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# A Study on Deep Shade Anthraquinone Dyes for Positive Colour Liquid Crystal Display

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# A Study on Deep Shade Anthraquinone Dyes for Positive Colour Liquid Crystal Display†

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## 1. INTRODUCTION

"Guest-Host" effect liquid crystal displays have many advantages, such as vivid colour, wide viewing angle and high brightness. They are used not only for colour display devices but also for the light valve array of full colour display devices.

There are two kinds of "Guest-Host" L. C. display: The negative type and the positive type.

The anthraquinone dyes with positive dichroism have been widely used in negative colour L. C. displays. The dyes with negative dichroism used in positive colour L. C. display have advantages over those with positive dichroism used in negative colour L. C. displays.

Anthraquinone dyes usually have the transition moment almost parallel to their molecular long axis and possess positive dichroism, but only a few anthraquinone dyes with orange to red shade exhibiting negative dichroism have been reported.[1]

In previous work, we have studied different series of anthraquinone dyes from yellow to red with negative dichroism. They are summarized in Table I.[2,3]

In the present work, three series of anthraquinone dyes with violet to blue shades have been designed and synthesized. All of them show negative dichroism.

In these molecules, different electro-donating or electro-withdrawing substituents, such as alkylamino, nitro and hydroxy groups are introduced to the α-position of anthraquinone molecule in order to reduce the transition energy of the molecule. Therefore the maximum absorption wavelength shifts to a longer wavelength area. On the other hand, substituted benzoylated amino or hydroxy groups

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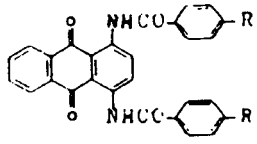
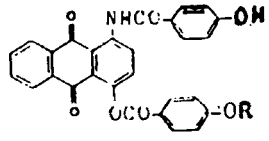
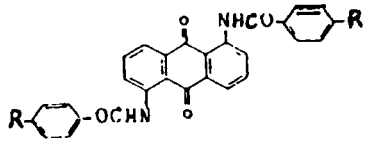
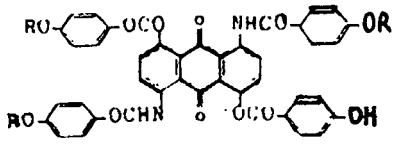
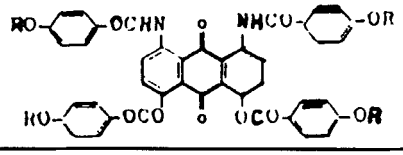
TABLE I

Yellow-red anthraquinone dyes with negative dichroism

| Series | Molecular structure | λ max nm | S |
|---|---|---|---|
| 1 |  | 500 505 | −0.33 −0.36 |
| 2 |  | 428 430 | −0.15 −0.22 |
| 3 |  | 446 | −0.07 |
| 4 |  | 462 | −0.30 |
| 5 |  | 458 461 | −0.29 −0.30 |

introduced to the other unsubstituted α-positions cause the transition moment of dyes to turn and be perpendicular to its molecular long axis.

These dyes are summarized in Table II.

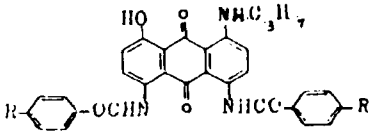
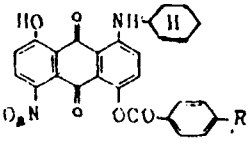
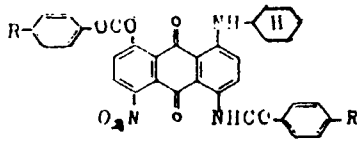
## 2. EXPERIMENTAL

The dichroic dyes have been synthesized starting from 1,8-dihydroxyanthraquinone. All dyes have been purified by thin layer chromatograph on silica gel G and/or recrystallization. The molecular structure of dyes are identified by IR, NMR, MS and elemental analysis. The syntheses and characterization of these dyes are described elsewhere.

The optical densities and maximum absorption wavelengths of the dyes are from a Shimadzu UV-240 spectrophotometer. The cell employed in the experiment is 15 × 35 mm in size. The thickness of the liquid crystal layer in the cell is 10 μm.

