# Abstract

The aspects of the molecular structure and conformational perspectives appear to be of fundamental importance in deciding the mesogenic behavior of liquid crystalline compounds. During past few decades, a number of exotic shaped liquid crystalline molecules encompassing a rich variety of mesophase morphologies with unusual molecular ordering and layer frustrations have been synthesized and studied extensively. Among them the ‘bent-core’ or ‘banana-shaped’ compounds have appeared as a field of considerable interest in soft matter research. The exceptional structure-induced mesomorphic behavior and unconventional mesophase sequences in these non-linear molecules have unveiled a stimulating new horizon in the science of thermotropic liquid crystals and set off a huge research effort in the area of banana-shaped or bent-core mesogens, especially after the remarkable discovery of electro-optic switching in such achiral mesogenic compounds. This dissertation is principally focused on an in-depth characterization of physical properties in several bent-core and hockey stick-shaped liquid crystals having nematic and smectic phases. Few multi-component systems and binary mixtures of the hockey stick-shaped compounds with calamitic molecules have also been formulated and systematic physical investigations have been carried out in their mesophases. Additionally, the influence of a hockey stick-shaped molecule as dopant on the phase-structure and hence, character of the different phase transitions in a chiral calamitic liquid crystal have also been explored. The following portray a brief overview of the contents of this dissertation along with salient features of the outcome.

**Chapter 1** gives an overview of the fundamentals of liquid crystals and their classification. Besides, basics of a few different mesophases and related molecular ordering have also been discussed.

**Chapter 2** describes the essentials of the experimental techniques and data analysis procedures employed for characterizing the mesomorphic behavior of the liquid crystals, supported by a few necessary theoretical backgrounds.

**Chapter 3** contains the experimental results obtained on the mesophases of three members of a homologues series having terminally alkyl substituted bent-core mesogens, 4-cyanoresorcinols (**1/7**, **1/9** and **1/10**) showing a broad nematic range. The nematic phase in these mesogens has appeared to be significantly different from those in the usual calamitics.

i. The temperature dependence of orientational order parameter ($<P_2>$) as obtained from the X-ray diffraction and birefringence measurements are although in agreement in the nematic phase, they show opposite trends in the low-temperature phases.

ii. Interestingly, the lower homologues (**1/7**, **1/9**) exhibit an inversion in sign of static dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) in the nematic phase while the higher homologue (**1/10**) possesses negative values of $\Delta\varepsilon$ throughout the mesomorphic range.

iii. The splay elastic modulus ($K_{11}$) has been found to be comparatively higher than the related bend elastic modulus ($K_{33}$).

iv. Measurements of relaxation time ($\tau_0$) have been performed from two different methods, *viz.* capacitive decay and optical phase-decay-time measurement methods, enabling a precise comparison.

v. The rotational viscosity ($\gamma_1$) values in the nematic phase were estimated to be more than an order of magnitude higher compared to that in conventional calamitic nematics.

The observed behavior has been explained by considering the strong dipolar correlation of the bent-core molecules and the existence of the short range

cybotactic clusters, their gradual growth and uniform alignment under the presence of strong surface anchoring.

In **Chapter 4**, the structure–property investigation in the mesophases of a few laterally methyl substituted hockey stick-shaped mesogens has been reported. Interestingly, introduction of a lateral methyl group in these compounds leads to the emergence of a high-temperature nematic phase. In addition they exhibit two polymorphic tilted smectic phases – the synclinic Sm-$C_s$ and the anticlinic Sm-$C_a$ phase.

i. The Sm-$C_s$–Sm-$C_a$ phase transition is accompanied by an only small calorimetric signal but causes a pronounced change in the optical textures.

ii. X–ray diffraction patterns in the nematic phase indicate the existence of cybotactic groups of the smectic type.

iii. Orientational order parameters determined from the $^{13}$C-NMR and birefringence measurements have been compared with those estimated from X–ray diffraction patterns.

iv. Dielectric measurements point to the formation of small "soft" ferroelectric clusters responsible for a low frequency absorption range.

**Chapter 5** aims to explore the dielectric and visco-elastic properties of the hockey stick-shaped liquid crystals as discussed in chapter 4. Interestingly, the nematic phase in these compound has been observed to be of dual character (i.e., partially calamitic like and partially bent-core like).

i. All the mesogens exhibit a temperature dependent inversion in $\Delta\varepsilon$ from positive to negative values on entering the Sm-$C_a$ phase.

ii. From an analysis of the temperature dependence of dielectric permittivity in the isotropic phase, the critical exponent ($\alpha$), characterizing the critical anomaly at the *N–I* phase transition have been found to be in agreement with the tricritical hypothesis.

iii. In the entire nematic range, $K_{33}$ values are relatively lower than the corresponding $K_{11}$ values.

iv. The $\gamma_1$ values were found to be slightly higher than those of many known calamitic molecules.

v. The activation energy ($E_a$) calculated from the viscosity data in the nematic phase was found to be considerably higher than those obtained for conventional rod-like compounds.

The observed behaviors have been accounted for by considering the intriguing shape-determined inter-molecular interactions in hockey stick-shaped compounds and molecular associations appearing in the mesophase.

In **Chapter 6**, the investigation of physical properties of a few multi-component eutectic mixtures consisting of the above mentioned hockey stick-shaped liquid crystals has been discussed. Three mixtures with varying number of pure components were prepared and their mesomorphic properties were characterized.

i. The nematic range in all the investigated mixtures were found to be around 7.5 °C – 9 °C which was consistently close to those of the shorter chain components, irrespective of the presence of the higher homologs with relatively lower nematic ranges.

ii. $\Delta\varepsilon$ and $K_{11}$ values are comparatively greater than those for the pure compounds.

iii. Magnitudes of $\gamma_1$ are either slightly higher or similar to those of the pure hockey stick-shaped mesogens.

**Chapter 7** deals with the study of influence of one of the above hockey stick-shaped molecules on the electro-optical properties of an anti-ferroelectric liquid crystal, (S)-MHPOBC from a polarization field reversal technique.

i. In these mixtures, the spontaneous polarization ($P_s$) values were found to be reduced significantly with increasing hockey stick-shaped molecule concentration.

ii. Interestingly, the response time and effective torsional bulk viscosity coefficient have been found to display a feeble dependence on the achiral mesogen concentration.

**Chapter 8** is devoted to study of critical behavior at the nematic–isotropic (*N*–*I*) and smectic-*A*–nematic (Sm-*A*–*N*) phase transitions in a binary system comprising the calamitic octylcyanobiphenyl and one of members of the above stated laterally methyl substituted hockey stick-shaped mesogens, from a high-resolution optical birefringence ($\Delta n$) measurement technique.

i. For the investigated mixtures, the critical exponent $\beta$ related to the limiting behavior of the nematic order parameter close to the *N*–*I* phase transition, was found to be in good conformity with the tricritical hypothesis.

ii. The yielded effective critical exponents ($\alpha'$, $\beta'$, $\gamma'$), characterizing the critical fluctuation near the Sm-*A*–*N* phase transition, have appeared to be non-universal in nature.

iii. With increasing hockey stick-shaped dopant concentration, the Sm-*A*–*N* phase transition was observed to demonstrate a strong tendency to be driven towards a first-order nature.

These outcomes have been explained by considering a modification of the effective intermolecular interactions and hence, the related coupling between the nematic and smectic order parameters, caused by the introduction of the angular mesogenic molecules in the calamitic environment.