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Research Article

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New materials based on imidazo[4,5-b]pyridine derivatives candidates for optoelectronic device applications: Theoretical investigations

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ABSTRACT

In recent years, organic materials have attracted much attention for potential use in a variety of optic, electronic and optoelectronic applications. Generally, target functionalities and the performance of devices created with such organic compounds strongly depend on the order of the active species over a range of length scales. Since their discovery, materials based on organic π-conjugated molecules have good properties such as thermal and photochemical stability ad high charge mobility, which make them promising candidates for research on optoelectronic device technology, such as LEDS, Transistors (TFTs) and low-cost solar cells. In this work a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on. 20 imidazo[4,5-b]pyridine derivatives. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO and energy Gap of the studied compounds have been calculated and reported. These properties suggest these materials as good candidates for organic solar cells.

Keywords: π-Conjugated molecules, Organic solar cells, DFT, Low band-gap, Electronic properties, Open-circuit voltage.

INTRODUCTION

Imidazo[4,5-b]pyridine derivatives represent an interesting class of compounds that possesses a wide spectrum of biological activities. A large number of imidazo[4,5-b]pyridine derivatives containing ring systems exhibited antibacterial, antifungal, antitubercular, analgesic, anti-inflammatory, anticancer, anti-convulsant, anti-viral, insecticide and anti-depressant activities [1-4].

For a long time heterocyclic compounds have constituted one of the largest areas of research in organic chemistry. These compounds are of particular importance as they are associated with a wide variety of physiological activities with wide variety of heterocyclic systems known today [5]. The research in new pi-conjugated molecules with specific applications has become one of the most interesting topics in the fields of chemical physics and materials science.

The use of low band gap materials is a viable method for a better harvesting of the solar spectrum and an improved raise of its efficiency. The control of this parameter of these materials is a research issue of ongoing interest. In this work a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on. 20 imidazo[4,5-b]pyridine derivatives [6].

The theoretical ground-state geometry and electronic structure of the studied molecules were investigated by the DFT method at B3LYP level with 6-31G (d,p) basis set. The effects of the ring structure and the substituents on the geometries and electronic properties of these materials are discussed with the aim of revealing the relationship between molecular structure and optoelectronic properties [7]. In this study, theoretical analysis on the geometries and electronic properties of these new conjugated compounds based on imidazo[4,5-b]pyridine (A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10} and A_{20}) is reported, as shown in figure 1.

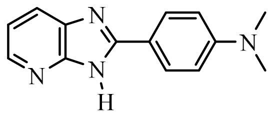
This investigation was used to drive next syntheses towards compounds more useful as active materials in optoelectronic. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells; so the HOMO, LUMO and E_{gap} energy and Voc (open circuit voltage) of the studied compounds have been calculated and reported.

EXPERIMENTAL SECTION

Materials

All of the 20 compounds and associated data involved in this study were obtained from literature by [3]. The inhibitory activity data were reported as IC_{50} against Aurora A. The IC_{50} values were converted into pIC_{50} according by Cichero [1]. The structures of the molecules are shown and associated inhibitory activities are shown in Table 1.

The data set implemented in this work consists of 20 imidazo[4,5-b]pyridine derivatives shown in figure 1. Half maximal inhibitory concentration (IC_{50}) is the quantity used for measuring in vitro potency of these compounds in inhibiting Aurora A kinase function.



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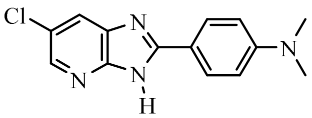

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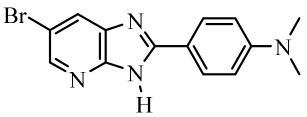

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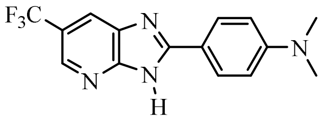

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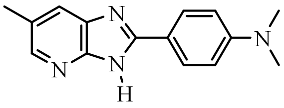

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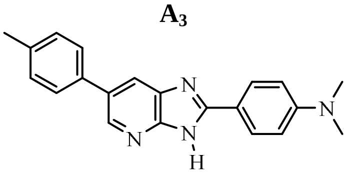

