Electro-optical Effect of the nCOOCB Liquid Crystal Molecules under the Terahertz Frequency Range: A Theoretical Approach

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ABSTRACT: *The homologous series of 4-cyano-4'-phenyl-phenol-alkanoates (nCOOCB) was studied under the influence of terahertz (THz) frequency range. The nCOOCB series has a re-entrant nematic phase, which is suitable for electro-optical properties under the THz frequency. The birefringence and order parameter expresses the twisting of the nematic phase at the higher frequency range. The director angle has fluctuated at a higher frequency range. The refractive index has remained constant at a higher frequency. The ionisation potential, electron affinity and Homo-Lumo energy gap continuously decrease with an extension of alkyl chain length; however, the dipole moment increases. The Homo-Lumo energy bandgap is reciprocal to the dipole moment.*

Keywords: nCOOCB liquid crystal, DFT, B3LYP, terahertz frequency, electro-optical effect

1. INTRODUCTION

The nitrile (CN) group and nitrogen oxide (NO_2) are used as the common polar groups in the liquid crystal (LC) molecules. However, the alkyl chain length is used as the non-polar group. The cyano group is a strongly polar substitution, which is an attribute to enhance the anisotropy of LC. The CN group has a tendency to be stable in the nematic phase. However, the alkyl or alkoxy derivatives contribute to the smectic phase.[1,2] The non-polar LCs are stable by the alkyl chain length, which increases the thermal geometry of the mesophase. The thermal substitutions of the LCs affect the stability of the mesophase. The hydrogen atom is used as the

terminal group of mesophase, which actively enhances the thermal stability of LC. The molecular packing and intermolecular forces are affected by the cause of charge distribution of the whole molecule.[3,4] The alkoxy and alkylamino biphenyl groups are mostly having higher nematic to isotropic (N-I) transition temperature in comparison with the alkyl derivates. The alkoxy and alkylamino biphenyl groups enhance the N-I transition temperature due to the electron-donating behaviour, and hence the molecular charge and polarizability are increased by the LC.[5]

The phenyl moiety replaced with the cyclohexane ring will enhance the transition temperature because of the lack of π-electron systems due to the decrease in molecular charge. The CN group attached to the cyclohexane ring reduces the thermal stability of molecules.[6] The smectic phase-based LC are enhancing Gibb's energy.[7] The extension of an alkyl chain length enhances the number of σ-bonds of the molecule due to increase in the geometrical anisotropy, intermolecular forces and thermal stability. The alkyl chain length derivative expresses the even-odd effect; this effect infers even and odd carbon atom number of alkyl chain length.[8] The even-odd effect has been observed in the N-I transition temperature, clearing point, order parameter, birefringence and refractive index. At the higher temperature, the alkyl chain length has obtained a higher degree of rotational and conformational order.[9,10] The 4 cyano phenyl phenol esters have a wide range of nematic phase.

The 8COOCB LC has a microscopic dielectric anisotropy, which is also suitable for the storage display applications. The 8COOCB LC monomer is having fluctuations inside the nematic phase. The 8COOCB LC also has a re-entrant nematic phase at high temperature. However, it does not express a re-entrant nematic phase with the effect of atmospheric pressure. The 8OCB LC reveals the anti-ferroelectric effect.[11,12] The OCB LC enhances the N-I transition temperature for the even members (2, 4, 6, 8) and reduces the N-I transition temperature for the odd members (1, 3, 5, 7).

The 4OCB LC has exhibited a higher degree of pairs conformation.[13] Wilk et al. have reported the cyanobiphenyl (CN) LC family suitable in the terahertz (THz) frequency region for absorption applications.[14] The ordinary and extraordinary refractive index of the nitrile group remains constant at the higher THz range.[15] Pan et al. have reported that the birefringence of 5CB LC molecules in the THz frequency range is 0.15.[16] In the present work, we have applied the electric field (THz frequency) to the LC molecules (nCOOCB) for searching the new molecules that are suitable for THz applications. The optical birefringence with adverse order is mostly ideal for the THz application. We are projecting a theoretical prediction for the unknown molecules which exist in future experiments.

