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Characterization of induced smectic G phase in a hydrogen bonded complex of p-n alkyloxy benzoic acids with tetradecane dicarboxylic acid

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ABSTRACT

A novel homologous series of hydrogen bonded liquid crystal (HBLC) has been synthesized and characterized. The HBLC is prepared by the complexation of mesogenic p-n alkyloxy benzoic acids with non-mesogenic tetradecane dicarboxylic acid. The series, thus, prepared is denoted as TDD + nOBA. This homologous series has been analyzed using polarizing optical microscope for the various textures. The phase transition temperatures are studied using differential scanning calorimeter. The Fourier transform infrared spectroscopy and H-NMR are also used to characterize and study the hydrogen bond formed in the complexes.

Keywords - Hydrogen Bonded Liquid Crystals, Mesogen, Textures, Smectic, Nematic

I INTRODUCTION

Liquid crystals are widely used as electro optic materials due to the property of birefringence [1,2]. The nematic liquid crystals perform at the speed of milli second as electro optic displays. However, many novel devices based on smectic liquid crystal phases have been prepared as these works on faster regimes (nano seconds). These devices are realized by sandwiching the tilted smectic phases between the pre treated substrates [3]. The smectic phases in the ambient temperature range are prepared by the proper selection of chemical moieties [4] (i.e., the rigid core or the terminal end chain parts). The hydrogen bond is used as a non-covalent interaction in the construction and ordering of liquid crystalline materials also called as mesogenic materials [5,6]. Hydrogen bonded liquid crystals (HBLC) showcase enhanced performance in the displays [7]. Kato and Frechet [8] were the first to demonstrate that hydrogen bonding between carboxylic group and pyridyl moieties was useful for the formation of supramolecular hydrogen bonded liquid crystals. Since then, many hydrogen bonded liquid crystals exhibiting rich polymorphism have been synthesized between various mesogenic and nonmesogenic compounds [9-15].

The present work involves the synthesis and characterization of HBLC between p-n- alkoxybenzoic acid and tetradecane dicarboxylic acid designated as TDD + nOBA (n = 4, 7-12; i.e., butyloxy, heptyloxy to dodecyloxy). The results of the synthesized complexes are exhibited through Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR), Polarizing Optical Microscope (POM) and differential scanning calorimeter (DSC).

II EXPERIMENTAL

The non mesogen tetradecane dicarboxylic acid, mesogenic p-n- alkyloxy benzoic acid and the solvent were purchased from Sigma Aldrich, India and used without further purification. The optical textures of the different phases were observed using Meiji POM equipped with a Mettler FP 82 HT hot stage and a Mettler FP 90 central processor. The sample was kept in silica crucible in air and the holding atmosphere for obtaining the curves was dry nitrogen. The DSC curves were obtained using Perkin Elmer simultaneous thermal analyzer (STA 6000), with scanning rate of 5 $^{O}C\ min^{-1}$ on heating. The sample was kept in isotropic state for five minutes to attain the thermal stability and then cooled at the same rate up to the room temperature. The respective equilibrium transition temperature and corresponding enthalpy values for each of the mesogens were recorded using the appropriate DSC software. Infrared spectra were recorded in the range of 4000-400 cm^{-1} on a Shimadzu FTIR spectrophotometer. Proton magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker Avance II and III 400 (400 MHz) using TMS as internal reference.

The intermolecular hydrogen bonded complex was synthesized by mixing 2 moles of p-n-alkyloxy benzoic acid with 1 mole of tetradecane dicarboxylic acid in dry dimethyl formamide (DMF) and stirred for 48 hours at room temperature. The excess solvent was removed by slow evaporation leaving behind the white crystalline solid as the product. The synthetic route and the general molecular structure of the homologous series of TDD + nOBA is depicted in Fig. 1.

