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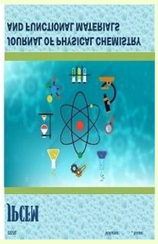

A Theoretical Study on Anthracene Molecule

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ABSTRACT

Computational quantum theory methods especially Hartree-Fock (HF) and Density functional theory (DFT) plays an important role in physical chemistry and theoretical physics. Anthracene is an antihistamine and has medicinal value, that is why it is important to understand its stability, reactivity and structure analysis. In this study, we optimize the energy band gaps using different basis sets for both DFT and HF methods. LanL2MB at DFT method was selected for the molecule. IR, NMR and UV were also investigated during the research.

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1. Introduction

Anthracene is a solid polycyclic aromatic hydrocarbon (PAH) of formula $C_{14}H_{10}$, consisting of three fused benzene rings. It is a component of coal tar. Anthracene is used in the production of the red dye alizarin and other dyes. Anthracene is colorless but exhibits a blue (400–500 nm peak) fluorescence under ultraviolet radiation. Anthracene, a wide band-gap organic semiconductor is used as a scintillator for detectors of high energy photons, electrons and alpha particles. Plastics, such as polyvinyltoluene, can be doped with anthracene to produce a plastic scintillator that is approximately water-equivalent for use in radiation therapy dosimetry. Anthracene's emission spectrum peaks at between 400 nm and 440 nm.

It is also used in wood preservatives, insecticides, and coating materials. Many researchers have focused on the development of a sensitive method to measurement anthracene which is important for certain diseases [12-14]. The resulting of nuclear magnetic resonance (NMR) and DFT was provided information of electrochemical properties of diphenhydramine and understanding its neurotransmitter activity in aqueous solutions. DFT theoretical calculation with the basis set of LanL2MB was analyzed various hydrogen bond of diphenhydramine. In this study, we will explain and find the energy band gaps by using Gaussian program software. The different basis sets (3-21G, 6-31G, 6-31G*, 6-311G, LanL2DZ, LanL2MB) for two methods (DFT and HF) performed on anthracene geometry. LanL2MB was chosen at the DFT method to show the IR and NMR spectra for the geometry structure.

2. COMPUTATIONAL METHODS

The Anthracene structure was drawn by Chem. Bio Draw Ultra 14.0 (Fig. 1). The structure of Anthracene was optimized by both density functional theory (DFT) and Hartree-Fock (HF) [9]. Different basis sets have been applied to find the energy band gaps of Anthracene. The reason why different basis sets were used is that each basis sets involves different functionalities and characteristics. Table 1 shows the energy band gaps for the two methods of different basis sets. The geometry system of anthracene at the B3LYP (DFT), LanL2MB basis set has been chosen [9,

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18]. The frequency and NMR were calculated to this basis set [19] The Gaussian 09 program has been used for all the calculations. Also, the origin program was performed for drawing the IR as in figure 3.

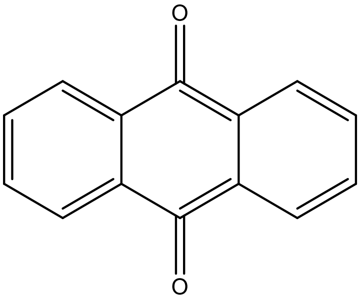

Figure 1. Structure of Anthracene

3. RESULT AND DISCUSSION

3.1. Energy bandgap

The first task of the computational work is to detct the optimized molecular structure using Gaussian 09 program. The energy band gaps associated with basis sets (3-21G, 6-31G, 6-31G*, 6-311G, LanL2DZ, LanL2MB) were listed in Table 1. The energy band gaps for the Hartree-Fock (HF) method have higher values compared with the density functional theory (DFT). The optimized structural parameter of anthracene with the LanL2MB was selected by the DFT method [9].

Table 1. The energy bandgap for different basis sets for both HF and DFT methods.

