Quantum Mechanical Study of 4-Alkyl 4'-Cyano Biphenyls: Part I: C_9H_{19}-C_6H_5-C_6H_5-CN

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Abstract

The quantum mechanical calcualtion werer carried out on 4-Alkyl 4'-Cyano Biphenyls (C_9H_{19}-C_6H_5-C_6H_5-CN). The IR spectra and Raman activities and its vibration association were discussed. The atomic charges with multipole moments were also computed and discussed.

Keywolds: Cyano Biphenyl, Liquid Crystals, Mesogen, IR Spectra, Raman Activities.

INTRODUCTION:

Alkyl and alkoxy cyano biphenyls are higly studied liquid crystals which are suitable for application in electro-optic devices and their properties as liquid crystal devices were well established [1,2]. Dunmur et al. [3] were 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. Merkel et al. [4] has calculated and analyzed the vibration spectra for cyanobiphenyl liquid crystals using DFT methods. Wu et al. [5] were studied the infra red applications of Perdeuterated cyanobiphenyl liquid crystals and found that it exhibits a much cleaner and reduced infrared absorption. Bernard et al. [6] studied the vibrational spectra of 4-octyloxy, 4'-cyanobiphenyl CN stretching in smectic, nematic, isotropic, and solution phases. Delabre et al. [7] studied the specificities of wetting behaviour of the series of cyanobiphenyl liquid crystals (LCs) on usual substrates, i.e. oxidized silicon wafers, water and glycerol, at both the macroscopic and microscopic scale, in the nematic range of temperature. Paterson et al. [8] synthesized and studied the role of a terminal chain in promoting the twist-bend nematic phase. Wang et al. [9] synthesised and studied the properties of hydroxy tail-terminated cyanobiphenyl liquid crystals.

In the this paper we will discuss about IR as well as Raman activities of 4-Alkyl 4'-Cyano Biphenyls (C_9H_{19}-C_6H_5-C_6H_5-CN; **9CB**). The geometry were taken from article by Murty et al. [10]

COMPUTATIONAL METHOD:

The geometry was optimized using DFT method B3LYP [11,12] using 6-31G** [13, 14] which was found suitable for these type of systems [15] with keeping all atoms free. The analytical frequencies as well as Raman activities were calculated. All calculation were done using Gaussian09 programme suit.[16]

RESULTS:

The optimized geometry of 9CB molecule is shown in figure 1. The inter ring angle between biphenyl is 37.1^o and inter ring seperation is 1.48Å. The angle between biphenyl and alkyl chain

is 88.3° and seperation is 1.52Å. The cyano group is planar to biphenyl ring and seperation is 1.43Å.

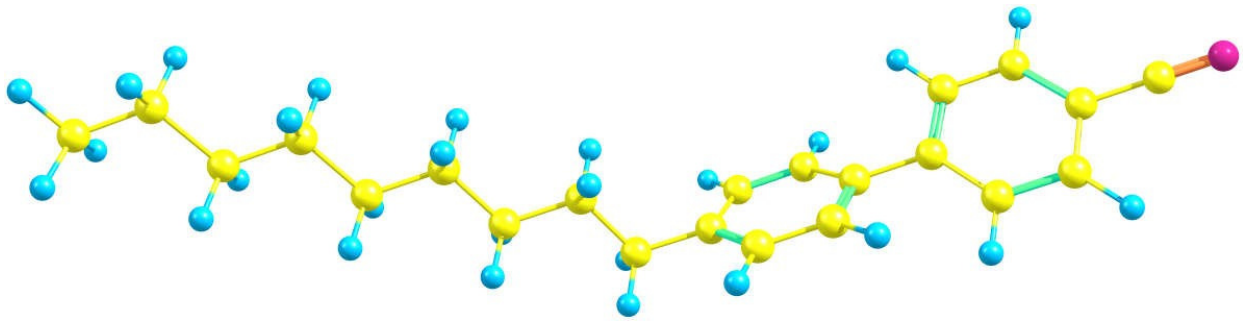

Figure 1: The optimized structure of the 9CB molecule.

Table 1 present the charges as well as multipoles corresponding each atoms of 9CB 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 9CB molecule.

