Theoretical Study as Nano Structure for Fluorine Phenanthrene Molecules(crystal) Group: by B_3LYP-DFT

Maan Ab.Saleh Almamory
Physics Department - College of Science - Babylon University.
E-mail: facemoon862@yahoo.com

Abstract

In this work, five molecules are optimized at B_3LYP/6-31G** density functional theory (DFT). Phenanthrene molecule was a reference. The electronic properties nano structure of fluorine Phenanthrene molecules group were investigated depending; include the bond molecules , nano structure for crystal, total energy, electronic states, electron affinity, chemical hardness, softness and electrophlicity index.Adding the fluorine atoms to the original ring (Phenanthrene molecule) leads to decrease the energy gap and the hardness of the molecule. The results show that these molecules are more effective with small energy gap compared with Phenanthrene molecule. This may indicates that these structures represent new electronic materials. The vibrational frequencies of fluorine Phenanthrene molecules group supplies new data.

Key words: DFT, energy gap, ionization potential, hardness and IR- spectrum.

Introduction

Aromaticity is a chemical property in which a conjugated ring of unsaturated bond, ions pairs, or empty orbital's exhibit stabilization stronger than would be expected by the stabilization and of resonance .There is usually considered to be because electrons are free to cycle around circular arrangements of atoms, which are alternately single-and double-bonded to one another. These bonds may be seen as a hybrid of a single and a double bond, each bond in the ring identical to every other [1].Thin commonly–seen model of aromatic rings, namely the idea that Phenanthrene was formed from a six-mamboed carbon ring with alternating single and double bonds, was developed by Kekule [2].The model for Phenanthrene consists of two resonance forums, which corresponds to the double and single bonds switching positions [3].

In present work , Phenanthrene is a reference for the new studied molecules ,in which they consist of fluorine atoms is replaced from to the hydrogen atoms, the new fluorine molecules have been exhaustively studied [4-9].There are many researches in aromatic molecules containing fluorine atoms [8,10]. (Mono fluorine Phenanthrene),(Di fluorine Phenanthrene),(Tri fluorine Phenanthrene)and (Titra fluorine Phenanthrene) have been synthesized [11-13].Many methods used to study the Aromaticity bossed on the structure or on the energetic behavior, such as, the harmonic oscillator model of Aromaticity [14],the aromatic stabilization energy[15].Other method ,based on the analysis of electron delocalization [16-17].In present work, fluorine Phenanthrene molecules group have been studied using DFT theoretical approach, and study the electronic properties of a new (fluorine - Phenanthrene) molecules.

Theory and computational Details

In this work, density functional theory has been used to calculate the electronic properties of the studied molecules at (B_3 LYP) functional with (6-31G**) basis sets. The geometry optimization, energies and IR-spectrum have been done using Gaussian 03 program [18].
According to the density functional theory, the total energy can be written as [19]:

$$E_0 = E_v(P_0) = T[\rho_0] + \int V_{en}(r)\,\rho_0(r)\,dr + J[\rho_0] + E_{NC}(\rho_0) \dots\dots\dots (1)$$

For a normalized wave function Ψ, the particle density is given by $\boldsymbol{\rho(r)}$

$$\rho(r) = \sum_i^{ni}[\Psi_i(r)]^2 \qquad \dots\dots\dots\dots\dots\dots \qquad .(2)$$

Where ni is the number of electrons in orbital (i), and the summation is over the occupied molecular orbital's .The kinetic energy of the system is [20]:

$$T[\rho] = T_s[\rho] + J[\rho] + V_{en}[\rho] + E_{XC}[\rho] \qquad \dots\dots\dots\dots\dots\dots \qquad (3)$$

Where $T_s[\rho], J[\rho], V_{en}[\rho]$ and $E_{XC}[\rho]$ are the kinetic energy of non interacting electrons system, classical coulomb energy, and exchange–correlation energy, respectively[19,20].

