Study of The Effect of Nitrogen Atoms on The Electronic Properties of Azulene Ring:B3LYP/ DFT Calculations

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(molecular theoretical physics)

Abstract

Theoretical study of the effect of adding nitrogen atoms in place of carbon atoms on the electronic properties of azulene ring was performed using DFT with B3LYP/6-31(d, p)basis sets. The optimized structure, total energies, electronic states, energy gaps, ionization potentials, electron affinities, chemical potentials, global hardness, softness, global electrophilictity, dipole moment and dipole polarizability were calculated. The harmonic vibration frequencies were calculated and compared with available experimental data. The results showed a decrease and increase in energy gap of azulene depends on the number and position of nitrogen atoms in the ring and improve the electronic properties for the new structures.

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

الخلاصة:

أجريت دراسة نظرية لتأثير استبدال ذرات النيتروجين بدلا من ذرات الكربون في حلقة الآزولين على الخصائص الإلكترونية باستخدام طريقة B3LYP / 6-31(d, p), DFT كمجموعات اساس. تم حساب الهيكل الأمثل، الطاقات الكلية، المستويات الإلكترونية، فجوة الطاقة، جهد التأين، الالفة الإلكترونية، الجهد الكيميائي، الصلابة، الليونة، عزم ثنائي القطب والاستقطاب. ترددات الاهتزاز التوافقي تم حسابها ومقارنتها مع البيانات التجريبية. وأظهرت النتائج انخفاض وزيادة فجوة الطاقة في الآزولين يعتمد على عدد ومواقع ذرات النيتروجين في الحلقة وتحسين الخصائص الإلكترونية للهياكل الجديدة .

1- Introduction

Organic compounds are important in industry and play key roles in the biochemistry of all living things [1,2]. 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 fabricated by using the organic semiconductors [12]. There are many organic materials 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 cynothiophene oligomers as a prototype of an organic conducting polymer using ab initio and DFT [19], they showed that the nitrogroup generally unreduced 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 effect of nitrogen atoms added to azulene ring and calculate some electronic properties of the new structures.

2- Theory and computational details

The structures of the molecules under study in this work are shown in figure 1, where the symbol 1 refers to azulene ring . 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 $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are the electronickinetic 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 ionization potential (IP), electron affinities (EA), chemical potential (μ) (the negative of electronegativity (χ)), hardness (η), softness (S),electrophilic index (ω) and the electric dipole

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polarizability (α) were calculated[30]. The HOMO and LUMO energies were used to estimate the IP and EA in the framework of Koopmans' theorem:

$$IP = E_{HOMO} \quad , \quad EA = E_{LUMO} \quad [31].$$

In the density functional theory (DFT), one of the global quantities is chemical potential (μ), 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 ν(r)[32]:

$$\mu = [\frac{\partial E}{\partial N}]_{V(r)} \tag{1}$$

The finite difference approximation to Chemical Potential gives,

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

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 ν(r) [32]:

$$\eta = \frac{1}{2}[\frac{\partial^2 E}{\partial N^2}]_{V(r)} = \frac{1}{2}[\frac{\partial \mu}{\partial N}]_{V(r)} \tag{3}$$

The finite difference approximation to Chemical hardness gives,

$$\eta = -\frac{(IP - EA)}{2} \tag{4}$$

The softness is given as [31] :

$$S = \frac{1}{2\eta} = [\frac{\partial^2 N}{\partial E^2}]_{V(r)} = [\frac{\partial N}{\partial \mu}]_{V(r)} \tag{5}$$

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

$$\omega = \frac{\mu^2}{2\eta} \tag{6}$$

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] :

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

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$< \alpha >$is evaluated using the equation [28].

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

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

3- Results and discussion

3.1 Energies

Table (1) shows the values of the total energy, electronic states (HOMO and LUMO) and the energy gap ($\varepsilon_{LUMO} - \varepsilon_{HOMO}$)of the studied structures. The total energy for all studied molecules as a linear function of the number of nitrogen N atoms adding in place of carbon atoms in the azulene ring. The final total energy of the product is the collection of the total energy of all small molecules which build the product molecule, that means:

$$E_{tot} \approx E_{tot}(azulene) + nE_{tot}(N) \qquad (9)$$

Where n is the number of nitrogen N atoms.

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 nitrogen atoms added in the ring causes decreasing the HOMO and LUMO energy [34],and energy gap decreased. Therefore, the presence of nitrogen atoms decreases the energy gaps improves the conductivities and also enhances the solubility of these molecules.

