

Three substituted (*Z*)-5-benzylidene-2-thioxothiazolidin-4-ones: hydrogen-bonded dimers that can be effectively isolated or linked into chains either by aromatic π – π stacking interactions or by dipolar carbonyl–carbonyl interactions

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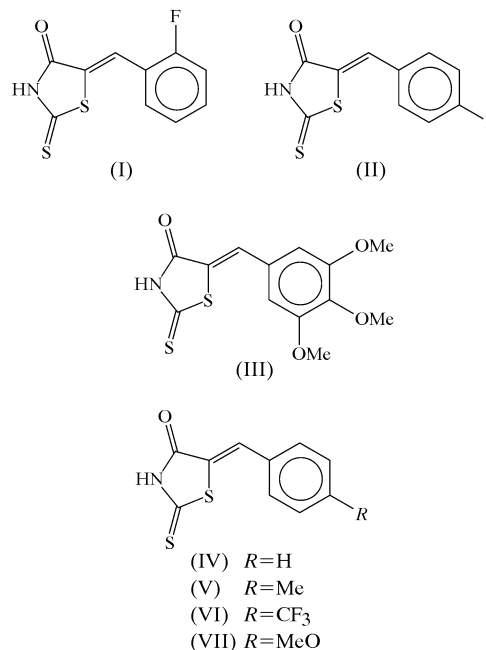
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In each of the isomeric compounds (*Z*)-5-(2-fluorobenzylidene)-2-thioxothiazolidin-4-one, C₁₀H₆FNOS₂, (I), and (*Z*)-5-(4-fluorobenzylidene)-2-thioxothiazolidin-4-one, C₁₀H₆FNOS₂, (II), there is a very wide C–C–C angle (*ca* 130°) at the methine C atom linking the two rings. In each isomer, paired N–H···O hydrogen bonds link the molecules into centrosymmetric *R*₂²(8) dimers; the hydrogen-bonded dimers are linked into chains by an aromatic π – π stacking interaction in isomer (I) and by an antiparallel dipolar carbonyl–carbonyl interaction in isomer (II). (*Z*)-5-(3,4,5-Trimethoxybenzylidene)-2-thioxothiazolidin-4-one, C₁₃H₁₃NO₄S₂, (III), which crystallizes with *Z'* = 2 in the space group *P* $\bar{1}$, shows the same very wide angle at the bridging methine C atom; the two independent molecules are linked into an isolated dimer having no crystallographic symmetry.

Comment

We report here the structures of three substituted (*Z*)-5-benzylidene-2-thioxothiazolidin-4-ones, namely two isomers of (*Z*)-5-(fluorobenzylidene)-2-thioxothiazolidin-4-one, (I) and (II) (Figs. 1 and 2), and (*Z*)-5-(3,4,5-trimethoxybenzylidene)-2-thioxothiazolidin-4-one, (III) (Fig. 3), and we briefly compare these with the structures of the four analogues (IV)–(VII) (see scheme), which have been reported recently (Delgado *et al.*, 2005). As for compounds (IV)–(VII), compounds (I)–(III) have been prepared by condensation of 2-thioxothiazolidin-4-one (rhodanine) with a substituted

benzaldehyde using microwave radiation in a solvent-free system.



The molecules of compounds (I)–(III) are all effectively planar, as shown by the values of the C_x5–C_x57–C_x51–C_x52 torsion angle, where *x* is nil for compounds (I) and (II), and *x* = 1 or 2, respectively, for the two independent molecules in compound (III) (Table 1); this angle defines the rotation of the aryl ring relative to the rest of the molecule. In each isomer, the C_x5–C_x57–C_x51 angle is very large, *ca* 130°, and these angles, together with the exocyclic angles at C_x5 and C_x51, are consistent with the occurrence of a repulsive intramolecular interaction between atoms S_x1 and H_x56 (Table 2). This behaviour closely mimics that in the analogues (IV)–

