

# Induced Smectic A Phase through Intermolecular Hydrogen Bonding: Part XVIII: Influence of *p-n*-Alkyl Benzoic Acids on Thermal and Phase Behavior of Hydrogen-Bonded Liquid Crystals

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A novel series of intermolecular hydrogen bonded liquid crystals was synthesized with the mesogens of *p-n*-alkyl benzoic acids (*n*BA where  $n = 5$  to 10) and *p*-(*p*'-octyloxy benzylidene)-cyano aniline (OBCA) moieties. The thermal and phase behaviors of these mesogens (*n*BA:OBCA) are studied by thermal polarizing optical microscopy and differential scanning calorimetry techniques. Induced smectic A phase with focal conic fan texture is observed in all the synthesized compounds. Moreover, the nematic phase present in all the pure *p-n*-alkyl benzoic acids (*n*BA where  $n = 6$  to 10) is quenched in all the hydrogen bonded compounds (*n*BA:OBCA) and smectic A phase is induced. But, in the compound 5BA:OBCA the nematic phase is also present along with the induced smectic A phase. The structural elucidation pertaining to the formation and stabilization of intermolecular hydrogen bonding is carried out by a detailed IR spectral investigation.

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## 1. Introduction

Aromatic carboxylic acids are the first compounds that exhibit liquid crystalline behavior due to hydrogen bond formation [1–5]. In recent years, supramolecular liquid crystals have been synthesized through hydrogen bonding of complementary molecules in a large number. The role of H-bonding interactions in the formation and/or stabilization of liquid crystalline phases has also been recognized [6]. Novel series of liquid crystalline materials involving interactions of intermolecular H-bonding between mesogens [7], mesogens and non-mesogens [8, 9] and non-mesogens [10] have been synthesized. In determining the structural packing, properties of molecular assemblies [11] and the variation of mesogenic behavior of molecules [12], these non-covalent H-bonding interactions between functional groups play a critical role [13]. Our present work deals with the synthesis of new series of novel liquid crystalline materials with the combination of two mesogens *p-n*-alkyl benzoic acids (*n*BA) and *p*-(*p*'-octyloxy benzylidene)-cyano aniline (OBCA). The molecular structure of the complexes under study is given in Fig. 1.

When a typical mesogenic compound is cooled, the more ordered phases, i.e., the phases having lower symmetries, are expected to occur at lower temperatures. Accordingly, in most of the liquid crystals, the usual sequence of phase transitions is (with K for solid crystal):

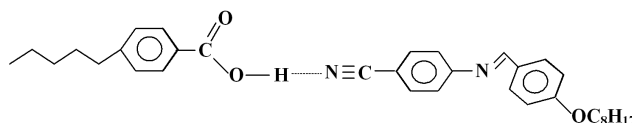


Fig. 1. Molecular structure of *n*BA:OBCA.

I–N–K or I–N–SmA–K. However, liquid crystals composed of molecules having *strongly polar* end groups show some unusual phase sequences. It is found that mixtures of certain compounds with strongly polar cyano or nitro end groups, on cooling from the isotropic phase, exhibit the sequence of transitions: I–N–SmA–N<sub>R</sub>–K. In some strongly polar pure compounds or binary mixtures, at temperatures below the range of existence of the re-entrant nematic phase, another smectic phase re-enters leading to the sequence: I–N–SmA<sub>d</sub>–NR–SmA<sub>1</sub>–K. This phenomenon is called double re-entrance. The lower temperature re-entrant smectic phase is called the smectic-A<sub>1</sub> (SmA<sub>1</sub>) phase, the lower temperature re-entrant smectic A phase after smectic-A<sub>1</sub> phase is called the smectic-A<sub>2</sub> (SmA<sub>2</sub>) phase and the higher temperature smectic phase is called the smectic-A<sub>d</sub> (SmA<sub>d</sub>).

In our experiment, the synthesized complexes follow the sequences of transitions: I–N–SmA–K ( $n = 5$ ) and I–SmA–K in ( $n = 6–10$ ). The induced smectic A phase

is not observed through *double re-entrance*. Therefore, it is concluded that it is smectic A<sub>d</sub> phase [14].

