LINEAR ACENES LINKED THIOPHENE, ELECTRONIC AND CHEMICAL PROPERTIES: PROSPECTS FOR MOLECULAR ORGANIC ELECTRONIC MATERIAL

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Graphical abstract

Total (GSE) Variation with number of electrons
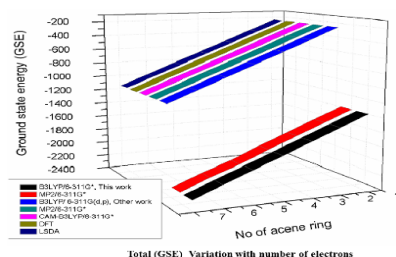
Abstract

We report a theoretical study of linear acene (n=1 to 7) linked thiophene properties functionality. The total ground state and band gap energies, Coulomb potential and nuclear repulsion energy are calculated by DFT, MP2 at B3LYP exchange level of the theory and 6-311G* basis set. The results are in good agreement with the experimental and theoretical values. It is found that the total ground state energy of the system and band gap energy decreases with an increasing number of electrons in the rings. The addition of thiophene molecules tends to improve the electronic and chemical properties of the linear acenes, the material exhibit potential application in the organic molecular electronic material.

Keywords: Ground state energy, coulomb potential, nuclear repulsion energy, Band gap energies

1.0 INTRODUCTION

Interest on π-conjugate organic semiconductor materials has potentially increased over a decade in chemistry, materials science and space physics. These materials got interest due to their promising advantages over a traditional inorganic material, such as low cost of production, light weight, flexibility, extensive coverage area [1], low temperature and soluble-based processes [2], and other favorable mechanical properties [3].

Π-conjugate organic materials display potential applications in organic light emitting diode (OLED), energy storage, photovoltaic cells, organic thin film transistors (OTFT), electrochromic devices, sensors and chemosensor [4-5], electronic paper and flat panel liquid crystal displays. In addition, printable transistors, smart card, and radio-frequency ID tags at a low cost are still under active investigation [6-7]. In addition, they are used in the fabrication of multifunctional graphene optoelectronic devices, which is capable of storing and detecting photo signal[8].

Moreover, organic semiconductors are used in an organic electrochemical transistor as biocompatible in brain-machine interface[9]. Oligocene derivatives showing high mobility and efficient quantum fluorescence are the best materials for hole transport

to design organic semiconductor devices [10]. Pentacene and rubrene hold the record for holes mobility of 5.5 cm^2/Vs in OTFTs transistors and 40 cm^2/Vs in single crystal OFETs. The delocalization of π-electron system makes them excellent charge transport materials [11-12]. As it was predicted, the increase in the acene length tends to rapidly decrease the exciton binding energy, this bodes well in the photovoltaic application for large acene [13].

Also, the replacement of the -CH group in the acenes backbones with hetero atoms makes it possible for scientists to modify their properties, which strongly affects the frontier orbital energy (FOE) of the new organic molecules by their number, position, and valences toward molecular material design[14].

Despite the merit displayed by the organic semiconductor material, there is a setback among organic electronic materials for device design, such as the intrinsic instability of radical ions in air, poor solubility and high barrier to inject electron for an electrode work function that uses noble metals, which are sensitive to light, oxygen, and polymerization[15-16]. Poor-electron material and scarce solubility are other difficulties concerning to molecular development for n-type materials [17]. A similar problem attached to pentacene and other high acenes molecules was reported[18]. However, there is some literature addressing the improvement of instability in the air, charge mobility and charge injection [19-21].

This work examines the additional effect of thiophene on linear acenes (n =1 to7) organic molecular semiconductor at a different position, in search for enhancement of electronic and chemical properties of linear acenes.

The computation is carried out at DFT and MP2 level of the theory with B3LYP exchange and 6-311G* basis set [22-25]. NWchem version 6.3 is used for the prediction of the ground state molecular energies and electronic properties. The molecular structure in question is shown in Figure 1, and the work is validated with available experimental and theoretical results.

Although, Figure 1 shows a range of acenes from two rings to seven rings, Heptacene, the single ring is also included, which is Benzene, one ring member for completeness of the work based on the definition of the linear acenes[26].

