GROUND STATE ENERGY, ELECTRONIC AND CHEMICAL PROPERTIES PREDICTION OF ACENES DERIVATIVES FOR ORGANIC ELECTRONIC: A DFT INSIGHT

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The ground state energies, energy gaps E_{gap}, HOMO and LUMO energies, electron affinity and ionization potential are calculated at the level of HF/6-311G and DFT-B3LYP/6-311G exchange level and basis set. The results show good agreement when compared with theoretical and the experimental values. It was found that the ground state energy of the system, gaps energy, electrophilicity, electronegativity and chemical hardness decreased with the increase in the number of acenes ring. From HOMO and LUMO energies, Ionization energies and electron affinity results, they show an improvement compare to the acenes molecules. Pentacene and the predicted molecules exhibit good electronic properties.

Keywords: HOMO and LUMO energy, DFT, electron affinity, ionization potential, Chemical potential, global hardness

1.0   INTRODUCTION

Interest in the research of π-conjugate organic semiconductor materials has potentially increased over a decade in materials science, chemistry as well as space physics. They display a promising over a traditional inorganic material such as lower cost of production, light weight, flexibility, large area of coverage [1], low temperature and soluble-based processes [2], and they possessed good promising mechanical properties [3]. The π-conjugate organic semiconductor materials demonstrate great important applications in light emitting diode (OLED), energy storage, photovoltaic cells, organic thin film transistors (OTFT), electrochromic devices, sensors [4], electronic paper and flat panel liquid crystal displays [5] and organic electrochemical transistor as biocompatible for brain-machine interface [6]

 In addition, low-cost 'smart cards', radio-frequency ID tags and printable transistors are under active investigation [5]. Ribeiro and Macedo [7] reported a fabrication of polyacenes capacitors with high capacity, rapid charge/discharge function and high reliability. Also, due to good quantum fluorescence efficiency and high mobility of hole transport, the acenes derivatives are among the most promising candidates for optoelectronic devices. These devices include organic light emitting diodes, organic field effect transistor and hole collectors in organic photovoltaic cells [8].

Consequently, molecular orbitals as highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) of organic semiconductor play important role in the determination of electronic and optical properties of organic electronic materials for the design of new organic electronic material [9]. where ionization potential (IP) and electron affinity (EA) for n- or p-type organic material conduction are mainly used to estimate the energy barrier for

injection of holes and electrons. Also to determine the efficiency in the design of the molecular electronics device such as OLED [10]. For an efficient electron injection from common metal electrodes, the electron affinity (EA) should be in excess of 3.00 eV [11].

The main setback in the developing organic semiconductor materials (OSMs) are; intrinsic instability of radical ions in the air and the high barrier for electron injection as considered work function [12]. Also, poor electrons, scarcely soluble and difficult to process them[13]. Similar problem with pentacene and other high acenes molecules reproted by Wang, Xu [14]. However, there are many efforts to overcome such drawback in the organic electronic molecular design. The earlier cited work to reduce instability in air was [14]. They used Bis (dithienobenzene) organic material with reasonable exhibited thin-film mobility of 0.04 $cm^2V^{-1}s^{-1}$ to reduce air stability, and the work of [15, 16]. Therefore, there is a need to further study the oligomers of acene properties due to their importance in organic electronic design. Here, we wish to report the theoretical ground state energy and electronic properties of the acenes (1 to 5) and the predicted molecules with in HF and DFT theory.

2.0   COMPUTATIONAL DETAIL

As part of adopted methodology, the predicted molecules was designed based on this work [12]. The results presented in this work are performed with the program package NWChem 6.1. The NWChem is an *ab intio* computational chemistry software package which also includes quantum chemical and molecular dynamic functionality. It is designed by EMSL (environmental molecular Science Laboratory) to run on high-performance parallel supercomputers, as well as conventional workstation clusters.