Basis sets	HF method Energy gaps (ev)	DFT method Energy gaps (ev)
3-21G	10.3986409	11.0609712
6-31G	10.9989287	10.2919714
6-31G*	10.9989287	10.2919714
6-311G	11.2919977	11.938001
LanL2DZ	11.4144499	11.8601759
LanL2MB	4.39140801	5.63144062

3.2. Molecular Structure:

The molecular structure and numbering of atom in the anthracene molecule was shown in Figure 2. The 72 vibration modes are present in the molecule. The first task of computational work was optimization of the molecule. The Gauss programs viewed the number of atoms scheme. To calculate the geometric structure DFT was used.

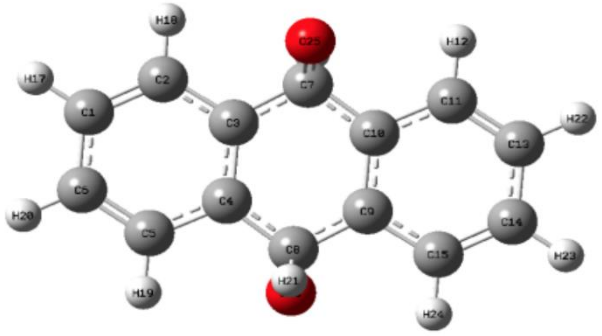

Figure 2: Optimized molecular structure of Anthracene

3.3. Vibrational Assignments:

The vibrational frequency was calculated by the DFT method at LanL2MB basis sets, FT-IR Figure 3 was observed with various vibration have been present in Table 2. The fundamental functional group present in the molecule vibrated at different frequencies as discussed below.

3.3.1. C-C /C=C vibrations:

The vibration carbon-carbon stretching in a ring usually occurs in a region 1400-1600 cm^{-1} [21]. In aromatic benzene ring the vibration carbon-carbon was occurring in the region 1420-1625 cm^{-1}. In the aromatic like benzene has six-member rings, there are two or more vibration are occur in a region due to the vibration of the skeletal, the strong vibration was started at 1500 cm^{-1}. Moreover, where the ring is conjugated by the groups the further vibration observed at 1580 cm^{-1}. In the present work, the carbon-carbon stretching vibration occurred in a region 1768.02-1839.39 cm^{-1}.The strong starching vibration of C=C in a ring occurred in a region 1579.42-1675.25 cm^{-1}. The vibration carbon-carbon single bond occurred in 1417.40-1488.18 cm^{-1} it is symmetrical vibration, but the stronger vibration for C-C in benzene ring was observed in region 1488.18 cm^{-1}. In 595.44, 649.6, 723.66 and 731.78 cm^{-1} C-C and C=C in a plane (in a ring) was rocking but in a region 884.88, 896.45 and 964.37 cm^{-1} was symmetrical Stretching.

3.3.2. C-H vibrations:

Commonly aromatic compounds in a region 3473-3468 cm^{-1} were observed multiple weak bonds due to the C-H stretching vibration of the aromatic rings [14]. The C-H bending vibration in a plan was observed in a region 990-1390 cm^{-1} and the peak was weak intensity [5]. This bond of C-H in a plane was very useful to found the characterization of compounds [26]. When the carbon and hydrogen are in a plane interaction was vibration above 1200 cm-1 usually moves in the opposite direction. [7, 8]. The C-H out of the plane usually occurs in a region 700-1000 cm^{-1} [19, 10]. In our anthracene molecule the C-H symmetrical stretching vibration out of the plane was observed between the regions 3027.75-3094.4 cm^{-1}, but the C-H in a plane was symmetrically vibrated between the regions 3181.27-3236.82 cm^{-1} this is an agreement with literature survey. In a region 3236.82- 526.53 cm^{-1} all C-H out of the plan was rocking vibrations. Also, al hydrogen was rocking vibration in diphenhydramine molecules in a region between 1181.68- 1256.21cm^{-1}**.**

3.3.3. C-N vibration

In this study of anthracene structure was shown the vibration of C-N in a region 996.46 cm^{-1} was symmetrical and in a region, 1152.66 cm^{-1} was scissoring._

Table 2. Various vibration of atoms calculated by DFT (LanL2MB)

