

6

Chapter 6

6.1 Physical Studies on Liquid Crystals with Dimeric Molecules

Liquid crystal dimers are composed of molecules containing two conventional mesogenic groups linked via *flexible* spacers[77]. The spacers are mainly alkyl chains. The phase transition behaviour of dimers exhibits a strong dependence on the length and parity of the flexible spacers. The dimers are broadly divided into two groups : (i) *symmetric dimers* in which the two mesogenic moieties are identical and (ii) *non symmetric dimers* which contain two different mesogenic units. These two groups can be further sub divided according to the molecular geometry of the mesogenic units. Dimers with two identical mesogens by far are the most widely synthesized and studied. There are several examples known in which two symmetric or non-symmetric calamitic

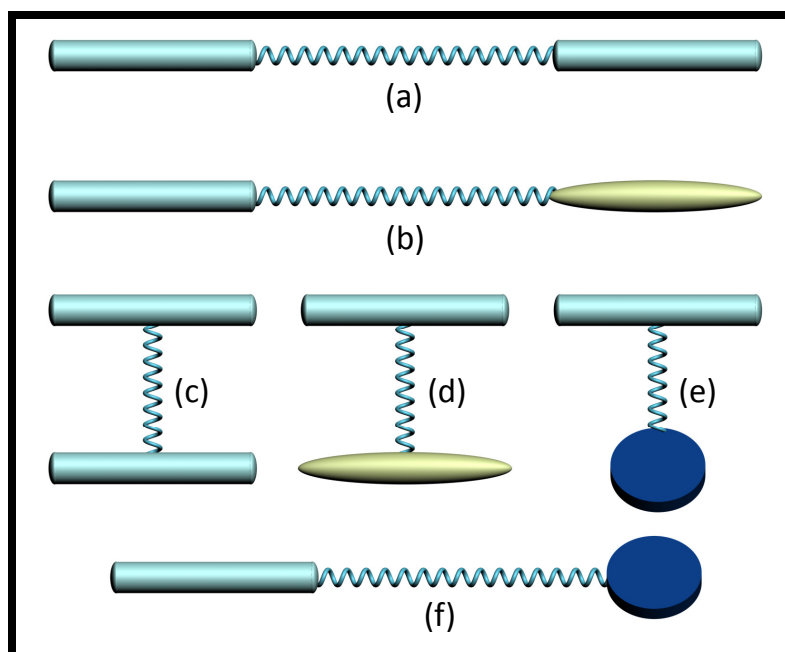


FIGURE 6.1: Schematic diagram of some possible structures of liquid crystal dimers : (a) symmetric calamitic dimer, (b) non-symmetric calamitic dimer, (c) and (d) laterally linked symmetric and non-symmetric calamitic dimer, (e) laterally linked discotic-calamitic dimer and (f) linearly attached discotic-calamitic dimer.

mesogens are connected laterally via a flexible spacer (see Figure 6.1). There are many possible combinations of discotic-calamitic and discotic-discotic molecules with linkage groups. In addition to these possibilities, several other combinations *viz.* banana-rod and banana-banana units[78–82] connected to each other via more than one spacer are also possible.

The dimers exhibit interesting phase behaviour depending on the length of the spacer and the structure of the linking groups. A large *odd-even* effect is seen in physical properties *viz.* nematic-isotropic transition temperature (T_{NI}), entropy change and order parameter at the T_{NI} of α, ω - bis(4'-cyanobiphenyl-4-yloxy)alkanes by varying the length and parity of the spacer. For the even number of carbon atoms, properties like birefringence, dielectric anisotropy exhibit higher values compared to those with odd number of carbon atoms[83, 84]. The former have rod-like conformation while the latter have a bent shape but now with a flexible linking group. The ratio of bend to splay (K_{33}/K_{11}) elastic constants are much smaller for the odd members compared to that for the neighbouring even members[85]. This has been theoretically analyzed by Terentev and Petchek[86].

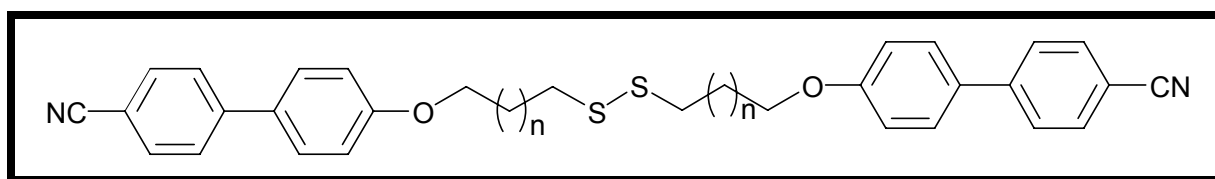


FIGURE 6.2: Schematic diagram of the dimeric compound used in our studies. n stands for the number of methylene units.

Sample	$T_{NI}(^{\circ}\text{C})$	$T_{AN}(^{\circ}\text{C})$	$T_{N_rA}(^{\circ}\text{C})$
D6 ($n = 4$)	126.8	-	-
D7 ($n = 5$)	112.2	-	-
D8 ($n = 6$)	116.1	-	-
D9 ($n = 7$)	107.6	84.9	70.0
D10 ($n = 8$)	108.7	101.1	-
Mix (94M% D10 + 6M% D6)	109.4	97.2	80.4

Table 6.1: Phase transition temperatures of different dimers and a mixture.

Most of the dimers exhibit liquid crystalline (LC) phases at a high temperature ($T_{NI} \gtrsim 150^{\circ}\text{C}$). Recently a series of thiol-functionalized disulphide-bridged alkoxy cyanobiphenyl dimers have been synthesized in our chemistry laboratory showing comparatively low temperature ($T_{NI} \sim 100^{\circ}\text{C}$) LC phases[87]. The structure of the dimeric molecule is shown in Figure 6.2. where 'n' is the number of methylene units. The monomer of the dimer contains one biphenyl with a $\text{C}\equiv\text{N}$ bond at one end and at the other end, an alkoxy chain is connected to a similar monomer through a disulphide bridge. All the dimers contain two sulfur atoms and an even number of carbon atoms in the chains; and as such all of them have *rod-like conformations*.

The phase transition temperatures of different dimers and the mixture which were used in our studies are shown in a Table 6.1. D6, D7 and D8 exhibit only the nematic phase. D9 exhibits a very interesting $\text{N-SmA}_d\text{-N}_r$ phase sequence as it is cooled. The SmA_d phase has a partial bilayer

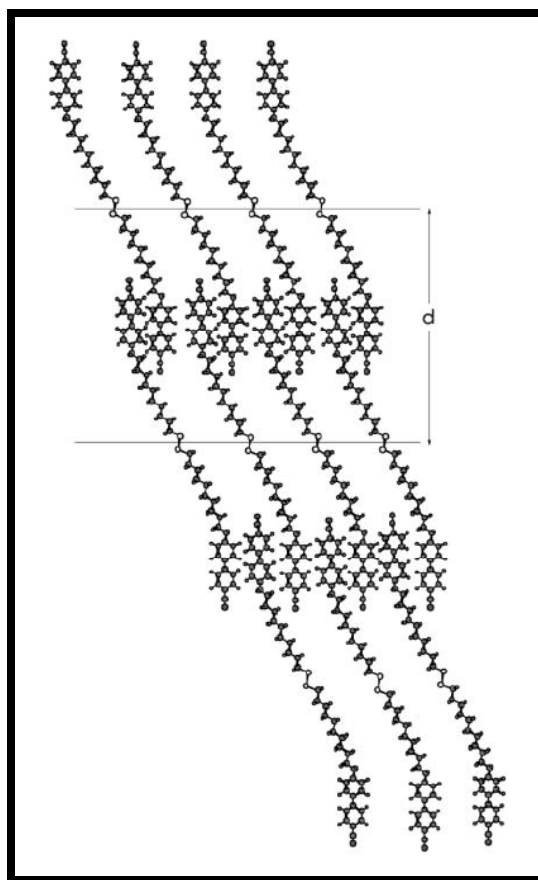


FIGURE 6.3: Partial bilayer intercalated structure in the smectic phase of D10 dimer determined by X-ray scattering studies (from reference[87])

structure, as determined by X-ray scattering studies[87](see Figure 6.3). This is caused by the tendency of compounds with highly polar end groups to form antiparallel pairs[45, 88] to lower the intermolecular interaction energy. Combined with the large dispersion energy between the aromatic parts and the nano segregation between the aromatic and aliphatic moieties, the partial bilayer structure results, as in the case of 8OCB mentioned in Chapter 3. In the present case, the partial bilayer structure of the dimers generates an intercalated structure in the SmA phase. There is a strong SmA-like short range order in the nematic phases of D7 and D8 also but not in the case of D6 with the shortest length of the spacer.