The LUMO-HOMO energy gaps of the new structures (molecules 2-6) are independent on the number of nitrogen atoms added to the original molecule in place of carbon atoms, molecule No. 3 has the smallest value of energy gap compared with others, the decreasing energy gap means the electrons can be easily excited from the ground state [35,36]. This effect of replacing atoms was the largest in molecule No.3, in which it has energy gap of (2.835 eV). The energy gap of azulene (3.324 eV), as see in figure 2.

Table 1 shows also the symmetry of studied molecules, the azulene molecule No. 1 is planar with inversion center and has C_{2v} symmetry (high symmetry) with lower electronegativity, while molecule 6 is planer and has C_1 symmetry (low

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symmetry) with higher electronegativity. All structures under study have not imaginary frequency, and this came from the accuracy of level used in optimization geometry for these structures (Berrny optimization). The shapes of HOMO and LUMO for the new structures (molecules 2-6) shown in figure 3 declare that the linear combination of atomic orbitals-molecular orbital comes from the contribution of the atoms in the ring and nitrogen atoms have more contributed in the electronic distribution for the structure.

3.2 Some electronic variables

In this paper we used 6-31G(d, p) basis sets with B3LYP density functional theory of high efficiency 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), electrophilic index (ω). The properties that are displayed in table 2 for each variable are computed by Koopmans method, in which it based on the differences between the HOMO and the LUMO energies of the neutral molecule and it is known as orbital-vertical method. 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 last three studied molecules 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 nitrogen atoms to the ring leads to increasing the ability of the electron affinity for molecule, EA for molecule **3** is the largest, as we see in Table 1.

The molecules dipole moment represents a generalized measure of bond properties and charge densities in a molecule [30]. Molecule with electron accepter group due to better charge distribution and increasing distance have higher dipole moment[32], from table 3 molecule **3** has higher dipole moment (5.321 Debye) . While the original molecule has small value of dipole moment (0.001 Debye). Adding the nitrogen atoms in place of carbon atoms changes the electronic distribution and the symmetry of the molecule.

The results of the calculated polarizability for (**1 – 6**) molecules in table 3 showed that all substitution groups leads to decrease the average polarizability and cause more change in the reactivity of the molecules in compared with the original molecule. The molecules **3** and **4** have average dipole polarizability equal 122.27 and 123.03 a.u, they have approximately the same polarizability.

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3.3 IR Spectra

The harmonic vibration frequencies calculated for studied molecules at B3LYP level using the 6-31(d, p) basis sets are were shown in the IR spectra in figure 3. As we know, the (C – H) stretching vibrations of aromatic molecules in the region (2900 – 3250) 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 stretching modes of vibration [30]. We summarized the vibration frequencies and the corresponding intensities for the studied molecules group in figure 3.The stretching (C – H) for molecules containing nitrogen atoms lies in the region (3150.60 – 3214.22) cm^{-1}, while for azulene molecule is in the region (3210.55–3985.65)cm^{-1}. The (N–H) stretching in the new structures was vibrates around the values between 3600 cm^{-1} and 3620 cm^{-1} depends on the number of nitrogen atoms added to the ring. The bending (C – H) bond in the new structures is in the region (1010.5 – 1260.5) cm^{-1}, and the stretching (C – C) is the region (1530.25–1660.5)cm^{-1}. Other vibrations due to stretching and bending bonds are appear in very low intensities regions for azulene and the other new structures and are shown in the spectra in mentioned figures.

4- Conclusions

The total energies for molecules under study are smaller than that for the original azulene molecule and adding nitrogen atoms in the azulene ring causes decreasing energy and more stability. The presence of these atoms change the electronic states and the (LUMO – HOMO) energy gap (decrease and increase the energy gap) depends on the number and position of nitrogen atoms added to the ring. This is one of the important properties obtained in this work, small energy gap means small excitation energies of manifold of the exited states and gave new electronic state for the compound, while the large value of energy gap in compared with the original structure may indicates new behavior appear for that compound. The electronic properties were calculated by orbital-vertical method. The results showed that all new groups of molecules have lowering value of the average polarizability and higher dipole moment compared with azulene. Adding the nitrogen atoms leads to increasing the vibration modes, and highest stretching vibration wave numbers and its gave suitable positions for nitrogen atoms with carbon atoms in azulene. Molecule **2** is the best option for n-type organic semiconductors because of its better LUMO-HOMO ratio and other electronic properties.

