

Photobehaviour of *Z*-1,2-di-(3'-methoxynaphth-2'-yl)ethene as model compound of biphotochromic supermolecules with *Z*-ethenic bridge

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ABSTRACT. This work is part of a research project aimed at investigating the behaviour of biphotochromic supermolecules where two photochromic units of the spirooxazine or chromene series are linked through a conjugated or unconjugated spacer. Preliminary investigations showed that the compounds with ethane, acetylene or ester bridges behave as classical photochromes while those with an ethene bridge showed good coloration accompanied by unusual thermal irreversibility at room temperature. The temperature effect on the spectral behaviour allowed such irreversibility to be explained by the occurrence of a cyclization process at the central ethene bond, typical of *Z*-diarylethenes. To better understand this photobehaviour, a deep investigation of a model molecule, *Z*-1,2-di-(3'-methoxynaphth-2'-yl)ethene, was carried out. This paper reports the results obtained on the model molecule and two biphotochromic systems containing benzo-chromene and spirooxazine units.

1. INTRODUCTION

Spiropyran, spirooxazines and chromenes have been largely investigated in the last decades because of their photochromic reactions which make them potentially suitable for different applications [1]. To increase colorability or tune the chromatic properties of these systems, a great number of substituted molecules have been synthesised and kinetically studied. The present work is part of a research project aimed at designing molecular structures containing two photochromic moieties (spirooxazine or chromene) linked through different molecular spacers thus leading to biphotochromic supermolecules [2, 3]. The final aim of this project is to find suitable compounds whose photocoloration is more intense with respect to compounds with only one photochromic unit and extends to the entire visible spectrum. Recently, some new compounds have been synthesised bearing rigid and flexible spacers (ethene, acetylene, ethane, ester). Those with the ethene bridge showed good coloration accompanied by unusual thermal irreversibility at room temperature. Under visible irradiation, decoloration, leading partially to the starting material, was observed, accompanied by extended degradation. On the basis of the temperature dependence of the spectral behaviour [2, 3] and of NMR measurements [4], the absence of thermal reversibility was explained by the occurrence of an electrocyclization process, typical of *Z*-1,2-diarylethenes [5]. To better understand such behaviour, this paper deals with a detailed photokinetic study of the model compound, *Z*-1,2-di-(3'-methoxynaphth-2'-yl)ethene (*Z*-DMNE). This compound was found to follow the known behaviour of several

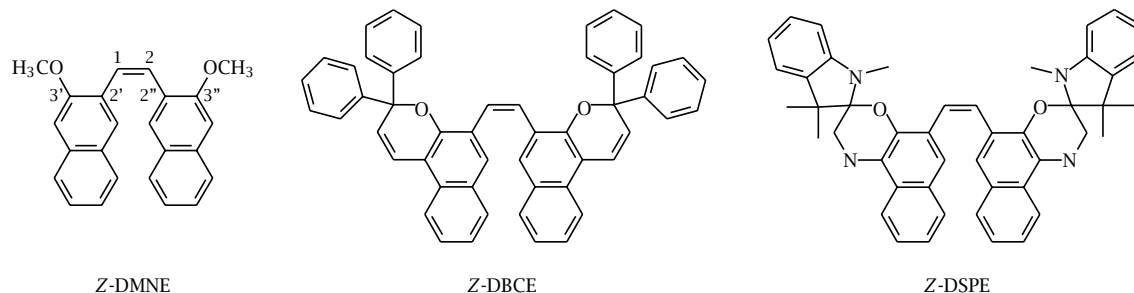
Z-diarylethenes giving parallel photocyclization to a phenanthrene-type product and photoisomerization to the *E* isomer. The results obtained were usefully compared with those obtained for compounds where the *Z*-ethenic bridge joins two photochromic benzo-[2H]-chromene moieties (*Z*-DBCE) or two spirooxazine moieties (*Z*-DSPE).

2. EXPERIMENTAL

The model molecule DMNE was prepared by a Wittig reaction, as described elsewhere [2]. HPLC analysis showed the presence of a mixture of 76% *Z* and 24% *E*. The photochromic compounds (Scheme 1) were prepared for previous works [2, 3]. Also in this case, according to NMR information [2, 4], the closed molecules are mainly present in *Z* geometry. HPLC analysis showed a weak peak (*ca.* 8.5% for DSPE), slightly increasing under UV irradiation, probably indicating the presence of small amounts of the *E* isomer. No evidence of the presence of *E* was found for DBCE.

The absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer. A Hewlett-Packard 8453 diode array spectrophotometer was used to analyse the time-evolution of the absorption spectra under irradiation and in the dark. The irradiation was carried out in toluene using a 75 W Xe lamp filtered by a Jobin-Yvon H10 UV monochromator.

