

Study of Supramolecule through Intermolecular Hydrogen Bond in 5OBA:TMD Liquid Crystals

Ch. Hemalakshmi and S. Sreehari Sastry*
Department of Physics, Acharya Nagarjuna University,
Nagarjunanagar -522510, India

Abstract— Intermolecular hydrogen bond in Supramolecular liquid crystal from mesogenic pentyloxy benzoic acid with non-mesogenic toulamide moieties that arise due to non-covalent interaction has been studied. Polarizing optical microscopic investigations revealed monotropic crystal G phase while enantiotropic nematic phase in the prepared compound and pure liquid crystal. The liquid crystalline phase transitions were confirmed differential scanning calorimeter. Intermolecular Hydrogen bonding and the structural determination in the liquid crystalline amide were performed by the FTIR spectroscopy. The detailed study of FTIR in 5OBA, TMD and 5OBA:TMD samples were carried out and revealed strong intermolecular hydrogen bond between the pentyloxy benzoic acid and Toulamide..

Keywords: Alkoxy benzoic acid, Induced crystal- G phase, Hydrogen bond, DSC, FTIR.

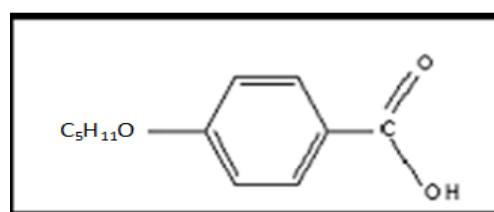
1. INTRODUCTION

Intermolecular hydrogen bonding play important role in the design and synthesis of many liquid crystalline materials [1] and [2]. The liquid crystalline behavior due to [3] hydrogen bonding that are synthesized include the conventional liquid crystals [4]. The formation of these hydrogen bonds played crucial role in self assembling process and building organized molecular structures [5,6]. In previous studies many liquid crystalline materials were synthesized with either mesomorphic or non-mesomorphic [7–10] compounds cross linked by non-covalent interactions [11,12] and with inducement of phases [13–17] attracted more interest that hold promise in potential applications [9] leading to supramolecular structures [18] due to its stability and directionality [19]. With untiring efforts and quest in the development, new liquid crystals are attributed between the pentyloxy benzoic acids and Toulamide. The chosen amide attributed the formation of supramolecular structures [20]. It is by fact that amide [21] resulted in hydrogen bonding with the decreased bond energies [22] due to the non-covalent coulomb interactions between the involved groups. The supramolecular hydrogen bonded liquid crystalline amide exhibit liquid crystalline nature between the – COOH group and the amide that turned by self assembly process that lead to structure in Fig. 1.

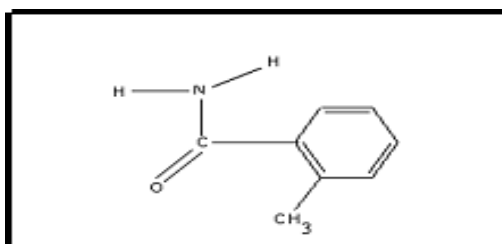
II. EXPERIMENTAL DETAILS

The present compound *p*-pentyloxy benzoic acid (5OBA) which is a mesogen and non mesogen *o*-toluamide (TMD) were supply by M/s Frinton laboratories, Inc., USA. Solvent pyridine was supply by Qualigens India. The complex, *p*-pentyloxy benzoic acid : *p*-toluamide (5OBA: TMD) was synthesized by

refluxing together in equimolar ratio (1:1) of *p*-pentyloxy benzoic acid and toulamide.. They are taken individually and mixed in the pyridine solvent (20ml). Now the two solutions are mixed and kept under constant stirring at 80°C for ~4hrs. Then most of the pyridine is removed by vacuum distillation process. It means the volume of the resultant homogeneous mixture was reduced to almost dryness by removing the excess pyridine under a controlled vacuum filtration. The white crystalline product was dried and re-crystallized from hot dichloromethane solution. The yielding is at about 85% with intermolecular hydrogen bonded structure . The Phase variants and the transition temperatures of *p*-pentyloxy benzoic acid : *p*-toluamide (5OBA: TMD) were determined from textural observation conducted under a thermal polarizing microscope (Meopta, DRU-3) provided with hot stage and a Canon colour Camera. Temperatures were determined by digital thermometer with an accuracy of $\pm 0.1^\circ\text{C}$. The temperature of the corresponding phase transitions were confirmed by Perkin-Elmer Differential Scanning Calorimeter (DSC) at a scan rate of $2^\circ\text{C}/\text{min}$. The infrared (IR) spectra in the solid state were recorded on a FTIR (FTIR 5300). Spectrometer (Jasco, Japan).



