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Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part IV: HO(CH₂)₆OC₆H₄.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)₆OC₆H₄.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

1. 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) (H_nCBPs). Loubser *et al.*^[7] investigated the unusual orientational behavior 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 compute 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)₆OC₆H₄.C₆H₄CN; H₆CBP). The geometry was generated from the work of Zugenmaier *et al.*^[5, 6].

2. 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].

3. Results

The optimized geometry of H₆CBP molecule is shown in Fig 1. The inter ring angle between biphenyl is 35.7° 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.

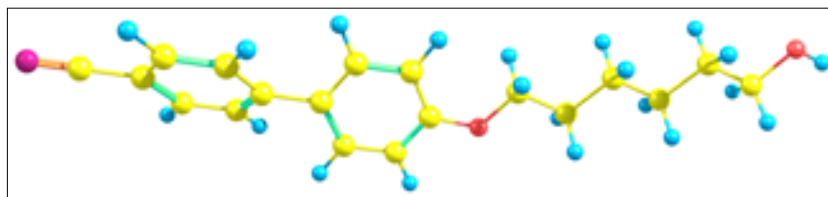


Fig 1: The optimized structure of the H6CBP molecule

Table 1 present the charges as well as multipoles corresponding each atom of H6CBP molecule. Since multipole depends on the coordinates of each atom therefore coordinates are also tabulated here.

Table 1: The charge, coordinates and multipoles corresponding each atom of H6CBP molecule

S No.	Atom	Coordinates			Charge		Multipole (au)	
		X	Y	Z				
1	C	-0.0220	-0.0130	-0.3270	-0.5244	1.6855	2.1381	0.3376
2	C	1.3724	0.0315	-0.4963	-0.5996	0.4086	-0.6065	-0.2321
3	C	2.0605	1.2206	-0.2901	0.1671	-0.5275	0.1167	0.1270
4	C	1.3904	2.3975	0.0939	0.1977	0.1635	1.0565	0.2468
5	C	-0.0058	2.3348	0.2626	0.0426	-0.1682	-0.7064	-0.1610
6	C	-0.7067	1.1536	0.0542	-0.4694	-0.8785	-0.4294	-0.0053
7	C	2.1313	3.6609	0.3129	-0.2952	0.2794	0.6520	0.0647
8	C	3.4246	3.6613	0.8722	-0.2325	-0.1074	-0.1975	-0.0606
9	C	4.1213	4.8420	1.0790	-0.3414	-0.2608	-0.1981	-0.0794
10	C	3.5474	6.0745	0.7278	0.4479	0.2338	-0.0202	0.0858
11	C	2.2630	6.0978	0.1690	-0.2518	-0.2205	0.1045	-0.1024
12	C	1.5738	4.9011	-0.0295	-0.2623	0.1916	-0.1024	0.1028
13	O	4.3114	7.1744	0.9672	-0.8964	0.1267	-0.4600	0.0869
14	C	3.7902	8.4630	0.6384	1.3355	-0.6166	-1.3273	-0.1206
15	C	4.8441	9.4985	1.0052	0.5863	0.1053	-0.2922	0.0094
16	C	4.3942	10.9296	0.6862	0.6459	-0.2810	-0.3954	0.0882
17	C	5.4498	11.9848	1.0414	1.3238	0.6107	0.6854	0.1933
18	C	5.0015	13.4147	0.7198	0.4729	-0.7174	0.3380	-0.2357
19	C	6.0516	14.4622	1.0684	0.3258	-0.6839	0.8100	-0.3928
20	O	5.5252	15.7391	0.7292	-1.1988	-0.2713	0.2367	-0.1357
21	C	-0.7384	-1.2352	-0.5407	0.5005	1.4081	2.5086	0.4410
22	N	-1.3203	-2.2282	-0.7136	0.5505	0.4194	0.6973	0.1208
23	H	1.9039	-0.8645	-0.7995	0.0352	0.0360	-0.0432	-0.0114
24	H	3.1331	1.2464	-0.4541	0.2325	-0.0600	-0.0259	0.0016
25	H	-0.5442	3.2194	0.5873	0.2372	0.0371	-0.0382	-0.0180
26	H	-1.7820	1.1215	0.1958	-0.0451	-0.1121	0.0187	0.0244
27	H	3.8784	2.7225	1.1757	0.1329	0.0222	0.0341	0.0108
28	H	5.1121	4.8405	1.5214	0.2652	-0.0700	-0.0091	-0.0316
29	H	1.7978	7.0318	-0.1224	0.0339	-0.0742	-0.0007	-0.0372
30	H	0.5906	4.9378	-0.4894	0.2251	0.0621	0.0221	0.0282
31	H	2.8574	8.6419	1.1928	-0.3795	-0.2031	0.1240	0.1454
32	H	3.5570	8.5098	-0.4353	-0.3828	-0.0297	0.0854	-0.2745
33	H	5.7683	9.2634	0.4633	-0.2352	0.1859	-0.0576	-0.0980
34	H	5.0730	9.4031	2.0736	-0.2288	0.0592	-0.0349	0.2144
35	H	3.4643	11.1528	1.2277	-0.3021	-0.2118	0.0858	0.1072
36	H	4.1507	11.0091	-0.3826	-0.2251	-0.0456	0.0456	-0.2030
37	H	6.3799	11.7598	0.5005	-0.4543	0.2476	-0.1376	-0.1752
38	H	5.6929	11.9060	2.1104	-0.5059	0.0600	-0.0906	0.3688
39	H	4.0804	13.6546	1.2656	-0.3810	-0.2477	0.0806	0.1617
40	H	4.7644	13.5058	-0.3477	-0.3557	-0.0459	0.0299	-0.3031
41	H	6.9826	14.2530	0.5148	0.1135	-0.0205	-0.0386	0.0526
42	H	6.2939	14.4014	2.1429	0.1112	0.0260	-0.0461	-0.0349
43	H	6.1873	16.4058	0.9490	0.5844	-0.0671	-0.0974	-0.0175

