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Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part I: $HO(CH_2)_3OC_6H_4.C_6H_4CN$

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Abstract: Most of the liquid crystals having a rod-like structure and contains one or more benzene rings. The dihedral angle betwixt the two benzene rings expresses the odd-even effect in Liquid Crystalline parameters. 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 ($HO(CH_2)_3OC_6H_4.C_6H_4CN$) 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] Wang et al. [4] synthesised and studied the properties of hydroxy tail-terminated cyanobiphenyl liquid crystals. 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). Unusual orientational behaviour of liquid crystals were investigated by Loubser et al. [7] and they studied of the effect of bipolar interactions on the ferroelectric properties Ojha et al. [8] investigated molecular ordering in a bipolar nematogenic cyanobiphenyl using computer simulation approach. Hussian et al. [9] investigated 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 this paper we will discuss about IR as well as Raman activities of 4, 4'-Disubstituted Biphenyl ($HO(CH_2)_3OC_6H_4.C_6H_4CN$; **H3CBP**). The geometry were taken from article 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 H3CBP 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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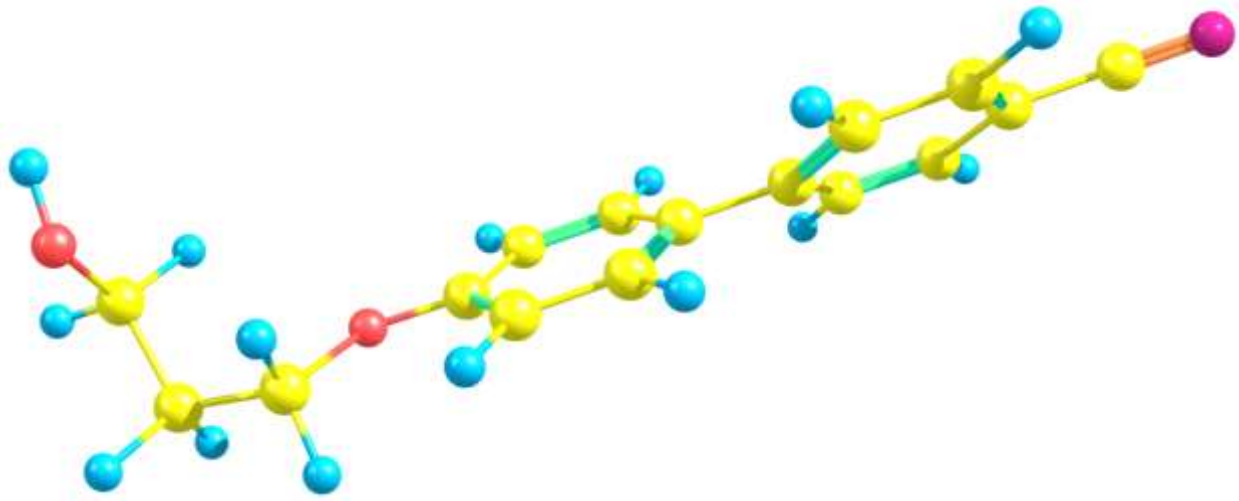

