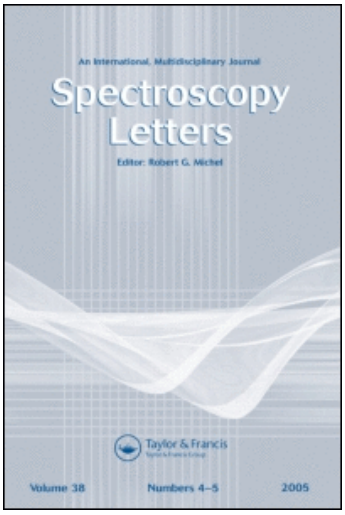

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Benzimidazo Quinolines - Potential Laser Dyes

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To cite this Article Bangar, Raju B. , Varadarajan, T. S. and Mukherjee, T.(1990) 'Benzimidazo Quinolines - Potential Laser Dyes', Spectroscopy Letters, 23: 7, 821 — 829
To link to this Article: DOI: 10.1080/00387019008054461
URL: http://dx.doi.org/10.1080/00387019008054461

SPECTROSCOPY LETTERS, 23(7), 821-829 (1990)

BENZIMIDAZO QUINOLINES - POTENTIAL LASER DYES

KEY WORDS: Laser dyes, Fluorescence quantum efficiency, Fluorescence lifetime, Cross-section of emission, Cross-section of absorption.

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ABSTRACT:

Various photophysical parameters of three substituted 7-diethylamino benzimidazo quinolines (I, II, and III) have been evaluated in three solvents: DMSO, DMF and chloroform. Based on these parameters, the probability of lasing action by the dyes is predicted and is confirmed from the preliminary laser investigations. Dye I (-CN Substitution in 3-position) and Dye III, which has an extended conjugated system in 3-position (- CH = C(CN)COOC H), have been found to be potential laser dyes, while Dye II (- CHO substitution in 3-position) is not.

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INTRODUCTION:

Some of the requirements for any good laser dye are [1]: Broad spectral region of fluorescence, high fluorescence quantum efficiency (ϕ_{fl}), high molar absorption co-efficient at the wavelength of absorption, a short fluorescence life time, (τ), preferably a few nanoseconds or less and a high cross section of fluorescence emission ($\sigma_e(\lambda)$). A dye can be classified as a laser dye if it satisfies these requirements. We herein report the various photophysical parameters like the fluorescence lifetime, the radiative and the non-radiative rate constants, the absorption and the emission cross sections of three 7-diethylamino benzimidazo quinolines (Dye I, II and III) and use these properties to predict the possible laser action from them.

EXPERIMENTAL:

The synthesis and purification of these dyes has been reported recently by Seshadri and co-workers [2]. The absorption and fluorescence spectra were recorded on a Bausch and Lomb Spectronic 2000 uv-visible absorption spectrophotometer and Aminco Bowman Spectrophotofluorometer respectively, and in three spectroscopy grade solvents Dimethyl Sulfoxide (DMSO), Dimethyl formamide (DMF) and Chloroform ($CHCl_3$). The method adopted for recording absorption and fluorescence spectra and for measuring fluorescence quantum efficiency has been described previously [3].

Fluorescence lifetimes were measured using a single photon counting spectrometer (Edinburough Instruments, U.K., model 199 spectrometer) consisting of a thyratron triggered metal bodied coaxial gated hydrogen or nitrogen discharge lamp as the excitation source, operating at a repetition rate of 30 kHz (FWHM~

1 ns), a Phillips XP 2020 Q stop photomultiplier tube and EG & G ORTEC data acquisition system, interfaced with a LSI 11/23 computer (Plessey, U.K.). An appropriate convolution fit programme, based on the true fluorescence decay function G (t) given by

$$G(t) = B \exp(-t/\tau) \qquad (1)$$

where B is the pre-exponential factor and τ, the fluorescence lifetime was used. The observed fluorescence decay function (Figure 1) F(t) is a convolution of G(t) and the instrument response function I(t). The computer fits were evaluated by minimum reduced χ^2 (chi square) values as well as by the distribution of the weighted residuals among the data channels. In all cases reported in this communication, $\chi^2 \sim 1$ was obtained.

RESULTS AND DISCUSSION:

The photophysical parameters of the three dyes in the three solvents are given in table I. The fluorescence decay profiles of all the three dyes in DMSO are shown in figure 1, along with the corresponding lamp response function and the best computer fit following equation (1). The dependence of the fluorescence lifetime on the solvent polarity is shown in figure 2.

The detailed solvent effects on the absorption and fluorescence spectra and fluorescence quantum efficiency of the three dyes are reported elsewhere [3].

