Theoretical study for the Electronic Properties of Tri-fluorine benzene Molecules Group and Adding CH$_3$ radical: by B3LYP-DFT Method

دراسة نظرية للخواص الإلكترونية لمجموعة جزيئات ثلاثي فلور البنزين بإضافة جذر CH$_3$ بمواقع مختلفة باستخدام طريقة B3LYP-DFT

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Abstract

   In this work, five molecules are optimized at B3LYP/6-31G** density functional theory. Benzene molecule was a reference. Electronic properties of tri-fluorine benzene molecules were investigated depending on the three parameters (B3LYP) by density functional theory method .The best geometry for all molecules were investigated at (6-31G**) basis sets. The total energies, energy gaps, ionization potentials, electron affinities and softness were calculated for the studied molecules. Adding the (CH$_3$) cluster to the tri-fluorine benzene leads to decrease the energy gap and the hardness of the studied molecules in comparison with the benzene molecule. The IR-spectra shows the effect of fluorine atoms in the ring on the vibrations of the reference molecule, the electronic properties and IR spectrum for all molecules were investigated by Gaussian 03 program.
Key words: DFT, energy gap, ionization potential, hardness and IR- spectrum.

الخلاصة :

   تم دراسة الخواص الالكترونية لخمس جزيئات من مجموعة ثلاثي فلورين البنزين وأضافة جذر CH$_3$ كمجموعة جانبية بالاعتماد على نظرية دالة الكثافة (DFT) عند المستوي **B3LYP/6-31G حيث أعتمد جزيئة البنزين كمرجع. تم تحقيق الخواص الألكترونية لمجموعة جزيئات ثلاثي فلورين البنزين بالأعتماد على ثلاث معاملات (B3LYP) بواسطة طريقة نظرية دالة الكثافة (DFT). التراكيب المثلى , الطاقات الكلية, فجوات الطاقة, جهود التأين, المرونة وأألفه الالكترونية الكيميائية, كل الخواص الألكترونية لهذة الجزيئات تم دراستها عند المستوي **6-31G . إضافة جذر (CH$_3$) بمواقع مختلفة إلى ثلاثي فلورين البنزين يقود إلى نقصان بفجوات الطاقة و الصلادة عند دراسة تلك الجزيئات ومقارنتها بجزيئه البنزين. طيف IR يبين تأثير إضافة ذرات الفلور في الحلقة على اهتزاز الجزيئات عند مقارنتها بالجريئة المرجع (البنزين), جميع الخواص الألكترونية تم دراستها بواسطة برنامج الكاوسيان (03) وطيف IR تم الحصول علية من هذا البرنامج .

1. Introduction

   Any problem in the electronic structure for any system treated by quantum mechanics; it is base on the Schrödinger equation. Some of the largest important applications of quantum mechanics is semiconductor physics and technology [1]. Engineers have incorporated the quantum mechanical into the design of new electronic devices [2].
   The hydrogen atom was Schrödinger's immediate goal when he develops his equation and the solution obtained in 1926 persuaded him [3].
   Physicists derived the physical laws and mathematical structure that constitute the basis of quantum mechanics, but subsequent applications became interest not just to the physicists but also chemists, biologists, medical scientists, engineers, and philosophers, where sophisticated computer

programs are routinely used for predicting the structures and geometries of large molecules [2]. The organic semiconductor materials, such as, conjugated organic molecules have been widely used as active materials for optoelectronic devices such as light emitting diodes[4-6], field effect transistor[6-8], and photovoltaic and solar cells[9,10]. The organic thin film transistors are one type of the so called organic devices, in which they fabricated by using the organic semiconductors [11]. These materials have advantages of easy fabrication, mechanical flexibility and low cost. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [12, 13].

Density function theory is one of the largest popular and successful quantum mechanical approaches [14]. It is a powerful computational quantum physical and chemical technique method that allows the calculation of the geometries and energies of reactants [15]. It has become a popular tool for electronic structure calculations in recent years due to its favorable combination of low computational cost and good accuracy for the calculated results. In analogy with wave mechanics methods, there are two main parameters controlling the accuracy of the results, the inherent approximations in the Hamiltonian and the size of the basis set used for expanding the Kohn–Sham (KS) orbital's [16,17]. The foundation of DFT was laid by Hohenberg and Kohn, who showed that a unique functional of the electron density determines the ground-state electronic energy exactly[18]. In present work, density functional theory has been performed to study the electronic properties of the fluorine benzene molecules to determine the effects of the substituent groups .