As the temperature is lowered in the SmA_d phase, the compound D9 and the mixture exhibit a reentrant nematic (N_r) phase (see Table 6.1). It has been argued that at higher densities, the dipole-induced dipole interactions effectively reduces the dipolar repulsion even for a *parallel*

orientation of dipoles and the competition between the monolayer and partial bilayer structure gives rise to the reentrant nematic phase[88, 89]. (Indeed in some cases, a *monolayer* SmA₁ phase is observed as the temperature is lowered from the reentrant nematic phase)[1].

In D9, the range of the N_r phase is very small and the sample crystallizes. On the other hand, D10 exhibits only a SmA_d phase and no reentrant nematic phase. We have made a mixture of 94 Mol% of D10 with 6 Mol% of D6 to obtain a reentrant nematic phase which is not exhibited by either D6 or D10. Further the useful temperature range of the reentrant nematic phase is larger than in the case of D9. This enables us to conduct physical studies on a wider range in the N_r phase of the mixture.

6.2 Experimental Procedure

All the dimers were synthesized and purified in our chemistry laboratory[87]. Two dimers D6 and D10 are weighed in appropriate quantities to make the mixture. All the samples are filled into the liquid crystal cell in the isotropic phase. Here we have used SiO coated ITO plates to get homogeneous alignment in the cell (see Section 2.2 of Chapter 2). We have used the electro optical setup described in Section 2.4 of Chapter 2 to measure 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.

6.3 Experimental Results and Discussions

6.3.1 Optical Birefringence

- (i) The values of birefringence (Δn) of all the dimers and the mixture increase with decreasing temperature. For clarity, we have shown the relative temperature variation of Δn for each sample separately in Figure 6.4. The birefringence of D9 dimer shows a small jump at the N-SmA transition point while in the D10 dimer and in the mixture only a change in slope is seen (see Figure 6.4). Only in the mixture a slope change is visible at SmA-N_r transition point, though there is no change in optical transmission. In the D6 dimer in the nematic

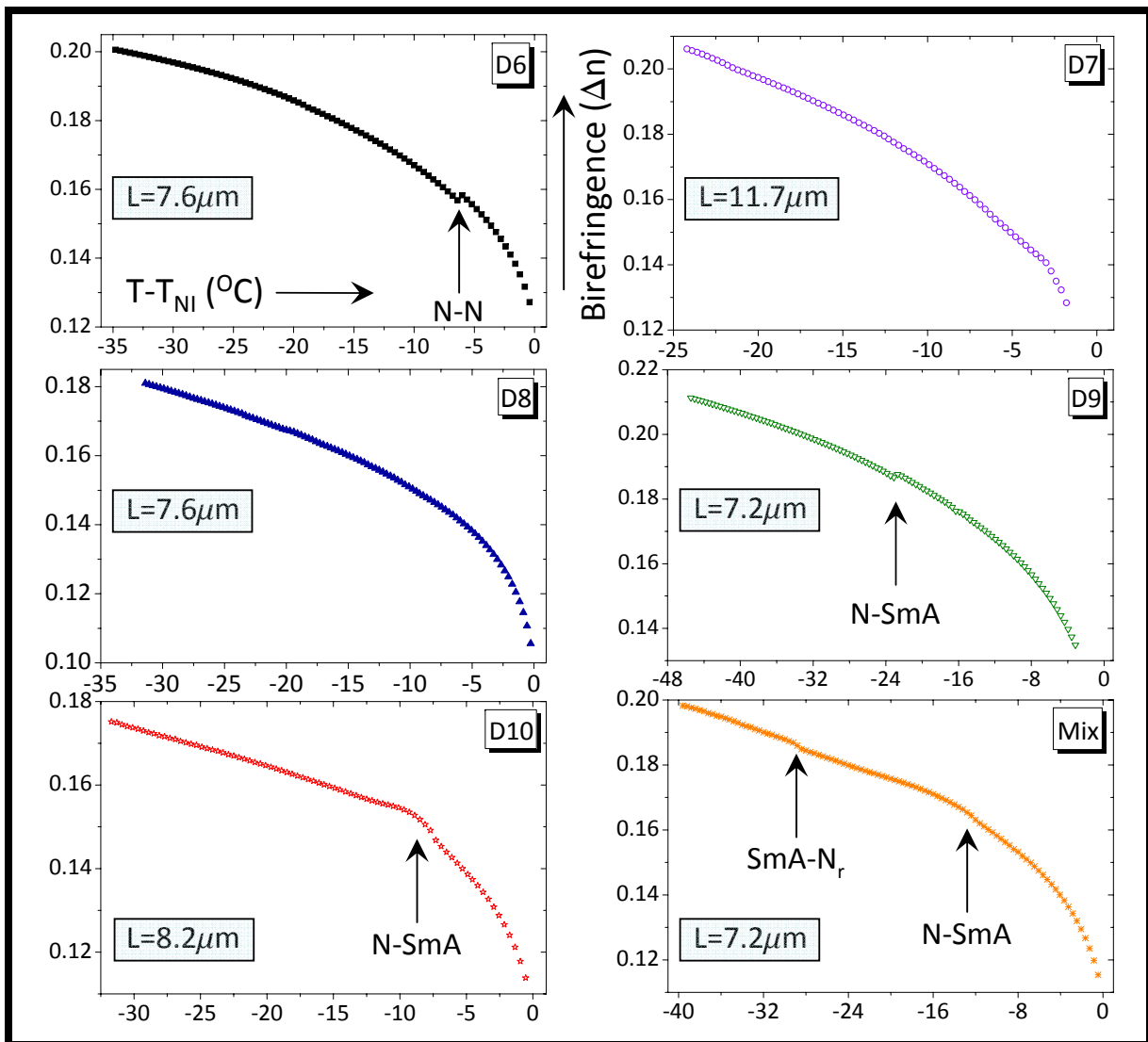


FIGURE 6.4: Dependences of the birefringence (Δn) of 5 dimers and the mixture on the relative temperatures.

range, a jump is seen in optical intensity reflecting that in birefringence (see Figure 6.4). Δn jumps to a *lower* value as temperature is lowered, indicating a nematic-nematic (N–N) transition.

- (ii) Even in D7 the birefringence exhibits a change of slope at $T - T_{NI} \simeq -2.5^\circ\text{C}$. The birefringence of the mixture (94 Mol% of D10 and 6 Mol% of D6) lies in between that of D10 and D6 (see Figure 6.5). A very interesting fact emerges when the relative temperature

