



Even–odd effect of the homologous series of nCHBT liquid crystal molecules under the influence of an electric field: A theoretical approach

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Abstract. In this work, we present the effect of electric field on 4-(trans-4'-n-alkyl-cyclohexyl) isothiocyanate-benzene (nCHBT) liquid crystal (LC) molecules. Under the influence of an electric field, the birefringence exhibits the even–odd effect while order parameter, HOMO–LUMO gap, magic angle, isotropic polarisability, range of director angle and the refractive index do not exhibit any even–odd effect. The extension of the alkyl chain length of the nCHBT liquid crystal molecule exhibits the even–odd effect for the dipole moment and temperature from nematic to isotropic phase transition while the HOMO–LUMO gap remains constant. Still, order parameters, isotropic polarisability and refractive index have continuously increased. The odd carbon atom numbers present higher values than the even carbon atom numbers of the alkyl chain for the phase transition temperature. The nCHBT LC molecule expresses the order parameter, and birefringence is reciprocal to each other. For the whole series, there is an increase in order parameter, and a decrease in birefringence. The influence of the external electric field is an alternative to the temperature for the optical parameter of nCHBT LC.

Keywords. Liquid crystal CHBT; even–odd effect; electric field; DFT (B3LYP and M062X); molecular spectroscopy.

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1. Introduction

The general structure of nCHBT consists of one phenyl ring attached to the cyclohexane ring with the chair conformation and the isothiocyanate (–NCS) group linked with the phenyl ring as well as the alkyl chain (C_nH_{2n+1}) attached to the cyclohexane ring. Based on technological applications, it has been found that the nematic LCs possess orientational order due to which they are used extensively in applications such as liquid crystal display (LCD) devices [1,2]. The refractive index and birefringence depend on the wavelength, temperature and structure of the particular material. But for the use of LC in the form of a display device, the temperature factor is important [3]. Simulation using computational techniques is used to know the transport properties of a particular LC.

The transfer of momentum gives rise to shear viscosity. In CHBT, viscosity is independent of the velocity gradient, whether it is in nematic or isotropic phase [4]. The strength of the odd–even effect decrease with the increase in the alkyl chain length of the compound. The clearing temperature also depends on the alkyl chain length. On increasing the temperature, the value of the extraordinary refractive index decreases while the value of the ordinary refractive index increases [5]. 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 form any dipole [6]. The infrared

(IR) spectrum of the isotropic LC is similar to the IR spectra of an LC in the nematic phase. The nematic LCs are capable of scattering light to a greater extent; its special appearance makes it more visible among others [7]. The NCS group has expressed better UV stability than the CN group. Their colour, conductivity and phase transition temperature remain the same. These contain a smectic layer spacing, which is similar to the length of one molecule. Its mixture with the CN group gives a high value of dielectric anisotropy [8]. An increase in melting point is observed when the number of carbon atoms in the alkyl chain is odd. The small changes in the rigid core structure lead to the change in attractive and repulsive forces [9]. 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 in their nematic range varies from 22.3 to 29.3 Å, which expresses the strong intermolecular interaction of 4CHBT LC. Short-range associations are highly dependent on the structure of the molecule. Quantitatively, by the Kirkwood correlation factor, it has been found that electron correlation is less in the isotropic case [10,11]. When two liquid crystals are similar in structure and length, but their polarity is different, then dielectric relaxation spectroscopy is required to study their orientational order. For comparing two LC compounds, the relative temperature is generally used [12]. Buchecker and Schadt [13] have revealed that the NCS group, along with the side chain, could help in the formation of homologous series in which a rigid core is free from double bonds. For compounds having odd number of alkyl groups, the range of temperature of mesogenic state is broad compared to the compounds having even number of alkyl groups. The mechanical properties of a liquid crystal-like elasticity depend upon the dipolar interaction. Schulz and Stolarz [14] have reported that whether the LC is thermally stable or not relies on the nature of its terminal group. The nCHBT compounds have –NCS as the terminal group, which fluctuates more in the high-temperature range. The objective of this work is to find out an unknown LC molecule for electro-optical applications. The motivation of the present work is to search for a new unknown LC molecule that is suitable in the terahertz (THz) applications because we are applying very high electric field (0.001 a.u.), which is equal to 6.5 THz.