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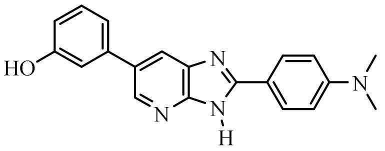

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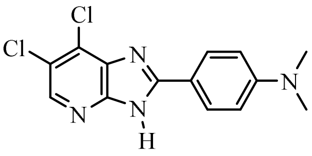

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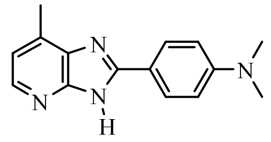

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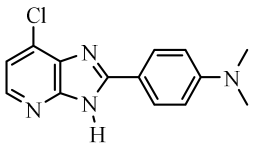

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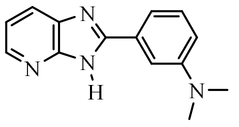

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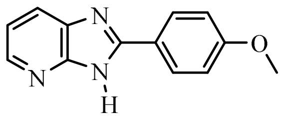

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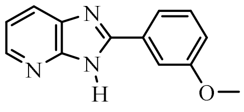

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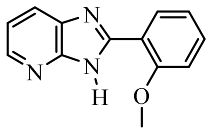

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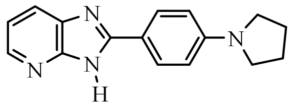

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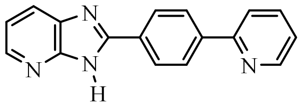
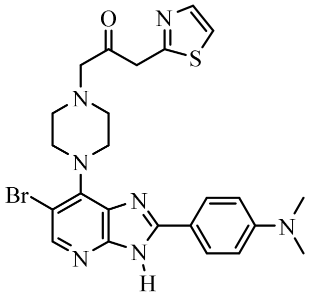
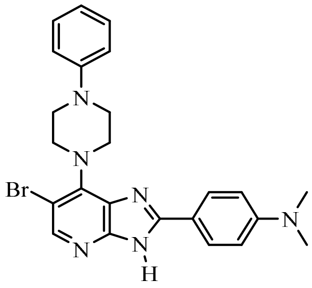
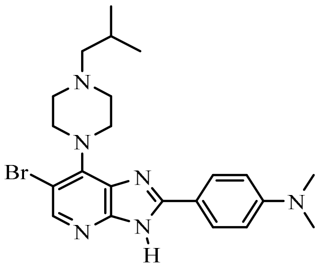






A_{16} **A_{17}** **A_{18}**



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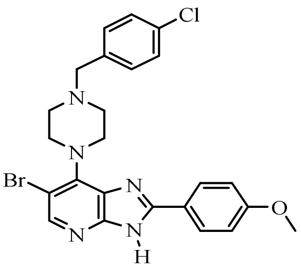


A_{20}

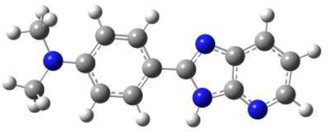
Figure 1: Chemical structure of imidazo[4,5-b]pyridine derivatives

Theoretical methodology

DFT method of three-parameter compound of Becke (B3LYP) [8] was used in all the study of the neutral 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 and doped 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 AND DISCUSSION

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.



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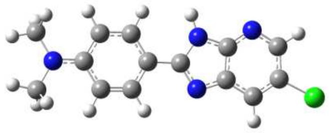

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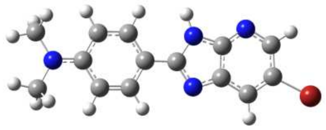

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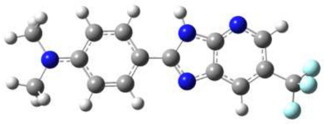

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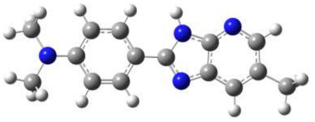

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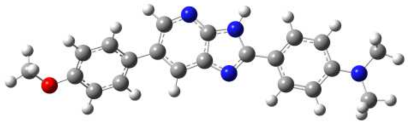

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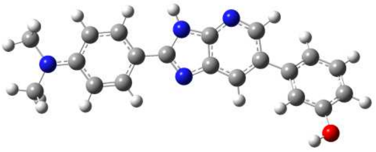

