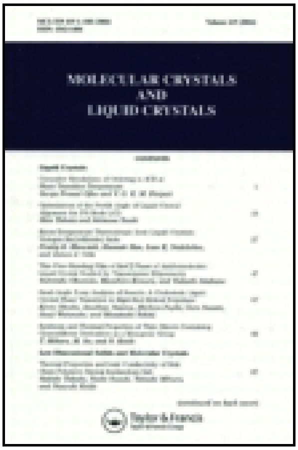

Molecular Crystals and Liquid Crystals

Alternating Intermolecular Hydrogen Bonding in Linear Liquid-Crystalline Complexes

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Alternating Intermolecular Hydrogen Bonding in Linear Liquid-Crystalline Complexes

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An extensive work for the realization of tilted liquid-crystalline (LC) phases of operational viability and display interest as tuned by the alternating (double) hydrogen bonding in the linear intermolecular complexes is presented. A new family of double-hydrogen-bonded liquid crystals formed between mesogenic p-n-alkoxybenzoic acids (nO.BAs) and nonmesogenic p-n-cyanophenol(CNΦOH) moieties is synthesized and studied systematically. Formation of H-bonding complex between proton acceptor/donor groups is confirmed through the corresponding IR spectroscopic shift. The phases and transitions exhibited by the H-bonded LC complexes are studied using polarizing thermal microscopy (TM) and differential scanning calorimetry (DSC). The impact of flexible chain length and the core part (both of the parent mesogenic moiety) is studied. The soft covalent bond interaction of H-bonding and its configuration are found to enhance the thermal stability of LC phases toward ambient temperatures with the simultaneous induction of tilted smectic G phase.

Keywords: hydrogen bonding, induced, intermolecular, liquid crystal, tilted smectic-e

INTRODUCTION

In the recent years, a spurt of research activity [1] in the field of supramolecular aspects of liquid crystals (LCs) has been witnessed in the

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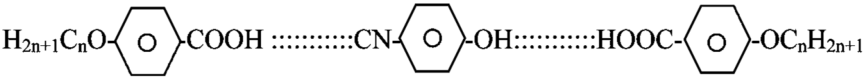
specific area of hydrogen bonding (HB), due to the inherent capability of this soft covalent interaction to impart a wide spectrum of design features to the constituent self-assembly [2–4] of the molecules. Although the first report of HBLCs by Kato and Frechet [5] between carboxylic acids and pyridine has triggered the activity in this field, fascination with this field is sustained by the subsequent reports regarding the H-bonding's capability to induce entirely new tilted LC phases relevant to display devices [6] with no prerequisite that one of the moieties need necessarily be mesogenic in nature. The LC properties exhibited by these HB complexes are understood as originating because of the spread of soft covalent interaction along the long molecular axis to enhance the fundamental and essential requirement of nonzero length-to-breadth ratio to the molecule. The relative advantage involved in this approach of addressing the problem of the influence of H bonding relies on the underlying simplicity of the synthetic procedure and the purity of the ingredients to result in the sustained and reproducible thermal stability. These aspects of H bonding in LCs has further motivated our present studies to investigate the influence of intermolecular double hydrogen bonding on the mesomorphism in the resulting linear LC complex.

EXPERIMENTAL

The proposed HBLC complex was synthesized from the inherently mesogenic p-n-alkoxybenzoic acids (for n = 3 to 10) and nonmesogenic p-cyanophenol as ingredient moieties. The p-n-alkoxybenzoic acids and p-cyanophenol (acquired from Frinton Laboratories, N.J., USA, 99% pure) along with the solvents (E-Merck) were mixed in 2:1 molar ratio in the presence of absolute pyridine as appropriate [7] solvent. The resulting HB complex was observed to be white and crystalline in appearance and is stable at room temperature. The molecular structure of the final product HBLC complex is given below:



The molecular formula for the present HBLC complexes used in the following discussion is nO.BA:CNΦOH:AB.On.

A Perkin-Elmer (BX series) Fourier Transform Infra-Red (FTIR) spectrometer was used for the confirmation of the formation of the H-bonded LC complex. An Olympus (BX-50) polarizing microscope supplemented with optical display (DP10) in conjunction with a PC-monitored Device Tech Instec temperature controller were used during the textural characterization of LC complexes. A Differential Scanning Calorimetry (Perkin-Elmer DSC-7) system was used for the calorimetric investigation ($5^{\circ}\mathrm{C\,min^{-1}}$) to determine the phase-transition temperatures and the heats of transitions involved with the present thermotropic HBLC complexes.

