

Crystal structure of (*E*)-3-allyl-2-sulfanylidenethiazolidin-4-one-5-[(thiophen-2-yl)methylidene]-

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Molecules of the title compound, C₁₁H₉NOS₃, are built up by one thiophene and one 2-thioxathiazolidin-4-one ring which are connected by a methylene bridge. In addition, there is an allyl substituent attached to nitrogen. The two rings are almost coplanar, making a dihedral angle between them of 0.76 (11)°. The allyl group is oriented perpendicular to the mean plane through both ring systems. The crystal structure exhibits inversion dimers in which molecules are linked by pairs of C—H...O hydrogen bonds. Additional π–π interactions between neighboring thiophene and 2-thioxathiazolidin-4-one rings [intercentroid distance = 3.694 (2) Å] lead to the formation of a three-dimensional network.

Keywords: crystal structure; rhodanine derivative; 2-thioxathiazolidin-4-one; hydrogen bonding; π–π interactions.

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1. Related literature

For pharmacological activities such as antimicrobial and anti-inflammatory of arylidene derivatives of rhodanine (2-thioxo-1,3-thiazolidin-4-one), see: Soltero-Higgin *et al.* (2004); Hu *et al.* (2004); Nasr & Said (2003); Johnson *et al.* (2001); Sortino *et al.* (2007); Insuasty *et al.* (2010); Tomasic & Masic (2009).

2. Experimental

2.1. Crystal data

C ₁₁ H ₉ NOS ₃	γ = 68.908 (1)°
M _r = 267.37	V = 601.44 (3) Å ³
Triclinic, P $\bar{1}$	Z = 2
a = 6.7342 (2) Å	Mo Kα radiation
b = 7.3762 (2) Å	μ = 0.59 mm ⁻¹
c = 13.2917 (5) Å	T = 296 K
α = 79.386 (2)°	0.37 × 0.35 × 0.28 mm
β = 80.104 (2)°	

2.2. Data collection

Bruker X8 APEX diffractometer	25223 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	3514 independent reflections
T _{min} = 0.700, T _{max} = 0.746	2557 reflections with I > 2σ(I)
	R _{int} = 0.042

2.3. Refinement

R[F ² > 2σ(F ²)] = 0.043	145 parameters
wR(F ²) = 0.111	H-atom parameters constrained
S = 1.07	Δρ _{max} = 0.35 e Å ⁻³
3514 reflections	Δρ _{min} = -0.26 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C3—H3...O1 ⁱ	0.93	2.54	3.304 (3)	140

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2009) and publCIF (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2466).

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supporting information

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Crystal structure of (*E*)-3-allyl-2-sulfanylidene-5-[(thiophen-2-yl)methylidene]thiazolidin-4-one

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S1. Comment

Rhodanine (2-thioxo-1,3-thiazolidin-4-one) is the key structural feature of a very important group of heterocyclic compounds for drug discovery programs. Arylidene derivatives of rhodanine have attracted great interest for synthetic organic chemists due to the broad biological activities of this class of compounds including antimicrobial (Sortino *et al.*; 2007, Hu *et al.*, 2004), anti-inflammatory (Nasr & Said, 2003; Johnson *et al.* 2001), and antifungal (Sortino *et al.*, 2007; Insuasty *et al.*, 2010) properties. Additionally, rhodanine derivatives may potentially be used in the treatment of diabetes, obesity, Alzheimer's disease, cystic fibrosis, thrombocytopenia, cancer, sleep, mood and central nervous system disorders as well as chronic inflammation (Tomasic & Masic, 2009).

The two five-membered rings (C1–C4, S1 and C6–C8, N1, S2) forming the molecule are almost coplanar, with a maximum deviation of $-0.023(2)$ Å for C7 (Fig.1). The allyl group is oriented perpendicular to the mean plane through the thioxothiazolidine cycle as indicated by the torsion angle C10–C9–N1–C7 of $90.2(3)^\circ$.

