Dyes and Pigments 5 (1984) 253–262

Spectral Properties of 7*H*,9*H*-Quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one

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(Received: 1 March, 1983)

SUMMARY

The basic spectral properties (absorption and emission spectra, emission anisotropy and emission lifetime) of 7H,9H-quinazolino[3,2-b]benz-[d,e]isoquinolin-7-one were measured and compared with theoretical predictions.

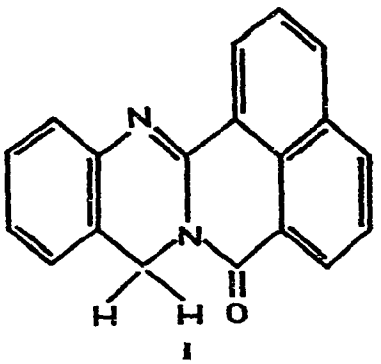
On the basis of Perrin's and Kawski's theories the rotatory motion of the dye was also studied. The electric dipole moments in both ground and excited states and the orientation of the transition moments were obtained.

1. INTRODUCTION

The synthesis and application of the disperse dyes derived from 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one have been investigated.[1]

Similar compounds have been used for dyeing synthetic fibres (polyesters, polyamides and polyacrylonitriles). Although some colour

Dyes and Pigments 0143-7208/84/$03·00



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and application properties of such compounds have been studied there is lack of information regarding their spectral characteristics.

This paper deals with the spectral effects of solvation and complexing of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one (**I**). A comparison of theoretical predictions with experimental data is also presented.

2. MATERIALS AND METHODS

The 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one was synthesised as already described.[1] The compound was thoroughly characterised and chromatographically purified.

The optical characteristics (absorption, emission spectra and fluorescence lifetime) of the dye were measured as previously described.[2,3] The fluorescence was excited at 405 nm and the wavelength of excitation was selected with an interference filter with 5·5 nm bandwidth. The emission anisotropy in methanol–glycerol mixtures was measured using a compensation polarimeter.[4]

To calculate charge distribution, bond orders and other molecular quantities the Pariser–Parr–Pople SCF–MO–CI method with the Mataga–Nishimoto integral approximation[5] and with the parameterisation of Kwiatkowski[6,7] was used. The molecular structure was taken to be planar with bond lengths of 1·397 Å and angles of 120°. The bond length of C=O was 1·24 Å. The resonance integrals β between given atoms were assumed to be:

$$\beta_{CC} = -2{\cdot}294\ \text{eV} \qquad \beta_{CN} = -2{\cdot}1\ \text{eV} \qquad \beta_{CO} = -2{\cdot}5\ \text{eV}$$

3. RESULTS AND DISCUSSION

To elucidate the charge distribution in both ground and excited singlet states and the bond orders the PPP–SCF–MO–CI calculations have been used. Results are shown in Fig. 1.

The absorption (A) and emission (F) spectra in methanol are shown in Fig. 2, which includes theoretical values of relative oscillator strengths calculated using the PPP method. As can be seen, the absorption spectrum has a broad band in the visible region with a maximum at about 400 nm. The position of band maxima and band shape of absorption are practically unchanged in different solvents or by changing the dye concentration. Such results indicate that the poorly resolved absorption band is probably associated with a monomeric form of the dye.

The fluorescence spectrum of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]-isoquinolin-7-one has two maxima (F_I,F_{II}; see Fig. 2). Both emission bands are shifted towards longer wavelengths as the polarity of the solvent increases (see Figs. 3 and 4). However, in both types of solvent (non-polar and polar) the shape of the emission spectra depends strongly on dye concentration (Figs. 3 and 4).

Fluorescence spectra which are shown in Figs. 3 and 4 were normalised at λ_{max} taken from the lowest dye concentration spectrum. Figure 5 shows the dependence of the ratio of the intensities of the two maxima of

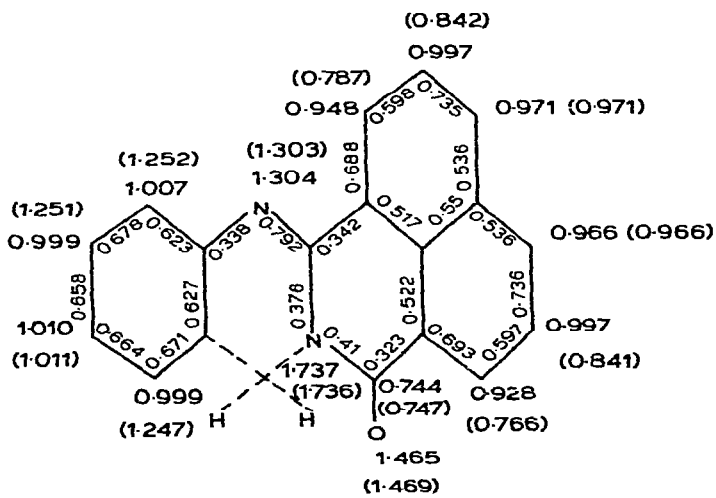

Fig. 1. Calculated values of π-electronic charge distribution in the ground and (in parentheses) first excited singlet states and bond orders of the dye.

