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## New organic materials based on TTF-pyrazine for photovoltaic applications: Quantum chemical investigations

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### ABSTRACT

To better understand and predict the properties of the  $\pi$ -conjugated compound especially in view of their use as organic solar cells, we have performed the investigation by using the DFT and TD-DFT quantum chemical calculations. The studied compounds are based on TTF- pyrazine , the aim is first to determine the geometries, electronic and optic properties by using the density functional theory (DFT/B3LYP) level with the correlation-consistent basis set 6-31G(d,p). Moreover, several physical parameters (HOMO, LUMO, E<sub>gap</sub>, Voc.....) were determined from the fully optimized structures. The absorption  $\lambda_{abs}$  is also calculated. This fundamental information is a valuable data in designing and making promising materials for organic solar cells.

**Keywords:**  $\pi$ -Conjugated molecules, TTF- pyrazine, organic solar cells, density function theory (DFT), low band-gap, electronic properties.

### INTRODUCTION

Solar energy has proven capacity to match the world's increasing energy needs [1-2]. Although several types of inorganic and organic materials, including semiconductors [3-4] and conducting polymers [5-6] are studied and proposed as a promising material in the field of organic solar cells. Especially, low band gap conjugated molecules or polymers because of their improved solar light harvesting ability [7-8].

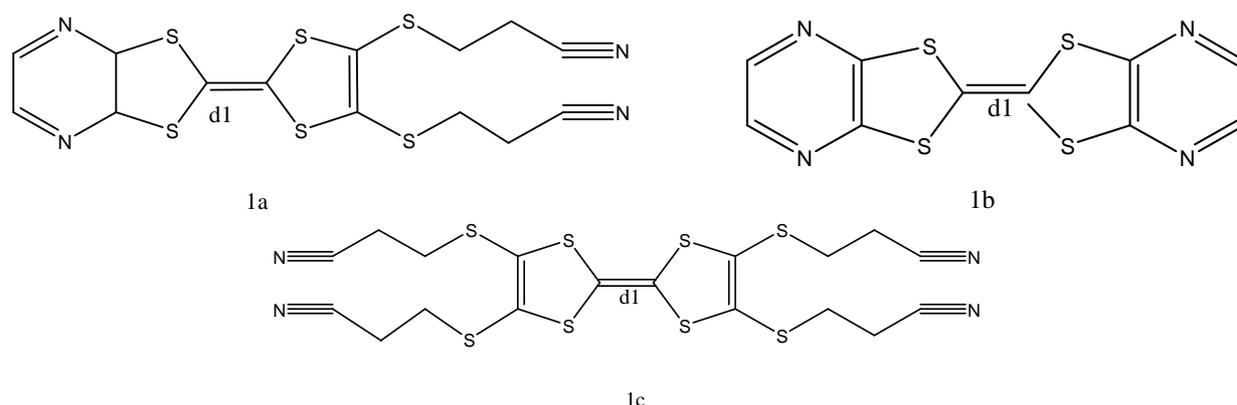
The new organic materials based on  $\pi$ -conjugated molecules specially carbazole or (and) thiophene have attracted interest and much attention because of their unique electronic properties, their high photoluminescence quantum efficiency, thermal stability and also their facile color tenability [9-10].

On the other hand, many researchers have become recently interested synthesizing short-chain compounds based on conjugated molecules because they are not amorphous and can be synthesized as well defined structures [11-12]. More, the short conjugated molecules based on thiophene and phenylene units have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency and thermal stability [13]. In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines. One of the most important factors of controlling physical properties is the band-gap, which is a current topic of research; In particular materials with a low band-gap are desired in optoelectronic applications. Many experimental and theoretical attempts have been made to modify the chemical structures [14].

At the same time 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. Recent work in this area has been focused on the synthesis and design of new molecules combining donor and acceptor blocks, or conjugated systems with narrow band gaps [15]. Theoretical studies on the electronic structures of  $\pi$ -conjugated compounds have given great contributions to the rationalization of the properties of known materials and to the properties prediction those of yet unknown ones. In this context, quantum chemical methods have been increasingly applied to predict the band gap of conjugated systems [16]. We note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic devices properties.

