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Structure effects on the photobehaviour of 2,2-diphenyl(2H)chromenes

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ABSTRACT

The photochromic behaviour of a series of 2,2-diphenyl(2H)chromenes, bearing different substituents (methyl, thienyl, $B(OH)_2$ and nitro groups), has been investigated. The photochromism of these molecules is described in terms of absorption spectra, photocolouration and photobleaching quantum yields, kinetics of thermal bleaching and competition between photochemical and photophysical relaxation. The quantum yield of UV photocolouration is generally fairly high (0.7–1.0), but decreases for compounds with thienyl and nitro substituents. The ring-open coloured form thermally rearranges to the closed uncoloured form, whereas visible photobleaching is substantially negligible ($\leq 10^{-3}$). The thermal bleaching process is markedly affected by the substituents and, in the case of the nitro-derivatives, is characterised by a drastic decrease of activation entropy and enthalpy.

1. Introduction

Photochromic compounds, that undergo reversible light-induced transformation between two structures exhibiting different absorption spectra, are currently receiving considerable attention due to potential technological applications, mainly as either optical switching systems or high-density optical storage devices, depending on whether their back reaction is induced by temperature or visible light. Owing to their ultrafast electrocyclization photoreactions, spirooxazines and chromenes are among the most important classes of organic photochromic compounds, that have shown promising properties such as colourability and fatigue resistance [1,2].

Among the various compounds which have been shown to exhibit photochromism, the class of benzopyrans (also called chromenes) has been one of the most extensively studied over the last decades. It is now well established that benzopyrans, as well as their structurally related naphthopyrans (benzo-chromenes), exhibit photochromic behaviour due to the electrocyclic ring-opening at the pyran C–O bond [1]. The photochromism of chromenes was first extensively studied and the mechanism determined by Becker and coworkers [3–10]. They showed that these molecules, upon UV irradiation, yield open metastable photoproduct(s), having the structure of *o*-quinone-allides [4], which are generally coloured due to increased electronic delocalisation. They can reconvert thermally and/or photochemically to the starting material.

In this work, a study of the photochromic behaviour of a series of 2,2-diphenyl(2H)chromenes (DPCs), bearing different substituents, is presented (Scheme 1). These molecules can be related to the parent 2,2-diphenyl-(2H)chromene (**1**), whose synthesis [11,12], dimerization reaction [13–15], photochromic behaviour [10,16–18] and time-resolved absorption studies by means of nanosecond [19], picosecond [19] and femtosecond [20] techniques have been already reported in the literature. The photochromic behaviour of DPCs chromium tricarbonyl complexes has also been studied [21,22]. Recently, a new alternative strategy for the synthesis of the nitro derivatives [23] of **1** and a spectral analysis of phenyl-substituted DPC have been published [24]. However, to the best of our knowledge, no quantitative study of the photochromic reaction of the aforementioned DPCs, has ever been reported.

In the present paper, a detailed study of the photochromism of these compounds is carried out with the aim to find out the effect of structure on their spectra, photochemistry and thermal bleaching kinetics. Changing the substituents in structurally related molecules may drastically change their photochromic properties either affecting the spectrum of the colourless form, or that of the coloured form, or the thermodynamics of the photochemical and thermal processes. Such modifications may provide molecules with enhanced commercial potential. Where fluorescence, which can provide a light-triggered signal alternative to colour, was observed, the corresponding quantum yield was measured.

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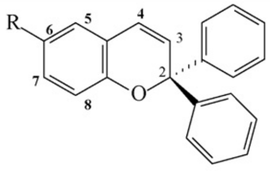
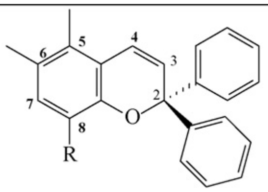
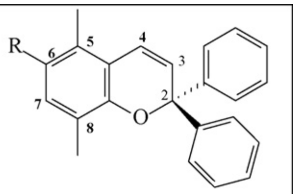
chromene skeleton R			
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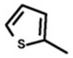
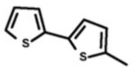
	6-Th-DPC **2**	5,6-diMe, 8-Th-DPC **3**	5,8-diMe, 6-Th-DPC **4**
	6-Th$_2$-DPC **5**	5,6-diMe, 8-Th$_2$-DPC **6**	5,8-diMe, 6-Th$_2$-DPC **7**
-B(OH)$_2$	6-B(OH)$_2$-DPC **8**	5,6-diMe, 8-B(OH)$_2$-DPC **9**	5,8-diMe, 6-B(OH)$_2$-DPC **10**
-NO$_2$		5,6-diMe, 8-NO$_2$-DPC **11**	5,8-diMe, 6-NO$_2$-DPC **12**

Scheme 1. Structures of the molecules investigated.

2. Materials and methods

2.1. Materials

The benzopyrans investigated were synthesized at the University of Marseille [23]. Their purity (>98%) was checked by HPLC. The photokinetic measurements were carried out in 3-methylpentane (3MP, BDH), distilled before use.

2.2. Apparatus

The absorption spectra were recorded using a HP 8453 diode-array spectrophotometer. Irradiation of the sample solutions was carried out in a 1 cm cell-path in the spectrophotometer holder, at a right angle to the monitoring beam, using a fibre-optic system. A 125 W Xe lamp, coupled with a Jobin-Yvon H10 UV monochromator, was used for irradiation and an Oxford Instruments cryostat for the temperature control. A grey filter (10% transmittance) was inserted between the sample and the spectrophotometer source, to avoid that a fraction of the UV light might reach the sample, thus inducing photochemistry.

