Theoretical study for the interactions of Coronene-Y interactions by using Density functional theory with hybrid function

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Abstract

Molecular geometry and contours have been investigated for Coronene and Coronene-Y molecules throughout the geometrical optimization procedure by using density functional theory (DFT) at 3-21G and B3LYP basis sets. Infrared spectra (IR) demonstrates new bonds belong to Carbon -Y atoms after the interaction. Contours show increasing electrons charges near Y atoms beyond the interaction. Donor and acceptor properties have been studied throughout comparison highest occupied molecular orbital energies of Coronene and individual atoms. Energyband gap for Coronene-P approach to the energy gap of Gallium Arsenide (GaAs). Electronegativity and electrophilicity calculate to the molecules under the study. Dipole moment and polarizability compute. Symmetry shows new point groups after adding Y atoms to Coronene. Density of states diagrams show the anti-ferromagnetic material property for Coronene-S and Coronene-Se.

Where Y: refer to atoms (P, S, Se, Zn, Cl, F)

Keywords: DFT, Infrared Ray, HOMO(Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital), DOS, Symmetry, Electrophilicity.

دراسة نظرية لتاثير تفاعل مادة الكورونين مع بعض العناصر باستخدام دالة DFT

م. محمد لطيف جبار

الخلاصة

تم نمذجة مادة الكورونين للحصول على افضل استقرار هندسي للجزيئات, ثم تمت اضافة عناصر انتقالية للمادة و كذلك نمذجتها, وقد تم ذلك باستخدام برنامج الكاوسين 09 للدالة DFT

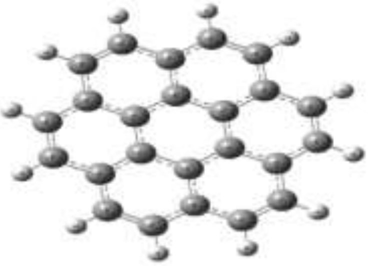
عند المستوي 3-21G وعند دالة الاساس B3LYP. حيث تم حساب طيف الاشعة تحت الحمراء لجميع المركبات و معرفة القمم للمركبات الجديدة التي ظهرت نتيجة تشكيل الاواصر بين الذرات المضافة و ذرات الكاربون الموجودة في مركب الكورونين و كذلك تم حساب دالة كثافة الحالة لمعرفة اي المركبات هو المانح وايها هو الواهب و معرفة فجوة الطاقة للمركبات التي تم حسابها وقد اظهرت النتائج النظرية ان فجوة الطاقة صغيرة مقارنة ببقية الذرات عند اضافة ذرة الفسفور للمركب.

1. Introduction

Thomas-Fermi model is the predecessor of density functional theory (DFT)[1]. Density functional theory is one from common, diversified and active methods at large areas in present days in computational physics, computational chemistry and even nuclear physics [2]. DFT is an approach used for description of the ground state properties of metals, insulators and semiconductors [3]. DFT has been succeeded not only encompasses standard bulk materials, but also complex materials such as proteins and carbon nanotube [4]. The main notion of DFT is describing an interacting system of fermions throughout density instead of many body wave function [5]. In solids for N-electron system, DFT obey Pauli's exclusion principle and repulsion potentials via Coulomb potential, i.e. the basic variable of the system depend on three spatial coordinates and rather than 3N degrees of freedom [6]. If someone know the exact electron density, the cusps of this density would occur at the positions of the nuclei[7] . Local density approximation (LDA), local spin density approximation and generalized gradient approximation are very important approximations in DFT [8]. Becke three parameters Lee-Yang-Parr (B3LYP) which is called the hybrid functional is good choice in order to investigate the geometry optimization in DFT [9].

2. Molecular structure

The molecular structure results from the electronic configuration of atoms in the molecules. It is proposed the molecular orbital theory to explain nature of the formation orbitals. One of the most effective rules contributes in the molecular structure such as Pauli's exclusion principle. Interelectronic repulsion, electron penetration toward the nucleus and nuclear shielding also effect on the molecular geometry[10] .



