

Theoretical Study of the Electronic Properties of Silabenzene Molecules Group: by B3LYP-DFT

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Abstract

The electronic properties of silabenzene molecules were investigated depending on the three parameters (B3LYP) density functional theory .The best geometry for all molecules was investigated using 6-31G** basis sets. The total energies, electronic states, energy gaps, ionization potentials and electron affinities were calculated for the studied molecules. Adding the sodium atoms to the hexasilabenzene lead to decrease the energy gap and the hardness of the molecule. This may indicates a new electronic material .The IR-spectrum shows the effect of silicon atoms in the ring on the vibrations of the reference molecule.

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, lone pairs, or empty orbital's exhibit stabilization stronger than would be expected by the stabilization and of resonance .The 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 benzene was formed from a six-membered carbon ring with alternating single and double bonds, was developed by Kekule [2].The model for benzene consists of two resonance forms, which corresponds to the double and single bonds switching positions [3].

In present work ,benzene is a reference for the new studied molecules ,in which they consist of silicon atoms in the ring ,the new silicon based molecules and clusters have been exhaustively studied [4-9].There are many researches in aromatic molecules containing silicon atoms [8,10].Silabenzene, silanaphthalene and silanthracene have been synthesized [11-13].Many methods used to study the aromaticity based 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, silabenzene molecules group have been studied using DFT theoretical approach, and study the electronic properties of a new silicon cluster,Si6Na6.

Theory and computational Details

In this work, density functional theory has been used to calculate the electronic properties of the studied molecules at B3LYP 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]:

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

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

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

Where n_i is the number of electrons in orbital (i), and the summation is over the occupied molecular orbitals. 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 electron system, classical coulomb energy, and exchange–correlation energy, respectively [19,20].

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

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

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

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

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

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

Where the three parameters $a_0 = 0.20$, $a_x = 0.72$, 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, 20]:

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

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

Where $E_{(+)}$ and $E_{(-)}$ are the positive and negative charged energy, $E_{(n)}$ is the neutral energy.

The electronic chemical potential (k), the hardness (η) and the softness (s) are given by:

$$K = IP + EA / 2 \quad (11)$$

$$\eta = IP - EA / 2 \quad (12)$$

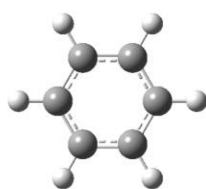
$$S = 1/2 \eta \quad (13)$$

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

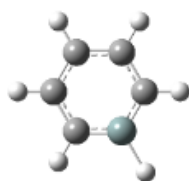
$$W = K^2 / 2 \eta$$

Results and Discussion

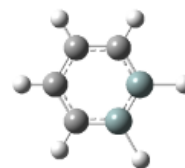
Figure (1) shows the studied molecules. The total energy and symmetry for these molecules are presented in table (1). The benzene molecule was included as reference.



