Photochromic properties of six 5-O-*n*-alkyl, 6'-CN substituted spironaphthoxazines

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ABSTRACT. The photochromic properties of a series of six 5-O-*n*-alkyl, 6'-CN substituted spironaphthoxazines has been investigated in toluene and methanol solution. The 6'-CN and 5-O-*n*-alkyl substitutions lead to a bathochromic shift of the UV spectra of the closed forms. The λ_{max} of the visible spectra of the open forms decrease with solvent polarity. Most of the photochromic parameters have been quantitatively determined. Among them, photocoloration and photobleaching quantum yields and molar absorption coefficients of the open forms have been derived from a numerical fitting of the photokinetic curves recorded under continuous monochromatic irradiation. Results show that the photo-steady-state properties are relatively independent of the 5-O-*n*-alkyl chain length, but are more sensitive to the size of the indolinic nitrogen substituent.

1. INTRODUCTION

It is well known that photochromic molecules undergo reversible rearrangements between two main states characterised by strongly differing spectral parameters [1]. For the purpose of practical applications, such as variable transmission glasses [2] and future optochemical memories [3], it is possible to identify among the numerous organic photochromic substances those exhibiting the required properties [4]. Once a photochromic series has been elected, its basic features can be modulated by playing with the nature and the position of a large variety of substituents [5].

Spirooxazines represent one of the most important photochromic series [6, 7]. Their photochromism can be understood by the presence of a photo-thermal equilibrium between the "closed" spiro isomer and the "open" planar merocyanine (Scheme 1).

Spirooxazines have a greater photostability than the more widely studied structurally similar spiropyrans. It has been shown recently that their photochromic and solvatochromic properties are very sensitive to the donor/acceptor character and the position of their substituents [8]. So, a spirooxazine with an acceptor substituent on the naphthoxazine side will be called: *pull-type*, while a spirooxazine with a donor substituent on the indoline side will be called *push-type*. In the same way, a donor on the indoline and an acceptor on the naphthoxazine gives rise to a *push-pull* compound [9]. Despite the great number of studies devoted to spirooxazines, information concerning structure-photochromic properties relationships is only available for a restricted number of compounds [10, 11].

The purpose of this paper is to investigate quantitatively the photochromic properties of six 5-O-*n*-alkyl, 6'-CN substituted spironaphthoxazines (*push-pull*). For the sake of comparison, one O-*n*-alkyl substituted compound (*push-type*), one 6'-CN substituted compound (*pull-type*) and the non-substituted spironaphthoxazine [12] (*neutral*) were also investigated in the same conditions. Table 1 gives the details of the substitutions for the whole set of molecules under investigation.

2. EXPERIMENTAL PART

2.1. Synthesis of the spironaphthoxazines. Spiro-naphthoxazines were synthesised by reaction of 2-methylene-1,3,3-trimethylindoline (Fischer's base) with the corresponding naphthols or amino-naphthols. Detailed synthesis of specific compounds are given in the following literature: compounds 1, 2, and 8 [14]; compounds 3, 4, 5, 6, and 7 [15]; compound 9 [16].

2.2. Spectral measurements. Absorption spectra were recorded on thermostated Varian Cary 50, Varian Cary 100 and Hewlett-Packard 8452A spectrophotometers. Solvents were of the highest available spectroscopic grade (Acros Organic).

2.3. Photokinetic monitoring. Photokinetic data (Abs vs. λ vs. t) matrices were recorded on an Ocean Optics fibre optic diode array spectrophotometer. The photochemical irradiation was derived at 90° from a 200 W high-pressure, IR filtered, mercury lamp equipped with single-line (313, 365, or 546 nm) interference filters. The monochromatic light intensity was determined directly in the stirred reactor using either an acidic aqueous solution of potassium ferrioxalate

Scheme 1.

Table 1. List of differently substituted spironaphthoxazines and their polar character.

Compounds [13]	R ¹ (N-)	R ⁵ (indoline)	R ^{6'} (oxazine)	Character
1	CH ₃	H	CN	pull-type
2	CH ₃	OCH ₃	CN	push-pull
3	CH ₃	OC ₃ H ₇	CN	push-pull
4	CH ₃	OC ₉ H ₁₉	CN	push-pull
5	CH ₃	OC ₁₆ H ₃₃	CN	push-pull
6	<i>n</i> -C ₃ H ₇	OCH ₃	CN	push-pull
7	<i>i</i> -C ₄ H ₉	OCH ₃	CN	push-pull
8	CH ₃	OCH ₃	H	push-type
9	CH ₃	H	H	neutral

