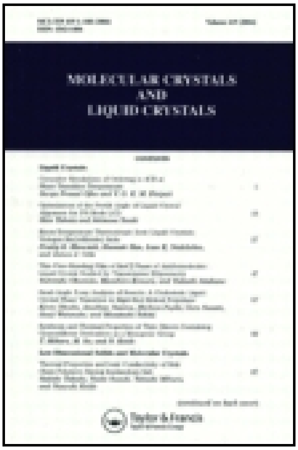

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Guest-Host Interactions in Nematic Liquid Crystals

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Guest-Host Interactions in Nematic Liquid Crystals

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RCA Laboratories
Princeton, New Jersey

Abstract—A new electro-optic effect based on guest-host interactions in nematic liquid crystals is described. The cooperative alignment of a nematic liquid crystal in an electric field is used to orient " guest " pleochroic dye molecules (molecules whose absorption spectrum is a function of the molecular orientation with respect to the polarization of the incident light). Electronic color switching was achieved using fields of the order of 10 kV/cm (dc through audio) with a variety of dyes. A detailed study of the optical density changes as a function of field strength and dye concentration for one guest-host system is also presented.

Introduction

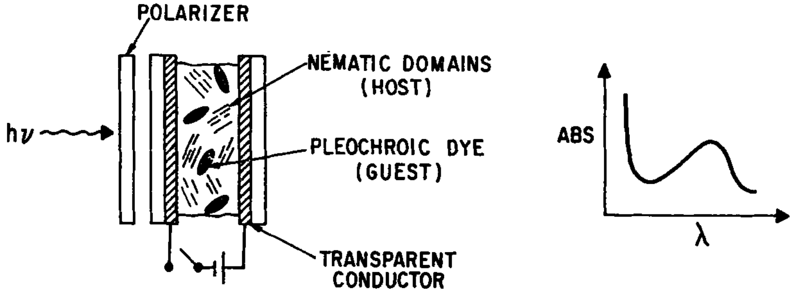
Cooperative phenomenon in nematic materials under electric fields has been the subject of several studies conducted in these laboratories over the past several years.[1,2,3,4] A systematic study of the relationship between molecular structure and the electrical properties of nematic liquid crystals has recently led to the discovery that cooperative alignment of certain mesomorphic " host " compounds by external electric fields can be used to orient pleochroic dye molecules (" guests ").[5] This orientation results in changes in the optical density of the material and consequently in the color of light transmitted through the medium. This report is a detailed account of our efforts to investigate the nature and scope of this new effect.

Discussion

The optical absorption spectrum of a pleochroic dye molecule is a function of its molecular orientation with respect to the polarization of the incident light. Materials which exhibit pleochroism are usually long, cylindrically shaped molecules containing chromophoric groups which form part of an extended aromatic system. Thus, if the pleochroic molecule is oriented with its long axis parallel to the electric vector of the incident polarized light, absorption of light by the molecule (low energy transition) occurs and the characteristic color of the dye is observed.

Conversely, orientation of the molecule with its long axis perpendicular to the electric vector results in little or no absorption by the visible transition and the incident light is transmitted unchanged.

The effect of electric fields on mixtures of these dyes with nematic hosts is illustrated in Fig. 1. The cell is constructed in the form of a parallel plate capacitor with transparent electrodes (Nesa coated glass). The nematic material containing a pleochroic dye serves as the dielectric. Typical electrode spacings are of the order of 0.5 mil (12.5 microns). Alignment of the molecules with their long axes parallel to the electric vector of the polarized light occurs merely through contact with the electrode surfaces. Stroking of the Nesa coated surfaced with a clean cotton swab prior to cell fabrication enhances the degree of alignment. This alignment procedure therefore results in a cell which has a color characteristic of the dissolved dye (Fig. 1a). The nematic compound selected as the host should have a very strong permanent dipole moment operating along its long molecular axis for maximum orientation effect. This feature enables the molecules to align in the direction of an applied electric field and in turn to orient the dissolved dye molecules with their long axes perpendicular to the electric vector of the incident polarized light. This produces a large decrease in the optical density and hence in the disappearance of color (Fig. 1b).



