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Ethyl (*E*)-2-(4-oxo-1,3-thiazinan-2-ylidene)ethanoate

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Key indicators

Single-crystal X-ray study
T = 163 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.099
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Each of the two independent molecules of the title compound, $C_8H_{11}NO_3S$, possesses an extended planar conformation, with an intramolecular N—H···O hydrogen bond.

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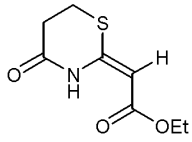
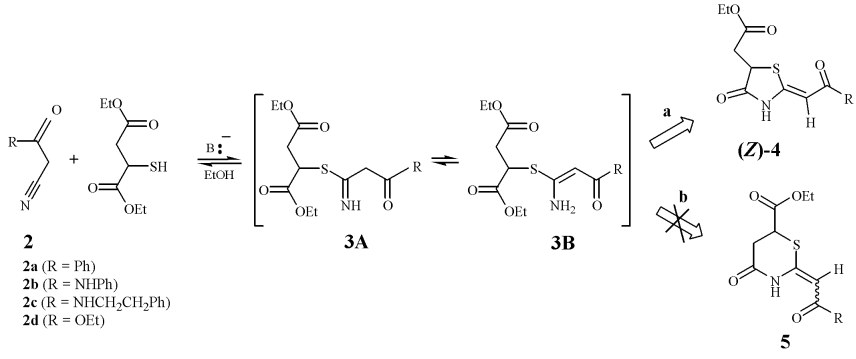
Comment

The title compound, (1), with an *E*-configured exocyclic double bond, was obtained in low yield from the heterocyclization of ethyl cyanoacetate with ethyl 3-mercaptopropanoate in ethanol solution (Marković *et al.*, 2003).



(1)

This reaction served as a model to confirm the regiocontrolled synthesis of (*Z*)-5-substituted-4-oxothiazolidine derivatives, (4), in good yields (60–80%), occurring *via* the base-catalysed heterocyclization of β-oxonitriles, (2), with diethyl mercaptosuccinate. These reactions were found to take place without detectable traces of the competing six-membered 6-substituted 4-oxo-1,3-thiazinane derivatives, (5). These derivatives could be formed from the key intermediates, (3), which possess two electrophilic centres. However, the intermediates (3) readily undergo intramolecular cyclization only by path (*a*), affording, under kinetic control, the stereodefined 4-oxothiazolidine derivatives, (4) (Marković & Baranac, 1998; Marković *et al.*, 2001). Therefore, both (i) the sluggish heterocyclization reaction giving rise to the title compound under relatively drastic reaction conditions and (ii) the exclusive formation of the five-membered heterocycles (4) without traces of (5) (see scheme below, path *a*) rely critically on the lower tendency towards cyclization of the common intermediates (3) to give the six-membered heterocycles (5) (path *b*).



2
2a (R = Ph)
2b (R = NHPh)
2c (R = $NHCH_2CH_2Ph$)
2d (R = OEt)

