New molecules for organic photovoltaic and solar cell applications based on N-(7-imidazolyl) -aryl sulfonamides : DFT / TD-DFT study

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Abstract

In the present work, we used theoretical methods density functional theory DFT and base set B3LYP/6-31G (d) to calculate the electronic properties of the five molecules based on N-(7-imidazolyl) -aryl sulfonamides. Some of these parameters are very interesting in the photovoltaic field, such as, energies of HOMO (E_{HOMO}), Energies of LUMO (E_{LUMO}) and Egap. On the other hand, we explored our results in the determination of electronic and spectroscopic properties of these organic molecules through the use of TD-DFT and base B3LYP/6-31G (d), indeed the object was to determine the molecules wavelengths, trace the visible, ultra-violet spectrum and determine the transition states. The established results and the elaborated properties shows that these molecules would be so efficient in the photovoltaic field.

1. Introduction

More recently, due to the interest in photo electronic [1-2], optoelectronic [3] and photochemical [4] characteristics, materials containing particular organic compounds, these fields have been designated as ones of more interesting studies [5].

These components, which are based on organic or conjugated compounds and have important and very interesting electronic and photovoltaic characteristics, are used in several applications [5] such as batteries [6], photovoltaic cells [7- 8], as well as field effect transistors [9].

Furthermore, in current technology, the synthesis of organic compounds with particular characteristics plays an essential role in the photovoltaic sector in particular, for understanding the link between electronic characteristics and molecular structure in order to find new components with interesting properties. [10-11]

Indeed, researchers in the photovoltaic sector have worked recently, on the synthesis and design of new organic compounds with narrow frequency bands and have established the relationships between the branching of molecules or the nature of donor groups in the molecule, the performance properties and photoelectric properties [12-13]. The electron donor molecules contain π electrons which can effect a π-π * transition [14-15] by absorbing the photons emitted between the HOMO and LUMO orbits. N-(7-indazolyl) -arylsulfonamides are very important compounds in many fields, their specific physical,

chemical and spectroscopic absorption and emission characteristics make them suitable for use in optoelectronics and in solar cell applications because of their high absorption in the excited state in the long term [15-16].

We used the theoretical method DFT in this work and on the five molecules of N-(7-indazolyl)-arylsulfonamide derivatives named P1, P2, P3, P4 and P5[17], we determined the electronic and photo electronic properties of these studied molecules (fig 1) in order to demonstrate the utility of these molecules in the photovoltaic field [15]. In general, for calculating its electronic and photo electronic properties, we used the DFT with base set 3-61(d) G.

