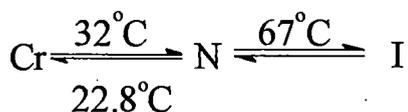
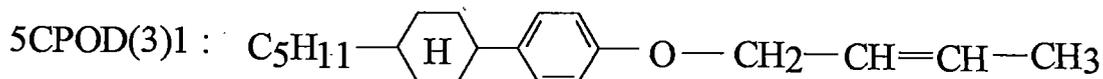
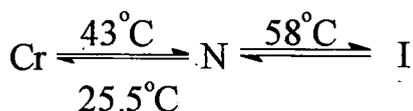
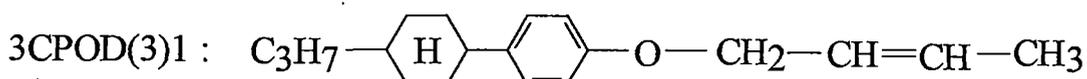


## **Chapter - 8**

### **SPLAY AND BEND ELASTIC CONSTANTS OF TWO NEMATOGENS**

## 8.1 INTRODUCTION

Numerous experiments in nematic liquid crystals based on field induced Fréedericksz transition have been performed in last thirty years keeping in mind that liquid crystal display devices depends among other things on its elastic properties. To formulate liquid crystals to meet device requirements it is desirable to understand the factors which determines the elastic constants. New types of non-polar as well as weakly polar nematic liquid crystals with alkenyl side chains have been prepared by Schadt et al<sup>[182-184]</sup>. The compounds have low optical anisotropy, low viscosity but high elastic constants and thus be used in display devices with short response times. With this view in mind I have undertaken this measurements of elastic constants of two alkenyl compounds namely, 3E-n-butane-phenyl- (4-cyclohexane-4'-n-propane) -ether (3CPOD(3)1 in short) and 3E - n - butane - phenyl - (4-cyclohexane-4'-n-pentane) -ether (5CPOD(3)1 in short). The structural formulae and the corresponding transition temperatures (°C) are given below:



Study of different physical properties of these two compounds had been undertaken by different workers in our laboratory. Using x-ray diffraction techniques, order parameters  $\langle P_2 \rangle$ ,  $\langle P_4 \rangle$  and other physical parameters have been determined by A.

Nath et al<sup>[185,186]</sup>. They have also measured density, refractive indices and  $\langle P_2 \rangle$  from optical birefringence study. N. K. Pradhan et al determined diamagnetic susceptibility anisotropy<sup>[133]</sup>. Elastic constants of the compound 3CPOD(3)1 has also been measured by Schadt<sup>[184,187,188]</sup>. This compound has negative dielectric anisotropy as has been reported by them. Samples of negative dielectric anisotropy are useful for positive contrast guest host displays and also for electric field controlled birefringence displays<sup>[189]</sup>.

## 8.2 ELASTIC CONSTANTS AND DISTORTION FREE ENERGY OF NEMATIC LIQUID CRYSTALS

The elastic properties of a liquid crystal are generated due to restoring torques which become apparent when the system is perturbed from its equilibrium position by some external stimuli like magnetic or electric field for instance. The director pattern is no longer uniform in space, but curved. If  $\mathbf{n}(\mathbf{r})$  changes noticeably only over large distances compared with the molecular dimensions, these curvatures can be described in terms of a continuum theory which disregards the details of the structure on a molecular scale. Based upon this point of view Zocher<sup>[190,191]</sup> and Oseen<sup>[192]</sup> initiated a phenomenological theory which was further developed by Frank<sup>[193]</sup>. This theory is in fact analogue to the continuum theory of elasticity of solids. According to the continuum theory of liquid crystals, the elastic part of the internal energy density of a perturbed liquid crystal is given by the equation

$$F_d = \frac{1}{2} \left[ k_{11} (\nabla \cdot \mathbf{n})^2 + k_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + k_{33} (\mathbf{n} \times \nabla \times \mathbf{n})^2 \right] \quad 8.1$$

The coefficients  $k_{11}$ ,  $k_{22}$  and  $k_{33}$  in this expression, the so called elastic constants are associated with the three basic types of distortions, viz., splay, twist and bend. The above equation is fundamental formula for the continuum theory of nematics. It is possible to generate deformations that are pure splay, pure twist or pure bend. Thus each constants should be positive, if not, the undistorted nematic conformation would not correspond to a minimum of the free energy  $F_d$ .

