Structure of Photochromic 3-Ethyl-8-methoxy-6-nitro-2*H*-1-benzopyran-2-spiro-2'-(3'-methylthiazolidine), C₁₅H₁₈N₂O₄S

Structure of Photochromic 3-Ethyl-8-methoxy-6-nitro-2H-1-benzopyran-2-spiro-2'-(3'-methylthiazolidine), $C_{15}H_{18}N_2O_4S$

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Abstract. $M_r = 322 \cdot 4$, $P\bar{1}$, $a = 6 \cdot 973$ (5), $b = 8 \cdot 884$ (4), $c = 13 \cdot 438$ (4) Å, $\alpha = 84 \cdot 48$ (5), $\beta = 110 \cdot 36$ (5), $\gamma = 86 \cdot 79$ (5)°, $V = 773 \cdot 2$ (12) Å³, $Z = 2$, $D_x = 1 \cdot 385$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1 \cdot 54051$ Å, $\mu = 1 \cdot 99$ mm⁻¹, $F(000) = 340$, room temperature, $R = 0 \cdot 048$ for 2344 observed reflexions. The spiro carbon atom is involved in two long bonds to S and O. The thiazolidine ring is in an almost perfect half-chair conformation. The conformation of the pyran ring is 1,3-diplanar. Its puckering parameters and torsion energy increase through introduction of such bulky substituents in positions 3 and 8 of the benzopyran that cannot avoid short intramolecular contacts through steric accommodations. Molecules are piled along the *b* axis, alternately reversed in orientation and nearly equally spaced. Both enantiomers are present in the crystalline state as implied by the centrosymmetric space group.

Introduction. Spiropyrans are colorless photochromic compounds, which transform under UV irradiation into strongly colored photomerocyanines. The reaction is reversible either by heat or by visible light absorption. It has been observed that the rate of decoloration depends on the electronic properties of the substituents introduced in the benzopyranic or heterocyclic part of the molecule. Guglielmetti, Mossé, Métras & Metzger (1968) have further shown that the activation energy of ring closure may also be lowered by introduction of bulky substituents, like C_2H_5, i-C_3H_7 or C_6H_5, in position 3.

To obtain a better insight into the correlation between molecular substitution, conformation and photochemical reactivity, the molecular structure of the title compound (I), synthesized and studied by Maguet, Garnier & Guglielmetti (1982), has been established and compared to the conformations of 8-bromo-6-nitroindolinespirobenzopyran (II) (Aldoshin, Atovmyan, D'yachenko & Gal'bershtam, 1981) and of the 8-nitro derivative (III) (Shibaeva, Rosenberg, Holmanskii & Zubkov, 1976).
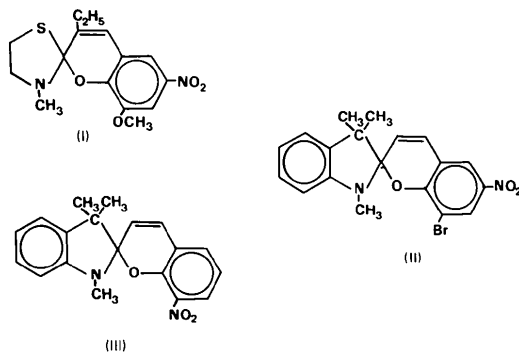
Experimental. Crystal size: $0 \cdot 2 \times 0 \cdot 3 \times 0 \cdot 1$ mm; cell constants: calculated from least-squares fit to 2θ values $(2\theta > 87°)$ of 13 reflexions measured manually on diffractometer. Data collection: Nonius CAD-3 automatic diffractometer by θ–2θ scan up to $2\theta = 132°$. Check reflexions: two, monitored every 40 reflexions, only random fluctuations noted. Each intensity was assigned an observational variance $\sigma^2(I) = S + B_1 + B_2 + (pI^2)$ (S, B_1, B_2 are total integrated and background counts, I net intensity, $p = 0 \cdot 04$). From 2690 measured reflexions, 346 $[I < 2\sigma(I)]$ classed as unobserved and excluded from refinement. Lp correction; absorption ignored. Index range: $0 \le h \le 8$; $-10 \le k \le 10$; $-15 \le l \le 14$. Structure solved with multisolution technique (Germain, Main & Woolfson, 1971). H atoms located from difference electron density map. Weighting scheme chosen so that averages of $w(\Delta F)^2$ constant for different ranges of $|F_o|$. Full-matrix least-squares refinement on F (*ORFLS*; Busing, Martin & Levy, 1962); heavy atoms anisotropically, H atoms isotropically; final $R = 0 \cdot 048$, $R_w = 0 \cdot 067$; final parameter shifts $<0 \cdot 1\sigma$, $S = 1 \cdot 06$ for $n = 271$, $m = 2344$. Scattering factors for heavy atoms from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). H-atom positions checked on difference Fourier synthesis, computed with contributions from all non-hydrogen atoms. Residual electron density in final difference map within

