Original Research Article

DENSITY FUNCTIONAL THEORY STUDY OF THE STRUCTURAL, ELECTRONIC, NON-LINEAR OPTICAL AND THERMODYNAMIC PROPERTIES OF POLY(3-HEXYLTHIOPHENE-2,5DIYL) IN GAS PHASE AND IN SOME SOLVENTS

Abstract

Poly(3-hexylthiophene-2,5-diyl) (P3HT) and its derivatives are polymer based materials with π conjugation framework. P3HT is useful photoelectric material and can be used in organic semiconductor devices such as PLED, OLED, Nonlinear optical devices and solar cells. In this work, a theoretical study of P3HT in the gas phase and in some solvents (methanol, thiophene,chloroform, toluene, and acetone**)**were investigated and reported based on Density Functional Theory (DFT) as implemented in Gaussian 09 package using B3LYP/6-31++G(d,p) basis set. Structural properties such as bond lengths and bond angles as well as the HUMO, LUMO, energy gap, global chemical index, thermodynamic properties, NLO and DOS of the P3HT molecule in order to determine the reactivity and stability of the molecule were obtained. The results obtained showed that the solvents have effects on the structural, electronic and non-linear-optical properties of the molecule. The optimized bond length revealed that the molecule has a stronger bond in methanol with smallest bond length of about 1.0840Å (C_{28}-H_{35})than in gas phase and the rest of the solvents. It was observed that the molecule is more stable in methanol with HOMO-LUMO energy gap and chemical hardness of 3.8338eV and 1.9169eV respectively. This indicates that the energy gap and chemical hardness of P3HT molecule increase with the increase in polarity and dielectric constants of the solvents. The energy gap obtained is compared with the one in literature (3.10eV). This indicates that the reported energy-gap leads by about 0.7eV. The calculationsof thermodynamic properties indicate that P3HT molecule has the highest value of specific heat capacity (Cv), that is 152.307C_V(Kcal/Mol) in methanol, toluene has the highest value of entropy as 266.960 (Kcal/Mol), and thiophene has the highest value of zero-point vibrational energy (ZPVE) as 455.37486 Kcal/Mol. The NLO properties show that methanol has the highest value of total dipole moment (μ_{tot}) as 1.01764 a.u while acetone has the highest value of first order hyperpolarizability (βtot) as 4.4447×10^{-30}esu than the rest of the solvents. The values obtained for thefirst order hyperpolarizability for P3HT in acetone is about 12 times than that of the urea molecule, (0.3728×10^{-30}esu)which is commonly used for the comparison of NLO properties.The results of the IR spectra show that the studied molecule was stable in both the gasphase and insolvents since no imaginary frequency was observed. It was also observed that the most intense frequency was found to be 3024.9421 cm^{-1} at an intensity of 140.2464 km/mol in methanol and 3088.6908 cm^{-1} at intensity of 77.6119km/mol in gas phase. The theoretical values of the opencircuit voltage were found to be 1.635 eV, 1.614 eV,1.605 eV,1.576 eV,.1514 eV,and 1.445 eVfor methanol, toluene, acetone, chloroform, thiophene and the gas phase respectively.These changes in the properties of the molecule are observed due to the differences in the dielectric constants of the solvents. The results show that careful selection of the solvents can enhance the properties of the molecule for Organic solar cells (OSC)s applications.

Keywords: Gaussian 09, P3HT, DFT, conducting polymer, and HOMO- LUMO Energy Gap

1.0Introduction

"The desire to manufacture more cost-efficient electronic devices with simple processing techniques has brought up the development of new materials to become an attractive and useful alternative to inorganic semiconductors. Recently, organic materials, including conjugated polymers, organic semiconductors, organic small molecules (SMs) and self-assembling, have received an increasing attention due to their ability to enable the fabrication of flexible, light weight, semi transparent and large-area devices"[1]."In

particular, organic materials based on conjugated polymers have attracted the interest of many scientists worldwide, because of their outstanding electrical and optical properties, reasonable chemical stability, and easy processability. These special properties of conjugated polymers enable the development of several electronic devices, such as organic light emitting diodes, organic solar cells, transistors, sensors and so on"[2]. "Polythiophene and its derivatives have been considered as one of the most promising conjugated polymers due to their high stability, ease of structural modification, and controllable optical and electrochemical properties"[3]. "Initially, the applications of non substituted Polythiophene were very limited because of its insolubility in many organic solvents, due to its extended conjugated structure. In addition, the alkyl chain has been incorporated into the thiophene units to obtain a functional monomer able to yield soluble polymers"[4]. "Among the thiophene family, poly(3-hexylthiophene-2,5diyl) (P3HT) is the most investigated donor polymer for solar cells applications due to its relatively higher carrier mobility"[5]."Poly (3-hexylthiophene-2,5-diyl) (P3HT) is a semiconducting polymer that is widely used in electronic applications. It belongs to a class of semicrystalline polymers referred to as regioregular poly (3-alkyl thiophene)s (P3AT)s"[6], and has "a molecular formula (C_{10} H_{14} S)n.The applications of P3HT are imperative in light-emitting diodes, thin film transistors, and OSCs due to the fact that it has a crystalline structure and good charge transport properties compared to the many materials used in OSCs"[7]."Research showed that P3HT properties such as optoelectronic properties and crystallinity and its OSCs performance can be altered by modification of its end groups"[8]. "Higher mobility in P3HT FET was as a result of self organizing nature of the P3HT molecules by thin film deposition, thus, P3HT coated channel film was more crystalline in nature compared to others which improved the conductivity as well as carrier mobility of the film"[9].

