

ABSTRACT

Various physical properties of some achiral and chiral liquid crystalline materials have been studied using optical polarizing microscopy, differential scanning calorimetry, 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.

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 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 explored. It is observed that thermal stability of nematic phase decreases substantially with increasing rigidity of the core structure and with increasing fluorination of the phenyl ring. Average intermolecular distance increases systematically with increasing fluorination and with increasing flexibility in the core structure. Effective molecular length (l) is found to be higher than the most extended length of the molecules, suggesting the presence of antiparallel-type dimers. Such molecular association is observed, to the best of our knowledge first time, in fluorinated compounds. In all the systems l increases with the chain length and with increasing flexibility in the core structure. l is found to be less in difluoro derivatives than in mono- and trifluoro derivatives. Molecular dipole moments are also found to increase systematically as one moves from $f \Rightarrow ff \Rightarrow fff$ derivative in all systems.

Density of the compounds decreases with increasing chain length and with increasing flexibility of the core. Also it decreases while moving from tri- to difluoro derivatives. 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. **5ccp-f**, having the lowest Δn and nematic phase over a large temperature, is expected to be useful for high-information-content display devices. 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.

It is observed that 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 $P2_1/c$. 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. 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 in **7CBB** crystal to SmA phase transition is reconstitutive type. Calculation of intermolecular distances strongly suggests existence of molecular packing in a head-to-tail configuration in all cases.

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 SmCA* 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 SmCA* phases it decreases with decreasing temperature. Spontaneous polarization is observed to be quite high and varies between 74.1 - 118.7 nC/cm². ϵ' and ϵ'' show discontinuous change at transition temperatures. Only Cole-Cole type Goldstone Mode relaxation is observed in

both ferroelectric and antiferroelectric phases. Soft Mode is observed near SmC^* - SmA^* transition only with bias field. 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^* , probable cause of which has been discussed. 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 different manner in ferro and antiferroelectric phases.

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. 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 $13\text{-}62\text{ nC/cm}^2$ 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.

Different types of dielectric absorption behaviour are observed in dielectric spectra. 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.