

Theoretical Study of the Electronic Properties for fluorine Azulene Molecules Group: by B₃LYP-DFT

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Abstract

In this work, five molecules are optimized at B₃LYP/6-31G** density functional theory (DFT). Azulene molecule was a reference. The electronic properties of fluorine azulene molecules group were investigated depending; include the total energy, electronic states, electron affinity, chemical hardness, softness and electrophilicity index. Adding the fluorine atoms to the original ring (azulene 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 azulene molecule. This may indicate that these structures represent new electronic materials. The vibrational frequencies of fluorine azulene molecules group supplies new data.

Keywords: 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 (B. P. v. R. Schleyer 2001). Thin commonly-seen model of aromatic rings, namely the idea that azulene was formed from a six-membered carbon ring with alternating single and double bonds, was developed by Kekule. The model for azulene consists of two resonance forms, which corresponds to the double and single bonds switching positions.

In present work, azulene 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. There are many researches in aromatic molecules containing fluorine atoms (E G.A. Jeffery 1991). (Mono fluorine azulene), (Di fluorine azulene), (Tri fluorine azulene), (Tetra fluorine azulene) and (Penta fluorine azulene) have been synthesized. Many methods used to study the Aromaticity based on the structure or on the energetic behavior, such as, the harmonic oscillator model of Aromaticity, the aromatic stabilization energy. Other method, based on the analysis of electron delocalization (F R.d. Green 1974). In

present work, fluorine azulene molecules group have been studied using DFT theoretical approach, and study the electronic properties of a new (fluorine - azulene) molecules.

Theory and computational Details

In this work, density functional theory has been used to calculate the electronic properties of the studied molecules at (B₃ LYP) functional with (6-31G**) basis sets. The geometry optimization, energies and IR-spectrum have been done using Gaussian 03 program.

According to the density functional theory, the total energy can be written as [19]:

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

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

$$\rho(r) = \sum_i^{n_i} |\Psi_i(r)|^2 \quad (2)$$

Where n_i 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]:

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

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

$$E_{XC}[\rho] = \int(\rho) E_{XC}[\rho] dr \quad (4)$$

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

$$J[\rho_0] = \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (6)$$

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$$V_{en}[\rho_0] = \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{|r_1-r_2|} dr_1 dr_2 + E_{xc}[\rho] \quad (7)$$

According to B3LYP function, the exchange correlation energy E_{xc}^{B3LYP} is given by :

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA}) \quad (8)$$

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 (F R.d. Green 1974):

$$IP = E_{(+)} + E_{(n)} \quad (9)$$

$$EA = E_{(n)} - E_{(-)} \quad (10)$$

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

$$\text{by: } \chi = \frac{IP+EA}{2} \dots (11), \eta = \frac{IP-EA}{2} \quad (12)$$

