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Photophysics of Thiacarbocyanine Dyes: Relaxation Dynamics in a Homologous Series of Thiacarbocyanines

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Fluorescence quantum yields and emission lifetimes have been measured at room temperature for a series of thiacarbocyanine dyes in various alcohol solvents. All radiationless deactivation events are accounted for by a process, e.g., torsional relaxation, whose rate is viscosity-dependent. The relaxation rate constant (k_η) and the exponent of viscosity dependence (α) in the Wirtz−Gierer analysis decrease with increasing polymethine chain length (n) in the dye series. Two dyes were further examined by time-resolved picosecond laser flash spectroscopy. Recovery of ground state in both cases is biphasic. In both cases, the short recovery time corresponds to the fluorescence lifetime. We infer that torsional relaxation of the vertical S_1 state is rate determining and does not cross between the S_1 and S_o potential surfaces in the relaxed S_1 conformation. The slower recovery process is identified with a pathway that leads to photoisomerization of the cyanine chromophores and implies involvement of a species intermediate between torsionally relaxed S_1 and the ground-state photoisomer. This intermediate is suggested to be an isomerized triplet state.

Introduction

In a preceding study in this series[1] we proposed that radiationless deactivation of the thiacarbocyanine cation involves intersystem crossing to an isomerized triplet excited state, together with internal conversion. Torsional motion of the polymethine chain is prerequisite to both processes, as illustrated schematically in Figure 1, based on the scheme proposed earlier by Ehrlich.[2] The central concept, namely degeneracy of the S_1 and T_1 states at the perpendicular minimum on the S_1 potential energy surface, was supported by the CS-INDO calculations of Momicchioli and co-workers.[3] The essential features of the Momicchioli model have been confirmed experimentally.[4] Some implications of the model are the following: (a) “vertical” intersystem crossing, i.e., from *trans*-S_1 to *trans*-T_1 dye should be very inefficient in competition with torsional relaxation on the S_1 surface; (b) *trans* → *cis* photoisomerization of dye does not involve the *trans*-T_1 state, owing to a large activation barrier; and (c) at least in part, the photoisomer should be formed in its T_1 state.

Prediction (a) has been confirmed independently by two groups.[5b,6] A recent study by Redmond and co-workers[7] has confirmed prediction (b), albeit for unsymmaterical cyanine dyes for which the potential surfaces may be quite different from those calculated by Momicchioli.[3] Our previous study[1] provided evidence of a metastable intermediate between the vertical S_1 state of the cyanine dyes studied and their ground-state photoisomers, which we interpreted in accord with prediction (c).

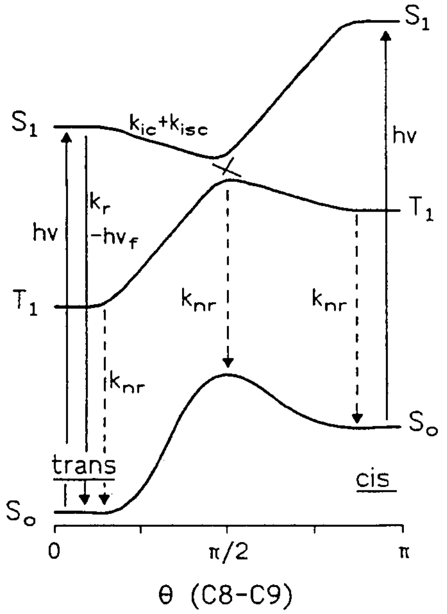

Figure 1. Schematic diagram of potential energy surfaces involved in radiative and nonradiative deactivation of a representative photoexcited cyanine dye (cf. ref 15, based on ref 3).

Even so, the idea of involvement of a spin unpaired intermediate in the photoisomerization of cyanine dyes remains controversial.[5,6] Most authors[5−9] assume a singlet pathway for *trans*−*cis* photoisomerization in cyanine dyes. According to the scheme of Figure 1, intersystem crossing should occur to a significant extent only from the torsionally relaxed singlet state, leading primarily to isomerized dye. Accordingly, intersystem crossing may be an important decay pathway for photoexcited cyanine dyes in solution, even though the measured[5b,6] vertical intersystem crossing quantum yields are low. Experiments designed to detect the excited species formed by triplet state sensitization of cyanine dyes[6] or to probe, for example, the effect of a heavy atom on the fluorescence quantum yields of these dyes,[5a,10] both of which address the efficiency of vertical intersystem crossing, do not provide a test of our proposal. Intersystem crossing should furthermore be inconsequential to, e.g., photographic applications, where the dyes function as photosensitizers in the adsorbed state. Adsorption restricts

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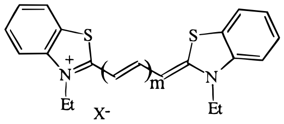
torsional relaxation[11,12] with a concomitant increase in the observable fluorescence quantum yields.