The emission spectra were taken using a Spex Fluorolog-2 1680/1 spectrofluorimeter; the quantum yield was determined using 9,10-diphenylanthracene in cyclohexane as a standard (quantum yield in deaerated solution: $\Phi_F = 0.90$ [25]). An uncertainty of 15% is estimated for the fluorescence quantum yield.

2.3. Methods

The quantum yields of the closed to open form photocolouration ($\Phi_{C\to O}$) and of the back photobleaching ($\Phi_{O\to C}$) were spectrophotometrically determined in 3MP using concentrations in the range of 10^{-4}–10^{-5} mol dm^{-3}. Potassium ferrioxalate actinometry was used to measure the radiation intensity, which was typically on the order of 2–3 × 10^{-7} moles of quanta dm^{-3} s^{-1}. The uncertainty in the quantum yield determinations is about 10%.

Eq. (1) [26] describes the colour-forming kinetics:

$$\frac{dA_O}{dt} = \varepsilon_O\ \Phi_{C\to O} I_C - k_\Delta A_O \tag{1}$$

A_O is the absorbance (1 cm cell-path) of the open (coloured) form at the analysis wavelength, I_C is the light intensity absorbed by the closed form at the irradiation wavelength, ε_O is the molar absorption coefficient of the coloured form at the analysis wavelength and k_Δ is the rate constant of thermal bleaching. Eq. (1) can be rearranged into the following equation:

$$\frac{dA_O}{dt} = \varepsilon_O\ \Phi_{C\to O}\varepsilon_{iso} I^0 F A^0 - A_O[I^0 F \varepsilon_{iso}\Phi_{C\to O} + k_\Delta] \tag{2}$$

where ε_{iso} is the molar absorption coefficient at the irradiation wavelength (isosbestic point), F is the photokinetic factor ($F = [1 - \exp(-2.3A')]/A'$, where A' is the total absorbance at the excitation wavelength (λ_{exc}) [26]), I^0 the intensity of the incident light and A^0 the initial absorbance at λ_{exc}. When possible, irradiation was carried out in the correspondence of an isosbestic point, in order not to change the total absorbance during the experiment. The absorbance-time data sets allow the values of ε_O and $\Phi_{C\to O}$ to be determined, once the k_Δ parameter is derived by plotting dA_O/dt vs. A_O, according to Eq. (2). An example of such linearization is shown in Fig. 1.

The kinetics of the thermal ring-closing reaction were recorded in the dark, following the colour-bleaching of the irradiated solution after switching off the UV source. The thermal bleaching kinetics were fitted using the experimental absorbance-time data which were interpolated with either mono- (Eq. (3)) or bi-exponential (Eq. (4)) functions, accounting also for the residual absorbance, R:

$$A_O = A_O^0\ \exp(-k_\Delta t) + R \tag{3}$$

$$A_O = A_{O1}^0\ \exp(-k_{\Delta 1} t) + A_{O2}^0\ \exp(-k_{\Delta 2} t) + R \tag{4}$$

Arrhenius diagrams were determined in the 250–280 K temperature range by plotting $\ln(k_\Delta)$ as a function of $1/T$. By using the

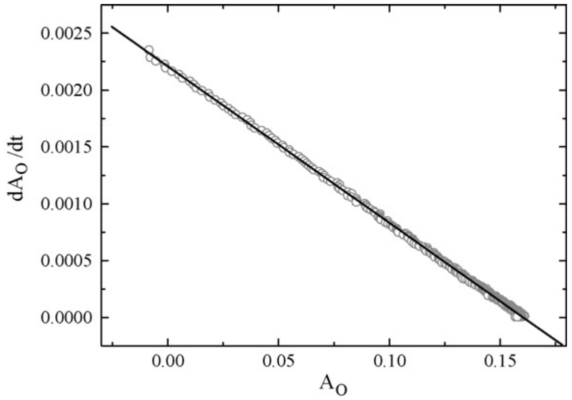


Fig. 1. Kinetic data of UV-photocolouration for **5** at 180 K in 3MP, treated according to Eq. (2).

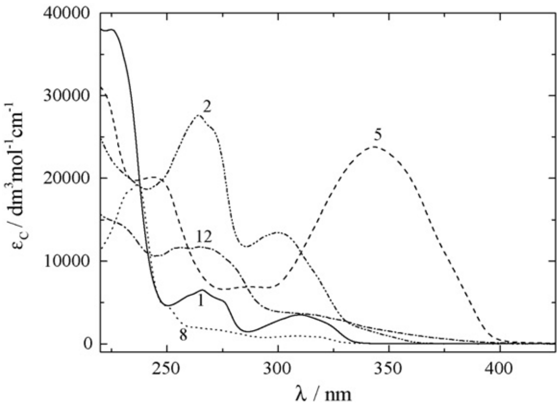


Fig. 2. Quantitative absorption spectra of the closed colourless forms of **1**, **2**, **5**, **8**, and **12** at 280 K in 3MP.

following Eyring equation:

$$\ln\left(\frac{k_\Delta}{T}\right) = \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} \qquad (5)$$

the thermodynamic activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) of the thermal bleaching process were obtained.

