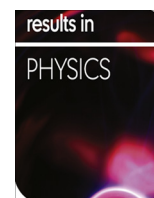


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Structure and electronic properties of substitutionally doped Cycloheptane molecule using DFT



Rajaa K. Mohammad, Rajaa A. Madlol, Nibras M. Umran, Fadhil I. Sharrad*

Department of Physics, College of Science, University of Kerbala, 56001 Karbala, Iraq

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ABSTRACT

A density functional theory (DFT) has been carried out of the calculation molecular structure of Cycloheptane molecule (C₇H₁₄) with Gaussian 09 and Gaussian view 5.08 programs. The effects of the substitution Silicon atom in place of the Carbon atom and substituting the one Hydrogen atom by one hydroxyl (OH) were performed using DFT at B3LYP level with CC-PVDZ basis set. The optimized structure, ionization potential, electron affinity, energy gap, electronegativity, total energies, force constant, reduces mass, Raman spectral, electrostatic potential surface and electron density surface were calculated. The results showed decrease in energy gaps, increases in the electron affinity, and discusses the effect of the substitution for all properties.

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Introduction

Cycloheptane is an organic semiconductor with the molecular formula C₇H₁₄, and has density 0.8110 g/cm³ and molar mass 98.19 g.mol⁻¹ [1].

Aromatic compounds are important in industry and play roles in the biochemistry of all living things, whereas solar cells and photovoltaic, organic light emitting diodes (OLEDs), thin film transistors [2,3]. Many studies had been done to calculate electronic properties. FT-Raman, UV, FT-IR and NMR spectra were measured in the condensed state as well as compared with the experimental data. It was done using DFT/B3LYP method with 6-311++G(d,p) as basis set of 2-(2-benzothiazolylthio)-ethanol [4]. Electronic properties and infrared spectra of diamondoids were calculated using DFT method [5]. The DFT method was used for the optimization structure of the ground state and simulation of the Raman and infrared spectra of trichloro cyclohexylsilane molecule [6]. The basic parameters of design and fabrication of an organic solar cell were HOMO and LUMO of organic compounds [7]. The DFT/B3LYP method with the 6-31G (d) basis set using the symmetry constraints had been used to calculate the harmonic vibrational frequencies, equilibrium molecular geometry, Raman scattering

activities and infrared intensities for tetraoxa [8] circulenes. The calculated quantum-chemical were in excellent agreement with the experimental spectra [8]. The investigation of the effects of a variety of substitutes (H, NH₂, NMe₂, OCH₃, CH₃, Cl, Br, CN and NO₂) on the electronic and structural properties of 2,4-diamino-5-*p*-substituted-phenyl-6-ethyl-pyrimidines had been used density functional theory (DFT) method at the level of B3LYP with 6-311G(d) basis set [9]. The complex heterogeneous nature of chars had confounded the complete analysis of the Raman spectra of these materials [10]. In other studies, the cyclic conformational coordinates are essential for the variation of molecular ring conformers as the use of Cremer-Pople coordinates have explain for five- and six-membered rings. So useful for correlating, the physical properties of macrocycles with their ring pucker and measuring the dynamic ring conformational behavior to varieties of canonical states were given for cycloheptane and cyclooctane which had been previously experimentally analyzed [11]. Femtosecond Raman rotational coherence spectroscopy (RCS) detected by degenerate four-wave mixing is a background-free method that allows to determine accurate rotational, vibration-rotation coupling constants, and centrifugal distortion constants of cyclopentane (C₅H₁₀). They are finding the lowest-frequency vibration in a pseudorotating ring deformation that interconverts 10 permutationally distinct but energetically degenerate “twist” minima interspersed by 10 “bent” conformers. While the individual twist and bent structures are polar asymmetric tops, the pseudorotation is

* Corresponding author.

E-mail address: fadhil.altai@gmail.com (F.I. Sharrad).

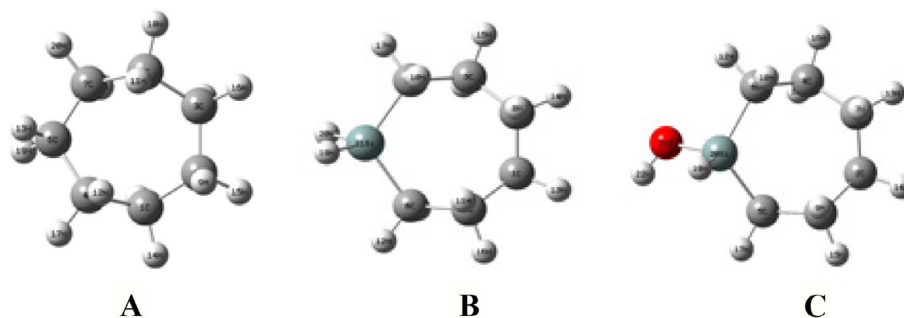


Fig. 1. The optimized structures of Cycloheptane (A), 7-monosilicon-Cycloheptane (B) and 7-monosilicon-7-hydroxyl-Cycloheptane (C) molecules using DFT method with CC-PVDZ basis set.

