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Synthesis and Properties of Benzanthrone Derivatives as Luminophore Dyes for Liquid Crystals

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ABSTRACT

The preparation in high yield and purity, and the photochemical and photophysical properties of some new azomethine and alkoxy derivatives of benzanthrone are reported, and their utility as luminophore dyes in liquid crystalline systems for displays of the 'guest–host' type is discussed. © 1998 Elsevier Science Ltd

Keywords: benzanthrone derivatives, luminophore dyes, liquid crystals.

INTRODUCTION

Fluorescent dyes of brilliant and clear colour have been intensively studied for use in various fields [1], and among them, benzanthrone dyes are well-known as luminophore dyes emitting in the region from yellow–green to red–purple fluorescence, depending on their structure [2]. Benzanthrone dyes exhibit, both in solution and in the solid state, bright fluorescence and high photostability and find use as daylight fluorescent pigments for synthetic textile materials [1], for mass and chemical colouration of other polymeric materials (see, for example, Ref. 3), etc.

This paper reports on the synthesis, and the photo-chemical and physical properties, of new benzanthrone derivatives containing azomethine and alkoxy groups in 3-position of the benzanthrone moiety, with respect to a new non-traditional application of the dyes in liquid crystalline (LC) systems for displays of the s.c. 'guest–host' type [4–7].

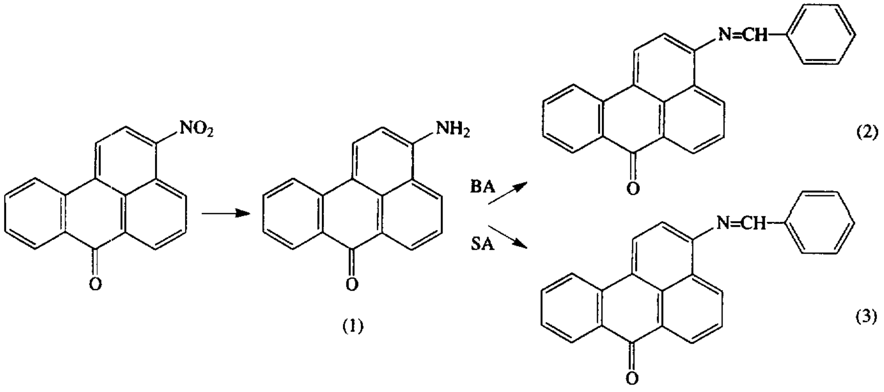
The introduction of the azomethine group extends the system of conjugated double bonds of the benzanthrone nucleus, thus increasing the chromophore length. A very important expectation with regard to the potential of benzanthrone dyes in liquid crystal displays is the design of a convenient disposition of their long molecular axis and the vectors of emission and/or absorption transition moments. This presumption is of interest for the dye orientation and function in a nematic LC display matrix [7]. The inclusion of alkoxy groups is additionally aimed at the synthesis of new benzanthrone dyes by extending the range in colour and brightness.

RESULTS AND DISCUSSION

Synthesis of the dyes

Synthesis of 3-amino substituted benzanthrones

The preparation of 3-amino substituted benzanthrone derivatives is outlined in Scheme 1.



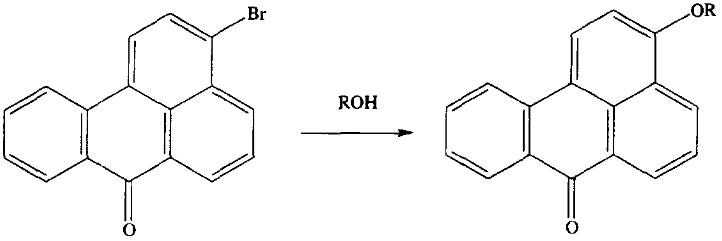
Scheme 1.