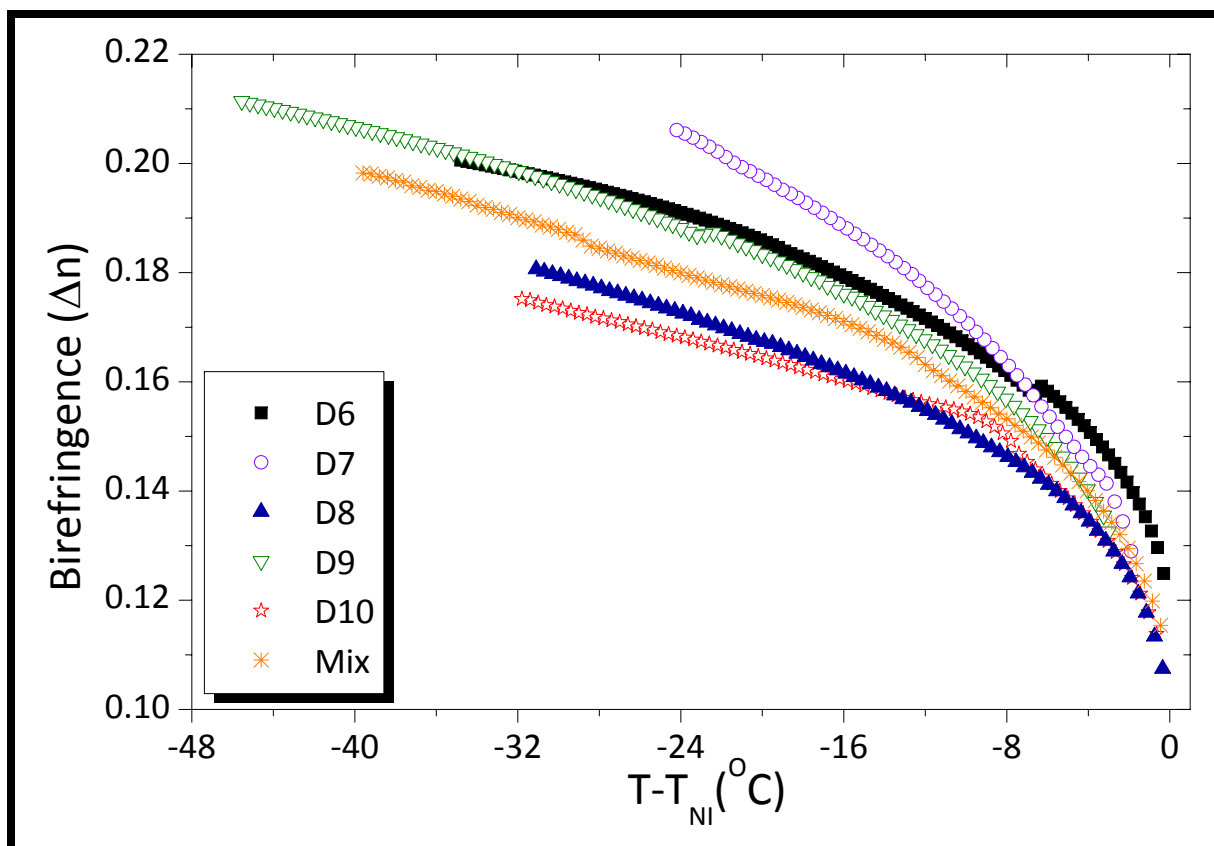


FIGURE 6.5: Dependences of the birefringence (Δn) of 5 dimers and the mixture on the relative temperatures, shown together.

Sample	$T_{NI} (^{\circ}K)$	$T^{**} (^{\circ}K)$	β	Δn_0
D6	400	400.7	0.12	0.26
D7	385.4	387.8	0.25	0.40
D8	389.3	389.8	0.13	0.24
D9	380.8	381.3	0.18	0.31
D10	381.9	382.9	0.15	0.25
Mixture	382.6	383.8	0.16	0.28

Table 6.2: Estimated values of T^{**} , the exponent β and Δn_0 for 5 dimers and the mixture. These are the parameters of Haller's extrapolation formula. Both β and Δn_0 exhibit odd-even effect.

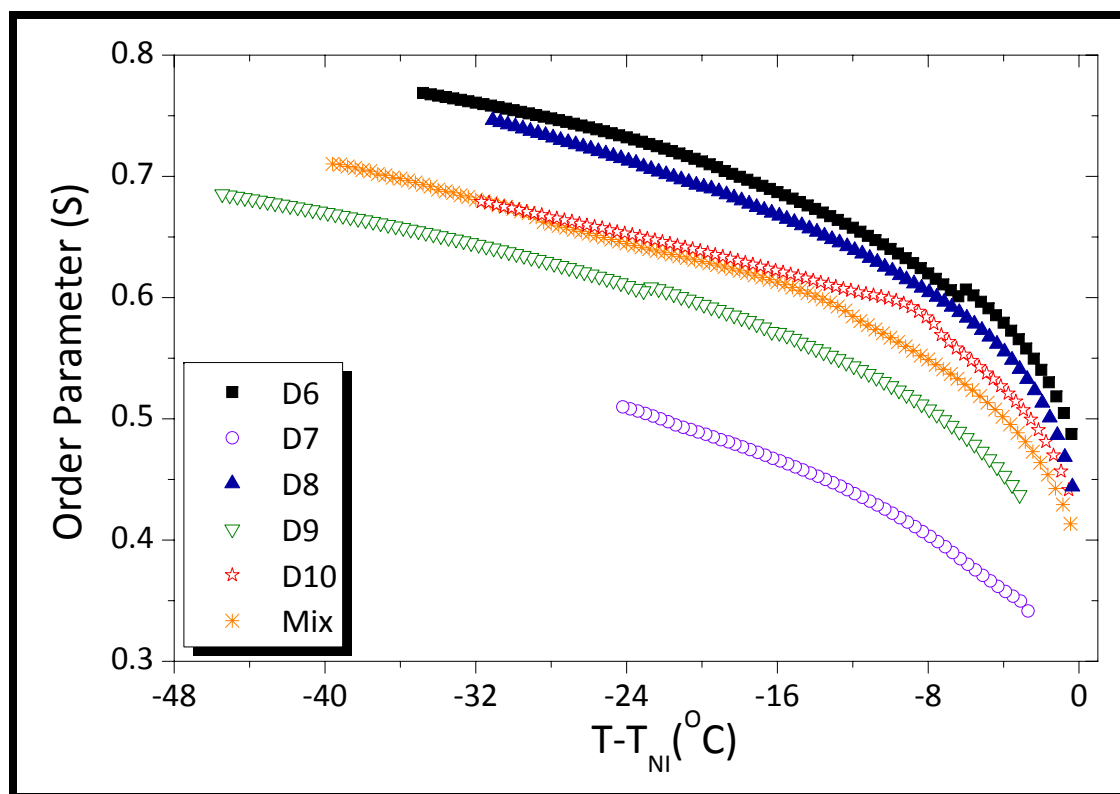


FIGURE 6.6: Dependences of order parameter (S) of 5 dimers and the mixture on the relative temperatures.

dependences of Δn of all the homologues are plotted in the same diagram (Figure 6.5). Even though all homologues have even number of carbon atoms in the chain, when the number of C atoms between the oxygen and the sulphur atoms of *one monomer is even*, Δn is lower than that of the next homologue with an *odd* number of C atoms, deep inside the nematic phase. Further, above the N–N transition in D6, the Δn values are higher than those of D7. The temperature variation of Δn in D7 has a higher slope at low temperatures than in all other cases.

- (iii) The order parameters are calculated by Haller extrapolation method[40] (for detailed description see Section 3.3.1) The order parameter of all the samples increase with decreasing temperature. The odd-even effect mentioned above for Δn is even more strongly evident in the order parameter data(Figure 6.5) *though surprisingly now the even homologues have higher values than the odd homologues*. The difference in the order parameters of D6 and

D7 is particularly large. The parameters of the Haller's extrapolation formula are shown in Table 6.2. Both the parameters β and Δn_0 exhibit odd-even effect showing low values for even dimers compared to those of the next homologues with odd monomers.

6.3.2 Dielectric Constants

- (i) The dielectric constants of all the samples are measured at frequency of 5.64 kHz. The dielectric constant in the isotropic phase decreases with increase in the chain length of the dimer (see Figure 6.7). $\epsilon_{\text{iso}}(\text{D6})$ has highest value and $\epsilon_{\text{iso}}(\text{D10})$ has the lowest value. In the mixture, $\epsilon_{\text{iso}}(\text{D6}) > \epsilon_{\text{iso}}(\text{Mix}) > \epsilon_{\text{iso}}(\text{D10})$. This is a result of weak polarizability of CH_2 units.
- (ii) In all the samples the dielectric constant perpendicular to the director (ϵ_{\perp}) decreases with decreasing temperature. This is characteristic of samples having *positive* dielectric

