

# STUDY OF THE EFFECT OF CYANO SUBGROUP ON THE ELECTRONIC PROPERTIES OF AZULENE MOLECULE: B3LYP-DFT CALCULATION

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## Abstract

Theoretical study of the effect of cyano subgroup on the electronic properties of azulene molecule was performed using DFT with B3LYP/6-31(d,p) basis set. The optimized structure, total energies, electronic states, energy gaps, ionization potentials, electron affinities, chemical potentials, global hardness, softness, global electrophilicity, dipole moment and dipole polarizability were calculated. The harmonic vibrational frequencies were calculated and compared with available experimental data. The results showed a decrease in energy gap and improve the electronic properties for the new structures.

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**Keywords:** DFT, Ionization potential, electron affinity, energy gap, and IR spectrum

## Introduction

Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [1]. Cyano-substituted aromatic molecules are members of a class of environmental contaminants found in airborne particulate matter, fossil fuel combustion products, coal fly ash, cigarette smoke, and vehicular emissions, formed by reactions of aromatic molecules with nitrogen oxide [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 [3-5], field effect transistor [6-9], and photovoltaic and solar cells [10,11]. These materials have advantages of easy fabrication, mechanical flexibility and low cost. The organic thin film transistors are one type of the so called organic devices, in which they are fabricated by using the organic semiconductors [12]. There are many organic materials that show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [13, 14].

Various studies on cyclic oligomers have been reported both experimentally and theoretically [15, 16], in [17] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. So, [18] studied the geometric and electronic properties for cyanothiophene oligomers as a prototype of an organic conducting polymer using *ab initio* and DFT [19], they showed that the cyano group generally reduced the band gap with variation of the substitution position.

Azulene molecule and its derivatives have been studied in this work. Therefore the main aim of this work is to examine the cyano group substituent effect on azulene molecule varying the number of the substituent in the molecule.

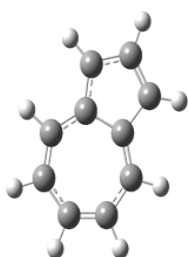
## Theory and computational details

The structures of the molecules under study in this work are shown in figure 1. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 suite of programs [21]. The molecular properties of the compounds had been computed by DFT using the standard 6-31G(d,p) basis set. Lee-Yang -

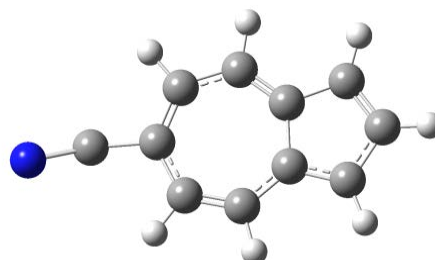
Parr correlation functional [22] is used together with Becke's three parameters[23]exchange functional B3LYP. Conformational analysis of the molecules had been performed to have an idea about the lowest energy structures of the species.

The geometrical structure was performed at the B3LYP density functional theory with the same basis set [22,24]. Harmonic vibration frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [25-27].The electronic energy as, where  $E_T$ ,  $E_V$ , and  $E_J$  are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT due to the exchange correlation term  $E_{xc}$ , which includes the exchange energy arising from the anti-symmetry of the quantum mechanical wave function and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [28].

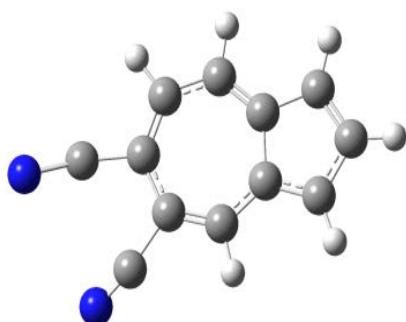
The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction, and vibration analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface[29]. In this investigation, the more relevant electronic potential (IP), electron affinities (EA), chemical potential ( $\mu$ ) (the negative of electronegativity ( $\chi$ )), hardness ( $\eta$ ), softness (S), electrophilic index ( $\omega$ ) and the electric dipole polarizability ( $\alpha$ ) were calculated. The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer and the respective neutral molecule;  $IP_v = E_{\text{cation}} - E_n$ . The EA was computed as the energy difference between the neutral molecule and the anion molecule:  $EA = E_n - E_{\text{anion}}$  [30]. The HOMO and LUMO energy was also used to estimate the IP and EA in the framework of Koopmans' theorem:  $IP = -\epsilon_{\text{HOMO}}$  and  $EA = -\epsilon_{\text{LUMO}}$  [31].