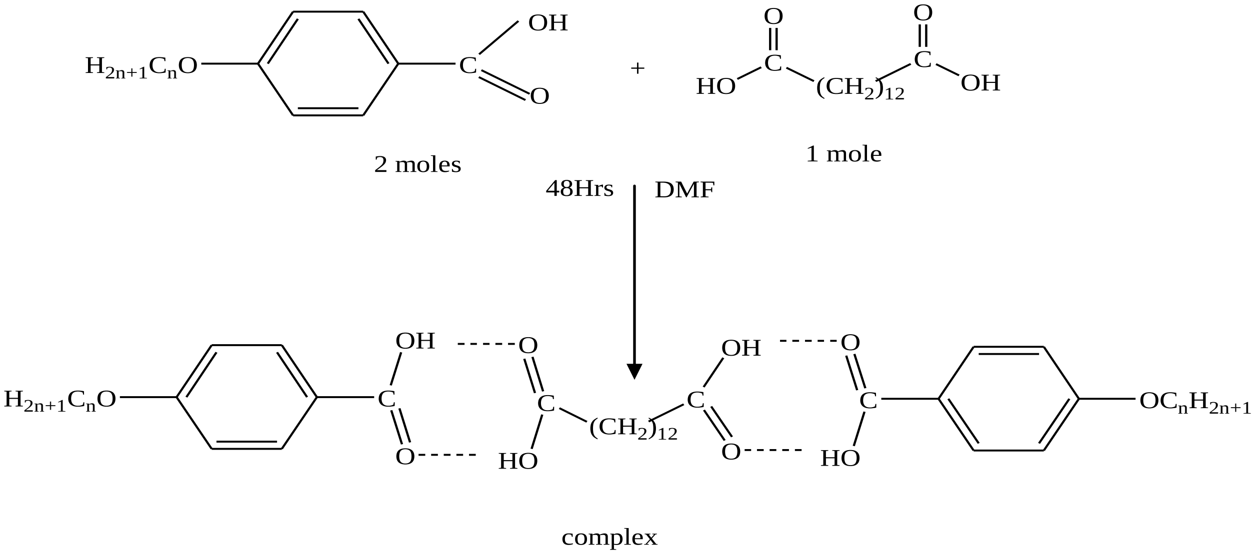

Fig. 1: General molecular structure of the homologous series of TDD + nOBA

III RESULTS AND DISCUSSION

3.1 THERMAL AND PHASE BEHAVIOUR (POM & DSC STUDIES)

The various phases of the homologous series of the complex obtained were identified using POM, the phase transition temperature data of which was further confirmed using DSC. The change in enthalpy values of the phase transitions are also given by DSC. In POM, the material is heated from the room temperature till the field of view becomes dark, i.e., to isotropic liquid followed by cooling the melt. The phase transition temperatures observed through POM are found to be in accordance with the DSC results. The Table 1 shows phase transition temperatures and enthalpy values of TDD + nOBA homologous series.

Table 1: Phase transition temperatures of TDD + nOBA homologous series obtained by DSC studies. Enthalpy values in J/g are shown in parenthesis.

