

Quantum yields of photocoloration and molar absorption coefficients of ferrocenyl substituted benzo and dibenzochromenes. Comparison with their phenyl-homologues

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ABSTRACT. The photochromic properties of three ferrocenyl-[2H]-benzopyrans were investigated under monochromatic irradiation and compared with those of their phenyl homologues. The UV/visible spectra of the closed and open forms are reported together with the quantum yields of photocoloration. It was shown that the ferrocenyl- substitution induces the formation of a new band in the 500-700 nm range in the open forms, however, it does not affect significantly the UV spectra of the closed forms. Ferrocenyl- substitution was also shown to increase the thermal bleaching rate constants and to decrease the photocoloration quantum yields. For most compounds, photochromic behaviour was not sensitive to the irradiation wavelength. However, for the methyl ferrocenyl chromene, the open form spectrum was slightly dependent of the irradiation wavelength. The influence of the ferrocenyl group and other structural features on the photochromic properties are discussed.

1. INTRODUCTION

[2H]-benzopyrans (elsewhere called 2H-chromenes) are photochromic compounds. They undergo a photocleavage of the C – O bond leading to a photomerocyanine form often referred as the open form (OF) (Scheme 1) [1]. Due to electronic delocalization, the absorption range of the open form is shifted towards longer wavelengths, i.e. from the UV to the visible region. The thermally reversible closure of the photomerocyanine gives the starting [2H]-benzopyran which is often referred as the closed form (CF).

Their photochromic behaviour is characterized by the UV spectra of the closed and open forms (ϵ_{CF}^λ and ϵ_{OF}^λ), by the thermal bleaching kinetic rate constants (k_Δ) and by the value of the quantum yield of the reversible photocoloration (ϕ_{col}). These photochromic parameters are greatly influenced by the nature of the R¹ and R² groups placed on the Csp³ in the 2-position [2] and by the size of the aromatic moiety (benzo[h] or dibenzo[f, h] chromene). Moreover, the replacement of a phenyl group by a ferrocenyl one at the 2-position [3] leads to open forms with two λ_{max} resulting in a strong absorption range extension in the visible region [4]. The back closure process is accelerated and some stabilized photomerocyanines are observed in alcohol solutions [5]. It was also shown that the resistance to the

photodegradation was increased. Three ferrocenyl-benzopyrans [3, 4] (**1a-3a**) and their phenyl-homologues [6] (**1b-3b**) (Scheme 2) were studied under monochromatic irradiation (313 and 366 nm) in order to determine their photocoloration quantum yields and the molar absorption coefficients of their transient open forms.

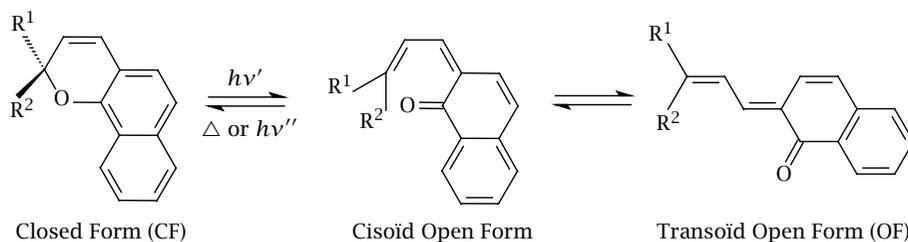
2. RESULTS AND DISCUSSION

2.1. UV spectra of the closed forms. Spectral analysis of the closed form [λ (nm), ϵ (L · mol⁻¹ · cm⁻¹)] has been realized in toluene and the results are reported in Table 1 (see Figure 1 for the detailed UV spectra of **2a** and **2b**).

