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## Electronic and photovoltaic properties of new materials based on 6-mono-substituted and 3,6-disubstituted acridines and their application to design novel materials for organic solar cells

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### ABSTRACT

The most research in new  $\pi$ -conjugated molecules with specific applications has become one of the interesting topics of the fields of chemical physics and materials science. The low band gap for these materials is one parameter influencing to enhancing the quality of device of the solar cells, so the control of this parameter for these materials is interesting. The knowledge the relationship between the electronic properties and molecular structure for these materials is very important to explore their suitability in electroluminescent devices. A theoretical study by using the DFT/6-31G (d) of several conjugated aromatic compounds based on 6-mono-substituted and 3,6-di-substituted acridines has been made in this work. The main objective is first to predict the HOMO, LUMO, Gap and energy  $V_{oc}$  (open circuit voltage) and then to study the possibility of application of these materials in the field of organic solar cells. The obtained values of the energy ( $E_{gap}$ ) range from 3.483 eV to 3.565 eV and those of the open-circuit voltage ( $V_{oc}$ ) range from 3.183 eV to 3.791 eV. The results show that the studied molecules can be used as BHJ solar cell and as sensitizers because the electron injection process from the molecule to the conduction band of fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is possible.

**Keywords:** Acridines, Organic solar cells, Conjugated molecules, Open-circuit voltage, DFT (B3LYP), low band gap.

### INTRODUCTION

Since their discovery, the organic materials based on conjugated molecules have attracted the interest of all scientists in the world this due to a result of their suitability in a broad range of much research leading to the growing interest in advanced electronic and photonic devices, as well as low-cost, large device densities, large-area fabrication of inexpensive, flexible and lightweight materials. These materials have exceptional properties optics and electronics for applications in microelectronics such as batteries, organic field-effect transistors (OFET), sensors, light-emitting diodes, photo-detectors and solar cells [1-3]. The synthesis the new organic materials with useful electronic properties always aim to enhance the devices electronics, this led a lot of scientists in the world to elucidate the further effect of ring substitution such as a variation of ring substituents on the relative photoconductivity. In this work we reported the theoretical analysis of the geometries and electronic properties of thirteen conjugated compounds based on 6-mono-substituted and 3,6-di-substituted acridines as shown in figure 1 ( $P_i$  ( $i= 1-13$ )), these compounds have already been synthesized by Di Giorgio [4], in which displays the effect of substituted groups on the structural and opto-electronic properties of these materials and leads to find potential sensitizers for use in organic solar cells. Acridines derivatives may exhibit large carrier mobility and excellent stability. Other theoretical study of Acridines derivatives has been reported in our previous work [5], and other works [6-7].

## MATERIALS AND METHODS

The quantum chemical investigation has been performed to the optical and electronic properties of these compounds. The 13 compounds are studied by using density functional theory (DFT) and time-dependent density functional theory (TD/DFT) with the aim to evidence the relationship between molecular structure and optoelectronic properties. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, Gap energy and  $V_{oc}$  (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as a good candidate for organic solar cells.

N°	R <sub>1</sub>	R <sub>2</sub>
P <sub>1</sub>	CH <sub>3</sub>	CH <sub>3</sub>
P <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
P <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>
P <sub>4</sub>		
P <sub>5</sub>		
P <sub>6</sub>		
P <sub>7</sub>		
P <sub>8</sub>		
P <sub>9</sub>		CH <sub>3</sub>
P <sub>10</sub>		CH <sub>3</sub>
P <sub>11</sub>		CH <sub>3</sub>
P <sub>12</sub>		CH <sub>3</sub>
P <sub>13</sub>		CH <sub>3</sub>

Figure 1: Chemical structure of studied compounds P<sub>i</sub> (i= 1–13)**Theoretical methodology**

DFT method of three-parameter compound of Becke (B3LYP) [8] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [9]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [10]. The geometry structures of neutral molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy  $E_{gap}$  is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the TD/DFT calculations on the fully optimized geometries [11].

## RESULTS

The results of the optimized structures (Figure.2) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the ring does not change the geometric parameters.

