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Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 131–136

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Effect of substituents on the photochromism of a spiro[indoline-naphthoxazine] under laser excitation

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Received 27 March 1995; accepted 3 May 1995

Abstract

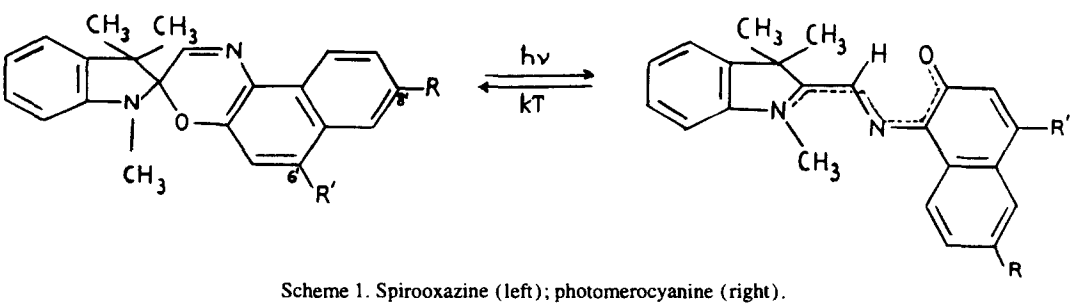
Spirooxazines have been extensively investigated in the last few years because of their remarkable photostability. Laser flash photolysis was used to study the mechanism of the photocoloration reaction of a spiro[indoline-naphthoxazine] substituted either with an electron-withdrawing group, the 8′-nitro derivative (compound **I**), or with electron-donating groups, the 6′-morpholino and 6′-piperidino derivatives (compounds **II** and **III**), in toluene solution at 297 K; the unsubstituted compound (**IV**) was also studied for comparison. The photomerocyanine is formed in the photocoloration process via a triplet pathway in the case of **I** with a high quantum yield (0.7), as was previously observed for homologous nitroindolinospiropyrans. In the case of electron-donating compounds (**II** and **III**) the photomerocyanine is formed exclusively via an excited singlet pathway; however, the quantum yields of photocoloration are much higher for compounds **II** and **III** (0.5) than for the unsubstituted one (0.2), but lower than for the nitro derivative.

Keywords: Photochromism; Laser; Excited states; Kinetics; Spirooxazines; Photomerocyanines

1. Introduction

Spirooxazines are a class of photochromic compounds closely related to spiropyrans in which the carbon atom in the methine bridge is substituted by a nitrogen atom. As in the case of spiropyrans, the photochromic reaction of spirooxazines consists of the UV-photoinduced breaking of the C–O bond of the non-conjugated orthogonal starting closed form, which leads to a planar highly conjugated open form with an all-trans structure, the photomerocyanine; the latter absorbs strongly in the visible, while the initial closed form absorbs only in the UV (Scheme 1).

In contrast with spiropyrans, spirooxazines present high light stability: almost no photodegradation has been observed after hundreds of photochromic cycles [1–3]. This property is an important feature in connection with applications in various fields, e.g. phototropic glasses, non-linear optics, biological probes [4,5]. These characteristics have prompted considerable interest in the mechanism of the photochromic reaction of these compounds over the last few years [6–15]. We reported in a previous paper [9] a photocoloration quantum yield of 0.2 for unsubstituted spirooxazine in toluene solution at 297 K, a value which was confirmed recently by Wilkinson et al. [16]. Such a low yield is a limitation to the use of spirooxazines as photochromic materials for practical applications. This yield could possibly be enhanced by substitution by electron-withdrawing or electron-donating groups giving rise to intramolecular charge transfer. The



Scheme 1. Spirooxazine (left); photomerocyanine (right).

