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Synthesis and Characterization of 9OBA : EBCA Intermolecular Hydrogen Bonded Mesogen

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ABSTRACT: The role of hydrogen bonding interaction in the formation and stabilization of mesophases has been recognized and significant work has been turned out. It was found that hydrogen bonds are successfully employed for the inducement of new mesophase and/or quenching of phase(s). The hydrogen bond has a striking influence on the phase behaviour as well as phase transition temperatures etc; Synthesis of hydrogen bonded liquid crystal consisting mesogenic+mesogenic, namely *p*-nonyloxy benzoic acid :*p*-(*p*'-ethoxy benzylidene – cyano aniline (9OBA:EBCA) is carried out. Characterization of the new compound is done through FTIR spectra for hydrogen bond formation, textural and phase transition studies through polarization optical microscope attached with hot stage and camera and confirmation of phase transition temperatures through differential calorimetry. From FTIR spectra, it is observed that hydrogen bond is formed between OH of 9OBA and NC of EBCA. The thermal polarizing microscope observations show that the three compounds 9OBA, EBCA and 9OBA: EBCA are enantiotopic liquid crystals exhibiting threaded marble nematic and schlieren smectic C phases, threaded nematic mesophase and threaded marble nematic and schlieren smectic C and marble smectic G phases respectively indicating induced phase in the synthesized compound along with changes in phase transition temperatures. Comparative study of 5OBA: EBCA and 8OBA: EBCA is discussed.

KEYWORDS: Polarizing optical microscope, Differential Scanning Calorimetry, hydrogen bond, Smectic –G, Infrared Spectroscopy,

I. INTRODUCTION

The role of hydrogen bonding interactions in the formation and stabilization of mesophases [1,2] has been recognized and significant work has been turned out. . The hydrogen bond has a striking influence on the phase behaviour as well as transition temperatures. The hydrogen bond liquid crystal (mesogen) may be synthesized with the combination of mesogenic + mesogenic, mesogenic + non- mesogenic and non-mesogenic + non-mesogenic but the present work is containing mesogenic+mesogenic , namely *p*-nonyloxy benzoic acid (9OBA) and: *p*-(*p*'-ethoxy benzylidene – cyano aniline (EBCA).

II RELATED WORK

Within the domain of liquid crystals prepared from multiple hydrogen bonding interactions[3-6], the synthesis and characterization of supramolecular liquid crystals and induced by the non-covalent electrostatic interaction involving intermolecular hydrogen bonding[7,8] have gained much attention. The liquid crystalline selforganization gives the material unique structures. Typically the dynamic character of linear calamatic hydrogen bonded liquid crystals are used as optical materials [9]. Induction and stabilization of liquid crystallinity through hydrogen bonding [10-12] are gaining momentum.

III. EXPERIMENTAL

The experimental work involves the synthesis of the compound and identification of textures with transition temperatures, confirmation of phase transition temperatures and confirmation of H-bond using thermal polarizing microscope attached with hot stage, Differential Scanning Calorimetry, and Fourier Transform Infrared (FTIR) Spectroscopy respectively. *p*- nonyloxy benzoic acid (9OBA) and *p*-(*p*'-ethoxy benzylidene – cyano aniline

which are mesogens obtained from M/s Frinton laboratories, New Jersey USA. Both 9OBA and EBCA are white crystalline compounds at room temperature. The complex *p* nonyloxy benzoic acid: *p*-(*p*'-ethoxy benzylidene – cyano aniline (9OBA: EBCA) is synthesized by refluxing together *p*-nonyl oxy benzoic acid (0.4406gms) and *p*-(*p*'-ethoxy benzylidene – cyano aniline (0.4200gms) in equimolar ratio 1:1. Each compound mixed in the pyridine solvent (20ml). Now the two solutions 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 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% The synthesis route is given in Fig 1

