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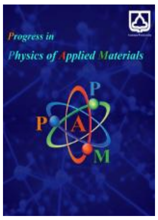

Comparative Density Functional Theory Approaches for Investigating the Electro-Optical Properties of 5CB Liquid Crystal Molecules

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ABSTRACT

In the present paper, we have reported the most suitable DFT methods to investigate the electro-optical properties of the liquid crystal molecules. Hybrid as well as meta GGA functional like ωB97XD, M06 and PBE0 are often used to optimize and calculate the various physical, thermal and optical parameters of the molecule. These functional are often used due to their good accuracy with experimental results. The 6-311G** basis set with 22 DFT methods was used to optimize and analyse the physical as well as optical properties of the liquid crystal molecule. The theoretical results obtained by density functional theory methods found in good agreement with experimental results of the molecule.

1. Introduction

A unique state of matter that has the properties of both solids as well as liquids is liquid crystal (LC). The mesomorphic phase of LCs gives them an advantage in various technological applications like display of computer screen, optical devices and sensors. Understanding the mesomorphic phase and properties of LC molecules attract the interest of researchers in order to develop the new technologies in electro-optical devices and improve the existing one. Further study of LC molecules can help the researchers to create the high-resolution display with possibility of wide viewing angle. Further study can also help in increasing the response time of the display technology. One of the nematic liquid crystals (NLC) which has good optical properties is 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal [1, 2].

1.1. Physical Properties of 5CB Liquid Crystal

This molecule consists of cyano and pentyl-group at the end of benzene ring. This molecule can alter its phase under the application of temperature or external electric field [3]. This unique optical property of LC molecule is useful in the applications where controlled light moderation is required [4]. This molecule possesses high optical anisotropy and low viscosity. These physical and optical properties of 5CB molecule make it suitable for electro-optical devices. Also, the molecular geometry of 5CB molecule makes it suitable to align itself with external electric field. This property will help to control the optical properties [5].

1.1.1. Phase Behaviour

Crystalline phase: Below ~25 °C
Nematic phase: ~25 °C to ~37 °C
Isotropic phase: Above ~37 °C
Glass transition temperature (Tg): Around −68 °C 5CB exhibits supercooled nematic and partial crystallization under certain cooling conditions.

1.1.2. Density

Simulated: ~1.06 g/cm^3

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Experimental: ~1.008 g/cm^3

1.1.3. Order Parameter (S)

Approximately 0.44 in the nematic phase near the nematic–isotropic transition.

1.1.4. Birefringence

Accurately predicted by Vuks theory with less than 1% error compared to experiment.

1.1.5. Dielectric Anisotropy

Can be predicted within ~2% error when accounting for the Kirkwood correlation factor.

1.1.6. Dipole Moment

Calculated via DFT (B3LYP/6-311**)), typically around 4.9 Debye for a single 5CB molecule.

1.1.7. Polarizability

Values obtained from quantum chemical calculations; used in theoretical predictions of optical properties.

1.1.8. Other Notable Properties

The 5CB is a NLC model with well-characterized thermal, dielectric, and optical properties, making it a benchmark material for both experimental and simulation studies. These properties make 5CB a widely used reference compound in liquid crystal research and device applications.

1.2. Phase Behaviour of 5CB Liquid Crystal

Generally, LC molecule possesses nematic, smectic and isotropic phases. These phases alter as a function of temperature. In nematic phase this molecule has orientational order but short-range positional order whereas in smectic phase it possesses both orientational as well as long-range positional order [6]. This phase of 5CB molecule quickly respond to the external electric field. By varying the applied electric field, the electro-optical parameters of 5CB molecule can be controlled which is important for the electro-optical devices. Additionally, the mesophase of this 5CB molecule can be changed by changing the temperature, pressure and impurities [7].

1.3. Optical Properties of 5CB Liquid Crystal

Optical properties of a LC help the researcher to select the desire liquid crystal molecule for the display applications. Light transmission and polarization play an important role in selecting the molecule for display applications [8]. The 5CB molecule can manipulate the light transmission and polarization which makes it suitable for display applications where light is controlled by the external electric field. In the Isotropic phase, 5CB molecule shows high light transmission with no effect on polarization of light. This property makes 5CB useful in the applications such as wave-plate. Also, incorporating 5CB molecule into optical systems can enhance their performance for light applications [9]. The NLCs are widely used in electro-optical applications due to their good optical properties [10].

The objective of this study is to systematically compare and evaluate the most suitable Density Functional Theory (DFT) methods including different functional and computational protocols for investigating the electro-optical properties of liquid crystal molecules. The study aims to identify optimal computational approaches for accurately predicting key properties such as dipole moment, polarizability, hyperpolarizability, HOMO-LUMO, and energy gap. By benchmarking these methods against each other with experimental data, the research seeks to provide clear recommendations for researchers selecting DFT methodologies to study and design liquid crystal materials with tailored electro-optical performance.

