IARJSET ISSN (O) 2393-8021, ISSN (P) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Impact Factor 7.105 ⁜ Vol. 9, Issue 1, January 2022

DOI: 10.17148/IARJSET.2022.9124

Quantum Mechanical Study of 4, 4' -Disubstituted Biphenyls: Part VII: $HO(CH_2)_9OC_6H_4.C_6H_4CN$

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Abstract: Geometrical anisotropy of small molecules with high polarizability may exhibit one or more liquid crystalline phases as well the familiar crystalline and isotropic phases. Structure and bonding in liquid crystals is important and diverse field in the interface between modern physics and chemistry. Structure–property relationship has been a key issue for the study of liquid crystals. Characteristically, it is observed that liquid crystalline compounds have a rigid core, which acts as the mesogenic unit and flexible alkyl chains at the terminal ends. 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 ($HO(CH_2)_9OC_6H_4.C_6H_4CN$) were calculated using DFT method. The vibration associated with peaks was discussed. The atomic charges with point dipoles were also computed. The Humo-Lumo gap as representation of band gap, thus computed.

Keywords: 4,4'-disubstituted biphenyl, Liquid Crystals, Mesogen, IR Spectra, Raman Activities

INTRODUCTION

Geometrical anisotropy of small molecules with high polarizability may exhibit one or more liquid crystalline phases as well the familiar crystalline and isotropic phases. [1] Incorporation of such moieties into the core chain or side group in a molecule can result in the formation of liquid crystalline phase at reasonable higher temperatures. The formation of such a phase, as well as its type, is closely related to the molecular structure.[2-4] Characteristically, it has been observed that liquid crystalline compounds have a rigid core, which acts as the mesogenic unit, and flexible alkyl chains at the terminal ends.[5] This feature is of main significance in the design and synthesis of new liquid crystalline compounds. These mesogens exhibit liquid crystalline behavior because of their high aspect ratio (length to breadth ratio). Zugenmaier et al. [6, 7] studied the crystal and molecular structures of ten 4, 4′-disubstituted biphenyls of the general formula HO-$(CH_2)_n$-O-C_6H_4-C_6H_4-CN (n=3−11) (H_nCBPs). Loubser et al.[8] invetigated the unusual orientational behaviour of liquid crystals and they also studied the effect of bipolar interactions on the ferroelectric properties. Ojha et al.[9] studied the molecular ordering in a bipolar nematogenic cyanobiphenyl using computer simulation approach. Hussian et al. [10] studied the liquid crystals based sensing platform-technological aspects. Chaudhary et al. calculated the electro-optical parameters with adverse order of 10CB liquid crystal molecules studied under the influence of an external high electric field.[11] Kumar et al. [12] has observed Odd−Even effect in the electro−optical properties of the homologous series of H_nCBP liquid crystal 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. [13] 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. [14] computed the 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 ($HO(CH_2)_9OC_6H_4.C_6H_4CN$; **H9CBP**). The geometry were generated from the paper by Zugenmaier et al. [6, 7]

COMPUTATIONAL METHOD

The geometry was optimized using DFT method B3LYP [15,16] using 6-31G** [17, 18] which was found suitable for these type of systems [19] with keeping all atoms free. The analytical frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit.[20]

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RESULTS

The optimized geometry of H9CBP 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 plannar to biphenyl and separation is 1.36Å. The cyano group is planar to biphenyl ring and separation is 1.43Å.

