

THE PHOTOPHYSICS OF RHODAMINE B

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Summary

The effects of solvent viscosity and dielectric constant on the photo-physics of rhodamine B in its protonated and zwitterion forms were studied. The internal conversion rate is dependent on the S_1-S_0 energy separation and increases when this gap is lowered through rotation of the diethylamino groups. Comparison is made with rhodamine 640 in which torsional motion about the C-N bond is not possible.

1. Introduction

Rhodamine B is extensively used as the active medium in continuous-wave and pulsed dye lasers. As water-soluble dyes sensitive to the local environment, some rhodamines have also found application as probes in biological and synthetic polyelectrolyte systems [1 - 4]. In order to interpret results in such systems a complete understanding of the factors affecting the photo-physics of the dye is needed. However, the literature is marked by a number of discrepancies. For example, the fluorescence quantum yield for rhodamine B has been claimed to be viscosity dependent [5], but elsewhere this has been denied [6]. The triplet state has sometimes been implicated in the radiationless processes [6] but other work pointing to very low triplet yields appears to contradict this [7]. Furthermore, from comparison of different rhodamines Viktorova and Gofman [8] noted a dependence of the fluorescent efficiency on the S_1-S_0 energy difference, while Drexhage [5] claimed that this interpretation was inadequate. Although spectra were published as early as 1956 for both the protonated and the zwitterion forms of rhodamine B [9], until quite recently there has been controversy as to the influence of acid-base equilibria and dimerization on the photophysics [10]. Reported spectra obtained by changing the rhodamine B concentration in alcohol solution [11] probably correspond to the base and acid dye forms rather than to the monomer and dimer species since the degree of dissociation increases at lower concentrations. The present work was undertaken to clarify the factors.

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affecting the photophysical behaviour of rhodamine B in its protonated and zwitterion forms.

2. Experimental details

Laser grade rhodamine B (Polysciences) and rhodamine 640 (Exciton), also known as rhodamine 101, were used without further purification as thin layer liquid chromatography showed them to have minimal impurity. Spectroscopic grade methanol (BDH), ethanol (Merck), glycerol for fluorescence microscopy (Merck), monodeuteromethanol (Merck) and D₂O (AAEC, 99.75% pure) were used as supplied. Normal propanol and butanol were freshly distilled and the water was triply distilled. The fluorescent background due to these solvents after excitation at 368 nm was negligible.

All dye solutions were freshly prepared in order to minimize adsorption of the dye on the silica cell walls. In aprotic solvents this is particularly important as a coloured complex forms in contact with the cell windows while the rhodamine B in bulk solution remains in the colourless lactone form. Dye concentrations of approximately 10^{-6} mol dm⁻³ and 5×10^{-7} mol dm⁻³ were used for fluorescence lifetime measurements and quantum yield determinations respectively. At these concentrations self-absorption and aggregation by the dye are insignificant [8]. An aqueous solution of rhodamine B was adjusted to pH 9 by the addition of a small amount of KOH so that only the zwitterion was present. Equal amounts of KOH solution were added to each solvent and the basic alcohols were dried over K₂CO₃. The alcohols were acidified to 10^{-2} mol dm⁻³ in HCl for study of the acid dye form. Deoxygenation of the alcohol solutions by freeze-pump-thaw cycles did not alter the results, as expected for the short fluorescence lifetimes and low oxygen concentrations in air-saturated solutions. However, it was preferable not to degas the solutions as oxygen inhibits the photodecomposition of rhodamines [12]. The poly(vinyl alcohol) (PVA) had a molecular weight of 40 000 (Polysciences). Rhodamine B was added to a 4% aqueous PVA solution which gave a transparent UV-stable film approximately 40 μm thick after evaporation of the solvent [13].

Absorption spectra were recorded on a Cary 17 spectrophotometer. A Perkin-Elmer MPF 44A spectrofluorometer measured the emission spectra which were uncorrected for spectral responses of the emission monochromator and the photomultiplier. The bandpasses of the excitation and emission monochromators were 1.5 nm and 3 nm respectively. Quantum yields were obtained by comparing the integrated fluorescence intensities with that of rhodamine B in ethanol which was taken as 0.68 [14]. A quadratic correction for the solvent refractive index at the exciting wavelength was applied. The relative error in the quantum yields was estimated to be 10%.

