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ELECTRONICALLY TUNED OPTICAL FILTERS

BY

JOSEPH A. CASTELLANO, GEORGE H. HEILMEIER,
EDWARD F. PASIERB, JR., AND MICHAEL T. MCCAFFREY

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BY

RCA LABORATORIES
PRINCETON, NEW JERSEY 08540

ELECTRONICS RESEARCH CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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TABLE OF CONTENTS

Section *Page*

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Continued)

LIST OF TABLES

ELECTRONICALLY TUNED OPTICAL FILTERS

By Joseph A. Castellano, George H. Heilmeier,
Edward F. Pasierb, Jr., and Michael T. McCaffrey
RCA Laboratories

SUMMARY

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 their molecular orientation with respect to the polarization of the incodent light). Electronic color switching at room temperature was achieved using fields of the order of 10 kV/cm (dc through audio) at powers of approximately 1 mW/cm^2 with a variety of dye structures. Thus, it was possible to produce electronically tuned, monochromic, optical filters with a variety of colors.

The preparation of dichromic optical filter was achieved using mixtures of a photochromic, pleochroic dye in a nematic host. This allowed us to electronically control two colors in the same nematic host.

Polychromic optical filters were prepared using layers of yellow and cyan guest-host systems. Thus, we could produce blue, green, white, yellow, and cyan by varying the voltage between the two layers.

A detailed study of the response and relaxation time of the effect was also conducted. Rise times of 1 to 5 msec and relaxation times of 30 to 200 msec were obtained. Dielectric dispersion measurements showed that approximately 1100 molecules of the nematic host material act collectively upon electronic excitation.

INTRODUCTION

Light-emitting and light-modifying effects provide the two main classes of electro-optic effects discovered to date. The cathode-ray tube and electroluminescent devices are examples of light-emitting effects. The former requires relatively high voltages to produce the electron beam, in addition to geometric and compositional requirements necessitated by the vacuum inside the tube. Electroluminescent devices are limited in varying degrees by spectral response, brightness, life, speed of response, and nature of the electrical drive.

Examples of light-modifying effects are mechanical shutters, saturable absorbers, Stark effect or Franz effect modulators, and effects based on field-induced changes of the index of refraction of a material (Pockels effect and the Kerr effect). Mechanical shutters are likely to be limited by their speed of response and drive requirements while saturable absorbers require intense optical radiation for operation. In general, the Stark and Franz effects require extremely high fields and voltages to produce minimal shifts in absorption spectra. In addition, single-crystal materials are needed for optimum performance. The linear electro-optic effect (or Pockels effect) also requires high voltages and fields in addition to strain-free single crystals lacking inversion symmetry. The Kerr effect shares the high-voltage requirements of the linear electro-optic effect.

This report is a detailed account of our efforts to investigate the nature and scope of a new electro-optic effect of the light modifying type which can electronically control color. The effect is based on the cooperative alignment of certain mesomorphic (liquid crystalline) host compounds by external electric fields which are used to orient guest dye molecules. This orientation results in changes in the optical density of the material and, consequently, changes in the color of light transmitted through the medium.

The research work performed during the year (April 1, 1968 to March 31, 1969) is described in this report. This work was conducted in the Consumer Electronics Research Laboratory, T. O. Stanley, Director, with J. A. Castellano as Project Scientist and G. H. Heilmeier as Project Supervisor. E. F. Pasierb, Jr., and M. T. McCaffrey also contributed to the effort during the report period.

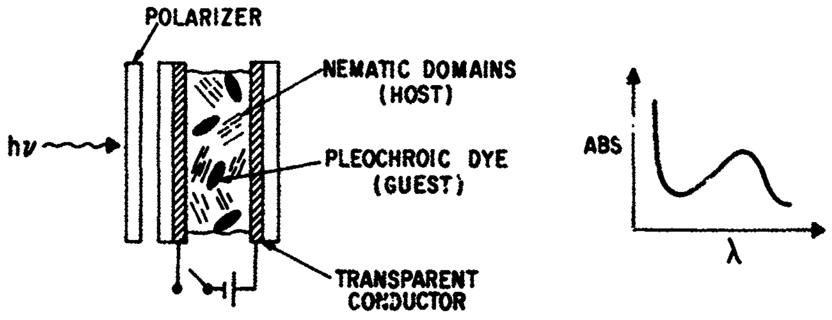
DISCUSSION

Cooperative phenomena in nematic materials under electric fields have been the subject of several studies conducted in these Laboratories over the past several years [Refs. 1-4]. 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[Refs. 5,6].

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 mixture of these dyes with nematic hosts is illustrated in Figure 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 surface with a clean cotton swab prior to cell fabrication enhances the degree of alignment. This alignment procedure, therefore, results in a cell that has a color characteristic of the dissolved dye [Figure 1(a)]. 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 [Figure 1(b)].



(a) GUEST-HOST SYSTEM - NO FIELD

(b) GUEST-HOST SYSTEM WITH FIELD

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

Our efforts during the past year have been directed toward the preparation of liquid crystalline compounds and selected pleochroic dyes which give fundamental color changes upon application of an electric field and which can be operated at or near room temperature. In an effort to further characterize this effect we have made measurements of the contrast ratio, rise and decay times, and dielectric dispersion.

MATERIALS

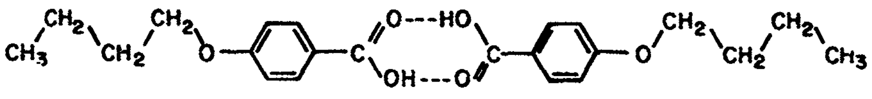
Single Nematic Hosts

The term "nematic" is derived from the Greek word meaning thread since it describes the thread-like lines which these materials exhibit under a microscope. A sample of nematic material contained in a vial appears as a viscous, turbid, off-white liquid. The molecules of a nematic compound are arranged with their long axes parallel. In contrast to smectic materials, however, the molecules are not arranged in layers and are free to slide past each other. The structural requirements which determine the type of mesomorphic behavior exhibited by particular molecules are adequately described elsewhere[Ref. 7].

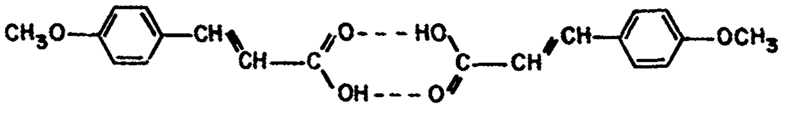
The nematic molecules selected for this study are cylindrically shaped and possess polarizable aromatic rings. In addition, they have a strong dipole moment operating along the long axis of the molecule. This enables the molecules to cooperatively align themselves parallel to the lines of force of the externally applied electric field.

Our initial studies were conducted with p-butoxybenzoic acid and p-methoxycinnamic acid (Figure 2) but the high operating temperatures required by these hosts prompted a search for other compounds with lower crystal→nematic transition temperatures. A class of compounds derived from p-ethoxybenzylidene-p'-aminobenzonitrile (PEBAB-2, Figure 2) was found to be suitable, and structural modifications of these molecules were therefore made. This involved the preparation of compounds with from 1 to 8 carbon atoms in the alkyl chain attached to the oxygen atom. This was accomplished by the sequence of reactions illustrated in Figure 3(a).

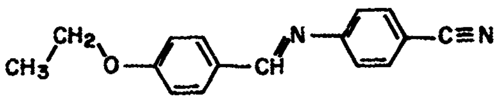
The crystal → nematic and nematic → isotropic liquid transition temperatures for all of these compounds are listed in Table VI (Appendix). A plot of phase transition temperatures as a function of chain length is illustrated in Figure 4. With the exception of PEBAB-3 which exhibits monotropic behavior, all of the compounds are enantiotropic (i.e., the CN point is below the NL point). This plot is characteristic of a homologous series of liquid crystalline compounds. It is well known that when the mesomorphic transition temperatures (e.g., NL points) for a homologous series of compounds (in a series of n-alkyl ethers or esters) are plotted against the number of carbon atoms in the alkyl chain, smooth curve relationships between even and odd members of the series are found to exist. This regular alternation of transition points has been explained by assuming that the alkyl chains adopt the "cog wheel" rather than the "zig-zag" conformation in the mesomorphic state.



P-BUTOXYBENZOIC ACID (NEMATIC RANGE, 147–161°C)



P-METHOXYCINNAMIC ACID (NEMATIC RANGE, 171–188°C)



P-ETHOXYBENZYLIDENE-P'-AMINOBENZONITRILE
(NEMATIC RANGE, 105–124°C)

Figure 2. Structures of nematic host materials.

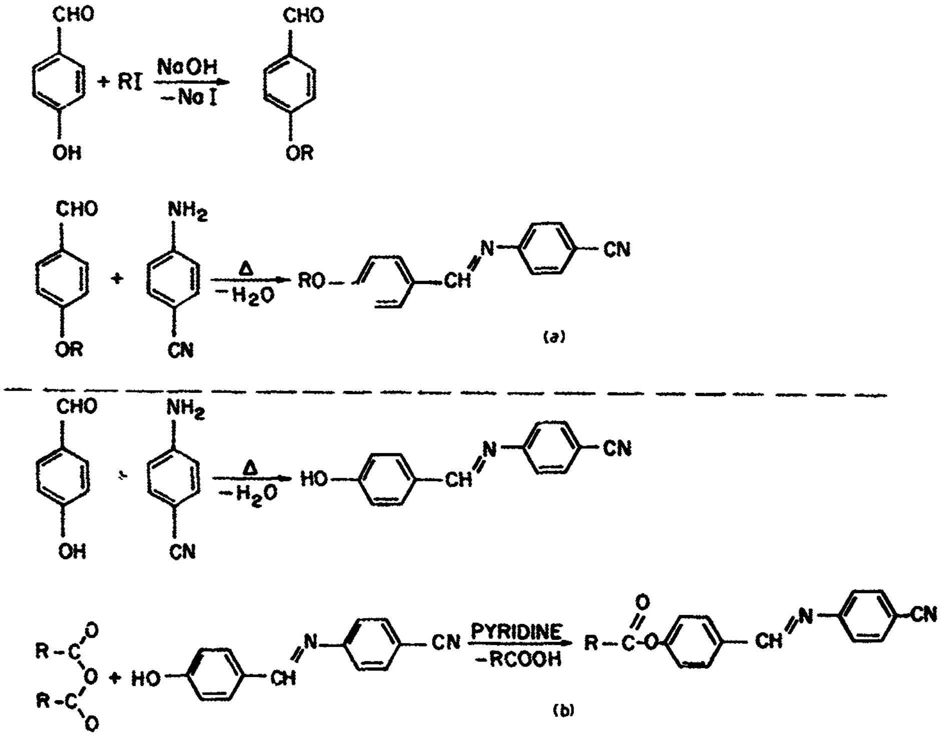


Figure 3. Synthesis of PEBAB type compounds.

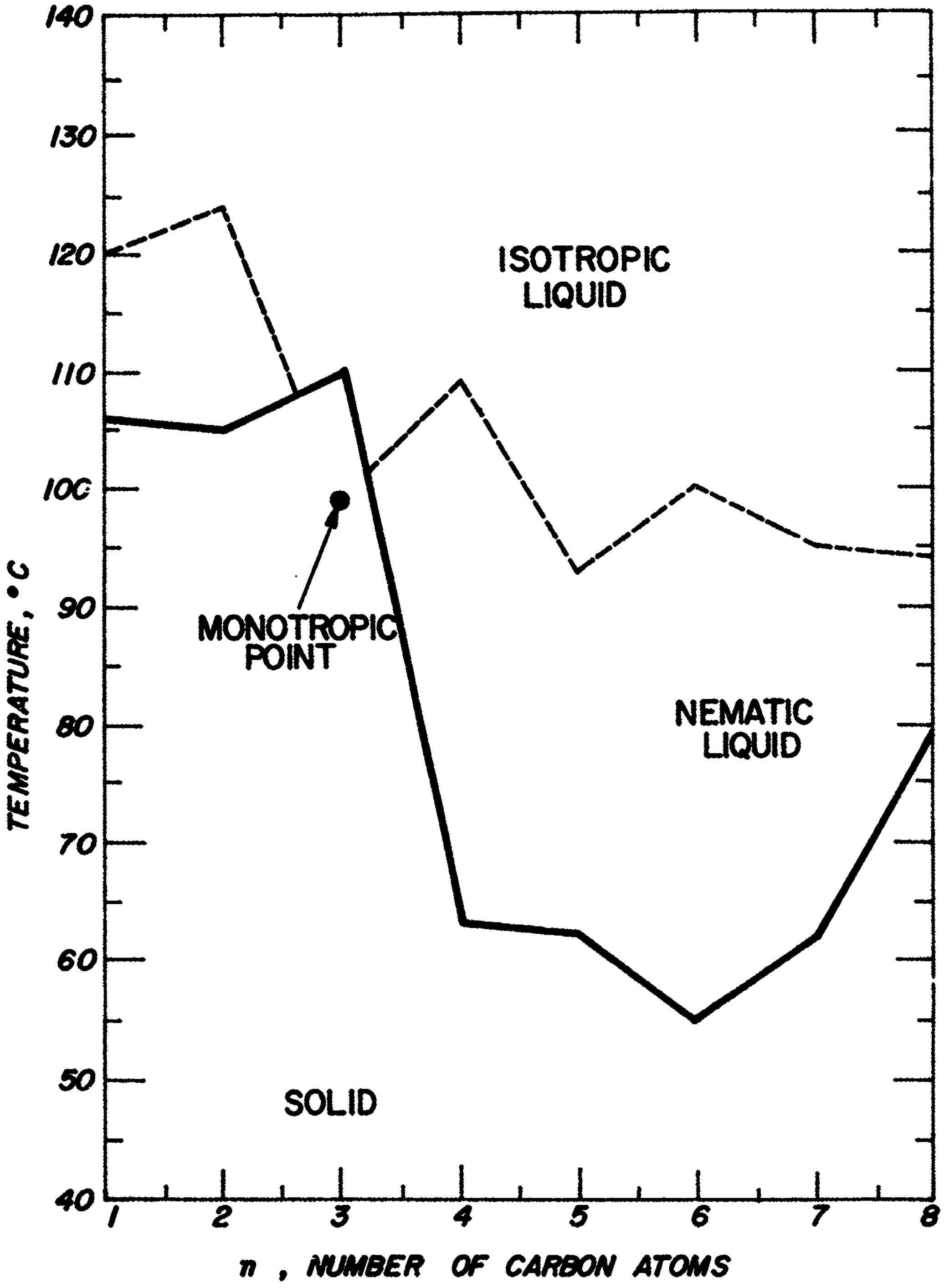


Figure 4. Phase transition plot for the series of p-alkoxybenzylidene-p'-aminobenzonitriles.

