

A Study OF the Electronic Structure of Azabenzen Molecules: by B3LYP-DFT Density Functional Calculation

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Abstract

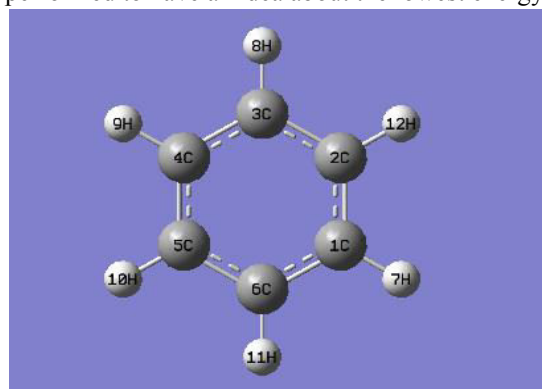
In this work, five molecules are optimized at B3LYP/6-31G** density functional theory. Benzene molecule was a reference. Electronic properties of azabenzene molecules were investigated depending on the three parameters (B3LYP) density functional theory. The best geometry for all molecules were investigated using (6-31G**) basis sets. The total energies, energy gaps, ionization potentials, electron affinities by use adiabatic and koopman methods . Adding CN cluster atoms in different position for the less Eg (pyridazine)molecular leads to decrease the energy gap in the second position comparison with the pyridazine molecular.

1.Introduction

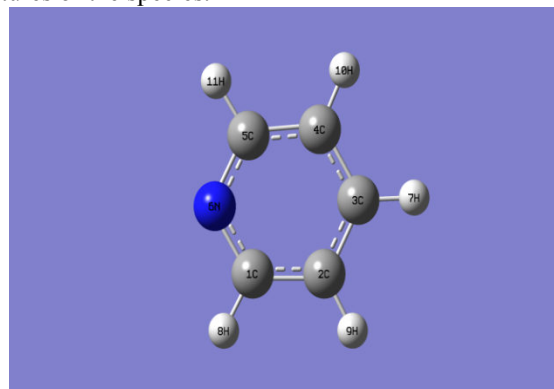
Aromatic compounds are important in industry. Key aromatic hydrocarbons of commercial interest are benzene ,toluene ,ortho-xylene and para-xylene.About 35 million tones are produced worldwide every year. They are extracted from complex mixtures obtained by the refining of oil or by distillation of coal tar ,and are used to produce arrange of important chemicals and polymers, including styrene ,phenol ,aniline,polyester and nylon.other aromatic compounds play key roles in the biochemistry of all living thing .four aromatic amino acids histidine,pheny lalanine,tryptophan ,and tyrosine,each serve as one of the 20 basic building blocks of proteins .Further ,all five nucleotides (adenine,thymine,cytosine,guanine,and uracil)that make up the sequence of the genetic code in DNA and RNA are aromatic purines or pyrimidines. In addition ,the molecule here contains an aromatic system with 2π electrons[1,2]

2. Computational details

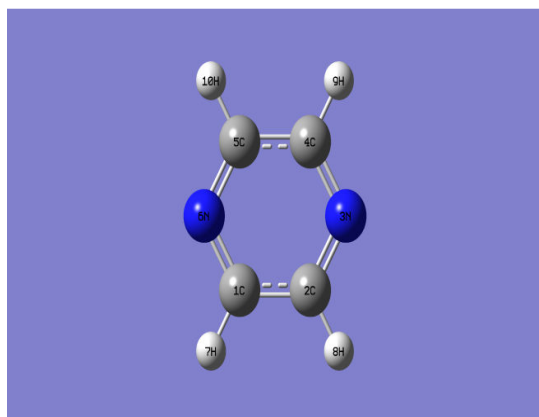
Figure(1) represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods. The molecular properties of the compounds had been computed by DFT using the standard 6-311G** basis set. In the DFT calculations, Lee, Yang and Parr correlation functional is used together with Becke's three parameters[3]exchange functional B3LYP. Conformational analysis of the molecules had been performed to have an idea about the lowest energy structures of the species.



