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Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part VI: HO $(CH_2)_8OC_6H_4.C_6H_4CN$

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ABSTRACT: The majority of the liquid crystals have a rod-like structure and have one or more benzene rings in its core. Structure and bonding in liquid crystals are significant and diverse field in the interface between modern physics and chemistry. Structure–property relationship is also a key issue for the study of liquid crystals. The strong dipole-dipole interaction shows the crystalline phase and has higher thermal stability. To understand the liquid crystalline properties, the IR spectra and Raman activities of 4,4'-Disubstituted Biphenyl ($HO(CH_2)_8OC_6H_4.C_6H_4CN$) were calculated using DFT method. The vibration associated with peaks was discussed. The atomic charges with point dipole were also computed and discussed. The Humo-Lumo gap as representation of ionization potential, thus computed.

KEYWORDS: Disubtituted Biphenyls, Liquid Crystals, Mesogen, IR Spectra, Raman Activities.

I. INTRODUCTION

There are a few materials which on heating do not go to liquid phase but remains in a intermediate phase between solid and liquid, which has fludity like liquid but maintans the orderness like solids. These matters are called the liquid-crystalline (LC) and it is also referred as the "fourth state of matter". Alkyl and alkoxy cyano biphenyls are appropriate for the use of electro-optic devices are broadly studied liquid crystals and their properties as liquid crystal devices are well known [1,2]. Dunmur et al. [3]. measured the electric permittivities, refractive indices and densities of the homologous series of alkyl-cyano-biphenyls as a function of temperature in the various phases. Mandal et al. [4] investigated using the X-Ray on the Mesogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile in the Solid Crystalline State and they established that the molecules are stacked along c-axis. Zugenmaier et al. [5, 6] studied the crystal and molecular structures of ten 4,4′-disubstituted biphenyls of the general formula HO-(CH2)n-O-C6H4-C6H4-CN (n=3−11) (HnCBPs). Loubser et al. [7] invetigated the unusual orientational behaviour of liquid crystals and they also studied the effect of bipolar interactions on the ferroelectric properties. Ojha et al.[8] studied the molecular ordering in a bipolar nematogenic cyanobiphenyl using computer simulation approach. Hussian et al. [9] studied the liquid crystals based sensing platform-technological aspects. Chaudhary et al. investiagted the electro-optical parameters with adverse order of 10CB liquid crystal molecules studied under the influence of an external high electric field.[10] Kumar et al. [11] has observed the Odd−Even effect in the electro−optical properties of the homologous series of H_nCBP liquid crystal under the influence of the electric field. Even–odd effect of the homologous series of nCHBT liquid crystal molecules under the impact of an electric field were calculated by Kumar et at. using DFT method. [12] The strong dipole-dipole interaction exhibits the crystalline phase and has higher thermal stability. The higher thermal stability of liquid crystal indicates a higher melting point and also presents the position of smectic liquid crystal. Kumar et al. [13] used DFT method to computed the spectroscopy existing behind the electro-optical properties with an even-odd effect of nCB liquid crystal molecules.

In the present work I will discuss about IR as well as Raman activities of 4, 4'-Disubstituted Biphenyl ($HO(CH_2)_8OC_6H_4.C_6H_4CN$; **H8CBP**). The geometry were generated from the work of Zugenmaier et al. [5, 6]

II. COMPUTATIONAL METHOD

The geometry was optimized using DFT method B3LYP [14,15] using 6-31G** [16, 17] which was found suitable for these type of systems [18] with keeping all atoms free. The analytical

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frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit.[19]

III. RESULTS AND DISCUSSION

The optimized geometry of H8CBP molecule is shown in figure 1. The inter ring angle between biphenyl is 35.3^{o} and inter ring seperation is 1.48Å. The alkoxy chain is plannar to biphenyl and seperation is 1.36Å. The cyano group is planar to biphenyl ring and seperation is 1.43Å. μ0 = 4π$\hat{}$10-7

- F is the force in Newtons
- N is the number of turns
- I is the current in Amps
- A is the area in length units squared
- g is the length of the gap between the solenoid and a piece of metal.

