



Effect of NH₂ Substituent Group on PC₆₁BM Properties Using DFT

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ABSTRACT

The effects of the substituents and substituent positions on the structure, electronic and spectral properties of the phenyl-C₆₁-butyric-acid-methyl-ester (PC₆₁BM) using Density functional theory (DFT) and time-dependent density functional theory (TD-DFT), with hybrid functional B3LYP and 6-31G(p,d) basis sets. The results show that the values of bonds length and angles have a good agreement with previous studies. The Koopman's method which is used to calculate some important electronic variables, such as the ionization energy, electron affinity, electronegativity, and energy gap. Also, the results showed that the location of addition subgroup on the PC₆₁BM molecule effect on the characteristics studied. The addition of the NH₂ caused a redshift to the visible spectrum due to reduces the energy gap that means construct new molecular electronic structures which can be used in applications of the organic solar cells.

Key words: PC₆₁BM, DFT, TD-DFT, IR, UV-Vis spectra, Organic Solar Cell.

1. INTRODUCTION

The fullerene-C₆₀ derivative, [6,6]-phenyl-C₆₁-butyric-acid-methyl-ester (PC₆₁BM), has been widely used as an electron acceptor in polymer solar cells [1,2]. However, for commercial applications, further increase of the power conversion efficiency of the solar cells is needed. Aiming toward this goal, much effort has been dedicated to the electronic structure of PCBM, including first-principles calculations [3-10]. These works provided important information about the electronic states in the vicinity of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), but knowledge of the entire occupied valence band is absent. The influence of the phenyl-butyrac-acid-methyl-ester side chain on the electronic states of the parent C₆₀ is far from thoroughly understood. A better understanding of the principles of these molecular devices requires the information of their conformations, electronic structures, and related properties. Here, the calculations of the

geometry, electronic structure, and optical spectra of PC₆₁BM using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with hybrid functional B3LYP with basis set 6-31G(p,d) are reported. The effect of the electron donor substituents on the geometries and electronic properties of these materials were investigated and discussed. Many organic and inorganic semiconductors have been used to make a solar cell. The selection was mostly based on known materials as, till lately, experimental data was the main source for screening materials for solar cell [11]. The competence of solar cell is partially dependent on their project as a whole, attractive into consideration a diversity of factors such as the intensity of concentrated sunshine and the stacking of multi-junction cells [12]. From above, in this research study, the impact of replacing the NH₂ group in different sites instead of a hydrogen atom in the vinyl ring for the purposes of examining this substitution in solar cell application.

2. COMPUTATIONAL METHODOLOGY

The calculations were carried out using the GAUSSIAN 09 package [13]. DFT with the three-parameter compound of Becke (B3LYP) and the 6-31G basis set [14,15]. Full geometry optimizations of PC₆₁BM and PC₆₁BM molecules group were performed with Berny optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates)[16,17], was used to optimize the geometries of the studied molecules, from the stable structures of these compounds; the HOMO/LUMO energies and the band gap energy (is evaluated as the difference between the LUMO and HOMO energies) were calculated and examined. The vertical electronic, including the ionization energy IE, electron affinity EA, electronegativity X, electrochemical hardness H, and softness S. These properties are calculated at the same level of theory, and the electronic spectra were systematically investigated using TD-DFT/B3LYP/6-31G(p,d) method, on the basis of the optimized ground-

state structures. All calculations were carried out in the gas phase.

3. RESULT AND DISSOCIATION

In this work, PC₆₁BM molecule is studied theoretically, to investigate the compositional characteristics structural, electronic and spectral properties, and then studied the influence of NH₂ group in the process of replacing a hydrogen atom in a vinyl ring to the same characteristics as above.

3.1 GEOMETRICAL STRUCTURE OF PC₆₁BM PURE MOLECULE.

At first, it will be referred to the results of PC₆₁BM pure molecule in which the optimized structure of the molecules is at minimum energy. So, it is necessary to find the relaxation of the molecule. All calculations have been found at B3LYP/6-31G(p,d) density functional theory. Figure (1) shows the optimized structure of the pure molecule and Table (1) contain the bond length in Angstrom (Å) and angles in degree (deg).

