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Quantum Mechanical Study of 4-Alkyl 4'-Cyano Biphenyls: Part II: $C_{11}H_{23}$-C_6H_5-C_6H_5-CN

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Abstract
The physical property and molecular structure of the liquid crystal (LC) molecules is responsible for the electro-optical response. The cyanobiphenyls (nCB) LCs are highly polar, so they have very high electrochemical and thermal stability. These LCs are very popular in liquid crystal device design. In this work the IR spectra and Raman activities of 4-Alkyl 4'-Cyano Biphenyls ($C_{11}H_{23}$-C_6H_5-C_6H_5-CN) were calculated using DFT method. The spectroscopy analysis was done for vibration associated with peaks were discussed. The atomic charges with point dipole were also computed and discussed. The optical polarizability of the nCB LC molecules is an important parameter and it was also computed. The Homu-Lumo gap represent the ionization potential was also computed.

Keywords: Cyano Biphenyl, Liquid Crystals, Mesogen, IR Spectra, Raman Activities

1. 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] Merkel *et al.* [4] has calculated and analyzed the vibration spectra for cyanobiphenyl liquid crystals using DFT methods. Grey et al. studied that when the nCB liquid crystals having a exclusive property for the alkyl chain length is changed, then the molecular properties of the mesophase change [5, 6]. 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. 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]. 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 this paper we will discuss about IR as well as Raman activities of 4-Alkyl 4'-Cyano Biphenyls ($C_{11}H_{23}$-C_6H_5-C_6H_5-CN; 11CB). The geometry was taken from article by Murty *et al* [14].

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].

Results
The optimized geometry of 11CB molecule is shown in Fig 1. The inter ring angle between biphenyl is 36.9º and inter ring separation is 1.48Å. The angle between biphenyl and alkyl chain is 89.4º and separation is 1.51Å. The cyano group is planar to biphenyl ring and separation is 1.43Å.

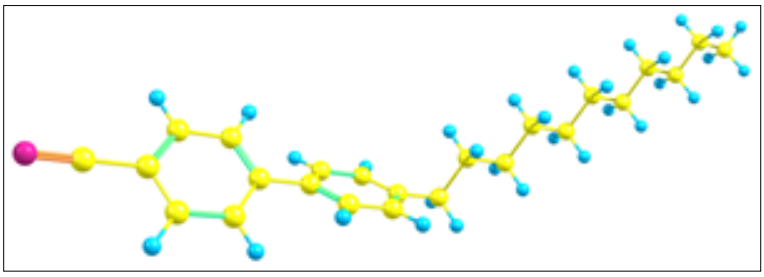

Fig 1: The optimized structure of the 11CB molecule

Table 1 present the charges as well as multipoles corresponding each atom of 11CB molecule. Since multipole depends on the coordinates of each atom therefore coordinates are also tabulated here.

Table 1: The charge, coordinates and multipoles corresponding each atom of 11CB molecule

