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Electo-optic and spectroscopic study of pyridine liquid crystal molecule and its deivatives

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Abstract: Four pyridine derivative and one simmilar but non-pyridine liquid crystal molecules with two aromatic and one cyclohexane ringed have been examined applying quantum mechanical tools like computational Density Functional Theory, to understand theirelectro-optical and spectroscopic details. The present article reports some liquid crystal moleculesnamely (1). 5-(4-butylcyclohexyl)-2-(4-methoxyphenyl)pyridine, (2). 5-(4-butylcyclohexyl)-2-(3-fluoro-4-methoxyphenyl)pyridine, (3). 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine, (4). 5-(4-pentylcyclohexyl)-2-(4-propylphenyl)pyridine and (5). 1-(4-pentylcyclohexyl)-4-(4-propylphenyl)benzene.having structure of pyridine and its derivative.it was found that differences at micro level will also be responsible for the changes in optical properties like birefringence, dielectric anisotropy, etc. as well as materialistic features like viscosity, elastic constant, etc.

Keywords: pyridine, liqid crystal, density functional theory, electro-optic, spectroscopic.

I. INTRODUCTION

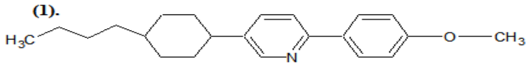
Liquid crystal is an intermediate phase of matter (between isotropic liquid and crystal). these molecules were originally discovered in chemical and biological system. Since long time, liquid Crystals (LCs) have been the subject of theoretical and experimental study. By their role in chemical, biological and elctro-optical system, they have many industrial applications. Liquid crystals arepowerful solvent in holding donor-spacer-acceptor systems as well as in maintain the fluid and order property over a wide range of temperatures too. Numerous electronic and optical properties of LC varies with change of substituent. These properties of molecules can be altered by the presence of different substituents. LC molecule have a dipole moment directly perpendicular to the molecular axis.[1-5]

The pyridine derivatives have been examined quantum mechanically to understand the possible reason for varying mesogenic character. The understanding the LC property of these pyridine is of fundamental importance in chemical physics.Raman scattering depends on the polarizability. The Homo-Lumo energy gap is effective for stability of the molecule. Also the electrical transport property determine by the Homo-Lumo gap. [6-7]A surficial study on the vibrational analysis and elctro-optical properties was necessary and has been performed successfully in our study.In this article, we have done geometry optimization, vibrational analysis and total energy calculation of some pyridine derivatives namely (1).5-(4-butylcyclohexyl)-2-(4-methoxyphenyl)pyridine, (2).5-(4-butylcyclohexyl)-2-(3-fluoro-4-methoxypheny l)pyridine, (3). 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine, (4).5-(4-pentylcyclohexyl)-2-(4-propylphenyl)pyridine and (5). 1-(4-pentylcyclohexyl)-4-(4-propylphenyl)benzene.

II. METHODOLOGY

The structures were designed using GaussView 5.0.

(1).



5-(4-butylcyclohexyl)-2-(4-methoxyphenyl)pyridine

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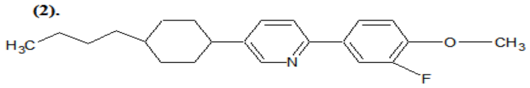

5-(4-butylcyclohexyl)-2-(3-fluoro-4-methoxyphenyl)pyridine

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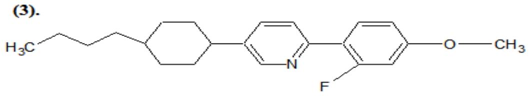
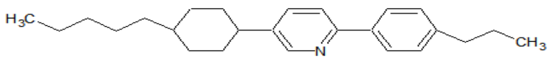


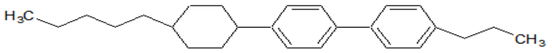
5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine

(4).



5-(4-pentylcyclohexyl)-2-(4-propylphenyl)pyridin

(5).



