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Study the Effect of Hydroxyl Radical on the Monogermacyclobutane Molecule by using Density Functional Theory

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Abstract

This work reports a theoretical study to investigate the electronic structure and optimized geometry for a saturated molecules group by using density functional theory (DFT) at B3LYP level with bases set 6-31G. Cyclobutane molecule is an original molecule before substitute one-carbon atom by one-germanium atom. The effect of substitute on cyclobutane molecule is discussed on the basis of the calculated electronic properties. The electronic properties included total energy, energy gap, ionization potential, electronic affinity, hardness and softness, which have been found with varying differences for each molecule, with comprehensive analysis of the calculated highest-occupied and lowest-unoccupied orbital (HOMO and LUMO respectively) energies. These properties also studied with substituting the one hydrogen atom by one hydroxyl (OH) radical in same molecular. The results in this study show that the calculated total energy, energy gap and ionization potential for cyclobutane 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.

Keywords: Cyclobutane, DFT, energy gap, ionization potential.

1. Introduction

Semiconductors are widely used and have important applications in manufacture and technology especially in instruction of the electronic devices, thus there are many studies for the electronic structure and physical properties of the semiconductors. The semiconductors have different uses according to the difference of their physical properties [Merdan, 2002]. Since the mid-20th Century, the electronics industry has enjoyed phenomenal growth and is now the largest industry in the world. The foundation of the electronics industry is the semiconductor device. To meet the tremendous demand of this industry, the semiconductor device field has also grown rapidly [Sze, 2007].

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 molecule. There are typical questions associated with the nature compounds of chemistry are: (i) different ring sizes, (ii) the magnitude of ring strain, (iii) the nature of the bonding and (iv), the chain lengths [Beckmann, 2001].

Cyclobutane molecule can be study as a semiconductor, because it is consisting from four-member carbon [Norman, 2002]. Cyclobutane is interesting because it provides a bridge between the very reactive for a hydrocarbon [Wiberg, 2005], and it is one of the important saturated rings molecules [Morrison, 2002], antiaromaticity [Bally,2003]. The dissociation of cyclobutane is form two ethylene molecules [Yusheng, 2007]. The structure of cyclobutane presents some interesting questions, the C−C−C bond angle is 88, indicating that it adopts the optimization of cyclobutane system is not planar conformation [Smith, 2007]. In 1885, Adolph von Baeyer studied the angle strain in cycloalkanes and show that the C−C−C bond angle of 90^o for cyclobutane [Daley, 2003].

Density function theory is one of the largest popular and successful quantum mechanical approaches [Capelle, 2006]. It is a powerful computational quantum physical and chemical technique method that allows the calculation of the geometries and energies of reactants [Ryan, 2001]. It has 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. In analogy with wave mechanics methods, 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].

In recent years, there has been a growing interest in (DFT) from the quantum chemistry community, It was given a theoretical basis in 1984, by Runge and Gross. They recently developed a density functional theory, which can be used for general molecules [Gisbergen, 1996].

2. Theoretical methods and computational details:

The molecular properties for the 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:

- 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 [Bittner, 2003]

$$IP = -E_{HOMO} \text{.........................} (1)$$

$$EA = -E_{LUMO} \text{.........................} (2)$$

From equations (1) and (2), we can calculate the hardness (μ) and the softness [Ali , 2009]:

$$\mu = (IP - EA)/2 \text{.........................} (3)$$

$$S = 1/(2\,\mu) \text{.........................} (4)$$

Where

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

S: is the softness of the molecules [Ghosh, 2004].

- 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].

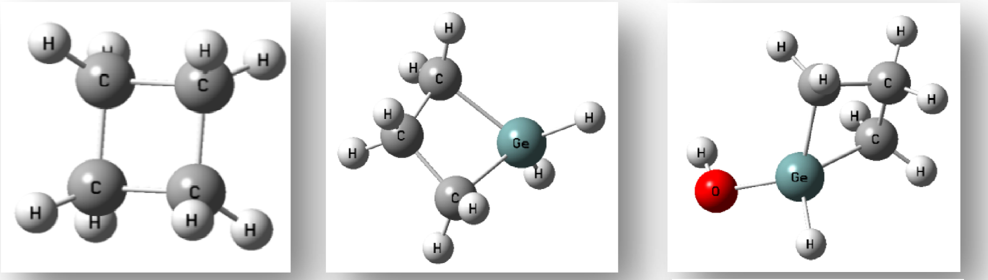
$$E_{gap} = E_{Lumo} - E_{Homo} \text{.........................} (5)$$