The spectral evolution with time was followed up to photostationary state attainment. The exposure to UV light was then discontinued in order to control whether some thermal bleaching occurred. The photobleaching reaction of the thermally equilibrated solution under irradiation with visible light was followed



Scheme 1.

from the absorbance decrease at the maximum of the coloured species.

An Oxford Instruments cryostat was used for the temperature control. Further details on the experimental procedures are reported in previous papers [3].

HPLC was employed for the analysis and separation of the thermostable products after irradiation of concentrated toluene solutions (*ca.* 10^{-4} mol dm $^{-3}$) with a Xenon lamp through an interference filter (366 nm, maximum transmittance 35%) and, in some experiments, through a cut-off ($\lambda > 400$ nm). The apparatus was a Waters 600E chromatograph with spectrophotometric detection. The column was a Waters C18 Symmetry for analytical purposes. Acetonitrile or a 95/5 v/v acetonitrile/water mixture were used as eluents.

The reaction quantum yields were determined from the absorbance/time curves, by various photokinetic approaches using potassium ferrioxalate as actinometer.

The molar absorption coefficients (ϵ) 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. This method clearly implies a significant uncertainty on the ϵ values, that could be estimated with an accuracy of about ± 15 –20%.

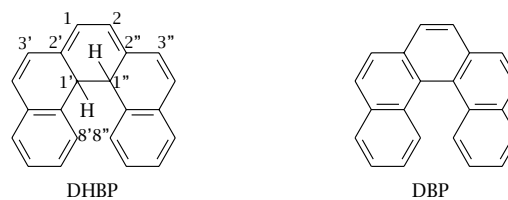
For laser flash photolysis measurements, the third harmonic (355 nm) from a Continuum Surelite Nd-YAG laser was used. The laser energy was less than 5 mJ per pulse; the time resolution was about 10 ns. The spectrophotometric analysing system was made up of a 150W Xenon source, a Baird-Tatlock monochromator blazed at 500 nm, a Hamamatsu R928 photomultiplier and a Tektronix DSA 602 digitised analyser.

3. RESULTS AND DISCUSSION

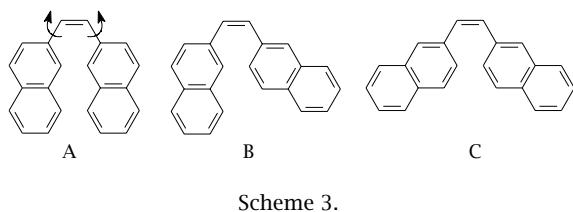
Preliminary results obtained with bichromophoric compounds bearing benzo-[2H]-chromene (BC) or spirooxazine (SP) photochromic units, linked by spacers other than ethene (such as acetylene, ethane and ester), showed a classical behaviour (photocoloration and back thermal bleaching) for the compounds BC-acetylene-

BC and SP-ester-BC and formation of two photoproducts (one thermally reversible and the other photoreversible) for the compounds BC-ethane-BC and BC-ester-BC [6]. The compounds studied in this work, having an ethene bridge, displayed a non-classical behaviour with the photoproduct(s) thermally stable for several hours or days (depending on the presence of oxygen). This unusual behaviour led us to investigate in more details the photochemistry of these ethene derivatives and to study in parallel an analogous (non photochromic) compound where the ethene bridge links two methoxy-substituted naphthyl groups, the *Z*-di-(3'-methoxynaphth-2'-yl)ethene (DMNE). The results obtained for this model molecule can be usefully compared with those obtained for the unsubstituted *Z*-1,2-di-(2'-naphthyl)ethene (DNE), whose photoisomerisation and photocyclisation have been widely investigated by various groups [5, 7–12]. Therefore, briefly summarising the photobehaviour of DNE before discussing the new results will be useful.

3.1. *Z*-1,2-di-(naphth-2'-yl)ethene. The photocyclisation of *Z*-DNE, through an allowed conrotatory electrocyclic process, is thermally and photochemically reversible and gives a sterically hindered dihydrobenzo[*c,g*]phenanthrene (DHBP, Scheme 2), stabilised by extended conjugation. The latter is characterised by a relatively strong absorption in the visible region (around 420 nm) and by the presence of two reactive hydrogen atoms, which can be removed, thermally and photochemically, in the presence of oxygen or other hydrogen acceptors leading to the oxidised product, dibenzo[*c,g*]phenanthrene (DBP, Scheme 2) [5, 7–12].



Scheme 2.



