Molecular Design, Geometry Structures and Stability for Pyrrole Substitutes, DFT study as Organic Solar cell system
(One Anchoring System)

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الخلاصة :

تم في هذا البحث دراسة نظرية للخصائص الالكترونية والتركيبية والفعالية الكيميائية للبايرول المعوض (S1, S2, S3, and S4). بواسطة كيمياء الكم. انجزت الموائمة الهندسية للتراكيب وفق نظرية دالة الكثافة الالكترونية DFT بطريقة B3LYP وعند مستوى المجموعة الاساسية DVZ(d) أظهرت الدراسة أن الجزيئة(S2) تمتلك أعلى عزم لثنائي القطب مقارنة مع الجزيئات. (S1,S3,S4) وتم حساب الخواص الالكترونية كطاقة المدار الجزيئية , LUMO. HOMO وقيمة ΔE والتي أظهرت ان استقرارية المركبات يكون (S4> S3> S2> S1). كذلك تمت في هذه الدراسة النظرية دراسة تداخلات المانح – المتقبل الالكترونية لهذه المركبات من خلال ادخال مجاميع الالكترونية جانبية مختلفة لدراسة تأثيرها على التركيب الالكتروني HOMO, LUMO, ΔE , الدراسة التركيبية والالكترونية لهذه المركبات يمكن ان تساعد في تصميم مركبات كيميائية كفوءة ضوئيا. كذلك تم دراسة طاقات الامتزاز لهذه المركبات على سطح اوكسيد التيتانيوم . ووجد ان افضل طاقة امتزاز كان المركب S2.

Abstract

The theoretical electron properties of Pyrrole Substitutes (S1, S2, S3, and S4) were carried out by using quantum chemical calculations. The optimized structures were obtained by the Density Functional Theory DFT/B3LYP level of theory using the basis set DVZ(d). The optimized structures of compounds have the global minimum energy. It was found that the dipole moment of compound (S2) have high values compared with the Compounds (S1,S3,S4). Global descriptors such as the MO energies of HOMO, LUMO levels and ΔE, were determined and used to identify the differences in the stability and reactivity of compounds. In general, the calculated values lead to the conclusion that on the one hand the stability of the compounds are S4> S3> S2> S1. On the other hand, the theoretical study of novel acceptor-donor organic materials based on these compounds has been investigated. Different electron side groups were introduced to investigate their effects on the electronic structure; HOMO, LUMO and energy gap. The structural and electronic study as shown in this paper in hand for these compounds could help to design more efficient functional photovoltaic organic materials. the adsorption energy between the compounds and the TiO_2 surface was studied. The most suitable adsorption configurations high value of adsorption energy was compound S2.

Keywords: Alkyl Chain Substituted, Pyrrole Substitutes, Structural and Electronic Properties, DFT/B3LYP, Band Gap.

Introduction

Aromatic heterocyclic compounds based on pyrrole or pyrdinium core including carboxylate derivatives, Schiff-bases and their metal complexes, are materials of much interest to researcher due to their wide applications in medicine[1-2], catalysis, luminescence[3], optical devices[4] and clean energy[5-6]. The π-conjugated molecules based on heterocyclic ring and characterized by an extended π- conjugation is of broad interest in many areas of research, for their applications in organic electronics, particularly, in the last decade, optoelectronic device technology [7,8], such as light-emitting diode (LEDS) [9], thin film transistors (TFTs) [10] and low-cost solar cells [11] Research in organic solar cells has attracted considerable interests in the past decade because of their potential applications as alternative light harvesting devices other than the conventional silicon-based solar cells [12-13]. However, the performance and lifetime most organic solar cells there are not satisfactory. In general, organic materials exhibit low carrier mobilities, low absorbance in near-IR region, short exciton diffusion length, and poor long-term stability. In order to improve the performance of organic photovoltaic devices, design of new photosensitizing/charge transport materials and fabrication of devices with improved architecture are essential. So, designing and synthesizing molecules involves connecting donor (D), π-bridge and acceptor (A) groups as D–π–A system to create highly polarized with more interesting properties play a crucial role in technology. It is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials. Nowadays much interest is devoted to the prediction and estimation of physicochemical properties of molecules, and materials by using computational. Computational chemistry (also known as molecular modeling) is the application of computer-based models to the simulation of chemical is the processes and the computation of chemical properties and to use this for predication and understanding how electrons, atoms, and molecules interact . Density Functional Theory (DFT) is one major method of computational chemistry which has been accepted by the ab initio quantum chemistry community as a cost effective general procedure for studying physical properties of the molecules. This is because it is based on total electron density rather than on wave functions[14-19]. The work in hand attempts to study and predication of structure and electronic properties, relative stabilities of structural modifications were investigated for the D–π–A system with an blend (alkyl chain substituted by C, O, N, S) as donor and pyrrole as π –spacer (π –conjugated) while carboxylic – as acceptor (an anchoring group) as imitation for organic solar cell system [20-23]. **As** strategy for designing solar cell analogues with reduced band gaps and whether to be materials for organic solar cell, by performing Density Functional Theory (DFT)/B3LYB level of theory using the basis set DZV(d).