3. Results and Discussion:

In this section, we refer to the results of cyclobutane molecule (the electronic structure and electronic properties) and study the affect of replacing one carbon atom by one germanium atom and replacing hydrogen atoms by hydroxyl radical. Before proceeding in electronic properties calculation, it is necessary to find the geometry optimum of the under study molecules, the optimization of geometry for each molecule is shows in Figure (1). The geometry optimum results for cyclobutane show a good agreement with the result of the previous studies results, as seen in table (1). It includes bond lengths and the bond angles results, where the letter R refers to the bond length, A refers to the bond angle and D refers to the dihedral angular. The geometry optimum shape of cyclobutane is show in figure (1).

Table (1): Optimum bond lengths and bond angles result for cyclobutane.

(Bond or Angle) Label	Present Study	Previous study		
		[Lee, 1999]	[Norman, 2002]	[Wiberg, 2005]
R_{C-C} (A°)	1.558	1.56	1.554	1.552
R_{C-H} (A°)	1.090	1.10	1.109	1.094
A_{C-C-C} (deg)	90.003	90	88.3	88
A_{H-C-H} (deg)	107.958	109	106.4	109.3
$D_{C-C-C-C}$ (deg)	0.077	---	---	---



Cyclobutane 4-monogermanium-cyclobutane 4-monogermanium-4-cyclobutanol

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

The total energy results included in table (2) and the electronic state (HOMO and LUMO) shows table (3) for studied molecules. The electronic properties of cyclobutane and new molecules are show in tables (4-6). Table (4) includes energy gap, table (5) included ionization potential and electronic affinity and table (6) included hardness and softness. Where the sample ŋ means the concatenation of the molecules.

Table (2): Total energy results for studied molecules group and comparison of the total energy result with previous studies for cyclobutane.

ŋ	Molecules	Total energy (a.u)	
		Present study	Previous study
1	cyclobutane	-157.232	-156.1390 [Kristyan, 2001] -157.24612 [Kenneth, 2001] -156.96467 [Curtiss, 1997]
2	4-monogermanium-cyclobutane	-2194.34484	---
3	4-monogermanium-4-cyclobutanol	-2269.61286	---

Table (3): HOMO and LUMO energy result for studied molecules group.

ŋ	Molecules	LUMO (eV)	HOMO (eV)
1	cyclobutane	-0.17116	-8.19486
2	4-monogermanium-cyclobutane	-0.2732	-7.51268
3	4-monogermanium-4-cyclobutanol	-0.4117	-7.29609

Table (4): Energy gap results for studied molecules group and comparison of the energy gap result with previous studies of cyclobutane.

ŋ	molecules	E.gap (eV)	
		Present work	Previous study
1	cyclobutane	8.02370	8.3 [Monica, 2007]
2	4-monogermanium-cyclobutane	7.23948	---
3	4-monogermanium-4-cyclobutanol	6.88438	---

Table (5): Ionization potential and electronic affinity result for studied molecules group and comparison of the ionization potential result with previous studies of cyclobutane.

ŋ	Molecules	IP (eV)		EA (eV)
		Present study	Pervious study	
1	cyclobutane	8.19486	9.92 [John, 1999]	0.17115
2	4-monogermanium-cyclobutane	8.19486	---	0.27319
3	4-monogermanium-4-cyclobutanol	7.29608	---	0.41170

Table (6): Hardness and softness result for studied molecules group.

ŋ	Molecules	μ (eV)	S (eV)
1	cyclobutane	4.01185	0.12463
2	4-monogermanium-cyclobutane	3.61974	0.13813
3	4-monogermanium-4-cyclobutanol	3.44219	0.14525

Figures (2-A) and (2-B) represent the decreasing total energy and energy gap. The opposite behaviors appear when we see HOMO level, but same behavior appear when we see LUMO level, as we see in figure (2-C). The ionization potential is smaller than organic cyclobutane but the electronic affinity of new molecule is larger than the organic cyclobutane, as we see in figure (3). The hardness is decreasing. Nevertheless, we see that the softness is increasing by small magnitude, and it is approximately amount constant as see in figure (4).

