

Simultaneous absorption and fluorescence analysis of the cyanine dye DOCI

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Abstract

Simultaneous application of laser absorption spectroscopy and laser induced fluorescence allowed us to obtain kinetic and spectroscopic properties of the dye 3,3'-diethyloxycarbocyanine iodide (DOCI). Photophysical and spectroscopic parameters of the photoisomeric species of DOCI, such as fluorescence quantum yield, isomerization and back-isomerization quantum yields, were obtained.

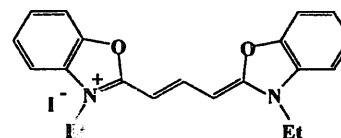
The method developed provides a complete quantitative description for a single photoisomerization process and an accurate value of the photoisomeric fluorescence quantum yield, relative to the corresponding value of the normal species. © 1997 Elsevier Science S.A.

Keywords: 3,3'-diethyloxycarbocyanine iodide (DOCI); Cyanine dyes; Laser absorption spectroscopy; Laser induced fluorescence; Photoisomerization

1. Introduction

In addition to their important technical applications, polymethine dyes present unique physical properties which provide an opportunity to analyze the radiative and non-radiative decay processes of excited states. Of particular importance for this analysis is the propensity of cyanine dyes to photoisomerize. The determination of photophysical parameters of the transient species shows intrinsic difficulties because both species present similar spectroscopic and photophysical characteristics. The error in the determination of the fluorescence parameters is generally large, particularly when the emission intensities of the analyzed species are low. Reliable measurements of absorption and emission properties of photoisomeric species such as absorption cross section, fluorescence quantum yield, fluorescence spectral distribution and lifetime of the excited state, require very sensitive techniques and a careful analysis of the results.

The analysis of photoisomeric species has been performed through extensive experimental studies by using various techniques namely flash photolysis, transient absorption, picosecond-time resolved spectroscopy, optoacoustics and others



3,3'-diethyloxycarbocyanine iodide (DOCI)

Scheme 1. Molecular structure of the dye 3,3'-diethyloxycarbocyanine iodide (DOCI).

[1–7]. The use of CW lasers in absorption and fluorescence techniques allows to obtain precise experimental data for photoisomers with long lifetimes ($\tau_p > 0.05$ ms) as it was shown by research work performed during the past years by our group [7–11].

The 3,3'-diethyloxycarbocyanine iodide cyanine dye (DOCI, Scheme 1) was previously studied by Ponterini and Momicchioli [12], who performed flash photolysis and fluorescence experiments in methanol–ethanol solutions, obtaining the isomerization and back-isomerization constant values in a low temperature range. In their work, they only observed fluorescence emission from the photoisomer at temperatures lower than 180 K. More recently, Ponterini et al. [13] and Aramendia et al. [14] investigated the dependence of the fluorescence emission of the DOCI normal species with the solvent viscosity and the sample temperature, for a group of primary *n*-alcohols.

In this work we have performed laser induced absorption and laser induced fluorescence measurements of DOCI in order to parametrize the absorption and emission properties of its photoisomer. The simultaneous use of these techniques

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together with an appropriate calculation procedure, reduces the number of parameters involved in the curve fitting. A global analysis of the data allows us to confirm the validity of the kinetic model employed, and to obtain accurate values for the parameters related to the radiative and non-radiative decay mechanisms of the photoisomer excited state.

2. Theory and methods

Fig. 1 shows the excitation mechanism and the decay processes involved in the kinetics of DOCI molecule. The mechanisms involved in the relaxation of the excited state of photoisomerizable cyanines were considered by Rullière [15] to be analogous to that proposed by Orlandi and Siebrand for stilbene [16]. According to this model, the excited state of the normal species undergoes photoisomerization through a barrier to a twisted minimum (*t*), from which the molecule decays very rapidly to the ground state either in the starting form S_0^N or in the photoisomer conformation S_0^P . It has recently been shown by Momicchioli et al. that the Orlandi–Siebrand model cannot account for all the characteristics of the excited state isomerization intermediate of the cyanines [17]. By using qualitative molecular orbital arguments supported by CS INDO calculations of the potential energy surface, they concluded that the perpendicular state of these dyes has twisted intramolecular charge transfer (TICT) character, rather than the biradicaloid character they predict for twisted stilbene [17,18]. However, similar to the stilbene case, the ground state surface for the cyanines at the twisted geometry is the transition structure for isomerization.