2. Computational methodology

All the molecules are optimised by the NWChem Software [15] with the help of density functional theory (DFT) method B3LYP [16,17] and M062X [18] by 6-31G** basis set [19–21]. After the optimisation of all

the molecules, we have applied the electric field (a.u.) to the CHBT LC compound series along the molecular axis (x -axis) and perpendicular axis (y -axis). The range of the applied electric field is 0.000–0.100 a.u. at the interval of 0.0020 a.u. [22] where 1 a.u. = 5.14×10^{11} V/m. After the electric field is applied, we have calculated the molecular polarisability of the CHBT LC molecule series. The molecular polarisability along the x -axis is considered as the extraordinary molecular polarisability (α_e) and along the y -axis is considered as the ordinary molecular polarizability (α_0). With the help of α_e and α_0 , we have calculated the order parameter, magic angle, refractive index and birefringence [23–30]. The finite-field approach framework predicts the total molecular energy under the impact of the electric field which is given below [31]:

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

where E_0 is the total energy in the absence of the electric field, and F_i , μ_i , α_{ij} and β_{ijk} are the components of the electric field, dipole moment, polarisability and first-order hyperpolarisability along the directions specified using the subscripts i , j and $k = x, y$ and z . The molecular anisotropy in polarisability ($\Delta\alpha$) can be expressed as numerical differentiation with an electric field of magnitude 0.002 a.u. The equations are given below [32]:

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

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_0,$$

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

where $\tilde{\alpha}$ is the mean isotropic polarisability.

Order Parameter (S):

$$S = \frac{\alpha_e - \alpha_0}{\alpha_e + \alpha_0}. \quad (1)$$

Birefringence (Δn):

$$\Delta n = \frac{(\alpha_e - \alpha_0)}{6.3631} \left[R^3 - \left(\frac{2\alpha_0 + \alpha_e}{20.244} \right) \right]^{-1}, \quad (2)$$

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):

$$\alpha = \frac{2\alpha_0 + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_0)}{3S},$$

$$\gamma_0 = \alpha - \frac{(\alpha_e - \alpha_0)}{3S},$$

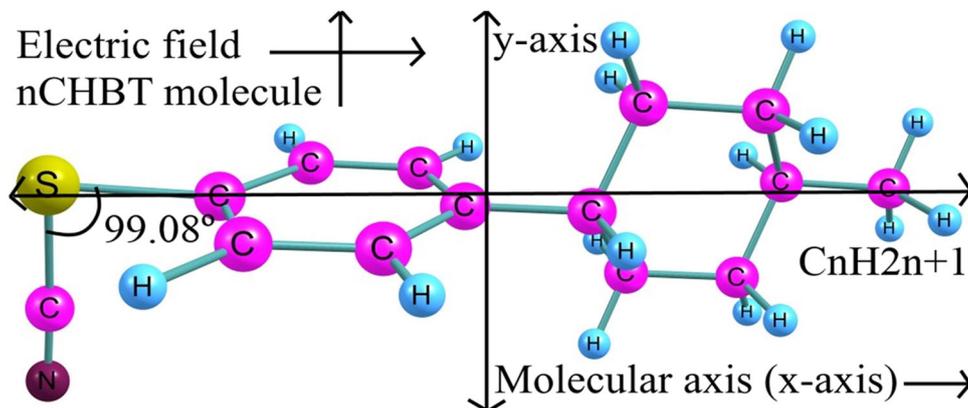


Figure 1. Optimised molecular structure of CHBT LC.

$$\begin{aligned}
 n_e &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} \\
 &\quad + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_0)}{1 - \frac{4\pi N\alpha}{3}}, \\
 n_0 &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} \\
 &\quad - \frac{(2\sqrt{10}/15)\pi NS(\gamma_e - \gamma_0)}{1 - \frac{4\pi N\alpha}{3}}, \\
 n &= \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}}, \tag{4}
 \end{aligned}$$

where $N = 300$ is the number of liquid crystal molecules and γ_e, γ_0 represent the extraordinary and ordinary internal field constant. The difference between γ_e and γ_0 serves as the differential molecular polarisability. n_e and n_0 represent the extraordinary and ordinary refractive indices.

