Physico-Spectroscopic Study of Pyridine Derivatives of Liquid Crystal Molecules

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Abstract: The pyridine derivative has been examined quantum mechanically to understand its physical and spectroscopic details along with various derivatives. The present work reports some liquid crystal molecules namely **(1).** 2-[4-(4-butylcyclohexyl)-2-fluorophenyl]-5-propylpyridine, **(2).** 2-[4-(4-ethylcyclohexyl)phenyl]-5-propylpyridine**, (3).** 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5-propylpyridine**, (4).** 2-[2-(4-butoxyphenyl) ethyl]-5-(4-ethylcyclohexyl) pyridine**, (5)** 2-{4-[2-(4-butylcyclohexyl) ethyl] phenyl}-5-ethylpyridine and **(6)** 4-ethylcyclohexyl 4-(5-pentylpyridin-2-yl) benzoate having structure of pyridine and its derivative. We have studied some physical and spectroscopic parameters (IR, Raman spectra) for analyzing its nature.

Keywords: Pyridine, Liquid Crystal, Density Functional Theory, Spectoscopic Study.

I. INTRODUCTION

The relation between the liquid crystal (LC) molecule and LC properties had long been of interest [1]. Mesomorphic behavior of LC depends upon the LC molecular structure. Many physical, electronic and optical properties of LC depend upon the nature of substituent. These properties of molecules can be altered by the presence of different substituents, therefore several derivatives of these molecule have been optimized. The effect of substituent depends on whether substituent is electron donating or withdrawing of conjugated systems as well as on the π conjugation length and inter-chain distance of the conjugated segments. LC molecule has a dipole moment directly perpendicular to the molecular axis [2-9]

Pyridine derivatives form an important class of molecules exhibiting liquid crystalline behavior. . The introduction of substituent group in lateral position at terminal and central benzene core decreases thermal stabilities. Theoretical study suggest that the potential around the pyridine molecule in symmetric in nature [10-14].

The present work reports some liquid crystal molecules namely **(1).** 2-[4-(4-butylcyclohexyl)-2-fluorophenyl]-5-propylpyridine, **(2).** 2-[4-(4-ethylcyclohexyl) phenyl]-5-propylpyridine**, (3)** 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine**, (4).**2-[2-(4-butoxyphenyl) ethyl]-5- (4ethylcyclohexyl) pyridine**, (5)** 2-{4-[2-(4-butylcyclohexyl) ethyl] phenyl}-5-ethylpyridine and **(6)** 4-ethylcyclohexyl 4-(5-pentylpyridin-2-yl) benzoate having structure of pyridine and its derivative.

The vibration states of a molecule are observed theoretically through infrared and Raman spectroscopy. These are dependent not only on the electronic properties of individual molecules but also on the properties that are determined in varies physical properties and effect of respective molecule.

II. THEORETICAL METHODOLOGY

Total-energy calculations and Optimization of molecular geometry were carried out through density-functional theory (DFT). It has been successfully applied in the past for characterization and explanation of properties of various class of molecules.[15,16,17] The structures were designed using Gauss View 5.0. The molecular structures were fully optimized without any constrain and frequency were calculated with B3LYP [18] hybrid functional for Gaussian type orbital's (GTOs) and 6-31G** basis set using Gaussian 09[19].

III. RESULTS AND DISCUSSION

Optimized geometry of these molecules has shown in figure 2. Physical and spectral properties of these compounds have been summarized in Table 1 and Table 2 respectively. Spectroscopic results namely Raman Activity and IR spectra have been presented in figure 3 and figure 4.

A. Physical Properties

Total energy of compounds lie in between -900 atomic unts (a.u.) to -1200 a.u. There is very little variation in HOMO-LUMO gap. Values of all these compounds vary from 0.17533 to 0.18797. Dipole moment of compound 1 is lowest and around 0.5 a.u. while values of dipole moment of other molecules are far away fom this and lie in between 1.0544 a.u. to 1.7247 a.u. Compound 5 is having lowest polarizability 222.6523 a.u. and for rest of compounds, it reaches towards around 300 a.u.

