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Journal of Photochemistry and Photobiology A: Chemistry 138 (2001) 123–128

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Photokinetic behaviour of biphotochromic supramolecular systems
Part 1. A bis-spirooxazine with a (*Z*)ethenic bridge between each moiety

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Received 3 October 2000; accepted 23 October 2000

Abstract

The photochromic behaviour of a bichromophoric molecule formed by two naphthospirooxazine moieties linked through an ethenic double bond has been studied. The photochemical and thermal evolution of this molecule and its model compound, a naphthospirooxazine linked by a double bond to a 2-methoxy-naphthalene group, was followed spectrophotometrically and by HPL chromatography. Photocoloration occurred with fairly high quantum yield ($\Phi \sim 0.2$) for both molecules. Identification of the photoproducts was helped by information from a parallel NMR study and by comparison with the results previously obtained on related monochromophoric compounds. The photoreaction was thermally irreversible at room temperature while a slow photobleaching ($\Phi \sim 10^{-3}$) accompanied by degradation was observed. A photoreaction mechanism is proposed implying the photocyclisation at the ethenic double bond level. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spirooxazines; Biphotochromes; Photokinetics; Reaction mechanism

1. Introduction

Spiroindolino-oxazines have been the object of extensive investigation because of their photochromic behaviour (for review articles, see [1,2]). High colourability and durability make these molecules very promising for a variety of applications. When two of these species are joined through a spacer to give an unique biphotochromophoric supermolecule, the photokinetic properties of the whole system might be markedly different from those of the free components.

A common project of our research groups is aimed at investigating the role that different photochromes and spacers of various nature (saturated and unsaturated, flexible and rigid) play in the photochromic behaviour.

The bichromophoric molecule investigated in this work is the bis-spiro[indoline-naphthoxazine] (bis-SPO) where the ethenic bridge joins two spiro[indoline-naphthoxazines] in 5′-position. For comparison purpose, a model molecule, formed by a single spirooxazine moiety and a 2-methoxy-naphthalene group, joined through an ethenic bridge (SPO–NPh) was also investigated (Scheme 1).

This study was mainly carried out in toluene using monochromatic irradiation light in the UV and visible ranges. The formation of photoproducts was followed by spectrophotometry and HPLC analyses. By using the empirical coefficients extracted from the experimental colour-forming curves obtained under UV irradiation, the quantum yields and absorption coefficients of the photoproducts were obtained. By using monochromatic visible light for irradiation, the quantum yields of photobleaching were also determined.

The photobehaviour of these molecules was found to be rather complicate. The absence of thermal reversibility and significant degradation make them unsuitable for applications as classical photochromes. Anyway, the results obtained are interesting for basic research and because they can drive the synthesis towards similar but more suitable compounds, in the area of dye printing.

2. Experimental

2.1. Materials

The molecules investigated were firstly synthesised by Chamontin [3] and resynthesised for the purpose by one of us (D. Levi) [4]. Their stereochemistry around the ethenic bridge is mainly *Z* (≈90%) and was checked by ^{1}H NMR

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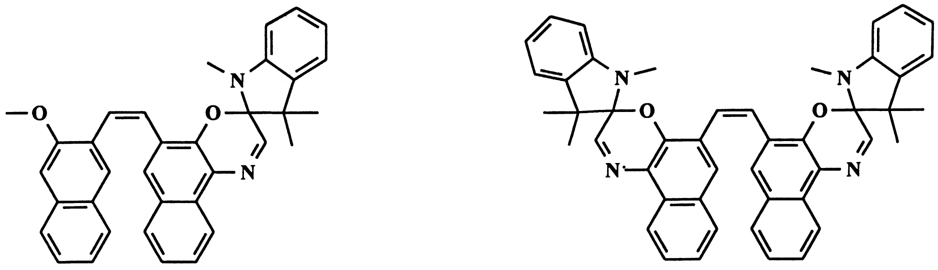
PII: S1010-6030(00)00398-1



SPO-NPh(Z)

bis-SPO(Z)

Scheme 1.

spectrometry. The solvent, toluene, an Uvasol Fluka product, was used without further purification.

2.2. *Apparatus*

The absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer and Beckman DU 7500 or Hewlett-Packard 8453 diode array spectrophotometers. A 150 W Xe lamp filtered by a Jobin-Yvon H10 UV monochromator was used as irradiating source. An Oxford Instruments cryostat was used for the temperature control.

