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Spectroscopic studies of 7-diethylamino-3-styryl coumarins

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Abstract

The absorption and fluorescence characteristics of four 7-diethylamino-3-styryl coumarins (dyes I–IV), containing either an extended formyl or acetyl substituent at the 3-position, in solvents of different polarity (chloroform, dimethylsulphoxide and dimethylformamide) were studied with regard to the influence of the flexibility of the chromophoric system in both the ground and excited states. The photophysical measurements show that the dyes are very weakly fluorescent. The fluorescence lifetimes are in the region of 0.01 ns and the non-radiative rate constant is very high when compared with the radiative rate constant. These observations indicate that the reduction of the acceptor strength of the substituent at the 3-position, as in the present case, in a 7-diethylaminocoumarin dye does not always result in sustained fluorescence in polar, aprotic solvents. Therefore these dyes are not technically important as laser dyes.

Keywords: Coumarins

1. Introduction

The group of widely used laser dyes emitting in the blue–green region of the spectrum are derived from the basic structural unit of the coumarin family by adding an electron-donating substituent at the 7-position and an electron-accepting substituent at the 3-, 4- and/or 6-position. The strong emission of the aminocoumarin dyes derives from the polar character of the low-lying excited states [1]. The Stokes shift, fluorescence yield and lasing potential are all influenced by the maintenance of a large excited state dipole moment. Dye substitution patterns and dye medium both play an important role in dipole stabilization.

The idea of linking coumarin and styryl systems originated [2] from the potential application of coumarins, substituted in the 3-position with various styryl derivatives of heterocycles, as fluorescent dyes for polyester, acrylic and polyamide fabrics [3–5].

Our special interest concerns the flexibility of the moiety connected to the 3-position of the aminocoumarin molecule. It was stimulated by similar studies indicating that the internal rotation of certain molecular fragments in aminocoumarins has a significant influence on their fluorescence behaviour [6]. To design efficiently fluorescing systems, for example laser dyes, it is essential to control the internal rotation of the molecule and hence the formation of the twisted intramolecular charge transfer (TICT) state because this often acts as an intramolecular fluorescence quencher. Two approaches have been proposed [7]: the first is to rigidize the system, thereby hindering the formation of the TICT state, and the second is to leave the system flexible, but increase the energy of the TICT state relative to that of the intramolecular charge transfer (ICT) state. This can be accomplished in two ways: (a) by reducing the donor strength of the amine group [7] and (b) by reducing the acceptor strength of the substituent [6].

Jones [6] has shown that in 7-aminocoumarins, displaying a delocalizing substituent at the 3-position (such as benzothiazole or benzimidazole), the "push–pull" substituent pattern is compromised by additional π-conjugation resulting in sustained fluorescence even in polar solvents.

The present work is a continuation of our search for new aminocoumarin laser dyes with wide wavelength coverage, greater stability and tunability [8,9], and investigates the photophysical properties of four 7-diethylamino-3-styryl derivatives (dyes **I, II, III** and **IV**) in solution. The solvent employed are chloroform ($CHCl_3$), dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Furthermore, we studied the effect of the extension of the π-electron system on the spectral

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behaviour of the aminocoumarins by including styryl and acetyl substituents at the 3-position.

2. Experimental details

2.1. Materials

The dyes were synthesized [2] and supplied in the pure form by Seshadri and Shenoy, Dyes Research Laboratory, UDCT, Bombay. The solvents used were all of spectroscopic grade from S.D. Fine Chemicals, India. The choice of solvents was based on the requirement of solubility in the range 10^{-4}–10^{-2} mol l^{-1} to achieve possible laser action from the dyes. Rhodamine B (BDH, UK) was used as a standard to determine the fluorescence quantum efficiency. The purity of the dyes and solvents was verified by spectroscopic and chromatographic (thin layer chromatography (TLC)) techniques prior to use. It was observed that the dyes exhibit very poor solubility in alcohols and water.

2.2. Measurements and methods

Absorption and steady state fluorescence spectra were recorded on a Milton Roy Spectronic 1201 UV–visible absorption spectrophotometer and an Aminco Bowman spectrofluorometer respectively. The fluorescence spectra were obtained, using front-surface reflection configuration, by exciting the dye at the wavelength of maximum absorbance in the respective solvent (the molar extinction coefficients of the dyes are listed in Table 1) and were recorded on a Riken Denshi F-3G X–Y/t recorder. The fluorescence spectra were corrected for the sensitivities of the grating, monochromator and photomultiplier tube (IP21) and also for the refractive index of the solvent. The fluorescence quantum efficiency (ϕ_{fl}) was determined from the corrected fluorescence spectra using rhodamine B in ethanol as a standard [10]. In all the cases reported in this paper, the estimated error for ϕ_{fl} is ±10%.

