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Fluorescent 3-oxy benzanthrone dyes in liquid crystalline media

I. Grabchev[a], I. Moneva[a,*], E. Wolarz[b], D. Bauman[b]

[a]*Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*
[b]*Faculty of Technical Physics, Poznan University of Technology, Poznan, Poland*

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Abstract

The behaviour of novel 3-oxy benzanthrone derivatives of intense fluorescence emission in liquid crystalline media has been studied with regard to their potential for display application. The optical properties of the dyes were examined both in organic solvents, nematic liquid crystal (LC) and polymer film. The influence of the dyes upon the phase transition temperatures and the electro-optical properties of LC in dye/LC systems was investigated in surface-stabilised display cells. The dichroism D(λ) and the orientational order parameters S_A and S_F of the dyes in LC were determined from absorption and fluorescence anisotropy. The effect of a polymer component added to the dye/LC systems upon the transition temperatures of LC was established.

Keywords: Fluorescent benzanthrone dyes; Liquid crystal displays; Guest–host effect

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1. Introduction

Benzanthrone derivatives have a wide variety of applications because of their excellent colour characteristics and high photostability [1]. Recent studies have shown that at least some benzanthrone derivatives (3-amino- and 3-azomethine substituted, with yellow-green or orange-red colour) have a potential for the non-traditional application as components in colour liquid-crystalline displays (LCDs) of the "guest-host" type [2–5].

This type of liquid–crystalline displays containing dichroic dyes (D) dissolved in low molar mass nematic liquid crystals (LC) were first described by Heilmeier and Zanoni [6]. They are based on the guest-host effect which utilises the easy alignment of LC under electric voltage and the close reorientation of the dye guest dissolved what causes selective absorption by the dyes. Due to the dye dopant, the LCDs of the guest-host type need only one polariser and have a wide viewing angle and good image contrast [7]. When fluorescent dyes are involved, the displays can work both in active and passive modes. One of the actual problems to be solved for their practical utilisation is the synthesis of suitable fluorescent dyes. From this point of view, it is of interest to investigate benzanthrone derivatives with oxy substituents in position C-3 of the chromophoric systems which are expected to have good fluorescence properties.

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* Corresponding author. Fax: +359-2-870-75-23.
E-mail address: itmoneva@bas.bg (I. Moneva).

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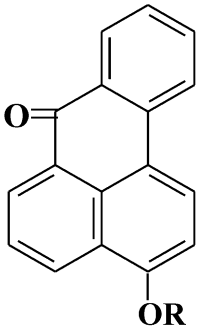
In this paper, we study the behavior of novel 3-oxy benzanthrone derivatives of intense fluorescence emission in liquid crystalline media, in relation to their usage in LCDs. Bi- and tri-component systems, dye/liquid crystal (dye/LC) and dye/liquid crystal/polystyrene (dye/LC/PS) systems, were under study. Their optical, thermal, and electro-optical properties were examined and discussed.

2. Experimental

Derivatives of 3-oxy benzanthrone dyes of the following structure were studied:



where R = –CH_3 (**D1**), –$CH_2CH_2OCH_3$ (**D2**) and –C_6H_5 (**D3**).

The oxy substituted dyes were synthesised by replacement of the bromo group in 3-bromo benzanthrone by alkoxy or aryloxy groups in an interphase catalysis reaction [8]. The reaction was run in DMF medium in the presence of solid KOH and catalytic amounts of 18-crown-6 at 60 °C, the molar ratio of KOH/R-OH/3-bromo benzanthrone being 4:2:1 [4].

Coloured fluorescent polystyrenes (PS + **D**) were obtained by free radical polymerisation of styrene in the presence of the dyes **D1**–**D3** what leads to inclusion of the dyes into the polymer mass [4]. The fraction of the dye in the polymer mass was equal to 0.5%. Thin isotropic films of 50 μm in thickness were prepared on a glass substrate from benzene solution of the polymers by evaporation of the solvent.

