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V. N. Vijayakumar [a], K. Murugadass [a] & M. L. N. Madhu Mohan [a]

[a] Liquid Crystal Research Laboratory (LCRL), Bannari Amman Institute of Technology, Sathyamangalam, India

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Study of Intermolecular Hydrogen Bonding in p-n-Alkoxybenzoic Acids and Alkyl Aniline Homologous Series – Part I

V. N. Vijayakumar, K. Murugadass, and M. L. N. Madhu Mohan
Liquid Crystal Research Laboratory (LCRL), Bannari Amman Institute of Technology, Sathyamangalam, India

A homologous series of interhydrogen bonded complexes between p-n-alkoxybenzoic acids (nABA) and alkyl anilines were isolated. The mesogenic nABA (where n represents the alkoxy carbon number from 5 to 12 except 6) formed a hydrogen bond with liquid crystal intermediate 4-hexyl aniline. The homologous series mesogens are analyzed by polarizing optical microscope, differential scanning calorimetry (DSC), and FTIR studies. An interesting feature of these homologous series is the drastic reduction of the mesogenic temperatures and the occurrence of smectic ordering just above ambient temperature. The phase diagrams of the nABA and the homologous series were computed and compared, respectively. A critical observation in all the binary compounds of the present homologous series reveals that there exists a correlation between the alkyl chain length and mesogenic phases induced. Further some of the mesogens exhibit monotropic Smectic F and Smectic G transition. The hydrogen bond formation was evinced through FTIR spectral studies. Results of free nABA and the hydrogen bonded homologous series were discussed in the light of increment in alkoxy carbon number, mesogenic phases exhibited, and mesogenic thermal span.

Keywords: hexyl aniline; hydrogen bonding; p-n-alkoxybenzoic acids

INTRODUCTION

Hydrogen bonded liquid crystals generated new interests among many research groups [1–6] because of their ease of synthesis, lower mesogenic temperatures, and fascinating properties. Discovery of H-bonded liquid crystals by Kato and Frechet [7] opened a new chapter in design,

Address correspondence to M. L. N. Madhu Mohan, Liquid Crystal Research Laboratory (LCRL), Bannari Amman Institute of Technology, Sathyamangalam 638-401, India. E-mail: mln.madhu@gmail.com

synthesis, and characterization of these mesogens. Most of the reported data [1–7] on H-bonded liquid crystals deals with some phase being induced. With our previous experience [8–10] in synthesizing liquid crystals, in the present work a successful attempt has been made to design and isolate homologous series of hydrogen bonded liquid crystals with the aim to lower the transition temperatures of the mesogens to the ambient temperatures. The mesogenic p-n-alkoxybenzoic acids nABA (where n represents the alkoxy carbon number from 5 to 12 except 6) formed a hydrogen bond with liquid crystal intermediate 4-hexyl aniline. Phase diagrams, the mesogenic phase, and thermal range are discussed for the isolated two different homologous series.

EXPERIMENTAL

Optical textural observations were made with a Nikon polarizing microscope equipped with Nikon digital CCD camera system with 5 mega pixels and 2560 * 1920 pixel resolutions. The liquid crystalline textures were processed, analyzed, and stored with the aid of ACT-2U 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 $\pm 0.1^{\circ}$C. This unit is interfaced to a computer by IEEE –STC 200 to control and monitor the temperature. The liquid crystal sample is filled by capillary action in its isotropic state into a commercially available (Instec, USA) polyamide buffed cell with 4 micron spacer. The transition temperatures and corresponding enthalpy values were obtained by differential scanning calorimetry (DSC) (Shimadzu DSC-60). The Fourier Transform Infrared Spectroscopy (FTIR) spectra was recorded (ABB FTIR MB3000) and analyzed with the MB3000 software. Dielectric studies were performed with HP 4192A impedance analyzer. The nABA and 4-hexyl aniline were supplied by Sigma Aldrich, Germany, and all the solvents used were E. Merk grade.

