

Effect of π -conjugated Molecules on Electronics Properties of Benzene-diamine Derivatives

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Abstract

The present work shows a theoretical results that have been used the functional Hybrid of three parameters Lee-Yang-Parr (B3LYP) of the quantum mechanical approach for density functional theory with (Spanish Initiative for Electronic Simulations with Thousands of Atoms) SIESTA code. All calculations were carried out employing the used method at the Gaussian 09 package of programs. It was reported the main point for research on dominance of the bandgap of elongated pi-conjugated molecules by using different chemical groups replacing hydrogen atom in the most molecules that used in this work. The side groups creates another factor that controls the value of the band gap. The dihedral angle between the two phenyl rings plays more important role in controlling the band gap in these molecules.

Article Info.

Keywords:

Electronic properties, dihedral angle, conjugated system, SIESTA code.

Article history:

Received: Dec. 03, 2020

Accepted: Apr. 11, 2021

Published: Sep. 01, 2021

1. Introduction

Understanding the effect of a chemical structure on the electronic properties of molecular devices that is more important for nanoelectronics. In the last decades, the band gap in molecular junctions was studied and made possible by techniques depending on statistics of distributions of considerable numbers of junction measurements [1-3]. Therefore, pi-conjugated molecules have gained significant interest due to their electronic properties, tunable and wide range of its applications [4, 5]. Particular attention has been dedicated to low-bandgap pi-conjugated orbitals firstly, due to their special electronic characteristics, and recently on account of their orbitals to interact in the two phenyl rings. In addition, the used technique of torsion angle is effective according to the affinity of determined chemical ligand groups. Thus, it has clearly been shown that variations in binding energy from junction to junction are responsible for the most width range of energy gap and for the nature of the linker-between two rings in the most molecules and dihedral angles [2, 6].

The band gap of pi-conjugated orbitals depends on the degree of an aromatic property of the backbone [6-8]. Therefore, to design low bandgap molecular devices, the donor/or acceptor groups [9] might be used to control the value of charge transport from/or molecules to side groups. Furthermore, the chemical structure aromaticity's of fused benzo/ or heterocyclic ring compels a pyridine structure on the main body, which produces a low bandgap and a substantial tendency to preserve planarity. Thus, the role of pi-conjugated system in these molecules is control value of bandgap energy that is more important in organic electronic [10, 11], and photovoltaic applications [12]. As well as, in the case of the amine (NH₂) anchor group for example, the nitrogen changes its attachment point, while maintaining binding energy as the junction is elongated due to remain bound to the under-coordinated C-C atoms.

This work presents the molecular structures of the series molecules that are used to calculate the band-gap energy at different side groups, which lead to various dihedral angles between two phenyl rings in the most molecules. Six molecules were used which are benzene-1, 4-diamine (1), biphenyl-4,4' -diamine (2), 2-methylbiphenyl-4,4'-diamine (3), 9H-fluorene-2,7-diamine (4), 2,2' -dimethylbiphenyl-4,4'-diamine (5), and 9,10-dihydrophenanthrene-2,7-diamine (6). The anchor group in these structures is amine (NH₂). Hence, we designed the molecules according to examine the effect of side groups on the band gap due to changes in bond length between the backbone and side group for each molecule as shown in Fig1.

In addition, we have seen the difference of side group in these structures, which appear to be another factor to change the value of the band gap that is called the twist angle, in particular (2, 3, 5, and 6) molecules. These molecules have different twist angle between rings due to the increased interactions between the pi orbitals for each ring, which leads to increase the overlap between adjacent rings.

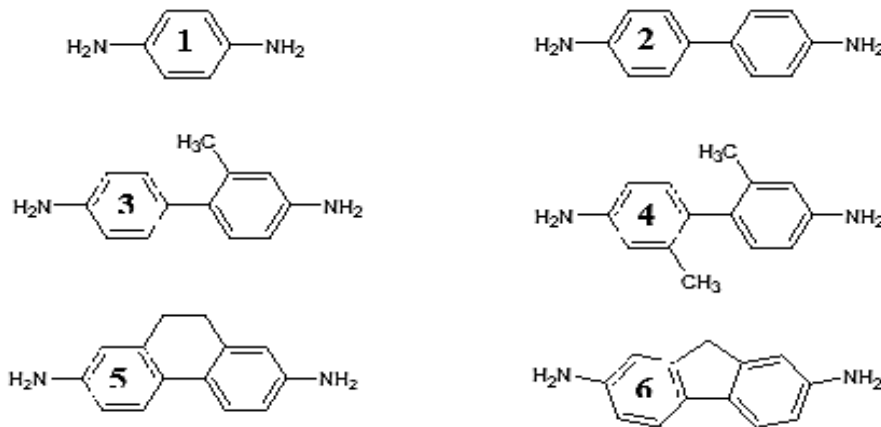


Figure 1: Molecular structures of biphenyl molecules with terminal group amine (NH₂) with varying bridge-link atoms [13].