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (Å^2)

The e.s.d.'s apply to the last significant digit. B_{eq} values were calculated with Hamilton's (1959) formula.

	x	y	z	B_{eq}
S(1')	7138 (1)	3189 (1)	8288 (0.5)	3.43
C(22')	5323 (3)	1754 (3)	7793 (2)	2.96
N(3')	4125 (3)	1717 (2)	8459 (2)	3.49
C(4')	3691 (4)	3255 (3)	8681 (2)	3.93
C(5')	5755 (5)	3885 (4)	9101 (2)	4.10
C(10')	2306 (5)	897 (4)	8096	4.68
C(3)	6549 (4)	281 (3)	7821 (2)	3.10
C(4)	7121 (4)	94 (3)	6990 (2)	3.00
C(4a)	6406 (3)	1199 (2)	6033 (2)	2.67
C(5)	7269 (3)	1216 (3)	5240 (2)	2.87
C(6)	6398 (3)	2265 (2)	4340 (2)	2.73
C(7)	4683 (3)	3268 (3)	4174 (2)	2.78
C(8)	3821 (3)	3248 (2)	4956 (2)	2.68
C(8a)	4755 (3)	2257 (2)	5911 (2)	2.59
O(1)	3951 (2)	2304 (2)	6694 (1)	3.15
C(11)	7290 (5)	−774 (3)	8857 (2)	4.17
C(12)	8641 (5)	−2175 (4)	8862 (3)	4.98
O(2)	2130 (2)	4144 (2)	4897 (1)	3.33
C(9)	1035 (4)	5045 (3)	3891 (2)	3.48
N	7343 (3)	2333 (2)	3527 (2)	3.31
O(3)	6436 (3)	3108 (2)	2667 (1)	4.84
O(4)	9005 (3)	1612 (2)	3721 (2)	4.77

± 0.4 e Å^{-3}. Final parameters of non-hydrogen atoms with e.s.d.'s are given in Table 1.* Geometrical parameters were computed with the program of Pippy & Ahmed (1968). Illustrations were prepared with *ORTEP* (Johnson, 1965).

Discussion. A perspective view of the title compound (I) with the atomic numbering is shown in Fig. 1(a) and the bond lengths and bond angles in Figs. 1(b) and (c).

The spiro carbon atom is involved in two long bonds: C(22')—S(1') [1.852 (3) Å] and C(22')—O(1) [1.469 (3) Å]. Structure determinations of a number of other spiro compounds have revealed even longer Csp^3—S^{II} bonds, such as 1.874 (Wong-Ng & Nyburg, 1978) and 1.90 Å (Cheng & Nyburg, 1978). This long-bond formation is related to the molecular crowding, the S(1')···O(1) distance [2.712 (3) Å] being shorter than the sum of van der Waals radii. The long C(22')—O(1) bond seems to be a common feature of photochromic spiropyrans and is in agreement with the photochemical reactivity of the molecule.

The bond angles around the spiro carbon vary from 104.4 to 116.1°. Such a distortion from tetrahedral geometry and the short C(22')—N(3') bond of 1.421 (4) Å suggest that the hybridization at C(22') contains a degree of sp^2 character.

The coordination geometry about N(3') is markedly pyramidal, the sum of valence bond angles being 338.4°.

