Experimental Investigations on Physical Properties of Some Novel Liquid Crystals with Banana-shaped and Rod-like Molecules

By

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for the degree of Doctor of Philosophy

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Declaration:

I hereby declare that the work reported in this thesis is entirely original. This thesis is composed independently by me at Raman Research Institute under the supervision of Dr. R. Pratibha. I further declare that the subject matter presented in this thesis has not previously formed the basis for the award of any degree, diploma, membership, associateship, fellowship or any other similar title of any university or institution.

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Certificate:

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Preface

This thesis reports some experimental investigations on physical properties of novel liquid crystals made of (i) banana-shaped and rod-like molecules and (ii) dimers made of rod-like molecules. Most of these studies have been made in the nematic phase.

Chapter 1 : We have given a general introduction to the topics which are relevant to the discussions in the later chapters.

Chapter 2 : We have described the experimental setup used in measuring (i) optical phase difference, (ii) dielectric constants $\epsilon_\perp$ and $\epsilon_\parallel$, and (iii) splay and bend elastic constants as functions of temperature, using a *single sample cell*. This is possible if the nematic liquid crystal has positive dielectric anisotropy, which is the case for all the materials studied in this thesis. In the electro-optical setup, the transmitted and reference intensities are measured using a dual frequency chopper along with a *dual-channel* lock-in amplifier using a *single* photo diode. The ratio of transmitted to reference intensity is taken to get rid of the intensity fluctuation of He-Ne laser. Another lock-in amplifier is used for the impedance analysis of the cell. All the instruments *ie.,* heater and two lock-in amplifiers are simultaneously *interfaced* with a computer. The heater is programmed following a proportional-integral-derivative (PID) algorithm. Perpendicular dielectric constant ($\epsilon_\perp$) is measured at different temperatures by applying a voltage which is well below the Fréedericksz threshold, and simultaneously the birefringence is also measured from optical data. Extrapolating the high voltage measurements of capacitance to infinite voltage $\epsilon_\parallel$ is also measured. At a fixed temperature, the voltage is increased in small steps, and from the Fréedericksz threshold

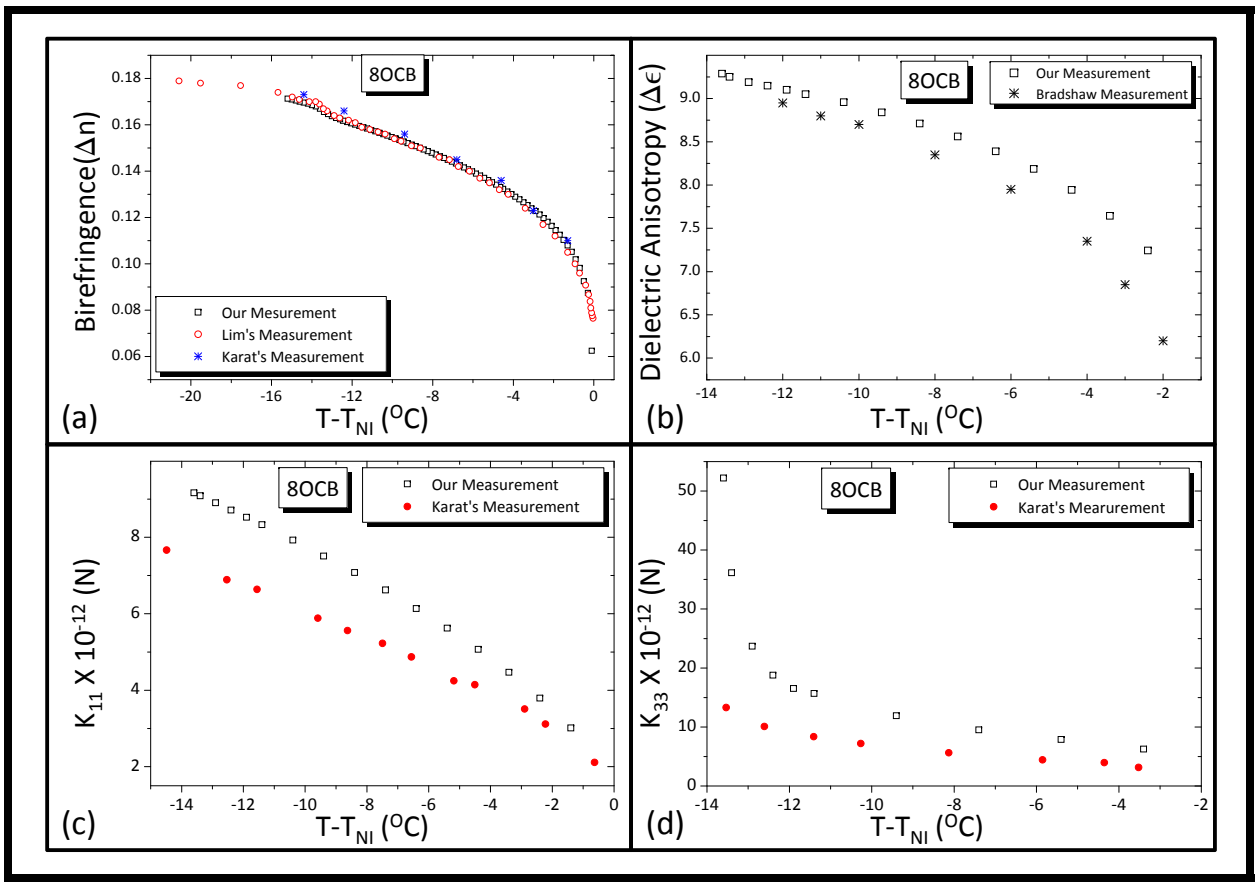

FIGURE 0.1: (a) Measured values of birefringence of 8OCB sample. □ represent our measurements, ○ represent Lim's[1] measurements and ✳ represent Karat's[2] measurements. (b) Measured values of dielectric anisotropy of 8OCB sample. □ represent our measurements and ✳ represent Bradshaw's[3] measurements. (c) Measured values of splay elastic constants of 8OCB sample. □ represent our measurements and ● represent Karat's measurements[2] (later re-analyzed by Madhusudana and Pratibha[4]) and (d) Measured values of bend elastic constants of 8OCB sample. □ represent our measurements and ● represent Karat's measurements[2] (later re-analyzed by Madhusudana and Pratibha[4])

voltage the splay elastic constant K_{11} is obtained. The optical phase differences at higher voltages are fitted to an appropriate theory by an iterative procedure to get the bend elastic constant K_{33}. All the data analysis and the iterative fitting algorithm are written in *Mathematica* software. To calibrate our setup we used the well known liquid crystal 4-*n*-octyloxy 4′-cyanobiphenyl (8OCB). Measurements of various physical properties of this material are available in the literature.

