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Structure of Photochromic Spiroxazines. II. 1',3',3'-Trimethylspiro{anthra[2,1-f][1,4]- benzoxazine-2,2'-indoline}-7,12-dione

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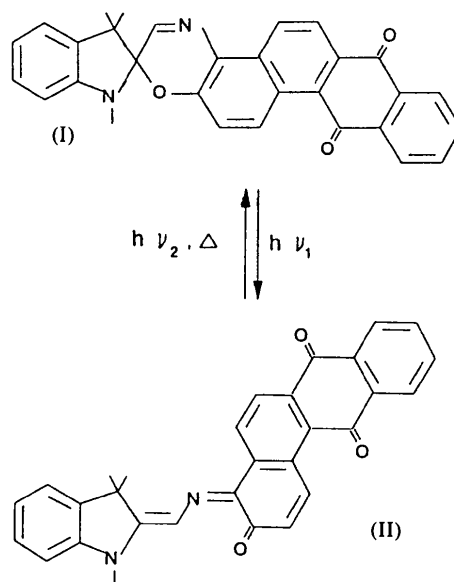
Abstract

The asymmetric unit comprises two crystallographically independent molecules. The molecule consists of a substituted indoline ring orthogonally linked to an anthraquinone–benzo–oxazine moiety through a spiro C atom having regular sp^3 hybridization. The length of the $C_{\text{spiro}}\text{—O}$ bond, that undergoes cleavage upon photoexcitation, is larger than that normally observed for other spiroxazines having lower photocolourability than the title compound.

Comment

The title compound (I), as for all other spiroindolinaphthoxazines, exhibits photochromism. Upon UV irradiation it undergoes a ring-opening reaction leading to a red-absorbing merocyanine-like struc-

ture (II). The reaction is reversible, (I) being restored by either thermal or photochemical bleaching.



The electrocyclic ring-opening reaction of spirobenzopyrans or spironaphthoxazines, leading to coloured merocyanines, has been extensively studied with a host of different spectroscopic techniques. There is now a general consensus on the reactive excited-state multiplicity, which has been identified as a singlet, that leads to the ring opening, and it is likely that the photocolouration is based on a charge-transfer process from the indoline N-atom lone pair, n_N , into the antibonding orbital of the $C_{\text{spiro}}\text{—O}$ bond, $\sigma^*_{C_{\text{spiro}}\text{—O}}$, of the oxazine moiety. This process should be maximized when the n_N is antiperiplanar to the $C_{\text{spiro}}\text{—O}$ bond. The length of the latter bond should increase with the extent of the $n_N\text{—}\sigma^*$ interaction and the $\text{N—}C_{\text{spiro}}$ bond length should concomitantly decrease. The efficiency of the photocolouration reaction may then correlate, among other things, to $C_{\text{spiro}}\text{—O}$ bond distance. To verify this hypothesis we have carried out the X-ray structure analysis of the anthraquinone-based spiroxazine (I).

Two crystallographically independent molecules exist in the asymmetric unit. The significant difference between them may reflect the extent to which the conformation of (I) is affected by crystal packing, but we found no significant differences for the bond involved in the ring-opening reaction.

On the other hand, the $C_{\text{spiro}}\text{—O}$ bond is much longer (1.473–1.475 Å) than those typically observed in oxygen-containing six-membered heterocycles [1.41–1.43 Å (Kennard, Watson & Town, 1973)]. These bonds are also longer than those observed in spiroindolinaphthoxazines [1.454 Å (Millini, Del

Piero, Allegrini, Crisci & Malatesta, 1991), 1.458–1.463 Å (Osano, Mitsuhashi, Maeda & Matsuzaki, 1991)] and their analogues [1.464–1.474 Å (Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991)]. This fact could, in principle, be indicative of a more polarized C_{spiro}—O bond in the ground state that results ultimately in better photochromic activity (Castaldi, Allegrini, Crisci & Renzi, 1989).

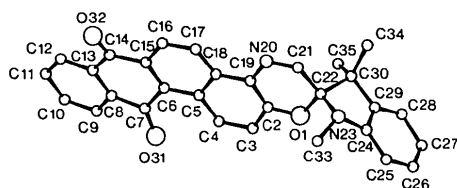


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) view of molecule *A*, showing the numbering scheme adopted.