In this paper, the values of the electronic and photo electronic properties have been determined by using the DFT and TD-DFT: B3LYP/6-31G (d) method. DFT to compute the electronic values and to optimize the geometry of the molecular structure and TD-DFT to examine the states of the transitions as well as the UV spectrum and photo electronic characteristics; for example, wavelength and excitation energy.
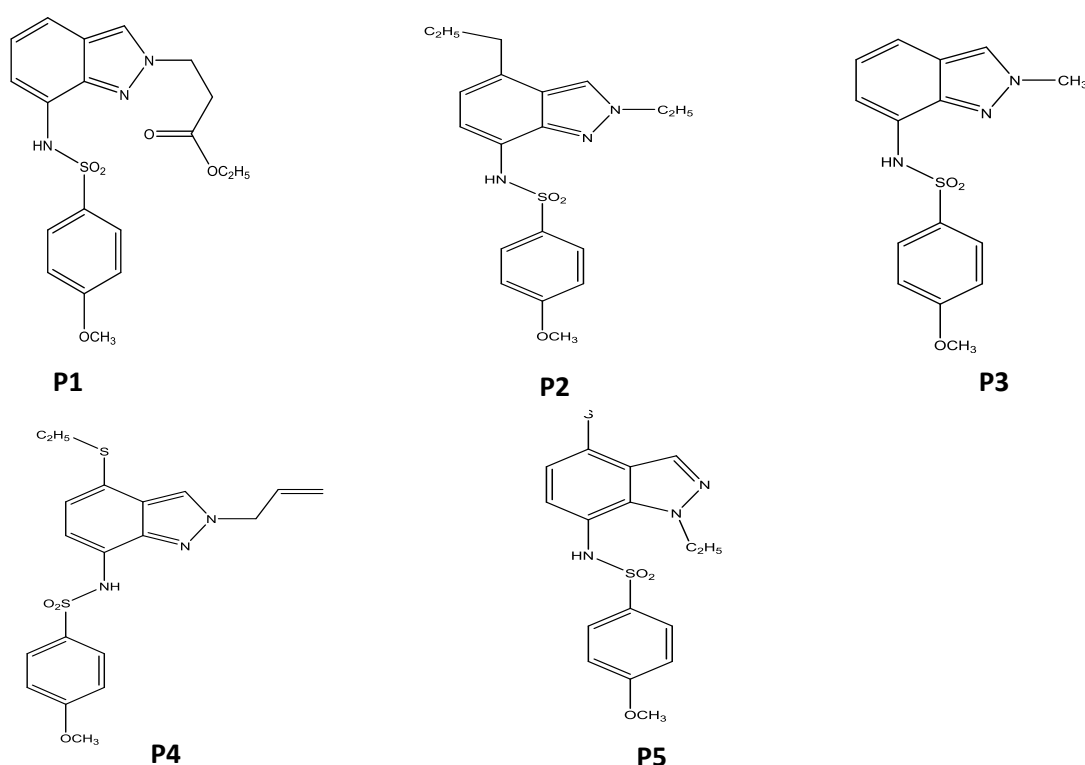

P1   **P2**   **P3**

P4   **P5**

Figure 1: Studied compounds P1; P2; P3; P4 and P5

2. Material and Methods

The properties and structural descriptors of the molecules have been calculated using Gaussian software [18] , through the density theory method (DFT) [19] with the function of the three parameters of Becke and the function of Lee Yang-Parr (B3LYP) [20 - 21] associated with 6-31G(d). this method has been applied to optimize the molecule geometry in the fundamental state, it has also been used to determine the minimum energies, Energies of HOMO; Energies of LUMO, and the Gap energies for molecules[22].

Electronic and photovoltaic parameters such as oscillator forces (OS) and optical transitions were calculated using the density-time functional theory (TD-DFT) [23]combined with the B3LYP/6-31 G (d). We were also able to establish and trace the ultraviolet absorption spectra of the studied molecules using GaussView software[24]. This method was essentially the same used in a previous work [25].

3. Results and discussion

3.1. Organic compounds optimization

To understand its electronic behaviour, we apply the analytic study of the charge distribution on the frontier orbital (FMO) of organic molecule, in particular the separate charge between the occupied and virtual orbitals to provide reasonably qualitative indication during the process of excitation[26] . We represent below the optimal geometry of the studied compounds (Fig. 2) by method DFT with GaussView software.