We have compared our 8OCB birefringence data with those of Lim *et al.* [1] and Karat *et al.* measurements[2]. Our results show good agreement with their data(see Figure 0.1a).

The dielectric anisotropy of 8OCB is compared with the data of Bradshaw *et al.* [3]. Our data are somewhat higher, and the difference increases close to T_{NI} (Figure 0.1b). Our K_{11} and K_{33} measured data of 8OCB are compared with the earlier measurements by Karat *et al.* [2] which were later reanalyzed by Madhusudana *et al.* [4]. Our values are higher by $\sim$15%. The present result shows a smoother variation of K_{11} with temperature compared to the earlier data as the temperature stability is higher(Figure 0.1c,d).

Our data on 8OCB compare very well with earlier measurements, as far as Δn is concerned. We believe that our measurements of $\epsilon_\perp$, $\epsilon_\parallel$, K_{11} and K_{33} are more accurate than the earlier measurements.

Chapter 3 : Compounds with molecules having two different shapes, viz, rod-like (R) and disc-like (D) have been studied in great detail in the past [5, 6]. The recently discovered liquid crystals (LCs) made of banana-shaped or bent-core (BC) molecules are being presently studied extensively [7, 8]. Unlike R and D molecules, the BC molecules have *shape polarity*. Recently detailed studies have been carried out on mixtures of a binary system of compounds having R and BC molecules[9]. The temperature-concentration phase diagrams of the BC compound 1,3-phenylene bis[4-(3-methyl-benzoyloxy)] 4′-*n*- dodecylbiphenyl 4′ -carboxylate (BC12) and R compound 4-*n*-octyloxy 4′-cyanobiphenyl (8OCB) are shown in Figure 0.2.

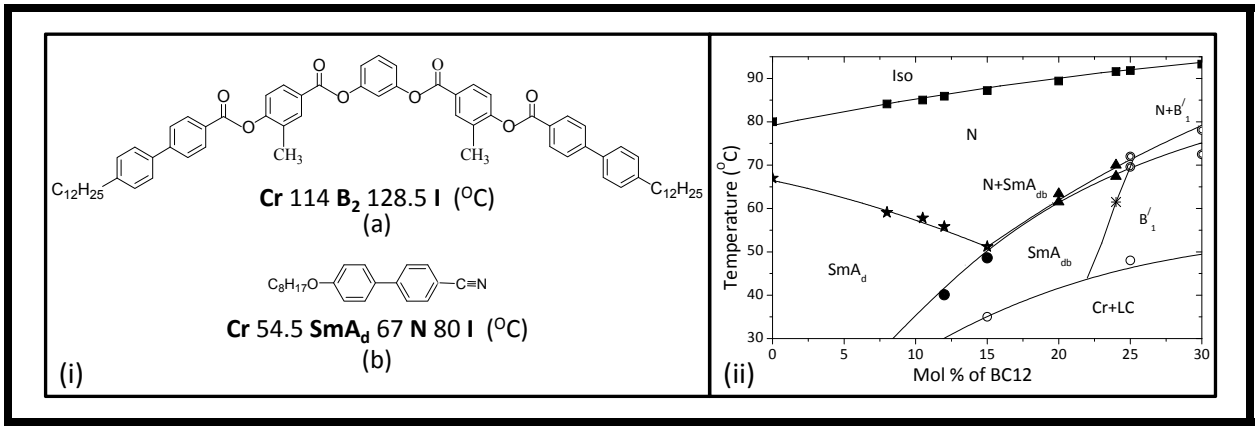

FIGURE 0.2: (i) Molecular structures and phase sequences exhibited by (a) 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4′-*n*- dodecylbiphenyl 4′ -carboxylate (BC12) and (b) 4-*n*-octyloxy 4′-cyanobiphenyl (8OCB). (ii) Temperature-concentration phase diagram of the binary mixture (reproduced from Ref. [9])

The 8OCB molecules have the strongly polar cyano end groups and neighbouring polar molecules have an antiparallel orientation and overlap at the aromatic cores [10] giving rise to the partial bilayer SmA_d phase. This system exhibits three induced phases, viz. the biaxial smectic-A (SmA_{db}) phase and two types of 2-dimensionally periodic phases B_1' and B_1 in appropriate concentration ranges of BC12. The mutual orientation of the R and BC molecules in the SmA_{db} phase has been established by other studies[9, 11]. It has been shown that the aromatic cores and aliphatic chains of BC12 molecules fit into the partial bilayer of 8OCB molecules with the arrow axes of the bent-core molecules preferentially lying parallel to the layer normal. In the R rich mixtures of the system, the nematic phase is exhibited over large temperature ranges and the mutual alignment of the two types of molecules can change with temperature, affecting various physical properties. We have undertaken the present work to explore this possibility.

We have studied 8OCB and its mixtures with 5, 11, 14 and 17 Mol% of BC12. In all further discussions these mixtures are denoted as 5M, 11M, 14M and 17M respectively.

At any given relative temperature ($T_{NI} - T$), birefringence (Δn) decreases with increasing concentration of the BC compound. This trend is a consequence of the lower anisotropy of polarizability of the BC molecule as compared to that of 8OCB molecule (see Figure 0.3a). The parallel dielectric constant $\epsilon_{\parallel}$ of 8OCB monotonically increases up to SmA_d. In 5M, $\epsilon_{\parallel}$ saturates at lower temperatures of the N phase. In 11M, 14M and 17M mixtures, as the nematic to SmA_d transition point is approached *within about* 3°C of the transition, $\epsilon_{\parallel}$ *decreases sharply* (see Figure 0.3b). This sharp decrease results from the smectic like short range order which builds up close to the transition point. The alignment of BC molecules in such short range ordered groups should be with their arrow axes along the director defined by the long axes of 8OCB molecules. The contribution of the BC molecules to the dielectric constant is sharply reduced. This reduction implies that there is a large barrier against the reorientation of the BC molecules about the bow axis in the smectic layers. This observation also implies that the *BC and 8OCB molecules may have a different mutual alignment in the high temperature nematic phase*.