(a) GUEST-HOST SYSTEM – NO FIELD

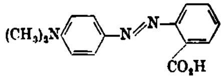
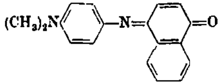
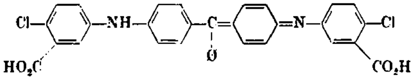
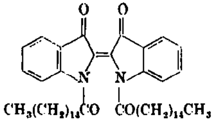
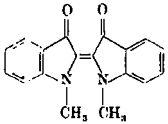
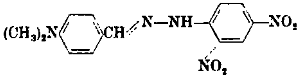
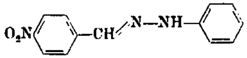
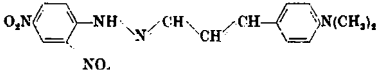
(b) GUEST-HOST SYSTEM WITH FIELD

Figure 1. Schematic representation of electro-optic cells exhibiting electronic color switching.

Three nematic compounds have been used to exhibit the desired alignment: *p*-*n*-butoxybenzoic acid (nematic range 147–161°) (**I**); *p*-methoxycinnamic acid (171–188°) and *p*-ethoxybenzylidene-*p*′-aminobenzonitrile (**II**) (105–124 °C). All of these compounds are essentially transparent in the visible portion of the spectrum. Initial studies[5] were conducted with **I** as the nematic host, but the lower crystal → nematic transition temperature of **II** dictated its use in most of the experiments described here.

The terminal dipolar cyano group provides the molecule with a strong dipole moment along the molecular axis. In addition the solvating power of the cyano group makes **II** a suitable solvent for a variety of dye structures.

TABLE 1 Pleochroic Dyes Included in this Study

Compound	Structure	Color Change Observed Field Off	 Field On	Nematic Host
Methyl Red		Red	Colorless	I
Indophenol Blue		Blue	Colorless	II
Isolar Green M		Green	Colorless	II
N-N′-Dipalmitoylindigo		Magenta	Colorless	II
N-N′-Dimethylindigo		Cyan	Colorless	II
4-Dimethylaminobenzylidene -2′, 4′-dinitrophenylhydrazone		Orange-Red	Pale Yellow	II
4-Nitrobenzylidenephenylhydrazone		Yellow	Colorless	II
4-Dimethylaminocinammylidene -2′, 4′-dinitrophenylhydrazone		Red	Pale Yellow	II

Several classes of organic dyes have been found to exhibit pleochroism and some of those which have been oriented in nematic hosts are illustrated in Table 1. The fundamental colors of the spectrum are represented but in principle any color can be obtained by suitable choice of guest dye. All of the compounds are long, rod-like molecules which possess highly polarizable terminal groups and aromatic rings. These features resemble those of mesomorphic compounds and thus make the molecules compatible with nematic hosts. In addition to being soluble in the nematic materials these dyes are non-ionic. This is an extremely important criterion since ionic materials must be excluded from electro-optic cells of this type as they produce irreversible electro-chemical processes which destroy the material. Thus a large number of known pleochroic dyes from the canine and related families which are ionic cannot be used for this effect.

Exploratory studies of electronic color switching of the guest-host mixtures shown in Table 1 were carried out with 1% concentrations of dye at the low temperature portion of the nematic range. The thickness of active area varied from 6–25 microns and excitation with 2–100 volts (DC through audio) at a power of approximately 1 milliwatt/cm^2 was employed. The speed of response varied from 1–5 milliseconds with relaxation times of the order of 20 milliseconds.

A detailed study of the changes in optical density as a function of field strength and dye concentration was conducted with cells prepared as described above containing mixtures of indophenol blue (III) and II. Measurements of the spectral changes were made with the aid of a device designed for spectrophotometric studies of electro-optic cells (Fig. 2). This piece of apparatus provides means for application of electric fields, rotation of polarizers and control of temperature. In the experiments described here, however, only one polarizer was used. The device was then placed into the sample compartment of the Cary 14R spectrophotometer and measurements of the absorption spectrum were made. This spectrum consisted of a broad Gaussian absorption with a $\lambda_{\max}$ at 6000 Å (Fig. 3). The polarizer