2.3. *Steady-state irradiation experiments*

The general procedure to study the photochemistry of these molecules consisted in irradiating toluene solutions, with monochromatic light of suitable wavelength for each compound, and following the spectral evolution with time by spectrophotometry up to photostationary state attainment. The irradiation was carried out in the spectrophotometer holder at a right angle to the monitoring beam, using a fiber-optic system. The absorbance–time datasets to be used for the interpolations were recorded following the absorbance changes under steady irradiation at the maximum of the colour bands of each compound.

After the steady-state conditions were attained, exposure to UV light was discontinued in order to control whether some thermal bleaching occurred.

The photobleaching reaction, induced by irradiating the thermally equilibrated solution with visible light, was kinetically followed by the absorbance decrease in the visible spectral region.

2.4. *HPLC separation of the thermostable photoproducts*

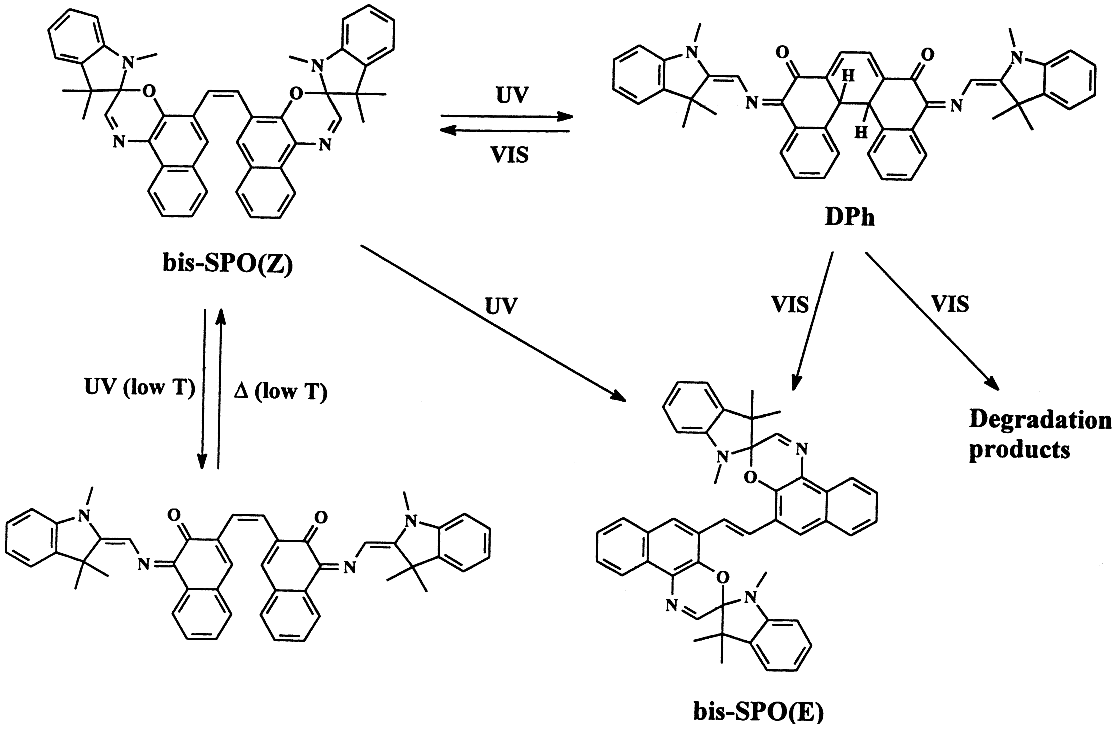
A Waters 600E chromatograph coupled with an HP 3390A integrator and spectrophotometric detection was used. The column was a Waters C18 Symmetry for analytical purposes. The photochromic solutions in toluene (ca. 10^{-4} mol dm^{-3}) were irradiated at room temperature with the Xenon lamp through an interference filter (366 nm, maximum transmittance 35%) and, in some experiments, through a cut-off ($\lambda > 400$ nm). The solutions were kept under irradiation and analysed from time to time. Pure acetonitrile or a 95/5 (v/v) acetonitrile/water mixture were used as the eluent.

2.5. *Quantum yield determinations*

The reaction quantum yields were determined from the absorbance–time curves, using potassium ferrioxalate actinometry for determining the radiation intensity (typically, of the order of 10^{-7} einstein dm^{-3} s^{-1} at the wavelength of irradiation). The photoreactions were irreversible and clean, thus the molar absorption coefficients could be obtained from the photostationary state absorbance and the initial concentration.