N		**Cr1-Cr (^{0}C)**	**Cr – Melt (^{0}C)**	**SmG (^{0}C)**	**SmC (^{0}C)**	**N (^{0}C)**	**SmC (^{0}C)**	**SmG (^{0}C)**	**Melt-Cr (^{0}C)**	**Cr-Cr1 (^{0}C)**
TDD + 4OBA	DSC (h)	-	114.64 (69.818)	122.63 (0.289)	-	-	-	-	-	-
	DSC (c)	-	-	-	-	-	-	111.13 (-11.24)	100.85 (-75.43)	-
TDD + 7OBA	DSC (h)	-	90.85 (58.06)	#	106.38 (44.33)	Peak not resolved	-	-	-	-
	DSC (c)	-	-	-	-	98.77 (-0.47)	91.56 (-48.60)	82.26 (-18.14)	75.22 (-30.42)	62.19 (24.76)
TDD + 8OBA	DSC (h)	75.07 (28.03)	95.09 (20.47)	#	107.10 (30.01)	120.88 (0.32)	-	-	-	-
	DSC (c)	-	-	-	-	102.68 (-2.39)	92.38 (-31.68)	88.01 (-14.86)	64.02 (-11.36)	50.93 (-23.88)
TDD + 9OBA	DSC (h)	-	93.83 (57.04)	#	104.91 (8.19)	117.30 (0.23)	-	-	-	-
	DSC (c)	-	-	-	-	99.79 (-2.76)	89.34 (-20.60)	85.74 (-9.80)	64.78 (-41.41)	49.23 (-25.76)
TDD + 10OBA	DSC (h)	86.86 (32.44)	96.29 (20.04)	#	107.75 (26.44)	118.03 (0.61)	-	-	-	-
	DSC (c)	-	-	-	-	107.48 (-1.25)	90.73 (-3.56)	87.43 (-20.00)	69.58 (-12.91)	52.03 (-28.36)

TDD + 11OBA	DSC (h)	-	92.02 (3.43)	#	97.35 (39.07)	105.00 (2.24)	-	-	-	-
	DSC (c)	-	-	-	-	99.45 (-2.32)	87.44 (-40.83)	80.58 (-3.24)	69.84 (-4.54)	56.07 (-32.38)
TDD+ 12OBA	DSC (h)	-	95.65 (53.06)	#	106.94 (41.39)	Peak not resolved	-	-	-	-
	DSC (c)	-	-	-	-	102.89 (-0.36)	88.26 (-29.27)	83.36 (-11.73)	65.28 (-5.37)	53.89 (-23.58)

Monotropic transition

The symbols used in the table and elsewhere stand for: Cr1 = crystalline solid 1, Cr = crystalline solid, N = nematic, Sm = smectic, I = isotropic liquid. The various phase transitions during heating as well as on cooling the material can be explained using different schematic diagrams shown below. The reversible arrow means that the phase transition is enantiotropic (appears during heating as well as cooling) while a single direction arrow means that the phase transition is monotropic (appears only during heating or cooling).

TDD + 4OBA

$$\begin{tikzcd}
\mathrm{Cr} \arrow[r, leftrightarrow] & \mathrm{SmG} \arrow[r, leftrightarrow] & \mathrm{I}
\end{tikzcd}$$

TDD + 7OBA

$$\begin{tikzcd}
\mathrm{Cr1} & \mathrm{Cr} \arrow[l] \arrow[r] & \mathrm{SmC} \arrow[r, leftrightarrow] \arrow[d] & \mathrm{N} \arrow[r, leftrightarrow] & \mathrm{I} \\
& & \mathrm{SmG} \arrow[ul] & &
\end{tikzcd}$$

TDD + 8OBA

$$\begin{tikzcd}
\mathrm{Cr1} \arrow[r, leftrightarrow] & \mathrm{Cr} \arrow[r] & \mathrm{SmC} \arrow[r, leftrightarrow] \arrow[d] & \mathrm{N} \arrow[r, leftrightarrow] & \mathrm{I} \\
& & \mathrm{SmG} \arrow[ul] & &
\end{tikzcd}$$

TDD + 9OBA

$$\begin{tikzcd}
\mathrm{Cr1} & \mathrm{Cr} \arrow[l] \arrow[r] & \mathrm{SmC} \arrow[r, leftrightarrow] \arrow[d] & \mathrm{N} \arrow[r, leftrightarrow] & \mathrm{I} \\
& & \mathrm{SmG} \arrow[ul] & &
\end{tikzcd}$$

TDD +10OBA

$$\begin{tikzcd}
Cr1 \arrow[r, leftrightarrow] & Cr \arrow[r] & SmC \arrow[r, leftrightarrow] \arrow[dl] & N \arrow[r, leftrightarrow] & I \\
 & SmG \arrow[u] & & &
\end{tikzcd}$$

