Molecular spectroscopy and adverse optical properties of \(N-(p\text{-hexyloxy-benzylidene})-p\text{-toluidine}\) (HBT) liquid crystal molecule studied by DFT methodology

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Abstract

In present work, we report the \(N-(p\text{-hexyloxy-benzylidene})-p\text{-toluidine}\) (HBT) liquid crystal (LC) molecule having maximum absorbance due to the O–C stretching (carbon atom of benzene ring) during the intermolecular interaction. Under the expansion of an external electric field, the HBT LC having nematic to smectic phase stability with adverse (negative values) order parameter and birefringence. The refractive index expresses stability in the nematic, smectic, and isotropic phases. The director angle maintains stability for the nematic phase in the adverse order and smectic phase stable in positive order.

1. Introduction

The Liquid crystal (LC) phase represents a different state of matter characterized by the mobility and order of the molecule. 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 [1]. 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 [2]. Liquid crystal (LC) phases are formed by anisotropic molecule, having one molecular axis very different from the other two [3]. 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 [4]. The impact of the external electric field on liquid crystal can be studied by analyzing the polarizability of the molecule [5, 6]. In liquid crystals, the molecular polarizability and its anisotropy are important inherent molecular properties because the intermolecular interaction energies depend on them [7]. LC materials may consist of polar and non-polar molecules that depend upon the physical structure of LC [8]. The LC molecules can possess permanent dipole along the long molecular axis, which enhances the dielectric anisotropy of LC. The dipole moment parallels to the long molecular axis, then \(\Delta \varepsilon > 0\), and the molecules tend to orient along the electric field direction because LC posses more significant dielectric anisotropy along the molecular axis (x-axis). If the molecule carries fewer dipole moments long molecular axis, then \(\Delta \varepsilon < 0\) and fragment tend to orient perpendicular to the electric field direction because of the polarity of the molecule is negligible [9]. 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 that causes the director angle to fluctuate [10].

Luckhurst et al [11] reported the Schiff base compound increases the polarity of the molecule, 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 [12, 13]. The molecular polarizabilities and the anisotropy of liquid crystal molecules are considered as an 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 increases 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. [14–16] Rao et al [17] reported with an increment of the magnetic field, the order parameter increases. 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 $\alpha_0$ increases, and $\alpha_e$ decreases with an increases temperature. The HBT is more stable as a comparison with other molecules. The HBT is having $-0.6$ order parameter and OBT having $-0.5$ order parameter. The HBT LC is having strong intermolecular forces that are responsible for the alignment of molecules. The HBT LC 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 [18].

2. Computational methodology

HBT liquid crystal molecules are optimized by density-functional theory (DFT) method B3LYP [19, 20] by 6–31 G** [21] basis set using NWChem software package [22]. After the optimization of all the molecules, we have applied the electric field to the HBT liquid crystals along the molecular axis ($x$-axis) and perpendicular ($y$-axis) to it from 0.0000 (a.u) to 0.1500 (a.u) at the interval of 0.0020 (a.u). After the applied electric field, we have calculated the molecular polarizability of the HBT LC molecule. X-axis considered as extraordinary molecular polarizability ($\alpha_e$), and Y-axis consider as ordinary molecular polarizability ($\alpha_o$) then we have calculated the order parameter, birefringence, refractive index, and magic angle as per the formula is given below [23];

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

$$\beta = [(\beta_{xx} + \beta_{yy} + \beta_{zz})^2 + (\beta_{xy} + \beta_{yz})^2]^{1/2},$$

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

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

$$\Delta \bar{\alpha} = \alpha_e - \alpha_o,$$

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

Where $\bar{\alpha}$ is mean isotropic polarizability.

Order Parameter ($S$):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o},$$

Birefringence ($\Delta n$):

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

Where $R$ is the radius of the liquid crystal molecule.

Magic angle ($\theta$):

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

Refractive index ($n$):

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

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

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

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

where $N$ is the number of liquid crystal molecules.
3. Result and discussion

3.1. Order parameter
The order parameter calculated under the influence of an external electric field by the mathematical equation (1). Rao et al [17] reported with an increment of the magnetic field, the order parameter increases. The nematic to the smectic phase transition, the order parameter decreases in the present work; the order parameter decreases from nematic to smectic phase transition shown in figure 1. The HBT LC has an adverse order parameter; the present work also indicates an adverse order parameter at the electric field 0.0480 (a.u.). Sarn et al [15] reported the \( \alpha_0 \) increases and \( \alpha_e \) decreases with an increment of temperature in the present work also the \( \alpha_0 \) increases and \( \alpha_e \) decreases under the influence of an external electric field. Sarn et al reported the positive order parameter of HBT LC is 0.68 in the present work; the positive order parameter is 0.67. The theoretical prediction is very accurate with the experimental evidence. The maximum order parameter of HBT LC is 0.6788, and the minimum is \(-0.3865\).

