

Induced Smectic-G Phase through Intermolecular Hydrogen Bonding Part IX: Comparative Thermal and Phase Behaviour Studies on Two Distinct Structural Isomers Possessing Linear and Bow Shapes

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Two novel intermolecular hydrogen bonding mesogenic series comprising two distinct structural isomers $n\text{ABA}:\text{R}:n\text{ABA}$ and $n\text{ABA}:\text{H}:n\text{ABA}$ (where R = resorcinol; H = hydroquinone; $n\text{ABA}$ = p - n -alkoxybenzoic acid with the alkyl carbon number varying from propyl- to decyl- and dodecyl-) have been synthesized using resorcinol and hydroquinone as central bent and linear cores, respectively. The thermal and phase behaviour of these complexes is studied by thermal microscopy and differential scanning calorimetry. The IR spectral data confirm the formation of intermolecular hydrogen bonding between the OH group of the non-mesogen and $-\text{COOH}$ group of the $n\text{ABA}$ moiety. Thermal studies reveal the existence of new phases: smectic-A and smectic-G. Comparative phase transition studies suggest that these isomers exhibit a different trend of mesomorphism.

Key words: Hydrogen Bonding; Thermal; Phase Behaviour; $n\text{ABA}:\text{R}:n\text{ABA}$, $n\text{ABA}:\text{H}:n\text{ABA}$.

Introduction

Among the various types of interaction involving non-covalent bonds in liquid crystalline (LC) materials, hydrogen bonds excel by their strong and directional nature. Besides playing a crucial role in inducing new mesophases with enhanced thermal stability, they also serve as powerful tools in the recognition and self-organization of liquid crystal molecules. Due to their low energies, they show a pronounced impact on the phase behaviour, clearing points, enthalpies of vaporization and thermal properties. The idea of fabricating a mesogenic molecule via hydrogen bonds by Kato and Frechet [1], paved the way for the development of many H-bonded systems including supramolecular liquid crystals [2], polymer liquid crystals [3, 4] and ferroelectric liquid crystals [5, 6].

It is well known that the mesophase of a liquid crystalline molecule is induced by the molecular packing at the micro level. The impact of such molecular contributions on the phase behaviour and the associated macroscopic structure can be shown either by increasing the additional transverse dipoles along the long molecular axis, or by the incorporation of C_{2v} molecular symmetry. In fact, such a polar symmetry paves a unique way of forming a helix which influences many physical and thermal properties of the tilted mesophases

and causes wide thermal ranges of induced phases. Moreover, the helicoidal structure can be altered by variation of the temperature and/or applied field, which in turn affects the molecular alignment, giving rise to new phases.

In fact, no comparative studies have been made to correlate the thermal and physical properties of conventional liquid crystalline materials having linear structure with those of compounds possessing C_{2v} symmetry (bow shaped). A proper correlation between the thermal and physical properties is possible only when the molecule possesses a structural isomerism which constitutes two distinct molecular symmetries (linear and bow shaped). This structural anomaly also facilitates to elucidate the role of a central bent molecule possessing C_{2v} symmetry.

In the present investigation, the linear and bowed LC materials $n\text{ABA}:\text{R}:n\text{ABA}$ and $n\text{ABA}:\text{H}:n\text{ABA}$, were obtained by designing their molecular skeletons in such a way that two p - n -alkoxybenzoic acids are attached selectively to the OH groups of the central resorcinol and hydroquinone moieties at the 1,3- and 1,4- positions, respectively, through intermolecular hydrogen bonding. In the continuation of our earlier work on the design and synthesis of intermolecular hydrogen bonding complexes with different proton donor acceptor groups [7–11], the present communication deals with the thermal and

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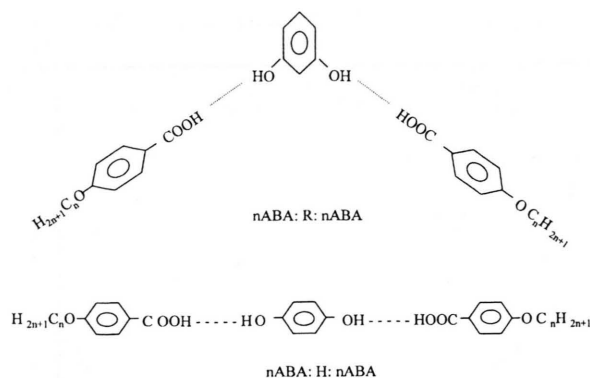


Fig. 1. Molecular structures of *n*ABA:R:*n*ABA and *n*ABA:H:*n*ABA.

phase behaviour of two novel liquid crystalline series involving hydrogen bonding between *p*-*n*-alkoxybenzoic acids (mesogen) and two non-mesogens (resorcinol and hydroquinone), see Figure 1.

