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Spectrokinetic study of a series of photochromic 2-ferrocenyl-2-methyl[2H]-chromenes

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Abstract

The study of the photochromic behaviour of a series of 2-ferrocenyl-2-methyl[2H]-chromenes has shown original spectrokinetic properties: the broadening of the absorption spectrum of the photomerocyanines with the appearance of a second band in the visible area and also important kinetic modifications in polar protic solvents giving to this series of chromenes a special interest. From spectrokinetic results, a structure of photomerocyanines stabilised by polar and protic solvent such as alcohols could be proposed.

Keywords: Chromenes; Benzoannellated [2H]-benzopyrans; Ferrocenyl; Photochromism; Hydrogen bonding; Spectrokinetics

1. Introduction

The [2H]-benzopyrans are an important family of photochromic pigments, the applications of which, for variable optical transmission materials, are well known [1]. The irradiation of such molecules by UV light involves the breaking of the C–O bond and their transformation into conjugated entities whose geometry is near planar, absorbing in the visible region (called photomerocyanines or open forms, OFs), whose reclosing is realised mainly by a thermal process but also by a photochemical process under visible irradiation (Scheme 1).

Photochromism can be defined by three main parameters: (i) the kinetic constant of thermal bleaching k_Δ, (ii) the λ_{max} of absorption of the OF, (iii) the colourability which corresponds to the absorbance at λ_{max} (A_∞ under continuous irradiation at photostationary state; A_0 under flash photolysis) [2].

The introduction of a ferrocenyl group (Fc) in the 2 position of the [2H]-chromenes modifies greatly the spectrokinetic parameters; indeed, the 2-ferrocenyl-2-phenyl benzochromenes annellated in (5–6) or (7–8) have two λ_{max} at about 460 and 600 nm in toluene while their diphenyl analogues present only one λ_{max} near 430 nm. The presence of the ferrocenyl group in 2 position modifies also the kinetic parameters [3,4]. We have modulated the substitution in the 2 position especially by introduction of methyl groups and we have prepared the (5–6) and (7–8) annellated compounds and (5–6/7–8) biannellated ones (compounds **1**–**3**) in order to check the influence of such modifications by reference to the phenyl-substituted series (compounds **4**–**6**).

2. Experimental

2.1. Materials

The synthesis has been realised using a previously described strategy [3] for the compounds **4**–**6**; the compounds **1**–**3** have been obtained with respective yields of 53, 15 and 23% (Fig. 1: an example is given for the synthesis of **1** and **4**).

In a typical experiment the ferrocenyl-propynol was first prepared as indicated and then reacted with the appropriate phenol.

Ferrocenyl-propynol. To a solution of ferrocenyl-ketone (1.5 mmol) in 100 ml of anhydrous THF was slowly added. The mixture was stirred for 2 h and 30 min then hydrolysed with saturated aqueous NH_4Cl. The organic phase was filtered on Celit, washed with H_2O, dried with $MgSO_4$ and evaporated. The residue was rapidly chromatographied (silica gel, hexane/ether: 75/15).

Ferrocenyl-[2H]-benzopyrans. A solution of the appropriate alcohol (1 mmol) in minimum of CH_2Cl_2 was added to a solution of the phenol (4 mmol) in minimum of CH_2Cl_2. The mixture was stirred until total consumption

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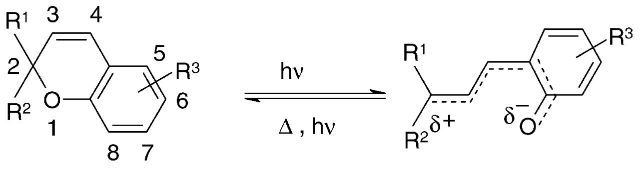


Scheme 1. Photochromic equilibrium for the chromene series.

of propargylic alcohol. The organic phase was washed with H_2O, dried and reduced under vacuum. The residue was chromatographied (silica gel, 100% hexane).

2.2. Apparatus and analytical methods

A Beckman DU-7500 spectrometer was used for recording the absorption spectra and measuring the thermal bleaching by following time-evolution under irradiation with an Oriel Xe lamp (150 W) using an optical fibre and a thermostated cell.