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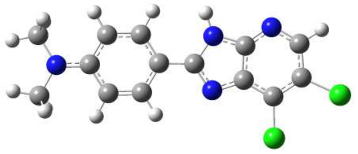

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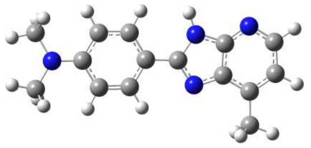

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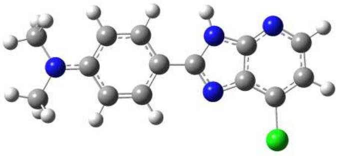
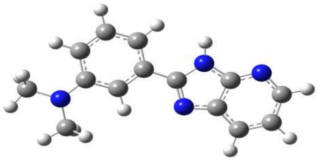


A_{10}



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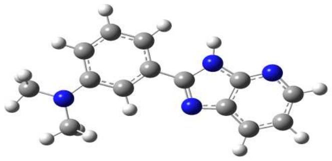

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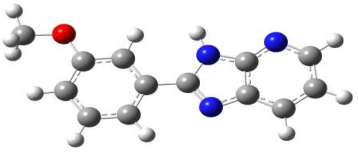
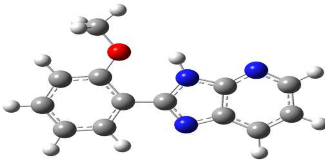
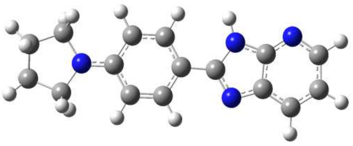


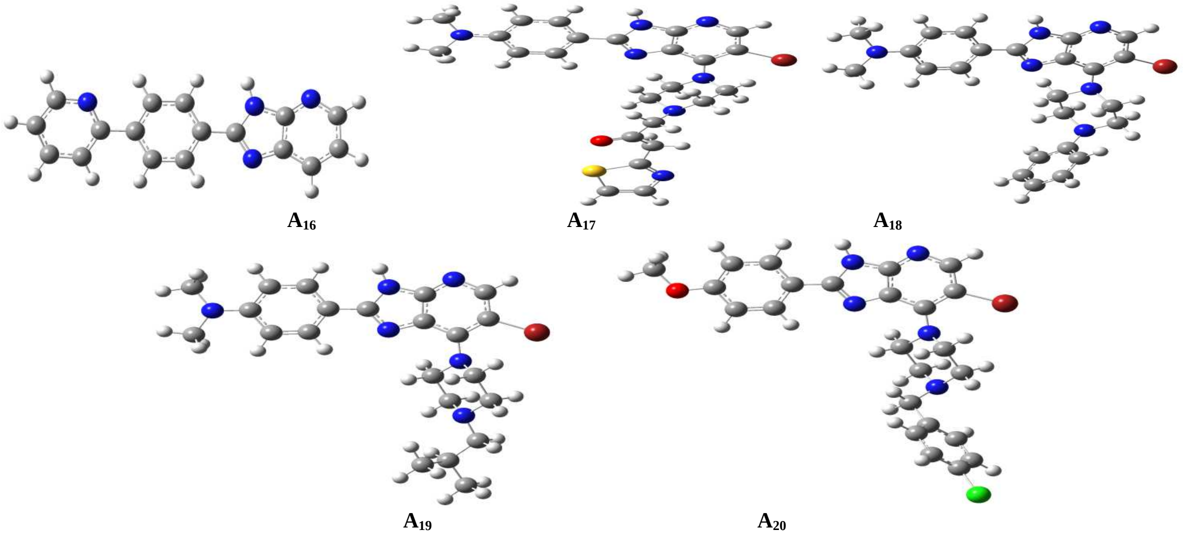
A_{13}



A_{14}



A_{15}


A_{16} **A_{17}** **A_{18}**

A_{19} **A_{20}**

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_{gap} between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the energy E_{gap} of the studied molecules, also the open circuit voltage V_{oc} (eV) and α = E_{LOMO} (Donor) –E_{LUMO} (Acceptor).These parameters will be discussed in the photovoltaic part.