Coronene

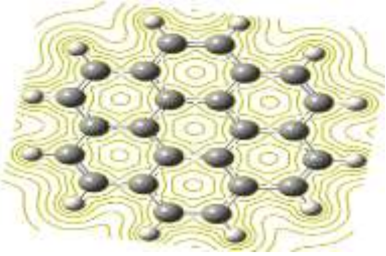
Coronene-P Coronene-S Coronene-Se

Coronene-Zn Coronene-Cl Coronene-F

Figure(1) The molecular structure for Coronene and Coronene-Y.

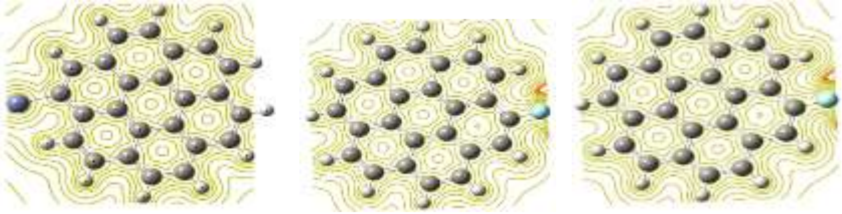
3. Electrostatic Potential (ESP)

It is very appropreiate to express of contours by the electrostatic potential because contours show the static charge distribution around the atoms. Contours also demonstrate the electron density at different regions of the molecule, one can say it denotes to electrons concentration at certain region. Electrostatic potential maps are bases on the molecular orbitals data [11].



Coronene

Coronene-P Coronene-S Coronene-S

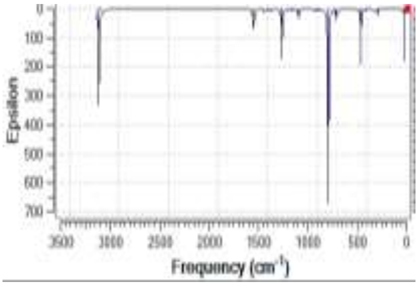


Coronene-Zn Coronene-Cl Coronene-F

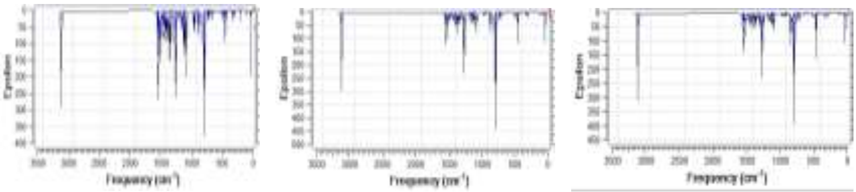
Figure(2) Electrostatic potential for Coronene and Coronene-Y

4. Infrared spectra

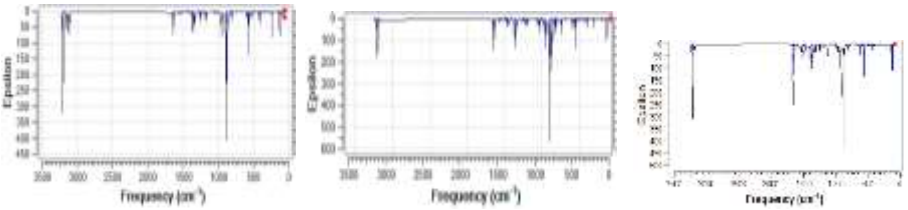
There are two kinds of stretching oscillations symmetric and asymmetric. The symmetric stretching is taking place when similar atoms oscillate in similar phase, while asymmetric stretching is happening when the bonds oscillate in variety phases. Infrared spectra yields harmonic vibrational frequencies. Low frequencies give torsion vibrations. The number of atomic modes depend on the number of atoms in the molecule. Vibration either elastic or inelastic [12]



Coronene



Coronene-P Coronene-S Coronene-Se



Coronene-Zn Coronene-Cl Coronene-F

Figure(3) Infrared spectra for Coronene and Coronene-Y.