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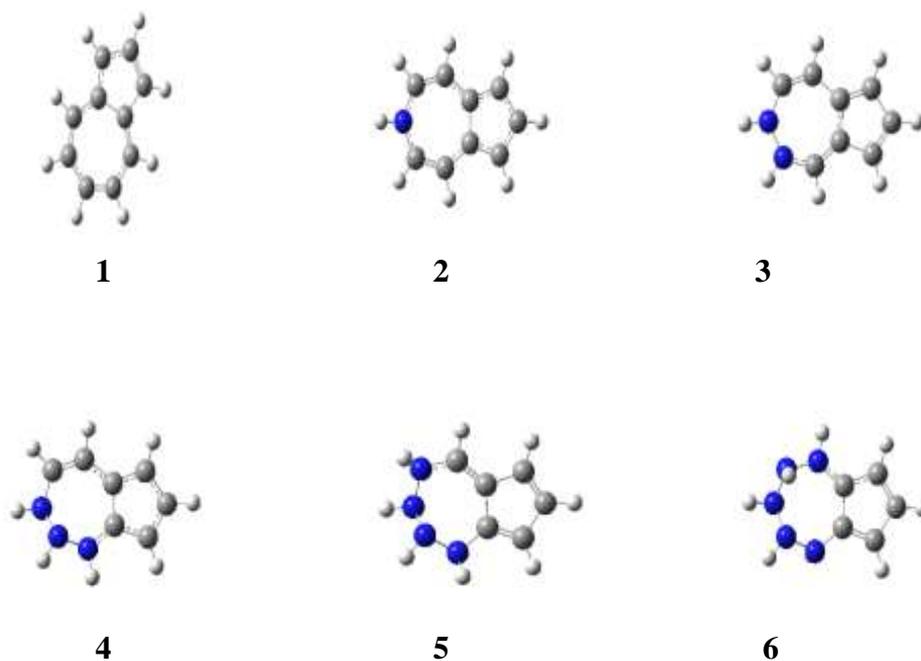
Figure 1: the molecules of azulene with nitrogen
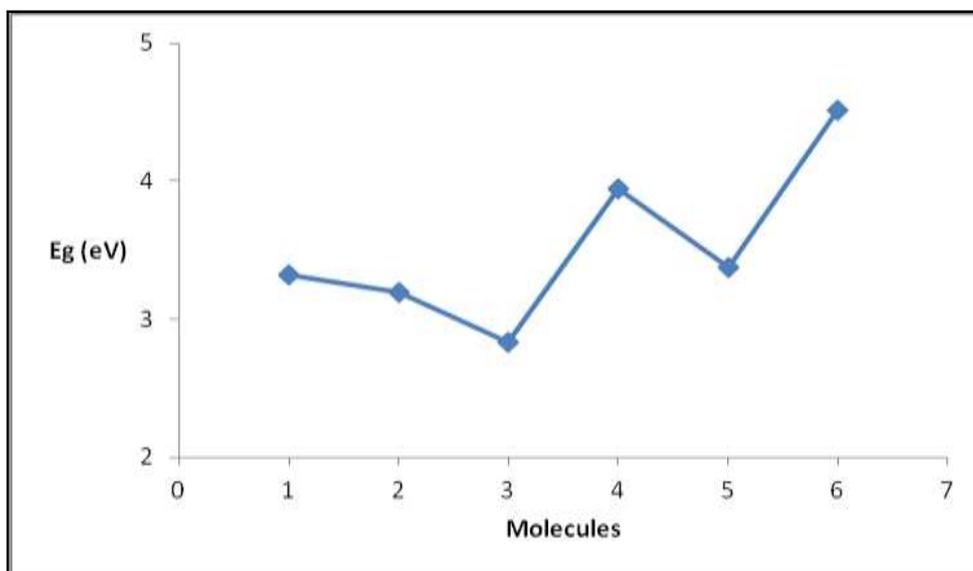
Figure 2: the relation between adding molecules and energy gap
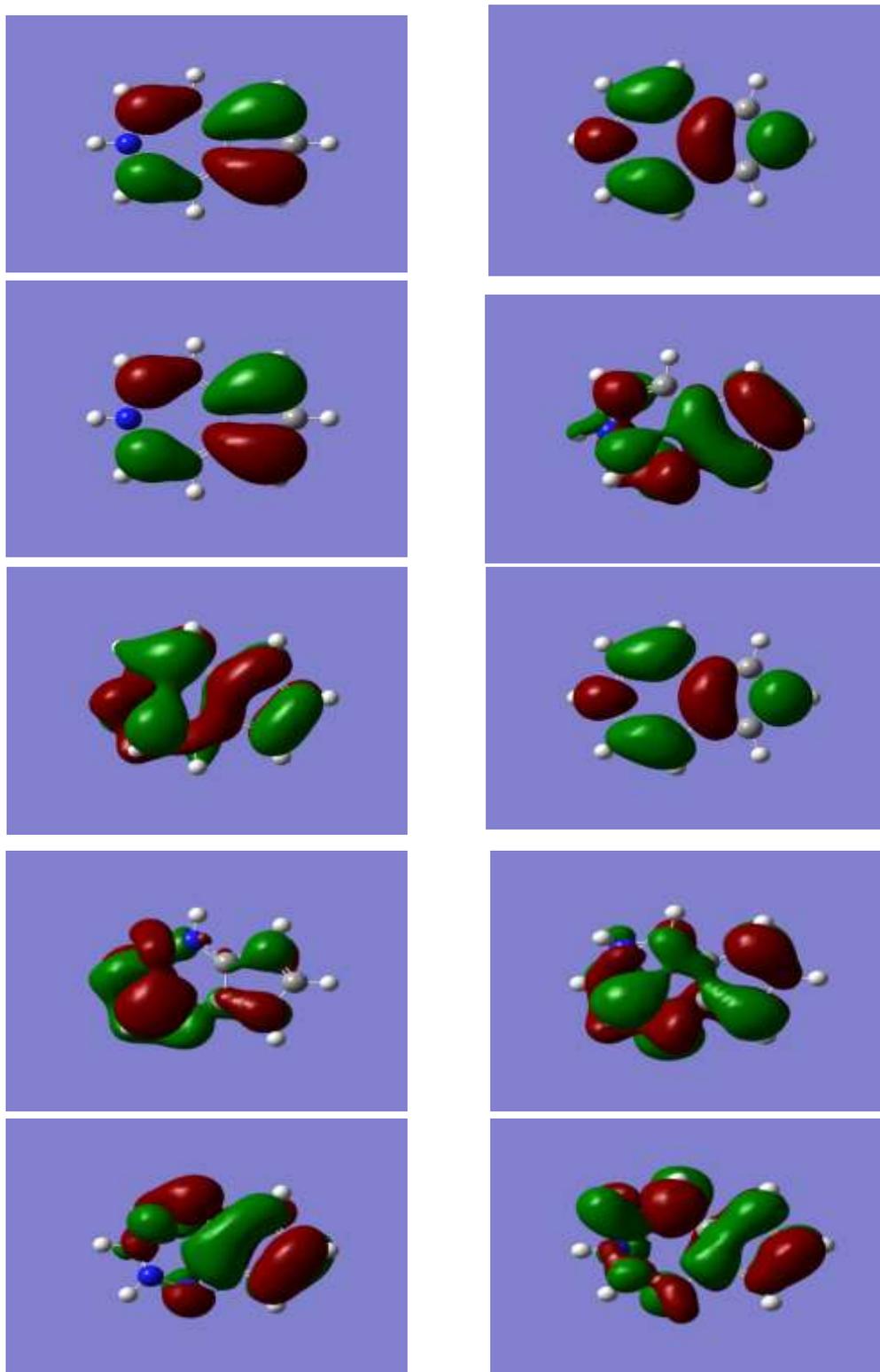
Figure 3: The shapes of HOMO (left) and LUMO (right) for molecules (2–6), respectively

