Orientation of the Absorption and Emission Transition Moments of Methine Dyes

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The emission anisotropies of the fluorescence of the prolate molecules 2[4(N,N-dimethyloamino)-α styrylo]benzothiazol and 2[4(N,N-dimethyloamino)α styrylo]benzoksazol in solvents of different viscosities were measured, yielding information about the rotational motion of the molecules.

The non-linear dependence of $1/r$ on T/η was confirmed. On the basis of a comparison of experimental and quantum chemical calculations the orientation of the transition moments of the dye molecules is proposed.

Introduction

Recently, studies of the dependency of the spectral characteristics of methine dyes on the molecular composition of the dyes, on the solvent polarity and on the temperature of the sample were made [1–3].

The aim of this study was to find out the orientation of absorption and fluorescence transition moments and their thermal motion in solvents with different viscosities. The experimental results are compared with Pariser-Parr-Pople SCF MO calculations.

Materials and Methods

The compounds examined were:

A) 2[4(N, N-dimethyloamino) α styrylo] benzothiazol

B) 2[4(N, N-dimethyloamino) α styrylo] benzoksazol.

The absorption and emission spectra and the lifetimes of the dyes were measured as previously described [2, 3]. The emission anisotropy of the solution was measured using a compensation polarimeter [4]. All spectral parameters were measured at room temperature in methanol with different amounts of glycerol to get solvents of different viscosities.

The PPP — SCF MO method with the Mataga and Nishimoto integral approximation [5] and with the parametrization of Kwiatkowski [6, 7] were used. The investigated molecule structures were taken the same as already described [8].

Results and Discussion

The absorption spectra measured in methanol and in methanol-glycerol mixtures are practically the same. A characteristic feature of the emission spectra is the increase of intensity of the second fluorescence band ($\lambda_{max} \approx 538$ nm in Fig. 1) caused by glycerol. This change is similar to previously observed emission variations in the case of methanol water mixtures [3].

The calculated electronic transition energies and relative oscillator strengths (f) are compared with the experimental spectra (A, F) in Figure 1. In this Figure the emission anisotropy spectrum r is also plotted. The absorption band agrees qualitatively with the calculated electronic transition. The emission anisotropy spectrum (see Fig. 4) clearly shows in the case of methine with the sulphur atom two different values of r throughout the dual fluorescence band. This indicates that the emission is composed of two electronic transitions.

To find out the angles between the absorption and fluorescence transition moments the emission anisotropy (EA) as a function of viscosity (η) was measured.

According to the theory [9] the rotational depolarization of fluorescence emitted by molecules in solution depends on the ratio of their lifetime τ in

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the excited fluorescent state to the rotational relaxation time θ'. As was shown by Perrin [10], the emission anisotropy r is governed by the equation

$$\frac{r}{r_0} = \frac{1}{1+\tau/\theta'}, \quad \text{with} \quad \frac{1}{\theta'} = \frac{kT}{V_{\text{eff}}\eta}, \qquad (1)$$

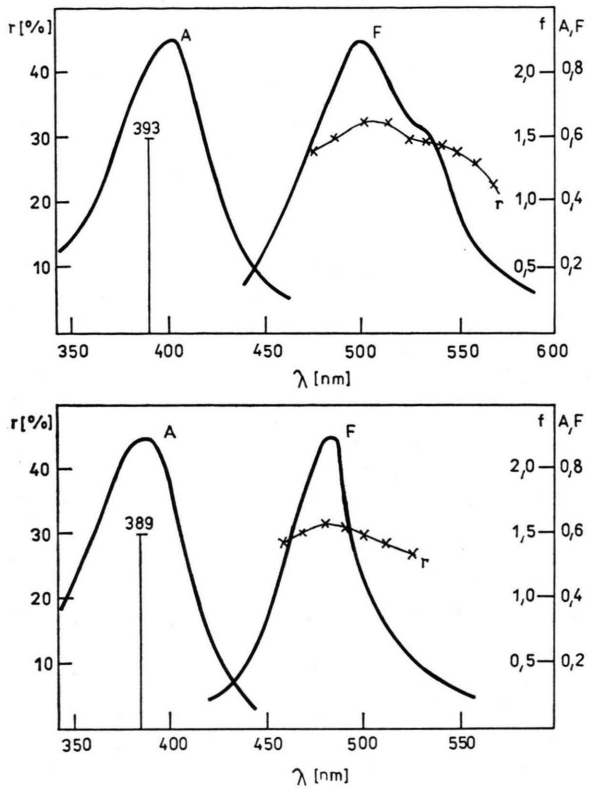

Fig. 1. The absorption (A) and emission (F) spectra, the emission anisotropy (r) measured throughout the fluorescence band and calculated values of absorption wavelength (393 nm and 389 nm) and oscillator strength for methines type IA and IVB from Figure 4.

where r_0 denotes the limiting emission anisotropy, i.e. the value observed when rotational depolarization is negligible, V_{eff} is an effective volume of the spherical molecule of the same volume as that of the prolate molecule. If the EA is measured as a function of temperature and (or) viscosity, one is able to estimate the values of r_0 and θ'. Using Perrin's equation for the fundamental emission anisotropy [10] and substituting this fundamental anisotropy by an experimental value of r_0 one can obtain an angle between the absorption and emission transition moments (β).