3.2. Birefringence
The birefringence calculated under the influence of an external electric field by the mathematical equation (2). Sarn et al [15] reported the birefringence decreases with increases temperature of the HBT LC molecule. The birefringence in the nematic phase exists between 0.2 to 0.1; the present work also indicates the birefringence of the nematic phase is 0.1119, shown in figure 2. The \( \alpha_0 \) increases and \( \alpha_e \) decrease with an extension of temperature; the present work indicates adverse or negative birefringence of HBT LC molecule. The HBT nematic phase is stable at the electric 0.0220 (a.u.) and 0.0240 (a.u.) and the smectic phase stable at the electric field 0.0580 (a.u.). The maximum birefringence of the HBT LC molecule is 0.1119, and the minimum is \(-0.0814\).

3.3. Refractive index
The refractive index calculated under the influence of an external electric field by the mathematical equation (4). Sarn et al [15] reported the refractive index of HBT LC is 1.58; the present work also indicates the refractive index of HBT LC is 1.58 as shown in figure 3.

3.4. Director angle or magic angle
The director angle or magic-angle calculated under the influence of an external electric field by the mathematical equation (3). The director angle decreases in the nematic phase and increases in the smectic phase with an expansion of the external electric field shown in figure 4. The magic angle of all the liquid crystals is 54.7; the present work also indicates the magic angle of HBT LC is 54.73. The maximum range of the director angle is 74.03°, and the minimum range is 27.56°. The director angle stable for the nematic and smectic phase.

![Figure 1. Calculated order parameter under the influence of an external electric field by density functional theory.](image-url)
3.5. IR spectroscopy of HBT LC

The C–O stretching expresses the maximum absorbance because oxygen atom transfers the charge to the benzene ring during the intermolecular interaction shown in figures 5 and 6, also given in table 1. Zhang et al reported [24] oxygen atom transfer the proton to the nitrogen atom during an intermolecular interaction, which is responsible for the maximum transmittance of the molecule.

The HBT liquid crystal molecule suitable for sensing and filtering applications because it expresses a broad range of frequencies given in table 1 and shown in figure 5. The whole molecule reveals Out of plane wagging of Hydrogen atom about the frequency of 845 cm\(^{-1}\). The whole molecule reveals O–C stretching (carbon atom of alkyl chain) about the frequency of 976 cm\(^{-1}\). The entire molecule reveals In-plane scissoring of C–H about the frequency of 1178 cm\(^{-1}\). The molecule as the whole shows O–C stretching (carbon atom of benzene ring) about the frequency of 1232 cm\(^{-1}\). The entire molecule reveals C–C stretching about the frequency of 1342 cm\(^{-1}\). The whole molecule reveals Out of plane wagging of C–H about the frequency of 1426 cm\(^{-1}\). The entire molecule represents In-plane scissoring of C–H about the frequency of 1539 cm\(^{-1}\). The entire molecule expresses C–N stretching and C–H In-plane scissoring about the frequency of 1631 cm\(^{-1}\). The molecule as the whole reveals the Symmetric stretching of C–H atom about the frequency of 3030 cm\(^{-1}\). The whole molecule reveals the Asymmetric stretching of C–H atom about the frequency range from 3092 cm\(^{-1}\) to 3191 cm\(^{-1}\).
Figure 4. Calculated director angle or magic-angle under the influence of an external electric field by density functional theory.

Figure 5. Calculated IR spectrum by density functional theory.

Figure 6. Charge distribution of HBT LC molecule (oxygen atom maximum electronegative and attached carbon atom maximum positive).
4. Conclusion

In this work, it has been found the HBT liquid crystal (LC) molecule has maximum absorbance during the intermolecular interaction because of charge transfer by an oxygen atom to the benzene ring. The order parameter and birefringence have adverse orders with an expansion of the external electric field. The HBT LC molecule is suitable for filtering and sensing applications because HBT LC is having a broad range of frequencies. With the help of this methodology, we can predict the optical and sensing properties of an unknown organic molecule. B. bahadur [25] reported HBT LC is diamagnetic, so it is suitable for the diamagnetic material applications. Molecular polarizability is the most crucial parameter in this manuscript, 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 present work is modified mathematical equations as a comparison with previously reported results. This theoretical model predicts 97 to 100% accuracy with the experimental evidence.

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The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Table 1. Vibrational mode of HBT LC calculated by DFT methodology.

| Frequency (cm$^{-1}$) | Modes of vibration |
|----------------------|--------------------|
| 565                  | C–H wagging in benzene |
| 845                  | Out of plane wagging of the hydrogen atom |
| 976                  | O–C stretching (carbon atom of alky chain) |
| 1178                 | In-plane scissoring of C–H atom |
| 1232                 | O–C stretching (carbon atom of benzene ring) |
| 1342                 | C–C stretching in benzene |
| 1426                 | C–H Out of plane wagging |
| 1539                 | C–H In-plane scissoring in benzene |
| 1631                 | C≡N Stretching and In-plane scissoring of C–H atom |
| 3030                 | C–H Symmetric stretching in the alky chain |
| 3092                 | C–H Asymmetric stretching in the alky chain |
| 3191                 | C–H Asymmetric stretching in benzene |
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