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# Studies on Optical and Molecular Orientations of Nano Molecular Self-assembly of Nematic Dimmer and Cholesteric Materials

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**Short running title: Studies on Optical and Molecular Orientations of Nano Molecular Self-assembly of Nematic Dimmer and Cholesteric Materials**

**Keywords: Molecular orientation; Molecular self assembly; Optical texture; Helical pitch; X-ray studies;**

**Studies on Optical and Molecular Orientations of Nano Molecular Self-assembly of Nematic Dimmer and Cholesteric Materials**

**Abstract: We report the results of our studies on optical and thermal properties of binary mixtures of nematic dimmer and cholesteric compounds, namely, cholestery Inonanoate (CN) and 1,7-bis-4-(4'-cyanobiphenyl) heptane (CB7CB). Different concentrations of the nematic dimmer show a very interesting spherulitic texture of cholesteric, induced chiral smectic and reentrantsmectic-A phase, sequentially when the specimen is cooled from its isotropic melt at different temperatures. The temperature variations of helical pitch and optical textures have also been discussed. Nano-aggregated size of the molecules has been confirmed by X-ray studies.**

**Keywords: Molecular orientation; Molecular self assembly; Optical texture; Helical pitch; X-ray studies;**

## I. INTRODUCTION

Orientational ordering of the molecules in liquid crystals gives rise to a rich variety of mesophases. The existent induced chiral liquid crystalline phases are formed either by self-assembly or when doped with a non-chiral liquid crystalline material, they are intrinsically characterized by an array of unique properties and structures: that are promising from both advanced technology and fundamental research points of view [1,2]. One of the most interesting groups of liquid crystalline compounds is that of the liquid crystal dimmers. The liquid crystal dimmers are different from conventional low molar mass mesogens in the manner that they are composed of molecules in which two anisotropic mesogenic groups are linked by a flexible spacer. They have been attracting a great deal of interest in recent years not only for their ability to act as model compounds for semi flexible main chain liquid crystal polymers but also because they exhibit quite fascinating and unusual properties [3, 4].

In the present investigation, our aim is to study the binary mixtures of nematic dimmer and cholesteric compounds, namely, cholestery Inonanoate (CN) and 1,7-bis-4-(4'-cyanobiphenyl) heptane (CB7CB). Different concentrations of these molecules exhibits an cholesteric and induced chiral smectic phases such as SmA, SmC\* SmC, reentrant SmA, and SmB respectively at different temperatures. These phases were observed by using microscopic technique. Optical and thermal studies have also been carried out to understand the intermolecular interactions of given molecules.

## II. EXPERIMENTAL STUDIES

In the present study, we use the materials, namely, cholestery Inonanoate (CN) and 1,7-bis-4-(4'-cyanobiphenyl) heptane (CB7CB). Mixtures of different concentrations of cholestery Inonanoate (CN) and 1,7-bis-4-(4'-cyanobiphenyl) heptane (CB7CB) were prepared and they were mixed thoroughly. These mixtures of concentrations were kept in desiccators for 6 hours. Samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures were measured with the help of a Gippon-Japan-polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [5,6]. The X-ray broadening peaks were obtained by using JEOL diffractometer. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

### III. RESULTS AND DISCUSSIONS

#### A. Optical Texture Studies

The molecular orientations of optical textures exhibited by the samples were observed and recorded using the leitz-polarizing microscope in conjunction hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The mixture of different concentrations of given molecules were slowly cooled from its isotropic melt. The genesis of nucleation starts in the form of small bubbles and slowly grows radially, which forms a spherulitic texture of cholesteric phase with large values of pitch [7, 8]. On further cooling the specimen, the cholesteric phase slowly changes over to focal conic fan shaped texture, which is the characteristics of SmA phase and is shown in Figure 1(a). The SmA phase is unstable and then it changes over to the SmC\* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of the chiral SmC\* phase. On further cooling the specimen, this phase slowly changes over to schlieren texture of SmC phase, as shown in Figure 1(b). The SmC phase is also unstable and then it changes over to bubbles in the form of battonnets, which are the characteristic of SmA phase and this phase has been termed as the reentrant SmA (ReSmA) phase. Sequentially on further cooling the specimen: the existence of reentrant SmA (ReSmA) phase slowly changes over to hexagonal close packed higher ordered SmB phase, which remains stable at room temperature [9].