The liquid crystalline mixture ZLI 1840, supplied by Merck (Darmstadt, Germany), was used as the host throughout the study. It exhibits a stable nematic phase over a broad temperature range (−15–90 °C) and is recommended for LCD application [9]. The dyes were initially screened for solubility in the LC. For further studies, the dyes were dissolved in the LC at a concentration of 0.5 wt.%, which is suitable for spectroscopic evaluation of the order parameter [10]. Dye/LC mixtures were studied in surface-stabilised “sandwich“ cells of 20 μm thickness. The mixtures formed thin oriented layers between the two glass plates of the cell with an area of 2×3 cm. Uniform planar orientation of the systems was achieved by coating the cell surfaces with polyimide layers which were additionally rubbed in one direction.

The electronic spectra of the dyes in ethanol, LC, and PS films were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. For recording the polarised absorption spectra, UV neutral polarisers were used. The fluorescence measurements were done at room temperature by using Perkin Elmer MPF 44 spectrophotometer. The concentration of the dyes in ethanol was equal to 10^{-6} mol l^{-1}. The orientational order parameters of the dyes dissolved in LC were calculated from the polarised components of the absorption and fluorescence spectra [11]

The measurements of the phase transition temperatures of dye/LC systems were performed under the polarising microscope Zetopan Pol, with an accuracy of ±0.1 K. The electro-optical parameters were estimated using a.c. voltage of 1 kHz.

3. Results and discussion

3.1. Spectral characteristics of 3-oxy benzanthrone dyes in isotropic and anisotropic media

The absorption properties of benzanthrone dyes largely depend on the electron donating power of the substituents at C-3 position [12–15]. They depend also on the nature of environment (polarity, viscosity, formation of hydrogen bonds or other intermolecular interactions). In this case, the long-wavelength band of the absorption spectrum in the visible region is a band of charge transfer

(CT), due to $\pi \rightarrow \pi^*$ electron transfer on $S_0 \rightarrow S_1$ transition.

Figs. 1 and 2 present the positions of the absorption (λ_A) and the fluorescence (λ_F) maxima of **D1**–**D3** dissolved in ethanol, in polymer film and in LC. In ethanol solution, the dyes absorb in the region 430–436 nm and re-emit fluorescence with maxima in the region 525–530 nm. The coloured PS films exhibit yellow colour with intensive green fluorescence. It is noted that the fluorescence intensities of the 3-oxy benzanthrone dyes under study are greater than those of 3-amino substituted benzanthrone derivatives having azomethine residue [2,4,5] due to the different polarisation of the chromophoric systems. In ethanol solution, the oxy benzanthrone dyes **D1**–**D3** exhibit much higher quantum yield of fluorescence ($\Phi_F = 0.42$–0.55) than the 3-amino- and 3-azomethyne substituted benzanthrones ($\Phi_F = 0.02$–0.008) [2,4]. In the whole, the 3-oxy substituted benzanthrone dyes have expectedly a higher yield of fluorescence than 3-amino benzanthrone because of the different donating ability of the amino and alkoxy groups.

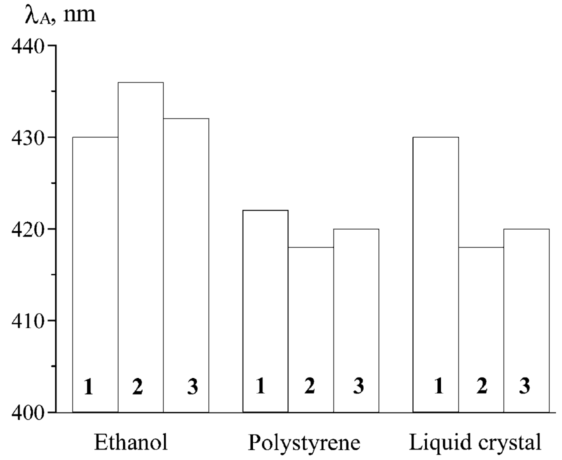


Fig. 1. Absorption maxima of 3-oxy benzanthrone dyes **D1**–**D3** in ethanol, polystyrene film and liquid crystal ZLI 1840.

