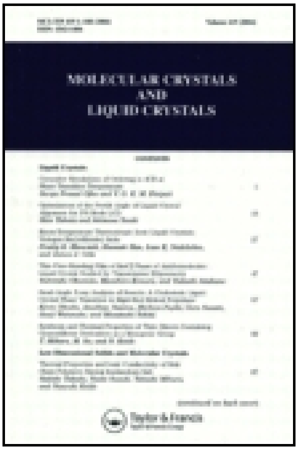

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Ester-Substituted Anthraquinone Dyes Soluble in Nematic Liquid Crystal Mixtures

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Ester-Substituted Anthraquinone Dyes Soluble in Nematic Liquid Crystal Mixtures

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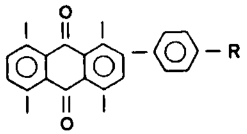
In liquid crystal mixtures of positive dielectric anisotropy, phenyl-substituted anthraquinones dyes have the properties required for Guest-Host applications. To display dark figures on a clear background (positive contrast), it is necessary to use mixtures of negative dielectric anisotropy. In these, the order parameters of the above mentioned dyes drop so much that they are not useful for practical applications. Ester derivatives have been synthesized in order to overcome this drawback. 3-Benzoyloxy-phenyl-and derivatives of 2-carboxy-substituted anthraquinones form a class of useful dyes for display applications.

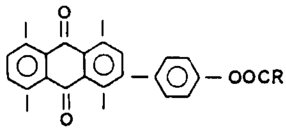
1. INTRODUCTION

The fabrication of displays using colored liquid crystals (L. C.) requires[1] suitable solutions of dyes in the liquid crystalline medium. It is stressed that not only to have the dye and the L. C. be stable, but also their mixture. Often one component acts as a photo-sensitizer toward the other.[2,3] Also the dichroic ratio of the dye, in solution, has to be greater than ten. Convenient dyes have been found for use in L. C. of positive dielectric anisotropy (positive L. C.)[4] A display presenting dark figures on a clear background through the use of negative liquid crystal mixtures (negative L. Cs) has been recently developed.[5] This led us to prepare solutions of the phenyl-substituted anthraquinones (Class I), that we had discovered earlier,[6] in negative L. Cs. We then observed that the order parameter of the dyes (Class I) in these solutions was very low,[7] but that this was not the case of azo dyes.



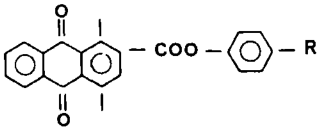
Formula of substituted anthraquinone dyes of Class I

We then hypothesized that this effect was due to the composition of negative L. C. mixtures that are formed of esters which decrease the dye order parameter even in positive L. Cs.[7] Two classes of ester-substituted anthraquinones:



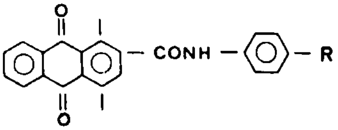
Formula of substituted anthraquinone dyes of Class II

alkanoyloxyphenyl substituted (II) and esters and amides (III and IV) derived from carboxy-substituted anthraquinones were synthesized in the hope that their interactions with the negative L. C. host would be higher than those of compounds of Class I.



Class III

Dye Formula



Class IV

The mode of preparation dictates the position of the ester-containing substituent. Thus all compounds of Class II are substituted in the 3-position, while compounds of Class III are substituted at position 2 of the anthraquinone ring.

This paper will describe the synthesis of the dyes, properties of their solution in L. Cs, and the interactions of these new dyes with the host. Examples of applications are given.

2. SYNTHESIS OF THE DYES

Structures II, III, and IV relate to already known classes of dyes. The preparation of the long chain (R) substituted compounds is adapted from the patent literature.[8] All the compounds described gave satisfactory analyses.

2.1. Preparation of the dyes II

Dyes II were readily obtained by acylating the 4,8-diamino-1,5-dihydroxy-3-(4′-hydroxyphenyl)anthraquinone with an appropriate alkanoic or benzoic acid anhydride. The common starting material itself was prepared by condensing the 4,8-diamino-1,5-dihydroxyanthraquinone-2,6-disulphonic acid with a phenol. The experimental procedure for the condensation and the structure determination of the product have been published.[9] Acylation under the conditions described below gives II and an *N*-acylated derivative of II. The two products can be separated and purified by column chromatography.

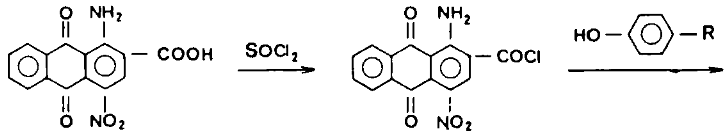
Preparation of 4,8-diamino-1,5-dihydroxy-3-(4′-heptanoyloxyphenyl) anthraquinone: 4,8-Diamino-1,5-dihydroxy-3-(4′-hydroxyphenyl)anthraquinone (1.0 g) was dissolved in dry pyridine (15 ml) at 80°C with good stirring. The resulting solution was cooled to 20°C and heptanoic anhydride (1.35 g) was added dropwise, under nitrogen. The mixture was stirred at 20°C for three h and then poured into water (150 ml). The precipitate was filtered off, washed with water, and dried in vacuum.

