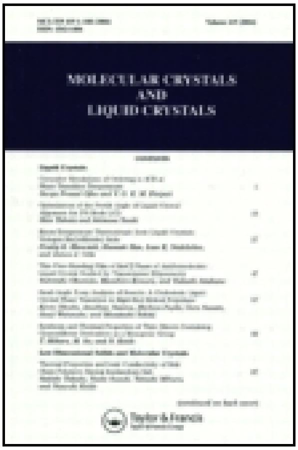

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Induced Smectic-G Phase Through Intermolecular H-Bonding: Part III. Influence of Alkyl Chain Length of p-n-Alkoxybenzoic Acids on Thermal and Phase Behaviour

Pisupati Swathi [a], S. Sreehari Sastry [a], P. A. Kumar [b] & V. G.K.M. Pisipati [b]

[a] Department of Physics, Nagarjuna University, Nagarjuna Nagar, 522 510, India

[b] Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar, 522 510, India

To cite this article: Pisupati Swathi, S. Sreehari Sastry, P. A. Kumar & V. G.K.M. Pisipati (2001): Induced Smectic-G Phase Through Intermolecular H-Bonding: Part III. Influence of Alkyl Chain Length of p-n-Alkoxybenzoic Acids on Thermal and Phase Behaviour, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 523-533

To link to this article: http://dx.doi.org/10.1080/10587250108025332

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 523-533
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Induced Smectic-G Phase Through Intermolecular H-Bonding: Part III. Influence of Alkyl Chain Length of *p-n*-Alkoxybenzoic Acids on Thermal and Phase Behaviour

PISUPATI SWATHI[a], S. SREEHARI SASTRY[a], P.A. KUMAR[b] and V.G.K.M. PISIPATI[b]*

[a]*Department of Physics, Nagarjuna University, Nagarjuna Nagar 522 510 India and* [b]*Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar 522 510 India*

A novel series of intermolecular hydrogen bonding complexes have been synthesized by using *p-n*-alkoxybenzoic acids (alkyl chain length varies from propyl- to decyl and dodecyl-) (ABA) and a non-mesogenic moiety, 2-amino-5-chloro-pyridine (ACP), The thermal and phase behaviour of these complexes are studied by thermal microscopy (TM) and differential scanning calorimetry (DSC) techniques. The stabilization of intermolecular hydrogen bonding is studied by IR spectra. A detailed IR spectral investigation in solid and solution states suggest that both acid and pyridine nitrogens are complementary to one another by acting as proton donor and acceptor respectively. The comparative thermal studies with free benzoic acids and the corresponding analogous hydrogen bonded complexes reveal the inducement of a monotropic smectic-G phase with simultaneous quenching of nematic and smectic-C phases.

Keywords: hydrogen bonding; smectic-G; phase behaviour

---

* Corresponding author.

INTRODUCTION

Despite the fact that the influence of the chemical interactions involving inter- and intramolecular hydrogen bonding has a striking influence on the mesomorphic behaviour, a considerable current interest has been focussed on the isolation of novel H-bonded liquid crystal materials[1-6]. Owing to their low bond energies and activation energies, these non-covalent interactions have pronounced impact on the induction and/or quenching of novel mesophases and their thermal distribution [7-9]. Nevertheless, the proton donor and acceptor capabilities of the functional groups and/or atoms which are being involved in the hydrogen bonding certainly show remarkable contributions towards the inducement of new phases.

Our previous investigations on two novel series[7] of H-bonded liquid crystalline systems involving ABA and *p*-hydroxy alkylbenzoates revealed that the induced smectic-G phase is equally distributed across the series in the higher homologues with simultaneous quenching of smectic-C phase. The detailed IR and NMR studies[7] confirmed that the –COOH and –OH groups are complementary to one another to act as proton donor and acceptor. Considering the scope of exploring the role of proton donor and acceptor capabilities of groups involved in H-bonding towards the thermal and phase behaviour of a newly induced phase, the present communication deals with the synthesis and characterization of phase behaviour of a novel series of liquid crystalline materials involving intermolecular hydrogen bonding between mesogenic *ABA* and the non-mesogenic ACP (figure1).

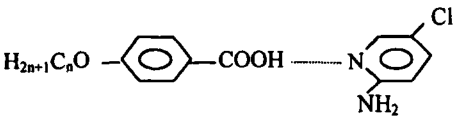

FIGURE 1 Molecular structure of ABA:ACP

EXPERIMENTAL

Materials and Methods

All the substituted *p-alkoxy benzoic* acids (of 99.9% purity) are supplied by Frinton Laboratories, New Jersy, USA. The non mesogen, 2-amino-5-chloro pyridine is purchased from Sigma Chemical Company, USA. The solvents used in the present study are of E. Merck grade and are used as such without further purification. The IR spectra (solid and solution states) are recorded on a Perkin Elmer (BX Series) FTIR spectrometer. Optical textural observations are carried out by thermal microscopy with an Olympus BX 50 supplemented by optical display (DP 10). Differential scanning thermograms are recorded on a Perkin Elmer DSC- 7.