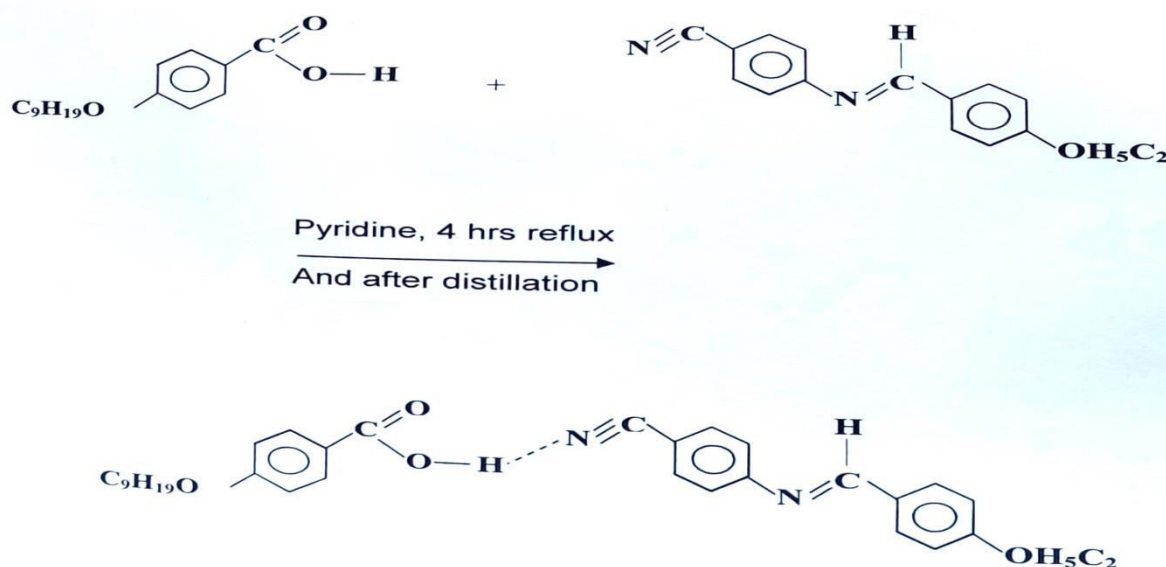


Fig1: Synthesis of 9OBA: EBCA

The phase variations and transition temperatures in the hydrogen bonded complexes are determined by textural observations made by a polarizing optical microscope (POM) (MEOPTA, ORE-MICROSCOPE-DRU-3, S.NO:56512) equipped with a hot stage. Different textures are photographed with the digital camera of Canon make with specifications (EOS (RebelXS/EOS 1000D)). A digital thermometer with the range -50°C to 300°C and with an accuracy of $\pm 0.1^{\circ}\text{C}$ is used to determine the temperature. The transition temperatures of the compounds under investigation were determined using Perkin-Elmer DSC, model Diamond and the weight of the samples were measured with single pan balance Metler Model AE 240 with an accuracy of 0.01mg. FTIR 5300 spectrometer of JASCO (Japan) instrument is used. Spectra are taken in solid KBr and liquid chloroform.

IV. RESULTS AND DISCUSSIONS

A novel mesogen *p* nonyl oxy benzoic acid *p*-(*p*'-ethoxy benzylidene – cyano aniline (9OBA:EBCA) containing mesogens *p* nonyloxy benzoic acid (9OBA) and *p*-(*p*'-ethoxy benzylidene – cyano aniline (EBCA) was synthesized and further characterized as given below.

Polarizing optical microscopy: -

Under crossed polarizers, different textures exhibited by liquid crystals for different temperatures. From POM studies, In heating cycle, the pure 9OBA which is enantiotropic in nature, exhibits schlieren smectic –C phase Fig. 2 in between the temperatures 95.8°C and 118.5°C . On further heating, it changes to threaded marble nematic phase at 118.5°C and this phase remains upto 142.3°C as shown in fig 3. On further heating it becomes isotropic. In cooling cycle the nematic droplets (Fig 4) separate from the isotropic melt at 141.9°C . These nematic droplets combined together to form the nematic phase which remains up to 118.2°C . On further cooling Schlieren Smectic –C phase exists in between the temperatures 118.2°C and 94.4°C . Afterwards it becomes solid phase. EBCA, which is also an enantiotropic liquid

