

# Photokinetic behaviour of biphotochromic supramolecular systems Part 2. A bis-benzo-[2H]-chromene and a spirooxazine–chromene with a (Z-)ethenic bridge between each moiety

F. Ortica<sup>a</sup>, D. Levi<sup>b</sup>, P. Brun<sup>b</sup>, R. Guglielmetti<sup>b</sup>,  
U. Mazzucato<sup>a</sup>, G. Favaro<sup>a,\*</sup>

<sup>a</sup> Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

<sup>b</sup> Faculté des Sciences de Luminy, Université de la Méditerranée, UMR CNRS 6114, 13288 Marseille Cedex 9, France

Received 17 November 2000; received in revised form 13 December 2000; accepted 21 December 2000

## Abstract

The photochromic behaviour of two new bichromophoric molecules (a symmetric one, formed by two 3,3-diphenyl-[3H]-naphtho[2,1-b]pyran moieties, and an asymmetric one, formed by a naphthopyran and a spiro[indoline-naphthoxazine] moiety) linked through an ethenic double bond has been studied. A model compound, where the chromene moiety is linked to a naphthalene group, was also investigated for comparison purpose. The photochemical and thermal evolution of the bichromophoric molecules were followed spectrophotometrically and by high performance liquid chromatography (HPLC). The photochromic reaction was found to be only partially photoreversible. Massive irradiation with visible light led to degradation. The reaction mechanism for these molecules containing a chromene moiety is characterised by an intermediate, which thermally evolves to different products. The quantum yield of formation and the first-order kinetic constant of the thermal evolution of the intermediate were determined. The identification of the photoproducts was helped by information from a parallel NMR study. Comparison of these results with those previously obtained on related monochromophoric and bichromophoric compounds allowed reasonable photoreaction mechanisms to be proposed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Chromenes; Naphthopyrans; Spirooxazines; Bi-photochromes; Photokinetics; Reaction mechanism

## 1. Introduction

The photochromism of spiroindolino-oxazines [1,2] and benzo-[2H]-chromenes or naphthopyrans [3,4] has been extensively studied. These classes of molecules exhibit chromatic properties and durability which make them potentially suitable for various applications. Joining two of these molecules through an ethenic bridge yields a bichromophoric supermolecule, that exhibits photochemical and dynamic properties different from those of the single components. The photochemical behaviour of a bis-spiro[indoline-naphthoxazine] (bis-SPO) and of the model molecule naphthospirooxazine linked to a naphthalene group (SPO–NPh), has been recently investigated and described in Part I [5]. These molecules, at room temperature, showed high colourability but no thermal reversibility, while photobleaching led to prevalent degradation. The

stability in the dark of the photoproduct(s) was attributed to light-induced cyclisation at the central double bond.

In this work, two bichromophoric molecules containing the benzo-[2H]-chromene moiety are investigated: bis-benzo-[2H]-chromene (bis-CHR) and spiro[indoline-naphthoxazine]–benzo-[2H]-chromene (SPO–CHR). For comparison purpose, the model molecule, formed by a single photochromic moiety (benzo-[2H]-chromene) and a 2-methoxy-naphthalene group, joined through an ethenic bridge (CHR–NPh) was also investigated. In bis-CHR, the ethenic bridge is between two 3,3-diphenyl-[3H]-naphtho[2,1-b]pyran units in the 5 position and in SPO–CHR the ethenic bridge joins the 5 position of chromene to the 5' position of spirooxazine.

The open-coloured forms (*ortho*-quinoneallide structure), derived from chromenes, absorb at shorter wavelengths compared with spirooxazines. The photoreaction often yields two coloured photoproducts, instead of one, which exhibit different thermal and/or photochemical reactivity [3,6–8].

This investigation was aimed at obtaining information on the photokinetic behaviour of these molecules, also in

\* Corresponding author. Fax: +390-75-585-5598.  
E-mail address: favaro@phch.chm.unipg.it (G. Favaro).

comparison with the previously investigated spirooxazine-derived bichromophoric compound [5], and at gaining more insights into the photo and thermal dynamics of these classes of supermolecules.

Spectrophotometry and high performance liquid chromatography (HPLC) analyses were used to follow the formation of products under irradiation and in the dark. The quantum yields of photoreactions, kinetic parameters of thermal reactions and absorption coefficients of the photoproducts were obtained. By using monochromatic visible light for irradiation, the quantum yields of the photobleaching processes were also determined.

The photo-behaviour of these molecules was found to be more complicated than that of the spirooxazine bichromophoric molecule [5]. Even in those cases, thermal reversibility was not operative at room temperature, while a slow photobleaching to the starting material, accompanied by side-products, was observed. The lack of thermal reversibility and partial degradation make them unsuitable for applications as classical photochromes. Their study is anyway worthwhile because they are interesting compounds from the point of view of the basic research.

## 2. Experimental

### 2.1. Materials

The super-molecules studied here were firstly synthesised by Chamontin [9] and resynthesised for the purpose by one of us (Levi [10]). Their stereochemistry around the ethenic bridge is mainly *Z* ( $\approx 90\%$ ) and was checked by  $^1\text{H}$  NMR spectrometry [11]. The formula of the three compounds investigated are represented in Scheme 1. All measurements were carried out in toluene (Uvasol Fluka), used without further purification.