$$E_{XC}[\rho] = \int(\rho)\,E_{XC}[\rho]\,dr \qquad \dots\dots\dots\dots\dots\dots \qquad (4)$$

$$T_s[\rho] = -\frac{1}{2}\sum_i\langle\emptyset_i|\nabla^2|\emptyset_i\rangle \qquad \dots\dots\dots\dots\dots\dots \qquad (5)$$

$$J[\rho_0] = \frac{1}{2}\iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1 - r_2|}\, dr_1\, dr_2 \qquad \text{………………..} \qquad (6)$$

$$V_{en}[\rho_0] = \frac{1}{2}\iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1 - r_2|}\, dr_1\, dr_2 + E_{XC}[\rho] \text{………………} \qquad ..(7)$$

According to B3LYP function, the exchange correlation energy E_{XC}^{B3LYP} is given by [21]:

$$E_{xc}^{B3LYB} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

… ………………… (8)

Where the three parameters $a_0 = 0.20,\ a_x = 0.27\ and\ a_c = 0.81$.

The ionization potential (IP) and the electron affinity (EA) of the molecule are calculated according to the following relations [19, 21]:

$$IP = E_{(+)} + E_{(n)} \qquad \text{………………..} \qquad (9)$$

$$EA = E_{(n)} - E_{(-)} \qquad \text{………………} \qquad .(10)$$

Where E (+) and E (-) are the positive and negative charged energy, E (n) is the neutral energy. The electronic chemical potential (χ), the hardness (η) and the softness (s) are given by: $\chi = \frac{IP+EA}{2}$….(11), $\eta = \frac{IP-EA}{2}$ ….(12), $S = \frac{1}{2\eta}$ ….(13)

And the electrophlicity (ω) of the molecular is given by:

$$\omega = \frac{\chi^2}{2\eta} \qquad \text{………………..} \qquad .(14)$$

Results and Discussion

Figure (1) shows the studied molecules .The total energy and symmetry for these molecules are presented in table (1).The Phenanthrene molecule was included as reference.

Energies

It is clear that from table (1), the total energy for all molecules depends on the number of fluorine atoms in the ring; it is decreasing with the decreasing of (F) atoms number, the total energy for all study molecules as a linear function of F 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} = E(Phenanthrene) +n E(fluorine) …………. (15)

Where n is the number of Floure atoms. As we see in figure (2).The (fluorine Phenanthrene) molecules group are more stable than Phenanthrene. And the table (1) show also the symmetry of study molecules, the first molecule is planar with inversion center and have D_{5h} symmetry (high symmetry), and have lower electro negativity, while the last molecule is planer and have C_{2v} symmetry (low symmetry), and have higher electro negativity. Also not found effects for the imaginary frequency all the molecules for equal $E_{LUMO} - E_{HOMO})$

It is clear that from Table (2), (from the table (1) the total energy for all fluorine Phenanthrene molecules are different from one to others in which this refer to that the total energy is dependent on the position of the fluorine atoms in the ring, and it is observed that substitution of fluorine atoms (electron with drawing) causes decreasing the HOMO and LUMO energy [14],and energy gap decreased. Therefore, the presence of substituent decreases the energy gaps improves the conductivities. The (LUMO-HOMO) energy gaps of fluorine molecules is less than that of the original molecules (Phenanthrene), with decreasing energy gap, electrons can be easily excited from the ground state [12-15]. And from figure (3) it's clear the energies per unit a.u (Eg , LUMO and HOMO) are decreasing with No. of molecules .

Some important variables

The function B_3LYP used in this work has a high efficient to calculate the electronic properties such as ionization potentials (IP) ,electron affinities (EA),chemical potentials or electro negativity(χ),hardness (η), electrophilicities (w) and softness (S).Table (3) lists the electronic properties for the molecules under study. It is clear from table (3) that the ionization potential for fluorine Phenanthrene molecules group is largest than that for Phenanthrene. The electron affinity for fluorine Phenanthrene group is more than that the electron affinity for Phenanthrene except. It is obvious from this table that all molecules under study have hardness less than that for

Phenanthrene; the behavior of (electro negativity, softness and electrophlicity) index for the studied molecules shows the magnitude large than these for the original ring (Phenanthrene), adding the atoms fluorine give the molecule more softness, it is a new electronic material.