crystal exhibits nematic phase (Fig. 5) in between the temperatures 102°C and 123.9°C on heating and in between the temperatures 122.5°C and 104.5°C on cooling. The compound 9OBA: EBCA exhibits three phases i.e. smectic –G (Fig. 6), smectic – C and nematic phase in between solid phase and isotropic phase. The induced smectic –G phase is observed in both heating and cooling cycles in addition to the Smectic –C and nematic phases. In heating cycle, induced smectic-G is observed in smooth mosaic texture at 73°C . Smectic –C phase is observed in between the temperatures 83.5°C and 115.5°C . On further heating, Smectic –C phase is changed to nematic phase in between the temperatures 115.5°C and 121°C . It becomes isotropic at 121°C . In cooling cycle, from the isotropic melt nematic phase is observed at 120.2°C . This phase remains upto 13.5°C . On further cooling smectic –C phase exists in between the temperatures 113.5°C and 83.6°C , smectic G phase is induced and it remains upto 61.1°C . The compound becomes solid below 61.1°C . Inducement of new phase and/or quenching of existing phase is a striking manifestation of hydrogen bond formation..

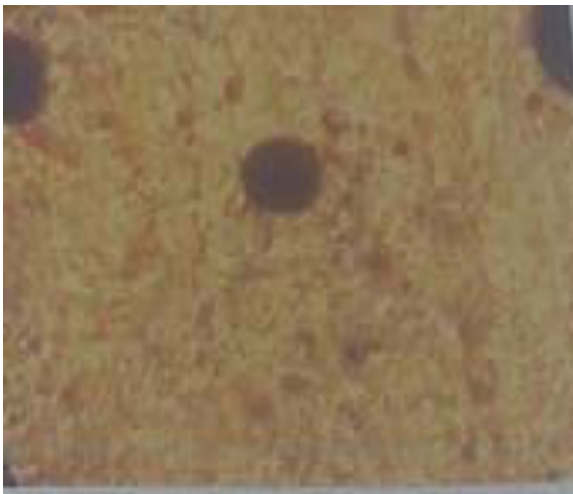


Fig 2 Schlieren smectic –C phase



Fig. 3 Threaded marble nematic mesophase

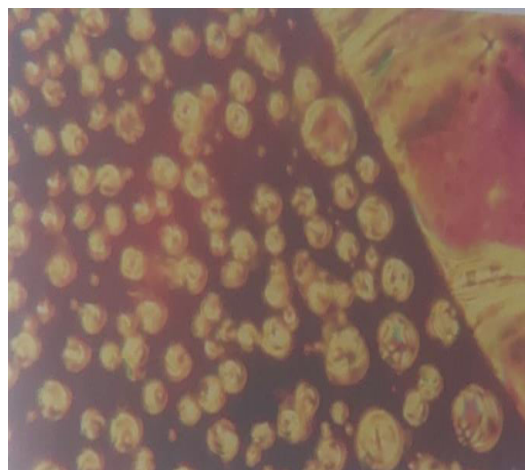


Fig. 4 Nematic droplets



Fig 5 Nematic phase

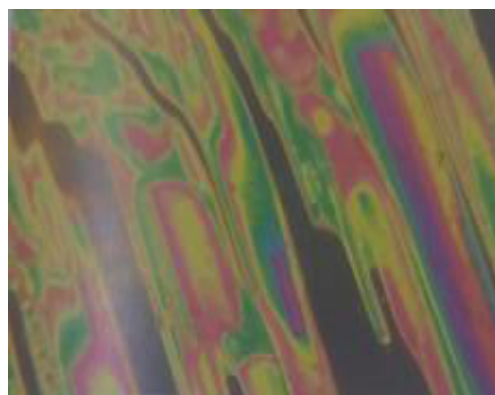


Fig 6 Smectic -G phase

Differential Scanning Calorimeter: -

In heating cycle, the pure 9OBA exhibits Smectic -C phase in between the temperatures 94.2^oC and 115.5^oC. On further heating, it changes to nematic phase at 115.5^oC and this phase remains upto 142.1^oC. On further heating it becomes isotropic. In cooling cycle the nematic phase separates from the isotropic melt at 141.3^oC and this phase remains up to 112.2^oC. On further cooling Smectic -C phase exists in between the temperatures 112.2^oC and 88.9^oC. On further cooling, it becomes as solid below 88.9^oC. The pure EBCA exhibits nematic phase in between the temperatures 103.8^oC and 126.3^oC on heating and in between the temperatures 116.3^oC and 76.6^oC on super cooling, which is enantiotropic. In heating cycle 9OBA: EBCA exhibits smectic -G phase but DSC peak is not well resolved. On heating the compound exhibits smectic-C phase at 86.7^oC and the peaks corresponding to smectic-C to nematic phase and nematic phase to isotropic are not well resolved. In cooling cycle, the transition peak corresponding to isotropic to nematic and nematic to smectic-C phase are not well resolved in DSC. On further cooling, the smectic-G phase separated from the smectic-C phase exists in between the temperatures 69^oC and 58.6^oC. Afterwards on further cooling it becomes a solid below 58.6^oC. DSC thermograms in heating and cooling cycles are shown in Fig 7-9, The

