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A. Ivashchenko^a & V. Titov^a

^a Organic Intermediates & Dyes Institute, Moscow, 103787, USSR
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Dichroic Dyes for Liquid Crystal Devices

A. IVASHCHENKO and V. TITOV

Organic Intermediates & Dyes Institute, Moscow 103787, USSR

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Using data on geometry of molecules and direction of electronic oscillator a large series of dichroic dyes have been synthesized exhibiting positive, negative or zero dichroism, as well as two colour dichroic dyes with opposite signs of dichroism of absorption bands. Ways of obtaining dichroic dyes with a higher solubility have been proposed.

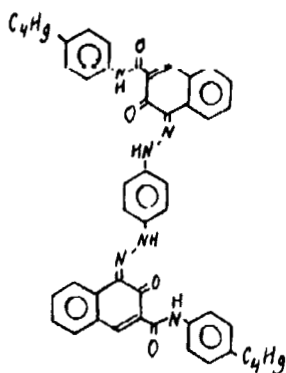
1. INTRODUCTION

Liquid Crystal Materials (LCM) for displays based on guest host electro-optic effect¹ contain one or more Dichroic Dyes (DD) in a liquid crystalline matrix; therefore their design is a more sophisticated scientific and technological problem than that of the ordinary LCM. Additional problems in this case are mainly connected with the order parameter (S), solubility and stability of DD in LCM. For a long time, relations between DD structure and properties have been studied in our research laboratory. As a result, we have worked out a methodology of DD design² which allows DD of all the four types to be obtained: L-type (DD of positive dichroism, $0 < S \leq 1$), T-type (DD of negative dichroism, $-0.5 \leq S < 0$), I type (isotropic DD, $S = 0$) and LT-type (DD with two or more absorption bands with opposite signs of dichroism).³ Besides, we have found ways of obtaining DD with a high solubility (C) in Liquid Crystals (LC). This paper reports the main results of our investigations.

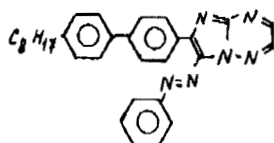
2. RESULTS AND DISCUSSION

2.1. Methodology of DD Design

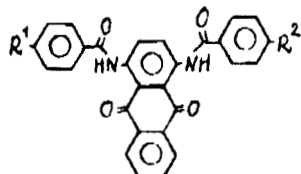
As a result of our studies we have shown that DD molecules can have not only rod-like (as in LC ones) but also a more complicated structure. As a rule, DD molecules have rod-like fragments bound by different groupments permitting LC molecules to penetrate partly into a DD molecule (see Figure 1). This and more complicated DD structures allow the achievement of high geometric ordering (S_r)



I $\lambda_1 = 603 \text{ nm}$, $\lambda_2 = 650 \text{ nm}$;
 $S_1 = S_2 = -0.33$



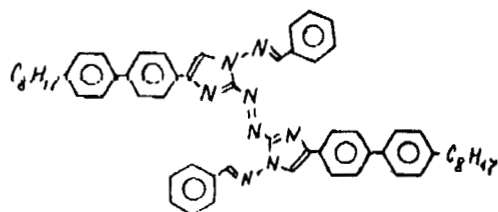
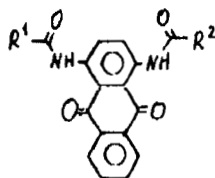
III $\lambda = 413 \text{ nm}$, $S = 0$



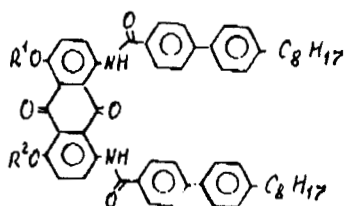
VII $R^1 = C_6H_{13}$, $R^2 = C_5H_{11}$ (cyclohexyl);
 $c = 3.1\%$