The ring-closure takes place in a stereospecific way with respect to the possible rotational conformers. In fact, *Z*-DNE exists in solution as an equilibrium mixture of three conformers (A, B, C, Scheme 3) due to the partially hindered rotation of the naphthyl groups around the single bonds with the ethenic carbons. The results of accurate investigations from different groups in the early seventies [7-9] indicated that only one of the possible conformers (A) is involved in the activated photocyclisation at room temperature (with a quantum yield $\phi_{\text{DHBP}} = 0.02$ and an activation energy of about 42 kJ mol^{-1}), probably taking place through an unstable isomeric precursor [10] (see below). However, a flash photolysis study of *Z*-DNE [9] in methylcyclohexane revealed the formation of another cyclized compound with half-life of 10^{-4} s at room temperature and a red-shifted absorption around 530 nm. This intermediate, assigned to the cyclised conformer B, namely to dihydrobenzo[b,g]phenanthrene, DHBP_B , is favoured by low temperature and high viscosity. It is undetectable at room temperature due to fast ring opening and back conversion to the starting *Z*-DNE compound. No traces of cyclisation implying the third conformer C were observed.

The photochemical ring-opening of the more stable intermediate produced by the A rotamer, DHBP_A , leads to the starting *Z* isomer with a quantum yield $\phi_Z = 0.008$ and an activation energy of 27 kJ mol^{-1} in a non-polar solvent at room temperature [9]. The thermal ring opening follows first order kinetics at a rate strongly dependent on temperature (the activation energy is 97 kJ mol^{-1} in hexane) [8].

The relatively high value (42 kJ mol^{-1}) of the activation energy for photocyclisation of *Z*-DNE leads to a remarkable sharp decrease of its quantum yield with temperature, the formation of DHBP_A being practically inhibited below -30°C . The half-life time of the cyclised compound at room temperature is rather long in the dark and in the absence of oxidants ($t_{1/2} = 36.8 \text{ days}$) [8]. It obviously depends on the rates of thermal and photochemical ring opening and of oxidation to DBP.

3.2. *Z*-1,2-di-(3'-methoxy-naphth-2'-yl)ethene.

After UV irradiation of the synthesized DMNE, four peaks were obtained by HPLC analysis. The corresponding four products were separated and characterised spectrophotometrically. Their absorption spectra in

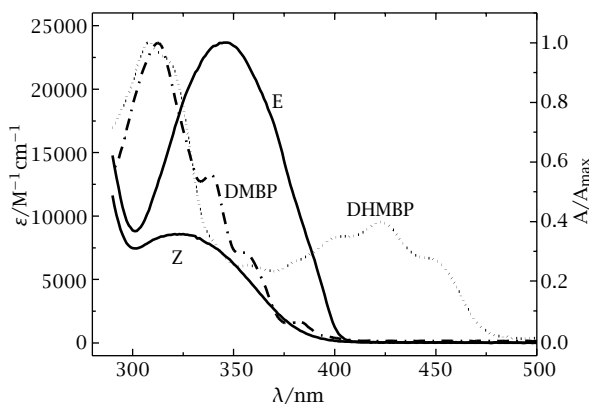
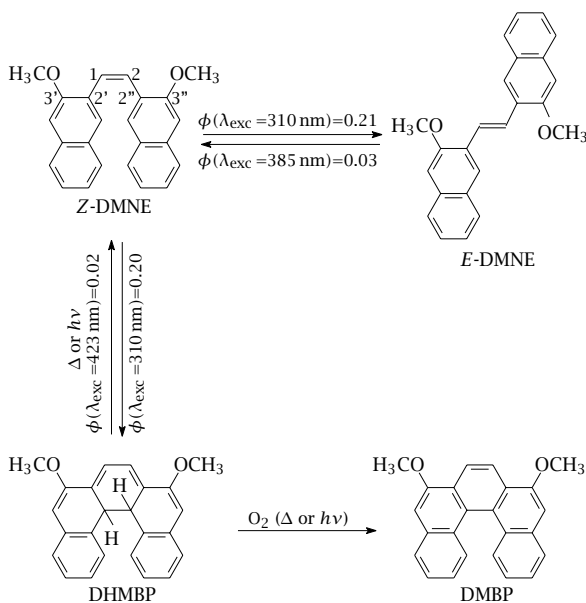


Figure 1. Absorption spectra of E and Z isomers of 1,2-di-(3'-methoxynaphth-2'-yl)-ethene (full line, left hand side) and normalized absorption spectra of the dihydrocyclized compound DHMBP (dot) and its oxidation product DMBP (dash-dot) in toluene.

toluene are shown in Figure 1. The quantitative spectra (full line) are assigned to the E and Z isomers, the normalised ones to the cyclised intermediate, dihydro-methoxybenzo[c,g]phenanthrene (DHMBP) and its final oxidation product (DMBP) (Scheme 4). Also with this methoxy-substituted compound, only the cyclised compound corresponding to the A conformer was observed. This intermediate, which is substantially stable at room temperature even in air-equilibrated solutions, displays a characteristic structured absorption band with maximum at 423 nm and a band in the UV region, at about 310 nm. As found for the unsubstituted DHBP, for which an unusually high fluorescence yield at



Scheme 4.

