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Methyl 4-acetoxy-2-methyl-2H-1,2-benzothiazine-3-carboxylate 1,1-dioxide

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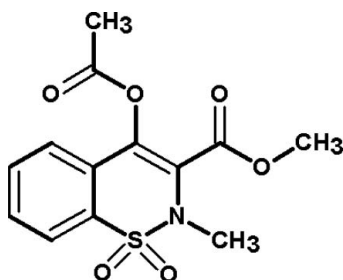
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.051; wR factor = 0.146; data-to-parameter ratio = 15.7.

In the title compound, $\text{C}_{13}\text{H}_{13}\text{NO}_6\text{S}$, the thiazine ring adopts a distorted half-chair conformation. Each molecule is linked to its neighbour through intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For related literature, see: Fabiola *et al.* (1998); Golič & Leban (1987); Kojić-Prodić & Ružić-Toroš (1982); Rajagopal & Seshadri (1990); Reck *et al.* (1988); Rehman *et al.* (2005, 2006); Turck *et al.* (1996).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{13}\text{NO}_6\text{S}$ $M_r = 311.30$ Monoclinic, $P2_1/c$ $a = 6.8917$ (5) Å $b = 24.1814$ (17) Å $c = 8.2861$ (5) Å $\beta = 97.876$ (4)° $V = 1367.86$ (16) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.26$ mm⁻¹ $T = 120$ (2) K $0.40 \times 0.20 \times 0.20$ mm

Data collection

Bruker Nonius KappaCCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.902$, $T_{\max} = 0.949$

12265 measured reflections
3032 independent reflections
2183 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.145$
 $S = 1.03$
3032 reflections

193 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C13}-\text{H13A}\cdots\text{O4}^i$	0.98	2.48	3.387 (3)	153
$\text{C5}-\text{H5}\cdots\text{O1}^i$	0.95	2.48	3.349 (3)	151

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

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CAMERON (Pearce & Watkin, 1993); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2156).

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supplementary materials

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Methyl 4-acetoxy-2-methyl-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide

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Comment

Among the vast class of benzothiazines, 1,2-benzothiazine 1,1-dioxides are the most versatile compounds due to their applications in various fields such as pharmaceuticals (Turck *et al.*, 1996), dyes (Rajagopal & Seshadri, 1990) and fungicides. In continuation of our investigation of the chemistry of 1,2-benzothiazine 1,1-dioxide derivatives (Rehman *et al.*, 2005; Rehman *et al.*, 2006) we have synthesized the title compound (**I**) and its crystal structure is reported here.

In (**I**) (Fig. 1), the benzene ring of the benzothiazine nucleus is planar (the maximum least square deviation from the plane of the atoms involved is 0.01 Å) while the thiazine ring adopts a distorted half chair conformation. N1 has a pyramidal geometry projecting the methyl group approximately perpendicular to the thiazine ring. Atoms O1, O3 and O5 lie approximately in the plane of the ring while O2 lies almost perpendicular to it.

The C7—O3 bond length in (**I**) is longer [1.389 (3)] than in the related molecules having no substitution at O3 [1.352 (9) Å; Golič & Leban, 1987; 1.350 (9) Å; Reck *et al.*, 1988].

C9—O4 bond length [1.201 (13) Å] is observed to be shorter than in its previously reported non acylated analogue [1.262 (10) Å; Golič & Leban, 1987] due to no involvement of O4 electrons in the hydrogen bonding. O4 lies almost perpendicular to the thiazine ring and the bond angle C7—C8—C9 [127.3 (2) Å] is greater than observed in the related hydrogen bonded oxicams [121.0 (3) Å; Kojić-Prodić & Ružić-Toroš, 1982; 120.9 (2) Å, Fabiola *et al.*, 1998]. Molecules are linked by C—H...O hydrogen bonds (Table 1) forming a chain along *a* axis.

Experimental

Acetyl chloride (1.57 g; 10 mmol) was slowly added to a mixture of methyl 4-hydroxy-2-methyl-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide (1.345 g; 5 mmol), triethylamine (0.71 g; 7 mmol) and carbon tetrachloride (25 ml) under nitrogen atmosphere at 273 K. The mixture was stirred for a period of three hours at room temperature and the solvent was evaporated under vacuum. A residue was poured over ice-water mixture to get the white coloured product which was washed with cold water and recrystallized from chloroform-methanol mixture (1:1). Yield 1.31 g; 84°; m.p. 422 K.

