Ph. D.

Thesis Abstract

"Chirality in achiral bent shaped molecules: synthesis and characterization of banana liquid crystals"

By

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Abstract:

The discovery of spontaneous polarity and chirality in smectic liquid crystals (LCs) of achiral bent shaped molecules has stimulated a new era in soft materials attracting both chemists and physicists alike because of spontaneously chiral and switchable polar phases; polarization splay modulated and layer undulated phases, and the potential applications of these materials in electro-optical devices. The manifestation of nematic phases among the mesophases in materials of bent core molecules is relatively scarce due to strong tendency for smectic layering generated by the close packing of the kinked molecules promoted by aromatic core interactions. Nematic phase is largely realized in derivatives of 1,3-disubstituted phenyl ring with a substituent in 2- or 4- positions. However, reduction of the molecular bent at the apex by the replacement of 1,3-substituted 6-membered phenyl ring by a 2,5-substitued 5-membered heterocycles like oxadiazole, or thiadiazole or unsymmetrical hockey stick molecules or dimesogens comprised of rod-like and bent units (with a overall reduction in bent angle) yielded the nematic phases at high temperatures above the layered smectic or columnar phases. Hence the realization of nematic phase in bent core molecules is dependent on the molecular architecture with extended aromatic cores and/or relatively shorter terminal chains or reduction of molecular bent promoted by rigid extended five-membered heterocycles ring at the centre. This thesis mainly deals with the nematic and layered phases in four ring bent core mesogens which falls in the boundary between bent shaped molecules and calamitic or rod-like molecules. The organized body of the thesis is as follows:

Chapter I deal with the introduction of bent shaped liquid crystals and its associated mesophases.

Chapter II describes the survey of literature of bent shaped liquid crystals in quest for nematic and smectic mesophases of opposite-handedness followed by proposed plan of research work.

Chapter III describes the elegant synthetic steps towards the successful synthesis of target compounds.

In Chapter- IV(A), the synthesis and mesomorphic properties of a newly designed achiral four-ring asymmetrical bent-core hockey-stick shaped compound has been studied using polarizing optical microscope (POM) observation, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis under an aligning magnetic field. The compounds exhibited the phase transition, Isotropic – nematic – orthogonal smectic (Sm) – crystal. We observed SmC-type layer reflection in the N phase particularly over a wide lower temperature range. In the vicinity of the temperature close to the transition to the smectic phase, a SmA-type layer reflection emerges in addition to the SmC-type one. The lower temperature smectic phase is an orthogonal one, which is proved by sharp layer reflection along the meridian direction (magnetic field direction) and optical extinction direction along the layer normal by POM observations. Curiously, the SmA and SmC in the clusters are not family fluid smectic phases with non-tilted and tilted molecules. The temperature dependent structural transition from N to N_{cybC} is associated with a change of the position and intensity of the SAXS patterns.

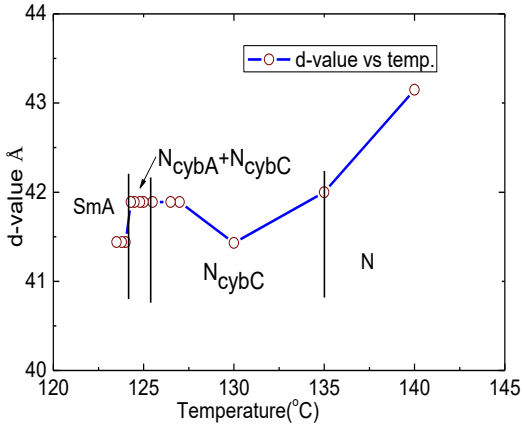


Figure: d-value vs Temperature.

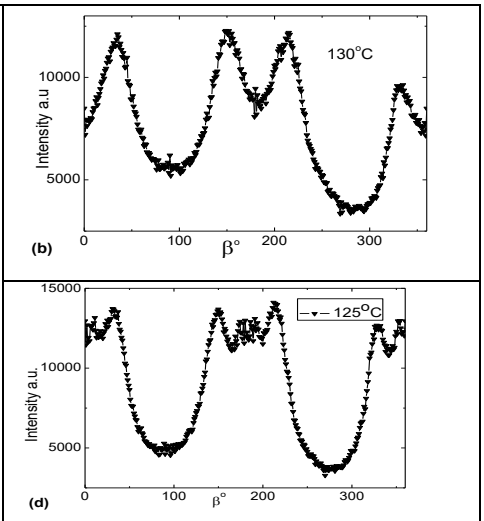
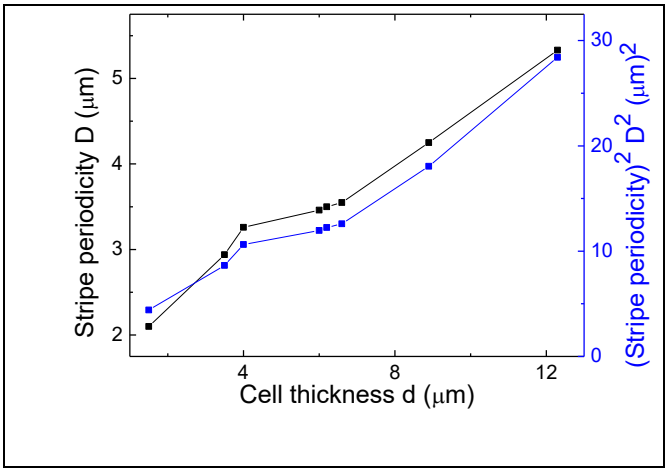


