)	0.86052 (5)	0.0565 (2)
O1	0.2602 (2)	0.41659 (14)	0.56207 (14)	0.0475 (4)
N1	0.2472 (2)	0.61507 (17)	0.54627 (17)	0.0448 (4)
C1	0.2587 (3)	0.54831 (19)	0.6176 (2)	0.0413 (4)
C2	0.2732 (3)	0.59454 (19)	0.7611 (2)	0.0406 (4)
C3	0.2779 (3)	0.8341 (2)	0.7357 (2)	0.0451 (5)
C4	0.2788 (3)	0.9705 (2)	0.7798 (2)	0.0544 (5)
H4	0.3011	1.0242	0.8717	0.065*
C5	0.2465 (3)	1.0268 (2)	0.6874 (3)	0.0609 (6)
H5	0.2477	1.1182	0.7170	0.073*
C6	0.2124 (4)	0.9460 (3)	0.5503 (3)	0.0611 (6)
H6	0.1905	0.9832	0.4876	0.073*
C7	0.2110 (3)	0.8105 (2)	0.5071 (2)	0.0530 (5)
H7	0.1870	0.7568	0.4148	0.064*
C8	0.2449 (3)	0.7522 (2)	0.5988 (2)	0.0430 (4)
C9	0.2521 (3)	0.5025 (2)	0.8113 (2)	0.0475 (5)
H9	0.2260	0.4115	0.7483	0.057*
C10	0.2635 (3)	0.5220 (2)	0.9482 (2)	0.0474 (5)
C11	0.3516 (3)	0.6452 (2)	1.0698 (2)	0.0546 (5)
H11	0.4089	0.7238	1.0673	0.065*
C12	0.3555 (4)	0.6529 (3)	1.1942 (3)	0.0641 (6)
H12	0.4148	0.7366	1.2742	0.077*
C13	0.2726 (4)	0.5379 (3)	1.2008 (3)	0.0652 (7)
H13	0.2745	0.5436	1.2847	0.078*
C14	0.1869 (4)	0.4144 (3)	1.0823 (3)	0.0692 (7)
H14	0.1311	0.3362	1.0862	0.083*
C15	0.1830 (4)	0.4058 (3)	0.9572 (3)	0.0599 (6)
H15	0.1259	0.3214	0.8780	0.072*
C16	0.2407 (3)	0.3562 (2)	0.4203 (2)	0.0442 (5)
H16A	0.3462	0.4064	0.4126	0.053*
H16B	0.1220	0.3589	0.3588	0.053*
C17	0.2411 (3)	0.2102 (2)	0.3825 (2)	0.0461 (5)
H17A	0.1413	0.1638	0.3982	0.055*
H17B	0.3627	0.2096	0.4427	0.055*
C18	0.2094 (4)	0.1319 (2)	0.2322 (2)	0.0559 (6)
H18A	0.0884	0.1335	0.1723	0.067*
H18B	0.3098	0.1781	0.2170	0.067*
C19	0.2077 (5)	−0.0158 (3)	0.1920 (3)	0.0771 (8)
H19A	0.1921	−0.0594	0.0973	0.116*

H19B	0.1037	−0.0637	0.2015	0.116*
H19C	0.3263	−0.0182	0.2519	0.116*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0843 (4)	0.0397 (3)	0.0369 (3)	0.0152 (3)	0.0219 (3)	0.0130 (2)
O1	0.0704 (9)	0.0385 (7)	0.0368 (7)	0.0201 (6)	0.0245 (7)	0.0170 (6)
N1	0.0552 (10)	0.0411 (9)	0.0409 (9)	0.0154 (7)	0.0217 (8)	0.0194 (7)
C1	0.0465 (10)	0.0361 (10)	0.0379 (10)	0.0116 (8)	0.0182 (8)	0.0132 (8)
C2	0.0444 (10)	0.0375 (10)	0.0376 (10)	0.0122 (8)	0.0168 (8)	0.0150 (8)
C3	0.0456 (10)	0.0407 (10)	0.0467 (11)	0.0098 (8)	0.0175 (9)	0.0202 (9)
C4	0.0560 (12)	0.0409 (11)	0.0530 (13)	0.0082 (9)	0.0189 (10)	0.0135 (10)
C5	0.0643 (14)	0.0381 (11)	0.0760 (16)	0.0154 (10)	0.0253 (12)	0.0250 (11)
C6	0.0744 (16)	0.0543 (13)	0.0695 (16)	0.0237 (12)	0.0308 (13)	0.0404 (12)
C7	0.0659 (14)	0.0512 (12)	0.0497 (12)	0.0203 (10)	0.0272 (10)	0.0267 (10)
C8	0.0447 (10)	0.0408 (10)	0.0457 (11)	0.0124 (8)	0.0192 (8)	0.0216 (9)
C9	0.0577 (12)	0.0406 (10)	0.0422 (11)	0.0130 (9)	0.0216 (9)	0.0167 (9)
C10	0.0538 (11)	0.0522 (12)	0.0457 (11)	0.0215 (9)	0.0236 (9)	0.0270 (10)
C11	0.0646 (13)	0.0537 (13)	0.0451 (12)	0.0118 (10)	0.0217 (10)	0.0253 (10)
C12	0.0822 (17)	0.0664 (15)	0.0439 (12)	0.0205 (13)	0.0265 (12)	0.0256 (11)
C13	0.0890 (18)	0.0771 (17)	0.0560 (14)	0.0359 (14)	0.0405 (13)	0.0438 (13)
C14	0.0971 (19)	0.0635 (16)	0.0714 (17)	0.0250 (14)	0.0448 (15)	0.0460 (14)
C15	0.0818 (16)	0.0500 (13)	0.0533 (13)	0.0198 (11)	0.0295 (12)	0.0275 (11)
C16	0.0555 (12)	0.0394 (10)	0.0360 (10)	0.0124 (8)	0.0208 (9)	0.0147 (8)
C17	0.0536 (12)	0.0420 (11)	0.0428 (11)	0.0159 (9)	0.0209 (9)	0.0180 (9)
C18	0.0669 (14)	0.0508 (12)	0.0472 (12)	0.0176 (10)	0.0292 (11)	0.0145 (10)
C19	0.099 (2)	0.0533 (15)	0.0715 (18)	0.0264 (14)	0.0441 (16)	0.0118 (13)