3. Results: evaluation of spectrokinetic parameters

The spectrokinetic parameters of compounds **1**–**3** have been measured under continuous irradiation, in three anhydrous solvents of different polarities (acetonitrile, toluene and ethanol), at a thermoregulated temperature of 25 °C and at a concentration of 2×10^{-4} M [5]. The λ_{max} are given in nm and the k_Δ in $10^{-3}\,s^{-1}$ (two values of kinetics: one fast, one slow) are determined at the wavelengths mentioned in brackets (Table 1). The colourability A_∞ is not given because these chromenes under continuous irradiation reach very slowly the photostationary state (6–12 h).

3.1. Spectroscopic properties

The 2-ferrocenyl-2-methyl[2H]-chromenes (**1**–**3**) present two principal characteristics:

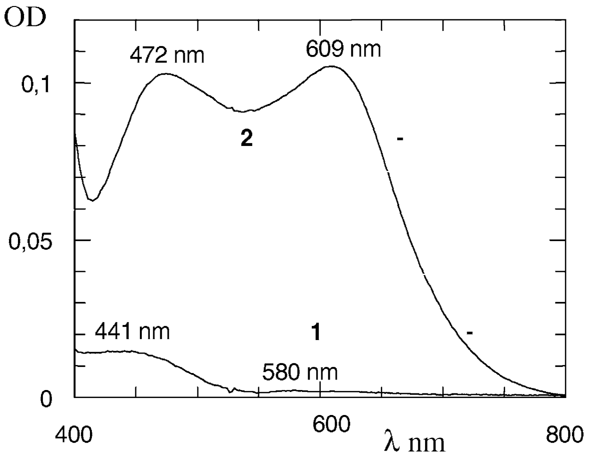


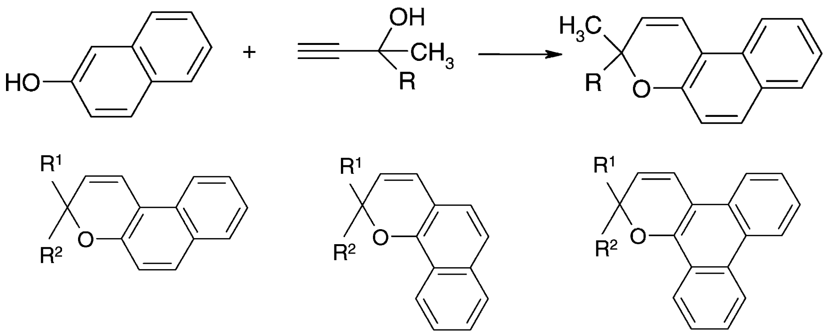
Fig. 2. Comparison of the visible absorption spectra in acetonitrile of the photomerocyanines of ferrocenyl-chromenes **1** and **2** having a different type of annellation.

- The visible spectrum of the OF has two λ_{max} (around 450 and 600 nm), while their diphenyl homologues (**4**–**6**) have only one λ_{max} of absorption.
- The presence of the second λ_{max} contributes to the considerable broadening of the visible spectrum of the OF.
- For the same time of irradiation, the (7–8) annellated compound **2** has an absorbance higher than that of the (5–6) annellated compound **1** (Fig. 2).

In the case of the (7–8) annellated compound **2**, the value of the absorbance for the second λ_{max} is comparable to that of the first λ_{max}. In contrast, for (5–6) annellated compound **1** and (5–6, 7–8) biannellated compound **3**, the value of the absorbance at 560–580 nm are lower than those measured at 440 nm.

3.2. Kinetic properties

A solution of photochromic compound was continuously irradiated by a UV beam until the photostationary state (equilibrium CF-OF) has been nearly reached. The



1 $R^1=CH_3$, $R^2=Fc$ **2** $R^1=CH_3$, $R^2=Fc$ **3** $R^1=CH_3$, $R^2=Fc$

Fig. 1. Synthesised chromenes.

