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Photophysical Properties of Ground-State Twisted Bicoumarins[†]

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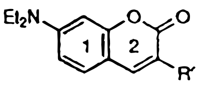
Photophysical properties of two selectively substituted bicoumarins bridged by a flexible single covalent bond have been investigated in solvents of varying polarity. The results show that the *second* coumarin moiety acts merely as a substituent to the *parent* coumarin—which is still the main chromophore—and has a minimal influence on the overall photophysical properties of the molecule. The solvent dependent spectral shifts are indicative of an intramolecular charge transfer nature of the lowest excited state of both the dyes. The sustenance of fluorescence of dye II—where the there are no additional electron-withdrawing substituents attached to the aminocoumarin nucleus, while the quenching of fluorescence along with a decrease in lifetime of dye I, − which has an additional electron-withdrawing cyano group in the 4-position of the *parent* coumarin—in highly polar solvents is explained in terms of the well-accepted ICT−TICT hypothesis.

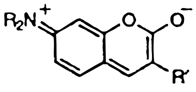
Introduction

The decrease in the fluorescence efficiency and lifetime of bichromophoric systems—comprised of donor and acceptor substituents—in highly polar solvents, has generally come to be accepted as due to charge transfer between the donor and acceptor moieties coupled with an internal twist (rotational relaxation) in the excited state leading to a nonplanar twisted conformation with a large dipolar character. On account of this large induced excited-state dipole moment, strong solute−solvent interactions have an efficient influence on this state: a polar solvent stabilizing the highly polar twisted conformation. Further, since the process involves a rotational relaxation of the bond linking the donor−acceptor pair, solvent viscosity would also affect the probability of formation of this state: a highly viscous solvent inducing a "viscosity drag" and hence retarding the relaxation to the twisted conformation. First observed by Lippert[1] as "anomalous" (dual) fluorescence in p-(*N*,*N*-dimethylamino)benzonitrile, it was later explained as due to the formation of an excited state with a large charge transfer nature with an almost perpendicular arrangement (twist) around a single bond and subsequently named the twisted intramolecular charge transfer (TICT) state by Grabowski *et al.*[2] This concept has, despite many challanges,[3−5] provided a satisfactory model for many experimental results on the photophysics of bichromophoric systems.[6−9]

The list of substances postulated to follow the TICT mechanism is steadily increasing. Among the most widely investigated class of compounds are the 7-aminocoumarins due to their wide importance as laser dyes[10] in the blue-green region, as probes for the study of solvent relaxations using ultrafast techniques,[11,12] and, more recently, as efficient nonlinear optical chromophores.[13] Simple 7-aminocoumarins are polar in the ground state, and electronic excitation is found to result in an excited species with a dipole moment that is approximately 2 times higher than the corresponding value in the ground state.[14] The existing knowledge of the TICT process in aminocoumarins is as follows:[6,15−17] the ground state of a typical aminocoumarin molecule is adquately described by the structure **A** (see below). Electronic excitation results initially in a locally excited (LE) state with a greater dipole moment than that in the ground state due to a partial charge transfer. This state is called the intramolecular charge transfer (ICT) state and is best described by structure **B** (R = Et$_2$). With increase in solvent polarity, the ICT states are sufficiently solvated, which decreases the energy gap between the lowest excited singlet state and the ground state, leading to a red shift in the fluorescence emission. In the presence of highly polar solvent molecules the planar polar molecule undergoes a further relaxation (a twist), which makes the donor lone pair orbital perpendicular to the acceptor π-orbital system. This leads to full charge separation and consequently to a large dipole moment and a high solvent reorientation energy,[18] resulting in the formation of the TICT state (structure **C**). The TICT state is thus more polar than the ICT state. Additional electron-withdrawing substituents (especially in the 3- and 4-positions: R′ for example) further enhance charge separation, which markedly accelerates the population of the TICT state. The magnitude of the change in dipole moment upon excitation or the sensitivity of the shift to the polarity of solvent is an indication of the charge transfer nature of the transition.

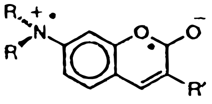


A



ICT

B



TICT

C

Despite its wide acceptance, detection of emission from the TICT states in aminocoumarins and in many other bichromophoric molecules has not yet been possible. There has been an instance when dual amplified spontaneous emission (ASE) has been reported for Coumarin 1 (C1)[19] and Coumarin 120 (C120)[20] in polar solvents, but this was later disproved.[21] Theoretical calculations on bichromophoric molecules show[7] that the π-system of the donor and acceptor are decoupled from each other at the twisted conformation, which makes the radiative relaxation from the TICT-state overlap forbidden. This induces difficulties in the detection of fluorescence from this state. In most cases, indirect methods need to be employed to characterize the formation of this state and to explain the photophysical properties observed thereafter.

