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(*Z*)-2-(2-Chlorobenzylidene)-4-(prop-2-ynyl)-2*H*-1,4-benzothiazin-3(4*H*)-one

Nada Kheira Sebbar,[a] Mohamed Ellouz,[a]* Younes Ouzidan,[b] Manpreet Kaur,[c] El Mokhtar Essassi[a] and Jerry P. Jasinski[c]

[a]Laboratoire de Chimie Organique Hétérocyclique URAC 21, Pôle de Compétence Pharmacochimie, Av. Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, [b]Laboratoire de Chimie Organique Appliquée, Faculté des Sciences et Techniques, Université Sidi Mohammed Ben Abdellah, Fès, Morocco, and [c]Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA. *Correspondence e-mail: ellouz.chimie@gmail.com

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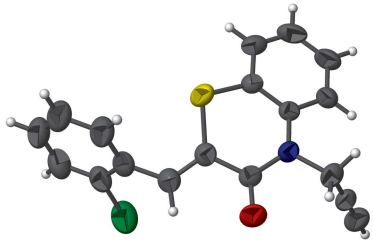
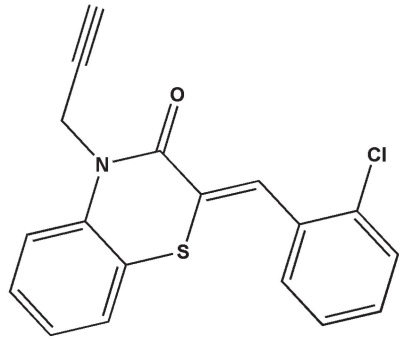
In the title compound, $C_{18}H_{12}ClNOS$, the thiazine-3-one ring of the 1,4-thiazin-3-one moiety adopts a slightly distorted twist-boat conformation. The dihedral angle between the benzene rings is 86.2 (1)°. In the crystal, the crystal packing features a single weak C—H···O interaction and weak π–π stacking interactions.

3D view



Chemical scheme



Structure description

The 1,4-benzothiazine ring system represents an important class of compounds, not only for their theoretical interest, but also for their analgesic (Wammack *et al.*, 2002); anti-viral (Malagu *et al.*, 1998; Rathore & Kumar, 2006) and anti-oxidant activities (Zia-ur-Rehman *et al.*, 2009). Recently, related research has been focused on existing molecules and their modifications in order to reduce their side effects and to explore their other pharmacological and biological effects (Sebbar *et al.*, 2016*a*; Armenise *et al.*, 2012). As a continuation of our research work on the development of N-substituted 1,4-benzothiazine derivatives and the evaluation of their potential pharmacological activities, we have studied the condensation reaction of propargyl bromide with (*Z*)-2-(2-chlorobenzylidene)-2*H*-1,4-benzothiazin-3(4*H*)-one under phase-transfer catalysis conditions using tetra-*n*-butylammonium bromide (TBAB) as a catalyst and potassium carbonate as the base, giving the title compound in good yield (Sebbar *et al.*, 2016*b*, Ellouz *et al.*, 2017*a*,*b*).

In the title compound (Fig. 1), the thiazine-3-one ring of the [1,4]thiazin-3-one moiety adopts a slightly distorted twist-boat conformation [puckering parameters: Q = 0.433 (2) Å, θ = 110.2 (2)° and φ = 196.4 (3)°]. The dihedral angle between the benzene

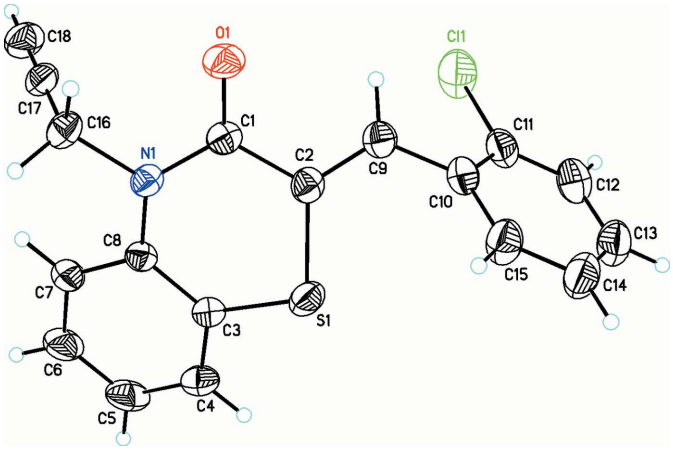


Figure 1
The structure of the title compound, showing the atom-numbering scheme, with displacement ellipsoids drawn at the 30% probability level.