TDD + 11OBA

$$\begin{tikzcd}
Cr1 & Cr \arrow[l] \arrow[r] & SmC \arrow[r, leftrightarrow] \arrow[dl] & N \arrow[r, leftrightarrow] & I \\
 & SmG \arrow[u] & & &
\end{tikzcd}$$

TDD + 12OBA

$$\begin{tikzcd}
Cr1 & Cr \arrow[l] \arrow[r] & SmC \arrow[r, leftrightarrow] \arrow[dl] & N \arrow[r, leftrightarrow] & I \\
 & SmG \arrow[u] & & &
\end{tikzcd}$$

The various combinations of TDD + nOBA give rise to textures which were observed using POM. These textures ware captured using a camera. The textures are represented as plate 1 (TDD + 7OBA) which show schlieren textures resembling smectic C phase. The multicolored mosaic textures (TDD + 9OBA; Plate 2) are of the monotropic smectic G phase. Similarly, nematic phase is shown as schlieren textures (Plate 3) in TDD + 11OBA system. The pattern of textures is similar in all other combinations.

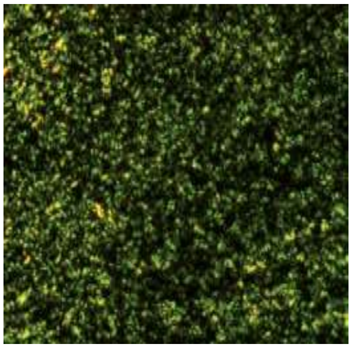

Plate 1

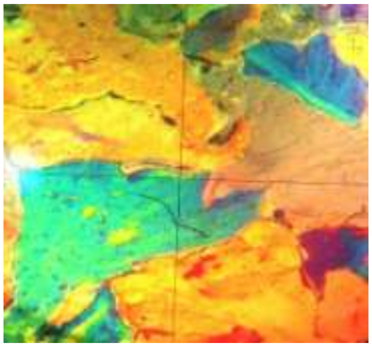

Plate 2

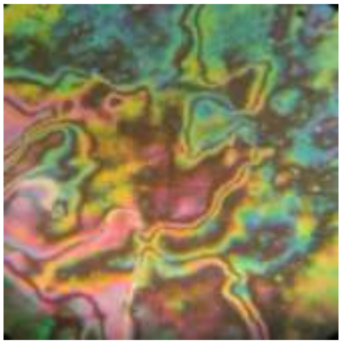

Plate 3

Plate 1: Schlieren textures of smectic C phase in TDD + 7OBA.

Plate 2: Smooth multicolored mosaic textures of smectic G phase in TDD + 9OBA.

Plate 3: Schlieren textures of nematic phase in TDD + 11OBA.

DSC thermograms are studied in heating and cooling cycle of the samples. The respective equilibrium transition temperature and corresponding enthalpy values for each of the mesogens and their mixtures are recorded using the software of the DSC. As a representative case, the thermograms during heating and cooling cycle for nonyloxy benzoic acid (9OBA) and one of the representative mixtures, namely, binary mixture of tetradecane dicarboxylic acid and nonyloxy benzoic acid, TDD + 9OBA are shown in Figs. 2 and 3, respectively.