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	-7.28584	-0.80234	0.15476	-0.41472	2.163058	0.691982	-0.11544
2	C	-6.38667	-1.44759	-0.71108	-0.50104	-0.21483	-0.37504	-0.23279
3	C	-5.0635	-1.02852	-0.77703	-0.11962	-0.38434	-0.08979	0.014535
4	C	-4.5959	0.04076	0.00895	0.219482	0.220105	-0.00987	-0.08415
5	C	-5.50887	0.67735	0.86973	-0.08879	-0.11159	-0.08467	-0.02069
6	C	-6.83393	0.26636	0.9474	-0.38713	-0.31934	0.335216	0.399678
7	C	-3.18298	0.48371	-0.06798	0.047686	-0.04294	-0.02514	0.052863
8	C	-2.49574	0.91927	1.07741	-0.22512	0.208283	0.123707	0.030561
9	C	-1.17016	1.3391	1.00067	-0.08564	0.100522	-0.14033	-0.81293
10	C	-0.47823	1.34461	-0.21811	-0.21578	0.214147	-0.00997	-0.56291
11	C	-1.16484	0.91069	-1.36052	-0.3303	0.004584	0.010291	-0.08672
12	C	-2.48937	0.48682	-1.28998	-0.1582	0.310566	0.104008	0.154252
13	C	0.97097	1.7706	-0.29216	0.34409	0.056441	-0.21283	0.092493
14	C	1.95936	0.60076	-0.10623	0.072314	-0.02917	-0.35917	-0.10706
15	C	3.42703	1.03913	-0.17753	0.576164	-0.03395	0.129852	0.065898
16	C	4.4207	-0.11506	0.00653	0.367397	0.016558	-0.22406	-0.07934
17	C	5.88816	0.32684	-0.06053	0.448017	0.067063	0.159798	0.025659

18	C	6.88614	-0.8233	0.12471	0.441548	0.044586	-0.17236	-0.03606
19	C	8.35254	-0.37821	0.06075	0.368786	0.152941	0.194639	0.011574
20	C	9.35283	-1.52603	0.24802	0.422943	0.040173	-0.09896	0.000419
21	C	10.8145	-1.0715	0.18519	0.203792	0.15885	0.043216	0.132542
22	C	-8.6515	-1.23012	0.22872	0.43628	2.397011	0.76076	-0.12408
23	N	-9.76053	-1.57736	0.28886	0.427409	0.721226	0.218077	-0.03794
24	H	-6.7302	-2.279	-1.31762	0.090106	-0.01444	-0.01722	-0.01298
25	H	-4.37292	-1.55349	-1.42927	0.184311	-0.00971	0.013136	0.020826
26	H	-5.17968	1.5221	1.46631	0.137122	-0.00099	0.004245	0.007679
27	H	-7.52786	0.77279	1.6101	0.017335	-0.05996	0.024739	0.042051
28	H	-2.99666	0.90659	2.04107	0.190506	0.048359	0.000917	-0.0351
29	H	-0.6615	1.66654	1.90434	0.320654	-0.10671	-0.04374	-0.06248
30	H	-0.65829	0.91855	-2.32275	0.091479	-0.00749	-0.01415	-0.04343
31	H	-3.00275	0.18698	-2.19895	0.218911	0.021614	0.012645	0.049773
32	H	1.16338	2.24901	-1.26089	-0.07481	0.014616	0.049808	-0.10014
33	H	1.16945	2.53028	0.47439	-0.02283	-0.01217	0.037203	0.045759
34	H	1.76235	-0.16085	-0.87262	-0.18355	-0.03212	-0.1146	-0.11754
35	H	1.76409	0.11617	0.85976	-0.11151	-0.01993	-0.04676	0.128001
36	H	3.61331	1.52824	-1.14444	-0.20531	0.03267	0.081659	-0.16491
37	H	3.61417	1.80497	0.58888	-0.22231	0.031661	0.129028	0.13119
38	H	4.23276	-0.60539	0.97235	-0.17949	-0.0251	-0.07481	0.150821
39	H	4.23578	-0.8797	-0.76141	-0.23067	-0.03566	-0.1404	-0.13508
40	H	6.07525	0.81748	-1.02649	-0.20819	0.031473	0.083667	-0.16556
41	H	6.07101	1.09263	0.70695	-0.2148	0.0281	0.128909	0.128165
42	H	6.6981	-1.31498	1.08999	-0.19458	-0.02826	-0.07817	0.155572
43	H	6.70523	-1.58848	-0.64385	-0.21816	-0.02982	-0.13244	-0.1296
44	H	8.54171	0.11272	-0.90485	-0.20136	0.024967	0.079249	-0.16537
45	H	8.53337	0.38787	0.82863	-0.20597	0.022361	0.124446	0.124902
46	H	9.16328	-2.01682	1.21251	-0.18056	-0.02925	-0.07851	0.148268
47	H	9.17382	-2.29076	-0.52023	-0.16411	-0.01312	-0.10628	-0.10909
48	H	11.5022	-1.9123	0.32345	-0.10087	0.087198	-0.11582	0.004587
49	H	11.04495	-0.60941	-0.78163	-0.05268	0.019451	0.036257	-0.09783
50	H	11.03326	-0.33169	0.96382	-0.12823	0.030914	0.106031	0.102167

