Bulg. J. Phys. **36** (2009) 274–285

Occurrence of Ambient Temperature and Re-Entrant Smectic Ordering in an Inter Molecular Hydrogen Bonding between Alkyl Aniline and Alkoxy Benzoic Acids

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Received *25 November 2009*

Abstract. A homologous series of inter hydrogen bonded complexes between p-n-alkoxybenzoic acids (12A+nBA) and alkyl aniline were isolated. The mesogenic p-n-alkoxybenzoic acids formed a hydrogen bond with liquid crystal intermediate 4-dodecyl aniline respectively. The isolated homologous series compounds were analyzed by FTIR, Polarizing optical microscope, dielectric studies and DSC. Interesting feature of these homologous series was the occurrence of an ambient smectic ordering in some of the isolated mesogens. The phase diagrams of the p-n-alkoxybenzoic acids and the present homologous series were computed and compared respectively. The hydrogen bond formation was evinced through FTIR spectral studies. Two higher member mesogens of the present homologous series were found to exhibit monotropic smectic G phase. Results of free p-n-alkoxybenzoic acids and the hydrogen bonded homologous series were discussed in the light of increment alkoxy carbon number, mesogenic phases exhibited and mesogenic thermal range.

PACS number: 42.70.Df, 61.30.Eb, 64.60.Q, 64.70.M, 77.22.Ch, 77.22Jp

1 Introduction

Since the discovery of the first ferroelectric liquid crystal by Meyer [1], the interest on these soft materials has grown enormously. In the recent times hydrogen bonded liquid crystals (HBLC) [2-13], are designed and synthesized from materials selected on the basis of their molecular reorganization and self assembly capability. The applicational aspects [14-17], and commercial viabilities made many research groups to work on these soft materials.

Hydrogen bonded liquid crystalline materials are known since early 1960 [3,4], however in the recent times [5-13, 18-22] much work has been done on these

complexes. Hydrogen bond, which is a fifth type of fundamental force, enables various mesogenic and non mesogenic compounds to form complexes which exhibit rich phase polymorphism. HBLC usually are composed of a proton donor and acceptor molecules. The reported data [5-12, 18-22] indicates the fact that if HBLC materials are to be mesogenic, it is enough either one of proton donor or the acceptor molecules to exhibit mesogenic property. The chemical molecular structure [10,18-22] of HBLC is co-related to the physical properties exhibited by it. The reported literature suggests the formation of HBLC through a carboxylic acids as well as from mixtures of unlike molecules capable of interacting through H-bonding [2,7,10,13-21]. Usually in all these HBLC the rigid core is made up of covalent and non covalent hydrogen bonding. The discovery of hydrogen bonded liquid crystal by Kato and Frechet [14] opened a new chapter in synthesis, design and characterization of these mesogens which facilitated by many research groups [27-32] to work in this field.

With our previous experience [24,25,33,34] in designing, synthesizing liquid crystals and in continuation of our efforts to understand hydrogen bonded mesogens which are earlier published as part I [23] and part II [26], in the present work a successful attempt has been made to design and isolate a homologous series of hydrogen bonded liquid crystals with an aim of lowering the transition temperatures of the mesogens to the ambient temperatures. The mesogenic p-n-alkoxybenzoic acids (where n represents the alkoxy carbon number from 5 to 12 except 4 and 6) formed a hydrogen bond with liquid crystal intermediate 4-dodecyl aniline respectively. Phase diagrams, mesogenic phase and thermal range are discussed for the isolated two different homologous series.

2 Experimental

2.1 Materials and Instrumentation

Optical textural observations were made with a Nikon polarizing microscope equipped with Nikon digital CCD camera system with 5 mega pixels and 2560×1920 pixel resolutions. The liquid crystalline textures were processed, analyzed and stored with the aid of ACT-2U imaging software system. The temperature control of the liquid crystal cell was equipped by Instec HCS402-STC 200 temperature controller (Instec, USA) to a temperature resolution of $\pm 0.1\,^{\circ}$C. This unit is interfaced to computer by IEEE–STC 200 to control and monitor the temperature the liquid crystal sample is filled by capillary action in its isotropic state into a untreated conducting cell with 4 micron spacer. The transition temperatures and corresponding enthalpy values were obtained by DSC (Shimadzu DSC-60). The FTIR spectra was recorded (ABB FTIR MB3000) and analyzed with the MB3000 software. The p-n-alkoxybenzoic acids (12A+nBA) and 4-dodecyl aniline were supplied by Sigma Aldrich, Germany and all the solvents used were E.Merk grade.