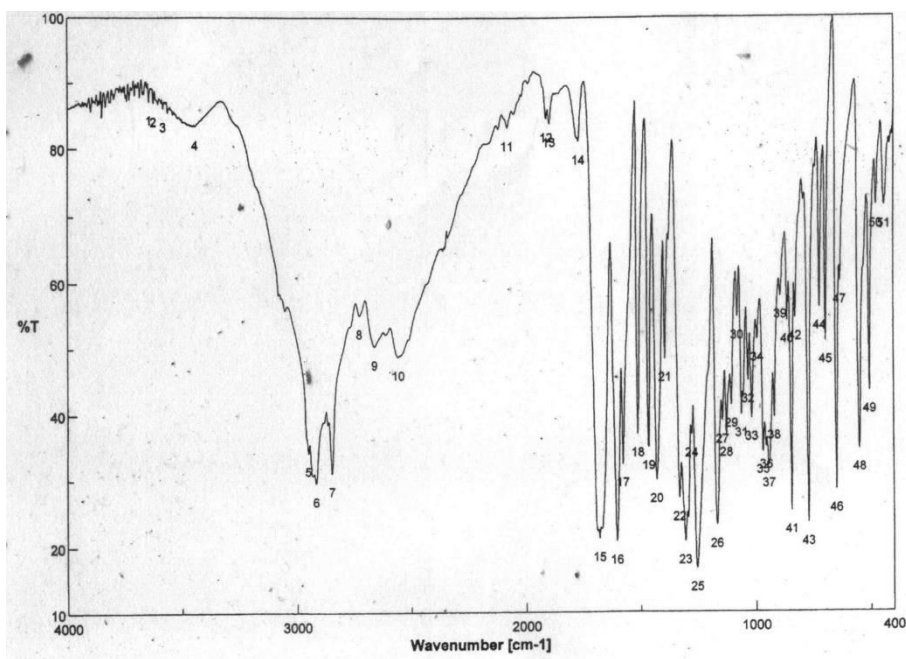


Fig. 7 DSC THERMOGRAM OF 9OBA

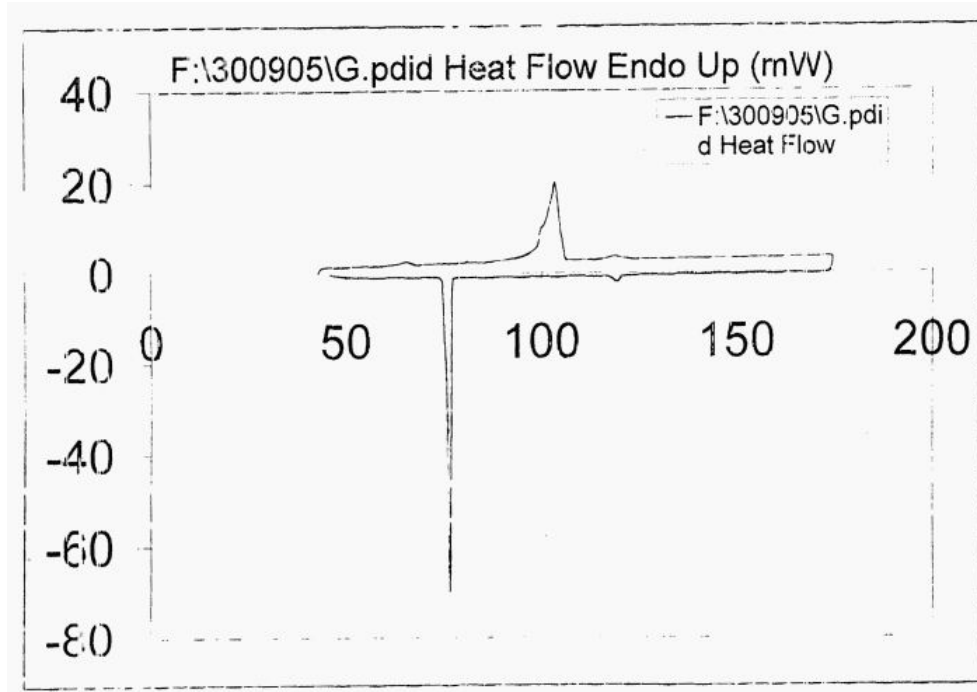


Fig. 8 DSC Thermogram of EBCA

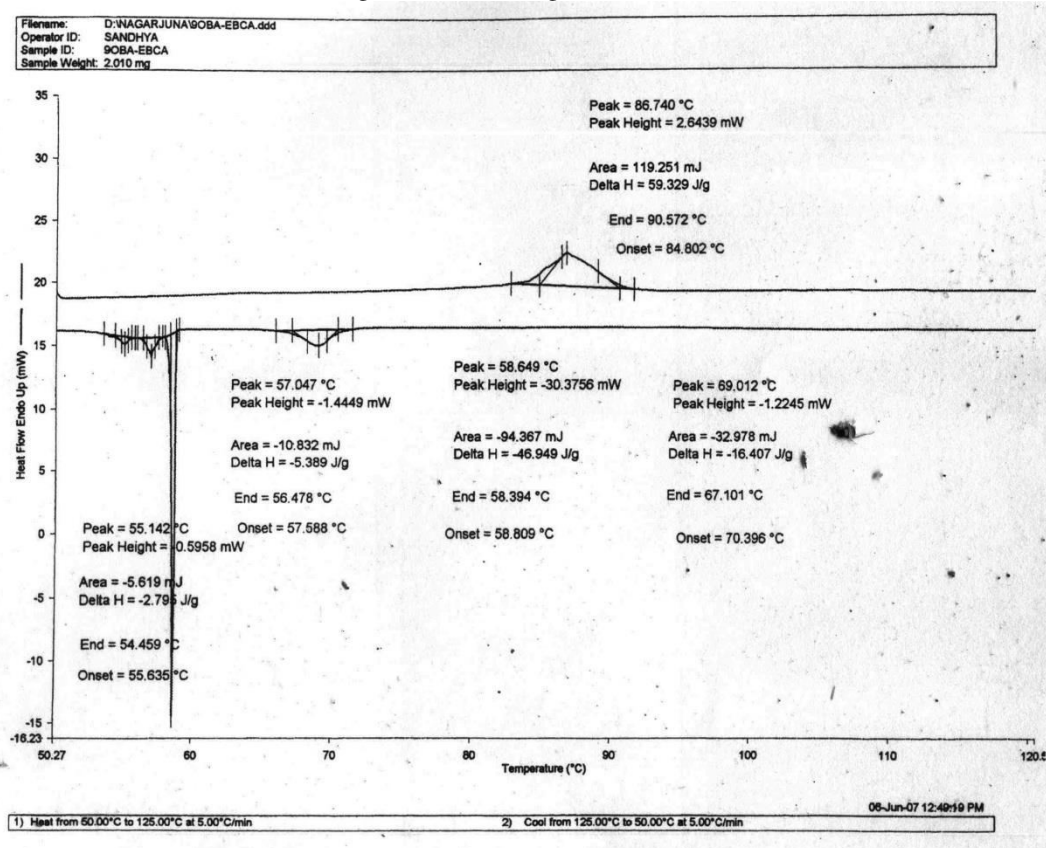


Fig 9



phase transition temperatures observed through thermal polarizing microscope are almost coinciding with DSC studies. The transition temperatures obtained from POM and DSC studies are given in Table 1

Table 1: Phase transition temperatures form POM and DSC

| <i>p</i> -nonyl oxy benzoic acid (9OBA) | | | | |
|---|-------------------------|----------------------------------|---------------------|----------------|
