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Infrared and Thermal Studies on Mesogenic *p*-Decyloxy Benzoic Acid:Hexyl *p*-Hydroxy Benzoate (10OBA:6HB)

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ABSTRACT: Formation of hydrogen bond due to intermolecular interactions between two compounds is potential topic and considerable amount of work was carried out. Inducement of novel phases and/or quenching of phases(s) because of hydrogen bonded mesogens have great deal of continuing interest. Further the characteristic of these mesogens are influence of phase behaviour and, stabilization and phase transition temperatures. Preparation of hydrogen bonded mesogen consisting mesogen = non-mesogen, namely, namely *p*-decyloxy benzoic acid :Hexyl *p*-hydroxy benzoate (10OBA:6HB) is carried out. Characterization of the novel compound is done through FTIR spectra for hydrogen bond formation, textural and phase transition studies through polarization optical microscope attached with hot stage and camera and confirmation of phase transition temperatures through differential calorimetry. From the present study the hydrogen bond is formed between OH of 10OBA and OH of 6HB. The thermal polarizing microscope observations show that the three compounds 10OBA, and 10OBA: 6HB are enantiotropic liquid crystals exhibiting threaded marble nematic and schlieren smectic C phases and ,threaded nematic mesophase and and marble smectic G phases respectively indicating induced phase in the synthesized compound along with changes in phase transition temperatures.

KEYWORDS: Infrared Spectroscopy Polarizing optical microscope, Differential Scanning Calorimetry, intermolecular hydrogen bond, Smectic -G,

I. INTRODUCTION

The role of hydrogen bonding interactions in the formation and stabilization of mesophases [1,2] has been recognized and significant work has been turned out. The hydrogen bond has a striking influence on the phase behaviour as well as transition temperatures. The hydrogen bond liquid crystal (mesogen) can be synthesized with the combination of mesogen + mesogen, mesogen + non- mesogen and non-mesogen + non-mesogen. In this communication consisting of mesogen+non-mesogen , namely *p*-decyloxy benzoic acid (10OBA) and: Hexyl *p*-hydroxy benzoate (6HB). is carried out.

II. RELATED WORK

Indrani et al [3] studied the hydrogen formation on 9OBA:EBCA, USHA ET AL [4] investigated on thermotropic hydrogen bonded liquid crystals while Sundaim [5] studied on hydrogen bonded supramolecular liquid crystal polymer, Luggar et al presented their work [6]. Recently thermal, infrared and NMR studies on hydrogen bonded mesogen was reported by Rani et al [7] and Ravi Shankar Kumar et al [8]. The liquid crystalline self-organization gives the material unique structures. Typically the dynamic character of linear calamatic hydrogen bonded liquid crystals are used as optical materials [9]. Induction and stabilization of liquid crystallinity through hydrogen bonding [10-12] are gaining momentum.

III. EXPERIMENTAL

The experimental work involves the synthesis of the compound, confirmation of hydrogen bond and identification of textures with transition temperatures, along with confirmation of phase transition temperatures. using Fourier

Transform Infrared (FTIR) Spectroscopy, thermal polarizing microscope attached with hot stage, Differential Scanning Calorimetry, and respectively. *p*-decyloxy benzoic acid (10OBA) which is a mesogen and Hexyl *p*-hydroxy benzoate (6HB) is non-mesogen obtained from M/s Frinton laboratories, New Jersey USA. Both 10OBA and 6HB are white crystalline compounds at room temperature. The complex *p*-decyloxy benzoic acid: Hexyl *p*-hydroxy benzoate (10OBA: 6HB) is synthesized by refluxing together *p*-nonyl oxy benzoic acid (0.4000gms) and *p*-(*p*'-ethoxy benzylidene – cyano aniline (0.3252 gms) in equimolar ratio 1:1. Details of same mechanism of dyndyhrdid id hibrn in [3]. The yielding is at about 85% The synthesis route is given in Fig 1

