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Phase Behaviour Studies of Intermolecular Hydrogen Bonded Binary Liquid Crystal Complex

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Abstract: A hydrogen bonded liquid crystal complex is designed and synthesized from the binary mixture of cholesteryl acetate (CHA) and 4- octyloxy benzoic acid (8BAO), and hydrogen bond formation in the complex has been confirmed by Fourier transform infrared (FTIR) spectroscopic studies. The thermal and textural characterization of the complex is carried out by polarizing optical microscope (POM) and differential scanning calorimetry (DSC). Transition temperatures and corresponding enthalpy values along with enantiotropic and monotropic transitions are elucidated from DSC. Interesting observation of the present work is that the identification of induced smectic G phase between smectic C and crystal, wider thermal span of the mesogenic phases and decreased enthalpy values in the binary mixture compared to the individual mesogens.
Keywords: Hydrogen bonded liquid crystals, Binary mixture, Nematic, Smectic, DSC, FTIR.

Introduction

Generally, the liquid crystal compounds of benzoic acids are found to exhibit mesomorphic phases with other mesogenic or non-mesogenic compounds through hydrogen bonding[1]. The formation of hydrogen bond (H-bond) through the non covalent interactions of molecules is a powerful tool for self assembling the molecules to form the liquid crystal complexes[2]. Mesomorphic phases in the hydrogen bonded liquid crystal complex play a vital role in designing the supramolecular liquid crystals. The hydrogen bonding interaction between molecules of supramolecular liquid crystal complexes have been studied extensively[3-6]. Synthesis of various liquid crystal complexes from the mixtures of mesogenic–mesogenic materials, mesogenic – non mesogenic material and non mesogenic– non mesogenic materials in different molecular ratios is a very active and vibrating area of the liquid crystal science[7-10].

A novel supramolecular hydrogen-bonded cholesteric mesogens have been investigated[11]. A supramolecular helical assembly of nematics in cholesteric liquid crystals (CLCs) cover a wide range of potential applications in displays, polarisers, organic pigments, thermography and photonic devices[12-14]. Most of the liquid crystals used in liquid crystal display technology are the eutectic mixtures that are developed by

mixing two or more mesogenic materials [15]. The alteration of the mixed mesomorphic ranges and thermal stabilities in the complex mesogens has drawn more attention among the various research groups [16-18].

With our previous research experience in synthesis and characterization of various types of hydrogen bonded liquid crystals (HBLC)[19-23] by following a well documented synthesis route, we obtained the binary mixture of HBLC complex. The field of hydrogen bonded liquid crystal (HBLC) is wide open for the design, synthesis and characterization of various new combinations of mesogens and non mesogens. The authors equipped such a possibility with mixing different mesogenic acids which enabled to understand the correlation between the physical and the chemical structure of the HBLC moieties. The demand of carrying out the present study lies in synthesize, analyze, and optical, thermal characterization of the complexes formed between two dissimilar mesogenic compounds which give an instant bound to numerous potential applications in the field of display devices such as optical shutters and light modulators [21, 22]

Experimental

4 - octyloxy benzoic acid (8BAO) and cholesteryl acetate (CHA) were supplied by Sigma Aldrich, Germany and all the solvents used were E.Merck grade. The LC sample is filled in its isotropic state to a homogenous alignment liquid crystal cell commercially available (Instec, USA) of 5 x 5 mm^2 indium tin oxide coated area with 4 μm spacer by capillary action.This LC cell is placed in a hot stage MHCS400 (MicrOptik) where the temperature is monitored by a MTDC600 temperature controller (MicrOptik) which is interfaced with a computer and controlled by a software program to a temperature resolution of $\pm$ 0.1^oC. The hot stage is placed under crossed polarizer of Ningbo polarizing microscope for optical textural studies equipped with digital unit (ToupTek). Optical images of mesogens are captured using a Sony CCD.17.UH310 USB CCD 3.1MP camera during heating and cooling runs at the rate of 1^oC min^{-1} and the corresponding textures are analyzed by software.

