

# Comparative Study by Image Analysis in Halogenated Schiff Base Liquid Crystals

L.N.V.H. Somasundar<sup>1</sup>, K.Mallika<sup>2</sup>, Sie Tiong Ha<sup>3</sup>, S.Sreehari Sastry<sup>4</sup>

Assistant Professor, Dept. of Physics, DVR & Dr.HS MIC College of Technology, Kanchikacherla, India<sup>1</sup>,

Research Scholar, Department of Physics, Acharya Nagarjuna University, Guntur (A.P), India<sup>2</sup>

Assistant Professor, Faculty of Science, Department of Chemical Science, University Tunku Abdul Rahman, Jalan University, Bandar Barat, Kampar, Perak, Malaysia<sup>3</sup>

UGC BSR Faculty Fellow, Department of Physics, Acharya Nagarjuna University, Guntur, A.P, India<sup>4</sup>

**ABSTRACT:** In this paper, a comparative study on thermo optical behavior of Schiff base liquid crystals with different halogen atoms is carried out using Image analysis technique. Schiff base liquid crystals: 4-chlorobenzylidene- 4'-alkanoyloxyaniline( $C_{n-1}H_{2n-1}COO-$ ,  $nClABn = 16$ ), 4-n-alkanoyloxybenzylidene-4'-bromoanilines ( $C_{n-1}H_{2n-1}COO-$ ,  $nABBA, n = 8$ ), 3-hydroxy-4-[[4-iodophenyl]imino]methyl}phenyl alkanooates ( $C_{n-1}H_{2n-1}COO-$ ,  $nABIA, n = 18$ ) comprising terminal chloro, bromo and iodo substituents is considered for the study. The presence of terminal substituent of with different halogen atoms chlorine, bromine and iodine either promote or suppress the mesomorphic properties. Thermo optical properties of the liquid crystals are computed from the textures of samples using MATLAB software. Results obtained from the comparative study tell that, 8ABBA is more suitable for applications of optical devices than the compound with 16ClAB, 18ABIA.

**KEYWORDS:** Schiff base compounds, Halogen atoms, Optical textures, molecular structure, Optical behaviour

## I. INTRODUCTION

Recently, liquid crystal research paid great attention towards structure property relationship of materials. It is essential requirement for synthesizing new mesogens to achieve the targeted properties and future applications [1-3]. Keeping this in mind, recently ester type Schiff based liquid crystals with two aromatic rings having different terminal substituents are often studied exclusively owing to their application in the fields of photonics and opto electronics. This kind of materials has the most suitable molecules which exhibits the mesomorphic properties useful in optical device applications [4-8]. The presence of different polarity of terminal substituents either suppresses or promotes the mesomorphic properties of the materials in terms of melting points and phase stabilities. The placement of a polar group in a terminal position of molecule modifies its thermal and optical properties effectively. Therefore, distinct properties of these compounds enable them promising candidate towards variety of applications involving photonic devices, nonlinear optics, optical data storage and information systems, optical switches, liquid crystal display etc. three synthesized Schiff base liquid crystals: 4-chlorobenzylidene- 4'-alkanoyloxyaniline( $C_{n-1}H_{2n-1}COO-$ ,  $nClABn = 16$ ), 4-n-alkanoyloxybenzylidene-4'-bromoanilines ( $C_{n-1}H_{2n-1}COO-$ ,  $nABBA, n = 8$ ), 3-hydroxy-4-[[4-iodophenyl]imino]methyl}phenyl alkanooates ( $C_{n-1}H_{2n-1}COO-$ ,  $nABIA, n = 18$ ) comprising terminal chloro, bromo and iodo substituents [9-11] is considered. In these Schiff base liquid crystals, azomethine and esters are useful linking units for generating mesomorphism in two or three aromatic ring compounds. By enhancing the rigidity of core system by azo compounds through metal complex formation improves the mesogenic properties. The presence of terminal substituent of electro negative halogen atoms chlorine, bromine and iodine either promote or suppress the mesomorphic properties depending on the structural property relationship.

Here, image analysis technique in conjunction with POM is reported to carry out the comparative study on thermo optical behavior Schiff base liquid crystals comprising terminal chloro, bromo and iodo substituents are considered. Thermo optical behavior is studied through computing the parameters like Optical transmittance, optical density, Phase retardation, Birefringence and its dispersion which are briefly explained in [12-14].

