Quantum Mechanical Study of 4, 4'-Disubstituted Biphenyls: Part III: HO (CH₂)₅OC₆H₄. C₆H₄CN

Devesh Kumar

Department of Physics, Siddharth University Kapilvastu, Siddharthnagar (U. P.) India 272 202

Abstract: 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. 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})₅ $OC_{6}H_{4}$, $C_{6}H_{4}CN$) were calculated using DFT method. The vibrations 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.

Keywords: Disubtituted 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 appropriate for purpose of electro-optic devices are higly studied liquid crystals and their properties as liquid crystal devices are well known [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] Studied 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 caxis. The molecules associate in pairs about the centre of inversion. Zugenmaier et al. [5, 6] determined 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] studied the unusual orientational behaviour of liquid crystals and they also studied the effect of bipolar interactions on the ferroelectric properties. The molecular ordering in a bipolar nematogenic cyanobiphenyl using computer simulation approach was done by Ojha et al. [8] Hussian et al. [9] investigated 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. [10] Kumar et al. [11] 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. [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] computed the spectroscopy existing behind the electrooptical 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 $(CH_2)_5OC_6H_4$. C_6H_4CN ; **H5CBP**). The geometry were generated from the paper by 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 H5CBP 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.



Figure 1: The optimized structure of the H5CBP molecule

Volume 11 Issue 1, January 2022 <u>www.ijsr.net</u> Licensed Under Creative Commons Attribution CC BY

International Journal of Science and Research (IJSR) ISSN: 2319-7064 SJIF (2020): 7.803

Table 1 present the charges as well as multipoles corresponding each atoms of H5CBP molecule. Since

multipole depends on the coordinates of each atoms therefore coordinates are also tabulated here.

Table 1: The charge.	coordinates and	l multipoles	corresponding	each atoms	of H5CBP	molecule.
0	,	1	1 0			

Sn No Atom	Coordinates		Change	Multipole (en)					
Sr. No.	Atom	Х	Y	Z	Charge	Munpole (au)			
1	С	-0.0244	-0.0477	0.0258	-0.5888	0.5968	1.0765	-0.0411	
2	С	1.3807	-0.0450	-0.0031	-0.3430	-0.1997	-0.1754	0.0098	
3	С	2.0733	1.1586	-0.0436	-0.2552	-0.1171	-0.4083	0.0216	
4	С	1.3966	2.3931	-0.0503	0.1001	-0.3286	-0.4292	0.0292	
5	С	-0.0106	2.3726	-0.0188	-0.2567	-0.3727	-0.3932	0.0026	
6	С	-0.7155	1.1759	0.0161	-0.3889	-0.1441	-0.2383	0.0112	
7	С	2.1410	3.6728	-0.0894	0.0636	-0.6965	-0.9767	-0.0571	
8	С	3.3647	3.8246	0.5781	0.1119	-0.0332	1.0478	-0.4401	
9	С	4.0739	5.0258	0.5511	-0.6359	0.1198	0.3994	-0.0577	
10	С	3.5620	6.1179	-0.1615	0.5711	-0.3984	0.1432	-0.2763	
11	С	2.3385	5.9844	-0.8375	-0.7906	-0.1972	0.3909	-0.2926	
12	С	1.6445	4.7849	-0.7983	0.0514	0.8819	0.5550	0.3604	
13	0	4.1640	7.3339	-0.2598	-0.9106	-0.3504	-0.1004	-0.1734	
14	С	5.4172	7.5405	0.3927	1.5422	-0.6534	-1.0482	0.0280	
15	С	5.8571	8.9701	0.1094	0.5926	-0.4516	0.0656	-0.2498	
16	С	7.2024	9.3099	0.7634	1.4059	0.1501	-0.1895	0.2369	
17	С	7.6481	10.7505	0.4875	0.2005	-0.1452	0.5687	-0.2597	
18	С	8.9847	11.0942	1.1334	0.8616	-0.1013	0.3537	-0.1901	
19	0	9.2902	12.4446	0.8105	-1.1255	-0.0854	0.2797	-0.1520	
20	С	-0.7447	-1.2856	0.0644	0.1971	1.0647	1.8439	-0.0517	
21	N	-1.3293	-2.2914	0.0951	0.3923	0.3648	0.6226	-0.0207	
22	Н	1.9181	-0.9876	-0.0061	0.1776	0.0064	0.0270	-0.0021	
23	Н	3.1572	1.1439	-0.0975	0.2344	-0.0747	0.0378	0.0044	
24	Н	-0.5578	3.3096	0.0048	0.2249	0.0656	-0.0323	-0.0061	
25	Н	-1.8000	1.1787	0.0477	0.1553	0.0088	0.0175	0.0002	
26	Н	3.7639	2.9982	1.1589	0.4113	-0.0755	0.1204	-0.0936	
27	Н	5.0093	5.1014	1.0923	0.1874	-0.0593	-0.0923	-0.0069	
28	Н	1.9606	6.8352	-1.3949	0.0945	-0.0178	0.0222	-0.0140	
29	Н	0.7140	4.6970	-1.3511	0.3741	0.1209	-0.0166	0.0754	
30	Н	6.1591	6.8217	0.0151	-0.4420	0.2520	-0.1459	-0.1160	
31	Н	5.3082	7.3739	1.4744	-0.4565	0.0041	0.0183	0.3274	
32	Н	5.0796	9.6544	0.4697	-0.3181	-0.2027	0.1713	0.0823	
33	Н	5.9202	9.1095	-0.9765	-0.2954	0.0131	0.0365	-0.2613	
34	Н	7.9716	8.6128	0.4013	-0.4587	0.2380	-0.2087	-0.1240	
35	Н	7.1319	9.1500	1.8488	-0.5064	-0.0181	-0.0465	0.3683	
36	Н	6.8936	11.4562	0.8564	-0.2581	-0.1611	0.1546	0.0808	
37	Н	7.7323	10.9194	-0.5932	-0.2443	0.0193	0.0303	-0.2298	
38	Н	9.7638	10.4070	0.7622	-0.1214	0.0729	-0.0661	-0.0257	
39	Н	8.9179	10.9480	2.2248	-0.1400	0.0000	-0.0193	0.1229	
40	Н	10.1365	12.6678	1.2171	0.5865	-0.1052	-0.0476	-0.0419	

