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Induced crystal G phase through intermolecular hydrogen bonding II. Influence of alkyl chain length of *n*-alkyl *p*-hydroxybenzoates on thermal and phase behaviour

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A new series of intermolecular hydrogen-bonded complexes have been synthesized using *p*-*n*-alkoxybenzoic acid (alkyl chain length varies from propyl- to decyl- and dodecyl-) and methyl *p*-hydroxybenzoate moieties. The thermal and phase behaviour of these complexes were studied by thermal microscopy and differential scanning calorimetry. Further, the stabilization of intermolecular hydrogen bonding in solution was studied by IR spectroscopy. A detailed IR spectral investigation in the solid and dissolved states suggests that the acid and phenol groups act as proton donor and proton acceptor, respectively. The thermal studies also reveal the inducement of a crystal G phase in the complexes.

1. Introduction

Because of their role as powerful tools for assembling molecules [1] and building organized molecular structures in biological systems [2, 3], considerable recent attention has been focused on the design and synthesis of new types of complexes involving intermolecular hydrogen bonding. This non-covalent interaction, with low bond energy, shows a pronounced impact on thermal properties, viz. melting points, enthalpies of vaporization and phase behaviour. Since Kato *et al.* [4] synthesized a new liquid crystal induced by intermolecular H-bonding between a substituted pyridine and a carboxylic acid, many other H-bonded materials including monomer liquid crystals (LCs), polymer liquid crystals [4–9] and ferroelectric liquid crystals (FLCs) [10, 11] have been reported. The literature on such intermolecular H-bonded complexes shows that the donor and/or proton acceptor molecules are not always themselves mesogenic. If one of the molecules is non-mesogenic, then the inducement of new phases and their thermal behaviour can be attributed without ambiguity to intermolecular H-bonding. In continuation of our earlier work on H-bonded complexes of butyl *p*-hydroxybenzoate (part I of this series [12]) and on other LC and FLC materials [13–15], we report here a new series of liquid crystalline complexes involving intermolecular hydrogen bonding between a *p*-*n*-alkoxybenzoic acid (mesogen) and methyl *p*-hydroxybenzoate (non-mesogen) (figure 1); the results are discussed in the light of the phase behaviour of the reported series of analogues.

2. Experimental

p-Alkoxybenzoic acids (99.9% purity) were supplied by Frinton Laboratories, New Jersey, USA; methyl *p*-hydroxybenzoate was purchased from CDH, Bombay, India.

IR spectra (solid and dissolved states) were recorded on a JASCO-5300 FTIR spectrometer. Optical textural observations were carried out using a Hertel-Reuss (super pan-II) polarizing microscope equipped with a PC-monitored Instec (Boulder) mk1 heating stage. The differential scanning thermograms were recorded on a Perkin-Elmer DSC-7. The present intermolecular H-bonded complexes were sythesized as reported earlier [12].

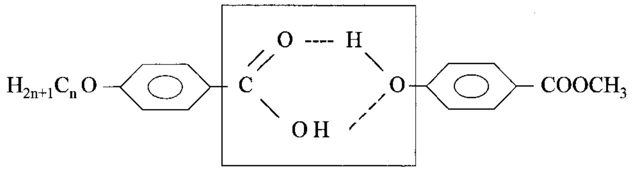

Figure 1. Molecular structure of intermolecular H-bonded complexes with $n = 3$ to 10 and 12.

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3. Results and discussion

The H-bonded complexes are white crystalline solids and are stable at room temperature. All the complexes are soluble in chloroform, dichloromethane, dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

