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Photochromic 8-Ethoxy-2-methylspiro(*syn*-5,6-benzo-2-azabicyclo[2.2.2]oct-5-ene-3,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine)

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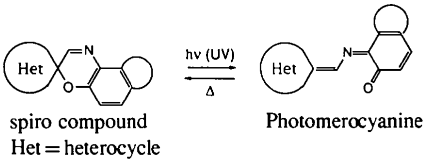
Abstract

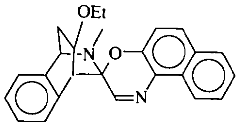
In the photochromic title compound, $C_{25}H_{24}N_2O_2$, the C_{spiro}—O bond can be broken on photoexcitation. Conformational parameters and oxazine-ring puckering have been investigated by considering similar photochromic compounds. It is shown that when the C_{spiro}—O bond is elongated, and therefore weakened, the ring-puckering coefficient is smaller and photochromic activity increases.

Comment

Spirooxazines are colourless photochromic compounds (Chu, 1990), which transform under UV irradiation into strongly coloured photomerocyanines. The reaction is reversible either by heat or by visible-light absorption.



The rate of decolouration depends on the electronic properties or steric hindrances of either the heterocyclic part or the annulation of the benzoxazinic ring (Tardieu, Dubest, Aubard, Kellmann, Tfibel, Samat & Guglielmetti, 1992; Rickwood, Marsden, Ormsby, Staunton, Wood, Hepworth & Gabbutt, 1994). Structural features, such as the C_{spiro}—O bond distance, the distances of oxazine N and O atoms from the adjacent phenyl ring mean plane, intramolecular short contacts, and oxazine ring planarity, which are related to the difference in photochromic behaviour are discussed here. In order to obtain a better insight into the correlation between molecular substitution, conformation and photochemical reactivity, the molecular structure of the title compound, (1), has been established and compared with the conformation of some other spirooxazinic compounds. The molecular conformation and atomic labelling are shown in Fig. 1.



(1)

The title molecule contains a naphthoxazine moiety linked to a substituted benzo-2-azabicyclo[2.2.2] fragment through the spiro atom, C12, which displays regular sp^3 hybridization. The bond angles at the C12 spiro carbon have a mean value of 109.4 (8)°. Table 3 shows that the O14—C12—C13 bond angle of the spiro C atom in the oxazine ring has a mean value of 109.1 (12)° for seven spirooxazines. The conformation of the oxazine ring of the title compoud is described as a twisted boat along the C13···C25 axis.

The phenyl and naphthyl moieties are planar (r.m.s. deviations of 0.002 and 0.006 Å, respectively) and are approximately orthogonal to each other [dihedral angle 87.1 (7)°]. The benzo-2-azabicyclo[2.2.2] fragment with its cage-like structure has a small degree of freedom. It displays D_3 symmetry with a mean torsion angle of 4.2 (3)°, probably as a result of the bulky naphthoxazine moiety linking through the spiro C12 atom.

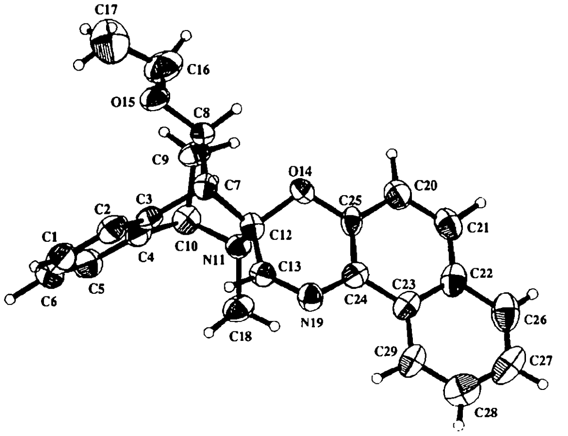


Fig. 1. Molecular view of the title compound drawn using *ORTEP* (Johnson, 1965) with displacement ellipsoids at 50% probability. H atoms are represented as spheres of arbitrary radii.

Atoms N19 and O14 are located 0.148 (6) and −0.016 (4) Å, respectively, from the mean plane of the adjacent phenyl ring (atoms C20–C25). Thus, the O atom is in the mean plane but the N atom is not. This is observed for five similar molecules, as shown in Table 3, and can be correlated to the O—C_{sp^2}—C_{sp^2}—N torsion angle [mean value 5 (4)°].