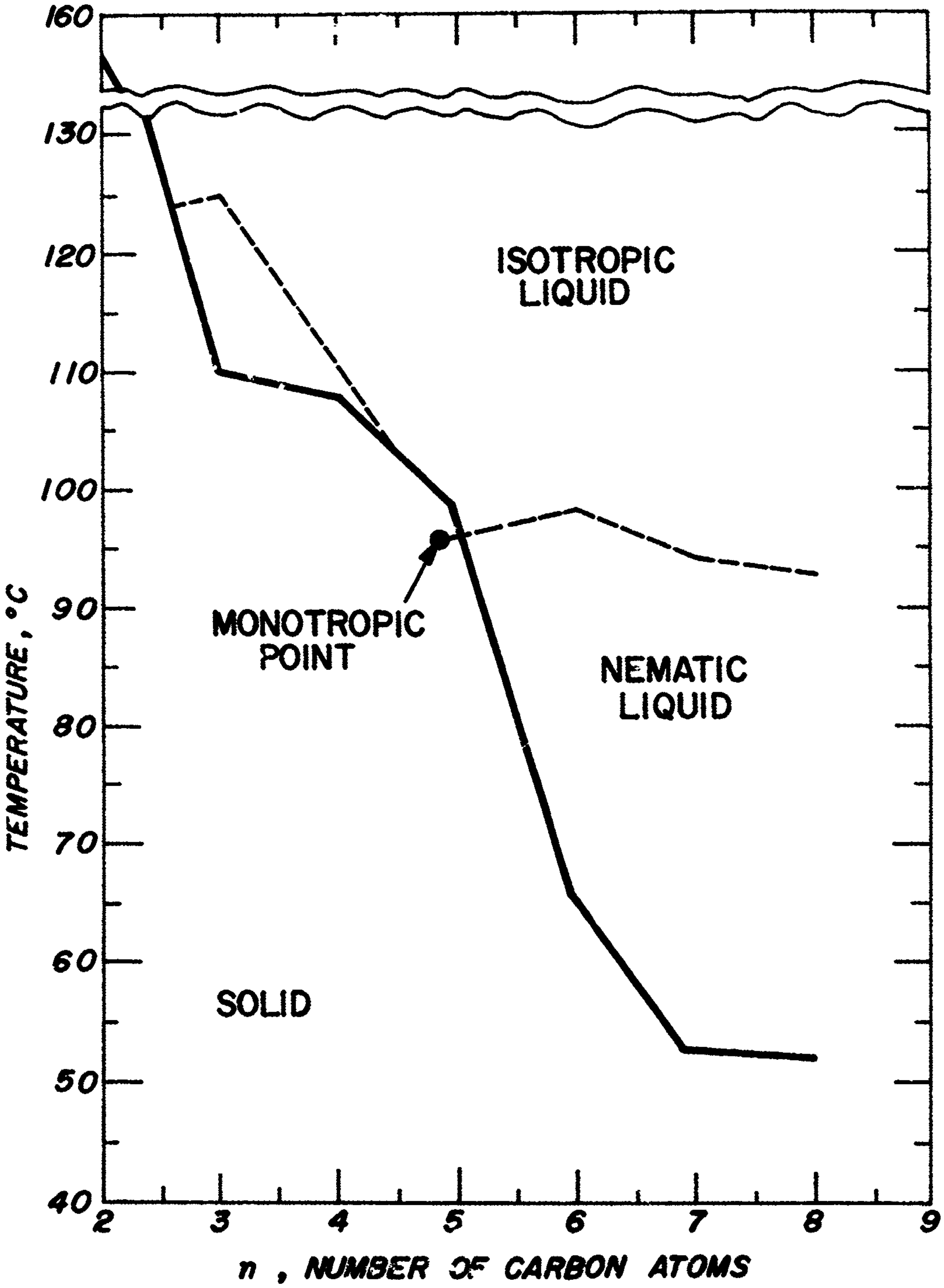
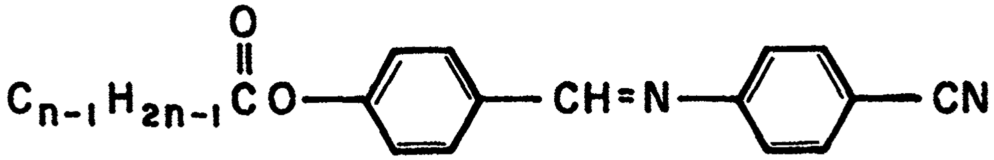


Figure 5. Phase transition plot for the series of p-acyloxybenzylidene-p'-aminobenzonitriles.

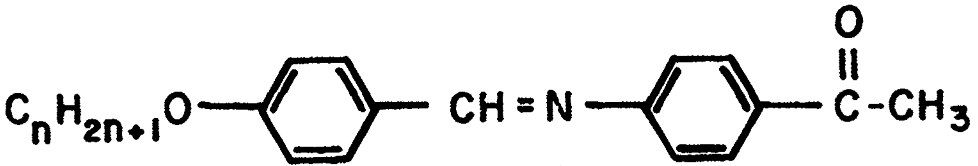
No such relationships exist, however, for the CN transition points since minor alterations in molecular structure can produce large changes in the energy required to disrupt the crystal lattice. In general, however, extended alkyl chains produce weak terminal intermolecular attractions which reduce the energy required to disrupt the crystal lattice structure. Thus, the compounds with the lowest CN points and the longest nematic ranges are PEBAB-4, -5 and -6. The higher CN point of PEBAB-8 relative to 4, 5, 6, and 7 is anomalous and suggests a special ordering of the chain of this molecule in the crystal lattice.

Another class of compounds in which the molecules orient themselves with their long axes in the direction of an applied electric field are the aliphatic esters of p-hydroxybenzylidene-p'-aminobenzonitrile (PEBAB-nO series). This series of compounds was prepared by the method shown in Figure 2(b). The results of transition temperature measurements are listed in Table VII (Appendix) while a phase transition plot is illustrated in Figure 5. The very large decrease in CN transition temperature with increasing chain length is a dramatic demonstration of reduced terminal interactions produced by shielding of the dipolar end groups. Indeed, the terminal interactions are so strong in PEBAB-10 that the molecule does not exhibit mesomorphic behavior.



PEBAB-nO (2<n<8)

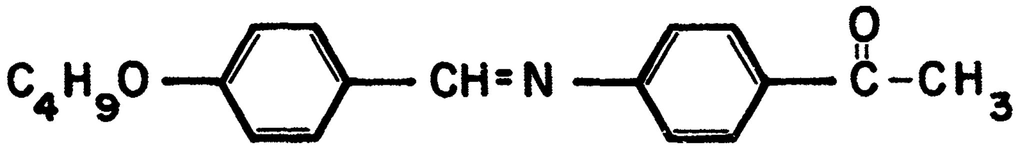
The presence of the cyano group in both the PEBAB-n and PEBAB-nO series provides the molecule with a hygroscopic site. Since the absorption of moisture is to be avoided, a search for other nematic molecules which contain groups that have strong dipole moments was initiated. Previous studies[Ref. 10] conducted at RCA Laboratories have yielded a new series of nematic compounds which contain the strongly dipolar carbonyl group and are based on the following structure:



ABAP

The preparation and purification of derivatives of ABAP containing 1, 2, 4, 6 and 8 carbon atoms in the alkoxy chain were carried out, and the transition temperatures are listed in Table VIII (Appendix). A plot of these results is illustrated in Figure 6. Although the first compound in the series appears to possess all the necessary requirements for mesomorphic behavior, it is in fact non-mesomorphic. As the length of the alkyl chain in the ether portion of the molecule is increased, however, mesomorphic behavior appears. An unusual feature of the phase transition plot for this series is the increased nematic as well as smectic thermal stability as the chain length is increased from four to eight carbon atoms. As the lateral interactions are increased by lengthening the chain from four to eight carbon atoms, disruption of the nematic state is prevented, and nematic thermal stability rises. That these lateral interactions are indeed increased is illustrated by the higher smectic thermal stability.

In an effort to modify the ABAP structure (to eliminate the smectic state) an extension of the alkyl chain in the ketone portion of the molecule was made. Thus, p-butoxybenzylidene-p'-aminopropiophenone was prepared, but the transition temperatures (CS-86°, SN-141°, NL-144°) indicated that the smectic thermal stability was rising rather than falling.



p-butoxybenzylidene-p'-aminoacetophenone

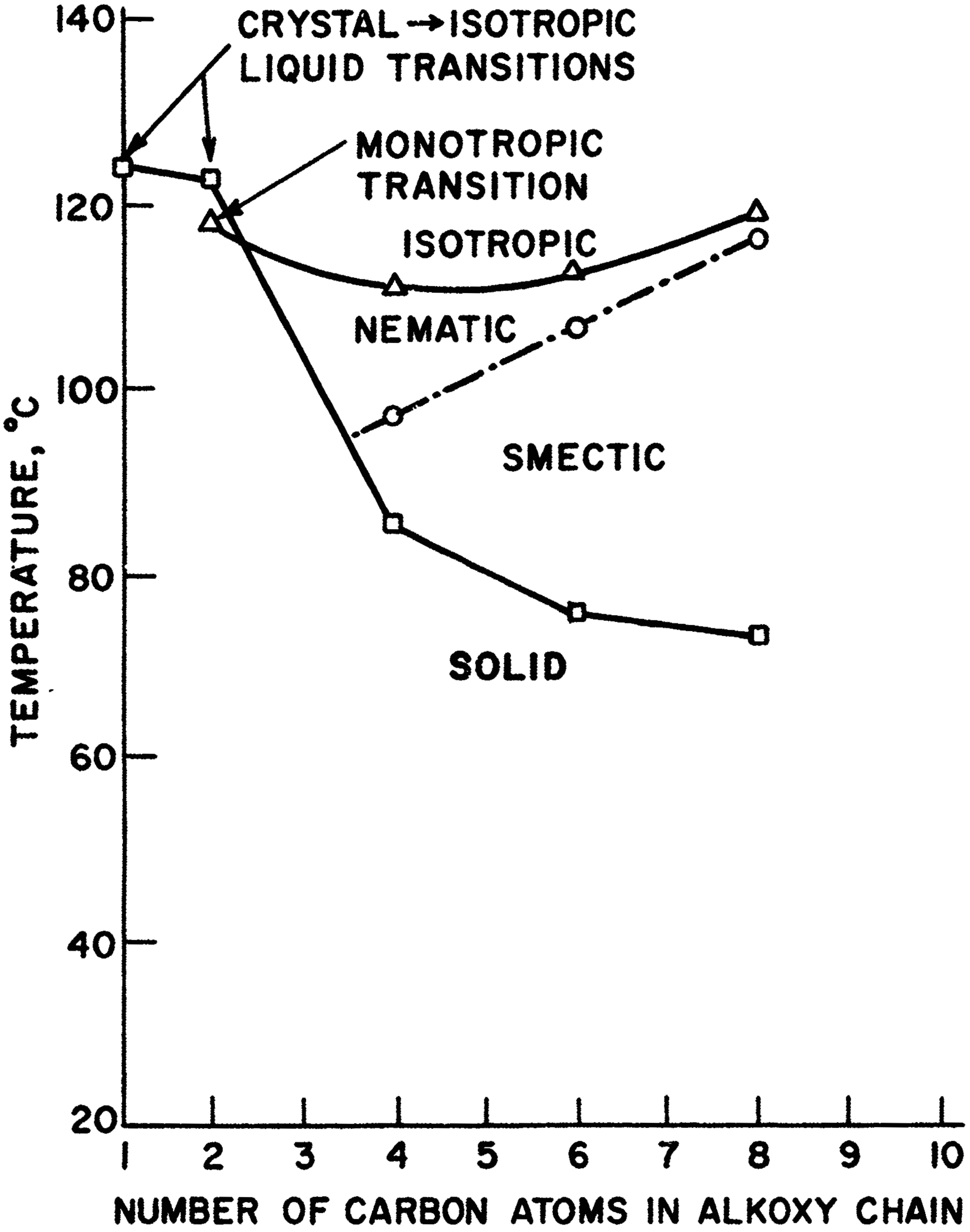
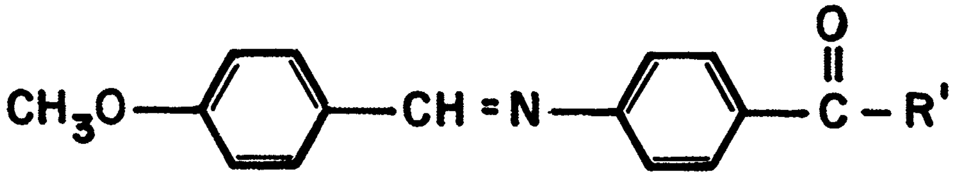


Figure 6. Phase transition temperature for the series:
p,p'-$C_nH_{2n+1}OC_6H_4CHNC_6H_4COCH_3$.

To counteract this effect, the series was continued with the preparation of derivatives (APAP) with an extended alkyl chain in the ketone portion of the molecule while the ether portion was kept at one carbon atom. The transition temperatures of these compounds are listed in Table IX (Appendix). The absence of smectic behavior in this group of derivatives is a dramatic demonstration of the necessity to investigate chain extension in both portions of a molecule in an effort to obtain the desired mesomorphic properties.



APAP COMPOUNDS – R' = C_2H_5, C_3H_7, C_4H_9

Mixtures of Nematic Compounds

Mixtures of linear, non-mesomorphic molecules with nematic compounds have been studied extensively in the past[Ref. 7]. These systems are always characterized by a sharp decrease in both the nematic → liquid and crystal → nematic transition temperature with increasing concentration of non-mesomorphic component. An example of this type of system has recently been reported[Ref. 8] with mixtures of p-azoxyanisole (nematic) and p-nitrobenzylidene-p'-chloroaniline (non-mesomorphic). The phase diagram for this binary mixture is illustrated in Figure 7.

Mixtures of two or more nematic compounds which possess subtle differences in molecular structure do not exhibit decreases in the nematic → liquid transition temperatures with molar composition although eutectic points for the crystal → nematic transition temperatures are obtained. An example of this phenomenon was first reported by Demus[Ref. 9]; a phase diagram for the binary system which he used is illustrated in Figure 8. Thus, the nematic → isotropic liquid transition temperatures form a smooth curve over the entire range of molar composition.

These effects can be explained by the following model. The molecules of a non-mesomorphic guest are randomly oriented in a nematic host, and the presence of small quantities is sufficient to cause disruption of nematic order. This is illustrated in Figure 9(b) where the dark ovals represent the non-nematic guest. On the other hand, mixtures of nematic compounds with almost identical structures have stable mesophases at all molar compositions because all the molecules are oriented in the same direction. This results in the formation of a "nematic lattice" as shown in Figure 9(c).

The concepts described above were successfully applied to binary and ternary mixtures of the PEBAB compounds mentioned earlier. A typical phase diagram for a ternary mixture of PEBAB type compounds is shown in Figure 10. Note that the nematic → isotropic liquid surface is continuous. This is consistent with the model described above for mixtures of nematic compounds.

Work on mixtures of compounds from both the PEBAB-n and PEBAB-nO family has led to the preparation of one mixture which has a nematic range of 26-88°C. This mixture, designated as PEBAB-RT, has one of the lowest crystal → nematic transition temperatures found to date. Detailed studies of guest-host interactions were carried out with this mixture as the nematic host.