3 Synthesis of Intermolecular Hydrogen Bonded Complexes

The intermolecular Hydrogen bonded complexes are synthesized by the addition of two moles of p-n-alkoxybenzoic acids (12A+nBA) with one mole of 4-dodecyl aniline in N,N-Dimethyl formamide (DMF) respectively. Further they are subject to constant stirring for 12 hours at ambient temperature of 30 °C till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF are then recrystallized. The yields varied from 85% to 95%. The yield of higher homologues compounds is observed to be more compared to its lower counterparts. The homologous series of p-n-alkoxybenzoic acids with 4-dodecyl aniline can be depicted as shown in Figure 1, where n represents alkoxy carbon number of benzoic acid.

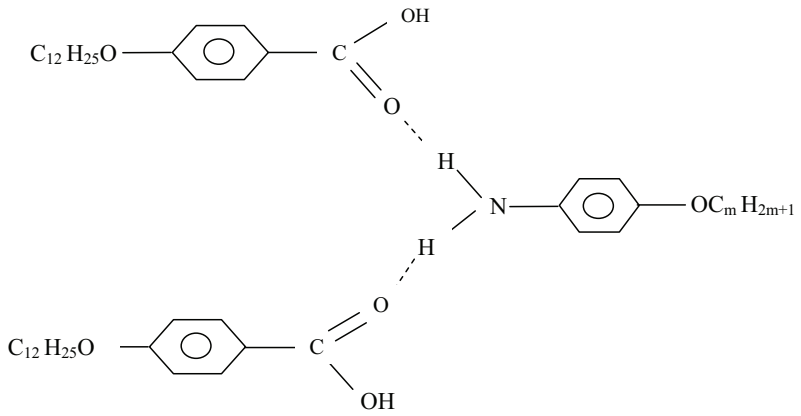

Figure 1. Molecular structure of dodecylaniline and alkoxy benzole acid homologous series.

4 Results and Discussion

All the mesogens isolated under the present investigation are white crystalline solids and are stable at room temperature. They are insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, benzene and dichloromethane. However they show a high degree of solubility in coordinating solvents like dimethylsulfoxide (DMSO), dimethylformamide (DMF) and pyridine. All these mesogens melt at temperatures around 100 °C (Table 1). They show high thermal and chemical stability when subjected to repeated thermal scans performed during thermal microscopy and DSC studies.

4.1 FT-IR Studies

The room temperature IR spectrum of free alkoxy benzoic acids and its H-bonded complexes were recorded in solid (KBr) state. The infrared frequencies of the pertinent bands are given in Table 1. The KBr spectra of p-n-alkoxy benzoic acid show sharp bonds at 1685 cm^{-1} and 1695 cm^{-1} due to the ν(C=O) mode and a strong intense band at 3012 cm^{-1} assigned to the ν(OH) mode of the carboxylic acid group [35]. This doubling nature of the ν(C=O) mode may be attributed to the dimeric nature of the acid group at room temperature [35]. The corresponding spectra in the solution state (chloform) show a strong intense band at 1712 cm^{-1} suggesting the existence of the monomeric form of benzoic acid in the solution state. Comparison of the spectra of complexes is made with the solution spectra of free alkoxy benzoic acids. The IR spectrum (KBr) of 4-dodecyl aniline shows characteristic bands for ν(C=O) ($\sim$ 1612 cm^{-1}), ν(N-H) ($\sim$ 3371 cm^{-1}) and νv(C-O)$_{\text{phenolic}}$ ($\sim$ 1265 cm^{-1}) stretching modes [12]. The solid state IR spectra of hydrogen bonded complex 12A+(11BA)2 complex as shown in Figure 2, exhibit a sharp band at 1682 cm^{-1} with the disappearance of the doubling nature due to the ν(C=O) mode of the benzoic acid moiety. This clearly suggests dissection of the dimeric p-n-alkoxy benzoic acids upon complexation. Further these complexes show bathochromic shifts in the ν(C=O) ($\sim$ 30 cm^{-1}) and ν(OH) ($\sim$ 96 cm^{-1}) modes of free alkoxy benzoic acid and the ν(N-H) mode ($\sim$ 46 cm^{-1}) group of aniline moiety, thereby indi-