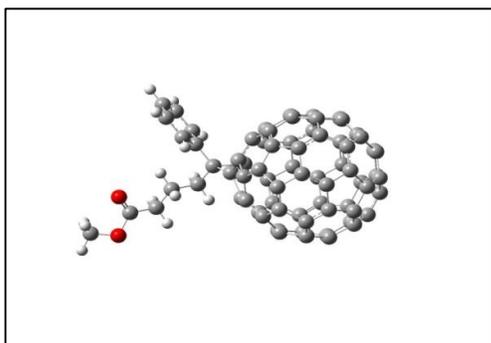


Figure 1: The optimized structure of the PC₆₁BM pure.

From Table (1) which represent the optimized structure of the pure molecule, it is clear that the bonds (C–C, C≡C, C–H, C=O, C–O) are found to be respectively (1.487, 1.309, 1.092, 1.235, 1.471) Å, where (C–C) bond is the longer than the other bonds in the molecule. Convergent bonds lengths with other some theoretical previous studies are proof that the accounts were accurate.

The angles ((C–C–C), (C–C≡C), (C–C–H), (C≡C–H), (H–C–H), (C–O–C), (C–C–O), (C–C=O), (O=C–O)) are calculated, and which have a range of dimensions between (108.452–107.981, 123.324–120.392, 110.004–109.178, 120.149–119.753, 106.302–105.277, 118.729, 111.058, 122.265, 122.675). It was a clear convergence of some corners with some previous theoretical studies, and this is proof that the accounts were accurate.

3.2 ELECTRONIC PROPERTIES OF PC₆₁BM PURE MOLECULE.

To study the electronic properties of the PC₆₁BM pure molecule. HOMO, LUMO band gap energies are useful parameters for the study. Also, the HOMO and LUMO energies were obtained by DFT/B3LYP/6-31G(p,d) were calculated according to the Koopman's theorem. The calculated energy gap of P C₆₁BM pure n-type semiconductor with energy gap equal 2.566eV, these properties are included the ionization energy IE, electron affinity EA, electronegativity X, electrochemical hardness H, and S, were calculated at the same level of theory. The results of measurements (-V/T) calculated to infer program V is the potential energy of the molecule and is twice the kinetic energy T negative tag, that corresponds to the operative part of the viral theory for molecules are non-relative, such as a molecule (PC₆₁BM) that means that electronic theory calculations were accurate.. as shown in Table (2).

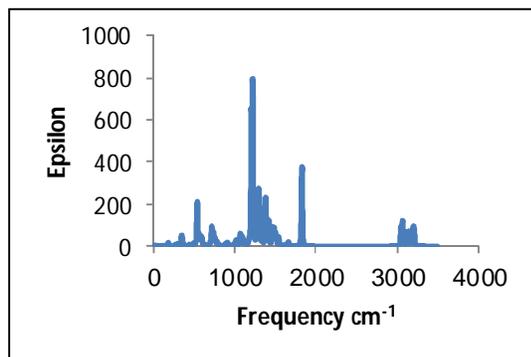
Table 2: The results of some electronic properties of PC₆₁BM.

Property	Current study
E _{HOMO} (eV)	-5.657
E _{LUMO} (eV)	-3.091
E _g (eV)	2.566
ET (a.u.)	-2902.354
-V/T	2.009
IE(eV)	5.657
EA(eV)	3.091
X(eV)	4.374
H(eV)	1.283
S(eV) ⁻¹	0.389

3.3 IR SPECTRUM OF PC₆₁BM PURE MOLECULE.

IR-Spectrum of a molecule PC₆₁BM are shown in Figure (2). Calculation of spectrum IR depends on the vibrational frequencies constituent atoms of a molecule, this Higher vibration this molecule was of type (C–C) bond, and the strong peak observed at (1220 cm⁻¹) as shown in Figure (2), and this vibration is the result of the vibration of the additives C₆₀ ball, and this vibration of type stretching.

Figure 2: The calculated IR-Spectrum of PC₆₁BM.



