Volume 5, Issue 3, July 2018 ISSN: 2348-8565 (Online)
International Journal of Modern Engineering and Research Technology
Website: http://www.ijmert.org Email: editor.ijmert@gmail.com

Study of Thermo-Optical Parameters for Device Applications by Image Analysis

L.N.V.H. Somasundar
Research Scholar
Department of Physics,
Acharya Nagarjuna University,
Guntur (A.P.) [INDIA]
Email: lanka.sundar@gmail.com

K. Mallika
Research Scholar
Department of Physics,
Acharya Nagarjuna University,
Guntur (A.P.) [INDIA]
Email: mallika.gudali@gmail.com

Ha Sie Tiong
Faculty of Science,
Department of Chemical Science
Universiti Tunku Abdul Rahman, Jalan Universiti
Bandar Barat, Kampar, Perak., [Malaysia]
Email: hast_utar@yahoo.com

Sreehari Sastry
Professor & UGC BSR Faculty Fellow
Department of Physics,
Acharya Nagarjuna University,
Guntur (A.P.) [INDIA]
Email: sreeharisastry@yahoo.com

ABSTRACT

Thermo optical behavior of two azomethine liquid crystals: 4-n-alkanoyloxybenzylidene-4′--bromoanilines ($C_{n-1}H_{2n-1}COO$-, n = 8); 8ABBA and 3-hydroxy-4-{[(4 iodophenyl) imino] methyl} phenyl alkanoates ($C_{n-1}H_{2n-1}COO$-, n = 18) ; 18ABIA comprising terminal bromo and iodo substituent's are investigated towards optical device applications by image analysis technique in conjunction with Polarizing Optical Microscopy which is based on intensities of the liquid crystal textures as a function of temperature. Thermal and optical properties of the liquid crystals are computed from the textures of samples using MATLAB software. Thermal properties such as transition temperatures, heat enthalpy, percentage of liquid crystallanity, phase stabilities and optical properties like transmittance, optical density, Birefringence and its dispersion are determined and results are discussed. The obtained results show that azomethine liquid crystals with terminal bromo substituent exhibit the good thermo optical behavior compared to terminal iodo substituent. Terminal bromo substituents are more suitable for optical device applications due to good optical properties.

Keywords:—*Azomethine mesogens; textures; image analysis; thermal and optical properties; device applications.*

I. INTRODUCTION

Mesomorphic materials 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 [1-5]. 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 [5-9].

Generally, applications of liquid crystal materials depend on their mesomorphic behavior under the application of external fields like temperature, pressure, electric field and magnetic field. Here, the external field is temperature [10-12]. On heating or cooling of the material from its solid to isotropic or isotropic to solid state via liquid crystalline state, the state or phase of the material will change. This can be observed in terms of variations in the textures of liquid crystal material and can be captured as textures using POM with camera attachment [13]. These variations are nothing but the changes in the intensities of colors. Analysis of these textural intensities with respect to temperature gives the information to investigate the thermo optical behavior of liquid crystals 8ABBA, 18ABIA.

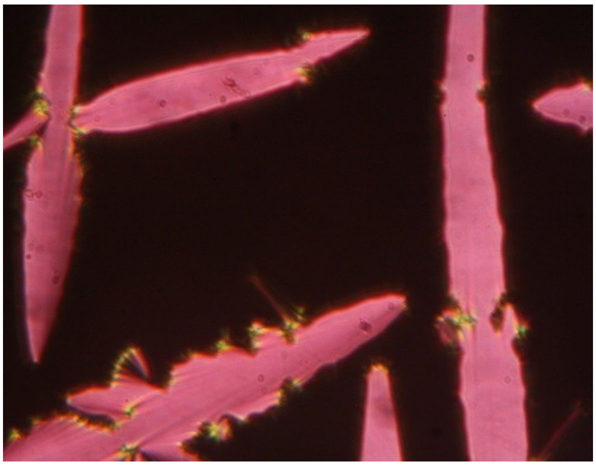
In this paper, thermo optical behavior of two azomethine liquid crystals: 4-n-alkanoyloxybenzylidene-4$^{/}$--bromoanilines *8*ABBA ($C_{n-1}H_{2n-1}COO$-, n = 8) and 3-hydroxy-4-{[(4-iodophenyl) imino] methyl} phenyl alkanoates 18ABIA ($C_{n-1}H_{2n-1}COO$-, n = 18) comprising terminal bromo and iodo substituents [14,15] are investigated using image analysis technique and other thermal analysis techniques available in literature. These microscopic textures are analyzed using MATLAB software (product by Math Works, Inc., (Natick, MA) [16-18]. This investigation includes the computation of thermal and optical properties. Such properties are Transition temperatures, heat enthalpy, percentage liquid crystallanity, phase stabilities and Optical transmittance, optical density, Birefringence and its dispersion.

