

Effect of some Substituents on the Optimization And Electronic Properties of Cyclopentane and Di-Cyclopentane.

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Abstract

This work reports a theoretical study to investigate the best geometric optimization and electronic structure for cyclopentane and di-cyclopentane molecules by using density functional theory (DFT) at B3LYP level with basis set 6-31G. Cyclopentane molecule is original molecule before replacing the carbon atoms by nitrogen and oxygen atoms. The effect of substitute on cyclopentane and di-cyclopentane molecules discussed based on the calculate of optimization parameters and the electronic properties. The electronic properties which included total energy, energy gap, ionization potential, electronic affinity, chemical potential, hardness, charge transfer, softness, electronegativity and electrophilicity, have been found with varying differences for each molecule.

In this work we found some of these properties (energy gap, total energy and hardness) increasing after replacing C atom by N and O atoms and (C₄H₅N) considered from insulation materials and more hardness than studied molecules because it has larger magnitude from energy gap and hardness, in addition to this molecule less affinity with the physical medium, while (C₈H₅NO) more affinity with the physical medium that makes it more stability comparing with other molecules. Calculations are carried out by employing the Gaussian 09 package of program.

Key word: Cyclopentane, DFT, energy gap, ionization potential, hardness

الخلاصة

تم خلال هذا البحث دراسة التركيب الإلكتروني وأفضل أمثلية هندسية لحلقة السايكلوبنتان والسايكلوبنتان المزدوجة باستخدام نظرية دالة الكثافة ذات المستوى (B3LYP/6-31G). جزيئة السايكلوبنتان هي الحلقة الأصلية قبل استبدال ذرات الكربون بذرات النيتروجين والأكسجين. وقد تم دراسة تأثير الاستبدال على السايكلوبنتان والسايكلوبنتان المزدوجة. كما تضمن البحث حساب الخواص الإلكترونية للجزيئات المدروسة وهذه الخواص هي الطاقة الكلية، فجوة الطاقة، جهد التأين، اللفة الألكترونية، الجهد الكيميائي، الصلادة، الانتقال في الشحنة، المرونة، الكهروسالبية والتآلف مع الوسط، ووجد إن قيم هذه الخصائص تتباين من جزيئة إلى أخرى حيث تم التوصل الى ان بعض من هذه الخصائص مثل فجوة الطاقة، الطاقة الكلية و الصلادة تزداد بعد التشويب وان الجزيئة (C₄H₅N) تعتبر من العوازل وأكثر الجزيئات المدروسة صلادة كونها امتلكت أكبر قيمة من فجوة الطاقة والصلادة اضافة الى كون هذه الجزيئة أقل تآلف مع الوسط بينما الجزيئة (C₈H₅NO) كانت أكثر تآلف مع الوسط وهذا يجعلها أكثر الجزيئات استقرارا. تم الحصول على الحسابات بواسطة برنامج كاس 09.

الكلمات المفتاحية: السايكلوبنتان، نظرية دالة الكثافة، فجوة الطاقة، جهد التأين، الصلادة

Introduction

Alkanes are hydrocarbons where all the carbon atoms are *sp*³-hybridized, all bonds are single bonds, and all carbons are tetrahedral shape. Because each carbon atom in an alkane bonds to four other atoms, chemists say they are saturated hydrocarbons. Pentane is the simplest alkane [Richard *et al.*, 2005]. Cyclopentane ring is a highly flammable alicyclic hydrocarbon with chemical formula C₅H₁₀ and CAS number 287-92-3, consisting of a ring of five carbon atoms each bonded with two hydrogen atoms above and below the plane. It occurs as a colorless liquid with a petrol-like odor. Its melting point is -94°C and its boiling point is 49°C. Cyclopentane is in the class of cycloalkanes, being alkanes that have one or more rings of carbon atoms. The typical structure of cyclopentane is the "envelope" conformation [Robert & Neuman, 1999].