3A **3B** **(*Z*)-4** **5**

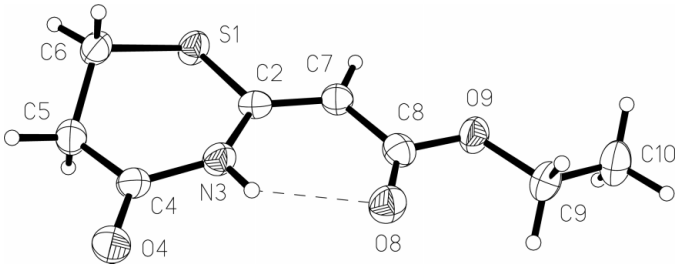


Figure 1
Perspective view of (1). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Compound (1) crystallizes in the monoclinic space group $P2/n$, with two independent molecules in the asymmetric unit, a perspective view of one of which is shown in Fig. 1. This unambiguously confirms the structure previously proposed for this compound (Marković *et al.*, 2003) and, for the first time, determines the stereochemistry of the exocyclic double bond. Interestingly, (1) has an *E* configuration, in contrast to the analogous five-membered thiazolidine compounds, which have a *Z* configuration, despite being formed under very similar experimental conditions (Marković *et al.*, 2003). The two independent molecules differ only slightly in their torsion angles. The molecules themselves are surprisingly planar, with the side chain extending out in the same plane as the thiazine ring. A contributing reason for this is the existence of an intramolecular hydrogen bond between the NH group and the carbonyl O atom of the side chain [H···O = 2.09 (3) and 2.16 (3) Å, N···O = 2.728 (2) and 2.731 (2) Å, and N—H···O = 131 (2) and 129 (2)° for the two independent molecules, respectively]. This stabilizing interaction may account for the observed formation of the *E* stereoisomer. A search of the Cambridge Structural Database (Version 5.25, November 2003 relaese; Allen, 2002) revealed that this is the first reported structure of a 2-alkylidene[1,3]thiazin-4-one.

Experimental

Compound (1) was synthesized as a colourless solid by the heterocyclization of ethyl cyanoacetate with ethyl 3-mercaptopropanoate (m.p. 339–340 K). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dilute ethanol solution of the title compound. IR (KBr): ν_{max} 3195, 3073, 1689, 1656, 1583, 1445, 1366, 1230, 1188, 1155, 793 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 1.19 (3H, *t*, J = 7.1 Hz, CH_3), 2.85 (2H, *m*, CH_2), 3.21 (2H, *m*, CH_2), 4.10 (2H, *q*, J = 7.1 Hz, CH_2O), 5.12 (1H, *s*, ═CH), 11.11 (1H, *s*, NH); ^{13}C NMR (DMSO-d_6): δ 14.4 (CH_3), 23.0 (CH_2S), 33.2 (CH_2CO), 59.9 (CH_2O), 90.1 (═CH), 154.5 (═CSN), 167.4 and 168.1 (2 × CO).; MS (EI): *m*/*z* (relative intensity): 201 (62) (M^+), 173 (10), 156 (33), 129 (75), 55 (100); UV (DMSO): λ_{max} (ε) 298.4 nm (17 900 M^{-1}cm^{-1}). Analysis calculated for $C_8H_{11}NO_3S$: C 47.75, H 5.51, N 6.96, S 15.93%; found: C 48.06, H 5.63, N 6.92, S 15.88%.

Crystal data

$C_8H_{11}NO_3S$	D_x = 1.424 Mg m^{-3}
M_r = 201.24	Mo $K\alpha$ radiation
Monoclinic, $P2/n$	Cell parameters from 9581 reflections
a = 14.0313 (8) Å	θ = 2.2–26.4°
b = 9.1124 (5) Å	μ = 0.32 mm^{-1}
c = 15.0553 (9) Å	T = 163 (2) K
β = 102.703 (1)°	Plate, colourless
V = 1877.84 (19) Å^3	0.66 × 0.41 × 0.05 mm
Z = 8	

Data collection

Bruker SMART CCD area-detector diffractometer	3298 independent reflections
φ and ω scans	2573 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	R_{int} = 0.020
T_{min} = 0.817, T_{max} = 0.984	θ_{max} = 25.0°
21 284 measured reflections	$h = -16 \rightarrow 16$
	$k = -10 \rightarrow 10$
	$l = -17 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.688P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$(\Delta/\sigma)_{max}$ = 0.004
$wR(F^2)$ = 0.099	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
3298 reflections	
241 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Crystal decay was monitored by the measurement of duplicate reflections. The N-bound H atoms were located in a difference Fourier map and their positions were refined with the restraint N—H = 0.85 (2) Å. C-bound H atoms were placed in calculated positions (C—H = 0.98 or 0.99 Å) and treated as riding, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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