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Spectroscopic analysis of 4, 4'-Methoxy Bis-Hydrazone: A DFT study

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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 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. 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'-Methoxy Bis-Hydrazone were calculated using DFT method. The vibration associated with peaks was discussed. The atomic charges with point dipoles were also computed and discussed. The Humo-Lumo gap as representation of ionization potential, thus computed.

Keywolds: *4, 4'-Methoxy Bis-Hydrazone, Liquid Crystals, Mesogen, IR Spectra, Raman Activities*

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I. 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). Some dihydrazides also show liquid crystalline properties at reasonable high temperatures. [6] Lakshmi et al. [7] synthesized and characterized the 4, 4'-methoxy bis-hydrazone which is a liquid crystalline material. Pang et al. [8] synthesized and investigated Smectic A liquid crystals from dihydrazide derivatives with lateral intermolecular hydrogen bonding. Xin et al. [9] investigated low molecular weight organogel from the cubic mesogens containing dihydrazide group. Che et al. [10] 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'-Methoxy Bis-Hydrazone (**MBH**). The geometry were generated from the paper by Lakshmi et al. [7]

II. 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]

III. RESULTS

The optimized geometry of MBH molecule is shown in figure 1. The molecule is planar and both the alkoxy chain is trans to each other at terminal end. The distance between oxygen and phenyl ring is 1.36Å in both case. The seperationn between both the nitrogen is 1.39Å.

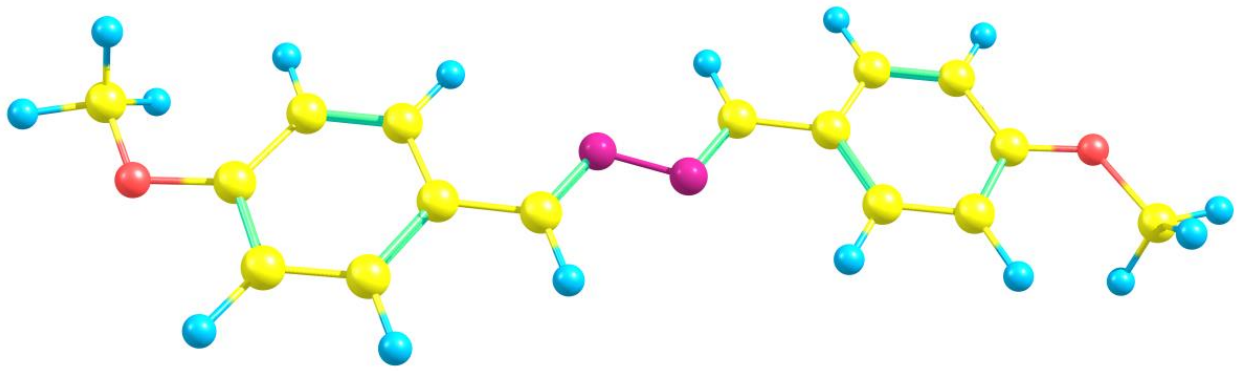

Figure 1: The optimized structure of the MBH molecule.