$$S = \frac{1}{2\eta} \quad (13)$$

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

$$\omega = \frac{\chi^2}{2\eta} \quad (14)$$

Results and Discussion

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

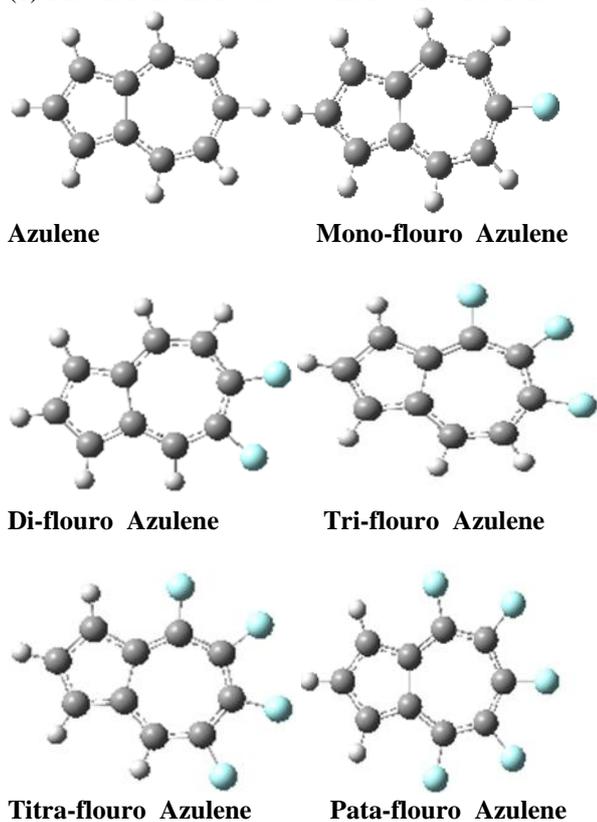


Figure 1: The structure of studied molecules

Energies

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

Mol.	Symbol	Total energy	Symmetry	No.of Imag
Azulene	0	-383.78263	D6h	0
1, fluorine azulene	1	-482.51485	C2v	0
1,2 fluorine azulene	2	-581.23306	C2v	0
1,2,3 fluorine azulene	3	-679.95221	C2v	0
1,2,3,4 fluorine azulene	4	-778.66727	C2v	0
1,2,3,4,5 fluorine azulene	5	-877.38401	C2v	0

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 increase 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:

$$E_{tot} = E_{tot}(\text{azulene}) + n E_{tot}(\text{Fluorine}) \quad (15)$$

Where n is the number of Fluore atoms. As we see in figure (2).The (fluorine azulene) molecules group are more stable than azulene. And the table (1) show also the symmetry of study molecules, the first molecule is planar with inversion center and have D_{6h} 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 zero.

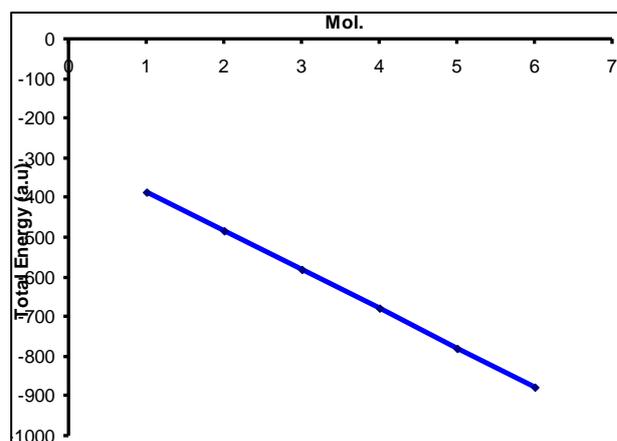


Figure 2: Total energy for fluorine azulene group molecules

Table (2) shows the values of the electronic states for the analyzed structures and the energy gap (E_LUMO-E_HOMO) of the studied molecules.

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

Mol.	HOMO(ev)	LUMO(ev)	E _g (ev)
C ₁₀ H ₈	-5.59493	-2.27051	6.58
C ₁₀ H ₇ F	-2.76646	-2.49909	6.37
C ₁₀ H ₆ F ₂	-2.77347	-2.84032	6.17
C ₁₀ H ₅ F ₃	-2.7974	-3.03706	6.183
C ₁₀ H ₄ F ₄	-2.80228	-3.3772	6.191
C ₁₀ H ₃ F ₅	-6.71035	-3.57802	5.172

It is clear that from Table (2), (from the table (1) the total energy for all fluorine azulene 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 (Azulene), with decreasing energy gap, electrons can be easily excited from the ground state (M G. R Desiraju 1997),And from figure (3) it's clear the energies per unit a.u (Eg , LUMO and HOMO) are decreasing with No. of molecules.

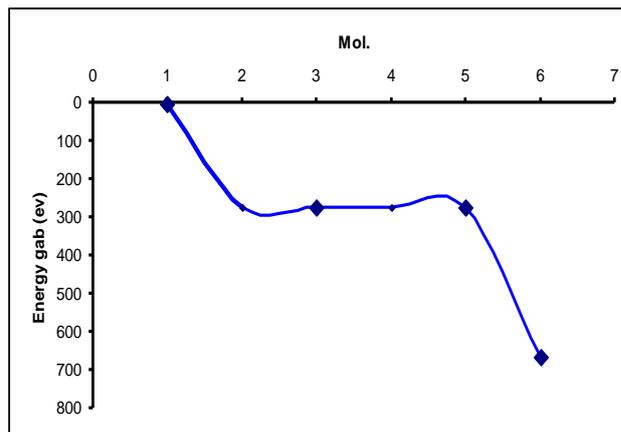


Figure 3: Energies per unit a.u corresponding the No. of molecule .