The angle between the spiro-planes passing through S(1'), C(22'), N(3') and C(3), C(22'), O(1) is 87.2 (2)°.

The bond lengths and bond angles in the benzopyran part of the molecule are in good agreement with
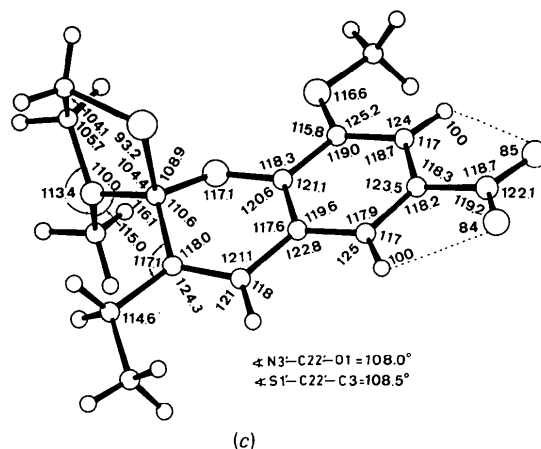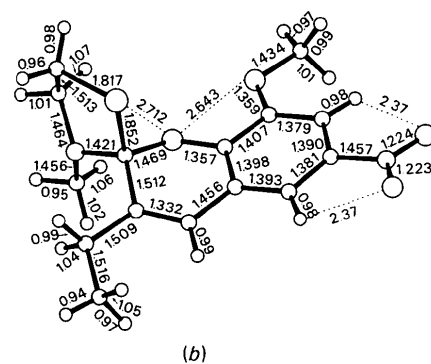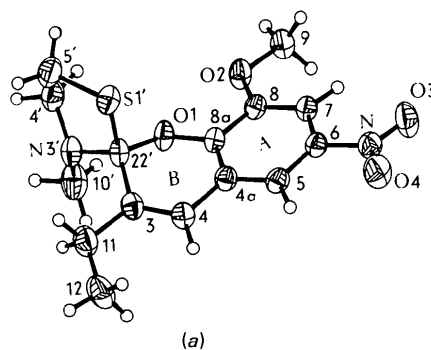

(a)

(b)

$\angle$ N3'—C22'—O1 = 108.0°
$\angle$ S1'—C22'—C3 = 108.5°

(c)

Fig. 1. (a) Perspective view and atomic numbering of the title compound. (b) Bond lengths (Å). The e.s.d.'s are 0.003 Å for S—C, O—C and O—N; 0.004 Å for C—N and C—C; and 0.04 Å for C—H. (c) Bond angles (°). The e.s.d.'s are 0.16° for C—S—C, S—C—N and S—C—O; 0.2° for C—C—C, C—N—C, C—O—C, C—N—O and O—N—O; and 2.0° for S—C—H, O—C—H, N—C—H and C—C—H.

expected values for nitro- and methoxy-substituted phenyl rings (Colapietro & Domenicano, 1977, 1978, 1980).

The geometry of the methoxy group is normal. The dihedral angle between planes passing through C(8), O(2), C(9) and the phenyl ring is 8·9 (3)°. The methyl C(9) is 0·241 (2) Å out of the phenyl-ring plane indicating a weakened interaction between the OCH$_3$ group and the aromatic ring. The structural features of the nitro group, longer C(6)—N bond, shorter N—O bonds and larger O—N—O angle, are also in favour of a weaker resonance interaction between the nitro group and the phenyl ring than in merocyanine (Miler-Srenger & Guglielmetti, 1982). The plane passing through C(6),N,O(3),O(4) forms an angle of 9·9 (3)° with the phenyl-ring plane.

Torsion angles are given in Table 2, and torsion angles, puckering parameters and mirror-plane asymmetry parameters of the pyran ring are compared with the corresponding values observed in the indoline-spiropyrans (II) and (III).

