Study the Effect of Amino Radicals on the Electronic Properties of Silabutadiene Rings

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Abstract:

The present work deals with the electronic structure of inorganic molecules in form ring, containing semiconductor atoms. Cyclobutadiene is the original ring before adding the silicon atoms and amino radicals. The present study includes six ring molecules . One quantum method is used to find the electronic properties of the studied molecules; it's: density functional theory with B3LYP/3-21G** level, it used to investigate the ionizations potential, electron affinity, chemical potential, total energy, energy gap, dipole moment and hardness. Calculations are carried out by employing the Gaussian 2003 program.

The silabutadiene molecules are more reactive, also hardness and energy gap decrease with increasing of silicon atoms and amino radicals added compare with the original ring, this means that adding silicon atoms lead to new electronic materials.

Key words: Silabutadiene, energy gap, ionization potential , electron affinity, chemical potential, IR spectra.

الخلاصة :

يتناول البحث الحالي التركيب الالكتروني لجزيئات لا عضوية على شكل حلقة تحتوي على ذرات شبة موصلة. ان البيوتادين الحلقة الاساسية قبل اضافة ذرات السيليكون وجذور الامين. يحتوي هذا البحث على ستة جزيئات حلقية. أستخدمت طريقة واحدة من طرق الكم لايجاد الخصائص الالكترونية للجزيئات المدروسة وهي طريقة دالة الكثافة ذات المستوى (B3LYP/3−21G**) هذه الطريقة أستخدمت لايجاد جهد التاين والالفة الاليكترونية والجهد الكيميائي و الطاقة الكلية و فجوة الطاقة و عزم ثنائي القطب والصلادة. تم الحصول على الحسابات بواسطة برنامج كاوس ٢٠٠٣.

ومن أهم ما توصلت أليه الدراسة هو إن استبدال ذرات الكربون بذرات السيليكون مع اضافة جذور الامين يجعل الجزيئة أكثر مرونة وتزداد فاعليتها مع المحيط مقارنة مع الحلقة الاصلية ، حيث تناقصت الصلادة بإضافة ذرات السيليكون إضافة إلى تناقص عرض فجوة الطاقة وهذا يعني الحصول على مواد الكترونية جديدة .

1- Introduction:

Cyclobutadiene ring is a four atoms of carbon bonded together by strong covalent bonds, in form cycle, it is an even attendant ring [V. I. Minkin, *et al*;1994], anti- aromatic [S. K. Ritter; 2004], the four identical bonds have a bond order of 0.5, which is significantly below the average for acyclics [Z. Chen, *et al*; 2003] ,this system have π-electron densities of unity in its ground neutral state [John P. Lowe, et al; 2006]. A series of theoretical and π interactions [M. Mascal, *et al*; 2002] and cation -π interactions [B. L. Schottel, *et al*; 2008] the interaction of anions and cations on different faces of the same π-system have been studied [I. Alkorta, *et al*; 2007].

Cation -π interactions that play important roles in many forefront sciences [K. S. Kim, *et al*; 2000] ,the importance of this kinds of interaction within various areas of scientific research is widely recognized ,and this mode of interaction has been the subject of several recent review and perspectives articles [P. Metrangolo, *et al*; 2008]. When replacing the carbon atoms by silicon atoms with rearrange cycle it's called silabutadiene ring and its transformed from organic to inorganic composites [L. Pavesi, *et al*; 2010, Yoshizawa, *et al*; 1999].

Silicon materials have many industrial uses. They are the base of component of most semiconductor devices; most importantly integrated circuits. Silicon is widely used in semiconductor devices because it remains a semiconductor at higher temperatures than the semiconductor germanium and because its native oxide is easily grown in a furnace and forms a better semiconductor dielectric interface than any other material [Ichinohe, *et al*; 2005, K. Hong, *et al*; 2010, P. Lorenzoand, *et al*; 2010, . L. Khriachtchev; 2009].

Free radical is an atom, a group of atoms or a molecule possessing one unpaired electron, which occupies an outer orbit [Beckman, *et al*; 1998, Aubrey D. N. J de Grey; 1999].

Amino Group is Nitrogen containing groups often have a significant impact on the physical-chemical properties and reactivates of relevant chemicals . A very important group is the amino group that is present in chemistry, radicals (often referred to as free radicals) are atoms, molecules, or ions with unpaired electrons on an otherwise open shell configuration [Egli, T., *et al*; 2001, Nowack, *et al*; 2000].

