

Chapter 8

SUMMARY AND CONCLUSION

The research on liquid crystals is multidisciplinary in nature and involves many branches of science viz. Chemistry, Physics, Biology, Electric and Electronic Engineering. The remarkable development in the liquid crystal science and technology is closely connected with specific physical properties of the liquid crystalline materials. The electro-optical parameters of liquid crystal displays, such as threshold voltage, response times, contrast ratio and multiplexity are strongly dependent on the anisotropy in optical, electrical, magnetic and elastic properties of liquid crystal materials. In this respect the relationships between molecular structure and various properties of the different liquid crystal phases are important. The nematic liquid crystal phase is technologically the most important of the many different types of liquid crystal phases and is used virtually in all commercially available liquid crystal displays. Accordingly, the structure-property relations of nematic liquid crystalline materials are extremely important. With this aim and objective I have determined few physical properties of some liquid crystalline materials from X-ray diffraction, optical birefringence, density and dielectric constant measurements. The salient features of the different works undertaken by me are briefly described below.

In chapter 1, I have presented a short review on liquid crystals especially thermotropic liquid crystal systems. Among the different modifications I have concentrated my discussions mainly on the nematic phase which is studied in this theses.

Different theories of liquid crystals which can be verified by X-ray diffraction, optical birefringence and dielectric studies, have been described in chapter 2. Brief description of the experimental techniques employed in this work have also been reported. Methods of calculations of different physical parameters viz., orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, apparent molecular length, interplaner spacing of cybotactic groups, length of the building unit constituting cybotactic group, intermolecular distance, refractive indices, molecular polarizabilities, dielectric parameters, dipole moments and their orientations, dipole correlation factors etc. have been outlined in this chapter.

In chapter 3, the results of the measurements of the transition temperatures from optical polarizing microscopic studies and transitional enthalpy and entropy values from DSC studies of the compounds *p*-n-pentylphenyl- 2-chloro- 4- (*p*-n-pentylbenzoyloxy)- benzoate and *p*-n-octylphenyl -2-chloro -4-(*p*-n-heptylbenzoyloxy) -benzoate and mixtures of different mole fractions of them have been obtained. All the compounds are found to exhibit nematic phase with supercooling effect far below room temperature. Marble textures were observed under a crossed polarizing microscope, however, near N-I transition typical schlieren textures, consisting entirely of $|s|=1$ disclinations were observed thereby indicating that the nematic phase is uniaxial in character. Mixtures of three different molefractions of them form nematic phase at well below room temperature and the equimolar mixture is found to be an eutectic mixture. Results of the small angle X-ray scattering studies on the magnetically aligned samples have been discussed throughout their mesomorphic ranges. X-ray diffraction patterns show that in each case the mesophase is skewed cybotactic nematic. The average intermolecular distance, D is found to be $\sim 5.10\text{\AA}$ slightly more than the usual value $4.9\text{-}5.0\text{\AA}$ and this may be due to the presence of bulky $-\text{Cl}$ group in the lateral position. The interplaner spacing of cybotactic groups l increases systematically from pure PCPB to OCHB through different compositions of OCHB. Molecular tilt angles are found to be in between 20 to 35 degrees. l 's in all cases are found to be less than the stereo model length of the molecules in all *trans*-configurations. This may be either due to the tilt of the molecules in the plane of a cybotactic group or the molecules may not be in most extended conformations or both. Temperature dependence of these parameters has been discussed. From the calculated size of the cybotactic group, it is observed that the transverse correlation in the group extends upto 5-6 molecular diameters. Orientational order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, for the pure compounds and their eutectic mixture have been determined and compared with Maier-Saupe theoretical values. $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values of the eutectic mixture have been found to lie in between those of the individual components and are more consistent with Maier-Saupe theoretical values than the pure compounds. Negative $\langle P_4 \rangle$ value was not found in any case.