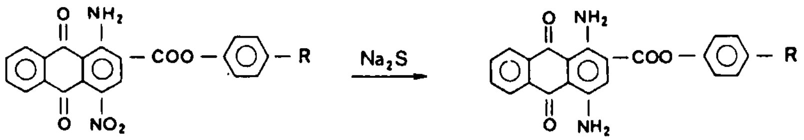
TLC showed two main products which could be separated by column chromatography on silica gel with chloroform + 5% ethyl acetate as eluent. Besides the described compound, another of higher Rf value was isolated. Nmr spectroscopy and MS showed that it was an *N*-acylated derivative of the first—see suggested structure V given later.

Preparation of 4,8-diamino-1,5-dihydroxy-3-(4′-(p-n-butyl benzoyl)oxyphenyl)-anthraquinone: Under nitrogen, a mixture of *p*-n-butylbenzoyl chloride (0.08 g) and sodium benzoate (0.72 g) in dry pyridine at 90–95°C for one h, cooled down to 50°C, and 4,8-diamino-1,5-dihydroxy-3-(4′-hydroxyphenyl)anthraquinone (1.0 g) added. The resulting mixture was stirred at 80–85°C for one h, then poured into water (150 ml). The precipitate was filtered off, washed with water, and dried in vacuum. TLC showed two main products which could be separated by column chromatography on silica gel with toluene + 10% ethyl acetate as eluent. The *N*-acylated compound has a higher Rf value under these conditions.

2.2. Preparation of the dyes III

Dyes III were prepared by the following scheme:





Preparation of p*-n-octylphenyl 1,4-diaminoanthraquinone-2-carboxylate:*

Acid chloride: Under nitrogen, thionyl chloride (10.0 g) was added to a mixture of 1-amino-4-nitroanthraquinone-2-carboxylic acid (4.0 g) in chlorobenzene (50 ml) and a few drops of *N*, *N*-dimethylformamide, heated at 65–70°C. Agitation was continued at this temperature overnight. The excess of thionyl chloride was removed under reduced pressure. The solution was then cooled and petroleum ether (200 ml) was added. The precipitate was filtered off, washed with petroleum ether, and dried in vacuum.

Esterification: A solution of *p*-n-octylphenol (8.12 g) in dry pyridine (100 ml) was stirred, 1-amino-4-nitroanthraquinone-2-carboxylic acid chloride (6.5 g) was added, and the mixture heated at 65–70°C for two h. After cooling down, the precipitate of the ester formed as added petroleum ether was filtered off, washed with petroleum ether, and dried.

Reduction: The nitro group of the anthraquinone ester was reduced by heating under reflux for one h a mixture of *p*-n-octylphenyl 1-amino-4-nitroanthraquinone-2-carboxylate (8.0 g) and sodium sulfide nonahydrate (19.0 g) dissolved in water (500 ml) and ethanol (25 ml). Cooling to room temperature and saturation of the solution with sodium chloride completed the precipitation of the resulting dye which was filtered off, washed with water, and dried in vacuum. The product was purified by column chromatography on silica gel with chloroform + 2% ethyl acetate as eluent.

2.3. Preparation of dye IV

*N-(*p*-Butylphenyl) 1,4-diaminoanthraquinone-2-carboxamide:* A solution of *p*-n-butylaniline (1.8 g) in chlorobenzene (40 ml) at 50°C was stirred. 1-Amino-4-nitroanthraquinone-2-carboxylic acid chloride (2.5 g) was added and the mixture heated at 60–65°C for three h. After cooling to room temperature, the precipitation of the amide was completed by adding hexane. The precipitate was filtered off, washed successively with water, 10% hydrochloric acid and water, and then dried. The reduction of the nitro group of the resulting anthraquinone amide was carried out with sodium sulfide as described above in the case of the anthraquinone ester. Purification of the amide dye was achieved by column chromatography on silica gel with chloroform + 5% ethyl acetate as eluent.

3. EXPERIMENTAL

3.1. Liquid crystal composition

Dye properties were measured using mixtures which were modified in order to optimize one or another property of the mixture. Some were commercial mixtures described in the first part of Table I. Tailored compositions indicated in part 3 were made from the single compounds listed in part 2 of Table I.

3.2. Physical measurements

Solubility: Our previous method[6] gave values that were too high. It has been modified as follows:

A solution of dye, 5 to 6 wt% was prepared by ultrasonic dispersion of the dye in the L. C., maintained at a controlled temperature of 19°C (twice for 15 min). The mixture was centrifuged at 10,000 r. p. m. at 20°C for 20 min. Some of the supernatant liquid (100 mg) was diluted with chloroform in a 10 ml flask. The dye concentration was determined from its optical density at the maximum wavelength by comparison with optical density of a standard solution of known concentration in chloroform.

