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The synthesis and application of fluorescent dyes based on 3-amino benzanthrone

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Abstract

The study reports a new method for the synthesis of 3-alkylamino benzanthrone derivatives and their basic photophysical properties. The novel benzanthrone dyes are suitable for the mass colouration of polymers and have potential for non-traditional use in liquid crystalline "guest–host" systems for colour displays. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Benzanthrone and its derivatives have been intensively studied because of the possibility of a wide variety of applications [1]. The presence of a polymerizable double bond in the benzanthrone molecule allows their usage in copolymerization processes with vinyl monomers [2]. Benzanthrone dyes are mainly used for the mass colouration of polymers. Because of their excellent colour characteristics and high photostability all benzanthrone dyes and their copolymers can be used as disperse dyes for textiles [3], daylight fluorescent pigments [4] and laser dyes [5].

Recently, it has been shown that some 3-oxy- and 3-azomethine substituted benzanthrone derivatives, of yellow-green or orange-red colour, exhibit properties which qualify them as appropriate components in liquid-crystal (LC) systems for electro-optic displays of the "guest–host" type [6–8]. Such systems consist of a nematic LC in which is dissolved a dichroic dye. The displays use the guest–host effect which utilises an electric field induced change in the absorption properties of the dichroic dye having high contrast and brightness [9]. If fluorescent, dichroic dyes are used in LC displays then the fluorescence intensity of the display can be controlled by changing the orientation of the guest and host molecules by means of an electric field. It was considered of interest to also investigate other derivatives of 3-amino benzanthrone, bearing at the C-3 position mono- and dialkylamino substituents. The expectation was that fluorescence emission and superior orientation of these dyes in the LC matrix would be achieved due to the stronger electron-donating alkylamino groups.

In this paper are reported the synthesis of some 3-amino substituted benzanthrone dyes, their spectral characteristics in organic solvents, in polystyrene solid films and in the commercial liquid crystal ZLI 1840, and some possible applications for the dyes. The applicability of the dyes

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for colouring polystyrene was also demonstrated. The utility of the benzanthrone dyes for colouring LC displays of the "guest–host" type is discussed on the basis of their spectral properties. The effect that the dyes have upon the phase transition temperature of the LC was evaluated using polarizing microscopy and their effect on the orientation parameter $<P_2>$ in surface stabilised display cells was determined using UV–visible absorption spectroscopy.

2. Results and discussion

2.1. Synthesis and characterisation of 3-alkylamino substituted benzanthrone dyes

The synthetic route used for the preparation of 3-alkylamino benzanthrone dyes is outlined in Scheme 1.

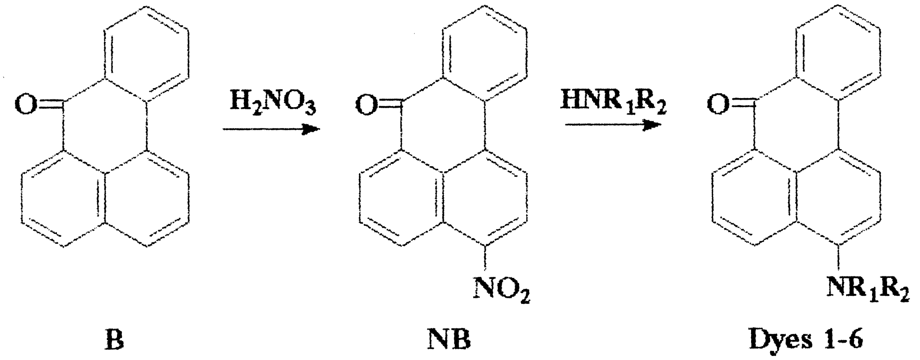
3-Nitro benzanthrone (NB), the initial product for the synthesis of the new dyes, was prepared by nitration of benzanthrone (B) [10]. The final products **1–6** were obtained in good yields by nucleophilic substitution of the nitro group in 3-nitro benzanthrone with primary and secondary aliphatic amines NHR_1R_2 in *N,N*-dimethylformamide (DMF). The same *method* has been used for the synthesis of some 4-alkylamino-1,8-naphthalimide dyes [11]. In this case, the electron-accepting carbonyl group of the benzanthrone molecule favours the nucleophilic substitution reactions of the nitro group with aliphatic amines NHR_1R_2. The products **1–6** were characterized by m.p., TLC (R_f), elemental analysis, FTIR and ^{1}H-NMR spectroscopy and the results obtained are as follows.