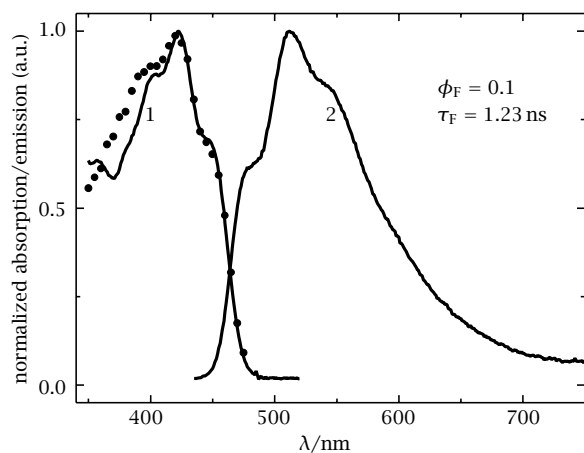


Figure 2. Normalized absorption, fluorescence emission and fluorescence excitation (dot) spectra of DHMBP in toluene.

room temperature was reported ($\phi_F = 0.5$) [9], the methoxy-substituted compound also emits (Figure 2) with a fluorescence maximum at 512 nm, a lower quantum yield ($\phi_F = 0.1$), a lifetime of 1.23 ns and a corresponding radiative parameter, $k_F = 8.1 \times 10^7 \text{ s}^{-1}$.

The 423 nm absorption band of DHMBP decreases in intensity very slowly (half-life time, $t_{1/2} = 16$ days) in deaerated solutions (by bubbling nitrogen or argon) kept in the dark. While the main product is the starting Z compound in deaerated solutions, in air-equilibrated solutions ($t_{1/2} = 8.7$ days) the oxidation product with benzophenanthrene structure is formed. Table 1 collects the spectral properties and the quantum yields of photoproduction of the DMNE isomers and the band maxima of the oxidised compound.

The quantum yields of the parallel photoreactions of Z (isomerisation to E and cyclisation to DHMBP) are comparable as well as the smaller ones of the back photoreactions of E and of the cyclised compound towards the starting Z isomer. Also with the methoxy-substituted compound, the photocyclisation of Z was found to be affected by temperature and to become inhibited at low temperature. Figure 3 shows the spectral behaviour found at room temperature and 200 K. At low temperature, the dihydro-derivative absorbing around 420 nm is no longer observable. Formation of a small amount of a photoproduct absorbing around 480 nm was instead observed (for the importance of this observation to understand the behaviour of the photochromic compounds, see below). It reconverts thermally to DHMBP, thus resembling the L precursor of DHBP_A described by Fischer and Muszkat for the DNE system [10–12]. Early observations by flash photolysis [10], followed by more recent studies with stationary methods on DNE bearing different substituents [11] and by detailed theoretical calculations [12], clearly indicated that steric hindrance brought about by disub-

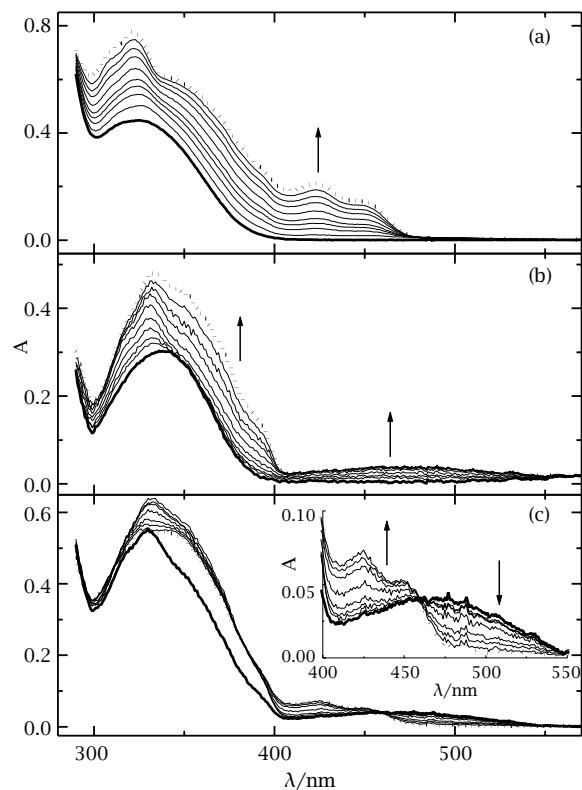


Figure 3. Time-evolution of the absorption spectrum of Z-DMNE in toluene: (a) under irradiation ($\lambda_{\text{exc}} = 310 \text{ nm}$) at room temperature; (b) under irradiation at 200 K; (c) increasing temperature (250–295 K) in the dark. Inset: visible spectral region expanded to show absorption details.

