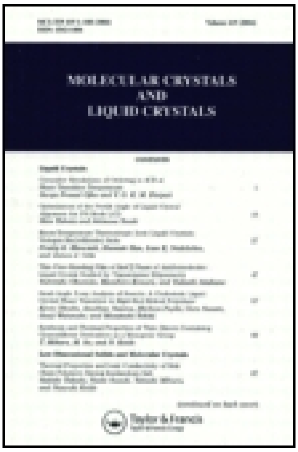

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New Photochromic 10′-Substituted Spiro[Indoline-Naphthoxazines]

Karine Chamontin [a], Vladimir Lokshn [a], Gilles Garros [a], Andre Samat [a], Robert Guglielmetti [a] & Roger Dubest [b]

[a] Laboratoire de Chimie et Matériaux Organiques, Modélisation-ERS CNRS 158. Faculté des Sciences de Luminy, Case 901, 13288, Marseille cedex, 9, FRANCE

[b] ITODYS, URA CNRS 34, Université de Paris VII, 75005, PARIS, FRANCE

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NEW PHOTOCHROMIC 10'-SUBSTITUTED SPIRO[INDOLINE-NAPHTHOXAZINES]

KARINE CHAMONTIN, VLADIMIR LOKSHIN, GILLES GARROS,
ANDRE SAMAT, ROBERT GUGLIELMETTI,
Laboratoire de Chimie et Matériaux Organiques, Modélisation-ERS CNRS 158 . Faculté des Sciences de Luminy, Case 901, 13288 Marseille cedex 9 -FRANCE

ROGER DUBEST
ITODYS, URA CNRS 34, Université de Paris VII, 75005 PARIS-FRANCE

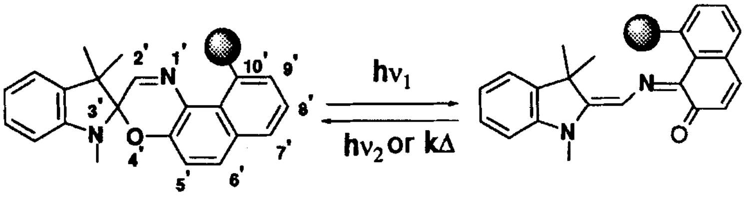
Abstract New photochromic 10'-substituted spiro[indoline-naphthoxazines] were synthesized and spectrokinetic parameters determined. Introduction of a substituent on the 10'-position have no significant influence on maximum wavelength absorption but the fading rate constant is highly increased. According to semi-empirical calculation, this behavior could be due to steric hindrance occuring, on the open form, between the methyl group linked on the indolinic nitrogen and the 10'-substituent.

INTRODUCTION

Spirooxazines, an important class of photochromic compounds, have been intensively studied during this last decade due to their high photostability[1] for optical devices.

In order to modify the spectrokinetic parameters a lot of structural variations on spirooxazine skeleton have been realized providing many patents and publications.[2-4] Nevertheless no examples dealing with spirooxazines substituted on the 10'-position (Scheme 1) have been described, although this position could influence photochromic equilibrium by steric hindrance.

Scheme 1



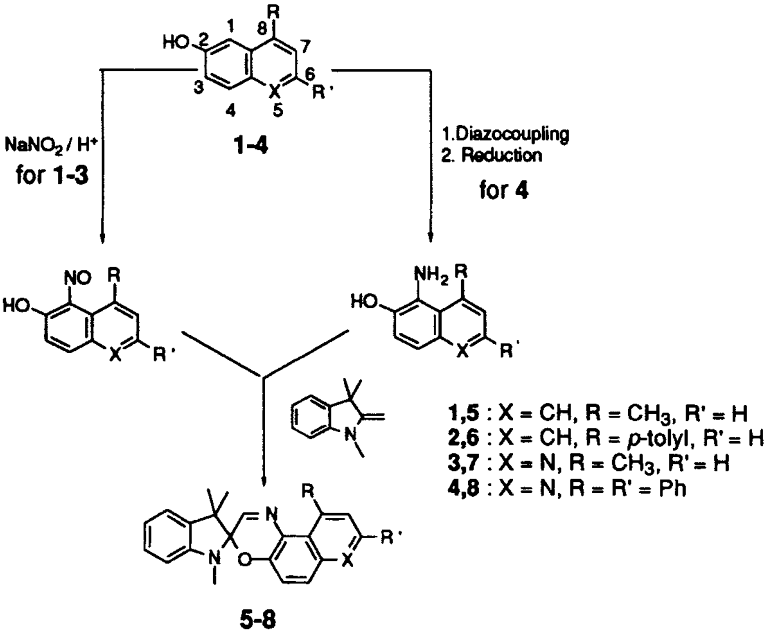
Our aim was to synthesize some spirooxazines substituted by alkyl or aryl group in 10'-position and to study their photochromic properties.

SYNTHESIS

To reach our goal, it was necessary to synthesize different β-naphthols substituted in 8-position and to prepare the corresponding α–nitroso or amino derivatives .

Some 8-substituted-2-naphthols are described in literature. 8-Methyl-2-naphthol **1** was synthesized[5] in three steps using 7-methoxy-1-tetralone as precursor, 8-p-tolyl-2-naphthol **2** was obtained by the same synthetic way. Ethers cleavage of 4-methyl-6-methoxyquinoline[6] and 2,4-diphenyl-6-methoxyquinoline[7] yielded the corresponding quinolinol **3** and **4**. Condensation of Fischer's base with nitroso derivatives of **1**, **2**, **3** and amino derivative of **4** gave the corresponding spiro[indoline-naphthoxazines] **5**, **6** and spiro[indoline-pyridobenzoxazines] **7**, **8** (Scheme 2). Compounds were purified by column chromatography, recristallization and characterized by ^1H, ^{13}C NMR and microanalysis.