Density functional theory (DFT) is a quantum mechanical modelling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry [Vondrášek *et.al.*, 2005].

DFT has been very popular for calculations in molecular and solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. In many cases the results of DFT calculations for solid-state systems agree quite satisfactorily with experimental data [Grimme & Stefan, 2006].

Theory and computational details:

Density functional theory is a quantum mechanical modeling method used in this work, there are many approximations in quantum mechanic such as local density approximation (LDA), local spin density approximation (LSDA), generalized gradient approximation (GGA) and hybrid functional [Jones, 2006], we will use the hybrid functional, and it should be approximated with a common density functional. The weighted sum of these two results is known as the functional of the Becke three parameters with Lee-Yang-Parr functional (B3LYP) [Tatsuo, 2002]:

$$E_{XC}^{BaLYP} = E_{xc}^{LDA} + a_0 (E_x^{HF} - E_x^{LDA}) + a_x (E_X^{GGA} - E_X^{LDA}) + a_c (E_C^{GGA} - E_C^{LDA}) \quad (1)$$

When B3LYP is Becke and Lee-Yang-Parr functional, LDA is Local Density Approximation, HF is Hartree-Fock, GGA is the General Gradient Approximation, E_X is the exchange-energy functional and E_C is the correlation-energy functional.

All constants are known, a_0 , a_x and a_c are three empirical parameters and the best value of these parameters had been found as follows ($a_0=0.20$, $a_x=0.72$ and $a_c=0.81$). It has shown to be highly successful for determination of properties such as: energy gap, ionization potential, electronic affinity, hardness, softness, electronic chemical potential and electrophilicity.

Where the energy gap (E_{gap}) is defined the difference between the lowest unoccupied molecular orbital and highest occupied molecular orbital according to the Koopmans theorem [Kampen, 1999].

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

Also the ionization potential (IP) is the amount of energy required to remove an electron from an isolated atom or molecule. Or it is expressed as the energy difference between the positive charged energy $E(+)$ and the neutral energy $E(n)$ [Head-Gordon & Head-Gordon 1994].

$$IP = - E_{\text{Homo}} \quad (3)$$

The electronic affinity (EA) which 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 $E(-)$ [Gong *et.al.*, 1994], as in the following relation:

$$EA = - E_{\text{Lumo}} \quad (4)$$

But the hardness (η) is defined as the measurement of molecule resistance to the change or deformation in molecular orbitals.

$$\eta = (IP - EA) / 2 \quad (5)$$

While the softness (S) is defined as property of molecules that measures the extent of chemical reactivity [Ghosh, 2004].

$$S = 1 / (2 \eta) \quad (6)$$

The electronic chemical potential (K) which is the fundamental variational principle in density functional theory.

$$K = (IP + EA) / 2 \quad (7)$$

The maximum electronic (ΔN_{max}) which is the property that means the translation of charge.

$$\Delta N_{\text{max}} = k / \eta \quad (8)$$

The Electrophilicity (w) is defined as the stabilization upon receiving an additional amount of electronic charge from the environment [Anupama Ghosh, 2010].

$$W = k^2 / (2 \eta) \quad (9)$$

Results and Discussion

The best geometric optimization and electronic properties of the cyclopentane and di-cyclopentane were studied and then replaced the carbon atom by nitrogen and oxygen atoms in cyclopentane and di-cyclopentane, these structures are shown in figure(1).

The geometric parameters obtained from the optimization of such structures under study were calculated. Table (1) represents the results of bond length between the single bonds, double bond and transfers bond, measured in Angstrom. The carbon atoms have quadruple valance, in cyclopentane molecule one of C atoms connects with two C atoms and one H atom therefore we see double bond, while in (C_4H_5N , C_4H_4O) also we see double bond because N and O atoms have high valance. Also we found difference in the bond length for (c-c) in cyclopentane because one of C atoms connects with two H atoms therefore we get two values for this bond that make this result better than the reference.