TDD is non mesogen, while 9OBA shows phase transitions at 95.91 ^{0}C, 118.05 ^{0}C and 140.47 ^{0}C during heating which corresponds to SmC, N and I phases, respectively. An additional peak corresponding to the solid-solid transition is clearly visible at 68.5 ^{0}C in 9OBA while cooling the sample. However, the binary combination of TDD + 9OBA exhibits an additonal peak during cooling of the sample (monotropic). The textures when observed using POM indicate the presence of multicoloured smooth mosaic textures of smectic G phase. Therefore, POM and DSC studies confirm the presence of smectic G phase in the binary mixture of TDD + 9OBA. The DSC thermogram of the binary mixture of TDD + 9OBA shows endothermic peaks during heating at 93.83 ^{0}C, 104.91 ^{0}C and 117.30 ^{0}C with enthalpy change values as 57.04, 8.25 and 0.28 Jg^{-1}, respectively. These peaks correspond to the Cr- SmC, SmC-N and N-I transitions. During cooling, the exothermic peaks observed are at 99.79 ^{0}C , 89.34 ^{0}C, 85.74 ^{0}C, 64.78 ^{0}C and 49.23 ^{0}C corresponding to isotropic to N phase, N - SmC phase, SmC - SmG phase, SmG -crystalline phase and finally from one crystalline form to another crystalline state. The corresponding enthalpy change values are -2.76, -20.60, -9.80, -41.41 and -25.76Jg^{-1}, respectively.