B. Spectroscopic Properties

Infra Red peaks of all compounds except (4) and (6) lies in between 1500 to 1550 cm^{-1} and molar extinction coefficient (epsilon) for these two are highest i.e 1200 and 1650 respectively. Raman lies in between 1650 to 1700 18 except for compound (4) whose intensity is also lowest i.e while for others intensity is between 90 to 130.
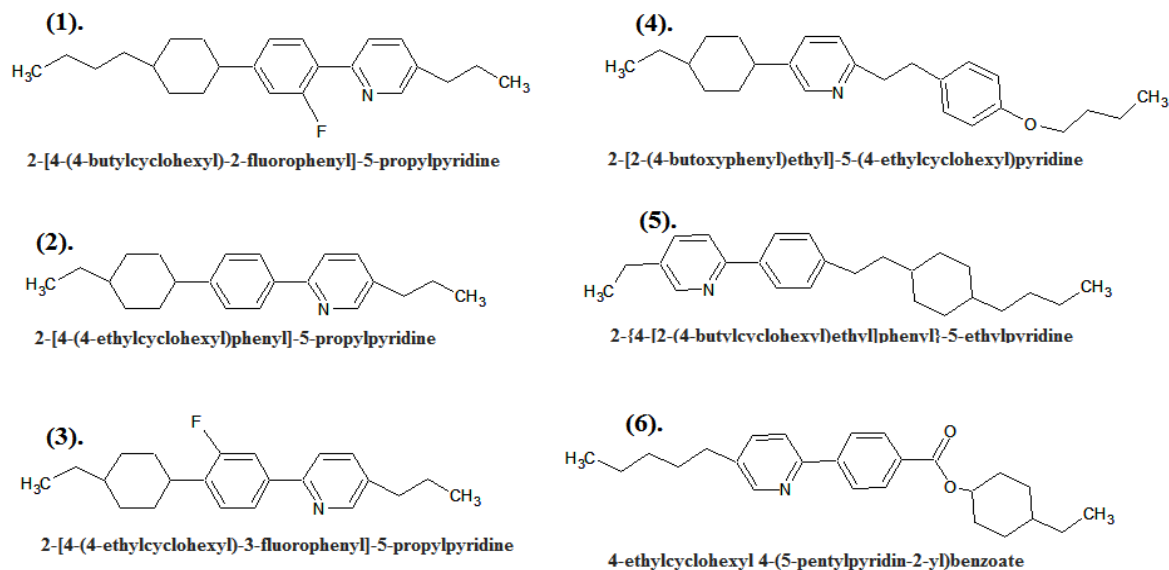
(1). 2-[4-(4-butylcyclohexyl)-2-fluorophenyl]-5-propylpyridine

(4). 2-[2-(4-butoxyphenyl)ethyl]-5-(4-ethylcyclohexyl)pyridine

(2). 2-[4-(4-ethylcyclohexyl)phenyl]-5-propylpyridine

(5). 2-{4-[2-(4-butylcyclohexyl)ethyl]phenyl}-5-ethylpyridine

(3). 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5-propylpyridine

(6). 4-ethylcyclohexyl 4-(5-pentylpyridin-2-yl)benzoate

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

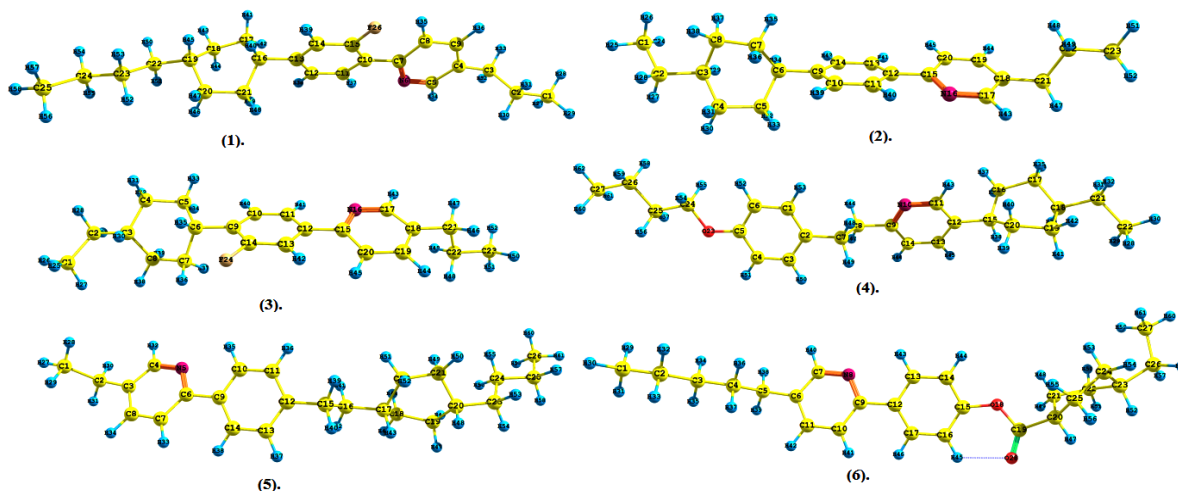(1). (2). (3). (4). (5). (6).

