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Thermally reversible photoconversion of spiroindoline-naphtho-oxazines to photomerocyanines: a photochemical and kinetic study

G. Favaro [a], V. Malatesta [b], U. Mazzucato [a], G. Ottavi [a], A. Romani [a]

[a] *Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy*
[b] *Great Lakes Chemical Italia S.r.l., Via Maritano 26, 20097 San Donato Milanese, Italy*

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Abstract

In this paper, a treatment of the spectroscopic data from thermoreversible photochromic systems is described which allows the molar absorption coefficient of the metastable photomerocyanine, the quantum yield of the colour-forming reaction and the kinetic parameters of the thermal bleaching to be determined. The results obtained for five spiroindoline-oxazines indicate that "colourability" on steady state irradiation depends on the photomerocyanine molar absorption coefficient, quantum yield and bleaching rate coefficient. For the molecules investigated, the "colourability" markedly depends on temperature, due to the temperature dependence of the bleaching reaction. The results obtained are compared with literature "colourability scales", determined empirically by comparison of different systems excited by pulsed light.

Keywords: Spiroindoline-naphtho-oxazines; Photomerocyanines; Photokinetics; Photochromism

1. Introduction

Determining the quantum yield of reversible photoreactions of photochromic systems following the mechanism

$$A \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} B$$

has always been considered as a non-trivial problem [1–6]. Difficulties arise because of the uncertainty in the molar extinction coefficient of the coloured species (B), produced on UV irradiation, which reconverts to the colourless molecule (A) within a few seconds. "Colourability" has often been taken as a measure of the goodness of a photochromic material [7]. This term refers to the propensity of the colourless molecule to be transformed into the coloured species on irradiation. It has often been expressed as the apparent absorption coefficient of the coloured form attained under fixed experimental conditions. Thus colourabilities of different photochromics have been compared by keeping the experimental conditions constant (excitation source, distance, filters, absorbance of the colourless form) [8–13]. More quantitatively, "colourability" has been equated to the product of the photoreaction quantum yield and the molar absorption coefficient of the coloured species, $\Phi\epsilon_B$ [14]. Although this definition appears to be independent of the irradiation conditions, it does not take into account the role of the thermal back reaction rate, which places a limit on the photoconvertible amount of the colourless form during steady irradiation and, therefore, on the maximum intensity of colour obtained at a given temperature.

In the general expression of the colour-forming rate of a thermally reversible photochromic system

$$d[B]/dt = I_A\Phi - k_\Delta[B] \qquad (1)$$

Φ can be determined provided that the concentration of the photoproduct can be obtained, generally from its absorbance. Therefore the molar absorption coefficient of B (ϵ_B) should be known in order to obtain the concentration of B and then Φ. Since the maximum colour intensity which can be obtained on stationary irradiation ("colourability") is also conditioned by the bleaching rate at a given temperature, the photochromic behaviour of a system can be completely characterized only by the knowledge of ϵ_B, Φ and k_Δ.

This problem was recently investigated in detail by Gauglitz and Scheerer [15] who, handling Eq. (1), obtained a relationship relating the maximum absorbance at the photostationary state with the temperature dependence of the thermal back reaction

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($k_\Delta = k_o \exp(-E_a/RT)$). In this way, they obtained an equation from which three parameters, containing ϵ_B, the activation energy (E_a) and the frequency factor (k_o) of the back reaction, were simultaneously determined by a mono-exponential fitting procedure according to Gauss–Newton. The knowledge of ϵ_B allowed the quantum yield of the photochemical forward reaction to be calculated by numerical integration of the rate law.

However, fitting an exponential curve by three parameters requires a large number of experimental measurements at different temperatures and very precise and accurate temperature determinations (± 0.1 °C) over a restricted temperature range (approximately 30 °C). Otherwise, convergency cannot be achieved (to be tested).

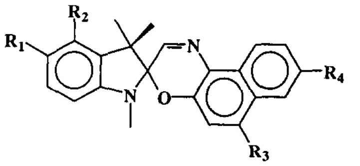
In this paper, starting from the idea of Gauglitz and Scheerer [15] of linking the photostationary state concentration with temperature, we propose a treatment of the spectrophotometric data from the thermoreversible photoreaction which does not require such demanding experimental prerequisites.

