

CHAPTER 9

Conclusions

The dissertation entitled “*Study of physical properties of bent-core mesogens having nematic and smectic phases*” submitted for the degree of Doctor of Philosophy (Physics) of the University of North Bengal embodies the results of experimental investigations on the physical properties of several pure bent-core and hockey stick-shaped liquid crystals and their mixtures exhibiting nematic and smectic phases. Nematic and calamitic like smectic phases are relatively rare among the mesophases formed by banana-shaped compounds and they have been found to be accompanied with a number of exotic features, finding no trace in classic calamitic liquid crystals. Although extensive research works have been carried out to investigate such unconventional mesophases, yet a number of questions remain unsolved so far. This dissertation is principally focused on determination of the structure-property correlation and characterization of mesomorphic properties in the nematic and smectic phases of several symmetric bent-core and hockey stick-shaped compounds. Additionally, the influence of bent-core molecules on the character of mesophase transitions and mesomorphic behavior of a few calamitic molecules has also been investigated. This thesis consists of eight chapters.

In chapter 1, a brief review of the fundamentals of liquid crystals, their classification, different mesophases and related molecular arrangements have been presented. However, this dissertation is restricted to the description of the general features and mesomorphisms of calamitic and bent-core liquid crystals which have been principally discussed here.

In chapter 2, an overview of the different experimental techniques, used for characterizing the liquid crystalline compounds and mixtures has been portrayed. The procedures for extracting different material parameters from different experiments have also been presented. Besides, few necessary theoretical approaches have also been discussed in brief.

Chapter 3, describes the physical characterization of three members of a homologues series having terminally alkyl substituted bent-core mesogens, 4-cyanoresorcinols (**1/7**, **1/9** and **1/10**) from birefringence, X-ray, static dielectric, splay & bend elastic moduli, relaxation time and rotational viscosity measurements. The principal objective of this work was to accomplish a systematic study of different mesomorphic properties in the mesophases of the compounds under investigation. All the three compounds exhibit a highly correlated nematic phase (N_{cybC}) over a wide temperature range followed by a phase (CybC) comprising elongated but not yet completely fused strings of cybotactic clusters. In addition, the higher homologues (**1/9** and **1/10**) exhibit one or more non-polar, tilted smectic phases ($\text{Sm-}C_{(\text{I})}$, $\text{Sm-}C_{(\text{II})}$). The temperature dependence of orientational order parameter ($\langle P_2 \rangle$) has been extracted from both X-ray diffraction and birefringence measurements and the values are found to be in agreement in the nematic phase. However, the $\langle P_2 \rangle$ values obtained from these two procedures exhibit opposite trends in the low-temperature CybC and Sm- C phases. The theoretical $\langle P_2 \rangle$ values, calculated using the McMillan's theory, have been found to concur well with those from X-ray diffraction measurements after introducing necessary correction for the presence of molecular tilt. Remarkably, the two lower homologues (**1/7**, **1/9**) demonstrate a temperature-dependent crossover in the two dielectric permittivity components ($\epsilon_{||}$ and ϵ_{\perp}) in the nematic phase while the higher homologue (**1/10**) exhibits negative values of dielectric anisotropy ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$) over the entire mesomorphic range. Such a crossover is possibly due to a combined influence of enhancement in the antiparallel dipolar correlation for the longitudinal dipolar component and formation of strong short range Sm- C

type layered structure. In all the investigated compounds, the splay elastic modulus has been observed to be relatively smaller (K_{11}) than the corresponding bend modulus (K_{33}), thus leading to negative values of elastic anisotropy ($K_{33} - K_{11}$). The yielded rotational viscosity (γ_1) values as obtained from two different techniques – the capacitive decay and optical phase-decay-time measurement methods, are nearly more than an order of magnitude higher compared to the conventional calamitic nematics. Such atypical γ_1 values may be owing to the formation of short range cybotactic clusters utilizing the shape anisotropy and strong transverse dipolar contribution from the bent-core molecules and also the existence of those clusters as an inherent part of the nematic phase structure. The strong temperature and chain length dependence of the cluster size has also clearly been reflected in the temperature variation of γ_1 . Eventually such strange ordering and hence, the huge induced flow reluctance and rotational hindrance of the molecules characterize the medium with a non-Newtonian like behavior.

