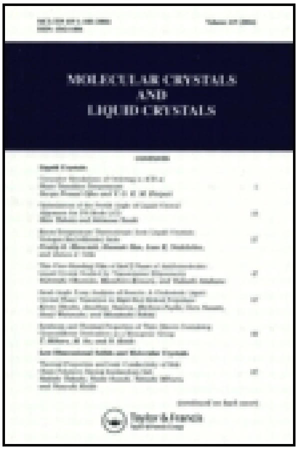


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism, Thermochromism and Solvatochromism of Spironaphthoxazines: Mechanistic Aspects

Dominique Eloy [a] & Pierre Jardon [a]

[a] Laboratoire de Photochimie, Université J. Fourier, BP 53 X, 38041, GRENOBLE Cedex, FRANCE

Version of record first published: 24 Sep 2006.

To cite this article: Dominique Eloy & Pierre Jardon (1994): Photochromism, Thermochromism and Solvatochromism of Spironaphthoxazines: Mechanistic Aspects, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 291-294

To link to this article: http://dx.doi.org/10.1080/10587259408037830

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 291–294
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PHOTOCHROMISM, THERMOCHROMISM AND SOLVATOCHROMISM OF SPIRONAPHTHOXAZINES : MECHANISTIC ASPECTS.

DOMINIQUE ELOY and PIERRE JARDON
Laboratoire de Photochimie, Université J. Fourier, BP 53 X,
38041 GRENOBLE Cedex, FRANCE.

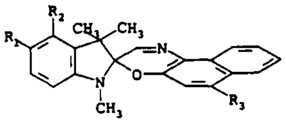
Abstract Mechanistic aspects of coloration and decoloration of some spironaphthoxazines have been studied. A schematic potential energy curve applicable to the photochromic reaction is presented

INTRODUCTION

The purpose of the present work was to study some mechanistic aspects of the photochromic reaction of spirooxazines.

The investigation involved the basic unsubstituted spirooxazine compound and two derivatives as shown in Table I.

TABLE I Chemical structure and absorption maxima of the spironaphthoxazines.



Compounds	Substituents R_1	R_2	R_3	λmax, nm (visible) toluene	ethanol
SPOA	H	H	H	590	610
SPOD	CH_3	CH_3	H	595	615
SPOP	H	H	pip.*	565	590

(*) pip. = piperidinyl

EXPERIMENTAL DETAILS

Materials and solutions

The three spirooxazines studied were supplied by Enichem Synthesis.

The solvents used were ethanol (Prolabo, Normapur grade) and toluene (Merck, Spectroscopy grade).

The concentration of the samples used were 2.10^{-4} $mol.dm^{-3}$ for irradiation in a 1 mm pathlength cell and 10^{-3} $mol.dm^{-3}$ for heating in a 1 cm pathlength cell.

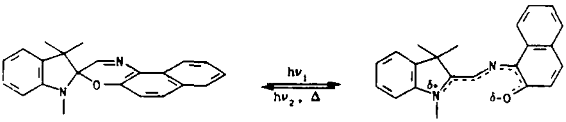
Instrumentation

Absorption spectra were recorded on a Perkin-Elmer Lambda 17 UV-visible spectrophotometer.

The equipment used for flash photolysis is described in detail in reference 1.

RESULTS AND DISCUSSION

The photochromism of spironaphthoxazine derivatives consists in a reversible photoisomerization involving the cleavage of the C(spiro)-O bond in the closed form (A) to form a colored open isomer, the photomerocyanine (B) :



A = colorless form B = colored form

This photomerocyanine form absorbs strongly in the visible region and reverts to its original form via both thermal and photochemical pathways.

Temperature dependence of the absorption of the colored form

There exists a thermal equilibrium between the colorless and colored form strongly temperature dependent. This thermochromic effect is illustrated in Figure 1.

The standard enthalpy of this equilibrium reaction can be calculating using the following equation :

$$\frac{d\ \mathrm{Log}A_B}{d(1/T)} = - \frac{\Delta H^0}{RT} \qquad [A] \gg [B]$$

Kinetics of the thermal decay

The value of the thermal rate constant was determined at different temperatures and according to the Arrhenius equation

$$\mathrm{Log}\ k_{BA} = - \frac{Ea}{RT} + \mathrm{Log}\ A \qquad \text{A is the frequency factor}$$

$$\Delta H^* = Ea - RT$$

the activation enthalpy, ΔH^*, can be calculated.