Figure 1: The optimized structure of the H3CBP molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of H3CBP 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 H3CBP molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	-0.0191	0.0115	0.0187	-0.6348	0.6464	1.0586	-0.0803
2	C	1.3852	-0.0360	-0.0074	-0.3562	-0.2185	-0.1282	0.0176
3	C	2.1199	1.1406	-0.0838	-0.3177	-0.1523	-0.4516	0.0324
4	C	1.4873	2.3974	-0.1305	0.0830	-0.2378	-0.5412	0.0530
5	C	0.0801	2.4273	-0.1007	-0.2470	-0.2860	-0.1792	-0.0038
6	C	-0.6664	1.2578	-0.0301	-0.3240	-0.0643	-0.1355	0.0185
7	C	2.2767	3.6478	-0.2094	0.0981	-0.7771	-0.9027	-0.0510
8	C	3.5047	3.7774	0.4554	0.0455	-0.0240	0.8689	-0.4315
9	C	4.2577	4.9498	0.3895	-0.6402	-0.1104	0.2265	-0.1288
10	C	3.7880	6.0348	-0.3623	0.5393	-0.1842	0.2018	-0.2204
11	C	2.5603	5.9237	-1.0349	-0.7243	-0.1155	0.4285	-0.2675
12	C	1.8219	4.7527	-0.9560	-0.0028	0.9791	0.5903	0.3508
13	O	4.4353	7.2229	-0.4986	-1.0043	-0.4070	-0.0457	-0.1578
14	C	5.7011	7.4012	0.1462	1.7113	-0.8104	-1.2959	0.1880
15	C	6.2249	8.7780	-0.2389	0.4618	0.4374	-0.7166	0.0589
16	C	6.5696	8.8936	-1.7199	0.6464	0.2470	-0.1340	0.1080
17	O	7.6270	7.9778	-1.9896	-1.0339	0.2430	-0.1824	-0.0190
18	C	-0.7828	-1.1983	0.0938	0.1741	1.2005	1.9488	-0.1119
19	N	-1.4031	-2.1812	0.1538	0.4544	0.4172	0.6440	-0.0426
20	H	1.8892	-0.9966	0.0202	0.1974	-0.0031	0.0371	-0.0034
21	H	3.2026	1.0860	-0.1352	0.2563	-0.0898	0.0441	0.0060
22	H	-0.4339	3.3831	-0.1071	0.1769	0.0362	-0.0183	0.0024

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23	H	-1.7502	1.2999	-0.0007	0.1715	0.0198	0.0091	-0.0020
24	H	3.8727	2.9571	1.0647	0.3839	-0.0616	0.1159	-0.0886
25	H	5.1948	5.0099	0.9293	0.2636	-0.1099	-0.0926	-0.0369
26	H	2.2137	6.7683	-1.6213	0.0814	-0.0191	0.0268	-0.0244
27	H	0.8889	4.6808	-1.5070	0.4246	0.1451	-0.0303	0.1045
28	H	6.4045	6.6285	-0.1856	-0.5354	0.2858	-0.2103	-0.1231
29	H	5.5762	7.3231	1.2347	-0.5651	0.0052	0.0512	0.3998
30	H	7.1258	8.9813	0.3518	-0.2330	0.1403	0.0807	0.1265
31	H	5.4799	9.5382	0.0220	0.0866	-0.0126	0.0314	-0.0179
32	H	6.8717	9.9284	-1.9452	-0.0973	0.0286	0.0753	-0.0234
33	H	5.6780	8.6649	-2.3209	-0.0506	-0.0628	-0.0315	-0.0230
34	H	7.7473	7.9259	-2.9453	0.5105	-0.0311	0.0163	0.0588

Various energies components with zero point corrections of H3CBP molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H3CBP molecules.

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-823.642634
Sum of electronic and thermal Energies	-823.625327
Sum of electronic and thermal Enthalpies	-823.624382
Sum of electronic and thermal Free Energies	-823.624382

Table 3 presents dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of H3CBP molecules.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of H3CBP molecules.

Dipole Monent	6.9241 debye
Exact Polarizability	91.130
Approx Polarizability	145.507

The IR spectra of H3CBP 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 1298.836 cm^{-1}. This frequencies is associated with twisting of alkyl chain attached with alkoxy chain. Second peak is at 1657.421 cm^{-1}. This frequencies is associated with twisting of alkyl chain attached with CN group. The next peak is at 1322.658 cm^{-1} and another peak hieght is at 2994.410 cm^{-1}. These are associated with twisting of alkoxy chain. Other peak hieght is at 2340.728 cm^{-1} which is associated with CN bond streching.

