

Comparative Study of Electro-Optical Properties of Liquid Crystal Molecules

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Chapter 1: Introduction

The states of matter are mainly classified into three categories: solid, liquid, and gas. Different properties are exhibited by these states of matter like solids have a definite shape, liquids can flow, and gases do not have fixed shape or volume. The concept of liquid crystal lies between a crystalline solid and an isotropic liquid. The Liquid crystal (LC) phase represents a different state of matter characterized by the molecule's mobility and order. All the particles in the crystalline state possess an orientational and three-dimensional positional order. Liquid crystal phases possess both orientational order and, in some cases, positional order in one or two dimensions. The molecules' behavior is responsible for the different types of intermolecular interaction acting between sides, planes, and ends of a molecule pair. LC phases are formed by anisotropic molecule, having one molecular axis very different from the other two. The rod-like molecule is the most common type of LC molecular shape. The nematic phase exhibits long-range orientational order but no positional order of the molecule. The external electric field's impact on liquid crystal can be studied by Vuk's theory and analyze the molecule's polarizability. In liquid crystals, the molecular polarizability and its anisotropy are important inherent molecular properties because the intermolecular interaction energies depend on them. LC materials may consist of polar and non-polar molecules that depend upon LC's physical structure. The LC molecules can possess permanent dipole along the long molecular axis, enhancing the LC's dielectric anisotropy. The dipole moment parallels the long molecular axis, then $\Delta\epsilon > 0$, and the molecules tend to orient along the electric field direction because LC possesses more significant dielectric anisotropy along the molecular axis (x-axis). The orientational order of the LC molecule does not change in the applied external electric field. The applied external electric field to the LC molecule causes the reorientation of the director angle. The LC molecule responds to

the applied external electric field E collectively, causing the director angle to fluctuate.

The calamitic thermotropic liquid crystals are classified into nematic and smectic liquid crystals. The subsequent class is discotic nematic and columnar. By the influence of solvents, the liquid crystals are named as Lyotropic liquid crystals. The role of a surfactant is very crucial in this case. The liquid crystals in the nematic phase do not change their propagation direction while going through the sample. But positional order is absent. If we take the case of isotropic liquid–nematic transition, the translational symmetry is maintained while the rotational symmetry is lost.

The liquid crystals in the smectic phase are obtained when the crystalline order is absent in two dimensions. By this, we get a stack of two-dimensional liquid. These have well-defined structures with well-defined interlayer spacing. In smectics, the positional and orientational ordering remains intact. This helps in translation in two directions and rotation in one direction. The strength of interlayer attractions was weak in comparison to lateral forces, so the layers of the molecules can slide over one another. This enhances the fluidity of smectics over the nematics as smectics have higher viscosity. Another key feature of the smectic phase is it has periodicity along one direction. One can find a large number of smectic phase as no point group is forbidden. From layer formation, one smectic phase is different from the other one another. Smectic A phase is considered to be the simplest phase in which the average molecular axis is perpendicular to the smectic layers. There is a random arrangement of different layers of the smectic phase, and they are capable of translating and rotating along their axes. One can observe optical patterns arising due to the distortion caused by the flexibility of layers. For getting a phase having a bit lower symmetry, the temperature must be decreased up to a certain level. These phases produce a crystalline structure when the long-axes of the molecule are orthogonal to the plane of the layers. One of the exceptions is the smectic D phase, which is a cubic phase but does not contain layers. Some smectic phases possess 2D character like smectic B, smectic I, and smectic F. The higher-order smectic phase possesses 3D character smectic L and smectic J.

Chapter 2 Methodology

All the molecules are optimized by the Gaussian 09 software package with the help of density functional theory (DFT) method B3LYP and M062X with 6-31G** basis set. After the optimization of all the molecules, we have applied the electric field to the nCB LC along the molecular axis (x-axis) and perpendicular (y-axis) to it from 0.0000 (a.u.) to 0.2000 (a.u.) at the interval of 0.0020 (a.u.). After the applied electric field, we have calculated the molecular polarizability of the nCB LC molecules. The X-axis has considered as extraordinary molecular polarizability (α_e), and Y-axis has considered as ordinary molecular polarizability (α_o). With the help of α_e and α_o , we have calculated the order parameter, birefringence, and refractive index as per the given formula. The finite-field approach framework predicts the total molecular energy under the impact of the electric field is given below.

$$E = E_0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k$$

Where E_0 is the total energy in the absence of the electric field. F_i , μ_i , α_{ij} , and β_{ijk} equivalent to the electric field components, dipole moment, polarizability, and first-order hyperpolarizability. Respectively directions specified along with the subscripts i, j and k=x, y and z. The α , β , μ , and $\Delta\alpha$ can be express as numerical differentiation with an electric field of magnitude 0.002 (a.u). respectively equations are given below;

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

where $\tilde{\alpha}$ is mean isotropic polarizability.

