Spectroscopic analysis of 2,5-Disubstituted Pyridine Derivatives: Part II

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ABSTRACT

Structure–property relationship has been a key issue for the study of liquid crystals. Structure and bonding in liquid crystals is important and diverse field in the interface between modern physics and chemistry. Geometrical anisotropy of small molecules with high polarizability may exhibit one or more liquid crystalline phases as well the familiar crystalline and isotropic phases. Characteristically, it is observed that liquid crystalline compounds have a rigid core, which acts as the mesogenic unit and flexible alkyl chains at the terminal ends. The strong dipole-dipole interaction exhibits the crystalline phase and has higher thermal stability.Pyridine derivatives form an important class of molecules exhibiting liquid crystalline behavior. The pyridine derivative has been examined quantum mechanically to understand its physical and spectroscopic details along with various derivatives. The present work reports a liquid crystal molecules namely 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine. This molecule undergoes mesogenic phase as Cr 47.6 N 127.5 I. Its IR spectra as well as Raman activities is analised. The atomic charges with point dipoles were also computed. The Humo-Lumo gap as representation of band gap, thus computed.

Keywolds: 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine, Liquid Crystals, Mesogen, IR Spectra, Raman Activities

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1. 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 a liquid crystal molecule namely 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine. 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. The vibration states of a molecule are observed theoretically through infrared and Raman spectroscopy.

2. COMPUTATIONAL METHOD

The geometry was optimized using DFT method B3LYP [15,16] using 6-31G** [17, 18] which was found suitable for these type of systems [19] with keeping all atoms free. The analytical frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit.[20]

3. RESULTS

The optimized geometry of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule is shown in figure 1. The inter ring angle between phenyl-pyridine ring is 15.9° and inter ring separation is 1.48Å. The alkyl

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chain is trans (83.3°) to biphenyl ring and separation is 1.51Å. The cylcohexane is also trans (102.5°) to phenyl with separation 1.52Å. The cyclohexane is in boat configuration.
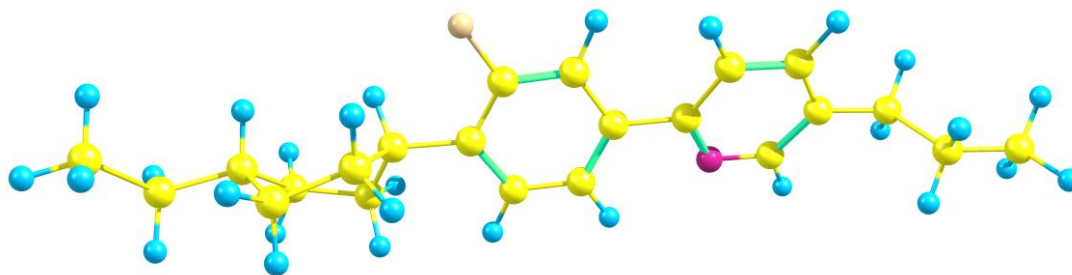

Figure 1: The optimized structure of the 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule. Table 1 present the charges as well as multipoles corresponding each atoms of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule. Since multipole depends on the coordinates of each atoms therefore coordinates are aslo tabulated here.

Table 1: The charge, coordinates and multipoles corresponding each atoms of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	10.13446	5.30511	-2.48502	0.53168	0.002396	0.013214	-0.12907
2	C	9.6714	4.07461	-1.69685	0.448652	0.142106	-0.14576	0.3311
3	C	8.1959	4.10095	-1.26023	0.521865	-0.08521	-0.4985	-0.51938
4	C	7.90769	2.97856	-0.22868	-0.40341	0.323393	1.050761	1.515512
5	C	6.42053	2.55646	-0.17326	3.499164	-0.14814	1.391981	-2.94826
6	C	5.50619	3.74802	-0.4954	-2.25231	-7.19645	-0.40099	0.925759
7	C	5.74218	4.19403	-1.97027	0.959114	0.94562	0.845334	0.777451
8	C	7.20444	3.98389	-2.42999	-0.20339	-0.30751	-0.90224	0.035992
9	C	4.03199	3.51603	-0.22598	-0.91624	-2.67959	-1.42546	0.382313
10	C	3.42736	2.2532	-0.15743	-0.56064	-0.03442	-1.0296	-0.02802
11	C	2.06164	2.10144	0.07358	-0.10393	-0.19993	0.369808	0.088039
12	C	1.229	3.21855	0.24165	-0.49168	0.664801	0.223911	-0.1274
13	C	1.81586	4.49299	0.18237	-0.19695	-0.15213	-0.22245	0.026872
14	C	3.1768	4.6076	-0.04828	0.433181	0.707892	1.100083	-0.07753
15	C	-0.22713	3.03313	0.47835	0.379664	1.209699	-0.15009	-0.11084
16	N	-0.62763	1.79732	0.83394	-0.21067	-0.51398	0.340126	-0.03811
17	C	-1.92368	1.58269	1.05897	-0.09764	0.291377	0.284491	-0.0766
18	C	-2.92558	2.55684	0.95503	-0.1411	-0.68438	-0.41179	0.146365
19	C	-2.5017	3.83535	0.57657	0.019222	0.585398	-0.58165	0.094691
20	C	-1.15455	4.07865	0.33295	-0.26892	0.094942	-0.26446	0.0507
21	C	-4.37841	2.2246	1.19698	0.197859	-0.08403	-0.01953	-0.29819
22	C	-5.15033	1.8913	-0.09646	-0.09343	-0.33084	-0.3026	-0.02244
23	C	-6.62246	1.55699	0.15998	0.437456	-0.15687	0.01268	0.040603
24	F	3.71049	5.85667	-0.09364	-0.55773	0.077442	0.296123	0.004985
25	H	9.98727	6.22358	-1.90504	-0.14383	-0.01723	0.136859	0.080969
26	H	11.1994	5.23611	-2.73043	-0.16663	0.172013	-0.00246	-0.03507
27	H	9.58917	5.41883	-3.42753	-0.21303	-0.08997	0.037611	-0.18257