In chapter 4, I have presented the refractive index and density values of PCPB, OCHB and their eutectic mixture (Mix-II) which happens to be equimolar mixture. The density of PCPB is highest but that of Mix-II is lowest. Thus like molecules with shorter but symmetric alkyl chains (PCPB) is packed more efficiently than the molecules with longer but asymmetric alkyl tails (OCHB). In the mixture the unlike molecules, though present in equal members, are less densely packed than the molecules of the pure compounds. Refractive indices (n_o , n_e) are measured at different temperatures for pure components and the eutectic mixture. At T_{NI} the refractive index and density values show first order phase transition. The average refractive index is found to decrease very slowly with temperature. In OCHB it is substantially less than that of PCPB over the entire nematic range and for the mixture it is further less. Thus \bar{n} follows the trend of density. The birefringence values of the eutectic mixture are less than the individual components at higher temperature region and are in-between at lower temperature region. It decreases fast with temperature. I have also calculated the optical polarizabilities (α_o , α_e) by Vuks' and Neugebauer's methods. The principal polarizability parameters of all the compounds have also been compared with those calculated from additivity rule of bond polarizability. Average polarizability $\bar{\alpha}$ shows higher value for the member having longer chain length and the mixture possesses intermediate value. The polarizability anisotropy ($\Delta\alpha$), like Δn , falls rapidly with temperature. Below the reduced temperature $T^*=0.19$ the $\Delta\alpha$ values of mix II lie in between the pure compounds but above that it is less. However, the normalised polarizability anisotropy ($\Delta\alpha/\bar{\alpha}$) is found to decrease with chain length suggesting that the core region mainly contributes to $\Delta\alpha$ but the chain part contributes more to $\bar{\alpha}$. The orientational order parameter $\langle P_2 \rangle$ at different temperatures has also been determined and compared with Maier-Saupe theoretical values. $\langle P_2 \rangle$ values of OCHB are found to be greater than those of PCPB and Mix-II at higher temperatures and are consistent with those determined from the X-ray studies, described in chapter 3. It is also found that OOP values of OCHB above $T^*=0.184$ are more than Maier-Saupe values, but those of PCPB and mixture are less. Thus

when 50% PCPB molecules are replaced by OCHB molecules (PCPB→Mix-II) almost no change of OOP takes place. However when both the pentyl chains of PCPB are replaced by octyl and heptyl chains (PCPB→OCHB) the OOP increases. Lower tilt angle of OCHB than PCPB and presence of asymmetrical chains might be the reason for this increase.

In chapter 5, the free molecule dipole moment of PCPB and OCHB have been determined by measuring the effective dipole moments of solution in a non-polar solvent and found to be 4.36D and 4.20D respectively. The results of the measurements of dielectric constants ϵ_{\parallel} and ϵ_{\perp} as functions of temperature at a frequency of 10 kHz have also been discussed. All the compounds show positive $\Delta\epsilon$ but it is considerably less than that for strong on-axis dipole like nCBs. In all cases a slight upward jump in $\bar{\epsilon}$ is found in the isotropic phase near T_{NI} suggesting the presence of antiferroelectric short-range order in nematic phase. Influence of structural modifications on the value of $\Delta\epsilon$ has also been discussed. All the permittivity parameters (ϵ_{\parallel} , ϵ_{\perp} , $\bar{\epsilon}$ and $\Delta\epsilon$) of the eutectic mixture are found to be less than those in pure components. Effective dipole moments μ and their inclination angles β with the molecular long axis within nematic phase are also determined following Maier and Meier equations. In each case μ values are found to be less than that of free molecules by about 1D thereby supplementing the idea that short range antiferroelectric order exists in the nematic phase in all the cases. Quantitative measurements of dipole correlation factor have been done using Bordewijk theory of anisotropy dielectrics. It is observed that there exists considerable antiparallel ordering of the molecular dipoles parallel to the nematic director and no significant correlation is observed perpendicular to it. Short range order parameters have also been evaluated at different temperatures. In the above three chapters properties of these materials have been compared with other structurally similar compounds.