## II. MATERIALS AND METHOD

Schiff base liquid crystals: 4-chlorobenzylidene-4'-alkanoyloxyaniline ( $C_{n-1}H_{2n-1}COO-$ ,  $nCIABn = 16$ ), 4-n-alkanoyloxybenzylidene-4'-bromoanilines ( $C_{n-1}H_{2n-1}COO-$ ,  $nABBA, n = 8$ ), 3-hydroxy-4-[(4-iodophenyl)imino]methyl}phenyl alkanooates ( $C_{n-1}H_{2n-1}COO-$ ,  $nABIA, n = 18$ ) comprising terminal chloro, bromo and iodo substituents [9-11] are used. Molecular structure of the samples are shown in Fig 1.

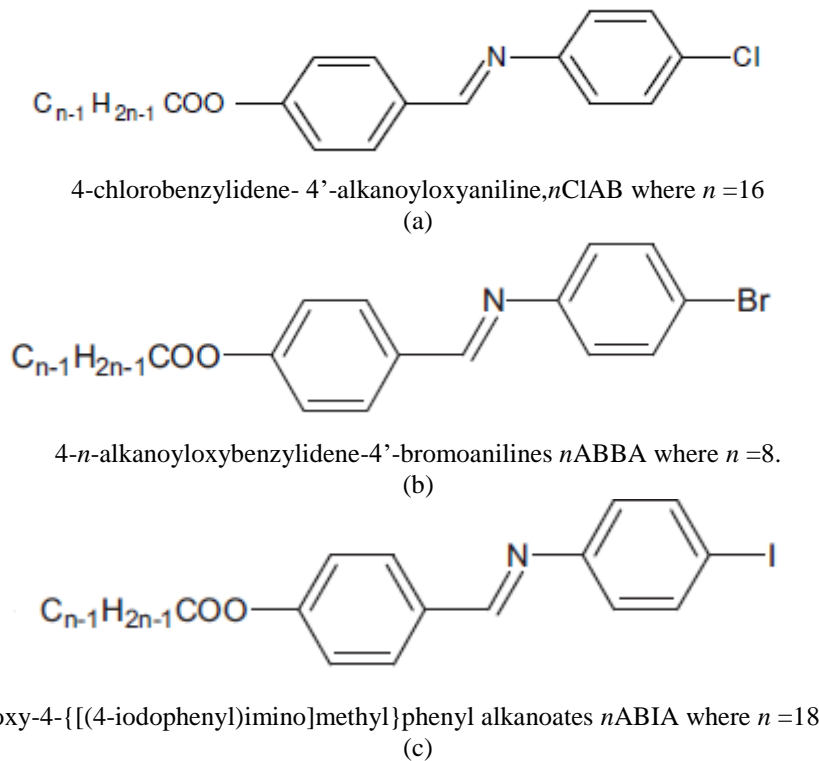


Fig .1. Molecular structures of compounds

The ITO coated homogeneous cell with  $5\mu m$  thickness (tolerance is  $\pm 0.2\mu m$ ) are obtained from Instec Inc., USA, is used to prepare liquid crystal sample for investigation. The experiment involve Meopta Polarizing optical microscope in the arthroscopic mode attached with hot stage described by Gray [15] and camera attachment for viewing, recording the textures as a function of temperature. The color image detected by the camera has a resolution of  $2592 \times 3888$  pixels which represents the 24bit true color pixel tone that ranges from 0 to 255 in R, G, and B colors under crossed and parallel polarizer's with the digital camera of canon made model (EOS Digital REBEL XS/ EOS1000D) of 10.10 mega pixel image sensor. To investigate the thermo optical behavior of samples, Textures of the sample from isotropic to solid phase are recorded in three monochromatic image planes (red, green and blue ) as a function of temperature [12-14]. Textures of the samples in a three monochromatic image planes show the greatest variations in intensity. The program was coded in MATLAB (implemented on P5 1.6GHz with 2GB RAM computer) for computational analysis of textures.