2. COMPUTATIONAL METHODOLOGY

The molecular structure of nCOOCB has been optimised by the Gaussian software package by the density functional theory (DFT) method using B3LYP and 6-31G basis set.[17–20] We have applied the electric field (THz frequency) to the nCOOCB LCs along the molecular axis (x-axis) and perpendicular (y-axis) to it from 0.0000 (a.u.) to 0.1500 (a.u.) with an interval of 0.0020 (a.u.) (where 0.001 a.u. = 6.5 THz, and 1 a.u. = 6.5 × 10^{15} Hz). Further, we have measured the molecular polarizabilities of the nCOOCB LC molecule. The x-axis is considered extraordinary molecular polarizabilities (α_e) and the y-axis is ordinary molecular polarizabilities (α_o). With the help of α_e and α_o, we calculated the birefringence, order parameter, magic angle and refractive index, as per the formula given in the following, where α, μ and β are equivalent to the components of the polarizability and dipole moment and first-order hyperpolarizability. [21,22]

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

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

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

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

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

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

In the equations, $\tilde{\alpha}$ is the mean isotropic polarizability.

Order parameter (S):

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

Birefringence (Δn):

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

From the equation, R is the radius of the LC molecule.

Magic angle (θ):

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

Refractive index (n):

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

$$n_e = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \dfrac{4\,\pi N\alpha}{3}} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \dfrac{4\,\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \dfrac{4\,\pi N\alpha}{3}} + \frac{(2\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \dfrac{4\,\pi N\alpha}{3}}$$

$$n = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \dfrac{4\,\pi N\alpha}{3}} \tag{4}$$

where N = 100 is the number of LC molecules.

3.   RESULTS AND DISCUSSION

The homologous series of nCOOCB is more suitable for the THz applications because all the optical parameters are affected under the impact of the THz frequency range, as given in the subsequent discussion. The physical parameters, i.e., dipole moment, ionisation potential, electron affinity and Homo-Lumo energy bandgap, indicate that the extended series of the present molecules also exist for the novel applications. The fluctuation of the director angle and twisting of birefringence at a higher frequency is most suitable for the filter and sensor device. The DFT methodology is most suitable for the organic compound (LC).[23] The optimised geometry of the LC is shown as Figure 1.
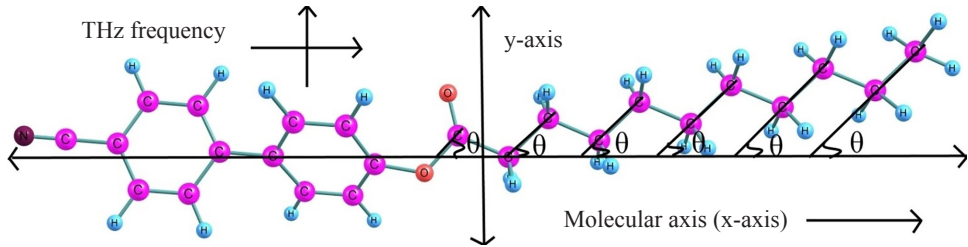
Figure 1: Optimised geometry of the nCOOCB LC molecule.

3.1   Birefringence

The birefringence of the homologous series is calculated with Equation 2, and shown in Figure 2. This LC has a re-entrant nematic phase, explaining the reason for negative behaviour. The cause of the re-entrant nematic phase is a more significant increase in the ordinary polarizability in comparison with the extraordinary polarizability. The geometry of the nCOOCB LC exhibits strong intermolecular interactions, which is the cause of the re-entrant nematic phase. The birefringence shows even-odd effect due to short range order intractions in the series of LCs. As the the alkyl chain increase, the viscosity of the series increases which shows the smectic phase of series and hence the series shows even-oddd effect due to possible short range interactions in the series. From the whole series, four LCs (2, 7–9) do not indicate any re-entrant phase because they are not predominant intermolecular forces in the series. The 4COOCB and 6COOCB LC are having strong intermolecular forces which cause the broad range re-entrant nematic phase. The maximum birefringence decreases continuously with an extension of alkyl chain length under the impact of an external electric field. Dubois and Zann report that the nematic to isotropic phase transition temperature does not express any even-odd effect; that is the reason in the present work, the homologous series also does not exhibit any even-odd effect.[24] The 9COOCB instant increases the birefringence due to the enhancement of molecular enthalpy.