### 2.2. Apparatus and analytical methods

A Perkin-Elmer Lambda 16 spectrophotometer and a Hewlett-Packard 8453 diode array spectrophotometer were used for recording the absorption spectra and following

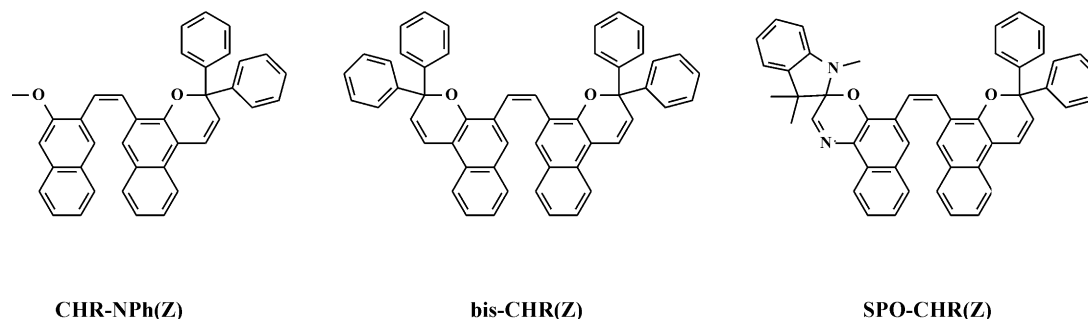
their time-evolution under irradiation and in the dark. The irradiation was carried out using a 150 W Xe lamp filtered by a Jobin–Yvon H10 UV monochromator at a right angle to the monitoring beam, using a fiber-optic system. The spectral evolution with time of toluene solutions containing the bichromophoric molecules ( $10^{-4}$  mol dm $^{-3}$ ) was followed under irradiation up to photostationary state attainment. Then, exposure to UV light was discontinued in order to control whether some thermal bleaching occurred. The rate constants of the thermal processes were determined from the first-order decay kinetics of the absorbance of each species at appropriate wavelengths.

The photobleaching reaction, induced by irradiating the thermally equilibrated solution with visible light, was kinetically followed. The kinetic analyses were carried out following spectrophotometrically the absorbance changes at the maximum of the colour-bands. HPLC was applied for the analysis and separation of the thermostable products using more concentrated toluene solutions (ca.  $10^{-3}$  mol dm $^{-3}$ ) and acetonitrile or a 95/5 (v/v) acetonitrile/water mixture as the eluent. The apparatus was a Waters 600E chromatograph coupled with an HP 3390A integrator and a spectrophotometric detection. The column was a Waters C18 Symmetry for analytical purposes. An Oxford Instruments cryostat was used for the temperature control.

### 2.3. Quantum yield and molar absorption coefficient determinations

The reaction quantum yields were determined from the absorbance/time curves, using various photokinetic approaches. Potassium ferrioxalate actinometry was used for determining the radiation intensity (typically, of the order of  $10^{-7}$  Einstein dm $^{-3}$  s $^{-1}$  at the wavelength of irradiation).

The molar absorption coefficients ( $\epsilon$ ) of most of photoproducts were determined by using the ratios of the peak area from HPL chromatograms, to obtain the concentrations, and the spectra recorded at the HPLC injection. The occurrence of thermal bleaching during elution was taken into account when necessary. This method clearly implies a significant uncertainty on the  $\epsilon$  values, that could be estimated about  $\pm 15$ –20%.



Scheme 1.

### 3. Results and discussion

#### 3.1. Bis-CHR and CHR-NPh

Like most of chromenes, which generally give rise to various photoproducts [3,6–8], the photo-behaviour of these molecules is more complex than that of compounds containing only the spirooxazine moiety.

The involvement of photochemical and thermal intermediates before photostationary state attainment and slow photobleaching with partial recovery of the starting closed species are common features in the photochemistry of these molecules.

Initially, the spectral changes of bis-CHR under UV irradiation mainly occurred in the 500 nm region giving rise to a characteristic, structured spectrum (Fig. 1, curve 2), that will be called “photochemical intermediate”, PI. For longer irradiation times of the bis-CHR solution, the absorbance also increased at 440 nm as well in the near UV region ( $\lambda_{\text{max}} = 354$  nm), attaining a photostationary state (Fig. 1, spectrum 4) with disappearance of PI. An apparently similar spectral change, consequent to PI photoproduction, was also observed when the briefly irradiated solution was kept in the dark (Fig. 1, spectrum 3).

These steps were also followed by HPLC. A briefly irradiated solution substantially showed only the peaks of the starting molecule and of PI. This solution, kept in the dark, did not show any change in the bis-CHR peak, while PI decreased and, instead, a new thermally stable compound (T) increased up to total consumption of PI; thus, finally, the thermally equilibrated solution contained unaltered bis-CHR and T (ca. 20%). The rate of the thermal step is  $k_{\text{PI} \rightarrow \text{T}} = 6.7 \times 10^{-4} \text{ s}^{-1}$ . Looking at the spectral features (Fig. 1, spectrum 3), the two absorption bands at 444 and 354 nm are assigned to T. If UV irradiation is carried out continuously, the HPLC chromatograms show that the photochemistry proceeds with consumption of bis-CHR, through PI formation. Beside T, two additional species are formed un-

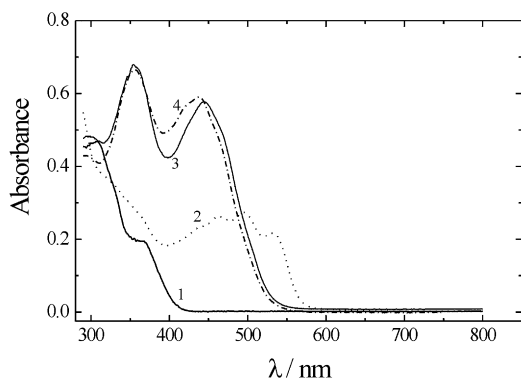


Fig. 1. Photochemistry of bis-CHR under UV irradiation in toluene,  $c = 2 \times 10^{-5} \text{ mol dm}^{-3}$ . Absorption spectrum: (1) before irradiation; (2) after 8 min irradiation (PI); (3) solution (2) kept over one night in the dark (T); (4) solution (2) UV irradiated up to photostationary state attainment (T + A + B) (see text).