## III. RESULTS AND DISCUSSION

Schiff base liquid crystals: 4-chlorobenzylidene-4'-alkanoyloxyaniline ( $C_{n-1}H_{2n-1}COO-$ ,  $n=16$ ), 4-n-alkanoyloxybenzylidene-4'-bromoanilines ( $C_{n-1}H_{2n-1}COO-$ ,  $n = 8$ ), 3-hydroxy-4-[(4-iodophenyl)imino]methyl}phenyl alkanooates ( $C_{n-1}H_{2n-1}COO-$ ,  $nABIA, n = 18$ ) comprising terminal chloro, bromo and iodo substituents exhibit the Smectic A and Smectic B on cooling. On cooling, 16CIAB, 8ABBA and 18ABIA exhibits three transitions between isotropic liquid and crystalline solid. The first transition from isotropic liquid to Smectic A transitions at temperatures  $103.5^{\circ}C$ ,  $106.78^{\circ}C$  and  $107.4^{\circ}C$ , second transition from smecticA to Smectic B at temperatures  $78.5^{\circ}C$ ,  $85.5^{\circ}C$  and  $102.5^{\circ}C$  and third transition from Smectic B to crystal phase at temperatures  $70.5^{\circ}C$ ,  $47.5^{\circ}C$  and  $78.0^{\circ}C$ . In this study, compounds were considered with different alkyl chain lengths. This is due to the fact that the compounds either with

lower members or higher members of the series exhibited the only enantiotropic smectic A phase, because they are too rigid to be mesogenic [9-11]. But, the drop in molecular polarity of liquid crystals and increase in alkyl chain length influences the level of association, leading often to the formation of a smectic phase layer structure. Therefore, smectic phase is observed for the compounds and is shown in Fig 2.

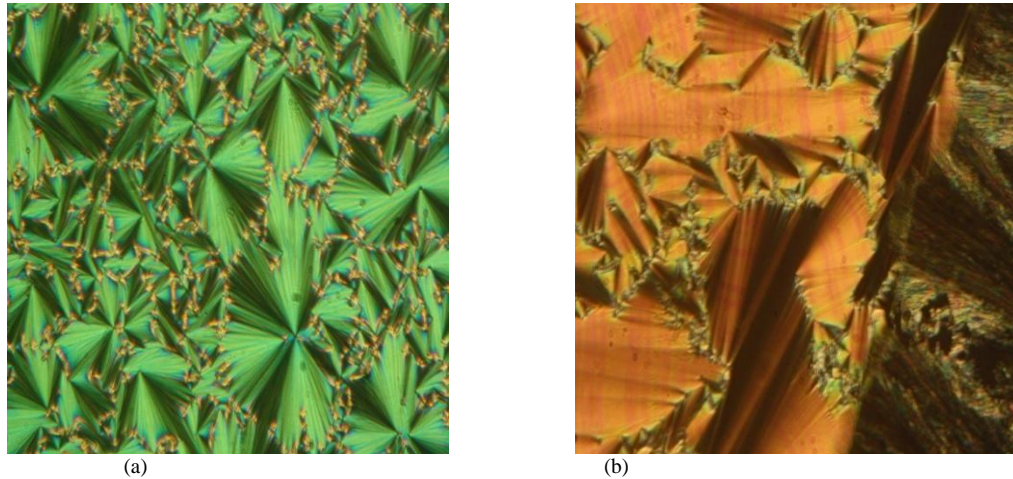
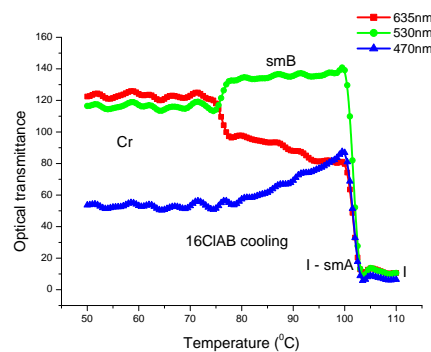


