

Synthesis and characterization of hydrogen-bonded mesogens between p-n- alkyloxy benzoic acid and sebacic acid

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Abstract: A series of thermotropic hydrogen-bonded liquid crystalline complex based on non mesogen sebacic acid and p-n-alkyloxy benzoic acid has been synthesized. The mesogenic properties of the series are demonstrated using polarizing optical microscope, differential scanning calorimeter, Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spectra. The so-formed complex shows monotropic mesophase which is not observed by any of the single components.

Key Words – Mesogens, smectic, nematic, polarizing microscope, supramolecular

1. Introduction

Liquid crystalline materials have a wide range of applications by virtue of which the global researchers have made it possible to design, synthesize, characterize and develop new materials. The proper combination of molecular interactions is a key factor for mesomorphism to appear in liquid crystals. The use of hydrogen bond, as a non-covalent interaction, can be an important tool in construction and ordering of liquid crystalline materials also called as mesogenic materials[1,2]. It is known to be an important force in many areas of chemistry and biology. Hydrogen-bonded interactions, for example, as observed in O – H \cdots N interaction, can be up to 36 kJ/mol for a linear hydrogen bond, stronger than van der Waals interactions (< 8 kJ/mol) [3,4]. At such strengths, they can bring about a self assembly of supramolecular aggregates. Kato and Frechet [5] 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 [6-12].

In the present study, the molecular recognition process between different molecular species is successfully used to form a new mesogenic molecular structure where the intermolecular hydrogen bonding occurs. Hence, this work involves synthesizing symmetric hydrogen-bonded liquid crystalline complexes based on sebacic acid (SA) and p-n-alkyloxy benzoic acid [nOBA, n representing alkyl substituent are 4 (butyl) and from 7 (heptyl) to 12 (dodecyl)], referred as SA + nOBA. The mesogenic properties are demonstrated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), while the existence of hydrogen-bond was verified by Fourier transform infrared (FTIR) spectra and proton magnetic resonance (PMR) spectra.

2. Experimental

The non mesogen sebacic acid, 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 differential scanning calorimeter (DSC) curves were studied using Perkin Elmer simultaneous thermal analyzer (STA 6000), with scanning rate of 5 °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 sample was kept in silica crucible in air and the holding atmosphere for obtaining the curves was dry nitrogen. 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 CDCl₃ 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 sebacic 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 SA + nOBA is depicted in fig. 1.