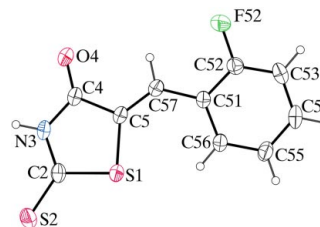


Figure 1

A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

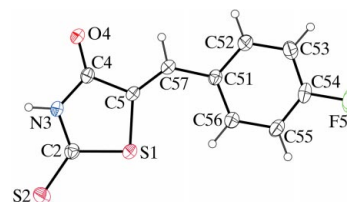


Figure 2

A molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

(VII). In each of the molecules in (III), the methoxy groups at Cx53 and Cx55 have their C atoms almost coplanar with the adjacent aryl rings (Table 1), but those at Cx54 have the C atoms well removed from this plane for steric reasons.

The supramolecular structures of compounds (I)–(III) are very simple. In the isomers (I) and (II), the molecules are linked by paired N–H···O hydrogen bonds (Table 2) into centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimers; in each isomer, the asymmetric unit was selected such that the dimer containing the reference molecule is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Figs. 4 and 5). The structures of (I) and (II) differ, however, in the manner in which the hydrogen-bonded dimers are linked into chains. In (III), the two independent molecules are again linked into a dimer but this does not exhibit even approximate centrosymmetry. There are no direction-specific interactions between the dimeric units in (III).

The hydrogen-bonded dimers in (I) are linked by an aromatic π – π stacking interaction. The aryl rings in the molecules at (x, y, z) and $(2 - x, -y, 1 - z)$, which lie, respectively, in the $R_2^2(8)$ dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, -\frac{1}{2}, \frac{1}{2})$, are strictly parallel, with an interplanar spacing of 3.366 (2) Å; the ring-centroid separation is 3.692 (2) Å, corresponding to an almost ideal ring offset of 1.515 (2) Å. Propagation by inversion of this interaction links the dimers into chains running parallel to the $[1\bar{1}0]$ direction (Fig. 6).

In (II), the hydrogen-bonded dimers are linked by an antiparallel carbonyl–carbonyl interaction, which is centro-

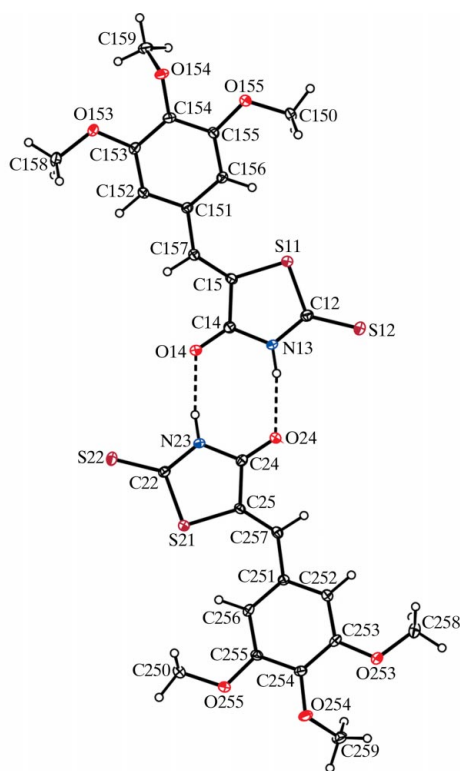


Figure 3

The two independent molecules of (III), showing the atom-labelling scheme and the N–H···O hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 30% probability level.

symmetric. The molecules at (x, y, z) and $(-x, 1 - y, 1 - z)$ are components of the dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively; their carbonyl groups are antiparallel, with a C···Oⁱⁱ distance of 3.181 (4) Å and an O–C···Oⁱⁱ angle of