Various energies components with zero point corrections of H5CBP molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of H5CBP molecules

Energies Components	Hartree
Sum of electronic and zero-point Energies	-902.218342
Sum of electronic and thermal Energies	-902.198303
Sum of electronic and thermal Enthalpies	-902.197359
Sum of electronic and thermal Free Energies	-902.269956

Table 3 presents dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of H5CBP molecules. The 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 monent, exact polarizability, and approx. polarizability of H5CBP molecules

Dipole Monent	7.2419debye
Exact Polarizability	110.682
Approx Polarizability	177.283

<u>www.ijsr.net</u>

Licensed Under Creative Commons Attribution CC BY

DOI: 10.21275/SR22118201140

The IR spectra of H5CBP 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 1299.261 cm⁻¹. This frequency is associated with twisting of phenyl ring attached with alkoxy chain. Second peak is at 1657.572 cm^{-1} . This frequency is associated with twisting of phenyl ring. Other peak height is at 2340.723 cm^{-1} which is associated with CN bond stretching.



Figure 2: IR Spectra of H5CBP molecule

Figure 3 represent Raman activities of H5CBP molecule. There are various peaks and the highest Raman activity is at 1318.024 cm⁻¹ and another peak is at 1657.687 cm⁻¹ which are associated with twisting of phenyl ring. Next peak is at 2340.723 cm⁻¹ which associated with CN bond stretching.



Figure 3: Raman activitty of H5CBP molecule

4.Conclusion

Electronic structure analysis of on 4, 4'-Disubstituted Biphenyl (HO (CH₂) $_5OC_6H_4$. C_6H_4CN) molecule was done with DFT methods. It is noted that increase in polarizabilities 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.

References

- [1] G. W. Gray, & P. A. Winsor, (1974). Liquid Crystals and Plastic Crystals, Vol.1, (New York: Wiley).
- [2] G. W. Gray, & P. A. Winsor, (1974). Liquid Crystals and Plastic Crystals, Vol.2, (New York: Wiley).
- [3] D. A. Dunmur, M. R. Manterfield W. H. Miller & J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.* 1978, 45, 127.
- [4] P. Mandal & S. Paul, *Mol. Cryst. liq. Cryst.* 1985, 131, 223.

Volume 11 Issue 1, January 2022

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

International Journal of Science and Research (IJSR) ISSN: 2319-7064 SJIF (2020): 7.803

- [5] P. Zugenmaier & A. Heiske, *Liquid Crystals* 1993, 15, 835
- [6] P. Zugenmaier, Liquid Crystals 2002, 29, 443
- [7] Christa Loubser and John W. Goodby, J. Mater. Chem.1995, 5, 1107
- [8] P. Lakshmi Praveen & Durga P. Ojha, *Phase Transitions* **2010**, *83*, 37
- [9] Zakir Hussain, Farah Qazi, Muhammad Imran, Ahmed Adil, Usman Asim, Riaz Amna and Didar Abbasi, *Biosensors and Bioelectronics* 2016, 85, 110
- [10] Shivani Chaudhary, Narinder Kumar, Pawan Singh, Khem B. Thapa and Devesh Kumar, *Jordan Journal* of *Physics* **2021**, *14*, 79.
- [11] Narinder Kumar, Pawan Singh, Khem Thapa and Devesh Kumar, *Iranian J. Math. Chem.*2020, *11*, 239.
- [12] Narinder Kumar, Shivani Chaudhary, Pranav Upadhyay, A K Dwivedi And Devesh Kumar, *Pramana - J. Phys.* 2020, 94, 106.
- [13] N. Kumar, P. Singh, S. Chaudhary, K. B. Thapa, P. Upadhyay, A. K. Dwivedi and D. Kumar, *Acta Physica Polonica A* 2020, *137*, 1135.
- [14] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [15] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- [16] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299.
- [17] H. D. Cohen, C. C. J. Roothaan, J. Chem. Phys. 1965, 43, S34.
- [18] Narinder Kumar, Shivani Chaudhary, Pawan Singh, Khem B. Thapa, Devesh Kumar, *Journal of Molecular Liquids* 2020, 318, 114254.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, et al., Gaussian 09, Revision A.02, Gaussian, Inc, Wallingford CT, 2010.
- [20] Devesh Kumar, Int. Adv. Res. J. Sc., Eng. and Tech.2022, 9, 38.
- [21] Devesh Kumar, Int. Adv. Res. J. Sc., Eng. and Tech. 2021, 8, 331