"Interestingly, many experimental and theoretical studies have been carried out in the synthesis and applications of poly(hexylthiophene-2,5-diyl) and its derivatives including Density Functional Theoryand Time-Depended Density Functional Theory.For example, in reference"[10], the study of electronic properties of P3HT by first principles density functional theory was carried out.A major breakthrough of over 10% power conversion efficiencies (PCEs) in both polymer and low molecular weight OPVs was reported [11].Similarly, reference[12] examined the behavior of poly (3-hexylthiophene-2,5- diyl) between the upper and lower gold electrodes using the Fowler-Nordhein model and reported that the HOMO level of P3HT was 5.2 eV and LUMO 3.1 eV. The heights of the hole barrier at the two interfaces was 0.085 eV for the lower and 0.013 eV = 0.5% for the upper contacts, which indicate a high density of the trap sites near the upper interface.Also reference[13] investigated "the effect of using single wall carbon nanotube (SWCNTs)-based hybrids as the hole transport layer on the performance of organic solar cells based on P3HT: PCBM blended using UV-Vis spectrophotometer.An investigation of the effects of Cul doping in P3HT: PCBM active layer in inverted OSC for low light application using fluorine tin oxide (FTO)-Coated glass substrates was also carried out" [14]."They reported that, the performance of the device with Cul-doped P3HT: PCMB enhanced the hole collection and reduced charge recombination, leading to increase in Jsc, FF and PCE of the device.In another work of reference"[15], they designed and synthesized a new NFA, ZY-4CL, by modifying the cyano substituted end group in BTP-4CL and found that, blend film-based separation on P3HT: ZY-4CL enhanced phase separation, that helped to improve the charge efficiency transport and reduced charge recombination in the corresponding OSC. This resulted in the improvement in the performance of photovoltaics made of P3HT: ZY-4CL based SOC significantly, obtaining a high PCE of 9.46%.

"Optical and electronic properties of organic semiconductor materials may be easily adjusted and tuned through chemical modifications. For instance, fluorine (F) substituentis attached to conjugated polymer donor materials for the purpose of lowering the LUMO energies and of increasing the open-circuit voltage in various polymers such as, PTB7, although the efficiency decreased due to poor compatibility of the derivative with PC61BM; PCDTBT, where a 25% increase in efficiency was observed using end-group fluorination; and BDT– DTBT, where as high as 75% increase in efficiency was observed for the

fluorinated derivative" [7]."However, lowering the LUMO energies using F were observed to be very limited in conjugated polymers with high intrinsic HOMO energies. Therefore, studies on stronger electron-withdrawing substituent are very much desired to improve thiophene-based and related materials for organic solar cells"[7]."Quantum chemical studies based on density functional theory (DFT) have been successful in evaluating the optical and electronic properties of π-conjugated systems. Although the results of DFT calculations have been observed to deviate from experimental values for these systems, the trends in the results are found to agree with the experimental findings. Thus, changes in the properties resulting from the chemical modifications can be satisfactorily addressed using this method"[7].

To the best of our knowledge, work on solvents effects on the global chemical index, non-linear optical properties, thermodynamics properties, and IR spectra of poly(3-hexylthiophene-2,5-diyl) have not been reported. In the present work, we investigated the effect of solvents (toluene, acetone, thiophene, methanol and chloroform) on the structural properties, molecular geometry, thermodynamic properties, nonlinear optical (NLO) properties, and chemical reactivity such as HOMO-LUMO energy gap, chemical hardness, chemical potential, density of state (DOS) and IR spectra of the P3HT and compared with the state of the molecule in the gas phase.

Figure 1: Optimized structure of poly(3-hexylthiophene-2,5-diyl) (P3HT)

2.0 Density Functional Theory (DFT)

"Density Functional Theory (DFT) is a computational method that derives properties of the molecules base on a determination of their electron density. DFT method has become the most widely-spread *ab-initio*method in Computational Material Science (CMS) and Solid-state Physics, due to its high computational efficiency and very good accuracy for the structure of molecules, crystals, surfaces and their interactions. In DFT method, the energy of the molecule is a function of the electron density"[16]. "Density functional theory (DFT) was proposed by Hohenberg and Kohn as a method to determine the electronic

structure of a system at groundstate with a theory stating that all ground-state properties for many-particle systems are functional of the electron density. In 1965, Kohn and Sham (KS) reformulated the problem in a more familiar form and opened the way to the practical applications ofDFT"[17].

2.1Global Reactivity Descriptors

The global reactivity descriptors parameters such as ionization potential (IP), electron affinity (EA), chemical potential (μ), electronegativity (χ), hardness (η), softness (S), electrophilicity index (ω) of the studied polymer are computed by using Koopmans' equations as;

$$IP = -E_{HOMO} \quad (1)$$

$$AE = -E_{LUMO} \quad (2)$$

The energy gap (E_g) is obtained using the relation;

$$E_g = E_{LUMO} - E_{HOMO} = IP\text{-}EA \quad (3)$$

Chemical hardness (η) is given by half of the energy of the band gap[18];

$$\eta = (E_{LUMO} - E_{HOMO})/2 = (IP - EA/2) \quad (4)$$

The softness of a molecule can be obtained by taking the inverse of its chemical hardness [19];

$$S = \frac{1}{-} \quad (5)$$

The chemical potential is given by [20];

$$\mu = -\left(\frac{IP+EA}{2}\right) \quad (6)$$

The electronegativity is obtained from[19];

$$\chi = \frac{IP+EA}{2} \quad (7)$$

The electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index is expressed as [19,21];

$$\omega = \frac{\mu^2}{2} \quad (8)$$

Nucleophilicity (υ) index is expressed as [20]

$$\nu = \frac{1}{\omega} \quad (9)$$

The maximum charge transfer which is the maximum amount of electronic charge that an electrophile system can accept is defined as

$$\Delta N_{max} = -\frac{\mu}{\eta} \quad (10)$$

"Other two parameters known as nucleofuge and electrofuge are used to study the reactivity of molecules. The nucleofuge is defined as the capacity of a molecule to accept an electron from a system while, the electrofuge measures the relative stability of the cation"[22,23]. Nucleofugality and electrofugality are defined as:

$$\Delta E_{nucleofuge} = \mathrm{sgn}(N + \eta)\left(\frac{\eta+\mu^2}{2\eta}\right) \quad (11)$$

