

1,4-Bis (β -Pyridyl-2-Vinyl) Benzene (P2VB) and 2,5-Distyryl-pyrazine (DSP) as Blue Laser Dyes

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Solutions of P2VB and DSP in dimethyl-sulphoxide (DMSO) of concentration *ca.* 10^{-3} M/l act as laser dyes on pumping with nitrogen laser. P2VB and DSP are lasing in the ranges 390-440 nm ($\lambda_{\max} = 416$ nm) and 435-465 nm ($\lambda_{\max} = 447$ nm) respectively. An equimolar mixture of P2VB and DSP behaves as an energy transfer dye laser (ETDL) and is lasing in the range 429-455 nm ($\lambda_{\max} = 438$ nm). Such ETDL system obeys a long range coulombic energy transfer mechanism with a critical transfer distance $R_0 = 7.5$ nm.

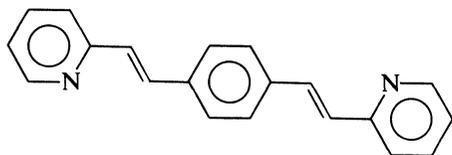
The fluorescence quantum yields of both dyes have been measured, and in DMSO $\phi_f = 0.46$ and 0.35 for P2VB and DSP respectively.

Both dyes show a remarkable photostability upon nitrogen laser excitation. This has been attributed to the role of the 337 nm light in inducing a back photo-chemical reaction of the initially formed photoproducts consisting mainly of photo-oligomers and *cis*-photoisomers.

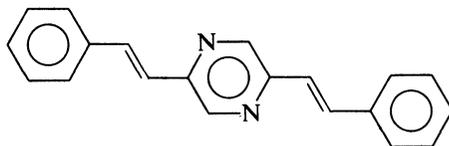
INTRODUCTION

Many blue-emitting laser dyes are now available. A widely used family of blue emitting dyes are 1,4-distyryl-benzene (DSB)¹⁻⁵ and stilbene derivatives.⁶⁻⁹ Such derivatives are characterized by their high photo-chemical stability compared with the widely used blue emitting coumarines.^{1,8}

In the present paper, we report two new efficient blue emitting laser dyes namely 1,4-bis (β -pyridyl-2-vinyl) benzene (P2VB) (I) and 2,5-distyrylpyrazine (DSP) (II) that lase in the blue region upon pumping with nitrogen laser.



(I)



(II)

A mixture of both dyes behaves as a typical energy transfer dye laser (ETDL). The mechanism of energy transfer has been examined. ETDL systems have the versatility of better photon harvesting and increased laser efficiency.¹⁰⁻¹²

The solution photoreactivity of both P2VB and DSP has been reported earlier.¹³⁻¹⁵ The photoreactivity is highly dependent upon excitation wavelength and material concentration.¹³⁻¹⁵ Irradiation with 365 and 403 nm light is believed to give photoproducts in the form of photo-oligomers and *cis*-photoisomers.¹³⁻¹⁵ The effect of the main nitrogen laser line at 337 nm, however, has not been reported and is examined in the present communication.

EXPERIMENTAL

Both P2VB and DSP were prepared by the methods described by Hasegawa *et al.*¹⁶ Extensive purification was achieved by recrystallization and column chromatography on silica gel using methylene chloride as eluent. The materials were then vacuum sublimed in the dark.

10^{-3} M/l solutions of P2VB and DSP in dimethylsulphoxide (DMSO, Anala R) were used as laser dyes without degassing. The dyes were pumped using a nitrogen laser system that is described elsewhere¹⁷ and the dye lasers were operated in the superfluorescence mode. Laser action was observed when a pump threshold was reached such that an intense collimated laser beam has been visually observed.

The beam was then allowed to pass through a Jobin Yvon monochromator before falling onto R446 Hamamatsu photomultiplier tube to measure the relative intensities.

