

Induced smectic-G Phase through Intermolecular Hydrogen Bonding, Part XV: Thermal and Phase Behaviour of *p*-hydroxybenzylidene-*p*-*n*-alkylanilines: *p*-*n*-alkoxybenzoic Acids

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Two novel series of liquid crystalline compounds involving intermolecular hydrogen bonding between mesogenic *p*-alkoxybenzoic acids (*nABA*) (where *n* denotes the alkoxy carbon number varying from propyl- to decyl- and dodecyl-) and *p*-hydroxybenzylidene-*p*-*n*-alkylanilines (HB*m*A) (where *m* represents the alkyl carbon numbers 4 and 9) were synthesized. The thermal and phase behaviour of these materials has been studied by thermal microscopy (TM) and differential scanning calorimetry (DSC). A detailed IR spectral investigation in solid and solution states confirms the formation of H-bonding between –OH and –COOH groups of HB*m*A and *nABA*, respectively. Comparative thermal analyses of both free *p*-*n* alkoxybenzoic acids and H-bonded complexes and their analogues series imply the induction of smectic-G phase in all the complexes.

Key words: Smectic-G; H-bonding; HB*m*A; *nABA*

Introduction

The synthesis of supramolecular liquid crystals involving hydrogen-bonding, which leads to complementary molecules, has widely been carried out in recent years owing to their applicability in electro-optic devices [1]. In addition to the complementarity of the components involved in the interaction, the directionality of the hydrogen bonds also plays a crucial role in exhibiting the liquid crystalline behaviour [1]. Apart from the striking influence on the physical properties such as melting points and enthalpies of vaporization, these non-covalent interactions have a pronounced impact on the induction and stabilization of new mesophases. In view of this, a considerable interest has been focused on the preparation and characterization of a wide variety of diversified supramolecular liquid crystal resulting from single hydrogen-bonding interaction of complementary components (viz. pyridyl and carboxyl moieties) [2–4],

multiple hydrogen bonding interactions (viz. dimerization of carboxylic acids) [5, 6], complexation between multi-functional components [7–9], polymer networks derived from bifunctional hydrogen-bonding [10–12], etc. In continuation of our systematic work on H-bonded liquid crystal materials involving different types of electron donors [13–19], the present communication deals with the synthesis and characterization of two novel series of liquid crystal complexes involving intermolecular hydrogen bonding between *p*-*n*-alkoxybenzoic acids (*nABA*) (where *n* denotes the alkoxy carbon number varying from propyl- to decyl- and dodecyl-) and non-mesogenic *p*-hydroxybenzylidene-*p*-*n*-alkylanilines (HB*m*A) (where *m* denotes the alkyl carbon numbers 4 and 9). The influence of the terminal functionalities on the thermal and phase behaviour is discussed in conjunction with the previously reported analogues [13, 14, 19]. The molecular structure of the complexes under study is given in Figure 1.

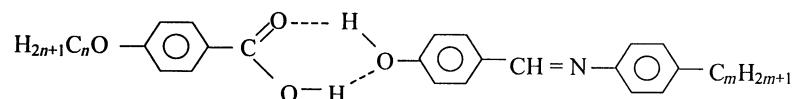


Fig. 1. Molecular structure of HB*m*A: *nABA* series.

Experimental

p-*n*-alkoxybenzoic acids (*n*ABA) of 99.9% purity were supplied by Frinton Laboratories, New Jersey, USA, while *p*-hydroxybenzaldehyde and *p*-*n*-alkylanilines were purchased from Sigma Aldrich Company, USA. The solvents used in the present study are of E. Merck grade and were used as such without further purification.

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

Synthesis

p-hydroxybenzylidene-*p*-*n*-alkylanilines (HBmA)

The *p*-hydroxybenzylidene-*p*-*n*-alkylanilines (HB4A and HB9A) were prepared by mixing equimolar absolute ethanol solutions containing *p*-hydroxybenzaldehyde (20.0 mmol) and the appropriate *p*-*n*-alkylanilines (20.0 mmol) in the presence of 1 or 2 drops of glacial acetic acid. The reaction mixture was then kept under reflux for ~ 2 h at 80 °C. The white crystalline product obtained on cooling the reaction mixture to room temperature was suction filtered and washed repeatedly with cold methanol solution and dried over CaCl₂. The crude product was then recrystallized from hot methanol solution to get a yield of ~ 89%.

