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Theoretical Study for the Effect of Hydroxyl Radical on the Electronic Properties of Cyclobutadiene Molecular

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Abstract

The present work deals with the electronic properties of organic molecules in form ring, containing semiconductor atoms. Cyclobutadiene is the original ring before replacing the hydrogen atom by hydroxyl radical. Density functional theory with B3LYP/6-21G level has been used to find the electronic structure and electronic properties of the studied molecules. The effect of substitute on cyclebutadiene molecule is discussed on the basis of the calculated electronic properties. It is included total energy, energy gap, ionization potential, electronic affinity and electrophilicity, with comprehensive analysis of the calculated highest-occupied and lowest-unoccupied orbital (HOMO and LUMO respectively) energies. The results in this study show that the calculated electronic properties for cyclebutadiene have been found a good agreement with the previous studies. For other molecules, we have not found a reference data, so this study supplies a new data in this aspect. These calculations have been performed using Gaussian 03 package.

Key words: cyclobutadiene, energy gap, ionization potential and electron affinity.

1. Introduction

The study of organic ring systems is an attractive research field that allows work on the solution of fundamental questions in chemistry and physical and the development of materials with interesting properties on a molecular. There are typical questions associated with the nature compounds of chemistry are: (i) preferences between different ring sizes (ii) the magnitude of ring strain (iii) the nature of the bonding and (iv) the chain lengths [Beckmann, 2001].

Cyclobutadiene is four atoms of carbon bonded together by strong covalent bonds, in form cycle, it is an even attendant ring, anti- aromatic, this system have π-electron densities of unity in its ground neutral state. A series of theoretical and π interactions and cation –π interactions the interaction of anions and cations on different faces of the same π-system have been studied [Minkin, 1994].

Free radicals are molecules or atoms that have an unpaired electron in their valence shell. The reactivity of an atom is determined by the number of electrons in its valence. Usually, electrons that are paired together in an orbital contain much less energy than an electron that sits in an orbital alone. For an atom, having less energy means being more stable, and since atoms are constantly trying to achieve greater stability, the unpaired electrons will try to pair themselves up with other free electrons. Hence, atoms or molecules which have unpaired electrons will react readily with other atoms and molecules [Beckman, 1997].

Density functional theory is a powerful computational quantum physical and chemical technique method that allows the calculation of the geometries and energies of reactants [Udhayakala, 2012]. It is become a popular tool for electronic structure calculations in recent years due to its favorable combination of low computational cost and good accuracy for the calculated results. There are two main parameters controlling the accuracy of the results, the inherent approximations in the Hamiltonian and the size of the basis set used for expanding the Kohn–Sham (KS) orbitals [Frank, 2002]. There are many approximations such as local density approximation (LDA), local spin density approximation (LSDA) and generalized gradient approximation [Jones, 2006].

2. Theoretical methods and computational details

The molecular properties for the cyclebutadiene and new molecules is computed under the Becke three parameters with Lee-Yang-Parr functional [B3LYP] level [Tatsuo, 2002] with large 6-31G basis set. However, a long time required for employing this level. The mathematical equations were use in the calculations included:

Total energy of a molecular system (T.E): Total energy is the first property calculated in this work, it is sum of the total electronic energy E_{ee}, and the energy of nucleus repulsion E_{nn} [Vladimir, 1999]. In KS-DFT, the total energy functional is partitioned as a

$$E[\rho] = T_s[\rho] + V[\rho] \qquad (1)$$

Where T_S: Kohn-Sham kinetic energy of the noninteracting electron gas and V contain the Hartree electron-electron repulsion energy, the electron exchange-correlation energy, and the external potential energy [Huang, 2010].

Energy gap (E.gap): is the different between the lowest unoccupied molecular orbital and highest occupied molecular orbital according to the Koopmans theorem [Kampen, 1999].

$$E_{gap} = E_{Lumo} - E_{Homo} \ldots\ldots(2)$$

Ionization potential (IP): is the amount of energy required to remove an electron from an isolated atom or molecule [Ali, 2009].

Electron affinity (EA): is the energy change when an electron is added to the neutral atom to form a negative ion [Ali , 2009].

According to Koopman's theorem the ionization potential and electron affinity are define as [Zhan, 2003]

$$IP = -E_{HOMO} \ldots\ldots(3)$$

$$EA = -E_{LUMO} \ldots\ldots(4)$$

From equations (3) and (4), we can calculate electrophilicity [Udhayakala, 2011]:

$$\omega = \kappa^2 /(2\mu) \ldots\ldots(5)$$

Where

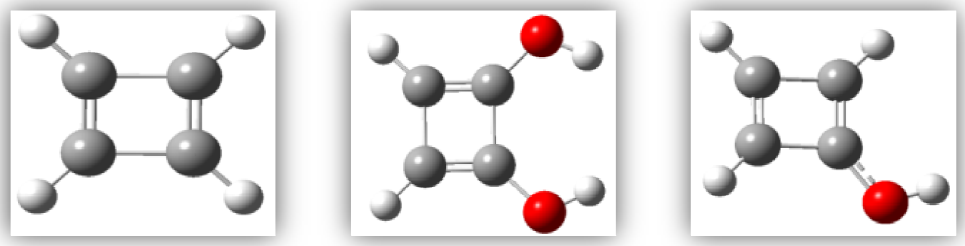
ω: is the electrophilicity which species that stabilize upon receiving an additional amount of electronic charge from the environment.