The analysis of absorption and emission process of both isomeric species under photoequilibrium conditions, using CW laser excitation, was described in previous works [7,10]. Absorbance and emission changes of the sample with the

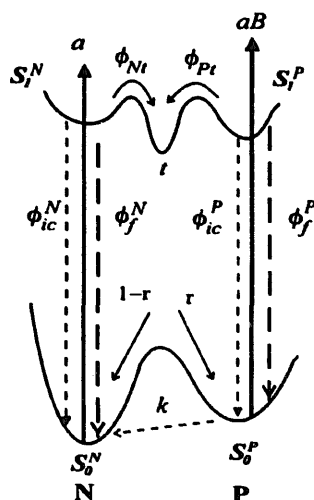


Fig. 1. Potential energy curve diagram. N and P symbolize the normal and the photoisomer species. S_0^N and S_0^P are the groundstates, S_1^N and S_1^P are the first excited states and ϕ_{ic}^N and ϕ_{ic}^P are the direct internal conversion quantum yield of species N and P, respectively. *t* is the twisted state and *r* is the branching ratio. The rest of the parameters are explained in the text.

laser fluence are related to the photophysical parameters of the dye through the photoisomeric model.

The inverse of the relative absorption coefficient as a function of the excitation fluence (α), can be expressed as [10]:

$$\frac{\alpha_o}{\alpha_o - \alpha_s} = \frac{1 + pB}{1 - B} \left(1 + \frac{a_s}{a} \right) \quad (1)$$

where

$$\alpha_i = \frac{1}{l} \ln \left(\frac{P_p}{P_{t,i}} \right) \quad (2)$$

$$B = \sigma_P / \sigma_N \quad (3)$$

$$a_s = \frac{k + w}{\phi_{np}(1 + pB)} \quad (4)$$

P_p and $P_{t,i}$ represent the power of the incident and transmitted probe beam, respectively. The subscript *i* takes the values o or s when the excitation laser beam is off or on, respectively; *l* [cm] is the optical path length in the sample; σ_P , σ_N [cm²] are the absorption cross section coefficients of the species P and N at the laser wavelength; $a = (P\sigma_N / Sh\nu_e)$ [photons s⁻¹] is the excitation rate; *P* [W] represents the pump power ($P \gg P_p$); *S* [cm²] is the excitation area; *h* [J s] is the Planck constant and ν_e [s⁻¹] is the laser excitation frequency; a_s is the excitation rate of saturation and can be defined as the value needed to obtain one half of the maximum photoisomer population; $p = \phi_{PN} / \phi_{NP}$ is the ratio between the quantum yield for the P to N and N to P isomerization; *k* [s⁻¹] is the rate constant of the $S_0^P \rightarrow S_0^N$ process; *w* [s⁻¹] is the rate of sample renewal within the irradiated volume by circulation of the solution.

Absorption changes expressed as a function of $1/a$ (Eq. (1)), represent a straight line when only two species are involved in the kinetics. A departure from this behavior could reveal the presence of an additional photoisomeric species [12]. Excitations at different wavelengths (at least two), should be used to obtain the values of *p*, *B* and ϕ_{NP} . The deactivation rate of the photoisomer ground state (*k* + *w*), can be known from the modulation of the absorption signal.

When emission spectra of isomeric species are strongly overlapped, as in the present case, fluorescence emission comes from the excited singlet state of the N and P species with efficiencies ϕ_f^N and ϕ_f^P , respectively. From Eq. (3) of Ref. [10], a new expression for the dependence of the ratio between the total fluorescence intensity, I_f , and the excitation rate, *a*, can be derived:

$$\frac{K}{K - I_f/a} = \frac{1 + pB}{1 - Bf} \left(1 + \frac{a_s}{a} \right) \quad (5)$$

where *K* is a constant that depends on the excitation wavelength, $f = \phi_f^P / \phi_f^N$, and *p* and a_s as were defined before. The correct value of *K* allows the data representation to take the form of a straight line when the left hand side of Eq. (5) is plotted as a function of $1/a$.