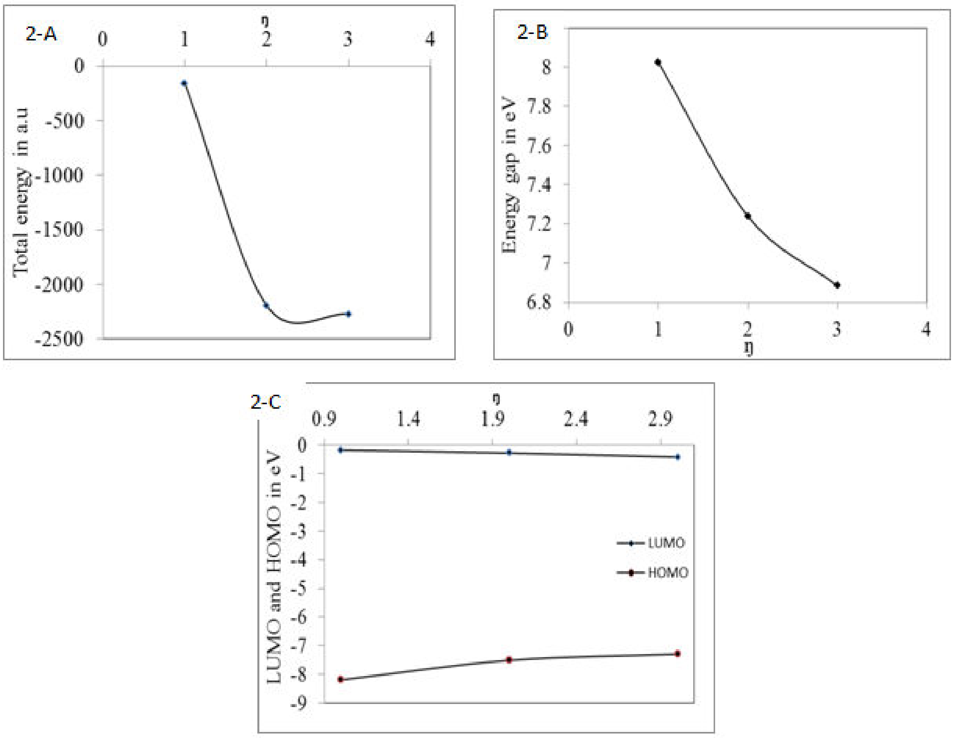


Fig. (2): Relationship, between total energy in (2-A), energy gap in (2-B), Cohesive energy in (2-C) and HOMO and LUMO energy in (2-D) with respect to the concatenation of the molecules

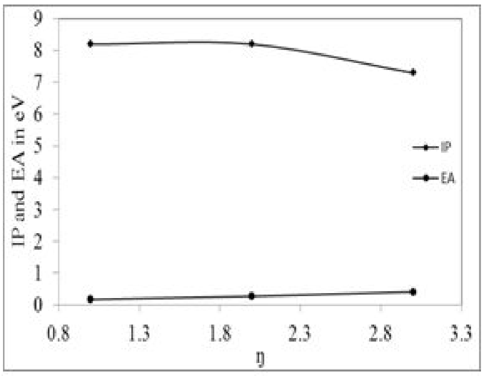


Fig. (3): Relationship, between ionization potential and Electronic affinity with respect to the number of the molecules

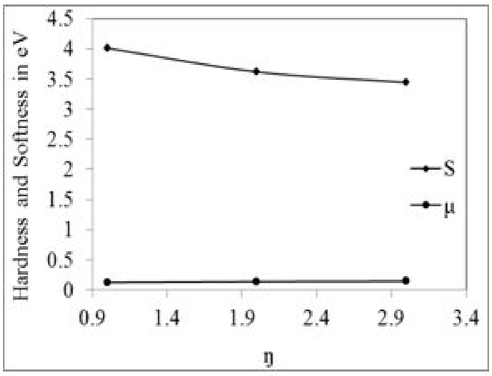


Fig.(4): Relationship, between hardness and softness with respect number of the molecules

4. Conclusions

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.

All the new studied molecules need small energy to become cation because ionization potential is smaller than original cyclobutane, but the electronic affinity are larger than the original cyclobutane.

The hardness for new molecules was lowering values as compared with cyclobutane, therefore all the new molecules are softer, and this reduces the resistance of species to lose electrons.

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