Since TICT states can act as intramolecular fluorescence quenchers, formation of such states is unhealthy for efficiently fluorescing systems, such as laser dyes. On the basis of the current knowledge of photophysics of TICT states, several

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[†] Dedicated to my father on his 75th birthday.

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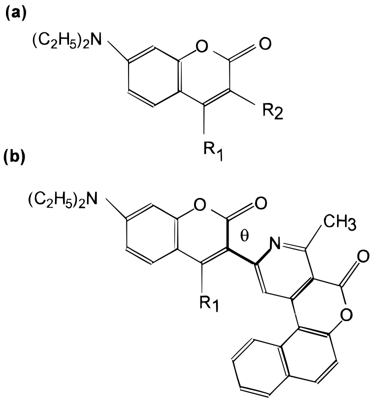
SCHEME 1



	DYE	R_1	R_2
(a)	C 1	CH_3	H
	C 35	CF_3	H
(b)	DYE I	CN	-
	DYE II	H	-

synthetic mechanisms have been proposed by which the population of these states can be restricted/controlled. These include (a) inhibition of the rotation of the bond around the amine group by rigidizing the substitution;[6,22] and (b) reducing the strength of either or both donor and acceptor substituents, leaving the system flexible.[6] This results in the lowering of the LE/ICT state compared to the TICT state. Thus 7-(diethylamino)-4-methylcoumarin has been found to show sustained fluorescence even in polar solvents, while the fluorescence of 7-(diethylamino)-4-(trifluoromethyl)coumarin has been found to undergo quenching in the same media.[6,18,22] Similarly 7-primary aminocoumarins have been shown to be fluorescing in the solvent media where 7-dialkyl aminocoumarins showed considerable quenching.[16] An extension of this method has been to compromise the "push−pull" pattern by increasing the π-conjugation of the delocalizing substituent.[16,23] However this has been found to be not always true.[24] Recently van Gompel and Shuster[25] have reported formation of a nonemissive TICT state in an aminocoumarin molecule having a rigid amino substitution at the 7-position and an ester at the 3-position. They attributed this to the rotation around the bond connecting the carbonyl groups. In a recent study on substituted aminocoumarins, Rechthaler and Köhler[26] have shown that population of TICT state is more plausible when a strong electron-withdrawing substituent is also present at the 4-position. In another study[18] of the solvent and substitution effects on several aminocoumarins, it has been shown that the role of solvent is more to stabilize the twisted state rather than to form it.

In this communication, the substitution and solvent effects on the photophysical properties of two new bicoumarins (coumarinylbenzopyranopyridine derivatives) are presented. The specialty of these compounds is that (a) both are bridged coumarins with a single covalent bond binding the two coumarin derivatives. They are denoted—strictly for the sake of simplicity of explanation—as follows: the coumarin nucleus having a diethylamino substitution as the *parent* coumarin and the phenyl-substituted coumarin as *second* coumarin. (b) The *second* coumarin molecule is highly rigidized due to additional substitutions (Scheme 1). (c) The main difference between the two dyes is the presence of an electron-withdrawing cyano group substituent in the 4-position of the *parent* coumarin nucleus in dye I and its absence in dye II. (d) Twist around the single covalent bond between the two coumarins is expected to provide an additional channel for the formation of the TICT state before the molecules fluoresce. This is analogous to the observations made earlier in triphenylmethane,[27] rhodamines, and other xanthene dyes.[6,28,29] The choice of solvents is such that the hydrogen-bonding effect, if any, in addition to the effect of polarity, could also be investigated. Such a study can, in principle, also explain how essentially changing the electron affinity of the acceptor moieties can influence molecular rearrangement of the molecule, after it has undergone an electronic excitation, leading to the formation of the TICT states. Since the donor moiety in the present case is held constant, it is possible to rationalize the energy of the TICT state (E_{TICT}) in these two dyes using the equation[6,30]

$$E_{\mathrm{TICT}} \sim \mathrm{IP_D} + \mathrm{EA_A} - C - E_{\mathrm{solv}} \tag{1}$$

where $\mathrm{IP_D}$ is the ionization potential of the donor (diethylamino in the present study), $\mathrm{EA_A}$ is the electron affinity of the acceptor, C is the negative Coulomb energy stabilizing the TICT state, and E_{solv} is the energy change through solvation of radical ions and of the strong TICT-state dipole. In the event of the donor moiety being the same, the probability of the formation of the TICT state is then influenced more by the strength of the acceptor group(s) present in the molecule and the polarity of the solvent medium surrounding the dye molecules.

In the present study, the substitution of the *second* coumarin induces (see below) steric hindrance and makes it out of plane with respect to the *parent* coumarin even in the ground state. The excited-state properties of such a molecule will make an interesting study in terms of the involvement of a possible twist, in the excited state, around the bond connecting the two nonplanar rings. It will be shown below that the photophysics of the two dyes obey, in principle, eq 1; however the differences in the behaviors of the two dyes (especially in regard to the formation of the TICT state) have a minimal influence on the *second* coumarin.

