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# Thermal and optical characterization of a novel series of supramolecular liquid crystals

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# ABSTRACT

Supramolecular hydrogen bonded liquid crystal (SMHBLC) homologous series is synthesized and characterized. Hydrogen bond is formed between p-*n*-alkyloxy benzoic acids (nOBA, where n=7 to 12) and Iodo substituted benzoic acid (I<sub>m</sub>BA) respectively. The isolated homologs are characterized by various techniques like Polarizing Optical Microscopy (POM), Differential Scanning Calorimetry (DSC), <sup>1</sup>H Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). From the POM and DSC studies phase diagram has been constructed and discussed. A new smectic ordering, labeled as smectic R, has been characterized which exhibits a ribbon like texture. This phase is observed in a complex pertaining to the undecyloxy carbon number. Tilt angle in smectic R phase and in traditional smectic C of all the complexes have been experimentally deduced and the results are fitted and so obtained  $\beta$  value concurrences with the Mean field theory predicted value.

# 1. Introduction

Liquid crystals [LC] are intermediate soft state materials that posses the properties of anisotropic crystals and isotropic liquids. As such, they exhibit distinct response. Materials scientists launched [1-6] their investigations for the utility of this soft matter through their design and adoptability in electro-optic devices [7-10] as optical shutters, light modulators etc. In the recent years, supra-molecular design of hydrogen bonded liquid crystals (HBLC) gained importance as functional materials for their synthesis and characterization with specific choice of chemical functional groups. Initiative of HBLCs by Kato [2,7] group has triggered the LC research to set in to a new direction of research activity. The lower activation energies involved with the HB interaction profoundly influence the thermal properties of LC phases, viz., melting points, enthalpies and thermal stability. The soft covalent (SC) interaction, if configured to spread adjacent and along the essential core region of the molecule, it is believed to originate to new mesophases with an operationally viability. Further, intermolecular HB of complementary type in LC materials is known to monitor the phase stability by the proper selection of interacting components. HB in LCs can be realized by the interaction between a proton donor moiety and a proton acceptor

moiety. Complementary type HBLCs can also be materialized [16-24] by the HB interaction of two organic acids, such that each of them possessing an acid (-COOH) moiety [11-19] bears a hydroxyl (-O-H $^{+\delta})$  group considered as a proton donor and a carbonyl (-C=O $^{-\delta})$  group considered as a proton acceptor. Nevertheless, HBLCs are also realized by the SC interaction between proton rich aniline moieties and proton acceptor aldehyde moieties. In order to realize the LC phases of phases of device interest in HBLC complexes, it is considered as a sufficient condition that at least one of the moieties should be inherently [18,21,24,25] mesogenic. Most of the reported cases [22,23] of HBLCs deal with both of the moieties exhibiting mesogenic [22,23] nature. However, HBLCs made up of two moieties which are inherently non-mesogenic [20,26,27] are also reported. Mono component [21,23] or multi component hydrogen bonded [21,22] LC systems are also reported. An overview of literature in HBLCs reveals HB interaction can enhance the thermal stability of device relevant tilted phases and better their operating parameters.

In the wake of the extensive reports of functional groups and their diversified utility, an attempt is made to design and isolate a novel homologous series of HBLCs especially made up of benzoic acids with meta-substitution (to promote transverse dipole moment) and mesogenic nOBAs. A series of meta-substituted (with lodine atom) HBLCs prepared from 3-lodobenzoic acids and N-p-*n*-alkyloxy benzoic acids (where *n* represents the alkyloxy chain length varied from 7 to 12) are presented, while the HB and LC phases are characterized by IR, proton NMR, Polarized Optical





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Microscopy (POM) and Differential Scanning Calorimetry (DSC) along with the device relevant optical properties exhibited are also determined.