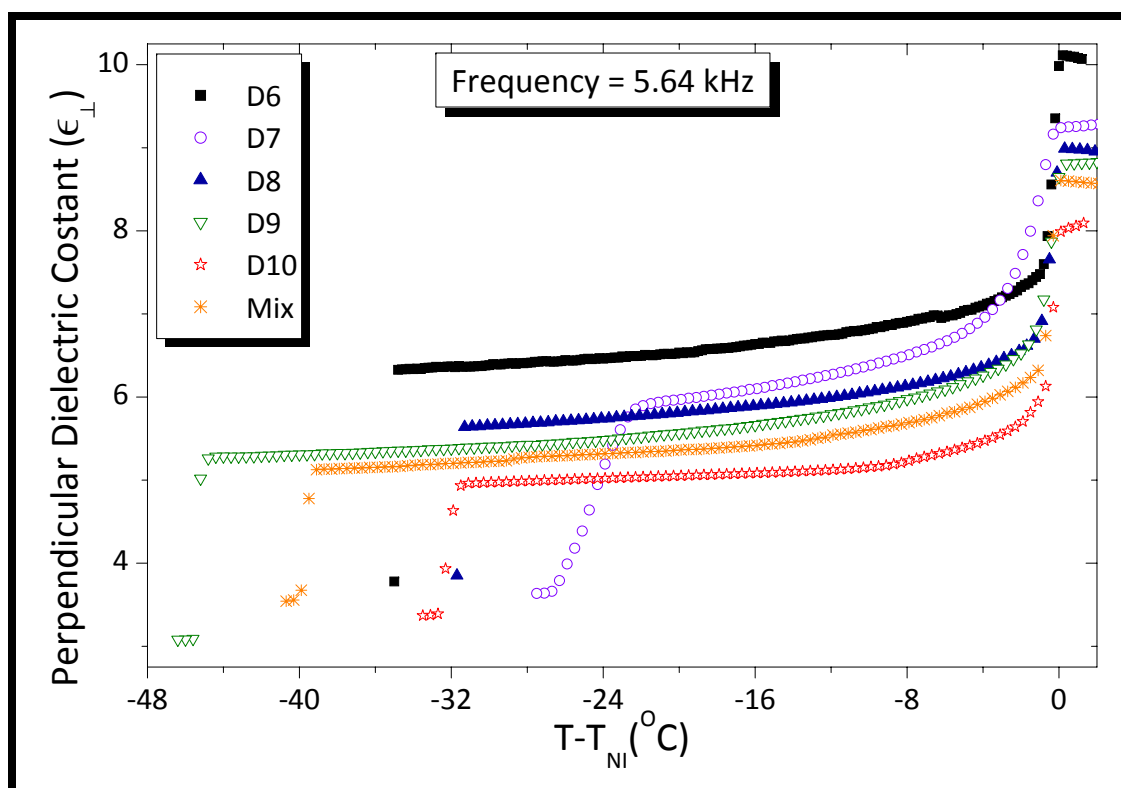


FIGURE 6.7: Dependences of ϵ_{\perp} of 5 dimers and the mixture on the relative temperatures. The steep fall at a lower temperature indicates crystallization. Frequency of measurement : 5.64 kHz

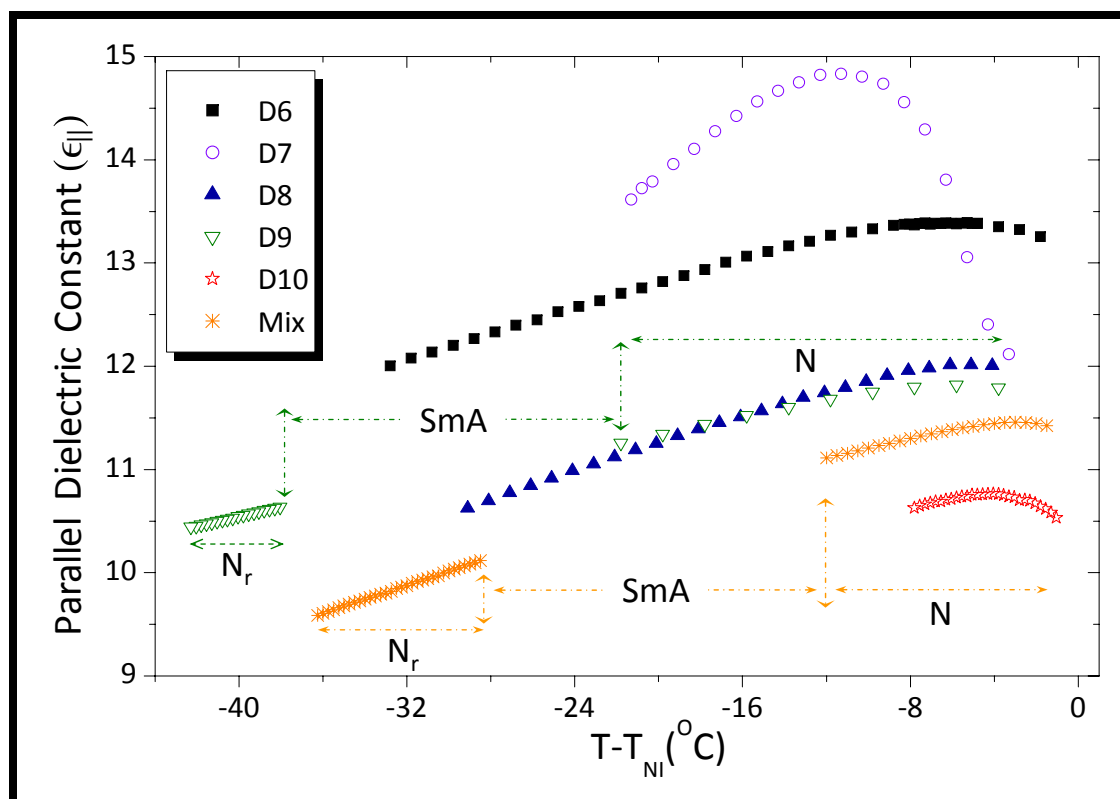


FIGURE 6.8: Dependences of $\epsilon_{||}$ of 5 dimers and the mixture on the relative temperatures.

anisotropy. In the nematic phase, ϵ_{\perp} values decrease with increase in chain length. Again the only exception is seen between D6 and D7 close to T_{NI} , in $\sim 3^{\circ}\text{C}$ temperature range. ϵ_{\perp} falls sharply close to crystallization temperature (see Figure 6.7). In D6 dimer a small jump is seen in ϵ_{\perp} in the nematic phase at the N–N transition temperature. Again in D7, ϵ_{\perp} has the steepest variation with temperature, as in the case of Δn .

- (iii) The dielectric constant parallel to the director ($\epsilon_{||}$) of all the samples are measured by applying high electric fields and extrapolating to $1/V = 0$. A detailed description of the method is given in Section 2.7 of Chapter 2. These measurements are possible only in the nematic phase. In all the cases as the temperature is lowered from T_{NI} , $\epsilon_{||}$ increases, reaches a maximum and then decreases slowly. There is a clear indication of odd-even effect in $\epsilon_{||}$, the values corresponding to even C atoms in the monomer moiety being lower than that of the preceding odd homologue (see Figure 6.8). $\epsilon_{||}$ of D7 exhibits the steepest increase

as the temperature is lowered from T_{NI} , and has the highest maximum value compared to all other samples (see Figure 6.8). $\epsilon_{||}$ can be measured only in the nematic and re-entrant nematic phases and $\epsilon_{||}$ decreases as the temperature is lowered in N_r phase also. $\epsilon_{||}$ values of the mixture lie between those of D6 and D10 (Figure 6.8).

The two linked monomers with the flexible spacer have cyano end groups pointing in *opposite* directions(see structure shown Figure 6.2). Nevertheless, $\epsilon_{||}$ shows fairly large values in all the dimers(Figure 6.8), implying that there is a significant contribution from orientation polarization of the two polar monomers(see Chapter 1). This in turn is possible only if the two monomers reorient relatively independently which appears to be possible as the disulphide bridging group makes the linkage chain extremely flexible. The decrease in $\epsilon_{||}$ at lower temperatures implies that the flexibility of the chain *decreases* at lower temperatures, thus reducing the contribution from orientation polarization to $\epsilon_{||}$. This trend is opposite to that shown by a pure monomer like 8OCB(see Figure 3.9).

- (iv) The dielectric anisotropy, ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$) of all the samples reflect the trends in $\epsilon_{||}$ (Figure 6.9a). $\Delta\epsilon$ increases with decrease in temperature, reaches a maximum and then decreases slowly. Again the temperature variation of $\Delta\epsilon$ of D7 dimer is extremely high both above and below the maximum.
- (v) The average dielectric constant, $\epsilon_{av} = (\epsilon_{||} + 2\epsilon_{\perp})/3$, of all the samples (except D7) slowly decreases with decrease in temperature(Figure 6.9). ϵ_{av} of D7 shows an anomalous trend : it sharply increases, reaches a maximum and falls comparatively faster than those of other dimers and the mixture (see Figure 6.9b). In the reentrant nematic phase, ϵ_{av} of the mixture decreases more rapidly compared to that of D9. The dielectric properties depend sensitively on the *short range* order[45], which is not taken into account in the Maier-Meier theory(see Equations 1.17 and 1.18)[18]. Δn is proportional to the order parameter while $\Delta\epsilon$ shows a more complicated variation, as the $\Delta\epsilon$ versus Δn plot in Figure 6.10 shows.
- (vi) In the nematic phase of the D6 dimer, a jump is seen in the optical transmitted intensity and the perpendicular dielectric constant at the same temperature ($T - T_{NI} \sim -6.2^\circ\text{C}$) indicating a nematic-nematic transition. We have conducted two independent experiments