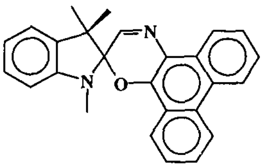
The method was applied to a number of spironaphtho-oxazine (SO) $\rightleftharpoons$ photomerocyanine (PM) systems in polar and non-polar solvents. In this case, the photochromism is due to photocleavage of the spiro bond of SO on UV irradiation to give the open PM structure which absorbs in the visible region. The results obtained (ϵ_{PM}, Φ and k_Δ) give an overview of the photochromic behaviour of these molecules and enable them to be tested with respect to potential applications.

2. Experimental details

2.1. Materials

The photochromic molecules studied were four naphtho-spiroindoline-oxazines (**1**, **2**, **3**, **4**) and one phenanthro-spiroindoline-oxazine (**5**), prepared according to literature methods [7].





	1	*2*	*3*	*4*	*5*
R1	H	H	CH3	H	
R2	H	H	CH3	H	
R3	H	piperidine	H	H	
R4	H	H	H	CO2Me	

The solvents methylcyclohexane (MCH) and ethanol (EtOH) were reagent grade Carlo Erba products.

2.2. Equipment

Absorption spectra were recorded on a Perkin–Elmer Lambda 16 spectrophotometer. For absorption measurements at varying temperatures, a cryostat (Oxford Instruments), equipped with a temperature controller operating between 77 K (if liquid nitrogen was used for cooling) and 500 K, was used. The temperature precision was within ± 1 °C; the accuracy in the temperature control was of the order of ± 0.2 °C. A 250 W medium pressure mercury lamp filtered by an interference filter ($\lambda = 366$ nm) was used for producing the coloured PM form. The irradiation intensity, which was constant during each run, was determined using potassium ferrioxalate actinometry (typically 10^{-6} einstein dm^{-3} s^{-1}).

2.3. Measurement procedures

The concentrations of the starting spiro-oxazines in MCH and EtOH were of the order of $(1\text{–}5) \times 10^{-5}$ mol dm^{-3}, corresponding to absorbances in the range 0.1–0.3 at the irradiation wavelength. The photoreactions were carried out in a fluorometric cell (path length, 1 cm) containing 1 cm^3 of solution. The irradiation was carried out in the spectrophotometer holder at right angles to the monitoring beam. The light was homogeneously spread on the cell window, and thus stirring was unnecessary. The increase in PM absorbance was followed, during stationary irradiation, at the absorption maximum wavelength (550–613 nm), where the excitation light did not disturb the absorbance measurement, up to photostationary state attainment. The absorbance signals (A_{PM}) were taken every 0.1 s and fitted by mono-exponential kinetics ($A_{PM} = A_{PM}^{\infty}[1 - \exp(-kt)]$). By using about 300 points for the fitting, the error in A_{PM}^{∞} was within 0.01% and that in k was less than 0.5%. Spectral changes were recorded at constant temperature and repeated on the same solution at temperature intervals of 3–4 °C over a temperature range of about 30 °C, waiting for about 30 min after resetting the temperature control to allow the solution to reach thermal equilibrium. The temperature range, chosen for each molecule relative to the bleaching rate, included room temperature (260–305 K). The kinetic rate parameters of the ring-closure reaction were determined at each temperature, following the disappearance of the coloured form at the wavelength of maximum absorbance, after having removed the irradiation source (zero time, approximately 2–3 s after the end of irradiation). First-order rate constants were obtained from linear log$A$ vs. time plots (correlation coefficient greater than 0.999 using about 100 experimental points). The activation energies, together with the frequency factors, of the thermal back reactions were determined from Arrhenius plots. An uncertainty of about 10% was evaluated for the activation energy, while the frequency factor was affected by more than 50% uncertainty.

3. Results and discussion

3.1. Kinetic details

Referring to the systems under study, for which the quantum yield of the reverse photoreaction is assumed to be negligible [3], Eq. (1) can be written in terms of the molar absorption coefficient (ϵ_{PM}) and the time dependence of the absorbance of the photomerocyanine (A_{PM}) at the analysis wavelength

$$dA_{PM}/dt = \epsilon_{PM}\Phi I_{SO} - k_{\Delta}A_{PM} \qquad (2)$$

I_{SO} represents the intensity of the monochromatic excitation light absorbed by SO per unit time (einstein dm^{-3} s^{-1}). Since PM also absorbs the excitation light (λ_{exc} = 366 nm), the fraction I_{SO}/I (I represents the total absorbed light) depends on the PM and SO concentrations according to