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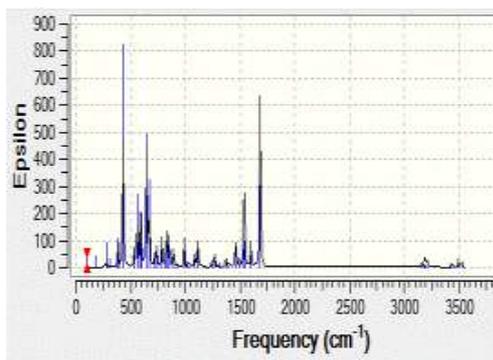
1
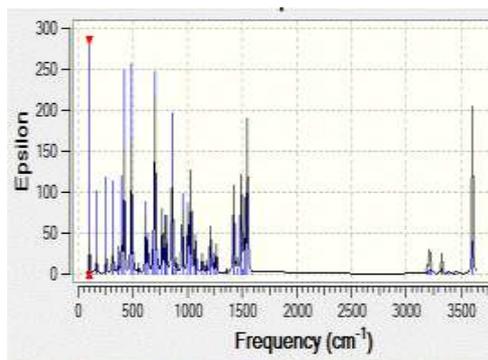
2
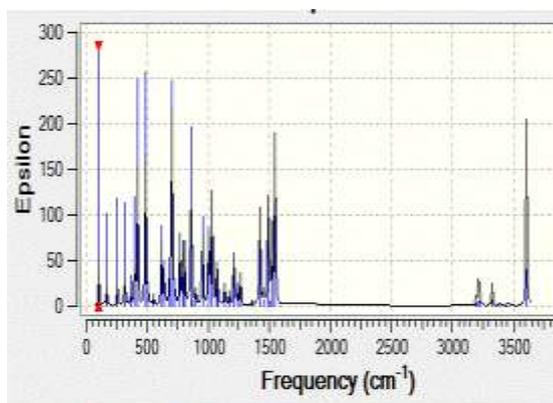
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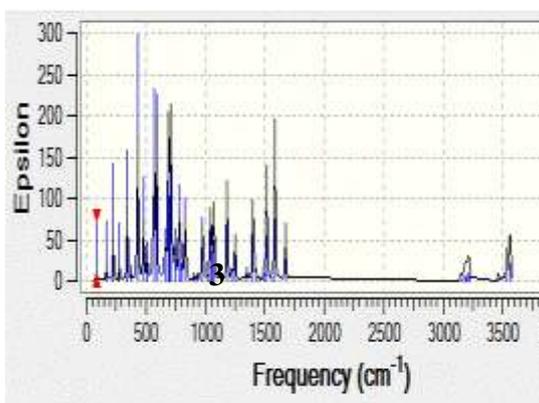
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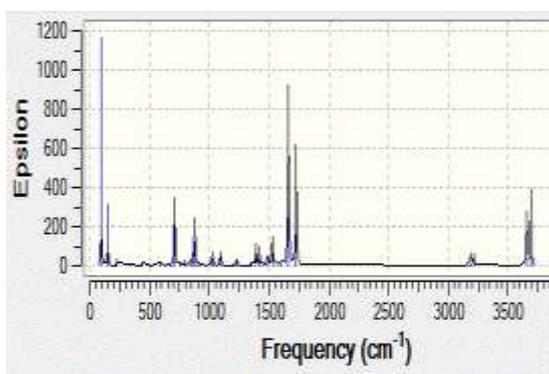
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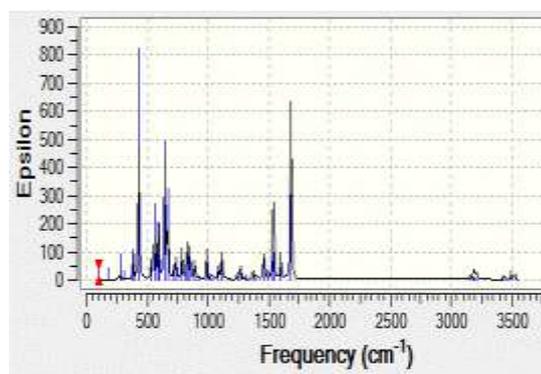
6