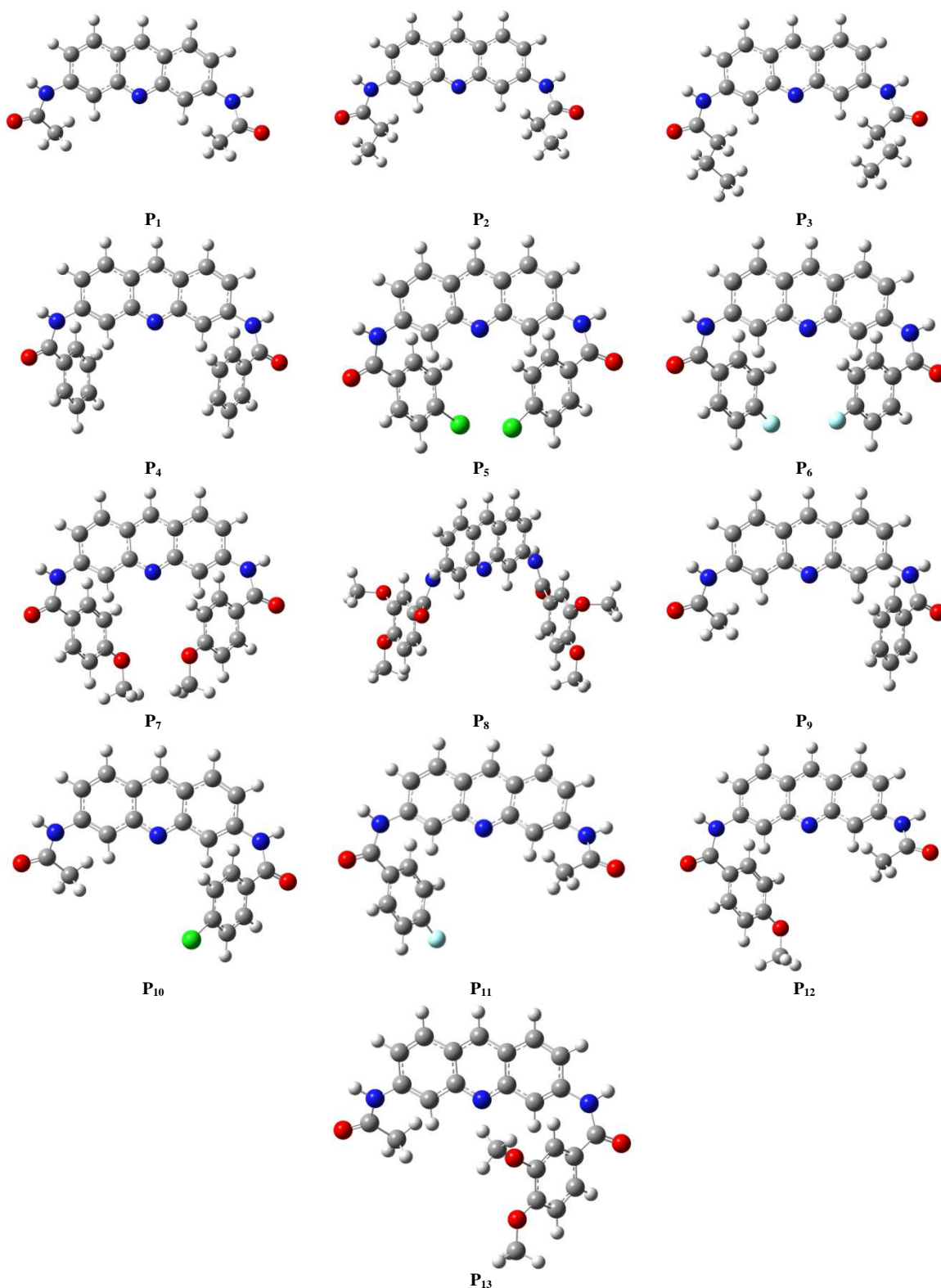


Figure 2: Optimized geometries obtained by B3LYP/6-31G (d) of the studied molecules

Table 1 lists the calculated frontier orbital energies and energy  $E_{\text{gap}}$  between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy  $E_{\text{gap}}$  of the studied molecules, also the open circuit voltage  $V_{\text{oc}}$  (eV) and  $\alpha = E_{\text{LUMO}}$  (Donor)  $- E_{\text{LUMO}}$  (Acceptor). These parameters will be discussed in the photovoltaic part.

