

Study of The Electronic Structure of di-Cyclobutadiene Molecule by Using Density Functional Theory

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Abstract

This work reports a theoretical study to investigate the electronic structure and electronic properties for unsaturated organic molecules group by using density functional theory (DFT) at B3LYP level with basis sets 6-31G(d,p). Cyclobutadiene is original molecule and then two Cyclobutadiene was linked, Studied the effect of linking on original cyclobutadiene molecule discussed based on the calculated electronic properties. The electronic properties included total energy, energy gap, ionization potential, electron affinity, have been found a striking variation in these values for these molecules, with comprehensive analysis of the calculated highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energies. These calculations have performed using Gaussian 09 package.

Keywords: Cyclobutadiene, DFT, energy gap, ionization potential, electronic affinity.

الخلاصة

تم خلال هذا البحث دراسة التركيب الإلكتروني و أفضل أمثلية هندسية نظريا لمجموعة جزيئات عضوية غير مشبعة، باستخدام نظرية دالية الكثافة (DFT) عند المستوي (B3LYP) مع الدوال الأساس 6-31G(p,d). جزيئة السايكلوبيوتاديين هي الحلقة الأصلية وبعدها تم ربط حلقتي سايكلوبيوتاديين. وقد دُرس تأثير الربط على جزيئة السايكلوبيوتاديين الاصلية، كما تضمن البحث حساب الخصائص الإلكترونية للجزيئات المدروسة، والتي تتضمن الطاقة الكلية وفجوة الطاقة وجهد التأين والألفة الإلكترونية ، ووجد تباين ملحوظ في تلك القيم بين تلك الجزيئات ، ثم يلي ذلك تحليل شامل لحسابات الطاقات المدارية الجزيئية الأعلى المشغولة HOMO والطاقات المدارية الأوطأ الغير مشغولة LUMO. تم تنفيذ هذه الحسابات باستخدام برنامج Gaussian 09. الكلمات المفتاحية : سايكلوبيوتاديين نظريه داله الكثافه، فجوة الطاقة، الجهد الأيوني، الألفة الإلكترونية.

Introduction

Semiconductor devices such as diodes, transistors and integrated circuits can be found everywhere in our daily lives, in Walkman, televisions, automobiles, washing machines and computers. We have come to rely on them and increasingly have come to expect higher performance at lower cost.

Personal computers clearly illustrate this trend. Anyone who wants to replace a three to five years old computer finds that the trade-in value of his or her computer is surprising low. On the bright side, one finds that the complexity and performance of the today's personal computers vastly exceeds that of their old computer and that for about the same purchase price, adjusted for inflation.

While this economic reality reflects the massive growth of the industry, it is hard to even imagine a similar growth in any other industry. For instance, in the automobile industry, no one would even expect a five times faster car with a five times larger capacity at the same price when comparing to what was offered five years ago. Nevertheless, when it comes to personal computers, such expectations are very realistic. [Zeghbroeck,2002].

The essential fact which has driven the successful growth of the computer industry is that through industrial skill and technological advances one manages to make smaller and smaller transistors. These devices deliver year after year better performance while consuming less power and because of their smaller size they can also be manufactured at a lower cost per device.

Cyclobutadiene can be used as a semiconductor because it is consisting from four atoms of carbon bonded together by strong covalent bonds. In all cyclic polyenes (C_nH_n), the p-molecular orbitals occur in degenerate pairs, except for the lowest p-orbital, and for the cyclic polyenes with even numbers of carbon atoms, the highest p-orbital, square molecule cyclobutadiene (C_4H_4) has four p-orbitals, a bonding orbital (p_1), two degenerate non-bonding orbitals (p_2 and p_3) and an anti-bonding orbital (p_4). Four electrons are placed into these four orbitals; into the bonding orbital, and one each with parallel spins into the degenerate non-bonding orbitals (Hund's rule). [Henry,1997].