Figure 4:The IR spectra of molecules under study, Epsilon≡ Intensity (Km/mol).

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Table 1: **Total energy, electronic states and energy gap for studied molecules**

Structure	Energy(a.u)	Symmetry	Electronic States(eV)		Energy Gaps (eV)
			HOMO	LUMO	
1	-381.7826	C_{2v}	-5.594	-2.270	3.324
2	-402.513	C_{2v}	-0.15992	-0.0425	3.1949
3	-419.114	C_s	-0.15758	-0.05336	2.8358
4	-435.724	C_1	-0.17671	-0.03161	3.9481
5	-452.361	C_1	-0.173	-0.04899	3.3743
6	-468.973	C_1	-0.18362	-0.01785	4.5106

Table2: **Some electronic variables for molecules under study.**

Molecules	IP(eV)	EA(eV)	X (eV)	H(eV)	$S(eV)^{-1}$	W(eV)
1	4.375	1.240	2.807	1.862	0.300	3.853
2	4.351	1.156	2.753	1.597	0.312	2.373
3	4.287	1.451	2.869	1.417	0.352	2.904
4	4.808	0.860	2.834	1.974	0.253	2.034
5	4.707	1.333	3.020	1.687	0.296	2.703
6	4.996	0.485	2.740	2.255	0.221	1.665

Table 3:Total dipole moment μ(Debye) and average polarizability$< \alpha >$ in

atomic units for molecules

molecules	μ	α_{zz}	α_{yy}	α_{xx}	$< \alpha >$
1	0.001	269.81	151.363	44.964	155.379
2	3.747	193.463	128.418	69.101	130.3273
3	5.321	176.356	121.999	68.465	122.2733
4	3.714	178.132	120.722	70.236	123.03
5	4.590	156.958	117.593	70.092	114.881
6	2.187	141.885	110.942	71.631	108.1527

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