ROTATIONAL DIFFUSION OF THE MODE-LOCKING DYE DODCI AND ITS PHOTOISOMER

G.R. FLEMING *, A.E.W. KNIGHT ‡, J.M. MORRIS, R.J. ROBBINS and G.W. ROBINSON #
Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

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Picosecond time dependent fluorescence depolarization has been used to measure the rotational diffusion time of 3,3'-diethyloxadicarbocyanine iodide (DODCI) in solution at 293 K: the stable form of DODCI was shown to have a "coiled" form, the cis,cis-1,5-conformation, whereas the photoisomer formed by irradiating DODCI in solution was shown to be the elongated all-trans-isomer. The stable form has a rotational correlation time of 160 ± 30 ps in ethanol and 320 ± 40 ps in isopropanol; the fluorescence lifetimes were 1.2 ± 0.1 ns (ethanol) and 1.6 ± 0.1 ns (isopropanol). The all-trans-photoisomer has a rotational correlation time of >700 ps in isopropanol and a fluorescence lifetime of 0.42 ± 0.05 ns. Furthermore, the rotational diffusion times agree closely with those predicted on the basis of the Stokes–Einstein hydrodynamic model, indicating a lack of any solvent attachment to DODCI in solution.

1. Introduction

In a previous paper [1] we reported that the fluorescein derivative dyes rose bengal and eosin rotate in polar solvents as if their volume is at least double that of the free molecule because of solvent attachment. Lessing and von Jenà [2] have used transient absorption spectroscopy to measure the rotational diffusion time of fluorescein 27 in alcohols of different viscosity and arrived at essentially the same conclusions. However, these general conclusions differ from those of Chuang and Eisenthal [3] who found that the molecular volume of rhodamine 6G is unaffected by hydrogen bonding interaction with the solvent. In order to test the generality of the phenomenon of solvent attachment, we have extended our measurements to differently shaped molecules with different molecular charges.

The photophysical properties of 3,3'-diethyloxadicarbocyanine iodide (DODCI) are of interest because of its widespread use as a saturable absorber for mode-locking rhodamine dye lasers operating in the spectral range 584–645 nm [4]. At the longer wavelengths (610–645 nm) mode-locking is due to the formation of a photoisomer [5]; both electronic relaxation [6,7] and rotational diffusion [8] of the DODCI photoisomer appear to be important for a full understanding of the mode-locking process. Using picosecond time-dependent fluorescence depolarization [1] it is possible to study the rotational diffusion of both the normal form of DODCI and its photoisomer. Rotational diffusion acts as a probe for the conformation of both species and also enables a measurement of their correct excited state lifetimes. This should help in the understanding of both the mechanism of photoisomerization and the mode-locking process. However, there are still some unexplained features of the photophysics of the DODCI photoisomer and thus the conclusions concerning the conformation of this species are tentative. Nevertheless, DODCI affords an interesting test of the phenomenon of solvent attachment and demonstrates the utility of rotational diffusion as a probe for molecular conformation.

* Present address: The Royal Institution, London, W1X 4BS, UK.
‡ Present address: School of Science, Griffith University, Nathan, Brisbane, Queensland 4111, Australia.
# Present address: Department of Chemistry, Texas Tech University, Lubbock, Texas, USA.
2. Theory of fluorescence depolarization

The problem of fluorescence depolarization has been treated in detail by Tao [9] and the relevant theoretical results were summarized in a previous paper [1]. The time dependent fluorescence polarization anisotropy \( r(t) \) is related to the experimentally observed intensities polarized parallel \( I_{\parallel}(t) \) and perpendicular \( I_{\perp}(t) \) to the polarization of the exciting light,

\[
r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t) + 1}.
\]

Note also that [9]

\[
r(t) = \frac{1}{3} \langle P_2 [\mathbf{e}(0) \cdot \mathbf{e}(t)] \rangle
\]

yielding directly the correlation function for the second Legendre polynomial of the dipole reorientation angle (the "rotational correlation function"); the \( \mathbf{e}'s \) are unit vectors along the transition dipole at times 0 and \( t \) respectively. The fluorescence decay law is obtained free from any interference from rotational diffusion as

\[
K(t) = I_{\parallel}(t) + 2I_{\perp}(t)
\]

and also can be obtained in a single measurement by setting the analyzer at an angle 54.7° from the direction of parallel polarization [1].