1-(4-pentylcyclohexyl)-4-(4-propylphenyl)benzene

Fig.1. Chemical structures of some pyridine liquid crystal molecules

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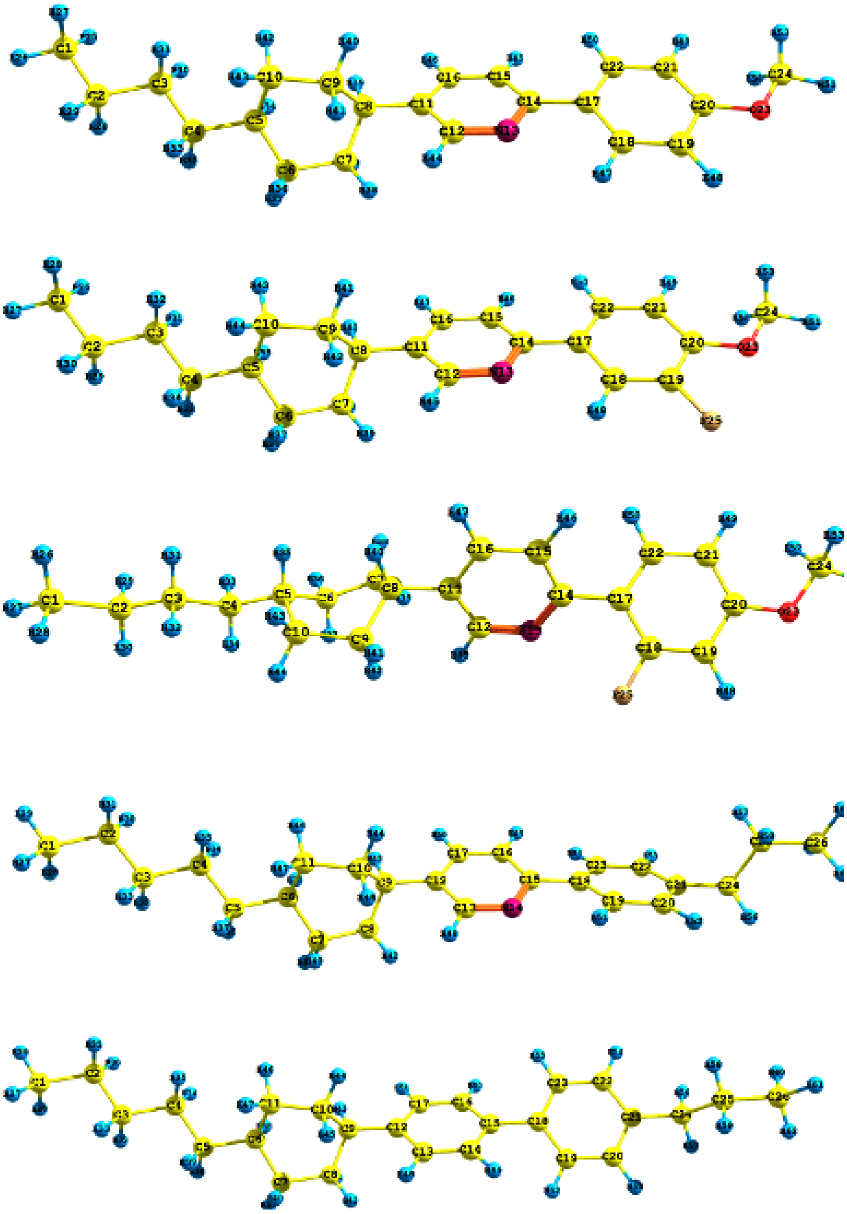

Fig.2. Optimized geometry of some pyridine liquid crystal molecules

Optimization of molecular geometry and frequencies as well as total energy calculations were carried out without any constraint through computational density-functional theory (DFT) method B3LYP [8,9] which is a hybrid functional for Gaussian type orbitals (GTOs) and 6-31G**[10] basis set using Gaussian 09[11] . So far DFT has been very successful in the past for predicting,characterizing and explaining the properties of various class of molecules, clusters, etc.[12,13]

III.RESULTS

Electro-optical properties likepolarizability, total energy, HOMO-LUMO gap and dipole moment of compounds (1) to (5) have been tabulated in table 1. Spectroscopic results namely IR and Raman, soobtained, has been shown in figure 2 and 3. It is summarized in table 3.

A. Electro-optical properties

Total energy is lowest for compound (2) and (3) which is around -1085.043 atomic units (a.u.) while it is highest for compound (1) at – 985.817 a.u. HOMO-LUMO gap of compound (5) is 0.18932 a.u. which is highest among these while at 0.17109, it is lowest for compound (2). Dipole moment shows large variation from 0.1768 a.u. to 3.8606 a.u. for compound (5) and (2) respectively. Polarizability of compound (5) is highest at 292.51533 a.u. (polarizability for compound (4), being at 291.574 a.u., is very near to that of compound (1)). It is lowest for compound (3) at 256.72933a.u.

B. Spectroscopic results

Infra-Red peak frequency is lowest for compound (1) at 1300 cm^{-1} and highest for compound (4) and (5) reaching to 1500 cm^{-1}. Molar extinction coefficient (ε) is greatest for compound (2) at 1100and smallest for compound 4 at 600. Frequency peak of Raman intensity spectra is maximum for compound (2) at 1700 cm^{-1} and rest all has 1650 cm^{-1}. Compound (3) is producing intensity 50 which least amongst all. Intensity moves upto 120 for compound (1) and (2).

