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SOME PROPERTIES OF DUAL FLUORESCENCE OF METHINE DYES

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SUMMARY

Studies of the dependence of methine dye absorption and fluorescence properties on the molecular composition of the dyes, on solvent polarity and on the temperature of the sample were made. The results have confirmed our recent suggestion that the emission band of methine dyes in polar solvents is composed of molecular and excimer fluorescence The spectral properties of different types of molecular composition of methine dyes indicated the centre in the dye molecule involved in excimer formation On the basis of a liquid nitrogen temperature spectrum and the lifetimes of fluorescence it is suggested that this type of methine dye which can form the excimers has a strong tendency to aggregate in the ground states These aggregates are able to quench the molecular fluorescence An increase of solvent polarity causes disaggregation of dye molecules giving an increase of molecular fluorescence and an increased probability of excimer formation. Thus, in polar solvents the long-wavelength emission band arises

1 INTRODUCTION

Recently, we have found that methine dyes in polar solvents emit a dual fluorescence [1] From the dependence of the fluorescence spectrum on the dye concentration it has been suggested that excimer formation is responsible for the second band of fluorescence [1] However on the basis of those results a contribution of a polar-solvent-assisted isomerisation of an excited molecule via internal rotation of the $N(CH_3)_2$ and $N(C_2H_5)_2$ groups to the observed dual fluorescence has not been excluded.[1]

In this paper we present the experimental results concerning the specific factors

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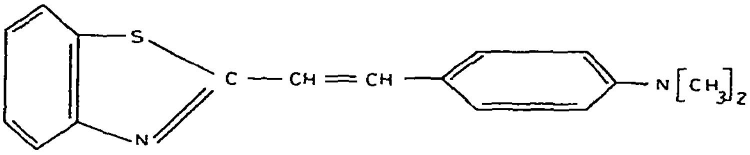
which control formation of the excited states responsible for the dual fluorescence We have measured the influence on spectral characteristics of methine dyes of (1) different rotamer groups (dyes **I**); (2) changing the sulphur for oxygen in the pigment molecule (dyes **II**) and (3) changing polarity and temperature of the sample

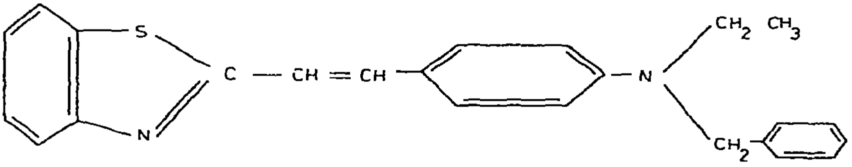
2 MATERIALS AND METHODS

The methine dyes used were



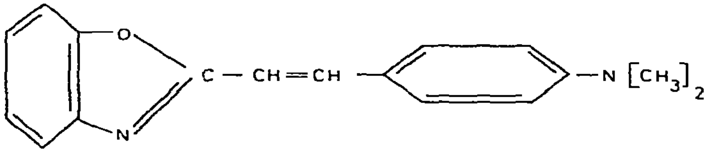
2-[4-(*N*,*N*-dimethylamino)-α-styryl]benzothiazole

Ia



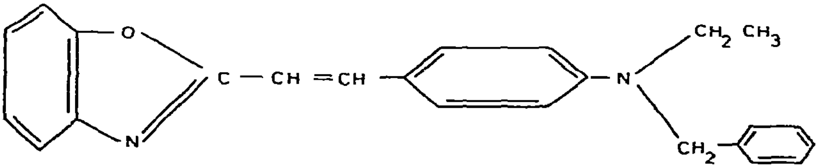
2-[4(*N*-ethyl-*N*-benzylamino)-α-styryl]benzothiazole

Ib



2-[4-(*N*,*N*-dimethylamino)-α-styryl]benzoxazole

IIa



2-[4-(*N*-ethyl-*N*-benzylamino)-α-styryl]benzoxazole

IIb

The dyes were synthesized as already described [2] The compounds were thoroughly identified and chromatographically purified The absorption spectra were measured with an UV-VIS Zeiss spectrophotometer The fluorescence spectra and quantum fluorescence yield were measured with an apparatus described elsewhere.[3] The liquid nitrogen temperature spectra were measured with a specially constructed Dewar device [4] The fluorescence was excited at 405 nm and the wavelength of excitation was selected with an interference filter (5·5 nm bandwith) Quantum yield of fluorescence was estimated by comparing the absorption and emission spectra of investigated dyes with those of fluorescein It was assumed that quantum yield of fluorescein emission equals 90 %.