In chapter 6, the results of the transition temperature measurements of the compounds of the series (nCHBT in short, n=2,4-9,11,12) have been presented. Nematic marble textures were observed with typical schlieren textures at T_{NI} . Some of them (4CHBT and 5CHBT) show monotropic transition. X-ray diffraction

photographs of magnetically oriented samples have been analysed and found to exhibit ordinary nematic phase. The average intermolecular distance is found to be $\sim 5.1\text{\AA}$ for all of them. Slight higher values of D may be due to presence of non-planer cyclohexyl ring in the core structure. The apparent molecular length, l varies from 22.71\AA for 4CHBT to 32.14\AA for 11CHBT at $0.98T_{NI}$. Temperature dependence of these parameters has been discussed. Average values of apparent molecular lengths in their nematic range are found to be ~ 1.15 times of their respective molecular model lengths indicating the presence of bimolecular association. However this ratio is smaller than the value, 1.4 found in nCBs; 1.3 in nPCH. So the molecular overlap in nCHBT is certainly more than that in both nCBs and nPCHs. Presence of molecular association has also been observed from dielectric studies, discussed in chapter 7. The orientational order parameters, $\langle P_2 \rangle$ were found to be slightly higher than Maier-Saupe theoretical values and lower than the values obtained from refractive index studies; whereas $\langle P_4 \rangle$ values were found to be comparable with Maier-Saupe values. The results have been discussed in relation to three other similar homologous series, viz., nCB, nPCH and nBT. For example, $\langle P_2 \rangle$ values at common reduced temperature $T^*=0.98T_{NI}$, of 5CHBT is found to be more than that of 5CB and 5PCH thereby indicating that the effect of change of the groups on order parameter is additive but the effect of terminal group predominates.

In chapter 7, the results of the temperature dependence of density and refractive indices n_o , n_e , n_{iso} of 11CHBT and dielectric permittivities, $\epsilon_{||}$, ϵ_{\perp} , ϵ_{iso} of 11CHBT and 12CHBT have been discussed. In 11CHBT density varies linearly with temperature on both sides of T_{NI} . \bar{n} remains almost constant with temperature in 11CHBT whereas in nCB, nPCH, PCPB and OCHB it decreases slowly. Optical polarizabilities have also been calculated. The orientational order parameter $\langle P_2 \rangle$ have been determined and found to be less than that of Maier-Saupe values unlike other members of the series. From dielectric measurements both 11CHBT and 12CHBT are found to show positive dielectric anisotropy. In both cases it is found that $\bar{\epsilon}$ is less than the extrapolated value of ϵ_{iso} . Moreover, effective values of dipole moment in nematic phase is found to be less than the free molecule dipole moment

These observations suggest the existence of short range antiferroelectric order in nematic phase. Calculated Kirkwood correlation factors indicate more antiparallel correlation along molecular axis than in the perpendicular direction.

In chapter 7, effect of chain length on some mesogenic properties have also been presented. It was reported earlier that isothiocyanatobenzene series show odd-even effect in the anisotropies of dielectric constants, conductivities and also in activation energy of ionic movement at temperatures 2°C below N-I transition. Comparing the different reported parameters it is further observed that all the temperatures T_m , T_{NI} and $T_{N\rightarrow K}$ (crystallization temperature) show OE effect but transition enthalpies ΔH_m and ΔH_C do not show such behaviour and T_m , T_{NI} , T_{N-K} and ΔH_m are found to increase with chain length though ΔH_C shows a maxima at $n=6$. At common reduced temperature $T^*\approx 0.98T_{NI}$, the density of the compounds are found to decrease monotonically with chain length while the polarizability parameters α_e , α_o and $\bar{\alpha}$ are found to increase. However, polarizability anisotropy in both solid and nematic phase and $\Delta\alpha/\bar{\alpha}$ show distinct OE effect. Similarly n_e decreases smoothly with chain length but n_o and Δn show OE effect. Dielectric parameter $\epsilon_{||}$, ϵ_{\perp} , and $\Delta\epsilon$ behaves in the same way. Orientational order parameter $\langle P_2 \rangle$, determined both from X-ray scattering and refractive indices data, show no OE effect, $\langle P_4 \rangle$ also does not show such behaviour. The ratio $\ln\langle P_2 \rangle/\ln\langle P_4 \rangle$ as a function of number of carbon atoms remains more close to the value predicted by Faber's theory than Maier-Saupe theory. The ratio of apparent molecular length to their respective model length, which is a measure of molecular overlap, is found to be more or less constant in the series, so also the effective dipole moments (μ) and their inclination angle β with the long axis. Antiparallel association is found to exist in all the members. Kirkwood correlation factors g_{\perp} and $\Delta g = g_{||} - g_{\perp}$, are found to exhibit OE effect but $g_{||}$ does not show such effect. In all cases where OE effects are observed the even members are found to have lower values than the odd members except in cases of n_o and $g_{||}$. The effects of substituting a phenyl ring by a

cyclohexane ring and -NCS terminal group by -CN group on the above properties have also been discussed.

