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Induced Crystal-G Phase through Intermolecular Hydrogen Bonding Part XIV: Influence of Alkyl Carbons of *p*-Hydroxybenzoates on Phase Distribution of Induced Phase

Two novel series of intermolecular hydrogen-bonded liquid crystal complexes resulting from equimolar combinations of *p*-*n*-alkoxybenzoic acids (*n*ABA) (where *n* represents alkoxy carbon numbers 3 to 10 and 12) and non-mesogens *viz.* ethyl-*p*-hydroxybenzoate (EHB) and propyl-*p*-hydroxybenzoate (PHB) have been synthesized. The formation and stabilization of the hydrogen bonding is confirmed by infrared spectral study, which reveals the terminal functionalities, -COOH and -OH moieties are complementary to each other by acting as both proton donor and acceptor. The results of comparative thermal and phase analyses of both the series are discussed in conjunction with free- *p*-*n*-alkoxybenzoic acids. The induction of crystal-G phase with wide thermal spans is observed in the present complexes.

Keywords: hydrogen bonding, nABA, EHB, PHB, crystal-G phase

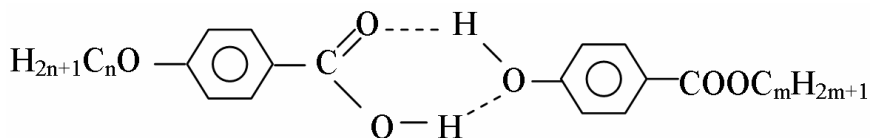
(Received February 18, 2002; Accepted April 9, 2002)

Introduction

Recent interest in the liquid crystal (LC) research involving supramolecular hydrogen-bonding and related applications in the area of electro-optic devices has led to the quest for new H-bonded liquid crystal materials (PALEOS et al. 2001). The low bond energies of these non-covalent interactions have a striking influence on physical properties such as melting points, enthalpies of vaporization and phase behaviour. Supramolecular liquid crystalline complexes resulting from these non-covalent interactions of either mesomorphic or non-mesomorphic components are reported (BENHARDT et al. 1998; KATO et al. 1995; WILSON et al. 1995; YU et al. 1991) and in fact, the induction of new phases in the systems involving a non-mesogen is attributed, without ambiguity, to the presence of intermolecular hydrogen bonding. As a part of our systematic investigations on supramolecular H-bonded liquid crystals (KUMAR et al. 1998; SWATHI et al. 2000; SWATHI et al. 2001a; 2001b; SRINIVASULU et al. 2000; SRINIVASULU et al. 2001; KUMAR et al. 2002) the present communication deals with synthesis and phase behaviour of two novel series of liquid crystalline complexes involving mesogenic *p*-*n*-alkoxybenzoic acids ($n = 3$ to 10 and 12) and non-mesogenic ethyl-*p*-hydroxybenzoate (EHB) and propyl-*p*-hydroxybenzoate (PHB) namely, ethyl-*p*-hydroxybenzoate: *p*-*n*-alkoxybenzoic acids (EHB:*n*ABA) and propyl-*p*-hydroxybenzoate: *p*-*n*-

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alkoxybenzoic acids (*PHB:nABA*) (Figure 1). The results are discussed in conjunction with the phase behaviour of *p-n-alkoxybenzoic acids*.



$$n = 3 \text{ to } 10 \text{ and } 12; m = 2 \text{ and } 3$$

Fig. 1: Molecular structure of *EHB:nABA* and *PHB:nABA* series

Experimental

p-n-Alkoxybenzoic acids (*nABA*) of 99.9% purity are supplied by Frinton Laboratories, New Jersey, USA while *alkyl-p-hydroxybenzoates*, *EHB* and *PHB* are purchased from BDH, Bombay, India. All the solvents used in the present study are of E. Merck grade.

The IR spectra in solid and solution states are recorded on a Perkin-Elmer (BX series) FT-IR spectrometer. The phase variants and their transition temperatures of free *p-n-alkoxybenzoic acids* and the corresponding series of hydrogen-bonded complexes are determined from the characteristic textural observations under polarized microscope (Olympus BX 50) equipped with optical display (DP-10) at a scan rate of 0.1°C per minute using Instec mk1 temperature controller. The temperatures of the corresponding phase transitions and their heat of transitions (in joules per gram) are further measured by scanning the compounds for DSC thermograms (Perkin-Elmer DSC-7) at a scan rate of 5 °C per minute.