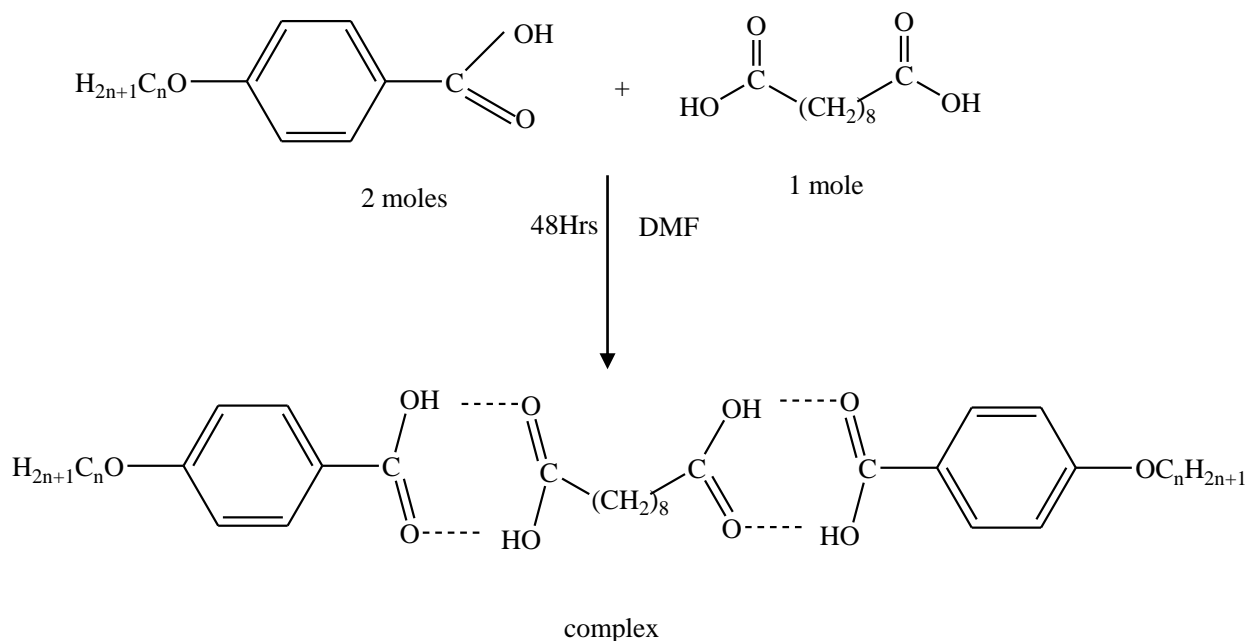


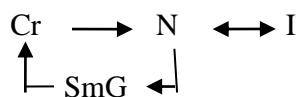
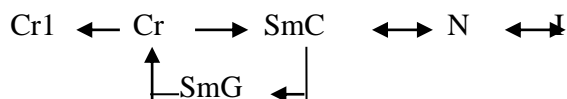
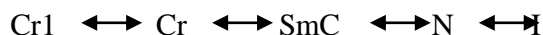
Figure 1: General molecular structure of the homologous series of SA + nOBA.

3. Results and discussion

3.1 Thermal and phase behaviour (POM & DSC studies)

The various substituents used in p-n- alkoxy benzoic acid (nOBA) are butyloxy (4OBA) and from heptyloxy (7OBA) to dodecyloxy (12OBA). The phase identification of sebacic acid (SA) and nOBA were initially monitored using POM by heating the material from room temperature till the field of view in POM becomes dark, i.e., to the isotropic liquid, at a uniform rate of $5\text{ }^{\circ}\text{C min}^{-1}$ followed by cooling the melt. The phases were identified by their characteristic textures. The phase transitions were later confirmed using DSC studies. In this manner, the different combinations were prepared and characterized for various phase transitions and phase variants. The phase transition temperatures observed through POM were found to be in accordance with the DSC results. The phase transition temperatures and enthalpy values of SA + nOBA homologous series are depicted in Table 1. 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 arrow in backward, and reversible (forward as well as backward directions) means that the phase transitions are monotropic (which appears upon cooling only) and enantiotropic (which appears on heating as well as cooling), respectively. The general phase sequence of various homologues of SA+nOBA in heating and cooling runs is shown as:

SA+ 40BA

**SA+ 70BA****SA+ 80BA****SA+ 90BA**

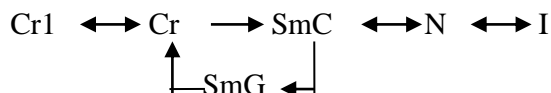
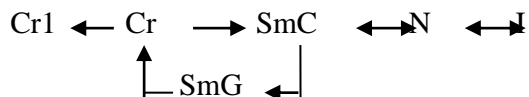
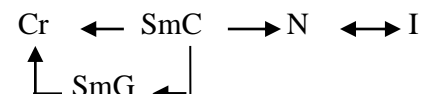
**SA +10OBA****SA+ 11OBA****SA + 12OBA**

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

N		Cr1-Cr (°C)	Cr – Melt (°C)	SmG (°C)	SmC (°C)	N (°C)	SmC (°C)	SmG (°C)	Melt-Cr (°C)	Cr-Cr1 (°C)
SA+4OBA	DSC(h)	-	122.16 (54.07)	#	-	125.0*	-	-	-	-
	DSC(c)	-	-	-	-	118.29 (-9.97)	-	111.57 (-2.19)	105.84 (-65.18)	-
SA+7OBA	DSC(h)	-	92.94 (71.31)	#	111.84 (11.44)	127.05 (0.60)	-	-	-	-
	DSC(c)	-	-	-	-	123.12 (-4.76)	108.11 (-0.96)	92.40 (-16.24)	81.28 (-34.80)	74.83 (-35.42)
SA+8OBA	DSC(h)	78.46 (39.60)	101.67 (34.29)	-	113.65 (8.71)	131.42 (1.09)	-	-	-	-
	DSC(c)	-	-	-	-	120.94 (-5.80)	88.13 (-0.04)	-	78.46 (-31.38)	59.18 (-16.63)
SA+9OBA	DSC(h)	-	94.07 (66.26)	#	113.35 (26.86)	122.63 (0.30)	-	-	-	-
	DSC(c)	-	-	-	-	113.79 (-1.23)	106.07 (-1.67)	94.53 (-25.75)	85.67 (-17.83)	66.11 (-45.95)
SA+10OBA	DSC(h)	87.01 (28.02)	94.82 (10.81)	#	113.04 (25.09)	121.42 (0.26)	-	-	-	-
	DSC(c)	-	-	-	-	118.15 (-1.75)	109.04 (-1.87)	91.78 (-19.74)	86.84 (-19.95)	70.91 (-14.85)
SA+11OBA	DSC(h)	-	96.95 (69.16)	#	113.36 (15.96)	121.46 (0.34)	-	-	-	-
	DSC(c)	-	-	-	-	117.44 (-0.06)	107.74 (-2.86)	93.13 (-26.75)	79.95 (-17.61)	67.60 (-9.51)
SA+12OBA	DSC(h)	84.40 (1.02)	94.75 (75.79)	#	113.08 (33.41)	127.80 (0.39)	-	-	-	-
	DSC(c)	-	-	-	-	120.03 (-1.89)	108.31 (-2.56)	90.74 (-33.71)	83.23 (-12.89)	64.87 (-6.77)