κ: is the electronic chemical potential.

μ: is the hardness and define that the measurement of molecule resistance to the change or deformation in molecular orbitals [Ghosh, 2004].

3. Results and Discussion

In this section, we refer to the electronic properties of cyclobutadienes and study the effect of replacing one and two hydrogen atom by one and two hydroxyl radical respectively. The optimization of geometry for each molecule is shows in Figure (1).



Cyclobutadiene 1- Cyclobutadienol 1,2-Cyclobutadienediol

Fig. (1): *The schematic representation for cyclobutadienes its group.*

The total energy results included in table (1) and the electronic state (HOMO and LUMO) shows table (2) for studied molecules. The electronic properties of cyclobutadiene and new molecules are show in tables (3-5). Table (3) includes energy gap, table (4) includes ionization potential and electronic affinity and table (5) included electronegativity. Where the sample ŋ means the concatenation of the molecules.

Table (1): *Total energy results for studied molecules group and comparison of the total energy for cyclobutadienes result with previous studies.*

ŋ	Molecules	Total energy (a.u)	
		Present study	Previous study [Hussien,2012]
1	Cyclobutadiene	-154.6956	-153.83
2	1- Cyclobutadienol	-229.9341	---
3	1,2-Cyclobutadienediol	-305.1588	---

Table (2): *HOMO and LUMO energy result for studied molecules group.*

ŋ	Molecules	LUMO (eV)		HOMO (eV)	
		Present study	Previous study [Hussien,2012]	Present study	Previous study [Hussien,2012]
1	Cyclobutadiene	-5.3513	-5.618	-1.8536	-1.903
2	1- Cyclobutadienol	-4.8903	---	-1.4552	---
3	1,2-Cyclobutadienediol	-4.5986	---	-1.2451	---

Table (3): *Energy gap results for studied molecules group and comparison of the energy gap of cyclobutadiene result with previous studies.*

ŋ	Molecules	Energy gap (eV)	
		Present study	Previous study
1	Cyclobutadiene	3.4977	3.715 [Hussien,2012] 3.419 [Al-Anber, 2005]
2	1- Cyclobutadienol	3.4351	---
3	1,2-Cyclobutadienediol	3.3534	---

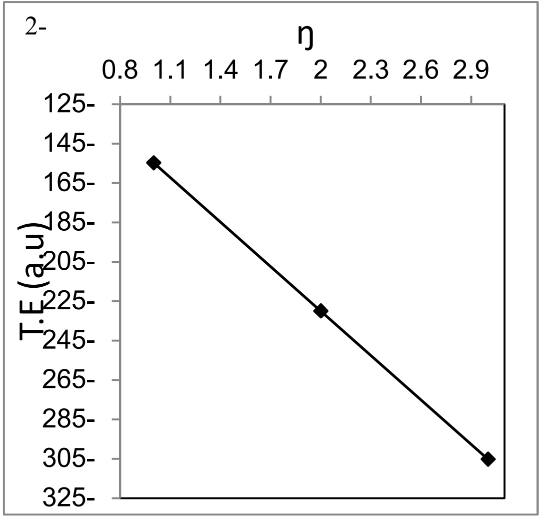
Table (4): Ionization potential and electronic affinity result for studied molecules group and comparison of their result with previous studies of cyclobutadiene.

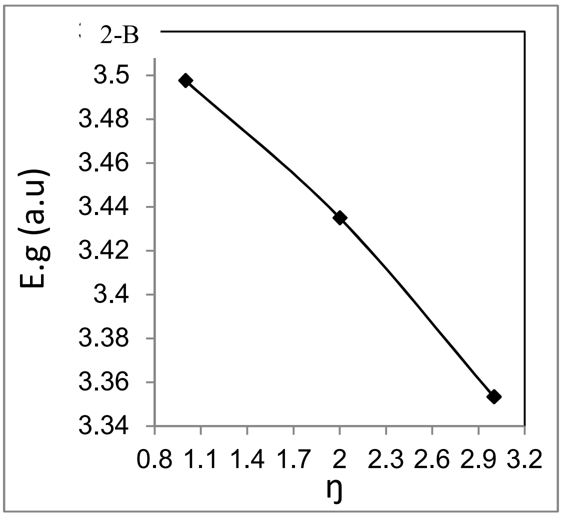
ŋ	Molecules	Ionization potential (eV)		Electronic affinity (eV)	
		Present study	Previous study [Hussien,2012]	Present study	Previous study [Hussien,2012]
1	Cyclobutadiene	5.3513	5.618	1.8536	1.903
2	1- Cyclobutadienol	4.8903	---	1.4552	---
3	1,2-Cyclobutadienediol	4.5986	---	1.2451	---

