$\theta/2\theta$ scans
Absorption correction: none
5946 measured reflections
4792 independent reflections
1909 reflections with
$\quad F > 6\sigma(F)$

$h = -1 \rightarrow 14$
$k = -1 \rightarrow 18$
$l = -17 \rightarrow 17$
3 standard reflections
every 97 reflections
intensity decay: 0.0001%

Refinement

Refinement on F
$R = 0.0462$
$wR = 0.0541$
$S = 1.1$
5946 reflections
218 parameters
H atoms not refined
$w^{-1} = \sigma^2(F) + 0.0008F_o^2$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

S(1)—C(2)	1.740 (3)	C(10)—C(24)	1.480 (5)
S(1)—C(9)	1.829 (3)	N(11)—C(12)	1.400 (4)
C(2)—C(3)	1.368 (4)	C(12)—C(13)	1.404 (4)
C(2)—C(7)	1.381 (4)	C(12)—C(21)	1.366 (4)
C(3)—C(4)	1.374 (5)	C(13)—C(14)	1.398 (4)
C(4)—C(5)	1.369 (6)	C(13)—C(18)	1.413 (5)
C(5)—C(6)	1.369 (5)	C(14)—C(15)	1.352 (5)
C(6)—C(7)	1.373 (4)	C(15)—C(16)	1.375 (7)
C(7)—N(8)	1.388 (4)	C(16)—C(17)	1.347 (6)
N(8)—C(9)	1.409 (4)	C(17)—C(18)	1.398 (5)
N(8)—C(23)	1.447 (4)	C(18)—C(19)	1.398 (5)
C(9)—C(10)	1.507 (4)	C(19)—C(20)	1.358 (5)
C(9)—O(22)	1.430 (4)	C(20)—C(21)	1.385 (5)
C(10)—N(11)	1.273 (4)	C(21)—O(22)	1.362 (4)
S(1)—C(9)—N(8)	105.0 (2)	S(1)—C(9)—O(22)	110.1 (2)
S(1)—C(9)—C(10)	107.7 (2)	N(8)—C(9)—O(22)	107.9 (2)
N(8)—C(9)—C(10)	116.2 (3)	C(10)—C(9)—O(22)	109.8 (2)

A variable scan rate, and a $\theta-2\theta$ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 50° were used.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXS*86; molecular graphics: *XP* (Siemens, 1990).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(Benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine 4-Oxide

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Abstract

The title compound, $C_{11}H_9NO_2S_2$, is a potent material preservative and contains the 1,4,2-oxathiazine ring system in a half-chair conformation with the methylene C atoms 0.510 (3) and −0.367 (3) Å from the plane of the other four oxathiazine ring atoms.

Comment

3-Aryl-5,6-dihydro-1,4,2-oxathiazines and their oxides are novel heterocyclic compounds active as agricultural fungicides, herbicides and plant growth regulants (Brouwer, Bell, Blem & Davis, 1986, 1987; Blem & Brouwer, 1987). Recently, 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine 4-oxide, (I), was found to possess potent material preservative properties (Davis, Valcke & Brouwer, 1995). These important compounds are therefore of interest from a structural viewpoint. To our knowledge, this is the first reported crystal structure determination of a molecule with a 1,4,2-oxathiazine ring system.

(I)
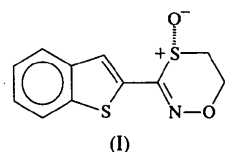
Molecule (I) as synthesized is a racemic mixture, but it undergoes spontaneous resolution on recrystallization from ethyl acetate to yield crystals in the chiral space group $P2_12_12_1$. Our X-ray data allowed determination of the absolute stereochemistry; a view of molecule (I) with the atomic numbering scheme is shown in Fig. 1. The 1,4,2-oxathiazine ring system adopts a slightly distorted half-chair conformation with the methylene C5 and C6 atoms 0.510 (3) Å and −0.367 (3) Å, respectively, from the plane of the other oxathiazine ring atoms; the torsion angle O1—N2—C3—S4 is −6.2 (3)°.
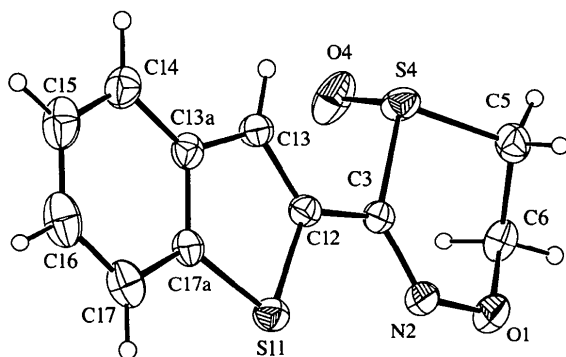

Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The bond lengths in the 1,4,2-oxathiazine ring system (Table 1) are mostly in agreement with expected values (Orpen et al., 1994) except for the C—S distances involving the oxathiazine S4 atom. The S—C_{sp^2} distance [S4—C3 1.813 (2) Å] is 0.021 Å longer than the S—C_{sp^3} distance [S4—C5 1.792 (2) Å]; this is not inconsistent with the presence of canonical forms such as (Ia) and (Ib) in the ground-state structure, with the form (Ib) making a minor contribution.

