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

N1—C2	1.4931 (13)	C2—C3	1.521 (2)
N1—C7	1.493 (2)	C3—O4	1.425 (2)
C2^i—N1—C2	109.93 (12)	O4—C3—C2	111.19 (10)
C2—N1—C7	111.71 (7)	C3—O4—C3^i	109.08 (13)
N1—C2—C3	109.48 (10)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Due to the instability of the crystals in air at room temperature, crystals were examined for quality after mounting in the cold stream of the diffractometer. A large (1.0 mm) crystal was used after the first several proved unsuitable. The crystal was optically centered with great care and an empirical absorption correction (*via* ψ scans) was used to account for intensity errors that may have resulted from small sections of the crystal not being fully bathed in the uniform X-ray beam. A partial data set for the corresponding bromide salt was also collected (the crystal was lost prior to completion). Solution and refinement of the truncated data gave results that were sufficiently conclusive to show that the compounds are isostructural. The lattice parameters of the hydrobromide [$a = 7.228\,(1)$, $b = 7.339\,(1)$, $c = 7.349\,(1)$ Å, $\beta = 92.92\,(1)°$] were determined from 35 reflections in the range $9.49 < \theta < 25.02°$. $(\Delta/\sigma)_{\max}$ may be regarded as being on the high side, but this is attributed to disorder in the C7 H atoms [$(\Delta/\sigma)_{\text{mean}} = 0.01$].

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Methylbenzothiazolinospiro-2,3′-(2-methyl[3*H*]phenanthr[9,10-*b*][1,4]oxazine) and 1-Methylbenzothiazolinospiro-2,3′-(2′-methyl[3*H*]naphth[2,1-*b*][1,4]oxazine)†

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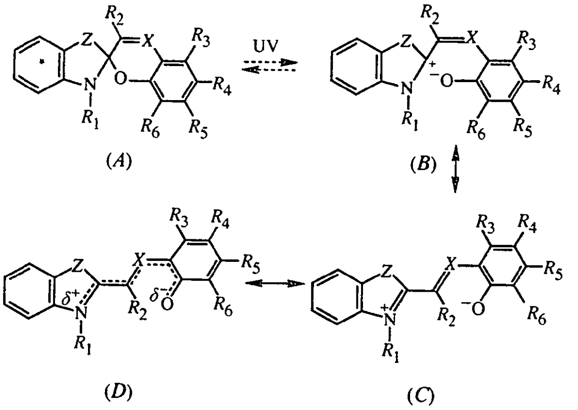
Abstract

The single-crystal X-ray structures of two thiazolinospiro derivatives, $C_{24}H_{18}N_2OS$ and $C_{20}H_{16}N_2OS$, suggest that their lack of photochromic behavior is due to electron-pair delocalization which reduces potential stabilization of a cationic intermediate.

Comment

Photochromic materials have been known since the 1950s (Hirshberg, 1950, 1956). Current interest stems from their potential application as optical information storage media based on the photochromic reaction.



Many spirooxazine compounds, (*A*), undergo this reversible change of color under the influence of UV radiation in solution. NMR evidence (Samat, Kister, Garnier, Metzger & Guglielmetti, 1975) supports the

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† Alternative names: 3-methyl-2,3-dihydro-1,3-benzothiazolespiro-2,2′-(3-methyl-2*H*-phenanthr[9,10-*b*][1,4]oxazine) and 3-methyl-2,3-dihydro-1,3-benzothiazolespiro-2,2′-(3-methyl-2*H*-naphth[2,1-*b*][1,4]-oxazine).

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thesis that this photochromism involves UV-induced dissociation of the spiro C—O bond, from the oxazine ring, to form a planar structure, (*B*), which is called the colored or open form. Form (*B*) is stabilized by electron-pair donation from the adjacent N atom, (*C*), and shows electron delocalization over an extended range if the structural framework is planar, (*D*). Return to the closed form (*A*) is driven by heat or visible light.