3. Results and discussion

The absorption and fluorescence characteristics (Figs. 1–4 and Table 1) show that the extension of the wavelength coverage of the aminocoumarins to the yellow–red region has been successfully achieved. With the exception of dye **III**, which has an absorption maximum and fluorescence in the blue–green region, the dyes (dyes **I**, **II** and **IV**) show absorption and fluorescence between 500 and 650 nm. A common feature observed in these styryl-substituted compounds is that the absorption band is relatively broad (with the exception of dye **III**), probably indicating the large flexibility of the chromophore. The solvatochromic shifts of the absorption bands are less pronounced than those of the fluorescence bands. This implies that the solvent

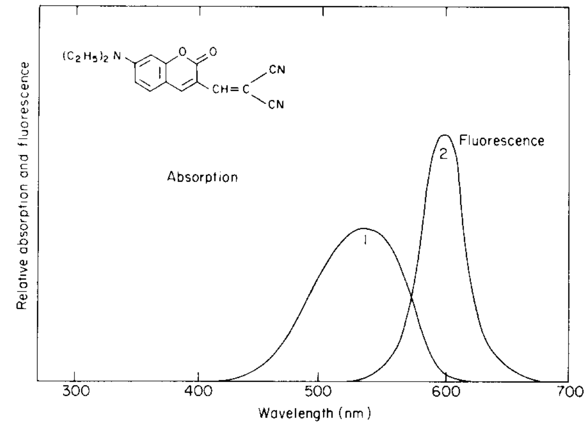


Fig. 1. Absorption (1) and fluorescence (2) spectra of dye **I** in DMSO.

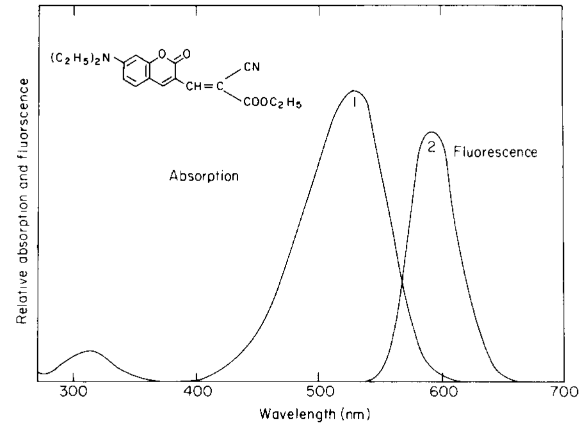


Fig. 2. Absorption (1) and fluorescence (2) spectra of dye **II** in DMSO.

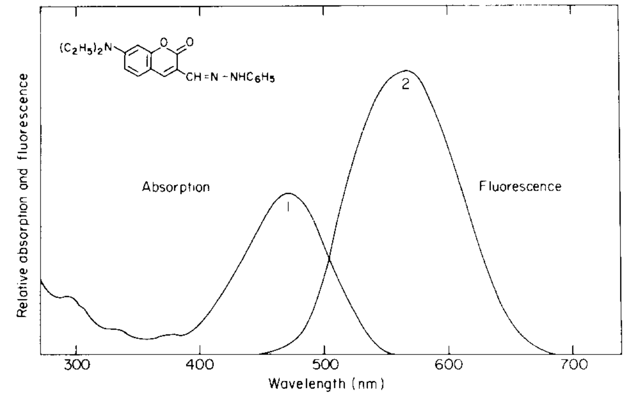


Fig. 3. Absorption (1) and fluorescence (2) spectra of dye **III** in DMSO.

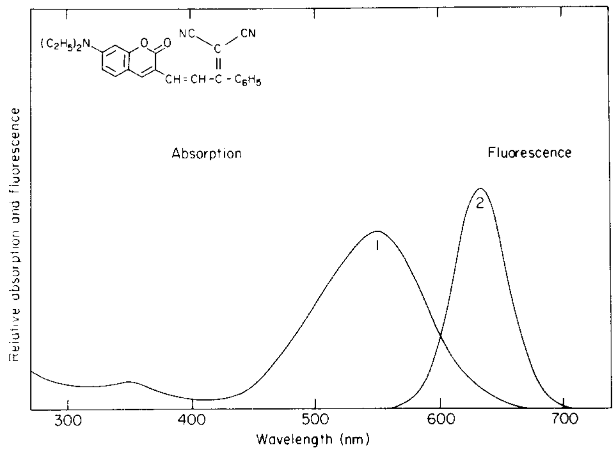


Fig. 4. Absorption (1) and fluorescence (2) spectra of dye **IV** in DMSO.

parameters do not affect the ground state energy distribution of the dye molecules possibly due to the relatively less polar nature of the solute in the ground state than in the excited state.

