

Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part V: HO(CH₂)₇OC₆H₄.C₆H₄CN

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Abstract

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. Most of the liquid crystals have a rod-like structure and contains one or more benzene rings in its core. The strong dipole-dipole interaction exhibits 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(CH₂)₇OC₆H₄.C₆H₄CN) were calculated using DFT method. The vibration associated with peaks were discussed. The atomic charges with point dipole were also computed and discussed. The HOMO-LUMO gap as representation of ionization potential, thus computed.

Keywords: Disubstituted Biphenyls, Liquid Crystals, Mesogen, IR Spectra, Raman Activities.

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I. INTRODUCTION

The liquid-crystalline (LC) state exists between the solid and the isotropic liquid phase of matter. It is also referred as the “fourth state of matter”. Alkyl and alkoxy cyano biphenyls are suitable for the use of electro-optic devices are extensively 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] investigated 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. investigated 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 al. 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(CH₂)₇OC₆H₄.C₆H₄CN; **H7CBP**). 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 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 H7CBP molecule is shown in figure 1. The inter ring angle between biphenyl is 35.2° and inter ring separation is 1.48Å. The alkoxy chain is planar to biphenyl and separation is 1.36Å. The cyano group is planar to biphenyl ring and separation is 1.43Å.

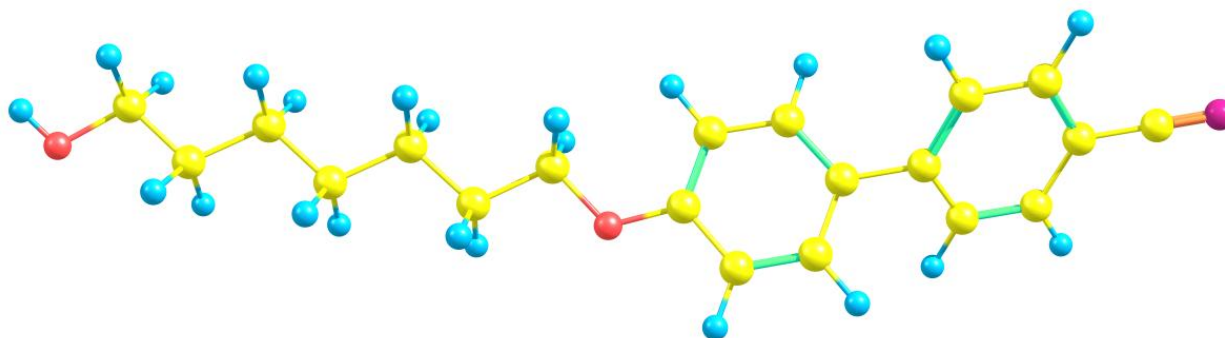


Figure 1: The optimized structure of the H7CBP molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of H7CBP 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 H7CBP molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.0901	-0.1275	0.3547	-0.7198	0.8261	1.4281	-0.2280
2	C	1.4907	-0.0698	0.2538	-0.3669	-0.0930	-0.2603	0.0462
3	C	2.1260	1.1537	0.0829	-0.2134	-0.3200	-0.1779	0.0221
4	C	1.3946	2.3538	0.0001	-0.0308	-0.0752	-0.0658	0.0129
5	C	-0.0076	2.2781	0.1012	-0.1927	0.0534	-0.4240	0.0631
6	C	-0.6549	1.0617	0.2782	-0.3147	-0.3364	-0.2729	0.0485
7	C	2.0777	3.6541	-0.1884	-0.0302	-0.3442	-0.4734	0.1426
8	C	3.2340	3.7619	-0.9744	-0.1725	-0.3121	0.3889	0.3408
9	C	3.8842	4.9815	-1.1637	-0.2983	0.0355	-0.0539	-0.0696
10	C	3.3800	6.1387	-0.5558	0.3504	-0.2446	0.0147	0.1792
11	C	2.2248	6.0500	0.2375	-0.3962	-0.1564	-0.3221	0.0686
12	C	1.5887	4.8307	0.4134	-0.3013	0.2314	-0.0469	-0.2157
13	O	3.9274	7.3786	-0.6706	-0.7623	-0.4858	-0.3220	0.2533
14	C	5.1051	7.5438	-1.4619	1.2732	-0.6775	-1.2479	0.2724
15	C	5.4873	9.0169	-1.4262	0.9163	-0.5392	-0.1612	0.2975
16	C	6.7481	9.3151	-2.2473	1.0241	0.0454	-0.5063	-0.1287
17	C	7.1379	10.7987	-2.2325	0.5863	-0.1191	-0.0613	0.1068
18	C	8.3983	11.1054	-3.0512	1.1486	0.5013	0.3004	-0.3263
19	C	8.7791	12.5902	-3.0379	0.2146	-0.1482	0.6683	0.3079
20	C	10.0314	12.8933	-3.8509	0.5913	-0.1492	0.8285	0.1349
21	O	10.2838	14.2904	-3.7631	-1.1751	-0.0688	0.3409	0.1196
22	C	-0.5712	-1.3856	0.5338	0.2598	1.1822	2.3152	-0.3124
23	N	-1.1083	-2.4079	0.6786	0.5331	0.3860	0.7169	-0.1069
24	H	2.0706	-0.9843	0.3226	0.1616	0.0070	0.0246	-0.0053
25	H	3.2099	1.1852	0.0385	0.2963	-0.1321	-0.0170	0.0046
26	H	-0.5990	3.1839	0.0133	0.2960	0.0552	-0.1093	0.0125
27	H	-1.7370	1.0211	0.3464	0.0899	-0.0284	0.0283	-0.0005
28	H	3.6238	2.8817	-1.4773	0.3469	-0.0355	0.1378	0.0667
29	H	4.7676	5.0197	-1.7895	0.0998	-0.0032	-0.0850	-0.0131