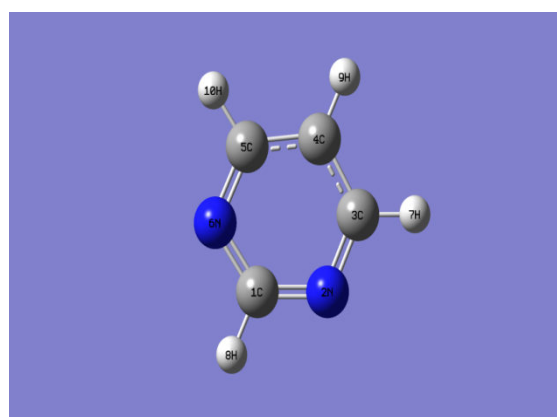
1(BZ)



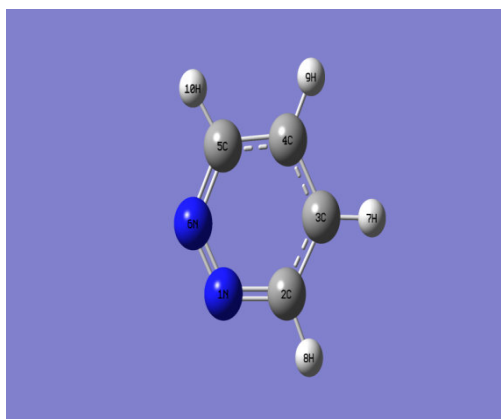
2(pyridine)



3(pyrimidine)



4(pyrazine)



5(pyridazine)

Figure(1).Structures of azabenzene discussed in this work.

3.THEARY

For molecular system of any size, direct solution of Hartree-Fock equation is impractical and more approximate methods are required to solve these equations. Therefore, the individual molecular orbitals are required to be expressed as linear combinations of a finite set of N_o prescribed one electron functions known as basis functions. If the basis functions are $\phi_1, \phi_2, \dots, \phi_n$, then an individual orbital ψ_i can be written [4,5,6].

$$\psi_i = \sum_{\mu=1}^{N_o} C_{\mu i} \phi_{\mu} \dots\dots\dots 2$$

$$S_{\mu\nu} = \int \phi_{\mu}(1) \phi_{\nu}(1) d\tau_1 \dots\dots\dots 1$$

where $C_{\mu i}$ are the molecular orbital expansion coefficients.

This method has a further advantage that it aids the interpretability of the result, since the nature of chemical problem frequently involves relating properties of molecules to those of the constituent atoms. The orthonormality condition in the LCAO approximation is given as,

$$\sum_{\mu\nu} C_{\mu i}^* C_{\nu j} S_{\mu\nu} = \delta_{ij} \dots\dots\dots 3$$

where δ_{ij} is the kronecker delta and $S_{\mu\nu}$ is the overlap integral for atomic function ϕ_{μ} and ϕ_{ν} ,
 Substituting the linear expansion of Eq. (2.1) in the molecular orbital integrals [7], yields:

$$H_{ii} = \sum_{\mu\nu} C_{\mu i}^* C_{\nu i} H_{\mu\nu} \dots\dots\dots 4$$

where $H_{\mu\nu}$ is the core Hamiltonian matrix elements,

$$H_{\mu\nu} = \int \phi_{\mu}(1) H^{\text{core}} \phi_{\nu}(1) d\tau_1 \dots\dots\dots 5$$

Similarly we may write

$$J_{ij} = \sum_{\mu\lambda\nu\sigma} C_{\mu i}^* C_{\lambda j}^* C_{\nu i} C_{\sigma j} (\mu\nu / \lambda\sigma) \dots\dots\dots 6$$

$$K_{ij} = \sum_{\mu\lambda\nu\sigma} C_{\mu i}^* C_{\lambda j}^* C_{\nu i} C_{\sigma j} (\mu\lambda / \nu\sigma) \dots\dots\dots 7$$

where $(\mu\nu / \lambda\sigma)$ is the differential overlap matrix elements

$$(\mu\nu / \lambda\sigma) = \iint \phi_{\mu}(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}(2) \phi_{\sigma}(2) d\tau_1 d\tau_2 \dots\dots\dots 8$$

