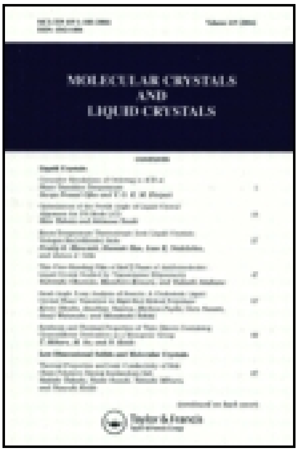

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KINETIC MODELLING OF THE PHOTOCHROMISM OF DIHYDROINDOLIZINES

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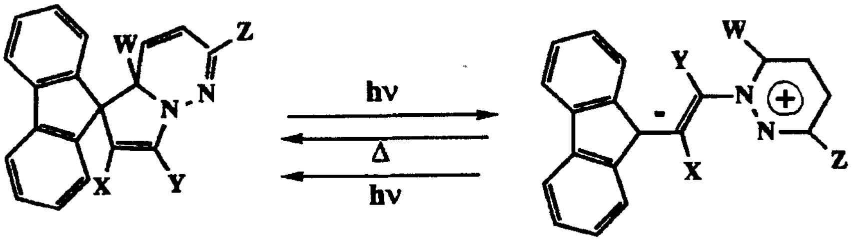
Abstract: Dihydroindolizines (DHI) are photochromic compounds, which on irradiation with long wavelength UV or visible light afford a colored open photoisomer, the betaïne. Light induces breaking of the azacyclopentene ring. In the dark, there is only one thermal back reaction (ring closure) The determination of photochromic parameters of these systems such as the quantum yields and the UV/visible spectra of the unstable photoisomers is not a trivial problem and requires appropriated methods. In this paper, we show that kinetic modelling and inverse treatment of experimental (**Abs** *vs* **t**) plots recorded under continuous irradiation can help to solve this problem (dynamic method).

INTRODUCTION

Dihydroindolizines (DHI) are photochromic compounds, which under UV or visible irradiation (blue light) undergo reversible opening of the azacyclopentene ring. The betaïne formed spontaneously recylizes in the dark[1] :



DHI **bétaïne**

Generally, this type of photochromism can be modelled by a « 2ϕ,1k » scheme (two photochemical reactions (2ϕ) and one thermal reaction (1k)). Quantitative parameters of the photochromism such as the quantum yields of the photochemical stages and the UV/visible spectrum of the betaïne can be extracted from this model.

The kinetic measurements required for modeling such systems are carried out under conditions of continuous irradiation resembling those commonly encountered in practical applications of photochromism (variable transmission or photosensitive glasses). Under these conditions of irradiation, the system reaches a photostationary state where the rate of photocoloration is exactly counterbalanced by the rate of the bleaching process. However, from simple observation of steady states absorbances, the true rate of conversion cannot be ascertained, namely the concentration of betaïne because its molar extinction coefficient is not known. Similarly, the quantum yields of all the photochemical processes involved are not known. These problems can be resolved using dynamic modeling which is based on a minimum of assumptions[2].

RESULTS AND DISCUSSION

We examined the 4 dihydroindolizines (DHI) bearing the following substituents:

TABLE I: Structure of the DHI investigated (A refers to the closed spiro form and B to the betaïne. DHI (I) and (IV) from Gauglitz and Scheerer's paper[3] were included for comparative purposes. (nB = norbornyl, Ad = adamentyl).

Compound	X	Y	Z	W
1A	**COO- nB**	**COO- nB**	**H**	**H**
2A	**COO- Ad**	**COO- Ad**	**H**	**H**
3A	**$COOCH_3$**	**$COOCH_3$**	**$-(CH_2)_6-CH_3$**	**CH_3**
4A	**$COO-CH_2-CH_3$**	**$COO-CH_2-CH_3$**	**$COOCH_3$**	**H**

I	**$COOCH_3$**	**$COOCH_3$**	**H**	**H**
IV	**$COOCH_3$**	**$COOCH_3$**	**CH_3**	**CH_3**

Qualitative analysis of this mechanism

Under irradiation, the four compounds photoisomerize into betaïnes, and recyclize spontaneously in the dark. The kinetics of the back reactions are monoexponential, and the rate constants k_{BA} in non-polar solvents (CH_2Cl_2 or toluene) at 25°C range from 1.8 to $5.7.10^{-2}\ s^{-1}$.

Furthermore, irradiation with visible light (546 nm) of the betaïne, the only species which absorbs at this wavelength, does not lead to any significant speeding up of the bleaching. There will thus be little or no quantum yield for the photobleaching reaction, which was also indicated by the quantitative kinetic analysis.