Fluorescence lifetimes were determined by the time-correlated single-photon counting method using an Applied Photophysics nanosecond spectrometer (model SP2X) and were reproducible to within 5%. Samples were

excited with vertically polarized light of 368 nm wavelength and the emission was observed at 90° to the excitation direction with a polarizer set at 54.7° to the vertical plane. Scattered excitation light was eliminated by Schott 420 and 550 nm cut-off filters. The calibration of the single-photon counting apparatus was such that a degassed quinine sulphate solution (10^{-5} mol dm^{-3} in 0.05 M H_2SO_4) gave a fluorescence lifetime of 18.9 ns. The experimental decay curves and the instrument response function were transferred to an on-line NOVA 2-10 computer and analysed using a non-linear least-squares iterative convolution method to fit a single-exponential decay function [4]. Unless otherwise stated, the measurements were made at 20°C .

3. Results and discussion

The energy of maximum absorption of a molecule depends both on the collective influence of the solvent and on specific short-range interactions between the molecule and its environment [15]. In a series of low viscosity alcohols the longest wavelength absorption maximum of rhodamine B shifts to lower energy with increasing dielectric constant (Fig. 1). In certain strongly hydrogen-bonding solvents the bulk dielectric constant gives an inadequate description of the solvent-solute interaction. In the case of glycerol, the low energy of maximum absorption of rhodamine B ($17\,860\text{ cm}^{-1}$ and $17\,730\text{ cm}^{-1}$ for the base and acid forms respectively) can be accounted for by the Kosower Z parameter [1]. Both the protonated and the zwitterion forms show the above dependence on solvent polarity but the effect is larger for

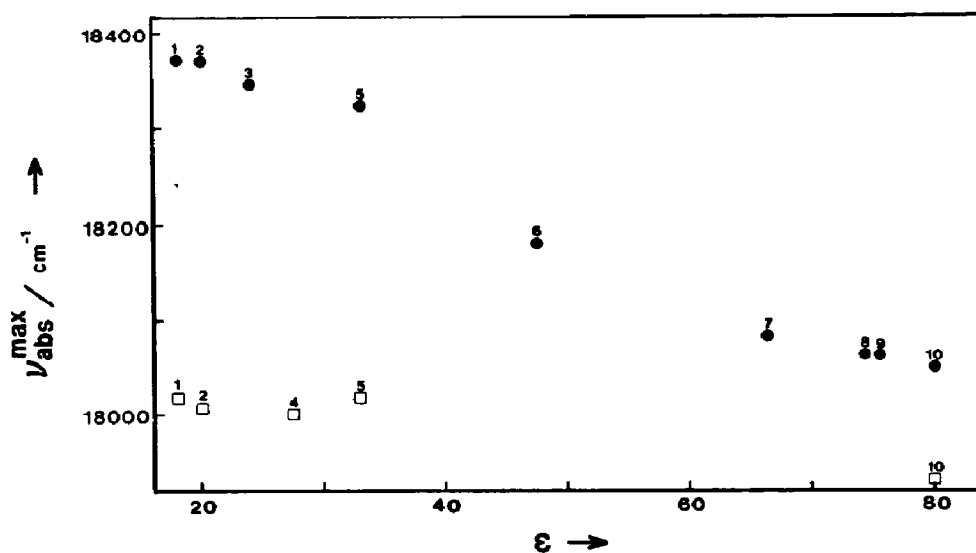


Fig. 1. Variation in the wavenumber of the absorption maximum of rhodamine B with the solvent dielectric constant (●, zwitterion form; □, protonated form) for the following solvents: 1, $\text{C}_4\text{H}_9\text{OH}$; 2, $\text{C}_3\text{H}_7\text{OH}$; 3, $\text{C}_2\text{H}_5\text{OH}$; 4, 94% $\text{C}_2\text{H}_5\text{OH}$ -water; 5, CH_3OH ; 6, 68% CH_3OH -water; 7, 24% CH_3OH -water; 8, 13% CH_3OH -water; 9, 8.5% $\text{C}_2\text{H}_5\text{OH}$ -water; 10, water.