## 2. Experimental

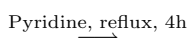
### 2.1. Materials and methods

All the substituted *n*BA and OBCA of 99.9% purity were supplied by Frinton Laboratories, USA.

The IR spectrum in solid state was recorded on THERMO NICOLET FTIR 5700 spectrometer. The phase variants and the transition temperatures of free *p-n*-alkyl benzoic acids and their corresponding series of intermolecular hydrogen-bonded complexes were determined from the characteristic textural observations under Olympus BX 50 thermal polarizing optical microscope with hot stage and equipped with a camera attachment to photograph the textures. A digital thermometer of  $-50^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  range with an accuracy of  $\pm 0.1^{\circ}\text{C}$  is used to determine the temperatures. The temperatures of the corresponding phase transitions and their heats of transition (in J/g) were further measured by scanning the compounds with differential scanning calorimetry (DSC) thermograms (Perkin-Elmer DSC Diamond Model) at a scan rate of  $5^{\circ}\text{C}/\text{min}$ .

### 2.2. Synthesis of intermolecular hydrogen bonding compounds

The intermolecular H-bonding complexes, *n*BA:OBCA, were synthesized by refluxing together the equimolar (1:1) mixture, of *p-n*-alkyl benzoic acids and OBCA, which is dissolved in 20 ml of pyridine, under constant stirring at  $80^{\circ}\text{C}$  for  $\approx 4$  h. The volume of the resultant homogeneous mixture was then reduced to dryness by removing the excess pyridine under a controlled vacuum filtration. The light yellow crystalline products were dried and re-crystallized from hot dichloromethane solution and dried over calcium chloride in a desiccator at room temperature.



where  $\text{R} = \text{C}_n\text{H}_{2n+1}$  and  $n$  varies from 5 to 10.

## 3. Results and discussion

### 3.1. IR spectra

The infrared frequencies of the corresponding groups of the pure *n*BA compounds, OBCA and *n*BA:OBCA series of complexes along with their assignments are included in Table I. The IR spectra of *p-n*-alkyl benzoic acids,

*n*BA, are recorded at room temperature in solid (KBr). The spectra of free *p-n*-alkyl benzoic acids (*n*BA where  $n = 8$ ) show two sharp bands at  $1423.9$  and  $944.3 \text{ cm}^{-1}$  corresponding to  $\bar{\nu}(\text{OH})$  in plane and out of plane bending modes [15].

TABLE I  
IR Spectral data of *n*BA, OBCA and *n*BA:OBCA

Sample no.	Compound (KBr)	$\bar{\nu}(\text{O-H})_{\text{acid}}$ [ $\text{cm}^{-1}$ ](OOPB)	$\bar{\nu}(\text{O-H})_{\text{acid}}$ [ $\text{cm}^{-1}$ ](IPB)	$\bar{\nu}(\text{C}\equiv\text{N})$ [ $\text{cm}^{-1}$ ]
1	OBCA			2224.2
2	5BA	943.02	1424.17	
3	5BA:OBCA	945	1420	2230
4	6BA	945	1424.1	
5	6BA:OBCA	947	1420	2230
6	7BA	938.6	1425	
7	7BA:OBCA	937	1430.4	2230
8	8BA	944.3	1423.9	
9	8BA:OBCA	947	1420	2230
10	9BA	944.7	1424.2	
11	9BA:OBCA	947	1430.5	2230
12	10BA	940.7	1421.8	
13	10BA:OBCA	946.1	1423.2	2223.8

IPB — in plane bending; OOPB — out of plane bending

The IR spectrum of *p*-(*p'*-octyloxy benzyldene)-cyano aniline is recorded at room temperature in solid (KBr). The spectrum of *p*-(*p'*-octyloxy benzyldene)-cyano aniline shows a sharp peak at  $2224.2 \text{ cm}^{-1}$  for  $\bar{\nu}(\text{CN})$  mode [15, 16].

