Available online at www.joac.info

ISSN: 2278-1862



Journal of Applicable Chemistry

2021, 10 (4): 460-465 (International Peer Reviewed Journal)

Optical Phase Transition and Tilt Angle Studies on Cyano Groups of Binary Mixture of Nematic Liquid Crystals

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Accepted on 15th July, 2021

ABSTRACT

Optical phase transition studies on thermal properties of binary mixtures of n-octyloxy-cyanobiphenyl (80CB) and 4-n-octyl-4-cyanobiphenyl (8CB) materials exhibits a re-entrant nematic and re-entrant smectic-Aphases sequentially when the specimen cooled from its isotropic melt at different concentrations and at different temperatures respectively. X-ray studies are helps us to understand the molecular layer spacing's of re-entrant nematic, re-entrant SmA and SmC phases at different temperature. Temperature variations of tilt angles have also been discussed.

Graphical Abstract:



Microphotographs obtained in between the crossed polars.

Keywords: Phase transition, Molecular orientation, layer spacing's, Tilt angle.

INTRODUCTION

Liquid crystal may be defined as a thermodynamically stable phase and it is characterized by anisotropy of properties without the existence of a three dimensional crystal lattice. For many organic materials, the transition from the solid to the liquid phase does not occur in a single step but takes place in a cascade of transitions. The molecular ordering in these intermediate phases, known as "mesophases," lies between that of a solid and an isotropic liquid. These ordered fluid mesophases are commonly called liquid crystals and are most often composed of elongated molecules. In these

mesophases: if the molecules shows some degree of rotational order (and in a few cases partial translational order as well) even though the crystal lattice does not exist. Lack of a lattice requires that these mesophases be fluid; they are, however, 'ordered fluid phases'. It is this simultaneous possession of liquid-like (fluidity) and solid-like (molecular order) character in a single phase that makes liquid crystals unique and gives rise to so many interesting properties as well as technological applications [1-6].

In the present investigation, we have been consider acyano groups of two compounds namely; noctyloxy-cyanobiphenyl (8OCB)and 4-n-octyl-4-cyanobiphenyl (8CB). Mixture of these molecules exhibits a re-entrant nematic and re-entrant smectic-A phases and also observed induced smectic phases such as SmA, SmC and SmE phases sequentially when the specimen is cooled from its isotropic melt. X-ray studies are helps us to study the molecular layer spacing's of re-entrant nematic, re-entrant SmA and SmC phases at different temperature. Temperature variations of tilt angles have also been discussed.

MATERIALS AND METHODS

In the present work: we have been considered two compounds namely:n-octyloxy-cyanobiphenyl (80CB) and 4-n-Octyl-4-Cyano-Biphenyl (8CB). Mixtures of different concentrations of 80CB and 8CB were prepared and were mixed thoroughly. These mixtures of various concentrations of 80CB and 8CB were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. The phase transition temperatures of these concentrations were measured with the help of 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 X-ray diffraction patterns were obtained using JEOL diffractometer [7].

RESULTS AND DISCUSSION

Optical studies: Binary mixtures of 80CB and 8CB exhibit a different liquid crystalline phases; the optical-phase transition studies were measured by Gippon-Japan polarizing microscope. The partial phase diagram is as shown in figure 1, which is obtained by plotting the concentrations against the phase transition temperatures. The partial phase diagram helps us to understand the stability of liquid crystalline phases and it has been found that: the concentrations ranging from 10% to 90% 8OCB and 8CB of given molecules shows a very interesting re-entrant nematic and re-entrant smectic-A phases and also it has been observed the smectic modifications: such as SmA, SmC and SmE phases sequentially when the specimen is cooled from its isotropic melt. The concentrations from 40% to 60% of cyano groups of this molecules exhibit a very interesting re-entrant nematic phase at below the smectic layer planes and it termed as the re-entrantnematic phase (N_{RE}). The existence of re-entrant nematic phase at lower temperature, the symmetry of thermodynamic stable phase decreases; in that region the molecules are invariant under decreasing a number of symmetry operations. The unstable re-entrant nematic phase exhibits as triped pattern focal conic domains of re-entrant SmA phase and then this phase produces a schlieren texture with disclinations (characterized by two dark brushes of extinction) and point defects-boojums (with four brushes of extinction) [8], these are the characteristics of characteristic of the SmC phase, when the sample is cooled from the re-entrant SmA phase. Microscopic observations of schlieren texture of SmC phase as shown in figure 2. The phase transition from re-entrant smectic-A-smectic-C phases are heralded by the appearance of a faint whitish background, the intensity of the transmitted light increasing at lower temperatures. This is caused by the increase of the tilt angle of the molecules as the temperature is lowered in the SmC phase. The molecules in chiral smectic phase form a layered structure, the thickness of each layer being typically of the order 20-30 Å. X-ray studies have shown that the molecular centers are packed randomly within the layers. The molecules are tilted from the layer normal by an angle. Eventually on this phase changes over to the crystalline SmE phase and this phase remains stable at room temperature [9-11].