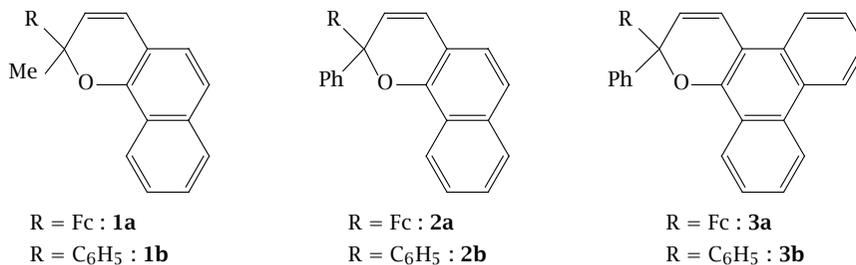
Table 1 shows that for each compound, there are several well-defined bands or shoulders that appear in the same narrow spectral range (1st λ_{max} : 315-317, 2nd λ_{max} : 326-333, 3rd λ_{max} : 340-345, 4th λ_{max} : 354-356, 5th λ_{max} : 374-375 nm). Spectra of the ferrocenyl substituted compounds **1a**, **2a**, **3a** are not significantly different from those of their phenyl homologues **1b**, **2b** and **3b**. On the other hand, phenanthreno-compounds **3a** and **3b** exhibit a characteristic strong band at 374-375 nm which appear to be specific for the phenanthreno-annellation. These results confirm that the pyranic moiety is responsible for the lower energy absorption bands of the closed form. Figure 1 shows the similarity between UV spectra of the closed forms of ferrocenyl- and phenyl-homologues.

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Scheme 1. Ring opening and ring closure of benzo-chromenes under irradiation.



Scheme 2. Structures of the studied compounds (Fc = ferrocenyl).

Table 1. UV spectra of compounds **1a–3b**.

no.	1 st λ_{\max} , ϵ_{\max}	2 nd λ_{\max} , ϵ_{\max}	3 rd λ_{\max} , ϵ_{\max}	4 th λ_{\max} , ϵ_{\max}	5 th λ_{\max} , ϵ_{\max}
1a (*)	317, 4250	327, 4800	340, 5000	354, 4270	(-)
1b	317(s), 4000	326, 4600	340, 4950	355, 4380	(-)
2a	(-)	328, 4360	340, 4500	354, 4100	(-)
2b	315, 4000	327, 4500	341, 4700	356, 4100	(-)
3a	(-)	(-)	344, 5950	354(s), 5560	375, 4090
3b	(-)	333(s), 4200	345, 4730	355(s), 4400	374, 3080

*: solvent: ma = methanol-acetonitrile 90–10 v/v; (s): shoulder, (-): no maximum.

2.2. Effect of the irradiation wavelength on UV-visible spectra of the open forms of compound **1a** in methanol.

The photochromism of these compounds has been investigated in four solvents: acetonitrile (a), ethanol (e) or methanol (m) and toluene (t) using independently two monochromatic irradiation wavelengths (313 and 366 nm). Usually, they lead to the same distribution of open forms with the same UV/visible spectra. However, in the case of **1a** in methanol, an unexpected effect has been observed. Both irradiation wavelengths lead to the formation of a broad spectrum exhibiting three bands at 387, 470 and 609 nm. But, when the irradiation is performed at 366 nm, the absorbances at 470 and 609 nm are smaller and the 387 nm band remains stable (i.e., there is no bleaching in the dark for this specific band) (Figure 2).

Such behaviour was already observed under polychromatic irradiation. A possible explanation would be the presence of a wavelength and irradiation time dependent proportion of the various expected photoisomers CCC, CTT, CTC, TTC and TTT (Figure 3). They are

able to undergo, either thermally or photochemically induced interconversions. If the thermal interconversion is slow, the photochemical interconversion prevails. Then, depending of their relative molar absorption coefficients at the UV irradiation wavelength, different distributions are likely to be established. The more energetic 313 nm irradiation could induce the partial photo-destruction of the long-lived photoisomer monitored at 387 nm letting it to accumulate under 366 nm irradiation.

