Density Functional Theory Investigation of the Cyclobutane Molecules

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Abstract:
The electronic structure, optimize geometry and electronic properties for cyclobutane have been studied by using density functional theory (DFT). The calculations were done with the commonly used exchange-correlation functional B3LYP with a bases set 6-31G. Followed a comprehensive analysis of the calculated highest-occupied and lowest-unoccupied Kohn-Sham orbital (HOMO and LUMO) energies. The electronic properties are include the total energy, ionization potential, electronic affinity, chemical potential, hardness, softness, bonding energy, electrophilicity and forbidden energy gap. This properties were studied with substituted the hydrogen atoms by hydroxide (OH) radical in same molecular with different numbers. The calculations have performed to know the addition effect of several numbers for (OH) radical on the molecular properties. The results in this study show that the new molecule has a soft property and semiconductor in better properties. In addition, the results show that the position of the radical has an effect on the electronic properties. Where the electronic properties of (Trans-1,2-cyclobutanediol) in general was more development. These calculations have performed using Gaussian 03 package.

Keyword: Cyclobutane, Density functional theory, 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. Cyclobutane semiconductors molecules have important uses due to its specific characteristics [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. Coincident with this growth, the semiconductor device literature has expanded and diversified [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 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, 2011].

Density function theory is one of the most popular and successful quantum mechanical approaches to matter. It is now adays routinely applied for calculating, e.g., the bonding energy of the molecules in chemistry and the band structure of solids in physics. first applications relevant for fields traditionally considered more distant from quantum mechanics, such as biology and mineralogy are beginning to appear. Superconductivity, atoms in the focus of strong laser pulses, classical liquids, magnetic properties of alloys have all been studied with DFT [capelle, 2006]. There are many approximations such as local approximation (LA), 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 use 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.
The mathematical equations were use in the calculations included:

$$IP = E(+) - E(n)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where (IP): is the Ionization potential for an molecule is the amount of energy required to remove an electron from an isolated atom or molecule, and expressed as the energy difference between the positive charged energy $E(+)$ and the neutral energy $E(n)$.

Electron affinity (EA) of an molecule is the energy change when an electron is added to the neutral atom to form a negative ion, and expressed as the energy difference between the neutral energy $E(n)$ and the negative charged energy $E(-)$, as in the following relation:

$$EA = E(n) - E(-)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

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

$$\kappa = (IP + EA)/2\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$
$$\mu = (IP - EA) /2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$
$$s = 1/(2\ \mu)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(5)$$
$$\omega = \kappa^{2}/ (2\ \mu) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where

κ: is the electronic chemical potential. It is that the quantity that measures the escaping tendency of electrons from species in its ground state.

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].

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

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].

$$E.gap = LUMO_{energy} - HOMO_{energy}\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

3. Results and Discussion:

Density functional theory used in this research at level B3LYP/ 6-31G. For study the electronic properties and electronic structure of saturated molecules. However, a large time required for employing this level and this time increases with increasing the radical used to describe the studied molecules, where characterizes by it is not economic time.

The electronic structure and electronic properties of the cyclebutane were studied and then addition the (OH) radical in different position and different number to the cyclobutane. The optimization of geometry of each molecule is shows in Figure (1). Table (1) is present the total energy and table (2) show the electronic state (HOMO and LUMO) for all studied molecules. The electronic properties of cyclobutane and all new molecules are shows in table (3) and table (4). Table (3) includes ionization potential, electronic affinitie, chemical potential and electrophilicitie, but table (4) includes hardness, softness, bonding energy and energy gap. Where the sample ŋ in tables (1, 2, 3 and 4) are means the number of the molecules.
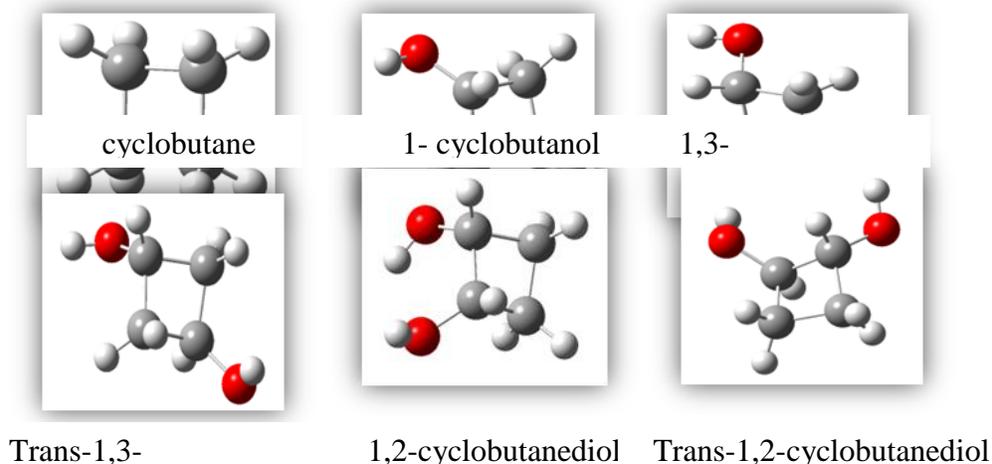
cyclobutane   1- cyclobutanol   1,3-