Various energies components with zero point corrections of 9CB molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of 9CB molecules.

Energies Components	**Hartree**
Sum of electronic and zero-point Energies	-908.962125
Sum of electronic and thermal Energies	-908.938789
Sum of electronic and thermal Enthalpies	-908.937845
Sum of electronic and thermal Free Energies	-909.01957

Table 3 presents dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of 9CB molecules.

Table 3: Dipole monent, exact polarizability, approx. polarizability and hyperpolarizability of 9CB molecules.

Dipole Monent	5.9993 debye
Exact Polarizability	186.209
Approx Polarizability	325.194
Hyperpolarizability	-1.80352607D+01

The IR spectra of 9CB molecule is shown in figure 2. From figure 2 it is visual that there are several peak and the highest peak (IR intensity) is at 3074.8659 cm^{-1}. Second peak is at 3086.036 cm^{-1}. The next peak is at 3106.3828 cm^{-1}. All these frequencies are associated with twisting of alkyl chain with respect to biphenyl plane. Another peak hieght is at 2341.886 cm^{-1}. This is associated with bond streching of CN group. Next peak is at 1659.8402 cm^{-1}. This is associated with twisting of phenyl group attached with CN group. Next peak is at 1539.8855 cm^{-1}. This frequency is assoicated with streching of inter bond separation of phenyl ring.

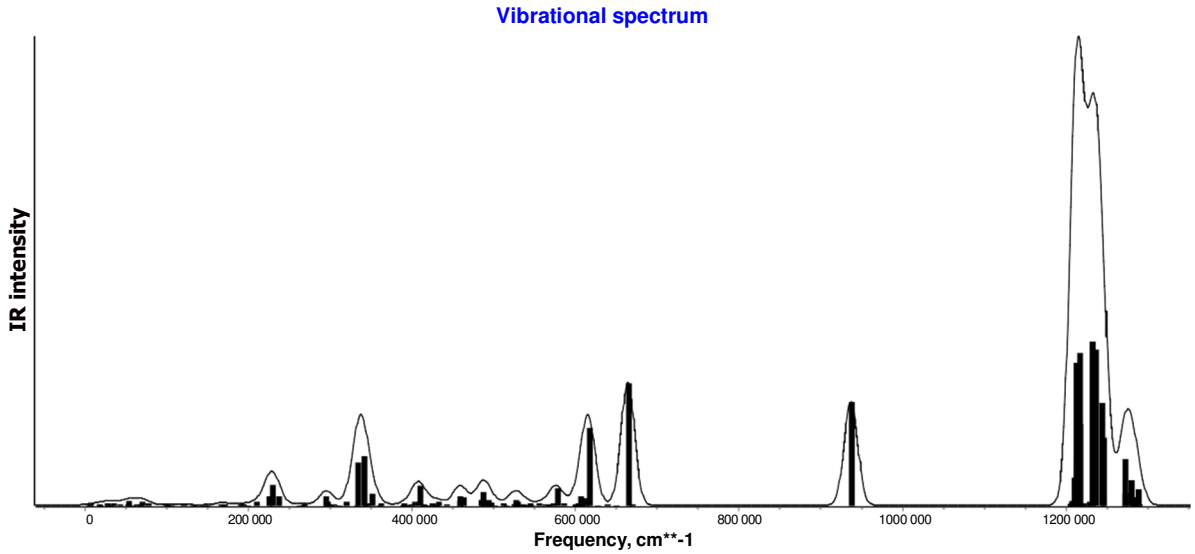

Figure 2: IR Spectra of 9CB molecule.