2. Computational details

Figure 1 represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 03 suite of programs [19]. The molecular properties of the compounds had been computed by DFT using the standard 6-31G** basis set. In the DFT calculations, Lee, Yang and Parr correlation functional is used together with Becke's three parameters[19]exchange functional B3LYP. Conformational analysis of the molecules had been performed to have an idea about the lowest energy structures of the species.
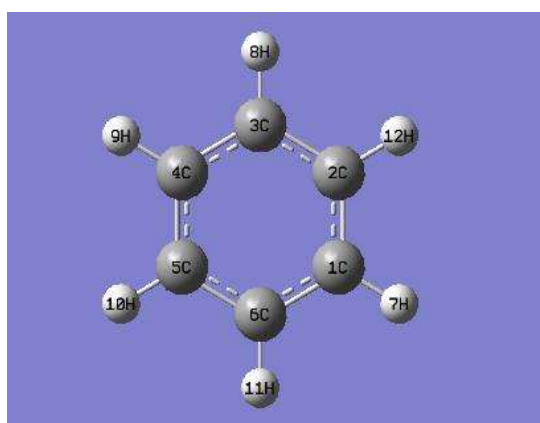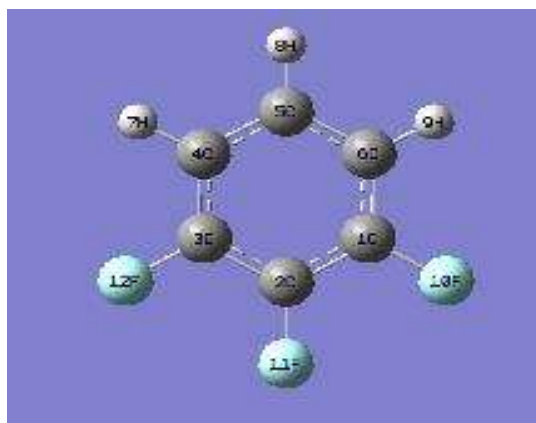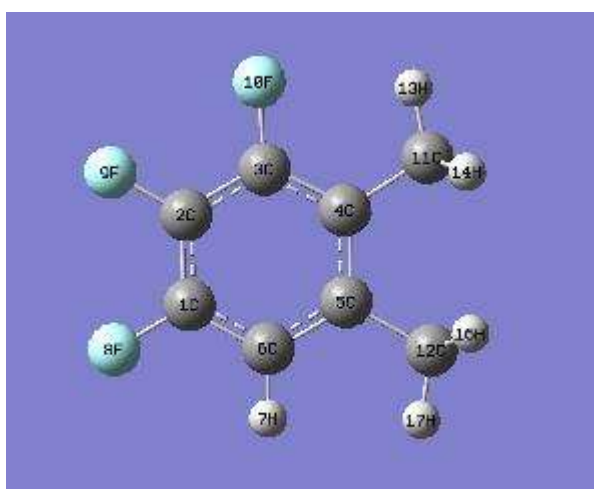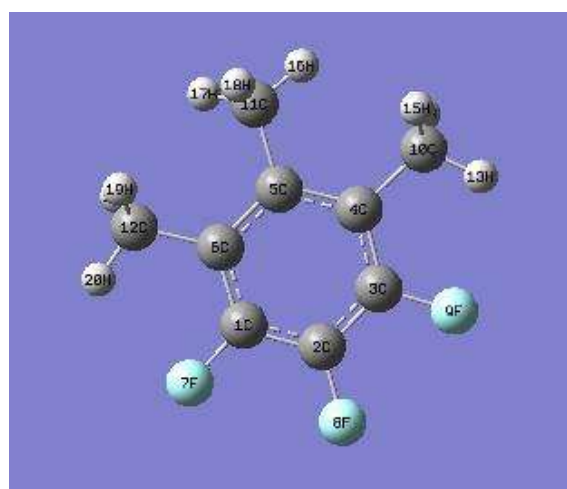