The total electronic energy can be written in terms of integral over atomic orbitals. By substituting the previous expressions in the equation of the electronic energy, we obtain

$$\varepsilon = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu / \lambda\sigma) - \frac{1}{2}(\mu\lambda / \nu\sigma)] \dots\dots\dots 9$$

where $P_{\mu\nu}$ is the density matrix elements,

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i}^* C_{\nu i} \dots\dots\dots 10$$

Applying the variational method to Eq. (2. 8), a small variation of the molecular orbital ψ_i can now be given as

$$\delta\psi_i = \sum_{\mu} \delta C_{\mu i} \phi_{\mu} \dots\dots\dots 11$$

And when applying the condition for a stationary point ($\delta\varepsilon = 0$), one can obtain the following final form, [4,8,9]

$$\sum_{\nu} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) C_{\nu i} = 0 \dots\dots\dots 12$$

where $F_{\mu\nu}$ is the Fock matrix

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left((\mu\nu / \lambda\sigma) - \frac{1}{2}(\mu\lambda / \nu\sigma) \right) \dots\dots\dots 13$$

The equations for LCAO which self-consistent field molecular orbitals, Eq. (2.11) are algebraic equations rather than differential equations (Hartree-Fock equations). They were set forth independently by Hall and by Roothaan, These equations are solved by first assuming an initial set of linear expansion coefficients $C_{\mu i}$, generating the density matrix $P_{\mu\nu}$ and computing the first guess at $F_{\mu\nu}$, then one can calculate a new matrix of $C_{\mu i}$. This procedure is continued until there is no change in $C_{\mu i}$ between iterations [7].

Koopman's theorem states that if the single particle energies are not affected by adding or removing a single electron, then the ionization energy is energy of the highest occupied single particle orbital (the HOMO) and the electron affinity is the energy of the lowest unoccupied orbital (the LUMO) with the negative sign as the following [10]

$$IP = - E_{\text{HOMO}} \dots\dots\dots 14$$

$$EA = - E_{\text{LUMO}} \dots\dots\dots 15$$

Where IP: ionization potential ,

EA: electronic affinity

E_{HOMO} : energy of the highest occupied orbital.

E_{LUMO} : energy of the lowest unoccupied orbital

Koopman's theorem is extremely useful in predicting ionization energies and spectra [10]. Energy gap generally refers to energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) according to the Koopmans theorem [11,12]

$$E_g = E_{LUMO} - E_{HOMO} \dots\dots\dots 16$$

Ionization energy (IP) defined as the minimum energy required to removing an electron from the atom in a gaseous phase. Ionization energy is expressed in units of electron volt (eV) [12].

Also, it can be define as the energy difference between the positive charged energy $E(+)$ and the neutral energy $E(n)$ [13].

$$IP = E(+) - E(n) \dots\dots\dots 17$$

Electron affinity can be defined as the energy released upon attachment of an electron to an atom or molecule resulting in the formation of the negative ion [12]. Also, it can be define as the energy difference between the neutral energy $E(n)$ and the negative charged energy $E(-)$, as in the following relation [14]:

$$EA = E(n) - E(-) \dots\dots\dots 18$$

Chemical hardness is the resistance of a species to lose electrons [15], for insulator and semiconductor, hardness is half of the energy gap [16]. From equations (1) and (2), we can calculate the chemical hardness (η):

$$\eta = (IP - EA)/2 \dots\dots\dots 19$$

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 [109, 111]

$$\eta = \frac{1}{2} (\partial^2 E / \partial n^2) \dots\dots\dots 20$$

The softness can be defined as the inverse of the hardness[15]

$$S = 1/(2\eta) \dots\dots\dots 21$$

Electro negativity is defined as "the power of an atom in a molecule to attract electrons to itself" by Pauling [11,17]. R. Mulliken defined electro negativity as the average of the ionization energy and electron affinity as follows [16,18]

$$\chi = (IP + EA)/2 \dots\dots\dots 22$$

Within the validity of Koopmans' theorem, we can be defined as the negative value for average of the energy levels of the HOMO and LUMO [11, 15].

