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Optical Activity of Chiral 4-Cyano 4'pentylbiphenyl: A Computational Study

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ABSTRACT
In this study, optical rotation of 4-cyano-4'-pentylbipenyl (5CB) which is a thermotropic liquid crystal has been investigated. On introducing chiral effect in 5CB liquid crystal, absolute configurations have been obtained with respect to optical rotation. We performed the theoretical specific rotation calculations using Gaussian 09 software along with B3LYP 6-31++g basis set. With the variation of electric field on different frequencies, specific rotation showed monotonically increasing trend and in a frequency range of 6000-8000 Å, it achieved saturation. From the molecular orbital analysis, it has been investigated that the electron cloud seems to be spread over cyano group attached to phenyl ring. A dip in energy band gap leads to the conductivity of 5CB chiral molecule. This study provides a deeper insight for chiral nematic liquid crystal to be utilized as a sensing and filtering device, organic photovoltaics and in many more devices.

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I. INTRODUCTION

The optical activity of any compound is directly connected with its chirality and in case of liquid crystal, this chirality leads to a dielectric tensor of the molecule capable of rotating in space. The liquid crystals are generally categorized in soft matter and have anisotropic properties [1]. For instance, cholesteric liquid crystals are considered as helical liquid crystals. To define the pitch of a helix, characteristic length needed to complete a 2π rotation has been utilized [2]. The rotation of polarized light after passing through optically active substance is known as optical rotation. On application of electric field, optical rotation is observed and this gives rise to electro-optic effect in a liquid crystal [3].

In the list of nematic liquid crystal, 5 cyano biphenyl is the first member. Its chemical name is 4-cyano 4'pentylbiphenyl. Its molar mass is 249.357g/mol and density is 1.008g/cc. It was discovered by George William Gray and his co-workers in 1972. It has readily accessible nematic range around room temperature [4]. The polar structure containing a cyano group attached to one benzene ring gives rise to a strong dipolar association. It is useful in the study of surface topography. The method which is adopted in the preparation of 5CB is the modification of biphenyl in a linear manner. Due to the presence of chiral groups, this compound can be easily supercooled. It shows non-linear dielectric effect [5]. When this compound is heated, subsequent possible appearance of Meta stable and cholesteric phases is observed. Finally, a glassy state is achieved. 5CB has high dielectric anisotropy and it is chemically very stable. To improve its electro-optical properties, 1D nanoparticle was added [6]. For finding the translational and rotational modes in a particular type of liquid crystal, Raman spectral analysis is required. The requirement of this analysis is a type of liquid crystal whose flexible parts does not contain any hydrogen and also it must be stable on exposure to atmospheric conditions. These properties are present in this compound [7]. On application of external electric field on 5CB, the alignment of molecule along nematic domains was observed. It also stabilizes the compound which gives rise to memory effect in 5CB. So, this compound is widely used in display devices [8]. A number of conformers exist in nature of 5CB. But, the most stable conformer is the one which has biphenyl core. One of the structural isomers of 5CB is a cholesteric liquid crystal [9]. On performing the differential scanning calorimetric studies on this structural isomer, phase transition from cholesteric to crystalline form is achieved. The molecules of 5CB are weakly associated, which results in effective breaking of dipoles on increasing the temperature [10]. Different phase transitions are observed in 5CB at different temperatures, i.e., at 296 K it changes from solid to nematic phase and at 308 K, it changes from nematic to isotropic phase [11]. On the basis of Raman study, it was observed that solid crystalline polymorphism exists in 5CB in C-N stretching region. At low temperatures, typical photoluminescence spectral band is observed. Further, new findings are being done on 5CB to improve its quality. Different methods are being adopted like

doping with polymers and other transition metals, spectroscopic studies etc. [12]-[14]. A molecular dynamics study is performed on 5CB at the air-water conjugation reveals that the orientational ordering is improved [15]-[16]. The dielectric constants and refractive indices are measured using external electric field; this is in good agreement with proposed result [17]-[18]. Different simulation performed under different conditions reveals that molecular properties are independent of time taken for simulation [19]-[20].

