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MEDIUM EFFECTS ON FLUORESCENCE QUANTUM YIELDS AND LIFETIMES FOR--ETC(U)

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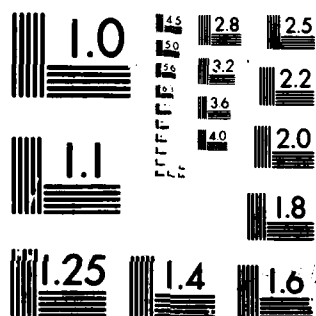
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TECHNICAL REPORT NO. 1

MEDIUM EFFECTS ON FLUORESCENCE QUANTUM YIELDS AND LIFETIMES
FOR COUMARIN LASER DYES

by

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MEDIUM EFFECTS ON FLUORESCENCE QUANTUM YIELDS AND LIFETIMES FOR COUMARIN LASER DYES

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Fluorescence quantum yields and lifetimes for a series of aminocoumarins have been measured. The characteristic red shift of fluorescence in polar solvents is accompanied by a marked decrease in emission yield and lifetime for coumarins in which the substituted amine group at the 7-position is free to rotate. Strong emission is maintained in structurally rigid dyes. The polar solvent effect is interpreted in terms of relaxation of dye excited singlets from an initial planar conformation to a twisted, non-emissive zwitterionic state.

1. Introduction

The importance of aminocoumarins as laser dyes for the blue-green spectral region has been recognized for some time.¹ Fundamental photophysical and photo chemical properties for this family of dyes have not been studied in detail, however, although fluorescence quantum yield²⁻⁵ and lifetime^{6,7} data are available. Interesting effects of medium and structure are apparent in the study of Reynolds and Drexhage.² We report a survey of emission parameters which further reveals the interplay of dye structure and solvent properties that governs the competition between radiative and non-radiative

decay for coumarin dyes. The results confirm the polar nature of the amino-coumarin fluorescent state and suggest a model for non-radiative decay which is consistent with recent proposals⁸ concerning excited species which exhibit intramolecular charge transfer.

2. Experimental

Coumarin dyes 1, 3, 4, and 5 were commercially available laser grade materials (Eastman Kodak coumarins 1, 102, 153, and 151, respectively). Coumarin 2 was prepared and purified as previously reported,⁹ and 6³ was a gift from Dr. R. L. Atkins. Solvents were spectrograde or purified by distillation and checked for absorbing or fluorescing impurities.

Emission spectra were recorded on a Perkin-Elmer MPF 44A fluorescence spectrophotometer equipped with a spectrum correction unit and a low temperature phosphorescence accessory and using quartz cells. Quantum yields were determined using quinine sulfate in 1.0 N H₂SO₄ ($\phi_f = 0.55$ ¹⁰) as the fluorescence standard with refractive index and differential absorption corrections. Fluorescence lifetimes were determined using single photon counting apparatus previously described¹¹ and employing analytical deconvolution methods which are reported.¹²

3. Results

Emission maxima for selected dyes obtained from corrected fluorescence spectra are shown in Table 1. A large red-shift of dye fluorescence emission in more polar solvents was observed as previously reported.¹ Similar shifts in emission wavelength have been recently observed for a number of aminocoumarins and interpreted in terms of solvent polarity-polarizability, hydrogen bonding, and cohesion parameters.^{13,14}

Fluorescence quantum yields and lifetimes for selected dyes for a variety

of solvents are shown in Table 2. Some reduction in fluorescence yields in more polar solvents was generally observed, but the effect was most striking for coumarins λ and ξ . Emission lifetime was sharply reduced (< 1 ns) for ξ as solvent polarity increased. The trend was less pronounced but continuous for λ in more polar media (note data for a 20-80 ethanol-water mixture.)

The effect on emission properties of a polar but viscous solvent was evaluated. In glycerol the usual polar solvent red shift of fluorescence was observed but emission yields and lifetimes were similar for all the dyes. Most noticeable was the continuation of reduction in fluorescence yield (ethanol-water vs. glycerol) for dyes with more rigid structures (λ and ξ) compared to the restoration of emission yield and lifetime for dyes with a flexible amine substituent (λ and ξ). Comparison was also made of the emission of ξ and λ in room temperature fluid solution and in a glassy matrix. In 50:50 ethanol-methanol relative fluorescence yields (ξ/λ) were 0.15 (RT) and 0.90 (77K). A sampling of data was also obtained for the NH_2 -substituted coumarin ξ with results which differ from the analogous structure ξ . Emission yields and lifetimes were sustained in polar solvents (acetonitrile, $\phi_f = 0.72$, $\tau_f = 5.2$ ns; ethanol-water, $\phi_f = .54$, $\tau_f = 5.3$ ns).

Special attention was paid to the possibility of dual emission for the dyes. A continuous pattern of emission red-shift ($\lambda_f = 522 - 534$ nm), a general broadening of the fluorescence band but no fundamental change in emission, structure or shape and a regular reduction of fluorescence yield ($\phi_f = 0.036 - 0.023$) were observed for coumarin ξ on changing the composition (20 - 90%) of water-ethanol solvent mixtures.