### 8.3 FRÉEDERICKSZ TRANSITION

The term Fréedericksz transition refers to the deformation of a thin layer of nematic liquid crystal with a uniform director field, in an external electric<sup>[194-196]</sup> or magnetic<sup>[197-203]</sup> field. It was first observed by Fréedericksz that such a layer would undergo an abrupt change in its optical properties when the strength of an external magnetic field, applied normal to the director, exceeded a well defined threshold value, known as the critical field. If the nematic liquid crystals have positive diamagnetic anisotropy or dielectric anisotropy, then as the field exceeds the critical value, the director starts to align along the external field. Depending on various geometrical arrangements one can determine splay, twist and bend elastic constants as shown in the Fig. - 8.1.

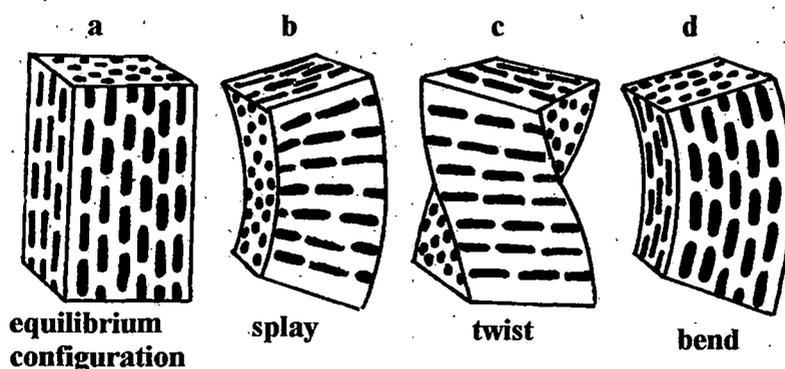


Fig. 8.1. a) An ordered liquid crystal in equilibrium configuration.  
The deformation states — b) splay, c) twist and d) bend

Fréedericksz transitions can be used to measure directly the elastic constants, provided the geometry i.e., the boundary conditions and the direction of the applied field are chosen in the appropriate way. Attention is to be paid to the calculation of the threshold values belonging to different geometries. From the geometry of arrangement as shown in the Fig.-8.2 we can determine splay, twist or bend elastic

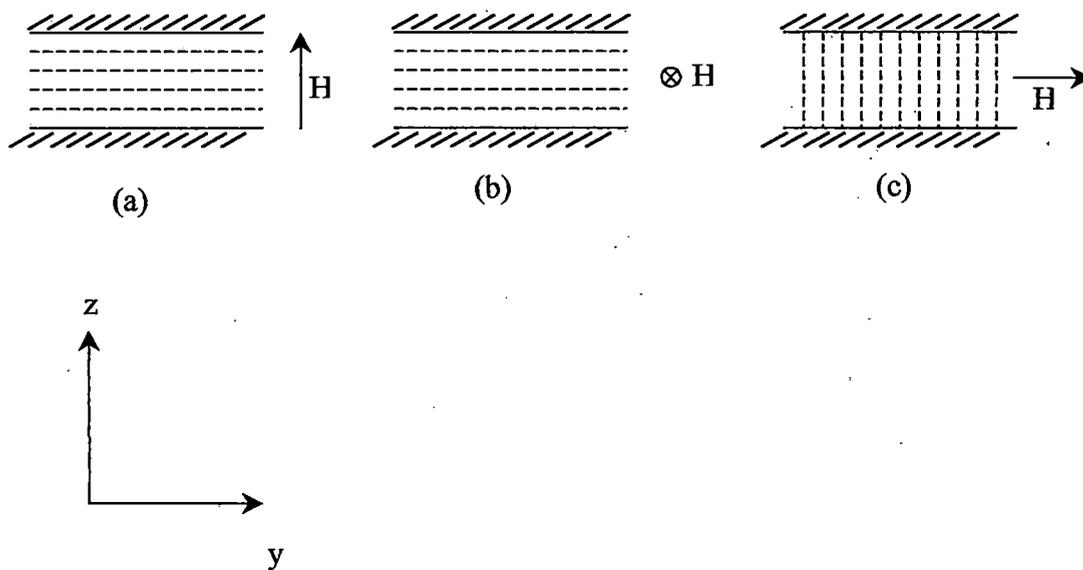


Fig. 8.2 Schematic experimental set-up for the determination of elastic constants from Fréedericksz transition: a) splay, b) twist and c) bend