Figure 0.3c shows K_{11} as a function of temperature for 8OCB and four mixtures. As the concentration of BC molecules is increased, K_{11} decreases. In all the mixtures the temperature dependence of K_{11} changes sign and K_{11} *decreases sharply* close to the N-SmA transition point. This **anomalous** behaviour reflects the reorientation of BC molecules in the smectic-like short

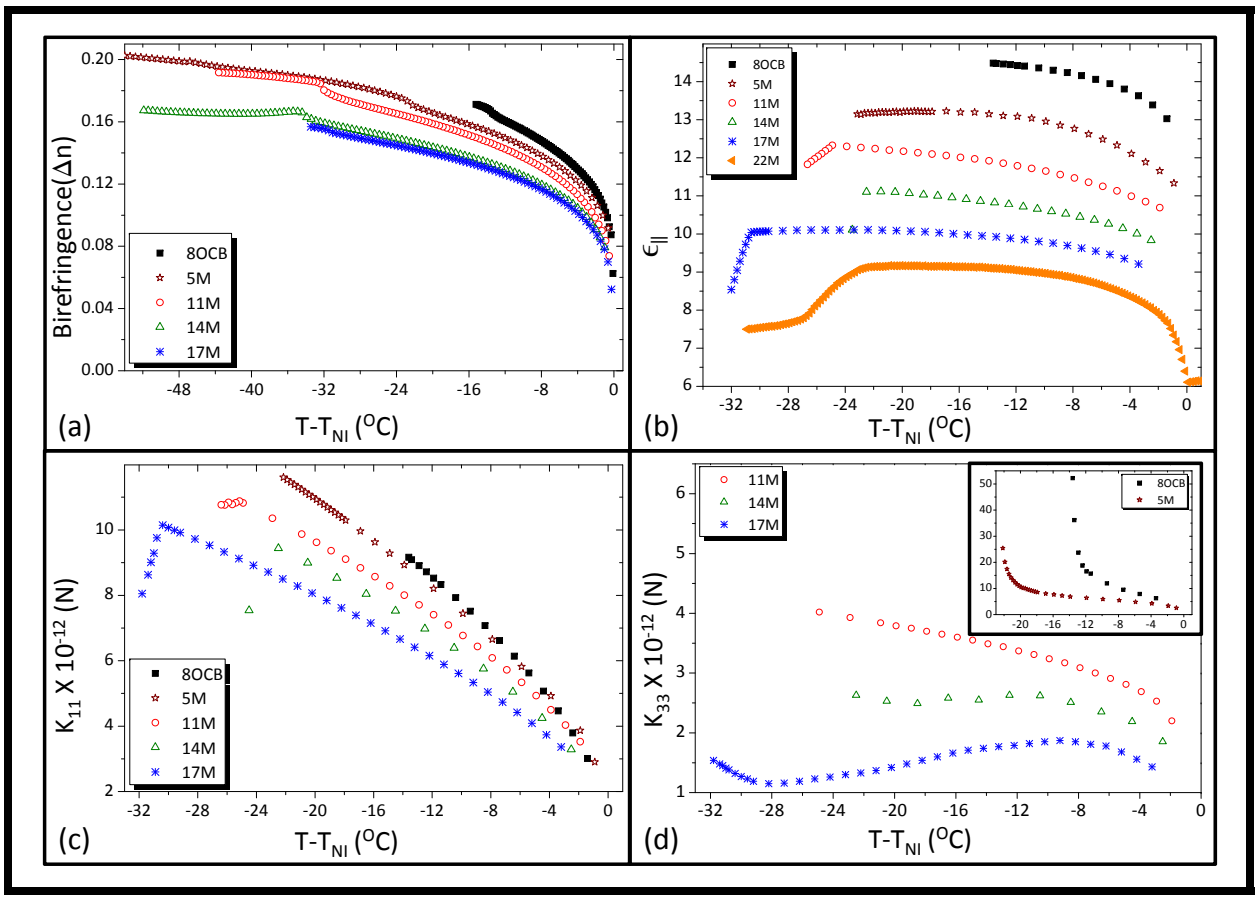

FIGURE 0.3: (a) Dependences of birefringence of pure 8OCB and four mixtures on the relative temperatures. (b) Dependences of $\epsilon_{\|}$ of pure 8OCB and five mixtures on the relative temperatures. $\epsilon_{\|}$ of 22M mixture is measured using a homeotropically aligned cell. (c) Dependences of K_{11} of pure 8OCB and four mixtures on the relative temperatures and (d) Dependences of K_{33} of pure 8OCB and four mixtures on the relative temperatures. The data for 8OCB and 5M mixture are shown in the inset.

range ordered (SRO) groups. As shown in Figure 0.4(b) the bent nature of the molecules can aid the splay deformation in the smectic like short range ordered groups in the nematic phase.

The bend elastic constant K_{33} decreases with the concentration of BC molecules. In 11 M mixture K_{33} decreases *four times* from that corresponding to 8OCB at 10°C below the isotropic-nematic transition point (see Figure 0.3d). This reduction is much more than the reduction of K_{11}. K_{33} also behaves **anomalously** with temperature. K_{33} initially increases and reaches maximum in 14M and 17M mixtures and then decreases slowly as the temperature is lowered from T_{NI}. Close to nematic-smectic transition point, K_{33} again increases.

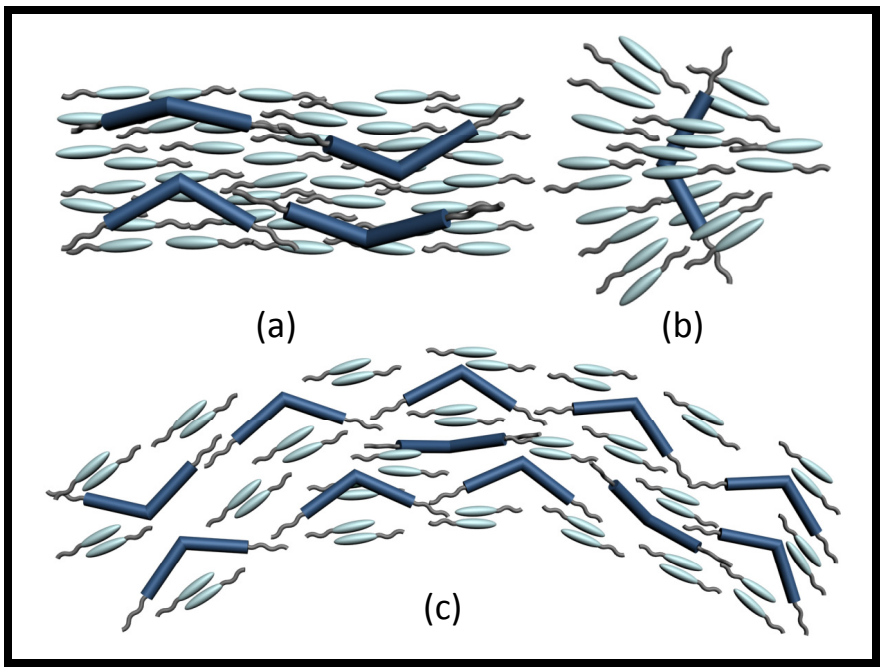

FIGURE 0.4: (a) Mutual alignment of R and BC molecules in the nematic phase (b) BC molecules reorient when smectic like short-range order builds up. The bent core molecules favour a splay distortion of the director field dominated by rods and (c) in the nematic phase the BC molecules fit very well in a director field with bend distortion.