Theoretical methods and computational details:

Several methods have been used for the calculation of ionization potential and electron affinities. Since available experimental electron affinities , the most direct theoretical method comes from calculation of the neutral energies their respective optimized geometries. We have used koopmans' theorem to calculate EA from LUMO energies and I_p from HOMO energies. In addition, the outer-valence Green's function (OVGF) method has been All calculations were performed using the Gaussian 09 program package.

All geometries were reoptimized using density functional methods using Becke's three-parameters exchange functional with the Lee, Yang, and Parr (B3LYP) correlation functional with basis sets 6-31G (d,p) level and frequency calculations carried out in order to verify that the stationary points thus obtained were true minima and to determine thermodynamic parameters for the determination of reaction energetics.

Schrödinger equation [Huda ,2011,Valeev, Sherrill,2003].

$$\hat{H} \Psi = E \Psi \dots \dots \dots (1)$$

Born Oppenheimer approximation

$$[\hat{H}_{el} = \hat{T}_e(r) + \hat{V}_{en}(r) + \hat{V}_{ee}(r) \dots \dots \dots (2)$$

then Schrödinger equation become:

$$[\hat{T}_e(r) + \hat{V}_{en}(r) + \hat{V}_{ee}(r)]\Psi = E \Psi \dots \dots \dots (3)$$

DFT provides an appealing alternative, being much more versatile, with $V_{ee}(r)$, onto a single-body problem without $V_{ee}(r)$. In DFT the key variable is the particle density $\rho(r)$ which for a normalized Ψ is given by

$$\rho(r) = \sum_i^{n_i} [\Psi_i(r)]^2 \dots \dots \dots (4)$$

Where the summation is over occupied molecular orbitals and n_i is the number of electrons in orbital (i). [Grotenders, 2005, Dorsett, White ,2000].

In molecular orbital (MO) theory with in the limitation of Koopman theorem the orbital energies of the frontier orbitals are given by: [Camargo, Honorio, Mercadante, Molfetta , Alves, dasilva, 2003, Huda, 2011].

$$I_P = - E_{HOMO} \dots \dots \dots (5)$$

$$E_A = - E_{LUMO} \dots \dots \dots (6)$$

Energy gap (E_{gap}): is the difference between the lowest unoccupied molecular orbital and highest occupied molecular orbital according to the Koopmans theorem [Kampen, 1999, Aqeel, 2009].

The energy difference between the HOMO and LUMO corresponds to the lowest excitation energy as following formula [Zeghbrouck,2002, Henry,1997].

$$E_{GAP} = E_{LUMO} - E_{HOMO} \dots \dots \dots (7)$$

Results and discussion

Chart 1 represents the geometrical structures of studied molecules at 6-31G(d,p) density functional theory with three parameters B3LYP . the ground state energy obtained by the same level of theory was illustrate in table 1, the total energy for the two structures are (-154.700 a.u) and (-308.235 a.u), respectively, as shown in figure 1. cyclobutadiene is a planar with high symmetry D_{2h} and it has a small value of electric dipole moment (.0001Debye), while di-cyclobutadiene has lower symmetry C_{2h} in compared with cyclobutadiene, it has electric dipole moment (.0003Debye). The two structures has not imaginary frequencies, this refers to good geometrical optimization done by the used level of theory. The C-C bond results by our method in present study B3LYP/6-31G(d, p) equals 1.57661 \AA in a good agreement with previous studies 1.579 \AA obtained by MP2/6-31G(d)[Alonso, Poater, Sola,2007] and 1.566 \AA results from CCSD(T)/cc-pVTZ [Levchenko, Krylov,2004]. C=C bond calculated in present study, 1.3356 \AA , also in a good agreement with other studies 1.334 \AA and 1.343 \AA from [Alonso, Poater, Sola,2007, Levchenko, Krylov,2004], respectively. One can see good optimization done in present study from the result of dihedral angle HCCC= 179.9808° calculated by B3LYP/6-31G(d, p) and in good agreement HCCC= 180° calculated from [Alonso, Poater, Sola,2007, Levchenko, Krylov,2004].