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

Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	V_{oc} (eV)	α (eV)
A_1	-5.084	-1.009	4.075	1.084	2.691
A_2	-5.239	-1.272	3.966	1.239	2.428
A_3	-5.237	-1.273	3.964	1.237	2.427
A_4	-5.308	-1.346	3.963	1.308	2.354
A_5	-5.025	-0.957	4.068	1.025	2.743
A_6	-5.024	-1.021	4.003	1.024	2.679
A_7	-5.114	-1.116	3.997	1.114	2.584
A_8	-5.32	-1.427	3.893	1.320	2.273
A_9	-5.03	-0.942	4.088	1.030	2.758
A_{10}	-5.202	-1.217	3.985	1.202	2.483
A_{11}	-5.275	-1.222	4.053	1.275	2.478
A_{12}	-5.600	-1.222	4.378	1.600	2.478
A_{13}	-5.851	-1.376	4.475	1.851	2.324
A_{14}	-5.674	-1.274	4.4	1.674	2.426
A_{15}	-4.987	-0.956	4.031	0.987	2.744
A_{16}	-5.799	-1.778	4.021	1.799	1.922
A_{17}	-5.114	-1.125	3.989	1.114	2.575
A_{18}	-4.899	-1.117	3.782	0.899	2.583
A_{19}	-5.054	-1.035	4.019	1.054	2.665
A_{20}	-5,347	-1,332	4,016	1,347	2,368
PCBM C_{60} (A)	-6,1	-3,7	-	-	-

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 A_1 to A_{20} change significantly, the LUMOs for A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10}, A_{11}, A_{12}, A_{13}, A_{14}, A_{15}, A_{16}, A_{17} A_{18}, A_{19} and A_{20}, are located at -1.009; -1.272; -1.273; -1.346; -0.957; -1.021; -1.116; -1.427; -0.942; -1.217; -1.222; -1.222; -1.376; -1.274; -0.956; -1.778; -1.125; -1.117; -1.035 and -1,332 eV, respectively. The HOMOs for A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10}, A_{11}, A_{12}, A_{13}, A_{14}, A_{15}, A_{16}, A_{17} A_{18}, A_{19} and A_{20} are located at -5.084; -5.239; -5.237; -5.308 ; -5.025; -5.024; -5.114; -5.320; -5.030; -5.202; -5.275; -5.600; -5.851; -5.674; -4.987; -5.799; -5.114; -4.899; -5.054 and -5,347 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 imidazo[4,5-b]pyridine ring on the HOMO and LUMO energies is clearly seen. In addition, energy (E_{gap}) of the studied molecules differs slightly from 3,782 eV to 4.475 eV depending on the different structures. They are studied in the following order:

$$\mathbf{A_{13}>A_{14}>A_{12}>A_9>A_1>A_5>A_{11}>A_{15}>A_{16}>A_{19}>A_{20}>A_6>A_7>A_{17}>A_{10}>A_2>A_3>A_4>A_8>A_{18}}$$

On the other hand and from the above analysis, we know that the LUMO energy levels of the molecules studied is much higher than that of the ITO conduction band edge (-4.7 eV). Thus, molecules in excited states of A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, A_9, A_{10}, A_{11}, A_{12}, A_{13}, A_{14}, A_{15}, A_{16}, A_{17} A_{18}, A_{19} and A_{20} have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [12]. This latter 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 HOMO level of PCBM. As shown in table 1, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosentizer. One side, the HOMO levels of the studied compounds A_i (i=1 to 20) are lower than that of PCBM. Else next, the LUMO levels of the studied compounds A_i (i=1 to 20) are lower than that of PCBM [13]. To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of PCBM, the HOMO and LUMO levels are compared. In addition, to effectively inject the electron into the CB of PCBM (-3.7 eV); the value of LUMO Donor must be greater than that of PCBM and accordingly $\alpha > 0$ [14]. 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. The maximum open circuit voltage (Voc) of the BHJ 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 [15]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression:

$$\mathbf{V_{oc} = \left| E_{HOMO}\ (Donor) \right| - \left| E_{LUMO}\ (Acceptor) \right| - 0.3} \tag{1}$$

The obtained values of Voc of the studied molecules calculated according to the equation (1) range from 0.899 eV to 1.851 eV (See table 1), these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as BHJ solar cell because the electron injection process from the studied molecule to the conduction band of PCBM and the subsequent regeneration is possible in an organic solar cell (Table 1, Figure3).