II. COMPUTATIONAL METHODOLOGY

The electronic structure of 5CB chiral liquid crystal is characterized by using Density Functional Theory (DFT), this helps in the analysis of total electronic energy, dipole moments and molecular orbitals. For this we utilized Gaussian 09 software and Gauss View 5 as graphical user interface (GUI). The hybrid functional B3LYP is very efficient in providing the results at low computational cost. The molecular orbital analysis has been done using Chemcraft software. The basis set for diffused functions 6-31++g has been adopted here [21-24].

III. RESULTS

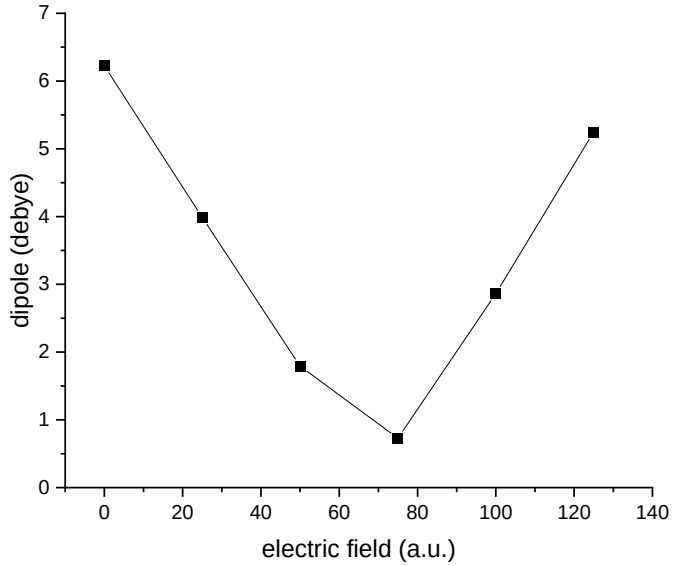
3.1 THEORETICAL CALCULATIONS OF SPECIFIC ROTATION

Table 1 summarizes the optical rotation of 5CB chiral molecule at different frequencies with the application of electric field. The method used here is B3LYP/6-31++G