SYNTHESIS OF INTERMOLECULAR HYDROGEN BONDED COMPLEX

The intermolecular hydrogen bonded mesogens are synthesized by the addition of one mole of nABA with one mole of 4-hexyl aniline in N,N-dimethyl formamide (DMF), respectively. Further, they are subject to constant stirring for 12 hours at ambient temperature of 30°C till a white precipitate in a dense solution is formed. The white crystalline crude complexes so obtained by removing excess DMF are then recrystallized. The yields varied from 85% to 95%. The yield of higher homologues compounds is observed to be more compared to its lower

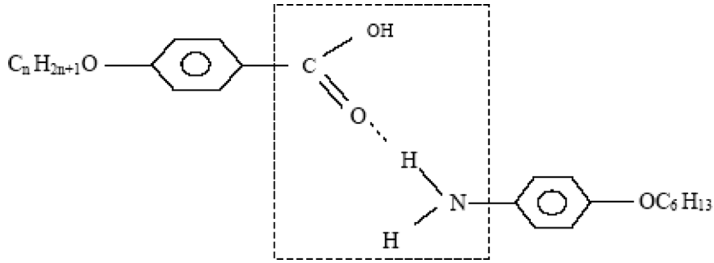

FIGURE 1 Molecular structure of 6 A + n BA homologous series.

counterparts. The molecular structure of the present homologous series of nABA with 4-hexyl aniline can be depicted as shown in the Fig. 1, where n represents the alkoxy carbon number.

RESULTS AND DISCUSSION

All the mesogens isolated under the 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, and dicholoro-methane. However, they

TABLE 1 Transition Temperatures Obtained by DSC 6 A + n BA Homologous Series. # Indicates Monotropic Transition

Carbon number	Phase variant	Technique	Crystal to melt	F	G	Crystal
3	F	DSC (h)	49.72 (87.57)	#		
		DSC (c)		47.33 (5.66)		42.88 (25.10)
5	FG	DSC (h)	47.28 (12.07)	57.60 (97.85)	#	
		DSC (c)		59.62 (10.77)	38.44 (28.85)	37.49 (8.06)
7	FG	DSC (h)	48.03 (194.12)	57.87 (3.80)	#	
		DSC (c)		54.20 (13.92)	43.33 (81.89)	39.90 (20.83)
8	FG	DSC (h)	53.23 (220.30)	75.21 (19.42)	#	
		DSC (c)		79.94 (4.62)	45.20 (36.75)	42.99 (11.28)
9	FG	DSC (h)	51.53 (11.49)	56.87 (34.22)	Merged with melt	
		DSC (c)		57.54 (29.30)	52.70 (2.65)	44.34 (73.74)
10	FG	DSC (h)	51.31 (9.75)	63.44 (10.31)	95.71 (3.97)	
		DSC (c)		79.03 (1.47)	75.29 (1.47)	44.47 (25.89)
11	FG	DSC (h)	61.84 (64.80)	96.53 (11.46)	93.11 (merged with F)	
		DSC (c)		78.92 (2.18)	74.52 (5.41)	46.28 (37.68)
12	G	DSC (h)	59.6 (157.97)		#	
		DSC (c)			84.04 (7.78)	43.24 (143.0)

show a high degree of solubility in coordinating solvents like dimethyl sulfoxide (DMSO), DMF, and pyridine. All these mesogens melt at specific temperatures below 100°C (Table 1). They show high thermal and chemical stability when subjected to repeated thermal scans performed during polarizing optical microscopy and DSC studies.

INFRARED SPECTROSCOPY (FTIR)

The IR spectra of nABA, 4-hexyl aniline, and their intermolecular H-bonded complex were recorded in the solid state (KBr) at room temperature. The solid state spectra of free alkoxybenzoic acid is reported [11] to have two sharp bands at 1685 and 1695 cm^{-1}, due to the frequency ν(C=O) mode. The doubling feature of this stretching mode confirms the dimeric nature of alkoxybenzoic acid at room temperature [11]. Further, a strong intense band appearing at 2924 cm^{-1} is assigned to ν(O-H) mode of the carboxylic acid group. The IR spectrum (KBr) of 4-hexyl aniline (Fig. 2) shows characteristic bands for ν(C=O) ($\sim$1628 cm^{-1}), ν(N-H) ($\sim$3371 cm^{-1}), and ν(C-O) ($\sim$1257 cm^{-1}) stretching modes [12]. The hypsochromic shift in ν(C=O) of acid ($\sim$62 cm^{-1}) and bathochromic shift in ν(OH) ($\sim$8 cm^{-1}) mode of acid in the present series suggest the formation of intermolecular H-bonding between the −COOH group of nABA and the −NH of 4-hexyl aniline. The presence of H-bonding in the present complexes was further inferred by the appearance of new band diagnostic of ν(O-H) at 2561 cm^{-1}.