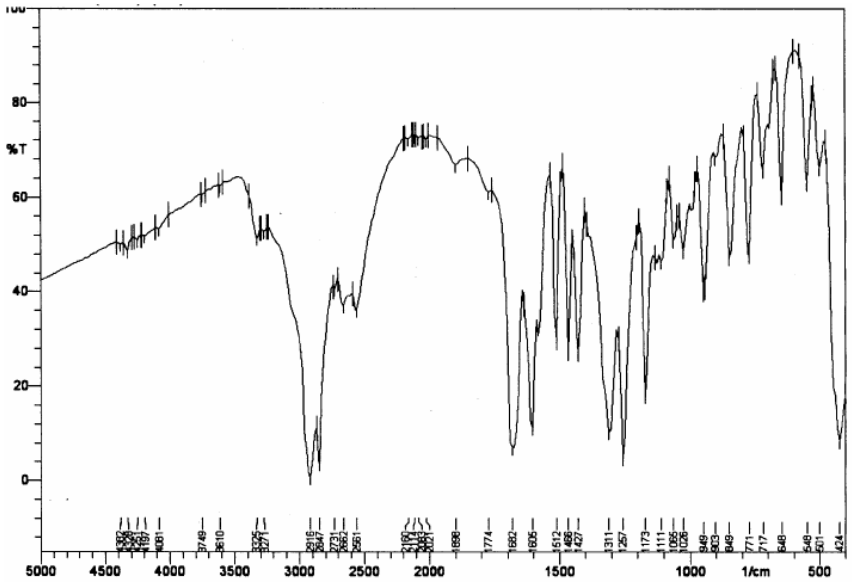

Figure 2. FTIR spectrum of 12A+(11BA)$_2$ hydrogen bonded complex.

Table 1. IR spectral frequencies of pertinent bands

Compound	nBA moiety		Aniline moiety		
	ν(C=O)	ν(OH)	ν(C–O)	ν(N–H)	ν(>C=N–)
p-dodecyloxy benzoic acid ($CHCl_3$)	1712	3012	—	—	—
Dodecyl aniline	—	—	1265	3371	1612
12A+12$(BA)_2$	1682	2918	1258	3331	1608
12A+11$(BA)_2$	1682	2916	1257	3325	1605
12A+10$(BA)_2$	1682	2916	1257	3333	1605

cating that both groups can form complementary H-bonding so as to accept as well as donate protons from one another [36]. The existence of the hydrogen bonding in the present series is further invoked by the bathochromic shift in the ν(C-O)$_{\text{phenolic}}$ mode of the aniline (~ 8 cm^{-1}).

4.2 Phase Identification

The observed phase variants, transition temperatures and corresponding enthalpy values obtained by DSC in cooling and heating run for the homologous series are presented in Table 2.

4.3 Dodecyl Aniline Benzoic Acids Homologous Series

The mesogens of the dodecyl aniline and benzoic acid homologous series on cooling from isotropic are found to exhibit characteristic textures [37], *viz.*, Smectic C (schlieren) Smectic F (broken focal conic), Smectic G (multi colored mosaic texture) and Smectic F re-entrant (chequered board texture) phases respectively. The general phase sequence of the dodecyl aniline and benzoic acid homologous series in the cooling run can be shown as

Isotropic $\longrightarrow$ Sm G $\longrightarrow$ Crystal (carbon number 3, 5 and 7)

Isotropic $\longrightarrow$ Sm C $\longrightarrow$ Sm F$\longrightarrow$ Sm G $\longrightarrow$ Crystal (carbon number 8 to 11)

Isotropic $\longrightarrow$ Sm C $\longrightarrow$ Sm F $\longrightarrow$ Sm G $\longrightarrow$ Sm F_r $\longrightarrow$ Crystal (carbon number 12)

It is clearly evident from the above phase sequences that new smectic phases have been induced compared to pure benzoic acid homologous series. In other words, from Carbon number 3 to 7, when compared to free alkoxy benzoic acid phase variance, in the present complex Nematic of the pure alkoxybenzoic has been quenched and Smectic G has been observed. Similarly from carbon number 8, smectic F phases is induced. Thus a good number of mesogenic phases have been induced in the lower and higher mesogens of the present series. Further the complex 12 of the present series exhibits a re-entrant smectic F ordering which