In the simplest case where the molecule undergoes brownian rotation as an Einstein sphere,

\[
\langle P_2 [\mathbf{e}(0) \cdot \mathbf{e}(t)] \rangle = \exp(-6Dt),
\]

where \( D = kT/6\nu \eta \) is the rotational diffusion constant, \( \nu \) is the molecular volume and \( \eta \) is the viscosity of the medium [10]. For the rotational diffusion of a symmetric rotor in the strong damping limit, \( \langle P_2 \rangle \) may consist of the sum of three exponentials [11]. However, for many cases of practical importance (oblate rotor with transition dipole parallel or perpendicular to the symmetry axis, prolate rotor with transition dipole parallel to the symmetry axis) \( \langle P_2 \rangle \) will decay, within experimental error, as a single exponential. In this case the rotational diffusion constant will depend not only on molecular volume, but also on the actual molecular shape.

3. Experimental

The Nd\(^{3+}\)-phosphate glass laser (Apollo) produces a train of about 100 pulses separated by 7.5 ns with durations of 6–8 ps (fwhm) [12,13]. For most of the experiments a single pulse is selected from near the beginning of the pulse train using a pulse selector of conventional design [12]. The 1054 nm laser fundamental is converted to the second harmonic at 527 nm with a temperature tuned cesium dihydrogen arsenate crystal (Quantum Technology Ltd.); an additional polarizer rejects any stray components of polarization from this vertically polarized exciting light.

Samples of DODCI \((10^{-5} \text{ in ethanol or isopropanol})\) are illuminated at 90° with respect to the optic axis of the streak camera (Electrophotonics Photchron II), the exciting beam being aligned as closely as possible to the viewing window of the sample cell to minimize the effects of reabsorption. Care is also taken to avoid stimulated emission by using dilute solutions \((10^{-5} \text{ M})\), low intensity excitation \(<10 \text{ MW cm}^{-2}\) and right-angle excitation geometry [14]. A rotatable polarizer in the streak camera collection optics selects the polarization component detected while a 3 mm Schott OG-570 filter in front of the streak camera slit removes any scattered 527 nm exciting light. The streaked image on the final phosphor of the streak camera is recorded with an optical multichannel analyzer (Princeton Applied Research) and the data transferred to an on-line computer for permanent storage and analysis. Lag problems [15] in the silicon vidicon can affect the linearity of the OMA response to pulsed light sources. After readjustment of the factory-set cathode voltage (from about \(-3 \text{ V to } -6 \text{ V}\)) the streak camera/OMA is linear to within \(\pm 5\%\) to pulsed light intensity in the range 100–2000 counts [12]. Errors in the time calibration of the streak camera have also been checked and found to be less than \(\pm 2\%\). A detailed description of the streak camera/optical multichannel analyzer detection system is published elsewhere [12].

4. Results and discussion

Fig. 1a shows the experimental \( I_{\parallel}(t) \) and \( I_{\perp}(t) \) curves for DODCI in isopropanol \((10^{-5} \text{ M, } 20.0 \pm 0.5^\circ \text{C})\) excited by a single 527 nm picosecond pulse.
Fig. 1. (a) $I_{\|}(t)$ (upper curve) and $I_{\perp}(t)$ (lower curve) for DODCI 10^{-5} M in iso propanol excited by a single 527 nm picosecond pulse. (b) Fluorescence decay (upper curve) and fluorescence polarization anisotropy (lower curve) calculated from experimental data in (a). The solid lines are best exponential fits. The vertical scale on the right refers to the anisotropy and the scale on the left to the decay function.

These curves represent the "raw" streak camera data — they are single shot results and no smoothing has been applied. Fig. 1b shows the $r(t)$ and $K(t)$ curves extracted from these data by the method of "leading edge matching" [1] which makes use of the relation

$$P_2[e(0)\cdot e(0)]=1,$$

which requires that $r(0)=0.4$. For this system, both $r(t)$ and $K(t)$ decay as single exponentials. The rotational correlation time and excited state lifetime calculated from a weighted least-squares fit to the $r(t)$ and $K(t)$ curves are given in table 1. Results obtained for DODCI in ethanol ($10^{-5}$ M, 20.0 ± 0.5°C) excited by a single 527 nm picosecond pulse are also summarized in table 1.