Order parameter (S):-

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \quad (1)$$

Birefringence (Δn):-

$$\Delta n = \frac{(\alpha_e - \alpha_o)}{6.3631} \left[R^3 - \left(\frac{2\alpha_o + \alpha_e}{20.244} \right) \right]^{-1} \quad (2)$$

where R is the radius of the liquid crystal molecule.

Magic angle (θ):-

$$\theta = \cos^{-1} \left[\frac{(2S+1)}{3} \right] \quad (3)$$

Refractive index (n):-

$$\begin{aligned} \alpha &= \frac{2\alpha_o + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S}, \quad \gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S} \\ n_e &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}} \\ n_o &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} - \frac{(2\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}} \\ n &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} \end{aligned} \quad (4)$$

where N=1, is the number of liquid crystal molecules studied with the variation of temperature and external electric field to find out the different phases of LC series.

The LC's temperature range is 300K to 400K used to study the phases of the LC series.

Chapter 3: Spectroscopy existing behind the electro-optical properties with an even-odd effect of nCB liquid crystal molecules

The electro-optical response depends on the physical property and molecular structure of the LC molecules. The cyanobiphenyl (nCB) LC's are highly polar, so it has very high thermal and electrochemical stability. The external electric field sufficiently affects the optical properties of rod shape LC's through both ends of molecules' polarization. Under an external electric field, the one end of the nCB molecule has favorable charges. In contrast, the other end is negatively charged and formed an electric dipole. The LC molecules director will reorient along the direction of the applied external electric field. The molecular polarizability increases with an increment of carbon atom number of the alkyl chain of the tail of the nCB LC molecules. The nCB LC's family first times synthesized by Gray et al. for the electro-optical application of the display technology. The nCB LC is colorless and stable to the moisture that is the best feature of these molecules. The nCB LC have a unique property for the alkyl chain length is changed, then the molecular properties of the mesophase changes. The nCB LC molecules are indicated an even-odd effect under the extension of the alkyl chain. The optical polarizability of the nCB LC molecule has followed the even-odd effect and gives the interchange polarizability. The order parameter also exhibits the even-odd effects for the even-odd number of the alkyl chain's carbon atom in the tail of the nCB LC. The birefringence is an electro-optical phenomenon used to find out the Kerr effect under the electric field's impact. The birefringence is a fundamental property of the LC, which gives LC's valuable information to use in various optical device applications. The electric field to the LC molecules has a rapid method to calculate birefringence and polarizability for the display technology's electro-optical application. The electro-optical effect is used to study the pretransitional behavior (related to the order parameter) of the nCB LC. The nCB LC has a positive Kerr constant because of the intense, permanent dipole moment and highly conjugated π -electrons. The polarization of LC molecules induced by an applied electric field to the molecule depends on the applied field's direction. The electric field corresponds to an essential parameter to determine the electro-optic property of the LC molecules. Rod shape LC molecules are lesser tilted as a comparison to the bent-core type LC molecules. The electrically induced tilt affects an observed in several types of bent-core and hockey-stick type LC molecules. The

polarization and bending plane of the molecules are parallel in the absence of an electric field, and it will be perpendicular to the plane in the presence of an electric field. The smectic phase of the LC molecule tilted continuously with the increased electric field. The switching behavior of the even-odd numbered carbon atom in the tail of the LC is different. The notation of nCB refers to the number of carbon atoms in the alkyl chain of nCB LC molecules. The Kerr constant measured with exploiting of birefringence under the impact of the electric field. The birefringence is equal to the product of light wavelength, Kerr constant, and the square of the electric field ($\Delta n = \lambda K E^2$), where λ =wavelength of light, E = strength of the electric field, K =Kerr constant. Karat et al. reported the even member of the nCB series is makes a larger angle with the long molecular axis. It will reduce the anisotropy of the molecule and thereby minimize the order parameter and nematic to the isotropic phase transition temperature. However, the odd member of the nCB series makes the least angle with the molecule's long molecular axis. Thus, it will enhance the anisotropy of the molecule, thereby increasing the order parameter and transition temperature. The present work also reveals the order parameter, and birefringence decreases for the even member. However, the order parameter and birefringence increase for the odd member of the nCB LC series. The nCB LC is a widely studied molecule, and all the optical parameters are readily available for comparison. With the help of the described method, we are explained that the electric field is another method to achieve the all-optical properties and phase transitions. Which is as shown in Fig. 3.1 by the variation of temperature to the LC. Electric polarizability is the most crucial factor in finding optical parameters.