Also, the code is capable of calculating of molecular electronic energies, analytical gradient using Hartree-Fock self-consistent field (SCF) theory, Gaussian density functional theory (DFT), and second-order perturbation theory. For all methods, geometry optimization is available to determine energy minima and transition state [17].

2.1 RESULTS AND DISCUSSIONS

The total ground state energies (Zero point energies) and HOMO and LUMO energies, HOMO-LUMO energy gap, Egap in the Hartree-Fock Density Functional Theory is presented. The molecule's properties were optimized and calculated at HF/6-311G and DFT-B3LYP/6-311G exchange level and basis set with NWchem version 6.1 [17, 18]. Molden is used for visualizing interface [19]. The result is compared with available theoretical and experimental results. Table 1 and 2 represent the total ground state energy and HOMO and LUMO energy compared with other experimental and theoretical values. While Table 3 and Table 4 is the HOMO-LUMO energy gaps, ionization potential and electron affinity for the acene. Table 5 shows the predicted results when thiophene is introduced to the acenes, which indicate a similar trend as the initial acenes. It shows the decrease in total ground state energy, increase in HOMO and LUMO energies. Also Table 6 indicates the variation of ionization potential and electron affinity of the predicted molecules. Thus, the predicted molecules show merit in term of energy gaps, HOMO and LUMO energies, Ionization potential, electron affinity and chemical properties, but not the ground state energies. The Figure 1. Shows the structure of the predicted molecules to be investigated.
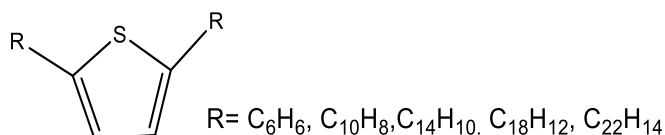
R= C_6H_6, $C_{10}H_8$, $C_{14}H_{10}$, $C_{18}H_{12}$, $C_{22}H_{14}$

Figure 1 predicted molecules with the acene (n = 1 to 5)

Table 1. Total ground state energies of the acenes (n= 1 to 5).

	Molecule	This work		Other works		
n		HF/6-311G	B3LYP/6-311G	HF [a]	DFT [a]	LSDA [a]
1	Benzene	-230.62	-232.20	-230.70	-232.25	-230.90
2	Naphthalene	-383.30	-387.81	-383.36	-385.89	-383.67
3	Anthracene	-535.79	-539.40	-536.00	-539.53	-536.42
4	Tetracene	-688.36	-693.01	-688.64	-693.17	-689.18
5	Pentacene	-840.95	-846.61	-841.28	-846.80	-841.93

[a] [20]

Table 2 HOMO and LUMO energies compared to other experimental and theoretical results.

		This Work				Other work			
Molecule		HF		B3LYP		Experiment		Theoretical	
n		HOMO	LUMO	HOMO	LUMO	IPES HOMO[b]	UPS LUMO [b]	HOMO [c]	LUMO[c]
1	Benzene	-7.49	-0.39	-7.49	0.39	-7.58	-0.40	-6.34	-1.19
2	Naphthalene	-5.88	-0.99	-5.88	-0.99	-6.40	-1.10	-5.50	-2.05
3	Anthracene	-4.99	-1.81	-4.99	-1.81	-5.70	-1.70	-5.00	-2.62
4	Tetracene	-4.45	-2.32	-4.45	-2.32	-5.10	-1.80	-4.67	-3.00
5	Pentacene	-4.24	-2.53	-4.24	-2.53	-2.80	-2.80	-4.45	-3.26

[b] [21], [c] [22]

Table 3 energy gap, Egap (eV) of the acenes (n= 1 to 5)

n	Molecule	HF/6-311G	DFT-B3LYP/6-311G	Experimental[d]	Other work [d]	
					DFT	HF
1	Benzene	7.10	7.88	6.20	6.82	12.78
2	Naphthalene	4.89	4.89	4.51	4.60	9.84
3	Anthracene	3.18	3.18	3.31	3.30	7.96
4	Tetracene	2.13	2.13	2.63	2.51	6.85
5	Pentacene	1.71	1.71			