30	H	1.8528	6.9522	0.7117	0.2362	0.0219	-0.0380	-0.0312
31	H	0.7121	4.7820	1.0524	0.2817	0.0956	0.0259	-0.0680
32	H	4.9110	7.2176	-2.4941	-0.3876	-0.0114	-0.0129	-0.2901
33	H	5.9167	6.9200	-1.0597	-0.4136	0.2610	-0.1187	0.0997
34	H	5.6371	9.3154	-0.3815	-0.3486	0.0335	0.0864	0.2786
35	H	4.6430	9.6065	-1.8036	-0.3762	-0.2380	0.1786	-0.0991
36	H	6.5941	8.9924	-3.2869	-0.4431	-0.0275	-0.0804	-0.3213
37	H	7.5867	8.7165	-1.8640	-0.4486	0.2677	-0.1773	0.1152
38	H	7.2913	11.1236	-1.1940	-0.2749	0.0173	0.0953	0.2247
39	H	6.3004	11.3972	-2.6170	-0.2586	-0.1741	0.1392	-0.0581
40	H	8.2445	10.7749	-4.0885	-0.4048	-0.0603	-0.1169	-0.2739
41	H	9.2356	10.5079	-2.6631	-0.3982	0.2041	-0.1948	0.1158
42	H	8.9462	12.9288	-2.0076	-0.2956	0.0512	0.0775	0.2415
43	H	7.9544	13.1955	-3.4349	-0.2630	-0.1784	0.1226	-0.0947
44	H	9.8798	12.5793	-4.8975	-0.0319	-0.0009	-0.0571	-0.0454
45	H	10.8798	12.3080	-3.4576	0.0378	-0.0093	-0.0343	-0.0130
46	H	11.0775	14.4858	-4.2760	0.5747	-0.0885	-0.0395	0.0552

The HOMO-LUMO gap for H7CBP is 0.162 hartree. Various energy components with zero-point corrections of H7CBP molecule are tabulated in Table 2.

Table 2: Energy Components such as electronic, thermal and Free energies of H7CBP molecules.

Energy Components	Hartree
Sum of electronic and zero-point Energies	-980.793048
Sum of electronic and thermal Energies	-980.770289
Sum of electronic and thermal Enthalpies	-980.769345
Sum of electronic and thermal Free Energies	-980.848923

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

Table 3: Dipole moment, exact polarizability, and approx. polarizability of H7CBP molecules.

Dipole Moment	6.7029 debye
Exact Polarizability	137.946
Approx Polarizability	212.270

The IR spectra of H7CBP molecule is shown in Figure 2. From Figure 2 it can be visualized that there are several peaks and the highest peak (IR intensity) is at 1297.365 cm⁻¹. This frequency is associated with twisting of the phenyl ring attached with the alkoxy chain. The second peak is at 1657.475 cm⁻¹. This frequency is associated with twisting of the phenyl ring. Other peak height is at 2340.667 cm⁻¹ which is associated with CN bond stretching.