Table (2) presents the number, type and values of angles in (degree) between the atoms and Table (3) included the number, type and values of dihedral angle in (degree) between the atoms, in this table we found that the value of dihedral angles (0.0003 – 179.998) approximately equal to zero that means the studied molecules lie in the plan except the angle (59°) in (C_4H_5N) and the angle (60°) in (C_4H_4O) because C atom connects with two H atoms that lead to be angle.

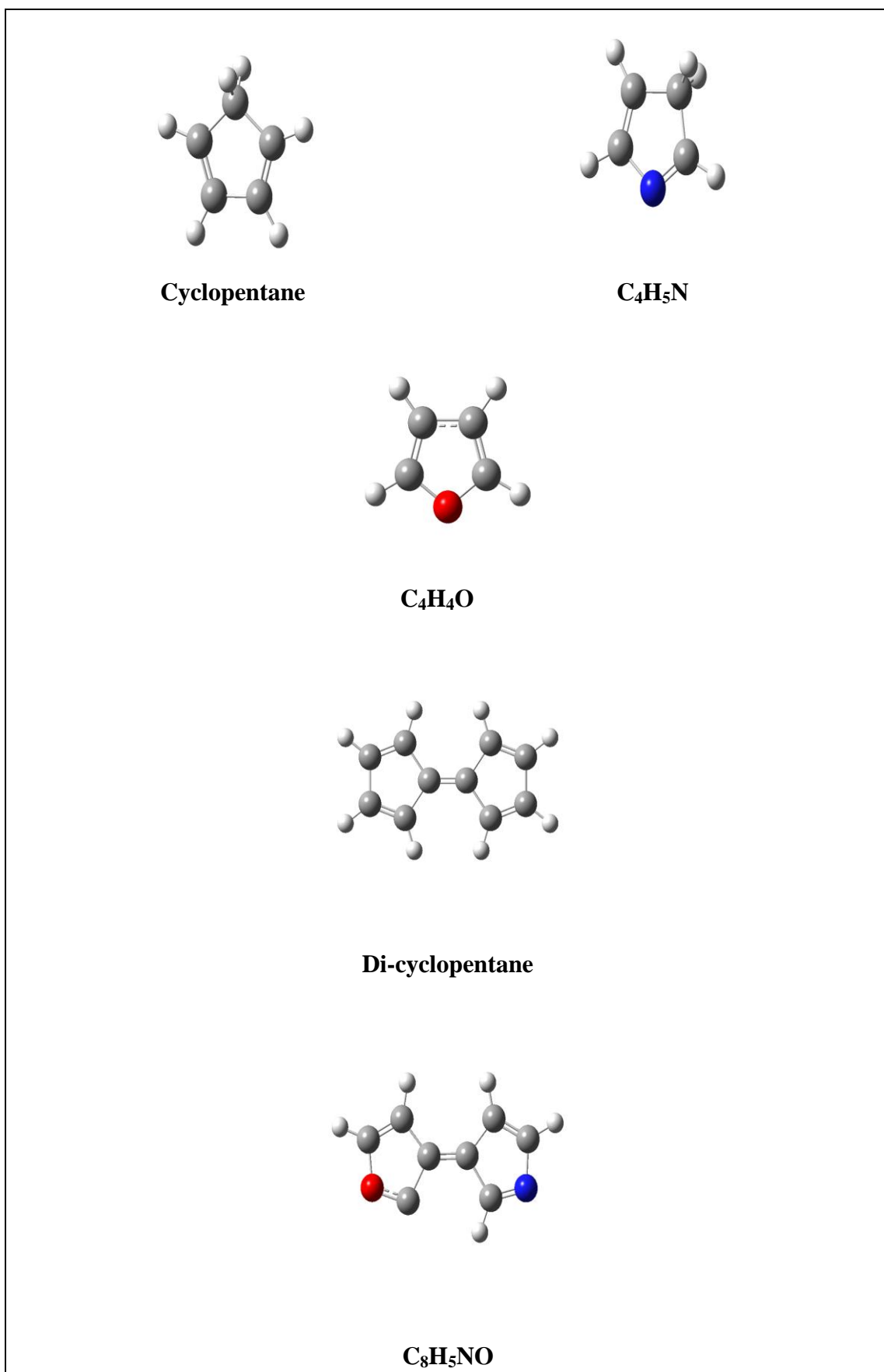


Fig. (1): The schematic representation for cyclopentane and di-cyclopentane before and after replacing C atom by N&O atoms.

