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2-(4-Oxo-3-phenyl-1,3-thiazolidin-2-ylidene)malononitrile

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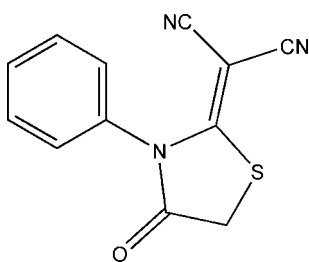
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.043; wR factor = 0.086; data-to-parameter ratio = 13.7.

In the title compound, $\text{C}_{12}\text{H}_7\text{N}_3\text{OS}$, the essentially planar thiazole ring (r.m.s. deviation = 0.022 Å) forms dihedral angles of 84.88 (9) and 1.8 (3)° with the phenyl ring and the $-\text{C}(\text{CN})_2$ group (r.m.s. deviation = 0.003 Å), respectively. The molecule has approximate local C_s symmetry. In the crystal, molecules are linked *via* $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds, forming chains propagating along [101]. The crystal studied was found to be an inversion twin with a refined 0.63 (1):0.37 (1) domain ratio.

Related literature

For background to 1,3-thiazolidin-4-ones and their properties, see: Singh *et al.* (1981); Liesen *et al.* (2010); Kocabalkanli *et al.* (2001); Kumar *et al.* (2007). For further synthetic details, see: Mohareb *et al.* (2012). For a related structure, see: Pomés Hernández *et al.* (1996).



Experimental

Crystal data

$\text{C}_{12}\text{H}_7\text{N}_3\text{OS}$
 $M_r = 241.27$
 Monoclinic, Cc
 $a = 17.0305$ (8) Å

$b = 9.5638$ (6) Å
 $c = 7.1651$ (4) Å
 $\beta = 104.199$ (4)°
 $V = 1131.37$ (11) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.27$ mm⁻¹

$T = 298$ K
 $0.20 \times 0.13 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 2136 measured reflections
 2136 independent reflections

1397 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.086$
 $S = 1.01$
 2136 reflections
 156 parameters
 2 restraints

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³
 Absolute structure: Flack (1983),
 835 Friedel pairs
 Flack parameter: 0.37 (1)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}10-\text{H}10\cdots\text{N}2^i$	0.93	2.62	3.504 (5)	159

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5577).

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supplementary materials

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2-(4-Oxo-3-phenyl-1,3-thiazolidin-2-ylidene)malononitrile

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Comment

1,3-Thiazolidin-4-ones are heterocyclic compounds that have an atom of sulfur and nitrogen at positions 1 and 3, respectively and a carbonyl group at position 4. Their presence in penicillin was the first recognition of their occurrence in nature (Singh *et al.*, 1981). They have found uses as antibacterial (Liesen *et al.*, 2010), antimicrobial (Kocabalkanli *et al.*, 2001) and anti-inflammatory agents (Kumar *et al.*, 2007). In continuation of our studies on this family of compounds, we now report the synthesis and crystal structure of the title compound, (I).

The heterocyclic ring (C1/C2/S1/C3/N1) in (I) is close to planar (r.m.s. deviation = 0.022 Å) and subtends dihedral angles with the phenyl ring and the C(CN)₂ group (r.m.s. deviation = 0.003 Å) of 84.88 (9) and 1.8 (3)°, respectively. An alternative analysis of the heterocyclic ring as a shallow envelope sees the S atom in the flap position displaced by 0.090 (5) Å from the other atoms (r.m.s. deviation = 0.004 Å). The molecule has approximate local C_s symmetry.

There is a short intermolecular contact [2.903 (2) Å] from the O atom of the carbonyl group to the centre of a nearby heterocyclic ring (symmetry: $x, 1 - x, z - 1/2$), but given the non-aromatic nature of the ring, this can hardly be regarded as a bond. No other significant intermolecular contacts occur in the crystal.

For a related structure, in which the thiazole ring was also found to be almost planar, see Pomés Hernández *et al.* (1996).