2-Theory:

Quantum Mechanic is a very successful model to understand the electronic structures of semiconductor structures, many models are used to study semiconductor structures properties in addition to other different kinds of models to resemble of any structures, Density functional theory is a quantum mechanical modeling method used in this work, there are many approximations such as local density approximation, generalized gradient approximations and hybrid functional, we will used the hybrid functional, and it should be approximated with a common density functional. The weighted sum of these two results is known as the functional of B3-LYP [Nzengung, *et al*; 2002, S.C. Miller; 1970, F. Brouwer; 1995]:

$$E_{xc}^{B3\text{-}LYP} = (1-a)E_x^{LDA} + aE_x^{B88} + cE_c^{LYP} + (1-c)E_c^{LDA}$$

All constants are known, and E_x^{B88} is the Becke exchange functional, LDA exchange–correlation density, a_o, a_x and a_c are three empirical parameters and the best value of these parameters had been found as follow (a_o=0.20, a_x=0.72 and a_c=0.81). It has shown to be highly successful for determination of properties such as energy gap, ionization potential , electron affinity and chemical potential [M. Head-Gordon, *et al*; 1994, X. G. Gong, *et al*; 1994].

The total energy (E_{tot}), ionization potential (IP), electron affinity (EA),chemical potential (K), hardness (η) and electrophilicity (W) for silabutadiene molecule are calculated in this work was calculated in B3LYP/3-21G** DFT in the following equations [J. huter; 2005, Anupama Ghosh, *et al*; 2010]:

$$IP = E_{(+)} - E_{(n)} \qquad\qquad (1)$$

where E(+)is the positive charged energy, E(n) is the neutral energy and E(-) is the negative charged energy.

$$EA = E(n) - E(-) \qquad\qquad (2)$$

$$K = (IP + EA) / 2 \qquad\qquad (3)$$

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

$$W = K^2/2\eta \qquad\qquad (5)$$

$$E_{gap} = E_{LUMO} - E_{HOMO} \qquad\qquad (6)$$

The dipole moment for neutral system is calculated from the atomic charges and the ion pairs as [X. G. Gong, *et al*; 1994] :

$$(7)$$

$$\mu_i = ce\sum_A (Q_A i_A) + 2cea_o\sum_A \rho(s-\rho_i)_A D(A) \quad , \quad i = x, y, z$$

Where c is speed of light, e is the electron charge, Q_A μi is total electron density, $\sum(Q_A i_A)$ is bond dipole, a_o is Bohr radius, $\rho(s-\rho_i)_A$ is one center electron density matrix element, and D(A) is the one center two electron integral [Anupama Ghosh, *et al*; 2010, Hong-Wei Xi, *et al*; 2008]:

The total dipole moment is:

$$\mu = \mu_x + \mu_y + \mu_z \qquad\qquad (8)$$

For any of amino groups molecules and the number of E_{tot} the total energy NH_2 groups:

$$Etot \approx E_{tot}(silabutadiene) + n\, Etot\,(NH_2) \qquad\qquad (9)$$

Where E_{tot} (silabutadiene) = - 1154.48 a.u.

n is the number of NH_2 groups, and $E_{tot}(NH_2)$ = - 55.579 a.u.

Infrared radiation (IR) is a radiation in the energy range between the visible and microwave regions of the electromagnetic spectrum. The portion of the IR spectral region between (2500-25000) nm [Huda B. H.; 2011]. Quantum mechanics places restrictions on microphysical systems.

These restrictions limit a molecule to having discrete energy levels. Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting, generally 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, most of the absorptions cited are associated with stretching vibrations [P. J. Stephens, *et al*;1994, Adil J. N.; 2011]:

3-Results and Discussion:

The number of the amino-silabutadiene groups molecules studied in this work are six, and we have been referred to every molecule as number in the figures and tables to the shortcut, table (1) shows the molecules, number of molecules and chemical formula for the molecules, figures (1-0, 1-1,1-2, 1-3, 1-4, 1-5) show the molecules.