| 1(BZ) | 2(Tri fluorine BZ) |
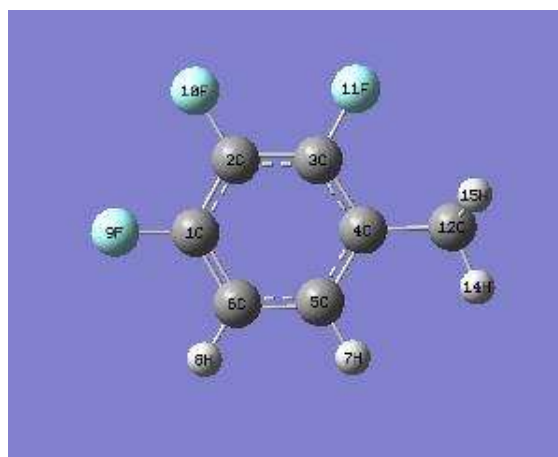
3(Tri fluorine BN 4CH$_3$)

4(Tri fluorine BN 4 ,5 CH$_3$)   5(Tri fluorine BN 4-6 CH$_3$)

Figure(1).Structures of Tri-fluorine benzene and its derivatives discussed in this work.

Koopman's theorem states that if the single particle energies are not affected by adding or removing a single electron, then the ionization energy is energy of the highest occupied single particle molecular orbital (the HOMO) and the electron affinity is the energy of the lowest unoccupied molecular orbital (the LUMO) with the negative sign as the following [20]

IP = - E$_{HOMO}$ …………………..(1)

EA= - E$_{LUMO}$ …………………..(2)

Where   IP: ionization potential , EA: electronic affinity
E$_{HOMO}$: energy of the highest occupied molecular orbital.
E$_{LUMO}$: energy of the lowest unoccupied molecular orbital

Koopman's theorem is extremely useful in predicting ionization energies and spectra [20].Energy gap generally refers to energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) according to the Koopmans theorem [21,22]

E$_g$ = E$_{LUMO}$ $^-$ E$_{HOMO}$ ………………(3)

Ionization energy (IP) defined as the minimum energy required to removing an electron from the atom in a gaseous phase. Ionization energy is expressed in units of electron volt (eV) [22]. The first ionization energy, IE_1, associated with the removal of the first valence electron as the equation [23,24]

$$X(g) \rightarrow X^+(g) + e^- \quad \dots\dots\dots\dots\dots(4)$$
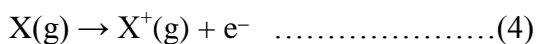
The second ionization energy, IE_2, of an atom refers to step (5). Note that this is equivalent to the first ionization of the ion X^+. Equation (6) describes the step corresponding to the third ionization energy, IE_3, of X and successive ionizations are similarly defined [22]:

$$X^+(g) \rightarrow X^{+2}(g) + e^- \quad \dots\dots\dots\dots\dots(5)$$

$$X^{+2}(g) \rightarrow X^{+3}(g) + e^- \quad \dots\dots\dots\dots\dots(6)$$
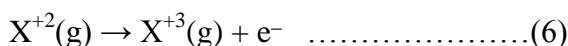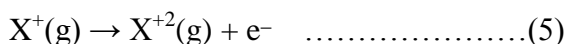
Also, it can be define as the energy difference between the positive charged energy E(+) and the neutral energy E(n) [2].

$$IP = E(+) - E(n) \quad \dots\dots\dots\dots\dots.(7)$$

Electron affinity can be defined as the energy released upon attachment of an electron to an atom or molecule resulting in the formation of the negative ion [22].The process of electron affinity shown in following equations [23,24]:

$$X(g) + e^- \rightarrow X^-(g) \quad \dots\dots\dots\dots\dots..(8)$$

$$X^-(g) + e^- \rightarrow X^{-2}(g) \quad \dots\dots\dots\dots\dots..(9)$$
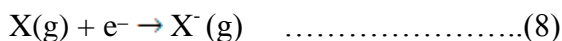
Also, it can be define as the energy difference between the neutral energy E(n) and the negative charged energy E(–), as in the following relation [25]:

$$EA = E(n) - E(-) \quad \dots\dots\dots\dots\dots...(10)$$

Chemical hardness is the resistance of a species to lose electrons [26], for insulator and semiconductor, hardness is half of the energy gap [27]. From equations (1) and (2), we can calculate the chemical hardness (η):

$$\eta = (IP - EA)/2 \quad \dots\dots\dots\dots\dots.(11)$$

The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons n [109, 111]

$$\eta = \frac{1}{2}(\partial^2 E/\partial n^2) \quad \dots\dots\dots\dots\dots.(12)$$