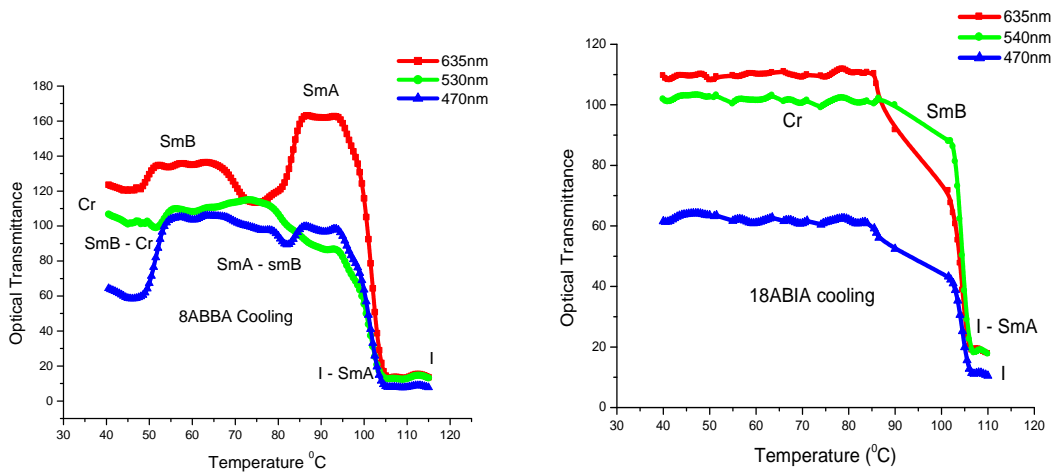
Fig. 2. (a) Smectic A; (b) Smectic B phase of Schiff base liquid crystals.

From the phase transition temperatures, it is observed that the mesophase range for the compound 8ABBA (57.0<sup>0</sup>C) is more compared to the compounds 16ClAB (32.4<sup>0</sup>C), 18ABIA (28.0<sup>0</sup>C). The difference in the clearing temperatures of the three liquid crystalline samples are very small and the temperatures of mesophase – crystalline solid transitions are varied based on their structure property relationship of samples and is shown in Figure 1. The difference in the linking groups (ester groups in 8ABBA, 18ABIA and ether group 16ClAB) between the phenyl ring and alkyl chain causes the changes in the liquid crystalline properties of the samples. The ether linking group such as Cl-AB provides the greater linearity to the molecules rather than the ester group. Thus results the wider phase ranges for the ether group compounds compared to the ester group compounds. In addition to that, the position of the imine linking group defines the direction of the carbonyl group. The different directions of the carbonyl groups between the phenyl and alkyl chain units strongly affect the smectic properties of molecules. From this we can tell that, mesogenic properties of the materials not only depends the electrostatic interactions but also on the geometrical structures of the molecules [16,17]. In addition to that, the increase of alkyl chain length from  $n = 8$  to 18, leads to the dilution of mesogenic core and depress the mesophase range of a compound 18ABIA.

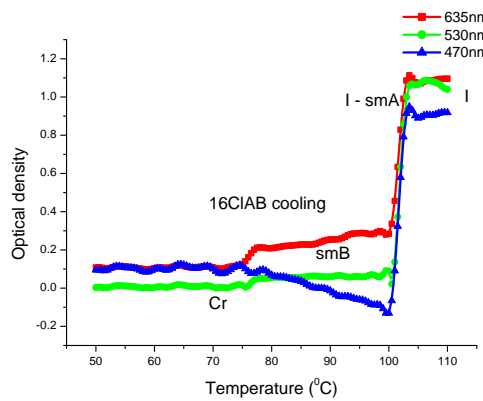
The nature of the terminal substituents or end groups in the molecule of the mesogen has profound influence on the optical properties also. As a function of temperature, optical behaviors of the compounds are studied by measuring the Optical transmittance, optical density, birefringence and its dispersion are computed using image analysis technique in conjunction with POM on MATLAB platform. Textures of the samples from isotropic to solid phase are recorded and analysis of these textural intensities with respect to temperature gives the information to investigate the thermo optical behavior of liquid crystals 16ClAB, 8ABBA and 18ABIA. Computed properties using Eqs [12-14] are plotted against the temperature which is shown in Figs 3 - 6



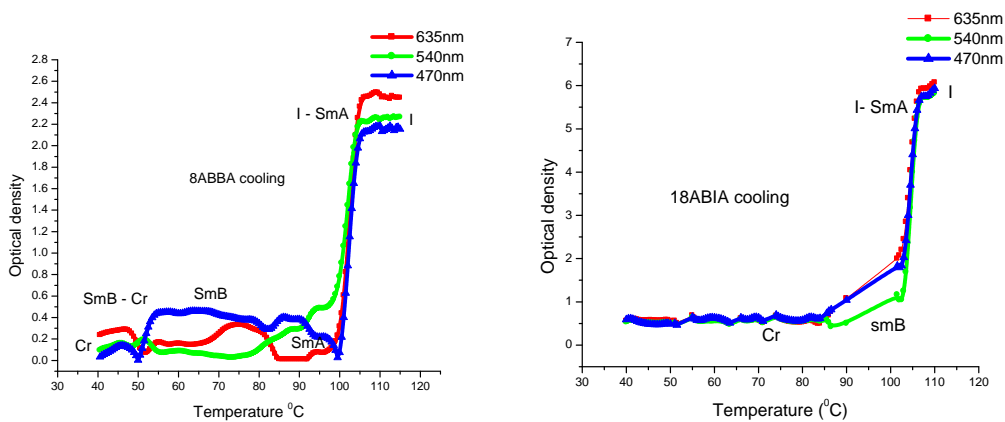
(a)