5. Calculations

5.1. Individual atoms

Table (1) shows HOMO, LUMO and electronegativity for the individual atoms.

atom	HOMO(eV)	LUMO(eV)	Electronegativity(eV)
P	-5.7306981	-4.8806577	5.3056779
S	-7.4370372	-6.5200602	6.9785487
Se	-6.5257743	-5.8675644	6.19666935
Zn	-5.7845739	-0.5779404	3.18125715
Cl	-11.059776	46.7914044	-17.8658139
F	-9.5624103	11.9427411	-1.1901654

5.2. Electronic states

HOMO and LUMO energies are the electronic states, it refers to certain places to existence of the electrons with quantized energies, in which HOMO energy indicates to high occupied molecular orbital, while LUMO energy point out low unoccupied molecular orbital, where the molecular orbitals are the linear combination to the atomic orbitals. The difference between HOMO and LUMO gives energy band gap (E_g) as the relation [13]:

$$E_g = E_{LUMO} - E_{HOMO} \qquad \ldots \quad (1)$$

Table (2) demonstrates electronic states for Coronene and Coronene-Y

System	HOMO(eV)	LUMO(eV)	Eg(eV)
Coronene	-5.6142393	-1.4818566	4.132383
Coronene-P	-4.3802658	-3.4616562	0.91861
Coronene-S	-5.6724687	-1.8306888	3.84178
Coronene-Se	-5.5758732	-1.7411679	3.834705
Coronene-Zn	-4.742703	-1.6062063	3.136497
Coronene-Cl	-5.809335	-1.7155905	4.093745
Coronene-F	-5.6659383	-1.6255254	4.040413

5.3. Electronegativity and Electrophilicity

The electronegativity can be defined as the measure of tendency of an atom to attract bonding pair of electrons, so one can say it describes the escaping tendency of the electrons from balance system such as atoms of molecules. Electronegativity and electrophilcity can be calculated respectively from the relations [14]

$$\chi = \frac{E_{HOMO} + E_{LUMO}}{2} \qquad \ldots \quad (2)$$

$$\omega = \frac{\chi^2}{2\eta} \qquad \ldots \quad (3)$$

Table (3)Electronegativity and electrophilicity for Coronene ad Coronene-Y

System	Electronegativity(eV)	Electrophilicity (eV)
Coronene	3.54804795	1.291590487
Coronene-P	3.920961	2.901358119

Coronene-S	3.75157875	1.479291083
Coronene-Se	3.65852055	1.42231135
Coronene-Zn	3.17445465	1.278957598
Coronene-Cl	3.76246275	1.429467061
Coronene-F	3.64573185	1.369346776

5.4. Dipole moment

Dipole moment represents the multiplying of the charge by the displacement. It appears I hetronuclear molecules, while homonclear molecules have no dipole moment. The dipole moment is given by the following equation [15]:

$$P = q * r \qquad \dots \quad (4)$$

Table (4) shows Dipole moment for Coronene and Coronene-Y

System	Dipole moment(Debye)
Coronene	0.0000
Coronene-P	5.1798
Coronene-S	4.7433
Coronene-Se	3.4471
Coronene-Zn	0.8359
Coronene-Cl	2.8214
Coronene-F	1.5937

5.5. Polarizability

Throughout the polarizability one can know that the molecule will be polarized or not. Polarizability determines the linear response to the electron density in presence an infinite seminal electric field F. It stands for second order variationin the energy. Polarizability is expressed by the relation [16]:

$$\alpha = \left(\frac{\partial^2 E}{\partial F_a \, \partial F_b}\right)_{a,b} = x, y, z \qquad \dots \quad (5)$$

Mean of the polarizability $\langle\alpha\rangle$ is given by the relation [17]:

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \qquad \dots \quad (6)$$

In which α_{xx} , α_{yy} and α_{zz} are the eigen values of the polarizability tensor. Polarizability is good property to give vision about the internal structure of the molecule.