[d] [23]

Table 4 calculated ionization energies (IP) and electron affinity (EA) for acenes.

n	Molecules	This work		Other work	
		IP (eV)	EA,(eV)	IP-UPS, Exp. [e],[f],[h]	EA-IPES, Exp.[e],[g], [h]
1	Benzene	7.492	0.389	8.96, (7.66), (6.70),(9.24)	
2	Naphthalene	5.884	0.991	6.4	1.100 (-0.20)
3	Anthracene	4.994	1.813	5.700 (5.7±0.2)	1.700 (0.53), 1.7
4	Tetracene	4.453	2.324	5.1	1.800 (1.07)
5	Pentacene	4.237	2.526	4.850 (5.1±0.6)	2.750 (1.39), 2.4±0.0.4

[e] [24], [f] [25], [g] [26], [h] [27]

Table 5 Total energies of the proposed molecules and HOMO and LUMO energies respectively.

n	Molecule	HF/6-311G	B3LYP/6-311G	HF/6-311G		B3LYP/6-311G	
				HOMO	LUMO	HOMO	LUMO
1	BThB	-1010	-1014.95	-5.187	-0.982	-5.187	-0.999
2	NThN	-1315	-1322.10	-5.057	-1.280	-5.057	-1.279
3	AThA	-1620	-1629.26	-5.060	-1.735	-5.060	-1.735
4	TThT	-1926	-1936.58	-4.441	-2.220	-4.441	-2.220
5	PThP	-2231	-2243.78	-4.267	-2.545	-4.267	-2.545

Table 6 calculated ionization energies (IP) of the predicted molecules and electron affinity (EA).

Molecules	BThB	NThN	AThA	TThT	PThP
Ionization energy Ip(eV)	5.1872	5.0574	5.0598	4.4411	4.2672
Electro Affinity EA(eV)	0.9989	1.2792	1.7347	2.2204	2.5450

However, Figure 2 shows the decrease in the zero-point energies (ground state energy) as the number of increase and there is a rapid decrease in the energy from the predicted molecules when the amount of carbon increase. Also, Figure 3 and Figure 4 show the decrease in the HOMO-LUMO energy gap, ionization potential (IP) and electron affinity (EA) with increase in the carbon of the acenes molecule. The predicted molecules exhibit a good energy gap, HOMO and LUMO energy, which is good for organic electronic material.
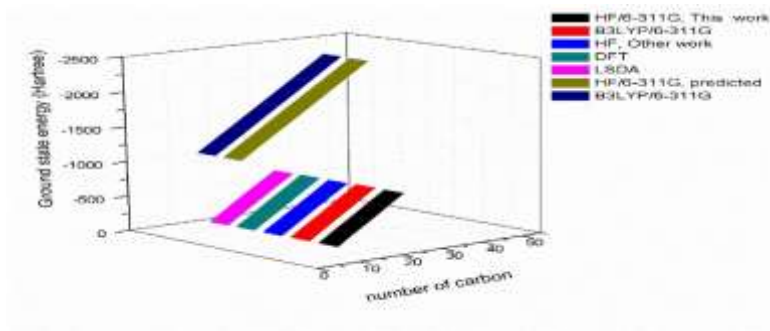
Figure 2 Graph of total ground state energy in the two theories compared with proposed molecules.
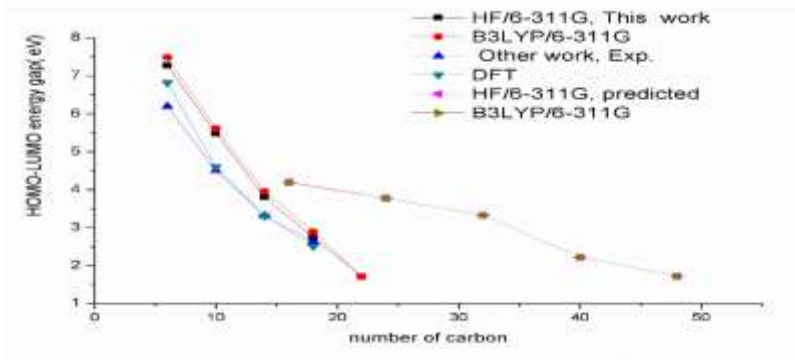