St. NO	vibration assignments	observed frequency (cm^{-1})	St. NO	vibration assignments	observed frequency (cm^{-1})
1	(C-H) out	43.77	32	(all H) ro	1181.68
2	(C-H) out	80.72	33	(all H) ro	1200.46
3	(C-H) out	128.26	34	(all H) ro	1227.25
4	(C-H) out	191.71	35	(all H) out,ro	1256.21
5	(C-H) out	249.98	36	(C1-O8)Sy,s	1281.71
6	(O7-H17)ro	273.63	37	(C4-C12)Sy,s	1326.77
7	(N14-H15,16)ro	283.72	38	(C12-C13)Sy,s	1358.67
8	(N14-H15,16)ro (C-O)ro	297.55	39	(C-C)in,Sy	1383.2
9	(C-H)out,ro	312.8	40	(all H)out, ro	1399.39
10	(C-H) out,ro	369.13	41	(C-C)in,Sy	1417.4
11	(C-H) out,ro	428.62	42	(C-C)in,Sy	1427.62
12	(C-H) out,ro	458.24	43	(C-C)in,Sy	1488.18
13	(C-H) out,ro	473.85	44	(C13-H21,22)sc	1527.34
14	(C-H) out,ro	490.4	45	(C12-H19,20)sc	1531.68
15	(C-H) out,ro	526.53	46	(C=C)in,Sy	1579.42
16	(N14-H15,16)ro	569.12	47	(C=C)in,Sy	1666.41
17	(C-C,C=C)in,ro	595.44	48	(C=C)in,Sy	1675.25
18	(C-C,C=C)in,ro	649.6	49	(N14-H15,16)sc	1709.1
19	(C-C,C=C)in,ro	723.66	50	(C12-H19,20)sy	3027.75
20	(C-C,C=C)in,ro	731.78	51	(C13-H21,22)sy	3043.08
21	(C-H) ro	794.48	52	(C12-H19,20)asy	3074.14
22	(C-H) ro	844.21	53	(C13-H21,22)asy	3094.4
23	(C-H) ro	857.95	54	(C5-H9)sy	3181.27
24	(C12-C13)sy	884.88	55	(C3-H10)sy	3199.5
25	(C12-C13)sy	896.45	56	(C2-H11)sy	3236.82
26	(C12-C13)sy	964.37	57	(N14-H15,16)sy	3551.73
27	(C-H)in,sc	976	58	(O8-H18)sy	3626.92
28	(C12-H19,20)ro	1020.82	59	(N14- H15,16)asy	3672.03
29	(C13-N14)sy	1103.82	60		
30	(O7-H17)ro	1126.49			
31	(C13-N14)sc				

Abbreviation: out: out of the plane, ro: rocking, sy: symmetrical, asy: anti-symmetrical, in: in the plan, sc: Scissoring.

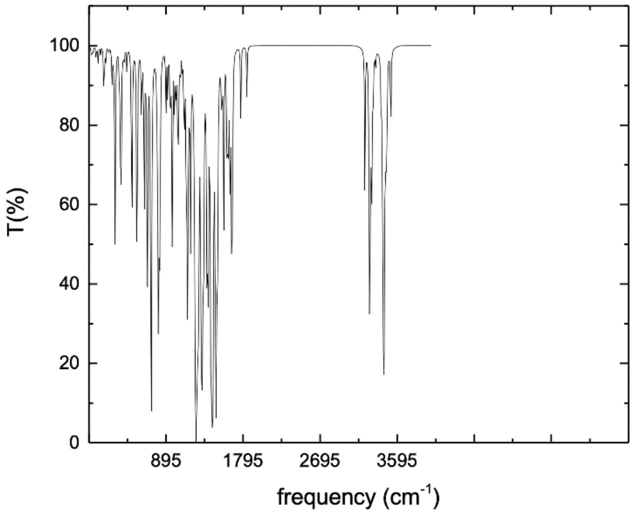

Figure 3. FT-IR Spectrum of Anthracene.

