

Influence of Benzoate on Substituent Benzoic Acids with Implications on Spectroscopic Studies through Inter Molecular Hydrogen Bonding

Ch.Ravi Shankar Kumar

Department of Physics, Institute of Science, GITAM University, Visakhapatnam, India.
Email: rskchaval@gmail.com

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ABSTRACT

Comprehensive study on the homologous series of compounds in the form A-R-HHB are synthesized with central rigid core as benzoic acids together with substituent's alkoxy (A) and alkyl (R) group of equal chain lengths from 5 to 10 are connected to hexyl-p-hydroxy benzoate (HHB). These complexes form supramolecular structures by self assembling process due to intermolecular hydrogen bonding. The formation is analyzed with techniques involving polarizing optical microscope, infrared spectroscopy, proton NMR spectroscopy and powdered X-ray diffraction. Results suggest that complexes arise from both A and R groups exhibit enantiotropic layered texture of crystal G phase observed by microscopic studies due to flexible nature of mesogenics. The conversion of free to molecular complexes is determined with variations in spectral shifts between its terminal groups COOH and OH of molecules involving inter molecular hydrogen bonding and its bonding index by FTIR spectra. The changes in structure and dynamics due to hydrogen bonding in complexes are convinced by proton NMR spectra with chemical shifts in specified range. The defects in crystal structure responsible for enantiotropic phenomena are analyzed by powdered X-ray diffraction.

Keywords: Phase Transitions, Microscopy, IR Spectra and Hydrogen Bonding

1. Introduction

Over the past decades the design and synthesis of new liquid crystalline molecules [1] has considerably broadened mesophase stability [2] especially with rod like molecules due to intermolecular interactions [3,4] that play vital role in the formation of liquid crystal textures [5]. These organized structures are built by strategic units leading to supramolecular structures [6,7] enable meaningful relationship cutting across its entities with their functional relationships attributed involves hydrogen bonding [8]. Liquid crystals possess fluid like properties are greatly influenced with non mesogenics stems the interaction leading to structural variations by self assembling [9-13] process that greatly influence the physical properties due to defects that exist in solid state where individual displacements of atoms are suppressed. The substituent liquid crystals or mesogenics exhibiting nematics under consideration are perfectly rigid [8,11,14] when associated with addition of benzoate (HHB) results with deviation in structure that occur due interaction between molecules. Many investigations lead to the forma-

tion of supramolecular structures due to hydrogen bonding due to its stability [2,15] and directionality that significantly change the molecules has drawn attention in development of new structures. In the present work mesomorphic properties [16] emphasized in terms of its features in normal state between hexyl-p-hydroxy benzoate and substituent liquid crystals A [17] and R [18] through hydrogen bonding as illustrated in **Figure 1**.

2. Experimental

The two mesogenics [19] that were chosen for conduct of experimental studies include the p-n-alkoxy benzoic acid (A), p-n-alkyl benzoic acid (R) and non mesogenic hexyl-p-hydroxy benzoate (HHB) are purchased from Frinton laboratories New Jersey, USA. These compounds possess a number of favorable properties in studies involving both crystalline and anisotropic states. The preparation is performed by dissolving in 1:1 ratio the compounds in pyridine under constant stirring for about 4 hours approximately at 80°C and the clear solution is obtained. The solvent was removed by fractional distillation with

resultant mixture was dried and re-crystallized by using dichloro-methane.

The phase transition temperatures and texture studies of synthesized materials were studied using Hertel Reuss super-pan II polarizing optical microscope (POM) equipped with optical display (DP10) at scan rate of 0.1°C/min. The liquid state (chloroform) and solid state (KBr) FT-IR-spectra were recorded on Perkin-Elmer (spectrum bX) series at room temperature from 400 - 4400 cm^{-1} with resolution 8 cm^{-1} . The proton nuclear magnetic resonance (^1H NMR) spectra were recorded on the Bruker Avance 400 MHz instrument in CDCl_3 with chemical shifts in ppm. X-ray studies were performed at room temperature using Phillips powdered XRD system in determining crystalline parameters.

3. Results and Discussions

Liquid crystals show unusual behavior due to variations in temperature. The transitions from crystalline to isotropic and back occur in single step in both heating and cooling process. Textures observed by polarizing optical microscope obtained in heating are much difficult to assign as they are complicated and natural textures in cooling are significant, of substituent's A and R and its complexes A-R-HHB are listed in **Table 1**. Realization of complexes by self assembling lead to supramolecular structures possess mechanical properties better than conventional liquid crystals by extending its flexible ends [19-21] with benzoate that gained positional order with layered texture of crystal G phase as illustrated in **Figure 2**.

