

Crystal structure of (Z)-3-allyl-5-(3-bromobenzylidene)-2-sulfanylidene-1,3-thiazolidin-4-one

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In the title compound, C₁₃H₁₀BrNOS₂, the rhodanine (systematic name: 2-sulfanylidene-1,3-thiazolidin-4-one) and the 3-bromobenzylidene ring systems are inclined slightly, forming a dihedral angle of 5.86 (12)°. The rhodanine moiety is linked to an allyl group at the N atom and to the 3-bromobenzylidene ring system. The allyl group, C=C—C, is nearly perpendicular to the mean plane through the rhodanine ring, making a dihedral angle of 87.2 (5)°. In the crystal, molecules are linked by pairs of C—H···O hydrogen bonds, forming inversion dimers with an R₂²(10) ring motif.

Keywords: crystal structure; rhodanine; hydrogen bonding.

CCDC reference: 1439611

1. Related literature

For pharmacological and biological activities of rhodanine-based molecules, see: Tomasić & Masic (2009); Sortino *et al.* (2007); Kesel (2003); Capan *et al.* (1996); Momose *et al.* (1991); Kawakami *et al.* (1998); Insuasty *et al.* (2010). For the crystal structure of a related compound, see: El Ajlaoui *et al.* (2015).

2. Experimental

2.1. Crystal data

C ₁₃ H ₁₀ BrNOS ₂	$\gamma = 76.732 (6)^\circ$
$M_r = 340.25$	$V = 685.60 (13) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.4044 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.2306 (13) \text{ \AA}$	$\mu = 3.29 \text{ mm}^{-1}$
$c = 11.7966 (13) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 80.100 (5)^\circ$	$0.31 \times 0.27 \times 0.21 \text{ mm}$
$\beta = 84.912 (6)^\circ$	

2.2. Data collection

Bruker X8 APEX diffractometer	25482 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	4181 independent reflections
$T_{\min} = 0.479$, $T_{\max} = 0.746$	2895 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	163 parameters
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.95 \text{ e \AA}^{-3}$
4181 reflections	$\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C7-H7\cdots O1^i$	0.93	2.42	3.310 (3)	159

Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS2014 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5249).

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Crystal structure of (Z)-3-allyl-5-(3-bromobenzylidene)-2-sulfanylidene-1,3-thiazolidin-4-one

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S1. Structural commentary

Rhodanine is an attractive scaffold unit because of its prestigious position in medicinal chemistry as it is responsible for numerous pharmacological and biological activities (Tomasic & Masic, 2009), *e.g.*, antimicrobial, antiviral, anti-convulsant, antidiabetic and antitumor activities (Sortino *et al.*, 2007; Kesel, 2003; Capan *et al.*, 1996; Momose *et al.*, 1991; Kawakami *et al.*, 1998; Insuasty *et al.* 2010). The unusual biological activity displayed by many rhodanine-based molecules have made them attractive synthetic targets.

The title compound, Fig. 1, is build up from a rhodanine ring (S1/N/1 C8–C10) linked to an allyl group (C11–C13) at the nitrogen atom and to a 3-bromobenzylidene ring system (C1–C6). The mean plane through the rhodanine ring is almost perpendicular to the allyl group (C11–C13) with a dihedral angle of 87.2 (5) °, and makes a dihedral angle of 5.86 (12)° with the 3-bromobenzylidene ring. A very similar arrangement has been observed in the crystal structure of (Z)-3-allyl-5-(4-methyl-benzylidene)-2-thioxothiazolidin-4-one, but with disorder in the allyl group (El Ajlaoui *et al.*, 2015).

In the crystal, molecules are linked by a pair of C—H···O hydrogen bonds forming inversion dimers with an $R^2_2(10)$ ring motif (Table 1 and Fig. 2).

S2. Synthesis and crystallization

To a solution of 3-allylrhodanine (1.15 mmol, 0.2 g) in 10 ml of THF, (3-bromobenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (1.38 mmol) was added and the mixture refluxed for 8 h, monitored by TLC. On completion of the reaction, with a yellow spot (TLC Rf = 0.3, using hexane/ethyl acetate 1:9) generated cleanly, the solvent was evaporated *in vacuo*. The crude product was purified on silica gel using hexane:ethyl acetate (1:9) as eluent. The title compound was recrystallized from ethanol giving colourless block-like crystals (yield: 76%; m.p. 390 K).