Steady state fluorescence, energy transfer and uv-irradiations were carried out using a Shimadzu RF-510 spectrofluorophotometer. Fluorescence quantum yield measurements were made using 9,10-diphenylanthracene as a reference standard.¹⁸

UV-visible absorption spectra were taken using a Unicam SP8000 spectrophotometer.

IR measurements were taken on a Shimadzu IR400 spectrophotometer using solution cells of NaCl plates 1 mm apart.

RESULTS AND DISCUSSION

The absorption spectra of P2VB, DSP and their mixture in DMSO are shown in Figure 1. The molar absorptivities, ϵ , at 337 nm are 4.5×10^4 , 2.5×10^4 l/mol · cm for P2VB and DSP, respectively. Due to high molar absorptivities, low dye concentrations of about 10^{-3} M/l

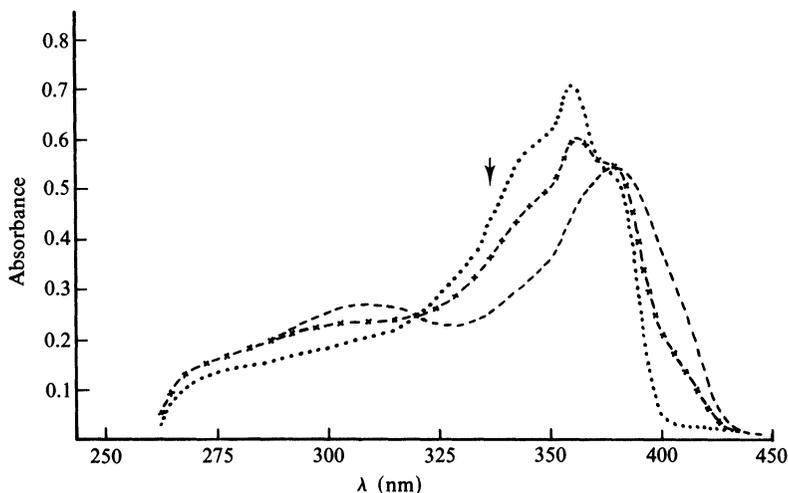


FIGURE 1 UV-visible spectra in DMSO of (---) 10^{-5} M DSP, (····) 10^{-5} M P2VB and (-·-·-) a mixture containing 5×10^{-6} M DSP + 5×10^{-6} M P2VB. The arrow shows the position of the pumping laser line at 337 nm.

were needed. In less polar solvents e.g., methanol, there is a slight blue shift (*ca.* 5 nm) compared with spectra in DMSO. The observed high molar absorptivities together with the slight red shifts in polar solvents indicates that the $S_1 \leftrightarrow S_0$ transitions are $\pi - \pi^*$ transitions as previously reported for DSP.¹⁹

Emission spectra of P2VB, DSP and their mixtures ($\lambda_{\text{ex}} = 337$ nm) are shown in Figure 2. A mixture of P2VB and DSP gives emission in the same spectral region as DSP indicating an energy transfer from excited P2VB to unexcited DSP molecules. Energy transfer is expected to occur because of the remarkable overlap between P2VB emission and DSP absorption spectra.

On pumping with nitrogen laser, the dyes lase at emission maxima comparable to steady state emission maxima in dilute solutions (concentrations *ca.* 10^{-6} M/l). In concentrated dye solutions (*ca.* 10^{-3} M/l) reabsorption occurs and the steady-state emission maxima are red shifted. The ranges of laser emission together with the corresponding laser emission maxima are summarized in Table 1.