Shimadzu DSC60 Plus with Ta60 software (version 2.21) and TAC-60i mechanical auto-cooling system is used for obtaining transition temperatures and enthalpy values of mesogens. Mass of about 4mg pure mesogens and mixture (CHA+8BAO) are accurately weighed by using a Shimadzu microbalance. The weighed mesogens and HBLC complex (CHA+8BAO) are sealed in aluminium pans and they are heated up to a temperature above the estimated clearing temperature and hold at its isotropic temperature for two minutes so as to attain thermal stability. Once a stable heat flow is sustained, the samples are cooled at a rate of 5$^oC min^{-1}$ to 30°C followed by a heating scan at a rate of 5$^oC min^{-1}$ to a temperature above the expected clearing temperature. All DSC curves are corrected using baselines recorded under identical conditions. FTIR spectra are recorded (ABB FTIR MB3000) by making pellet of the mesogens and (CHA+8BAO) complex along with KBr and analyzed them using the MB3000 software to identify the formation of H-bond in the (CHA+8BAO) complex.

Synthesis of CHA+8BAO HBLC complex

Intermolecular HBLC is synthesized by adding of one mole of 8BAO in N,N-Dimethyl formamide (DMF) and then with one mole of CHA in ethyl acetate respectively as shown in Figure 1. Further, the mixture is subjected to constant stirring (magnetic stirrer) for 12 hours with 750rpm at ambient temperature of 30^oC till white precipitate is formed. The white crystalline crude complex so obtained by removing excess DMF and then recrystallized with dimethyl sulfoxide. The yield is about 95%. The designed molecular structure of the HBLC complex (CHA+8BAO) is depicted in Figure 1.

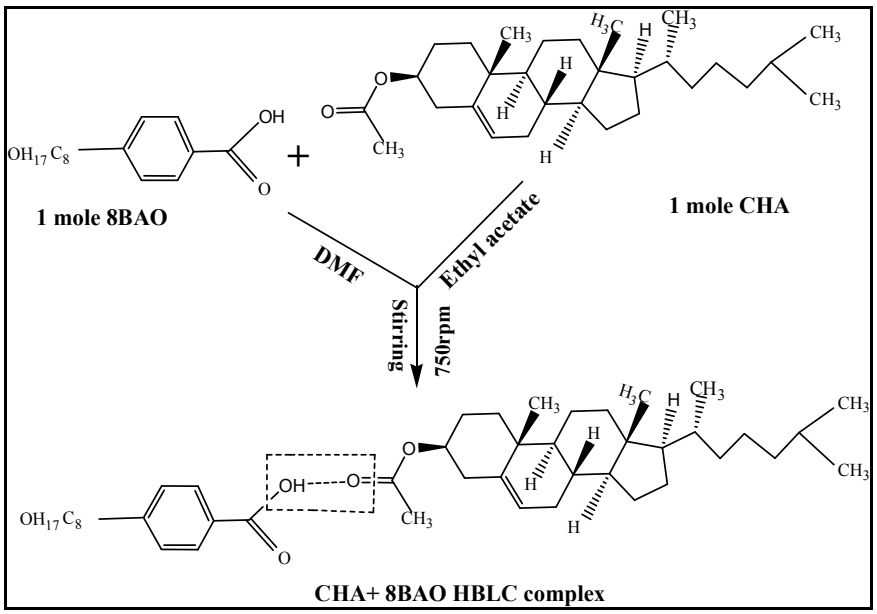

Figure 1 Molecular structure of CHA+8BAO hydrogen bonded complex

Results and Discussion

Infrared Spectroscopy (FTIR)

The FTIR spectrum of intermolecular H- bonded (CHA+8BAO) complex is recorded in the solid state (KBr) at room temperature as shown in Figure 2. The IR solid state spectra of 4 - octyl benzoic acid (8BAO) is reported[24] that there are two sharp bands at 1685 and 1695 cm^{-1} due to the frequency ν(C=O) mode. The doubling characteristic of this stretching mode confirms the dimeric nature of alkyloxybenzoic acid at room temperature[24]. The presence of H-bond in the present complex is further inferred by the appearance of new band shows the carboxylic acid group ν(O---H) at 2854cm^{-1} and the same is not observed in the pure CHA and pure 8BAO[25,26] mesogens.

