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Synthesis and phase transition studies on hydrogen bonded liquid crystal *p*-propoxy benzoic acid :*p*-chloro benzoic acid (3OBA:CIBA)

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ABSTRACT: Liquid crystal and non-liquid crystal combination class of *p*-propoxybenzoic acid :*p*-chlorobenzoic acid was synthesised. Monotropic nematic phase of textural identification was observed using polarizing microscopic studies. Phase transition temperature investigations were carried out using polarizing microscopy and differential scanning calorimetry (DSC). First order of the phase transition is noticed using Navard and Haudin parameter. FTIR studies reveal in solid (KBr) and solution (chloroform) state that there is a hetero dimer formation of acid moieties in the two compounds.

KEYWORDS: Phase, transitions temperatures, DSC, FTIR, Hydrogen bond, Navard and Haudin parameter.

I. INTRODUCTION

To bring down the transition temperature and to increase the phase range and to induce and/or quench the phases can be achieved significantly in complex liquid crystals. If the complex is formed through inter molecular hydrogen bond, lengthening of rigid rod segments occurs as a property of liquid crystalline behaviour. Induced mesomorphism due to non-covalent electrostatic interaction involving intermolecular hydrogen bonding type work is gained momentum [1-4]. Mesogen and mesogen as well as mesogen and non mesogen systems [5,6] were carried out by our group. In continuation of research, this work is taken up to prepare complex liquid crystal via hydrogen bond through the type of mesogen and nonmesogen combination, namely *p*-propoxy benzoic Acid and *p*- chloro benzoic acid.

II. EXPERIMENTAL

Textural and transition temperature studies is carried out using Mopta polarizing optical microscope with hot stage which is indigenously designed [7] and camera attachment. Temperature is measured with a digital thermometer with an accuracy $\pm 0.1^\circ\text{C}$. The transition temperatures under study are determined using M/s Thermal Analysis Instruments, UK of Differential Scanning Calorimeter (DSC). Fourier transformation Infrared spectrometer (FTIR): The Fourier transformation and Infrared Spectrometer is useful in obtaining wave numbers of different bonds. The instrument used was model FTIR-5300 of JASCO (Japan). One can obtain FTIR graph in a computer showing several peaks for different bonds in the compound.

Preparation of *p*-propoxy benzoic acid :-*p*-chloro benzoic acid (*p* – 3OBA : *p* –CIBA):-

p-Propoxy Benzoic Acid (3OBA) and *p*- chloro benzoic acid (CIBA) are purchased from Frinton Laboratories Vineland, New Jersey, USA and from M/s Loba Chemicals, India respectively. The intermolecular hydrogen (H) bonding complex, *p*-propoxybenzoic acid and *p*- chloro benzoic acid (3OBA : CIBA) was synthesized by refluxing together equimolar ratio(1:1) of *p*-Propoxy benzoic acid (0.4505 gm) and *p*- Chloro benzoic acid (0.3914 gm) and 20 ml of pyridine under constant stirring at 80°C for ~4hrs and the detailed procedure is reported in [6,7]. The yielding is of about 85 %.

III. RESULTS AND DISCUSSION

Thermal polarizing microscopy:-

Enantiotropic nematic phase is observed in 3OBA which is in good agreement with the reported values.[8,9] . *p*-chloro benzoic acid is non mesogenic and the melting point is 242 °C. The compound 3OBA: CIBA exhibits a single phase variant in between solid phase and isotropic phase. The observed phase is schliere texture indicating nematic phase (Fig. 1) and nematic droplets (Fig. 2). The nematic texture is observed only on heating, no phase is observed on cooling. DSC also confirmed the same observation. Hence the synthesised compound exhibits monotropic.. On heating from solid phase, a liquid crystalline phase nematic separates the solid at 114.2 °C. The nematic phase consists of threaded like structure. On further heating the nematic phase is changed to isotropic phase at 149.3 °C. Textural change and transition temperatures are given in heating and cooling for 3OBA, CIBA and 3OBA : CIBA (Table 1).