3. RESULTS AND DISCUSSION

If an internal rotation of the NR groups (where R represents the different substituents) is responsible for the dual fluorescence, different substituents R would be expected to influence the shape of the fluorescence spectra of methine dyes The fluorescence spectra should be affected differently by rotamer groups of different mass Figures 1 and 2 show the absorption and emission spectra of dyes **I** in polar (methanol) and non-polar (benzene) solvents As can be seen from those results, the spectral parameters of absorption and emission of both types of dyes **I** are quite similar. In the polar solvents both types of dyes exhibit a second fluorescence band

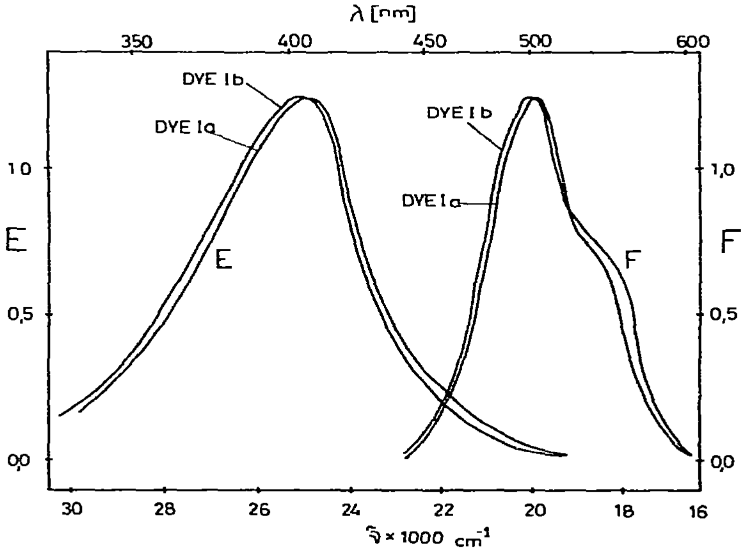


Fig 1 The absorption (E) and emission (F) spectra of dyes **I** in methanol

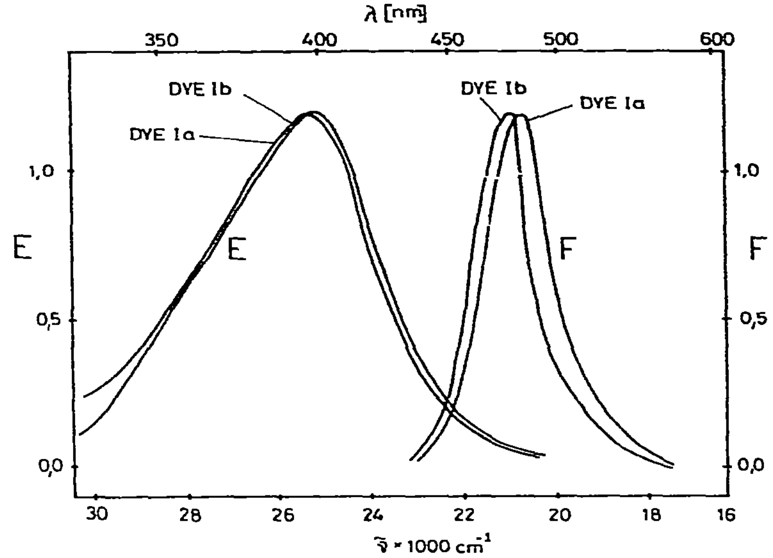


Fig 2 The absorption (E) and emission (F) spectra of dyes **I** in benzene

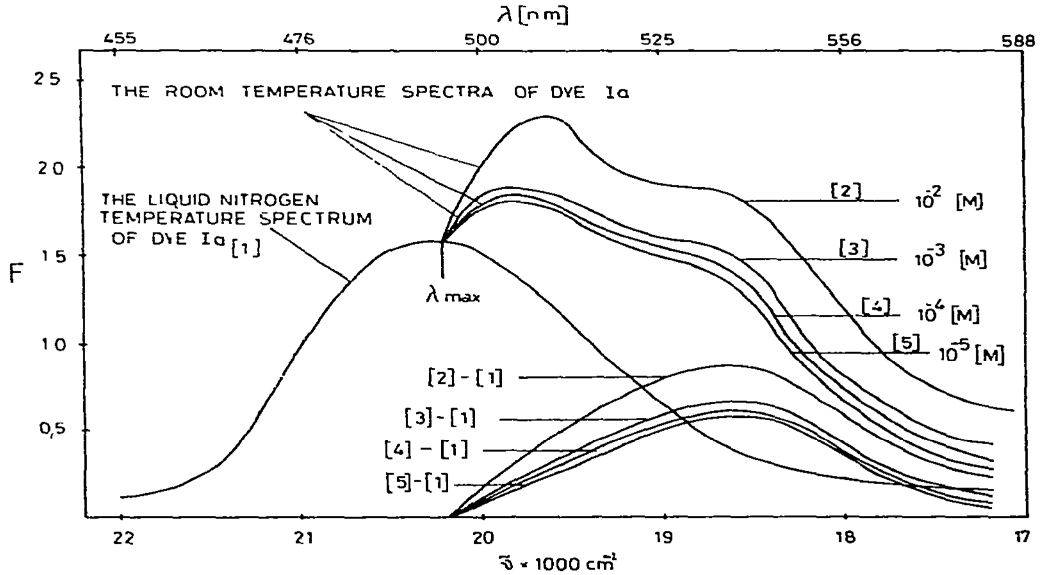


Fig 3 Effect of the dye **Ia** concentration on the fluorescence spectra in methanol Curves [2] – [1], [3] – [1], [4] – [1] and [5] – [1] represent the difference between respective emission spectra giving the second fluorescence band