The thiazolidine ring is in a nearly perfect half-chair conformation. Its twofold asymmetry parameter (Duax, Weeks & Rohrer, 1976) ΔC_2 [N(3')—C(4')] is 2·4 (2)°. The puckering parameters (Cremer & Pople, 1975) q_2 and φ_2 are 0·432 (5) Å and 273·7 (5)°, respectively. The phase angle φ_2 of a pure twist conformation is 270°. N(3') and C(4') are on opposite sides of the plane passing through C(5'), S(1'), C(22'), at 0·290 (2) and 0·391 (3) Å, respectively. The centrosymmetric space group implies the presence of both enantiomers in the crystalline state. It should be noted that solutions of the title compound do not show optical activity either.

Owing to substitution and fusion strains, the phenyl ring (A) of the benzopyran portion is slightly puckered, assuming a sofa conformation. C(8a) is 0·070 (2) Å from the best least-squares plane passing through C(4a), C(5), C(6), C(7) and C(8) ($\chi^2 = 28$).

The conformation of the pyran ring of thiazolidine- and indoline-spiropyrans is intermediate between sofa and boat conformations and could best be defined as 1,3-diplanar (Bucourt & Hainaut, 1965) or screw-boat (Boeyens, 1978). The ring-puckering amplitudes depend mostly on the size of substituents in positions 8 and 3 of the benzopyran. Bulky substituents which cannot avoid short intramolecular contacts through steric accommodations enhance the pyran-ring puckering and reactivity. Short intramolecular contacts are observed in (I) and (II), where the O(1)···O(2) and O(1)···Br distances [2·643 (3) and 3·00 Å respectively] are shorter than the sum of van der Waals radii. The torsion angles and ring-puckering coefficients are consequently increased with respect to the value observed in (III), where the nitro group can twist out of the molecular plane in order to avoid short contacts with O(1). Indeed, the angle between the planes passing

Table 2. *Conformational parameters*

The e.s.d.'s of the torsion angles are 0·2°.

Thiazolidine

S(1')—C(22')—N(3')—C(4')	−38·6
C(22')—N(3')—C(4')—C(5')	52·6
N(3')—C(4')—C(5')—S(1')	−39·0
C(4')—C(5')—S(1')—C(22')	15·5
C(5')—S(1')—C(22')—N(3')	12·2
S(1')—C(22')—O(1)—C(8a)	−74·5
S(1')—C(22')—C(3)—C(4)	84·9
N(3')—C(22')—O(1)—C(8a)	172·6
N(3')—C(22')—C(3)—C(4)	−157·9

Ring A

C(4a)—C(5)—C(6)—C(7)	1·9
C(5)—C(6)—C(7)—C(8)	−1·6
C(6)—C(7)—C(8)—C(8a)	−2·5
C(7)—C(8)—C(8a)—C(4a)	6·3
C(8)—C(8a)—C(4a)—C(5)	−6·0
C(8a)—C(4a)—C(5)—C(6)	2·0
C(5)—C(4a)—C(8a)—O(1)	177·1
C(7)—C(8)—C(8a)—O(1)	−176·7
C(5)—C(4a)—C(4)—C(3)	−166·9
C(8)—C(8a)—C(4a)—C(4)	172·7
O(1)—C(8a)—C(8)—O(2)	2·0

Substituents

C(9)—O(2)—C(8)—C(7)	−7·6
C(9)—O(2)—C(8)—C(8a)	173·8
O(4)—N—C(6)—C(5)	9·3
O(3)—N—C(6)—C(7)	10·3
C(12)—C(11)—C(3)—C(4)	4·8
C(12)—C(11)—C(3)—C(22')	175·7

Pyran ring

	(I) $\sigma = 0·2°$	(II) $\sigma = 0·3°$	(III)*
C(22')—C(3)—C(4)—C(4a)	6·5	3·6	3·7
C(3)—C(4)—C(4a)—C(8a)	14·4	7·8	4·8
C(4)—C(4a)—C(8a)—O(1)	−4·2	−0·6	−1·2
C(4a)—C(8a)—O(1) C(22')	−26·4	−17·9	−10·7
C(8a)—O(1)—C(22')—C(3)	44·6	26·6	17·5
O(1)—C(22')—C(3)—C(4)	−34·5	−19·4	−13·9