The softness can be defined as the inverse of the hardness[26]

$$S = 1/(2\eta) \quad \dots\dots\dots\dots\dots.(13)$$

Electro negativity is defined as "the power of an atom in a molecule to attract electrons to itself" by Pauling [22,23]. R. Mulliken defined electro negativity as the average of the ionization energy and electron affinity as follows [27]

$$\chi = (IP + EA)/2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Within the validity of Koopmans' theorem, we can be defined as the negative value for average of the energy levels of the HOMO and LUMO [21, 26].

$$\chi = -(E_{HOMO} - E_{LUMO}) \ldots\ldots\ldots\ldots\ldots(15)$$

The Electrophilicity is definition as a index measures the stabilization in energy when the system acquires an additional electronic charge from the environment. On the other word, it can be defined as a measure of energy lowering due to maximal electron flow between donor and acceptor [28].

$$\omega = \chi^2/(2\eta) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

3. Results and discussion

3.1. Energies

Table (1) shows the values of the total energy and electronic states for the analyzed structures and the energy gap ($E_{LUMO} - E_{HOMO}$) of the studied molecules. The total energy for all study molecules as a linear function of (F & CH$_3$) side group number adding to the molecule. The final total energy of the product is the collection of total energy of all small molecules which build the product molecule, that means:

$$E_{tot} \approx E_{tot}(molecule) + nE_{tot}(radical) \ldots\ldots\ldots\ldots (17)$$

Where n is the number of (F & CH$_3$) radicals.

It is clear that from table (1), the total energy for all molecules study is approximately the same in which this refer to that the total energy is independent on the position of the (F & CH$_3$) radical in the ring, and it is observed that substitution of fluorine and CH$_3$ groups (electron with drawing) causes decreasing the HOMO and LUMO energy [22],and energy gap decreased are less than that of the original molecules. Therefore, the presence of substituent decreases the energy gaps improves the semi conductivities and also enhances the solubility's of these molecules, with decreasing energy gap, electrons can be easily excited from the ground state . This effect of the side group was the largest in molecule **5** it has energy gap of (3.636 eV). The table (1) show also the symmetry of study molecules, the molecule **1** is planar with inversion center and have D$_{6h}$ symmetry (high symmetry), and have lower electro negativity, while molecule **5** is planer and have C$_{2v}$ symmetry (low symmetry), and have higher electro negativity.

Table1: Total energy, electronic states and energy gap for molecules.

