

HARMONIZATION OF NEMATIC'S FILLED WITH ESTERS THROUGH HYDROGEN BONDING

Ch. Ravi Shankar Kumar

Faculty of Physics, Institute of Science, GITAM University, Visakhapatnam, Andhra Pradesh, India 530045

Email: rskchaval@gmail.com

ABSTRACT

Anisotropic nature with fluidity and its inability to support shear is studied with harmonization between nematics and esters in transformation to layered textures through intermolecular hydrogen bonding. The anisotropy include molecular properties of liquid crystalline materials such as its texture, phase transitions, structure, interactions and index with interrelationships responsible for supramolecular structures. The harmonization behavior is dependent on its chemical intuition that are characterized with numerous techniques like polarizing optical microscope, differential scanning calorimetry, Fourier transform infrared spectroscopy, proton Nuclear magnetic resonance spectroscopy and powdered X-ray diffraction. Interestingly the flexibility of nematics with higher energy when filled with esters transform to layered textures due to non covalent interaction with reduced energy on harmonization.

Keywords – FTIR, Hydrogen Bonding, Phase transition and Crystal G phase.

1. INTRODUCTION

Liquid crystals greatly influence the molecular structure [1] with its interactions [2], symmetry and phase transitions [3]. In particular nematics[4] occupy its pace due to its functional group, weak interlayer coupling, strong in plane interactions characterized with high orientational order and in particular with aromatics due to displaced centre of gravities. The self aggregation [5-7] of aromatics with preferred molecular orientation transform to layered textures with indirect interaction exceeding the energy of vander waals interaction [8] have significant impact on the physical properties. The existence of structural inhomogenities in formation of supramolecular structures [9] is best attributed by hydrogen bonding [10-11] with crucial role of nematics. These orient with respect to director when filled with ester distortion occur due to flexible nature by intermolecular interactions [12] through hydrogen bonding resulting in stack of molecules. These hydrogen bonds gained importance in many physical, chemical and biological processes are acceptable when associated with liquid crystal lead to self assembled supramolecular structures. In present paper the harmonization [13] through intermolecular hydrogen bonding between the *p-n*-alkyl benzoic acid (PABA) that exhibit nematic phase on association with ester hexyl-*p*-hydroxy benzoate (SHB) transform to layered texture is attributed with its synthesis, thermal studies, infrared studies and powdered x-ray diffraction is shown in figure1. The constituent nematics, esters and harmonized structures exhibit high degree of thermal stability with repeated scans.

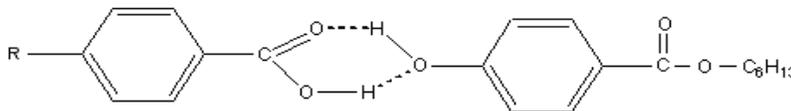


Figure 1. Intermolecular hydrogen bonded structure

2. EXPERIMENTAL

Two types of compounds *p-n*- alkyl benzoic acid (*n* the alkyl chain from pentyl to decyl) and hexyl-*p*-hydroxy benzoate of 99.9% purity used as such without purification for synthesis. The solid state (KBr) spectra were recorded on Perkin-Elmer (spectrum bX) Fourier transform infrared spectrometer at room temperature from 400-4400 cm^{-1} with resolution 8cm^{-1} . Complete molecular level properties are obtained with thermal studies involving phase transitions and textures using Meopta polarizing optical microscope fitted with heating stage and optical display at the rate of $0.1^\circ\text{C}/\text{min}$. The sample is placed on the glass plate rubbed uniformly by piece of linen cloth and further with lens paper. Calorimetric studies were performed by Differential Scanning calorimetry with thermograms recorded on SDT Q600 TA under nitrogen atmosphere at scan rate of $5^\circ\text{C}/\text{min}$ both in heating and cooling for transition temperatures. The structural conformations of harmonized structures are analyzed with proton NMR technique with Bruker Avance 400 MHz instrument in CDCl_3 with chemical shifts in ppm The x-ray diffraction measurements were carried at room temperature using Phillips powdered XRD system to analyze

interplanar spacing (Angstrom units), intensity (arbitrary units) and thickness (Angstrom units) using Scherrer's formula [14] with CuK α radiation of wavelength $\lambda = 1.54056$ AU.