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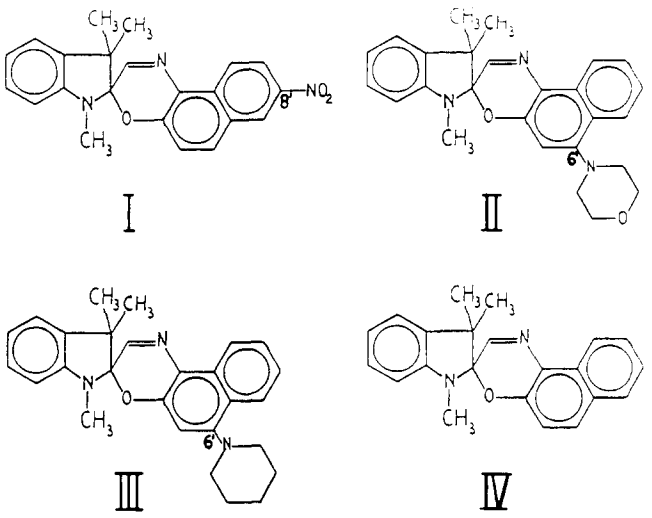
effect of such substituents on the photocoloration yields has received only little attention [15–17].

The purpose of the present study was to investigate the photocoloration mechanism by nanosecond laser photolysis and to determine the quantum yield of photomerocyanine formation for three substituted spiro[indoline-naphthoxazine] compounds, the 8′-nitro (**I**), the 6′-morpholino (**II**) and the 6′-piperidino (**III**), and the unsubstituted one (**IV**) for comparison.



It was observed from the results that nitro substitution in position 8′ on the naphthoxazine moiety induces a triplet channel for photomerocyanine formation and enhances the quantum yield of the photomerocyanine. Substitution by electron-donating groups in position 6′ also enhances the photomerocyanine quantum yield significantly, but in these cases (**II** and **III**) the photocoloration proceeds exclusively via an excited singlet pathway as previously observed for the unsubstituted compound [6–15].

2. Experimental details

2.1. Materials and solutions

The compounds investigated were synthesized and purified according to Refs. [18] and [19]. The solvents used were Merck Uvasol grade. The concentrations used were $(1.25–2.5)\times10^{-5}$ M. Sample solutions were contained in 1 cm × 1 cm silica cells and were deoxygenated by bubbling argon prior to laser excitation.

2.2. Nanosecond laser flash photolysis

The third harmonic (355 nm) of a pulsed YAG laser (Quantel YG 441; pulse width at half-maximum, 2 ns) was used as the excitation light source. Relative values of the laser energy were obtained by focusing a small fraction of the laser light onto a pyroelectric joulemeter (Laser Precision Corporation model RK 3230 with an RE 335 probe). Transmission changes were monitored at right angles to the excitation path using a xenon flash lamp (VQX N 65). The detection system consisted of a monochromator (Jarrell–Ash type 82-410; $f=3.5$; bandwidth 2 nm) and a photomultiplier (HTV R 928). The photomultiplier signal was fed to a digital scope (Tektronix 2440) through a field effect transistor probe (Tektronix P6021). The time resolution of the detection system was 1–2 ns. The digitized signal from the scope was stored on diskettes for kinetic analysis on a microcomputer.

2.3. Absorption and fluorescence

Conventional absorption and fluorescence measurements were performed using a Cary 210 spectrophotometer (Varian) and an MPF-3 spectrofluorimeter (Perkin–Elmer) respectively.

2.4. Quantum yields of photomerocyanine formation

The quantum yield of photomerocyanine (PM) formation was determined by comparing the PM concentration obtained after laser excitation at 15 μs after the end of the laser pulse with that obtained on excitation at the same laser energy of a solution of acridine in benzene chosen as a standard. The triplet quantum yield for acridine in benzene is reported to be 0.73 ± 0.07 [20]. This method of determining quantum yields is only valid provided that a small fraction of the molecules are excited, so that the optical density (OD) obtained remains linear with the laser energy; in these measurements less than 10% of the spirooxazine and acridine molecules were converted into PM and triplet respectively. The acridine concentration was chosen to give the same OD at 355 nm as that of the compound investigated; the concentration of acridine triplet was monitored at its absorption maximum (442 nm) using a triplet extinction coefficient of $2.7\times10^{4}\ M^{-1}\ cm^{-1}$ [20]. The PM concentration was monitored at its absorption maximum in the visible region. Various values have been reported in the literature for the absorption coefficient ϵ_{PM} of PM at the wavelength of maximum absorption [3,7,16,17,21]. We used a value for ϵ_{PM} of $5\times10^{4}\ M^{-1}\ cm^{-1}$ for all the spirooxazines investigated; this value is an extrapolation at room temperature of the measurements for **III** and **IV** carried out at 223 K by Favaro et al. [21]. This value of $5\times10^{4}\ M^{-1}\ cm^{-1}$ is consistent with the determinations of Kholmanskii and Dyumaev for **IV** [7] and of Ovcharenko et al. for **I** [17].