Figures

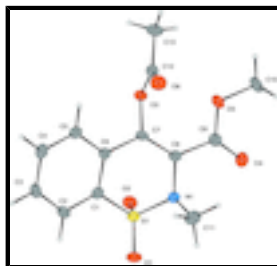


Fig. 1. The molecular structure of (**I**), showing displacement ellipsoids at the 50% probability level for non-H atoms. Dashed lines denote hydrogen bonds.

Methyl 4-acetoxy-2-methyl-2H-1,2-benzothiazine-3-carboxylate 1,1-dioxide

Crystal data

$C_{13}H_{13}NO_6S$	$F(000) = 648$
$M_r = 311.30$	$D_x = 1.512 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ybc	Cell parameters from 15145 reflections
$a = 6.8917 (5) \text{ \AA}$	$\theta = 2.9\text{--}27.5^\circ$
$b = 24.1814 (17) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 8.2861 (5) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 97.876 (4)^\circ$	Block, colourless
$V = 1367.86 (16) \text{ \AA}^3$	$0.40 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Bruker Nonius CCD camera on κ -goniostat diffractometer	3032 independent reflections
Radiation source: Bruker Nonius FR591 Rotating Anode	2183 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.057$
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$
φ and ω scans to fill the asymmetric unit	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (SADABS; Shelldrick, 2007)	$k = -31 \rightarrow 30$
$T_{\text{min}} = 0.902$, $T_{\text{max}} = 0.949$	$l = -10 \rightarrow 9$
12265 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.145$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 0.6225P]$
3032 reflections	where $P = (F_o^2 + 2F_c^2)/3$
193 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$

Special details

Experimental. *SADABS* was used to perform the Absorption correction Estimated minimum and maximum transmission: 0.6195 0.7456 The given Tmin and Tmax were generated using the *SHELX SIZE* command

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5172 (4)	0.43090 (10)	0.7387 (3)	0.0183 (5)
C2	0.7043 (4)	0.45347 (10)	0.7686 (3)	0.0213 (6)
H2	0.7629	0.4616	0.8766	0.026*
C3	0.8032 (4)	0.46376 (10)	0.6369 (3)	0.0213 (5)
H3	0.9315	0.4790	0.6544	0.026*
C4	0.7153 (4)	0.45192 (10)	0.4788 (3)	0.0219 (6)
H4	0.7836	0.4597	0.3893	0.026*
C5	0.5299 (4)	0.42895 (9)	0.4508 (3)	0.0183 (5)
H5	0.4719	0.4211	0.3425	0.022*
C6	0.4276 (4)	0.41729 (9)	0.5809 (3)	0.0167 (5)
C7	0.2364 (3)	0.39001 (9)	0.5570 (3)	0.0162 (5)
C8	0.1613 (4)	0.36162 (10)	0.6749 (3)	0.0181 (5)
C9	-0.0253 (4)	0.32911 (10)	0.6577 (3)	0.0202 (6)
C10	-0.2808 (4)	0.28845 (11)	0.4788 (3)	0.0301 (6)
H10A	-0.2544	0.2510	0.5215	0.045*
H10B	-0.3298	0.2865	0.3622	0.045*
H10C	-0.3793	0.3061	0.5364	0.045*
C11	0.3594 (4)	0.30948 (11)	0.8954 (3)	0.0294 (7)
H11A	0.2711	0.2784	0.8643	0.044*
H11B	0.3914	0.3107	1.0143	0.044*
H11C	0.4800	0.3048	0.8464	0.044*
C12	0.1291 (4)	0.35858 (10)	0.2862 (3)	0.0207 (6)
C13	-0.0222 (4)	0.37189 (12)	0.1456 (3)	0.0307 (7)
H13A	-0.0128	0.3455	0.0572	0.046*
H13B	-0.0008	0.4094	0.1073	0.046*
H13C	-0.1526	0.3695	0.1796	0.046*
N1	0.2622 (3)	0.36187 (8)	0.8366 (2)	0.0185 (5)
O1	0.4912 (3)	0.41115 (8)	1.04687 (19)	0.0263 (4)
O2	0.2249 (3)	0.46261 (7)	0.8823 (2)	0.0234 (4)
O3	0.1272 (2)	0.39845 (6)	0.40526 (18)	0.0184 (4)