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

TABLE1. Physical properties of pyridine liquid crystal molecules

COMPOUND	TOTAL ENERGY (a.u.)	HOMO-LUMO GAP (a.u.)	DIPOLE MOMENT (a.u.)	POLARIZABILITY (a.u.)
1	- 1088.477352	0.17888	0.4659	280.5273
2	- 910.614177	0.1784	1.655	256.4026
3	- 1009.846259	0.1773	1.7247	256.2623
4	- 1103.76640406	0.18797	1.0544	283.6263
5	- 1028.55954086	0.17908	1.5985	222.6523
6	- 1177.80098178	0.17533	1.1658	298.0916

TABLE2. Spectroscopic properties of pyridine liquid crystal molecules

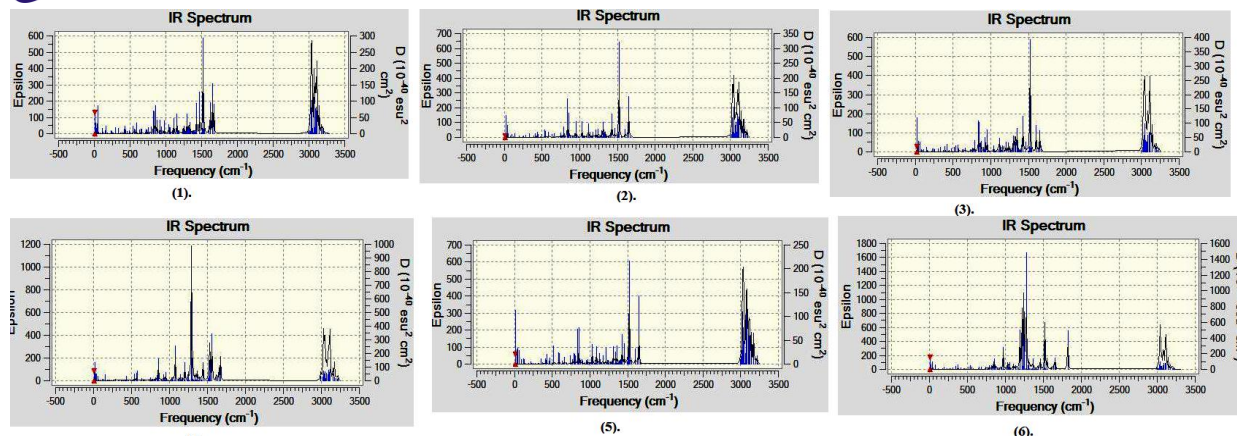| COMPOUND	INFRA RED		RAMAN (cm^{-1}) peak	
	Frequency peak (cm^{-1})	Molar extinction coefficient (ε)	Frequency peak (cm^{-1})	Intensity
1	1550	600	1650	100
2	1500	650	1700	110
3	1550	600	1650	90
4	1300	1200	1350	18
5	1500	600	1700	90
6	1250	1650	1650	130

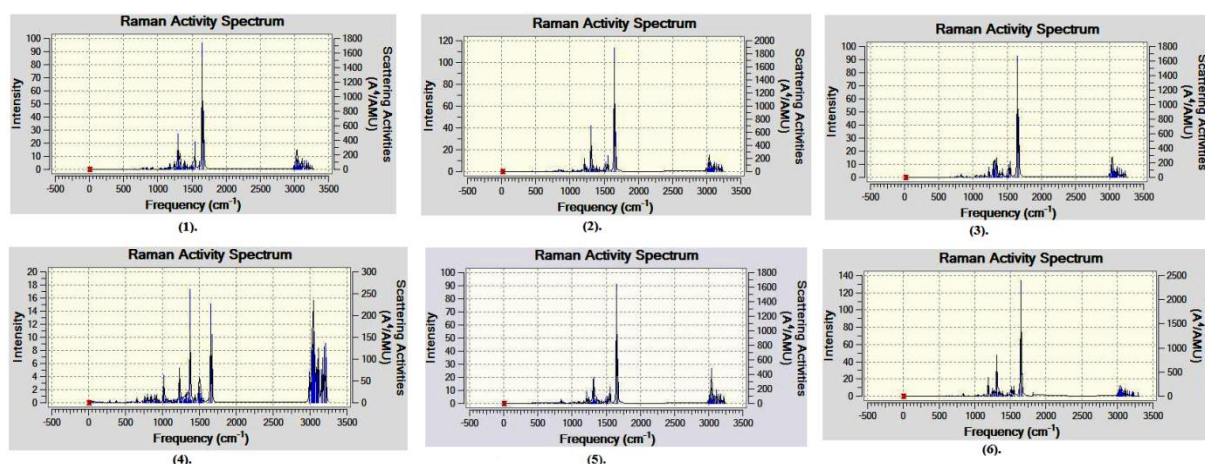Fig.3. IR spectra of some pyridine liquid crystal molecules

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

IV. CONCLUSION

Total energy of compound (6) is lowest due to presence of acetyl group, making itnot only most stable but also has the highest polaizability amongst all. As we can see compound (4) which also has oxygen atom towards one end has the second highest polarizability. In compound (1), both nitrogen as well as fluorine are on the same side producing lowest dipole moment while in compound (3), when both are on opposite, producing highest dipole moment. HOMO-LUMO gap of compound (5) is highest due to absence of nitrogen or oxygen atom like in other compounds.

Peak frequencies of IR spectra for compounds (4) and (6) are lower than others due to oxygen atoms, for the same reason their molar extinction coefficient (ε) is highest. Peak frequency and intensity for Raman is lowest for compound (4). We can see from optimized structure of compound (6), there is a hydrogen bond between oxygen of acetyl and hydrogen of cyclohexane.

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