S No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	-8.3721	-1.0132	-0.1931	-0.5010	1.6234	0.4368	0.2791
2	C	-7.4547	-1.5921	0.7001	-0.4294	-0.1475	-0.2916	0.1738
3	C	-6.1560	-1.1038	0.7761	-0.2045	-0.2824	-0.1095	0.0293
4	C	-5.7315	-0.0289	-0.0266	0.1617	-0.4272	-0.1419	-0.0406
5	C	-6.6625	0.5408	-0.9146	-0.1765	-0.0869	0.2511	-0.2712
6	C	-7.9633	0.0601	-1.0026	-0.2051	-0.2148	-0.0041	-0.0854
7	C	-4.3444	0.4875	0.0607	0.2157	-0.5091	-0.1930	-0.2137
8	C	-3.6639	0.9368	-1.0835	-0.1518	0.5087	0.2372	0.0469
9	C	-2.3622	1.4239	-0.9973	-0.1743	0.4340	0.0241	0.7624
10	C	-1.6879	1.4849	0.2300	-0.1533	-0.3382	-0.2346	0.8739
11	C	-2.3681	1.0381	1.3711	-0.4638	-0.0851	-0.0855	0.4053
12	C	-3.6690	0.5478	1.2913	-0.0842	0.1746	0.1019	-0.3017
13	C	-0.2612	1.9796	0.3139	0.5146	-0.0372	-0.1923	-0.1709
14	C	0.7809	0.8574	0.1276	-0.0222	-0.0414	-0.3466	0.1299
15	C	2.2274	1.3585	0.2170	0.4493	-0.1566	0.0599	-0.1472
16	C	3.2701	0.2488	0.0299	0.3023	-0.0209	-0.1911	0.1188
17	C	4.7178	0.7476	0.1225	0.3113	-0.0629	0.1262	-0.0827
18	C	5.7619	-0.3603	-0.0664	0.3569	-0.0323	-0.1066	0.0809
19	C	7.2094	0.1387	0.0283	0.2143	-0.0102	0.1021	-0.0559
20	C	8.2543	-0.9680	-0.1624	0.4238	-0.0435	-0.1006	0.0389
21	C	9.7016	-0.4691	-0.0671	0.2607	0.0579	0.1611	-0.0344
22	C	10.7472	-1.5749	-0.2596	0.4933	0.0018	-0.1023	-0.0372
23	C	12.1897	-1.0678	-0.1641	0.1996	0.1232	0.0976	-0.1381
24	C	-9.7125	-1.5129	-0.2775	0.2878	2.1390	0.8324	0.1023
25	N	-10.8010	-1.9188	-0.3460	0.4238	0.6954	0.2502	0.0481
26	H	-7.7644	-2.4269	1.3200	0.0956	-0.0040	-0.0221	0.0206
27	H	-5.4500	-1.5785	1.4500	0.1914	-0.0203	0.0204	-0.0323
28	H	-6.3682	1.3885	-1.5251	0.0187	0.0078	0.0626	-0.0485
29	H	-8.6717	0.5156	-1.6866	0.1055	-0.0190	0.0107	-0.0196
30	H	-4.1498	0.8817	-2.0533	0.2538	0.0429	0.0013	0.0803
31	H	-1.8581	1.7601	-1.9004	0.2735	-0.1062	-0.0464	0.0379
32	H	-1.8757	1.0878	2.3395	0.0458	0.0124	-0.0034	0.0579
33	H	-4.1795	0.2392	2.1989	0.2073	0.0278	0.0112	-0.0301
34	H	-0.0965	2.4615	1.2859	-0.0802	0.0089	0.0446	0.1053
35	H	-0.0946	2.7514	-0.4482	-0.0541	-0.0170	0.0461	-0.0586
36	H	0.6108	0.0811	0.8856	-0.1484	-0.0273	-0.0966	0.0998
37	H	0.6162	0.3730	-0.8441	-0.0815	-0.0212	-0.0384	-0.1157
38	H	2.3840	1.8442	1.1908	-0.1302	0.0252	0.0614	0.1261
39	H	2.3886	2.1398	-0.5396	-0.1737	0.0301	0.1099	-0.1011
40	H	3.1067	-0.5336	0.7848	-0.1963	-0.0292	-0.1231	0.1149
41	H	3.1141	-0.2349	-0.9449	-0.1482	-0.0171	-0.0654	-0.1412
42	H	4.8733	1.2302	1.0981	-0.1409	0.0236	0.0635	0.1324
43	H	4.8801	1.5315	-0.6311	-0.1588	0.0248	0.1026	-0.0949
44	H	5.5987	-1.1449	0.6862	-0.1788	-0.0241	-0.1152	0.1065
45	H	5.6072	-0.8419	-1.0426	-0.1521	-0.0146	-0.0673	-0.1389
46	H	7.3641	0.6193	1.0050	-0.1223	0.0175	0.0604	0.1205
47	H	7.3719	0.9244	-0.7235	-0.1347	0.0184	0.0957	-0.0848
48	H	8.0915	-1.7541	0.5889	-0.1831	-0.0218	-0.1157	0.1097
49	H	8.0998	-1.4482	-1.1394	-0.1776	-0.0167	-0.0737	-0.1513

50	H	9.8574	0.0100	0.9104	-0.1539	0.0147	0.0654	0.1417
51	H	9.8650	0.3177	-0.8177	-0.1646	0.0157	0.1091	-0.0978
52	H	10.5849	-2.3606	0.4910	-0.1635	-0.0134	-0.1023	0.1056
53	H	10.5912	-2.0534	-1.2362	-0.2176	-0.0268	-0.0882	-0.1751
54	H	12.3935	-0.3063	-0.9256	-0.1435	0.0304	0.1123	-0.1061
55	H	12.3867	-0.6152	0.8146	-0.0521	0.0148	0.0298	0.0950
56	H	12.9106	-1.8798	-0.3054	-0.0845	0.0779	-0.0998	-0.0019

Various energies components with zero-point corrections of 11CB molecule is tabulated in Table 2.

Table 2: Energies Components such as electronic, thermal and Free energies of 11CB molecules

Energies Components	Hartree
Sum of electronic and zero-point Energies	-987.536573
Sum of electronic and thermal Energies	-987.510579
Sum of electronic and thermal Enthalpies	-987.509635
Sum of electronic and thermal Free Energies	-987.597533

Table 3 presents dipole moment, exact polarizability, approx. polarizability and hyperpolarizability of 11CB molecules.