Figure 3 represent Raman activities of 9CB molecule. There are various peaks and the highest Raman activity is at 1659.8402 cm^{-1}. The frequency is associated twisting of phenyl ring as well as streching of phenyl and CN bond.

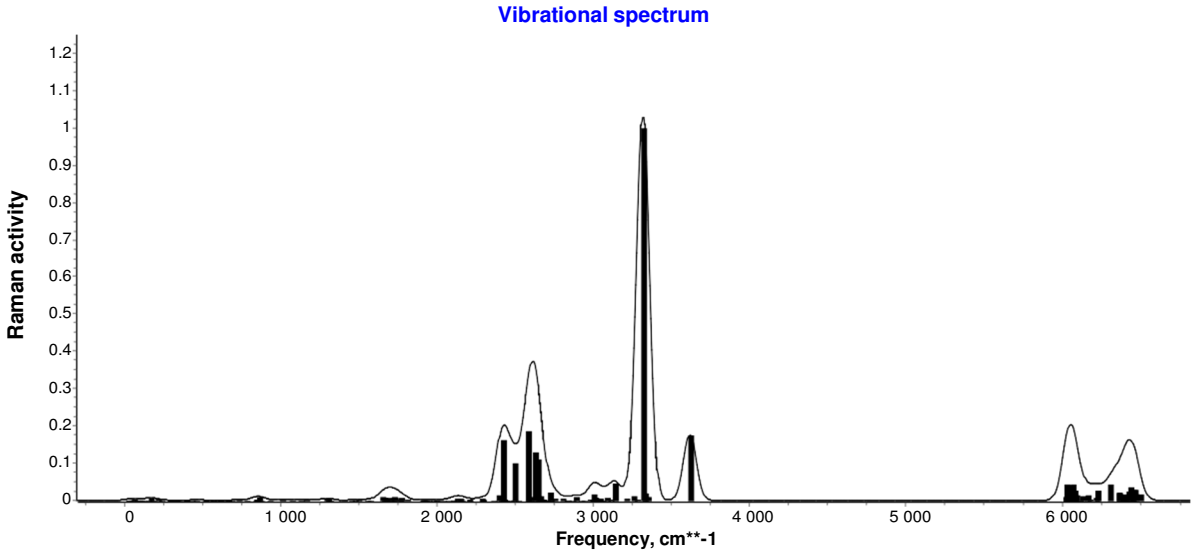

Figure 3: Raman activitty of 9CB molecule.

CONCLUSION:

Electronic structure analysis of on 4-Alkyl 4’-Cyano Biphenyls (C_9H_{19}-C_6H_5-C_6H_5-CN) molecule is carried out using DFT methods. The IR spectra and Raman activities 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. K. Merkel,R. Wrzalik, A. Kocot, *Journal of Molecular Structure* **2001**, *563–564*, 477.
5. Shin-Tson Wu and Qiong-Hua Wang, *Journal of Applied Physics* **2002**, *92*, 7146.
6. Bernard J. Bulkin and Kenneth Brezinsky, *J. Chem. Phys.* **1978**, *69*, 15.
7. U Delabre, C Richard and A M Cazabat, *J. Phys.: Condens. Matter* **2009**,*21*, 464129.
8. Daniel A. Paterson, Catriona A. Crawford, Damian Pociecha, Rebecca Walker, John M.D. Storey, Ewa Gorecka & Corrie T. Imrie, *Liquid Crystals* **2018**, *45*, 2341.
9. Kunlun Wang, Matthew Jirka, Prabin Rai, Robert J. Twieg, Tibor Szilvási, Huaizhe Yu, Nicholas L. Abbott, **Liquid Crystals 2019**, *46*, 397.
10. K. V. G. K. Murty, T. Manisekharan, and T. K. K. Srinivasan, *Mol. Cryst. Liq. Cryst.* **2004**, *408*, 83.
11. A.D. Becke, *J. Chem. Phys. 1993*, *98*, 5648.
12. C. Lee,W. Yang, R.G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
13. P.J. Hay,W.R.Wadt, *J. Chem. Phys.* **1985**, *82*,299.
14. H.D. Cohen, C.C.J. Roothaan, J. Chem. Phys. **1965**, *43*,S34.
15. Narinder Kumar, Shivani Chaudhary, Pawan Singh, Khem B. Thapa, Devesh Kumar, *Journal of Molecular Liquids* **2020**, *318*, 114254.
16. 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.