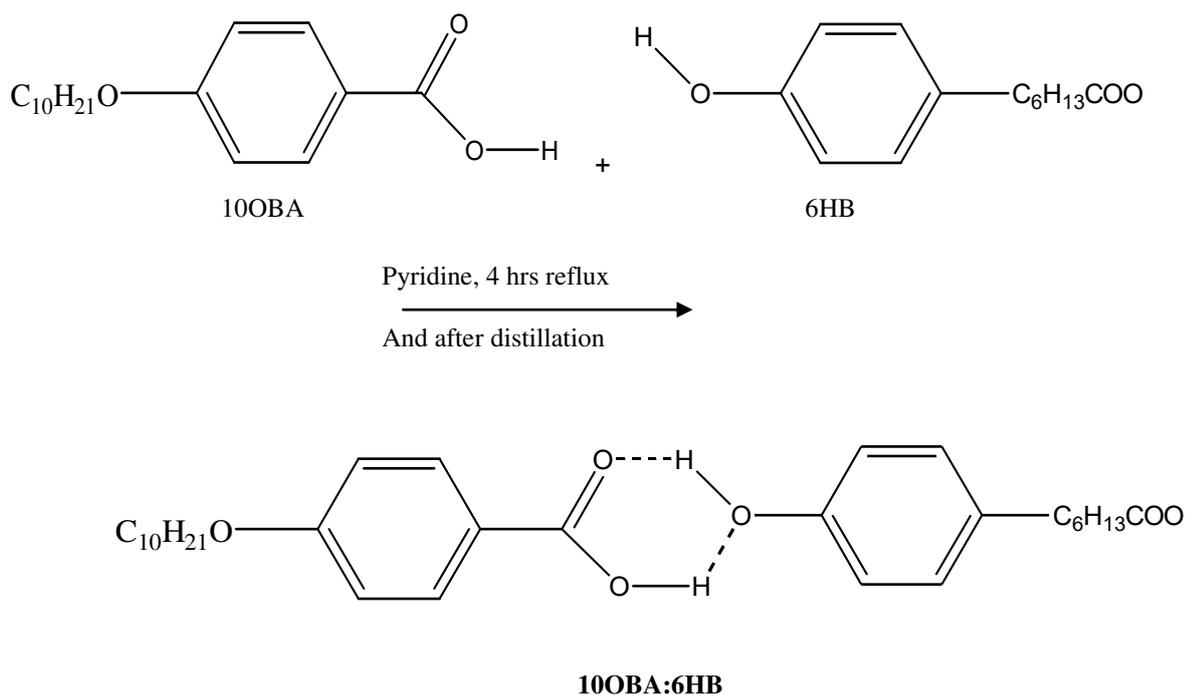


Fig1: Synthesis of 10OBA:6HB

JASCO (Japan) spectrometer model FTIR 5300 with solid KBr and liquid chloroform a polarizing optical microscope (POM) (MEOPTA,ORE-MICROSCOPE-DRU-3,S.NO:56512) equipped with a hot stage and Canon digital colour camera are used to record FTIR spectra, textures with phase transitions and to confirm phase transitions (Perkin-Elmer DSC, model Diamond) respectively. ± 0.1 accuracy of digital thermometer and Metler balance Model AE240 having accuracy of 0.01 mg are utilized for temperature and weighing of the samples respectively.

III. RESULTS AND DISCUSSIONS

A novel mesogen, *p*-decyl oxy benzoic acid Hexyl *p*-hydroxy benzoate (6HB) (10OBA:6HB) containing mesogens *p*-decyloxy benzoic acid (10OBA) and Hexyl *p*-hydroxy benzoate (6HB) was synthesized and further characterization is presented below.