Fig.(1-0)   (1-1)   (1-2)   (1-3)   (1-4)   (1-5)
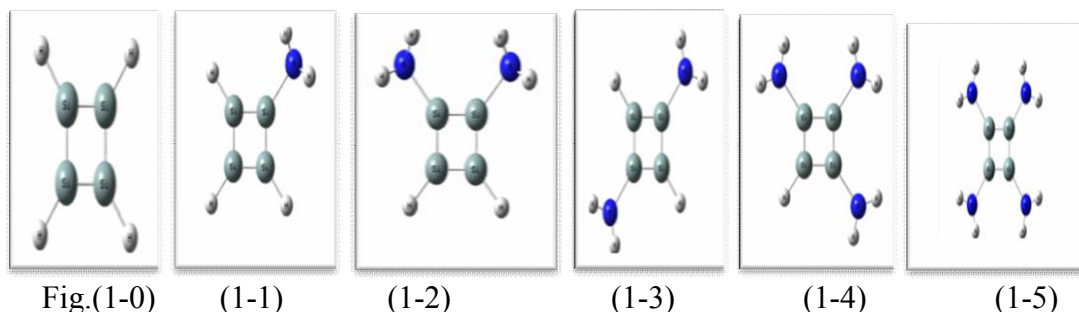
Before proceeding in physical properties calculation, it is necessary to find out the geometry optimization of the studied molecules, Table (2) shows the bond length and Angles between the bonds for this molecules, Table (3) shows HUMO, LOMO, E_{gap}, IP, EA, K, η, W, E_{tot} and Dipole moment for this molecules.
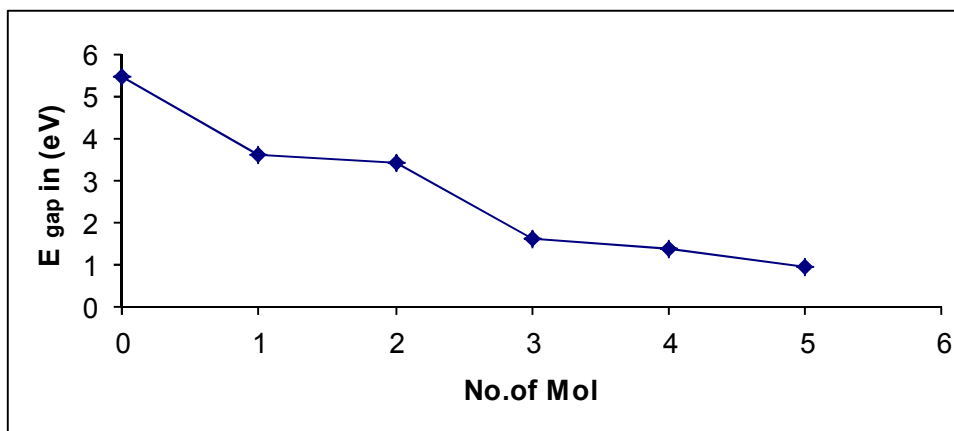
Figure(2): The relation between energy gap and no. of mol.

From the calculations, it has been found that the energy gap for the silabutadiene molecule decreasing with adding and replacing of location of NH_2 .This is one of the important results obtained in the present study, 1,2,3,4-tetraamino-silabutadiene) has smaller energy gap than the others this may indicate a new electronic material, small energy gap means small excitation energies of manifold of the excited states, as shows figure(2) .
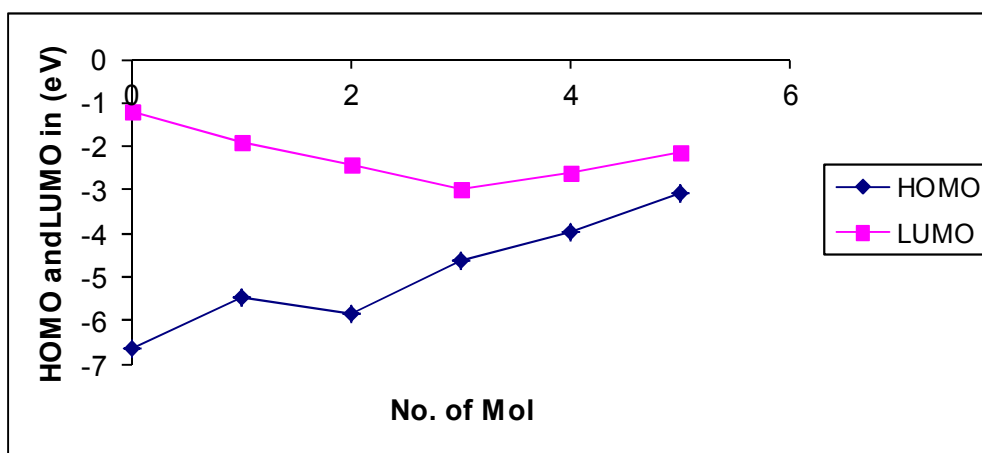

Figure(3): The relation between E_{HOMO} and E_{LUMO} and no. of mol.

The main change occurs at HOMO level compared with LUMO level and this change depends on the number of NH_2. Figure (3) shows the HOMO and LUMO level of the silabutadienes molecules. The molecular orbitals are localized on the same part of the silicon atoms and NH_2 positions, and this localization gives the active site an ability to interact with other atoms , such as, hydrogen and hydrogen like atoms.