(a) Molecular Structure of *p*-pentyloxy benzoic acid



(b) Molecular Structure of *ortho*- Toluamide

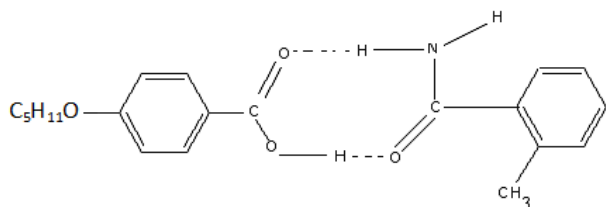


Figure-1: Molecular texture of (a) 5OBA, (B) Toluamide (c) 5OBA:TMD

III. RESULTS AND DISCUSSION

All compounds are isolated under investigation and are stable at room temperature. The infrared frequencies in solid state (KBr) which are correlated to bonds with the free *p*-pentyloxy benzoic acid and *o*-toluamide along with its complex is tabulated in Table 1 which is recorded at room temperature.. The sharp peaks of pentyloxy benzoic acid (5OBA) [14] with wave number assignments related to (C=O) at 1678 cm⁻¹ reveal the dimeric nature [11] due to two component absorption band in crystal phase and frequency of 2955 is assigned to the (OH) mode. The identified wave numbers Toulamide [23,24] with peaks occur at 1394 cm⁻¹ due to (CN) mode with the asymmetric (ASY) and symmetric (SY) at 3367 and 3580cm⁻¹ due to NH mode together with 682 cm⁻¹ to the NH out of plane bending (OPB). Hydrogen bonding is convinced in the homologous series with pentyloxy benzoic acid as reference. The bonded frequencies corresponding to the acid and amide reveal a bathochromic shift* 20 cm⁻¹ due to C=O, * 80 cm⁻¹.