Figure 3 shows detailed data of energy of the frontier orbitals for studying compounds and [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) (substituted C_{60}).

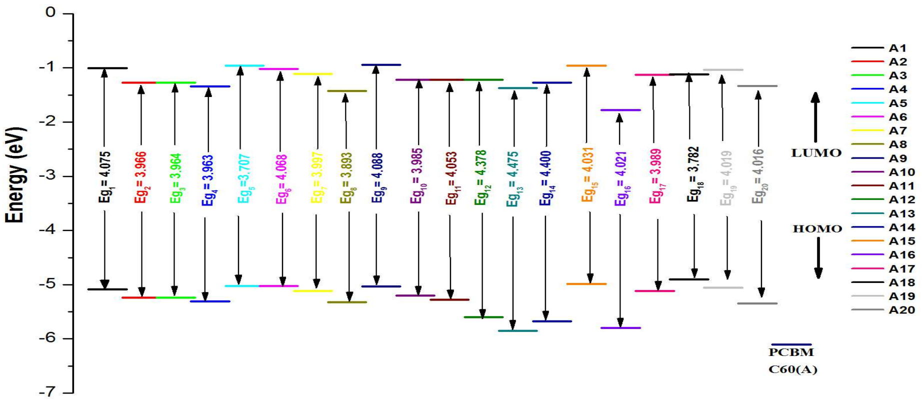
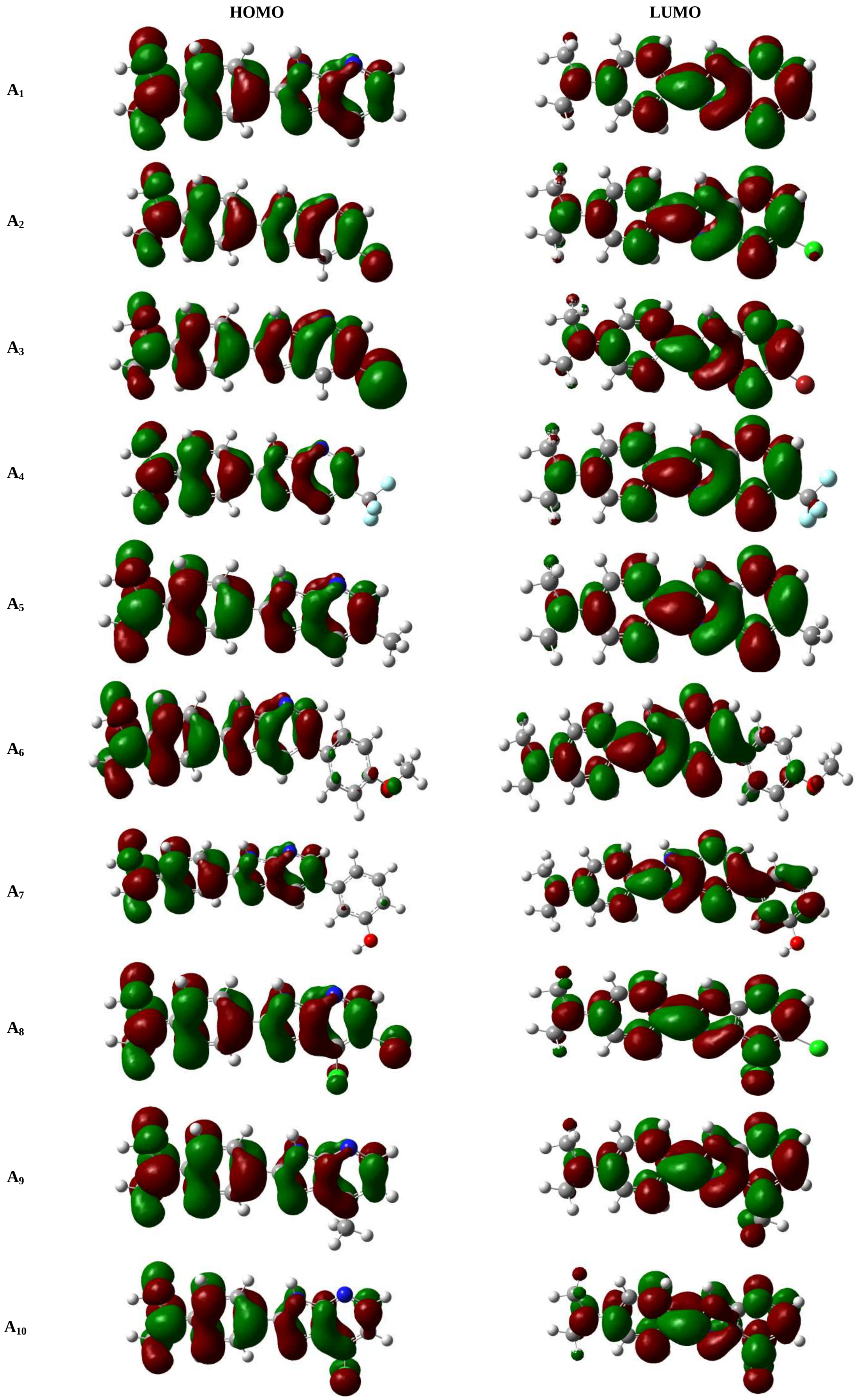