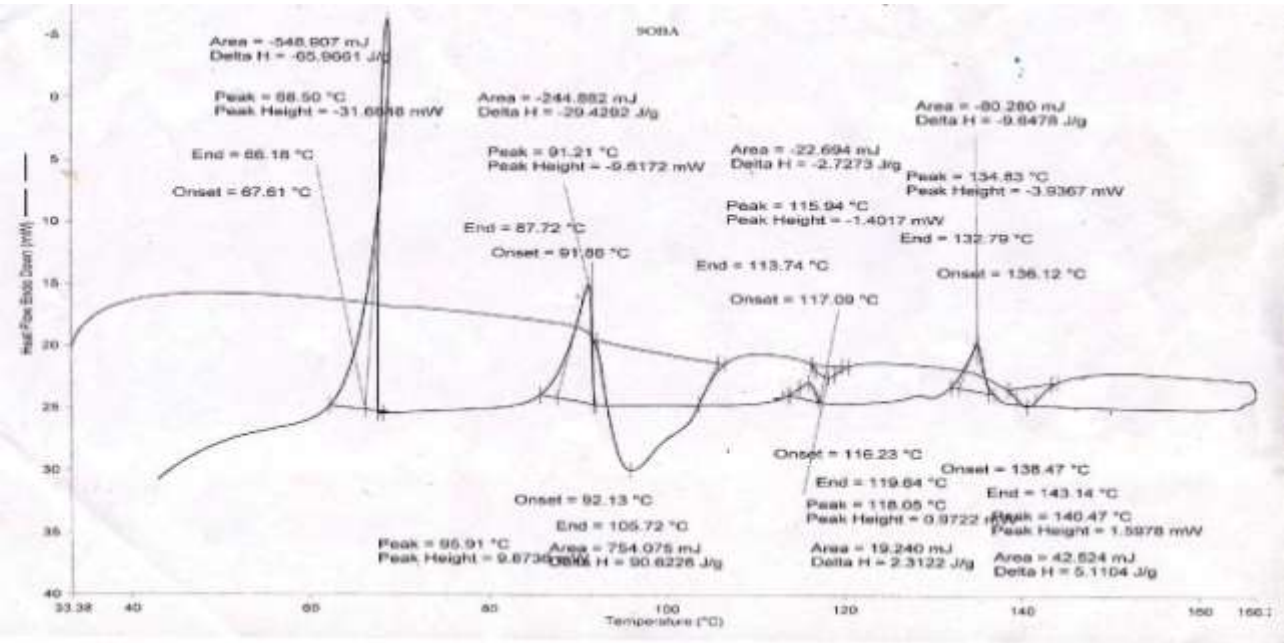

Fig. 2: DSC of 9OBA

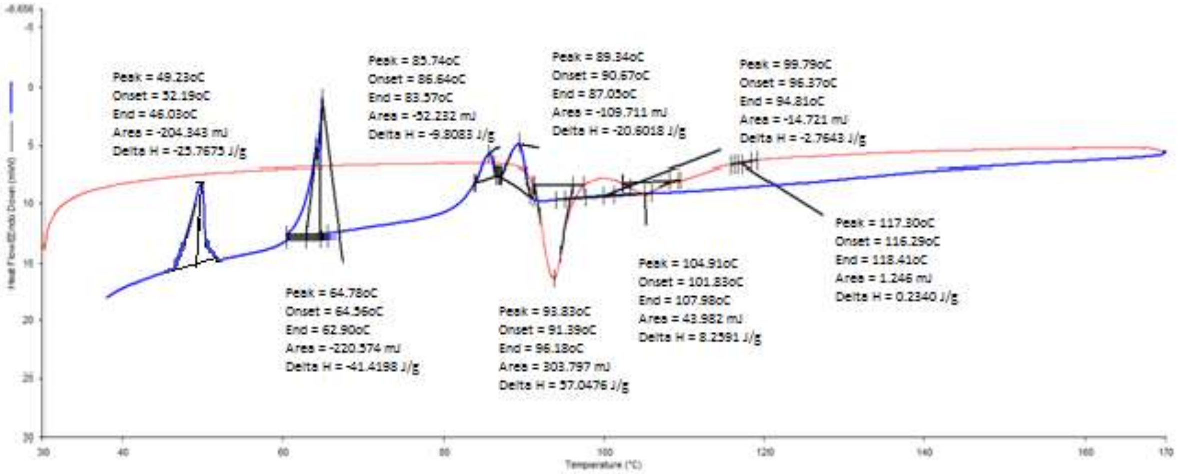

Fig. 3: DSC of the complex TDD + 9OBA

3.2 FTIR SPECTRA

The FTIR spectra of pure alkyloxy benzoic acids, TDD and their mixtures (TDD+nOBA) were recorded in the solid state (KBR) at room temperature. As a representative case, FTIR spectra of undecyloxy benzoic acid (11OBA) (Fig.4) and its complex with TDD (TDD+11OBA) (Fig.5) are illustrated. The solid state spectra of the free undecyloxy benzoic acid shows two sharp peaks at 1681 cm^{-1} and 1695 cm^{-1} due to ν (C=O) mode [16]. The double peaks observed confirm the dimeric nature of alkyloxy benzoic acid in general and undecyloxy benzoic acid in particular at room temperature. The O-H stretching absorption band appears at 2933cm^{-1} in pure undecyloxy benzoic acid. As a result of complexation of hydrogen bonded complex, the FTIR spectra of TDD + 11OBA shows single broad band at 1689.72 cm^{-1} (1690 cm^{-1}). Therefore, the FTIR spectra shows non appearance of the doubling nature of ν(C= O) mode of benzoic acid moiety. This significant feature confirms that the dimeric nature of the alkyloxy benzoic acid dissociates and prefers to exist in a monomeric form upon comlexation [17]. Moreover, there is a shift in the values of O-H stretching frequencies in the complex TDD + 11OBA from 2933.73 to 2923.25cm^{-1}. The bathochromic shift from 2933.73 cm^{-1} to 2923.25 cm^{-1} in the ν(OH) (~10 cm^{-1}) mode of acid in the mesogen suggest the formation of intermolecular hydrogen bonding between the –COOH group of 11OBA and TDD [18]. A similar trend is followed in all other synthesized hydrogen bonded complexes of p- n- alkyloxy benzoic acid and TDD confirming the formation of hydrogen bonded complexes.