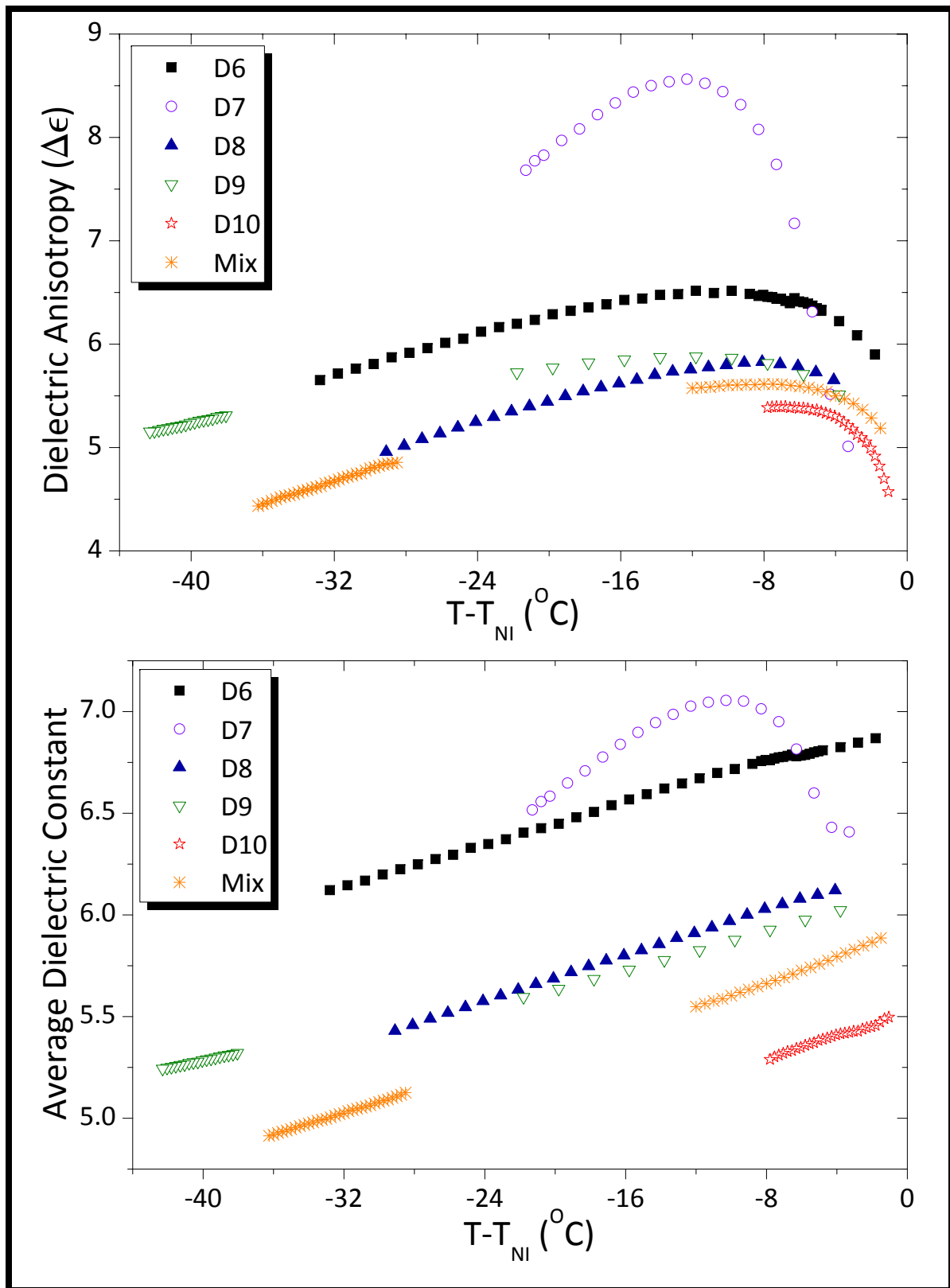


FIGURE 6.9: (a) Dependences of dielectric anisotropy ($\Delta\epsilon$) of 5 dimers and the mixture on the relative temperatures. (b) Dependences of average dielectric constant (ϵ_{avg}) of 5 dimers and the mixture on the relative temperatures.

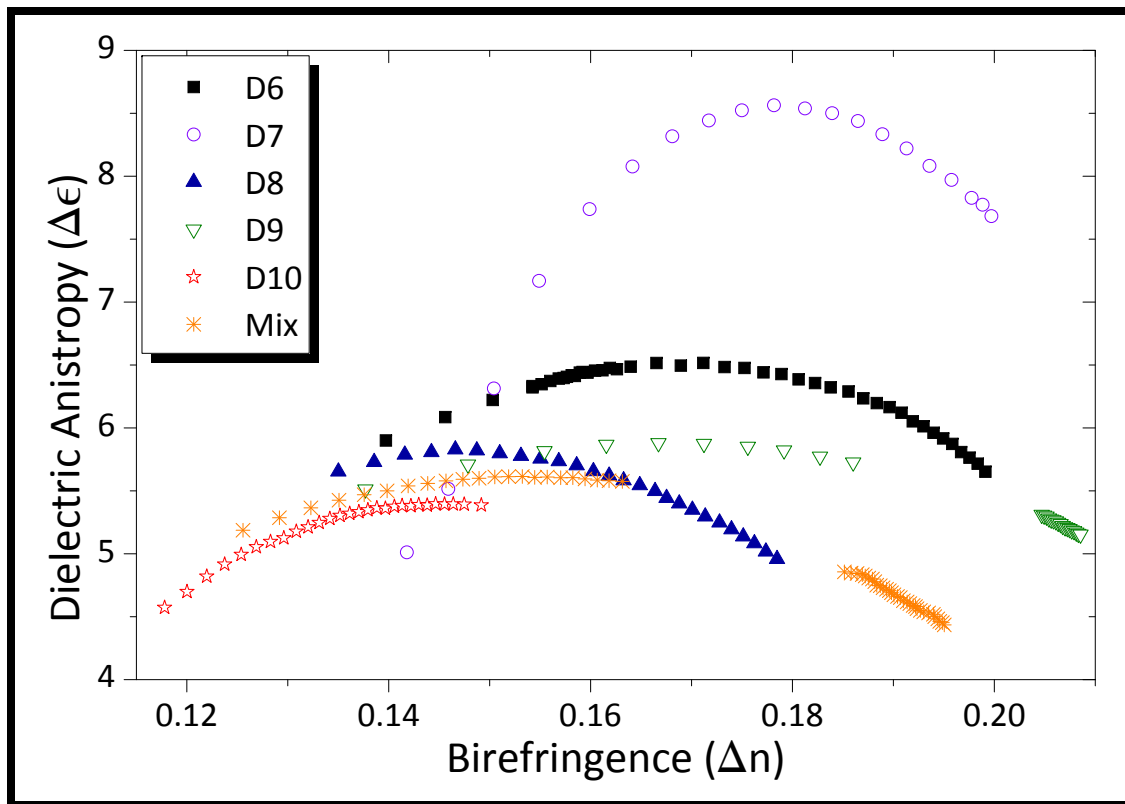


FIGURE 6.10: Dielectric anisotropy ($\Delta\epsilon$) versus birefringence (Δn) of all the samples.

with different cell thicknesses ($L = 7.6 \mu\text{m}$ and $13.3 \mu\text{m}$). In both the cells the jump is seen at the same temperature of 120.5°C (see Figure 6.11). Optical intensity jumps to a higher value indicating that the birefringence and hence the order parameter have jumped to a *lower* value. ϵ_{\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 (see Figure 6.12). It signifies a weakly first order N–N transition, which occurs because of a change in the *short range order* in the medium[1, 88].