In the earlier paper,[1] assignment of the triplet intermediate was based on indirect evidence: namely the disappearance of the emissive, vertical singlet states of the dyes on a much faster time scale than appearance of either isomerized or unisomerized ground state. The utility of cyanine dyes in photodynamic therapies[12] which are generally thought to involve singlet oxygen production *in vivo*[13] provides additional support for the idea that spin unpaired intermediates may be involved in radiationless deactivation of photoexcited cyanine dyes. The experimentally determined quantum yield for singlet oxygen production from a representative cyanine dye is, however, quite low.[12] Singlet oxygen has however been implicated in the direct photooxidation of representative cyanine dyes.[14]

In another study,[15] the simplest member of the series, 3,3′-diethyl-2,2′-thiacyanine tosylate (dye **I**), showed no evidence of intersystem crossing under our conditions. Radiationless deactivation of this dye could be accounted for simply in terms of torsional relaxation to a funnel state on the singlet potential surface, followed by partitioning of this intermediate between the two possible ground state isomers. Even so, crossing from the excited singlet to ground state at this funnel appeared to be remarkably slow ($k_{nr} = \sim 2 \times 10^9$ s^{-1} in methanol) compared to the corresponding transition in other systems studied, e.g., stilbene.[16] Thus intersystem crossing, though not observed in this case, could, in principle, compete with radiationless decay to ground state. The 1,1′-diethyl-4,4′-cyanine cation behaves similarly.[17] Its relaxation has also been modeled computationally by the same authors and assigned to overdamped wave packet motion, though this interpretation does not seem consistent with the significant solvent effects usually observed in cyanine dye radiationless relaxation.[8]



Dye **I** m = 0 X = tosylate
Dye **II** m = 1 X = iodide
Dye **III** m = 2 X = iodide
Dye **IV** m = 3 X = iodide

The work reported in this paper was undertaken using the methodologies of both previous papers in this series:[1,15] (a) to explore whether the results previously reported[1] also extend to other members of the thiacarbocyanine series; and (b) to confirm through additional and convincing evidence the scheme embodied in Figure 1.

Experimental Section

For the present study we selected the homologous series of 3,3′-diethyl-2,2′-thiacarbo-cyanine iodides:

dye **II**: 3,3′-diethyl-2,2′-thiacarbocyanine iodide (H. W. Sands and Co.)

dye **III**: 3,3′-diethyl-2,2′-thiadicarbocyanine iodide (Eastman Kodak Co.)

dye **IV**: 3,3′-diethyl-2,2′-thiatricarbocyanine iodide (Pfalz and Bauer, Inc.)

The dye samples were used as received from the indicated vendors, and were pure to thin-layer chromatography. Absorption maxima and extinction coefficients derived from spectra recorded at 2.5 × 10^{-6} M concentration in a 1 cm cell were in good agreement with literature values and are given in Table 1. Spectroscopic grade solvents (EM Omnisolv^{R} methanol and ethanol, Aldrich "spectrophotometric grade" 1-propanol, and Aldrich "99+%" 1-pentanol) were used throughout; control experiments demonstrated that the solvents alone produced no fluorescence or light absorbing transients under the conditions of our experiments. Solutions prepared for steady-state emission spectroscopy were ca. 10^{-6} M in dye, and the concentration of solutions used for fluorescence lifetime and transient absorption studies was ca. 10^{-5} M. The dye solutions obeyed Beer's law over this concentration regime.

TABLE 1: Spectroscopic Characteristics of Dyes II−IV

dye	solvent	λ_{max}(nm)	ϵ (10^5 M^{-1} cm^{-1})	$\Delta\nu_{1/2}$ (fwhm) (cm^{-1})
II	CH_3OH	554	1.80	1128
	C_2H_5OH	556	1.80	1070
	C_3H_7OH	557	1.80	1050
	$C_5H_{11}OH$	558	1.80	1079
	avg		1.80	(1082 ± 29)
III	CH_3OH	654	2.25	945
	C_2H_5OH	657	2.25	936
	C_3H_7OH	659	2.40	930
	$C_5H_{11}OH$	662	2.25	900
	avg		(2.28 ± 0.07)	(928 ± 17)
IV	CH_3OH	754	2.50	985
	C_2H_5OH	759	2.40	1038
	C_3H_7OH	762	2.60	922
	$C_5H_{11}OH$	764	2.50	1040
	avg		(2.50 ± 0.07)	(996 ± 48)

Fluorescence emission and excitation spectra were recorded at room temperature (22 ± 1 °C) under ambient atmosphere on a Perkin-Elmer MPF44B spectrofluorimeter enhanced with a Hamamatsu R936 photomultiplier tube (in order to obtain spectral response to 930 nm) operating in the ratio mode. A "look up" table for correcting the spectra was created by the white card method. For estimation of fluorescence quantum yields, integrated, corrected emission spectra were compared to the integrated, corrected emission spectra of the calibration compounds, Coumarin 343 (Eastman Kodak Co.) and Nile Red (Aldrich), recorded in methanol and toluene, respectively, under conditions where the optical density of the calibration compound was the same as that of the test compound at the wavelength of excitation (adjusted to ca. 0.20 in the 1 cm quartz fluorimeter cell).

