DEPENDENCE ON THE VISCOSITY AND THE NATURE OF THE SOLVENT OF THE RELAXATION PATHWAYS OF THE FIRST SINGLET EXCITED STATE OF 3,3'-DIETHYLOXADICARBOCYANINE IODIDE

J. JARAUDIAS

Département Recherche et Analyse, S. R. I. R. M. A., Centre D'Études Nucléaires de Saclay, Boîte Postale No. 2, 91190 Gif-sur-Yvette (France)

Summary

The relaxation processes of the first excited singlet state of 3,3'-diethyloxadicarbocyanine iodide are investigated in this work. The viscosity effect of the medium is studied by applying the Oster–Nishijima relation which is modified to include photoisomerization. We show that, when the oscillator strength is constant and the spectral shift is small, the natural lifetime τ_0 in various solvents can be calculated from the spectrum of a reference solution. This is carried out by applying the well-known Strickler and Berg formula and introducing corrections for the refractive index and the spectral shift.

The lifetime of the S_1 state is measured by means of picosecond fluorescence techniques and the photoisomerization is measured using classical laser flash photolysis.

The Oster–Nishijima model applies well to unbranched alcohol solutions, from methanol to decanol. In glycerol, glycol or their mixtures with water all the relaxation processes except photoisomerization are accelerated. We suggest that a short range interaction occurs in these solvents, in keeping with the hypothesis that internal conversion via torsional movement and photoisomerization do not occur from the same molecular conformation.

1. Introduction

The photoisomerization of cyanine dyes is a well-known process following electronic absorption to an upper level S_1 of the singlet manifold [1 - 3]. A particularly important example is 3,3'-diethyloxadicarbocyanine iodide (DODCI), a dye which is used in the mode-locking rhodamine 6G dye laser [4].

Other pathways for the S_1 state relaxation are internal radiationless conversion, fluorescence and intersystem crossing; intersystem crossing is a process of low quantum yield for the dye DODCI [1].

In the S_1 state the conjugated π electronic structure is broken; this allows movement of the substituents at each end of the pure σ bonding system thus created which destroys the initial planar structure. The excited electronic structure of the polymethinic chromophore can be obtained using Hückel molecular orbital calculations. This method has allowed Tani [5] to determine that, for a nine-membered polymethinic chromophore such as DODCI, the electronic population of the central atom only becomes zero. Consequently only out-of-plane twisting movements are allowed.

The effect of intramolecular twisting has been evoked to explain, in terms of steric hindrance, the higher probability for internal conversion when the molecules have a short conjugated chain, $e.g.$ in the lower polymethine dyes [6 - 8] or tetraphenylbutadiene [9]. As a consequence, the ability of such molecules to undergo deviation from the planar structure may be directly correlated with the internal conversion processes of the S_1 state towards the S_0 ground state and with the photoisomerization quantum yield.

In this work we attempted to establish such correlations using a method based on the viscosity effect of the solvents; as a rough hypothesis we assumed that the higher was the viscosity the smaller the amplitude of molecular movements.

The fluorescence quantum yield of DODCI was obtained from fluorescence lifetime measurements using a picosecond technique. A laser flash photolysis method was used to obtain the photoisomerization quantum yield ϕ_P^S for various solutions. Special attention was paid to the thermalization rate k_{ISO} of the photoisomer from its ground state S_0^P to the ground state S_0^N of the normal isomer.

The solvents employed were the unbranched alcohols up to decanol, water–glycol mixtures and water–glycerol mixtures; these solvents cover a viscosity range of four orders of magnitude.

2. Experimental

The Kodak laser-grade dye DODCI was used without further purification.

The solvents were the following Merck quality products: methanol (for spectroscopy); ethanol (Uvasol quality); n-propanol, n-pentanol, n-octanol, n-decanol and 1,2-ethanediol (analytical grade); n-butanol (for fluorescence spectroscopy). Water-free glycerol was used as the 1490 cP viscosity reference and glycerol–etwa 87% was used as the 150 cP reference.

The compositions of the water–glycerol mixtures which were necessary to obtain given viscosities were taken from ref. 10.

3. Apparatus

Absorption spectra of DODCI in the various solvents were recorded on a Cary 114 spectrophotometer; they exhibited no change in the dye concen-

tration range 2×10^{-4} - 10^{-7} M. However, to prevent interference from possible dimerization [11], all experiments were performed in 2×10^{-5} - 10^{-4} M solutions.