Trans-1,3-   1,2-cyclobutanediol   Trans-1,2-cyclobutanediol

Figure (1) shows the optimized structure of studied molecules.

Table (1) Total energy of the molecules

ŋ	Molecules	Total energy (e.V)	Total energy* (e.V)
1	Cyclobutane	-157.23191	-157.25654
2	1- Cyclobutanol	-232.46214	-
3	cis-1,3-Cyclobutanediol	-307.68948	-
4	trans-1,3-Cyclobutanediol	-307.68737	-
5	cis-1,2-Cyclobutanediol	-307.68892	-
6	trans-1,2-Cyclobutanediol	-307.69037	-

* Theoretical result of Previous studies from reference [Lydia, 2001]

Table (2) the electronic state for optimized molecules

ŋ	Molecules	electronic state	
		HOMO (e.V)	LUMO (e.V)
1	Cyclobutane	-8.19486	-0.17115
2	1- Cyclobutanol	-7.34370	-0.29877
3	cis-1,3-Cyclobutanediol	-7.35050	-0.41197
4	trans-1,3-Cyclobutanediol	-7.39159	-0.45768
5	cis-1,2-Cyclobutanediol	-7.25091	-0.59401
6	trans-1,2-Cyclobutanediol	-6.97145	-0.45768

Table (3) the calculated electronic properties for studied optimized molecules

ŋ	Molecule	IP(e.V)	IP(e.V)**	EA(e.V)	K(e.V)	W(e.V)
	Cyclobutane	8.19486	9.92	0.17115	4.18301	2.18073
2	1- Cyclobutanol	7.34370	-	0.29877	3.82124	2.07267
3	cis-1,3-Cyclobutanediol	7.35050	-	0.41197	3.88124	2.17106
4	trans-1,3-Cyclobutanediol	7.39159	-	0.45768	3.92464	2.22137
5	cis-1,2-Cyclobutanediol	7.25091	-	0.59401	3.92246	2.31124
6	trans-1,2-Cyclobutanediol	6.97145	-	0.45768	3.71457	2.11829

** Theoretical result of Previous studies from reference [Dean, 1999]

Table (4) the calculated electronic properties for studied optimized molecules

ŋ	Molecule	μ(e.V)	s(e.V)	B.E(e.V)	Egap(e.V)	Egap *** (e.V)
1	Cyclobutane	4.01185	0.12463	-2.07720	8.02370	8.3
2	1- Cyclobutanol	3.52246	0.14194	-2.33804	7.04492	-
3	cis-1,3-Cyclobutanediol	3.46926	0.14412	-2.59599	6.93853	-
4	trans-1,3-Cyclobutanediol	3.46695	0.14421	-2.59388	6.93390	-
5	cis-1,2-Cyclobutanediol	3.32845	0.15022	-2.59542	6.65689	-
6	trans-1,2-Cyclobutanediol	3.25688	0.15352	-2.59103	6.51376	-