Experimental

Materials and Methods

p-*n*-alkoxy benzoic acids (99% purity) were supplied by Frinton Laboratories, New Jersey, USA. Resorcinol and hydroquinone were purchased from Sd-fine chemicals India. The IR spectra (KBr and chloroform) were recorded on a Perkin-Elmer (BX series) FTIR spectrometer. The optical textural observations were carried out by a thermal microscope with an Olympus BX-50 supplemented by optical display (DP10). The DSC thermograms were recorded on a Perkin Elmer DSC-7.

The intermolecular hydrogen bonding complexes were synthesized by stirring together pyridine solutions containing an appropriate *p*-*n*-alkoxybenzoic acid (~5.5 g/20.0 mol) and a non-mesogen (resorcinol/hydroquinone) (1.1 g/10.0 mol) for ~6 h at room temperature. The white crystalline crude complexes, obtained by removing the pyridine by distillation under reduced pressure, were purified by recrystallization from hot dichloromethane solution and dried over calcium chloride in a desiccator at room temperature for ~12 h to get a yield of 1.2 g (88%).

The H-bonded complexes thus obtained are white crystalline solids in nature and are stable at room temperature. Further, they show a high degree of thermal

stability when subjected to repeated thermal scans during TM and DSC studies.

Results and Discussion

IR Spectra

The room temperature IR spectra (KBr pellets) of free *p*-*n*-alkoxy benzoic acids show two sharp bands associated with the stretching modes of the carbonyl group at 1685 and 1695 cm⁻¹, which are assigned to the dimeric nature of the acid group [12]. The chloroform spectra show disappearance of the corresponding bands and appearance of a single sharp band at ~1712 cm⁻¹, revealing the stabilization of the monomeric form of the acids in the solution state. The presence of a sharp band at 3012 cm⁻¹ is assigned to the stretching mode of the OH group. Resorcinol and hydroquinone exhibit pertinent bands at ~3650 and ~1200 cm⁻¹, due to $\nu(\text{OH})$ and $\nu(\text{C}-\text{OH})$ modes of vibration, respectively.

When compared to the solution state spectra of the free acids, the complexes exhibit bathochromic shifts in the stretching modes of the carbonyl group (~25 cm⁻¹), of the *p*-*n*-alkoxy benzoic acids and the C-OH (~50 cm⁻¹) group of the non-mesogenic moieties. This clearly suggests the formation of intermolecular hydrogenbonding between the COOH group of the *p*-*n*-alkoxy benzoic acids and the OH groups of resorcinol/hydroquinone.

Thermal and Phase Behaviour

The phases and their transition temperatures of the H-bonded complexes are determined [13] from characteristic textural observations under a polarizing microscope equipped with a temperature controller system at a scan rate of 0.1 °C/min. As reported earlier [7–9], the phases of the free *p*-*n*-alkoxybenzoic acids are nematic (marble) as the unique mesophase in the lower homologues (*n* = 3 to 6) and smectic-C (schlieren) in the higher members of the series.

On cooling from the isotropic melt, all the complexes of *n*ABA:R:*n*ABA series exhibit nematic droplets followed by a threaded marble texture of nematic phase. The higher members of the series (*n* = 7, 9 and 10) show the appearance of focal conic fans, characteristic of smectic-A phase as an induced orthogonal phase. On

Table 1. Transition temperatures (°C) from TM and DSC of *n*ABA:R:*n*ABA complexes. Enthalpy values are given in parentheses. (N = nematic, A = smectic A, G = smectic G).

Complex [#]	Phase variant	Phase transition temperatures/°C of TM and DSC (ΔH J/g)			
		Iso.-N/A/G	N-A/G	A-G	G-Cryst.
I	NG	139.2 [*]	137.8 [134.6 (76.33)]	–	101.8 [99.8 (40.79)]
II	NG	147.3 [*]	137.6 [135.3 (84.7)]	–	– [–]
III	NG	138.2 [*]	115.2 [112.1 (71.25)]	–	– [–]
IV	NG	128.8 [*]	96.3 [93.9 (57.26)]	–	86.3 [*]
V	NAG	130.3 [*]	92.7 [91.4 (5.04)]	89.5 [87.9 (41.79)]	84.3 [84.3 (60.10)]
VI	NG	128.4 [*]	96.2 [95.4 (33.4)]	–	64.8 [52.9 (43.9)]
VII	NAG	128.2 [*]	113.2 [106.7 (5.53)]	95.2 [90.11 (35.49)]	69.6 [65.4 (76.8)]
VIII	NAG	128.6 [*]	118.5 [113.3 (2.96)]	95.9 [92.33 (34.11)]	79.3 [73.9 (22.57)]
IX	NG	125.2 [117.5 (32.68)]	84.7 [84.2 (41.87)]	–	64.8 [62.9 (67.91)]

[#] I–IX represent alkyl chain lengths of ABA: propyl-, butyl, pentyl-, hexyl-, heptyl-, octyl-, nonyl-, decyl-, and dodecyl-, respectively.