3.4 ABSORPTION SPECTRUM OF PC61BM PURE MOLECULE.

UV-Vis spectrum of the investigated reference molecule (PC₆₁BM pure) using DFT-B3YLP/6-31G(p,d), as shown in Figure (3). The figure shows high absorption in the UV region occurs within a wavelength (366.6nm). This wavelength is not used in the application of solar cell being located in the UV area and far from the visible area, so that this material was not helpful being pure and always be useful when mixed into polymer material for obtaining spectral shift, Its gentle absorption within the visible region as the reference (23).

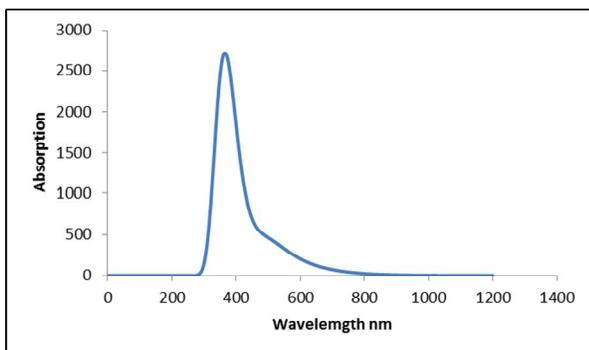


Figure 3: The UV-Vis Spectrum of PC₆₁BM.

3.5 SUBSTITUENT OF A HYDROGEN ATOM BY COMPENSATING NH₂ GROUP.

Will substitute a unit of hydrogen atoms in the benzene ring terminals in C₆₀ substitution group like NH₂. for the purpose to know the impact of this group on the molecule's properties and its applications. The replacement process was different positions with a benzene ring (Ortho, Meta, and Para), in order to study this effect, we study the following characteristics the structure, electronic, and spectral properties.

3.5.1 GEOMETRICAL STRUCTURE AFTER SUBSTITUENT NH₂ GROUP.

When added NH₂ substituent to the PC₆₁BM pure molecule at a different position in the benzene ring at the sites (Ortho, Meta, and Para), it is expected to appear on new properties. Figure (4) show the optimized structure of the new molecules after addition of the NH₂ group (Ortho, Meta, and Para). Table (3) represented some of the new bonds in (Å) and angles in (deg) that have appeared after the addition of NH₂ group in the positions (Ortho, Meta, and Para). The Table shows some bonds and angles that appeared after substituting a hydrogen atom in benzene ring with a compensating group (NH₂), and there was a similarity with some previous theoretical studies.

3.5.2 ELECTRONIC PROPERTIES AFTER SUBSTITUENT NH₂ GROUP.

Table (4) illustrates the high occupied molecular orbital energy E_{HOMO}, lower unoccupied molecular orbital energy E_{LUMO}, and the energy gap of molecules after addition NH₂ group (Ortho, Meta, and Para). From this table, the addition of NH₂ groups affects both HOMO and LUMO energies, but its effect on HOMO energy is more than on LUMO energy. In general, the main change that occurs at the HOMO level depends on NH₂ groups located in the PC₆₁BM pure. All molecules after the addition have an energy gap smaller than that of the pure molecule, but the smallest is at (Ortho).

Table 4: The E_{HOMO}, E_{LUMO}, and Eg in eV of (Ortho, Meta, and Para) molecules after substituent NH₂ group.

Molecule	E _{HOMO} (eV)	E _{LUMO} (eV)	Eg(eV)
Ortho	-5.499	-3.213	2.286
Meta	-5.459	-3.169	2.290
Para	-5.479	-3.142	2.337

Table (5) declares the results of the total energy E_T in a.u. and some computed electronic properties in eV of molecules after the addition of the NH₂ group (Ortho, Meta, and Para), calculated depending on Koopman's theorem. These calculations included the ionization energy IE, electron affinity EA, electronegativity X, electrochemical hardness H and electronic softness S and -V/T. It is clear from this table that the total energy of the substituent group is less than the total energy of the reference molecule (PC₆₁BM). The total energy decreased with different location of NH₂ groups added to the reference molecule, the substituent group have low values of IE and high values of EA in comparison with the reference molecule. Adding the NH₂ groups reduced the IE and increased the EA of the PC₆₁BM. Meta molecule has the smallest value of IE; this means that molecule needs small energy to become cations in comparison with the others. The electronegativity X of the studied molecules

after addition that has less than that for a pure molecule. It is clear from the table that the electrochemical hardness of all studied molecules is smaller than that for PC₆₁BM. The decreasing of electrochemical hardness is the main upcoming, and as shown to that band gap goes to be rather soft and lowering the resistance of these structures to lose an electron. The increasing of softness corresponds to the decreasing in the hardness refers to that these molecules have small band gaps compared with PC₆₁BM.