supplementary materials

O4	-0.0967 (3)	0.31203 (8)	0.7727 (2)	0.0353 (5)
O5	-0.1014 (3)	0.32064 (7)	0.5028 (2)	0.0266 (4)
O6	0.2420 (3)	0.32061 (7)	0.3014 (2)	0.0282 (5)
S1	0.37225 (9)	0.42031 (2)	0.89441 (7)	0.0197 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0191 (13)	0.0190 (12)	0.0169 (12)	0.0010 (10)	0.0030 (10)	0.0017 (9)
C2	0.0201 (14)	0.0197 (12)	0.0222 (13)	-0.0006 (10)	-0.0035 (10)	-0.0003 (10)
C3	0.0138 (13)	0.0196 (12)	0.0302 (14)	-0.0010 (10)	0.0021 (10)	0.0026 (11)
C4	0.0205 (14)	0.0207 (12)	0.0260 (13)	0.0023 (10)	0.0082 (10)	0.0032 (10)
C5	0.0193 (14)	0.0183 (12)	0.0175 (12)	0.0029 (10)	0.0034 (10)	0.0009 (9)
C6	0.0162 (13)	0.0149 (11)	0.0182 (12)	0.0021 (9)	-0.0003 (10)	0.0017 (9)
C7	0.0146 (12)	0.0198 (12)	0.0135 (11)	0.0019 (10)	-0.0006 (9)	-0.0019 (9)
C8	0.0204 (14)	0.0183 (12)	0.0151 (11)	0.0004 (10)	0.0009 (9)	-0.0017 (9)
C9	0.0214 (14)	0.0197 (12)	0.0201 (13)	0.0000 (10)	0.0047 (10)	-0.0040 (10)
C10	0.0250 (16)	0.0325 (15)	0.0320 (15)	-0.0132 (12)	0.0013 (12)	-0.0068 (12)
C11	0.0372 (17)	0.0243 (14)	0.0257 (14)	0.0046 (12)	0.0006 (12)	0.0038 (11)
C12	0.0186 (14)	0.0267 (13)	0.0175 (12)	-0.0040 (11)	0.0046 (10)	-0.0015 (10)
C13	0.0280 (16)	0.0437 (17)	0.0190 (13)	-0.0027 (13)	-0.0015 (11)	-0.0039 (12)
N1	0.0192 (12)	0.0202 (10)	0.0157 (10)	-0.0012 (8)	0.0013 (8)	0.0007 (8)
O1	0.0243 (11)	0.0390 (11)	0.0141 (9)	-0.0034 (8)	-0.0023 (7)	0.0010 (8)
O2	0.0248 (10)	0.0230 (9)	0.0223 (9)	0.0011 (7)	0.0031 (7)	-0.0041 (7)
O3	0.0176 (9)	0.0218 (9)	0.0152 (8)	0.0003 (7)	-0.0003 (7)	-0.0008 (7)
O4	0.0386 (13)	0.0458 (12)	0.0225 (10)	-0.0196 (10)	0.0080 (9)	0.0008 (9)
O5	0.0222 (10)	0.0351 (10)	0.0223 (9)	-0.0119 (8)	0.0020 (7)	-0.0044 (8)
O6	0.0308 (11)	0.0284 (10)	0.0259 (10)	0.0028 (8)	0.0054 (8)	-0.0049 (8)
S1	0.0207 (4)	0.0234 (3)	0.0147 (3)	-0.0017 (2)	0.0014 (2)	-0.0012 (2)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.391 (3)	C10—O5	1.451 (3)
C1—C6	1.407 (3)	C10—H10A	0.9800
C1—S1	1.755 (3)	C10—H10B	0.9800
C2—C3	1.386 (4)	C10—H10C	0.9800
C2—H2	0.9500	C11—N1	1.484 (3)
C3—C4	1.396 (3)	C11—H11A	0.9800
C3—H3	0.9500	C11—H11B	0.9800
C4—C5	1.384 (3)	C11—H11C	0.9800
C4—H4	0.9500	C12—O6	1.199 (3)
C5—C6	1.396 (3)	C12—O3	1.380 (3)
C5—H5	0.9500	C12—C13	1.488 (3)
C6—C7	1.463 (3)	C13—H13A	0.9800
C7—C8	1.353 (3)	C13—H13B	0.9800
C7—O3	1.389 (3)	C13—H13C	0.9800
C8—N1	1.422 (3)	N1—S1	1.644 (2)
C8—C9	1.498 (3)	O1—S1	1.4258 (17)
C9—O4	1.203 (3)	O2—S1	1.4354 (18)

