

Electronic Properties of Hydrogen Adsorption on the Silicon- Substituted C₂₀ Fullerenes: A Density Functional Theory Calculations

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ABSTRACT

The B3LYP/6-31++G** density functional calculations were used to obtain minimum geometries and interaction energies between the molecular hydrogen and nanostructures of fullerenes, C₂₀ (cage), C₂₀ (bowl), C₁₉Si (bowl, penta), C₁₉Si (bowl, hexa). The H₂ molecule is set as adsorbed in the distance of 3Å at vertical position from surface above the pentagonal and hexagonal sites of nanostructures. By comparing of gap energies, electronic chemical potential, hardness and results of QTAIM (Quantum Theory of Atom in Molecules) analysis, the Si atom substitution in hexa two-fold position of C₂₀ (bowl) may be suitable for the adsorption of hydrogen molecule.

Keywords: C₂₀ Fullerenes, Silicon substitution, Hydrogen Adsorption, NBO, QTAIM Analysis.

INTRODUCTION

Pure hydrogen may be the final destination in the evolution of fuel usage from coal to petroleum to natural gas, which has followed a trail of increasing hydrogen content [1]. A major bottleneck for the hydrogen vehicle is the problem of hydrogen storage. Jena describes the fundamental modes in which the H₂ molecule can be attached to a storage material [2]. He discusses the stringent requirements of the reversibility of the hydrogen uptake and release using each type of mechanism and emphasizes the use of nano sized configurations to improve the kinetics and thermodynamics of the candidate materials [2, 3]. Recently, considerable attention has been driven to

porous materials such as zeolites, carbon nano tubes, and fullerenes as possible materials for hydrogen storage. C₂₀ is regarded as the smallest experimentally synthesized carbon fullerene with 12 pentagons and bowl form of C₂₀ with 6 hexagonal rings and a pentagon at center of structure [4]. Experimentally, each of these C₂₀ isomers can be produced under suitable reaction conditions, For example, C₂₀ fullerenes from its perhydrogenated form, dodecahedrane, C₂₀H₂₀ [5]. By comparing experimental photo-electron spectra with theoretical results, Saito and Miyamoto concluded that C₂₀ fullerene should be a cage-type structure [6]. On the other hand, An et al, based on Hartree –

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Fock based CCSD (T) and MP4 results, concluded that bowl type structure would be the most stable structure [7, 8]. For C₂₀ the most stable isomer can have a ring-shape, a bowl or a cage structure, depending on the computational method. Huda and co-workers found that bowl shaped C₂₀ structure is more stable than the cage shaped [9]. The theoretical reports are available in the literature where carbon fullerenes were taken as base models for SiC fullerene structures. In Si substituted C₂₀ clusters, the binding energies are higher for cage-type structure by almost 0.1 eV/atom over the bowl type structures [10, 11].

COMPUTATIONAL METHODS

In our study, the B3LYP/6-31++G** density functional calculations were used to obtain minimum geometries and interaction energies between the molecular hydrogen and nanostructures of fullerenes C₂₀ (cage), C₁₉Si (cage), C₂₀ (bowl), C₁₉Si (bowl, hexa two-fold), C₁₉Si (bowl, hexa three-fold) and C₁₉Si (bowl, Penta) by Gaussian 03 package [12]. Then, H₂ molecule is adsorbed above the pentagonal and hexagonal sites. Using Natural Bond Orbitals (NBO) analysis, HOMO-LUMO gaps (HLG), electronic chemical potential, hardness and adsorption energies are obtained. A quantitative comparison of the bond strength can be given in terms of the bond topological properties. So, the wave functions obtained are evaluated with the program package AIMALL [13].