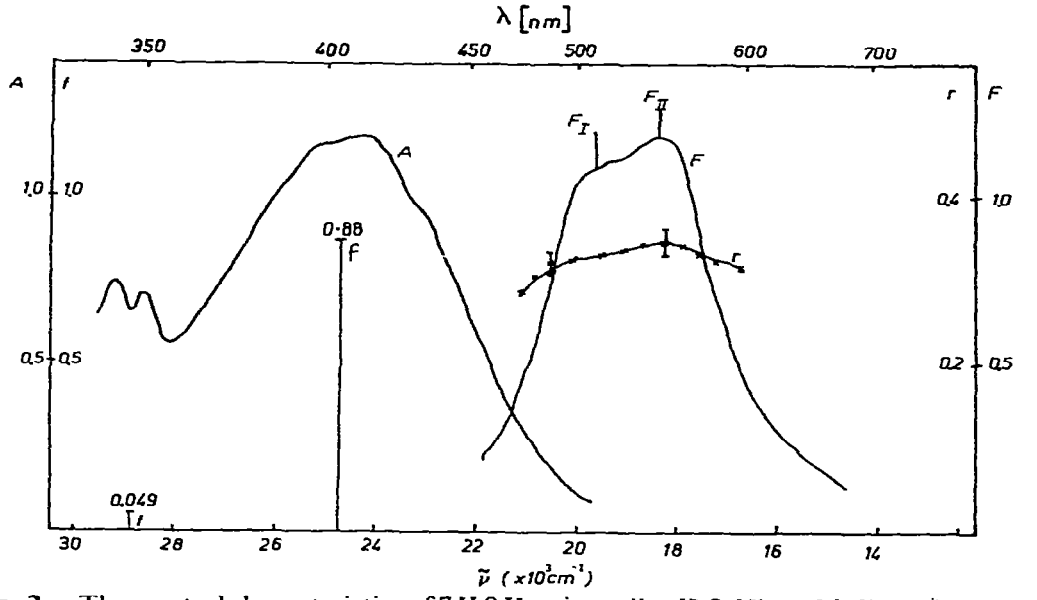

Fig. 2. The spectral characteristics of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one. *A* and *F* represent the absorption and emission spectra respectively, *r* is the emission anisotropy and *f* the oscillator strength.