II. Materials and Method

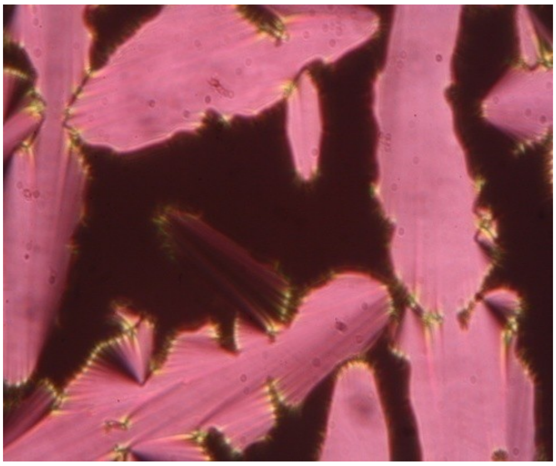
Synthesized azomethine liquid crystals:4-n-alkanoyloxybenzylidene-4$^{/}$-bromoanilin- es *n*ABBA ($C_{n-1}H_{2n-1}COO$-, n = 8) and 3-hydroxy-4-{[(4-iodophenyl)imino]methyl} phenyl alkanoates *n*ABIA ($C_{n-1}H_{2n-1}COO$-, n = 18) comprising terminal bromo and iodo substituents [14,15] are used. The ITO coated homogeneous cell having area of 5mm X 5mm with 5mm spacing (tolerance is ± 0.2 µm) 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 [19] 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 x 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. Textures of the samples in a three monochromatic image planes show the greatest variations in intensity [13,20]. The program was coded in MATLAB (implemented on P5 1.6GHz with 2GB RAM computer) for computational analysis of textures.

III. Results and Discussion

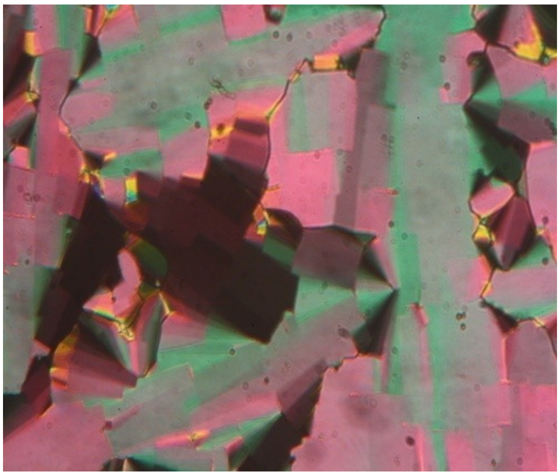
Azomethine liquid crystals 8ABBA and 18ABIA, exhibited enantiotropic smectic A and smectic B phases. They are shown in figures 1 and 2. Here, the compound *n*ABIA, considered instead of lower members of series. This due to the fact that, the compounds of the lower members of the series *n*ABIA where n = 8 to 16 exhibited the only enantiotropic smectic A phase, because they are too rigid to be mesogenic [15].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. The enhancement of rigidity of the core system by its azo compounds attributed to the change in the part of the chemical structure which in turn influences the phase transition temperatures of compounds also. The presence of terminal substituent's of halogen atoms also having the ability to enhance the stability of lattice and melting temperatures. Phase transition temperatures and phases of azomethine liquid crystals *8*ABBA and 18ABIA are given in Table 1. The mesophase range for the compound 8ABBA (57.0^{0}C) is more compared to the compound 18ABIA (28.0^{0}C). This is due to the fact that, the increase of alkyl chain length from n = 8 to 18, leads to the dilution of mesogenic core.