with a maximum at 538 nm and 545 nm, respectively (Fig. 1). However, in polar solvents, shape of emission spectra depends strongly on dye concentration (Figs 3 and 4).

Fluorescence spectra which are shown in Figs. 3 and 4 were normalized at λ_{max} taken from a liquid nitrogen temperature spectrum.

Those results are in good agreement with our recent data[1] and favour the excimer fluorescence as against the rotamer hypothesis It is worth noting that at low temperatures the fluorescence spectrum of methine dyes in methanol becomes similar to the emission spectrum of dyes in the non-polar solvent This observation, taken with that in a liquid crystal matrix,[6] indicates that a dual fluorescence comes from the excimers formed in polar solvents by a diffusion-controlled collision process

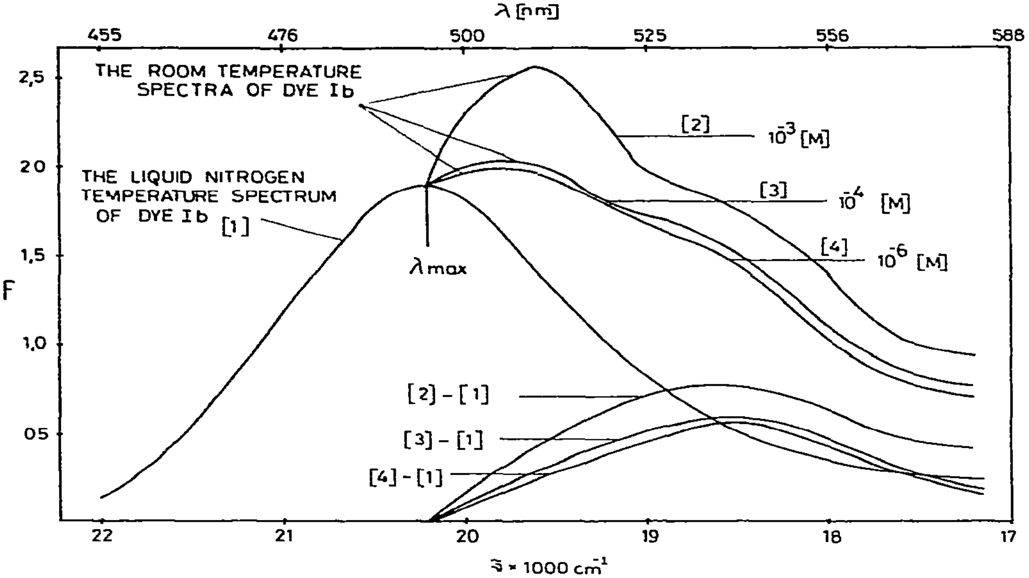


Fig 4 Effect of the dye **Ib** concentration on the fluorescence spectra in methanol Curves [2] – [1] [3] – [1] and [4] – [1] represent the difference between respective emission spectra giving the second fluorescence band