$$\chi = -(E_{HOMO} - E_{LUMO}) \dots\dots\dots 23$$

The Electrophilicity is definition as a index measures the stabilization in energy when the system acquires an additional electronic charge from the environme. On the other word, it can be defined as a measure of energy lowering due to maximal electron flow between donor and acceptor [19].

$$\omega = \chi^2 / (2\eta) \dots\dots\dots 24$$

4.results and discussion

4.1 The Geometry Optimization

In the present work ,there are five molecules that are studied ,including benzene (c_6h_6),pyridine(c_5h_5N),Pyrimidine($c_4H_4N_2$),Pyrazine($c_4H_4N_2$),pyrdizane($c_4H_4N_2$). Before proceeding in physical properties calculation ,it is necessary to find out the geometry optimization of the studies molecules . this includes the calculation of the wave function and energy at a starting geometry and then proceeds to move to anew geometry to give a lower energy .Ideally this geometry calculated the forces on the atoms by evaluating the gradient of the energy with respect to atomic coordinates. Table (4-1) Show the optimized coordinates of azabenzene molecules group calculated by B3YP/6-31G** density functional theory.

Table (4-1a):the optimized coordinates in (\AA) of benzene molecules by using B3LYP/6-31G**

Molecules	Symbols	Atom number	x	y	z
Benzene c_6H_6	1	C1	-1.3902	-0.0875	0
		C2	-0.7708	1.1599	0
		C3	0.6191	1.2475	0
		C4	1.3902	0.0875	0
		C5	0.7708	-1.1599	0
		C6	-0.6192	-1.2474	0
		H7	-2.4695	-0.1555	0
		H8	-1.3694	2.0607	0
		H9	1.0999	2.2163	0
		H10	2.4695	0.1555	0
		H11	1.3693	-2.0607	0
		H12	-1.0998	-2.2163	0

Table (4-1b):the optimized coordinates in (A°) of Pyridine molecules by using B3LYP/6-31G**

Molecules	Symbols	Atom number	x	y	z
Pyridine c ₅ H ₅ N	2	C1	1.1412	-0.7200	0
		C2	1.1950	0.6709	0
		C3	0.0002	1.3806	0
		C4	1.1952	0.6705	0
		C5	1.1410	-0.7204	0
		N6	-0.0002	-1.4140	0
		H7	0.0004	2.4620	0
		H8	-2.0543	-1.3030	0
		H9	-2.1497	1.1782	0
		H10	2.1497	1.1773	0
		H11	2.0538	-1.3043	0

Table (4-1c):the optimized coordinates in (A°) of molecules by using pyrimidine B3LYP/6-31G**

Molecules	Symbols	Atom number	x	y	z
Pyrimidine C ₄ H ₄ N ₂	3	C1	1.3087	-0.0000	0
		N2	0.7130	-1.1930	0
		C3	-0.6210	-1.1819	0
		C4	-1.3510	0.0000	0
		C5	-0.6215	1.1819	0
		N6	0.7130	1.1930	0
		H7	-1.1146	-2.1469	0
		H8	2.3919	0.0000	0
		H9	-2.4310	0.0000	0
		H10	-1.1146	2.1469	0

Table (4-1d):the optimized coordinates in (A°) of pyrazine molecules by using B3LYP/6-31G**

Molecules	Symbols	Atom number	x	y	z
Pyrazine c ₄ H ₄ N ₂	4	C1	-1.1315	-0.6965	0
		C2	-1.1315	0.6965	0
		N3	0.0000	1.4015	0
		C4	1.1315	0.6965	0
		C5	1.1315	-0.6965	0
		N6	0.0000	-1.4015	0
		H7	-2.0611	-1.2524	0
		H8	-2.0612	1.2524	0
		H9	2.0110	1.2524	0
		H10	2.0612	-1.2524	0

Table (4-1e):the optimized coordinates in (A°) of pyridazine molecules by using B3LYP/6-31G**

Molecules	symbol	Atomic number	x	y	z
Pyridazine c ₄ H ₄ N ₂	5	N1	0.6652	-1.2266	0
		C2	1.3211	-0.0674	0
		C3	0.6896	1.1755	0
		C4	-0.6896	1.1755	0
		C5	-1.3211	-0.0674	0
		N6	-0.6652	-1.2266	0
		H7	1.2659	2.0899	0
		H8	2.4002	-0.1519	0
		H9	-1.2659	2.0899	0
		H10			0

