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Fluorescence Properties of Methine Dyes in a Nematic Liquid Crystal Matrix

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The spectral properties of methine dyes in a homogeneously aligned nematic liquid crystal matrix with respect to the external electric fields were studied.

It is shown that the order parameter calculated from the polarized fluorescence (S_F) of the guest molecules is greater than that obtained from the absorption data (S_E). S_E becomes zero in the isotropic region, whereas the order parameter S_F still has a finite value even at temperatures above the clearing point. Results indicate a more-ordered state near the surface than in the bulk of the liquid crystal cell.

INTRODUCTION

In a previous paper[1] it was shown that methine dyes investigated in organic solvents fluoresce in the region of 460–550 nm. The fluorescence characteristics of this type of dyes are interesting both from the basic molecular physics[1] and for practical reasons, because they are finding increased application in display devices.[2,3]

The purpose of this investigation was to get more details about the spectral properties of methine dyes (absorption, emission and lifetime) in "guest-host" type liquid crystal cells. It will be also shown that an order parameter calculated from the polarized fluorescence of the dye molecules is significantly greater than that obtained from the absorption measurements indicating a more-ordered state near the surface than in the bulk of the liquid crystal cell.

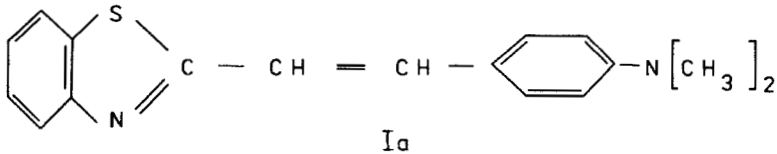
MATERIAL AND METHODS

As a host the following liquid crystal with a positive dielectric anisotropy was used:

4-cyano-4′-pentylbiphenyl (PCB).

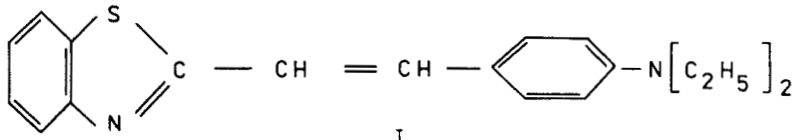
As a quest we used the following methine dyes:

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



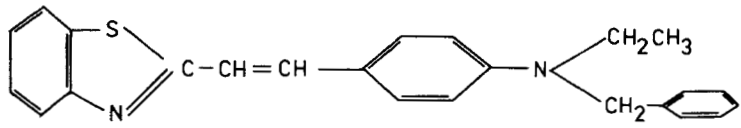
Ia

2[4(N,N-diethyloamino)α-styrylo]benzotiazol



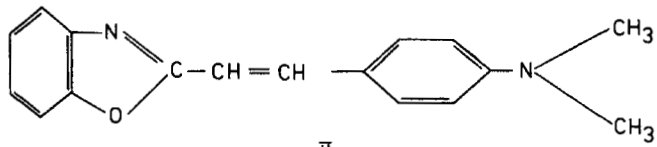
Ib

2[4(N-ethylo, *N*-benzyloamino)α-styrylo]benzotiazol



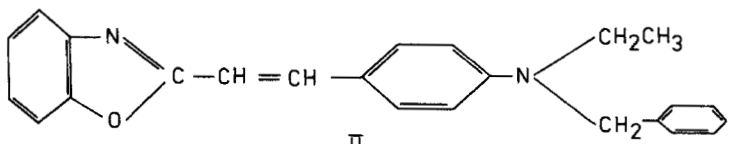
Ic

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



IIa

2[4(N-ethylo, N-benzyloamino)α-styrylo]benzoksazol



IIb

The methine dyes were synthesized, thoroughly identified, and chromatographically purified.[4]

The "guest-host" mixture was placed into a liquid crystal cell. The surfaces of the glass plates of the cell were coated with SiO_2 to obtain homogeneous alignment of the liquid crystal. The thickness of the sample was 20 μm. The absorption spectra were measured with a UV-Vis Zeiss spectrophotometer equipped with two polaroid sheets. The emission was excited through an interference filter (405 nm, 5.5 nm bandwidth). The excitation and fluorescence observation directions were both on the same side of the cell and perpendicular to one another. The excitation was performed with an unpolarized light beam. Two polarized components of fluorescence $F_{\parallel}$ and $F_{\perp}$ (referring to an electric vector of the emitted light parallel and perpendicular to the direction of liquid crystal initial orientation) were measured. Fluorescence lifetimes were measured with a phase shift fluorometer.[5] All the measurements were performed at room temperature and an a.c. voltage of 1 kHz was applied. Other details of the technique of measurements are described elsewhere.[6]

