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Induced Crystal G Phase Through Intermolecular Hydrogen Bond Constructed by *p-n*-Alkoxy Benzoic Acids with *Ortho*-Toluamide (*n*OBA:TMD)

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Abstract **- A new series of supra molecular liquid crystals (*nOBA:TMD n* = 4 to 12) were synthesized with mesogenic *p-n* alkoxy benzoic acids (nOBAS) and non-mesogenic ortho toluamide (TMD) moieties. Intermolecular interaction between the proton donor (COOH) of *n*OBA and proton acceptor (OH) of TMD results the hydrogen bond. Newly formed complexes are characterized by polarizing optical microscope and differential scanning calorimetry, along with the conformational studies of hydrogen bonding through vibrational spectroscopy (FTIR). The IR spectral study confirms that the formation of hydrogen bond between proton donor (- COOH) of nOBA and proton acceptor (OH) of TMD. The formation of hydrogen bond is attributed to the quenching of the nematic and Smectic phase and inducement of crystal G phase in liquid crystal complex. A comparative study of phase abundance is presented with respect to the pure *p-n* alkyloxy benzoic acids (*n*OBA) and other hydrogen bonded liquid crystal complexes of *n*BAs.**

Key words--Supra molecular liquid crystals,ntermolecular interactions, hydrogen bond,Differential Scanning Calorimetry, Fourier Transform Infrared Spectroscopy.

I. INTRODUCTION

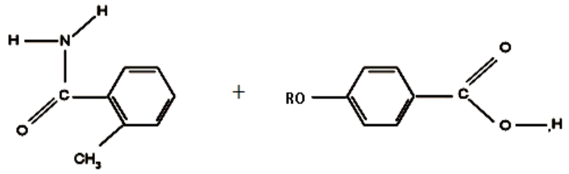
Unique materials that have large number of applications in the field of Engineering, technology and medicine are liquid crystals [1-5]. As these materials possess good number of applications, there is always vigorous research in developing novel liquid crystalline materials with different molecular structures and phases. Preparing novel liquid crystals involve various techniques like synthesizing using organic compounds and mixing two different compounds, metals and halogenated compounds etc [6-9]. In most of the cases chemists keep keen observation on the synthesis of hydrogen bond [10-21], as well as *p-n* Alkoxy Benzoic acids [19]. Among these novel liquid crystals, Hydrogen bonded liquid crystals have distinctive nature to show mesomorphic behavior due to their strong and directional nature in different types of interactions [22]. The alkoxy benzoic acids exhibit liquid crystalline nature. The same nature was observed in the in all hydrogen bonded liquid crystals obtained from the combinations of mesogen and mesogen, non mesogen and non mesogen, mesogen and non mesogen materials. The non-covalent interactions exhibit superficial effects on physical and thermal properties i.e., mesomorphic behavior and transition temperatures [15]. In the present article, a novel homologous series of liquid crystal complexes are prepared through the development of hydrogen bond between COOH of liquid crystal compounds *p,n*-alkoxy benzoic acids when *n* = 4 to12 and OH of non liquid crystalline compound *Ortho*-Toluamide (TMD). Fourier Transform Infrared (FTIR) spectroscopy is used to confirm the formation of hydrogen bonding and the prepared complexes mesomorphism is characterized by polarizing optical microscope (POM), Differential Scanning Calorimetry (DSC).

II. EXPERIMENTAL

The *p-n*-alkoxy benzoic acid (99% purity) and *o*-TMD supplied by M/s. frinton, Inc., USA. Solvent pyridine from M/s. Qualigens, India. The transition temperatures and phase variant of *p-n*-alkoxy benzoic acid and corresponding hydrogen bonded complexes were found from textural observations carried out using thermal optical polarizing microscope (Meopta, DRU-3) with a hot stage and HD Canon camera attachment. Methodology for sample cell preparation and observation of mesophase of the samples as a function of temperature has been given in [9],[16], and [19]. Phase transition temperatures were compared with temperatures of Perkin-Elmer Diamond Differential Scanning Calorimeter (DSC) at a scan rate of 2°C/min and confirmed. The IR spectrum in solid state was recorded on FTIR (FTIR 5300) Spectrometer (JASCO, Japan).

