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Research Article

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Theoretical Study of The Optical and Photovoltaic Properties of Molecules Based on 1,3-Diaza-Azulene by DFT Calculations

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ABSTRACT

In this study, we carried out theoretical study of electronic properties and geometry of twelve conjugated compounds based on 1,3-diaza-azulene. The effect of the substituted groups (Cl, F, Br, CH_3) on the optoelectronic and structural properties, dipole moment, HOMO, LUMO and E_{gap} are discussed. The geometry at the ground state and the electronic structure of studied molecules are obtained by density functional theory (DFT) and density functional theory time-dependent (TD-DFT) with the B3LYP / 6-31G (d, p). The results of this study show that these compounds are good candidates for organic solar cells.

Keywords: 1,3-diaza-azulene; Electronic properties; DFT; HOMO; LUMO; Photovoltaic; Organic solar cells

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INTRODUCTION

The cheapest current technology for generating electricity from the sun is the use of the photoelectric effect. Solar panels on silicon are currently the most popular, this technology is limited by its high cost. An emerging technology that can address the current gaps in the field is organic photovoltaics in which semiconductors are carbon-based. These compounds are much less expensive to manufacture and require a lower initial investment [1,2]. They also exhibit the ability to be dissolved and incorporated into inks. They may benefit from the enormous expertise in printing technology, low cost and high speed of production. In addition, organic devices can be fabricated on flexible or semi-transparent substrates, and can benefit from new applications, such as solar textiles that wrap for easy transport, solar tinted windows [3,4].

The main limitation of organic photovoltaics is its low efficacy compared to its inorganic counterparts. To be economically viable and competitive, it is crucial to increase this effectiveness. To do this, we need to find organic compounds, which have the most relevant electronic properties, including optimum band gap and energy levels allowing heterojunction effective.

The synthesis of all compounds is completely impossible, and it is crucial to probe how the theoretical properties for better effectiveness. Scharber et al. proposed a semi-empirical model in 2006 to explain the operation of the organic devices and provide an efficiency maximum of 11% based on this model [5]. It is useful from first principles and solving the Schrödinger equation. These calculation methods that are not based on experimental data are called ab-initio. An interesting technique to solve the Schrödinger equation is the density functional theory (DFT) [6].

Organic semiconductors have attracted the attention of researcher's theorists and experimentalists in recent years, due to their excellent optical and electronic properties [7]. These materials can be used for producing such diverse devices as photovoltaic cells, field effect transistors, and light emitting diodes [8-13]. Most research of new π-conjugated molecules with specific applications has become one of the interesting topics in the fields of physical and chemical materials [14].

A fundamental understanding of the ultimate relationship between structure and properties of these materials is required to exploit their properties for photovoltaic cells. In this study, twelve compounds based on 1,3-diaza-azulene (DA_0, DA_1, DA_2, DA_3, DA_4, DA_5, DA_6, DA_7, DA_8, DA_9, DA_{10}, DA_{11}) are considered. These compounds were studied using DFT and TD-DFT calculations. HOMO, LUMO, gap energies and open circuit voltage (V_{oc}) of all molecules are investigated.

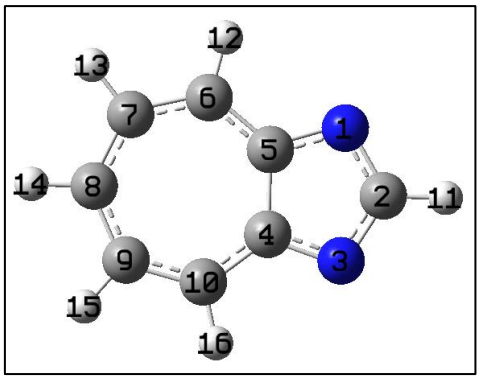

Figure 1: Structure of 1,3-diaza-azulene (DA_0)

EXPERIMENTAL SECTION

The optimized of the geometries of the studied molecules were carried by using DFT method with the hybrid functional of exchange correlation with the three-parameter compound of Becke (B3LYP) and the 6-31G (d, p) basis set was used for all calculations [15]. The electronic absorption spectra are investigated using TD-DFT calculations at the B3LYP. The calculations were carried out using the GAUSSIAN 03 program [16].
The power conversion efficiency (η) is mainly determined by the short-circuit current density (Jsc) and the open circuit photovoltage (V_{oc}). The η can be expressed by the following equation:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{J_{\max} . V_{\max}}{P_{in}} = \frac{FF . V_{OC} . J_{SC}}{P_{in}}$$

where, P_{in} is the incident power density, FF is the fill factor and J_{sc} is the short circuit current.