3.1 Effect of the temperature with an extension of alkyl chain length

This subsection describes the different phase transition of nCB liquid crystal with the variation of temperature. The red line is indicating the crystalline to the nematic phase transition from 1CB to 7CB. The 8CB to 12CB showing crystalline to smectic phase A transition indicated by the pink line. The 8CB to 9CB leading smectic A to nematic phase transition marked by the green line. Nematic to the isotropic phase transition of 1CB to 9CB shown by the blue line, and lastly, smectic A to the isotropic phase transition of 10CB to 12CB indicated by the brown line. The temperature variation

expresses the even-odd effect for the phase transition of the nCB series. Which is also shown by the application of the electric field on the nCB series. Dalmolen et al. , Dunmur et al., and Lin et al. are reported the nCB series expresses an even-odd effect under the impact of the temperature of LC. The nCB LC molecules reveal an even-odd effect under the temperature's influence by an extension of alkyl chain length. Karat et al. already reported that even member of the nCB series is making a larger angle with the long molecular axis. Thus, it will reduce the molecule's anisotropy and thereby minimize the nematic to the isotropic phase transition temperature. However, the odd member of the nCB series is making a lower angle with the molecule's long molecular axis. Thus, it will be enhancing the anisotropy of the molecule, thereby increasing the transition temperature shown in Figure 3.1. The C-C symmetric scissoring in the benzene ring is responsible for crystalline to the nematic phase transition. Because the IR frequency corresponds to the absorbance is continual increases from 1CB to 7CB. However, the absorbance decreases for the 8CB because it is expressed crystalline to the smectic A phase transition indicates by the pink line. The C-C and C-H atom's stretching has contributed to the anisotropy of polarizability for the new compound compared with the previous molecule.

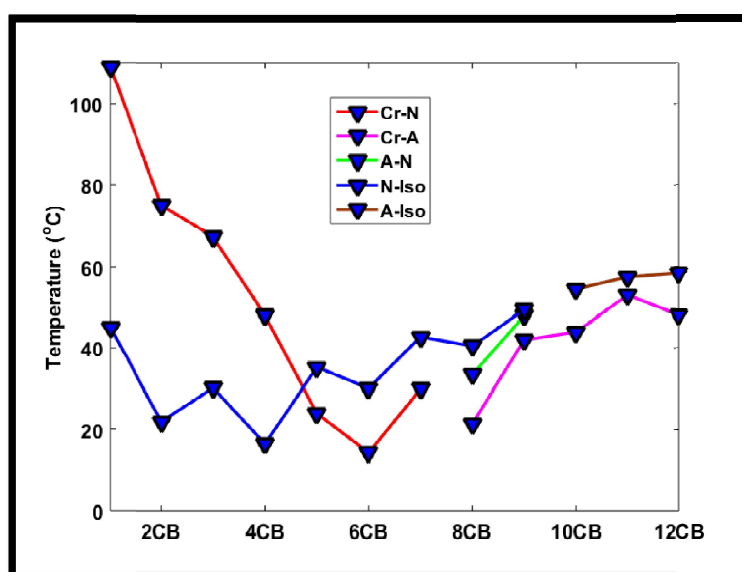


Figure 3.1. Effect of temperature under the expansion of alkyl chain length {red line indicates crystalline to nematic phase (Cr-N), the blue line indicates nematic to isotropic phase transition (N-iso), the green line indicates smectic A to nematic phase

transition (A-N), the pink line indicates crystalline to smectic A phase transition (Cr-A), the brown line indicates smectic A to isotropic phase transition (A-Iso)}

3.2 Birefringence

We have calculated birefringence with the help of Eq. No. 2 under the external electric field with an extension of the alkyl chain length. Coles reported the birefringence is decreasing under the influence of the external electric field with an extension of alkyl chain length. In present work, the birefringence is decreasing continuously with an extension of the alkyl chain, as shown in Figure 3.14. Dunmur et al. have reported under the impact of temperature, the dielectric anisotropy, and birefringence decreased. And the nCB series are showing an even-odd effect with the extension of the alkyl chain length. Under the influence of an electric field, the birefringence of nCB LC molecules decreases with the even-odd effect, as shown in Figure 3.14. Wu et al. reported the birefringence of 5CB is 0.22. In the present work, the birefringence of 5CB is 0.20. From 1CB to 5CB, the birefringence steadily decreases but does not show the even-odd effect. Still, after the 5CB LC, the birefringence exhibits the perfectly even-odd effect express by the DFT methods B3LYP, as shown in Figure 3.14. However, the even-odd effect is expressing by the DFT method M062X. The odd carbon atom number of the alkyl chain has a higher birefringence as compared to the even member of the alkyl chain. The birefringence decreases with an increase of carbon atom numbers of the alkyl chain length. The C-H asymmetric stretching corresponds to IR absorbance in the benzene ring, an improvement for the odd member, and falls for the even member of the alkyl chain. The 10CB LC is an even member of the nCB series. The IR absorbance is increasing instead of decreasing of 10CB LC that is the reason for sharply reducing birefringence.