Because the experimental arrangement used for the fluorescence spectroscopy has been widely described elsewhere [12] only a brief comment is given here.

A mode-locked rhodamine 6G dye laser was used to deliver a 2 μs train of picosecond pulses of 20 - 30 μJ measured at the sample cell. A Pockels cell situated between the exciting source and the sample cell enabled single-pulse experiments to be carried out. A fast Electrophonics streak camera associated with a PAR optical multichannel analyser (OMA) was used to record the fluorescence decay curves. In agreement with the results of the critical study of Fleming *et al.* [13] for signal processing, only shots of intensity below 2000 counts were recorded.

Measurements of photoisomerization quantum yields and spectra were performed using a classical laser flash photolysis set-up. A flash-lamp-pumped dye laser operating in a relaxing regime generated a 1.5 μs (full width at half-maximum) pulse which was the photolysing source. The emission wavelength was 480 nm when a 2.2×10^{-4} M methanolic solution of Coumarin 102 was used as the amplifying medium. The pulse energy was in the range 20 - 30 mJ.

We used a small 2 mm diameter glass sphere, into which was focused the light emitted by a quartz lamp, as the analysing source. The light from this quasi-point source was passed through a coupling lens to the 1 mm thick sample cell. A diaphragm placed in front of this cell defined the volume traversed by both the exciting and the probe beams. An optically matched Bausch and Lomb monochromator placed behind the sample cell was used to select the analysing wavelength.

The filtered part of the spectrum was directed to a RTC XP 1016 photo-multiplier and the output signal was displayed on a Tektronix 7704 (7B70-7A11) oscilloscope screen.

Because of their non-colinearity, the exciting and probe beams were arranged so that the analysed volume was smaller than that excited. As both beams were incident on the same side of the sample cell, the exciting light was focused in front of the cell and the analysing light was focused behind the cell. A beam splitter inserted in the exciting beam directed a part of the light to a radiometer which was used to monitor the intensity.

4. Results

4.1. Fluorescence kinetics

When the samples were excited by a single picosecond pulse, the recorded signals had the form of an exponential decay characteristic of a single unmolecular process. The excited state lifetime values were obtained by correcting for the apparatus response [14].

The results are presented in Table 1 and values of the lifetime $\tau_f(S_1^N)$ of the normal species are plotted against the viscosity η in Fig. 1 for the unbranched alcohols and for the water-glycol mixtures used as solvents. The curves obtained show that the lifetime increases monotonically with η.

The values obtained in this work for $\tau_f(S_1^N)$ support that obtained by Fleming et al. [13] in isopropanol (1.6 ± 0.1 ns), the viscosity of which is close to that of n-propanol. However, in pure glycol solution a higher value (2 ns) than that reported by Derkacheva et al. [15] (1.6 ns) was found. Furthermore the values of $\tau_f(S_1^N)$ for methanol, ethanol and n-propanol solutions have been confirmed [16] by measuring the absorption recovery rate.

Whole pulse train excitation previously carried out [2] for an ethanolic solution of DODCI was repeated with n-propanol and n-decanol, giving 500 and 630 ps respectively for the excited state lifetime $\tau_f(S_1^P)$ of the photoisomer in these media.

Fleming et al. [13] have not reported a viscosity dependence for $\tau_f(S_1^P)$ probably because the viscosity range used was too narrow.

4.2. Absorption spectroscopy and kinetics

The absorption spectrum of $(DODCI)_N$ showed no significant modification in the various solvents and mixtures employed. The molar extinction coefficient of the absorption maximum remained constant. The position of the maximum shifted slightly (12 nm) in going from methanol to n-decanol; $\lambda(\epsilon_{max}) = 578$ nm in methanol and 590 nm in decanol. In water-