Experimental

Crystal data

C₃₀H₂₂N₂O₃

M_r = 458.52

Monoclinic

*P*2₁/*c*

a = 21.778 (3) Å

b = 16.707 (2) Å

c = 12.367 (2) Å

β = 97.89 (3)°

V = 4457.1 (11) Å³

Z = 8

D_x = 1.367 Mg m⁻³

Cu *K*α radiation

λ = 1.54178 Å

Cell parameters from 30 reflections

θ = 15–25°

μ = 0.673 mm⁻¹

T = 298 K

Irregular

0.8 × 0.6 × 0.5 mm

Red

Crystal source: synthesis according to Castaldi, Allegrini, Crisci & Renzi (1989); crystallized from MeOH

Data collection

Siemens AED diffractometer

θ/2θ scans

Absorption correction:

none

6614 measured reflections

6248 independent reflections

2381 observed reflections

[*F* > 4σ(*F*)]

R_{int} = 0.0277

θ_{max} = 60°

h = -24 → 24

k = 0 → 18

l = 0 → 12

1 standard reflection (231)

monitored every 100

reflections

intensity variation: none

Refinement

Refinement on *F*

Final *R* = 0.049

wR = 0.043

S = 1.67

2381 reflections

631 parameters

H-atom parameters not refined

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.06

Δρ_{max} = 0.29 e Å⁻³

Δρ_{min} = -0.18 e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O(1A)	0.4315 (1)	0.1374 (1)	0.1484 (2)	0.0567 (6)
C(2A)	0.4040 (1)	0.1133 (1)	0.2336 (2)	0.0477 (9)
C(3A)	0.4391 (1)	0.0664 (2)	0.3102 (2)	0.0498 (8)
C(4A)	0.4163 (1)	0.0387 (1)	0.3990 (2)	0.0483 (9)
C(5A)	0.3564 (1)	0.0618 (2)	0.4210 (2)	0.0430 (8)
C(6A)	0.3298 (1)	0.0371 (1)	0.5155 (2)	0.0421 (8)
C(7A)	0.3649 (1)	-0.0142 (2)	0.6013 (2)	0.0460 (9)
C(8A)	0.3310 (1)	-0.0512 (1)	0.6841 (2)	0.0429 (8)
C(9A)	0.3588 (1)	-0.1107 (2)	0.7528 (2)	0.0497 (9)
C(10A)	0.3288 (1)	-0.1453 (2)	0.8310 (2)	0.0613 (11)
C(11A)	0.2713 (1)	-0.1168 (2)	0.8472 (2)	0.0598 (10)
C(12A)	0.2428 (1)	-0.0566 (2)	0.7801 (2)	0.0552 (9)
C(13A)	0.2721 (1)	-0.0228 (1)	0.6994 (2)	0.0420 (9)
C(14A)	0.2431 (1)	0.0396 (1)	0.6288 (2)	0.0492 (9)
C(15A)	0.2714 (1)	0.0644 (1)	0.5319 (2)	0.0397 (8)
C(16A)	0.2382 (1)	0.1150 (2)	0.4545 (2)	0.0484 (9)
C(17A)	0.2620 (1)	0.1372 (1)	0.3634 (2)	0.0454 (8)
C(18A)	0.3205 (1)	0.1115 (1)	0.3423 (2)	0.0456 (9)
C(19A)	0.3458 (1)	0.1366 (1)	0.2490 (2)	0.0426 (8)
N(20A)	0.3105 (1)	0.1870 (1)	0.1730 (2)	0.0487 (7)
C(21A)	0.3356 (1)	0.2095 (1)	0.0899 (2)	0.0508 (9)
C(22A)	0.3956 (1)	0.1816 (2)	0.0577 (2)	0.0500 (10)
N(23A)	0.4336 (1)	0.2477 (1)	0.0329 (2)	0.0479 (7)
C(24A)	0.4765 (1)	0.2152 (1)	-0.0296 (2)	0.0405 (8)
C(25A)	0.5332 (1)	0.2468 (2)	-0.0487 (2)	0.0553 (9)