Table 1
Spectrokinetic characteristics of the chromenes **1–6**

	Acetonitrile	Toluene	Ethanol
Chromene **1**			
λ_{max}	441, 580	425, 587	437, 584
k_{Δ}	–	–	–
Chromene **2**			
λ_{max}	472, 609	473, 608	400, 425, 608
k_{Δ}	10.8/4.2 (472 nm)	0.9 (473 nm)	0 (400 nm)/1.4 (609 nm)
Chromene **3**			
λ_{max}	440, 563	440, 563	400, 530, 609
k_{Δ}	157.9/1.6 (440 nm)	144.1/0.1 (440 nm)	0 (400 nm)/1.4 (609 nm)
Chromene **4**			
λ_{max}	410	411	417
k_{Δ}	100/0.2	160/0.4	210/0.9
Chromene **5**			
λ_{max}	458	450	461
k_{Δ}	21.9/1.1	14.8/0.5	5.6/0.8
Chromene **6**			
λ_{max}	400	400	400
k_{Δ}	60.8/0.8	40.5/0.2	65.9/22.8

irradiation is stopped and the thermal bleaching constant k_{Δ} is determined (first-order kinetics). The results (Table 1) show that, for the compound **1**, the closure thermal kinetics is too rapid for being observed by this method.

It is difficult to find a correlation between the structure of the chromenes and their thermal bleaching kinetics; the kinetics depend on the substituents in 2 position, the type of annellation and the solvent.

The compounds **2** and **3** have a bleaching kinetics equal to 0 in ethanol at 400 nm. Indeed when the compound **2** in ethanol is no more irradiated (Fig. 3) the absorbance at 400 nm does not vary while a decrease of the absorbance in the area from 450 to 650 nm is observed. This area corresponds to the classical visible spectrum for this type of compound (Fig. 2). The k_{Δ} kinetics measured at 609 nm for compounds **2** and **3** in ethanol have a value of $1.4 \times 10^{-3}\ s^{-1}$.

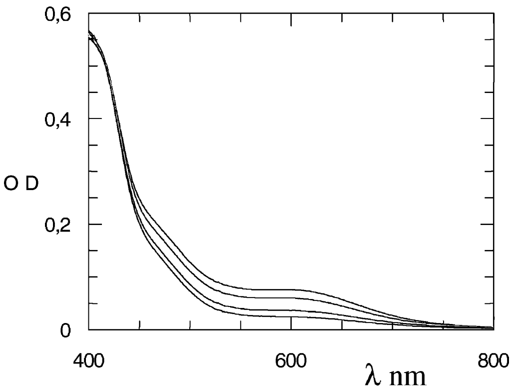


Fig. 3. Spectrum describing the thermal bleaching of compound **2** in ethanol.

The absorbance at 400 nm increases with time of irradiation. We verify that this absorption is not related with the formation of a degradation by-product. Indeed a solution of **2**, previously irradiated in ethanol, evaporated to dryness and again dissolved in ethanol shows no absorption in the 400 nm area. After irradiation, this same solution absorbs again at 400 nm. These results show that the absorption at 400 nm is induced by a permanent coloured species. This phenomenon is not observed in toluene or acetonitrile.

The general outline of the visible spectrum of the compound **2** in ethanol, after irradiation is related to the presence of at least two photomerocyanine stereoisomers: one or several classical stereoisomers absorbing between 450 and 650 nm, having a bleaching kinetic constant different from zero and one isomer absorbing at 400 nm having probably a structure weakly conjugated (see Fig. 7).

In order to have a better understanding of the effect of alcohols on the bleaching kinetics of compounds **2** and **3**, we have tested a series of alcohols with different steric hindrances (methanol, ethanol, propanol, *iso*-propanol, butanol and *iso*-butanol) (Table 2, Fig. 4).

The results obtained show that the closure kinetics is directly related to the alcohol used. Indeed when the hydrocarbon chain of the alcohol is increasing, the kinetics is different from zero, this phenomenon is particularly sensitive with the

Table 2
Closing kinetics of compounds **2** and **3** in different alcohols at 400 nm

Compound	MeOH	EtOH	PrOH	*i*PrOH	BuOH	*i*BuOH
2	$k_{\Delta} = 0$	$k_{\Delta} = 0$	$k_{\Delta} = 0$	$k_{\Delta} \neq 0$	$k_{\Delta} \approx 0$	$k_{\Delta} \neq 0$
3	$k_{\Delta} = 0$	$k_{\Delta} = 0$	$k_{\Delta} \approx 0$	$k_{\Delta} \neq 0$	$k_{\Delta} \neq 0$	$k_{\Delta} \neq 0$

