Dyes and Pigments 92 (2012) 807–816

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The role of temperature in the photochromic behaviour

Fausto Ortica*

Università di Perugia, Dipartimento di Chimica, via Elce di Sotto, 8 - 06123 Perugia, Italy

A R T I C L E I N F O

Article history:
Received 22 December 2010
Received in revised form
28 March 2011
Accepted 1 April 2011
Available online 20 April 2011

Keywords:
Photochromism
Thermochromism
Temperature effect
Kinetics
Colourability
Quantum yield

A B S T R A C T

This paper reviews a series of photochromic systems belonging to the classes of spirooxazines, chromenes and arylethenes, which have been recently investigated in our laboratory. Temperature variations may have very significant and different effects on the behaviour of photochromic systems, which depend on their type of reversibility (T or P systems). For thermoreversible photochromic molecules, increasing the temperature increases the rate of the thermal bleaching reaction, thus decreasing light-stimulated colouration. For systems being both photochromic and thermochromic, such as spirooxazines and chromenes, a combination of the experimental data gathered from temperature effect studies can bring about a complete description of the kinetics and thermodynamics of the ground state reaction, in terms of activation energies, frequency factors, thermodynamic activation parameters, equilibrium constants of the ground state reaction. Lowering the temperature may either reduce a complex photochemical reaction, which yields several photoproducts, to a simpler one giving a single photoproduct, as observed for some chromenes, or transform a thermo- and photoreversible system into one which is only photoreversible, as found for some dipyrrolylperfluorocyclopentenes: thermal decolouration dominates bleaching at room temperature and above; whilst at low temperature thermostability and photoreversibility are established. For photoreversible systems, such as photochromic arylethenes, the quantum yields for both UV colouration, $\Phi_{O\rightarrow C}$, and visible decolouration, $\Phi_{C\rightarrow O}$, were found to depend on the temperature. An in depth understanding of the reaction mechanisms and the design of synthetic strategies for possible practical applications entail a careful analysis of all of these aspects.

1. Introduction

Temperature variations may induce very significant and different effects on the behaviour of photochromic systems. Such effects are no doubt of fundamental importance in this research field. First because, as it is well established, they constitute one of the possible ways to distinguish and classify different photochromic compounds, thereby allowing them to be labelled as T-type and P-type systems [1], based on their reversibility. Although an extended and general in depth analysis of temperature variations on these molecules is hard to find in the scientific literature, the role of temperature, at least indirectly, has been always taken into account by researchers either planning synthetic strategies for the design of new photochromic materials or investigating their photobehaviour. As a matter of fact, in light of the peculiar practical application for which a molecule is designed, the full, partial or lack of thermal reversibility of a photochromic system may alternatively be required. Consequently, compounds that exhibit full or partial thermal bleaching processes, such as spiropyrans [2], spirooxazines [3,4] and chromenes [5,6] are currently employed, for example, as optical filters, ophthalmic lenses, smart windows, whilst systems like photochromic diarylethenes, which have received increasing attention over the last two decades [7–10], may find some interesting applications as permanent memories, optical switches, etc. Besides these features, a temperature increase may also induce spontaneous coloration in a photochromic system (thermochromism) [11].

This review article highlights the effects of the temperature on the photobehaviour of various molecular systems, belonging to different classes of photochromic compounds, namely spirooxazines, chromenes and arylethenes. For thermoreversible photochromic molecules, increasing the temperature increases the rate of the thermal bleaching reaction, thus decreasing light-stimulated colouration. Given that temperature raising can also induce spontaneous colouration of thermochromic compounds, a combination of thermochromism and photochromism data can provide a complete description of the kinetics and thermodynamics of the thermal reaction of such molecular systems.

---

* Tel.: +39 075 585 5576; fax: +39 075 585 5598.
E-mail address: ortica@unipg.it.

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.04.002

Lowering temperature may even reduce a complex photochemical reaction, which yields several photoproducts, to a simpler one giving a single photoproduct, or transform a thermo- and photoreversible system into a purely photoreversible one. On the other hand, although temperature is not directly involved in the fading process of photoreversible photochromic compounds, nevertheless an in depth study of its effects on the behaviour of these molecules, in terms of an analysis of possible thermal activation barriers in the colouration and/or decolouration pathways may give interesting information about the reaction mechanism of such systems.

2. The molecules

The molecules object of this report are shown in Scheme 1.

The two spirooxazines (1,3-dihydro-3,3-dimethyl-1-isobutyl-6′-(2,3-dihydro-1*H*-indol-1-yl)spiro[2*H*-indole-2,3′-3*H*-naphtho[2,1-*b*][1,4]oxazine], **SO-1**, and 1,3-dihydro-3,3-dimethyl-1-neopentyl-6′-(4″-N,N-diethylanilino)spiro[2*H*-indole-2,2′-3*H*-naphtho[1,2-*b*][1,4]oxazine], **SO-2**), and the two chromenes (2-(4′-piperidinophenyl)-2-phenyl-5-carbomethoxy-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, **NP-1**, and 2-(4′-dimethylaminophenyl)-2-(4′-methoxyphenyl)-5-hydroxymethyl-9-pyrrolidino-2*H*-naphtho[1,2-*b*]pyran, **NP-2**) were purchased from James Robinson Ltd. The 2,2-diphenyl-5,6-dimethyl-8-nitro(2*H*)chromene (**8-nitro-DPC**) and 2,2-diphenyl-5,8-dimethyl-6-nitro(2*H*)chromene (**6-nitro-DPC**) were synthesized at the laboratories of the University of Marseille [12]. The 5,6-benzo(2*H*)dimethyl-chromene (**5,6-DMBC**) was received from PPG Industries (Monroeville, PA, USA) and kindly supplied by Dr. B. Van Gemert. The five dipyrrolyl perfluoro cyclopentenes (**DPFC**), bearing different substituents, namely CN-DPFC, CO_2CH_3-DPFC, phenyl-DPFC, thienyl-DPFC and thienylethynyl-DPFC, were synthesized at the University of Marseille [13]. The arylethenes 3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-1,1-dimethyl-2,5-dihydro-1*H*-silole (**BTSi**) [14], 3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-1-phenyl-2,5-dihydrophosphole 1-oxide (**BTPO**) [14], 1-benzyl-3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-[1*H*]-2,5-dihydropyrrol-2,5-dione (**SYM**) [15], tetra(2,5-dimethyl-3-thienyl)ethene (**tetrakis**) [16], were all synthesized at the University of Marseille.

3. Methodologies and data treatment

Most data were obtained by using continuous monochromatic irradiation to promote the photoreactions and spectrophotometric techniques to kinetically follow the photochemical and thermal processes under controlled temperatures. Graphical and mathematical methods were applied to the obtained absorbance/time datasets.

In studying thermoreversible photochromic systems, the rate constants of thermal bleaching were obtained by means of a first-order treatment of the decay kinetics, according to Eq. (1):

$$A = A^0 e^{-k_\Delta t} \tag{1}$$

where A^0 and k_Δ indicate the absorbance value at the photostationary state and the rate constant for thermal bleaching, respectively. A linear treatment of Eq. (1) (Arrhenius equation, Eq. (2)), was used in order to determine the activation energy, E_a, and the frequency factor, *A*, of the thermal back reaction.