In this study, we have used family molecules, which are shown in Fig.1. Each molecule has structural characteristics, electronic properties, and dihedral angle. The frontier orbitals were drawn for each structure. Switching and electronics devices are the main applications for these molecules as represents control value of pi-orbitals between two phenyl rings.

2. Computational methods

The band gap for family molecules was calculated. All molecular structures were carried out using DFT-based SIESTA code [14], as well as the Generalized Gradient Approximation (GGA)–PBE functional, double- ξ polarized basis set, and mesh cutoff 250 Ry. These were used to calculate the total energy for each molecule. In addition, the Gaussian 09 package with the B3LYP level was used to calculate the band gap between HOMO and LUMO energy level for each molecule, using Eq. (1) [15]:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

where E_{gap} denotes the energy gap. The ionization potential (I_E) is defined as the quantity of energy needed to remove an electron from an isolated atom (or molecule). It is expressed as the difference between the positive-charged energy (E^+), and the neutral (E_n) as the relation: $I_E = E^+ - E_n$. Also, the electron affinity (EA) of an atom (molecule) is the energy change when an electron is added to the neutral atom to form a negative ion and is expressed as the energy difference between the neutral. Energy (E_n)

and the negative-charged energy (E_-) according to the relation: $E_n = E_n - E_-$. Thus, the HOMO and LUMO energies were used to compute in the framework of Koopmans theorem as shown [16]:

$$I_E = -E_{\text{HOMO}} \quad (2)$$

$$E_A = -E_{\text{LUMO}} \quad (3)$$

3. Results and discussions

The electronic properties were calculated for the six molecules. DFT-based SIESTA code²⁴ was used to calculate the total energy for each molecule with different dihedral angles according to the various side groups. In addition, the Gaussian 09 package [17] with the B3LYP level was used to calculate the band gap between HOMO and LUMO energy levels for each molecule. Using Eq. (1), the band gap was calculated, as shown in Table 1. It can clearly be seen that the lowest value is (0.16186 eV) for molecule 4, while the highest value is (0.1925 eV) for molecule 5. This is reasonable to reach to know the factor behind this difference between these molecules. The lowest value of the band gap for molecule 4 is due to the dihedral angle, which is 0° in this structure, as shown in Table 2. This means that the overlap in this case is of maximum value. The charge transport through molecule 4 is greater than the other molecules due to the 0° angle between the two rings [18] as shown in Fig.2. A new map for bandgap control in the pi-conjugated molecules is represented by substituting the (CH_3) atoms with a hydrogen atom in the main body and/or phenyl rings as shown in Fig.1.

Table 1: E_{HOMO} , $E_{\text{HOMO}-1}$, E_{LUMO} , $E_{\text{LUMO}+1}$, and E_{gap} in eV of six molecular structures.

Ms	HOMO (eV)	HOMO-1 (eV)	LUMO (eV)	LUMO+1 (eV)	$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)
1	-0.14660	-0.23068	0.02346	0.06731	0.17006
2	-0.17212	-0.19043	0.01353	0.02605	0.18565
3	-0.17071	-0.18968	0.01575	0.02646	0.18646
4	-0.15524	-0.20119	0.00662	0.01695	0.16186
5	-0.17086	-0.18699	0.02164	0.02655	0.1925
6	-0.15890	-0.20040	0.01216	0.01561	0.17106

Table 2: Ionization Potential I_E , Electron Affinity E_A , and Dihedral angle (α) of family molecular structures.