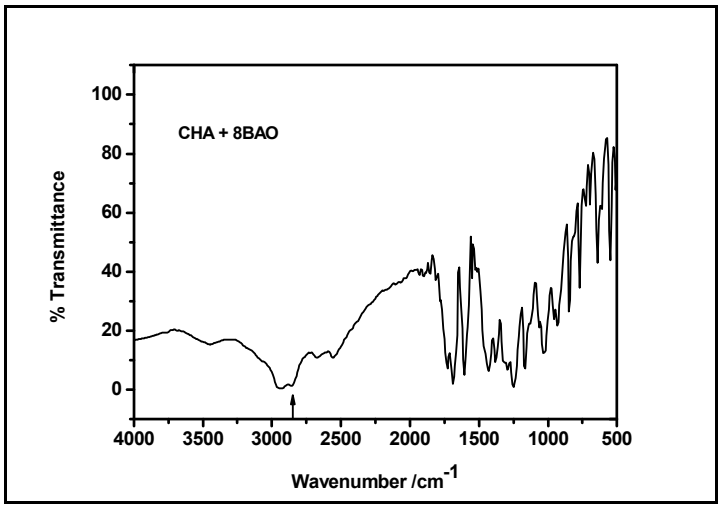

Figure 2 FTIR spectra of CHA+8BAO hydrogen bonded complex

Textural observations-POM

The synthesized HBLC complex is highly stable at ambient temperature (~30^{o}C). The prepared HBLC complex melts at specific temperature below ~85^{o}C and it shows high thermal and chemical stability when subjected to repeated thermal scans performed during POM and DSC studies. The POM is used to observe the thermal behaviors and textures exhibited by the mesogens and HBLC complex. The pure CHA mesogen is

found to exhibit characteristic textures like cholestric, and crystal texture as shown in Figure 3a-3c respectively. The pure 8BAO mesogen is found to exhibit characteristic like threaded Nematic (N), twisted Smectic (Sm C), Smectic G (Sm G) and crystal texture as reported[27] by author.

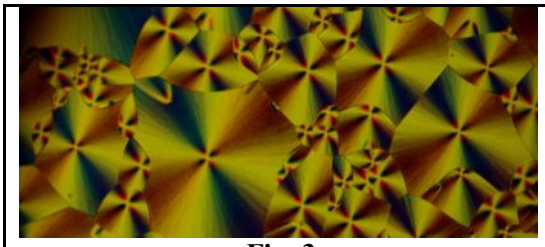

Fig. 3a

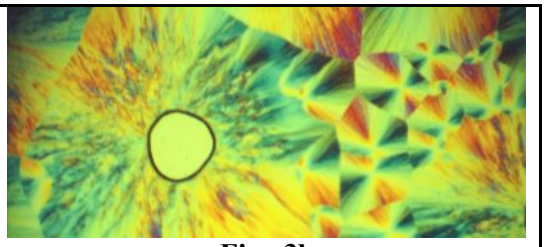

Fig. 3b

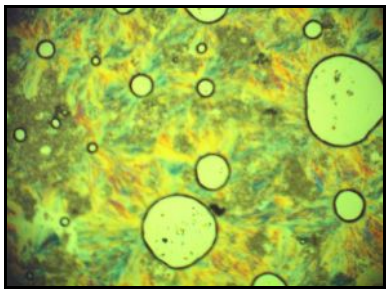

Fig. 3c

Figure 3 Characteristic texture of pure cholesteryl acetate

The HBLC complex is found to exhibit characteristic textures[28] like Smectic C (Schlieren texture), Smectic G (mosaic texture) and crystal texture as shown in Figure 4a-4d, respectively. Formation of H-bond between two mesogens leads to change in transition temperatures without much affecting mesophase structures. Nearly the cholesteric phases are very similar to the nematic LCs. As significance, the system acquires a helical ordering perpendicular to the long axis of the molecules. Also the helix may be right or left-handed depending on the molecular average orientation.