2.3. Kinetic study of the thermal decay.

Under continuous monochromatic irradiation, a rather large proportion (from 42 to 95%) of the open forms was reached at steady state. As it has been shown with compound **1a** in methanol, depending on the nature of the irradiated compound, the irradiation wavelength, the photon flux, the solvent and the duration of the irradiation, several isomers are likely to be present. After the irradiation has been shut down, the system undergoes a thermal bleaching, however this process is not 100%

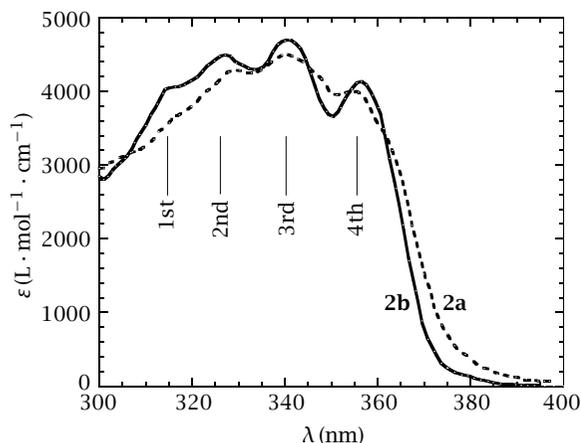


Figure 1. Spectra of typical closed forms in toluene (compounds **2a** (ferrocenyl-) and phenyl-homologue **2b**). Note the presence on the two homologue compounds of the similar intensity and wavelength range for the four spectral bands.

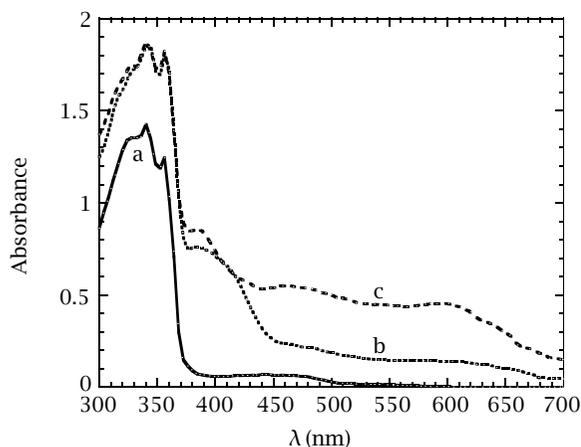


Figure 2. Comparison of the UV/visible spectra obtained after irradiation at 313 or 366 nm of a $3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ methanolic solution of **1a**. Spectra: a: initial; b: after irradiation at 366 nm; c: after irradiation at 313 nm.

reversible, a certain amount of the coloured species (hereby specified as long-lived species) remains relatively stable within the time-scale of observation and do not participate to the mono-exponential decay that has been recorded for all the compounds. Results are gathered in Table 2.

Within the time-scale of our kinetic technique (i.e., 0.1 s to 10000 s), a large amplitude thermal decay has been recorded for all compounds under investigation. These kinetics were characterised by a first-order rate constant k_{Δ} . Lower k_{Δ} values are for compounds **2a** and **2b** in toluene, while higher k_{Δ} is in the more polar solvent acetonitrile (**1b**). Our measurements show also

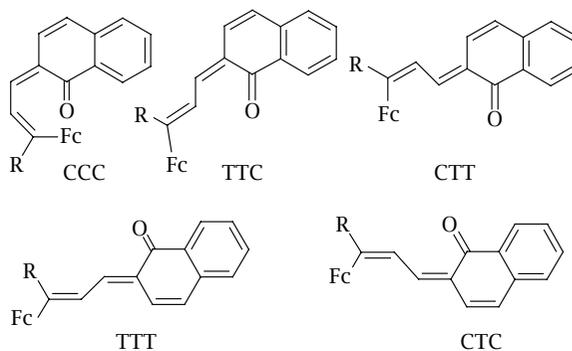


Figure 3. Main stereoisomers of the open form.

that the replacement of the phenyl group by a ferrocene increases the thermal bleaching: $k_{\Delta}(\mathbf{2a}) > k_{\Delta}(\mathbf{2b})$ and $k_{\Delta}(\mathbf{3a}) > k_{\Delta}(\mathbf{3b})$. The same effect is observed when a methyl group replaces a phenyl one: $k_{\Delta}(\mathbf{1b}) > k_{\Delta}(\mathbf{2b})$ and when a phenanthrene nucleus replaces a naphthalene one: $k_{\Delta}(\mathbf{3b}) > k_{\Delta}(\mathbf{2b})$ and $k_{\Delta}(\mathbf{3a}) > k_{\Delta}(\mathbf{2a})$.