TABLE 1

	Viscosity (cP)	Φ_P^S	k_{ISO}^{-1} (ms)	τ_f (ns)
Methanol	0.6	0.9	2.53	0.92[a]
Ethanol	1.2	1	2.97	1.2[a]
n-Propanol	2.2	–	3.71	1.58[a]
n-Butanol	2.9	–	4.44	1.70
n-Pentanol	4	0.92	4.58	2.03
n-Octanol	9	–	5.46	2.2
n-Decanol	14	0.88	5.56	2.38
Glycol	19.9	0.28	2.60	1.98
Glycerol (water free)	1490	0.09	3.09	1.77
Glycerol–13% H_2O	130	0.22	2.96	–
Glycerol–20% H_2O	62	0.35	2.44	1.27
Glycerol–40% H_2O	11	0.60	2.71	–
Glycerol–50% H_2O	6	0.61	2.24	–
Glycerol–75% H_2O	2.1	0.59	2.03	–
Glycol–40% H_2O	5	–	–	1.61
Glycol–60% H_2O	2.8	–	–	1.58
Glycol–80% H_2O	1.7	–	–	1.24
Glycol–90% H_2O	1.3	–	–	1.1

[a] These results have been confirmed using the recovery absorption technique.
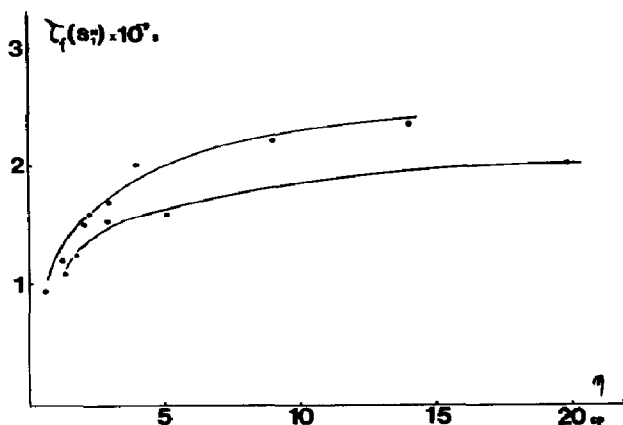
Fig. 1. Plots of $\tau_f(S_1^N)$ vs. η: ●, in pure unbranched alcohols at 293 K; ○, in neat glycol and water–glycol mixtures.

free glycerol $\lambda(\epsilon_{max}) = 585$ nm and in the 2 cP solution $\lambda(\epsilon_{max}) = 576$ nm.

When excited by the blue flash, a long-lived transient absorption (2 - 5 ms) was observed only at the red side of the spectrum and extending to 645 nm. The transmission of the sample increased in the 500 - 530 nm region indicating a decrease of the $(DODCI)_N$ concentration. The rate constant for recovery of the initial optical density of the sample was the same at both 620 and 530 nm.

The red transient absorption is attributed to the photoisomer $(DODCI)_P$. Because of the low value for the quantum yield of intersystem crossing [1] ($\phi_T < 5 \times 10^{-3}$), at times longer than a few nanoseconds the concentrations of the two species satisfy the relation

$$\Delta C_P = -\Delta C_N \tag{1}$$

where ΔC_P and ΔC_N refer to concentration changes of the two species. The results obtained using this procedure are in good agreement with those found previously [1].

The induced optical density ΔD_{620}^S in solvent S measured at 620 nm obeys the relation

$$\Delta D_{620}^S = a_S \phi_P^S I_0^{480} \tag{2}$$

where ϕ_P^S is the photoisomerization quantum yield in solvent S, I_0 is the exciting beam intensity and a_S is a proportionality factor defined by

$$a_S = a(1-10^{-D\,{}_{480}^S})\epsilon_{620}^{SP} \exp\,(t/\tau_{ISO}^S) \tag{3}$$

Here a is a proportionality term which relates the reading given by the radiometer to the exciting beam intensity, D_{480}^S is the optical density in solvent S at the exciting wavelength and ϵ_{620}^{SP} is the molar extinction coefficient of the photoisomer at 620 nm in this solvent. The term $\exp\,(t/\tau_{ISO}^S)$ was introduced because the measurement was made at time t (greater than 500 μs)

after excitation.

Because ϕ_P in an ethanolic solution is known, the relative value of Φ_P in the other solvents can be deduced using eqn. (2):

$$\Phi_P^S = \frac{\Delta D_s}{\Delta D_r}\bigg|_{I_0} \frac{a_r}{a_s} \tag{4}$$

Φ_P^S is the ratio of the slopes of the straight lines obtained using eqn. (2) for the two solvents when I_0 is varied. The index r denotes a reference solution, ethanol in this work.