Order parameter (O. P.): Optical densities of L. C.-dye solutions were measured with a Perkin Elmer 555 Spectrophotometer at the wavelength of maximum absorption. For these measurements the solutions were contained in glass frit-sealed cells. The cell thickness employed was either 15 μ or 30 μ. A matching cell filled with the pure L. C. was positioned in the reference beam, the polarization of both beams being defined using two HN32 polarizers (Polaroid Corp.). Homogeneous alignment of the L. C. mixtures was assured by the use of a 4,000 Å thick rubbed polyimide layer. The homogeneity of the alignment was controlled with the aid of crossed polarizers. The polarization of the spectrophotometer beams was arranged so as to be parallel with the alignment directions of the cells, by examining the position of the absorption maximum. The optical densities (D) of a solution were measured with the light beam polarized either parallel ($D_{\parallel}$) or perpendicular ($D_{\perp}$) to the L. C. alignment direction by means of a 90° rotation of the cells.

TABLE I

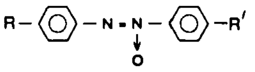
Compositions of the L. C. mixtures mentioned in the text:

Part 1 Commercial mixtures

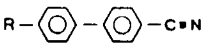
Code	Composition	T_{NI}°C	$\Delta\varepsilon$	Source
NP V	Azoxy	73	−0.2	Merck
ZLI1132	PCH	70	10.3	Merck
ZLI1275	E	80	−0.8	Merck
ZLI1221	PCH, E	90	8.0	Merck
ZLI1291	PCH, E	107	8.6	Merck
ZLI1565	PCH, CPCH	85	6.0	Merck
ZLI1840	PCH, CPCH	90	12.2	Merck
E7	CB	60	11	BDH
E8	CB	72	18	BDH
E38	CB, E	85	–	BDH
E43	CB	84	12	BDH
E55	CB, E	60	–	BDH
ROTN-101	E	73	17.6	Roche
ROTN-103	E	81	25.6	Roche
N-24	E	71	−1.1	Chisso
EN-24	E, *o*-diCN	66	−5.6	Chisso

Part 2 Single compounds

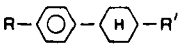
Azoxy



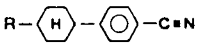
Cyanobiphenyle (C. B.)



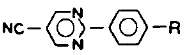
phenyl cyclo hexane (PCH)



cyano phenyl cyclo hexane (CPCH)

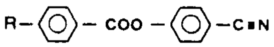


cyano pyrimidine (Cpy)

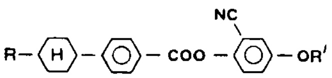


Ester (E)

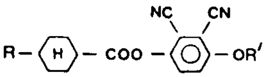
cyano-ester (C. E.)



m-cyano ester (*m*-C. E.)



o-dicyano ester (*o*-diCN)



where RR′ are alkyl or alkoxy substituent

Part 3 Host mixtures

Code	Composition	T_{NI}°C	$\Delta\varepsilon$	Source
ALP2	PCH, CPy	105	13.9	ASULAB
ALP5	CE, CB	85	12.3	ASULAB
ALP10	CB, PCH, CPy	111	14.1	ASULAB
ALP12	CE	60	15.1	ASULAB
ALP13	CE, CPy	150	13.7	ASULAB
ALN4	E, *m*-CN	115	−2.2	ASULAB
ALN5	E, *m*-CN	133	−2.5	ASULAB
ALN10	PCH	72.5	−0.25	ASULAB
ALN29	E	73.6	−1.5	ASULAB
ALN31	E	89	−1	ASULAB
ALN76	E, *o*-diCN	80.6	−2.5	ASULAB

The dye order parameter, S_D, was calculated from the dichroic ratio r, using the following relationships:

$$r = \frac{D_{\parallel}}{D_{\perp}}$$

and

$$S = \frac{r - 1}{r + 2}$$

No correction was made for the anisotropy of the L. C. polarization field. Even when great care is paid to the experimental conditions, variations in the value of S_D of 0.05 units are common. The higher values from measurements are normally quoted, as the lower values are normally caused by imperfect experimental conditions, *e.g.*, L. C. misalignment, cell birefringence, etc.

In this work the cell temperature was thermostatted at 20°C. In the range 20° to 30°C, order parameter values decrease by 0,01 every 5°C.

Stability to light: The photodegradation of L. C.-dye solutions is activated by the presence of oxygen. The cells employed for O. P. measurements were not therefore suitable for use in evaluations of the stability of dyes to sunlight. For this evaluation, cells similar to commercial displays, with a 90° twisted parallel alignment, were employed. The solutions of the dye were degassed, under vacuum and the cells filled under nitrogen. After filling, the aperture was plugged with an epoxy adhesive. Both plates of each cell included an In_2O_3 coating beneath an aligning layer of rubbed polyimide. During the evaluations, the filled cells were placed on a black background in a Leybold-Heraeus "Sun Test apparatus." The cell tray was maintained at 30°C, although the cell temperature was, in fact, higher. The optical density and cell current (under 3 V, 32 Hz excitation) were measured after appropriate periods of exposure. The time after which the optical density decreased to one half of its initial value was deduced from the diagram representing the optical density as a function of time of exposure (Figure 2).

