

Chapter IX

SUMMARY AND CONCLUSION

Liquid crystal is currently an important field of research from the view of basic sciences as well as from application point of view. In this context studies on different physical properties of liquid crystals and understanding them in relation to their structures are important. Since mixtures are used in commercial display devices studying the properties of mixtures are also of much interest. Phase behaviour exhibited by a compound and the thermal stability of a particular phase depends upon the nature of intermolecular phases. Keeping this in view several physical properties of nine pure thermotropic liquid crystals and four binary mixtures have been studied in the thesis by employing optical microscopy, DSC, X-ray diffraction techniques as well as dielectric constants measurements. Crystal and molecular structure analysis and interaction energy calculation have also been done in few compounds. A chapter wise summary and important conclusions are given below.

In Chapter I, a general introduction to the field of liquid crystals has been given with a short review on liquid crystals, especially thermotropic liquid crystal systems. Different modifications of liquid crystals have been described briefly. Emphasis has been given on the discussions on the nematic, smectic A, smectic B and other smectic like soft crystal phases which have been studied in the present work. A brief survey of applications of liquid crystals in various fields have also been given. List of investigated compounds are also given in this chapter.

In Chapter II, Maier-Saupe mean field theory of nematic phase and McMillan's theory of smectic A phase have been discussed because some of the experimental results have been compared with the observations of these theories. Theory of X-ray diffraction from liquid crystals and methods of analysis of X-ray photographs to identify different phases and to calculate various molecular parameters have been described in detail. Maier-Meier theory of dielectric properties of liquid crystals and theoretical basis of calculation of the effective dipole molecular moment in nematic phase as well as the dipole-dipole correlation factors have also been described. Theory of crystal structure analysis by direct methods from CAD4 diffractometer data have been outlined. Details of the used experimental set up have been described.

In Chapter III, results of texture, DSC and X-ray studies on two di-Schiff's base compound, BMBT and BBBT, have been presented. The compound BMBT shows only ordinary nematic phase, whereas, BBBT forms a highly ordered smectic like tilted crystal phase and a skewed cybotactic nematic phase. Another di-Schiff's base compound BOCP, which forms only skewed cybotactic nematic phase, showed parallel imbricated mode of molecular packing in the crystalline state. However, in BBBT the molecules are arranged in tilted layers as precursor to the observed tilted smectic like crystal phase. In both the compounds supercooling effect has been observed. However, thermal range of supercooling of smectic phase, observed from DSC and X-ray measurements, is found to differ to some extent. This anomalous behaviour might be due to difference in container geometry, sample thickness and external alignment field. Two crystal phases are also observed in BBBT. The transition temperatures and the thermodynamic parameters observed by us differ slightly from those reported previously, particularly at T_{NI} . The average intermolecular distance (D) in the nematic phase is found to increase slightly with temperature in both cases. Observed D values are in the range 5.12-5.53 Å in BMBT and 5.02-5.24 Å in BBBT. In both the systems the apparent molecular length (l) is found to be less than the model lengths (L) of the respective molecules. This suggests that either the molecules are not in the most extended conformation or the molecules are tilted or both. If the molecules are assumed to be in most extended conformation then the tilt angle (β_t) is found to decrease by about 9° from a value of $\sim 50^\circ$ over the nematic range of BBBT. Value of β_t measured directly from X-ray photograph is found to be almost equal to the mean of the above β_t values. However, in BMBT the observed β_t is about half the above value. In BBBT the transverse correlation length in the cybotactic groups is found to be about five molecular diameters. Moreover, an abrupt change in the values of the above molecular parameters is observed at T_{SM-N} signifying a first order phase transition, ΔH and ΔS values also support this observation. Orientational order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, are found to agree well with MS theory and Faber's theory in BBBT but the agreement is not so well in BMBT. In both the systems the $\langle P_2 \rangle$ values are

on the higher side of the normal range. These compounds were found to be effective in GLC phase separation. High melting point, long range of nematic phase and high $\langle P_2 \rangle$ values are the possible factors for their effectiveness in GLC phase separation.