3. Results and discussion

3.1. Spectra and kinetics

Transient OD changes following laser excitation at 355 nm of toluene solutions of **I–IV** at 297 K were monitored in the spectral region 400–800 nm over a time range of a few

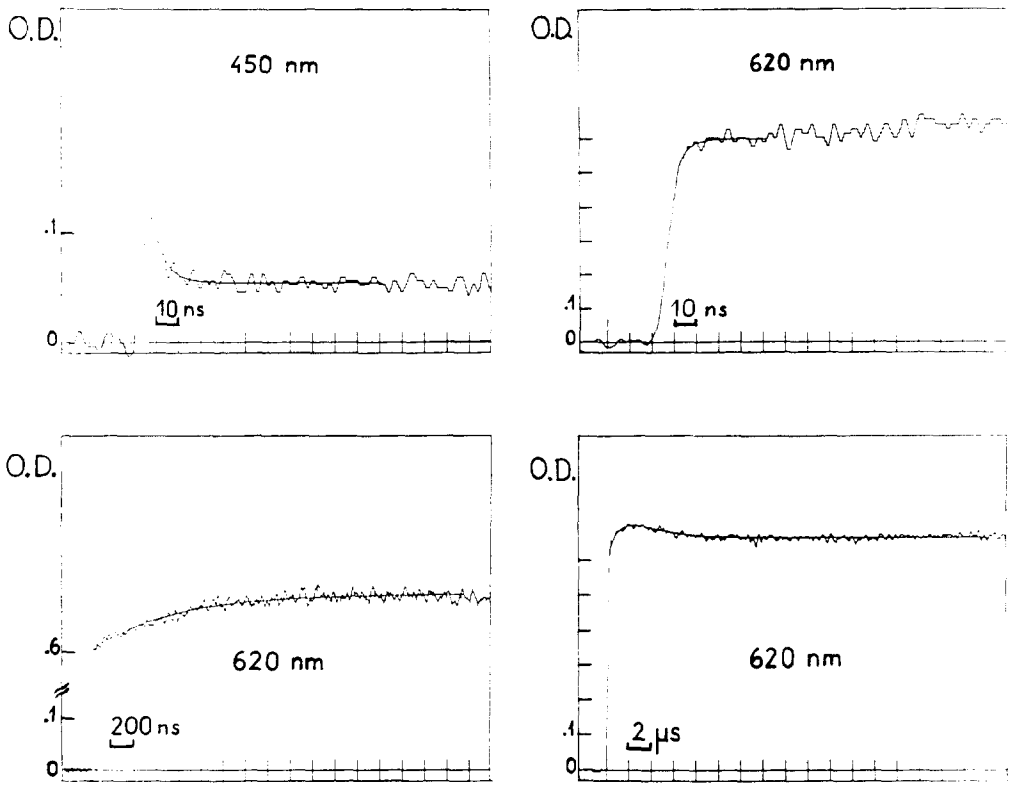


Fig. 1. Time evolution of the transient optical density at selected wavelengths of compound **I** in degassed toluene at 297 K after laser excitation at 355 nm: nanosecond and microsecond time scales.

nanoseconds to a few milliseconds after the end of the pulse. Typical oscillograms at selected wavelengths are shown in Fig. 1 and 3. The transient absorption spectra measured immediately after the end of the pulse and at 15 μs after the end of the pulse are shown in Figs. 2 and 4. The time evolution of the OD changes was found to differ according to the electron-withdrawing or electron-donating character of the substituent.