Synthesis of Intermolecular Hydrogen-bonded Complexes

The intermolecular H-bonded complexes are synthesized by mixing together appropriate *p-n-alkoxybenzoic acids* (20.0 mmol) and *alkyl-p-hydroxybenzoates* (20.0 mmol) in ~ 20 mL of absolute pyridine under constant stirring at 80 °C for ~2h. White crystalline crude complexes, obtained by removing excess pyridine by distillation under reduced pressure, are then recrystallized from hot dichloromethane solution and dried over calcium chloride in a desiccator at room temperature. The yields obtained are ~92%.

Results and Discussion

All the compounds isolated under 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, dichloromethane etc. However, they show a high degree of solubility in the coordinating solvents like dimethyl sulfoxide (DMSO), dimethylformamide (DMF), pyridine etc. All these complexes melt at specific

temperatures below 135 °C. They show high degree of thermal and chemical stability when subjected to repeated thermal scans performed during thermal microscopy (TM) and Differential Scanning Calorimeter (DSC) studies.

Infrared Spectra

The room temperature IR spectra of *nABA* and their corresponding H-bonded complexes are recorded both in solid (KBr) and solution (chloroform) states. The infrared frequencies of the pertinent bands are summarized in Table 1. The KBr spectra of free *p-n-alkoxybenzoic acids* show two sharp bands at 1685 and 1695 cm^{-1} due to $\nu(\text{C}=\text{O})$ mode and a strong intense band at 3012 cm^{-1} assigned to $\nu(\text{OH})$ mode of carboxylic acid group (NAKAMAOTO, 1978). This doubling nature of $\nu(\text{C}=\text{O})$ mode may be attributed to the dimeric nature of the acid group at room temperature (KUMAR et al. 1998). The corresponding spectra recorded in chloroform show a strong intense band suggesting the existence of monomeric form of benzoic acid in the solution state. To avoid further complications due to such intermolecular interactions, comparison of spectra of complexes is made with the solution state spectra of free *nABA*.

The IR spectrum of *ethyl-p-hydroxybenzoate* shows characteristic bands for $\nu(\text{C}-\text{O})_{\text{phenolic}}$ (1280 cm^{-1}), $\nu(\text{OH})$ (3311 cm^{-1}) and $\nu(\text{C}=\text{O})_{\text{ester}}$ (1681 cm^{-1}) while *propyl-p-hydroxybenzoate* exhibits the corresponding bands at 1281, 3273 and 1675 cm^{-1} (NAKAMAOTO, 1978).

The solid state IR spectra of *EHB:nABA* and *PHB:nABA* exhibit a sharp band at $\sim 1691 \text{ cm}^{-1}$ with disappearance of doubling nature due to $\nu(\text{C}=\text{O})$ mode of benzoic acid moiety. This clearly implies the dissociation of dimeric nature of *p-n-alkoxybenzoic acids* upon complexation. Further, these complexes show bathochromic shifts in the $\nu(\text{C}=\text{O})$ mode of *nABA* ($\sim 20 \text{ cm}^{-1}$) and hypsochromic shift ($\sim 50 \text{ cm}^{-1}$) in the $\nu(\text{OH})$ mode of non-mesogen in the present 1:1 complexes. This suggest the formation of hydrogen bond between $-\text{COOH}$ group of *nABA* and the $-\text{OH}$ group of *EHB/PHB* moiety thereby both groups can form a complementary H-bonding so as to accept as well as donate protons from one another (KUMAR et al. 1998; SWATHI et al. 2000). The existence of hydrogen bonding in the present series is further inferred from the bathochromic shift in the $\nu(\text{C}-\text{O})_{\text{phenolic}}$ mode of non-mesogen ($\sim 25 \text{ cm}^{-1}$). The degree of stabilization of intermolecular hydrogen bonding is studied by recording the spectra of complexes in chloroform solution. The spectra show the re-appearance of the stretching modes of acidic $>\text{C}=\text{O}$ group and $-\text{OH}$ group of the ester suggesting the destruction of intermolecular H-bonding in solution state.

Thermal and Phase Behaviour

The phase identification and the corresponding transition temperatures of both the series under present study are determined from the characteristic textural observation (GRAY et al. 1984) using a polarizing thermal microscope. The optical microscopic observations reveal: *p-n-alkoxybenzoic acids* exhibit nematic (marble) as a unique mesophase in the lower homologues ($n = 3$ to 6) and smectic-C (schilieren) in higher members of the series. It is noticed that the thermal distribution of smectic-C phase increases with the increase of alkoxy carbon number.

Table 1: IR spectral frequencies (cm^{-1}) of pertinent bands.