E_{HOMO}, E_{LUMO} and Band gap energies calculated by B3LYP/6-31(d) G are represented in Table 1. The energy gap (E_{gap}) was evaluated theoretically as the difference between the HUMO and LOMO levels. E_{HOMO} and E_{LUMO} of organic molecules are very important to limit and determine the way of charge transfer that was found between the acceptors and donors of the molecules. In table 1: the values of the energy levels HOMO of the molecules are: -5.29;-5.08;-5.50;-5.81 and -5.42 of P1 to P6 respectively, and while values of ELUMO are -0.89;-0.85;-1.66;-1.09;-1.22 respectively for the same molecules, P1 to P5. We observe that the LUMO energies of the tested molecules are larger than ITO which equals (-4.7 ev), Thus, the excited state molecules have a strong ability to inject electrons into the ITO electrodes [19].   On one hand, the energies of gap of all compounds range from 4.72 eV to -3.84 eV in the following order: P3<P5 <P2< P1< P4. Comparing with the P4 molecule, there is a destabilization of the HOMO energy and a stabilization of the LUMO energy levels.
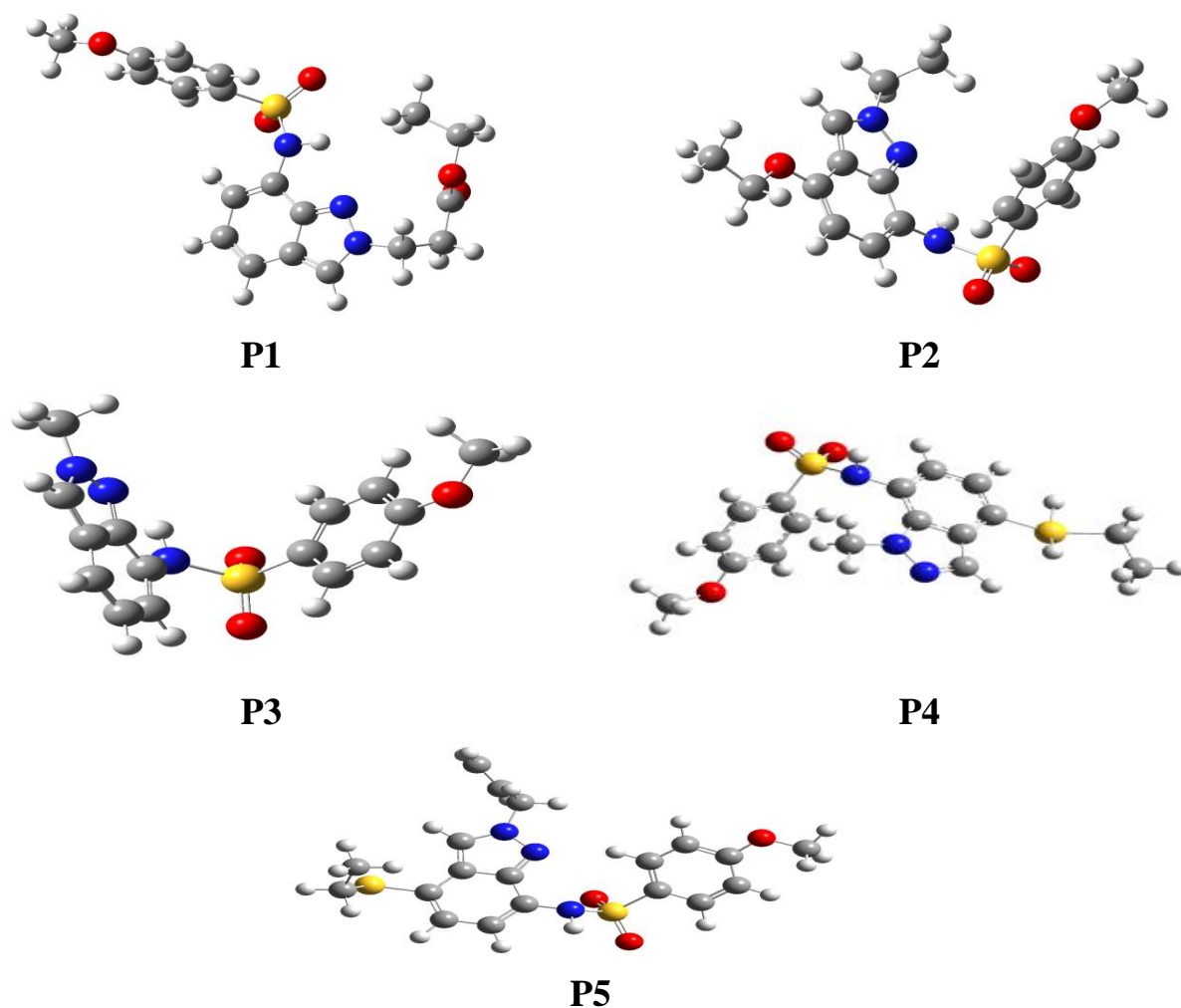
P1

P2

P3

P4

P5

Figure 2: The optimized geometrical structures of the studied molecules.