4-2 Electronic State and energy Gap

Table (4-2a) Mulliken atomic charges for azabenzene molecules group

Molecules	Mulliken atomic charges											
benzene	C1	C2	C3	C4	C5	C6	H7	H8	H9	H10	H11	H12
	0.0758	0.0772	0.0758	0.0758	0.0772	0.0758	-0.07630	-0.0762	-0.0762	-0.0763	-0.0762	-0.0762
Pyridine	C1	C2	C3	C4	C4	N6	H7	H8	H9	H10	H11	
	0.1995	0.3310	0.1870	0.3310	0.1995	-.8365	-0.0873	-.0844	-0.0919	-0.0873	-0.0880	
primidine	C1	N2	C3	C4	C5	N6	H7	H8	H9	H10		
	0.6700	-0.718	0.3297	0.4583	0.3297	-.7183	-0.0873	-0.0844	-0.0919	-0.0873		
Pyrazine	C1	C2	N3	C4	C5	N6	H7	H8	H9	H10		
	0.4619	0.4619	-0.746	0.4619	0.4619	-.7469	-0.0884	-0.0884	-0.0884	-0.0884		
Pyridazine	N1	C2	C3	C4	C5	N6	H7	H8	H9	H10		
	-0.470	0.1207	0.5114	0.5114	0.1207	-.0470	-0.0803	-0.0816	-0.0803	-0.0816		

Table (4-2b) Total energy, electronic states and energy gap for molecules.

Molecules	Symbols	$E_{TOTAL}(e.v)$	$E_{HOMO}(e.v)$	$E_{LUMO}(e.v)$	$E_g(e.v)$
benzene	1	-6321.5061	-7.0800	-0.4897	6.5903
PrYidine	2	-6757.9572	-7.2296	-1.1237	6.1055
pyrimidine	3	-7194.5063	-7.2732	-1.6053	5.6679
pyrazine	4	-7194.3294	-7.1638	-1.8614	5.3002
pyridazine	5	-7193.5213	-6.7181	-1.8276	4.8923

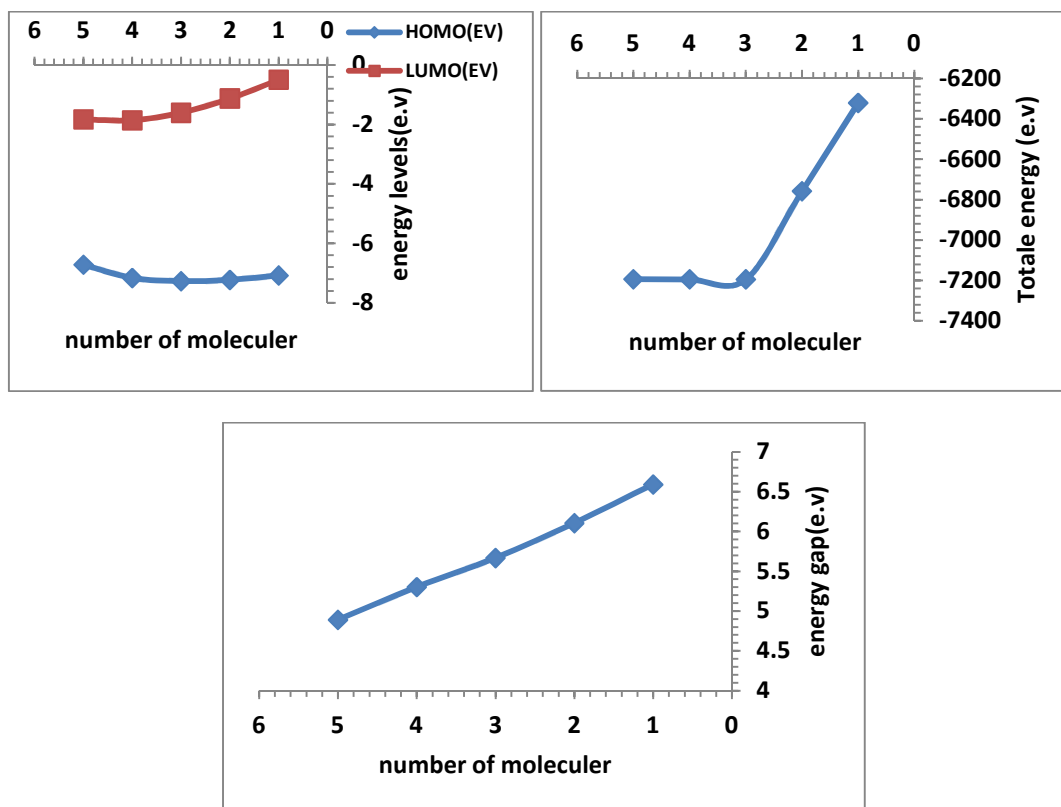
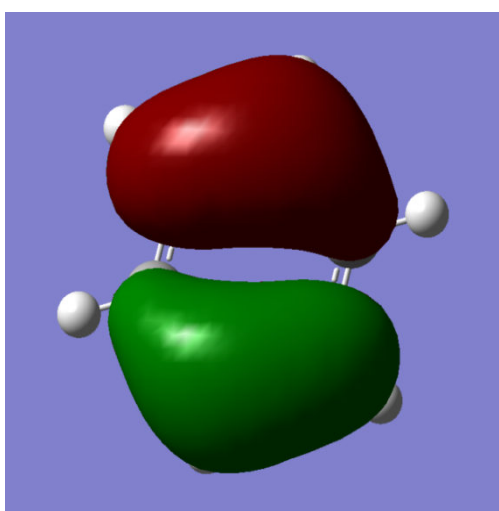