The total energy of silabutadiene as alinear function of NH_2 side group number adding to the molecules as shows in figure (4).
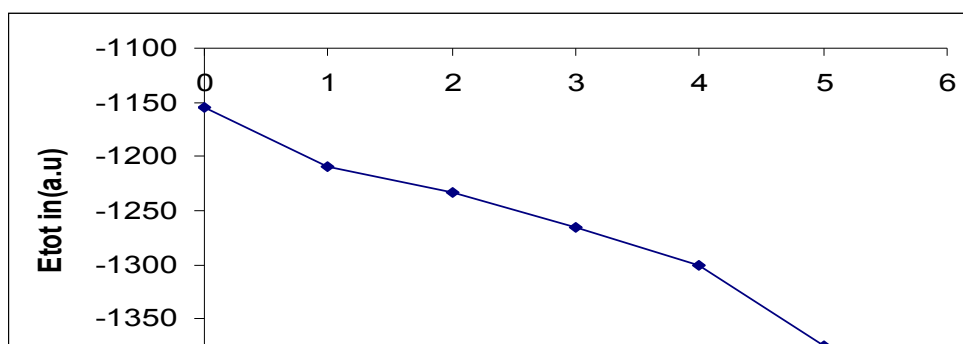
**Figure(4): The relation between total energy and no. of mol.**
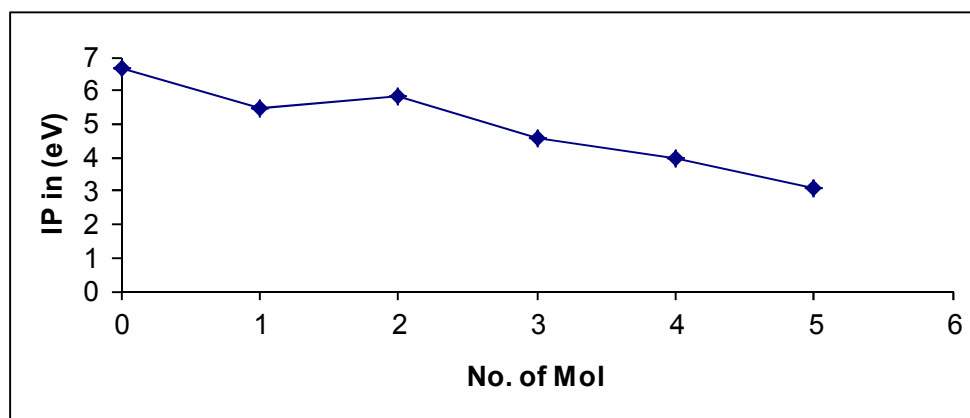
Figure(5): The relation between ionization potential and no. of mol.

By depending on the results of electron states for the studied molecules, figure(5) shows the ionization potential for the radicals-silabutadiene molecules IP for new molecules is less than that for the original molecule this indicates that it needs small energy to become cation comparing with the others.
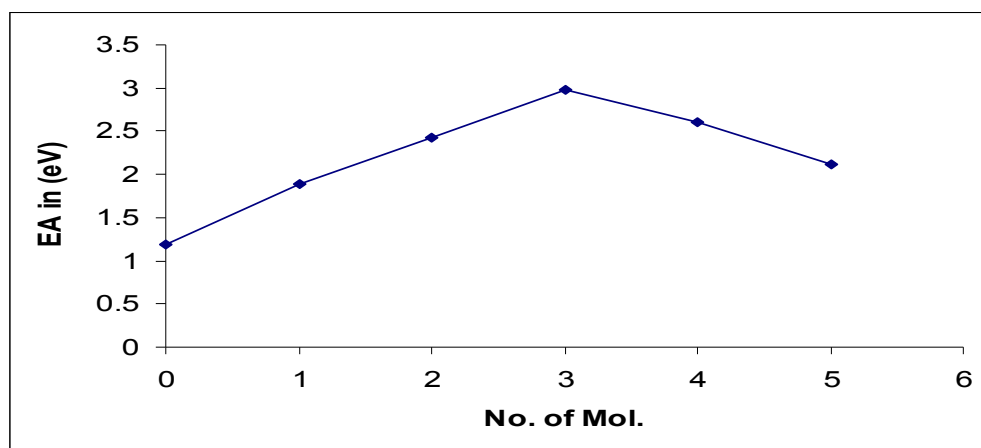

Figure(6): The relation between electron affinity and no. of mol.