rings is 86.2 (1)°. In the crystal, a single weak C18—H18···O1^{i} interaction links the molecules into chains along the *c*-axis direction (Fig. 2, Table 1). In addition, π–π stacking interactions [*Cg*3···*Cg*3^{iii} = 3.8766 (2) Å; *Cg*3 is the centroid of the C10–C15 benzene ring; symmetry code: (iii) $1-x, -y, -z$] are also observed.

Synthesis and crystallization

To a mixture of (*Z*)-2-(2-chlorobenzylidene)-2*H*-1,4-benzothiazin-3(4*H*)-one (0.49 g, 1.5 mmol), potassium carbonate (0.41 g, 3 mmol) and tetra-*n*-butyl ammonium bromide (0.048 g, 0.15 mmol) in DMF (15 ml) was added propargyl bromide (3 mmol). Stirring was continued at room temperature for 24 h. The salts were removed by filtration and the filtrate was concentrated under reduced pressure. The residue was separated by chromatography on a column of silica gel with ethyl acetate–hexane (1/9) as the eluent. The solid product was purified by recrystallization from ethanol solution to afford yellow crystals in 90% yield.

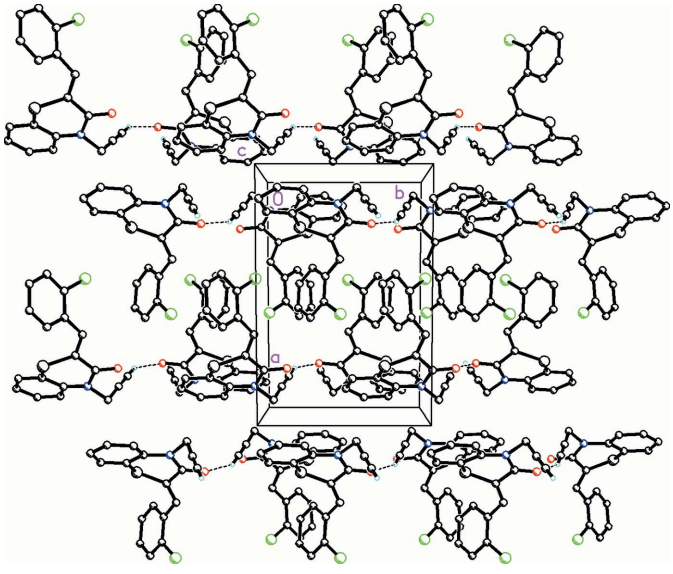


Figure 2
The molecular packing of the title compound, viewed along the *c* axis. Dashed lines indicate weak intermolecular hydrogen bonds. H atoms not involved in these interactions have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···O1^{i}	0.93	2.33	3.191 (3)	154

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{12}ClNOS$
M_r	325.80
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	13.3937 (8), 8.9106 (4), 13.3940 (7)
β (°)	99.765 (5)
V (Å^3)	1575.36 (15)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.38
Crystal size (mm)	0.24 × 0.18 × 0.12
Data collection	
Diffractometer	Rigaku Oxford Diffraction
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
T_{min}, T_{max}	0.481, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10186, 3031, 2559
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.138, 1.03
No. of reflections	3031
No. of parameters	199
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.29

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170889 [https://doi.org/10.1107/S2414314617008896]