The spectral characteristics of the second type of methine dye (dyes **II**) have been measured to find out any influence of molecular composition on the excimer formation The molecules of the dyes **II** contain in their structure oxygen instead of sulphur atoms and give the absorption and emission spectra shown in Figs. 5 and 6. In this case the second band of fluorescence does not arise even in polar solvents. Polarity of the solvents caused slight changes in position and in half-width of the

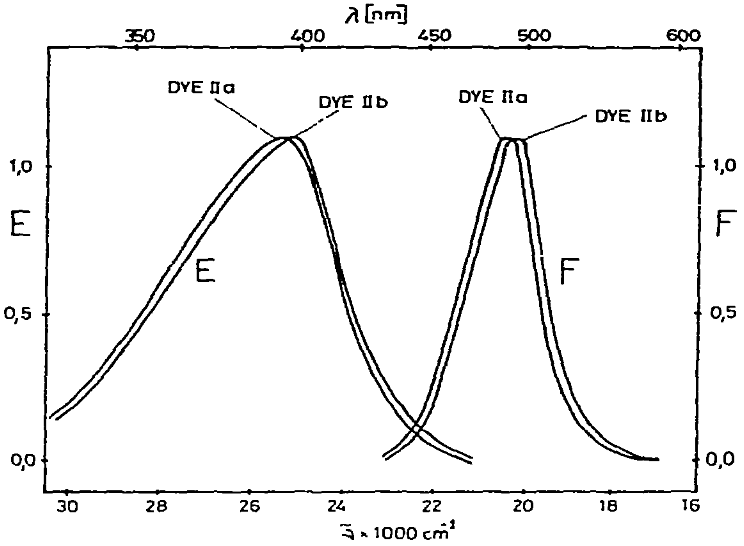


Fig 5 The absorption (E) and emission (F) spectra of dyes **II** in methanol

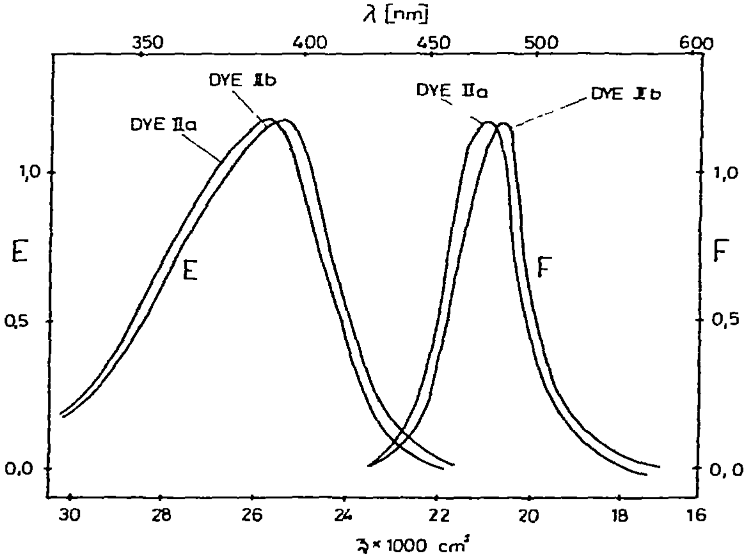


Fig 6 The absorption (E) and emission (F) spectra of dyes **II** in benzene

absorption and emission bands of dyes **II** (Figs. 5 and 6). The observed changes could be simply explained in terms of solute–solvent interactions.[7,8] Therefore the position in the molecular structure of the methine dyes that is connected with an excimer formation has been located.

An influence of the solvent polarity on the fluorescence of dye **Ib** is shown in Fig. 7. Emission spectra given in Fig. 7 were normalized at λ_{max} taken from a liquid nitrogen temperature spectrum. The results have clearly shown that the intensity of the second band of methine dye fluorescence depends on the polarity of solvent It is important to point out that an increase of solvent polarity causes the increase of fluorescence yield measured at λ_{max} (Fig 8). It means that the short-wavelength band of fluorescence increases too with increasing solvent polarity A quantum fluorescence yield of dye **Ia** in methanol is higher (20 %) than that in the non-polar solvent, benzene (13 %) This indicates that the short-wavelength maximum of emission is connected with the fluorescence of excited dye monomers The variation of solvent polarity causes alterations in the degree of methine dye aggregation changing the fluorescence yield of monomers and increasing the probability of the excimer formation A process of aggregation seems to take place even at quite low dye concentrations. Unpublished results have shown that the quantum fluorescence yield of the 'short-wavelength' band decreases, starting from a dye concentration of