The amplified noise in the $r(t)$ curve at long times is due to the functional form of eq. (1) as a difference divided by an exponentially decaying function. However, the rotational correlation time is insensitive to these errors in the tail of the curve because the least-squares fitting procedure weights the earlier points much more than those at longer times. Fig. 1b also reveals that $r(t)<0.4$ at the maximum of the fluorescence polarization anisotropy curve: this is due to convolution effects which means that the fit cannot be started $t=0$. In fact, the "leading edge matching" method ensures that the condition given by eq. (5) is satisfied.

Shank and Ippen [16] have also measured the rotational correlation time of DODCI and obtained the results: 95 ps (MeOH) and 200 ps (EtOH); based on solvent viscosities this implies a value of ≈400 ps in isopropanol. These values are in reasonable agreement with the values of 160 ± 30 ps (EtOH) and 320 ± 40 ps (t-PrOH) obtained in the present work. However, Lessing and von Jena [2] have recently re-evaluated Shank and Ippen’s data [16] and obtained 50 ps for the rotational correlation time of DODCI in methanol. This seems inconsistent both with our data and that predicted on the basis of the hydrodynamic model. The measured excited state lifetimes for DODCI are 1.6 ± 0.1 ns (t-PrOH) and 1.2 ± 0.1 ns (EtOH). Previously reported values are ≈1.2 ns (EtOH) [5,14,16–18] and 0.56 ns (H2O) [18].

For DODCI there are several conceivable molecular conformations with respect to cis—trans isomerization of the polymethine chain. Two conformations

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solvent</th>
<th>$\eta$(cP)</th>
<th>$\tau_{or}$(ps)</th>
<th>$\tau_{et}$(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DODCI a)</td>
<td>t-PrOH</td>
<td>2.37</td>
<td>320 ± 40</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>DODCI b)</td>
<td>t-PrOH</td>
<td>2.37</td>
<td>700 ± 100</td>
<td>1.6 ± 0.1, 0.42 ± 0.05</td>
</tr>
<tr>
<td>DODCI c)</td>
<td>EtOH</td>
<td>1.20</td>
<td>160 ± 30</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

a) Excited by a single pulse.
b) Excited by a train of pulses.
that are favourable for their lack of steric hindrance—the all-trans-isomer and the cis,cis-1,5-isomer derived from the former by two trans → cis isomerizations of the polymethine chain—are shown in fig. 2 and are approximately prolate and oblate rotors respectively. The calculated rotational correlation times are 770 ± 70 ps for the all-trans-isomer (prolate rotor, semi-axes ≈ 2.8 Å and 12 Å) and 330 ± 30 ps for the cis,cis-1,5-isomer (oblate rotor, semi-axes ≈ 6.5 Å and 2 Å) in isopropanol solution (η = 2.37 cP at 20°C) *. Comparison with the experimental value of 320 ± 40 ps (i-PrOH) suggests that the normal form of DODCI has the cis,cis-1,5-conformation or possibly some other coiled up conformation in isopropanol. The experimental value of 160 ± 30 ps (EtOH), although less accurate, implies that DODCI has the same conformation in ethanol as in isopropanol. In contrast to this, structurally similar molecules such as stilbene [19] and butadiene [20] derivatives and the retinyl polyenes [21] are known to preferentially adopt the all-trans conformation.

These results also indicate that the molecular volume of DODCI in both ethanol and isopropanol is unaffected by solvent attachment. This may be compared with results for the fluorescein derivative dyes [1,2] which rotate in polar solvents as if their volume is at least double that of the free molecule because of solvent attachment. However, it is possible to envisage an increase in the effective molecular volume by a kind of molecular paddle wheel effect [1]. This effect should depend only on the molecular shape (not molecular charge, polarizability etc.) and is expected to be more important for oblate rotors than for prolate rotors. The fluorescein derivative dyes and cis,cis-1,5-DODCI are both approximately oblate rotors and so the lack of any solvent attachment to DODCI implies that the increase in the molecular volume of the fluorescein derivative dyes is due to a strong, specific solute—solvent interaction rather than a molecular paddle wheel effect. In fact, the rotational correlation time of water and the small alcohols [26] is much shorter than the rotational correlation time of the solute and therefore a molecular paddle wheel effect seems unlikely. Furthermore, Chuang and Eisenthal [3] found that the molecular volume of rhodamine 6G is unaffected by hydrogen bonding interactions with the solvent. A possible reason for these differences in behaviour is the charge on the molecules: the fluorescein derivatives are dianions whereas DODCI and rhodamine 6G are both mono-cations. Further work is necessary to establish whether it is the sign or the magnitude of the molecular charge which controls solvent attachment to dye molecules in polar solvents.