For the short-circuit current density Jsc it is determined as:

$$J_{SC} = \int_{\lambda} LHE(\lambda)\, \Phi_{inject}\, \eta_{collect}\, d\lambda$$

where *LH*E (λ) is the light harvesting efficiency, Φ_{inject} is the electron injection efficiency and $\eta_{collect}$ is the charge collection efficiency.

LHE can be expressed as:

$$LHE = 1 - 10^{-f}$$

where f is the oscillator strength.

RESULTS AND DISCUSSION

The optimized molecular structures are presented in Figure 2. The Geometric display shows the planar conformation for all compounds.
Table 1 shows the calculated orbital energies and energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as well the open circuit voltage V_{oc} and difference between the LUMO energy levels of the donor (DA_i / i=0,…,11) and acceptor (PCBM C60) :

$$\alpha = E_{LUMO}(\text{donor}) - E_{LUMO}(\text{acceptor})$$

In organic solar cells, the open circuit voltage (V_{oc}) is found to be linearly depending on the HOMO donor and LUMO acceptor energies [14-15] which are important factors in determining whether effective charge transfer will occur between the donor and acceptor .The theoretical values V_{oc} is calculated from the following expression:

$$V_{OC} = |E_{HOMO}(Donor)| - |E_{LUMO}(Acceptor)| - 0.3$$

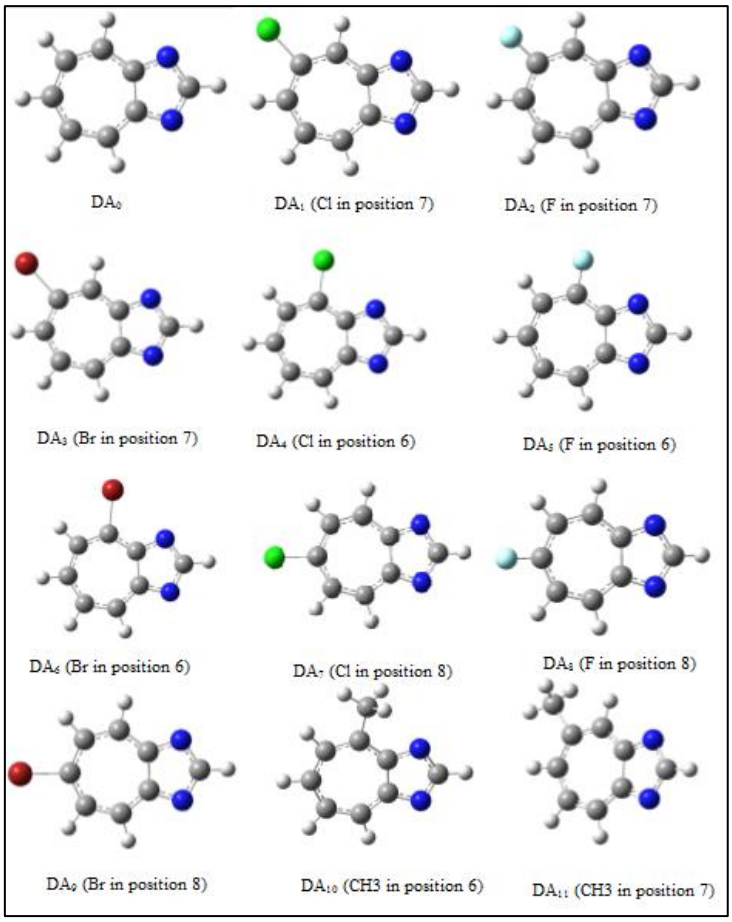

Figure 2: Optimized molecular structures computed by DFT/B3LYP/6-31 G(d,p)

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

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	V_{oc}(eV)	α (eV)
DA_0	-6.72	-2.44	4.28	2,72	1,26
DA_1	-6.84	-2.75	4.09	2,84	0,95
DA_2	-6.76	-2.67	4.09	2,76	1,03
DA_3	-6.79	-2.74	4.05	2,79	0,96
DA_4	-6.9	-2.67	4.23	2,90	1,03
DA_5	-6.84	-2.53	4.31	2,84	1,17
DA_6	-6.85	-2.66	4.19	2,85	1,04
DA_7	-7.01	-2.72	4.29	3,01	0,98
DA_8	-6.93	-2.49	4.44	2,93	1,21
DA_9	-6.98	-2.72	4.26	2,98	0,98
DA_{10}	-6.61	-2.32	4.29	2,61	1,38
DA_{11}	-6.52	-2.33	4.19	2,52	1,37
PCBM C60	-6.1	-3.7	-	-	-

The HOMO and LUMO energies values of the compounds are different. This is due to structural modifications following substitution. Energy gap (Egap) of studied molecules varies from 4.44 to 4.05eV. The corresponding values are in the order:

$$DA_3 < DA_1 < DA_2 < DA_6 < DA_{11} < DA_4 < DA_9 < DA_0 < DA_7 < DA_{10} < DA_5 < DA_8$$

The obtained V_{oc} values are in the range of 2.52-3.01 eV. These values are sufficient for an injection of electrons efficiently as possible and therefore, all the studied molecules can be used as organic bulk heterojunction (BHJ) solar cells.