3-aminobenzanthrone (1) was prepared by reduction of 3-nitrobenzanthrone with sodium sulfide [8]. The azomethine derivatives 2 and 3 were prepared by reacting 3-aminobenzanthrone with benzaldehyde (BA) or with salicyl aldehyde (SA) in boiling ethanol.

Synthesis of 3-alkoxybenzanthrone derivatives

The 3-alkoxy benzanthrone derivatives prepared are shown in Scheme 2 where R is $-CH_3$ (4), $-CH_2CH_2OCH_3$ (5), and $-C_6H_5$ (6).

Replacement of the bromo group by alkoxy was carried out under the conditions of interphase catalysis [9]. The reaction was run under selected conditions, viz., in DMF medium in the presence of solid potassium hydroxide



Scheme 2.

and catalytic amounts of 18-crown-6 at 60°C, the molar ratio of KOH/ROH/3-bromobenzanthrone being 4/2/1 [10].

The reaction time was 4 h when using 2-methoxyethanol (dye 5), and 6 h with phenol (dye 6), the reactivity of the hydroxy group depending on the substituent (see Experimental section).

The four benzanthrone dyes 2, 3, 5, 6 thus obtained were of high yield and purity (Table 1). They were characterized by IR, UV/Vis and fluorescence spectroscopy, ^{1}H-NMR, elemental analysis, M.p. and TLC (see Table 1, Fig. 1 and Experimental section). The dyes 1 and 4 are known compounds, in use for polymeric materials [1].

TABLE 1
Yield, Melting Point *M. p.*, R_f (TLC) and IR-absorption of Benzanthrone Dyes 1–6

Dye	*Yield (%)*	M.p. *(°C)*	R_f[a]	*IR absorption (cm^{-1})*				
				$\nu_{C=O}$	ν_{C-O-C}	$\nu_{C-C(ar)}$	$\nu_{CH=N}$	$\delta_{CH(ar)}$
1	73	244–246	0.45	1635	—	1585	—	785
						1528		760
						1470		718
2	93	207–208	0.49	1650	—	1575	1623	790
						1520		760
						1470		719
								690
3	92	199–201	0.51	1648	—	1572	1620	790
						1500		755
						1470		715
4	84	176–178	0.16	1645	1268	1580	—	775
					1172	1515		750
					1039	1470		705
5	89	110–112	0.52	1645	1268	1582	—	778
					1179	1515		750
					1040	1470		705
6	84	172–174	0.61	1651	1255	1580	—	777
					1039	1520		750
						1470		702

[a] The solvent used for dyes 1–3 was *n*-heptane/acetone (1/1) and for dyes 4–6 was *n*-hexane/benzene/chloroform (3/2/1).

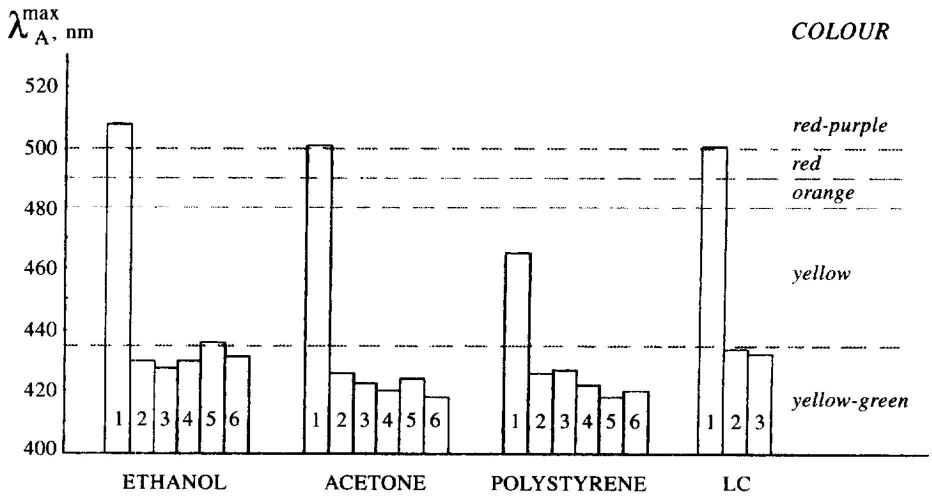


Fig. 1. Absorption maxima of benzanthrone dyes 1-6 in isotropic and anisotropic (liquid crystal ZLI 1840) media.