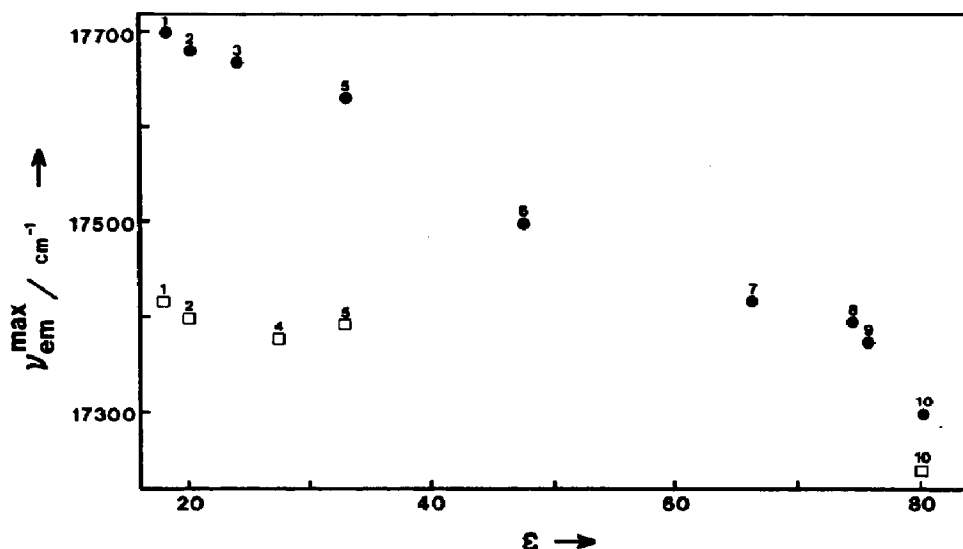


Fig. 2. Variation in the wavenumber of the emission maximum of rhodamine B with the solvent dielectric constant: ●, zwitterion form; □, protonated form (solvents as in Fig. 1).

the zwitterion. The emission bands also show a similar red shift with increasing solvent polarity. The foregoing solvent shift of the absorption maxima is as expected for a $\pi\pi^*$ absorption and can be explained by an increased polarity in the excited state. The position of the emission maxima may be further influenced by excited state solvent relaxation [1]. In very viscous solvents where slow relaxation might be anticipated a somewhat smaller red shift is expected. However, where the viscosities are low, the emission band positions will essentially follow the solvent dielectric constant (Fig. 2). The difference between the band maxima for the acid and the base forms is marked, and this fact may well provide a more plausible explanation for some earlier results which were interpreted in terms of a surprisingly high lactone contribution for rhodamine B in methanol and ethanol [16]. In this earlier work a comparison of the absorbance at 550 nm for methanol and ethanol solutions with that for acetic acid solution was made. However, results in the present study show that the absorbance at 550 nm will be influenced firstly by the shift in acid-base equilibrium in favour of the zwitterion on passing from acetic acid to the alcohols and secondly by the different band positions for the acid and base forms in the various solvents. These effects may well be more significant than effects due to lactone formation in the alcohols.