Benzene



mono-silabenzene



di-silabenzene

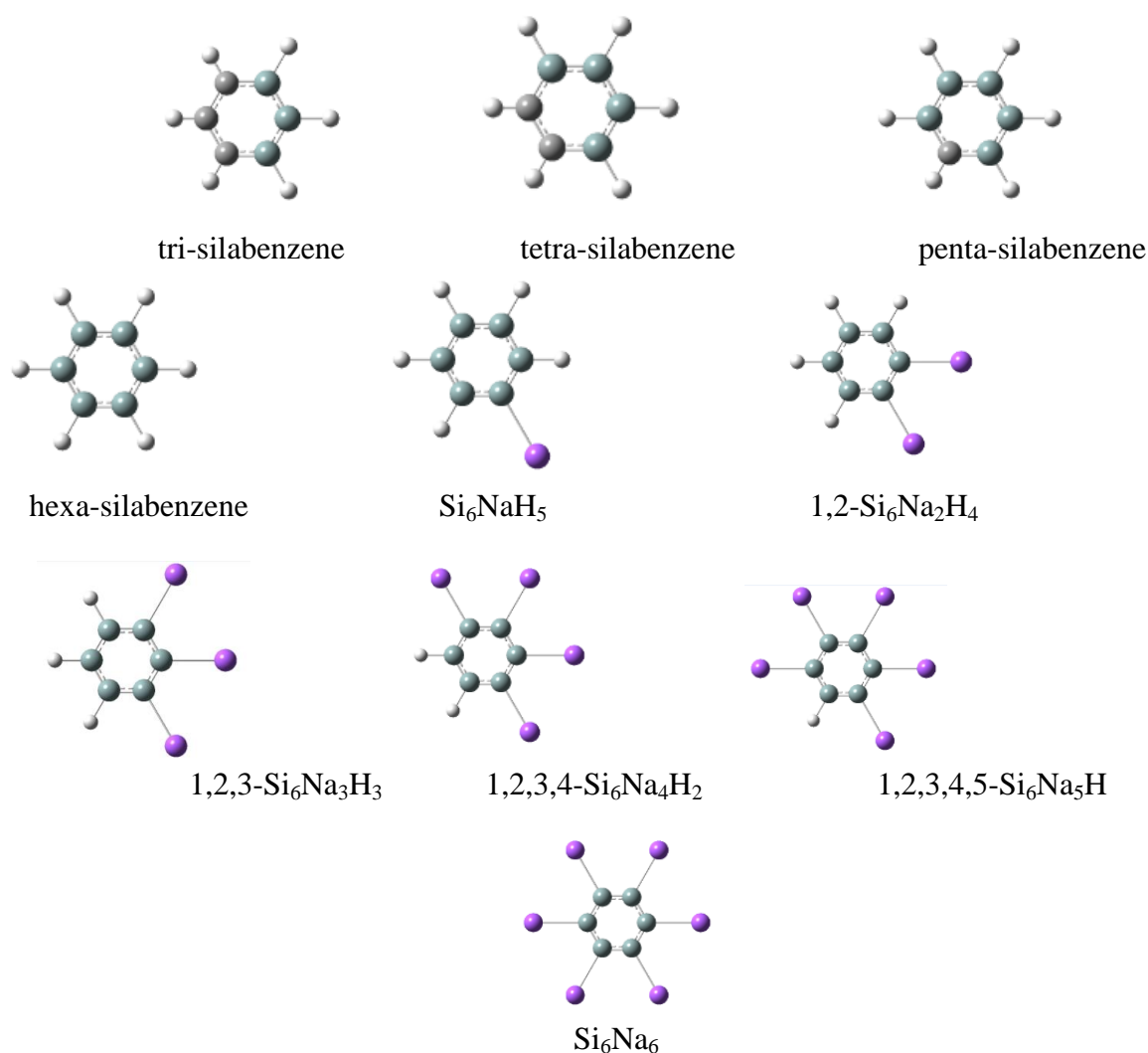


Figure 1: The structure of studied molecules

Table 1: Total energy and symmetry for molecular

Mol.	Symbol	Energy (au)		Symmetry
		Present Work	Ref (22)	
C_6H_6	0	-232.2582	-232.2979	D_{6h}
SiC_5H_6	1	-483.6045	-483.6600	C_{2v}
$1,2\text{-Si}_2\text{C}_4\text{H}_6$	2	-734.9695	-735.0387	C_{2v}
$1,2,3\text{-Si}_3\text{C}_3\text{H}_6$	3	-986.3451	-986.4407	C_{2v}
$1,2,3,4\text{-Si}_4\text{C}_2\text{H}_6$	4	-1237.7188	-1237.8159	C_{2v}

1,2,3,4,5-Si ₅ CH ₆	5	-1489.1043	-1489.2161	C _{2v}
Si ₆ H ₆	6	-1740.4929	-1740.6167	D _{6h}
Si ₆ NaH ₅	7	-1902.2133	-1898.278	C _{2v}
1,2-Si ₆ Na ₂ H ₄	8	-2063.9176	-2059.547	C _{2v}
1,2,3-Si ₆ Na ₃ H ₃	9	-2225.6181	-2220.809	C _{2v}
1,2,3,4-Si ₆ Na ₄ H ₂	10	-2387.323	-2382.080	C _{2h}
1,2,3,4,5-Si ₆ Na ₅ H	11	-2549.0120	-2539.355	C ₂
Si ₆ Na ₆	12	-2710.6999	-2704.568	C _{6h}

It is clear that from table (1), the total energy for all new molecules depends on the number of silicon atoms in the ring, it is decreasing with the increase of Si atoms number, as we see in figure (2). The silabenzene molecules group are more stable than benzene.