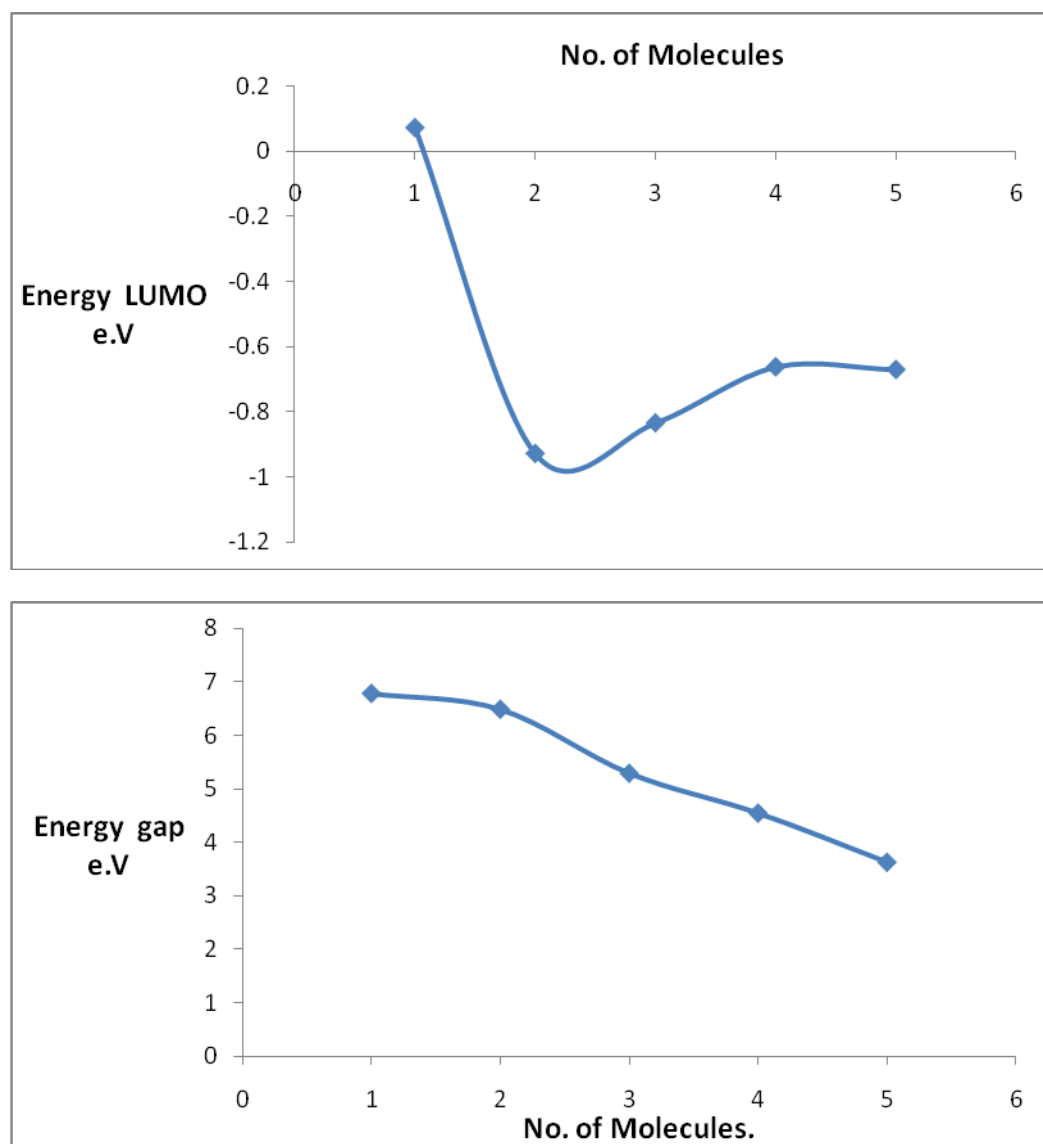| Structure molecule	Total Energy(a.u)	Symmetry	Electronic States(eV)		Energy Gaps (eV)
			HOMO	LUMO	Our data
1	-232.258	D$_{6h}$	-6.718	0.0718	6.789
2	-529.991	C$_{2v}$	-7.423	-0.929	6.493
3	-569.315	C$_s$	-6.123	-0.835	5.298