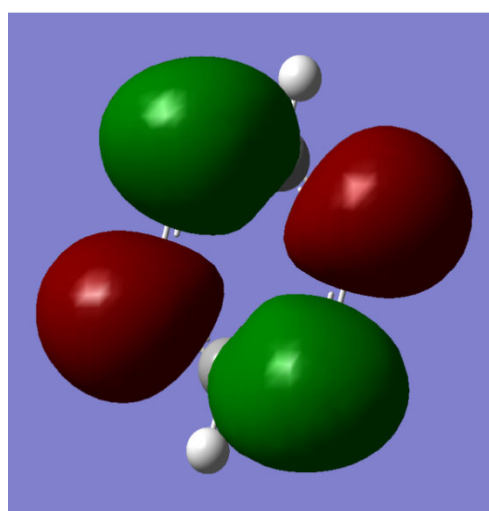
Figure (2) : Energies per unit e.V corresponding the No. of molecule .

The total energy for the new ring is decrease with the addition of nitrogen atoms number ,this give that the molecule becomes more stable with increasing of nitrogen but in the ring of the same number of atoms (pyrimidine,pyrazine,pyridazine) pyridazine is more stable from other rings, Table(4-2a) contains main change of distribution charge on the each atoms, Table (4-2d) show the change occurs at HOMO Level compared with LUMO level and this change depends on the number and position of N atoms instead of carbon and hydrogen atoms from the calculation ,it has been found that the forbidden energy gap for the benzene molecule decreases

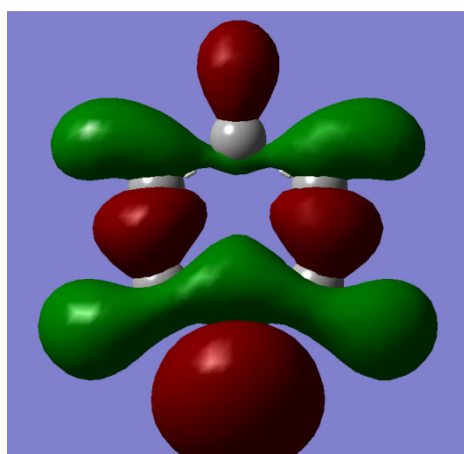
with replacing c-H atoms by nitrogen atoms. The energy gap is to be lowered from 6.59 eV for benzene to 4.89 eV for pyridazine as shown in figure (2). This is one of the important results obtained in the present study. Pyridazine may indicate a new electronic material, in which it has a smaller energy gap than benzene and the other studied molecules. A small energy gap means small excitation energies of manifold of the excited states. Figures (3) show the HOMO and LUMO levels of the new ring calculated by B3LYP/6-31G**DFT. The molecular orbitals are localized on the same part of the nitrogen atoms positions, and this localization gives the active site an ability to interact with other atoms, such as hydrogen and hydrogen-like atoms.



