Electro-optical and Physical Properties of Liquid Crystal Molecules studied by Quantum Mechanical Methodology

Summary of the Thesis

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Summary

Condensed matter which exhibits an intermediate thermodynamic phase between the crystalline solid and the isotropic liquid is termed as liquid crystal or mesophase. This contains orientational or weak positional order which produces several physical properties of crystals, but flow like liquids [1-4]. This liquid crystal phase was first discovered by Austrian botanist, Friedrich Reinitzer, when he was investigating the derivatives of cholesterol. Since then, a large number of studies have been done in order to understand the variety of liquid crystalline phases [5-7].

The electronic and optical properties of liquid crystals were first utilized to convey information via a graphics display. Nowadays, liquid crystal displays are widely used in computers, television, pocket calculators and in many appliances to deliver the alphanumeric information to the user [8-12]. One of the fundamental properties of liquid crystal is an orientational order parameter (S), this single property has a capability to govern all physical properties.

The physical properties observed at macroscopic level can be accounted in terms of electrical, optical, diamagnetic and dielectric properties [13-17]. These properties are anisotropic in nature and contributes to the diversity of liquid crystals. Liquid crystals possess large dielectric and electro-optical properties owing to their large anisotropy coupled with the collective molecular reorientation. Liquid crystals have wide application in the field of Physics, Chemistry and Biology due to their high sensitivity to the change in surrounding medium [18-22]. In recent years materials with high order optical nonlinearity are under investigation due to their applications in optical communications, image processing, switching, 3D data storage and optical limiting. Dielectric data and data of electro-optical study were the various tools used to study the behavior of liquid crystals [23-25].

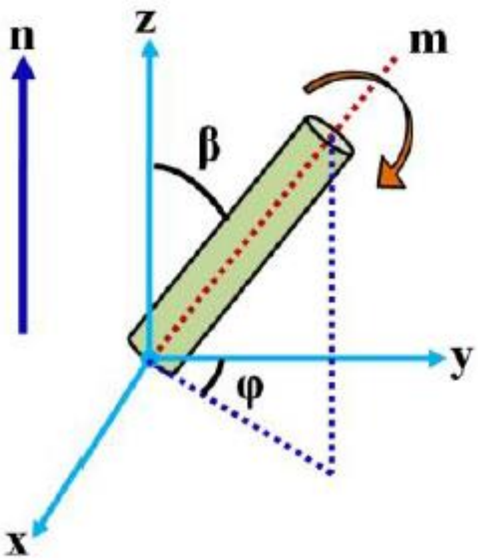


Figure 1. Representation of liquid crystal orientation along with director (n) and azimuthal angle (φ)

Birefringence is the optical property of an anisotropic material under which a ray of light entering with a propagation direction, other than parallel to the optical axis, is divided into two rays, viz. ordinary ray (o-ray) and extra-ordinary ray (e-ray) [26-29]. Both the rays travel with different velocities through the material, and therefore have different refractive indices. This phenomenon is called double refraction or birefringence and the material is termed as birefringent or birefractive material. The two emerging rays are polarized in planes perpendicular to each. The o-ray is coupled to the molecular optic axis, whereas e-ray is perpendicular to the optic axis [30-34].

Liquid crystals are classified into the thermotropic liquid crystal which is obtained within a temperature range, and lyotropic liquid crystals which are obtained within the concentration range [35-38]. Thermotropic liquid crystals are further classified into nematic, smectic, cholesteric liquid crystals depending upon the molecular symmetry and orientation of the molecules. The nematic liquid crystal is an anisotropic fluid and the molecules in the nematic are free to move in any direction as they don't have an orderly position [39-41].

The liquid crystals are very susceptible to an electric field regarding which the liquid crystal molecules are widely used in electro-optical applications or flat panel display devices based on their various molecular chemistry [42-45].

The thesis present here is divided into six chapters which all are briefly described below:

Chapter 1 describes the "Introduction" of the liquid crystal molecules as liquid crystals exhibit the various properties of the crystalline solid and isotropic liquid. The molecular structure of liquid crystal consists of a side chain with a terminal group that interacts with aromatic rings, attached to linkage groups. The liquid crystal is classified into different types based on molecular symmetry or arrangement of molecules [45-48].

The nematic phase of liquid crystal is the simplest form in which there is no orientational order and the molecules align themselves in the preferred direction. In smectic liquid crystals, molecules have positional as well as directional order and exhibit soap-like properties [49-55]. Cholesteric LC's have long-chain chirality order in molecules and are structured in the helical form. These liquid crystals exhibit the property of diffraction of light.

The chapter also includes the physical properties of the liquid crystal-like optical anisotropy, dielectric anisotropy, elastic constants, viscosity, order parameter, etc.

On applying the electric field, the molecules of liquid crystal orient themselves in the direction of the field which is applied in a certain direction.

Liquid crystals are widely used in the discipline of technology, science, and also in medicine. They are used in display devices, optical imaging, medical science, and temperature sensors, etc. A brief introduction of applications like liquid crystal display (LCD) and other applications are discussed in the chapter [56-57].

Chapter 2 gives the “Computational methodology” of the molecules to calculate the physical properties from the optimization of the liquid crystal. It starts from the computational Quantum mechanics in which we solve the minimum energy of the molecules from the density functional theory, method using the preferred basis set and the methods. The main basis of DFT depends on the electron density, i.e., if the electron density is found, then other possible parameters are also calculated. The mathematical formulation of the physical properties like order parameter, birefringence, refractive index, the magic angle is derived which are described in the chapter. Gaussian 09 software is used for the optimization of the molecules. For designing of the molecules Gauss View5 is used as it is a graphical user interface of Gaussian 09 software.

Chapter 3 concludes that the different parameters of E7 liquid crystal changes on application of electric field in THz frequency range. The main physical properties; order parameter and birefringence vary in negative as well as positive directions. The director angle above a value of θ=450 showed fast fluctuations and this rapid change may be utilized in fast switching devices. The refractive index remains stable in the THz frequency range in case of E7 liquid crystal. A eutectic mixture of four liquid crystals may be used in optical shutters. The four components are 5CB, 7CB, 8OCB and 5CT with percentage composition 51%, 25%, 16% and 8% respectively. Using Gaussian 09 software the E7 liquid crystal mixture is fully optimized and different parameters like dipole moment, polarizability anisotropy, magic angle has been calculated. The range of order parameter calculated theoretically is from -0.1456 to 0.2313 with the variation of electric field. The range of birefringence is from -0.2845 to 0.3103 and range of director angle is from 45.710 to 60.910. Refractive index lies between 1.57 to 1.58 and this range correctly matches with the experimental findings.