Figure 3: Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules

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 [16]. In general, as shown in figure 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π-bonding character within subunit and a π-antibonding character between the consecutive subunits while the LUMOs possess a π-antibonding character within subunit and a π-bonding character between the subunits whereas it is the opposite in the case of doped forms.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LUMO
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A_8
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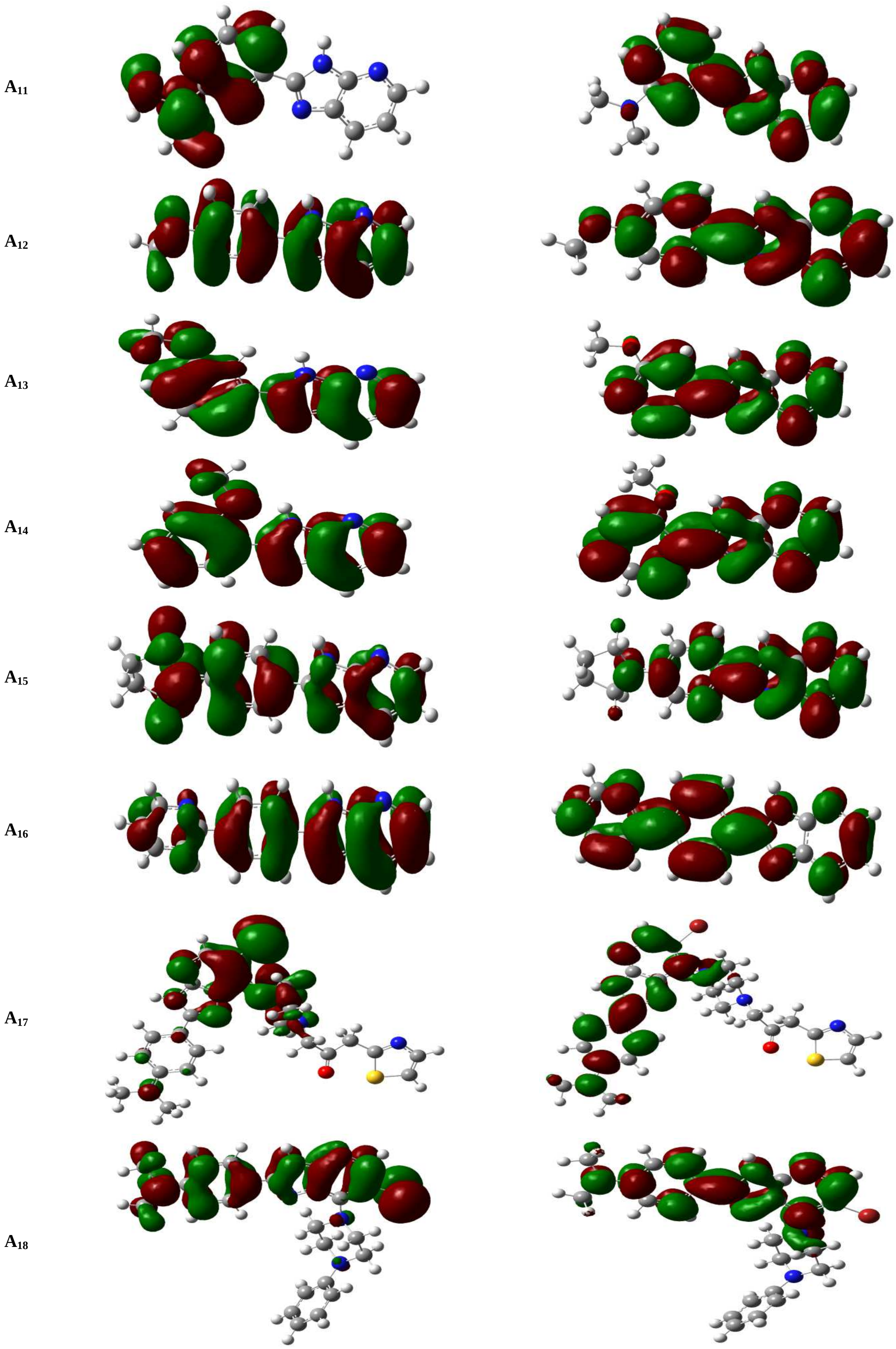
A_{10}


