

B3LYP/DFT calculations of C₅OH₅ and C₄O₂H₄ molecules

Wasan Mnati Mohammed

Physics Department-College of Science for Women-Babylon University,Babal, P.O.BOX4 . Iraq

Abstract

This work include the study of five molecules. The density function theory at B3LYP with 6-31G (d,p) was employed to calculate the effect of replacing oxygen atoms instead of the carbon in the benzene molecule on the electronic properties in two different ways: Koopmans and adiabatic. These properties included the total energy, electronic states, energy gap, ionization potential, electron affinity, electronegativity, hardness, softness and electrophilic index. As a result note increase the overall energy with change the location of two oxygen atoms and the highest energy emerged in the molecule (1,2 O-C₄H₄), the molecule (1,2 O- C₄H₄) is more soft (S) with small energy gap (E_g) in comparison with benzene ,and it more electrophilicity (χ) and more reactivity (ω).

Introduction

Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit a stabilization stronger than would be expected by the stabilization of conjugation alone. It can also be considered a manifestation of cyclic delocalization and of resonance [1,2]. An aromatic compound contains a set of covalently-bound atoms, and the definition of an aromatic molecule is given by Huckle's rule[3]. In order to be considered aromatic, a molecule must be cyclic, planer, each atom of the ring must have a P orbital which is perpendicular to the plane of the ring, and it must contain $(4n+2) \pi$ electrons (where $n=0,1,2,3,\dots$).

Aromatic hydrocarbons can be monocyclic (MAH) or polycyclic (PAH)[4]. Benzene is a MAH with molecular formula C₆H₆. It is an important industrial solvent and precursor in the production of drugs, plastic , dyes and synthetic rubber [5].

The five molecules group are aromatic compounds possessing the ring structure of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior. These compounds are manufactured on a large scale for use in high octane gasoline and in the production of polymers, insecticides, detergents, dyes and many miscellaneous chemicals[6].

Detailed calculation

There are five molecules studied in this work, the optimized structure for the studied molecules was shown in figure (1)

All calculations was carried out using the method of density function theory in the Gaussian 09 suit of programs[7]. The properties of the molecules calculated manner (DFT) using the standerd 6-31G(d,p) basis sets. The harmonic vibrational frequencies and the geometry optimization were performed at the B3LYP (DFT) with the same basis sets. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [8-12].The DFT partitions

the electronic energy as $E = E_T + E_V + E_J + E_{xc}$, 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 hybrid function B3LYP has shown to be highly successful for determination of properties such as ionization potentials (IP), electron affinities (EA), chemical potential (K), it is the negative of electronegativity (χ), hardness (η), softness (S), electrophilic index (ω), electric dipole polarizability (α), total dipole moment (μ)[13-16]. The properties for each molecule are computed by two method :Koopmans and adiabatic. The first method based on the differences between the HOMO and LUMO energies of the neutral molecules and is known as orbital-vertical (Koopmans theorem), $IP = -\epsilon_{HOMO}$ and $EA = -\epsilon_{LUMO}$ [17]

And the second method based on computing the energies foreach molecule in three states (anion ,neutral and cation)

$$IP = \epsilon_{(+1)} - \epsilon_{(0)} \text{ and } EA = \epsilon_{(0)} - \epsilon_{(-1)}$$

According to density function theory (DFT) the electronic chemical potential (K) is a measure to escaping tendency of an electronic cloud.

$$K = \frac{1}{2} (\epsilon_{HOMO} + \epsilon_{LUMO}) = -1/2 (IP+EA) \quad \dots\dots 1$$

$$K = -\chi = - (IP+EA)/2 \quad \dots\dots 2$$

The definition chemical hardness (η) is half of the energy gap between two frontier orbitals, in terms of ionization potentials (IP) and electron affinities (EA) [18,19].

$$\eta = (IP-EA)/2 \quad \dots\dots 3$$

The electron density for a soft molecule changes easier than a hard molecule, and due to that ,soft molecules will be more reactive than hard molecules [19].

$$S = 1/2\eta \quad \dots\dots 4$$

Electrophilicity index is measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index (ω) is defined as[20]

$$\omega = \chi^2/2\eta \quad \dots\dots 5$$

The total dipole moment (μ) is a measure of the symmetry in molecule charge distribution, and is given as a vector in three dimensions

$$\mu = \mu_x + \mu_y + \mu_z \quad \dots\dots 6$$

The electric dipole polarizability $\langle \alpha \rangle$ is measure of linear response of the electron density in the presence of an infinitesimal electronic field and it represents a second order variation in energy[19].

$$\langle \alpha \rangle = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \dots\dots 7$$

Results and discussion

1- Total energy, symmetry, imaginary frequencies and energy gap

It's obvious from table (1) that the total energy of the studied molecules increases when adding one oxygen atom in place of carbon. And when add two atoms of oxygen takes energy to decreasing, Its clear from table (1), that the total energy for (1,3O-C₄H₄,1,4O- C₄H₄,1,2O- C₄H₄) is approximately the same which indicates that the total energy is independent on the location of the oxygen atoms in the ring.