For different N values we get different solenoid force for valve operating

I=5amp, g=0.5, A=πdl. (d =2mm,l=5cm,)

Figure 1: The optimized structure of the H8CBP molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of H8CBP molecule. Since multipole depends on the coordinates of each atoms therefore coordinates are also tabulated here.

Table 1: The charge, coordinates and multipoles corresponding each atoms of H8CBP molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.0735	-0.0926	-0.4730	-0.4878	0.7557	1.4190	0.2656
2	C	1.4728	-0.0496	-0.3501	-0.2797	0.0026	-0.1334	-0.0212
3	C	2.1147	1.1621	-0.1274	-0.3215	0.0293	-0.1850	-0.0244
4	C	1.3910	2.3644	-0.0133	0.1930	0.0948	-0.1278	0.0323
5	C	-0.0101	2.3032	-0.1369	-0.1095	-0.0451	-0.5064	-0.1124
6	C	-0.6637	1.0989	-0.3655	-0.3900	-0.5767	-0.2922	-0.0758
7	C	2.0807	3.6522	0.2294	-0.0991	-0.3276	-0.1819	-0.1764
8	C	3.2262	3.7246	1.0350	-0.1158	-0.2443	0.1763	-0.2486
9	C	3.8829	4.9320	1.2740	-0.2130	-0.0302	-0.0623	0.0208
10	C	3.3964	6.1128	0.6979	0.3536	-0.2354	0.2317	-0.2114
11	C	2.2518	6.0596	-0.1141	-0.4226	-0.1678	-0.4143	-0.0848
12	C	1.6091	4.8520	-0.3395	-0.3946	0.3189	-0.0750	0.2887
13	O	3.9511	7.3436	0.8613	-0.8417	-0.4746	-0.2657	-0.2737
14	C	5.1226	7.4734	1.6690	1.2643	-0.7662	-1.2092	-0.3656
15	C	5.5193	8.9429	1.6808	0.9158	-0.5447	-0.0656	-0.3233
16	C	6.7747	9.2053	2.5222	0.8936	-0.0517	-0.6362	-0.0750
17	C	7.1809	10.6844	2.5516	0.5869	-0.1268	0.0280	0.0142
18	C	8.4349	10.9566	3.3916	0.2258	-0.0033	-0.2922	-0.1267
19	C	8.8421	12.4347	3.4160	-0.0338	-0.3268	-0.3334	0.1003
20	C	10.0940	12.7036	4.2599	0.4191	0.0648	-0.3606	-0.4289