At first sight, the planarity of the oxazine may be related to photochromic properties. Planarity can be evaluated with the χ^2 Pearson test (a flat fragment has a small χ^2 value). For the first three oxazinic compounds described in Table 3, it has been shown experimentally (Tardieu *et al.*, 1992; Laréginie, Samat & Guglielmetti, 1993) that photochromic activity decreases from (1) to (3) [(3*A*) and (3*B*) are crystallographically independent molecules]. This is in agreement with the increase in χ^2: the more planar the oxazinic ring, the less the molecule is photocolourable. Clegg *et al.* (Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991) state that the non-methyl-substituted compound, (4), exhibits photochromic properties and that the methylated derivatives, molecules (5*A*) and (5*B*), do not. An additional methyl group on the oxazine ring sterically hinders the formation of the merocyanine form and therefore decreases photochromic activity. One can observe that the methyl-substituted molecules, (5*A*) and (5*B*), have indeed increased χ^2 values.

These observations have to be compared and, perhaps, related to previous work by Aldoshin (1994), who correlated the cleavage of the C—O bond with specific *n*–σ^* orbital interactions involving indolinic N and O on the one hand, and the unoccupied σ^* orbitals of the C—O bond on the other.

The C_{spiro}—O mean bond distance [1.468 (5) Å; Table 3] is longer than the normal value (1.41–1.43 Å) and seems to be a common structural feature of photochromic spirooxazines. The long C_{spiro}—O distance explains the easy cleavage of this bond. The calculated C_{spiro}—C_{sp^2} mean distance [1.512 (13) Å] retains its normal value (C_{sp^3}—C_{sp^2} = 1.52 Å) and the C_{sp^2} atom conserves its hybridization in the spiro and merocyanine forms.

Experimental

The synthesis of the title compound will be described elswhere (Laréginie, Samat & Guglielmetti, 1995). Crystals suitable for X-ray analysis were obtained by recrystallization from methanol solution. The density D_m was measured by flotation.

Crystal data

$C_{25}H_{24}N_2O_2$
M_r = 384.48
Monoclinic
$P2_1/c$
a = 7.957 (5) Å
b = 11.920 (3) Å
c = 21.533 (3) Å
β = 99.72 (1)°
V = 2013.1 (1) Å^3
Z = 4
D_x = 1.268 Mg m^{-3}
D_m = 1.26 (1) Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 2.00–56.00°
μ = 0.650 mm^{-1}
T = 293 K
Parallelepiped
0.42 × 0.12 × 0.08 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
θ scans
Absorption correction: none
4942 measured reflections
4389 independent reflections
1325 observed reflections [$I > 3.0\sigma(I)$]

R_{int} = 0.02
θ_{max} = 56°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.052
wR = 0.052
S = 0.19
1325 reflections
334 parameters
All H-atom parameters refined

Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.3
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.2 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C1	−0.0796 (9)	0.3945 (6)	0.3805 (4)	4.6 (5)
C2	0.0970 (9)	0.3732 (6)	0.3969 (3)	3.6 (4)
C3	0.1509 (8)	0.2982 (5)	0.4442 (3)	2.7 (3)
C4	0.0341 (9)	0.2422 (5)	0.4753 (3)	2.9 (3)
C5	−0.1401 (9)	0.2648 (7)	0.4588 (4)	4.0 (4)
C6	−0.1949 (9)	0.3388 (7)	0.4113 (4)	4.7 (4)
C7	0.3319 (8)	0.2616 (5)	0.4676 (3)	2.7 (3)
C8	0.3420 (8)	0.1322 (6)	0.4585 (3)	3.1 (3)
C9	0.2219 (9)	0.0759 (6)	0.4980 (3)	3.5 (3)
C10	0.1226 (9)	0.1677 (6)	0.5265 (3)	3.2 (3)

N11	0.2446 (6)	0.2338 (4)	0.5709 (2)	2.7 (2)
C12	0.3730 (8)	0.2876 (5)	0.5387 (3)	2.7 (3)
C13	0.3931 (9)	0.4120 (6)	0.5500 (3)	3.0 (3)
O14	0.5387 (5)	0.2345 (3)	0.5607 (2)	3.2 (2)
O15	0.2845 (5)	0.1025 (4)	0.3942 (2)	3.8 (2)
C16	0.4071 (9)	0.1288 (9)	0.3544 (4)	6.0 (5)
C17	0.3286 (9)	0.1188 (9)	0.2889 (5)	7.5 (7)
C18	0.1575 (9)	0.3079 (7)	0.6101 (4)	3.9 (4)
N19	0.4941 (7)	0.4553 (4)	0.5959 (3)	3.2 (2)
C20	0.7338 (9)	0.1981 (6)	0.6549 (4)	3.7 (4)
C21	0.8157 (9)	0.2334 (7)	0.7123 (4)	4.0 (4)
C22	0.7888 (9)	0.3429 (7)	0.7351 (3)	3.6 (4)
C23	0.6765 (9)	0.4166 (6)	0.6972 (3)	3.1 (3)
C24	0.5942 (8)	0.3812 (6)	0.6372 (3)	2.9 (3)
C25	0.6200 (8)	0.2716 (7)	0.6189 (3)	3.0 (4)
C26	0.8687 (9)	0.3814 (9)	0.7958 (4)	5.0 (6)
C27	0.8368 (9)	0.4854 (9)	0.8161 (4)	5.5 (5)
C28	0.7260 (9)	0.5562 (7)	0.7786 (5)	5.1 (4)
C29	0.6475 (9)	0.5247 (7)	0.7199 (4)	3.9 (4)