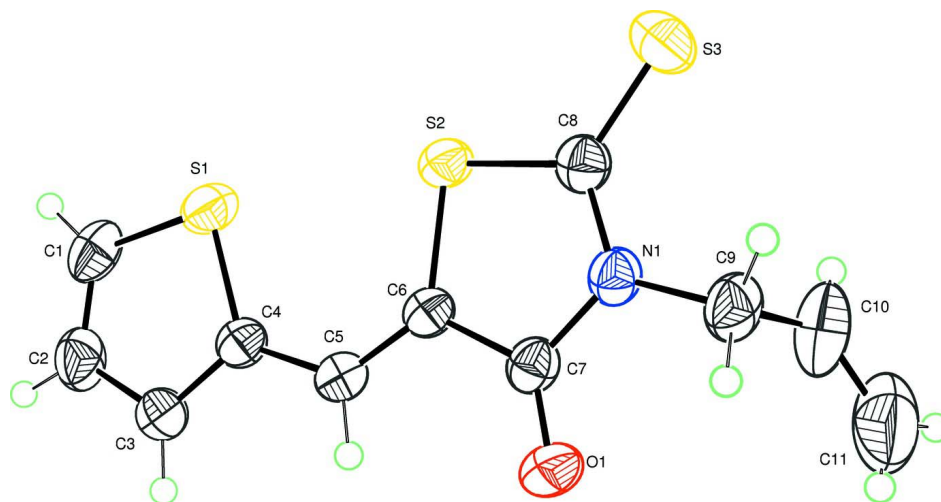
The cohesion of the crystal structure is ensured by C3–H3 \cdots O1 hydrogen bonds between molecules forming a dimers and π – π interactions between heterocycles [intercentroid distance = $3.69(2)$ Å], forming a three-dimensional network as shown in Fig.2 and Table 1.

S2. Experimental

To a solution of 3-allyl-2-thioxo-1,3-thiazolidin-4-one (1.15 mmol, 0.2 g) in 10 ml of THF methyl-2-(thiophen-2-yl-methylene)-5-oxopyrazolidin-2-ium-1-ide (1.38 mmol) was added. The mixture was refluxed for 8 h and was monitored by TLC. After the reaction was completed only one yellow spot (TLC $R_f = 0.3$, hexane/ethyl acetate 1:9) was generated cleanly. The solvent was evaporated *in vacuo*. The crude product was purified on silica using hexane: ethyl acetate (1/9) as eluent. The product was obtained as a yellow crystal solid (Yield: 55%, m.p.: 403 K).

S3. Refinement

H atoms were located from the difference Fourier map and treated as riding with C–H = 0.97 Å and C–H = 0.93 Å for methylene and aromatic, respectively. All hydrogen atoms were included into the refinement with $U_{iso}(H) = 1.2 U_{eq}$ of the parent carbon atom.

**Figure 1**

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small circles of arbitrary radius.