The formation of inter-molecular hydrogen bonding between OH group of *n*BA and CN group of OBCA can be invoked on the basis of bathochromic shifts in  $\bar{\nu}(\text{CN})$  mode ( $\approx 6 \text{ cm}^{-1}$ ) of OBCA [7, 17] and  $\bar{\nu}(\text{O-H})$  in plane bending mode ( $\approx 4 \text{ cm}^{-1}$ ) of carboxylic acid group and a hypsochromic shift of ( $\approx 3 \text{ cm}^{-1}$ ) in  $\bar{\nu}(\text{O-H})$  out of plane bending mode [18] upon complexation which strongly supports the existence of H-bonding. The existence of H-bonding is strongly confirmed due to the strong broad induced frequency of  $3465.5 \text{ cm}^{-1}$  [15, 18], lying in the frequency range of stretching OH-group due to H-bonding.

### 3.2. Thermal and phase behavior

The phase transition temperatures along with the characteristic textural observations of pure *n*BA compounds, OBCA and synthesized series of *n*BA:OBCA complexes are determined under a thermal polarizing optical microscope. From the optical microscopic investigations, it is observed that the pure *p-n*-alkyl benzoic acids [19] and OBCA [20] are enantiotropic liquid crystalline compounds exhibiting only threaded nematic mesophase (Fig. 2).

The thermal microscopic studies indicate that the *n*BA:OBCA series of compounds exhibits nematic and

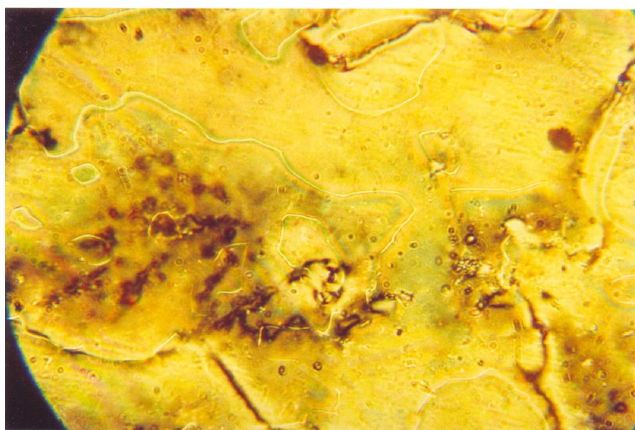


Fig. 2. Threaded nematic mesophase.

induced smectic A (SmA) phases. The nematic phase present in the pure compounds of  $n$ BA (where  $n = 6$  to 10) has been quenched in the synthesized compounds of the  $n$ BA:OBCA series (where  $n = 6$  to 10) and only smectic A phase is induced in all the compounds. Smectic A phase with focal-conic fan texture is induced in all the compounds of the present series. In the case of 5BA:OBCA compound, the nematic phase is also present with the induced smectic A phase.

In 5BA:OBCA liquid crystal, the nematic phase separates from the isotropic melt in the form of small droplets which on further cooling leads to the formation of threaded nematic texture as shown (Fig. 2). On further cooling, the phase transition from nematic to smectic A phase is observed with the formation of a focal-conic fan texture (Fig. 3).

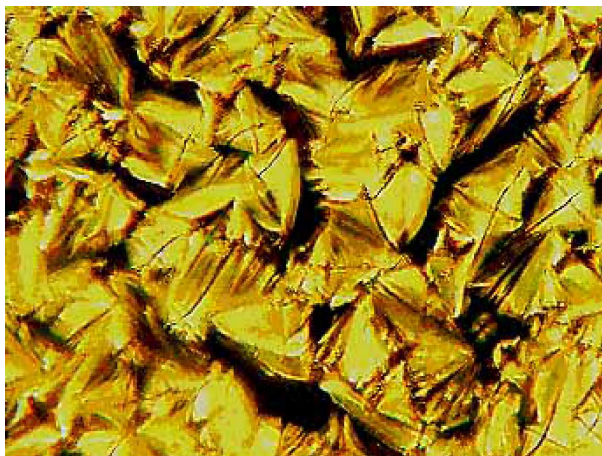


Fig. 3. Focal conic fan texture of SmA phase in  $n$ BA:OBCA ( $n = 5-10$ ).

In the remaining compounds ( $n = 6$  to 10) the smectic A phase separates from the isotropic melt in the form of small battonnets which on further cooling combine to

TABLE II  
Transition temperatures of  $n$ BA:OBCA observed through polarizing optical microscope and DSC.