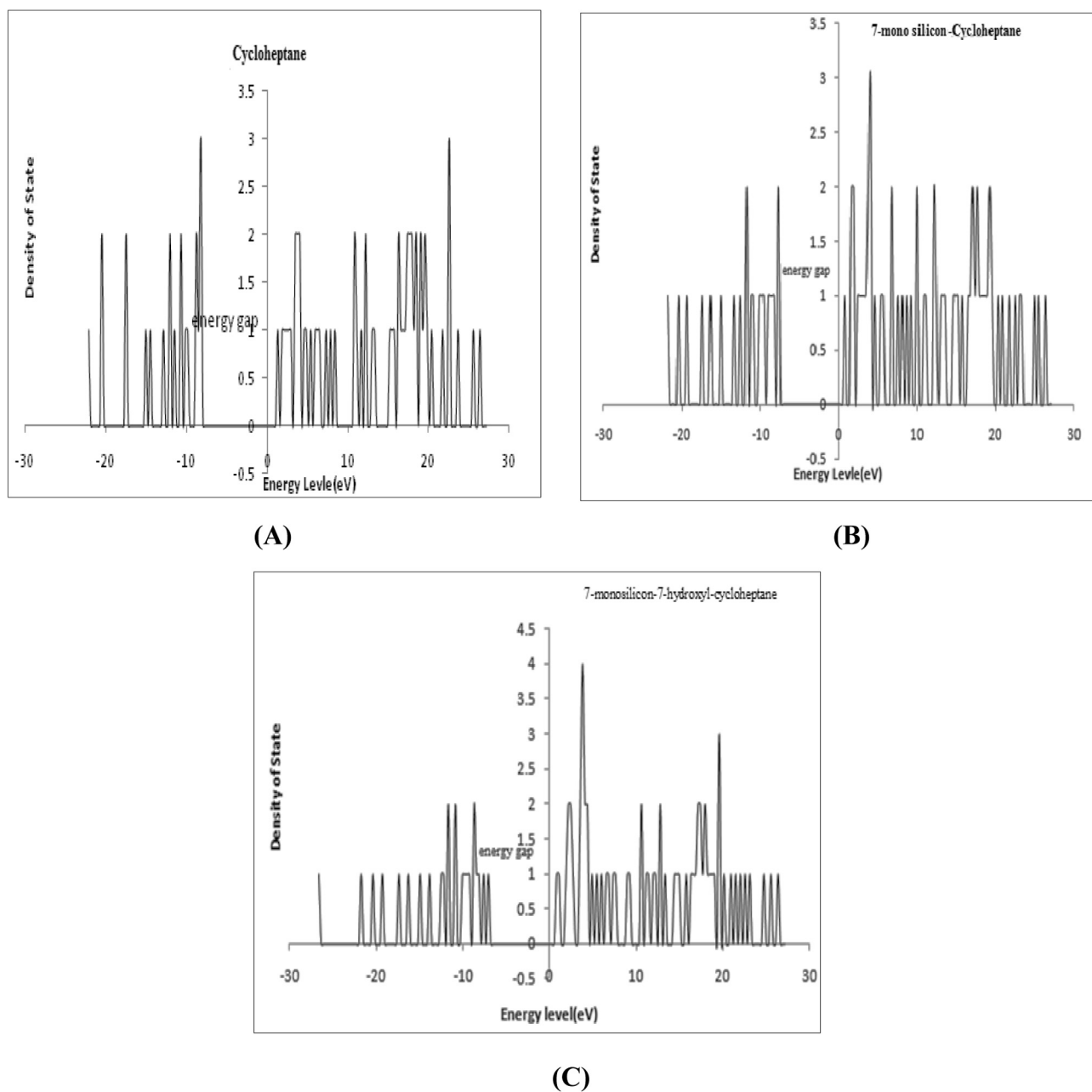
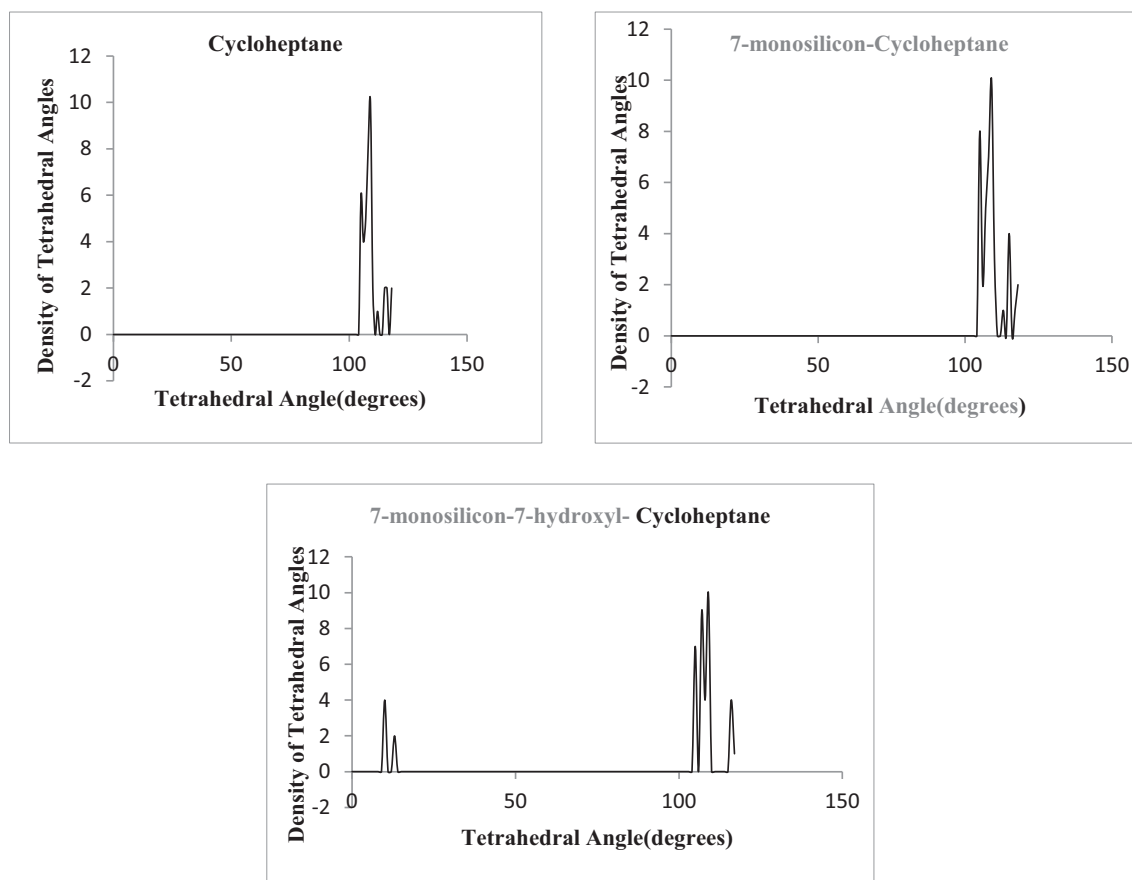