#### 2. Materials and methods

A Varian 300 MHz <sup>1</sup>H NMR spectrometer is used to verify the HBLC complex formation and to estimate the H-atom abundance. An ABB FTIR MB3000 spectrometer and the MB3000 software are used to confirm the hydrogen bonding. Optical textural observations were made with a Nikon polarizing optical microscope (POM) equipped with Nikon digital CCD camera in conjunction with an ACT-2U imaging software. An Instec HCS402-STC 200 temperature controller ( $\pm 0.1$  °C) system is used for textural studies. The liquid crystal sample is filled in to the cells (made up of polyimide buffed pre-treated and conductive coated 4 µm spaced transparent glass plates) in its high temperature isotropic state. The transition temperatures and corresponding enthalpy values were obtained by DSC (Shimadzu DSC-60, Japan). Optical extinction technique is used for the determination of tilt angle. The p-n-alkyloxy benzoic acids (nOBA) and m-substituted benzoic acid (ImBA) and solvents of HPLC grade for the synthesis were procured from Sigma Aldrich, (Germany) and all the solvents used were of HPLC grade.

# 3. Synthesis of I<sub>m</sub>BA:nOBA series of HBLCs

Iodine substituted hydrogen bonded mesogens, viz., ImBA: nOBA series of HBLCs are synthesized by the addition of one mole of p-*n*-alkyloxy benzoic acids (nOBA, where n=7-12) and 1 mole of Iodo substituted benzoic acid (I<sub>m</sub>BA) in N, N-Dimethyl formamide (DMF). The dimeric form of nOBA is first converted in to the monomeric form by dissolving nOBA in DMF. Then, they are reacted with the ImBA dissolved in DMF. Further, the reactants were subjected to constant stirring for 12 h at ambient temperature (30 °C) till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF. The product is then re-crystallized with dimethyl Sulfoxide (DMSO). The synthetic route and molecular structure of the present HBLCs made up of p-n-alkyloxy benzoic acids with m-iodo benzoic acid (ImBA:nOBA) is presented in Scheme 1, where *n* represents the number of methyline  $(-CH_2-)$  units in alkyloxy chain of nOBA. It is anticipated that the meta-position of Iodine atom on the molecular frame is expected to enhance the

transverse dipole moment ( $\mu_t$ ) to influence the variance and thermal stability of LC phases. They are found to be insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, and benzene and dichloromethane. However, I<sub>m</sub>BA:nOBAs exhibited a high degree of solubility in coordinating solvents like dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and Pyridine. All members of the present series of HBLCs are found (Table 1) melt at temperatures below 97 °C.

# 4. Results and discussion

## 4.1. <sup>1</sup>H NMR studies

The <sup>1</sup>H NMR spectrum exhibited by the I<sub>m</sub>BA:nOBA series of HBLCs is presented in Fig. 2 (for n=9 as representative). The salient features of NMR spectrum are

- (1) A singlet at  $\delta \sim 0$  ppm infers the standard absorption corresponding to the TMS.
- (2) A singlet in the vicinity of  $\delta \sim 8.5$  ppm infers the presence of one H-atom of benzene ring of I<sub>m</sub>BA situated between carboxylic acid moiety and I-atom. The higher value of Chemical shift due to de-shielding effect (which is caused by neighboring groups (i.e.–COOH and iodine moieties).
- (3) A multiplet in the range of  $\delta \sim 8.0-8.2$  infers the presence of three H-atoms of aromatic moieties in the adjacent C-atoms to the acid moieties, i.e., one-H-atom adjacent to the I<sub>m</sub>BA's acid moiety and two-H-atoms corresponding to the nOBA's acid moiety.
- (4) A singlet at  $\delta \sim$ 7.9 indicates the presence of one H-atom attached to the C-atom of the aromatic ring of I<sub>m</sub>BA situated in para position of –COOH moiety.
- (5) A multiplet around  $\delta \sim$  7.25 indicates the presence of one-H-atom of aromatic ring of I<sub>m</sub>BA (total integrated intensity  $\sim$  2.0 is resolve as that from one-H-atom of I<sub>m</sub>BA moiety, while the other-H-atom relevant to the residual H-atoms of CDCl<sub>3</sub> used as solvent).
- (6) Multiplets at  $\delta \sim 6.9$  evinces the presence of two H-atoms each on the C-atoms of the aromatic ring situated at the p-position of –COOH moiety of nOBA.