There is a slight irradiation wavelength effect on the percentage of stable long-lived species formed after irradiation. The origin of this effect is likely to be the same than for compound **1a** in methanol solution (i.e., a variable distribution of several possible photoisomers). However, after standing for a long time in the dark (several hours or days), a slow thermal bleaching occurs [7]. This spontaneous long-time decay was never complete, ferrocenyl compounds **1a**, **2a** and **3a** appeared always to contain, in toluene solution and at room temperature 1, 4.8, and 10% of the open forms, respectively. This long-term stable proportion was less important for the phenyl-homologues, respectively 0.4, 0.8 and 1% for **1b**, **2b**, and **3b**. The presence of such small quantities of stable open form is likely to be related to a thermal equilibrium between the closed and open stereoisomers (i.e., a slight thermochromic effect).

2.4. Kinetic modelling of the Absorbance vs time curves under continuous monochromatic irradiation. From kinetic modelling of Absorbance vs time photokinetic curves [8], quantitative UV-visible spectra of the reversible open forms (lifetime < 1000 s) and quantum yields of photocoloration can be extracted.

2.4.1 Quantitative UV/visible spectra of the opened forms

The molar absorption coefficients of the reversible open forms (OF) that have been obtained after kinetic modelling are gathered on the Table 3.

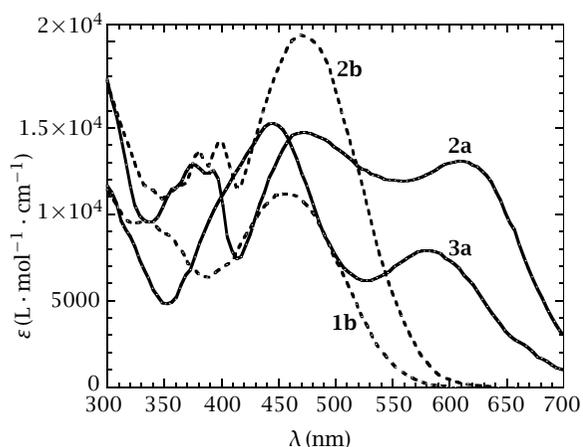
Figure 4 presents the calculated spectra of compounds **1b**, **2a**, **2b** and **3a** as they have been obtained from the kinetic modelling. For ferrocenyl-containing compounds **2a** and **3a**, the main feature is the presence

Table 2. % (after irradiation) of long-lived isomers of the open form and thermal bleaching rate constant k_{Δ} for compounds **1**–**3** (both monitored at λ_{obs}) ($T = 298\text{K}$).

no.	solvent	% long-lived isomers after irradiation at 313; 366 nm	k_{Δ} (10^{-3} s^{-1})	λ_{obs} (nm)
1a	m	6; 8	8.3	600
1b	t	31; 26	11.0	450
1b	a	48; 51	16.6	458
1b	e	47; 34	9.2	461
2a	t	12; -	2.4	470
2b	t	23; 24	1.45	472
3a	t	14.4; 9.1	9.0	447 or 600
3b	t	5; 12	4.0	472

Table 3. Molar absorption coefficients of the transient open forms (OF).

	Solvent	λ_{irr}	ϵ_{OF} ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	(λ_{max})	OF(nm)
1a	m/a	313	11600(358), 12100(386),	5800(466),	4800(600)
1b	m/a	366	9900(356), 8800(390),	1600(466),	1000(600)
1b	a	313/366	10650(330), 11500(460)		
1b	t	313/366	9800(336), 11850(454)		
1b	e	313/366	10300(336), 11100(460)		
2a	t	313/366	12600(374), 12250(392),	14350(474),	12750(608)
2b	t	313/366	13450(380), 14200(400),	20250(470)	
3a	t	313/366	15450(446), 7950(582)		