RESULTS AND DISCUSSION

Confirmation of HB LC Complex Formation

The IR spectra of p-cyanophenol and the HBLC complexes are recorded in solid state (KBr) at room temperature. The solid state (KBr) IR spectrum of nonmesogenic moiety (viz., p-n-cyanophenol) is presented as Fig. 1. The IR spectrum of HBLC complex (viz., nOBA:CNΦOH:ABO.n for n = 8) is presented as a representative in Fig. 2. The corresponding spectral data is presented in Table 1. It may be recalled that IR spectra of free p-n-alkoxybenzoic acids is reported [8] with double-peak sharp absorption at $\nu \sim 1700\,\mathrm{cm^{-1}}$ and is attributed to the –C=O– stretching mode, whereas the doubling feature of the peak is inferred as due to the dimeric abundance of p-substituted benzoic acid. The solid state (KBr) IR spectrum of p-cyanophenol (Fig. 1) is found to exhibit two characteristic bands (viz., one of medium intensity at $\nu \sim 1583\,\mathrm{cm^{-1}}$ and another of broad nature at $\nu \sim 3289\,\mathrm{cm^{-1}}$). The former one is inferred as due to –C≡N stretching and the latter to the –OH stretching modes. The formation of alternating or double H-bonding between the ingredient moieties is confirmed by recording the RT solid state (KBr) IR spectrum

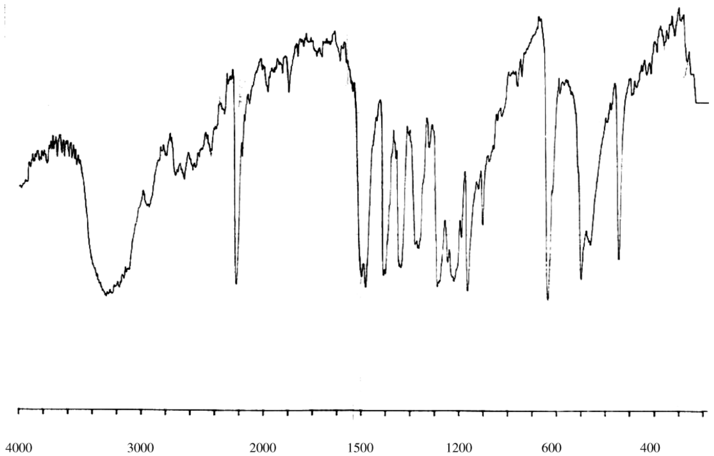


FIGURE 1 Solid-state (KBr) infrared spectrum of p-cyanophenol.

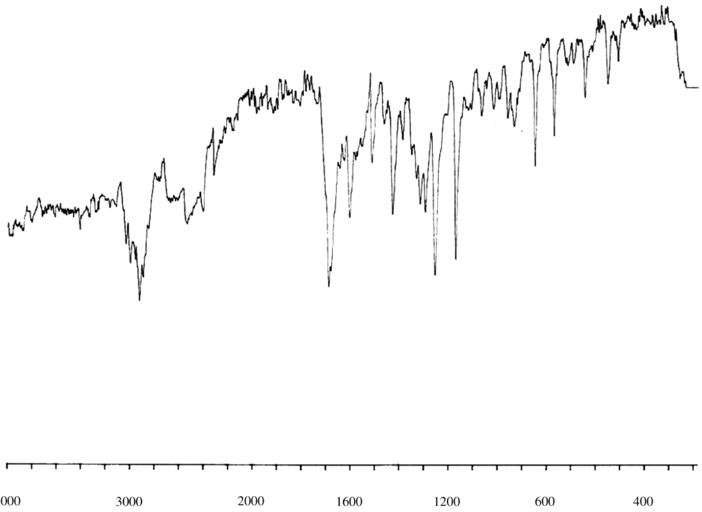


FIGURE 2 Solid-state (KBr) infrared spectrum of hydrogen-bonded LC complex (i.e., nO.BA::CNΦOH::AB.On) for n = 8.