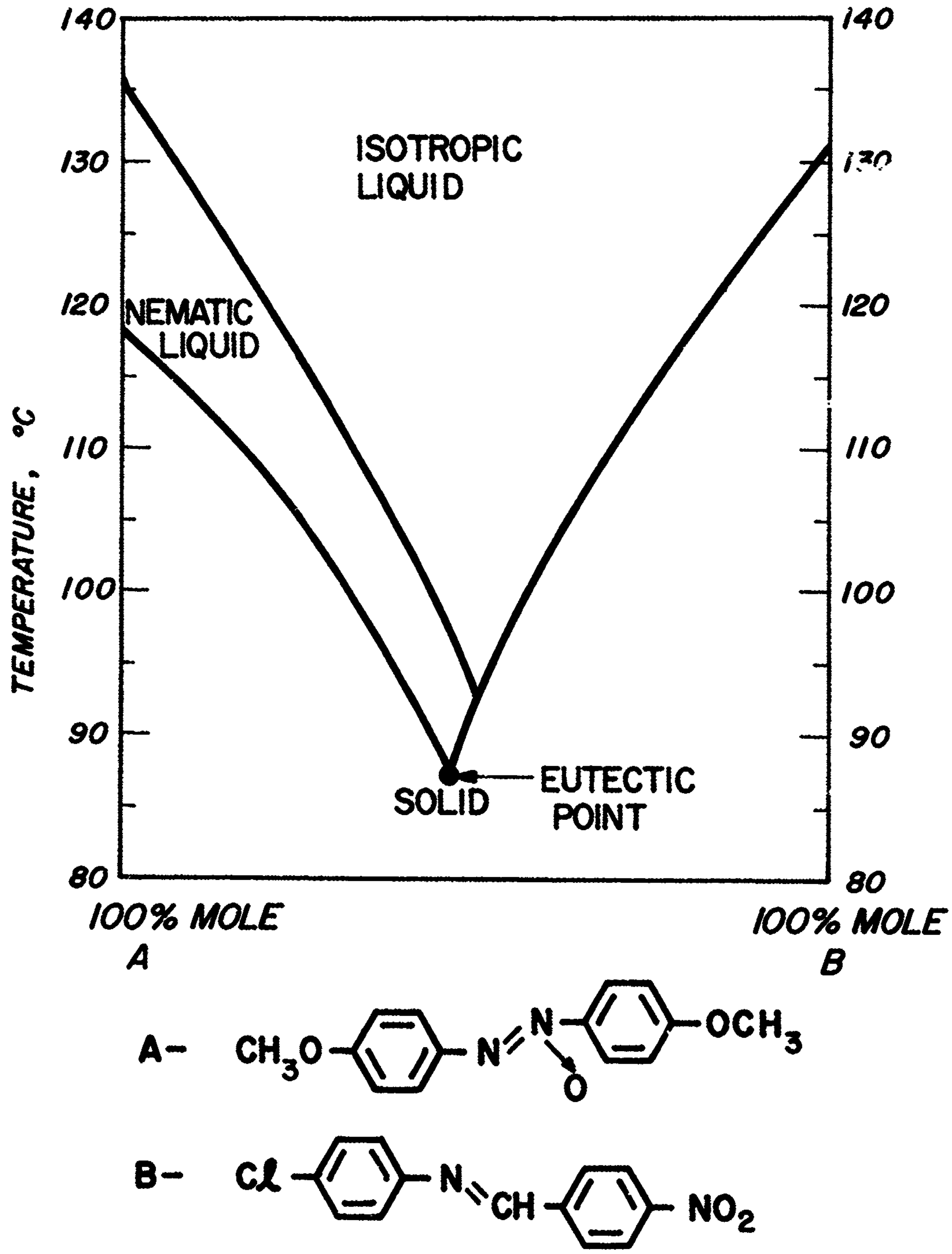


Figure 7. Phase diagram of binary mixture of nematic compound with non-mesomorphic compound.

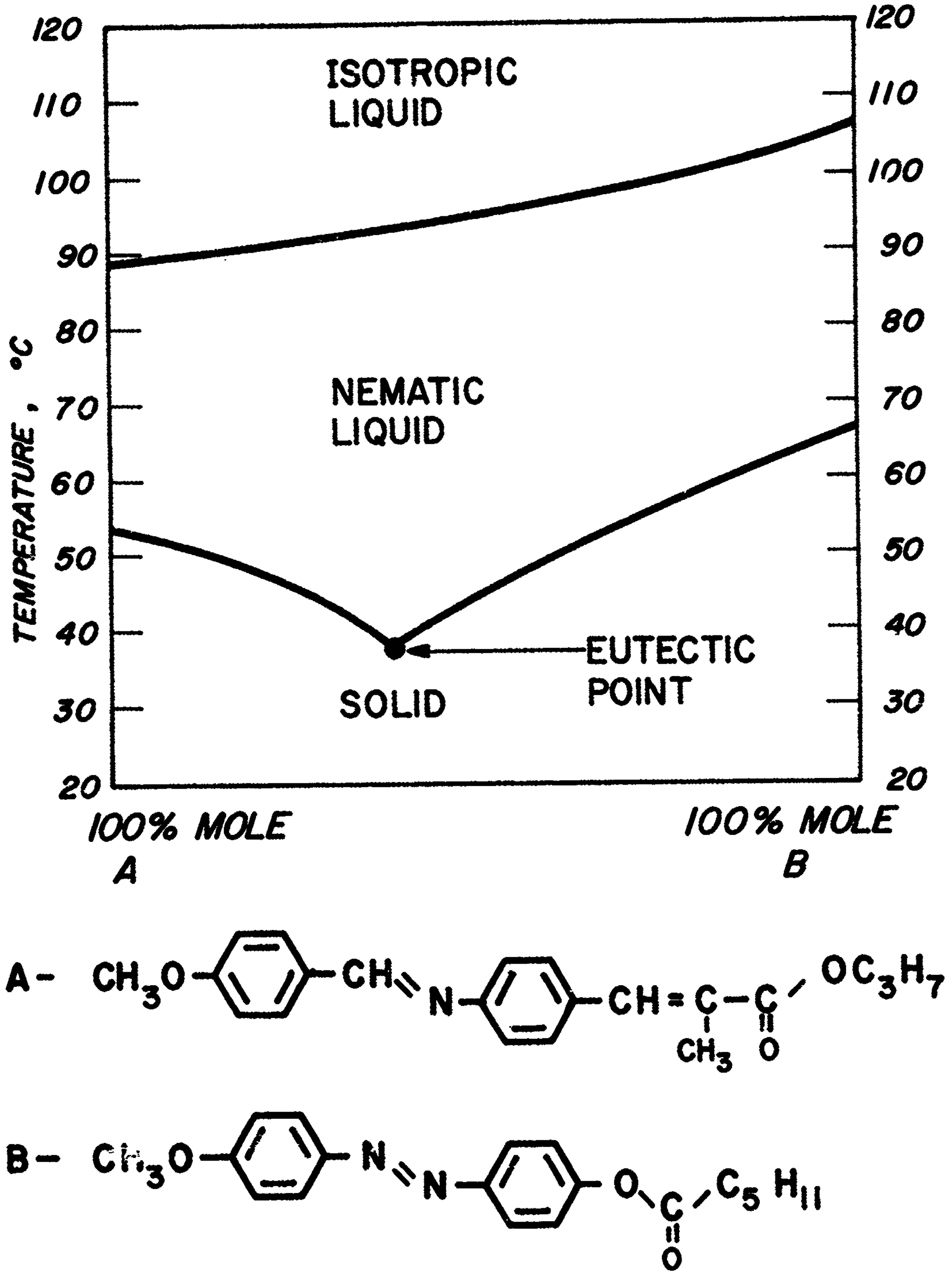
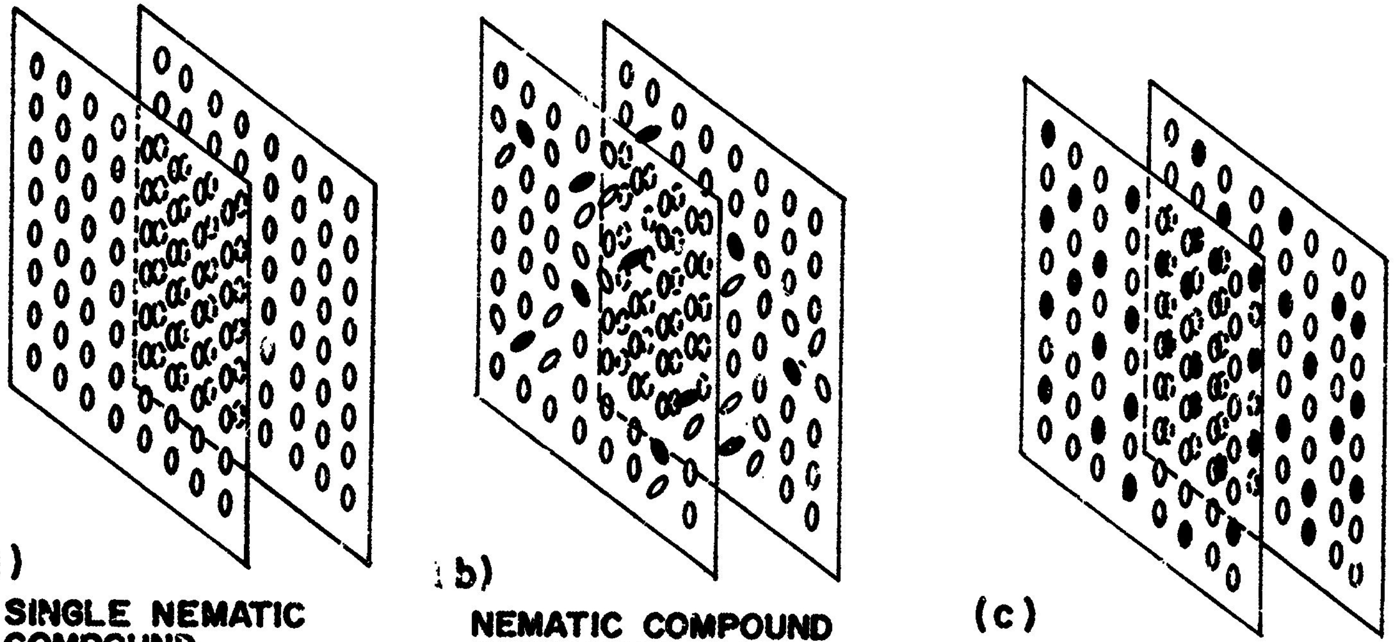


Figure 8. Phase diagram of binary mixture of nematic compounds.



(a) SINGLE NEMATIC COMPOUND

(b) NEMATIC COMPOUND CONTAINING NON-MESOMORPHIC GUEST

(c) BINARY MIXTURE OF NEMATIC COMPOUNDS

Figure 9. *Structure of nematic mesophases.*

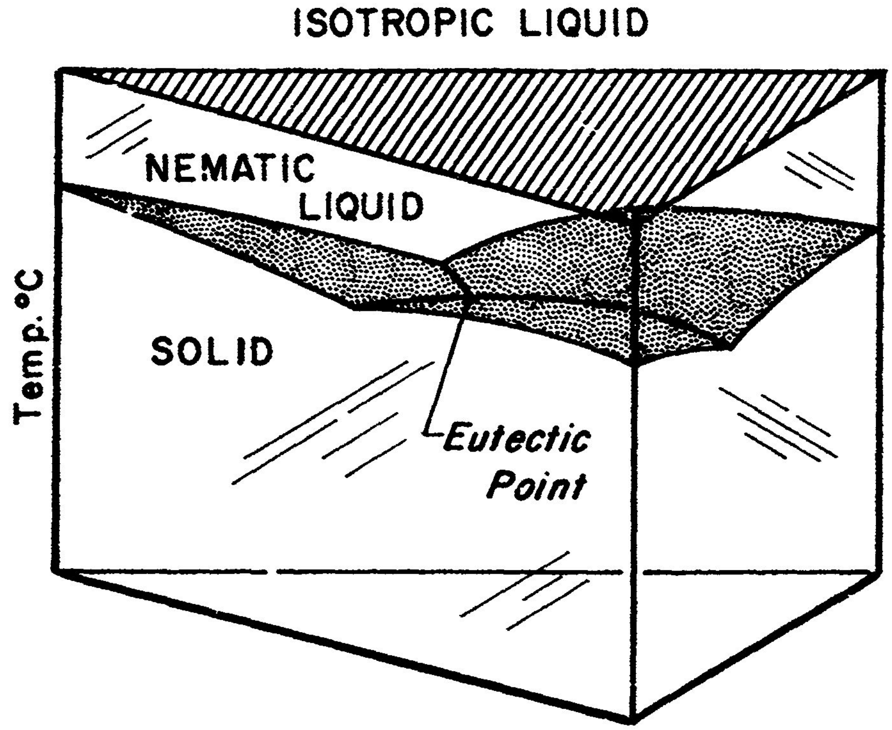


Figure 10. Phase diagram of a ternary PEBAB mixture.

Although each compound of the ABAP series possesses smectic behavior as well as nematic behavior, we believed that mixtures of these compounds would exhibit depression of the smectic → nematic transition temperatures. A series of binary and ternary mixtures containing these compounds were therefore prepared and the transition temperatures measured. The phase diagram constructed from these data, however, showed no depressions in the smectic → nematic or nematic → isotropic transition temperatures although eutectic points for the crystal → smectic transition were obtained.

Mixtures of the three compounds from the APAP series were made but no room-temperature materials were found. The lowest crystal → nematic transition temperature found for this series was 75°. These results are listed in Table X (Appendix).

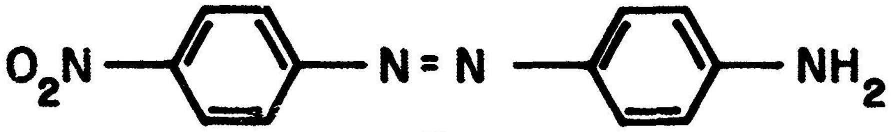
Pleochroic Dyes

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 I. 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 aromatc 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 nonionic. This is an extremely important criterion since ionic materials must be excluded from electro-optic cells of this type as they produce irreversible electrochemical processes which destroy the material. Thus, a large number of known pleochroic dyes from the cyanine and related families which are ionic cannot be used for this effect.

All of these dyes were purified by recrystallization followed by millipore filtration. Methyl red, indophenol blue, and isolar green M were obtained from a local supply house. N,N'-dipalmitoylindigo and N,N'-dimethylindigo were prepared by Dr. D. L. Ross of these Laboratories. The two 2,4-dinitrophenylhydrazone derivatives were prepared by conventional condensation techniques using the appropriate aldehydes and hydrazine derivatives.

Dyes representing several other classes of organic compounds were obtained from commercial sources, and purification of each by recrystallization was carried out. Compounds related to anthraquinone and isoviolanthrone were not found to be pleochroic. A list of the dyes is given in Table II.

The azo dyes contained free amino and hydroxyl groups which were protected prior to study in electric fields. Consequently, disperse orange 3 (I) was reacted with p-butoxybenzaldehyde to give lustrous red



I

TABLE I

PLEOCHROIC DYES INCLUDED IN THIS STUDY

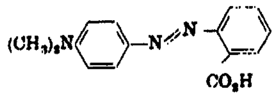
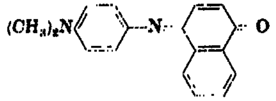
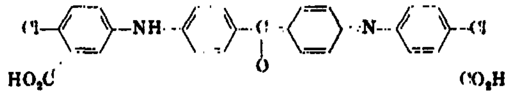
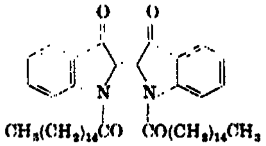
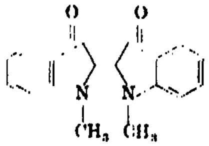
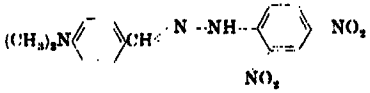
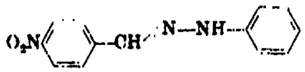
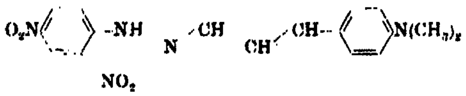
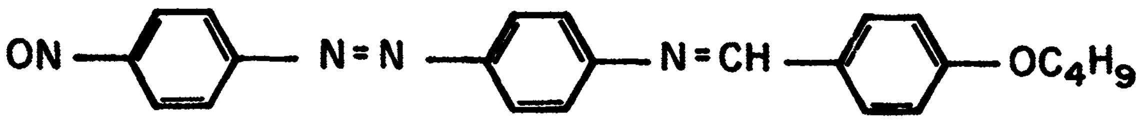
Compound	Structure	Color Change Observed		Nematic Host
		Field Off	Field On	
Methyl Red		Red	Colorless	I
Indophenol Blue		Blue	Colorless	II
Isolar Green M		Green	Colorless	II
N-N'-Dipalmitoylindigo		Magenta	Colorless	II
N-N'-Dimethylindigo		Cyan	Colorless	II
4-Dimethylaminobenzylidene -2', 4'-dinitrophenylhydrazone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

TABLE II

COMMERCIAL DYES STUDIES

Name	Color Index No.	Class	Pleochroism
Dynacolor 17A	--	Merocyanine	Yellow → Colorless
Dynacolor 17B	--	Merocyanine	Red → Yellow
Disperse Orange 3	11005	Azo	Orange → Pale Yellow
Disperse Red 13	11115	Azo	Red → Pale Yellow
Oil Yellow	11160	Azo	Yellow → Colorless
Acetamine Scarlet B	11110	Azo	Red → Pale Yellow
Jade Green	59825	Isoviolanthrone	None
Ponsol Violet BND	--	Anthraquinone	None
Direct Black 13	--	Anthraquinone	None

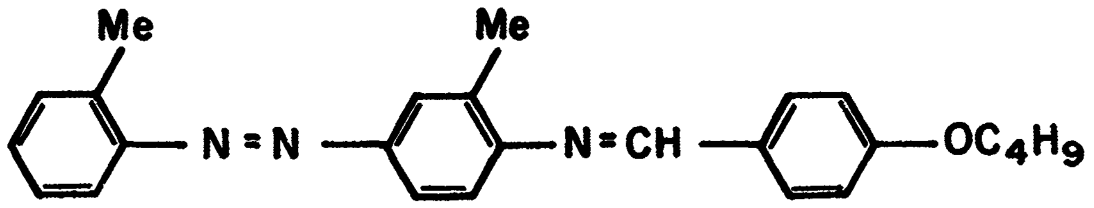
plates of the expected Schiff base (II). This compound (PNAZA) exhibited pleochroism from red to pale yellow.