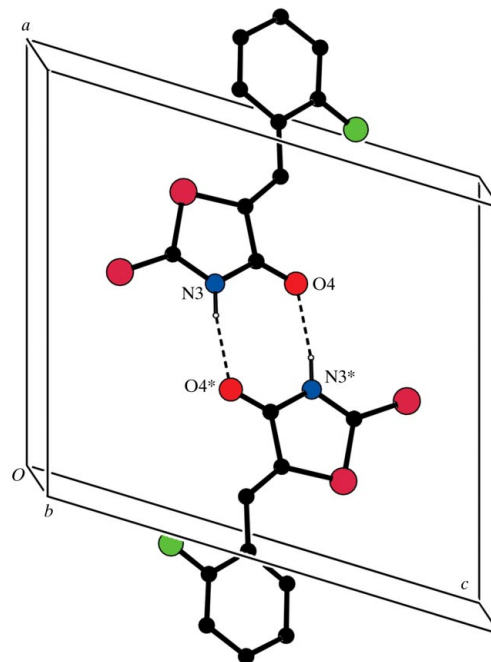


Figure 4

Part of the crystal structure of (I), showing the formation of a centrosymmetric hydrogen-bonded dimer. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

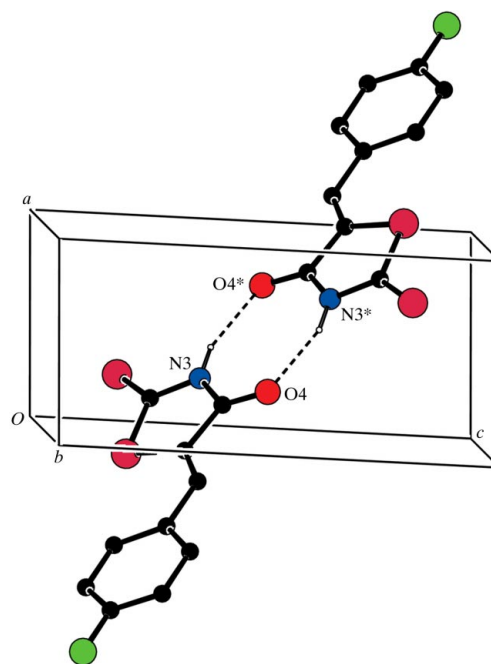


Figure 5

Part of the crystal structure of (II), showing the formation of a centrosymmetric hydrogen-bonded dimer. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

100.5 (2)° [symmetry code: (ii) $-x, -y + 1, -z + 1$], producing a slightly sheared interaction of type II (Allen *et al.*, 1998), which links the dimers into chains running parallel to the [100] direction (Fig. 7).

We note very briefly the different patterns of supramolecular aggregation in the analogues (IV)–(VII) (Delgado *et al.*, 2005). In (IV), which crystallizes with $Z' = 2$ in the space group $P2_1/n$, the two independent molecules are linked by N—H···O bonds into a dimer, as in (III), but these dimers are not isolated; instead they are linked by C—H··· π (arene) hydrogen bonds into sheets. Compound (V) is effectively isomorphous with (III) and the molecules form centrosymmetric dimers, which are linked into chains by a dipolar carbonyl–carbonyl interaction. No dimers formed by paired

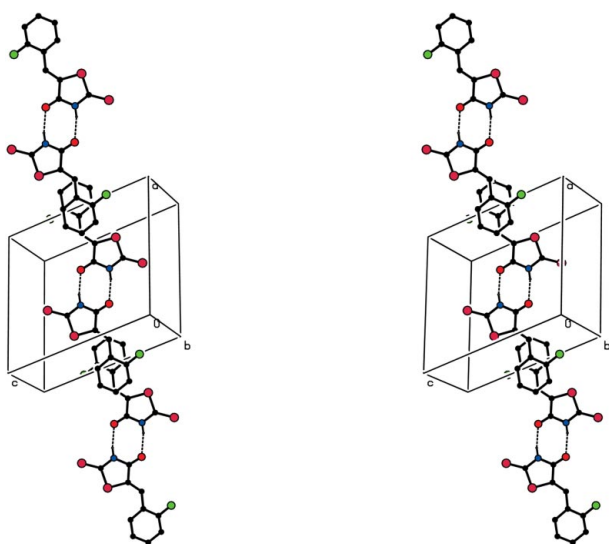


Figure 6

A stereoview of part of the crystal structure of (I), showing the formation of a π -stacked [110] chain of hydrogen-bonded dimers. For the sake of clarity, H atoms bonded to C atoms have been omitted.