The HOMO and LUMO energy levels of the donor and of the acceptor components for photovoltaic devices are very important factors to determine whether effective charge transfer will happen between donor and acceptor. The offset of band edges of the HOMO and LUMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

In this paper and in order to guide the synthesis of novels materials, three compounds based on TTF-pyrazine and other  $\pi$ -conjugated molecules (1a, 1b and 1c) shown in scheme1, are designed. These compounds were prepared by S. Rabaça et al [17]. The geometries, electronic properties, absorption spectra of these studied 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 Voc (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as a good candidate for organic dye-sensitized solar cells.



Scheme1: Structure of the studied compounds (1a, 1b and 1c)

## MATERIALS AND METHODS

DFT method of three-parameter compound of Becke (B3LYP) [18] was used in all the study of the neutral and polaronic compounds. The 6-31G (d,p) basis set was used for all calculations[19-20]. 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 [21]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy 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.

## RESULTS

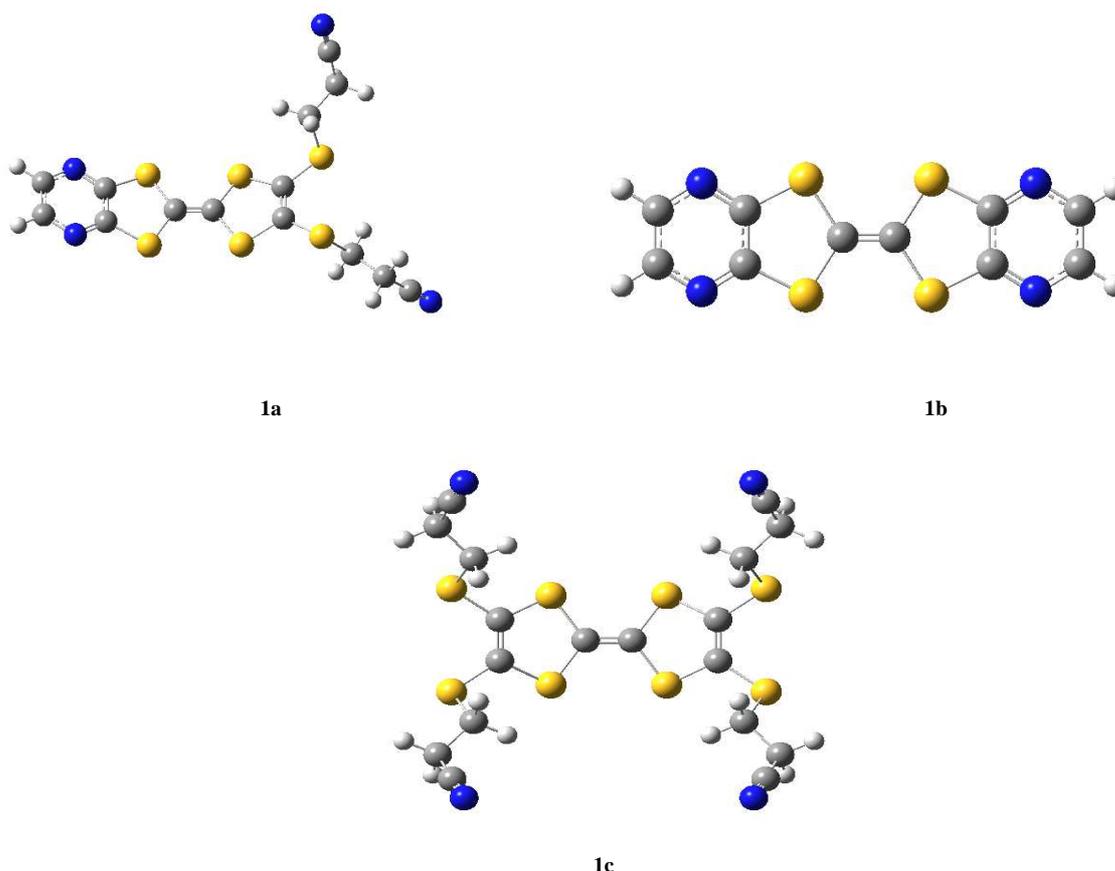
### Geometric parameters:

The chemical structures of all studied molecules in this work are displayed in scheme1. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d,p) basis sets using Gaussian 03 program suite, and the optimized geometries are given in Figure 1. The calculated bond lengths of molecules 1a, 1b and 1c are listed in table 1. For each model inter-ring bond lengths  $d_1$  which greatly contribute to the internal energy, were compared in table 1. It was found in other works [22] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses.

**Table 1:** geometrical parameters of studied compounds 1a, 1b and 1c obtained by b3lyp/6-31G (d,p) in their neutral states

bond length (Å) and Angle (°)	$d_1$ $\theta_1$
1a	1.348 179.99
1b	1,3488 179.99
1c	1.349 176.9

The results of the optimized structures for all studied compounds show that they have similar conformation (quasi planar conformation) (Figure 1). We found that the consecutive units have dihedral angles  $\theta = 179.99^\circ$  for all compounds, and inter-ring distances ( $d_1 = 1,348 \text{ \AA}$  for 1a;  $d_1 = 1,349 \text{ \AA}$  for 1b;  $d_1 = 1,349 \text{ \AA}$  for 1c).

**Figure 1:** Optimized structure of the studied compound obtained by B3LYP/6-31G (d) level**Electronic properties :****Table 2:** The HOMO, LUMO and HOMO–LUMO gaps energy (eV) by B3LYP/6-31 G\*

Compounds	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)
1a	-5.2779	-2.2180	3.0599
1b	-5.4632	-1.6729	3.790
1c	-5.1489	-2.2868	2.8621

The calculated frontier orbital energies (four occupied orbital and four unoccupied orbital) and energy gaps between HOMO and LUMO are shown in Table 2. As shown in Table 2. The calculated electronic parameters (Gap, LUMO, HOMO) of compounds 1a, 1b, and 1c are (3.0599 eV, -2.2180 eV, -5.2779 eV); (3.790 eV, -1.6729 eV, -5.4632 eV) and (2.8621 eV, -2.2868 eV, -5.1489 eV) respectively.

**Absorption Properties :**

Based on the optimized molecular structures with B3LYP/6-31G (d,p) method. We have calculated the UV-vis spectra of each studied compounds: 1a, 1b and 1c using TD-DFT method.