Table(5) Polarizability for Coronene and Coronene-Y

System	α_{xx}	α_{yy}	α_{ZZ}	$\langle\alpha\rangle$
Coronene	349.857	349.82	51.266	250.3143333
Coronene-P	480.356	357.738	62.423	300.1723333
Coronene-S	478.791	353.961	57.641	296.7976667
Coronene-Se	483.543	354.756	58.762	299.0203333
Coronene-Zn	402.263	354.645	56.919	271.2756667
Coronene-Cl	388.769	351.841	53.745	264.785
Coronene-F	350.813	348.911	51.451	250.3916667

5.6. Symmetry

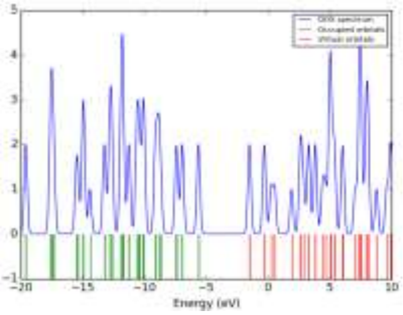
Some geometrical figures demonstrate more symmetric than the others, one can say the sphere is more symmetric than the cube since the sphere looks the same after rotation throughout any angle about the diameter. Symmetry operations implies rotation, reflection and inversion. Symmetry elements are point symmetry, axis symmetry and plane symmetry. In order to say the molecule is symmetric, it must be exist at least one common point unchanged beyond the symmetry operation. Symmetry is very important characterstic because it gives informations about dipole moment and degenerate states without calculations [18].

Table (6) Point group symmetry for Coronene and Coronene-Y

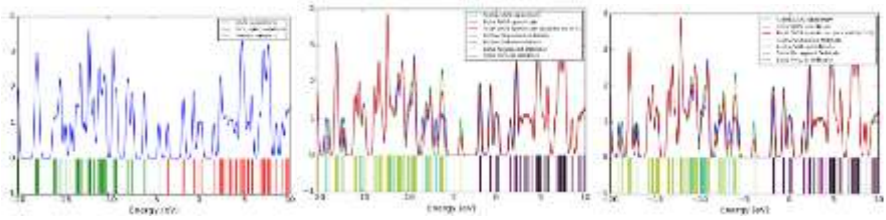
System	Symmetry
Coronene	D6h/C1
Coronene-P	Cs/C1
Coronene-S	Cs/C1
Coronene-Se	Cs/C1
Coronene-Zn	Cs/C1
Coronene-Cl	Cs/C1
Coronene-F	Cs/C1

5.7. Density of states

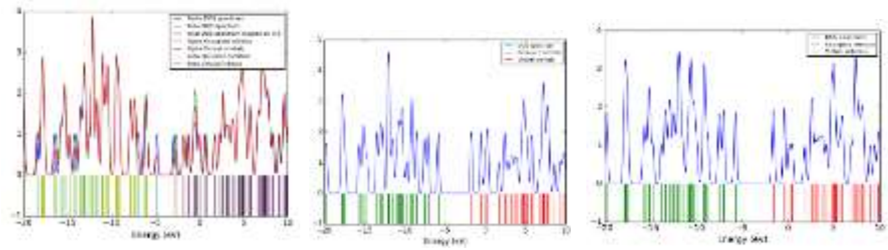
DOS of the system stands for the number of states per interval of energy at each energy level in which this energy level available to be occupied. In quantum mechanics waves , the waves like particles can occupy modes or states with wavelengths and directions of propagation indicated by the system, only specific states are allowed[19]. Some systems permit to only electrons of certain wavelengths to exist, but other systems allow to the waves to propagate in one direction because of the crystalline structure. DOS is very necessary property in solid state physics [20].