FTIR Spectral Studies:

The FTIR spectra of 10OBA, 6HB AND 10OBA:6HB are given in figs 2-4. The spectrum of *p*-decyloxy benzoic acid shows a sharp peak at 1681cm^{-1} for $\bar{\nu}$ (C = O) mode and 1255cm^{-1} for $\bar{\nu}$ (C – O) due to KBr. Another strong intense band assigned to $\bar{\nu}$ (OH) mode of carboxylic acid group is obtained at 2923cm^{-1} due to KBr. The spectrum of hexyl-*p*-hydroxy benzoate shows sharp peaks at 3374.90cm^{-1} for $\bar{\nu}$ (OH) mode, 1230cm^{-1} for $\bar{\nu}$ (C-O), 1395cm^{-1} for



In plane bending of $\bar{\nu}$ (OH) mode and 608 cm^{-1} for Out of plane bending of $\bar{\nu}$ (OH) mode in KBr. The wavenumbers of 10OBA: 6HB exhibit the presence of a strong intense band due to $\bar{\nu}$ (C = O) mode of benzoic acid moiety at 1682 cm^{-1} . This strongly supports the existence of 10OBA moiety in a monomeric form upon complexation. The formation of inter molecular hydrogen bonding between COOH group of 10OBA and OH group of 6HB can be invoked on the basis of hypsochromic shifts in $\bar{\nu}$ (C-O)_{acid} mode (31 cm^{-1}), $\bar{\nu}$ (O-H)_{benzoate} In plane of bending mode (7 cm^{-1}), $\bar{\nu}$ (OH)_{benzoate} out of plane bending mode (18 cm^{-1}), $\bar{\nu}$ (C-O)_{benzoate} mode is (26 cm^{-1}), [10] of 6HB in KBr which strongly supports the existence of H – bonding. A thorough IR spectral study in solid indicates the acid as proton donor and phenol groups act as proton donor and proton acceptor. This is similar to the reported by Koga, et al., [11], Kumar et al [12] and Swathi et al [13].

It is clearly understood that the synthesized compound is a mixture of the two components 10OBA and 6HB.. The formation of intermolecular hydrogen bonding between COOH group of 10OBA and COOH group of 6HB can be invoked in the hypochromic and bathochromic shifts shown in Table 1.