C(26A)	0.5684 (1)	0.2011 (2)	-0.1115 (2)	0.0634 (11)
C(27A)	0.5482 (1)	0.1296 (2)	-0.1551 (2)	0.0502 (9)
C(28A)	0.4904 (1)	0.0998 (1)	-0.1390 (2)	0.0458 (9)
C(29A)	0.4561 (1)	0.1435 (1)	-0.0757 (2)	0.0386 (9)
C(30A)	0.3931 (1)	0.1267 (1)	-0.0454 (2)	0.0424 (9)
O(31A)	0.4197 (1)	-0.0267 (1)	0.6067 (2)	0.0381 (8)
O(32A)	0.1944 (1)	0.0712 (1)	0.6460 (2)	0.0373 (7)
C(33A)	0.4540 (1)	0.3058 (2)	0.1174 (3)	0.0697 (11)
C(34A)	0.3435 (1)	0.1576 (2)	-0.1349 (2)	0.0533 (10)
C(35A)	0.3792 (1)	0.0416 (2)	-0.0204 (2)	0.0602 (9)
O(1B)	0.0029 (1)	-0.1242 (1)	0.8021 (1)	0.0400 (6)
C(2B)	0.0426 (1)	-0.1249 (2)	0.7265 (2)	0.0492 (9)
C(3B)	0.0358 (1)	-0.0611 (1)	0.6528 (2)	0.0427 (10)
C(4B)	0.0741 (1)	-0.0562 (1)	0.5753 (2)	0.0401 (8)
C(5B)	0.1218 (1)	-0.1130 (1)	0.5688 (2)	0.0399 (8)
C(6B)	0.1642 (1)	-0.1117 (1)	0.4877 (2)	0.0368 (7)
C(7B)	0.1531 (1)	-0.0611 (2)	0.3891 (2)	0.0516 (8)
C(8B)	0.1979 (1)	-0.0630 (1)	0.3087 (2)	0.0398 (9)
C(9B)	0.1871 (1)	-0.0195 (2)	0.2131 (2)	0.0501 (9)
C(10B)	0.2284 (1)	-0.0224 (2)	0.1381 (2)	0.0575 (9)
C(11B)	0.2820 (1)	-0.0675 (2)	0.1605 (2)	0.0385 (9)
C(12B)	0.2945 (1)	-0.1102 (1)	0.2561 (2)	0.0452 (9)
C(13B)	0.2516 (1)	-0.1069 (1)	0.3296 (2)	0.0407 (9)
C(14B)	0.2638 (1)	-0.1557 (1)	0.4305 (2)	0.0423 (9)
C(15B)	0.2153 (1)	-0.1614 (1)	0.5013 (2)	0.0374 (8)
C(16B)	0.2219 (1)	-0.2204 (1)	0.5835 (2)	0.0419 (9)
C(17B)	0.1786 (1)	-0.2291 (1)	0.6502 (2)	0.0476 (10)
C(18B)	0.1290 (1)	-0.1749 (1)	0.6471 (2)	0.0374 (8)
C(19B)	0.0875 (1)	-0.1814 (2)	0.7252 (2)	0.0451 (9)
N(20B)	0.0928 (1)	-0.2466 (1)	0.7966 (2)	0.0396 (8)
C(21B)	0.0536 (1)	-0.2496 (2)	0.8633 (2)	0.0571 (11)
C(22B)	0.0049 (1)	-0.1912 (1)	0.8806 (2)	0.0633 (9)
N(23B)	0.0174 (1)	-0.1573 (1)	0.9878 (2)	0.0547 (8)
C(24B)	-0.0380 (1)	-0.1371 (2)	1.0262 (2)	0.0485 (10)
C(25B)	-0.0469 (1)	-0.0909 (2)	1.1131 (2)	0.0571 (11)
C(26B)	-0.1052 (1)	-0.0835 (2)	1.1348 (3)	0.0452 (12)
C(27B)	-0.1547 (1)	-0.1167 (2)	1.0765 (3)	0.0255 (11)
C(28B)	-0.1471 (1)	-0.1646 (2)	0.9846 (2)	0.0464 (10)
C(29B)	-0.0863 (1)	-0.1741 (1)	0.9598 (2)	0.0577 (8)
C(30B)	-0.0612 (1)	-0.2250 (1)	0.8744 (2)	0.0464 (10)
O(31B)	0.1060 (1)	-0.0226 (1)	0.3650 (2)	0.0707 (8)
O(32B)	0.3148 (1)	-0.1871 (1)	0.4574 (2)	0.0496 (6)
C(33B)	0.0745 (1)	-0.1151 (2)	1.0245 (3)	0.0743 (11)
C(34B)	-0.0989 (1)	-0.2189 (2)	0.7625 (2)	0.0730 (12)
C(35B)	-0.0596 (1)	-0.3120 (2)	0.9139 (3)	0.0666 (10)