Table 2. Transition temperatures obtained by DSC of 12A+ nBA homologous series. Enthalpy (ΔH) values are given in J/g while temperature is measured in degrees centigrade

Carbon number	Phase variant	Technique	Crystal to melt	ΔH	C	ΔH	F	ΔH	G	ΔH	F_r	ΔH	Crystal	ΔH
		DSC (h)												
3	G	DSC (c)	#	#					108.3	12.36			#	
		POM (c)							107.5					
		DSC (h)	47.7	48.17										
5	G	DSC (c)							64.7	77.24			29.8	42.5
		POM (c)							65.5				28.5	
		DSC (h)												
7	G	DSC (c)	#	#					88.3	10.60				
		POM (c)							89.5					
		DSC (h)	74.3	21.49	96.7	0.32	95	0.88	⋆					
8	CFG	DSC (c)			91.3	♯	89.5	16.94	45.1	†			44	26.6
		POM (c)			92.5		90.4		46.3				42.9	
		DSC (h)	93.4	64.04	104.1	0.20	⋆		⋆					
9	CFG	DSC (c)			93.1	‡	90.4	0.81	86.1	14.83			61.6	41.3
		POM (c)			94.2		91.5		87.2				62.4	
		DSC (h)	34.6	9.29	96.2	4.94	93.5	3.49	86.7	13.51				
10	CFG	DSC (c)	—		100.6	1.65	92.9	0.29	88.4	9.28	—		76.3	10.85
		POM (c)			101.4		93.8		89.6				77.6	
		DSC (h)	35.3	26.28										
11	CFG	DSC (c)			100.2	3.18	80.2	13.82	74.1	10.19	—		40.1	32.8
		POM (c)			101.5		81.6		75.4				41.2	
		DSC (h)	38.8	25.24	—		109.0	1.79	94.5	53.29	47.8	0.18	—	
12	$CFGF_r$	DSC (c)			117.9	2.67	103.3	6.50	82.6	21.92	64.3	11.3	42.5	25.17
		POM (c)			118.5		103.9		83.2		64.9		43.1	

– room temperature liquid crystal
⋆ – monotropic transition
♯ – merged with F
† – merged with crystal
‡ – not resolved

has been confirmed by DSC and optical textural studies. Two complexes namely octyl and nonyloxy benzoic acid complexes exhibit monotropic smectic G transition where, in the heating cycle the smectic G phase is observed while it is not observed during the cooling cycle.

4.4 DSC Studies

DSC thermograms are obtained in heating and cooling cycle. The sample is heated with a scan rate of 10°C/min and hold at its isotropic temperature for one minute so as to attain thermal stability. The cooling run is performed with a scan rate of 10°C/min. The respective equilibrium transition temperatures and corresponding enthalpy values of the mesogens corresponding to the homologous series are listed separately in Table 2.

4.5 Re-Entrant Phenomenon

DSC Study

The phase transition temperatures and enthalpy values of dodecyloxybenzoic acid complex [12A+$(12BA)_2$] are discussed. As shown in Figure 3, in the cooling run the DSC thermo gram exhibits five distinct transitions namely isotropic to smectic C, smectic C to smectic F and smectic F to smectic G, smectic G to smectic F (re-entrant) and smectic F (re-entrant) to crystal with transition temperatures 117.9°C, 103.3°C, 82.6°C, 64.3°C and 42.5°C with corresponding enthalpy values 2.67 J/g, 6.50 J/g, 21.92 J/g, 11.29 J/g and 25.17 J/g, respectively. While in the heating cycle four distant transitions namely crystal to melt, melt to smectic F (re-entrant), smectic F (re-entrant) to smectic G, smectic G to smectic F are observed at 38.8°C, 47.8°C, 94.5°C and 109°C with the corresponding enthalpy values 25.24 J/g, 0.18 J/g, 53.29 J/g and 1.79 J/g, respectively. These transition temperatures and corresponding thermal spans of individual phases concur with polarizing optical microscopic studies.