Prior to photoisomerization quantum yield measurements, the decay rate k_{ISO} of the photoisomer ground state towards the ground state of the normal form was measured. The results are plotted in Fig.2. In alcoholic media the inverse of the decay rate k_{ISO} increases rapidly with the viscosity. No such effect is observed for glycol, glycerol and their water mixtures; the values of k_{ISO}^{-1} all lie in the range 2 - 3 ms in spite of the very extended viscosity range.

The photoisomerization quantum yield remains constant (within 20% experimental error) in all the alcohols employed (Fig. 3). In the other solvents the results are all lower in the corresponding viscosity range and decrease markedly as the viscosity is increased from 10 cP to the highest values.

5. Discussion

Our results fit well into the framework of the four classical levels of photoisomerization, the levels involved being S_0^N, S_1^N, S_0^P and S_1^P. In this work intersystem crossing [1] is not a sufficiently important process to contribute significantly.
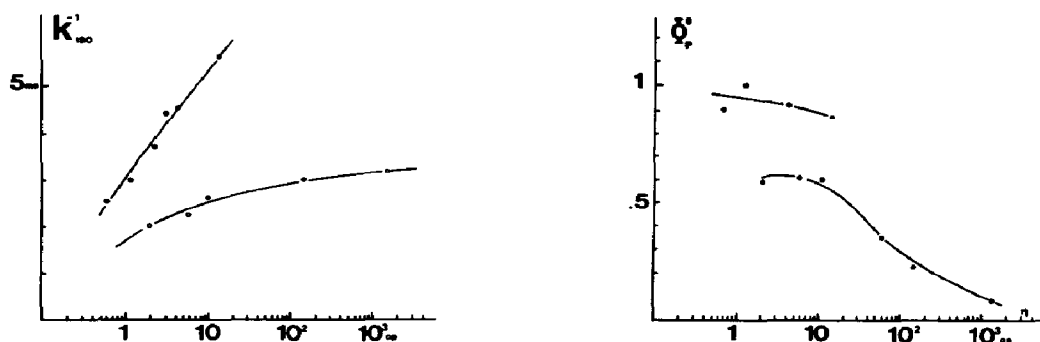

Fig. 2. Plots of k_{ISO}^{-1} against η: ●, in pure unbranched alcohols; ○, in glycerol and water—glycerol mixtures at 293 K.

Fig. 3. Plots of the normalized photoisomerization quantum yield Φ_P^S as a function of η: ●, in pure unbranched alcohols; ○, in glycerol and water—glycerol mixtures.

Chibisov [17] has demonstrated that the process of *cis–trans* photo-isomerization occurs via singlet excited levels for some unsubstituted cyanines, in particular for diethyloxacarbocyanine iodide (DOCI).

The suggested decay mechanism for the excited S_1^N state of DODCI is as follows:

$$S_1^N \xrightarrow{k_{NR}} S_0^N \tag{5}$$

$$S_1^N \xrightarrow{k_R} S_0^N + h\nu_f \tag{6}$$

$$S_1^N \xrightarrow{k_P} S_0^P \tag{7}$$
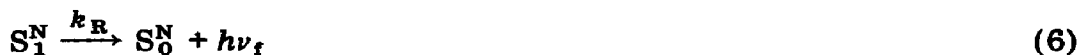
where k_{NR}, k_R and k_P are respectively the non-radiative rate constant, the radiative rate constant and the isomerization rate constant.

The fluorescence quantum yield ϕ_f is given by

$$\phi_f = \frac{k_R}{k_{NR} + k_R + k_P} \tag{8}$$

ϕ_f can also be calculated from

$$\phi_f = \frac{\tau_f(S_1^N)}{\tau_0(S_1^N)} \tag{9}$$

where τ_f is the fluorescence lifetime and τ_0 is the natural radiative lifetime. τ_0 can be calculated using Forster's formula, as was carried out by Dempster *et al.* [1], with the Strickler and Berg relation [18] (see later). τ_0 can also be obtained by calculating the ratio of the measured excited state S_1^N lifetime to the fluorescence quantum yield ϕ_f obtained using fluorescence spectroscopy.