(b) (c)  
Fig. 3. Optical Transmittance of (a) 16CIAB; (b) 8ABBA ; (c) 18ABIA.  
( Cr:Crystal;SmA: Smectic A; I:Isotropic).



(a)



(b) (c)

Fig. 4. Optical density of (a) 16CIBA; (b) 8ABBA; (c) 18ABIA  
( Cr:Crystal;SmA: Smectic A; I:Isotropic).

Figs 3 and 4 show the variations in the values of optical transmittance and optical density [18]. These two properties give the emission and absorption of light from the liquid crystal material. Depending on wavelengths and molecular structure, the interaction between the light and atoms of molecules will take place. This can be useful to investigate the optical behavior of the samples. For the sample 8ABBA, the value of optical transmittance is high at all three wavelengths in the liquid crystal range. In these azomethine liquid crystals, the terminal substituent of halogen atoms attributed to the change in the part of the chemical structure which in turn influences the optical transmittance of compounds. The higher alkyl chain length of the compound 16CIAB, 18ABIA dilutes the mesogenic core and exhibits the mesomorphic phase with decreasing intensity values. Figure 4 shows the optical density of compounds 16CIAB, 8ABBA and 18ABIA. On cooling of the sample, sharp texture transformations of I - Smectic A - Smectic B - Cr give the jump like changes in the values of optical density. This is due to the fact that, the transmission of light takes place in smectic phase alignment of molecules. This can observe clearly for the compound 8ABBA and is useful for the fabrication of tunable optical filters compared to the 16CIAB, 18ABIA. Absorption of the liquid crystal molecules for the compound 16CIAB, 18ABIA is linear at all three wavelengths. Optical transmittance of the sample is inversely proportional to the optical density and clearly observed in Fig 3.