Wilk et al. have reported the cyanobiphenyl LC family most suitable for the THz applications that is the reason for choosing this molecular series (present work).[25] Vieweg and Deninger have reported that the birefringence of 5CB LC under THz frequency exists between 0.10 and 0.12. Similarly, in the present work, the birefringence of 5COOCB is 0.13, which is near about the experimental evidence.[26] The birefringence is enhanced in 5COOCB LC because it has two extra oxygen atoms in comparison with 5CB LC.
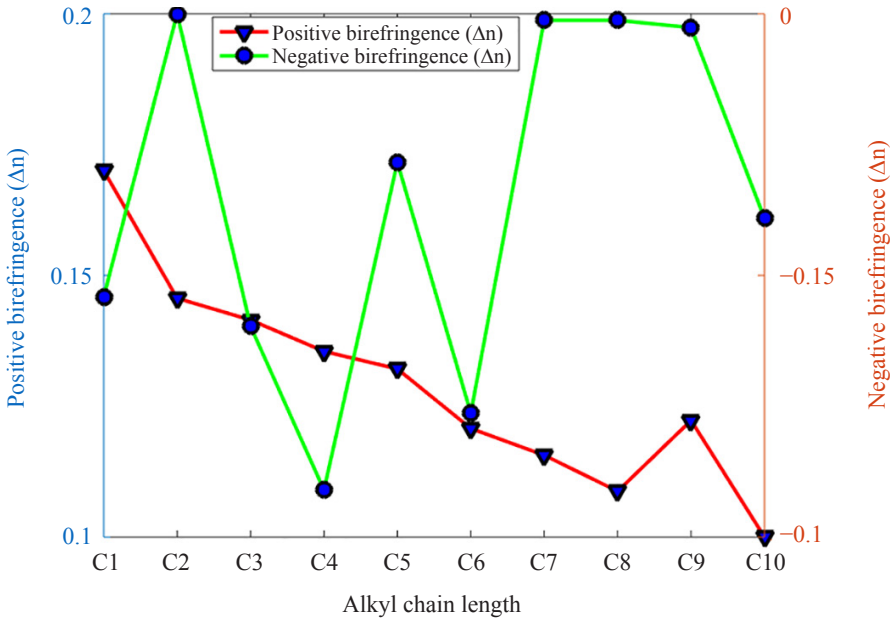
Figure 2:   Birefringence of the nCOOCB LC molecules calculated under the influence of an external electric field with the extension of alkyl chain length (the birefringence of LC has been measured by the DFT method B3LYP, and calculated using Equation 2 under the influence of an electric field).

3.2   Refractive Index

The refractive index has been calculated with the help of Equation 4 under the impact of an external electric field, as shown in Figure 3. The minimum (green line) and maximum (red line) refractive index nCOOCB > 5 remain constant for the value of 1.57. The refractive index decreases in 5COOCH because intermolecular forces break the symmetry. Vieweg and Deninger have reported that the refractive index of 5CB LC exists between 1.60 and 1.57; similarly, the refractive index of 5COOCB is 1.57, which has correlated with the experimental evidence.[26] Reuter et al. have reported the refractive index increases with an increase in the THz frequency range.[27] In the present work, the refractive index also increases with an expansion of THz frequency range. Li et al. have reported that the ordinary, and the extraordinary refractive index remains constant in the THz frequency region.[15] The 6COOCB and 10COOCB LC are more suitable for the THz frequency range because the refractive index remains constant at a higher frequency range. The minimum values of refractive index show even-odd effect due to considering higher order terms to calculate the refractive index.
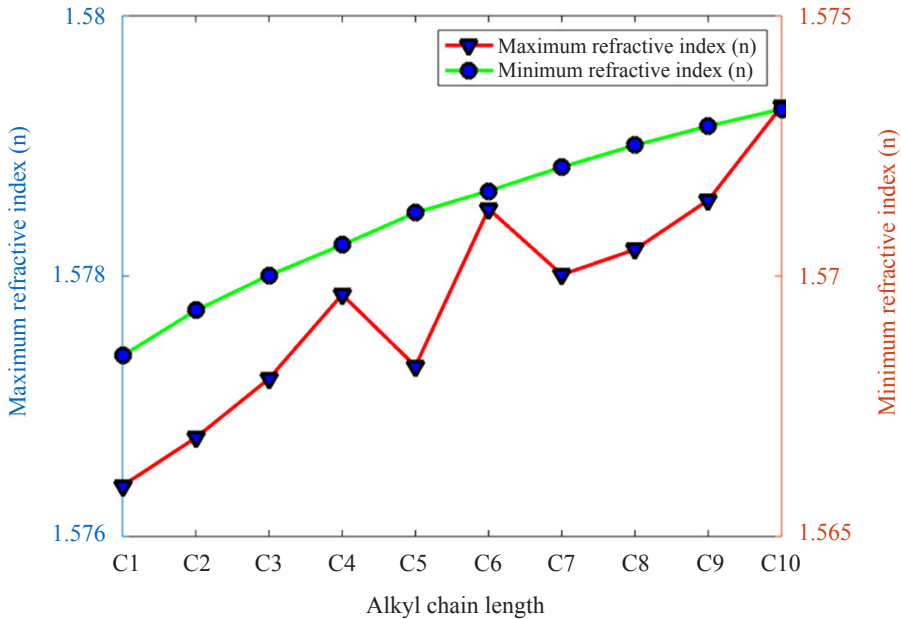
Figure 3:   Refractive index of the nCOOCB LC molecules calculated under the influence of an external electric field with the extension of alkyl chain length (the refractive index of LC has been measured by the DFT method B3LYP, and calculated using Equation 4 under the influence of an electric field).