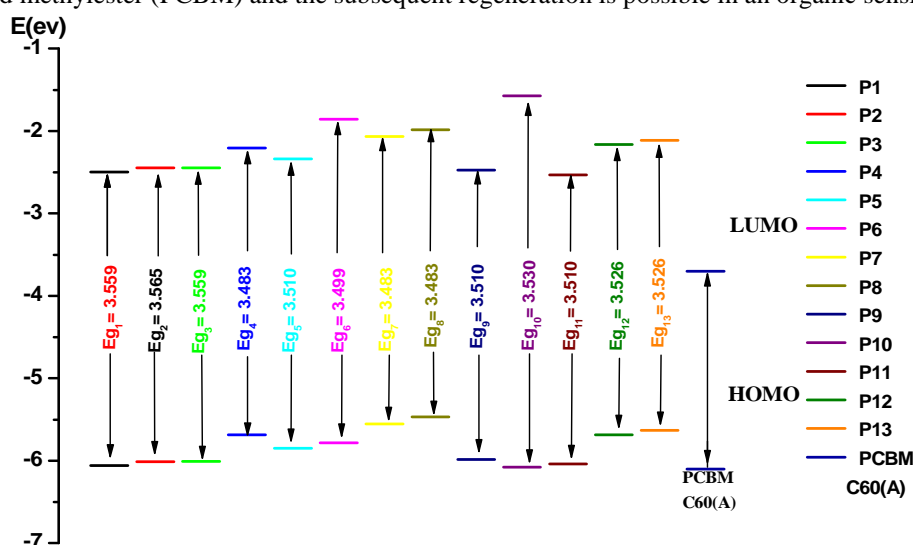
**Table 1: Energy values of  $E_{\text{LUMO}}$  (eV),  $E_{\text{HOMO}}$  (eV),  $E_{\text{gap}}$  (eV),  $\alpha$  (eV) and the open circuit voltage  $V_{\text{oc}}$  (eV) of the studied molecules obtained by B3LYP/6-31G (d)**

Compound	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)
P <sub>1</sub>	-6.06	-2.50	3.56	2.06	1.20
P <sub>2</sub>	-6.01	-2.45	3.56	2.01	1.25
P <sub>3</sub>	-6.01	-2.45	3.56	2.01	1.25
P <sub>4</sub>	-5.69	-2.20	3.48	1.69	1.50
P <sub>5</sub>	-5.85	-2.34	3.51	1.85	1.36
P <sub>6</sub>	-5.79	-2.29	3.50	1.79	1.41
P <sub>7</sub>	-5.55	-2.07	3.48	1.55	1.63
P <sub>8</sub>	-5.47	-1.99	3.48	1.47	1.71
P <sub>9</sub>	-5.99	-2.48	3.51	1.99	1.22
P <sub>10</sub>	-6.08	-2.55	3.53	2.08	1.15
P <sub>11</sub>	-6.04	-2.53	3.51	2.04	1.17
P <sub>12</sub>	-5.69	-2.16	3.53	1.69	1.54
P <sub>13</sub>	-5.63	-2.11	3.52	1.63	1.59
PCBM C <sub>60</sub> (A)	-6.10	-3.70	-	-	-

To study the photovoltaic properties and to evaluate the possibilities of electron transfer from the studied molecules to the conductive band of an acceptor (PCBM), the HOMO and LUMO levels are compared. As shown in table 1, the change of molecular structure affects greatly on the HOMO and LUMO levels. The experiment phenomenon is quite consistent with previous literature [12], 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 ( $V_{\text{oc}}$ ). As shown in Figure 3, both the HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. On the one hand, the HOMO levels of the studied compounds are higher than that of PCBM. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor [13]. The maximum open circuit voltage ( $V_{\text{oc}}$ ) of the organic solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the donor (our studied molecules) and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [14]. The theoretical values of open-circuit voltage  $V_{\text{oc}}$  have been calculated from the following expression:

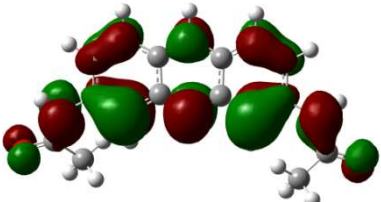
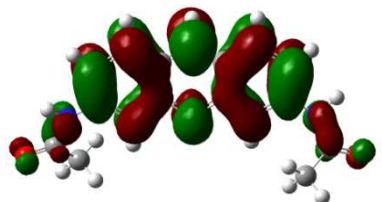
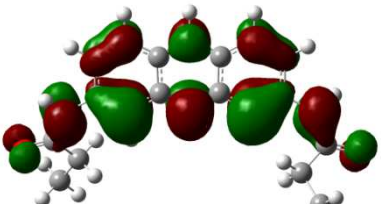
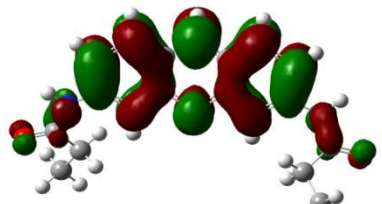
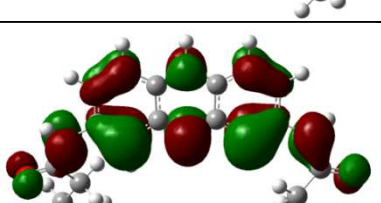
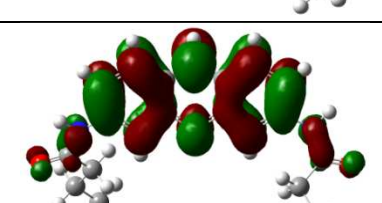
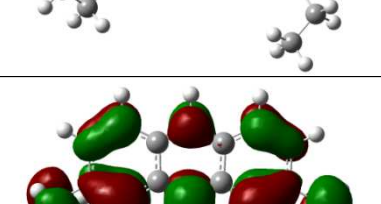
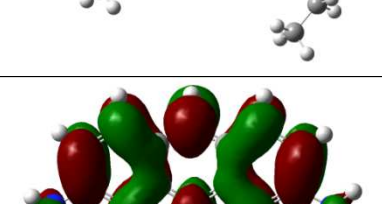
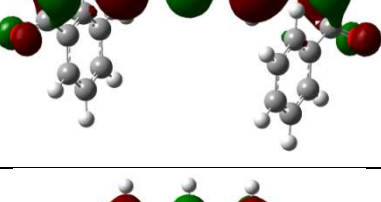
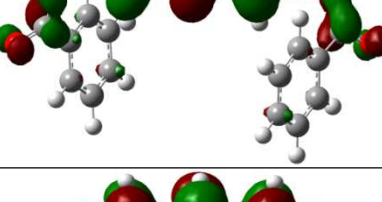
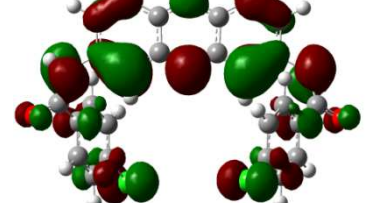
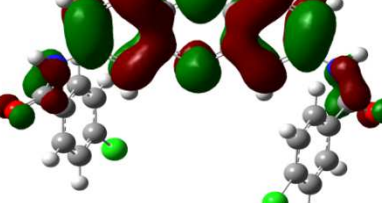
$$V_{\text{oc}} = |E_{\text{HOMO}} (\text{Donor})| - |E_{\text{LUMO}} (\text{Acceptor})| - 0.3 \quad (1)$$

The obtained values of  $V_{\text{oc}}$  of the studied molecules range from 3.18 eV to 3.79 eV, these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of fullerene derivative [6,6]-phenyl-C61-butyric acid methylester (PCBM) and the subsequent regeneration is possible in an organic sensitized solar cell.