The Humo Lumo gap for H6CBP is 0.163 Hartree. Various energies components with zero-point corrections of H6CBP

molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H6CBP molecules.

Energies Components	Hartree
Sum of electronic and zero-point Energies	-941.505812
Sum of electronic and thermal Energies	-941.484423
Sum of electronic and thermal Enthalpies	-941.483479
Sum of electronic and thermal Free Energies	-941.559588

Table 3 presents dipole moment, exact polarizability, approx. polarizability and hyperpolarizability of H6CBP molecules. From table 3 it is apparent that polarizabilities increased in comparison with H3CBP and H4CBP^[20, 21] which clearly indicate that optical activity of H5CB is higher than H3CBP and H4CBP.

Table 3: Dipole moment, exact polarizability, and approx. polarizability of H6CBP molecules

Dipole Moment	7.7921 Debye
Exact Polarizability	117.753
Approx. Polarizability	186.524

The IR spectra of H6CBP molecule is shown in Fig 2. From Fig 2 it can be visualized that there are several peak and the highest peak (IR intensity) is at 1298.230 cm^{-1} . This frequency is associated with twisting of phenyl ring attached with alkoxy chain. Second peak is at 1657.579 cm^{-1} . This frequency is associated with twisting of phenyl ring. Other peak height is at 2340.869 cm^{-1} which is associated with CN bond stretching.

