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

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ABSTRACT
Geometrical anisotropy of small molecules with high polarizability may exhibit one or more liquid crystalline phases as well the familiar crystalline and isotropic phases. Structure and bonding in liquid crystals is important and diverse field in the interface between modern physics and chemistry. Structure–property relationship has been a key issue for the study of liquid crystals. 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)phenyl]-5-propylpyridine. This molecule undergoes mesogenic phase as Cr 51 Sm 94 N 157.8 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)phenyl]-5-propylpyridine, Liquid Crystals, Mesogen, IR Spectra, Raman Activities*

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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 a liquid crystal molecule namely 2-[4-(4-ethylcyclohexyl) phenyl]-5-propylpyridine. 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.

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]

II. RESULTS

The optimized geometry of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine molecule is shown in figure 1. The inter ring angle between phenyl-pyridine is 16.3^o and inter ring separation is 1.48Å. The alkyl chain is trans (81.6^o) to biphenyl ring and separation is 1.51Å. The cylcohexane is also trans (121.3^o) to phenyl with separation 1.52Å. The cyclohexane is in boat configuration.

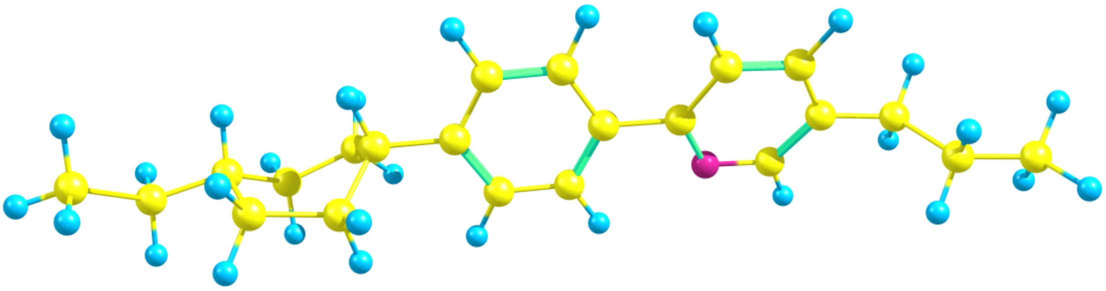

Figure 1: The optimized structure of the 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine 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) phenyl]-5- propylpyridine molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	10.20914	5.09556	-2.51381	0.494302	-0.1579	0.139213	-0.02728
2	C	9.69301	3.94456	-1.64216	0.551102	-0.02756	-0.14596	-0.11201
3	C	8.21752	4.07041	-1.22727	0.460027	-0.40503	-0.31135	0.374421
4	C	7.79266	2.94474	-0.27023	-0.30467	0.19059	-0.40793	0.059363
5	C	6.3796	3.17849	0.31214	0.777711	0.347495	0.466261	-0.1776
6	C	5.44313	3.94752	-0.66445	-0.42612	-1.44314	-0.23985	0.439865
7	C	5.83077	3.60988	-2.11946	0.59486	-0.19701	0.138558	0.080877
8	C	7.25946	4.104	-2.4479	-0.18701	-0.36175	0.036616	0.137553
9	C	3.97418	3.70807	-0.36599	0.016942	-0.38912	0.512954	0.203359
10	C	3.38533	2.44272	-0.52389	0.045346	-0.75451	0.200055	0.194299
11	C	2.03765	2.23209	-0.25475	-0.39989	-0.42408	-0.0333	0.144189
12	C	1.21405	3.28301	0.18491	-0.09971	-0.64912	-0.56642	-0.00888
13	C	1.80159	4.54561	0.35558	-0.15788	-0.04977	-0.82964	-0.18643
14	C	3.15305	4.75005	0.08197	-0.37339	-0.59457	0.346435	0.223125
15	C	-0.22589	3.03034	0.45548	-0.19459	-0.10818	0.040859	0.118331
16	N	-0.60334	1.74244	0.57376	-0.08159	-0.47239	0.319698	0.011858
17	C	-1.88496	1.4675	0.81672	-0.08338	-0.10144	0.264533	0.052145
18	C	-2.89497	2.42684	0.96473	-0.05138	-0.11797	0.61404	-0.03428
19	C	-2.49645	3.76184	0.83274	-0.29399	0.230082	0.490881	-0.03804
20	C	-1.16584	4.06921	0.57343	-0.35288	0.053484	-0.523	-0.02585
21	C	-4.33213	2.03228	1.20739	0.579523	0.180697	0.112085	-0.29964
22	C	-5.18018	1.99971	-0.08087	-0.10607	-0.17588	-0.07033	-0.29108
23	C	-6.63693	1.60489	0.17759	0.703892	-0.06233	-0.0507	0.177174
24	H	10.08962	6.05983	-2.00581	-0.19151	-0.00834	0.162513	0.081965
25	H	11.27312	4.97106	-2.74061	-0.09948	0.128742	-0.01236	-0.03404
26	H	9.67492	5.1558	-3.46762	-0.20927	-0.08664	0.018082	-0.19568
27	H	10.30942	3.87881	-0.73548	-0.1745	0.096527	-0.00863	0.132053
28	H	9.83184	2.99191	-2.17356	-0.26115	0.03717	-0.18681	-0.08918
29	H	8.11211	5.0216	-0.68239	-0.12744	-0.0089	0.109793	0.010941