($I_0^{313} = (5 \pm 0.1) \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$, $I_0^{365} = (6 \pm 0.1) \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$) or a fresh toluene solution of Aberchrom 540 ($I_0^{546} = (3.5 \pm 0.1) \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$). The relative photon flux at the output of the irradiation fibre was checked by a home-made semi-conductor photosensor before and after each experiment. Experiments must be designed in order to reveal the effect of the direct and reverse quantum yields, i.e., using at least two different irradiation wavelengths λ' and λ'' . These wavelengths must be selected so that $\epsilon'_B/\epsilon'_A \neq \epsilon''_B/\epsilon''_A$ as in Fischer's classical method [17]. Moreover, to take into account the possible variations of the photokinetic factor, the evolution of the absorbance at the irradiation wavelength (Abs') must be monitored continuously throughout the irradiation process. The photochemical reactor was a 1 cm $\times$ 1 cm optical path quartz cell containing 2 cm³ solution, it was closed with a Teflon bung. The whole set-up was enclosed inside a thermostatic block (T = 283–323 K).

2.4. Data treatment. The photokinetic system under consideration included three global processes:

from which three equations can be established according to the photokinetic laws [18, 19].

$$d[A]/dt = -\Phi_{AB}\epsilon'_A I_0 F[A] + \Phi_{BA}\epsilon'_B I_0 F[B] + k_{BA}[B] \quad (1)$$

where Φ_{AB} = quantum yield of the $A \rightarrow B$ photochemical reaction, ϵ'_A = molar absorption coefficient of the photosensitive substrate A at the irradiation wavelength,

l = optical path, I_0 = incident photon flux and F = photokinetic factor.

$$[A] + [B] = [A_0] \quad (2)$$

$$\text{Abs} = (\epsilon_A[A] + \epsilon_B[B])l \quad (3)$$

Their combination is the basis for the data treatment. An home-made software [20] was used for the numerical integration of the differential equation and parameter optimisation.

Photochromic parameters were extracted during a numerical curve fitting procedure. To start the fitting procedure, all the unknown parameters are put at arbitrary values, then they are optimised by iteration until a minimum is reached between the experimental photokinetic curves and the model. Two quantum yields: Φ_{AB} and Φ_{BA} and three molar absorption coefficients of the open form: ϵ'_B (first irradiation wavelength), ϵ''_B (second irradiation wavelength) and $\epsilon_B(\lambda_{\text{max}})$ are to be determined. All the other parameters, such as the closed form spectrum (ϵ_A vs. λ) and the thermal bleaching rate constant (k_{BA}) are known from independent measurements. The reliability of the solution is ensured by showing that whatever the initial starting values the same optimised parameters are obtained.

3. RESULTS AND DISCUSSION

3.1. Analysis of the absorption spectra of the closed forms. The spectra were recorded in toluene and methanol. Figure 1 shows that 6'-CN substitution leads to a bathochromic shift of the less energetic band (compounds 1 and 2 vs. 8 and 9). Among each group,

Table 2. Spectral characteristics of the closed forms in toluene (tol) and methanol (met) solutions.

Compounds	1	2	3	4	5	6	7	8	9
$\lambda_{\max}$ (tol)	368	372	372	372	372	373	373	347	319
$\varepsilon\lambda_{\max}$ (tol)	7300	7765	7630	7660	7350	7270	7650	6270	7640
$\lambda_{\max}$ (met)	369	370	370	371	370	372	372	347	318
$\lambda_{\max}$ (met)	7560	7260	7910	7840	7110	7360	8000	5180	6800

Figure 1. Closed form UV spectra of compounds 1, 2, 8, and 9 in toluene solution.

Figure 2. Absorbance of a $2.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ toluene solution of compound 6 versus time under 365 nm irradiation ($\Delta t = 1 \text{ s}$).

5-OCH₃ substitution (electron donating) leads to the appearance of a longer wavelength shoulder (compounds 2 and 8 vs. 1 and 9).

Complete results, gathered in Table 2, confirm the 6'-CN bathochromic shift ($\lambda_{\max} = 368\text{--}373 \text{ nm}$ (1 to 7) vs. $319\text{--}347 \text{ nm}$ (8 and 9).

3.2. Analysis of the absorption spectra of the open form. During the continuous UV irradiation of a photochromic solution, the photoisomerisation of the

Figure 3. Plot of the maxima of absorption wavenumbers of the open forms (ν_B) vs. the Brooker's blue parameter (χ_B) of various solvents for push-pull compounds 2, 5, and 6 and for neutral compound 9.

closed form gives rise to an open form (Scheme 1). There is a strong variation of the absorption spectrum in the visible region (Figure 2).

From such records, the $\lambda_{\max}$ of the open forms can be measured directly while specific photokinetic curves can be extracted. Leaving the solution in the dark allows thermal bleaching to be monitored. $\lambda_{\max}$ and k_{BA} are solvent sensitive.