(Fig. 2) at room temperature of the final product HBLC complex and the following analysis of it. The observed bathochromic shift (in comparison with free p-n-cyanophenol IR spectrum in Fig. 1) of −CN stretching band by $\Delta\nu \sim 70\,\mathrm{cm}^{-1}$ and the −OH band by $\Delta\nu \sim 300\,\mathrm{cm}^{-1}$ confirms the participation of cyano and hydroxyl groups respectively in the formation of H bonding along the long molecular axis as tuned by proton acceptor/donor interaction. It is also observed that the carbonyl group relevant to the >C=O stretching, which appeared as a double peak at ($\nu \sim 1700\,\mathrm{cm}^{-1}$) in the IR spectrum of dimeric form of p-n-benzoic acid, reduces to a single absorption band at $\nu \sim 1689\,\mathrm{cm}^{-1}$. The observed change of carbonyl group's double peak in the IR spectrum of HBLC into a single peak along with its bathochromic shift (in comparison with the −OH absorption reported in the IR spectrum for p-n-alkoxybenzoic

TABLE 1 Solid (KBr) IR Spectroscopic Data of p-n-Cyanopnenol and HB LC Complex (nO.BA::CNΦOH::AB.On for n = 8O.BA::CN as Representative)

Compound	$\nu(\mathrm{CO})_{\mathrm{acid}}$	$\nu(\mathrm{OH})_{\mathrm{acid}}$	$\nu(\mathrm{CN})_{\mathrm{phenolic}}$	$\nu(\mathrm{OH})_{\mathrm{phenolic}}$
8O.BA	1685 & 1695	3014	—	—
CNΦOH	—	—	1583	3289
nO.BA–CNΦOH–nO.BA, H-bond complex with n = 8	1689	2924	1513	2996

acids) of $-$OH group by $\Delta\nu \sim 90\,\mathrm{cm}^{-1}$ (at $\nu \sim 2924\,\mathrm{cm}^{-1}$) confirms the dissociation of inherent bonding dimeric form and stable formation of Hydrogen between mesogenic p-n-substituted octyloxybenzoic acid and nonmesogenic p-n-cyanophenol moiety. Hence, the compound so formed is viewed as a linear intermolecular alternating (i.e., along the long molecular axis) H bonded (double) complex capable of exhibiting LC nature.

Thermal Stability and Phase Variance

The LC phase variance and the corresponding transition temperatures as observed through polarized microscopic textures [9] and DSC during the heating and cooling scans in the present series of HBLC complexes (viz., nO.BA:CNΦOH:AB.On for $n = 3$ to 10) are presented in Table 2. A representative DSC thermogram for one of the HBLC complexes (say, for $n = 9$) recorded during the cooling and heating runs is presented in Fig. 3. The phase-transition temperatures determined from thermal microscopy are found to agree with the values of DSC. The data of total LC thermal stability and specified tilted LC phase stability exhibited by the free p-n-alkoxybenzoic acids along with the corresponding HB complexes reported [10,11] with them are presented in Table 3.

An overview of the results of phase-transition temperatures in Table 2 throws light on the trend of gradually increasing the thermal range of the nematic phase (~25°C) and the quenching of tilted smectic C (SmC) thermal range with increasing n value, (i.e., with increasing chain length as one goes from lower homologues to higher homologues). However, the observed abundance of the various phases exhibited by the present HBLCs reflects upon the increasing LC thermal range (to a maximum of ~29°C) with the increasing length of the flexible alkoxy end chain length of mesogenic moiety. This increase in the LC thermal stability is due to the prevalence of soft covalent interaction along the long molecular axis, which in turn results in the increasing length-to-breadth ratio of the core in the present case of intermolecular double H-bonding. The soft covalent interaction mediated H-bonding in these compounds also spreads symmetrically on either side of the cyanophenol moiety as shown in the molecular formula. Although the hydrogen bond direction is rather off the board (with regard to the phenol ring of mesogenic nO.BA moiety), this interaction is argued to spread along the long molecular axis of the mesogenic moiety. In summary, the nonmesogenic moiety here serves as a spacer between two mesogenic moieties. In contrast to other HBLC complexes reports [11–14] formed by p-n-alkoxy benzoic acids (Table 3), the double but, alternating intermolecular linear HBLC

TABLE 2 LC Phase Variance, Transition Temperatures, and Heats of Transition of HBLC Complexes (i.e., nO.BA::CNΦOH::AB.On for n = 3 to 10)