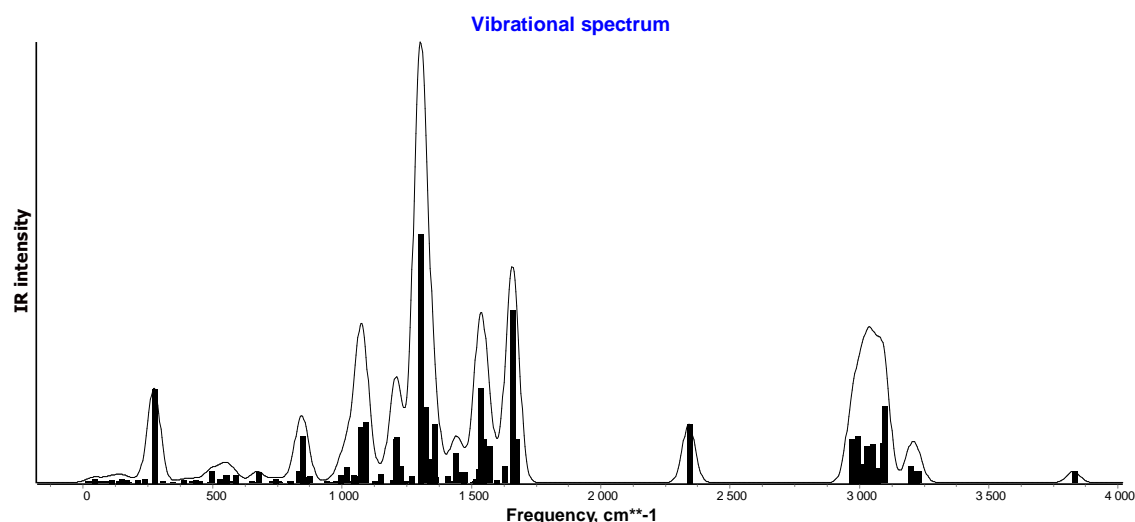


Figure 2: IR Spectra of H7CBP molecule.

Figure 3 represent Raman activities of H7CBP molecule. There are various peaks and the highest Raman activity is at 1657.475 cm^{-1} which are associated with twisting of phenyl ring. Next peak is at 2340.667 cm^{-1} which associated with CN bond stretching.

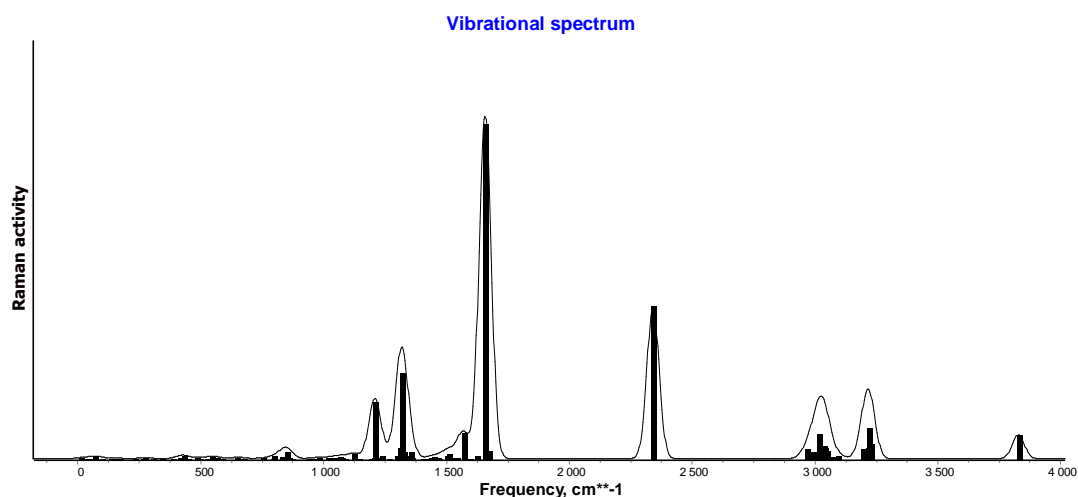


Figure 3: Raman activity of H7CBP molecule.

IV. CONCLUSION

DFT study of electronic structure analysis of on 4, 4'-Disubstituted Biphenyl ($\text{HO}(\text{CH}_2)_7\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$) molecule was done. It is interesting to note that there is increase in polarizabilities of H7CBP in comparison with H3CBP, H4CBP, H5.CBP. and H6CBP which means optical activities of H7CBP is more than H3CBP, H4CBP, H5.CBP. and H6CBP. The IR peaks and Raman activities peaks were explained.

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