Fig. 2. The density of state of (A) Cycloheptane, (B) 7-monosilicon-Cycloheptane and (C) 7-monosilicon-7-hydroxyl-Cycloheptane molecules using DFT method with CC-PVDZ basis set.

Table 1The HOMO, LUMO, and Energy gap (E_g) in eV values units, while the total energy in a.u. unit.

Molecules	HOMO (eV)	LUMO (eV)	E_g (eV)	Total energy (a.u.)
Cycloheptane	-8.1665	1.3744	9.5409	-275.1897
7-monosilicon-Cycloheptane	-7.6966	1.0443	8.7409	-526.5910
7-monosilicon-7-hydroxyl-Cycloheptane	-7.3461	0.9395	8.2857	-601.8635

**Fig. 3.** The density of tetrahedral angles for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules using DFT method with CC-PVDZ basis set.

fast on the time scale of external rotation, rendering cyclopentane a fluxionally nonpolar symmetric top molecule [12]. In more details conformational analysis of cyclopentane and its derivatives were performed using DFT (ω b97xd/6-311+G (d, p)) level of theory. The researchers found, the concept of a spherical conformational and scape represents two concentric ring coordinates for twisting and bending pathways in cyclopentane and its derivatives which helped fully explain their fluxional nature, confirmed by 1100–1600 cm^{-1} region of their Raman spectra [13].

In the present work, we have studied the optimized structure, ionization potential, electron affinity, energy gap, electronegativity, total energies, force constant, reduces mass, Raman spectral, electrostatic potential surface and electron density surface using DFT for Cycloheptane molecule (C_7H_{14}) with the effects of the substitution Silicon atom in place of the Carbon atom and substituting the one Hydrogen atom by one hydroxyl (OH). Furthermore, we are interest to study the properties of Cycloheptane because of the scarcity of research. The aromatic compounds are important in industry for multiple uses, such as in the biochemistry of all living things, whereas solar cells and photovoltaic, organic light emitting diodes (OLEDs), thin film transistors.

