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Structure of Photochromic Spiroxazines. I. 1,3,3-Trimethylspiro[indoline-2,3'-[3H]-naphtho[2,1-b][1,4]oxazine]

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Abstract. $C_{22}H_{20}N_2O$, $M_r = 328.4$, orthorhombic, *Pbca*, $a = 17.120$ (3), $b = 16.818$ (3), $c = 12.405$ (2) Å, $V = 3571.7$ (11) Å^3, $Z = 8$, $D_x = 1.221$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1.54178$ Å, $\mu = 0.558$ mm^{-1}, $F(000) = 1392$, $T = 295$ K, $R = 0.053$ for 1762 reflections with $F > 2\sigma(F)$. The molecular structure consists of an indoline ring linked to a naphthoxazine ring through a spiro C atom. No significant distortion from the tetrahedral coordination was detected for the spiro C atom. All intermolecular distances agree with normal van der Waals interactions.

Introduction. Spiroindolinonaphthoxazines (I) exhibit photochromism and have higher durability with respect to photo-excitation than spiroindolinobenzopyrans. The better fatigue resistance renders this class of compounds most interesting for practical applications such as optical switches, filters, coatings for lenses and windows, optical memories *etc.*

The photochemical ring opening which results in the formation of red-absorbing merocyanine-like structures (II) has been extensively studied by ultrafast transient absorption and emission spectroscopy
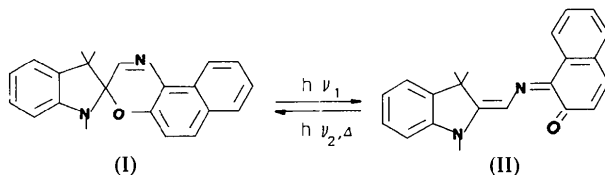
(Schneider, Mindl, Elfinger & Melzig, 1987; Schneider, Baumann, Klüter & Melzig, 1987; Kelmann, Tfibel, Dubest, Levoir, Aubard, Poitier & Guglielmetti, 1989; Bohne, Fan, Li, Lusztyk & Scaiano, 1990), nanosecond time-resolved spontaneous and coherent anti-Stokes Raman scattering (Albert, Bertigny, Aubard, Dubest & Dubois, 1985) and picosecond time-resolved resonance Raman spectroscopy (Aramaki & Atkinson, 1990). There is now a general consensus on the involvement of the excited singlet state S_1 in the cleavage of the C_{spiro}—O bond (Aramaki & Atkinson, 1990; Kelmann *et al.*, 1989; Schneider, Baumann *et al.*, 1987; Schneider, Mindl *et al.* 1987) with the only exception, in the class of spiropyran, for nitro-substituted indoline derivatives, for which the reactive state is T_1 (Sakuragi, Aoki, Tamaki & Ichimura, 1990). It was found that in the class of indoline spiropyrans the C_{spiro}—O bond is longer than the corresponding bond in the six-membered heterocycles (Aldoshin & Atovmyan, 1985). This may indicate an effective n_N-σ^* interaction between the indole nitrogen lone pair and a pyran C—O antibonding orbital in the ground state. The strength of this electronic interaction may be magnified in the excited state, providing the driving force for the photoinduced coloration reaction.

We have undertaken an extensive study of the molecular properties (photochromic activity, fatigue resistance *etc.*) of spirobenzoxazines, with the aim of evidencing structure–performance relationships

(I)   (II)

involving geometric differences in the crystal and/or in the merocyanine forms. The present paper reports the crystal structure of the parent compound of photochromic spirobenzoxazines.

Experimental. The title compound was prepared according to Chu (1983). Crystallization from methanol at room temperature produced a mixture of platelets and regular octahedral crystals, with melting points 399.5 and 416 K, respectively (determined by DSC analysis). Preliminary inspection with Weissenberg photographs indicated that only the latter were suitable for X-ray analysis. A crystal with an edge of *ca* 0.5 mm was used for data collection on a Siemens AED diffractometer; Ni-filtered Cu *Kα* radiation ($\lambda = 1.54178$ Å) was used. Refined unit-cell parameters were obtained from the angular setting of 30 intense reflections ($10 \leq \theta \leq 25°$). The data were collected to $\theta_{max} = 70°$, using a θ–2θ scan, index range h $0 \rightarrow 20$, k $0 \rightarrow -20$, l $0 \rightarrow 15$. The intensity of the (220) reflection, monitored every 50 measurements, varied within ±2%. 3392 unique reflections measured, 1762 with $F > 2\sigma(F)$. The data were corrected for Lp effects but not for absorption.

The structure was solved by direct methods (*SIR*88 program, Burla *et al.*, 1989), and refined by block-matrix least squares (Immirzi, 1973). In the final refinement cycles, the H atoms were included in the structure-factor calculations with $U_{iso} = 0.06$ Å^2 and positions fixed on geometrical grounds. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $1/w = 12 + F_o + 0.019F_o^2$. The final cycles of refinement included atomic coordinates and anisotropic thermal parameters of all non-H atoms (226 parameters). The final R index was 0.053. $wR = 0.059$, $S = 1.41$, $(\Delta/\sigma)_{max} = 0.05$, $\Delta\rho_{min} = -0.22$, $\Delta\rho_{max} = 0.27$ e Å^{-3}. Scattering factors from *International Tables for Crystallography* (1974, Vol. IV). Other computer programs used: *ORTEP* (Johnson, 1965) and *PARST* (Nardelli, 1983).