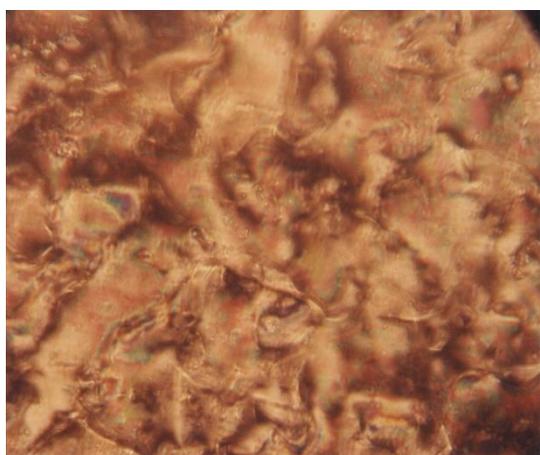


Fig. 1: Nematic texture of 3OBA: CIBA

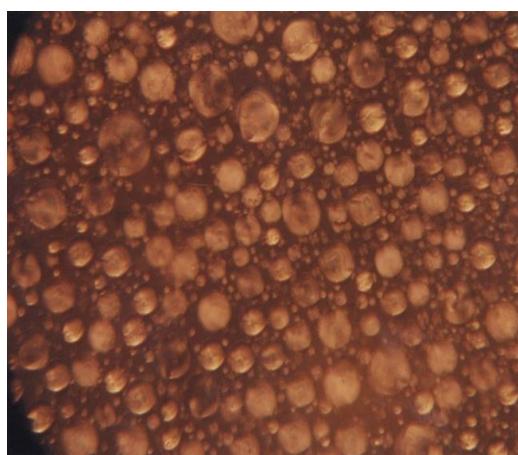


Fig. 2: Nematic droplets of 3OBA

Characterization of phase identification:-

On heating the solid phase to nematic phase transition is observed at 108.1 °C while the nematic phase to isotropic phase transition is observed at 145.14 °C. In the cooling cycle no peak is observed. This indicates that the prepared compound is monotropic which is in good agreement with the polarizing microscopic studies. In the both heating and cooling cycles the DSC thermograms are presented in the Figs.3 and 4. The compound 3OBA: CIBA exhibits a single phase variant in between solid crystal and isotropic phase in the heating cycle and hence it is monotropic. It means that the textural phase is observed only on heating and no phase has been observed on cooling. In DSC also the same thing has been observed. On heating from solid phase, a liquid crystalline phase nematic separates the solid at 114.2 °C. The nematic phase consists of threads. On further heating the nematic phase is changed to isotropic at 149.3 °C. This data is presented in Table 1 along with the reported values in the literature.

Table: 1: DSC and TM data of the present study on 3OBA and 3OBA: CIBA

p- 3OBA (p-Propoxy Benzoic Acid)					
Name of the reporter// Present study	Experiment	Solid to Solid	Solid to Nematic	Nematic to Isotropic	Nematic Range
A.J.Herbert [8 9]	DSC	121°C	146.5°C	153.5°C	7 °C
Robert.F.Bryan and Paul Hartley [9 8]	X-ray	122°C	147 °C	153.5°C	6.5°C
M.Srinivasulu[10 14]	T.M.	-----	145.2°C	154.9°C	9.7°C
	DSC	-----	150.6°C	158.8°C	8.2°C
Frinton Laboratories	-----	-----	145°C	156°C	11 °C

Present study	T.M. (H)		144.3 °C	154.1 °C	9.8 °C
	T.M. (C)		132.2 °C	152.5 °C	
	DSC (H)	121.9 °C	149.02 °C	157.7 °C	8.7 °C
	DSC (C)	-----	136.7 °C	153.6 °C	
Synthesized compound <i>p</i> -3OBA: <i>p</i> -ClBA (<i>p</i> -propoxy benzoic acid and <i>p</i> -chloro benzoic acid)					
Present study	T.M. (H)	-----	133.1 °C	151.9 °C	18.8 °C
	DSC (H)	126.9 °C	136.6 °C	152.8 °C	19.2 °C

