

Chapter 7

Experimental determination of
the flexoelectric coefficients
of some nematics

CHAPTER 7

EXPERIMENTAL DETERMINATION OF THE FLEXOELECTRIC COEFFICIENTS OF SOME NEMATIC LIQUID CRYSTALS

7.1 INTRODUCTION

In connection with our experimental studies on the electrohydrodynamic instabilities, we have measured the flexoelectric coefficients of two nematics. As described in chapter 3, splay and bend distortions of the director field can induce a flexoelectric polarization in a nematic, given by [1]

$$\vec{P} = e_1 \hat{n} (\text{div } \hat{n}) + e_3 \text{curl } \hat{n} \times \hat{n},$$

where e_1 and e_3 are the two flexoelectric coefficients corresponding to splay and bend, respectively. This flexoelectric polarization cannot be directly measured because of the screening of the polarization charges by the small traces of impurity ions present in the sample. Therefore, the flexoelectric coefficients are usually estimated by using the inverse effect, ie, by measuring the flexoelectric distortion of the director field induced by an external electric field. It should, however, be noted here that only a few measurements of these coefficients have been reported.

We have used the method of Dozov et al. [2] to measure $(e_1 - e_3)$. The sample geometry used is shown in Fig.1. The nematic is taken in a hybrid aligned cell with the director lying in the XZ plane. The anchoring at the two surfaces is assumed to be strong. The director field in such a cell (shown by the solid line in the figure) has a permanent splay-bend distortion, which gives rise to a flexoelectric polarisation \vec{P} along X, given by

$$\vec{P} = (e_1 - e_3) \hat{n} \operatorname{div} \hat{n}.$$

When an electric field \vec{E} is applied along Y, additional twist distortion is created in the medium due to the action of \vec{E} on \vec{P} . Since the dielectric free energy is second order in E, the influence of the dielectric anisotropy can be neglected as long as the field strength is small. Using the one elastic constant approximation, the equations describing the nematic are [2]:

$$K \left(\frac{d^2 \theta}{dZ^2} \right) - \sin \theta \cos \theta \left(\frac{d\phi}{dZ} \right)^2 + (e_1 - e_3) E \sin^2 \theta \cos \phi \left(\frac{d\phi}{dZ} \right) = 0 \quad (1)$$

$$\left(\frac{d}{dZ} \right) [K \sin^2 \theta \left(\frac{d\phi}{dZ} \right)] - (e_1 - e_3) E \cos \phi \sin^2 \theta \left(\frac{d\theta}{dZ} \right) = 0 \quad (2)$$

where K is the elastic constant and the angles θ and ϕ are

defined in Fig.1. From Eq.(2) we find that when ϕ is small, it is linear in E. Eq.(1) describes the change in the initial splay-bend distortion due to the field. This change is second order in E and can be neglected for low twist. Then from Eq.(1) we get

$$d^2\theta/dz^2 = 0 \quad \text{and hence} \quad \theta = \frac{1}{2} a Z/d.$$

Linearizing Eq.(2) in ϕ and using the above solution for θ , we get

$$d\phi/d\theta = [(e_1 - e_3) E d / (\pi K)] [\theta - \frac{1}{2} \sin 2\theta] \sin^{-2} \theta \quad (3)$$

The maximum value of ϕ occurs close to the plate with homeotropic alignment and on integrating Eq. (3) it is found to be [2]

$$\phi(o) = - (e_1 - e_3) E d / (\pi K) \quad (4)$$

$\phi(o)$ can be measured using the waveguide property of the twisted structure. If a light beam, which is linearly polarized along X, is sent in through the upper plate with homogeneous alignment, the polarization direction of the transmitted beam will be rotated by an angle $\phi(o)$. $(e_1 - e_3)/K$ can be obtained from the slope of the plot of $\phi(o)$ vs. E. The sign of $(e_1 - e_3)$ can be deduced from the direction of twist of the structure, for a given sign