*Microscopic data

#Monotropic transition

The various combinations show features of characteristic textures. As representative of it, plate 1 (SA + 7OBA) shows schlieren textures which resemble to smectic C phase. The monotropic smectic G phase which has been observed in most of the combinations shows multicolored mosaic textures (SA + 9OBA; Plate 2). Similarly, nematic phase shows schlieren textures (Plate 3) which has been seen in SA + 11OBA system. The pattern of textures is similar in all the combinations.

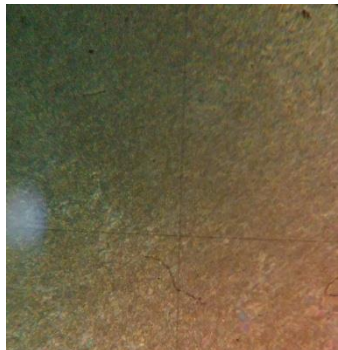


Plate 1.

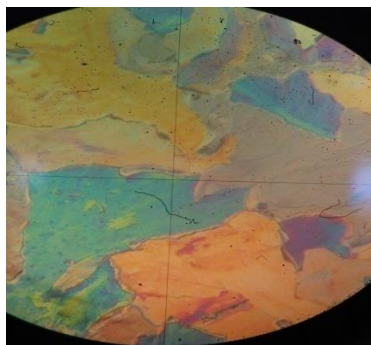


Plate 2.

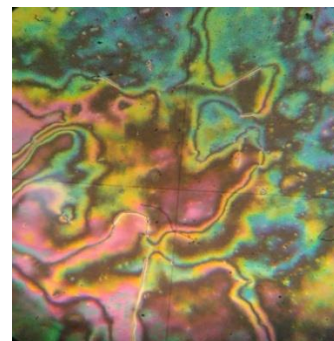


Plate 3.

Plate 1. Schlieren textures of smectic C phase texture in SA+7OBA.

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

Plate 3. Schlieren textures of nematic phase in SA+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. Figures 2 and 3 show the DSC thermograms during heating and cooling cycle for heptyloxy benzoic acid (7OBA) and one of the representative mixtures, namely, binary mixture of sebacic acid and heptyloxy benzoic acid, SA + 7OBA.

Sebacic acid (SA) is non mesogen, while 7OBA shows smectic C phase from 98.5 °C to 101.2 °C and nematic phase in the range of 146.2 °C- 148.5 °C upon heating. During cooling, an additional peak corresponding to the solid-solid transition is clearly visible in 7OBA. However, the binary combination of SA + 7OBA shows a new transition during cooling of the sample (monotropic). The textures when observed using POM indicated the presence of multicoloured smooth mosaic textures of smectic G phase. Therefore, POM and DSC studies confirmed the presence of smectic G phase in the binary mixture of SA + 7OBA. The thermogram in the heating cycle shows endothermic peaks at 92.94 °C, 111.84 °C and 127.05 °C with enthalpy change values as 71.31, 11.44 and 0.60 Jg⁻¹, respectively. These peaks correspond to the Cr- SmC, SmC-N and N-I transitions. During cooling, the exothermic peaks observed are at 126.5 °C (microscopic data only), 108.11 °C, 92.40 °C, 81.28 °C and 74.83 °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 depicted in Table 1.