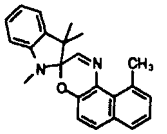
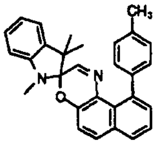
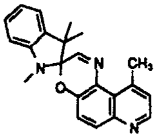
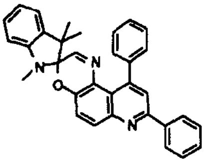
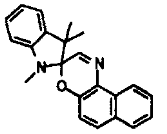
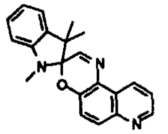
Scheme 2



SPECTROKINETIC RESULTS

All compounds exhibit photochromic properties. The photochromic characteristics (fading rate constant K_Δ and absorption wavelength λ_{max} of open form) were determined by flash photolysis coupled to a fast spectrophotometer.[8] Results are summarized in Table 1.

TABLE I Spectrokinetic parameters of 10'-substituted spironaphthoxazines **5**, **6** and spiropyridobenzoxazines **7**,**8** (compounds **9** and **10** are given as reference). Experimental conditions: c = 2.5.10^{-5} mol.l^{-1} in toluene at 25°C.

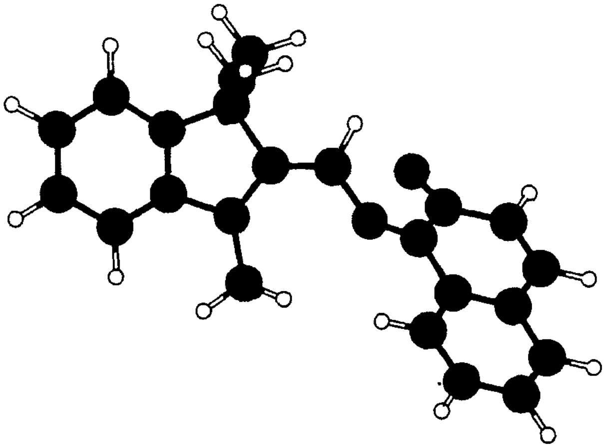
N°	Coumpound	K_Δ (s^{-1})	λ_{max} (nm)
5		20	593
6		4.2	605
7		16	590
8		4.3	617
9		0.54	594
10		0.34	590

RESULTS AND DISCUSSION

Compared to reference coupounds **9** and **10**, results obtained for new spirooxazines **5**-**8** (Table 1), show that substitution on 10'-position by methyl or aryl group has no significant influence on maximum absorption wavelengths.

On the other hand, introduction of these substituents leads to an important destabilization of colored forms as indicated by a dramatic acceleration of fading rates : 40 to 50 times more for methyl and 10 times more for aryl derivatives. To explain this behavior, certainly due to steric influence rather than electronic effects, we performed molecular modelling through quantic semi-empirical calculation (PM3).[9] Previous theoretical and experimental results[10,11] have shown that among the different possible isomers of photomerocyanines of spiro[indoline-naphthoxazines], one is energetically favored: the conformation of which being represented on Scheme 1. In this respect, we verified that the introduction of a methyl or a phenyl group on the 10'-position did not change the relative stability of the different isomers. Moreover the formation energy of the most stable isomer is not highly modified (E_{form}= 57.4 kcal and 51.6kcal respectively for open forms of **9** and **5**). In fact, we found that during the photochromic reaction path[12] the formation of the different isomers of the open form (after C-O breaking) involves doubtless a twisted transoïd intermediate (Figure 1). Now, on this conformation, the methyl group linked to the nitrogen atom of indolinic ring and the 10'-hydrogen atom are rather close. The introduction of a methyl group on the 10'-position would hinder rotations leading to planar trans isomers and favour the ring closure, giving rise to the initial spiro form, thus justifying the drastic increase of the fading rates.

FIGURE I



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REFERENCES

1. N. Y. C. Chu, in "Photochromism: Molecules and Systems ", H. Dürr, H. Bouas-Laurent, Eds, Elsevier (Amsterdam 1990), Chap 10 et 24.
2. P. Tardieu, R. Dubest, J. Aubard, A. Kellmann, F. Tfibel, A. Samat and R. Guglielmetti, Helv. Chim. Acta, 75, 1185, (1992).
3. M. Rickwood, S.D. Marsden, M.E. Ormsby, A.L. Staunton, D.W. Wood, J.D. Hepworth, C.D. Gabbut, Mol. Cryst. Liq. Cryst., 246, 17 (1994).
4. P. Lareginie, V. Lokshin, A. Samat, R. Guglielmetti, E. Zaballos-Garcia, WO Patent, 96/04590
5. F. Snyckers, H. Zollinger, Helv. Chim. Acta, 53, 1294, (1970).
6. K. N. Campbell and I. J. Schaffner, J. Am. Chem.Soc., 67, 86 (1945).
7. B. Bortolotti, R. Leardini, D. Nanni and G. Zanardi, Tetrahedron, 49, 10157 (1993).
8. E. Pottier, R. Dubest, R. Guglielmetti, P. Tardieu, A. Kellmann, F. Tfibel, P. Levoir, J. Aubard, Helv. Chim. Acta, 73, 303, (1990).
9. J. J. P. Stewart, J. Comput. Chem., 10, 209 (1989).
10. S. Nakamura, K. Uchida, A. Murakami, M. Irie, J. Org. Chem., 58, 5543 (1993).
11. P. Lareginie, V. Lokshin, A. Samat, R. Guglielmetti, G. Pèpe, J. Chem. Soc. Perkin Trans. 2, 107 (1996).
12. G. Garros, I. Chuev, A. Samat, M. Rajzmann, R. Guglielmetti (to be published).