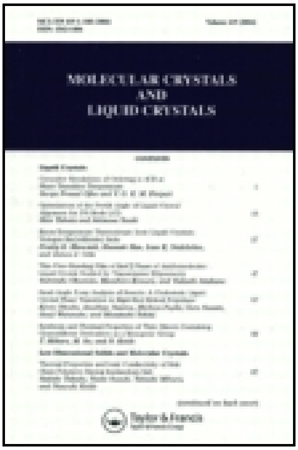

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Computer Analysis of the Thermoreversible Photochromism of Spiropyranne Compounds: Evaluation of Absorption Spectrum and Quantum Yield

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COMPUTER ANALYSIS OF THE THERMOREVERSIBLE PHOTOCHROMISM OF SPIROPYRANNE COMPOUNDS: EVALUATION OF ABSORPTION SPECTRUM AND QUANTUM YIELD

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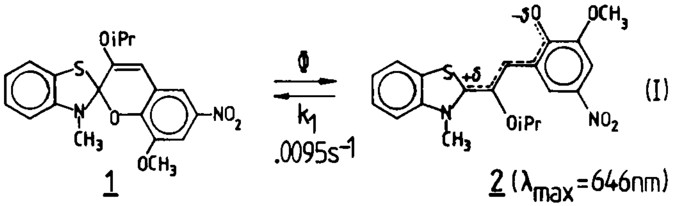
Abstract We propose a general method for the computer analysis of the thermoreversible photochromism. By combining numerical integration of the photokinetic equations and least square adjustement of the quantum yield (Φ) and absorption coefficients (ϵ), it is possible to fit accurately the experimental absorbance vs time curves recorded during continuous monochromatic irradiation. The method is applied to a spiro [benzothiazoline - benzopyranne] compound.

INTRODUCTION:

The mechanism of most thermally reversible photochromic systems[1] can be encompassed in:

$$A \dashrightarrow B\ (\Phi_1) \qquad (I)$$
$$B \dashrightarrow A\ (k_1)$$

which describes the kinetic behavior of spiro [benzothiazoline - benzopyranne] (1)...



1

2 (λ_{max}=646nm)

(I)

In the absence of further information from independent experiments, evaluation of both quantum yield (Φ) and molar absorption coefficients (ϵ) must be resolved from photokinetic considerations[2,3,4,5,6].

GENERAL PHOTOKINETIC THEORY OF TYPE (I) THERMOREVERSIBLE PHOTOCHROMIC SYSTEM.

Assuming the reaction medium is stirred uniformly, the kinetics are represented by a unique differential equation

(1) which is the algebraic sum of the photochemical rate $-\Phi I_a(A)$ and the thermal return $k_1[B]$:

$$d[A]/dt = -\Phi I_a(A) + k_1[B] \qquad (1)$$

where $I_a(A)$ is the photon flux absorbed by the photosensitive product A. The matter conservation equation (2) is:

$$[A] + [B] = [A]_0 \qquad (2)$$

l^{irr} (optical path of irradiation) and = 1 (optical path length of monitoring) are assumed to be 1 cm. For all wavelengths λ, Beer's law applies :

$$Abs^{\lambda} = \epsilon^{\lambda}{}_{A}[A] + \epsilon^{\lambda}{}_{B}[B] \qquad (3)$$

The relationship (4) governing the change in absorbance is obtained by combining equations (1), (2) and (3):

$$dAbs^{\lambda}/dt=-\Phi I_0 \epsilon^{irr}{}_{A} F^{irr}(Abs^{\lambda}-\epsilon^{\lambda}{}_{B}[A_0])+k_1(\epsilon^{\lambda}{}_{A}[A_0]-Abs^{\lambda}) \qquad (4)$$

where I_0 is the monochromatic incident photon flux of wavelength λ^{irr}; $\epsilon^{irr}{}_{A}$: the molar extinction coefficient of A at λ^{irr}; $[A_0]$: the initial concentration; Abs^{λ}: the absorbance of the reaction medium at λ at time t; the photokinetic factor is $F^{irr} = (1 - 10^{-Abs\lambda irr})/Abs^{\lambda irr}$. Some of these terms are either known or readily measured:

- known terms: $[A_0]$ and $\epsilon^{\lambda}{}_{A}$,
- measurable terms: I_0, Abs^{λ} (as well as at λ^{irr}) and k_1,
- terms to be adjusted: Φ, $\epsilon^{\lambda}{}_{B}$ and $\epsilon^{\lambda irr}{}_{B}$.