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were located in a difference Fourier map and treated as riding: C–H = 0.93–0.97 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Two reflections, (0 1 0) and (0 0 1), affected by the beam-stop were removed during the final cycles of refinement.

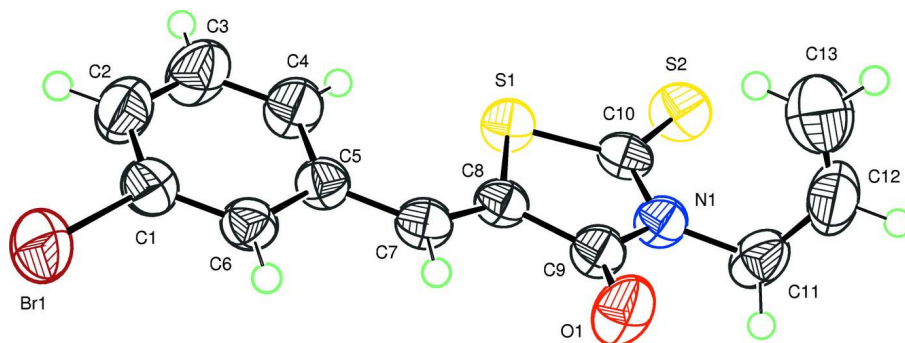


Figure 1

A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

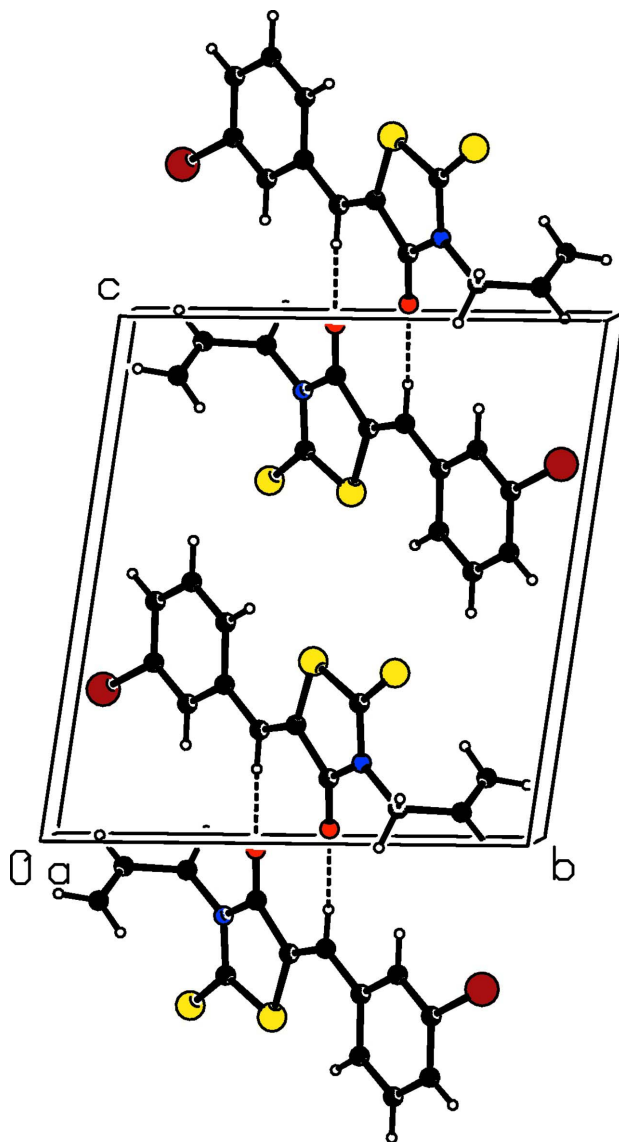


Figure 2

A view along the *a* axis of the crystal packing of the title compound, showing the hydrogen bonds as dashed lines (see Table 1).

