

CHAPTER 7

SUMMARY AND CONCLUSIONS

The nematic liquid crystals and ferroelectric liquid crystals are nowadays used virtually in all commercially available liquid crystal displays. Accordingly, studies on their structure-property relationships are extremely important. With this aim and objective, physical properties of some achiral and chiral liquid crystalline materials have been studied using OPM, DSC, X-ray diffraction, optical birefringence, dielectric spectroscopy and electrooptic methods. Crystal and molecular structures of some these mesogenic compounds in solid state have also been investigated. Finding optimized geometry by molecular mechanics calculation various physical properties have also been calculated.

Nine phenyl bicyclohexyl or biphenyl cyclohexyl based fluorobenzene derivatives (3ccp-f, 3ccp-ff, 3ccp-fff, 5ccp-f, 5ccp-ff, 5ccp-fff, 3cpp-ff, 5cpp-ff, 5cpp-fff), one isothiocyanatobenzene based compound (11CHBT) and one four ring cyano compound (7CBB) have been studied in the achiral system all of which exhibit nematic phase. One partially fluorinated terphenyl based chiral compound [5F6T(2',3'F)], which exhibits antiferroelectric, ferroelectric and paraelectric phases, have also been investigated. In addition, using two different types of host mixtures and three different types of dopants six multi-component room temperature FLC mixtures (LAHS1 to LAHS6) have been formulated and characterized.

From thorough investigation of the nine mono-, di- or tri-fluorinated compounds influence of molecular core structure, chain length and fluorination on their various physical properties have been investigated in detail. It is observed that:

- thermal stability of nematic phase decreases substantially with increasing rigidity of the core structure (i.e. when a cyclohexyl ring is replaced by a phenyl ring) and with increasing fluorination of the phenyl ring.
- average intermolecular distance increases, indicating a decrease in the molecular packing, systematically with increasing fluorination and with increasing flexibility in the core structure. Increasing temperature has similar effect on molecular packing.
- Effective molecular length (l) is found to be higher than the most extended length of the molecules, suggesting the presence of antiparallel-type dimers. Although antiparallel bimolecular association was observed before in polar compounds like cyanobiphenyls and isothiocyanatobenzenes, such association is observed, to the best of our knowledge first time, in fluorinated compounds. However, extent of overlap is found to be intermediate between those of cyanobiphenyls and isothiocyanatobenzenes.

It is further observed that in all the systems l increases with the chain length and with increasing flexibility in the core structure. l is also found to be less in difluoro derivatives

than in mono- and trifluoro derivatives, indicating that the overlap between dimerized molecules in ff derivatives is more than in f and fff derivatives. In all compounds l is found to decrease slightly with temperature.

- Molecular dipole moments (μ) increase systematically as one moves from f \Rightarrow ff \Rightarrow fff derivative in all systems. However increment is more in f \Rightarrow ff derivative than in ff \Rightarrow fff derivative and there is almost no change in dipole moment with chain length. μ is substantially tilted in difluoro derivatives, while in mono- and trifluoro derivatives it is along the molecular axis. In **ccp-f** derivatives μ increases from 1.93D to 3.21D to 3.72D while going from singly to triply fluorinated derivatives.
- Density of the compounds decreases (i.e. molecular packing is less efficient) with increasing chain length and with increasing flexibility of the core. Also it decreases while moving from tri- to difluoro derivatives. Density is found to decrease linearly with temperature. Singly fluorinated compounds show stronger temperature dependence of density than ff and fff compounds.
- Refractive indices (n_e , n_o and n_{av}) exhibit normal dispersive behavior.
- The optical anisotropy (Δn) is found to be larger in ff system compared to f and fff systems in **5ccp** and **5cpp** series, but the opposite behavior is observed in **3ccp** series. It decreases with increasing chain length (except in **3ccp-ff** and **5ccp-ff** systems) but increases with increasing rigidity of core. With temperature Δn decreases, decrement rate is different in different compounds.
- **5ccp-f**, having the lowest Δn (about 0.067 at 80°C) and nematic phase over a large temperature, is expected to be useful for high-information-content display devices.
- Polarizability anisotropy ($\Delta\alpha$), like Δn , is larger in ff system compared to f and fff systems in **5ccp** and **5cpp** series, however in **3ccp** series ff system possesses least value. It is also observed that contributions of increased chain length and enhanced core rigidity to $\Delta\alpha$ are additive. $\Delta\alpha$ is found to decrease with temperature, nature of variation is similar to that observed in Δn .
- The orientational order parameters $\langle P_2 \rangle$ obtained from refractive indices measurements are found to be slightly more, whereas the X-ray order parameters are found to be close to the mean field values in all the systems. A decreasing trend of $\langle P_2 \rangle$ is observed as one moves from f \Rightarrow fff \Rightarrow ff system while it increases with increasing rigidity of the core.
- $\Delta n^2 = n_e^2 - n_o^2$ shows perfect linear dependence on orientational order parameter in all compounds as expected from theory.