3. Results and discussion

The transition temperature, dipole moment and birefringence express an even–odd effect due to the increment of the alkyl chain of the CHBT LC. However, the HOMO–LUMO gap is not affected. The present work shows that birefringence is inversely related to the order parameter. However, the refractive index, order parameter, range of director angle ($\Delta\theta^\circ$) and refractive index continuously increase with an increment of alkyl chain length while birefringence steadily decreases. Rozga [36] has reported a very high electric field (10^9 V/m) for the liquid crystal ion separation, which increases the propagation rate of streamers. Therefore, in the present work we used 10^{10} V/m electric field for the charge separation of the molecules. Baran *et al* [6] have reported that the nematogen nCHBT series displayed a very high

electrical resistance of $10^9 \Omega \text{ cm}$, which is the reason for applying an unusually high electric field (10^{10} V/m) in the present work. The optimised molecular structure of CHBT LC is shown in figure 1.

3.1 Transition temperature

The transition temperature from the nematic to isotropic phase shows the even–odd effect (see figure 2). Dabrowski *et al* [8,9] have reported that the melting point increases 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 and Schadt [13] reported that when the nCHBT compounds have odd number of alkyl groups, the range of temperature of mesogenic state is broad compared to the compounds having an even number of alkyl groups. The transition temperature expresses the even–odd effect when the alkyl chain length of nCHBT LC increases. The odd carbon atom number has a higher prospective; however, even carbon atom number has a lower prospective. The odd carbon atom number of the alkyl chain increases the transition temperature and even number decreases the transition temperature because even member of the nCHBT series makes 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 makes a lower angle with the long molecular axis of the molecule. Thus, it will be enhancing the anisotropy of the molecule, thereby increasing the transition temperature.

3.2 Dipole moment

Wang *et al* [22] have reported that the dipole moment of the molecule decreases with the applied electric field.

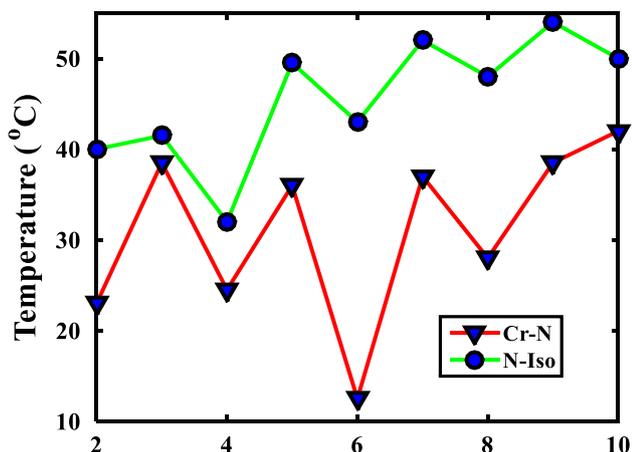


Figure 2. Transition temperature of nCHBT LC calculated with the extension of alkyl chain length (crystalline-to-nematic phase transition (Cr-N) and nematic-to-isotropic phase transition (N-Iso) show that alkyl chain with odd carbon atom number has higher melting point. However, alkyl chain with even carbon atom number has lower melting point [8]).

The present work also indicates that the dipole moment increases for alkyl chains with even number of carbon atoms. However, under the influence of the electric field, the birefringence increases for the odd carbon atom number, as shown in figure 6, the experimental evidence also increases for the odd carbon atom number (1, 3, 5, ...) of the alkyl chain as shown in figure 2. The dipole moment expresses the even–odd effect with the increased alkyl chain length, as shown in figure 3. The even carbon atom number of the alkyl chain expresses higher value of dipole moment while odd carbon atom number expresses lower value because the C–H atom wagging and C–C twisting frequencies increase for the even carbon atom number of the benzene ring but twisting frequency decreases for odd carbon number. The C–S stretching frequency is also responsible for the even carbon atom in the upward direction and odd carbon atom number in the downward direction. The variance of the dipole moment indicates that the CHBT LC molecules change shape and size due to the increment of the alkyl chain length.