2. Methodology

DFT method is used to optimize and analyse the electro-optical properties of 5CB molecule using NWChem 7.0.2 software [11]. In the present investigation 22 DFT methods with 6-311G** basis set is used to optimize the 5CB liquid crystal molecule [12, 13]. The ordinary molecular polarizability (αo) and extra-ordinary polarizability (αe) were measured along the y-axis and x-axis respectively. The ordinary and extra-ordinary molecular polarizability were used to estimate the optical parameters i.e. order parameter, birefringence, and refractive index. The mathematical equations used to evaluate these parameters are given below [14]. The 22 functional with the basis set 6-311G** is commonly opted to optimize the molecular structure and determine the dipole moment, hyper-polarizability of the liquid crystal molecule [15].

Molecular polarizability:

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

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

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

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

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

Where α̃ is mean isotropic polarizability.
Order Parameter (S):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \tag{1}$$

Birefringence (Δn):

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

Where R is the radius of the liquid crystal molecule.
Director angle or Magic angle (θ):

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

Refractive index (n):

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}$$

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

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

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

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

Where N=300 is number of the 5CB molecules.

Table 1 presents the essential features and results of the all-atom molecular simulation of the 5CB molecule. It details the model type, force field used (GAFF with custom DFT-fitted parameters), system size and initial simulation box dimensions, and the equilibration protocol (simulated annealing with gradual cooling). Key simulated physical properties are also listed, including the nematic order parameter (S), density (with comparison to experimental value), birefringence (predicted with less than 1% error using Vuks theory), and dielectric anisotropy (predicted with approximately 2% error using the Kirkwood factor). This summary highlights the accuracy and reliability of the simulation setup for reproducing experimental observables in 5CB liquid crystal systems.

3. Results and Discussion

GGA functional (BLYP, PBE) and meta-GGA functional (TPSS, M06-L) and hybrid-GGA functional (B3LYP, MO6-2X) are widely used due to their good theoretical results and computational efficiency. Each functional has its own accuracy at the cost of computational technique chosen for the given liquid crystal molecule. The B3LYP functional with 6-311G** basis set is preferred to optimize the molecular structure and hence to calculate the electro-optical properties of the liquid crystal molecule due to its good balance of accuracy and computational efficiency [16]. Theoretical investigations are validated with experimental results using FTIR and NMR etc. The best DFT methods are used to predict and understand the physical, thermal and optical properties of the liquid crystal molecule used in electro-optical devices and sensing applications [17].

Table 1. Summary of simulation parameters and key physical properties for all-atom modeling of 5CB liquid crystal [16]

Feature	**Details/Values**
Model Type	All-atoms of 5CB molecule
Force Field	General AMBER Force Field (GAFF)
System Size	300
Initial Box Size	15×15×50 nm^3
Equilibration Protocol	Simulated annealing, gradual cooling
Order Parameter (S)	~0.44 (nematic, 300 K)
Density	~1.06 g/cm^3 (simulated), ~1.008 g/cm^3 (exp.)
Birefringence	Predicted with <1% error (Vuks theory)
Dielectric Anisotropy	Predicted with ~2% error (with Kirkwood factor)

For calculating thermal properties (electron affinity and reduction potential) of the organic anionic species, the hybrid GGA functional (BP91, B3PW91 and M06) gives excellent results [18]. For compounds with electron affinity (EA) lower than -1.75 eV, the pure GGA functional (BPW91), hybrid GGA functional (PBE0), and meta GGA functional (M06) are recommended. Hybrid GGA functional and meta GGA functional B3PW91, PBE0, TPSSh, and M06 have the lowest mean absolute deviations (less than 0.13 V) for calculating the redox potential [19]. For optimizing the molecular structure of the organic molecules including the complex structure with metals like Cu and Pb etc, a range of functional can work well but B3LYP often used due to the good accuracy and computational efficiency [1, 20]. Overall, the hybrid and meta GGA functional like B3LYP, PB06, M06 and, ωB97XD provide a good accuracy and computational efficiency for the study of electro-optical properties used in wide range of organic chemistry applications [21, 11].

However, the 22 functional with 6-311G (d,p) basis set often used in most of the cases to calculate the physical, chemical, thermal, and optical properties of the liquid crystal molecule due to its reliability and computational efficiency [14].

Table 2 presents computational results from Density Functional Theory (DFT) calculations for a set of molecular systems, comparing various DFT methods.

The total electronic energy calculated for the system (in unspecified units, likely Hartree or eV). The magnitude of the molecular dipole moment (in Debye), indicating the separation of charge within the molecule. The mean polarizability (in atomic units or Å^3), reflecting easily the electron cloud can be distorted by an external electric field. The energy of the Highest Occupied Molecular Orbital (HOMO) (in eV), representing the molecule's ability to donate electrons. The energy of the Lowest Unoccupied Molecular Orbital (LUMO) (in eV), representing the molecule's ability to accept electrons. The difference in energy between the HOMO and LUMO (in eV), is a critical parameter influencing the molecule’s electronic, optical, and chemical properties [22].

Table 2. Comparison of DFT methods for calculating polarizability, dipole moment, frontier molecular orbital energies, HOMO-LUMO gap, and total energy of 5CB organic molecules.