The photophysical characteristics of dyes **I** and **II** show similarities in the absorption and fluorescence maxima and also in the fluorescence quantum efficiency in all three solvents studied. This can be understood from the similar substituents in the extended styryl derivative. Dye **I** has two –CN groups attached at the 3′-position and dye **II** has a –CN group and a $-COOC_2H_5$ group attached at the 3′-position of the same chromophore skeleton. Thus the absorption maxima of dyes **I** and **II** are in the region between 510 and 530 nm. The fluorescence maxima are in the region between 556 and 596 nm. In contrast with the very moderate bathochromic shift of the absorption maxima with an increase in solvent polarity, the fluorescence maxima show a significant increase and are clearly red shifted with an increase in solvent polarity.

The fluorescence quantum efficiency is very low in these dyes (and also in the other two dyes under consideration), with a maximum efficiency of 0.04 being observed in the less polar solvent chloroform. The quantum efficiency falls off, gradually in the case of dye **I** and rapidly in the case of dye **II**, with an increase in solvent polarity.

In the case of dye **III**, both the absorption and fluorescence maxima are hypsochromically shifted when compared with those observed in dyes **I** and **II**. Again, a moderate bathochromic shift in the absorption and a significant (70 nm) red shift in the fluorescence are observed with an increase in polarity of the solvent from chloroform to DMSO. The fluorescence quantum efficiency is found to be higher in the less polar solvent (0.15 in chloroform) than in more polar solvents (0.005 in DMSO).

Dye **IV** shows an absorption maximum between 519 and 537 nm in the solvents studied. The corresponding fluorescence maximum is found between 588 and 632 nm. The fluorescence wavelength is again found to be more sensitive to changes in solvent polarity. The fluorescence quantum efficiency is very low, between 0.01 and 0.04, in the solvents studied.

Thus although attempts to obtain fluorescence in the red region from a substituted coumarin molecule have

Table 1
Photophysical properties of 7-diethylamino-3-styryl coumarins in various solvents

Dye	Solvent	λ_a (nm)	$\epsilon_a \times 10^{-4}$ (l mol^{-1} cm^{-1})	λ_{fl} (nm)	ϕ_{fl}	τ_{fl} (ns)	$k_r \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})
I	$CHCl_3$	312	0.88					
		527	5.35	564	0.040	0.075	5.35	128.00
	DMF	296	0.41					
		529	3.39	588	0.037	0.109	3.39	88.35
	DMSO	314	0.41					
		529	3.65	596	0.007	0.019	3.65	522.63
II	$CHCl_3$	310	3.54					
		510	4.82	556	0.040	0.083	4.82	115.66
	DMF	517	3.54	578	0.020	0.056	3.54	175.00
	DMSO	523	2.15	580	0.017	0.079	2.15	124.43
III	$CHCl_3$	303	1.23					
		455	3.65	492	0.150	0.411	3.65	20.51
	DMF	287	1.84					
		460	4.50	550	0.007	0.015	4.50	662.00
	DMSO	291	1.41					
		465	3.90	566	0.005	0.013	3.90	765.38
IV	$CHCl_3$	519	4.71	588	0.030	0.064	4.71	151.56
	DMF	528	3.68	624	0.040	0.109	3.68	88.89
	DMSO	537	4.24	632	0.010	0.024	4.24	412.50

been successful, the fluorescence quantum efficiency is found to be very low.

We assume that the bathochromic shift of the dyes is due to the electronic substituent effect and the special type of bridging (these molecules are somewhat twisted around the C–C single bond at the 3-position of the coumarin molecule; according to molecular orbital (MO) theory, mode twisting around a single bond should give rise to a bathochromic shift [11]). This conclusion is further supported by the very low fluorescence quantum yields.

The fluorescence quantum yields are strongly dependent on the environment. A critical examination of Table 1 reveals that, in solvents of low polarity, the fluorescence quantum yield is higher (although not very high) than in solvents of high polarity. On going to solvents of higher polarity, a drastic decrease in ϕ_{fl} is observed in all four dyes.