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21	C	10.5351	14.1627	4.2458	0.9471	-0.2358	-0.2369	-0.5141
22	O	10.8939	14.5068	2.9112	-1.1449	0.0927	-0.0255	-0.3461
23	C	-0.5944	-1.3385	-0.7058	0.2983	0.9938	1.8435	0.3430
24	N	-1.1369	-2.3506	-0.8945	0.3588	0.3235	0.6036	0.1119
25	H	2.0469	-0.9656	-0.4426	0.1491	-0.0058	0.0008	-0.0002
26	H	3.1980	1.1835	-0.0665	0.1918	-0.0626	-0.0062	-0.0014
27	H	-0.5959	3.2101	-0.0259	0.2793	0.0628	-0.0873	-0.0078
28	H	-1.7450	1.0693	-0.4507	0.0188	-0.0755	0.0217	-0.0047
29	H	3.6019	2.8251	1.5136	0.2376	-0.0014	0.0812	-0.0221
30	H	4.7572	4.9423	1.9135	0.0993	-0.0005	-0.0822	0.0127
31	H	1.8936	6.9801	-0.5633	0.2714	0.0282	-0.0605	0.0463
32	H	0.7416	4.8317	-0.9924	0.3486	0.1308	0.0214	0.0987
33	H	5.9319	6.8538	1.2560	-0.3890	0.2521	-0.1096	-0.0911
34	H	4.9149	7.1185	2.6889	-0.3713	-0.0103	-0.0265	0.2778
35	H	4.6768	9.5296	2.0669	-0.3816	-0.2374	0.1734	0.1080
36	H	5.6824	9.2703	0.6468	-0.3671	0.0369	0.0909	-0.2899
37	H	7.6108	8.6084	2.1310	-0.4297	0.2673	-0.1609	-0.1049
38	H	6.6070	8.8561	3.5511	-0.3639	-0.0266	-0.0690	0.2758
39	H	6.3445	11.2812	2.9419	-0.2577	-0.1689	0.1226	0.0634
40	H	7.3493	11.0346	1.5237	-0.2322	0.0172	0.0729	-0.2007
41	H	9.2699	10.3574	3.0012	-0.1903	0.1426	-0.0861	-0.0484
42	H	8.2659	10.6057	4.4202	-0.1412	-0.0075	-0.0282	0.1463
43	H	8.0078	13.0359	3.8061	-0.0875	-0.0784	0.0704	0.0225
44	H	9.0241	12.7874	2.3944	0.0367	0.0266	0.0368	-0.0450
45	H	10.9272	12.0895	3.8942	-0.2967	0.1855	-0.1395	-0.0733
46	H	9.9169	12.4073	5.3027	-0.0657	-0.0094	-0.0030	0.0985
47	H	9.7141	14.8014	4.6131	-0.1689	-0.0716	0.0788	0.0550
48	H	11.3870	14.2978	4.9318	-0.0522	0.0508	0.0297	0.0335
49	H	11.1191	15.4447	2.8914	0.5600	-0.0275	-0.0982	0.0325

The Humo Lumo gap for H8CBP is 0.162 hartree.Various energies components with zero point corrections of H8CBP molecule are tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H8CBP molecules.

Energies Components	Hartree
Sum of electronic and zero-point Energies	-1020.080919
Sum of electronic and thermal Energies	-1020.056876
Sum of electronic and thermal Enthalpies	-1020.055932
Sum of electronic and thermal Free Energies	-1020.139080

Table 3 presents dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of H8CBP molecules. From table 3 it is apparent that polarizabilities increased in comparison with H3CBP, H4CBP, H5.CBP. H6CBP and H7CBP [20, 21] which clearly indicate that optical activity of H8CB is higher than H3CBP, H4CBP, H5.CBP, H6CBP and H7CBP.

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Table 3: Dipole monent, exact polarizability, and approx. polarizability of H8CBP molecules.

Dipole Monent	8.9222 debye
Exact Polarizability	152.152
Approx Polarizability	232.770

The IR spectra of H8CBP 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 1295.802 cm^{-1}. This frequency is associated with twisting of phenyl ring attached with alkoxy chain. Second peak is at 1657.349 cm^{-1}. This frequency is associated with twisting of phenyl ring. Other peak height is at 2340.661 cm^{-1} which is associated with CN bond stretching.