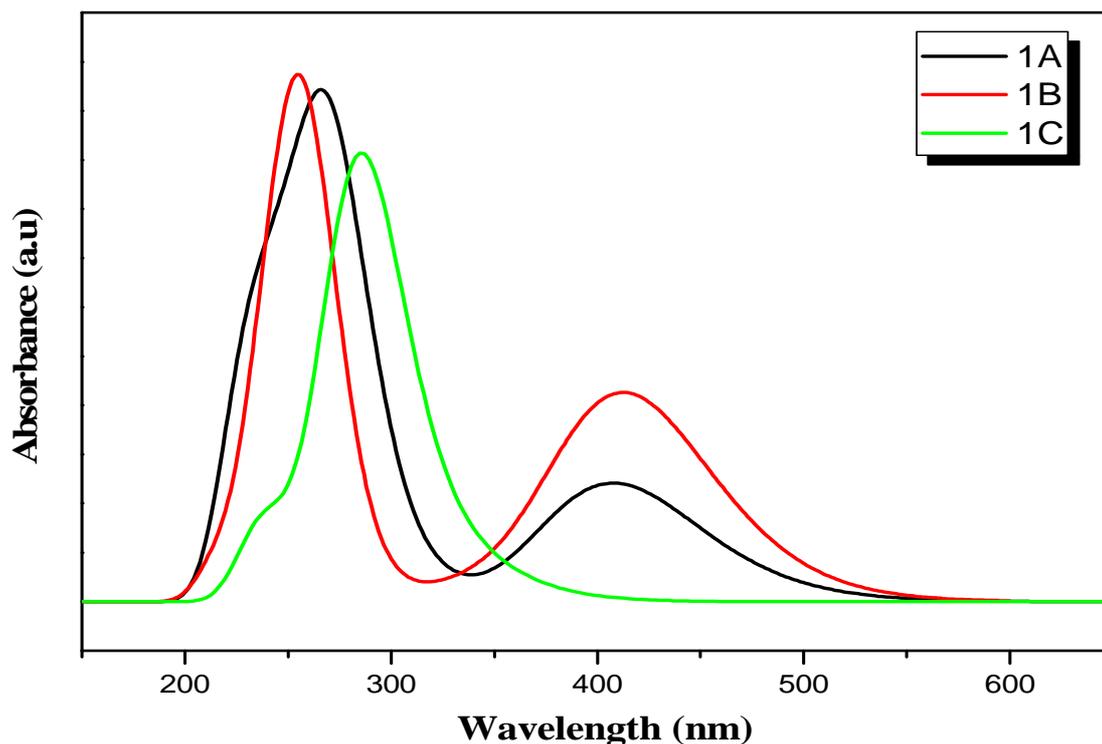


Figure 2: Simulated UV-visible optical absorption spectra of each compound with the calculated data at the TD-DFT B3LYP/6-31G (d,p) level

The corresponding simulated UV-Vis absorption spectra of all compounds, presented as oscillator strength against wavelength, are shown in Fig. 2. We can find the values of the absorption  $\lambda_{\text{max}}$  (nm) and oscillator strength (O.S) along with main excitation configuration of the studied compounds. In addition, we note that the broader absorption peak means that there is a distribution of energy level corresponding to the  $\pi-\pi^*$  transition. 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  $S_0 \rightarrow S_1$  electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO  $\rightarrow$  LUMO transition is predominant in  $S_0 \rightarrow S_1$  electronic transition Table 3; the results are a decrease of the LUMO and an increase of the HOMO energy.

Table 3: Transition states, assignments, the corresponding wavelength and oscillator strength for the title compounds by TD-DFT/B3LYP/6-31G (d, p)

Compounds	Transition	Wavelength ( $\lambda$ , nm)	Ea (eV)	O.S	MO/character
1c	$S_0 \rightarrow S_1$	610.81	2.029	0.0002	HOMO $\rightarrow$ LUMO (95%)
		290.13	4.273	0.2132	HOMO $\rightarrow$ LUMO <sub>+8</sub> (35%)
1a	$S_0 \rightarrow S_1$	433.92	2.857	0.0175	HOMO $\rightarrow$ LUMO <sub>+2</sub> (75%)
		270.91	4.576	0.2443	HOMO $\rightarrow$ LUMO <sub>+6</sub> (31%)
1b	$S_0 \rightarrow S_1$	429.88	2.884	0.0001	HOMO $\rightarrow$ LUMO <sub>+2</sub> (97%)
		260.57	4.758	0.4073	HOMO <sub>-1</sub> $\rightarrow$ LUMO <sub>+1</sub> (65%)

Table 4: Energy values of  $E_{\text{LUMO}}$  (eV),  $E_{\text{HOMO}}$  (eV),  $E_{\text{gap}}$  (eV),  $\alpha$  and the open circuit voltage  $V_{\text{oc}}$  (eV) of the studied molecules obtained by B3LYP/6-31G (d)

Compounds	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	PCBM C <sub>60</sub> (A)		PCBM C <sub>60</sub>		PCBM C <sub>70</sub>		PCBM C <sub>76</sub>	
				$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)	$V_{\text{oc}}$ (eV)	$\alpha$ (eV)
1a	-5,277	-2,218	3,0599	1,277	1,481	1,508	1,252	1,438	1,322	1,188	1,572
1b	-5,463	-1,672	3,79	1,463	2,027	1,693	1,797	1,623	1,867	1,373	2,117
1c	-5,148	-2,286	2,862	1,148	1,413	1,379	1,183	1,309	1,253	1,059	1,503
PCBM C <sub>60</sub> (A)	-6.100	-3.700									
PCBM C <sub>60</sub>	-	-3.470									
PCBM C <sub>70</sub>	-	-3.540									
PCBM C <sub>76</sub>	-	-3.790									