Spectral studies on benzanthrone dyes 1-6

IR spectroscopy

Stretching and deformation vibrations of the main functional groups of all dyes are listed in Table 1.

IR spectra of dyes 1–3 show an intensive absorption band at 1635–1651 cm^{-1} characteristic of the carbonyl group of the benzanthrone moiety. Dye 1 has a split peak with maxima at 3370, 3265 and 3154 cm^{-1}, characteristic of its primary amino group. These peaks are absent in the spectra of dyes 2 and 3, which show a band at 1620–1623 cm^{-1} typical for the -N = CH residue. In the spectra of dyes 4–5, there are asymmetric vibrations at 1172 and 1179 cm^{-1}, 1039–1040 and 1268 cm^{-1} from the ether C–O–C group, while in dye 6 the asymmetric vibrations at 1255 cm^{-1} are from the ether group C–O–Ar.

The bands at 750–760, 775–790, 1468–1470, 1575–1586 and 3046–3062 cm^{-1} observed for all dyes are characteristic of the aromatic system of the benzanthrone molecule. The bands at 690 and 702 cm^{-1} are characteristic of the monosubstituted benzene rings in dyes 2 and 6. The intense bands at 1384–1385 cm^{-1} in dyes 4 and 5 are characteristic of the CH_3 group.

Owing to the intramolecular hydrogen bonding in the case of dye 3, a large band in the region 2000–3600 cm^{-1} is observed, within which there are bands characteristic of the valent C–H bonds in the aromatic structure. No characteristic peaks for NH, nor a band for the carbonyl group connected with a quinoid form of the dye were found.

UV/Vis spectrometry and fluorescence

The absorption spectra of dyes 1–6 were recorded in ethanol, acetone, LC (ZLI 1840- Merck) and on thin polystyrene film. Figure 1 presents their absorption maxima in the various environments. The polarization of the benzanthrone molecule is governed by the donor–acceptor interactions of the electron-donating substituents in 3-position and the electron-accepting carbonyl group, while charge transfer along the chain of conjugated double bonds leads to absorption in the visible region.

Thus, dye 1 having a strong electron-donating primary amino group absorbs in ethanol at 508 nm. Replacement of the amino group by the azomethine group in dyes 2 and 3 significantly affects the absorption properties since a decrease in the electron-donating ability of the nitrogen in the azomethine fragment alters the molecular polarization. As a result, absorption maxima are hypsochromically shifted to the yellow–green region.

The alkoxy benzanthrone derivatives obtained display absorption maxima at 430–436 nm, the nature of the substituent *R* only slightly affecting the position of the absorption maxima.

The effect of the π-donating groups (N and O) in the 3-position of the benzanthrone molecule and of the π-accepting carbonyl group upon absorption properties depends on the polarity of solvent (Fig. 1). A hypsochromic shift is observed from the more polar ethanol to the less polar acetone, which is likely due to different solvation of the dyes. The effect is most pronounced in the case of dye 1, which in ethanol absorbs in the red–purple region, but in polystyrene there is a shift to the yellow region.