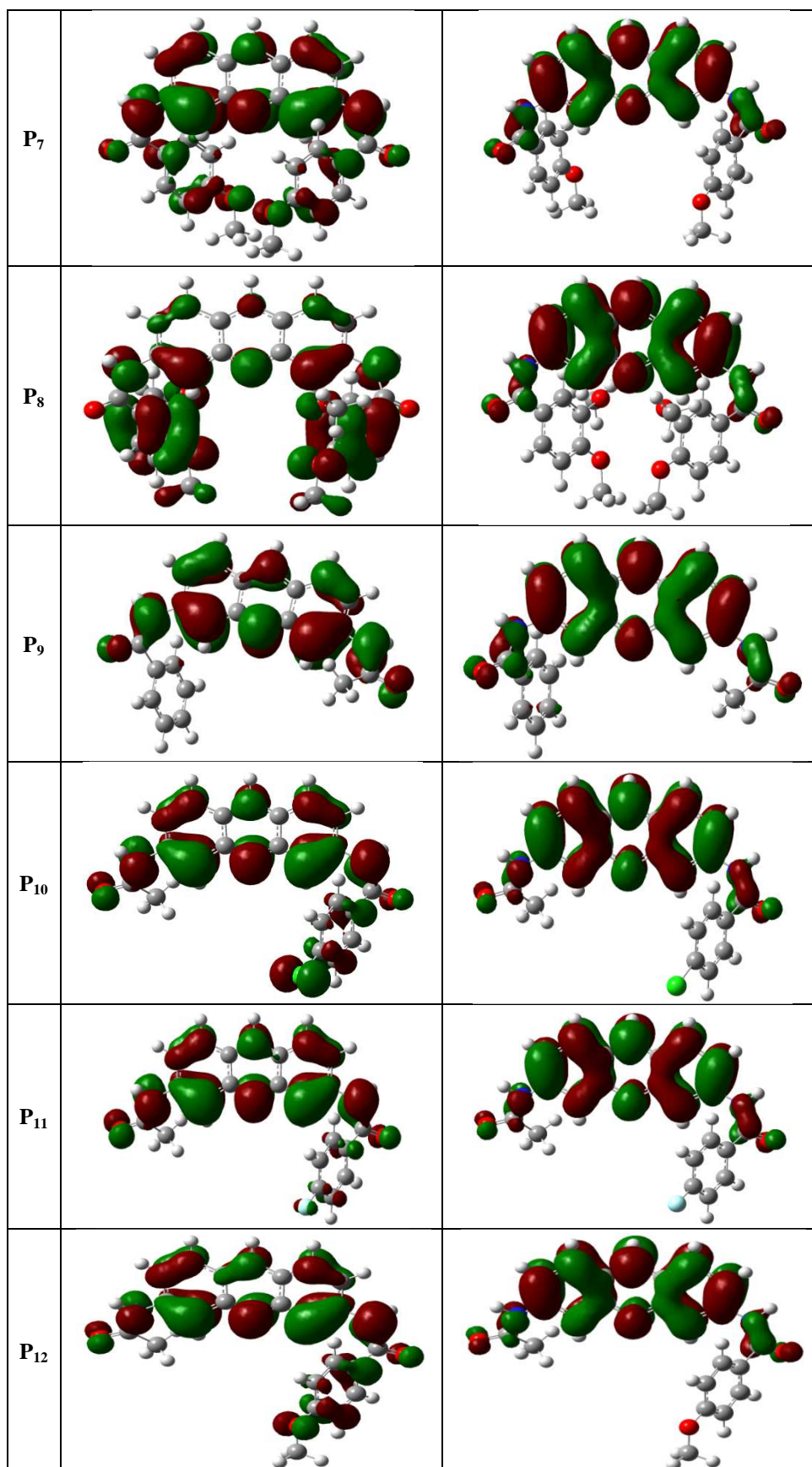


**Figure 3: Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules**

The frontier molecular orbital (MO) contribution is very important in determining the charge-separated states of the studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [15]. In general, as shown in figure 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a  $\pi$ -bonding character within subunit and a  $\pi$ -antibonding character between the consecutive subunits while the LUMOs possess a  $\pi$ -antibonding character within subunit and a  $\pi$ -bonding character between the subunits whereas it is the opposite in the case of doped forms.

N°	HOMO	LUMO
P <sub>1</sub>		
P <sub>2</sub>		
P <sub>3</sub>		
P <sub>4</sub>		
P <sub>5</sub>		
P <sub>6</sub>		





