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Dyes with Negative Dichroism for Liquid Crystal Displays Based on the Guest-Host Effect

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The novel approach is proposed to the synthesis of dyes with negative dichroism. The molecular models, which are adequate to the dichroic dyes, are shown. As an example of the approach, the synthesis and dichroic properties of some derivatives of the 2,2′-azoimidazole are described. The time and contrast characteristics of the displays, based on the guest-host effect, are presented.

1. INTRODUCTION

Widely used twist-effect liquid crystal displays provide only black and white image and have low brightness and limited view angle. Color displays based on the electric field induced reorientation of dye molecules, together with liquid crystalline matrices (the guest-host effect)[1] are, to some extent, free of these disadvantages. Moreover, different colors of dichroic dyes allow us to increase the information content and to make better the aesthetic appearance of the display.

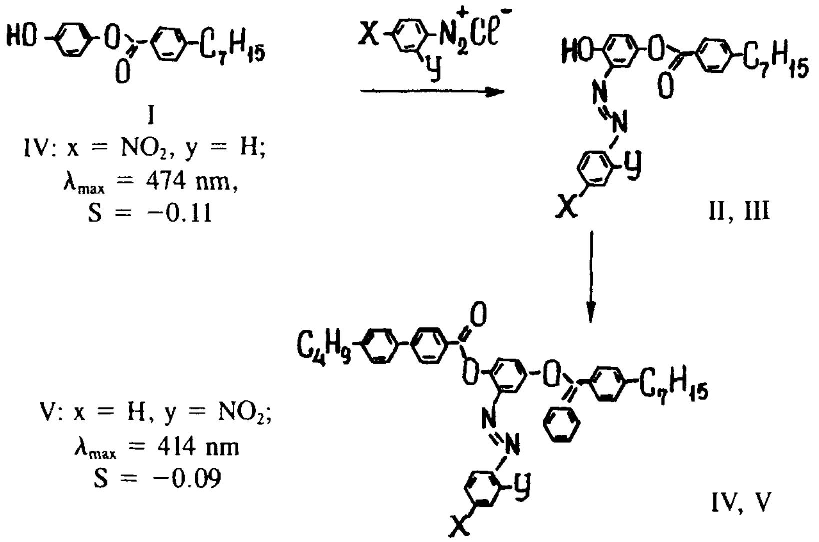
At the present time, there have been discoveries of a number of dichroic dyes having positive dichroism.[2,3] Such dyes provide a negative contrast in most of color displays.[3] Serious technological difficulties do not allow obtaining good positive contrast using cells with slightly tilted homeotropic orientation of liquid crystals doped with positive dichroic dyes. The simplest way to have a positive contrast is the utilization of dyes with negative dichroism in usual twist-cells. In addition, one can have the color switching using dyes with two absorption bands having dichroism of opposite signs.[4,5]

The choice of such dyes is limited by certain bis-merocyanine derivatives having narrow absorption bands and low solubility[6] and tetrazines having low extinction coefficients.[7] So, the aim of the present paper is to carry out new dyes with negative dichroism, as well as liquid crystalline mixtures, based on their display applications.

2. A NOVEL APPROACH TO CONSTRUCTING THE DYES WITH NEGATIVE DICHROISM AND EXPERIMENTAL RESULTS

The novel approach[8] is based on the idea that the dye molecule can have, in principle, more complicated, not to be a rod-like, spatial structure consisting of some "blocks". Each of the blocks can have an isolated chromophore conjugation chain providing an electronic transition in the visible spectral range with a certain direction of the absorption oscillator. In addition, a special type of the mutual packing of dye and liquid crystalline molecules must take place, which increases the orientational order parameter for the dye molecules; see for example Figure 1m.

In the framework of this approach, we have synthesized the substituted azobenzenes IV and V having negative dichroism. The synthesis was done as follows (for details see Appendix)



I

IV: x = NO_2, y = H;
λ_{max} = 474 nm,
S = −0.11

II, III

V: x = H, y = NO_2;
λ_{max} = 414 nm
S = −0.09

IV, V

The negative dichroism is accounted for by the perpendicular orientation of the electronic oscillator of the azo-moiety with respect to the longest molecular axis of the compounds IV and V as a whole.