Fig. 1. Molecular structure of ImBA: nOBA series.



Scheme 1. Scheme of I<sub>m</sub>BA: nOBA synthesis.



Fig. 2. <sup>1</sup>H NMR spectra of I<sub>m</sub>BA:90BA complex.

- (7) A triplet in the vicinity of  $\delta \sim 4.1$  infers the presence of two-H-atoms situated on the first  $-CH_2$  unit (adjacent to the aromatic ring) of the alkoxy chain of nOBA.
- (8) A triplet at  $\delta \sim 3.1$  confirms the presence of three-H-atoms corresponding to the CH<sub>3</sub> group of at the end of alkyl chain.
- (9) Multiplets in the range from δ~1.28 to 1.8 infer the presence of 14 H-atoms pertaining to the remaining 7-methyline units each possessing 2-H-atoms.

The singlet at  $\delta \sim 2.1$  infers the presence of two H-atoms attributed to the trace level impurity of acetone used as cleaner. The absence of NMR response (for  $\delta > 10$ ) possibly to infer the presence of two H-atoms of both of the hydroxyl moieties (corresponding to the –COOH groups of I<sub>m</sub>BA and nOBA) is attributed to the limitation of the NMR instrument (i.e., being operated at 300 MHz). Hence, in the wake of the agreement between the observed (points 1–9) number of H-atoms (through the <sup>1</sup>H NMR) and the expected (Fig. 1) number of H-atoms in the HBLC complex, the purity of the HBLC product (to the extent of H-atom abundance at spectroscopic levels) is confirmed.

# 4.2. Fourier transform infrared spectroscopy (FTIR) studies

The solid state (KBr) IR spectra recorded at RT for I<sub>m</sub>BA: nOBAs are presented in Fig. 3 (for n = 11, as representative). The presence of an intense peak at 2924 cm<sup>-1</sup> is attributed [25,29–30] to the possible shift of OH stretching and the participation of H-atom of hydroxyl group of acid moiety. The IR absorption relevant to the carbonyl stretching ( > C==O) frequency is found to shift towards lower side from 28 to 36 cm<sup>-1</sup> for the present cases of I<sub>m</sub>BA:nOBAs. The shift of frequency and its appearance as single absorption line confirms the participation of O-atom of carbonyl group of –COOH moiety in its monomeric form.

#### 4.3. Phase identification

The observed phase variance, transition temperatures and corresponding enthalpy values through the POM and DSC (in cooling and heating cycles) studies for the  $I_mBA$ :nOBA series are presented in Table 1.

#### 4.3.1. Phase characterization through POM

 $I_m$ BA:nOBAs are found to exhibit characteristic [28] textures as presented in Plate 1–8. The Nematic phase exhibited schlieren four brush (Plate 1) texture. Cooling of nematic phase in n=11



Fig. 3. FTIR spectra for I<sub>m</sub>BA:110BA complex.

resulted for the appearance of black transmitted intensity (Plate 2) implying the homeotropic arrangement of molecules. This texture is frequently referred (Ref) as pseudo-isotropic texture. It appears more black in color than that of isotropic brown color, and somewhat less black than homeotropic jet black. As this phase is originated from the nematic phase during the cooling process, this phase is tentatively labeled as N<sub>h</sub> phase. Further, cooling of this homeotropic phase results for the growth of a texture (Plates 3a and b) with ribbon like appearance. Hence, this phase is labeled as Smectic-R (Sm R). The texture shows large continuous curved ribbons with considerable width, while texture possesses canal like appearances. In each ribbon, disclination lines are observed to vouch and evince for the possible helicoidal structure. The dark part of the canal and its opposite handed viz; brighter part is clearly visualized in the plates 3a and 3b characterize the phase to be tilted. Such a texture is characterized and previously reported by us [14] in HBLC mesogens which is referred as ribbon phase and abbreviated as Smectic R. However, on further cooling of Sm R phase, a cacoon like regions are observed (swarms in Plate 4) are observed to grow. Since, the cacoon like textural appearance is uncommon to the calamitic LCs, under the consideration that it may be one or other form of smectic phases (to be investigated) this cacoon phase is named as smectic- $X_1$  phase.