Modeling and Geometry Optimization

The quantum chemical calculations were performed for 4 compounds using the PC Gamess (Firefly) .program [24]. optimal geometry of all compounds under study computed using density functional theory with double zeta valence DZV(d) basis set and Becke's 3-parameter exchange functional with Lee-Yang-Parr correlation energy functional(B3LYP) [25-26]. All calculations were performed on the Pentium (R)4/IPM-PC- CPU 3.00GHz, 2.00GB . The structures of compounds are shown below in Figure 1:

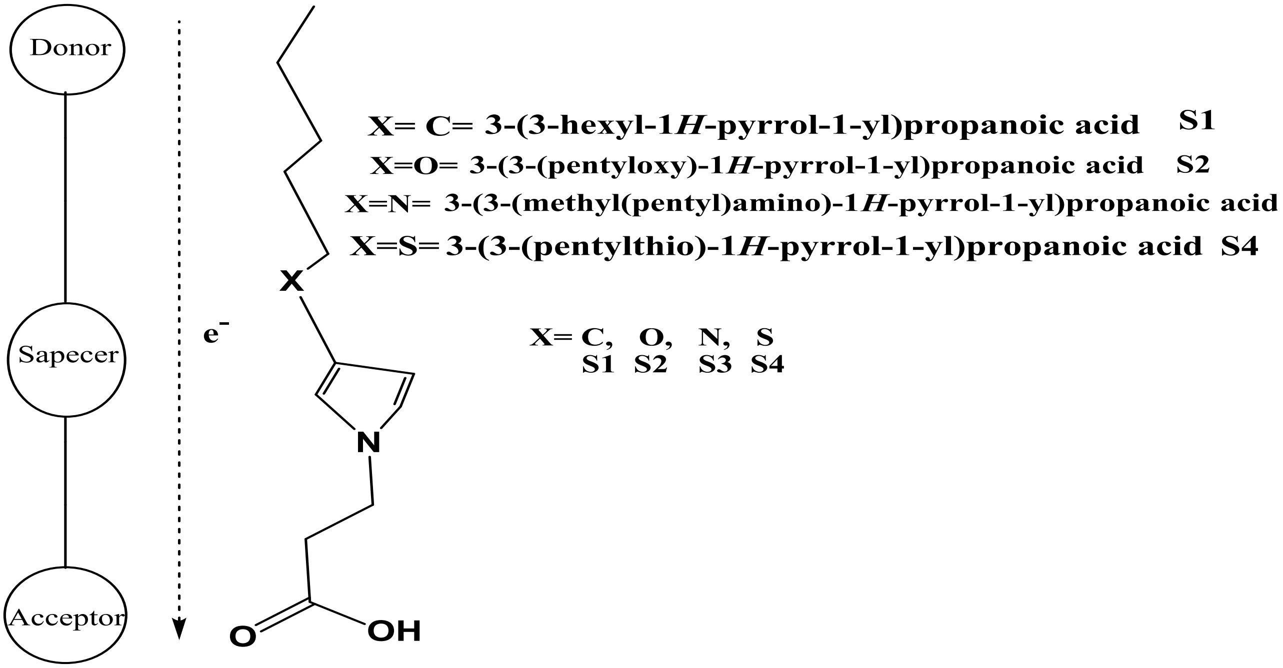
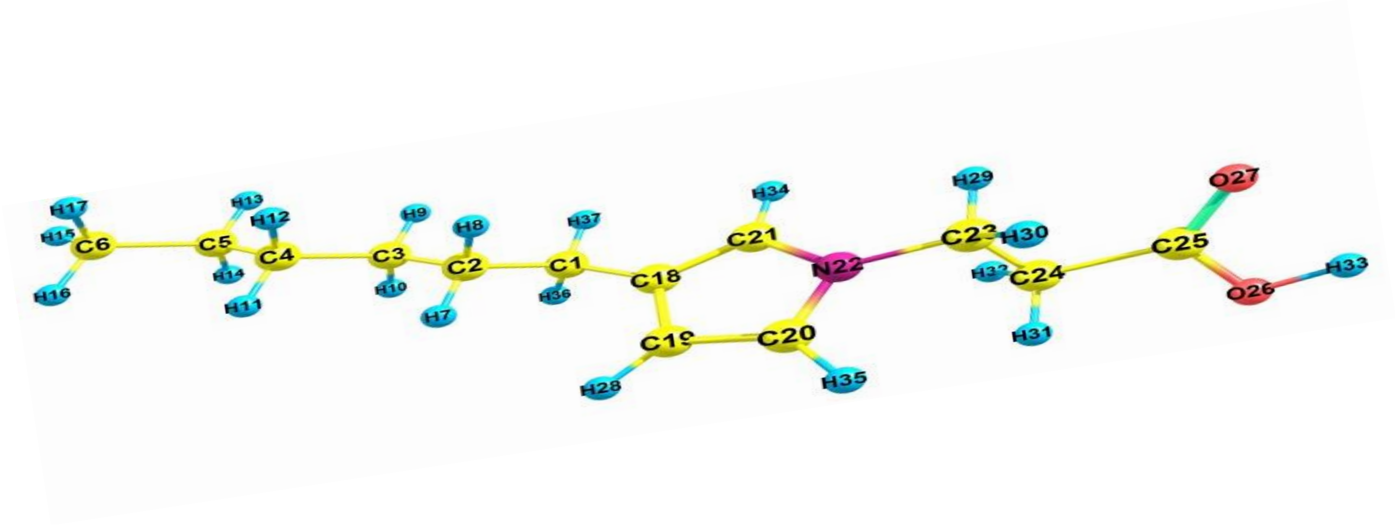


Figure 1: Molecular Structure of Compounds

Results and Discussion

The geometry optimized structures (S1, S2, S3 and S4) are visualized in Figure (2) below while the selected parameters of their structural data are summarized in Table 1.