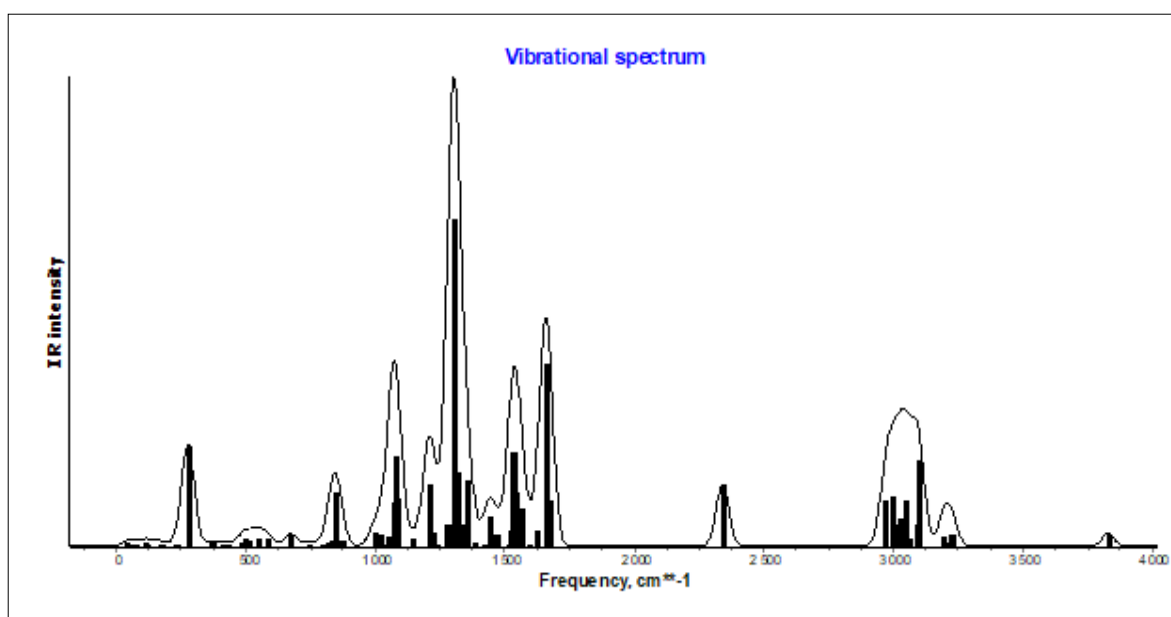
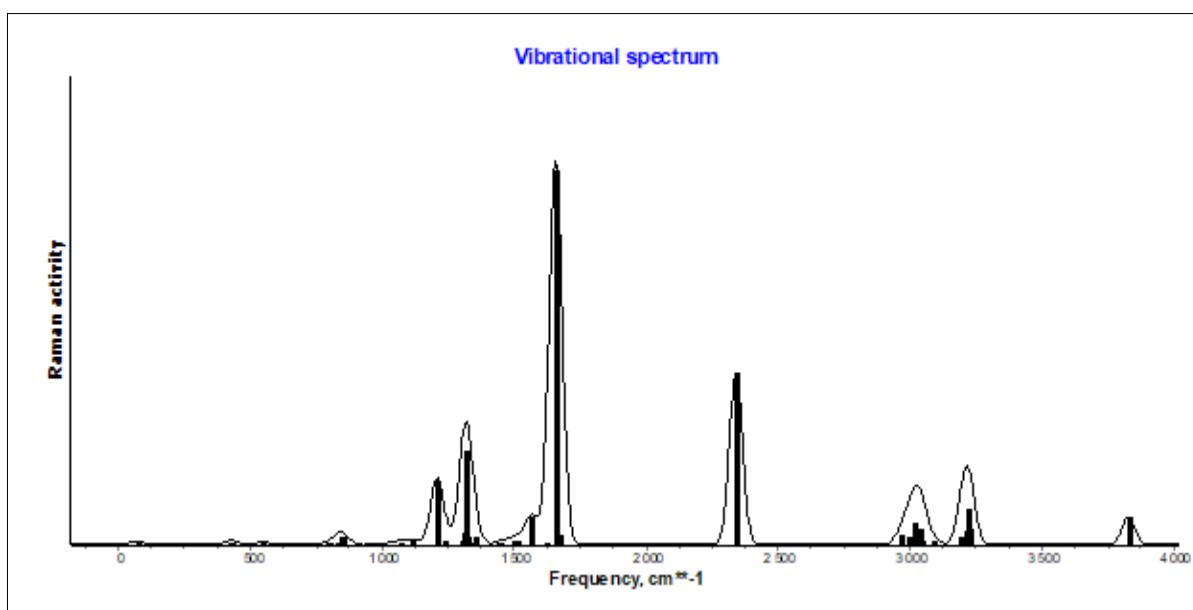
**Fig 2:** IR Spectra of H6CBP molecule

Figure 3 represent Raman activities of H6CBP molecule. There are various peaks and the highest Raman activity is at 1657.519 cm^{-1} which are associated with twisting of phenyl

ring. Next peak is at 2340.869 cm^{-1} which associated with CN bond stretching.

**Fig 3:** Raman activity of H6CBP molecule

4. Conclusion

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

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