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Characterization of a new smectic ordering in supramolecular hydrogen bonded liquid crystals by X-ray, optical and dielectric studies

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ABSTRACT

A novel series of linear supramolecular hydrogen bonded liquid crystals (SMHBLC) has been investigated. Complimentary hydrogen bonds are formed between various alkyloxy benzoic acids. Formation of hydrogen bond is confirmed by FTIR spectroscopic studies. These homologs exhibit rich phase variance as evinced by various textures by polarizing optical microscopic (POM) studies. DSC studies revealed the transition temperatures and corresponding enthalpy values which are elucidated from the DSC thermograms. Phase diagram has been constructed through POM and DSC data. An interesting finding is the observation of a new smectic ordering labeled as smectic X. This phase has been characterized by various techniques which includes XRD. Optical tilt angle in smectic C and smectic X phases of various homologs has been measured and fitted to a power law. Dielectric relaxations have been carried out in nematic and smectic C phases of different mesogens and their activation energies are calculated. An interesting observation is the optical shuttering action of the mesogens in the nematic phase. In addition to the above phenomenon the light filtering action of these mesogens in the nematic phase has been studied.

1. Introduction

Synthesis and application of fascinating liquid crystals earned a tremendous growth in the past few decades. Several thousands of organic compounds are now known to exhibit mesogenic properties [1,2]. It is clear from the literature [3] that the strength of hydrogen bonding existing between neighboring molecules plays a decisive role in the self assembly of supramolecular aggregates. H-bond is an important agent for engineering directional elements in to supramolecular assemblies of noncovalently connected molecules [4]. Kato and his group prepared a variety of liquid crystals induced by this intermolecular hydrogen bonding between pyridyl moieties which are proton acceptors and carboxylic acid groups which are proton donors [5]. Many supramolecular hydrogen bonded liquid crystal (SMHBLC) systems like molecular liquid crystals [6–10], polymer liquid crystals [11–14], ferroelectric liquid crystals [15] and room temperature liquid crystals are reported [16]. Single bond [17–19], double bond [20–23] and multiple bond [24,25] supramolecular hydrogen bonded liquid crystals are synthesized and reported.

The central theme of the aimed research work involves the design, synthesis and characterization of eight homologous series of SMHBLC formed between p-n-alkyloxy benzoic acids (nBAO) and p-n-alkyloxy benzoic acids (mBAO) referred as nBAO + mBAO, where m varies from 5 to 12. These eight series can be referred as 5BAO + mBAO, 6BAO + mBAO, 7BAO + mBAO, 8BAO + mBAO, 9BAO + mBAO, 10BAO + mBAO, 11BAO + mBAO and 12BAO + mBAO which give rise to 56 different supramolecular hydrogen bonded complexes. In this paper, the systematic study of the mesogenic properties exhibited by seven complexes of 10BAO + mBAO homologous series is discussed. The mesogenic materials find its wide application not only in display devices but also as optical shutters, optical modulators and optical filters to the desired wavelength as reported by us in our earlier studies [26,27].

2. Material and methods

Optical textural observations were made with a Nikon polarizing microscope (POM) equipped with Nikon digital CCD camera system with 5 megapixels and 2560 × 1920 pixel resolutions. The liquid crystalline textures were analyzed and stored with the aid of NIS 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 ±0.1 °C. This unit was interfaced to a computer by IEEE-STC 200 to control and monitor the temperature. The liquid crystal sample was filled by capillary action in its isotropic state into a commercially available (Instec, USA) polyamide buffed cell with 4 μm spacer. Optical extinction technique [18] was used for determination of tilt angle. Transition temperatures and corresponding enthalpy values were obtained by DSC (Shimadzu DSC-60, Japan). FTIR spectra was recorded (ABB FTIR MB3000) and analyzed with the MB3000 software. XRD measurements were done with CuKα radiation (1.54 Å) (Rigaku Ultrax-18) fitted with a

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graphite fitted monochromator with a resolution of 0.02°. The p-n-decyloxy benzoic acid (10BAO) and p-n-alkyloxy benzoic acids (mBAO, where m = 5 to 12) were supplied by Sigma Aldrich, (Germany) and all the solvents were of high performance liquid chromatography (HPLC) grade.

2.1. Synthesis of SMHBLC

All the inter hydrogen bonded complexes examined in the present study are prepared by mixing 1:1 molar ratio decyloxy benzoic acid with various alkyloxy benzoic acids in DMF as described in the reported literature [28–30]. The synthesis route of nBAO + mBAO is represented as Scheme 1. The molecular structure of p-n-decyloxy benzoic acid (10BAO) with p-n-alkyloxy benzoic acids (mBAO, where m = 5 to 12) is depicted in Fig. 1, where m represents the alkyloxy carbon number.