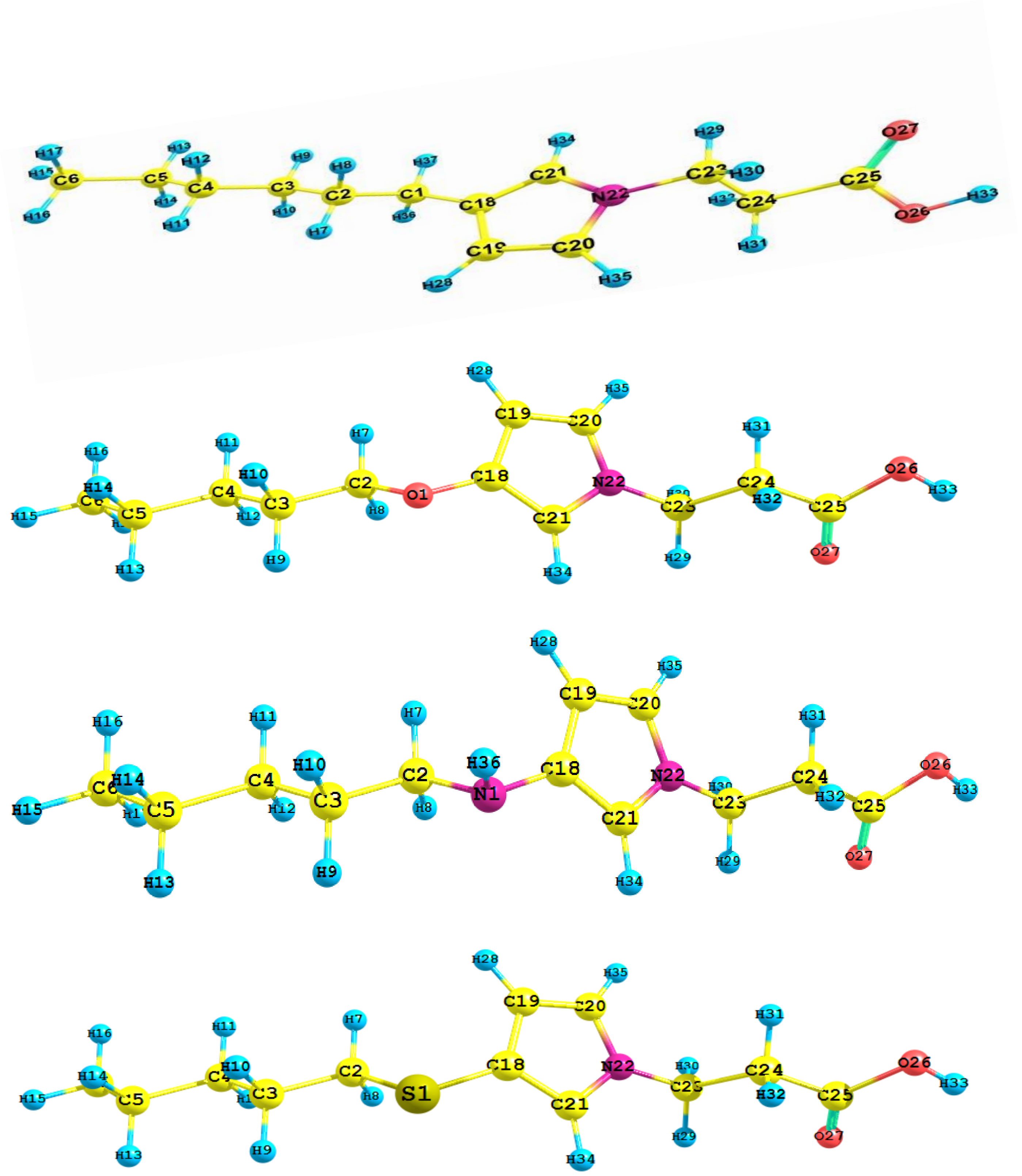


Figure 2: DFT/B3LYP –DZV(d) Calculated Optimized Structures of the Possible Predication for the Compounds in Gas Phase.

For all molecules, pyrrole substitutes ((S1, S2, S3 and S4)), optimized geometric structures, dipole moments, total energies, the HOMO, LUMO and energy band gap (ΔE) calculation have been investigated after total optimization by B3LYP/ DZV.