Table (5): *Electrophilicity results for studied molecules group and comparison of the electrophilicity for cyclobutadienes result with previous studies.*

ŋ	Molecules	Electrophilicity (eV)	
		Present study	Previous study [Hussien,2012]
1	Cyclobutadiene	3.7103	1.264
2	1- Cyclobutadienol	2.9305	---
3	1,2-Cyclobutadienediol	2.5458	---

Figures (2-A) and (2-B) represent the decreasing total energy and energy gap. Nevertheless, when we see LUMO and HOMO level where it is increasing as figure (2-C). The ionization potential and electronic affinity are smaller than organic, as we see in figure (3). The opposite behaviors appear when we see the electrophilicity, where it is less than the electrophilicity of organic cyclobutadiene, as we see in figure (5).





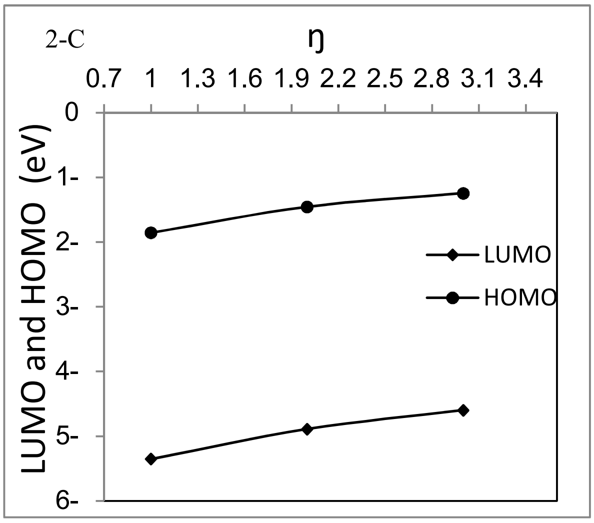


Fig. (2): *Relationship, between total energy in (2-A), energy gap in (2-B), and HOMO and LUMO energy in (2-C) with respect to the concatenation of the molecules*

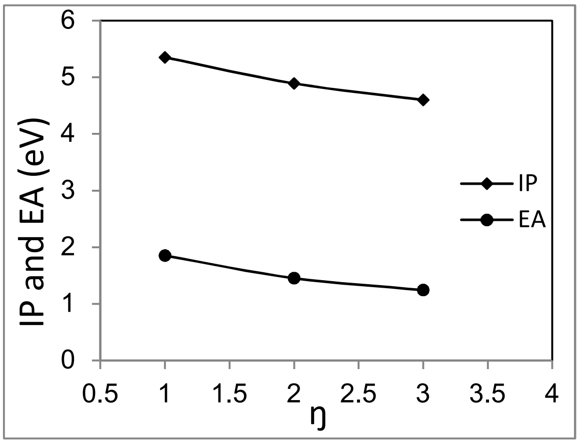


Fig. (3): Relationship, between ionization potential and electronic affinity with respect to the number of the molecules

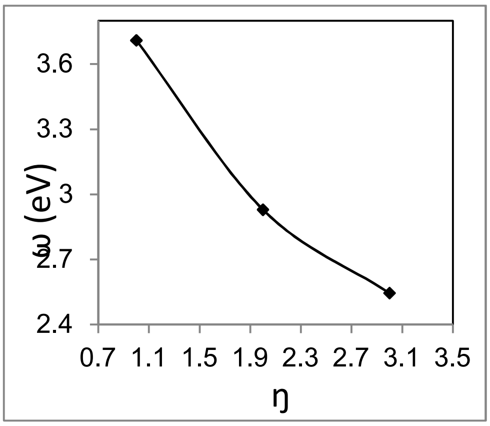


Fig.(4): Relationship, between electrophilicity and the number of the molecules

4. Conclusions

1. Decreasing the total energy with increasing the number of hydroxyl radical refers to new molecules is more stable than cyclobutadiene.
2. One of the important results was obtain in this study, is the decreasing of the energy gap. This declares that these molecules are the nearest to semiconductor because the both HOMO and LUMO levels become more adjacent.
3. All the new studied molecules need small energy to become cation because ionization potential is smaller than original cyclebutadiene.
4. The new molecular are more reactive according to the increasing of the electrophilicity.
5. Hydroxyl radical effect on the electronic properties depended on the increasing the number of hydroxyl radical.

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