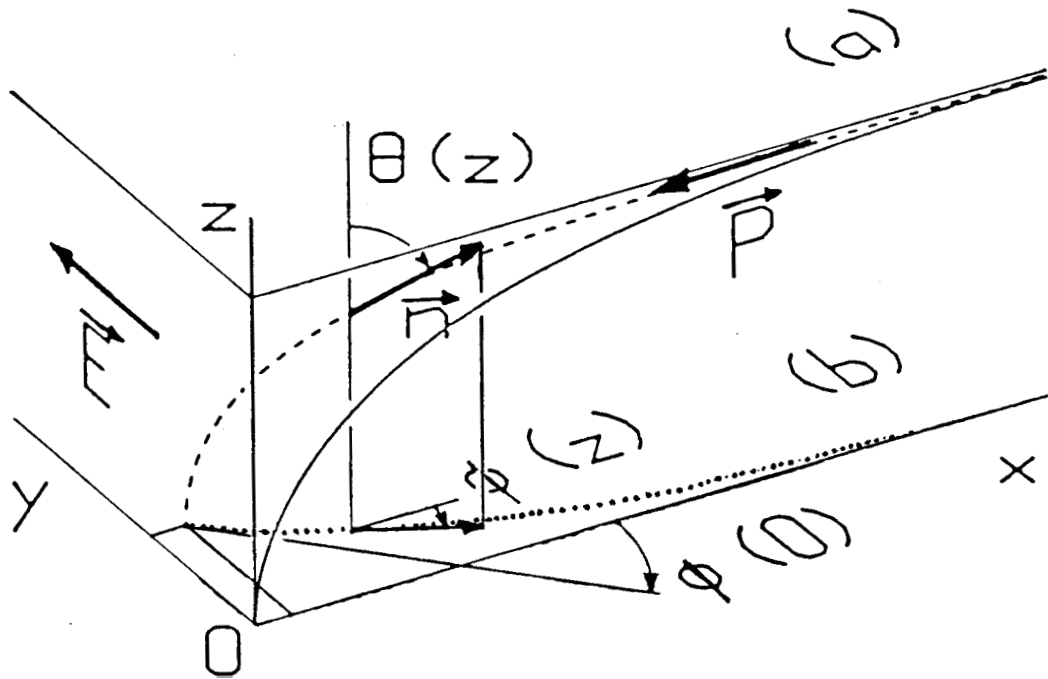


Fig.1. Sample geometry for the measurement of $(e_1 - e_3)$. The unperturbed director profile is in the xz plane (solid line). Under the action of \mathbf{E} it twists continuously along y (dashed line). The twist $\Phi(z)$ is visible on the xy projection of the director profile (dotted line). (from Ref.2).

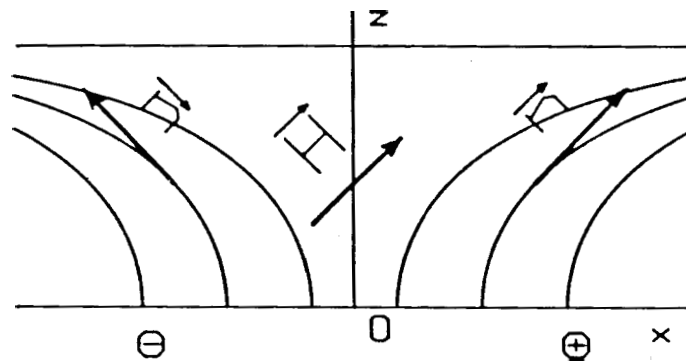


Fig.2. The twin domains of splay-bend in a hybrid cell. Under the action of the magnetic field \mathbf{H} , the (+) domain grows at the expense of the (-) domain. (from Ref.2).

of the applied field.

It should be noted here that two types of domains are possible in a hybrid aligned cell, as shown in Fig.2. The flexoelectric polarization \vec{P} in these two domains are in opposite directions. Hence they twist in opposite directions when the field is applied. A monodomain sample can be obtained by applying a strong magnetic field in an oblique direction or by cooling the sample from the isotropic phase in the presence of a relatively weak oblique magnetic field.

The sum ($e_1 + e_3$) of the flexoelectric coefficients of some nematics have been measured [3,4,5] by studying the director distortion induced in a sample by the gradient of an external electric field or by using a hybrid aligned cell with weak anchoring at one of the surfaces [6]. In Refs. 3 and 4 interdigitated electrodes were used to produce the field gradients and in Ref.5 the gradient was created using a quadrupolar arrangement of electrodes. We have used a simpler set up, where the field gradient is produced by using a wedge shaped cell. The nematic is aligned homeotropically with strong anchoring at the two plates. The field gradient that can be produced in this geometry is relatively small. Therefore, the dielectric

anisotropy of the material under study must be quite small, so as to reduce the direct dielectric coupling to the applied field. Neglecting the dielectric anisotropy the flexoelectric distortion of the director field can be estimated by equating the elastic and flexoelectric torques.