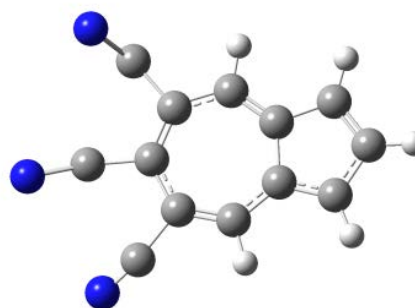
Azulene



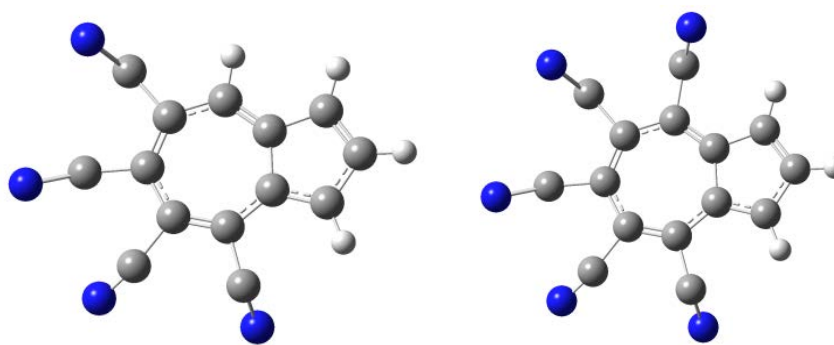
mono-cyano azulene



di-cyano azulene



tri-cyano azulene



tetra- cyano azulene                      penta- cyano azulene  
**Figure 1.** Geometrical structures of the studied molecules

In the density functional theory (DFT), one of the global quantities is chemical potential ( $\mu$ ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the Energy versus N(number of electrons) curve at external potential  $v(r)$ [32]:

$$\mu = \left[ \frac{\partial E}{\partial N} \right]_{(v(r))} \quad (1)$$

The finite difference approximation to Chemical Potential gives,

$$\mu \approx -\chi = -\frac{IP + EA}{2} \quad (2)$$

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, for a constant external potential  $v(r)$  [32]:

$$\eta = \frac{1}{2} \left[ \frac{\partial^2 E}{\partial N^2} \right]_{(v(r))} = \frac{1}{2} \left[ \frac{\partial \mu}{\partial N} \right]_{(v(r))} \quad (3)$$

The finite difference approximation to Chemical hardness gives,

$$\eta = (IP - EA)/2 \quad (4)$$

The softness is given as [31] :

$$S = \frac{1}{2\eta} = \left( \frac{\partial^2 N}{\partial E^2} \right)_{(v(r))} = \left( \frac{\partial N}{\partial \mu} \right)_{(v(r))} \quad (5)$$

The electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index ( $\omega$ ) is defined as [28],

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

One of the other global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy, viz.[32] :

$$\alpha = - \left( \frac{\partial^2 E}{\partial F_a \partial F_b} \right)_{a,b = x, y, z} \quad (7)$$

If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability  $\langle \alpha \rangle$  is evaluated using the equation [28].

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

Where  $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$  are the eigenvalues of the polarizability tensor.

## Results and discussion

### I. Energies.

Table (1) shows the values of the total energy and electronic states and the energy gap ( $E_{LUMO} - E_{HOMO}$ ) of the studied molecules. The total energy for all studied molecules as a linear function of CN side group number adding to the azulene 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:

$$E_{tot} \approx E_{tot}(\text{azulene}) + nE_{tot}(\text{CN}) \quad (9)$$

Where n is the number of CN radicals.

It is clear that from Table 1, the total energy for all mentioned molecules are small when compared with the original azulene molecule, and the substitution of cyano groups causes decreasing the HOMO and LUMO energy [34], and energy gap decreased. Therefore, the presence of substituent decreases the energy gaps improves the conductivities and also enhances the solubilities of these molecules.

The LUMO-HOMO energy gaps of cyano-azulene molecules are less than that of the original molecule, with decreasing energy gap, electrons can be easily excited from the ground state [35,36]. This effect of the side group was the largest in molecule No.6 it has energy gap of (2.524 eV). The energy gap of azulene (3.324 eV). The table 1 shows also the symmetry of studied molecules, the molecule 1 is planar with inversion center and have  $C_{2v}$  symmetry (high symmetry), and have lower electronegativity, while molecule 6 is planar and have  $C_1$  symmetry (low symmetry), and have higher electronegativity. The results showed that the energy gap here is a linear function to the cyano subgroup adding to the molecule.