$$\frac{I_{SO}}{I} = \frac{A'_{SO}}{A'} = \frac{\epsilon'_{SO}[SO]}{\epsilon'_{SO}[SO] + \epsilon'_{PM}[PM]} \qquad (3)$$

where A'_{SO} and A' represent the SO absorbance and the total absorbance at λ_{exc} respectively and ϵ'_{SO} and ϵ'_{PM} are the molar absorption coefficients of the two molecules at λ_{exc} (note that the prime is used to represent the absorbances and molar absorption coefficients at λ_{exc}). By expressing the total absorbed light I as $I^0[1-\exp(-2.3A')]$, and substituting I_{SO} in Eq. (2) by Eq. (3), the following relationship is obtained

$$dA_{PM}/dt = \epsilon_{PM}\Phi I^0 F A'_{SO} - k_{\Delta}A_{PM} \qquad (4)$$

where $F = [1-\exp(-2.3A')]/A'$ represents the photokinetic factor [15,16]. When λ_{exc} corresponds, or is close to, an isosbestic point, F remains constant with irradiation time and can be directly evaluated from the spectrum of the closed form. Otherwise, it is unknown and depends on the degree of photoconversion.

When the photostationary state is attained, namely $dA_{PM}/dt = 0$, the PM absorbance has reached its limiting value at the temperature of the experiment (A_{PM}^{∞})

$$\epsilon_{PM}\Phi I^0 F^{\infty} A'^{\infty}_{SO} = k_{\Delta}A_{PM}^{\infty} \qquad (5)$$

The superscript ∞ refers to photostationary conditions.

Considering that the instantaneous SO concentration is related to that of PM and to the initial SO concentration (c_o)

$$A'_{SO} = \epsilon'_{SO}[SO] = \epsilon'_{SO}(c_o - [PM]) = \epsilon'_{SO}(c_o - A_{PM}/\epsilon_{PM})$$

Eq. (5) can be rearranged in the following form

$$\frac{1}{A_{PM}^{\infty}} = \frac{1}{\epsilon_{PM}c_o} + \frac{k_{\Delta}}{\Phi I^0 \epsilon'_{SO} F^{\infty}} \times \frac{1}{\epsilon_{PM}c_o} \qquad (6)$$

The equation of Gauglitz and Scheerer [15] is formally different from Eq. (6) only because the rate of the thermal back reaction has been substituted by its Arrhenius temperature dependence ($k_{\Delta} = k_o \exp(-E_a/RT)$). Therefore temperature and A_{PM}^{∞} have been taken as the independent and dependent variables respectively.

In this work, we preferred to choose k_{Δ} as the independent variable, because it can be determined with high precision (correlation coefficient, better than 0.999), provided that the temperature is rigorously kept constant independent of its absolute value.

3.2. Molar absorption coefficient and quantum yield determinations

Assuming that Φ is independent of temperature in the limited temperature range used, Eq. (6) represents a linear relationship between $1/A_{PM}^{\infty}$ and k_{Δ}/F^{∞}. It allows ϵ_{PM} to be obtained from the intercept and Φ from the intercept to slope ratio, since ϵ'_{SO} can easily be obtained from the spectrum of the non-irradiated SO solution and I^0 is determined by actinometry. Plotting Eq. (6) requires A_{PM}^{∞} and the corresponding k_{Δ} and F values to be determined at several temperatures. The photokinetic factor, which varies during the course of the reaction, attains a constant value at the photostationary state, which depends on temperature because of the effect of temperature on the degree of photoconversion. Depending on the relative magnitude of ϵ'_{SO} and ϵ'_{PM}, the F^{∞} value increases ($\epsilon'_{SO} > \epsilon'_{PM}$) or decreases ($\epsilon'_{SO} < \epsilon'_{PM}$) with decreasing temperature and attains the limit 2.303 when $A'^{\infty} \to 0$, that is for a hypothetical complete conversion of SO to PM and a negligible ϵ'_{PM} value. Experimentally, this limit is reached for $A'^{\infty} \leq 0.05$, that is when the series expansion of $\exp(-2.303A'^{\infty})$ can be stopped at the first term. This condition could be achieved, in rare cases, by a suitable choice of the initial concentration, irradiation intensity and temperature range. In these cases, the experimental $1/A_{PM}^{\infty}$ values and the corresponding k_{Δ} values, measured at each temperature, allow ϵ_{PM} and Φ to be determined easily from Eq. (6).