Sadkowski and Fleming [10], in an attempt to explain the blue shift of the absorption spectrum of the zwitterion relative to the protonated form, suggested that this was due to the large solvent stabilization experienced by the zwitterion S_0 level in comparison with the zwitterion S_1 level and the protonated molecule levels. This argument appears to be invalid as it suggests that more polar solvents would cause a blue shift of the absorption spectrum. It is also at odds with the earlier Förster cycle calculation of the same researchers. Implicit in this is the assumption that the shift is due to a dif-

ference in the electronic properties of the two species rather than to different solvent effects. The differences between the nuclear magnetic resonance spectra for the acid and base forms of xanthene dyes [17] show that the negative charge on the carboxyl group significantly influences protons on the chromophore. Thus a change in S_1-S_0 energy separation on the loss of the carboxyl proton might be expected. The idea that a negative charge on the carboxyl group influences the chromophore had earlier been proposed by Drexhage [5] who suggested that the non-radiative process in rhodamine B involved torsional motion of the diethylamino groups and that this motion was restricted in the zwitterion owing to the higher excited state $C=N$ bond order. However, as will be seen, the exponential dependence of internal conversion on the S_1-S_0 gap may also be of significance in explaining the observed difference between the acid and the base forms.

The fluorescence decay time and quantum yield of rhodamine B were measured for a range of solvents and the radiative and non-radiative rates were calculated. Table 1 contains the same solvents referred to in Figs. 1 and 2 and shows that in the series water to butanol (where the viscosities are low and range only over a factor of 5) the non-radiative rate decreases steadily with decreasing dielectric constant and with increasing S_1-S_0 energy gap. The radiative rate stays constant throughout. For the zwitterion, Table 1 shows that for glycerol the non-radiative rate is lower than would be expected from the dielectric constant and, more particularly, is low in relation to the small S_1-S_0 energy gap. This points to the influence of solvent viscosity, a conclusion which is reinforced by the observation that k_{nr} falls to zero in the rigid PVA [18]. In Table 2, two sets of water-alcohol mixtures are used to demonstrate the effect of the solvent dielectric constant on the non-radiative decay rate of the zwitterion without the complication of varying solvent viscosity.

The foregoing results are generally compatible with the major non-radiative channel being internal conversion, which is increasingly efficient as the S_1-S_0 energy gap decreases except where very high solvent viscosity intervenes. The proportionally more significant change in the non-radiative rate for the zwitterion is consistent with the larger solvent shift observed in that case, while the viscosity effect accords with Drexhage's suggestion that torsional motion of the diethylamino groups is also involved in the non-radiative process. For those dyes where torsional motion of the $C=N$ group is possible, Drexhage has denied the importance of the S_1-S_0 gap in determining the non-radiative rate and has attributed the effect of polar solvents to micro-rigidity. However, this suggests an increase in the fluorescence quantum yield with increasing solvent polarity in contradiction to the present results. It is interesting to note that Drexhage records as a curiosity the high quantum yield (0.91) of rhodamine 3B in low viscosity dichloromethane. However, this effect can readily be explained by the large S_1-S_0 energy gap being the dominant factor.

Two other possibilities for the non-radiative process were considered but rejected on the available evidence. The increase in the non-radiative rate

TABLE 1

Dependence of the photophysical properties of rhodamine B on solvent dielectric constant and viscosity

Solvent	Dielectric constant	Acid form		Base form		$k_{nr} \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})
		ϕ_f	τ_f (ns)	$k_r \times 10^{-8}$ (s^{-1})	ϕ_f			
H ₂ O	80	0.27	1.6	1.7	4.6	0.32	1.7	1.9
D ₂ O	80	0.32	1.8	1.8	3.8	0.35	1.9	1.8
CH ₃ OH	33	0.43	2.3	1.9	2.5	0.53	2.4	2.2
CH ₃ OD	33	0.44	2.3	1.9	2.4	0.55	2.6	2.2
C ₂ H ₅ OH (94%)	27	0.46	2.2	2.1	2.5	0.68	2.7	2.5
C ₃ H ₇ OH	20	0.54	2.5	2.2	1.8	0.74	3.0	2.5
C ₄ H ₉ OH	18	0.55	2.6	2.1	1.7	0.75	3.1	2.4
Glycerol	43					0.78	3.6	2.1
PVA	40					1.0	5.1	2.0

TABLE 2

Dependence of the photophysical properties of rhodamine B on solvent dielectric constant for constant viscosity