Adding the side groups of amino radicals to the silabutadiene molecules leads to increasing the electron affinity.2,4-diamino-silabutadiene molecule has the largest of electron affinity value that is mean this molecule needs large energy to become anion comparing with other molecules as shown in figure(6).
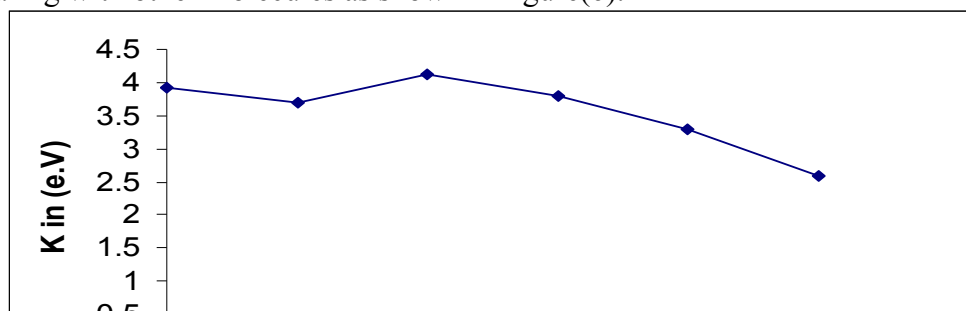
Figure(7):The relation between chemical potential and no. of mol.

The chemical potential for all radicals-silabutadiene molecules groups is less than that for the original molecule this refers to that the electrons in these molecules have a large escaping tendency as shows figure (7).
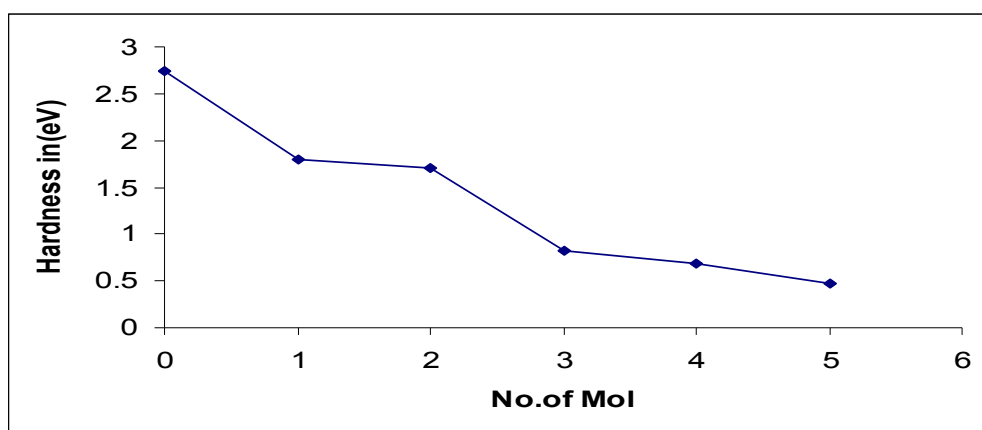
**Figure(8): The relation between the hardness and no. of mol.**

It is clear from figure (8) that the hardness of all molecules is small but for tetraamino-silabutadiene the hardness is the smallest with respect to others. The decreasing of hardness is the main future as a sign for that band gap goes to be rather soft and lowering the resistance of a species to lose an electron.
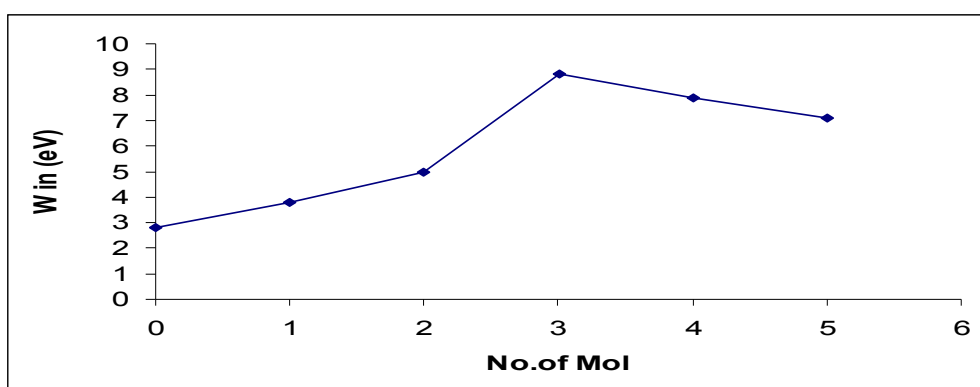
**Figure(9):The relation between electrophilicity and no. of mol.**