From the determination of crystal and molecular structures of four compounds *viz.* **3ccp-ff** and **3ccp-fff**, **11CHBT** and **7CBB** by direct methods it is observed that

- While difluorinated **3ccp-ff** crystallizes in monoclinic space group $P2_1/n$, trifluorinated **3ccp-fff** crystallizes in triclinic system with space group $P\bar{1}$; both the non-fluorinated compounds **11CHBT** and **7CBB** crystallize in monoclinic space group $P2_1/c$.
- Two carbon atoms of the alkyl chain are in disordered condition in **7CBB**, no such disorder is observed in the other three compounds, not even in **6CBB**.
- All bond lengths and bond angles agree well with values reported in Cambridge Structural Database and in other mesogenic compounds.
- Molecules of **3ccp-ff**, **3ccp-fff** and **11CHBT** are almost in their most extended conformations while in **7CBB** length of the molecules in crystalline state is slightly less than the most extended model length.
- All the phenyl rings are found to be planar and the cyclohexyl rings are in chair conformation.
- Dihedral angle between the phenyl and nearby cyclohexyl ring decreases (122.1° to 83.2°) on the introduction of additional fluorine atom in the phenyl ring (**3ccp-ff** to **3ccp-fff**) while it increases from 60.7° to 122.1° or 83.2° with additional cyclohexyl group in the core (**11CHBT** to **3ccp-ff** or **3ccp-fff**).
- From the structural results of **11CHBT** nature of the resonance structure of isothiocyanato group is established for the first time.
- Parallel imbricated mode of molecular packing is observed as precursor to nematic phase in **3ccp-ff**, **3ccp-fff** and **11CHBT** compounds while packing of **7CBB** molecules in crystalline is not strictly precursor to smectic A structure. Crystal to nematic transition is displacive type in first three compounds while that in **7CBB** is reconstitutive type.
- Calculation of intermolecular distances strongly suggests existence of molecular packing in a head-to-tail configuration in all cases. Conclusive evidence of existence of antiparallel bimolecular associations has been reported for the first time in both the crystalline and nematic phases for fluorobenzene systems and in crystalline system of isothiocyanato compounds. For cyanobiphenyls and isothiocyanates the existence of such molecular associations in nematic phase well established.
- It is found that in **3ccp-ff** and **3ccp-fff** molecular geometry and conformation, values of molecular dipole moments and their inclination with long axes, packing and extent of overlap of the molecules in the crystalline state differ from each other. These differences may be responsible for the substantial difference in the melting points. Moreover, the

molecular volume of **3ccp-fff** is greater than **3ccp-ff** but the molecular geometry is more symmetrical. This results in better and efficient packing of the **3ccp-fff** molecules both in crystalline and nematic phase, which is evident from the fact that the density in both the phases is less in **3ccp-fff** than in **3ccp-ff**. Possibly this explains the higher melting point in **3ccp-fff** than **3ccp-ff**. On the other hand, the existence of larger overlapping cores in the nematic phase is expected to increase T_{NI} . Since overlapping is more in **3ccp-ff** than that in **3ccp-fff**, the clearing temperature of the former is found to be more than the later.

It may thus be concluded that increased melting point due to more efficient packing in the crystalline state and decreased clearing point due to less overlapping cores in the nematic state is the reason for substantially lower nematic range in **3ccp-fff** than its bifluorinated analogue.