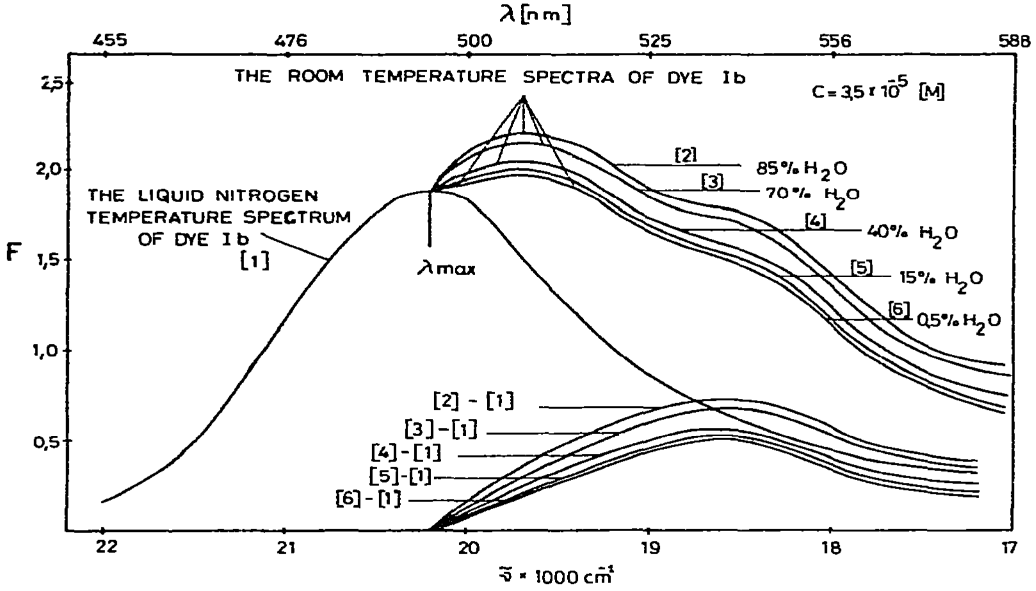


Fig 7 Effect of the water in methanol (v/v) concentration on the fluorescence spectra of dye **Ib**

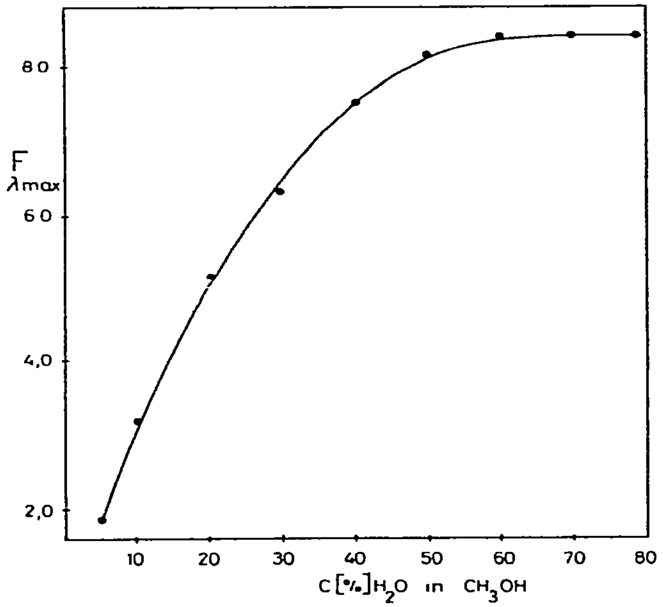


Fig 8 Dependence of the fluorescence intensity of dye **Ib** measured at λ_{max} (see Fig 7) on the water in methanol (v,v) concentration