4	-608.637	C$_s$	-5.216	-0.663	4.553
5	-602.639	C$_{2v}$	-4.307	-0.671	3.636
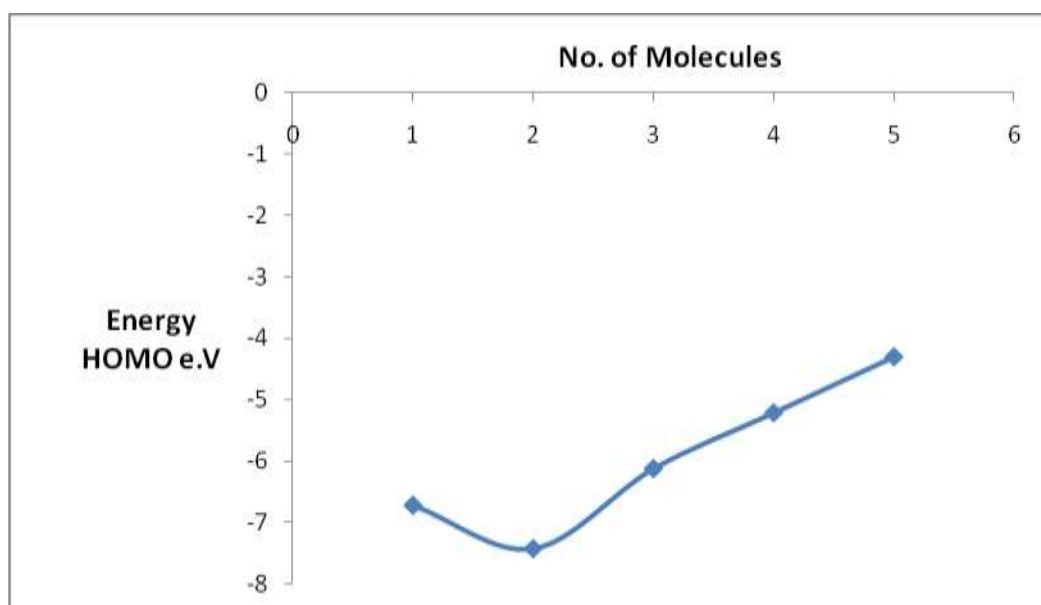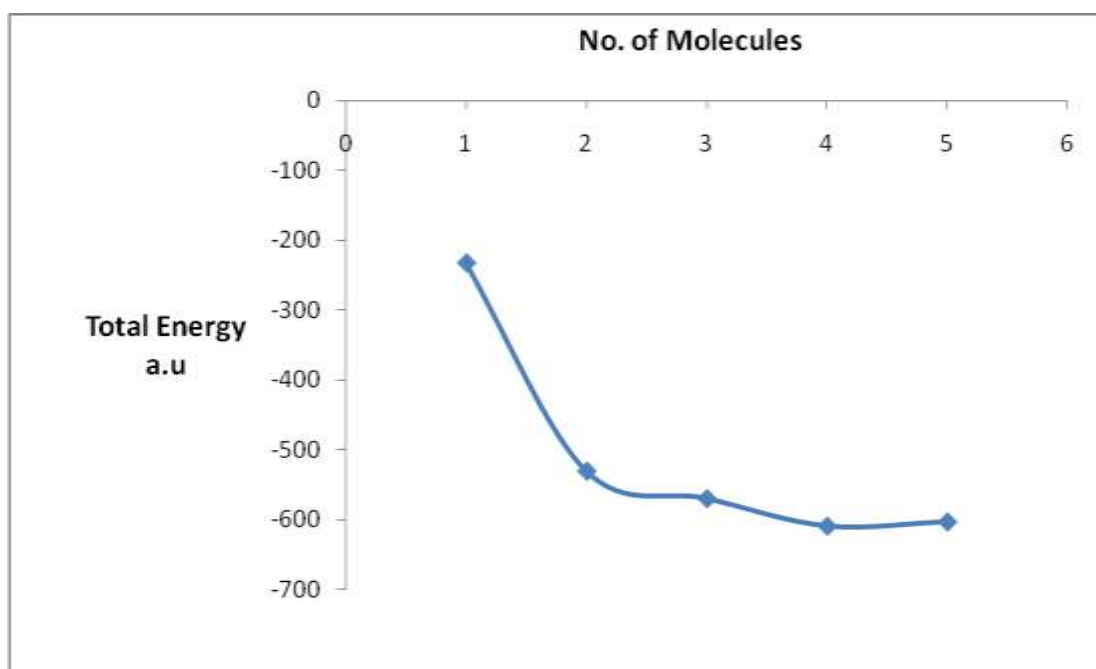
Figure (2) : Energies per unit a.u & e.V corresponding the No. of molecules .