TABLE II

Violet-blue anthraquinone dyes with negative dichroism

| Series | Molecular structure | λ max$_1$ nm | $S_1$ | λ max$_2$ nm | $S_2$ |
|---|---|---|---|---|---|
| A |  | 680 | −0.34 ∫ −0.38 | 630 | −0.33 ∫ −0.40 |
| B |  | 664 | −0.27 ∫ −0.28 | 615 | −0.27 ∫ −0.28 |
| C |  | 663 | −0.34 ∫ −0.39 | 613 | −0.34 ∫ −0.39 |

A liquid crystal E63 is used as a host in this work. The properties of these dyes are illustrated in Table III.

## 3. RESULTS AND DISCUSSIONS

### *Solubility of Dyes in Liquid Crystal*

One of the important factors for colour L. C. displays is sufficient solubility of the dye in liquid crystals.

Of the dyes synthesized in this work, the solubilities of dichroic dyes of the *B* series, in which there is one acyl group, are higher than 4% by weight. Dyes of the *B* series have greater solubility than the *C* series, in which there are two acyl groups in the molecule. It was similarly found that the dyes were nearly insoluble in L. C. when three acyl groups were introduced into the dye molecules of the *A* series. In the *A* and *C* series, *R* in the side chains are alkyl groups, the solubilities are higher than when *R* is an alkoxy group.

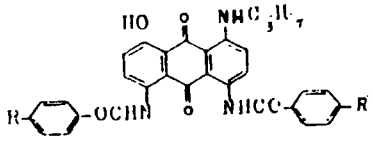
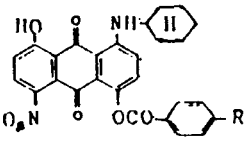
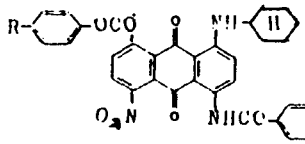
### Order Parameter

The key factor for negative dichroic anthraquinone dyes is that acylated amino or hydroxy groups must be present in the molecule. In our case substituted benzoyl group was introduced.

Dyes of *A* and *C* series contain two benzoyl groups with long chain alkyl or alkoxy substituents. The absolute values of their order parameters are as high as $-0{,}34 \rightarrow -0{,}38$. There is only one benzoyl group in the dyes of the *B* series. The

TABLE III

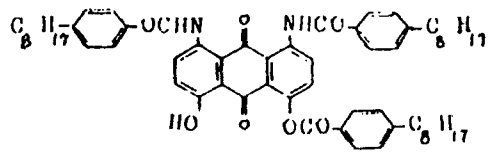
Maximum absorption and order parameter of the dyes

| No. | Molecular structure | R | Content wt% | $S_1$ $\lambda$ max$_1$ | $S_2$ $\lambda$ max$_2$ |
|---|---|---|---|---|---|
| 1 |  | $-C_4H_9$ | 0.5 | −0.34 | −0.33 |
| 2 | | $-C_5H_{11}$ | 0.5 | −0.34 | −0.34 |
| 3 | | $-C_6H_{13}$ | 0.5 | −0.34 | −0.34 |
| 4 | | $-C_7H_{15}$ | 0.5 | −0.35 | −0.35 |
| 5 | | $-C_8H_{17}$ | 0.5 | −0.36 | −0.37 |
| 6 | | $-C_9H_{19}$ | 0.5 | −0.36 | −0.38 |
| 9 | | $-OC_8H_{18}$ | 0.3 | −0.38 | −0.40 |
| 19 |  | $-C_4H_9$ | 1.5 | −0.27 | −0.27 |
| 20 | | $-C_6H_{13}$ | 1.5 | −0.27 | −0.27 |
| 21 | | $-C_7H_{15}$ | 1.5 | −0.27 | −0.27 |
| 22 | | $-C_9H_{19}$ | 1.5 | −0.27 | −0.27 |
| 23 | | $-OC_4H_9$ | 1.5 | −0.27 | −0.27 |
| 24 | | $-OC_5H_{11}$ | 1.5 | −0.27 | −0.27 |
| 25 | | $-OC_6H_{13}$ | 1.5 | −0.27 | −0.27 |
| 26 | | $-OC_7H_{15}$ | 1.5 | −0.28 | −0.28 |
| 27 | | $-OC_8H_{11}$ | 1.5 | −0.28 | −0.28 |
| 28 | | $-OC_9H_{19}$ | 1.5 | −0.28 | −0.28 |
| 29 | | $-C_4H_9$ | 1.0 | −0.36 | −0.37 |
| 30 | | $-C_6H_{13}$ | 1.0 | −0.38 | −0.38 |
| 31 | | $-C_7H_{15}$ | 1.0 | −0.38 | −0.37 |
| 32 |  | $-C_8H_{18}$ | 1.0 | −0.39 | −0.38 |
| 33 | | $-OC_4H_9$ | 0.8 | −0.34 | −0.34 |
| 34 | | $-OC_5H_{11}$ | 0.8 | −0.37 | −0.38 |
| 35 | | $-OC_6H_{13}$ | 0.8 | −0.38 | −0.39 |
| 36 | | $-OC_8H_{17}$ | 0.8 | −0.39 | −0.37 |
| 37 | | $-OC_9H_{19}$ | 0.8 | −0.39 | −0.38 |

