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Induced smectic G phase through intermolecular hydrogen bonding

POLURI A. KUMAR, M. SRINIVASULU and VENKATA G. K. M. PISIPATI*

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences,
Nagarjuna University, Nagajunanagar 552 510, India

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A new series of mesomorphic complexes formed through intermolecular hydrogen bonding between *p*-*n*-alkoxybenzoic acids (where alkoxy denotes chains from propoxy- to decyloxy- and dodecyloxy-) and non-mesogenic *p*-hydroxybutyl benzoate, have been synthesized and characterized by thermal microscopy, differential scanning calorimetry, infrared spectroscopy (IR) and ¹H NMR studies. A detailed IR spectral investigation in the solid state and in solution suggests that the acid and phenol groups are complementary to each other, each acting as both proton donor and proton acceptor. The results of comparative thermal analyses of both free *p*-*n*-alkoxybenzoic acids and H-bonded complexes exhibited an induced crystal smectic G phase in the complexes throughout the series, its thermal range increasing with alkoxy carbon number.

1. Introduction

Hydrogen bonds, usually considered as the fifth fundamental type of chemical interaction, have attracted much attention in recent years owing to their importance as powerful tools for self-assembling molecules [1]. Despite their low bond energy, these hydrogen bonds are of great significance both in biochemical systems and normal chemical reactions. Since the first discovery of a H-bonded liquid crystal compound by Kato *et al.* [2], many other materials, including liquid crystals (LCs) [3–7] and ferroelectric liquid crystals (FLCs) [8, 9], have been reported. Because of their low bond and activation energies H-bonded complexes play a crucial part in many reactions at normal temperatures. Further, these intermolecular systems have a striking effect on physical properties such as melting point, boiling point and enthalpies of vaporization and sublimation, etc. These interesting aspects have motivated us to undertake systematic studies regarding the synthesis and characterization of some intermolecular H-bonded complexes. As part of a research programme on the synthesis [10] and characterization [11, 12] of LC and FLC materials, the present communication deals with the synthesis and properties of a new series of liquid crystalline complexes involving intermolecular H-bonding between mesogenic *p*-*n*-alkoxybenzoic acids and the non-mesogenic *p*-hydroxybutyl benzoate (figure 1).

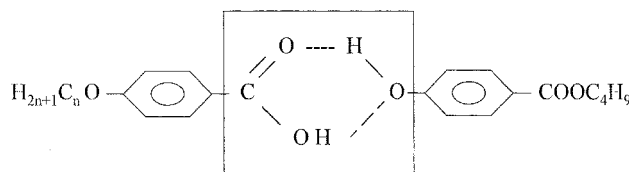


Figure 1. Molecular structure of intermolecular H-bonded complexes with $n = 3$ to 10 and 12.

2. Experimental

2.1. Materials and instrumentation

All the substituted *p*-alkoxybenzoic acids (of 99.9% purity) were supplied by Frinton Laboratories, New Jersey, USA; *p*-hydroxybutyl benzoate was purchased from BDH, Bombay, India. Pyridine was purified by standard literature methods [13]. The IR spectra on the solid and its solution were recorded on a JASCO-5300 FTIR spectrometer. The ¹H NMR spectra in DMSO-*d*₆ were obtained on a Jeol-GSX 400 (400 MHz) multinuclear spectrometer. Optical textural observations were carried out by thermal microscopy with a Hertel-Reuss (super pan-II) polarizing microscope equipped with a PC-monitored Instec (Boulder) mk 1 heating stage. Differential scanning thermograms were recorded on a Perkin-Elmer DSC-7 instrument.

2.2. Synthesis of intermolecular hydrogen bonded complexes

The intermolecular H-bonded complexes were synthesized by mixing the appropriate *p*-*n*-alkoxybenzoic acid

* Author for correspondence.

(20 mmol) and *p*-hydroxybutyl benzoate (3.3 g, 20 mmol) in absolute pyridine (~20 ml); the mixture was stirred for ~6 h at room temperature. White crystalline crude complexes were obtained by removing the pyridine by distillation under reduced pressure. The crude complexes were then recrystallized from hot dichloromethane solution and dried over calcium chloride in a desiccator at room temperature. The yields obtained were ~88%.