Fluorescence lifetimes were measured using a Hamamatsu streak camera[18] protected with a 450 nm cutoff filter. Dye solutions in a 2 mm quartz cuvette were excited by a frequency doubled (532 nm), passively mode-locked Nd:YAG laser generating ca. 30 ps (fwhm) pulses. Instrumentation and data analysis procedures for transient absorption spectroscopy have been described previously.[19] Each reported transient absorption spectra represents an average of at least eight individually determined spectra. As the absolute magnitudes of the light absorbing transients are extremely sensitive to focus and alignment of the pump and probe beams, all data points to be compared with one another, e.g., delay times for a kinetic analysis, were obtained in one session. For laser flash excitation the same Nd:YAG laser used for fluorescence lifetime measurements was used in the frequency-doubled mode (532 nm) with two-stage secondary amplification, focused to an 0.3 cm spot on the 2 mm sample cuvette. Pulse energies incident on the sample were adjusted by use of neutral density filters; an energy of (1.4 ± 0.3) mJ/pulse was used for the kinetic experiments. Dyes **II** and **III** were studied in this manner at 1 × 10^{-5} and 3 × 10^{-5} M concentration, respectively, so as to provide equivalent absorbances at 532 nm (ca. 0.10 in the 2 mm cell).

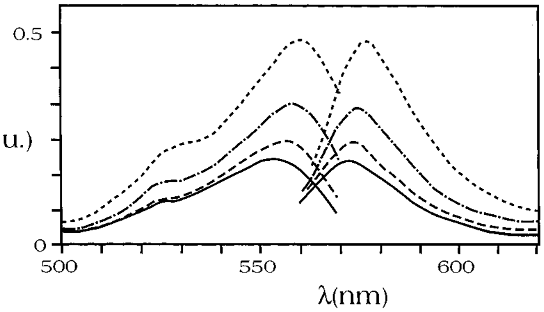


Figure 2. Fluorescence excitation (left) and emission (right) spectra for dye **II** in (top to bottom) 1-pentanol, 1-propanol, ethanol, and methanol.

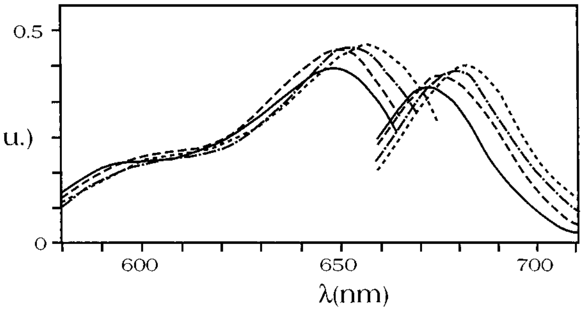


Figure 3. Fluorescence excitation (left) and emission (right) spectra for dye **III** in (top to bottom) 1-pentanol, 1-propanol, ethanol, and methanol.

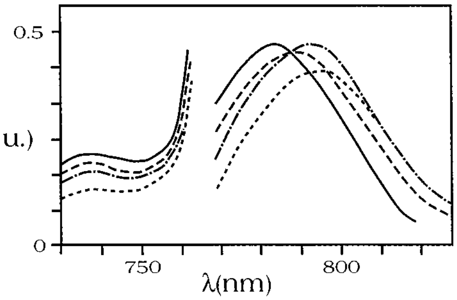


Figure 4. Fluorescence excitation (left) and emission (right) spectra for dye **IV** in (top to bottom) 1-pentanol, 1-propanol, ethanol, and methanol.

Results and Discussion

Fluorescence Quantum Yields and Lifetimes. The emission (excited at λ_{max} of the absorption spectrum) and excitation (monitored at λ_{max} of the emission spectrum) spectra for dyes **II**, **III** and **IV** are shown in Figures 2−4, respectively. Fluorescence quantum yields, Φ_f, natural radiative lifetimes, τ_{nat}, estimated from the data of Table 1 by the method of Strickler and Berg,[20] and estimated fluorescence lifetimes (as $\tau_f = \Phi_f \tau_{nat}$) are given in Table 2. Lifetimes obtained as single-exponential fits with residual variation, $(1 - r^2) \leq 0.014$, to streak camera decay traces recorded for methanol and pentanol solutions of dyes **II** − **IV** are also summarized in Table 2. No evidence of biexponential decay previously[6] reported for dye **II** was found in the data obtained on our samples. Agreement between the two estimates of τ_f is within experimental error (±10%).

Our earlier measurements[15] of fluorescence quantum yields and lifetimes for dye **I** are also in reasonable agreement with the quantum yields[6,8,9a,11] and lifetimes[6,9a,11] reported in the literature. By contrast, our values of Φ_f for dye **III** differ by about a factor of 2 from the literature values;[8,11] our τ_f estimates are correspondingly smaller. Quenching by trace impurities is unlikely for emissive states of subnanosecond duration, so that the discrepancies cannot be attributed to this source. Note, however, that the values of Φ_f and τ_f reported by Fassler and Baezold[11] are for the cation of dye **III** with chloride as the counterion. In this regard, it is worth noting that Tatikolov and co-workers[21a] reported accelerated nonradiative decay of S_1 for a series of benzimidazolocyanine dyes when the counterion is iodide, vis-a-vis chloride or perchlorate. To our knowledge, fluorescence quantum yield and lifetime data do not appear to have been published previously for dye **IV**, though a lifetime of 1.2 ns has been reported for the analogous hexamethylindotricarbocyanine cation.[21b]