Dividing Eq. (5) by Eq. (1), we obtain

$$\frac{K/(K-I_f/a)}{\alpha_o/(\alpha_o-\alpha_s)} = \frac{1-B}{1-Bf} \quad (6)$$

The right hand side of Eq. (6) is a constant that depends on the excitation wavelength through the factor $B(\lambda)$, but is independent of the excitation intensity in the case of two interacting isomers. When $B(\lambda)$ is obtained from the absorption measurements, the ratio between the fluorescence quantum yield of the P and N isomers, f , can be easily determined.

3. Experimental details

DOCI was used in solutions of analytical grade ethanol at room temperature. The purity of dye has been confirmed by spectrophotometric and chromatographic techniques prior to use. Measurements were performed by using low concentration samples ($2\text{--}10 \times 10^{-6} \text{ M}$). DOCI solutions flowed through a standard fluorescence cuvette. Special caution was taken to control the temperature and the flow speed, owing to the strong dependence of some photophysical constants on these parameters. Absorbances were measured with a Beckman spectrophotometer DU-65.

The general arrangement employed for both laser techniques was previously described [7,10,11]. CW laser excitation was carried out with an Ar ion laser at three different wavelengths: 476.5, 488 and 496.5 nm.

Absorption measurements were performed by using a silicon photodiode as power detector. A photomultiplier (Hamamatsu 446 multialkali) was employed in the fluorescence measurements. Experimental data were acquired and analyzed by using a PC.

4. Results and discussion

Fig. 2 shows experimental values from differential absorption measurements obtained at two excitation wavelengths:

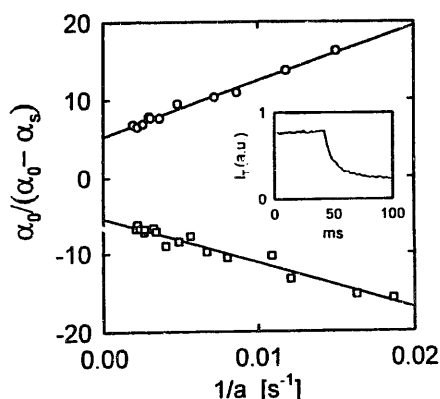


Fig. 2. Experimental values from differential absorption measurements excited at two different wavelengths: 476.5 nm (O) and 496.5 nm (□). The sign of the slope and the ordinate to the origin depends on the factor $(1-B)$ in Eq. (1). The inset shows the decay of the photoisomer absorption signal (see text).

476.5 nm and 496.5 nm. The sign of the slope and the ordinate to the origin depend on the factor $(1-B)$ in Eq. (1). Slope signs corresponding to the mentioned excitation wavelengths were opposite: positive for excitation at 476.5 nm and negative for the other. This means that σ_P is lower than σ_N in the first case and larger in the second case. The absorption difference $(\alpha_o - \alpha_s)$ was very close to zero at 488 nm, independent of the excitation fluence, which indicates that $B \approx 1$ (or $\sigma_N = \sigma_P$) at that wavelength.

The inset to Fig. 2 shows the decay of the photoisomer absorption signal $\tau_P = 1/(k+w)$, which depends both on the speed of sample renewal from the excited region w and on the thermal back-isomerization constant k . The τ_P value was 13.3 ms ($k+w = 75 \text{ s}^{-1}$). At room temperature in non-viscous solvents, the τ_P value has a strong dependence with w , because the k value is much lower ($k = 4 \text{ s}^{-1}$) [14].

The best fit of experimental points of Fig. 2 was obtained by using Eq. (1) with $p = 1.2$, $B(476.5 \text{ nm}) = 0.70$, $B(496.5 \text{ nm}) = 1.53$ and $\phi_{NP} = 0.34$. Photoisomeric absorption cross section values at both wavelengths were obtained from the B values and the normal species absorption cross section values. σ_N values were taken from Ref. [19] and checked by spectrophotometric measurements. The results, $\sigma_P(476.5 \text{ nm}) = 2.69 \times 10^{-16} \text{ cm}^2$ and $\sigma_P(496.5 \text{ nm}) = 5.13 \times 10^{-16} \text{ cm}^2$, are in qualitative agreement with the spectral shift to longer wavelengths shown in Ref. [12], where the contribution of both species was not separated. As $p = \phi_{PN}/\phi_{NP} = 1.2$, the value of the calculated back-isomerization constant at 25 °C was $\phi_{PN} = 0.41$.