* Transition peaks are not resolved.

further cooling, a smooth multicoloured mosaic texture of smectic-G phase is induced throughout the series.

On the other hand, the *n*ABA:H:*n*ABA series displays the presence of nematic (threaded marble), smectic-C (broken focal conic fans) and smectic-G (mosaic) phases. However, in the complex-I (*n* = 3) a new phase variant, Iso.-Smectic-G is observed. Non-occurrence of the smectic-C phase is noticed in the homologues *n* = 3 to 6.

The phase transition temperatures of both series observed through thermal microscopy are in reasonable agreement with the corresponding DSC thermograms (Tables 1 and 2).

The phase diagrams are constructed using the observed transition temperatures from thermal microscopy. Figures 2, 3, and 4 present the phase diagrams of free *p*-*n*-alkoxybenzoic acids, *n*ABA:R:*n*ABA and *n*ABA:H:*n*ABA series, respectively.

As in the case of free-*p*-*n*-alkoxybenzoic acids, the *n*ABA:R:*n*ABA series clearly shows (Fig. 3) wide thermal ranges of the nematic phase for the complexes III to VI (*n* = 5 to 8) and relatively narrow ranges in the case of the complexes I, II, VII, and VIII. However, a sudden increment of the nematic thermal range is seen in complex IX (*n* = 12). An increase of the thermal range of the

smectic-A phase is observed in the complexes V, VII, and VIII (*n* = 7, 9, and 10). The thermal distribution of smectic-A phase among these individual members of the series requires the spectral mention that this induced orthogonal phase originates in the complex-V (*n* = 7), as is the case with the smectic-C phase in free-*p*-*n*-alkoxybenzoic acids. Moreover, it is interesting to note that quenching of smectic-C phase is observed in the present series. The complex VII (*n* = 9) exhibits all the three phases (NAG) with maximum thermal ranges, while complexes II and III (*n* = 4 and 5) show smectic-G phase at ambient temperature.

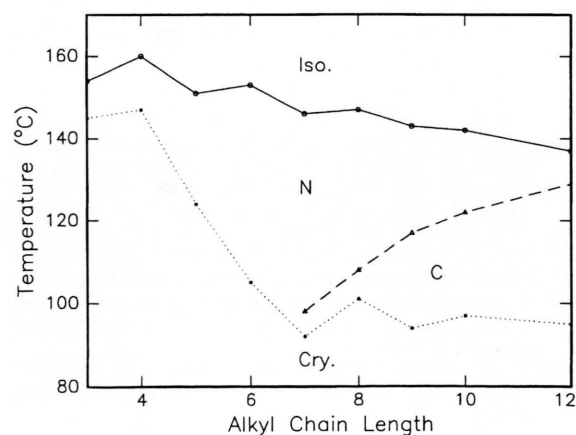
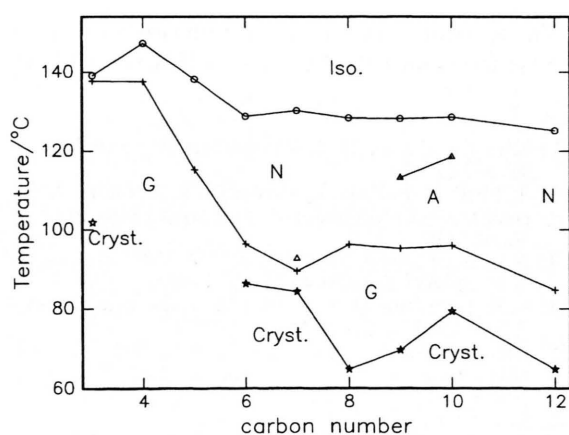
A glance at the phase behaviour of *n*ABA:H:*n*ABA (Fig. 4) reveals that the nematic range gradually increases from complex II to VI (*n* = 4 to 8) and then decreases in the higher homologues of the series. This also matches the phase profile of *n*ABA:R:*n*ABA (Fig. 3) except for complex-IX (*n* = 12). However, a gradual increment in the thermal ranges of the smectic-C phase is observed in both series. The phase diagram clearly shows that smectic-C and smectic-G are the more dominant phases in the higher members of the series, from complex VII to IX (*n* = 9, 10, and 12), and smectic-G in the lower members of the series. The interesting feature

Table 2. Transition temperatures ($^{\circ}\text{C}$) from TM and DSC of *n*ABA:H:*n*ABA complexes. Enthalpy values are given in parentheses. (N = nematic, C = smectic C, G = smectic G).