RESULTS AND DISCUSSION

Previous results[1] have shown that the fluorescence characteristics of investigated dyes are strongly dependent on the polarity of solvent in isotropic systems. We have found that methine dyes which contain the S atoms (like dyes I) exhibit in polar solvents two emission bands in contrast to only one fluorescence band in non-polar solvents.[1] Moreover, the observed lifetimes of fluorescence are much longer in polar than non-polar solvents. Methine dyes with the O atoms instead of S (like dyes II) do not show any changes in a shape and in the lifetimes of fluorescence caused by solvents.[7]

On the basis of these observations we have suggested[1] that an excimer fluorescence is responsible for the second longwavelength emission band in polar solvents.

Since the liquid crystal matrix used may be considered rather polar in nature, one can expect the fluorescence characteristics which are typical of polar solvents. However, both types of dyes studied (I and II) have shown quite similar absorption and fluorescence spectra. The examples of absorption and emission spectra of both polarized components ($E_{\parallel}$, $E_{\perp}$ and $F_{\parallel}$, $F_{\perp}$) are shown in Figure 1. Other spectral parameters are listed in Table I. These results (Figure 1) indicate that both types of dye molecules exhibit the molecular fluorescence and that the excimer fluorescence normally observed in polar solvents for dyes I under our experimental conditions (room temperature and dye concentration of about 10^{-4} mol/L) is negli-

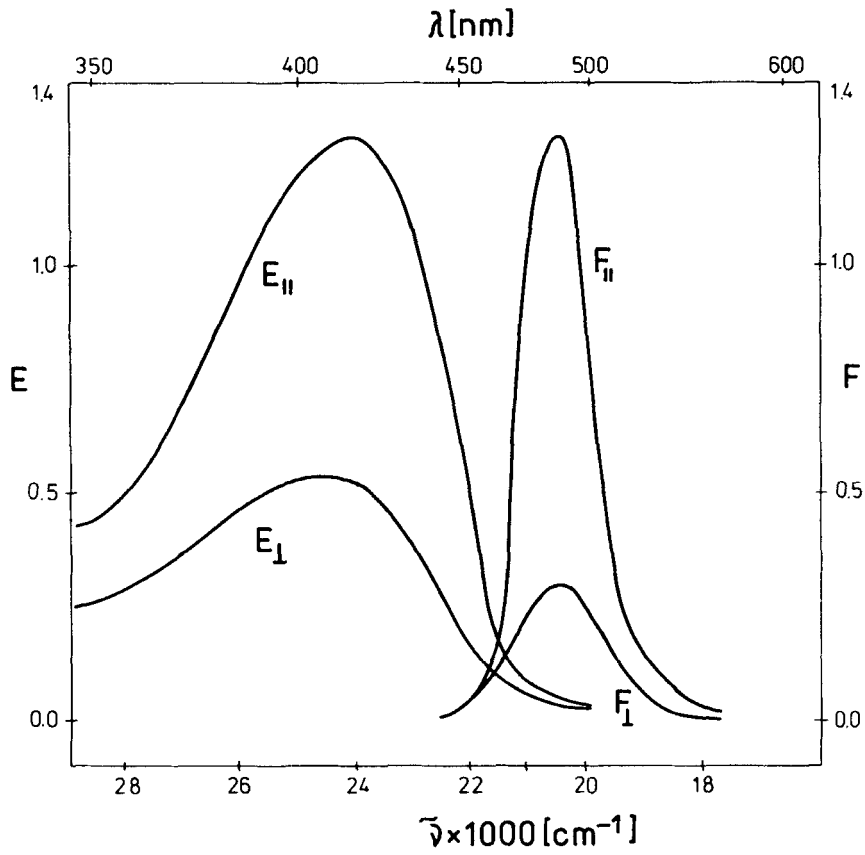


FIGURE 1 Absorption [E] and fluorescence [F] spectra of methine dye Ib in the PCB matrix ($E_{\parallel}F_{\parallel}$; $E_{\perp}F_{\perp}$—parallel and perpendicular components).

gible. This conclusion is supported by the lifetime values (τ in Table I) which are very similar to the values in non-polar solvents.[1,7] Fluorescence spectra obtained in a liquid crystal matrix confirm our suggestion that an excimer fluorescence, and not the polarity of the solvent, is responsible for the second long-wavelength emission band in the case of dye I.