Compound	$\nu(\text{C}=\text{O})$		$\nu(\text{C}-\text{O})_{\text{phenolic}}$	$\nu(\text{OH})_{\text{ester}}$
	Acid moiety	Ester moiety		
<i>p</i> -Octyloxy benzoic acid (CH_3Cl)	1712	--	--	
Ethyl <i>p</i> -hydroxy benzoate (<i>EHB</i>)	--	1681	1280	3311
<i>EHB:nABA</i> ($n=8$)	1691	1685	1256	3352
Propyl <i>p</i> -hydroxy benzoate (<i>PHB</i>)	--	1675	1281	3273
<i>PHB:nABA</i> ($n=3$)	1689	1672	1254	3341

On cooling from the isotropic melt, *EHB:nABA* complexes (except in $n = 4$ and 5) display nematic droplets followed by a threaded marble texture of nematic phase. On further cooling, a broken focal conic texture characteristic of smectic-C phase is observed in the higher homologues of the series (complexes VI to IX). Further cooling leads to the induction of a higher ordered tilted crystal-G phase in the form of mosaic texture in all the complexes.

On the other hand, the *PHB:nABA* series exhibit the presence of nematic (threaded marble), smectic-C (broken focal conic fans) and induced crystal-G (multi-coloured mosaic) phases. However, in the complex, a new phase variant, isotropic to crystal-G is observed. Non-occurrence of the smectic-C phase observed in the lower homologues, $n = 3$ to 6.

The phase transition temperatures observed through thermal microscopy are found to be in reasonable agreement with the corresponding DSC data.

Phase Diagrams

The phase diagrams are constructed using the observed transition temperatures from thermal microscopy in the cooling cycle. Figures 2, 3 and 4 represent such phase illustrations for free *p-n-alkoxybenzoic acids*, *EHB:nABA* and *PHB:nABA* series, respectively.