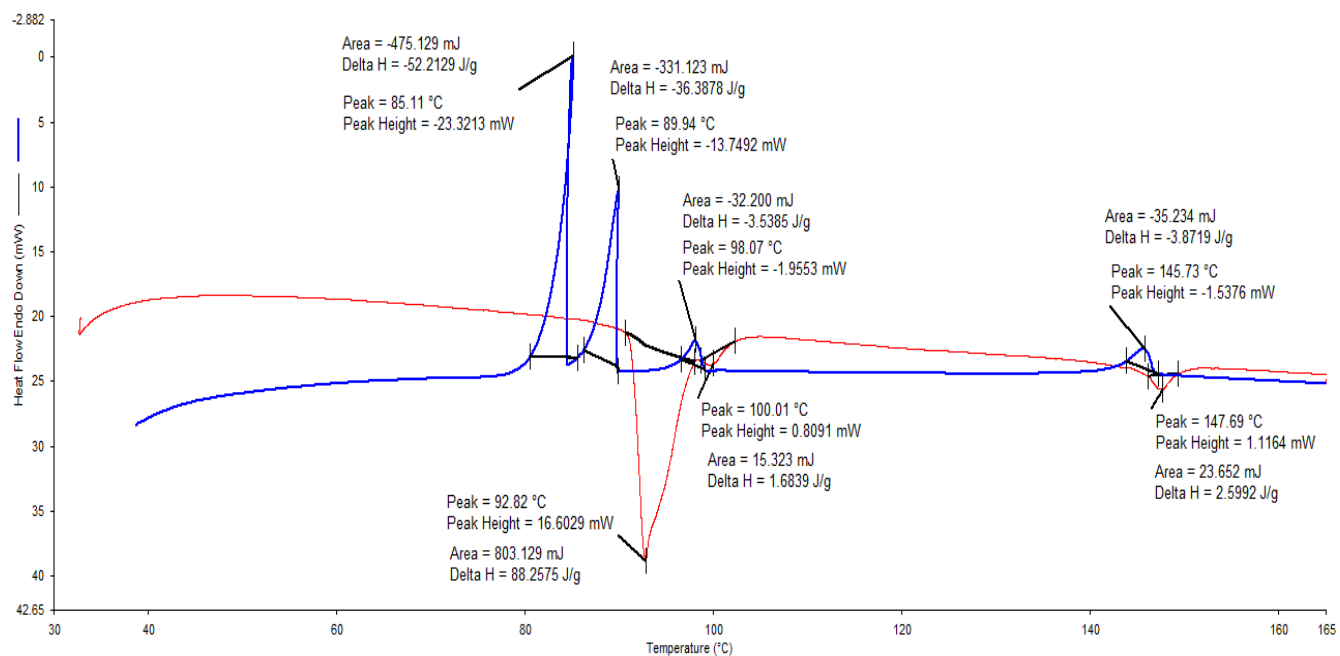


Figure 2: DSC Curve of 7OBA

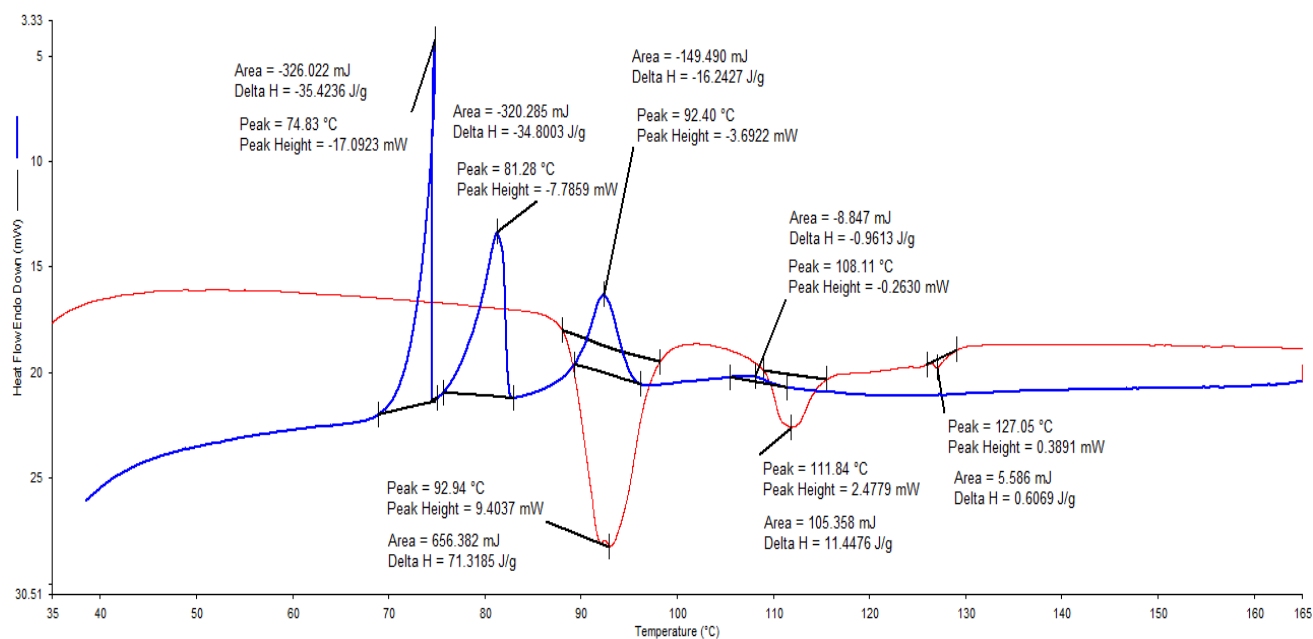


Figure 3: DSC Curve of 7OBA + SA

3.2 FTIR spectra

The FTIR spectra of pure alkyloxy benzoic acid, sebacic acid and their mixtures were recorded in the solid state at room temperature. The solid state spectra of the free alkyloxy benzoic acid should show two peaks at 1685 cm^{-1} and 1695 cm^{-1} due to $\nu(\text{C}=\text{O})$ mode [13]. As a representative of alkyloxy benzoic acid, for example nonyloxy benzoic acid (9OBA), the two peaks in the vicinity of 1687 cm^{-1} are shown. The doubling feature of this symmetrical stretching mode confirms the dimeric nature of alkyloxy benzoic acid in general and nonyloxy benzoic acid in particular at room temperature. The sharp peaks stretching from 3000 cm^{-1} and 2500 cm^{-1} are due to carboxylic acid $-\text{OH}$ stretching frequency. The C-H stretching frequencies in the pure component (9OBA) appear at 2848 cm^{-1} and 2918 cm^{-1} . As a result of complexation of hydrogen-bonded complex, the FTIR spectra of SA+ 9OBA (Fig. 