The vibration analysis indicates that most molecules (C₆H₆,1,O- C₅H₅,1,3O- C₄H₄,1,4O- C₄H₄) are global minimum without imaginary frequencies. except (1,2O- C₄H₄) molecule is characteristic of transition structures

in which it has one imaginary frequency (-152.2578 cm⁻¹). Table (1) shows the behavior of energy gap E_g . All new molecules (1,O- C₅H₅,1,3O- C₄H₄,1,4O- C₄H₄,1,2O- C₄H₄) have a small energy gap in which as compared with the original molecule (C₆H₆). The energy gap reduced from (6.6678105 eV) for molecule (C₆H₆) it is an insulator material to (3.24969 eV) for molecule (1,2O- C₄H₄) in which it has the smallest energy gap in this work. The new molecules are electronic materials with small value of energy gap.

2- Electronic properties

Table (2) shows the IP,EA , χ , η ,S, ω for molecules under study calculation in both ways (Koopmans, adiabatic) as show in the table the result of ionization potential (IP) have a tendency to **donate** electrons. The IP for (1,2O- C₄H₄) is less than the original molecules and (1,O- C₅H₅) is less value of ionization potential. This dicates that this molecule needs low energy to become **cation** as compared with other.

Electron affinity (EA) is a measure of the power of the molecule to granting electron when adding the electron LUMO. Adding the oxygen atoms in the ring in place to carbon atoms lead to increasing the ability of the electron affinity for the molecule. the largest value of the electron affinity appear in the molecule (1,2O- C₄H₄), and it become more reactive and may refer to new electronic states of materials.

The behavior of electronegativity, softness and electrophilic index for the (1,O- C₅H₅,1,3O- C₄H₄,1,4O- C₄H₄,1,2O- C₄H₄) molecules shows the magnitude large than these for the original ring. Adding oxygen atoms in place of carbon atoms give the molecule more softness, and less hardness from benzene (C₆H₆). while the electronegativity increased from (2.052108) for (C₆H₆) to (5.18620) for (1,2O- C₄H₄) molecule.

3- Total dipole moment and polarizability

The total dipole moment for (C₆H₆) and (1,4O- C₄H₄) molecule equals zero because they have high symmetry (D_{6h} , D_{2h}) respectively. due to the inherent tendency of π -electron for strong delocalization. these calculation are shown in table 3 and fig 2 (a).

The result of polarizability for studied molecules in table (3) shows that the average polarizability for (1,2O- C₄H₄) molecule is small than that for benzene. Adding the oxygen atoms in place of carbon atoms leads to few lowering in the polarizability of the molecules. This is because the oxygen atoms have a high value of electronegativity (3.44) eV. Fig 2 (a,b) shows the behavior of total dipole moment and average polarizability of the molecules under study.

4- Geometrical parameters and electronic states

Adding the oxygen atoms to the benzene ring in place of carbon atoms leads to changing the optimized parameters for the original (benzene) molecule. Table (4) shows the bond lengths and bond angles for the new molecules.

5- Electronic state

The effect of added oxygen atoms on both high occupied molecular orbitals HOMO and lowest unoccupied molecular orbitals LUMO was shown in figer (3),but the effect on LUMO energy is more than that on HOMO energy ,the change occurs at LUMO level as compared with HOMO depends on the number and location of atoms added in place of carbons ring.

Conclusion:-

In this study we have use DFT to compute geometry optimization and electronic properties of (C₆H₆, 1,O- C₅H₅,1,3O- C₄H₄,1,4O- C₄H₄,1,2O- C₄H₄) molecules by using B3LYP function with (6-31G) (d,p).The important conclusions are:-

1. geometry optimization for benzene molecule has been found in a good agreement with experimental data.
2. The total energies for di-(1,3O- C₄H₄,1,4O- C₄H₄,1,2O- C₄H₄) molecules found not dependent on the position of the oxygen atoms ,the addition of oxygen atoms to the ring instead of carbon causing an increase in the total energy, of the molecule.
3. The process of replacing oxygen atoms instead of the carbon atoms caused a decrease in the energy gap, As decreased energy gap from (6.6678105 eV) for benzene to (3.24969 eV) for molecule (1,2O- C₄H₄). A small energy gap means small excitation energies of manifold of the exited states.