$$\ln k_\Delta = \ln A - \frac{E_a}{RT} \tag{2}$$

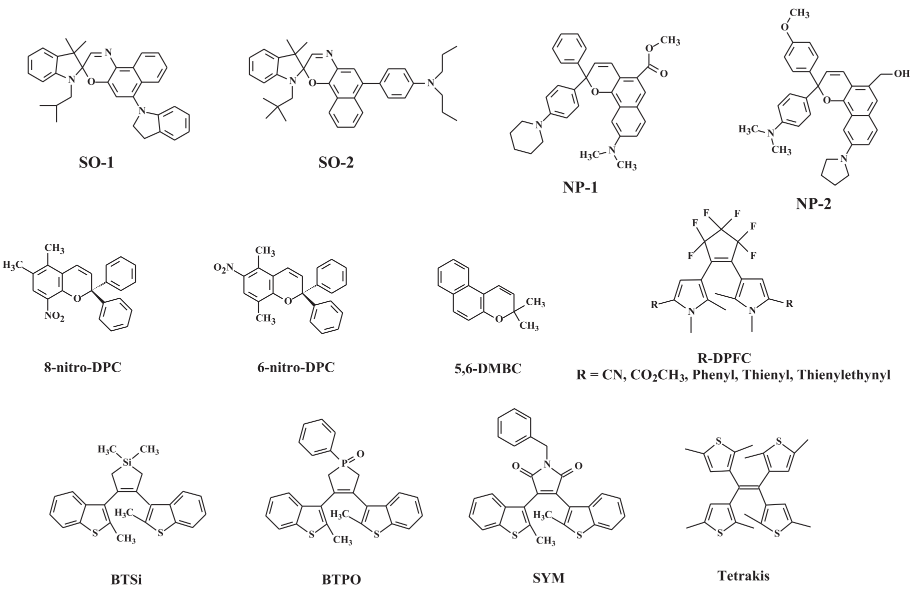
The maximum wavelength absorbance values of the open coloured forms, measured as a function of temperature, allowed the enthalpies of reaction to be determined, making use of the van t'Hoff equation [17,18], by plotting ln *A* vs T^{-1}, Eq. (3):

$$\frac{d\ln K}{d\left(T^{-1}\right)} = \frac{d\ln A}{d\left(T^{-1}\right)} = -\frac{\Delta H^\circ}{R} \tag{3}$$

where the equilibrium constant *K* can be derived, for a given analytical concentration of the photochrome c_0, once the absorbance *A* and the molar absorption coefficient ε of the open form in the visible are known, Eq. (4).

$$K = \frac{[coloured]}{[colourless]} = \frac{A/\varepsilon}{c_0 - A/\varepsilon} \cong \frac{A}{c_0 \varepsilon} \tag{4}$$

Hence, all thermodynamic parameters of the thermal reaction are determined, including the rate constant k_Δ' and activation energy E_a' for the forward thermal reaction (Eqs. (5) and (6)):



Scheme 1. Structures of the thermoreversible and photoreversible molecules investigated.

$$k'_{\Delta} = k_{\Delta} \times K \tag{5}$$

$$E'_a = \Delta H^0 + E_a \tag{6}$$

Using the Eyring Eqs. (7) and (8), where k_B is the Boltzmann constant:

$$\ln\left(\frac{k'_{\Delta}}{T}\right) = \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H'^{\neq}}{RT} + \frac{\Delta S'^{\neq}}{R} \tag{7}$$

$$\ln\left(\frac{k_{\Delta}}{T}\right) = \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} \tag{8}$$

the activation thermodynamic parameters of both thermal colouration ($\Delta H'^{\neq}$, $\Delta S'^{\neq}$, $\Delta G'^{\neq}$) and bleaching ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) can then be evaluated from the slope and the intercept of the $\ln(k_{\Delta}/T)$ vs. $1/T$ linear correlation.

Concerning the photoreversible photochromic systems, the quantum yields for UV photocolouration and photodecolouration and the molar absorption coefficient of the ring-closed isomer were determined by means of the following algorithm. Eq. (9) describes the formation of the coloured isomer C in terms of its absorbance A_C and molar absorption coefficient, ε_C, at the analysis wavelength, of the photokinetic factor $F = A_{\text{total}}/(1-10^{-A\text{total}})$ [19–21], the initial absorbance at the irradiation wavelength A^0, the monochromatic light intensity I^0 (number of photons dm^{-3} s^{-1}) and the quantum yields of the forward ($\Phi_{O\rightarrow C}$) and back ($\Phi_{C\rightarrow O}$) reactions.

$$\frac{dA_C}{dt} = \varepsilon_C \Phi_{O\rightarrow C} I^0 F A^0 - \left[I^0 F \varepsilon_{iso}(\Phi_{O\rightarrow C} + \Phi_{C\rightarrow O})\right] A_C \tag{9}$$

A plot of dA_C/dt vs A_C provides a straight line, from which the sum ($\Phi_{O\rightarrow C} + \Phi_{C\rightarrow O}$) is obtained from the slope and $\Phi_{O\rightarrow C}$ from the intercept, once ε_C is known. The photobleaching quantum yield can be also obtained by irradiating the photostationary solution (or the solution of the pure colored form) with visible light and following the color fading by means of Eq. (10) [22]:

$$-\frac{dA_C}{dt} = \varepsilon_C \Phi_{C\rightarrow O} I^0 \left(1 - 10^{-A'_C}\right) \tag{10}$$

where A'_C is the absorbance of the coloured form at the irradiation wavelength. From the straight line of the $-dA_C/dt$ vs. $10^{-A'_C}$ plot, equal slope and intercept are obtained, wherefrom the quantum yield of the closed to open photobleaching ($\Phi_{C\rightarrow O}$) is achieved.

At low transformation percentage, an initial rate method was considered to be the most reliable and was therefore preferred to determine the quantum yields, Eq. (11):

$$\frac{\Delta A_C}{\Delta t} = \varepsilon_C \Phi_{O\rightarrow C} I^0 F A^0 \tag{11}$$

The quantum yields were treated according to an Arrhenius-type equation (Eq. (11)) [23]:

$$\ln\left[\frac{1}{\Phi_{C\rightarrow O}} - 1\right] = \frac{E_a}{RT} + const \tag{12}$$

The linear treatment based on Eq. (12), allows the activation energies (E_a) for the ring opening reaction in the excited state and the limit yields ($\Phi^{\text{lim}}_{C\rightarrow O}$, virtually at T→ ∞) to be determined from the slope and the intercept, respectively.

4. Thermoreversible systems

In this section, the photobehaviour of some photochromic systems which exhibit full or partial thermal reversibility will be discussed. The effects of the temperature on two spirooxazines **SO-1**, **SO-2**, and two chromenes **NP-1**, and **NP-2**, were investigated in MeCN solution [24]. The spectral features of the four compounds in their closed colourless forms and at the photostationary state, are shown in Fig. 1. The spectral evolution under UV irradiation (λ_{exc} = 295, 301, 320 and 324 nm for **SO-1**, **SO-2**, **NP-1** and **NP-2**, respectively) and the colour bleaching in the dark were kinetically followed at different temperatures, in the 266-245 K range. The kinetic profiles of UV colouration and thermal bleaching, recorded in this temperature interval, are shown in Fig. 2 for **SO-2.**

The quantum yields of UV colouration and the molar absorption coefficients of the open coloured forms were determined by making use either of the integral [19], or the initial rate [25], or the photostationary [26] method. Quantum yields values ranging from 0.10 to 0.53 and from 0.59 to 0.71 were found for the spirooxanines and chromenes, respectively [24]. The back reaction turned out to be completely thermal for the spirooxazines, whilst a very small residual absorbance was observed for the naphthopyrans. The rate constants of thermal bleaching, measured by Eq. (1), were treated according to Eq. (2) (Arrhenius) in order to determine the activation energy, E_a, and the frequency factor, A, of the thermal back reaction for the four molecules (Table 1).

These compounds also exhibited thermochromic behaviour, due to an endothermal ring–opening reaction, which was investigated by recording the absorption spectra of concentrated solutions ($1–5 \times 10^{-3}$ mol dm^{-3}) in the 243–343 temperature range, as shown in Fig. 3 in the case of **SO-1**.

By using Eqs. (3) and (4), the equilibrium constant K and all the thermodynamic parameters of the thermal reaction were determined (Table 1). Furthermore, the rate constant k_{Δ}' and activation energy E_a' for the forward thermal reaction were calculated through Eqs. 5 and 6. These parameters are collected in Table 2. Using the Eyring equations 7 and 8, the activation thermodynamic parameters of both thermal colouration ($\Delta H'^{\neq}$, $\Delta S'^{\neq}$, $\Delta G'^{\neq}$, Table 2) and bleaching ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$, Table 1) were evaluated. Examples of the linear correlation for Eqs. 2 and 8 are depicted in Fig. 4.