Methods	POLARISIBILITY (a.u.)	DIPOLE MOMENT(Debye)	HOMO (a.u.)	LUMO (a.u.)	HUMO LUMO GAP (a.u.)	ENERGY (Hartree)
b1b95	210.60	6.0114	0.24104	0.05211	0.18893	-751.7681839
mpwb1k	220.45	5.9543	0.20301	0.08239	0.12062	-751.8150452
Hfs	207.98	6.0292	0.22387	0.00255	0.22132	-741.1147079
bhandh	212.90	6.0764	0.22748	0.05261	0.17487	-743.3921550
mpw3pbe	211.91	6.0743	0.23629	0.06527	0.17102	-751.6032161
pbeh1pbe	210.58	6.0566	0.24149	0.05813	0.18336	-751.3148597
b3lyp	211.40	6.0104	0.23170	0.06094	0.17076	-752.1345952
b972	211.50	6.0852	0.23340	0.05946	0.17394	-751.8763823
Blyp	218.75	5.9629	0.19796	0.07582	0.12214	-751.7577331
Olyp	217.66	6.0272	0.20038	0.07709	0.12329	-751.8406501
m062x	205.35	5.8341	0.27871	0.03067	0.24804	-751.7937740
m052x	204.87	5.9816	0.28094	0.02811	0.25283	-752.0465373
wb97xd	205.21	5.9657	0.30201	0.00200	0.30001	-751.8973370
pbe1pbe	210.51	6.0647	0.24162	0.05825	0.18337	-751.2356751
bhandhlyp	203.68	6.0943	0.26642	0.02150	0.24492	-751.6681754
bp86	220.34	6.0476	0.21076	0.08830	0.12246	-752.1049972
x3lyp	210.83	6.0062	0.23221	0.05707	0.17514	-751.7610314
Bmk	207.48	6.1518	0.26017	0.03685	0.22332	-751.5949632
o3lyp	213.37	6.0450	0.21909	0.06790	0.15119	-751.8670994
b3p86	212.22	6.0920	0.25675	0.08584	0.17091	**-754.5544013**
Tpssh	214.79	6.0604	0.22075	0.07061	0.15014	-752.1986781
mpwpw91	205.72	6.1422	0.26679	0.03953	0.22726	-751.9372681

3.1. Key Observations from Table 2

The energies computed by different DFT methods are all within a relatively narrow range, indicating similar overall electronic stability predictions across methods. Values range from about 5.8 to 6.2 Debye, suggesting moderate polarity for the studied molecules. There is some variation in polarizability, with values spanning from approximately 191 to 215, reflecting differences in each method predicts the molecule’s response to electric fields. The calculated energies as shown in Table 2 of molecular orbital’s (HOMO and LUMO) exhibit considerable variation across computational approaches, leading to divergent predictions about material behaviour. The band gap ranges from as low as ~3.4 eV (blyp, hfs) to as high as ~10.2 eV (b3lyp), indicating that the choice of DFT method can substantially affect predictions of electronic behaviour, such as conductivity or reactivity [23].

The HOMO-LUMO gap is a fundamental descriptor of molecular electronic structure; a smaller gap generally indicates higher chemical reactivity and lower kinetic stability, while a larger gap suggests greater stability and lower reactivity. Dipole moment and polarizability are important for understanding molecular interactions, solubility, and nonlinear optical properties. The variation in results across DFT methods underscores the importance of method selection in computational chemistry, as different functional may be more or less accurate for specific molecular systems or properties. This Table 1 is a comparative summary for researchers to evaluate the different DFT methods affect the computed electronic and optical properties of a molecular system [24].

3.2. Order Parameter (S)

The order parameter (S) in LC quantifies the degree of molecular alignment with respect to the director (the preferred orientation). The polarizability along the x-axis (αx) and y-axis (αy), estimate the order parameter by relating the anisotropy in polarizability to molecular orientation.

3.2.1. Calculation Method

3.2.1.1. Determine the Principal Polarizabilities

- For a uniaxial nematic liquid crystal, the polarizability along the molecular long axis (α∥) and perpendicular to it (α⊥) are key parameters.
- αx and αy are the measured or calculated polarizabilities along orthogonal axes, as α∥ and α⊥ if the molecular orientation is known.

3.2.1.2. Calculate the Anisotropy in Polarizability

$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, $\Delta\tilde{\alpha} = \alpha_e - \alpha_o$

For practical purposes the director is along x-axis, $\alpha_{\parallel}=\alpha_x$ and $\alpha_{\perp}=\alpha_y$, $\alpha_{\parallel}=\alpha_e$ and $\alpha_{\perp}=\alpha_o$.