Finally, we report results obtained for DODCI in isopropanol (10−5 M, 20.0 ± 0.5°C) excited by a train of 527 nm picosecond pulses. Fig. 3a shows the experimental I(t) and K(t) curves obtained when the streak camera is triggered on a pulse ≈ 250 ns after the beginning of the pulse train, while fig. 3b shows the r(t) and K(t) curves extracted from the experimental data by the method of “leading edge matching” [1]. In this case r(t) decays within experimental error as a single exponential, but the rotational correlation time (700 ± 100 ps) is much longer than that obtained.

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* The error limits on the calculated times are estimations based on errors in measuring molecular models and in approximating the molecular shape as a symmetric ellipsoid.

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Fig. 2. Scale molecular drawings of (a) all-trans-DODCI, and (b) cis,cis-1,5-DODCI. The solid outline represents the size of a scale molecular model. See text for actual dimensions.
under conditions of single pulse excitation ($320 \pm 40$ ps). In addition, the decay function is non-exponential. Using a nonlinear least-squares curve fitting procedure [22], $K(t)$ can be fitted as the sum of two exponentials with lifetimes $1.6 \pm 0.1$ ns and $0.42 \pm 0.05$ ns and relative weights $0.5 \pm 0.1$ and $0.5 \pm 0.1$ respectively. Although in general it is difficult to fit a unique pair of exponentials to such a decay function, this particular situation was favourable because of the large difference in lifetimes and approximately equal weights of the two exponentials. These results are summarized in table 1.

It is now well established that excitation of the normal form of DODCI ($\lambda_{\text{abs}} \approx 580$ nm) results in the formation of a photoisomer with reported quantum yields of 0.08 [5] and 0.01 [23]. The lifetime of the photoisomer ground state is $1.3 \text{ ms}$ [5] and its absorption [5] and emission [24] spectra are similar to those of the normal form but shifted $\approx 40$ nm to the red. Because of the low photoisomerization quantum yield, little photoisomer is formed within a single picosecond pulse. However, excitation with a train of picosecond pulses leads to the rapid buildup ($<200$ ns [23]) of a steady state concentration of 15–20% photoisomer [17,23]. Recently, Mialocq et al. [17] measured the fluorescence decay of DODCI in ethanol excited by a train of picosecond pulses at 605 nm and also obtained a two component decay with lifetimes $1.2 \pm 0.3$ ns and $0.42 \pm 0.06$ ns and approximately equal relative intensities. These authors attributed the faster component to the fluorescence of the DODCI photoisomer and the slower component to the fluorescence decay of the normal form of DODCI. Our results in isopropanol are also consistent with this explanation: the slower component of $K(t)$ has a lifetime ($1.6 \pm 0.1$ ns) identical to that obtained under conditions of single pulse excitation, while the faster component has a lifetime ($0.42 \pm 0.05$ ns) in agreement with that obtained by Mialocq et al. [17] for the DODCI photoisomer. Thus, while the fluorescence lifetime of the normal form of DODCI shows quite a strong solvent dependence, it appears that there is no such effect on the fluorescence lifetime of the photoisomer form, although the experimental data are not sufficiently accurate to rule out the possibility of a weaker solvent dependence.