PHASE IDENTIFICATION

The observed phase variants, transition temperatures, and corresponding enthalpy values obtained by DSC in cooling and heating cycles for the homologous series are presented in Table 1.

HEXYL ANILINE AND ALKOXY BENZOIC ACIDS HOMOLOGOUS SERIES

The mesogens of the hexyl aniline and alkoxy benzoic acid homologous series are found to exhibit characteristic textures [13], viz., Smectic F (multicolored mosaic texture with sharp boundaries) and Smectic G (multicolored mosaic texture), respectively. The general phase sequence of the hexyl aniline and alkoxy benzoic acid homologous series in the cooling run can be shown as:

$$\text{Isotropic} \rightarrow \text{Sm F} \rightarrow \text{Sm G} \rightarrow \text{Crystal}$$

(compound with alkoxy carbon number 5 and 11)

Isotropic → SmG → Crystal
(compound with alkoxy carbon number 12).

DSC STUDIES

DSC thermograms are obtained in the heating and cooling cycles. The sample is heated with a scan rate of 10°C/min and held at its isotropic temperature for one minute so as to attain thermal stability. The cooling run is performed with a scan rate of 10°C/min. The respective equilibrium transition temperatures and corresponding enthalpy values of the mesogens corresponding to the homologous series are listed separately in Table 1. Smectic G is observed to be monotropic in petnyl, heptyl, octyl, and dodecyl benzoic acids, and hexyl aniline homologous series in the heating cycle, while Smectic F is observed to be monotropic in propyl benzoic acid, and hexyl aniline in the heating cycle. Polarizing optical microscopic studies also confirm these DSC results of the monotropic transitions. Further, the higher members, namely, nonyloxy, decyloxy, and undecyloxy benzoic acid of the hexyl aniline homologous series exhibit enantiotropic transitions.

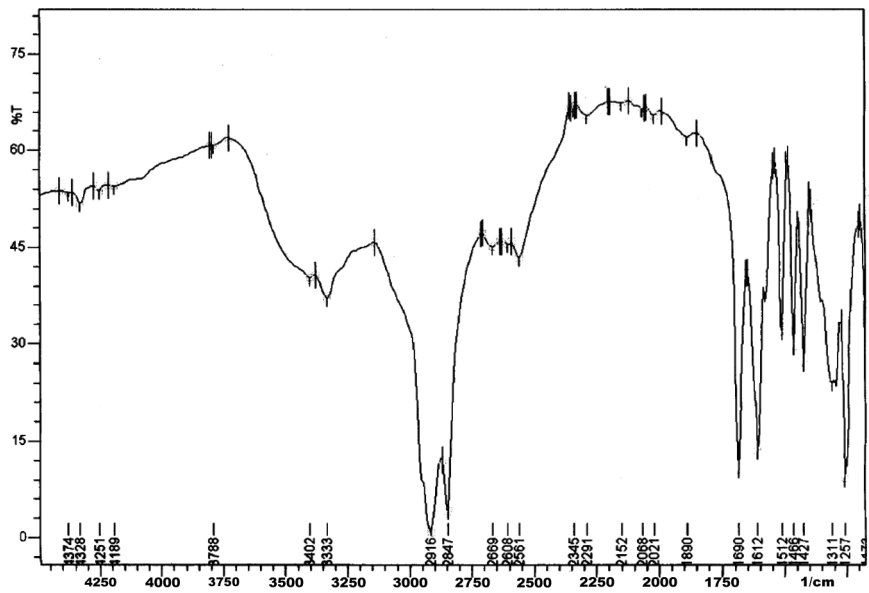

FIGURE 2 FTIR spectrum of 6 A + 8 BA mesogen.