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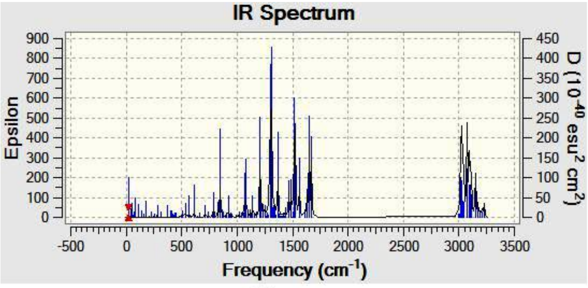
TABLE 1**.** Elctro-optical propertiesofpyridine liquid crystal molecules

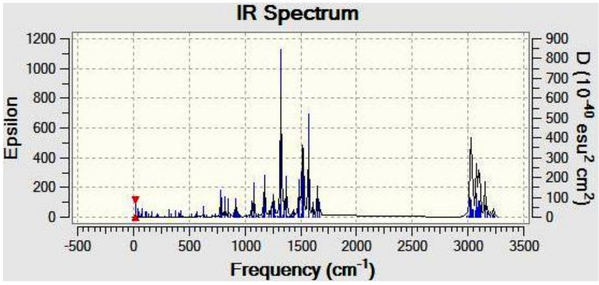
COMPOUND	**POLARIZABILITY (a.u.)**	**TOTAL ENERGY (a.u.)**	**HOMO-LUMO GAP (a.u.)**	**DIPOLE MOMENT (a.u.)**
1	261.31233	-985.81772412	0.17297	2.5430
2	262.18166	-1085.04374730	0.17109	3.8606
3	256.72933	-1085.04356918	0.18457	3.4265
4	291.574	-1028.56133046	0.17937	1.8105
5	292.51533	-1012.52375221	0.18932	0.1768

TABLE 2**.** Spectroscopic propertiesofpyridine liquid crystal molecules

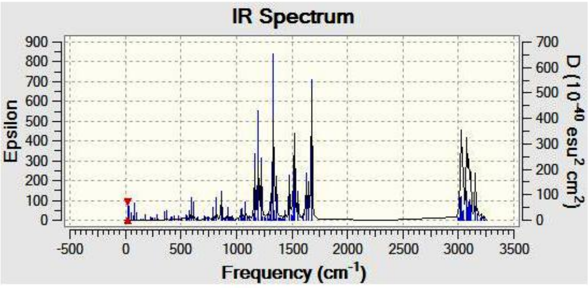
COMPOUND	**INFRA RED**		**RAMAN INTENSITY**	
	Frequency peak (cm^{-1})	**Molar extinction coefficient(ε)**	**Frequency peak (cm^{-1})**	**Intensity**
1	1300	850	1650	120
2	1400	1100	1700	120
3	1400	850	1650	50
4	1500	600	1650	110
5	1500	750	1650	110



(1).



(2).