3.3 HOMO–LUMO gap

The HOMO–LUMO energy gap will not be affected due to the increment of alkyl chain length, as shown in figure 4. The DFT methodology (B3LYP and M062X) exhibits the same characteristics. The HOMO–LUMO energy gap remains constant for 6.25 eV in the B3LYP method, and by the M062X method, the energy gap remains constant for 8.20 eV. All kinds of molecular

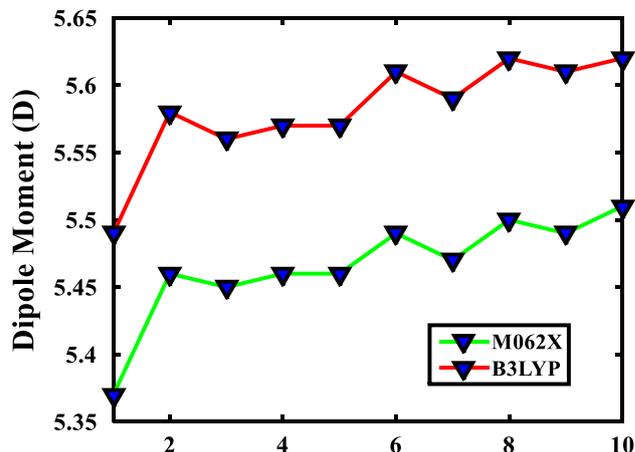


Figure 3. Dipole moment of nCHBT LC calculated with the extension of alkyl chain length (the dipole moment expresses an even–odd effect when the alkyl chain length of CHBT LC increases. The dipole moment is studied by DFT methodology (B3LYP and M062X) and the nature of both the methods is similar. B3LYP and M062X methods are suitable for organic molecules and that is the reason for selecting these methods).

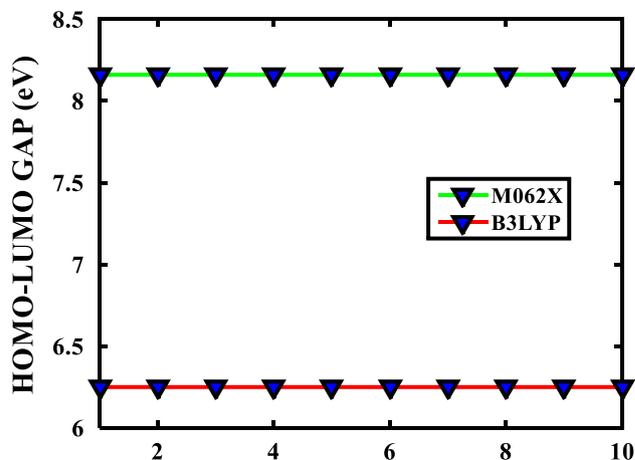


Figure 4. HOMO–LUMO gap of nCHBT LC calculated with the extension of alkyl chain length (the HOMO–LUMO gap is studied by DFT methodology (B3LYP and M062X) when the alkyl chain length of CHBT LC is extended. HOMO–LUMO gap is not considered under the influence of the electric field; it is considered only under the extension of alkyl chain length. The nature of both methods is similar).

stretching do not deflect the HOMO–LUMO energy gap, and it does not express any odd–even effect; it remains constant for all the series because the nCHBT LC is an insulating material. Baran *et al* [6] have reported that the nematogen nCHBT series display a very high electrical resistance of $10^9 \Omega \text{ cm}$. The number of monomers of the nCHBT series does not affect the insulating behaviour, which is the reason for the constant band gap.