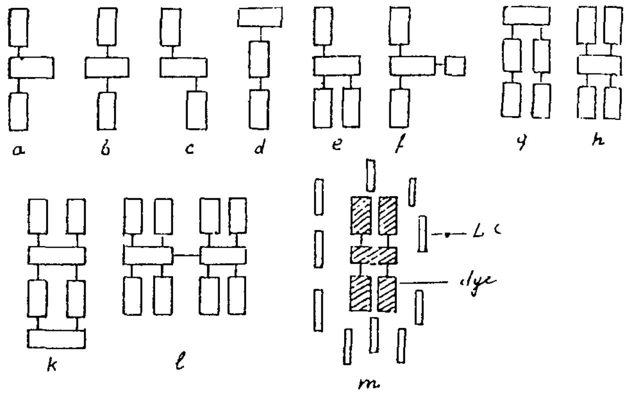
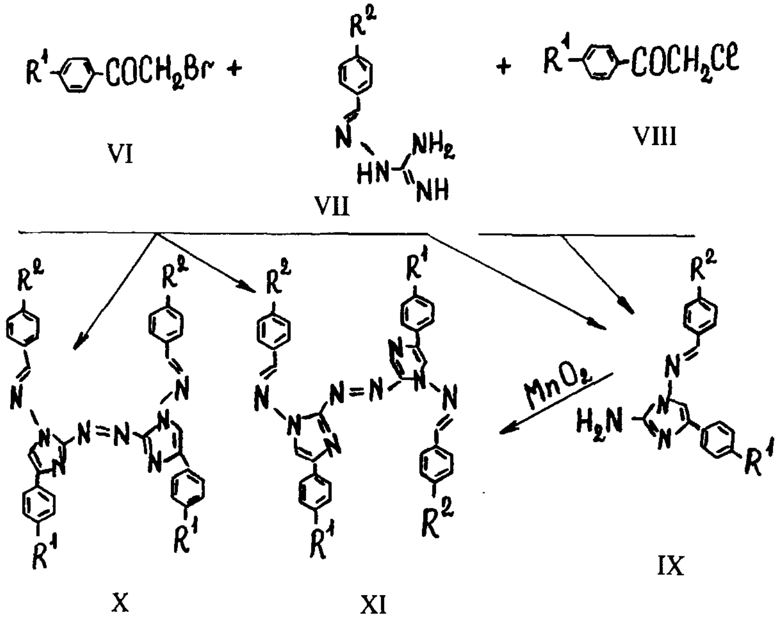


FIGURE 1 Molecular models for dichroic dyes for liquid crystal display applications.

The substituted 2,2′-azoimidazoles (X, XI) provide examples of more complicated dichroic dyes (Fig. 1h) synthesized according to the following scheme:[9,10]



Absorption spectra of 2,2′-azoimidazoles in the visible range have two bands, the short wave band and the long wave band, which are due to the absorption by the benzylidene and azo-groups, respectively.

The typical polarization absorption spectrum for a derivative of the 2,2′-azoimidazole (KD-5) in a homogeneously oriented liquid crystalline layer is shown in Figure 2. One can see that the short wave band at $\lambda_{max} = 430$ nm has positive dichroism with a dichroic ratio $D_{\parallel}/D_{\perp} = 6.7$ (the corresponding "apparent" order parameter for the longitudinal absorption oscillator calculated without any corrections on the local field anisotropy, $S_1 = 0.64$). The long wave band at $\lambda_{max} = 540$ nm has negative dichroism with a dichroic ratio $D_{\perp}/D_{\parallel} = 3.2$ (the "apparent" order parameter for the transverse oscillator $S_2 = -0.29$). The latter value can be considered as a rather high one for the saturation value of S_2 is -0.5.

The spectra shown can easily be accounted for by the molecular structure of 2,2′-azoimidazoles. It is obvious that the longest molecular axis is directed along the benzylidene groups —CH=N—. Thus, the short wave absorption oscillator is also directed along this axis (positive dichroism) while the long wave oscillator is perpendicular to the long molecular axis (negative dichroism).