2.0 METHODOLOGY

NWchem is a quantum chemistry and physics software employed for quantum and molecular mechanics calculation using the standard approach of the quantum mechanical method of electronic wavefunction or density. It is used for single point energy calculation, *ab-initio* molecular dynamics on potential energy surface, geometry optimization with constraints at minimization and transition state. Moreover, it provides an automatic computation of

numerical first and second derivatives, Conductor-like Screening Model (COSMO) calculation, ONION hybrid calculation, the normal mode vibrational analysis in Cartesian coordinates. Electrostatic potential from fit atomic partial charges, electron transfer (ET), spin-free one-electron Douglas-Kroll calculation, vibrational SCF and DFT can be achieved. Also, at the DFT and SCF level of theory various (response) properties are available, including indirect spin-spin coupling and NMR shielding tensors.

The calculation of the ground state energies and electronic properties are performed with NWChem within the Restricted Hartree-Fock (RHF) and Density Functional Theory (DFT) theories [27-28]. Molden is utilized for the visualization of the molecules [29]. The molecular structure of the organic semiconductor was first optimized at DFT-B3LYP, and MP2 exchange levels of the theories with 6-311G* basis sets [30-31]. A theoretical investigation is carried out at DFT with B3LYP exchange-correlation functional and used the same basis set for the ground state energy and frontier molecular orbital (FMO) energies, which ensured accuracy in the calculation.
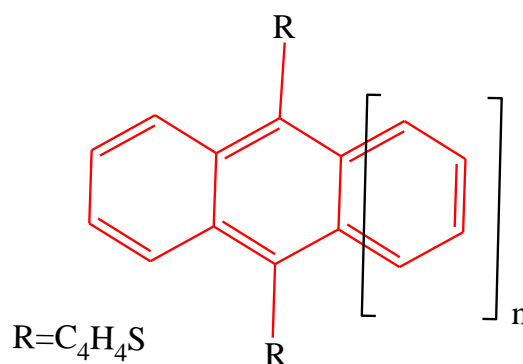

Figure 1 Predicted molecular structure for investigation

3.0 RESULTS AND DISCUSSION

3.1 Ground State Energy Property

The calculated total (GSE) ground state energy, Coulomb energy, and nuclear repulsion energy in the two theories with 6-311G* basis set is listed in Table 1. Figure 2(a) shows the variation of the total ground state energy when thiophene introduced to the acenes molecules. Figure 2(b) indicates the decrease in GSE when compared with other results. The energies tend to decrease the amount of the number of electrons. The results show a linear dependency with a number of carbon increases.
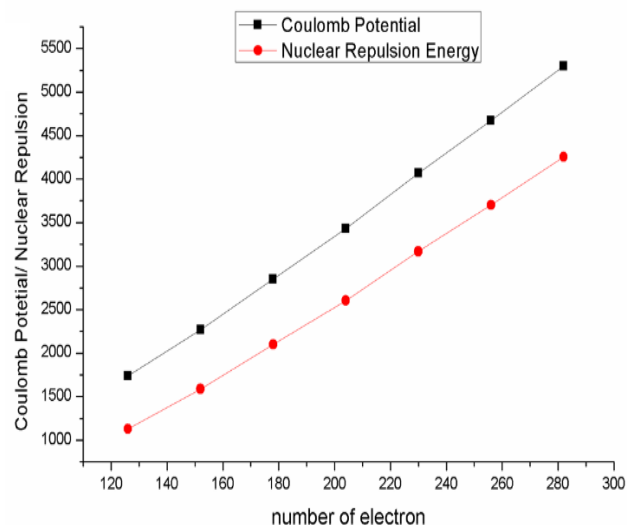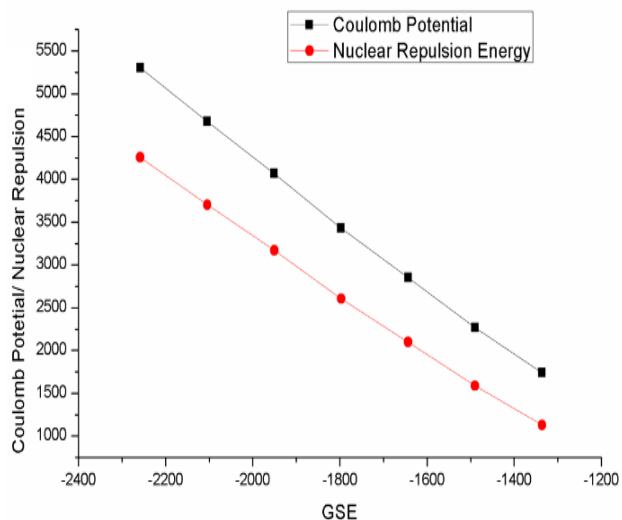
Table 1 Total GSE, Coulomb potential, and nuclear repulsion energies in (Ha)

