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

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Abstract

The structure and stereochemistry of the title compound have been determined at 163 K. The two independent molecules each possess an extended planar conformation with an intramolecular NH[⋯]O hydrogen bond.

Comment

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

[Structure of (1) here]

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-catalyzed 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), which 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, (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) (Scheme, path a), rely critically on the lower tendency towards cyclization of the common intermediates (3) to give the six-membered heterocycles (5) (path b).

[Scheme here]

Compound (1) crystallizes in the monoclinic space group $P2_1/n$, with two independent molecules in the asymmetric unit, a perspective view of one of which is shown in Figure 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, this has the *E*-configuration, in contrast to the analogous five-membered thiazolidine compounds which have the *Z*-configuration, despite being formed under very similar experimental conditions (Marković *et al.*, 2003). The two independent molecules differ only in small torsional angle differences within the molecules. 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 oxygen of the side chain, as defined by the following parameters: H—O 2.09 (3) and 2.16 (3) Å, N—O 2.728 (2) and 2.731 (2) Å, 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 (Allen, 2002) revealed that this is the first reported structure of a 2-alkylidene[1,3]thiazin-4-one.

[Fig.1 here]

Experimental

Compound (1) was synthesized as a pale yellow solid by the heterocyclization of ethyl cyanoacetate with ethyl 3-mercaptopropanoate; m.p. 66–67 °C. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dilute ethanol solution of the title compound. Spectroscopic data: IR (KBr): ν_{\max} 3195, 3073, 1689, 1656, 1583, 1445, 1366, 1230, 1188, 1155, 793 cm^{-1} ; ^1H 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 \times CO); MS (EI): m/z (rel. intensity): 201 (62) (M^+), 173 (10), 156 (33), 129 (75), 55 (100); UV (DMSO): λ_{\max} (ϵ) 298.4 nm (17900 $M^{-1}\cdot\text{cm}^{-1}$); Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{NO}_3\text{S}$: 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%.

Refinement

Crystal decay was monitored by the measurement of duplicate reflections. The NH hydrogen was located from a difference Fourier and its position refined. CH hydrogen were placed in calculated positions and refined as riding, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached carbon.

Computing details

Data collection: Bruker *SMART*; cell refinement: Bruker *SMART*; data reduction: Bruker *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Figures

Figure 1. Perspective view of (1).

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Crystal data

$\text{C}_8\text{H}_{11}\text{NO}_3\text{S}$	$V = 1877.84 (19) \text{ \AA}^3$
$M_r = 201.24$	$Z = 8$
Monoclinic, $P2_1/n$	Mo $K\alpha$
$a = 14.0313 (8) \text{ \AA}$	$\mu = 0.32 \text{ mm}^{-1}$
$b = 9.1124 (5) \text{ \AA}$	$T = 163 (2) \text{ K}$

$c = 15.0553 (9) \text{ \AA}$
 $\beta = 102.7030 (10)^\circ$

$0.66 \times 0.41 \times 0.05 \text{ mm}$

Data collection

CCD area detector
diffractometer
Absorption correction: multi-scan
SADABS (Sheldrick, 2002)
 $T_{\min} = 0.817$, $T_{\max} = 0.984$
21284 measured reflections

3298 independent reflections

2573 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.099$
 $S = 1.04$
3298 reflections

241 parameters

H atoms treated by a mixture of
independent and constrained refinement

$\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruker (1997). *SMART*, *SAINT* and *SADABS*. Area Detector Control and Integration Software. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Marković, R. & Baranac, M. (1998). *Heterocycles*, **48**, 893–903.
- Marković, R., Baranac, M., Džambaski, Z., Stojanović, M. & Steel, P. J. (2003). *Tetrahedron*, **59**, 7803–7810.
- Marković, R., Džambaski, Z. & Baranac, M. (2001). *Tetrahedron*, **57**, 5833–5841.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.