For practical reasons it is important to have a dye with a very high ability of orientation in a liquid crystal matrix. This ability depends on the interaction between the dye and liquid crystal molecules (e.g. the guest-host effect)[8] and depends also on the interaction between the dye molecules and an electrode surface of the cell.[6,9] As a basic quantitative parameter for characterization of the colour-switching property of the liquid crystal display devices a polarized absorption is usually used. However, this quantity is

TABLE I

A summary of the main parameters of the studied "quest-host" type of liquid crystal cell

Liquid crystal	Dye	E_{max} (nm)	F_{max} (nm)	S_E	S_F	τ (ns)	$U_{1/2}(V)$
PCB	Ia	420	495	0.39	0.50	0.8	0.6 (from absorption Figure 2) 2.6 (from fluorescence Figure 3)
	Ib	420	495	0.32	0.49	0.3	0.6 (from absorption Figure 2) 2.0 (from fluorescence Figure 3)
	Ic	417	488	0.32	0.48	0.7	0.8 (from absorption Figure 2) 1.8 (from fluorescence Figure 3)
	IIa	400	481	0.31	0.45	0.8	0.7 (from absorption Figure 4) 2.5 (from fluorescence Figure 5)
	IIb	400	481	0.30	0.46	0.9	0.7 (from absorption Figure 4) 2.5 (from fluorescence Figure 5)

an insufficient parameter for comparing the dichroic property of "guest-host" liquid crystal cells because it does not give any information about the interaction between the molecules of the matrix and the surface of the cell. The optical properties and also the dynamic behaviour of liquid crystal cells are strongly influenced by this interaction.[9-12] The surface effects can be shown using the fluorescence measurements and comparing these results with the corresponding absorption data.[9]

With the aim of clarifying this problem, the dependence of parallel and perpendicular components of the absorption and the emission, referred to an electric vector of light and a liquid crystal director, on a voltage applied, were measured. Since we have used a nematic liquid crystal with a positive dielectric anisotropy, an external electric field should cause the transition moments for absorption and emission (parallel components $E_{\parallel}$ and $F_{\parallel}$) to tip out of the polarization direction of the exciting beam and the polarization direction of an analysing polarizer, resulting in a decrease of absorption and emission intensities. The dependence of the two components of absorption and fluorescence on the applied voltage is shown in Figures 2–5. From

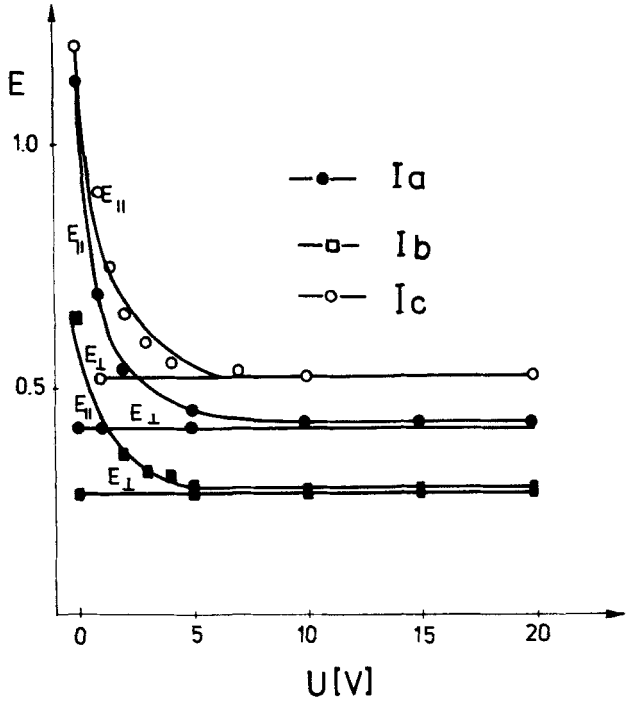


Figure 2 The dependence of polarized components of absorption of the dyes I, in the PCB matrix on voltage applied.

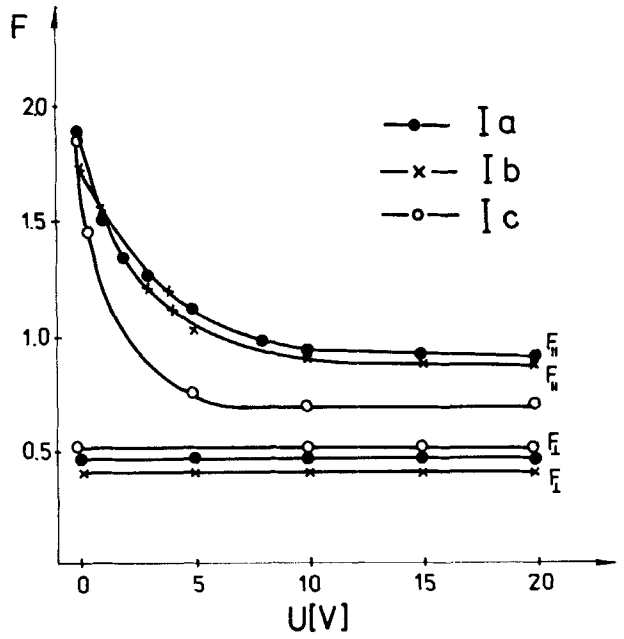


FIGURE 3 The dependence of polarized components of the fluorescence of the dyes I, in the PCB matrix on voltage applied.