Experimental

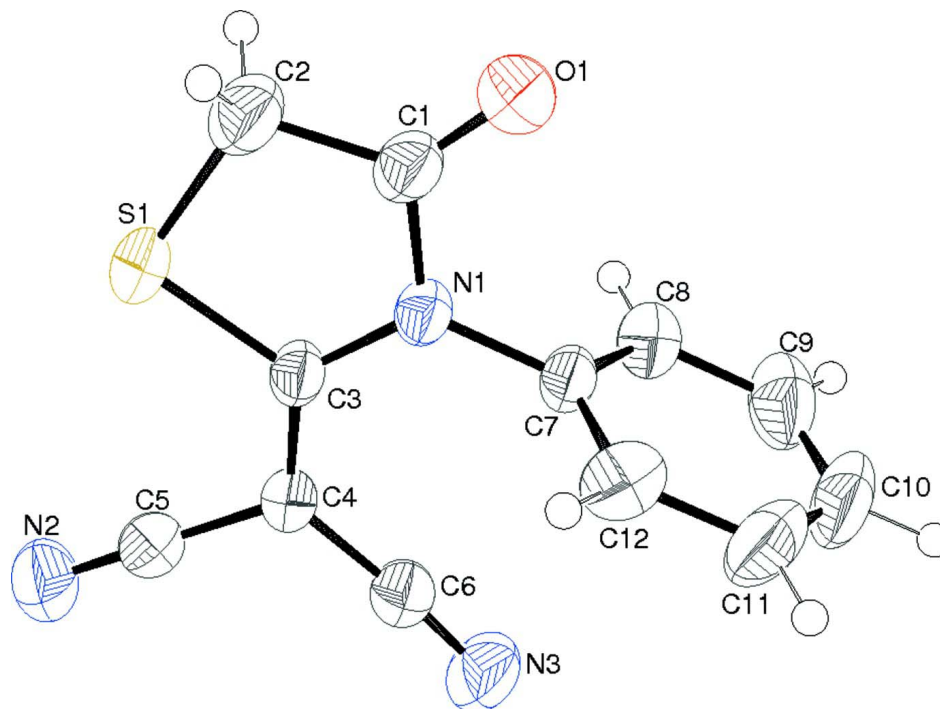
To a solution of malononitrile (0.66 g, 0.01 mol) dissolved in dimethylformamide (15 ml), potassium hydroxide pellets (0.56 g, 0.01 mol) and phenylisothiocyanate (1.35 g, 0.01 mol) were added. The reaction mixture was covered and stirred at room temperature overnight. *N'*-(2-chloroacetyl)-2-cyanoacetohydrazide (1.75 g, 0.01 mol) (Mohareb *et al.*, 2012) was stirred in the following day, and the solution was covered for another night, after which the reaction mixture was poured onto ice, neutralized with dil. HCl and the precipitated solid filtered off. Yellow blocks were obtained by slow evaporation of an ethanol solution.

Refinement

The H atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and refined as riding. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ was applied.

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Figure 1**

The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level.

2-(4-Oxo-3-phenyl-1,3-thiazolidin-2-ylidene)malononitrile

Crystal data

$C_{12}H_7N_3OS$

$M_r = 241.27$

Monoclinic, *Cc*

Hall symbol: *C* -2yc

$a = 17.0305$ (8) Å

$b = 9.5638$ (6) Å

$c = 7.1651$ (4) Å

$\beta = 104.199$ (4)°

$V = 1131.37$ (11) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.416$ Mg m⁻³

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 1133 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.27$ mm⁻¹

$T = 298$ K

Block, yellow

$0.20 \times 0.13 \times 0.05$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