The molecules are bent and when there is a bend deformation they can more easily get accommodated with the director field of the rods (Figure 0.4c). The bend elastic constant decreases by the presence of BC molecules in the medium. As the temperature is lowered the order parameter increases and the influence of BC molecules becomes even stronger. Instead of the bend constant increasing with that of the orientational order, it actually *decreases*. Very close to N-SmA transition point K_{33} shows an increasing trend, because of the build up of smectic like SRO. In this case, the bend distortion of the director field becomes more difficult, as is well known[5, 6]. A simple model has been proposed to account for the anomalous trend in K_{33}.

In view of the anomalous trends in the temperature variations in the elastic constants found in the mixtures with 14 and 17 mol % BC12 molecules, it is of obvious interest to investigate mixtures with even higher concentrations of BC molecules. We undertook measurements on 24M mixture.

Birefringence of 24M is lower compared to that of other mixtures. The dielectric constant 24M

in the isotropic phase is ~ 8.5, which is *much above* that of other mixtures, and almost similar to that of pure 8OCB. $\epsilon_\perp$ is also *much larger* than that of 8OCB and other mixtures, at any relative temperature. At same relative temperature the Fréedericksz threshold voltage is higher for 24M than that of 17M mixture. This implies that the dielectric anisotropy of 24M should be lower than that of 17M mixture near the threshold voltage though the measured $\Delta\epsilon$ of 24M is similar to that of 17M mixture, where $\epsilon_\parallel$ is measured by extrapolation of ϵ at high voltages to $1/V = 0$. In order to investigate this difference further, we conducted other experiments. A mixture with 20M of BC molecules was taken in a *homeotropically* aligned cell. The temperature dependent dielectric constant $\epsilon_\parallel$ was now directly measured using this cell for various applied AC voltages

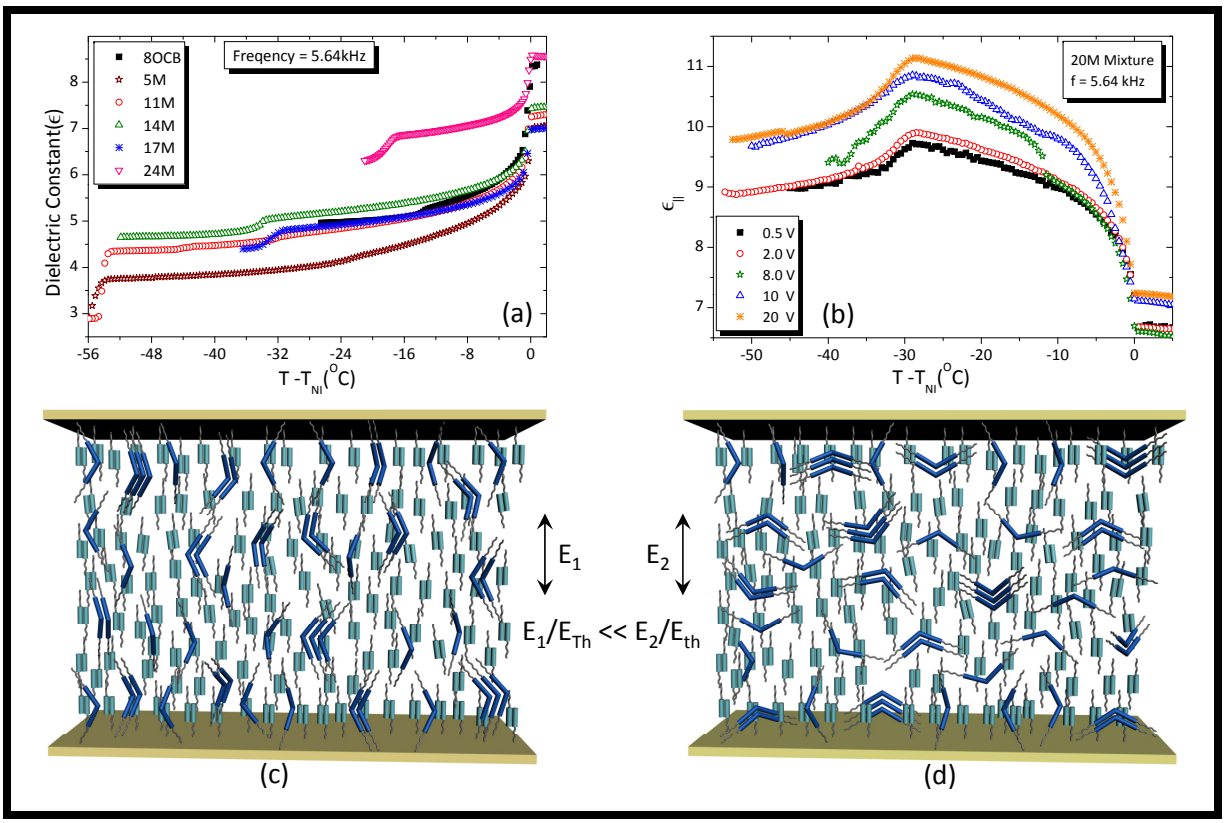

FIGURE 0.5: (a) Dependences of $\epsilon_\perp$ of pure 8OCB and five mixtures on the relative temperatures. $\epsilon_\perp$ of 24M exhibits highest values, (b) Temperature variations of $\epsilon_\parallel$ at different applied electric fields of 20M mixture. $\epsilon_\parallel$ increases with increasing electric field. The result implies formation of clusters of BC molecules in a mixture with high concentration of BC molecules. (c) At the low voltages the clusters are oriented with their bow axes along **n** enhancing $\epsilon_\perp$. (d) In high fields the clusters reorient and the arrow axes align along **n**, enhancing $\epsilon_\parallel$. The optical birefringence measured in a direction perpendicular to the plane of the figure is higher for (c) than for (d).

of frequency 5.64 kHz (Figure 0.5b).

With decrease in temperature, $\epsilon_{\|}$ increases in the nematic phase. At close to T_{AN}, $\epsilon_{\|}$ falls rapidly as smectic like short range order build up. This trend is seen in all the graphs where $\epsilon_{\|}$ are measured in various different applied voltages. More surprisingly $\epsilon_{\|}$ increases with increase of applied voltage (see Figure 0.5b). At higher applied voltages 10V and 20V, even in the isotropic phase, ϵ_{iso} shows a *higher value* which is $\sim$ 6% larger compared to the value measured at lower voltages. In the nematic phase as well as SmA_{db} phase, $\epsilon_{\|}$ is higher at all temperatures compared to the values measured at lower applied voltages.