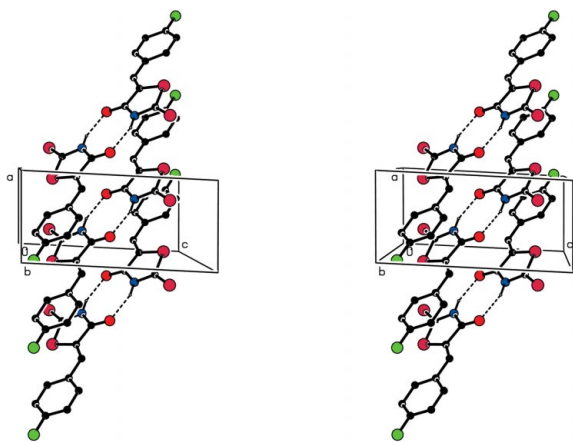


Figure 7

A stereoview of part of the crystal structure of (II), showing the formation of a [100] chain of hydrogen-bonded dimers linked by dipolar carbonyl–carbonyl interactions. For the sake of clarity, H atoms bonded to C atoms have been omitted.

N—H···O hydrogen bonds are discernible in the structure of (VI); instead the molecules are linked into chains of rings by a combination of N—H···S and C—H···O hydrogen bonds. In (VII), the usual $R_2^2(8)$ dimers are formed and these are linked into chains of rings by C—H···S hydrogen bonds. Thus, within the extended series (I)–(VII), it is apparent that rather modest changes to the peripheral substituents can have a significant influence on the overall supramolecular aggregation.

Experimental

Equimolar quantities (1 mmol of each component) of 2-thioxothiazolidin-4-one and the appropriate substituted benzaldehyde were placed in open Pyrex glass vessels in the absence of any solvent and irradiated in a domestic microwave oven for 3 min (at 600 W); the reactions were monitored by thin-layer chromatography. The reaction mixtures were extracted with ethanol; after removal of this solvent, the products were recrystallized from dimethylformamide to give crystals suitable for single-crystal X-ray diffraction. (I): orange crystals, m.p. 438 K, yield 53%; MS (70 eV) m/z (%): 239 (4, M^+), 152 (100), 108 (2). (II): orange crystals, m.p. 495 K, yield 88%; MS (70 eV) m/z (%): 239 (24, M^+), 152 (100), 107 (2). (III): orange crystals, m.p. 474 K, yield 85%; MS (70 eV) m/z (%): 313 (18, $M+2$), 312 (11, $M+1$), 311 (88, M^+), 224 [100, ($M - C_2HNO_2$) $^+$], 209 (94), 181 (16), 166 (9).

Compound (I)

Crystal data

$C_{10}H_6FNOS_2$
 $M_r = 239.28$
 Monoclinic, $P2_1/c$
 $a = 11.1848$ (4) Å
 $b = 7.7651$ (4) Å
 $c = 12.3611$ (5) Å
 $\beta = 107.417$ (3)°
 $V = 1024.35$ (8) Å 3

$Z = 4$
 $D_x = 1.552$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.50$ mm $^{-1}$
 $T = 298$ (2) K
 Plate, orange
 $0.36 \times 0.32 \times 0.04$ mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.869$, $T_{\max} = 0.980$

9920 measured reflections
 2337 independent reflections
 1768 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.105$
 $S = 1.04$
 2337 reflections
 141 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.3103P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22$ e Å $^{-3}$
 $\Delta\rho_{\min} = -0.32$ e Å $^{-3}$

Compound (II)

Crystal data

$C_{10}H_6FNOS_2$
 $M_r = 239.28$
 Monoclinic, $P2_1/c$
 $a = 4.9173$ (2) Å
 $b = 19.8906$ (10) Å
 $c = 10.4976$ (6) Å
 $\beta = 92.929$ (3)°
 $V = 1025.41$ (9) Å 3

