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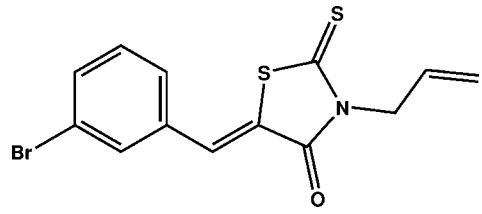

Crystal structure of (*Z*)-3-allyl-5-(3-bromobenzylidene)-2-sulfanylidene-1,3-thiazolidin-4-one

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In the title compound, $C_{13}H_{10}BrNOS_2$, 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, maling 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 $R_2^2(10)$ 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

$C_{13}H_{10}BrNOS_2$
M_r = 340.25
Triclinic, $P\overline{1}$
a = 5.4044 (6) Å
b = 11.2306 (13) Å
c = 11.7966 (13) Å
α = 80.100 (5)°
β = 84.912 (6)°
γ = 76.732 (6)°
V = 685.60 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.29 mm^{-1}
T = 296 K
0.31 × 0.27 × 0.21 mm

2.2. Data collection

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

2.3. Refinement

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···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).

Acknowledgements

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

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supporting information

Acta Cryst. (2015). E**71**, o1010–o1011 [https://doi.org/10.1107/S2056989015022884]

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

Rahhal El Ajlaoui, El Mostapha Rakib, Issam Forsal, Mohamed Saadi and Lahcen El Ammari

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/1C8–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 $U_{iso}(H) = 1.2U_{eq}(C)$. Two reflections, (0 1 0) and (0 0 1), affected by the beam-stop were removed during the final cycles of refinement.

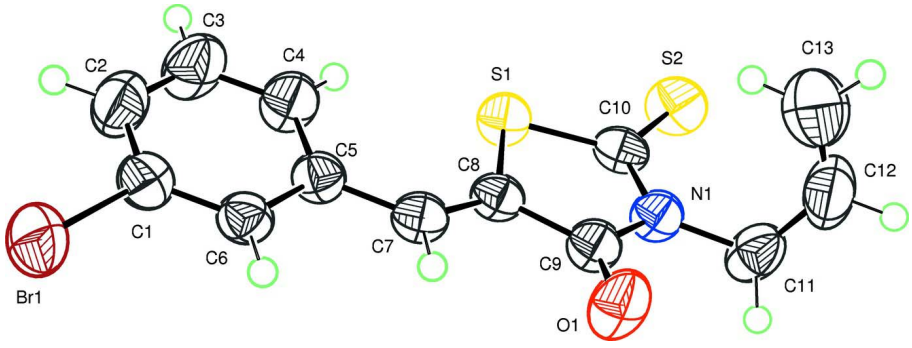

Figure 1

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

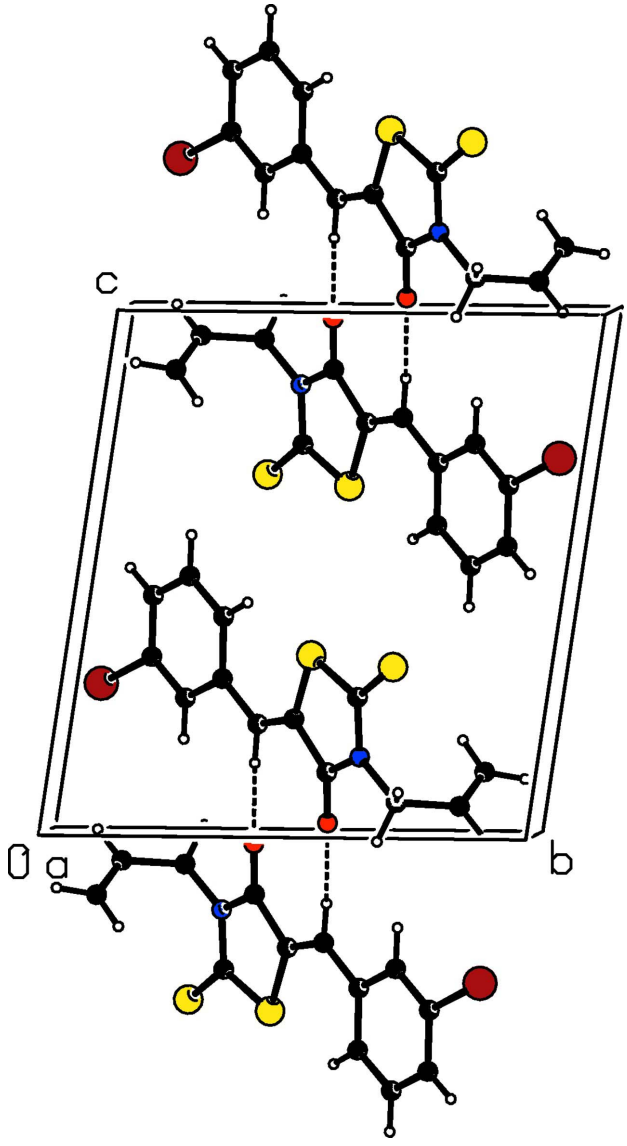

Figure 2

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, $P\overline{1}$
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$b = 11.2306$ (13) Å
$c = 11.7966$ (13) Å
$\alpha = 80.100$ (5)°
$\beta = 84.912$ (6)°
$\gamma = 76.732$ (6)°
$V = 685.60$ (13) Å^3
$Z = 2$
$F(000) = 340$
$D_x = 1.648$ 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
Block, colourless

0.31 × 0.27 × 0.21 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.479, T_{max} = 0.746

25482 measured reflections
4181 independent reflections
2895 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 30.5°, θ_{min} = 2.8°
h = −7→7
k = −16→16
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.098
S = 1.01
4181 reflections
163 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.492P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 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}
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, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O1^{i}	0.93	2.42	3.310 (3)	159

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.