stitution at the 4 and 5 positions of Z-stilbene analogues or by benzo-annellation at the [c] and [g] bonds, as in the case of these naphthyl-derivatives, allows observation of two dihydro-intermediates [11, 12] derived from the A rotamer. They absorb in the visible region at short (S, around 420 nm) and longer (L, around 480 nm) wavelengths, respectively. S is more rigid, as indicated by the vibrationally resolved spectrum, while L shows a broad absorption spectrum. L is formed primarily but it is generally not observable at room temperature because it undergoes fast ring-cleavage towards the starting Z isomer accompanied by fast (even if activated) equilibration with S, which in turn converts to Z thermally or by visible light. At lower temperatures, below -30°C , only L is formed by irradiation of Z-DNE. It is thermally stable at this temperature and photoconverts to Z-DNE with visible light. Theoretical calculations [12] allowed the geometries of the (relatively) stable DHBP (S) and its precursor (L) to be assigned to the two minimum energy conformers, denoted as ac (“anticlinal” or “twisted”) and ap (“antiperiplanar” or “extended”), differing by the extent of planarity of the polyenic unit. The steric in-

Table 1. Absorption and fluorescence properties of the Z and E isomers of DMNE and of the products of photochemical and thermal reactions in toluene together with the quantum yields of the photoconversions involved.

Compounds	λ_{\max} /nm	$\epsilon/M^{-1} \text{ cm}^{-1}$	λ_{\max}^F /nm	ϕ_{form}
Z	325	8600	not observed	0.03 (E → Z) 0.02 (DHMBP → Z)
E	346	23700	399,423	0.21 (Z → E)
DHMBP	423,450	7300,6000	512	0.2 (Z → DHMBP)
DMBP	312,338,355,382		413,435	

teractions of L (8' – 8'' repulsion, see numeration in Scheme 2) are released in S by skeletal deformation (see Figure 7 in reference [12]) involving significant torsion about the 1' – 1'' bond accompanied by torsion about the 2' – 3' and 2'' – 3'' bonds, probably facilitated by substituents at the 3', 3'' positions, as in DMNE (next section).

Even for the methoxy-substituted DNE, the spectral and kinetic behaviour of the primary photoproduct clearly indicates that it is the L precursor (absorbing at longer wavelengths) of the more stable dihydroderivative observed at room temperature (S). Laser flash photolysis experiments allowed the L precursor to be detected even at room temperature (Figure 4). It exhibits an absorption maximum around 470 nm and decays with first order kinetics ($k = 20 \text{ s}^{-1}$), not affected by the presence of oxygen. Again, these results resemble those found by E. Fischer *et al.* for DNE by conventional flash photolysis [10, 11]. Therefore, the photochemical and thermal behaviour of DMNE (see Scheme 4) is quite similar to that summarised above for the unsubstituted compound DNE.

3.3. Z-1,2-di-(benzo-[2H]-chromene)ethene. Like most of chromenes, which generally give rise to various

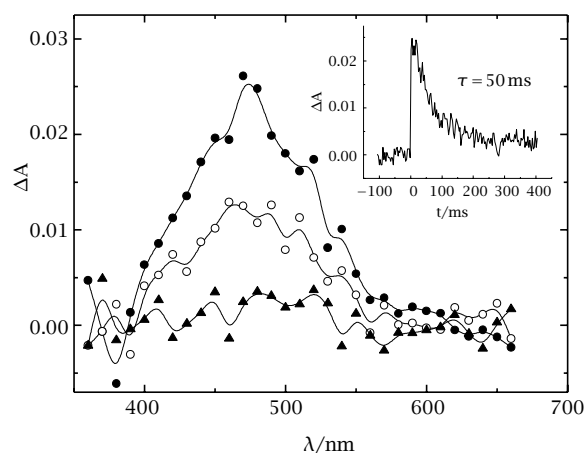


Figure 4. Transient absorption spectra obtained by laser flash photolysis of Z-DMNE in toluene ($\lambda_{\text{exc}} = 355 \text{ nm}$) at different delay times after the laser pulse: 5 ms (●●●), 59 ms (○○○) and 400 ms (▲▲▲). Inset: transient decay monitored at 480 nm.

photoproducts [13–16], the photo-behaviour of Z-DBCE is rather complex. 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.