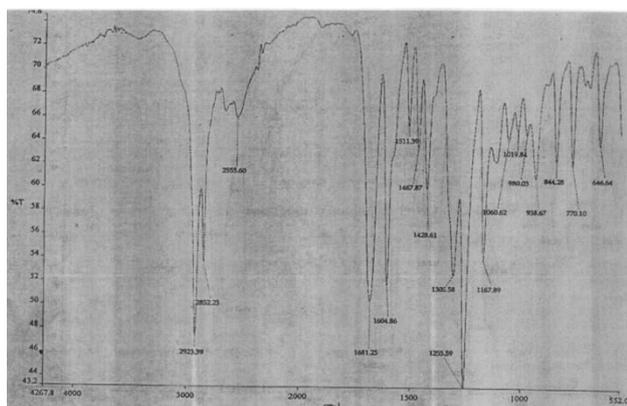


Fig 2. FTIR Spectrum of 10OBA

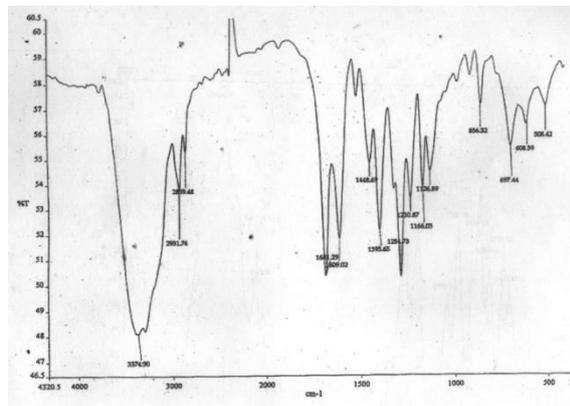


Fig 3. FTIR Spectrum of 6HB

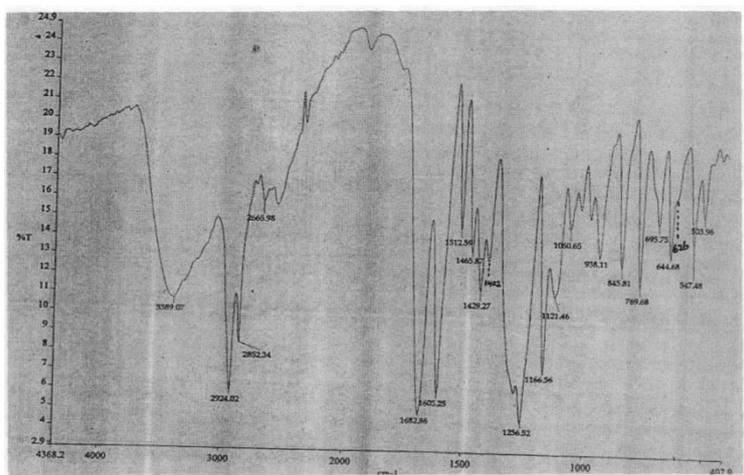


Fig 4. FTIR Spectrum of 10OBA:6HB

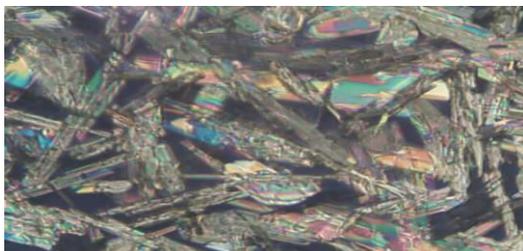


Plate 5: Smectic G of 10OBA:6HB

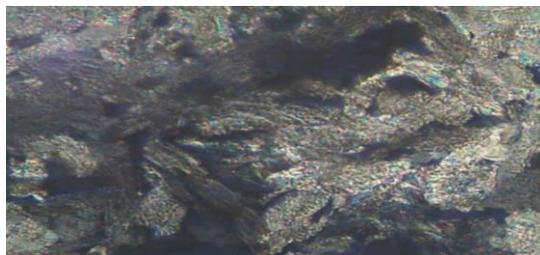


Plate 6: Solid of 10OBA:6HB

Differential Scanning Calorimeter: -

The transition temperatures of pure 10OBA, 6HB and the synthesized compound 10OBA: 6HB according to the Differential Scanning Calorimetry (DSC) are given as follows. In heating cycle, the pure 10OBA exhibits smectic C phase at 91.9 °C and this phase extends up to 116.6 °C to change to nematic phase. Afterwards, on further heating, it becomes isotropic at 141.8 °C. In cooling cycle, the nematic phase separates from the isotropic phase at 140.6°C and this phase remains up to 118.4°C. On further cooling, it becomes smectic C in between 118.4 and 93.9 °C, with further cooling it becomes solid below 93.9°C. The DSC thermogram of 10OBA is shown in Fig. 5 in both heating and cooling cycles. The pure 6HB is non mesogen and has melting point of 54.5°C. In heating cycle, 10OBA:6HB exhibits smectic G phase in between temperature 88.94 and 97.27. On further heating Smectic G phase is changed to Nematic phase is on above 97.27. Afterwards, on further heating, it becomes isotropic and its peak is not resolved in DSC thermogram. In cooling cycle, the nematic phase separates from the isotropic phase at 99.34°C. On cooling, nematic phase is changed to smectic G phase in between the temperatures 92.7°C and 75.94°C. Afterwards, on further cooling, it becomes as solid below 75.94°C. The DSC thermogram of 10OBA: 6HB is shown in Fig 6 in both heating and cooling cycles at a scan rate of 5°C/min. The transition temperatures obtained from the DSC studies are shown in Table 2. The phase transition temperatures observed through thermal polarizing microscope are almost coinciding with DSC studies. Hence the synthesized complex exhibits enantiotropic liquid crystal nature with Inducement of smectic-G phase in addition to the nematic phase.

