

Electro-optic and spectroscopic study of pyridine liquid crystal molecule and its derivatives

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Abstract: Four pyridine derivative and one similar 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 their electro-optical and spectroscopic details. The present article reports some liquid crystal molecules namely (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, liquid 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 systems. Since long time, liquid crystals (LCs) have been the subject of theoretical and experimental study. By their role in chemical, biological and electro-optical systems, they have many industrial applications. Liquid crystals are powerful solvents in holding donor-spacer-acceptor systems as well as in maintaining the fluid and order property over a wide range of temperatures too. Numerous electronic and optical properties of LC vary with change of substituent. These properties of molecules can be altered by the presence of different substituents. LC molecules 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 of the LC property

of these pyridines is of fundamental importance in chemical physics. Raman scattering depends on the polarizability. The HOMO-LUMO energy gap is effective for the stability of the molecule. Also, the electrical transport property is determined by the HOMO-LUMO gap. [6-7] A superficial study on the vibrational analysis and electro-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-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.

II. METHODOLOGY

The structures were designed using GaussView 5.0.

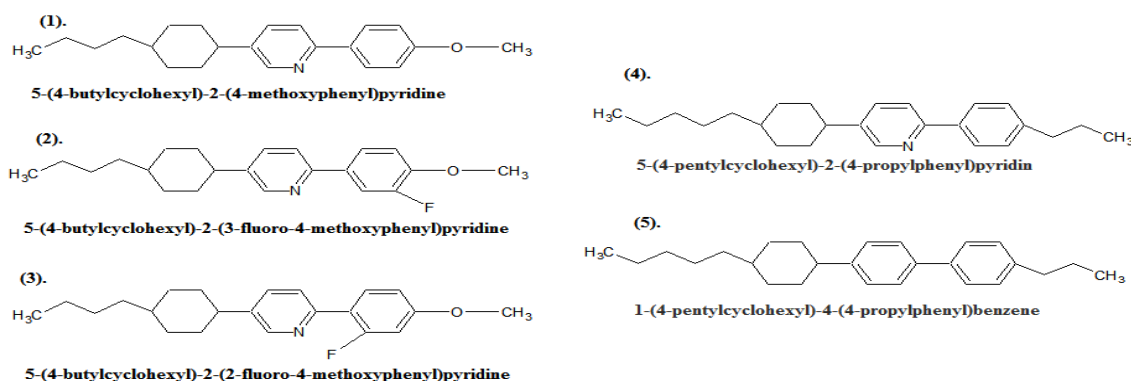


Fig.1. Chemical structures of some pyridine liquid crystal molecules

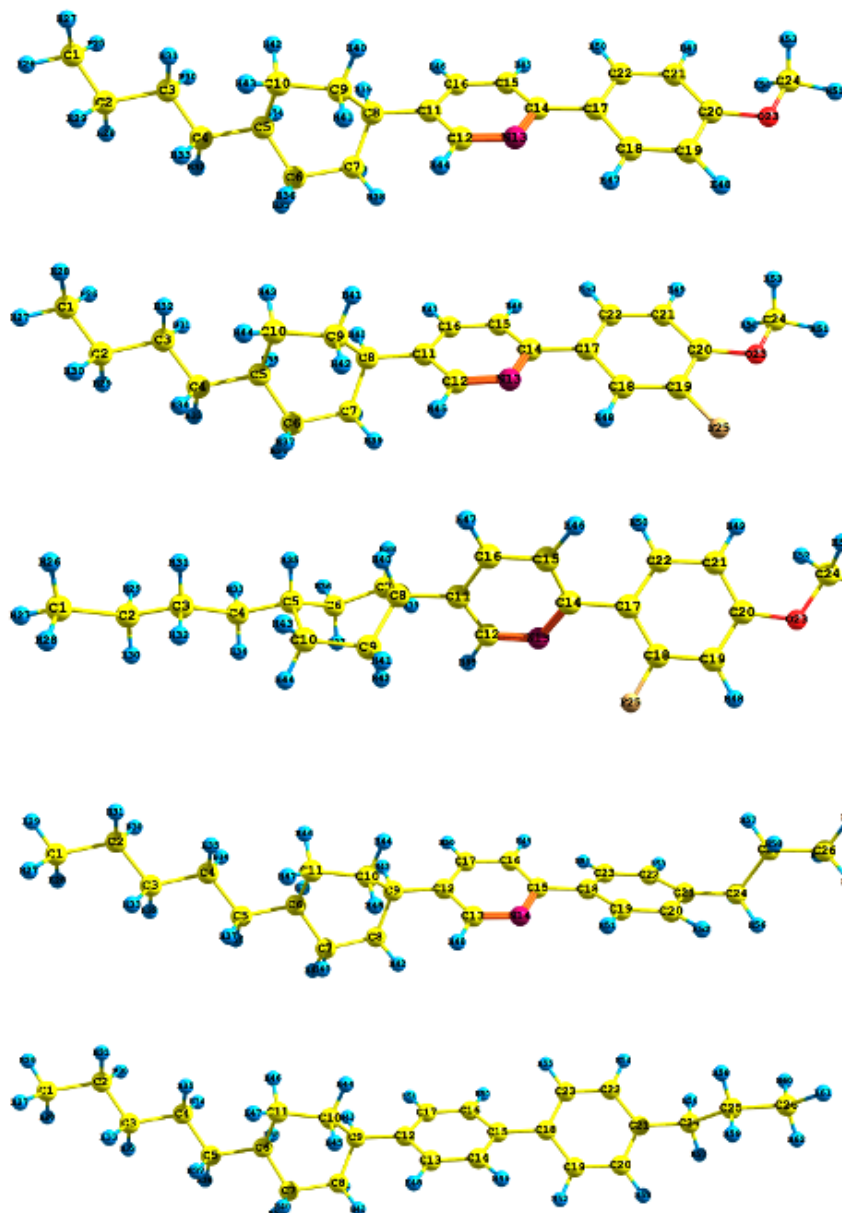


Fig.2. Optimized geometry of some pyridine liquid crystal molecules

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 like polarizability, 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, so obtained, 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

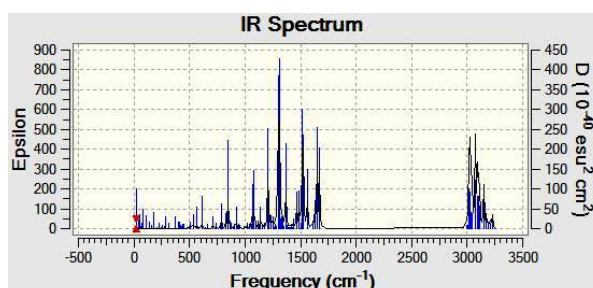
Infra-Red peak frequency is lowest for compound (1) at 1300 cm^{-1} and highest for compound (4) and (5) reaching to 1500 cm^{-1} . Molar extinction coefficient (ϵ) is greatest for compound (2) at 1100 and smallest for compound 4 at 600. Frequency peak of Raman intensity spectra is maximum for compound (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).

TABLE 1. Electro-optical properties of pyridine liquid crystal molecules

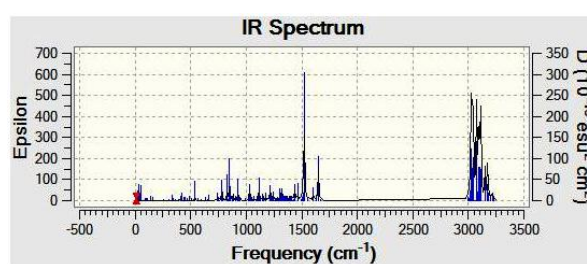
COMPOUND	POLARIZABILITY (a.u.)	TOTAL ENERGY (a.u.)	HOMO-LUMO GAP (a.u.)	DIPOLE MOMENT (a.u.)
1	261.31233	-985.81772412	0.17297	2.5430
2	262.18166	-1085.04374730	0.17109	3.8606
3	256.72933	-1085.04356918	0.18457	3.4265
4	291.574	-1028.56133046	0.17937	1.8105
5	292.51533	-1012.52375221	0.18932	0.1768

TABLE 2. Spectroscopic properties of pyridine liquid crystal molecules

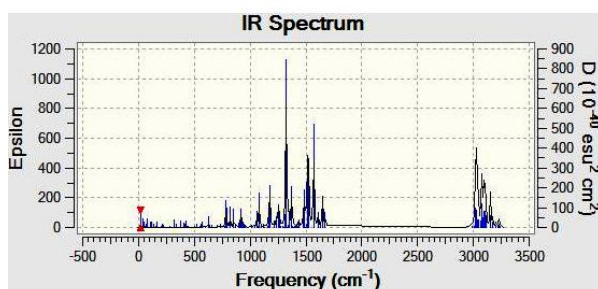
COMPOUND	INFRA RED		RAMAN INTENSITY	
	Frequency peak (cm ⁻¹)	Molar extinction coefficient (ε)	Frequency peak (cm ⁻¹)	Intensity
1	1300	850	1650	120
2	1400	1100	1700	120
3	1400	850	1650	50
4	1500	600	1650	110
5	1500	750	1650	110



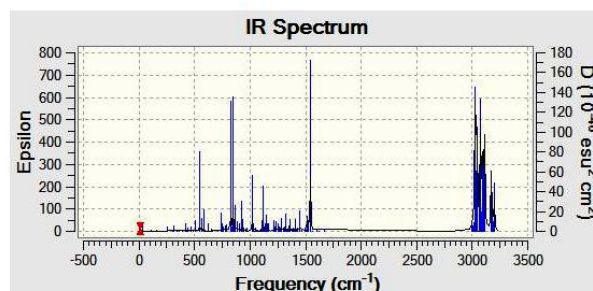
(1).