3.5.3 IR SPECTRUM AFTER SUBSTITUENT NH₂ GROUP

According to $3N-6$ was calculated the number of vibrational modes of the spectrum, where N is the number of atoms in the molecule, Figure (5-7) show the infrared IR-Spectrum of PC₆₁BM molecule and the addition of subgroups in the PC₆₁BM pure included the relationship between the intensity of the spectrum and the corresponding frequency. The vibrational modes have been increased with increasing of bonds in the molecule. The IR-Spectra of PC₆₁BM pure and substituent group of molecules showed that the differences between them are coming from the addition (NH₂) of PC₆₁BM pure in a different position. The vibrational modes have been increased with increasing of bonds in the molecule. The strong peaks from IR come from very different normal modes. The frequency range of the normal modes. The strongest IR absorption corresponds to the high-frequency vibrational mode 246 with a frequency of 3044cm⁻¹, which is the stretch movement of C-H bond in the carbonyl group. The next stronger IR absorption is attributed to the vibrational mode 263 at 3640cm⁻¹, corresponding to the bond bending movement of N-H bonds in butyric acid methyl ester.

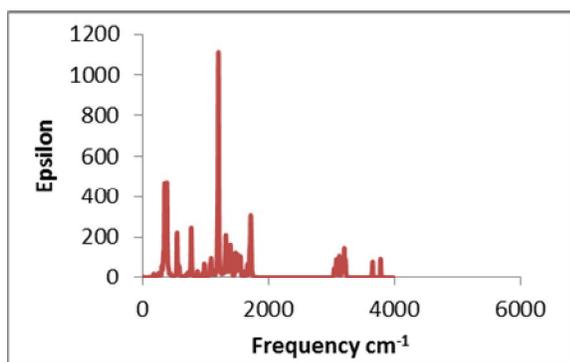


Figure 5: The calculated IR-Spectrum of Ortho molecule after substituent NH₂ group.

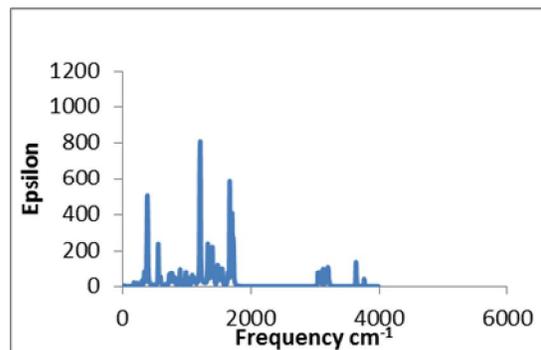


Figure 6: The calculated IR-Spectrum of Meta molecule after substituent NH₂ group.

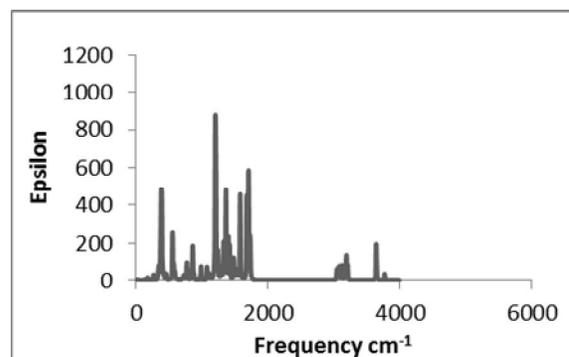


Figure 7: The calculated IR-Spectrum of Para molecule after substituent NH₂ group.