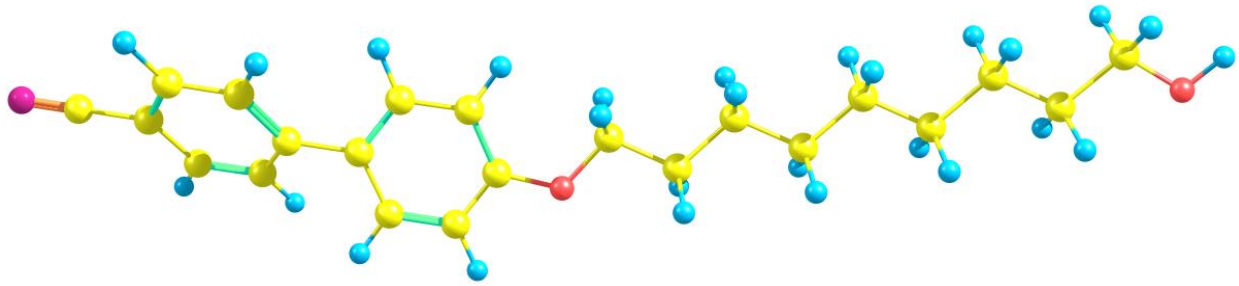

Figure 1: The optimized structure of the H9CBP molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of H9CBP 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 H9CBP molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.0890	-0.1436	-0.4427	-0.5150	0.7561	1.4491	0.2517
2	C	1.4886	-0.0904	-0.3268	-0.2490	-0.0077	-0.0951	-0.0131
3	C	2.1237	1.1276	-0.1197	-0.3662	0.1885	-0.1735	-0.0161
4	C	1.3930	2.3264	-0.0146	0.2185	0.1203	-0.3440	0.0088
5	C	-0.0082	2.2551	-0.1312	-0.1132	0.0227	-0.2692	-0.0695
6	C	-0.6552	1.0444	-0.3443	-0.3229	-0.5150	-0.2282	-0.0577
7	C	2.0757	3.6209	0.2120	-0.0027	-0.2471	-0.0187	-0.1360
8	C	3.2245	3.7083	1.0114	-0.1804	-0.2087	-0.0212	-0.1844
9	C	3.8743	4.9222	1.2359	-0.1251	-0.1360	-0.0846	-0.0516
10	C	3.3772	6.0943	0.6511	0.3163	-0.2192	0.3582	-0.2238
11	C	2.2294	6.0260	-0.1551	-0.3563	-0.1790	-0.5752	-0.0556
12	C	1.5937	4.8122	-0.3662	-0.4786	0.1760	-0.1503	0.1926
13	O	3.9244	7.3304	0.8009	-0.8846	-0.4898	-0.2544	-0.2861
14	C	5.0957	7.4758	1.6054	1.3276	-0.7763	-1.2888	-0.3507
15	C	5.4787	8.9491	1.6077	1.0120	-0.5423	-0.0655	-0.2710
16	C	6.7326	9.2283	2.4459	0.9098	-0.0020	-0.6876	0.0391
17	C	7.1218	10.7122	2.4694	0.5519	-0.0916	-0.1450	0.0098
18	C	8.3754	11.0014	3.3047	0.5390	0.2533	-0.1187	0.1452
19	C	8.7591	12.4862	3.3352	0.4645	-0.1821	0.0265	-0.1628
20	C	10.0128	12.7774	4.1701	1.0374	0.4989	0.3281	0.2973
21	C	10.3879	14.2636	4.1986	0.1440	-0.1293	0.6690	-0.2837
22	C	11.6331	14.5501	5.0281	0.5910	-0.1549	0.8057	-0.1043
23	O	11.8824	15.9499	4.9783	-1.1596	-0.0656	0.3365	-0.1086
24	C	-0.5721	-1.3960	-0.6592	0.3092	1.0020	1.8932	0.3245
25	N	-1.1096	-2.4133	-0.8344	0.3691	0.3240	0.6120	0.1056
26	H	2.0682	-1.0037	-0.4125	0.1546	-0.0089	0.0028	-0.0004