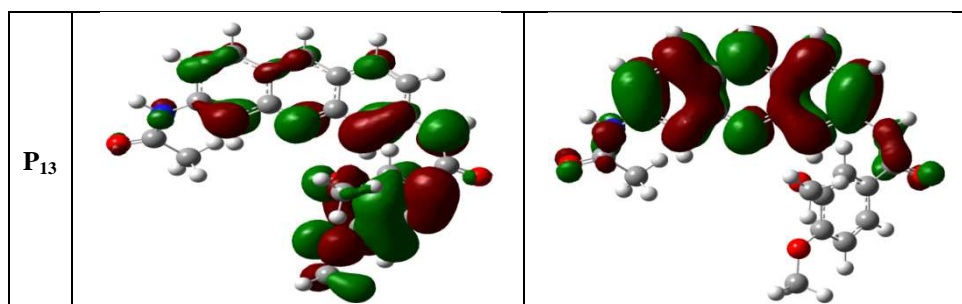


Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level

On the other hand and how the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material, and a good photovoltaic material should have broad and strong visible absorption characteristics. From the optimized structure obtained with the method B3LYP/6-31G (d) of each studied compound, we have calculated the UV-Vis spectra of the studied molecules  $P_i$  ( $i=1$  to 13) using TD-DFT method. The corresponding simulated UV-Vis absorption spectra of  $P_i$ , presented as oscillator strength against wavelength, are shown in Figure 5. As illustrated in table 2, we can find the values of calculated absorption  $\lambda_{\max}$  (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds  $P_i$ .

Table 2: Absorption spectra data obtained by TD-DFT methods for the  $P_i$  ( $i=1$  to 13) compounds at B3LYP/6-31G (d) optimized geometries

Compound	$\lambda$ (nm)	$E_{\text{activation}}$	O.S	MO/character
$P_1$	362.22	3.42	0.25	H-1 $\rightarrow$ LUMO (78%)
$P_2$	362.90	3.42	0.26	H-1 $\rightarrow$ LUMO (78%)
$P_3$	363.04	3.42	0.26	H-1 $\rightarrow$ LUMO (78%)
$P_4$	363.73	3.41	0.22	H-1 $\rightarrow$ LUMO (79%)
$P_5$	362.91	3.42	0.21	H-1 $\rightarrow$ LUMO (79%)
$P_6$	363.62	3.41	0.22	H-1 $\rightarrow$ LUMO (80%)
$P_7$	368.52	3.36	0.21	H-1 $\rightarrow$ LUMO (84%)
$P_8$	366.08	3.39	0.20	H-1 $\rightarrow$ LUMO (83%)
$P_9$	363.57	3.41	0.23	H-1 $\rightarrow$ LUMO (85%)
$P_{10}$	362.93	3.42	0.22	H-1 $\rightarrow$ LUMO (84%)
$P_{11}$	363.43	3.41	0.23	H-1 $\rightarrow$ LUMO (79%)
$P_{12}$	364.72	3.40	0.23	H-1 $\rightarrow$ LUMO (81%)
$P_{13}$	364.49	3.40	0.19	H-1 $\rightarrow$ LUMO (73%)

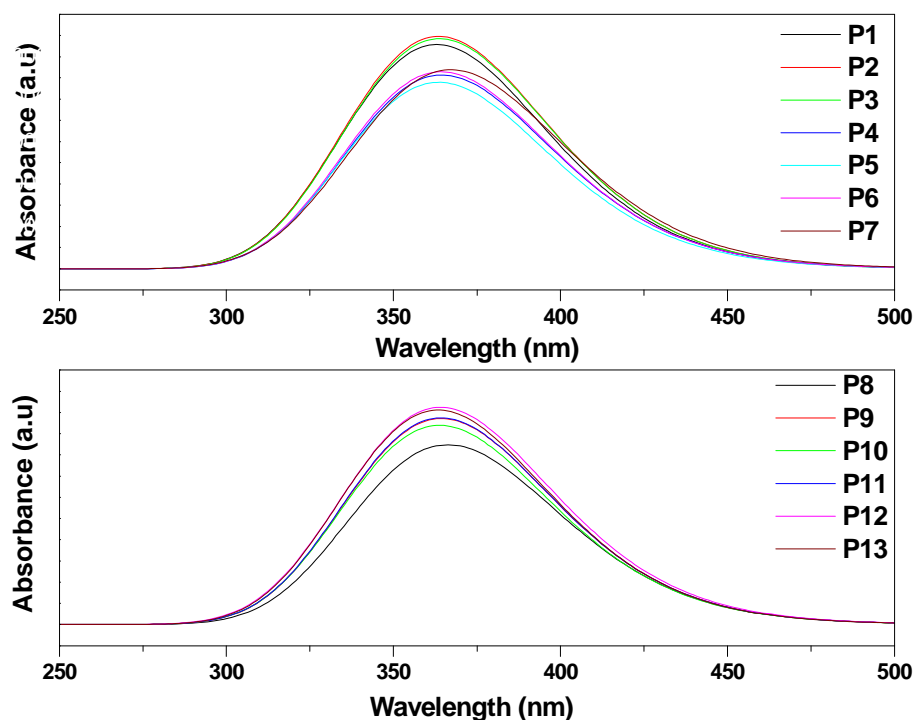


Figure 5: Simulated UV-visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d)

## DISCUSSION

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.