TABLE 2: Fluorescence Quantum Yields for Dyes II−IV

dye	solvent	τ_{nat} (ns)	Φ_f	$\tau_f{}^a$ (ns)	$\tau_f{}^b$ (ns)	$\tau_f{}^c$ (ns)
II	CH_3OH	3.15	0.046	0.145	0.12	0.16 (11) 0.10 (8)
	C_2H_5OH	3.15	0.055	0.173		0.28 (7) 0.15 (8)
	C_3H_7OH	3.15	0.075	0.24		
	$C_5H_{11}OH$	3.15	0.10	0.32	(0.32 ± 0.03)	0.35 (8)
III	CH_3OH	4.3	0.15	0.64	(0.58 ± 0.08)	1.2 (11) 1.07 (8)
	C_2H_5OH	4.3	0.17	0.73		1.45 (8)
	C_3H_7OH	4.3	0.20	0.86		
	$C_5H_{11}OH$	4.3	0.23	1.00	(1.23 ± 0.07)	1.87 (8)
IV	CH_3OH	5.8	0.21	1.22	(1.62 ± 0.15)	
	C_2H_5OH	5.8	0.22	1.28		
	C_3H_7OH	5.8	0.24	1.39		
	$C_5H_{11}OH$	5.8	0.26	1.51	1.45	

[a] Estimated as $\tau_f = \Phi_f \tau_{nat}$. [b] Single-exponential fit to streak camera data. [c] Literature values; references indicated in parentheses. Values of τ_f attributed to ref 8 are calculated from values of τ_{nat} and Φ_f at 25° reported therein.

The solvents chosen for the fluorescence quantum yield and lifetime measurements represent a series in which viscosity approximately doubles with each increment. Given the expectation that competing nonradiative processes should involve torsional relaxation of the cyanine chromophores, we analyzed the data for fluorescence quantum efficiency according to the model of Gierer and Wirtz[22] (as formulated by Vogel and Rettig[23]) whereby

$$\Phi_f{}^{-1} = 1 + (k_o \tau_{nat}) + (k_\eta \tau_{nat}) \eta^{-\alpha} \qquad (1)$$

where k_o is the rate constant for the viscosity-independent pathway for radiationless deactivation, k_η is the rate constant for the viscosity-dependent torsional relaxation pathway, and α is an empirical measure of the contribution of Stokes diffusion of the rotating molecular fragment relative to that of diffusion of the dye molecule into free volume where there is no frictional barrier to isomerization.

The data of Table 2 could be fitted to eq 1 with correlation coefficients r ≥ 0.995, and in all cases with $k_o = 0$; that is, with no viscosity-independent contribution to radiationless deactivation. In this result, as also noted by Aramendía and co-workers,[8] we differ from analyses published for dimethylindocarbocyanine dyes[24] wherein finite values of k_o are inferred. The latter authors associate the nonzero k_o values with processes involving energy acceptance by stretching modes of the polymethine chain. Parameters for our fits are presented in Table 3. An estimate of α = 0.65 was reported for S_1 relaxation of dye **II** in a series of nitrile solvents.[25] It is relevant to note that a significantly lower value of this parameter would be expected in an alcohol solvent series, owing to the different average values for the infinite frequency shear modulus in these solvents.[24,25] To the extent that dyes **II**−**IV** are all likely to exist in solution in the all-trans isomer form,[2,26,27] for purposes of comparison we have included in Table 3 the data obtained from a similar

TABLE 3: Solvent Viscosity Dependence of Nonradiative Deactivation in Thiacyanine Dye Cations

dye	n^a	$k_\eta\tau_{\text{nat}}$	α	k_η (s^{-1})	r
I^b	1	232	0.67	1.6×10^{11}	0.999
II	3	17.7	0.39	5.6×10^9	0.995
III	5	5.8	0.21	1.35×10^9	0.999
IV	7	4.5	0.11	0.78×10^9	0.995

[a] Number of carbon atoms in the polymethine chain. [b] Data for *syn*-3,3′-diethyl-2,2′-thiacayanine tosylate (dye **I**)[15] are included for comparison; other data from this work.

analysis of the fluorescence behavior of dye **I** in its corresponding *syn*-conformation.[15]

It is immediately apparent from the data of Table 3 that both the rate of the viscosity-dependent relaxation process, defined by k_η, and the relative contribution of the Stokes diffusion thereto, measured by the parameter α, decrease monotonically with increasing polymethine chain length (n) in this series of dyes. Both of these inferences are consistent with chemical intuition. Note that ln k_η scales approximately with $1/n$ ($r = 0.989$). From the point of view of the ven der Zwan–Hynes theory,[28] as applied to the photoisomerization of the Merocyanine 540 dye by the Quitevis and Robinson groups,[29] these trends correspond to a transition from strong solvent coupling (polarization caging) to weak solvent coupling (nonadiabatic solvation) of the relaxation with increasing chain length (n) in our series. Dye **II**, for which $\alpha = 0.39$, must fall close to the critical point in the van der Zwan–Hynes model, from which we expect[29] that $\alpha = 0.33$. This effect corresponds to increasing participation of modes of the polymethine chain which do not involve dipole–dipole coupling to solvent with increasing n. Thus, for dyes possessing a longer chain length ($n = 5,7...$) the picture of S_1 relaxation as simple twisting about one C–C bond (with concomitant change in the dihedral angle between the aromatic nuclei of the dye by ca. $\pi/2$ as shown in Figure 1) becomes an oversimplification.[10b]