3.3   Director Angle or Magic-angle

The minimum range of director angle decreases continually with an extension of alkyl chain length, as shown in Figure 4. The 1COOCB and 2COOCB mostly show crystalline behaviour because the nematic phase does not exhibit stability. The 6COOCB and 10COOCB have a maximum range of director angle, hence they are suitable for sensing or filtering applications in the THz frequency range. Wang et al. have reported that under the applied field, the director angle is reoriented due to an inherent behaviour of the nematic LCs.[28] The nCOOCB LCs do not have any homogeneous alignment under the applied high electric field due to its internal geometry with intermolecular forces. The even-odd effect in the director angle is also related with the shape and size of LCs in the series. As the size increases, the interractions also vary and hence the even-odd effect appears in the series. The certain odd members show some specific fluctuations while the even members show some other cases. Due to such variation, the director angle shows even-odd effect. The fluctuation of the director angle is more suitable for filtering, sensing, switching and imaging applications.
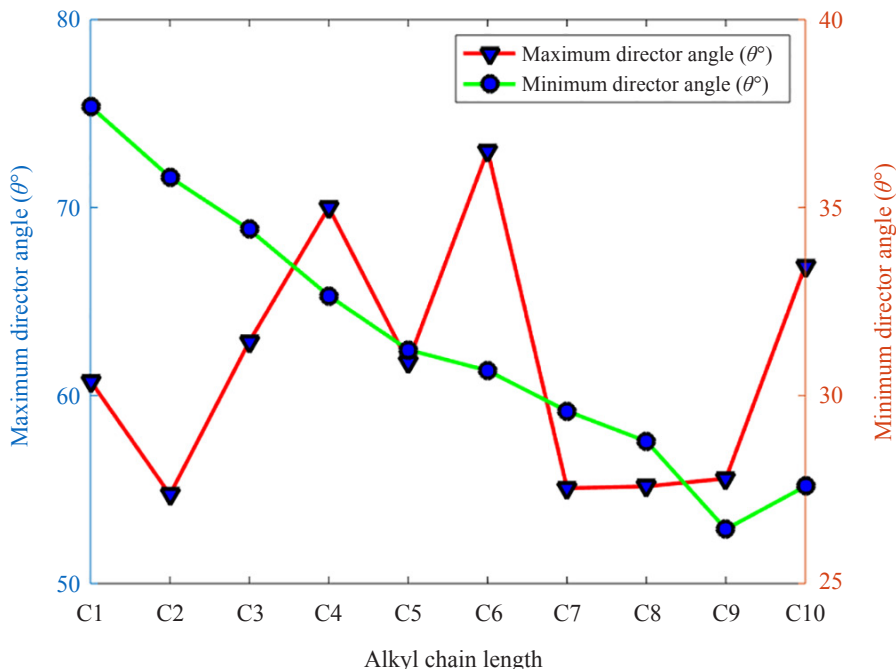
Figure 4:   Director angle or magic-angle of the nCOOCB LC molecules calculated under the influence of an external electric field with the extension of alkyl chain length (the director angle of LC was measured by the DFT method B3LYP, and calculated using Equation 3 under the influence of an electric field; the director angle does not indicate any even-odd effect).