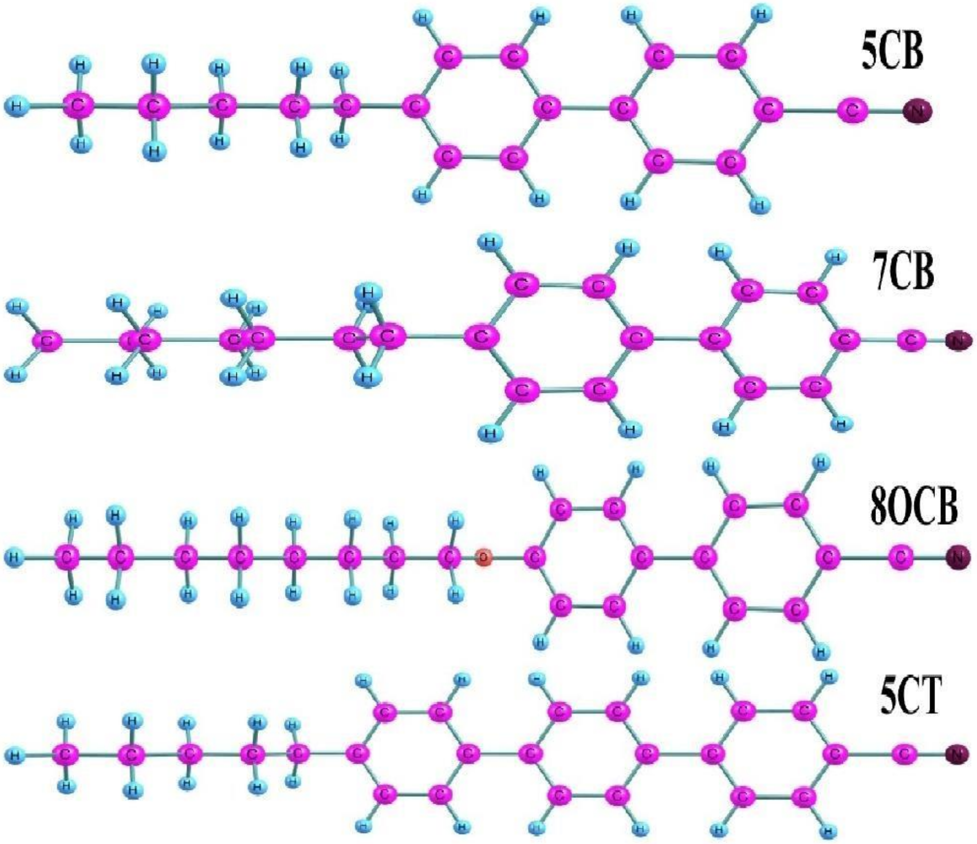


Figure 2. The composition of E7 LC mixtures; 5CB, 7CB, 8OCB and 5CT.

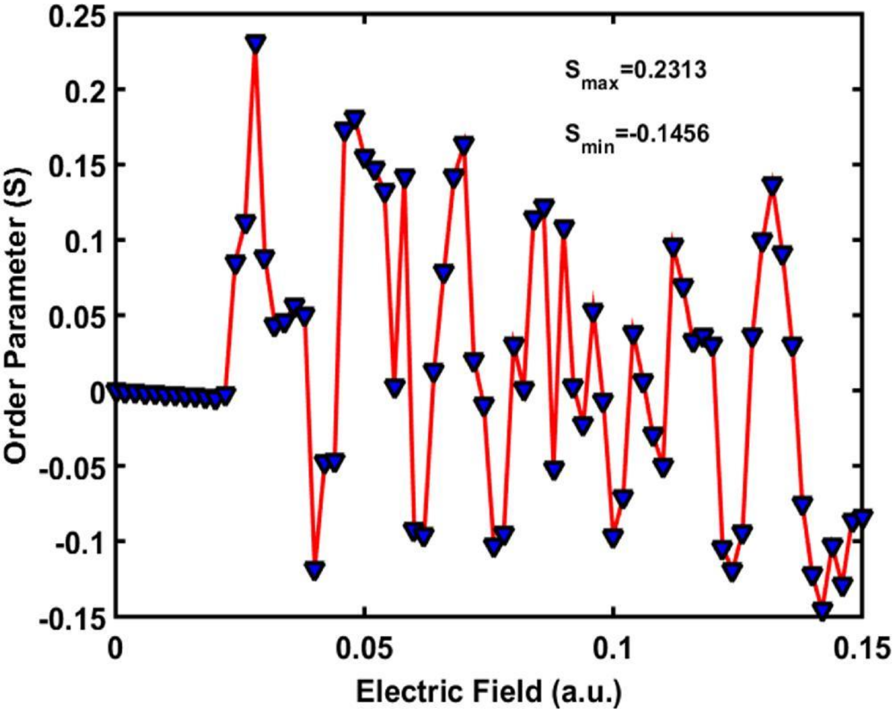


Figure 3. Order parameter of E7 LC calculated under the influence of an electric field.