Intermolecular H-bonding Complexes

HBmA:*n*ABA complexes were synthesized by refluxing together appropriate *p*-alkoxybenzoic acids (6.0 mmol) and *p*-*n*-alkylanilines (6.0 mmol) in 20.0 ml of absolute pyridine under constant stirring at 80 °C for ~ 2 h. The volume of the resulting homogeneous mixture was then reduced to almost dryness by removing the excess pyridine under a controlled vacuum distillation. The white crystalline products were dried and re-

crystallized from a hot dichloromethane solution. The yields obtained were ~ 94%.

Results and Discussion

The white crystalline HBmA:*n*ABA complexes were found to be stable at room temperature. They are insoluble in water and sparingly soluble in common organic solvents such as methanol, ethanol, benzene, dichloromethane, etc. Further, they showed a high degree of solubility in coordinating solvents like dimethylsulfoxide (DMSO), dimethylformamide (DMF), pyridine, etc. The complexes, when subjected to repeated thermal scans, showed a high degree of thermal and chemical stability.

Infrared Spectra

The room temperature IR spectra of *n*ABA and its H-bonded complexes were 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 three *p*-*n*-alkoxybenzoic acids show two sharp bands at 1685 and 1695 cm⁻¹ due to the $\nu(\text{C=O})$ mode and a strong intense band at 3012 cm⁻¹ assigned to the $\nu(\text{OH})$ mode of the carboxylic acid group [20]. This doubling nature of the $\nu(\text{C=O})$ mode may be attributed to the dimeric nature of the acid group at room temperature [20]. The corresponding spectra in the solution state (chloroform) show a strong intense band at 1712 cm⁻¹, suggesting the existence of the monomeric form of benzoic acid in the solution state. To avoid further complications due to such intermolecular interactions, comparison of the spectra of complexes was made with the solution state spectra of free *n*ABA.

Table 1. IR spectral frequencies (cm⁻¹) of pertinent bands.

Compound	<i>n</i> ABA moiety		HBmA moiety		
	$\nu(\text{C=O})$	$\nu(\text{OH})$	$\nu(\text{C-O})_{\text{phenolic}}$	$\nu(\text{OH})$	$\nu(>\text{C=N-})$
<i>p</i> -Octyloxy benzoic acid (CHCl ₃)	1712	3012	—	—	—
HB4A	—	—	1284	3476	1601
HB4A: <i>n</i> ABA (n = 8)	1690	2926	1254	3428	1607
HB9A	—	—	1281	3472	1599
HB9A: <i>n</i> ABA (n = 8)	1687	2928	1255	3426	1607

The IR spectrum of HB4A shows characteristic bands for $\nu(\text{C}-\text{O})_{\text{phenolic}}$ (1284 cm^{-1}), $\nu(\text{OH})$ (3476 cm^{-1}) and $\nu(>\text{C}=\text{N}-)$ (1601 cm^{-1}) groups, while HB9A exhibits the corresponding bands at 1281, 3472 and 1599 cm^{-1} , respectively [20].

The solid state IR spectra of HB4A:*n*ABA and HB9A:*n*ABA exhibit a sharp band at $\sim 1690 \text{ cm}^{-1}$ with disappearance of the doubling nature due to the $\nu(\text{C}=\text{O})$ mode of the benzoic acid moiety. This clearly suggests dissociation of the dimeric *p*-*n*-alkoxybenzoic acids upon complexation. Further, these complexes show bathochromic shifts in the $\nu(\text{C}=\text{O})$ ($\sim 20 \text{ cm}^{-1}$) and $\nu(\text{OH})$ ($\sim 80 \text{ cm}^{-1}$) modes of free-*n*ABA and the $\nu(\text{OH})$ mode ($\sim 50 \text{ cm}^{-1}$) of non-mesogen in the present 1:1 complexes. This suggests the formation of hydrogen bonds between $-\text{COOH}$ group of *n*ABA and the $-\text{OH}$ group of the HB*m*A moiety, thereby indicating that both groups can form complementary H-bonding so as to accept as well as donate protons from one another [20]. The existence of hydrogen bonding in the present series is further invoked by the bathochromic shift in the $\nu(\text{C}-\text{O})_{\text{phenolic}}$ mode of the non-mesogen ($\sim 30 \text{ cm}^{-1}$). The non-involvement of the imino group in the formation of hydrogen bonding is confirmed by the unaltered frequencies of the $\nu(>\text{C}=\text{N}-)$ mode [20].