3.4   Order Parameter

The order parameter was calculated with the help of Equation 1 under the influence of an external electric field, as shown in Figure 5. The positive order parameter increases with an extension of the alkyl chain length. The homologous series has a negative and positive order parameter due to the re-entrant nematic phase. From the whole series, only two LCs (2, 7) do not have a re-entrant nematic phase; however, they have a nematic phase. Vieweg et al. have reported that the order parameter of 6CB in the THz frequency range is 0.6.[29] Similarly, the present work also indicates that the positive order parameter of 6COOCB is 0.6.

The 6COOCB LCs are having a broad range of re-entrant nematic phase; however, the 6CB only has a nematic phase, and it does not express any re-entrant behaviour. Levelut and Druon have reported the 8COOCB LC having a re-entrant nematic phase.[11] The order parameter has a higher value for higher alkyl chains in the

series. The higher values are due to smectic phase occurring for higher members which have high viscosity in the series. The present work indicates the re-entrant nematic phase behaviour of LCs. The work also suggests that the 6COOCB is better for the THz applications in comparison with 8COOCB because 6COOCB has a broad range re-entrant nematic phase compared with 8COOCB.
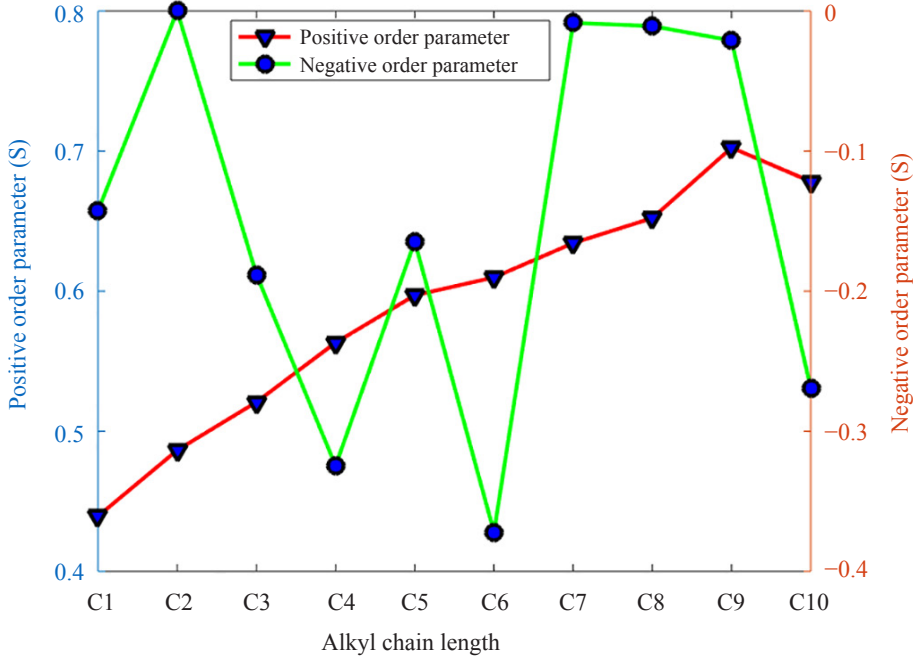

Figure 5: Order parameter or magic-angle of the nCOOCB LC molecules calculated under the influence of an external electric field with the extension of alkyl chain length (the order parameter of LC was measured by the DFT method B3LYP, and calculated using Equation 1 under the influence of an electric field; the even-odd effect is indicated with minor deviation).