A combination of these thermochromic and photochromic results can be exploited to bring about a complete description of the kinetics and thermodynamics of the ground state reaction. This study [24] shows that the compounds investigated behave as high-performance thermochromic compounds at high temperatures, while they exhibit efficient photochromic behaviour at low temperatures. All the compounds exhibited excellent photochemical and thermal colourability, which can be suitably tuned upon changing

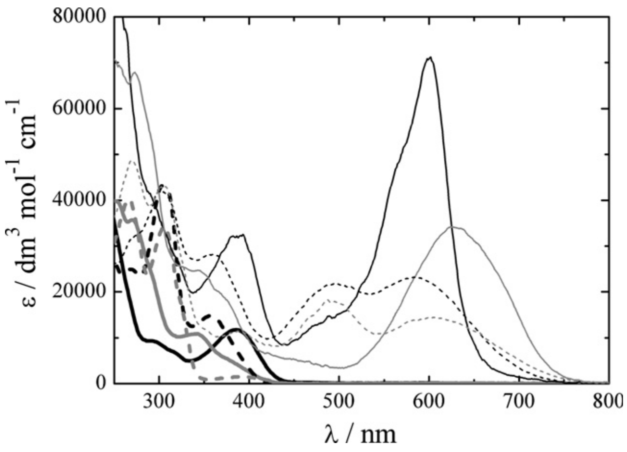


Fig. 1. Absorption spectra of the two spirooxazines (full lines: SO-1, black; SO-2, grey) and the two chromenes (dashed lines: NP-1, black; NP-2, grey) in their closed colourless forms (thick lines) and at the photostationary state (thin lines), in acetonitrile at 263 K.

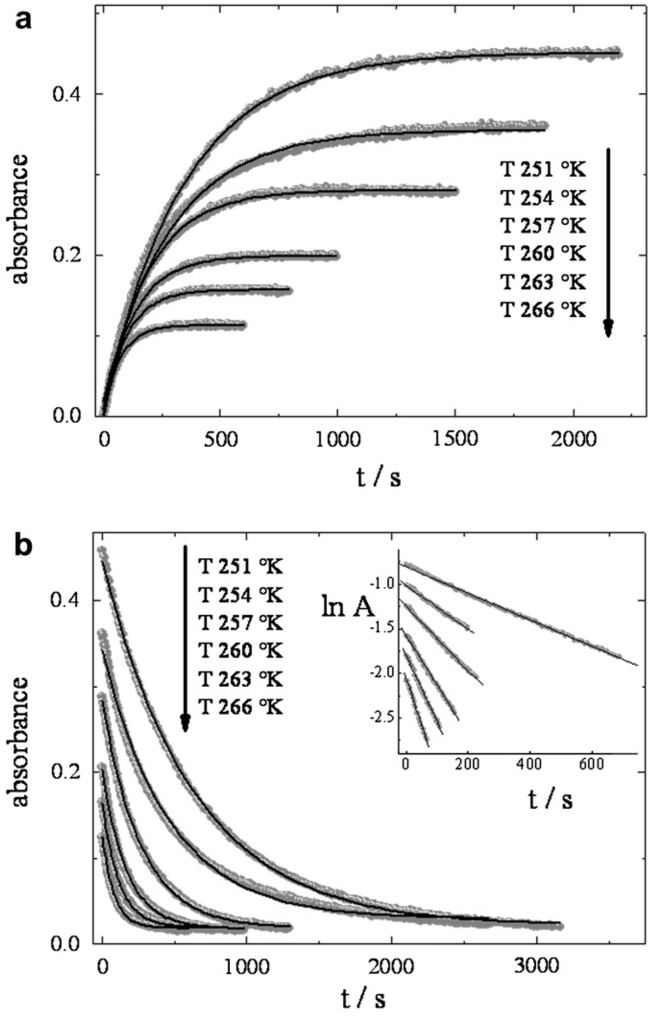


Fig. 2. UV photocolouration (a) and thermal bleaching (b) profiles of SO-2 in acetonitrile as a function of temperature. Inset: linear treatment of bleaching kinetics.

irradiation and temperature conditions. The colourability can be conveniently expressed in terms of the absorbance of the coloured form at the photostationary state, A^{∞}, relative to the concentration of the photochromic compound c_0, according to Eq. (13):

$$\frac{A^{\infty}}{c_0}=\frac{I_0\bullet\varepsilon\bullet\varepsilon_0\bullet\Phi\bullet F^{\infty}}{I_0\bullet\varepsilon_0\bullet\Phi\bullet F^{\infty}+k_{\Delta}} \tag{13}$$

where I_0 is the intensity of the irradiation light, F^{∞} is the photokinetic factor at the photostationary state ε and ε_0 represent the molar absorption coefficients of the open and closed form, respectively. From Eq. (13) it can be seen that, the smaller k_{Δ} and the larger Φ and ε are, the greater the maximum colour intensity attainable. As a consequence, a strong dependence of colourability on temperature is normally observed if the activation energy of thermal bleaching is high. Anyway, there might be some applications where a photochrome with low thermal bleaching activation energy can be required, in order not to have a large temperature dependence of colourability.

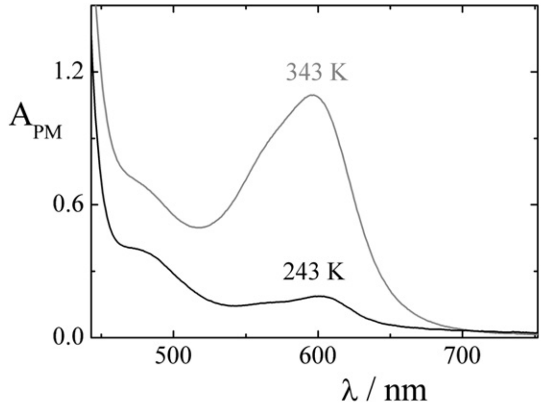


Fig. 3. Thermal evolution of the visible portion of the absorption spectrum of SO-1 in acetonitrile.

In a wide series of 2,2-diphenyl-2*H* [1]benzopyrans, bearing different substituents (methyl, thienyl, $B(OH)_2$ and nitro groups) recently studied in our laboratory [27], two examples of compounds having this particular photobehaviour, **8-nitro-DPC** and **6-nitro-DPC**, were found. The measurements were carried out in the 250–280 K temperature interval, and at 180 K, in order to weaken the thermal contributions to the overall mechanism. The absorption spectra of the two DPC in 3-methylpentane at 180 K, along with the corresponding open forms at the photostationary state, are illustrated in Fig. 5.

The colouration kinetics were well-fitted by bi-exponential curves in the whole temperature range, whereas, at 180 K, a single exponential function allows a good interpolation of the experimental data. The quantum yields, calculated at 180 K by using the integral method, provided values of 0.55 and 0.66 for 8-nitro-DPC and 6-nitro-DPC, respectively [27]. A very significant difference was observed when recording the colouration kinetics and the absorbance photostationary values in the 280–250 K interval for the nitro-substituted compounds and the other molecules investigated, belonging to the same DPC series [27]. This feature can be easily evidenced from a comparison between the photobehaviour of one of the nitro-DPC, e.g. 6-nitro-DPC, and another DPC containing a different substituent on the same position, for instance 6-$B(OH)_2$-DPC (Fig. 6).

It can be seen that colouration is scarcely influenced by the temperature for the nitro-substituted molecule (Fig. 6a), which possesses an uncommon low value of E_a of the thermal back reaction (see Table 3), whilst is markedly dependent on *T* for the $B(OH)_2$ analogue (Fig. 6b) that, on the contrary, is characterized by a “normal” E_a value of 75.9 kJ mol^{-1} [27]. The conversion percentage at the photostationary state is almost constant for **6-nitro-DPC**, whereas it undergoes a tenfold increase upon decreasing temperature from 280 K to 250 K for 6-$B(OH)_2$-DPC. The ring open coloured forms thermally reconvert to the colourless starting material with visible photobleaching almost inefficient

Table 1
Activation energies (E_a) and frequency factors (A) for the thermal bleaching reactions, equilibrium constants (K), thermodynamic parameters (ΔH^0, ΔG^0, ΔS^0) and thermodynamic activation parameters ($\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$) of the thermal bleaching reactions for the two spirooxazines and chromenes investigated. Data from ref. [24].