On the other hand, we evaluated the possibility of the electron transfer from the LUMO levels or the studied compounds in the excited state to LUMO of the acceptor [6.6]-phenyl-C61-butyric acid

methyl ester (PCBM) or to conduction band TiO2 (Titanium dioxide). In order to compare their LUMO levels with the PCBM's LUMO and the TiO2 conduction band in which we use butyric acid methyl ester (PCBM) or the TiO2 band conduction in (Fig. 3).
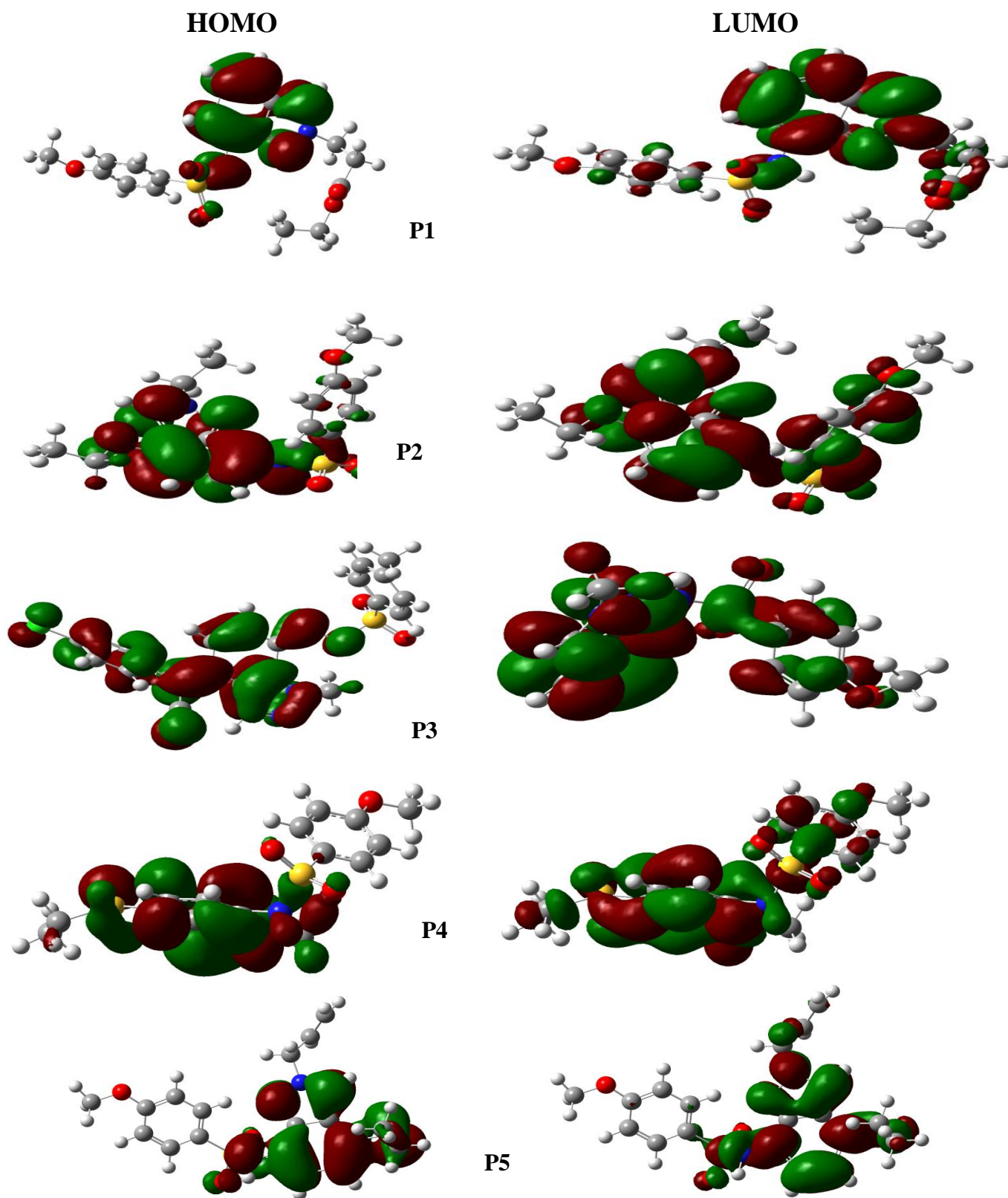
HOMO   **LUMO**