Solvent	η/η_0	ϵ	τ_f (ns)	ϕ_f	$k_r \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})	λ_{abs}^{max} (nm)
94% C ₂ H ₅ OH-H ₂ O	1.40	27.4	2.7	0.68	2.5	1.2	546
68% CH ₃ OH-H ₂ O	1.41	47.5	2.3	0.46	2.0	2.3	550
13% CH ₃ OH-H ₂ O	1.42	74.4	2.0	0.38	1.9	3.1	554
8.5% C ₂ H ₅ OH-H ₂ O	1.41	75.6	1.9	0.38	2.0	3.2	554
100% C ₃ H ₇ OH	2.22	20.0	3.0	0.74	2.5	0.9	544
24% C ₂ H ₅ OH-H ₂ O	2.36	66.3	2.0	0.42	2.1	2.9	554

with increase in solvent dielectric constant might be thought to be indicative of photoionization. Photoionization has been found to be important in the probe molecule 1,8-anilino naphthalene sulphonate (1,8-ANS) [19, 20] and other molecules containing electron-donating groups [21]. However, the considerably lower energy of the first absorption in rhodamine B compared with the foregoing molecules argues against this. Moreover, rhodamine B does not show the large solvent-dependent Stokes shift which characterizes 1,8-ANS. This was taken by Robinson *et al.* [19] as pointing to, although not proving, the existence of a large excited state solute-solvent interaction. Sadkowski and Fleming [20] have subsequently confirmed that the stabilized state from which photoionization occurs in 1,8-ANS is the result of a strong hydrogen-bonding interaction with the solvent. Robinson *et al.* studied 1,8-ANS in mixed $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$ solvents and found a markedly non-linear dependence of the non-radiative rate on solvent composition. Their results pointed to a dependence of photoionization on the number of water molecules in the solvation sphere of the 1,8-ANS, with the non-radiative rate dropping by a factor of approximately 50 in going from pure water to 95% $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$. By contrast, for the same solvent change the non-radiative rate in rhodamine B drops by less than a factor of 2. Thus, while rhodamine B is certainly subject to hydrogen bonding by the solvent, as is indicated by the conversion to the lactone form that occurs in aprotic solvents, the interaction seems to be considerably weaker than that which precedes photoionization in 1,8-ANS. To confirm the absence of photoionization, aqueous rhodamine B was flash photolysed. The apparatus consisted of a Q-switched Nd:phosphate glass laser operating in either the second or the fourth harmonic. When this apparatus was operated at the fourth harmonic (264 nm) to flash a degassed aqueous solution containing 10^{-4} mol dm^{-3} tryptophan, clear evidence of hydrated electron was obtained during monitoring at 680 nm. However, when the same apparatus operating in the second harmonic (527 nm) was used to flash photolyse an aqueous degassed solution containing 2×10^{-6} mol dm^{-3} rhodamine B (pH 10) no trace of hydrated electron was seen.

Another possibility that we believe can be rejected has been raised by Mostovnikov *et al.* [12] who suggested that in hydrogen-donating solvents certain dye molecules may abstract hydrogen atoms from the solvent to form a colourless "leuco" form. Apart from the intrinsic improbability of hydrogen abstraction from water by a molecule with an S_1 energy of only about 210 kJ mol^{-1} , several other observations rule out this possibility. Hydrogen abstraction would be expected to occur more readily in methanol than in water because of the lower bond energy of the C-H bonds, thus leading to a higher fluorescence quantum yield for the latter solvent. The reverse is the case. Moreover, rhodamine 110 would be expected to be just as efficient as rhodamine B as a hydrogen abstractor, yet its quantum yield is very much higher.