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Crystal data

$C_{18}H_{12}ClNOS$
$M_r = 325.80$
Monoclinic, $P2_1/c$
$a = 13.3937$ (8) Å
$b = 8.9106$ (4) Å
$c = 13.3940$ (7) Å
$\beta = 99.765$ (5)°
$V = 1575.36$ (15) Å^3
$Z = 4$
$F(000) = 672$
$D_x = 1.374$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 3922 reflections
$\theta = 3.4$–$71.2°$
$\mu = 3.38$ mm^{-1}
$T = 293$ K
Prism, yellow
0.24 × 0.18 × 0.12 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)
$T_{min} = 0.481$, $T_{max} = 1.000$
10186 measured reflections
3031 independent reflections
2559 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 71.7°$, $\theta_{min} = 3.4°$
$h = -15\rightarrow16$
$k = -7\rightarrow10$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.138$
$S = 1.03$
3031 reflections
199 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.4736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ 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}
Cl1	0.42965 (6)	0.52359 (13)	0.25072 (7)	0.0975 (3)
S1	0.77650 (5)	0.76330 (7)	0.34112 (4)	0.0610 (2)
O1	0.78762 (15)	0.34054 (17)	0.26884 (13)	0.0621 (5)
N1	0.86271 (13)	0.53717 (19)	0.20648 (13)	0.0432 (4)
C1	0.79562 (16)	0.4761 (2)	0.26214 (15)	0.0447 (5)
C2	0.73317 (17)	0.5795 (2)	0.31387 (15)	0.0475 (5)
C3	0.82700 (15)	0.8022 (2)	0.23221 (15)	0.0435 (4)
C4	0.83237 (19)	0.9512 (3)	0.2039 (2)	0.0568 (6)
H4	0.8051	1.0256	0.2399	0.068*
C5	0.8780 (2)	0.9898 (3)	0.1227 (2)	0.0715 (8)
H5	0.8823	1.0900	0.1044	0.086*
C6	0.9169 (3)	0.8799 (3)	0.0693 (2)	0.0763 (9)
H6	0.9479	0.9058	0.0147	0.092*
C7	0.9106 (2)	0.7318 (3)	0.0955 (2)	0.0603 (6)
H7	0.9364	0.6584	0.0575	0.072*
C8	0.86627 (15)	0.6896 (2)	0.17806 (15)	0.0415 (4)
C9	0.64950 (19)	0.5274 (3)	0.34302 (17)	0.0555 (5)
H9	0.6326	0.4276	0.3283	0.067*
C10	0.58172 (19)	0.6140 (3)	0.39636 (18)	0.0563 (6)
C11	0.4785 (2)	0.6218 (3)	0.3599 (2)	0.0633 (6)
C12	0.4138 (2)	0.7054 (4)	0.4076 (3)	0.0773 (8)
H12	0.3451	0.7098	0.3812	0.093*
C13	0.4521 (3)	0.7823 (4)	0.4946 (3)	0.0824 (9)
H13	0.4090	0.8391	0.5273	0.099*
C14	0.5533 (3)	0.7758 (4)	0.5334 (2)	0.0815 (9)
H14	0.5789	0.8271	0.5926	0.098*
C15	0.6173 (2)	0.6930 (4)	0.4845 (2)	0.0707 (7)
H15	0.6861	0.6900	0.5113	0.085*
C16	0.92210 (18)	0.4284 (3)	0.15800 (18)	0.0537 (5)
H16A	0.9874	0.4722	0.1533	0.064*
H16B	0.9341	0.3399	0.2005	0.064*
C17	0.87254 (19)	0.3833 (2)	0.05696 (18)	0.0535 (5)
C18	0.8334 (2)	0.3439 (3)	−0.0242 (2)	0.0689 (7)
H18	0.8025	0.3128	−0.0883	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0702 (5)	0.1452 (9)	0.0770 (5)	−0.0216 (5)	0.0127 (4)	−0.0267 (5)
S1	0.0887 (5)	0.0493 (4)	0.0499 (3)	−0.0049 (3)	0.0256 (3)	−0.0109 (2)
O1	0.0877 (12)	0.0381 (9)	0.0631 (10)	0.0014 (7)	0.0204 (9)	0.0090 (7)
N1	0.0483 (9)	0.0386 (9)	0.0429 (9)	0.0043 (7)	0.0087 (7)	−0.0007 (7)
C1	0.0551 (12)	0.0402 (11)	0.0380 (9)	0.0020 (8)	0.0053 (8)	0.0035 (8)
C2	0.0568 (12)	0.0504 (12)	0.0358 (9)	0.0017 (9)	0.0096 (8)	0.0036 (8)
C3	0.0462 (10)	0.0394 (10)	0.0440 (10)	−0.0017 (8)	0.0047 (8)	−0.0015 (8)