Figure (5) show the vibration frequencies calculated of the studied molecules using $B_3LYP/6\text{-}31G^{**}$ 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 (5) that the IR spectrum for group molecules characters from that of tri fluorine Phenanthrene 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.

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 Phenanthrene and fluorine Phenanthrene molecules 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 Phenanthrene molecules group is lowers' values in compare with Phenanthrene.

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

4- The presence of the substituents decreases the energy gap of the molecules study; this is one of the important properties obtained in this work.

5- The results showed that all substitution groups leads to decrease the average polarizability and increase dipole moment and cause to unreactive than original molecules.

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

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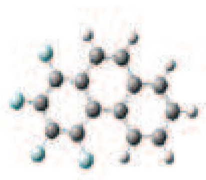
Mon

Di- Fluoro Phenanthrene **Tri- Fluoro Phenanthrene**



Titra- Fluoro Phenanthrene

Figure (1): The structure of studied molecules

Table 1: Total energy (a.u), symmetry and number of Imaginary frequency for molecular

Mol.	Symbol	Total energy	Symmetry	No.of Imag
C14H10	0	-539.5983	D6h	0
C14H9F	1	-638.8403	C2v	0
C14H8F2	2	-738.0749	C2v	0
C14H7F3	3	-837.3094	C2v	0
C14H6F4	4	-936.5390	C2v	0

Table 2: electronic states (HOMO, LOMO) and Energy gaps for molecular

Mol.	HOMO(ev)	LUMO(ev)	E_g (ev)
C14H10	-6.0414	-1.3796	4.6618
C14H9F	-6.2349	-1.5850	4.6498
C14H8F2	-6.3160	-1.7140	4.6019
C14H7F3	-6.3886	-1.7483	4.6403
C14H6F4	-6.4281	-1.8822	4.5459

Table (3): The electronic properties for molecules (all in electron volts)

Mol.	IP	EA	χ	η	S	ω
C14H10	6.0414	1.3796	3.7105	23309	0.2145	2.9533
C14H9F	6.2349	1.5850	3.9100	2.3249	0.2150	3.2878
C14H8F2	6.3160	1.7140	4.0150	2.3009	0.2172	3.5029
C14H7F3	6.3886	1.7483	4.0685	2.3201	0.2155	3.5671
C14H6F4	6.4281	1.8822	4.1551	2.2729	0.2199	3.7980