The photobleaching quantum yields were measured by irradiating the thermally bleached solution with visible monochromatic light ($I^0 \sim (0.6–1) \times 10^{-6}$ moles of quanta dm^{-3} s^{-1}) and following the colour fading up to at least 30% transformation, based on Eq. (6) [27]:

$$-\frac{dA_O}{dt} = \varepsilon_O \; \Phi_{O\to C} I^0 (1 - 10^{-A'_O}) \qquad (6)$$

where A'_O is the absorbance of the coloured form at λ_{exc}. Both A_O and A'_O are time dependent variables. Based on Eq. (6), the quantum yield was obtained from the linear plot of $-dA_O/dt$ vs. $10^{-A'_O}$, which gives $\varepsilon_O \times \Phi_{O\to C}$ from both the intercept and slope.

3. Results

3.1. Spectrokinetic behaviour

The absorption spectra of the closed colourless forms of the compounds investigated generally show an increase in molar absorption coefficient, with respect to the parent molecule, and a red-shift, particularly marked for the dithienyl derivatives (Table 1). Some examples of absorption spectra are shown in Fig. 2.

Colouration of the samples, upon UV irradiation, was studied in the 250–280 K temperature range. The kinetics fit well a bi-exponential function over a large temperature interval. Only lowering temperature down to 180 K, the kinetics fit a single exponential function. An example of such behaviour is illustrated in Fig. 3, where the colouration kinetics of compound **5**, at 275 K (a, bi-exponential) and 180 K (b, mono-exponential), are shown. At 180 K, where the thermal bleaching is slowed down and the mono-exponential treatment can be applied, the quantum yield of photocolouration and the molar absorption coefficient of the coloured form, produced at faster rate, could be determined (Table 2).

The absorption spectra at the photostationary state show, in the visible region, the spectral features of the open coloured forms, which are rather similar to each other in shape, showing a narrow vibrationally structured band around 400 nm and a broader absorption between 450 and 700 nm; the spectra obtained upon irradiation of the thienyl and dithienyl derivatives are somewhat red-shifted (Fig. 4).

The ring-open coloured forms, produced upon UV irradiation, spontaneously rearrange back to the closed uncoloured form. The thermal bleaching process always consists of two components but,

Table 1
Molar absorption coefficients of the colourless closed forms (ε_C) at the maximum absorption wavelengths (λ_{max}) of the DPCs in 3MP

Compound	ε_C (λ_{max}) dm^3 mol^{-1} cm^{-1} (nm)
1	6500 (266); 3500 (310)
2	27,600 (264); 13,500 (300)
3	20,100 (277); 3700 (343)
4	21,200 (240); 19,500 (259); 1300 (327)
5	20,100 (244); 23,800 (344)
6	15,600 (249); 12,600 (284); 18,100 (342); 18,000 (363)
7	19,500 (239); 12,000 (293); 16,700 (325)
8	19,200 (237); 950 (309)
9	21,600 (234); 5100 (272); 2500 (324)
10	21,000 (242); 1000 (317)
11	14,800 (260); 3500 (345)
12	11,800 (257); 12,000 (265)

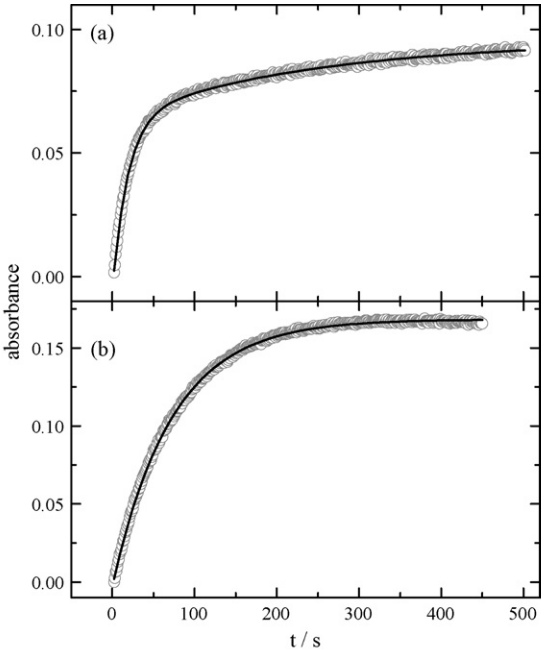


Fig. 3. UV-photocolouration kinetics of **5** monitored at λ = 555 nm at 275 K (a) and 180 K (b) in 3MP.

Table 2
Spectral (molar absorption coefficient of the coloured open forms (ε_O) at the maximum absorption wavelength, λ_{max}), photochemical (quantum yield of UV photocolouration, Φ_{col}, and visible photobleaching, Φ_{bl}) and kinetic (rate constant at 280 K, k_{280}, activation energy, E_a, frequency factor, A) parameters of the DPCs in 3MP