The degree of stabilization of intermolecular hydrogen bonding was studied by recording the spectra of complexes in chloroform solution. The spectra show the reappearance of the stretching modes of the acidic $>\text{C}=\text{O}$ group and the $-\text{OH}$ group of the HB*m*A moiety, suggesting destruction of intermolecular H-bonding in the solution state.

Thermal and Phase Behaviour

Phase Variants

The phase identification [21] was done from characteristic textural observations using a polarizing thermal microscope. The thermal and phase behaviour of HB4A:*n*ABA and HB9A:*n*ABA were compared with that of free *p*-*n*-alkoxy benzoic acids. The microscopic textural observations on free *p*-*n*-alkoxybenzoic acids revealed the existence of a nematic marble texture as the dominant mesophase across the series, and a smectic-C phase with its characteristic schlieren texture was observed in the higher homologues ($n = 7$ to 12). It was observed from the phase diagram of the free *p*-*n*-alkoxy benzoic acids (Fig. 2) that the thermal distribution of the

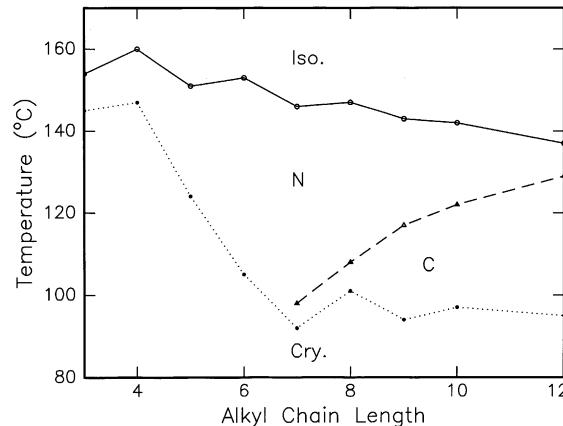


Fig. 2. Phase diagram of *p*-*n*-alkoxy benzoic acids (*n*ABA).

Table 2. Transition temperatures by TM and DSC of HB4A:*n*ABA complexes.

HB4A: <i>n</i> ABA (<i>n</i>)	Phase variant	Phase transition temperatures/°C by TM and [DSC ($\Delta H/\text{J/gm}$)]		
		Iso-N/G	N-G	G-Cryst.
I (3)	G	123.5 [121.3 (25.4)]	—	100.3 [100.2 (18.3)]
II (4)	G	135.2 [132.6 (92.0)]	—	75.3 [68.18 (27.92)]
III (5)	G	111.8 [107.7 (39.6)]	—	75.8 [*]
IV (6)	NG	109.2 [104.2 (2.1)]	94.3 [90.4 (24.5)]	92.1 [*]
V (7)	NG	105.3 [102.8 (1.2)]	102.4 [*]	85.3 [78.9 (18.8)]
VI (8)	NG	107.3 [103.8 (1.2)]	96.1 [92.1 (16.8)]	53.4 [48.2 (25.5)]
VII (9)	NG	103.8 [100.9 (5.6)]	88.8 [85.3 (16.1)]	65.4 [59.7 (21.3)]
VIII (10)	NG	110.4 [108.7 (5.1)]	93.3 [89.6 (16.2)]	78.1 [74.5 (12.1)]
IX (12)	NG	115.1 [110.5 (4.3)]	85.3 [80.3 (18.3)]	70.3 [65.6 (8.1)]

I-IX represent alkyl chain lengths of ABA: propyl-, butyl-, pentyl-, hexyl-, heptyl, octyl-, nonyl-, decyl-, and dodecyl-, respectively. * DSC peaks are not well resolved

smectic-C increases with increase of the alkoxy carbon number.

The microscopic observations on HB4A:*n*ABA reveal the induction of a highly ordered three-dimensional smectic-G phase across the series. On cooling from the isotropic melt, the lower homologues ($n = 3$ to 5) exhibit the smooth multi-coloured mosaic texture characteristic of the smectic-G phase, while the higher homologues ($n = 6$ to 12) display the marble texture characteristic of the nematic phase in addition to the newly in-

Table 3. Transition temperatures by TM and DSC of HB9A: *n*ABA complexes.