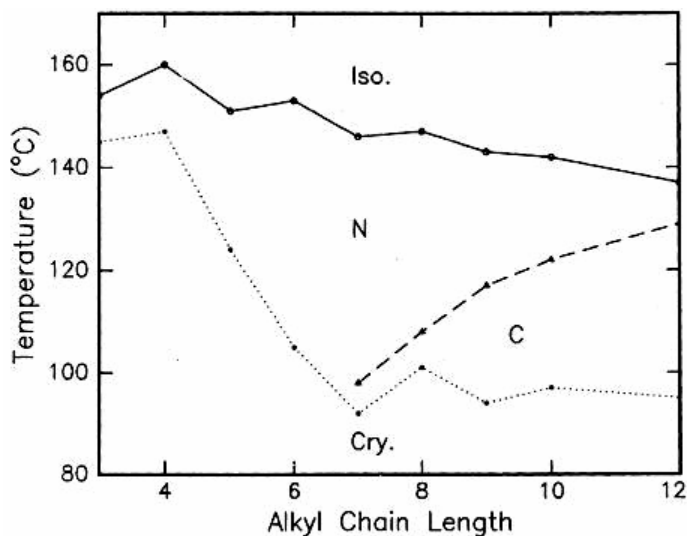


Fig. 2: Phase diagram of *p-n*-alkoxy benzoic acids (*nABA*) series

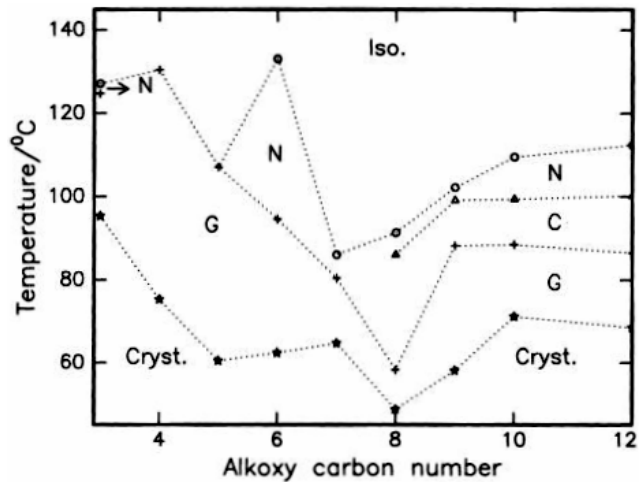


Fig. 3: Phase diagram of *EHB:nABA* series

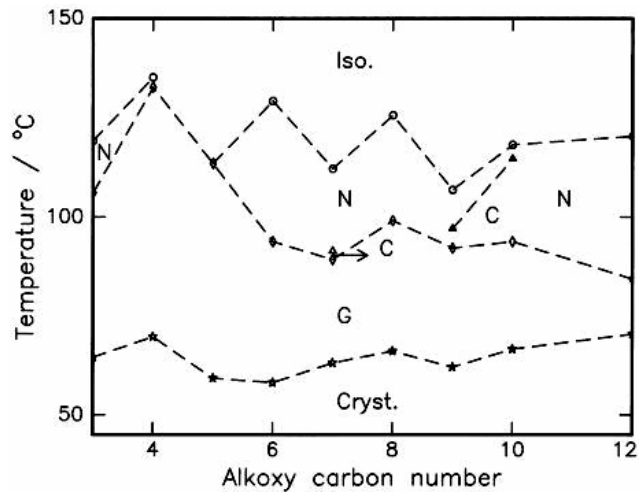


Fig. 4: Phase diagram of *PHB:nABA* series

When compared with the phase behaviour of free-*nABA* series (Figure 2) it is clearly evident that *EHB:nABA* series display a decreasing trend in the thermal spans of nematic phase in the middle members. On the other hand, the higher homologues exhibit well-stabilized smectic-C phase with wide thermal spans. The thermal distribution of induced crystal-G across the series follows an interesting trend: wide thermal ranges are observed for the lower homologues ($n = 3$ to 6) followed by narrow thermal spans in middle members ($n = 7$ and 8) and a gradual stabilization in the higher homologue members ($n = 9, 10$ and 12). It is further noticed that the complex-IV ($n = 6$) displays a wide thermal range of liquid crystallinity (~ 70 °C), which is almost equally contributed by nematic (~ 38 °C) and crystal-G (~ 32 °C) phases. In the higher members of the series ($n = 10$ and 12) an equal distribution of nematic and tilted phases is observed. As expected, the thermal range of liquid crystallinity is increased in the individual members of the present series with relatively low clearing temperatures when compared to free-*ABA* series.

On the other hand, the *PHB:nABA* series (Figure 4) show altogether a different trend of phase behaviour. The thermal spans of nematic phase is being unaffected among middle members of the series ($n = 6$ to 8). However, the thermal distribution of nematic and smectic-C phases follow a discontinuous trend with increase in alkoxy carbon number. For instant, the thermal distribution of smectic-C phase across the series follows an interesting trend: a narrow range (~ 2 °C) for complex-V ($n = 7$) and its non-occurrence in complexes VI and IX ($n = 8$ and 12) and a sudden appearance in the complexes VII and VIII ($n = 9$ and 10). Further, it can be clearly emphasized from the phase diagram that the induced crystal-G phase is the dominant phase in the series with wide thermal spans. The present series exhibit an odd-even effect with respect to thermal range of nematic phase. Nevertheless, the clearing temperatures among the individual members of the series are found to be low when compared with the free *nABA* series. As expected, the thermal range of liquid crystallinity is increased in the members of the present series when compared to free-*nABA* series. As in the case of *EHB:nABA* series, complex-IV shows a wide thermal range of liquid crystallinity (~ 70 °C).

Conclusion

Thermal and phase behaviour studies on newly synthesized hydrogen-bonded complexes viz. *EHB:nABA* and *PHB:nABA* reveal the inducement of a well-stabilized crystal-G phase in all the complexes with wide thermal spans. Thermal studies also confirm the existence of new phase transitions, viz., *isotropic to crystal-G*, *nematic to crystal-G* and *smectic-C to crystal-G* in the series when compared to the phase behaviour of free *p-n-alkoxybenzoic acids*. Induction of a three-dimensional crystal-G phase and occurrence of new phase variants in the present series can best be accounted on the basis of significant molecular contributions originated from the presence of additional transverse dipole ($>C=O$ group) of *benzoate* moiety, which in turn enhances the polarity across the molecular length. The detailed IR structural study confirms the existence of intermolecular hydrogen bonding between terminal *-COOH* and *-OH* groups of *p-n-alkoxybenzoic acids* and *alkyl p-hydroxybenzoates*, respectively which are complementary to each other by acting as both proton donor and acceptor.

Acknowledgements

This work is supported by Council for Scientific and Industrial Research (Grant No.13(7544-A)/Pool), Department of Science and Technology (Grant No: SP/S2/M-45/94) and University Grants Commission (under Faculty Improvement Program) for financial assistance. Authors are grateful to Prof. K.G.Subhadra of Kakatiya University, Warangal, for recording IR spectra.

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