3.5   Ionisation Potential and Electron Affinity

The ionisation potential and electron affinity continuously decrease with an extension of alkyl chain length, as shown in Figures 6 and 7. The homologous series of nCOOCB indicates that more stable LCs also exist in nature for the novel applications.
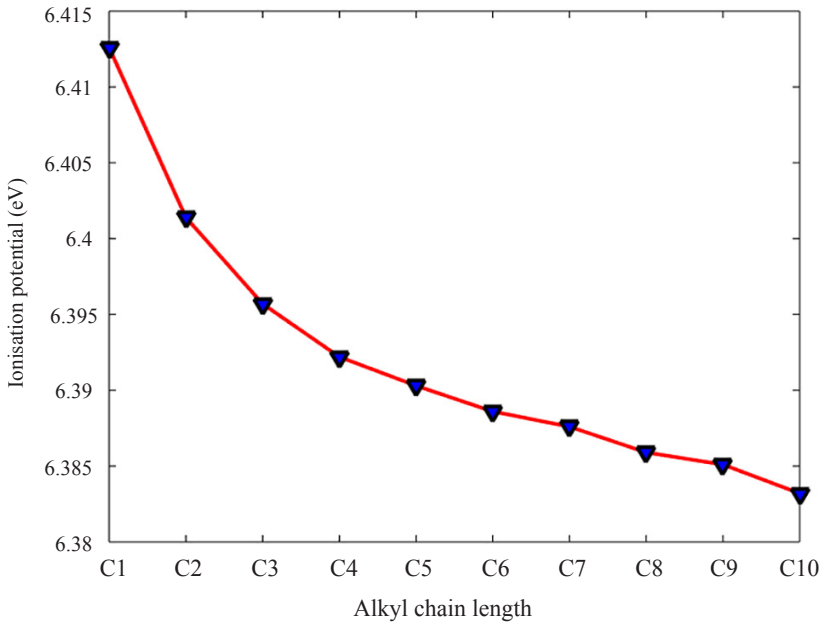
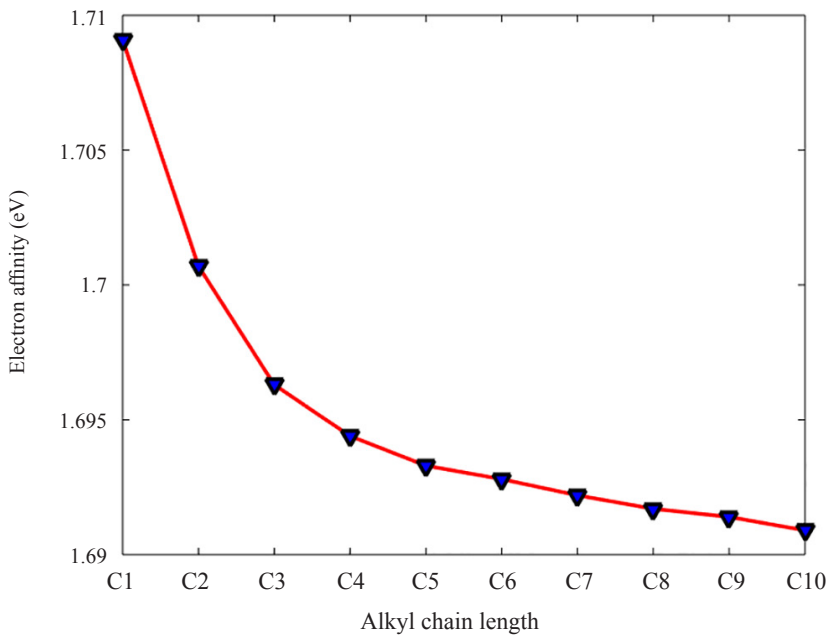Figure 6: Ionisation potential of the homologous series of nCOOCB LC.

Figure 7: Electron affinity of the homologous series of nCOOCB LC.