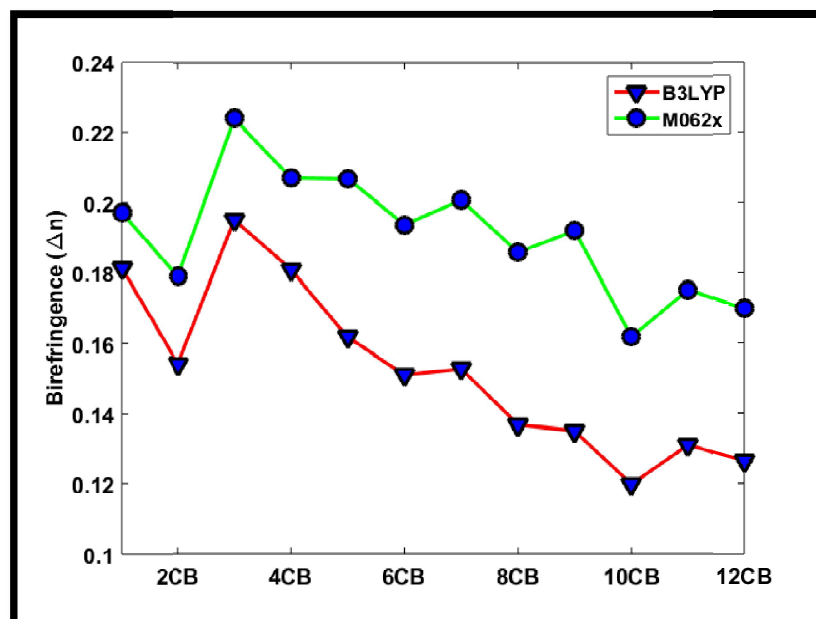


Figure 3.14. Calculated birefringence of nCB series under the effect of the external electric field with an extension of the alkyl chain length using B3LYP (red line) and M062X (green line) methods.

Chapter 4: Molecular spectroscopy and adverse optical properties of HBT liquid crystal molecule

The Liquid crystal (LC) phase represents a different state of matter characterized by the molecule's mobility and order. All the particles in the crystalline state possess an orientational and three-dimensional positional order. Liquid crystal phases possess both orientational order and, in some cases, positional order in one or two dimensions. The liquid crystal behavior of molecules is responsible for the different types of intermolecular interaction acting between sides, planes, and ends of a pair of the molecule. Liquid crystal (LC) phases are formed by anisotropic molecule, having one molecular axis very different from the other two. The rod-like molecule is the most common type of LC molecular shape. The nematic phase exhibits long-range orientational order but no positional order of the molecule. The impact of the external electric field on liquid crystal can be studied by analyzing the polarizability of the molecule. In liquid crystals, the molecular polarizability and its anisotropy are important inherent molecular properties because the intermolecular interaction energies depend on them. LC materials may consist of polar and non-polar molecules

that depend upon LC's physical structure. The LC molecules can possess permanent dipole along the long molecular axis, enhancing the dielectric anisotropy of LC. The dipole moment parallels to the long molecular axis, then $\Delta\epsilon > 0$, and the molecules tend to orient along the electric field direction because LC possesses more significant dielectric anisotropy along the molecular axis (x-axis). If the molecule carries fewer dipole moments long molecular axis, then $\Delta\epsilon < 0$ and fragment tend to orient perpendicular to the electric field direction because of the polarity of the molecule is negligible. The orientational order of the LC molecule does not change in the applied external electric field. The applied external electric field to the LC molecule causes the reorientation of the director angle. The LC molecule responds to the applied external electric field E collectively, causing the director angle to fluctuate.

Luckhurst et al. reported the Schiff base compound increases the molecule's polarity, which enhances the dielectric anisotropy. The dielectric anisotropy is suitable for the electro-optical effect in display applications. Alkyl chain also increased the liquid crystal properties, such as the nematic-isotropic or nematic, to a smectic phase transition temperature. According to different theoretical models, the molecular polarizabilities and the anisotropy of liquid crystal molecules are considered essential characteristic inherent molecular properties because the intermolecular interaction energies, according to different theoretical models, are dependent on them. The refractive index of HBT LC is 1.58. The birefringence decreases with the increased temperature of the HBT LC molecule. The birefringence in the nematic phase exists between 0.2 to 0.1. The OBT has a smectic B phase. Rao et al. reported that the order parameter increases with an increment of the magnetic field. The nematic to the smectic phase transition, the order parameter decreases. The HBT LC has an adverse order parameter within the range of 0.45 to 0.58. The α_0 increases, and α_c decreases with increased temperature. The HBT is more stable as a comparison with other molecules. The HBT has a -0.6 order parameter, and OBT has a -0.5 order parameter. The HBT LC has strong intermolecular forces that are responsible for the alignment of molecules. The HBT LC is also having greater translational flexibility, which is dominant in the nematic phase. The HBT LC is an excellent molecule for high-speed optical switching devices; that is the reason for choosing this molecule as shown in fig 4.1.

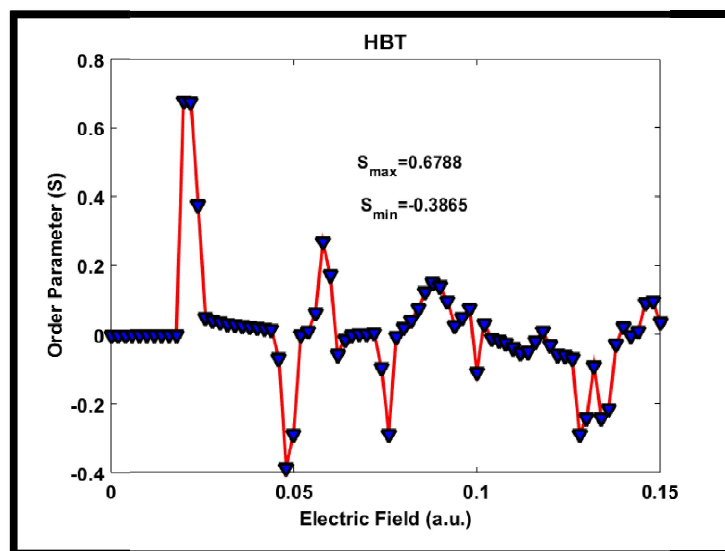


Figure 4.1. Calculated order parameter under the influence of an external electric field by density functional theory.