Table (1): Types and lengths of bonds between the atoms.

Molecules	Bond	Number	Value (Å)	
			Present study	Previous study
Cyclopentane	C – C	3	1.469 - 1.505	1.540 [Kenneth, 2005] 1.55 [Changyol, 1999] 1.54 [Hafied, 2008]
	C = C	2	1.348	---
	C – H	6	1.103 - 1.084	1.095 [Kenneth, 2005] 1.1 [Changyol, 1999] 1.10 [Hafied, 2008]
C ₄ H ₅ N	C – C	2	1.506	---
	C = C	1	1.345	---
	C – H	5	1.081- 1.099	---
	C – N	1	1.428	---
	C = N	1	1.289	---
C ₄ H ₄ O	C = C	2	1.360	---
	C ⋯ C	1	1.435	---
	C – H	4	1.078 - 1.080	---
	C – O	2	1.364	---
Di-cyclopentane	C – C	6	1.471 - 1.477	---
	C = C	5	1.353 - 1.364	---
	C – H	8	1.081 - 1.083	---
C ₈ H ₅ NO	C – C	4	1.448 - 1.502	---
	C = C	3	1.340 - 1.364	---
	C – H	5	1.079 - 1.083	---
	C – N	1	1.436	---
	C = N	1	1.291	---
	C – O	1	1.415	---
	C ⋯ O	1	1.339	---

Table (2): Types and values of angles between the atoms.

Molecules	Angle	Number	Value (Degree)	
			Present study	Previous study
Cyclopentane	C – C – C	5	103.269 -109.316	108 [Changyol, 1999]
	C – C – H	12	111.990 - 126.977	---
	H – C – H	1	105.743	106 [Changyol, 1999]
C ₄ H ₅ N	C – C – C	2	107.420	---
	C – C – H	7	111.74 - 128.359	---
	C – C – N	2	113.667	---
	C – N – C	1	106.029	---
	H – C – H	1	106.238	---
	N – C – H	2	118.608- 121.714	---
C ₄ H ₄ O	C – C – C	2	106.099	---
	C – C – H	6	126.505 - 133.693	---
	C – C – O	2	110.514	---
	C – O – C	1	106.771	---
	O – C – H	2	115.792	---
Di-cyclopentane	C – C – C	14	106.397 - 108.967	---
	C – C – C	16	124.533 - 127.286	---
C ₈ H ₅ NO	C – C – C	8	103.943 - 132.083	---
	C – C – H	7	124.081 - 133.533	---
	C – C – N	2	111.885 - 113.479	---
	C – N – C	1	105.413	---
	N – C – H	2	118.514 - 124.032	---
	C – C – O	2	102.988 - 110.969	---
	C – O – C	1	112.218	---
	O – C – H	1	115.497	---

Table (3): Types and values of the dihedral angle between the atoms.