Compound	Φ_{col}	ε_O (λ_{max}) dm^3 mol^{-1} cm^{-1} (nm)	k_{280} (s^{-1})	E_a (kJ mol^{-1})	A (s^{-1})	$\Phi_{photobl}$
1	1.00	11,900 (500)	0.141	60.1	3.4×10^{10}	10^{-2}
2	0.59	15,750 (523)	0.0757, 0.0114	63.6, 56.6	6.1×10^{10}, 4.7×10^{8}	$<10^{-4}$
3	0.79	7,900 (580)	0.196	58.7	2.0×10^{10}	9×10^{-3}
4	0.70	8,300 (510)	0.135	58.4	9.8×10^{9}	5×10^{-3}
5	0.44	12,530 (555)	0.0468, 0.00096	69.1, 20.5	3.5×10^{11}, 6.4	$<10^{-4}$
6	0.54	6,800 (645)	0.157	58.7	1.6×10^{10}	1.5×10^{-3}
7	0.35	12,400 (528)	0.126	51.8	6.1×10^{8}	8.5×10^{-3}
8	1.0	2,200 (530)	0.187	73.6	1.2×10^{13}	1×10^{-3}
9	0.81	4,820 (550)	0.0973	56.6	4.2×10^{9}	$<10^{-4}$
10	0.79	3,200 (495)	0.0484	75.9	1.4×10^{13}	1×10^{-3}
11	0.55	7,500 (510)	0.0025	36.3	1.4×10^{4}	$<10^{-4}$
12	0.66	11,700 (503)	0.0026	15.7	2.2	$<10^{-4}$

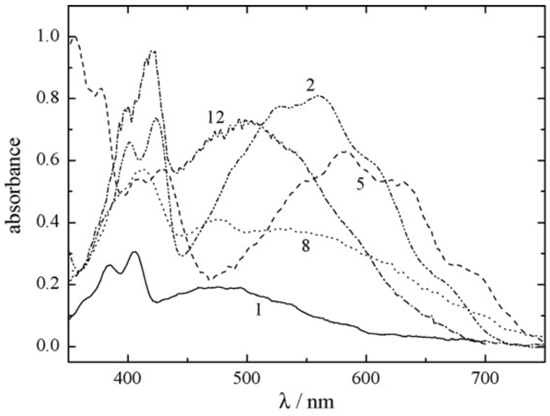


Fig. 4. Absorption spectra at the photostationary state of **1**, **2**, **5**, **8**, and **12** under irradiation at λ = 309, 279, 343, 310 and 283 nm, respectively, at 180 K in 3MP.

whilst in the case of the thienyl-substituted compounds both of them have comparable kinetics, for the other molecules they are characterised by very different rate constants. In the latter cases, only the bleaching parameter of the faster process was determined (Table 2).

The activation energies and frequency factors of the thermal bleaching were determined from Arrhenius plots ($r \geq 0.99$, see Table 2); two meaningful graphical examples are shown in Fig. 5.

The thermodynamic activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) for the thermal bleaching are reported in Table 3.

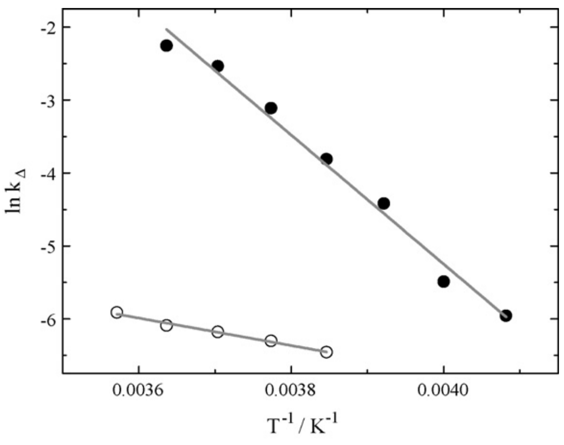


Fig. 5. Examples of Arrhenius plots for **8** (●) and **12** (○) in 3MP.

The slower thermal process can be slightly accelerated by visible irradiation even though, in this case, the bleaching of the coloured form occurs without full recovery of the starting spectrum, thus indicating a probable side reaction triggered by visible light. Anyway, visible photobleaching is substantially negligible and characterised by very low quantum yields (10^{-3}–10^{-4}, Table 2). For some naphthopyrans, by NMR analysis, an allene intermediate has been recognized which is formed by VIS irradiation of the *transoid-cis* and reconverts to the *transoid-cis* form through an inactivated dark reaction [28 and references therein]. Such intermediate can be only tentatively hypothesized in the present case, since it was impossible to accumulate it in a significant concentration.

3.2. Fluorescence emission

Among the molecules investigated, only the dithienyl derivatives were found to exhibit fluorescence emission upon UV light excitation of the closed form (Fig. 6).

The quantum yields of fluorescence (ϕ_F), are on the order of magnitude of 10^{-3}. They show a regular dependence on λ_{exc}, increasing with decreasing the excitation energy (Table 4).

The normalized fluorescence excitation spectra, monitored at different emission wavelengths, match with each other, showing that they arise from the same excited species. Nevertheless, they do not overlap the corresponding absorption spectra, as shown for **5** in Fig. 7.