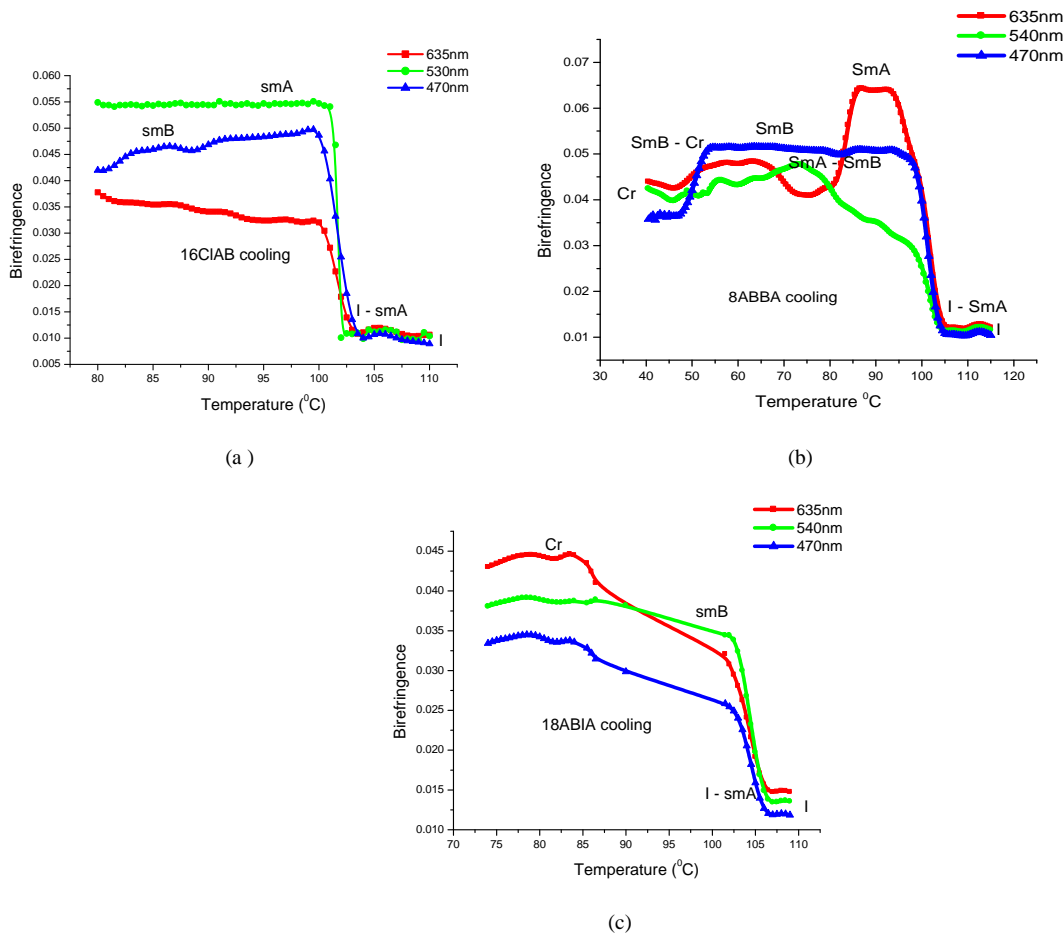


Fig. 5. Temperature dependence of Birefringence of (a)16CIAB; (b) 8ABBA; (c) 18ABIA.

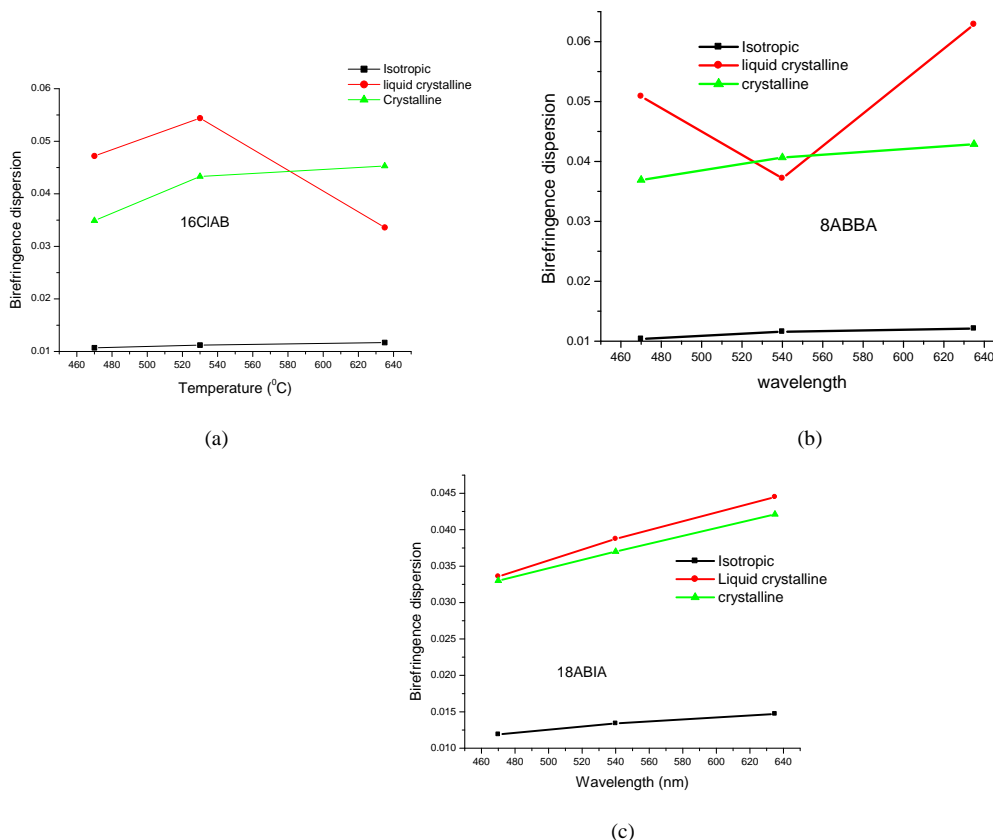


Fig. 6. Wavelength dependence of Birefringence dispersion of (a) 16CIAB; (b) 8ABBA; (c) 18ABIA.