Figure 4. UV-visible spectra of the reversible open forms of compounds **1b**, **2a**, **2b** and **3a** in toluene solution.

of a specific band within the 580–610 nm range [5]. For compounds **2a** and **2b**, another characteristic is the presence on the lower wavelength part of the spectra of a small “pattern” more or less similar to the UV spectra of the corresponding closed form, but red-shifted by $\approx 33 \text{ kJ} \cdot \text{mol}^{-1}$ in **2a** and $\approx 41 \text{ kJ} \cdot \text{mol}^{-1}$ in **2b**. It is likely that this pattern would be related to the 12 electrons system of the vinyl-naphthalene moiety encountered either in the closed or open forms. Moreover, as expected, replacement of a methyl by a phenyl increases the conjugation and hence the molar absorption coefficient ($\epsilon_{\text{OF}}(\mathbf{2b}) > \epsilon_{\text{OF}}(\mathbf{1b})$); λ_{max} is also red-shifted ($\lambda_{\text{max}}(\mathbf{2b}) > \lambda_{\text{max}}(\mathbf{1b})$). This effect is no

longer true for ferrocenyl-compounds **2a** and **3a**, where phenanthryl- (to naphthyl-) substitution induces a blue-shift ($\lambda_{\text{max}}(\mathbf{2a}) > \lambda_{\text{max}}(\mathbf{3a})$) and decreases the molar absorption ($\epsilon_{\text{OF}}(\mathbf{2a}) > \epsilon_{\text{OF}}(\mathbf{3a})$).

2.4.2 Determination of the quantum yields of the reversible photocoloration process

It was assumed that these quantum yields were not irradiation wavelength sensitive for 313 and 366 nm (Table 4). This hypothesis was justified because the values that have been extracted independently from the two irradiation wavelength were not significantly different within our experimental accuracy. Values given have been obtained by averaging data from 313 and 366 nm irradiation. Quantum yield for compound **3b** is not given because it cannot be extracted with a sufficient precision due to lack of convergence in the iterative calculation. Ferrocenyl-compounds **2a** and **3a** exhibit low quantum yields. For compound **2a** and **2b** we have obtained ($\phi(\mathbf{2b}) \approx 4 \times \phi(\mathbf{2a})$). A possible explanation for this weak photoreactivity would be a deactivation of the excited state (either thermally, by fluorescence or by intersystem crossing to a low reactive triplet intermediate) due to the presence of the ferrocene group. Quantum yields are also solvent sensitive, being higher in the less polar solvent. This effect could be interpreted by the presence of a non-reactive short lived state (triplet or transient photoisomer) giving rise to deactivation in the more polar solvent as already described for spiropyran systems [9]. ϕ_{col} also increases slightly when a phenanthrene nucleus replaces a naph-

Table 4. Photocoloration quantum yields of various compounds in various solvents.

n°	1a	1b	1b	1b	2a	2b	3a
solvent	m/a	t	e	a	t	t	t
$\phi_{\text{coloration}}$	0.06 ± 0.05	0.70 ± 0.10	0.50 ± 0.20	0.42 ± 0.10	0.15 ± 0.05	0.62 ± 0.05	0.20 ± 0.05

thalene one $\phi_{\text{col}}(\mathbf{3a}) > \phi_{\text{col}}(\mathbf{2a})$. As the exact molar absorption coefficient of the photoisomers responsible for the non-reversible photocoloration (Figure 2) was not known, the corresponding quantum yields were not determined.

The quantum yield of photocoloration ϕ_{col} and the thermal fading rate constant k_{Δ} can be correlated to the experimental photosteady state absorbance (Abs_{PSS}). Highly colourable compound **2b** ($\text{Abs}_{\text{PSS}}(470) \approx 1.9$) exhibits a high ϕ_{col} with a low k_{Δ} . On the other side, weakly colourable compound **3a** ($\text{Abs}_{\text{PSS}}(582) \approx 0.45$) has a low photocoloration quantum yield and a high thermal fading rate constant. In between, lie medium colourable compounds **1b** and **2a** ($\text{Abs}_{\text{PSS}}(\lambda_{\text{max}}) \approx 0.9$ – 1.1). The origin of such behaviour can be understood from the photosteady state equation, which shows that Abs_{PSS} is an increasing function of the ratio $\phi_{\text{col}}/k_{\Delta}$. The coloration of the solution is proportional to the open form concentration ([OF]) [10]. Then at the photosteady state (PSS), eq. (1) (derived from eq. (3) = 0) holds. It shows that $[\text{OF}]_{\text{PSS}}$ is proportional to the ratio $\phi_{\text{col}}/k_{\Delta}$:

$$([\text{OF}]/[\text{CF}])_{\text{PSS}} = (\phi_{\text{col}}/k_{\Delta}) \times (\epsilon'_{\text{CF}} I_0 F) \quad (1)$$

3. CONCLUSION

Kinetic modelling of Absorbance vs time curves recorded under monochromatic irradiation of a series of ferrocenyl-benzopyrans and their phenyl-homologues has provided interesting results about their quantitative spectral, kinetic and photochromic properties.

It has been shown that the UV spectra of the closed forms was not sensitive to the presence of the ferrocenyl-group at the 2-position. Kinetic measurements have also shown that the rate constant of thermal fading was higher with ferrocenyl compounds than with their phenyl-homologues. However, an unexpected stable open form has been observed with the methyl ferrocenyl-compound **1a** in methanol solution. A wavelength and solvent dependent long-lived photoisomer distribution has been assumed.

The molar absorption coefficients of the reversible open forms and the corresponding quantum yields of photocoloration have been determined. The presence of a ferrocenyl-group in the 2-position of the benzopyrans decreases the quantum yield but it leads to a new visible absorption band in the 550–700 nm range. The photocoloration behaviour can be quantitatively correlated to their photochromic parameters.

4. EXPERIMENTAL PART

4.1. Chromenes. Their synthesis and characterization has been already published elsewhere [3, 4, 6].

4.2. Photochromic solutions. The photochromic solutions were obtained by dissolving the corresponding chromenes in spectroscopic grade anhydrous solvents. All the concentrations were in the $3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ range.

4.3. Monochromatic irradiations. The monochromatic irradiation was derived from a filtered 200 W high pressure mercury lamp using a liquid optical fibre able to deliver around $\approx 130 \text{ W} \cdot \text{m}^{-2}$ in the 300–400 nm mercury UV lines with a 10 nm bandwidth. Potassium ferrioxalate was used to determine the photon flux with a precision better than 5%.

at 313 nm: $I_0 = 5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$,

at 366 nm: $I_0 = 6 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$.

The photon flux was checked periodically using a home-made semiconductor light sensor. The photochemical reactor was a 1 cm \times 1 cm thermostated and stirred quartz cell placed in the compartment of a HP8451A diode array spectrophotometer. Several wavelengths including the irradiation one were monitored simultaneously. The data as Abs vs time photokinetic curves were stored and processed using a home-made software.

4.4. Thermal relaxation. Thermal decay occurred after the irradiation photon flux was shut down. Absorbance vs time were recorded during this process. The thermal bleaching constants k_{Δ} at 25 °C were calculated using monoexponential eq. (2) [11–13]

$$\text{Abs}_t = \text{Abs}_{\text{PSS}} - (\text{Abs}_{\text{PSS}} - \text{Abs}_0) e^{-k_{\Delta} t} \quad (2)$$

In this equation Abs_t is the absorbance measured at a time t , Abs_0 is the absorbance measured at time 0 and Abs_{PSS} is the absorbance at the photo-steady state. Short irradiation times (less than 300 s) were selected in order to minimise photodegradation and long-lived species formation.