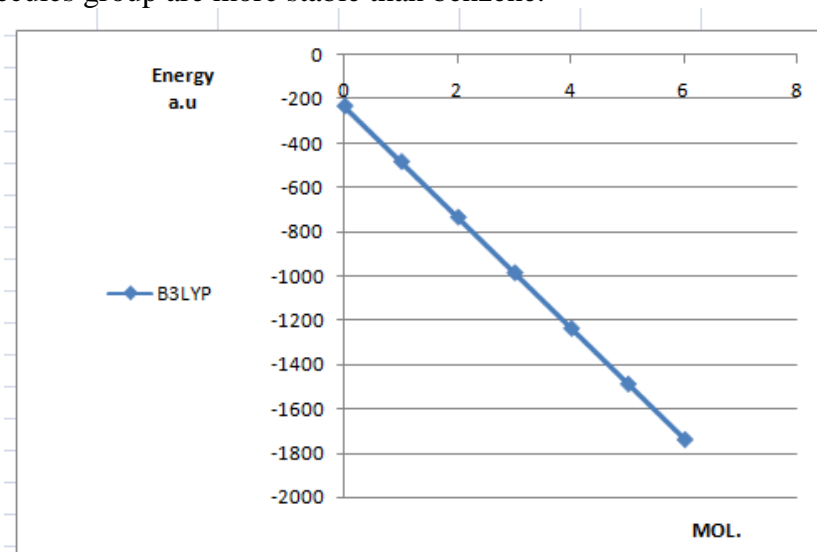


Figure 2: Total energy for silabenzene group molecules

For the comparing between the carbon atom and silicon atom, the SP hybridization of silicon is weaker than of carbon, this may lead to differences in the behavior of bonding for two atoms. C-H bond differ to Si-H bond. For hexasilabenzene Si_6H_6 . The bond to silicon atom is the same bond for C-H. The new molecule Si_6Na_6 has been studied here.

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 (K), hardness (η), electrophilicities (w), softness (s), and energy gap (Eg). Table (2) lists the electronic properties for the molecules under study. It is clear from table (2) that the ionization potential for silabenzene molecules group is less than that for benzene, but pentasilabenzene has the least, this means that this molecule needs small energy to become cation comparing with other molecules. The electron affinity for silabenzene group is more than that the electron affinity for benzene except the disilabenzene. It is obvious from this table that all molecules under study have hardness less than that for benzene. It has been found that the forbidden energy gap for all silabenzene molecules group is less than that for benzene. Pentasilabenzene has approximately half value of energy gap for benzene; it is a new electronic material.

Table 2: The electronic properties for molecules (all in electron volts)