C4	0.0645 (14)	0.0392 (11)	0.0653 (14)	−0.0018 (10)	0.0071 (11)	−0.0022 (10)
C5	0.092 (2)	0.0446 (13)	0.0768 (17)	−0.0206 (13)	0.0122 (15)	0.0107 (12)
C6	0.103 (2)	0.0625 (16)	0.0707 (17)	−0.0347 (15)	0.0358 (16)	−0.0021 (13)
C7	0.0701 (15)	0.0547 (14)	0.0624 (14)	−0.0176 (11)	0.0296 (12)	−0.0089 (11)
C8	0.0419 (10)	0.0409 (10)	0.0411 (9)	−0.0041 (8)	0.0049 (8)	−0.0012 (8)
C9	0.0640 (14)	0.0562 (13)	0.0488 (12)	−0.0022 (10)	0.0162 (10)	0.0012 (10)
C10	0.0605 (13)	0.0621 (14)	0.0497 (12)	−0.0031 (11)	0.0191 (10)	0.0042 (10)
C11	0.0627 (14)	0.0744 (17)	0.0567 (13)	−0.0089 (12)	0.0214 (11)	0.0065 (12)
C12	0.0582 (15)	0.097 (2)	0.0812 (19)	0.0009 (14)	0.0240 (14)	0.0061 (16)
C13	0.081 (2)	0.092 (2)	0.082 (2)	0.0075 (17)	0.0384 (17)	−0.0062 (17)
C14	0.086 (2)	0.098 (2)	0.0651 (17)	−0.0004 (17)	0.0264 (15)	−0.0181 (15)
C15	0.0638 (15)	0.094 (2)	0.0554 (14)	0.0017 (14)	0.0125 (12)	−0.0096 (13)
C16	0.0530 (12)	0.0488 (12)	0.0595 (13)	0.0125 (9)	0.0098 (10)	−0.0043 (10)
C17	0.0679 (14)	0.0395 (11)	0.0581 (13)	0.0045 (9)	0.0253 (11)	−0.0025 (9)
C18	0.099 (2)	0.0580 (15)	0.0535 (14)	−0.0054 (14)	0.0238 (14)	−0.0074 (11)

Geometric parameters (Å, º)

Cl1—C11	1.734 (3)	C7—C8	1.393 (3)
S1—C2	1.755 (2)	C9—H9	0.9300
S1—C3	1.744 (2)	C9—C10	1.467 (3)
O1—C1	1.217 (3)	C10—C11	1.388 (4)
N1—C1	1.374 (3)	C10—C15	1.388 (4)
N1—C8	1.414 (3)	C11—C12	1.379 (4)
N1—C16	1.473 (3)	C12—H12	0.9300
C1—C2	1.492 (3)	C12—C13	1.374 (5)
C2—C9	1.331 (3)	C13—H13	0.9300
C3—C4	1.386 (3)	C13—C14	1.369 (5)
C3—C8	1.392 (3)	C14—H14	0.9300
C4—H4	0.9300	C14—C15	1.377 (4)
C4—C5	1.378 (4)	C15—H15	0.9300
C5—H5	0.9300	C16—H16A	0.9700
C5—C6	1.367 (4)	C16—H16B	0.9700
C6—H6	0.9300	C16—C17	1.459 (3)
C6—C7	1.372 (4)	C17—C18	1.177 (4)
C7—H7	0.9300	C18—H18	0.9300
C3—S1—C2	99.97 (10)	C2—C9—C10	125.5 (2)
C1—N1—C8	125.59 (17)	C10—C9—H9	117.3
C1—N1—C16	115.49 (18)	C11—C10—C9	121.1 (2)
C8—N1—C16	117.93 (17)	C11—C10—C15	116.9 (2)
O1—C1—N1	120.5 (2)	C15—C10—C9	122.0 (2)
O1—C1—C2	121.0 (2)	C10—C11—Cl1	118.8 (2)
N1—C1—C2	118.49 (18)	C12—C11—Cl1	119.1 (2)
C1—C2—S1	118.78 (16)	C12—C11—C10	122.0 (3)
C9—C2—S1	121.98 (18)	C11—C12—H12	120.3
C9—C2—C1	119.1 (2)	C13—C12—C11	119.3 (3)
C4—C3—S1	117.71 (17)	C13—C12—H12	120.3

