

Fluorescence Quantum Yield and Free Rotor Effect

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It was found that the weakly fluorescent trans-2(4'-*N,N*-dimethylaminostyryl)-pyridinium betaine dyestuff (1) becomes efficiently fluorescent in very viscous media. The fluorescence quantum yield (ϕ_F) for dyestuff (1) approaches unity in ethanol-ether (1:1) glass at 98 K. Moreover, the fluorescence wave-length is blue shifted (1874 cm^{-1}) when the temperature is lowered to 98 K. The results are rationalized as being due to solvent viscosity dependent rate constant for a radiationless internal conversion process, involving rotation of the different parts of the molecule, a free rotor effect. The rate of internal rotation was estimated to be $3.4 \times 10^{11}\text{ s}^{-1}$. The results suggest that this molecule can be used as a fluorescent probe to study microscopic structural changes in surrounding media occurring on the picosecond time scale.

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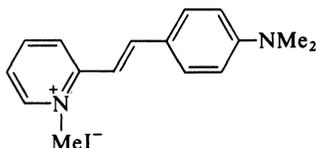
INTRODUCTION

There is considerable current interest in the photo-physical relationship between fluorescence quantum yield (ϕ_F) of donor-acceptor (D-A) chromogens and the molecular rigidity, solvent viscosity and temperature.^{1,2}

It has been previously shown that the mechanism proposed for deactivation of the singlet excited state of some molecules (e.g., stilbene derivatives,³ γ -*N,N*-dialkylaminobenzylidenemalonitriles derivatives¹ and 3,5-dialkyl-4-methoxybenzylidenemalonitrile,⁴ involves rotation about a bond in the S_1 state and decay from a twisted singlet state S'_1 . Intersystem crossing to the triplet states is considered inefficient, and the only process competing with twisting about the bond from the S_1 states is fluorescence. The requirement, that inhibition of geometrical relaxation results in a corresponding increase in

the fluorescence quantum yield, is a consequence of this mechanism. Consequently, such compounds (probes) may be thought of as sensors of microenvironments.⁵ The photons emitted by such probes are reporters of the local structure in the vicinity of the probe at the time of emission. Fluorescence methods are often outstanding in terms of sensitivity for the investigation of chemical and physical dynamic processes such as rotational motion, solvent reorganization, and energy transfer often occur in this time domain and have been investigated by means of fluorescence probes.

Here we report some results on the fluorescence spectra and quantum yields of dyestuff (1) in different solvents at ambient and 98 K temperatures. These results have a significant bearing on the photo-physical and dynamic properties of dyestuff (1).



(1)

EXPERIMENTAL

Dyestuff (1) was the courtesy of Prof. Dr. Z. H. Khalil and its purity was checked on TLC on silica gel with CH_2Cl_2 as eluant. Spectroscopic pure solvents were used for all measurements. Absorption spectral data were reported before.⁶ Fluorescence spectra were taken on a Fica 55 and Shimadzu 510 spectrofluorimeters. Fluorescence quantum yields were determined by comparing with a fluorescence standard Rhodamine B ($\phi_F = 0.69$).

RESULTS AND DISCUSSION

It has been previously shown⁶ that dyestuff (1) exhibits an intense $S_0 \longrightarrow S_1$ absorption band in the visible region. This band undergoes considerable hypsochromic and hypochromic shifts in media of increasing polarity, indicating that the S_0 state is more polar than the S_1 state. Also, it has been shown that these solvent-induced shifts are

consistent with a transition having significant charge-transfer (electron pump) character. These spectral data are used in the present study to calculate the radiative lifetime (τ_0) of the emitting S_1 state by making use of the formula

$$\tau_0 = \frac{1}{k_F} = \frac{3.5 \times 10^8}{\bar{\nu}^2 \cdot \epsilon_{\max} \cdot \Delta\bar{\nu}_{1/2}}$$

where k_F is the first excited singlet state radiative rate constant, $\bar{\nu}$ is the wavenumber of maximum absorption, ϵ_{\max} is molar absorptivity at $\bar{\nu}$ and $\Delta\bar{\nu}_{1/2}$ is the half-band width. The data are listed in Table 1. There is practically no difference in the radiative lifetime of dye (1) in different solvents which reflect a similarity in the ground state dipole moment.

The wavelength and quantum yield of fluorescence of dye (1) are sensitive to both solvent polarity and temperature. Therefore, fluorescence spectra (Figure 1) and quantum yield determinations were made in a number of solvents at ambient and 98 K temperatures (Table 1). Within the limited number of solvents used, the fluorescence yield is

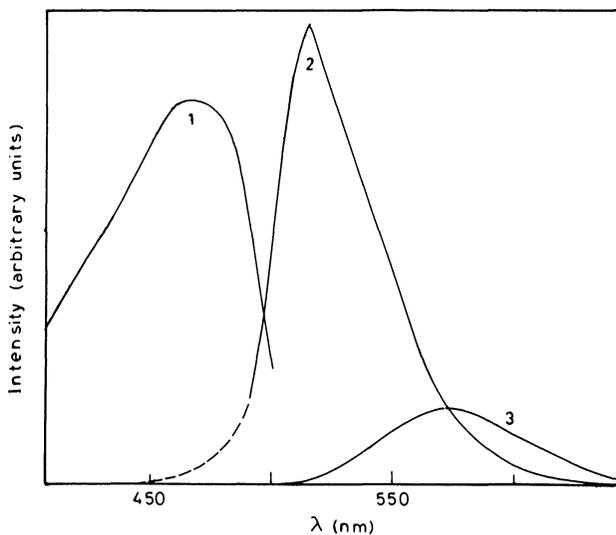


FIGURE 1 Excitation (1) and fluorescence spectra (2) of a dilute solution (10^{-6} M) of the dye at 98 K (2) and at ambient temperature (3).