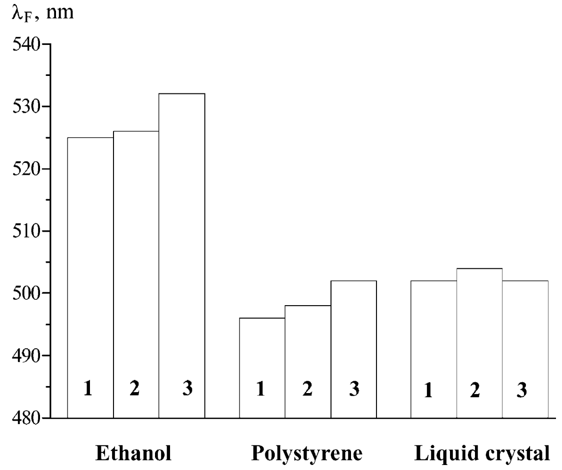


Fig. 2. Fluorescence maxima of 3-oxy benzanthrone dyes **D1**–**D3** in ethanol, polystyrene film and liquid crystal ZLI 1840.

In LC, the dyes are of yellow colour too. They emit in LC intense yellow-green fluorescence with maxima in the region 502–504 nm. The absorption and fluorescence maxima of all dye/LC mixtures and coloured PS show a hypsochromic shift with respect to the maxima of the relevant dyes in ethanol. Exact determination of the fluorescence quantum yield of the dyes in oriented LC is very difficult because many factors (also anisotropic) have to be taken into account.

3.2. Dichroism and orientational order of the dyes in liquid crystal systems

It is known that substances added to nematic LC affect its orientational order. Particularly convenient for measuring orientation parameters in LC systems involving dichroic dyes is the method based on polarised light spectra. The orientation of the dyes in guest–host liquid crystalline systems depends on their molecular structure [16], concentration [17] and intermolecular interactions between the molecules of the dye guest and the LC host [18].

The orientational order parameters S_A and S_F of liquid crystalline systems containing the dichroic dyes **D1**–**D3**, are determined from the polarised absorption and fluorescence measurements.

The orientational order parameter S_A of a dye in LC can be calculated by measuring the polarised absorbancies at λ_A and utilisation of the following Eq. (1) [19,20]:

$$S_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} - \left(1 - \frac{3}{2}\sin^2\beta\right)^{-1} \quad (1)$$

Here, $A_{\parallel}$ and $A_{\perp}$ are the corresponding absorbancies at $\lambda_{\max}$, at parallel and perpendicular orientation of the polariser according to the macroscopic orientation of LC, and β is the angle between the long molecular axis of the dye and the direction of its absorption transition moment.

If $\beta = 0$ Eq. (1) reduces to the following Eq. (2):

$$S_A = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{2}$$

Assuming that the lifetime of the excited state of the fluorescent dye is greater than the rotational correlation time, Baur at al. [21] showed that the order parameter can also be calculated from the fluorescence measurements by using Eq. (3):

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

Here, $F_{\parallel}$ and $F_{\perp}$ are the corresponding fluorescence intensities at $\lambda_{\max}$, with the polarisation direction parallel and perpendicular to the macroscopic orientation of the LC sample, respectively. Eq. (3) holds only for the angle between the absorption and emission oscillators $\delta = 0°$.

The angles β and δ are still unknown for the benzanthrone dyes under study. To a first approximation, we assume that β and $\delta \rightarrow 0°$, and estimate the absorption and fluorescence order parameters of the dichroic dye molecules dissolved in a liquid crystalline matrix by using Eqs. (2) and (3).

Table 1 presents the values of the dichroic ratio $D(\lambda)$ and the orientational order parameters S_A and S_F for dyes **D1**–**D3**. From the data presented, it is seen that the terminal substituents R affect significantly the dichroic ratio $D\lambda_A$ and, consequently, the order parameter S_A. The values of S_A are found to be in the range between 0.35 and 0.48 while the values of S_F are less. This may indicate that the assumption about the relation between the lifetime of the excited state and the rotational correlation time does not hold in this case. The highest order parameter is obtained for dye **D3** with the phenyl ring stabilising the orientation of the chromophoric system. Relatively low values of these parameters for **D1** can be related to the presence of the shortest substituent ($R = CH_3$). These results are in accordance with our previous investigation on the influence of the substituents upon the orientation of dyes in liquid crystalline media [2,3,5].

