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Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part II: $HO(CH_2)_4OC_6H_4.C_6H_4CN$

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Abstract: Structure and bonding in liquid crystals is highly rich and diverse field in the interface between modern physics and chemistry. Structure–property relationship has been a central 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 ($HO(CH_2)_4OC_6H_4.C_6H_4CN$) were calculated using DFT method. The vibration associated with peaks were discussed. The atomic charges with point dipole were also computed and discussed. The Humo-Lumo gap as representation of ionization potential, thus computed.

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

INTRODUCTION:

Alkyl and alkoxy cyano biphenyls which are suitable for application in electro-optic devices are higly studied liquid crystals and their properties as liquid crystal devices are well established [1,2]. The electric permittivities, refractive indices and densities of the homologous series of alkyl-cyano-biphenyls as a function of temperature in the various phases were measured by Dunmur et al. [3] Mandal et al. [4] did the X-Ray Studies on the Mesogen 4′-n-Pentyloxy-4-Biphenylcarbonitrile in the Solid Crystalline State and they found that The molecules are stacked along c-axis. The molecules associate in pairs about the centre of inversion. Zugenmaier et al. [5, 6] determined the crystal and molecular structures of eight 4,4′-disubstituted biphenyls of the general formula HO-(CH2)n-O-C6H4-C6H4-CN (n=3−11) (HnCBPs). Loubser et al. [7] investigated unusual orientational behaviour of liquid crystals and they also studied of the effect of bipolar interactions on the ferroelectric properties. The molecular ordering in a bipolar nematogenic cyanobiphenyl using computer simulation approach was investigated by Ojha et al.[8] Hussian et al. [9] stdied the liquid crystals based sensing platform-technological aspects. Chaudhary et al. computed 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] Odd−Even effect observed in the electro−optical properties of the homologous Series of H_nCBP liquid crystal studied under the impact of the electric field. Even–odd effect of the homologous series of nCHBT liquid crystal molecules under the influence of an electric field were computed 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. Using DFT method Kumar et al. [13] calculated spectroscopy existing behind the electro-optical properties with an even-odd Effect of nCB Liquid Crystal Molecules.

In the present paper I will discuss about IR as well as Raman activities of 4, 4'-Disubstituted Biphenyl ($HO(CH_2)_4OC_6H_4.C_6H_4CN$; **H4CBP**). The geometry were generated from the paper by Zugenmaier et al. [5, 6]

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]

RESULTS:

The optimized geometry of H4CBP molecule is shown in figure 1. The inter ring angle between biphenyl is 35.6° 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.

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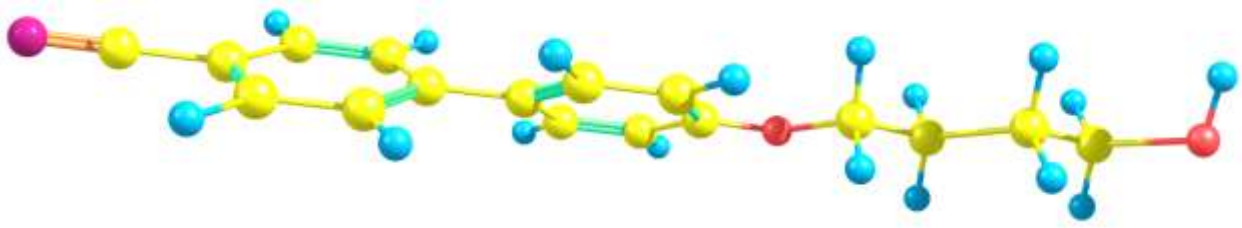