3.6   Homo-Lumo Energy Gap and Dipole Moment

The Homo-Lumo energy gap is continuously decreasing with an extension of alkyl chain length; however, dipole moment steadily decreases. The decreasing Homo-Lumo energy gap indicates that this homologous series is suitable for the semiconducting or conducting polymer applications. The Homo-Lumo energy gap and dipole moment express even-odd effect, as shown in Figures 8 and 9. The Homo-Lumo energy gap expresses the odd-even effect with minor deviation; however, the dipole moment expresses a perfectly even-odd effect. The dipole moment increases for the even carbon atom number of the alkyl chain. However, the Homo-Lumo energy gap increases for the odd carbon atom number. Shang et al. have reported the dipole moment, and energy bandgap are inversely proportional to each other.[30] In the present work, the dipole moment is inversely proportional to each other because it increases for the even members and the Homo-Lumo gap increases for the odd members.
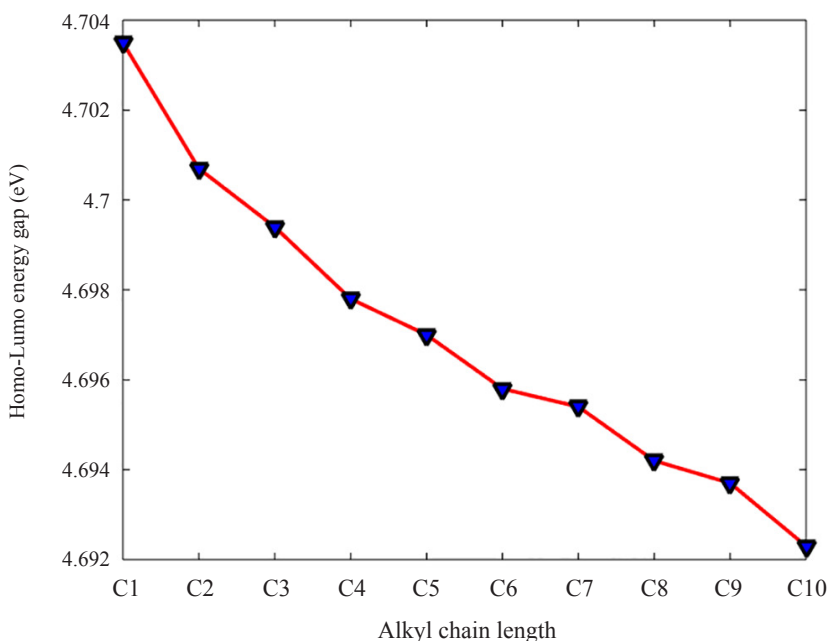

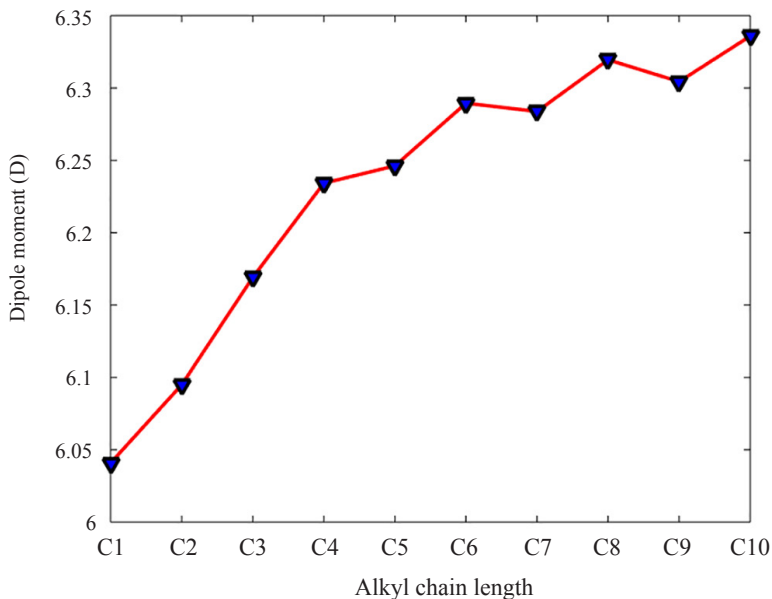Figure 8: Homo-Lumo energy gap for the homologous series nCOOCB.

Figure 9: Dipole moment of the homologous series nCOOCB.

4. CONCLUSION

In the present work, it has been found that the homologous series is most suitable for electro-optical device applications in THz frequency regions because all the optical parameters are affected under the THz frequency region. The series shows dispersions in the lower frequency region and the optical parameters of the series are also frequency dependent. As the frequency is applied on the LCs, the molecules show fluctuations in the orientation resulting molecular polarizablities and hyper-polarizabilities; the values of these polarizabilies are related to the amplitude of applied frequency, size and shape of the LC. For the large molecules, the large induced field occurs on the LCs having corresponding polarizibilities, order parameters, refractive index and so on. The obtained frequency parameters show even-odd effect depending on the range of frequencies. The homologous series has a re-entrant nematic phase, which is suitable in the THz frequency region for the sensing, filtering, imaging and switching applications. The 6COOCB and 10 COOCB LCs are best for the applications due to constant refractive index and a broad range of director angle. The physical parameters dipole moment, ionisation potential, electron affinity and Homo-Lumo energy bandgap indicate that the extended series of the present molecules also exists for the novel applications. The motivation of this work is to find out unknown molecules that are suitable for the THz frequency range.

5. ACKNOWLEDGEMENTS

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