Magde and Windsor [19] have reported a value of ϕ_f of 0.42 ± 0.02 for an ethanolic solution of DODCI. We determined the fluorescence lifetime to be 1.2 ± 0.1 ns in this solvent which yields $\tau_0(S_1^N)$ = 2.86 ± 0.37 ns. Dempster *et al.* [1] have calculated a value for $\tau_0(S_1^N)$ of 2.54 ± 0.25 ns. However, changing the solvent results in a spectral shift and the value of $\tau_0(S_1^N)$ is modified.

The Strickler and Berg formula takes account of this modification:

$$\tau_0^{-1} = 2.880 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle_{av}^{-1} \int \epsilon(\nu_a) d\ln\nu_a \tag{10}$$

where n is the refractive index of the solvent, and ν_f and ν_a refer to emission and absorption wavenumbers respectively. $\epsilon(\nu_a)$ is the molar extinction coefficient and $\langle \nu_f^{-3} \rangle_{av}^{-1}$ is defined as follows:

$$\langle \nu_f^{-3} \rangle_{av}^{-1} = \frac{\int I_f(\nu_f) d\nu_f}{\int \nu_f^{-3} I_f(\nu_f) d\nu_f} \tag{11}$$

The numerator represents the area of the fluorescence spectrum.

If the whole emission spectrum is shifted by a constant amount $\Delta\nu'_f$, eqn. (11) may be rewritten as

$$\langle\nu_f'^{-3}\rangle^{-1} = \left(1 + \frac{3\Delta\nu_f}{\nu_{rf}}\right)\langle\nu_f^{-3}\rangle^{-1} \qquad (12)$$

where the prime indicates the new value of $\langle\nu_f^{-3}\rangle^{-1}$ calculated with respect to a reference solution. ν_{rf} is taken to be the wavenumber of the emission maximum, the spectral shift of which is $\Delta\nu_f$.

In this work a maximum (blue) shift of 248 cm^{-1} was found for the emission of DODCI in methanol when the reference solvent was ethanol. Because the fluorescence spectra were spread over the range 17 000 - 14 000 cm^{-1}, this procedure introduced only a slight error (0.5%) into the correction factor.

When the same procedure was applied to correct $\int\epsilon(\nu_a)d\ln\nu_a$ for changes in ν_a due to a change of solvent it was easy to demonstrate that

$$\int\epsilon'(\nu_a)d\ln\nu_a' = \left(1 - \frac{\Delta\nu_a}{\nu_a}\right)\int\epsilon(\nu_a)d\ln\nu_a \qquad (13)$$

Combination of eqns. (12) and (13) with eqn. (10) gave a new relation for τ_0' and, after solving for τ_0, it was found that

$$\tau_0' = \left(1 + \frac{\Delta\nu_a}{\nu_{ra}}\right)\left(1 - \frac{3\Delta\nu_f}{\nu_{rf}}\right)\left(\frac{n}{n'}\right)^2 \tau_0 \qquad (14)$$

It is evident that this relation holds when both the emission and the absorption spectra in a given solvent are only slightly displaced with respect to the spectra in a reference solvent and when the oscillator strength for absorption is independent of the solvent.

Fluorescence spectra were recorded using a technique analogous to that described by Rulliere [20] with the DODCI concentration in the 10^{-7} M range. The power of the Ar$^+$ laser beam (514.5 nm) was reduced so that only a few milliwatts were incident on the sample, in order to avoid any contribution of the photoisomer spectrum [21].

The results presented in Table 2 are for ethanol as the reference solvent. ϕ_f was calculated for both values of τ_0 (S_1^N) in ethanol (see earlier). For the dye DODCI the major part of the correction for the τ_0 values arises from the change of the refractive index. The contribution of the spectral shift is of the opposite sign and reduces the correction.

The values reported in this work for the unbranched alcohols exhibit a variation of about 10% over the whole range in the two cases.