3.3. Solvatochromic effect on the open form spectra. Figure 3 shows that for *push-pull* compounds like 2, 5, and 6, there is a very significant linear correlation between the wavenumber $\nu_{\max}(B)$ and the Brooker's blue parameter (χ_B) [21]. Such behaviour, where the $\lambda_{\max}$ decreases with the solvent polarity is known as negative solvatochromism [22]. On the other hand, *neutral* compound 9 was confirmed to exhibit positive solvatochromism by the existence of an excellent linear correlation of its $\nu_{\max}(B)$ with the Brooker's red parameter (χ_R) (not shown).

3.4. Kinetic study of the thermal bleaching. Thermal bleaching occurs when a previously irradiated solution is kept in the dark. Careful data treatment of the thermal bleaching kinetics show that in all cases more than 98% of the decay can be interpreted accurately by a monoexponential curve (Figure 4). This result excludes the occurrence of aggregation process of the open forms in our experimental conditions [23].

Table 3. Thermal bleaching rate constants ($\times 10^{-2} \text{ s}^{-1}$) at 20°C and E_a in $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds	1	2	3	4	5	6	7	8	9
k_{BA} (tol)	5.85	1.23	1.007	1.033	1.029	0.841	0.781	19.5	19.1
E_a (tol)	97	95.3	97.7	97.2	97.4	97.8	96.1	66.8	62.8
k_{BA} (met)	0.34	0.031	0.028	0.027	0.027	0.024	0.021	4.3	27.2
E_a (met)	86.2	96.1	96.6	96.7	96.6	98.5	100.5	94.3	83.3

Figure 4. Variation of the absorbance during the thermal bleaching of compound 7 in toluene solution. The solid line corresponds to fitting (insert: the linearity of the same kinetics with an ordinate log scale shows its mono-exponential character).

Activation energies of the thermal decays were determined from Arrhenius plots. Figure 5 shows the plot obtained in toluene and methanol during the investigation of compound 7.

The main results are gathered in Table 3. For all the molecules, the thermal bleaching rate constant k_{BA} is solvent sensitive. On the other hand, all the *push-pull* compounds (2 to 7) give rise to similar activation energies without any significant solvent effect. For *pull-type* compound 1, E_a decreases with solvent polarity, while it increases with *push-type* and *neutral* molecule 8 and 9. These reverse effects are compensated on *push-pull* molecules.

3.5. Determination of the quantum yields of photoreactions and absorption coefficients of the open form. Because the photoconversion rate (i.e., the percentage of open form) is not known, neither the molar absorption coefficient (ϵ_B) nor the photocoloration and photobleaching quantum yields (Φ_{AB} and Φ_{BA}) can be reached directly. A quantitative kinetic analysis of the photokinetic curves recorded under continuous monochromatic irradiation is needed. This analysis involves a curve fitting procedure based on differential kinetic equation established from the macroscopic mechanism of the reaction.

Figure 5. Arrhenius plot for the thermal bleaching of compound 7 in methanol and toluene.

Several photokinetic curves were recorded using three different irradiation wavelengths successively, two in the UV region: 313 and 365 nm and one in the visible region: 546 nm. In each experiment, three wavelengths were monitored simultaneously: one corresponds to the irradiation wavelength; the two others are close to the λ_{max} of the open form. For each experiments, nine photokinetic curves need to be fitted simultaneously (Figure 6).

After the fitting procedure has succeeded, photochromic parameters such as quantum yields and molar absorption coefficients of open form are delivered. They are gathered in Table 4.

The results show that all the *push-pull* molecules (2 to 7) behave very similarly with a photocoloration quantum yield ranging from 0.11 to 0.135 and a molar absorption coefficient from 60800 to 67700. On the other side, *push-type* 8 and *neutral* 9 compounds are more difficult to investigate due to their faster thermal decay [24, 25]. Higher photocoloration quantum yield, but lower molar absorption coefficient is observed for the *pull-type* compound 1.

3.6. Structure-properties relationship: effect of the CN, O-alkyl and N-alkyl substitutions. From the careful examination of Table 1 some structural similarities can be seen. Compounds 2 to 7 are *push-pull* type molecules, while 1 is *pull-type*, 8 *push-type* and 9 *neutral*. These structural features are reflected by their

Table 4. Quantum yields of photocoloration (Φ_{AB}) and photobleaching (Φ_{BA}) and molar absorption coefficients ($\epsilon(\lambda_{\max})$ in $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) of the various spirooxazines in toluene (tol) and methanol (met).