Puckering parameters	(I)	(II)	(III)	$^1S_6$	^1E	$^{1,4}B$
Q (Å)	0·346 (6)	0·221 (8)	0·146			
φ_2 (°)	347·3 (5)	338·8 (7)	344·0	330	360	360
θ (°)	69·2 (5)	65·9 (7)	64·9	67·5	54·7	90

Mirror-plane asymmetry parameter (°)

ΔC_s|C(22')|	14·2 (2)	10·1 (3)	5·0
ΔC_s|C(3)—C(4)|	31·9 (2)	20·1 (3)	13·2

* E.s.d.'s of atomic parameters were not published by the authors.

through C(8),N,O(3),O(4) and the phenyl ring is 55·5° in 8-nitroindolinespirobenzopyran (III).

The planes passing through C(3),C(22'),O(1) and C(3),C(4),C(8a),O(1) form an angle of 144·6 (2)°. Rings A and B are *cis*-fused.

The molecular packing is illustrated in Fig. 2. The molecules are stacked along the b axis. Alternate molecules are reversed in orientation and nearly equally spaced. The molecular pair at 1 − x, −y, 1 − z and x, y, z shows an extensive overlap of the benzopyran's part. A short van der Waals contact of 3·444 (3) Å is observed between C(4) and C(6). The mutual lateral displacement of the next pair's benzopyran portion at x, y, z and 1 − x, 1 − y, 1 − z is by about 2·5 Å more pronounced than in the preceding pair. The shortest van
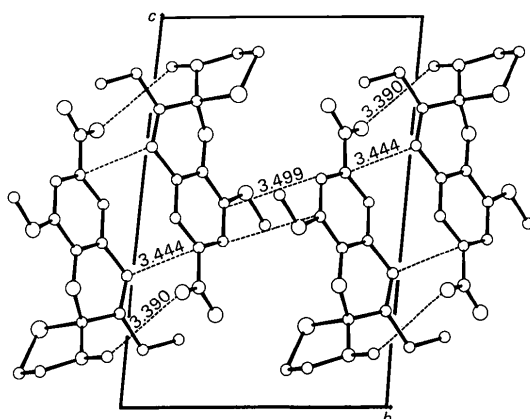
Fig. 2. Molecular packing of the title compound viewed along **a.** (Distances in Å.)

der Waals contact, 3·499 (3) Å, is between C(7) and C(8). The molecular stacks are further cross-linked through short contacts: $O(2)\cdots C(9^i)$ 3·255 (3), $C(9)\cdots C(9^i)$ 3·733 (4), $C(4)\cdots C(10'^{ii})$ 3·541 (4) Å; (i) and (ii) correspond to symmetry positions $-x, 1-y, 1-z$ and $1+x, y, z$, respectively.

H(5) is involved in short intra- and intermolecular contacts to O(4). The geometry of this weak asymmetrical bifurcated interaction is:

	d (Å)	d (Å)	$\angle$ (°)	$\angle$ (°)
			$C(5)-H(5)\cdots$	$O(4)\cdots H(5)\cdots$
	C(5)-H(5)	O(4)$\cdots$H(5)	O(4)	$O(4^{iii})$
C(5)-···-O(4)		2·37 (3)	100 (2)	
C(5)-H(5)	0·98 (3)			113 (1)
·-·O(4^{iii})		2·47 (3)	146 (2)	

(iii) refers to symmetry position $2-x, -y, 1-z$.

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Structure of *cyclo*(-L-Leucyl-L-tyrosyl-) Monohydrate, C₁₅H₂₀N₂O₃.H₂O

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Abstract. $M_r = 294·3$, monoclinic, $P2_1$, $a = 8·883$ (5), $b = 6·105$ (3), $c = 14·582$ (5) Å, $\beta = 99·53$ (4)°, $U = 779·9$ Å³, $Z = 2$, $D_m = 1·25$, $D_x = 1·25$ Mg m⁻³, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·666$ mm⁻¹, $F(000) = 316$, room temperature, $R = 0·075$ for 1147 significant reflections. One of the *cis* peptide units shows significant non-planarity with $\omega = -11·7$ (10)°, the other is planar with $\omega = -2·8$ (10)°. The diketopiperazine ring