Chapter 5: Electro-optical odd-Even effect of the homologous series of 7O.m liquid crystal compound

The electronegative oxygen atom plays a crucial role in the compound series of *N(p-n-Heptyloxy-Benzylidene) p-Toluidine* nO.m ($n=7$, $m=1-10$); the presence of an oxygen atom in the series of 7O.m is responsible for the nematic phase. On increases the length of alkoxy or alkyl chain, then the dipole moment increases with the liquid-crystalline range of molecules. The nematic to smectic-A (N-A) phase transition has been observed if the alkyl chain length increased. The nO.m compound series shows the odd-even effect under the applied Temperature. The order parameter (S) has been studied by the optical birefringence and molecular polarizability. The removal of an oxygen atom from both sides of the NO.Om compound series is responsible for the reduction of dipole moment and transition temperature. The presence of oxygen atoms on both sides of the compounds NO.Om causes the growth of the clearing temperature and liquid crystalline range. The Schiff base compounds are (NO.O.m, nO.m, and n.m) very sensitive to the atmosphere. The nO.m compounds show the orthogonal phase for the $n \leq 6$, and $m \geq 7$, and they exhibit the smectic-F and smectic-G phases. The 7O.1 liquid crystals molecules express the nematic and monotropic-A and smectic-B phase under the effect of temperature. The 7O.1 *N(p-n-heptyloxy-*

benzylidene)p-toluidine (HyBT) liquid crystal compound is a weakly polar compound. It exhibits the nematic phase in heating while cooling of the sample expresses the smectic-A and smectic-B phases. With reduced temperature, the density and ultrasonic velocity in the isotropic phase linearly increased. No hysteresis loop has been observed in the density during heating and cooling cycles. The alkoxy and alkyl-substituted Schiff bases liquid crystal molecules express the liquid crystalline behavior above the room temperature. The compound series is denoted by nO.m where n and m represent the numbers of carbon atoms in the alkyl and alkoxy the groups, respectively linked with the benzylidene-aniline frame in the para-positions. The n=7 number has fixed, and m numbers vary from 1 to 5, which is showing the nematic phase, and m=6 indicating only smectic phases (smectic-A, smectic-C, smectic-F, and smectic-G). The n=7 and m \geq 5 exhibit the nematic and smectic phase while the m \geq 8 does not express any nematic phase. They are exhibit only a series of smectic phases. The extended homologous series (m>8) represents the smectic-A phase at a higher temperature and a narrow range of smectic-C or smectic-B and finally smectic-G phase at a lower temperature [16-17]. The 7O.4 compound expresses the ultrasonic velocity in the isotropic phase, which is enhanced linearly with decreasing temperature. The peculiar decrease in the ultrasonic velocity has been observed in the environs of the isotropic-nematic (I-N) phase transition. The ultrasonic velocity firstly reduces in the isotropic phase adjacent to the transition temperature, and further enhanced with decreased temperature in the nematic phase. The nematic phase liquid crystal molecules possess long-range orientational order. At the same time, the smectic molecules contain three, two, or one-dimensional periodic order addition with the orientational order. The ultrasonic velocity and molecular volume in a range of temperatures predict the phase transition and also predict molecular packing and molecular interaction. In 7O.5, the compound's density decreases linearly, with increases in the smectic-G phase's temperature. The smectic-G to the smectic-B phase transition is the first-order transition in which the structures changed abruptly. The density change at the transition temperature is due to the structural deformation from three dimensional (3D) with smectic-G phase to two dimensional (2D) smectic-B phase. The smectic-C to smectic-A phase transition expresses the second-order phase transition because the density changes continuously from smectic-A-smectic-C. In the smectic-A phase, the density decreases linearly with the enhancement of temperature continuously. The smectic-A to the nematic

phase transition is the first-order phase transition because of the molecules' parallel arrangement. The present work theme is searching for the new liquid crystals, which is maybe suitable for the optical shutters, beam steerers, limiters, and switchable optical filters applications. The present work shows the correlation between the theoretical prediction of the electric field's external effect with the experimental evidence under the impact of temperature.