4. DYE-LIQUID CRYSTAL INTERACTIONS

Although often discussed, the interactions of dyes and L. Cs have not been clearly elucidated. With known dyes, concentration in an L. C. cannot be higher than 8% for solubility reasons, and is generally on the order of 2–3%. Then, these interactions do not affect strongly the characteristic physical properties of the L. C. The nematic to isotropic transition temperature (T_{NI} of the solution, for instance, is the same as that of the pure L. C. although it occurs over a much larger temperature range. This corresponds to the two-phase region that has been calculated[10] from the thermodynamics of L. C. solutions. Nevertheless, it has been shown[7] that the apparent dye order parameter of compounds of class I is increased by their interactions with cyanobiphenyl L. Cs. Therefore, before describing the dye properties, the conditions of measurements and the interactions have to be specified. The two classes of dye II and III are considered together with L. Cs of practical use[†] of either positive or negative dielectric anisotropy (D. A).

4.1. Order parameter

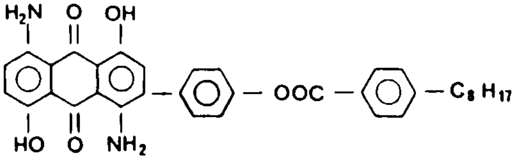
4.1.1. Compounds of structure II

The behavior of the octyl derivative is a representative example for all compounds of that structure. Results are shown in Table II. There is little influence of the L. C. host on the dye order parameter (O. P.) which varies between 0.72 and 0.66. Higher T_{NI} values give a higher O. P., but as soon as T_{NI} is higher than 70°C, the value does not increase further. In most mixtures, the molecular composition does not change the O. P. value. In general, these dyes have the order parameter of the host, as already observed with other anthraquinone derivatives, whose structure is not adapted to the Guest-Host effect.[7]

[†] Practical use means large nematic range (< -10; $> +60$°C) and high dielectric anisotropy.

TABLE II

Order parameter of dyes in various host mixtures



L. C. ($\Delta\varepsilon > o$)	Composition	T_{NI} (°C)	Order parameter
E7	CB	60	0.66
E38	CB, E	85	0.69
ALP-12	CE	60	0.65
ALP-5	CE + CB	85	0.68
ALP-13	CE + CPy	150	0.72
L. C. ($\Delta\varepsilon < o$)			
NP V	Azoxy	73	0.55
ZLI1275	Ester	80	0.69
N24	Ester	71	0.68
EN-24	Ester, *o*-diCN	66	0.65
ALN-76	Ester, *o*-diCN	80.6	0.70
ALN-4	Ester, *m*-CN	115	0.70
ALN-5	Ester, *m*-CN	113	0.71
ALN-10	PCH	72.5	0.70
ALN-29	Ester	73.6	0.70
ALN-31	Ester	89	0.70

4.1.2. Compounds of class III

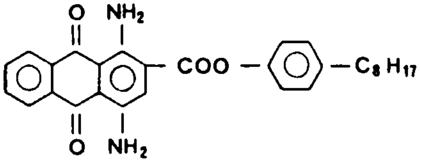
These compounds, which are substituted in the 2-position behave in a way that recalls their 2-phenyl-substituted homologue as shown in Table III for the compound R = C_8H_{17}. They have, in positive L. C. mixtures, an order parameter ($S \sim 08$) which is higher than that of the L. C. and drops in negative L. Cs. These observations may be summarized as follows:

- The order parameter is the highest in L.C. having a cyano-substituent directed along the long molecular axis.
- Among L. Cs of the same chemical constitution, O. P. increases as T_{NI} increases.
- The presence of esters lowers the order parameter. In L. Cs of negative D. A, the order parameter decreases, but stays at a level which is still useful.

Fig. 1 illustrates the behavior of the two classes of compounds compared with their 2- and 3-phenyl-substituted homologues.

TABLE III

Order parameter of dyes in various host mixtures



L. C. ($\Delta\varepsilon > o$)	Composition	T_{NI} (°C)	Order parameter (20°C)
ZLI1132	PCH	70	0.78
ZLI1565	PCH, CPCH	85	0.78
ZLI1840	PCH, CPCH	90	0.80
ZLI1221	PCH, E	90	0.79
ZLI1291	PCH, E	107	0.78
E7	CB	60	0.75
E8	CB	72	0.78
E43	CB	84	0.78
E55	CB, E	60	0.68
ROTN-101	CE	73	0.70
ROTN-103	CE	81	0.75
ALP-12	CE	60	0.72
ALP-2	PCH, CPy	105	0.80
ALP-10	CB, PCH, CPy	111	0.81
L. C. ($\Delta\varepsilon < o$)			
MBBA	Schiffs Base	47	0.45
NP V	Azoxy	73	0.58
ZLI1275	Ester	80	0.66
EN-24	Esters, *o*-diCN	66	0.68
ALN-29	Ester	73.6	0.71
ALN-76	Ester, *o*-diCN	80.6	0.71

5. PROPERTIES OF THE DYES

Knowing the influence of the L. C. as solvent, the properties of the dyes may be compared for two mixtures representative of positive and negative L. Cs.