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27	H	3.2072	1.1564	-0.0641	0.1476	-0.0356	-0.0104	0.0012
28	H	-0.5994	3.1593	-0.0269	0.2280	0.0312	-0.0721	-0.0032
29	H	-1.7367	1.0070	-0.4241	0.0299	-0.0682	0.0206	-0.0035
30	H	3.6085	2.8159	1.4966	0.1918	0.0095	0.0638	-0.0081
31	H	4.7516	4.9443	1.8709	0.1147	-0.0065	-0.0846	0.0093
32	H	1.8631	6.9398	-0.6113	0.2938	0.0347	-0.0661	0.0512
33	H	0.7233	4.7800	-1.0147	0.3186	0.1173	0.0244	0.0906
34	H	5.9102	6.8612	1.1949	-0.4133	0.2632	-0.1156	-0.0977
35	H	4.8934	7.1253	2.6280	-0.4027	-0.0156	-0.0346	0.2972
36	H	4.6311	9.5298	1.9918	-0.4192	-0.2609	0.1850	0.1108
37	H	5.6371	9.2720	0.5716	-0.3719	0.0362	0.0891	-0.2914
38	H	7.5746	8.6393	2.0553	-0.4451	0.2744	-0.1616	-0.1142
39	H	6.5706	8.8813	3.4764	-0.4157	-0.0266	-0.0734	0.3113
40	H	6.2800	11.3003	2.8609	-0.2149	-0.1488	0.1193	0.0515
41	H	7.2820	11.0609	1.4395	-0.2037	0.0137	0.0782	-0.1785
42	H	9.2181	10.4163	2.9097	-0.2859	0.1719	-0.1324	-0.0849
43	H	8.2163	10.6466	4.3331	-0.2662	-0.0321	-0.0680	0.2093
44	H	7.9167	13.0709	3.7309	-0.2231	-0.1478	0.1105	0.0689
45	H	8.9177	12.8420	2.3074	-0.2415	0.0290	0.0813	-0.1923
46	H	10.8552	12.1935	3.7723	-0.3496	0.1778	-0.1734	-0.1122
47	H	9.8538	12.4191	5.1973	-0.3370	-0.0606	-0.1035	0.2296
48	H	9.5579	14.8551	4.6054	-0.2306	-0.1649	0.1044	0.0913
49	H	10.5606	14.6297	3.1787	-0.2664	0.0489	0.0740	-0.2211
50	H	12.4863	13.9776	4.6264	0.0406	-0.0123	-0.0317	0.0114
51	H	11.4748	14.2091	6.0652	-0.0362	-0.0022	-0.0561	0.0470
52	H	12.6716	16.1335	5.5022	0.5670	-0.0835	-0.0367	-0.0539

Various energies components with zero point corrections of H9CBP molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H9CBP molecules.

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-1059.367690
Sum of electronic and thermal Energies	-1059.342200
Sum of electronic and thermal Enthalpies	-1059.341256
Sum of electronic and thermal Free Energies	-1059.427779

Table 3 presents dipole moment, exact polarizability, approx. and polarizability of H9CBP molecules. The band gap (Humo-Lumo) is 4.46 eV. The ionization potential is 5.97 eV and electron affinity is 1.51 eV.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of H9CBP molecules.

Dipole Monent	7.7736 debye
Exact Polarizability	160.171
Approx Polarizability	243.623

The IR spectra of H9CBP 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 1298.726 cm^{-1}. This frequency is associated with twisting of phenyl ring

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attached with alkoxy chain. Second peak is at 1657.342 cm^{-1}. This frequency is associated with twisting of phenyl ring. Other peak height is at 2340.671 cm^{-1} that is associated with CN bond stretching.