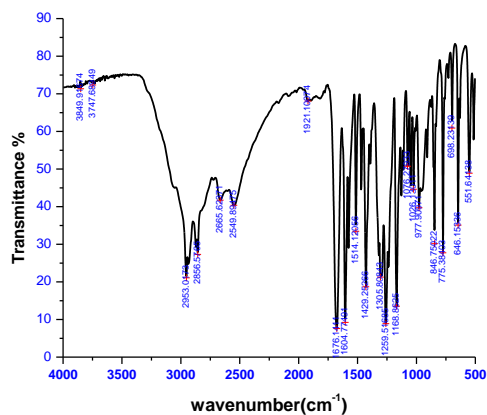


Fig 2(a). Ftir Spectra of 5oba

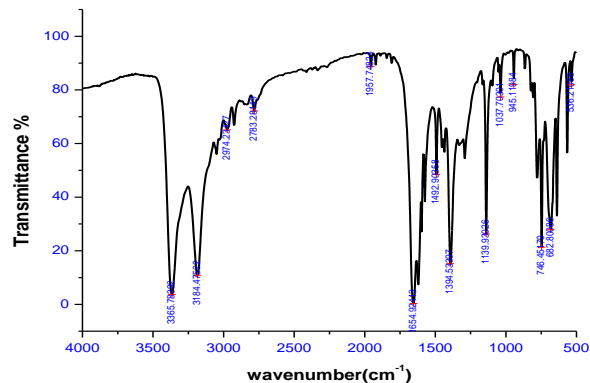


Fig.2(b) Ftir Spectra of Tmd

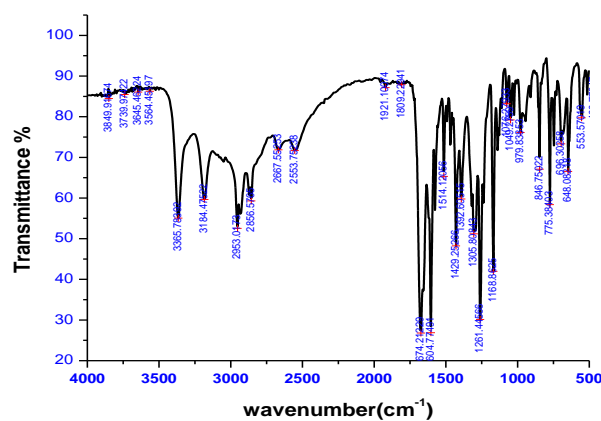


Fig.2(c) Ftir Spectra of 5oba:Tmd

Table 1: FT-IR ANALYSIS FOR THE NON-MESOGEN, MESOGEN AND HYDROGEN BONDED MESOGEN TMD, 5OBA AND 5OBA:TMD. (in cm⁻¹)

Compound	TMD	5OBA	5OBA :TMD
Functional Group			
(NH) _{ASY}	3530		3483
(NH) _{SY}	3185		3184
C=O		1678	1665
(NH) _{IPB}			1612
C-N	1394		1421
C-O	1137	1290	1294
(NH) _{OPB}	682		676
O-H		2955	2953
(CH) _{IPB}		1510	1514
(OH) _{IPB}		1422	1429
(COC) _{SY}		1173	1168
(COC) _{ASY}		1011	1074
(OH) _{OPB}		908	978
C-C		851	846