Compd	E_a (kJ mol^{-1})	A (s^{-1})	K	ΔH^0 (kJ mol^{-1})	ΔG^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
SO-1	51	1×10^{9}	2×10^{-3}	12.3	16.0	−12	48.5	72.2	−80
SO-2	77	1.5×10^{13}	3×10^{-3}	15.7	14.5	4	74.5	74.7	−0.7
NP-1	66.5	5×10^{10}	0.5×10^{-3}	18.5	18.9	−1	64.0	78.5	−49
NP-2	61	3×10^{9}	5×10^{-3}	13.4	13.2	~0	58.7	80.1	−72

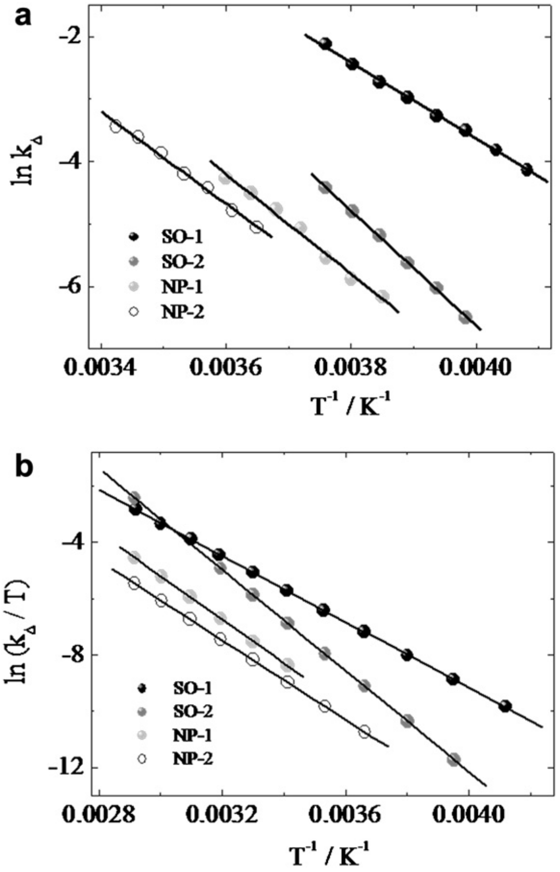


Fig. 4. Arrhenius (a) and Eyring (b) plots for the thermal bleaching process of the four photochromes in acetonitrile.

($\Phi \leq 10^{-3}$ [27]). The effects of temperature variations on thermal bleaching were monitored in the 280–250 K interval and treated according to the Arrhenius and Eyring equations, to estimate k_{Δ} at different T, A, E_a, and the thermodynamic activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ (Table 3).

Beside the aforementioned interesting effect on colourability, the temperature also showed a pronounced influence on the mechanism of reaction. The bi-exponential trend of colouration kinetics, observed in the 280–250 K temperature range, indicates the presence of at least two photoproducts, which are generally reported in the literature as the *transoid-cis* and *transoid-trans* isomers, formed either in a consecutive or in a parallel pathway from the starting chromene molecule [25,28–37]. However, when the temperature was decreased to 180 K, the kinetic data of UV photocolouration had a single exponential nature and this peculiar behaviour, ascribed to the presence of an activation barrier in the *transoid-cis* to *transoid-trans* photoisomerization, allowed the quantum yield of photocolouration and the molar absorption coefficient of the *transoid-cis* open form to be easily measured.

Table 2
Activation energies (E_a), frequency factors (A) and thermodynamic activation parameters ($\Delta H'^{\neq}$, $\Delta G'^{\neq}$, $\Delta S'^{\neq}$) of the thermal colouration for the two spirooxazines and chromenes investigated. Data from ref. [24].

Compd	E_a' (kJ mol^{-1})	A' (s^{-1})	ΔH'$^{\neq}$ (kJ mol^{-1})	ΔG'$^{\neq}$ (kJ mol^{-1})	ΔS'$^{\neq}$ (J mol^{-1} K^{-1})
SO-1	63.2	3×10^{8}	60.9	88.3	−92
SO-2	92.7	3×10^{13}	90.5	88.9	5
NP-1	85.1	4×10^{10}	82.6	97.5	−50
NP-2	74.7	3×10^{9}	72.2	93.2	−70

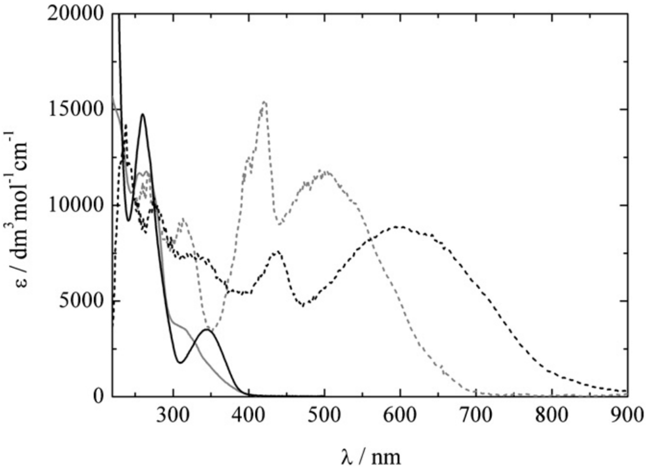


Fig. 5. Absorption spectra of 8-nitro-DPC (black) and 6-nitro-DPC (grey) in the colourless form (full lines) and at the photostationary state (dashed lines) in 3-methylpentane at 180 K ($\lambda_{\text{exc}} = 283$ nm).

This evidence suggests that lowering temperature may somehow reduce a complex photochemical reaction, which yields several photoproducts, to a simpler one giving a single photoproduct, thereby allowing an easier mathematical analysis of the experimental data from the photochromic system itself. This was also observed in a study carried out for **5,6-DMBC** in 3-methylpentane solution [38]. Due to the very fast rate of the thermal back reaction at room temperature ($k_{\Delta} > 10^2$ s^{-1} [38]) this molecule could only be investigated at relatively low temperatures, whereby the behaviour upon UV photocolouration ($\lambda_{\text{exc}} = 318$ nm) was monitored in the 235–219 K and 160–140 K intervals. This photochromic system turned out to be rather complicated and, in the higher temperature range, the colouration process led to a photostationary state where both a *cisoid-cis* and a *transoid-cis* open species were simultaneously present, along with the parent **5,6-DMBC**. When the UV irradiating source was removed, a thermostationary state constituted by the *transoid-cis* form and the **5,6-DMBC** was attained. Only irradiation with visible light could reconvert the *transoid-cis* to the original **5,6-DMBC**. When the

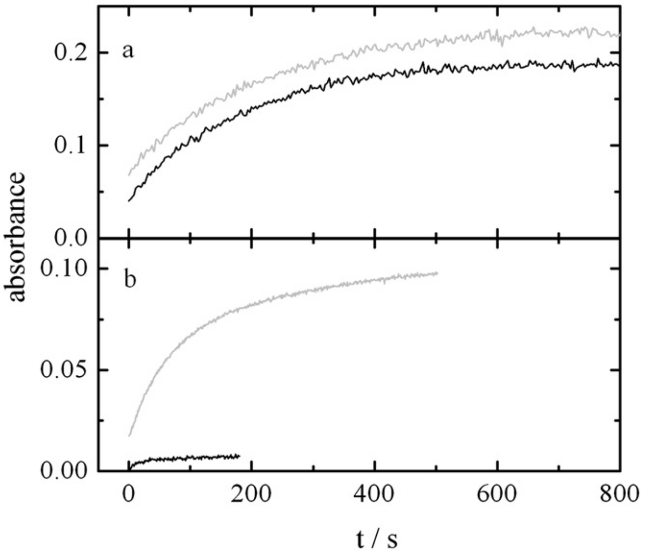


Fig. 6. UV colouration of 6-nitro-DPC (a, $\lambda_{\text{exc}} = 283$ nm) and 6-B(OH)$_2$-DPC (b, $\lambda_{\text{exc}} = 310$ nm) at 280 K (black) and 250 K (light grey) in 3-methylpentane.

Table 3
Activation and thermodynamic activation parameters of the thermal bleaching reactions for the two nitro-DPC in 3 MP. Data from ref. [27].