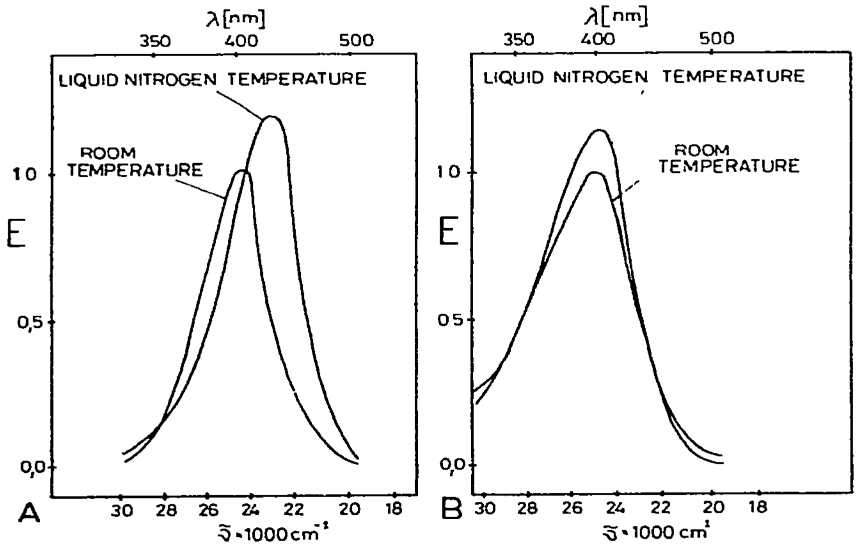


Fig 9 The absorption spectra of dyes **Ia** (A) and **IIa** (B) in methanol

the order of 10^{-5}M. Such results suggest that the concentration of non-fluorescent dye aggregates is high enough even at a dye concentration of 10^{-5}M to change the monomeric fluorescence yield The strong tendency of methine dye to aggregate provides a good explanation for the short lifetimes of excited electronic states[1] measured at dye concentrations of the order of 10^{-5}M The longer 'true' lifetimes of methine dyes are shortened by non-fluorescent aggregates in dynamic quenching of excited monomers.

The concentration of methine dye aggregates can be changed not only by solvent polarity but also by changing the temperature of the solution In Fig 9 the absorption spectra of the dyes measured at liquid nitrogen and room temperatures in methanol are compared Similar results have been obtained with dyes **Ib** and **IIb**. A maximum absorption of those dyes at low temperature is shifted towards a longer wavelength in the case of dyes **I**, whereas it is practically unaffected for the dyes **II** Assuming that the observed long-wavelength shift of the absorption maximum is due to an increase of aggregate concentration the results shown in Fig 9B mean that either the concentration of dye **II** aggregates is very high at room temperature and in this case the lifetimes of fluorescence should be very short because of quenching processes, or a tendency for the aggregation of dyes **II** is weaker than that of dyes **I** so that the lifetime of fluorescence of these dyes should be much longer The values of the lifetimes given in Table 1 have shown that the second possibility is the more plausible In a non-polar solvent (benzene) where dyes **I** show marked tendency for aggregation and where the lifetime of fluorescence is very short,[1] temperature of the sample does not affect the absorption spectra. Therefore, it is reasonable to suggest that the methine dyes with the S atoms in their molecular structure have a marked tendency for complexation The complexes formed with unexcited molecules are non-fluorescent aggregates which caused a quenching of monomeric fluorescence whereas complexes formed with the help of excited electronic levels emit a long-wavelength fluorescence Intensity of emission of long-wavelength fluorescence increases with increasing probability of excimer formation

TABLE 1
FLUORESCENCE LIFETIME OF METHINE DYES

Dye	*Lifetime of fluorescence (ns)*		
	Benzene	*Methanol*	
		First band	*Second band*
Ia	0.50 ± 0.25	1.00 ± 0.25	1.50 ± 0.25
Ib	0.75 ± 0.25	1.75 ± 0.25	2.00 ± 0.25
IIa	2.50 ± 0.25	2.50 ± 0.25	—
IIb	2.50 ± 0.25	2.50 ± 0.25	—

4 CONCLUSIONS

It has been shown that methine dyes with S atoms in their molecular composition give a dual fluorescence in polar solvents The short-wavelength band of the dual fluorescence has shorter lifetime of emission than the long-wavelength The intensity of the long-wavelength band of fluorescence increases with increasing either the dye concentration or the solvent polarity The fluorescence yield of the first band of emission decreases even in a non-polar solvent with increasing dye concentration This indicates that the methine dyes have a strong tendency to aggregate giving non-fluorescent complexes That idea seems to be confirmed by the very short lifetimes of the short-wavelength band of emission, by the increase of the fluorescence yield of this emission band caused by increase of the solvent polarity and by the low temperature absorption spectra

Therefore, in non-polar solvents, this type of dyes even at low dye concentration have formed the non-fluorescent complexes The complex stability is strongly affected by solvent polarity Thus, in polar solvents the probability of an excimer formation increases and fluorescence of the excimers can be seen giving the long-wavelength emission band

We have also shown that excimers cannot be formed with molecules of methine dyes based on benzoxazoles compared with benzothiazole residues

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