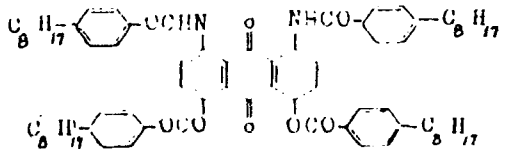
absolute values of their parameters are in the range of $-0{,}27 \rightarrow -0{,}29$, which are obviously lower than those of the *A* and *C* series. It was found that in each series the dyes substituted with alkoxy groups in the side chain have slightly higher order parameters than those substituted with alkyl groups containing the same number of carbon atoms. The side chain has an influence on the value of order parameter; in all series, increasing the number of carbon atoms in the side chain increases the absolute value of order parameter until the number of carbon atoms reaches 7 or 8.

### Absorption Spectra

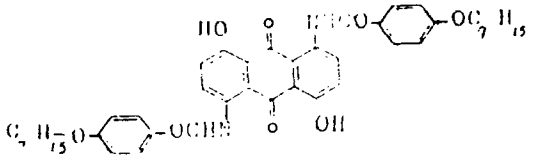
As a general rule the maximum absorption wavelength shift to short wavelength due to the result of acylation of either the amino or hydroxy group. For example, in our previous work, it was found that the maximum absorption wavelength of the dye of formula



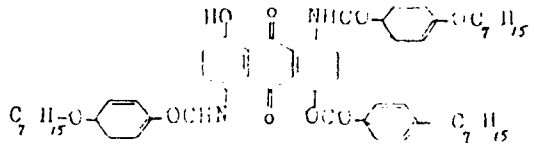
is 526 nm, while that of dye of formula



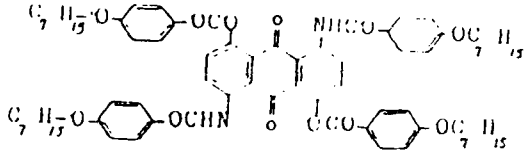
decreases to 458 nm. A similar relationship occurs in dyes of



λmax. 526 nm



λmax. 475 nm



λmax. 462 nm

But in our present work it has been found that the introduction of acylated hydroxy group has little influence on the maximum absorption, viz the maximum absorption of acylated dye is 663 nm and 613 nm while that of the nonacylated is only 664 nm and 615 nm (see Table II).

## References


1. A. V. Ivashchenko *et al.*, *Mol. Cryst. Liq. Cryst.*, **129**, 259 (1985).
2. Guo Du Ren, Wei Wu, Jia Ru Wang, presented at the First International Symposium on Chemistry on Functional Dyes. June, 1989 in Osaka.
3. Wei Wu, Guo Du Ren, Jia Ru Wang, *Journal of Dalin University of Technology*, **29**, 645 (1989).