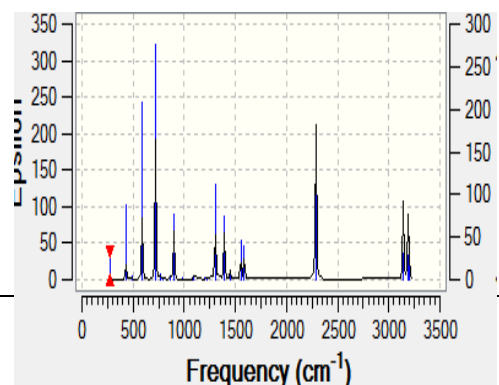
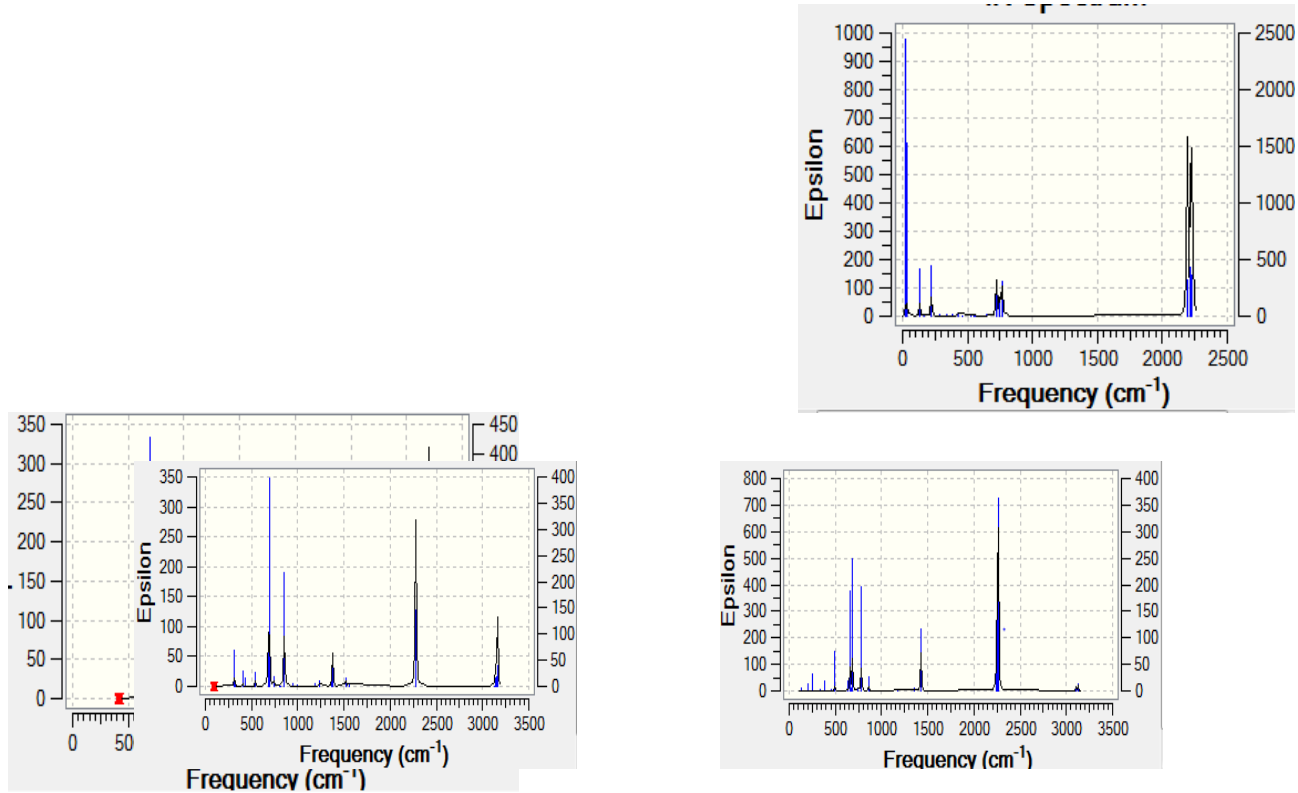
Mol.	IP	EA	K	η	W	S	E _g
C_6H_6	6.718	-.072	3.323	3.395	1.626	.147	6.788
SiC_5H_6	6.982	0.326	3.654	3.328	2.005	.150	5.027
1,2- $\text{Si}_2\text{C}_4\text{H}_6$	6.648	0.913	3.780	2.867	2.491	.174	4.366
1,2,2- $\text{Si}_3\text{C}_3\text{H}_6$	5.882	1.391	3.636	2.245	2.944	.222	4.34
1,2,3,4- $\text{Si}_4\text{C}_2\text{H}_6$	5.998	1.709	3.853	2.144	3.462	.233	3.565
1,2,3,4,5- Si_5CH_6	5.964	1.830	3.897	2.067	3.673	.483	3.235
Si_6H_6	5.596	2.245	3.920	1.675	4.586	.298	3.346
Si_6NaH_5	4.702	1.565	3.133	1.568	3.130	.318	2.299
1,2- $\text{Si}_6\text{Na}_2\text{H}_4$	4.080	1.893	2.986	1.0935	4.074	.457	2.119
1,2,3- $\text{Si}_6\text{Na}_3\text{H}_3$	3.780	1.526	2.653	1.127	3.122	.443	2.045
1,2,3,4- $\text{Si}_6\text{Na}_4\text{H}_2$	3.171	1.450	2.310	0.860	3.102	.575	1.666
1,2,3,4,5- $\text{Si}_6\text{Na}_5\text{H}$	3.101	1.363	2.232	0.869	2.866	.591	1.484
Si_6Na_6	2.940	1.248	2.094	0.846	2.591	.591	1.332