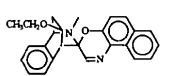
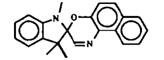
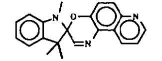
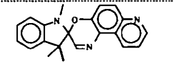
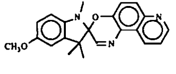
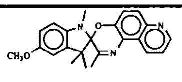
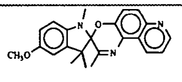
Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.413 (9)	C12—O14	1.467 (7)
C1—C6	1.388 (9)	C13—N19	1.273 (8)
C2—C3	1.369 (9)	O14—C25	1.382 (8)
C3—C4	1.403 (8)	O15—C16	1.438 (9)
C3—C7	1.508 (8)	C16—C17	1.448 (9)
C4—C5	1.398 (9)	N19—C24	1.402 (8)
C4—C10	1.496 (9)	C20—C21	1.363 (9)
C5—C6	1.365 (9)	C20—C25	1.397 (9)
C7—C8	1.559 (9)	C21—C22	1.423 (9)
C7—C12	1.542 (8)	C22—C23	1.411 (9)
C8—C9	1.537 (9)	C22—C26	1.429 (9)
C8—O15	1.428 (7)	C23—C24	1.411 (9)
C9—C10	1.537 (9)	C23—C29	1.411 (9)
C10—N11	1.471 (8)	C24—C25	1.390 (9)
N11—C12	1.475 (7)	C26—C27	1.353 (9)
N11—C18	1.473 (9)	C27—C28	1.379 (9)
C12—C13	1.507 (9)	C28—C29	1.365 (9)

C2—C1—C6	120.3 (7)	N11—C12—C13	114.5 (5)
C1—C2—C3	118.5 (6)	N11—C12—O14	108.5 (4)
C2—C3—C4	121.1 (6)	C13—C12—O14	107.9 (5)
C2—C3—C7	126.8 (6)	C12—C13—N19	124.1 (6)
C4—C3—C7	112.0 (5)	C12—O14—C25	114.3 (4)
C3—C4—C5	119.7 (6)	C8—O15—C16	112.7 (5)
C3—C4—C10	111.5 (5)	O15—C16—C17	109.8 (7)
C5—C4—C10	128.7 (6)	C13—N19—C24	117.0 (5)
C4—C5—C6	119.5 (7)	C21—C20—C25	118.4 (7)
C1—C6—C5	120.9 (7)	C20—C21—C22	121.3 (7)
C3—C7—C8	108.1 (5)	C21—C22—C23	119.3 (6)
C3—C7—C12	107.7 (5)	C21—C22—C26	122.7 (7)
C8—C7—C12	108.5 (5)	C23—C22—C26	118.0 (6)
C7—C8—C9	108.2 (5)	C22—C23—C24	119.6 (6)
C7—C8—O15	110.6 (5)	C22—C23—C29	119.5 (6)
C9—C8—O15	107.5 (5)	C24—C23—C29	120.8 (6)
C8—C9—C10	108.6 (5)	N19—C24—C23	121.2 (6)
C4—C10—C9	109.8 (5)	N19—C24—C25	120.5 (6)
C4—C10—N11	109.8 (5)	C23—C24—C25	118.2 (6)
C9—C10—N11	108.3 (5)	O14—C25—C20	117.6 (6)
C10—N11—C12	111.2 (4)	O14—C25—C24	119.3 (6)
C10—N11—C18	111.8 (5)	C20—C25—C24	123.0 (6)
C12—N11—C18	116.0 (5)	C22—C26—C27	120.7 (8)
C7—C12—N11	109.4 (5)	C26—C27—C28	120.5 (8)
C7—C12—C13	110.9 (5)	C27—C28—C29	121.4 (8)
C7—C12—O14	105.2 (4)	C23—C29—C28	119.7 (7)