Some important variables

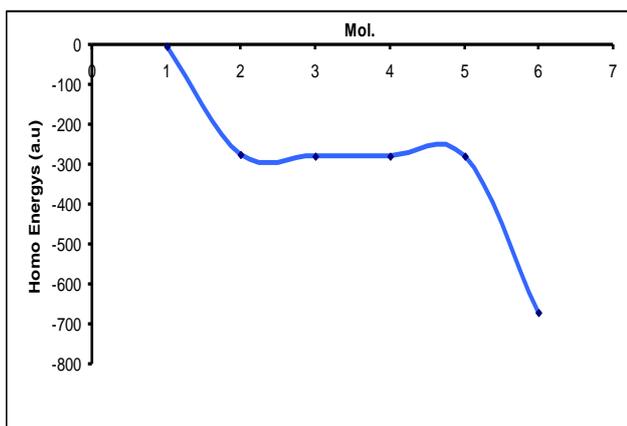
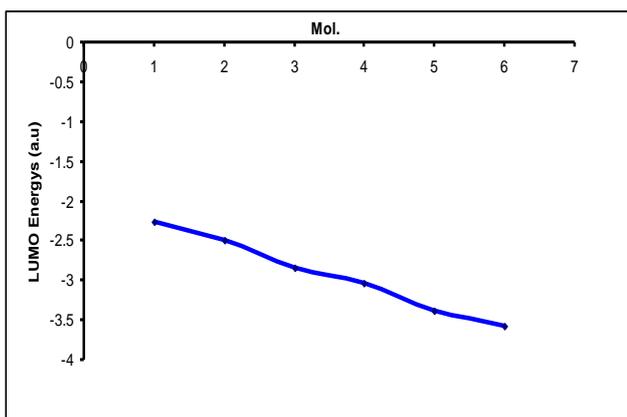
The function B₃LYP used in this work has a high efficient to calculate the electronic properties such as ionization potentials (IP), electron affinities (EA), chemical potentials or electro negativity (χ), hardness (η), electrophilicities (w) and softness (S). Table (3) lists the electronic properties for the molecules under study. It is clear from table (3) that the ionization potential for fluorine azulene molecules group is largest than that for azulene. The electron affinity for fluorine azulene group is more than that the electron affinity for azulene except. It is obvious from this table that all molecules under study have hardness less than that for azulene; the behavior of (electro negativity, softness and electrophilicity) index for the studied molecules shows the magnitude large than these for the original ring (azulene), adding the atoms fluorine give the molecule more softness, it is a new electronic material.

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

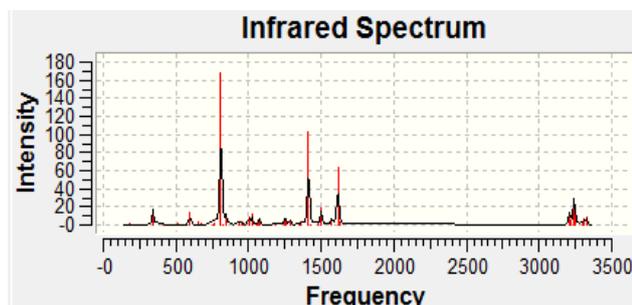
Mol.	IP	EA	χ	η	S	ω
C ₁₀ H ₈	5.59493	2.27051	3.93272	1.6622	0.3008	1.326
C ₁₀ H ₇ F	276.646	2.49909	139.572	137.073	0.00364	2.554
C ₁₀ H ₆ F ₂	277.347	2.84032	140.093	137.253	0.003642	2.738
C ₁₀ H ₅ F ₃	279.774	3.03706	141.405	138.368	0.003613	3.065
C ₁₀ H ₄ F ₄	280.228	3.3772	142.202	138.425	0.003612	3.329
C ₁₀ H ₃ F ₅	671.035	3.57802	337.306	138.53	0.003608	3.519

IR Spectra

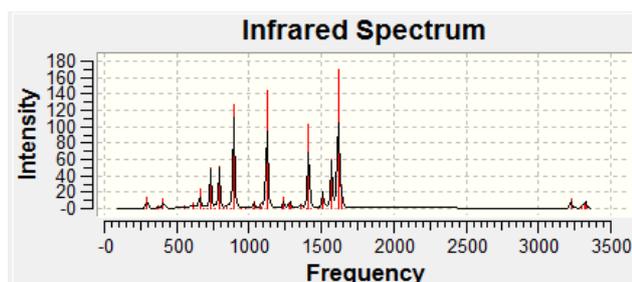
Figure (4) show the vibration frequencies calculated of the studied molecules using B₃LYP/6-31G** method..The strong peak computed by B3LYP/6-31G** observed due to the bending of (C---H) bond, and due to the stretching of (C---C) bond. It is clear from figure (4) that the IR spectrum for group molecules characters from that of tri fluorine azulene 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