Ms	I_E (eV)	E_A (eV)	Dihedral angle (α)	Total energy (eV)
1	0.14660	-0.02346	-	-1660.34
2	0.17212	-0.01353	41°	-2696.89
3	0.17071	-0.01575	51°	-2891.44
4	0.15524	-0.00662	0°	-2859.28
5	0.17086	-0.02164	66°	-3086.02
6	0.15890	-0.01216	19°	-3053.91

Fig.3 (a) shows the total energy as a function of molecular structures that were used in this work. The total energies for family molecules were calculated, and the difference between these structures is clearly seen. This is because of the chemical group at the edge of these molecules. Fig.3 (b) illustrates the total energy as a function of the dihedral angle of family molecules. The vibrational values of the total energy due to different dihedral angle can be deduced from this figure and are listed in Table 2.

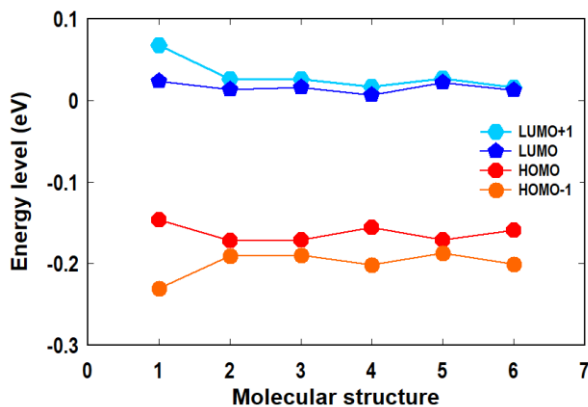


Figure 2: Comparison of the calculated energy levels of family molecular groups.

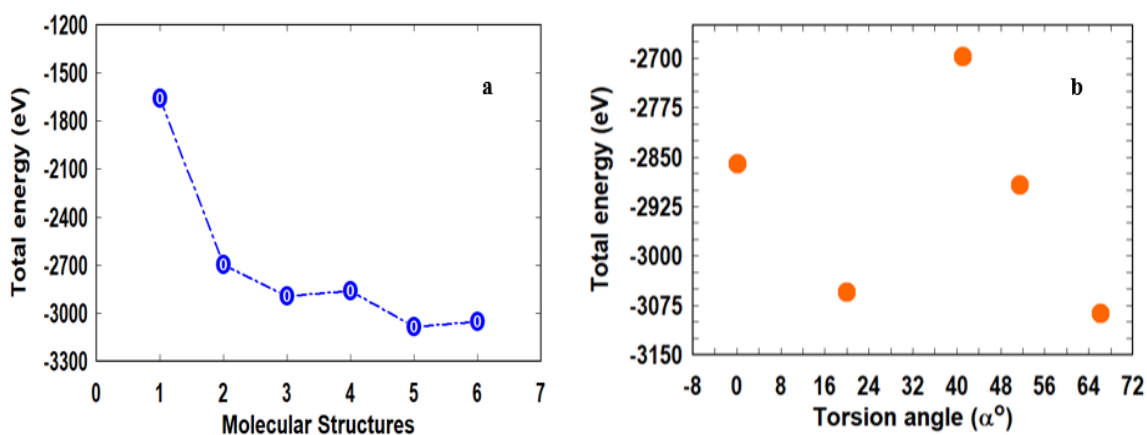


Figure 3: (a) The total energy as a function of molecular structures at different chemical group, (b) Total energy as a function of dihedral angle for six molecules.

Fig. 4 shows the various values of the dihedral angle for six molecules due to the side groups that were using it to know and study the special interest has been dedicated to low-bandgap pi-conjugated in organic materials due to their especial electronic properties and lately on account of their ability to efficiently absorb solar light. Thus, the promise they present as structures to enhance photovoltaic cells.

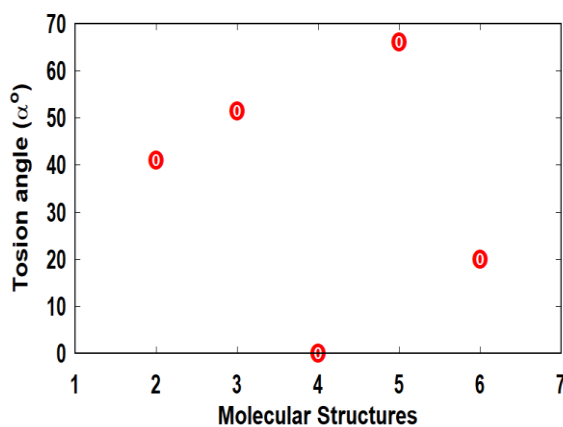
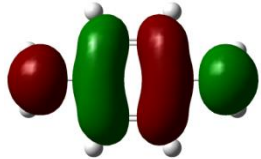
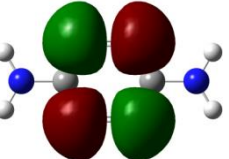