3.1. *Infrared spectra*

The IR spectra of the *p*-*n*-alkoxybenzoic acids, methyl *p*-hydroxybenzoate and their intermolecular H-bonded complexes were recorded both in the solid (KBr) and dissolved (chloroform) states at room temperature. The infrared frequencies (only pertinent bands) along with their assignments are summarised in table 1. The solid state spectra of free alkoxybenzoic acids show two sharp bands at 1685 and 1695 cm^{-1} due to the ν(C=O) mode. The doubling feature of this stretching mode confirms the dimeric nature of the benzoic acid at room temperature [16]. Further, a strong intense band appearing at 3012 cm^{-1} is assigned to the ν(OH) mode of the carboxylic acid group. The IR spectrum (KBr) of methyl *p*-hydroxybenzoate shows characteristic bands for $\nu(\mathrm{C{-}O})_{\mathrm{phenolic}}$ (~ 1285 cm^{-1}), ν(OH) (3315 cm^{-1}) and $\nu(\mathrm{C{=}O})_{\mathrm{ester}}$ (1684 cm^{-1}) stretching modes [16]. The hypsochromic shift in the ν(C=O) of acid (~ 50 cm^{-1}) and bathochromic shift in the $\nu(\mathrm{C{-}O})_{\mathrm{phenolic}}$ mode of ester (~ 25 cm^{-1}) and ν(OH) (~ 30 cm^{-1}) mode of acid, in the present series, suggest the formation of intermolecular H-bonding between the −COOH group of *p*-hydroxybenzoic acid and the −OH group of methyl *p*-hydroxybenzoate. The presence of H-bonding in the present complexes was further inferred from the absence of a band at 3315 cm^{-1} due to the ν(OH) mode of ester and the appearance of a new band diagnostic of a ν(H---OH) mode at ~ 2552 cm^{-1} [16]. A noteworthy feature is the appearance of a sharp band at ~ 1712 cm^{-1} and the disappearance of the doubling nature of the ν(C=O) mode of benzoic acid. This implies that the dimeric nature of the benzoic acid transforms to a monomeric form upon complexation.

The degree of stabilization of intermolecular H-bonding was further studied by recording spectra of the complexes in chloroform solution. The spectra show the reappearance of the stretching modes of the > C=O acid group and the −OH ester group suggesting the destruction of H-bonding in solution [17].

3.2. *Thermal and phase behaviour*

The phase variants (and their transition temperatures) of free *p*-*n*-alkoxybenzoic acids and their corresponding complexes (tables 2 and 3) were determined [18] from textural observations by thermal microscopy (TM) under a polarizing microscope using a heating or cooling rate of 0.1°C min^{-1}. The free *p*-*n*-alkoxybenzoic acids exhibit the nematic (marble) as the unique mesophase in the lower homologues ($n = 3$ to 6) and the smectic C phase (schlieren) in higher members of the series [8].

On cooling from the isotropic melt, the present series of compounds exhibited the formation of nematic droplets which on further cooling proceeded to the formation of a threaded nematic texture. The transition from the nematic to smectic C phase shows schlieren ($n = 12$) and broken focal-conic fan ($n = 7$ to 10) textures. On further cooling, the appearance of a smooth multicoloured mosaic texture implies inducement of the G phase in the complexes.

Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms (table 3).

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

Compound[a]	ν(C=O) Acid moiety	ν(C=O) Ester moiety	$\nu(\mathrm{C{-}O})_{\mathrm{phenolic}}$	$\nu(\mathrm{OH})_{\mathrm{acid}}$
p-Octyloxybenzoic acid	1685, 1695	—	—	3012
Methyl *p*-hydroxybenzoate	—	1689	1289	—
I	1710	1680	1251	2985
II	1712	1682	1255	2987
III	1712	1683	1259	2984
IV	1710	1693	1248	2987
V	1708	1682	1255	2987
VI	1709	1693	1253	2987
VII	1710	1685	1255	2984
VIII	1712	1684	1255	2986
IX	1710	1687	1257	2986

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

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

		Phase transition temperatures/°C of TM and [DSC (ΔH/J g^{-1})]		
Acid	Phase variant	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.