The calculated dipole moment of the studied compounds respectively DA_0(4.1736D), DA_1(3.1789D), DA_2(3.3978D), DA_3(3.2235D), DA_4(4.4262D), DA_5(4.5418D), DA_6(4.2459D), DA_7(2.3967D), DA_8(2.8941D), DA_9(2.5913D), DA_{10}(4.0149D), DA_{11}(4.5667D)

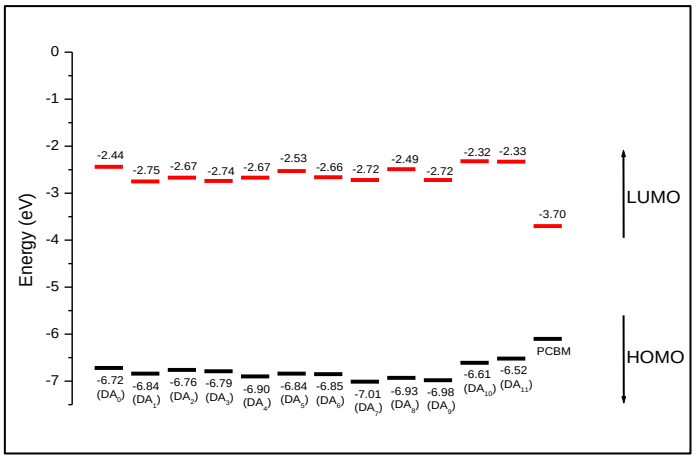

Figure 3: HOMO and LUMO energy levels of the studied compounds, by DFT/B3LYP/6-31G(d,p) basis set

As shown in Table 2, we can find the values of wavelengths λ_{abs} calculated and oscillator strengths (OS). Excitation state S_1 corresponds almost exclusively to the allocation of an electron from the orbital HOMO of LUMO. The wavelengths of absorption wave resulting from electronic transition $S_0 \rightarrow S_1$ that increases progressively with the increase of conjugation lengths. It is reasonable, the transition between HOMO→LUMO is predominant in $S_0 \rightarrow S_1$ electronic transition, and the results are a decrease of LUMO and an increase of HOMO energy.

Table 2: Absorption spectra data obtained by TD-DFT methods for compounds at B3LYP/6-31G (d) optimized geometries

Compound	λ (nm)	$E_{activation}$(eV)	f	MO/character
DA_0	371.54	3.337	0,212	HOMO->LUMO (91%)
DA_1	386.27	3.209	0,294	HOMO->LUMO (89%)
DA_2	385.07	3.219	0,367	HOMO->LUMO (90%)
DA_3	388.93	3.187	0,307	HOMO->LUMO (89%)
DA_4	371.3	3.339	0,316	HOMO->LUMO (80%)
DA_5	363.1	3.414	0,283	HOMO->LUMO (83%)
DA_6	372.28	3.33	0,386	HOMO->LUMO (73%)
DA_7	373.72	3.317	0,144	HOMO->LUMO (89%)
DA_8	362.16	3.423	0,076	HOMO->LUMO (88%)
DA_9	374.6	3.309	0,141	H-1->LUMO (88%)
DA_{10}	368.13	3.367	0,313	HOMO->LUMO (87%)
DA_{11}	377.42	3.285	0,267	HOMO->LUMO (90%)