The above results clearly confirms the trends noticed in the 24M mixture in which $\epsilon_{\|}$ was obtained by extrapolating the ϵ data to $1/V = 0$ in a sample which was homogeneously aligned in the field free state. $\epsilon_{\|}$ *strongly* depends on the applied field, increases by $\sim$ 15% for a voltage of 20V, which corresponds to a modest field of $\sim$ 1.35 V/μm or $\sim$ 45 esu. The implication of the above result is that there is a structural change in the medium as a function of applied voltage. In 20M and 24M, the volume fraction of BC molecules exceeds that of 8OCB and the mutual interactions between BC molecules becomes dominant. This leads to the formation of clusters of 2 or more BC molecules, which enhance $\epsilon_{\perp}$ in 24M to high values. In 20M a sufficiently large electric field applied along the director reorients the clusters such that their arrow axes point along the field direction, which increases $\epsilon_{\|}$ (see Figure 0.5d).

Chapter 4 : The rod-like (R) and bent-core (BC) molecules can be expected to have different order parameters in the nematic phase. The BC molecule which deviates strongly from cylindrical symmetry requires two different order parameters for a full description even in a uniaxial phase. When the molecules are cylindrically symmetric a single order parameter S can describe the orientational order parameter. The orientational order of the BC molecules must be described by two order parameters S and D where D is called the *molecular biaxiality order parameter*. A measurement of D using the infrared dichroism technique is possible but would require two independent vibrational modes from the same molecule which can give rise to isolated bands in the IR spectrum[12]. We have used the $C_{Ph} - O$ bonds attached to the phenyl rings and the $C = O$ bonds present in the BC12 molecule to estimate S and D order parameters of the BC12 molecules in a mixture with 11 Mol% of BC12(Figure 0.6a). This method requires a knowledge

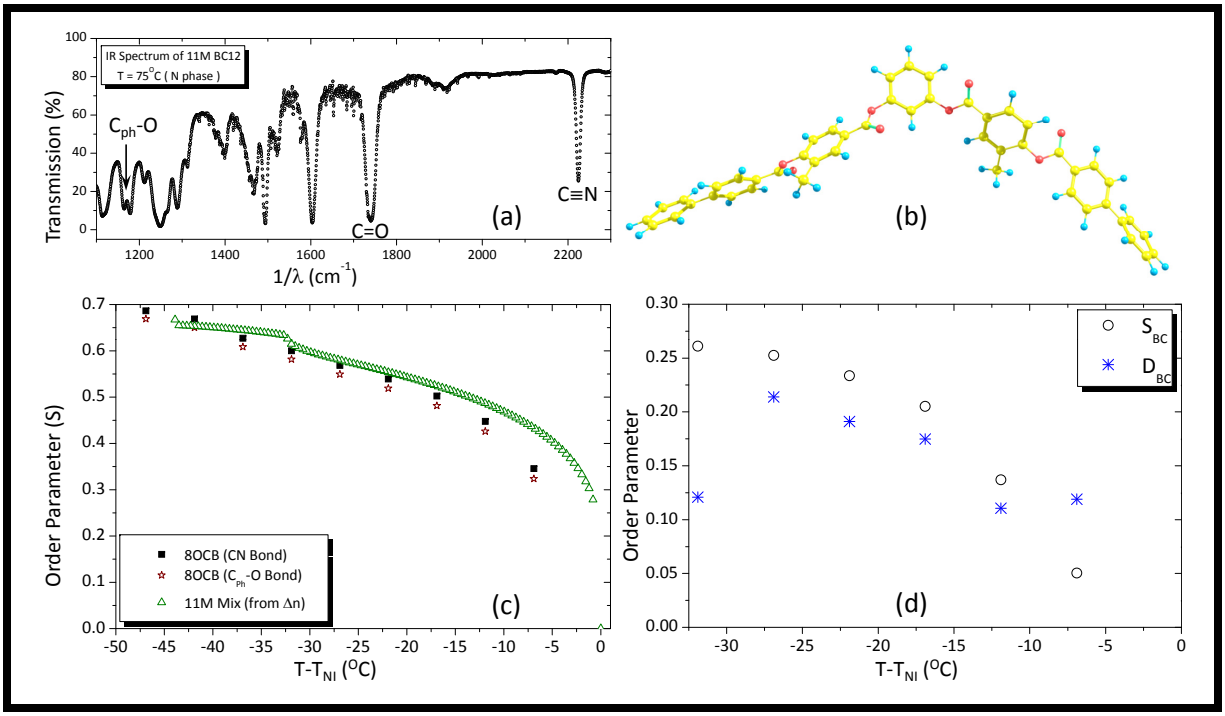

FIGURE 0.6: (a) IR spectrum of 11M mixture in the nematic phase, (b) energy minimized molecular structures of a BC12 molecule (only core), (c) Order parameter of 8OCB using 2 different bonds compared with the average order parameter of the 11M mixture calculated from optical birefringence and (d) Uniaxial and biaxial order parameters of BC12, estimated from IR data.

of the molecular structure.

We have calculated the S order parameter of 8OCB molecules using the absorption bands of both C $\equiv$ N and $C_{ph} - O$ bonds for different temperatures. Both the bonds are along the long axes of the 8OCB molecule. These two order parameter values are very close (see Figure 0.6c). These numbers are also very similar to, though somewhat smaller than the average order parameter of the mixture estimated from optical birefringence. The difference between the IR data and the optical data estimates increases at higher temperatures in the nematic phase.

In order to calculate the two order parameters S and D of BC molecules we should know the geometrical structure of the molecule. We have used the *Spartan 04* software to get the minimum energy conformation of a BC12 molecule. From the minimized energy of molecular structure, we calculate the angles made by all the four C = O bonds and all the four $C_{ph} - O$ bonds with the Bow, Arrow and C axes. These angles and IR absorptions of the corresponding bonds are related

with S and D of BC molecule. Using these we get S and D order parameters of the BC molecules. Both S and D of BC12 are positive and increase with decreasing temperature in the nematic phase(Figure 0.6d). In the smectic phase we could not get any reasonable values for S and D order parameters with the known mutual arrangement *viz.* the arrow axes along the director. From the NMR studies on a nematic liquid crystal made of only BC molecules, Xu *et al.* [13] have found very low value ($\sim$ 0.025) of the order parameter D. Indeed in order to get reasonable values of the S order parameter, they had to use a molecular geometry which was different from the energy minimized geometry of a single molecule. We believe that the values of S that we have got are clearly underestimated compared to the values obtained from optical measurements and IR data on 8OCB molecules. Further, D parameters are also overestimated. The attempt to measure both S and D molecular orientational order parameters of the BC molecules in the 11M mixture shows that the average geometrical conformations of the molecule may be quite different from the one got on the basis of energy minimization of a single BC molecule. The packing effects are likely to change the molecular structure to favour entropic gain in the free energy. Since BC12 has four relatively flexible O$-$C=O groups, such a change of structure which may also depend on temperature, is highly likely.