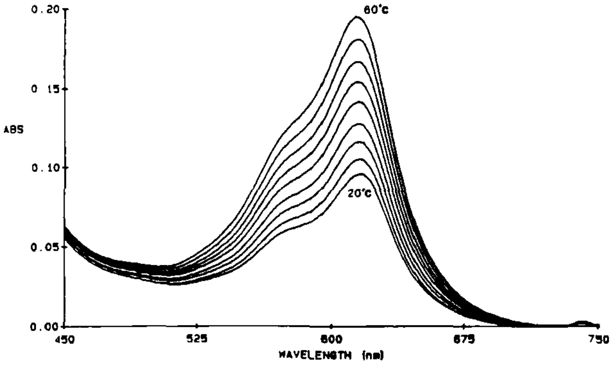


FIGURE 1 The absorption spectrum of the colored form of SPOD in ethanol at several temperatures

TABLE II Calculated standard enthalpy and activation enthalpy

	ΔH^0 (k.J.mol^{-1})	
	toluene	ethanol
SPOA	-	16.36
SPOD	18.65	14.20
SPOP	16.29	11.97

	ΔH^{*} (k.J.mol^{-1})	
	toluene	ethanol
SPOA	60.82	91.95
SPOD	80.16	97.33
SPOP	61.55	62.50

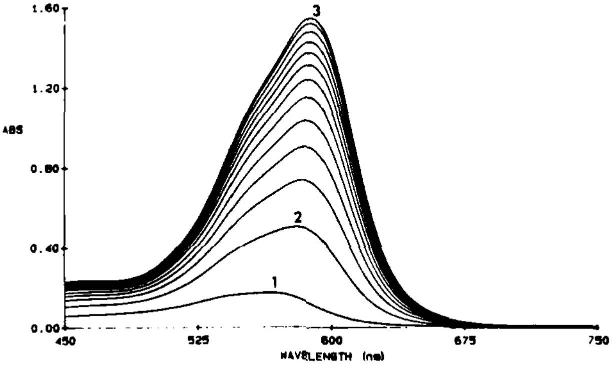


FIGURE 2 Progressive absorption spectral change of SPOP as a fonction of methanol concentration

1 methanol = 0

2 methanol = 0.6 M

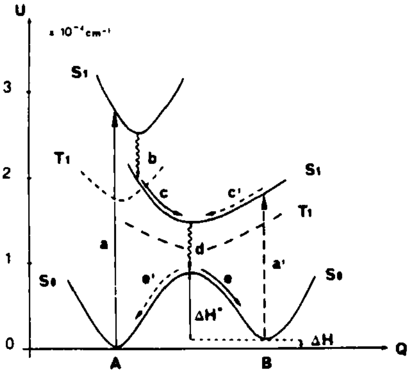
3 methanol = 7.4 M solvent = toluene

Solvent dependence of the absorption of the colored form

The absorption maximum of spirooxazines is solvent dependent (Figure 2). The red shift is probably due to a higher dipole moment for excited spirooxazines with respect to its ground state, thus leading to increased excited stabilization in polar solvents.

CONCLUSION

The kinetic and thermodynamic data strongly suggest an energy level schema as shown in the figure.



ENERGY DIAGRAM

a : $S_0 \longrightarrow S_1$ absorption of A

a' : $S_0 \longrightarrow S_1$ absorption of B

b : breakage of the CO linkage

c, c' : relaxation of the vibrational levels of S_1 (B)

d : internal conversion

e, e' : relaxation of the vibrational levels of S_0 (B) and S_0 (A)

photocoloration : a, b, c, d, e

photodecoloration : a', c', d, e'

thermal decoloration : - e, e'

thermochromism : - e', e

This diagram can explain the main properties of the SPO studied :

- the colored species are mainly formed from the singlet state in direct photocoloration and can be formed from the triplet state in sensitized photocoloration
- the photocoloration appears very shortly (< 1 ns) after the irradiating flash
- the colorless and colored forms show no fluorescence and no phosphorescence
- color formation and decoloration are reactions proceeding via electronically excited states (S_1 or T_1) and via vibrationally excited ground state.
- the colored form is mainly quinoid

REFERENCE

1. D. Eloy, P. Escaffre, R. Gautron and P. Jardon, J. Chim. Phys., 89, 897 (1992).