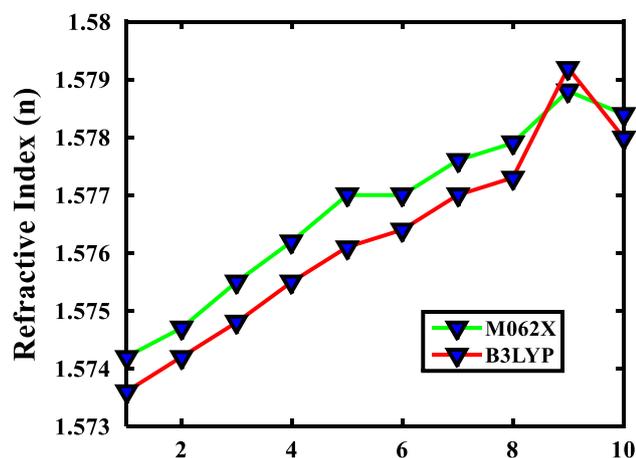


Figure 5. Refractive index of nCHBT LC calculated with the extension of alkyl chain length (the refractive index is studied by DFT methodology (B3LYP and M062X) when the alkyl chain length of CHBT liquid crystal is extended. The refractive index is calculated using eq. (4) under the influence of the electric field. The nature of both methods is similar).

3.4 Refractive index

The refractive index is calculated using eq. (4). The refractive index continuously increases with alkyl chain length, as shown in figure 5. Devi *et al* [3] reported that the refractive indices and birefringence depend on wavelength, temperature and structure of the particular material. Still, the refractive index also depends on the electric field (present work). Baran *et al* [6] have reported that the refractive index increases with temperature; the present work also shows that refractive index increases with electric field, as shown in figure 5. The 9CHBT shows that the refractive index sharply increases and the IR absorbance is found to be very high in the 9CHBT LC because of the C–H wagging frequency of the benzene ring. The rocking frequency corresponding to IR absorbance is found to be very high in the tail of 9CHBT. The C–N stretching corresponding to the IR absorbance shows a continuous increase for the nCHBT series, but C–N stretching decreases in the 9CHBT LC, which is the reason for the enhanced refractive index. M062X methodology predicts the same refractive index for 5CHBT and 6CHBT because they are having one transition state (i.e. ready to react with any material). Still, the refractive index continuously increases in B3LYP methodology. 9CHBT does not have any transition state, but 5CHBT to 8CHBT and 10CHBT LC have one transition state. The refractive index is an optical parameter used for measuring the electro-optical effect of LC.

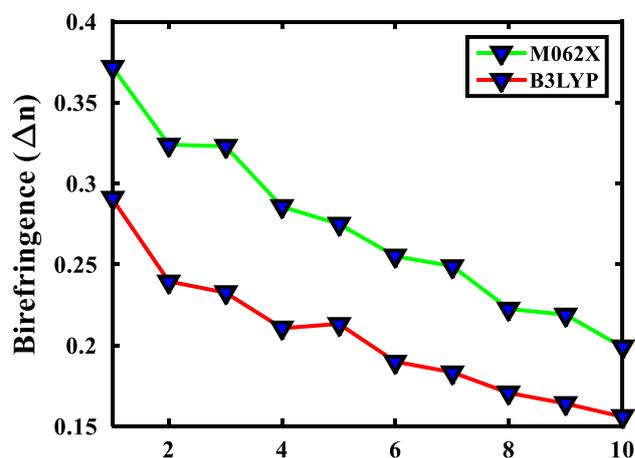


Figure 6. Birefringence calculated with the extension of alkyl chain length (the birefringence is studied by DFT methodology (B3LYP and M062X) when the alkyl chain length of CHBT LC is extended. The birefringence is calculated using eq. (2) under the influence of the electric field. The nature of both methods is similar).

3.5 Birefringence

The birefringence is calculated with the help of eq. (2). Dabrowski *et al* [35] reported that the birefringences of 5CHBT and 6CHBT LC are 0.19 and 0.15 under the influence of temperature. In the present work, the birefringences of 5CHBT and 6CHBT LC are 0.21 and 0.18 which are very close to the experimental values (0.19 and 0.15) [6] as shown in figure 6. Sielezin *et al* [2] have reported that the birefringence decreases by the extension of the alkyl chain length. In the present work also birefringence decreases and expresses even–odd effect due to the increment of alkyl chain length because the C–C symmetric and asymmetric stretching corresponding to IR absorbance increases for the odd carbon atom number and decreases for the even carbon atom number of benzene and cyclohexane ring. Buchecker *et al* [13] have reported that birefringence, dielectric anisotropy and elastic constant increase for the odd number and decrease for the even number of carbon atom of the alkyl chain length. The present work also predicts the same as shown in figure 6. The M062X method expresses more even–odd effect compared to the B3LYP method because the M062X method studies the non-bonded molecular interactions while the B3LYP method studies the Vanderwall forces and hydrogen bond interaction. The birefringence continuously decreases with the extension of the alkyl chain length. According to the M062X method, 2CHBT and 3CHBT, 6CHBT and 7CHBT, and 8CHBT and 9CHBT have the same birefringence because of the dispersion interaction by the molecules, but according to the B3LYP

method, 4CHBT and 5CHBT have approximately same value of birefringence because of the equal amount of intermolecular forces. The birefringence is an optical parameter used for measuring the electro-optical effect of LC.