| Experiment | Solid to S _C | S _C to N | N to Isotropic | |
| POM (H) | 95.8 | 118.5 | 142.3 | |
| POM (C) | 94.4 | 118.2 | 141.9 | |
| DSC (H) | 94.2 | 115.5 | 142.1 | |
| DSC (C) | 88.9 | 112.2 | 141.3 | |
| EBCA <i>p</i> -(<i>p</i> '-ethoxy benzylidene – cyano aniline | | | | |
| | Solid to N | N to Isotropic | | |
| POM (H) | 102 | 123.9 | | |
| POM (C) | 104.5 | 122.5 | | |
| DSC (H) | 103.8 | 126.3 | | |
| DSC (C) | 76.6 | 116.3 | | |
| Synthesized compound <i>p</i> -nonyl oxy benzoic acid (9OBA) <i>p</i> -(<i>p</i> '-ethoxy benzylidene – cyano aniline | | | | |
| | Solid to S _G | S _G to S _C | S _C to N | N to Isotropic |
| POM (H) | 73 | 83.5 | 115.5 | 121 |
| POM (C) | 61.1 | 83.6 | 113.5 | 120.2 |
| DSC (H) | * | 86.7 | * | * |
| DSC (C) | * | * | * | * |

- Peaks not resolved in DSC

FTIR Spectral Studies:

The FTIR spectra of 9OBA, EBCA AND 9OBA:EBCA are given in figs 10-12. Changes in the form of band shifts are observed in the spectra. It is clear that the synthesized compound is a mixture of the two components 9OBA and EBCA.. The formation of intermolecular hydrogen bonding between COOH group of 9OBA and CN group of EBCA can be invoked in the hypochromic and bathochromic shifts shown in Table 2