2.1.1. *3-*N,N*-dimethylamino benzanthrone* (**1**)

Yield: 66%; m.p. 202–205°C: FTIR (KBr) 3051, 2890, 1660, 1600, 1580, 1500 cm^{-1}. ^{1}H NMR (DMSO-d_6, 100 MHz) δ: 2.92 (s, 6H): 2×CH_3; 6.74 (d, 1H, $J=8.0$ Hz): 2-H: 7.32 (m, 3H): 5-H, 8-H and 10-H: 7.82 (m, 2H): 4-H and 9-H: 8.24 (m, 2H): 6-H and 7-H: 8.68 (d, 1H, $J=8.0$ Hz): 1-H. Anal. Calcd. for $C_{19}H_{14}NO$ (272.2) C 83.82%. H 5.14%. N 5.14%. Found C 83.61%. H 5.03%. N 5.09%.

2.1.2. *3-*N,N*-diethvlamino benzanthrone* (**2**)

Yield: 73%, m.p. 186–188°C; FTIR (KBr) 3050, 2950, 2881, 1645, 1600, 1582, 1502 cm^{-1}. ^{1}H NMR (DMSO-d_6, 100 MHz) δ: 1.12 (t, 6H):



$R_1=$	$R_2=$	
CH_3	CH_3	(1)
CH_2CH_3	CH_2CH_3	(2)
H	CH_2CH_3	(3)
H	$CH_2CH_2CH_2CH_3$	(4)
H	$CH_2CH_2CH_2CH_2CH_2CH_3$	(5)
H	CH_2CH_2OH	(6)

Scheme 1.

2×CH_3; 3.20 (q, 4H): 2×CH_2; 6.70 (d, 1H $J=8.0$ Hz): 2-H: 7.28 (m, 3H: 5-H, 8-H and 10-H: 7.76 (m, 2H): 4-H and 9-H; 8.20 (m, 2H): 6-H and 7-H; 8.66 (d, 1H, $J=8.0$ Hz): 1-H. Anal. Calcd. for $C_{21}H_{19}NO$ (301.2) C 83.72%, H 6.31%. N 4.65%. Found C 83.50%. H 6.21%. N 4.49%.

2.1.3. *3-*N*-ethylamino benzanthrone* (**3**)

Yield: 69%; m.p. 108–110°C: FTIR (KBr) 3360, 3040, 2920, 2860, 1655, 1600, 1580, 1510 cm^{-1}, ^1H NMR (DMSO-d_6, 100 MHz) δ: 1.14 (t, 3H): CH_3; 3.24 (q, 2H): CH_2; 3.78 (s, 1H): NH; 6.72 (d, 1H, $J=8.0$ Hz): 2-H; 7.30 (m, 3H): 5-H, 8-H and 10-H: 7.78 (m, 2H): 4-H and 9-H: 8.22 (m, 2H): 6-H and 7-H; 8.70 (d, 1H, $J=8.0$ Hz): 1-H. Anal. Calcd. for $C_{19}H_{15}NO$ (273.2) C 83.51%, H 5.49%, N 5.12%. Found C 83.29%, H 5.39%, N 5.01%.

2.1.4. *3-*N*-butylamino benzanthrone* (**4**)

Yield: 67%; m.p. 224–226°C; FTIR (KBr) 3350, 3040, 2930, 2890, 1650, 1602, 1570, 1503 cm^{-1}. ^1H NMR (DMSO-d_6, 100 MHz) δ: 0.98 (t, 3H): CH_3 1.54 (m, 4H): 2×CH_2; 3.26 (t, 2H): NCH_2; 3.66 (s, 1H): NH; 6.68 (d, 1H, $J=8.0$ Hz): 2-H; 7.28 (m, 3H): 5-H, 8-H and 10-H; 7.78 (m, 2H): 4-H and 9-H; 8.18 (m, 2H): 6-H and 7-H; 8.64 (d, 1H, $J=8,0$ Hz): 1-H. Anal. Calcd. for $C_{21}H_{19}NO$ (301.2) C 83.72%, H 6.31%, N 4.65%. Found C 83.50%, H 6.21%, N 4.49%.