Finally the properties of the two group of materials studied in the thesis might be compared here. I have investigated two groups of nematogenic systems:

System-I : p-n-alkylphenyl- 2-chloro- 4- (p-n-alkylbenzoyloxy)- benzoates and their mixtures viz., PCPB, OCHB and Mix I, II and III.

System-II : 4-(*trans*-4'-n-alkylcyclohexyl)isothiocyanatobenzenes (nCHBT with n=3-12).

System-I is a three ring system with off axis dipole ($\mu \approx 4.3D$ and angle $\sim 40^\circ$) whereas system-II is a two ring system with almost axial dipole moment ($\mu \approx 3.50D$ and angle $\sim 10^\circ$). System-II compounds have low nematic range ($\sim 20^\circ C$) whereas system-I compounds have the high range ($>90^\circ C$). Mix II of the system-I has the highest temperature range spanning from -8 to $109^\circ C$. Nematic marble textures are exhibited by all the compounds, however, typical schlieren texture was observed near N-I transition temperature. Though higher homologues of system-I shows smectic and nematic phases the members of system-II posses only nematic phase.

X-ray diffraction studies confirm that system-I compounds posses skewed cybotactic nematic modification but nCHBT system exhibit normal nematic phase. In both systems the average intermolecular distance is found to be slightly greater than 5\AA , the value found in n-alkyl cyanobiphenyls. Presence of lateral bulky -Cl atom is assumed to be responsible for this in system-I and in system-II it is due to the replacement of the phenyl ring by a bulkier cyclohexane ring. In system-I, both the interplaner spacing and length of the building unit of the cybotactic groups are found to be slightly less than their respective model lengths in all-*trans* configurations. However, dielectric study reveals antiparallel correlation among the nearest neighbours. These indicate the presence of bimolecular association with almost complete overlap of the molecules which are tilted and are not in their most extended configurations. In nCHBT system, however, the apparent molecular length is found to be slightly higher than their respective model lengths suggesting almost complete overlap of the most extended molecules in bimolecular association.

Mass density of system-I is greater than that of system-II but the number density shows opposite behaviour. Density of Mix-II is found to be less than that of the individual components in system-I. In both systems density values are found to decrease with increasing chain length.

Though there is no similarity of the structure between the two systems, extraordinary refractive index is found to decrease with temperature in both systems. Ordinary refractive index values are, however, found to increase with temperature in system-II but in system-I it decreases though increases near T_{NI} . Optical anisotropy values of both systems is found to be more or less same. However optical polarizabilities (α_e , α_o), average polarizability ($\bar{\alpha}$) and polarizability anisotropy $\Delta\alpha$ values of system-I is found to be greater than that of system-II. While the polarizability parameters α_e , α_o and $\bar{\alpha}$ are found to increase in both systems, but in system-I, $\Delta\alpha$ decreases with increasing chain length and in system-II an overall increment is noted. However the normalised polarizability anisotropy ($\Delta\alpha/\bar{\alpha}$) of the two systems is comparable.

Dielectric anisotropy $\Delta\epsilon$ in system-II is higher than that in system-I. This is expected because stronger dipole moments of system-I are off-axis. Dipole moments of the molecules in nematic phase are found to be less than that of free molecule in all cases, non-zero value of inclination angle with the molecular long axis is also observed. This angle is found to be much larger in system-I than in nCHBT system. Antiparallel dipolar correlation between nearest neighbour molecules are found in all cases. This correlation parallel to the nematic director is more in system-II, however, the correlation perpendicular to it is less in both the systems.

In system-II most of the members show higher values of $\langle P_2 \rangle$ than Maier-Saupe values whereas in system-I these are close to Maier-Saupe values. In no case, however, negative $\langle P_4 \rangle$ values are found. Moreover, in system-II, it is observed that the values of $R = \ln\langle P_2 \rangle / \ln\langle P_4 \rangle$ remain more close to the values predicted by Faber's continuum theory than by Maier-Saupe's mean field theory. However, in case of system-I the values of R are found to be in between those predicted by Maier-Saupe and Faber's theories.