The synthesis of harmonized structures PABA: SHB is performed by refluxing both *p-n*-alkyl benzoic acids and hexyl *p*-hydroxy benzoate in pyridine under constant stirring for about 3 hours approximately. The volume of resultant homogenous mixture was reduced to solid powder by removing excess pyridine by fractional distillation. The crystalline products were dried and recrystallized with dichloro-methane.

3. RESULTS

FTIR spectrum presents vibration contributions [15] of free *p-n*-alkyl benzoic acid, hexyl-*p*-hydroxy benzoate and harmonized structures recorded in Table 1 at room temperature. The stretching vibration (cm^{-1}) of P8BA is the broad OH at 3441 with characteristic peak of 1644 due to C=O and filled in ester at 1230 of C-O, in plane bend (IPB) and out plane bend (OPB) at 1395, 697 cm^{-1} respectively.

Temperature dependence of the rigid *p-n*-alkyl benzoic acid in both heating and cooling that exhibit nematic phase is listed in Table 2 with phase diagram [16] in figure 2. This phase is characterized with long axis of molecules parallel to one another with preferred orientation throughout the medium.

Table 1: Infrared spectral data of free and harmonized structures

Compound	(C=O) _{acid}	(OH) _{acid}	(OH) _{ester}		(C-O) _{ester}
			IPB	OPB	
P8BA	1644	3441			
SHB			1395	697	1230
P5BA: SHB	1604	3294	1429	639	1255
P6BA: SHB	1619	3439	1399	642	1245
P7BA: SHB	1608	3297	1402	698	1232
P8BA: SHB	1607	3295	1444	698	1230
P9BA: SHB	1616	3440	1400	700	1245
P10BA: SHB	1608	3395	1398	697	1285

Table 2: Thermal studies of *p-n*-alkyl benzoic acid (PABA)

Mesogen	Phase	Phase transition temperatures/ $^{\circ}\text{C}$ TM, [DSC (ΔH Wg $^{-1}$)]			
		Heating		Cooling	
		Crys-N	N-Iso	Iso-N	N-Crys
P5BA	N	89[87.89(0.103)]	126[121.46(0.707)]	124[117.24(1.13)]	84[82.36(1.17)]
P6BA	N	99.2[95.76(0.166)]	114.1[118.97(0.623)]	112.5[112.9(1.15)]	94.5[88.5(2.01)]
P7BA	N	105.3[102.66(0.649)]	123.3[120.76(0.193)]	121.7[117.5(0.75)]	102.2[97.5(1.41)]
P8BA	N	104.1[100.29(0.551)]	113.5[112.25(1.412)]	110.3[109.6(1.53)]	98.9[92.9(2.14)]
P9BA	N	91.5[96.71(0.585)]	118.5[115.07(1.643)]	115.8[111.5(2.04)]	90.1[93.8 (2.88)]
P10BA	N	92.5[96.07(1.078)]	110.1[107.5(2.006)]	108.8[103.9(2.45)]	93.3[88.5(3.24)]

The nematic phase is initiated with droplet texture further transformed to threaded texture before reaching isotropic state from crystal and back due to flexible nature of rigid rods. On disturbing the cover slip the nematic phase executed Brownian motion. DSC measurements showed strong endothermal peaks in heating exothermal in cooling with enthalpies at respective temperatures in concordance with transitions observed by microscope reveal enantiotropic nature of compound with clearing temperatures extending from 89 to 126 $^{\circ}\text{C}$. The transitions from Isotropic (Iso) to Nematic(N) and reverse exhibit even odd behavior and further with uniform trend in crystal to nematic and its reverse. The enthalpy values in cooling are much higher in cooling than in heating which reveal that larger energies are required for paramorphosis[17].