30	H	8.51805	2.84367	0.546	-0.06268	0.070212	0.00795	0.082573
31	H	7.82025	1.9925	-0.8179	-0.13509	0.000552	-0.13985	-0.06549
32	H	6.44475	3.74109	1.25104	-0.2838	0.007655	0.087281	0.224059
33	H	5.92677	2.21398	0.56802	0.016901	-0.05292	-0.02849	-0.00553
34	H	5.62438	5.02219	-0.52841	0.179276	0.056535	-0.0555	-0.03701
35	H	5.10908	4.0499	-2.81602	-0.24504	-0.13229	0.084823	-0.15385
36	H	5.76715	2.52368	-2.26179	-0.04654	0.000381	-0.06715	0.034961
37	H	7.21129	5.1248	-2.84453	0.000072	0.030249	0.058207	-0.0351
38	H	7.67535	3.48339	-3.25298	0.089691	0.030201	0.016175	0.004532
39	H	3.98973	1.60641	-0.86602	0.258953	-0.02451	0.059642	0.027811
40	H	1.5958	1.24978	-0.37799	0.099688	0.066191	-0.03746	-0.03581
41	H	1.213	5.37952	0.72533	0.333246	0.104578	-0.08056	-0.0571
42	H	3.58032	5.73954	0.22713	0.099518	0.020127	0.016294	0.001395
43	H	-2.13332	0.40931	0.90866	0.203335	0.056718	0.052359	-0.01482
44	H	-3.22859	4.56069	0.92932	0.066509	-0.02722	0.02618	0.002174
45	H	-0.86637	5.10389	0.44975	0.322962	-0.04394	-0.11357	0.027487
46	H	-4.79189	2.73105	1.91871	-0.1163	-0.06873	0.075572	0.091129
47	H	-4.36465	1.04289	1.68086	-0.05242	0.011169	-0.07865	0.045876
48	H	-5.14039	2.98609	-0.56049	-0.05853	0.014863	0.096212	-0.03673
49	H	-4.72254	1.29888	-0.79035	-0.08734	0.072987	-0.0704	-0.07521
50	H	-7.12476	2.31056	0.85983	-0.22663	-0.09478	0.146561	0.122036
51	H	-7.21492	1.5869	-0.7519	-0.16679	-0.09839	-0.00267	-0.15514
52	H	-6.70359	0.60901	0.63033	-0.23679	-0.01092	-0.20491	0.079834

Various energies components with zero point corrections of H9CBP molecule is tabulated in Table 2.

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

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-910.152351
Sum of electronic and thermal Energies	-910.129918
Sum of electronic and thermal Enthalpies	-910.128974
Sum of electronic and thermal Free Energies	-910.207479

Table 3 presents dipole moment, exact polarizability, approx. and polarizability of H9CBP molecules. The band gap (Humo-Lumo) is 4.46 eV. The ionization potential is 5.97 eV and electron affinity is 1.51 eV.

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

Dipole Monent	3.2359 debye
Exact Polarizability	156.01
Approx Polarizability	232.319

The IR spectra of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine 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 1521.8309 cm^{-1}. This frequency is associated with twisting of pyridine ring attached with alkyl chain. Second peak is at 1651.4277 cm^{-1}. This frequency is associated with twisting of phenyl ring. Other peak height is at 3041.4470 cm^{-1} that is associated with twisting of alkyl chain.