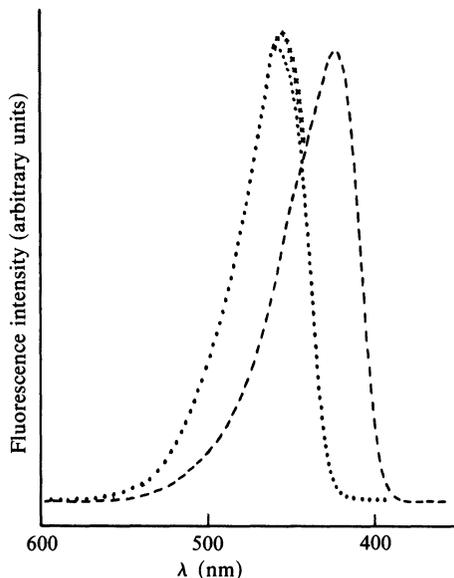


FIGURE 2 Emission spectra ($\lambda_{\text{ex}} = 337$ nm) of (\cdots) 10^{-3} M DSP, ($---$) 10^{-3} M P2VB and ($\times \times \times$) a mixture containing (5×10^{-4} M DSP + 5×10^{-4} M P2VB) in DMSO.

TABLE I
Laser emission characteristics of P2VB, DSP and their mixture
(concentrations = 10^{-3} M/l in DMSO)

Laser dye	Lasing range λ (nm)	Laser maximum λ_{\max} (nm)
P2VB	390-440	416
DSP	435-465	447
Mixture	429-455	438

Fluorescence quantum yields (ϕ_f) of P2VB and DSP dyes in DMSO are $\phi_f = 0.46$ and 0.35 respectively ($\lambda_{\text{ex}} = 337$ nm). It is clear that P2VB is a more efficient emitter compared with DSP upon excitation with 337 nm light. This may be correlated with the higher molar absorptivity of P2VB at 337 nm.

Protonated P2VB obtained by bubbling HCl gas in concentrated (ca. 10^{-3} M/l) P2VB solution in DMSO gives a remarkably intense green emission ($\lambda_{\max} = 490$ nm, $\lambda_{\text{ex}} = 337$ nm, $\phi_f = 0.32$ in DMSO). The emission is considerably red shifted with respect to unprotonated P2VB. Unfortunately the protonated form does not give laser action upon pumping with nitrogen laser. We are trying to modify such a pH-sensitive system.

Figure 3 shows the Stern-Volmer plot of P2VB fluorescence quenching using DSP as a quencher. Fluorescence quenching is efficient even at very low concentrations of DSP. From the Stern-Volmer rate constant and the solution lifetime of P2VB ($\tau = 1.0$ ns),²⁰ we calculate an energy transfer rate constant k_{ET} as ca. 7.5×10^{13} ($1 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) which is much larger than the limiting diffusion rate constant i.e., $k_{ET} \gg k_{\text{diff}}$. This means that a long-range coulombic energy transfer mechanism is prevailing.²¹ This is also in agreement with the observation that energy transfer rate constants are highly sensitive to the medium refractive index (n). The Förster formula²¹ indicates that the energy transfer rate constant is inversely proportional to the fourth power of the refractive index (n). Figure 3 shows that k_{ET} increases on adding ethylene glycol ($n = 1.4314$, $\eta = 9.4$ poise) to DMSO ($n = 1.4785$, $\eta = 1.8$ poise).

The critical transfer distance (R_0) has been calculated using the Förster formula²¹ and was found as $R_0 = 7.5$ nm. This value lies within the accepted values for long-range coulombic energy transfer mechanism.