Preparation of p-n alkoxy benzoic acid (nOBA):ortho toluamide (TMD) complexes (where n=4 to 12):

Supra molecular Hydrogen bonded liquid crystalline complexes namely, *n*OBA: TMD (where n=4 to 12) are prepared by the following procedure given in scheme 1. Required amount of samples for synthesis are weighed on a single pan electronic balance Dhona make, ER-180A with an accuracy of 0.01mg.Equimolar (1:1) ratio of *n*OBA and TMD are used for the preparation of liquid crystal complexes 4OBA: TMD to 12OBA:TMD. Compounds are taken individually and mixed in the pyridine solvent (20ml). Thus the naturally existing dimeric forms of *n*OBA compounds with complementary hydrogen bond are converted into the monomeric form. Now the two solutions are mixed and kept under constant stirring at 80^0C for 4hrs. Then most of the pyridine is removed by vacuum distillation process. It means the resultant homogeneous mixture was reduced to almost dryness by removing the excess pyridine under a controlled vaccum filtration. The white crystalline product was dried and re- crystallized from hot dichloromethane solution. The yielding is at about 85%. The entire process involved in synthesis of given liquid crystal complexes are shown in the form of chemical reaction as follows.

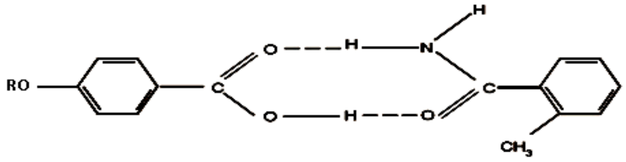


ortho toluamide (TMD) *p,n* - alkoxy benzoic acids (*n*OBA)

Pyridine, 4 hrs reflux (at 80^0C)

$\longrightarrow$

And after distillation



Liquid crystal complex - *n*OBA : TMD ,Where R= C_nH_{2n+1}, and *n* = 4 to 12.

Newly synthesized *n*OBA : TMD complexes are characterized by different thermal analysis techniques: POM and DSC. Structural characterization is done by the FTIR studies. Complexation of mesogenic *n*OBA and non mesogenic TMD influences the thermal and phase behavior of pure mesogens. The resultant *n*OBA:TMD complexes shows the interesting and completely novel phases which are not present in the pure samples.

III. RESULTS AND DISCUSSION

Characterization of novel homologous series of liquid crystal complexes *n*OBA:TMD are explained in the preceding section.

In detail, all the pure series of samples possess nematic phase and samples with *n*=7 – 12 additionally exhibit Smectic C phase. It was observed that phase transition temperatures of all the complex samples were decreased compared to their pure counterparts. Astonishingly, nematic phase was quenched in the complexes n= 4-6 and Crystal G phase was induced in whole series of the samples and nematic phase also observed in complexes with *n* = 7to12. As a representative case nematic droplets and Crystal G phases of 8OBA :TMD was shown in Figs 1 and 2. Quenching of old phases, inducement of new phases and change in transition temperatures in the prepared complexes were identified which has helped us to conclude that certainlyintermolecular hydrogen bond is formed between *n*OBA and TMD [23-26]. Crystal G phase [27] consisting of molecules packed in different layers with long axis tilted with respect to normal layer planes characterized by C centered monoclinic cell with tilt molecules having pseudo hexagonal close packing [27]. Thermal span of all the Crystal G phases induced in complexes range is around 10^0C – 20^0C which is a remarkable feature of these samples. Thermal span of the nematic phase was reduced from the pure mesogens (*n*OBA).