The evolution of the system under UV irradiation ($\lambda_{\text{exc}} = 366 \text{ nm}$) was followed by spectrophotometry and HPLC. Initially, photocoloration leads to an absorption spectrum in the 500 nm region (Figure 5(a), curve 3, after 8 min irradiation), thereafter called “photochemi-

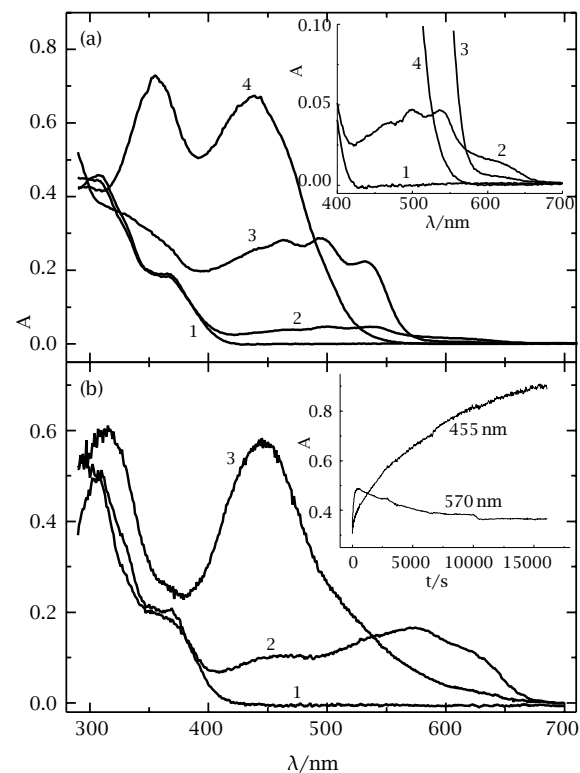
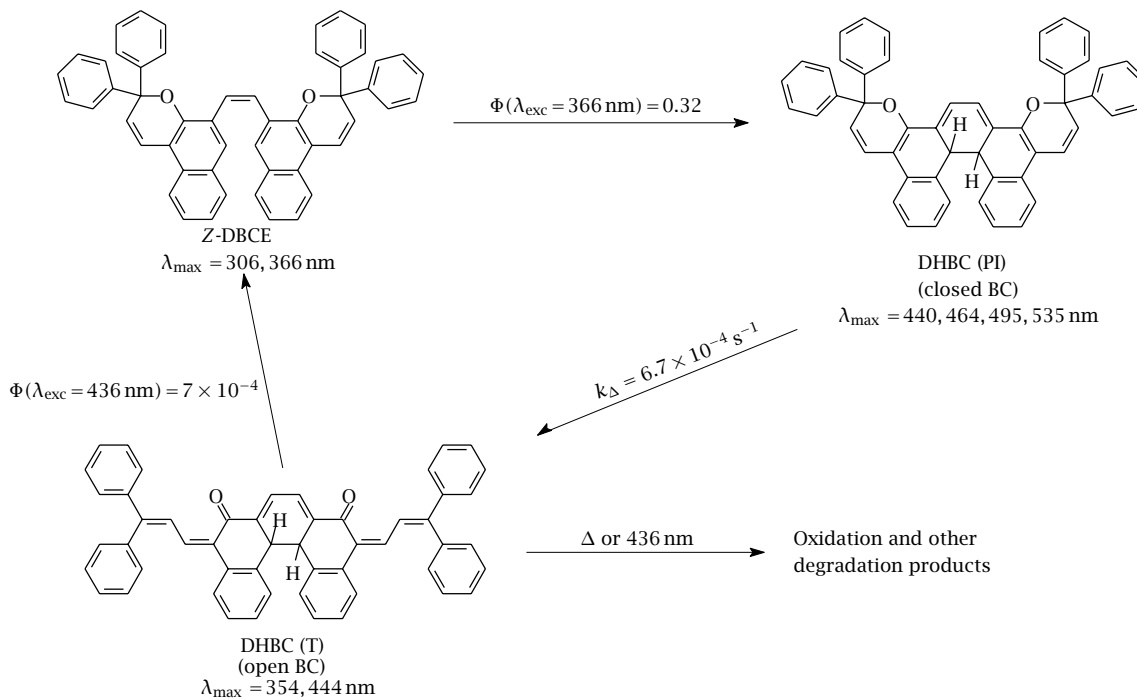


Figure 5. Photochemical ($\lambda_{\text{exc}} = 366 \text{ nm}$) and thermal reactivity of Z-DBCE in toluene. (a) at room temperature: starting compound (1); after 40 s irradiation (2); after 10 min irradiation (3) and after 2 hours in the dark (4); (b) at 200 K: starting compound (1); after 10 min irradiation (2) and after 4 hours irradiation (3). Insets: (a) visible part of the spectrum enlarged to show absorption details; (b) kinetic behaviour at different wavelengths.