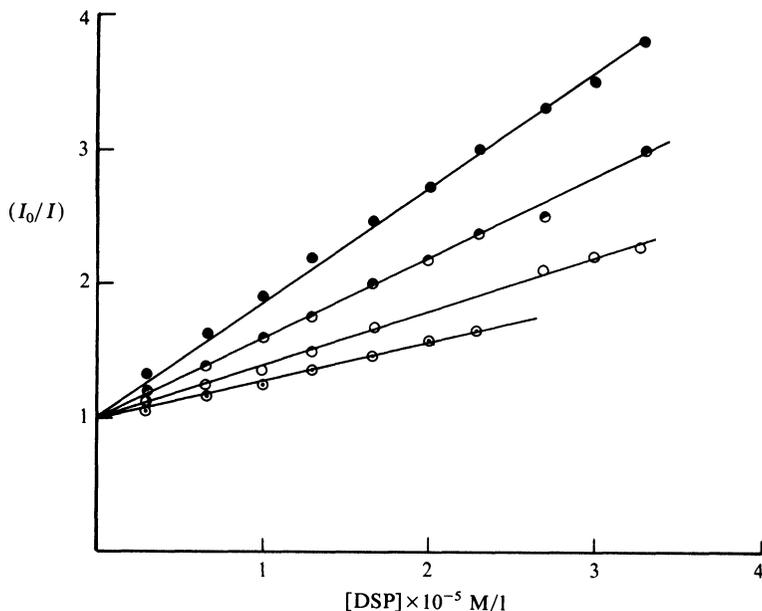


FIGURE 3 Stern-Volmer plots showing fluorescence quenching of a 10^{-5} M P2VB solution using DSP as a quencher, ($\lambda_{\text{ex}} = 337$ nm, $\lambda_{\text{em}} = 420$ nm). The solvents are: \odot ; DMSO, \circ ; 9 ml DMSO + 1 ml ethylene glycol, \bullet ; 7 ml DMSO + 3 ml ethylene glycol and \bullet ; 5 ml DMSO + 5 ml ethylene glycol.

In this mechanism, molecules diffuse in order to come within a critical transfer distance $R_0 = 7.5$ nm. In concentrated solutions, however, diffusion is less important and in the ETDL system of P2VB and DSP, the refractive index of the medium is a major factor compared with the medium viscosity.

Temperature also affects the energy transfer rate constants. Figure 4 shows the change in the value of the Stern-Volmer quenching rate constant (k_q/k_0) as a function of temperature. The trend of the change cannot be explained in terms of viscosity changes. The behaviour shown in Figure 4 can be satisfactorily explained by assuming that k_0 increases with increasing temperature k_q and k_0 are the quenching rate constants (in s^{-1}) in the presence and absence of DSP quencher respectively.

Solutions of P2VB or DSP in DMSO (concentration *ca.* 10^{-3} M/l) show high stability when subjected to nitrogen laser. The dyes continue

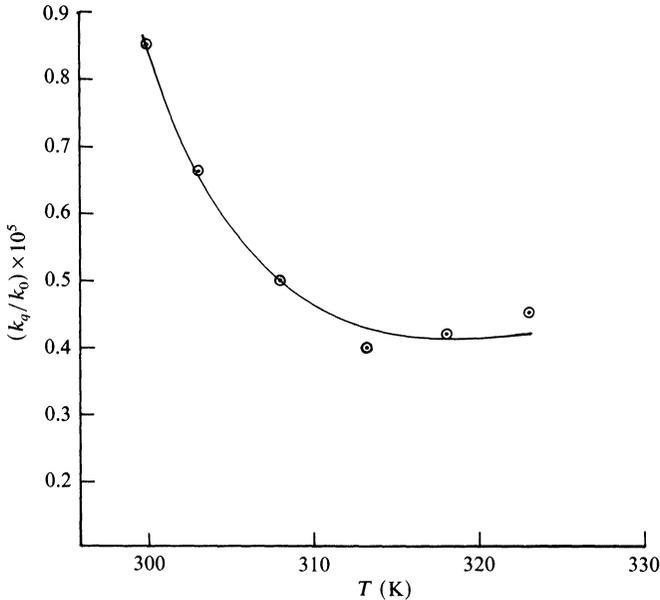


FIGURE 4 Effect of temperature on the Stern-Volmer rate constant (k_q/k_0).

to lase even after being subjected to *ca.* 10^6 nitrogen laser pulses. Irradiation using 337 nm light obtained from a medium-pressure xenon lamp (intensity *ca.* 4×10^{-5} Einstein \cdot min $^{-1}$) for an hour gave virtually no significant changes in fluorescence, excitation or IR spectra. This is not the case when 365 nm is used in irradiation. It seems that the 337 nm light lies within the excitation range of the photoproducts. The main expected photoproducts are photo-oligomers and *cis*-photoisomers¹³⁻¹⁵ that absorb at shorter wavelengths compared with the fresh material.

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