TABLE 1
Fluorescence spectral data of (1) in organic solvents

Solvent	η/cP	$10^3 \phi_F$	λ_F/nm	τ_0/ns	$\tau \times 10^{11} \text{ s}$
Acetone ^a	0.32	3.6 ^a	584	4.94	1.77
CH ₂ Cl ₂	0.44	4.3	570	6.61	2.87
Ethylacetate	0.45	4.3	548	4.97	2.14
MeOH	0.60	4.1	564	5.15	2.11
EtOH ^a	1.20	6.2 ^a	562	4.95	3.07
EtOH: ether RT		0.6	570	4.90	$2.94 \times 10^{-12} \text{ s}$
EtOH: ether 98 K		888	515	4.90	$4.35 \times 10^{-9} \text{ s}$

^a Preliminary experiments showed that deaeration of dye solution has practically no effect on the ϕ_F value, a result which eliminates the possibility of bimolecular quenching by dissolved oxygen.

generally dependent of solvent viscosity; it increases as solvent viscosity increases. Interestingly, about three order of magnitude increase in the quantum yield of fluorescence of dye (1) in ethanol–ether (1 : 1) on going from ambient temperature to 98 K was observed. Moreover, the fluorescence lifetime of dye (1) in different solvents and temperatures can be estimated by using the radiative lifetime and the ϕ_F according to

$$\tau_F = \frac{1}{k_F + k_{ic}} = \tau_0 \phi_F$$

where k_{ic} is the rate constant of the radiationless internal conversion process. The results (lie in picosecond time scale) are given in Table 1. So far we have the following experimental observations (Table 1): first, an increase of ϕ_F value as the solvent medium becomes more viscous; second, a large ϕ_F value as the medium becomes rigid; and third, the blue shift of the fluorescence spectrum (1874 cm^{-1}) as the temperature is lowered to 98 K.

In order to interpret these observations, we refer to a qualitative potential energy diagram representing the solvent interaction with the dye molecule in the S_0 and S_1 states, Figure 2. The interaction energy is assumed to depend on two coordinates representing the degree of twisting or rotation around a bond symbolized by θ and the other representing the orientation of the polar solvent molecules with respect to the solute dipole moment (or the solute–solvent intermolecular separation) symbolized by R . The dependences of the interaction

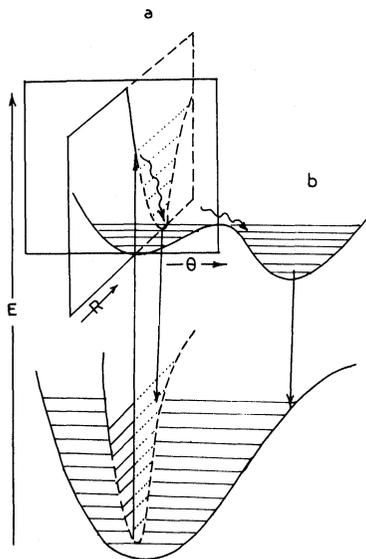


FIGURE 2 Ground and excited state potential energy curves for different conformations: (a) planar and (b) nonplanar, differing in the rotation (θ) but have the same (R).

energy with respect to θ and R are drawn in two perpendicular planes. In the excited state the magnitude of the interaction energy of the equilibrium configuration is smaller than that of the ground state reflecting a decrease in the dipole moment of the solute. Excitation results in a sudden decrease in the dipole moment of the solute giving rise to a strained Franck-Condon state which will relax along the coordinate R to the equilibrium excited state planar configuration (a) followed by either emission or relaxation along the twisting coordinate θ to the equilibrium excited state nonplanar configuration (b) followed by emission. Emission leads to a sudden increase in the dipole moment of the solute giving rise to strained Franck-Condon ground state which will relax along R and/or θ to the equilibrium ground state. Configuration (b) represents the most favorable orientation with the largest interaction energy while conformation (a) represents the least favorable orientation. In a fluid medium the lifetime of the various conformations is short compared to the excited state lifetime and a dynamic equilibrium exists. One may think of a viscosity-dependent barrier²

between (a) and (b), the height of which depends on the rigidity of the medium. Excitation of the solute dye molecule will lead to a fast relaxation and emission originates from the equilibrium excited state configuration corresponding to the most stable site, i.e., site (b). This accounts for the observed small value of ϕ_F in fluid media in which excitation energy is dissipated by free rotor effects. If the medium is made rigid such that the relaxation rate constant along θ is smaller than the fluorescence rate constant, emission will occur from a strained Franck-Condon excited state (or from site (a)). In rigid media the dynamic equilibrium between sites (a) and (b) is lost. In other words internal relaxation along θ is prohibited and ϕ_F value, therefore, is maximized. Since any free rotor effect will be strongly prohibited at 98 K because of the rigidity, the rate of internal conversion (rotation) can be estimated to be $3.4 \times 10^{11} \text{ s}^{-1}$, from the difference in decay rates of dye (1) in ethanol:ether at room temperature and at 98 K.

Finally, the dependence of fluorescence emission maxima upon solvent viscosity can also be used to confirm the suggested mechanism above. When the solvent relaxation rate is too slow for the process to be completed before emission (at 98 K), a shift to higher energy in the emission is observed (Table 1). This accounts for the third observation mentioned above.

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