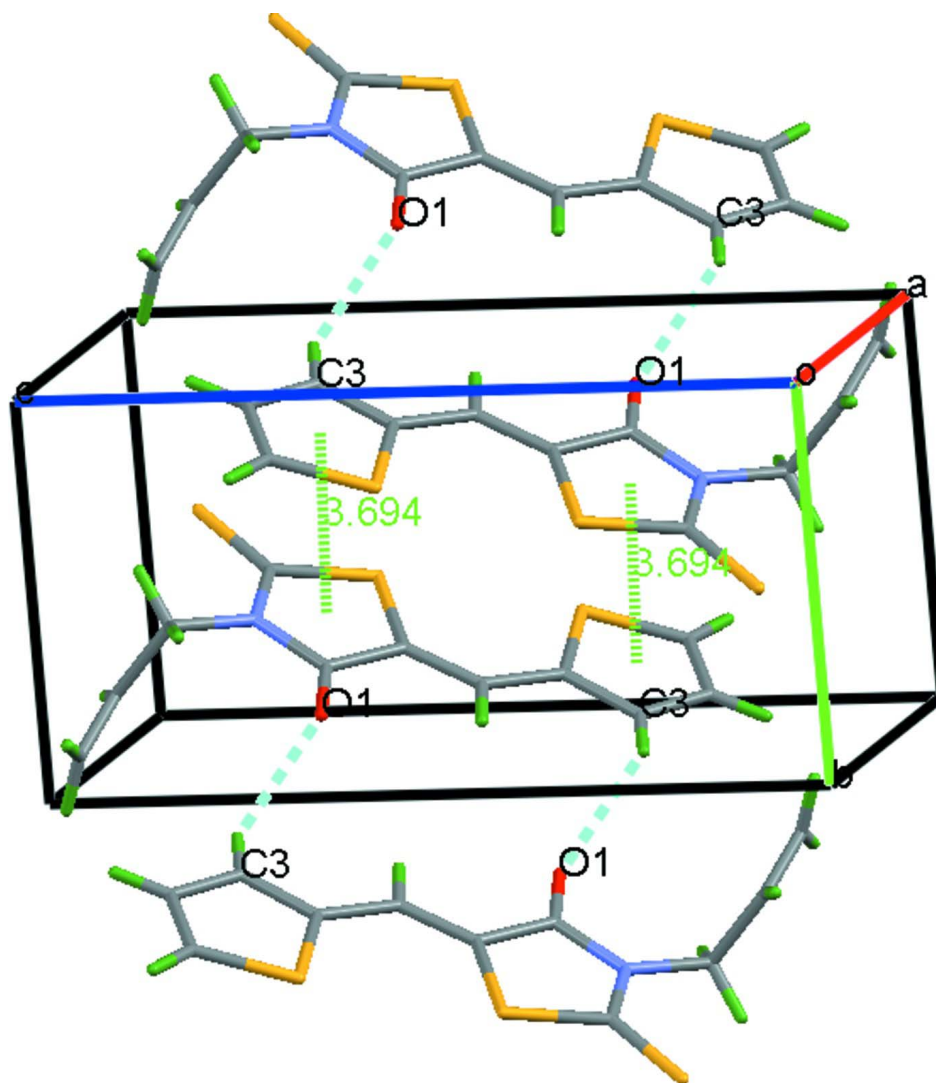


Figure 2

Partial crystal packing of the title compound showing hydrogen bonds and π - π interactions between molecules.

(E)-3-Allyl-2-sulfanylidene-5-[(thiophen-2-yl)methylidene]thiazolidin-4-one

Crystal data

$C_{11}H_9NOS_3$

$M_r = 267.37$

Triclinic, $P\bar{1}$

$a = 6.7342$ (2) Å

$b = 7.3762$ (2) Å

$c = 13.2917$ (5) Å

$\alpha = 79.386$ (2)°

$\beta = 80.104$ (2)°

$\gamma = 68.908$ (1)°

$V = 601.44$ (3) Å³

$Z = 2$

$F(000) = 276$

$D_x = 1.476$ Mg m⁻³

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

Cell parameters from 3514 reflections

$\theta = 3.0$ – 30.0 °

$\mu = 0.59$ mm⁻¹

$T = 296$ K

Block, yellow

$0.37 \times 0.35 \times 0.28$ mm

Data collection

Bruker X8 APEX diffractometer	25223 measured reflections
Radiation source: fine-focus sealed tube	3514 independent reflections
Graphite monochromator	2557 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.042$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.700$, $T_{\text{max}} = 0.746$	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 10$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 0.3716P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3514 reflections	$\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
145 parameters	$\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$
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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1345 (4)	0.1860 (4)	0.70306 (19)	0.0518 (6)
H1	-0.0046	0.2033	0.7342	0.062*
C2	0.3105 (4)	0.0861 (4)	0.75114 (18)	0.0523 (6)
H2	0.3058	0.0267	0.8192	0.063*
C3	0.5018 (4)	0.0808 (3)	0.68783 (17)	0.0428 (5)
H3	0.6372	0.0182	0.7094	0.051*
C4	0.4669 (3)	0.1785 (3)	0.59025 (16)	0.0350 (4)
C5	0.6327 (3)	0.1940 (3)	0.50925 (16)	0.0358 (4)
H5	0.7718	0.1321	0.5264	0.043*
C6	0.6167 (3)	0.2849 (3)	0.41203 (16)	0.0341 (4)
C7	0.8086 (3)	0.2828 (3)	0.33909 (16)	0.0366 (4)
C8	0.5339 (3)	0.4692 (3)	0.23605 (17)	0.0399 (5)
C9	0.9117 (4)	0.4146 (4)	0.15934 (19)	0.0491 (6)
H9A	0.8550	0.5408	0.1181	0.059*
H9B	1.0355	0.4141	0.1876	0.059*
C10	0.9801 (6)	0.2599 (5)	0.0927 (2)	0.0743 (9)
H10	0.8740	0.2392	0.0646	0.089*
C11	1.1737 (7)	0.1513 (6)	0.0701 (3)	0.1111 (16)
H11A	1.2845	0.1674	0.0967	0.133*
H11B	1.2038	0.0562	0.0272	0.133*
N1	0.7483 (3)	0.3913 (3)	0.24437 (13)	0.0382 (4)