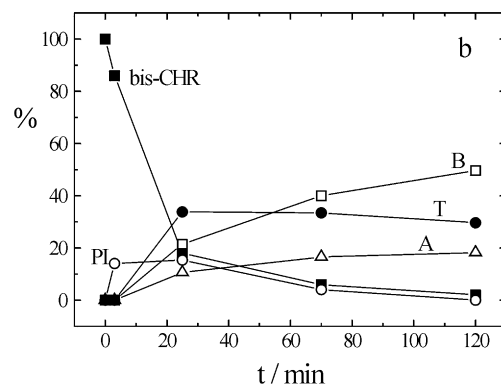
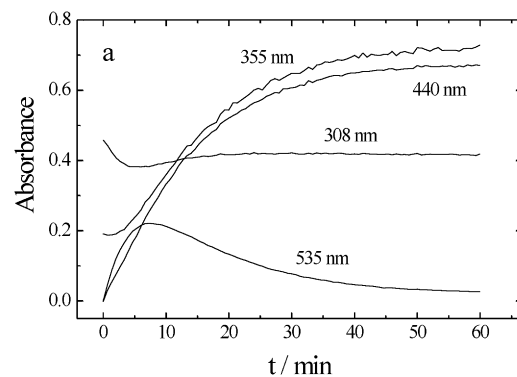


Fig. 2. (a) Spectrophotometric kinetics under UV irradiation of bis-CHR in toluene followed at wavelengths where PI prevails (535 nm), where T prevails (355 and 440 nm) and at a quasi isobestic point (308 nm); (b) HPLC analysis during irradiation of bis-CHR in toluene: (■) bis-CHR; (○) photochemical intermediate, PI; (●) thermal product, T; (△) photoproduct A; (□) photoproduct B.

der irradiation, A and B, and their amounts increase up to total consumption of both bis-CHR and PI. Thus, it can be established that all processes originate from the primarily photoproduct PI. The time-evolution with irradiation of the spectrum at different wavelengths and of the HPLC peaks is shown in Fig. 2. At the photostationary state attained under UV irradiation, the solution contains T (~30%), A (~20%) and B (~50%). The three species were separated by HPLC and their absorption spectra recorded. The spectra of the individual species are shown in Fig. 3. The similarity of the spectra obtained justifies the scarce spectral changes found after thermal-stationary state (Fig. 1, spectrum 3) and photostationary state (Fig. 1, spectrum 4) attainment and suggests that the three species, A, B and T are structurally similar. All spectra undergo slow thermal evolution: the thermal product derived from A and B is clearly the same.

The molar absorption coefficient and formation quantum yield of PI were determined using a photokinetic method [12], assuming that initially only this species absorbs at 535 nm. This is a reasonable assumption in the light of the HPLC results. The kinetic equation for PI formation, in terms of time-dependence of the PI absorbance ( $A_{\text{PI}}$ , 1 cm

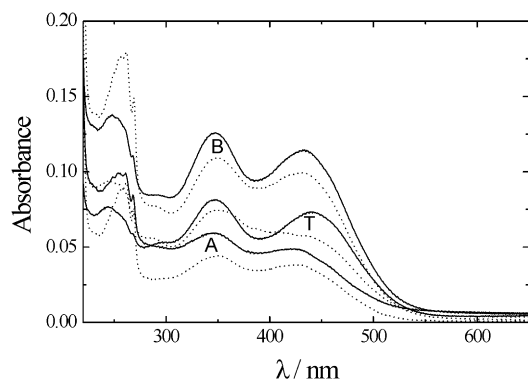


Fig. 3. Absorption spectra, recorded after HPLC separation of the photoproducts obtained from a toluene solution of bis-CHR (full lines) and after 3-day thermal evolution (dotted lines).

path) at the analysis wavelength (535 nm), is given by Eq. (1), if the thermal conversion to T ( $k_{PI \rightarrow T}$ ) is assumed to be the main decay path.

$$\frac{dA_{PI}}{dt} = \varepsilon_{PI} \Phi I^0 F \varepsilon_{bis-CHR} C_0 - (\Phi I^0 F \varepsilon_{bis-CHR} + k_{PI \rightarrow T}) A_{PI} \quad (1)$$