5.1. Viscosity dependence of ϕ_f

Oster and Nishijima [22] have noted the existence of two radiationless pathways for the de-excitation of the excited state of Auramine 0; one pathway is caused by a vibrational process with a mean duration of τ_2 and the

TABLE 2

	$\nu_m(cm^{-1})$	$\Delta\nu_a$	ν_f	$\Delta\nu_f$	$(n/n')^2$	$\tau_0{}^a$	$\tau_0{}^b$
CH_3OH	17 301	+90	16 391	+248	1.050	2.56	2.88
C_2H_5OH	17 211	0	16 639	0	1	2.54[a]	2.86[b]
C_3H_7OH	17 153	−58	16 521	−118	0.966	2.50	2.81
C_4H_9OH	17 123	−88	16 511	−148	0.947	2.46	2.77
$C_5H_{11}OH$	17 094	−117	16 486	−153	0.933	2.42	2.72
$C_8H_{17}OH$	17 007	−204	16 461	−178	0.908	2.35	2.65
$C_{10}H_{21}OH$	16 949	−262	16 447	−192	0.899	2.33	2.62

[a] The literature value of Dempster *et al.* [1] was used as the reference value in the calculations for the other solvents using eqn. (14).
[b] For the reference solvent the ϕ_f value of Magde and Windsor [19] and our value of $\tau_f(S_1^N)$ were used in order to calculate (eqn. (14)) τ_0 for the other solvents.

other pathway, which is caused by molecular twisting movements, is characterized by a relaxation time τ_3.

If the second pathway is controlled by diffusion it should be viscosity dependent. Application of Stokes's law, which links τ_3 to η, and combination with eqn. (8) gives the Oster–Nishijima relation:

$$\phi_f{}^{-1} = 1 + \frac{\tau_0}{\tau_2} + a\tau_0\frac{T}{\eta} \tag{15}$$

where a is a proportionality constant.

In the excited state the π electronic structure of DODCI is broken [5] and intramolecular twisting becomes possible. If eqn. (15) is obeyed, a plot of $\phi_f{}^{-1}$ against η^{-1} should give a straight line when T is kept constant.

However, DODCI undergoes isomerization when it is photoexcited. The photoisomerization is brought about by the rotation of part of the molecule around the central pure bond formed in the polymethinic chain of the excited state, *i.e.* by an intramolecular twisting movement.

If in turn this movement is controlled by rotational diffusion, eqn. (15) may be rewritten as

$$\phi_f{}^{-1} = 1 + \frac{\tau_0}{\tau_2} + (a + b)\tau_0\frac{T}{\eta} \tag{16}$$

In this case the photoisomerization contributes to the slope of the straight line by an additional factor b.

In the alternative case eqn. (15) is simply modified giving

$$\phi_f{}^{-1} = 1 + \frac{\tau_0}{\tau_2} + \frac{\tau_0}{\tau_P} + a\tau_0\frac{T}{\eta} \tag{17}$$

The isomerization process now contributes to the intercept of the straight line on the y axis.

In general the orientational relaxation time of dye molecules is very sensitive to the viscosity of the medium. The Debye diffusion model describes very well the rotational movements of molecules in both their excited states [13] and their ground states [23, 24].

5.2. Unbranched alcohols

In unbranched alcohols the orientational relaxation time of $(DODCI)_N$ increases by a factor of 30 in going from methanol to decanol [21], as predicted by Stokes's law for a rotating spheroid. However, the Φ_P values obtained in these solvents do not exhibit such a viscosity effect. Consequently only eqn. (17) is expected to provide an adequate description of the relaxation processes.

The values of ϕ_f^{-1} for the various alcohols as a function of η^{-1} are given in Fig. 4. for a constant temperature.

Using the corrected values for τ_0 (S_1^N) given in Table 2, good straight line fits are obtained in both cases. Thus the Oster function defined by eqn. (17) is well obeyed whichever of the two reference values [1, 19] is taken.