2.1.5. *3-*N*-hexylamino benzanthrone* (**5**)

Yield: 79%; m.p. 147–150°C; FTIR (KBr) 3360, 3050, 2920, 2840, 1645, 1607, 1582 cm^{-1}. ^1H NMR (DMSO-d_6, 100 MHz) δ: 0.96 (t, 3H): CH_3; 1.48 (m, 8H): 4×CH_2; 3.22 (t, 2H: NCH_2 3.46 (s, 1H): NH; 6.70 (d, 1H, $J=8.0$ Hz): 2-H: 7.32 (m, 3H): 5-H, 8-H and 10-H: 7.82 (m, 2H): 4-H and 9-H: 8.22 (m, 2H): 6-H and 7-H; 8.62 (d, 1H, $J=8.0$ Hz): 1-H. Anal. Calcd. for $C_{23}H_{23}NO$ (329.2) C 83.89%, H 6.99%. N 4.25%. Found C 83.75%, H 6.80%, N 4.19%.

2.1.6. *3-*N*-2-hydroxyethyl-amino benzanthrone* (**6**)

Yield: 83%; m.p. 128–130°C: FTIR (KBr) 3362, 3048, 2910, 1645, 1603, 1582, cm^{-1}. ^1H NMR (DMSO-d_6 100 MHz) δ: 2.43 (s, 1H): OH: 3.54 (t, 2H): NCH_2; 3.72 (t, 2H): OCH_2; 4.16 (s, 1-H): NH; 6.66 (d, 1H, $J=8.0$ Hz): 2-H; 7.26 (m, 3H): 5-H, 8-H and 10-H; 7.80 (m, 2H): 4-H and 9-H; 8.24 (m, 2H): 6-H and 7-H: 8.56 (d, 1H, $J=8.0$ Hz): 1-H. Anal. Calcd. for $C_{19}H_{15}NO_2$ (289.3) C 78.89%, H 5.19%, N 4.84%. Found C 78.71%, H 5.05%, N 4.80%.

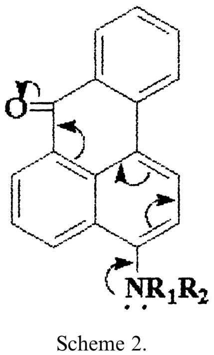
2.2. *UV–visible absorption and fluorescence of the benzanthrone dyes measured in different solvents*

As the absorption properties of the benzanthrone dyes are related to the extent of the polarisation of the benzanthrone molecule upon irradiation, resulting from the electron donor–acceptor interaction within the chromophoric system and so may be influenced by the environmental effect of the media upon this interaction [9, 12–14]. The electron donor–acceptor interaction within 3-substituted benzanthrone occurs between its electron-accepting carbonyl group and the electron-donating groups in the C-3 position of the chromophoric system [8]. The path of the charge transfer is given on Scheme 2.

Clearly the bands of absorption and emission of the dyes largely depend on the electron donating power of the substituents R_1 and R_2 at the C-3 position. The spectral properties of the benzanthrone dyes depend also on the nature of the environment (polarity, viscosity, formation of hydrogen bonds or other intermolecular interactions).

The 3-substituted benzanthrone derivatives exhibited the following disposition of the energetic levels [15,16]:

$$T\pi\pi^* < S\pi\pi^* < Tn\pi^* < Sn\pi^*$$



Scheme 2.

In this case, the long-wave band of the absorption spectrum in the visible region is a band of charge transfer (CT), due to $\pi \rightarrow \pi^*$ electron transfer during $S_0 \rightarrow S_1$ transition.