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

Sr. No.	Atom	Coordinates			Charge	Multipole (au)		
		X	Y	Z				
1	C	0.1149	-0.0703	-0.2455	1.1435	-0.0302	1.1160	0.1031
2	O	1.5147	-0.0314	-0.0103	-0.5792	-0.0496	-0.0615	-0.0210
3	C	2.1285	1.1820	0.0587	0.6185	0.0347	-0.1733	0.0155
4	C	3.5126	1.1519	0.2903	-0.7127	-0.0121	0.3883	-0.0266
5	C	4.2260	2.3377	0.3766	-0.2209	-0.5895	-0.2426	-0.0758
6	C	3.5868	3.5843	0.2358	-0.3915	0.5359	0.0626	0.0770
7	C	2.2010	3.5978	0.0044	-0.1307	0.7324	-0.4225	0.1211
8	C	1.4730	2.4159	-0.0845	-0.4378	0.0896	0.5043	0.0134
9	C	4.3673	4.8123	0.3323	-0.1618	-0.4931	-0.3783	-0.0545
10	N	3.8349	5.9809	0.2121	-0.0896	0.6786	-0.1963	0.0964
11	N	4.7724	7.0027	0.3404	-0.1517	-0.6265	-0.0027	-0.0817
12	C	4.2402	8.1713	0.2197	-0.1062	0.4433	0.1567	0.0508
13	C	5.0208	9.3993	0.3160	-0.4595	-0.6381	-0.3356	-0.0864
14	C	6.4065	9.3857	0.5477	-0.0931	-0.8673	0.6307	-0.1505
15	C	7.1346	10.5675	0.6365	-0.5695	-0.0183	-0.5335	-0.0005
16	C	6.4793	11.8015	0.4928	0.6700	-0.0056	-0.0629	-0.0079
17	C	5.0953	11.8317	0.2608	-0.6524	-0.1492	-0.1738	-0.0012
18	C	4.3818	10.6459	0.1747	-0.1389	0.7182	0.1375	0.0938
19	O	7.0932	13.0149	0.5617	-0.4661	0.0445	-0.0195	0.0207
20	C	8.4930	13.0537	0.7970	0.9620	0.0895	-0.7829	-0.0805
21	H	-0.1461	0.3857	-1.2089	-0.3597	-0.0509	0.0550	-0.2679
22	H	-0.1575	-1.1266	-0.2629	0.1469	0.0495	-0.0047	-0.0042
23	H	-0.4438	0.4333	0.5535	-0.4658	-0.1906	0.1059	0.2865

24	H	3.9988	0.1880	0.3980	0.4315	-0.1249	0.1617	-0.0197
25	H	5.2977	2.3056	0.5562	0.3196	-0.1201	-0.0053	-0.0229
26	H	1.7042	4.5560	-0.1049	0.4073	0.0689	-0.1661	0.0249
27	H	0.4054	2.4607	-0.2640	0.2042	0.0842	0.0368	0.0107
28	H	5.4436	4.7183	0.5139	0.2462	-0.0896	0.0161	-0.0193
29	H	3.1639	8.2653	0.0377	0.2303	0.0746	-0.0342	0.0177
30	H	6.9033	8.4275	0.6574	0.4802	-0.0800	0.2154	-0.0241
31	H	8.2022	10.5227	0.8163	0.2326	-0.0971	-0.0175	-0.0133
32	H	4.6092	12.7956	0.1528	0.3280	0.0980	-0.0953	0.0147
33	H	3.3101	10.6780	-0.0053	0.3380	0.1217	0.0009	0.0255
34	H	9.0517	12.5498	-0.0018	-0.3739	0.1546	-0.1034	-0.2409
35	H	8.7654	14.1100	0.8141	0.0891	-0.0423	0.0350	0.0019
36	H	8.7539	12.5980	1.7606	-0.2867	0.0346	-0.0603	0.2278

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	-878.946651
Sum of electronic and thermal Energies	-878.928429
Sum of electronic and thermal Enthalpies	-878.927484
Sum of electronic and thermal Free Energies	-878.995023

Table 3 presents dipole moment, exact polarizability, approx. polarizability and hyperpolarizability of MBH molecules. The Humo-Lumo gap is 0.139 hartree.

Table 3: Dipole monent, exact polarizability, and approx. polarizability of H5CBP molecules.

Dipole Monent	0.3976 debye
Exact Polarizability	79.376
Approx Polarizability	122.462

The IR spectra of MBH 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 1303.321 cm^{-1}. This frequency is associated with twisting of both of phenyl rings as well as both alkoxy chains. Second peak is at 1191.316 cm^{-1}. This frequency is associated with twisting of both phenyl ring. Other peak hieght is at 1558.773 cm^{-1} that is associated with twisting of both of phenyl rings as well as both alkoxy chains also.