Molecules	DFT-B3LYP	MP2	Coulomb energy	Nuclear repulsion energy
M1	-1336.0665	-1333.2683	1737.0216	1128.8689
M2	-1489.7475	-1486.4862	2268.0271	1587.1853
M3	-1643.4243	-1639.6955	2851.2649	2097.9824
M4	-1797.1002	-1792.9002	3429.8972	2604.2613
M5	-1950.7729	-1958.1393	4068.0184	3169.9406
M6	-2104.4464	-2099.3039	4672.338	3701.9268
M7	-2258.1196	-2252.5059	5298.6927	4255.9532
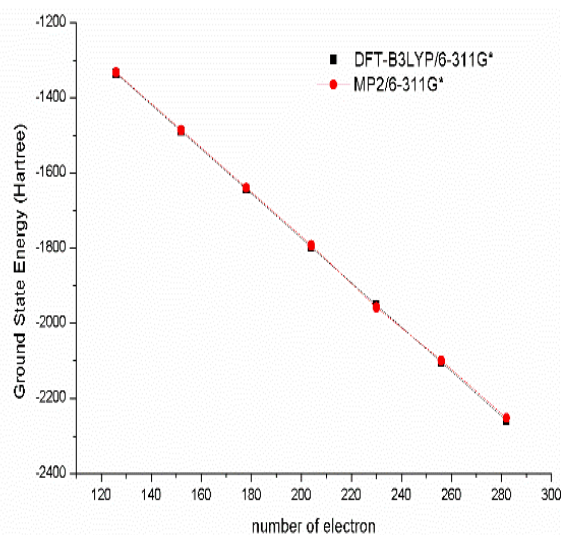
Figure 2 (a) Total GSE plotted against the number of electrons
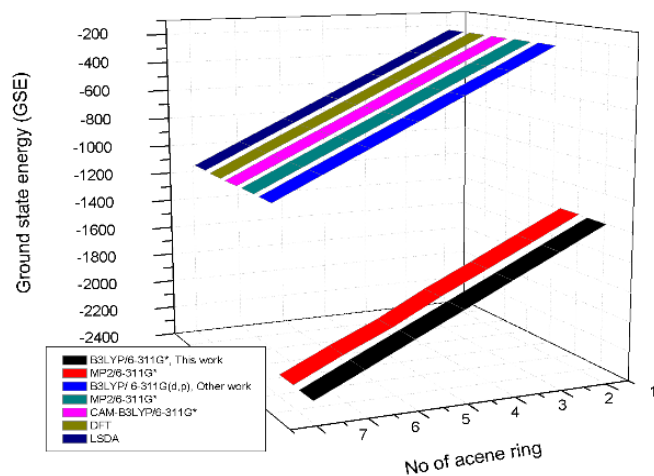
Figure 2 (b) GSE results compared with other work [32]

However, Figure 3(a) shows a linear increase in the Coulomb potential and nuclear repulsion energy as a number of electrons increase. Thus, possibly, the graph illustrates the approximation in Quantum mechanics method; a Born-Oppenheimer approximation that neglects the motion of the nucleus, which are denser in their composition[33]. Moreover, at a ground state energy level in Figure 3(b), the potential energy, and nuclear repulsion were decreasing with an increase in the acenes ring.

Figure 3 (a) Coulomb potential and nuclear repulsion energy plotted against the number of electrons and GSE in Hartree

Figure 3 (b) Coulomb potential and nuclear repulsion energy plotted against the number of electrons and GSE in Hartree unit.