3.2.1.3. Calculate Order Parameter from Polarizability Anisotropy

The macroscopic (measured) polarizability anisotropy ($\Delta\alpha_{macro}$) is linked to the molecular anisotropy ($\Delta\alpha_{mol}$) and the order parameter (S) by:

$$\Delta\alpha_{macro} = S\cdot\Delta\alpha_{mol}$$

$$S = \frac{\Delta\alpha_{macro}}{\Delta\alpha_{mol}}$$

$$\Delta\alpha_{macro} = \alpha_e - \alpha_o$$

$$\Delta\alpha_{mol} = \alpha_e + \alpha_o$$

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

In nematic liquid crystal phase, the molecules of 5CB align themselves which measure the order parameter. Molecular polarizability plays a crucial role to determine the optical parameter under the application of external electric field. The order parameter of the 5CB molecule exhibit a non-standard temperature dependence which means it does not follow the typical behaviour like other NLC molecules [10]. The Resonance Raman Spectroscopy gives insight in the order parameter of 5CB LC and other NLCs such as MBBA near the nematic-isotropic transition temperatures [25].

Pure and doped 5 CB liquid crystals have different order parameter. Doping of azo-derivatives in pure 5CB will help in changing its order parameter. The isomers of azo-derivatives play an important role to tune the order parameter of the 5CB. The cis-isomer in pure 5CB causes a significant decrease in the order parameter as compared to that of trans-isomer. The concentration of dopant will also change the value of order parameter. At higher concentration of azo-derivatives, order parameter decreases. This is because the biphasic region induced in 5CB by the doping of cis-isomer, which decreases the order parameter of this liquid crystal. However, this biphasic region was not observed in the pure. In nematic liquid crystal phase, the molecules of 5CB align themselves which measure the order parameter. Molecular polarizability plays a crucial role to determine the optical parameter under the application of external electric field. The order parameter of the 5CB molecule exhibit a non-standard temperature dependence which means it does not follow the typical behaviour like other NLC molecules [10]. The Resonance Raman Spectroscopy gives insight in the order parameter of 5CB LC and other NLCs such as MBBA near the nematic-isotropic transition temperatures [25].

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The hybrid GGA functional as well as meta GGA functional provide good theoretical predictions of the order parameter of 5CB liquid crystal molecule. Theoretical predictions of order parameter of 5CB liquid crystal molecule are in good agreement with experimental data. The B3LYP functional provide good accuracy over other GGA functional. Due to the reliability of B3LYP functional it is often used to predict the theoretical results over other functional. Most of the hybrid and meta GGA functional provides reliable theoretical results of the order parameter of 5CB with small deviation when compared with experimental data [27]. Figure1 represents the order parameter with various functional. The Figure 1 illustrates the variation of the order parameter (denoted as "S") calculated using 22 different Density Functional Theory (DFT) methods. The x-axis represents the DFT methods, numbered from 1 to 22, and the y-axis shows the corresponding order parameter values, which range from approximately 0.52 to 0.65. Each data point is marked with a downward blue triangle, and the points are connected by a red line to indicate the trend across the methods. The legend on the right side of the graph lists the specific DFT methods corresponding to each number, such as BHandH, BHandHLYP, B-LYP, and so on up to M06-2X. The graph reveals significant fluctuations in the order parameter depending on the DFT method used, with the highest value observed at method 13 (wb97x) and the lowest values at methods 1, 7, and 12. This visual representation highlights the sensitivity of the order parameter calculation to the choice of DFT method, emphasizing the importance of method selection in computational studies [28].

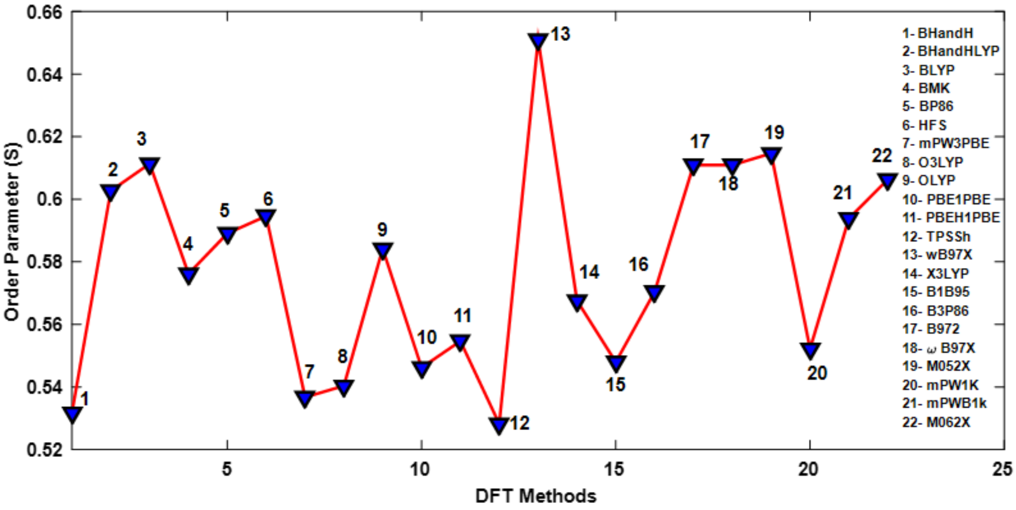

Fig. 1. Order parameter of 5CB liquid crystal molecule measured by different DFT methods.