If the above analysis is correct, it should be possible to calculate the rotational correlation time for the DODCI photoisomer $\tau_{\text{OR,P}}$ from the known fluorescence lifetimes of the two species ($\tau_{\text{FL,N}} = 1.6 \pm 0.1$ ns, $\tau_{\text{FL,P}} = 0.42 \pm 0.05$ ns), the rotational correlation time of the normal form ($\tau_{\text{OR,N}} = 320 \pm 40$ ps), the fraction of photoisomer fluorescence ($R = 0.5 \pm 0.1$) and the measured rotational correlation time for excitation with a train of picosecond pulses ($\tau_{\text{OR,M}} = 700 \pm 100$ ps). For a decay function of the form

$$K(t) = (1 - R) \exp(-t/\tau_{\text{FL,N}}) + R \exp(-t/\tau_{\text{FL,P}}),$$

(6)

the fluorescence polarization anisotropy calculated according to eq. (1)

$$r(t) = 0.4[1 - R] \exp(-t/\tau_{\text{FL,N}} + 1/\tau_{\text{OR,N}})] + R \exp(-t/\tau_{\text{FL,P}} + 1/\tau_{\text{OR,P}})]/K(t)$$

$$\approx 0.4 \exp(-t/\tau_{\text{OR,M}}),$$

(7)

which decays to a good approximation as a single exponential. However, the value of the photoisomer rotational correlation time calculated from this expres-
sion is very sensitive to errors in the other parameters. Nevertheless, it is relatively easy to show that if \( \tau_{\text{OR,N}} < \tau_{\text{OR,M}} \) then \( \tau_{\text{OR,M}} < \tau_{\text{OR,P}} \) which sets a lower limit for the rotational correlation time of the DODCI photoisomer, \( \tau_{\text{OR,P}} > 700 \) ps. This lower limit is sufficient to establish the conformation of the DODCI photoisomer. Comparison of the estimated rotational correlation time (>700 ps) with those calculated for the all-trans-isomer (770 ± 70 ps) and for the cis,cis-1,5-isomer (330 ± 30 ps) suggests that the DODCI photoisomer has the all-trans conformation. The photoisomerization of DODCI apparently involves a transition from the coiled cis,cis-1,5-conformation to the elongated all-trans conformation, requiring two cis → trans isomerizations of the poly-methine chain.

In conclusion, it must be pointed out that the photophysical properties of the DODCI photoisomer are not yet fully understood. For example, excitation of DODCI with a train of pulses at 527 nm, 590 nm [24] or 605 nm [1,2,24] results in fluorescence from both photoisomer and normal forms of DODCI in approximately equal proportions (within a factor of two). Yet the relative extinction coefficients of the two species [5] change by more than two orders of magnitude over this wavelength range, suggesting that the photoisomer may not be excited directly. In fact, from a study of the photoisomer fluorescence as a function of concentration, Rullière [25] concluded that radiative energy transfer does occur between DODCI normal form and the photoisomer and, that this is the predominant process for photoisomer excitation even at concentrations of \( 10^{-5} \) M or less. That is, photons emitted by the normal form of DODCI are absorbed by the photoisomer, which should lead to an apparent quenching of the DODCI fluorescence. Thus the kinetics for the fluorescence decay may well be more complex than the sum of two exponentials when exciting with a train of picosecond pulses. Until the photophysics of DODCI is more completely understood the assignment of the all-trans conformation to the photoisomer must be regarded as tentative.

5. Conclusion

The rotational correlation time for DODCI excited with a single laser pulse suggests that the molecular conformation is compact in both ethanol and isopropanol solutions. The cis,cis-1,5-isomer is an oblate rotor whose calculated rotational correlation time is in good agreement with the experimental value, and we suggest that the normal form of DODCI has this conformation. The photoisomer formed when exciting with a train of pulses rotates much more slowly and is tentatively assigned the prolate all-trans conformation. Solvent attachment does not affect the rotational diffusion of DODCI, in line with Chuang and Eisenthal’s results for rhodanine 6G [3] (also a monocation) but in contrast to results obtained for the fluorescein derivatives (dianions) where solvent attachment has been observed [1,2].

Using picosecond time dependent fluorescence depolarization we have been able to assign molecular conformations in fluid solution. Whereas previously no information was available about the photoisomerization process in DODCI or the exact nature of the photoisomer, we have been able to assign the conformations of both species and identify the photoisomerization process as involving two cis → trans isomerizations. Although our results are in qualitative agreement with the potential curves for DODCI photoisomerization proposed by Rullière [25], these potential curves must be revised to take into account the fact that photoisomerization of DODCI probably occurs by twisting of a pair of ethylenic bonds rather than twisting of a single ethylenic bond (as occurs in substituted ethylene derivatives such as stilbene).

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