DISCUSSIONS

1. Geometry Optimization: In this research, the full optimization of geometries at B3LYP/6-31++G** method show that C₂₀ cage (Fig.1) with -761.467 a.u. energy is more stable than C₂₀ bowl (Fig.2) with -761.293 a.u. The Si substitution in both bowl and cage shape,

of fullerene increase the stability. The Si substituted bowl structure at penta (Fig.3), hexa three-fold (Fig.4) and hexa two-fold (Fig. 5) positions are more stable than C₁₉Si cage (Fig.6) by 6.5676 a.u., 6.2909 a.u. and 6.648 a.u., respectively. The Si substitution at hexa two-fold position is more stable over the hexa three-fold by 0.358 a.u. in energy. The heteroatom substitution in the bowl fullerene may be suitable for the adsorption of hydrogen molecule. We study hydrogen molecule adsorption on all of structures. One hydrogen molecule is placed in the distance of 3 Å at vertical position from surface (Carbon or Silicon atom) in optimized configuration. One of the optimized structures of H₂ interaction with Fullerene is shown in Fig. 7. From our results, the effects of adsorption of H₂ on C₁₉Si (bowl, two-fold) at hexa position with 0.0814 a.u. and 0.358 a.u. change of the energy is stronger than C₁₉Si (bowl) at penta position and C₁₉Si (bowl, hexa three-fold), respectively. The adsorption energy, E_{ads}, is calculated using eq. (1). By definition, E_{ads} < 0 corresponds with more stability and exothermic chemical bonding and E_{ads} > 0 corresponds with endothermic chemical bonding. These energies show that the interaction between the H₂ molecule and C₁₉Si hexa, two-fold) is stronger than other interactions, Table 1.

2. NBO Analysis: The natural bond orbital (NBO) analysis were performed at the B3LYP/6-31++G** level using Gaussian 03. Using NBO analysis, HOMO-LUMO gaps, HLG (eq. (2)), electronic chemical potential (eq. (3)) and hardness (eq. (4)) are obtained [14].

The electronic chemical potential and hardness are defined as the following first-order [15, 16] and second-order [17, 18] derivatives, by (eq. (5)) and (eq. (6)) respectively.

$$E_{\text{ads}} = E_{\text{(structure, H}_2\text{)}} - (E_{\text{structure}} + E_{\text{H}_2}) \quad (1)$$

$$\text{HLG} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (2)$$

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2 \quad (3)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (4)$$

$$\mu = - \left(\frac{\partial E}{\partial n} \right) \quad (5)$$

$$\eta = 1/2 (\partial^2 E / \partial N^2) \quad (6)$$

Table 1 presents the results of NBO analysis obtained by the DFT calculations. The energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), known as the HOMO–LUMO gap or simply HLG, is a critical parameter in determining molecular electrical transport properties,

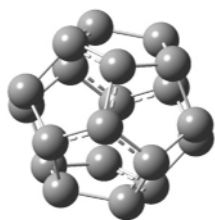


Fig. 1. C₂₀ (cage).

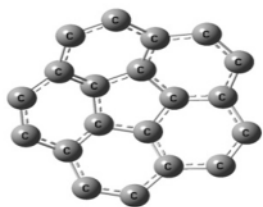


Fig. 2. C₂₀ bowl.

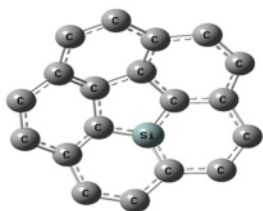


Fig. 3. C₁₉Si (bowl, penta).

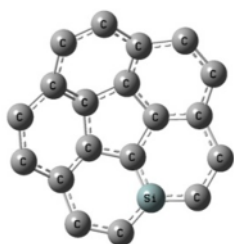


Fig. 4. C₁₉Si (bowl, hexa, three-fold).

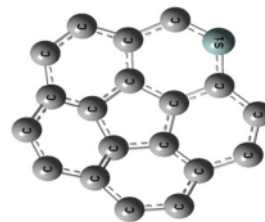


Fig. 5. C₁₉Si (bowl, hexa, two-fold).

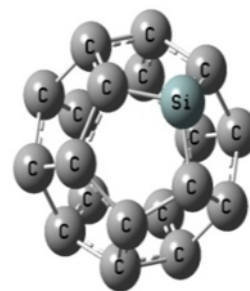


Fig. 6. C₁₉Si cage.