5.1. Influence of the substituent chain length on the dye order parameter

5.1.1. Compounds of structure II (3-alkanoyloxyphenyl)

The results are collected in Table IV which shows that the order parameter is independent of the chain length and of whether the chain is alkyl or alkoxy. This is the case for the positive (E7), (ALP12) or negative

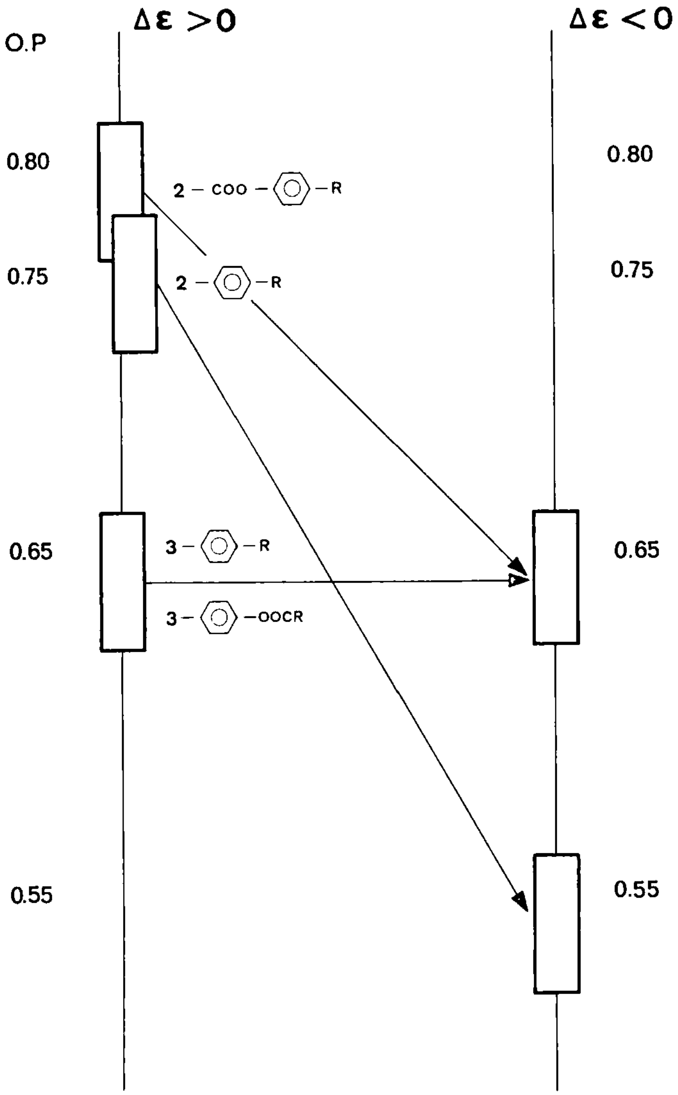
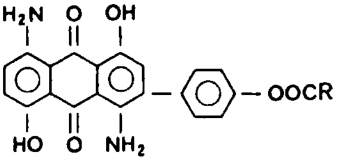


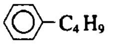
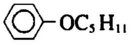
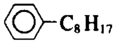
FIGURE 1 The order parameter of substituted anthraquinone dyes in L. C. of varying dielectric anisotropy. The variation depends upon the substituent in the anthraquinone dye.

(ZLI 1275) mixtures, confirming the absence of interactions with the host mentioned in Section 4.1. The measured value of the order parameter (0.66 ±0.02) is similar to that of the corresponding 3-phenyl-substituted compound and equal to that of the host.

TABLE IV

Order parameter of dyes of class II in typical hosts of positive or negative dielectric anisotropy: influence of chain length.



DYE	L.C. ($\Delta\varepsilon > o$)		L.C. ($\Delta\varepsilon < o$)
R	E7 (CB)	ALP-12 (CE)	ZLI1275 (E)
	T_{NI} : 60°C	T_{NI} : 60°C	T_{NI} : 80°C
 $-C_4H_9$	0.68	0.66	0.68
 $-OC_5H_{11}$	0.66	0.66	0.68
 $-C_8H_{17}$	0.66	0.66	0.69
C_5H_{11}	0.64	0.65	0.67
C_6H_{13}	0.65	0.64	0.68

5.1.2. Compounds of Class III (alkyl-phenyl anthraquinone-2-carboxylate)

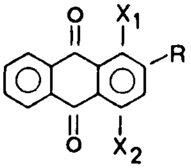
Whereas a slight influence of the chain length is seen in negative L. C., there is in a positive L. C. an increase of the O. P. value from 0.65 to 0.74 as the chain length increases from R = H to R = C_8H_{17} (Table V). This recalls the behavior of the 2-substituted compound (I) already mentioned.

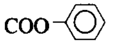
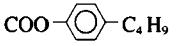
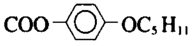
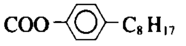
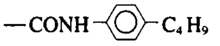
5.2. Stability toward sunlight

The change in the optical density of a cell filled with a solution of the dyes under study and submitted to the light of a Sun Test apparatus is shown in Figure 2. The octylphenyl- and octyl-substituted compounds of Class II and III respectively dissolved in the positive ZLI 1840 and the negative ZLI 1275 have been chosen as representative. While dye II is stable with a half-life of 1,500 h, dye III degrades. During the degradation, the conductivity of the solution increases, indicating the formation of ionizable products. The particular stability of some anthraquinone dyes bearing a substituent (with a mobile hydrogen) in the 1-position is due to the formation, in the excited state, of an enol which deactivates by returning to the ground state. The decrease in optical density with time is different for

TABLE V

Order parameter of dyes of class III in typical hosts of positive or negative dielectric anisotropy: influence of substituents.