Synthesis of Intermolecular Hydrogen Bonding Complexes

The intermolecular hydrogen bonded complexes are synthesized by mixing together appropriate *p*-*n*-alkoxy benzoic acid (20 mmol) and 2-

amino-5-chloro pyridine (20 mmol) in absolute pyridine in (~ 20 ml). The mixture is stirred for ~ 6h at room temperature. After removing the excess pyridine by vaccum distillation under reduced pressure, a white crystalline product is obtained. The crude complexes are then recrystallized from hot dichloromethane solution to get a yield of 88%.

RESULTS AND DISCUSSION

IR Spectra

The room temperature IR spectra of ABA, ACP and their H-bonded complexes are recorded both in solid (KBr) and solution (chloroform) states. The infrared frequencies of the pertinent bands are summarized in table 1. The KBr spectra of free *p*-*n*-alkoxybenzoic acids show two sharp bands at 1685 and 1695 cm^{-1} due to ν(C=O) mode and a strong intense band at 3032 cm^{-1} assigned to ν(OH) mode of carboxylic acid group. This doubling nature of ν(C=O) mode may be attributed to the dimeric nature of the acid group at room temperature [10]. The corresponding spectra in the solution state (chloroform) show a strong intense band suggesting the existence of monomeric form of benzoic acid in the solution state. To avoid further complications arising due to such intermolecular interactions, comparison of spectra of complexes are made with the solution spectra of the free *ABA*. A noteworthy feature in the spectra of complexes is the appearance of a sharp band at ~ 1680 cm^{-1} and non-occurrence of the doubling nature of ν(C=O) mode of benzoic acid moiety. This clearly suggests that the dimeric nature of benzoic acid dissociates and prefers to exist in a monomeric form upon complexation.

The IR spectrum (KBr) of ACP shows two bands of medium intensity at 3152, 3295 cm^{-1} due to symmetric and asymmetric stretching modes, respectively of NH_2 group and two strong bands at 669 and 639 cm^{-1} are assigned to pyridine ring deformation modes [10].

TABLE 1 IR Spectral data (cm^{-1}) of ABA:ACP complexes

Compound/ Complex	$\nu(NH)_{sym}$	$\nu(NH)_{asym}$	$\nu(OH)$	$\nu(CO)$	Pyridine deformation modes	
					in plane	out plane
OBA(KBr)	---	---	3032	1685, 1695	---	---
OBA (CH_3Cl)	---	---	3040	1712		
ACP	3295	3455		---	639	669
I	3291	3445	3148	1679	640	695
IV	3288	3454	3146	1683	647	701
VIII	3285	3445	3148	1687	648	695

OBA = *p*-octyloxybenzoic acid; ACP = ACP

The spectra of the present H-bonded series show bathochromic shifts in ν(C=O) mode of acid (~ 30 cm^{-1}) and hypsochromic shifts in the pyridine deformation (~ 30 cm^{-1}) mode of 2-amino-5-chloro-pyridine strongly suggest the formation of intermolecular hydrogen bonding between the –COOH group of *p*-*n*-alkoxy benzoic acid and nitrogen atom of ACP. Further, the band associated with ν(OH) mode of carboxylic acid group suffered a hypsochromic shift (table 1) upon complexation which supports the formation of H-bonding. The presence of intermolecular H-bonding is further invoked on the basis of appearance of a new intense band at 2920 cm^{-1} diagnostic of ν(H---N) in all the complexes[10]. Moreover, it is clearly seen that the stretching modes of $-NH_2$ group of 2-amino-5-chloro pyridine remain almost unaltered in the spectra of the complexes providing a substantial evidence towards the non-involvement of this group in the intermolecular hydrogen bonding.

The degree of stabilization of intermolecular H-bonding is further studied by recording spectra of complexes in chloroform solution. The spectra show the re-appearance of the stretching modes of the >C=O and pyridine ring deformation modes of free ABA and ACP moieties, respectively suggesting the destruction of H-bonding in solution state.

Thermal and Phase Behaviour

The phase variants and their transition temperatures of free *p-n*-alkoxybenzoic acids and the corresponding complexes (table 2 and 3) are determined[11] from the characteristic textural observations under polarized microscope equipped with a temperature controller system at a rate of 0.1 °C/min. The *p-n*-alkoxybenzoic acids exhibit nematic (marble) as a unique mesophase in the lower homologues (n = 3 to 6) and smectic-C (schilieren) in higher members of the series [3].