Table 1 shows the basic electronic characteristics of the dyes in toluene; the values of the absorption maximum (λ_A), the molecular extinction coefficient ($\log \epsilon$), the fluorescence maximum (λ_F), the Stokes shift ($\nu_A - \nu_F$), the oscillator strength (f) for the long-wave absorption band and the energy of activation of the singlet state (E_{S1}) are shown.

The benzanthrone dyes studied were of orange-red colour and displayed intense fluorescence in toluene. The absorption maximum λ_A were in the visible region at 450–486 nm being bathochromically shifted with regard to the oxy- and azomethine substituted benzanthrone dyes [7]. The λ_A values for dyes bearing dimethyl- and diethylamino groups (dyes **1** and **2**) at the C-3 position in the benzanthrone molecule were hypsochromically shifted in comparison with those for dyes **3**–**6** bearing a secondary amino group, due to conformational changes. These refer to the possible rotation of alkylated groups from dialkylamino groups around a 3-(C–N) bond which leads to stretching of the molecule beyond its plane and to corruption of its planar structure. The orbital interaction between the substituents $-N(CH_3)_2$ or $-N(C_2H_5)_2$, and the π-electron system of the dye becomes weaker, resulting in a decrease of the dipole transition moment of the dye molecule and, correspondingly, a hypsochromic shift of λ_A.

The benzanthrone dyes **1**–**6** displayed fluorescence emission at room temperature in the region 500–650 nm with well pronounced maxima λ_F at 564–574 nm (Table 1). The emission was the mirror image of the absorption spectra (in toluene), in the long-wave region. The R substituents had a smaller effect upon λ_F, which is evidence that the benzanthrone molecule was more stable in the exicted state S_1.

Table 1
Photophysical characteristics of the benzanthrone dyes **1**–**6** recorded in toluene (see text)

Dyes	1	2	3	4	5	6
λ_A nm	450	458	474	486	476	462
$\log \epsilon$	4.12	4.07	4.07	4.18	4.19	4.15
λ_F nm	564	568	574	574	572	570
$(\nu_A - \nu_F)$ cm^{-1}	4492	4228	3675	3154	3526	4101
E_{S1} kJ mol^{-1}	222	222	218	216	218	219

The Stokes shift (ν_A − ν_F) indicates the difference in properties and structure of the dyes in the ground state S_0 and the first excited state S_1 [Eq. (1)]

$$\nu_A - \nu_F = (1/\lambda_A - 1/\lambda_F) \times 10^7\,\mathrm{cm}^{-1} \qquad (1)$$

The calculated values of the Stokes shift were between 3154 and 4492 cm^{-1} as is common for this type of dye [7,14]. The observed larger Stokes shift for dyes **1** and **2** is connected with the energy losses during the transition to the excited state.

The energy of activation of the first excited state E_{S1} was calculated from the point of intersection of absorption and fluorescence spectra at the corresponding wavelength λ_{S1}. There was only a small difference in the values obtained for dyes **1**–**6** which were between 216 and 222 kJ mol^{-1}.

The interaction of the π-donating amino groups at C-3 of the benzanthrone molecules with the π-accepting carbonyl group and its effect upon absorption depends on the polarity of solvents. Fig. 1 shows the dependence of the absorption maximum of the CT band in the case of dye **5**, as an example, upon solvent polarity $E_T(30)$ [17]. The

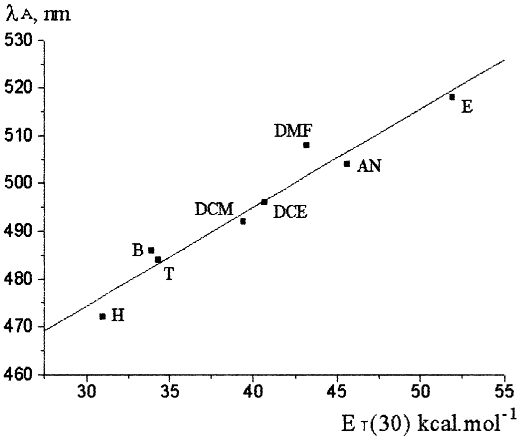


Fig. 1. λ_A-dependence of dye **5** on the empirical parameters of solvent polarity $E_T(30)$: Solvents used: H = hexane, B = benzene, T = toluene, DCM = dichloromethane, DCE = dichloroethane. DMF = *N,N*-dimethylformamide, AN = acetonitrile, E = ethanol.