Dye			L. C. ($\Delta\varepsilon > o$)		L. C. ($\Delta\varepsilon < o$)
X_1	X_2	R	E7	ALP-12	ZLI1275
NH_2	NH_2		0.65	0.65	–
NH_2	H		0.67	0.61	0.67
NH_2	NH_2		0.73	0.73	0.65
NH_2	NH_2		0.74	0.73	0.65
NH_2	NH_2		0.71	–	0.64

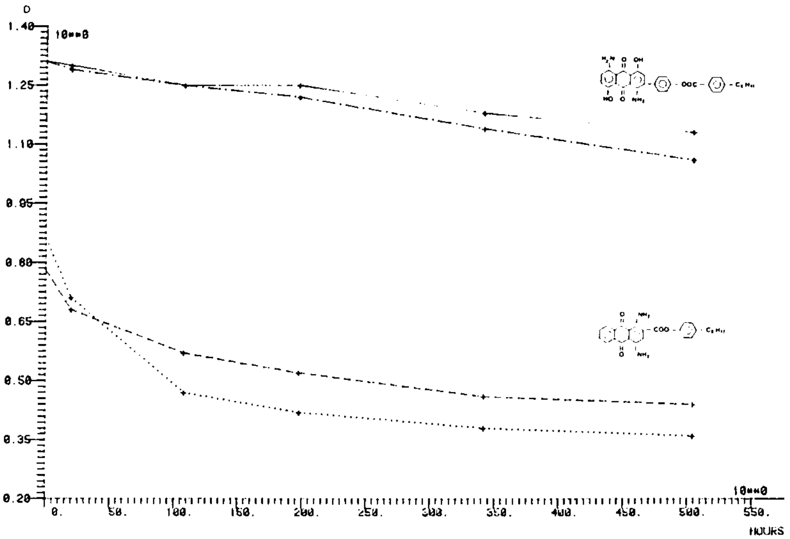


FIGURE 2 The decrease in optical density of a colored (dyed) L. C. solution exposed to sunlight with time a) dye II (R = Octylphenyl) -·-·- in ZLI 1840; ______ in ZLI 1275; b) dye III (R = Octyl) - - - - - in ZLI 1840; · · · · · in ZLI 1275.

dyes II and III as shown in Figure 2. This means that their excited states follow, at least partially, two different paths to return to the ground state. In the case of dye III, we think that the difference resides in the hydrogen bonding of the amino-group with the 2-ester linkage. This bond causes the hydrogen atom of the amino-group to move onto the carbonyl group by absorption of the energy of incident photons. The excited state is no longer an enol, and its deactivation leads to unknown products as shown in Figure 3.

5.3. Maximum solubilities in L. C. mixtures

The dye solubility in itself is not a criterion of applicability of the dye for a Guest-Host display. It is, in fact, the maximum optical density that counts. As the anthraquinone ring substitution only slightly affects the absorption coefficient ε, maximum solubility is, however, a good indication of the maximum optical density. Also the values of solubility at room temperature give an indication of the risk of precipitation of the dye at lower temperatures. In Table VI, solubility values are reported for dyes of both Class II and III, and show a fair, 4 wt%, value in positive mixtures. In negative mixtures of low dielectric anisotropy such as ZLI 1275, this maximum solubility is only 1.5 wt%, which is still sufficient for practical applications taking into account their high absorption coefficient.

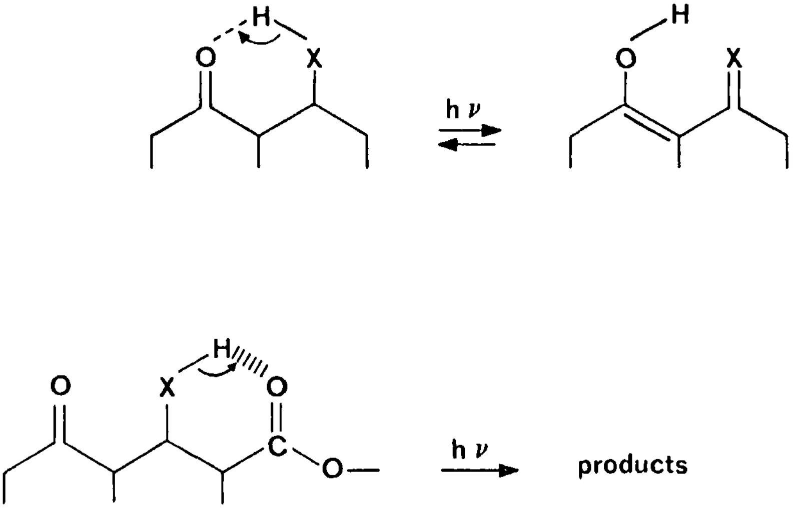
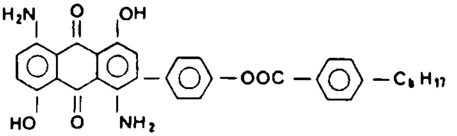
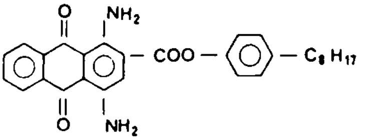
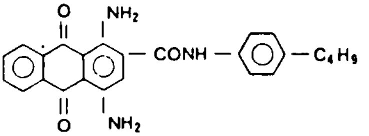


FIGURE 3 An anthraquinone dye is stable because of the reversible exchange of the mobile hydrogen of the 1-substituent. Hydrogen bonding with a 2-acceptor substituent competes with the stabilization mechanism.