In general, ϵ_{PM} and Φ can be obtained by an iterative method. The problem is the evaluation of F^{∞} which requires the knowledge of the total amount of excitation light absorbed at the photostationary state, and therefore the knowledge of ϵ'_{SO}, ϵ'_{PM} and the system composition (Eq. (3)). While ϵ'_{SO} can be easily obtained from the absorption spectrum of the non-irradiated system at the temperature of the experiment, ϵ'_{PM} and ϵ_{PM} can only be obtained, by first approximation, from low temperature spectra in conditions of total photoconversion of SO to PM. Using these values, an approximate PM concentration is determined from the visible spectrum, where only PM absorbs, and it is used to calculate an approximate F^{∞} value. By inserting this value in Eq. (6), an approximate ϵ_{PM} value is extrapolated. Extrapolations of ϵ_{PM} and recalculation of the corresponding F^{∞} value are iterated until the intercept (Eq. (6)) corresponds to the given $(\epsilon_{PM}c_0)^{-1}$ value. Also ϵ'_{PM}, taken at low temperature, may change at room temperature; however, by using simulated data sets, it was demonstrated that variations in ϵ'_{PM} up to 50% did not appreciably affect the final results.

Once ϵ_{PM} has been determined, the quantum yield can be obtained from the intercept to slope ratio of the linear plot (Eq. (6)) or, alternatively, by extrapolating the colour-forming rate at zero time from

$$\Phi = \frac{(dA_{PM}/\,dt)_{t\to 0}}{\epsilon_{PM}I^0[(1-\exp(-2.3A'_{SO})]} \tag{7}$$

3.3. Results and comparison with the literature

Owing to the abovementioned difficulties, only a few ϵ_{PM} data, and therefore Φ data, have been reported in the literature for this kind of system. Two methods were used to determine ϵ_{PM} values. One takes advantage of the slowness of the bleaching reaction at low temperature (230–200 K) and assumes complete conversion into the coloured form under this condition. By this method, the ϵ_{PM} values are generally overestimated, owing to the effect of temperature on the absorption spectrum [17]. The second widely used method is that of laser saturation at room temperature. Since the laser energies required for reaching saturation are generally rather high, the ϵ_{PM} value can be underestimated by this method.

In this work, the absorption coefficients (ϵ_{PM}) of five merocyanines were obtained by the iterative method described. Generally, 5–6 iterations were sufficient for convergence. The quantum yields of the photoreaction Φ were determined from Eqs. (6) and/or (7). Results obtained by the two procedures agreed within the uncertainty of the individual methods (±15%).

Typical results obtained by following the colour-forming and colour-bleaching kinetics at different temperatures are illustrated in Figs. 1 and 2 for **2** in MCH. In Fig. 3, the linear fit (Eq. (6)) of the experimental data for **2** in MCH, treated by the iterative procedure, is shown (correlation coefficient, better than 0.99).

The colour-rising rates exhibit first-order kinetics for all the molecules investigated. In reality, this was unexpected, due to the variation of F during each run at fixed temperature. However, this variation (typically 5% or less during a complete run under the experimental conditions used) is too small to affect the first-order trend. Only if the irradiation wavelength corresponds to an isosbestic point can the colour-rising kinetics be rigorously first order.

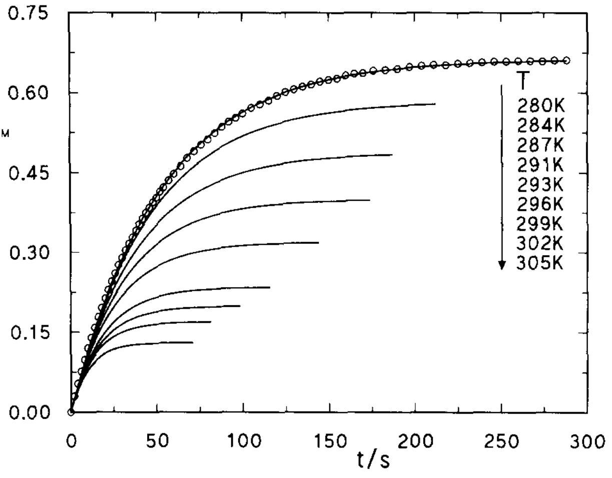


Fig. 1. Temperature dependence of the colour-forming kinetics on stationary irradiation of **2** in MCH, followed at the maximum absorbance (λ = 550 nm). Full lines represent first-order kinetics best-fit curves. The experimental points on the top curve (280 K) demonstrate the goodness of fit (the number of points reported is much less than those monitored experimentally).