3. Results and discussion

The colour-forming kinetics in toluene solution were spectrophotometrically followed on the maximum of the colour band under continuous monochromatic UV irradiation at room temperature (20 ± 2°C). After attainment of the photostationary state, the coloured solutions were kept in the dark to control if any thermal evolution occurred and then further irradiated with monochromatic visible light and/or the whole visible emission of the Xenon lamp up to total fading. In parallel experiments, small volumes (10 μl) of the solution were taken up from time to time during irradiation and analysed by HPLC. Both molecules (bis-SPO and SPO–NPh) showed no thermal bleaching under the experimental conditions used (toluene solution, UV irradiation, room temperature). Our work hypothesis is that the photoproduct has a dihydrophenanthrene (DPh)-type structure (Scheme 2) due to the electrocyclic photoreaction which is typical of *cis*-stilbene-like molecules (for a review article, see [5]). It can return thermally to the starting *cis*-isomer or, alternatively, can easily lose two hydrogen atoms in the presence of suitable acceptors, e.g. in aerated solutions,



Scheme 2.

thus giving irreversibly oxidised phenanthrene-type products. DPh absorbs in the visible due to its more extended conjugation system. By visible irradiation, the excited DPh* can revert to DPh or undergo ring-opening to the starting *cis*-isomer or react with a hydrogen acceptor.

It has to be noted that, in the last 12 years, Irie et al. [6,7] have developed a new type of durable and thermally irreversible photochromes (diarylethene derivatives with heterocyclic rings) which could have practical application in the field of optical data storage. The colour formation in these compounds is just due to the electrocyclic ring closing photoreaction. The aim of the authors was to use different substituents to prevent such oxidation, to make the coloured dihydrocyclised compound thermally stable and to reconvert it to the starting material by irradiation with visible light.

In the case of *cis*-1,2-di-(2-naphthyl)ethene, a parent compound of the present molecules, widely investigated by Knittel et al. [8,9], it was found that the formation of the cyclised isomer (leading to a cyclohexadiene central ring) is sharply temperature dependent and does not occur below 243 K. At lower temperatures a thermally unstable cyclised isomer (with the structure of a different conformer) was observed by laser flash photolysis [10].

In the present compounds, we believe that a particular thermal stability of the cyclised dihydro-derivative is the main reason of the irreversibility of the colour-forming reaction at room temperature [11]. This hypothesis was nicely confirmed by the fact that at lower temperatures, where the thermally activated photocyclisation is no longer operative, the colour-bleaching process was observed by NMR measurements [12].

Under UV irradiation (366 nm) at room temperature, the colourless molecules yielded coloured photoproducts (λ_{max} = 446 and 613 nm for bis-SPO and 578 nm for SPO–NPh). The reactions were clean, as shown by the isosbestic points maintained during irradiation, and substantially complete, as demonstrated by the HPL chromatograms. The spectra of the colourless closed forms and of the coloured open forms for both molecules are shown in Fig. 1.

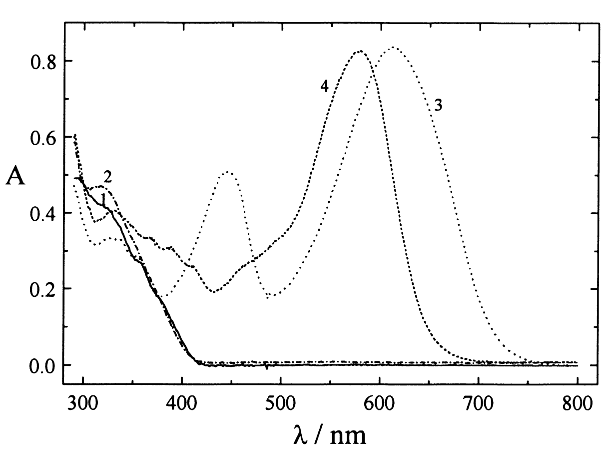


Fig. 1. Spectra of bis-SPO (2×10^{-5} mol dm^{-3}) and SPO–NPh (3×10^{-5} mol dm^{-3}) in toluene before UV irradiation (1, bis-SPO; 2, SPO–NPh) and at the photostationary state (3, bis-SPO; 4, SPO–NPh).

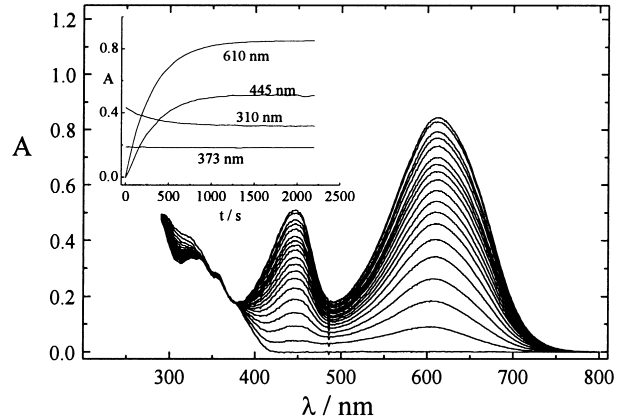


Fig. 2. Spectral evolution and kinetics (inset) followed from absorbance changes of bis-SPO under UV irradiation at various wavelengths: 373 nm wavelength corresponds to an isosbestic point.