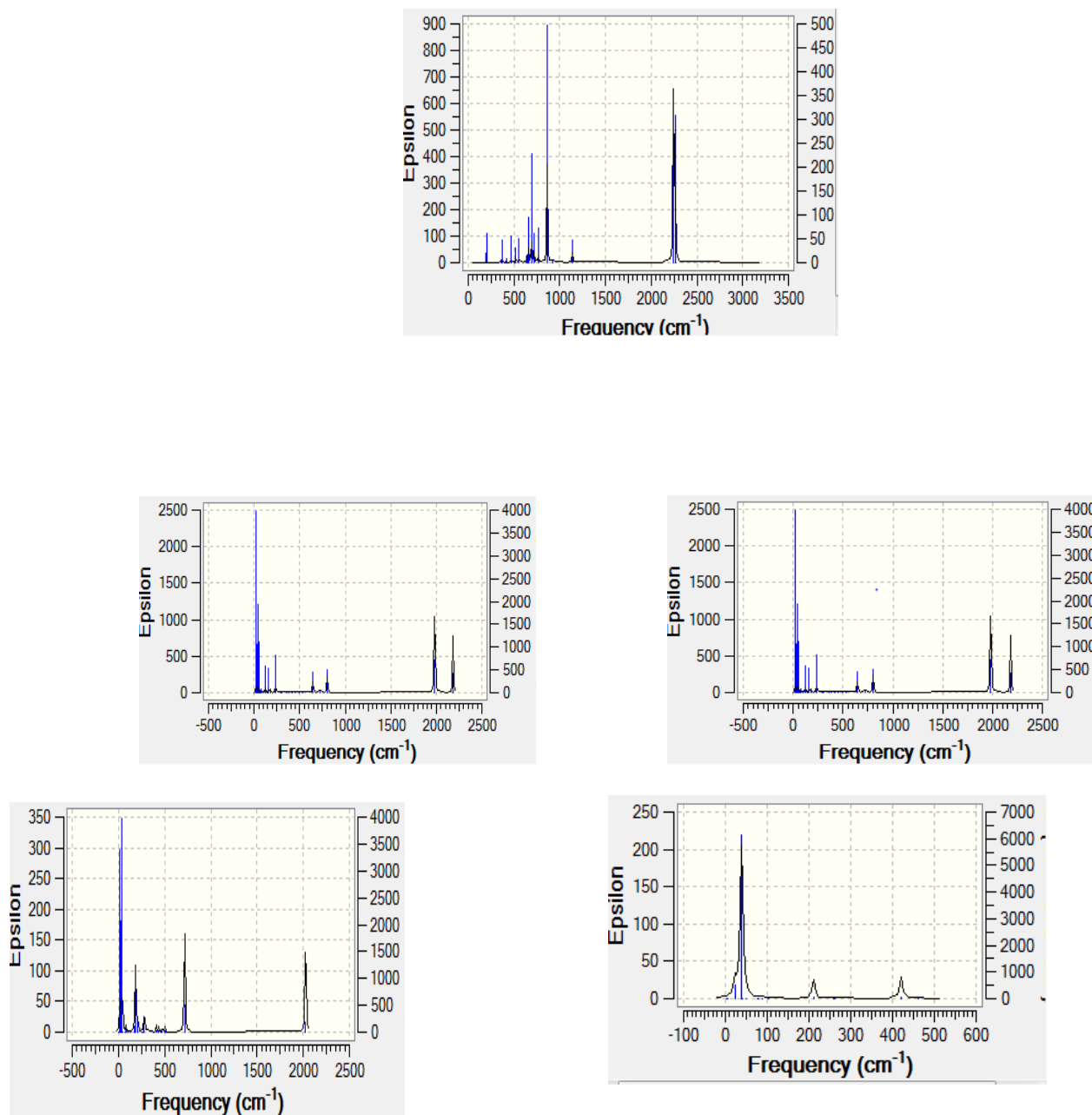
The new aromatic structure, hexasilabenzene, differs from other silabenzenes, there is no difference in the electro negativity. The interaction of sodium (Na) atoms as a cation with the new aromatic molecule has been studied here. (Si_6Na_6) has the same symmetry (D_{6h}) for benzene and hexasilabenzene.

Figure (3) shows the vibrational frequencies calculated of benzene using B3LYP/6-31G** DFT. The peak appears at (691, 1066.3, 1528.28 and 3202.34) cm^{-1} . These results have been found in good agreement with experimental data [23]. The strong peak observed at 691 cm^{-1} and the weak at 1066 cm^{-1} are due to the bending of C-H bond, the peak observed at 1528 cm^{-1} is due to the stretching of C-C bond, but the peak at 3202 cm^{-1} is due to the stretching of C-H bond.

It is clear from figure (3) that the IR spectrum for silabenzene molecules group characters from that the number of vibration modes due to existing Si-Si, Si-H and

Si-C bond. The spectra appear the 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.





Figure(3): The IR spectra for studied molecules
Epsilon = Intensity in Km/mol

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 benzene and silabenzene 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 silabenzene molecules group is lowers' values in compare with benzene.
- 3- The energy gaps for all silabenzene molecules are smaller than for benzene .Pentasilabenzene may be a candidate as a new electronic material, in which it has a smaller energy gap than the others, this is one of the important results obtained in this study, a small energy gap means small excitation energies of manifold of the excited states, this global property is a field for more researchers.
- 4- B3LYP/6-31G** DFT given a large approach in IR spectra calculations for observed peaks computed experimentally of benzene ,and for new silabenzenes this study supplies new data for IR spectrum.

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