TABLE VI

Solubilities of the various dyes in typical hosts

Dye structure	Liquid crystal	Solubility (20°C) % w/w
	E43	4,3
	ZLI1840	4,8
	ZLI1275	1,5
	E43	4,8
	ZLI1840	4,0
	ZLI1275	1,8
	E43	1,7
	ZLI1840	1,1
	ZLI1275	1,0

5.4. Absorption of visible light

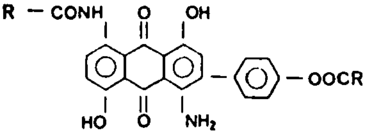
The compounds under investigation are derived from an anthraquinone nucleus which, depending upon its various substituents, determines the color of the dye. With the starting materials available to us, only a few compounds could be made, and no systematic study of the influence of the substituent was feasible.

Compounds of Class II are derived from 1,5-dihydroxy-4,8-diamino-anthraquinone and type III are substituted 1,4-diaminoanthraquinones. In fact, both visible spectra look similar with a wide absorption band of width at half height $\Delta\lambda = 90$ nm, differing in the resolution of the vibration maxima. The spectrum is not influenced measurably by the chain length. Table VII reports the value of the wavelength of that maximum which has the higher wavelength value (and has also the highest optical density) for the two types of compounds with $R = C_8H_{17}$. The maximum absorption coefficient in chloroform is $2 \pm 0.4 \cdot 10^4$ for compounds of Class II and about half this value for type III ($\varepsilon \sim 1.2 \cdot 10^4$). The shade is greenish blue.

Solution of dyes of type II in chloroform absorb at 618 nm and those of Class III at 628 nm. The wavelengths of the maxima (λ max) are shifted in the nematic medium by some 20 nm. The slight variations[†] of λ max from one L. C. to another, are in the experimental uncertainty range of the apparatus. Thus, although our measurements give generally a high precision, we do not know their significance. The broad range of absorption which is characteristic of the anthraquinone dyes is useful in the formulation of mixtures.

6. SOME FURTHER RESULTS

During the syntheses of the alkylbenzoyloxyphenyl derivatives (dyes II), an *N*-acylated compound is formed as a by-product; the structure can only be tentatively represented by V[‡], as the exact position of the amido-group cannot be determined.



Compounds of structure V

For the purpose of evaluation, it was separated from compound II by chromatography. Surprisingly, the properties of both II and V in solution in L. Cs are the same. For practical use the separation may not be required.

Alkyl esters of type II (R = C_nH_{2n+1}) have also been tested; their order parameter is low. In that case the *N*-acylated derivative has a lower order parameter than its non-acylated homologue.

Finally, the influence of the substituent in the 4-position of dyes of Class III has been considered for X = H, NO_2, and Br. The latter dye is insoluble and the others have low O. P. The amido-derivative (IV) has the interest of offering a deep blue shade (λmax = 576 nm) together with a high order parameter. Solubility of 1 wt% in either positive or negative mixtures and $\varepsilon = 1.26 \cdot 10^4$ makes it an interesting dye which we could not consider further in this work.

7. PRACTICAL APPLICATION (DYES OF CLASS II)

A main concern in visualization is to write black characters on a white background. This requires a black dichroic mixture. A common way

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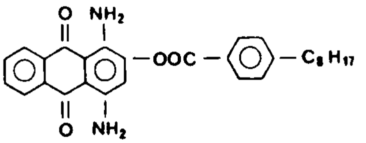
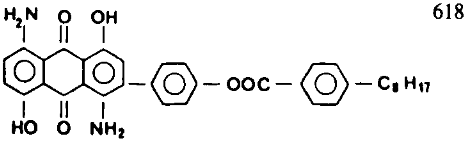
[†] Dye I absorbs at 640 ±2 nm in MBBA and 646 ±2 nm in E7.

[‡] The light stability of compounds V has not been studied.

TABLE VII

Optical properties of the two class of dyes

Dye	CHCL₃		L. C.	
	λmax. nm	ε mole^{-1} l cm^{-1}	λmax. nm	ε∥*
	628	$1{,}2 \cdot 10^4$	642	$5{,}4 \cdot 10^4$ (in E_7)
	618	$2{,}4 \cdot 10^4$	638	$3 \cdot 10^4$ (in 1275)

*ε∥ is absorption coefficient in the parallel direction it depends upon the host and the order parameter.

to obtain the black color is to mix a yellow, a red and a blue dye. We have shown that yellow and red azo dyes have acceptable stability[2] and good order parameter which, furthermore, does not change with the sign of the dielectric anisotropy of the L. C. host. A mixture of $CH_3O—C_6H_4—N=N—C_6H_3(2—CH_3)—(N=N—C_6H_4—)_2OCH_3$ (yellow), $(CH_3)_2N—C_6H_4—N=N—C_6H_3(2—CH_3)—(N=N—C_6H_4)_2—N(CH_3)_2$ and II $R=C_6H_4—C_4H_9$ provides the required composition, as its visible spectrum in a mixture of negative anisotropy shows (Figure 4).