In the chiral compound, **5F6T(2',3'F)** typical fan shaped texture in SmA^* phase, domains with equidistant line patterns due to helicoidal structure in SmC^* phase and broken fan texture with sign of helical pattern in SmC_A^* phase are observed. Rigidity of the core structure and its lateral fluorination are found to have pronounced effect on the phase behavior and on the stability of the antiferroelectric and ferroelectric phases. X-ray studies reveal that the layer thickness remains almost constant in SmA^* phase but within SmC^* and SmC_A^* phases it decreases with decreasing temperature, a step jump is observed only at $SmA^* - SmC^*$ transition which corresponds to about 3.3% layer shrinkage. As a result, tilt angle in SmC_A^* phase decreases slowly with increasing temperature, varies from 22.2° to 19.5° , in SmC^* phase it decreases from 18.8° to 5.5° , the rate of decrement is very sharp near $SmC^* - SmA^*$ transition. Thus the compound behaves like regular ferroelectric, not de-Vries type. Molecular mechanics calculation reveals that the molecules possess a dipole moment of 1.80 D. Spontaneous polarization is observed to be quite high and varies between 74.1 - 118.7 nC/cm². Real and imaginary parts of dielectric constants, ϵ' and ϵ'' show discontinuous change at transition temperatures. Only Goldstone Mode relaxation is observed in both ferroelectric and antiferroelectric phases. Fitted data shows that the GM peak is Cole-Cole type. Soft Mode is not observed in SmC^* without bias field, but on application of bias field SM is observed near $SmC^* - SmA^*$ transition. Temperature dependence of GM and SM is found to be consistent with the predictions of generalized Landau model. No SM or antiphase azimuthal angle fluctuation mode is observed in SmC_A^* .

Due to surface interactions under the confined geometry of thin dielectric cell (5.2 μm) the material is probably showing ferroelectric type behavior although in bulk it shows antiferroelectric phase, hence no SM or anti-phase antiferroelectric mode is observed. High

value of ϵ' in SmC_A^* absence of DSC signal and relaxation behavior related to antiphase azimuthal angle fluctuation as well as continuous change in layer thickness and spontaneous polarization at SmC^* - SmC_A^* transition support this view.

GM relaxation frequency is found to decrease with increasing cell thickness which indicates that the molecular motion is restricted in thin cells due to strong surface interactions. Rotational viscosity is found to decrease quite fast in a non-linear manner, rate of decrement is different in ferro and antiferroelectric phases. In SmC^* phase activation energy for the process is found to be 48.14 kJ/mole.

All the FLC mixtures show ferroelectric SmC^* phase at or below room temperature with a varying degree of overall mesophase thermal stability and stability of SmC^* phase. Effect of host molecules and various dopants on the occurrence and thermal stability of different phases has been discussed. Chirality of the dopant is found, as expected, to be the key factor for induction of ferroelectric behaviour in a tilted smectic system. On the other hand, a considerable enhancement of SmC^* phase is observed when a singly fluorinated compound possessing SmC^* phase with chiral centers at one or both ends is used as dopant. In the mixture LAHS1 SmC^* phase continues upto 80.6 °C, while in LAHS4 it is upto 75.5 °C. LAHS1 and LAHS5 will be easier to align in bookshelf geometry since they possess SmA^* and N^* phases at higher temperatures.

Values of spontaneous polarization are found to vary between 13-62 nC/cm² at room temperature. It is observed that mixtures with dopants having chiral centres at both ends possess relatively high P_s compared to mixtures with dopant having one chiral centre. Mixture with two chiral compounds having opposite optical rotations is found to have minimum spontaneous polarization. Minimum X-ray tilt (θ) is observed in mixture LAHS5. Thus by choosing proper host and chiral dopant, θ and P_s can be controlled to get faster switching time.

Different types of dielectric absorption behaviour were observed in planar geometry of the FLC cells. Goldstone mode critical frequencies are found to vary widely in the mixtures - from 0.7 kHz to 10.6 kHz. Rigidity of the core structure, nature of chirality and extent of fluorination of the constituent molecules are found to have pronounced effect on the collective mode relaxation behaviour of the mixtures.

All of the results incorporated in this dissertation have already been published in different international scientific journals, a list of which is given in **Appendix B**.