THEORETICAL DFT STUDY THE OPTO-ELECTRONIC PROPERTIES OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE)

Mohanned J. Al-anber*, Aqeel M. Ali*, Norri S. Al-Maliky* and Ali H. Al-Mowali*

*Department of Physics, College of Science, Basrah University, Karmet Ali, Basrah, Iraq.

Abstract: Some of poly(3,4-ethylenedioxythiophene) (PEDOT) properties were studied with respect to the chain length of the polymer. The density functional theory is used for examining these properties. The increase of the PEDOT's chain lengths led to decreasing in its energy gap, chemical potential, global hardness and ionization potential. While the electron affinity showed increasing.

Keywords: Poly(3,4-ethylenedioxythiophene); DFT; Energy gap; Ionization potential; Global hardness.

INTRODUCTION

Due to its chemical stability, high conductivity on doping, and their non-linear optical properties, poly(3,4-ethylenedioxythiophene) is among the few studied conjugated organic polymers, experimentally and theoretically [1]. The studies focus to synthesis new polymers with low energy gap. During the recent years systematic efforts were aimed at investigating the molecular and electronic structure of poly(3,4-ethylenedioxythiophene) oligomers and its derivatives [2-7]. The energy gap between valence and conduction band of polymer is related to the lowest allowed energy of its monomer units and to the bandwidth resulting from the overlap among the monomer orbitals [2]. The energy band gaps obtained from band structure calculations for solids are analogous of the energy differences between the highest occupied molecular orbital and lowest unoccupied molecular orbital energy differences in molecules. To design a polymer with low band gap, it is desirable to start with monomer units with small excitation energies, therefor a prior idea on the estimate is often useful. One way to obtain excitation energies are to calculate the energy of the ground and excited state explicitly and to take the energy difference. The commonly accepted structure of poly(3,4-ethylenedioxythiophene) is a linear chain of monomers [3]. An initial estimate of the band gap can be carried out using density functional theory (DFT). DFT is very attractive in calculations involving finite system because even the lowest level of DFT, the Local Spin Density Approximation (LSDA), includes some electron correlation. This is extremely important in the design of conducting organic polymers which have an extended π-system. Although the LSDA eigenvalue differences underestimate the band gap compared to the experiment, the shift is almost and very systematic [2]. DFT method had successfully been used to study band gaps of conjugated organic polymers, where the HOMO/LUMO difference provide good estimate of the excitation energy. While there is some controversy surrounding the interpretation of DFT orbitals energies, we found that HOMO/LUMO energy difference offers a very good estimate of band gaps. It should be noted that the HOMO/LUMO energy difference at ab initio level does not closely relate to excitation energies due to the absence of orbital relaxation effects [8].

In this regard, we investigated the geometric and electronic structures of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites. The results of B3LYP/ CEP-31G studies of relative stability, energy gap, ionization potential, electron affinity, chemical potential, and global hardness.

THEORETICAL BACKGROUND

Within the framework of DFT, the ground state energy of a molecule can be expressed in terms of electron density, $\rho(r)$ as [9]:

$$E[\rho] = F_{HK}[\rho] + \int v(r)\,\rho(r)\,dr$$

where $v(r)$ is the external potential and $F_{HK}[\rho]$ is universal Hohenberg–Kohn functional. Global reactivity descriptors (GRD) such as chemical potential, μ and hardness, η for a system can be defined as the first and second partial derivative of $E[\rho]$ with respect to the amount of electron N constant external potential $v(r)$, respectively, as [10-12]:

$$\mu = (\partial E[\rho]/\partial N)_{v(r)} \text{ and } \eta = \tfrac{1}{2}(\partial^2 E[\rho]/\partial N^2)_{v(r)}$$

The energy of a molecule as a function of ΔN can be written as a Taylor series expansion:

Author for Correspondence: Mohanned J. Al-anber, epartment of Physics, College of Science, Basrah University, Karmet Ali, Basrah, Iraq. E-mail: mohanned. mohammed@uobasrah.edu.iq.