Computational approach

All computational procedure was carried out using Gaussian 09 and Gaussian view 5.08 programs [14]. The optimization structure of Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules with substitution Silicon and hydroxyl in positions of Hydrogen atom have been performed with B3LYP/CC-PVDZ level in the gas phase and DFT method. The energy of the highest occupied molecular orbital is E^{HOMO} and the energy of the lowest unoccupied molecular orbital is E^{LUMO} . The energy gap computed using the following equation [15]:

$$\Delta E_{gap} = E^{LUMO} - E^{HOMO} \quad (1)$$

Ionization potential (IP) and electron affinity (EA) can have been calculated using equations [16].

$$IP = -E^{HOMO} \quad (2)$$

$$EA = -E^{LUMO} \quad (3)$$

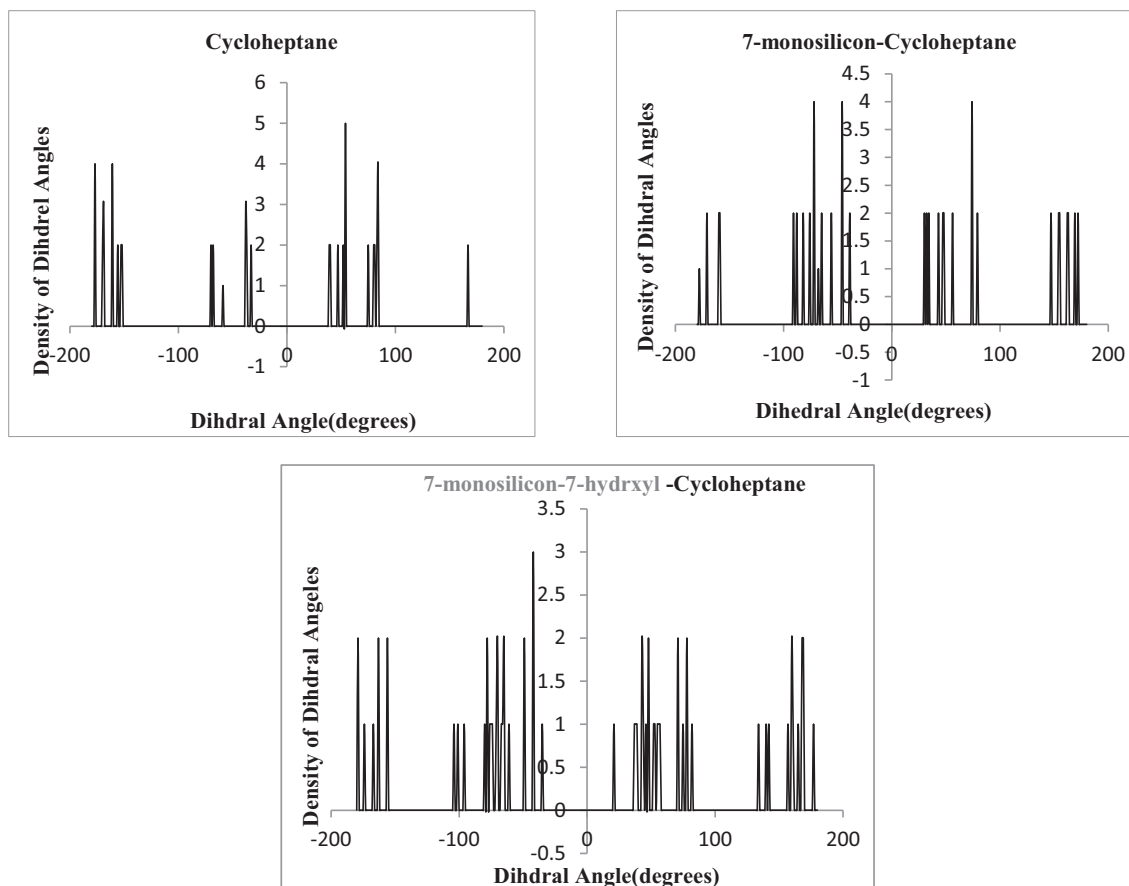


Fig. 4. The density of dihedral angles for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules using DFT method with CC-PVDZ basis set.

Table 2

The ionization potential (*IP*), electron affinity (*EA*) and electronegativity (*X*) values of values in eV units.

Molecules	<i>IP</i> (eV)	<i>EA</i> (eV)	<i>X</i> (eV)
Cycloheptane	8.1665	−1.3744	3.3960
7-monosilicon-Cycloheptane	7.6966	−1.0443	3.3261
7-monosilicon-7-hydroxyl-Cycloheptane	7.3461	−0.9396	3.2032

While, the electronegativity (*X*) can be calculated using the following equation [17].

$$X = -1/2(E^{HOMO} + E^{LUMO}) \quad (4)$$

Results and discussion

The specific type of basis set has accuracy in the calculations and considered the valence electrons in the bound. In addition, this model is treated the deformation and polarization of the dopant Cycloheptane molecule. From this treatment, the composite will have a polarization type of double Zeta. The optimized structures of Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules in gas phase are computed using DFT methods with CC-PVDZ basis set, and it is shown in Fig. 1A, B and C, respectively.

Energy level and the energy gap

The energy level and the energy gap for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules have been shown in Fig. 2. In doping case, the electronic bands are continuous and the energy levels are increasing, while the energy gaps are decreasing for the substitution atom (also, see Table 1). The energy gap indicated to the activity of molecule in computed results and the 7-monosilicon-7-hydroxyl-Cycloheptane molecule has small energy gap 8.2857 eV, small energy gap indicated to the activity of molecule, while Cycloheptane has high energy gap 9.540 eV.