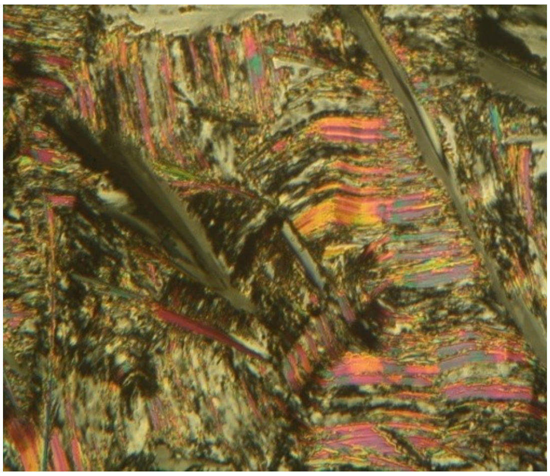
(a)



(b)

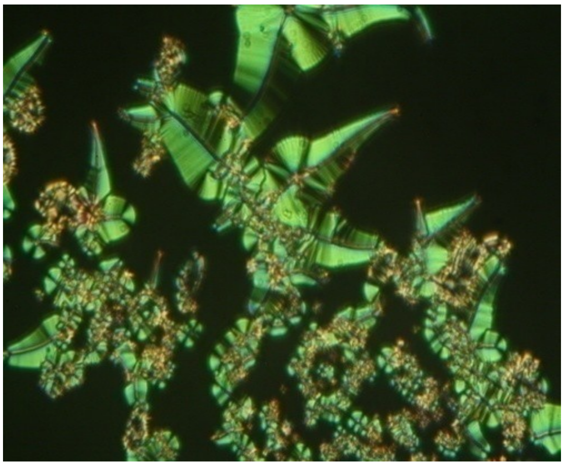


(c)

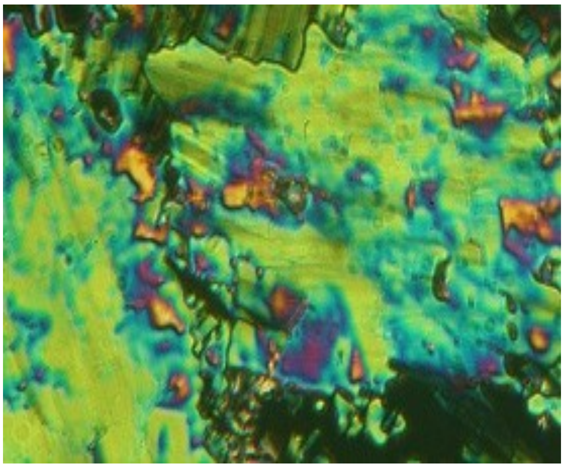


(d)

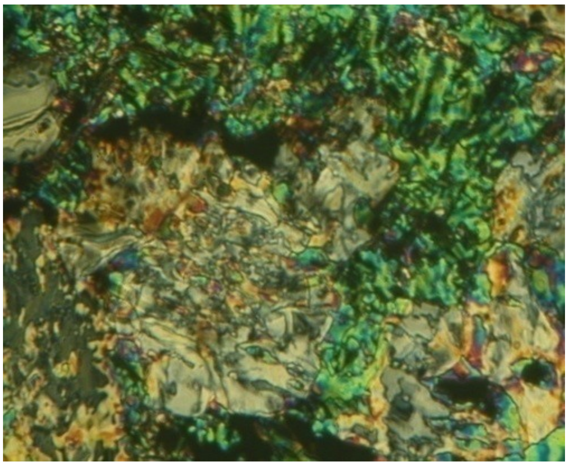
Figure 1. optical textures of Liquid crystal4-n-alkanoyloxybenzylidene-4$^{/}$--bromoanilines nABBA ($C_{n-1}H_{2n-1}COO$-, n = 8) (a) I - Smectic A phase, (b) Smectic A phase ; (c) Smectic B phase, (d) Crystal phase.