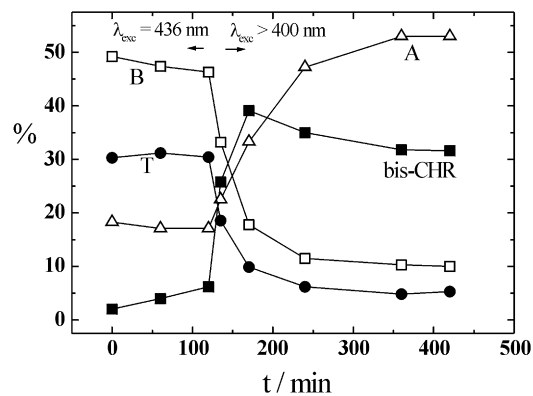
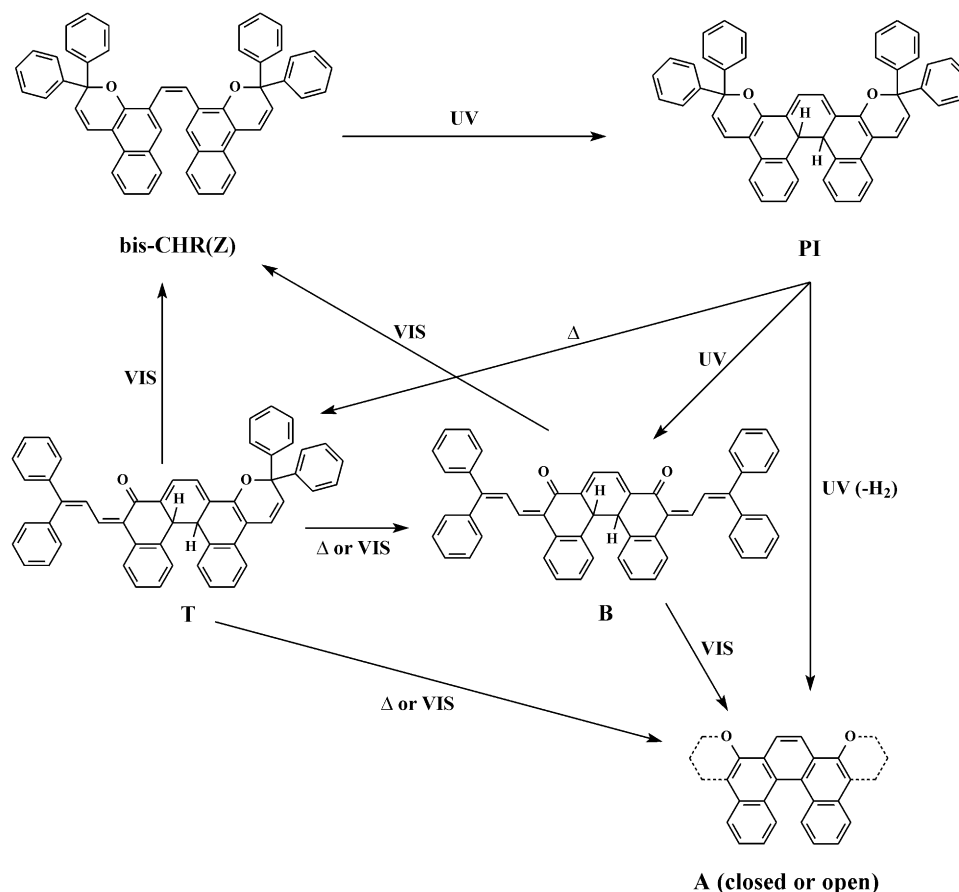


Fig. 4. Photobleaching kinetics of bis-CHR followed by HPLC analysis: (■) bis-CHR; (●) thermal product T; (△) photoproduct A; (□) photoproduct B. The first three points (120 min) were recorded under monochromatic irradiation ( $\lambda = 436$  nm) while the successive points were recorded by using the whole visible light (cut-off at  $\lambda < 400$  nm) emitted by the Xe lamp.

In Eq. (1),  $\varepsilon_{PI}$  ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) is the molar absorption coefficient of PI at the analysis wavelength,  $\Phi$  the quantum yield of the photoreaction,  $I^0$  the intensity of the monochromatic excitation light ( $\lambda_{exc} = 366$  nm) per time unit ( $\text{Einstein dm}^{-3} \text{s}^{-1}$ ),  $\varepsilon_{bis-CHR}$  the bis-CHR molar absorption



Scheme 2.

coefficient at  $\lambda_{\text{exc}}$ ,  $C_0$  the bis-CHR analytical concentration and  $F = [1 - \exp(-2.3A')]/A'$  represents the photokinetic factor ( $A'$  is the total absorbance at  $\lambda_{\text{exc}}$ ), which accounts for the variation of the absorbed fraction of the total incident light,  $I = I^0[1 - \exp(-2.3A')]$  during the reaction course [12–14]. The photokinetic factor is rigorously a time-independent parameter only if irradiation is carried out on, or near to, an isosbestic point in the absorption spectra of the colourless and the coloured forms. Under our experimental conditions ( $\lambda_{\text{exc}} = 366 \text{ nm}$ ), the absorbed light did not appreciably change during PI formation and  $F$  could be considered as a time-independent parameter. Thus, the plot of  $dA_{\text{PI}}/dt$  vs.  $A_{\text{PI}}$ , is a straight line. The  $\Phi$  value (0.23) could be obtained from the slope, while the  $\varepsilon_{\text{PI}}$  value was determined from the  $\Phi\varepsilon_{\text{PI}}$  product given by the intercept.

The photostationary solution, which was stable in the dark, slowly reacted when exposed to monochromatic visible light ( $\lambda_{\text{exc}} = 436 \text{ nm}$ ). The quantum yield of the photobleaching (referred to T,  $\Phi_{-T} = 7 \times 10^{-4}$ ) was determined at 500 nm at low conversion percentage, using the kinetic equation (2),

$$-\frac{dA_{\text{T}}}{dt} = \varepsilon_{\text{T}}\Phi_{-T}I^0(1 - 10^{-A'_{\text{T}}}) \quad (2)$$

where  $A_{\text{T}}$  and  $\varepsilon_{\text{T}}$  are the absorbance and molar absorption coefficient at the analysis wavelength,  $I^0$  the intensity of the monochromatic light at the excitation wavelength, where the absorbance is  $A'_{\text{T}}$ . Based on Eq. (2), from the linear plot of  $-dA_{\text{T}}/dt$  vs.  $10^{-A'_{\text{T}}}$ ,  $\varepsilon_{\text{T}}\Phi_{-T}I^0$  was obtained from both the intercept and the slope. The excellent correspondence of the two values supports the reliability of the results.