4. NMR analysis

The ^{13}C NMR chemical shifts used to identify chemical compounds [35]. GIAO (Gauge Including Atomic Orbital) is the faster procedure to calculation upon the basis set used. A GIAO method was preferable for many aspects state of the subject [19]. NMR was used to calculation chemical shift for the title compound best on TMS HF/LanL2MB(d) GIAO, TMS B3LYP/LanL2MB(2d, P)GIAO, and CH4 HF/LanL2MB(d) GIAO for carbon atoms. Hydrogen best on TMS HF/LanLMB(d) GIAO, TMS B3LYP/LanLMB(2d,P)GIAO and oxygen best on the H2O B3LYP/LanL2MB(2d, P) GIAO, H2O HF/LanL2MB(d) GIAO. Table 3 showed the 13C NMR for all references. According to TMS HF/LanL2MB(d) reference, the carbon was ordered from C3>C1>C4>C6>C5>C2>C12>C13 that means carbon number C3 was higher ppm lower filed but C13 was lower ppm higher filed. However, for TMS b3LYP/LanL2MB(2d,P) reference to carbon atoms was order from C6>C1>C3>C4 >C2>C5>C13>12 in this reference C6 was observed at higher ppm lower filed but C12 was lower ppm higher filed. For the reference, CH4 HF/6-31 G(d), C1>C6>C4>C3>C2>C5>C13>C12, carbon number one (C1) was found in higher ppm and carbon number twelve found in lower ppm higher filed.

For H-NMR Table 4 used two references TMS HF/LanL2MB G(d) GIAO and TMS B3LYP/LanL2MB+G(2d, P) GIAO. According to the reference TMS HF/LanLMB (d) GIAO the observation hydrogen peak started from higher filed (H15) to the end of lower filed (H11).H11>H10>H9>H18>H22>H17>H21>H19>H20>H16>H15. Besides for reference TMS B3LYP/LanL2MBG(2d,P) GIAO the order of hydrogen peak is the same as the previse reference with a little be different in a lower ppm for all hydrogen atoms. The NMR for nitrogen shown in Table 5, the peak was observed at 19.98 ppm for TMS HF/6-31 G(d)GIAO, but for TMS B3LYP/LanL2MB(2d, P) GIAO was observed at 17.5ppm.

Table 3. The observed C NMR chemical shifts in ppm for Anthracene

C. NO	NONE ppm	TMS HF/LanL2MB(d) GIAO Ppm	TMS B3LYP/LanL2MB(2d,P) GIAO ppm	CH4 HF/LanL2MB(d) GIAO ppm
C1	54	146	151.9	145
C2	80.9	120.7	102	118.3
C3	75	155	132.7	124.1
C4	55.7	145.8	123	133.9
C5	84	124	98.3	115
C6	56	144	153.9	143.1
C12	151	71	31.9	48.1
C13	149	69	33.8	50.1

Table 4. The observed H NMR chemical shifts in ppm for Diphenhydramine

H. NO	NONE ppm	TMS HF/LanL2MB(d) GIAO ppm	TMS B3LYP/LanL2MB(2d,P) GIAO ppm
H9	26.79	5.81	5.1
H10	26.1	6.5	5.78
H11	25.83	6.7	6.0
H15	33.2	- 0.6	- 1.31
H16	32.41	0.9	- 0.58
H17	29.85	2.75	2.05
H18	27.6	5.0	4.28
H19	30.25	2.31	1.61
H20	30.8	1.8	1.1
H21	30.05	2.55	1.58
H22	29.78	2.82	2.13

5. CONCLUSION

In this work, all basis sets with both HF and DTF methods investigated to calculation bandgap energy for anthracene molecule. Proposed the better basis set is LanL2MB according to the literature previous. The IR shows the vibration for all atoms that is good agreement with the kinds of literature. NMR has determined the identity of the molecular structure. The peaks of atoms in NMR were the relation with the types of references which was used on it. For example, C1 has different shifted in a ppm for all three references. The reference H2O HF/LanL2MB(d)GIAO and H2O

B3LYP/LanL2MB(2d,P)GIAO show the oxygen's ppm and it is closed to each other.

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