The fluorescence lifetimes of the dyes could not be precisely determined using the conventional single-photon-counting technique [12], as they were outside the resolution limit of the instrument available (this is approximately 100 ps [13]). Hence these values were determined theoretically in the following manner.

The radiative rate constant (k_r) can be estimated from the absorption coefficient (ϵ_a) by the relation [14]

$$k_r = 10^4 \epsilon_a \tag{1}$$

The fluorescence lifetime (τ_{fl}) and the non-radiative rate constant (k_{nr}) can then be calculated by

$$\tau_{\mathrm{fl}} = \phi_{\mathrm{fl}}/k_r \tag{2}$$

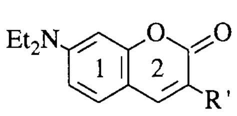
and

$$k_{nr} = (1 - \phi_{\mathrm{fl}})/\tau_{\mathrm{fl}} \tag{3}$$

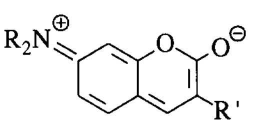
These results are summarized in Table 1.

The intersystem crossing probability of 7-aminocoumarins is very small [15]; thus the non-radiative deactivation of these dyes is mainly due to internal conversion. Table 1 shows that the rate constant of this process is very high (and always much greater than k_r). Internal rotation (twisting) of the molecule is one of the possibilities of internal conversion.

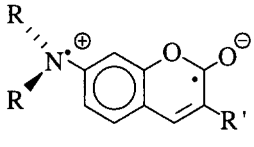
The large Stokes shift indicates an increase in the dipole moment on excitation. This behaviour has been attributed to a charge redistribution in the excited state with respect to the ground state [1,8,17]. Thus the statistical weight of the resonance structures **A** and **B** changes from predominantly structure **A** in the ground state to predominantly structure **B** in the first excited state. The latter structure can be described as a planar ICT state, explaining the greater solvent polarity effect observed at the maximum emission wavelength than at the absorption wavelength (Table 1).



A



ICT
B



TICT
C

The observed changes in the photophysical properties of the dyes can be rationalized in terms of the existing knowledge of TICT processes in 7-aminocoumarins [7,18]. On electronic excitation of a bichromophoric molecule containing an electron donor (usually a dialkylamino group) and an electron-withdrawing group, an ICT state with partial electron transfer is formed initially. The ICT states of the dyes are more polar than their ground states. With an increase in solvent polarity (ϵ), the ICT states are sufficiently solvated. This decreases the energy gap between the ground and the ICT state, which results in a red shift of the ICT emission. In polar media, the dialkylamino group sequentially undergoes twisting which makes the donor orbital perpendicular to the acceptor orbital. This leads to complete electron transfer, resulting in the formation of a TICT state **C** [19,20]. Again the TICT state and the transition state leading to it are more polar than the corresponding ICT state. With an increase in polarity of the medium, the transition state for the TICT process is stabilized to a greater extent than the ICT state. The substituent at the 3-position can be interpreted as a second electron-withdrawing group which can facilitate charge transfer from the electron-donating moiety of the diethylaminocoumarin molecule, resulting in an increase in charge separation. This markedly accelerates the TICT process. Since TICT is the main non-radiative process in the ICT state of aminocoumarins, the acceleration of TICT automatically implies a decrease in ϕ_{fl} and τ_{fl} of the ICT fluorescence. This is observed in the present case.

The extremely large values of k_{nr} for all the dyes in the solvents studied indicate the predominance of radiationless deactivation via a non-fluorescent TICT state. However, τ_{fl} and k_{nr} do not show any dependence on the solvent parameters. These experimental results suggest that other medium effects, such as specific solute–solvent interactions [21], have an important influence on the non-radiative deactivation process of these dyes.

4. Conclusions

It can be concluded that the absorption and fluorescence characteristics of the dyes show a significant dependence on their molecular structure and the medium. The fluorescence of the dyes is considerably red shifted when compared with other known coumarin laser dyes, but the fluorescence quantum efficiency is very low. These observations indicate that the reduction of the acceptor strength of the substituent at the 3-position, as in the present case, in a 7-diethylaminocoumarin dye does not always result in sustained fluorescence in polar, aprotic solvents. Thus these dyes are not technically important as laser dyes; however, the extreme sensitivity of dye **III** to the medium polarity (a red shift of the fluorescence maximum by approximately 70 nm in the range of solvents studied) could provide an opportunity to probe the microenvironment experienced by this molecule.

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