Complex [#]	Phase variant	Phase transition temperatures/ $^{\circ}\text{C}$ from TM and DSC (ΔH J/g)			
		Iso.-N/C/G	N-C/G	C-G	G-Cryst.
I	G	131.5 [129.3 (65.18)]	—	—	112.2 [110.4 (72.4)]
II	NG	143.4 [*]	142.9 [135.2 (62.19)]	—	—
III	NG	134.5 [*]	114.6 [112.3 (97.5)]	—	—
IV	NG	123.1 [125.2 (29.2)]	98.2 [93.8 (52.3)]	—	—
V	NCG	129.2 [124.4 (38.5)]	97.8 [94.1 (5.24)]	89.2 [87.4 (37.17)]	86.2 [83.6 (52.3)]
VI	NCG	138.2 [132.8 (1.19)]	98.9 [101.0 (4.06)]	95.8 [95.0 (40.35)]	52.2 [52.6 (50.61)]
VII	NCG	126.4 [*]	109.3 [110.0 (4.64)]	90.8 [89.2 (31.87)]	67.5 [65.3 (70.57)]
VIII	NCG	128.8 [*]	118.5 [120.6 (6.59)]	92.3 [89.8 (25.37)]	75.2 [70.71 (18.09)]
IX	NCG	125.5 [122.5 (16.94)]	112.3 [*]	82.7 [81.8 (24.59)]	59.6 [60.5 (18.28)]

[#] I–IX represent alkyl chain lengths of ABA: propyl-, butyl-, pentyl-, hexyl-, heptyl-, octyl-, nonyl-, decyl-, and dodecyl-, respectively.

* Transition peaks are not resolved.

Fig. 2. Phase diagram of free *p*-*n*-alkoxybenzoic acids (N = nematic, C = smectic C).Fig. 3. Phase diagram of *n*ABA:R:*n*ABA complexes (N = nematic, A = smectic A, C = smectic C).

of the series is that the complexes II to IV exhibit smectic-G phase at room temperatures, while complex IX ($n = 12$) displays all the three phases (N, smectic-C and smectic-G) with maximum thermal ranges. Further, the transition temperatures of all the phases across the series exhibit the odd-even effect.

Moreover, the phase behaviour of complex V ($n = 7$) in both the analogous series represents a similar feature in the sense that the smectic phases exhibit very narrow ranges, which matches with the phase profile of free benzoic acid (Fig. 2). This clearly suggests that the alkyl chain length of the benzoic acid moiety may play a

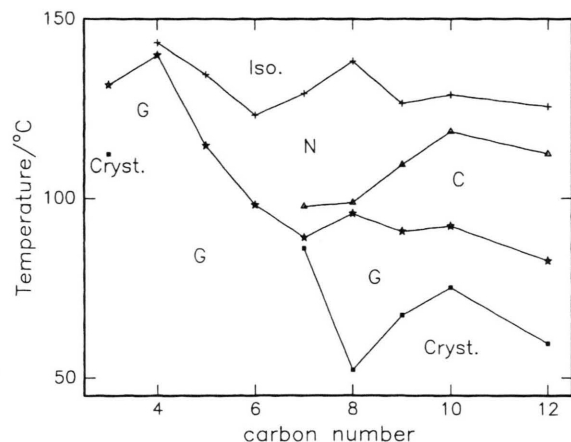


Fig. 4. Phase diagram of $n\text{ABA}:\text{H}:\text{nABA}$ complexes (N = nematic, C = smectic C, G = smectic G).

crucial role in the phase behaviour of complex V. It is also noticed that the complexes in both series show enhanced thermal ranges of liquid crystalline phases when compared to free *p-n*-alkoxybenzoic acids.

Conclusion

The thermal studies performed on two distinct isomer series, $n\text{ABA}:\text{R}:\text{nABA}$ and $n\text{ABA}:\text{H}:\text{nABA}$, re-

veal that the chemical constitution of the central non-mesogenic moiety has a pronounced impact on the phase behaviour of the liquid crystal molecule. The incorporation of a central core possessing intermolecular hydrogen bonding with a mesogen also promotes the occurring of new phases. A comparative systematic thermal study of the present series also implies that the $n\text{ABA}:\text{R}:\text{nABA}$ series shows the occurrence of an orthogonal molecular ordering (smectic-A) as an additional induced phase. This can best be interpreted in terms of molecular symmetry (C_{2v}) of the bent molecule, promoting a unique way for forming a helix in the adjacent molecular layers, which certainly influences many physical and thermal properties of the mesophases. Furthermore, the advent of this molecular symmetry of the liquid crystalline properties is realized by new phase variants with relatively wide thermal spans of the induced phases. Further conformational studies regarding the ferroelectric ordering in the observed smectic phases in the $n\text{ABA}:\text{R}:\text{nABA}$ series are in progress.

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