The substitutents in the 3 position cause a significant change in the photophysical characteristics of the dyes in ethanol (Table 2). The fluorescent maxima of dyes 1–6 are in the region 525–568 nm, dependent on their molecular structure. The energy in the first excited state E_{S_1} was estimated from the cross points of absorption and fluorescence spectra and the corresponding

TABLE 2
Photophysical characteristics of benzanthrone dyes 1–6 in ethanol (see text)

	1	*2*	*3*	*4*	*5*	*6*
λ_A^{max} (nm)	508	430	428	430	436	432
log ε						
in ethanol	3.96	4.20	4.23	4.01	4.02	4.04
in acetone	3.89	4.12	4.11	3.98	4.00	4.02
λ_F^{max} (nm)	568	525	569	525	526	532
E_{S_1} (kJ mol^{-1})	224.1	253.6	252.5	246.8	247.3	245.3
$\bar{\nu}_A - \bar{\nu}_F$ (cm^{-1})	2079	4208	9884	4244	4136	4139
Quantum yield Φ_F	0.006	0.008	0.02	0.55	0.49	0.42
Oscillator strength f						
in ethanol	0.181	0.279	0.326	0.186	0.186	0.188
in acetone	0.165	0.243	0.281	0.171	0.169	0.175

wavelength. It has the lowest value with dye 1 and is connected with the large effect which the environment has upon its optical properties.

The substituents in the 3 position also have a strong influence on the quantum yield Φ_F of fluorescence. For dyes 1–3, the relative quantum yield is very low, within 6.10^{-3}–2.10^{-2}, which could be due to emissionless deactivation processes during the transition from the excited state S_1 to ground state S_0. As known with alkoxy derivatives, dyes 4–6 display a more intensive fluorescence, with quantum yields within 0.42–0.55 (standard Rhodamine 6G, $\Phi_0 = 0.88$ [11]).

An important dye parameter is the oscillator strength (f) which relates to the absorption ability of chromophoric systems. It is calculated [12] according to the relationship

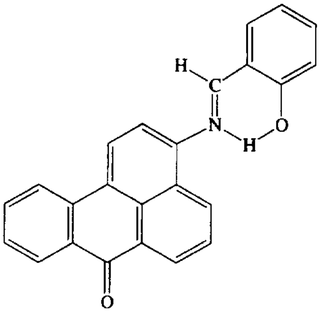
$$f = 4.32 \cdot 10^{-9} \Delta\nu_{1/2} \varepsilon_{\max},$$

where $\Delta\nu_{1/2}$ is the halfwidth of the absorption band (in cm^{-1}) and $\varepsilon_{\max}$ is the maximum extinction. The f values found were within the range 0.181–0.326 in ethanol (Table 2) and lower (0.165–0.281) in acetone and correlate well with the hypochromic effect observed.

The considerably higher Stokes shift for dye 3 can be related to the formation of an intramolecular hydrogen bond between the hydroxy group and the unshared electron pair of the nitrogen atom in the azomethine fragment; the H-bond stabilizes the molecule and leads to a much higher quantum yield of fluorescence (×4) than that of dye 2.

The spectral properties of dyes 1–6 in polystyrene

The spectral properties of the benzanthrone dyes were also recorded in polystyrene (Fig. 1) since it was expected like other polymers, to stabilize LC-based systems (see, for example, Ref. 6).



Scheme 3.

By radical polymerization of styrene in the presence of dyes 4–6, yellow–green fluorescing transparent polymers were produced whose absorption and fluorescence spectra were recorded on films 40 μm thick prepared from solution (Table 3). In the polystyrene matrix, dyes 4–6 absorb at 418–422 nm, have fluorescence emission at 496–502 nm and their Stokes shift ($\bar{\nu}_A - \bar{\nu}_F$) is at 3535–3898 cm^{-1}. The results do not evidence any structural changes in the chromophores owing to the polystyrene matrix and/or the process of polymerization such that can alter their spectral properties.

In the case of dye 1 and the amino substituted derivatives, the spectral properties were recorded on films obtained from solution of the dyes and separately prepared polystyrene because of the higher lability of their amino group against radicals involved in the polymerization process. Dye 1 has absorption in the yellow region with the maximum at 465 nm (Fig. 1), its large hypsochromic shift in polystyrene with regard to ethanol being related to conformational changes. Dyes 2 and 3 have absorption in the yellow–green region, with maxima at 426–427 nm, and a slight bathochromic shift with respect to ethanol is observed.