28	H	10.29732	3.97337	-0.7997	-0.3044	0.153576	-0.01522	0.18251
29	H	9.84882	3.16647	-2.29078	-0.18626	0.034236	-0.12031	-0.1015
30	H	8.01694	5.07066	-0.77089	0.024048	-0.07512	0.040067	0.023202
31	H	8.23611	3.31434	0.76273	-0.48512	0.113715	0.065524	0.286436
32	H	8.51954	2.09976	-0.47074	0.193404	-0.03965	-0.00355	-0.03895
33	H	6.18407	2.13999	0.81218	0.023894	0.035663	-0.03012	0.076552
34	H	6.23704	1.75368	-0.89902	-1.00159	-0.11479	-0.49311	-0.21059
35	H	5.81306	4.58037	0.15071	1.133089	0.248406	-0.42762	-0.46294
36	H	5.45697	5.24729	-2.06398	-0.26884	-0.11279	0.165705	-0.01683
37	H	5.06891	3.63063	-2.62687	0.160604	-0.00638	0.000725	0.010863
38	H	7.44281	4.70081	-3.22288	0.16726	0.050712	0.008601	0.036371
39	H	7.31689	2.98706	-2.87873	-0.31178	0.028952	-0.17273	-0.1532
40	H	4.03947	1.36572	-0.28322	-0.11668	0.038348	-0.13239	-0.01153
41	H	1.61753	1.1148	0.13106	0.187499	0.037332	0.007071	-0.01171
42	H	1.24607	5.4025	0.33428	0.163833	0.035951	0.023131	-0.01692
43	H	-2.19204	0.5666	1.35085	0.190584	0.037336	0.026831	-0.01715
44	H	-3.22607	4.63986	0.47033	0.346841	0.101586	-0.08594	0.00112
45	H	-0.83309	5.06588	0.02041	0.237259	-0.05666	-0.05084	0.026447
46	H	-4.87072	3.06791	1.69875	-0.02559	-0.01959	0.056322	0.043919
47	H	-4.44856	1.37181	1.88406	-0.04659	0.003488	-0.06551	0.072549
48	H	-5.07595	2.74122	-0.78696	0.06111	0.037956	0.022219	-0.00852
49	H	-4.65762	1.04906	-0.59833	-0.08269	0.078967	-0.0753	-0.07459
50	H	-7.14382	2.39577	0.63527	-0.17304	-0.08339	0.146123	0.07721
51	H	-7.14534	1.32646	-0.77371	-0.14749	-0.07874	-0.0371	-0.14594
52	H	-6.72344	0.68848	0.82076	-0.14572	-0.01889	-0.12701	0.094366

Various energies components with zero point corrections of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecules.

Energies Components	Hartree
Sum of electronic and zero-point Energies	-1009.39
Sum of electronic and thermal Energies	-1009.37
Sum of electronic and thermal Enthalpies	-1009.37
Sum of electronic and thermal Free Energies	-1009.45

Table 3 presents dipole moment, exact polarizability, approx. and polarizability of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecules. The band gap (Humo-Lumo) is 4.83 eV. The ionization potential is 5.91 eV and electron affinity is 1.08 eV.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecules.