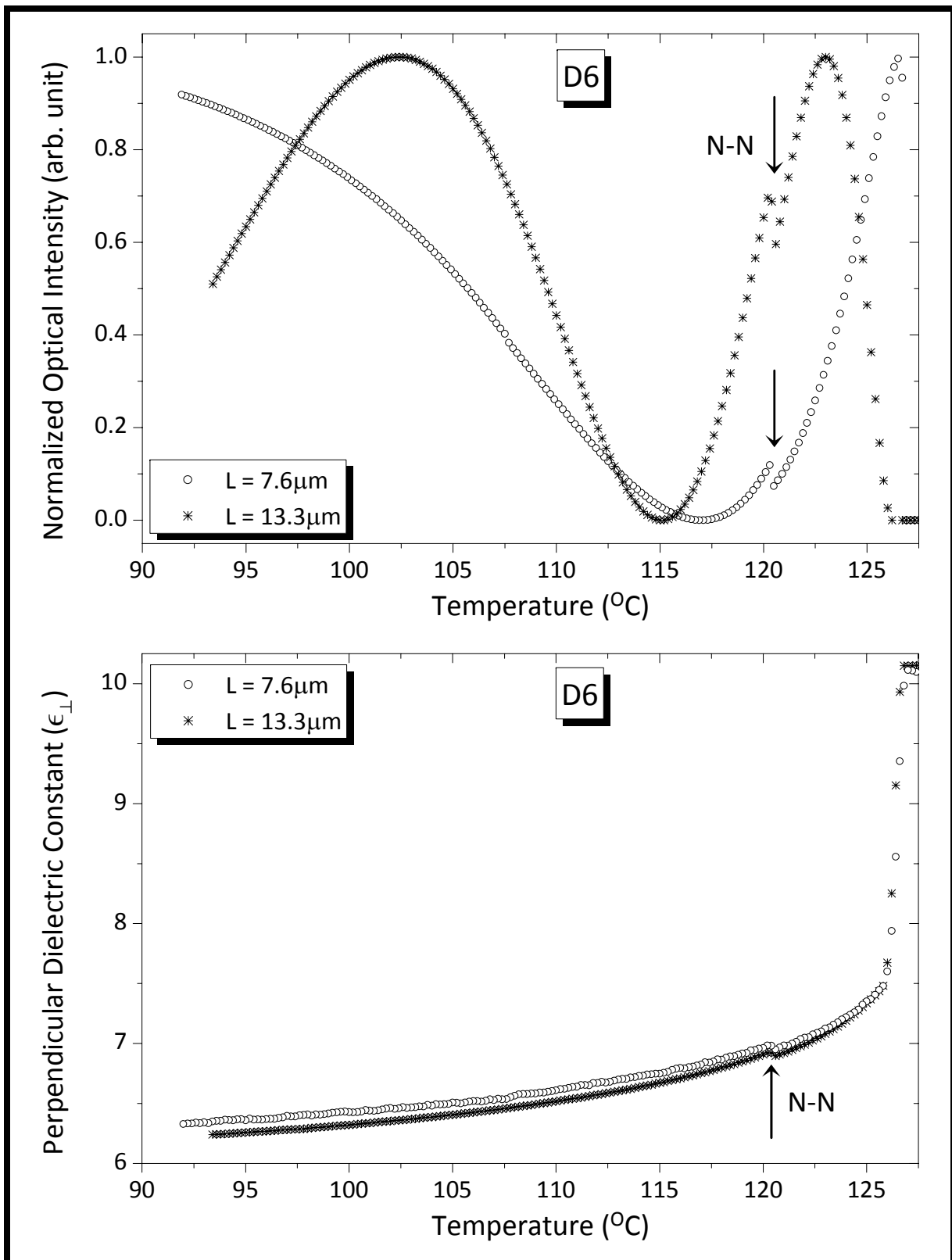


FIGURE 6.11: Detection of N–N transition of D6 dimer in two cells of different thicknesses, using optical (upper section) and dielectric (lower section) measurements.

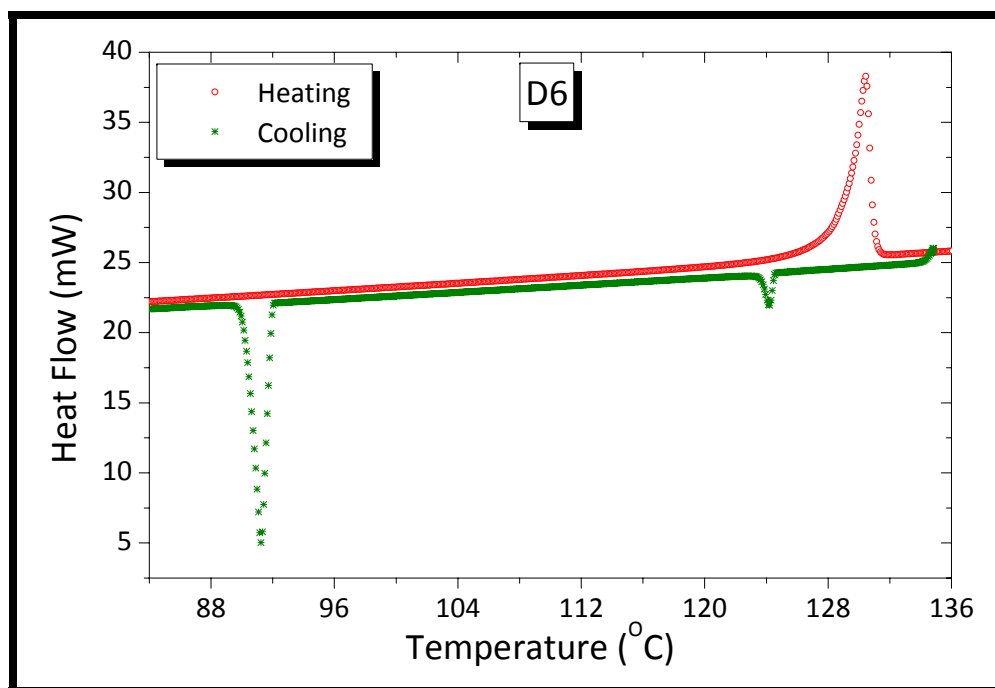


FIGURE 6.12: DSC thermogram of D6 dimer. The large peak in the heating run is from crystal to isotropic transition. The I-N transition occurs only on cooling at $\sim 124^{\circ}\text{C}$. The large peak in the cooling run corresponds to crystallization. There is no evidence of N-N transition.

6.3.3 Elastic Constants

- (i) The splay elastic constant is measured using Fréedericksz threshold voltage. Figure 6.13 and 6.14 show K_{11} as functions of temperature for D9 and the mixture and all other dimers respectively. Only D9 and the mixture exhibit the re-entrant nematic phase. In all the samples K_{11} increases with decrease in temperature. At any relative temperature, K_{11} of the mixture is higher than that of D9 dimer. The higher temperature nematic range is smaller in the mixture compared to D9 but the reentrant nematic (N_r) range is larger. Again D7 dimer shows a very rapid variation of K_{11} as the temperature is lowered from T_{NI} and reaches a *saturation* close to the crystallization temperature. In the N_r phase also K_{11} increases with decrease in temperature (see Figure 6.13). In the D6 dimer very close to N-N transition point K_{11} varies smoothly, and no indication of a transition is seen in Figure 6.14. At the same relative temperature, K_{11} shows a small odd-even effect close to T_{NI} , the even members having higher values.

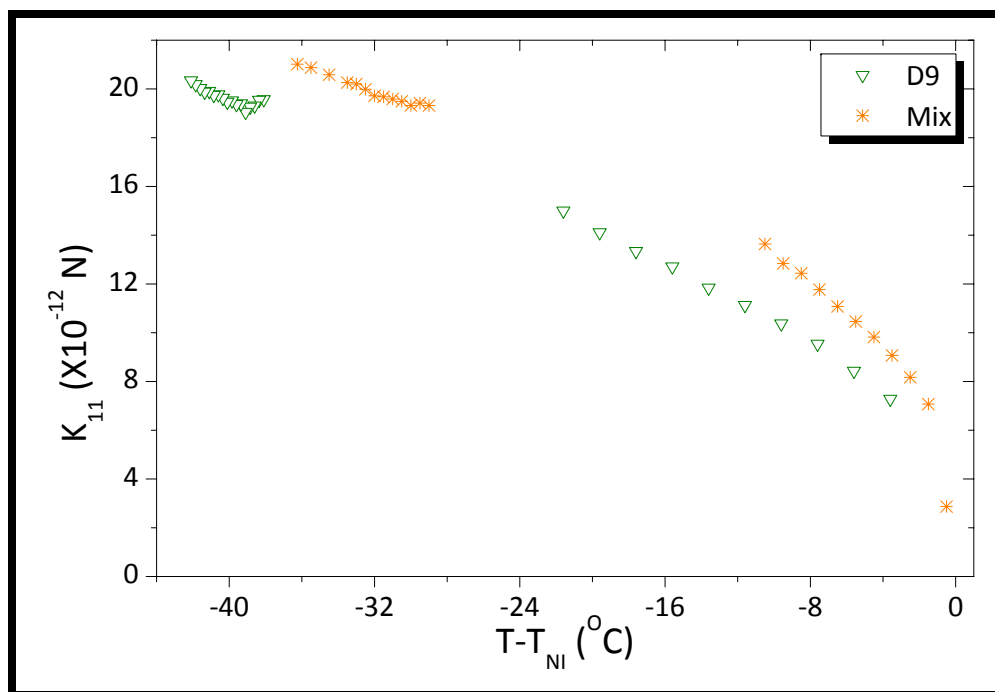


FIGURE 6.13: Dependences of K_{11} of D9 and the mixture on the relative temperatures. These two samples exhibit the re-entrant nematic phase.