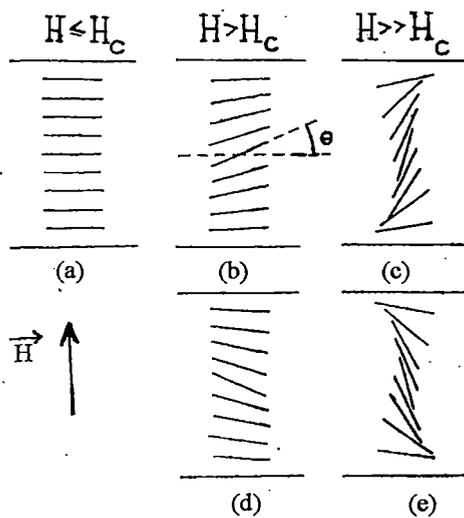


Fig. 8.3 Deformation of the director pattern above the threshold field in the splay mode

constants in the magnetic field  $H$ . The critical magnetic field for Fréedericksz transition is

$$(H_c)_i = \left( \frac{k_{ii}}{\Delta\chi} \right)^{1/2} \frac{\pi}{d} \quad 8.2$$

where  $d$  is the sample thickness,  $\Delta\chi$  is the diamagnetic anisotropy, the subscript  $i = 1, 2, 3$  refers to splay, twist and bend deformation respectively. In splay mode, for a magnetic field  $H > H_c$ , applied along  $Z$  direction, the uniform planar structure (Fig.- 8.3a) is unstable and the system jumps into one of the two possible states Fig. - 8.3b or 8.3d. If the field is increased further these states develop into Fig. - 8.3c and 8.3e respectively. In my calculation  $\Delta\chi$  values have been taken from N. K. Pradhan's work<sup>[133]</sup>.

#### 8.4 EXPERIMENTAL TECHNIQUE AND SET-UP FOR DETERMINATION OF $K_{11}$ AND $K_{33}$

The apparatus for the determination of the elastic constants ( $k_{11}$  and  $k_{33}$ ) has been designed and fabricated in our laboratory by Das and Paul<sup>[204]</sup>. The block diagram of the set-up has been shown in Fig.-8.4. Details of the cell preparation

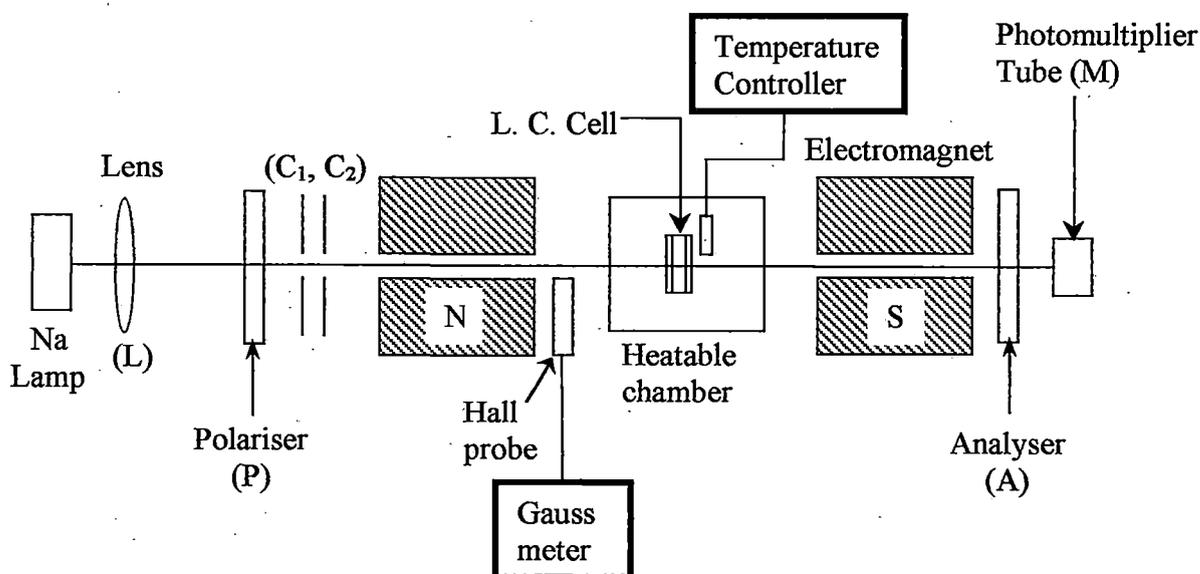


Fig. 8.4 Block diagram of experimental set-up for measuring elastic constants by Fréedericksz transition

