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Three new spirooxazines derivatives have been investigated in neutral and acidic ethanol solution. Besides, the classical photochromic and thermochromic properties of spirooxazines compounds, a strong reversible visible-light photobleaching of the protonated open form has been found. A global mechanism is proposed.

Keywords: acidichromism; photochromism; spirooxazine

INTRODUCTION

Among the photochromic compounds, spirooxazines are currently applied for manufacturing light sensitive materials [1]. Spirooxazines derivatives applicable to such devices should possess some specific properties such high photocoloration quantum yield, specific association properties and low degradability. Hence, there is a constant demand of new synthetic molecules exhibiting the required features. In this paper, we present a qualitative preliminary study of the photochromism of three novel spiroxazines derivatives bearing two oxygen-containing substituents (Fig. 1).

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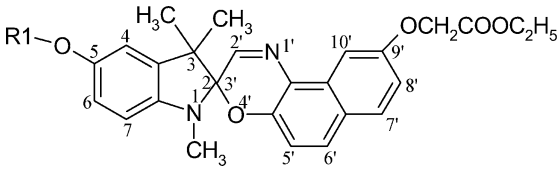

R1	CH_3	C_9H_{19}	$C_{16}H_{33}$
n°	1	2	3

FIGURE 1 Structure of the spirooxazines under investigation.

In ethanol solution, these molecules exhibit the expected spirooxazines photochromic properties, namely: photocoloration under UV irradiation, thermal bleaching in the dark [2] and acidichromism [3]. However, some unprecedented responses such as negative photochromism in acid medium have been observed.

The aim of this paper is to investigate the reversible photobleaching under visible light irradiation of acidified solutions of these compounds (negative photochromism).

EXPERIMENTAL

The synthesis of ethyl 5-methoxy-1,3,3-trimethylspiro[indoline-2, 3′-[3H]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (1), ethyl 5-nonyloxy-1,3,3-trimethylspiro[indoline-2,3′-[3H]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (2) and ethyl 5-hexadecyloxy-1,3,3-trimethylspiro [indoline-2,3′-[3H]naphtho[2,1-*b*][1,4]oxazine]-9′-yloxyacetate (3) was described in a previous paper [4].

The samples were dissolved in absolute ethanol of highest spectroscopic grade. A solution of HCl in the same solvent and an aqueous solution of NaOH were used. Absorption spectra and kinetic curves were recorded with an Ocean Optics fibre optic diode array spectrophotometer. Photochemical irradiation was derived from a 200 W high pressure mercury lamp enabling selection of a single emission line using appropriate interference filters. The photochromic solution was stirred continuously with a magnetic bar in the 1 cm $\times$ 1 cm reactor cell. The whole set-up was equipped with a thermostatic block. All the experiments were carried out at 27°C (300 K).

RESULTS AND DISCUSSION

Photochromism

The three compounds have similar UV spectra whatever the length of the alkyl-chain. Their UV-region absorption characteristics are given in Table 1.

TABLE 1 Molar Absorption Coefficients (in $L.mole^{-1}.cm^{-1}$) of the Three Spirooxazines in Ethanol Solution at 300 K at Some Selected Wavelengths. (a), (c), (e): Hg Lines; (b): Valley Minimum; (d): Maximum

Compound	$\varepsilon^{254}{}_{(a)}$	$\varepsilon^{287}{}_{(b)}$	$\varepsilon^{313}{}_{(c)}$	$\varepsilon^{323}{}_{(d)}$	$\varepsilon^{365}{}_{(e)}$
1	11330	4795	9145	9580	3790
2	11795	4675	9090	9615	3830
3	10050	4405	8630	9000	3650

Whatever the UV irradiation wavelength (254, 313 or 365 nm), photocoloration led to the appearance of the well-known photomerocyanine absorption band ($\lambda_{max} = 621$ nm + a shoulder at 580 nm) (Fig. 2).

A magnification of the spectrum (a) in Fig. 2 showed that a small quantity of merocyanine (B) was already present in the initial ethanol solution, indicating that there is a thermal equilibrium between the merocyanine (B) and the closed spiro-forms (A). This equilibrium is strongly shifted towards A. ($K_{eq} = [B]/[A] \ll 1$)

After switching-off of the UV excitation source, the well-known relaxation (ring closure to A) of the merocyanine open form (B) occurs. Moreover, another interesting property of B is its visible light