## 3.2 Some important variables

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials(IP), electron affinities(EA), electronegativity (χ), absolute hardness(η), absolute softness (S) and electrophilic index (ω). The properties are displayed in table (2) lists the electronic properties for the molecules under study. It is clear from table (2) that the ionization potential for fluorine benzene molecules group is largest than that for benzene but after adding the CH_3 cluster in the ring BZ I have that the IP is less than for BZ. The electron affinity for fluorine benzene group is more than that the electron affinity for benzene except until after adding the CH_3 cluster . It is obvious from this table that all molecules under study have hardness less than that for benzene; The behavior of electro negativity but in the (2,3) molecules are largest from BZ, (softness and electrophlicity) index for the studied molecules shows the magnitude large than these for the original ring (benzene), adding the atoms fluorine and CH_3 cluster give the molecule more softness, it is a new electronic material.

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**Table (2): Computed energies for BZ& Fluorine BZ &Fluorine BZCH$_3$ molecules.**

|	Species	IP (eV)	EA (eV)	χ(eV)	η (eV)	S (eV)$^{-1}$	ω (eV)
1	C_6H_6	6.718	-0.0718	3.323	3.394	0.147	1.626
2	$C_6H_3F_3$	7.423	0.929	4.176	3.247	0.154	2.685
3	$C_6H_2F_34(CH_3)$	6.123	0.835	3.479	2.649	0.188	2.284
4	$C_6HF_34,5(CH_3)$	5.216	0.663	2.939	2.276	0.219	1.897
5	$C_6HF_34,6(CH_3)$	4.307	0.671	2.489	1.818	0.275	1.703

3.3 Infrared spectra

The harmonic vibrational frequencies calculated for studied molecules at B3LYP functional using the 6-31G** basis sets. The (C-H) stretching vibrations of aromatic molecules in the region (2900-3 250) cm^{-1} which is characteristic region for ready identification of (C-H) stretching vibrations and particularly the region (3250-3100) cm^{-1} for asymmetric stretching and (3100-2900) cm^{-1} for symmetric modes of vibration. Figure (3) shows the vibration frequencies calculated of the studied molecules using B3LYP/6-31G** method..The strong peak computed by B3LYP/6-31G** observed due to the bending of (C---H) bond, and due to the stretching of (C---C) bond. It is clear from figure (3) that the IR spectrum for group molecules characters from that of tri fluorine benzene molecule, the stretching and bending of these bonds caused to new peaks or band of peaks to be appeared. There are two types for stretching vibration symmetric and asymmetric, the symmetric stretching is happened when the bonds of the same atoms vibrate in the same phase, and the asymmetric stretching is happened when the bonds vibrate in different phases.
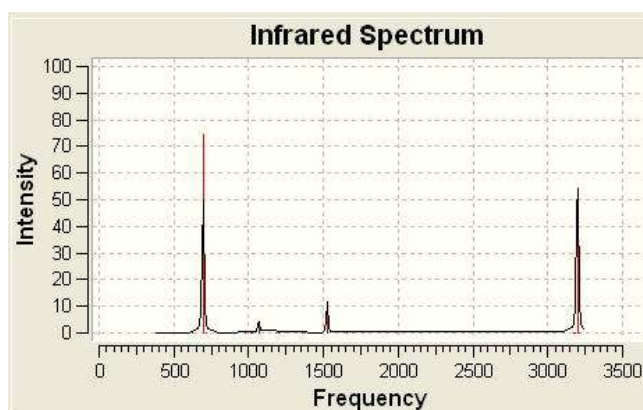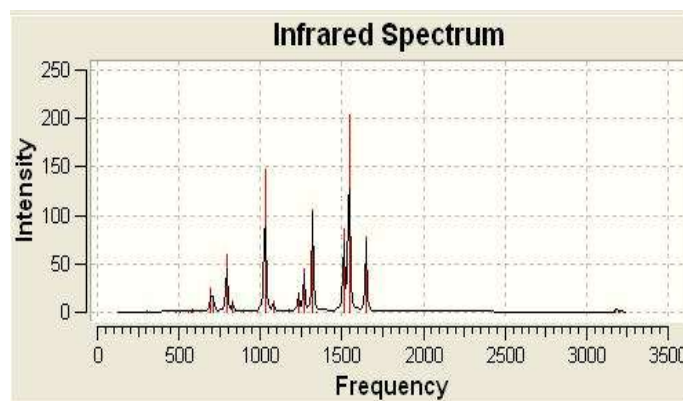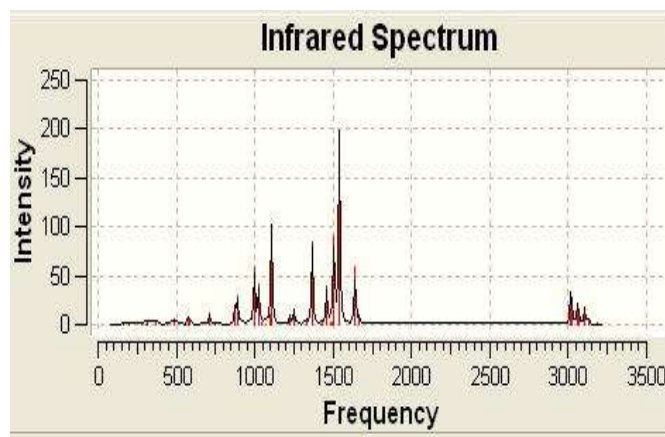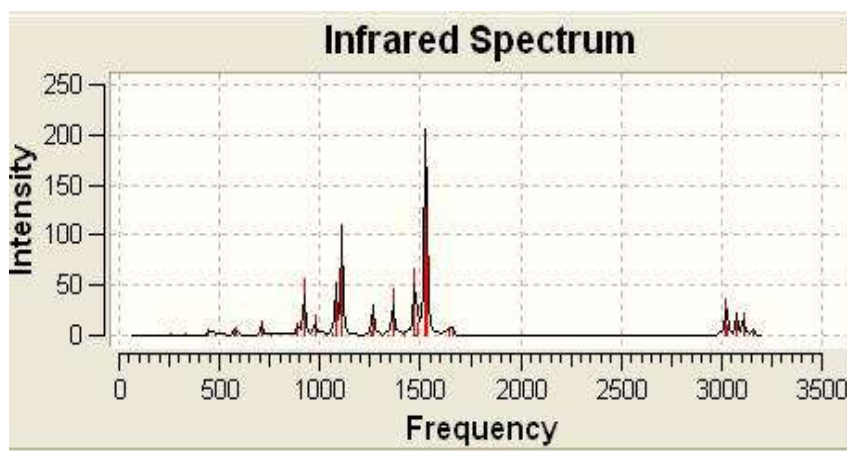