Materials and Methods

The two dyes (Scheme 1) have been synthesized[31] and supplied in pure form by Pal and Seshadri. The solvents used were all of spectroscopy grade (Merck or Aldrich) and used as received. Rhodamine B (Merck) in ethanol was used as fluorescent standard for determining the fluorescence quantum efficiency of the two dyes. The purity of the dyes has been confirmed by thin layer chromatography. Absorption spectra of the dyes have been recorded on a Beckman DU 70 dual-beam UV−visible absorption spectrophotometer. Steady-state fluorescence spectra were recorded in highly diluted solutions (optical density at excitation wavelengths ~0.2) using right angle geometry on a Spex Fluorolog 112 spectrofluorimeter, equipped with Glan-Thompson polarizers and a cooled Hamamatsu R928 photomultiplier tube. Excitation was vertically polarized while the emission was measured at the magic angle. The bandwidth of the excitation and emission slits (2 on each side) was 3.7 and 1.6 nm, respectively. Fluorescence spectra were corrected for the nonlinearities in the response of the photomultiplier tube, monochromator, and refractive index of the solvent. Fluorescence quantum efficiency (Φ_f) was determined from the corrected fluorescence spectra using Rhodamine B in ethanol as a standard.[32] The estimated error for Φ_f is ±5%. Fluorescence lieftimes were measured in selected solvents (see below) with a PRA 3000 series nanosecond fluorescence spectrometer using the time-correlated single photon counting method. A

TABLE 1: Results of Semiempirical Calculations Using the SPARTAN Program[a]

dye	ΔH_f (kcal/mol)	μ_g (D)	θ (deg)
dye I	+21.6	8.85	−40.5
dye II	−13.54	10.2	49.0

[a] ΔH_f = heat of formation, μ_g = dipole moment of the dye in the ground state, θ = the dihedral angle between the two nonplanar coumarin moieties (see Scheme 1).

deuterium-filled flash-lamp was used as an excitation source. The excitation wavelength, corresponding to the S_0-S_1 transition, was selected by interference filters (Omega/Saven AB, Sweden) (bandwidth 6 nm). Fluorescence emission was observed above 550 nm through a long pass filter (Schott, Germany) and a Lee filter (HT) 008 Dark Salmon (in cases where the emission maximum was beyond 600 nm). Magic angle polarization was used for all fluorescence decay measurements. Further details are given elsewhere.[33] Analysis of the fluorescence decay measurements was carried out using Spectra software (S. Savikhin Software) to determine the excited-state lifetimes. The goodness of the fit was judged from the reduced chi-squared value and plots of the residuals. The response of the instrument and accuracy of data analysis were confirmed by determining the lifetime of standard samples (Rhodamine 101 in ethanol and Coumarin 515 (Exciton) in acetonitrile) prior to making the final measurements.

Theoretical Calculations

Austin Model 1 (AM1) semiempirical quantum mechanical calculations were performed using the Spartan 4.0 program.[34] Geometry of the dye molecule in the ground state was optimized prior to performing the calculations. The dipole moment of the molecules in the ground state was determined for the geometrically optimized conformation that gave a low heat of formation. The results of the semiempirical calculations are tabulated in Table 1. More reliable results were obtained for the ground state, and the excited-state calculations were found to be failing before nearing completion.

Results

Absorption and Fluorescence Spectra. The absorption and fluorescence spectra of the dyes show a regular bathochromic shift with increase in the polarity of the solvent. Representative spectra of the dyes, each in three solvents, are shown in Figures 1 and 2. The details in other solvents are tabulated in Table 2. Spectral changes in the absorption spectra are, however, found to be generally small and do not correlate with any specific solvent polarity (π^*) or hydrogen-bonding (α) parameter. Larger changes in the fluorescence maxima (λ_f) than in the absorption maxima (λ_a) as a result of change in the polarity of the solvent are observed in both the dyes, implying a greater polarity (dipole moment) for the dyes in the excited state compared to that in the ground state.

The Stokes shift, which is the difference between the absorption and emission frequencies, is thus mainly due to the changes in the latter. The Lippert–Mataga equation relates the Stokes shift to the polarity function of the solvent—with the assumption that the solute is a point dipole centered in a spherical cavity whose size does not alter on excitation—in the following manner:[35–37]

$$\Delta\tilde{\nu} = (2\Delta\mu^2/hca_0^{\,3})\Delta f + A \tag{2}$$

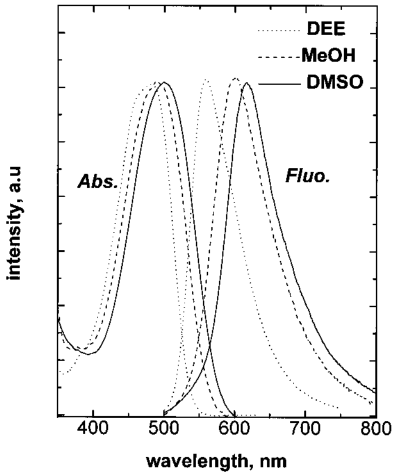


Figure 1. Normalized absorption (Abs.) and fluorescence (Fluo.) spectra of dye I in diethyl ether, DEE (dotted line); methanol, MeOH (dashed line); and dimethyl sulfoxide, DMSO (solid line).