Figure 1: The optimized structure of the H4CBP molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of H4CBP 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 H4CBP molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.0073	-0.0454	-0.0097	-0.3292	1.0696	1.8593	-0.0074
2	C	1.3926	-0.0290	-0.2459	-0.7943	0.1678	-0.7297	-0.1246
3	C	2.0825	1.1769	-0.2537	0.2850	-1.7614	-0.4179	0.3031
4	C	1.4236	2.3991	-0.0219	0.1807	1.7953	2.9577	-0.0028
5	C	0.0364	2.3647	0.2150	0.3629	0.4512	-1.6997	-0.2871
6	C	-0.6664	1.1663	0.2198	-0.8100	-0.7598	-0.2219	0.1361
7	C	2.1660	3.6806	-0.0269	-1.0191	0.4735	1.1613	-0.0640
8	C	3.4757	3.7657	0.4667	-0.0347	-0.1462	0.5989	-0.2287
9	C	4.1847	4.9674	0.4697	-0.4889	0.3325	0.1218	0.1201
10	C	3.5839	6.1282	-0.0337	0.7272	-0.4787	0.2493	-0.2364
11	C	2.2736	6.0626	-0.5337	-0.7191	-0.3822	0.2858	-0.2406
12	C	1.5815	4.8612	-0.5270	-0.1241	0.5194	0.2474	0.1745
13	O	4.1763	7.3526	-0.0821	-1.0246	-0.3320	0.0947	-0.1450
14	C	5.5141	7.4934	0.3951	1.7417	-0.8067	-1.8337	0.1109
15	C	5.9165	8.9503	0.2134	1.2148	-0.0058	0.2149	-0.1660
16	C	7.3450	9.2284	0.6963	-0.1606	-0.1289	-0.3396	0.3131
17	C	7.7507	10.6947	0.5247	0.9581	0.4856	-0.0289	0.1432
18	O	9.0929	10.9446	0.9145	-1.1508	0.2569	0.1098	-0.2100
19	C	-0.7107	-1.2853	-0.0031	0.3713	1.2383	2.1482	-0.0122
20	N	-1.2934	-2.2926	0.0021	0.4484	0.3781	0.6494	-0.0025
21	H	1.9150	-0.9613	-0.4334	0.0905	0.0218	-0.0121	0.0004
22	H	3.1462	1.1764	-0.4692	0.5824	-0.2563	0.0263	0.0581
23	H	-0.4927	3.2890	0.4241	0.5324	0.1312	-0.1811	-0.0483
24	H	-1.7343	1.1574	0.4116	0.0738	-0.0321	0.0113	0.0018
25	H	3.9481	2.8827	0.8870	0.3217	-0.0609	0.1007	-0.0483
26	H	5.1901	4.9884	0.8724	0.0582	-0.0092	-0.0996	0.0211
27	H	1.8259	6.9675	-0.9311	0.1038	-0.0028	0.0196	-0.0003
28	H	0.5793	4.8292	-0.9438	0.2986	0.1041	-0.0062	0.0432
29	H	6.1860	6.8302	-0.1686	-0.5843	0.2989	-0.1427	-0.2219
30	H	5.5675	7.2045	1.4550	-0.5774	0.0721	0.0157	0.3890

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31	H	5.2011	9.5796	0.7570	-0.3444	-0.2123	0.1328	0.1444
32	H	5.8195	9.2092	-0.8480	-0.3775	-0.0463	0.0480	-0.2946
33	H	8.0643	8.6056	0.1500	-0.0205	0.0901	-0.0372	-0.0460
34	H	7.4369	8.9549	1.7583	-0.1764	0.0468	-0.0437	0.1693
35	H	7.0451	11.3444	1.0687	-0.1704	-0.1130	0.0937	0.0675
36	H	7.6927	10.9757	-0.5326	-0.0700	0.0049	0.0086	-0.0817
37	H	9.1611	10.7767	1.8633	0.6247	-0.0085	0.0234	-0.1501

Various energies components with zero point corrections of H4CBP molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H4CBP molecules.

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-862.931356
Sum of electronic and thermal Energies	-862.912764
Sum of electronic and thermal Enthalpies	-862.911820
Sum of electronic and thermal Free Energies	-862.980545

Table 3 presents dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of H4CBP molecules. The polarizabilities increased in comparison with H3CBP which clearly indicate that optical activity of H4CB is higher than H3CBP.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of H4CBP molecules.

Dipole Monent	5.9805 debye
Exact Polarizability	98.728
Approx Polarizability	156.118

The IR spectra of H4CBP 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 1298.172 cm^{-1}. This frequencies is associated with twisting of alkyl chain attached with alkoxy chain. Second peak is at 1657.687 cm^{-1}. This frequencies is associated with twisting of phenyl ring attached with CN group. The next peak is at 1087.0744 cm^{-1}. This are associated with twisting of alkoxy chain. Other peak hieght is at 2341.089 cm^{-1} which is associated with CN bond streching.