Time-Resolved Spectroscopy. Transient absorption spectra recorded after ps-laser excitation of dyes **II** and **III** at 532 nm were recorded in methanol and in 1-pentanol. Representative spectra are shown in Figures 5 and 6. The salient feature in these spectra of both dyes is the bleaching and recovery of the dye ground state, where the magnitude of the bleaching signal recorded at various delay times t is $-\Delta A(t)$. Both ground-state bleaching and formation of light absorbing transients occurred outside the probe window of our instrumentation for dye **IV**. Attempted analyses of ground-state recovery at $\lambda_{\max}$ of the absorption spectrum as a first-order kinetic process led, in all cases, to bifurcated plots suggestive of a biexponential process. Accordingly, the recovery data was analyzed by eq 2:

$$-\Delta A(t) = -\Delta A_{\text{o}}[\Phi_1 \exp(-t/\tau_1) + \Phi_2 \exp(-t/\tau_2)] \quad (2)$$

Fits of the experimental data to eq 2 (including $-\Delta A(t)$ values derived from spectra recorded at delay times not represented in Figures 5 and 6) are shown in Figure 7. The second time constant for recovery, τ_2, could not be estimated in our experiments, as this process occurs on too long a time scale (>10 ns). We accordingly used $\tau_2 = \infty$ in these fits. Values for τ_1, Φ_1, and Φ_2 are given in Table 4.

The fast stage of the recovery of ground-state absorption occurs with a time constant, τ_1, and in all cases is comparable to the measured fluorescence lifetimes, τ_f. The coefficient Φ_1 corresponds to the quantum yield for deactivation of S_1 by a pathway (including but not limited to fluorescence) leading to fast ground-state recovery. Accordingly, the slow process accounts for a fraction of the total excitation energy dissipation given by Φ_2. To a first approximation, values of Φ_1 and Φ_2 appear to be independent of either the polymethine chain length or the nature of the solvent. They are also in reasonable agreement with the corresponding parameters for the thiacarbocyanine dyes examined previously, albeit in methylene

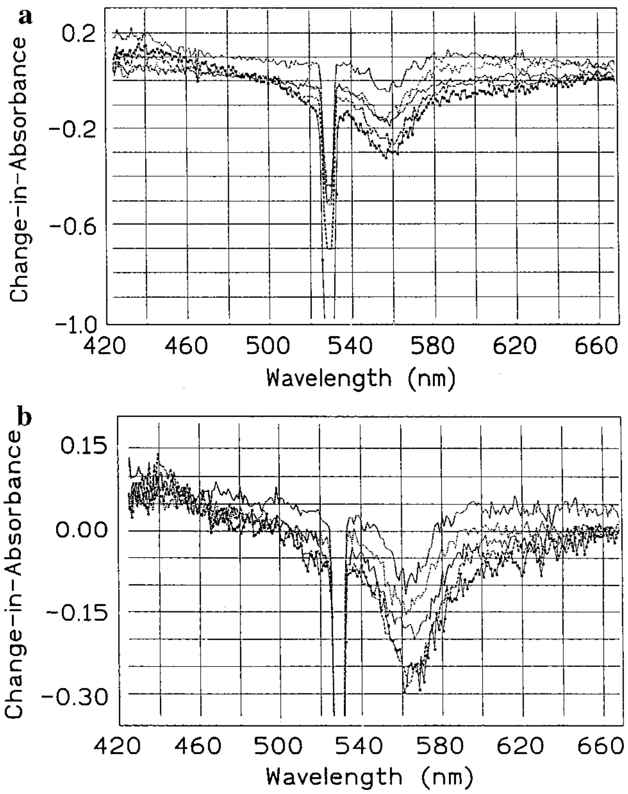


Figure 5. Transient absorption spectra recorded following 30 ps laser flash excitation of dye **II** at 532 nm. Delay times are (top to bottom) 1 ns, 500, 200, 100 and 50 ps in methanol (a) and 1-pentanol (b).