A_{11}
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A_{17}
A_{18}

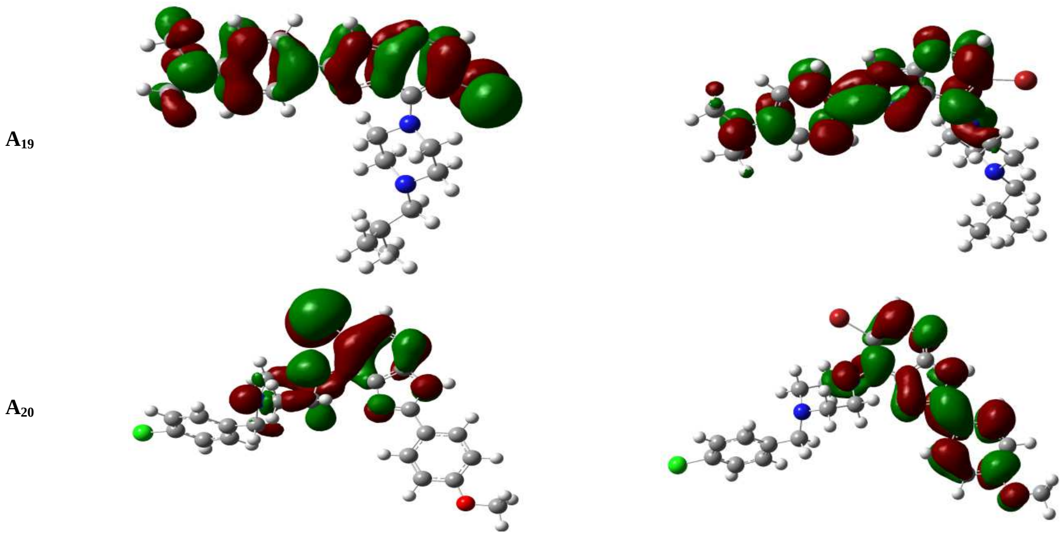

Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level

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. In fact, we have calculated the UV-Visible spectra of the studied compounds A_i (i=1 to 20) using TD-DFT starting with optimized geometry obtained at B3LYP/6-31(d) level. As illustrated in table 2, we can find the values of calculated wavelength λ_{max} and oscillator strengths O.S. Recall that excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

Data in table 2 shows that there is a bathochromic shift when passing from A_1 (263 nm) to A_8 (341 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.