3. Results and discussion

Seven 10BAO + mBAO hydrogen bonded complexes isolated under the present investigation are white crystalline solids and are stable at room temperature (30 °C). They melt at specific temperatures below ~88.8 °C (Table 1) and show high thermal and chemical stability when subjected to repeated thermal scans performed during polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) studies.

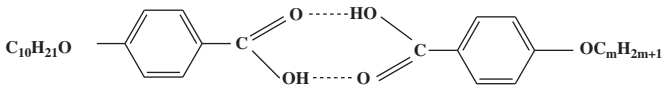


Fig. 1. Molecular structure of the 10BAO + mBAO homologous series.

3.1. Phase identification

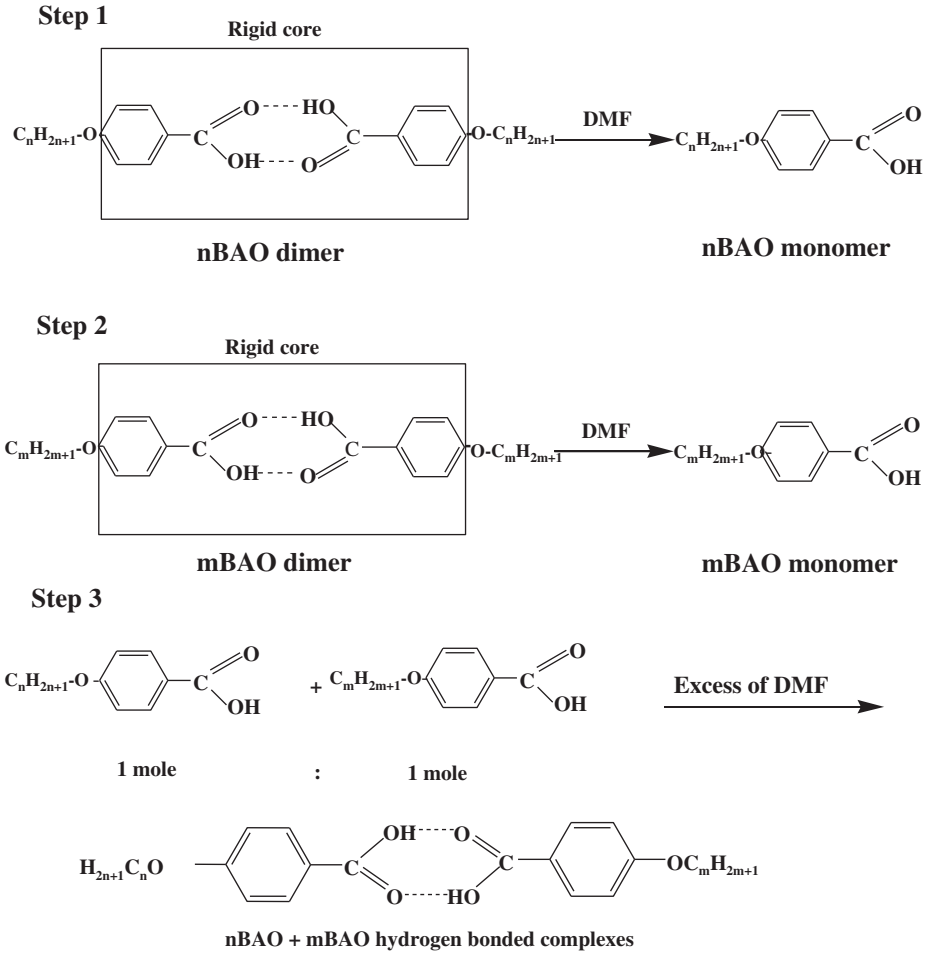
The observed phase variants, transition temperatures and corresponding enthalpy values obtained by DSC in the cooling and heating cycles for the 10BAO + mBAO complexes are presented in Table 1 along with POM cooling data.

3.2. Phases exhibited by 10BAO + mBAO homologous series

The mesogens of the p-n-decyloxy benzoic acid (10BAO) with p-n-alkyloxy benzoic acids (mBAO, where m = 5 to 12) designated as 10BAO + mBAO homologous series are found to exhibit characteristic textures [31], viz., nematic (N) (threaded texture, Plate 1), smectic X (worm like texture, Plate 2), smectic C (schlieren texture, Plate 3) and smectic F (chequered board texture, Plate 4) respectively. The general phase sequence of various homologs of 10BAO + mBAO series in cooling and heating runs can be shown as:

Isotropic⇌N→Sm C→Sm F⇌Crystal (10BAO + 5BAO)

Isotropic⇌N→Sm X⇌Sm C⇌Crystal (10BAO + 6BAO)



Scheme 1. Scheme representing the formation of 10BAO + mBAO hydrogen bonded series.