Figure: azimuthal angle scan.

Chapter- IV (B) report the observation of spontaneous periodic modulations of the nematic director in cybotactic nematic phase (Nx) possessing two distinct molecular arrangements of N_{cybC} and $N_{cybA,}$ in homeotropic cells when surface aligning agents to produce homeotropic alignment is not achieved. The Nx phase range is found to be dependent

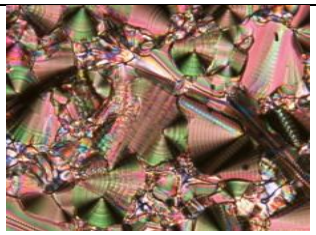
upon the sample exposure to UV-Visible light. The measured stripe period (**D**) is found to be linearly proportional to the square root of sample thickness. Further temperature dependent measurements of dielectric anisotropy splay (K_{11}) and bend (K_{33}) elastic constants of mixtures of rod-like 7CB and achiral four-ring bent-core molecules (5M and 7M) are also reported. K_{11} increases monotonically in the nematic phase with decreasing temperature in pure 7CB and mixtures. However, we observed an anomalous trend in the variation of K_{33} with temperature in two mixtures viz., K_{33} increases initially with decreasing temperature, then decreases and finally increases on further cooling. Another anomaly is the increase in K_{33} with the increase in concentration of bent-core molecules in 7CB in the entire nematic range. The results are discussed relating the molecular alignment of bent core molecules in nematic phase and strong coupling of bent shape of the molecules with the bend distortion.



Chapter- IV(C) gives the detailed study of the conformation of nematic phase by electric field study, magnetic field and free standing film study. The most plausible structure for N_b device to realize both fast response and wider viewing angle is the homeotropically aligned cell with an in-plane switching of the minor director. Lee *et al.* reported fast switching of the minor director with bent core liquid crystal (LC), ODBP-Ph-C7, confirmed already by NMR and x-ray experiments, but results of Lee at were strongly criticized by Stannarius for their incorrect interpretation. Recently Le *et al.* reported optical study of the bent core LC, A131, which was confirmed as showing biaxiality in its nematic phase. However, they did not find any evidence of the optical biaxiality in this material. Optical studies like free standing film suggests that the absence of disclinations of unit strength, $|s| = 1$, in the

nematic schlieren texture is evidence of biaxiality in the phase. Application of electric field induces electro-convection patterns in the nematic phase due to hydrodynamic instabilities. The nematic phase presented in this thesis is uniaxial as evidenced from in-plane switching study and magnetic field study. Large 4-brush disclinations $|s| = 1$ appeared readily in the uniaxial Nu films. Nematic fluid in a droplet of glycerol was also observed under polarising microscope, where 4-brush disclinations $|s| = 1$ appeared in the uniaxial nematic phase.

Chapter-V deals with the influence of polar substituent in mesomorphism in four ring achiral bent shaped molecule. Despite the high polarity, the fluoro substituent has a low polarizability which confers low intermolecular dispersion interactions. The fluoro substituent is the smallest, after hydrogen, of all possible substituents, and like hydrogen it is monoatomic. So although a fluoro substituent obviously causes a steric effect, the size influence is not too drastic, which enables it to be usefully incorporated into parent molecules for beneficial modification of properties. Lateral substituents, particularly fluoro, are frequently employed in liquid crystal structures to modify melting point, liquid crystal transition temperatures and mesophase morphology and to modify the physical properties of liquid crystals to enable their use in applications. Fluoro substituents have been so successfully and usefully incorporated into liquid crystal molecules because of the combination of small size and high polarity and because the high strength of the C–F bond confers excellent stability. Achiral molecules based on a novel four-ring core with an ester linkage at the molecular bend and fluorine substituent in the side wings are shown to exhibit smectic liquid crystal phases including their polarization splay modulated and layer undulated (PMLU) variants, B7 as evidenced from polarising optical microscopy study. Additionally, these compounds exhibit strong photoluminescence, the first family of SmCP phases to do so.



B7 phase