4. Discussion

4.1. Effects of the substituent

The absorption spectra of the colourless forms of the chromenes examined are affected by the substituents in both intensity and

Table 3
Thermodynamic activation parameters for the thermal bleaching process of the DPCs in 3MP

Compound	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta G^{\neq}_{280}$ (kJ mol^{-1})
1	58.0	−50	72.0
2	60.7, 54.6	−48, −86	74.1, 78.7
3	56.5	−55	71.9
4	56.2	−61	73.3
5	66.5, 18.3	−31, −237	75.2, 84.7
6	56.5	−57	72.5
7	49.6	−84	73.1
8	71.4	−1.4	71.8
9	54.4	−68	73.4
10	73.7	−0.5	73.8
11	34.0	−173	82.4
12	13.4	−246	82.3

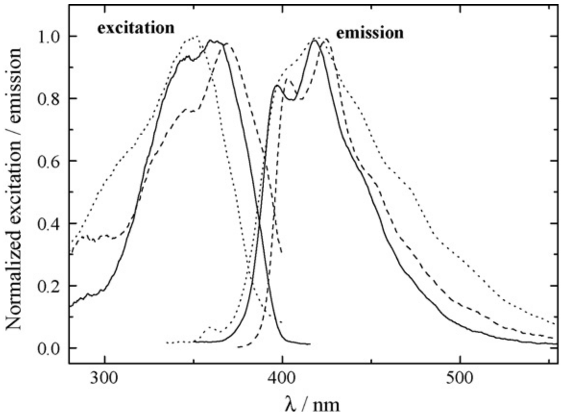


Fig. 6. Normalized fluorescence emission and fluorescence excitation spectra of **5** (full, $\lambda_{exc} = 340$ nm), **6** (dash, $\lambda_{exc} = 370$ nm), **7**(dot, $\lambda_{exc} = 330$ nm) at room temperature in 3MP.

Table 4
Quantum yields of fluorescence as a function of λ_{exc} for the three dithienyl-DPCs in 3MP

λ_{exc} (nm)	Φ_F ($\times 10^3$)		
	5	**6**	**7**
270	1.8		3.4
290			3.1
300			4.1
310			3.8
325			4.2
330	3.8		4.5
340	4.7	1.2	
350	5.9	1.6	8.5
360	7.0	2.1	
370	8.8	3.2	
380		5.1	
390		9.2	

position, compared with that of the parent molecule **1**. A general increase of molar absorption coefficient and a neat bathochromic shift are exhibited by the thienyl and dithienyl derivatives, whereas molecules with $B(OH)_2$ as substituent have significantly lower absorption coefficients (Table 1). The marked hyperchromic effect of compounds **2** and **5** is due to the thienyl group(s) in 6 position which have a lowest excited state of allowed ^1B_u character [29] and enhance the conjugation of the overall molecular system. Similarly, we have found that, in naphthopyrans, the thienyl substitution in 8 position results in a bathochromic shift and an increase of molar absorption coefficient of the long-wavelength absorption band of the colourless form [28].

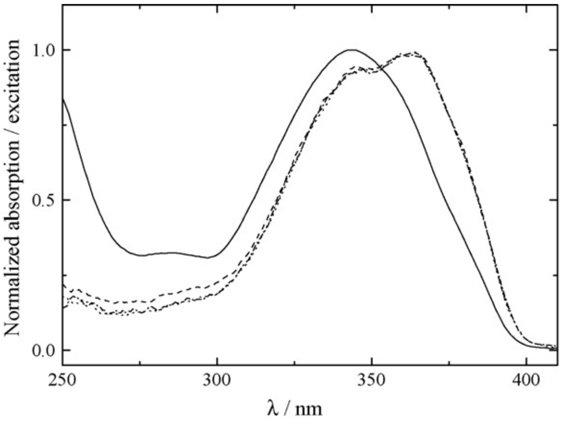


Fig. 7. Normalized absorption (full) and fluorescence excitation spectra of **5** monitored at $\lambda_{em} = 400$ nm (dash), 420 nm (dot) and 450 nm (dash-dot) in 3MP.

As far as the coloured forms are concerned, all spectra are red-shifted with respect to the reference compound, especially those of thienyl and dithienyl derivatives. This effect can be ascribed to the extended π conjugation induced by the thienyl group(s) [28,30–32] and is more pronounced when substitution occurs in the 8 position, molecules **3** and **6**.

The quantum yields of photocolouration are all notably high (in some cases almost one), but they are lowered by thienyl substitution and decrease with the number of thienyl units. This effect, already observed for some thienyl-substituted naphthopyrans [28], can be attributed to the presence of additional relaxation processes occurring from the lowest excited singlet state, such as fluorescence emission and intersystem crossing to the triplet state, that compete with photocolouration. Attempts to detect the triplet, using laser flash photolysis with nanosecond time resolution, were unsuccessful, whereas fluorescence was observed, showing an interesting λ_{exc} effect (Table 4). Such behaviour has been previously observed for an analogous thiophene-substituted chromene [28] as well as for several naphthopyrans [5,33,34] and is attributed to the competition between photoreaction and vibrational relaxation at each vibrational level of an electronically excited state. This competition reduces the population of the $S_1(0)$ level, from where fluorescence occurs, as much as higher is the excitation energy. As a consequence, the fluorescence excitation spectrum is different from the absorption spectrum since it looses intensity towards the short wavelength region.