Chapter 5: We have made flexoelectric studies on mixtures of rod-like and bent-core molecules. Splay or bend distortion of a nematic liquid crystal can create an electric *polarization*. This was first shown by Meyer[14] and this effect is known as flexoelectric effect. The flexoelectric polarization **P** induced by a weak distortion of a nematic director field is given by,

$$\mathbf{P} = e_1 \left(\boldsymbol{\nabla} . \mathbf{n}\right) \mathbf{n} + e_3 \left(\boldsymbol{\nabla} \times \mathbf{n}\right) \times \mathbf{n} \tag{0.1}$$

where e_1 and e_3 are flexoelectric coefficients corresponding to the splay and bend distortions respectively with the dimensions of charge/length or electric potential and of *arbitrary sign*. This expression is the most general polar vector that can be constructed from the *apolar* director **n**.

Recently Harden *et al.* [15] have measured the flexoelectric coefficients of pure bent-core nematic 4-chloro-1,3-phenylene bis 4-[4′-(9-decenyloxy) benzoyloxyl] benzoate (C1Pbis10BB) by a mechanical technique where an oscillatory bend deformation is induced by periodically flexing a thin layer of NLCs contained between nonrigid conducting surfaces and then measure the induced

electric voltage which is generated by the e_3 coefficient. The magnitude of e_3 was found to be *3 orders of magnitude larger than in calamitics*.

We are interested in measuring flexoelectric coefficients of nematic mixtures made of 8OCB (R) and BC12 (BC) molecules. The mixtures exhibit large nematic ranges (see Figure 0.2b). Using the Dozov technique[16], where we have used a hybrid aligned cell and a planar DC electric field, we have measured e^*/K of pure 8OCB, 5M and 8M mixtures, where $e^* = (e_1 - e_3)$. The signs of e^*/K of 8OCB and the two mixtures are all negative. In magnitude, e^*/K of 5M is ~2 times larger than that of pure 8OCB (Figure 0.7). From this data we get, $\left(\frac{e^*}{K}\right)_{\text{BC}} \approx 20 \left(\frac{e^*}{K}\right)_{\text{8OCB}}$, which is very much smaller than Harden's[15] result.

Our measurements of (e^*/K) in 8OCB and two mixtures 5M and 8M show that (i) the BC molecule has a much larger flexoelectric coefficient than that of a rod like molecule like 8OCB. The main contribution to e^* should be of dipolar origin, as originally envisaged by Meyer. However the estimated value of e^* is much smaller than that of the pure compound. The large value in the latter case may be due to enhancement by cluster formation, which is essentially absent in our

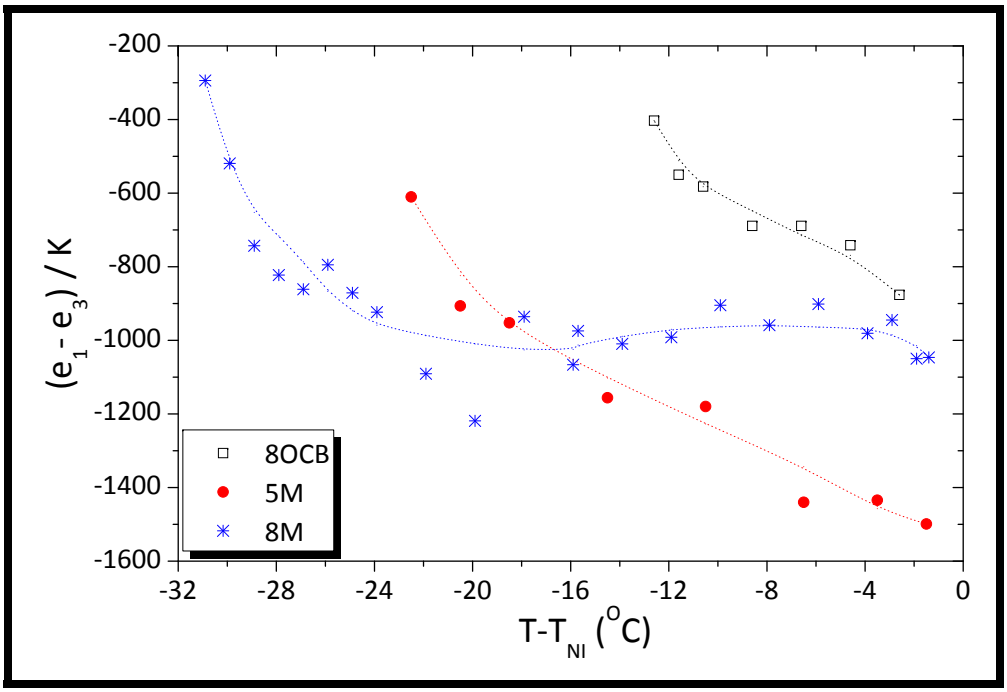

FIGURE 0.7: Variations of flexoelectric coefficient of pure 8OCB and two mixtures with relative temperature

mixtures 5M and 8M. (ii) The relatively large value of (e^*/K) of the BC molecules also gives rise to an increased internal field in the hybrid aligned cell when the concentration of BC molecules is increased. This in turn leads to a full reorientation of the director on the plate treated for planar alignment to give only homeotropically aligned cells for concentrations $>$ 11 Mol % of BC molecules.

Chapter 6: Liquid crystal dimers are composed of molecules containing two conventional mesogenic groups linked via flexible spacers. The physical properties of nematic liquid crystals made of dimeric molecules are expected to be different from those made of monomers. Recently a few disulphide-bridged alkoxycyanobiphenyl dimers

$[N \equiv C - (C_6H_4) - (C_6H_4) - O - (CH_2)_n - S - S - (CH_2)_n - O - (C_6H_4) - (C_6H_4) - C]$ [17] have been synthesized in our chemistry laboratory, where 'n' is the number of methylene units. These dimers exhibit relatively low temperature liquid crystalline phases compared to other dimers. Lower homologues exhibit only the nematic phase while higher homologues exhibit nematic as well as smectic phases. The ninth homologue indicated by (D9) exhibits the reentrant nematic (N_r) phase over a short temperature range ($\sim 3^\circ$C). We have made a mixture of 94 Mol % of D10 with 6 Mol % of D6 which shows the reentrant nematic over a large temperature range ($\sim 8^\circ$C). We have undertaken some measurements of the optical birefringence, both parallel and perpendicular dielectric constants, and the splay and bend elastic constants in the nematic phase of different dimers and one mixture(94 Mol % of D10 and 6 Mol % of D6).