# Table 1ImBA:nOBA series of HBLCs.

I <sub>m</sub> BA:nOBA <b>HBLC</b> <b>Complexes for </b> <i>n</i>	Phase variance	Technique	Melt	N	N <sub>h</sub> /Sm X	Sm R	Sm X <sub>1</sub>	Sm C	Sm F	K
12	NXCF	DSC (h)	94.5 (65.92)	a				a	a	
		DSC (c)		119.4 (1.46)	100.7 (0.26)			96.7	87.1	78.5 (21.43)
		POM		119.9	101.1			97.00	87.3	78.6
11	NN <sub>h</sub> RX <sub>1</sub> CF	DSC (h)	96.0 (56.85)	a	a	104.0 (1.79)	a	a	a	
		DSC (c)		123.2 (0.87)	104.2 (0.27)	102 (0.59)	97.1 (1.27)	95.3 (0.20)	78.2 (11.99)	73.9 (28.16)
		POM		123.9	104.8	102.5	97.5	95.6	78.4	74.00
10	-	DSC (h) DSC (c) POM	88.5 (23.97)							83.3 (16.57) 83.6
9	NXCF	DSC (h)	91.4 (70.50)	a	104.5 (1.34)			a	a	
		DSC (c)		143.2 (1.52)	100.7 (0.89)			88.9 (16.74)	84.3 (2.74)	80.5 (22.08)
		POM		143.8	101.2			89.3	84.6	80.7
8	-	DSC (h) DSC (c) POM	88.1 (14.00)							85.5 (19.65) 85.9
7	Ν	DSC (h) DSC (c) POM	88.2 (32.39)	102.0 (7.96) 102.0 (2.05) 102.5						78.4 (21.72) 78.7

It is interesting to note that two even complexes viz., ImBA:80BA and ImBA:100BA do not exhibit any mesogenic phases. The numbers given in parenthesis are the enthalpy values in J/g.

<sup>a</sup> monotropic, @ not resolved.



Plate 1. Nematic schlieren texture of the ImBA:110BA at 123.9 °C.

The swarms of cacoon like regions coalesce with further cooling, as they manifest with a homogeneous textural pattern in plate 5. On cooling the Sm X phase, a broken focal conic texture characteristic of smectic C phase (Plate 6) originates which is found to get established (Plate 7) as characteristic texture. Further cooling of Sm C phase is found to result in the growth of colored chequered board texture (Plate 8) characteristic of Smectic F phase. As to ascertain the structural details and response for the either to unknown smectic R and smectic X phases in the present I<sub>m</sub>BA:nOBA series of HBLCs, further experimental investigations are aimed whose results are presented in the up-coming sections.

# 4.3.2. Transition temperatures and enthalpy of LC phase transitions by DSC

DSC thermograms of all the complexes are recorded in heating and cooling cycle at scan rate of 5 °C/min and is presented in Fig. 4 (for n=11 as representative), while the corresponding data of



Plate 2. Psuedo-isotropic texture of Sm D phase for I<sub>m</sub>BA:110BA at 104.8 °C.

transition temperatures and the enthalpy ( $\Delta H$ ) are presented in Table 1. Initially, the sample is heated and held in its isotropic phase for 2 min as it is allowed to attain thermal equilibrium. The results of DSC are found to concur with the values from POM studies. From Fig. 4, the thermogram for n=11 seems to be rather complex as it involves seven distinct transitions, viz., isotropic to Nematic; Nematic to homeotropic nematic; homeotropic nematic to Sm R; Sm R to Sm X<sub>1</sub>; Sm X<sub>1</sub> to Sm C; Sm C to Sm F and Sm F to crystal, with transition temperatures earmarked as 123.2 °C, 104.2 °C, 102.0 °C, 97.1 °C, 95.3 °C, 78.2 °C, 73.9 °C, with corresponding enthalpy values of 0.87 J/g, 0.27 J/g, 0.59 J/g, 1.27 J/g, 0.2 J/g, 11.99 J/g and 28.16 J/g, respectively. While in the heating cycle, two distinct transitions namely crystal to melt and Sm X<sub>1</sub> to Sm R are obtained at 96.0 °C and 104.0 °C, with corresponding enthalpy values of 56.85 J/g and 1.79 J/g, respectively. For a clear visualization of the DSC peaks relevant to the nematic to homeotropic nematic, homeotropic nematic to Sm R, and Sm R to Sm X<sub>1</sub> phase transitions, the thermogram is expanded in the corresponding region as