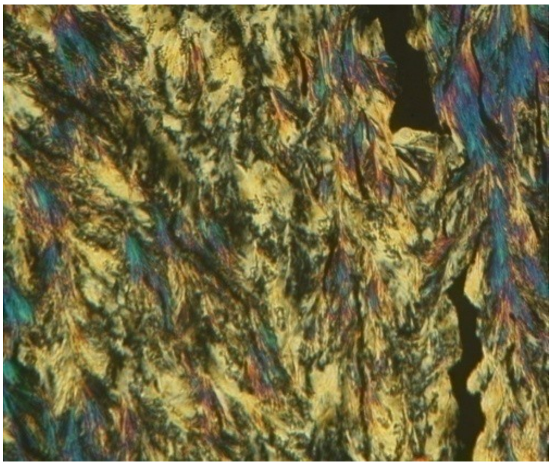
(a)



(b)



(c)



(d)

Figure 2: optical textures of Liquid crystal: 3-hydroxy-4 -{[(4-iodophenyl)imino]methyl}phenyl alkanoates ($C_{n-1}H_{2n-1}COO$-, n =18) (a) I - Smectic A phase, (b) Smectic B phase ; (c) Smectic B – Crystal phase, (d) Crystal phase.

Table 1. Phases and Phase Transition Temperatures of Azomethine Liquid Crystals.

Compound	Phases I-Sm A-Sm B-Cr DSC	Transition temperatures (°C) POM and Image analysis
8ABBA	106.78 – 91.03–46.16	104.5 –85.5 –47.5
18ABIA	107.4 –104.6 –79.5	106.0-102.5 –78.0

(Cr:Crystal;sm A – Smectic A; sm B – Smectic B; I:Isotropic).

The phase transition temperatures measured are in good agreement with the standard techniques like DSC and literature [14,15]. The enthalpy changes of the samples are used to calculate the percentage of crystallinity and are given in Table 2. It is an important property of the materials which exhibits the optical activity [21,22]. Percentage of the liquid crystallinity is calculated from the equation (1).

$$\text{Liquid crytsallinity\%} = \frac{\Delta H_f - \Delta H_c}{\Delta H_{f100\%}} * 100 \quad (1)$$

where ΔH_f is the enthalpy change of melting to liquid crystal phase, ΔH_c is the enthalpy change of crystallization from liquid crystal phase and $\Delta H_{f100\%}$ is the enthalpy of melting of a reference liquid crystal material. Here the considered reference material is Cholesteryl myristate which is good system in which to study transitions between liquid crystal phases [22].

Table 2. Enthalpy changes of of Azomethine liquid crystals on heating and cooling.

Compound	Enthalpy change (KJ/mol)	Liquid crystal-linit (%)
8ABBA	cooling: 6.53 – 3.02 – 10.64 heating: 25.09 – 2.27 – 6.39	30.67
18ABIA	cooling: 11.93 – 4.52 – 69.16 heating: 73.88 – 4.12 – 11.44	15.68

From Table 2, the percentage of liquid crystallinity of the compounds 8ABBA is high compared to the 18ABIA. Therefore, sample 8ABBA exhibit good optical activity property.

Phase stability is useful to study the optical behavior of the liquid crystal samples calculated from [23]. It is an important parameter that governs the utility of the mesogens in opticl device applications. For long-time operating devices, it is necessary to maintain high phase stability in materials. Phase stability is high for the liquid crystal 8ABBA compared to the 18ABIA. The increase in chain length increases the dispersion forces and shielding of terminal dipolar attractions of terminal groups that elevates the mesogenic range. This can be observed clearly from Table 3 (Column of ΔT).