Table 1
Dichroic ratios $D\lambda_A$ and $D\lambda_F$ and orientational order parameters S_A and S_F of 3-oxy benzanthrone dyes **D1**–**D3** in liquid crystal ZLI 1840 at room temperature

Dye	$D\lambda_A$	$D\lambda_F$	S_A	S_F
D1	3.64	1.84	0.35	0.22
D2	3.04	2.06	0.40	0.26
D3	3.76	2.82	0.48	0.38

Fig. 3 presents the order parameter S_A as a function of temperature for the dyes **D1**–**D3** in LC. The orientational order parameters of the dyes decrease with increasing temperature that corresponds with the disordering processes taking place in the nematic phase.

3.3. Effect of guests upon the phase transition behaviour of liquid crystal

The addition of a nonmesogenic solute to a nematic LC changes its normal nematic-isotropic phase transition temperature, in most cases causing its decrease. Another specific feature of the phase transition is the presence of the two-phase region predicted by theory and observed experimentally [22].

The results from the temperature investigations on pure LC and on dye/LC mixtures are given in

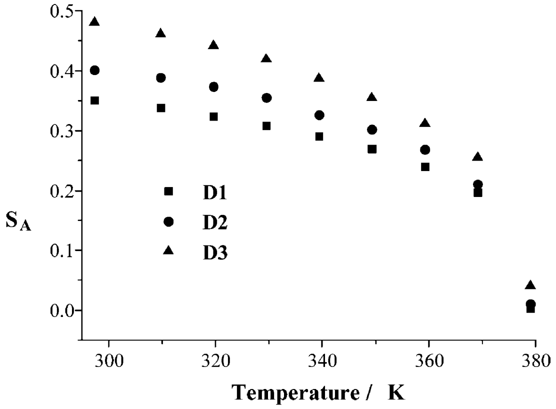


Fig. 3. Order parameters S_A of 3-oxy benzanthrone dye + LC systems as a function of temperature T.

Table 2. The following temperature charateristics of the nematic-isotropic phase transition are determined: T_N, at which the first drop of the isotropic liquid appears, and T_I, at which the last drop of the nematics disappears. Their difference, $(T_I - T_N)$, is the range of the two-phase region, and ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the relevant temperatures of pure LC. $T_{NI} = 1/2(T_N + T_I)$ is the average temperature of the nematic-isotropic transition of the dye/LC mixtures, and ΔT_N is the shift with respect to pure LC.

The temperature investigations on the binary systems showed that **D1**–**D3** very slightly decrease the phase-transition temperatures T_N and T_I of the pure LC and have a minor effect upon the width of the two-phase region of LC.

The decrease is much greater in the case of the tricomponent systems when a polymer component is added. This behaviour is definitely due to the polymer introduced and can be closely related to theoretical predictions (based on Helfand's lattice model [23]) which describe the effect of flexible polymer guests upon the nematic-isotropic phase transition of low-molecular mass LCs.

3.4. Electro-optical properties of dye/liquid crystal systems

The reorientation of LC under applied voltage is very important from technical point of view. This effect can be described by measuring absorption or fluorescence changes of initially oriented dye/LC mixtures in LC display cells.

The parallel component, $A_{\parallel}$, of the absorption, measured at the wavelength corresponding to the maximum, λ_A, for **D1**–**D3** in ZLI 1840 is decreased as the applied voltage rises. Simultaneously, the perpendicular component, $A_{\perp}$, is not changed within experimental uncertainty. This observation is typical for the guest–host LCDs which contain a LC with positive dielectric anisotropy. At a large voltage, the parallel and perpendicular components should become equal. We report the voltage giving x% of absorbance (for $A = A_{\parallel} - A_{\perp}$ normalised to 100%) in the form:

$$V_x(\alpha, \ T),$$

where α is the angle measured to the cell normal (degrees) and T is the temperature.