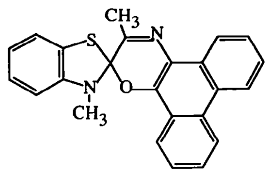
Abstraction from details of the solid-state structure to solution behavior is always open to question because it is unclear what specific role solvation might play in the mechanism of C—O bond breaking. However, previous investigators have analyzed structures of spirooxazines and have identified specific details which might presage photochromic and non-photochromic behavior. Electron-withdrawing substituents are often present at R_4 and R_6 in photochromic materials. R_1 is normally a methyl group. There appear to be no special requirements for R_3, R_5 and R_6.

When R_2 is a bulky alkyl group, the lifetime of the open form has been reported to diminish (Guglielmetti, Mossé, Métras & Metzger, 1968; Mentienne *et al.*, 1973). The comparison of photochromic behavior of three compounds [Z = $(CH_3)_2C$, X = N] in which R_2 = H, with their non-thermochromic counterparts in which R_2 = CH_3, suggested that steric strain in planar state (*C*) due to the bulk of R_2 might increase the rate of return to form (*A*) (Clegg *et al.*, 1991). However, 3-ethyl-8-methyl-6-nitro-2*H*-1-benzopyran-2-spiro-2′-(3′-methylthiazolidine), (III), with R_2 = ethyl, is photochromic (Miler-Srenger & Guglielmetti, 1984). Compound (III) represents the only previously reported structure of a spiro compound with Z = S (R_1 = CH_3, R_4 = NO_2, R_6 = OCH_3, R_3, R_5 = H, X = CH, unsubstituted aromatic ring labeled * not present).

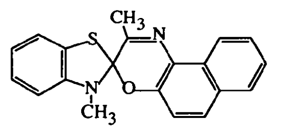
Other authors have examined bond lengths at the spiro C atom, speculating that photochromic compounds might display longer and thus weaker C—O bonds reflecting their incipient breakage (Millini, Del Piero, Allegrini, Malatesta & Castaldi, 1993) and shorter C—N distances, an omen of donation of the unshared pair on N towards the cation developing at the spiro C atom (Osano, Mitsuhashi, Maeda & Matsuzaki, 1991). Photochromic spiro compounds show C—O bonds of 1.46 Å or greater. C—N bonds of 1.425 (6)–1.434 (3) Å or shorter have been cited as supportive of photochromism.

Similarly, the sum of the bond angles at N has been examined for evidence that the sp^3 hybridized (angle total: 3 × 109 or 327°) N atom is becoming planar or sp^2 hybridized (angle total: 360°) in preparation for electron-pair donation to stabilize the cation seen in (*B*). Thus, higher angle totals suggest potential thermochromism.

We have prepared two benzothiazolinospirooxazines which do not display photochromism; 1-methylbenzothiazolinospiro-2,3′-(2-methyl[3*H*]phenanthr[9,10-*b*]-[1,4]oxazine), (I) (Fig. 1), and 1-methylbenzothiazolinospiro-2,3′-(2′-methyl[3*H*]naphth[2,1-*b*][1,4]oxazine), (II) (Fig. 2), and have determined their single-crystal X-ray structures to verify the connectivities of the molecules and to seek an explanation for their unexpected lack of photochromic behavior. The synthesis and IR characterization of (II) has previously been reported (Arnold & Paal, 1971).



(I)



(II)

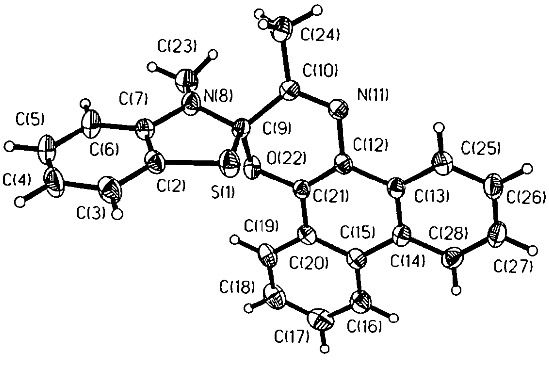


Fig. 1. Projection view of (I). Ellipsoids are shown at the 50% probability level.