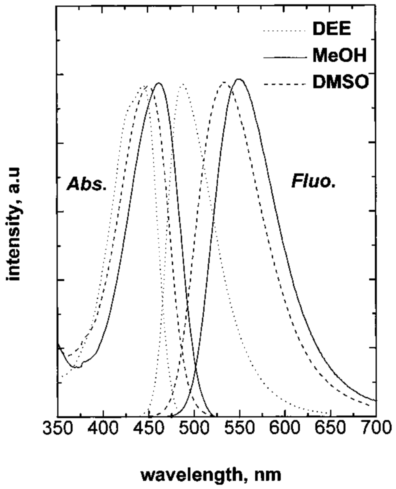


Figure 2. Normalized absorption (Abs.) and fluorescence (Fluo.) spectra of dye II in diethyl ether, DEE (dotted line); methanol, MeOH (dashed line); and dimethyl sulfoxide, DMSO (solid line).

where $\Delta\tilde{\nu}$ is the Stokes shift (in cm^{-1}) and is given by $\Delta\tilde{\nu} = \tilde{\nu}_a - \tilde{\nu}_e$, where $\tilde{\nu}_a$ and $\tilde{\nu}_e$ are the spectral positions (frequencies) of the absorption maxima and solvent-equilibrated fluorescence maxima, respectively. The terms in the parentheses in eq 1 are Planck's constant (h), speed of light (c), Onsager cavity radius of the solute molecule (a_0), and the square of the magnitude of the change in its dipole moment on excitation from a ground state to an excited state ($\Delta\vec{\mu} = \vec{\mu}_e - \vec{\mu}_g$), where $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moments of the molecule in the ground and excited states, respectively. This is obtained directly as the slope of the plot of the Stokes shift versus the polarity function. Δf is the polarity–polarizability parameter of the solvent and is expressed in terms of the refractive index and dielectric constant of the solvent, according to the following relation:

$$\Delta f = \frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} \tag{3}$$

where ϵ and n are, respectively, the dielectric constant and refractive index of the solvent (at room temperature).

The Lippert–Mataga plots for the two dyes, as plotted in Figure 3, phenomenologically, reflect a higher dipolar character for the molecule in the excited state than in the ground state. A linear least-squares regression analysis of $\Delta\tilde{\nu}$ versus Δf gives a

TABLE 2: Absorption and Fluorescence Spectral Data of Dye I and Dye II in Various Solvents[a]

Dye I

solvent	ϵ	λ_a (nm)	λ_f (nm)	$\Delta\tilde{\nu}$ (cm^{-1})
diethyl ether (DEE)	4.19	480	559	2944
chloroform	4.81	500	571	2407
dioxane[b]	2.02/7.0	474	564	3367
tetrahydrofuran	7.58	487	583	3380
dichloromethane (DCM)	9.08	480	579	3562
dimethylformamide	36.7	490	605	3879
acetonitrile	38.8	485	601	3979
dimethyl sulfoxide (DMSO)	46.7	490	617	4148
ethanol	24.6	492	601	3686
methanol (MeOH)	32.7	490	601	3797

Dye II

solvent	Δf[c]	λ_a (nm)	λ_f (nm)	$\Delta\tilde{\nu}$ (cm^{-1})
diethyl ether (DEE)	0.161	445	489	2022
chloroform	0.148	455	497	1857
dioxane[b]	0.02/0.2	450	492	1897
tetrahydrofuran	0.21	453	512	2544
dichloromethane (DCM)	0.218	450	508	2537
dimethylformamide	0.275	450	530	3354
acetonitrile	0.305	451	534	3446
dimethyl sulfoxide (DMSO)	0.267	462	550	3463
ethanol	0.288	453	530	3207
methanol (MeOH)	0.310	450	537	3460

[a] See text for details of colum titles. [b] Bulk dielectric constant of dioxane in 2.02 (at room temperature), and this corresponds to a Δf of 0.02. However, it's known to have a dynamic dielectric constant varying between 5 and 7 in the presence of strongly polar solute dipoles.[48] A dielectric constant value of 7 has been considered in the present study. [c] Polarity function for each solvent is based on the value of the dielectric constant and refractive index of the solvents given in ref 49.