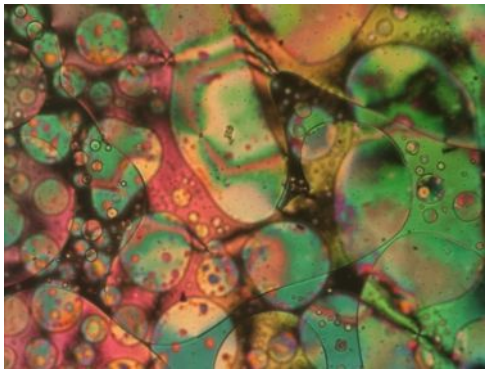

Fig. 4a

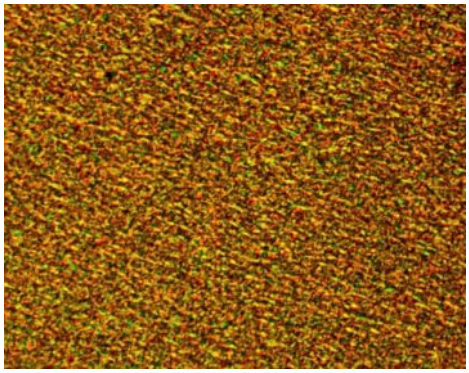

Fig. 4b

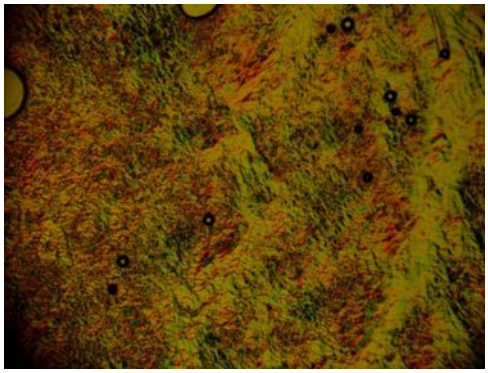

Fig. 4c

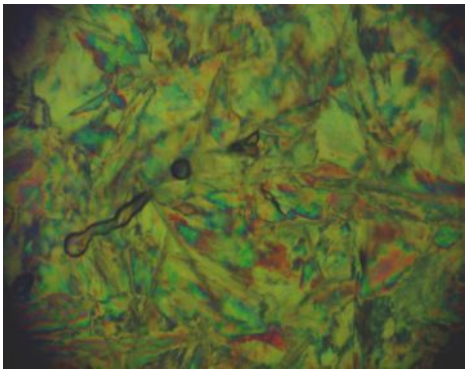

Fig. 4d

Figure 4 Characteristic texture of CHA +8BAO hydrogen bonded complex

Table 1 Transition temperatures in centigrade obtained by POM and DSC techniques along with enthalpy values given in J/g

Compound	Phase Variance	Technique	Cycle	Crystal-Melt	N	Sm C	Sm G	Crystal
8 BAO	NC	POM	Heating	73.1	108.2	101.3		
			Cooling		105.4	92.5		53.9
	NC	DSC	Heating	72.4 (111.71)	107.8 (7.14)	100.9 (65.87)		
			Cooling		105.2 (0.59)	92.1 (0.16)		53.4 (10.4)
CHA	N	POM	Heating	107.3	#			
			Cooling		81.3			80.6
	N	DSC	Heating	106.1 (158.3)	#			
			Cooling		81.0 (Merged with crystal)			80.3 (73.9)
CHA+8BAO	NCG	POM	Heating	75.2	93.3	52.7	#	
			Cooling		92.9	52.4	48.9	47.0
		DSC	Heating	74.4 (134.24)	94.9 (1.37)	#	#	
			Cooling		92.7 (0.26)	52.1 (0.77)	48.6 (Merged with crystal)	46.2 (2.57)