$\Delta E\,[\rho]\ =\ (\partial E\,[\rho]/\partial N_i)_{v(r)}\ \Delta N_i\ +\ \tfrac{1}{2}(\partial^2 E\,[\rho]/\partial N_i\partial N_j)_{v(r)}$ $\Delta N_i\Delta N_j\ +\ \tfrac{1}{3}(\partial^3 E[\rho]/\partial N_i\partial N_j\partial N_k)_{v(r)}\ \Delta N_i\Delta N_j\Delta N_k\ +\dots$

where $\mu\ =\ (\partial E\,[\rho]/\partial N_i)_{v(r)}$ in one direction, $\eta\ =\ \tfrac{1}{2}(\partial^2 E\,[\rho]/\partial N_i\partial N_j)_{v(r)}$ in two directions and $\kappa\ =\ \tfrac{1}{3}\,(\partial^3 E[\rho]/\partial N_i\partial N_j\partial N_k)_{v(r)}$ in three directions, so the κ as the compassion term. When the ΔN becomes very small the equation becomes:

$\Delta E[\rho] = \mu\,\Delta N + \eta\,\Delta N^2 + \kappa\,\Delta N^3$

Inverse of hardness is the global softness, S, expressed as:

$S = 1/(2\eta)$

To compute μ and η, the finite difference approximation is helpful [13]:

$\mu \approx -\tfrac{1}{2}(\text{IP+EA})$ and $\eta \approx \tfrac{1}{2}(\text{IP-EA})$

where IP and EA are ionization potential, $IP = E\,[\rho]^{N-1} - E\,[\rho]^{N}$, and electron affinity, $EA = E\,[\rho]^{N+1} - E\,[\rho]^{N}$ respectively. The global hardness (η) is reflected the overall stability of a system. However, the site selectivity and reactivity can only be studied using the local reactivity descriptors. One such descriptor is local softness $s(r)$ [82], which is defined as:

$s(r) = (\partial\rho(r)/\partial\mu)_{v(r)} = (\partial\rho(r)/\partial N)_{v(r)}\ (\partial N/\partial\mu)_{v(r)} = f(r)\,S$

$S = \int s(r)\ \mathrm{d}r$

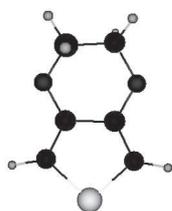where $f(r)$ is the Fukui function(FF) [14].

Figure 1: The optimized structure of (3,4-ethylenedioxy thiophene) monomer calculated at B3LYP/CEP-31G.

COMPUTATIONAL METHODS

First geometries for all cases were optimized at Restricted Hartree-Fock (RHF) method with basis set CEP-31G and then we optimized using B3LYP method to include correlation corrections with basis set CEP-31G. Density functionals are used, the Becke's three-parameter functional which defines the exchange functional as the linear combination of Hartree-Fock, local and gradient-corrected exchange terms. The B3 hybrid functional was used in combination with the correlation functionals of Lee, Yang and Parr and non-local correlation expression provided by the Perdew 86. Some previous calculations [6] suggest about the basis set CEP-31G gave their results good agreement. For that, we used the basis set CEP-31G is that of Stephens/Basch/Krauss ECP split valence. All geometries and calculations were carried out using the Gaussian98 [15].
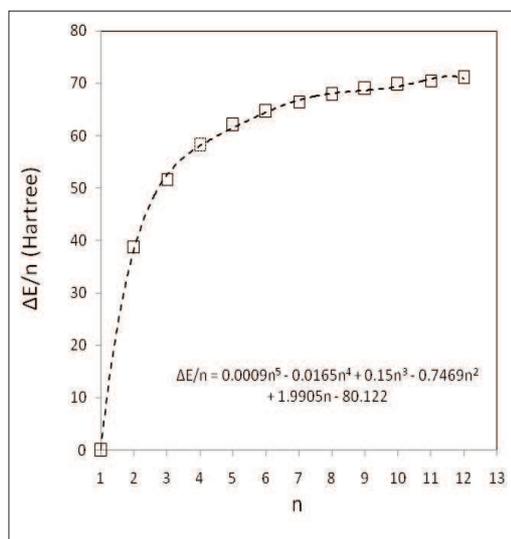