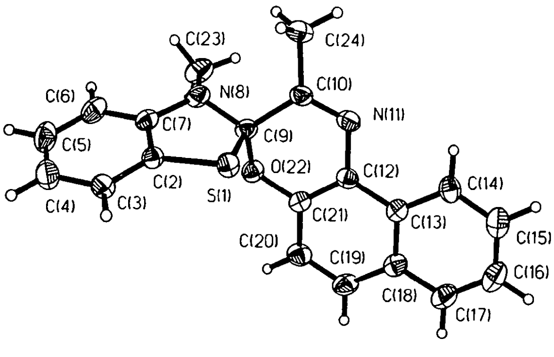


Fig. 2. Projection view of (II). Ellipsoids are shown at the 50% probability level.

Compounds (I) and (II) crystallize with two relatively planar moieties (atoms 1–9 and atoms 9–24) which display interplanar angles close to perpendicular [respective standard deviations of 0.065 and 0.087, and an interplanar angle of 93.3° for (I); respective standard deviations of 0.085 and 0.090, and an interplanar angle of 105.0° for (II)].

The S—C bonds in the title compounds [S—C 1.838 (5) in (I) and 1.829 (3) Å in (II)] are shorter than the distance of 1.852 (3) Å seen for (III). Both compounds display short C—O and C—N bonds at the spiro C atom; 1.422 (6) and 1.402 (6) Å, respectively, for (I), and 1.430 (4) and 1.409 (4) Å for (II). The C—N shortening may be attributed to the presence of the S atom. A similar short C—N bond of 1.421 (4) Å is seen in (III) (Miler-Srenger & Guglielmetti, 1984). The C—O bonds of the title compounds are significantly shorter than those characteristic of photochromic spiropyrans.

Compounds (I) and (II) display considerable flattening at N8; 350.9 (4) for (I) and 349.2 (2)° for (II) compared with the 338.4° total reported for (III).

Compounds (I) and (II) are bright red in color, suggesting significant amounts of bond delocalization involving the S and N atoms, and the adjacent aromatic ring. The shortness of the bonds between the heteroatoms and this ring [N8—C7 1.385 (7) and S1—C2 1.743 (5) Å for (I), and N8—C7 1.388 (4) and S1—C2 1.740 (3) Å for (II)], coupled with the relative planarity of bonds at N8, suggests a degree of rehybridization at S1 and N8 to facilitate delocalization of their lone pairs. Thus, the ability of either heteroatom to stabilize a cation developing at the spiro C atom is severely reduced. In compound (III), which lacks the aromatic ring adjacent to the heteroatoms, unshared pairs on the N and S atoms are available to stabilize the cation developing at the spiro C atom in the photochromic mechanism.

Experimental

N-Methyl-2-ethylbenzothiazolium iodide (5 mmol) and 9-nitroso-10-hydroxyphenanthrene (5 mmol) [1-nitroso-2-hydroxyphenanthrene (5 mmol) for (II)] were mixed in a 100 ml flask followed by the addition of 50 ml anhydrous ethyl alcohol and 3 ml triethylamine and heating under reflux (4 h). After removal of the solvent, the residue was dissolved in chloroform and chromatographed on silica gel. The major product was recrystallized from chloroform/petroleum ether. Single crystals were obtained by dissolving the solid product in a 1:1 mixture of chloroform and petroleum ether which was allowed to concentrate at room temperature. Red cubic single crystals were obtained.