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Density of tetrahedral angles

The values of density of tetrahedral angles of Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules are shown in Fig. 3. From this figure, the tetrahedral angles at the range 105.24–117.11° of Cycloheptane, while for 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules at 105.39–118.49° and 105.07–118.46°, respectively, It is clear from Fig. 3 that the substitution of Silicon and hydroxyl atoms in place of Carbon atom leads to small differences of density tetrahedral angles for this molecule.

Density of dihedral angles

The density of dihedral angle is considered a measure of the value of change for dihedral angle. From these calculations, the dihedral angle is in the range of pure molecule or deformation occurred in it. The density of dihedral angles for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules computed using DFT method with CC-PVDZ basis set at 167°, and −177° for Cycloheptane and −178.68° and

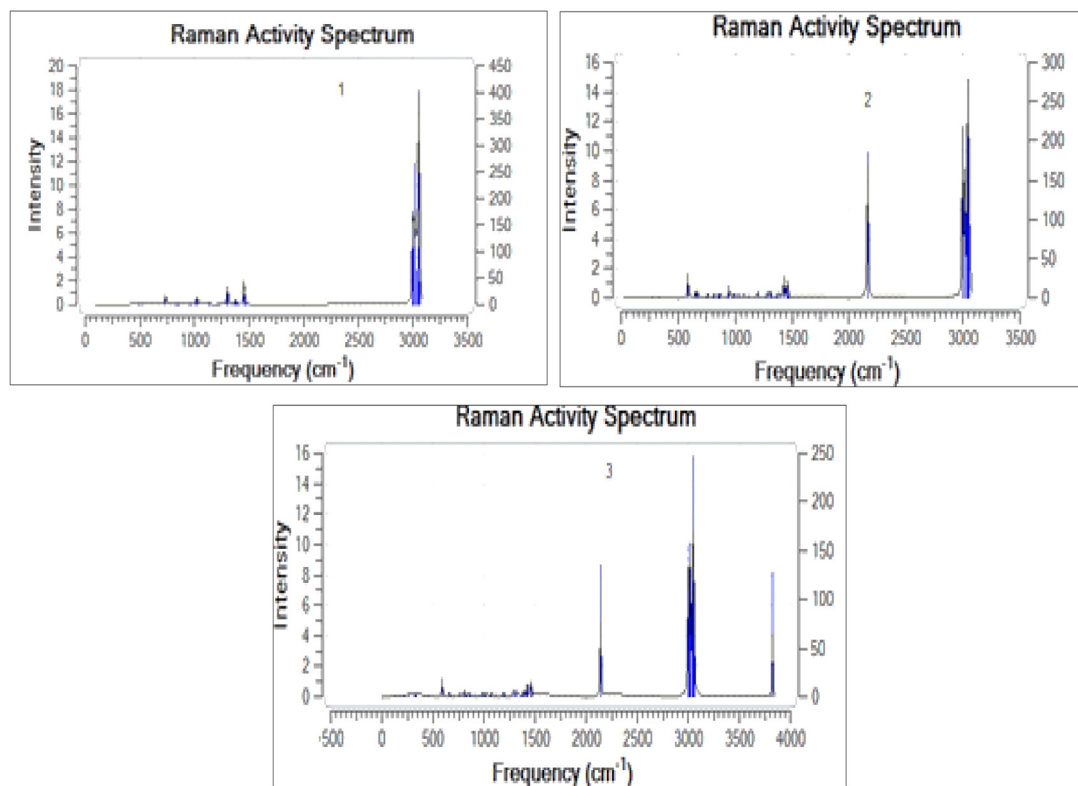


Fig. 5. Raman spectra for Cycloheptane (1), 7-monosilicon-Cycloheptane (2) and 7-monosilicon-7-hydroxyl-Cycloheptane (3) molecules using DFT method with CC-PVDZ basis set.