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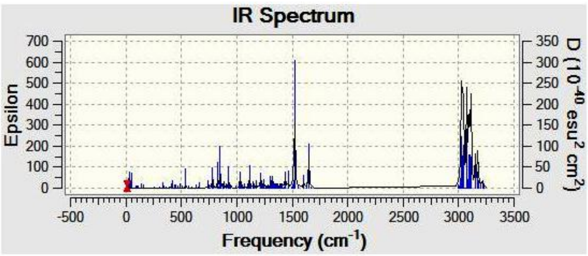
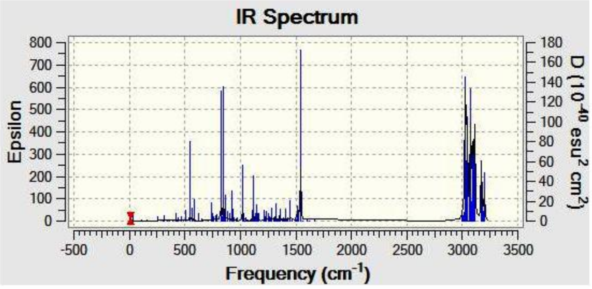
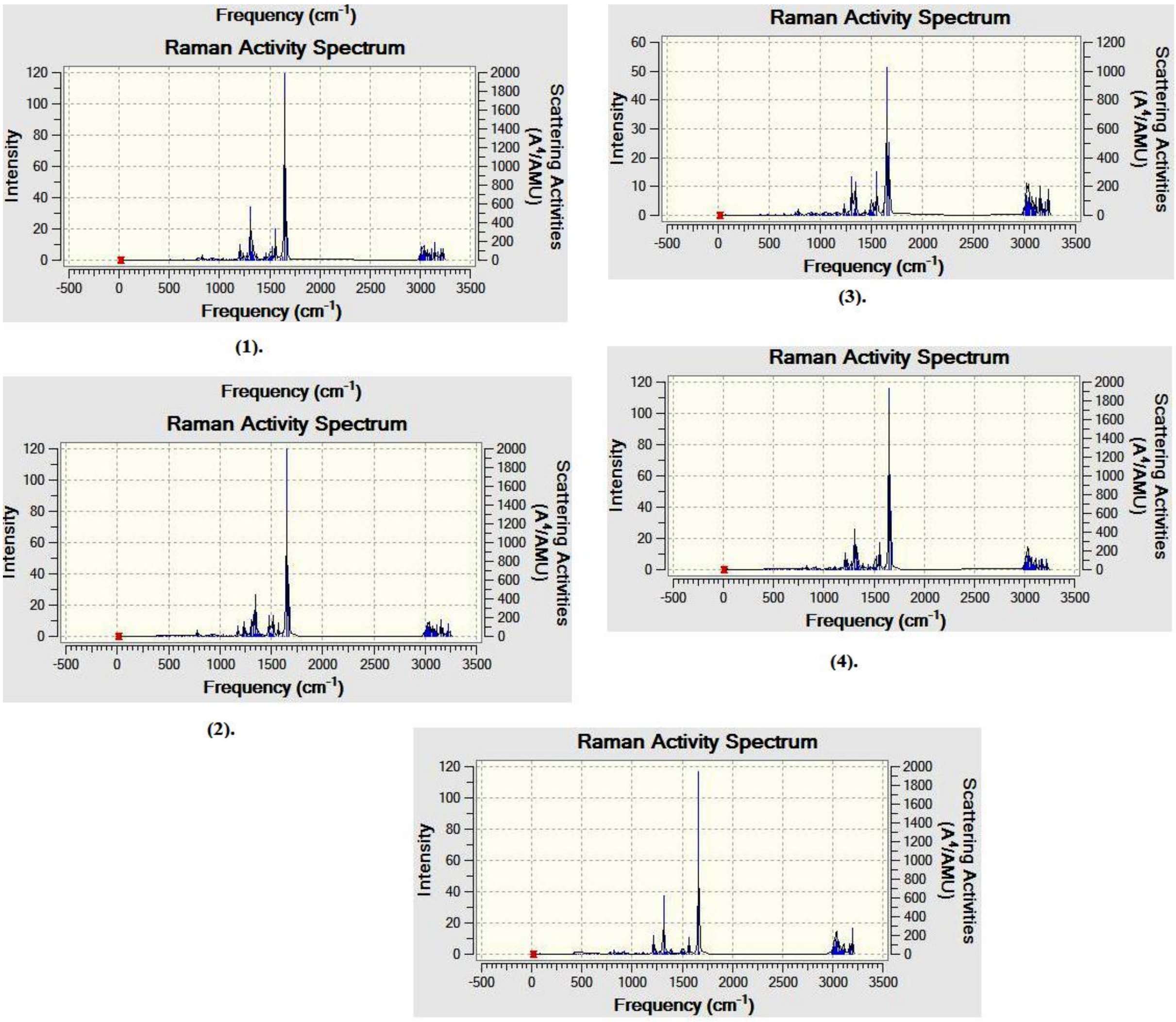


(4).



(5).

Fig.3. IR spectra of some pyridine liquid crystal molecules



(1).

(2).

(3).

(4).

(5).

Fig.3. Raman spectra of some pyridine liquid crystal molecules

IV. DISCUSSION

Total energy of compound (1) is highest and that of compound (2) and (3) is lowest although all these are having almost same basic structure, only difference is the presence of fluorine in (2) and (3) at different positions of benzene ring. HOMO-LUMO gap of compound (5) is greater than all others though HOMO-LUMO gapof compound (3) is very near to that of former. This may be due to absence of any atom having lone pair electrons in former and presence of nitogen in the vicinity fluorine in the latter. This above said reason is also determining factor in generating dipole moment, as we can see dipole moment of compound (5) is lowest and that of compound (2) is highest which is due to presence of oxygen as well as fluorine (two most electronegative atoms) on same side of the molecule. Compound (4) and (5) have most no. of atoms thus having most no. of electrons, leading to higher polarizability amongst all.

All the molecules have same basic structure that is two side by side aromatic rings along with third aromatic ring an alkyl chains at the both ends in (4) and (5) or at one end in (1), (2)and (3). That's why, we are getting simmilar IR and Raman spectra for all these molecules with some minor differences pertaining to presence or absence of atoms like nitrogen, oxygen and fluorine.

V. CONCLUSION

Not only mere presence but also the position of subtituent is affecting the elctro-optical as well as spectroscopic results that will lead to some major differences when present in bulk. These differences at micro level will also be responsible for the changes in optical properties like birefringence, dielectric anisotropy, etc. as well as materialistic features like viscosity, elastic constant, etc.

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