Table 3: Dipole moment, exact polarizability, approx. polarizability and hyperpolarizability of 11CB molecules

Dipole Moment	6.1850 Debye
Exact Polarizability	205.179
Approx. Polarizability	356.900
Hyperpolarizability	3269.533

Homo-Lumo gap of 9CB, 10CB and 11CB molecules

Table 4: Homo-Lumo gap of 9CB, 10CB and 11CB molecules in Hartree. It is interesting to note that the Humo-Lomo gap of all the three molecules is same.

	Molecules		
	9CB	10CB	11CB
Homo-Lumo Gap	0.3588	0.3588	0.3588

The IR spectra of 11CB molecule is shown in Fig 2. From Fig 2 it is visual that there are several peak and the highest peak (IR intensity) is at 3076.848 cm^{-1}. Second peak is at 3076.848 cm^{-1}. These frequencies are associated with twisting of alkyl chain. The next peak is at 2341.8323 cm^{-1}. This is associated with bond stretching of CN group. Another peak height is at 1659.8025 cm^{-1}. This is associated with twisting of phenyl group attached with CN group.

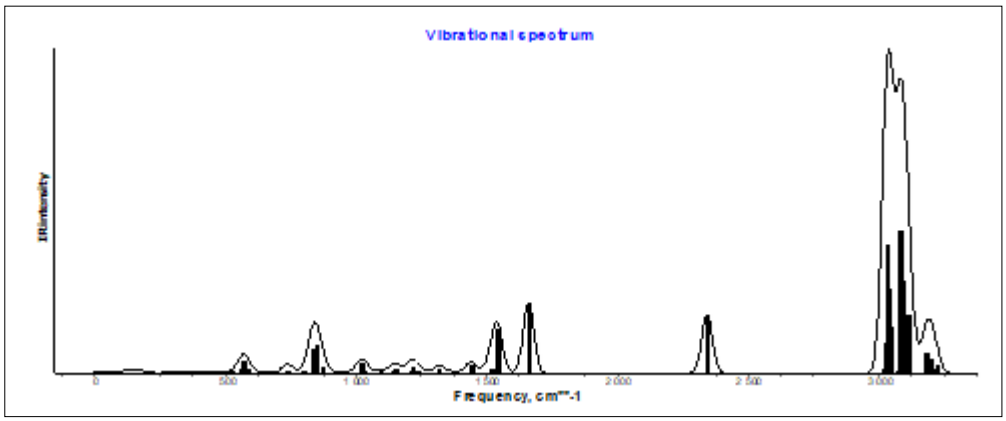

Fig 2: IR Spectra of 11CB molecule

Fig 3 represent Raman activities of 11CB molecule. There are various peaks and the highest Raman activity is at 1659.8025 cm^{-1}. This is associated with twisting of phenyl group attached with CN group. Next peak is at 2341.8323 cm^{-1} which associated with CN bond stretching.

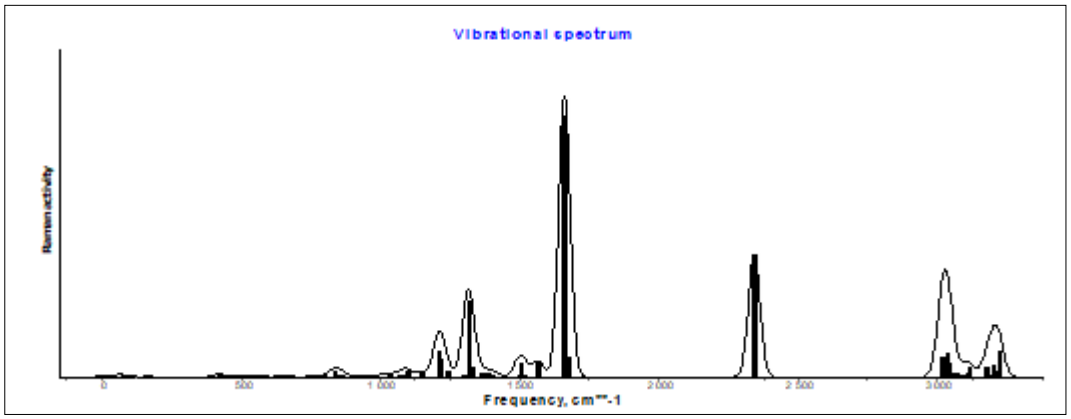

Fig 3: Raman activity of 11CB molecule

Conclusion

Electronic structure analysis of on 4-Alkyl 4'-Cyano Biphenyls ($C_{11}H_{23}$-C_6H_5-C_6H_5-CN) molecule is carried out using DFT methods. The IR spectra and Raman activities were explained.

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