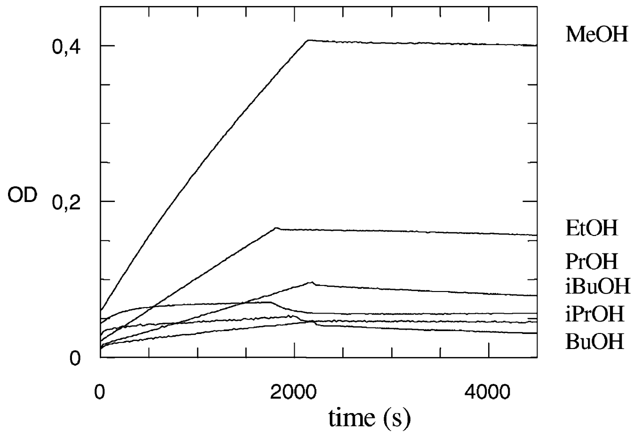


Fig. 4. Comparison of kinetic behaviour of compound **2** in function of the size of the alcohol at 400 nm.

solvents whose hydrocarbon chain is branched. The addition of a small quantity of acid (*p*-TsOH) to a solution of **2** in an alcohol (e.g. *i*PrOH) which does not complex the OF does not modify the closing kinetics. The presence of a permanent OF is thus not related to the protic character of the alcohols.

During these studies another original behaviour has been observed. After irradiation of a solution of the compound **2** in ethanol and registration of the typical spectrum of the OF, the ethanol solution has been evaporated with a nitrogen stream. The residue is then dissolved in acetonitrile. This solution turns spontaneously from yellow to a blue colour. The visible absorption spectrum of this new solution not irradiated shows that the λ_{max} at 400 nm has disappeared while a new absorption at 609 nm (Fig. 5) has appeared. This absorption corresponds to a transoïd OF which slowly closes. When this solution is irradiated, the intensity at 609 nm decreases and a second λ_{max} appears at 472 nm (Fig. 6).

Under irradiation by UV light two species appear to be in equilibrium, one has a λ_{max} at 472 nm and one has a λ_{max} at 609 nm. When equilibrium is finally reached the classical spectrum of 2 in acetonitrile is observed (Fig. 2).

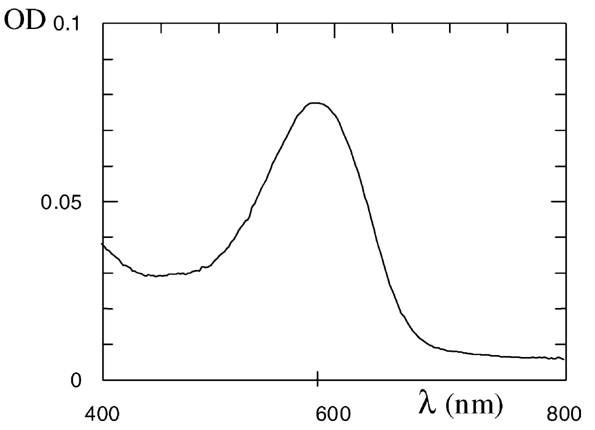


Fig. 5. Absorption spectrum of the compound **2** irradiated in ethanol, evaporated and again dissolved in acetonitrile.

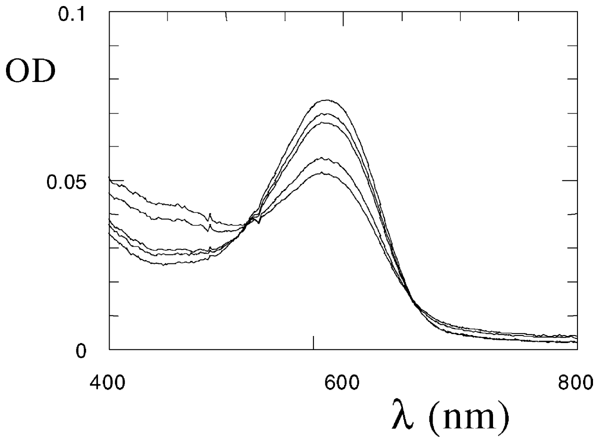


Fig. 6. Absorption spectrum under irradiation of a solution of compound **2** in acetonitrile, previously irradiated in ethanol.

In order to have more information about the structure of the permanent merocyanine that is formed in methanol or ethanol, the IR spectrum of an irradiated solution of **2** in methanol has been recorded by using an FT-IR spectrometer and a bromine and iodine thallium cell. The IR of the OF of **2** shows a vibration band at 1664 cm^{-1} which could be assigned to a quinoid form of the photomerocyanine (carbonyl function).