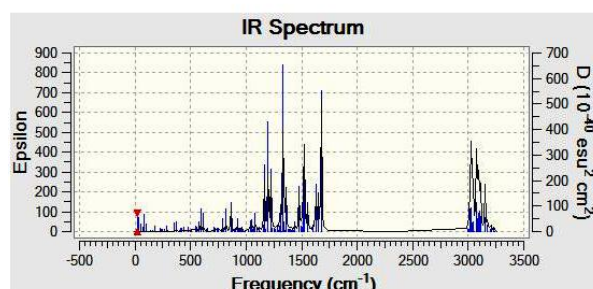
(4).



(2).



(5).



(3).

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

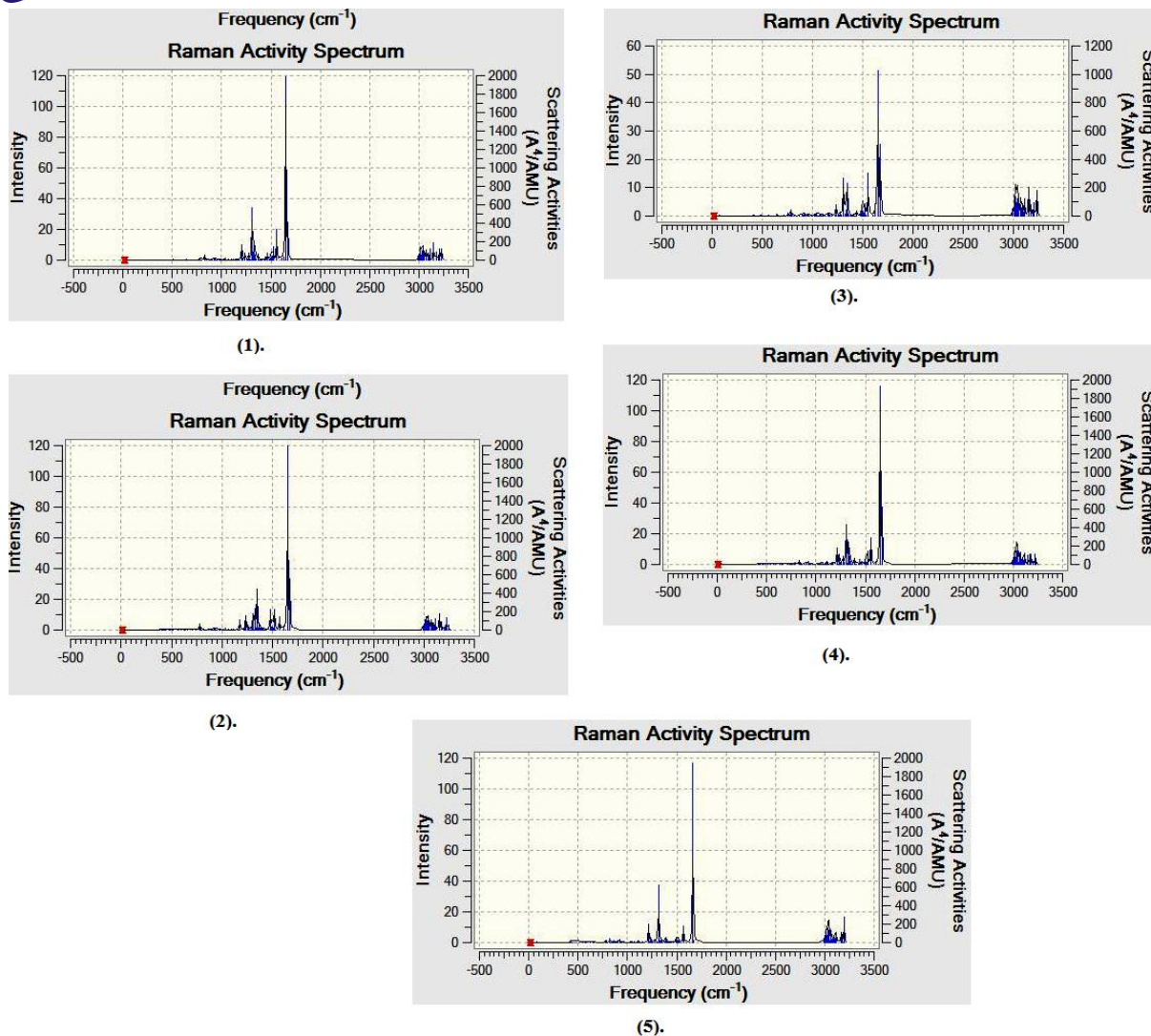


Fig.3. Raman spectra of some pyridine liquid crystal molecules

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 gap of 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 nitrogen in the vicinity of 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 and 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 similar 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 substituent is affecting the electro-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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