monotropic transition

The observed phase variants and transition temperatures (POM) in cooling and heating cycles for the pure mesogens and prepared HBLC complex is given in Table 1. The general phase sequences of the pure mesogens and the HBLC complex in the cooling run are observed as,

Isotropic ⟵ N ⇋ Crystal **(CHA)**
Isotropic ⇋ Nematic ⇋ Sm ⇋ Crystal **(8BAO)**
Isotropic ⇋ Nematic ⟵ Sm C ⟵ Sm G ⇋ Crystal **(CHA+8BAO)**

DSC STUDIES

Pure cholesteryl acetate (CHA)

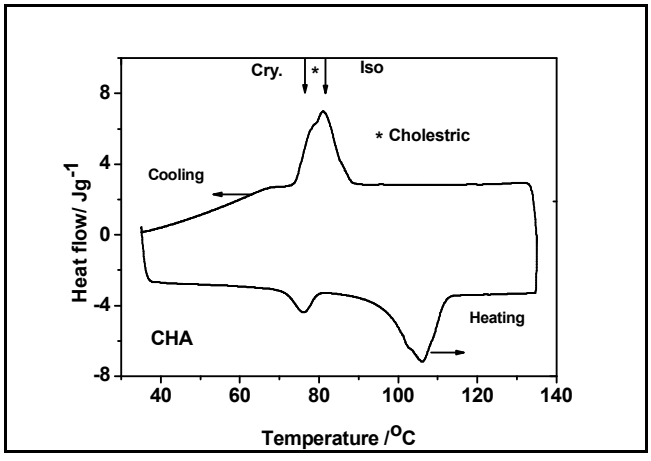

Figure 5 DSC thermogram of pure cholesteryl acetate

The DSC heating scan for pure CHA in Figure 5 shows a peak at 105.8°C indicating transition from crystal to melt and the cholestric mesophase region is not identified (monotropic) during heating scan and POM observation. The DSC cooling scan for pure CHA in Figure 5 shows a peak at 81.0°C for the transition from the isotropic phase to mesophase which is merged with crystal. From observations of POM, literature data[26] and DSC curve, we have identified the threaded nematic texture (Figure 3a) as mesophase. Also the transition from cholesteric to disturbed cholestric texture is shown in Figure 3b and the corresponding peak (DSC) at 80.3°C represents transition from the disturbed cholestric texture to solid phase as shown in Figure 3c. LC phase transitions such as melting, and other phase transition temperatures are found to be invariant in successive cooling and heating cycle. This clearly shows that the synthesized intermolecular HBLC complex is chemically more stable and purity.

Pure 4- decyloxy benzoic acid (8BAO)

