International Journal of Engineering Inventions
e-ISSN: 2278-7461, p-ISSN: 2319-6491
Volume 11, Issue 12 [December. 2022] PP: 85-89

Spectroscopic analysis of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl) pyridine

Vinod Kumar Singh[1], R.K.Singh*[2], A.K. Dwivedi[3]
[1]*Deparment of Chemistry,*
Shivpati Degree College,ShohratGarh,SiddharthNagar (U.P.) 272205 INDIA
[2]*Deparment of Chemistry,*
M. L. K. P. G. College Balrampur (U.P.) 271201 INDIA
[3]*Deparment of Physics,*
M. L. K. P. G. College Balrampur (U.P.) 271201 INDIA

ABSTRACT

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. 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. 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 strong dipole-dipole interaction exhibits the crystalline phase and has higher thermal stability. The present work reports a liquid crystal molecules namely 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine. This molecule undergoes mesogenic phase as Cr 45.2 N 174.5 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: 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine, Liquid Crystals, Mesogen, IR Spectra, Raman Activities

---

Date of Submission: 04-12-2022 Date of Acceptance: 16-12-2022

---

1. 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 are powerful 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]

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 [8-12].

The present work reports a liquid crystal molecule namely 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine. 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 [13,14] using 6-31G** [15, 16] which was found suitable for these type of systems [17] with keeping all atoms free. The analytical frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit.[18]

3. RESULTS

The optimized geometry of 2-[2-(4-butoxyphenyl) ethyl]-5- (4ethylcyclohexyl) pyridine molecule is shown in figure 1. The phenyl ring and pyridine ring is connected with ethyl group and phenyl ring and pyridine ring separated with ethyl group by 1.51Å. The alkoxy chain is plannar (06.3^{o}) to phenyl ring and separation is 1.137Å. The cylcohexane is also trans (102.6^{o}) to pyridine ring with separation 1.52Å. The cyclohexane is in boat configuration.

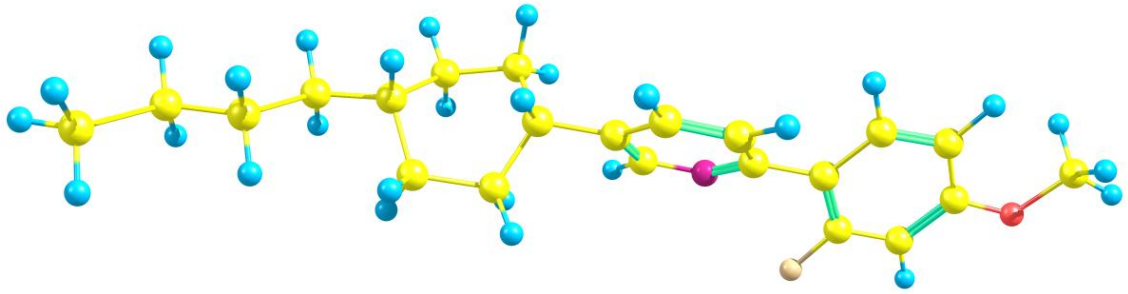

Figure 1: The optimized structure of the 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine.

Table 1 present the charges as well as multipoles corresponding each atoms of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine 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 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.422604	0.36263	1.044781	-0.132649	0.27708	0.05816	-0.24931
2	C	-0.514991	1.398043	0.994958	0.113982	-0.24114	0.023404	0.131429
3	C	-0.318067	2.405579	0.036591	-0.121991	0.64141	-0.29357	-0.29642
4	C	0.765013	2.378834	-0.833703	-0.121315	0.19927	-0.01136	-0.14781
5	C	1.693991	1.329922	-0.769921	0.333589	-0.14473	-0.07613	0.210586
6	C	1.51927	0.316171	0.179015	-0.142085	-0.05268	-0.06936	0.088506
7	C	-1.715896	1.409038	1.914357	-0.239563	-0.09116	0.14476	-0.19335
8	C	-2.944279	0.681617	1.312715	-0.203368	-0.01337	-0.07408	0.338624
9	C	-4.099604	0.59997	2.284044	0.219607	-0.0345	0.294845	-0.34202
10	N	-3.910823	-0.17242	3.369748	-0.400078	-0.7375	0.31882	-0.00034
11	C	-4.899678	-0.26915	4.260784	0.016973	0.13224	-0.42004	0.613332
12	C	-6.139297	0.381751	4.156062	0.113636	1.31571	0.710417	-2.26581
13	C	-6.316557	1.184221	3.025893	-0.101321	-0.26174	0.511185	-0.53917
14	C	-5.295701	1.29682	2.083259	-0.113061	-0.18892	0.000383	0.099271
15	C	-7.221043	0.224162	5.207587	-0.124816	2.09797	0.375937	-1.94192
16	C	-7.770456	-1.23064	5.279336	-0.179673	-0.98174	0.419994	-0.21222
17	C	-8.416966	-1.55985	6.644027	-0.183005	-0.03875	-0.59664	0.105945