Table 2. Geometric parameters (Å, °)

O(1A)—C(2A)	1.343 (4)	O(1B)—C(2B)	1.358 (3)
O(1A)—C(22A)	1.474 (3)	O(1B)—C(22B)	1.478 (3)
C(2A)—C(3A)	1.377 (3)	C(2B)—C(3B)	1.397 (4)
C(2A)—C(19A)	1.364 (3)	C(2B)—C(19B)	1.361 (4)
C(3A)—C(4A)	1.348 (4)	C(3B)—C(4B)	1.357 (3)
C(4A)—C(5A)	1.422 (3)	C(4B)—C(5B)	1.417 (3)
C(5A)—C(6A)	1.434 (4)	C(5B)—C(6B)	1.454 (3)
C(5A)—C(18A)	1.428 (3)	C(5B)—C(18B)	1.411 (3)
C(6A)—C(7A)	1.491 (3)	C(6B)—C(7B)	1.476 (4)
C(6A)—C(15A)	1.392 (3)	C(6B)—C(15B)	1.380 (3)
C(7A)—C(8A)	1.478 (4)	C(7B)—C(8B)	1.486 (3)
C(7A)—O(31A)	1.204 (3)	C(7B)—O(31B)	1.212 (3)
C(8A)—C(9A)	1.391 (4)	C(8B)—C(9B)	1.380 (3)
C(8A)—C(13A)	1.405 (3)	C(8B)—C(13B)	1.375 (3)
C(9A)—C(10A)	1.367 (4)	C(9B)—C(10B)	1.379 (3)
C(10A)—C(11A)	1.380 (3)	C(10B)—C(11B)	1.385 (4)
C(11A)—C(12A)	1.394 (4)	C(11B)—C(12B)	1.376 (4)
C(12A)—C(13A)	1.377 (4)	C(12B)—C(13B)	1.391 (3)
C(13A)—C(14A)	1.448 (3)	C(13B)—C(14B)	1.484 (3)
C(14A)—C(15A)	1.480 (3)	C(14B)—C(15B)	1.465 (4)
C(14A)—O(32A)	1.229 (3)	C(14B)—O(32B)	1.232 (3)
C(15A)—C(16A)	1.401 (3)	C(15B)—C(16B)	1.409 (3)
C(16A)—C(17A)	1.355 (4)	C(16B)—C(17B)	1.343 (4)
C(17A)—C(18A)	1.402 (3)	C(17B)—C(18B)	1.406 (3)
C(18A)—C(19A)	1.409 (3)	C(18B)—C(19B)	1.415 (4)
C(19A)—N(20A)	1.409 (3)	C(19B)—N(20B)	1.397 (4)
N(20A)—C(21A)	1.285 (3)	N(20B)—C(21B)	1.267 (4)
C(21A)—C(22A)	1.492 (3)	C(21B)—C(22B)	1.478 (4)
C(22A)—N(23A)	1.438 (4)	C(22B)—N(23B)	1.433 (3)
C(22A)—C(30A)	1.565 (4)	C(22B)—C(30B)	1.538 (3)
N(23A)—C(24A)	1.401 (3)	N(23B)—C(24B)	1.397 (3)
N(23A)—C(33A)	1.451 (4)	N(23B)—C(33B)	1.447 (3)
C(24A)—C(25A)	1.393 (4)	C(24B)—C(25B)	1.358 (4)
C(24A)—C(29A)	1.374 (3)	C(24B)—C(29B)	1.388 (3)
C(25A)—C(26A)	1.392 (4)	C(25B)—C(26B)	1.339 (3)
C(26A)—C(27A)	1.358 (4)	C(26B)—C(27B)	1.333 (4)
C(27A)—C(28A)	1.393 (3)	C(27B)—C(28B)	1.418 (5)
C(28A)—C(29A)	1.365 (3)	C(28B)—C(29B)	1.408 (3)
C(29A)—C(30A)	1.498 (3)	C(29B)—C(30B)	1.515 (3)
C(30A)—C(34A)	1.526 (3)	C(30B)—C(34B)	1.512 (3)
C(30A)—C(35A)	1.495 (4)	C(30B)—C(35B)	1.532 (4)
O(1A)—C(22A)—C(21A)	110.2 (2)	O(1B)—C(22B)—C(21B)	111.2 (2)
C(21A)—C(22A)—C(30A)	117.8 (2)	C(21B)—C(22B)—C(30B)	115.8 (2)
C(21A)—C(22A)—N(23A)	111.6 (2)	C(21B)—C(22B)—N(23B)	110.2 (2)
O(1A)—C(22A)—C(30A)	106.4 (2)	O(1B)—C(22B)—C(30B)	107.6 (2)
O(1A)—C(22A)—N(23A)	106.6 (2)	O(1B)—C(22B)—N(23B)	107.0 (2)
N(23A)—C(22A)—C(30A)	103.5 (2)	N(23B)—C(22B)—C(30B)	104.4 (2)

The structure was solved by direct methods (SIR88; Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and refined by block-matrix least squares (Immirzi, 1973). Other programs used: PLUTO (Motherwell & Clegg, 1978) and PARST (Nardelli, 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55948 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1026]

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β -Homopipitzolone

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Abstract

The structure of β -homopipitzolone (one of the two isomers of an intermediate product in the homocycle synthesis) has been unequivocally established as 10-hydroxy-2,6,9-trimethyltricyclo[6.3.1.0^{1,6}]dodeca-9-ene-5,11,12-trione with relative 1R,2R,6R,8S configuration.

Comment

The thermal (Walls, Padilla, Joseph-Nathan, Giral & Romo, 1965; Joseph-Nathan, Mendoza & Garcia, 1977) and catalytic (Sanchez, Yanez, Enriquez & Joseph-Nathan, 1981) transformations of perezone produce a mixture of α - and β -pipitzols. In continuation of our investigations in this field, we have prepared the new α - and β -homopipitzolone mixture from modified perezone (Mendoza, Garcia, Reyes &