$$\Delta E_{electrofuge} = \frac{(\mu-\eta)^2}{2\eta} \quad (12)$$

2.2 Open-Circuit Voltage (VOC)

"The maximum open-circuit voltage (V_{OC}), is a crucial photovoltaic parameter that can be obtained theoretically by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor. The theoretical value of V_{OC} has been calculated from the expression"[24]

$$V_{OC} = E_{HOMO}^{Donor} - E_{LUMO}^{Acceptor} - 0.3 \quad (13)$$

2.3 Vibrational Frequency

The vibrational frequencies are calculated with the following equations [16]:

$$V_{ij} = \frac{1}{\sqrt{m_i m_j}}\left(\frac{\partial^2 V}{\partial_{qi}\partial_{qj}}\right) \quad (14)$$

where V_{ij} is the Hessian matrix,m_i refers to the mass of atom i, *and* ∂_{qi} refers to a displacement of atom *i* in the x-, y-, or z-direction,

$$VU = \lambda U \quad (15)$$

Where *U is* a matrix of eigenvectors and λ is a vector of eigenvalues, and

$$\lambda_{k=(2\pi\upsilon_k)^2} \quad (16)$$

Where λ_k is the k_{th}eigenvalue and ν_k is the k_{th}vibrational frequency.

The infrared intensities can be computed with the equation [16]

$$\frac{\partial E_{SCF}}{\partial f \partial a} = 2\sum_{i}^{d.o} h_{ij}^{fa} + 4\sum_{i}^{d.o}\sum_{j}^{all} U_{ji}^{a} h_{ij}^{f} \quad (17)$$

$$h_{ij}^{fa} \sum_{\mu\upsilon}^{AO} C_{\mu}^{i0} C_{\upsilon}^{i0}\left(\frac{\partial^2 h_{\mu\upsilon}}{\partial f \partial a}\right) \quad (18)$$

E_{SCF} is the self-consistent field energy, f is the electric field, a is a nuclear coordinate, $h_{\mu\upsilon}$ is the one-electron atomic orbital integral, U^a is related to the derivative of the molecular orbital coefficients with respect to a by $\frac{\partial c_{\mu}^{i}}{\partial a} = \sum_{m}^{all} U_{mi}^{a} C_{\mu}^{m0}$ (19)

The term "all" in the above summations refers to all occupied and virtual molecular orbitals and .d.o... Refers to doubly occupied orbitals such as those found in the ground state of a closed-shell system. Terms such as C_{μ}^{i0} refers to the coefficients of the atomic orbital m in the ith unperturbed molecular orbital.

2.4 Non-Linear Optical (NLO) Properties

To have clearer picture of the non-linear optical properties (NLO) of poly(3-hexylthiophene-2,5-diyl), the dipole moment (μ), polarizability (α), anisotropic polarizability ($\Delta\alpha$), and First-order hyperpolarizability (β) and second-order hyperpolarizability (γ) were also computed.

For molecular systems, dipole moment can be obtained from [19];

$$\mu_{tot} = \left[\mu_x + \mu_y + \mu_z\right]^2 \quad (20)$$

where μ_x, μ_y and μ_z are the components of dipole moment in x, y and z coordinates.

The electric dipole polarizability is given by [25];

$$\alpha = \frac{\partial^2 E}{\partial F_a \partial F_b} \quad (21)$$

The mean polarizability is calculated using [25];

$$< \alpha >= \frac{1}{2}\left(a_{xx} + a_{yy} + a_{zz}\right) \quad (22)$$

where a_x, a_y, and a_z quantities are known as principal values of polarizability tensor.

The anisotropic polarizability is given by [19];

$$\Delta\alpha = 2^{-1/2}\left[\left(a_{xx} - a_{yy}\right)^2 + \left(a_{yy} - a_{zz}\right)^2 + (a_{zz} - a_{xx})^2 + 6\left(a_{xz} + a_{xy} + a_{yz}\right)\right]^{1/2} \quad (23)$$

The first-order hyperpolarizability is defined as [26];

$$\beta = \left[\left(\beta_{xxx} + \beta_{yyy} + \beta_{zzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{xzz} + \beta_{zyy}\right)^2\right]^{1/2} \quad (24)$$

The second-order hyperpolarizability is given by [25];

$$\gamma = \frac{1}{5}\left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right)\right] \quad (25)$$

3.0 Computational Method

All computations were carried out using windows version of Gaussian 9W[27]software package and Gauss View, Rev 5.0.9 [28]molecular visualization tool. The Density Functional Theory (DFT) calculations were performed using Becke's three-parameter hybrid functional [29] with the Lee-Yang-Parr correlation functional [29], a combination that "gives rise to the well-known B3LYP method. In addition, geometry optimization was carried out using Ab-initio quantum mechanical technique at DFT. Stability check was

performed on the molecule to confirm its stability. All parameters were allowed to relax and each calculation converged to an optimized geometry.For the study of solvation effects, a Self-Consistent Reaction Field (SCRF) approach based on Polarizable Continuum Model (PCM) was used. The effects of five solvents (toluene, acetone, methanol, thiophene and chloroform) were investigated by means of the SCRF method based on PCM as implemented in the Gaussian 09"[30]."The structures wereentirely optimized and studied at the DFT level of theory using B3LYP method with basis set 6-311++G(d,p).The DFT methodhas proven to be one of the most accurate methods for the computation of the electronic structure of solids and molecules"[31]. "In addition, the vibrational frequencies for the optimized molecular structures were also calculated. The optimized geometry of the molecule has no imaginary vibrational frequencies which imply that minimum potential energy was found which further confirmed the stability of the molecule.The parameters such as Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO),energies wereobtained from the eigenvalues and were used to compute the Ionization Potential (IP), Electron Affinity (EA), energy band gap (or global hardness), chemical potential (μ), chemical hardness (η) and electrophilicity index (ω)"[32].The nonlinear optical properties of the molecule such as dipole moment (μ), isotropic polarizability(α), anisotropic polarizability(Δα) and first order polarizability (β and γ)were calculated using equations 22-25. The Ir-Spectra were also plotted and interpreted.