Dipole Monent	3.6149 debye
Exact Polarizability	153.196
Approx Polarizability	230.454

The IR spectra of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecules molecule is shown in figure 2. From figure 2 it can be visualized that there are several peak and the highest peak (IR intensity) is at

1522.7660 cm^{-1}. This frequency is associated with twisting of pyridine ring attached with alkyl chain. Second peak is at 1604.5138 cm^{-1}. This frequency is associated with twisting of phenyl ring. Other peak height is at 3034.4780 cm^{-1} that is associated with twisting of cyclohexane.
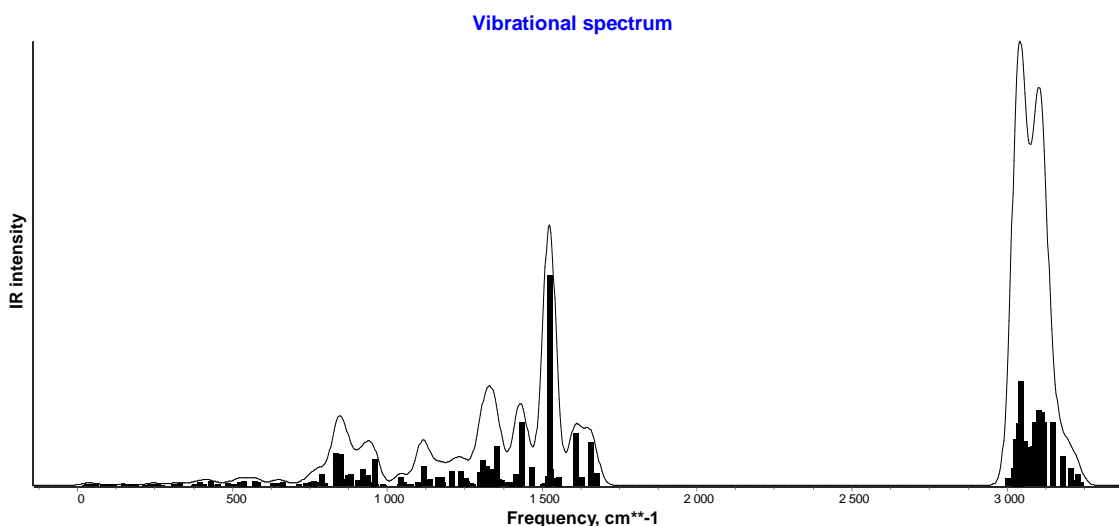

Figure 2: IR Spectra of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule.

Figure 3 represent Raman activities of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule. There are various peaks and the highest Raman activity is at 1651.8520 cm^{-1} which are associated with twisting of pyridine ring. Next peak is at 3029.6096 cm^{-1} that associated with alkyl chain stretching.
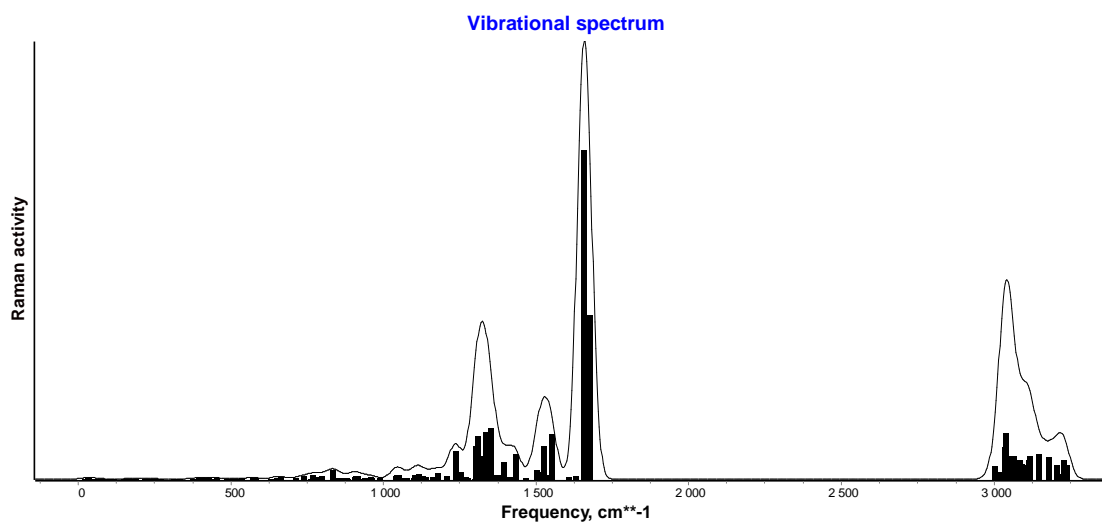

Figure 3: Raman activity of 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine molecule.

4. CONCLUSION

The electronic structure analysis of on 2-[4-(4-ethylcyclohexyl)-3-fluorophenyl]-5propylpyridine. The IR peaks and Raman activities peaks were explained.

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