Kinetic model of photochromism

Assuming that the photochromism of the DHI is governed by a « $2\phi,1k$ » mechanism, and referring to the DHI as A and the betaïnes as B, the change in concentration of A under continuous monochromatic irradiation of A is given by:

$$-d[A]/dt = [k_{BA} + (\Phi_{AB}.\varepsilon'_A + \Phi_{BA}.\varepsilon'_B).l.I_0.F].[A] - (k_{BA} + \Phi_{BA}.\varepsilon'_B.l.I_0.F).[A]_0 \quad (1)$$

where ϕ_{AB} and ϕ_{BA} are the quantum yields of photocoloration and photobleaching respectively, and ε'_A and ε'_B are the molar extinction coefficients of A and B at the irradiation wavelength, l is the optical path length of the photochemical reactor and $F = (1 - 10^{-Abs'})/Abs'$ is the photokinetic factor, which only depends on the total absorbance at the irradiation wavelength :λ'. I_0 is the incident photon flux (in $mol.l^{-1}.s^{-1})^2$.
From Beer-Lambert's law and the equation for the conservation of matter:

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

there is a relationship between the observable absorbance at any wavelength Abs and [A]:

$$Abs - \varepsilon_B.[A]_0 = (\varepsilon_A - \varepsilon_B).[A] \quad (3)$$

where $[A]_0$ is the concentration of the pure compound A.

We thus have a relationship between the photochemical parameters: ϕ_{AB}, ϕ_{BA}, ε'_A, ε'_B, ε_A, ε_B, and the change in absorbance under continuous monochromatic irradiation.

Some of these parameters are known such as ε'_A and ε_A (the absorption spectra of the DHI are known) or k_{BA} (recyclization reaction), while the others can be obtained by inverse treatment of the experimentally observed absorbances. (For more details concerning this method, see ref 2b).

Simulation and fitting of the plots of Abs vs t

In order to extract ϕ_{AB} and ϕ_{BA}, two independent experiments must be carried out at two different wavelengths such that the ratios $\varepsilon'_B/\varepsilon'_A \neq \varepsilon''_B/\varepsilon''_A$. These experiments are designed such that relative importance of the two photochemical processes (photocoloration and photobleaching) differ, but the irradiation wavelengths are selected to be sufficiently close for the quantum yields to be independent of λ. For dihydroindolizine **1A**, (see figure 1), the two irradiation wavelengths are 400 and 366 nm. In both cases, the absorbances at the irradiation wavelengths are recorded to determine the change in photokinetic factor and that of λ^{max} of the open form (betaïne **1B** at 514 nm) thus indicating the amplitude of the process.

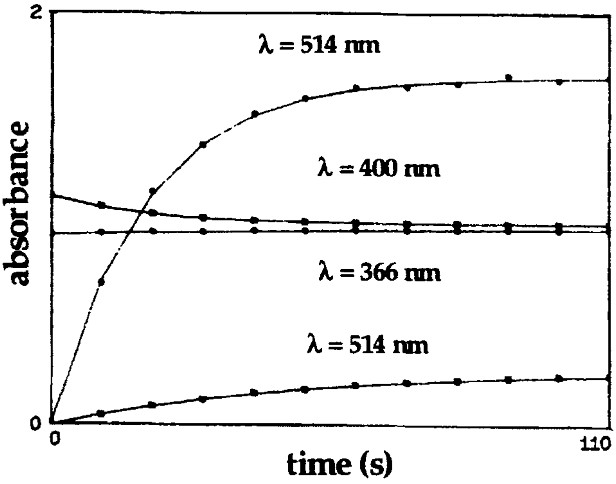


FIGURE 1 Kinetics of photocoloration of **1A** (• : λ' = 366 nm, o: λ' = 400 nm).

The experimental points can be fitted by a « 2ϕ, 1k » model. The optimized parameters are listed in table II.

TABLE II: Values of the photochromic parameters for **1A** after fitting the kinetic curves shown in figure 1. The solution is unique and is independent of the initial values used in the fitting procedure.

Paramètres	**Valeurs**
Φ_{AB}	0,80
Φ_{BA}	0,00
ε^{366}_{B}	6500 L.mol^{-1}.cm^{-1}
ε^{400}_{B}	10000 L.mol^{-1}.cm^{-1}
ε^{514}_{B}	25000 L.mol^{-1}.cm^{-1}

The results indicate the absence of a photobleaching process ($\phi_{BA} = 0$) and the model « 2ϕ, 1k » is in fact reduced to a « 1ϕ, 1k » one.

Extraction of the UV/visible absorption spectrum of an unstable betaïne

The value of ε_B obtained in the procedure described above corresponds to the observation wavelength λ^{max} (ε_B^{max} in this case). The complete spectrum of B is calculated from the spectrum of the reaction mixture at time t employing relationship (3) in form (3'):

$$\varepsilon_B = (\varepsilon_A[A] - Abs_t)/([A]_t - [A]_0) \qquad (3')$$

where ε_A is the current spectrum of A, Abs_t the absorbance of the reaction mixture at time t, Abs_0 at time t = 0 and $[A]_t$ the concentration of A at time t, (this latter value is obtained during inverse treatment).