#### B. Helical Pitch Measurements In Smectic And Cholesteryl Layers

Helical pitch measurements were performed on the cholesteric phase following the well-known Grandjean–Cano wedge method [10, 11]. The given mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly ( $0.2^{\circ}\text{C min}^{-1}$ ) from isotropic cholesteric to smectic phase, which induces an array of equidistant Grandjean–Cano lines. The pitch of cholesteric phase was determined by measuring the distance between the Grandjean–Cano lines as a function of temperature. As the temperature was lowered, the mesophase changes from cholesteric to smectic phase and the spacing between lines are increased, indicating that: pitch in the cholesteric phase is also increasing. Temperature variation of pitch for the mixture of 50% CN in CB7CB is shown in Figure 2. From this figure, it is evident that, the variation of pitch from cholesteric to smectic phase is smooth and continuous. But gradually, the value of pitch increases from 0.17 to 0.19 mm upon cooling the sample from cholesteric to smectic phase. The value of pitch increases steeply and reaches a maximum of 0.54 mm at the cholesteric to smectic phase transition. In this study, we have noticed that: the sequence is Iso-Cho-SmA-SmC-SmC\*-ReSmA-SmB on cooling. Most of the data about helical pitch are available in literature [12]. The pitch is continuous at the cho-smectic transition in spite of a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the SmA, SmC, SmC\*, ReSmA and SmB phases. This divergence is related to second-order nature of the transition. It exhibits a steep decrease, close to cholesteric phase which is usually the characteristics of second-order SmA, SmC, SmC\*, ReSmA and SmB phase transitions.

#### C. Characterization Of Nano aggregated Grains

X-ray diffraction studies on liquid crystalline materials were carried out to confirm the existing phase of liquid crystals and hence it suggested by DSC and also optical texture to identify the structural properties of various liquid crystalline phases such as Cho, SmA, SmC, SmC\*, ReSmA and SmB. X-ray diffractometer traces obtained for the mixture of 50% CN in CB7CB at temperature  $63^{\circ}\text{C}$  is shown in Figure 3. The diffraction peaks at this temperature corresponds to Reentrant Smectic-A phases respectively by using JEOL diffractometer. The x-rays used had a wavelength of  $1.54066\text{\AA}$ .

In the present work, X-ray diffraction study is an important method to determine the nano-aggregated grain size of molecules for different liquid crystalline phases [13, 14]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate nano-aggregated grain size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks we have used the Scherrer's formula

$$L = K\lambda/\beta \cos\theta,$$

where L is the nano -aggregated grain size,  $\lambda$  is the wave length of X-ray, K is usually taken as 0.89,  $\beta$  is the line width at half maximum and  $\theta$  is the diffraction angle. Usually with decrease of temperature [15, 16], the nano-aggregated grain size of the molecules increases. Temperature dependent molecular orientations of focal conic fan texture of Reentrant Smectic-A phase is more stable and hence the molecular ordering of this phase shows two peaks at temperature  $63^{\circ}\text{C}$ . The nano-aggregated grain size of liquid crystalline material for Reentrant Smectic-A phase for 50% of given mixtures are comes out to be 37.38 nm. From the X-ray studies, we have been observed that, molecular ordering of liquid crystalline phase increases with decreasing the temperature. X-ray

studies clearly shows that; nano-aggregated grain size of given molecules are big enough to indicates the molecular ordering [17-19] of layer structure increases as well as decrease the temperature.

#### IV. CONCLUSIONS

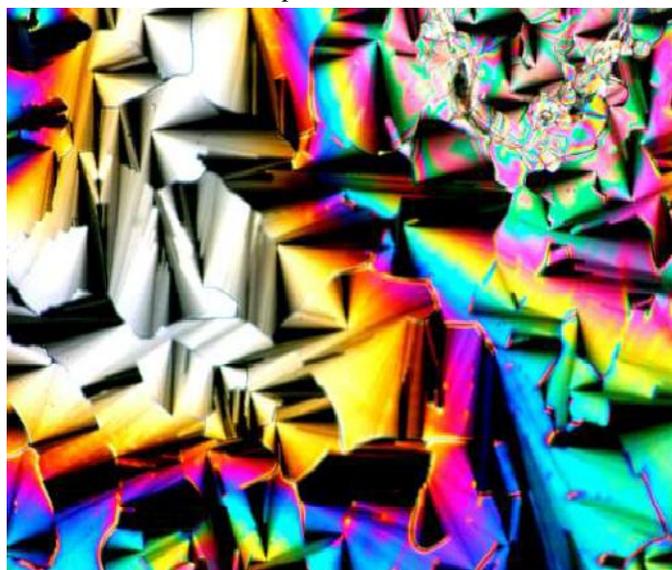
In light of the above results, we have drawn the following conclusions. The binary mixture of nematic dimmer and cholesteric material sexhibits different liquid crystalline phases, showing the formation of spherulitic texture of cholesteric, induced chiral smectic and reentrant smectic-A phase respectively at different temperatures. The value of pitch increased steeply at the cholesteric to smectic phase transition. The X-ray study lends support to found nano aggregated size of molecules for re-entrant smectic-A phase to be 37.38 nm.