II

MP 132°C

The azo dye known as oil yellow was treated in a similar fashion to give compound III which exhibited pleochroism from orange → colorless.



III

MP 87-88°C

GUEST-HOST INTERACTIONS

Monochromic Cells

Spectral Response. -- Exploratory studies of electronic color switching of the guest-host mixtures shown in Table I were carried out with 1% concentrations of dye at the low-temperature portion of the nematic range of PEBAB-RT. The thickness of the active area varied from 6 to 25 microns, and excitation with 2 to 100 volts (through audio) at a power of approximately 1 mW/cm^2 was employed.

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 and PEBAB-RT. Measurements of the spectral changes were made with the aid of a device designed for spectrophotometric studies of electro-optic cells (Figure 11). 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 (Figure 12), and measurements of the absorption spectrum were made. This spectrum consisted of a broad Gaussian absorption with a λ_{max} at 6000 Å (Figure 13). The polarizer 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 Figure 14. The threshold for switching was between 1 and 2 V for all concentrations except 5.0%, for which a threshold of 5 V 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 to 8 V). These results are in agreement with those obtained from a study of the infrared dichroism of a nematic compound of almost identical structure (Ref. 11). 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 Figure 14. 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 Figure 15. The maximum effect, a change in absorbance 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

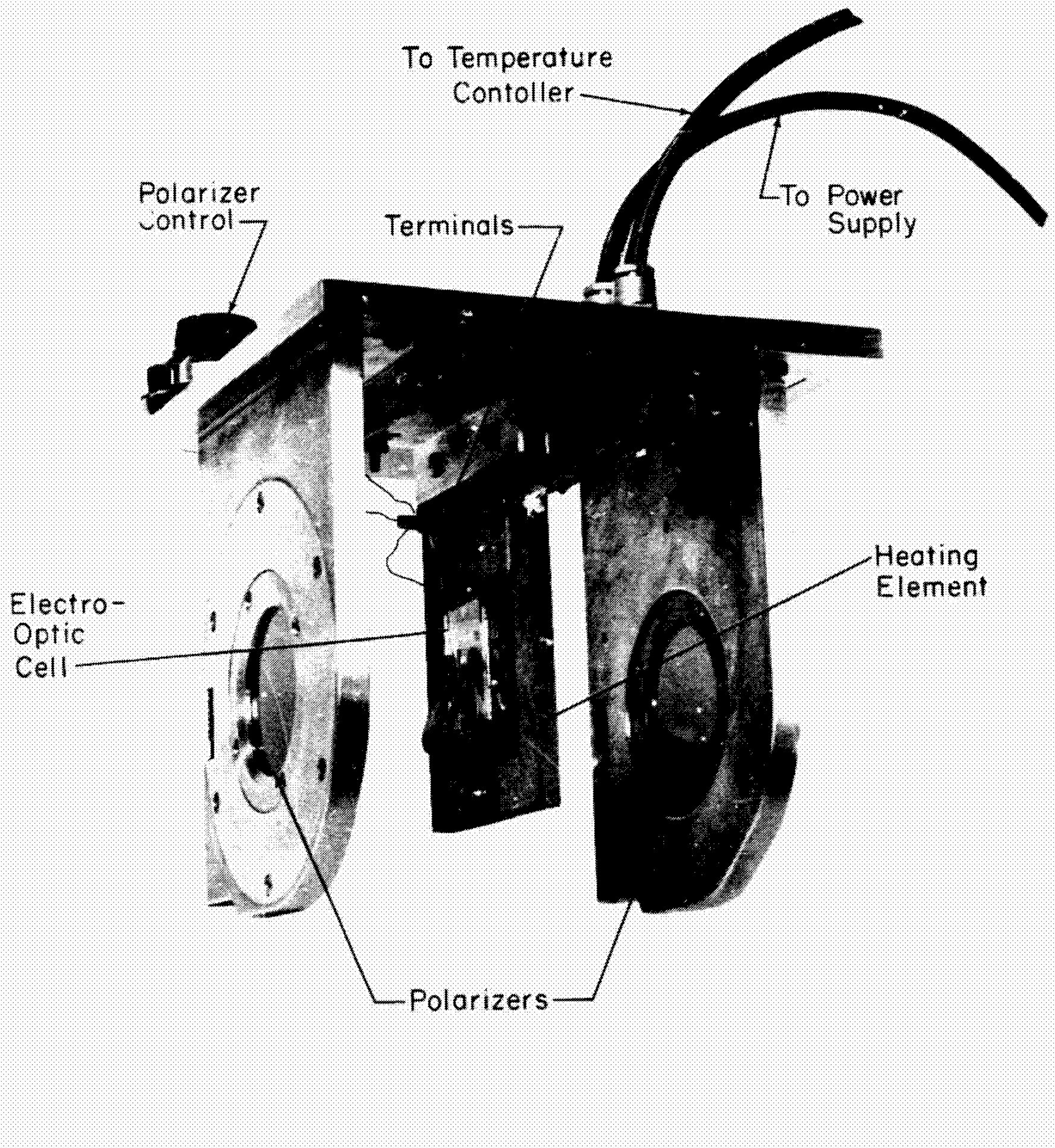


Figure 11. Apparatus designed for spectrophotometric measurements of electro-optic cells (SEO device).

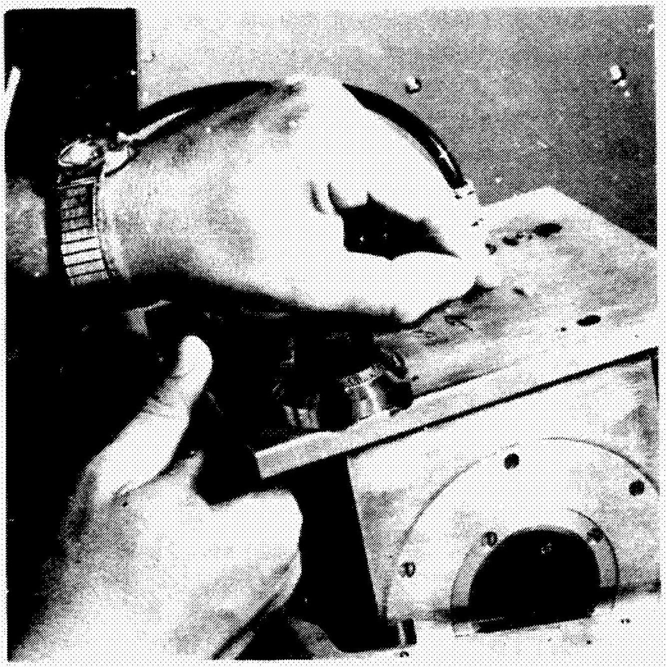


Figure 12. Insertion of SEO device in Cary 14R spectrophotometer.

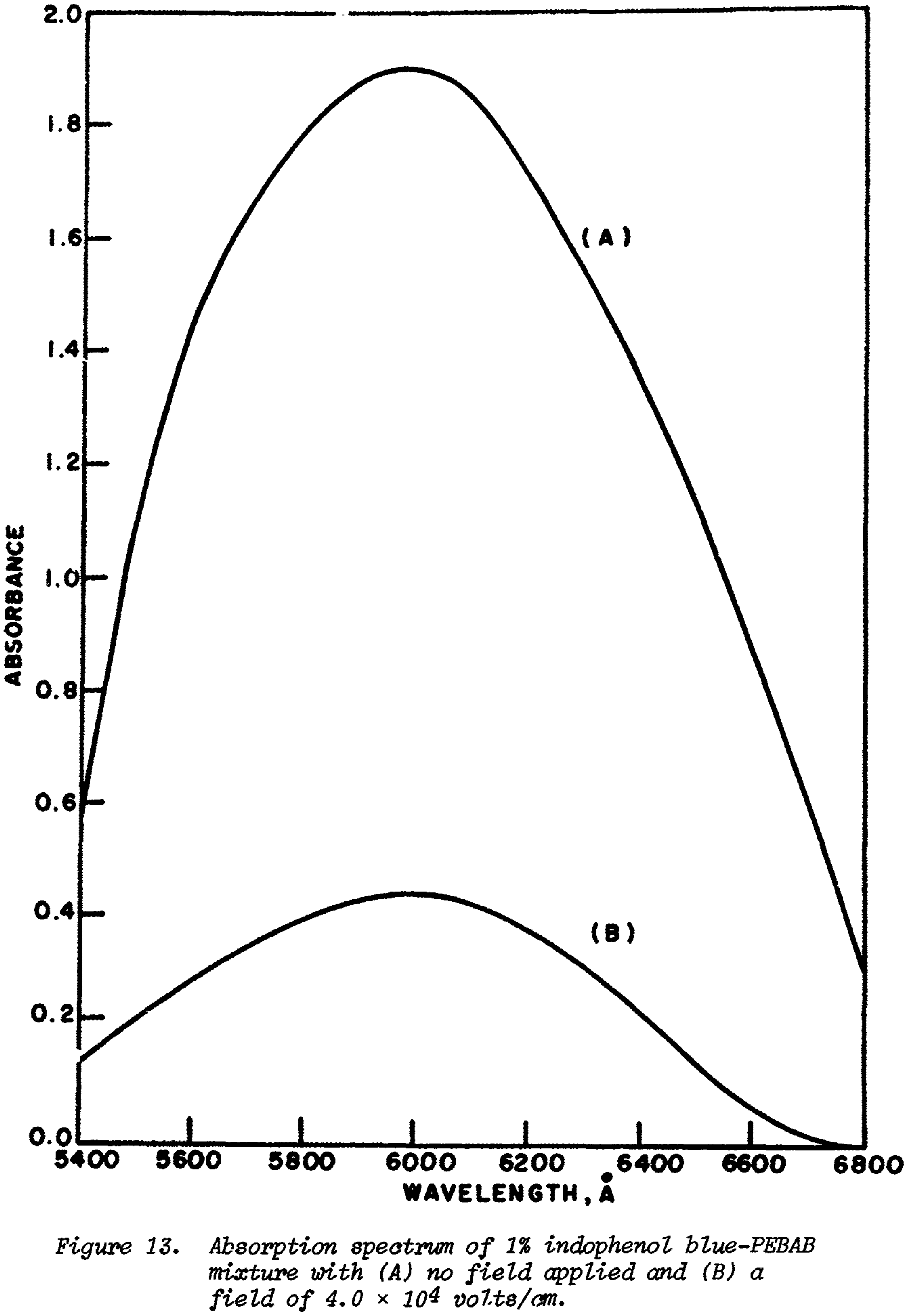


Figure 13. Absorption spectrum of 1% indophenol blue-PEBAB mixture with (A) no field applied and (B) a field of 4.0 × 10^4 volts/cm.

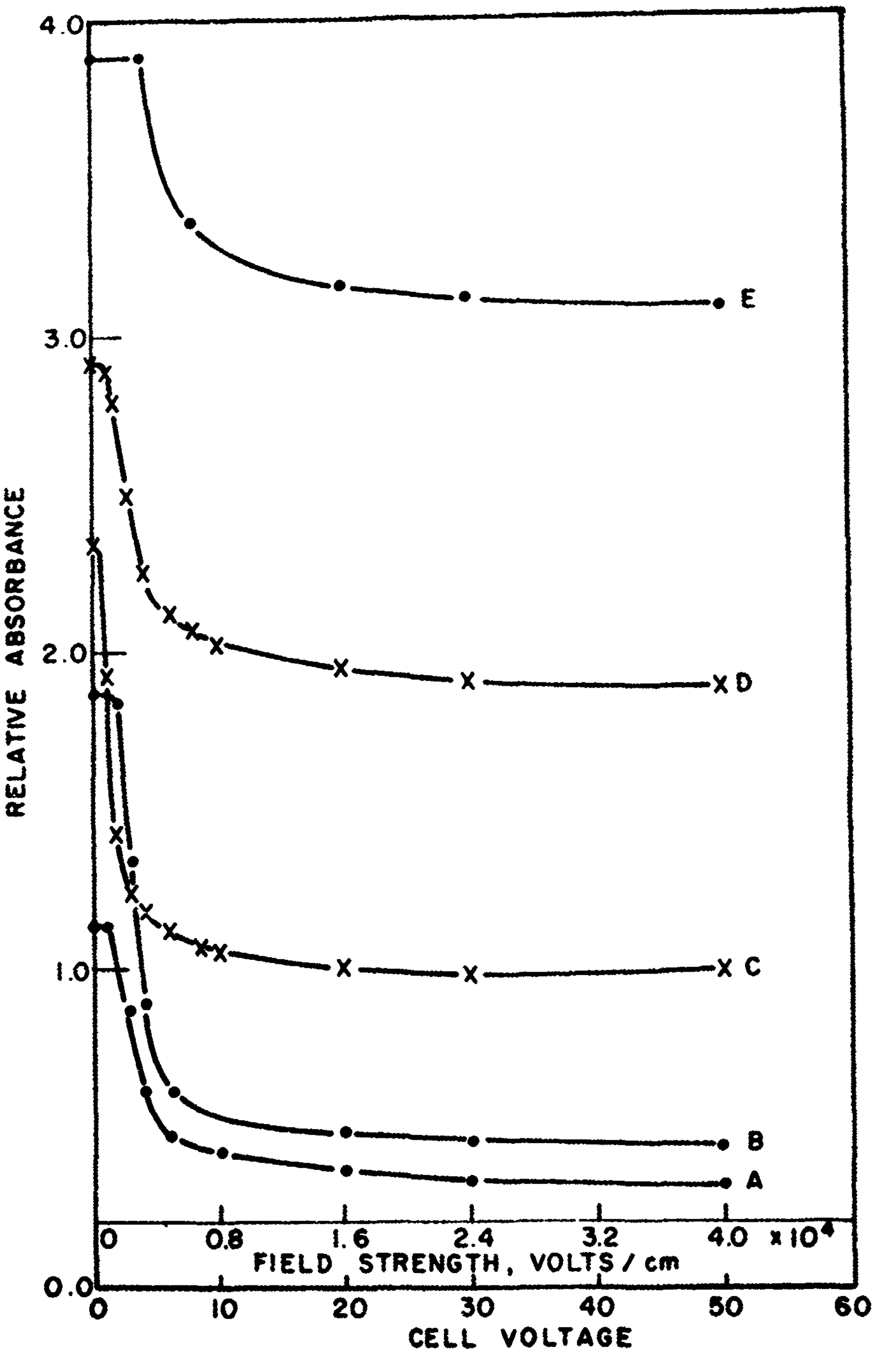


Figure 14. Changes in absorbance as a function of field strength for mixtures of PEBAB-RT and A - 0.5%, B - 1.0%. C - 1.5%, D - 2.5% and E - 5.0% of indophenol blue (cell thickness 12.5 microns).