**Plate 3.** a and b Ribbon like texture of Sm R phase with extinction positions for tilt angle in  $I_m$ BA:110BA at 102.5 °C.



Plate 4. Origin of cacoon like swarms of Sm X phase in I<sub>m</sub>BA:110BA.



Plate 5. Cacoon-like textured swarms grown for Sm X phase in  $I_{\rm m}BA:110BA$  at 97.5 °C.

re-presented in Fig. 5. Owing to the following observations and their comparison with the reports LCs that;

- (a) The involvement of comparable and considerable amount of enthalpy across the nematic to homeotropic nematic phase transition.
- (b) Pseudo-isotropic textural appearance which is comparable to the reported characteristic textures [28] attributed to smectic D phase.



**Plate 6.** Transition of Sm X phase to Sm C phase with broken focal conic texture for  $I_mBA:110BA$ .



Plate 7. Broken focal conic texture of Sm C in  $I_mBA$ :110BA at 95.6 °C.

- (c) Occurrence of homeotropic nematic phase (n=11) at a lower temperature than that of nematic phase, the homeotropic nematic phase  $(N_h)$  observed for n=11 is reassigned as Sm D phase.
- (d) Sm D to Sm R transition in cooling scan is found to accompany with an enthalpy value of 0.59 J/g confirming its first order nature. But, in heating scan transition is observed to accompany with an enthalpy value of 1.9 J/g. Hence, occurrence of Sm-R is confirmed as enantiotropic.



Plate 8. Colored chequred board texture of Sm F in ImBA:110BA at 78.4 °C.



Fig. 4. DSC thermogram of I<sub>m</sub>BA:110BAcomplex in exothermic run.



Fig. 5. Clear visualization of DSC exothermic thermogram of I<sub>m</sub>BA:110BA complex.

#### 4.4. Phase diagram for I<sub>m</sub>BA:nOBA series of HBLCs

Phase diagram constructed with the results of transition temperatures and thermal stability (Table 1) exhibited by the



Fig. 6. Phase diagram of I<sub>m</sub>BA:nOBA series. Nematic, Smectic X, Smectic C, Smectic F, Smectic D and Smectic R phases are abbreviated as N, X, C, F, D and R respectively.

 $I_mBA:nOBAs$  is presented in Fig. 6. The salient features of the phase diagram for the  $I_mBA:nOBAs$  reflects up on

- (a) The HBLCs viz., I<sub>m</sub>BA:nOBAs exhibit nematic phase with orientational order, Sm D LC phase with homeotropic orthogonal alignment, titled smectic phases with layering order, smectic-R, smectic-X and smectic F respectively. Nematic phase prevails in all complexes which exhibited LC nature with varying thermal spans.
- (b) LC phases are quenched in even numbered intermediate homologs (n=8 and10).Quenching is attributed to the effective transverse dipole moment  $\mu_t$  inherently possessed by the molecule as I-atom is substituted at meta position of the 3-iodobenzoic acid.
- (c) Two new phases, viz., Sm R and Sm X exhibiting hither to un-reported textures along with a rarely reported Sm D phase are exhibited by I<sub>m</sub>BA:nOBAs, which is assumed due to the strategic position occupied to the electro-negative I-atom with respect to the rigid core part of the LC complex.
- (d) A quasi-2D ordered tilted hexagonally ordered Sm F phase is found to follow and occur by cooling the tilted 1-D tilted Sm C phase in the I<sub>m</sub>BA:nOBAs prevalently in odd-numbered higher homologs.
- (e) Odd-even effect is found to occur at the crystal melting points (where crystal or solid phase changes in to LC phase with heating) as a consequence of alternating contributions of axial polarizabilities.