HB9A: <i>n</i> ABA (<i>n</i>)	Phase variant	Phase transition temperatures/°C by TM and [DSC ($\Delta H/J/gm$)]		
		Iso-N/G	N-G	G-Cryst.
I (3)	G	103.8 [107.8 (23.5)]	—	47.5 [*]
II (4)	G	123.6 [126.3 (27.6)]	—	44.8 [*]
III (5)	G	96.3 [94.2 (29.5)]	—	79.4 [*]
IV (6)	G	90.8 [88.9 (22.2)]	—	68.5 [*]
V (7)	G	83.3 [80.4 (45.3)]	—	32.4 [*]
VI (8)	G	91.6 [91.8 (16.2)]	—	43.1 40.2 (17.9)
VII (9)	G	87.7 [82.2 (7.4)]	—	62.4 [54.7 (23.8)]
VIII (10)	NG	100.7 [98.8 (2.5)]	89.2 [87.8 (11.7)]	70.9 [68.7 (12.8)]
IX (12)	NG	103.5 [102.3 (4.3)]	83.3 [80.9 (12.3)]	68.4 [67.4 (15.4)]

I-IX represent alkyl chain lengths of ABA: propyl-, butyl-, pentyl-, hexyl-, heptyl, octyl-, nonyl-, decyl-, and dodecyl-, respectively. * DSC peaks are not well resolved

duced smectic-G phase. On the other hand, in the cooling cycle the HB9A: *n*ABA series exhibits nematic phase (threaded marble texture) for higher homologues (*n* = 10 and 12) and an induced smectic-G phase (multicoloured mosaic) for all the complexes across the series.

The phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC data. The phase variants and their corresponding temperatures are summarized in Tables 2 and 3.

Phase Diagrams

In order to study the thermal behaviour of the mesophases observed in the present complexes, phase diagrams were constructed for HB4A: *n*ABA and HB9A: *n*ABA, which are illustrated in Figs. 3 and 4, respectively.

A glance at Fig. 3 reveals the HB4A: *n*ABA exhibits low clearing temperatures when compared to free *n*ABA series (Fig. 2). A gradual increase in thermal span of nematic phase is observed as the alkoxy chain length of the benzoic acid moiety increases from *n* = 8 to 12. The thermal range of smectic-G phase follows an irreg-

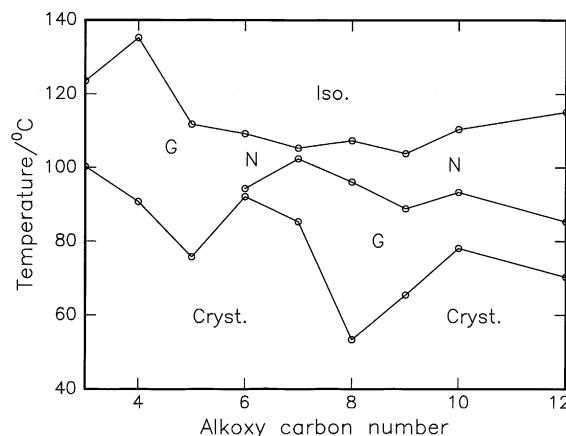


Fig. 3. Phase diagram of HB4A: *n*ABA.

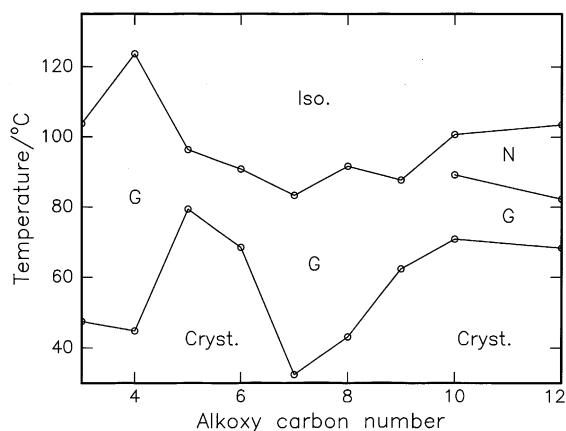


Fig. 4. Phase diagram of HB9A: *n*ABA.

ular trend in the lower homologues and is stabilized in the higher members of the series. When compared to free acids (Fig. 2), the present series exhibit a decreasing trend in thermal spans of the nematic phase. A wide thermal span of ~ 45 °C is observed for the induced smectic-G phase of the complexes III and VI (*n* = 4 and 8). It is further noticed that the smectic-C phase, which is the dominant phase in the higher members of the free *n*ABA series, completely disappears in the HB4A: *n*ABA series.