We regard the display to be completely OFF or ON if [24]:

$$\text{OFF:} \quad V < V_{90} \ (0°, \ T)$$

$$\text{ON:} \quad V > V_{10} \ (0°, \ T)$$

The measured values of V_{90} (0°, 25 °C) and V_{10} (0°, 25 °C) for the systems are listed in Table 3. It is seen that all dye/LC mixtures investigated have very similar values of V_{90} and V_{10}, found to be between 1.20–1.30 and 3.40–3.90 V, respectively. As a measure of the contrast ratio, one can accept to a first approximation the change of the absorbance by on–off control of the applied voltage, measured at λ_A. In Table 3 is listed also the ratio $A_{\parallel}$ (OFF)/$A_{\parallel}$ (ON) for the mixtures studied.

Table 2
Effect of the guests, 3-oxy benzanthrone dyes D1–D3 and coloured polystyrenes PS + (D1–D3), upon the temperatures of the nematic-isotropic phase transition of liquid crystal ZLI 1840, in K (see text)

System	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	T_{NI}	ΔT_{NI}
LC	362.5	368.5	6.0	–	–	365.5	–
LC + D1	361.8	367.9	6.1	−0.7	−1.6	364.9	−0.6
LC + D2	362.1	368.3	6.2	−0.4	−0.2	365.2	−0.3
LC + D3	361.8	368.3	6.5	−0.7	−0.2	365.1	−0.4
LC + PS	357.1	366.0	8.9	−5.4	−2.5	361.6	−4.0
LC + PS + D1	357.3	367.1	9.8	−5.7	−1.4	362.2	−3.9
LC + PS + D2	357.8	365.8	8.0	−4.7	−2.7	361.8	−3.7
LC + PS + D3	358.3	367.1	8.8	−4.2	−2.8	362.7	−2.8

Table 3
Characteristic voltages for ZLI 1840 doped with 3-oxy benzanthrone dyes **D1**–**D3**

Systems	V_{90} (0°, 25 °C) V $\Delta V = \pm 0.1V$	V_{10} (0°, 25 °C) V $\Delta V = \pm 0.1V$	$A_{\parallel}$ (OFF)/ $A_{\parallel}$ (ON)
LC + **D1**	1.30	3.40	1.87
LC + **D2**	1.20	3.60	1.10
LC + **D3**	1.22	3.90	1.87

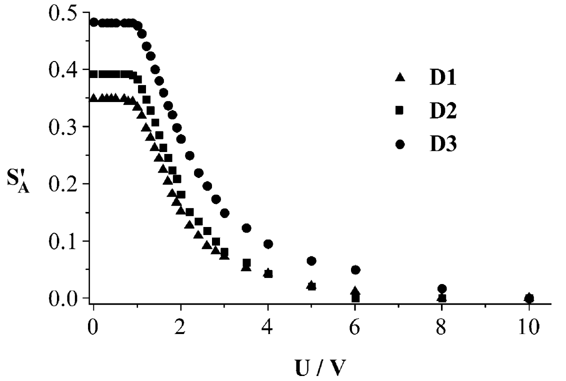


Fig. 4. Order parameter S'_A of 3-oxy benzanthrone dye + LC systems as a function of applied voltage U.

Fig. 4 presents the dependence of the values of the order parameter S'_A for **D1**–**D3** in LC on the applied voltage. The threshold effect is observed at about 0.7–0.8 V. The switch-OFF and -ON voltage values were determined also from the fluorescence components of the dye/ZLI 1840 systems. The shape of the relative fluorescence anisotropy curve was very close to that for the absorption anisotropy. As a result, the OFF- and ON- voltages obtained using both methods are equal, within the limits of experimental error.

4. Conclusion

In this paper, results have been presented of optical, thermodynamical and electro-optical studies on systems composed of novel highly fluorescent 3-oxy benzanthrone dyes in the commercial nematic liquid crystal ZLI 1840, with regard to their usage in liquid-crystal displays. In addition, the optical and thermal properties of coloured polystyrenes containing the dyes in their mass are given. The orientation of the dyes in liquid crystal is related to the substituent in position C-3. In the case of Dye/LC systems is observed a weak destabilising effect of the dyes on the nematic phase whereas this effect is stronger in the tricomponent system additionally comprising polystyrene. The results obtained and the intense fluorescence emission of the dyes show that they can be suitable components of colour liquid-crystal displays operating both in passive and active modes.

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