Figure(9) shows the relation between the electrophilicity and the number of molecules, from this figure the electrophilicity computed decreasing with increasing of NH_2 groups, for silabutadiene has

small electrophilicity and 2,4-diamino-silabutadiene has the largest value of electrophilicity, all new silabutadienes are strong electrophones.
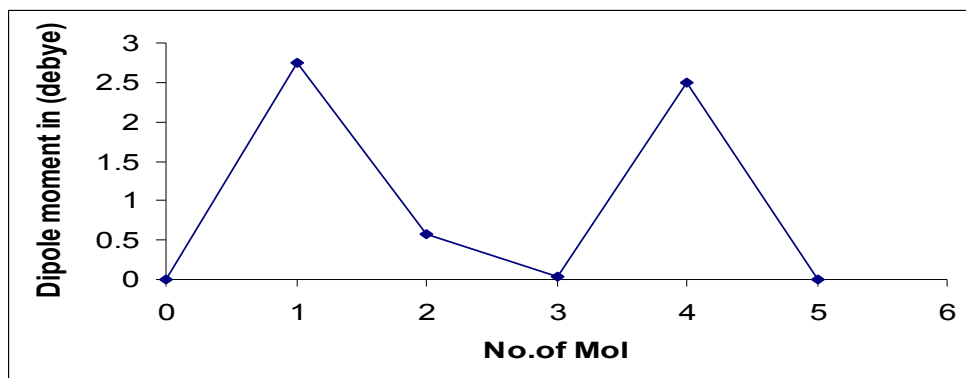

**Figure(10):The relation between total dipole moment and no. of mol.**

In this study, we have found that dipole moment of (1-monoamino-silabutadiene and 1,2,3-triamino-silabutadiene)molecules approximately similar, and for (1,2-diamino-silabutadiene has 0.5) , while for (silabutadiene ,2,4-diamino-silabutadiene and 1,2,3,4-tetraamino-silabutadiene) molecule have been found approximately zero as shows figure(10). These results explain the symmetry for each molecule, and they exhibit bond localizations and their geometries are non-uniform, exhibiting alternating (Si---Si) bond lengths.
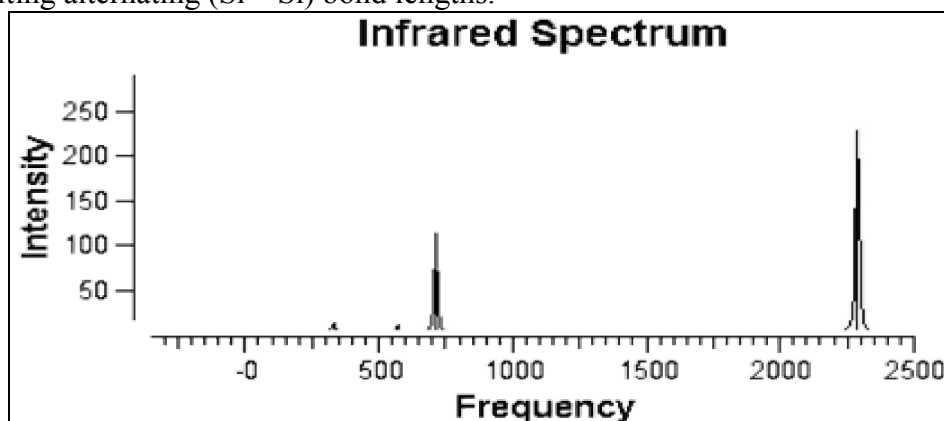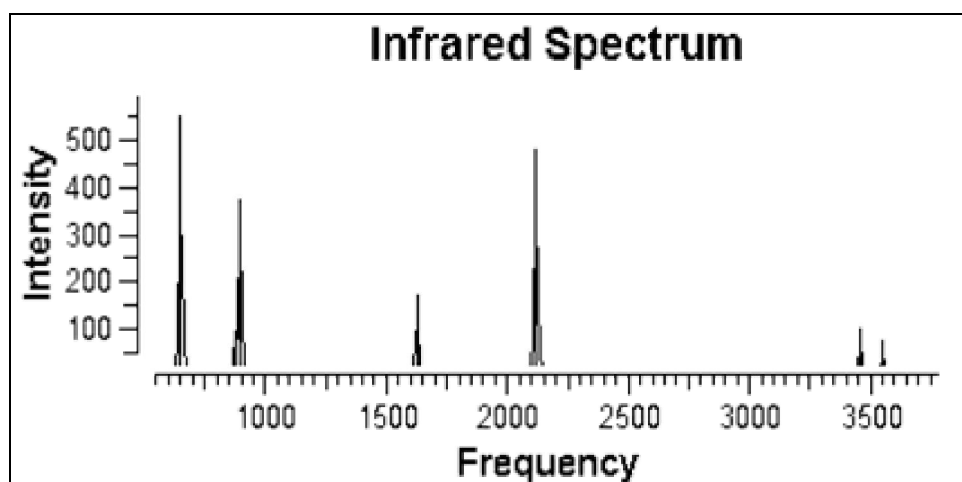