		Phase transition temperatures from TM and DSC (°C) and ΔH (J/gm)			
N	Phase variant	Iso-N	N-C/G	C-G	G-Cryst.
3	TM NG	120.4	113.2	—	83.0
		117.04	109.19	—	61.2
		[0.87]	[0.65]	—	[13.27]
4	NG	106.9	95.7	—	33.6
		105.02	90.73	—	$
		[0.57]	[0.43]	—	[0.02]
5	NG	102.1	81.4	—	35.1
		100.09	80.1	—	$
		[0.69]	[0.56]	—	—
6	NG	110.2	72.1	—	40.1
		109.1	69.91	—	$
		[0.59]	[0.51]	—	—
7	NCG	116.4	77.0	74.6	33.4
		115.1	76.4	75.0	$
		[0.68]	[1.7]	[#]	—
8	NCG	130.0	83.1	77.2	41.0
		128.53	80.32	71.3	$
		[0.22]	[0.48]	[1.7]	—
9	NCG	105.1	77.8	51.9	36.0
		101.3	73.7	48.93	$
		[0.10]	[4.0]	[10.21]	—
10	NCG	115.2	84.98	62.1	
		113.36	113.36	63.83	42.0
		[0.02]	[0.83]	[0.10]	—

#, no transition peak is observed.
$, transition peaks not resolved.
[] enthalpy value

complexes are found to exhibit maximum LC thermal phase stability. The occurrence of tilted smectic polymorphism (i.e., thermal range of SmC, SmG, etc.) is also profoundly influenced by the double H-bond formation rather than the single H-bonding in nO.BAs. As such, the present case also falls into the category of LCs that account for the predominance of tilted LC phases as contributed by the in-plane, outboard polarizability [15] observed with the LC homologues with odd numbers of methyline units. The melting temperatures of three-dimensional crystals into LC phases are also found to be depressed with a simultaneous induction [10] of the smectic G phase. Hence, the observations from Table 2 speak about the impact of double H bonding on the LC thermal stability toward enhanced operational

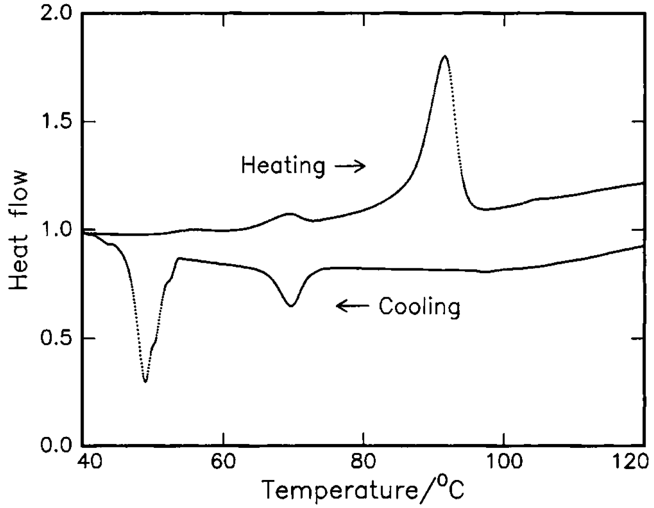


FIGURE 3 DSC thermogram of hydrogen-bonded LC complex (i.e., nO.BA::CNΦOH::AB.On) for n = 9 as representative.

viability at room temperature and to induce tilted LC phases (i.e., SmG phase). The odd–even effect [16] as contributed from axial polarizabilities, which is found [11–14] almost unfailing in the case of free nO.BAs at the LC clearing and three-dimensional crystal melting (into

TABLE 3 LC Phase Thermal Stability of nO.BAs and Their HB Complexes (Formed by Single and Double Hydrogen Bonding by nO.BAs as Meogenic Moiety)

					Single H-bond complexes with nO.BAs					
	nO.BA, Ref. [10]		Double H-bond, present work		Ref. [12]		Ref. [13]		Ref. [14]	
n	$(\Delta T)_{LC}$	$(\Delta T)_{tilt}$	$(\Delta T)_{LC}$	$(\Delta T)_{tilt}$	$(\Delta T)_{LC}$	$(\Delta T)_{tilt}$	$(\Delta T)_{LC}$	$(\Delta T)_{tilt}$	$(\Delta T)_{LC}$	$(\Delta T)_{tilt}$
3	9	—	37.4	40.2	19.8	19.8	50.6	50.6	22.9	22.9
4	13	—	73.3	62.1	3.3	3.3	48.9	48.9	49.3	49.3
5	27	—	67	46.3	52.2	52.2	36.2	36.2	38.1	23.5
6	48	—	60.1	32	22.2	1.9	38.7	38.7	57.6	17
7	54	6	83	43.6	25.7	44	36.2	28.1	56.2	26.7
8	46	7	89	42.1	56.7	38.2	24	24	80.2	69.7
9	49	23	69	41.8	29.9	12.9	27.8	27.8	80.1	35.9
10	45	25	73.2	41	31.9	27.8	20.7	20.7	54.2	36.6

LC phase) transitions, appears to be dominant at the interfaces involving three-dimensional crystal melting (into LC phase) only in the case of double HBLC complexes.