4.0Results and Discussion

4.1Optimized Bond Lengths (Å) of poly(3-hexylthiophene-2,5-diyl) (P3HT) in Gas Phase and in some solvents

"The distance between the nuclei of two atoms covalently bonded together is known as bond length whereas bond angle is the angle between two adjacent bonds of an atom in a molecule"[26]. "The optimized values of bond lengths and bond angles of the studied molecule were calculated and shown in Tables 1 and 2 at DFT/B3LYP level using 6-311++G (d, p) basis set in the gas phase and in different solvents (acetone, chloroform, methanol, thiophene and toluene).From Table 1, there are small variations in bond lengths of P3HT when optimized with solvents compared with that in gas phase. The result shows that the lowest value obtained was 1.0841Å(C_{28}-H_{35}) in methanol. However, when compared withthe results of P3HT molecule in gas phase with other solvents, the bond lengths in the mentioned solventare a bit lower than that in the gas phase and in other solvents. It is worth noting that, the smaller the bond length, the higher the bond energy and stronger the bond will be"[33]. "Accordingly, this has shownthat the bond energy of P3HT in methanol isslightly stronger than that in gas phase and in the other solvents.

Hence, sufficient amount of energy is needed to break these bonds. It was also observed that the bond length increases with a decrease in the polarity of the solvents under study. However, the longest bond length is 1.7659Å(C_{21}-S_{23}). This is the weakest bond energy of P3HT in both gas phase and in solvents. Hence, a littleamount of energy is enough to break these bonds. The structural geometry of the studied molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work reported by"[34,35].

Table 1. Selected bond lengths (Å) of the optimized structure of P3HT molecule in the gas phase and in different solvents using B3LYP/6-311++G (d, p) basis set

Bond length	Gas phase	Methanol	Thiophene	Chloroform	Toluene	Acetone	Previous work [34,35]
C_1-C_2	1.5433	1.5343	1.5343	1.5343	1.5343	1.5335	
C_1-H_3	1.3973	1.097	1.0969	1.0969	1.097	1.0984	
C_{18}-C_{21}	1.3824	1.3837	1.3834	1.3835	1.3837	1.3827	
C_{18}-C_{22}	1.4327	1.4359	1.4352	1.4355	1.436	1.434	1.43
C_{22}-C_{24}	1.3673	1.3694	1.3693	1.3693	1.3694	1.3674	1.37
C_{21}-S_{23}	1.7629	1.7659	1.7644	1.765	1.7659	1.7657	
C_{28}-H_{35}	1.0847	1.0840	1.0841	1.0841	1.0841	1.0846	
S_{23}-C_{24}	1.7454	1.7479	1.7463	1.747	1.748	1.7486	1.70
S_{29}-C_{31}	1.7587	1.7609	1.7592	1.7598	1.7608	1.7619	
C_{40}-H_{48}	1.0976	1.0975	1.0972	1.0973	1.0975	1.0979	

4.2Selected bond angles(°) ofthe optimized structure of poly(3-hexylthiophene-2,5-diyl) (P3HT) in gas phase and in different solvents

The optimized bond angles of P3HT molecule in gas phase and in different solventsare listed in Table 2. The bond angle is the average angle between the orbitals of the central atom containing the bonding electron pairs in the molecule [36]. It is expressed in degrees. The bond angle throws more light on the distribution of orbitals around a central atom in a molecule. The bond angles also contribute to the shape of a molecule. From Table 2, there is a slight increase in the bond angles of the studied molecule in solvents when compared with the one in gas phase. From the results obtained, the values obtained in methanol are a bit higher than the one obtained in gas phase and other solvents. This indicates that, in terms of bond angles, P3HT molecule has the highest stability in methanol than in gas phase and other solvents.The bond angles were found to have an average value of110° in both gas phase and in solvents. The structural

geometry of the titled molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work reported by [37].

Table 2. Selected bond angles (˚) of the optimized structure of P3HT molecule in the gas phase and in different solvents using B3LYP/6-311++G (d, p) basis set

Bond angles	Gas phase	Methanol	Thiophene	Chloroform	Toluene	Acetone	Previous work [37]
C_2-C_1-H_3	112.0958	110.9579	110.9963	110.9821	110.9614	111.0398	
C_{15}-C_{18}-C_{22}	122.2284	121.9226	122.0081	121.9742	121.9202	122.0689	
C_{21}-C_{25}-C_{28}	129.2423	129.3251	129.2225	129.2625	129.3375	129.3339	129.0000
C_{25}-S_{29}-C_{31}	92.39860	92.3619	92.3472	92.3543	92.3631	92.3257	
C_{36}-S_{39}-C_{44}	92.43290	92.5171	92.5054	92.5108	92.5163	92.4548	
H_{56}-C_{50}-H_{60}	108.9110	106.1997	106.0559	106.1072	106.2011	106.1282	
C_{15}-C_{12}-H_{16}	108.9888	108.9942	108.9456	108.9623	108.9947	109.0756	109.000
C_{15}-C_{12}-H_{17}	109.2197	109.1195	109.1459	109.1372	109.1181	109.1842	
$H_{47}C_{40}$-H_{48}	107.0998	106.3561	106.2505	106.2872	106.3437	106.2459	
C_{38}-C_{43}-C_{44}	112.3680	112.2971	112.2698	112.2811	112.2931	112.3229	113.0000