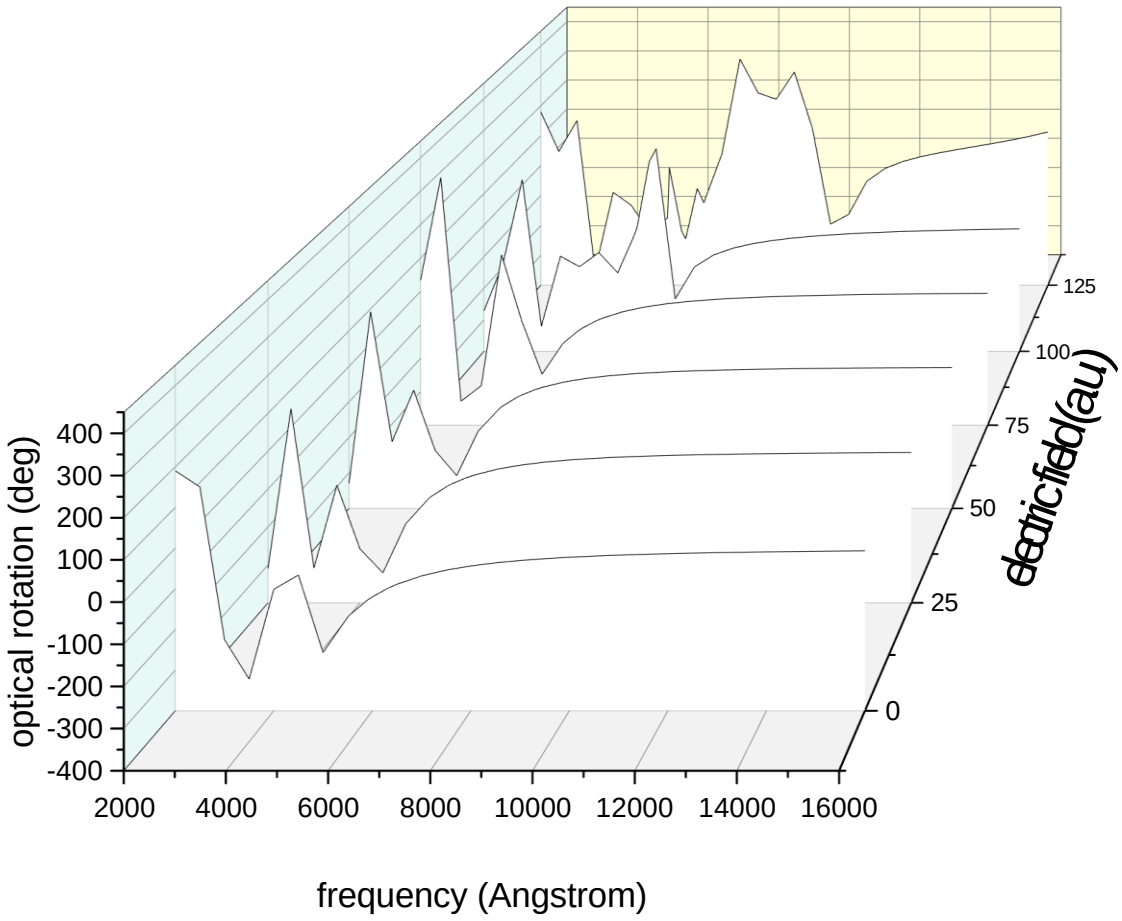
	B3LYP					
FREQUENCY (Å)	ELECTRIC FIELD (a.u.)					
	0	25	50	75	100	125
16000	-6.68	-3.85	-3.38	-5.41	-12.09	112.8
15500	-7.21	-4.17	-3.67	-5.85	-13.04	98.18
15000	-7.8	-4.54	-4	-6.35	-14.12	85.71
14500	-8.47	-4.96	-4.38	-6.91	-15.34	74.6
14000	-9.23	-5.44	-4.82	-7.55	-16.73	64.18
13500	-10.1	-6	-5.33	-8.29	-18.34	53.85
13000	-11.11	-6.65	-5.92	-9.14	-20.2	42.9
12500	-12.28	-7.41	-6.61	-10.14	-22.37	30.25
12000	-13.65	-8.31	-7.44	-11.31	-24.95	14.07
11500	-15.28	-9.38	-8.42	-12.71	-28.03	-9.73
11000	-17.21	-10.68	-9.62	-14.38	-31.76	-52.46
10500	-19.55	-12.27	-11.09	-16.42	-36.36	-162.9
10000	-22.42	-14.24	-12.91	-18.92	-42.15	-195.62
9500	-25.97	-16.71	-15.21	-22.05	-49.62	124.37
9000	-30.46	-19.86	-18.16	-26.03	-59.61	313.05
8500	-36.22	-23.97	-22.01	-31.18	-73.64	221.94
8000	-43.8	-29.45	-27.17	-38.01	-95	243.26
7500	-54.03	-36.93	-34.23	-47.32	-132.95	356.45
7000	-68.25	-47.48	-44.23	-60.42	-234.05	38.68
6500	-88.8	-62.89	-58.89	-79.61	241.78	-124.47
6320	-98.47	-70.19	-65.85	-88.74	200.9	-76
6000	-119.9	-86.46	-81.4	-109.18	-8.79	-244.89
5890	-128.85	-93.28	-87.93	-117.81	-43.15	-219.38
5550	-163.61	-119.86	-113.42	-151.81	-136.36	-7.06
5500	-169.84	-124.64	-118.01	-157.99	-151.84	-174.78
5000	-256.74	-191.36	-182.26	-247.34	-87.16	-222.66
4500	-66.14	-321.03	-307.74	-88.65	-132.1	-132.93
4000	-101.34	-257.7	-237.07	109.27	-98.78	-89.23
3500	-322.25	-89.94	-67.26	-281.7	-320.52	-350.69
3000	-225.19	-308.29	-212.05	-328.03	143.41	151.02
2500	150.49	111.74	153.25	340.69	-120.54	47.2
2000	190.19	-309.71	-329.12	33.25	-271.47	179.52

The optical rotation connects the microscopic property of molecular configuration and the rotation of light through the polaroid.