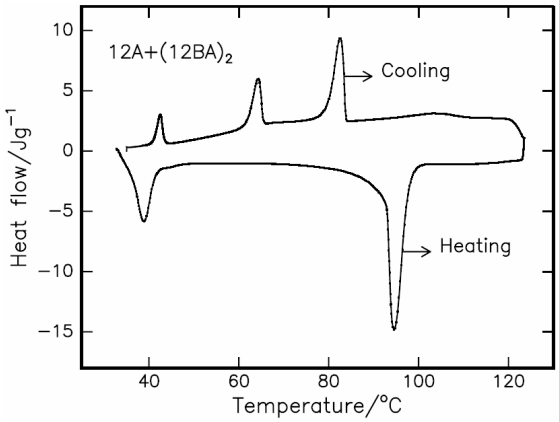

Figure 3. DSC thermogram of 12A+$(12A)_2$ mesogen.

Polarizing Optical Microscopy

The optical textural observations also confirm the re-entrant DSC results. The phase sequence of the dodecyloxy benzoic acid complex is cited above. Schlieren smectic C is observed which transformed to broken focal conic texture of smectic F on further cooling smooth multi colored mosaic texture of smectic G is observed. Further cooling resulted in the re-entrant smectic F with chequered board texture as depicted in Figure 4.

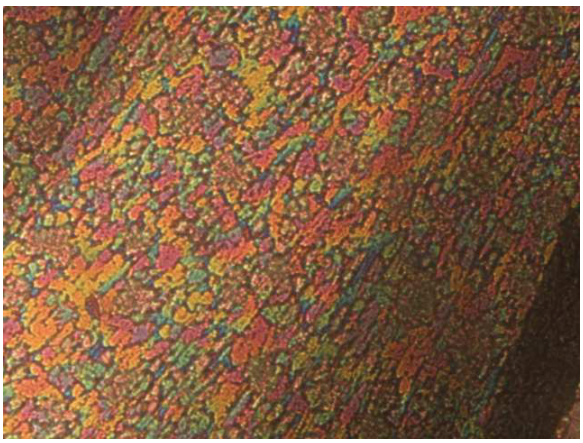

Figure 4. Chequered board texture of re-entrant smectic F.

4.6 Phase Diagrams

The phase diagrams of pure p-n-alkoxybenzoic acids and the dodecyl aniline homologous series are constructed through optical polarizing microscopic studies by the phase transition temperatures observed in the cooling run of the mesogens of the present homologous series. The phase diagram of pure p-n-alkoxybenzoic acids is composed of three tilted phases namely, nematic, smectic C and smectic G as shown in Figure 5.

From a close observation of the phase diagram of the complex illustrated in Figure 6, the following observation are made.

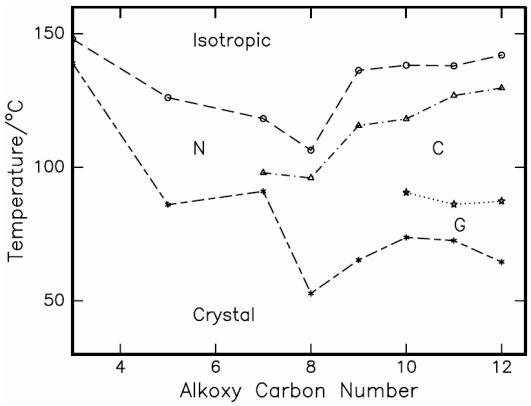

Figure 5. Phase diagram of alkoxy benzoic acids.

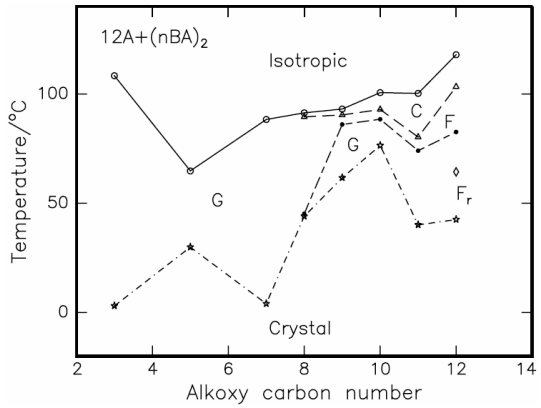

Figure 6. Phase diagram of 12 + $(nBA)_2$ hydrogen bonded complex.