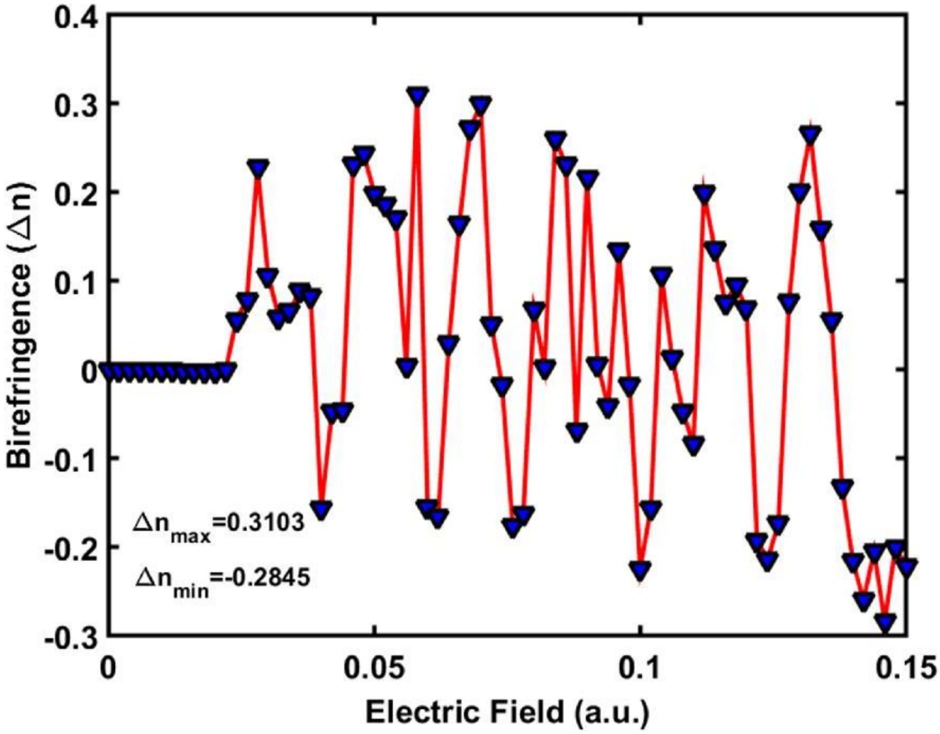


Figure 4. The birefringence of E7 LC calculated under the influence of an electric field.

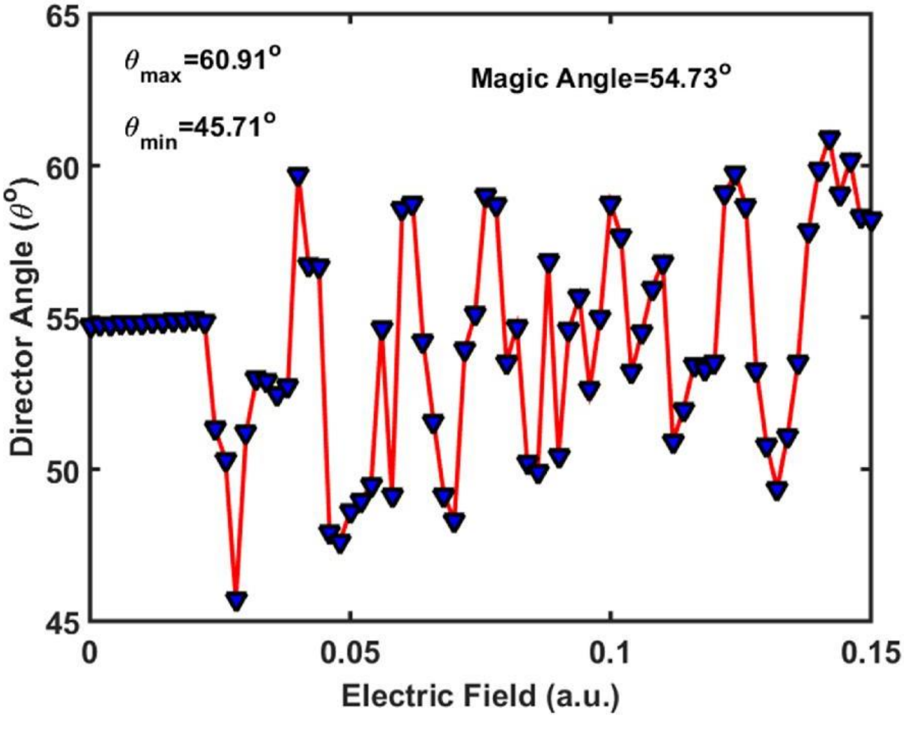


Figure 5. Director angle of E7 LC calculated under the influence of an electric field

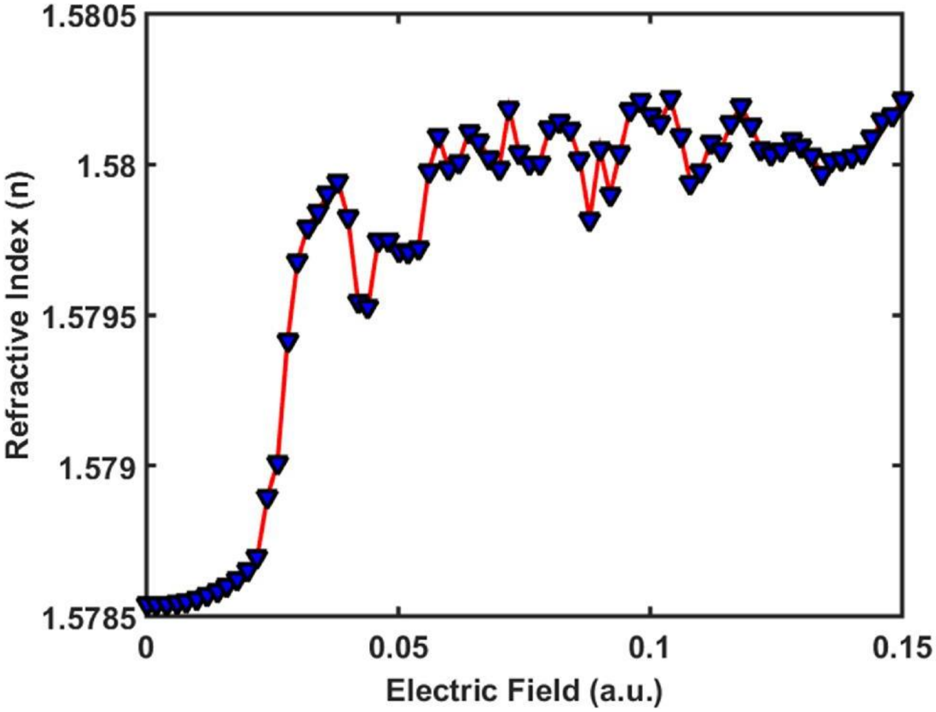


Figure 6. Refractive index of E7 LC calculated under the influence of an electric field.