Figure 3: The contour plots of HOMO and LUMO orbitals of the studied compounds

We note that the LUMOs levels of all dyes are higher than PCBM one (_3.7 eV), [27] as far as the conduction band of semiconductor TiO2 (_3.9 eV) [28]. We can see a good electron injection from these dyes to the acceptors PCBM and TiO2, indicating that these dyes may be good candidates for application in photovoltaic devices.

Table1: The E_{HOMO}, E_{LUMO} and Egap obtained by B3LYP/6-31(d)G of the studied molecules ..

Pi	HOMO (eV)	LUMO (eV)	Egap (eV)
P1	-5.29	-0.89	4.40
P2	-5.08	-0.85	4.24
P3	-5.50	-1.66	3.84
P4	-5.81	-1.09	4.72
P5	-5.42	-1.22	4.20

Among the very important parameters in the photovoltaic domain, we will find the maximum open circuit voltage (Voc) which is calculated theoretically by the difference between E_{HOMO} of the compounds and the E_{HUMO} of the electron acceptor [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) or to conduction band TiO$_2$ (Titanium dioxide), using the expressions below (1)[29][30][31]:

$$V_{OC} = \left|E_{HOMO}^{Donor}\right| - \left|E_{LUMO}^{acceptor}\right| - 0.3 \qquad \text{equation (1)}$$

Table 2 represents the values of Voc of the studied dyes calculated by equation (2). It ranges from 1.084 eV to 1.811 eV for PCBM, and from 0.884 eV to 1.611 eV for TiO2. Which means that the electron transfer will be easy from the studied compounds Pi to PCBM or TiO2. Furthermore, these values are sufficient to obtain the high efficient electron injection, then we calculated parameter ^aI for all the compounds Pi=1-5 by following equation (3) [32]:

$$^aI = E_{LUMO\,Pi=1-5} - E_{LUMO\,PCBM} \qquad \text{equation (2)}$$

The spatial tracing of the HOMO and LUMO distributions of the five organic molecules, which are analyzed theoretically by DFT method, is shown in Fig. 4. The molecules distribution is identical for all compounds whether for HOMO or LUMO, we can clearly observe a localized destructions on all molecules N-(7-imidazolyl) -aryl sulfonamides, except a part, which means that all the molecules represent a strong electronic coupling ...
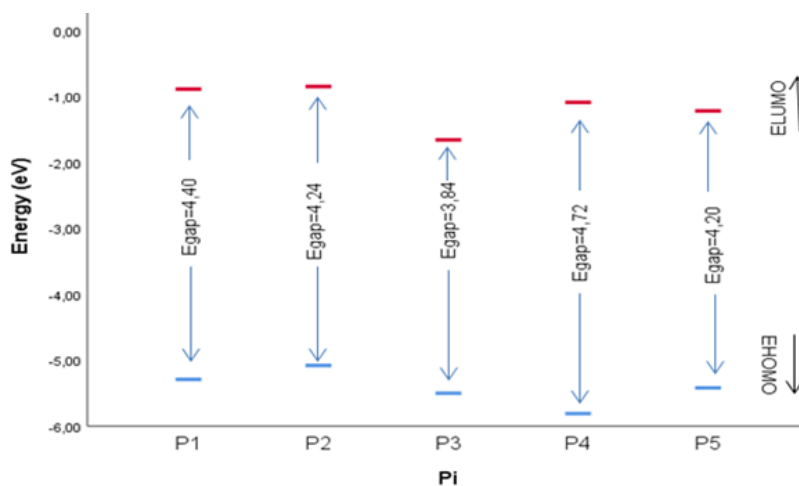

Figure 4: Energies of HOMO , Energies of LUMO and Egap of the studied molecules.