Compounds	E <sub>HOMO</sub> (ev)	E <sub>LUMO</sub> (ev)	E <sub>gap</sub> (ev)	PCBM C <sub>78-C2V</sub>		PCBM C <sub>78-D3</sub>		PCBM C <sub>84-D2</sub>	
				Voc (ev)	$\alpha$ (ev)	Voc (ev)	$\alpha$ (ev)	Voc (ev)	$\alpha$ (ev)
1a	-5,277	-2,218	3,0599	1,038	1,722	0,978	1,782	0,997	1,762
1b	-5,463	-1,672	3,79	1,223	2,267	1,163	2,327	1,183	2,307
1c	-5,148	-2,2686	2,282	0,909	1,653	0,849	1,713	0,869	1,693
PCBM C <sub>78-C2V</sub>	-	-3.94							
PCBM C <sub>78-D3</sub>	-	-4.00							
PCBM C <sub>84-D2</sub>	-	-3.98							

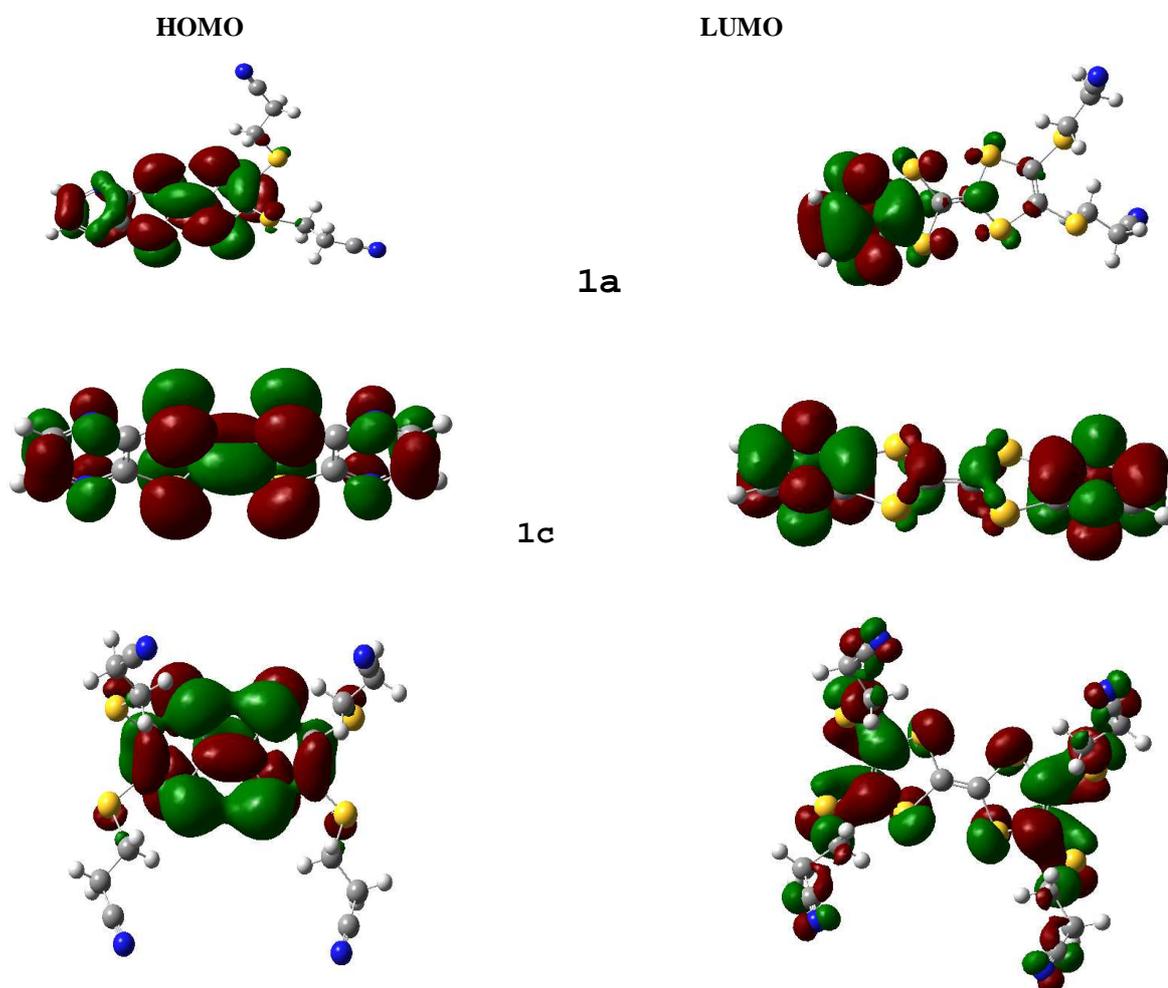
### Photovoltaic Properties :

