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Ethyl *cis*-3-(2-methoxyphenyl)-1-4-thiazine-2-carboxylate 1,1-dioxide at 150 K

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.100
Data-to-parameter ratio = 15.9

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

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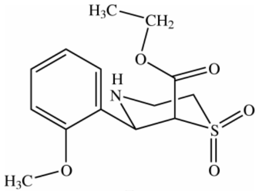
The thiazine ring in the title compound, $C_{14}H_{19}NO_5S$, adopts a slightly distorted chair conformation. The substituents, *viz*. the ethoxycarbonyl and methoxyphenyl groups, are located *cis* to one another. In the crystal structure, the inversion-related molecules exist as C—H···O hydrogen-bonded dimers, and these are linked by N—H···O and C—H···O interactions to form layers parallel to the *ac* plane.

Comment

Thiazines are heterocycles containing an S and an N atom and two double bonds. Because of their various biological applications [for example, as antitumour, antiviral (Shehata *et al.*, 1996), bactericidal, parasiticidal (Boulton & Mckillop, 1984) and antituberculotic agents (Bukowski, 2001), as well as antiepileptics, tranquilizers, sedatives, cardiovascular agents (Yamamoto *et al.*, 2000), herbicide antidotes (Foery *et al.*, 1986), antihypertensives (Faull, 1996) and anaesthetics (Bojar *et al.*, 1987), and in gastric ulceration studies (Tozkoparan *et al.*, 2002)], thiazine derivatives have attracted considerable interest. Studies of heterocycles report potent cerebral protectant and calcium antagonist activities (Erker, 1998) for substituted 1,4-thiazine derivatives, and they also show inhibitory activity on the central nervous system (Grandolini *et al.*, 1997; Malinka *et al.*, 2002). Since structural data on thiazines are limited, X-ray crystallographic studies of a series of thiazine derivatives have been undertaken. We report here the crystal and molecular structure of the title thiazine derivative, (I).



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The torsion angles (Table 1) indicate that the thiazine ring in (I) adopts a slightly distorted chair conformation, with the ethoxycarbonyl and 2-methoxyphenyl groups located *cis* to one another. This relative configuration of the groups is probably fixed in the cyclization step during the formation of the six-membered ring of (I) from the acyclic starting material, in order to minimize the steric and/or electronic interactions. The methoxyphenyl substituent adopts an equatorial position and the ethoxycarbonyl substituent adopts an axial position. The other chair conformation, which could arise from ring flipping, with equatorial ethoxycarbonyl and axial *o*-methoxyphenyl groups, is not preferred by the molecules, presumably because the steric requirements of the methoxyphenyl ring are larger than those of the ethoxycarbonyl group.

The C—S bond lengths of 1.7874 (14) and 1.7678 (15) Å in the present structure are comparable with the corresponding distances of 1.793 (3) and 1.798 (3) Å in methyl 6-benzoyl-3,5-diphenyl-1,4-thiazine-2-carboxylate- 1,1-dioxide (Krishnaiah & Jagadeesh Kumar, 1995) and 1.795 (3) and 1.795 (2) Å in thiazine-3-one (Ramasubbu *et al.*, 1988). The C—C and C—N distances agree with the standard expected values, except for a slight deviation in the C1—C2 bond, which can be attributed to the effect of the bulky substituents at these C atoms of the thiazine ring. The C9—C8—C13 bond angle [118.65 (13)°] deviates slightly from the usual value of 120°, which may be due to the fact that atom C8 is attached directly to the thiazine ring and may experience some steric effect.

In the crystal, the inversion-related molecules are linked by C7—H7*A*···O3^{i} hydrogen bonds to form centrosymmetric dimers, and these dimers are linked by N1—H1N···O1^{ii} and C9—H9···O1^{ii} interactions to form molecular chains along the *c* axis. Adjacent chains are linked along the *a* axis *via* C14—H14*A*···O2^{iii} hydrogen bonds to form layers parallel to the *ac* plane (Fig. 2; see Table 2 for symmetry codes).

Experimental

A mixture of diethyl ethane-1,2-disulfonylacetate (6.6 g), *o*-methoxybenzaldehyde (5.6 ml) and ammonium acetate (1.6 g) in ethanol (100 ml) was heated under reflux for 20 h. The excess of solvent was removed by distillation and the mixture was kept overnight. The separated solid was filtered off, washed with water and dried. The product upon crystallization from ethanol afforded (I) as colourless single crystals in the form of transparent plates (yield 15%; m.p. 416–418 K).