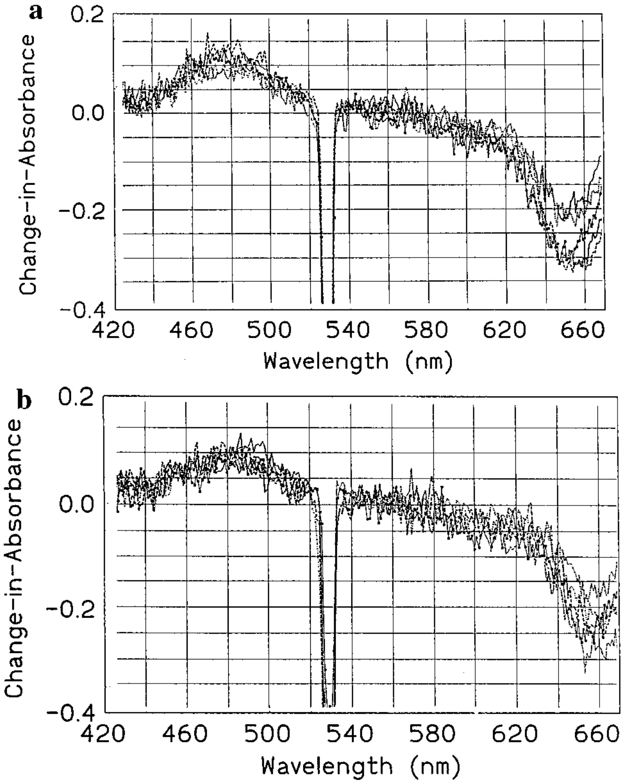


Figure 6. Transient absorption spectra recorded following 30 ps laser flash excitation of dye **III** at 532 nm. Delay times are (top to bottom) 1 ns, 500, 200, 100 and 50 ps in methanol (a) and 1-pentanol (b).

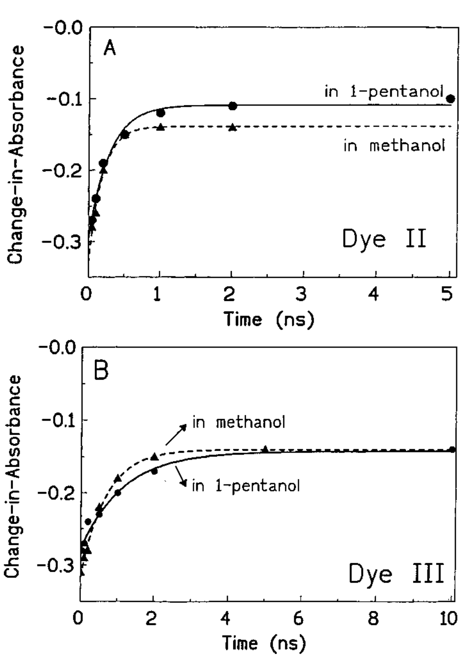


Figure 7. Fit of the data to eq 2 for the ground-state recovery of the thiacarbocyanine dyes in methanol (▲) and 1-pentanol (●), using parameters from Table 4. Absorbance change, $-\Delta A$, at room temperature following 30 ps pulsed laser excitation at 532 nm: (A) dye **II** at 556 nm; (B) dye **III** at 658 nm.

TABLE 4: Parameters for Ground-State Recovery in Dyes II and III

dye	solvent	τ_1 (ns)	Φ_1	Φ_2
II	CH_3OH	(0.19 ± 0.03)	(0.58 ± 0.04)	(0.42 ± 0.04)
	$C_5H_{11}OH$	(0.37 ± 0.05)	(0.63 ± 0.04)	(0.37 ± 0.04)
III	CH_3OH	(0.68 ± 0.06)	(0.56 ± 0.02)	(0.44 ± 0.02)
	$C_5H_{11}OH$	(1.19 ± 0.09)	(0.52 ± 0.04)	(0.48 ± 0.04)
avg			(0.57 ± 0.04)	(0.43 ± 0.04)

chloride solution.[1] We therefore expect dye **IV** to exhibit a similar behavior.

Estimates of Φ_1 are consistently larger than the measured values of Φ_f (Table 2). Hence, the process must also include a component of radiationless decay. It follows that insofar as torsional relaxation limits the lifetime of the emissive excited state, this process must also be rate determining in fast, radiationless ground-state recovery; that is, the rate constant, k_{nr}, for the $S_1 \rightarrow S_0$ potential crossing at the funnel must in all cases be fast compared to $1/\tau_1$. For the case of a simple hemicyanine dye, which fluoresces from its torsionally relaxed state, Fromherz and co-workers[30] measured nonradiative decay, that is, crossing from the S_1 to the S_0 potential surface, in butanol solvent: k_{nr} = ca. 7×10^9 s^{-1} in reasonable agreement with our estimate of 2×10^9 s^{-1} for dye **I** in methanol.[15] The goal of measuring it directly for the compounds of present interest, however, remains elusive.

Trans−*cis* (E→Z) isomerization has long been recognized as a major pathway for deactivation of photoexcited cyanine dyes,[2,27,31] although we now recognize this to be an oversimplification for the dyes possessing longer polymethine chains (see above).[10b] More than one photoisomerization pathway may also be available to the longer-chain homologs, e.g., di- and tricarbocyanines, where isomerization about different double bonds may compete for dissipation of the excitation energy.[32] Under our conditions, isomerization must be accounted for within Φ_2. Quantum yields have been reported for formation of mono-*cis*-**II** ($\Phi_{iso} = 0.25$)[4,5b] and **III** ($\Phi_{iso} \leq 0.50$).[33] Laser flash photolysis of dye **III** on the nanosecond time scale does not lead to detectable isomer formation, however, although persistent bleaching of the ground-state remains observable.[33] A time scale of up to microseconds is usually required for observation of isomer absorption in pump−probe experiments.[8a,33] Dempster[34] has estimated the first-order rate constant for the appearance of the mono-*cis* isomer of the oxa-analogue of dye **III** from its vertical S_1 state as $k_{iso} = 1 \times 10^7$ s^{-1}. If the isomerization pathway involves crossing from S_1 to S_0 in the perpendicular conformation, followed by partitioning between the all-trans (i.e., unisomerized) and mono-*cis* ground states, k_{iso} would correspond to $1/\tau_1$, ca. 10^9 s^{-1} for dye **III**. Taken together, these observations require an intermediate on the isomerization pathway between the torsionally relaxed S_1 state and the ground-state mono-*cis* isomer. (Note that small amounts of the photoisomer formed directly from the relaxed S_1 state without the intervention of this intermediate would probably not be detectable under our conditions. The absorption spectra for mono-*cis*-**II** and **III** are essentially coincident with the absorption spectra of their unisomerized all-*trans* isomers[9a,33]).