To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared. Table 4 lists the calculated frontier orbital energies highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), the E<sub>gap</sub> energy of the studied molecules, the open circuit voltage Voc (eV) and The difference between both the energy levels LUMO of the donor and acceptor noted  $\alpha$  [26].

### DISCUSSION

Firstly, by studying the different results obtained for geometrical parameters (table 1), we have noted that the incorporation of several groups does not change inter-ring distances d1, and it is obvious that the torsion angle constitutes a compromise between the effects of conjugation on crystal packing energy, which favours a planar structure. Then, knowing that electronic structures are fundamental to the interpretation and understanding of the absorption spectra, we have determined the electronic properties (table 2); Comparing the molecules 1a, 1b and 1c by studying these properties, we have noticed that the increased ICT characters make the energies of HOMO stabilized and LUMO destabilized when passing from 1c to 1b. Therefore, the energy gaps between HOMO and LUMO decrease, which would make the Optical absorption spectra red shifted. The order of energy gaps is 1c (2.8621 eV) < 1a (3.0599 eV) < 1b (3.7903 eV).

On the other hand, it is important to examine the HOMO and the LUMO for these compounds because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and the ability of electron hole transport. In general, as plotted in Fig. 3, the HOMO possesses an antibonding character between the consecutive subunits; whereas the LUMO of all compounds generally shows a bonding character between the subunits.



Finally and based on the optimized molecular structures with B3LYP/6-31G (d,p) method. We have calculated the UV-vis spectra of each studied compounds: 1a, 1b and 1c using TD-DFT method (table 3, fig 2). The calculated wavelength  $\lambda_{\text{max}}$  of the studied compounds decreases in the following order  $\lambda_{\text{max}}(1c) > \lambda_{\text{max}}(1a) > \lambda_{\text{max}}(1b)$ , which is the same order of the reduction of the acceptor strength. This bathochromic effect from 1b to 1c is obviously due to a higher mean conjugation length and to inter-chain electronic coupling [23].

Concerning the study of Photovoltaic Properties and knowing that generally, the most efficient material solar cells are based on the bulk hetero-junction structure of the blend of pi-conjugated molecule or polymer donors and fullerene derivative acceptors [24-25]. Here, we studied and discuss the photovoltaic properties of the compounds 1a, 1b and 1c as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the most broadly used as an acceptor in solar cell devices. 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. Figure 5 shows detailed data of absolute energy of the frontier orbitals for the studied compounds and PCBM derivatives. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/LUMO energies in agreement with their electron character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared.