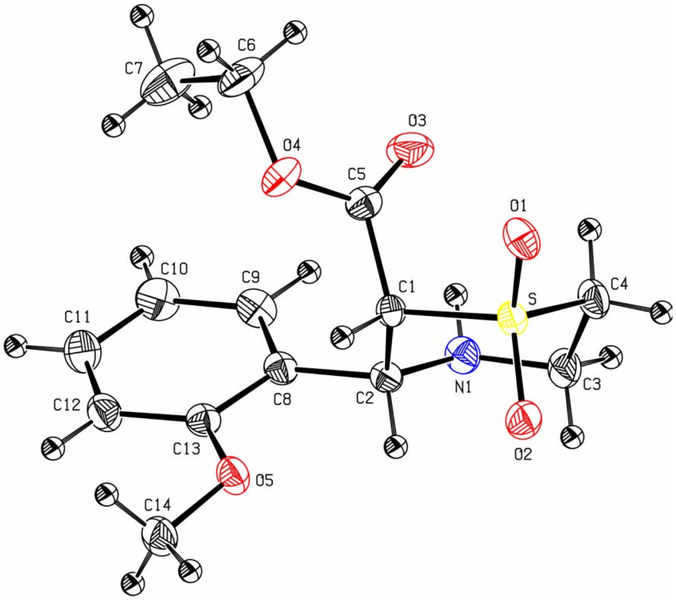


Figure 1
The structure of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Crystal data

$C_{14}H_{19}NO_5S$
M_r = 313.37
Monoclinic, $C2/c$
a = 25.706 (5) Å
b = 9.7180 (19) Å
c = 12.245 (2) Å
β = 93.44 (3)°
V = 3053.4 (10) Å^3
Z = 8

D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
θ = 1.6–26.4°
μ = 0.23 mm^{-1}
T = 150 (2) K
Plate, colourless
0.48 × 0.40 × 0.14 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min}$ = 0.90, $T_{\max}$ = 0.97
15 899 measured reflections

3132 independent reflections
2870 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 26.4°
$h = -32 \rightarrow 32$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.100
S = 1.15
3132 reflections
197 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 2.1671P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.42 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0092 (6)

Table 1
Selected geometric parameters (Å, °).

S—O2	1.4440 (11)	O4—C6	1.4682 (18)
S—O1	1.4476 (11)	O5—C13	1.3677 (17)
S—C4	1.7678 (15)	O5—C14	1.4325 (17)
S—C1	1.7874 (14)	N1—C2	1.4501 (17)
O3—C5	1.2039 (19)	N1—C3	1.4599 (19)
O4—C5	1.3341 (18)		
C5—C1—C2	111.56 (11)	C8—C2—C1	106.95 (10)
C5—C1—S	110.54 (9)	C9—C8—C13	118.65 (13)
C2—C1—S	110.42 (9)	C9—C8—C2	123.01 (13)
N1—C2—C8	112.97 (11)	C13—C8—C2	118.28 (12)
N1—C2—C1	115.03 (11)		
C4—S—C1—C2	−47.87 (10)	N1—C3—C4—S	−59.42 (15)
C3—N1—C2—C1	−59.62 (15)	C1—S—C4—C3	49.94 (12)
S—C1—C2—N1	54.88 (13)	C1—C2—C8—C9	−102.39 (14)
C5—C1—C2—C8	57.88 (14)	C1—C2—C8—C13	74.76 (14)
C2—N1—C3—C4	62.44 (16)		

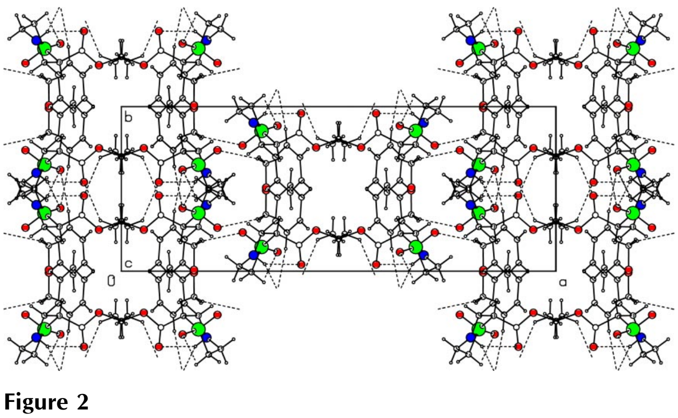


Figure 2
The molecular packing in (I), viewed along the *c* axis.

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···O3$^{\rm i}$	0.96	2.59	3.339 (2)	135
N1—H1N···O1$^{\rm ii}$	0.87 (2)	2.47 (2)	3.204 (2)	142 (2)
C9—H9···O1$^{\rm ii}$	0.97	2.51	3.481 (2)	173
C14—H14A···O2$^{\rm iii}$	0.96	2.54	3.343 (2)	142
C1—H1···O5	0.98	2.47	3.054 (2)	118

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x, -y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Atom H1N was found in a difference Fourier map and its positional parameters and $U_{\rm iso}$ value were refined. All other H atoms were placed in calculated positions and allowed to ride on their parent C atoms, with C—H distances in the range 0.94–0.98 Å; the $U_{\rm iso}$(H) values were set to 1.5$U_{\rm eq}$(parent atom) for the methyl H atoms and 1.2$U_{\rm eq}$(parent atom) for the other H atoms. A rotating-group model was used for the methyl groups.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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