Discussion. The molecular conformation and atomic labelling scheme are shown in Fig. 1. Atomic coordi-

Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule (60% probability), showing the numbering scheme adopted.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
O(1)	0.8530 (1)	0.0700 (1)	0.0680 (1)	0.0550 (4)
C(2)	0.9007 (1)	0.1322 (1)	0.0434 (2)	0.0426 (6)
C(3)	0.8876 (1)	0.1706 (2)	-0.0554 (2)	0.0497 (6)
C(4)	0.9342 (1)	0.2326 (1)	-0.0853 (2)	0.0499 (7)
C(5)	0.9950 (1)	0.2598 (2)	-0.0178 (2)	0.0442 (6)
C(6)	1.0425 (1)	0.3251 (2)	-0.0465 (2)	0.0550 (7)
C(7)	1.1016 (2)	0.3497 (2)	0.0193 (2)	0.0644 (8)
C(8)	1.1153 (2)	0.3104 (2)	0.1167 (2)	0.0632 (8)
C(9)	1.0706 (2)	0.2474 (2)	0.1474 (2)	0.0509 (6)
C(10)	1.0092 (1)	0.2208 (1)	0.0809 (2)	0.0401 (5)
C(11)	0.9604 (1)	0.1554 (1)	0.1094 (2)	0.0411 (5)
N(12)	0.9778 (1)	0.1123 (1)	0.2046 (2)	0.0505 (5)
C(13)	0.9306 (2)	0.0578 (2)	0.2315 (2)	0.0537 (7)
C(14)	0.8554 (1)	0.0364 (2)	0.1760 (2)	0.0440 (6)
N(15)	0.8490 (1)	-0.0483 (1)	0.1644 (2)	0.0497 (5)
C(16)	0.7687 (1)	-0.0679 (1)	0.1612 (2)	0.0440 (6)
C(17)	0.7349 (2)	-0.1380 (2)	0.1281 (3)	0.0610 (8)
C(18)	0.6553 (2)	-0.1438 (2)	0.1345 (3)	0.0730 (9)
C(19)	0.6109 (2)	-0.0825 (2)	0.1729 (3)	0.0751 (9)
C(20)	0.6452 (2)	-0.0120 (2)	0.2067 (3)	0.0600 (7)
C(21)	0.7258 (1)	-0.0058 (1)	0.2003 (2)	0.0432 (5)
C(22)	0.7799 (1)	0.0590 (1)	0.2375 (2)	0.0461 (6)
C(23)	0.9048 (2)	-0.0915 (2)	0.0999 (3)	0.0771 (10)
C(24)	0.7531 (2)	0.1435 (2)	0.2141 (3)	0.0700 (8)
C(25)	0.7928 (2)	0.0490 (2)	0.3605 (3)	0.0710 (9)

nates for non-H atoms are given in Table 1,* bond distances and angles are reported in Table 2.

The molecule contains a naphthoxazine moiety linked to a substituted indoline fragment through the spiro C(14) atom. The geometry for the atoms involved in the opening of the oxazine ring (Fig. 1) is normal including the spiro C(14) atom, which displays a regular sp^3 hybridization.

The indoline fragment has a compressed envelope conformation with the C(14) atom 0.46 Å above the mean plane. The dihedral angle between planes through C(22), C(14), N(15) and C(17)–C(20) is 29.6°. Phenyl and naphthyl moieties are planar (r.m.d.'s 0.0025 and 0.011 Å respectively) and approximately orthogonal to each other (dihedral angle 81.8°).

The naphthoxazine moiety is bent towards the *gem*-dimethyl groups along the O(1)···C(13) and O(1)···N(12) lines by 16.0 and 3.8° respectively. Such a conformation ensures a significant $n_{N(15)}$–$\sigma^*_{[O(1)—C(14)]}$ orbital interaction in the spiro unit favoring an easy phototransformation to the merocyanine form (II).

Bond lengths and angles of the present molecule are similar to those reported for 1,3,3,5,6-pentamethyl[indoline-2,3'-3H-pyrido[3,2-f][1,4]benzoxazine] (Clegg, Norman, Lasch & Kwak, 1987). The
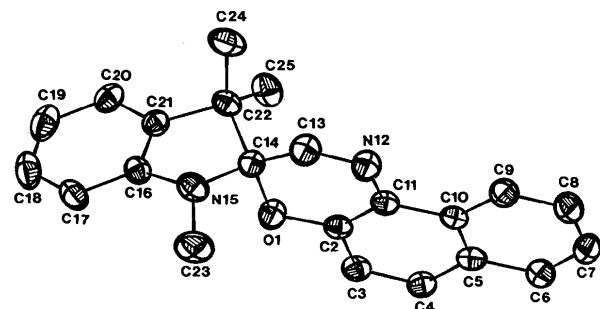