The colourability of photochromes depends on the quantum yield of the colouration reaction, Φ_{col}, the absorption coefficient of the coloured form, ε_O, as well as the kinetic constant of the thermal back reaction, k_Δ. The smaller k_Δ and the larger ε_O and Φ_{col} are, the greater the maximum colour intensity attainable. The effect of k_Δ on colourability implies that it strongly depends on the temperature when the activation energy of bleaching is high. For some applications, a photochrome with low bleaching activation energy would be desirable in order not to have a strongly temperature-dependent colourability. The k_Δ values determined at 280 K for the compounds investigated (Table 2) are all in the range of 10^{-2}–10^{-1} s^{-1}, with the exception of the two nitro-derivatives for which they are notably smaller, despite their lower activation energies. This is due to the unusually low frequency factors. As a consequence, the colourability of these two compounds is scarcely temperature-dependent in a wide temperature range. This behaviour is illustrated in Fig. 8, where the photocolouration kinetics of **12** ($E_a = 15.7$ kJ mol^{-1}) are compared with those of **10**, which has a "normal" activation energy ($E_a = 75.9$ kJ mol^{-1}), in the temperature range of 250–280 K. It can be observed that the conversion percentage at the photostationary state is almost constant for **12**, whereas it increases from 0.01 at 280 K to 0.1 at 250 K for **10**.

The activation parameters of the thermal bleaching reflect the kinetic behaviour (Table 3). Free energy, $\Delta G^{\neq}$, is scarcely affected by substitution, its value ranging from 72 to 85 kJ mol^{-1}, whereas significantly different values are obtained for the activation entropy, $\Delta S^{\neq}$, which is *quasi*-zero for compounds substituted with $B(OH)_2$ in 6 position (**8** and **10**). In all the other cases, $\Delta S^{\neq}$ is negative, indicating a transition state with a more constrained structure than the open form. For the nitro derivatives, extremely low frequency factors ($\leq 10^4$ s^{-1}) were found, which are associated to markedly negative activation entropies. The activation enthalpy, $\Delta H^{\neq}$, is also structure dependent, ranging from 13 to 74 kJ mol^{-1}and being especially low for the NO_2-derivatives. The NO_2 effect on the kinetic and thermodynamic parameters can be understood considering its strong electron-withdrawing prop-

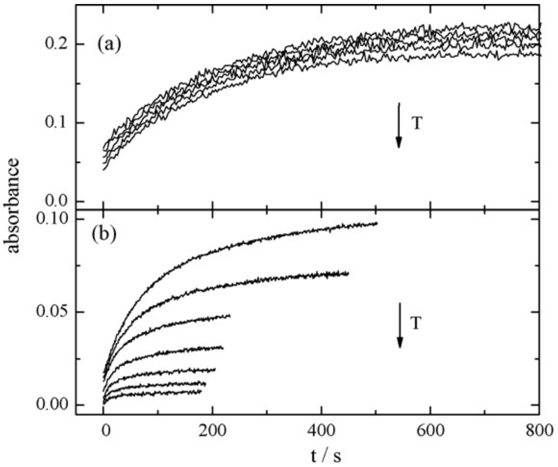


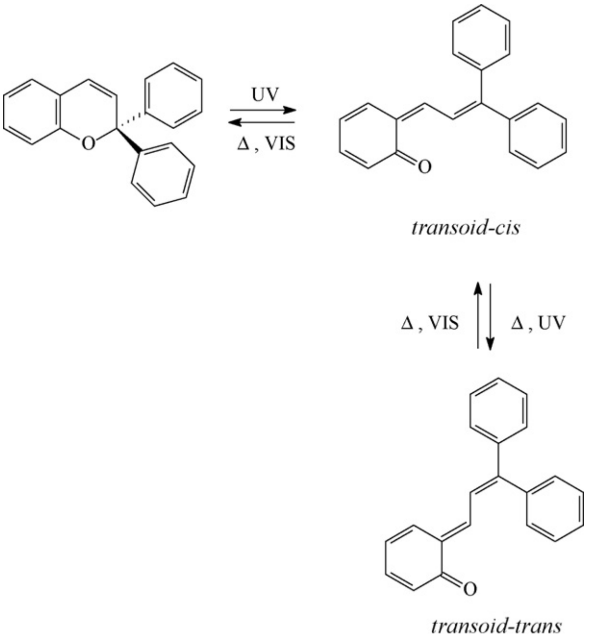
Fig. 8. Colour-forming kinetics for (a) **12** and (b) **10** as a function of the temperature.

erties. A comparison with structurally related spiro-compounds will be useful. It is known that these molecules generally exhibit positive solvatochromic effect (bathochromic shift on increasing polarity) because the contribution of low-polar quinoid forms dominates in the ground state [35,36]. However, with the NO_2 substituent, negative solvatochromism (hypsochromic shift with polarity) has been observed [37]. The blue shift in polar solvents indicates that the dipole moment, from the value characteristic of a highly polar ground state (zwitterionic-type), decreases considerably in the excited state (quasi charge recombination). This implies that the transition state is structurally more similar to the closed form than to the open molecular species. The highly negative $\Delta S^{\neq}$ is related to the decreased torsional freedom in the transition state. A positive contribution to entropy, expected from the randomization of the solvent molecules organized around the more polar ground state open form, appears completely negligible.

4.2. Mechanism

Despite the differences induced by changes of substituents in the spectral, photochemical and kinetic parameters, the mechanism of the photochromic behaviour of these compounds can be illustrated by a common scheme (Scheme 2).