3.1.1. Electron-withdrawing substituent: nitro compound

Three time phases can be distinguished on the oscillograms for **I** (Fig. 1); they follow strict first-order kinetics. Since these time phases could be fitted at all wavelengths by three exponentials with the same time constants (6 ns, 700 ns and 3 μs respectively), these time constants were assigned to the lifetimes of three transient species presumably formed sequentially one after the other. A plateau in OD was reached about 15 μs after the end of the pulse and the OD then remained constant over more than 200 μs. The absorption spectrum at $t = 15$ μs (Fig. 2a) was assigned to the photomerocyanine of the spirooxazine, i.e. the longest-lived open isomer with an all-trans planar configuration. The absorption spectrum of the shorter-lived transient (lifetime 6 ns) was obtained from the difference of the transient spectra recorded at the end of the pulse and at 30 ns after the pulse (Fig. 2b); this spectrum has a maximum around 450 nm and extends into the near IR (the absorption band around 450 nm is shown in the inset of Fig. 2b). The shorter-lived absorption bands vanish within the first 30 ns following the end of the pulse, giving rise to an OD increase in the region of main absorption of the PM and of its stereoisomers. A short-lived (25–30 ns) transient absorbing around 450 and 700 nm has been observed previously in the case of nitro-substituted indolinospironaphthopyrans and assigned to the lowest triplet of an isomer precursor of PM [22]. Compound **I** is the spirooxazine homologue of a nitro-substituted spironaphthopyran and presents similar photophysical properties — no fluorescence, easily detectable phosphorescence at 77 K [23] — and presumably has a high intersystem-crossing yield due to the mixing of the $\pi\pi^*$ states with the $n\pi^*$ states localized on the NO_2 group. Thus it seems reasonable to make the same assignment for the shorter-lived transient species observed in the present case, i.e. a triplet state. The other two longer-lived transients (lifetimes 700 ns and 3 μs) were not affected by oxygen saturation of the solutions and their absorption spectra were found to be similar to that of PM, except for a small spectral shift. On these grounds both transients were assigned to isomers of PM, the first being generated from the triplet and evolving into the second which in turn leads to PM. Thus in the case of compound **I** PM is formed via a triplet pathway as previously observed in the case of homologous nitro-substituted spiropyrans [22,24,25].

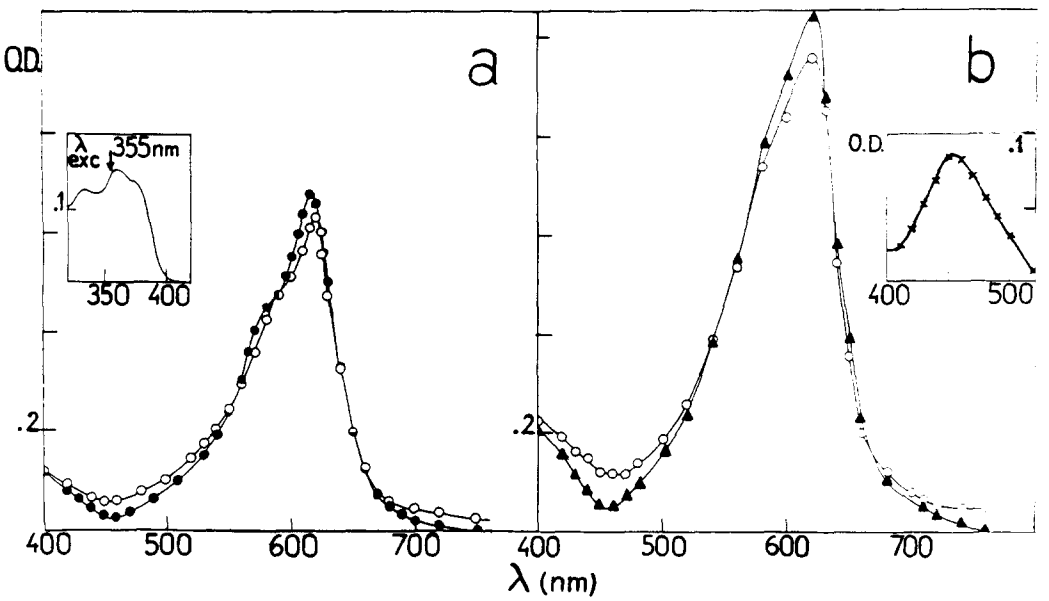


Fig. 2. Transient absorption spectra recorded upon laser excitation at 355 nm of compound I in degassed toluene at 297 K. (a) 1.25×10^{-5} M; ○, at the end of the pulse; ●, 15 μs after the end of the pulse. The absorption spectrum of I is shown in the inset; the arrow indicates the wavelength of laser excitation. (b) 2.5×10^{-5} M; ○, at the end of the pulse; ▲, 30 ns after the end of the pulse. The absorption band of the 6 ns transient in the region 400–500 nm is shown in the inset.