technique has been given by de Jeu<sup>[205]</sup>. The splay elastic constant was measured by using homogeneous planar aligned cell where inner side of both the glass plates were treated by  $\sim 1\%$  PVA solution, dried and gently rubbed the layer in one direction by bond paper. For bend elastic constant measurement, homeotropic aligned cell was taken. In this case inner sides of the cell were treated by lecithin. Filled in cell with the sample was placed inside a thermostated block. Sample thickness was measured with the help of screw gauge. Temperature was measured and controlled within an accuracy of  $\pm 0.5$  °C by means of a copper-constantan thermocouple inserted in the brass block and temperature controller (Indotherm Model 457). A sodium D light was used as a source which was allowed to incident on the sample through a lens (L), polariser (P) and collimating circular slits ( $C_1$ ,  $C_2$ ). The polariser (P) and the analyser (A) (i.e., a combination of quarter wave ( $\lambda/4$ ) plate and a linear polariser) were crossed at  $\pm 45^\circ$  relative to the vertical axis for better sensitivity. The transmitted light was monitored by photomultiplier tube (M) which counts photon and corresponding current was measured by a nano-ammeter. Applied magnetic field was set always perpendicular to the aligned sample and during experiment it was changed slowly so that the nematic orientation remains in equilibrium with the applied magnetic field. To ensure this exact alignment, the brass block was mounted on a specially constructed platform whose alignment with respect to the field could be adjusted to an accuracy of 1-2' of arc. Further, the platform itself rested on levelling screw so that the alignment of the sample could be varied in every possible manner. For a desired temperature, when field (H) exceeded critical value ( $H_c$ ), an abrupt change in current corresponding to abrupt change in optical properties took place. We could measure  $H_c$  from field H versus intensity curve within an accuracy of  $\pm 10$  Gauss. The magnetic field was measured using a Hall-probe Gaussmeter (Model DGM-102).

If the field was increased gradually beyond its critical value, the transmitted light intensity exhibits oscillations due to the change of phase relation.

In our present set-up it is not possible to measure  $k_{22}$  till now. The threshold value for twist deformation cannot be detected optically when viewed along the twist axis. Due to the large birefringence of the medium for this direction of

propagation, the state of polarisation of the transmitted beam is indistinguishable from that of the emerging beam from the untwist nematics. A total internal reflection technique can be used to measure the  $k_{22}$  values of the twist deformation.

Both the chemicals were donated by Hoffmann La-Roche, Switzerland. I have used these samples without further purification. Transition temperatures of the pure compounds were determined with the help of Mettler Fp 80/82 thermo system by observing the texture under polarising microscope.

## 8.5 RESULTS AND DISCUSSIONS

Elongation of the molecular shape is a vital factor for elastic curvature. It can occur in two ways — by elongation of rigid core of structurally similar thermotropic liquid crystals (TLC) or by elongation of alkyl chain part. It is well known that elastic constants of the molecules with flexible chain part is something special due to the contribution of chain part to the elasticity of the molecule. In previous experimental works<sup>[201,203]</sup>  $k_{33}/k_{11}$  has been found to increase when rigid core of structurally similar TLCs is elongated. But for homologous samples where elongation of the molecules take place due to increase in chain length,  $k_{33}/k_{11}$  has been observed to decrease with the increase of alkyl chain length<sup>[199,206-212]</sup>.

The temperature variations of both the elastic constants are shown in Fig. - 8.5 – 8.6 for the compounds. It is found that both  $k_{11}$  and  $k_{33}$  decrease with increasing temperature (Table 8.1 – 8.4) which is in agreement with other reported values. The ratio  $k_{33}/k_{11}$  is also found to decrease with increasing temperature as shown in Fig. - 8.7 and Table 8.5 – 8.6. It is noted that  $k_{33}$  is larger than  $k_{11}$  for both the samples over the entire range. This is consistent with the observation of previous workers<sup>[201,208,211,212]</sup>. It is also noted that  $k_{33}/k_{11}$  is larger in 3CPOD(3)1 than in 5CPOD(3)1 in accordance with previous observation that the ratio decrease with increasing chain lengths in a homologous series. In addition I observe that temperature variation of  $k_{33}/k_{11}$  for 5CPOD(3)1 is much smaller than that for 3CPOD(3)1.