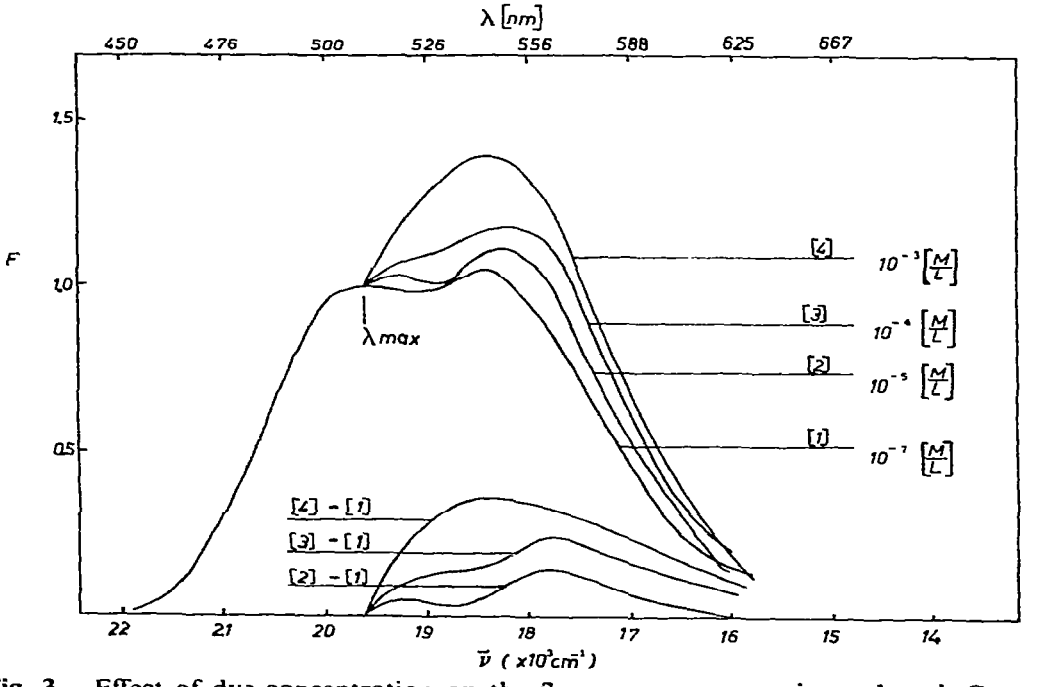

Fig. 3. Effect of dye concentration on the fluorescence spectra in methanol. Curves [2] – [1], [3] – [1], [4] – [1] represent the differences between respective emission spectra.

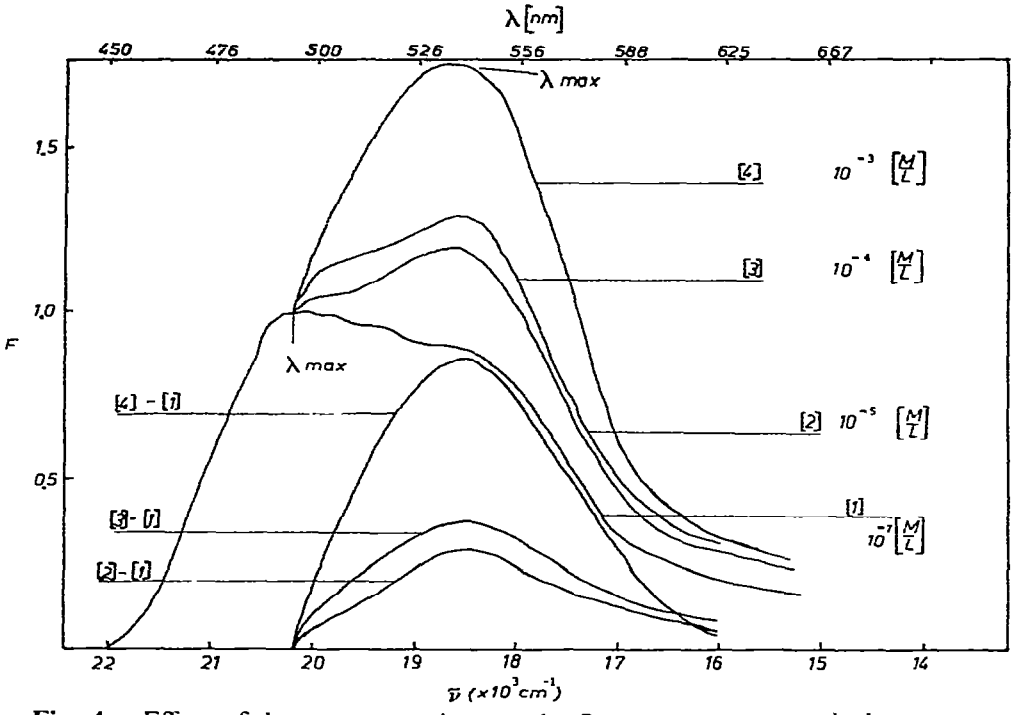

Fig. 4. Effect of dye concentration on the fluorescence spectra in benzene.

fluorescence bands. A relative increase of the second band with higher concentrations is observed. This effect of dye concentration on the emission spectrum is stronger in non-polar solvents than in polar ones. In benzene large increases of the long wavelength emission band are observed at low dye concentrations (*ca.* 10^{-4}M; Fig. 4) whereas in polar solvents this increase is much lower. These results suggest that:

(i) the second band of fluorescence (the long wavelength band) can be attributed to the excimer emission, and that
(ii) the excited state of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one is characterised by a higher dipole moment (μ_e) than the ground state (μ_g).

To clarify the above two suggestions the following measurements have been carried out

(i) an emission anisotropy spectrum (r in Fig. 2)
(ii) the emission anisotropy as a function of viscosity (η), and
(iii) estimation of dipole moments (μ_e and μ_g).