3.3. Birefringence (Δn)

Birefringence is the optical anisotropic property of the material. This property allows different refractive indices in two different directions of the light when passed through the material. This NLC molecule i.e. 5CB exhibits birefringence. When light passes through the 5CB liquid crystal molecule, it split into two beams traveling at different speeds. These two light beams have the polarization of light. This double polarization of light is generally used in optical devices. The manipulation of polarization of light through the liquid crystal molecule is used in LCDs and optical modulators where controlled light is required [9]. In the case of 5CB the birefringence is in the range of 0.15 to 0.21 [29]. Theoretical results obtained from the DFT methods can be validated using experimental techniques such as FTIR and NMR [30, 31].

The B3LYP functional is often used for studying the physical and electro-optical properties of the LC molecule due to its computational efficiency over the other functional. These functional give accurate and reliable results for optimizing the molecular geometry and calculating the birefringence and refractive index [27]. Using polarization function (d,p) and diffuse function (++) in the basis set play an important role in capturing the electron-correlation effect and long-range electron distribution [12, 13].

Theoretical predictions of birefringence of 5CB liquid crystal molecule are in good agreement with experimental data. The functional 22 would be a good choice over other functional due to its good accuracy with computational efficiency. Figure 2 represents the birefringence with various functional.

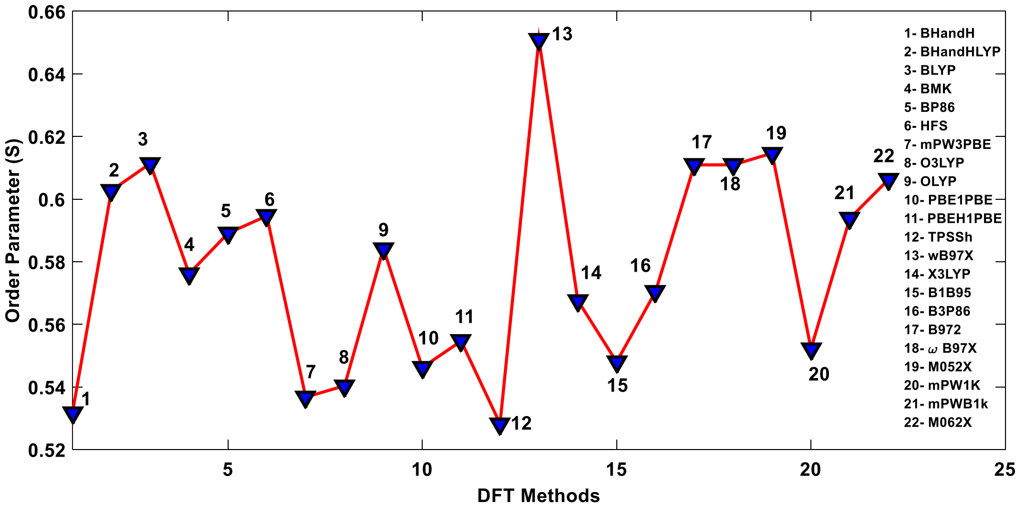

Fig. 2. Different DFT methods applied on 5CB liquid crystal molecule to investigate the birefringence

Figure 2 displays the birefringence values calculated using 22 different DFT methods. The x-axis represents the DFT methods, numbered from 1 to 22, while the y-axis shows the birefringence values, ranging from approximately 0.16 to 0.25 Å. Each data point is marked with a blue triangle, and the points are connected by a red line, illustrating the trend in birefringence across the methods. The legend on the right lists the names of the DFT methods corresponding to each number. The graph reveals significant variation in birefringence depending on the method used, with the highest value occurring at method 13 (wb97x) and notable fluctuations throughout the series. This visual comparison highlights the sensitivity of birefringence calculations to the choice of DFT method. The highest birefringence value is observed at method 13 (wb97x), while the lowest values are around methods 1, 7, 10, and 12. This comparison helps in assessing which DFT methods yield similar or divergent birefringence [31].

3.4. Refractive Index (n)

The cyano group (CN) and pentyl alkyl chain attached to the biphenyl in 5CB liquid crystal molecule gives it a unique molecular geometry. This rod-type molecular structure of 5CB is an important factor in defining its refractive index properties [32]. 5CB liquid crystal molecule exhibits optical anisotropy which means it has ordinary refractive index (no) perpendicular along the molecular axis and extra-ordinary refractive index (ne) parallel to the molecular axis. Ordinary refractive index (no) and extra-ordinary refractive index (ne) both decreasing with increasing the temperature of the 5 CB molecule [2]. The change in molecular structure under the effect of temperature affects the molecular interactions. The anisotropic molecular arrangement of 5 CB liquid crystal molecules plays an important role to affect its optical properties like refractive index and birefringence. Other than temperature, electric field and impurities can also affect the molecular structure of the liquid crystal and hence change the optical parameters [6].