Total Energy: The structure optimization (minimum energy) obtained by the DFT(B3LYP) presented in Table 1.The total energy determines the occurrence or non-occurrence of chemical reactions and stereospecific paths in intra- and intermolecular processes. The total energy of the system composed of the internal, potential, and kinetic energy[27]. the total energy (absolute values) for compounds are S4> S3> S2> S1.

Dipole Moment: The dipole moment (μ in Debye) is another important electronic parameter used to describe the polarity of the molecule. This parameter that helps in the understanding of interaction between atoms in the same or different molecules dipole moment increases with the increase in electronegativity of atoms. Also is related to the distribution of electrons in a molecule. The dipole moment (μ in Debye) for compounds are S2 > S4> S1> S3. Chemical reactivity usually increases with the increase in dipole moment as well as attractive for the interaction with other systems and to form complexes, from Table 1 that, the dipole moment has maximum values for compound (S2) compared with compounds (S1, S3, S4). The high dipole moment may make the compound (S2) attract other systems to interact, to form complexes, and to indicate highly polar molecules.[28-29].

HOMO-LUMO Energy Gap: The electron distribution for the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO and LUMO energy gaps (ΔE) for compounds (S1, S2, S3, and S4) are depicted in figure3.The even values of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, while HOMO as an electron donor represents the ability to donate an electron. The smaller the LUMO, HOMO and energy gaps are the easier is it for the HOMO electrons to be excited; the higher the HOMO energies, the easier it is for HOMO to donate electrons; the lower the LUMO energies are the easier is it for LUMO to accept electrons. So from the energies band gaps it results that the stabilities of compounds are (S4> S3> S2> S1). Compounds (R1&R2) with a small HOMO-LUMO gap and A large HOMO–LUMO gap implies a high kinetic stability and low chemical reactivity, because it is energetically unfavorable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO. Generally it is said that low Egap leads to red shift remarkably by lowering the LUMO energy level [30-32].

Photovoltaic Properties

Here, we studied the photovoltaic properties of the all studied compounds as donor blended with TiO_2 which is used as an acceptor in solar cell devices. To elucidate the parameters that influence the photovoltaic efficiency toward better understanding of the structure–property relationships. The presented study of structural, electronic and optical properties for these compounds could help to design more efficient functional photovoltaic organic materials. The conjugated linker in a D–π–A system acts as both a component for light harvesting and a channel for charge transport. A good conjugated linker should promote the absorption of light over a wide region, and at the same time, facilitate charge transfer. The pyrrole unit is an appealing class of conjugated linker used in photovoltaic cells. It provides effective conjugation without affecting of the stability. In this model in hand present itself as D–π–A system with an blend (alkyl chain substituted by C, O, N and S) as donor and pyrrole as π –spacer (π –conjugated) while carboxylic – as acceptor (an anchoring group)as well as TiO_2 as surface of the conduction band, as application of intermolecular charge transfer (ICT). The ICT property of a D–π–A dye is strongly dependent on the electron-donating ability of D, the electron-withdrawing ability of A, as well as the electronic characteristic of the π-conjugated bridge. It can be tuned through chemical modification of each component. The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. In these compounds, the HOMO is mainly localized on the pyrrole and electron donating ligands, and the

LUMO is mainly distributed over the carboxylic (Figure 4). The distribution of LUMO and HOMO is favorable for efficient electron injection into TiO_2 via chemical bonding. Our strategy for designing solar cell analogues with reduced band gaps was based upon the observation that the HOMO in all compounds has slight change from compound S1 to S4, with high HOMO on the sulfur heteroatom, whilst the LUMO has minor slight changed on contribution on the heteroatom. We thereby reasoned that replacement of sulfur by another atom (C, O, N) have a good influence on the HOMO energy level which would primarily result from the small difference in electronegativity between sulfur and another atom (C, O, N) . The band gap of S4 is much smaller than that of the other substituted compounds. This may be attributed to the number of electron attracting sulfur atom which put in side groups, and also the resonance effect tends to confine the π-electrons within the pyrrole ring and hence to prevent their delocalization along the whole conjugated chain and leads to the destabilisation of both the HOMO level and LUMO levels with decrease in the energy gap, another concepts to the small energy gap is the relative distance between the donor alkyl chain substituted, (π-pyrrole) and (carboxylic)acceptor which responsible for the strongest localized contribution to the population transfer is the LUMO orbital of the donor[33-35]. Table 1, show the change of the electron-donor a great effect on the HOMO and LUMO levels.

Open-Circuit Voltage (Voc).