C1—C2—C3—C4	0.9 (4)	C7—C8—O15—C16	75.1 (5)
C1—C2—C3—C7	178.3 (6)	C7—C12—C13—N19	−147.5 (6)
C2—C3—C4—C5	−1.4 (4)	C7—C12—O14—C25	163.9 (5)
C2—C3—C4—C10	−178.1 (6)	C8—O15—C16—C17	−168.1 (7)
C2—C3—C7—C8	−120.2 (5)	C12—C13—N19—C24	1.4 (3)
C2—C3—C7—C12	122.8 (5)	O14—C25—C20—C21	179.7 (7)
C3—C2—C1—C6	−1.0 (4)	C20—C21—C22—C23	−0.7 (4)
C3—C4—C10—N11	56.3 (4)	C20—C21—C22—C26	178.1 (7)
C3—C7—C8—C9	−61.3 (4)	C21—C22—C23—C29	179.1 (7)
C3—C7—C8—O15	56.3 (4)	C21—C22—C26—C27	−178.6 (8)
C3—C7—C12—C13	−72.3 (4)	C22—C21—C20—C25	−0.9 (4)
C3—C7—C12—O14	171.3 (5)	C22—C26—C27—C28	0.2 (5)
C4—C10—N11—C18	72.2 (5)		

Table 3. *Seven crystallographic spirooxazine structures*

Code	Molecule	IUPAC Molecule Name	C_{spiro}-O (Å)	C_{spiro}-C_{sp^2} (Å)	O-C_{spiro}-C angle in oxazine ring (°)	C-O-C angle in oxazine ring (°)	Torsional angle (O-C-C-N) in oxazine ring (°)	χ^2 Pearson test	Distance of O from phenyl mean plane (Å)	Distance of N from phenyl mean plane (Å)	Ref.
(1)		See *Title*	**1.467**	**1.507**	**107.9**	**114.3**	**3.3**	**6241**	**0.016**	**0.148**	**(a)**
(2)		1,3,3-trimethylspiro [indoline-2,3'-[3H] naphth[2,1-b] [1,4]-oxazine]	**1.465**	**1.504**	**110.7**	**119.2**	**3.4**	**7761**	**0.001**	**0.117**	**(b)**
(3*A*)		1,3,3-trimethylspiro [indoline-2,3'-[3H] pyrido[5,4-f] [1,4]-benoxazine]	**1.464**	**1.498**	**109.7**	**117.6**	**2.8**	**14417**	**0.005**	**0.088**	**(c)**
(3*B*)		1,3,3-trimethylspiro [indoline-2,3'-[3H] pyrido[5,4-f] [1,4]-benoxazine]	**1.465**	**1.499**	**109.2**	**116.7**	**2.9**	**19059**	**0.042**	**0.092**	**(c)**
(4)		5 - methoxy - 1,3,3 - trimethylspiro [indoline-2,3'-[3H] pyrido [5,4-f] [1,4] benzoaxine]	**1.467**	**1.517**	**110.4**	**120.6**	**1.3**	**500**	**0.021**	**0.095**	**(c)**
(5*A*)		5-methoxy-1,2',3,3-tetramethylspiro [indoline-2,3'-[3H] pyrido [5,4-f] [1,4] benzoaxine]	**1.475**	**1.534**	**108.3**	**116.6**	**8.6**	**20484**	**0.048**	**0.220**	**(c)**
(5*B*)		5-methoxy-1,2',3,3-tetramethylspiro [indoline-2,3'-[3H] pyrido [5,4-f] [1,4] benzoaxine]	**1.474**	**1.524**	**107.8**	**116.9**	**11.2**	**21202**	**0.072**	**0.263**	**(c)**

References: (*a*) present work; (*b*) Millini, Del Piero, Allegrini, Crisci & Malatesta (1991); (*c*) Clegg *et al.* (1991).

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: local program. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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8-Methylspiro(*syn*-10,11-benzo-8-azatricyclo[5.2.2.0^{1,5}]undec-10-ene)-9,3′-[3*H*]naphth[1,2-*b*][1,4]oxazine

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Abstract

The title compound, $C_{26}H_{24}N_2O$, is of interest in the study of the effects of steric hindrance on photochromic properties.

Comment

In the field of organic photochromic compounds, spiro[indoline–naphthoxazines], (1) (Chu, 1990), have been studied extensively for several years because of their good photochromic properties (Tardieu *et al.*, 1992; Rickwood *et al.*, 1994). In order to study the effect of the heterocyclic part, *H*, on the photochromic characteristics, we recently synthesized (Laréginie, Samat & Guglielmetti, 1995) and studied the three-dimensional structure (Reboul *et al.*, 1995) of a spiro[azabicyclonaphthoxazine], (2). To extend this preliminary work and to develop the correlation between the