3.6 Order parameter

The order parameter of LC is in the range of 0.3–0.8. Below 0.3, it is a perfect liquid, and above 0.8, it is a perfect crystal. The order parameter is calculated with the help of eq. (1) under the influence of an external electric field. Bauman *et al* [33] have reported the order parameter of 7CHBT LC as 0.61 under the influence of temperature. The present work also reports the order parameter of 7CHBT LC as 0.64, which is close to the experimental value [34] shown in figure 7a. Raszewski *et al* [37] have reported the order parameter of 6CHBT LC as 0.68. The present work also expresses the order parameter of 6CHBT as 0.68, which supports the experimental evidence shown in figure 7a. The DFT method M062X expresses the nematic phase stability due to the contribution of molecular anisotropy. Sarkar *et al* [11] have reported that the order parameter increases with the extension of alkyl chain length under the influence of temperature in the present work. Also, under the influence of electric field, the order parameter continuously increases by increasing the alkyl chain length. The order parameter continuously increases with the increment of alkyl chain length because C–N and C–C atom stretching corresponding to the IR absorbance continuously increases for the nCHBT series. The order parameter has expressed the even–odd effect with minor deviation. The order parameter is an essential parameter for calculating the physical state of LC with the help of this methodology; we can predict the state of unknown molecules. The extension of alkyl chain length under the influence of the electric field reduces the range of nematic phase stability, as shown in figure 7b.

3.7 Magic angle

Dabrowski *et al* [9] have reported that 1CHBT does not have LC property. However, 2CHBT to 10CHBT have LC property because as the present work shows, the magic angle of 1CHBT LC is higher and very close to 54.80° as shown in figure 8. The magic angle is calculated with the help of eq. (3). The standard value of the magic angle is 54.7° for all LC molecules. The magic angle depends on the order parameter. The 1CHBT LC molecule shows approximately 54.8° magic angle, but the others in the series express 54.7° magic angle as