# 4.5. Order parameter in tilted LC phases

#### 4.5.1. Smectic-C phase

Temperature variation of tilt angle  $\theta(T)$  reflecting the growth of order parameter (Fig. 7) in SmC phase is measured by optical extinction method [19] in I<sub>m</sub>BA: nOBAs ( for n=9, 11 and 12). The tilt angle is found to increase with decreasing temperature. It is observed that  $\theta(T)$  attains a characteristic maximum value. For higher homologs, viz., n=11 and 12, the  $\theta(T)_{max}$  is observed to be ~16, while for the intermediate member viz., n=9, it is found to be ~11°. The large magnitudes of the tilt angle in higher homologs are attributed to the enhanced orientational disorder introduced by the lengthy flexible part of the molecule. Hence, higher homologs with extended flexible part in HBLCs are argued to contribute positively to the inclined [31] soft covalent hydrogen



**Fig. 7.** Temperature variation of tilt angle in smectic C phase for  $I_mBA:nOBA$  complexes (where n=9, 11 and 12). Solid line denotes the theoretical fit, error bars are shown to experimental points with respect to values predicted by mean field theory.

bonding interaction for the realization of tilted phases of applicational interest.

The observed temperature variation of  $\theta(T)$  appears to follow a power law relationship given by

$$\theta(T)\alpha(T_{\mathsf{C}}-T)^{\beta},\tag{1}$$

where  $T_{C}$  represents the transition temperature,  $\beta$  is the critical exponent component value and *T* is the temperature at which  $\theta(T)$  is experimentally determined.

The data of  $\theta(T)$  for the members of  $I_mBA:nOBAs$  in Sm C phase is fitted (Fig. 7) to the Eq. 1 to study the growth of order parameter in Sm C phase. The estimated values of  $\beta$  for n=9, 11 and 12 are found to be  $0.45 \pm 0.05$ ;  $0.55 \pm 0.03$  and  $0.45 \pm 0.01$ , respectively. The solid line (drawn for the fit parameters) and the error bars superposed (Fig. 7) over the observations reflect up on the goodness of the fit and the consistency of the observations. The estimated values of  $\beta$  for the present members of  $I_mBA:nOBAs$ are found to be in the vicinity of Mean Field theory [32,33] prediction to infer the long-range interaction of transverse dipole moment for the stabilization of tilted smectic C phase.

# 4.5.2. Smectic R phase

Temperature variation of tilt angle in SmR phase exhibited by I<sub>m</sub>BA:110BA determined by optical extinction method is presented in Fig. 8. Tilt angle reflects [22,24] the order parameter of a tilted smectic phase. It is noticed that the order parameter increases with decreasing temperature and attains a maximum value. Growth of the order parameter with decreasing temperature in I<sub>m</sub>BA:110BA is analyzed by fitting the data ((Fig. 8) of  $\theta(T)$ to Eq. (1). The estimated values of  $\beta$  is found to be 0.45  $\pm$  0.01. The solid line (drawn for the fit parameters) and the error bars superposed (Fig. 8) over the observations reflect up on the goodness of the fit and the consistency of the measurements. The estimated value of  $\beta$  for I<sub>m</sub>BA:110BAs is found to agree with the Mean Field [32,33] predictions to infer growth of long range order parameter in tilted smectic R phase.

# 5. Conclusions

 A novel series of halogen substituted benzoic acid (lodo) with p-n alkyloxy benzoic acids are synthesized and characterized.



**Fig. 8.** Temperature variation of tilt angle in smectic R phase of  $I_m$ BA:110BA complex. Solid line denotes the theoretical fit, error bars are shown to experimental points with respect to values predicted by mean field theory.

- (2) <sup>1</sup>H NMR study confirms the environmental hydrogen atoms existing in the complexes.
- (3) Three new smectic orderings are noticed and characterized.
- (4) The tilt angle measurements in smectic C and smectic R phases are performed and the goodness of the fit is tested with error bars.

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