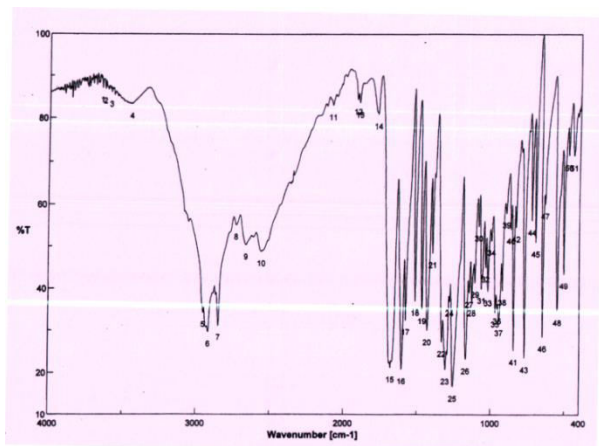


Fig. 10 FTIR of 9OB

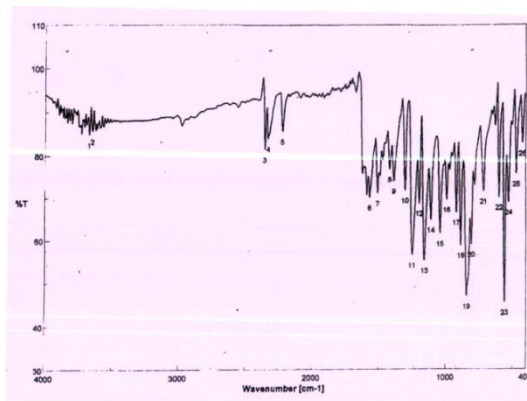


Fig. 11 FTIR of EBCA

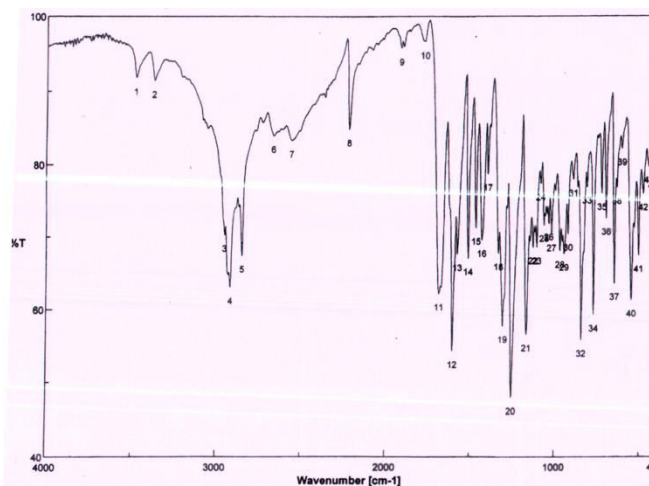


Fig. 12FTIR of 9OBA: EBCA

Table 2:FRTR spectral data in KBr

| Compound | $\bar{\nu}$ (C=O) _{acid} cm ⁻¹ | $\bar{\nu}$ (O-H) _{acid} cm ⁻¹ | $\bar{\nu}$ (C=N)cm ⁻¹ |
|----------------|---|---|--------------------------------------|
| 9OBA(KBR) | 1681.62 | 3444.24 | ---- |
| EBCA(KBR) | ---- | ----- | 2253.52 |
| 9OBA:EBCA(KBR) | 1686.44 | 3477.03 | 2216.77cm ⁻¹ |

Further, the results of 9OBA: EBCA are compared in cooling cycle with that of 8OBA: EBCA and 5OBA: EBCA using thermal polarizing microscope as shown in Table 3. The thermal span of smectic-G phase in 9OBA: EBCA is 22.5⁰ C where as in 8OBA: EBCA and 5OBA:EBCA it is in 33.5⁰ C and 19.5⁰ C respectively., The thermal span of smectic-C phase in 9OBA: EBCA is 30⁰ C where as in 8OBA: EBCA 8⁰ C and this range is very less than that of 9OBA: EBCA.

Table3:Transition temperatures and liquid crystalline range

| Compound | Phase variant | Cr to S _G /S _C /N | S _G to S _C | S _G /S _C / to N | N to I | LC range |
|------------------|---------------|---|----------------------------------|---------------------------------------|--------|----------|
| 9OBA: EBCA (C) | GCN | 61.1 | 83,6 | 113.5 | 120.2 | 59.1 |
| 8OBA: EBCA (C) | GCN | 57.1 | 90.5 | 98.5 | 133.5 | 76.4 |
| 5OBA:EBCA(H) (C) | GN | 74 | ----- | 93.5 | 111.1 | 37.1 |

V. CONCLUSIONS

From the present study it is noted that the three compounds 9OBA, EBCA and 9OBA: EBCA are enantiotropic liquid crystals. The phase transition temperatures observed through Polarizing Optical microscope are in reasonable agreement with the transition temperatures obtained from Differential Scanning Calorimetry. An induced Smectic-G phase is observed in both heating and cooling cycles. The Smectic-G phase is due to the inducement of intermolecular hydrogen bonding between the OH group of 9OBA and CN group of EBCA. The thermal span of induced smectic-G phase in 9OBA: EBCA is 22.5⁰ C where as in 8OBA: EBCA and 5OBA:EBCA it is in 33.5⁰ C and 19.5⁰ C respectively.