Compd	E_a kJ mol^{-1}	A s^{-1}	ΔH$^{\#}$ kJ mol^{-1}	ΔS$^{\#}$ J K^{-1} mol^{-1}	ΔG$^{\#}$ kJ mol^{-1}
8-nitro-DPC	36.3	1.4×10^4	34.0	−173	82.4
6-nitro-DPC	15.7	2.2	13.4	−246	82.3

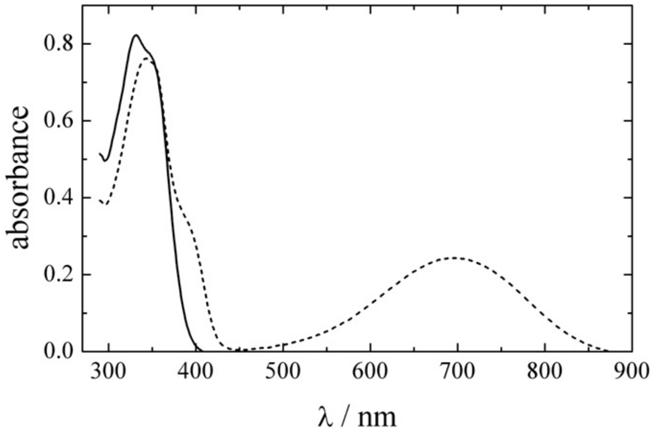


Fig. 7. Absorption spectra of CN-DPFC in toluene at 280 K: before irradiation (full line) and at the photostationary state (dashed line).

temperature was low enough to reduce the contribution of the thermally activated processes, only the *cisoid-cis* open form was observed, which remained stable in the dark. In this case, visible irradiation did not allow the reconstitution of the starting material whilst a side product was formed, whose nature was tentatively assigned either to a hydroxyphenyl [39] or to an *o*-allenylnaphthol [40–42] structure.

5. Thermo- and photoreversible systems

Not only can changes in temperature rule out a particular reaction pathway, thus leading to a simplification of the overall mechanism but, in some cases, it may even transform a thermo- and photoreversible (T & P) system into a molecule which is only photoreversible, as we found for some dipyrrolylperfluorocyclopentenes (**DPFC**) [22,43]. Concerning the diarylethene photochromes, it has been shown [9,44–51] that they can either be photo- and thermoreversible or exclusively photoreversible, depending on the aromatic stabilization energy of the aryl groups, which influences the thermal stability of the coloured form. From this point of view, the dipyrrolyl compounds have been classified as systems where the cycloreversion reaction can occur both thermally and photochemically [9,52]. We investigated the photobehaviour of five molecules belonging to this class, where different substituents, such as CN, CO_2CH_3, phenyl, thienyl and thienylethynyl are present on the two pyrrol rings [22,43]. The absorption spectra of the CN substituted molecule in toluene, before and after UV photocolouration at 280 K, are shown in Fig. 7.

The most interesting effect of temperature variations on this systems, in addition to the expected increase of the absorbance value at the photostationary state with decreasing the temperature, was observed in the bleaching process. After attainment of the photostationary state, if the UV irradiation was discontinued, thermal bleaching occurred at rates strongly dependent on the temperature (activation energy ranging from 65 to 83 kJ mol^{-1} [22], Table 4). The kinetic results obtained for CN-DPFC are depicted in Fig. 8.

At 320 K (Fig. 8a), bleaching is thermal ($k_\Delta = 2.4 \times 10^{-3}$ s^{-1}) while at 280 K (Fig. 8b) the thermal process is markedly slowed down ($k_\Delta = 8 \times 10^{-5}$ s^{-1}) and the back conversion to the open form is accelerated by visible irradiation. If the temperature is lowered to 200 K (Fig. 8c), the photoproduct obtained by UV irradiation becomes thermally stable and only irradiation with visible light induces cycloreversion to the starting molecular structure. This study evidences that these **DPFC** exhibit relatively high quantum yields for both UV photocolouration and visible photobleaching, their values ranging from 0.37 to 0.81 and from 0.11 to 0.27, respectively [22]. These molecules also underwent thermal bleaching at sufficiently high temperature and this behaviour was more pronounced for the three compounds bearing aromatic substituents. The kinetic and thermodynamic parameters of thermal bleaching were obtained as usual by Arrhenius and Eyring treatments and are collected in Table 4.

On first examination the data in Table 4 might indicate that the slow thermal back reaction observed for the aromatic derivatives is probably ascribed to the entropy factor.

6. Photoreversible (bistable) systems

The effects of temperature variations were investigated on two types of photoreversible photochromic arylethenes. In the compounds of the first type, the photochromic activity is accomplished by inhibiting the *cis-trans* isomerization through a five-membered ring which constrains the molecular geometry in the *cis* position, as in the above dipyrrolyl compounds. In the systems of the second type, although no rigid constraint is present, the peculiar symmetry of the molecule renders the *cis-trans* photoisomerization inactive. A few isolated examples of studies on the temperature effect can be found in the literature, mainly by Irie and coworkers, for molecules which belong to the first class, whereas, to the best of our knowledge, no studies dealing with temperature effects have been reported for the second type of compounds. The thermal effects on the interconversion between the antiparallel (a-p) and parallel (p) isomers of photochromic diarylethenes were investigated by NMR [53]. The effect of the temperature on quantum yields of both photocyclization [54] and photocycloreversion [54–57] as

Table 4
Activation and thermodynamic activation parameters of the thermal bleaching reactions for the DPFC in toluene. Data from ref. [22].

Compd	E_a kJ mol^{-1}	A s^{-1}	ΔH$^{\#}$ kJ mol^{-1}	ΔS$^{\#}$ J K^{-1} mol^{-1}	ΔG$^{\#}$ kJ mol^{-1}
CN	83 ± 4	4×10^{12}	80.6	−11.7	84.0
CO_2CH_3	71 ± 4	5×10^{11}	68.6	−29.0	77.0
Phenyl	79 ± 4	5×10^{9}	75.6	−67.3	95.1
Thienyl	67 ± 3	5×10^{8}	64.6	−86.4	89.6
Thienylethynyl	65 ± 5	7×10^{7}	62.6	−103	92.5

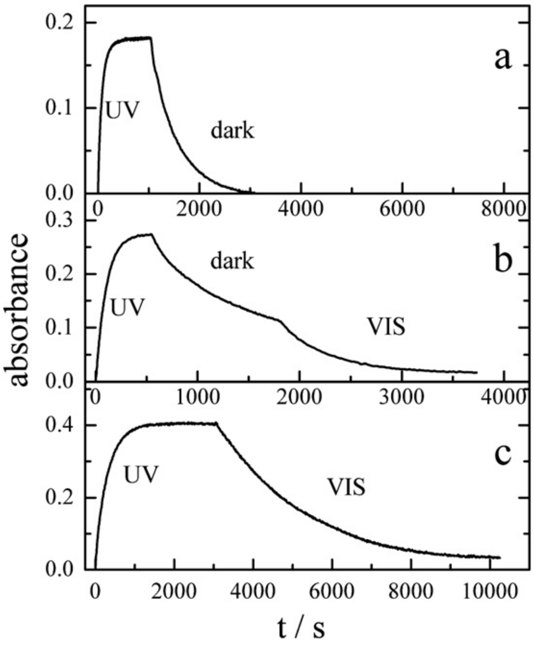


Fig. 8. Kinetic profiles of CN-DPFC in toluene: a) 320 K; b) 280 K; c) 200 K.

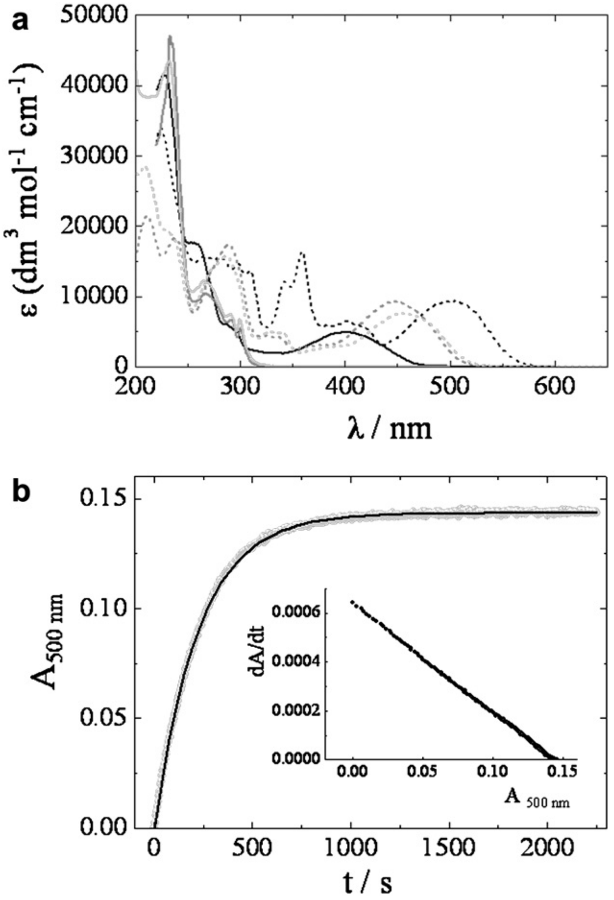


Fig. 9. a) Absorption spectra of the colourless (full line) and coloured (dashed line) forms of SYM (black, $\lambda_{exc} = 265$ nm), BTSi (grey, $\lambda_{exc} = 266$ nm) and BTPO (light grey, $\lambda_{exc} = 267$ nm) in 3-methylpentane at room temperature; b) photocolouration kinetics of SYM in 3-methylpentane ($\lambda_{exc} = 265$ nm) at 200 K and linear treatment (inset) according to Eq. (9).