Generally energy gap more than 0.2 eV between the LUMO of the organic molecules and the conduction band of the TiO_2 is necessary for effective electron injection [36].As well as the experiment phenomenon was quite consistent with previous literature [37], which reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the LUMO level of PCBM (acceptor was reported to be between−3.47 eV, PCBM C70 -3.54 eV, PCBM C78-D3 -4.0 eV, table2[38] As it's known, the most efficient organic solar cells are based on the bulk heterojunction (BHJ) structure of the blend of organic material donors and fullerene derivative acceptors (PCBM) (open circuit voltage, Voc) is the maximum voltage that can be generated by the device. Although Voc is an important criterion with which we can estimate the efficiency of composite (donor/PCBM), we must take into account the difference between the LUMO of conjugated-π compound donor and those of (PCBM) acceptor noticed α gap. This is an indicator for optimization of the open circuit voltage (Voc), which should be maximal for efficiency of solar cells. Maximizing the open-circuit voltage in a low-bandgap compound is one of the critical factors towards enabling high-efficiency solar cells so that from table 1, the Maximizing the open-circuit voltage was the molecule S1 blended with C78-D3. which mean to increase of power conversion efficiency for solar cell. The theoretical values of Voc were calculated from the following expression:

$$\mathbf{Voc} = \left| \mathbf{E_{HOMO}\ (Donor)} \right| - \left| \mathbf{E_{LUMO}\ (Acceptor)} \right| - \mathbf{0.3} \quad (1)$$

$$\alpha = \left| \mathbf{E_{LUMO}\ (Acceptor)} \right| - \left| \mathbf{E_{LUMO}\ (Donor)} \right| \quad (2)$$

The maximum open circuit voltage of the Bulk Hetero Junction solar cell is related to the difference between the HOMO of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation. knowing that in organic solar cells, the Voc is considered linearly as a function of the HOMO level and the donor level of the LUMO of the acceptor. The obtained values of Voc of the studied molecules calculated according to the equation (1) (table 1) these values are sufficient for a possible efficient electron injection. Therefore, all the studied can be used as sensitizers because electron injection process from the exited molecule to the condition band of PCBM and subsequent regeneration is possible in sensitized solar cells. It can also be found that, the HOMO and LUMO energies of the studied compounds are slightly different. This implies that different structures play key roles on electronic properties and the effect of slight structural variations, especially the effect of the motifs branched to the molecule on the HOMO and LUMO energies is clearly seen[39-40].On the other hand the molecules of one anchoring system S1, S2, S3 and S4 ($-CH_2$-CO-OH-terminated) can be desorption on surface TiO_2 (layers) by mono anchoring and this lead to increase a sufficient crosslinking or coordination of the carboxylic groups molecules with TiO_2 surface to formation one substrate-CH_2-CO-O-TiO_2 surface and more stability. From energy gap value table 1, it can see the compound S4 have small energy gap more stability more coordination of the carboxylic groups molecules with TiO_2 surface and this also obviously from geometry optimization.

Table 1. The Total Energy, Dipole moment(μ), E_{HOMO}, E_{LUMO}, Energy Gap (eV), of (S1,S2,S3 and S4) Obtained by B3LYP/ DZV(d).

Co	$T_{E\ a.u}$	$(\mu)_{D.M}$	E_{LUMO} eV	E_{HOMO} eV	ΔE
S1	-713.34501	1.622811	-0.307491	-5.578378	5.27088
S2	-729.37607	2.074038	-0.329260	-5.657291	5.32803
S3	-749.25059	1.576536	-0.321096	-5.502185	5.18108
S4	-1072.2131	2.011611	-0.394568	-5.382454	4.98788

Table 2. The PCBM (C60, C70, C78-D3),the Voc (ev) and α gap

Co	PCBM C60 LUMO −3.47 eV		PCBM C70		PCBM C78-D3	
	Voc	α	Voc	A	Voc	α
S1	3.0925	3.3925	2.93250	3.2325	3.3925	3.6925
S2	3.0707	3.3707	2.91074	3.2107	3.3707	3.6707
S3	3.0789	3.3789	2.91890	3.2189	3.3789	3.6789
S4	3.0054	3.3054	2.84543	3.1454	3.3054	3.6054

The variation of Voc of the compound understudy as a function of HOMO level is shown in figure 3. It can be seen that in general Voc of compounds varies inversely with HOMO level of the electron donor material[41].

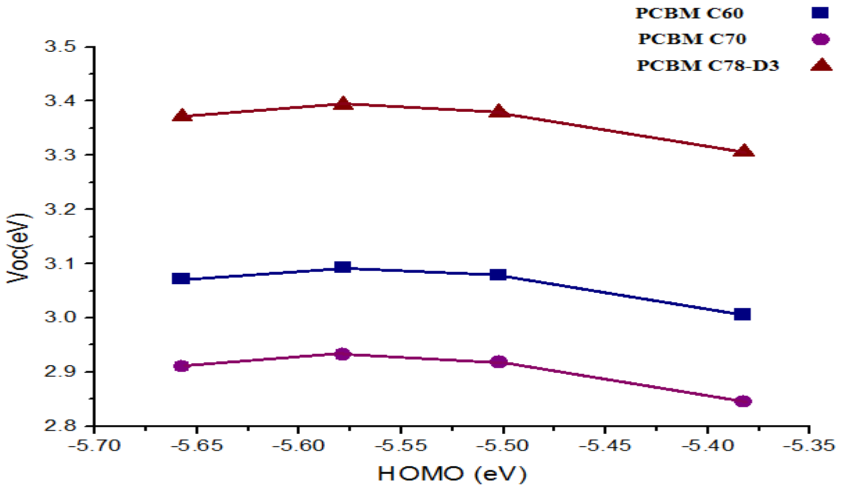


Figure 3. Plots of the Open-circuit voltage distribution versus the HOMO energy levels