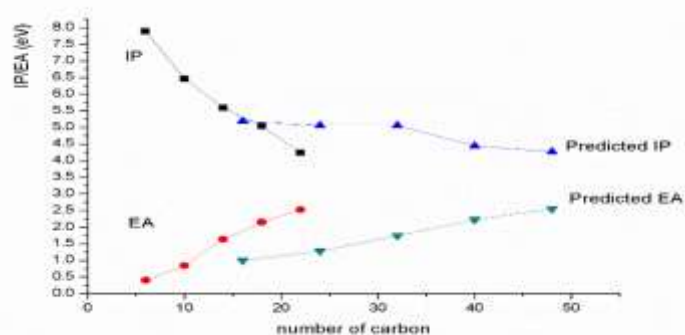Figure 3. Energy gap of the acenes compared to other work

Figure 4. Ionization potential (IP) and electron affinity (EA) of the acene and the predicted molecules.

Chemical Indices

Apart from the density functional theory, several important properties of molecules such as, ionization potential (IP), electron affinity (EA), chemical potential (μ), hardness index (η), softness index (S), electronegativity index (χ), electrophilicity index (ϖ) and Fukui function are needed to accurately predict chemical and electronic behaviours of the organic semiconductor molecules .

Further, according to Koopmans' theorem, global descriptors or chemical indices for a close shell molecule, one may use Hartree-Fock theory to get ionization potential (IP) and electron affinity (EA) in the forms of molecular orbital energies and redefined μ, η and χ [28-31].

$$IP = -E_{HOMO} \text{ and } EA = -E_{LUMO} \qquad (1.0)$$

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \approx \frac{1}{2}(IP - EA) \qquad (1.2)$$

$$\chi = \frac{1}{2}(IP + EA) \qquad (1.3)$$

$$\mu = \frac{1}{2}(E_{HOMO} + E_{LUMO}) \approx -\frac{1}{2}(IP + EA) \qquad (1.4)$$

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In addition, according to Koopmans' theorem the energy gap E_{gap} is defined as the difference between HOMO energy (Highest occupied molecular orbital) and LUMO energy (Lowest unoccupied molecular orbital) that is given by:

$$E_{gap} = E_{LUMO} - E_{HOMO} \approx IP - EA \qquad (1.5)$$

However, the chemical indices are evaluated based on Koopmans' theorem relation. Here, Table 7 indicates the variation of the electronegativity index (χ), hardness index (η), chemical potential (μ), softness index (S), electrophilicity index (ω) with the increase of the carbon in the ring. The result shows the decrease and increase of the individual paramter as the number of carbon increases.

Table 7. Computed chemical Indices of the predicted acenes' molecules.

Molecules	Electronegativity χ	Hardness η	Chemical Potential μ	Softness S	Electrophilic ω
BThB	3.0931	4.1883	-3.0931	0.2388	20.0348
NThN	3.1683	3.7782	-3.1683	0.2647	18.9632
AThA	3.3973	3.3251	-3.3973	0.3007	19.1888
TThT	3.3308	2.2207	-3.3308	0.4503	12.3180
PThP	3.4061	1.7222	-3.4061	0.5807	9.99010

Conclusion

The total ground state, electronic properties of the series of linear acenes and the predicted acenes derivatives at ground state were studied from a theoretical framework. The property was investigated as the function of the increased number of carbon in the acenes and the predicted molecules. Among the acene rings, pentacene shows a promising result for organic electronic material application and the predicted molecular exhibited a good result when compared to the original acenes molecules.

Acknowledgment

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