changes in the position of the CT band of dye **5** in various solvents are caused by the solvatochromic effect of the solvent. The absorption maxima of the dye in polar solvents are, as expected bathochromically shifted with regard to those in apolar solvents. The explicit formula obtained upon averaging is Eq. (2).

$$\lambda_A = 412 + 2.07E_T(30) \qquad (2)$$

which was derived by a least squares method, with a correlation coefficient of $R = 0.97$ and a standard deviation of S.D. = 3.79 nm ($N = 8$).

From Fig. 1 it can also be seen that dye **5** exhibited positive solvatochromism as did the other dyes. The linear character of the dependence indicates that dipole–dipole interactions prevail in dye solution.

2.3. Mass colouration of polystyrene and spectral characteristics of the benzanthrone dyes in a thin solid film

Previous studies have been published on the mass colouration of polystyrene (PS) during its synthesis in the presence of some alkoxy benzanthrone derivatives [8,18]. Using free radical polymerization of styrene in the presence of the amino benzanthrone dyes **1**–**6**, orange-red fluorescing transparent polymers were produced. The spectral properties of the benzanthrone dyes in solid polystyrene films were determined as it was expected that introduction of polymers could stabilise LC-based systems [19,20]. Thin dye (0.5%) polystyrene films (40 μm thick) obtained from toluene solution were used. In such solid polystyrene films, the dyes **1**–**6** exhibited orange-red colour and their absorption maxima were between 462 and 484 nm (Table 2). They displayed intensive fluorescence with maxima λ_F at 572–590 nm and their Stokes shifts were 3712–4256 cm^{-1}. The dyes **1**–**6** exhibited similar absorption properties in toluene solution and in solid polystyrene film, as a result of the similar polarity of the two media values of dielectric constants; ϵ (toluene) = 2.38, ϵ (PS) = 2.40–2.65 [21]. The fluorescence spectra of the solid polymer films, however, differed significantly from those in toluene solution, being bathochromically shifted which is connected with the rigidity of the polypropylene structure. Evidently, the results do not provide evidence of any structural changes in the chromophoric system owing to the polystyrene matrix and/or to the process of polymerization.

Table 2
Spectral characteristics of the benzanthrone dyes recorded in thin polystyrene film

Dyes	1	2	3	4	5	6
λ_A nm	462	460	478	480	484	468
λ_F nm	572	572	588	590	590	574
$(\nu_A - \nu_F)$ cm^{-1}	4162	4256	3914	3884	3712	3945

2.4. Functional properties of the benzanthrone dyes in liquid crystal systems

Some properties of bi- and tricomponent dye/liquid crystal systems (including a polymeric component) have been studied with regard to their application for LC displays. The dyes under study (**1**–**6**) were initially screened for solubility in LC and then were dissolved in the medium at a concentration of 0.5 w/v%, to ensure an accurate determination of the orientational parameter S_A [22]. The measurements on the dyes in LC were carried out in "sandwich" cells of 20 μm in thickness [19]. The dye/LC mixtures formed thin oriented layers between two glass plates with an area of 2×3 cm. Planar, homogeneous molecular orientation of the systems in the cells was achieved by coating the cell surfaces with polyvinylalcohol layers which were previously orientated by rubbing [23].

Commercial LC ZLI 1840 (Merck) was used as host material which exhibits a stable nematic phase over a broad temperature range (−15–90°C) and high positive dielectric anisotropy [24].

2.4.1. Spectral characteristics of the dyes in liquid crystal

In LC, all dyes **1**–**6** retained their red-orange colour, with absorption maxima λ_A at 458–500 nm and re-emitted an intense fluorescence with maxima λ_F at 590–598 nm (Table 3). The absorption and fluorescent maxima of the dyes were bathochromically shifted with regard to λ_A and λ_F in the apolar toluene and in polystyrene film, and hypsochromically shifted in the polar ethanol. The data obtained for the dyes studied were bathchromically shifted with regard to the 3-oxy and 3-azomethine substituted benzanthrone dyes [25], indicating their stronger polarization.