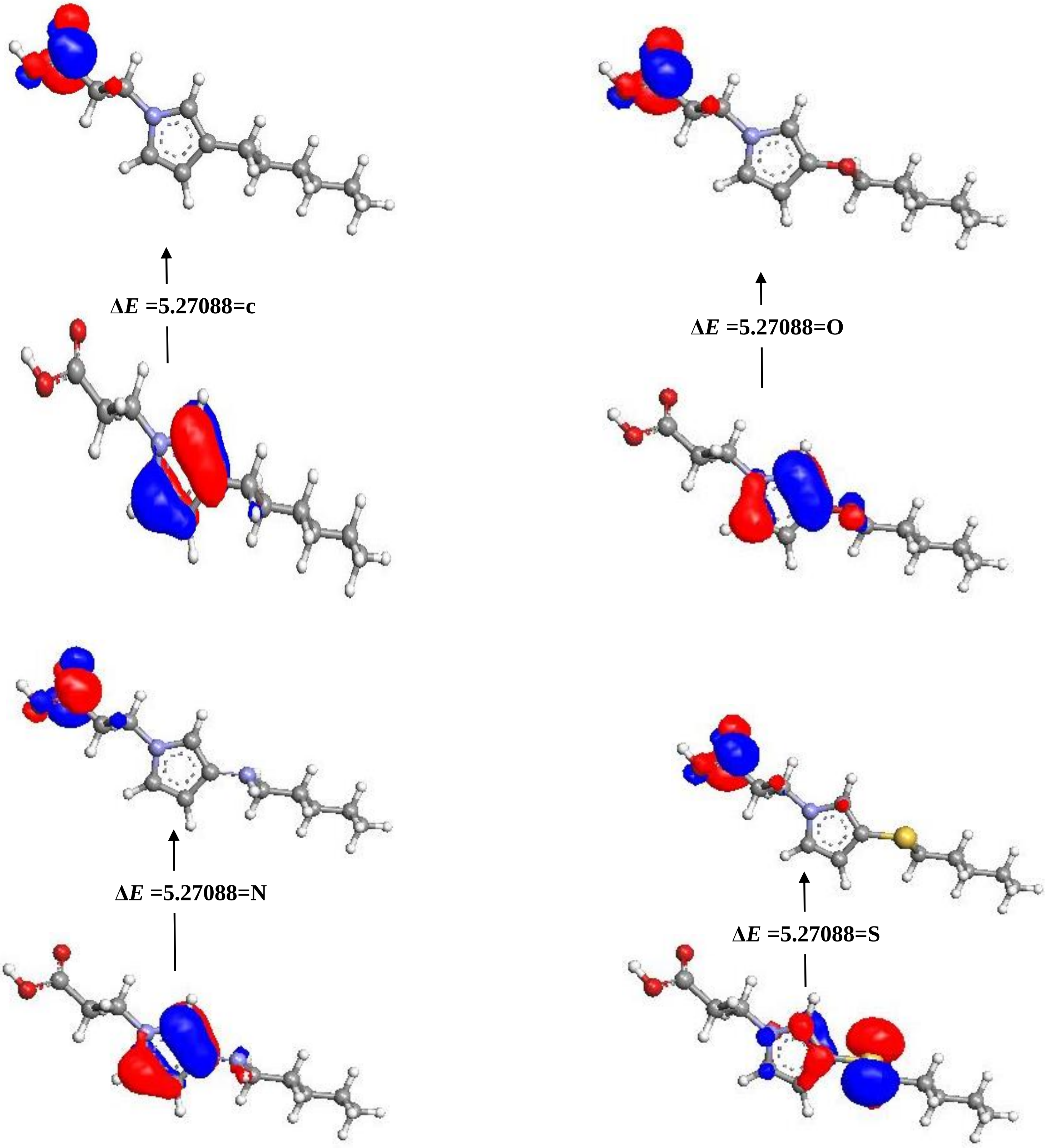


Figure 4. Electronic Distribution in HOMO and LUMO Orbitals.

On the other hand the bond length between the Donor moieties and π-spacer is very important for loading and transfer charge between the donor and acceptor group in the device solar cells. The bond lengths and angles for compounds are listed in Table 3; As shown, there are slight changes in the bond lengths and angles of compounds, like the changes of the bond length and angles in the ring indicate the presence of -conjugation which causes of the electrostatic attraction between atoms. As well as when the replacing the carbon atom by atoms oxygen and nitrogen in the bond (1-2), this lead to short the bond while when replacing carbon by silver lead to increase in the bond distance (be week), also this happen to the bond (1-18).Also the effect of substitution on the ring leads to redistribution of electron cloud in the ring of the compounds (S1, S2, S3, and S4)[42-45]. These results show that the connection between donor moieties (D) via π-bridge (pyrrole) is crucial which enhance the (ICT) character .

Table 3: Selected Structural Parameters of The Optimized Compounds, Bond Distance(A°) and Bond Angles(°) Obtained By B3LYP/DZV(d).