Though all the dimers have an even number of carbon atoms in the flexible chains, the birefringence, the order parameter, $\epsilon_\parallel$ and dielectric anisotropy show clear odd-even effects, depending on the number of carbon atoms in the alkoxy chain of a monomeric unit. Birefringence, $\epsilon_\parallel$ and $\Delta\epsilon$ are lower for a given even monomer than those of next odd monomer (Figure 0.8a, c). Surprisingly the order parameter shows exactly the *opposite odd-even effect*, the even homologues having higher values than the neighbouring odd homologues (Figure 0.8b). D7 exhibits unusual temperature dependences. It has the steepest variations in Δn, S and $\epsilon_\parallel$ (Figure 0.8). The dielectric constant in the isotropic phase and $\epsilon_\perp$ decreases with increase in the chain length of the dimer.

In the nematic phase of the D6 dimer, a jump is seen in the optical transmitted intensity and

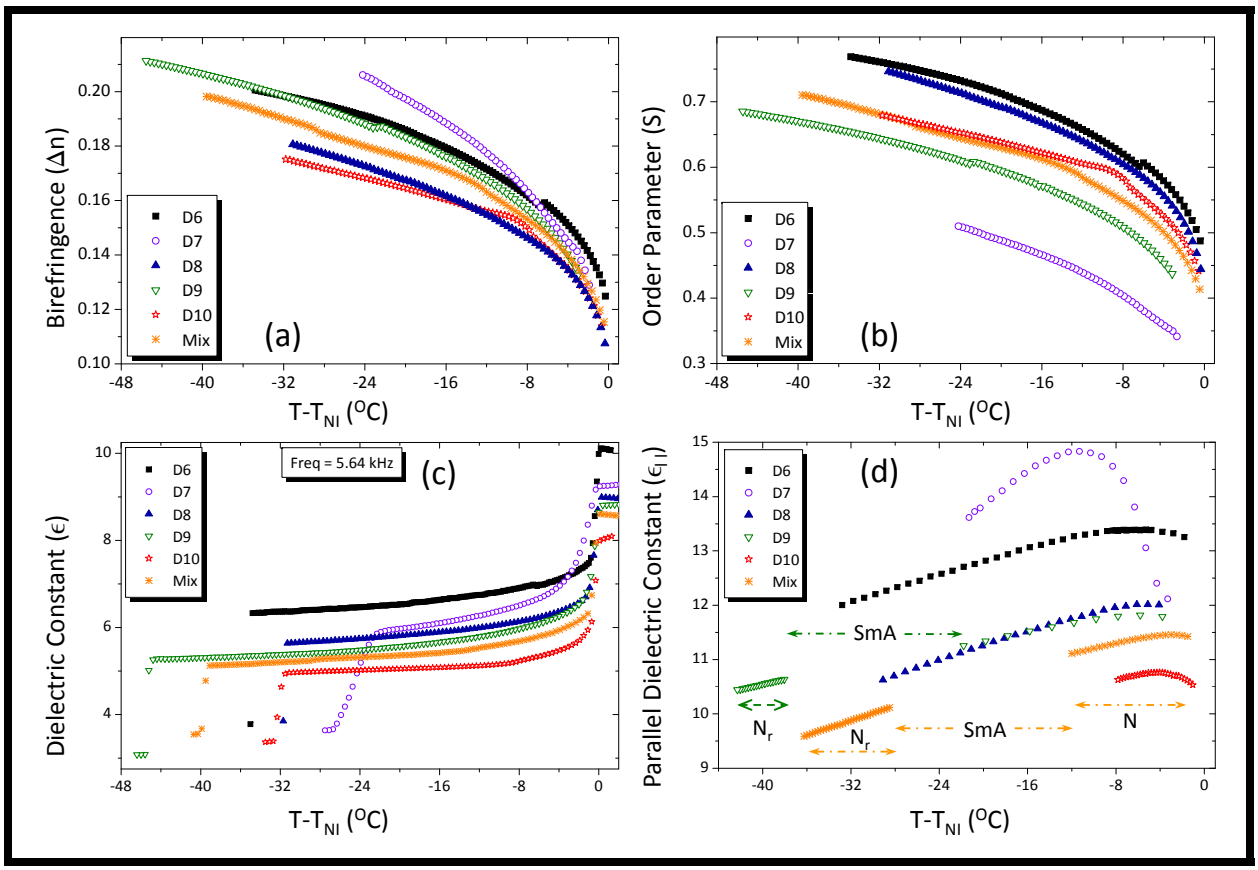

FIGURE 0.8: Dependences of (a) the birefringence (Δn), (b) order parameter (S), (c) $\epsilon_{\perp}$, and (d) $\epsilon_{\parallel}$ of 5 dimers and the mixture on the relative temperatures.

the perpendicular dielectric constant at the same temperature ($T - T_{NI} \sim -6.2^{\circ}C$) indicating a nematic-nematic transition. We have conducted two independent experiments with different cell thicknesses. In both the cells the jump is seen at the same temperature of 120.5°C (see Figure 0.9). Optical intensity jumps to a higher value indicating that the birefringence and hence the order parameter have jumped to a *lower* value. $\epsilon_{\perp}$ jumps to a higher value again corresponding to decrease in the order parameter. This phenomenon occurs within the nematic phase, without any signature in the calorimetric data. It signifies a weakly first order N–N transition, which occurs because of a change in the *short range order* in the medium[5, 18].