4. In DFT ,B3LYP function (6-31G) (d,p) the electronic properties (IP,EA, χ , η ,S, ω) are calculated. The new molecular are more reaction than benzene and they have semiconductor properties.
5. molecule (1,2O- C₄H₄) is the best from among the other of the studied molecules, being the owned smaller energy gap and better electronic properties.

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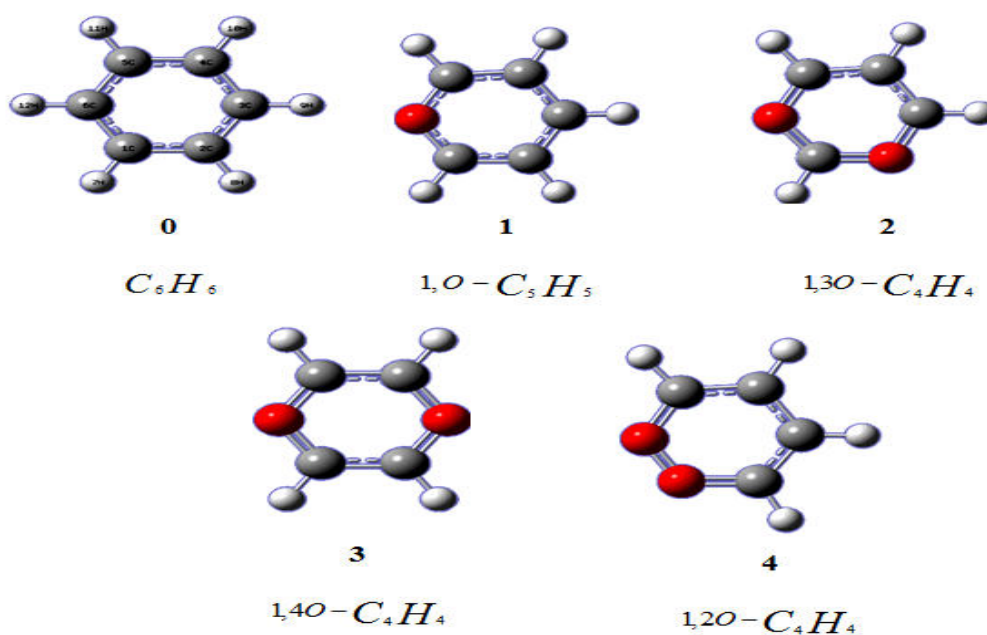


Figure :1 Optimized Structures of benzene and its derivatives discussed in this work

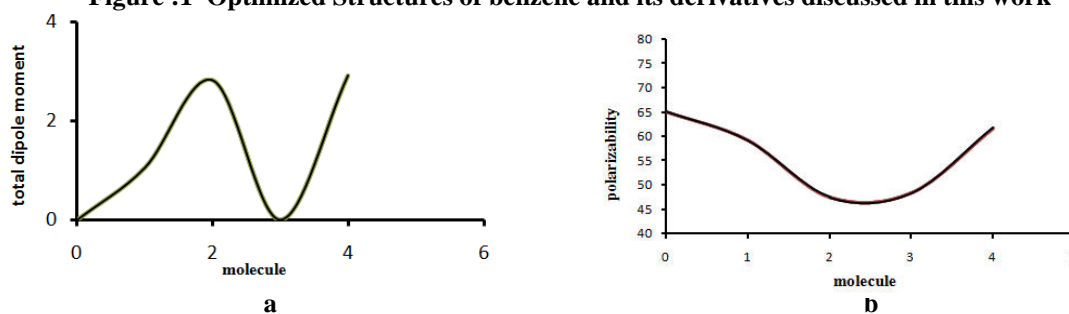


figure 2 : (a) dipole moment and (b) polarizability calculations for analyzed molecules.