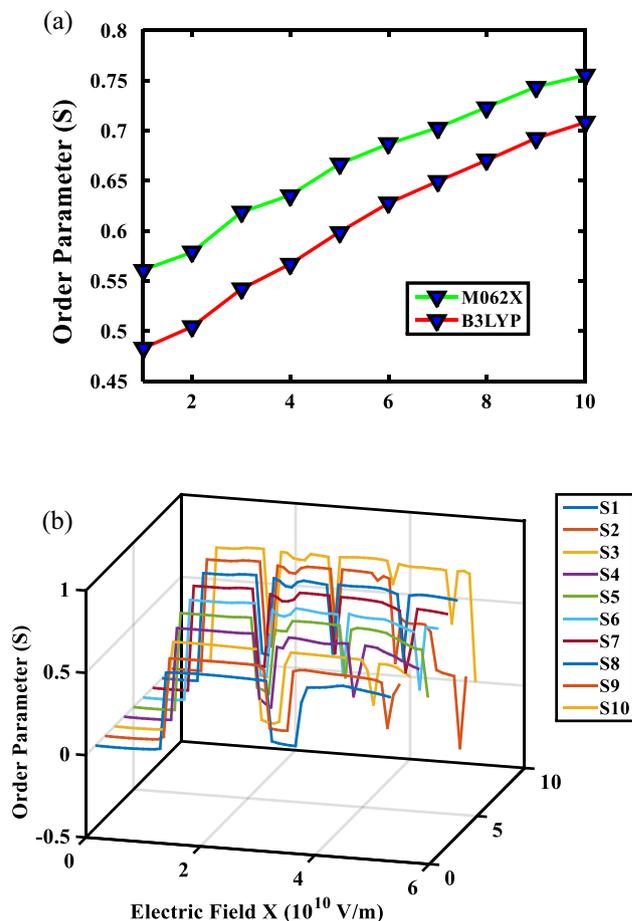


Figure 7. (a) Order parameter when the length of the alkyl chain is extended (the order parameter is studied using DFT methodology (B3LYP and M062X) when the alkyl chain length of CHBT liquid crystal is extended. The order parameter is calculated using eq. (1) under the influence of the electric field. The nature of both methods is similar) and (b) the order parameter is calculated when the alkyl chain length is extended (the order parameter is studied by DFT methodology (B3LYP) of nCHBT liquid crystal. The order parameter is calculated using eq. (1) under the influence of the electric field).

shown in figure 8. The magic angle decreases continuously with the increased length of the alkyl chain, but it increases again in 10CHBT. However, nCHBT maintains 54.7° magic angle for all the others in series. The magic angle of the LC molecule depends on the molecular anisotropy. The molecular anisotropy continuously decreases with an increase in alkyl chain length and that is the reason for the decrement of the magic angle. The nCHBT LC series is uniaxial; however, 9CHBT is biaxial. The magic angle of the 9CHBT decreases, and 10CHBT increases due to biaxial and uniaxial behaviour of LC.

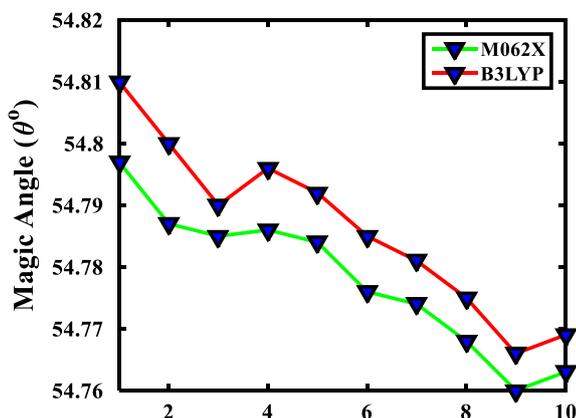


Figure 8. The magic angle of nCHBTLC calculated with the extension of alkyl chain length (the magic angle is studied by DFT methodology (B3LYP and M062X) when the length of the alkyl chain of CHBT LC is increased. The magic angle is calculated under the influence of the electric field using eq. (3). The nature of both methods is approximately similar).

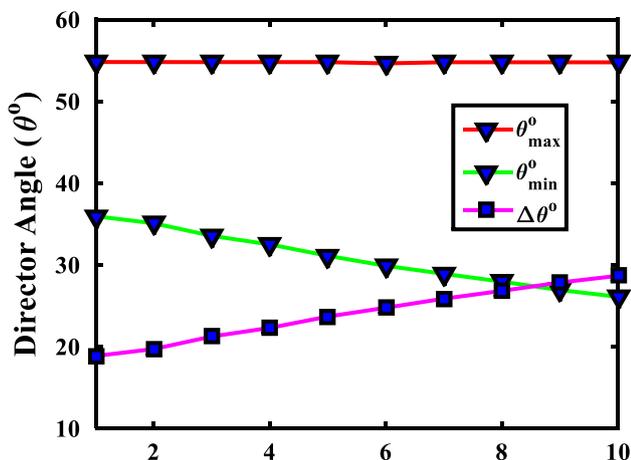


Figure 9. Range of director angle of nCHBT LC calculated with the extension of alkyl chain length (the range of the director angle (magic angle) is studied by DFT methodology (B3LYP) when the length of the alkyl chain of CHBT LC is extended. The range of the director angle is calculated by eq. (3) under the influence of the electric field. The difference of the director angle ($\Delta\theta^\circ$) continuously increases, but the minimum director angle (θ_{\min}°) continuously decreases. However, the maximum director angle (θ_{\max}°) remains constant).