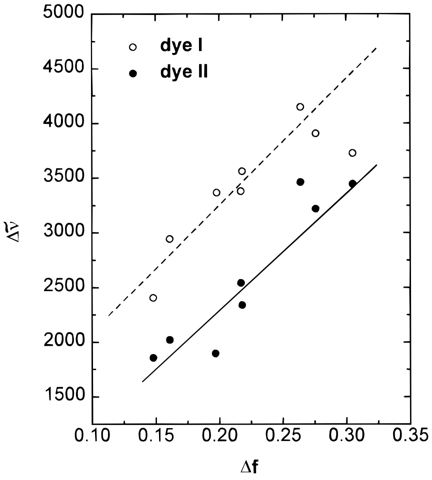


Figure 3. Lippert–Mataga plots relating the Stokes shift ($\Delta\tilde{\nu}$ in cm^{-1}) to the solvent polarity–polarizability parameter (Δf).

good correlation when only aprotic solvents are considered, in accordance with the following relation:

$$\Delta\tilde{\nu} = 11594\Delta f + 933\ (r = 0.95), \quad \text{for dye I}$$

and

$$\Delta\tilde{\nu} = 10700\Delta f + 149\ (r = 0.96), \quad \text{for dye II}$$

The deviations from the above plots observed in the case of alcohols characterize specific solvent effects arising from specific solute–solvent interactions (hydrogen bonding, etc.). (In regard to the hydrogen bond influences on the observed differences in the photophysical properties of the two dyes, since both dyes have the same hydrogen-bonding sites—the carbonyl O and the amine N, both good hydrogen bond acceptors in the ground state—on the *parent* coumarin, the observed differences in the photophysical properties of the two dyes (see below) cannot be directly attributed to the effect of hydrogen bonding.) The magnitude of the slope is an indication of the increase in the excited-state dipole moment and in the present case implies that the two dyes are (almost) equally polar in the excited state. An approximation of the magnitude of the change in the dipole moment of the dye molecules on excitation can be made on the basis of available data on a_0 for various aminocoumarins. On the basis of the suggestion of Lippert,[38] the Onsager cavity radius of the dye molecule is usually taken approximately as 40% of its long molecular axis. On account of nonplanarity (Scheme 1), the long axis of the dye molecules, I and II, can be considered to be either that of the *parent* coumarin or that of the *second* coumarin. In a gross underestimation, assuming that the *parent* coumarin has a longer molecular axis, a value of 5 Å can be assumed for a_0. This is in accordance with the values of 5.7 and 5.01 Å for 7-(diethylamino)-4-methylcoumarin (C1)[39] and 7-(diethylamino)-4-(trifluoromethyl)coumarin (C35),[26] respectively. This approximation leads to a calculated value of 12 and 11.53 D as the change in dipole moment on excitation for dyes I and II, respectively, and corresponds to a μ_e value of 20.9 D for dye I and 21.7 D for dye II.

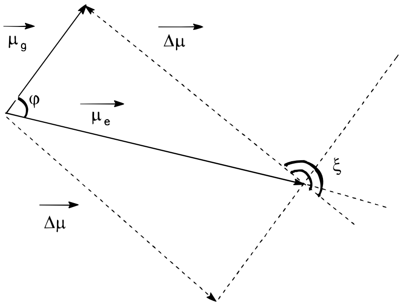


Figure 4. Definition of angles between the ground-state ($\vec{\mu}_g$) and excited-state ($\vec{\mu}_e$) dipole moment vectors.

A more accurate determination of the magnitude of the change in dipole moment on excitation would require a precise estimate of the Onsager cavity radius since an uncertainty introduced by this parameter has been shown to result in great anomalies in the calculation of excited-state dipole moments.[40] Such a difficulty can be circumvented by adapting the method proposed by Suppan,[41] which, in a simplified form, can be represented by eq 4:

$$\tilde{\nu}_a/\tilde{\nu}_e = -\mu_g \cos \xi/\mu_e \cos \varphi \tag{4}$$

The angles ξ and φ define the difference in directions between the vectors $\vec{\mu}_g$, $\vec{\mu}_e$, and $\Delta\vec{\mu}$ (see Figure 4). When the spectral shifts for fluorescence are much greater than those observed for absorption, and on a simple assumption that the ground- and excited-state dipoles are collinear (i.e. $\varphi = 0$ and $\xi = 180°$),[26,41] the ratio of $\vec{\mu}_e/\vec{\mu}_g$ can be obtained directly from the slopes of the plots shown in Figure 5. Least-squares analysis of the data gave a good linear correlation, resulting in a slope of 1.71 for dye I ($r = 0.93$) and 1.80 ($r = 0.82$) for dye II. The ground-state dipole moment of these two dyes, calculated theoretically using AM1, is found to be almost the same (Table 1). The two dyes thus have (almost) similar excited-state dipole moments. Qualitatively, this is the same result that is obtained from the Lippert–Mataga treatment. Thus μ_g(dye I) ~ μ_g(dye II) and μ_e(dye I) ~ μ_e(dye II). The excited-state dipole moments calcualted by the above two methods are 2.6 times the corresponding values in the ground state. This magnitude of