3.5.4 ABSORPTION SPECTRUM AFTER SUBSTITUENT NH₂ GROUP.

The absorption spectrum for molecules (Ortho, Meta, and Para) after substituent NH₂ group in gas phase mod with different position, was recorded compared, as shown in Figure (8). The figure shows three spectra in the visible region at the range about (590.3-612.2-628.8) nm. The reason for red shifting in UV-Vis spectra addition subgroups (NH₂) in a different location for PC₆₁BM pure amount 610.4nm due to decreasing energy gap, due to generating secondary levels between (HOMO and LUMO) around Fermi level. The peak maxima in UV-Vis spectra move from (366.6 nm) for a pure molecule to (628.8 nm) for Ortho. The reason for high shifting for Ortho molecule in comparison with other molecules under study due to of high ionic charges on Ortho caused by the position of addition with respect to another location of the subgroup.

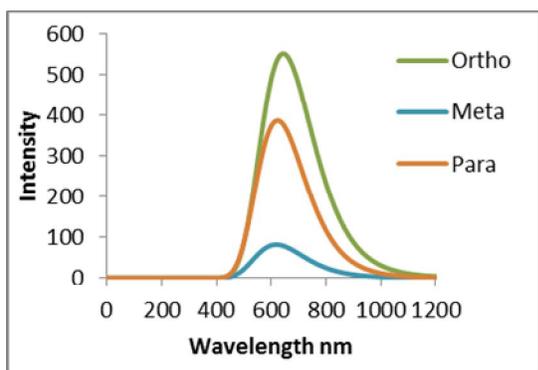


Figure 8: The UV-Vis Spectrum of molecules (Ortho, Meta, and Para) after substituent NH₂ group.

4. CONCLUSION

From the results, the strong peaks from IR come from very different normal modes. The strongest IR absorption corresponds to the high-frequency vibrational mode, which is the stretch movement of C-H bond in the carbonyl group. The next stronger IR absorption is attributed to the vibrational mode, corresponding to the bond bending movement of N-H bonds in butyric acid methyl ester. Also, the results show that the designed molecules after addition NH₂ group to reference molecule are possible can be used as solar cells, but the Ortho molecule is better than the other molecules under study. The absorption spectra of Ortho calculated in a maximum absorption, for decreasing the gap and consequently increase the absorbance of emitted photons for any molecules. The addition of NH₂ to three different location improved the properties of the molecule due to a redshift in the UV-Vis spectrum, and this is useful in the work of the solar cells. Ortho molecule was the preferred location for the three sites because it had the highest absorption.

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Table 1: The bond length (in Å) and angle length (in degree) of PC₆₁BM pure.

Bonds	Value	Previous studies	Angle	Value	Previous studies
c-c	1.487	1.534-1.456 [18]	(C-C-C)	108.452-107.981	108.012 -107.986 [21]
C...C	1.309	1.437-1.306[19]	(C-C...C)	123.324-120.392	126.170 -120.186 [20]
C-H	1.092	1.100-1.093[20]	(C-C-H)	110.004-109.178	----
C=O	1.235	1.247 -1.231 [21]	(C...C-H)	120.149-119.753	----
C-O	1.471	1.478 -1.374 [22]	(H-C-H)	106.302-105.277	-----
			(C-O-C)	118.729	118.986 -118.866 [22]
			(C-C-O)	111.058	-----
			(C-C=O)	122.265	123.525 -120.172 [22]
			(O=C-O)	122.675	-----