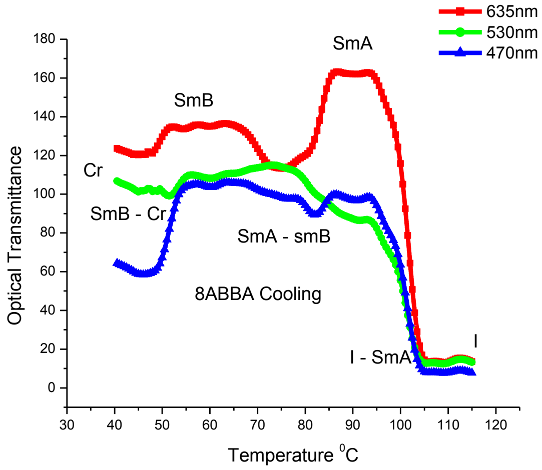
Table 3: Thermal stability factor obtained from present technique and DSC

Compound	ΔT [DSC] T_{mid} [DSC]	S[DSC]
8ABBA	57 [60.62] 76[76.47]	4332 [4635.6]
18ABIA	28[27.9] 92 [93.45]	2576 [2607.25]

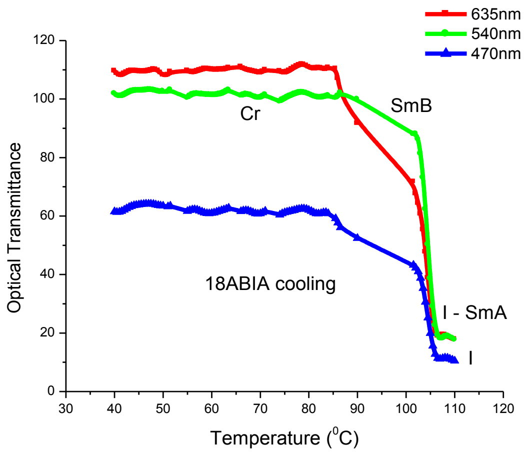
(ΔT: temperature difference, T_{mid} : middle phase of temperature, S: thermal stability factor)

The nature of the terminal substituents or end groups in the molecule of the mesogen has profound influence on the optical properties also. Here, optical behaviors of the compounds are studied with respect to temperature. As a function of temperature, phase change occurs due to disturbance in directions of the molecules. In solid phase liquid crystal molecule directors remain undisturbed and no phase change occurs. While passing the phase, orientation of molecular directions results phase transitions. In this region, the optical behaviors of the compounds are vary from the initial phase This can be investigated using different techniques. By using the standard optical microscopic technique, these transitions can observe as beautiful textures. Here, optical transmittance, optical density, birefringence and its dispersion are computed using image analysis technique in conjunction with POM on MATLAB platform. Optical behavior of such properties considerable towards the applications involving photonic devices, nonlinear optics, optical data storage and information systems, optical switches, liquid crystal display etc. For small values of temperature, there is no change in the textures and recorded textures remain same.

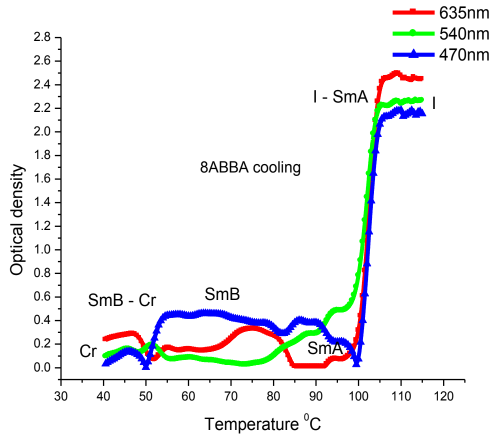
As the temperature is increased, changes in textural features occurred reveals the phase transition. While passing a phase from initial phase (isotropic phase) to other liquid crystal phase or liquid crystal phase to solid phase, orientation of the molecules with respect to the temperature affects the transmitted intensity values of the textures in terms of textural feature changes. Analysis of these textural intensities with respect to temperature gives the information to investigate the thermo optical behavior of liquid crystals 8ABBA and 18ABIA. This can be observed from Figures 1 and 2 as a representative case. Computed properties using Equations given in [24-27] are plotted against the temperature which is shown in Figures 3, 4 and 5.