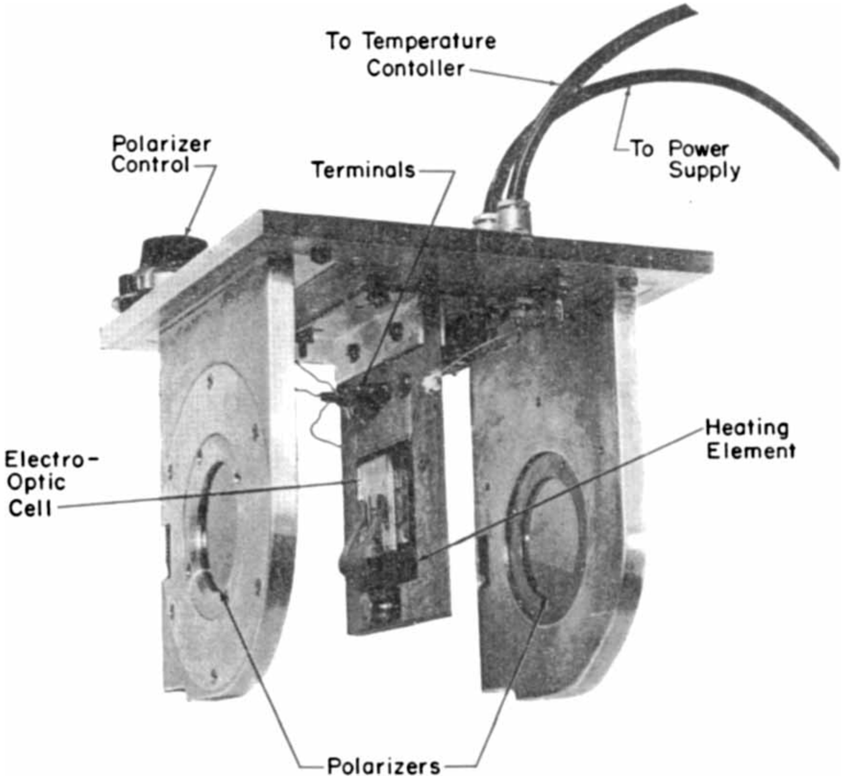


Figure 2. Apparatus designed for spectrophotometric measurements of electro-optic cells. The device is inserted into the sample compartment of the Cary 14R spectrophotometer.

was rotated until the maximum absorption at 6000 Å was obtained. Measurements of the absorbance at the λ_{max} as a function of applied dc electric field were then made for each concentration of dye and the results are shown in Fig. 4. The threshold for switching was between 1 and 2 volts for all concentrations except the 5.0%, for which a threshold of 5 volts was obtained. That fine color tuning at low power is possible with systems of this type is indicated by the decrease in relative absorbance at very low voltages (2–8 volts). These results are in agreement with those obtained from a study of the infrared dichroism of a nematic

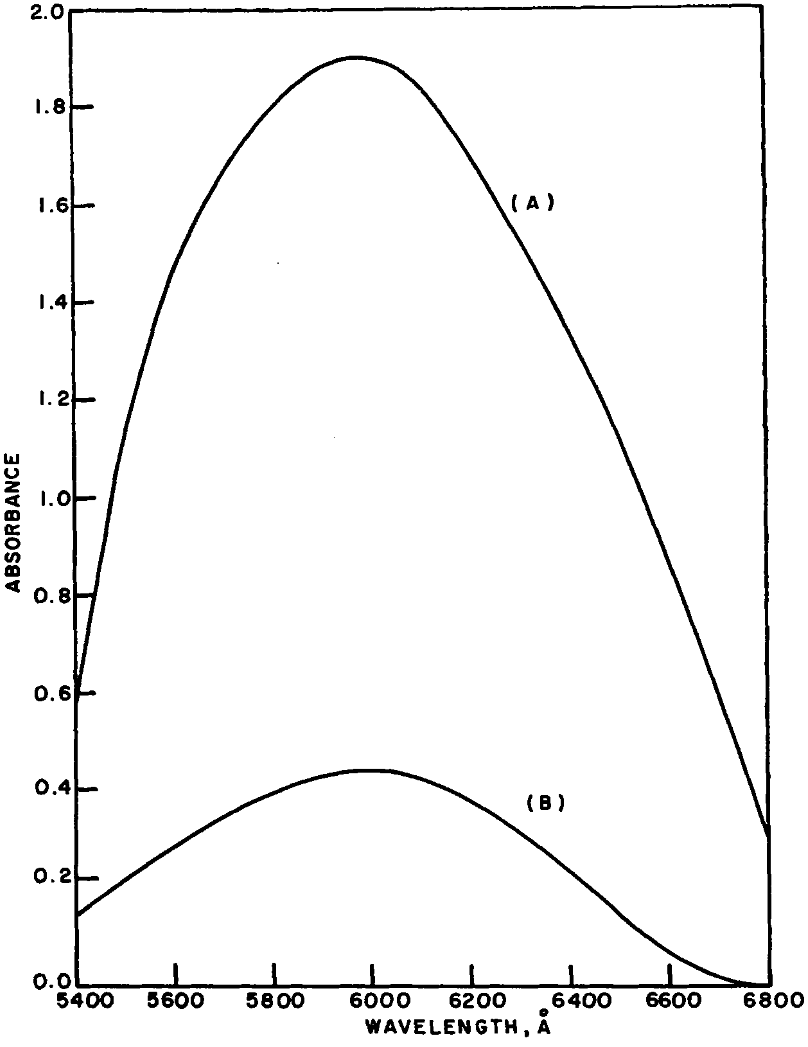


Figure 3. Absorption spectrum 1% indophenol blue-PEBAB mixture with (A) no field applied and (B) a field of 4.0 × 10^4 volts/cm.