It can be observed from figure 2 that the τ values of the non-rigid dyes I and II decrease with increasing solvent polarity, while an opposite dependence is observed in the case of dye III.

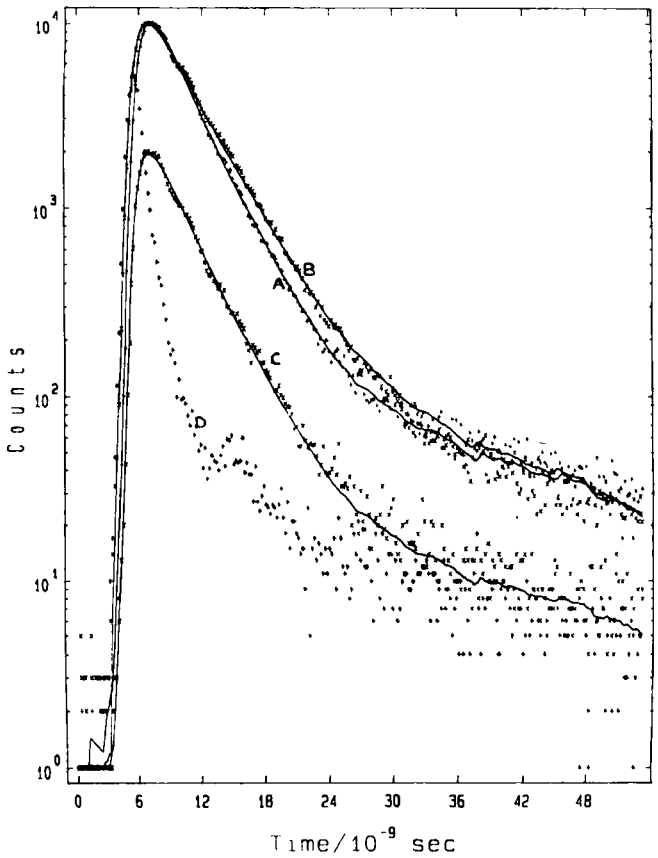

FIG. 1. Fluorescence decay profiles of dyes I(A), II(B) and III(C) in DMSO, along with the instrument profile (D). The solid lines give the computer best fit with $\chi^2 \sim 1.5$. $\lambda_{exc} \sim$ 337 nm., using a N_2-discharge lamp (FWHM ~ 1 ns).

TABLE I

SPECTRAL CHARACTERISTICS OF THE DYES.

DYE	SOLVENT	λ_{ab}^{*} (nm)	λ_{fl} (nm)	ϕ_{fl}	τ (ns)	$k_r \times 10^{-8}$ (s^{-1})	$k_{nr} \times 10^{-8}$ (s^{-1})	$\sigma_e(\lambda) \times 10^{16}$ (cm^2)	$\sigma_a(\lambda) \times 10^{16}$ (cm^2)
I	DMSO	437	488	0.65	3.11	2.09	1.13	0.43	2.86
	DMF	435	486	0.35	3.42	1.02	1.96	0.15	4.88
	CHCl	434	478	0.50	5.34	0.94	0.94	0.16	8.60
II	DMSO	427	486	0.32	3.73	0.86	1.82	0.09	1.14
	DMF	425	484	0.29	3.80	0.76	1.97	0.08	2.08
	CHCl	424	476	0.30	4.28	0.70	1.64	0.08	2.23
III	DMSO	529	622	0.71	3.78	2.20	0.94	1.40	1.79
	DMF	525	618	0.49	2.79	1.76	1.83	0.89	2.40
	CHCl	515	596	0.60	1.64	3.56	2.44	1.52	3.84

* longest wavelength maximum of absorption, an absorption band near 337 nm., is present in all the three dyes in all the three solvents.