4.3Frontier Molecular Orbital Energies

Table 3 gives the Highest Occupied Molecular Orbital (HOMO)and Lowest Unoccupied Molecular Orbital(LUMO)and Energy gap (E_{gap}) in electron volt (eV) of the studied molecule in gas phase and insomesolvents calculated at the DFT/B3LYP level using 6-311++G (d, p) basis set. The values of HOMO, LUMO and HOMO-LUMO energy gap reflect the chemical activity of the molecule. Compounds with lower HOMO-LUMO gap value tend to have higher stability [17]. Both HOMO and LUMO are the main orbitals taking part in chemical reaction. HOMO energy characterizes the capability of electron giving; LUMO characterizes the capability of electron accepting. The frontier orbital gap helps to characterize the chemical reactivity, optical polarizability, chemical hardness and softness of a molecule. The HOMO-LUMO gap,that is the difference in energy between the HOMO and LUMO, is an important stability index. It is clear from Table 3 that the HOMO-LUMO energy gap for the P3HT molecule is lower in methanol with value of about 3.8338eV follow byacetone, chloroform, thiophene, toluene, and then in gas phase with values of 3.8365 eV, 3.8531 eV, 3.8629 eV, 3.8657 eV and 3.8827 eV respectively. The results show that, P3HT has smaller band gap energy in methanol (3.8338 eV) than in gas phase and the rest of the solvents. Therefore, the electron transfer from HOMO to LUMO of the molecule in methanol is relatively harder than that in the gas phase. This shows that P3HT molecule is having higher stability in methanol than in gas phase and in other solvents. However, P3HT has larger energy gap in gas phase than in solvents thus, the electron jumps from the HOMO to the LUMO energy orbital more easily in the gas phase than in the solvents. Interestingly, the order of stability increases with an increase in polarity of the solvents under

study. The HOMO-LUMO gap of P3HT obtained in methanol is a bit comparable to 3.10 eV reported by[38].

The ionization potential (IP) and electron affinity (EA) measure the tendency of compounds to lose or gain an electron [39]. The higher the ionization potential (IP), the more difficult it is to remove an electron to form an ion. The lower the electron affinity (EA), the less easy it is to add an electron. In Table 3, it can be observed that it is more difficult to remove an electron from the gas phasethan in acetone, chloroform, methanol, thiophene and toluene to form an ion. Similarly, it is more difficult to add an electron in terms of their EAs, to the molecule in the gasphase<acetone<chloroform<methanol<thiophene<toluenein that order. It was observed that the ionization potential increases with an increase in the polarity of the solvents while the electron affinity decreases as the polarity of the solvents decreases.

Table 3: Calculated HOMO, LUMO, IP, AE, and Energy gap in (eV) of the Optimized Structure of Poly(hexylthiophene-2,5-diyl) using B3LYP/6-311++G (d, p) basis set

Solvents	Dielectric (ε)	HOMO (eV)	LUMO (eV)	IP (eV)	EA (eV)	E_{gap} (eV)	Previous work
Gas phase		-5.2148	-1.3875	5.2148	1.3875	3.8273	[38]
Methanol	32.6130	-5.4052	-1.5693	5.4052	1.5693	3.8359	3.10
Thiophene	2.7270	-5.2842	-1.4651	5.2842	1.4651	3.8191	
Chloroform	4.7113	-5.3459	-1.4909	5.3459	1.4909	3.8550	
Toluene	2.3741	-5.3843	-1.5720	5.3843	1.5720	3.8123	
Acetone	20.4930	-5.3748	-1.5598	5.3748	1.5598	3.8150	

4.4Global Chemical Reactivity Descriptors (GCRD)

The Global Chemical Reactivity Descriptors parameters of molecules such as hardness (η), softness (ʃ), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) of P3HT molecule in gas phase and in some solvents are reported in Table 4. Chemical hardness is proportional to the HOMO-LUMO energy gap. An increase in the chemical hardness makes the molecule more stable and less reactive.As seen in Table 4, P3HT molecule in the gas phasewith slightly higher value of chemical hardness of 1.9414eV is considered to be harder and more stable than, follow by toluene,thiophene, chloroform, acetone and methanol with chemical hardness of 1.9329eV, 1.9315eV,1.9266eV, 1.9183eV and 1.9169eV respectively. This indicates that P3HTin the gas phase is more stable. Electronegativity and chemical potential are important parameters in the quantum chemical reaction. The higher the value of electronegativity, the greater the ability of theatoms or molecules to attract electrons, whereas the greater the value of chemical

potential, the more the reactivity and less stable the molecule[40]. P3HT molecule in the gas phase has a higher electronegativity than in the solvents as reported in Table 4. The molecule also has thegreatest value of chemical potential in acetone and methanol. Consequently, this molecule is more reactive and less stable in both acetone and methanol. The electrophilicity index value is used for the determination of chemical reactivity of molecules. The result indicatesthat the electrophilicity index with value of 3.1704(eV) was highest in methanol.This affirm the stability of the molecule in methanol than in the gas phase and other solvents.

Table 4: Global chemical indices of the optimized structure of poly(hexylthiophene-2,5-diyl) using B3LYP/ 6-311++G (d, p) basis set

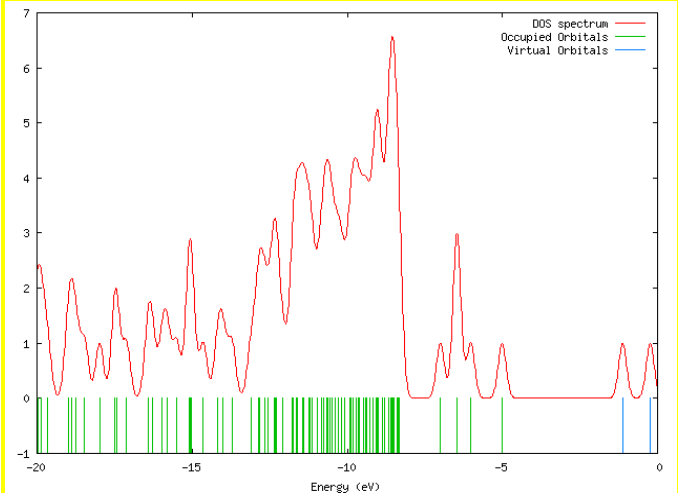
Gas phase/Solvents	**η (eV)**	**∫(eV)**	**χ (eV)**	**μ (eV)**	**ω(eV)**
Gas phase	1.9137	0.5225	-3.3012	3.3012	2.8473
Methanol	1.9179	0.5214	-3.4873	3.4873	3.1704
Thiophene	1.9096	0.5237	-3.3746	3.3746	3.0313
Chloroform	1.9275	0.5188	-3.4184	3.4184	3.0313
Toluene	1.9062	0.5246	-3.4782	3.4782	3.0313
Acetone	1.9075	0.5242	-3.4673	3.4673	3.1512