$$\Delta E/n = 0.0009n^5 - 0.0165n^4 + 0.15n^3 - 0.7469n^2 + 1.9905n - 80.122$$

Figure 3: Relative stability energy of poly(3,4-ethylenedioxy thiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.

RESULT AND DISCUSSION

Initial geometry optimized for monomer of poly(3,4-ethylenedioxythiophene) (PEDOT) using B3LYP/CEP-31G, see figure 1, then for two monomers, …, until the chain with ten monomer as shown in Figure 2. These are the stable geometries of (3,4-ethylenedioxy thiophene) monomer, dimer,…and PEDOT. Spectroscopic data for organic -systems are usually determined either in solution or in the solid state (crystal or thin film). Since our calculations are for isolated molecules in the gas phase, we have attempted to compare our calculation to experimental results in solution. The relative stability energy (ΔE) per periodic unit (n), $\Delta E/n = (E^{monomer}-E^n)/n$, as a function of periodic unite number, n, shows in Fig. 3. Where n is number of periodic units that made the polymer chain. Generally, as the chain length increases
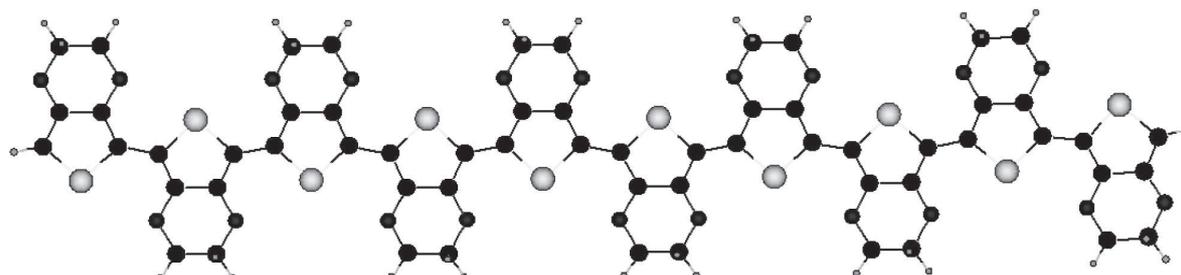

Figure 2: The optimized structure of (3,4-ethylenedioxy thiophene) chain calculated at B3LYP/CEP-31G.
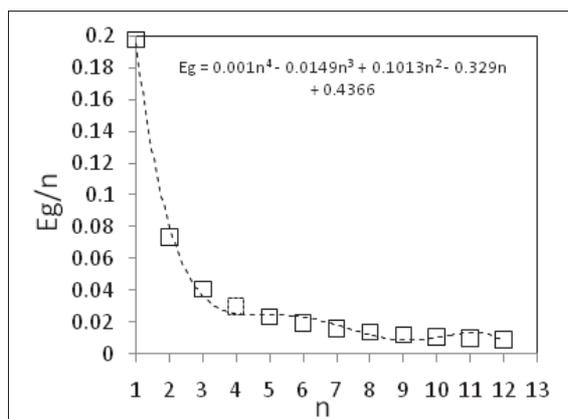
Figure 4: Energy gap of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.
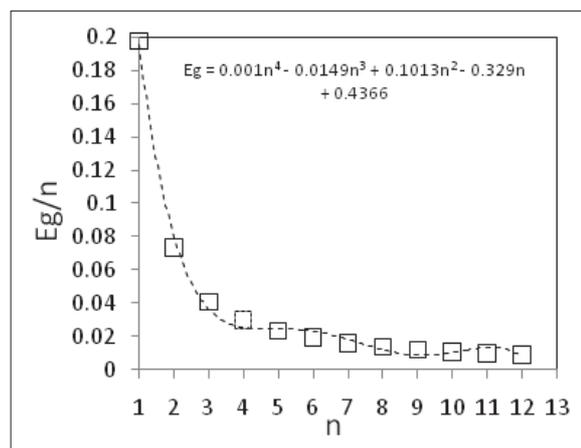