A schematic diagram of the experimental set up is shown in Fig.3. The initial bend distortion of the director is very small since the wedge angle is $\sim 1^\circ$. On applying an electric field between the two glass plates, we assume a small distortion of the director so that $\hat{n} = 0 \quad 1$. The resulting flexoelectric polarization along X and Z are:

$$P_x = (e_1 + e_3) \theta \left(\frac{\partial \theta}{\partial X} \right) + e_3 \left(\frac{\partial \theta}{\partial Z} \right)$$

$$P_z = - (e_1 + e_3) \theta \left(\frac{\partial \theta}{\partial Z} \right) + e_1 \left(\frac{\partial \theta}{\partial X} \right)$$

Minimizing the flexoelectric free energy density, $f^{fl} = - \vec{P} \cdot \vec{E}$, and keeping the lowest order terms, the flexoelectric torque is found to be

$$\Gamma^{fl} = e_3 \left(\frac{\partial E_x}{\partial Z} \right) + e_1 \left(\frac{\partial E_z}{\partial X} \right)$$

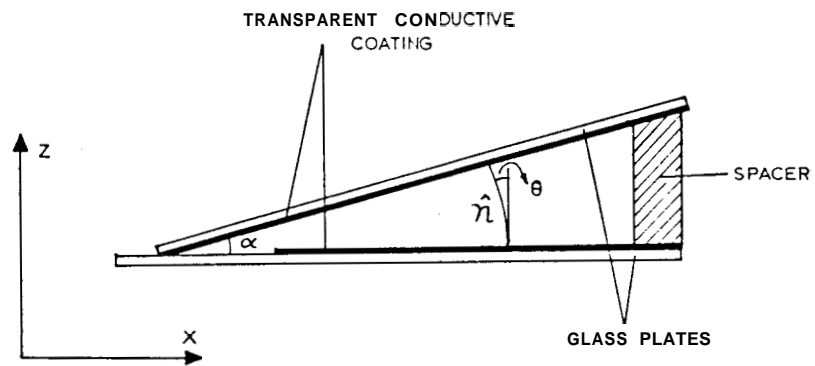


Fig.3. Schematic diagram of the experimental set up used to measure $(e_1 + e_r)$.

From the Maxwell relation, $\text{curl } \vec{E} = 0$, we get

$$(\partial E_x / \partial Z) = (\partial E_z / \partial X)$$

Using this in the above relation, the flexoelectric torque is obtained as

$$\Gamma^{fl} = (e_1 + e_3) (\partial E_z / \partial X) \quad (5)$$

In the one elastic constant approximation the elastic free energy density is

$$f^d = \frac{1}{2} K (\partial \theta / \partial Z)^2$$

Therefore the elastic torque is given by

$$\Gamma^d = -K (\partial^2 \theta / \partial Z^2) \quad (6)$$

Equating the two torques given by Eqs. (5) and (6), we get the following relation

$$(e_1 + e_3) (\partial E_z / \partial X) = K (\partial^2 \theta / \partial Z^2) \quad (7)$$

The boundary conditions on θ are:

$$e(Z = 0) = 0 \quad \text{and} \quad \theta(Z = d) = a.$$

where α is the wedge angle. Using these conditions, Eq.(7) can be solved to get

$$\theta(Z) = [(e_1 + e_3) V \alpha / (2 K)] [Z/d - (Z/d)^2] + \alpha Z/d \quad (8)$$

where V is the applied voltage.

θ can be obtained from the **tilt** of the conoscopic pattern observed between crossed polarizers. For small θ the conoscopic pattern can be expected to rotate by an angle $n_o \bar{\theta}$, where n_o is the ordinary index of refraction and $\bar{\theta}$ is the average **tilt** angle in the sample, given by

$$\bar{\theta} = (1/d) \int_0^d \theta(Z) dZ = (\alpha/2) [1 + (e_1 + e_3) V / (6K)] \quad (9)$$

The sign of $(e_1 + e_3)$ is obtained from the direction of **tilt** of the conoscopic pattern, for a given sign of the applied field. The first term on the right hand side of Eq.(9) gives the **tilt** of the conoscopic figure due to the initial bend distortion of the director and the second term gives the additional **tilt** due to the **flexoelectric** distortion. Since the latter depends on the sign of the applied voltage, when the field is reversed the pattern should shift in the opposite direction. Hence by measuring the shift of the conoscopic pattern for both signs of the