Molecules	Angle	Number	Value (Degree)
Cyclopentane	C – C – C – C	5	-0.043 – 0.040
	C – C – C – H	12	-180.072 – 180.045
	H – C – C – H	7	-59.297 – 59.316
C ₄ H ₅ N	C – C – C – C	1	-0.0007
	C – C – C – H	4	-179.983 – 180.096
	H – C – C – H	5	-60.579 – 60.753
	C – C – C – N	2	-0.0051 – 0.0058
	C – C – N – C	2	-0.0091 – 0.0085
	N – C – C – H	3	-180.066 – 120.526
	H – C – N – C	2	-180.0003 – 179.987
C ₄ H ₄ O	C – C – C – C	1	0.0036
	C – C – C – H	4	-180.021 – 180.069
	H – C – C – H	3	-0.003 – 0.093
	C – C – C – O	2	-0.008 – 0.002
	C – C – O – C	2	-0.0073 – 0.0097
	O – C – C – H	1	180.0165
	H – C – O – C	2	-180.052 – 179.982
Di-cyclopentane	C – C – C – C	18	-179.998 – 179.995
	C – C – C – H	20	-180.036 – 180.039
	H – C – C – H	6	-0.0742 – 0.0384
C ₄ H ₅ NO	C – C – C – C	8	-180.023 – 179.99
	C – C – C – H	8	-180.033 – 180.0006
	H – C – C – H	2	-0.0515 – -0.0342
	C – C – C – O	3	-179.992 – 0.002
	C – C – O – C	2	-0.002 – 0.0021
	O – C – C – H	1	-180.0018
	H – C – O – C	1	180.0282
	C – C – C – N	3	0.003 – 180.014
	C – C – N – C	2	-0.0133 – 0.0055
	H – C – N – C	2	179.995

In Table (4) we explain some of electronic properties like: ionization potential, electronic affinity, energy gap in (electron volt) and total energy in (atomic unit). While Table (5) represents the chemical formula for the studied molecules and other electronic properties like: chemical potential, hardness, electrophilicity in (electron volt), charge transfer (ΔN_{\max}) and softness in (electron volt inverse).

Table (4): Ionization potential, electronic affinity, energy gap and total energy for cyclopentane and di-cyclopentane.

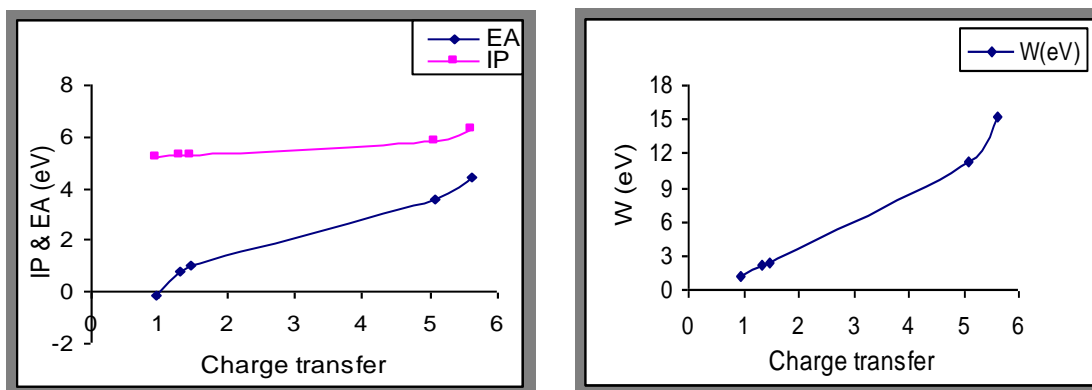
Molecules	IP(eV)	EA(eV)	E _{gap} (eV)		E _{tot} (a.u)	
			Present study	Previous study	Present study	Previous study
Cyclopentane	5.22	1.006	4.223	4.217 [Hafied, 2008]	-194.11069	- 196.836 [Hafied, 2008]
C ₄ H ₄ O	5.82	0.79	5.004	---	-230.02737	---
C ₄ H ₅ N	5.25	-0.13	5.349	---	-210.17633	---
Di-cyclopentane	5.31	3.56	1.741	---	-385.80907	---
C ₈ H ₅ NO	6.31	4.408	1.887	---	-437.67093	---

Table(5): The Chemical formula, chemical potential, hardness, charge transfer (ΔN_{\max}), softness and electrophilicity for cyclopentane and di-cyclopentane.