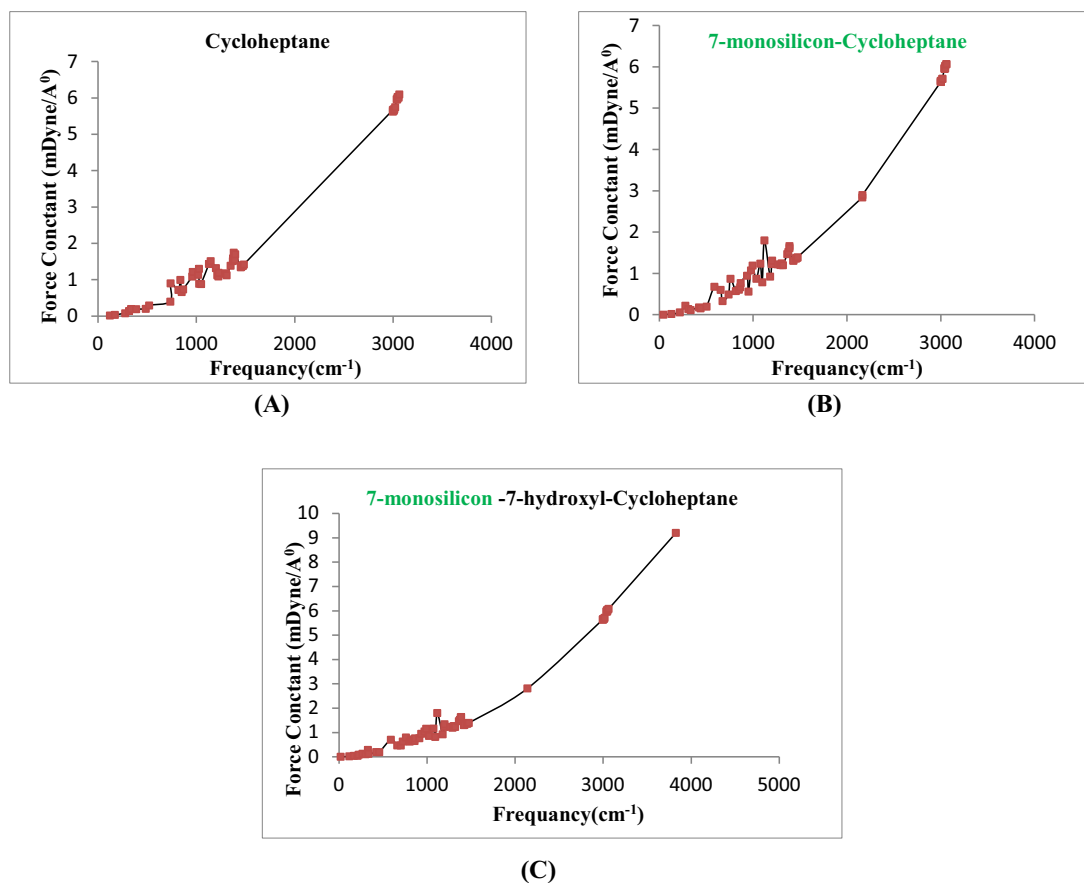


Fig. 6. The force constant for Cycloheptane (A), 7-monosilicon-Cycloheptane (B) and 7-monosilicon-7-hydroxyl-Cycloheptane (C) molecules using DFT method with CC-PVDZ basis set.

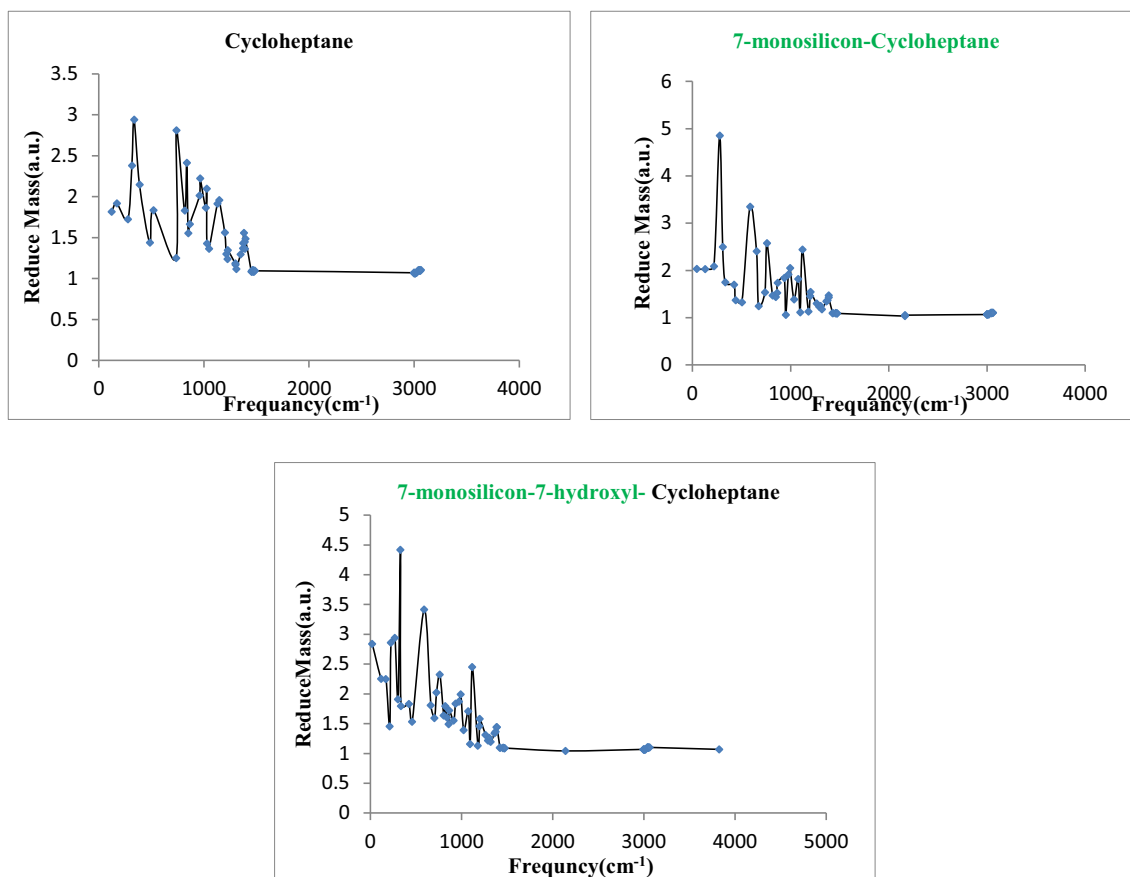


Fig. 7. The reduce mass for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules using DFT method with CC-PVDZ basis set.