Figure(12-0): IR spectrum for silabutadiene
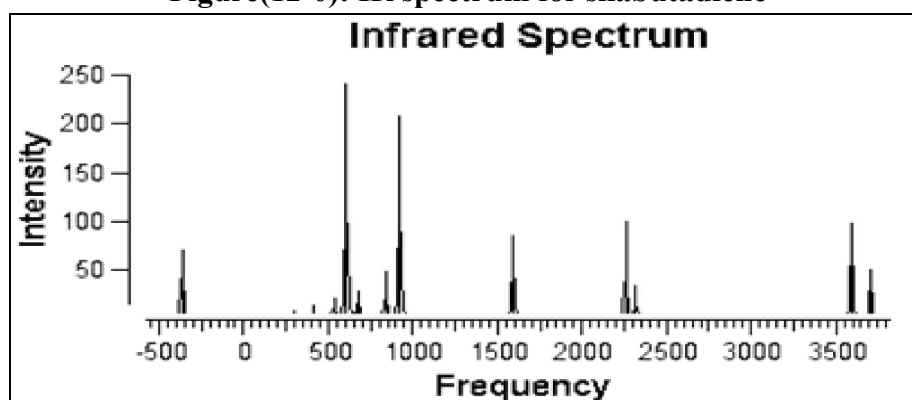
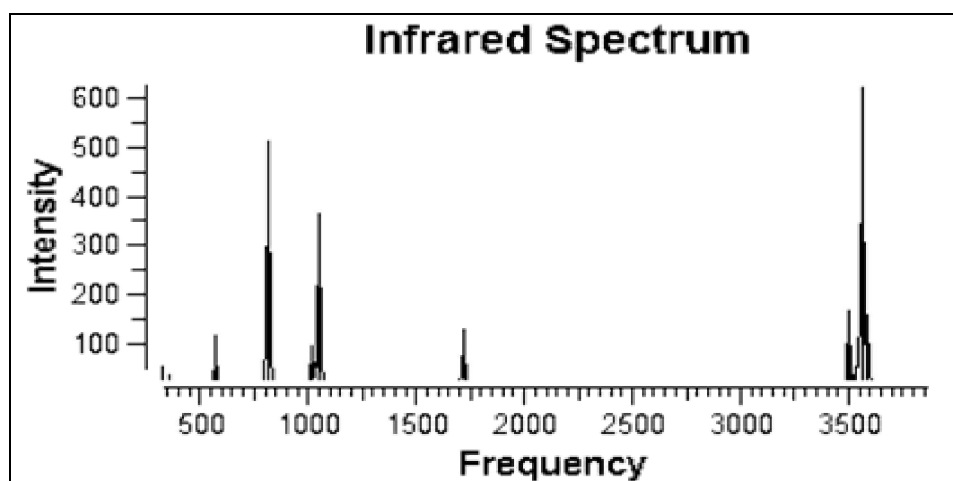**Figure(12-1): IR spectrum for 1-monoamino-silabutadiene**
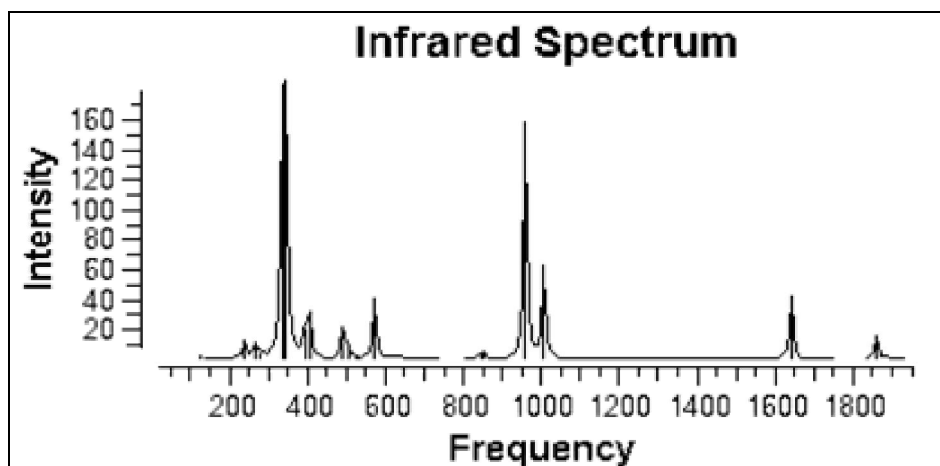
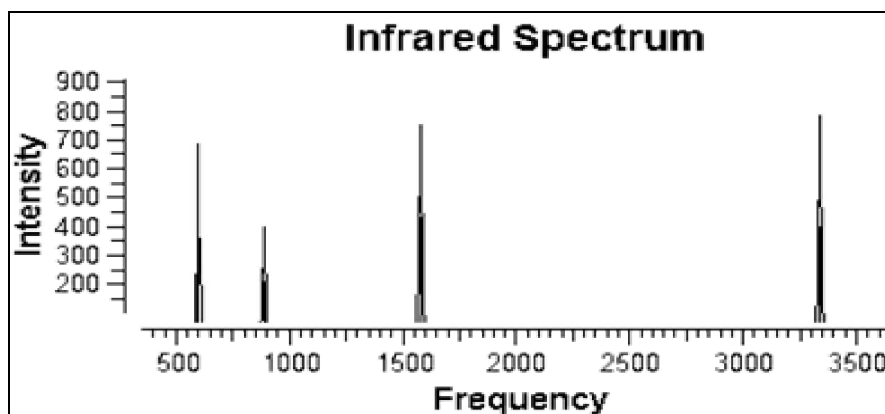**Figure(12-2): IR spectrum for 1,2-diamino-silabutadiene**