The experimental results obtained with both types of dyes are shown in Figures 2 and 3. These results exhibit a non-linear dependence of $-1/r$ on T/η. The non-linear dependence observed for several luminescent systems [9, 10, 11, 12, 13, 14, 15] has been attributed to the asphericity in the Brownian rotation at low viscosity and to solvation effects. Recently, Kawski et al. [16] hav obtained similar data using prolate luminescent molecules. Kawski et al. [16] have developed a theory based on the assumption that the prolate luminescent molecules perform irregular rotational motions within a limited solid angle ($\langle\beta_{\max}\rangle$). According to this theory

$$\frac{r}{r_0} = A + \frac{1-A}{1+\tau/\theta}, \quad \text{with} \quad \frac{1}{\theta} = \frac{6D}{1-A},$$

and $6D = kT/V_{\text{eff}}\eta$,

where V_{eff} (in m^3) is an effective volume of a spherical molecule of the same volume as that of the prolate one.

On comparison of the theory with the experimental results, the parameter A of the investigated molecules was evaluated from the r_0/r dependence

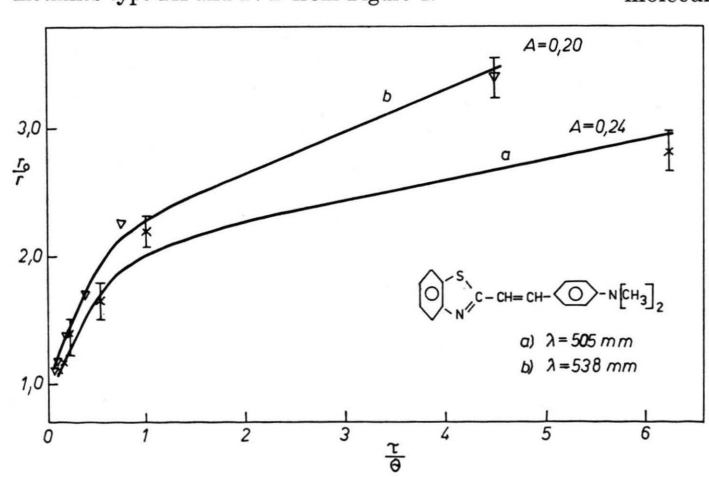

Fig. 2. Reciprocal of emission anisotropy versus τ/θ. The points are the experimental values and the drawn lines are the theoretical curves for a) $A = 0.24$; b) $A = 0.20$.

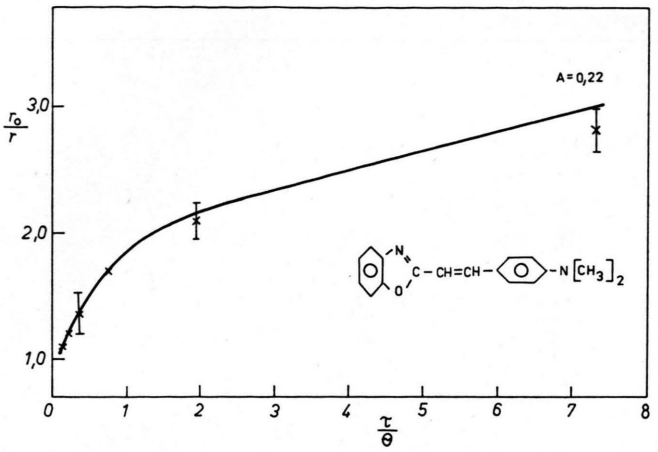

Fig. 3. Reciprocal of emission anisotropy versus τ/θ. The points are the experimental values and the drawn line is the theoretical curve for $A = 0.22$.

on $\tau/\theta = cT/\eta$, where $c = k\tau(1-A)V_{\text{eff}} = \text{const.}$ The parameter A depends on the solid angle $\langle\beta_{\max}\rangle$ for the rotational relaxation time [16]. Therefore, having A one can find out the values of $\langle\beta_{\max}\rangle$. Table 1 shows the determined quantities.

These EA results demonstrate that:

1) the fluorescence bands can be attributed to two different electronic excited states with different β angles.

2) the investigated methines undergo more than one kind of rotational motion in solvents with different viscosities, giving a non-linear relationship between $1/r$ and T/η.

In order to correlate the directions of the transition moments of absorption and emission with the structure of the dye molecule we have calcu-

Table 1. The determined quantities of the investigated methines.

Dye	Maximum of fluorescence	r_0	$V_{\text{eff}} \times 10^{-30}\,\text{m}^3$	$\langle\beta_{\max}\rangle$	β
A	505 nm	0,3571	1497	45°38′	15°57′
	538 nm	0,3293	1348	47°31′	20°12′
B	476 nm	0,3636	1758	46°15′	14°26′

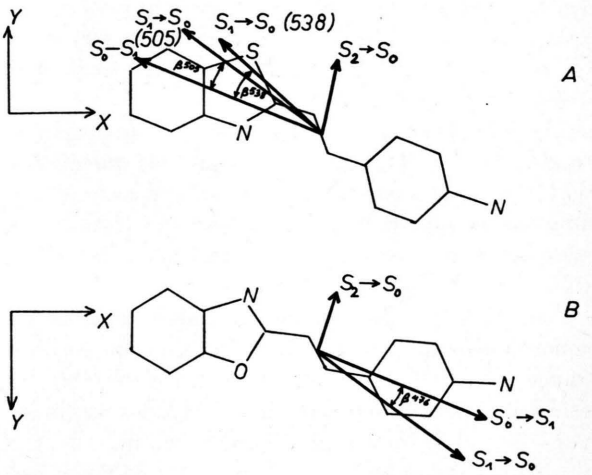

Fig. 4. The molecular structures with their transition moments.

lated, using the PPP method, the polarization of absorption transition moments. Assuming that the theoretical transition moments of absorption give the directions of experimentally obtained absorption transitions we are able to visualize the orientation of the transition moments for different molecular structure [8] of dyes (Figure 4).

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