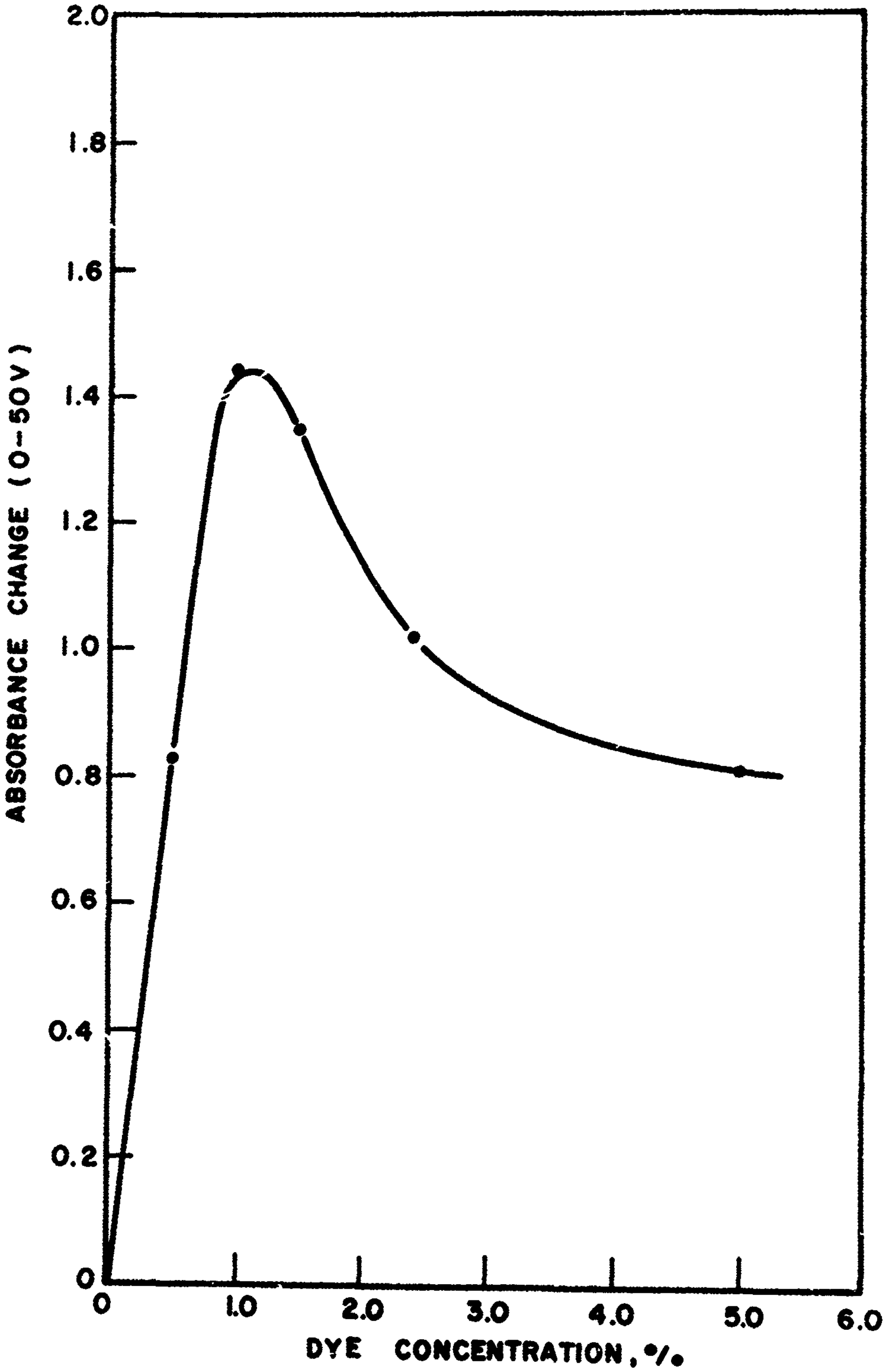


Figure 15. Maximum absorbance change (0-50 V) as a function of indophenol blue concentration in PEBAB-RT.

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 the PEBAB-RT host we require

$$\varepsilon = N \vec{\mu} \cdot \vec{E} \sim kT \qquad (1)$$

where $\vec{\mu}$ = molecular dipole moment ($\sim$3)

$\vec{E}$ = field strength ($\sim$ 4.0 kV/cm)

and N = number of dipoles cooperatively aligned ($\sim$ 100).

Thus, it is implied from these measurements that this nematic liquid exhibits a cooperative behavior involving approximately 100 molecules.

In an effort to further elucidate the interactions of dye molecules in liquid crystals, the absorption characteristics of indophenol blue in PEBAB-RT as a function of concentration and cell thickness were determined. The Beer-Lambert plot (absorbance vs. concentration) showed only a slight deviation from linearity at concentrations above 1 to 1.5%. This deviation is probably due to association of the dye molecules in the nematic host and is well known to occur with many organic molecules dissolved in isotropic solvents at these concentrations (5.0×10^{-2}M). The absorbance of a mixture containing 0.5% indophenol blue in PEBAB-RT was measured as a function of cell thickness ranging from 1/4 mil to 2.0 mils, but no deviation from linearity was observed as expected.

A study of the spectral response as a function of field strength was also made with the PNAZA (yellow → colorless) dye dissolved in PEBAB-RT. The visible absorption spectrum consisted of a long tail from 4000 to 5000 Å. The results were similar to those obtained for the indophenol blue-PEBAB-RT mixtures. The maximum contrast ratio was obtained at a dye concentration of 1 to 1.5%.

The presence of a keto group in the terminal position of molecules of ABAP and APAP provides them with strong dipole moments along the molecular axis, and cooperative alignment effects similar to those exhibited by PEBAB-RT should occur. An examination of the behavior of p-ethoxybenzylidene-p'-aminoacetophenone (ABAP, n = 2) in mixtures with indophenol blue were therefore initiated. The nematic molecules are initially oriented with their long axes perpendicular to the electrode surfaces. This is in contrast to the behavior of PEBAB and its derivatives which give orientation parallel to the electrodes. When a field was applied across the material the molecules aligned with their long axes perpendicular to the direction of the field. Hence, when a mixture with indophenol blue was subjected to an applied electrical field, the material changed from colorless to blue. The contrast ratio, however, was not as high as previously demonstrated. Further work on these materials is planned.

Response and Relaxation Time. -- A study of the effect of dye structure and concentration as well as of temperature and field strength on the rise and decay times of electro-optic cells was made during the past year. The measurements were made with mixtures of PEBAB-80 and the dyes, indophenol blue and PNAZA. A single nematic host was chosen for these experiments in order to avoid complications in interpretation of the results. The experimental apparatus consisted of a mercury arc beam directed through a Corning type 7-59 broad-bandpass filter focused onto the cell under test and detected by an RCA 935-S photomultiplier tube. The output voltage of the photomultiplier tube, proportional to the incident light intensity, was sampled by a type 503 Tektronix oscilloscope. Listed below are the salient features of the accumulated results.

1. No significant differences in rise times are noted for dye concentrations of 1.2, 2.5, and 5.0%. At 10 V (0.8 x 10^4 V/cm) the rise time at 60°C is ~2 msec and ~0.2 msec at 45 V.
2. The relaxation time of all the cells made with dye concentrations of 2.5, 5.0, and 10.0% is ~30 msec and is independent of the magnitude of the initially applied voltage pulse.
3. For applied voltages of 45 V (3.6 x 10^4 V/cm) the rise time for all cells (dye concentrations 0 to 10%) is less than 1 msec and relatively insensitive to temperature changes. At 10 V, a dye concentration of 10% responds in ~5 msec but decreases rapidly to ~0.5 msec at voltages greater than 25 V.
4. Cells made with either undoped host material or a 1.2% dye concentration relax about 2 to 3 times slower than the units with higher dye concentrations, but again no voltage dependence was observed A slight decrease in relaxation time was noted at higher temperatures (80 to [illegible]°C).

The compiled data listed in Table III show the speed of response time for seven different electro-optic cells at three different applied voltage pulses and at two temperatures. All of the cells had an active area of approximately 1.3 cm^2 with a 0.5-mil separation between TIC-coated glass electrodes.

TABLE III

RISE TIME MEASUREMENTS OF PNAZA-PEBAB MIXTURES

PNAZA Dye Concentration in PEBAB-80	Voltage pulse = 10V		Voltage pulse = 22.5V		Voltage pulse = 45V	
	Temp 60°C (msec)	Temp 80°C (msec)	Temp 60°C (msec)	Temp 80°C (msec)	Temp 60°C (msec)	Temp 80°C (msec)
1.2%	2-3	1-2	0.5-1	0.1-0.5	0.1-0.5	0.1-0.5
2.5%	1-2	1-2	0.5-1	0.1-0.5	0.1-0.5	0.1-0.5
4.0%	1-2	1-2	0.5-1	0.1-0.5	0.1-0.5	0.1-0.5
5.0%	1-2	1-2	0.5-1	0.1-0.5	0.1-0.5	0.1-0.5
7.5%	4	4	0.5-1	0.1-0.5	0.1-0.5	0.1-0.5
10.0%	5	5	1-2	1-2	0.1-0.5	0.1-0.5
1.0% Indophenol Blue	6	3-4	1-2	0.1-0.6	0.1-0.5	0.1-0.5

A detailed investigation was made of speed of response time as a function of cell temperature. Two different electro-optic units on one double grooved split substrate minimized potential differences that might be introduced in the cell fabrication process. Dye concentrations of 2.5% PNAZA and 2.2% indophenol blue in PEBAB-80 allowed comparative measurements to be made between the two different dye materials. The temperature range of interest was dictated by the nematic range of the host PEBAB-80 material, between 56°C and 90°C (Figures 16 and 17).

The relaxation time remains relatively constant at 30 to 50 msec, independent of the initially applied electric field pulse (>5 x 10^3 V/cm) or the cell temperature in its nematic state. Rise time characteristics were affected only at the lower temperatures <u>and</u> at low electric field pulses. For an applied voltage pulse of 10 V across a 1/2-mil cell, a rise time of 6 msec is measured near the C-N temperature at 55°C. At 65°C the rise time is reduced significantly to about 2 msec and remains relatively unaffected as the cell temperature is increased further to $\sim$92°C.

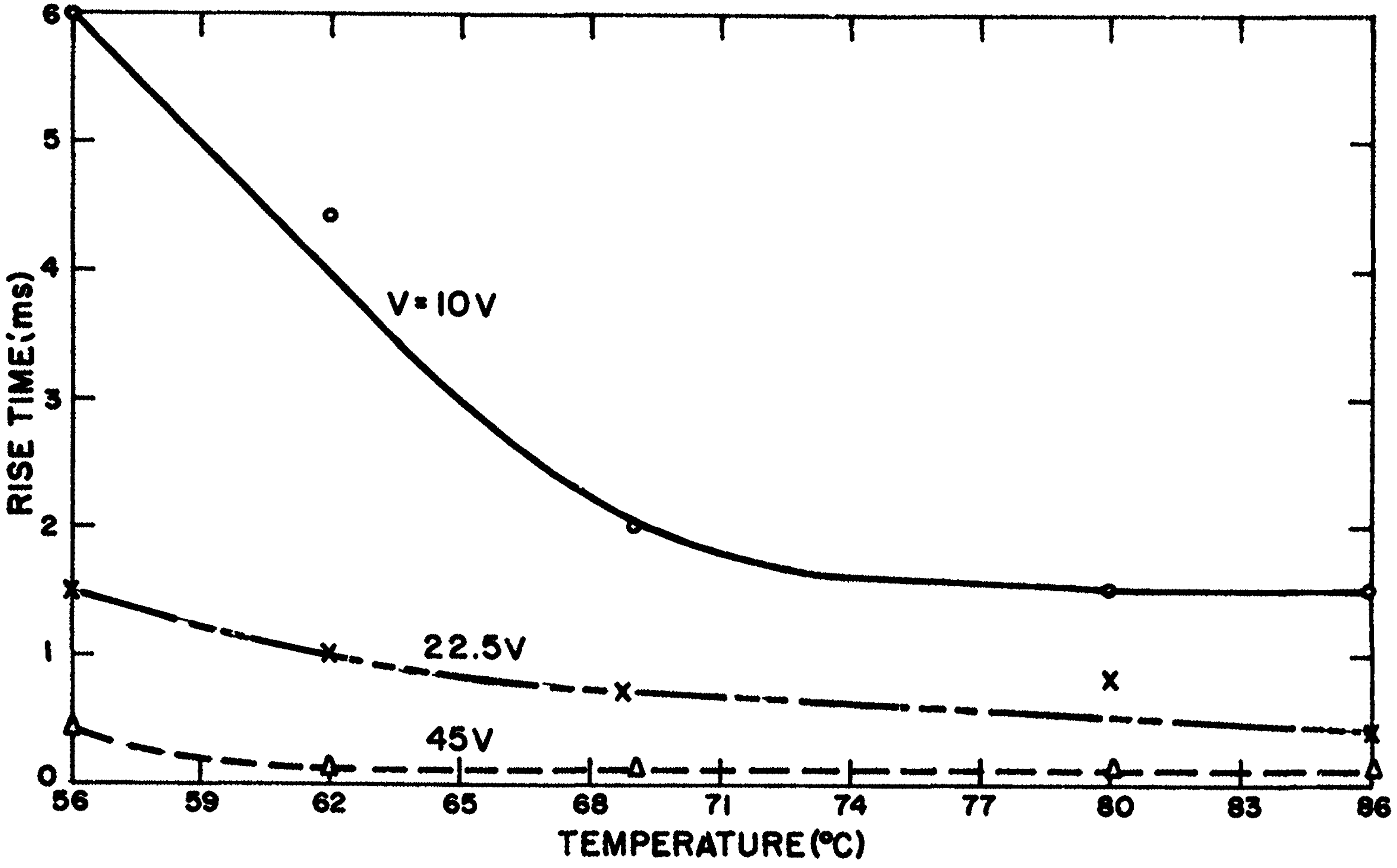


Figure 16. Rise time vs. temperature, 2.5% PNAZA in PEBAB-80.