VIII $R^1 = R^2 = C_6H_{13}$; $c = 0.5\%$

IX $R^1 = R^2 = C_5H_{11}$ (cyclohexyl); $c = 1.0\%$



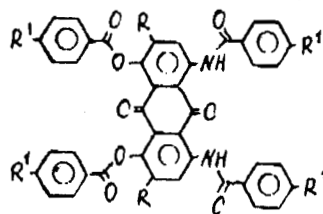
II $\lambda_1 = 426 \text{ nm}$, $\lambda_2 = 545 \text{ nm}$;
 $S_1 = +0.66$, $S_2 = -0.28$



IV $R^1 = R^2 = H$, $\lambda_1 = 560 \text{ nm}$,
 $\lambda_2 = 600 \text{ nm}$; $S_1 = S_2 = -0.34$

V $R^1 = C_8H_{17}$ (phenyl), $R^2 = H$;
 $\lambda = 535 \text{ nm}$, $S = -0.35$

VI $R^1 = R^2 = C_8H_{17}$ (phenyl);
 $\lambda = 470 \text{ nm}$; $S = -0.36$



X $R = R^1 = C_4H_9$; $S = -0.32$, $c > 9\%$

XI $R = H$, $R^1 = C_4H_9$; $S = -0.33$, $c = 0.5\%$

XII $R^1 = R^2 = C_4H_9$ (cyclohexyl)

XIII $R^1 = C_4H_9$ (cyclohexyl), $R^2 = C_5H_{11}$ (cyclohexyl)

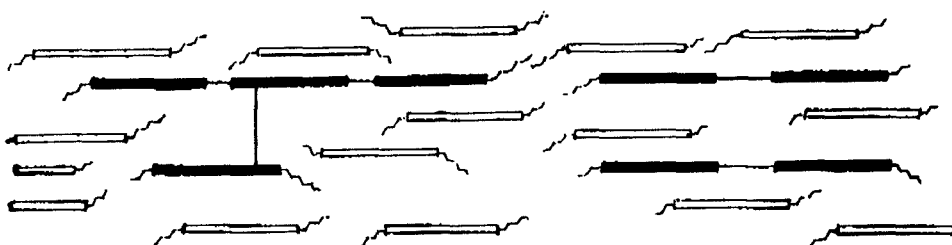


FIGURE 1 Package of DD molecules^{1, 2} in the oriented layer of LC molecules.³

of DD molecules in the LC up to a theoretical value of $S^r \approx 1$. By knowing, from quantum-chemical calculations or experimental data, the direction of the oscillator of the long-wave electronic transition in a dye, we can obtain a dye with a fixed value and sign of dichroism by introduction of appropriate substituents in particular parts of the dye molecule. Using this methodology we have obtained different DD, the most significant of them being azo dyes I–III^{4–6} and anthraquinona dyes IV–VI⁷ of T-, LT- and I-types.

2.2. DD Solubility

Analysis of the published data and our own investigations allowed us to separate out the three most effective ways of obtaining DD with a high solubility in LC:

1. It was stated that asymmetrically substituted DD have higher solubility than their symmetric analogues. For example, the solubility of DD VII in the LC mixture ZK-807 is six times higher than that of DD VIII and three times higher than that of DD IX.⁹
2. It was shown that introduction of lateral alkyl substituents in DD molecules enhances their solubility in LC.¹⁰ Thus, for instance, the solubility of DD X in ZK-807 is almost 20 times higher than that of the analogous dye XI lacking similar lateral substituents.^{8–10}
3. A higher DD solubility in LC can be achieved using a mixture of DD absorbing in the same spectral range (homologous series of DD). Similar mixtures can be specially synthesized instead of mixing individual DD. Thus, for example, the mixture of DD IX, XII and XIII obtained by acylation of 1,4-diaminoanthraquinone with the mixture of trans-4-butylcyclohexanecarbonyl and 4-(trans-4-pentylcyclohexyl)-benzoyl chlorides (1:1) has a solubility in ZK-807 three times higher than the solubility of DD IX and six times higher than that of DD XII.⁹

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