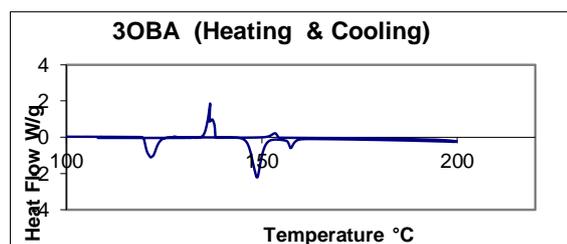


Fig. 3: DSC thermogram of 3OBA

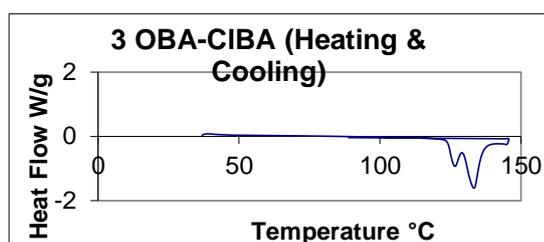


Fig. 4: DSC thermogram of 3OBA:ClBA

The Differential Scanning Calorimetry is an extensive technique not only for the detection of phase transitions, quantitative determination of the associated enthalpy changes at the transition and for the qualitative analysis of materials (purity, isothermal crystallization etc.,) but also for the determination of the order of transition whether first order or second order .

An elegant and simple method to determine the order of phase transition temperatures from the DSC peak heights of material quantities was reported by Navard and Haudin [11-10]. The order of phase transition can be determined from the magnitude of the ratio (N) of different enthalpy peak heights h_2/h_1 , performed with two different scan rates (T_1 and T_2), which is a function of the ratio of the scanning rates, ($T_2/T_1 = R$), keeping the weight of the compound constant. It follows that for a first order transition, N varies as the square root of R, while for the second order transition, N should be directly proportional to R: Here we have used $R = 2$ (i.e., keeping the mass of the sample constant the DSC thermogram (Fig.5) are obtained for scan rates 10 °C and 5 °C

For the synthesized compound, we have used $R = 2$ (i.e., keeping the mass of the sample constant) and the DSC thermograms are obtained for scan rates 10 °C and 5 °C. DSC thermogram scanned at 5 °C /min (h_1) and 10 °C /min (h_2) are shown in figure 3. The height calculated for 5 °C /min (h_1) and 10 °C /min (h_2) are 0.63 and 1.76 respectively. The Navard and Haudin parameter is $h_2/h_1 = 2.77$. This value suggests that the order of isotropic - nematic transition in this compound is the second order.

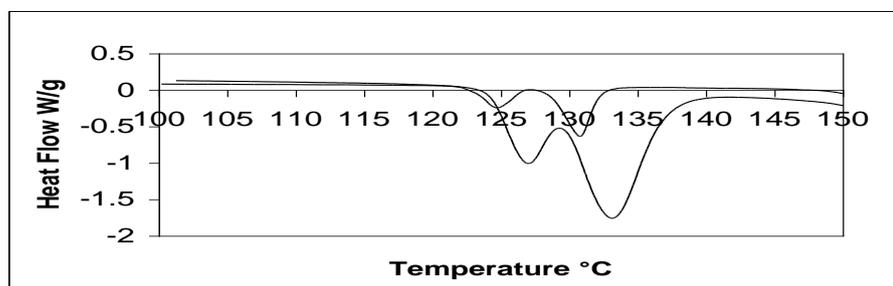


Fig. 5: DSC thermograms for scan rates 10 °C and 5 °C

FTIR SPECTRA :

Important structural information can be get from the powerful technique of Infrared spectroscopy [12-14]. Intra and inter molecular hydrogen interactions can be observed in the structural elucidation of organic molecules. Molecular vibrations and rotations due to the excitations, the absorption bands in the infrared region of the electro- magnetic radiation are obtained. The IR spectrum of a particular free organic compound is the characteristic of the entire molecule and it is true that certain functional groups of the molecule give rise to the bands at or near the same frequency regardless of structure of the rest of the molecule. When an organic compound binds to another molecule, at

least one additional atom is introduced into the vibrational system of the other compound. As a consequence the bond angles, bond lengths and inter atomic force constants associated with the individual compounds would be expected to alter slightly in their complexes. The IR spectrum of a coordinated compound differs from that of a free molecule and thus, it should be possible to correlate the changes in the form of band shifts observed in the spectra with the changes in bonding. Thus the information regarding the bonding nature of the constituent molecule in a particular complex may be obtained. Our aim is to establish the existence of inter molecular hydrogen bonding using this IR spectra.