5) shows single broad band at 1689.64 cm^{-1} (1690 cm^{-1}). The significant feature of this figure is non-appearance of the doubling nature of $\nu(\text{C}=\text{O})$ mode of benzoic acid moiety. Moreover, there is a shift in the values of C-H stretching frequencies in the complex SA+ 9OBA as 2846 cm^{-1} and 2914 cm^{-1} . The carboxylic acid $-\text{OH}$ stretch in the complex becomes more broad over the range of 3000 cm^{-1} and 2500 cm^{-1} indicating the presence of strong hydrogen bonding

between the sebacic acid and nonyloxy benzoic acid. The hypsochromic shift from 1685 cm^{-1} to 1690 cm^{-1} in $\nu(\text{C}=\text{O})$ of acid ($\sim 5\text{ cm}^{-1}$) and bathochromic shift from 2918 cm^{-1} and 2848 cm^{-1} to 2914 cm^{-1} and 2846 cm^{-1} in the $\nu(\text{OH})$ ($\sim 4\text{ cm}^{-1}$) mode of acid in the mesogen suggest the formation of intermolecular hydrogen bonding between the $-\text{COOH}$ group of nonyloxy benzoic acid and sebacic acid. A similar trend is followed in all other synthesized hydrogen bonded complexes of p- n- alkyloxy benzoic acid and sebacic acid.