One interesting possibility of displaying a positive contrast with a Guest-Host system is to use a mixture of a nematic L. C. having negative dielectric anisotropy, dichroic dyes, and a chiral compound inducing a cholesteric structure. Choosing a ratio $d/p < 1$ (p: pitch of the cholesteric structure, d: thickness of the cell) and homeotropic boundary conditions, the cholesteric structure unwinds giving a transparent homeotropic structure. The cholesteric structure reappears by application of an electrical field. Thus the areas submitted to the field are colored by the dichroic dye oriented in the homogeneous helical structure.[5]

The physical properties of two typical mixtures are reported in the lower part of Table VIII. In the upper part the threshold voltages of two mixtures A and B are reported, without chiral agent, in a homeotropically aligned, 8-micron thick cell.

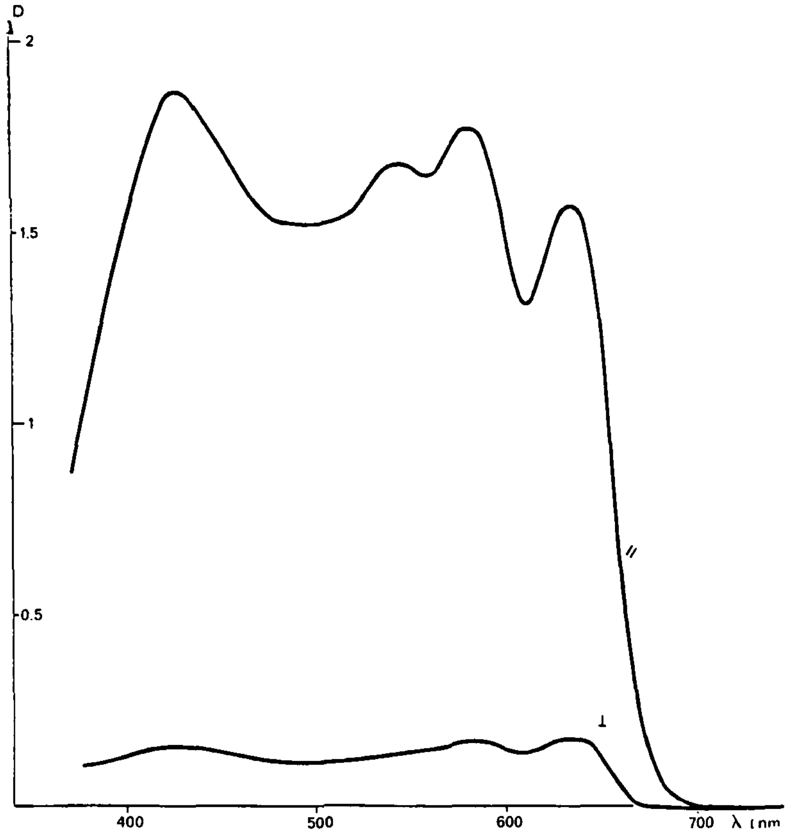


FIGURE 4 Visible spectrum of a black mixture of negative dielectric anisotropy; 16.5 μ cell, parallel orientation, polarized light parallel (||) and perpendicular (⊥) to the nematic director.

8. CONCLUSION

There are, at present, many dyes that have been shown compatible with Guest-Host applications. The favorable molecular geometry of the blue azo dyes has not allowed their practical use, as their solutions in L. Cs are too sensitive to light, and their decomposition produces charged species. Among the substituted anthraquinones, only a few have interactions with the host that make them useful. Host composition varies, depending upon the application sought. Thus the dye structure has to be adapted to the host composition. In many cases the ester derivatives of 3-(*p*-hydroxyphenyl) anthraquinone will prove the best choice.

TABLE VIII

Physical properties of typical black negative L. C. mixtures, and electro-optical properties of positive contrast Guest-Host displays, (cell 8 μ thick, cholesteric pitch p : $d/p=0.7$).

		Mixture A	Mixture B
	Black mixture without chiral agent		
Clearing point (°C)		66	80.5
Viscosity (cP, 20°C)		64	40
Threshold voltage $V_{10}^{(1)}$ (V)		1,40	2,15
	636 nm	0,71	0,74
Order parameters (at 25°C)	580 nm	0,76	0,79
	430 nm	0,76	0,79
	Positive contrast guest host display		
Operating voltage (V)		>2	>3
Threshold voltage (V)		1	1,6
Contrast$^{(2)}$ V=3V		49	45
V=4, 5V		51	53
Brightness$^{(3)}$		45	50
Viewing angle		~±90°C	±90°C
Response time (ms) at 4,5V	+on	60	90
	+off (50%)	400	150

(1) Corresponding to homeotropic alignment (2) Contrast=$(1-I_{on}/I_{off})\times 100$. I_{on} and I_{off} denote respectively the intensities of light reflected corresponding to the ON and OFF states.[11] (3) Brightness=$I_{off}/I^{*}\times 100$ where I^{*} is the light intensity corresponding to a white reflector.[11]

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