3. Results and discussion

3.1. Intermolecular hydrogen bonding

The room temperature IR spectra of *p*-*n*-alkoxybenzoic acids, *p*-hydroxybutyl benzoate and their intermolecular H-bonded complexes were recorded both in the solid (KBr pellet) and solution (chloroform) states. The infrared frequencies (only pertinent bands) along with their assignments are summarized in table 1. The solid state spectra of the free alkoxybenzoic acids show two sharp bands at 1685 and 1695 cm^{-1} due to the $\nu(\text{C}=\text{O})$ mode and a strong intense band at 3032 cm^{-1} assigned to the $\nu(\text{OH})$ mode of the carboxylic acid group. The doubling feature of this stretching mode may be attributed to the dimeric nature of the substituted benzoic acid at room temperature [14]. The IR spectrum (KBr pellet) of *p*-hydroxybutyl benzoate shows characteristic bands for $\nu(\text{C}-\text{O})_{\text{phenolic}}$ (~1289 cm^{-1}), $\nu(\text{OH})$ (3320 cm^{-1}) and $\nu(\text{C}=\text{O})_{\text{ester}}$ (1689 cm^{-1}) stretching modes [14]. The hypsochromic shifts in the $\nu(\text{C}=\text{O})$ of acid (~20 cm^{-1}) and $\nu(\text{OH})$ of ester (~50 cm^{-1}), and the bathochromic shift in the $\nu(\text{C}-\text{O})_{\text{phenolic}}$ mode of ester (~25 cm^{-1}) in the present 1:1 complexes, suggest the formation of intermolecular H-bonding between the $-\text{COOH}$ group of the *p*-alkoxybenzoic acid and the $-\text{OH}$ group of *p*-hydroxybutyl benzoate; both groups can form complementary H-bonding so as to accept as well as donate protons from each other. The presence

of H-bonding in the present complexes was further implied by hypsochromic shifts (~40 cm^{-1}) of the OH stretching mode of the acid group in the IR spectra of the complexes. A noteworthy feature in the IR spectra is the appearance of a sharp band at ~1712 cm^{-1} and the disappearance of the doubling nature of the $\nu(\text{C}=\text{O})$ mode of the benzoic acid. This implies that the dimeric nature of the benzoic acid disappears upon complexation.

The degree of stabilization of intermolecular H-bonding was further studied by observations in chloroform solution. The spectra showed the reappearance of the stretching modes of the acidic $>\text{C}=\text{O}$ group and of the $-\text{OH}$ group of the ester (figure 2) suggesting the destruction of H-bonding in solution [15].

Spectral evidence for the absence of intermolecular H-bonding in solution was also obtained by measuring ^1H NMR spectra in $\text{DMSO}-d_6$ solution at room temperature. The ^1H NMR spectra of the complexes show signals due to the $-(\text{CH}_2)_n-$, $-\text{CH}_3$ and $-(\text{C}_6\text{H}_4)$ groups of both acid and ester moieties at their expected order of multiplicities. A broad signal appearing at ~12.5 δ (with its integration equal to one proton) due to $-\text{OH}$ of the ester moiety confirms the absence of intermolecular H-bonding in solution.

3.2. Thermal studies

The phase identification and phase variants of the present series of compounds were determined [16] by cooling the isotropic melt at a rate of 0.1 $^\circ\text{C min}^{-1}$, using a polarizing microscope with a temperature controller system. The phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. The phase variants and the transition temperatures of both the *p*-alkoxybenzoic acids and their analogue complexes are given in tables 2 and 3.

Table 1. IR spectral data (cm^{-1}) of intermolecular H-bonded complexes.

Compound ^a	$\nu(\text{C}=\text{O})$		$\nu(\text{C}-\text{O})_{\text{phenolic}}$	$\nu(\text{OH})$
	Acid moiety	Ester moiety		
<i>p</i> -Octyloxybenzoic acid	1685, 1695	—	—	—
<i>p</i> -Hydroxybutyl benzoate	—	1689	1289	3320
I	1712	1685	1260	3460
II	1712	1685	1263	3472
III	1713	1683	1265	3476
IV	1712	1689	1263	3467
V	1712	1681	1264	3474
VI	1715	1681	1264	3461
VII	1716	1685	1264	3467
VIII	1714	1683	1265	3472
IX	1712	1683	1259	3475

^a I–IX represents the alkyl chain length: propyl-, butyl-, pentyl-, hexyl-, heptyl-, octyl-, nonyl-, decyl- and dodecyl-, respectively.

Table 2. Thermal microscopy and DSC data for *p-n*-alkoxybenzoic acids.

Acid	Phase variant	Phase transition temperatures/ $^{\circ}\text{C}$ by TM and [DSC($\Delta H/J^{-1} \text{g}^{-1}$)]		
		I-N	N-C	N/C-Cr
I	N	154.9 [158.8 (10.0)]	—	145.2 [150.6 (79.8)]
II	N	160.1 [160.5 (12.6)]	—	147.1 [149.9 (92.7)]
III	N	151.4 [153.5 (10.5)]	—	123.9 [123.6 (92.4)]
IV	NC	153.8 [155.1 (11.0)]	—	105.1 [109.3 (56.1)]
V	NC	146.8 [148.7 (6.7)]	98.3 [99.2 (5.2)]	91.8 [94.8 (104.4)]
VI	NC	147.5 [150.4 (8.4)]	97.8 [100.3 (4.0)]	101.9 [104.5 (41.0)]
VII	NC	142.9 [141.3 (9.5)]	117.1 [113.2 (6.2)]	94.5 [95.1 (148.6)]
VIII	NC	138.3 [135.1 (9.4)]	115.6 [111.4 (3.3)]	97.0 [95.7 (25.3)]
IX	NC	137.2 [136.4 ^a]	128.9 [136.4 ^a]	95.1 [94.4 (127.3)]

^a The transitions peaks are not resolved.