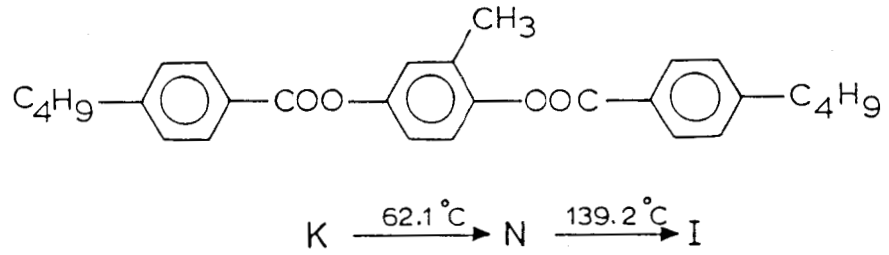
applied field, the shift due to the initial bend distortion of the director can be eliminated and $(e_1 + e_3)$ can be estimated.

7.2 EXPERIMENTAL

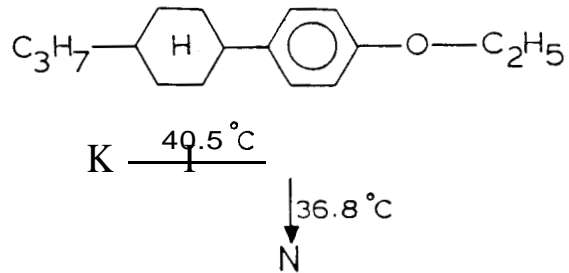
We have measured $(e_1 - e_3)$ and $(e_1 + e_3)$ of a room temperature nematic containing 48 mole % (2-methylphenyl)-bis 4-n-butylbenzoate (RO-CE 1700) and 52 mole % 1-n-propyl-4[4-n-ethoxyphenyl]-cyclohexane (PCH 302), which was used in our studies on the EHD instabilities. For the measurement of $(e_1 + e_3)$, 4% of 4'-n-pentyl-4-cyanobiphenyl (5CB) was added to the above mixture to make the dielectric anisotropy approximately zero. It should be noted here that the addition of 5CB did not lead to any qualitative changes in the domain pattern observed at the threshold of the EHD instability. We have also measured $(e_1 - e_3)$ of a pure compound, viz, 4-pentylphenyl-trans-4-pentylcyclohexylcarboxylate (S 1497), at 40° C in the nematic phase. RO-CE 1700, PCH 302 and 5CB were obtained from Hoffman La Roche and S 1497 from Merck. The structural formulae and the transition temperatures of these compounds are given in Fig.4.

Homogeneous alignment was obtained by vacuum deposition of SiO₂ on the glass plates at an oblique angle.

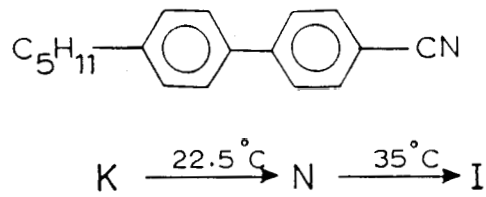
RO - CE 1700



PCH 302



5 CB



S 1497

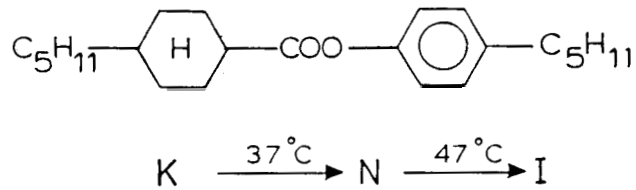


Fig.?. Structural formulae and the transition temperatures of the compounds studied.

Homeotropic alignment was produced by coating the glass plates with octyldecyl triethoxy silane (see chapter 1, section 4). The transverse electric field required for the $(e_1 - e_3)$ measurement was applied between two phosphor-bronze wires, which also served as spacers. The diameter of the wire was 25 μm . All the optical measurements were made using a Leitz Ortholux II POL - BK polarizing microscope. A Mettler hot stage (FP52) was used to control the temperature of the sample.