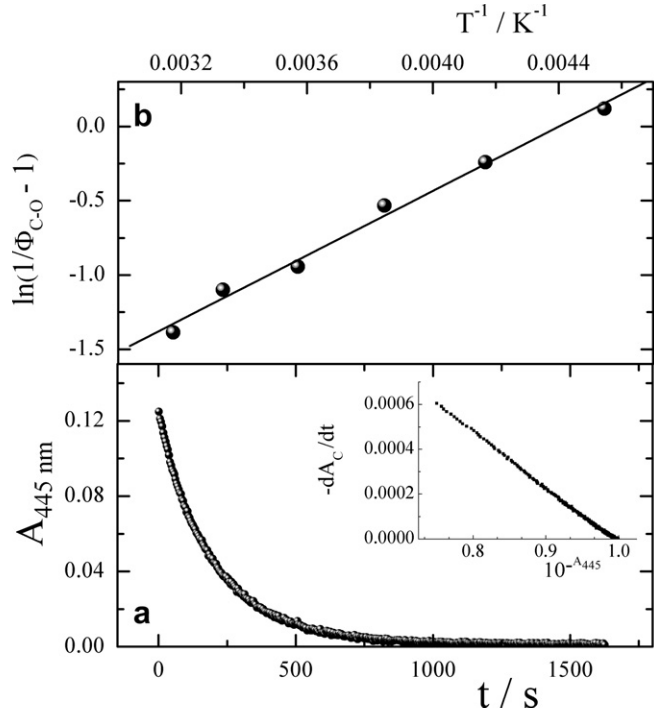


Fig. 10. Photobleaching kinetics of BTPO in 3-methylpentane ($\lambda_{exc} = 445$ nm) at 200 K (a); linear treatment according to Eq. (11) (inset); photobleaching quantum yields as a function of temperature, according to Eq. (12) (b).

well as the activation energy for the visible light-stimulated cycloreversion [54] were also determined.

Among the photochromic arylethenes of the first type, the effects of temperature on the photobehaviour of some compounds bearing various substituents in the five-membered ring, namely (**BTSi**) [23], (**BTPO**) [23] and (**SYM**) [58] have been investigated. The absorption spectra of the colourless open forms and those of the ring-closed species obtained upon UV irradiation are shown in Fig. 9a. The investigation was carried out over a large temperature range, from 315 K down to 180 K in liquid solution, and in a rigid matrix of 3-methylpentane (77–80 K). The quantum yields for UV photocolouration ($\Phi_{O \rightarrow C}$) and visible photobleaching ($\Phi_{C \rightarrow O}$) were determined by means of the algorithm described above, employing Eq. (9) and (10). An example of data treatment based on Eq. (9) is shown in Fig. 9b for **SYM**, while an application of Eq. (10) is displayed in Fig. 10a.

Table 5
Quantum yields for visible stimulated photobleaching of SYM, BTSi and BTPO in 3-methylpentane solution and rigid matrix. Data from ref [23,58].

T/K	$\Phi_{C \rightarrow O}$ (visible light)		
	SYM	BTSi	BTPO
$T \rightarrow \infty$	0.92	0.95	0.99
315	0.52	0.80	0.80
300	0.51	0.58	0.75
290		0.56	0.76
280	0.47	0.56	0.72
260	0.43	0.52	0.63
250	0.40		
240	0.38	0.50	0.56
230	0.33		
220	0.31	0.39	0.47
200	0.24_5	0.31	0.45
180	0.16		
80 (matrix)	~0	0.001	0.04

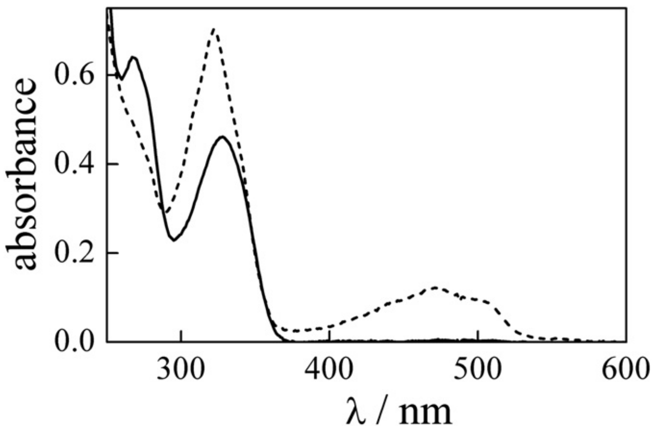


Fig. 11. Absorption spectra of the colourless (full line) and coloured (dashed line) forms of Tetrakis in 3-methylpentane at 77 K.

For the systems examined, the quantum yield of photocolouration was only barely affected by changing the operative temperature, the main effect being an increase of $\Phi_{O\to C}$ (from 0.37 to 0.99 for **BTSi** [23]) on passing from a 3-methylpentane fluid solution at 290 K to a glassy solution at 77 K. This might be interpreted taking into account the percentage of the reactive a-p conformation which is actually present in the system, that has already been reported to undergo a slight increase with decreasing temperature [53] and that is the only reactive species giving the cyclized photoproduct under UV irradiation [50,59]. On the contrary, the quantum yield for visible induced photodecolouration ($\Phi_{C\to O}$) turned out to be extremely sensitive to temperature variations, as can be seen from Table 5, where a regular decrease of $\Phi_{C\to O}$ with decreasing temperature can be observed for the three molecules. The values become almost immeasurable in a rigid matrix, where the cycloreversion is practically absent. The quantum yields were treated according to the Arrhenius-type equation (Eq. (12), Fig. 10b) [23], which allowed the activation energies (E_a) for the ring opening reaction in the excited state and the limit yields ($\Phi^{\mathrm{lim}}_{C\to O}$, virtually at $T\to\infty$, see Table 5) to be determined. The activation energy values range from 6.0 [58] to 8.5 [23] kJ mol^{-1}, and are of the same order of magnitude as those previously found by Irie and coworkers in a single-crystalline phase [54].

Recently, we have been studying some relatively new photochromic arylethenes where the competition between the photocolouration and *cis-trans* photoisomerization pathways is annulled due to the particular symmetry of the molecular system [60]. An initial analysis of the photochromism of **Tetrakis** has been reported by Krayushkin [61], while Ikeda et al. [62–64] reported studies on compounds having similar structures. Our work was focused on the effects of temperature variations on the quantum yields of both photocolouration and photobleaching processes of **Tetrakis**; the experiments were performed in 3 MP over a wide temperature interval, from 315 to 180 K (liquid solution) and 80 K (rigid matrix). The absorption spectra of **Tetrakis** in a 3-methylpentane rigid matrix, before and after UV irradiation at 286 nm, are displayed in Fig. 11.

Upon irradiation with visible light ($\lambda_{\mathrm{exc}} = 445$ nm) the bleaching was only partial and a residual absorption remained after the irradiation was discontinued. As a consequence, the initial rate method, based on Eq. (11), was preferred to determine the quantum yields of photobleaching. The results obtained are summarized in Table 6.

The quantum yield for the visible decolouration shows a progressive decrease as the temperature is lowered and the process is completely inhibited in a rigid matrix. By means of Eq. (12) the activation energy of the closed to open reaction ($E_a = 3.1$ kJ mol^{-1}) and the limit yield (0.7) are determined from the slope and intercept, respectively, of linear plots of ln $(1/\Phi_{C\to O} - 1)$ vs T^{-1} [60]. Unlike the aforementioned photochromic diarylethenes having a pentatomic ring to the double bond, for **Tetrakis** an increase of the quantum yield for UV colouration $\Phi_{O\to C}$ with decreasing the temperature was also observed. This “negative” temperature effect probably reflects an increase of the reactive a-p isomer as the temperature is lowered.

Table 6
Quantum yields for UV photocolouration and visible photobleaching of Tetrakis in 3-methylpentane solution and rigid matrix. Data from ref [60].