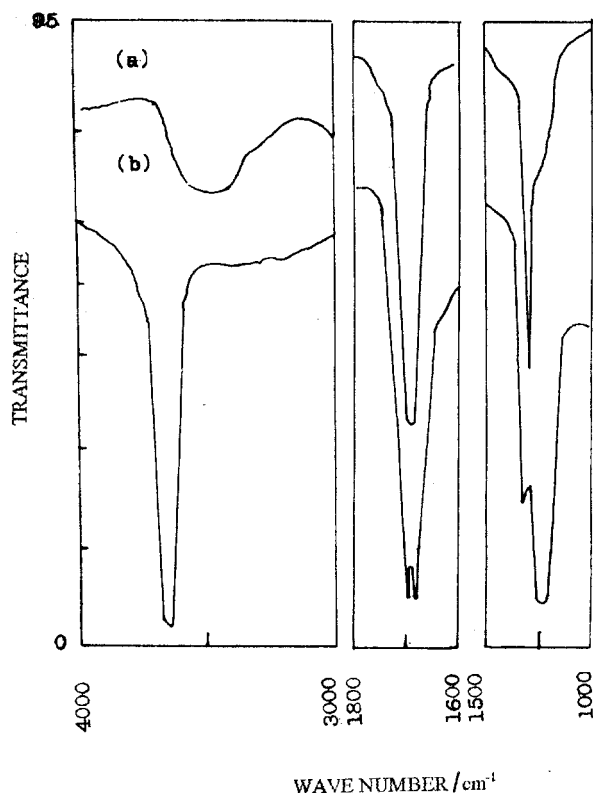


Figure 2. IR spectra of a representative complex ($n = 10$): (a) in solid state (KBr pellet) and (b) in chloroform solution.

The optical microscopic observations revealed that *p-n*-alkoxybenzoic acids exhibit nematic (marble) as the unique mesophase in the lower homologues (number of

carbon atoms in alkoxy group, $n = 3$ to 6); in higher members of the series, the thermal distribution of the smectic C phase increases with the simultaneous quenching of the nematic phase [6].

Phase diagrams were constructed from the transition temperatures observed by thermal microscopy. Figures 3 and 4 illustrate the phase behaviour of the free *p-n*-alkoxybenzoic acids and the analogous complexes, respectively. Figure 4 shows that the smectic C and smectic G phases are dominant in the compounds from complex-VI to -IX while the nematic is the major phase for complex-III to -VII. Complex-VII showed all three phases (N, SmC and SmG) with maximum thermal ranges. The transition temperatures across the series show an odd-even effect.

4. Conclusion

The experimental results on the new complexes reveal the following salient features:

- (1) The smectic-G phase with a smooth multicoloured mosaic texture (figure 5) is induced in all the complexes.
- (2) In the case of complex-I, a direct smectic G phase is observed on cooling from the isotropic melt, bypassing the nematic phase present in the analogue acid.
- (3) In all the complexes, the nematic and smectic C phases exhibit threaded marble ($n = 7$ to 10) and schlieren brushes textures ($n = 7$ to 10 and 12), respectively.

Table 3. Thermal microscopy and DSC data for intermolecular H-bonded complexes.

Complex	Phase variant	Phase transition temperatures/ $^{\circ}\text{C}$ by TM and [DSC($\Delta H/J\text{ g}^{-1}$)]			
		I-N/C/G	N-C/G	C-G	G-Cr
I	G	142.6 [140.4 (50.7)]	—	—	110.1 [122.9 (25.6)]
II	NG	142.6 [138.2 (1.5)]	130.1 [^a]	—	126.4 [132.5 (65.4)]
III	NG	138.9 [139.3 (1.0)]	116.2 [^a]	—	110.5 [124.3 (80.2)]
IV	NG	146.1 [142.7 (9.7)]	97.9 [107.2 (48.5)]	—	96.7 [76.2 (22.7)]
V	NCG	138.6 [135.0 (2.2)]	91.3 [89.3 ^b]	90.5 [88.4 ^b]	90.1 [96.3 (102.9)]
VI	NCG	138.5 [140.3 (0.4)]	120.4 [119.8 (0.26)]	98.2 [^a]	61.0 [102.0 (43.2)]
VII	NCG	120.4 [115.5 (3.4)]	107.6 [104.0 (7.7)]	92.0 [^a]	71.4 [87.7 (73.4)]
VIII	NCG	114.4 [119.5 ^b]	107.8 [116.1 ^b]	95.0 [97.7 (15.6)]	79.2 [88.3 (35.4)]
IX	CG	111.0 [113.6 (19.0)]	—	90.1 [^a]	65.7 [81.2 (31.1)]

^a No transition peak observed in DSC.