Chapter 4 summarizes the structure–property investigation in the mesophases of a few laterally methyl substituted hockey stick-shaped compounds by polarizing microscopy, X-ray diffraction, $^{13}\text{C-NMR}$, optical birefringence, dielectric and electro-optical methods. Interestingly, the introduction of a lateral methyl group in the obtuse angle, between the *meta*-alkyloxy chain and azomethine connection group in these molecules, results in the emergence of a nematic phase at higher temperatures. Steric interactions between the methyl group and the neighbouring alkoxy chain in the *meta*-position conceivably induce a more rod-like shape thereby facilitating the formation of the nematic phase. The nematic–smectic C_a ($N\text{-Sm-}C_a$) phase sequence, as observed in compounds **1** and **2**, is also quite remarkable. In addition to the nematic phase, compounds **3-5** demonstrate two tilted smectic phases – $\text{Sm-}C_s$ with synclinic and $\text{Sm-}C_a$ with anticlinic molecular arrangement. The two-dimensional X-ray diffraction pattern in the $\text{Sm-}C_s$ phase clearly proves the synclinic structure, the pattern in the $\text{Sm-}C_a$ phase is

caused by an anticline arrangement of the molecules in adjacent layers. The orientational order parameter ($\langle P_2 \rangle$) values determined from the birefringence and NMR measurements agree well with one another and decrease at the Sm- C_s -Sm- C_a transition. However, the $\langle P_2 \rangle$ values determined from X-ray diffraction measurements on compound **4** increase in going from Sm- C_s to Sm- C_a phase and the obtained values are significantly large relative to the other two measuring procedures. This apparent contradiction may be owing to the uncertainties in these methods suffering mainly (but not only) from a differing alignment of the surface-aligned samples in the smectic phases and a differing change in this alignment with temperature for the different experimental settings. Furthermore, a more precise extraction of the X-ray intensity distribution data [$I(\chi)$] and elimination of the background contribution from the same employing other more refined techniques may also help in eliminating such contradicting outcomes. The dielectric measurements show a low frequency absorption, which has been interpreted as signal from small “soft” ferroelectric clusters in analogy to the Sm-*CP* phases of banana-shaped molecules. Possibly the clusters formed by hockey stick molecules exhibit stronger fluctuations. Therefore, it may be difficult to detect ferroelectricity by the reversal current methods.

Chapter 5 deals with the study of dielectric and visco-elastic properties in the nematic phase of four members of the hockey stick-shaped liquid crystals as discussed in chapter 4. Remarkably, the nematic phase in these compound demonstrate a dual character (i.e., partially calamitic like and partially bent-core like appearance). Birefringence measurements indicate that the Sm- C_a -*N* transition is of first order while the Sm- C_s -*N* transition is either of second order or weakly first order. The temperature dependence of dielectric permittivity exhibits a strong dependence on the anisotropic correlations among the hockey stick-shaped molecules and a temperature dependent inversion in the static dielectric anisotropy has been observed from positive to negative values on entering the Sm- C_a phase. From an analysis of the temperature dependence of

dielectric permittivity in the isotropic phase, related critical exponent (α), characterizing the critical fluctuations at the N - I phase transition have been appeared to be in agreement with the tricritical hypothesis. Similar to previous banana-shaped compounds, here as well, in the nematic phase, the bend elastic modulus (K_{33}) has been found to be relatively lower than the corresponding splay modulus (K_{11}) probably owing to the collective influence of both the coupling between the curved molecular profile and the bend deformation in the medium as well as the existence of comparatively short-range highly ordered molecular domains within this mesophase. Surprisingly, the measured nematic rotational viscosity (γ_1) values have been found to be slightly higher than those obtained for several usual calamitic molecules and thereby contradict the banana like appearance as asserted by the elastic constant measurements. Such a fascinating outcome can merely be accounted for by considering the fact that like in conventional bent core compounds, for hockey stick-shaped nematogens as well, different shape correlated molecular interactions and eccentric phase-structure modifications (e.g., strong rotational hindrance, significant clustering within the mesophase) take place but to a somewhat less extent and that is why they promote a number of such remarkable phenomena some of which pertain to calamitic liquid crystals while some other are related to the bent core compounds, again some are completely intermediate between both of them.

In chapter 6, a comprehensive study of physical properties of a few multi-component liquid crystal mixtures incorporating the previously mentioned laterally methyl substituted hockey stick-shaped compounds, has been presented. Three eutectic mixtures, comprising varying number of pure components were formulated. They demonstrate a nematic (N) phase in addition to an anticlinic smectic C ($Sm-C_a$) phase or the I - N - $Sm-C_s$ - $Sm-C_a$ phase sequence. Interestingly, despite the sufficient proportions of the higher homologs (those with longer terminal chain) in them, all of the mixtures have found to demonstrate a relatively broad nematic range. The optical birefringence in them assumes comparatively lower values than that of the pure

components. Furthermore, the obtained dielectric anisotropy and splay elastic modulus values have been observed to be relatively greater than those obtained for the pure hockey stick-shaped molecules. At a fixed reduced temperature, the rotational viscosity values are either somewhat higher or nearly identical to those of the pure components. In spite of the difference in composition of the mixtures and also the major variation in concentration of the constituents from one mixture to another, no significant departure has been detected in magnitude of different material parameters from those for the pure compounds. Probably, it is the structural similarity of the component hockey stick-shaped molecules which promotes such alike behavior. These outcomes also indicate the key role of the molecular structure in deciding the phase-structure and mesomorphic behavior of liquid crystalline compounds.