2.4.2. Ordering in dye/liquid crystal systems

It has been found that substances added to a nematic LC affect its orientation order. Particularly convenient for measuring the orientation parameters in LC systems that include dichroic dyes is the method based on polarised absorption spectra. The orientation of the dyes in "guest–host" LC systems depends on their molecular structure [26], concentration [27] and intermolecular interactions between the molecules of the dye guest and the LC host [28].

The orientation order parameter S_A of a dye in an LC can be calculated by measuring the polarized absorbences at λ_A [29,30] [Eq. (3)].

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

where $A_\parallel$ and $A_\perp$ are the corresponding absorbencies in polarized light (at λ_{max}) of the polariser both parallel to and vertical to the LC director, and β is the angle between the long molecular axis of the dye and the vector of its absorption transition moment.

At $\beta = 0$, Eq. (2) reduces to Eq. (4):

$$S_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} \equiv \frac{N(\lambda) - 1}{N(\lambda) + 2} \tag{4}$$

where $N(\lambda) = A_\parallel / A_\perp$ is the dichroic ratio of the dye molecule in polarized light.

Table 3
Spectral characteristics, dichroic ratio $N(\lambda_A)$ and orientation order (S_A) of the benzanthrone dyes recorded in LC (see text)

Dyes	1	2	3	4	5	6
λ_A nm	458	462	489	498	500	478
λ_F nm	590	592	594	596	598	592
(ν_A–ν_F) cm^{-1}	4885	4753	3615	3302	3276	4028
$N(\lambda_A)$	3.44	3.44	5.14	5.50	6.11	4.25
S_A	0.46	0.46	0.58	0.60	0.63	0.52

It is accepted that elongation of a dye molecule affords better orientating in an LC. Table 3 displays the values of the dichroic ratio $N(\lambda)$ and the orientation parameter S_A of the benzanthrone dyes **1**–**6**. From the data presented it is evident that the terminal substituents R_1R_2 affected the order parameter S_A, the values varying in the range 0.46–0.63. Thus, the long alkyl chains in dyes **4** and **5** caused an increase of S_A (0.60–0.63) which is related to the elongation of the molecules. The order paramaters S_A were of satisfactory value for dyes **3**–**6** but were low for dyes **1** and **2**, which can be attributed to steric effects. The effect of the amino substituents upon the order parameter S_A were in the order $NH_2 < NR_1R_2 < NHR$.

It is noteworthy that the orientation parameters determined for some of the benzanthrone dyes under study were higher than those of 3-amino-substituted benzanthrone derivatives having an azomethine residue [7,8].

2.4.3. 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 a decrease. Another specific feature of the phase transition is the appearance of two-phase regions as predicted by theory and observed experimentally [31].

The results from the temperature investigations on pure LC and on dye (0.5%)/LC mixtures are given in Table 4. The following temperature characteristics of the nematic–isotropic phase transition were determined: T_N, at which the first drop of the isotropic liquid appeared, and T_I, at which the last drop of the nematics disappeared. 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 its shift with respect to pure LC.

The temperature investigations of binary dye/LC systems showed that dyes **1**–**6** slightly lowered the phase transition temperatures T_N and T_I of the pure LC. The observed depression was enhanced

Table 4
Effect of benzanthrone dyes **1**–**6** and polystyrene (PS) upon the temperatures of the nematic–isotropic phase transition of liquid crystal ZLI 1340, in K (see text)