Chapter 4 concludes an investigation of a hydrogen-bonded liquid crystal compound 7OBA and its composites with graphene and reduced graphene oxide (rGO). The π-π* transitions the phenyl ring of 7OBA and π-π* transitions in C=C bonds of graphene superimposed each other thereby providing enhanced UV absorption. These composites have vital applications in non-linear electronics. These studies very well explained that the physical properties of liquid crystal are dependent on structure - property relationships. In our study, presence of hydrogen bonding in the structure of molecule lead to superior properties. The idea to investigate this composite lies in lesser reporting in this similar kind of composites. For the determination of electronic structure, density functional theory has been utilized, it helps in calculating the overall electron density distribution as well as total energy. According to the First law of thermodynamics, whenever a phase transition occurs in a compound enthalpy of the system changes and gives an insight about what amount of heat has been converted into useful work. So, in our study, composite system (Graphene + 7OBA) has a lesser amount of energy than 7OBA. The principal absorption peak has been observed at 255 nm and this is due to π-π* transitions in phenyl ring part. The absorption in 7OBA has been increased by the interaction of graphene and reduced graphene oxide. The superposition of C=C and π-π* transition peaks increase the magnitude of absorbance. By introducing guest material like graphene, the poor dielectric nature of liquid crystal has been enhanced. The orientation of 17 Ȧ long 7OBA and graphene (100-600 nm) has been analyzed so that physical properties can be studied. This composite system study is helpful in non-linear electronic devices or voltage regulated electronic devices.

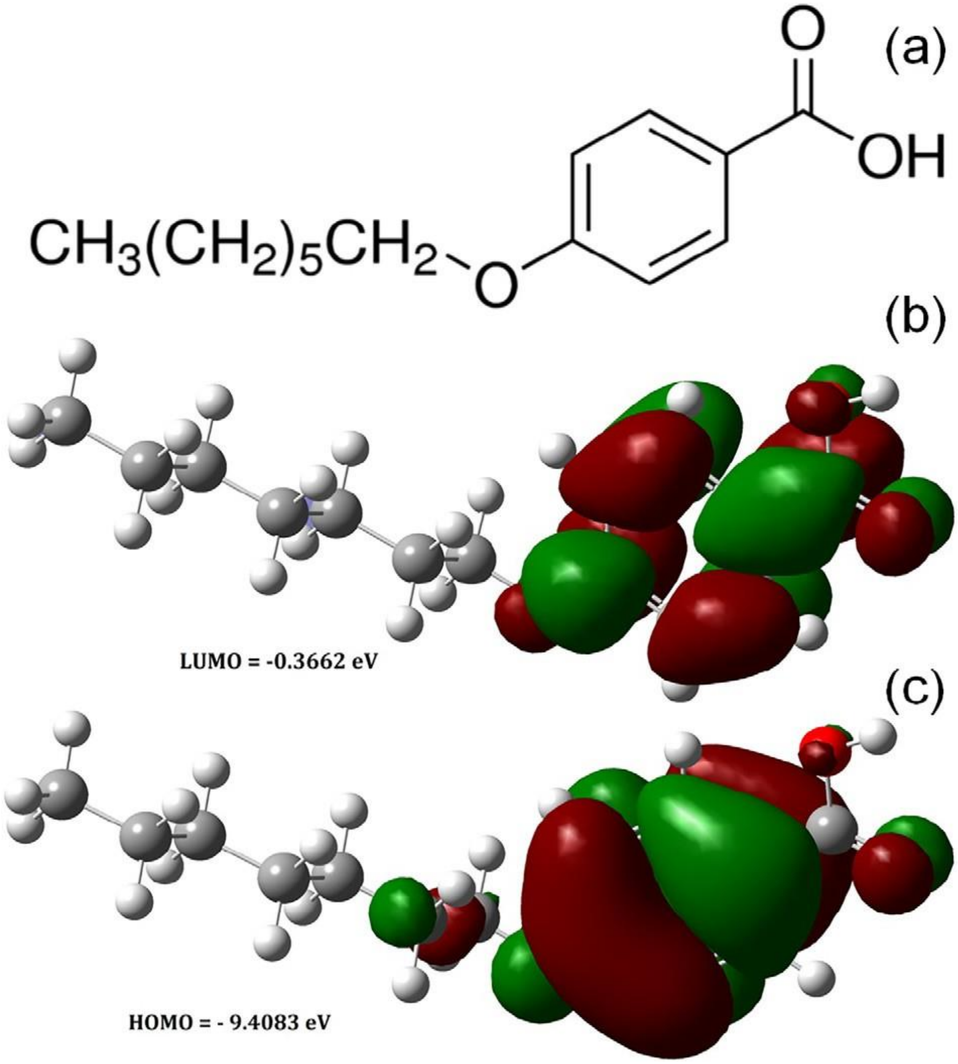


Figure 7. (a) Chemical structure, (b) LUMO, and (c) HOMO of the 4-(Heptyloxy) benzoic acid (7OBA) liquid crystalline compound. The LUMO (−0.3662 eV) and HOMO (−9.4083 eV) values were obtained from the DFT-B3LYP/6-31G(d, p) simulation using a hybrid function AM1/opt +freq level with the help of Gaussian 09 W software-package.

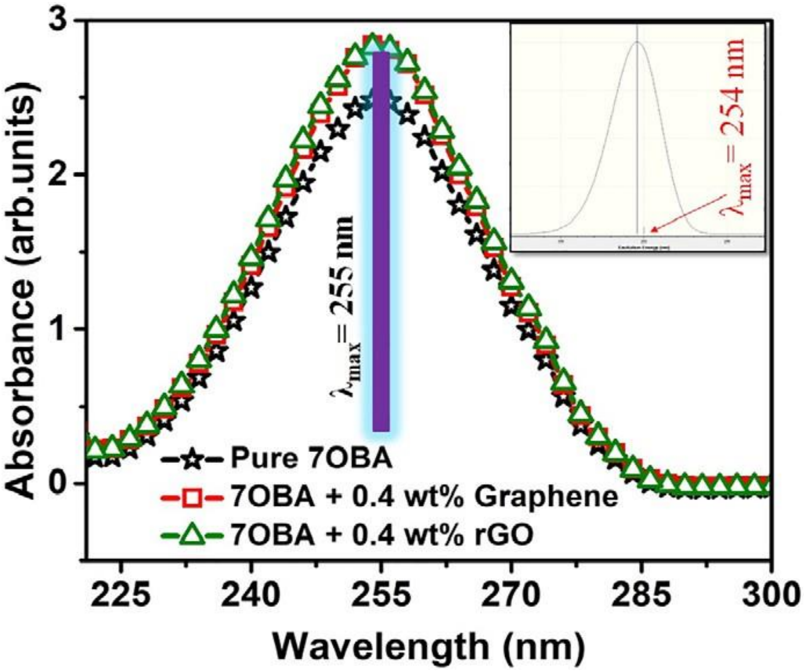


Figure 8. UV–visible absorbance of 7OBA liquid crystalline compound and its composites with graphene and rGO. Inset represents the theoretically obtained UV–visible absorption spectrum.