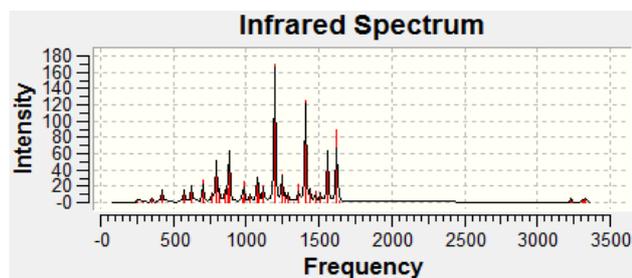
symmetric and asymmetric, the symmetric stretching is happened when the bonds of the same atoms vibrate in the same phase, and the asymmetric stretching is happened when the bonds vibrate in different phases.



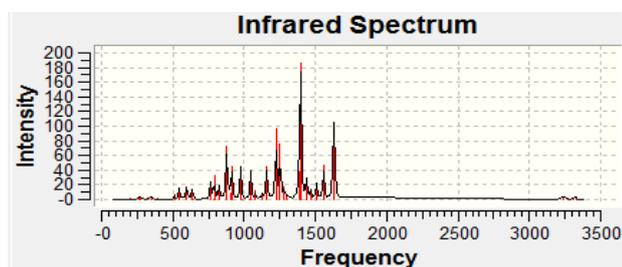
(1)



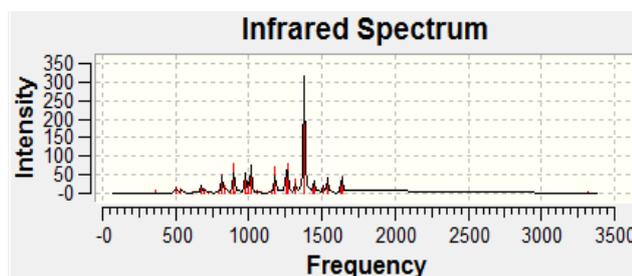
(2)



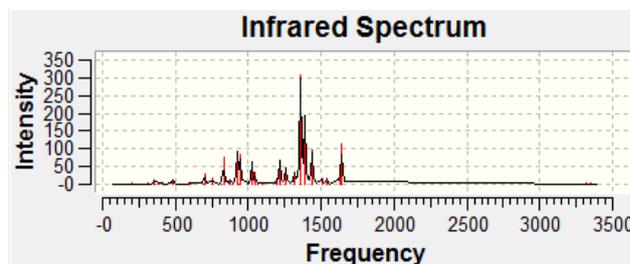
(3)



(4)



(5)



(6)

Figure (4) Vibration frequencies calculated of the studied molecules using B₃LYP/6-31G** method.

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 azulene and fluorine azulene 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 azulene molecules group is lowers' values in compare with azulene.
- 3- The total energies for fluorine azulene 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 azulene, and for new fluorine azulene this study supplies new data for IR spectrum.

References

- B. P. v. R. Schleyer (2001), Aromaticity (Editorial), *Chemical Reviews*, Vol.101, P.1115-1118.
- C A. T. Balaban, P. v. R. Schleyer and H. S. Rzepa(2005), Crocker, Armit and Robinson, *Chemical Reviews*, Vol.105, P.3436-3447.
- E G.A. Jeffery(1991), W. Saenger, Hydrogen Bonding in Biological structures, *Springer, Berlin*.
- F R.d. Green(1974)., Hydrogen Bonding by C-H groups, *Wiley-Inter-Science, New York*.
- G S. Scheiner(1974), Hydrogen Bonding: a Theoretical Perspective, *Oxford University Press, Oxford*.
- K P. Hobza, Z. Havlas(2000), *Chem. Rev.* 100 4253.
- M G. R Desiraju(1997), T. Steiner, The Weak Hydrogen Bond, *Oxford University Press, Oxford*.
- O A. T. Balaban, P. v. R. Schleyer and H. S. Rzepa, Crocker, Armit and Robinson, (2005) *Chemical Reviews*, Vol.105, P.3436-3447.
- P K. Sadasivam, R. Kumaresan, (2011), *Computational and Theoretical Chemistry* 963 227-235.