The bi-exponential behaviour of the colouration kinetics in the temperature range explored (250–280 K) indicates the formation of at least two photoproducts, as found in other cases, which exhibit different thermal and/or photochemical reactivity [27,38–47]. For some naphthopyrans (5,6-benzochromenes [39,41–45], 7,8-benzochromenes [27,38,45], fluorenone-derived [46] and benzoindene-fused [47] benzochromenes), the structures of the two photoproducts have been assigned to the *transoid-cis* and *transoid-trans* isomers. According to the mechanisms proposed, the two isomers are formed in sequence upon UV irradiation: the *transoid-cis* is generally thermoreversible and the *transoid-trans* photoreversible, although an alternative reaction pathway has also been suggested, where both species are formed in a parallel process [27,38,42]. In the present case, where benzopyrans instead of naphthopyrans are involved, a consecutive mechanism is proposed. The bi-exponential character of the colouration curves is in agreement with the formation of two coloured species, even though the spectral difference between the two isomers is not straightforward, as also reported in the literature [39,42]. Another experimental evidence, to take into account in order to clarify the reaction mechanism, is that the colouration curves become mono-exponential at low temperature (180 K). This can be reasonably due to the presence of a thermal process and/or a thermally activated photochemical process on passing from the *transoid-cis* to the *transoid-trans* stereoisomer. The activation barrier to this photoisomerization would become insurmountable at low temperature, thereby blocking the UV-photoinduced transformation of the *transoid-cis* to the *transoid-trans* form. In contrast with the reaction mechanism proposed by others for naphthopyrans [32], we do not have any evidence for direct thermal conversion of the long-lived *transoid-trans* isomer to the closed form. The slow thermal step observed would correspond to the conversion *transoid-trans* → *transoid-cis*, which is the bottle-neck of the overall ring-closure process.



Scheme 2. General reaction mechanism.

With regard to the thermal bleaching process, all kinetics show a bi-exponential trend, which can be attributed to conversion of the two coloured stereoisomers to the starting molecule. The contribution of the slower process changes along the series but remains always of minor importance. However, whereas the fast component of the decay can always be readily monitored, the slow one is characterised by a much smaller rate coefficient and requires a prolonged period in the dark (at least one night at room temperature) in order to completely bleach. Therefore, the experimental determination of the kinetic parameter of the slow component is hard to be performed. An exception is represented by molecules bearing thienyl substituents in 6 position, that exhibit a two-component thermal bleaching which is clearly visible in the “normal” time window employed. This feature is in agreement with recent findings by Moorthy et al., who observed a bi-exponential pattern in the thermal decays of 6- and 7-arylchromenes [24].

5. Conclusions

The results obtained for the DPCs investigated in terms of their spectral, photochemical and kinetic parameters, allow structural effects on their photochromic behaviour to be evaluated. The substituent effect is reflected in the absorption spectra of the coloured and colourless forms, photocolourability, and kinetics of the thermal bleaching. Due to the presence of specific substituents, such as thienyl and nitro groups, the solar response is enhanced compared to the unsubstituted compound and the spectra of the coloured forms extend over a wide range of the visible radiation.

The photocolouration quantum yield is generally fairly high (0.7–1.0), but drastically decreases for di-thienyl substituted compounds, which also exhibit wavelength-dependent fluorescence. This behaviour, which is attributed to competition between photocolouration and vibrational relaxation, can offer the possibility of tuning the deactivation pathways by changing the excitation wavelength.

The bleaching process is markedly affected by the substituents. In the case of the nitro-derivatives, it is characterised by unusually low frequency factors and activation energies and this leads to photocolourability which is almost constant in a wide temperature range, thus giving excellent photochromic performance even at relatively high temperatures.