Table 2 also shows that the compound **3** is more sensitive to the steric hindrance of the alcohols when compared with compound **2**. This phenomenon could be attributed to the presence of an additional fused phenyl group in position 5–6. On the other hand when the methyl group is replaced by a phenyl group [3], a closure kinetics different from zero is observed in methanol and ethanol. These observations indicate that the steric interactions between groups in positions 2 and (5–6) of ferrocenyl-chromenes are directly related with the closure kinetics.

4. Discussion

In order to give some explanations for the existence of a coloured permanent OF depending on the nature of substitution on positions 2 and 5–6, some molecular mechanic calculations have been performed using GENMOL software [6–8] on five OFs of compound **2** (CCC, CTT, CTC, TTC and TTT) (Fig. 7).

The free energies of the molecules in vacuum and in different solvents were calculated. The purpose was to determine the most probable molecule form depending on the system free energy at room temperature. This energy can be estimated by the sum of the molecule strain energy and the solvatation enthalpy (Table 3).

The enthalpies are calculated with different solvents, i.e. the molecule is dipped in a solvent box, the form of which is similar to the molecule and contains at least three layers of solvent molecules. Some molecular dynamics cycles

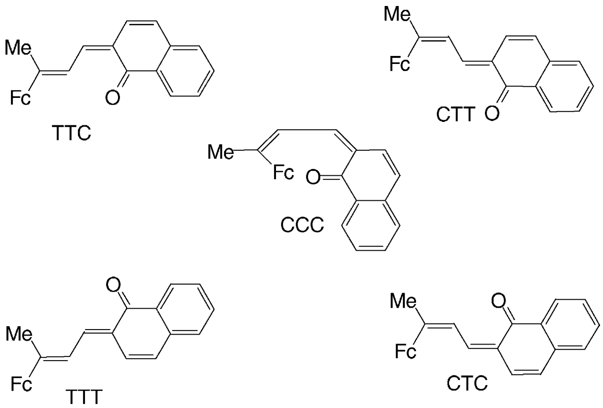


Fig. 7. Possible stereoisomers of OF.

Table 3
Calculation of molecule free energy at room temperature for the five OFs

Free energy (kcal/mol)	TTC	CTT	TTT	CTC	CCC
In vacuum	−103	−103	−104	−107	−102
In CH_3CN	−147	−144	−158	−142	−150
In MeOH	−145	−167	−167	−157	−160
In *i*BuOH	−151	−141	−136	−134	−137

have been performed in order to obtain a coherent physical representation of the system. The solvatation enthalpy corresponds to the non-bonding interaction between the chromene and the solvent molecules. The entropy contribution to the solvatation free energy is equivalent for all the forms and the molecular entropy is negligible for such rigid molecules.

The most probable forms in solution will correspond to a minimum for the system free energy.

The results show that, in not solvated state, the CTC form is slightly more stable, while the TTC, CTT, TTT and CCC forms have similar energies. In solution, the energies are modified. So, in acetonitrile, the energy of the TTT form is markedly decreased while the energy of the CTT and CTC forms are higher than those of the CCC or TTC forms.

In methanol, the CTT and TTT forms are markedly stabilised; in *iso*-butanol only the TTC form is stabilised.

In all cases, the energy of the CCC form is a function of the solvent and this form is stabilised in methanol relatively to acetonitrile. The geometry of the CCC form is very similar to the geometry of the closed form which absorbs at about 360 nm; it is also the first one produced on opening of the closed form [9,10].

Our hypothesis is that under irradiation in methanol, ethanol or propanol, the CCC form having in these solvents a low energy is relatively stable and may have an absorption at 396 nm (a bathochromic shift of 36 nm as compared with the more conjugated closed form). A stable CCC form has been already characterised from similar compounds [11]. In solvents like acetonitrile, toluene or *iso*-butanol, this CCC form evolves under irradiation to give more stable forms absorbing at 472 and 609 nm. Chelation of the carbonyl group and iron atom by a molecule of alcohol could explain, in the CCC form, the different effects observed (Fig. 8).