C9—O5	1.334 (3)		
C2—C1—C6	122.4 (2)	O5—C10—H10C	109.5
C2—C1—S1	122.25 (18)	H10A—C10—H10C	109.5
C6—C1—S1	115.33 (18)	H10B—C10—H10C	109.5
C3—C2—C1	118.3 (2)	N1—C11—H11A	109.5
C3—C2—H2	120.8	N1—C11—H11B	109.5
C1—C2—H2	120.8	H11A—C11—H11B	109.5
C2—C3—C4	120.4 (2)	N1—C11—H11C	109.5
C2—C3—H3	119.8	H11A—C11—H11C	109.5
C4—C3—H3	119.8	H11B—C11—H11C	109.5
C5—C4—C3	120.8 (2)	O6—C12—O3	121.9 (2)
C5—C4—H4	119.6	O6—C12—C13	128.5 (2)
C3—C4—H4	119.6	O3—C12—C13	109.5 (2)
C4—C5—C6	120.3 (2)	C12—C13—H13A	109.5
C4—C5—H5	119.9	C12—C13—H13B	109.5
C6—C5—H5	119.9	H13A—C13—H13B	109.5
C5—C6—C1	117.9 (2)	C12—C13—H13C	109.5
C5—C6—C7	121.9 (2)	H13A—C13—H13C	109.5
C1—C6—C7	120.2 (2)	H13B—C13—H13C	109.5
C8—C7—O3	121.0 (2)	C8—N1—C11	116.50 (18)
C8—C7—C6	123.9 (2)	C8—N1—S1	115.14 (15)
O3—C7—C6	114.97 (19)	C11—N1—S1	117.95 (17)
C7—C8—N1	119.5 (2)	C12—O3—C7	119.17 (18)
C7—C8—C9	127.3 (2)	C9—O5—C10	115.4 (2)
N1—C8—C9	113.2 (2)	O1—S1—O2	119.20 (10)
O4—C9—O5	124.0 (2)	O1—S1—N1	108.13 (11)
O4—C9—C8	123.0 (2)	O2—S1—N1	107.37 (10)
O5—C9—C8	113.0 (2)	O1—S1—C1	110.97 (12)
O5—C10—H10A	109.5	O2—S1—C1	108.25 (11)
O5—C10—H10B	109.5	N1—S1—C1	101.39 (11)
H10A—C10—H10B	109.5		
C6—C1—C2—C3	1.3 (4)	C7—C8—N1—C11	-108.8 (3)
S1—C1—C2—C3	-175.79 (18)	C9—C8—N1—C11	72.3 (3)
C1—C2—C3—C4	0.4 (4)	C7—C8—N1—S1	35.6 (3)
C2—C3—C4—C5	-1.1 (4)	C9—C8—N1—S1	-143.34 (17)
C3—C4—C5—C6	0.1 (4)	O6—C12—O3—C7	-10.5 (3)
C4—C5—C6—C1	1.6 (3)	C13—C12—O3—C7	170.6 (2)
C4—C5—C6—C7	-176.3 (2)	C8—C7—O3—C12	-86.4 (3)
C2—C1—C6—C5	-2.3 (3)	C6—C7—O3—C12	98.0 (2)
S1—C1—C6—C5	175.01 (17)	O4—C9—O5—C10	-0.2 (4)
C2—C1—C6—C7	175.6 (2)	C8—C9—O5—C10	178.9 (2)
S1—C1—C6—C7	-7.1 (3)	C8—N1—S1—O1	-170.76 (17)
C5—C6—C7—C8	157.1 (2)	C11—N1—S1—O1	-27.0 (2)
C1—C6—C7—C8	-20.7 (4)	C8—N1—S1—O2	59.42 (19)
C5—C6—C7—O3	-27.4 (3)	C11—N1—S1—O2	-156.78 (18)
C1—C6—C7—O3	154.8 (2)	C8—N1—S1—C1	-54.01 (19)
O3—C7—C8—N1	-169.13 (19)	C11—N1—S1—C1	89.79 (19)
C6—C7—C8—N1	6.2 (4)	C2—C1—S1—O1	-28.5 (2)

supplementary materials

O3—C7—C8—C9	9.6 (4)	C6—C1—S1—O1	154.23 (17)
C6—C7—C8—C9	-175.1 (2)	C2—C1—S1—O2	104.1 (2)
C7—C8—C9—O4	-168.4 (3)	C6—C1—S1—O2	-73.2 (2)
N1—C8—C9—O4	10.4 (3)	C2—C1—S1—N1	-143.1 (2)
C7—C8—C9—O5	12.4 (4)	C6—C1—S1—N1	39.6 (2)
N1—C8—C9—O5	-168.8 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C13—H13A \cdots O4 ⁱ	0.98	2.49	3.387 (3)	153
C5—H5 \cdots O1 ⁱ	0.95	2.48	3.349 (3)	151

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

Fig. 1