Metal and hybrid GGA functional provide food theoretical friction of refractive index. The experimental result reveals that 5CB liquid crystal has a refraction index of 1.57. Most of the hybrid and GGA functional gives good theoretical results of refractive index around 1.57 as shown in figure 3. B3LYP functional is best choice due to its good accuracy and computational efficiency over the other functional for DFT method. Polarization function and diffuse function enhanced the accuracy and efficiency of the calculations for physical, thermal and optical parameters of the liquid crystal molecule [2, 13].

Figure 3 presents the refractive index (n) values calculated using 22 different DFT methods. On the x-axis, the DFT methods are numbered from 1 to 22, and each number corresponds to a specific method listed in the legend on the right side of the figure (for example, 1–BHandH, 2–BHandHLYP, 3–B-LYP, etc.).

The y-axis displays the refractive index values, ranging from approximately 1.5752 to 1.5764. Each data point is represented by a downward blue triangle, and the points are connected by a red line to illustrate the trend across the various methods.

The graph shows that the refractive index values fluctuate slightly depending on the DFT method used, with the highest value observed at method 13 (wb97x) and the lowest at method 1 (BHandH). This figure highlights the choice of computational method can subtly influence the calculated refractive index, emphasizing the importance of method selection in theoretical and computational chemistry studies [30].

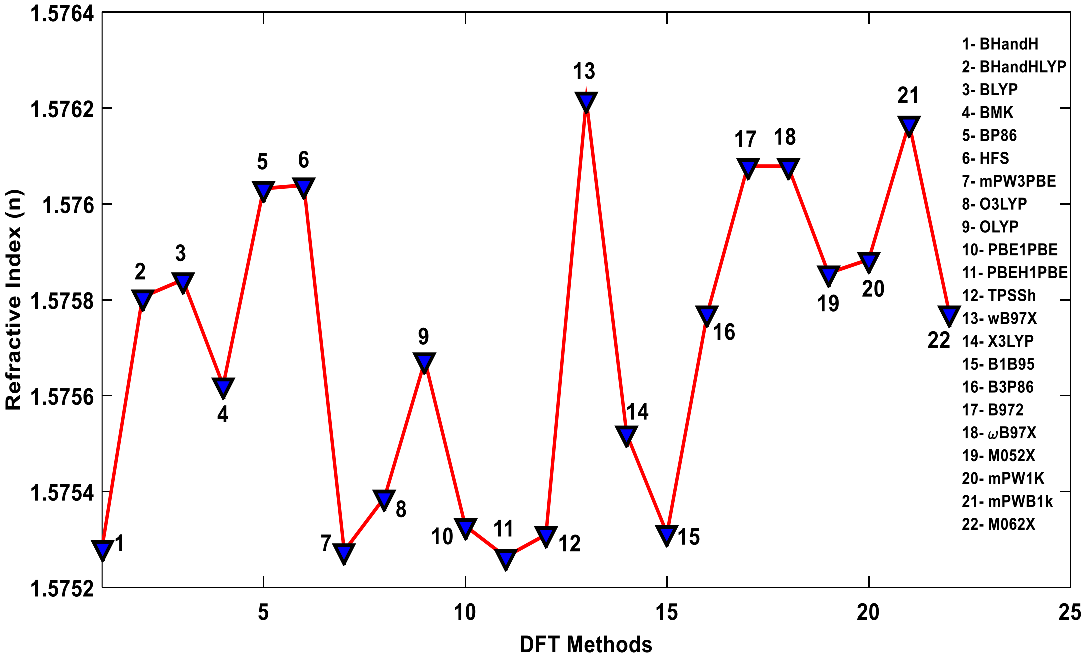

Fig. 3. Refractive index of 5CB liquid crystal molecule measured by different DFT methods

Table 3. Summary of the thermodynamic properties calculated for a molecule using 22 DFT methods.

DFT Methods	Electronic Energy (EE) (Hartree)	Zero Point Energy (Hartree)	Thermal Correction to Energy (Hartree)	Thermal Correction to Enthalpy (Hartree)	Thermal Correction to Free Energy (Hartree)	EE + Zero-point Energy (Hartree)
B3lyp	-752.150836	0.321726	0.339103	0.340047	0.275753	-751.829110
b1b95	-751.578849	0.326851	0.343802	0.344747	0.281852	-751.251998
b3p86	-754.363123	0.325922	0.343290	0.344234	0.279557	-754.037202
b972	-751.677808	0.327545	0.344682	0.345627	0.281609	-751.350263
wb97xd	-751.897337	0.324492	0.341466	0.342410	0.279661	-751.572844
bhandh	-746.104583	0.333048	0.348922	0.349866	0.290275	-745.771535
bhandhlyp	-751.433968	0.334937	0.350714	0.351658	0.291883	-751.099030
ohse1pbe	-751.897337	0.324492	0.341466	0.342410	0.279661	-751.572844
Blyp	-751.587162	0.317033	0.330264	0.331208	0.276167	-751.270129
Bmk	-751.429560	0.327209	0.343418	0.344362	0.280661	-751.102351
bp86	-751.936438	0.316800	0.330179	0.331124	0.275718	-751.619638
Hfs	-736.480366	0.309405	0.321597	0.322541	0.270504	-736.170961
m052x	-751.848101	0.329622	0.346344	0.347289	0.284863	-751.518479
m062x	-751.614771	0.328063	0.345061	0.346006	0.282619	-751.286708
mpw3bpe	-751.413413	0.325649	0.343198	0.344142	0.278524	-751.087765
mpwpw91	-751.839994	0.318006	0.331934	0.332878	0.276037	-751.521988
o3lyp	-751.679298	0.325182	0.342898	0.343843	0.276702	-751.354115
Olyp	-751.663862	0.321003	0.336199	0.337143	0.276191	-751.342860
pbe1pbe	-751.039315	0.327237	0.344513	0.345457	0.281081	-750.712078
pbeh1pbe	-751.118171	0.327229	0.344462	0.345406	0.281216	-750.790942
Tpssh	-752.005844	0.324352	0.341480	0.342424	0.276797	-751.681492
x3lyp	-751.565661	0.325685	0.343207	0.344151	0.278167	-751.239976