Prolonged irradiation with polychromatic visible light (cut-off at 400 nm) partially recovered the starting supermolecule ( $\approx 32\%$ ) along with an increased amount of A ( $\approx 53\%$ ), while B was reduced to 10% and T to 5% (Fig. 4).

The vibronically resolved PI spectrum is typical of rigid, conjugated structures. Based on the hypothesis, put forward in the case of bis-SPO [5], that photocyclisation occurred at the central double bond [15], PI could be assigned to the centrally cyclised closed form. The latter has a dihydrophenanthrene-type structure (DPh) and is formed by the electrocyclic photoreaction which is typical of *cis*-diarylethenes [17].<sup>1</sup> Its marked stability, related to extended conjugation, prevents thermal bleaching to occur. However, since the DPh formation is thermally activated, experiments carried out at low temperature led to normal behaviour, by-passing the central cyclisation.

The thermal product T, which slowly photobleaches upon visible irradiation, could result from opening of one of the side rings, while A and B correspond to opening of both the chromene rings, one in the DPh form (B), the other in the oxidised form (A). Based on the results of the spectrophotometric and kinetic analysis, the reaction mechanism proposed, Scheme 2, accounts for all experimental findings.

<sup>1</sup> For review article, see [16].

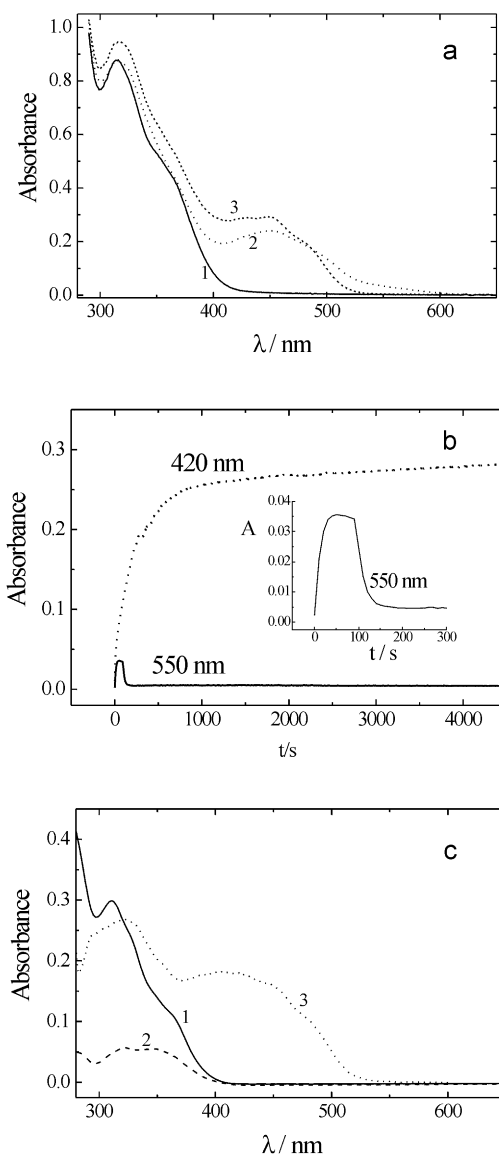
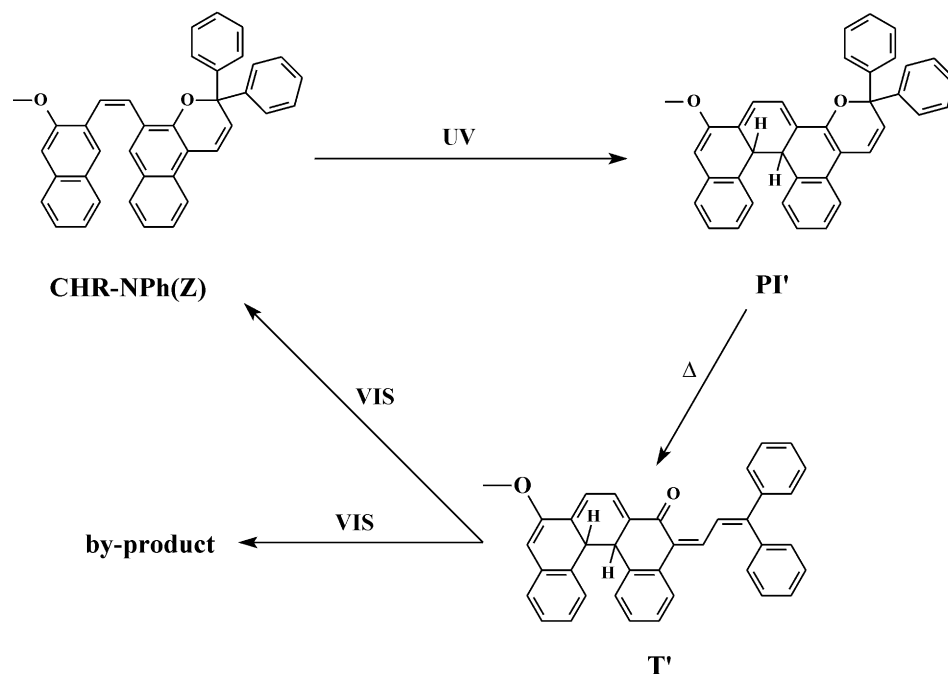


Fig. 5. (a) Absorption spectra obtained during UV irradiation of CHR–NPh in toluene: (1) before irradiation; (2) after 1 min irradiation (PI'); (3) after 1 h and 30 min in the dark, T'; (b) thermal kinetics of the UV-irradiated CHR–NPh solution followed at two wavelengths. Insert: zoomed kinetics at 550 nm; (c) spectra obtained by HPLC separation from a toluene solution of CHR–NPh: (1) main compound present in the initial sample; (2) minor compound; (3) product T'.