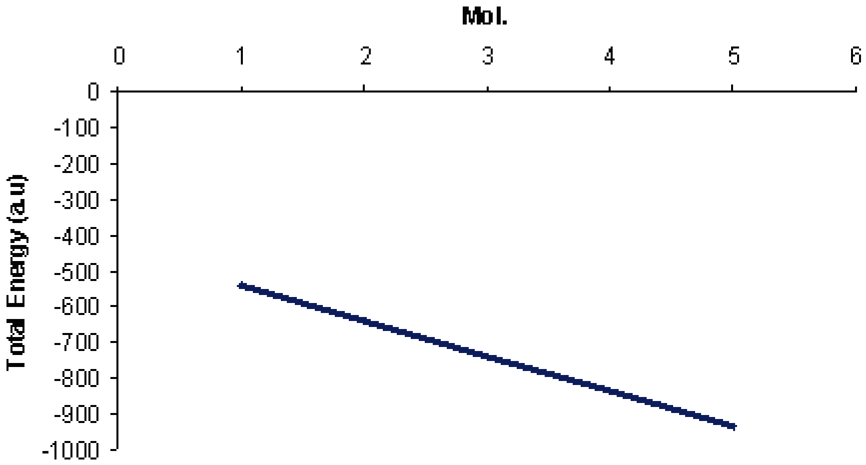


Figure 2: Total energy for fluorine Phenanthrene group molecules

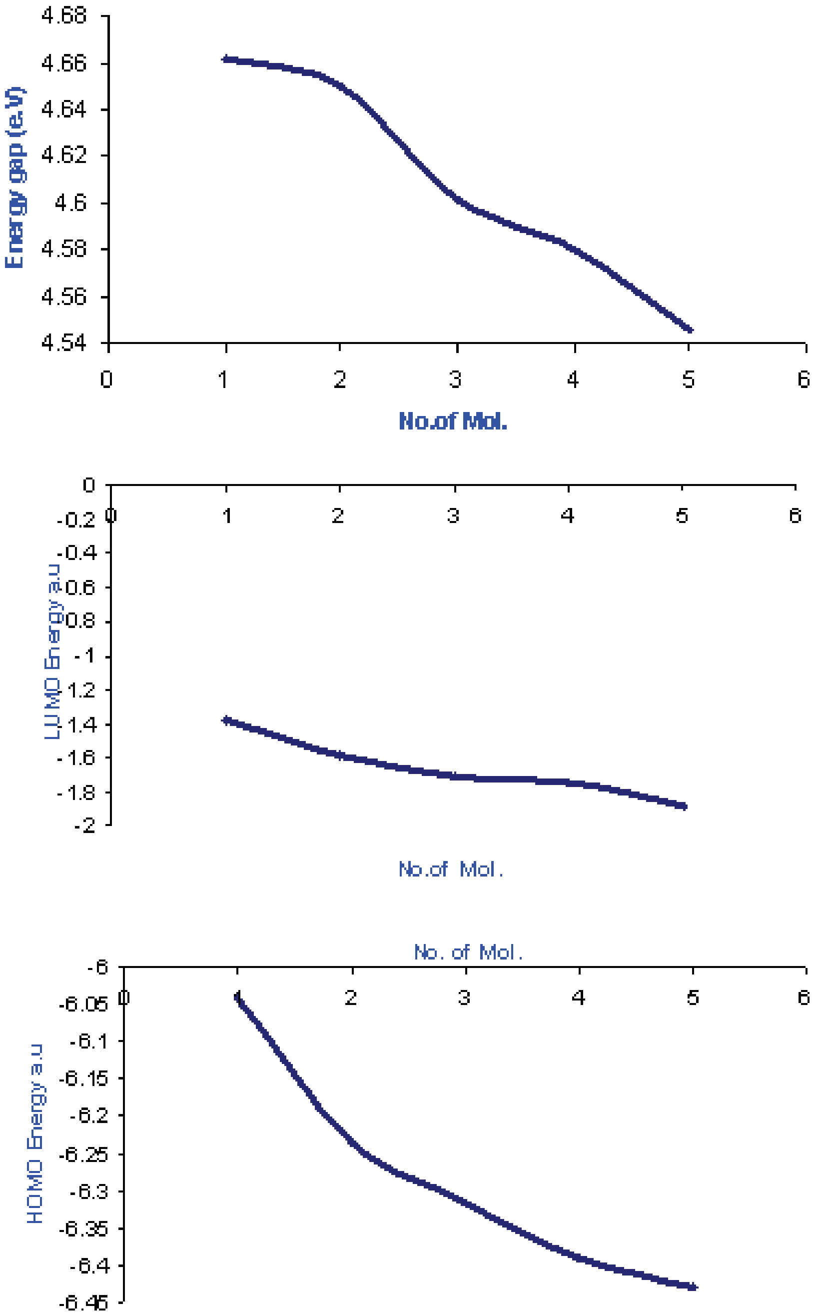
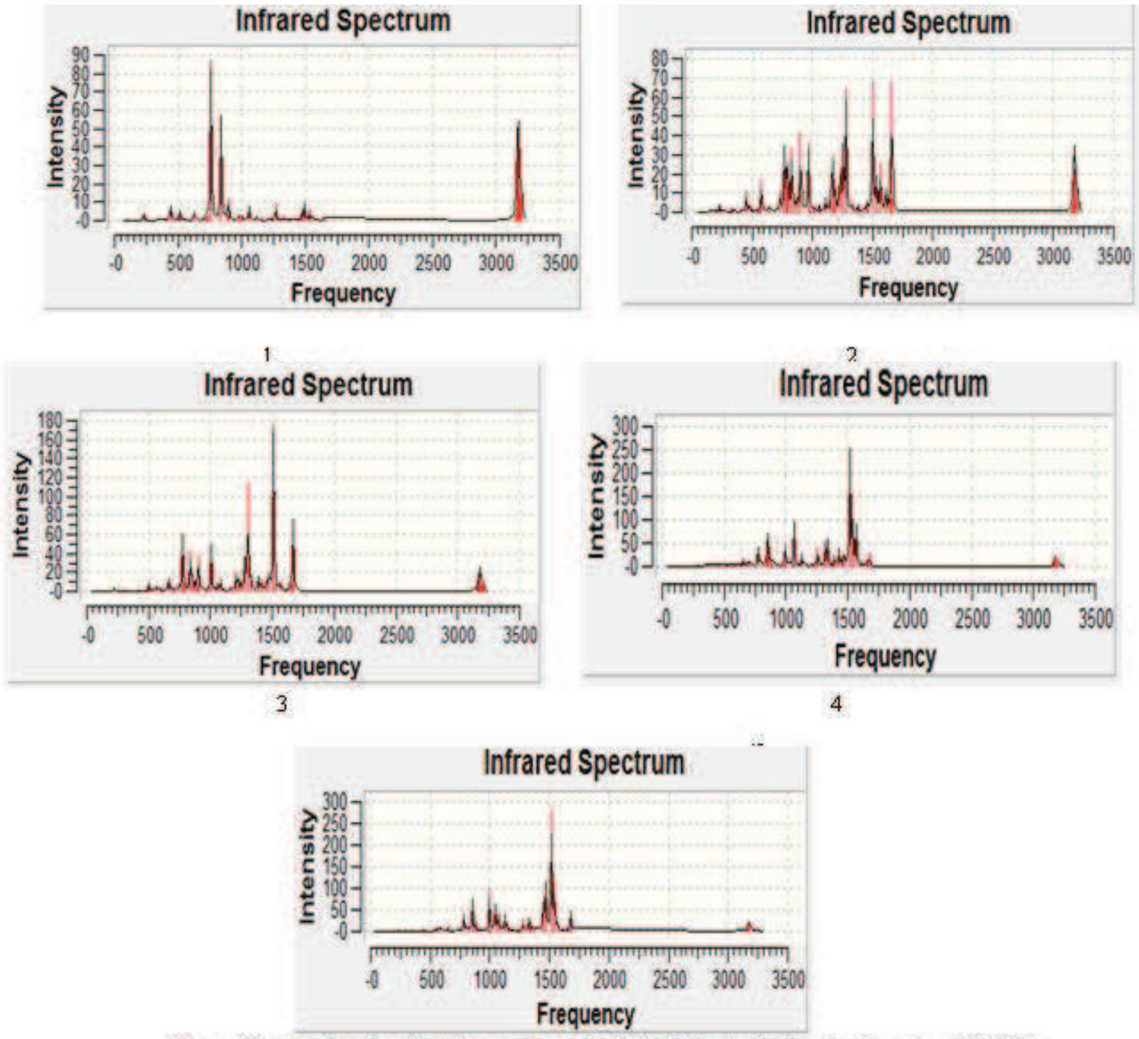


Figure (3) : Energies per unit a.u corresponding the No. of molecule .



1

2

3

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Figure (5) show the vibration frequencies calculated of the studied molecules using $B_3LYP/6\text{-}31G^{**}$ method

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