All the mesogens of the present complex exhibit liquid crystallinity. Complexes 3 and 7 are found to exhibit wide thermal range of smectic G phase upto $\sim 5\,^{\circ}$C far beyond ambient temperatures. Smectic G phase is induced in the lower homologous series while smectic F is induced in the higher homologous complexes. A re-entrant smectic F is observed in dodecyl carbon complex with wide thermal span. The thermal span of the series is maximum in lower carbon numbers and minimum for nonyl complex. In general the isotropic temperatures of the present series are much lower than the isotropic temperatures of the free alkoxy benzoic acids.

4.7 Dielectric Studies

Dielectric studies enable to detect second order transitions which cannot be resolved by DSC studies. In the present study, as a representative case, 12A+$(11BA)_2$ hydrogen bonded complex is presented. This compound is filled in a untreated conducting cell of 4 micron spacer with an active area of 1 mm ^{2} under capillary action. Silver wires are drawn from the cell as leads. Empty cell is calibrated with temperature and with a known substance (benzene) to calculate the leads capacitance. The cell with the sample is placed in Instec hot stage (HCS 402) whose temperature is monitored by Instec stand alone temperature controller (STC 200), interfaced with a computer, to an accuracy of $\pm 0.1\,^{\circ}$C. The sample is taken to its isotropic state and held for two minutes so as to attain thermal stability. Simultaneous textural observations are made to ascertain the phase of the mesogen. The readings are noted in the cooling run with a scan rate of 0.1°C/min. The 12A+$(11BA)_2$ compound in the cell is provided with a sinusoidal stimulus of 1.1 V obtained from HP 4192A impedance analyzer. The variation of the capacitance at two different frequencies namely 10 KHz and 100 KHz is plotted in Figure 7. From the careful observation of the figure 6 the

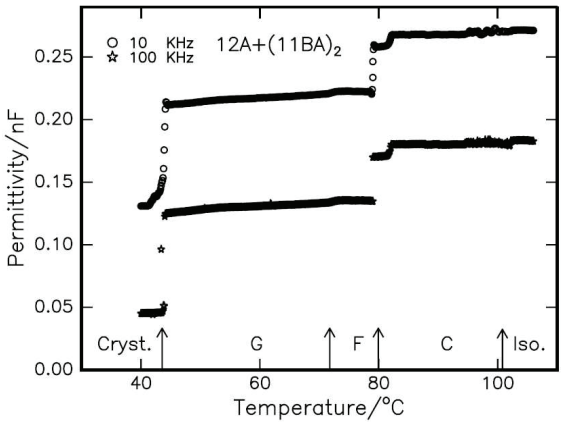

Figure 7. Temperature variation of permittivity for 12A+$(11BA)_2$ mesogen at 10 KHz and 100 KHz.

following points are noted.

a) As the temperature is decreased from isotropic, smectic C phase is formed. This is manifested in the form of a small kink at 101.0 °C in the dielectric spectrum.

b) In the entire thermal range of smectic C capacitance value is unaltered indicating the stabilization of the smectic C phase

c) The sudden step like decrement followed by a steep fall in the magnitude of the permittivity in the dielectric spectrum at 80.0 °C is attributed to the onset of smectic F phase. From 80.0°C to 75.4°C, the thermal range of smectic F, the variation of capacitance is almost linear.

d) The onset of smectic G phase is seen in the dielectric spectrum as an anomaly at 75.4°C. In entire thermal range of smectic G the capacitance is unaltered indicating the stabilization of the smectic G phase.

e) A sudden steep fall in at 41.2 °C in the magnitude of the permittivity indicates the onset of crystal.

These variations in the magnitude of the permittivity are observed in both 10 KHz and 100 KHz frequency spectrum. Further similar variations are noted in the dielectric loss spectrum pertaining to the corresponding frequencies. The transition temperatures obtained by this technique are in good agreement with those obtained from other techniques namely POM and DSC.

5 Conclusions

Inter hydrogen bonded liquid crystalline complex between alkoxy benzoic acid and alkyl aniline has been successfully isolated and characterized. Smectic G phase is observed to be induced in the lower homologous series of the complex while smectic F and smectic re-entrant F are observed in the higher homologous series. DSC, dielectric and textural studies confirm the above observations.

Acknowledgements

The authors acknowledge the financial support rendered by All India Council of Technical Education, Department of Science and Technology, and Defence Research Development Organization, New Delhi. Infrastructural support provided by Bannari Amman Institute of Technology is gratefully acknowledged.

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