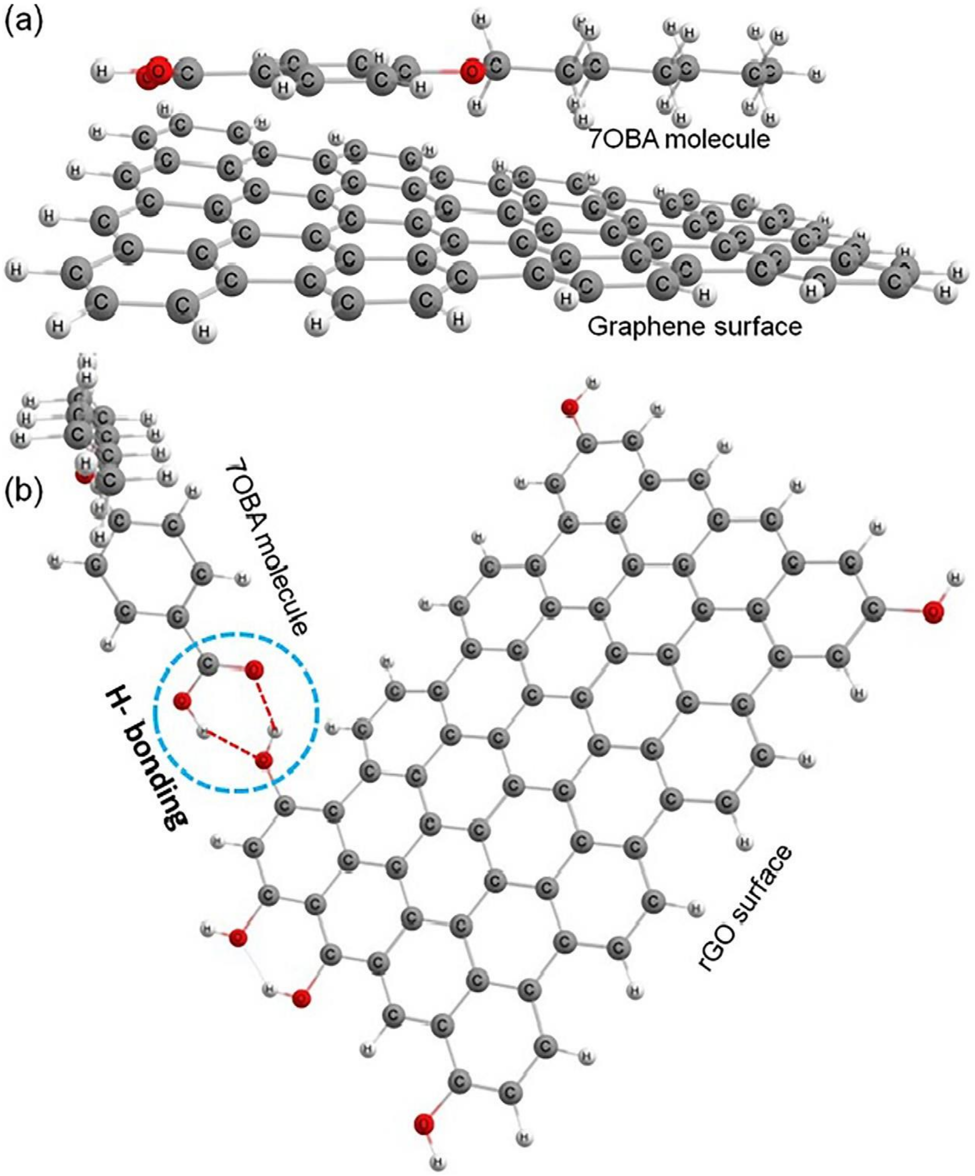
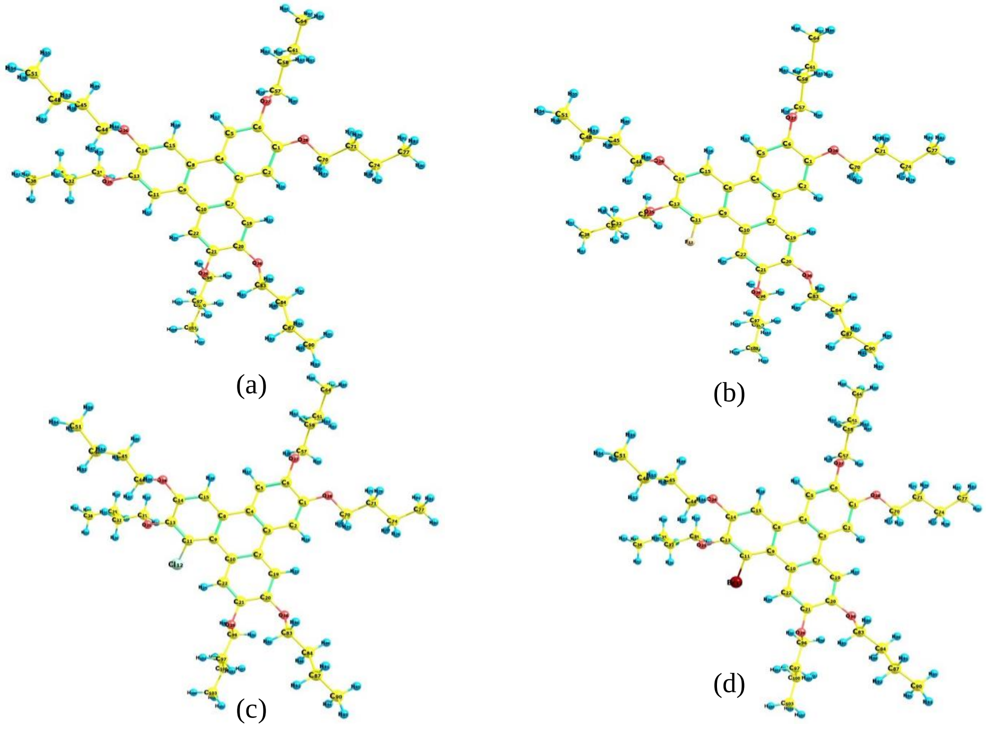


Figure 9. (a) and (b) represent the optimized geometries of molecular interactions between the 7OBA+graphene and 7OBA+rGO, respectively.

Table 1 A comparison of the experimental and simulation results. The abbreviations, E and S refer to the experimental and the DFT-B3LYP/6-31G (d, p) simulated values, respectively. The refractive indices were measured at 24°C.