4.5Density of States (DOS)

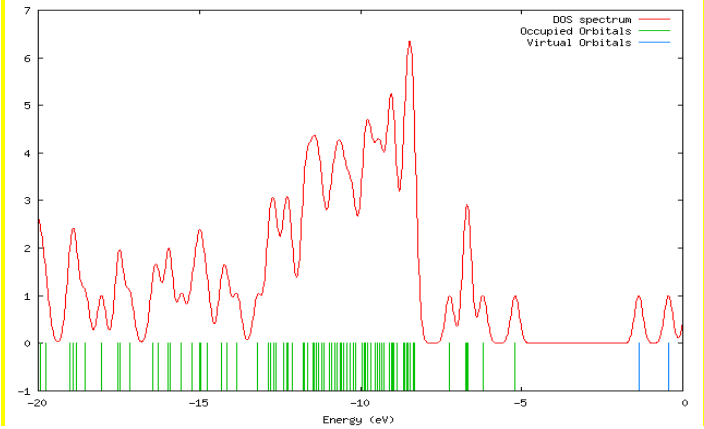
The Density of State (DOS) is an ingredient of critical importance for the accurate physical understanding of the optoelectronic properties of organic semiconductors. The application of DOS plot is to demonstrate the molecular orbital and their contribution of chemical bonding through the Overlap Population Density of States (OPDOS) plot [17]. The DOS plot results show overlapping population in the molecular orbital. The OPDOS result shows nonbonding, bonding and anti-bonding interactions between the two orbital atom groups. The positive value of OPDOS indicates the bonding interaction and negative value indicates the anti-bonding interactions and zero value indicates the nonbonding interactions.The DOS plot gives thecomposition of group of orbitals contributing to the molecular orbital. The graph exhibits the orbital characteristics of different energy range. It is the major contribution from s orbital and p orbital basic function of carbon in the frontier molecular orbital.

From the DOS of the P3HT molecule in the gas phase and in solvents, the population of charges is becoming denser in the order gas phase<methanol (as seen from Fig. 2). This suggests that the existence of the solvents molecule, free charges and the weak intermolecular forces within methanol clearly affect the charges population compared to gas phase and other solvents. As observed in the entire DOSs, the

chargepopulation is highly concentrated in the valence region, which indicates that P3HT in the gasphase and in solvents possesses high tendency to behave as n-type semiconductor materials. Moreso, the presence of strong hybridization has elevated the charges population near the zero Fermi energy level and consequently, the valence band maxima of the molecule in methanol are pushed to higher energies. Since charges population is denser near zero Fermi energy, the possibility to succeed in transmitting the charges from valence region to conduction region is increased as well. As we compared, the gaps produced in DOS are in agreement with the previously found on the HOMO–LUMO energy gaps and band gap values for all the solvents.



(a) In Gas Phase



(b) In Methanol

Figure 2 computed density of state (DOS) of P3HT molecule in gas phase and in solvent

4.6Thermodynamic Properties

The thermal stability of organic solar cells is critical for practical applications of this emerging technology. Thus, effective approaches and strategies need to be found to alleviate their inherent thermal instability.At

a higher entropy, a material exhibits less disorder behavior or molecular disruptions and thus energetically stable. Similarly, a gradual improvement in the heat capacity of a material makes it an outstanding material for optoelectronic devices [41].Table 5 presents the components and total contributions of the electronic, translational, rotational and vibrational energies to the entropy (S) and heat capacity (Cv) as well as the rotational constants and zero-point vibrational energies (ZPVE) of P3HT in the gas phase and in different solvents.The results obtained show that the molecule has the highest value of specific heat capacity in methanolas 152.307(Kcal/Mol) and the molecule intoluene has the highest value of entropy as 266.960 (Kcal/Mol), while in thiophene the molecule has the highest value of zero-point vibrational energy (ZPVE) as 455.37486 Kcal/Mol. It can be observed that the specific heat capacity of P3HT is found to increase with an increase in the polarity of the solvents, while the entropy decreases as the dielectric constant increases. The zero-point vibrational energy (ZPVE) also decreases with an increase in the polarity of the solvents. The variation of thermodynamic properties changes slightly due to the effect of the solvents.Thus, we conclude that the solvents have influence on the thermodynamic properties of the molecule. The results verified that the molecule has higher chemical reactivity and thermal resistivity in solvents than in gas phase due to the increase in their kinetic energy.

Table 5: Thermodynamics properties of the optimized structure of P3HT molecule in the gas phase and different solvents usingB3LYP/ 6-311++G(d)

	Gas		Acetone		Chloroform	
	Cv (Kcal/Mol)	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**
Electronic	0.000	0.000	0.000	0.000	0.000	0.000
Translational	2.981	44.680	2.981	44.680	2.981	44.680
Rotational	2.981	38.995	2.981	38.993	2.981	38.993
Vibrational	145.245	180.491	145.105	180.026	145.091	180.012
Total	**151.207**	**263.766**	**151.067**	**263.699**	**151.052**	**263.685**
Rotational Constants (GHz)	0.09787,0.04271,0.03268		0.09772, 0.04277, 0.03274		0.09771, 0.04278,0.03274	
ZPVE (Kcal/Mol)	**458.61913**		**458.97986**		**459.01914**	

Solvents Positions	Methanol		Thiophene		Toluene	
	Cv (Kcal/Mol)	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**	**Cv (Kcal/Mol)**	**S (Kcal/Mol)**
Electronic	0.000	0.000	0.000	0.000	0.000	0.000
Translational	2.981	44.680	2.981	44.680	2.981	44.680
Rotational	2.981	39.009	2.981	38.993	2.981	39.008
Vibrational	146.346	182.835	145.105	180.026	146.334	183.272
Total	**152.307**	**266.523**	**151.067**	**263.699**	**152.296**	**266.960**
Rotational Constants (GHz)	0.097560.042410.03257		0.097720.042770.03274		0.097610.042380.03258	