O1	0.9933 (2)	0.2023 (3)	0.35541 (13)	0.0515 (4)
S1	0.19548 (9)	0.27676 (9)	0.57905 (5)	0.04606 (16)
S2	0.38596 (8)	0.41472 (8)	0.35129 (4)	0.03895 (14)
S3	0.41977 (12)	0.59688 (12)	0.13403 (5)	0.0646 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0437 (13)	0.0519 (14)	0.0552 (15)	-0.0171 (11)	0.0135 (11)	-0.0117 (11)
C2	0.0583 (15)	0.0566 (14)	0.0374 (12)	-0.0213 (12)	0.0061 (11)	-0.0020 (10)
C3	0.0425 (12)	0.0437 (12)	0.0389 (11)	-0.0123 (10)	-0.0042 (9)	-0.0028 (9)
C4	0.0343 (10)	0.0315 (10)	0.0392 (11)	-0.0108 (8)	-0.0029 (8)	-0.0065 (8)
C5	0.0316 (10)	0.0343 (10)	0.0406 (11)	-0.0101 (8)	-0.0032 (8)	-0.0054 (8)
C6	0.0304 (9)	0.0340 (10)	0.0377 (10)	-0.0111 (8)	-0.0022 (8)	-0.0060 (8)
C7	0.0337 (10)	0.0393 (11)	0.0389 (11)	-0.0156 (9)	-0.0002 (8)	-0.0077 (9)
C8	0.0402 (11)	0.0412 (11)	0.0394 (11)	-0.0151 (9)	-0.0030 (9)	-0.0063 (9)
C9	0.0447 (13)	0.0555 (14)	0.0469 (13)	-0.0242 (11)	0.0066 (10)	-0.0024 (10)
C10	0.084 (2)	0.086 (2)	0.0568 (17)	-0.0438 (19)	0.0266 (15)	-0.0216 (15)
C11	0.133 (4)	0.086 (3)	0.067 (2)	0.002 (2)	0.025 (2)	-0.0083 (19)
N1	0.0360 (9)	0.0424 (9)	0.0370 (9)	-0.0165 (8)	0.0006 (7)	-0.0051 (7)
O1	0.0298 (8)	0.0662 (11)	0.0532 (10)	-0.0130 (7)	-0.0035 (7)	-0.0032 (8)
S1	0.0340 (3)	0.0453 (3)	0.0515 (3)	-0.0083 (2)	-0.0008 (2)	-0.0031 (2)
S2	0.0291 (2)	0.0432 (3)	0.0410 (3)	-0.0101 (2)	-0.0029 (2)	-0.0024 (2)
S3	0.0557 (4)	0.0842 (5)	0.0448 (4)	-0.0184 (4)	-0.0133 (3)	0.0101 (3)

Geometric parameters (Å, °)

C1—C2	1.347 (4)	C7—O1	1.208 (2)
C1—S1	1.701 (3)	C7—N1	1.400 (3)
C1—H1	0.9300	C8—N1	1.364 (3)
C2—C3	1.405 (3)	C8—S3	1.638 (2)
C2—H2	0.9300	C8—S2	1.743 (2)
C3—C4	1.377 (3)	C9—C10	1.468 (4)
C3—H3	0.9300	C9—N1	1.468 (3)
C4—C5	1.433 (3)	C9—H9A	0.9700
C4—S1	1.729 (2)	C9—H9B	0.9700
C5—C6	1.344 (3)	C10—C11	1.278 (5)
C5—H5	0.9300	C10—H10	0.9300
C6—C7	1.473 (3)	C11—H11A	0.9300
C6—S2	1.749 (2)	C11—H11B	0.9300
C2—C1—S1	112.36 (18)	N1—C8—S3	126.87 (17)
C2—C1—H1	123.8	N1—C8—S2	110.96 (16)
S1—C1—H1	123.8	S3—C8—S2	122.17 (13)
C1—C2—C3	113.0 (2)	C10—C9—N1	113.0 (2)
C1—C2—H2	123.5	C10—C9—H9A	109.0
C3—C2—H2	123.5	N1—C9—H9A	109.0
C4—C3—C2	112.6 (2)	C10—C9—H9B	109.0

C4—C3—H3	123.7	N1—C9—H9B	109.0
C2—C3—H3	123.7	H9A—C9—H9B	107.8
C3—C4—C5	124.61 (19)	C11—C10—C9	125.3 (4)
C3—C4—S1	110.43 (16)	C11—C10—H10	117.4
C5—C4—S1	124.96 (16)	C9—C10—H10	117.4
C6—C5—C4	129.47 (19)	C10—C11—H11A	120.0
C6—C5—H5	115.3	C10—C11—H11B	120.0
C4—C5—H5	115.3	H11A—C11—H11B	120.0
C5—C6—C7	121.35 (19)	C8—N1—C7	116.63 (17)
C5—C6—S2	128.78 (16)	C8—N1—C9	122.99 (19)
C7—C6—S2	109.86 (15)	C7—N1—C9	120.37 (18)
O1—C7—N1	123.06 (19)	C1—S1—C4	91.64 (11)
O1—C7—C6	126.9 (2)	C8—S2—C6	92.49 (10)
N1—C7—C6	110.02 (17)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C3—H3...O1 ⁱ	0.93	2.54	3.304 (3)	140

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