When the steric hindrance of the alcohol is increasing, a non-bonding interaction with the substituent in positions 2 and 5–6 in the chromene prevents the stabilisation by chelation of this OF.

The increase of the steric hindrance on the 2 or 5–6 positions has the same effect. When the methyl group in 2 position is replaced by a phenyl group, the hydrocarbon chain of the alcohol is directly in non-bonding interaction with the phenyl group, preventing the formation of a chelate stabilising the CCC geometry. When this stabilised CCC form is dissolved in acetonitrile with some traces of ethanol, the energy increases strongly. With the change in polarity, the CCC stereoisomer becomes a CTT or TTC transoïd forms still stabilised by the alcohol molecule and absorbing at 609 nm (Fig. 9).

The CTT and TTC configurations are the only possible transoid forms that may be stabilised by the position of the alcohol molecule. Indeed, the ferrocenyl and the oxygen of the quinone being on the same side, it is possible for the alcohol to develop two stabilising interactions. For the TTC form, the approach of the alcohol is certainly more difficult considering the relative configurations. Under UV irradiation, there is isomerisation and an absorption band appears at 472 nm and the absorbance at 609 nm decreases.

In the total absence of small size alcohol, these two forms absorbing at 472 and 609 nm are present under UV irradiation. In more bulky alcohols, we are in the same case as in acetonitrile.

We could think that the stereoisomer absorbing at 609 nm in the other solvents (bulky alcohols, acetonitrile, toluene) has probably a CTT or TTC configuration. The configuration of the stereoisomer corresponding to the first λ_{max} (450 nm)

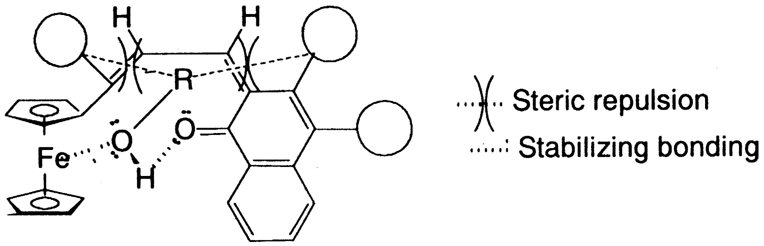


Fig. 8. Stabilisation of the CCC form.

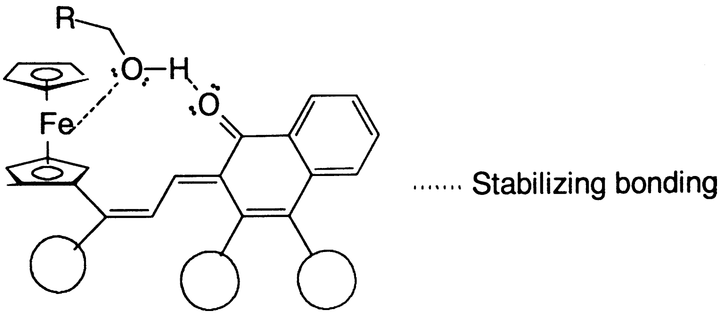


Fig. 9. Hypothesis about the structure of the transoid CTT OF stabilised by the alcohol, corresponding to the second absorption band (609 nm).

is certainly very near of that of the stereoisomer absorbing at 609 nm because the closure kinetics are very similar at the two λ_{max}. This stereoisomer is transoid and probably of the TTT type having the lowest energy. The hypothesis on the structure of stereoisomers corresponding to the two λ_{max} allows to explain the originality of the absorption spectra of these 2-ferrocenyl-2-methyl benzochromenes.

In conclusion, the hypothesis we propose is that a CCC form absorbing at 400 nm is formed in alcohol solvent. When the alcohol is evaporated and a new solution is prepared in acetonitrile without irradiation, this form evolves towards a CTT or TTC form after change of the polarity of the solvent and could absorbs at 609 nm. After irradiation of this form, an equilibrium is realised between the form responsible of the absorption at 609 nm and the TTT form absorbing at 470 nm having important non-bonding interactions at the level of the planar conjugated form. It must be noted that this behaviour is observed mainly for compound **2** and to a less extent for compound **3** (Table 3). The explanation lies on the fact that the chromenes annellated in the 7–8 positions lead to photomerocyanine forms much more stable than the photomerocyanines issued from 5–6 annellated compounds because of less strong non-bonding interactions.

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