Coronene



Coronene-P Coronene-S Coronene-Se



Coronene-Zn Coronene-Cl Coronene-F

Figure(4) Density of states for Coronene and Coronene-Y

6. Discussion

From table(1) and table(2) one can conclude throughout the values of HOMO energies that Coronene represents an acceptor, while Phosphorus, Sulfur, Selenium, Zinc, Clourine and Fluorine stand for donors in coronene-Y interactions because HOMO energy for any individual atom among Y atoms is greater than HOMO energy of Coronene, hence the electrons will release to unoccupied orbitals [21].

The energy gap of Coronene-P approximates to the energy gap of GaAs as shown in table(2), the energy gap of GaAs equal to (0.78eV), and the energy gap for Coronene-Y approaches to (0.92eV) , this makes Coronene-P has great advantages in the electronic devices. The other individual atoms also affect on the energy gap when they are added to Coronene [22].

One can visualize from table(1) and table(3), the electronegativity for Coronene is larger than the electronegativity of Zinc, Clourine, and Fluorine, therefore, atoms of Coronene will adsorb on Zinc, Clourine and Fluorine. In the other hand, the electronegativity of Phosphorus, Sulfur and Selenium is less than the electronegativity of Coronene, hence those atoms will adsorb on Coronene, i.e. in the two cases resonance charge transfer will get throughout the surfaces of individual atoms and Coronene [23].

In table(3) Coronene-P is the most electrophilicity molecule, but Coronene-Zn is the less electrophilicity molecule among all. Except Zinc, dding all individual atoms to Coronene make the electrophilicity larger, i.e. the electrophilicity of Coronene-Zn is less than the electrophilicity of Coronene[24] .

The values of dipole moment of Coronene and Coronene-Y molecules as revealed in table (4) . Coronene has no dipole moment it like homonuclear molecule. Coronene-Zn has dipole moment, it is hetronuclear molecule. Coronene-S has the highest value of dipole moment, the dipole moment of Coronene-S is able to interact with the electric field of the electromagnetic radiation. All molecules that have dipole moment are hetronuclear molecules [25].

In table(5) Coronene-P is the most reactivity molecule because it has the largest value of polarizability, while Coronene-F is the smallest reactivity among Coronene-Y molecules. The polarizability increase with increasing of the size that will be occupied by the electrons. Polarizability is very important property in molecular physics, it gives useful informations about the molecular structure [26].

In table(6) the symmetry of Coronene is D6h, this means Coronene has horizontal mirror plane because it is from the point group symmetry Dnh, so Coronene have six fold principal axes and six fold axes perpendicular to Cn, Because the element C1 Coronene is able to rotate by 360^o. One can visualize clearly when any Y atom adds to Coronene the point group symmetry become Cs/C1, that is to say Coronene-Y molecules is able to rotate by 360^o, but it consists of two elements identity and mirror plane[27].

Figure(4) illustrate DOS for Coronene and Coronene-Y molecules. Coronene-S and Coronene-Se as the anti-ferromagnetic material properties because it has beta orbitals, the magnetic moments resultant will be zero, this means at zero Kelvin every atom of those molecules which surround by another atom will have magnetic moments with the same magnitude, but opposite direction to the magnetic moments, i.e the two atoms will have similar quantity of magnetic moment but with opposite direction. Density of states gives the energy level that are available to occupy by electrons[28] .

7. Conclusions

Contours maps demonstrate increasing of electron density near Phosphorus, Sulfur, Selenium, Zinc, Cluorine and Fluorine atoms, hence one can conclude increasing the charges that surround Y atoms. New bonds between Coronene and Y atoms demonstrate beyond adding Y atoms to Coronene. Coronene-P and Coronene-Z have energy band gaps approximates to the semiconductor band gap. Resonance charge transfer gets throughout the interactions. Electronegativity property appear some Y atoms will adsorb on Coronene. Coronene-P has the highest value of dipole moment and polarizability, hence it is the highest reactivity molecule. All Coronene-Y molecules have Cs point group symmetry, this demonstrates influence Coronene which has D6h point group symmetry beyond the interaction with Y atoms.

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9. References

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