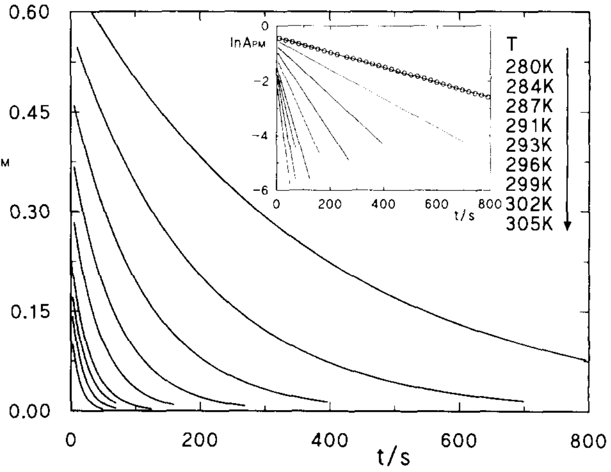


Fig. 2. Temperature dependence of the colour-bleaching kinetics on stationary irradiation of **2** in MCH. Inset: data fit by first-order kinetics (experimental points on the top line).

The photostationary state absorbance increases as the temperature is decreased (by about a factor of four over a 25 °C temperature range for the example illustrated in Fig. 1). The greater the activation energy of the bleaching reaction, the larger the temperature effect on $A_{PM}{}^{\infty}$.

The absorption coefficients and quantum yields of the PMs determined are reported in Table 1 (see below) and compared with some literature values.

For **1** and **2**, Wilkinson et al. [3] determined molar absorption coefficients of 31 000 and 32 000 dm^3 mol^{-1} cm^{-1} respectively in toluene, while the value found for **1** in ethanol was 51 000 dm^3 mol^{-1} cm^{-1}, which is equal to that determined by Kholmanskii and Dyu-

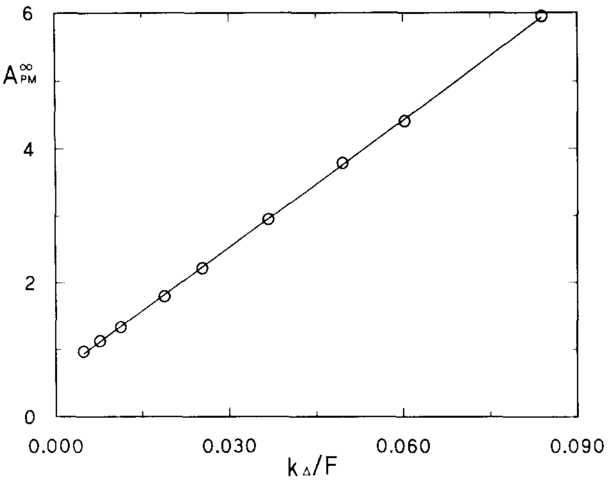


Fig. 3. Linear fit of the data from Figs. 1 and 2 according to Eq. (6), after the interative procedure.

Table 1
Molar absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) at λ_{max} (nm) and quantum yields of the coloured forms in two solvents

Compound	ϵ_{PM} (λ_{max})		ϕ	
	MCH	EtOH	MCH	EtOH
1	38000 (585) ± 1500 (31000 ± 3000) [a]	61000 (613) ± 1000 (51000) [b] (71000) [f]	0.41 ± 0.06 (0.23 ± 0.10) [a] (0.22) [d] (0.9) [g] (0.51) [h]	0.32 ± 0.05 (0.44) [c] (0.19) [e]
2	42000 (550) ± 1000 (32000 ± 3000) [a]	67000 (589) ± 1000	0.55 ± 0.07 (0.42 ± 0.20) [a] (0.4) [i] (0.91) [h]	0.65 ± 0.07
3	35500 (585) ± 1500	63000 (613) ± 2000	0.25 ± 0.04 (0.26) [h]	0.18 ± 0.03
4	45500 (591) ± 2000	48800 (609) ± 1000	0.35 ± 0.04	0.36 ± 0.04
5	51000 (566) ± 1000	87000 (600) ± 2000	0.49 ± 0.06 (0.44) [h]	0.29 ± 0.06

[a] Measured in toluene, Ref. [3].
[b] From Ref. [3].
[c] From Ref. [18].
[d] Measured in toluene, Ref. [22].
[e] Measured in methanol, Ref. [22].
[f] From Ref. [19].
[g] From Ref. [19], no solvent given.
[h] From Ref. [21].
[i] Measured in toluene, Ref. [23].