Compound $n$ BA:OBCA where $n = (5-10)$	Phase	I-N/SmA	N-SmA	SmA-solid
5BA:OBCA (TM)	NA	74.7	60.1	50
(DSC)		79.9	65.2	54.2
6BA:OBCA (TM)	A	77.8		56
(DSC)		70.6		61.4
7BA:OBCA (TM)	A	95.9		62
(DSC)		94.5		57.8
8BA:OBCA (TM)	A	83.1		63.6
(DSC)		72.7		63.6
9BA:OBCA (TM)	A	96.5		72
(DSC)		94.6		76
10BA:OBCA (TM)	A	79.9		62.5
(DSC)		79.6		68.7

form a focal conic fan texture of SmA phase (Fig. 3). The phase transition temperatures observed through thermal microscopy are in reasonable agreement with those in the DSC thermograms [16] and the data is given in Table II.

### 3.3. Phase diagram

From phase diagram (Fig. 4), the following results are observed.

As the alkyl chain length increases from  $n = 6$  to 10, the nematic phase has been quenched with the simultaneous growth in the induced smectic A phase [21-23].

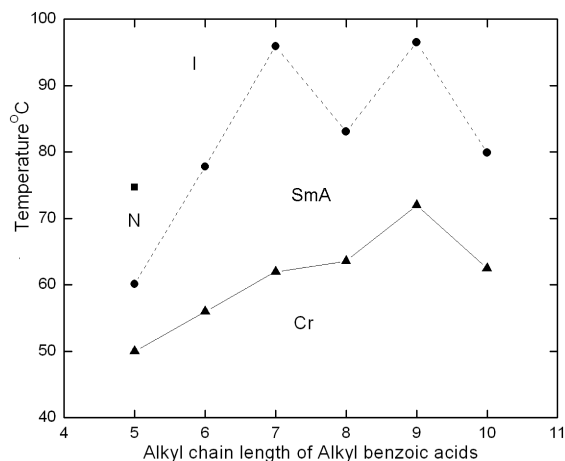


Fig. 4. Phase diagram of intermolecular H-bonded complexes.

The temperature range of the nematic phase decreases with the induced SmA phase in the 5BA:OBCA compound than in the pure 5BA compound.

In all the compounds, the thermal spans of induced SmA phase show odd-even effect which indicates the intrachain constraints on the tail-chain flexibility [24, 25].

The clearing temperatures of all *n*BA:OBCA series of compounds are lowered when compared with those in the pure *n*BA series and odd members exhibit wide thermal ranges of induced smectic A phase [16].

#### 4. Conclusions

All the compounds of *n*BA:OBCA series ( $n = 5, 6, 8,$  and  $10$ ) are enantiotropic liquid crystals with induced SmA phase. The compounds  $n = 7$  and  $9$  are monotropic liquid crystalline compounds, i.e., they exhibit induced smectic A phase only in cooling cycle. In heating cycle, they directly become isotropic from solid phase without exhibiting any liquid crystalline phase [10]. The liquid crystalline range is increased in all the synthesized compounds when compared with the pure *n*BA series except in the 5BA:OBCA compound.

The growth in the inducement of SmA phase with increase in alkyl chain length shows the influence of the non-polar tails on the rigid cores i.e., the semi-flexible tail chains cause enough disorder and keep the cores to obtain partial positional order from isotropic phase which leads to SmA phase.

From FTIR and polarizing optical microscopy (POM) investigations, it is concluded that the hydrogen bond is formed between the O-H group of *p*-*n*-alkyl benzoic acids (**1**) and CN group of OBCA (**2**). The intermolecular H-bonding interactions between the terminal functional groups of the molecule **1** (O-H) and **2** (CN) influence their molecular packing, i.e., each molecule of **1** is regularly arranged head-to-tail with adjacent molecule **2** in the same layers [18, 26].

In such a way, the terminal groups of the adjacent dimers come close together through thermal motions and rearrangement of H-bonds into the open structures takes place offering a good degree of stabilization also in solid state [18].

The complexes with odd alkyl carbon numbers show wide liquid crystalline ranges. This shows the influence of the alkyl carbon number on the intermolecular H-bonding.