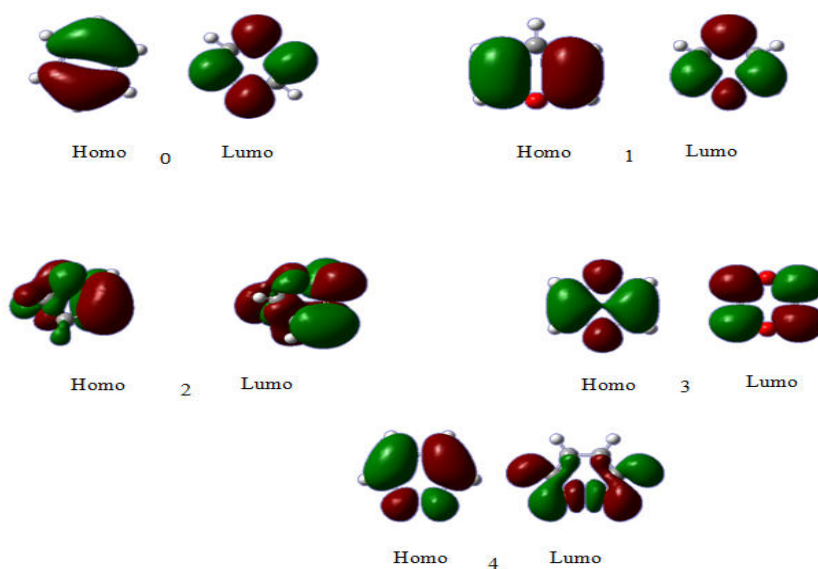


figure 3 : HOMO and LUMO for analyzed molecules.

Table 1: Total energy, symmetry imaginary frequency and energy gap for analyzed molecules.

molecules	E (a.u)	Eg (eV)	Symmetry	im-freq.
0	-232.208692	6.6678105	D6h	0
1	-268.6317282	3.5343069	C2v	0
2	-305.1028637	6.0436131	C1	0
3	-305.1109653	4.8860997	D2h	0
4	-305.0486185	3.2496903	C2v	1(-152.2578)

Table 2 : Electronic properties for analyzed molecules.

molecules	IP		EA		X		η		S		ω	
	Koopman	Adiupatic	Koopman	Adiupatic	Koopman	Adiupatic	Koopman	Adiupatic	Koopman	Adiupatic	Koopman	Adiupatic
0	7.0329687	0.3350203	0.3651582	-0.02279394	3.6990635	0.1561132	3.33390525	0.17890714	0.14997427	2.79474588	2.052108471	0.068111681
1	4.1729256	0.2310007	0.6386187	-0.00153604	2.4057722	0.1147324	1.76715345	0.11626839	0.28294091	4.3003949	1.637588303	0.056608302
2	7.0509273	0.2936922	1.0073142	-0.04807242	4.0291208	0.1228099	3.02180655	0.17088234	0.16546393	2.92598997	2.686110734	0.044130583
3	5.5551936	0.2864974	0.6690939	-0.02186225	3.1121438	0.1323176	2.44304985	0.1541798	0.20466222	3.24296687	1.982243367	0.056777654
4	5.7301539	0.2917837	2.4804636	-0.02160794	4.1053088	0.1350879	1.62484515	0.15669581	0.30772163	3.19089579	5.186204954	0.058229801

Table 3 : dipole moment and polarizability calculations for analyzed molecules.

Species	Dipole Moment(μ) Debye	Polarizability (a.u)			
		α_{zz}	α_{yy}	α_x	α_{ave}
0	0	77.702	77.694	39.843	65.07967
1	1.052	69.37	69.991	38.348	59.23633
2	2.8142	53.145	52.335	37.052	47.51067
3	0	53.066	58.999	33.088	48.38433
4	2.9106	65.96	59.636	59.636	61.744

Table 4 : Geometrical parameters for analyzed molecules.

Species	Bond length (A ⁰)		Species	Angel (degree)	
0	C-C	1.4023	0	C-C-C	119.9941
	C-H	1.086		C-C-H	120.0054
1	C-C	1.4235	1	C-C-H	120.7548
	C-H	1.0582		C-C-O	121.6623
	C-O	1.4235		H-C-O	111.0689
2	C-H	1.0787	2	C-C-C	120.9925
	C-O	1.4412		C-C-H	125.7465
	C-C	1.478		C-C-O	113.181
3	C-C	1.3342	3	H-C-O	118.2547
	C-H	1.0785		C-C-C	107.8689
	C-O	1.4213		O-C-O	115.2335
4	C-C	1.3393	4	C-C-H	124.808
	C-H	1.0841		C-C-O	123.1788
	C-O	1.4126		H-C-O	112.0134
4			4	C-C-H	120.452
				C-C-O	125.1334
				H-C-O	107.4164