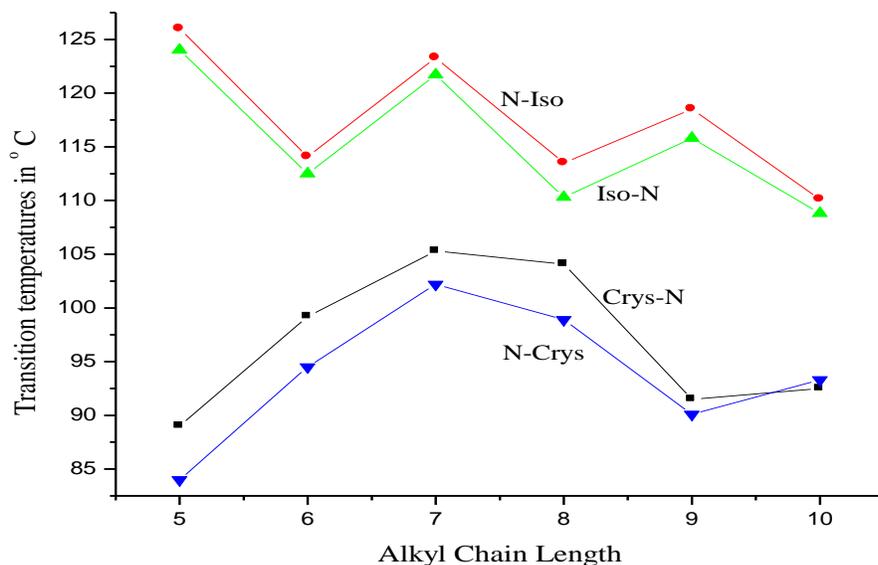


Figure.2. Phase diagram of free p-n-alkyl benzoic acid (PABA)

4. DISCUSSION

The harmonization of nematics with esters reveal interesting features in spectral shifts, transmittance studies, hydrogen bonding index [18 -19], phase transitions, enthalpy and crystalline parameters. The infrared studies of harmonized structure reveal the intermolecular hydrogen bonding with intense sharp peaks, lowered vibration shift of ($\approx 40 \text{ cm}^{-1}$) due to C=O and ($\approx 150 \text{ cm}^{-1}$) due to the OH of acid. An intense sharp peak associate's raised shift of C-O ($\approx 50 \text{ cm}^{-1}$) in ester group confirms the extensive nature of intermolecular hydrogen bonding. A feature of the strong hydrogen bonding in harmonization is further inferred from absence of a band at 3374 cm^{-1} due to OH mode of SHB in PABA: SHB.

A significant feature on harmonization is the maximum stretching frequency indicates that both OH groups in para positions are involved in intermolecular hydrogen bonding influence the stable mesomorphic nature. The changes in peak positions and area of (C=O), (OH) and (C-O) is responsible for the thermally induced phase changes through hydrogen bonding[20] that gained vital importance with miscibility enhancement lead to harmonized structure illustrated in Figure1.

The spectra is further analyzed for transmittance (inverse of absorption) in Table 3 and bonding index studies Table 4 of harmonized structures between the groups. The focus on transmittance studies show variations of both groups and particularly OH of acid with pronounced variation indicating its participation in hydrogen bonding. The studies of hydrogen bonding index exhibit contrast behavior of the nematics and ester molecules on harmonization.

Table 3: Transmittance studies of free and harmonized structures

Compound	(C=O) _{acid}	(C-O) _{acid}	(OH) _{acid}	(OH) _{ester}		(C-O) _{ester}
				IPB	OPB	
P8BA	40.8	47	28.7			
SHB				52.3	55.6	53.5
P5BA: SHB	41	38	62.4	56	52	38
P6BA: SHB	97.6	97.7	94.5	98.4	99.6	99
P7BA: SHB	53.5	50.5	54.5	52.6	56	55
P8BA: SHB	45	34	54	55	56	47
P9BA: SHB	65.7	66.5	60.5	64	67	67.5
P10BA: SHB	58.5	57	56	58.3	62	57

Table 4: Hydrogen bonding Index studies with free and harmonized structures

Compound	(%A) _{acid}	Bonding Index with acid	(%A) _{ester}		Bonding Index with Ester	
			IPB	OPB		
P8BA	62.71					
SHB			28.32	25.49		
P5BA: SHB	20.76	0.33	30.10	27.57	1.06	1.08
P6BA: SHB	24.10	0.38	29.59	26.23	1.04	1.02
P7BA: SHB	26.20	0.41	27.74	24.95	0.97	0.97
P8BA: SHB	26.76	0.42	25.34	23.81	0.89	0.98
P9BA: SHB	21.75	0.34	19.38	17.2	0.68	0.67
P10BA: SHB	25.10	0.40	23.51	20.62	0.83	0.80

The thermal studies of harmonized units reveal a number of interesting features listed in Table 5 with phase diagram that helps to study the behavior in different thermodynamic paths influencing mesomorphic properties due to conformations [21-22] like unsaturated nature, mobility and fluctuation on harmonization as illustrated in figure 3.