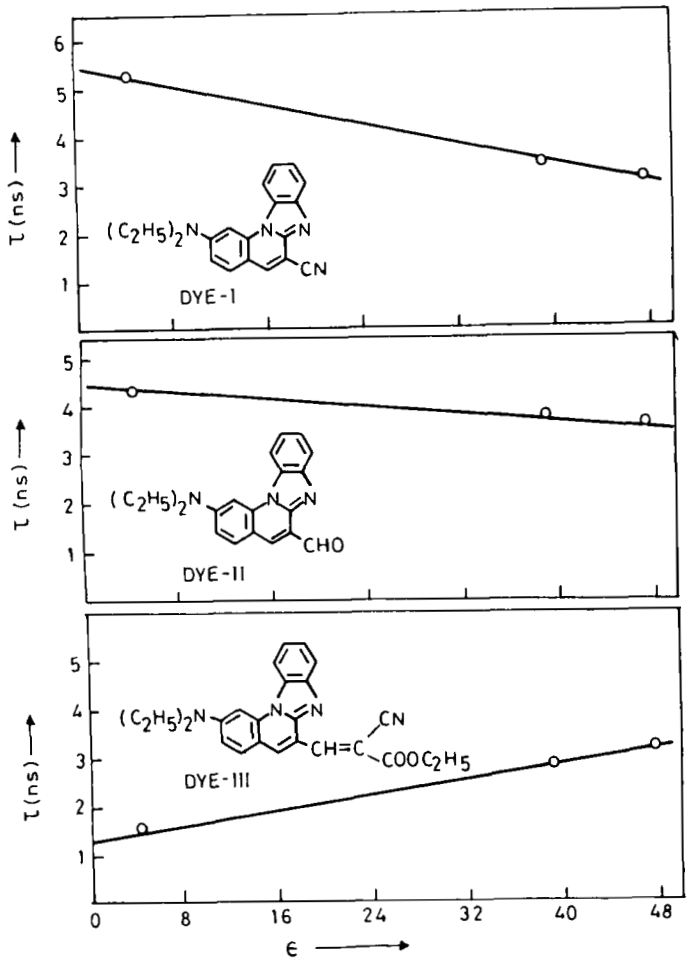

FIG. 2: PLOTS OF FLUORESCENCE LIFE TIME OF DYES AS A FUNCTION OF THE DIELECTRIC CONSTANT OF SOLVENTS.

This can be understood in terms of the extended rigid conjugate structure of the dye (III) molecule.

When Φ_{fl} and τ values are both available, the solvent effects can be resolved in terms of the influences on the radiative (k_r) and the non-radiative (k_{nr}) rate constants [4], given by

$$k_r = 1/\tau_o = \Phi_{fl}/\tau \quad (2)$$

and

$$k_{nr} = (1-\Phi_{fl})/\tau \quad (3)$$

In all the three dyes, although k_r can be accounted to a certain extent, for the changes in Φ_{fl}, the stronger influence involves k_{nr}. This is increased by nearly three times in dye III on going from highly polar solvent (DMSO) to weakly polar solvent ($CHCl_3$).

An important indication for the quality of laser dyes is the cross section of fluorescence emission ($\sigma_e(\lambda)$) given by [5]

$$\sigma_e(\lambda) = \lambda_{fl}^4 E(\lambda)\Phi_{fl}/8\pi c n^2 \tau \quad (4)$$

where $E(\lambda)$ is the normalised fluorescence line shape function, such that, $\int E(\lambda)d\lambda = 1$, 'n' is the refractive index of the solvent and 'C' is the velocity of light in the particular solvent.

The cross section of absorption ($\sigma_a(\lambda)$) is given by [6]

$$\sigma_a(\lambda) = 0.385 \times 10^{-20} \varepsilon_{max} \quad (5)$$

where, ε_{max} is the molar extinction co-efficient of the longest wavelength maximum of absorption.

It can be observed from table I that the cross section of fluorescence emission decreases with decrease in the solvent polarity. This may be explained as due to either a decrease in Φ_{fl} or an increase in τ in weakly polar solvents. The cross section of absorption increases with decrease in solvent polarity and this may be due to the increase in the absorptions of the dyes in weakly/non-polar solvents [3].

The values of $\sigma_e(\lambda)$ of dye III are comparable with that of the standard laser dye, Rhodamine 6G in ethanol, ($\sigma_e(\lambda) = 2.2 \times 10^{-16} cm^2$ at 565 nm[7]) and hence dye III promises to be a potential laser dye. This is supported by a large k_r and a short τ value. Dye II has a very low $\sigma_e(\lambda)$ value and an equally low k_r value, hence it cannot be classified as a laser dye. The behavior of dye I appears to be in between those of dye III and dye II.

Preliminary investigations confirm that Dye III lases when pumped by a Nitrogen laser (Jobin Yvon), while dye I lases by Energy Transfer mechanism and dye II does not lase at all.

It can hence be concluded that the evaluation of the photophysical parameters can be successfully employed to predict the possible laser action of these dyes.

ACKNOWLEDGMENTS:

The authors are extremely thankful to Prof. S. Seshadri, Dyes Research Laboratory, UDCT, Bombay, India, for providing the dyes in the pure form. One of the authors (BRB) is thankful to the University Grants Commission for the award of research fellowship.

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Date Received: 03/19/90
Date Accepted: 04/20/90