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

Marija Baranac\textsuperscript{a}, Rade Marković\textsuperscript{a} and Peter J. Steel\textsuperscript{b}

\textsuperscript{a}Faculty of Chemistry, University of Belgrade, Studenski trg 16, P.O. Box 158, 11001 Belgrade, Serbia and Montenegro, and Center for Chemistry ICTM, P.O. Box 815, 11000 Belgrade, Serbia and Montenegro, and \textsuperscript{b}Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Correspondence email: peter.steel@canterbury.ac.nz

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\textsuperscript{−}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 \textit{et al.}, 2003). 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 \textit{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 \textit{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).

Compound (1) crystallizes in the monoclinic space group P2\textsubscript{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 \textit{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 \textit{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.

Experimental

Compound (1) was synthesized as a pale yellow solid by the heterocyclization of ethyl cyanoacetate with ethyl 3-mercapto-
propanoate; 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); ^13C 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 x 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}.cm^{-1}); Anal. Calcd. 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, 15.85%.

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_{iso} = 1.2 U_{eq}
of the attached carbon.

Computing details

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

Figures

Figure 1. Perspective view of (1).

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

Crystal data

C_8H_{11}NO_3S

M_r = 201.24

Monoclinic, P2/n

a = 14.0313 (8) Å

b = 9.1124 (5) Å

V = 1877.84 (19) Å^3

Z = 8

Mo Ka

μ = 0.32 mm^{-1}

T = 163 (2) K
$c = 15.0553 (9) \, \text{Å}$

$\beta = 102.7030 (10)^{\circ}$

0.66 $\times$ 0.41 $\times$ 0.05 mm

**Data collection**

CCD area detector
diffractometer
3298 independent reflections

Absorption correction: multi-scan
SADABS (Sheldrick, 2002)
2573 reflections with $I > 2\sigma(I)$

$T_{\text{min}} = 0.817$, $T_{\text{max}} = 0.984$

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

21284 measured reflections

**Refinement**

$R[F^2 > 2\sigma(F^2)] = 0.035$

241 parameters

$wR(F^2) = 0.099$

H atoms treated by a mixture of
independent and constrained refinement

$S = 1.04$

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

3298 reflections

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

**References**