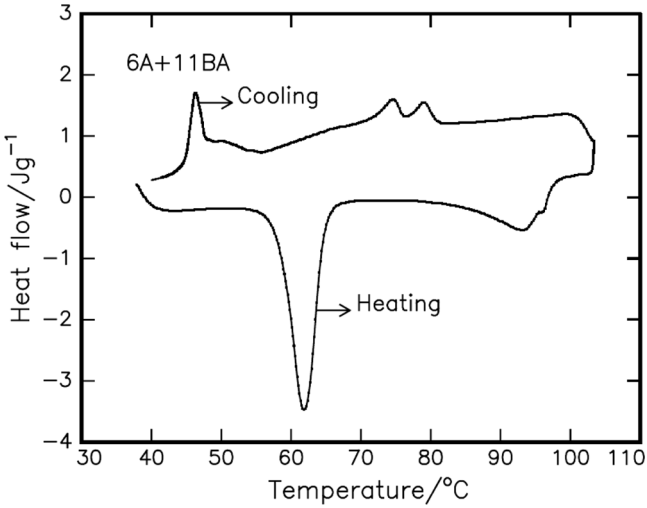

FIGURE 3 DSC thermo gram of 6 A + 11 BA mesogen.

DSC STUDIES OF UNDECYLOXY BENZOIC ACID WITH HEXYL ANILINE

As a representative case, the phase transition temperatures and enthalpy values of undecyloxy benzoic acid and hexyl aniline mesogen are discussed Figure 3 illustrates the thermogram of the mesogen recorded at a scan rate of 10°C/min for the heating and cooling runs. In the cooling run of DSC thermogram, the above compound possesses three distinct transitions, namely, isotropic to Sm F, Sm F to Sm G, and Sm G to crystal, with transition temperatures 78.92°C, 74.52°C, and 46.28°C, with corresponding enthalpy values 2.18 J/g, 5.41 J/g, and 37.68 J/g, respectively. While in the heating cycle three distant transitions, namely, crystal to melt, melt to Sm F, Sm F to Sm G are obtained at 61.84°C, 96.53°C, and 93.11°C with corresponding enthalpy values of 64.80 J/g and 11.46 J/g, respectively. The enthalpy values corresponding to temperatures 96.53°C and 93.11°C are merged. All these transition temperatures of the present homologous series concur with polarizing microscopic studies.

PHASE DIAGRAMS

Phase Diagram of Pure nABA

The phase diagrams of pure nABA and the hexyl aniline homologous series are constructed through optical polarizing microscopic studies

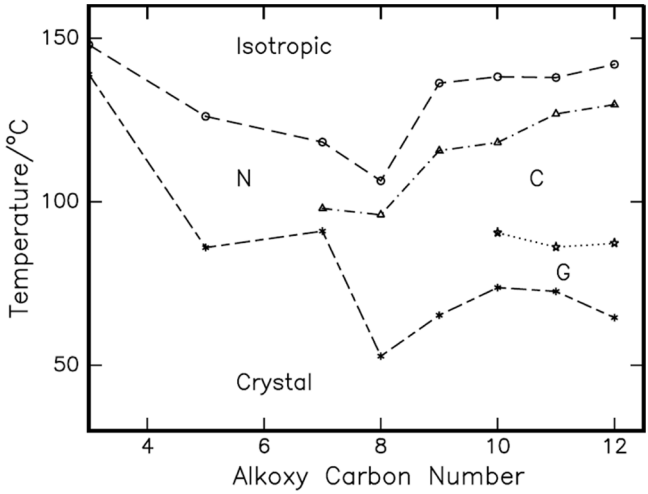

FIGURE 4 Phase diagram of nABA.

by the phase transition temperatures observed in the cooling run of the mesogens of the present homologous series. The phase diagram of pure nABA is composed of three tilted phases, namely, nematic, Smectic C, and Smectic G, as shown in Fig. 4.

Phase Diagram of Hexyl Aniline and Alkoxy Benzoic Acids Homologous Series

The phase diagram of hexyl aniline with nABA is depicted in Fig. 5. A careful observation of Fig. 5 reveals the following points:

1. The first and last members of the series, namely, propyloxy and dodecyloxy benzoic acids exhibit only single phase variance.
2. The first members of the present series, namely, propyloxy benzoic acid exhibit Smectic G, while the last members, namely, dodecyloxy benzoic acid exhibit Smectic F phase.
3. All other intermediate members of the homologous series exhibit two phase variance, namely, Smectic F and Smectic G.
4. In the lower members of the homologous series, with alkoxy carbon number from 5 to 8, the thermal span of Smectic F is abundant, while the thermal span of Smectic G is minimal.
5. Further, in this part of the phase diagram, it can be observed that the thermal span of Smectic F phase drastically increased and