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

		Phase transition temperatures/°C of TM and [DSC (ΔH/J g^{-1})]			
Complex	Phase variant	I–N/C/G	N–C/G	C–G	G–Cr
I	NG	142 [131.4 (76.4)]	140	—	112 [102.1 (41.31)]
II	NG	146 [142.3 (1.2)]	139 [134.2 (80.4)]	—	115 [53.2 (16.9)]
III	NG	135 [134.5 (2.0)]	108 [115.5 (67.9)]	—	105 [[a]]
IV	NG	142 [125.9 (.7)]	96 [91.6 (49.9)]	—	68 [[a]]
V	NCG	137 [137.0 (4.2)]	89 [89.7 (1.0)]	88 [86.6 (1.3)]	87 [83.3 (95.6)]
VI	NCG	138 [135.9 (1.7)]	102 [91.8[b]]	100 [90.5[b]]	65 [47.3 (48.5)]
VII	NCG	129 [120.3 (5.4)]	105 [104.4 (4.3)]	93 [88.5 (31.5)]	89 [62.9 (83.0)]
VIII	NCG	129 [127.3 (6.1)]	104 [104.1 (2.9)]	94 [89.0 (35.1)]	76 [71.1 (25.1)]
IX	CG	125 [125.3 (20.1)]	—	87 [83.1 (33.3)]	65 [65.9 (12.8)]

[a] No transition peak is observed in DSC.
[b] The transition peaks are not well resolved.

The data revealed that the thermal distribution of the smectic C increases with the simultaneous quenching of the nematic phase [8].

The phase diagrams were constructed from the temperatures transition observed from thermal microscopy. Figures 2 and 3 illustrate the phase behaviour of the

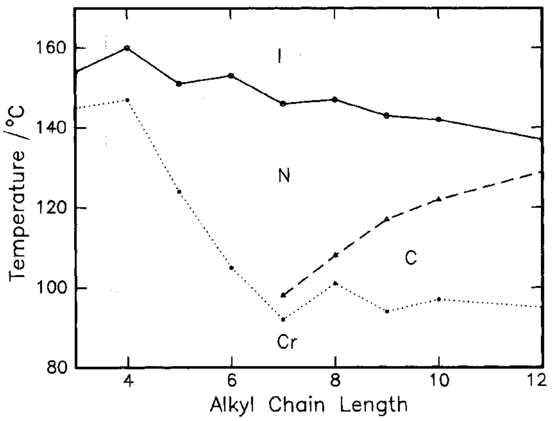

Figure 2. Phase diagram of *p*-*n*-alkoxybenzoic acids.

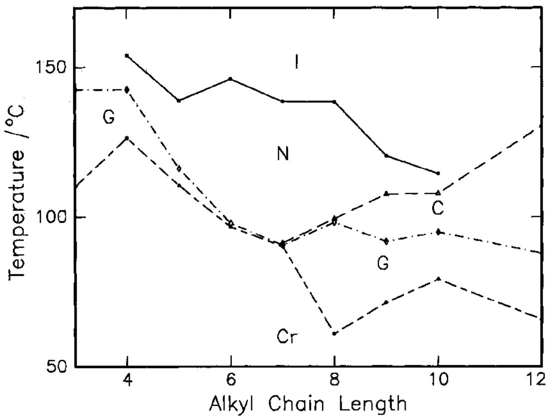

Figure 4. Phase diagram of reported intermolecular H-bonded complexes of butyl *p*-hydroxy benzoate.

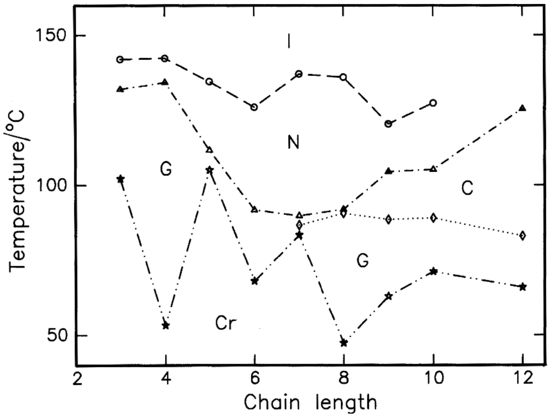

Figure 3. Phase diagram of intermolecular H-bonded complexes.

free *p*-*n*-alkoxybenzoic acids and the analogous complexes, respectively. Figure 3 shows that the smectic C and G phases are more dominant in the complexes VI to IX while the nematic is the major phase for complex III to VII. Further, complex III shows a wide thermal range for the induced G phase. Complex VIII shows all three phases (N, SmC and G) with maximum thermal ranges. Moreover, the transition temperatures across the series show an odd–even effect.