Figure 6: Electron affinity of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.
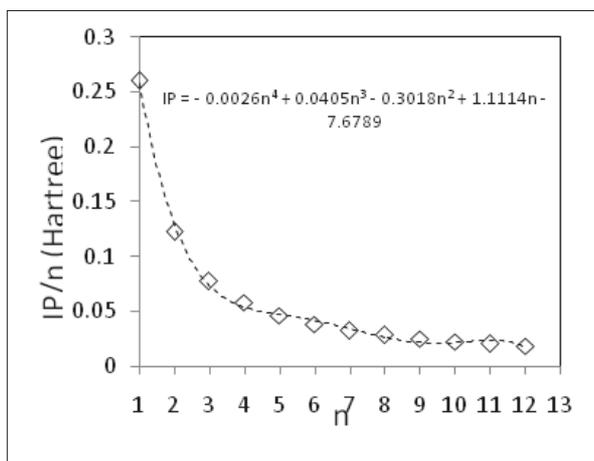

Figure 5: Ionization potential of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.CEP-31G.CEP-31G.
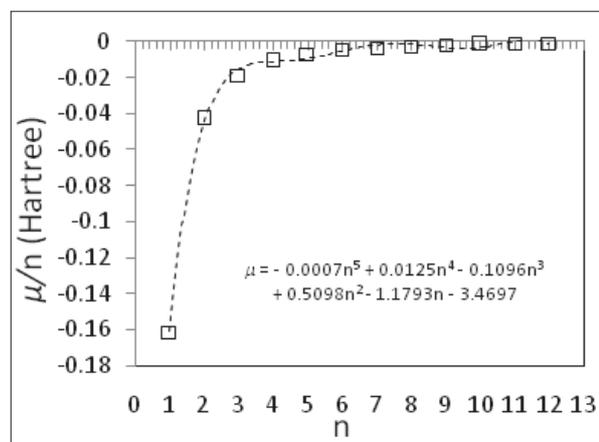

Figure 7: Chemical potential of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.

the relative stability increases too. The operation of add periodic unites, n = 2, 3, the relative stability increase rapid, but beyond n > 2 there lower in these increases. So we may note after few units, n > 9, a saturated case. In other word, the increasing of chain length is not supported the stability. With the B3LYP/CEP-31G the energy gap per periodic unit (n), ($Eg = E_{LUMO} - E_{HOMO}$)/n, for PEDOT as a function of add periodic unites, n, is shown in Fig. 4. When we transport from monomer to dimer the energy gap showed rapid decrease after few periodic unites. Then as the chain length increases, the n increases, the energy gap will not shows interest deceases, so there is saturated case. This behavior may lead to note that the large length does not give narrow energy gap. As comparison with experimental value of 0.095 Hartree, which will corresponds to the number of unit 8< n < 12[16]. Figure 5 shows the ionization potential (IP) per periodic unit (n) for the PEDOT as a function of add periodic unites n. Where, it shows rapid decrease until add the third periodic unit, n=3, and then low decreases, n > 3. The decreases in the ionization potential of the PEDOT with the chain length increases led to increase the ability of doping it with