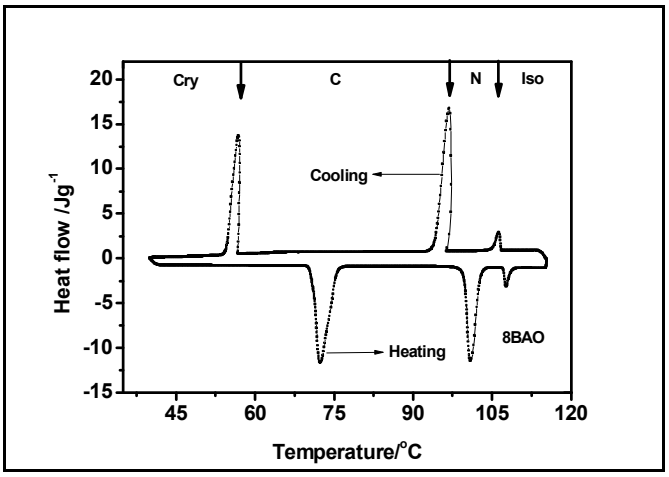

Figure 6 DSC thermogram of pure 4 - octyloxy benzoic acid

The DSC heating and cooling cycle of pure 8BAO (Figure 6) shows there are four well-known peaks. During DSC cooling cycle , transition temperatures for the mesomorphic phases in 8BAO are evaluated as 105.2°C, 92.1°C, and 53.4°C for Iso to N, N to Sm C and Sm C to crystal respectively.

HBLC complex (CHA+8BAO)

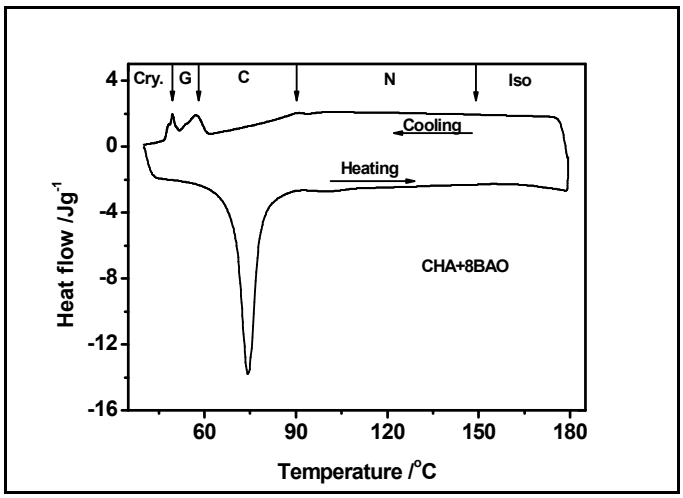

Figure 7 DSC thermogram of CHA +8BAO hydrogen bonded complex

The DSC curve (Figure 7) for the HBLC complex (CHA+8BAO) during cooling cycle at 92.7°C, 52.1°C, 48.6°C and 46.2°C shows mesophases corresponding to threaded Nematic (Figure 4a), schlieren texture of Sm C (Figure 4b), multicolored mosaic like texture of Sm G (Figure 4c) and crystal phases (Figure 4d) respectively. We identified that the induced Sm G phase due to the increasing the chain length and

texturally disturbed phases in the CHA+8BAO complex while compared to pure CHA and pure 8BAO, in addition to that the increased thermal span of 40.6°C in the nematic region while compared to pure 8BAO of 13.1°C. Also the induced Sm G phae thermal span is observed as 2.4°C. This observation clearly shows that the stabilization of phases is due to the formation of intermolecular hydrogen bond between the mesogens which creates the systematic reorientation of molecules themselves. Increasing chain length in the intermolecular hydrogen bonded liquid crystals could induce a frustration in the layer smectic liquid phase structures.

At the eutectic point, the melting point reaches its minimum and also clearing point of the liquid crystal complex is usually the linear average of composition, thus the mixture of two liquid crystal can offer a much larger temperature range that exhibit the nematic phase for display applications. The observed phase variants, transition temperatures and corresponding enthalpy values are obtained by DSC in cooling and heating cycles for the pure mesogens and HBLC complex is presented in Table 1. Polarizing optical microscopic studies are concurrent with DSC results.

Conclusions

Thermal and optical properties of two pure mesogens and the binary mixture of HBLCs have been analyzed. This molecular design strategy gave a wonderful method to modulate the phase behavior and transition temperatures of HBLC mesogenic complex. The induced Sm G phase, corresponding textures and transition temperature along with enthalpy values are analyzed through POM and DSC studies respectively. Abundant reduction of enthalpy values across isotropic to nematic, nematic to Sm C, Sm C to Sm G and Sm G to crystal phase are found in the HBLC (CHA+8BAO) complex.

Acknowledgements

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