The 7O.m compound series expresses a perfectly odd-even effect by an order parameter, birefringence, and dipole moment under the effect's electric field. But the isotropic polarizability, Homo-Lumo gap, and refractive index do not express any odd-even effect. The 7O.m compound series has low birefringence and small order parameter in the presence of an electric field. The Homo-Lumo gap remains constant during the extension of the alkyl chain length of the 7O.m compound. The refractive index and isotropic polarizability are continuously enhanced with the extent of the alkyl chain. The DFT methods reveal the same nature of characteristics for all the parameters but different values. The M062X method expresses the higher values for the refractive index, birefringence, Homo-Lumo gap, and order parameter compared with the B3LYP method, while dipole moment and isotropic polarizability having higher values for the B3LYP method as a comparison with the M062X method. The B3LYP and M062X are the most excellent organic compounds; they express good accuracy with the experimental results. The 7O.m compound series has a 54.74° magic angle, and it is calculated by Equation number 3.

3.1 Order parameter

The order parameter has been calculated with Equation no. 1 under an external electric field's influence. The 7O.1 and 7O.2 ($m > 2$) liquid crystal molecules do not exhibit any odd-even effect, and after the 7O.2 molecule, the odd-even effect is observed correctly shown in Figure 5.1. The order parameter of the 7O.m series sharply decreases for the 7O.6 liquid crystal molecule expressed by both methods B3LYP and M062X shown in Figure 5.1. because bond orientational order breaks rotational symmetry and represents the smectic-F phase. Rao et al. have reported that the order parameter of 7O.1 exists between 0.42 and 0.63. In the present work, the order parameter of 7O.1 is 0.41, shown by the B3LYP method. Gasparoux et al. have reported the order parameter of 7O.4 existing between 0.42 to 0.63, and by the Vuks

methods, the order parameter of 7O.4 is 0.41. In the present work, the order parameter of 7O.4 is 0.40, shown by the B3LYP method, which is approximately equal to the experimental evidence. Rao et al. reported the order parameter of 7O.5 is 0.44 in the present work; the order parameter of 7O.5 is 0.46. The B3LYP method is suitable for $m < 5$, and the M062X method suitable for $m > 5$. Godzwon et al. reported the transition temperature nematic to isotropic (N-I) phase transition is also express the odd-even effect under the impact of temp. In contrast, the present work also indicates the odd-even effect under the influence of an electric field's external effect. The impact of temperature on the liquid crystals is correlated with the external impact of the electric field.

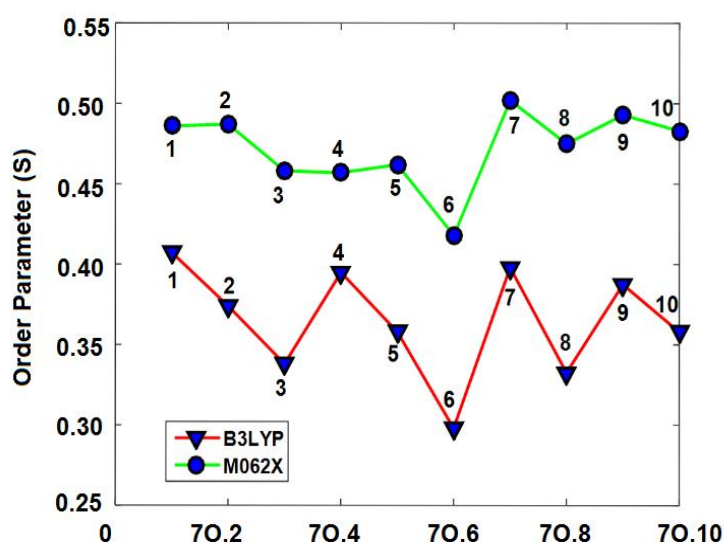


Figure 5.1. Order parameter generated under the applied electric field (a.u) by the B3LYP and M062X methods.

Chapter 6: Even-odd effect of the homologous series of nCHBT liquid crystal molecules

The general structure of nCHBT consists of one phenyl ring attached by the cyclohexane ring with the chair conformation and the isothiocyanate ($-NCS$) group linked with the phenyl ring and the alkyl chain (C_nH_{2n+1}) attached to the cyclohexane ring. Based on technological applications, it has been found the nematic liquid crystals possess orientational order due to they have used for the extensive applications in liquid crystal display (LCD) devices. The refractive index and