3.1.2. *Electron-donating substituents: morpholine and piperidine*

Oscillograms for compound **II** at various wavelengths are shown in Fig. 3 (similar oscillograms were observed for compound **III**). At all wavelengths the same bi-exponential time evolution of OD was observed after laser excitation with time constants of 500 ns and 3 μs respectively. The transient absorption spectra at the end of the pulse and at 15 μs after the pulse are shown in Fig. 4 for the morpholino and piperidino compounds. They display only small spectral and amplitude changes between these two times, the latter time corresponding to the completion of PM formation. The

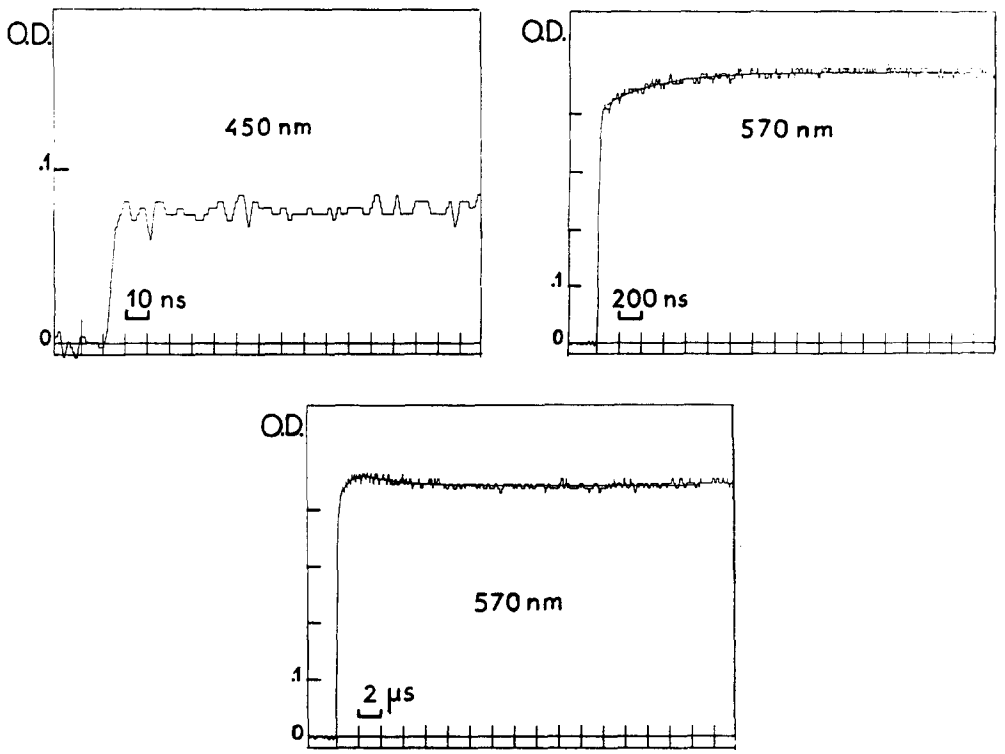


Fig. 3. Time evolution of the transient optical density at selected wavelengths of compound **II** in degassed toluene at 297 K after laser excitation at 355 nm: nanosecond and microsecond time scales.