18	C	-9.063373	-0.32392	7.290157	-0.039518	0.60493	-0.43436	0.277222
19	C	-7.970301	0.735969	7.591656	-0.1828	-0.21675	1.041634	-0.51098
20	C	-6.772901	0.675995	6.613678	-0.181594	-0.33333	-1.75415	0.055013
21	C	-9.884709	-0.69168	8.537525	-0.170122	-0.18209	0.142315	0.079087
22	C	-10.63422	0.484537	9.173962	-0.31653	-0.10295	0.125745	-0.03066
23	O	2.725638	1.391444	-1.664272	-0.509655	-0.5642	0.289096	0.226844
24	C	3.700451	0.352557	-1.654816	0.068862	-0.96931	0.10867	0.817322
25	C	4.715642	0.65357	-2.749157	-0.19073	-0.59868	0.558258	0.007693
26	C	5.818044	-0.40901	-2.837288	-0.179447	-0.11849	-0.0973	0.320536
27	C	6.841697	-0.11401	-3.938284	-0.309898	0.08505	-0.02135	-0.06596
28	H	-9.948022	1.259277	9.531115	0.10446	0.08719	0.071981	0.029822
29	H	-11.31715	0.952825	8.45533	0.098289	-0.1047	0.069537	-0.10085
30	H	-11.23116	0.153986	10.03024	0.098951	-0.05808	-0.03742	0.095699
31	H	-10.60825	-1.47142	8.264316	0.085871	-0.08984	-0.12231	-0.01772
32	H	-9.215205	-1.14612	9.282089	0.086126	0.05426	-0.06423	0.095459
33	H	-9.76317	0.103731	6.554884	0.077222	-0.03595	0.055753	-0.06462
34	H	-9.158427	-2.35802	6.519528	0.087739	-0.11339	-0.0946	-0.01987
35	H	-7.658031	-1.95707	7.33211	0.088774	0.10952	-0.04733	0.049539
36	H	-8.498125	-1.37092	4.471082	0.094301	-0.18982	-0.08206	-0.24874
37	H	-6.958432	-1.93927	5.081325	0.096126	0.04516	0.028079	0.027009
38	H	-8.048759	0.882369	4.910413	0.083469	-0.07427	-0.03105	0.089307
39	H	-6.280318	1.652789	6.559099	0.094974	-0.01502	0.025163	0.014664
40	H	-6.016695	-0.02522	6.988429	0.094783	0.25489	-0.13495	0.125063
41	H	-8.415615	1.737233	7.56447	0.094113	-0.05664	0.130937	0.023674
42	H	-7.600125	0.594501	8.615812	0.088847	-0.01787	-0.03031	-0.04859
43	H	-4.695482	-0.91051	5.117975	0.08821	0.07603	-0.08543	0.079377
44	H	-5.424782	1.914875	1.199369	0.084169	0.00648	-0.00963	0.013452
45	H	-7.253401	1.718497	2.882751	0.08651	-0.07285	0.019596	0.018285
46	H	-2.643527	-0.33612	1.038294	0.116083	0.01526	-0.01044	0.027891
47	H	-3.25779	1.185657	0.391733	0.090586	0.01366	-0.00758	0.020182
48	H	-1.472171	0.920562	2.86352	0.120049	-0.00598	-0.01139	-0.0189
49	H	-1.996542	2.442586	2.152156	0.092193	-0.00507	0.094977	0.023149
50	H	-1.024682	3.230463	-0.02447	0.074738	0.07414	-0.09728	0.020759
51	H	0.917657	3.161584	-1.56997	0.088322	-0.0326	-0.01967	0.041373
52	H	2.223926	-0.50321	0.257596	0.085019	-0.0591	0.016967	0.040327
53	H	0.301792	-0.43030	1.779406	0.083292	-0.00946	0.043012	-0.02174
54	H	4.192698	0.305123	-0.671778	0.09346	0.19237	-0.02553	0.243895
55	H	3.21737	-0.62015	-1.831871	0.093339	-0.07417	-0.24031	-0.07215
56	H	5.157077	1.639536	-2.557925	0.105885	0.14556	0.278013	0.046163
57	H	4.18654	0.727723	-3.707342	0.105826	-0.13592	0.010867	-0.29932
58	H	5.363706	-1.39312	-3.015533	0.093587	-0.09957	-0.23968	-0.04788
59	H	6.333475	-0.48265	-1.870043	0.093653	0.14889	-0.03214	0.260282
60	H	7.337771	0.84837	-3.769701	0.103427	0.08453	0.161813	0.016919
61	H	6.362396	-0.07035	-4.922682	0.103392	-0.07446	0.015205	-0.16041

62	H	7.616813	-0.88591	-3.978929	0.100779	0.13545	-0.1254	-0.01209

Various energies components with zero point corrections of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecules.