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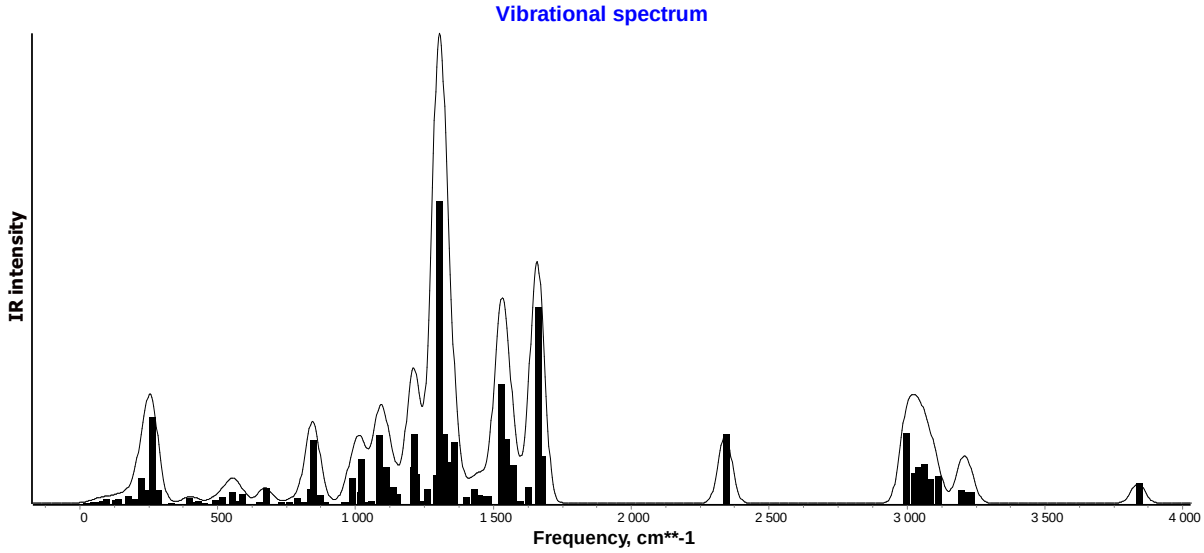

Figure 2: IR Spectra of H3CBP molecule.

Figure 3 represent Raman activities of H3CBP molecule. There are various peaks and the highest Raman activity is at 1657.421 cm^{-1}. This is associated with twisting of phenyl group attached with CN group. Next peak is at 2340.817 cm^{-1} which associated with CN bond strechingh.

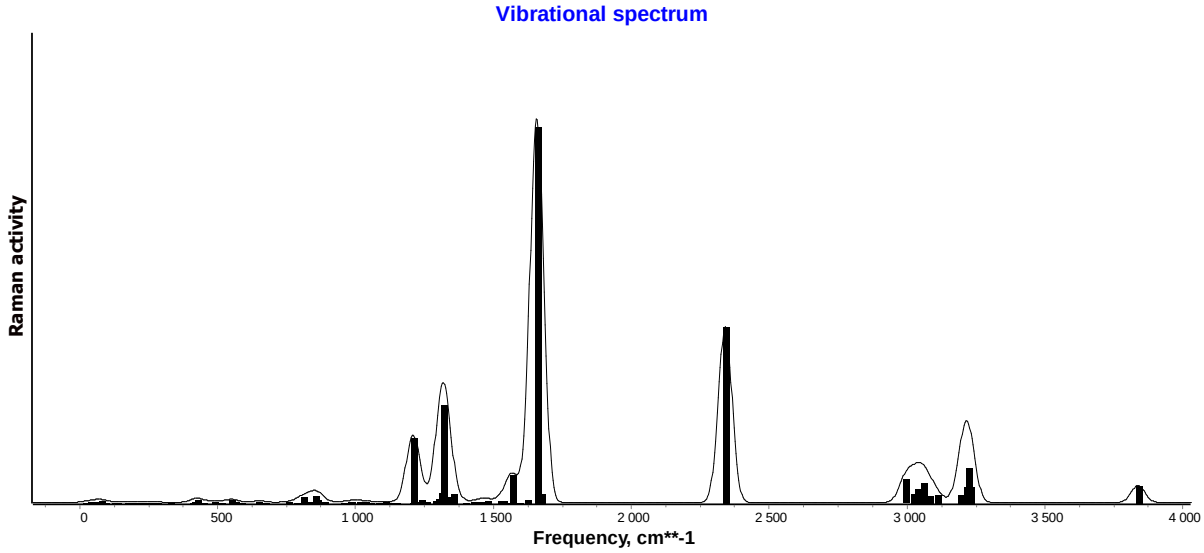

Figure 3: Raman activitty of H3CBP molecule.

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. The IR peaks and Raman activities peaks were explained.

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