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#### References

[1] G.W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London 1969, p. 163.

- [2] H. Kelker, R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980, p. 59.
- [3] D. Vorlander, *Ver. Deutsch. Chem. Ges.* **41**, 2033 (1908).
- [4] G.W. Gray, B. Jones, *J. Chem. Soc.*, 1467 (1954).
- [5] G.W. Gray, B. Jones, *J. Chem. Soc.*, 4179 (1953).
- [6] C.M. Paleos, D. Tsiourvas, *Liq. Cryst.* **28**, 1127 (2001).
- [7] P.A. Kumar, P. Swathi, V.G.K.M. Pisipati, A.V. Rajeswari, S. Sreehari Sastry, *Phase Transit.* **76**, 625 (2003).
- [8] P.A. Kumar, V.G.K.M. Pisipati, A.V. Rajeswari, S. Sreehari Sastry, *Z. Naturforsch. A* **57**, 184 (2002).
- [9] P.A. Kumar, P. Swathi, V.G.K.M. Pisipati, A.V. Rajeswari, S. Sreehari Sastry, *Z. Naturforsch. A* **57**, 797 (2002).
- [10] M. Parra, P. Hidalgo, J. Barbera, J. Alderete, *Liq. Cryst.* **32**, 573 (2005).
- [11] (a) C.A. Hunter, *Angew. Chem. Int. Ed. Engl.* **32**, 1584 (1993); (b) C.A. Hunter, *Chem. Soc. Rev.* **23**, 101 (1994).
- [12] (a) K.M. Lee, C.M. Lee, I.J.B. Lin, *Angew. Chem. Int. Ed. Engl.* **36**, 1850 (1997); (b) J. Chang, J.S. Moore, *J. Am. Chem. Soc.* **116**, 2655 (1994).
- [13] (a) G.R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York 1989; (b) G.R. Desiraju, *Chem. Commun.*, 1475 (1997).
- [14] A.S. Govind, Ph.D. thesis, RRI, Bangalore, 2002.
- [15] R.M. Silverstein, G.C. Bassler, T.C. Morrill, *Spectroscopic Identification of Organic Compounds, Fifth Edition*, Wiley, Singapore 1991.
- [16] M. Xie, C. Zhang, *Liq. Cryst.* **34**, 1275 (2007).
- [17] C.S. Cassidy, L.A. Reinhardt, W.W. Cleland, P.A. Frey, *J. Chem. Soc., Perkin Trans. 2*, 635 (1999).
- [18] L. Carpaneto, C. Peluffo, P. Piaggio, B. Valenti, *J. Chem. Soc., Faraday Trans. 93*, 1095 (1997).
- [19] C. Weygand, R. Gabler, *Z. Phys. Chemie B* **46**, 270 (1940).
- [20] Private Communication from M/S Frinton Laboratory, USA.
- [21] (a) L.L. Lai, C.H. Ho, Y.J. Lin, E. Wang, Y.H. Liu, Y. Wang, Y.C. Lin, K.L. Cheng, *Liq. Cryst.* **29**, 1477 (2002); (b) V.F. Petrov, *Liq. Cryst.* **28**, 217 (2001).
- [22] D.W. Bruce, D.A. Dunmur, S.A. Hudson, E. Lalinde, P.M. Maitlis, M.P. McDonald, R. Orr, P. Styring, A.S. Cherodian, R.M. Richardson, J.L. Feijoo, G. Ungar, *Mol. Cryst. Liq. Cryst.* **206**, 79 (1991).
- [23] H. Loc Nguyen, P.N. Horton, M.B. Hursthouse, D.W. Bruce, *Liq. Cryst.* **31**, 1445 (2004).
- [24] F. Dowell, *Phys. Rev. A* **38**, 382 (1988).
- [25] E. Bialecka-Florjanczyk, D. Melon-Ksyta, A. Orzeszko, I. Sledzinska, J. Przedmojski, E. Gorecka, *Liq. Cryst.* **31**, 1227 (2004).
- [26] Long-Li Lai, Feng-Ya Su, Chen-Hsiung Hung, *Liq. Cryst.* **31**, 773 (2004).