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-1103.214289
Sum of electronic and thermal Energies	-1103.186873
Sum of electronic and thermal Enthalpies	-1103.185928
Sum of electronic and thermal Free Energies	-1103.277012

Table 3 presents dipole moment, exact polarizability, approx. and polarizability of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecules. The band gap (Humo-Lumo) is 5.12 eV. The ionization potential is 5.57 eV and electron affinity is 0.45 eV.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecules.

Dipole Monent	0.7918 debye
Exact Polarizability	287.957
Approx Polarizability	391.521

The IR spectra of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine 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 1288.9152 cm^{-1}. This frequency is associated with twisting of phenyl ring attached with alkoxy chain. Second peak is at 1560.8452 cm^{-1}. This frequency is associated with twisting of alkoxy chain. Other peak height is at 3030.0207 cm^{-1} that is associated with twisting of cyclohexane.

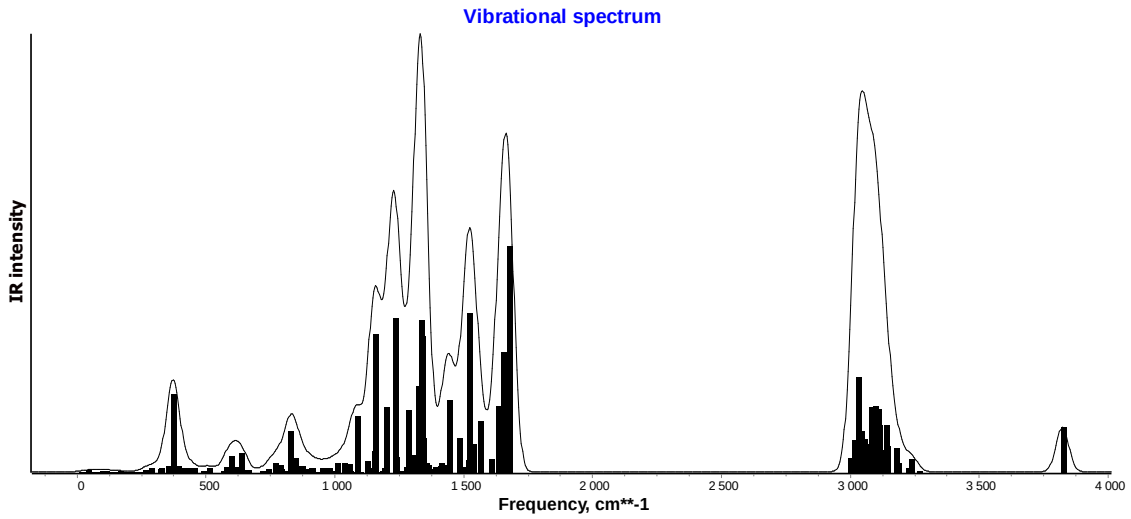

Figure 2: IR Spectra of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule.

Figure 3 represent Raman activities of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule. There are various peaks and the highest Raman activity is at 1233.2506 cm^{-1} which are associated with twisting of phenyl ring with alkoxy group. Another peak is at 1652.551 cm^{-1}, which is accosiated with twisting of pyridine ring. Next peak is at 3040.0893 cm^{-1} that associated with twisting of alkoxy chain tail.