In this case, at low GSE energy level, the calculated electron affinities (EAs), ionization potential (IPs) and chemical indices are presented in Table 2. The relationship between these global chemical indices has been extensively discussed in the following work [34-37]. A rational design of an optimized light-emitting diode lies in controlling both the holes and electrons for a proper charge transfer and efficient charge injection. The electron affinities (EAs) and ionization potential (IPs) play such role.

They are used to estimate the energy barrier for injection of charges, both holes and electrons into organic material. In general, the amount of energy required to create a hole is about ~5.1eV, and the extraction of an electron from the anion require ~2.4eV in the polymer [31].

Figure 4(a) and (b) display the plots of IPs and EAs as the function of the number of electrons and GSE. As the thiophene introduced to the acene molecules, the IPs tend to decrease across the molecules and increase with GSE as the amount of ring increase, which indicating the hole injection property significantly improved. Thus, it shows the agreement with guess made for E_{HOMO} energies. While for EAs in the same figures indicated, the EAs energy increase with the number of electrons and decrease at the ground state level with the increase in the number of the linear acene rings. This indicates the ability by the molecules to accept more electrons.

Table 2 Calculated chemical indices at DFT-B3LYP theory with 6-311G* basis set

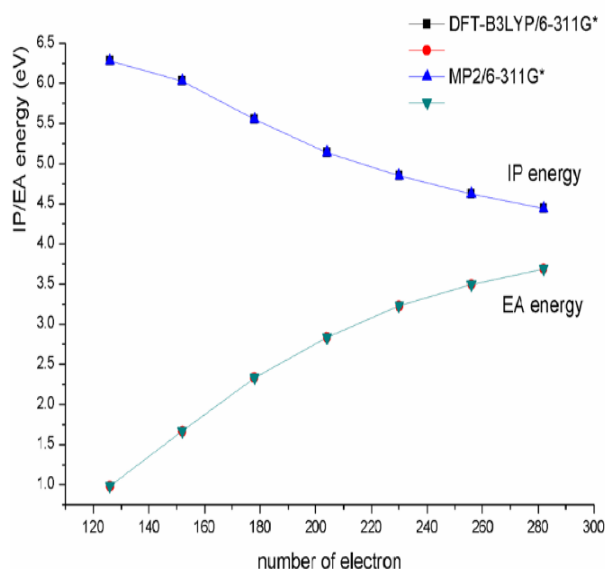| Molecule	IP(eV)	EA(eV)
M1	6.2778	0.9807
M2	6.0270	1.6653
M3	5.5506	2.3307
M4	5.1388	2.8336
M5	4.8513	3.2281
M6	4.6259	3.4930
M7	4.4429	3.6877

Figure 4 (a) Variation of IPs and EAs with the number of electrons and Total GSE
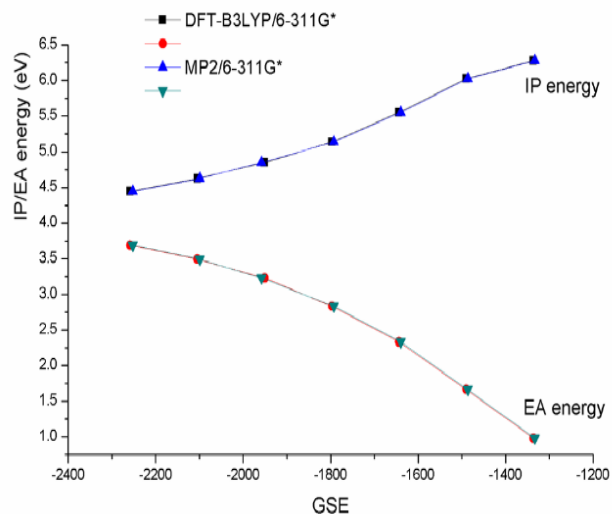

Figure 4 (b) Variation of IPs and EAs with the number of electrons and Total GSE

4.0 CONCLUSION

The total ground state energy and electronic properties of the linear acenes (n= 1 to 7) linked thiophene predicted at DFT and MP2 were studied from the theoretical framework. The properties investigated as the function of increasing number of electrons of acene rings. GSE decreases with the rise in the number of electrons where the potential energy and nuclear repulsion energy increase with the number of electrons. Thus, our results support Born-Oppenheimer approximation from the quantum mechanics of many-body theory.

Acknowledgement

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