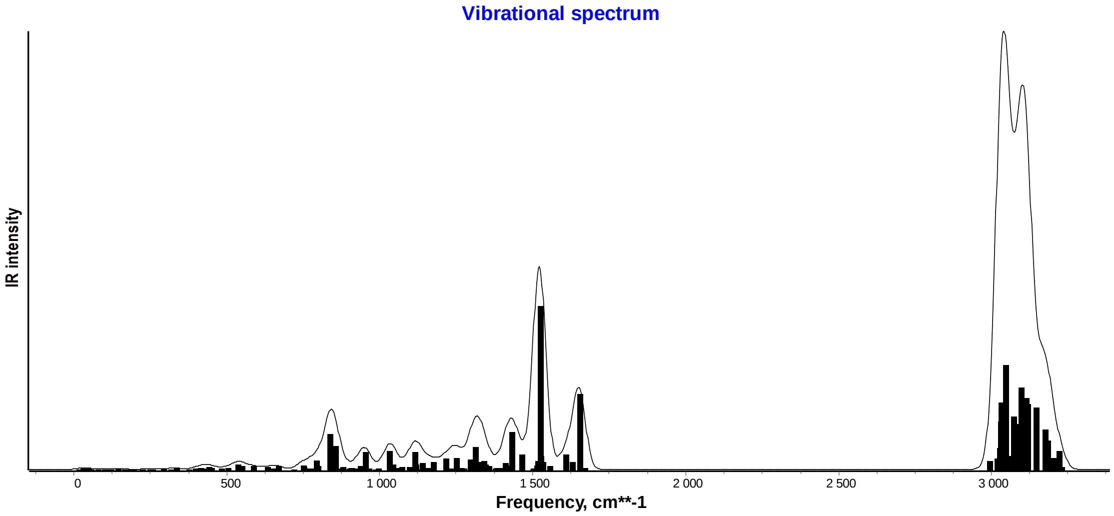

Figure 2: IR Spectra of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine molecule.

Figure 3 represent Raman activities of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine molecule. There are various peaks and the highest Raman activity is at 1651.4277 cm^{-1} which are associated with twisting of pyridine ring. Next peak is at 1390.7178 cm^{-1} that associated with alkyl chain stretching.

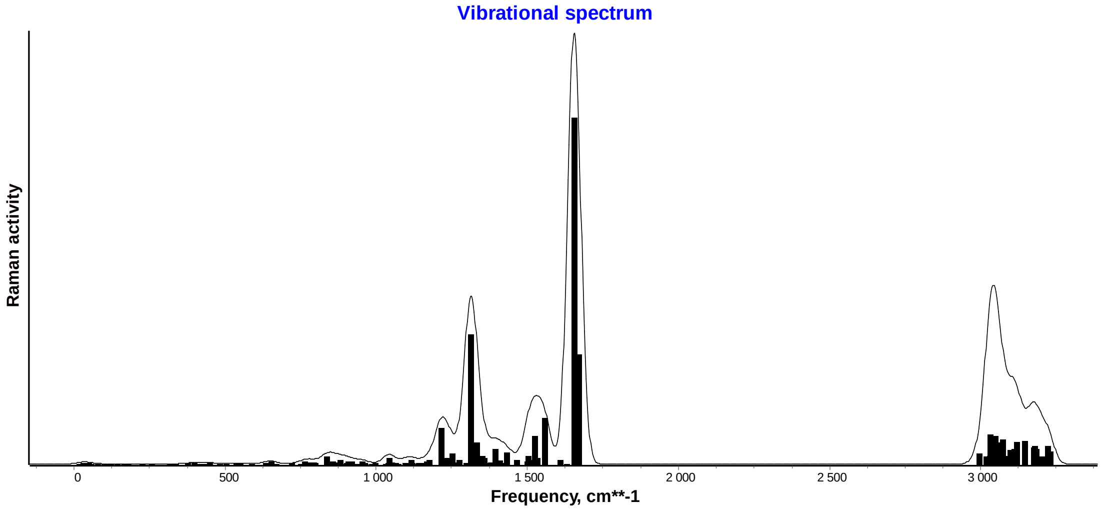

Figure 3: Raman activity of 2-[4-(4-ethylcyclohexyl) phenyl]-5- propylpyridine molecule.

III. CONCLUSION

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

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