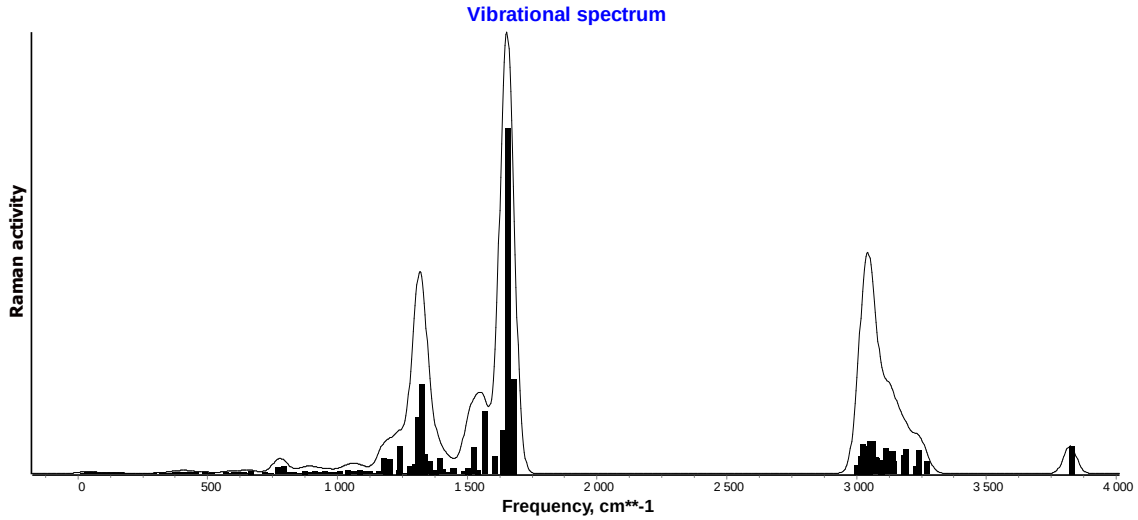

Figure 3: Raman activity of 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule.

4. CONCLUSION

The electronic structure analysis of on 5-(4-butylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)pyridine molecule. The IR peaks and Raman activities peaks were explained.

REFERENCES

[1]. ND Mermin, in "The topological theory of defects in ordered media".inRev Mod Phys.,vol. 51. pp. 591–648. 1979
[2]. H-R Trebin, in "The topology of non-uniform media in condensed matter physics" in Adv Phys., vol. 31.pp.195–254. 1982
[3]. U. Heinen, T. Berthold, G. Kothe, E. Stavitski, T. Galili, H. Levanon, G. Wiederrecht,| and M. R. Wasielewski, in "High Time Resolution Q-Band EPR Study of Sequential Electron Transfer in a Triad Oriented in a Liquid rystal" inj. Phys. Chem.. A, vol.106, pp.1933-1937., 2002
[4]. MihirRoychoudhury , Shailendra Kumar Thakur, Pankaj Kumar Gaurav , "Estimation of mesogenic character of disubstituted pyridine derivatives on the basis of intermolecular interaction energy calculations Journal of molecular Liquids" in vol.161,pp. 55–62 , 2011
[5]. M. Roychoudhury, P. K. Gaurav, R. Manohar and A. K. Prajapati," Analysis of Mesogenic Characteristics of 6-Chloro-benzothiazol-2-yl-(4-exadecyloxyphenyl) Diazene—A Smectic Liquid Crystal Mol. Cryst. Liq. Cryst.,in Vol. 537, pp. 3–21, 2011
[6]. Vladimir F. Petrov study of some liquid crystalline 2,5-disubstituted pyridine derivatives Mol. Cryst. Liq. Cryst.,in vol. 383, pp. 63–79,2002
[7]. P. L. Praveen And D. P. Ojha, In "Effect Of Molecular Interactions And Homologue Number On Uv Absorption Spectra Of Liquid Crystalline Alkyl Cyanobiphenyl Dimers: Dft Calculations" in ., Mol. Cryst. Liq. Cryst., Vol. 606: Pp. 75–89, 2015
[8]. F.V. Petrov, "Study of some Liquid crystalline 2, 5-disttituted pyridine derivatves" in Mol. Cryst. Liq. Cryst., Vol. 383, pp. 63–79.
[9]. Durga, P. Ojha, "A First Principle Study of Electronic Structure of In_2ZnTiO_6" in American Journal of Materials Science, vol 4(4), pp 165-168. 2014
[10]. V. F. Petrov, A. I. Pavluchenko, and N. I. Smirnova, "New Liquid Crystalline Pyridine Derivatives" in Mol. Cryst. Liq. Cryst., 265, 47 (1995).
[11]. M. Roychoudhury, S. K. Thakur and P K Gaurav in "Estimation of mesogenic character of disubsituted pyridine derivatives on the basis of intermolecular association energy calculations." in Journal Of Molecular Liquids , Vol. 161, pp. 55-62, 2011
[12]. M. Roychoudhury, P. K. Gaurav, Rajiv Manohar, and A. K. Prajapati "Estimation of mesogenic character of disubstituted pyridine derivatives on the basis of intermolecular interaction energy calculations" in Mol. Cryst. Liq. Cryst., Vol. 537: pp. 3–21, 2011
[13]. A.D. Becke, J. Chem. Phys. 1993, 98, 5648.
[14]. C. Lee,W. Yang, R.G. Parr, Phys. Rev. B **1988**, 37, 785.
[15]. P.J. Hay,W.R.Wadt, J. Chem. Phys. **1985**, 82,299.
[16]. H.D. Cohen, C.C.J. Roothaan, J. Chem. Phys. **1965**, 43,S34.
[17]. N. Kumar, S. Chaudhary, P. Singh, K. B. Thapa, D. Kumar, Journal of Molecular Liquids **2020**, 318, 114254.
[18]. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, et al., Gaussian 09, Revision A.02, Gaussian, Inc, Wallingford CT, 2010.