T/K	$\lambda_{exc} = 286$ nm	$\lambda_{exc} = 445$ nm
	$\Phi_{O\to C}$	$\Phi_{C\to O}$
315	0.39	0.38
300	0.42	
280	0.48	0.38
260	0.41	0.34
240	0.58	0.32
220	0.59	0.27
200	0.59	0.27
180	0.62	0.20
77	1.0	0.0

7. Conclusion

The results reported in this paper represent a brief collection of examples where the temperature exerts a significant influence on the photobehaviour of photochromic systems. For molecules which undergo thermal colouration, such as some spirooxazines and chromenes, a complete description of the kinetics and thermodynamics of the ground state reaction can be achieved through a combination of the thermochromic and photochromic data obtained. The usually complex reaction mechanism reported for chromenes may sometimes be simplified by reducing the operative temperature, thereby rendering the thermal pathways completely inefficient. Colourability may also be influenced by temperature variations, in a way that depends on the substitution to the molecular structure, as we observed for some nitro-substituted chromenes. In the case of dipyrrolylperfluorocyclopentenes, the temperature range where measurements are carried out is fundamental in determining the kind of reversibility of the photochromic system: purely thermal, photo-thermal, purely photoreversible. Even for photoreversible molecules, such as photochromic arylethenes, the light activated processes are sensitive to the temperature. We have found that the quantum yields of photobleaching may be significantly influenced by the temperature. Generally, the quantum yield for decolouration, $\Phi_{C\to O}$, decreases with decreasing the temperature, due to a barrier (of the order of a few kJ mol^{-1}) to the ring opening reaction, which even hampers the cycloreversion in a rigid matrix at 80 K. In contrast, in some cases the photocolouration quantum yield $\Phi_{O\to C}$ was found to increases with decreasing the temperature. This “negative” effect is assigned to an increasing amount of the most easily isomerizable rotamer in the conformational equilibrium as the temperature decreases.

Acknowledgements

This research was funded by the Italian “Ministero per l’Università e la Ricerca Scientifica e Tecnologica” in the framework of a FIRB project (“Spectroscopic and kinetic study of organic photochromic compounds in solution, micro-heterogeneous media and polymeric films") and a PRIN-2006 project ("Photophysics and photochemistry of chromogenic compounds for technological applications"). The author thanks Prof. G. Favaro and all the colleagues of the "Laboratorio di Fotofisica e Fotochimica" at the University of Perugia for their valuable and helpful contribution to the research work reported in the manuscript. People of Université de la Mediterranée, Faculté de Sciences de Luminy, Marseille, are gratefully acknowledged for synthesizing and supplying most of the compounds investigated. The author also wishes to thank James Robinson Ltd. for providing the spirooxazines and two of the naphthopyrans analyzed and PPG Industries for the 5,6-DMBC sample.

References

[1] Bouas-Laurent H, Dürr H. Organic photochromism (IUPAC technical report). Pure Appl Chem 2001;73:639–65.

[2] Guglielmetti R. $4n+2$ systems: spiropyrans. In: Dürr H, Bouas-Laurent H, editors. Photochromism. Molecules and systems. Amsterdam: Elsevier; 1990. p. 314–466.

[3] Chu NYC. $4n+2$ systems: spirooxazines. In: Dürr H, Bouas-Laurent H, editors. Photochromism. Molecules and systems. Amsterdam: Elsevier; 1990. p. 493–513.

[4] Maeda S. Spirooxazines. In: Crano JC, Guglielmetti RJ, editors. Organic photochromic and thermochromic compounds, Vol. 1. , New York: Kluwer Academic/Plenum Publishers; 1999. p. 85–109.

[5] Van Gemert B. Benzo and naphthopyrans (Chromenes). In: Crano JC, Guglielmetti RJ, editors. Organic photochromic and thermochromic compounds, Vol. 1. , New York: Kluwer Academic/Plenum Publishers; 1999. p. 111–40.

[6] Hepworth JD, Heron BM. In: Kim S-H, editor. Functional dyes. Amsterdam: Elsevier; 2006. p. 85–135.

[7] Irie M, Mohri M. Thermally irreversible photochromic systems. Reversible photocyclization of diarylethene derivatives. J Org Chem 1988;53:803–8.

[8] Irie M. Diarylethenes with heterocyclic aryl groups. In: Crano JC, Guglielmetti RJ, editors. Organic photochromic and thermochromic compounds, Vol. 1. , New York: Kluwer Academic/Plenum Publishers; 1999. p. 207–22.

[9] Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100: 1685–716.

[10] Matsuda K, Irie M. Diarylethene as a photoswitching unit. J. Photochem. Photobiol. C: Photochemistry Reviews 2004;5:169–82.

[11] Samat A, Lokshin V. Thermochromism of organic compounds. In: Crano JC, Guglielmetti RJ, editors. Organic photochromic and thermochromic compounds, Vol. 2. , New York: Kluwer Academic/Plenum Publishers; 1999. p. 415–66.

[12] Bougdid L, Heynderickx A, Delbaere S, Moustrou C. First synthesis of nitro-substituted 2,2-diphenyl-2H-1-benzopyrans via the ipso-nitration reaction. Tetrahedron 2007;63:8242–9.

[13] Heynderickx A, Kaou AM, Moustrou C, Samat A, Guglielmetti R. Synthesis and photochromic behaviour of new dipyrrolylperfluorocyclopentenes. New J Chem 2003;27:1425–32.

[14] Bougdid L. Ph.D. dissertation. Marseille, France.

[15] El Yahyaoui A, Félix G, Heynderickx A, Moustrou C, Samat A. Convenient synthesis of photochromic symmetrical or unsymmetrical bis(heteroaryl) maleimides via the Suzuki–Miyaura cross-coupling reaction. Tetrahedron 2007;63:9482–7.

[16] Bougdid L., Terrier A, Heynderickx A, Maurel F, Shilova EA, Moustrou C. Synthesis and photochromic properties of tri-thienyl substituted ethylene: combined experimental and theoretical study. In Book of Abstract, ISOP-2007, p 38.

[17] Favaro G, Masetti F, Mazzucato U, Ottavi G, Allegrini P, Malatesta V. Photochromism, thermochromism and solvatochromism of some spiro [indolinoxazine]-photomerocyanine systems: effects of structure and solvent. J Chem Soc Faraday Trans 1994;90:333–8.

[18] Favaro G, Malatesta V, Mazzucato U, Miliani C, Ottavi G. A comprehensive kinetic, thermodynamic and photochemical study of some spiro-indoline-oxazines. Proc Indian Acad Sci Chem Sci 1995;107:659–72.

[19] Ottavi G, Ortica F, Favaro G. Photokinetic methods: a mathematical analysis of the rate equations in photochromic systems. Int J Chem Kinet 1999;31: 303–13.

[20] Gauglitz G, Scheerer E. Method for the determination of absorption coefficients, reaction rate constants and thermodynamic data in the system AB. J Photochem Photobiol A 1993;71:205–12.

[21] Borderie B, Lavabre D, Micheau JC, Laplante JP. Nonlinear dynamics, multiple steady states, and oscillations in photochemistry. J Phys Chem 1992;96: 2953–61.

[22] Ortica F, Smimmo P, Mazzucato U, Favaro G, Heynderickx A, Moustrou C, et al. Photoinduced processes in dipyrrolyl-perfluoro-ciclopentenes. Photochem Photobiol 2006;82:1326–33.

[23] Cipolloni M, Ortica F, Bougdid L, Moustrou C, Mazzucato U, Favaro G. New thermally irreversible and fluorescent photochromic diarylethenes. J Phys Chem A 2008;112:4765–71.

[24] di Nunzio MR, Gentili PL, Romani A, Favaro G. Photochromic, thermochromic, and fluorescent spirooxazines and naphthopyrans: a spectrokinetic and thermodynamic study. Chem Phys Chem 2008;9:768–75.

[25] Favaro G, Romani A, Becker RS. Photochromic behavior of 2,2-spiro-adamantylidene-2H-naphtho[1,2-b]pyran: a new thermoreversible and photoreversible photochromic system. Photochem Photobiol 2000;72: 632–8.

[26] Favaro G, Malatesta V, Mazzucato U, Ottavi G, Romani A. Thermally reversible photoconversion of spiroindoline-naphtho-oxazines to photomerocyanines: a photochemical and kinetic study. J Photochem Photobiol A 1995;87: 235–41.