Theoretical calculations for rigid rods<sup>[213]</sup> based on spherocylindrical model, predicts that  $k_{33}/k_{11}$  should decrease if the molecular aspect ratio  $R = (L-W)/W$

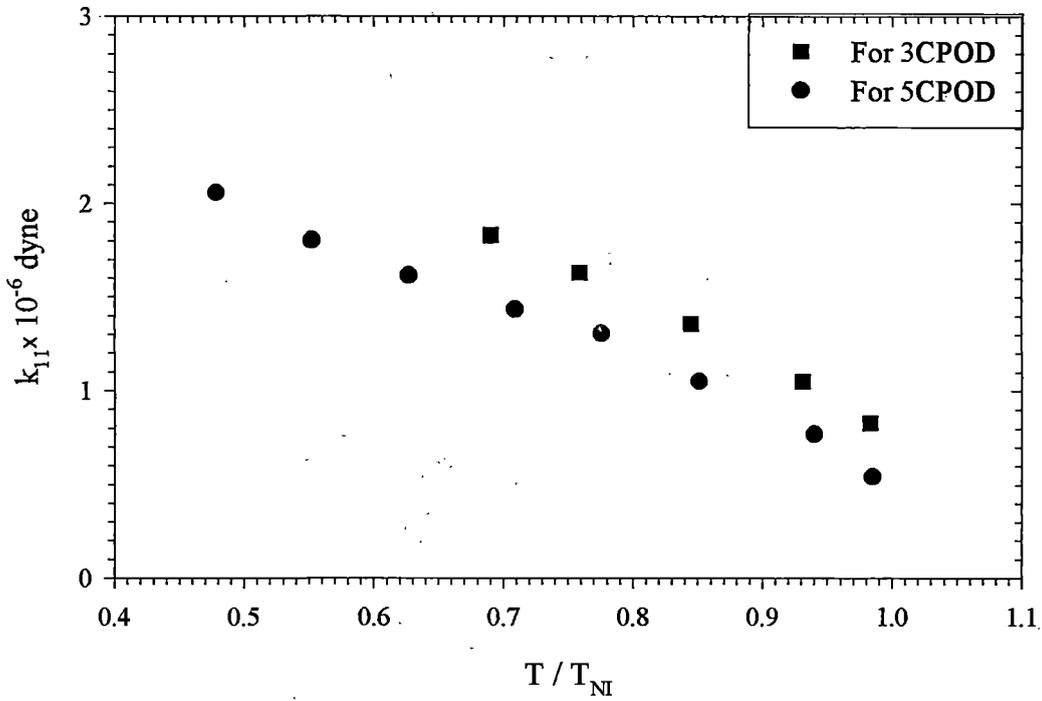


Fig. 8.5 Variation of splay elastic constant ( $k_{11}$ ) with temperature

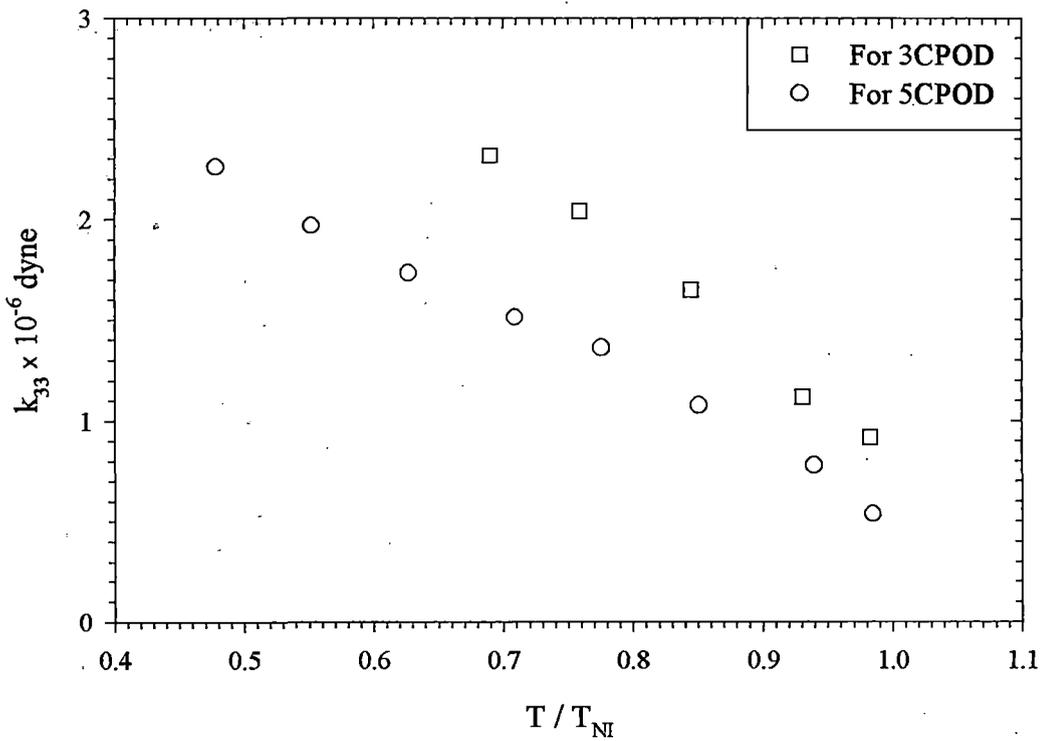


Fig. 8.6 Variation of bend elastic constant ( $k_{33}$ ) with temperature

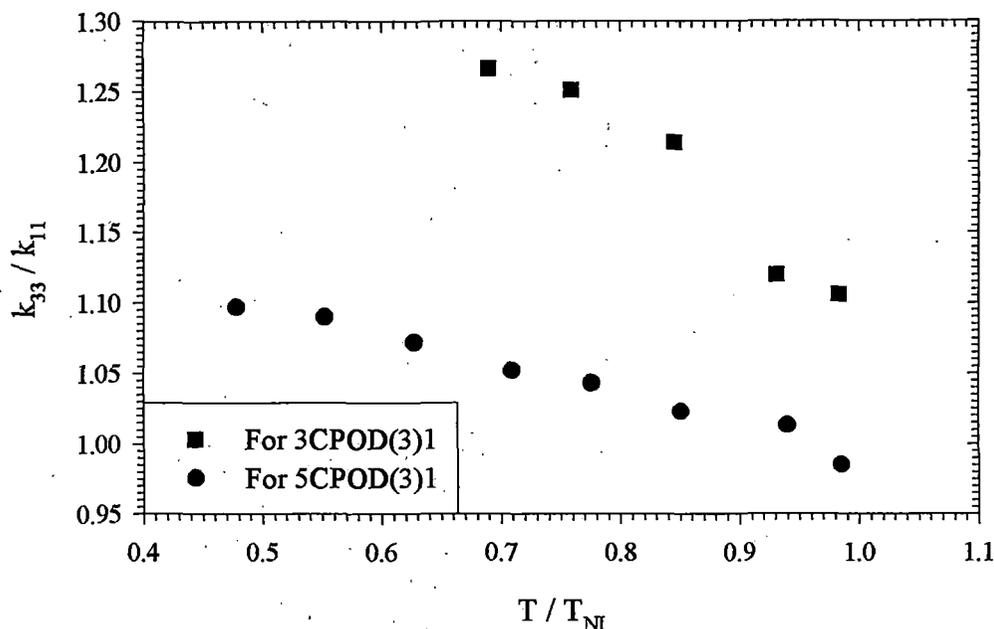


Fig. 8.7 Variation of  $k_{33}/k_{11}$  with temperature for sample 3CPOD(3)1 and 5CPOD(3)1

decreases where  $L$  and  $W$  represent the molecular length and width respectively. Though Leenhouts' previous work<sup>[201]</sup> supports this but later<sup>[203]</sup> his experimental results contradict it. Generally the width of the molecule is taken to be the nearly same as the width of the rigid core ( $\cong 4.83 \text{ \AA}$ ) if the chain has five or less carbon atoms in it<sup>[203]</sup>. Apparent molecular length of two molecules 3CPOD(3)1 and 5CPOD(3)1 are  $16.8 \text{ \AA}$  and  $19.1 \text{ \AA}$  respectively. So according to the theory in my case  $k_{33}/k_{11}$  should decrease with decrease in  $R$  which is in contradiction to the experimental result.