From the first glance, it seems surprising that the values S_1 and S_2 are high enough, though the molecules of 2,2′-azoimidazoles are rather extended along the transverse direction. However, we believe that the specific spatial structure of these dye molecules allow the rod-like molecules of a liquid crystalline matrix to be built into their frames (Figure 1h). Such a penetration markedly increases the orientational order parameter of our guest molecules as compared to the order parameter of guest molecules having

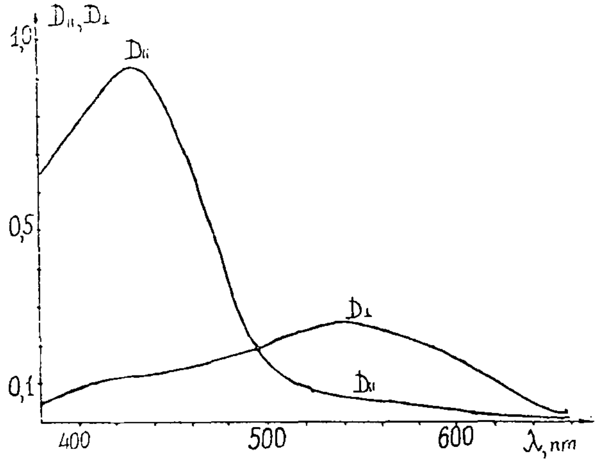


FIGURE 2 Polarization absorption spectrum of dye KD-5 in a mixture of alkyl- and alkoxy-cyanobiphenyls; A homogeneously oriented layer, thickness = 20 μ, temperature = 22°C, dye concentration = 0.7 wt%.

TABLE I

Parameters of dichroic dyes (substituted 2,2'-azoimidazoles X,XI), measured at 22°C in a mixture of *p*-alkyl- and *p*-alkyloxy-cyanobiphenyls (CB).

Compound N	R^1	R^2	λ^2_{max}	S_2	λ^1_{max}	S_1
Xa	n-C_6H_{13}	H	536	−0.24	395	0.66
Xb	n-C_7H_{15}	H	530	−0.24	400	0.57
Xc	n-C_8H_{17}-	H	530	−0.28	395	0.58
XIa	n-C_8H_{17}-	H	545	−0.28	426	0.66
XIb	H	H	530	−0.14	430	0.50
XIc	n-C_7H_{15}	C_2H_5O	540	−0.13	430	0.50
XId	n-C_7H_{15}	O_2	550	−0.15	400	0.47
XIe	n-C_8H_{17}	C_2H_5O	560	−0.21	440	0.66

simple rectangular form with the same dimensions. The other derivatives of the 2.2'-azoimidazole listed in Table I show analogous polarization spectra.

The dichroic dyes X,XI shown in Table I have strong absorption bands (the extinction coefficient $\varepsilon \approx 0.8 - 1.7 \cdot 10^4 cm^{-1} \cdot M^{-1} \cdot l$) in the visible range and high "apparent" order parameters. When used in liquid crystal twist displays with only one polaroid, these dyes allow us to have bright red-violet symbols against yellow background. Without any polaroids one can have a twist display with red-violet symbols against brown background.

We also synthesized other dyes of more complicated structure (Figure 1a, c, e, h) having negative dichroism and high order parameter,[11] Table II.

TABLE II

Parameters of some novel dyes measured at 22°C in the same CB mixture.

Code :	KD-36 :	KD-53 :	KD-54 :	KD-77 :	KD-81 :	KD-92
λ_{max}, nm	512	446	$\frac{580}{617}$	535	470	$\frac{580}{614}$
$D_\perp/D_\parallel$	4.2	2.4	$\frac{4.0}{3.8}$	4.8	4.8	$\frac{4.0}{3.8}$
S	−0.35	−0.22	−0.32	−0.36	−0.36	−0.32
$\varepsilon \cdot 10^4$ $(M^{-1} \cdot cm^{-1} \cdot l)$	0.68	0.57	1.1	....	0.8	1.1
Color	red	yellow	blue	ruby-red	orange	blue

All of the dyes are photochemically stable and easily soluble in liquid crystalline mixtures.