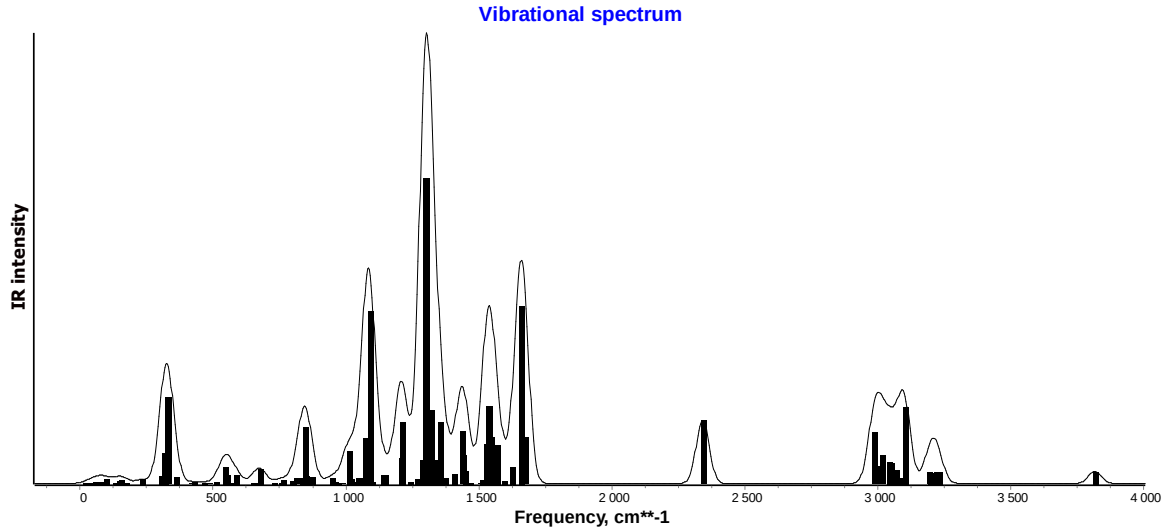

Figure 2: IR Spectra of H4CBP molecule.

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Figure 3 represent Raman activities of H4CBP molecule. There are various peaks and the highest Raman activity is at 1657.687 cm^{-1}. This is associated with twisting of phenyl group attached with CN group. Next peak is at 2341.089 cm^{-1} which associated with CN bond strechingh. Next peak is at 1208.554 cm^{-1}. This is associated with twistung of phenyl ring.

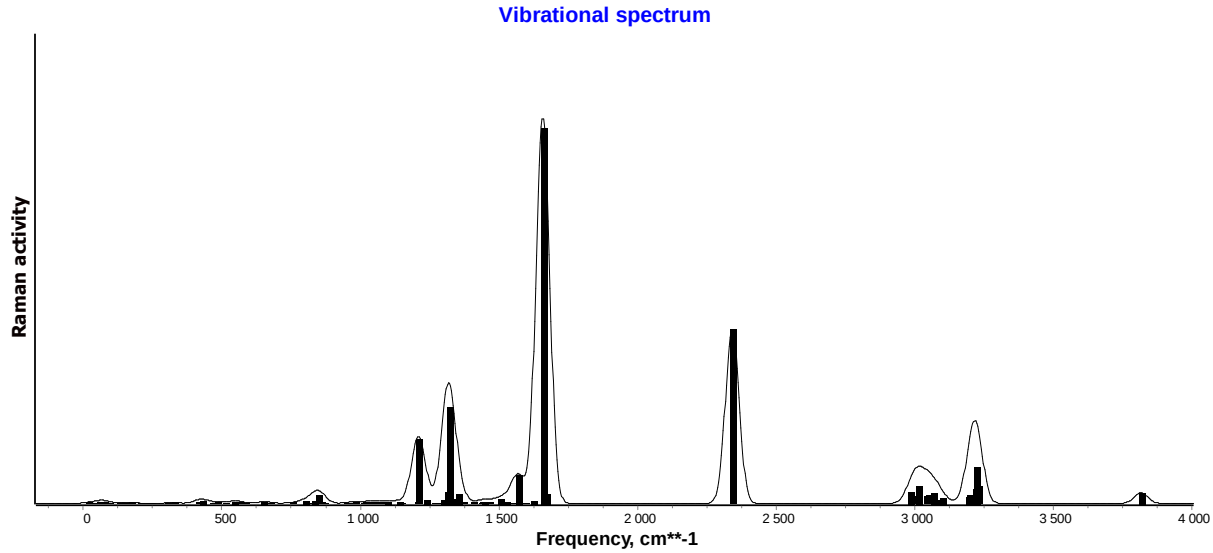

Figure 3: Raman activitty of H4CBP molecule.

CONCLUSION:

Electronic structure analysis of on 4-Alkyl 4'-Cyano Biphenyls ($C_{11}H_{23}$-C_6H_5-C_6H_5-CN) molecule was done with DFT methods. It is noted that increase in polarizabilities in comparison with H3CBP which means optical activities is more than H3CBP. The IR peaks and Raman activities peaks were explained.

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