Compound (I)

Crystal data

$C_{24}H_{18}N_2OS$
$M_r = 382.5$
Monoclinic
$P2_1/n$
$a = 6.286\,(3)$ Å
$b = 12.033\,(5)$ Å
$c = 24.523\,(14)$ Å
$\beta = 95.31\,(4)°$
$V = 1846.9\,(16)$ Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 66 reflections
$\theta = 3.69–12.43°$
$\mu = 0.193$ mm^{-1}
$T = 298$ K
Cubic
0.2 × 0.2 × 0.2 mm
Red

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7195 measured reflections
5365 independent reflections
1634 reflections with $F > 6\sigma(F)$

$R_{\rm int} = 0.0572$
$\theta_{\rm max} = 30°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 16$
$l = -34 \rightarrow 30$
3 standard reflections every 97 reflections intensity decay: 0.0001%

Refinement

Refinement on F
$R = 0.0545$
$wR = 0.0570$
$S = 1.30$
5365 reflections
253 parameters
H atoms not refined
$w^{-1} = \sigma^2(F) + 0.0008F^2$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S(1)—C(2)	1.743 (5)	C(12)—C(21)	1.331 (7)
S(1)—C(9)	1.838 (5)	C(13)—C(14)	1.388 (8)
C(2)—C(3)	1.376 (8)	C(13)—C(25)	1.391 (8)
C(2)—C(7)	1.367 (8)	C(14)—C(15)	1.450 (8)
C(3)—C(4)	1.369 (9)	C(14)—C(28)	1.400 (8)
C(4)—C(5)	1.354 (11)	C(15)—C(16)	1.377 (9)
C(5)—C(6)	1.372 (9)	C(15)—C(20)	1.405 (7)
C(6)—C(7)	1.380 (8)	C(16)—C(17)	1.356 (9)
C(7)—N(8)	1.385 (7)	C(17)—C(18)	1.380 (9)
N(8)—C(9)	1.402 (6)	C(18)—C(19)	1.350 (10)
N(8)—C(23)	1.441 (7)	C(19)—C(20)	1.384 (8)
C(9)—C(10)	1.501 (7)	C(20)—C(21)	1.413 (8)
C(9)—O(22)	1.422 (6)	C(21)—O(22)	1.363 (6)
C(10)—N(11)	1.272 (7)	C(25)—C(26)	1.353 (8)
C(10)—C(24)	1.487 (8)	C(26)—C(27)	1.370 (9)
N(11)—C(12)	1.399 (7)	C(27)—C(28)	1.356 (9)
C(12)—C(13)	1.429 (7)		
C(7)—N(8)—C(9)	113.1 (4)	N(8)—C(9)—O(22)	108.1 (4)
C(7)—N(8)—C(23)	119.5 (4)	C(10)—C(9)—O(22)	109.5 (4)
C(9)—N(8)—C(23)	118.3 (4)	C(9)—C(10)—N(11)	120.0 (5)
S(1)—C(9)—N(8)	104.9 (3)	C(9)—C(10)—C(24)	120.0 (4)
S(1)—C(9)—C(10)	106.7 (3)	N(11)—C(10)—C(24)	119.8 (5)
N(8)—C(9)—C(10)	116.1 (4)	C(10)—N(11)—C(12)	118.0 (4)
S(1)—C(9)—O(22)	111.4 (3)		

Compound (II)

Crystal data

$C_{20}H_{16}N_2OS$
$M_r = 332.4$
Monoclinic
$P2_1/c$
$a = 10.237\,(3)$ Å
$b = 13.364\,(7)$ Å
$c = 12.296\,(7)$ Å
$\beta = 102.16\,(3)°$
$V = 1646.6\,(14)$ Å^3
$Z = 4$
$D_x = 1.341$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 3.65–12.83°$
$\mu = 0.205$ mm^{-1}
$T = 298$ K
Cube
0.2 × 0.2 × 0.2 mm
Red–orange

Data collection

Syntex *P*4 four-circle diffractometer

$R_{\rm int} = 0.0383$
$\theta_{\rm max} = 25°$

$\theta/2\theta$ scans
Absorption correction: none
5946 measured reflections
4792 independent reflections
1909 reflections with $F > 6\sigma(F)$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 18$
$l = -17 \rightarrow 17$
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 θ–2θ 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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Acta Cryst. (1997). C**53**, 823–825

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.