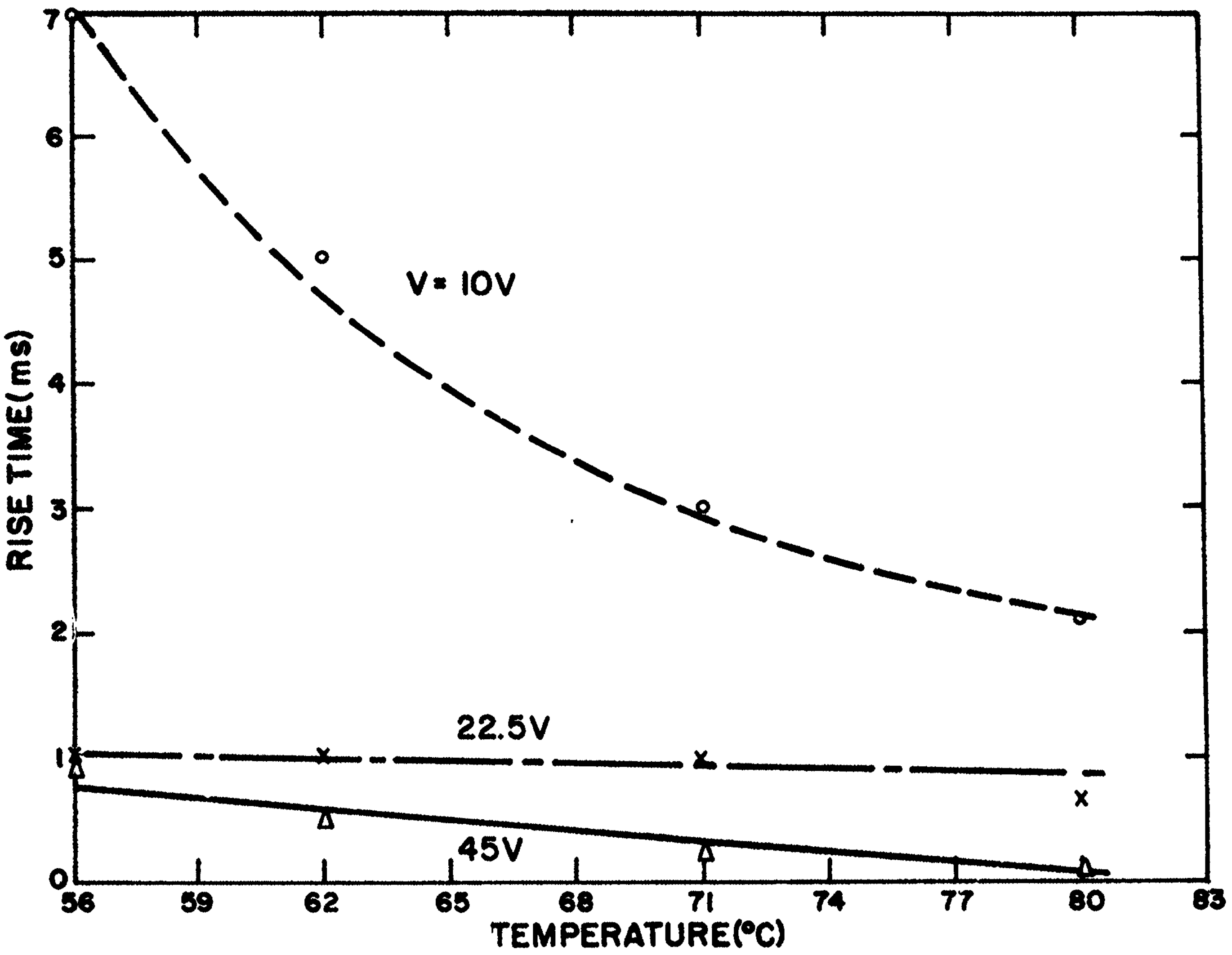


Figure 17. Rise time vs. temperature, 2.2% indophenol blue in PEBAB-80.

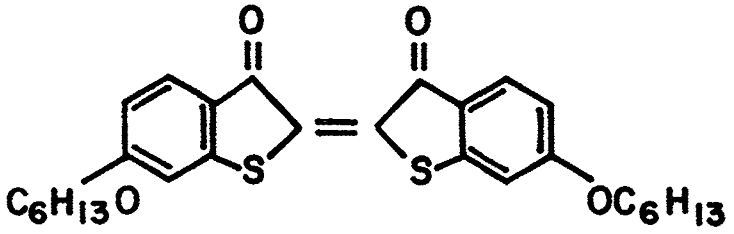
Although no important temperature restrictions could be imposed on cell performance relating to speed of response to an applied electric field, an apparent reduction of "on-off" contrast ratio is observed at elevated temperatures.

These results indicate that both the speed of response and decay are dependent on the nature of the host material and independent of the structure of the guest dye molecule. The long relaxation time may be due to the high viscosity of the nematic material. Future work will be directed toward ways and means to reduce the relaxation time by lowering the viscosity of the medium and/or by application of reversed pulses of ac or dc fields

Dichromic Cells

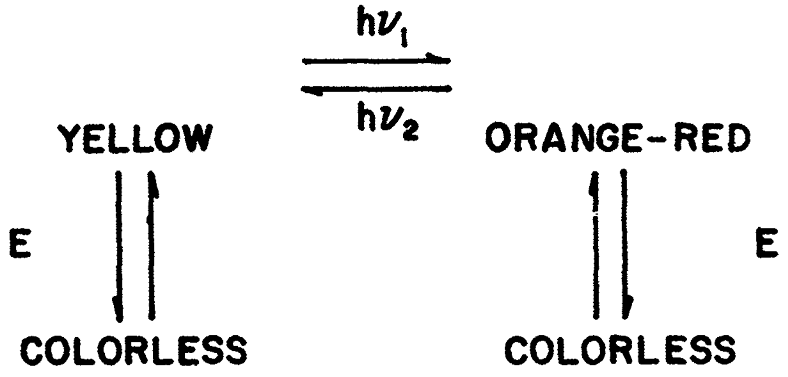
The use of liquid crystals in orienting pleochroic dye molecules should also be applicable to photochromic dyes. It should therefore be possible to control the photochromic reaction by changing the orientation of the dye with respect to the incident light.

An examination of the behavior of photochromic, pleochroic dyes in the PEBAB-RT host was therefore initiated during the past year. Mixtures of PEBAB-RT with 6,6'-dihexyloxythioindigo (Ref. 12) (IV) were prepared at concentrations of 1, 2, and 5% of dye. Crystallization of the dye from the nematic material occurred, however, in the 5% mixture due to poor solubility of the compound in PEBAB-RT. An electro-optic cell was nevertheless prepared with the 2% mixture, and the spectral changes were studied with the GEO device previously described (Figure 11). The spectrum of the dye exhibits a peak at 4600 Å due to the *cis* form and one at 5100 Å due to the *trans* form. Irradiation of the cell with light of the proper wavelength produces conversion of one form to the other. This reversible process occurs in the nematic host to the same degree as it does in solution. Since both *cis* and *trans* forms of the guest molecule are pleochroic, it is possible to achieve electronic color switching of either form by application of electric fields of the order



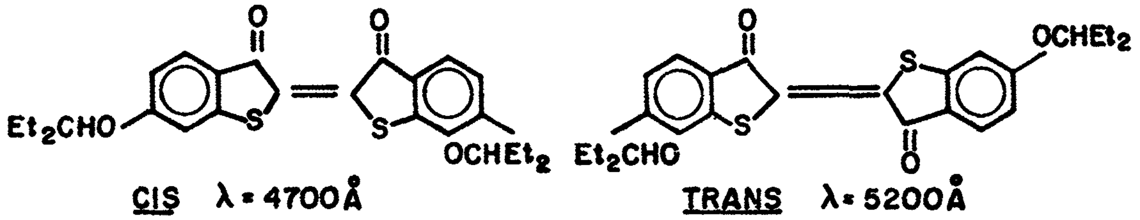
IV

of 10 to 40 kV/cm. This adds another dimension to our electronic color switching effect since it now provides us with means for conversion of one color to another photolytically in addition to changing the optical density electronically. A schematic diagram of these changes is illustrated:



The low extinction coefficients of these absorption bands as well as the poor solubility of the dye in PEBAB-RT resulted in low contrast ratios. In addition, these factors hampered efforts to study photochromic behavior as a function of field strength.

In order to circumvent these difficulties a new compound, 6,6'-di-3-pentyloxythioindigo (Ref. 12) (V) which had a higher solubility in PEBAB-RT than IV was prepared. Two different electro-optic cells containing concentrations of 1.25 and 2.0% of V in PEBAB-RT were fabricated and their absorption spectra measured with the SEO device inserted in the Cary 14R spectrophotometer. The spectrum of the dye exhibits a peak at 4700 Å due to the *cis* form and one at 5200 Å due to the *trans* form.



V

The initial optical density vs. wavelength characteristics were recorded and similar measurements repeated after illuminating the particular cell at wavelengths either above or below ∿5000 Å. Corning type CS 3-70 and CS 5-60 filters, which were inserted between the light source (Hanovia 150-W Hg vapor lamp) and the electro-optic cell under test, were used to select the desired wavelength of incident radiation. Within reasonable limits, neither the magnitude of the radiant energy nor the time of irradiation were critical for these measurements. Table IV shows the optical density changes at 5200 Å and 4700 Å of each cell after two cycles of irradiation. Electronic color switching of each form was also accomplished and these results are shown in Table V.

TABLE IV

OPTICAL DENSITY CHANGES AT 4700 Å AND 5200 Å AFTER TWO CYCLES OF IRRADIATION

		Dye Concentration			
		1.25%		2.0%	
Order of Irradiation	Irradiation Conditions	O.D. of cis	O.D. of trans	O.D. of cis	O.D. of trans
0	Initial optical density	0.64	0.44	1.45	1.50
1	Filter CS 3-70 $\lambda > 5000$ Å 1 minute	0.72	0.32	1.55	1.00
2	Filter CS 5-60 $\lambda < 5000$ Å 1 minute	0.60	0.62	1.20	1.72
3	Filter CS 3-70 1 minute	0.72	0.32	1.55	1.00
4	Filter CS 5-60	0.60	0.62	1.20	1.72

TABLE V

OPTICAL DENSITY vs. APPLIED ELECTRIC FIELD WITH NO CHANGE IN ILLUMINATION CONDITIONS

	1.25% cell		2.0% cell	
	cis	trans	cis	trans
Optical density with V = 0	0.61	0.42	1.00	1.60
Optical density with V = 22 volts	0.25	0.17	0.63	0.90

Thus, we have demonstrated that good contrast ratios can be obtained with photochromic, pleochroic dyes in liquid crystals. In all of these experiments, however, the optical density of the cells was so high that enough light was absorbed to produce photochromism in both orientations ($E_{||}$ and $E_{\perp}$) of the dye molecules. This is undoubtedly due to the fact that at high concentration of dye (above 1%) a large number of molecules are not oriented by the liquid crystal and contribute to the absorbance of the medium. This effect was observed with the indophenol blue-PEBAB-RT mixture described above (see Figure 15).

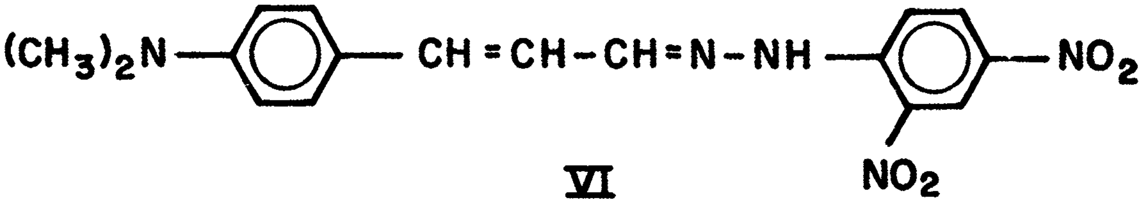
After about six cycles of irradiation between the two isomeric forms the changes in optical density began to decrease. This "fatigue" is known to occur when this photochromic dye is dissolved in an acidic medium. Thus, the liquid crystalline system may be too acidic for this particular dye. Future work in this area must therefore be devoted toward the use of dyes with higher extinction coefficients and greater stability.

Polychromic Cells

For practical utility in color switching applications, it would be desirable to fabricate a single unit which would exhibit a desired color of the spectrum by application of an electric field of specific magnitude. One way this may be accomplished is to fabricate a unit which contains separated layers of material (dye and host) that transmit the three primary subtractive colors -- yellow, cyan, and magenta. Variation of the voltage among the layers should then produce all the colors of the spectrum in the light transmitted through the unit. For this reason, a considerable effort was devoted to means of obtaining dye mixtures (and electro-optic cells) that would exhibit the desired spectral characteristics.

A partial demonstration of this concept was provided by electronic color switching of two different cells placed one upon the other. Thus, we were able to observe four primary colors by placing a cell (A) containing 1% of the PNAZA dye (yellow) in PEBAB-RT over one (B) containing 1% indophenol blue in PEBAB-RT and examining the light transmitted through both cells (initially green) as a function of a 40-kV/cm electric field applied to both cells (white), to A (blue) and to B (yellow). Variation of the voltage between the two cells produced shades of color among these four.

Since we have not been able to obtain a dye which exhibits an absorption spectrum similar to that of the "standard" cyan (Kodak Wratten Filter #44A), our efforts were directed toward the use of two pleochroic dyes in the same nematic host. Thus, mixtures of indophenol blue and PNAZA (yellow) were prepared with the PEBAB-RT host, and the resulting electro-optic cells exhibited spectral characteristics which closely approximated those of the standard (Figure 18). A similar effort to obtain the standard magenta was also made. This work involved the preparation of additional mixtures of indophenol blue and the red hydrazone VI with PEBAB-RT. However, we have still been unable to achieve the desired color. Several other red dyes will be investigated soon in an effort to meet this objective.



VI

Another mode of operation using electronic color switching involves the use of a mixture of a pleochroic and nonpleochroic dye in the same nematic host. In this case, a mixture of indophenol blue ($\sim$0.5%) and 4-methoxybenzylidene - 2',4'-dinitrophenylhydrazone (VII) ($\sim$0.5%) in

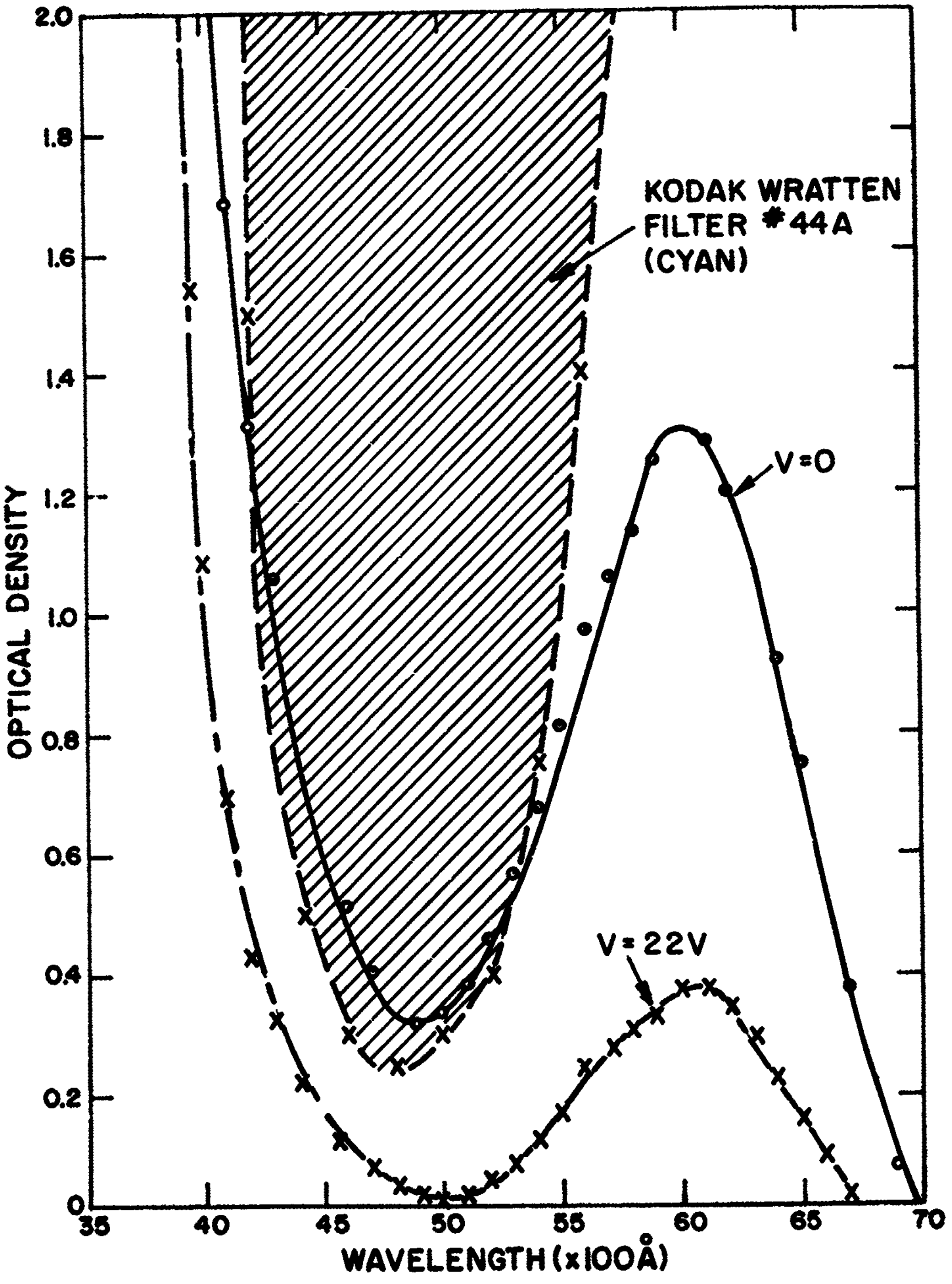
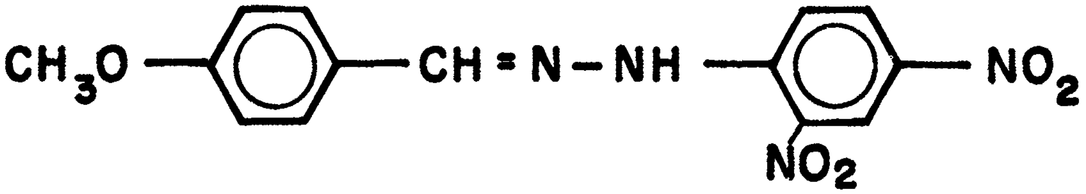