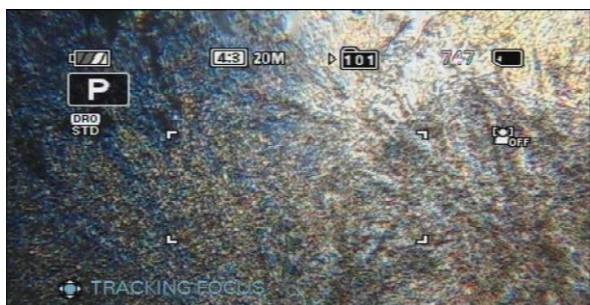


Fig 3. Texture of nematic phase of 5OBA

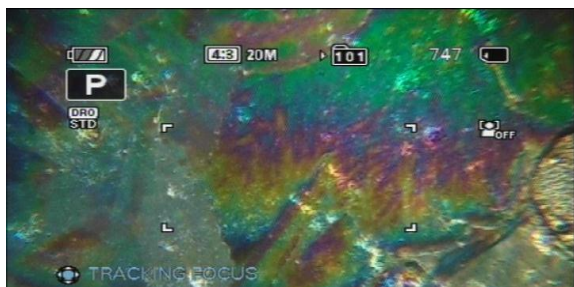


Fig 4 Texture of crystal G phase of 5OBA: TMD

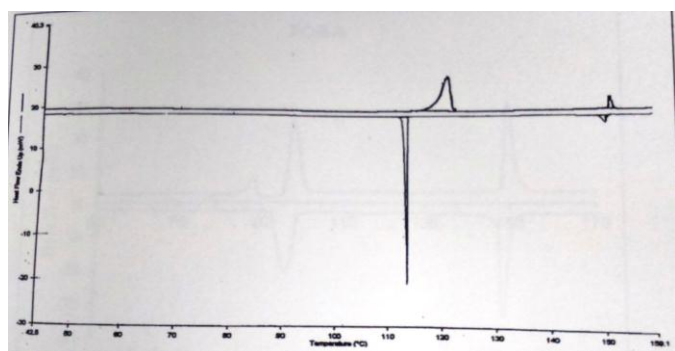


Fig.5(a) DSC thermogram of 5OBA:TMD

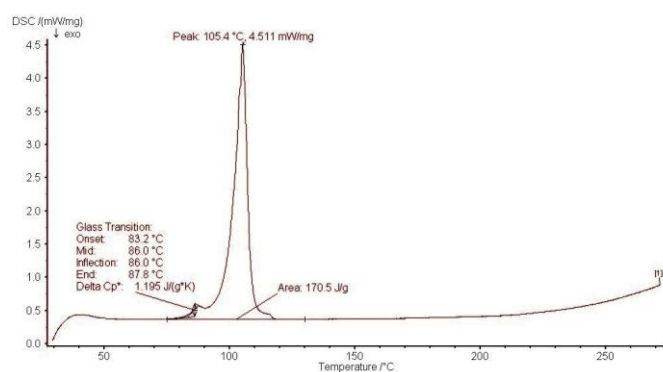


Fig.5(b) DSC thermogram of 5OBA:TMD in cooling cycle

Table 2: The phase transition temperatures in heating (H) and cooling (C) Cycles for, 5OBA TMD and 5OBA:TMD using Polarizing Optical Microscope

Compound	Cr to N/G	N/G to I
5OBA (H)	121.6 °C	146.5 °C
5OBA (C)	114.6 °C	145.4 °C
TMD	--	143-145 °C (melting point)
5OBA:TMD(C)	87.6 °C	105.1 °C

corresponding to the OH mode of acid and 80 cm^{-1} due NH out of plane bending. Further hydrogen bonding is enhanced due to the CN stretching exhibiting hypsochromic shift of 15 cm^{-1} . These shift in frequencies with simultaneous increase and decrease confirm the fact that hydrogen bonding takes place between the acid and amide group. The IR spectral studies in chloroform reveal the destruction of hydrogen bonding with increase in stretching frequencies of CN confirming the destruction of hydrogen bonding in solution. All the peak integrations are well suitable for the hydrogen bonded acid and amide structure Fig. 1 with unaltered stretching modes of NH. The stretching assignments of associated wave numbers of (C=O) ACID, (OH)ACID,(CN)AMIDE and (NH)OPB, the hydrogen bonding may be expected between (C=O)ACID and (CN)AMIDE that lead to structure in Fig. 1. The thermodynamic behavior of phases in cooling cycle are characterized by the textural observations [26] with their transition temperatures determined by polarizing optical microscope of pentylxy benzoic acid and the designed hydrogen bonded toulamide (5OBA:TMD) are tabulated in Table.2.pentylxy benzoic acid [13] exhibiting marble nematic phase. These members of series show enantiotropic liquid crystalline nature over wide range of temperature from the isotropic melt. The toulamide is non-mesogenic and does not exhibit any phase. The bonded amide resulted in crystal G phase. In the cooling process isotropic to threated nematic transition occurs which is shown in Fig. 3, on further cooling nematic phase nucleates to a growth patterns and subsequently to form layer texture of crystalline G phase by hydrogen bonding is shown in Fig 4.

Crystal G phase [27] has molecules packed in layers with their long axis tilted with respect to normal to layer planes characterized by C centered monoclinic cell with tilt molecules having pseudo hexagonal close packing. Molecules of this phase undergo reorientational motion about long axes with herring bone local structure with superposition of three different orientations of local orthorhombic cells that contributes to hexagonal symmetry [28]. This phase nucleates with dendritic growth pattern forming elongated platelets that result in layered texture which is very ordered. The texture characteristically forms elongated platelets as mesophase separates from preceding medium which are rectangular in shape. The phase is very viscous and sheared that crumple into another retaining some of the original shape with cover slip subjected to mechanical displacement. Crystal G phase exhibits microscopic textures as it is formed from large

variety of precursor phases like nematic's and smectic's. These exhibit a high degree of thermal and chemical stability when subjected to repeated observations with polarizing optical microscope and differential scanning calorimetry. DSC flow chart is show in Fig .5(b)

The transition temperatures of pure 5OBA and the synthesized compound 5OBA: TMD according to the Differential Scanning Calorimetry (DSC) [31-32], in heating cycle, the pure 5OBA exhibits enantiotropic nematic phase at 121.6 °C and this phase extends up to 146.5 °C to change to isotropic phase. In cooling cycle, the nematic phase separates from the isotropic phase at 145.0°C and this phase remains up to 114.6°C and becomes solid. The DSC thermogram of 5OBA is shown in Fig. 5(a) in both heating and cooling cycles.