BZ   Tri Fluorine BZ
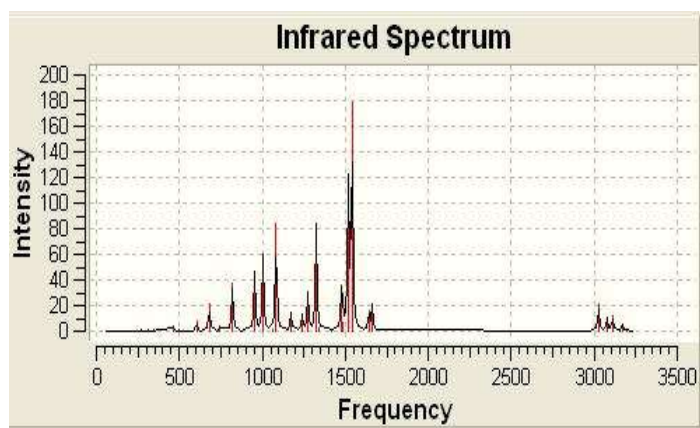
Tri Fluorine BZ (4CH₃)

Tri Fluorine BZ (4,5CH₃)

Tri Fluorine BZ (4,6 CH₃)

Figure (3):(continued) The IR spectra of molecules under study, Epsilon≡ Intensity (Km/mol).

4. Conclusions

1- The density functional theory is a powerful method three parameters Lee-Yang-Par (B3LYP) functional is a suitable and an efficient function for studying the electronic properties of aromatic structures.

2- The geometric structures, symmetry and total energies for benzene and fluorine benzene molecules and (CH₃) group are in a good agreement with those in other references. But for other molecules they have not been found similar studies, thus this study supplies new data in this aspect. The hardness for fluorine benzene and fluorine BZ (CH₃) molecules group is lowers' values in compare with benzene.

3- The total energies for fluorine benzene found dependent on the position of the fluorine atom and CH₃ cluster in the ring and substitution fluorine group causes decreasing total energy and more stability.

4- The presence of the substituent's decreases the energy gap of the molecules study, this is one of the important properties obtained in this work.

5- B3LYP/6-31G** DFT given a large approach in IR spectra calculations for observed peaks computed experimentally of benzene, and for new fluorine benzenes this study supplies new data for IR spectrum.

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