On the other hand and from the above analysis, we know that the LUMO energy levels of the studied molecules is much higher than that of the ITO conduction band edge (-4.7 eV). Thus, the studied molecules 1a, 1b and 1c have a strong ability to inject electrons into ITO electrodes. The experiment phenomenon is quite consistent with previous literature [27], 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 several acceptor PCBM. ( $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78-C2V}$ ,  $C_{78-D3}$ ,  $C_{84-D3}$ ,  $C_{84-D2}$ ,  $C_{84-D2d}$ ) (Figure.5).

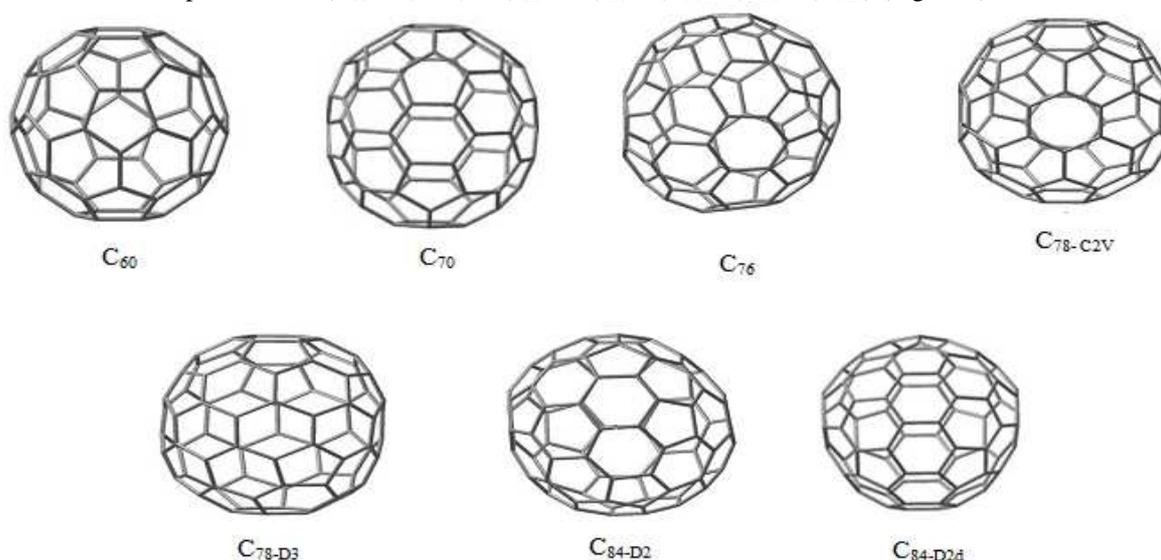


Figure 4: Structure of the investigated fullerenes

As shown in table 4, both HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosensitizer. It should be noted that the LUMO levels of the studied compounds are higher than that of PCBM derivatives which varies in literature from -4.0 to -3.47 eV ( $C_{60}$  (-3.47 eV),  $C_{70}$  (-3.54),  $C_{76}$  (-3.79),  $C_{78-C2V}$  (-3.94),  $C_{78-D3}$  (-4.0),  $C_{84-D2}$  (-3.98)) [28].

To evaluate the possibilities of electron transfer from the studied molecules to the conductive band of the proposed acceptors, the HOMO and LUMO levels are compared. 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 ( $V_{oc}$ ) 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 (PCBM derivatives in our case), taking into account the energy lost during the photo-charge generation [29-30]. The theoretical values of open-circuit voltage  $V_{oc}$  have been calculated from the following expression:

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

The obtained values of  $V_{oc}$  of the studied molecules (1a, 1b and 1c) calculated according to the equation (1) range respectively from (1.277 eV, 1.463 eV, 1.148 eV) for PCBM C60(A); (1.508 eV, 1.693 eV, 1.379 eV) for PCBM C60; (1.438 eV; 1.623 eV, 1.309 eV) for PCBM C70; (1.188 eV; 1.373 eV, 1.059 eV) for PCBM C76; (1.038 eV; 1.223 eV; 0.909 eV) for PCBM C78-C2V; (0.978 eV; 1.163 eV; 0.849 eV) for PCBM C78-D3; (0.997 eV; 1.183 eV; 0.869 eV) for PCBM C84-D2 (see Table 4). These values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as BHJ because the electron injection process from the studied molecule to the conduction band of PCBM derivatives and the subsequent regeneration is possible in an organic solar cell. We noted that the best values of  $V_{oc}$  are indicated for the studied compounds blended with C60 (1.623 eV) and C70 (1.693 eV), and the higher value are given for molecule **1b** blended with C70.