Table 2: Absorption spectra data obtained by TD-DFT methods for the A_i (i=1 to 20) compounds at B3LYP/6-31G (d) optimized geometries

Molecules	λ_{abs}(nm)	$E_{activation}$ (eV)	O.S
A_1	263.55	4,704	0.1395
A_2	333.32	3.720	0.9689
A_3	334.81	3.703	1.0020
A_4	331.31	3.742	0.9399
A_5	325.19	3.813	1.0282
A_6	328.79	3.771	1.1543
A_7	335.91	3.691	1.1647
A_8	341.37	3.632	0.9368
A_9	322.01	3.850	1.0083
A_{10}	333.22	3.721	0.9434
A_{11}	297.68	4.165	0.8018
A_{12}	298.20	4.158	0.8591
A_{13}	298.74	4.150	0.6459
A_{14}	300.38	4.128	0.6805
A_{15}	328.14	3.778	1.0393
A_{16}	297.59	4.166	0.9855
A_{17}	334.53	3.706	0.9171
A_{18}	332.90	3.724	0.8643
A_{19}	337.16	3.677	0.8590
A_{20}	305.58	4.057	0.7380

The corresponding simulated UV–Vis absorption spectra of A_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 λ_{max}(nm) and oscillator strength (O.S) of the studied compounds A_i.

The calculated wavelength λ_{abs} of the studied compounds decreases in the following order:

$A_8>A_{19}>A_7>A_3>A_{17}>A_2>A_{10}>A_{18}>A_4>A_6>A_{15}>A_5>A_9>A_{20}>A_{14}>A_{13}>A_{12}>A_{11}>A_{16}>A_1$

This is the same order of the reduction of the acceptor strength. This bathochromic effect from A_i is obviously due to increased π delocalization. This interesting point is seen both by analyzing electronic and absorption results. Excitation to the S_1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. The absorption wavelengths arising from S_0-S_1electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO-LUMO transition is predominant in S_0-S_1electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy [17].

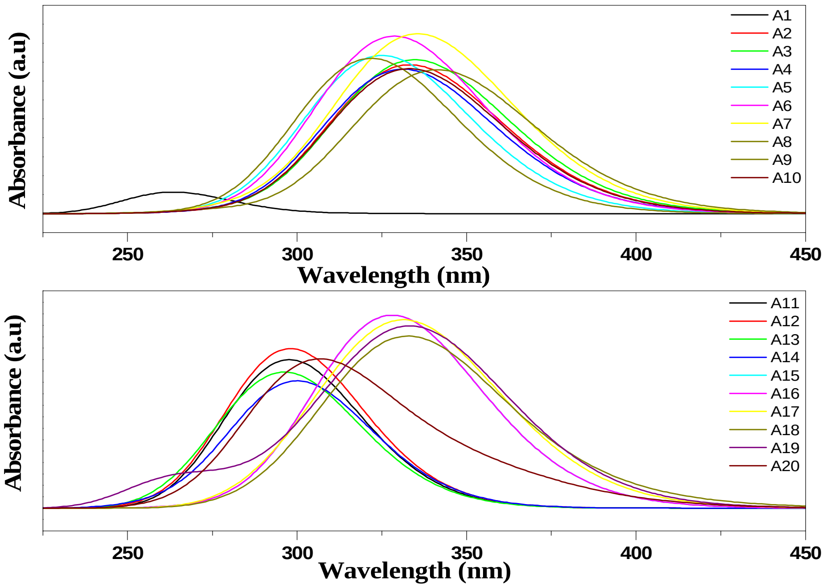

Figure 5: Simulated UV–visible optical absorption spectra of title compounds with calculated data at the TD-DFT/B3LYP/6-31G(d)

CONCLUSION

This study is a theoretical analysis of the geometries and electronic properties of three various compounds based on the imidazo[4,5-b]pyridine 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:

***** The results of the optimized structures for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups does not change the geometric parameters.
***** The calculated frontier orbital energies HOMO and LUMO and energy E_{gap} showed that the energy E_{gap} of the studied molecules differ slightly from 4.475 eV to 3.782 eV depending on the different structures. Also we can remark that the energy E_{gap} decreases, this is probably due to the effect of the conjugated system and aromaticity in the studied compounds.
***** The energy E_{gap} of A_{18} is much smaller than that of the other compounds.
***** Molecule A_8 witch have a relatively high value of λ_{max} (absorption), is expected to have the most outstanding photophysical properties.
***** All the studied molecules can be used as BHJ solar cell because the electron injection process from the 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 applications. 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 new materials for organic solar cells.

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