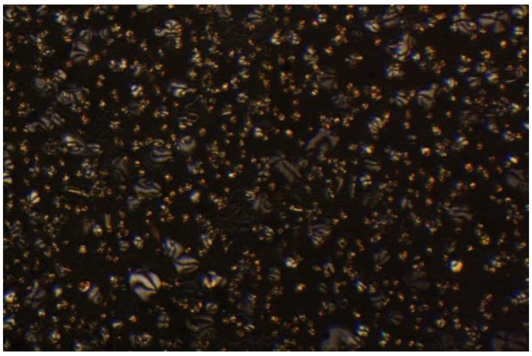


Fig 1..Nematic phase in 8OBA:TMD

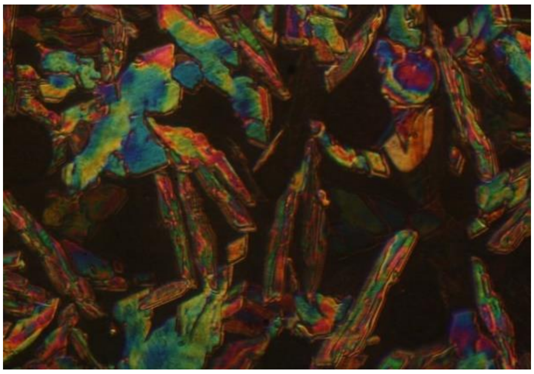


Figure3. Smectic-G phase in 8OBA:TMD

The Phase Transition temperatures recorded using thermal microscope was in good agreement with the recordings using DSC thermo grams given in Table 1. As a representative case DSC thermo gram of 8OBA: TMD was shown in Fig 3.

TABLE 1. Observed Phase Transition temperatures of *n*OBA:TMD using DSC and POM

Compound nOBA:TMD	Phase	Isotropic (I)^{0}C	I – N (^{0}C)	I-G (^{0}C)	N/G-Cr (^{0}C)
n =4 (TM) (DSC)	S_G	116.1 112.4			97.8
n =5 (TM) (DSC)	S_G	110.7 105.1			94
n =6 (TM) (DSC)	S_G	112		99.6 103.7	85.4
n =7 (TM) (DSC)	N,S_G	103	92.6 94.6	86 96.1	73
n =8 (TM) (DSC)	N,S_G	108	90.2 89.5	86.8 76.8	72.1
n =9 (TM) (DSC)	N,S_G	103	101 100.1	95.2 95.8	84.2
n =10 (TM) (DSC)	N,S_G	106	100.3 102.3	91.6 95.4	78.2
n =11 (TM)	N,S_G	105.8	94.2	94.5	75.3