In 5OBA:TMD monotropic crystal G phase is exhibited which is induced crystal G phase in between temperature 105.4°C. On further cooling, it becomes crystal at 86.7. The transition temperatures obtained from the DSC study and POM study are in good agreement.

IV. CONCLUSIONS

The intermolecular hydrogen bonded carboxylic acid dimmers aid the formation of bonded amides exhibiting crystal G phase due to dynamic nature of non-covalent interactions and reduced bond energies between the two polar groups. The pronounced effect of between the C=O, OH of acid and NH, CN group of amide is functional in the formation of intermolecular hydrogen bonding. These explanations suffice the liquid crystalline amide through inter molecular hydrogen bonding with crystal G phase.

. ACKNOWLEDGEMENTS

The authors acknowledge T. Kalyani and M. Sailaja for their help rendered in this work. The authors gratefully acknowledge University Grants Commission Departmental Special Assistance at Level I program No. F.530/1/ DSA-1/2015 (SAP-1), dated 12 May 2015, and Department of Science and Technology-Fund for Improving Science and Technology program No.DST/FIST/ PSI-002/2011 dated 20-12-2011, New Delhi, to the department of Physics, Acharya Nagarjuna University for providing financial assistance.

REFERENCES

- [1] T. Kato, in: D. Demus, G. Goodby, W. Gray, H.W. Spiess, V.W. Vill (Eds.), *Hand Book of Liquid crystals*, Wiley-VCH, 1998.
- [2] C.M. Paleos, D. Tsiourvos, *Supramolecular Hydrogen Bonded Liquid Crystals*.Liq. Cryst. Vol.28, 1127.-1161, 2001.
- [3] L.M. Wilson, "A highly ordered Hydrogen bonded Net- work Liq. Cryst. 18 381-385 .1995
- [4] Z. Sideratou, D. Tsiourvas, C.M. Paleos, *Liquid crystalline behaviour of hydrogen bonded complexes of a non-mesogenic anil with p-n-alkoxybenzoic acids*, Liq. Cryst. Vol.22, 51- 60 1997
- [5] G.W. Gray, *Molecular Structures and Properties of Liquid Crystals*, Academic,London, 1962.
- [6] C.M. Paleos, T. Siourvas, *Thermotropic Liquid Crystals Formed by Intermolecular Hydrogen Bonding Interactions*, Angew. Chem., Soc. Int. Ed. Vol.34, 1696-1711 1995
- [7] Hong Chen Lin, Chung-Wen Ko, Kermin Go, Tze-Wen Cheng, *Supramolecular liquid crystals containing isoquinoline hydrogen-bonded Acceptors*, Vol. Liq. Cryst. Vol.26, 613-618, 1999.