In Chapter IV, X-ray studies on another two Schiff's bases 6OBPAA and 8OBPAA and their equimolar mixture have been reported. In both the compounds and the mixture N, SmA and SmB phases have been observed over a wide range of temperatures. No change in phase sequence or no appreciable change in transition temperatures is observed between the two homologues except that the temperature T_{NI} is 10°C less in 8OBPAA than in 6OBPAA and in the mixture SmB phase is enhanced by about 15°. Moreover, it is observed that replacement of the flexible butyl chain of the Schiff's base 6O.4 (or 4O.4) by a rigid azophenyl group in 6OBPAA or in 8OBPAA increases the transition temperatures and the stability of the different phases substantially, however, the SmH/SmG phase is suppressed altogether. From X-ray studies it is observed that in all cases d (layer spacing) or l decreases as one moves from SmB to N phase, reverse trend is observed in D. All these parameters show higher values in the higher homologue and the mixture show intermediate values. Systematic increment of D values from SmB to I phase suggests that the molecules are most efficiently packed in SmB phase and in isotropic phase the packing is least efficient. In the mixture the packing is of intermediate nature. Since l/L or d/L ratio is observed to be slightly higher than unity in all phases, a bimolecular association of the molecules, with almost complete overlap, are assumed to exist in the mesophases. The orientational order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, calculated from X-ray data of the samples have been compared with those obtained from McMillan's theory in SmA phase and Maier-Saupe theory in N phase and found to be in good agreement. The values of the adjustable parameter α are found to increase with chain length as is expected from McMillan's theory, in the mixture α values are found to be in between the pure compounds. Moreover, the values of T_{SmA-N} calculated from McMillan's theory are found to be in excellent agreement with observed values. SmA-N transition is found to be of first order type.

In Chapter V, results of X-ray diffraction and dielectric studies on binary mixtures of a carboxylate and a cyanobiphenyl (BPPCC+2CB) in three concentrations have been presented. Dielectric behaviour of pure BPPCC has also been studied. It is observed that replacement of only 25% 2CB molecules, which exhibit virtual nematic phase, by nematogenic BPPCC molecules induces monotropic nematic phase but to get enantiotropic nematic phase 50% molecules have to be replaced (Mixtures II). Since this mixture and another with 75% BPPCC (Mixture III) are found to be nematic at ambient temperature with long range (36° and 51°), they are expected to be useful in commercial display devices. The apparent molecular length (l) and the average intermolecular distance (D) are found to increase very slowly with temperature in all mixtures. Mean value of D is found to be 5.13 \AA in Mixture II and 5.19 \AA in Mixture III which are more than the value 5.0 \AA usually found in N phase of nCB compounds. It is also observed that the packing of the dissimilar molecules in the mixtures is less efficient than that in the pure components. The average l value of the molecules is found to be 19.6 \AA in both the mixtures, considerably different from the value expected from simple additive rule. In both the pure components some sort of bimolecular association is reported to exist in the nematic phase. If the associated lengths of those pairs are taken as the effective lengths of the molecules within nematic phase, then the calculated l values in the mixtures become 20.15 \AA and 19.43 \AA respectively, very close to the observed value (19.6 \AA). Thus bimolecular association within same type of molecules (homo dimmers) is likely to be present in the mixtures as well. The orientational order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, values at different temperatures agree well with those obtained from Maier-Saupe theory. In the mixtures no significant change in order parameters is observed. Moreover, in these mixtures the molecules are found to be less ordered than the mono- and di-Schiff's base molecules described in Chapter III and IV. Since the molecules of the previous systems are longer and less rigid than the present molecules, they are expected to be less ordered as observed.

The compound BPPCC shows small but negative anisotropy, however, all the three mixtures show large positive anisotropy. 2CB molecules are expected to have

large positive dielectric anisotropy like all other members of the **nCB** series. Thus the dielectric behaviour of the mixtures is dominated by the 2CB component. Even when only 25% of the BPPCC molecules are replaced by the 2CB molecules substantial positive anisotropy is yielded. Replacement of 50% and 75% BPPCC molecules by 2CB molecules results in larger $\Delta\epsilon$. In all the mixtures dielectric permittivity in the isotropic phase ϵ_{iso} is found to be larger than $\bar{\epsilon}$ in the nematic phase, no such jump is observed in BPPCC. But effective value of the dipole moment within nematic phase of BPPCC, calculated from Maier and Meier equations, is found to be about 20% less than the free molecule value. These suggest presence of some sort of anti-parallel dipolar associations within nematic phase of the mixtures and BPPCC. In mixtures this dipolar association breaks down completely or partially in the isotropic phase resulting in the increase of effective dipole moment of the molecules and thereby increasing the permittivity. In BPPCC probably no such change in molecular associations takes place during the N-I transition. Slight change in the value of effective dipole moment at T_{NI} also suggests this. In BPPCC the values of dipole-dipole correlation factors (g_{\parallel} and g_{\perp}) in nematic phase were also calculated using Bordewijk theory. These values suggest parallel components of the molecular dipole moments are strongly correlated in antiferroelectric fashion at low temperatures but at high temperatures this correlation is almost negligible. However, over the entire nematic range the correlation of the perpendicular component is ferroelectric type but almost negligible.