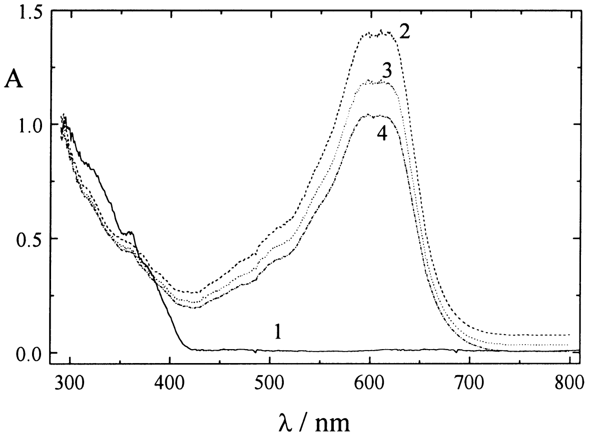


Fig. 3. Thermal reversibility of bis-SPO at low temperature ($T = 230\,\mathrm{K}$): (1) spectrum before irradiation; (2) photostationary state (end of irradiation); (3) and (4) after 1 and 2 h, respectively, in the dark.

Examples of the spectral evolution under UV irradiation and of the colour-forming kinetics (inset) are illustrated in Fig. 2.

No thermal bleaching was observed, since the photoproducts were stable in the dark. This behaviour allowed the molar absorption coefficients and quantum yields of the coloured forms to be determined (Table 1).

The absorption spectra of bis-SPO and SPO–NPh are significantly different from those of the single photochrome (SPO) [13–15]. Two colour bands are present in the biphotochrome, while one band, broadened on the blue side, is observed in the model molecule SPO–NPh. The typical merocyanine band, which is located at 601 nm in the single photochrome SPO, is hypsochromically shifted in SPO–NPh and bathochromically in bis-SPO, indicating increased and decreased contributions, respectively, of zwitterionic forms to the resonance hybrid describing the ground state molecule. The spectral feature of bis-SPO, never observed with differently substituted SPOs, indicates the simultaneous occurrence of the central ring closing at the ethenic bridge and of the side rings opening in the photochromic moieties. The greater ε value for bis-SPO than for SPO–NPh (Table 1) is in agreement with the hypothesis that in the former both photochromic moieties are in the open form and both contribute to the absorption. The spectral evolution and kinetics (equal rate at all wavelengths), shown in Fig. 2, support the view of simultaneous occurrence of the closing and opening processes.

Table 1
Spectral and photochemical parameters for bis-SPO and SPO–NPh: wavelengths and molar absorption coefficients of the maxima of the coloured forms and quantum yields of the photocoloration and photobleaching processes

	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ ($\mathrm{M^{-1}\,cm^{-1}}$)	$\Phi_{\text{colour-forming}}$	$\Phi_{\text{photobleaching}}$
bis-SPO	446 613	25900 44000	0.23	9×10^{-4}
SPO–NPh	578	30300	0.19	4×10^{-3}

It is noteworthy that irradiation with monochromatic UV light ($\lambda_{\mathrm{irr}} = 373\,\mathrm{nm}$) of bis-SPO at low temperature (230 K) led to a coloured open form characterised by a single absorption band in the visible ($\lambda_{\max} = 607\,\mathrm{nm}$), while no peak was observed in the 450 nm region (Fig. 3). When UV irradiation was discontinued, slow thermal bleaching occurred ($k_{\Delta} = 5 \times 10^{-5}\,\mathrm{s^{-1}}$), leading to the starting material as the main product. The NMR experiments [12], carried out at low temperature, also showed the occurrence of thermal bleaching.

The above observation (formation of stable photoproducts at room temperature) was also supported by parallel HPLC measurements.

These results are consistent with the assignment of the 450 nm band to the cyclised dihydro-derivative formed during the photocolouration process. In the light of these facts, it can be reasonably concluded that the formation of the DPh is a thermally activated process, which occurs at room temperature, leading to a rather stable cyclised photoproduct. Stabilisation is due to increased conjugation which prevents thermal bleaching from occurring.