ZPVE (Kcal/Mol)	**455.29132**	**455.37486**	**455.31561**

4.7 Non-Linear Optical Properties

Non-linear optical (NLO) effect arises from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude and other propagation characteristics from the incident fields [42]. Also, dipole moment in a molecule is an important electronic property which results from non-uniform distribution of charges on the various atoms in the molecule [43]. It is worth noting that, the molecule with higher dipole moment tends to be a polar material. Our investigation highlighted the effects of solvents on the non-linear optical properties of P3HT. This is necessary for fully understandingof the nonlinear optical response of the molecule.Table 6 shows the non-linear optical propertiesof P3HT in the gas phase and in somesolvents. It can be observed from the table that there is an increase in values of total dipole moments(μ_{tot}), anisotropy of polarizability$\langle\Delta\alpha\rangle$, first-order hyperpolarizability (β_{tot}), and second order hyperpolarizability(γ_{tot}), while the mean polarizability$\langle\alpha\rangle$ decreases due to the effects of the solvents. From the results obtained, methanol has the highest values of dipole moment with a value of1.01764 Debye. The increase in the dipole moments of P3HT in solvents affirm to us that the molecule may behave as polar material in solvents. Our finding reveals that P3HT molecule in the gas phase has slightly higher value of mean polarizability when compared with the results obtained in solvents. However, the results obtained for total anisotropic polarizability show that P3HT in methanol has slightly higher value ($5.05\text{x}10^{-24}\ esu$)when compared with the results obtained inthe gas phase and in other solvents. Therefore, the polarizability of P3HT molecule increases as the polarity of the solvents decreases whereas the anisotropic polarizability increases with an increase in the polarity of the solvents. Also, from the results in Table 6, P3HT molecule in acetone has slightly higher value of first-order hyperpolarizability ($4.44\text{x}10^{-30}$esu), follow by chloroform, thiophene, methanol, gas phase and then in toluene with values$(1.36 \times 10^{-30} esu)$, $(1.30 \times 10^{-30} esu)$,$(1.12 \times 10^{-30} esu)$,$(9.38 \times 10^{-30} esu)and(4.84 \times 10^{-30} esu)$ respectively. This shows that, there is an increase in the value of the first-order hyperpolarizability in the order oftoluene<gas-phase<methanol<thiophene<chloroform<acetone. The values obtained for the first order hyperpolarizability for P3HT in acetone ($4.44\text{x}10^{-30}$esu), is about 12 times than that of the urea molecule (0.3728×10^{-30}esu), which is commonly used for the comparison of NLO properties. Therefore, the result indicates that the first order hyperpolarizability of P3HT increases with an increase in the polarity of the solvents. From the foregoing, we conclude that the presence of the solvents actually improved the NLO properties of the studied molecule.

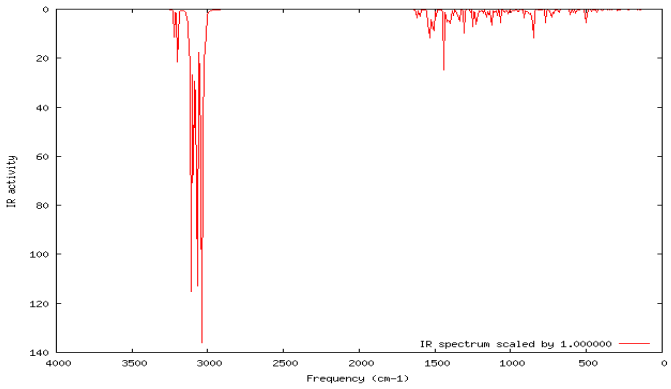
Table 6. Non-linear optical properties (in electrostatic unit, esu) and dipole moment in (Debye) of the optimized P3HT Molecule in the gas phase and different solvents

Molecule	μ_{tot}	$\langle\alpha\rangle$	$\langle\Delta\alpha\rangle$	β_{tot}	γ_{tot}
Gas Phase	0.69378	$-3.37\text{x}10^{-23}$	$3.77\text{x}10^{-24}$	$9.38\text{x}10^{-31}$	$-2.475\text{x}10^{-17}$
Acetone	1.001749	$-1.31\text{x}10^{-23}$	$5.00\text{x}10^{-24}$	$4.44\text{x}10^{-30}$	$-7.520\text{x}10^{-20}$
Chloroform	0.93575	$-3.33\text{x}10^{-23}$	$4.64\text{x}10^{-24}$	$1.36\square10^{-30}$	$-7.539\text{x}10^{-20}$
Methanol	1.01764	$1.33\text{x}10^{-28}$	$5.05\text{x}10^{-24}$	$1.12\text{x}10^{-30}$	$-7.517\text{x}10^{-20}$
Thiophene	0.83003	$-3,34\text{x}10^{-23}$	$4.39\text{x}10^{-24}$	$1.30\text{x}10^{-30}$	$-7.553\text{x}10^{-20}$
Toluene	0.81221	$-3.34\text{x}10^{-23}$	$4.31\text{x}10^{-24}$	$4.84\text{x}10^{-31}$	$-7.559\text{x}10^{-20}$

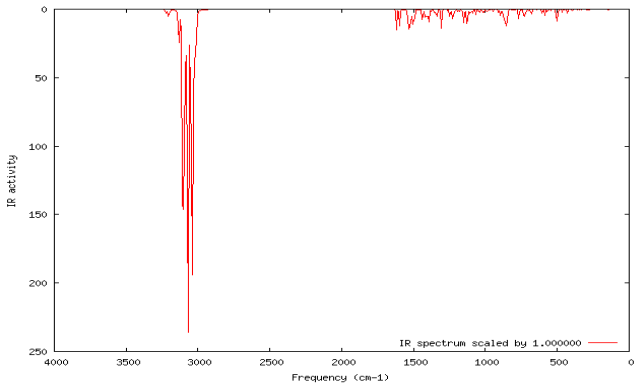
4.8 IR Intensities

IR spectroscopy deals with the study of interaction of infrared light with matter. When a molecule absorbs infrared radiation, its chemical bonds vibrate and may either be stretch, contract or bend [44]. The main