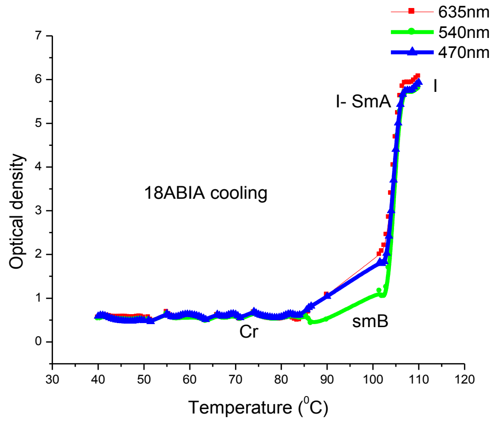
(a)



(b)



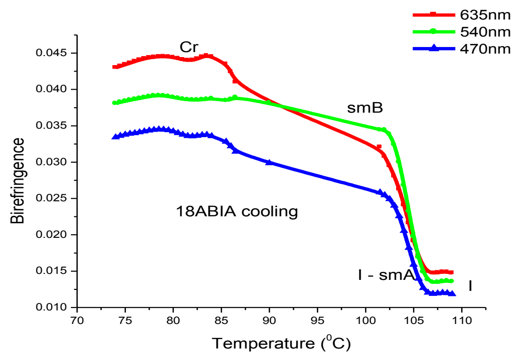
(c)



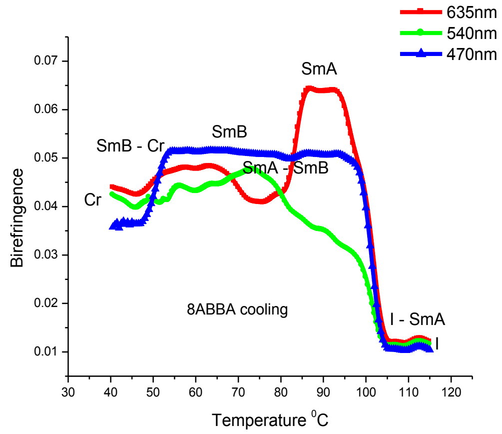
(d)

Figure 3: Optical Transmittance of (a) 8ABBA ; (b) 18ABIA, Optical density of (c) 8ABBA; (d) 18ABIA (Cr:Crystal;SmA: Smectic A; I:Isotropic).

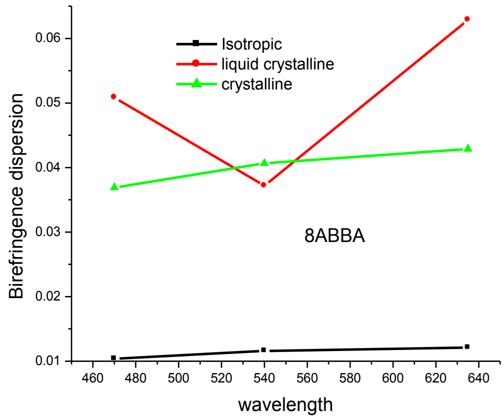
Figures: 3(a and b) and 3(c and d) show the variations in the values of optical transmittance and optical density [24]. These two properties give the emission and absorption of light from the liquid crystal material. Depending on wavelengths and molecular structure, the interaction between the light and atoms of molecules will take place. This can be useful to investigate the optical behavior of the samples. For different phases, this can be observed as changes in the textural features as function of temperature. On cooling, the value of optical transmittance increases near the isotropic phase to liquid crystal phase transition and show a sudden decrement or increment in the transmission values based on molecular alignments of the phases. 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 of the compound 18ABIA dilutes the mesogenic core and exhibits the mesomorphic phase with decreasing intensity values. Figure 3 (c,d) shows the optical density of compounds 8ABBA and 18ABIA. In Isotropic phase the molecular orientation is random and there is no transmission of light and the light is absorbed by the random orientations of the molecules. 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 18ABIA. Absorption of the liquid crystal molecules for the compound 18ABIA is linear at all three wavelengths. Optical transmittance of the sample is inversely proportional to the optical density and clearly observed in Figure 3.