GRAPH 1 The variation of electric field Vs dipole moment



GRAPH 2 The variation of optical rotation with electric field along with different frequencies

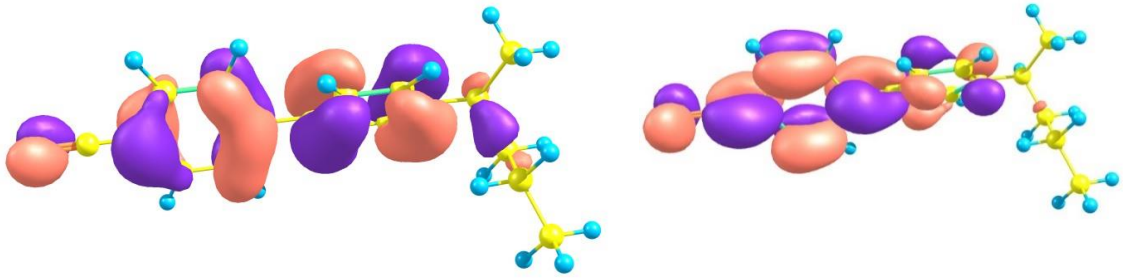


3.2 MOLECULAR ORBITAL

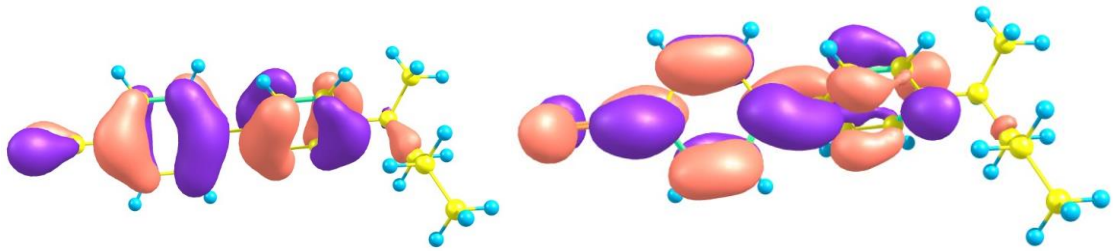
The electron cloud is distributed over the phenyl rings showing most of the charge of the molecule has been acquired by both the phenyl rings. The HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) diagrams has been investigated and we concluded that on increasing the electric

field (a.u.) the electron cloud in LUMO shifts from phenyl rings to alkyl chain. Molecular orbital analysis revealed the bonding nature in an intermolecular interaction even the hydrogen bonding can also be understood. Nitrogen with an electronegative nature is a suitable site for electrophilic attack.

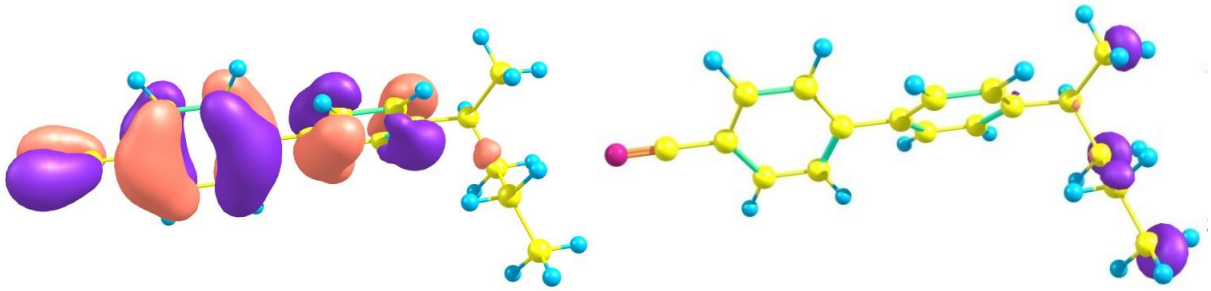
The different molecular orbitals indicating electron density mapping are shown



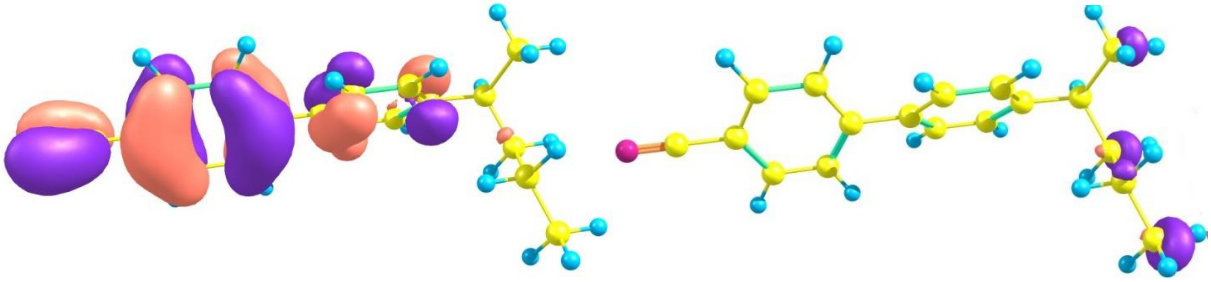
Molecular orbital of 5CB chiral at 0 field using B3lyp