Table 2
Kinetic parameters of the thermal back reaction in two solvents at 298 K

Compound	E_a ($kJ\ mol^{-1}$)		k_{Δ} (s^{-1})	
	MCH	EtOH	MCH	EtOH
1	71	81	0.24	0.23
2	88	41	0.04	0.58
3	78	92	0.06	0.06
4	70	80	0.16	0.03
5	79	66	0.07	3.2

maev [18], but disagrees with that quoted by Chu [19] (71 000 $dm^3\ mol^{-1}\ cm^{-1}$) from low temperature measurements. Since a similar value was determined by us (73 000 $dm^3\ mol^{-1}\ cm^{-1}$) [17] under similar conditions, it is evident that the temperature effect on the molar absorption coefficients cannot be disregarded. As can be seen, the ϵ_{PM} values are larger in polar solvents than non-polar, as previously found from low temperature determinations under stationary conditions [17], or from room temperature determinations by pulsed techniques [3]. For the same molecules (**1** and **2**), the ϵ_{PM} values obtained using the method described here are in reasonable agreement with, even if somewhat larger than, the determinations of Ref. [3]. Moreover, they are also of the same order of magnitude as those recently reported by Pozzo et al. [20] for a similar molecule, obtained by nuclear magnetic resonance (NMR) determinations of the ratio of the open to closed forms in thermal equilibrium at room temperature.

As can be seen from Table 1, the solvent polarity effect on the PM absorption maxima confirms the positive solvatochromism, already reported for some of the molecules investigated [17].

The photoreaction quantum yields are in the range 0.2–0.6: the polarity effect is modest, almost of the order of the experimental uncertainty. With the exception of **3**, the quantum yields are close to 0.5. The comparison with values previously determined in our laboratory, using low temperature absorption coefficients [21], shows a large discrepancy for **2** only, due to an overestimation of the ϵ_{PM} value in this case. Other literature values of the quantum yields of **1** in ethanol or methanol (0.44 [18], 0.19 [22]) or toluene (0.23 [3], 0.22 [22]) and of **2** in toluene (0.42 [3], 0.4 [23]) are difficult to compare because of the different ϵ_{PM} values assumed and the excitation wavelengths used. As previously suggested [18], the wavelength effect can be very important in these molecules where excitation energy transfer from one moiety to another should be of low probability owing to the rigidity with which the two moieties are held orthogonally. Thus lower energy light ($\lambda > 300$ nm), which is absorbed by the oxazine moiety, is expected to be more efficient in breaking the C–O bond, leading to PM formation, than higher energy light absorbed by the indoline moiety.

The kinetic parameters of the thermal back reaction, the activation energy (E_a) and rate coefficient at 298 K (k_{Δ}), are reported in Table 2. It can be seen that the substituents and the solvent may play an important role in determining the thermal bleaching rate. As observed previously, the rate coefficient tends to increase in polar solvents, but **4** represents an exception to this trend. The k_Δ values determined here are in satisfactory agreement with those reported in the literature for some of these molecules [3,11,12,19,22,24].

4. Concluding remarks

Compared with the methods used previously for determining ϵ_{PM} (low temperature or laser saturation), this procedure takes advantage of temperature ranges and irradiation conditions which are closer to those of operation. Thus the temperature effect on the absorption spectrum (and therefore on ϵ_{PM}) is minimal, as are the negative consequences due to high intensity laser excitation (side photoreactions, local heating, inhomogeneity).

Also the procedure of Gauglitz and Scheerer [15] is unaffected by these inconveniences, since it utilizes steady irradiation in a limited temperature range. However, their method works only if extremely accurate experimental data (in particular, temperature readings) are available, because it is based on an exponential fit to obtain three parameters, from which the absorption coefficient, activation energy and frequency factor are calculated. The quantum yield is evaluated by a separate integration procedure.