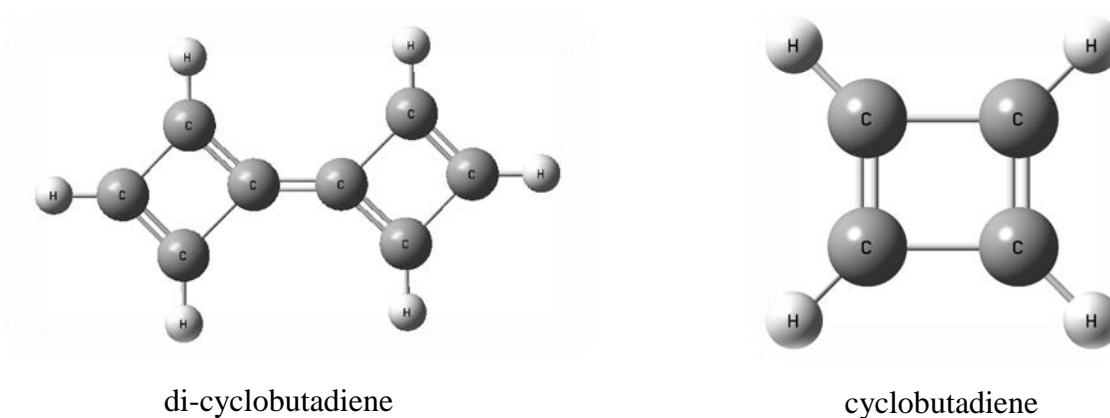


Chart (1): The optimized structures for studied molecules.

Table (1) : Total energy and symmetry for studied molecules.

Chemical Name	Symbol	molecular mass (amu)	Et (a.u.)	Symmetry
Cyclobutadiene	C_4H_4	52.0313	-154.700	D_{2h}
Di-cyclobutadiene	C_8H_6	102.04695	-308.2351381	C_{2h}

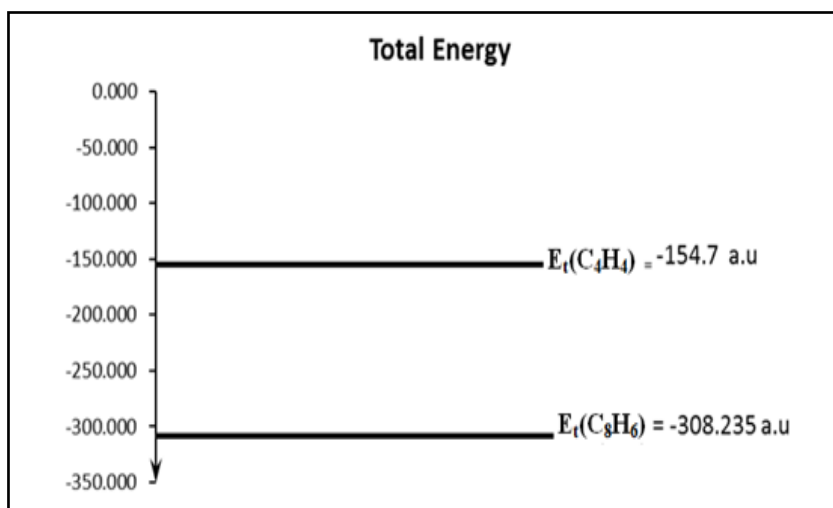


Figure (1): total energy for studied molecules.

Table (2) shows the results of electronic states (HOMO and LUMO), energy band gap (LUMO – HOMO), ionization potential and electron affinity for cyclobutadiene and di-cyclobutadiene calculated in eV by employing 6-31G (d,p). The interaction of two cyclobutadiene rings leads to change the energy of both HOMO and LUMO, the LUMO and HOMO are change from (-5.37553305 and -1.88735496) eV, respectively, for cyclobutadiene to (-4.65879531 and -2.76110017) eV , as in figure (2).