In Chapter VI, the crystal and molecular structure of the biphenyl 2CB, which exhibits virtual nematic phase, is described which was determined by direct methods from single crystal X-ray diffraction data. The crystal belongs to monoclinic system with space group $P2_1$, cell parameters being $a=8.584(4)$, $b=5.865(3)$, $c=11.833(3)$ (Å) and $\beta=92.30(3)^\circ$. Refinement led to $R=0.079$ with $I>2\sigma(I)$. The molecules are found to be in the most extended conformation. The phenyl rings are highly planar and the dihedral angle between them is 1.46° . Antiparallel pairs of 2_1 symmetry related molecules are arranged in layers and the layers are stacked along $[001]$. The thickness of these layers is equal to the length of

crystallographic *c*-axis. van der Waals' type of contact is found to exist between the 21 symmetry related molecules and length of such paired molecules is found to be 1.13 times the molecular length. However, in several *n*CB or *n*OCB compounds, where monotropic or enantiotropic mesophases are observed, dipole-dipole or dipole-induced dipole type contact is found to exist and the associated pair length is about 1.4 times the molecular length. Moreover, imbricated type of molecular packing is observed which is assumed to be necessary for the formation of nematic phase. In contrast 2CB molecules are arranged in tilted smectic type layers. Moreover, van der Waals' type of contact encompasses all the molecules within a layer. So the melting point is well above the range of thermal stability of the nematic phase. However, while cooling from isotropic melt, dipole-dipole interaction may give rise to parallel imbricated mode of packing as observed in the fifth member onwards of *n*OCB series of compounds and this in turn may sets in nematic phase.

In Chapter VII the crystal and molecular structure of BPPCC, a nematogenic compound, determined by direct methods has been presented. The crystal belongs to monoclinic type with space group $P2_1/a$, $a = 11.2483(22)$, $b = 20.2968(44)$, $c = 17.6311(14)$ Å, $\beta = 100.342(11)^\circ$ and two independent molecules within unit cell. Refinement converged to an R-value of 0.106. Some bond lengths and angles are found to deviate considerably from the standard values as has been reported earlier in mesogenic compounds. The molecules are in the most extended conformation and are roughly in the *a-c* plane. But unlike 2CB the molecules are packed in parallel-imbricated manner. Crystal – nematic transition may thus be of displacive type. Presence of bimolecular association due to van der Waals' interaction is found in both crystalline and nematic phases. It is inferred that as a result of van der Waals' interactions bimolecular associations exist in the crystalline state as well as in the nematic phase and play a dominant role in the mesophase stability.

In Chapter VIII, the pair intermolecular interaction energy of ECCPP, PCCPP and HCCPP, three pyrimidine mesogenic compounds, has been calculated in the crystalline state by atom-atom potential method taking into account van der Waals' and electrostatic interactions and considering the molecules as rigid bodies.

Stacking, in-plane and overall minimum energy configurations have been calculated to find the most favourable arrangements for both parallel and anti-parallel dimers. For each compound it is observed that in all cases (stacking, in-plane and overall minimum) main contribution to the total interaction energy comes from van der Waals' interaction, the contribution of the electrostatic interaction in no case is greater than 4%. Energetically most favourable configurations of the dimers have been compared with the data obtained from crystal structure analysis and X-ray scattering studies in mesophases. It is concluded that the dispersion forces play the key role in stabilizing both the stacking and in-plane interactions and the dimer energy do not change drastically when the stacking distance is increased by $\sim 1 \text{ \AA}$ and molecular overlap is decreased by $\sim 3 \text{ \AA}$ which indicate that the compounds are capable of retaining molecular order up to a considerable extent against thermal agitations. Thus the compounds exhibit mesogenic behaviour. In case of HCCPP in-plane interaction energy is much stronger compared to the other two compounds. The stacking energy plays a major role in mesophase stability, the significant contribution of in-plane interaction may be responsible for the formation of smectic phase in HCCPP.