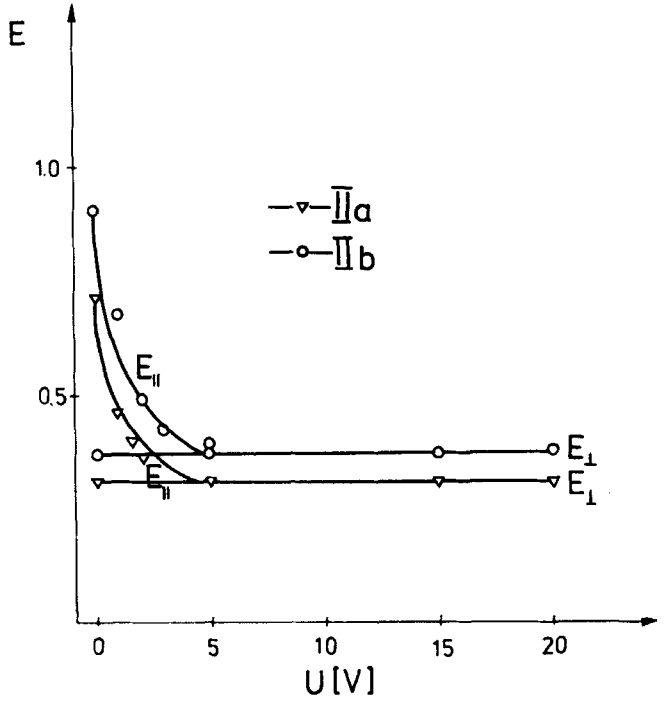


FIGURE 4 The dependence of polarized components of the absorption of the dyes II in PCB matrix on voltage applied.

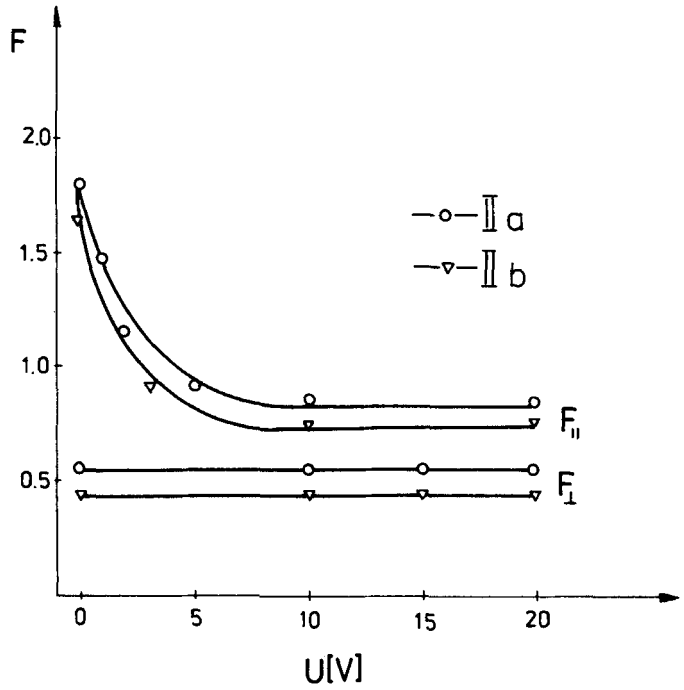


FIGURE 5 The dependence of polarized components of the fluorescence of the dyes II in PCB matrix on voltage applied.

these results it should be noted that:

1) The perpendicular components of both the absorption and emission intensities are independent of the external electric field.

2) For the reoriented dye molecules (by the external electric field) the parallel components of absorption reach practically the values of the perpendicular components.

3) The parallel components of fluorescence $[F_{\parallel}]$ of both type of dyes (I, II) do not reach the perpendicular values $[F_{\perp}]$ even at very high applied voltage.