Properties	**Pristine 7OBA**	**7OBA + Graphene**	**7OBA + rGO**
Refractive index (in toluene)	1.5084 (E) -(S)	1.5010 (E) -(S)	1.5011 (E) -(S)
λ_{max} (nm)	255 (E) 254 (S)	255 (E) 254 (S)	255 (E) 254 (S)
Dipole moment (Debye)	- (E) 3.18(S)	- (E) 1.16(S)	- (E) 9.27(S)
ν (cm^{-1})	1168; O-H scissoring (E)	1167 (E)	1166 (E)
	1292; C-O alkoxy stretching (E)	1293 (E)	1291 (E)
	1427-1466; rocking in C-H (E)	1426-1466 (E)	1410-1467 (E)
	1664; aromatic C-C sym. Stretching (E)	1666 (E)	1659 (E)
	1724; C=O stretching (E)	1724 (E)	1724 (E)
	2847-3100; sym. and asym. C-H stretching (E)	2847-3100 (E)	2847-3100 (E)
	3638; sym O-H stretching (E)	3640 (E)	3608 (E)
	1197; O-H scissoring (S)	1215; rocking in C-H bond (S)	1207; rocking in O-H (S)
	1391; C-O alkoxy stretching (S)	1342 (S)	Not observed
	1393-1462; rocking in C-H (S)	1388-1400 (S)	1380-1384 (S)
	1667; aromatic C-C sym. stretching (S)	1648 (S)	1647 (S)
	1722; C=O stretching (S)	1693; scissoring in C-O (S)	1662 (S)
	3000-3114; sym. and asym. C-H stretching (S)	2999-3100 (S)	3000-3124 (S)
	3630; sym. O-H stretching (S)	3648 (S)	3353-3694 (S)

Chapter 5 concludes the studies of molecular properties of hexabutyloxytryphenylene (HAT4) and halogenated hexabutyloxytryphenylene (HAT4) using density functional theory (DFT). For the generation of non-linear optical and electronic parameters, the method used is B3LYP along with 6-31G, 6-31G* and 6-31G** basis sets. The electro-optical parameters like dipole moment, mean polarizability, anisotropy in polarizability and hyperpolarizability has been studied. Some global parameters like ionization potential, electron affinity, electronegativity, chemical hardness and electrophilicity index are also calculated. The effect of halogenation on linear, non-linear as well as thermodynamical properties was analyzed. Preferably stating the effect on the introduction of halogens like fluorine, chlorine and bromine were investigated. Non-linear optical properties in halogenated HAT4 are larger in value as compared to pure HAT4.



(a) (b)

(c) (d)

Figure 10. Optimized geometry of (a) HAT4 (b) Fluorinated HAT4 (c) Chlorinated HAT4 (d) Brominated HAT4 molecules.

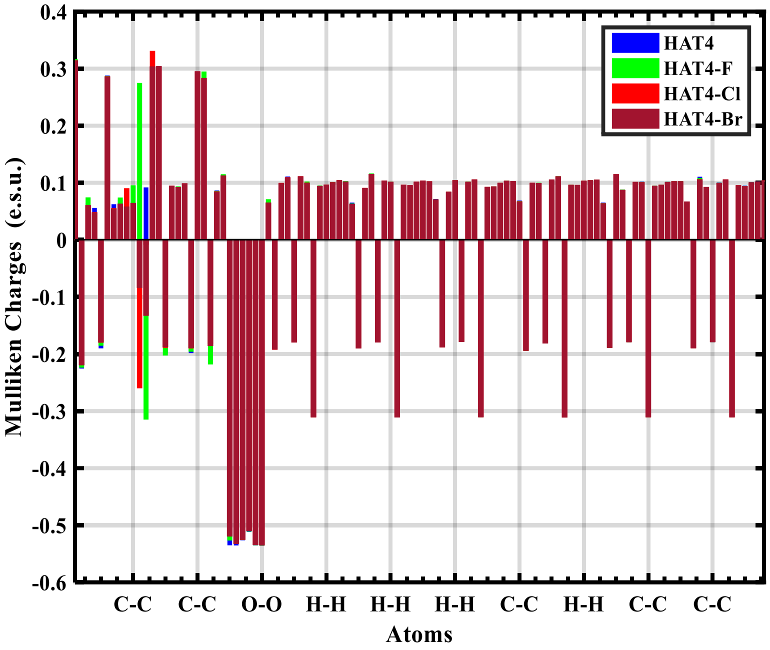


Figure 11. Mulliken charges Analysis of HAT4 molecule, Fluorinated HAT4, Chlorinated HAT4 and Brominated HAT4 molecules.