	Compounds			
Bond/Angle	**S1**	**S2**	**S3n**	**S4**
(1-2)	**1.533**	**1.430**	**1.431**	**1.830**
(1-18)	**1.494**	**1.368**	**1.431**	**1.762**
(18-19)	**1.380**	**1.431**	**1.469**	**1.428**
(18-21)	**1.425**	**1.385**	**1.431**	**1.383**
(19-20)	**1.386**	**1.381**	**1.383**	**1.384**
(20-22)	**1.381**	**1.378**	**1.382**	**1.378**
(22-21)	**1.381**	**1.387**	**1.381**	**1.456**
(2-1-18)	**111.5**	**113.7**	**113.3**	**101.0**
(1-18-19)	**125.8**	**127.5**	**128.3**	**127.5**
(1-18-21)	**127.0**	**124.3**	**124.6**	**125.2**

we study the relationship between adsorption geometry and electron injection properties of one of the most successful metal-organic, on the TiO_2 (111) surface(the most commonly used DSSC semiconductor). We systematically construct all possible adsorption configurations of the (S1, S2, S3, and S4) molecule (bidentate) on this surface by connected to TiO_2 through the carboxylic acid.. we find that a large number of adsorption configurations are possible – more than ten structures, with one(anchoring group carboxylic groups (bidentate)adsorbed on the TiO_2 (111) surface.

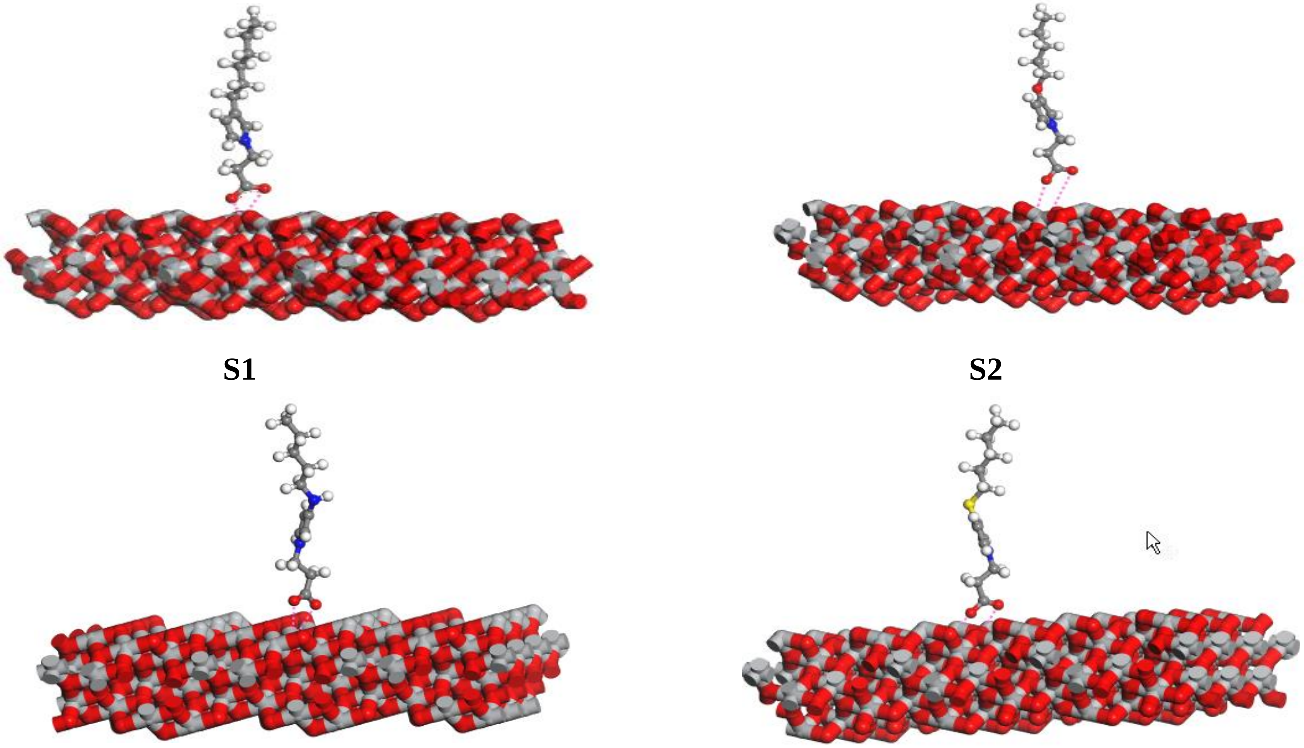
In this computational work the Monte Carlo simulation techniques is used to find the preferential adsorption sites on the TiO_2 surface by finding the low-energy adsorption sites on the TiO_2 surface(111) Molecular mechanics (force field) tools are used to investigate the simulated adsorption system[17].

Geometry optimization was achieved using COMPASS force field and the Smart minimize method by high-convergence criteria. This was followed by modelling the molecular electronic structures, including the distribution of frontier molecular orbitals and Fukui indices to establish the active sites as well as the local reactivity of the molecules. This computational study aims to find low-energy adsorption sites to investigate the preferential adsorption of molecule on TiO_2 surface aiming to find a relation between the effect of its molecular structure and its compounds efficiency.

Table 4: The output and descriptors calculated by the Monte Carlo simulation of compounds confirmations on TiO_2 (111) surface.