172° for 7-monosilicon-Cycloheptane and -179.1° and 177° for 7-monosilicon-7-hydroxyl-Cycloheptane and it is shown in Fig. 4. From this figure, the substitution lead to the difference of density for this molecule.

Quantum chemical parameters

The values of the calculated quantum chemical parameters such as the highest occupied molecular orbital (E^{HOMO}), lowest unoccupied molecular orbital (E^{LUMO}), energy gap and total energy are presented in Table 1. From this table, the values of LUMO, energy gap and total energy are decreasing, while the values of HOMO are increasing, this refers to corresponds to the more reactive molecule in the reactions with electrophiles. The 7-monosilicon-7-hydroxyl-Cycloheptane has high HOMO and this value depend on the type of substitution atoms.

Electronic properties

The values of electronic properties such as IP , EA and X are computed by DFT/B3LYP with CC-PVDZ. The ionization potential have been computed by making 7-monosilicon-Cycloheptane one electron deficit. These quantities give us an idea about the chemical reactivity of substitute Cycloheptane [18], basis set and it is shown in Table 2. From this table, the electron distribution of Silicon is $3s^2 3p^2$ and Oxygen $2p^4$ are assumed to be inactive in chemical bonding with the Carbon atoms. For this, the electron substitution leads to decreasing the values of ionization potential (IP) and electronegativity (X), while the values of electron affinity (EA) are increasing.

Raman spectra

The Raman spectra of the C–H stretching week studied in the region $3036.08\text{--}3037.08\text{ cm}^{-1}$ for Cycloheptane, you can see Fig. 5 (1), the 7-momosilicon-Cycloheptane and the 7-monosilicon-7-hydroxyl-Cycloheptane molecules and the C–C studied in the region $1145.03\text{--}119.53\text{ cm}^{-1}$ for original molecule, you can see Fig. 5(2 and 3). The substitution leads to new vibration modes for molecules understudy. The 7-momosilicon-Cycloheptane molecules have C–Si–C and Si–H stretching studied in the region 586.414 and 737.625 cm^{-1} , while for the 7-monosilicon-7-hydroxyl-Cycloheptane found O–H stretching, rocking and H–O–Si–H wagging in region 3826.39 , 211.231 and 821.653 cm^{-1} . From this figure, we can see the effect of Silicon and hydroxyl atoms are lead to the vibration harmonic are week.

Force constant and reduced masses

The force constant and reduce mass of Cycloheptane, 7-monosilicon-Cycloheptane and the 7-monosilicon-7-hydroxyl-Cycloheptane molecules calculated using DFT methods with CC-PVDZ basis set and are shown in Figs. 6 and 7. In Fig. 6, force constant can be divided into two regions; the first part range is from 0 to 1471.9 cm^{-1} . The second part range is from 1450 cm^{-1} to near 4000 cm^{-1} , except the 7-monosilicon-7-hydroxyl-cycloheptane molecule at near 5000 cm^{-1} . The 7-monosilicon-Cycloheptane has highest force constant at $1.662\text{ mDyne/\AA}^\circ$. In Fig. 7, the 7-monosilicon-Cycloheptane molecule has highest reduce mass at 4.850 a.u. . From this figures, the values of reduced mass for all molecules are decreasing, this shows that some vibrations might include one kind of atoms and exclude the other, while the force