On cooling the isotropic melt, the present series exhibited the formation of multi coloured smooth mosaic texture of smectic-G phase as an induced monotropic phase. However, the re-appearance of nematic phase in the form of marble texture is observed in complex-V.

The phase transition temperatures observed through thermal microscopy are found to be in reasonable agreement with the corresponding DSC thermograms (Table 3). The data revealed that the thermal distribution of induced smectic-G phase (plate 1) decreases with increasing alkyl chain length of benzoic acid moiety.

TABLE 2 TM and DSC data of ABA

ABA*	Phase	Phase transition temperatures/°C of TM and DSC (ΔH/J/gm)		
		Iso. - N	N - Sm-C	N/C - Cryst.
I	N	154.9	---	145.2
		[158.8 (10)]		[150.6 (79.8)]
II	N	160.1	---	147.1
		[160.5 (12.6)]		[149.9 (92.7)]
III	N	151.4	---	123.9
		[153.5 (10.5)]		[123.6 (92.4)]
IV	N	153.8	---	105.1
		[158.9 (11.0)		[109.3 (56.1)]
V	NC	146.8	98.3	91.8
		[148.7 (6.7)]	[99.2 (5.2)]	[94.8 (104.4)]
VI	NC	147.5	97.8	101.9
		[150.4 (8.4)]	[100.3 (4.0)]	[104.5 (41.0)]
VII	NC	142.9	117.1	94.5
		[141.3 (9.5)]	[113.2 (6.2)]	[95.1 (148.6)]
VIII	NC	138.3	115.6	97.0
		[135.1 (9.4)]	[111.4 (3.3)]	[95.7 (25.3)]
IX	NC	137.2	128.9	95.1
		[136.4]$^{\#}$	[136.4]$^{\#}$	[94.4 (127.3)]

$^{\#}$Transition peaks are not well resolved

The phase diagrams are constructed from the transition temperatures. Figures 2 and 3 illustrate the phase behaviour of the free

ABA and their analogue complexes, respectively. A glance at figure 3 reveals that except in complex-V, the quenching of nematic phase, which is a dominant phase in free ABA, is equally substituted by the induced smectic-G phase in all the complexes. The thermal range of induced smectic-G phase is high in lower homologues and a gradual decrement of its thermal distribution is observed when the carbon number of benzoic acid alkyl chain length increases. At this juncture, it is worth mention to recall the thermal distribution of induced smectic-G phase among the reported analogue complexes[7] derived from *p*-alkoxy benzoates (non-mesogen moieties) where a non-uniform trend is observed. This observation, however, serves as a token of evidence

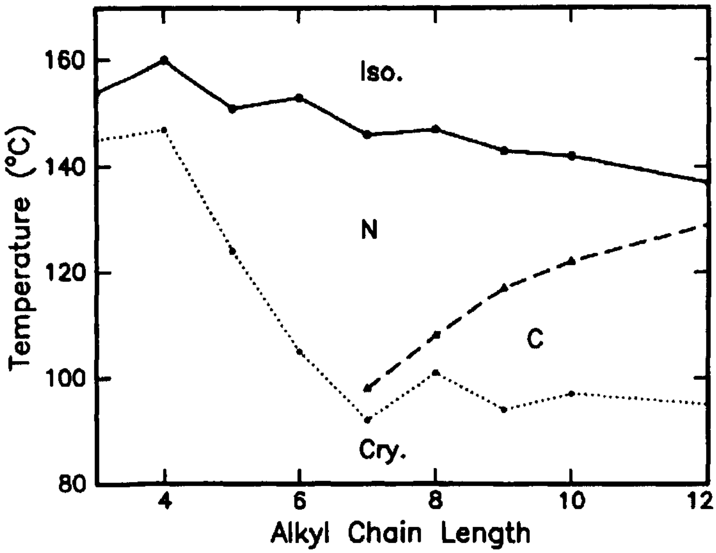

FIGURE 2 Phase diagram of ABA

towards the significant contribution of non-mesogenic ACP moiety on the phase behaviour of the present series of compounds. Further, the stabilization of this induced phase among the individual members of this series clearly suggests the important role of hydrogen bonding associated with the electron rich hetero atom (nitrogen) and an acid group of ABA.