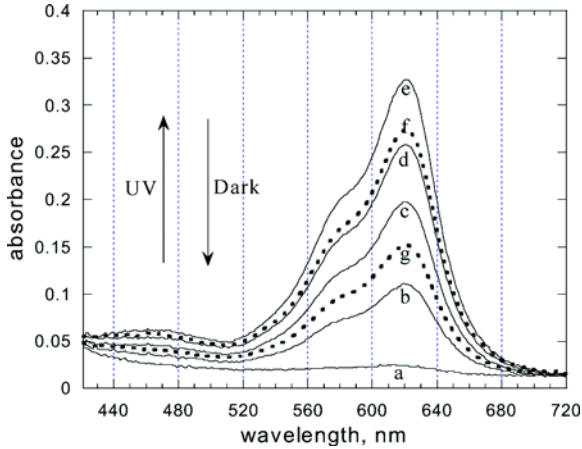

FIGURE 2 Evolution of the absorption spectra of a 1.3×10^{-4} M solution of spirooxazine (1) in neutral EtOH medium during 365 nm continuous irradiation (a: 0; b: 9; c: 16; d: 24; e: 73 s) and consecutive thermal bleaching at 300 K after switch-off of the UV irradiation (f: 7; g: 17 s).

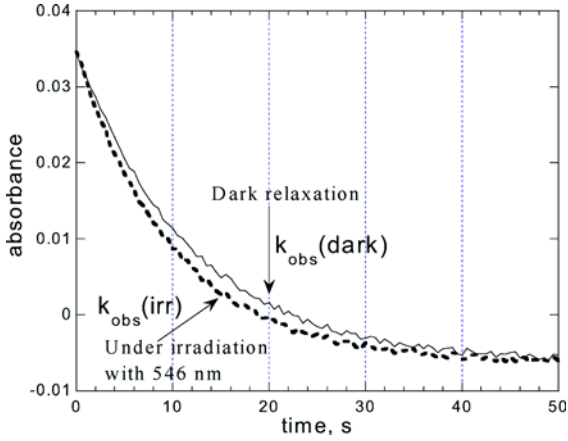

FIGURE 3 Relaxation kinetic curves recorded during the ring closure of the merocyanine B to the spiroform A. Note the acceleration under visible light irradiation (lower dotted curve).

photo-bleaching capability. It was shown that the thermal relaxation was accelerated by a 546 or 577 nm irradiation (Fig. 3).

All these experimental results suggest that the spiro (A) and the merocyanine (B) forms are coupled by two thermal (k_{AB} and k_{BA}) and two photochemical (Φ_{AB} and Φ_{BA}) reversible isomerisation process [5].

Acidichromism

Spironaphthoxazines are pH sensitive compounds due to the protonation of the merocyanine open form (Fig. 4).

Protonation shifts the thermal equilibrium between the closed A and open B form towards B (Fig. 5). Although protonation is usually

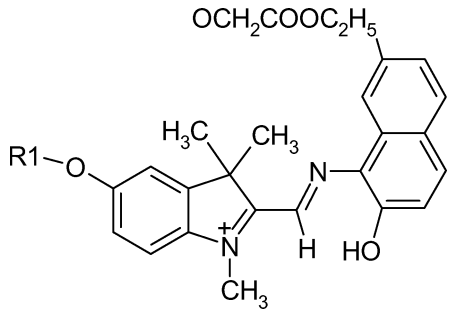

FIGURE 4 Molecular structure of the protonated merocyanine (BH^+).

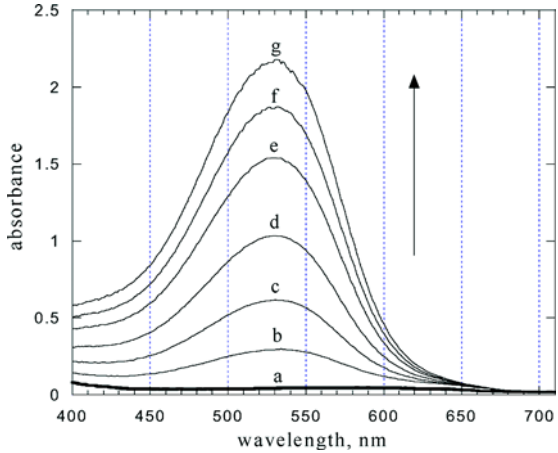

FIGURE 5 Slow evolution at 300 K of the absorption spectra of a 1.3×10^{-4} M solution of the spirooxazine (1) in EtOH induced by addition of 10^{-3} M HCl (a: 0; b: 370; c: 980; d: 2000; e: 3890; d: 5920; g: 9070 s).

assumed to be a rapid process, the slow equilibration between the spiro A and the open B forms plays the role of rate limiting step.

In acid medium, the merocyanine spectrum was significantly blue shifted ($\lambda_{max} = 532$ nm). The protonated open form (BH^+) seemed to be relatively long-lived. However, after an apparent accumulation, its concentration decreased slowly after long-time standing in the dark (not shown). This effect may be assigned to a second protonation giving rise to the lost of conjugation as it has been proposed by Gentili *et al.* [6]. However, when irradiated with UV-light, the intensity of the residual absorption band was partially recovered.