To elucidate the nature of the non-radiative processes further, rhodamine B was studied in D_2O and CH_3OD (see Table 1). Perhaps surprisingly, in view of the fact that the only exchangeable proton is not directly attached

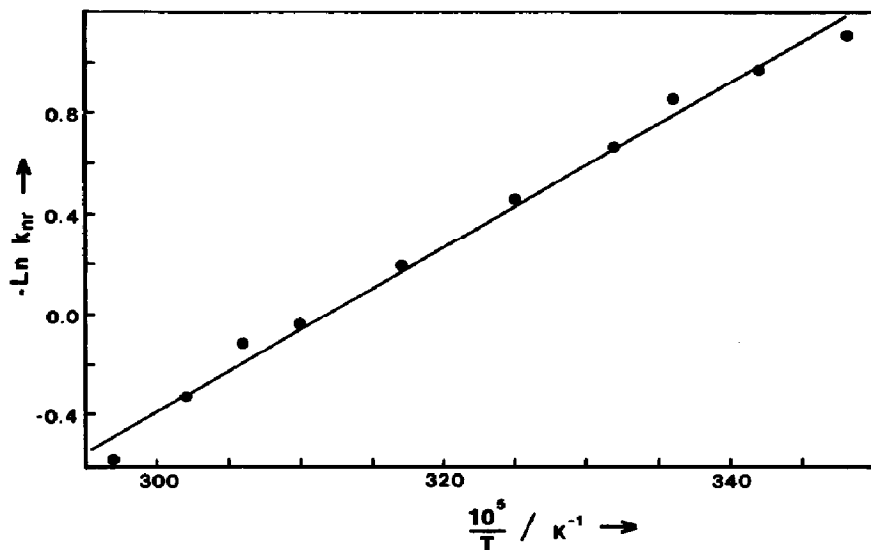


Fig. 3. Arrhenius plot for the zwitterion form of rhodamine B in water.

to the chromophore, there was a significant change in going from H_2O to D_2O for both forms of the dye. These results suggest that coupling occurs between the hydrogenic modes of the solvent and the vibrations of the dye responsible for taking up energy in internal conversion. In rhodamine 640, where the rigid structure precludes torsional motion, a much larger isotope effect on the non-radiative rate occurs despite the fact that again there are no exchangeable protons attached to the chromophore. In aqueous solution the fluorescence decay time is 4.3 ns and the quantum yield has been reported as 0.71 [22]. The lifetime increases to 4.9 ns and the quantum yield to 0.9 in D_2O . Interestingly, the isotope effect appears to be no more marked in rhodamine 110, which like rhodamine 640 is thought to have a rigid structure (in this case due to the high $\text{C}=\text{N}<$ bond order) but where there are exchangeable hydrogens.

The temperature dependence of the non-radiative rate for the zwitterion form of rhodamine B was investigated and an Arrhenius plot is given in Fig. 3. As the quantum yield of rhodamine B in solution at low temperatures is unity [23], there is no need to consider any temperature-independent non-radiative decay process. The apparent activation energy is 26 kJ mol^{-1} which compares favourably with the values of 28 kJ mol^{-1} [23] and 30 kJ mol^{-1} [24] determined for the zwitterion in ethanol.

Drexhage had earlier distinguished rhodamine B, in which torsional motion of the $\text{C}=\text{N}<$ group is possible, from those dyes in which the chromophore is rigid and planar (rhodamine 110, rhodamine 6G and rhodamine 640). Rhodamine B was thought to be characterized by an increase in the non-radiative decay rate at higher temperatures due to increased torsional mobility of the $\text{C}=\text{N}<$ groups [5]. The precise role of torsional motion in the non-radiative decay was not discussed nor was the relation between this motion and the observed activation energy. In the other group the non-

radiative process was thought to be internal conversion promoted by the high frequency hydrogenic modes and to a first approximation independent of temperature [5]. This distinction now appears to be a little misleading. The distinction between rigid and non-rigid structures accords with the observation that the rhodamine dyes tend to divide into a group with fluorescence quantum yields approaching unity (rhodamine 110) and a group with much lower quantum yields (rhodamine B). However, it seems likely that in both groups the dominant non-radiative process is internal conversion involving the high frequency hydrogenic vibrations. What distinguishes rhodamine B is the mediating role of torsional motion of the diethylamino groups. The implication of the present results is that torsional motion of the diethylamino groups can cause a narrowing of the S_1-S_0 gap thus facilitating internal conversion. In denying the importance of the S_1-S_0 gap Drexhage cited rhodamine 640 which has a small S_1-S_0 separation but a quantum yield of approximately unity. However, in rhodamine 640 torsional motion of the $C=N$ group is not possible. The present results indicate a correlation between the internal conversion rate and the S_1-S_0 gap. The situation may be one in which this gap is influenced by solvent stabilization effects, with the possibility of further narrowing as a result of torsional motion of the diethylamino groups.