In the former case the corrected value for the radiative lifetime in decanol is very close to the measured lifetime of 2.34 ns. The intercept on the y axis is slightly less than unity. In the second case the straight line is displaced so that it cuts the ordinate at a value greater than unity; this is in better accord with the mathematical description of the processes involved.
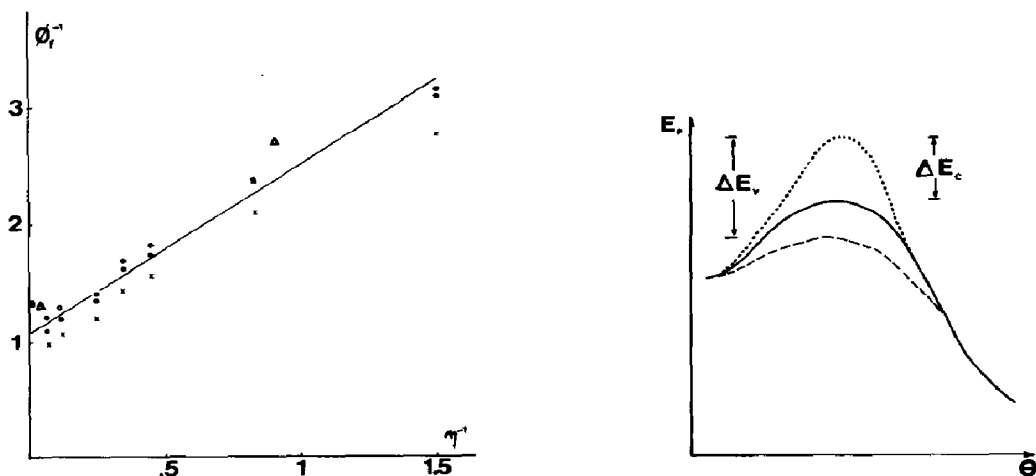

Fig. 4. The inverse of the fluorescence quantum yield ϕ_f^{-1} as a function of η^{-1}: x, corrected τ_0 values, column 7 of Table 2; ●, corrected τ_0 values, column 8 of Table 2; ○, for a constant value of τ_0; △, water–glycol mixtures; ■, pure water-free glycerol.

Fig. 5. Modification of the potential barriers for intramolecular twisting: ΔE_v is the viscosity contribution; ΔE_c is related to short range solute–solvent interaction.

In this case, and taking into account the overall error, the maximum intercept on the y axis is 1.1. Applying eqn. (17) it is easy to demonstrate that

$$\tau_P \geqslant 10\tau_0 \tag{18}$$

This procedure predicts a value $k_P \leqslant 3.5 \times 10^7 \text{ s}^{-1}$, which is smaller than that obtained previously [1] ($k_P = 6.45 \times 10^7 \text{ s}^{-1}$). The value found in this work is in better agreement with the photoisomerization quantum yield ϕ_P of 0.01 measured by Arthurs et al. [25].

5.3. Non-alcoholic solvent and mixtures

In these solvents the $\tau_f(S_1^N)$ values are all lower than those obtained in unbranched alcohols with the same viscosity (Fig. 2). Furthermore in pure glycerol ($\eta = 1490$ cP) the measured value of $\tau_f(S_1^N)$ is lower than that in pure decanol ($\eta = 14$ cP) (Table 1).

The calculated values for ϕ_f^{-1} in pure glycol and in glycol–90% H_2O are 1.31 and 2.69 respectively. These points are plotted in Fig. 4 and it can be seen that they are situated above the curve drawn for the unbranched alcohols. If they are to agree with the Oster–Nishijima relation (eqn. (17)) then the other parameters would have to be altered.

The value of ϕ_f^{-1} in pure glycerol is 1.36, which is close to that obtained in pure glycol in spite of the higher viscosity. Since the corresponding point (Fig. 4) is very close to the y axis, a smaller value for k_P in this solvent is predicted using eqn. (17). This is confirmed by our results (Fig. 3), which show that the quantum yield for photoisomerization is smaller in these solvents over the whole viscosity range and decreases markedly at higher values of η.

In contrast the measured values of k_{ISO}^{-1} are also lower than those obtained in the pure alcohols (Fig. 2).

Thus the type of interaction occurring in the polyhydric solvents appears to accelerate all the relaxation processes except isomerization regardless of whether DODCI is in the excited or ground state. Chuang and Eisenthal [23] have measured the orientational relaxation time of rhodamine 6G in glycol and unbranched alcohols. They observed that Stokes's law is well obeyed in the unbranched alcohols, whereas in glycol the value is lower than that expected. They concluded that rhodamine 6G "does not view the full frictional effects of the polymeric structure of the solvent which are however contained in the value of the viscosity" and, on the basis of our results, the same may be said of DODCI.

Although the lower values of $\tau_f(S_1^N)$ and k_P^{-1} may be explained in terms of a local reduction of the viscosity, this seems difficult to justify for a solvent such as pure glycerol. An alternative explanation is one involving the chemical nature of the solvent.