The spectral properties of dyes 1–3 in LC

In LC, dye 1 absorbs at 496 nm and its maximum is red. All other dyes are yellow–green and their maxima are hypsochromically shifted with respect to dye 1 ($\Delta\lambda = 62$, 64 nm). In LC, like in PS, only dye 1 is hypsochromically shifted ($\Delta\lambda = 12$ nm) with respect to ethanol, while dyes 2 and 3 are slightly bathochromically shifted ($\Delta\lambda = 4$ nm). This effect is related to possible formation of intermolecular H-bonds in the case of dye 1 but not in the case of dyes 2 and 3.

Colouring liquid crystalline systems with benzanthrone dyes

Some properties of bi- and tricomponent liquid crystal systems of the 'guest–host' type have been studied. The dyes were 'hosted' by the commercial liquid crystal mixture ZLI 1840 as supplied by Merck which has a broad temperature range of nematic phase (−15–90°C). The tricomponent systems additionally include polystyrene. The dyes amounted in both systems to

TABLE 3

Spectral characteristics of benzanthrone dyes 4–6 in polystyrene (PS) of the viscosity-average mol. mass M_v

Dyes	λ_A^{max} *(nm)*	λ_F^{max} *(nm)*	$\bar{\nu}_A - \bar{\nu}_F$ *(cm^{-1})*	$\bar{M}_v \times 10^{-5}$ *of PS*
4	422	496	3535	3.16
5	418	498	3843	2.90
6	420	502	3889	3.25

0.5 wt.%, while the content of polystyrene in the tricomponent system was 40 wt.% with respect to LC. The preparative methods were as described in previous papers [6,7].

Table 4 presents the results from the thermal measurements on dye/LC and dye/LC/polystyrene mixtures using dye 3 as an example. T_N is the temperature at which the first drop of the isotropic liquid appears on sample heating, whereas T_I is the temperature at which the last drop of the nematics disappears. (T_I–T_N) describes the range of the two-phase region known for 'guest–host' LC systems [13]. ΔT_N and ΔT_I are the shifts of T_N and T_I with respect to the pure liquid crystal. The average values of the nematic–isotropic transition temperature for the mixtures studied $\langle T_{NI}\rangle = \langle (T_N + T_I)/2\rangle$ and the shift with respect to the pure LC, $\langle \Delta T_{NI}\rangle$, are also presented. These data show that the investigated dye introduced into the LC at a concentration at 0.5 wt.% causes a slight decrease of both T_N and T_I temperatures and slightly widens the two-phase region in comparison to the pure LC. The introduction of the polymer, however, enhances change in T_N and T_I: T_N and T_I become lower (with respect to the pure LC) and the widening of the two-phase region is larger.

The orientational order S_A of dye 3 in LC matrix was determined by means of polarized absorption spectrometry [6]. The found value of $S_A = 0.57$ indicates a good orientational order of dye 3 in LC.

On the basis of the good order of dye 3 in the LC matrix and the minor effect it has on the thermodynamic properties of LC, one can conclude that it is a suitable species in display systems working in the passive mode, while dyes 4–6, having much higher quantum yields of fluorescence, are suggestive for utility in displays working both in passive and active modes.

EXPERIMENTAL

Characterization

The electronic spectra in ethanol, acetone, LC and on films of polystyrene were recorded at room temperature using a Hewlett Packard 8452 A

TABLE 4
Transition Temperatures of Bi- and Tricomponent LC Systems Containing Dye 3 and/or Polystyrene (PS) (See Text). The Temperatures are Given in K