(Ia)   (Ib)
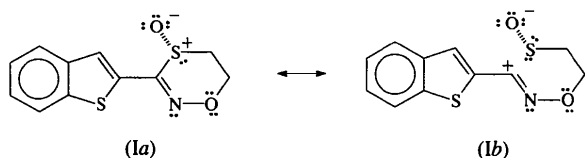
The atoms of the benzo[b]thienyl moiety are close to being coplanar [the interplanar angle between the five- and six-membered rings is only 2.0 (1)°]. The O1, N2, C3, S4 plane forms a dihedral angle of 4.1 (1)° with the plane of the benzo[b]thienyl ring system.

There are two short intermolecular C—H···O interactions to O4 (Table 2). There is also a short intramolec-

ular contact between H13 (on C13) and S4, with H···S 2.73 Å, some 0.27 Å shorter than the sum of the van der Waals radii (Bondi, 1964); the exocyclic angle C3—C12—C13 is enlarged [to 127.46 (14)°]. Examination of the structure with *PLATON* (Spek, 1996a) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Crystal data

$C_{11}H_9NO_2S_2$	Mo $K\alpha$ radiation
$M_r = 251.31$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.4730 (11)$ Å	$\theta = 10.3$–$18.3°$
$b = 8.2860 (11)$ Å	$\mu = 0.472$ mm^{-1}
$c = 17.527 (2)$ Å	$T = 294 (1)$ K
$V = 1085.3 (3)$ Å^3	Plate
$Z = 4$	$0.40 \times 0.40 \times 0.24$ mm
$D_x = 1.538$ Mg m^{-3}	Very pale yellow
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.014$
diffractometer	$\theta_{max} = 27°$
$\theta/2\theta$ scans	$h = -9 \rightarrow 9$
Absorption correction:	$k = 10 \rightarrow 10$
Gaussian by integration	$l = 22 \rightarrow 22$
$T_{min} = 0.805$, $T_{max} = 0.905$	3 standard reflections
2717 measured reflections	frequency: 120 min
2393 independent reflections	no intensity decay;
2186 reflections with	variation 0.5%
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.204$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{min} = -0.155$ e Å^{-3}
$wR(F^2) = 0.073$	Extinction correction:
$S = 1.060$	*SHELXL93*
2393 reflections	Extinction coefficient:
146 parameters	0.0053 (18)
H atoms riding (C—H 0.93–	Scattering factors from
0.97 Å)	*International Tables for*
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2$	*Crystallography* (Vol. C)
$+ 0.0452P]$	Absolute configuration:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983)
$(\Delta/\sigma)_{max} < 0.001$	Flack parameter = −0.01 (7)

Table 1. *Selected geometric parameters (Å, °)*

S4—O4	1.485 (2)	O1—C6	1.437 (2)
S4—C3	1.813 (2)	N2—C3	1.284 (2)
S4—C5	1.792 (2)	C3—C12	1.450 (2)
S11—C12	1.742 (2)	C5—C6	1.496 (3)
S11—C17a	1.741 (2)	C12—C13	1.362 (2)
O1—N2	1.385 (2)		

O4—S4—C3	107.68 (9)	S4—C3—C12	113.69 (12)
O4—S4—C5	106.91 (10)	N2—C3—C12	117.11 (14)
C3—S4—C5	93.83 (8)	S4—C5—C6	108.21 (13)
C12—S11—C17a	90.76 (8)	O1—C6—C5	110.9 (2)
N2—O1—C6	117.29 (13)	S11—C12—C3	119.55 (12)
O1—N2—C3	121.78 (14)	S11—C12—C13	112.99 (13)
S4—C3—N2	129.07 (13)	C3—C12—C13	127.46 (14)
O1—N2—C3—S4	−6.2 (3)		

Table 2. *Short C—H···O and C—H···S contacts (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···O4^i	0.97	2.47	3.311 (2)	145
C13—H13···O4^{ii}	0.93	2.45	3.321 (2)	156
C13—H13···S4	0.93	2.73	3.063 (2)	102

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

A complete Friedel data set ($\pm h$, $+k$, $+l$ reflections) was collected to aid in the determination of the absolute configuration of the structure reported here and also to ensure a suitable excess of reflection data to parameters in the refinement (16.4 reflections per parameter).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996a) and *PLUTON* (Spek 1996b). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *WordPerfect* macro *PREPCIF* (Ferguson, 1996).

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