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REFERENCES

- [1] K.S.Usha, P.Rohini, J.Vivekanandan, N.Pongali Satya Prabhu, M.L.N.Madhu Mohan, "Investigations on thermotropic hydrogen bond liquid crystals", Mol. Cryst. Liq. Cryst, Vol.755, Issue-1, pp 1-13 2023
- [2] S.Sundaram, P.Subhasri, R.Jayaprakasam and V.N.Vijaykumar, "Thermal and optical characterization of multiple hydrogen bonded liquid crystals derived from mesogenic and non-mesogenic compounds: experimental and theoretical (DFT) studies", Canadian Journal of Physics, Vol. 98, Issue 5, pp 413-424 2020
- [3] Ch.Hemalakshmi and S.Sreehari Sastry, "Study of Supramolecule through Intermolecular Hydrogen Bond in 5OBA:TMD Liquid Crystals", IJERT, Vol.6, pp.225-228, 2017
- [4] S.Chandrasekhar, "Liquid Crystals" Cambridge University Press, 2ed. 1992
- [5] C.M. Paleos., and D. Tsiourvas, "Supramolecular hydrogen-bonded liquid crystals", Liq. Cryst. Vol.28 pp.1127-1167, 2001
- [6] A.J.Gopunath, T. Chitravel, C. Kavitha, N. Pongali Sathya Prabu, and M.L.N. Madhu Mohan M. L. N., "Thermal Optical And Dielectric Analysis of Hydrogen -Bonded Liquid Crystals formed by Adipic and Alkyloxy Benzoic Acids", Mol. Cryst. Liq. Cryst., Vol.592, Issue 1, pp.63-81, 2014
- [7] S. Salma Begum, T. Vindhya Kumari, C. Ravi Shankar Kumar, and S. Sreehari Sastry, "Liquid crystalline G phase of self assembled donor-acceptor molecules by intermolecular hydrogen bonding", J.Non-Cryst.Sol. Vol.357, pp.1745-1749, 2011.
- [8] Mohamad Hagar, Hoda A.Ahmed, Rua B. Alnoman, Mariusz Jaremko, Abdul-Hamid Emwas, Salim Sioud and Khulood A.AbuAl-Ola, "New Liquid Crystal Assemblies Based on Cyano-Hydrogen Bonding Interactions", Front.Chem, Vol. 9, Issue 4, PP 1-14 2021 ArticleNo. 679885
- [9] S J.D. Lugger, S J.A. Houben, Y Foelen, M G. Debije, A P.H. J.Schenning and D .J.Mulder "Hydrogen - Bonded Supramolecular liquid crystal Polymer: Smart materials with Stimuli - Responsive, Self Healing and Recyclable Properties", Chem. Rev. Volume 5, issue 5, pp. 4946-4975, 2022
- [10] S.Sreehari Sastry, S.Salma Begum, K.Mallika, K.B.Mahalakshmi, and HaSieTiong, "Image analysis to Detect phase transition temperatures of *p-n*-alkylbenzoic acids", IJIRSET, Vol.2(9), pp.4641-4647, 2013 [11]
- [11] T..Kalyani, and S.Sreehari Sastry, "Investigations on Mesogenic 10BA: TMD (p-Decyl Benzoic Acid: O-Toulamide)", IJIRSET, Volume 10, Issue 6, pp.8100-8107, 2021
- [12] M.S.Fedorov, N I Giricheva, S.A. Syrbu, E.A. Belova, I. A. Filippov, and M.R.Kiselev, "New supramolecular hydrogen-bonded liquid crystals based on 4-alkylbenzenesulfonic acids and 4-pyridyl 4'-alkyloxybenzoates: Quantum: Quantum chemical modeling and mesomorphic properties. J. Mol. Struct. Vol. 1244. Article 130890. pp 1-7. 2021



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