The fluorescence quantum yield of the DOCI photoisomer was obtained as follows. First, values of K that adjust the left hand side of Eq. (5) to a straight line for each excitation wavelength, were found. An example is shown in the inset to Fig. 3 for excitation at 476.5 nm. Second, the ratio expressed by the left hand side of Eq. (6) was performed. As we expressed in Section 2, the result of this operation should give a constant value independent of the excitation fluence. Thus, horizontal straight line plots should be obtained.

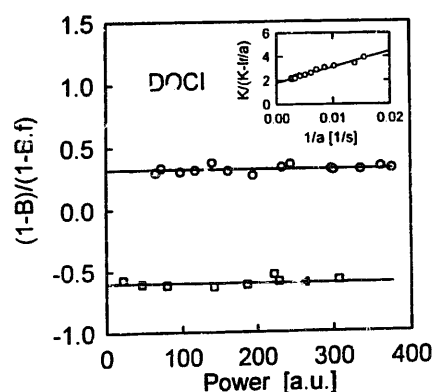


Fig. 3. Experimental results by using simultaneously fluorescence and absorption techniques. The horizontal straight lines, expressed by Eq. (6), at two different wavelength 476.5 nm (O) and 496.5 nm (□), are shown. Inset shows the representation of the Eq. (5) that adjust the $K/(K-I_f/a)$ variable to a straight line.

Results are shown in Fig. 3 for 476.5 and 496.5 nm excitation wavelengths, in terms of the excitation power. Knowing the corresponding B values from the absorption analysis, we obtain the fluorescence quantum yield ratio f , by using Eq. (6). A value of $f=0.09$ was obtained at room temperature. Taking into account that the fluorescence quantum yield of DOCI in ethanolic solutions is $\phi_f^N=0.05$ at 21 °C [13], we obtain $\phi_f^P=0.0045$. This value confirms the general notion that the *cis* isomers of carbocyanines have negligible fluorescence at room temperature.

Knowing the ϕ_f^N value, and neglecting the direct internal conversion of the N species [12,14], we can derive the quantum yield of population transfer from S_1^N to t twisted state as $\phi_{Nt}=1-\phi_f^N=0.95$. Now, considering that $\phi_{NP}=\phi_{Nt}r=0.34$, we obtain $r=0.36$ for the branching ratio in agreement with the Ref. [12], where a value of 0.32 ± 0.08 was obtained. Also, a ϕ_{Pt} value (quantum yield of population transfer from S_1^P to t twisted state) of 0.64, can be calculated from $\phi_{PN}=\phi_{Pt}(1-r)$.

Analyzing the S_1^P state and neglecting the fluorescence contribution of the P species, we calculated a value of the quantum yield corresponding to the direct internal conversion, $\phi_{ic}^P=0.36$. 41% of the molecules are transferred from the S_1^P state to the S_0^N state through the channel $S_1^P \rightarrow t \rightarrow S_0^N$ and 23% of the molecules decay by activated internal conversion to the S_0^P state through the channel $S_1^P \rightarrow t \rightarrow S_0^P$.

5. Conclusion

The methodology used in this work, based in the application of simultaneous absorption and fluorescence techniques, provides a complete quantitative description of the photo-physical processes in the photoisomerizable dyes, even when the spectra of both species are strongly overlapped, such as the DOCI case.

The isomerization and the back-isomerization values reported in this work at room temperature are consistent with extrapolated values obtained from Ref. [12] where a similar system was analyzed at low temperature. The obtained value for the photoisomeric emission efficient, agrees with the

assumption given in the Ref. [12], that it should be very low. This value had not been reported before.

Straight lines obtained with absorption and fluorescence data of DOCI clearly show that the results are consistent with the two-species photoisomerization model. The methodology adopted in order to obtain photophysical parameters relative to the corresponding values of the normal species, allows to fit equations with the fewest number of parameters.

Acknowledgements

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