Table 3 summarizes thermodynamic properties calculated for a molecule using various DFT methods. Each row corresponds to a different DFT functional, and the columns report key energetic and thermodynamic corrections relevant to computational chemistry. The total electronic energy (EE) of the molecule, typically reported in Hartree. This is the energy from the quantum mechanical calculation before any corrections. The Zero Point Energy is the quantum mechanical energy correction accounting for the lowest possible vibrational energy (even at absolute zero), in Hartree. The Thermal Correction to Energy is additional energy correction due to thermal effects (vibrational, rotational, and translational) at a standard temperature, in Hartree. The Thermal Correction to Enthalpy is correction to convert the internal energy to enthalpy, reflecting the energy required to create the molecule at constant pressure, in Hartree. The Thermal Correction to Free Energy is correction applied to obtain the Gibbs free energy, which accounts for entropy effects at a given temperature, in Hartree. The EE + Zero-point Energy is sum of the electronic energy and the zero-point energy, representing the molecule's energy at 0K including quantum vibrational effects, in Hartree [18].

3.4.1. Key Observations from Table 3

All the electronic energies are having large negative numbers, indicating stability, bound systems of molecules. The differences between functional reflect each DFT method approximates electron correlation and exchange. The Zero point energy corrections are positive and relatively similar across methods, typically around 0.32–0.34 Hartree, reflecting similar vibrational structures. The Thermal corrections (to energy, enthalpy, and free energy) are also positive and closely clustered, showing that thermal effects are consistent for this molecule across DFT methods. The sum of electronic and zero-point energies (EE + Zero-point Energy) provides a more physically meaningful value for comparing molecular stabilities, as it includes both electronic and quantum vibrational contributions [31]. The Table 3 allows researchers to systematically compare the different computational methods affect the predicted thermodynamic properties of a molecular system.

Table 4. Thermodynamic and statistical mechanical properties of a molecule, calculated using 22 DFT methods.

DFT Methods	EE + Thermal Energy Correction (Hartree)	EE + Thermal Enthalpy Correction (Hartree)	EE + Thermal Free Energy Correction (Hartree)	E (Thermal) (kcal/mol)	Heat Capacity (Cv) (cal/mol-kelvin)	Entropy (S) (cal/mol-kelvin)
B3lyp	-751.811733	-751.810789	-751.875083	212.790	67.517	135.318
b1b95	-751.23505	-751.234103	-751.296997	215.74	65.954	132.373
b3p86	-754.01983	-754.018889	-754.083566	215.42	66.468	136.125
b972	-751.33313	-751.332181	-751.396199	216.29	65.848	134.737
wb97xd	-751.555870	-751.554926	-751.617675	214.27	66.721	132.066
bhandh	-745.75566	-745.754717	-745.814307	218.95	63.659	125.419
bhandhlyp	-751.08325	-751.082310	-751.142085	220.08	62.713	125.807
ohse1pbe	-751.555870	-751.554926	-751.617675	214.273	66.721	132.066
Blyp	-751.2569	-751.255954	-751.310995	207.24	55.727	115.844
Bmk	-751.08614	-751.085199	-751.148900	215.5	62.553	134.070
bp86	-751.60626	-751.605314	-751.660720	207.19	56.250	116.611
Hfs	-736.15877	-736.157825	-736.209862	201.81	54.790	109.522
m052x	-751.50176	-751.500813	-751.563239	217.33	65.082	131.386
m062x	-751.269710	-751.268766	-751.332152	216.53	65.682	133.408
mpw3bpe	-751.07022	-751.069271	-751.134889	215.360	66.661	138.105
mpwpw91	-751.508060	-751.507116	-751.563957	208.29	57.628	119.632
o3lyp	-751.3364	-751.335455	-751.402596	215.17	66.777	141.310
Olyp	-751.32766	-751.326719	-751.387671	210.97	60.441	128.284
pbe1pbe	-750.6948	-750.693858	-750.758234	216.19	66.187	135.492
pbeh1pbe	-750.77371	-750.772765	-750.836955	216.15	66.132	135.099
Tpssh	-751.66436	-751.663420	-751.729047	214.28	65.085	138.124
x3lyp	-751.22245	-751.221509	-751.287494	215.37	66.363	138.875