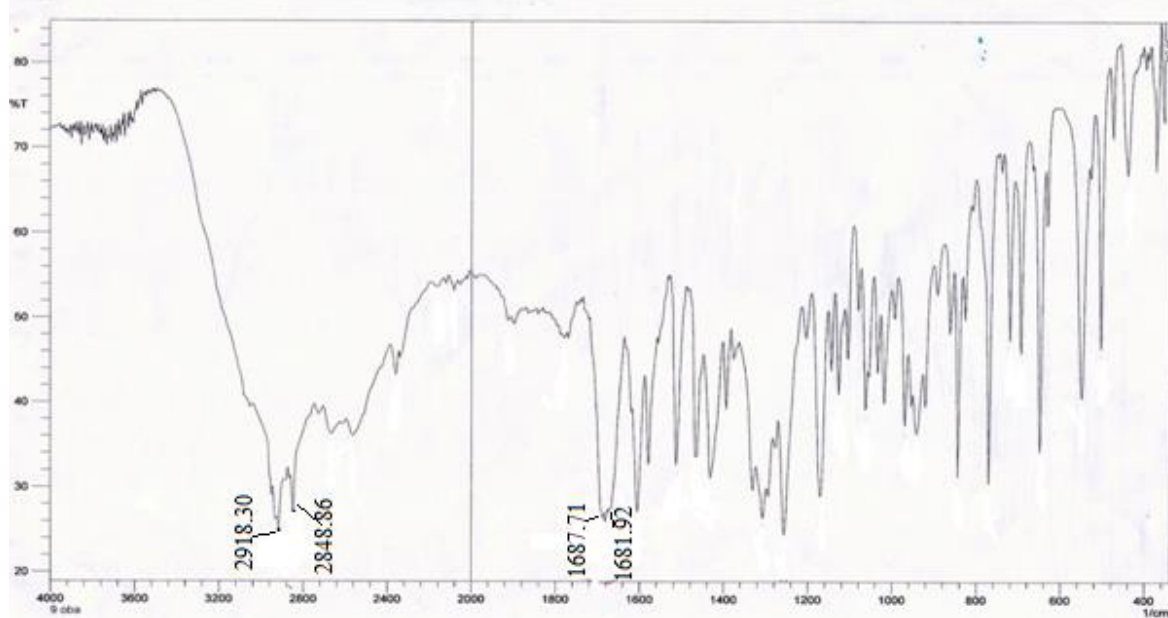


Figure 4: FTIR Spectrum of 9OBA

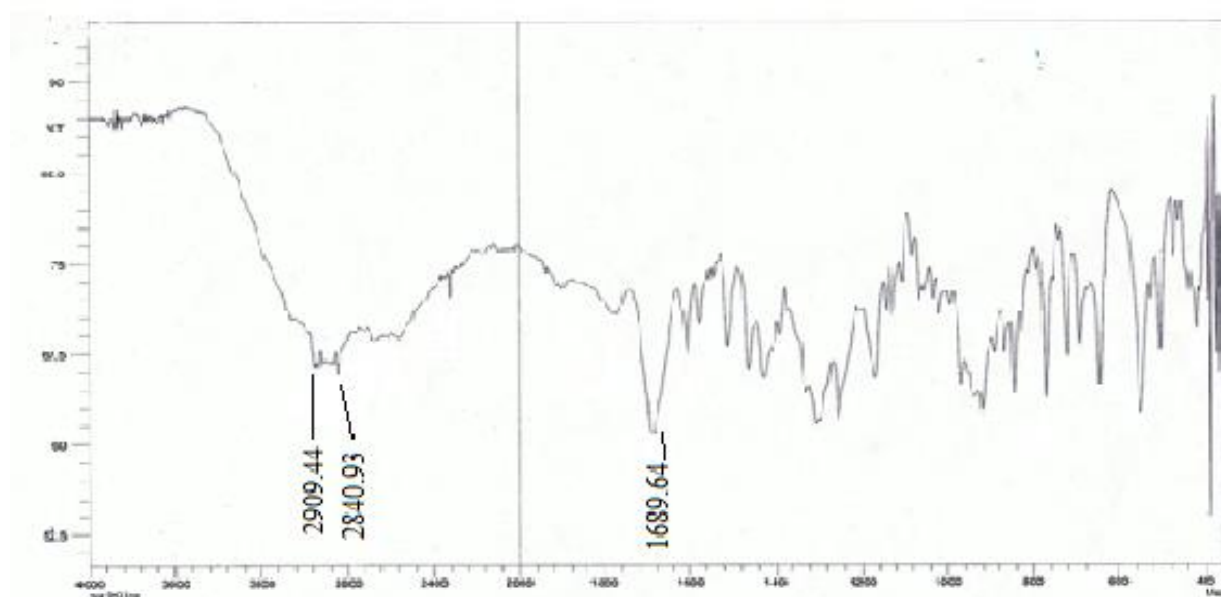


Figure 5: FTIR Spectrum of 9OBA + SA

3.3 Proton nuclear magnetic resonance (^1H -nmr)

The chemical structures for SA+nOBA series have been verified by ^1H -NMR studies. As a representative case, ^1H -NMR for SA+8OBA is discussed. The recorded spectra is shown in the Fig. 6. Some of the generalisations which can be interpreted from this figure may be summarized as: (a) the peaks observed between 2.4 and 0.85 ppm correspond 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 ^1H -NMR spectra agrees well with the expected number of hydrogen atoms, the complex between SA+8OBA and likewise for other members of the series are considered to be formed.

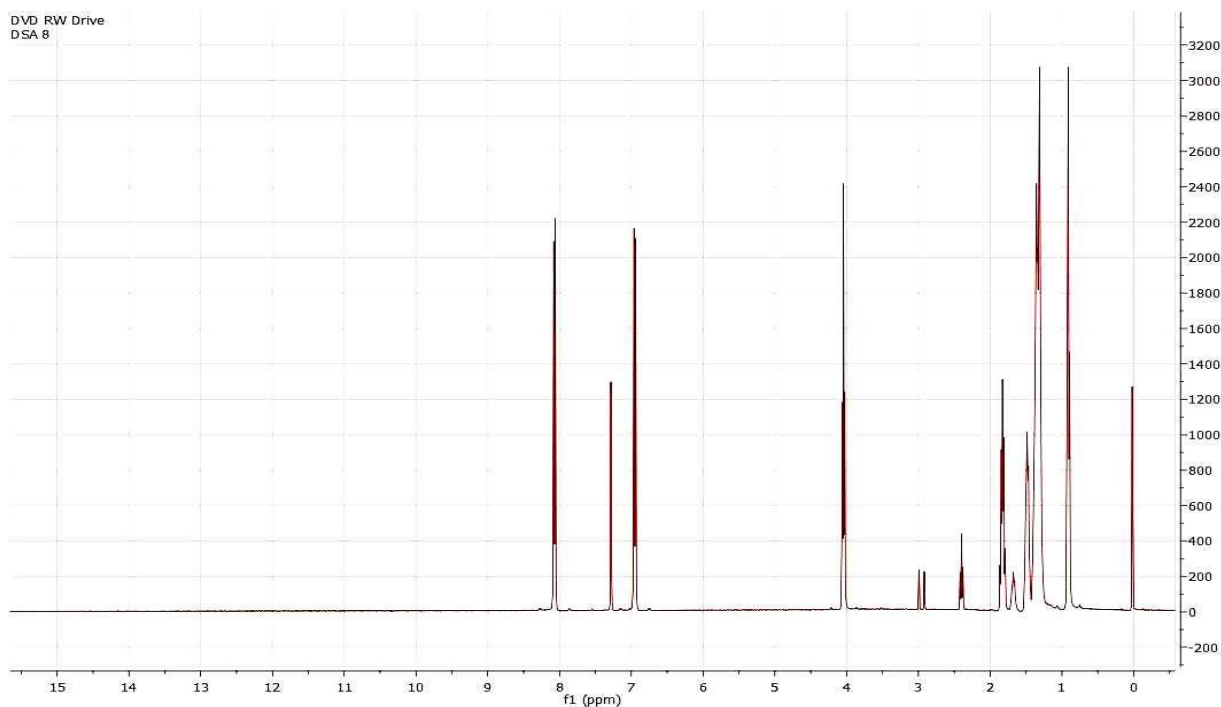


Figure 6: ^1H -NMR spectra of SA + 8OBA.

Conclusion

The study of the hydrogen bonded liquid crystalline complexes of SA + nOBA and TDD + nOBA can be concluded as follows.

1. All the complexes of SA + nOBA were found to have intermolecular hydrogen bond between $-\text{COOH}$ of the benzoic acids and the dioic acids used.
2. The hydrogen bonded liquid crystalline complexes prepared were found to have a new phase induced during cooling the binary mixture.
3. The phase obtained was seen to be SmG phase when it was observed for its texture under PLM.
4. Many novel devices based on smectic liquid crystal phases have been prepared as these works on faster regimes (nano seconds). Since the complexes formed are rich in smectic phases, these can be exploited for their applications in the field of technology.

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