Thus it is concluded that calculations based on spherocylindrical model is not so useful for explanation of experimental results. It is better to consider the suggestion proposed by de Jeu et al<sup>[208]</sup> and Karat et al<sup>[199]</sup> that the lengthening of the alkyl chain leads to an increase of the positional correlation in a plane perpendicular to the director and is the cause for decreasing the ratio of  $k_{33}/k_{11}$ .

**Table - 8.1**

**Experimental values of splay elastic constant (  $k_{11}$  ) for different values of temperature  $T / T_{NI}$  for sample 3CPOD(3)1**

$T_{NI} = 58.0^\circ\text{C}$ , Sample thickness = 162  $\mu\text{m}$

$T / T_{NI}$	$H_c$ in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit*	$k_{11} \times 10^{-6}$ dyne
0.983	770	5.255	0.8293
0.931	830	5.731	1.0508
0.845	880	6.595	1.3594
0.759	930	7.086	1.6313
0.690	960	7.465	1.8312

\*data have been taken from reference [133].

**Table - 8.2**

**Experimental values of splay elastic constant (  $k_{33}$  ) for different values of temperature  $T / T_{NI}$  for sample 3CPOD(3)1**

$T_{NI} = 58.0^\circ\text{C}$ , Sample thickness = 162  $\mu\text{m}$

$T / T_{NI}$	$H_c$ in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$k_{33} \times 10^{-6}$ dyne
0.983	810	5.255	0.918
0.931	880	5.731	1.180
0.845	970	6.595	1.650
0.759	1040	7.086	2.040
0.690	1080	7.465	2.318

**Table - 8.3**

**Experimental values of splay elastic constant (  $k_{11}$  ) for different values of temperature  $T / T_{NI}$  for sample 5CPOD(3)1**

$T_{NI} = 67.0^\circ \text{C}$  , Sample thickness = 162  $\mu\text{m}$

$T / T_{NI}$	$H_c$ in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$k_{11} \times 10^{-6}$ dyne
0.985	690	4.2965	0.544
0.940	790	4.6355	0.770
0.851	870	5.2266	1.053
0.776	940	5.5538	1.306
0.709	965	5.7965	1.437
0.627	995	6.1370	1.617
0.552	1025	6.4600	1.806
0.478	1060	6.8960	2.060

**Table - 8.4**

**Experimental values of splay elastic constant (  $k_{33}$  ) for different values of temperature  $T / T_{NI}$  for sample 5CPOD(3)1**

$T_{NI} = 67.0^\circ \text{C}$  , Sample thickness = 162  $\mu\text{m}$

$T / T_{NI}$	$H_c$ in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$k_{33} \times 10^{-6}$ dyne
0.985	685	4.2965	0.537
0.940	795	4.6355	0.780
0.851	880	5.2266	1.077
0.776	960	5.5538	1.362
0.709	990	5.7965	1.512
0.627	1030	6.1370	1.733
0.552	1070	6.4600	1.969
0.478	1110	6.8960	2.260

**Table - 8.5**

**Ratio of bend to splay (  $k_{33} / k_{11}$  ) elastic constants of sample 3CPOD(3)1 for various  $T / T_{NI}$  values.**

$T / T_{NI}$	$k_{11} \times 10^{-6}$ dyne	$k_{33} \times 10^{-6}$ dyne	$k_{33} / k_{11}$
0.983	0.8293	0.918	1.106
0.931	1.0508	1.180	1.120
0.845	1.3594	1.650	1.214
0.759	1.6313	2.040	1.251
0.690	1.8312	2.318	1.266

**Table - 8.6**

**Ratio of bend to splay (  $k_{33} / k_{11}$  ) elastic constants of sample 5CPOD(3)1 for various  $T / T_{NI}$  values.**

$T / T_{NI}$	$k_{11} \times 10^{-6}$ dyne	$k_{33} \times 10^{-6}$ dyne	$k_{33} / k_{11}$
0.985	0.544	0.537	0.985
0.940	0.770	0.780	1.013
0.851	1.053	1.077	1.023
0.776	1.306	1.362	1.043
0.709	1.437	1.512	1.052
0.627	1.617	1.733	1.072
0.552	1.806	1.969	1.090
0.478	2.060	2.260	1.097