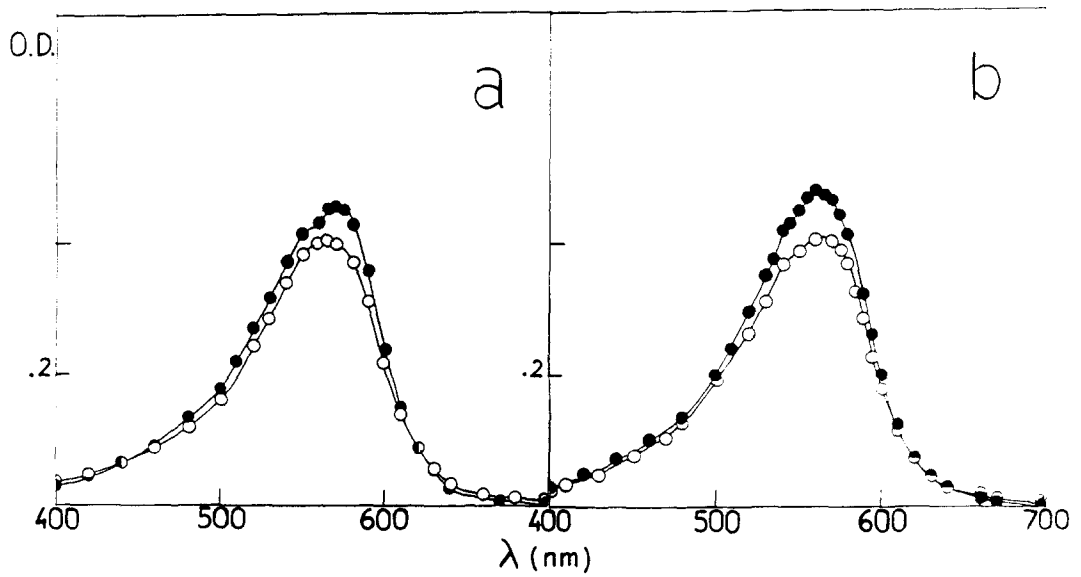


Fig. 4. Transient absorption spectra recorded upon laser excitation at 355 nm of compounds (a) **II** and (b) **III** in degassed toluene at 297 K (1.25×10^{-5} M): ○, at the end of the pulse; ●, 15 μs after the end of the pulse.

absorption spectrum present immediately after the pulse is similar to the PM absorption spectrum and was therefore assigned to a transoid isomer of PM as in the previously reported study of unsubstituted spirooxazine [9]; since the transients observed were not affected by oxygen, it was concluded that the transoid isomer already present at the end of the pulse is in its ground state and undergoes successive structural rearrangements towards PM. Thus, in the case of electron-donating substituents, PM formation proceeds exclusively via an excited singlet pathway, in contrast with the triplet pathway observed for compound **I**.

3.2. Quantum yields

The quantum yields of photomerocyanine formation were determined in toluene at 297 K by comparing the PM concentrations obtained upon excitation of solutions of compounds **I–IV** with the concentration of the triplet of acridine obtained in benzene and used as a standard (see Section 2.4). The values obtained are listed in Table 1 and are given with an experimental error of about 20%.

The quantum yield of PM formation is quite high for NO_2 substitution in position 8′ on the naphthoxazine. Similar high values have been reported for nitro-substituted spiropyrans [22,25–27]: the photocoloration of these compounds involves an efficient triplet pathway as in the case of **I**. No value has been given previously for the quantum yield of PM formation for **I** in solution; only a much smaller value has been reported for this compound in polymeric films at low temperature [17]. In the case of electron-donating substituents in position 6′, photocoloration occurs via an excited singlet channel as in the case of the unsubstituted compound **IV** [6–15]. However, the quantum yield is significantly enhanced as compared with the latter case. The same yield was obtained for 6′-morpholino- and 6′-piperidino-substituted spirooxazines; compared with the piperidine, the oxygen atom in the morpholine cycle apparently does not increase the electron-donating character. The quantum yields for **III** and **IV** can be compared with values reported in the literature. Our results are similar to the values obtained by Wilkinson et al. [16] under the same experimental conditions. Favaro et al. [15] have reported higher quantum yields for these two compounds. However, it is worth noting that all three determinations give the same value of 2 for the ratio of the quantum yields of **III** and **IV**.

Table 1
Quantum yields of photomerocyanine formation in toluene at 297 K

Compound	PM λ_{max} (nm)	Φ_{PM}
I	615	0.7
II	570	0.5
III	560	0.5
IV [a]	590	0.2

[a] From previous work [9].

4. Conclusions

It was shown in the present study that high photocoloration quantum yields can be obtained by substitution of spirooxazine either with an electron-withdrawing group such as NO_2 or with electron-donating groups such as morpholine and piperidine on the naphthoxazine cycle. Although PM formation occurs for **II** and **III** exclusively via a singlet pathway as for the unsubstituted compound **IV**, it is observed that the quantum yield of photocoloration is markedly enhanced with respect to that of **IV**. The highest quantum yield was obtained in the case of the nitro compound with a triplet mechanism

for PM formation; this result is consistent with the high quantum yields well established for homologous nitro-substituted spiropyrans whose photocoloration also occurs via a triplet pathway [22,25–27].

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