$Z = 4$
 $D_x = 1.550$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.50$ mm $^{-1}$
 $T = 298$ (2) K
 Lath, orange
 $0.60 \times 0.35 \times 0.12$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.753$, $T_{\max} = 0.942$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.110$
 $S = 1.09$
 2287 reflections
 137 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 1.095P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0071 (17)

Compound (III)

Crystal data

$\text{C}_{13}\text{H}_{13}\text{NO}_4\text{S}_2$
 $M_r = 311.36$
 Triclinic, $P\bar{1}$
 $a = 10.3432$ (4) Å
 $b = 10.9105$ (4) Å
 $c = 13.4621$ (4) Å
 $\alpha = 100.399$ (2)°
 $\beta = 91.572$ (2)°
 $\gamma = 110.301$ (2)°

$V = 1394.72$ (9) Å³
 $Z = 4$
 $D_x = 1.483 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.39 \text{ mm}^{-1}$
 $T = 120$ (2) K
 Plate, orange
 $0.10 \times 0.08 \times 0.03 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.952$, $T_{\max} = 0.988$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.119$
 $S = 1.00$
 6377 reflections
 367 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond angles and torsion angles (°) for compounds (I)–(III).

Parameter	(I)	(II)	(III)	(III)
x	nil	nil	1	2
Cx5–Cx57–Cx51	129.25 (17)	130.6 (3)	131.3 (3)	130.6 (3)
Sx1–Cx5–Cx57	130.48 (14)	130.1 (2)	130.0 (2)	130.2 (2)
Cx4–Cx5–Cx57	120.50 (17)	121.1 (3)	120.8 (2)	120.9 (2)
Cx52–Cx51–Cx56	115.44 (16)	118.6 (3)	119.4 (2)	117.8 (2)
Cx57–Cx51–Cx56	124.47 (17)	123.6 (3)	123.0 (2)	123.0 (2)
Cx5–Cx57–Cx51–Cx52	–174.60 (19)	179.9 (3)	179.9 (3)	179.5 (3)
Cx52–Cx53–Ox53–Cx58	–	–	5.1 (4)	–15.8 (4)
Cx53–Cx54–Ox54–Cx59	–	–	–77.3 (3)	–48.1 (3)
Cx54–Cx55–Ox55–Cx50	–	–	–179.3 (2)	174.3 (2)

For each of (I) and (II), the space group $P2_1/c$ was uniquely assigned from the systematic absences. Crystals of (III) are triclinic; the space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. All H atoms were located in difference maps. H atoms bonded to C atoms were treated as riding atoms, with C–H distances of 0.93 Å for (I) and (II), and 0.95 (aromatic) and 0.98 Å (methyl) for (III), and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ or

Table 2

Hydrogen bonds and short intramolecular contacts (Å, °) for compounds (I)–(III).

Compound	$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
(I)	C56–H56··S1	0.93	2.51	3.226 (2)	134
	N3–H3··O4 ⁱ	0.86	2.00	2.843 (2)	168
(II)	C56–H56··S1	0.93	2.51	3.230 (3)	135
	N3–H3··O4 ⁱ	0.87	2.00	2.831 (3)	159
(III)	C156–H156··S11	0.95	2.50	3.237 (2)	134
	N13–H13··O24	0.88	1.95	2.814 (3)	168
	C256–H256··S21	0.95	2.49	3.227 (2)	134
	N23–H23··O14	0.88	1.96	2.807 (3)	162

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

$1.5U_{\text{eq}}(\text{methyl C});$ H atoms bonded to N atoms were allowed to ride at the distances found from the difference maps [$\text{N}–\text{H} = 0.86–0.88 \text{ Å}$ with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$].

For all compounds, data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SIR2004 (Burla *et al.*, 2005); program(s) used to refine structure: OSCAIL (McArdle, 2003) and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3027). Services for accessing these data are described at the back of the journal.

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