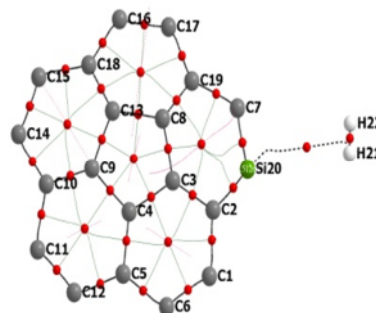


Fig. 7. H₂ interaction with C₁₉Si (bowl, hexa, two-fold).

because it is a measure of electron conductivity. The energy gaps were determined by simply taking the differences in energy between HOMO and LUMO energy levels, (eq. (2)).

The gap energies of the bowl shapes decrease after adsorption, but these gaps increase for cage shapes. Since HLG is a measure of electrical conductivity, i.e. the decreasing trend in the HLG value means that electrical conductivity increases when the Hydrogen is adsorbed. After adsorption, the change of HLG (HLG fullerene +H₂ –HLG fullerene), change of

electronic chemical potential ($\mu_{\text{fullerene}+\text{H}_2} - \mu_{\text{fullerene}}$), and change of hardness ($\eta_{\text{fullerene}+\text{H}_2} - \eta_{\text{fullerene}}$), due to the polarization interaction between the charged Si atom and H₂ molecule at C₁₉Si (hexa, two- fold) is stronger than other Hydrogen interactions. The gap energy of the C₁₉Si (hexa, two- fold) after hydrogen adsorption, decreased from 88.621 kcal/mol to 81.462 kcal/mol, with ΔHLG equal to -7.159 kcal/mol. Therefore expected value of gap between valence and conduction band is shorter than other structures, so it indicates a maximum conduction in this structure.

Also the values for gap energy and hardness for all of the fullerene structures are smaller than the H₂ molecule (HLG for H₂ is 298.69 kcal/mol and η is 149.345 kcal/mol); these lead fullerene structures have higher polarizability than the H₂ molecule. Thus fullerene structures could accept electron from H₂. When hydrogen adsorbs on structures, electronic chemical potentials of C₁₉Si (hexa, two- fold) will be decrease from -93.792 to -89.230 kcal/mol, with maximum of $\Delta\mu$ (4.518 kcal/mol), which is related to the highest stability of C₁₉Si (hexa, two- fold), with H₂ system. The value of hardness for fullerene-H₂ is differing from the individual fullerene and H₂ molecule. The hardness of the C₁₉Si (hexa, two- fold), with H₂ system was decreased ($\Delta\eta = -3.5767$ kcal/mol), this means that, the hardness of the fullerene is larger than the fullerene-H₂ system, and we can predict that the fullerene is relatively more stable and a physisorption process is dominant. So, in this system it shows, the H-H bond length expands slightly from 0.74252 Å to 0.74375 Å, (Table1).

3. AIM Analysis: The quantum theory of atoms in molecules (QTAIM) [19] (developed by Professor Richard F. W. Bader and his coworkers), relies on quantum observables such as the electron