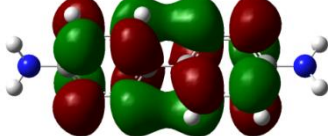
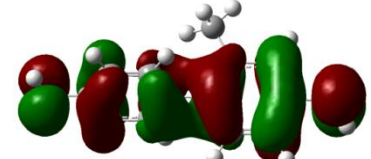
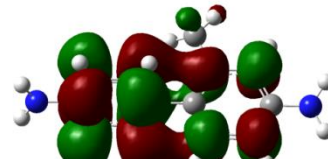
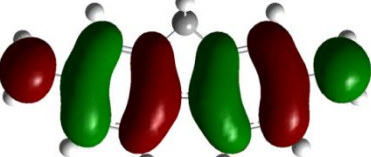
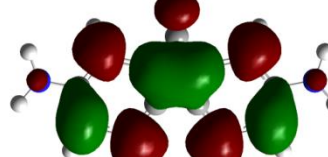
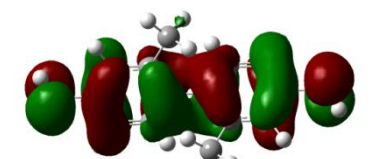
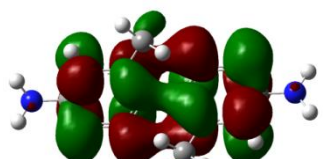
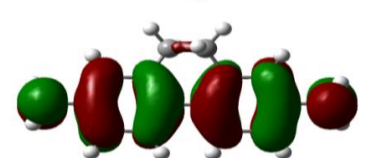
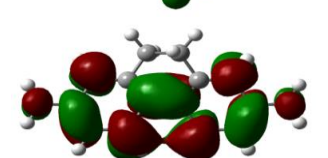


Figure 4: Dihedral angle as a function of molecular structures for six molecules.

Table 3 shows the Frontier Orbitals for these structures with the band gap, and explains the amount or the weight of the focus of charges either in the backbone or at the ends of molecules.

Table 3: The Frontier Orbitals for six molecular structures at different side groups with band gap energy by eV.

No.	HOMO (eV)	LUMO (eV)	$E_g = E_{LUMO} - E_{HOMO}$ (eV)
1			0.17006
2			0.18565
3			0.18646
4			0.16186
5			0.19741
6			0.17451

4. Conclusions

In this paper, the electronic properties of geometrical structures for biphenyl molecules were calculated using theoretical method, this indicates to a good relax obtained for these molecules. The study presents a strategy for the bandgap domination in very low value of bandgap (less than 1.0 eV) molecular structures. A family of latest low-bandgap pi-conjugated molecular structures, which produces to significant and expected, varies in the bandgap of the molecules. In addition, we have seen that the charge transport was important in order to know the central charge either in the backbone or in the side groups. Thus, to control the range of the bandgap, these structural parameters define the range and pi-pi conjugation, and the electronic distribution in the pi-conjugated molecule, as well as here the charge transport properties of the materials.

Acknowledgements

The authors would like to thanks College of Science at University of Babylon to support us to do this work.

Conflict of interest

Authors declare that they have no conflict of interest.

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تأثير الجزيئات المترافقة-pi على الخواص الالكترونية لمشتقة البنزين-ثنائي الامين

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الخلاصة

يعرض العمل الحالي النتائج النظرية التي استخدمت دوال الهجين لثلاث معلمات (B3LYP) Lee-Yang-Parr للنهج الميكانيكي الكمومي للنظرية الوظيفية للكثافة للحالة مع برنامج السياسة SIESTA. تم إجراء جميع الحسابات باستخدام الطريقة المستخدمة في حزمة برامج الكاوسيين Gaussian 09. ان النقطة الرئيسية للبحث هيمنة حزمة فجوة للجزيئات المترافقة pi الممدودة باستخدام مجاميع كيميائية مختلفة لتحل محل ذرة الهيدروجين في معظم الجزيئات المستخدمة في هذا العمل. عملت المجموعات الجانبية عاملاً آخر يتم التحكم في قيمة فجوة النطاق. لعبت زاوية الالتواء بين حلقتين في نيل دوراً أكثر أهمية في التحكم في فجوة النطاق في هذه الجزيئات.