Table 5: Thermal studies of harmonized structures (PABA: SHB)

*represents peak not resolved

Complexes	Phase	Phase transition temperatures/°C TM, [DSC (ΔH Wg ⁻¹)]			
		Heating		Cooling	
		Crys-G	G-Iso	Iso-G	G-Crys
P5BA:SHB	G	61.3[54.91(0.0962)]	142[137.76(0.099)]	136[130.90(1.018)]	70.2[66.17(0.2696)]
P6BA:SHB	G	58.6[51.36(1.408)]	138[148.36(2.509)]	71[74.83(2.198)]	68[67.06(0.2143)]
P7BA:SHB	G	59.2[54.17(0.067)]	91.4[100.44(0.874)]	83.5[*()]	80[80.45(1.12)]
P8BA:SHB	G	58.3[54.91(0.334)]	86.5[86.75(0.0492)]	83[81.12(0.3718)]	77[77.07(0.489)]
P9BA:SHB	G	62.6[55.99(0.264)]	88[92.51(0.650)]	83[81.44(0.962)]	79[72.84(0.843)]
P10BA:SHB	G	60.2[54.83(0.572)]	84.8[86.56(1.332)]	81.4[*()]	75[75.98(1.921)]

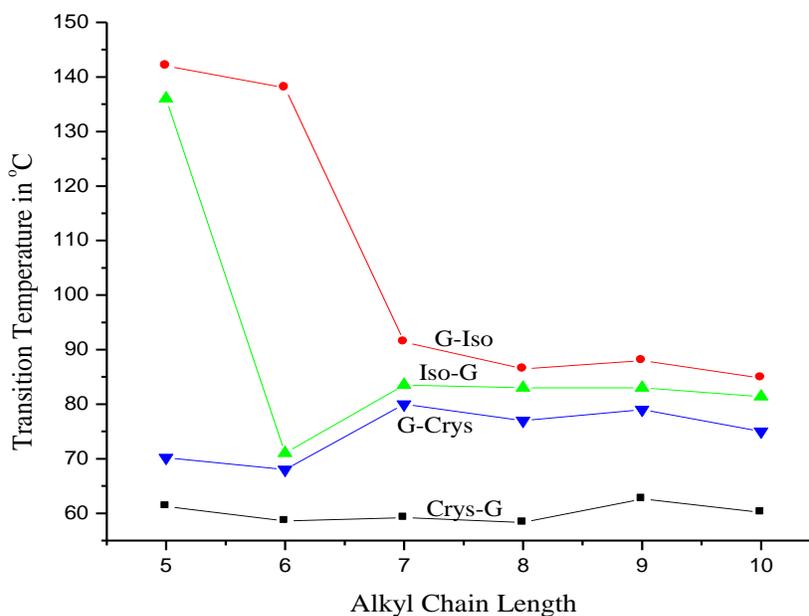


Figure 3. Phase diagram of harmonized structure PABA: SHB

The harmonization nucleated in two steps from crystalline to G phase [23] and to isotropic state altering orientation of nematics from respective direction in formation of new crystal G phase illustrated in figure 4 in both heating and cooling with reduced transition temperatures. The homogenous nucleation extended the interplanar spacing with filled in esters hindering the nematic phase forming crystal G phase. The phase is characterized by elongated platelets with hexagonal packed structure. The even odd behavior is completely lost from G phase to Isotropic and back preserving the uniform behavior in both the processes. A noteworthy feature of the elongated texture is due to harmonization of nematics with esters enabled to stretch the molecules with reduced enthalpy in its formation revealing the non covalent interactions of the involved molecules.