The "growing in" of a second emission component¹⁵ as a function of medium was not apparent. Lifetime results were obtained from excellent fits of single exponential decay curves to experimental data over 2-3 decades of

photon counting. Possible deviations from singlet exponential behavior were found in a few cases when fluorescence decay was monitored at different wavelengths using interference filters. For example, the decay of emission of λ_2 in acetonitrile (500 ± 10 nm) was composed of the 0.6 ns decay and as much as 5% of a 3.0 ns component. Similarly small second components were apparent for λ_2 and λ_4 in glycerol (500 or 550 nm filters) but, significantly, all emissions were cleanly single exponential when monitored at 600 nm.

The temperature dependence of emission parameters for λ_1 , λ_2 , and λ_4 was examined. Fluorescence yields for λ_2 in acetonitrile decreased (0.12 - 0.05) with a moderate increase ($4 - 58^\circ$) in temperature whereas the yield of emission of λ_4 was temperature independent in this range.

The fluorescence quantum yield for λ_1 in glycerol was significantly reduced (0.56 - 0.23) between $20 - 80^\circ$, in parallel with a drop in measured emission lifetime (3.8 - 1.6 ns).

4. Discussion

Coumarin dyes are readily divided into two families on the basis of the response of fluorescence lifetime and quantum yield to increase in solvent polarity. For dyes having a substituted amine function which is not restricted by substituent linkage, emission yield and lifetime are sharply reduced in a polar solvent but recover in viscous or glassy media. The effect is more pronounced for a more polar dye (λ_2 vs. λ_1). The family of rigid dye structures (λ_3 , λ_4 , and λ_5) responds more moderately to medium polarity and the effect of a viscous polar solvent (glycerol) is to further reduce rather than fortify emission yield.

Rate constants for radiative and non-radiative decay are readily calculated from the relationships, $k_f = \phi_f/\tau_f$ and $k_{nd} = 1 - \phi_f/\tau_f$. Values for k_f

and k_{nd} shown in Table 3 range close to $1 \times 10^8 \text{ sec}^{-1}$ except for the non-radiative decay parameters for λ and ζ in the most polar solvents. The >200-fold range of k_{nd} for ζ including the return to a relatively slow non-radiative decay in glycerol is most revealing. The quantum yield data alone suggest that coumarin λ follows the pattern of solvent independence set by the other rigid dyes.

The results are readily interpreted in terms of a rotation dependent non-radiative decay which links excited state conformations having different requirements for solvent stabilization. Thus, dye excitation is followed by preliminary relaxation to a moderately polar, planar intramolecular charge transfer state (ICT) state (represented below by a single resonance form). For dyes with less rigid geometries, rotation at the amine function follows, leading to a non-planar conformation, a twisted charge transfer (TICT) state. Both polar states are stabilized by substituents (electron donation at nitrogen and at the aniline ring and electron withdrawal for the lactone ring) and by interaction with solvent dipoles. For the fully charged TICT state, larger requirements for substituent and solvent charge delocalization are expected.

The ICT - TICT model is one adopted from the current proposal of Grabowski, Cowley, and Baumann⁵ concerning the behavior of a variety of polar excited species. The emission profile for coumarin ICT and TICT states differs from a prototype such as p-dimethylaminobenzonitrile^{5,15} in that the twisted form is non-emissive or at best very weakly emissive (The inherent relative strength of ICT emission remaining in polar solvents could mask the small contribution expected for fluorescence of the twisted state⁵). Two important exceptions to the decay pattern for the coumarin dyes are found in the NH_2 - (5) and 2- thiazole^{1,6} substituted systems both of which maintain robust fluorescence in a polar medium. The apparent reluctance for rotation

dependent radiationless decay in 5 is consistent with the prediction of a recent theoretical study¹⁶ of $N(CH_3)_2^-$ vs. NH_2 - substituted benzonitrile and related systems.

The temperature dependence of emission yield and lifetime for 1 and 2 is consistent with the proposed rotatory radiationless decay. The extent of thermal activation for the ICT $\rightarrow$ TICT conversion is revealed in plots of $\ln k_{nd}$ vs. $1/T$. Values for 2 in acetonitrile, calculated from quantum yield data and assuming a temperature independent k_f , result in the Arrhenius parameters, $A = 1 \times 10^{11} \text{ sec}^{-1}$ and $E_a = 2.5 \text{ kcal/mol}$. A higher activation barrier for radiationless decay expected for 1 in glycerol is obtained from the temperature dependence of k_{nd} with $A = 6 \times 10^{11} \text{ sec}^{-1}$ and $E_a = 4.9 \text{ kcal/mol}$.

The behavior of the coumarins is reminiscent of observations concerning rhodamine laser dyes. Thus, rhodamines such as Rho B and 6G with non-rigid structures undergo a solvent polarity and viscosity dependent reduction in fluorescence quantum yield whereas emission is sustained for the rigid Rho 101 in various media.¹ The temperature dependence of fluorescence yield for Rho B and 6G¹⁷ is similar to that observed for the coumarins.

Further studies of the medium dependence of photophysical properties of coumarin dyes are continuing.