Figs 5 and 6 show the birefringence and its dispersion at three wavelengths and are plotted against the temperature. Here, computation of birefringence relies on observing an intensity change in the textures of liquid crystals. On cooling of the sample from its isotropic phase, the value of birefringence increases abruptly in the biphasic region of I – Smectic temperature interval and there are small fluctuation in the value of birefringence at Smectic - Cr phases on further cooling. The small variations in the optical parameter curves other than transitions are due to change in the refractive index of the samples which results the continuous color changes of textures with respect to the wavelength and temperature. This can be clearly observed for two samples from Figs 3 – 6. From the Birefringence and its dispersion of samples, it is observed that compound 8ABBA exhibits the high birefringence value compared to the compound 16CIAB, 18ABIA. This is due to the fact that, the high ionic radius of the terminal substituent (iodine) in adjacent rings causes the twisting of rings and the birefringence to fall at all three wavelengths. The obtained results reveal that, optical behavior of the compounds towards the device applications are effected by chain length, size of the molecules and position of terminal substituents. Generally, the higher electro negative atoms (chlorine) gives the high mesomorphic properties compared to the less electro negative atoms Bromine and Iodine. And also the longer spacer groups of the liquid crystal compounds play a key role in determining good thermal and optical behavior which are suitable towards the optical device applications. But, here azomethine liquid crystals with lesser spacer groups 8ABBA exhibits the good thermo optical behavior in terms of phase stability, liquid crystallinity and anisotropic properties compared to compound with higher spacer groups 16CIAB, 18ABIA . Therefore, this governs the utility of mesogen 8ABBA in long-time operating devices, optical filters and good optical activity property materials. The compound with higher spacer groups 16CIAB, 18ABIA destroys the liquid crystallinity by diluting the ordering effect of rigid core and eventually the compound is not able to maintain the liquid crystal ordering. The molecular structure of reverse imine group also affects the optical properties of 16CIAB. The variations in birefringence for the compound 18ABIA are small and linear in all the three wavelengths when compared for the compound 8ABBA, 16CIAB. It means the birefringence is same for all the wavelengths at a given temperature. But the compound 8ABBA exhibited the tunable birefringence [19-21]. So, the compound with 8ABBA is more suitable for applications of optical devices than the compound with 16CIAB, 18ABIA.

#### IV. CONCLUSIONS

Comparative study on thermo optical behavior of Schiff base liquid crystals comprising terminal chloro, bromo and iodo substituents is carried out successfully towards the optical device applications through image analysis. The azomethine liquid crystals with lesser spacer groups 8ABBA exhibit the good thermo optical behavior compared to longer spacer groups of the liquid crystal compounds. The compound with higher spacer groups 16CIAB, 18ABIA destroys the liquid crystallinity by diluting the ordering effect of rigid core and eventually the drops the liquid crystalline optical properties.

#### ACKNOWLEDGEMENTS

One of the author (SSS) is grateful to University Grants Commission for providing BSR Faculty fellowship No.:F.18-1/2011(BSR) dated: 04/01/2017.and No.F.4-5(11)/019(BSR) dated 17-8-2020. The authors also gratefully acknowledge University Grants Commission Departmental Special Assistance program at Level I program No.F.530/1/DSA- 1/2015 (SAP-1), dated 12th May 2015.