Figure 1. Partial phase diagram for the sample of 8OCB in 8CB.



Figure 2. Microphotographs obtained in between the crossed polars

X-ray studies: X-ray diffraction patterns were taken to understand the change in layer spacing's of re-entrant nematic, re-entrant SmA and SmC phases with temperature. The obtained x-ray traces for samples of 50% of 8OCB in 8CB at different temperatures correspond to re-entrant nematic, re-entrant SmA and SmC phases respectively. From the figure 3, it has been observed that: as the temperature increases the molecular layer spacing's of re-entrant smectic-A phase are constant, but in



Figure 3. Variations of layer spacing's with temperature for the sample of 50% 80CB in 8CB at the transition from re-entrant smectic-A to re-entrant nematic phases.

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re-entrant nematic phase and molecular layer spacing's are abruptly increases. In contrast to the birefringence cyano groups of given molecules are abruptly changes at re-entrant smectic-A to re-entrant nematic transition. This suggests that a general increase in orientational order. The increase in orientational order and tilt angle may explain low shrinkage of smectic layers. From the figure 4, it is very clear that:the molecular layer spacing's of smectic-C phase increases with increasing temperature and then transition from smectic-C to re-entrant smectic-A phase, themolecular layer spacing's are constant. In the re-entrant smectic-A to smectic-C phase transition, when temperature decreases, the tilt angle increases from $\theta=0$ (ReSm_A) to $\theta > 0$ (SmC), the smectic layer spacing's are almost constant [12, 13].



Figure 4. Variations of layer spacing's with temperature for the sample of 50% 80CB in 8CB at the transition from smectic-C to re-entrant smectic-A phases.

Temperature variations of tilt angle studies on smectic-c phase: Measurements of temperature variations of tilt angle on smectic phase of liquid crystalline materials are good test for theory. In the tilted smectic planes, the tilt angle can be measured by using x-ray diffraction data to determine the change in interlayer spacing distance due to the tilting of molecules. Temperature variations of tilt angle on smectic-c phase for the sample of 50% 80CB and 8CB are shown in figure 5. The tilt angle increases with increasing temperature and it attains a saturation value. The saturation value of tilt angle for the smectic-C phase is found to be 3.63° is shown in the figure. The tilt angle values are attributed to the directions of soft covalent bond interaction and it extends along the molecular axis



Figure 5. Temperature variations of tilt angle on smectic-c phase for the sample of 50% 8OCB in 8CB.

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molecular self assembly, which provides larger dipole-dipole interaction between the molecules. Sometimes A small discontinuity of the tilt angle has been observed at every phase transition between tilted smectic planes. The tilt angle studies helps us to understand polar interactions between the neighboring layers provides excellent agreement with the experiment for phase transitions between smectic-A and smectic-E phases [14-19].

APPLICATION

This study shows how microscopic technique and optical anisotropy of binary mixtures of cyano groups of nematic liquid crystalline materials changes with variations of temperature.

CONCLUSION

Microscopic investigation of binary mixture of cyano groups of molecules shows the existence of reentrant nematic and re-entrant smectic-A phases for some concentrations respectively at different temperatures. he x-ray data of intermolecular layer spacing's are helps us to understand the tiltangles studies on smectic-C phase: it shows a strong coupling of aggregated nano-molecular self assembly: which provides larger dipole-dipole interaction between the central core and side chain of liquid crystalline molecules.

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