Scheme 5.

cal intermediate", PI. A weak absorption at longer wavelength was also detected (see Figure 5(a), curve 2, inset). By HPLC, only one peak was observed in addition to that of the starting molecule.

For longer irradiation times, new absorption bands grow at 444 nm and in the near UV region ($\lambda_{\max} = 354 \text{ nm}$), accompanied by disappearance of PI. An apparently similar spectral change, following PI photoproduction, was also observed when the briefly irradiated solution was kept in the dark. The decrease of the PI peak was replaced by a new peak of a thermally stable compound (thereafter called T, spectrum 4 in Figure 5(a)) which increased up to total consumption of PI.

Based on the new information obtained from the study of the model molecule, PI was assigned to the cyclised dihydro-derivative (DHBC) with photochromic units still *closed*. Traces of its L precursor (see above) can be responsible for the weak bathochromic absorption noted around 600 nm . It fastly reacts to give the starting Z-DBCE and DHBC. The photochemical and thermal evolutions of the latter towards T (stable for days) correspond to the irreversible opening of the side chromene moieties to form DHBC with *open* photochromic units. Bleaching was obtained by visible irradiation (leading to the starting Z) or by thermal oxidation (leading to the dehydrogenated cyclised compound and to other degradation products).

Support to this working hypothesis came from experiments at low temperature. UV irradiation at 200 K (Figure 5(b)) led to formation of the L precursor photoequilibrated with Z (spectrum 2) and to opening of the

chromene moieties (spectrum 3) without photocyclisation at the central Z-ethene bond. Inset in Figure 5(b) shows that the two photoreactions occurred in parallel at different rates, the formation of L (monitored at 570 nm) being the fastest. By heating the solution up to room temperature, the photochromic units reversibly returned to the closed forms but the small amount of L which did not return to Z yielded the centrally cyclised DHBC with open side units. The latter remained stable for several days and is responsible for the residual coloration observed.

A simplified picture of these processes is shown in Scheme 5, where some spectral and kinetic parameters from reference [3] are also reported.

3.4. Z-1,2-di-(spirooxazine)ethene. The main reaction of DSPE under UV irradiation ($\lambda_{\text{exc}} = 373 \text{ nm}$) is the almost quantitative conversion (HPLC analysis) to coloured photoproducts with absorption bands at 446 and 613 nm . No thermal bleaching was observed, the photoproduct (one peak observed by HPLC) being stable in the dark for several days. On the basis of previous results on the single SP molecule [17, 18], NMR data [2, 4] and the present results on the model compound, the colour-forming reaction can be assigned to cyclisation at the Z-ethene bond (band at 446 nm) and opening of the spiro-bonds of the SP moieties (band at 613 nm , typical of a photomerocyanine), while the small amount of the E isomer initially present (see Experimental Section) slightly increases by low-yield Z \rightarrow E photoisomerization.

The spectral evolution and kinetics (equal rate at all wavelengths) of the colour forming process (Figure 6(a)) showed that the two bands grow at the same rate ($k = 3.3 \times 10^{-3} \text{ s}^{-1}$, under the experimental conditions used), thus indicating that the ring opening of the side photochromic moieties to give the photomerocyanine chromophore occurs practically simultaneously to the ring closing of the central ethenic bridge [3].

Upon prolonged irradiation with visible light at room temperature, the coloured solutions completely faded with a low quantum yield of about 0.001 [3]. In addition to formation of small amounts of the starting closed form, the photobleaching led to extensive decomposition, due, at least in part, to slow formation of the dehydrogenated product with phenanthrene-type structure in the air-equilibrated solutions. Also internal rotation around the ethenic double bond leading to the E isomer partially occurs.

UV irradiation at low temperature (200 K) produced the coloured open form ($\lambda_{\text{max}} = 607 \text{ nm}$). No net absorption bands in the 450 nm region were observed, indicating that, if the L precursor is formed, as shown above for benzo-chromene derivatives, its concentra-

tion is probably too low to be detected and, in any case, its absorption remains hidden under the intense band of the photomerocyanine units. In fact, the absorbance increases with the irradiation time in the 450 nm region too. Monitoring the growing at both wavelengths, as done at room temperature, the band at 446 nm was found to follow a mono-exponential kinetics ($k = 4.2 \times 10^{-3} \text{ s}^{-1}$), probably corresponding to the primary cyclization step, while that at 607 nm showed a bi-exponential decay. The fast component corresponded to that at 446 nm, and the slow one ($k = 6.9 \times 10^{-4} \text{ s}^{-1}$) was ascribed to the photochromic process of the side units.