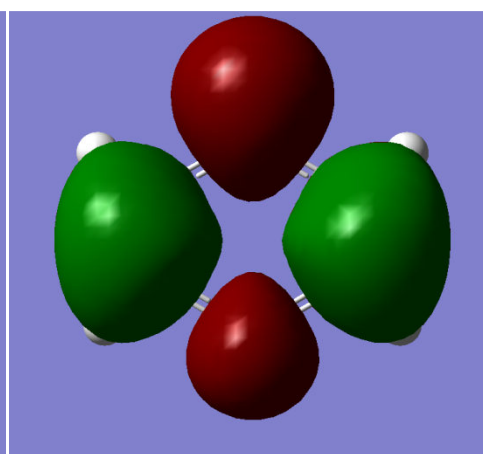
Benzene(LUMO)



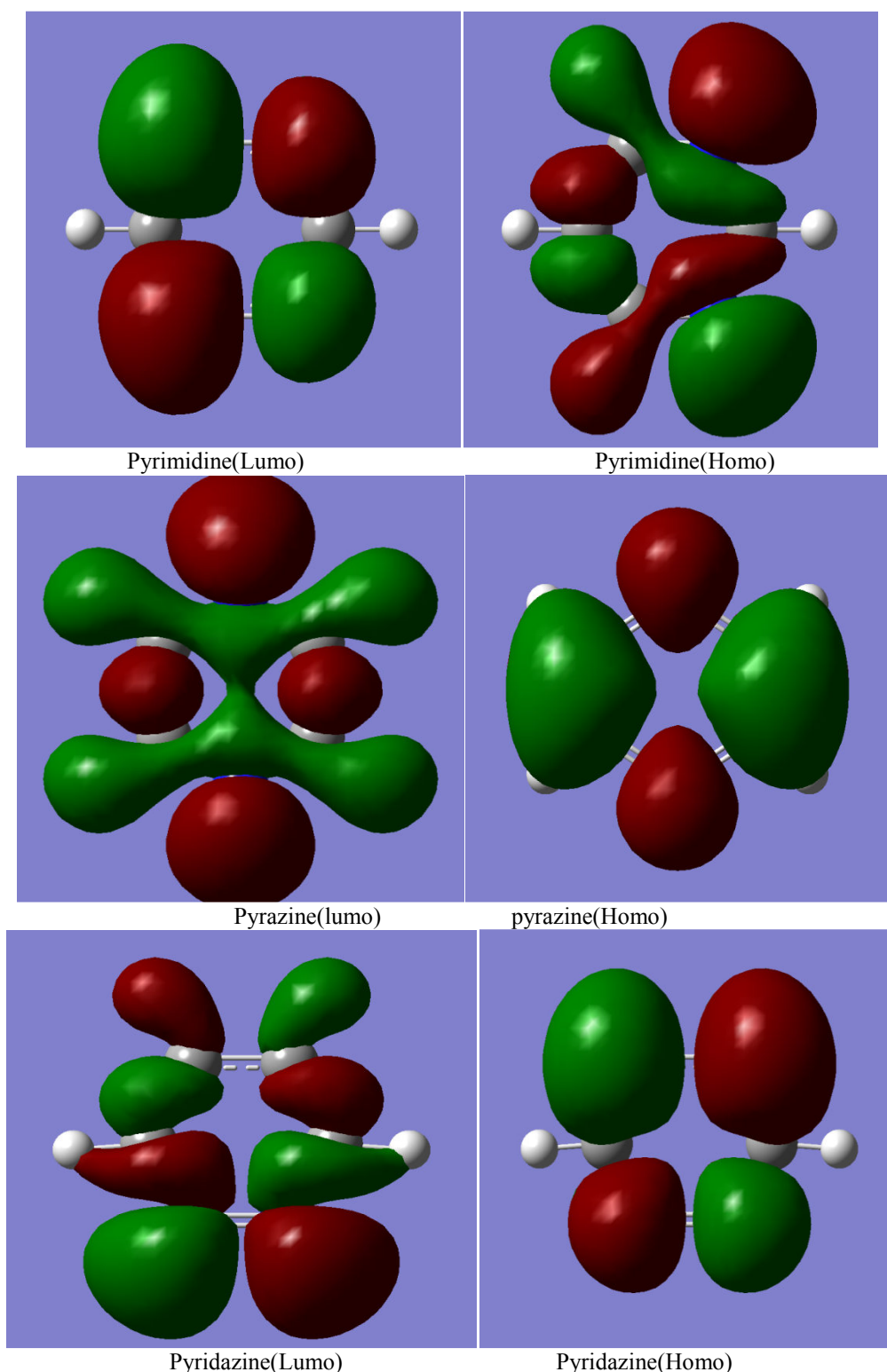
Benzene(HOMO)