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

Structure	Energy(a.u)	Symmetry	Electronic States(eV)		Energy Gaps (eV)
			HOMO	LUMO	
1	-383.7826	$C_{2v}$	-5.594	-2.270	3.324
2	-461.1120	$C_s$	-5.292	-2.081	3.211
3	-536.3485	$C_s$	-5.295	-2.190	3.105
4	-611.5643	$C_s$	-5.245	-2.201	3.044
5	-686.7933	$C_s$	-5.004	-2.112	2.892
6	-762.0060	$C_1$	-5.005	-2.481	2.524

### II. Some electronic variables.

B3LYP density functional theory used in this work has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials(IP), electron affinities(EA), electronegativity ( $\chi$ ), absolute hardness( $\eta$ ), absolute softness (S), electrophilic index ( $\omega$ ). The properties that are displayed in table 2 for each variable are computed by adiabatic method only, in which the two different ways used in the calculation are : The first one being energy-vertical is based on the differences of total electronic energies when an electron is added or removed in accordance with the neutral molecule. The second one is based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as orbital-vertical (Koopmans' theorem). The calculated properties for each variable as shown in table 2 clearly reveal that these compounds have a tendency to capture electrons instead of donating them. The ionization potential for the studied molecules group is greater than that for the original azulene molecule, but the molecule No.6 has the largest value of ionization potential, this indicates that this molecule needs high energy to become cation comparing with the others. The strength of an acceptor molecule is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the CN radical to the ring leads to increasing the ability of the electron affinity for the molecule, EA for molecule 6 is the largest, as we see in Table 1.

Few interesting observations have been made from the results that are shown in table 2 obtained through the energy-vertical method. The electron affinities (EA) computed from the energy of the lowest unoccupied molecular orbital (LUMO) are higher for all studied molecules than that of the energy-vertical method. The ionization potential (IP) that results from the highest occupied molecular orbital is smaller for all studied molecules than that of the energy-vertical method. From the previous investigations, it has been found that for almost all the commonly used exchange-correlation functional such as B3LYP, B3PW91, Koopman's theorem is not satisfied accurately [30]. The two results obtained by the calculation of electronegativities and electrophilicities also agreed very well with the difference in the result. This could be the reason for the low hardness values obtained from the orbital-vertical method than from the method of energy-vertical. Koopman's theorem neglects the relaxation effect by using the frozen-orbital approximation. However, this error is frequently compensated by the oppositely directed error due to the electron correlation effect, neglected in the Hartree-Fock (HF) method. Therefore, the Koopmans' theorem is a crude but useful and fast approach [38]. The behavior of electronegativity, softness and electrophilic index for the studied molecules shows the magnitude larger than these for the original ring, adding the radicals give the molecule more softness. The results in table. 2 are due to adiabatic method.

**Table2: The electronic properties for molecules.**

Molecules	IP(eV)	EA(eV)	X (eV)	H(eV)	S(eV) <sup>-1</sup>	W(eV)
1	4.375	1.240	2.807	1.862	0.300	3.853
2	4.675	1.993	3.334	1.749	0.285	4.004
3	5.295	2.054	4.484	1.620	0.308	4.064
4	4.225	1.916	3.886	1.521	0.435	3.856
5	5.053	3.104	4.266	1.334	0.825	4.025
6	6.135	3.854	4.994	1.042	2.206	5.345

The molecules dipole moment represents a generalized measure of bond properties and charge densities in a molecule [30]. Molecule with electron acceptor group due to better charge distribution and increasing distance have higher dipole moment[32], from table 3 molecule **2** has higher dipole moment (8.204 Debye) .

The results of the calculated polarizability for (**1 – 6**) molecules in table 3 showed that all substitution groups leads to increase the average polarizability and cause more reactive than the original molecule. The molecules **2** and **3** have average dipole polarizability equal 203.947 and 207.516 a.u, they have the highest polarizability and have highest reactivity. This due to the ring delocalizing  $\pi$  electron resonance from the ring groups [32].

**Table 3:calculated dipole moment  $\mu$ (Debye) and average polarizability  $\langle \alpha \rangle$  in atomic units for molecules.**

molecules	$\mu$	$\alpha_{zz}$	$\alpha_{yy}$	$\alpha_{xx}$	$\langle \alpha \rangle$
1	0.001	269.81	151.363	44.964	155.379
2	8.204	362.363	182.565	68.913	203.947
3	0.003	379.652	185.604	57.292	207.516
4	0.204	304.58	218.748	59.763	194.364
5	0.012	281.341	203.679	76.989	167.003
6	3.234	303.656	216.695	66.582	195.644

### III. IR Spectra

The IR spectra of (**1- 6**) molecules are provided in fig. (2). The harmonic vibrational frequencies calculated for studied molecules at B3LYP level using the 6-31(d,p) basis sets. The (C – H) stretching vibrations of aromatic molecules in the region (2900 – 3250) cm<sup>-1</sup> which is characteristic region for ready identification of (C – H) stretching vibrations and particularly the region (3250 – 3100) cm<sup>-1</sup> for asymmetric stretching and (3100 – 2900) cm<sup>-1</sup> for symmetric stretching modes of vibration [30]. We summarized the vibrational frequencies and the corresponding intensities for cyano-azulene molecules group in fig. 2.