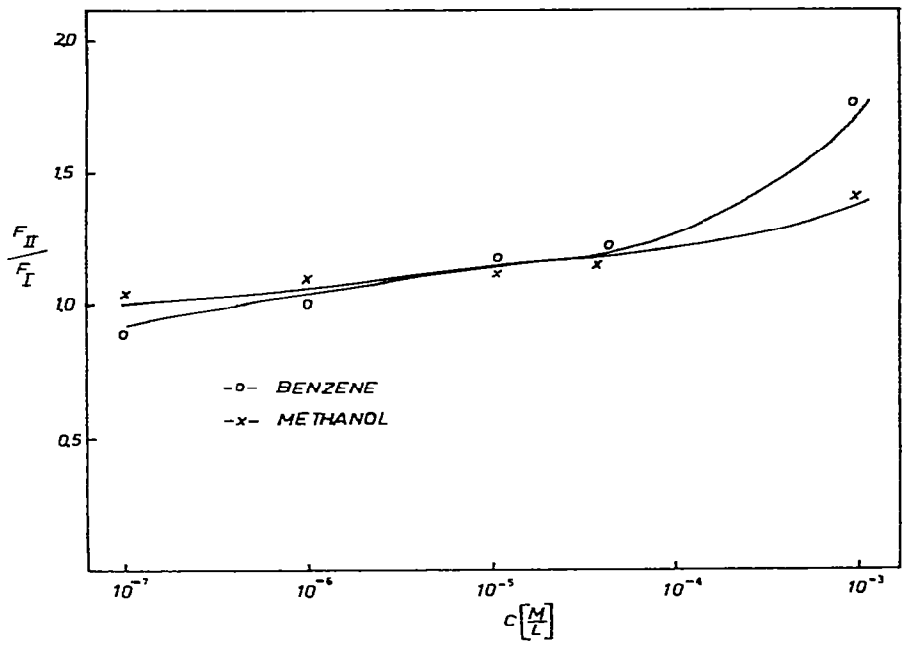

Fig. 5. Dependence of the ratio of the intensities of the two fluorescence band maxima on the dye concentration.

As can be seen from Fig. 2 the emission anisotropy spectrum shows two different values of r for two fluorescence bands. Such results strongly indicate that emission derives from two electronic transitions, in support of the concept of excimer formation.

To find out the angles between absorption and fluorescence transition moments and to examine the effects of motion of the dye molecule, emission anisotropy as a function of solvent viscosity was measured. According to theory[8] the rotation depolarisation of fluorescence emitted by molecules in solution depends on the ratio of their lifetime τ in an excited fluorescent state to a rotational relaxation time θ'. Perrin[9] has shown that the emission anisotropy, r, is governed by the equation

$$\frac{r}{r_0} = \frac{1}{1 + (\tau/\theta')} \tag{1}$$

where

$$\frac{1}{\theta'} = \frac{kT}{V_{\text{eff}}\eta}$$

and r_0 denotes a limiting value of r (i.e. the value observed when

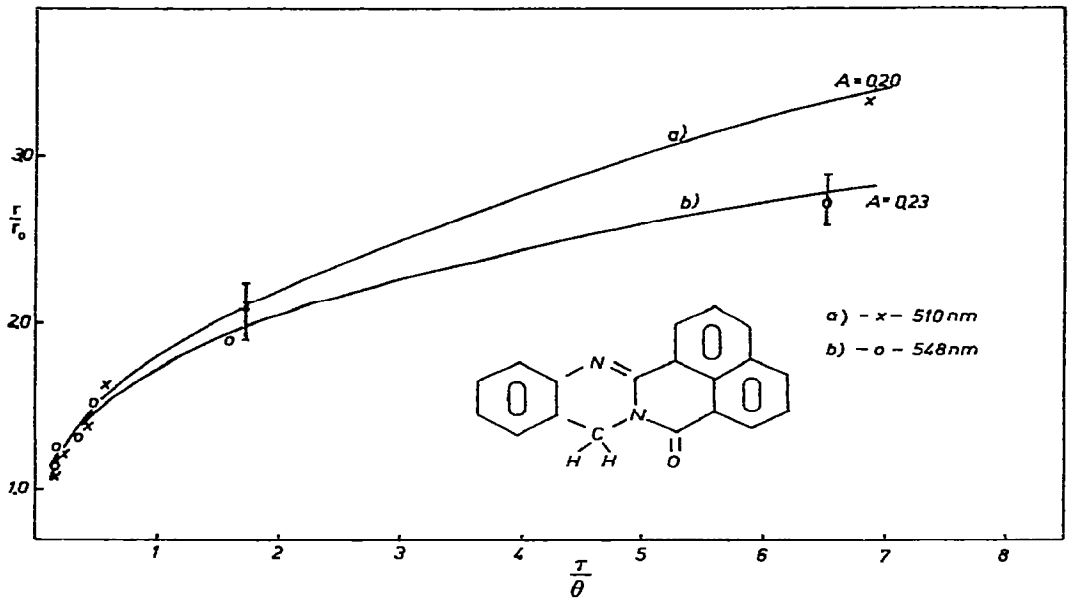

Fig. 6. Reciprocal of emission anisotropy (r) versus ratio of the fluorescence lifetime to the rotational time (τ/θ). The points are the experimental values and the drawn lines are the theoretical curves.

rotational depolarisation is negligible), V_{eff} is an effective volume of the molecule and T is the temperature of the sample. If the emission anisotropy is measured as a function of temperature and (or) viscosity, one is able to estimate the values of r_0 and θ' (or V). Using Perrin's[9] equation for a fundamental emission anisotropy and substituting this fundamental anisotropy by an experimental value of r_0 one can obtain an angle between absorption and emission transition moments, β.