Co.	Total Energy	Adsorption Energy	Rigid Adsorption Energy	Deformation Energy	dE_{ad}/dN_i	Ti-O A^0
S1C	**-53.64188**	**-2.518391e+003**	**-46.477876**	**-2.471913e+003**	**-2.518391e+003**	**2.319**
S2O	**-48.70808**	**-2.577284e+003**	**-54.558436**	**-2.522726e+003**	**-2.577284e+003**	**3.637**
S3N	**-58.88136**	**-2.555580e+003**	**-65.263290**	**-2.490540e+003**	**-2.555803e+003**	**3.994**
S4S	**-64.74342**	**-2.537333e+003**	**-64.252604**	**-2.473081e+003**	**-2.537333e+003**	**3.921**

As seen in Table 4, The parameters presented in including total energy, in kcal mol^{-1}, of the substrate–adsorbate configuration[30]. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy and the deformation energy. In this study, the substrate energy (TiO_2 surface) is taken as zero. In addition, adsorption energy in kcal mol−1, reports energy released when the relaxed adsorbate on the substrate. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate 2 components[30]. The rigid adsorption energy reports the energy, in kcal mol^{-1}, released when the unrelaxed adsorbate components (i.e., before the geometry optimization step) are adsorbed on the substrate. The deformation energy reports the energy, in kcal mol , released when the adsorbed adsorbate components are relaxed on the substrate surface. Table4 shows also (dE /dNi), which reports the energy, in kcal mol^{-1} ads , of substrate–adsorbate configurations where one of the adsorbate components has been removed[46-50].



S1 **S2**

S3 **S4**

Figure 3. Most suitable configuration for adsorption in bridged bidentate (one anchoring groups) of compounds on TiO_2 surface substrate obtained.

As seen in table 4, the adsorption energy. Figure3, Table 4 shown the most suitable adsorption configurations for the oxygen compounds on TiO_2 . It can be seen from Table 4 that the values of adsorption energy for compounds are S2 > S3> S4> S1, the compounds and TiO2 surface are determined by the van der waals forces while the electrostatic energies are as the sum of the energies of the adsorbate components and the adsorption energy. The van der Waals interactions are dominant in adsorption of lone-pair electrons of oxygen on metal surfaces. Indicate that the adsorption energies between the oxygen in carboxylic functional group in compounds and TiO_2 surface are determined by the van der Waals forces. The electronegativity and the tow lone-pair of electron in oxygen lead to get high value of adsorption energy for compound S2 (containing oxygen group) is related to the distribution of electrons in a molecule and indicate that the oxygen compounds are likely to adsorb on the TiO_2 surface and form stable films to design organic solar cell system.

Conclusion

In this study, the quantum chemical investigation of the geometries and electronic properties of pyrrole substitutes(S1, S2, S3, S4 and S5), optimized geometric structures, dipole moments, total energies, the HOMO, LUMO and also the energy band gap (ΔE) calculation have been investigated after total optimization by B3LYP/DZV(d). This study is a theoretical analysis of the geometries and optoelectronic properties which displays the effect of substituted groups on the structural and optoelectronic properties of these materials and leads to the possibility to suggest these materials for organic solar cells application. The concluding remarks are:

1-The results of the optimized structures for all studied compounds show that they have similar conformations. We found that the modification of several groups does change the geometric parameters.
(bond lengths and angles)of compounds, indicate the presence of -conjugation which causes of the electrostatic attraction between atoms. And this leads to redistribution of electron cloud in the ring of the compounds (S1, S2, S3, and S4)

2- The calculated frontier orbital energy HOMO and LUMO and energy gap showed that the energy gap of the studied molecules differ slightly from 5.27088 to 4.98788 depending on the different structures. Depend on the energies band gaps, the stabilities of compounds are (S4> S3> S2> S1). Compounds (S4) with a small HOMO-LUMO gap and A large HOMO–LUMO gap implies a high kinetic stability and low chemical reactivity.

3-The donor moieties improve the electronic properties of the studied molecules by reducing the energy gap, making them more conductive systems. also improves the charge transfer along the molecular chain. So that the best reducing of band gap (favorable state) was compound S4.

4- The best values of Voc are indicated for the studied compounds blended with C60, C70 or C78-D3,and higher value are given for molecule S1 blended with C78-D3. which mean to increase of power conversion efficiency for solar cell.

5-Values of Voc of the studied molecules calculated range from 2.845 eV to 3.392 eV these values are sufficient for a possible efficient electron injection. Therefore, all the studied can be used as sensitizers because electron injection process.

This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Finally, the procedures of theoretical calculations can be employed to predict the electronic properties on the other compounds, and further to design novel materials for organic solar cell.

6- Monte Carlo simulation studies help to find the most stable conformation and adsorption sites for a broad range of materials, The results indicated that the studied compounds could adsorb onto TiO_2 surface by the van der Waals force, and The high value of adsorption energy for compound S2.

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تصميم جزيئي وهندسي والاستقراية لمعوضات البايرول, دراسة باستخدام نظرية دالة الكثافة الالكترونية كنظام للخلايا الشمسية العضوية (نظام احادي الرسو)

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