(DSC)			96.0	87.5	
n =12 (TM) (DSC)	N,S_G	110	103.5 104.6	89.5 94.2	70.9

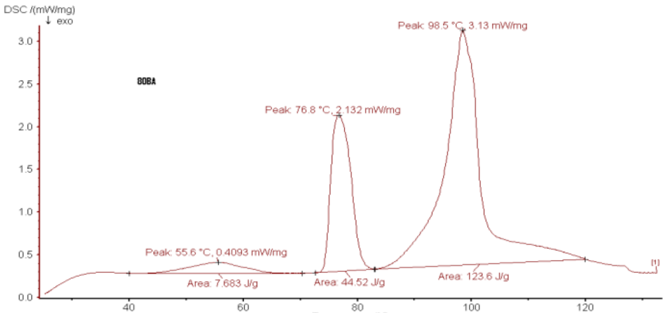


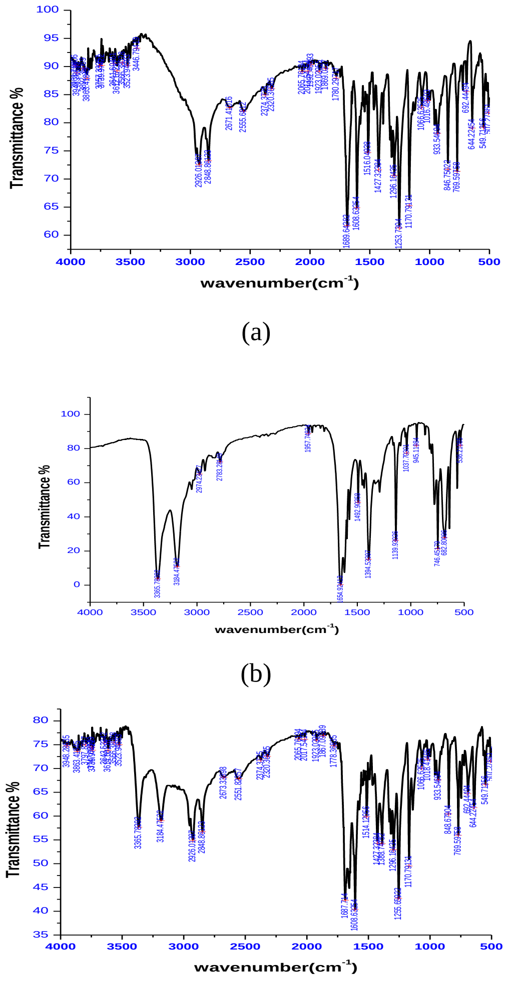
Fig 3. DSC Graph of 8OBA:TMD

A. Fourier Transform Infrared spectroscopy (FTIR):

The IR Spectra of the *p-n*-alkoxy benzoic acids (*n*OBA), ortho toluamide (TMD) and their inter molecular H-bonded complexes were recorded both in solid (KBr) and dissolved (in chloroform) states at room temperature and was shown in Fig 4. The summaries of infrared frequencies along with their assignments were shown in Table 2. The IR spectra of TMD exhibit the strong characteristic absorptions bands at 3369.0 cm^{-1} for N-H stretching along with (out plane bend) OPB modes of NH at 618.02 cm^{-1} [28,29] *n*OBA : TMD complexes show the absorption bands in the range of 620 – 698 cm^{-1} for (NH) OPB modes, strong intense bands due to C-H mode of benzoic acid moiety in the range of 2954-2916 cm^{-1}which supports the existence of *n*OBA moieties in monomeric form upon complexation. The stretching, bending vibrations involving the proton donating groups (NH_2) and proton acceptor groups (O-H) showed shifts in their absorption frequencies, confirms the formation of hydrogen bonding in liquid crystal complexes. TMD with proton accepting substituents O-H, the intra molecular H-bond in TMD disturbs the symmetry of the amino group. Therefore, the formation of intermolecular H-bond with acceptor substituent is formed by the free N-H group. Stability of the hydrogen bonding is observed by IR peak shift of the in plane bend (IPB) mode of N-H and C-H towards the higher frequency side.

TABLE 2. IR spectral data (cm^{-1}) for TMD and *n*OBA:TMD

Sample No.	Compound *n*OBA: TMD	(C=O)		(NH) AMIDE		(NH) OPB	(CH) ACID
		Acid	Amide	(NH) ASY	(NH) SY		
0	TMD		1654	3365.	3184	618	
1	4OBA: TMD	1669	1729	3365	3181	620	2954
2	5OBA: TMD	1662	1729	3367	3184	686	2953
3	6OBA: TMD	1669	1663	3365	3165	698	2931
4	7OBA: TMD	1668	1562	3365	3184	751	2931
5	8OBA: TMD	1689	1687	3365	3184	693	2931
6	9OBA: TMD	1662	1668	3365	3180	682	2918
7	10OBA :TMD	1669	1662	3365	3184	694	2918
8	11OBA :TMD	1668	1662	3365	3182	696	2918
9	12OBA :TMD	1669	1667	3365	3183	698	2916



(a)

(b)

(c|)

Fig 4. (a) FTIR Spectrum of 8OBA;(b). FTIR Spectrum of TMD; b). FTIR Spectrum of TMD;(c) FTIR spectrum of 8OBA:TMD.