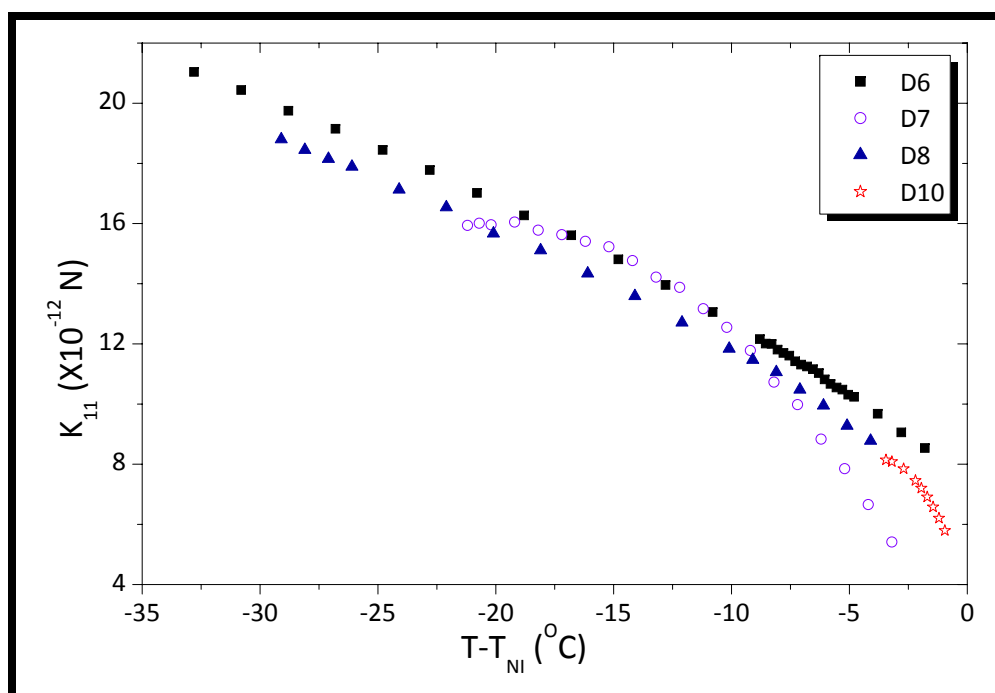


FIGURE 6.14: Dependences of K_{11} of D6, D7, D8 and D10 dimers on the relative temperatures.

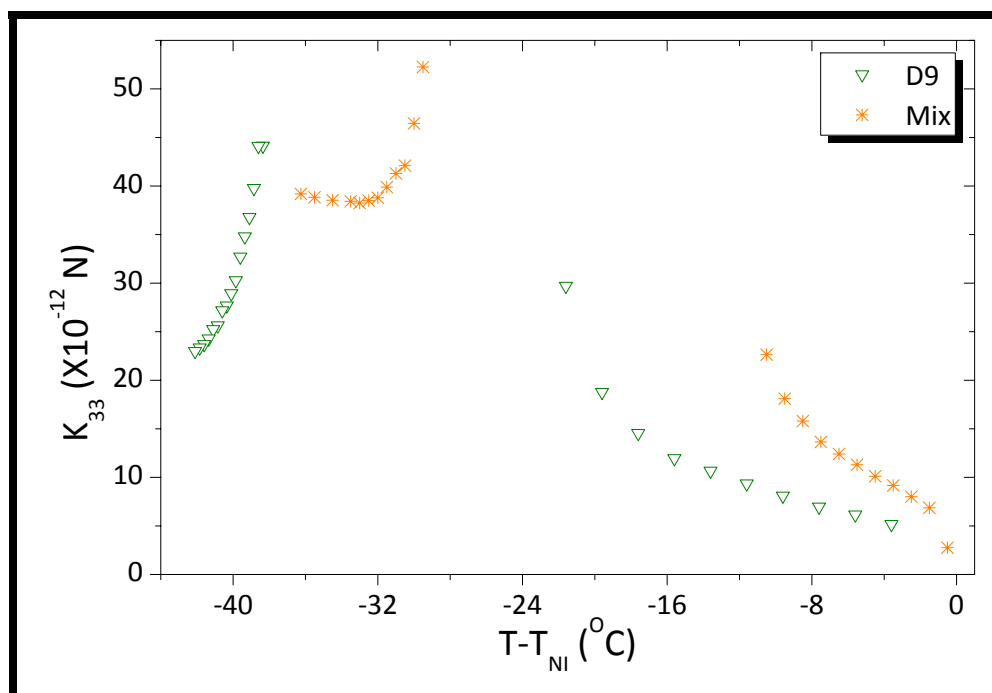


FIGURE 6.15: Dependences of K_{33} of D9 and the mixture on the relative temperatures. These two samples exhibit the re-entrant nematic phase.

- (ii) The bend elastic constant (K_{33}) is obtained by the electro optic measurement above the Fréedericksz threshold voltage and an iterative fitting procedure. The detailed description of the method is given in Section 2.9 of Chapter 2. In the higher temperature nematic phase, K_{33} increases with decrease in temperature in D9 and the mixture (see Figure 6.15). D9, D10 and the mixture exhibit the SmA_d phase, and K_{33} diverges close to nematic-smectic transition temperature (T_{AN}) (see Figure 6.15). Close to T_{AN} , as the smectic-like short range order builds up, it is very difficult to bend the director. This causes the divergence of the bend elastic constant[1, 2]. In other dimers (*viz.* D6, D7 and D8) with decrease in temperature, K_{33} increases smoothly(see Figure 6.16). The divergence of K_{33} is also observed when the temperature in the N_r phase approaches T_{AN} (Figure 6.15) 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. Also, as in the case of K_{11} , K_{33} has a much steeper variation with temperature in the higher temperature range of the nematic phase of D7

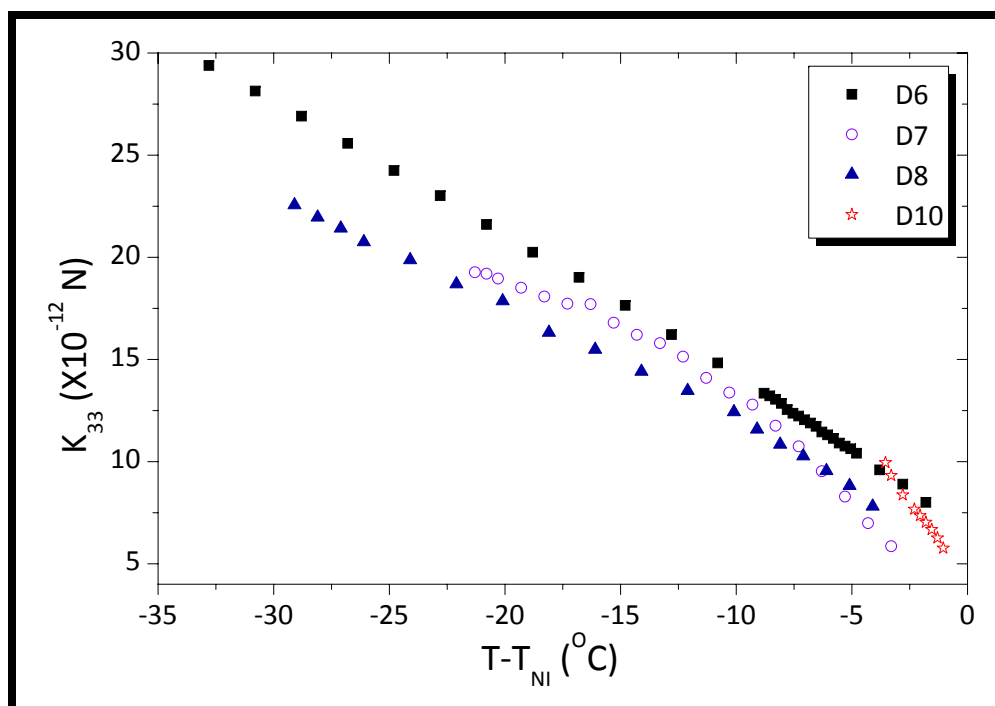


FIGURE 6.16: Dependences of K_{33} of D6, D7, D8 and D10 dimers on the relative temperatures.

than in the lower temperature range.

The temperature dependences of the elastic constant ratio K_{33}/K_{11} of all the dimers and the mixtures are calculated and shown in Figure 6.17. It is larger than 1 in most cases. Only in D9, the ratio significantly less than 1 close T_{NI} , and diverges as T_{AN} is approached. The low value indicates a layered *cybotactic* short range order with only a few molecules[31, 90, 91], and a divergence indicates a pretransitional effect[1].