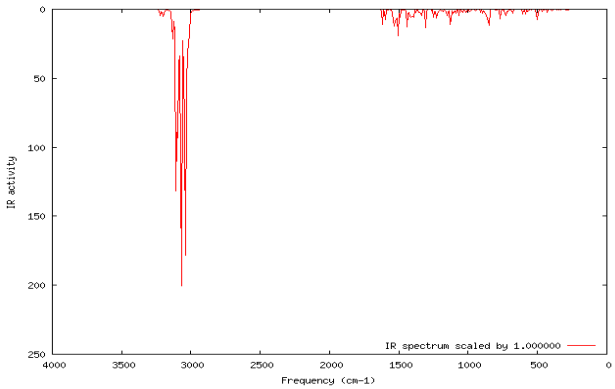
focus of vibrational analysis is to get vibrational modes connected with the precise molecular structure of the measured compound [45].Figure 3 shows the graphical representations of the calculated vibrational frequencies and intensities of P3HT molecule in solvents and in gas phase. Anharmonicity effects in real system are neglected, thus DFT method systematically overestimates the vibrational wave numbers. Thus, generic frequency scale factors have to be applied in fitting the calculated v In addition, increasing frequency overestimation of DFT in the high frequency regions (>3000 cm−1) was reported in several research papers [46-47]. Consequently, the frequencies of C–H stretching vibrations in this study were scaled down by multiplying a factor of 0.958 while other frequencies were scaled down by a factor of 0.9682 [46].The representation shows that there is slight increase in the peak values of the frequencies of the studied molecule in solvents when compared with gas phase. From the graphs, P3HT in methanol has the most intense frequency with value of 3024.9421cm^{-1} with corresponding intensities of 140.2464 km/mol follow by acetone, chloroform, toluene, thiophene and thengas phase with values of frequencies at 3025.0710cm^{-1},3025.9678 cm^{-1},3026.6927cm^{-1}, 3026.5349cm^{-1} and 3088.6908cm^{-1} withcorresponding intensities of 137.3717 km/mol, 118.4580 km/mol, 117.0428 km/mol, 112.1323 km/mol and 77.6119 km/mol respectively. From the results obtained, the frequency of P3HT molecule in gas phase and in solvents are in the order of methanol>acetone>chloroform>toluene>thiophene>gas phase.For all the solvents and gas phase under investigation, the frequency ranges between 3024.9421cm^{-1} and 3088.6908cm^{-1} with corresponding intensities between 140.2464 km/mol and 77.6119 km/mol. At these frequencies, w =C-H stretch, s[broad] dimer OH, s Ar-H stretch and m =C-H stretch, s =C-H stretch were observed. Comparing the graphs presented, P3HT in methanol has slightly higher peak values of frequencies with corresponding intensities than in gas phase and the rest of the solvents.



Gas phase



ChloroformMethanol



ThiopheneToluene

Figure 3: IR spectra of P3HT molecule

Open-circuit Voltage (VOC)

The open-circuit voltage of an organic solar cell is obtained from the difference between the HOMO of the donor and the LUMO of the electron acceptor, considering the energy loss during photo charge generation [39]. The obtained values of Voc of the studied molecules calculated according to equation (13) range from1.445 eV to 1.635 eV. Specifically the calculated values are ofthe $V_{OC}$for the gas phase and in different solvents were obtained as 1.445 eV in the gas phase, 1.635 eV in methanol, follow 1.614 eV in toluene, 1.605 eV in acetone, 1.576 eV in chloroform and 1.514 eV in thiophene.These obtained Voc values are sufficient for possible efficient electron injection. Therefore, the studied molecule can be used as an organic solar cell, because the process of electron injection of the studied excited molecule to the conduction band of the acceptor (PCBM derivatives) and the subsequent regeneration can be done. We observed that the best values of Vocare 1.635 eV, 1.614 eV and 1.605 eV for methanol, toluene and acetone respectively.

5.0Conclusion

Inthis work, optimized parameters, electronic properties, density of states, thermodynamic parameters, non-linear optical properties, and vibrational frequencies of P3HT in solvents and in gas phase have been calculated. The global and local descriptors have been used to investigate the reactivity of the molecule in different solvents. The descriptors obtained could also provide more information and may contribute to a better understanding of the electronic structure of this compound. The HOMO-LUMO energy gapof 3.8338 eV shows that the titled compound is more stable in methanol than in the gasphase

and the rest of the solvents. The energy-gap was compared with the ones in literature (3.10eV). The ionization potential, electron affinity, chemical potential, electronegativity, hardness, softness and electrophilicity of the studied molecule were calculated and reported. The results indicate high stability and low reactivity of the molecule in chemical reaction and also indicate that the studied molecule is a good electrophile. The result of the IR spectrum shows that the studied molecule was stable in both the gas and solvents since no imaginary frequency was observed. It was also observed that the most intense frequency was found to be 3024.9421 cm^{-1} at an intensity of 140.2464 km/mol in methanol and 3088.6908 cm^{-1} at intensity of 77.6119 km/mol in gas phase. The theoretical values of the open circuit voltage were found to be 1.635 eV, 1.614 eV, 1.605 eV, 1.576 eV, .1514 eV, and 1.445 eV for methanol, toluene, acetone, chloroform, thiophene and the gas phase respectively. These valuesare sufficient for possible electron injection, therefore poly (3-hexylthiophene -2,5- diyl) can be used for solar cell application. We recommend further study of the properties of this molecule in anionic and cationic forms so as to give us a deeper insight of its relevance in organic semiconductor applications. Finally, we are also convinced that the systematic use of this theoretical approach can be employed to predict the optoelectronic properties on the other materials organic, and further to design novel materials for organic solar cells.

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