Pyridine(LUMO)



Pyridine(HOMO)



Figure(3):DFT calculation: HOMO and LUMO level for azabenezen

4-3 Some important variables

B3LYP functional used in this study has a high efficient 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 (4-1) lists the electronic properties for the molecules under study. It is clear from that the ionization potential for all molecules is less than for BZ. The electron affinity for the molecules under study is more than that the electron affinity for benzene these results mean that these molecules are more reactive and may be a signal to new states

of material . It is obvious from this table that all molecules under study have hardness less than that for benzene the decreasing of hardness is the main feature ,as assigned for that band gap goes to be rather soft and lowering the resistance of azabenzene to lose an electron, (softness and electrophilicity) index for the studied molecules shows the magnitude large than these for the original ring (benzene), All new molecules strong electrophiles , it is a new electronic material.

Table(4-1):Computed energies for BZ& azabenzene molecules.

Species	IP (eV)	EA (eV)	κ (eV)	η (eV)	S (eV) ⁻¹	ω (eV)
1 benzene	9.2435	-2.4800	3.3817	5.8617	0.085	0.9720
2 pridine	9.10664	-0.7040	4.2013	4.9053	0.1019	1.7986
3 primidine	9.1697	-0.2865	4.4416	4.7281	0.1057	2.0852
4 pyrazine	9.1667	-0.0391	4.5638	4.6029	0.1086	2.2619
5 pyridzine	8.5463	-0.0625	4.2419	4.3044	0.1161	2.0890

5. 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- Decreasing of the total energy with increasing the number of nitrogen atoms refers to more stable azabenzene molecules than benzene .
- 3-Azabenzene molecules have low ionization potential and high electron affinity compared with the original aromatic molecule.This(according to adiabatic method)related to chemical potential and low hardness will accept electrons .
- 4- The electrophilicity increases when adding the nitrogen atoms and it is still the good descriptor ,which may predict the reactive molecules with other atoms ,molecules and groups. The electrophilicity is approximately slightly increasing from (0.9720ev) for benzene to (2.0890) ev for pyridazine
- 5- Energy gap is auseful global property .soft molecules with small energy gaps ,their electron density change more easily than hard molecule. Adding nitrogen atoms lead to decrease the energy gap ,but pyridazine has lowest forbidden energy gap.This may indicated anew electronic material,and when adding(CN) radical to the lest molecule obtaining low energy gap (4.5786) ev .

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Molecules	Symbols	Atom number	x	y	z
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		C2	1.3211	-0.0674	-0.0000
		C3	0.6896	1.1755	0.0000
		C4	-0.6896	1.1755	0.0000
		C5	-1.3211	-0.0674	0.0000
		N6	-0.6652	-1.2266	-0.0000
		H7	1.2659	2.0899	0.0000
		H8	2.4002	-0.1519	-0.0000
		H9	-1.2659	2.0899	0.0000
		H10	-2.4002	-0.1519	0.0000

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