This phase has molecules packed in layers with their

long axis tilted with respect to normal to layer planes with tilt molecules performing reorientational motion about long axes that contributes to hexagonal symmetry. A consequence of transition temperatures of the free and complexes is that orientational textures with long axes of molecules perpendicular to glass substrate involve higher transition temperatures than layered textures where long axes are at an angle with glass substrate. The transition temperatures are plotted against chain length are illustrated in **Figure 3**. The lowered nature of temperatures is an implication of loss in rigidity, reducing fluidity and change in symmetry of free molecules due to participation of flexible ends with benzoates with thermal span lesser by 8°C. A feature in transition temperatures of molecular complexes associates contrast behavior in members of substituent's A and partial even odd effect [22] with R group that reveal the length of flexible terminals had influenced in occurrence of the said phase.

The Fourier transform infrared spectral interpretation [23-25] is used in exploiting the structural defects responsible for change in orientation is realized with spectral shifts (cm^{-1}) due to hydrogen bonding (OH) of substituent's and its complexes are listed in **Table 2**. The solid state spectral studies reveal OH of A and R groups is much less in comparison with HHB indicating their intact nature. On complexation there is tremendous change in spectral shifts of complexes A-R-HHB formed with A are contrary with R group. On structural level these shifts enabled terminal groups of aromatic rings to participate in hydrogen bonding that has nucleated in formation of layered texture.

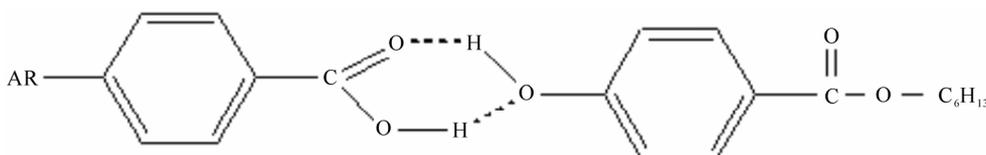


Figure 1. Bonded structure of substituted benzoic acid with hexyl-*p*-hydroxy benzoate.

Table 1. Polarizing optical microscope studies of free and complexes.

Chain Length	Type of texture			Transition Temperatures °C			
	A	R	(A-R-HHB)	A	R	(A-R-HHB) _A	(A-R-HHB) _R
5	N	N	G	151.4	124	98.4	96
6	N	N	G	153.8	112.5	85	71
7	N	N	G	146.8	121.7	80	83.5
8	N	N	G	147.5	110.3	85.7	83
9	N	N	G	142.9	115.8	87.2	83
10	N	N	G	138.3	108.8	90.6	81.4

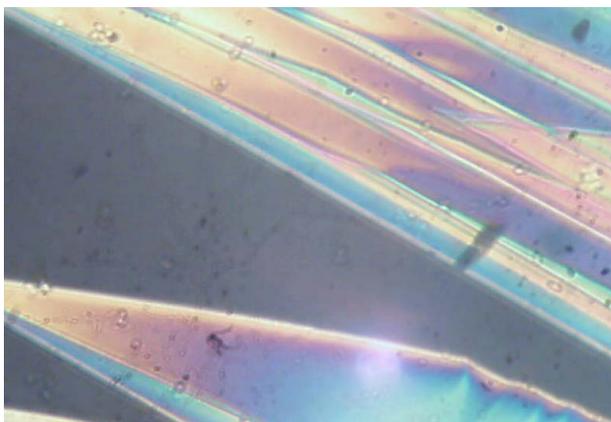


Figure 2. Texture of crystal G phase.

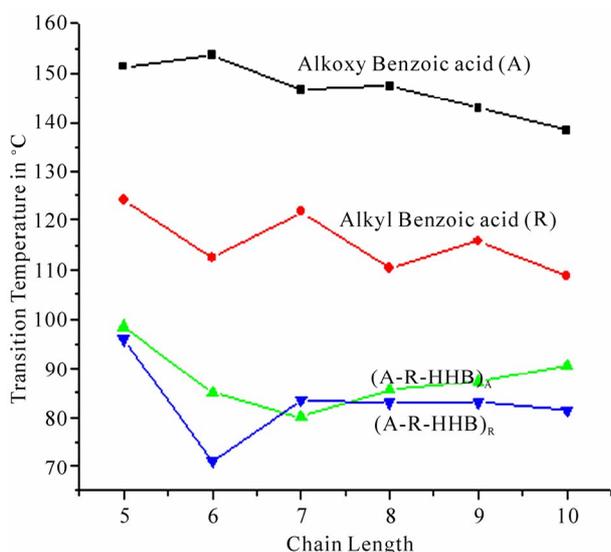


Figure 3. Plot of transition temperatures vs chain length.