p-Propoxy benzoic acids (3OBA):-

The IR spectrum of p – propoxy benzoic acids are recorded [10] at room temperature both in solid (KBr) and solution (Chloroform) (Fig.6) states. The spectra of p-propoxy benzoic acid show a sharp peak at 1680.15cm⁻¹ due to KBr and 1672.92 due to chloroform for ν (C = O) mode. Another strong intense band assigned to ν (OH) mode of carboxylic acid group is obtained at 2966.79 due to KBr and 2956.91 due to chloroform.

p-Chloro benzoic acids (CIBA):-

The IR Spectrum of p-chloro benzoic acid is recorded at room temperature both in solid (KBr) and solution (chloroform) states (Fig. 7). The spectra of p- chloro benzoic acid show a sharp peak at 1682.08cm⁻¹ due to KBr and 1683.55 cm⁻¹ due to chloroform for ν (C = O) mode. Another strong intense band assigned to ν (OH) mode of carboxylic acid group is obtained at 2925.48 cm⁻¹ due to chloroform. To avoid further complications due to such intermolecular interactions, comparison of spectra complexes are made with the solution state spectra of free CIBA.

p – Propoxy benzoic acid : p – chloro benzoic acids (3OBA : CIBA):-

The infrared frequencies of 3OBA:CIBA (Fig. 8) show the presence of a strong intense band due to (C = O) mode of benzoic acid moiety at ~1682.08cm⁻¹. This strongly supports the existence of 3OBA moiety in a monomeric form upon complexation. The formation of inter molecular hydrogen bonding between COOH group of 3OBA and COOH group of CIBA can be invoked on the basis of hypsochromic shift in ν(C=O) mode (~10 cm⁻¹) of 3OBA and ν(OH) mode of carboxylic acid group also suffered a hypsochromic shift of (~2Cm⁻¹) upon complexation which strongly supports the existence of weak H – bonding between COOH of p-propoxy benzoic acid and COOH of p-chloro benzoic acid due to hetero dimer formation [1].

Table – 2: IR Spectra data cm⁻¹ of 3OBA, CIBA and 3OBA: CIBA

S.No.	Compound	ν(C = O) _{acid} cm ⁻¹	ν(OH) _{acid} cm ⁻¹	ν(C – O) cm ⁻¹
1.	3OBA(CH ₃ Cl)	1672.92	2965.98	1287.25
2.	3OBA(KBr)	1680.15	2966.79	1288.56
3.	CIBA(CH ₃ Cl)	1683.55	2925.48	1283.59
4.	CIBA (KBr)	1682.06	-----	1282.78
5.	3OBA : CIBA (CH ₃ Cl)	1678.73	2966.95	1283.39
6.	3OBA : CIBA (KBr)	1682.08	2976.69	1286.64