Compounds	1	2	3	4	5	6	7	8	9
$\lambda_{\max}$ (tol)	645	661	662	662	662	662	662	612	596
$\epsilon(\lambda_{\max})$ (tol)	57500	65900	62800	63000	60800	65600	67700	-	40000
Φ_{AB} (tol)	0.17	0.11	0.13	0.13	0.135	0.13	0.12	-	0.3–0.5
Φ_{BA} (tol)	0.01	0.02	0.02	0.015	0.02	0.01	0.01	-	-
$\lambda_{\max}$ (met)	642	649	650	651	651	655	657	623	613
$\epsilon(\lambda_{\max})$ (met)	60800	67150	-	-	-	-	-	59500	-
Φ_{AB} (met)	0.11	0.05	-	-	-	-	-	0.13	-
Φ_{BA} (met)	0.03	0.02	-	-	-	-	-	0.025	-

Figure 6. Kinetic analysis of the absorbance vs. time curves recorded during continuous monochromatic irradiation of compound 4 in toluene. Dots are experimental points and solid lines the result of the numerical fitting. The nomenclature of the nine curves is the following:

$\lambda_{\text{irr}} = 313 \text{ nm}$ and $\lambda_{\text{obs}} = 662 \text{ nm}$ (a), 615 (c), 313 (f);
 $\lambda_{\text{irr}} = 365 \text{ nm}$ and $\lambda_{\text{obs}} = 662 \text{ nm}$ (b), 615 (d), 365 (e);
 $\lambda_{\text{irr}} = 546 \text{ nm}$ and $\lambda_{\text{obs}} = 662 \text{ nm}$ (g), 615 (h), 546 (i).

kinetic and spectral parameters. This structure effect can be illustrated by plotting the activation energies in methanol vs. the activation energies in toluene E_a (met) vs. E_a (tol) (Figure 7).

5-O-*n*-Alkyl, 6'-CN substituted *push-pull* compounds 2, 3, 4, 5, 6, and 7 behave similarly while *pull-type*, *push-type* and *neutral* compounds 1, 8, and 9 do not. Looking more carefully at the [2–7] cluster shows that the effect of the O-*n*-alkyl chain length from O-methyl to O-hexadecyl is negligible (sub-cluster [2, 3, 4, 5]). On the contrary, the effect of the substituents on the nitrogen atom of the indoline moiety seems to be more prominent: on the sub-cluster [2, 6, 7] it can be seen that the activation energy in methanol increases with the size of the nitrogen substituent. A possible explanation is related to the charge distribution within the open forms. Compounds 2 to 7 are expected to exhibit larger charge delocalisation as they bear a donor sub-

Figure 7. E_a (met) vs. E_a (tol) diagram showing the structure properties relationship of the various compounds under consideration.

stituent on the indoline moiety and an acceptor on oxazine. Such *push-pull* like molecules are known to give rise to zwitterionic merocyanine forms. These zwitterionic merocyanines are of interest because they are expected to self-aggregate in appropriate solvents [26]. On the other hand, a donor substituent on the indoline moiety (*push-type* compound 8) or acceptor substituent on the oxazine side (*pull-type* compound 1) exhibit a lesser charge delocalisation. They are consequently qualified of “intermediate” in the diagram in Figure 7. In the case of unsubstituted spironaphthoxazine 9 (*neutral*), the corresponding merocyanine is mainly under a quinoïd form.

Such splitting into separate sub-sets would also appear by plotting several other photochromic properties [27], for instance ϵ_B vs. Φ_{AB} , k_{BA} (tol) vs. k_{BA} (met) or $\lambda_{\max}(B)$ (tol) vs. k_{BA} (tol).

4. CONCLUSION

5-O-*n*-alkyl, 6'-CN substituted spironaphthoxazines are characterised by very strong photochromic behaviour due to some favourable parameters. The bulky

alkyl nitrogen substituent increases this feature. Small bleaching parameters (k_{BA} and Φ_{BA}) and rather high coloration parameters (ϵ_B and Φ_{AB}) are responsible of this effect. From the whole set of photochromic parameters an absolute classification of the set of 6'-CN-substituted spirooxazines (**1** to **7**) was obtained. Considering the photo-steady-state colorability in toluene solution, the following sequence was found: **7** $\approx$ **6** > **2** $\approx$ **3** $\approx$ **4** $\approx$ **5** > **1**. It has been shown that a less than 10^{-4} molar solution of *push-pull* compounds (**2** to **7**) in methanol solution can easily reach an intense blue colour ($Abs \approx 2$ in a 1 cm cell) under 365 nm irradiation (filtered high pressure 200 w mercury arc). Another very interesting property is that their open form has a zwitterionic structure giving a chance for future observation of self-aggregation.

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