Systems	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 + dye **1**	360.5	367.4	6.9	−2.0	−1.1	364.0	−1.5
LC + dye **2**	360.8	367.6	6.8	−1.7	−0.9	364.2	−1.3
LC + dye **3**	361.0	367.6	6.6	−1.5	−0.9	364.3	−1.2
LC + dye **4**	361.4	367.8	6.4	−1.1	−0.7	364.6	−0.9
LC + dye **5**	361.6	367.8	6.2	−0.9	−0.7	364.7	−0.8
LC + dye **6**	361.8	368.0	6.2	−0.7	−0.5	364.9	−0.6
LC + PS	357.1	366.0	8.9	−5.4	−2.5	361.6	−4.0
LC + dye **1** + PS	356.8	365.2	8.4	−5.7	−2.2	361.0	−4.5
LC + dye **2** + PS	356.6	365.2	8.6	−5.9	−2.2	360.9	−4.6
LC + dye **3** + PS	356.8	365.4	8.6	−5.7	−3.1	361.1	−4.4
LC + dye **4** + PS	356.8	365.6	8.8	−5.7	−2.9	361.2	−4.3
LC + dye **5** + PS	356.4	365.6	9.2	−6.1	−2.9	361.0	−4.5
LC + dye **6** + PS	356.4	365.8	9.4	−6.1	−2.7	361.1	−4.4

through the introduction of a polymeric component into the system (dye/LC/PS), being between 5.7 and 6.1 K for T_N, and 2.2 and 3.1 K for T_I. This behaviour can be closely related to theoretical predictions [32] (based on Helfand's lattice model) that describe the effect of flexible polymer guests on the nematic–isotropic phase transition of low-molecular mass LC systems.

The investigations of the binary systems showed that many of the dyes **1–6** either do not, or very slightly, lower the phase-transition temperatures T_N and T_I of the pure LC and had a minor effect upon the two-phase region of the LC.

3. Experimental

3.1. General method for the synthesis of 3-amino-alkyl benzanthrone dyes **1–6**

A mixture of 3-nitro benzanthrone (0.01 M) and the respective amines (0.01 M) in 50 ml DMF was stirred at 80°C, and the reaction was monitored *by* TLC. After 8 h the mixture was poured into 200 ml water. The final product was filtered, and washed.

The reaction course and purity of the final products were followed using TLC on silicagel (Fluka F_{60} 254 20×20; 0.2 mm), using as eluent the solvent system *n*-heptane:acetone (1:1). Melting points were determined using a Kofler microscope.

3.2. Characterisation of the dyes

IR spectra were taken on a Perkin–Elmer 1600 FTIR spectrometer at 4 cm^{-1} resolution using KBr pellets. ^{1}H-NMR spectra were recorded on a JEOL JNM-PS spectrometer, operating at 100 MHz in d_6-DMSO and using TMS as internal standard (chemical shifts δ in ppm).

The electronic spectra of the dyes in various media including organic solvents, solid polymer film and LC were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution, at room temperature. For recording the polarised absorption spectra, UV neutral filters were used.

Fluorescence measurements of dyes **1**–**6** in toluene at a concentration of 10^{-6} mol l^{-1} and on coloured thin polymer films of polystyrene (dye content 0.5%) were recorded on a Perkin–Elmer MPF 44 spectrophotometer at room temperature.

The measurements of the phase-transition temperatures of dye/LC systems were performed using a Zetopan Pol polarising microscope with an accuracy of 0.1 K.

4. Conclusions

Novel 3-amino substituted benzanthrone dyes were synthesized in good yield and purity by nucleophilic substitution of the nitro group in 3-nitro benzanthrone with aliphatic amines. All the dyes were of excellent red-orange colour and displayed intense fluorescense in isotropic (organic solvents and solid polymer film) and anisotropic LC media.

The radical polymerization of styrene in the presence of 3-amino benzanthrone dyes gave bright, uniform colouration of the polymer, with no evidence of structural changes to the chromophoric system of the dyes.

The potential of the novel benzanthrone dyes for use in LC systems for displays was proven. The orientation of the dyes in a ZLI 1840 liquid crystalline matrix depended on the substituents at the

C-3 position; the more elongated dye molecules showed satisfactory values of the order parameter S_A, exhibiting values in the range 0.46–0.63. The monoalkyl substituted dyes values showed the highest values of benzanthrone dyes studied. The dyes did not destabilise the mesomorphic phase of the LC host although the introduction of a polymeric component into the system (dye/LC/PS) depressed the mesomorphic phase.

The fluorescent 3-alkylamino benzanthrone derivatives under study are suitable luminophores both for the mass colouration of polymer materials and for guest–host liquid-crystal systems.

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