However, experimental results exhibit a non-linear dependence of $1/r$ and T/η (Fig. 6). Such non-linearity observed for several systems[10-12] has been attributed either to the asphericity of the law of Brownian rotation at low viscosity or to solvation effects. Recently, Kawski *et al.*[13] have obtained similar data using prolate luminescent molecules. They have developed the theory based on the assumption that the prolate molecules perform irregular rotation motions within a limited solid angle, $\langle\beta_{\max}\rangle$. According to this theory,

$$\frac{r}{r_0} = A + \frac{1-A}{1+(\tau/\theta)} \qquad (2)$$

TABLE 1
Calculated Light Emission Values for 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]isoquinolin-7-one

Fluorescence maximum (nm)	r_0	$V_{eff} \times 10^{-30}$ (m^3)	β	$\langle\beta_{max}\rangle$
510	0·3643	2372	14°18′	47°31′
548	0·3851	2588	9°10′	46°16′

where

$$\frac{1}{\theta} = \frac{6D}{1 - A}$$

and

$$6D = \frac{kT}{V_{eff}\eta}$$

On comparison of the theory with the experimental results, the parameter A was evaluated from the r_0/r dependence on $\tau/\theta = c(T/\eta)$, where $c = k\tau(1 - A)V_{eff} = \text{constant}$. The parameter A depends on a solid angle $\langle\beta_{max}\rangle$. Therefore, from A the values of $\langle\beta_{max}\rangle$ can be obtained. Table 1 shows the calculated quantities.

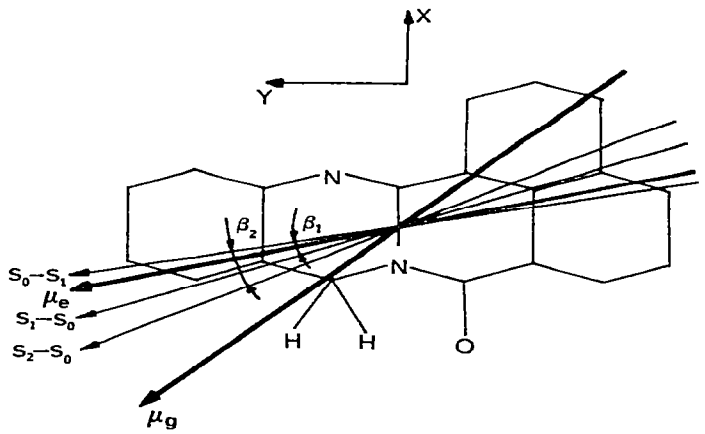

Fig. 7. The orientation of transition moments and the π-electron dipole moments in the molecular structure. $\mu_g = 4{\cdot}15\text{D}$; $\mu_e = 7{\cdot}40\text{D}$.

These results suggest again that the fluorescence bands can be attributed to two different electronic excited states with different β angles.

In order to correlate the directions of the transition moments of absorption and emission with a structure of the dye molecule, the polarisation of the absorption transition moment was calculated using the PPP method. Assuming that theoretical polarisation of absorption gives the direction of experimentally obtained absorption transition and knowing the angles β, one is able to visualise the orientation of transition moments for the dye (Fig. 7).

4. CONCLUSIONS

It may be concluded from the results that 7*H*,9*H*-quinazolino[3,2-*b*]-benz[*d*,*e*]isoquinolin-7-one gives two fluorescence bands. The intensity of the long wavelength band of fluorescence increases with increasing dye concentration. This indicates that 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]-isoquinolin-7-one has a tendency to aggregate in the excited state giving excimers. This effect is stronger in non-polar than in polar solvents, indicating that in non-polar solvents the probability of excimer formation is higher. A second conclusion is that the dye molecules undergo more than one kind of rotational motion in solvents with different viscosities giving a non-linear relationship between $1/r$ and T/η. Additionally it has been shown that the excited state of 7*H*,9*H*-quinazolino[3,2-*b*]benz[*d*,*e*]-isoquinolin-7-one is characterised by a higher dipole moment than the ground state.

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