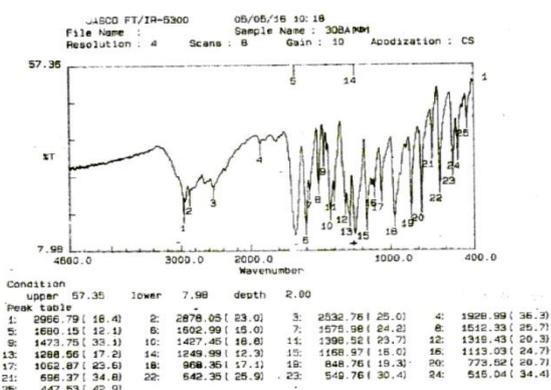


Fig.6a: FTIR Spectrum of 3OBA in KBr

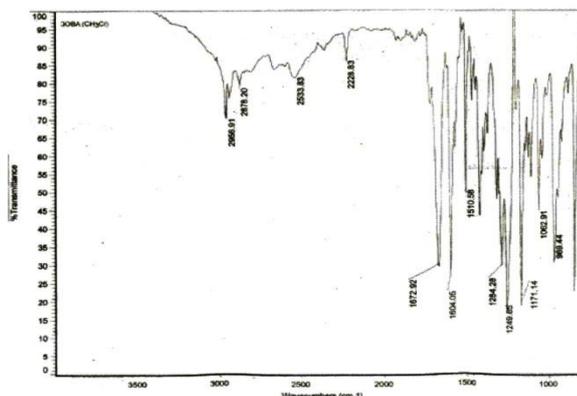


Fig 6b: FTIR Spectrum of 3OBA in CHCl₃

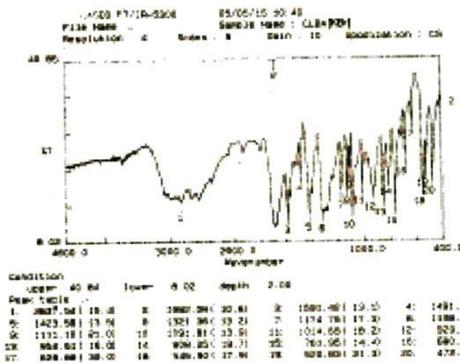


Fig 7a:. FTIR Spectrum of CIBA in KBr

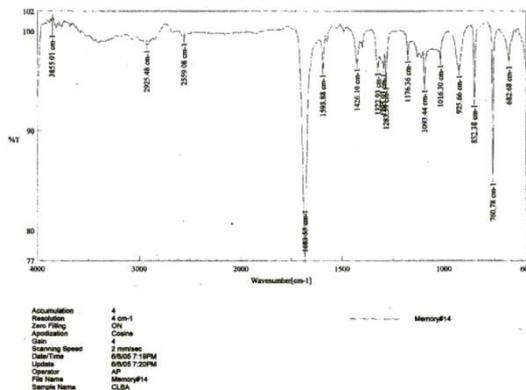


Fig 7b:. FTIR Spectrum of CIBA in CHCl3

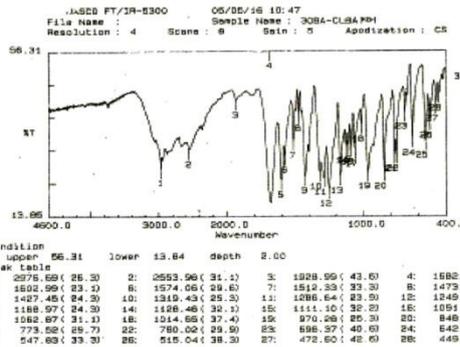


Fig 8a:. FTIR Spectrum of 3OBA:CIBA in KBr

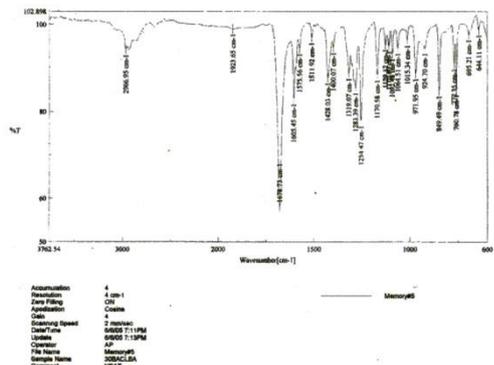


Fig 8b:. FTIR Spectrum of 3OBA:CIBA in CHCl3

IV. CONCLUSIONS

A monotropic nematic phase in the heating cycle exhibited by 3OBA:CIBA due to intermolecular hydrogen bond. It is confirmed through DSC study also. Intermolecular hydrogen bond is also confirmed through FTIR study formed between COOH of *p*-propoxy benzoic acid and COOH of *p*-chloro benzoic acid due to hetero dimer formation. The thermal span has been increased from pure compound 6 °C to hydrogen bond compound 37 °C. It observed that the transition favours second order phase transition using Navard and Haudin parameter.

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