compound of almost identical structure.[6] The field strength required to obtain maximum orientation of domains was reported to be approximately 5 kV/cm which corresponds closely to the values shown in Fig. 4. In addition the value for the dichroic ratio at maximum orientation is in the same order of magnitude as that for the ratio of the absorption of the dye without and with an applied field. Since the orientation of nematic domains can be obtained from this value, it appears that the degree of orientation of dye molecules is closely related to the degree of orientation of the host.

The effect of dye concentration on absorbance change is shown in Fig. 5. The maximum effect, a change of 1.4 units, was obtained at a dye concentration of 1.0%. The gradual decrease in absorbance change with increasing dye concentration above 1.0% indicates that the nematic host can produce alignment of only a maximum number of guest molecules. As the number of dissolved dye molecules increases beyond this maximum, unoriented molecules contribute to the absorbance of the medium in the presence of an applied electric field. The optimum concentration suggests that each dye molecule is associated with approximately 100 host liquid crystal molecules. Furthermore, optimum alignment implies that the alignment energy is of the order of kT. For this to be the case with host (II) we require:

$$\bullet = \mathrm{N}\vec{\mu}\cdot\vec{\mathrm{E}} \sim \mathrm{kT}$$

where μ = molecular dipole moment

E = field strength

and N = number of dipoles cooperatively aligned ~ 100

Thus it is implied from these measurements that this nematic liquid exhibits a cooperative behavior involving approximately 100 molecules. Further studies of this effect with other guest-host systems are in progress.

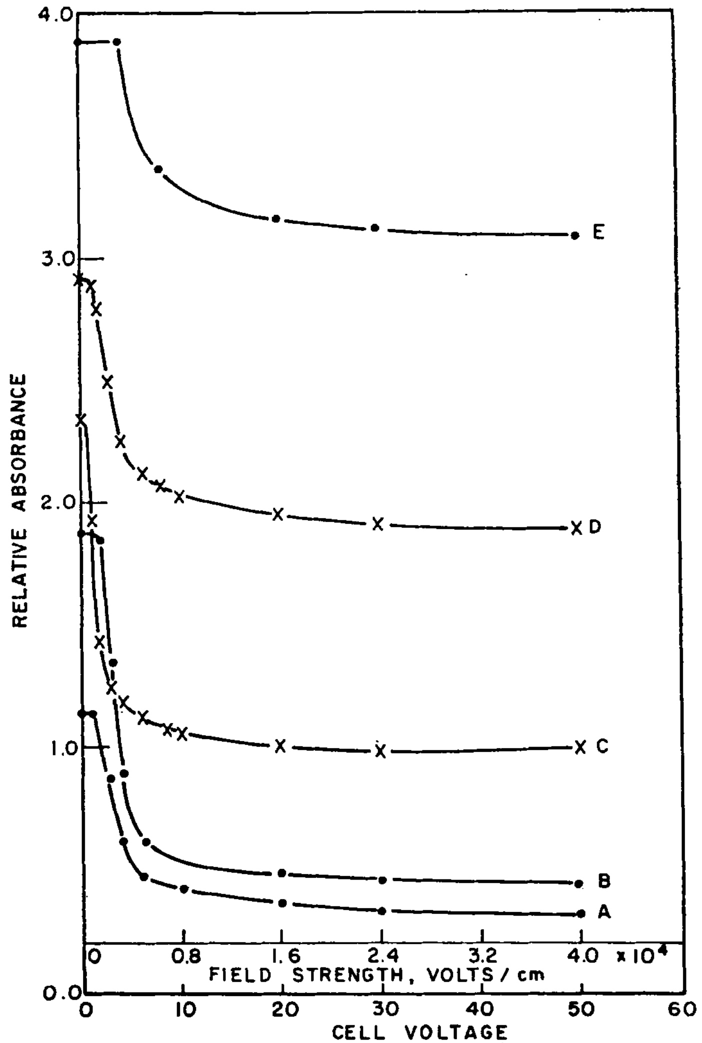


Figure 4. Changes in absorbance as a function of field strength for mixtures of II and A–0.5%, B–1.0%, C–1.5%, D–2.5%, and E–5.0% of III (cell thickness—12.5 microns).