Formula (4) is the basis of all UV/visible photokinetic studies related to thermoreversible photochromic systems (I).

RESULTS

We develop a new method considering the dynamic information contained into the absorbance vs time curves recorded under continuous irradiation. Unlike the classical steady method[7,8], our method is a non stationnary one, based on numerical integration. Its main advantage is to be not strictly limited to type (I) photochromic systems.

By adding new kinetic equations, one takes account of mechanistic complications such as photodegradation. With a diode array detector[9] $Abs^{\lambda irr}$ can be easily monitored. This is a very profitable feature because it allows to take into account the value and the variations of F^{irr} during the integration of (4).

The spiro [benzothiazoline - benzopyranne] (1) is a thermally reversible photochromic compound[10]. At 20°C, in toluene solution, the thermal decay is first order (k_1 = 9.5×10^{-3} s^{-1}). The evolution of the spectrum of the solution is recorded continuously in order to get an absorbance matrix whose raws are wavelengths and columns are times of irradiation.

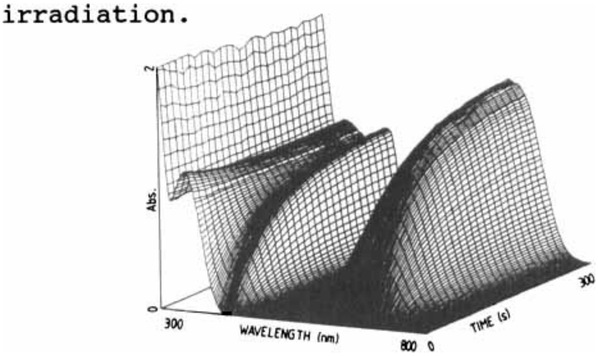


FIGURE 1 Three dimensional spectra (Abs., λ, t) of compound (1), under continuous irradiation: I_0(366nm)=5.9 x 10^{-6} Ms^{-1}).$[A]_0$ = 1.45 x 10^{-4}M in toluene solution.

The kinetic curves at 366nm and 646nm (λ_{max} of 2) are extracted and fitted (see exp. part).

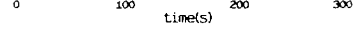


FIGURE 2 Simulation and least square fitting. Circles are experimental values at 366 and 646nm; solid lines: fitting using equation (4) and three adjusted parameters: Φ=.14, ϵ^{646}_B = 28500 and ϵ^{366}_B=5800 $M^{-1}cm^{-1}$).

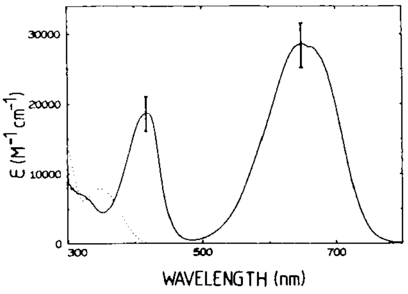


FIGURE 3 UV/visible absorption spectra in toluene solution at room temperature: solid line: 2 (errors bars are estimated from 9 independent experiments). Dotted line: 1

The whole UV/visible spectrum of 2 (B) (ϵ^{λ}_{B}) is calculated from (2) and (3) using [B] = $Abs^{646}(t)/\epsilon^{646}_{B}$ (B is the only absorbing species at this wavelength), $\epsilon^{\lambda}_{B} = (Abs^{\lambda}(t) - \epsilon^{\lambda}_{A}[A](t))/[B](t)$. t is choosen near the steady state. The mean value of $\Phi = .14 \pm .02$.

EXPERIMENTAL

Toluene was of spectroscopic grade and used as reference. Irradiation was performed using a filtered (366nm) 200 W high pressure mercury vapour lamp focused on a quartz light pipe to a 1 cm square-sided quartz cell (vol. = 2 ml). The cuvette was stirred magnetically and placed in a HP 8451 diode-array spectrophotometer. The analysis and irradiation beams are perpendicular. The data sampling rate must be fast enough to deliver more than 20 points all over the curved part of the plot. The data ($Abs^{\lambda}(t)$) were transferred to a HP9000/330 workstation. The fitting algorithm minimises the residual error $RE = \Sigma_j\Sigma_p(Y_{jp}^{calc} - Y_{jp}^{obs})^2/pj$, where j is the number of experimental points per kinetic and p the number of kinetics. The values Y_{jp}^{calc} were obtained by numerical integration of (4). Iterative calculations using starting values for the three parameters were performed until a minimum value of RE was reached. The final result does not depend on the starting values.

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