#### REFERENCES

- [1] Gowda A, ArunRoy, SandeepKumar, "Synthesis and mesomorphic properties of novel Schiff base liquid crystalline EDOT derivatives", *J. Mol. Liq.*, vol.225,pp: 840-847,2017.
- [2] Nagwa H.S, Ahmed, Gamal R. S, Hoda A Ahmed, Mohamed Hagar," New wide-stability four-ring azo/ester/Schiff base liquid crystals: synthesis, mesomorphic, photophysical, and DFT approaches", *RSC Advances*,vol.10,pp: 9643-9656,2020.
- [3] Sherif S. Nafee, Mohamed Hagar,Hoda A. Ahmed, Reda M. El-Shishtawy, Bahaudin M. Raffah,"The Synthesis of New Thermal Stable Schiff Base/Ester Liquid Crystals: A Computational, Mesomorphic, and Optical Study",*Molecules*,vol. 24,pp: 3032(1-19),2019.
- [4] Martin Stalder, Oberwil, Martin Schadt, Seltisberg, "Nematic liquid crystal electro- optical element and device", U.S. Patent A1 0147033, 2003.
- [5] Ernst Lueder, "Liquid crystal displays – Addressing schemes and electro optic Effects", John Wiley & Sons, United Kingdom, 2005.
- [6] Scott J.W, Gregory D.J, Gregory P.C," Liquid Crystals: Frontiers in Biomedical Applications",World Scientific Publishing Co.Pte.Ltd, Singapore, 2007.
- [7] Ford M.J, Penny Hale, Shapter J.G, Voelcker N.H, Waclawik E.R, "Liquid crystal displays: Fabrication and measurement of a twisted nematics liquid crystal cell", *Journal of Chemical Education*, vol.81, pp:854-858, 2004.
- [8] Liquid crystals and advanced organic materials, Department of chemistry, University of York. Heslington:York. Available from: <http://www.york.ac.uk/chemistry/staff/academic/d-g/jgoodby/>.
- [9] .Sie-Tiong Ha, Lay-Khoon Ong, Yasodha Sivasothy, Guan-Yeow Yeap, Hong-Cheu Lin, Siew-Ling Lee, Peng-Lim Boey and Nilesh L. Bonde, "Mesogenic Schiff base esters with terminal chloro group: Synthesis, thermotropic properties and X-ray diffraction studies,*International Journal of the Physical Sciences*, vol. 5(5), pp: 564-575, 2010
- [10] Ha S.T, Lee T.L,Yeap G.Y, Lee S.L,Win Y.F, Ong S.T," Mesomorphic behavior of new azomethine liquid crystals having terminal bromo substituent",*Chinese Chemical Letters*, vol. 23, pp: 177–180,2012.
- [11] Ha S.T, Lee T.L,Yeap G.Y, Ito M.M, Ayumu Saito, Masaaki Watanabe "Mesomorphic behavior of new azomethine liquid crystals having terminal iodo group", *Chinese Chemical Letters*, vol: 22, pp:260-263, 2011.
- [12] Eccher J, Sampaio A.R, Viscovini R.C, Conte G, Westphal E, Gallardo H, Bechtold I.H, "Image processing as a tool for phase transitions identification", *Journal of Molecular Liquids*, vol.153, pp:162-166, 2010.
- [13] Sreehari Sastry S, Ha S.T , Gowri Sankara Rao B , Mallika. K, Vindhya Kumari T, "Optical properties of a mesogen by image analysis", *Liquid Crystals*, vol: 39, pp:1414-1419, 2012.
- [14] Sreehari Sastry S, Sandeep Kumar , Vindhya Kumari T , Mallika. K , Gowri Sankara Rao. B, Ha Sie Tiong, "Liquid crystal parameters through image Analysis", *Liquid Crystals*, vol: 39, pp:1527-1537, 2012.
- [15] Gray G.W, "Molecular Structure and the properties of Liquid Crystals", Academic press, New York, 1962.
- [16] Elena Perju , Vasile cozen , Daniel Timpu and Maria Bruma , "The influence of methoxy side groups and halogen nature on the mesomorphic and optical properties", *Liquid Crystals*,vol.44, pp:798-808, 2017.
- [17] Sakurai Y, Takenaka S, Miyake H, Morita H, Ikemoto T,"Molecular structure and smectic properties. Part 1. The effect of linkages on smectic A thermal stability in three aromatic ring compounds linked by ester groups", *Journal of the Chemical Society, Perkin Transactions*,vol.2, pp. 1199–1204, 1989.



- [18] Optical density, [Internet], (accessed 15-3-2017) available from : [https://physics.tutorvista.com/fluid-dynamics/optical\\_density.html](https://physics.tutorvista.com/fluid-dynamics/optical_density.html).
- [19] Roman Dąbrowski, Przemysław Kula, Jakub Herman, “High Birefringence Liquid Crystals”, Crystals, vol.3, pp: 443-482, 2013.
- [20] Greg A.K, Michael J.D, Graham A, “Liquid crystal tunable birefringent filters”, Proceedings of SPIE, optical spectroscopic techniques and instrumentation for atmospheric and space research II, vol. 2830. Bellingham (WA): SPIE; 1996.
- [21] Tomasz A, “Tunable highly birefringent solid-core photonic liquid crystal Fibers”, Optical and Quantum electronics, vol: 39, pp:0121- 0132, 2007.