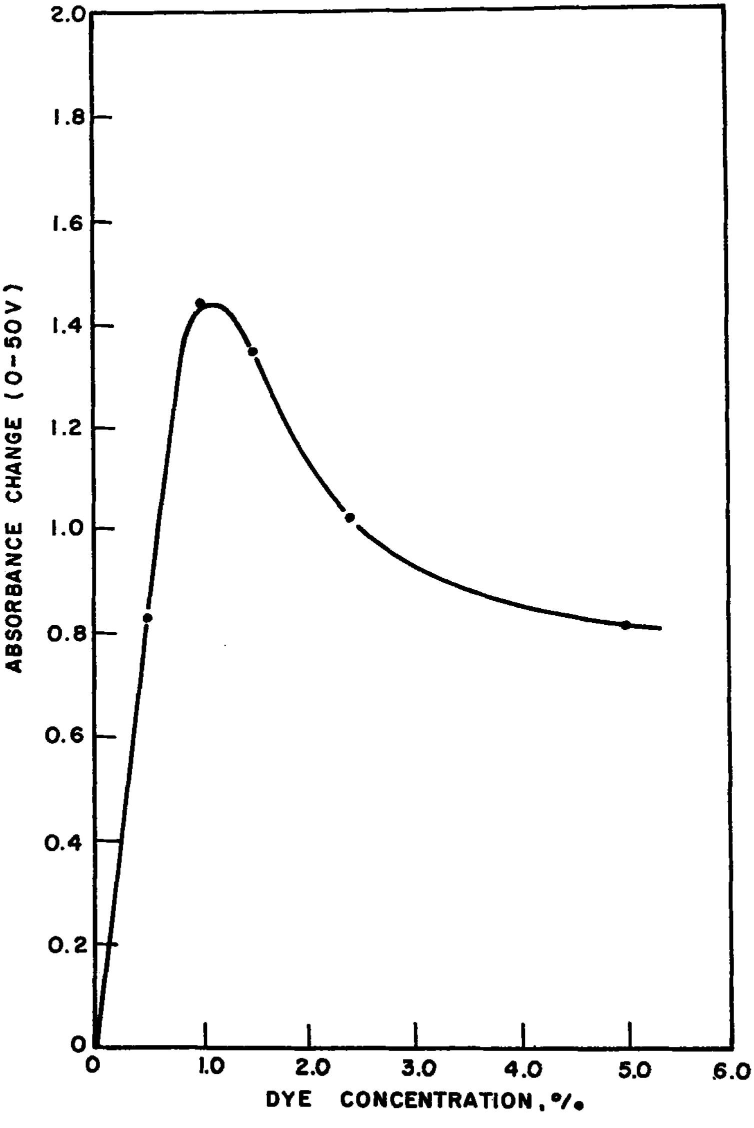


Figure 5. Maximum absorbance change (0–50 V) as a function of indophenol blue concentrations for mixtures of II and III.

Experimental

Materials. *p*-Butoxybenzoic acid and *p*-methoxycinnamic acid were obtained from Distillation Products (Eastman Kodak) and were purified further by several recrystallizations. These materials had resistivities of the order of 10^9 ohm-cm. *p*-Ethoxybenzylidene-*p*′-aminobenzonitrile was prepared by acid-catalyzed condensation of *p*-ethoxybenzaldehyde with *p*-aminobenzonitrile. After purification by recrystallization the compound was zone refined to given material with a resistivity of 10^{10} ohm-cm.

Methyl red, indophenol blue and isolar green M were obtained from commercial sources and were purified by recrystallization to constant melting point. The remaining dyes listed in Table 1 were prepared by conventional organic chemical techniques[7] and were purified as above. All of the dyes had measured resistivities in the range 10^9–10^{10} ohm-cm.

Measurements. The electro-optic cells were prepared by techniques previously described.[2,3] The optical density measurements were made with the electro-optic cell mounted in the device shown in Fig. 2. A typical absorption spectrum obtained with this device inserted in the Cary 14R spectrophotometer is shown in Fig. 3.

Acknowledgment

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6. Neff, V. D., Gulrich, L. W. and Brown, G. H., Proc. of 1st Int. Liq. Cryst. Conf., Kent State University, 1965, p. 21–35. These workers report almost complete (0.95) orientation of the domains of *p*-methoxybenzylidene-*p'*-aminobenzonitrile molecules parallel to a surface in the absence of an applied field.
7. The indigo dyes were prepared by Dr. D. L. Ross of RCA Laboratories.