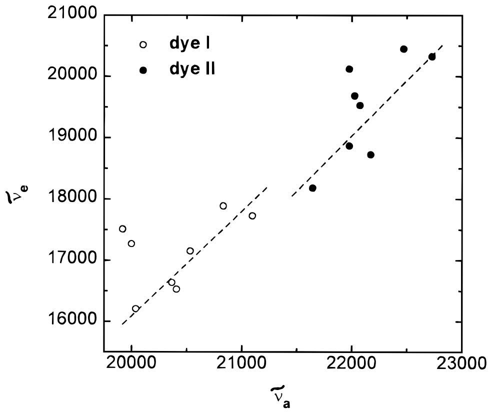


Figure 5. Representative plots of the linear dependence between absorption and fluorescence maxima for dyes I and II. $\tilde{\nu}_a$ = absorption frequency corresponding to the longest wavelength absorption band; $\tilde{\nu}_e$ = emission frequency (both in cm^{-1}).

increase is comparable to that reported for several substituted aminocoumarins.[14,16,22,26,39] However, these are the values obtained out of a highly simplified analysis, since neither a change in the direction of $\vec{\mu}_e$ nor the orientation of $\Delta\vec{\mu}$ with respect to $\vec{\mu}_g$ and $\vec{\mu}_e$ is considered in this treatment. Nevertheless, this treatment gives an estimate of the possible nature of the excited state in the two dyes.

Fluorescence Quantum Efficiency and Lifetime. The major differences in the photophysics of the dyes in different solvents evolve at this stage. Dye I shows a strong long-lived fluorescence in weakly polar solvents, which falls off very rapidly as the solvent is made more polar. There is a limiting value (dielectric threshold) above which the changes in the fluorescence quantum efficiency (Φ_f) as well as the fluorescence lifetime (τ_f) are more susceptible to the changes in the polarity of solvent. In highly polar solvents (DMSO), Φ_f decreases to one-fifth of the value obtained in weakly polar solvents (DEE) and τ_f decreases nearly by one-half for the same change in solvent polarity. The most important observation in the case of dye II is that it shows a sustenance of fluorescence in all the solvents studied. A small decrease in fluorescence efficiency can, however, be noticed in highly polar solvents. The same dependence is, however, not observed in the case of excited-state lifetime, which is found to be lower in less polar solvents.

Excited-state characteristics can be better understood on the basis of the rate constants for radiative (k_r) and nonradiative (k_{nr}) emission, which explain the various competing processes for the molecules relaxing from an excited state to a ground state. While the former describes the electric dipolar coupling of the excited states with the ground states, vibronic and spin–orbit interactions are considered in the latter case. The two quantities are related to Φ_f and τ_f in the following manner:

$$k_r = \Phi_f/\tau_f \tag{5}$$

and

$$k_{nr} = (1 - \Phi_f)/\tau_f \tag{6}$$

The values of the above parameters, obtained in the present study, are listed in Table 3. The dependence of these two parameters on the solvent polarity is varying not only within a dye but also from one dye to another. More interesting results are in the dependence of k_{nr}, which while it remains almost constant for dye II, increases monotonically by 2 orders of magnitude in the case of dye I when the polarity of the solvent is increased.

TABLE 3: Fluorescence Quantum Efficiency, Lifetime of the Lowest Excited Singlet State, and Radiative and Nonradiative Rate Constants of the Dyes in the Solvents Studied[a]

solvent	Φ_f	τ_f (ns)	$k_r \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})
Dye I				
diethyl ether	0.99	4.18	2.37	0.024
chloroform	0.82	4.14	1.98	0.44
dioxane	0.79	3.89	2.03	0.54
tetrahydrofuran	0.66	3.97	1.66	0.86
dichloromethane	0.76	4.21	1.81	0.57
dimethylformamide	0.27	2.33	1.16	3.13
acetonitrile	0.48	2.42	1.98	2.14
dimethyl sulfoxide	0.21	2.08	1.01	3.80
ethanol	0.42	2.27	1.85	2.56
methanol	0.19	1.78	1.07	4.55
Dye II				
diethyl ether	0.63			
chloroform	0.67	1.93	3.47	1.71
dioxane	0.78	1.93	4.04	1.14
tetrahydrofuran	0.67			
dichloromethane	0.69	2.33	2.96	1.33
dimethylformamide	0.57	2.54	2.24	1.69
dimethyl sulfoxide	0.59	2.80	2.10	1.46
methanol	0.62	2.21	2.81	1.72

[a] For an explanation of column titles, see text.