The degree of orientation of the dye molecules studied can be described by an order parameter S defined as:[13]

$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{1}$$

where θ is the angle between the molecular long axis and the average direction of the long axis of the liquid crystal molecules. The order parameter can be calculated using either the polarized absorption or the polarized fluorescence spectra of guest molecules. In the case where the angle between

the long molecular axis and the direction of the electronic absorption transition moment equals null, the order parameter S_E, calculated from the absorption, is given by Ref. 13:

$$S_E = \frac{E_{\parallel} - E_{\perp}}{E_{\parallel} + 2E_{\perp}} \tag{2}$$

where $E_{\parallel}$ and $E_{\perp}$ denote parallel and perpendicular components of absorption.

The evaluation of S values from fluorescence measurements is more complicated. However, if one assumes $\tau_R < \tau$ (where τ_R is the time required for the excited molecules to relax to an equilibrium state, τ is the lifetime of excited state of guest molecules) and both transition moments responsible for the absorption and emission are parallel to each other, then one can estimate the S_F values using the following formula:[13]

$$S_F = \frac{F_{\parallel} - F_{\perp}}{F_{\parallel} + 2F_{\perp}} \tag{3}$$

where $F_{\parallel}$ and $F_{\perp}$ denote parallel and perpendicular components of emission intensities. The order parameter has been computed from the polarized absorption (S_E) and from the polarized fluorescence (S_F), and the results are listed in Table I. From the results shown in Figures 2–5 one can also determine the values $U_{1/2}$ of the electric potential applied which causes a half change of the parallel components of absorption and emission. The values obtained are also given in Table I.

In order to understand the above results one should remember that the fluorescence is observed from the front surface of the liquid crystal cell. Therefore, the fluorescence measurements give an information about the alignment of dye molecules lying on this surface of the cell ($S_F \approx S_S$; S_S—a surface order parameter) while the absorption measurements contain the information on the average orientation alignment of the dye molecules in the whole volume of the cell ($S_E \approx S_B$; S_B—a bulk order parameter.)[12] Thus, the results indicate that even at high voltages applied, a thin surface layer of guest molecules remains still nonreoriented—the parallel fluorescence component is greater than the perpendicular one (Figures 3, 5). In such a situation the S_E value as an averaged value is smaller than it should be (Table I) and the $U_{1/2}$ for the fluorescence is greater than that value for absorption (Table I).

The above conclusion is confirmed by a temperature dependence of the order parameter obtained from the fluorescence data Figure 6. The ordering at the surface is not destroyed completely even in the isotropic temperature

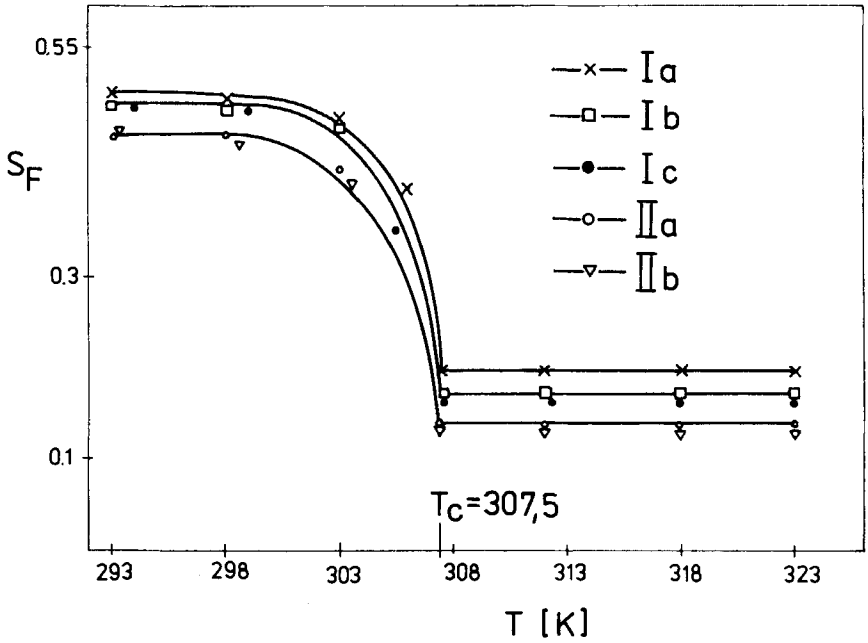


FIGURE 6 The temperature dependence of order parameters at the surface of the cell.

(S_F has a finite value at temperatures above the clearing point T_c) whereas S_E becomes zero.

These results are in qualitative agreement with our previous data,[6] with observations of Mada and Kobayashi.[12] Furthermore, our recent results[9] with other liquid crystal materials have shown that the order parameters at the surface of the cell are usually larger than those in the bulk.

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