In the wake of the following observations, namely

1) increased overall LC thermal span,
2) increased nematic thermal span,
3) relative increments in the thermal stabilty of tilted LC phases,
4) induction of new tilted SmG-like phases,
5) enhanced operational viability with the shut down of LC phases at ambient temperatures, and
6) dominant odd–even effects at melting transition,

We conclude that

1) the present case of double H bonding increases the length-to-breadth ratio of the LC molecule with prevalently soft covalent interaction to result in the increase of mesogenic character, and
2) the double H-bond in the present case (which is tuned alternatively by the soft covalent interaction along the LC molecule's long axis) influences the axial polarizabilities to result in the pronounced odd–even effect observed at melting temperatures of HBLC complexes involving the growth of three-dimensional crystal.

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REFERENCES

[1] Suriyakala, R. & Pisipati, V. G. K. M. (2004). *Phase Trans.*, *77*, 281 and the references there in.

[2] Kato, T. & Kawakimi, T. (1997). *Chem. Lett.*, *211*; Kato, T. & Frechet, J. M. J. (1995). *Macro. Mol. Symposium.*, *98*, 311.

[3] Pasenkiewicz, G., Yakaoka, Y., Miyagawa, H., Kitamuro, K., & Kusumi, A. (1977). *J. Phys. Chem.*, *101*, 3677.

[4] (a) Etter, M. C. (1990). *Acc. Chem. Res.*, *23*, 120; (b) Whitesides, G. M., Mathias, J. P., & Seto, C. T. (1991). *Science*, *254*, 1312; (c) Lehn, J. M. (1988). *Angew. Chem. Intl. Ed. Engl.*, *27*, 89.

[5] Kato, T. & Frechet, J. M. J. (1989). *J. Am. Chem. Soc.*, *111*, 8533.

[6] (a) Demus, D. (1976). In: *Non-emissive Electro-Optic Displays*, Knetz, A. R. & von willison, E. K. (Eds.), Plenum Press: New York, p. 94; (b) Mosley. (1993). *Displays*, *14*(2), 67; (c) Goodby, J. W., Osipov, M. A., Blinc, R., Clark, N. A., Lagerwall, S. T., Osopov, S. A., Pikin, S. A., Sakurai, T., Yushino, K., & Zeks, B. (1991). In: *Ferroelectric Liquid Crystals, Principles, Properties and Applications*, Gordon and Breach: Philadelphia.

[7] Kumar, P. A., Srinivasulu, M., & Pisipati, V. G. K. M. (1998). *Liq. Cryst.*, *26*, 859.

[8] Nakamoto, K. (1978). In: *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 4th ed., InterScience: New York.

[9] Gray, G. W. & Goodby, J. W. (1984). In: *Smectic Liquid Crystals: Textures and Structures*, Leonard Hill: London.

[10] Kumar, P. A., Srinivasulu, M., & Pisipati, V. G. K. M. (1999). *Liq. Cryst.*, *26*, 1339.

[11] Sideratou, Z., Tsiourvas, D., Paleos, C. M., & Skoulios, A. (1997). *Liq. Cryst.*, *22*, 51.

[12] Kumar, P. A., Pisipati, V. G. K. M., Rajeswari, A. V., & Sastry, S. S. (2002). *Z. Naturforsh.*, *57a*, 184.

[13] Swathi, P., Sastry, S. S., Kumar, P. A., & Pisipati, V. G. K. M. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 523.

[14] Srinivasulu, M., Satyanarayana, P. V. V., Kumar, P. A., & Pisipati, V. G. K. M. (2001). *Z. Naturforsch.*, *56a*, 685.

[15] Luckhurst, G. R. & Gray, G. W. (1979). In: *The Molecular Physics of Liquid Crystals*, Academic Press, Chap. 12, 267, 275.

[16] Marcelja, S. (1974). *J. Chem. Phys.*, *60*, 3599.