Geometric parameters (Å, º)

S1—C2	1.754 (2)	C11—H11	0.9300
S1—C3	1.754 (2)	C11—C12	1.379 (3)
O1—C1	1.349 (2)	C12—H12	0.9300
O1—C16	1.443 (2)	C12—C13	1.376 (4)
N1—C1	1.275 (3)	C13—H13	0.9300
N1—C8	1.403 (3)	C13—C14	1.374 (4)
C1—C2	1.480 (3)	C14—H14	0.9300
C2—C9	1.352 (3)	C14—C15	1.385 (3)
C3—C4	1.390 (3)	C15—H15	0.9300
C3—C8	1.390 (3)	C16—H16A	0.9700
C4—H4	0.9300	C16—H16B	0.9700
C4—C5	1.384 (3)	C16—C17	1.498 (3)
C5—H5	0.9300	C17—H17A	0.9700
C5—C6	1.387 (4)	C17—H17B	0.9700
C6—H6	0.9300	C17—C18	1.516 (3)
C6—C7	1.380 (3)	C18—H18A	0.9700
C7—H7	0.9300	C18—H18B	0.9700

C7—C8	1.393 (3)	C18—C19	1.509 (3)
C9—H9	0.9300	C19—H19A	0.9600
C9—C10	1.465 (3)	C19—H19B	0.9600
C10—C11	1.389 (3)	C19—H19C	0.9600
C10—C15	1.395 (3)		

C3—S1—C2	103.27 (10)	C11—C12—H12	119.7
C1—O1—C16	117.28 (15)	C13—C12—C11	120.5 (2)
C1—N1—C8	122.00 (17)	C13—C12—H12	119.7
O1—C1—C2	111.21 (17)	C12—C13—H13	120.3
N1—C1—O1	119.64 (17)	C14—C13—C12	119.4 (2)
N1—C1—C2	129.15 (18)	C14—C13—H13	120.3
C1—C2—S1	116.55 (14)	C13—C14—H14	119.8
C9—C2—S1	123.02 (16)	C13—C14—C15	120.4 (2)
C9—C2—C1	120.40 (18)	C15—C14—H14	119.8
C4—C3—S1	117.21 (17)	C10—C15—H15	119.5
C4—C3—C8	120.7 (2)	C14—C15—C10	120.9 (2)
C8—C3—S1	122.03 (16)	C14—C15—H15	119.5
C3—C4—H4	119.9	O1—C16—H16A	110.3
C5—C4—C3	120.2 (2)	O1—C16—H16B	110.3
C5—C4—H4	119.9	O1—C16—C17	106.89 (16)
C4—C5—H5	120.2	H16A—C16—H16B	108.6
C4—C5—C6	119.6 (2)	C17—C16—H16A	110.3
C6—C5—H5	120.2	C17—C16—H16B	110.3
C5—C6—H6	120.1	C16—C17—H17A	109.2
C7—C6—C5	119.9 (2)	C16—C17—H17B	109.2
C7—C6—H6	120.1	C16—C17—C18	112.25 (18)
C6—C7—H7	119.3	H17A—C17—H17B	107.9
C6—C7—C8	121.4 (2)	C18—C17—H17A	109.2
C8—C7—H7	119.3	C18—C17—H17B	109.2
C3—C8—N1	124.66 (18)	C17—C18—H18A	109.0
C3—C8—C7	118.15 (19)	C17—C18—H18B	109.0
C7—C8—N1	117.17 (19)	H18A—C18—H18B	107.8
C2—C9—H9	114.6	C19—C18—C17	112.9 (2)
C2—C9—C10	130.9 (2)	C19—C18—H18A	109.0
C10—C9—H9	114.6	C19—C18—H18B	109.0
C11—C10—C9	125.5 (2)	C18—C19—H19A	109.5
C11—C10—C15	117.6 (2)	C18—C19—H19B	109.5
C15—C10—C9	116.9 (2)	C18—C19—H19C	109.5
C10—C11—H11	119.4	H19A—C19—H19B	109.5
C12—C11—C10	121.2 (2)	H19A—C19—H19C	109.5
C12—C11—H11	119.4	H19B—C19—H19C	109.5

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C3–C8 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···S1	0.93	2.51	3.155 (2)	127

C17—H17*A*···*Cg*2^{i}	0.97	2.82	3.665 (3)	146

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.