In bis-CHR, the initial chromatogram showed no trace of other species that could be assigned to the *trans*-geometric isomer. In CHR–NPh, an additional component was present in consistent amount (11%). UV irradiation (300 nm) did not affect the minor component, while the principal one, probably the *cis*-isomer, decreased yielding a photochemical intermediate, PI', similarly to bis-CHR. In this case, PI' was only revealed by spectrophotometric analysis (Fig. 5a, spectrum 2) since its thermal decay to a stable form (T', Fig. 5a, spectrum 3) was too fast ( $k_{\text{PI}' \rightarrow \text{T}'} = 5.3 \times 10^{-2} \text{ s}^{-1}$ ) to allow HPLC detection. The spectrophotometric kinetics, shown in Fig. 5b, indicate a continuous absorbance increase



at 420 nm, where both PI' and T' absorb, while at 550 nm, where only PI' absorbs, the absorbance first increases and then decreases. The quantum yield of formation of PI' and its thermal decay rate were determined at 550 nm (see Fig. 5b, insert). The spectra of the compounds obtained by HPLC separation from the initial sample and that of T' are shown in Fig. 5c. Given the region where they absorb, PI' and T' can be reasonably identified as cyclised and/or open forms,

while the species which are present in the non-irradiated sample are the closed *cis*-form and a minor impurity (see NMR [11]).

Photobleaching occurred upon irradiation with visible light; the spectrum of the bleached solution showed another product, possibly the *trans*-isomer, in significant amount, even though the original *cis*-isomer should be formed as well. Further support to this interpretation is given by the

Table 1

Spectral and photochemical parameters for bis-CHR and CHR-NPh: wavelengths and molar absorption coefficients of the maxima of the coloured metastable forms and quantum yields of the photocoloration and photobleaching processes

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Colour-forming	Thermal ( $k$ ) and photochemical ( $\Phi$ ) colour-bleaching
Bis-CHR				
PI	440	18300	$\Phi = 0.23$	$k_{\text{PI} \rightarrow \text{T}} = 6.7 \times 10^{-4} \text{ s}^{-1}$
	464	21500		
	495	24100		
	535	20000		
T	354	31500	$\Phi_{-\text{T}} = 7 \times 10^{-4}$	
	444	33800		
A	347			
	426			
B	348			
	435			
CHR-NPh				
PI'	450	12500	$\Phi \sim 1$	$k_{\text{PI}' \rightarrow \text{T}'} = 5.3 \times 10^{-2} \text{ s}^{-1}$
T'	322	22700		
	428	13600		
	450	13400		
	480(sh)	9100	$\Phi_{-\text{T}'} = 5 \times 10^{-3}$	

HPLC analysis, carried out during the photobleaching reaction, which showed that visible irradiation leads to the starting material as the main product. In conclusion, as for bis-CHR, the photochemistry proceeds starting from the photochemical intermediate. The proposed reaction mechanism is illustrated in Scheme 3.

The spectral, photochemical and kinetic parameters of these two molecules are reported in Table 1. It can be observed that the quantum yield of formation of the intermediate PI' is rather high, compared with those found for similar molecules. However, this value must be taken with caution since its uncertainty may be as large as 30% in such a system where the photoproduct undergoes fast thermal transformation and the measurements had to be done in a low absorbance region (550 nm) to avoid overlapping of the spectra of PI' and T' (see Fig. 5b, insert).

### 3.2. SPO-CHR

Two compounds (86 and 14%, respectively), both absorbing in the UV region, were isolated from the synthesised sample of SPO-CHR by HPLC separation; they probably are the two *cis*- and *trans*-geometric isomers of SPO-CHR in the closed form. They did not directly interconvert upon UV irradiation ( $\lambda_{\text{exc}} > 300$  nm), while photocoloration occurred in two steps: a fast photochemical step and a slower

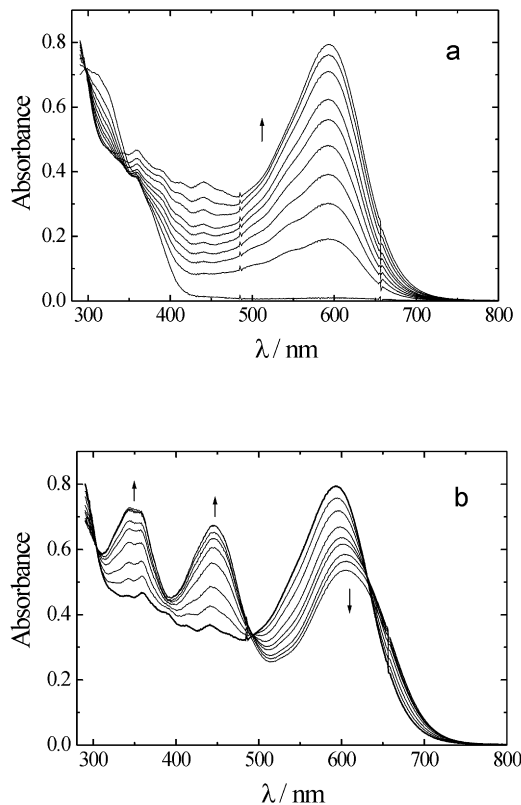


Fig. 6. Time evolution of the spectra of SPO-CHR in toluene: (a) under steady irradiation (10 min total,  $\lambda_{\text{exc}} = 329$  nm), prevalent PI'' absorption; (b) final solution of (a) during 40 min further irradiation or in the dark.