- [8] P.A. Kumar, P. Swathi, V.G.K.M. Pisipati, A.V. Rajeswari, S. Sreehari Sastry, *Induced smectic-G phase through intermolecular hydrogen bonding part XIII: Impact of a nematogen on phase behaviour of hydrogen bonded liquid crystals*. Phase Transitions Vol.76, 625-632, 2003.
- [9] Kato, J.M.J. Frechet, *a new approach to mesophase stabilization through hydrogen bonding molecular interactions in binary mixtures* J. Am. Chem. Soc. Vol. 111 8533-8334, 1989.
- [10] L. Cher, T. Ling, Jianwei Xu, Xuehong Lu, Chaobin He, *Synthesis and characterisation of main-chain hydrogen-bonded supramolecular liquid crystalline complexes formed by azo-containing*, Liq. Cryst. Vol.35 241-251, 2008.
- [11] Seung Koo Kang, Edward T. Samulski, *Liquid crystals comprising hydrogen-bonded organic acids i. mixtures of non-mesogenic acids* Liq. Cryst. Vol.27 371-376 2000
- [12] Takashi Kato, M. Fukumasa, J.M.J. Fretchet, *Supramolecular liquid-crystalline complexes exhibiting room-temperature mesophases and electrooptic effects. hydrogen-bonded mesogens derived from alkyipyridines and benzoic acids* Chem. Mater. Vol. 7, 368-372 1995
- [13] P.A. Kumar, M. Srinivaulu, V.G.K.M. Pisipati, *Induced Smectic-G Phase through Intermolecular H-bonding* Liq. Cryst. Vol. 26., 1339-1999.
- [14] P.A. Kumar, P. Swathi, V.G.K.M. Pisipati, A.V. Rajeswari, *Induced smectic-G phase through inter molecular hydrogen bonding Part XIV: Influence of alkyl carbons on phase distribution of induced phase* Cryst. Res. Technol. Vol. 37, 595-601 2002.
- [15] P.A. Kumar, V.G.K.M. Pisipati, A.V. Rajeswari, S. Sreehari Sastry, *Induced smectic-G phase through intermolecular hydrogen bonding part XII#: Thermal and phase Behaviour of p-aminobenzonitrile:p-n-alkoxybenzoic acid* Z. Naturforsch. Vol. 57a, 184-189, 2001.
- [16] P. Swathi, P.A. Kumar, V.G.K.M. Pisipati, *Induced Smectic-G Phase through Intermolecular H-bonding Part II. Influence of alkyl chain length of p-hydroxy-n-alkylbenzoates on thermal and phase behaviour* Liq. Cryst. Vol.27, 665 2000.
- [17] P. Swathi, P.A. Kumar, V.G.K.M. Pisipati, *Induced smectic-G phase through intermolecular hydrogen bonding Part IV. A study of Crystallization kinetics* Liq. Cryst. Vol.28, 1163-1169.2001.
- [18] T. Kato, J.M.J. Frechet, *Hydrogen-bonded liquid crystals built from hydrogen-bonding donors and acceptors infrared study on the stability of the hydrogen bond between carboxylic acid and pyridyl moieties* Liq. Cryst. Vol.33,1429-1437 2006.
- [19] M. Lehn, *supramolecular chemistry—scope and perspectives molecules, supermolecules, and molecular devices (nobel lecture)* Angew. Chem., Int. Ed. Engl. Vol.27, 89 1988.
- [20] M. Masahiko, K. Yoshinori, A. Harada, *Formation of Supramolecular polymers constructed by cyclodextrins with cinnamide* *J. Inclusion Phenom. Macroyclic Chem.*Vol. 50, 57-62 2004
- [21] Y. Mastunaga, M. Terada, *Liquid crystal phases exhibited by n,n'-Dialkanoyldiaminomesitylenes*, Mol. Cryst. Liq. Cryst. Vol.141, 321-326 1986.
- [22] S. Lifson, A.T. Hagler, P. Dauber, *Consistent force field studies of intermolecular forces in hydrogen-bonded crystals. 1. carboxylic acids, amides, and the c:o.cntdot.cntdot.cntdot.h- hydrogen bonds* J. Am. Chem. Soc Vol.101, 5111-5121 1979.
- [23] Robert M. Silverstein, Francis X. Webster, *Spectrometric Identification of Organic Compounds*, 6th Ed., 1997.
- [24] H. Williams, Ian Fleming, *Spectroscopic Methods in Organic Chemistry*, TMH,2004.
- [25] F. Scheinmann, *An introduction to spectroscopic methods for identification of organic compounds*, Nuclear Magnetic Resonance and Infrared Spectroscopy, vol. 1, Pergamon, 1970.
- [26] G.W. Gray, J.W. Goodby, *Smectic Liquid Crystals*, Leonard Hill, 1984.
- [27] Iam Choon Khoo, Francesco Simoni, *Physics of Liquid Crystal Materials*, Gordon and Breach Science, 1991.
- [28] A.J. Dianoux, F. Volino, *Molecular orientational order in the mesophases of TBBA : Results of a consistent analysis of neutron, NQR and NMR data*, J. Phys. Vol.40, 181-190, 1979..
- [29] Thermal Analysis <http://liqcryst.chemie.uni-hamburg.de/icionline/liqcryst/icintro/topics/CH1B7.html>
- [30] Y Zheng., S.Ren., Y.Ling and M.Lu, *DSC study on thermotropic liquid crystalline compounds with alkyl substituents*, Molecular Crystals and Liquid Crystals Vol.452, 3 – 9, 2006