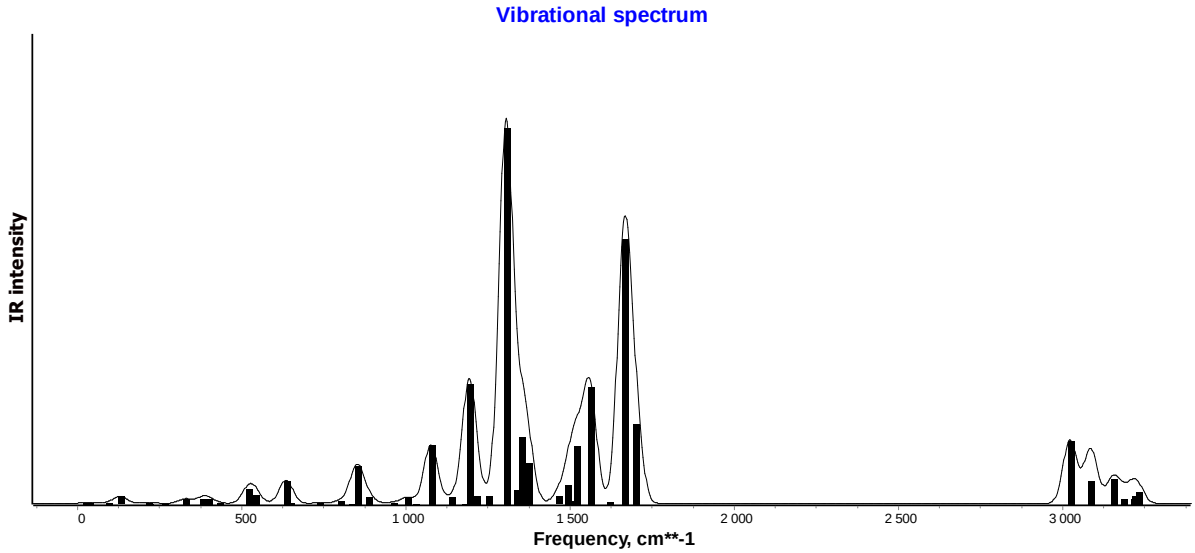

Figure 2: IR Spectra of H5CBP molecule.

Figure 3 represent Raman activities of MBH molecule. There are various peaks and the highest Raman activity is at 1633.055 cm^{-1} and another peak is at 1598.623 cm^{-1} which are associated with twisting of both phenyl rings and hydrazones. Next peak is at 1194.465 cm^{-1} that is associated with twisting of both the phenyl rings.

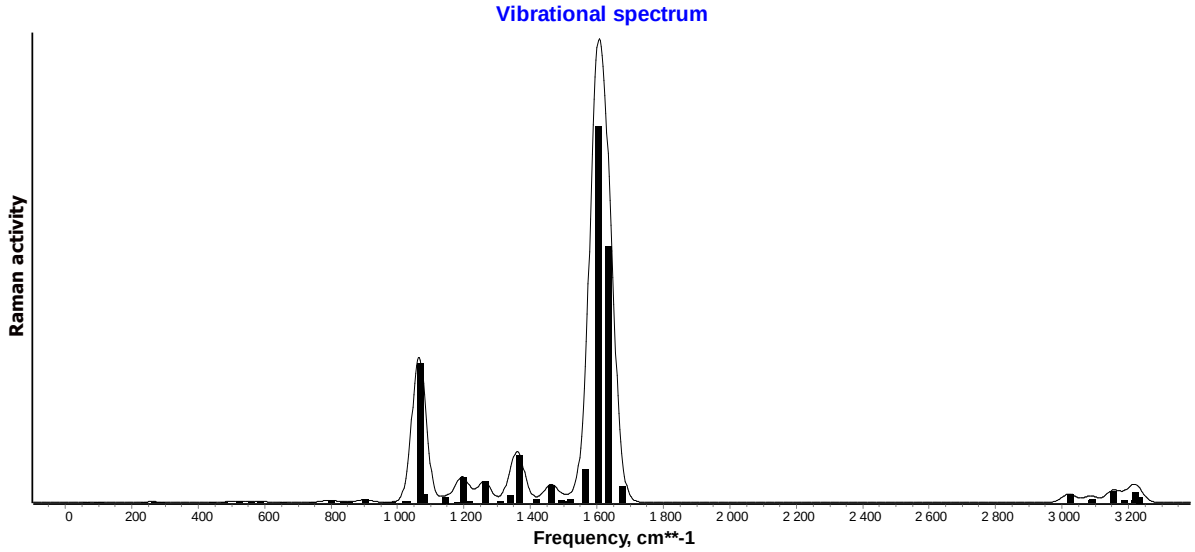

Figure 3: Raman activity of MBH molecule.

IV. CONCLUSION

Electronic structure analysis of on 4, 4'-Methoxy Bis-Hydrazone molecule was done with DFT methods. The IR peaks and Raman activities peaks were explained.

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