accepters. The long chain of conjugated polymer such as PEDOT will not interested in lower the IP. Figure 6 shows the electron affinity (EA) per periodic unit (n) for the PEDOT as a function of add periodic unites n. Where contribution of each periodic unite that add to chain will lowers as n increases, so its behavior likes exponent. Where, the ability of PEDOT to get electrons interests as n < 9. Generally, the increases in the electron affinity led to higher the ability of doping with donors. Figure 7 shows the chemical potential (μ), per periodic unite n, for the PEDOT as a function of add periodic unites n. The transfer from monomer lower the chemical potential, so we can note the role of the second periodic unite, and then the third once in this lower. The added periodic unites more than three, n > 3, did not show any effect interesting. Figure 8 shows the global hardness (η) for the PEDOT, per periodic unite n, as a function of add periodic unites n. The global hardness for PEDOT decreases as increasing of the number of the periodic unites, with note that for n=1 and 2 there is rapid lowering in the stability of the system, while for n > 2 there is no influence.
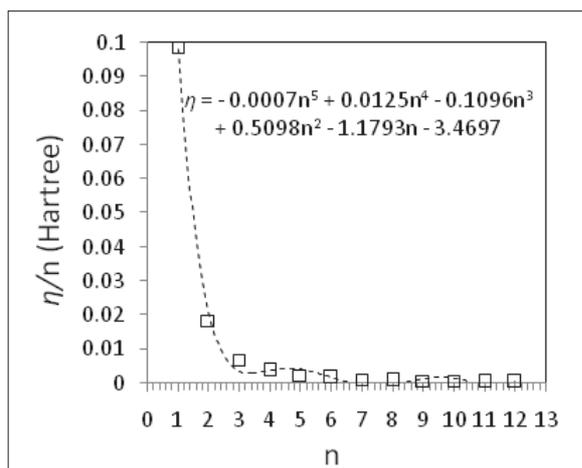
68

Figure 8: Global hardness of poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of added periodic unites, n, calculated at B3LYP/CEP-31G.

CONCLUSION

The density functional theory, B3LYP/CEP-31G, is the best method for the geometry optimization of the conjugated polymers. The energy gap, chemical potential, global hardness and ionization potential will decrease according to increase the length of the poly(3,4-ethylenedioxy thiophene) (PEDOT). While the electron affinity showed increasing.

REFERENCES

[1] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A. 1998. *Synth. Met.* **96**: 177-189.

[2] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A., *J.* 1997. *Comp. Chem.* **18**.15: 1943-1953, .

[3] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A. 1999 . *Synth. Met.* **98.** : 221-227.

[4] Nakanishi, H, *et al.J.* 1998. *Org. Chem.* **63**: 8632-8633.

[5] Lathti, P. M., Obrzut, J., Karasz, F. E. *Macromolecules.* **20**: 1987. 2023.

[6] Smith, James Richard. *Electrosynthesis of Novel Polyheterocycles*, Ph.D. Dissertation, Unpublished, School of Pharmacy & Biomedical Sciences, University of Portsmouth, Portsmouth, UK.1995.

[7] Irle, Stephan and Lischka, Hans. *J.* 1995. *Chem. Phys.* **103** (4).

[8] Foresman, J. B. and Frisch, A. F. 1995. *Exploring Chemistry with Electronic Structure Methods, 2ⁿᵈ ed.* Gaussian, Inc., Pittsburgh, PA.

[9] Hohenberg, K. Kohn, W. 1964. Phys Rev. **B 136**:864

[10] Parr RG, Pearson, RG.1983. J Am Chem Soc. **105**:7512.

[11] Pearson RG. 1985. J Am. Chem. Soc. **107**: 6801.

[12] Parr RG, Donnelly RA, Levy M, Palke WE. 1978. J Chem Phys. **68**:3801.

[13] Parr R. G, Yang w. 1989. Density functional Theory of atoms and molecules. Oxford University Press, New York.

[14] Parr R. G, Yang, w. 1984. J Am. Chem. Soc. **106**:4049.

[15] *Gaussian 98, Revision B.2.* M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. HeadGordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[16] Sankaran, B. Reynolds, J.R. Macromolecules.1997. **30:** 2582.