Pi	HOMO(eV)	LUMO(eV)	VOC (eV)		α_i/PCBM (eV)
			PCBM	**TIO2**	
P1	-5.292	-0.887	1.292	1.092	2.813
P2	-5.084	-0.846	1.084	0.884	3.054
P3	-5.367	-0.991	1.367	1.167	2.709
P4	-5.811	-1.094	1.811	1.611	2.606
P5	-5.419	-1.222	4.197	1.919	1.219
PCBM	-6.100	-3.200			
TIO2		-3.900			

3.2. Absorption proprieties

Table 3 shows that the E_{HOMO} values of all the compounds are much higher than that of the E_{HOMO} value of PCBM. the values of the open voltage (Voc) of the studied molecules are 1.292;1.084;1.367;1.811;1.419 for P1 to P5 respectively in the case of PCBM (Table 2), values are sufficient for possible efficient electron injection.

Table 2: Data absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31G (d) with Eex: Excitation energy; O.S: Oscillator strength.

	Electronic transitions	**∡abs (nm)**	**Eex (eV)**	**O.S (eV)**
P1	$S_0 \rightarrow S_1$	309.06	4.0116	0.0957
	$S_0 \rightarrow S_2$	302.29	4.1015	0.0859
	$S_0 \rightarrow S_3$	289.05	4.2893	0.0021
P2	$S_0 \rightarrow S_1$	325.68	3.8069	0.2203
	$S_0 \rightarrow S_2$	305.17	4.0628	0.0181
	$S_0 \rightarrow S_3$	293.51	4.2243	0.0143
P3	$S_0 \rightarrow S_1$	311.85	3.9758	0.1948
	$S_0 \rightarrow S_2$	289.04	4.2895	0.0171
	$S_0 \rightarrow S_3$	278.37	4.4539	0.0140
P4	$S_0 \rightarrow S_1$	294.51	4.2099	0.2396
	$S_0 \rightarrow S_2$	291.30	4.2562	0.0086
	$S_0 \rightarrow S_3$	277.82	4.4628	0.0040
P5	$S_0 \rightarrow S_1$	327.90	3.7812	0.2646
	$S_0 \rightarrow S_2$	293.18	4.2290	0.0531
	$S_0 \rightarrow S_3$	279.81	4.5827	0.0066

The contribution of the molecular boundary orbital (MO) is important in the determination of the separate charge states of the studied molecules (Table 3), since the relative order of the occupied and virtual orbitals provides a reasonable qualitative indication of the excitation properties as well as the capacitance.

The HOMO and LUMO energy levels are interesting for all studies molecules (Table 1). These are very important factors in determining charge transfer exists between donors and acceptors as the Egap. In this work we applied the DFT/6-31G (d) method to determine the electron and spectroscopic

properties by TD-DFT for all organic compounds, and to understand the influence of parameters on photovoltaic efficiency for a better understanding of structure-property relationships. In addition, from our theoretical results we can deduce that these molecules are useful in the photovoltaic application basing on the geometric, electronic and optical properties.