Figure 4(a) depicts one way in which torsional motion could narrow the S_1-S_0 gap. The potential energy minimum shown corresponds to coplanarity of the $C=N$ group and the xanthene ring system, *i.e.* to maximum π -type overlap. The barrier to rotation round the $C=N$ bond is expected to be lower in the excited state owing to a decrease in the $C=N$ bond order. Thus the upper state potential energy curve is shallower. Thermal excitation in the upper electronic state changes the torsional angle to a new value where the S_1-S_0 gap is smaller. If this model were correct, then the temperature dependence of internal conversion would be expected to be complex and the fitting of the non-radiative rate to an Arrhenius equation must be considered as a first approximation only. There would be contributions to the apparent activation energy from the internal energy barrier and from the energy required for rotational diffusion in the solvent. It should be noted that the activation energy observed here is considerably higher than the activation energy of the solvent viscosity [25]. However, it is smaller than would be expected for complete rotation of the diethylamino group, even allowing for the expected lowering of the $C=N$ bond order in the excited state [26]. The model proposed here, however, does not require complete rotation.

In recent publications on the related dye Fast Acid Violet 2R (FAV2R) a double potential minimum model was proposed (Fig. 4(b)) [27] in which a narrowing of the S_1-S_0 energy gap, with consequent fast internal conversion, was envisaged on moving from an initial non-coplanar configuration ($\theta = \theta'$) to one in which the planes of the substituents were more nearly coplanar. In the case of FAV2R the activation energy for the non-radiative process has not been measured. Moreover, in FAV2R the nitrogen substituents are extremely bulky and the measurements were made in very viscous solutions.