The assignment of k_{nd} to ICT $\rightarrow$ TICT bond rotation is not strictly required. A fast reversible rotation followed by rate determining TICT decay (fluorescence decay still single exponential) is not ruled out.

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Table 1. Fluorescence Emission Maxima for Coumarin Dyes^a

Solvent	λ		λ		λ		λ		λ		λ	
	λ_f	ν_f	λ_f	ν_f	λ_f	ν_f	λ_f	ν_f	λ_f	ν_f	λ_f	ν_f
cyclohexane	395	25.3	433	23.1	455	22.0	440	22.7	407	24.6		
ethyl acetate	416	24.0	479	20.9	500	20.0	487	20.5	432	23.2		
acetonitrile	434	23.0	510	19.6	521	19.2	506	19.8	458	21.8		
ethanol	451	22.2	509	19.7	531	18.8	515	19.4	473	21.1		
ethanol-water	458	21.8	525	19.1	542	18.5	528	18.9				
glycerol	463	21.6	525	19.1	547	18.3						

^a λ_f in nm, ν_f in cm^{-1} ; ethanol-water = 50:50 (v/v).

Table 2. Coumarin Fluorescence Quantum Yields and Lifetimes^a

Solvent	λ		λ		λ		λ		λ	
	ϕ_f	τ_f	ϕ_f	τ_f	ϕ_f	τ_f	ϕ_f	τ_f	ϕ_f	τ_f
cyclohexane	0.32	2.8	1.04	4.1	0.73	4.3	0.93	4.2	1.05	
ethyl acetate	0.93	3.1	0.64	4.6	0.88	5.4	0.72		0.70	
acetonitrile	0.73	3.4	0.09	0.60	0.43	5.6	0.68	5.6	0.59	
ethanol	0.59	3.1	0.09	0.85	0.26	3.4	0.65	5.1	0.74	
ethanol-water ^b	0.22	1.4	0.03	0.45	0.26	4.7	0.43	4.5	0.77	
glycerol	0.53	3.8	0.14	2.7	0.17	3.5	0.27			

^a τ_f in ns; dye concentration = $1-5 \times 10^{-5}$ M.

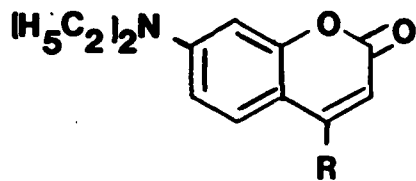
^b 50:50 (v/v) mixture; for λ in 20:80 ethanol-water, $\phi_f = 0.11$ and $\tau_f = 0.70$ ns.

Table 3. Rate Constants for Radiative and Non-radiative Decay^a

Solvent	λ		ξ		A		ϕ	
	k_f	k_{nd}	k_f	k_{nd}	k_f	k_{nd}	k_f	k_{nd}
cyclohexane	1.1	2.4	2.4	<.10	1.7	0.63	2.2	.17
ethyl acetate	3.0	.23	1.4	.78	1.6	0.22		
acetonitrile	2.2	.79	1.5	15.	0.77	1.0	1.2	.57
ethanol	1.9	1.3	1.1	11.	0.77	2.2	1.3	.69
ethanol-water ^b	1.6	5.6	0.67	22.	0.55	1.6	.96	1.3
glycerol	1.4	1.2	0.52	3.2	0.49	2.4		

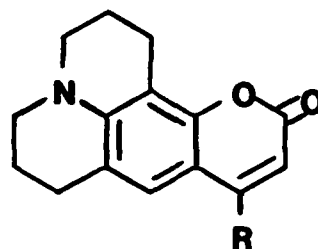
^a k 's $\times 10^{-8} \text{ sec}^{-1}$.

^b50:50 (v/v) mixture; for λ in 20:80 ethanol-water, $k_f = 1.6 \times 10^8$ and $k_{nd} = 13 \times 10^8 \text{ sec}^{-1}$.



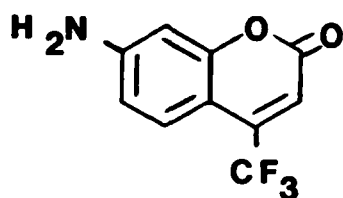
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2, R=CF₃

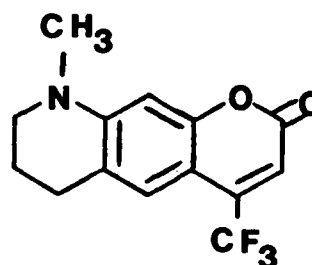


3, R=CH₃

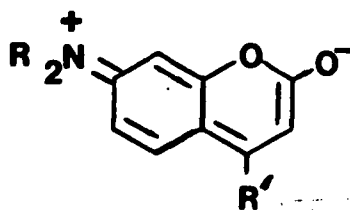
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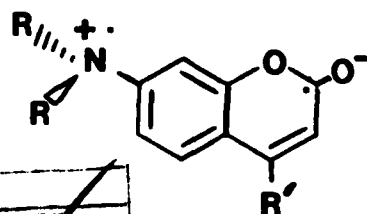
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