TABLE 4: Comparative Analysis of the Absorption (λ_a) and Fluorescence (λ_f) Maxima of Selected 7-(Diethylamino)coumarins in Acetonitrile

dye	λ_a (nm)	λ_f (nm)
Cl[a]	367	430
C35[a]	396	501
dye I[b]	485	601
dye II[b]	451	534

[a] Data taken from ref 16. [b] Present study.

TABLE 5: Transition Dipole Moments for Absorption (M_a) and Emission (M_f) for the Two Dyes in Dichloromethane (DCM) and Dimethyl Sulfoxide (DMSO)[a]

	solvent			
dye	DCM M_a (D)[b]	DCM M_f (D)	DMSO M_a (D)	DMSO M_f (D)
dye I	7.3	6.2	8.1	4.8
dye II	6.9	6.5	6.1	5.9

[a] The percentage of error in the estimation of the values is ±10%. [b] Debye units.

Transition Dipole Moments. As a measure of the probability of radiative transitions, transition dipole moments for absorption (M_a) and fluorescence (M_f) have been calculated for the two dyes in two different solvents: a weakly polar solvent, dichloromethane (DCM), and a strongly polar solvent, dimethyl sulfoxide (DMSO). M_a can be estimated according to the equation[42]

$$M_a = 0.0958(\epsilon_{max}\Delta\tilde{\nu}^a{}_{1/2}/\tilde{\nu}_a)^{1/2} \tag{7}$$

where ϵ_{max} is the maximum value of the molar decadic extinction coefficient and $\Delta\tilde{\nu}^a{}_{1/2}$ is the full width at half-maximum of the absorption band.

When k_r is known, M_f can be calculated using the equation[43]

$$M_f = (3hk_r/64\pi^4\tilde{\nu}_f^3n^3)^{1/2} \tag{8}$$

where the symbols have their usual meanings. The values obtained for the dyes, given in Table 5, indicate that the probability of radiative transitions in dye I are indeed different when compared to dye II. A very similar value of M_a and M_f in both the solvents in the case of dye II indicates that the fluorescence emission is from the same state to which the molecule has been excited, while the situation is found not to be so in the case of dye I in DMSO.

Discussion

The lowest excited state of 7-aminocoumarins is of a highly polar character, resulting from a π,π^* transition. The transition dipole moment for absorption to this state is also high. This state is widely separated from the respective triplet state.[14,26] The transition dipole moment for fluorescence emission is found to be varying—depending on the extent of charge transfer in the excited state—between one-half to three-halves of the transition dipole moment for absorption.[14] 7-Aminocoumarins with extended π-conjugated substituents in the 3-position are closely related to the styryl dyes[44] in that they may be considered as possessing a ring type styryl structure. Such additional π-conjugation has proven to be useful[16,23] in weakening the strength of the acceptor, thereby reducing the charge transfer induced by the push−pull conformation of the donor alkylamino group and the acceptor coumarin ring.

In the present study a large dipole moment for the dyes in the ground state signifies that they are strongly solvated in the ground state. However the observed spectral shifts in the absorption spectra with increase in solvent polarity do not completely reflect such a situation. The lack of structure in fluorescence spectra is similar to the broad fluorescence observed in several highly polar probes used in spectral shift studies.[11,12] Maroncelli and Fleming[45] conclude, from a similar observation on Coumarin 153, that this is perhaps on account of a *feedback* character of the dye molecule due to a very strong interaction between a highly polar solute and a highly polar solvent.

In the case of 7-aminocoumarins at least three excited triplet states are found to be lying close to the corresponding singlet states;[14,16,26] however, spin−orbit interactions leading to intersystem crossing to triplet states have been found to have a low probability.[46] The main nonradiative deactivation funnel, then, is internal conversion. Internal rotation (twisting) is one possible mechanism of internal conversion. On the basis of the observations summarized in Table 3, a similar dependence of k_r on solvent polarity can be seen in the case of dye I and II. The high Φ_f and short τ_f observed in dye II indicate a large transition dipole moment for emission. Hence, the nonradiative decay is less efficient.