As a comparative study between the *n*BA:TMD [16] and *n*OBA:TMD (*n*= 4 to 12) , the data given in Table 3 reveals that in case of NH (IPB) there is a increased shift of 74cm^{-1} for *n*BA:TMD and 513cm^{-1} for *n*OBA:9HB. And also by comparing the FTIR Spectra of *n*BA:TMD and *n*OBA:TMD, the below table shows that *n*BA:TMD exhibits the 12cm^{-1} hypochromic shift in (NH) bond stretch and *n*OBA:TMD shows 25cm^{-1} bathochromic shift with respect to the (NH) bond stretch respectively.

TABLE 3. FTIR data of *n*BA:TMD and *n*OBA:TMD

Compound	(c=o)		(NH) amide		$(NH)_{opb}$	$(CH)_{acid}$
	Acid	Amide	$(NH)_{asy}$	$(NH)_{sy}$		
TMD	-	1655	3367	3185	682	-
8BA	1644	-	-	-	-	2926
8OBA	1684	-	-	-	946	2928
4BA:	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

TMD 4OBA: TMD	1679	1616	3361	3182	685	2954
5BA: TMD 5OBA: TMD	1655 1678	1617 1617	3367 3367	3184 3184	686 686	2863 2953
6BA: TMD 6OBA: TMD	1657 1691	1607 1607	3375 3375	3165 3165	696 682	2855 2931
7BA: TMD 7OBA: TMD	1658 1678	1612 1612	3366 3366	3184 3184	694 696	2851 2931
8BA: TMD 8OBA: TMD	1658 1689	1612 1687	3367 3365	3185 3184	693 694	2852 2931
9BA: TMD 9OBA: TMD	1662 1681	1617 1612	3369 3369	3180 3180	682 693	2853 2918
10BA: TMD 10OBA: TMD	1658 1681	1610 1612	3366 3362	3184 3184	694 682	2851 2918

From the below Table 4 it is observed that, the thermal span for alkoxy complexes is more than alkyl complexes further that thermal stability is comparatively more in *n*OBA:TMD complexes and is around 50ºC. crystal G phase is dominant in *n*BA:TMD complex and *n*OBA:TMD series. Further, theremal stability for *n*BA:TMD complexes lie in between 25ºC. Hence, *n*OBA:TMD complexes are thermally and texturally more stable than *n*BA:TMD.

TABLE 4. Comparison of transition temperatures obtained from POM for *n*OBA:TMD and *n*BA:TMD

Molecular complexes	Phase Variant	I/N– S_G (ºC)	N/S_G – Cr (ºC)
4BA:TMD 4OBA:TMD	NA S_G	NA 116.1	NA 97.8
5BA:TMD 5OBA:TMD	G S_G	68.1 110.7	67.6 94
6BA:TMD 6OBA:TMD	G S_G	82.2 99.6	68 85.4
7BA:TMD 7OBA:TMD	G N,S_G	80 92.6	67.7 73
8BA:TMD 8OBA:TMD	G N,S_G	93.7 86.8	80.3 72.1
9BA:TMD 9OBA:TMD	G N,S_G	85 95.2	76 84.2
10BA:TMD 10OBA:TMD	G N,S_G	83 95.4	75 78.2
11BA:TMD 11OBA:TMD	NA N, S_G	NA 96	NA 75.3
12BA:TMD 12OBA:TMD	NA N, S_G	NA 94.2	NA 70.9

***NA represents Not Available**

IV. CONCLUSION

A new series supra molecular hydrogen bonded liquid crystal complexes have been synthesized from *p*-*n*-alkoxy Benzoic acid (*n*OBA) where *n*=4 to 12 and TMD. (The Crystal G phase induced in all the complexes, and threaded nematic phase is induced in 12OBA:TMD compound.) Hydrogen bond is established between the OH group of the *p*-*n*-Alkoxy Benzoic acid and NH group of TMD, leads to an orthorhombic arrangement of the molecules. Hence, the molecular packing was influenced by the intermolecular Hydrogen Bonding, due to this influence in each layer of the molecule of *n*OBA an arrangement was created like head–to–tail and TMD as an adjacent molecule, a condition which induce crystal G mesomorphism.