The absorption of a solar cell is essential for the application of a photovoltaic material from the optimized structure from the B3LYP / 6-31G(d) method; we calculated and plotted the UV-Vis spectra of P1;P2;P3;P4 and P5 using the TD-DFT method. The simulated UV-Vis absorption spectra are identical to the previous figure. (Fig 5). Based on TD–DFT theoretical method, (table 3) we found that wavelengths range from 291nm to 327 nm these values are 309.06 nm ; 325.68 nm ; 311.85 nm ; 294.51nm ; 327.90 nm respectively for P1 to P5. When it comes to the force of the scout (OS) values, we found : 0.0957 eV ; 0.220 eV; 0.1948 eV ; 0.2396 eV ; 0.2646 eV for the same molecules order, finally the excitation energy values are as follows 4.0116 eV;3.806 eV ;3.9758 eV;3.7812eV ;4.2099eV, always for the same order (P1;P2;P3;P4 and P5) are given in (table 3) .
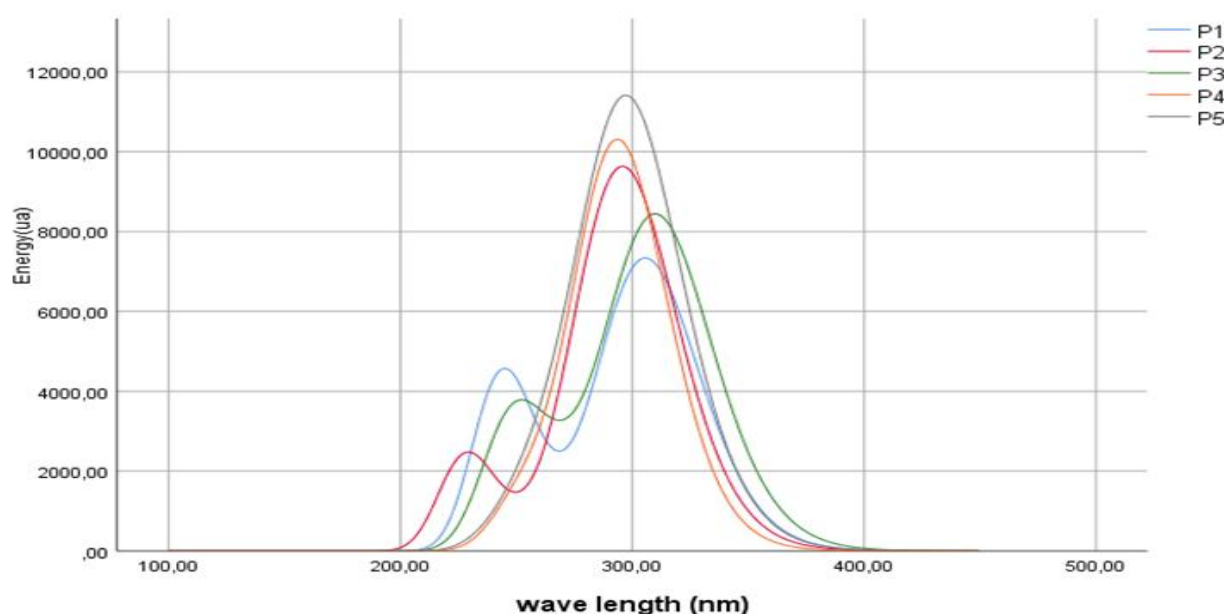

Figure 1: The absorption spectra ⊀max of the studied compounds

Conclusion

In this work, we were interested to use TD-DFT / B3 LYP method and the base set 6-31G (d) to study the theoretical analysis of the five organic molecules synthesize of N-(7-imidazolyl) -aryl sulfonamides: P1; P2; P3; P4; P5.

- The UV−Vis absorption properties have been obtained by TD/DFT calculations. The obtained absorption maximums are important in the range of 327 nm – 291nm.
- The calculated band gap Egap of the studied molecules was in the range of 4.492 eV to 5.008 eV as far as E_{HOMO} and E_{LUMO} energies.
- The calculated values of Voc of the studied molecules range from 1.479 eV to 2.092 eV in the case of PCBM. Moreover, it range from 1.279 eV to 1.892   eV in the case of TiO2.

The calculated theoretical liner is used to understand relationships between electrochemical properties and molecular structure; it can also be used to assume electronic properties of materials still in preparation and to design new materials for solar cells.

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