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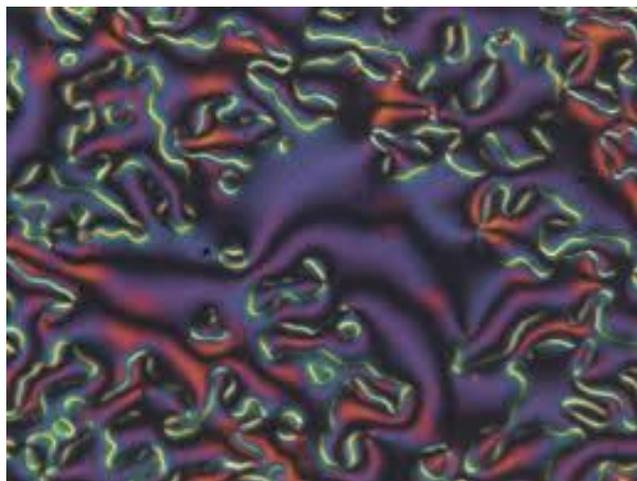
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#### Figure Captions

Figure1. Microphotographs obtained in between the crossed polars.



Focal conic fan-shaped texture of SmA phase (250X).



1) Schlieren texture of SmC phase (250X).

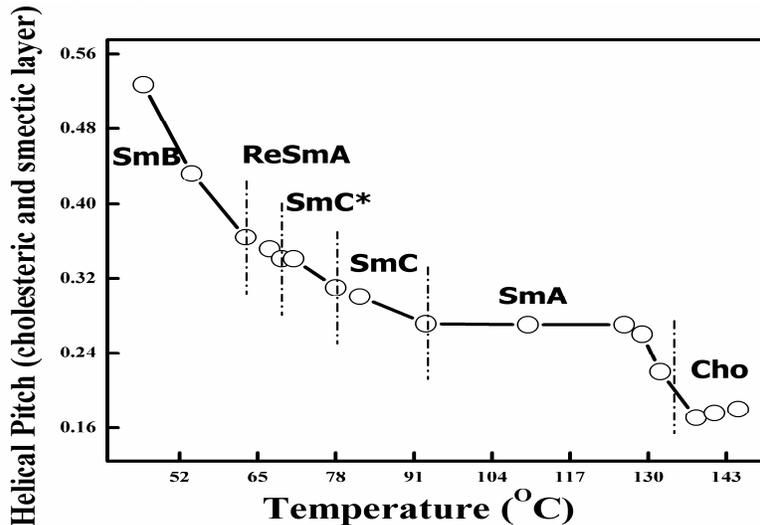


Figure 2. Temperature variations of pitch for the mixture of 50% CN in CB7CB.

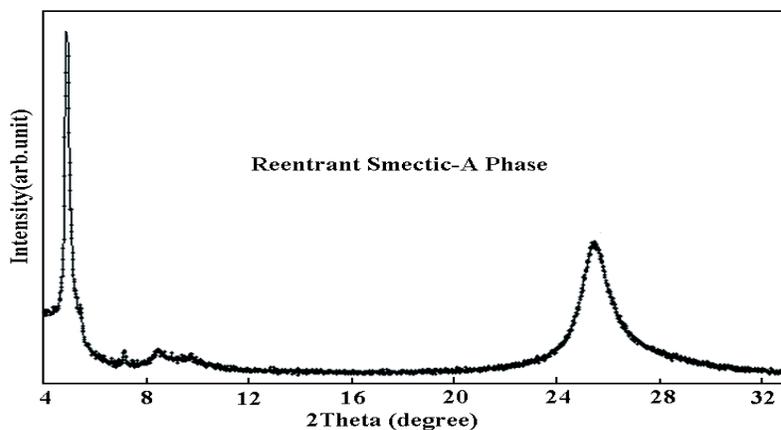


Figure 3. X-ray broadening spectrum for the sample of 50% CN in CB7CB at 63 °C of Reentrant SmA phase.



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