(*Z*)-3-Allyl-5-(3-bromobenzylidene)-2-sulfanylidene-1,3-thiazolidin-4-one

Crystal data

$C_{13}H_{10}BrNOS_2$

$M_r = 340.25$

Triclinic, $P\bar{1}$

$a = 5.4044$ (6) Å

$b = 11.2306$ (13) Å

$c = 11.7966$ (13) Å

$\alpha = 80.100$ (5)°

$\beta = 84.912$ (6)°

$\gamma = 76.732$ (6)°

$V = 685.60$ (13) Å³

$Z = 2$

$F(000) = 340$

$D_x = 1.648$ Mg m⁻³

Melting point: 390 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4181 reflections

$\theta = 2.8$ – 30.5 °

$\mu = 3.29$ mm⁻¹

$T = 296$ K $0.31 \times 0.27 \times 0.21$ mm
 Block, colourless

Data collection

Bruker X8 APEX diffractometer	25482 measured reflections
Radiation source: fine-focus sealed tube	4181 independent reflections
Graphite monochromator	2895 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.044$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$\theta_{\text{max}} = 30.5^\circ$, $\theta_{\text{min}} = 2.8^\circ$
$T_{\text{min}} = 0.479$, $T_{\text{max}} = 0.746$	$h = -7 \rightarrow 7$
	$k = -16 \rightarrow 16$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.492P]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4181 reflections	$\Delta\rho_{\text{max}} = 0.95 \text{ e } \text{\AA}^{-3}$
163 parameters	$\Delta\rho_{\text{min}} = -0.71 \text{ e } \text{\AA}^{-3}$
0 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7585 (5)	0.8474 (2)	0.6704 (2)	0.0449 (5)
C2	0.7277 (6)	0.8621 (3)	0.5535 (2)	0.0578 (7)
H2	0.7974	0.9201	0.5025	0.069*
C3	0.5914 (6)	0.7891 (3)	0.5138 (2)	0.0625 (8)
H3	0.5704	0.7977	0.4352	0.075*
C4	0.4861 (5)	0.7039 (3)	0.5885 (2)	0.0516 (6)
H4	0.3934	0.6562	0.5601	0.062*
C5	0.5173 (4)	0.6882 (2)	0.70721 (19)	0.0379 (5)
C6	0.6565 (4)	0.7623 (2)	0.7469 (2)	0.0392 (5)
H6	0.6799	0.7540	0.8253	0.047*
C7	0.4177 (4)	0.5987 (2)	0.79133 (19)	0.0386 (5)
H7	0.4638	0.5940	0.8663	0.046*
C8	0.2693 (4)	0.5212 (2)	0.77866 (18)	0.0358 (4)
C9	0.1983 (4)	0.4349 (2)	0.87829 (19)	0.0402 (5)
C10	-0.0140 (4)	0.3884 (2)	0.7315 (2)	0.0385 (5)
C11	-0.0559 (5)	0.2749 (3)	0.9303 (2)	0.0538 (7)
H11A	-0.2218	0.2691	0.9094	0.065*
H11B	-0.0769	0.3018	1.0051	0.065*
C12	0.1173 (8)	0.1500 (3)	0.9393 (3)	0.0717 (9)

H12	0.0739	0.0898	0.9972	0.086*
C13	0.3193 (8)	0.1155 (3)	0.8769 (3)	0.0845 (11)
H13A	0.3724	0.1716	0.8176	0.101*
H13B	0.4125	0.0343	0.8909	0.101*
N1	0.0372 (4)	0.36716 (18)	0.84606 (16)	0.0398 (4)
O1	0.2673 (4)	0.42021 (19)	0.97577 (14)	0.0579 (5)
S1	0.13666 (12)	0.50102 (6)	0.65523 (5)	0.04169 (14)
S2	-0.18899 (14)	0.31940 (7)	0.67061 (6)	0.05491 (18)
Br1	0.94248 (6)	0.94874 (3)	0.72543 (3)	0.06670 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0478 (14)	0.0440 (13)	0.0461 (13)	-0.0140 (11)	-0.0009 (10)	-0.0110 (10)
C2	0.0697 (18)	0.0600 (17)	0.0465 (14)	-0.0269 (14)	0.0026 (13)	-0.0013 (12)
C3	0.080 (2)	0.079 (2)	0.0341 (13)	-0.0327 (17)	-0.0068 (13)	-0.0022 (13)
C4	0.0625 (16)	0.0627 (16)	0.0376 (12)	-0.0268 (13)	-0.0082 (11)	-0.0086 (11)
C5	0.0402 (12)	0.0407 (12)	0.0345 (11)	-0.0097 (9)	-0.0058 (9)	-0.0077 (9)
C6	0.0424 (12)	0.0420 (12)	0.0356 (11)	-0.0106 (10)	-0.0030 (9)	-0.0105 (9)
C7	0.0418 (12)	0.0450 (12)	0.0319 (10)	-0.0102 (10)	-0.0087 (9)	-0.0097 (9)
C8	0.0381 (11)	0.0397 (11)	0.0315 (10)	-0.0072 (9)	-0.0077 (8)	-0.0093 (9)
C9	0.0434 (12)	0.0455 (12)	0.0359 (11)	-0.0142 (10)	-0.0071 (9)	-0.0091 (9)
C10	0.0346 (11)	0.0436 (12)	0.0403 (12)	-0.0059 (9)	-0.0075 (9)	-0.0152 (9)
C11	0.0588 (16)	0.0713 (18)	0.0417 (13)	-0.0359 (14)	0.0026 (11)	-0.0107 (12)
C12	0.106 (3)	0.0573 (18)	0.0569 (18)	-0.0387 (18)	-0.0014 (18)	0.0050 (14)
C13	0.098 (3)	0.060 (2)	0.082 (3)	-0.0004 (19)	-0.008 (2)	0.0036 (18)
N1	0.0432 (10)	0.0464 (11)	0.0345 (9)	-0.0159 (9)	-0.0060 (8)	-0.0085 (8)
O1	0.0756 (13)	0.0754 (13)	0.0335 (9)	-0.0392 (11)	-0.0177 (8)	0.0004 (8)
S1	0.0471 (3)	0.0495 (3)	0.0328 (3)	-0.0148 (3)	-0.0131 (2)	-0.0066 (2)
S2	0.0547 (4)	0.0703 (4)	0.0517 (4)	-0.0268 (3)	-0.0135 (3)	-0.0194 (3)
Br1	0.0796 (2)	0.0688 (2)	0.0663 (2)	-0.04359 (17)	0.00513 (15)	-0.01814 (15)