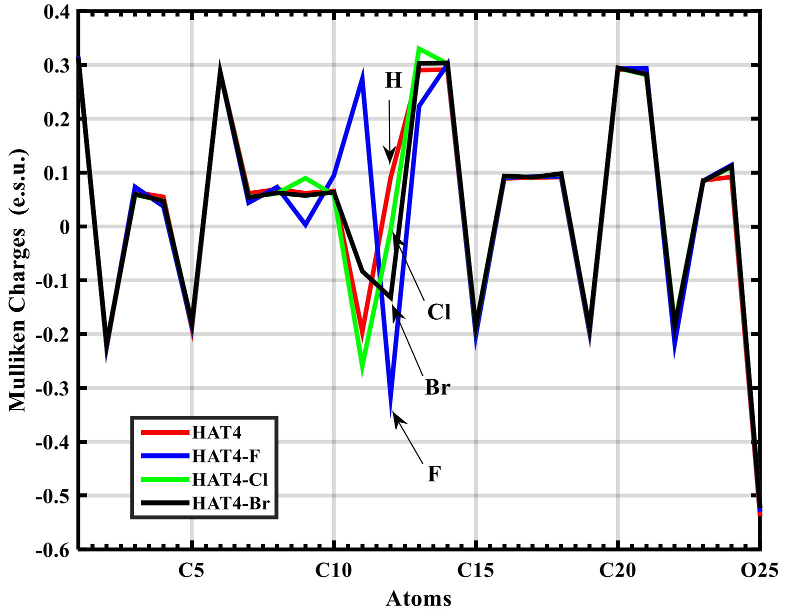
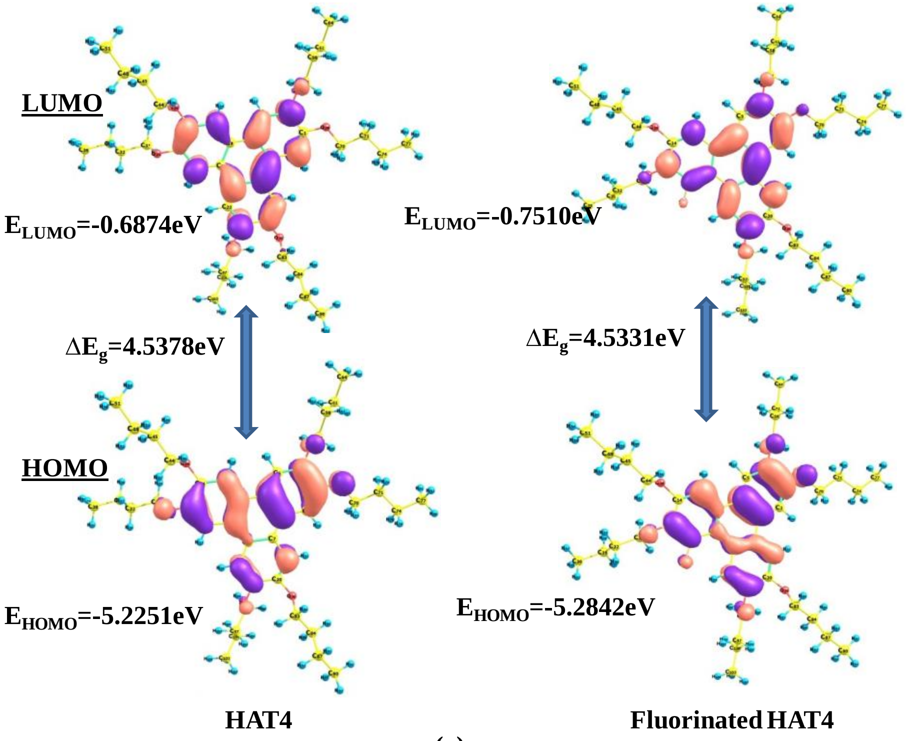


Figure 12. Mulliken charges of most affected atoms in the core geometry of non-halogenated and halogenated HAT4 molecule.



(a)

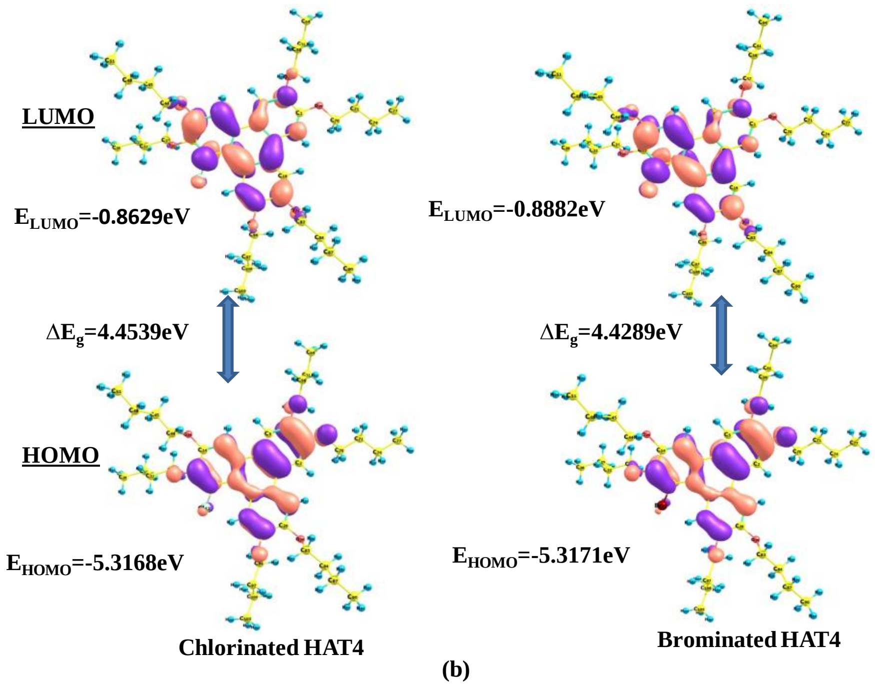


Figure 13. HOMO-LUMO diagram for HAT4 and Halogenated HAT4 DLC molecules (B3LYP/6-31G**).

Table 2. Global parameters of pure HAT4 and halogenated HAT4 molecules using 6-31G** basis set.

Global Parameters	**HAT4**	**Fluorinated HAT4**	**Chlorinated HAT4**	**Brominated HAT4**
HOMO (eV)	-5.2251	-5.2842	-5.3168	-5.3171
LUMO (eV)	-0.6874	-0.7510	-0.8629	-0.8882
Ionization Potential (eV)	5.2251	5.2842	5.3168	5.3171
Electron Affinity (eV)	0.6874	0.7510	0.8629	0.8882
Electronegativity χ (eV)	2.9562	3.0176	3.0899	3.1026
Electronic Chemical Potential μ (eV)	-2.9562	-3.0176	-3.0899	-3.1026
Global Hardness η (eV)	2.2689	2.2666	2.2269	2.2145

Global Softness (eV^{-1})	0.2204	0.2206	0.2245	0.2258
Electrophilicity index ω(eV)	1.9259	2.0087	2.1435	2.1735
ΔN_max	1.3029	1.3313	1.3875	1.4011
Band Gap ΔEg (eV)	4.5378	4.5331	4.4539	4.4289
Local softness (nucleophilic attack) of atomic centre being halogenated (S_k^+) [NPA]	-0.0247	0.0407	0.0072	0.0023
Local softness (electrophilic attack) of atomic centre being halogenated (S_k^-) [NPA]	0.0291	0.0354	0.0059	0.0146

Table 3. Electro-optical properties of HAT4 and halogenated HAT4 molecules using different basis sets