Molecules	Ch.formula	K(eV)	η (eV)	ΔN_{\max}	S(eV ⁻¹)	W(eV)
Cyclopentane	C ₅ H ₆	3.102	2.12	1.46	0.23	2.31
C ₄ H ₄ O	C ₄ H ₄ O	3.29	2.5	1.32	0.2	2.17
C ₄ H ₅ N	C ₄ H ₅ N	2.58	2.7	0.96	0.18	1.25
Di-cyclopentane	C ₁₀ H ₈	4.43	0.87	5.09	0.57	11.23
C ₈ H ₅ NO	C ₈ H ₅ NO	5.36	0.95	5.63	0.53	15.31

In this study we found the relationship between ionization potential and electronic affinity with respect to the charge transfer, we found that the probability of the molecule tendency to form a positive ion is almost constant with increasing in charge transfer and the greater the probability of the molecule tendency to form a negative ion transmission occurs clear in the charge. That is shown in Table (4) and in figure (2-A), then we found there is proportional relationship between electrophilicity and charge transfer, i.e. that the transition in the charge occurs when the molecule affinity with the physical medium in addition to possessing a chemical high effort. That is shown in figure (2-B).

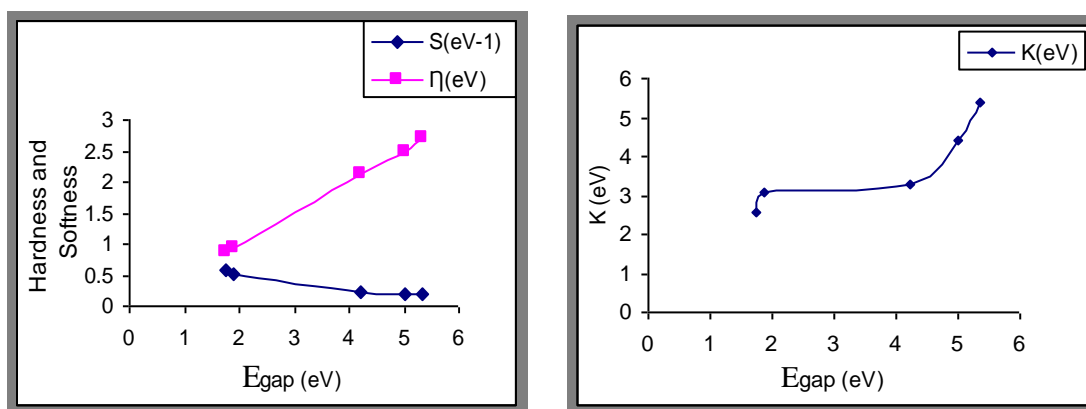
From figure (3-A) we found that there is a proportional relationship between hardness and the energy gap but it was inverse between softness and the energy gap, ie the molecule when it has a high value of the energy gap become more hardness. Conversely, if the energy gap of little value, the molecule to be softer, then in figure (3-B) we found that the chemical potential for molecules increased when the energy gap increased too.



2-A

2-B

Fig.(2):Relationship, between ionization potential and electronic affinity in (2-A) and electrophilicity in (2-B) with respect to charge transfer (ΔN_{max}).



3-A

3-B

Fig.(3):Relationship,between hardness and softness in (3-A) and chemical potential in (3-B) with respect to the energy gap.

Conclusions

1. Di-cyclopentane molecule before and after replacing C atom by N and O atoms has small energy gap comparing with cyclopentane molecule, therefore the di-cyclopentane molecule is within the semiconductor materials, while the cyclopentane molecule is within the insulation materials.
2. The total energy of the last molecule is greater than the other molecules, although the number of its atoms decreased this is caused by the energy of N and O atoms is greater than the energy of C and H atoms. In addition to the fact that these molecules have electrophilicity greater than the other molecules.
3. The relationship between hardness and softness is always inverse relationship. The (C₄H₅N) molecule has greater magnitude for energy gap so this molecule tends to be more hardness.
4. The results in this study show that the calculated total energy, energy gap, bond's length and value of angle for cyclopentane 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.

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