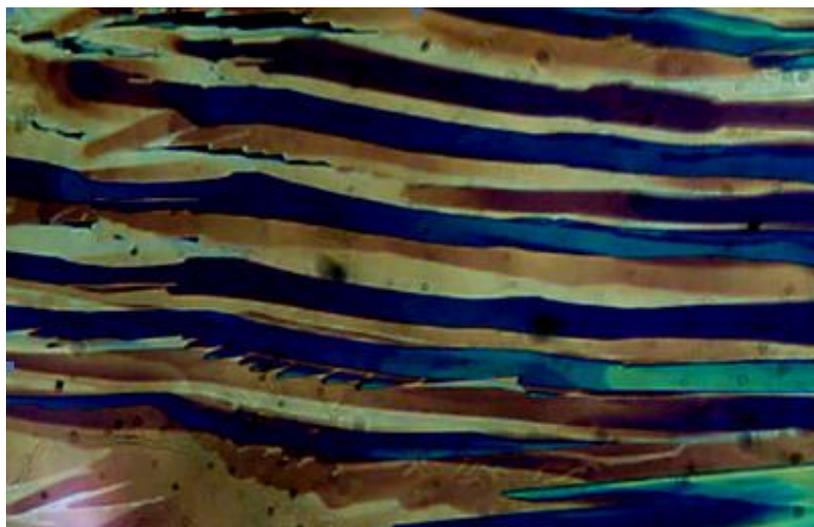


Figure.4. Crystal G Phase

With the filled in esters having interstices randomly distributed resulted in

- (i) Harmonization of host molecules results with occupation of its lattice sites leading the molecules to glide over one another gaining complete positional order disturbing the symmetry of nematics.
- (ii) Lowered temperatures and enthalpy is indication of interacting with acids, occupying its lattice sites and altering the transition due to harmonization.
- (iii) Significantly complex associated with hexyl chain in both techniques involving IR and thermal studies reveal equal occupation of interstices with lattice sites of acid lead to increased values by significant amount in comparison with other chain lengths.

Proton NMR studies [24] suggest nematics filled with esters alter and possible to measure the chemically shifted species of CH_3 , CH_2 around 0.8 triplet, 1.2 multiplets and contribution of 7.0 doublet due to aromatic protons of groups with down field shift. The OH of harmonized at 4.3 ppm convinced with infrared peak in the range 680-730 cm^{-1} .

The powdered X-ray studies of representative P6BA and ester with harmonized structures are performed to determine crystalline parameters are listed in Table 6.

Table 6: Powdered x-ray studies of free and harmonized structures

Compounds	Bragg angle	FWHM	Intensity (Arbitrary Units)	Interplanar spacing (AU)	$\langle t \rangle$ AU
P6BA	22.402	9.3295	64611	4.0423	0.1678
SHB	22.657	20.452	224	3.9992	0.0767
P5BA:SHB	12.285	1.3457	582	7.2404	1.1013
P6BA:SHB	22.810	9.1980	201	3.9738	0.1707
P7BA:SHB	19.103	1.6082	962	4.7074	0.9529
P8BA:SHB	22.916	1.5251	465	3.9564	1.0308
P9BA:SHB	12.596	2.2565	949	7.0643	0.6575
P10BA:SHB	22.289	7.2628	715	4.0619	0.2154

These include inter-planar spacing $d = n \lambda / \sin \theta$ and thickness $\langle t \rangle = 0.94 \lambda / \text{FWHM} \cos \theta_B$ measured in angstrom units(AU) with FWHM as full width half maximum and θ_B is the corresponding bragg angle in degrees. The interplanar studies of harmonized structures reveal an even odd behavior associated with increase in thickness interplanar spacing and intensity due to filled in ester. The phase obtained at low temperatures in thermal studies associates an increased thickness in comparison with nematics. These studies characterize positional order with elongated platelets further with reduced scattering due to harmonization.

5. CONCLUSIONS

The stabilization and induction of new textures have been extensively studied with hydrogen bonding. These reflected with reduced vibration shifts, absorption and enhanced bonding index. The hetero intermolecular hydrogen bonding enriched in harmonization between nematics and esters with elongated platelets. The temperatures of nematic phase are high compared to crystal G phase with in plane and interlayer correlations are more anisotropic that transforms to elongated textures. Larger enthalpy is responsible for orientation along director due to harmonization with ester allowed for self assembling due to non covalent interaction with reduced energy. The spectral analysis gave significant evidences for phase transitions and has proven efficient method. The chemical shifts in respective range for hydrogen bonding interprets structural formation between the groups convinced with associated shifts in FTIR spectra. The studies are attributed with harmony except with temperature dependence of phase performed with powdered x-ray diffraction.