Chapter 7 is devoted to explore the effect of hockey stick-shaped molecules on the electro-optical properties of a chiral anti-ferroelectric liquid crystal. Four binary liquid crystal mixtures consisting of the hockey stick-shaped mesogenic 4-(3-*n*-decyloxy-2-methyl-phenyliminomethyl)phenyl 4-*n*-dodecyloxycinnamate and the antiferroelectric liquid crystal, (S)-MHPOBC were prepared and their physical characterization has been performed from the study of temperature dependences of spontaneous polarization, relaxation time, effective torsional viscosity and anchoring energy coefficients from a polarization field reversal technique. In these mixtures, the spontaneous polarization (P_s) has found to be significantly influenced by the introduction of bent-mesogenic molecules in chiral environment, where an enhancement in concentration of the hockey stick-shaped molecules causes a significant reduction in P_s value. Such a drop may be due to the dilatation effect of spontaneous polarization caused by addition of the achiral hockey stick-shaped compound. There may also be a weakening of the core-core correlation among the molecules in these combined systems along with additional contribution from mismatch in terminal chain length between the guest and host molecules. An extrapolation of the linear fit to the P_s values yields a zero polarization

value for the investigated hockey stick-shaped compound, confirming the non-polar character of the same. Interestingly, the response time (τ) and effective torsional bulk viscosity coefficient (η) are found to demonstrate only a feeble dependence on achiral compound concentration. Moreover, for a specific mixture, the magnitudes of dispersion and polarization anchoring strength coefficients have been found to be close to one another suggesting nearly equal share in anchoring energy from electrostatic and non-electrostatic parts of interaction. Hence, the asymmetric bent-shaped molecules have been found to induce a considerable reduction in magnitude of spontaneous polarization and hence, a related elongation of the helix in investigated antiferroelectric systems without affecting the molecular relaxation time considerably. Perhaps, hockey stick-shaped molecules suffer a relatively weak perturbation in the investigated chiral environment leading to such captivating outcomes. Even though a number of issues are to be resolved, such rod-like–bent-core combined systems may emerge as a viable route for designing materials with potential for different electro-optic applications.

Chapter 8 focuses on an extensive optical investigation of critical behavior at the nematic–isotropic (N – I) and smectic- A –nematic (Sm- A – N) phase transitions in a binary system comprising calamitic octylcyanobiphenyl (8CB) and one of members, 4-(3-*n*-decyloxy-2-methyl-phenyliminomethyl)phenyl 4-*n*-dodecyloxyxinnamate (compound **5**), of the above discussed hockey stick-shaped liquid crystals, from a high-resolution measurement of optical birefringence (Δn). The precise Δn data have been quite successful in characterizing the transitional anomaly associated with both the N – I and Sm- A – N phase transitions. For the investigated mixtures, the critical exponent β related to the limiting behavior of the nematic order parameter close to the N – I phase transition, has come out to be in good conformity with the tricritical hypothesis. No visible discontinuity was observed in the temperature dependence of Δn at the Sm- A – N phase transition implying a second-order nature of that transition. A power-law analysis has

found to describe successfully the divergence of the temperature dependence of a differential quotient $Q(T)$ extracted from Δn data on both sides of the transition, over a broad range of reduced temperature. It has been observed that the introduction of the angular mesogenic dopant leads to a contraction of the nematic range with a corresponding enhancement in the $Q(T)$ anomaly near the Sm- $A-N$ phase transition. The effective critical exponents (α' , β' , γ') characterizing the critical fluctuation near the Sm- $A-N$ phase transition, have appeared to be non-universal in nature i.e., being intermediate between those predicted for 3D-XY and tricritical systems. Here, the introduction of the hockey stick-shaped molecules in the rod-like environment has been found to cause a significant modification in effective intermolecular interactions in the host medium, thus affecting the order of the transition, where perhaps the kinked molecular shape of the dopant also plays a vital role. Now, enhancement of concentration of the dopant compound causes an augmentation of such resultant effect which again is facilitated through a consequent enhancement in the associated Sm- $A-N$ phase transition temperature. Besides, such a revision in the intermolecular interactions is also followed by a corresponding strengthening of the coupling between the nematic and smectic- A order parameters, thus driving the transition towards a first-order nature.

In the past two decades, the bent-core or banana-shaped compounds have emerged as a very intriguing class of compounds in the field of soft-condensed matter. They have found to demonstrate a rich variety of phase topologies with exotic molecular arrangement having no counterpart elsewhere. Even the calamitic like mesophases in them have also been appeared to be coupled with a number of exclusive features finding no trace in traditional rod-like molecules. Such bent-mesogenic molecules are much promising not only for obtaining the knowledge of molecular behavior from the theoretical view point, but they are also crucial because some of them are of immense potential for technological applications. In the frame of this thesis it not becomes possible to answer a number of questions, for example – the exact nature and

structural behavior of the cybotactic cluster in bent-core nematic phases and their rigorous influence on the mesophase behavior or the detailed dependence of the mesogenic features on the molecular curvature, which necessitates further seminal research works encompassing both theoretical and experimental approaches.