The spectra of dihydroindolizine **1A** and the corresponding betaïne **1B** are shown in figure 2.

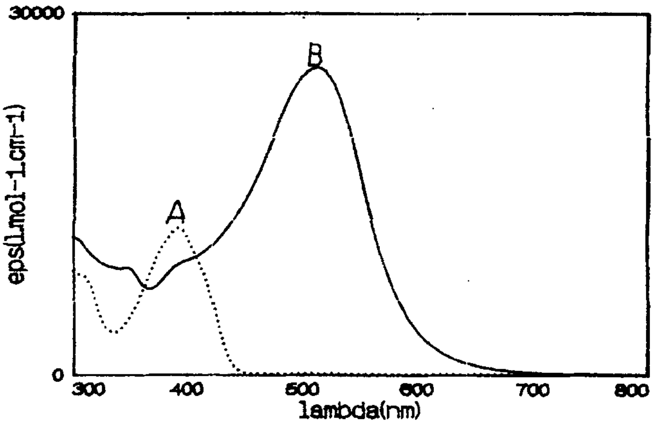


FIGURE 2 UV/visible absorption spectra of the closed (**1A**; dotted line) and open forms (**1B**; full line).

Photochromic parameters of the four DHI derivatives

The other dihydroindolizines were analyzed in a similar way, and the results obtained are listed in table III.

TABLE III: Values of the photochromic parameters of the DHI derivatives. for I and IV, from reference 3a.

Compound	λ_A^{max} (nm)	ε_A^{max} ($\text{L.mol}^{1}.\text{cm}^{-1}$)	k_{BA},25°C (s^{-1})	ϕ_{AB}	ϕ_{BA}	l_B^{max} (nm)	ε_B^{max} ($\text{L.mol}^{1}.\text{cm}^{-1}$)	Solvent
<u>**1A**</u>	394	12200	$1{,}8.10^{-2}$	0,80	0,00	514	25000	Toluène
<u>**2A**</u>	394	14200	$5{,}7.10^{-2}$	0,74	0,00	514	25000	Toluène
<u>**3A**</u>	400	12300	$2{,}9.10^{-2}$	0,70	0,00	630 444	10300 14000	CH_2Cl_2
<u>**4A**</u>	418	13700	$2{,}0.10^{-2}$	0,19	0,00	510	21000	CH_2Cl_2
I	388	≈10000	1.10^{-3}	0.7	0	518	20000	THF
IV	396	≈10000	2.10^{-4}	0.6	0	620 450	≈12000 ≈15000	THF

The absorption peaks λ^{max} of the closed forms A lay between 394 and 418 nm, the highest wavelengths corresponding to the derivatives with bulky or polar substituents at position Z. The molar extinction coefficients ε_A^{max} were little affected by the nature of the substituent (between 12,200 and 14,200 $\text{l.mol}^{-1}.\text{cm}^{-1}$).

The compounds <u>1A</u>, <u>2A</u> and I with similar molecular structures gave comparable results, with differences solely in k_{BA}. On the other hand for betaïne <u>3B</u>, the lowest molar extinction coefficient (10,000 instead of 20,000 to 25,000) and a higher λ^{max} was of note. It was attributed to the presence of CH_3 groups at the W position and a bulky substituent on position Z.

It should also be noted that several betaïnes bearing a CH_3 group at the W position displayed two absorption bands in the visible region. This splitting could be accounted for by the non-planar nature of the betaïne giving rise to two rotamers (e.g. <u>3B</u> and **IV**).

Compound <u>4A</u> bears an attractant group on position Z, which hampers opening of the heterocyclopentene ring. This gives rise to a lower quantum yield of photocoloration (0.2 instead of 07-0.8).

The results presented here are in line with those of Gauglitz and Scheerer for similar compounds[3a].

CONCLUSION

Dynamic analysis of these four DHI derivatives showed that they obey a «1ϕ,1k» reaction mechanism The values of the quantum yield of photocoloration and the spectrum of the betaïne formed (non-isolable chemically) could be obtained by a complete treatment of the kinetic curves under continuous monochromatic irradiation. The method described here only involves a minimum of approximations. The most important condition is that the mixture is well stirred and homogenous, that the quantum yields within the same absorption band are independent of the irradiation wavelength and assuming that Beer-Lambert's law is applicable.

The dynamic method may still be used if the mechanism is complicated by the presence of several photoisomers or photodegradation reactions. It can also help discriminate between various possible reaction mechanisms.

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