Geometric parameters (Å, °)

C1—C6	1.374 (3)	C8—S1	1.749 (2)
C1—C2	1.381 (4)	C9—O1	1.213 (3)
C1—Br1	1.896 (2)	C9—N1	1.394 (3)
C2—C3	1.380 (4)	C10—N1	1.372 (3)
C2—H2	0.9300	C10—S2	1.631 (2)
C3—C4	1.374 (4)	C10—S1	1.739 (2)
C3—H3	0.9300	C11—N1	1.453 (3)
C4—C5	1.401 (3)	C11—C12	1.489 (5)
C4—H4	0.9300	C11—H11A	0.9700
C5—C6	1.401 (3)	C11—H11B	0.9700
C5—C7	1.447 (3)	C12—C13	1.283 (5)
C6—H6	0.9300	C12—H12	0.9300
C7—C8	1.345 (3)	C13—H13A	0.9300
C7—H7	0.9300	C13—H13B	0.9300

C8—C9	1.472 (3)		
C6—C1—C2	121.4 (2)	C9—C8—S1	109.66 (16)
C6—C1—Br1	119.79 (18)	O1—C9—N1	122.5 (2)
C2—C1—Br1	118.8 (2)	O1—C9—C8	127.0 (2)
C3—C2—C1	118.7 (2)	N1—C9—C8	110.44 (18)
C3—C2—H2	120.7	N1—C10—S2	126.32 (19)
C1—C2—H2	120.7	N1—C10—S1	110.91 (16)
C4—C3—C2	121.1 (3)	S2—C10—S1	122.77 (14)
C4—C3—H3	119.5	N1—C11—C12	113.0 (2)
C2—C3—H3	119.5	N1—C11—H11A	109.0
C3—C4—C5	120.6 (2)	C12—C11—H11A	109.0
C3—C4—H4	119.7	N1—C11—H11B	109.0
C5—C4—H4	119.7	C12—C11—H11B	109.0
C6—C5—C4	118.1 (2)	H11A—C11—H11B	107.8
C6—C5—C7	117.89 (19)	C13—C12—C11	127.9 (3)
C4—C5—C7	124.0 (2)	C13—C12—H12	116.1
C1—C6—C5	120.2 (2)	C11—C12—H12	116.1
C1—C6—H6	119.9	C12—C13—H13A	120.0
C5—C6—H6	119.9	C12—C13—H13B	120.0
C8—C7—C5	130.5 (2)	H13A—C13—H13B	120.0
C8—C7—H7	114.8	C10—N1—C9	116.30 (19)
C5—C7—H7	114.8	C10—N1—C11	123.3 (2)
C7—C8—C9	120.37 (19)	C9—N1—C11	120.27 (19)
C7—C8—S1	129.97 (18)	C10—S1—C8	92.61 (11)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C7—H7 \cdots O1 ⁱ	0.93	2.42	3.310 (3)	159

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