birefringence depend upon the wavelength, temperature, and structure of the particular material. But for the use of liquid crystal in the form of a display device, the temperature factor is essential. A simulation using computational techniques has used to know the transport properties of a particular liquid crystal. The transfer of momentum gives rise to shear viscosity. In CHBT, viscosity is independent of the velocity gradient, whether it is nematic or isotropic phase. The strength of the odd-even effect has undermined with the increase in the alkyl chain of the compound. On increasing the temperature, the value of the extraordinary refractive index decreases while the ordinary refractive index's value increases. With the introduction of the NCS group, the value of polarisability increases in the case of CHBT, as phenyl ring combines with π electron. In the nematic phase of CHBT, the antiparallel association of the molecule is not present. The antiparallel conformation has generated the dipole between the cyanobiphenyl (CN) group; however, the NCS group does not create any dipole. The infrared spectrum of the isotropic liquid crystal is similar to the IR spectra of a liquid crystal in the nematic phase. The nematic liquid crystals are capable of scattering light to a greater extent; its special appearance makes it more visible, among others. The NCS group exposed to UV radiation, it has found that it resist exposure. Their color, conductivity, and phase transition temperature remains the same. These contain a smectic layer spacing, which is similar to the length of one molecule. Its mixture with the CN group yields a high value of dielectric anisotropy. The small changes in the rigid core structure lead to the change in attractive and repulsive forces. The transfer of momentum in liquids is different from the transport phenomenon in solids. The rigid core in CHBT is known as the mesogenic core. The ratio of apparent molecular length and calculated the molecular distance indicates that some biomolecule associates with CHBT. Short-range associations are highly dependent on the structure of the molecule. Quantitatively, founded by a Kirkwood correlation factor, and this reveals that correlation is less in the isotropic phase. When two liquid crystals have a resemblance in structure and length, but their polarity is different, then dielectric relaxation spectroscopy is required to study their orientational order. For the comparison between two liquid crystal compounds, the relative temperature is generally used. Buchecker et al. have revealed that the isothiocyanates group and the side chain could help form a homologous series in which a rigid core is free from double bonds. The compounds having an odd number of alkyl groups, the range of mesogenic state temperature is broad compared to the

compounds having an even number of alkyl groups. The mechanical properties of a liquid crystal-like elasticity depend upon the dipolar interaction. Schulz et al. have reported that the liquid crystal is thermally stable or not; it relies on its terminal group's nature. The nCHBT compounds are having –NCS as the terminal group, which is more fluctuates in the high-temperature range. The objective of this work is to find out an unknown liquid crystal molecule for electro-optical applications. The present work's motivation is searching for a new unknown liquid crystal molecule that is suitable in the terahertz (THz) applications because we are applying a very high electric field 0.001 a.u, which is equal to 6.5 THz.

The transition temperature, birefringence, and dipole moment reveal an even-odd effect due to the increment of the alkyl chain of CHBT liquid crystal; however, the HOMO-LUMO gap not affected. The present work is indicating birefringence is inversely related to the order parameter. However, the order parameter, refractive index, range of director angle ($\Delta\theta^\circ$), and refractive index continuously increase with an increment of alkyl chain length while birefringence steadily decreases. Rozga et al. have reported an unusually high electric field used for ion separation, which increases the propagation rate of streamers to be at least 10^9 V/m; the present work used 10^{10} V/m electric field for the charge separation of the molecules. Baran et al. have reported that the nematogen nCHBT series displayed a very high electrical resistance 10^9 Ω cm, which is why applied an unusually high electric field 10^{10} V/m in the present work.

3.1 Transition Temperature:

The transition temperature from the nematic to isotropic phase shows the even-odd effect shown in figure 6.1 Dabrowski et al. have reported the increased amount of the melting point observed when the number of carbon atoms in the alkyl chain is odd, and the small changes in the rigid core structure lead to the change in attractive and repulsive forces. Buchecker et al. reported the nCHBT compounds having an odd number of alkyl groups; the range of mesogenic state temperature is broad compared to the compounds having an even number of alkyl groups. The transition temperature expresses the even-odd effect under the extension of the alkyl chain length of nCHBT LC. The odd carbon atom number has a higher prospective; however, even the carbon atom number has a lower prospective. The odd carbon atom number of the alkyl chain

length increases the transition temperature and even number decreases the transition temperature because the even member of the nCHBT series is making a larger angle with the long molecular axis; thus, it will reduce the anisotropy of the molecule, and it will also reduce the nematic to the isotropic phase (N-Iso) transition temperature. However, the odd member of the nCHBT series is making a lower angle with the long molecular axis; thus, it will enhance the anisotropy of the molecule, thereby increasing the transition temperature.

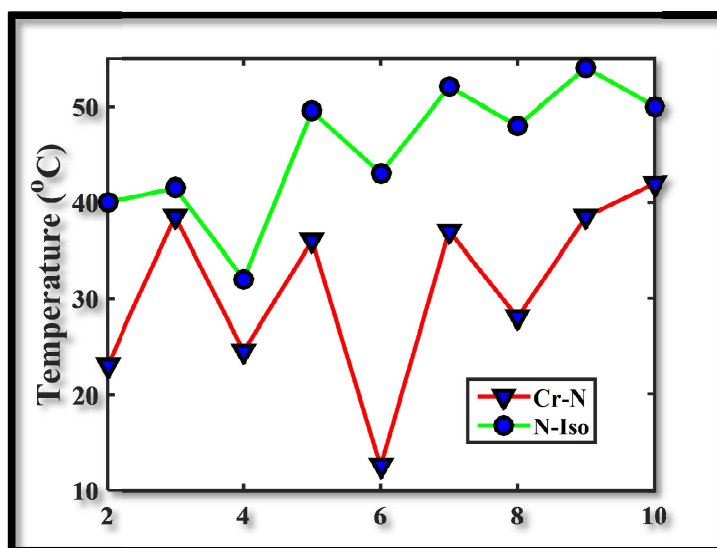


Figure 6.1. Transition temperature of nCHBT LC under the extension of alkyl chain (Crystalline to Nematic phase transition (Cr-N) and Nematic to Isotropic phase transition (N-Iso) expresses the odd carbon atom number has a higher melting point; however, even the carbon atom number has a lower melting point)