The possibility of observed fluorescence due to complex formation either in the ground or excited states (dimers, excimers) can be ruled out on the basis of the following: (a) Neither the emission spectrum nor the absorption spectrum shows any dependence on the concentration. However as mentioned in the experimental section, care has been taken to maintain the optical density of the samples below 0.2 to avoid formation of any complexes. (b) Fluorescence (maxima, full width at half-maximum, fwhm) was found to be independent of the excitation wavelength. (c) Global analysis of the time-resolved fluorescence measurements, collected at different wavelengths, did not resolve any additional emitting species. (Global analysis has been found to be very effective in extracting information on the minimum number of emitting species as well as their individual spectra.[47])

I now draw attention to the primary aim of the present study: the role of the *second* coumarin moiety, if any, on the overall photophysical properties of the dye molecule. As is evident from the semiempirical quantum mechanical calculations, the two coumarin moieties are nonplanar even in the ground state. The dihedral angles for the dyes are given in Table 1. Both the dyes have the same conjugated *second* coumarin moiety attached at the 3-position of the *parent* coumarin. If this substitution were to be the main electron-withdrawing group involved in the charge transfer in the excited singlet state, from the positively charged diethylamino group, then the two dyes would have displayed identical fluorescence characteristics. A very large and identical value of μ_e indicates that the lowest excited state of both the dyes has an ICT electronic configuration. The magnitude of displacement of the positive charge from the donor to the acceptor moiety (~2.45 Å) reflects a situation where the charge transfer is more likely within the *parent* coumarin nucleus. The absorption and fluorescence of the dyes I and II are found to be strongly red-shifted (when compared to the analogous 7-(diethylamino)-4-methylcoumarin (C1) and 7-(diethylamino)-4-(trifluoromethyl)coumarin (C35), Table 4), and the absorption and fluorescence of dye I are at longer wavelengths when compared to that in dye II. This is, evidently, a result of the type of substitution at the 3- and 4-position of the *parent* coumarin, which introduces a significant conjugative effect. These observations in combination with the other observations[14,26] on aminocoumarins imply that the *second* coumarin has minimal or no influence on the observed differences in the photophysical properties of the two dyes and performs the mere role of a substituent that extends the π-conjugation and shifts both the absorption and fluorescence toward the red region. An extension of π-conjugation weakens the push−pull interaction between the diethylamino donor and the coumarin acceptor ring, and thus dyes with such a substitution retain a high fluorescence yield even in highly polar solvents. Coumarin 6 (C6) and laser dye C515 (also represented as C30) are well-known examples. This analogy however still does not explain the differences in the fluorescence efficiency and lifetime of the two dyes.

To argue the observations on the basis of the ICT−TICT analogy that serves very well in many cases pertaining to bichromophoric molecular systems would imply that the twist around the single bond connecting the donor and acceptor groups should lead to the relaxation of the molecules from the planar ICT conformation to the TICT conformation in the excited state. Since the electron-donating substituent in the two dyes is the same diethylamino group, rotation of the bond formed between this group and *parent* coumarin is still possible in both the dyes. Similarly, in view of the identical composition of the *second* coumarin moiety, the extent of free rotation about the bond connecting the two coumarin moieties can be assumed to be the same.

On the basis of the existing knowledge of the fluorescence quenching of aminocoumarins in highly polar solvents, the possible explanation of the observed differences is as follows: in the present study the two dyes have the same electron-donating amino substituent on the *parent* coumarin. For positional isomers, the Coulomb energy for stabilization (term C in eq 1) depends strongly on the electron affinity of the acceptor group. EA_A is certainly higher for the −CN (dye I) than for the −H (dye II) anion. From the present study we find that μ_g(dye I) ~ μ_g(dye II) and μ_e(dye I) ~ μ_e(dye II). Thus ΔE_{solv} (eq 1), the solvation energy for the stabilization of the dipoles in the excited state, is the same for both the dyes.[39] In such a situation the left-hand-side parameter in eq 1 (E_{TICT}) is then primarily dependent on the electronegative strength (EA_A) of the acceptor involved in the intramolecular charge transfer. Evidently dye I should show a greater stabilization of the TICT state than dye II. According to the concept of ICT−

TICT states in bichromophoric molecules whose chromophores are linked essentially by a single bond, for the excited molecules to occupy the TICT state and to relax from it to the ground state, it is required that the following condition be satisfied.[6]

$$E_{\mathrm{TICT}} - E_{\mathrm{ICT}} < 0 \tag{9}$$

where E_{ICT} is the energy of the ICT state.

Equation 9 means that even though twisting is still favorable in the case of flexible bichromophoric molecules, if the energy of the twisted state is greater than that of the planar ICT state, twisting relaxation to the former state cannot take place. On the other hand if the ICT state is higher lying than the TICT state, the molecule can relax to the low lying TICT state. Extending this explanation to the present study then leads to the approximation that in the case of dye II it could be that $E_{\mathrm{TICT}} > E_{\mathrm{CT}}$, and hence the fluorescence is still from the planar ICT state even in polar solvents. Since dye I shows considerable quenching of fluorescence in highly polar solvents, it could be due to spontaneous relaxation to the TICT state, which must be lower lying that the ICT state.

In view of the failure of semiempirical calculations for the molecules in the excited state using the available molecular mechanics software, a qualitative treatment such as the one presented here becomes unavoidable. A precise estimation of the energies of the ICT and TICT states for various geometrical conformations of the dye molecules would have certainly been very useful for better explanation of the differences in the photophysical properties of the two dyes.

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