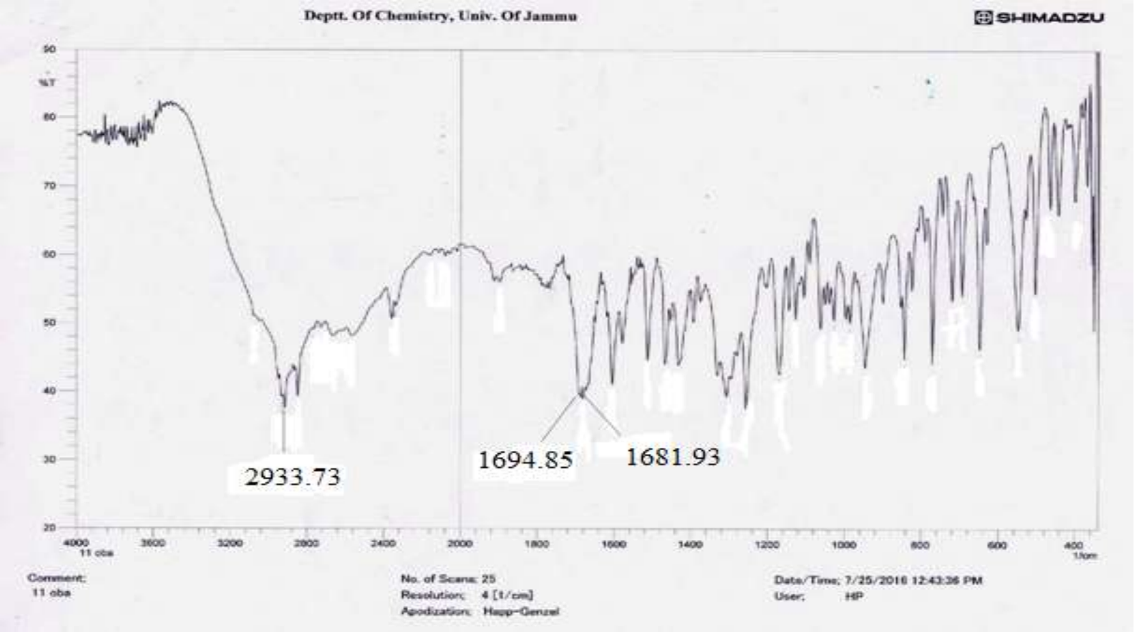

Fig. 4: FTIR spectra of undecyloxy benzoic acid (11OBA)