Figure(12-3): IR spectrum for 1,3-diamino-silabutadiene

Figure(12-4): IR spectrum for 1,2,3-triamino-silabutadiene

Figure(12-5): IR spectrum for 1,2,3,4-tetramino-silabutadiene

The shaking modes for amino-silabutadiene molecule groups are shown in figure (12-0) by B3LYP/3-21G** method. By comparison the IR spectrum of 1-monoaminobutadiene molecule with that of butadiene molecule, figure (12-1), it will be noted the differences between them, and it has been deduced that the differences due to the addition of NH_2 groups, where the vibration modes have been increased with increasing of bonds, consequently the peaks have been increased. 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.

4-conclusions :

1- B3LYP functional level is an efficient of density functional theory to studying the properties of
   these molecules.

2- Geometric structures, symmetry and total energies for silabutadiene are suitable results for even elternant rings, and this work supplies new data in this aspect because they have not been found similar studies for NH_2 radicals-silabutadiene molecules group.

3- The energy gaps for all new molecules are change with adding and replacing the location of NH_2 radical, molecule has the smallest energy gap than the others, this is one of the important property obtained in this work, a small energy gap means small excitation energies of mani-fold of the excited states.

4- Present work are also supplies new data for the total energy (E_{tot}), ionization potential (IP), electron affinity (EA), chemical potential (K), hardness (η), electrophilicity (w) and IR spectra of the studied molecules.

Table (1):The molecules, number of molecules and chemical formula

for amino-silabutadiene mol.

No. of Mol	Name of Mol.	Chemical formula
0	Silabutadiene	Si_4H_4
١	1-monoamino-silabutadiene	$Si_4H_3NH_2$
٢	1,2-diamino-silabutadiene	$Si_4H_2(NH_2)_2$
٣	1,3-diamino-silabutadiene	$Si_4H_2(NH_2)_2$
٤	1,2,3-triamino-silabutadiene	$Si_4H(NH2)_3$
٥	1,2,3,4-tetraamino-silabutadiene	$Si_4(NH_2)_4$

Table (2):The bond length and angles between the bond

for amino-silabutadiene mol.

No. of Mol.	Bond	Bond length(Å)	Exp.[Vladimir Ya. Lee, et al;2007]	Bond	Angles (degree)
0	Si----Si	2.37	2.39	Si--Si--Si	89.99
	Si==Si	2.17	2.17	——	——
1	Si----Si	2.23	——	Si--Si--Si	98.50
76.30	Si--Si--Si	——	2.40	Si----Si	2
——	——	——	1.47	Si==Si	
72.60	Si--Si--Si	——	2.28	Si----Si	3
74.15	Si--Si--Si	——	2.30	Si----Si	4
89.99	Si--Si--Si	——	2.17	Si----Si	5

Table(3):parameters of analyzed molecules.

Dipole Mom.	E_{gap} (eV)	E_{tot} (a.u)	W(eV)	η(eV)	K(eV)	EA(eV)	IP(eV)	LOMO (eV)	HUMO (eV)	No. of Mol.
0	5.468	-1154.5	2.823	2.734	3.929	1.195	6.664	-1.195	-6.663	**0**
2.75	3.600	-1209.6	3.773	1.800	3.685	1.885	5.486	-1.885	-5.486	**1**
0.57	3.422	-1232.6	4.985	1.711	4.130	2.419	5.842	-2.419	-5.842	**2**
0.04	1.631	-1264.8	8.806	0.815	3.790	2.974	4.606	-2.974	-4.606	**3**
2.49	1.361	-1300.8	7.904	0.681	3.281	2.600	3.961	-2.600	-3.961	**4**
0	0.951	-1374.8	7.085	0.475	2.596	2.120	3.072	-2.120	-3.072	**5**

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