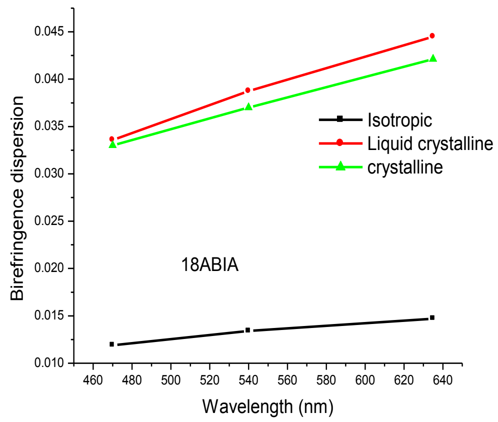
(a)



(b)



(c)



(d)

Figure 4. Birefringence of (a) 8ABBA; (b) 18ABIA; birefringence dispersion of (c) 8ABBA; (d) 18ABIA

Figure 4 shows the birefringence values 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. In all, a general trend is observed for isotropic and meso phases. The destruction and ordering of molecular alignment from their respective phases lead to the variations in the B values. 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. Liquid crystal coexistence regions (I - LC, LC - Cr) are commonly marked by an abrupt change in birefringence due to an immediate loss of all birefringence in a particular region of the sample. 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 Figure 1, 2, 3, and 4. From the Birefringence and its dispersion of samples, it is observed that compound 8ABBA exhibits the high birefringence value compared to the compound 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 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 interms of phase stability, liquid crystallinity and anisotropic properties compared to compound with higher spacer groups 18ABIA (Table 1, 2 and 3). 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 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 variations in birefringence for the compound 18ABIA are small and linear in all the three wavelengths when compared for the compound 8ABBA. It means the birefringence is same for all the wavelengths at a given temperature. But the compound 8ABBA exhibited the tunable birefringence by showing more variations in the birefringence values of each wavelength with linearity. The tunable birefringence is the variation of birefringence that should be large and linear with respect to temperature [28-30]. So, the compound with 8ABBA is more suitable for applications of optical devices than the compound with 18ABIA.

IV. Conclusion

Thermo optical behavior of two azomethine liquid crystals comprising terminal bromo and iodo substituents are investigated 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 18ABIA destroys the liquid crystallinity by diluting the ordering effect of rigid core and eventually the drops the liquid crystalline anisotropic properties.

Acknowledgements

One of the author (SSS) grateful to University Grants Commission for providing BSR Faculty fellowship No.F.18-1/2011(BSR) Dt: 4/01/2017. The authors also 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,

REFERENCES:

[1] Yen-Chen Liu, Ko-Ting Cheng, Hsin-Fu Chen and Andy Ying-Guey Fuh, Photo- and electro-isomerization of azobenzenes based on polymer-dispersed liquid crystals doped with azobenzenes and their applications, Journal of Optic Express,22,4404-4411, 2014.

[2] Smart window using a thermally and optically switchable liquid crystal cell, Proceedings of SPIE 10555 - Emerging Liquid Crystal Technologies XIII, 8th February 2018; doi: 10.1117/12.2289457; https://doi.org/10.1117/12.2289457

[3] J.W. Scott, D.J. Gregory, P.C. Gregory, Liquid Crystals : Frontiers in Biomedical Applications, (World Scientific Publishing Co.Pte.Ltd, Singapore, 2007).

[4] M.J. Ford, Penny Hale, J.G. Shapter, N.H. Voelcker, E.R. Waclawik, Liquid crystal displays: Fabrication and measurement of a twisted nematics liquid crystal cell, Journal of Chemical Education, 81, 854-858, 2004.

[5] Liquid crystals and advanced organic materials, Department of chemistry, University of York. Heslington:York; [Internet], (accessed 12-3-2018) Available from:http://www.york.ac.uk/chemistry/staff/academic/d-g/jgoodby/.

[6] S.M.Kelly, Hand book of Advanced Electronic and Photonic Materials and Devices, (Academic Press, U.S.A, 2000).

[7] Quan Li, Liquid Crystals Beyond Displays – Chemistry, Physics and Applicatiions,(John Wiley & sons, New Jersy, 2012).

[8] VG. Chigrinov, Liquid Crystal Devices: Physics and Applications, (Boston, MA, USA: Artech House, 1999).

[9] JA.Castellano. Handbook of Display Technology, (Amsterdam, The Netherlands: Elsevier, 2012).