For fresh acidified solutions, the observed protonation was completely reversible as it was demonstrated by neutralisation with an equivalent quantity of the base. An instantaneous transformation of the "acidified" gaussian-shaped spectrum (532 nm) into the "non-protonated" spectrum (621 nm) was observed. Then, the expected thermal decay of this spectrum towards the spiro form took place (Fig. 6).

An unexpected feature of the protonated form was its reversible photobleaching capability (Fig. 7) under visible-light irradiation (negative photochromism). During this process, a deep-purple solution lost quasi instantaneously its coloration which could be then slowly recovered in the dark. From pH measurements carried-out under visible irradiation, proton release was observed. It is likely that the

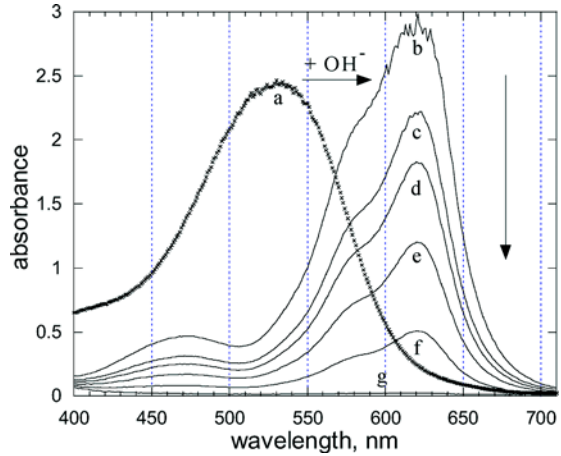

FIGURE 6 Visible absorption of an acidified solution of (1) (a: 0 s) and spectral evolution after neutralization (b: 3; c: 5; d: 6; e: 8; f: 12; g: 42 s). $[1] = 1.3 \times 10^{-4}$ M; $[HCl] = 10^{-3}$ M; $[NaOH] = 10^{-3}$ M.

protonated merocyanine undergoes direct rearrangement to the spiro-form A without any noticeable accumulation of the non-protonated open-form B.

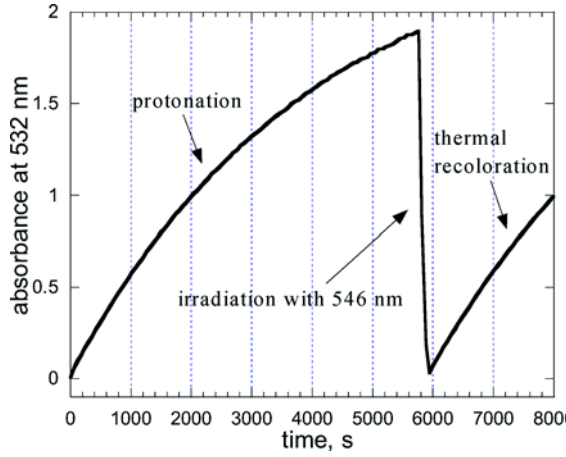

FIGURE 7 Characteristic kinetic curve of a 1.3×10^{-4} M spirooxazine (1) solution after addition of acid ($[HCl] = 10^{-3}$ M) followed by the irradiation with 546 nm and consecutive thermal relaxation.

TABLE 2 List of Processes Involved in the Proposed Mechanism

$A \rightarrow B$
$A + h\nu\,(UV) \rightarrow B$
$B \rightarrow A$
$B + h\nu(VIS) \rightarrow A$
$B + H^+ \rightarrow BH^+$
$BH^+ \rightarrow B + H^+$
$BH^+ + h\nu(VIS) \rightarrow A + H^+$
$BH^+ + H^+ \rightarrow C$
$C \rightarrow BH^+ + H^+$

Proposition of a Mechanism

Based on the qualitative results mentioned above, the following mechanistic steps can be assumed during the photochromism and acidichromism of spirooxazine (1) (Table 2).

It appears that under irradiation in acidified solution several processes are coupled making the dynamics of the photochromism of these oxyacetate alkoxy-spirooxazines to be relatively complex. Numerical modelling of the coupled differential equations which express the general photochromic behaviour whatever the experimental conditions (UV and/or visible irradiation, photosteady state (PSS), thermal relaxation, equilibrium...) would be required to verify the validity of these assumptions and to extract some useful kinetic and photochromic parameters.

CONCLUSION

The photochromism of oxyacetate alkoxy spirooxazine compounds has been investigated in neutral and acidified ethanol solution. Besides the usual positive photochromism, the presence of a slow ring-opening step has been found in neutral medium. The light-blue neutral ethanol solution turns into deep-purple under protonation. These acid solutions exhibit a strong negative photochromism. A general mechanism involving several coupled thermal and photochemical steps is under investigation.

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