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

O(1)—C(2)	1.362 (3)	O(1)—C(14)	1.454 (3)
C(2)—C(3)	1.403 (3)	C(2)—C(11)	1.366 (3)
C(3)—C(4)	1.365 (3)	C(4)—C(5)	1.411 (3)
C(5)—C(6)	1.412 (3)	C(5)—C(10)	1.410 (3)
C(6)—C(7)	1.363 (4)	C(7)—C(8)	1.397 (4)
C(8)—C(9)	1.362 (4)	C(9)—C(10)	1.410 (3)
C(10)—C(11)	1.425 (3)	C(11)—N(12)	1.416 (3)
N(12)—C(13)	1.267 (3)	C(13)—C(14)	1.504 (4)
C(14)—N(15)	1.436 (3)	C(14)—C(22)	1.548 (3)
N(15)—C(16)	1.414 (3)	N(15)—C(23)	1.442 (4)
C(16)—C(17)	1.375 (3)	C(16)—C(21)	1.366 (3)
C(17)—C(18)	1.369 (4)	C(18)—C(19)	1.366 (4)
C(19)—C(20)	1.388 (4)	C(20)—C(21)	1.387 (3)
C(21)—C(22)	1.503 (3)	C(22)—C(24)	1.521 (3)
C(22)—C(25)	1.551 (3)		

C(2)—O(1)—C(14)	119.2 (2)	O(1)—C(2)—C(11)	122.2 (2)
O(1)—C(2)—C(3)	117.0 (2)	C(3)—C(2)—C(11)	120.8 (2)
C(2)—C(3)—C(4)	119.7 (2)	C(3)—C(4)—C(5)	121.1 (2)
C(4)—C(5)—C(10)	119.4 (2)	C(4)—C(5)—C(6)	121.8 (2)
C(6)—C(5)—C(10)	118.8 (2)	C(5)—C(6)—C(7)	120.8 (2)
C(6)—C(7)—C(8)	119.9 (3)	C(7)—C(8)—C(9)	121.1 (2)
C(8)—C(9)—C(10)	120.1 (2)	C(5)—C(10)—C(9)	119.2 (2)
C(9)—C(10)—C(11)	122.4 (2)	C(5)—C(10)—C(11)	118.3 (2)
C(2)—C(11)—C(10)	120.6 (2)	C(10)—C(11)—N(12)	118.6 (2)
C(2)—C(11)—N(12)	120.7 (2)	C(11)—N(12)—C(13)	117.4 (2)
N(12)—C(13)—C(14)	126.7 (2)	O(1)—C(14)—C(13)	110.6 (2)
C(13)—C(14)—C(22)	115.5 (2)	C(13)—C(14)—N(15)	110.4 (2)
O(1)—C(14)—C(22)	109.6 (2)	O(1)—C(14)—N(15)	106.9 (2)
N(15)—C(14)—C(22)	103.3 (2)	C(14)—N(15)—C(23)	120.3 (2)
C(14)—N(15)—C(16)	108.0 (2)	C(16)—N(15)—C(23)	120.7 (2)
N(15)—C(16)—C(21)	109.5 (2)	N(15)—C(16)—C(17)	128.2 (2)
C(17)—C(16)—C(21)	122.3 (2)	C(16)—C(17)—C(18)	117.6 (2)
C(17)—C(18)—C(19)	121.3 (3)	C(18)—C(19)—C(20)	121.0 (3)
C(19)—C(20)—C(21)	117.9 (2)	C(16)—C(21)—C(20)	119.9 (2)
C(20)—C(21)—C(22)	130.5 (2)	C(16)—C(21)—C(22)	109.4 (2)
C(14)—C(22)—C(21)	100.7 (2)	C(21)—C(22)—C(25)	108.1 (2)
C(21)—C(22)—C(24)	115.7 (2)	C(14)—C(22)—C(25)	109.9 (2)
C(14)—C(22)—C(24)	112.8 (2)	C(24)—C(22)—C(25)	109.4 (2)

replacement of C(6) by an N atom does not alter the geometry of the spiro system; the slower ring-closure kinetics observed for the merocyanine form of the pyridobenzoxazine (Malatesta, 1991) presumably arises from a change in electronic structure.

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Structure of β-Ammoniumpropionitrile Hemifumarate

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Abstract. 2-Cyanoethylammonium hemifumarate, $C_3H_7N_2^+.\frac{1}{2}C_4H_2O_4^{2-}$, $M_r = 128.12$, monoclinic, $P2_1/n$, $a = 5.163$ (2), $b = 23.472$ (13), $c = 5.458$ (3) Å, $\beta = 97.08$ (4)°, $V = 656.4$ Å^3, $Z = 4$, $D_x = 1.296$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1.54179$ Å, $\mu = 8.19$ cm^{-1}, $F(000) = 272$, $T = 293$ K, $R = 0.0534$ for 860 independent data. The crystal structure shows layers of β-ammoniumpropionitrile held together by antiparallel stacking of the nitrile groups, alternating with layers of fumarate dianions whose carboxyl groups form

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