4.5. Photocoloration quantum yields and molar absorption coefficients of the transient OF. In order to extract the photochromic parameters (ϕ_{col} and ϵ_{OF}), experimental photokinetic curves (Abs vs t) were fitted using a kinetic modelling procedure. The model was derived from the simplest photochromic mechanism: $\text{CF} \rightarrow \text{OF} (h\nu)$; $\text{OF} \rightarrow \text{CF} (\Delta)$ which gives rise to

the differential and phenomenological equations:

$$-d[CF]/dt = \phi_{col}I_0\varepsilon'_{CF}F[CF] - k_{\Delta}[OF] \quad (3)$$

$$Abs = \varepsilon_{CF}[CF] + \varepsilon_{OF}([C]_0 - [CF]) \quad (4)$$

$$[CF] + [OF] = [C]_0 \quad (5)$$

ε'_{CF} is taken at the irradiation wavelength, F is the photokinetic factor [8, 11], $F = (1 - 10^{-Abs'})/Abs'$ and $[C]_0$ is the total concentration of the photochromic compound.

The calculated Abs values were obtained by numerical integration using "guessed" values of the unknown parameters, then they were fitted on the experimental ones using a minimisation algorithm able to adjust the initial "guessed" values of the parameters at their optimum. At the end of the fitting procedure, the estimated values of the parameters were delivered. The uniqueness of the solution was tested by showing that whatever the initial values of the guessed parameters the calculation arrived to the same minimum at convergence.

REFERENCES

- [1] (a) J. C. Crano and R. J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Vols. 1 and 2, Kluwer Academic-Plenum Publishers, New York, 1998-1999.
 (b) R. S. Becker and J. Michl, *J. Am. Chem. Soc.* **88** (1966), 5931.
 (c) G. Favaro, A. Romani, and R. S. Becker, *Photochem. Photobiol.* **72** (2000), 632.
- [2] (a) B. Van Gemert, in *Organic Photochromic and Thermochromic Compounds*, (J. C. Crano and R. J. Guglielmetti, Eds.), Vol. 1, Kluwer Academic-Plenum Publishers, New York, 1998, Chapter 3.
 (b) A. Kumar, *Mol. Cryst. Liq. Cryst.* **297** (1997), 139.
- [3] S. Anguille, Ph.D. Thesis, Marseille-Luminy, France, 2000.
- [4] S. Anguille, P. Brun, R. Guglielmetti, Y. P. Strokach, A. A. Ignatin, V. A. Barachevsky, and M. V. Alfimov, *J. Chem. Soc. Perkin Trans. 2* (2001), 639.
- [5] P. Brun, R. Guglielmetti, G. Pèpe, and S. Anguille, *J. Photochem. Photobiol. A, Chem.* (in press).
- [6] J. L. Pozzo, Ph.D. Thesis, Marseille-Luminy, France, 1994.
- [7] (a) G. Ottavi, G. Favaro, and V. Malatesta, *J. Photochem. Photobiol. A, Chem.* **115** (1998), 123.
 (b) B. Luccioni-Houze, M. Campredon, R. Guglielmetti, and G. Giusti, *Mol. Cryst., Liq. Cryst.* **297** (1997), 161.
- [8] V. Pimienta, D. Lavabre, G. Levy, A. Samat, R. Guglielmetti, and J. C. Micheau, *J. Phys. Chem.* **100** (1996), 4485.
- [9] R. C. Bertelson, *Photochromic Processes involving heterocyclic cleavage in: Photochromism* (G. H. Brown, Ed.), Wiley-Interscience, New-York, 1971, Chapter 3, pp. 45-431.
- [10] N. Rebière, C. Moustrou, M. Meyer, A. Samat, R. Guglielmetti, J. C. Micheau, and J. Aubard, *J. Phys. Org. Chem.* **13** (2000), 1.
- [11] M. H. Deniel, D. Lavabre, and J. C. Micheau, in *Organic Photochromic and Thermochromic Compounds*, Vol. 2, (J. C. Crano and R. J. Guglielmetti, Eds.), Kluwer Academic-Plenum Publishers, New York, 1999, chapter 3, pp. 167-209.
- [12] A. V. Metelitsa, J. C. Micheau, N. A. Voloshin, E. N. Voloshina, and V. I. Minkin, *J. Phys. Chem. B.* **105** (2001), 8417.
- [13] V. Pimienta and J. C. Micheau, *Mol. Liq. Liq. Cryst.* **344** (2000), 157.



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