Chapter 7: Conclusion and future prospects

The work's motivation has studied the reason behind the even-odd effects obtained by temperature and electric field variation. The temperature and electric field both parameters are shown the odd-even effect in the LC series. Hence, the study's interesting part is the correlation between the electric field and temperature to cause the even-odd effect in the LC series. This strategy is useful for the electro-optical effect of future molecules. The present theoretical model predicts the optical parameters of the unknown organic molecule. The novelty of the current work is modified mathematical equations as a comparison with previously reported results. This theoretical model predicts 97 to 100% accuracy with the experimental evidence.

Chapter 3: In this chapter, it has been found that the electric field's effect on the nCB LC series. Which is reveals an even-odd effect in optical applications. It has been found that the electric field is another method to find out the optical parameters of the nCB series. The optical parameters are obtaining using derived equations from Vuk's theory. The birefringence of nCB series is decreased continuously and showing an even-odd effect with the extension of the alkyl chain length of the nCB LC molecules. The order parameter of the nCB is steadily increasing with an extension of the alkyl chain length of the nCB series. The stretching of C-C and C-H atom corresponds to higher IR absorbance for odd members and lowers IR absorbance for even members of the nCB series. The C-C and C-H, atom stretching, is contributing to the anisotropy of polarizability. The order parameter and birefringence of the nCB LC molecules are inversely proportional to each other. Under the electric field effect, the birefringence and order parameters are different for different carbon atom numbers. The order parameter, birefringence, and transition temperature of the nCB series reveal a higher value for odd carbon members, which corresponds to the benzene ring's C-H asymmetric stretching. Our results help to investigate the optical parameters of LC, which can be obtained through electric field and temperature. It is also explaining the correlation between microscopic parameters to mesoscopic parameters of LC, which can be obtained by variation of external electric field and temperature of liquid crystals.

Chapter 4: In this chapter, it has been found that the HBT LC molecule has maximum absorbance during the intermolecular interaction because of charge transfer by an oxygen atom to the benzene ring. The birefringence and order parameter have adverse orders with an expansion of the external electric field. The HBT LC molecule is suitable for sensing and filtering applications because HBT LC has a broad range of frequencies. With this methodology's help, we can predict an unknown organic molecule's optical and sensing properties. Molecular polarizability is the most crucial parameter in this chapter, which is responsible for the optical properties of the organic molecule. This theoretical model predicts the optical parameters of the unknown organic molecule. The novelty of the current work is modified mathematical equations as a comparison with previously reported results. This theoretical model predicts 97 to 100% accuracy with the experimental evidence.

Chapter 5: In this chapter, it has been found that the 7O.m compound series express a perfectly odd-even effect by order parameter (S), birefringence (Δn), and dipole moment under the impact of the electric field. But the isotropic polarizability, HOMO-LUMO gap, and refractive do not express any odd-even effect in the 7O.m series. This compound series has low birefringence and order parameter. The HOMO-LUMO gap remains constant on increasing the length of the alkyl chain. The isotropic polarizability and refractive index continuously improve with an extension of the alkyl chain length. The M062X method produces higher values for the refractive index, HOMO-LUMO gap, order parameter, and birefringence, while dipole moment and isotropic polarizability having higher values which have been calculated by the B3LYP method. The DFT method expresses the perfectly electro-optic and odd-even effect under the applied electric field computed using Eq. 1, 2, 3, and 4. Most probably, it has been found that when the alkyl chain length increased, then the HOMO-LUMO gap some time increased or some time decreased, but in the series of 7O.m compound, the HOMO-LUMO gap remains constant. The homologous series of 7O.m liquid crystal molecules may be suitable for the THz applications. The 7O.m liquid crystals are also ideal for the limiters, optical shutters, beam steerers, and switchable optical filters applications.

Chapter 6: In the present chapter, it has been found that under the extension of alkyl chain length, the transition temperature, dipole moment, and birefringence exhibits the even-odd effect. At the same time, the HOMO-LUMO energy gap remains stable due to insulating behavior. The range of director angle, order parameter, refractive index, and isotropic polarizability of the CHBT molecule increases gradually with an extension of alkyl chain length because C-N atom stretching corresponds to IR absorbance continuously increases. The order parameters and birefringence are inversely related to each other. Hence the birefringence decreases and the order parameter increases of the CHBT series due to the continuous extension of alkyl chain length under an electric field. The birefringence and magic angle continually decrease with the increment of alkyl chain length. The influence of an electric field is an alternative to the temperature for optical applications. The present chapter strategy can predict all the optical parameters of the unknown molecules. The current chapter strategy can predict the physical parameters isotropic polarizability, dipole moment, state density, and Intermolecular interactions of the unknown molecules. This work's

motivation is to search for new liquid crystal molecules that are suitable under the terahertz (THz) applications.