Table 4 presents thermodynamic and statistical mechanical properties of a molecule, calculated using various DFT methods. Each row corresponds to a different DFT functional, and the columns display key energetic and thermodynamic corrections relevant for computational chemistry and molecular modeling. The sum of the electronic energy and the thermal correction to energy, representing the total energy of the molecule at a given temperature 298 K, in Hartree. The sum of the electronic energy and the thermal correction to enthalpy, which includes the energy required to create the molecule at constant pressure, in Hartree. The sum of the electronic energy and the thermal correction to Gibbs free energy, accounting for entropy effects, in Hartree. This value is crucial for predicting reaction spontaneity. The calculated thermal energy contribution (in kJ/mol) includes vibrational, rotational and translational components. The constant-volume heat capacity (in cal/mol·K) indicates the amount of energy required to raise the temperature of the molecule by one Kelvin. The entropy of the molecule (in cal/mol·K) reflects the degree of disorder or randomness in the molecular system [32].

3.4.2. Key Observations from Table 4

The EE + Thermal Energy, Enthalpy and Free Energy corrections are all large negative numbers (in Hartree), as expected for stability, bound molecules. Small differences between these values reflect the different ways energy is partitioned in thermodynamic calculations. The thermal energy values range from about 201.8 to 225.9 kJ/mol, showing some variability depending on the DFT method used. The heat capacity ranges from about 54.8 to 66.8 cal/mol·K. Higher values indicate greater ability of the molecule to store thermal energy. Entropy values span from approximately 109.5 to 141.3 cal/mol·K, with higher entropy indicating more possible microstates or greater molecular flexibility. The Table 4 provides a comprehensive comparison of the various DFT methods, which predict the thermodynamic properties of a molecule, aiding in the selection of appropriate computational approaches for accurate modelling and analysis in chemistry and materials science. The Experimental parameter of 5cb liquid crystal molecule given in the Table 5.

Table 5. Experimental parameter of 5cb liquid crystal molecule [30]

Band gap	4.38 eV
Dipole Moment	3.7 to 4.3 Debye
Polarizability	33 x 10^{-24} cm^3 (33 Å)
Ionization Potential	4.70 eV
Electron affinity	1.61 eV
Order Parameter	0.5 to 0.6
Birefringence	0.15 to 0.21
Refractive index	N_e-1.77, N_o-1.58, Average- 1.76

The 5CB liquid crystal exhibits a range of electronic and optical properties that are highly relevant for optoelectronic and photonic applications. It has a band gap of 4.38 eV, indicating it is a wide-band-gap semiconductor, which is typically associated with transparency in the visible region and strong ultraviolet absorption. The dipole moment ranges from 3.7 to 4.3 Debye, suggesting moderate molecular polarity, while the polarizability is 33 × 10^{-24} cm^3 (or 33 $Å^3$), reflecting the material's ability to be distorted by external electric fields a key factor in nonlinear optical responses. The ionization potential is 4.70 eV, and the electron affinity is 1.61 eV, the parameters that define the material's ability to donate or accept electrons, crucial for electronic device performance. The order parameter, ranging from 0.5 to 0.6, indicates a moderate degree of molecular alignment, which can influence anisotropic optical properties.

The birefringence, between 0.15 and 0.21, points to significant optical anisotropy, enabling applications in polarization control. The refractive indices are listed as extraordinary (n_e) 1.77, ordinary (n_o) 1.58, with an average of 1.76, values that support efficient light manipulation and wave guiding. Collectively, these properties suggest the material is well-suited for use in advanced optoelectronic devices, photonic crystals, and nonlinear optical applications.

4. Conclusions

The hybrid GGA functional and metal GGA functional like PBOE, B3LYP, ωB97XD, MO6, BPW91 etc. are good choice due to their good accuracy and computational efficiency for studying the wide range of properties like physical, thermal and optical properties of the liquid crystal molecules. DFT methods mentioned above are widely used to study the phase transition and thermal stability of the liquid crystal molecule. Most of the DFT methods mentioned above provide theoretical values of birefringence in the range of 0.15 to 0.21. Also, the theoretical values of refractive index using various DFT methods mentioned above are in good agreement with experimental result. The best DFT methods are employed to optimize the molecule and calculate the dipole moment, polarizability, order parameter, birefringence etc. The understanding of the phase transition, thermal stability and optical properties will help in determining electro optical properties of liquid crystal molecules used in electro optical devices such as liquid crystal display (LCD) and sensing devices.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors contribution statement

Yogesh Kumar, Tikaram, Narinder Kumar did Conceptualization and methodology and applied software, formal analysis, investigation and data curation. Yogesh Kumar wrote the initial draft of the manuscript; TikaRam did the review and editing; Narinder Kumar is the supervisions of the project administration. All authors have read and agreed to the published version of the manuscript.

Availability of Data and Materials

All data included in this paper are available upon request by contacting the corresponding author.

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