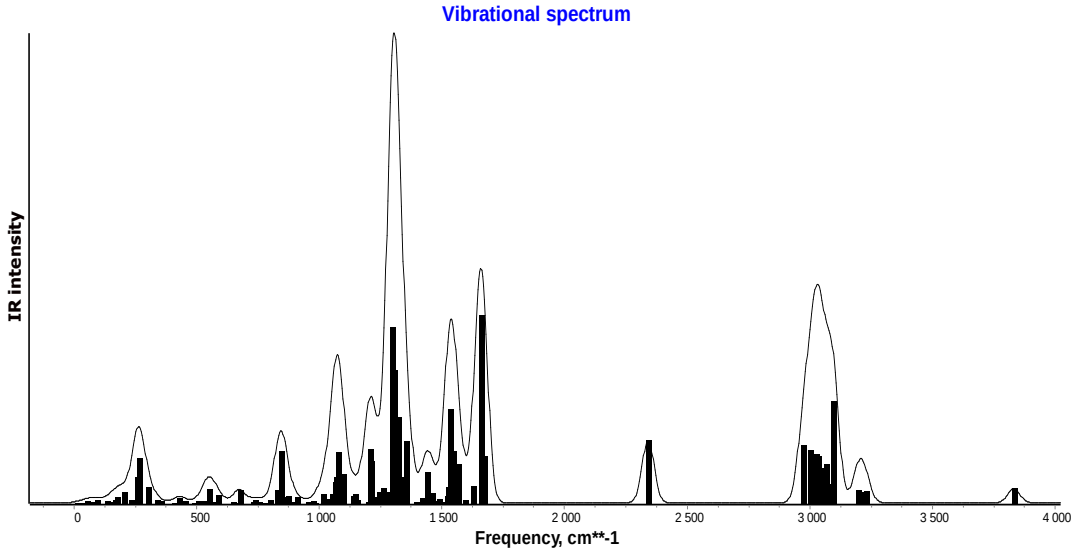

Figure 2: IR Spectra of H8CBP molecule.

Figure 3 represent Raman activities of H8CBP molecule. There are various peaks and the highest Raman activity is at 1657.349 cm^{-1} which are associated with twisting of phenyl ring. Next peak is at 2340.661 cm^{-1} which associated with CN bond stretching.

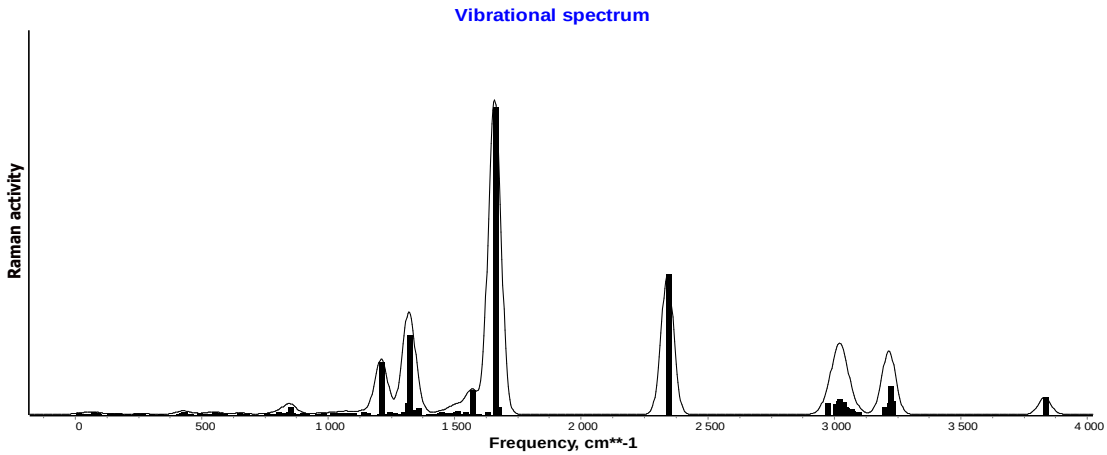

Figure 3: Raman activitty of H8CBP molecule.

IV. CONCLUSION

DFT stduy of electronic structure analysis of on 4, 4'-Disubstituted Biphenyl ($HO(CH_2)_8OC_6H_4.C_6H_4CN$) molecule was done. It is interesting to note that there is increase in polarizabilities of H8CBP in comparison with H3CBP, H4CBP, H5.CBP. H6CBP and H7CBP which means optical activities of H8CBP is more than H3CBP, H4CBP, H5.CBP. H6CBP and H7CBP. The IR peaks and Raman activities peaks were explained.

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