7.3 RESULTS AND DISCUSSION

The dependence of the angle of rotation of the polarization direction, $\phi(o)$ (see Eq.4), with the applied voltage, observed in the RO-CE 1700 - PCH 302 mixture at room temperature, is shown in Fig.5. Note that $\phi(o)$ varies linearly with the applied voltage and changes sign when V is reversed, confirming the flexoelectric origin of the distortion. $(e_1 - e_3)$ is obtained from the slope of the straight line fit, using Eq.4. $(e_1 - e_3)/K$ is found to be 100 cgs units. Assuming $K = 10^{-6}$ dyne, we get $(e_1 - e_3) = 1.0 \times 10^{-4}$ cgs units. Note that this is equal to the MBBA value [2] and is of the same sign.

The variation of $\phi(o)$ with the applied voltage, observed in S 1497 at 40' C is shown in Fig.6. From the

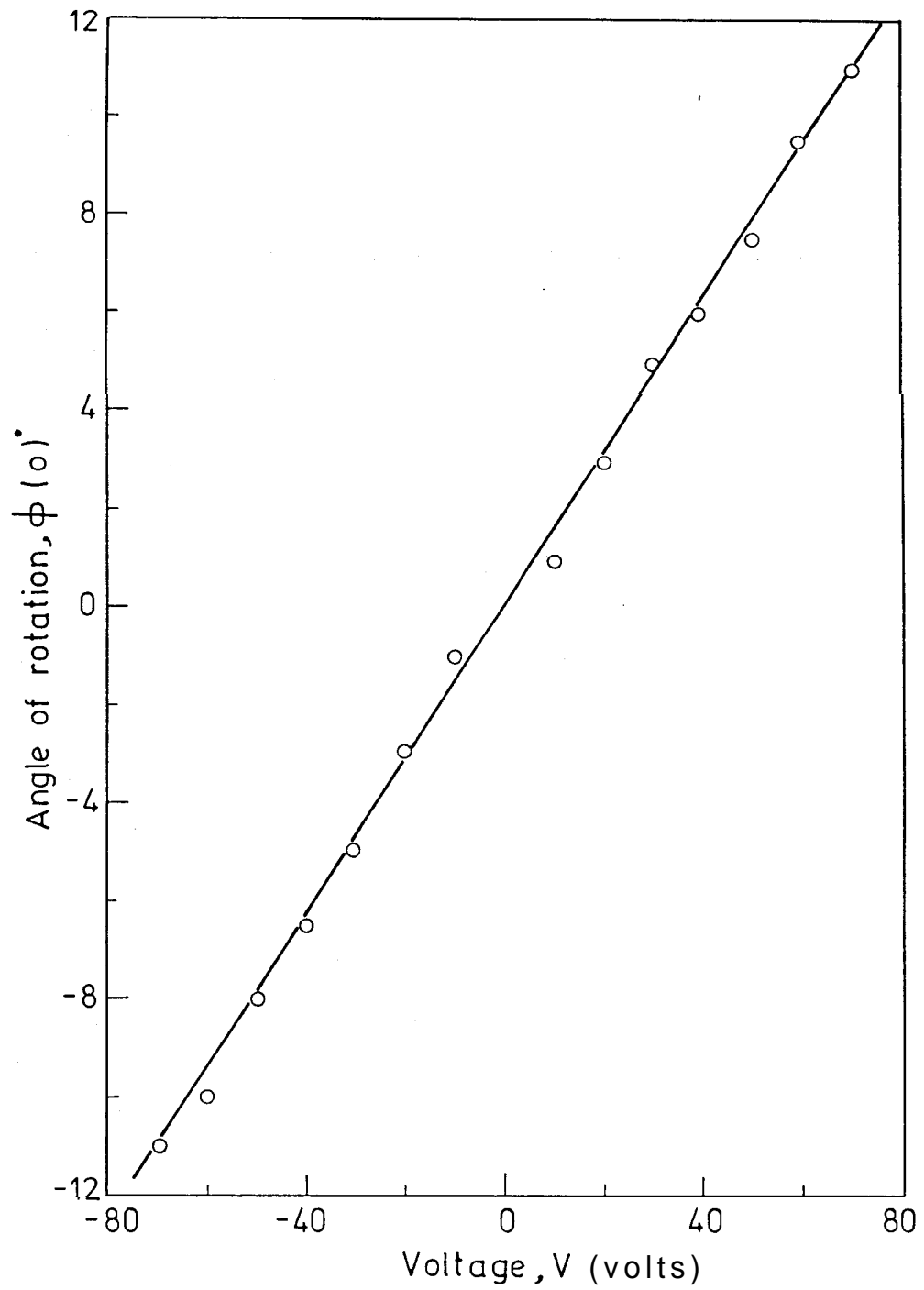


Fig.5. Variation of the angle of rotation of the plane of polarization with the applied voltage, observed in the RO-CE 1700 - PCH 302 mixture at room temperature.