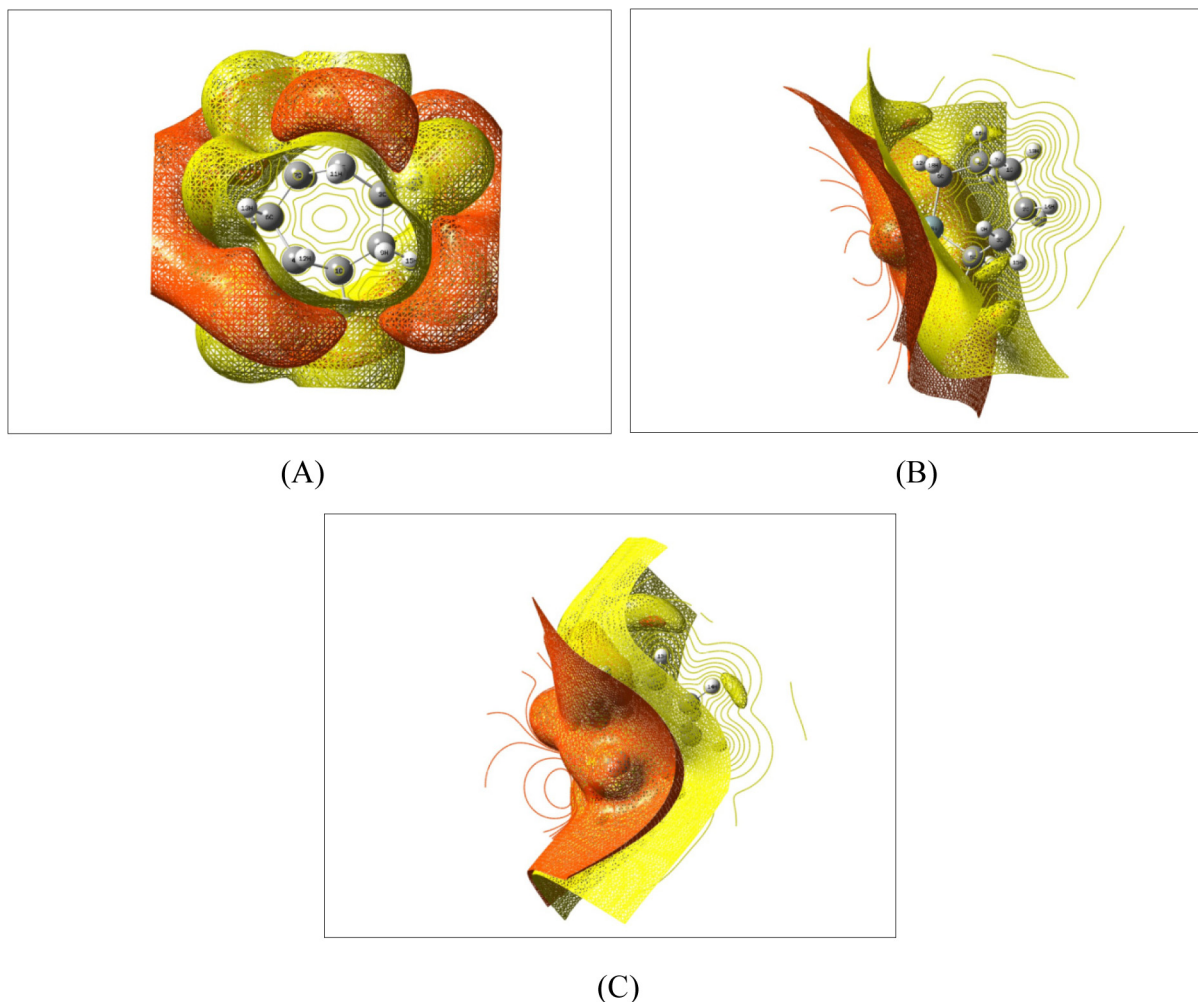


Fig. 8. The electrostatic potential and electron density surfaces for Cycloheptane (A), 7-monosilicon-Cycloheptane (B) and 7-monosilicon-7-hydroxyl-Cycloheptane (C) molecules using DFT method with CC-PVDZ basis set.

constant are increasing. The reason of these results because of the reduced mass is inversely proportional to the frequency, while the force constant is directly proportional to the frequency according to the $\nu = 1/2\pi\sqrt{\frac{k}{\mu}}$.

Electrostatic potential and electron density surfaces

The Electrostatic potential and electron density surfaces for Cycloheptane, 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxy 1-Cycloheptane molecules computed using DFT method with CC-PVDZ basis set and are shown in Fig. 8. The distribution of electrostatic potential and electron density surfaces depends on the type of substitution atoms; also depend on negative and positive charges. From this figure, the density distribution on Cycloheptane molecule is homogenous, while in 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules distribution on the silicon and hydroxyl atoms. It is because these atoms have a high electronegativity therefore, it is attract charge toward them.

Conclusions

In this paper, a density functional theory (DFT) has been carried out of calculation molecular structure of Cycloheptane molecule (C7H14). The calculated values of density of tetrahedral angle and dihedral angle are different and depended on the substitution

of atoms. The values of LUMO and total energy are decreasing, while the values of HOMO are increasing, these refer to corresponds to the more reactive molecule in the reactions with electrophiles. The values of *IP* and *X* are decreasing, while the values of *EA* are increasing. Rama spectra, the substitution lead to new vibration modes and small different of stretching vibration, also the effect of Silicon and hydroxyl atoms are lead to the vibration harmonic are week. The values of reduce mass for all molecules are decreasing and the force constant are increasing. The distribution of electrostatic potential and electron density surfaces depends on the type of substitution atoms; also depend on the negative and positive charges and electronegativity, electrostatic potential and electron density surfaces in 7-monosilicon-Cycloheptane and 7-monosilicon-7-hydroxyl-Cycloheptane molecules distribution on the Silicon and hydroxyl atoms.

Acknowledgments

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