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REFERENCES

[01] Frederic J. Kahn, Electric Field Induced Orientational Deformation of Nematic Liquid Crystals: Tunable Birefringence, Applied Physics Letters 20, 199 (1972); doi: 10.1063/1.1654107

[02] G. Singh, G. Vijaya Prakash, S. Kaur, A. Choudhary, A.M. BiradarMolecular relaxation in homeotropically aligned ferroelectric liquid crystalsPhysica B 403 (2008) 3316– 3319

[03] Faten Al-Hazmi, Ahmed A. Al-Ghamdi, Noruh Al-Senany, Fowzia Alnowaiser, Fahrettin Yakuphanoglu Dielectric anisotropy and electrical properties of the copper phthalocyanine (CuPc): 4–40-n-Heptylcyanobiphenyl (7CB) composite liquid crystals, Composites: Part B 56 (2014) 15–19

[04] Chih-Hsin Chena, Kun-Lin Yang A liquid crystal biosensor for detecting organophosphates through the localized pH changes induced by their hydrolytic products, Sensors and Actuators B 181 (2013) 368– 374

[05] Mashooq Khan and Soo-Young ParkLiquid Crystal-Based Proton Sensitive Glucose Biosensordx.doi.org /10.1021/ ac402916v | Anal. Chem. 2014, 86, 1493−1501

[06] Alicia Gamble Synthesis of Liquid Crystals Filling Forms with Function University of Colorado Boulder Liquid Crystals Materials Research Center

[07] Synthesis and mesogenic properties of liquid crystals with bent core-tail substitution geometry Thesis written by Richard Davis B.S., Westminster College, 2008 M.S., Kent State University, 2013

[08] S. Salma Begum, T. Vindhya Kumari, C. Ravi Shankar Kumar, S. Sreehari Sastry, Liquid crystalline G phase of self assembled donor–acceptor molecules by intermolecular hydrogen bonding Journal of Non-Crystalline Solids 357 (2011) 1745–1749

[09] K. Vijayalakshmi and S. Sreehari Sastry Induced Smectic A Phase through Intermolecular Hydrogen Bonding: Part XVIII: Influence of p-n-Alkyl Benzoic Acids on Thermal and Phase Behavior of Hydrogen-Bonded Liquid Crystals Acta Physica Polonica A Vol. 115 (2008) xxxx

[10] Vijayakumar VN, Madhu Mohan MLN. Synthesis and characterization of double hydrogen bonded ferroelectric liquid crystals exhibiting reentrant smectic ordering. Ferroelectrics. 2009; 392:81–97.