[27] Ortica F, Bougdid L, Moustrou C, Mazzucato U, Favaro G. Structure effects on the photobehaviour of 2,2-diphenyl(2H)chromenes. J Photochem Photobiol A 2008;200:287–93.

[28] Favaro G, Mazzucato U, Ottavi G, Becker RS. Kinetic analysis of the photochromic behavior of a naturally occurring chromene (Lapachenole) under steady irradiation. Mol Cryst Liq Cryst 1997;298:137–44.

[29] Ottavi G, Favaro G, Malatesta V. Spectrokinetic study of 2,2-diphenyl-5,6-benzo(2H)chromene: a thermoreversible and photoreversible photochromic system. J Photochem Photobiol A Chem 1998;115:123–8.

[30] Luccioni-Houze B, Campredon M, Guglielmetti R, Giusti G. Kinetic analysis of fluoro-[2H]-chromenes at the photostationary states. Mol Cryst Liq Cryst 1997;297:161–5.

[31] Hobley J, Malatesta V, Millini R, Giroldini W, Wis L, Goto M, et al. Photochromism of chromene crystals; a new property of old chromenes. Chem Commun; 2000:1339–40.

[32] Görner H, Chibisov AK. Photoprocesses in 2,2-diphenyl-5,6-benzo(2H)chromene. J Photochem Photobiol A Chem 2002;149:83–9.

[33] Delbaere S, Luccioni-Houze B, Bochu C, Teral Y, Campredon M, Vermeersch G. Kinetic and structural studies of the photochromic process of 3H-naphthopyrans by UV and NMR spectroscopy. J Chem Soc, Perkin Trans 1998;2: 1153–7.

[34] Delbaere S, Micheau JC, Teral Y, Bochu C, Campredon M, Vermeersch G. NMR structural and kinetic assignment of fluoro-3H-naphthopyran photomerocyanines. Photochem Photobiol 2001;74:694–9.

[35] Hobley J, Malatesta V, Hatanaka K, Kajimoto S, Williams SL, Fukumura H. Picosecond and nanosecond photo-dynamics of a naphthopyran merocyanine. Phys Chem Chem Phys 2002;4:180–4.

[36] Coelho PJ, Carvalho LM, Rodrigues S, Oliveira-Campos AMF, Dubest R, Aubard J, et al. Synthesis and photochromic behaviour of novel 2H-chromenes derived from fluorenone. Tetrahedron 2002;58:925–31.

[37] Martins CI, Coelho PJ, Carvalho LM, Oliveira-Campos AMF, Samat A, Guglielmetti R. Photochromic properties of new benzoindene-fused 2H-chromenes. Helv Chim Acta 2003;86:570–8.

[38] Favaro G, Romani A, Ortica F. The complex photochromic behaviour of 5,6-benzo(2H)dimethyl-chromene in 3-methylpentane solution. Photochem Photobiol Sci 2003;2:1032–7.

[39] Padwa A, Au A, Lee GA, Owens W. Photochemical ring-opening reactions of substituted chromenes and isochromenes. J Org Chem 1975;40:1142–9.

[40] Delbaere S, Vermeersch G. NMR proofs of the involvement of an allenyl-naphthol as a key-intermediate in the photochromic process of [3H]naphthopyran. Tetrahedron Lett 2003;44:259–62.

[41] Delbaere S, Micheau JC, Vermeersch G. Multinuclear NMR structural characterisation of an unprecedented photochromic allene intermediate. Org Lett 2002;4:3143–5.

[42] Ortica F, Smimmo P, Favaro G, Mazzucato U, Delbaere S, Venec D, et al. Effect of oligothiophene substituents on the photophysical and photochromic properties of a naphthopyran. Photochem Photobiol Sci 2004;3:878–85.

[43] Smimmo P, Ortica F, Mazzucato U, Favaro G, Heynderickx A, Moustrou C, et al. Photophysics and photochemistry of some dipyrrolylperfluorociclopentenes. Mol Cryst Liq Cryst 2005;430:267–72.

[44] Tian H, Yang S. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97.

[45] Muszkat KA. The 4a, 4b-dihydrophenanthrenes. Top Curr Chem 1980;88: 89–143.

[46] Saltiel J, D'Agostino J, Megarity ED, Metts L, Neuberger KR, Wrighton M, et al. Cis-trans photoisomerization of olefins. Org Photochem 1973;3:1–113.

[47] Mallory FB, Mallory CW. Photocyclization of stilbenes and related molecules. Org Reactions 1984;30:1–456.

[48] Laarhoven WH. Photocyclizations and intramolecular photocycloadditions of conjugated arylolefins and related compounds. Org Photochem 1989;10: 163–308.

[49] Laarhoven WH. $4n+2$ systems: molecules derived from Z-hexa-1,3,5,-triene/cycloexa-1,3-diene. In: Dürr H, Bouas-Laurent H, editors. Photochromism. Molecules and systems. Amsterdam: Elsevier; 1990. p. 270–313.

[50] Nakamura S, Irie M. Thermally irreversible photochromic systems. A theoretical study. J Org Chem 1988;53:6136–8.

[51] Kellogg RM, Groen MB, Wynberg H. Photochemically induced cyclization of some furyl- and thienylethenes. J Org Chem 1967;32:3093–100.

[52] Uchida K, Matsuoka T, Sayo K, Iwamoto M, Hayashi S, Irie M. Thermally reversible photochromic systems. Photochromism of a dipyrrolylperfluorocyclopentene. Chem Lett; 1999:835–6.

[53] Uchida K, Nakayama Y, Irie M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-bis(benzo[b]thiophen-3-yl)ethene derivatives. Bull Chem Soc Jpn 1990;63:1311–5.

[54] Irie M, Lifka T, Kobatake S, Kato N. Photochromism of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase. J Am Chem Soc 2000;122:4871–6.

[55] Chen Q, Zhang D, Zhang G, Yang X, Feng Y, Fan Q, et al. Multicolour tunable emission from organogels containing tetraphenylethene, perylenediimide, and spiropyran derivatives. Adv Funct Mater 2010;20:3244–51.

[56] Irie M, Sakemura K, Okinaka M, Uchida K. Photochromism of dithienylethenes with electron-donating substituents. J Org Chem 1995;60:8305–9.

[57] Irie M, Eriguchi T, Takada T, Uchida K. Photochromism of diarylethenes having thiophene oligomers as the aryl groups. Tetrahedron 1997;53:12263–71.

[58] Cipolloni M, Ortica F, El Yahyaoui A, Heynderickx A, Moustrou C, Favaro G. New photochromic symmetrical and unsymmetrical bis(heteroaryl)maleimides: a spectrokinetic study. Chem Phys 2009;358:258–64.

[59] Goldberg A, Murakami A, Kanda K, Kobayashi T, Nakamura S, Uchida K, et al. Rotational isomerization of dithienylethenes: a study on the mechanism determining quantum yield of cyclization reaction. J Phys Chem A 2003;107:4982–8.

[60] Cipolloni M, Ortica F, Bougdid L, Moustrou C, Maurel F, Favaro G. Tetra- and tri-thienyl ethenes: new fluorescent photochromic compounds. Photochem Photobiol Sci. 2011; doi:10.1039/C0PP00328J.

[61] Beleńkii LI, Gromova GP, Kolotaev AV, Nabatov BV, Krayushkin MM. Synthesis and photochromic properties of tetrakis(3,5-dimethyl-2-thienyl)- and tetrakis(2,5-dimethyl-3-thienyl)ethylenes. Russ Chem Bull, Int. Ed 2005;54:1208–13.

[62] Ikeda H, Sakai A, Namai H, Kawabe A, Mizuno K. Synthesis, X-ray crystallographic analysis, and theoretical structure analysis of tetrathienylethenes designed for photo- and electro-chromism. Tetrahedron Lett 2007;48:8338–42.

[63] Ikeda H, Sakai A, Kawabe A, Namai H, Mizuno K. Photochromic properties of tetrakis(2-methylthien-3-yl)ethene and its tetrakis(methylthio) derivative. Tetrahedron Lett 2008;49:4972–6.

[64] Ikeda H, Kawabe A, Sakai A, Namai H, Mizuno K. Photochromic behaviour of tetrathienylethene in condensed systems - attempts to control 1,2-dyotropic rearrangement of the closed isomer. Res Chem Intermed 2009;35:893–908.