Table (2) : Electronic properties for studied molecules.

Molecule	HOMO (eV)	LUMO (eV)	E_{gap} (eV)	IP(eV)	EA(eV)
C_4H_4	-5.37553305	-1.88735496	3.488	5.375533	1.88735496
C_8H_6	-4.65879531	-2.76110017	1.898	4.658795	2.76110017

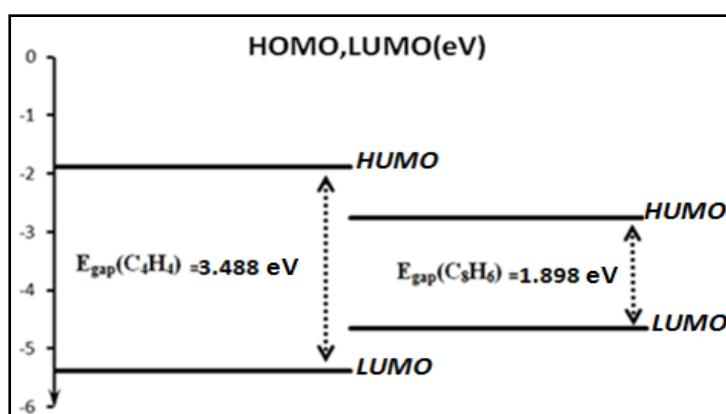


Figure (2): HOMO and LUMO energies for studied molecules.

The behavior of energy band gap for the two structures under study declare that the di-cyclobutadiene has small energy gap E_{gap} in compared with cyclobutadiene. The energy gap was decreased from (3.488 eV) for cyclobutadiene to approximately the half value (1.898 eV for di-cyclobutadiene), as shown in figure (3).

This feature result maybe refers to that, di-cyclobutadiene is a good molecular semiconductor.

Table (2) shows the ionization potential and electron affinity for molecules under study. The decreasing of ionization potential from (5.375533 eV) for cyclobutadiene to (4.658795 eV) for di-cyclobutadiene refers to that di-cyclobutadiene needs to small energy to capture an electron and it behaves as acceptor semiconductor, this conclude is very agree with the increasing in electron affinity for di-cyclobutadiene.

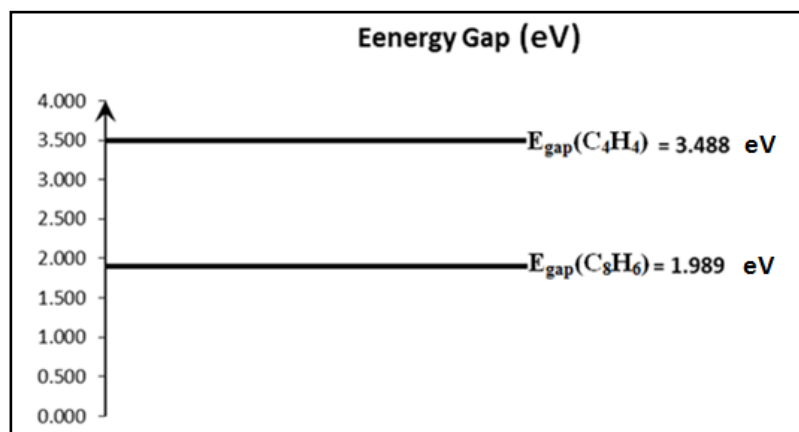


Figure (3) : Energy gap for studied molecules.

Conclusions

From the above results, one can conclude that:

1. The geometrical optimization treatments by B3LYP/6-31G (d,p) in a good agreement with other studies for the same structures.
2. Di-cyclobutadiene is a stable molecule with small ground state energy compared with the reference cyclobutadiene molecule.
3. B3LYP/6-31G (d,p) is a suitable function to describe the molecules under study, the geometry optimization done by this method gave good result without imaginary frequency.
4. Di-cyclobutadiene has small energy gap, it is a semiconductor with good electronic properties such as high electron affinity in compared with cyclobutadiene.

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