To illustrate the results in Table 2, we also simulated the UV-visible absorption spectrum for twelve compounds studied for the TD-DFT method / B3LYP / 6-31G (d) (Figure 5).We studied the UV-vis spectra of each compound studied: DA_i (i=0 to 11) using the TD-DFT method (Figure 5). These values are calculated by TD-DFT method starting with optimized geometry obtained at B3LYP / 6-31G (d).The wavelength λ_{abs} calculated of the test compounds decreased in the following order:

$$DA_8<DA_5<DA_{10}<DA_4<DA_0<DA_6<DA_7<DA_9<DA_{11}<DA_2<DA_1<DA_3$$

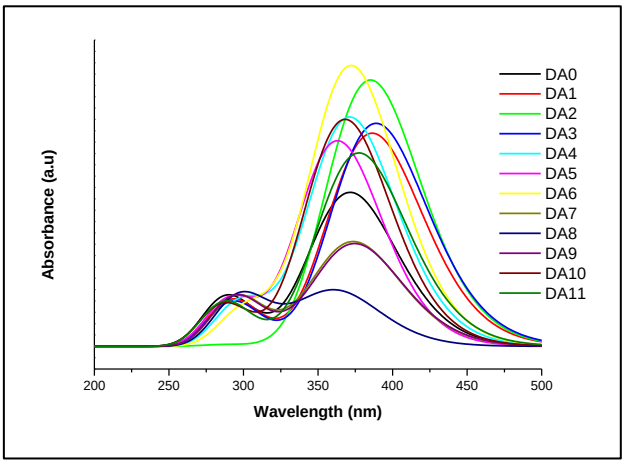

Figure 5: Simulated UV–visible optical absorption spectra of title compounds withcalculated data at the TD-DFT/B3LYP/6-31G(d)

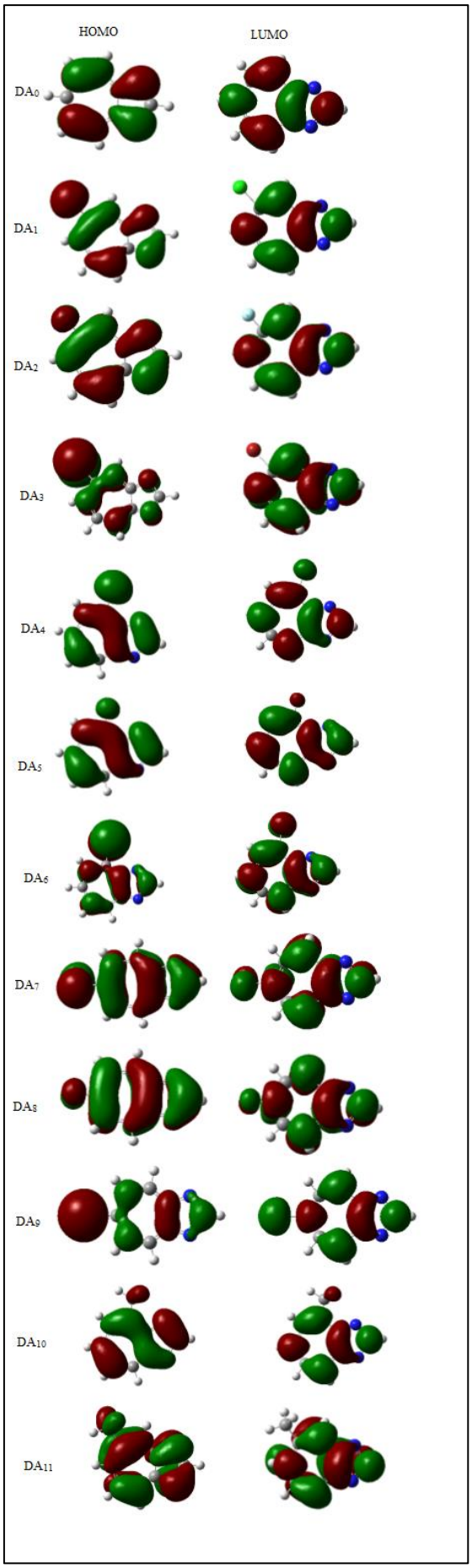

Figure 4: Obtained isodensity plots of the frontier orbital HOMO and LUMO of the studied compounds obtained at B3LYP/6-31(d) level

Finally we note that the DA3 molecule has the largest wavelength (λmax) among these studied molecules so it can have remarkable properties in the photo-physical domains.

CONCLUSION

In this study, the properties of the electronic structure and optical absorption of twelve compounds based on 1,3-diaza-azulene were studied using DFT and TD-DFT methods. We noticed the changes of several donor or acceptor groups do not change the geometric parameters and the energies of the orbital HOMO, LUMO and Egap showed that Egap studied molecules differ slightly from 4,05 eV to 4,44 eV for the different structures, and Egap of DA_3 is much lower than other compounds. From these results, we can conclude that these molecules have shown significant optoelectronic properties, which leads to offer these materials for application of organic solar cells. This calculation procedure can be used as a model system for understanding the relationship between the electronic properties and molecular structure and can also be used to study their aptitude in electroluminescent devices. The results suggest these materials as candidate for organic solar cells.

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