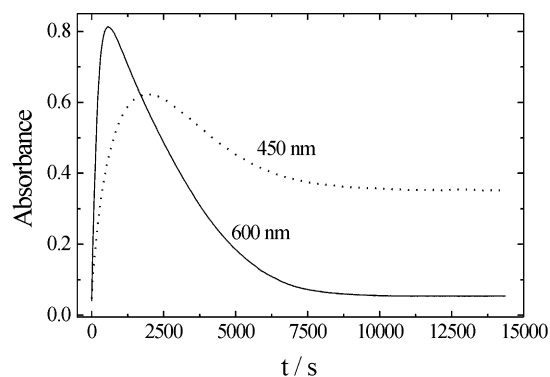


Fig. 7. Kinetics of the photoreaction of SPO-CHR in toluene under UV irradiation at two monitoring wavelengths.

thermal step. The results illustrated in Fig. 6 refer to 329 nm excitation, a wavelength corresponding to a quasi isosbestic point in the spectra of the briefly irradiated solutions.

The spectra (Fig. 6a) and kinetics (Fig. 7), after a short irradiation time, show a different time-evolution by changing the analysis wavelength. A fast absorbance increase was initially observed at 600 nm (typical of the SPO moiety) and a slower one at 450 nm (typical of CHR or the cyclised molecule). Upon longer irradiation times (40 min), a new band appeared at 350 nm and the absorbance increased around 450 nm, while the absorption band at longer wavelengths decreased in intensity and shifted to the red (Fig. 6b). At this point, the spectrum is characterised by three well-defined absorption bands, at 343–352 nm (two peaked), 447 and 614 nm. This second step is exclusively thermal, since it also occurred at the same rate ( $k_{\Delta} = 4 \times 10^{-4} \text{ s}^{-1}$ ) when irradiation was discontinued after the first step and the solution was kept in the dark. HPLC separation showed that the three bands belong to the same photoproduct. After thermal equilibration, the major component of the starting sample was reduced to 82%, the remaining was constituted by the minor component (14%) and one coloured product (4%). In Fig. 8, the spectra of the three species, separated by HPLC, are shown.

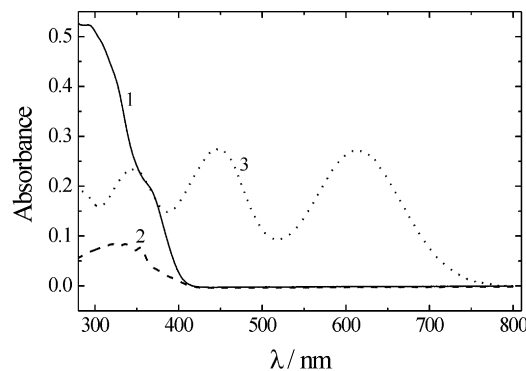
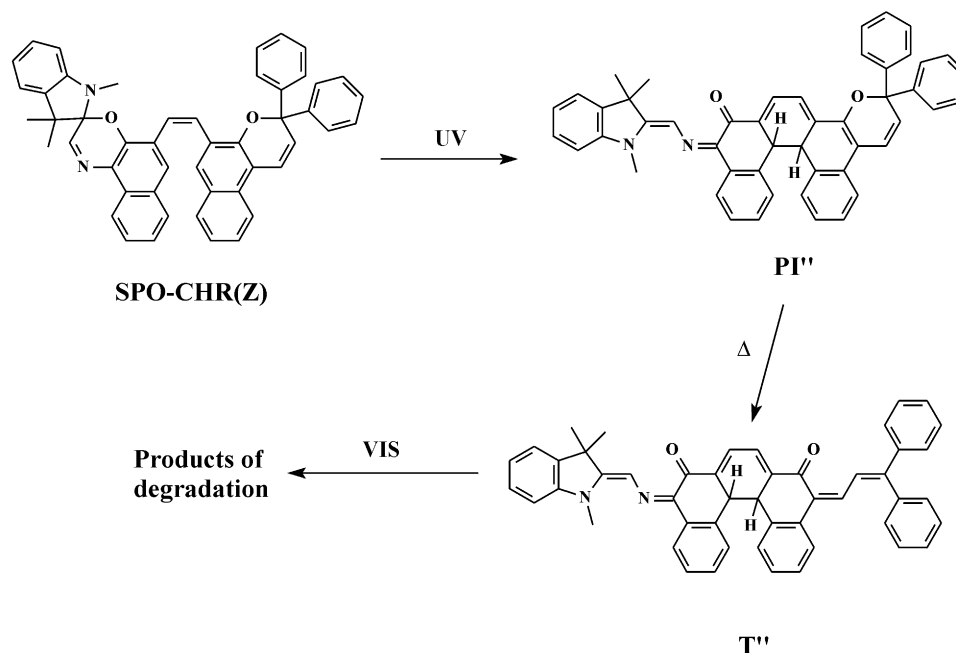


Fig. 8. Spectra obtained by HPLC separation from a toluene solution of SPO-CHR: (1) main compound present in the initial sample; (2) minor compound; (3) thermal product (T'').