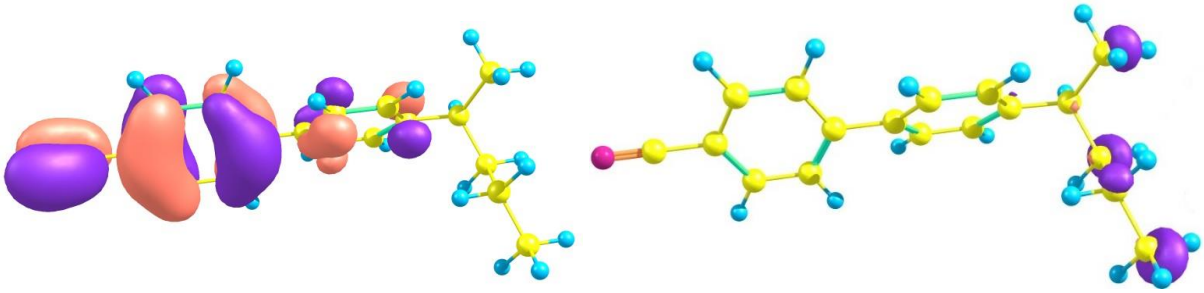
Molecular orbital of 5CB at 25 field using B3lyp



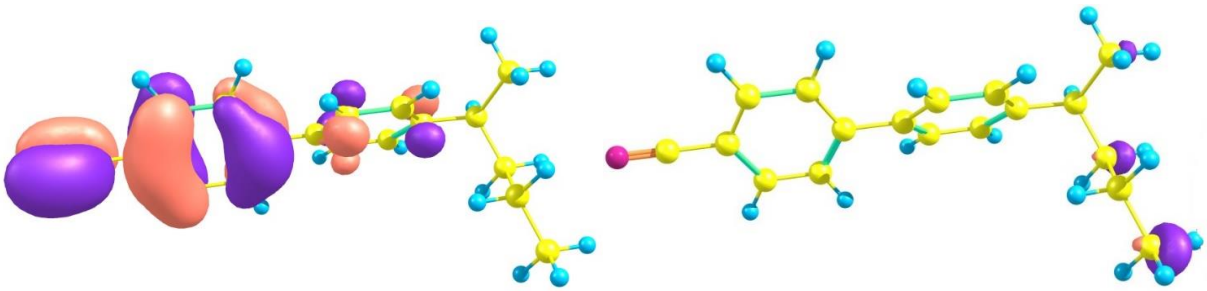
Molecular orbital of 5CB chiral at 50 field using B3lyp



Molecular orbital of 5CB at 75 field using B3lyp



Molecular orbital of 5CB chiral at 100 field using B3lyp



Molecular orbital of 5CB chiral at 125 field using B3lyp

TABLE 3 DIPOLE MOMENT with different method on different electric field

ELECTRIC FIELD	B3LYP
0	6.2256 debye
25	3.9892 debye
50	1.7916 debye
75	0.7294 debye
100	2.863 debye
125	5.2468 debye

IV. CONCLUSION

In medical chemistry and biochemistry, chiral compounds are of great importance. In our study, the optical rotation of 5CB chiral compound has been investigated. In a certain electric field, the optical responses with the variation of frequency showed monotonically increasing trend. Molecular geometry is directly connected with optical rotation. The chiral 5CB liquid crystal molecule shows optical rotation on different fields along with different frequencies. The analysis reveals that on increasing the frequencies, the optical activity saturates for the electric fields up to 100 a.u. The constant value of optical rotation shows that the 5CB chiral liquid crystal molecule may be utilized in calculating the pitch of a liquid crystal molecule. The electron cloud as shown by molecular orbital diagram has been spread over cyano group which is attached to the phenyl ring. The variation of dipole moment with electric field indicates the electronegative nature.

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