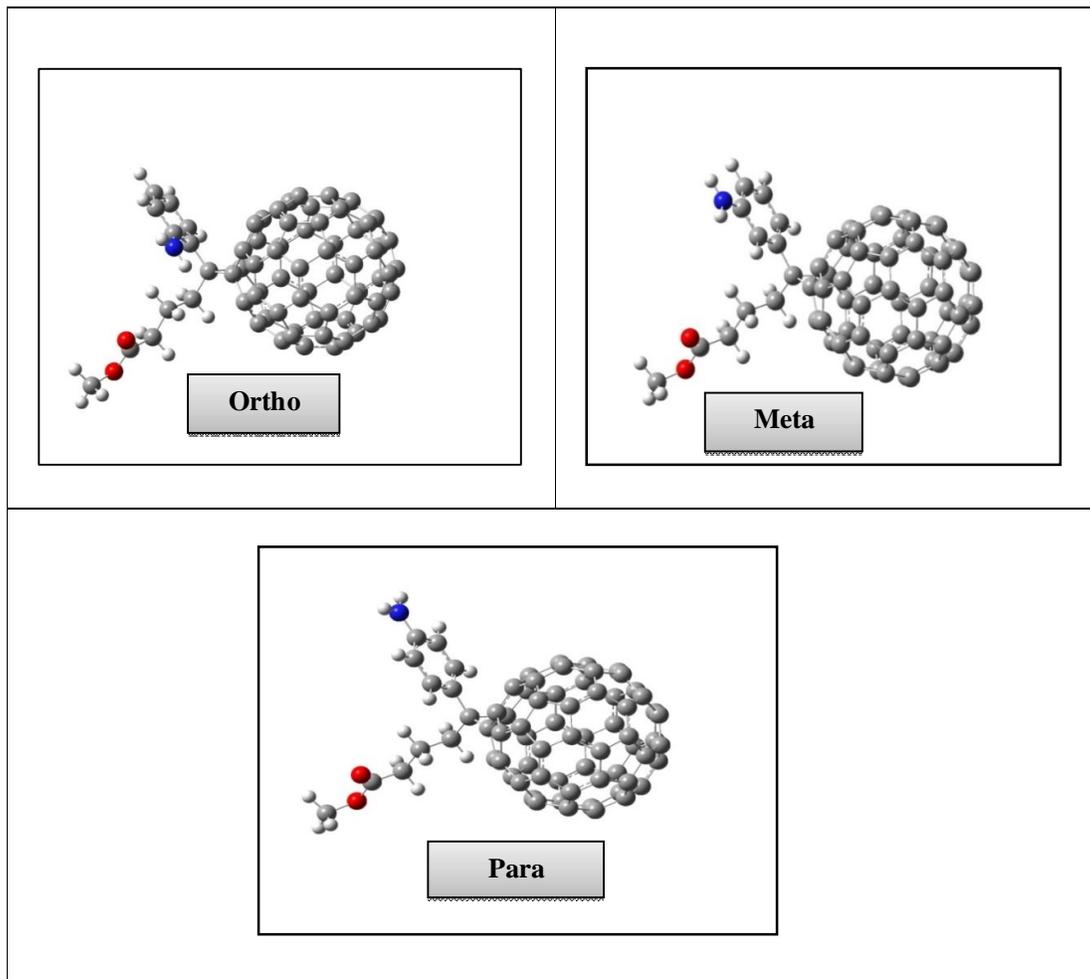


Figure 4: The optimized structure of the molecules after additional NH₂ group.

Table 3: The bond length (in Å) and angle length (in deg) after substituent NH₂ group (Ortho, Meta, and Para).

Molecule	Bonds	Value	Previous studies	Angle	Value	Previous studies
Ortho	N-H	1.004	----	(C-N-H)	122.675 120.201	120.121 -119.782 [22]
	C-N	1.382	1.467-1.365 [22]	(H-N-H)	117.543	----
				(C=C-N)	119.835	----
Meta	N-H	1.004	----	(C-N-H)	121.053	----
	C-N	1.383	1.467 -1.365 [22]	(H-N-H)	117.909	----
				(C=C-N)	120.481	----
Para	N-H	1.004	----	(C-N-H)	121.058	----
	C-N	1.352	1.467 -1.365 [22]	(H-N-H)	117.916	----
				(C=C-N)	120.918	----

Molecule	ET (a.u.)	-V/T	IE (eV)	EA (eV)	X(eV)	H (eV)	S (eV) ⁻¹
PC ₆₁ BM-Ortho	-2956.913	2.0052	5.499	3.213	4.356	1.143	0.437
PC ₆₁ BM-Meta	-2956.916	2.0052	5.449	3.169	4.309	1.140	0.438

Table 5: The calculated electronic properties in eV of (Ortho, Meta, and Para) molecules group.