Table 2

Spectral and photochemical parameters for SPO–CHR: wavelengths and molar absorption coefficients of the maxima of the coloured forms and quantum yields of the photocolouration and photobleaching processes and rate of the thermal formation of T

	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Colour-forming	Thermal ( <i>k</i> ) and photochemical ( $\Phi$ ) colour-bleaching
SPO–CHR				
PI''	593	52100	$\Phi = 0.1$	$k_{PI'' \rightarrow T''} = 4 \times 10^{-4} \text{ s}^{-1}$
T''	606–614	35200		$\Phi_{-T''} = 4 \times 10^{-3}$
	447	35600		
	347	30400		



Scheme 4.

Prolonged irradiation produced complete fading in the 600 nm region, but not at shorter wavelengths. It is worth noting that  $\lambda_{\text{exc}}$  is strongly absorbed by photoproducts that are likely to undergo photobleaching. Further irradiation at longer wavelength (500 nm) caused a spectral blue shift, without any recovery of the starting material, accompanied by extended degradation, as also shown by HPLC analysis. Undetectable back formation of SPO–CHR was unexpected in view of the results obtained with the other compounds.

Some spectral and kinetic parameters are reported in Table 2. A tentative reaction mechanism is proposed in Scheme 4. Based on Scheme 4, the SPO moiety is easily opened as the photocyclisation occurs (fast process in Fig. 7), while the thermal CHR opening follows slowly. The initially formed photoproduct, P'', is thermally unstable and yields T'', which is stable and could be separated by HPLC. Prolonged irradiation with visible light produced degradation compounds.

#### 4. Conclusions

As pointed out for the bichromophoric molecule derived from spiro[indoline-naphthoxazine] (bis-SPO) and its model molecule (SPO–NPh), the photokinetic behaviour of these supermolecules markedly differs from that of the free components. The systems are no more reversible, therefore they cannot work as classical photochromes. The compounds previously investigated [5], only containing the SPO photochromic moiety, showed a clean photocolouration process and slow irreversible photobleaching, without participation of thermal steps in the reaction mechanism at room temperature.

The photochemistry of the compounds investigated here, which contain one or two chromene units, is characterised by primary formation of a coloured intermediate. This intermediate evolves in the dark leading to a thermal-stationary state. The intermediate is more stable in the molecules containing two photochromic moieties (bis-CHR and



CHR–SPO), while the thermal decay of PI' (photochemical intermediate from CHR–NPh) is about two orders of magnitude faster than those of PI and PI'. Therefore, PI' could be hardly detected spectrophotometrically while it was wholly undetectable by HPLC.

Visible photobleaching of the thermally equilibrated solutions leads to prevalent degradation in CHR–SPO, similarly to the previously studied bis-SPO and SPO–NPh [5], while significant back-formation of the starting material is observed for CHR–NPh and bis-CHR.

The common, peculiar behaviour of all the bichromophoric molecules investigated, which was put forward in this and in a previous paper [5], is the competition of the central double bond reactivity with the side photochromic moiety reactivity. The main difference between spirooxazine and chromene containing compounds is the different opening rate, which is faster for the photochromic SPO moiety, not allowing the cyclised intermediate to be detected in bis-SPO. This view is supported by the behaviour of the mixed compound SPO–CHR, where the SPO moiety is open in the primarily formed intermediate (centrally cyclised), while the opening of the chromene moiety occurs in a successive thermal step.

The assignment of irreversibility to the reactivity of the ethenic double bond is supported by the reversible behaviour of systems where the photochromic moieties are joined through a flexible (as an ester bridge) or a rigid (as an acetylenic bridge) spacer [10].

### 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.

### References

- [1] R. Guglielmetti, in: H. Dürr, H. Bouas-Laurent (Eds.), *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, 1990, p. 314 (Chapter 8).
- [2] J.C. Crano, R.J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Vols. 1/2, Plenum Press, New York, 1998–1999.
- [3] B. Van Gemert, in: J.C. Crano, R.J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Vol. 1, Plenum Press, New York, 1998, p. 111 (Chapter 3).
- [4] J. Kolc, R.S. Becker, *J. Phys. Chem.* 71 (1967) 4045.
- [5] F. Ortica, D. Levi, P. Brun, R. Guglielmetti, U. Mazzucato, G. Favaro, *J. Photochem. Photobiol. A* (2000).
- [6] G. Favaro, U. Mazzucato, G. Ottavi, R.S. Becker, *Mol. Cryst. Liq. Cryst.* 298 (1997) 137.
- [7] G. Ottavi, G. Favaro, V. Malatesta, *J. Photochem. Photobiol. A* 115 (1998) 123.
- [8] G. Favaro, A. Romani, R.S. Becker, *Photochem. Photobiol.* 72 (2000) 632.
- [9] K. Chamontin, Ph.D. Thesis, Université de la Méditerranée, Marseille Luminy, France, 1997.
- [10] D. Levi, Ph.D. Thesis, Université de la Méditerranée, Marseille Luminy, France, 2000.
- [11] G. Vermeersch, et al., unpublished results.
- [12] G. Ottavi, F. Ortica, G. Favaro, *Int. J. Chem. Kin.* 31 (1999) 303.
- [13] A. Bar, G. Gauglitz, *J. Photochem. Photobiol. A* 46 (1989) 15.
- [14] B. Borderie, D. Lavabre, J.C. Micheau, J.P. Laplante, *J. Phys. Chem.* 96 (1992) 2953.
- [15] M. Irie, in: J.C. Crano, R.J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Vol. 1, Plenum Press, New York, 1998 (Chapter 5).
- [16] K.A. Muszkat, *Top. Curr. Chem.* 88 (1979) 91.
- [17] M. Irie, *Chem. Rev.* 100 (2000) 1685.