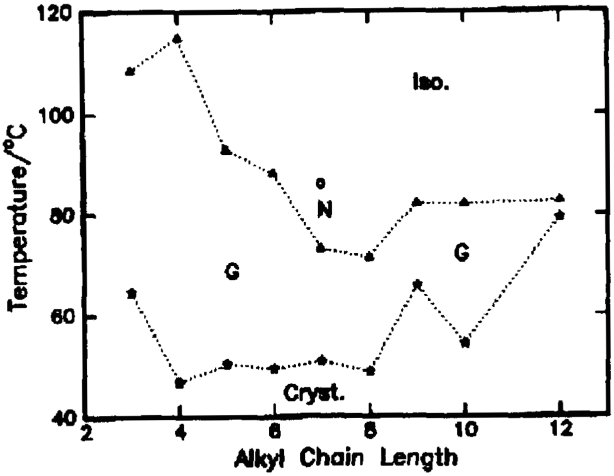

FIGURE 3 Phase diagram of ABA:ACB complexes

Unlike in free ABA, wide liquid crystalline thermal ranges are noticed for the complexes having even number of alkyl carbons and the present series show an odd-even effect in the thermal ranges of induced phase.

TABLE 3 TM and DSC data of ABA:ACP

ABA:ACP*	Phase	Phase transition temperatures/°C of TM and DSC (ΔH/J/gm)		
		Iso.- N/Sm-G	N - Sm-G	Sm-G - Cryst.
I	G	108.5		64.6
		[101.1 (22.1)]		[49.5 (79.5)]
II	G	114.8		46.7
		[97.0 (7.9)]		[48.1 (67.6)]
III	G	92.8		50.3
		[86.5 (10.8)]		[50.3 (83.7)]
IV#	G	88.1		49.4
		[84.3 (10.6)]		
V	NG	86.1	84.9	50.8
		[81.2 (15.8)]	[73.1 (39.4)]	[45.0 (39.8)]
VI	G	71.4		48.7
		[72.7 (2.6)]		[48.7 (84.9)]
VII	G	82.2		65.7
		[56.0 (44.2)]		[49.2 (38.5)]
VIII	G	82.0		54.2
		[70.8 (11.5)]		[50.1 (71.6)]
IX	G	82.6		79.2
		[63.7 (9.2)]		[49.9 (59.8)]

*Compounds I – IX represent alkyl chain length as propyl-, butyl-, pentyl-, hexyl-, heptyl-, octyl-, nonyl-, decyl- and dodecyl-

No crystal transition is observed

SUMMARY

The thermal studies on ABA:ACP series imply the inducement of a smectic-G phase with simultaneous quenching of nematic and smectic-C phases. The induction of this smectic- G phase may best be accounted on the basis of possible molecular contributions from the intermolecular H-bonding between the electron rich hetero atom (nitrogen) and an acid group. Apart from this non-covalent interaction, the tendency of permanent transverse dipoles (viz., chlorine and amino groups) in delocalizing the electron cloud may also have a significant role towards the origin of the new phase.

Acknowledgements

Financial support rendered by Council of Scientific and Industrial Research (CSIR), University Grants Commission (UGC) under DRS scheme and Department of Science and Technology (DST), New Delhi is gratefully acknowledged. Thanks are also due to Prof. K.G. Subhadra of Kakatiya University, Warangal, India for IR spectral recording.

References

[1] T. Kato, K. Toshiyuki, J. Fumiko and J. M. J. Frechet, *Liq. Cryst.*, **14,** 1311 (1994).

[2] E. B. Barmatov, D. A. Pebalk, M. V. Barmatova and E. P. Shibaeb, *Liq. Cryst.*, **23,** 447 (1997).

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

[4] S. V. N. Raju, S. A. Mule, C. R. Rajan and S. Ponrathnam, *Ind. J. Chem.*, **36 A & B**, 525 (1997)..

[5] Y. Tian, X. Xu, Y. Zhao, X. Tang and T. Li, *Liq. Cryst.*, **22,** 87 (1997).

[6] L. J. Yu, *Liq. Cryst.*, **14,**1303 (1993).; T. Kato, H. Kihara, T. Turyu, S. Ujie, K. Imura, J. M. J. Frechet and U. Kumar, *Ferroelectrics*, **148,** 161 (1993).

[7] P. A. Kumar, M. Srinivasulu and V. G. K. M. Pisipati, *Liq. Cryst.*, **26,** 1339 (1999); P. Swathi, P. A. Kumar and V. G. K. M. Pisipati, *Liq. Cryst.*, **27** (2000) (in press).

[8] A. Treybig, H. Bernhardt, S. Diele, W. Weissflog, H. Kresse, *Mol. Cryst. Liq. Cryst. Sci. Technol.*, Sec. A,, **293,**7, (1997).

[9] C. Yang, D. Zhao, X. Tang, X. Zhao and E. Zhou, *Jilin Daxue Ziran Kexue Xuebao (Ch)*, **2,** 123, (1992).

[10] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* 4th Edn., (New York Interscience) 1978.

[11] A. Addison, *Techniques and Experiments for Organic Chemistry*3rd Edn., (Allyn and Bacon).

[12] G. W. Gray and J. W. G. Goodby, *Smectic Liquid Crystals: Textures and Structures* London, Leonard Hill 1984.