6.4 Odd-Even Effects in the Observed Properties

As we have noted earlier, all the dimers studied have an even number of carbon atoms, and two sulphur atoms in the flexible chain connecting the two aromatic cyanobiphenyl end groups. This means that all of them have rod-like conformations. Nevertheless, some odd-even effect is seen in various physical properties, depending on the number of carbon atoms in each monomer. The N-I transition temperature itself shows this trend (Table 6.1), with the even numbers having larger

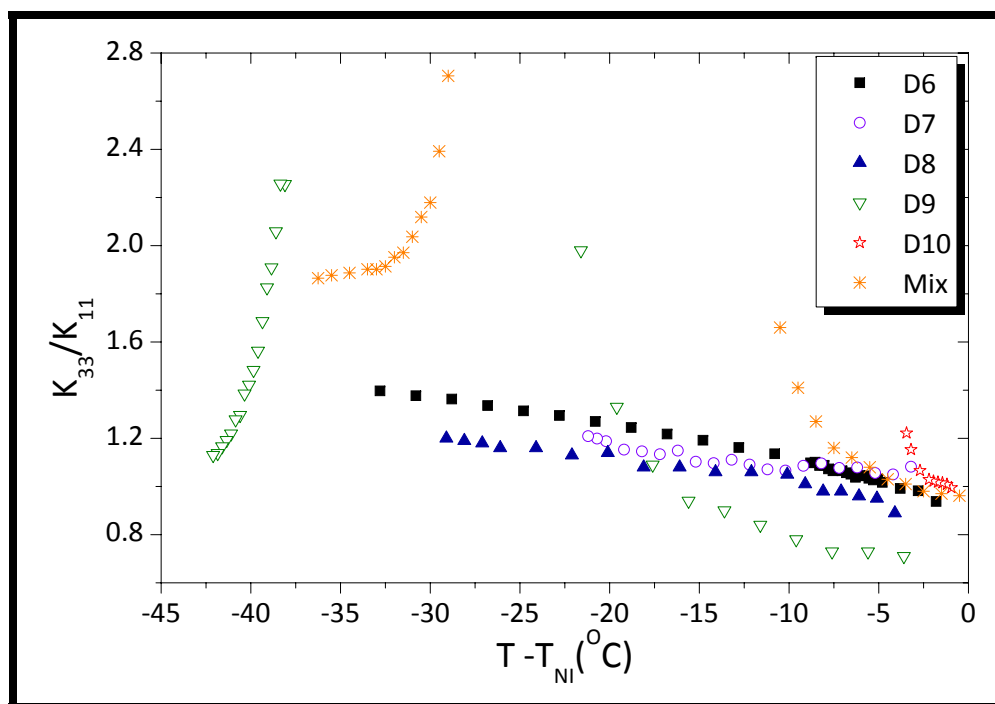


FIGURE 6.17: Relative temperature variations of the ratio of elastic constants (K_{33}/K_{11}) of all the system studied.

T_{NI} values. This is similar to the odd-even effect seen in the alkoxycyanobiphenyl monomers themselves[2]. This arises because the lowest energy all-trans configuration of the alkoxy chain leads to an alignment of the end C–C bond along the molecular long axis in the case of a chain with even number of carbon atoms increasing the overall anisotropy of the molecule. On the other hand, in the homologue with odd number of carbon atoms the end C–C bond makes a large angle with the molecular long axis, reducing the overall anisotropy of the molecule. This trend is reflected in the dimer also. The sulphur atoms of the bridging group do not change this relative anisotropy of even and odd homologues. The dimers of course have a much larger length to width ratio, thus increasing the nematic to isotropic transition temperature compared to that of a monomer. We can compare the properties of 8OCB and D8 dimer, as the monomeric moiety of D8 has an 8-carbon atom chain like 8OCB. While 8OCB exhibits both N and SmA_{db} phases, D8 exhibits only a nematic phase with a smectic A_d like cybotactic short range order. The order parameter follows the same odd-even effect as in the alkoxycyanobiphenyl series, *ie.*, the even members have higher order parameters. But curiously, Δn , $\epsilon_{||}$ and $\Delta\epsilon$

show exactly the *opposite odd-even effect*, the odd homologues having higher values than the neighbouring even homologues. This is 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 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 ϵ_{\parallel} (Figure 6.18). 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 CH₂–CH₂ bond as the sulphur atoms are much smaller in size compared to the bulky CH₂ groups. Indeed the sharp increase in ϵ_{\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 $\sim 100^{\circ}\text{C}$, and ϵ_{\parallel} starts to decrease sharply. As the temperature is lowered, the conformational freedom of chains reduces and the orientation contribution to ϵ_{\parallel} decreases.

The elastic constants K_{11} and K_{33} which strongly depend on the order parameter are higher for the even members than the neighbouring odd members close to T_{NI} . The elastic constants have the lowest values for D7 near T_{NI} , as the two moieties are decoupled somewhat better in this case at the higher temperatures of the nematic range and the dimers can adopt their shape to the splay and bend distortions in the medium.

We can compare the properties of 8OCB with D8, both of which have 8 carbon atom long chains in the monomeric units. At $T_{NI} - 10^{\circ}\text{C}$, ϵ_{\parallel} of 8OCB is ~ 14.3 while that of D8 is ~ 12 due to the restricted reorientation in the dimer. The dimer has a much larger length to width ratio and as such, K_{11} of dimer is $12 \times 10^{-12}\text{N}$ at $T_{NI} - 10^{\circ}\text{C}$ (Figure 6.14), which is about 1.5 times larger than that of 8OCB[92] at $T_{NI} - 10^{\circ}\text{C}$ (Figure 3.11). On the other hand, K_{33} has similar values in both cases (see Figures 3.12 and 6.16), due to the easier adaptation of the bend distortion in the dimer.

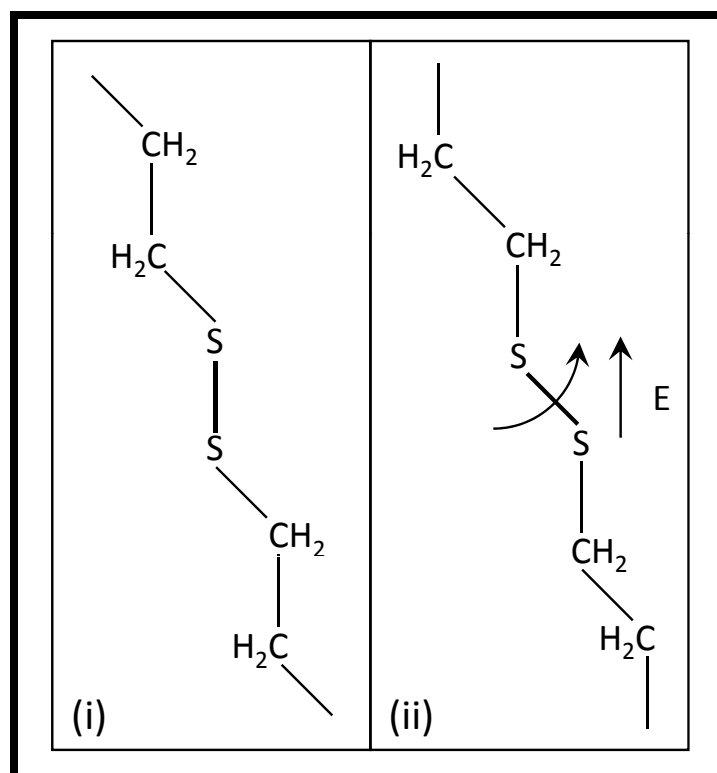


FIGURE 6.18: The configuration near the central disulphide linkage group in (i) even homologues and (ii) odd homologues. The long axis of the dimer is vertical. In the odd homologue, a reorientation about the S-S bond is easier under an external field.

6.5 Conclusions

The studies on the dimers made of two alkoxy cyanobiphenyl moieties linked through a flexible disulphide bridge have brought out several unusual features. Though all the dimers have an even number of carbon atoms in the flexible chains, the birefringence, the order parameter and ϵ_{\parallel} show clear odd-even effects, depending on the number of carbon atoms in the alkoxy chain of a monomeric unit. The lowest homologue D6 exhibits an N–N transition. D9 and a mixture exhibit the reentrant nematic phase. D7 exhibits unusual temperature dependences. It has the steepest variations in Δn (and S), K_{11} and K_{33} near T_{NI} . The elastic constants K_{11} and K_{33} tend to get saturated at lower temperature in the nematic phase. It also exhibits the highest value of ϵ_{\parallel} in the entire series. These trends show that the short range order varies with temperature in all the dimers, giving rise to N–N transition in D6, unusual temperature dependence of physical properties in D7 and the reentrant nematic phase in D9 dimer.

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