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References

[1] S. Maeda, in: R.J. Guglielmetti, J.C. Crano (Eds.), Benzo Organic Photochromic and Thermochromic Compounds, vol. 1, Kluwer Academic/Plenum Publishers, New York, 1999, pp. 85–109;
B. Van Gemert, in: R.J. Guglielmetti, J.C. Crano (Eds.), Benzo Organic Photochromic and Thermochromic Compounds, vol. 1, Kluwer Academic/Plenum Publishers, New York, 1999, pp. 111–140.
[2] N.Y.C. Chu, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990, pp. 493–509.
[3] R.S. Becker, J. Michl, J. Am. Chem. Soc. 88 (1966) 5931–5933.
[4] J. Kolc, R.S. Becker, J. Phys. Chem. 71 (1967) 4045–4048.
[5] R.S. Becker, E. Dolan, D.E. Balke, J. Chem. Phys. 50 (1969) 239–245.
[6] N.W. Tyer, R.S. Becker, J. Am. Chem. Soc. 92 (1970) 1289–1294.
[7] N.W. Tyer, R.S. Becker, J. Am. Chem. Soc. 92 (1970) 1295–1302.
[8] J. Kolc, R.S. Becker, Photochem. Photobiol. 12 (1970) 383–393.
[9] L. Edwards, J. Kolc, R.S. Becker, Photochem. Photobiol. 13 (1971) 423–429.
[10] C. Lenoble, R.S. Becker, J. Photochem. 33 (1986) 187–197.
[11] A. Lowenbein, E. Pongracz, E.A. Spiess, Ber. Dtsch. Chem. Ges. B. 57B (1924) 1517–1526.
[12] R. Guglielmetti, Proceedings of the SPIE—The International Society for Optical Engineering, vol. 3227, 1997, pp. 212–216.
[13] J. Cottam, R. Livingston, M. Walshaw, K.D. Bartle, D.W. Jones, J. Chem. Soc. (1965) 5261–5265.
[14] R. Livingston, D. Miller, S. Morris, J. Chem. Soc. (1960) 602–604.
[15] C.S. Barnes, M.I. Strong, J.L. Occolowitz, Tetrahedron 19 (1963) 839–847.
[16] R.S. Becker, US Patent 3,567,605 19,710,302 (1971).
[17] A.L. Padwa, G.A. Lee, J. Chem. Soc., Chem. Commun. (1972) 795–796.
[18] A.L. Padwa, G.A. Lee, W. Owens, J. Org. Chem. 40 (1975) 1142–1149.
[19] Y. Kodama, T. Nakabayashi, K. Segawa, E. Hattori, M. Sakuragi, N. Nishi, H. Sakuragi, J. Phys. Chem. A 104 (2000) 11478–11485.
[20] P.L. Gentili, E. Danilov, F. Ortica, M.A.J. Rodgers, G. Favaro, Photochem. Photobiol. Sci. 3 (2004) 886–891.
[21] P. Hannesschlager, P. Brun, Appl. Organometal. Chem. 13 (1999) 447–451.
[22] P. Hannesschlager, P. Brun, Appl. Organometal. Chem. 14 (2000) 686–690.
[23] L. Bougdid, A. Heynderickx, S. Delbaere, C. Moustrou, Tetrahedron 63 (2007) 8242–8249.
[24] J.N. Moorthy, P. Venkatakrishnan, S. Samanta, D.K. Kumar, Org. Lett. 9 (2007) 919–922.
[25] G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi, F. Momicchioli, J. Phys. Chem. 91 (1987) 4733–4743.
[26] G. Ottavi, F. Ortica, G. Favaro, Int. J. Chem. Kin. 31 (1999) 303–313.
[27] G. Favaro, A. Romani, R.S. Becker, Photochem. Photobiol. 72 (2000) 632–638.
[28] F. Ortica, P. Smimmo, G. Favaro, U. Mazzucato, S. Delbaere, D. Venec, G. Vermeersch, M. Frigoli, C. Moustrou, A. Samat, Photochem. Photobiol. Sci. 3 (2004) 878–885.
[29] R.S. Becker, J. Seixas de Melo, A.L. Maçanita, F. Elisei, Pure Appl. Chem. 67 (1995) 9–16.
[30] C. Moustrou, N. Rebière, A. Samat, R. Guglielmetti, A.E. Yassar, R. Dubest, J. Aubard, Helv. Chim. Acta 81 (1998) 1293–1302.
[31] N. Rebière, C. Moustrou, M. Meyer, A. Samat, R. Guglielmetti, J.-C. Micheau, J. Aubard, J. Phys. Org. Chem. 13 (2000) 523–530.
[32] M. Frigoli, V. Pimienta, C. Moustrou, A. Samat, R. Guglielmetti, J. Aubard, F. Maurel, J.-C. Micheau, Photochem. Photobiol. Sci. 2 (2003) 888–892.
[33] R.S. Becker, G. Favaro, A. Romani, P.L. Gentili, F.M.B. Dias, Chem. Phys. 316 (2005) 108–116.
[34] G. Favaro, A. Romani, R.S. Becker, Photochem. Photobiol. 74 (2001) 378–384.
[35] G. Favaro, F. Masetti, U. Mazzucato, G. Ottavi, P. Allegrini, V. Malatesta, J. Chem. Soc., Faraday Trans. 90 (1994) 333–338.
[36] A. Kellmann, F. Tfibel, R. Dubest, P. Levoir, J. Aubard, E. Pottier, R. Guglielmetti, J. Photochem. Photobiol. A: Chem. 49 (1989) 63–73.
[37] S.-R. Keum, M.-S. Hur, P.M. Kazmaier, E. Buncel, Can. J. Chem. 69 (1991) 1940–1947.
[38] G. Favaro, U. Mazzucato, G. Ottavi, R.S. Becker, Mol. Cryst. Liq. Cryst. 298 (1997) 137–144.
[39] G. Ottavi, G. Favaro, V. Malatesta, J. Photochem. Photobiol. A: Chem. 115 (1998) 123–128.
[40] B. Luccioni-Houze, M. Campredon, R. Guglielmetti, G. Giusti, Mol. Cryst. Liq. Cryst. 297 (1997) 161–165.
[41] J. Hobley, V. Malatesta, R. Millini, W. Giroldini, L. Wis, M. Goto, M. Kishimoto, H. Fukumura, Chem. Commun. (2000) 1339–1340.
[42] H. Görner, A.K. Chibisov, J. Photochem. Photobiol. A: Chem. 149 (2002) 83–89.
[43] S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon, G. Vermeersch, J. Chem. Soc., Perkin Trans. 2 (1998) 1153–1157.
[44] S. Delbaere, J.-C. Micheau, Y. Teral, C. Bochu, M. Campredon, G. Vermeersch, Photochem. Photobiol. 74 (2001) 694–699.
[45] J. Hobley, V. Malatesta, K. Hatanaka, S. Kajimoto, S.L. Williams, H. Fukumura, Phys. Chem. Chem. Phys. 4 (2002) 180–184.
[46] P.J. Coelho, L.M. Carvalho, S. Rodrigues, A.M.F. Oliveira-Campos, R. Dubest, J. Aubard, A. Samat, R. Guglielmetti, Tetrahedron 58 (2002) 925–931.
[47] C.I. Martins, P.J. Coelho, L.M. Carvalho, A.M.F. Oliveira-Campos, A. Samat, R. Guglielmetti, Helv. Chim. Acta 86 (2003) 570–578.