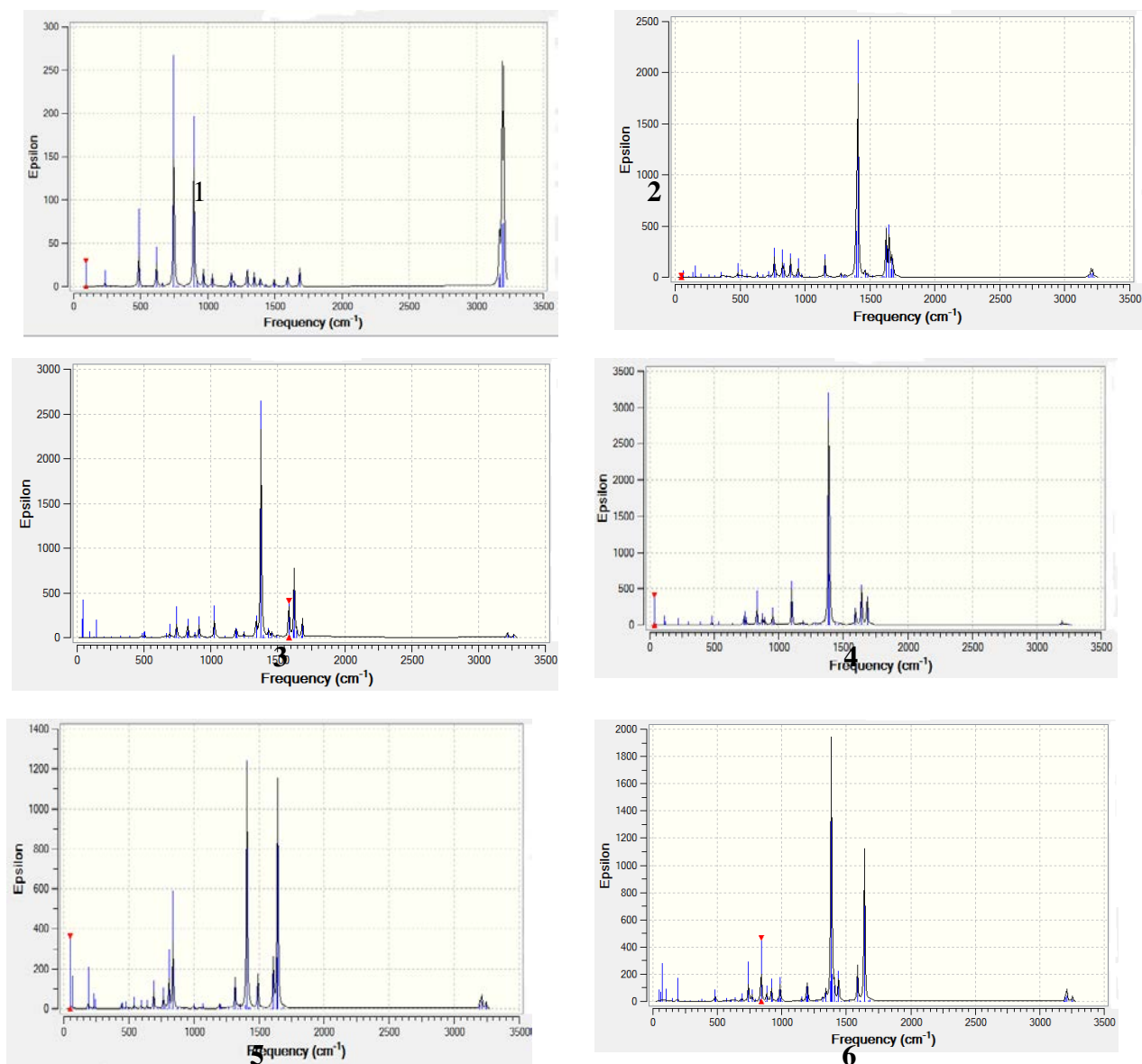


Figure 2: The IR spectra of molecules under study,  $\text{Epsilon} \equiv \text{Intensity (Km/mol)}$ .

#### IV. Conclusions:

The total energies for molecules under study are smaller than that for the original azulene molecule and substitution cyano group causes decreasing energy and more stability. The presence of the substituents decreases the energy gap of the studied molecules, this is one of the important properties obtained in this work, and a small energy gap means small excitation energies of manifold of the excited states. The electronic properties were calculated by two methods, energy-vertical method and orbital-vertical method and Koopman's theorem is not satisfied accurately. The results showed that all substitution groups leads to increase the average polarizability and dipole moment and cause to more reactive than original molecule. Adding the cyano groups leads to increasing the vibrational mode, and highest stretching vibrational wave numbers and its gave suitable positions for CN with carbon atoms in phenyl ring. Molecule **6** is the best option for n-type organic semiconductors because of its better HOMO – LUMO ratio and other electronic properties.

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