System	T_N	T_I	$T_I - T_N$	ΔT_N	ΔT_I	$T_{N,I}$	$\Delta T_{N,I}$
LC	362.5	368.5	6.0	—	—	365.5	—
LC + Dye3	360.8	367.9	7.1	−1.7	−0.6	364.4	−1.1
LC + PS	358.1	366.3	8.2	−4.4	−2.2	362.2	−3.3
LC + Dye3 + PS	357.3	366.0	8.7	−5.2	−2.5	361.7	−3.8

spectrophotometer with 2 nm resolution. Fluorescence spectra were obtained on a Perkin–Elmer M40 spectrophotometer in ethanol using Rhodamine 6G as a standard. FT-IR spectra were taken at 4 cm^{-1} resolution on a Perkin–Elmer 1600 FT-IR spectrophotometer, using KBr pellets. ^1H-NMR spectra were recorded on a YEOL JNM-PS 100 spectrometer operating at 100 MHz in DMSO and using TMS as internal standard (chemical shifts δ in ppm). All melting points given are uncorrected.

The reaction course and purity of the final products were followed by TLC on silica gel (Fluka $F_{60}254$ 20×20; 0.2 mm) using as eluant the solvent systems *n*-heptane/acetone (1/1) for dyes 1–3 and hexane/benzene/chloroform (3/2/1) for dyes 4–6.

Synthesis of 3-aminobenzanthrone (1)

The dye was prepared [8] by nitration of benzanthrone with fuming nitric acid and subsequent reduction of the nitro group by Na_2S. M.p. 244-6°C (cc. [8] 246°C).

Synthesis of 3-amino substituted benzanthrones

2.45 g (0.01 M) 3-aminobenzanthrone was dissolved in 100 ml absolute ethanol. 1.52 ml (0.015 M) benzaldehyde or salicyl-aldehyde were added at boiling point and stirred for 6 h. The final products were filtered and washed with diethyl ether.

3-(Benzylidenamino)benzanthrone (2)

Elemental analysis ($C_{24}H_{15}NO$): calculated %: C, 86.48; H, 4.50; N, 4.20; found %: C, 86.31; H, 4.43; N, 4.16

3-(2-Hydroxybenzylidenamino)benzanthrone (3)

Elemental analysis ($C_{24}H_{15}NO_2$): calculated %: C, 82.52; H, 4.29; N, 4.01; found %: C, 82.30; H, 4.21; N, 3.94

Synthesis of 3-methoxybenzanthrone (4)

The dye was prepared according to the method reported in Ref. 10. *M.p.* 176–178°C (cc. [10] 177–178°C).

Synthesis of 3-alkoxybenzanthrone derivatives

0.01 M Benzanthrone was dissolved in 50 ml DMF; 0.04 M potassium hydroxide, 0.001 M 18-crown-6 and 0.02 M of the corresponding alcohol ROH were added and the mixture stirred at 60°C for 4 h and then poured into 150 ml water, pH = 3 (HCl). The precipitates were filtered and dried after recrystallization from benzene.

3-(2-Methoxyethyloxy)benzanthrone (5)
The reaction time was 4 h.

Elemental analysis ($C_{20}H_{16}O_2$): calculated %: C, 83.33; H, 5.55; found %: C, 83.12; H, 5.38.

^{1}H NMR (DMSO) ppm: 3.42 (s, 3H, CH_3); 4.18–4.30 (q, 4H, OCH_2); 6.84–6.93 (d, lH); 7.08–8.16 (m, 8H).

3-Phenoxybenzanthrone (6)
The reaction time was 6 h.

Elemental analysis ($C_{23}H_{14}O_2$): calculated %: C, 85.71 H, 4.34; found C, 85.59; H, 4.29.

^{1}H NMR (DMSO) ppm: 6.58–6.44 (d, lH); 6.90–6.94 (s, 5H); 7.12-8.68 (m, 8H).

Radical polymerization of styrene in the presence of dyes 4–6
Styrene (10 g), 0.05 g of dye 4–6 and, as initiator, 0.05 g dibenzoylperoxide, were placed in a glass ampoule and the system was purged with nitrogen. The sealed ampoule was heated in a thermostat for 8 h at 80°C to produce the polymers having a yellow–green fluorescence.

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