Coordinating the absorption studies from FTIR spectra of substituent's and complexes in determination of hydrogen bonding index [26,27] responsible for altered texture are listed in **Table 3**. These absorption studies reveal even odd behavior in substituent groups A and R that is lost on complexation with benzoate. The studies involving hydrogen bonding index determines the extent of participation between the molecules that increases slowly in chain length with A group due to paramorphosis and an even odd behavior associates with R group. These variations signify that flexible terminals of both groups influenced the occurrence of phase due to dispersed non covalent interaction.

The studies of complexes with NMR spectra [28] provide rich structure and dynamic information that is lost due to its swift averaging in the liquid phase. Chemical shifts provide the first signature to understand the pack-

ing and hydrogen bonding formation [29] in the solid state. The ^1H NMR spectra of the free and its complexes exhibit different regions are well resolved in the spectrum. The structural studies for complexes indicate chemical shifts around 0.9 attributed to the CH_3 , multiplets in range 1.3 - 1.8 attributes to $(\text{CH}_2)_n$ of both the groups and 4.3 triplet for bonded OH. The shifts at 6.9 - 7.0 contribute to aromatic protons. The OH of phenolic is assigned to 8.2 suggests the down field shift due to inter molecular hydrogen bonding. These chemical shifts reveal the convinced IR with peak around $680 - 730 \text{ cm}^{-1}$.

Finally with X-ray diffraction [30] involving small angle regions reveal the information of the anisotropic properties between parallel and perpendicular incident directions. These properties arise due to defects existing in solid state which are the crystalline parameters determined in angstrom units (AU) are listed in **Table 4**.

The inter planar spacing $d = n\lambda/\sin\theta$, the thickness (t) = $0.94 \lambda/(B\cos\theta_B)$ are determined with $\lambda = 1.54056$ angstroms units, (B) is full width half maximum and θ_B is bragg angle. The studies reveal drastic change in intensity, interplanar spacing and thickness irrespective of the substituent group in comparison with the benzoate. The influence of functional molecules is integrated into system by involving the crystalline properties for the obtained texture with reduced scattering. The choice of benzoate enabled in generation of new molecular structure that helped to expand the properties of liquid crystals that arise from aromatics due to displaced center of gravities with increased variation in size and planar separation.

With increase in chain length the influence of benzoate on the core molecule enabled greater degree of conformational freedom [31,32]. These parameters articulate that the benzoate group has successfully disturbed the oriented texture of its molecules to layered texture.

4. Conclusions

The work resulted in influence of benzoate successfully leading with enantiotropic layered texture in both alkoxy and alkyl groups. The disturbed symmetry with reduced transition temperatures gained positional order by self assembling process. The hydrogen bonding with narrow peaks and enhanced shifts lead the aromatic rings to nucleate its structure together with bonding index has increased molecular packing. The liquid crystal on complexation with benzoate has lead to new molecular and supramolecular structure with properties that are dependent of aromatics that are mesogens. The explanation is valid with necessary support in altering the texture and its confirmation with various techniques due to hexyl-*p*-hydroxy benzoate and further studies in control of self assembling process need to be performed.

Table 2. Solid state IR spectra.

Chain Length	(OH) _A	(OH) _R	(OH) _{HBB}	(A-R-HHB) _{OHA}	(A-R-HHB) _{OHR}
			3374		
5	2955	2958		3300	3294
6	2933	3120		3435	3439
7	2932	2926		3441	3297
8	3130	2926		3399	3295
9	2924	2924		3412	3440
10	2923	2923		3389	3395

Table 3. Hydrogen bonding index.

Chain Length	(OH) _A	(OH) _R	(A-R-HHB) _A	(Bonding index) _A	(A-R-HHB) _R	(Bonding index) _R
5	65.76	19.93	14.56	0.221	20.67	1.037
6	28.07	70.07	30.89	1.100	24.1	0.343
7	72.19	19.38	84.77	1.174	26.20	1.351
8	35.07	37.47	69.04	1.968	26.76	0.714
9	37.26	11.75	91.72	2.461	21.75	1.851
10	33.07	16.75	96.6	2.9210	25.10	1.498

Table 4. Crystalline parameters.

Name of Compound	Bragg angle	Intensity	Interplanar distance	Thickness
HHB	22.657	224	3.999	0.0767
(A-R-HHB) _A				
5	20.053	473	4.4918	0.765
6	23.008	789	3.9407	3.7004
7	14.194	2731	6.2828	1.829
8	20.024	1146	4.499	0.7356
9	9.577	148	9.258	0.0394
10	4.449	98	19.86	0.3800
(A-R-HHB) _R				
5	12.285	582	7.2404	1.1013
6	22.810	201	3.9738	0.1707
7	19.103	962	4.7074	0.9529
8	22.916	465	3.9564	1.0308
9	12.596	949	7.0643	0.65758
10	22.289	7157	4.0614	0.2154

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