C4—C3—C8	120.4 (2)	C12—C13—H13	119.9
C8—C3—S1	121.80 (16)	C14—C13—C12	120.2 (3)
C3—C4—H4	119.8	C14—C13—H13	119.9
C5—C4—C3	120.4 (2)	C13—C14—H14	120.0
C5—C4—H4	119.8	C13—C14—C15	120.0 (3)
C4—C5—H5	120.2	C15—C14—H14	120.0
C6—C5—C4	119.6 (2)	C10—C15—H15	119.2
C6—C5—H5	120.2	C14—C15—C10	121.6 (3)
C5—C6—H6	119.6	C14—C15—H15	119.2
C5—C6—C7	120.7 (3)	N1—C16—H16A	108.9
C7—C6—H6	119.6	N1—C16—H16B	108.9
C6—C7—H7	119.5	H16A—C16—H16B	107.7
C6—C7—C8	121.0 (2)	C17—C16—N1	113.30 (19)
C8—C7—H7	119.5	C17—C16—H16A	108.9
C3—C8—N1	121.27 (18)	C17—C16—H16B	108.9
C3—C8—C7	118.0 (2)	C18—C17—C16	178.6 (3)
C7—C8—N1	120.7 (2)	C17—C18—H18	180.0
C2—C9—H9	117.3		

Cl1—C11—C12—C13	179.5 (3)	C4—C5—C6—C7	0.2 (5)
S1—C2—C9—C10	2.5 (3)	C5—C6—C7—C8	−1.2 (5)
S1—C3—C4—C5	175.4 (2)	C6—C7—C8—N1	−178.1 (3)
S1—C3—C8—N1	2.9 (3)	C6—C7—C8—C3	1.1 (4)
S1—C3—C8—C7	−176.23 (18)	C8—N1—C1—O1	168.0 (2)
O1—C1—C2—S1	157.24 (18)	C8—N1—C1—C2	−12.0 (3)
O1—C1—C2—C9	−19.0 (3)	C8—N1—C16—C17	−80.1 (3)
N1—C1—C2—S1	−22.8 (2)	C8—C3—C4—C5	−1.0 (4)
N1—C1—C2—C9	161.0 (2)	C9—C10—C11—Cl1	1.3 (3)
C1—N1—C8—C3	23.2 (3)	C9—C10—C11—C12	−178.4 (3)
C1—N1—C8—C7	−157.7 (2)	C9—C10—C15—C14	179.1 (3)
C1—N1—C16—C17	89.1 (2)	C10—C11—C12—C13	−0.8 (5)
C1—C2—C9—C10	178.7 (2)	C11—C10—C15—C14	−0.3 (4)
C2—S1—C3—C4	154.52 (19)	C11—C12—C13—C14	0.0 (5)
C2—S1—C3—C8	−29.14 (19)	C12—C13—C14—C15	0.6 (5)
C2—C9—C10—C11	126.8 (3)	C13—C14—C15—C10	−0.5 (5)
C2—C9—C10—C15	−52.6 (4)	C15—C10—C11—Cl1	−179.3 (2)
C3—S1—C2—C1	38.40 (18)	C15—C10—C11—C12	0.9 (4)
C3—S1—C2—C9	−145.5 (2)	C16—N1—C1—O1	−0.3 (3)
C3—C4—C5—C6	0.8 (4)	C16—N1—C1—C2	179.71 (18)
C4—C3—C8—N1	179.2 (2)	C16—N1—C8—C3	−168.79 (19)
C4—C3—C8—C7	0.0 (3)	C16—N1—C8—C7	10.4 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···O1^{i}	0.93	2.71	3.486 (4)	142

C18—H18···O1^{ii}	0.93	2.33	3.191 (3)	154

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