By means of the method described here, both ϵ_{PM} and Φ are determined from the same linear regression iterative procedure. Handling the data is simpler and the uncertainty in the quantum yields is of the same order of magnitude (10%–15%) as that obtained by Gauglitz and Scheerer [15]. A reliable comparison of the molar absorption coefficient accuracy is not possible because the uncertainties in these values are not reported in Ref. [15]. However, as pointed out above, the ϵ_{PM} values determined here are in reasonable agreement with the most reliable values determined by the laser saturation method [3].

As regards the evaluation of "colourability", a clearcut distinction is observed which depends on the irradiation conditions. If colouration is observed immediately after flash excitation, the product $\epsilon_{PM}\Phi$ gives a criterion of comparison between different photochromics, independent of temperature. On the other hand, when colour is formed and maintained under steady irradiation, as in most practical applications (glasses, containers for photosensitive products, coating materials), the bleaching rate must be accounted for when evaluating the "colourability". In such conditions, the smaller the bleaching rate ($k_o \exp(-E_a/RT)$) and the larger ϵ_{PM} and Φ, the greater the maximum colour intensity attainable. As a consequence, the colourability becomes markedly dependent on temperature. In order not to obtain too large a colour intensity change with temperature, a photochromic with a small bleaching activation energy is desirable. Interestingly, a spiro-oxazine has recently been synthesized for which the temperature effect is practically negligible [20].

Under stationary conditions, "colourability", expressed as A_{PM}^{∞}/c_o, can be calculated for any experimental condition (starting SO concentration c_o and irradiating light intensity I^0) from Eq. (6) rearranged into the form

$$\frac{A_{PM}^{\infty}}{c_o} = \frac{I^0\epsilon_{PM}\epsilon'_{SO}\Phi F^{\infty}}{I^0\epsilon'_{SO}\Phi F^{\infty} + k_\Delta} \qquad (8)$$

The photokinetic factor F^{∞} depends on the experimental conditions and cannot be evaluated exactly a priori. However, for this kind of molecules at the irradiation

Table 3
"Colourability" scales for the SOs investigated: comparison of parameters obtained in this work with some experimental data from the literature

Compound	Solvent	This work		From refs. [10, 11]	From Ref. [12]
		$\epsilon_{PM}\Phi$ [a]	A/c_o [b]	ϵ_A [c]	ϵ_A [c]
1	Non-polar	15600	460	19000	12000
	Polar	19500	600	35000	
2	Non-polar	23100	9000	32500	24200
	Polar	43500	1450	79000	
3	Non-polar	8900	990	21000	11350
	Polar	11300	1480		
4	Non-polar	15900	530		
	Polar	17600	2890		
5	Non-polar	25000	3000	33500	25850
	Polar	25200	74		

[a] Calculated from the parameters of Table 1.

[b] Obtained from Eq. (8) at 298 K, assuming $I^0 = 10^{-6}$ einstein dm^{-3} s^{-1} and $F^{\infty} = 2$.

[c] "Apparent" molar absorption coefficient of the coloured form obtained on flash excitation in fixed conditions.

wavelength used here ($\lambda_{\rm exc}=366$ nm, $\epsilon'_{\rm SO}=3000$–9000 dm^3 mol^{-1} cm^{-1}; $\epsilon'_{\rm PM}=2000$–4000 dm^3 mol^{-1} cm^{-1}), the range of F^{∞} is 2 ± 0.2 (for initial concentrations within 10^{-5}–5×10^{-5} mol dm^{-3}) and this value can be used for the calculation.

On the basis of the present experimental results, the calculated parameters for colourability evaluation on flash ($\epsilon_{\rm PM}\Phi$) and steady state (Eq. (8)) excitation are reported in Table 3 and compared with some literature values determined by flash excitation as apparent molar extinction coefficients ($\epsilon_{\rm A}=A_{\rm PM}/c_{\rm o}$) [10–12]. As expected, the agreement is qualitatively satisfactory with the $\epsilon_{\rm PM}\Phi$ calculated parameters. It can be observed that, on flash excitation, the colour-forming efficiency is better in polar than non-polar solvents, as previously outlined [8]. During steady irradiation, the situation is reversed in some cases (molecules **2** and **5**), due to the faster bleaching rate in polar solvents than non-polar.

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