[10] P.J. Collings, M. Hird, Introduction to Liquid Crystals: Chemistry and Physics, (Taylor & Francis Ltd., UK, 1998).

[11] Tsujimura T,OLED Display: Fundamentals and Applications 2nd edn.(Hoboken, NJ, John Wiley & Sons, USA, 2017).

[12] Birenda Bahadur, Liquid Crystals: Applications and Uses, Vol. 3,(World Scientific Publishing, Singapore, 1992).

[13] I.Dierking, Textures of liquid crystals, (Wiely-VCH Verlag GmbH Co., Weinheim, 2003).

[14] S.T. Ha, T.L. Lee, G.Y.Yeap, S. L.Lee,Y.F.Win, S.T. Ong, Mesomorphic behaviour of new azomethine liquid crystals having terminal bromo substituent, Chinese Chemical Letters, 23, 177–180,2012.

[15] S.T. Ha, T.L. Lee, G.Y.Yeap, M.M.Ito, Ayumu Saito, Masaaki Watanabe, Mesomorphic behavior of new azomethine liquid crystals having terminal iodo group, Chinese Chemical Letters, 22, 260-263, 2011.

[16] Introduction to Image Processing and Applications, [Internet], (accessed 29-3-2018). Available from: http://www.engineersgarage.com/ articles/

image-processing-tutorial-applications?page=3.

[17] C.John, J.Russ,Christian Russ, Introduction to Image processing and Analysis, (CRC Press, London,2008).

[18] Introduction to MATLAB – Mathworks, 2018. [Internet], (accessed 2-4-2018) Availble from: www.mathworks.in/support/ learn-with-matlab-tutorials.html.

[19] G.W.Gray, Molecular Structure and the properties of Liquid Crystals, (Academic press, New York, 1962)

[20] R.N. Clark, Implications of Digital Photography Technology, Clarkvision Articles, 2010.

[21] W.J. Sichina, DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics, PE-Tech 40, Thermal analysis, 2000.

[22] Phase Transitions and Differential Scanning Calorimetry, Chemistry 75, pp:1-12, 2010, [Internet], (accessed 27 -7-2017) Available from: http:// www.dartmouth.edu/~pchem/75/ pdfs/ DSC.pdf

[23] A.J. Gopunath A.J, T. Chitravel, C. Kavitha C, N. Pongali Sathya Prabu, M.L.N.Madhu Mohan, Thermal, Optical, and Dielectric Analysis of Hydrogen-Bonded Liquid Crystals Formed by Adipic and Alkyloxy Benzoic Acids, Molecular Crystals and Liquid Crystals, 592, 63-81, 2014.

[24] Optical density, [Internet], (accessed 15-3-2017) Available from : https:// physics.tutorvista.com/fluid-dynamics/optical density.html

[25] J. Eccher, A.R.Sampaio, R.C.Viscovin, G.Conte, E. Westphal, H.Gallardo,I.H. Bechtold, Image processing as a tool for phase transitions identification, Journal of Molecular Liquids, 153, 162-166, 2010.

[26] S. Sreehari Sastry, S. T. Ha, B. Gowri Sankara Rao, K. Mallika and T. Vindhya Kumari, Optical properties of a mesogen by image analysis, Liquid Crystals, 39, 1414-1419, 2012.

[27] S. Sreehari Sastry, Sandeep Kumar, T. Vindhya Kumari, K. Mallika, B. Gowri Sankara Rao and Ha Sie Tiong, Liquid crystal parameters through image analysis, Liquid Crystals, 39, 1527-1537, 2012.

[28] Roman Dąbrowski, Przemysław Kula and Jakub Herman, High Birefringence Liquid Crystals, Crystals, 3, 443-482, 2013.

[29] A.K. Greg, J.D. Michael, A.Graham, Liquid crystal tunable birefringent Filters, Proceedings of SPIE, optical spectroscopic techniques and instrumentation for atmospheric and space research II, 2830, Bellingham (WA): SPIE; 1996.

[30] R. Tomasz, Tunable highly birefringent solid-core photonic liquid crystal fibers, Optical and Quantum electronics, 39, 1021-1032, 2007.

* * * * *