As shown in Table 1, The HOMO and LUMO energies of P<sub>1</sub> to P<sub>13</sub> change significantly, the LUMOs for P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>, P<sub>5</sub>, P<sub>6</sub>, P<sub>7</sub>, P<sub>8</sub>, P<sub>9</sub>, P<sub>10</sub>, P<sub>11</sub>, P<sub>12</sub> and P<sub>13</sub> are located at -2.50; -2.45; -2.45; -2.20; -2.34; -2.29; -2.07; -1.99; -2.48; -2.55; -2.53; -2.16 and -2.11 eV, respectively. The HOMOs for P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>, P<sub>5</sub>, P<sub>6</sub>, P<sub>7</sub>, P<sub>8</sub>, P<sub>9</sub>, P<sub>10</sub>, P<sub>11</sub>, P<sub>12</sub> and P<sub>13</sub> are located at -6.06; -6.01; -6.01; -5.69; -5.85; -5.79; -5.55; -5.47; -5.99; -6.08; -6.04; -5.69 and -5.63 eV, respectively.

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. In addition, energy ( $E_{\text{gap}}$ ) of the studied molecules differs slightly from 3.48 eV to 3.56 eV depending on the different structures. They are studied in the following order:

$$P_2 > P_1 > P_3 > P_{10} > P_{12} > P_{13} > P_5 > P_9 > P_{11} > P_6 > P_8 > P_7 > P_4$$

Data in table 2 shows that there is a bathochromic shift when passing from P<sub>7</sub> (368.52 nm) to P<sub>1</sub> (362.22 nm). This effect is obviously due to the aromaticity in the studied compounds. Those interesting points are seen both in the studying the electronic and absorption properties [16].

The calculated wavelength  $\lambda_{\text{abs}}$  of the studied compounds decreases in the following order P<sub>1</sub> > P<sub>2</sub> > P<sub>5</sub> > P<sub>10</sub> > P<sub>3</sub> > P<sub>11</sub> > P<sub>9</sub> > P<sub>6</sub> > P<sub>4</sub> > P<sub>13</sub> > P<sub>12</sub> > P<sub>8</sub> > P<sub>7</sub> which is the same order of the reduction of the acceptor strength. This bathochromic effect from P<sub>i</sub> is obviously due to increased  $\pi$  delocalization. This interesting point is seen both by analysing electronic and absorption results. Excitation to the S<sub>1</sub> state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from S<sub>0</sub>-S<sub>1</sub> electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in S<sub>0</sub>-S<sub>1</sub> electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

## CONCLUSION

In this study, the quantum chemical investigation on the geometries and electronic properties of various compound based on 6-mono-substituted and 3,6-di-substituted acridines which displays the effect of substituted groups on the structural and opto-electronic properties of these materials and leads to the possibility to suggest these materials for organic solar cells application. The concluding remarks are:

The results of the optimized structures for all studied compounds show that they have similar conformations (quasi planar conformation). We found that the modifications of several groups Donor or Acceptor does not change the geometric parameters.

The calculated frontier orbital energies HOMO and LUMO and energy  $E_{\text{gap}}$  showed that the energy  $E_{\text{gap}}$  of the studied molecules differ slightly from 3.48 eV to 3.57 eV depending on the different structures. Also we can remark that the energy ( $E_{\text{gap}}$ ) decreases, this is probably due to the effect of the conjugated system and aromaticity in the compounds studied.

The gap energy  $E_{\text{gap}}$  of P<sub>4</sub> is much smaller than that of the other compounds.

The Molecule P<sub>7</sub> witch have a relatively high value of  $\lambda_{\text{max}}$  (absorption), is expected to have the most outstanding photo physical properties.

All the studied molecules can be used as BHJ solar cell because the electron injection process from each studied molecule to the conduction band of PCBM and the subsequent regeneration are possible.

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 application. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved the other materials, and further to design novel materials for organic solar cells.



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