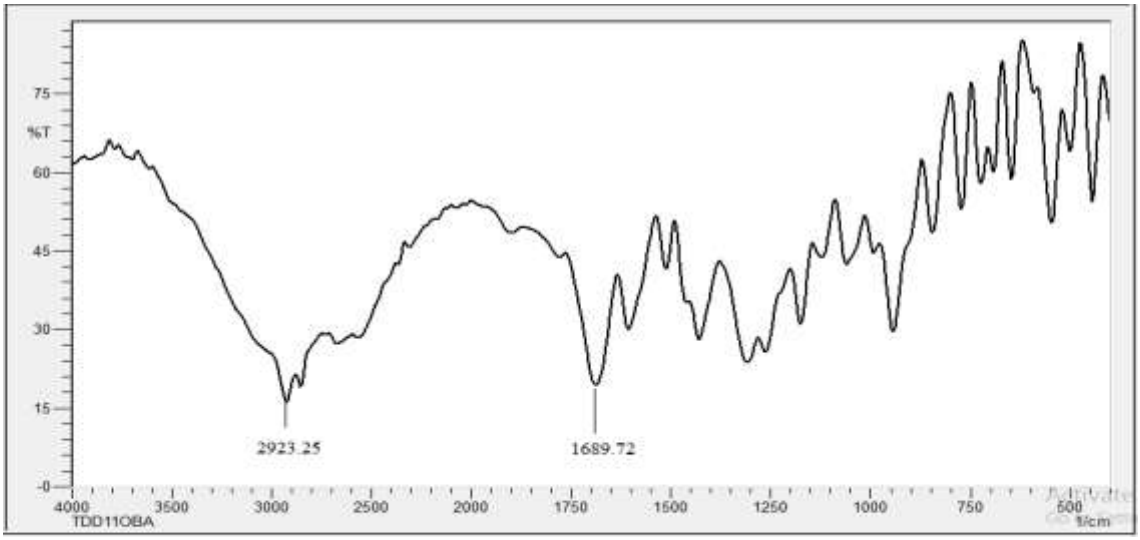

Fig. 5: FTIR spectra of the complex TDD+11OBA

3.3 PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H- NMR)

The chemical structure for TDD + nOBA series have been verified by ^{1}H-NMR studies. As a representative case, ^{1}H-NMR for TDD+10OBA is discussed. The recorded spectra is shown in Fig. 6. Some of the generialisations which can be interpreted from this figure may be summarized as: (a) the peaks observed between 2.4 and 0.85 ppm coresspond to the methylene protons, (b) two set of multiplets between 6.883–6.913 ppm and 7.957–7.986 ppm are due to aromatic protons, and (c) the characteristic peaks between 3.985–4.02 ppm correspond to methoxy proton unit. Since the observed ^{1}H-NMR spectra agrees well with the expected number of hydrogen atoms, the complex between TDD+10OBA and likewise for other members of the series are considered to be formed.

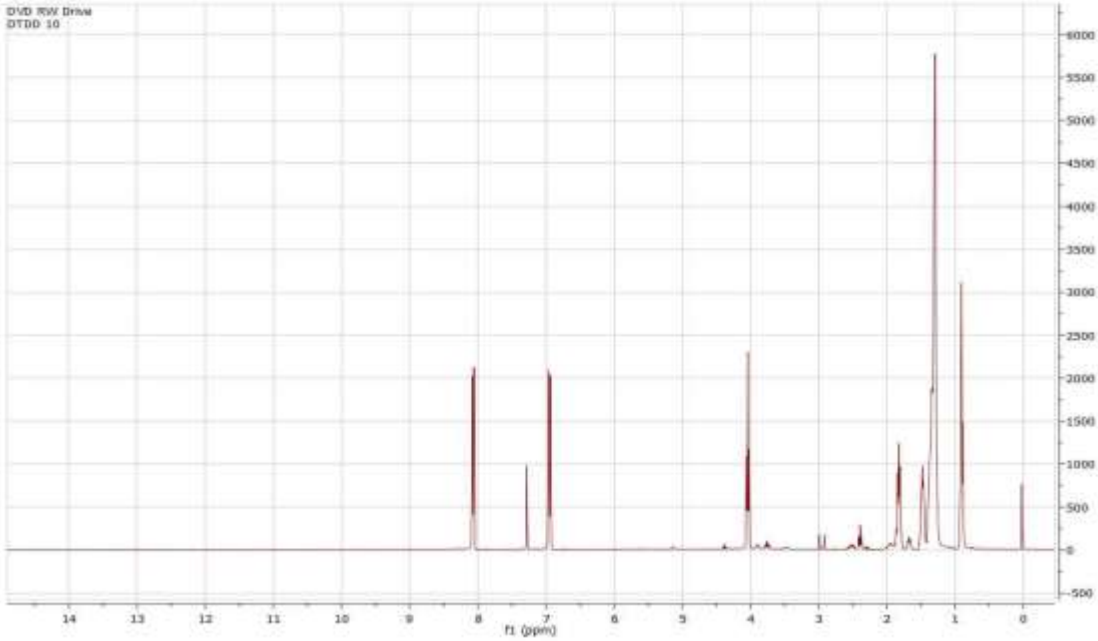

Fig. 6: ^{1}H-NMR of the complex TDD + 10OBA

IV CONCLUSION

A successful attempt has been made in preparing a homologous series of hydrogen bonded liquid crystal between p-n- alkyloxy benzoic acids and tetradecane dicarboxylic acid (n = 4, 7-12). There is an induction of a new phase in the complexes prepared which when characterized for its textures using POM was observed to be smectic G phase. This Phase is seen during cooling the sample material and hence called monotropic phase, except for TDD + 4OBA where it appears during haeting as well. The complexes synthesized are bonded through a hyrdogen bond which is confirmed by FTIR and NMR studies.

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