2136 measured reflections

2136 independent reflections

1397 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$

$\theta_{max} = 27.5$ °, $\theta_{min} = 3.6$ °

$h = -21$ → 22

$k = -12$ → 11

$l = -9$ → 9

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.086$

$S = 1.01$

2136 reflections

156 parameters

2 restraints

Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.0674P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.008 (2)
 Absolute structure: Flack (1983), 835 Friedel pairs
 Flack parameter: 0.37 (1)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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	0.40086 (17)	0.3723 (3)	0.3314 (5)	0.0435 (8)
C2	0.31911 (18)	0.3591 (4)	0.3709 (4)	0.0542 (9)
H2A	0.2827	0.3104	0.2657	0.065*
H2B	0.2969	0.4511	0.3830	0.065*
C3	0.43425 (18)	0.2567 (3)	0.6297 (4)	0.0357 (7)
C4	0.48151 (17)	0.1984 (3)	0.7933 (4)	0.0395 (8)
C5	0.4414 (2)	0.1387 (4)	0.9303 (5)	0.0487 (8)
C6	0.5676 (2)	0.1857 (3)	0.8434 (5)	0.0444 (8)
C7	0.54465 (17)	0.3210 (3)	0.4754 (4)	0.0368 (7)
C8	0.58860 (18)	0.4396 (4)	0.5395 (4)	0.0465 (8)
H8	0.5650	0.5143	0.5884	0.056*
C9	0.6685 (2)	0.4455 (5)	0.5297 (5)	0.0669 (11)
H9	0.6994	0.5242	0.5746	0.080*
C10	0.7026 (2)	0.3359 (5)	0.4543 (5)	0.0689 (13)
H10	0.7563	0.3411	0.4470	0.083*
C11	0.6581 (2)	0.2197 (5)	0.3901 (5)	0.0657 (12)
H11	0.6816	0.1456	0.3394	0.079*
C12	0.5784 (2)	0.2111 (4)	0.3998 (4)	0.0534 (10)
H12	0.5480	0.1318	0.3557	0.064*
S1	0.32943 (5)	0.26310 (9)	0.59038 (11)	0.0515 (3)
O1	0.41623 (12)	0.4253 (2)	0.1924 (3)	0.0585 (7)
N1	0.46104 (13)	0.3139 (3)	0.4828 (3)	0.0363 (6)
N2	0.40992 (18)	0.0906 (3)	1.0384 (5)	0.0703 (9)
N3	0.63584 (18)	0.1710 (3)	0.8969 (4)	0.0671 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0331 (18)	0.039 (2)	0.0570 (19)	-0.0008 (15)	0.0092 (15)	-0.0014 (17)
C2	0.036 (2)	0.071 (3)	0.0535 (19)	0.0005 (17)	0.0065 (14)	0.0031 (18)
C3	0.0287 (16)	0.0350 (19)	0.0452 (17)	-0.0036 (15)	0.0126 (13)	-0.0012 (14)
C4	0.0327 (18)	0.042 (2)	0.0459 (19)	0.0010 (14)	0.0142 (15)	0.0074 (15)
C5	0.0362 (19)	0.050 (2)	0.0577 (19)	0.0011 (16)	0.0074 (16)	0.0099 (17)
C6	0.040 (2)	0.048 (2)	0.0461 (17)	-0.0002 (16)	0.0109 (14)	0.0044 (17)
C7	0.0283 (17)	0.045 (2)	0.0386 (17)	-0.0005 (15)	0.0110 (13)	0.0027 (15)
C8	0.042 (2)	0.051 (2)	0.0490 (18)	-0.0055 (17)	0.0144 (14)	-0.0015 (16)
C9	0.047 (2)	0.095 (3)	0.060 (2)	-0.020 (2)	0.0139 (18)	0.007 (2)
C10	0.030 (2)	0.122 (4)	0.057 (2)	0.003 (2)	0.0147 (16)	0.012 (2)
C11	0.046 (2)	0.098 (3)	0.057 (2)	0.026 (2)	0.0199 (19)	0.003 (2)
C12	0.049 (2)	0.057 (3)	0.052 (2)	0.0062 (18)	0.0080 (17)	-0.0045 (15)
S1	0.0288 (4)	0.0603 (6)	0.0661 (5)	-0.0030 (5)	0.0131 (3)	0.0097 (5)
O1	0.0528 (15)	0.0679 (18)	0.0571 (13)	0.0059 (12)	0.0178 (10)	0.0173 (13)
N1	0.0280 (14)	0.0374 (16)	0.0442 (14)	-0.0027 (11)	0.0103 (11)	0.0005 (12)
N2	0.0528 (19)	0.085 (3)	0.076 (2)	-0.0039 (18)	0.0208 (15)	0.030 (2)
N3	0.040 (2)	0.092 (3)	0.067 (2)	0.0083 (17)	0.0091 (15)	0.0192 (18)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.202 (3)	C7—C12	1.372 (4)
C1—N1	1.412 (4)	C7—C8	1.374 (4)
C1—C2	1.492 (4)	C7—N1	1.439 (3)
C2—S1	1.792 (3)	C8—C9	1.381 (4)
C2—H2A	0.9700	C8—H8	0.9300
C2—H2B	0.9700	C9—C10	1.372 (6)
C3—N1	1.361 (4)	C9—H9	0.9300
C3—C4	1.367 (4)	C10—C11	1.361 (5)
C3—S1	1.739 (3)	C10—H10	0.9300
C4—C6	1.426 (4)	C11—C12	1.378 (5)
C4—C5	1.444 (5)	C11—H11	0.9300
C5—N2	1.142 (4)	C12—H12	0.9300
C6—N3	1.140 (4)		
O1—C1—N1	122.6 (3)	C7—C8—C9	118.7 (3)
O1—C1—C2	126.5 (3)	C7—C8—H8	120.7
N1—C1—C2	110.9 (3)	C9—C8—H8	120.7
C1—C2—S1	108.3 (2)	C10—C9—C8	120.5 (4)
C1—C2—H2A	110.0	C10—C9—H9	119.8
S1—C2—H2A	110.0	C8—C9—H9	119.8
C1—C2—H2B	110.0	C11—C10—C9	120.1 (4)
S1—C2—H2B	110.0	C11—C10—H10	119.9
H2A—C2—H2B	108.4	C9—C10—H10	119.9
N1—C3—C4	126.1 (3)	C10—C11—C12	120.4 (4)
N1—C3—S1	112.7 (2)	C10—C11—H11	119.8
C4—C3—S1	121.2 (2)	C12—C11—H11	119.8
C3—C4—C6	127.1 (2)	C7—C12—C11	119.2 (4)

C3—C4—C5	117.8 (3)	C7—C12—H12	120.4
C6—C4—C5	115.1 (3)	C11—C12—H12	120.4
N2—C5—C4	179.5 (4)	C3—S1—C2	92.06 (15)
N3—C6—C4	174.6 (3)	C3—N1—C1	115.8 (2)
C12—C7—C8	121.1 (3)	C3—N1—C7	124.7 (2)
C12—C7—N1	119.5 (3)	C1—N1—C7	119.4 (2)
C8—C7—N1	119.3 (3)		

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>
C10—H10 \cdots N2 ⁱ	0.93	2.62	3.504 (5)	159

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