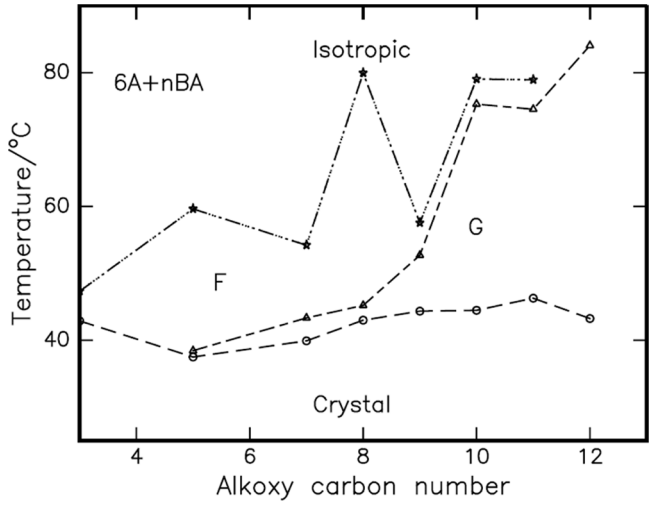

FIGURE 5 Phase diagram of the 6 A + n BA homologous series.

attained maximum value at alkoxy carbon number 8, while the thermal span of Smectic G is unaltered.

6. In the higher members of the homologous series, with alkoxy carbon number from 9 to 12, the thermal span of Smectic G is abundant, while the thermal span of Smectic F is minimal.
7. Further, in this part of the phase diagram, it can be observed that the thermal span of Smectic G phase increased, while the thermal span of Smectic F remained unaltered.
8. It can also inferred from the entire phase diagram, the mesogenic thermal range increased drastically with the increment of alkoxy carbon number.
9. Interestingly, the odd–even effect is visible in the isotropic transitions but is suppressed at crystal transition temperatures.
10. It is interesting to note that the present homologous series mesogens exhibit only Smectic F and Smectic G phases, while the pure nABA exhibit three phases, namely, nematic, Smectic C, and Smectic G.
11. The lower mesogens of the homologous series when compared tothe alkoxy benzoic acid mesogens, where nematic and Smectic C are completely quenched by Smectic G and Smectic F phases.
12. In summary, it can be concluded that the Smectic F thermal span is quenched by Smectic G in the entire homologous series with the increment of the alkoxy carbon number.

INFLUENCE OF ALKOXY CARBON NUMBER

From Fig. 5 it can be inferred that alkoxy carbon chain length has a pronounced effect on the phase variance, mesogenic thermal span, and favored phase. In other words, as the alkoxy carbon number increased, the following facts are noticed:

1. In the present homologous series, the transition temperatures of all the mesogens are observed to be below 100°C, while the alkoxy benzoic acid mesogens transition temperatures are much higher, at 150°C.
2. The first mesogen of the series, i.e., 6 A + 3 BA shows Smectic F phase while the last mesogen of the series, i.e., 6 A + 12 BA is found to exhibit Smectic G phase. Thus as the alkoxy carbon increased the quenching of the Smectic F by Smectic G phase progressively increased.
3. However, the higher members of the present homologous series favored the Smectic G phase, while the lower members favored the Smectic F phase.
4. The overall mesogenic range increased drastically from ~5°C in the 6 A + 3 BA to ~40°C in 6 A + 12 BA mesogen. Thus the increment of the carbon number favored the increment in the mesogenic thermal range.
5. Interestingly, the nematic and the Smectic C phases observed in the free alkoxy benzoic acid mesogens are quenched, and the Smectic G and Smectic F phases are induced in the present homologous series.

CONCLUSIONS

1. A new series of hydrogen bonded complexes between nABA and hexyl aniline have been isolated and characterized.
2. The mesogens are characterized by FTIR, DSC, and polarizing optical microscopic and dielectric studies.
3. The Smectic G and Smectic F phases are observed, while the pure alkoxy benzoic acids exhibit nematic, Smectic C, and Smectic G phases.
4. Hydrogen-bond formation has influenced the mesogenic temperatures of the present homologous series which are drastically reduced when compared to the pure nABA.

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