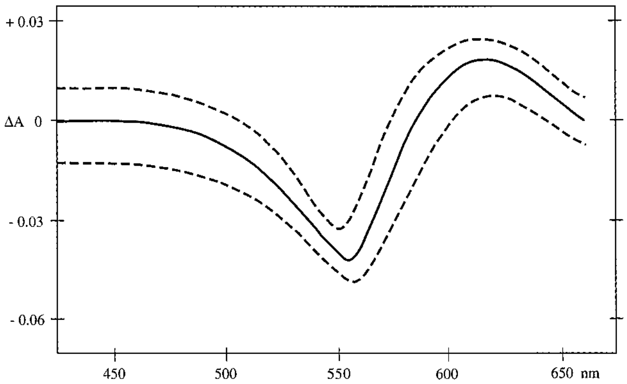


Figure 8. Smoothed transient absorption spectrum recorded 5 ns after laser excitation of dye **II** at 532 nm (3.0 mJ/pulse). Dashed lines indicate envelopes of ±1 standard deviations for the population of individual spectral determinations averaged to obtain the solid line. Absorption centered on 620 nm is assigned as the triplet of *cis*-**II** on the basis of ref 35.

We propose that the intermediate in the photoisomerization process lies on the T_1 potential surface, and is formed by rapid intersystem crossing at the funnel, where the S_1 and T_1 states become degenerate[2,3] as shown in Figure 1. Intersystem crossing is accordingly followed by barrierless[3] torsional relaxation. The *cis*-photoisomer accordingly forms, at least in part, in its T_1 state. In support of this inference we show an expanded view of the smoothed transient absorption spectrum of dye **II**, recorded 5 ns after laser excitation at 532 nm with 3 mJ/pulse, in Figure 8. An absorption centered on 620 nm is readily apparent, consistent with the observation by Chibisov et al.[35] of a T_1−T_n band centered on 640 nm for *cis*-**II**.

Quenching of isomeric T_1 by dissolved oxygen should occur in ca. 0.1 μs, if we assume that $[O_2] = \sim 10^{-3}$ M and that the reaction is diffusion-limited. This estimate is consistent with the reported appearance of the photoisomer on the time scale of up to microseconds[9a,33] and with the measured rate of formation of the photoisomer in the oxa-analogue of dye **III**.[29] Formation of a spin-unpaired species which is oxygen quenched is consistent with the implied intermediacy of singlet oxygen in the direct photooxidation of cyanine dyes.[14]

High quantum yields of isomerization should accordingly correlate with high quantum yields for intersystem crossing, but the quantum yield for intersystem crossing of dye **II** has been estimated variously[5b,6] as 0.001−0.004. These estimates, however, refer to intersystem crossing without isomerization, i.e., formation of *trans*-T_1 from *trans*-S_1, whereas our proposal posits formation of *cis*-T_1 in concerted fashion from *trans*-S_1,

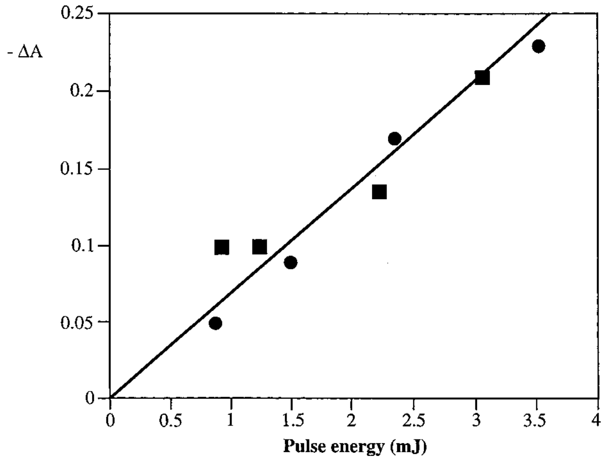


Figure 9. Linear dependence of initial bleaching of ground state **II** (squares) and **III** (circles), measured at λ_{max} 50 ps after laser excitation, on laser pulse energy.