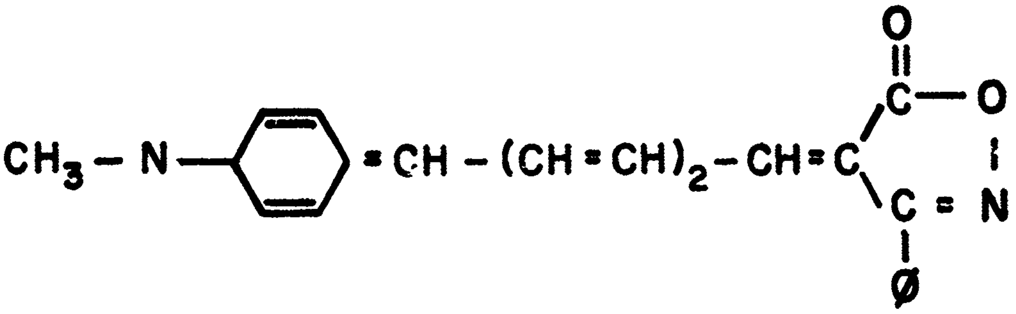
Figure 18. Absorption spectrum of mixture of indophenol blue and PNAZA in PEBAB-RT.



VII

PEBAB-RT was examined in the normal cell configuration. The material could be switched from violet to red with fields of ~40kV/cm. Thus, the red dye is oriented by the nematic material but its color does not change since its absorption spectrum is not a function of its orientation with respect to the polarized light. The indophenol lue, however, operates in the usual way.

A dye which is known to exhibit extensive solvatochromic behavior (change in color with change in polarity of solvent) has the structure VIII.



VIII

Since the PEBAB-RT host changes its dielectric constant upon the application of a dc bias, it should be possible to electronically produce changes in the color of mixtures of VIII and the nematic host. An attempt to accomplish this was made but the poor solubility of VIII in the nematic host reduced the absorption characteristics to such a degree that no color changes were observed.

DIELECTRIC DISPERSION MEASUREMENTS

Color switching by means of guest-host interactions in nematic liquid crystals has at its very foundation the orientation of the nematic host in an external electric field. A fundamental tool in the study of molecular behavior is the measurement of the dielectric dispersion. Thus dielectric studies of the PEBAB family were conducted with and without the presence of a bias field.

Measurements were made on the sandwich type cells used in all of our guest-host experiments. The dielectric dispersion was measured using a Boonton capacitance bridge. Measurements were not made above 1 MHz. The Hewlett-Packard (302A) impedance meter was used to check the data. The Boonton bridge had a provision for introducing an external dc bias. The measuring signal was of the order of a few millivolts and had no effect on the measurements. The data with and without bias are shown in Figure 19 and can be summarized as follows:

1. With no bias present the material has a dielectric constant of 7 with a relaxation which occurs around 1 to 5 MHz.
2. With bias present the dielectric constant is increased to 21 while a relaxation is observed to occur at about 50 kHz.
3. In the isotropic state the dielectric constant is 10.5. Bias has no effect.

In the unbiased state the molecular alignment, as confirmed by observing the sample in transmitted light between crossed polarizers, is such that the molecular axes are essentially parallel to the electrodes. In the biased state the molecular axes lie perpendicular to the electrodes and parallel to the bias field. This type of alignment is to be expected since the PEBAB family has a strong permanent dipole moment due to the pressure of the cyano group along the molecular axis.

The nature of the relaxation data requires some consideration. For example, is the relaxation due to interfacial phenomena or is it true Debye relaxation? Relaxation data are generally interpreted in terms of a complex dielectric constant and the admittance is given by

$$Y = j\omega\varepsilon^* = j\omega(\varepsilon' - j\varepsilon'') \qquad (2)$$

For Debye type relaxation at frequencies below relaxation[Ref.14]

$$\varepsilon'' \propto \omega$$

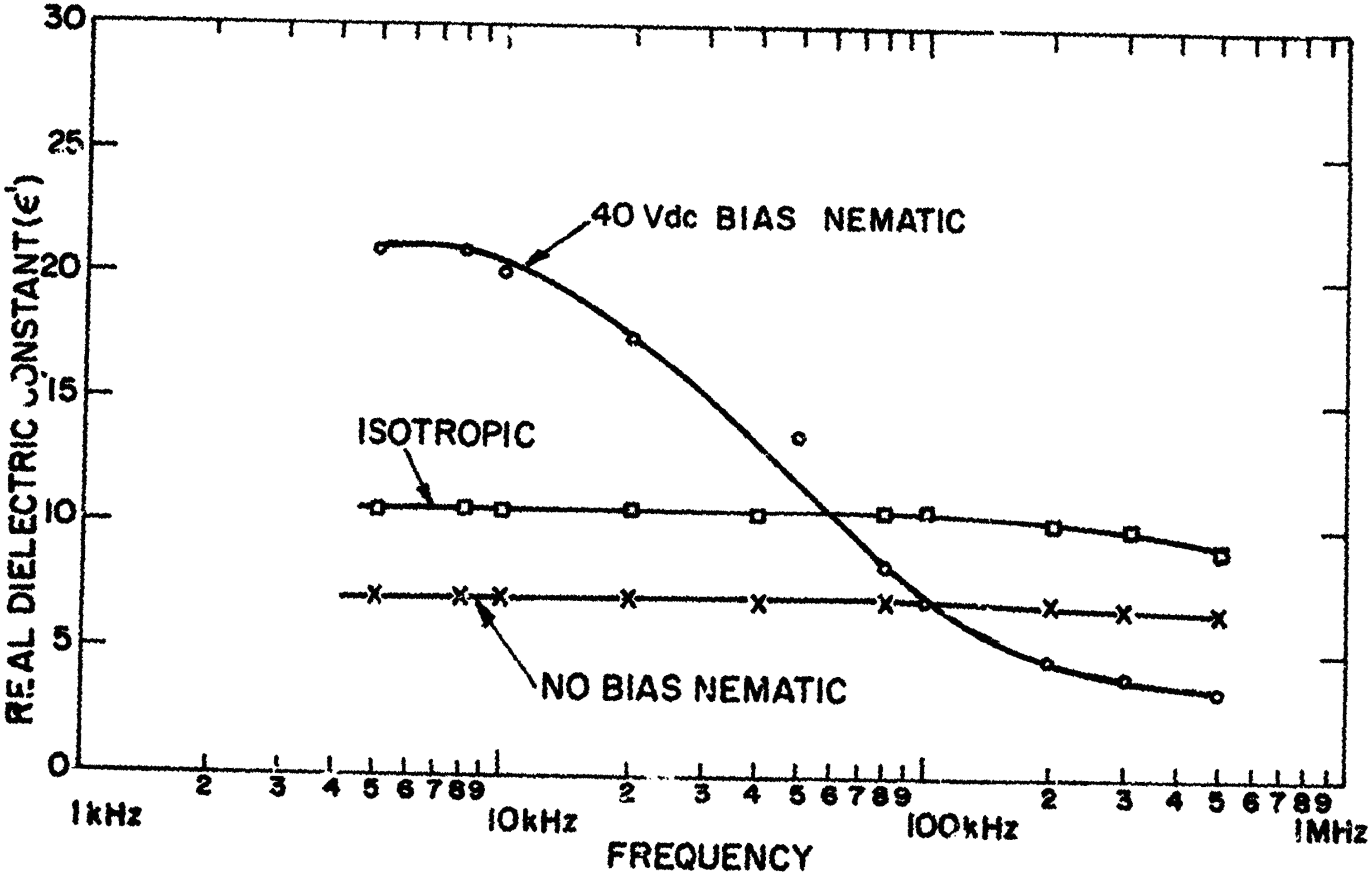
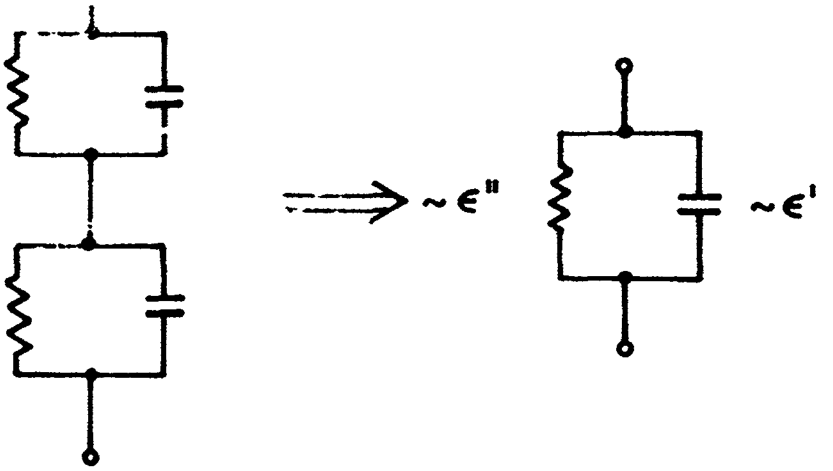


Figure 19. Real dielectric constant vs. frequency of PEBAB-PT.

In the case of interfacial polarization



and

$$\varepsilon'' \propto \frac{1}{\omega}$$

Thus, the behavior of the imaginary part of the complex dielectric constant as a function of frequency (Figure 20) can be used to differentiate between a true relaxation and interfacial polarization. Our data indicate that the relaxations of concern in our experiments are of the former type.

Maier and Meier[Ref. 15] have calculated the anistropy of the dielectric constant for nematic materials using Onsager's model of a liquid dielectric. While their calculation is in error, the approach is correct. The corrected equations are:

$$\frac{\varepsilon_1 - 1}{4\pi} = \mathrm{NhF} \left\{ \bar{\alpha} + \frac{2}{3} \Delta \alpha S + \frac{F\mu^2}{3kT} \left[1 - (1 - 3 \cos^2\beta)S \right] \right\} \qquad (3)$$

and

$$\frac{\varepsilon_2 - 1}{4\pi} = \mathrm{NhF} \left\{ \bar{\alpha} - \frac{1}{3} \Delta \alpha S + \frac{F\mu^2}{3kT} \left[1 + \frac{1}{2} (1 - 3 \cos^2\beta)S \right] \right\} \qquad (4)$$

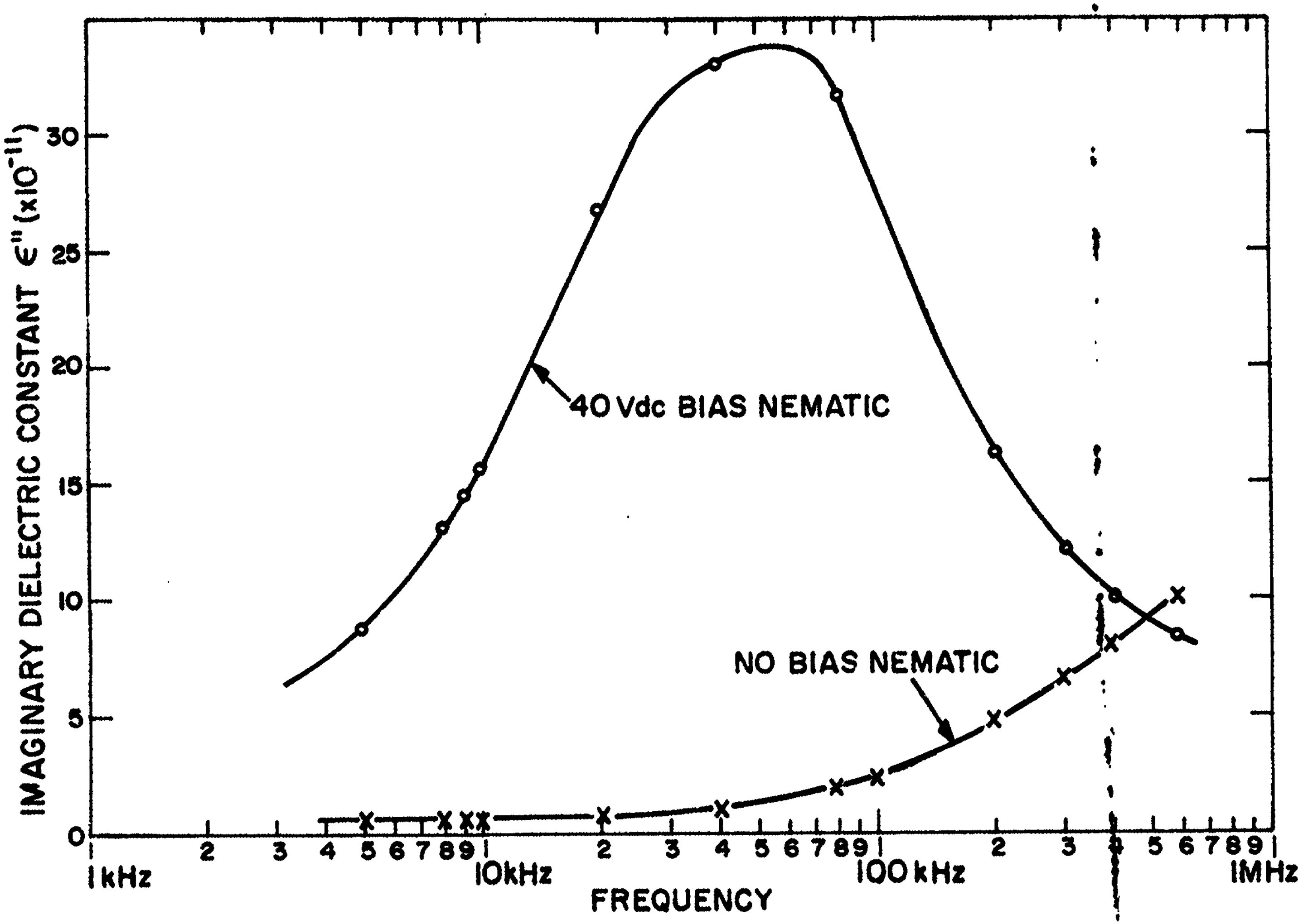


Figure 20. Imaginary dielectric constant vs. frequency of PEBAB-RT.

where

ε = dielectric constant

α = electronic polarizability

μ = molecular dipole moment

$S = 1 - 3/2\ \overline{\sin^2\theta}$

$h = \frac{3\bar{\varepsilon}}{2\bar{\varepsilon} + 1}$

$f = \frac{2\bar{\varepsilon} - 2}{2\bar{\varepsilon} + 1}\ \frac{4\pi}{3}\ \frac{N_L\rho}{M}$

$F = \frac{1}{1 - \bar{\alpha} f}$

$\bar{\alpha} = 1/3\ (\alpha_{||} - 2\alpha_{\perp})$; $\bar{\varepsilon} = 1/3\ (\varepsilon_1 + 2\varepsilon_2)$

θ = angle of molecular axes with field

β = angle of dipole with molecular axis

and the orientations are as shown in Figure 21.