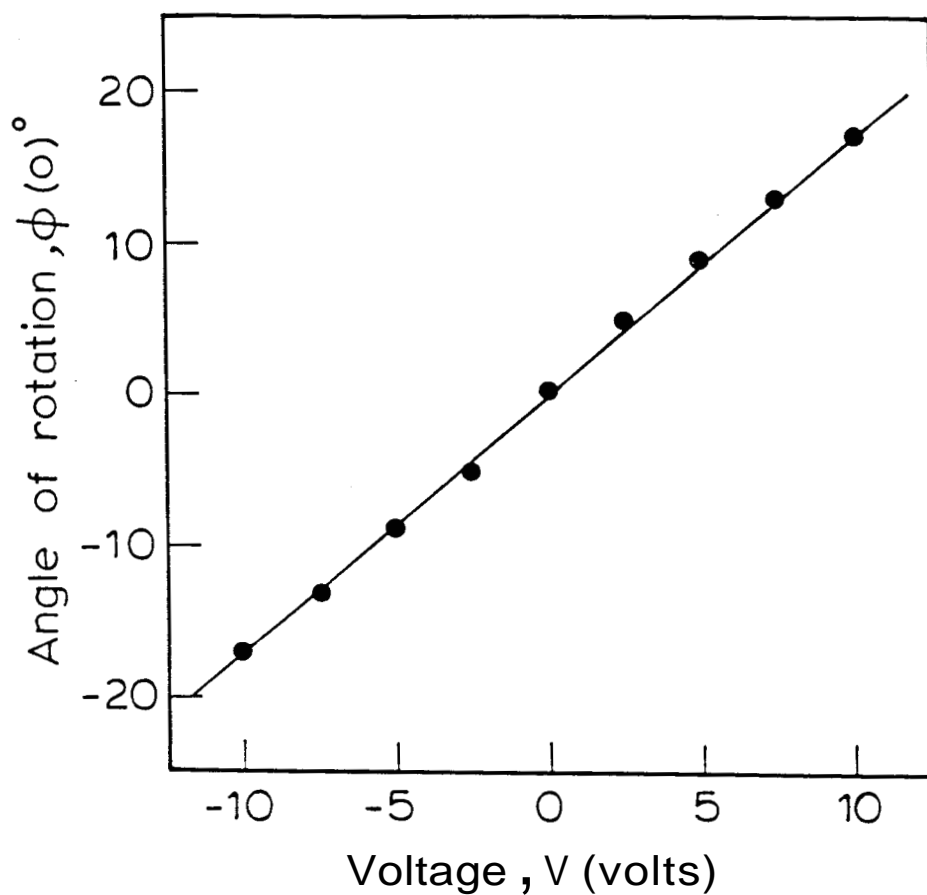


Fig.6. Variation of the angle of rotation of the plane of polarization with the applied voltage, observed in S 1497 at 40 $^\circ$ C.

slope of the plot we get $(e_1 - e_3)/K$ to be 940 cgs units. The relatively large value of $(e_1 - e_3)$ of this compound may, result from the transverse component of the ester dipole moment.

As described in the introduction, the combination $(e_1 + e_3)$ of the RO-CE 1700 - PCH 302 mixture at room temperature was estimated by measuring the shift of the conoscopic pattern on applying the electric field. The pattern was found to shift along X when the field was applied. On reversing the field the pattern shifted in the opposite direction, confirming that the director distortion is due to the flexoelectric effect. For an applied voltage of 5 Volts, the observed shift of the pattern corresponds to $\bar{\theta} = 0.25'$. Then from Eq.(8) we get $(e_1 + e_3)/K = -180$ cgs units. Taking $K = 1.0 \times 10^{-6}$ dynes, we get $(e_1 + e_3) = -1.8 \times 10^{-4}$ cgs units. Note that this value is comparable to the MBBA value of -7.0×10^{-4} cgs units [6] and is of the same sign.

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