A comparative study with the phase behaviour of the reported analogous butyl *p*-hydroxybenzoate series [12] (figure 4) has been made to estimate the influence of the end chain length of the benzoate moiety on the mesomorphic behaviour and degree of stabilization of the newly induced G phase. From the phase diagrams (figures 3 and 4), it appears that the present series shows a wider liquid crystalline thermal ranges than the previous analogous complexes. Further, the impact of the chain length of the ester moiety is significant in the early members of the series ($n = 3$ to 7). Figure 3 shows the appearance of wide thermal ranges for the G phase in the present series when n is even. On the other hand, in the previously reported analogues (figure 4) the thermal range is narrow until the carbon chain length reaches seven. This provides substantial evidence towards the significant role of the ester end chain. However, it is interesting to note that the phase behaviour of complex V ($n = 7$) of both series is critical in the sense that the smectic C and G phases have very narrow ranges exactly matching the phase profile of the free *p*-*n*-alkoxybenzoic acid (figure 2). In other words, the alkyl chain length of the benzoic acid moiety has a pronounced effect on the phase behaviour of complex V.

4. Conclusion

Thermal analysis shows that a G phase with a smooth multicoloured mosaic texture (figure 5) is induced in all the complexes studied. Complex I exhibits a wide thermal range (32°C) G phase, as compared with the previously reported analogous series. Further, it is observed that the complexes with even alkyl carbon number show wide thermal ranges of the induced phase. Thermal studies also confirm the presence of new phase transitions, viz. I–G, I–SmC and N–G in the complexes, as compared with the free *p*-*n*-alkoxybenzoic acids. This can best be explained on the basis of a significant contribution from an additional transverse dipole (>C=O group) of the ester moiety which in turn enhances the polarity across the molecular length [18]. This approach provides a possible explanation of the inducement of a three-dimensional G phase.

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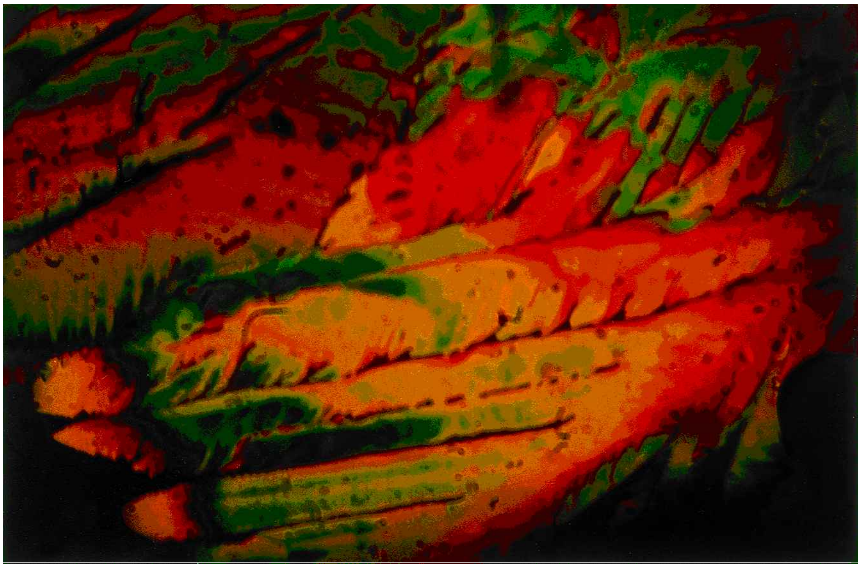

Figure 5. Smooth mosaic texture of the G phase.

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