^b The transition peaks were not well resolved.

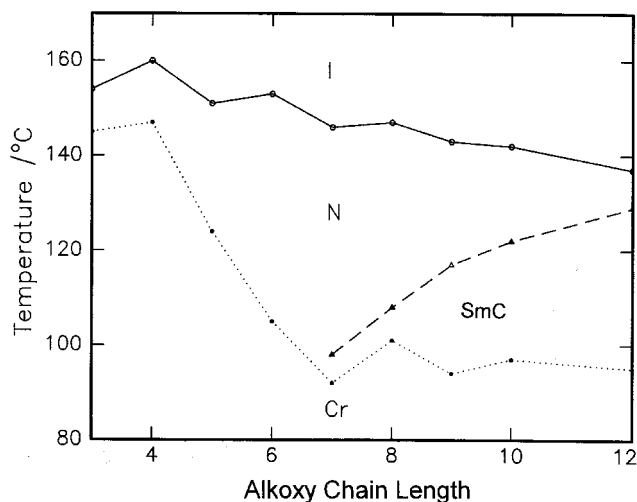
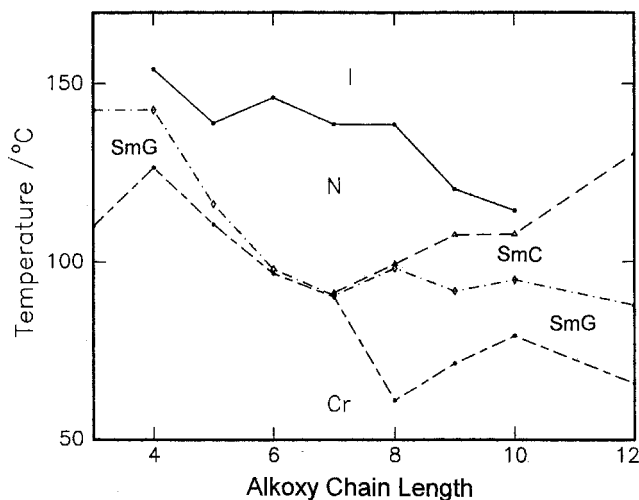
Figure 3. Phase diagram of *p-n*-alkyloxybenzoic acids.

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

- (4) It is observed that the thermal range of the nematic phase increases from complex-I to -IV, decreases from complex-V to -VIII, and is finally lost in complex-IX (table 3).
- (5) In general, the clearing points for a related series of compounds increase with increasing alkoxy carbon number, owing to increasing dispersive force. However, in the present complexes the clearing points decrease as the alkoxy chain length increases. This anomaly in the observed trend of clearing points may be attributed to the inverse stability of H-bonding vs. chain length.

- (6) The presence of new phase variants, viz. I-SmG, I-SmC and N-SmG in these complexes may best be interpreted at the molecular level in terms of the enhanced polarity across the molecular length achieved by the incorporation of an additional transverse dipole ($>\text{C}=\text{O}$ group) [16]. This approach can also provide a possible explanation of the induction of a three dimensional SmG phase.
- (7) The mesomorphic behaviour (thermal range of liquid crystallinity) of the complexes is enhanced compared with the free acids (figure 3).

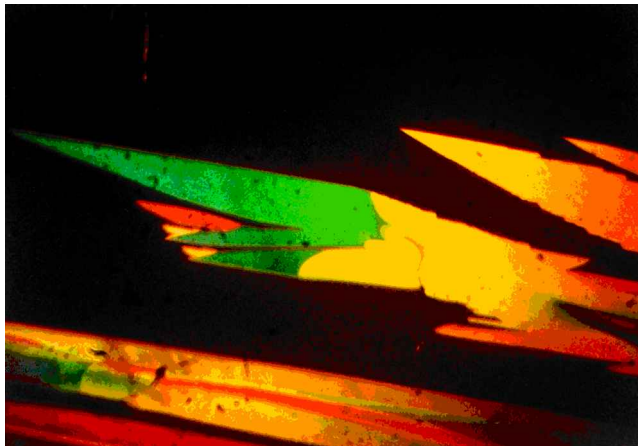


Figure 5. Smooth mosaic texture of smectic G phase.

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