[11] Chitravel T, Madhu Mohan MLN. Occurrence of ambient temperature and re-entrant smectic ordering in an inter-molecular hydrogen bonding between alkyl aniline and alkoxy benzoic acids. Mol. Cryst. Liq. Cryst. 2010; 524:131–143.
[12] Vijayakumar VN, Madhu Mohan MLN. Design, synthesis and characterization of hydrogen bonded ferroelectric liquid crystals. Mol. Cryst. Liq. Cryst. 2010; 524:54–67.
[13] Subhapriya P, Vijayakumar VN, Madhu Mohan MLN, Vijay anand PS. Study and characterization of double hydrogen bonded liquid crystals comprising of p-n alkoxy benzoic acids with azelaic and dodecane dicarboxlic acid. Mol. Cryst. Liq. Cryst. 2010; 53:36–50.
[14] Kumar PA, Pisipati VGKM, Rajeswaria AV, Sreehari Sastry S. Induced smectic-G phase through intermolecular hydrogen bonding, part XII: thermal and phase behaviour of p-aminobenzonitrile: p-n-alkoxybenzoic acids. Liquid Crystals Today Z. Naturforsch. 2002; 57a:184–188.
[15] Swathi P, Kumar PA, Pisipati VGKM, Rajeswaria AV, Sreehari Sastry S. Induced smectic-G phase through intermolecular hydrogen bonding, part XV: thermal and phase behaviour of p-alkyl anilines: p- n-alkoxybenzoic acids, Z. Induced smectic-G phase through intermolecular hydrogen bonding, part XV: thermal and phase behaviour of p-alkyl anilines: p-n- alkoxybenzoic acids, Naturforsch. 2002;57a:797–802.
[16] Swathi P, Kumar PA, Pisipati VGKM. Induced smectic-G phase through intermolecular hydrogen bonding, part III: influence of alkyl chain length of p-n-alkoxybenzoic acids on thermal and phase behaviour. Mol. Cryst. Liq. Cryst.2001;365:523–533.
[17] Paleos CM, Tsiourvas D. Thermo tropic liquid crystals formed by intermolecular hydrogen bonding interaction. Angew. Chem. Int. Ed. Engl. 1995; 34:1696–1711.
[18] Gray GW. Molecular structure and the properties of liquid crystals. London: London Academic Press; 1962. p. 163.
[19] Kelker H, Hatz R. Handbook of liquid crystals. Weinheim: Verlag Chemie; 1980. p.59.
[20] Vijayakumar VN, Madhu Mohan MLN. Study of inter molecular hydrogen bonding in p-n-alkoxybenzoic acids and alkyl aniline homologous series–part-I Mol.Cryst. Liq. Cryst. 2009;515:39–48.
[21] Swathi P, Kumar PA, Pisipati VGKM. Induced smectic-B phase through intermolecular hydrogen bonding part IX: comparative thermal and phase behaviour studies on two distinct structural isomers possessing linear and bow shapes. Z. Naturforsch. 2001; 56a:692–696.
[22] K. Vijayalakshmi and S. Sreehari Sastry, Induced smectic phase trhough intermolecular hydrogen bnonding Part XVIII: Influence of *p*-*n*-alkyl benzoic acid on thermal and phase behavior of hydrogen bonded liquid crystals. Acta Physica Polonica A Vol. 115 (2009) 690-693-
[23] S. Salma Begum, T. Vindhya Kumari, C. Ravi Shankar Kumar, S. Sreehari Sastry Liquid crystalline G phase of self assembled donor-acceptor molecules by intermolecurlar hydrogen bonding Journal of Non-Crystalline Solids 357 (2011) 1745–1749,
[24] S. Sreehari Sastry, S. Salma Begum, K. Mallika, K.B. Mahalakshmi, Ha Sie Tiong Image analysis to detect phase transition temperatures of *p*-*n*-alkyl bnenzoic acids International Journal of Innovative Research in Science, Engineering and Technology Vol. 2, Issue 9, September 2013, 4641-4647
[25] S. Sreehari Sastry, S. Salma Begum, T. Vindhya Kumari,V.R.K. Murthy, and Sie Tiong Ha, Effect of mage\netitel nano particles on *p*-*n*-alky benzoic acid mesogens, E-Journal of Chemistry, 2012, 9(4), 2462-2471,
[26] Ch. Hemalakshmi and S. Sreehari Sastry Study of Supramolecule through Intermolecular Hydrogen Bond in 5OBA:TMD Liquid Crystals, IJERT, 2017, 6, 225-228
[27] Robert M. Silverstein, Francis X. Webster, Spectrometric Identification of Organic Compounds, 6th Ed., 1997.
[28] H. Williams, Ian Fleming, Spectroscopic Methods in Organic Chemistry, TMH, 2004.
[29] William K. Organic Spectroscopy. Haryana: Replika Press; rr 2008.