Upon prolonged irradiation with visible light, the coloured solutions completely faded. The photobleaching quantum yields ($\sim 10^{-3}$) were determined at low transformation percentage using monochromatic light (509 nm), based on the rate equation (1):

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = \varepsilon \Phi_{\mathrm{bleach}} I^0 (1 - 10^{-A'}) \tag{1}$$

where A' is the absorbance of the coloured form at the irradiation wavelength, while A is the absorbance and ε is the molar absorption coefficient at the analysis wavelength. Both A and A' are time dependent variables. Based on this equation, the quantum yield was obtained from the linear

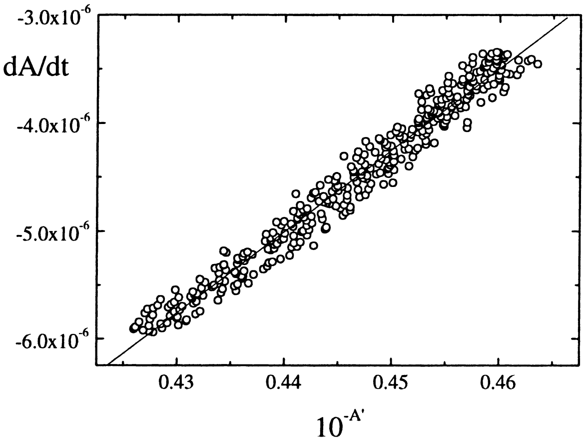


Fig. 4. Graphical treatment employed to obtain the photobleaching quantum yield for SPO–NPh: irradiation wavelength 509 nm; monitoring wavelength 580 nm.

plot of $-\mathrm{d}A/\mathrm{d}t$ versus $10^{-A'}$, which gives $\varepsilon\Phi_{\mathrm{bleach}}I^0$ from both the intercept and slope [16]. An example of the graphical treatment is shown in Fig. 4 for SPO–NPh.

Continuing the irradiation with the polychromatic visible emission of the Xe-lamp, filtered with a cut-off ($\lambda >$ 400 nm) to eliminate excitation of the colourless form, production of small amounts of the starting closed form with very low quantum yield was initially observed, followed by decomposition.

According to NMR information [12], the closed molecules are mainly present in *cis*-geometry. In the chromatograms taken before irradiation, a weak peak was observed (ca. 5% for SPO–NPh and 8.5% for bis-SPO) which slightly increased under UV irradiation. Considering the present and previous results for the corresponding spirooxazine molecule [14,15] and NMR data [12], the colour-forming reaction can be assigned to opening of the spiro-bonds of the spirooxazine moieties in the *cis*-form, while a small amount of the *trans*-closed isomer is initially present and increases by low-yield photoconversion from the *cis*-form. Photobleaching is due to the closure of the photochrome rings; however, the final colourless back products obtained at room temperature were different from the starting supermolecules. Internal rotation around the ethenic double bond partially occurs but most of these unidentified back products are due to extensive photodegradation. The proposed reaction mechanism which matches results from different sources is shown in Scheme 2.

4. Conclusions

The photokinetic behaviour of the bis-SPO supermolecule investigated is more complicated than that of the single components. Colourability upon UV irradiation increases, since thermal reversibility is lost. Photobleaching occurs by irradiation with visible light, but the back products are different from the starting materials. Thus, the supermolecule does not work as a photochrome but, due to its sensitivity to a large range of excitation wavelengths, may find application in other fields, for example in non-conventional image-reproduction systems. The model molecule exhibits a similar behaviour.

The two compounds (bis-SPO and SPO–NPh) investigated at room temperature show a fast opening of the photochromic moiety in the firstly formed centrally cyclised intermediate. This leads to a clean photocoloration process and slow photobleaching, without participation of thermal steps in the reaction mechanism. Due to prevalent degradation, the bleached solutions cannot be newly coloured by UV irradiation.

The irreversibility is due to the presence of the ethenic double bond, since, when the two photochromic moieties are joined through a flexible spacer (as an esteric bridge) or a rigid spacer (an acetylenic bridge), reversibility is recovered [4]. Thus, competition of the central double bond reactivity with the side moiety reactivity is mainly responsible for the irreversibility of the photochromic behaviour.

Acknowledgements

The research of the Perugia group was funded by the Ministero per l'Università e la Ricerca Scientifica e Tecnologica (Rome) and the Perugia University in the framework of the Programmi di Ricerca di Interesse Nazionale (project: 'Mechanisms of Photoinduced Processes in Homogeneous Media and in Complex Matrices'). A grant from the Italian Consiglio Nazionale delle Ricerche (Rome) is also acknowledged.

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