The high activation energy of the photocyclisation process does not enable the formation of the "stable" dihydro-intermediate (S) to take place at low temperature, as reported for DNE [5, 7-12] and found for DMNE in the present work. Therefore, normal (reversible) photochromism of the SP units takes place. When UV irradiation was discontinued, slow thermal bleaching occurred even at low temperature ($t_{1/2} = 230 \text{ min}$), leading to the starting material as the main product, in agreement with NMR results [2, 4] at low temperature.

The reaction mechanism of DSPE (already reported in reference [3]) is similar to that shown above for DBCE.

4. CONCLUSIONS

The photokinetic behaviour of the supermolecules investigated, with two photochromic units linked through an ethenic bridge, markedly differs from that of the free components. The systems are no more reversible, therefore they cannot work as classical photochromes. They showed a photocolouration process and slow irreversible photobleaching, apparently without participation of thermal steps in the reaction mechanism at room temperature.

The parallel study of the methoxy-substituted "non-photochromic" model allowed the unusual irreversibility to be explained by the formation of a dihydrophenanthrene-type intermediate, originated from photocyclisation at the central ethene bridge and stable for hours or days at room temperature. This intermediate can be oxidized to the dehydrogenated product in air-equilibrated solutions, thus explaining the large extent of photodegradation observed over long times. Only by pulsed techniques, or at low temperatures, it was possible to detect small amounts of a precursor of the intermediate. Since the activated formation of the photocyclised intermediate is practically inhibited at low temperatures, the compounds exhibit an almost normal behaviour below -30°C (mainly, photoisomerization to E for the model molecule and reversible formation of the coloured species for the compounds bearing BC and SP units).

The two bichromophoric compounds investigated

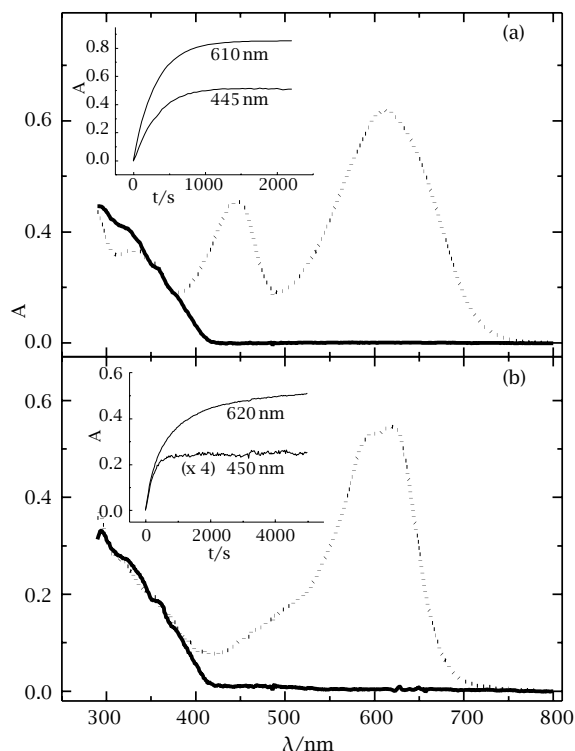


Figure 6. Photochemical ($\lambda_{\text{exc}} = 373 \text{ nm}$) and thermal reactivity of Z-DSPE in toluene: (a) at room temperature: starting compound (full line); after 40 min irradiation at the isosbestic point of 373 nm (dot); (b) at 230 K: starting compound (full line); after ca. 70 min irradiation (dot). The insets show the kinetic behaviour at different wavelengths.

behave similarly to the model compound in some aspects, but also display some peculiar differences in others, depending on the relative rates of the processes occurring at the central ethene bond and at the side photochromic units, respectively. The opening rate of the photochromic units is slower for the chromene derivative, thus allowing a better separation of the two steps of central cyclization and opening of the side units. The opening process is faster for the SP moiety, not allowing the cyclised intermediate to be easily detected.

Comparison with the results obtained for the model molecule indicates that the presence of the Z-ethene structure strongly affects the photobehaviour of the bichromophoric supermolecules at an extent which depends on the stability of the photoproduct dihydro-intermediate. As recalled above, DNE gives one of the most stable dihydro-intermediates (half time of decay: about 37 days in deaerated solutions) and the stability of the methoxy-substituted compound is only slightly reduced in comparison. Even if this stability is drastically reduced in the presence of oxidants or in air-equilibrated solutions, it still prevents thermal bleaching from occurring for hours or days and remains the reason of the apparent irreversibility of the photocoloration process.

In conclusion, cyclisation at the central ethene bridge is mainly responsible for the observed behaviour of these ethenic supermolecules. They do not work as photochromes but, due to their sensitivity to a large range of excitation wavelengths, may find application in other fields, for example in non-conventional image-reproduction systems.

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