At any relative temperature, K_{11} of the mixture is higher than that of D9 dimer. In the D6 dimer very close to N–N transition point K_{11} varies smoothly, and no indication of a N–N transition is seen in Figure 0.9. At the same relative temperature, K_{11} shows a small odd-even

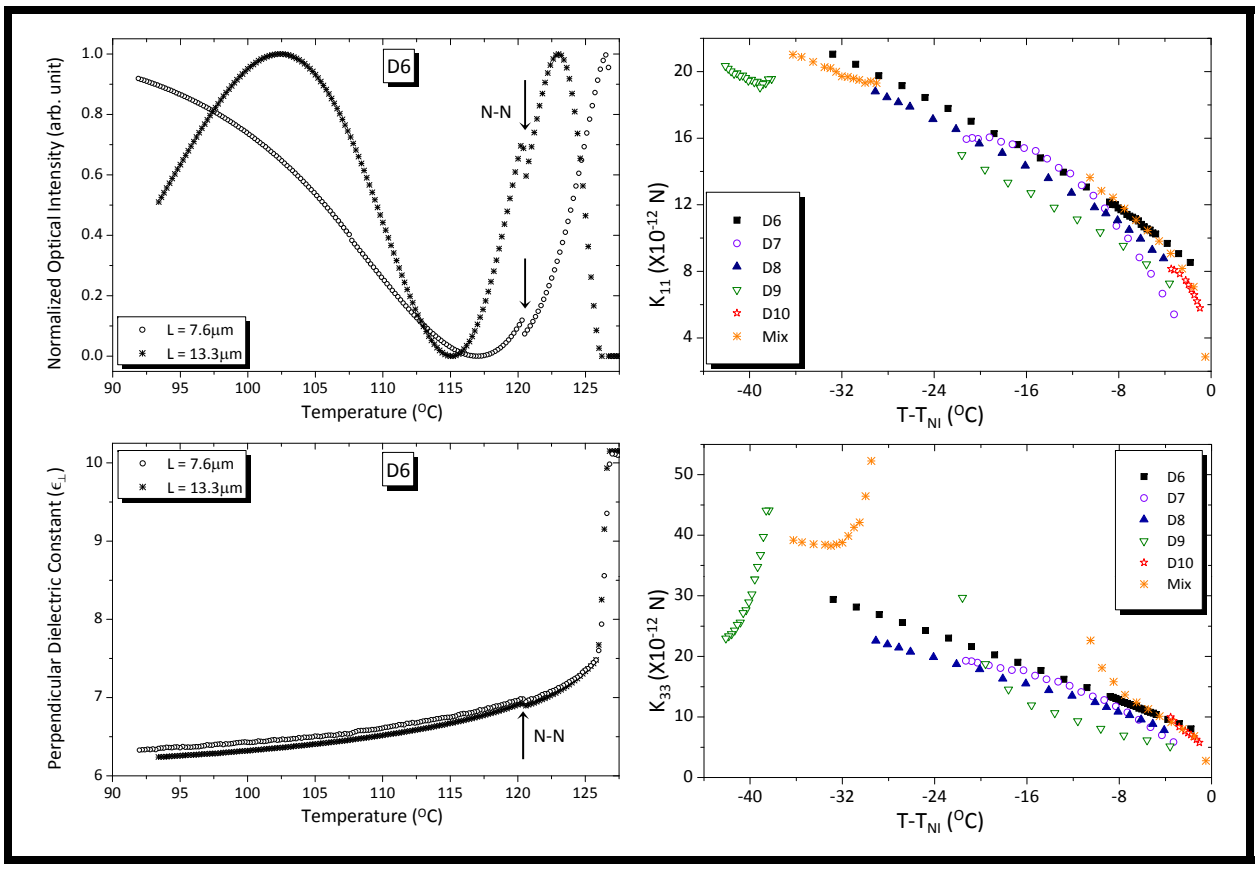

FIGURE 0.9: Detection of N–N transition of D6 dimer in two cells of different thicknesses, using optical (upper section) and dielectric (lower section) measurements. Dependences of K_{11} of all the samples on the relative temperatures. Dependences of K_{33} of all the samples on the relative temperatures.

effect close to T_{NI}, the even members having higher values.

The divergence of K_{33} is observed when the temperature in the N_r phase approaches T_{AN} (Figure 0.9) in D9 and the mixture. In the nematic phase at any given relative temperature, K_{33} of the mixture is larger than that of D9 dimer. Again as in the case of K_{11}, there is no evidence of N–N transition in the D6 compound.

The odd-even effects are probably connected with the disulphide bridging group. In the case of even homologues, the –S–S– bond itself is aligned along the long axis of the dimer on average, and the two C–S bonds on either side are oriented at a large angle to this axis. The C–S bond polarizabilities subtract from that of the polarizability along the long axis, and the birefringence is lowered. In the odd homologues, the C–S bonds are aligned along the long axes, and add to

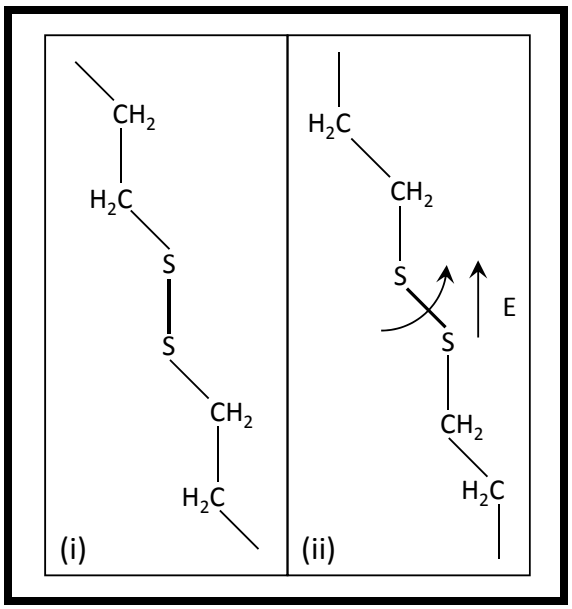

FIGURE 0.10: The configuration near the central disulphide linkage group in (i) even homologues and (ii) odd homologues. The long axis of the dimer is vertical. In the odd homologue, a reorientation about the S–S bond is easier under an external field.

the anisotropy, increasing the Δn value, but not to the overall order parameter of the medium. Moreover, the S–S bond makes a large angle to the long axis and it is easier for each alkoxy-cyanobiphenyl moiety to reorient under the action of a low frequency electric field, thus increasing the orientation contribution to $\epsilon_{\parallel}$(Figure 0.10). Further, the fluctuations about the S–S of odd members lowers the order parameter to a greater extent than in the case of even members in which the bond is aligned along the long axis of the dimers. The reorientation about the S–S bond should be much easier compared to that about a CH_2–CH_2 bond as the sulphur atoms are much smaller in size compared to the bulky CH_2 groups. Indeed the sharp increase in $\epsilon_{\parallel}$ as the temperature is lowered from T_{NI} in D7 which is the lowest odd homologue studied, reflects this tendency for a facile reorientation about the S–S bond till the conformational stiffening takes over at $\sim 100^{\circ}$C, and $\epsilon_{\parallel}$ starts to decrease sharply. As the temperature is lowered, the conformational freedom of chains reduces and the orientation contribution to $\epsilon_{\parallel}$ decreases in all the homologues studied (Figure 0.8).

Some of the results in this thesis have been published in the following paper:

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