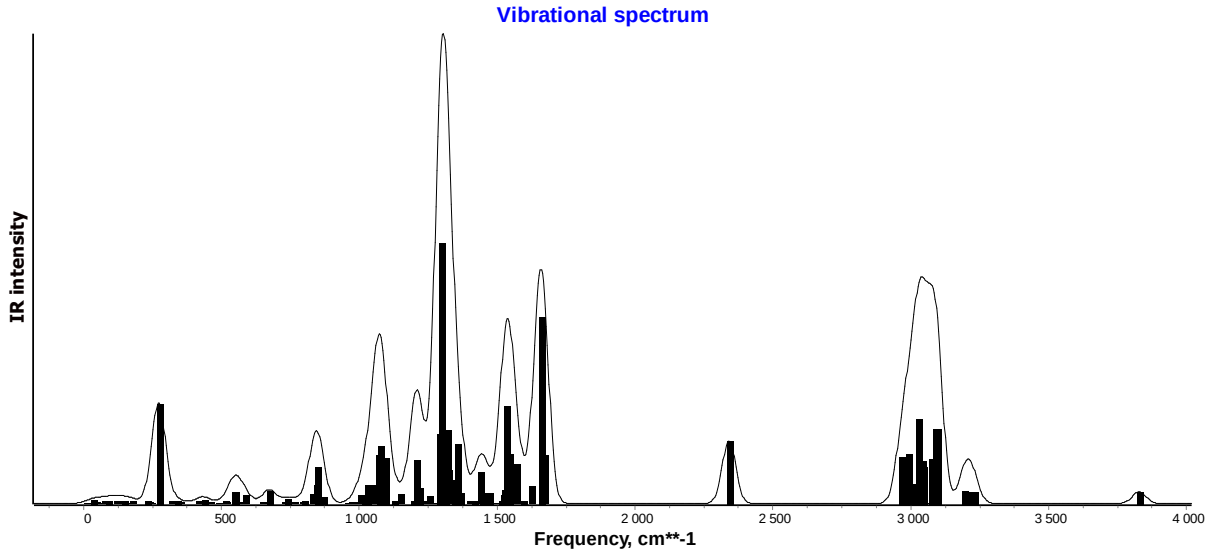

Figure 2: IR Spectra of H9CBP molecule.

Figure 3 represent Raman activities of H9CBP molecule. There are various peaks and the highest Raman activity is at 1317.390 cm^{-1} which are associated with twisting of phenyl ring. Next peak is at 2340.617 cm^{-1} that associated with CN bond stretching.

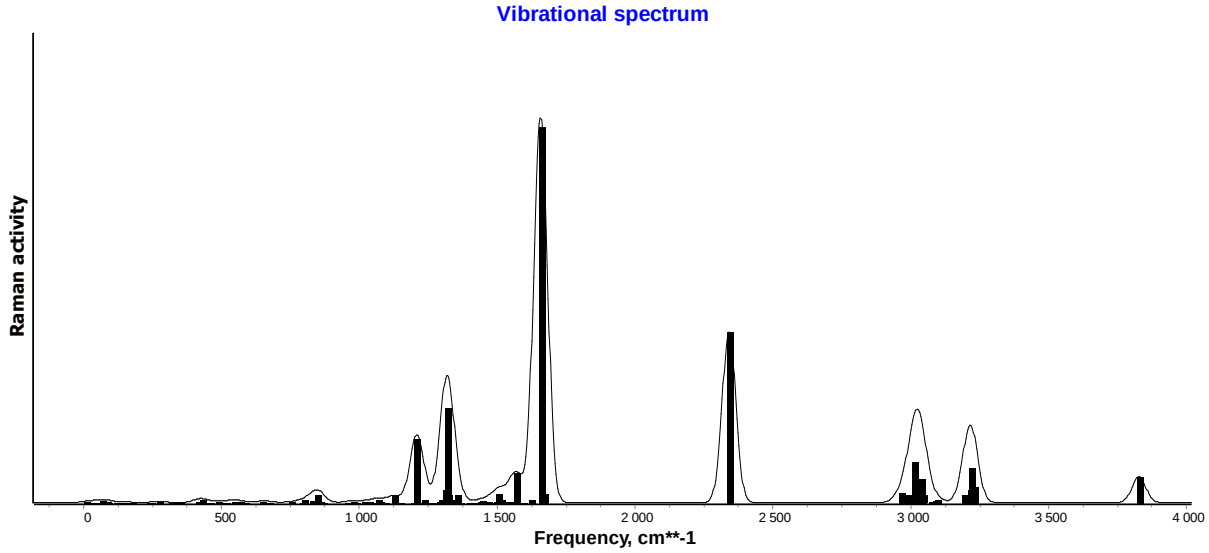

Figure 3: Raman activity of H9CBP molecule.

CONCLUSION

The electronic structure analysis of on 4, 4'-Disubstituted Biphenyl ($HO(CH_2)_9OC_6H_4.C_6H_4CN$) molecule was done. It is interesting to note that there is increase in polarizabilities of H9CBP in comparison with H3CBP, H4CBP, H5CBP, H6CBP, H7CBP and H8CBP [21-26] which means optical activities of H9CBP is more than H3CBP, H4CBP, H5CBP, H6CBP, H7CBP and H8CBP. The IR peaks and Raman activities peaks were explained.

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