Compared with unbranched alcohols, polyhydric solvents and their mixtures with water are characterized by a greater concentration of OH groups. If a short range interaction is evoked to explain the faster relaxation observed, these groups may contribute to dissipate the excess energy of DODCI in the

S_1^N state. Such an effect would be strong in pure glycol, glycerol and solvents of intermediate viscosity where the measured τ_f (S_1^N) is reduced to values lower than that obtained for the decanol solution.

Saltiel and D'Agostino [26], in their study of viscosity effects on the singlet pathway to stilbene photoisomerization, have compared the results obtained for solutions of different viscosities; they have proposed potential energy curves for the intramolecular twisting movement (Fig. 5). According to their scheme the thermal contribution to the barrier E_t, which is that encountered in liquids of low viscosity, is enhanced in liquids of high viscosity by the viscosity-dependent contribution ΔE_v. Thus the measured height of the energy barrier E_{obs} is $E_t + \Delta E_v$.

The results presented in Figs. 2 and 3 show that such a relationship is not sufficient to give an overall description of the solvent effect for the various systems studied; the chemical nature of the solvents also appears to be a contributing factor. This means that another term ΔE_c has to be introduced into the potential energy relationship to account for this contribution so that $E_{obs} = \Delta E_v + E_t + \Delta E_c$.

Because the results for the S_1^N lifetimes of DODCI in alcoholic solutions are in good agreement with the predictions based on a simple viscosity effect, ΔE_c must be very much smaller than ΔE_v and its contribution to the potential energy barrier appears to be negligible in this solvent family. The data of Table 1 and Fig. 1 show that, in the polyfunctional solvents, τ_f (S_1^N) is reduced relative to the values found in the simple alcohols; this shows that the contribution of ΔE_c to the energy barrier acts to reduce that of ΔE_v.

The results given in Fig. 3 show that the photoisomerization yield in glycol, glycerol and their mixtures with water is strongly viscosity dependent, unlike that observed in the simple alcohols. However, this dependence on viscosity is evident in the range above 10 cP, i.e. at viscosities much higher than those encountered in the unbranched alcohols employed.

The contribution of the chemical effect to the potential barrier is certainly present since the photoisomerization yield measured in these systems is always lower than that found in the monohydroxylic solvents of corresponding viscosity. These data also indicate that ΔE_v remains of greater importance than ΔE_c and becomes the controlling factor as the aqueous content of the mixtures decreases. Although the viscosity effect is predominant for photoisomerization, it evidently has less controlling influence over the radiationless relaxation indicating that these processes are of a different nature.

A theoretical calculation [5] has shown that only two adjacent pure σ bonds exist, one on either side of the central atom of the chromophore, in the electronic π^* structure. Thus this atom is the only possible site of torsional movements to give either internal conversion or isomerization.

This structural consideration lends support to the idea that these two relaxation pathways originate from different torsional states as proposed by Rulliere [20]. In his model the internal conversion occurs from a slightly distorted structure. This result is similar to that previously obtained [22]

for Auramine O, where the torsional angle of the out-of-plane structure was found to be only 2.2°.

Photoisomerization occurs via a completely crossed structure which is intermediate between the planar conformations of the two isomers in their excited states.

6. Conclusion

We studied the effect of solvent on the relaxation processes of DODCI in its excited state. The effect of the medium on the radiative lifetime τ_0 was introduced in terms of two parameters, the spectral shift and the refractive index. The role of the refractive index has been investigated previously [27], and we applied the n^{-2} correction. However, a more accurate study would have to consider that both the fluorescence and the absorption spectra extend from 700 to 450 nm, and over this wide wavelength range the refractive index may not be constant. In this respect the modified Strickler and Berg equation obtained by Birks and Dyson [28] is more rigorous.

Corrected values for τ_0 (S_1^N) were used to calculate the fluorescence quantum yield ϕ_f of DODCI in various solvents. In this case the Oster–Nishijima description for the viscosity effect on ϕ_f satisfactorily explains the results obtained for the unbranched alcohols. This point was not discussed for the polyhydric alcohols and their mixtures with water, which all accelerate the internal conversion. This effect was attributed to a high density of OH groups showing that, in addition to the viscosity, the chemical nature of the solvent is important. Although the results are in general agreement with the Rulliere model [20] for photoisomerization, further extensive investigations of other systems must be carried out to establish a quantitative model for the influence of the chemical structure of the solvent.

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