Acknowledgements

The author thanks the management of university and all the technical members for assistance in recording the spectra, thermograms and data of the involved experimental techniques.

REFERENCES

- [1]. S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.* **124** pp1-20 (1985)
- [2]. A.H. Pakiari, S.M. Aazami, A. Ghanadzadeh *Jor. Of Molecular Liquids* **139**, No.1-3, pp 8-13,(2008)
- [3]. Shri Singh *Physics Reports* **324** pp107-269(2000)
- [4]. N. Hijikuro, K. Miyakawa and H. Mori *Physics Letters A* **45** Issue 3, pp257-258 (1973)
- [5]. Takashi Kato, Norihiro Mizoshita *Current Opinion in Solid State and Materials Science* **6**, Issue 6, pp579 -587 (2002)
- [6]. Mitsuharu Kotera, Jean-Marie Lehn and Jean-Pierre Vigneron *J. Chem. Soc., Chem. Commun.,* Issue 2 pp197-199 (1994)
- [7]. Johan Hoogboom, Johannes A.A.W Elemans, Alan E Rowan, Theo H.M Rasing, and Roeland J.M Nolte *Phil. Trans. R. Soc. A* **365** pp1553-1576 (2007)
- [8]. S.Lifson., A.T. Hagler and P.Dauber *Jor. of American Chem. Soc.* **101** Issue 18 pp 5111-5121 (1979)
- [9]. Takashi Kato *Surpramolecular Science* **3** Issue 1-3 pp53-59 (1996)
- [10]. Ming Jiang, Mei Li, Maoliang Xiang and Hui Zhou *Advances in Polymer Science* **146** pp121-197 (1999)
- [11]. Shimei Jiang, Weiqing Xu, Bing Zhao, Yanqing Tian, Yingying Zhao *Materials Science and Engineering: C* **11**, Issue 2 pp85-88 (2000)
- [12]. Jason R. Greuel, Timothy E. Andrews, Justin J. Wichman, Joshua D. Tessner and Kurt N.Wiegel *Liquid Crystals*, **37** Issue 12 pp1515-1520 (2010)
- [13]. Agnieszka Iwan, Damian Pocięcha, Andrzej Sikora, Henryk Janeczek and Marcin Węgrzyn *Liquid Crystals* **37** Issue 12 pp1479-1492 (2010)
- [14]. Elements of X-ray Diffraction B.D.Cullity and S.R.Stock 3rd Edition Prentice Hall Publishers, New Jersey 2001
- [15]. Robert M. Silverstein and Francis X. Webster *Spectrometric Identification of organic compounds* 6th Edition Wiley Publishers NewYork 2005
- [16]. M. Papoular *Solid State Communications* **7** Issue 23 pp 1691-1692 (1969)
- [17]. Panos Vlachos, Bassam Mansoor, Matthew P. Aldred, Mary O'Neill and Stephen M. Kelly *Chem. Commun.,* Issue 23 , pp2921-2923(2005)
- [18]. X.Dai, J.Xu, X. Guo, Y. Lu, D.Shen, N. Zhao, X. Luo, and X.Zhang *Macromolecules* **37** Issue 15 pp5615-5623 (2004).
- [19]. C.B.Wang and S. Cooper *Macromolecules* **16** Issue 5 pp775-786 (1983)
- [20]. Shigeo Kohmoto, Yasunobu Someya and Keiki Kishikawa *Liquid Crystals*, **37** Issue 2 pp209-216 (2010)
- [21]. P.Minary ,M.Levit *Jor. Comput Biol.* **17** Issue 8 pp993-1010 (2010)
- [22]. A.P. Ivashin , M.Yu. Kovalevsky and L.V. Logvinova *Journal of Molecular Liquids* **120** Issue 1-3 pp115 -118 (2005)
- [23]. G.W. Gray and J.W.G. Good By *Smectic Liquid Crystals* Leonard Hill Press, Glasgow and London 1984
- [24]. F.Scheinmann *An Introduction to Spectroscopic Methods for Identification of Organic Compounds Volume 1 Nuclear Magnetic Resonance and Infrared Spectroscopy* 1st Edition Pergamon Press Oxford 1970