*** Excremental result of Previous studies from reference [Monica, 2006]

Figure (2-A) represent the decreasing total energy with respect to the increasing of radical. The same behaviors appear when we see LUMO level, but opposite behavior appear when we see HOMO level, as we see in figure (2-B). the bonding energy decreasing to (-2.6 e.V) if adding two (OH) radical, as we see in figure (2-C), also the energy gap is decreasing by addition two radical, as we see in figure (2-D), that means the new molecules were more stable than the organic molecular. The ionization potential is smaller than organic cyclobutane but the electronic affinity of new molecule is larger than the organic cyclobutane, as in figure (3), this means that the new molecule needs small energy to become cation comparing with organic molecule. The chemical potential and electrophilicity of the new molecules in case addition one radical is less than the chemical potential of organic cyclobutane then began increasing by small magnitude with increasing the number of the radical as we see in figure (4), that means the electrons in these molecules have a small escaping tendency then organic molecular. Also the hardness of new molecular is smaller than cycolobutane but softness of new molecules approximately amount constant, as figure (5), this mean that the new molecules is soften than organic cyclobutane.
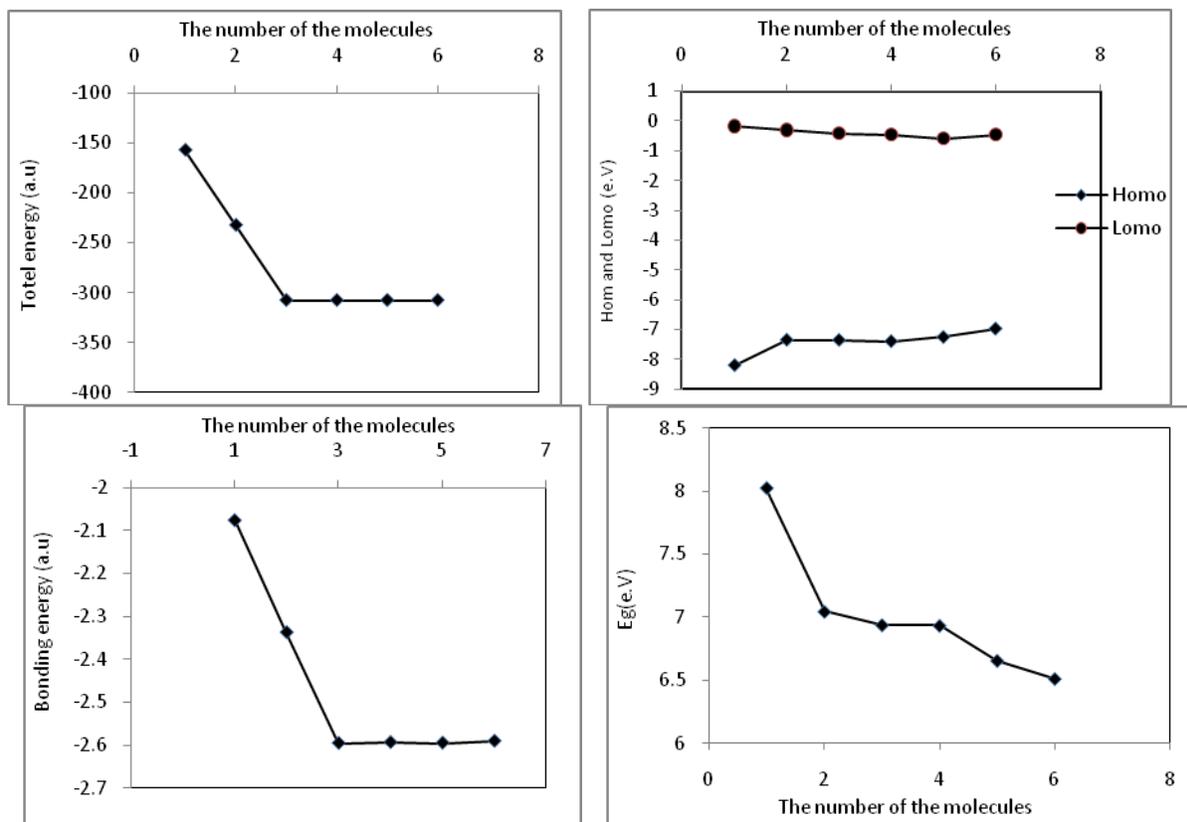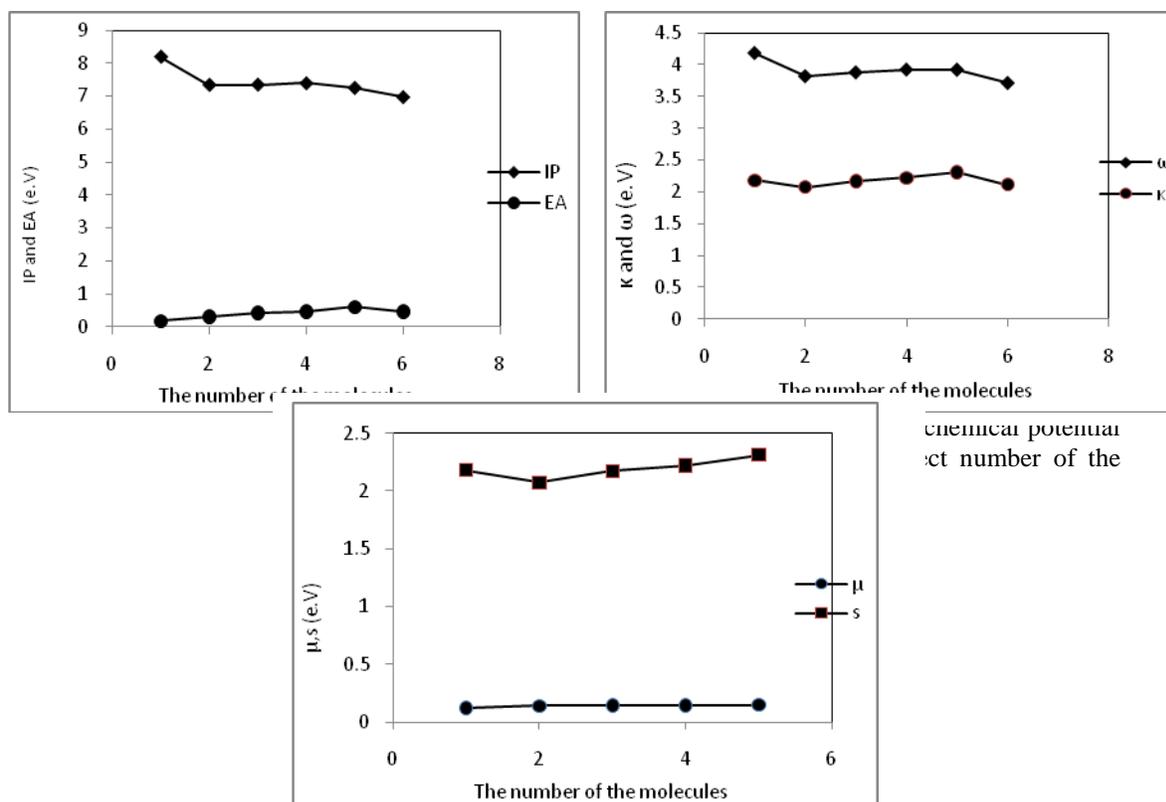
Fig. (2): Relationship, between total energy in (2-A), HOMO and LUMO energy in (2-B), bonding energy in (2-C) and energy gap in (2-D) with respect to the numbernumber of the molecules

4.   Conclusions

1. One of the important results was obtain in this study, is the decreasing of the total energy, bonding energy and forbidden energy gap for all molecules. This declares that these molecules have more stable than organic molecule, also lead to get   new semiconductor with more conductivity because the both HOMO and LUMO levels become more adjacent. The molecular trans-1,2-cyclobutanediol may candidate as a new electronic material and more stable.

2.   All new studied molecules need small energy to become cartio and have incline for receiving an electron because ionization potential is smaller than organic cyclobutane, but the electronic affinity is larger than organic cyclobutane.

3.   Decreasing the quantity of the escaping tendency of electrons from species in its ground state, but species was stabilize upon receiving an additional amount of electronic charge from the environment.

4.   The hardness for new molecules was lowering values comparing with cyclobutane, therefore the all new molecules are soft, and this eased chemical reaction process.

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