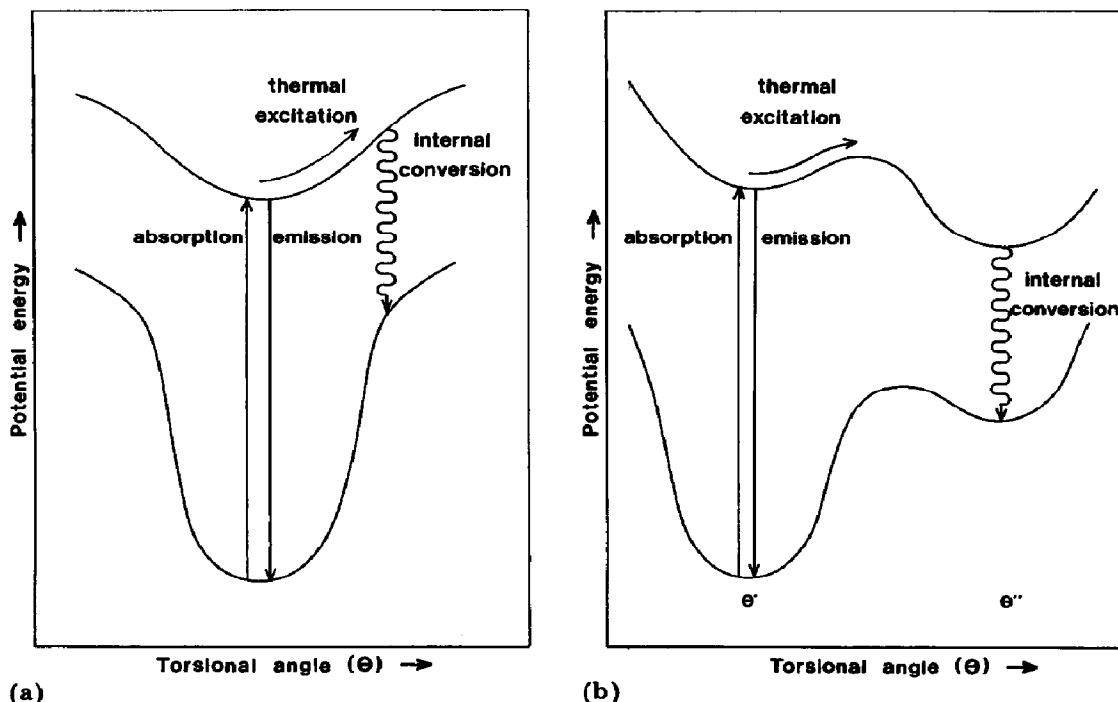


Fig. 4. (a) Variation in the potential energy in the ground and excited electronic states with the torsional angle of the diethylamino groups. (b) Variation in the potential energy in the ground and excited electronic states with the torsional angle (double minimum model).

The height of the potential barrier and the energy difference between the initial and final states were considered unimportant as the movement to the second potential energy minimum was thought to be hydrodynamically controlled. If a double potential minimum model was to be applied to rhodamine B in aqueous solution, then the much smaller rotating groups would mean that the movement to the second potential minimum, with subsequent internal conversion, would be kinetically controlled and an activation energy associated with the energy barrier to rotation would be expected. In the FAV2R work no detailed consideration of the nature of the potential energy curves was made, the only assertion being that the S_1-S_0 energy gap was narrowed on moving to a potential minimum corresponding to greater π overlap. However, there are difficulties in applying a double potential minimum model to rhodamine B. These difficulties relate to observations on rhodamine 640. Here the structure ensures that the $C=N$ group is in the "coplanar" position of maximum π overlap. Moreover, the S_1-S_0 energy gap is considerably smaller than in rhodamine B. Despite this, the fluorescence quantum yield is very high in rhodamine 640. Thus it appears that simply achieving the position of maximum π overlap is not in itself likely to reduce the S_1-S_0 energy gap to the point where internal conversion becomes appreciable. This supports the idea that a reduction of the energy gap in the way described in Fig. 4(a) is necessary. Although it might be argued that FAV2R is a different

case, in which attainment of the coplanar configuration does lead to a decrease in energy gap such that internal conversion becomes appreciable, a number of difficulties remain. Figure 4(b) shows what appears to be the only possible arrangement of ground and excited state potential energy curves. In Fig. 4(b) the θ'' minimum corresponding to maximum π overlap lies below the excited state potential maximum by an amount corresponding to the barrier to rotation of the C=N< group away from the coplanar position. Because the C=N< bond order is expected to decline on excitation, any decrease in the S_1-S_0 energy gap on moving to this coplanar configuration cannot be attributed to an increase in depth of the θ'' minimum in the excited state. Rather, it must be attributed to the fact that the potential energy minimum initially occupied is shallower in the excited state than in the ground state. In the ground state the θ'' minimum must be considerably shallower than the θ' minimum in order to explain the fact that all absorption occurs out of the latter. The θ' minimum would have to be attributed to least steric hindrance, and passage out of this minimum in the excited state would be associated with the observed activation energy for internal conversion.

Examination of molecular models of rhodamine B shows that as well as the coplanar configuration of the C=N< group there is likely to be a second stable configuration. Whether potential energy curves of the form shown in Fig. 4(b) are possible for either rhodamine B or FAV2R is much more problematical. There is a further requirement applicable to both the models considered above. There is no blue shift in the emission maximum on moving to a more viscous solvent of the same dielectric constant. If movement away from the Franck-Condon configuration achieved immediately after excitation is associated with a decrease in the S_1-S_0 gap, then a red shift in emission might be expected in those solvents of low viscosity in which such torsional motion most readily occurs. The lack of emission shift with viscosity indicates that, at configurations other than the Franck-Condon configuration, the processes of thermal deactivation and/or internal conversion are very rapid, *i.e.* emission is only competitive from the Franck-Condon state. This is certainly to be expected in the case of rhodamine B in aqueous solution where the torsional motions are expected to be very rapid indeed.

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