Electro-optical properties	**Basis set**	**HAT4**	**Fluorinated HAT4**	**Chlorinated HAT4**	**Brominated HAT4**
Dipole Moment (μ) (Debye)	6-31G	2.40	2.65	2.21	2.15
	6-31G*	2.07	2.28	2.03	1.99
	6-31G**	2.07	2.28	2.03	1.99
Mean Polarizability (<α>) $\times 10^{-24}$ e s u	6-31G	76.88	77.00	78.48	79.08
	6-31G*	78.40	78.56	80.18	81.10
	6-31G**	79.21	79.35	80.97	81.90
Anisotropy in Polarizability (Δα) $\times 10^{-24}$ e s u	6-31G	49.05	49.34	48.52	48.77
	6-31G*	50.05	50.31	49.51	49.78
	6-31G**	50.41	50.67	49.85	50.12
Hyperpolarizability (β) $\times 10^{-33}$ e	6-31G	5888.46	6293.99	7725.00	7816.40
	6-31G*	5510.40	5694.076	7488.89	8028.07

s u	6-31G**	5543.72	5724.02	7519.42	8058.86
Molar Refractivity (M R) e s u	6-31G	193.91	194.21	197.95	199.47
	6-31G*	197.76	198.15	202.23	204.56
	6-31G**	199.80	200.17	204.26	206.58
Dielectric constant (ε)	6-31G	2.94	2.37	2.89	2.64
	6-31G*	2.61	2.93	2.77	3.90
	6-31G**	2.36	3.17	2.75	2.89

Table 4. Thermal energy ($E_{Thermal}$), Specific heat capacity (C_V) and Entropy (S) of pure HAT4 and halogenated HAT4 molecules using different basis sets

Molecules	**Basis set**	**Free energies (incl. elec. energy) (Kcal/Mol)**	**Thermal enthalpies (incl. elec. energy) (Kcal/Mol)**	**$E_{Thermal}$ (Kcal/Mol)**	**Specific heat capacity C_V (Cal/Mol-Kel)**	**Entropy S (Cal/Mol-Kelvin)**
HAT4	6-31G	-1309317.254	-1309243.128	626.011	164.175	248.618
	6-31G*	-1309037.438	-1309572.598	627.739	185.796	309.744
	6-31G**	-1309720.841	-1309623.861	628.328	196.033	325.274
Fluorinated HAT4	6-31G	-1371576.374	-1371499.752	621.468	167.335	256.992
	6-31G*	-1371933.255	-13071842.809	622.606	186.852	303.358
	6-31G**	-1371991.475	-1371892.537	623.822	199.065	331.841
Chlorinated HAT4	6-31G	-1597701.281	-1597624.344	620.793	167.831	258.044
	6-31G*	-1598059.269	-1597966.119	622.427	189.569	311.856
	6-31G**	-1598115.517	-1598016.461	623.064	199.775	332.235
Brominated HAT4	6-31G	-2922503.833	-2922426.761	620.676	168.045	258.499
	6-31G*	-2922865.754	-2922771.936	622.310	189.810	314.669
	6-31G**	-2922922.133	-2922822.272	622.946	200.016	334.934

At the end of the thesis, I would like to do some final conclusions on the basis of theoretical studies done during the entire course of work.

The mixture of four liquid crystals 5CB, 5CT, 7CB and 8OCB is known as E7 liquid crystal and its properties varied under the influence of electric field.

A hydrogen bonded liquid crystal compound 4-(heptyloxy) benzoic acid (7OBA) interacts with graphene and reduced graphene oxide. This interaction showed π-π* transitions in phenyl ring of 7OBA and π-π* transitions in C=C bonds of graphene, both the transitions superimposed giving an enhanced UV absorption at 255 nm.

The molecular properties of hexabutyloxytryphenylene (HAT4) and halogenated HAT4 using Density Functional Theory (DFT) has been investigated. The effect of halogenation also leads to understand the modification of nonlinear parameters of HAT4 for the interaction of nonlinear fields.

LIST OF PUBLICATIONS

Part of the thesis published and communicated in refereed journals:

1. Dharmendra Pratap Singh, Abhishek Kumar Misra, Kamal Kumar Pandey, **Bhavna Pal**, Narinder Kumar, Devendra Singh, Kirill Kondratenko, Benoit Duponchel, Paul Genevray, Redouane Douali, "Spectroscopic, dielectric and nonlinear current–voltage characterization of a hydrogen-bonded liquid crystalline compound influenced via graphitic nanoflakes: An equilibrium between the experimental and theoretical studies", **Journal of Molecular Liquids**, 302, 112537, (2020).
2. Narinder Kumar, **Bhavna Pal**, Pawan Singh, Khem B. Thapa, Devendra Singh, Devesh Kumar, "Electrical Characterization of E7 Liquid Crystal Molecules under the Impact of an External Electric Field (THz): A Theoretical approach", **Jordan Journal of Chemistry**, 15, 101, (2020).
3. **Bhavna Pal**, Mirtunjai Mishra, Devendra Singh, Devesh Kumar, "A theoretical investigation of nonlinear optical and electronic molecular parameters of hexabutyloxytryphenylene and halogenated hexabutyloxytryphenylene molecules using density functional theory (DFT) for nonlinear device applications", **Physica Scripta**, 97, 065808, (2022).

Work not included in the thesis:

1. A.K. Dwivedi, **Bhavna Pal**, Shivani Chaudhary, Pawan Singh, Khem B. Thapa, Narinder Kumar, Devendra Singh, "Molecular spectroscopy of 5CB (cyano biphenyl) liquid crystal molecule studied by DFT methodology", **Adalya Journal**, 08, 08, (2019).
2. A.K. Dwivedi, **Bhavna Pal**, Narinder Kumar, Asheesh Kumar, Pawan Singh, Khem B. Thapa, Devendra Singh, "Spectroscopic Properties of PCH liquid crystal molecule stuied

by DFT methodology", **Journal of Information and Computational Science**, 09, 07, (2019).

3. A.K. Dwivedi, **Bhavna Pal**, Shivani Chaudhary, Pawan Singh, Asheesh Kumar, Khem B. Thapa, Narinder Kumar, Devendra Singh, "Molecular Stretching of 4- methoxy-4'-n-alkyl-tolan liquid crystal molecule studied by DFT Methodology", **Journal of Information and Computational Science**,09, 08, (2019).
4. A. K. Dwivedi , **Bhavna Pal** , Narinder Kumar , Asheesh Kumar , Pawan Singh, Khem B Thapa , Devendra Singh, "Spectroscopic Analysis of PAA (paraazoxy anisole) liquid crystal molecule studied by DFT Methodology", **Infokara Research Journal**, 08, 08, (2019).
5. Narinder Kumar, **Bhavna Pal**, Shivani Chaudhary, Devendra Singh, Devesh Kumar, "Reduced graphene oxide contains a minimum of six oxygen atoms for higher dipolar strength: A DFT study", **French-Ukrainian Journal of Chemistry**, 08, 01, (2020).

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