Figure 6 shows detailed data of energy of the frontier orbitals for studying compounds with PCBM and its derivatives.

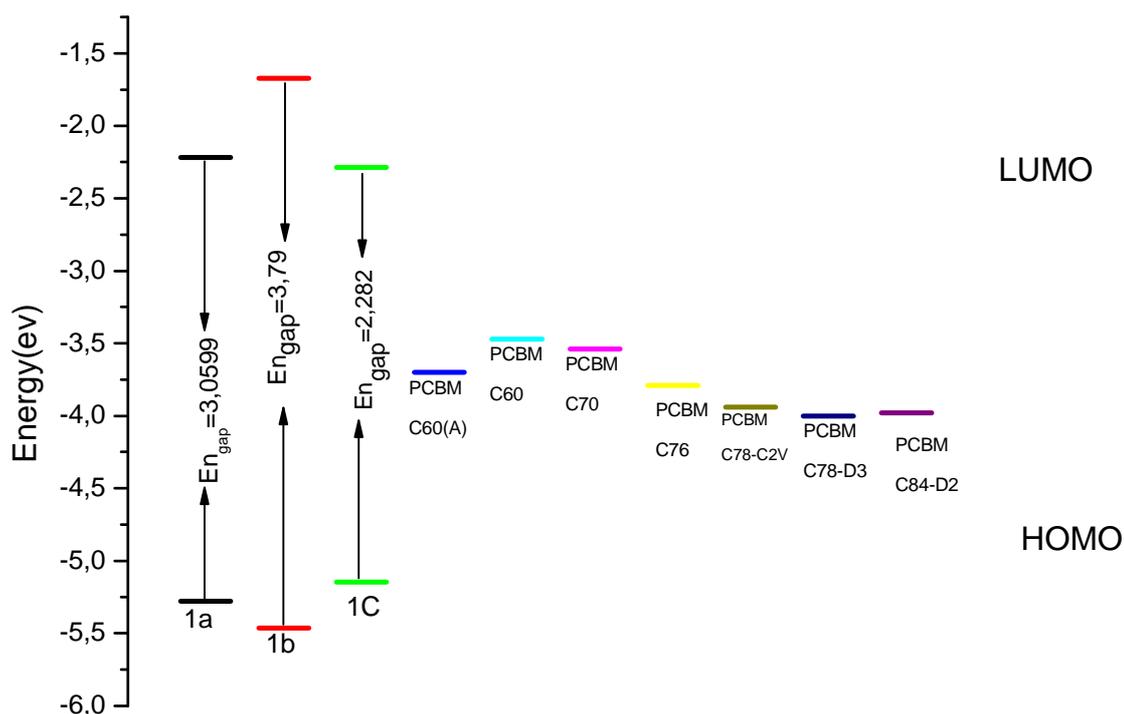


Figure 5: Sketch of DFT/B3LYP/6-31G (d) calculated energy of the HOMO, LUMO levels of studied molecules

## CONCLUSION

This study is a theoretical analysis of the geometries and electronic properties of the compounds based on TTF-pyrazine 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 the studied compounds show that they have similar conformations (quasi planar conformation). We found that the modification of the groups does not change the geometric parameters.

\* The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 3.79 eV to 2.862 eV depending on the different structures. The calculated band gap  $E_{gap}$  of the studied compound increases in the following order

1b > 1a > 1c.

\* All the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and derivatives and the subsequent regeneration are feasible in the organic sensitized solar cell.

\* The best values of Voc are indicated for the studied compounds blended with C60 (1.623eV) or C70 (1.693eV), and higher value are given for molecule **1b** blended with C70.

\* 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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