3.8 Range of director angle

Equation (3) calculates the range of director angle ($\Delta\theta^\circ$) under the influence of the electric field. The range of $\Delta\theta^\circ$ is taken from the magic angle, as shown in figure 9. The range of director angle ($\Delta\theta^\circ$) continuously increases with the extension of the alkyl chain

length. The C–C and C–N atom stretching contribute to the enhancement of frequency when $\Delta\theta^\circ$ increases continuously. The minimum director angle (θ_{\min}°) continuously decreases with the extension of alkyl chain length. However, the maximum director angle (θ_{\max}°) remains constant with the extension of alkyl chain length. The maximum director angle remains constant for 55° because the C–H atom stretching of the benzene ring remains constant for all the series. However, the minimum director angle decreases from 35° to 25° . The difference of director angle ($\Delta\theta^\circ$) is continuously increased from 19° to 29° and expresses the broad range of director angle due to the extension of the alkyl chain.

3.9 Isotropic polarisability

Baran *et al* [6] have reported that the π -electron conjugation of the phenyl ring with terminal –NCS group gives stronger polarisability than with –CN group. Jadzyn *et al* [34] have reported that the external electric field aligns the nematogen molecules in the applied axis with maximum polarisability, and the parallel molecular axis (x -axis) gives a minimum moment of inertia of the molecule. The 6CHBT LC expresses three absorption bands with a 0.61 order parameter for the nematic phase; the present work also supports the experimental evidence. The isotropic polarisability increases continuously with alkyl chain length because C–N atom stretching corresponding to IR absorbance continuously increases. The C–C twisting frequency of benzene continuously increases, and so the isotropic polarisability increases continuously with alkyl chain length. Both DFT methodologies give the same prediction with minor deviation (figure 10). Baran *et al* [6] have reported that the isotropic polarisability continuously increases with the alkyl chain length because the alkyl chain contributes to the molecular polarisability with the help of phenyl ring and –NCS terminal group. That is the reason for continuous enhancement of isotropic polarisability.

4. Conclusion

In the present work, it has been found that when the length of the alkyl chain is extended, the dipole moment, transition temperature and birefringence exhibit even–odd effect while the HOMO–LUMO energy gap remains stable due to the insulating behaviour. The refractive index, order parameter, range of director angle and isotropic polarisability of the CHBT molecule increase gradually with an extension of alkyl chain length because C–N atom stretching corresponding to

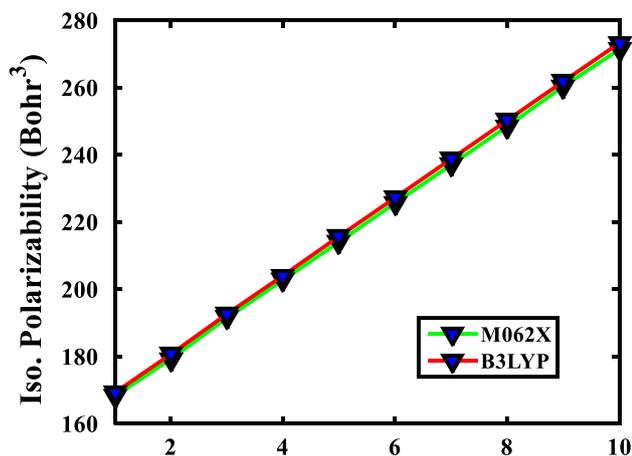


Figure 10. Isotropic polarisability of nCHBT LC calculated with the extension of alkyl chain length (the isotropic polarisability is studied by DFT methodology (B3LYP and M062X) when the length of the CHBTLC alkyl chain is extended. The isotropic polarisability is not calculated under the influence of the electric field; it is calculated only when the length of the alkyl chain is extended. The nature of both methods is similar).

IR absorbance continuously increases. The birefringence and order parameter are inversely related to each other; hence the birefringence decreases and the order parameter increases for the CHBT series due to the continuous extension of alkyl chain length under the influence of electric field. The magic angle and birefringence continuously decrease with the increment of alkyl chain length. We can study the electro-optical effect by the temperature as well as the influence of the electric field. The present work strategy can predict all the optical parameters of the unknown molecules and also the physical parameters such as dipole moment, density of state, isotropic polarisability and intermolecular interactions of the unknown molecules. The motivation of this work is to search for new LC molecules which are suitable in terahertz (THz) applications.

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