3. ELECTRO-OPTICAL PROPERTIES

The electro-optical characteristics of liquid crystalline materials containing dyes at all, and dyes with negative dichroism in particular, markedly differ from that for the usual twist effect. Two different regimes are compared in Figure 3. Curve 1 is a normalized contrast-voltage characteristic for a CB mixture doped simultaneously with two dyes (1 wt % of KD-54, and 0.5 wt % of KD-92) placed into a conventional twist-cell of thickness 20 μ with only one polaroid. Curve 2 is the corresponding characteristic for a pure CB mixture in the same twist cell placed between two polaroids. It is easy to see that the threshold for the guest-host effect is lower than that for the twist-effect as the former corresponds to the onset of the director distortion, while the latter coincides with the cut-off of the Mauguin regime.[12]

The steepness of contrast-voltage curves is smaller in the case of the guest-host effect (Figure 3). In particular, the parameter $P_{50} = (U_{50} - U_{90})/U_{90}$ is 0.26 and 0.16 for the guest-host and twist-effect respectively (here U_{50} and U_{90} are external voltages corresponding to the 50%- and 90%-optical transmissions).

In addition, the time characteristics for the guest host effect are somewhat worse than those for the twist-effect. For instance, the rise time for

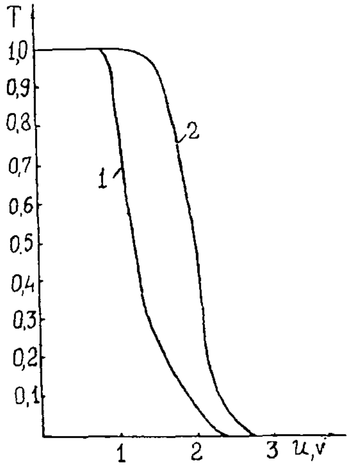


FIGURE 3 Normalized optical transmission curves as functions of the voltage across the twist cell: 1 – guest-host effect, 2 – twist-effect.

the conventional E7 and NP-1565 mixtures doped with our KD-54 dye are 120 and 115 ms respectively (a 10 μ twist-cell with one polaroid in the guest-host regime, voltage $U = 4$V, temperature is 22°C). The corresponding rise times for the twist-effect under the same conditions are 85 and 70 ms. The decay times for the guest-host effect are 170 ms(E7) and 90 ms (NP-1565), while for the twist-effect they are 90 ms(E7) and 40 ms(NP-1565). This difference is also accounted for by different criteria for the degree of the director reorientation (full reorientation in the case of the guest-host effect and only partial reorientation near cell boundaries responsible for the optical rotation in the Mauguin regime for the twist-effect).[12]

APPENDIX

Synthesis of the azo-dyes with negative dichroism

The diazo-solution obtained by diazotation of 1.4 g(0.01 M) *p*-nitroaniline is added (with mixing) to the solution of 3.12 g (0.01 M) monoheptylbenzoylhydroquinone in 50 ml ethanol. The 25% solution of sodium carbonate is used to increase pH of the mixture up to 8. The deposition is filtered, washed with water, and recrystallired from 70% acetic acid. The result is 4 g of 4-heptylbenzoyloxy-2(4′-nitrophenyl)-azo-1-oxybenzene (II) with m.p. 113–114°C. Found, %: C 67.95, H 5.77, N 8.97; $C_{26}H_{27}N_3O_5$. Calcul, %: C 67.66, H 5.90, N 9.11.

3 g chloroanhydride of the butyldiphenyl-carboxylic acid is added (with mixing) to the solution of 4 g 4-heptylbenzoyloxy 2-(4′-nitrophenyl)-azo-1-oxybenzene in 15 ml pyridine, temperature was not allowed to be higher than 25°C. The reaction mixture is remained for a night, then is poured into the hydrochloric acid. The dye is extracted by chloroform. The chloroform extract is washed until neutral reaction, chloroform is evaporated, and the deposition is recrystallired from ethanol and acetone. The result is 0.8 g(13.22%) dye IV with transition temperatures 160-198.5°C. Found, %: C 73.92, H 6.34, N 6.21: $C_{43}H_{43}N_3O_6$. Calcul., %: C 74.01, H 6.21, N 6.02.

Compound III is obtained the same way as II from monoheptylbenzoylhydroquinone and O-nitroaniline.

0.9 g (19.84 %) compound *V* is obtained from 2.5 g 2-oxy-5-(4′-heptylbenzoyloxy)-2″-nitroazobenzene (III) and 3.0 g chloroanhydride of the *p*-butyldiphenylcarboxylic acid. The transition temperature is 90.8-143.7°C. Found, %: C 74.11, H 6.43, N 6.30; $C_{43}H_{43}N_3O_6$. Calcul.,%: C 74.01, H 6.21, N 6.02.

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