From Eqs. (3) and (4)

$$\frac{\Delta\varepsilon}{4\pi} = \varepsilon_1 - \varepsilon_2 = NhF\left[\Delta\alpha - \frac{F\mu^2}{2kT}(1 - 3\cos^2\beta)S\right] \qquad (5)$$

In the isotropic liquid S = 0; hence,

$$\frac{\varepsilon_{\text{isotropic}}}{4\pi} = NhF\ (\bar{\alpha} + \frac{F\mu^2}{3kT}) \qquad (6)$$

Neglecting the anisotropy of the electronic polarizability which is possible if $\varepsilon_{\text{isotropic}} \gg 1$ (roughly the case in the PEBAB family)

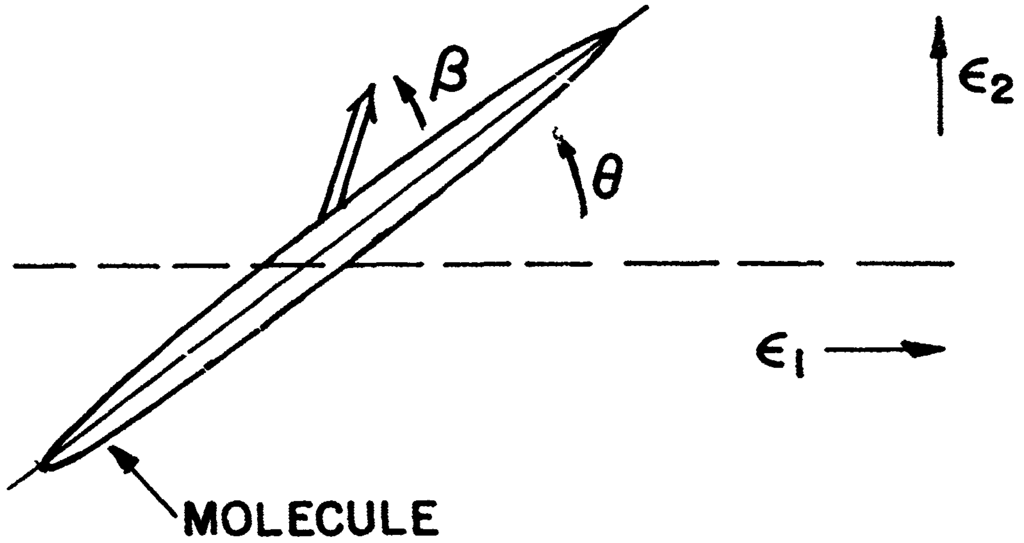


Figure 21. Molecular orientation of PEBAB-RT.

$$\frac{\epsilon_1-1}{4\pi} = \frac{\epsilon_{isotropic}-1}{4\pi} - \frac{NhF^2\mu^2}{3kT}\left(1 - 3\cos^2\beta\right) S \qquad (7)$$

Hence, $\epsilon_1 \geq \epsilon_{isotropic}$ for $\beta \leq 55°$

For the PEBAB family, $\beta \sim 0$ and assuming $S \sim .5$ we obtain

$$\epsilon_1 = \epsilon_{isotropic} + \frac{4\pi NhF^2\mu^2}{3kT} \quad 2\epsilon_{isotropic} \qquad (8)$$

and

$$\frac{\epsilon_1+2\epsilon_2}{3} = \epsilon_{isotropic} \qquad (9)$$

With bias present the molecules are aligned along the direction of the field and we measure $\epsilon_1 = 21$. For the case of no bias, the molecules lie essentially parallel to the electrodes and we measure $\epsilon_2 = 7$. Now the measured value of $\epsilon_{isotropic}$ is = 10.5 which is roughly $\epsilon_{1/2}$ as required by Eq. (8). Using the experimental values for ϵ_1 and ϵ_2 and Eq. (9)

$$\frac{\varepsilon_1 + 2\varepsilon_2}{3} = 11.7 = \varepsilon_{\text{isotropic}} \tag{10}$$

This is in good agreement with the experimental value of 10.5, and gives us confidence in the approach.

The interpretation of the relaxation shifts with bias is more complex and only a simple model is available at the present time. It is felt that the presence of an orienting bias field gives rise to an additional energy barrier to rotation. Thus

$$\tau_E = \tau_o \exp(U/kT) \tag{11}$$

where

τ_E = relaxation time with bias present

τ_o = relaxation time without bias

U = barrier energy

kT = thermal energy

Experimentally

$$\tau_E \sim 100\ \tau_o \tag{12}$$

This implies that

$$\exp(U/kT) \sim 100$$

and

$$U \sim 4.6\ kT$$

Now suppose the additional barrier energy is due solely to dipolar orientation; then

$$U = n\mu E_{\text{bias}} = 4.6\ kT \tag{13}$$

where

μ = molecular dipole moment $\sim$ 4 debye

$E_{dc} = 1.3 \times 10^6$ V/m

n = number of cooperatively orienting dipoles

At 300°K

$n \sim 1100$

This approach suggests that the alignment energy in the bias field is equivalent to that of 1100 molecules acting collectively. The barrier energy of 4.6 kT which is introduced by the bias field seems reasonable since the orientation pattern is stable with respect to thermal fluctuations. Thus, the increase in the relaxation time possibly can be accounted for by the field-induced barrier.

STATE-OF-THE-ART DEVICES

Several devices designed to demonstrate the utility of electronic color switches were constructed during the past year. A cell containing the 1.0% indophenol blue-PEBAB mixture described in the text was used successfully to modulate the beam of a 1-mW helium-neon laser. This laser has an output at 6328 Å which corresponds to the absorption of the dye. With no field applied, therefore, 97% of the laser light was absorbed. A field of 4.0 x 10^4 V/cm applied to the cell produces cooperative alignment, and the medium absorbs only 50% of the laser light. This inexpensive device provides a simple method for laser modulation in the kHz range with only minimal power requirements.

The numeric display shown in Figure 22 is another representative state-of-the-art device using the indophenol blue:PEBAB-RT mixture. The complete range of single digit numbers (0 through 9) is possible by photoetching the usual seven-segment pattern onto one of the TIC-coated surfaces of the 1/2-mil spaced electro-optic cell. Automatic sequential counting is achieved using commercially available circuits consisting of a timer (clock), binary counter, and a seven-segment decoder suitable for addressing the seven-segment display element. A flat, 2-inch square fluorescent panel capable of 8 to 12 W continuous operation provides ample back illumination for viewing the display.

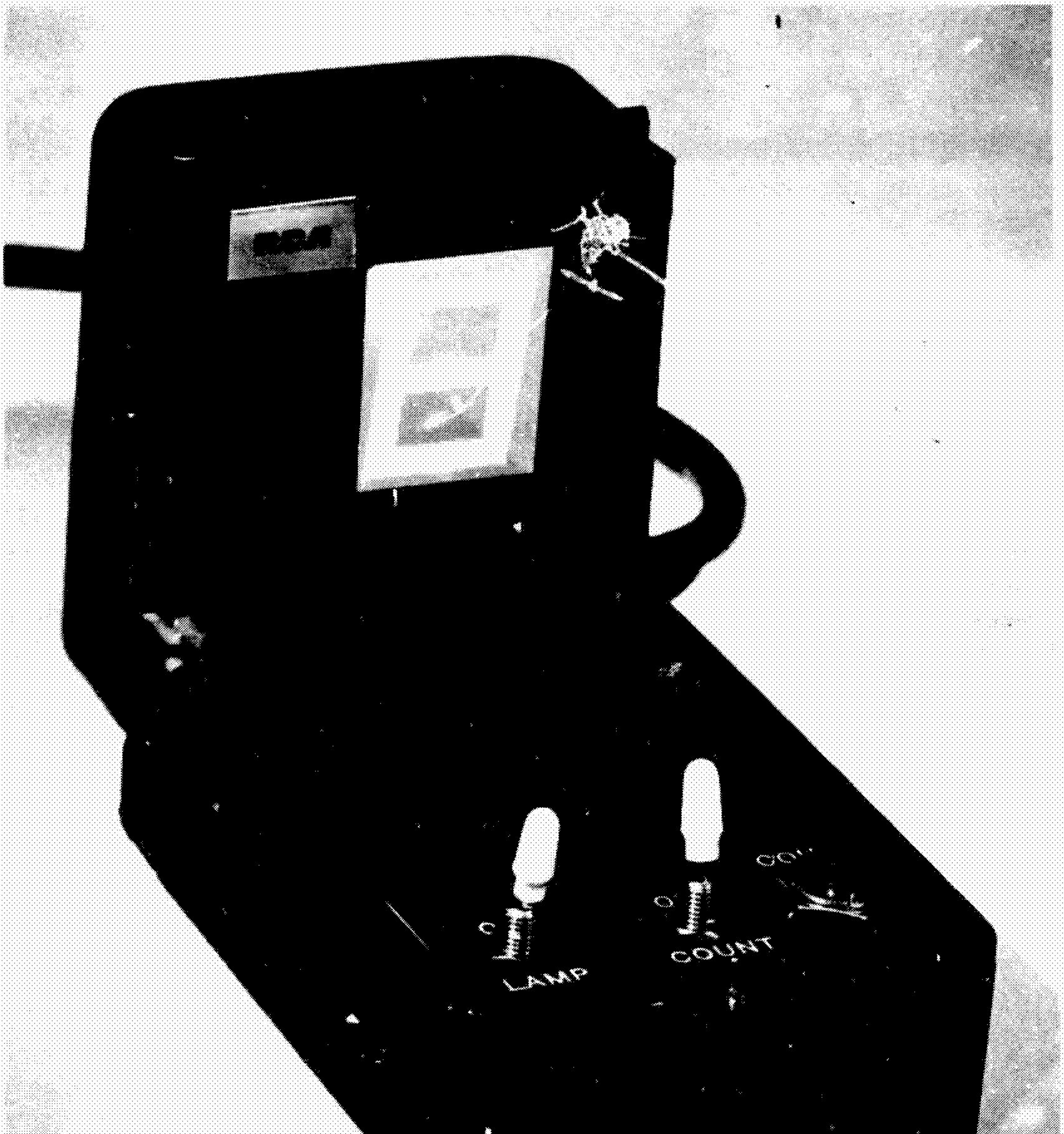


Figure 22. Numeric indicator with indophenol blue:PEBAB-RT electro-optic cell.

CONCLUSIONS

The development of electronically tuned optical filters using the interaction between pleochroic guest molecules and liquid crystalline (nematic) host materials has been achieved. The preparation of new nematic compounds has led to the discovery that mixtures of certain Schiff bases yield host materials which can be operated at room temperature. In addition, we have found that a variety of dyes could be used to produce a number of monochromic electro-optic cells. The use of two dyes in the same nematic host has allowed us to produce electro-optic cells with any desired shade of color. We have also demonstrated photochromism in liquid crystals.

The speed of response and decay of the monochromic electro-optic cells was found to be a function of the nematic host material with little or no effect of the dissolved dye. The response was of the order of 1 to 5 msec, while the relaxation time was 30 to 200 msec (depending on the temperature).

FUTURE PLANS

We plan to devote a considerable effort in the coming year to the development of a single unit which controls light over the entire visible region of the spectrum. We feel that this can be accomplished by utilizing layers of guest-host materials which exhibit the primary subtractive colors: cyan, magenta, and yellow.

Efforts to reduce the relaxation time of the guest-host systems will also be a major objective of our research. This will involve the use of both electrical and chemical techniques. In addition, experiments will be conducted in an effort to obtain a better understanding of the rise and decay phenomena.

NEW TECHNOLOGY

A. Title: Helium-Neon Laser Modulator

Page Reference: 47

Comments: A cell containing a 1% indophenol blue-PEBAB mixture was used successfully to modulate the beam of a 1 mW helium-neon laser.

B. Title: Numeric Indicator with Liquid Crystal Display

Page Reference: 48

Comments: An indophenol blue:PEBAB-RT mixture has been utilized in a device displaying the complete range of single digit numbers.

C. Title: Electronically Tuned Monochromic Filters

Page Reference: 21-27

Comments: An electro-optic cell prepared with 1% indophenol blue in PEBAB-RT can be used to control light of 6000-Å wavelength.

D. Title: Electronically Tuned Dichromic Filters

Page Reference: 32-35

Comments: An electro-optic cell prepared with a photochromic, pleochroic dye in PEBAB-RT can be used to electronically control light at 4700 Å and at 5200 Å.

E. Title: Electronically Tuned Polychromic Filters

Page Reference: 35-38

Comments: Electronic control of four primary colors using a single unit has been achieved.

APPENDIX

TABLE VI

PHASE TRANSITION TEMPERATURES FOR PFBAB - n COMPOUNDS

n	Transition Temperatures, °C		Nematic
	CN (crystal → nematic)	NL (nematic → liquid)	Range, °C
1	106	120	14
2	105	132	27
3	110	(98) monotropic	--
4	63	108	45
5	62	93	31
6	55	100	45
7	66.5	95	28.5
8	78	91.5	13.5

TABLE VII

PHASE TRANSITION TEMPERATURES FOR PEBAB - nO COMPOUNDS

n	Transition Temperatures, °C		Nematic
	CN (crystal → nematic)	NL (nematic → liquid)	Range, °C
2	158	Not mesomorphic	--
3	111	125	14
4	108	112	4
5	99	(96) monotropic	--
6	66	98	32
7	54	94	40
8	52	93	41

TABLE VIII

PHASE TRANSITION TEMPERATURES FOR ABAP COMPOUNDS

m	Transition Temperatures, °C CS*	SN**	NL	Nematic Range, °C
1	--	--	123 (not mesomorphic)	--
2	--	--	119 (115) monotropic	--
4	85	97	109	12
6	74	108	111	3
6	71	113	116	3

* crystal → smectic
** smectic → nematic

TABLE IX

PHASE TRANSITION TEMPERATURES FOR APAP COMPOUNDS

R'	Transition Temperatures, °C CN	NL	Remarks
CH_3CH_2	115	132	--
$CH_3CH_2CH_2$	101	(96)	monotropic
$CH_3CH_2CH_2CH_2$	87	105	--

TABLE X

PHASE TRANSITION TEMPERATURES FOR MIXTURES OF APAP COMPOUNDS

	$R' = C_2H_5 (A); C_3H_7 (B); C_4H_9 (C)$				
	Molar Composition			Transition Temperature, °C	
No.	%A	%B	%C	C-N	N-L
1	50	50	0	93-5°	114-115.5°
2	0	50	50	83-5°	102-102.5°
3	50	0	50	81°C	116.5-118°
4	33	33	33	80.5°	109-10°
5	10	15	75	7	106-7°
6	15	75	10	90°	100-101.5°
7	75	10	15	103°	122-5°
8	40	40	20	76°	112-3°
9	40	20	40	73°	113.5-114.5°
10	20	40	40	82°	108.5-111.5°
11	50	25	50	84°	116-17°
12	25	25	50	78°	110.5-111.5°
13	25	50	25	83°	107.5-109°

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