On the other hand, the HB9A: *n*ABA series (Fig. 4) shows an altogether different trend in the phase behaviour. The most striking feature of the phase behaviour is seen from the thermal distribution of nematic phase, where the existence of this phase is realized in the higher members of the series (*n* = 10 and 12). A well-

stabilized induced smectic-G phase with wide thermal spans is observed for all the complexes. The thermal distribution of induced phase follows an irregular trend in the lower homologues and is gradually stabilized in the higher members. Comparison of the HB9A:*n*ABA series (Fig. 4) with free acids (Fig. 2), reveals that the nematic phase, which is the most dominant phase in free *n*ABA, has lost its prominence among the complexes, and its existence is confined to the higher members. As in the HB4A:*n*ABA series, the complex II (*n* = 4) shows a maximum thermal range of induced phase. Non-existence of the smectic-C phase is observed in the present series when compared to free *n*ABA. Further, the present series display low clearing temperatures for all the members when compared to free *n*ABA series.

The influence of the alkyl carbon number of the aniline moiety on the thermal and phase behaviour of both series under the present investigation was studied in the light of phase distribution among the individual members of the series (Figs. 3 and 4). A detailed comparative study suggests that, as the alkyl chain length increases from -butyl to -nonyl, the individual members of the series show a decrease in the clearing temperature. The striking influence of the alkyl chain length of the aniline moiety can be seen in the distribution of nematic phase in both series. Moreover, the HB9A:*n*ABA series shows wide thermal spans of the newly induced smectic-G phase when compared to HB4A:*n*ABA. This clearly implies the impact of the alkyl carbon number of the aniline moiety on the thermal and phase behaviour.

Influence of the imino Group on Thermal and Phase Behaviour

In order to understand the effective role of the imino group on the degree of stabilization of the phases, a comparative analysis was made with the phase behaviour of reported analogous series of H-bonded complexes [13, 14, 19] having -OH and -COOH groups as proton donors and acceptors. The impact of the imino group is clearly seen from the low clearing temperatures observed in the series under present study when compared to the reported analogues. Further, the striking influence of the moiety can further be realized by the non-occurrence of smectic-C phase of the present complexes, which is one of the dominant phases in the higher homologues of the reported series [13, 14, 19]. Moreover, the thermal span of the induced smectic-G phase is found to be low when compared to that of the

reported analogues. It is well known that the origin of new phases and their thermal distribution depends to a great extent on the proton donor and acceptor capabilities of the terminal functional groups. The presence of strong polar rigid groups (-C=N-) certainly plays a crucial role in ascertaining the overall mesomorphic behaviour. Nevertheless, the stabilization of the induced phases among the individual members of the series clearly implies the effective role of hydrogen bonding.

Conclusion

Two novel series of hydrogen-bonded complexes were isolated, using *p*-*n*-alkoxybenzoic acids as common mesogenic systems. The detailed IR spectral study reveals the presence of intermolecular hydrogen bonding in the form of a complementary six member ring formed between the terminal -COOH and -OH groups of *p*-*n*-alkoxybenzoic acids and the *p*-hydroxybenzylidene-*p*-*n*-alkyl aniline moieties, respectively. Thermal and phase studies suggest the occurrence of new phase variants, viz. G and NG. Comparative thermal analyses with the phase behaviour of free acids and the reported analogues suggest the induction of a well-stabilized, highly ordered, three-dimensional, tilted smectic-G phase in both series with wide thermal spans. The occurrence of this induced phase can best be accounted for on the basis of significant molecular contributions originated from the electron rich imino group (-CH=N) as a central rigid core, which in turn enhances the polarity across the molecular length. Apart from the significant contributions from intermolecular hydrogen bonding, various combinational steric factors, associated with varied denticities of phenyl rings in the vicinity of stable six member-rings formed through intermolecular hydrogen bonding, have a profound impact on the thermal and phase behaviour.

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