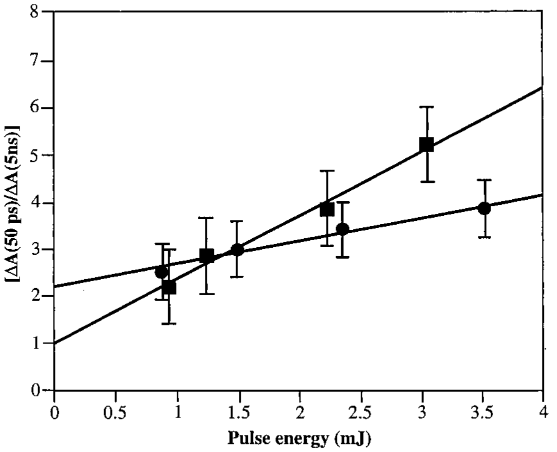


Figure 10. Photoquenching of persistent ground-state bleaching for dyes **II** (squares) and **III** (circles), shown as dependence of [Δ*A*(50 ps)/Δ*A*(5 ns)] on laser pulse energy.

and, presumably,[1] vice versa. The low quantum yields previously reported for vertical intersystem crossing in dye **II** are, in our opinion, not only valid estimates, but to be expected from the potential energy surface diagram developed by Momicchioli and co-workers.[3]

Multiphoton Effects. Redmond and co-workers[7] recently published results indicating unusually facile back intersystem crossing between higher excited states of some cyanine dyes. Efficient intersystem crossing from biphotonically excited coumarin laser dyes has also been reported.[36] These results suggested to us that multiphoton excitation to higher excited states might be involved in the generation of the state responsible for persistent bleaching of the absorption of dyes **II** and **III** under conditions of laser excitation. Accordingly we undertook to study the pump−probe response of dyes **II** and **III** under conditions of varying pump energy. The initially observed, i.e., 50 ps after excitation, bleaching at λ_{max} for both dyes, ΔA(50 ps), was found to vary linearly with laser pulse energy, as shown in Figure 9. The depedendence of the absolute magnitude of the persistent bleaching, still observable 5 ns after excitation, Δ*A*(5 ns), on laser power was less straightforward. When, however, Δ*A*(5 ns) was expressed in a normalized, reciprocal fashion, as [Δ*A*(50 ps)/Δ*A*(5 ns)], shown for both dyes in Figure 10, it can be seen that the yield of persistent bleaching actually decreases with increasing laser pulse energy. The linear relationships exhibited by both sets of data in this Figure are characteristic of photoquenching[37] of the process responsible for formation of the metastable species. That the photoquenching slopes for the two dyes are significantly different is unsurprising, insofar as biphotonic excitation requires resonance between $2h\nu$ and the energy of transition to a higher excited state. Thus biphotonic excitation to higher excited states in the singlet manifold of both dyes leads directly to ground state by emissive and radiationless pathways, without intervention of intersystem crossing, consistent with the results of the Redmond group.[7]

Conclusions

We have measured quantum yields and lifetimes of fluorescence at room temperature of thiacarbocyanine dyes in a series of alcohol solvents, and found that we can account for all radiationless deactivation by a process whose rate is viscosity-dependent, i.e, torsional relaxation. The relaxation rate constant, k_η, and the exponent, α, of the viscosity dependence in the Wirtz−Gierer analysis,[22] decrease with increasing polymethine chain length, *n*, in the dye series.

Dyes **II** and **III** have also been examined by time-resolved picosecond laser flash spectroscopy. Recovery of ground state is biphasic; the short recovery time corresponds to the fluorescence lifetime. We infer that torsional relaxation of the vertical S_1 state, not crossing between the S_1 and S_o potential surfaces in the relaxed S_1 conformation, is rate-determining in both cases. The opposite was found in a previous study of dye **I**.[15] We believe that the difference between dye **I** and dyes **II** and **III** in this regard reflects the much faster rate of torsional relaxation (k_η) in dye **I**.

The slower recovery process is identified with a pathway involving the well-known photoisomerization of the cyanine chromophores and infers involvement of an intermediate species between the torsionally relaxed S_1 state of the dye and the ground-state photoisomer. We propose that this intermediate is an isomerized triplet state, consistent (a) with our earlier observations on analogues of dye **II**,[1] and (b) with the degeneracy of S_1 and T_1 potential surfaces at the global minimum on the S_1 potential surface corresponding to the perpendicular conformation of the chromophore[2,3] (Figure 1). An intermediate assignable[35] as the triplet of *cis*-**II** has been observed under our conditions. Formation of this species for both dyes is subject to photoquenching.

The present results and our proposed interpretation are consistent with our previous observations on analogues of dye **II**.[1] On the other hand, no evidence of intersystem crossing at the funnel was observed in the case of the 3,3′-diethyl-2,2′-cyanine dye,[15] perhaps because the rate of torsional relaxation in this dye ($k_\eta = {\sim}10^{11}\ s^{-1}$) is too rapid. Given this interpretation, the rate of intersystem crossing at the point of S_1-T_1 degeneracy. i.e., in the twisted conformation, in these chromophores must be of the order of about $10^{10}\ s^{-1}$ (a reasonable estimate), comparable to k_{nr}.

Since our interpretation of these results is dependent on the model of Momicchioli and co-workers[3] it would be desirable to see their quantum chemical strategy extended to a study of the potential surfaces for relaxation of cyanine dyes of longer chain length. Thereby the chain length dependence of the principal features of the potential surfaces which these authors have proposed could be established.

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