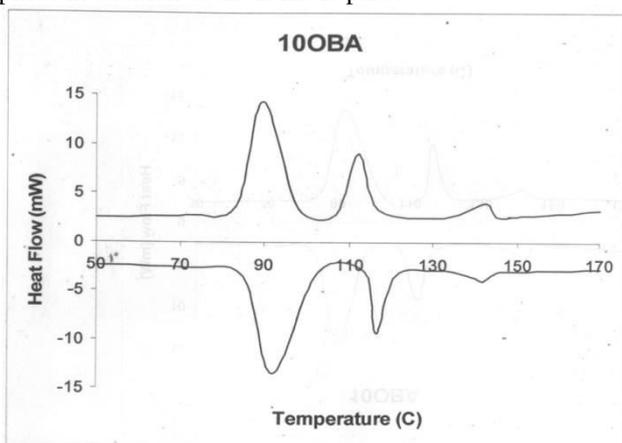


Fig. 5. DSC thermogram of 10OBA

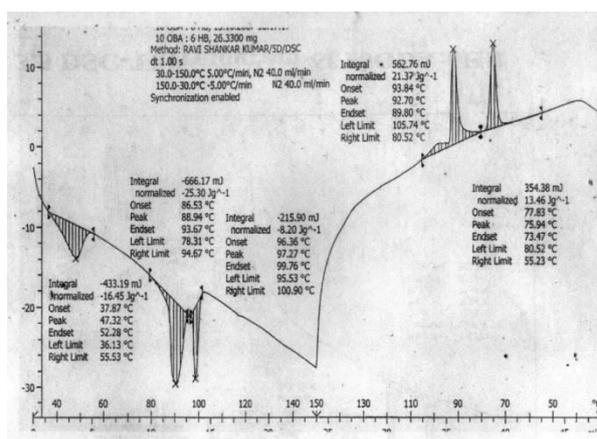


Fig.6. DSC thermogram of 10OBA:6HB

Thermal polarizing microscope values are almost coinciding with DSC studies. The transition temperatures obtained from POM and DSC studies are given in Table 2



Table21:Phase transition temperatures form POM and DSC

10OBA (<i>p</i> - <i>n</i> - decyloxy benzoic acid)				
Name of The Publisher/ Present Study	Expt.	Solid to S _c	S _c / N	N to Isotropic
Frinton Laboratories [14]		97°C	122°C	142°C
Present Study	T.M (H)	98.9°C	117.9°C	140.5°C
	T.M(C)	97°C	115.6°C	138.3°C
	DSC(H)	91.9°C	116.6°C	141.8°C
	DSC(C)	93.9°C	118.4°C	140.6°C
Synthesized compound 10OBA:6HB (<i>p</i> - <i>n</i> -decyloxy benzoic acid:hexyl <i>p</i> - hydroxybenzoate)				
		Solid to S _G	S _G to N	N to Isotropic
Present Study	T.M (H)	88°C	94.8°C	100.9°C
	T.M(C)	76.9°C	91.3°C	97.4°C
	DSC(H)	88.9°C	97.2°C	[a]
	DSC(C)	75.94°C	92.7°C	99.34°C

IV. CONCLUSIONS

From the present study it is noted that the intermolecular hydrogen bond may be attributed between the COOH group of *p*-decyloxy benzoic acid (10OBA) and OH of hexyl *p*-hydroxyl benzoate (6HB). The phase transition temperatures observed through Differential Scanning Calorimetry studies are in reasonable agreement with the transition temperatures obtained from the thermal polarizing microscope observations. The thermal polarizing microscope observations show that the three compounds 10OBA, 6HB and 10OBA: 6HB are exhibiting the following phases. *p*-decyloxy benzoic acid (10OBA) showed schlieren smectic C and Threaded marble nematic phases and it was an enantiotropic liquid crystal. Hexyl *p*-hydroxy benzoate (6HB) showed a non mesogenic. *p*- decyloxy benzoic acid: Hexyl *p*-hydroxy benzoate (10OBA: 6HB) exhibited enantiotropic threaded marble nematic and mosaic smectic G phases. In heating and cooling cycles, induced smectic G phase is observed due to intermolecular interaction of hydrogen bond.

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