density $\rho(r)$ and energy densities. A substantial aspect of Bader's theory of atoms in molecules (AIM; Bader, 1994) is the partitioning of a molecule into submolecular or even atomic regions [20, 21]. There is one BCP between each pair of atoms that are bonded, i.e., two atoms linked by a bond path and sharing a common interatomic zero-flux surface. In addition to the set of trajectories which terminate at the BCP and define an interatomic surface, a pair of trajectories originates at the BCP with each member of the pair terminating at one of the nuclei of the chemically bonded atoms. Chemical bonding interactions are characterized and classified according to the properties of the electron and energy densities at the BCP, collectively known as "bond properties". The Electron Density at the BCP (ρ_b) has been shown to be strongly correlated with the binding energy for several types of bonding interaction [22, 23]. Because the Laplacian is essentially a second derivative, its sign indicates regions of local electronic charge concentration or depletion with respect to the immediate neighborhood. Thus, where $\nabla^2\rho(r) > 0$ the density is locally depleted and expanded relative to its average distribution; where $\nabla^2\rho(r) < 0$ the density is locally concentrated, tightly bound, and compressed relative to its average distribution. The Laplacian of the electron density at the BCP ($\nabla^2\rho_b$) in covalent bonding is negative, $\nabla^2\rho_b < 0$. In contrast, in closed-shell bonding, for example ionic, hydrogen-bonding or van der Waals interactions, the interaction is characterized by a depletion of density in the region of contact of the two atoms and $\nabla^2\rho_b > 0$ [24]. A quantitative comparison of the covalent bond strength can be given in terms of the bond topological properties. Table 2 presents the results for the values of the charge density, the Laplacian at the

bond critical points, change of atom's charge (Δq) and change of kinetic energy of atom (Δk) obtained by the B3LYP/6-31++G** method. At all of the molecules the values of $\nabla^2\rho_b$ for adsorbent atom from fullerene structures and H from H₂ molecule at the adsorption site are positive, and that the bond character is physisorption with van der Waals

interactions. The results obtained also showed large charge transfer from the H₂ to Si atom at the C₁₉Si (hexa, two- fold), so that change of Si charge is -0.13132 a.u., and the most decrease of kinetic energy of Si at this system to predict a strong interaction of H₂ with C₁₉Si (hexa, two- fold), (Fig.8).

Table 1. Energy of structures, adsorption energy, bond length, ΔHLG , μ & $\Delta\mu$ and η & $\Delta\eta$ for systems.

Structure	E /a.u.	E _{ads} / kcal.mol ⁻¹	¹ Bond length H-H /Å	ΔHLG / kcal.mol ⁻¹	μ / kcal.mol ⁻¹	$\Delta\mu$ / kcal.mol ⁻¹	η / kcal.mol ⁻¹	$\Delta\eta$ / kcal.mol ⁻¹
C ₂₀ cage	-761.4678		-		-105.125		21.805	
C ₂₀ cage,H ₂	-762.6462	+0.313	0.74336	0.0188	-105.206	-0.0627	21.818	0.00941
C ₁₉ Si cage	-1012.914		-		-94.457		8.869	
C ₁₉ Si cage,H ₂	-1014.0920	+0.564	0.74344	1.7507	-93.290	0.6275	9.745	0.8753
C ₂₀ bowl	-768.1884		-		-94.463		49.873	
C ₂₀ bowl,H ₂	-769.3490	-0.188	0.74362	0.9977	-94.903	-0.4392	49.377	-0.4957
C ₁₉ Si penta	-1019.4816		-		-99.960		33.201	
C ₁₉ Si penta,H ₂	-1020.6605	0.000	0.74370	0.01255	-99.910	0.0502	33.194	-0.00627
C ₁₉ Si hexa, three-fold	-1019.2049		-		-95.208		42.054	
C ₁₉ Si,H ₂ hexa, three-fold	-1020.3837	+0.062	0.74369	0.8602	-94.602	0.6067	43.774	1.7204
C ₁₉ Si hexa, two-fold	-1019.5619		-		-93.792		44.307	
C ₁₉ Si,H ₂ hexa, two-fold	-1020.7419	-0.690	0.74375	-7.1535	-89.230	4.518	40.724	-3.5767

Table 2. The Electron Density, Laplacian of the Electron Density at the BCP, (Δq) and Δk obtained by AIM analysis for systems.

structure	Connected atoms	ρ	$\nabla^2\rho$	¹ Δq	² Δk /a.u.
C ₂₀ cage, H ₂	C ₁₆ -H ₂₁	0.00341	+0.00956	C ₁₆ = 0.00836	C ₁₆ =0.0114
	H ₂₁ -H ₂₂	0.26753	-1.3362		
C ₂₀ ,H ₂ bowl, penta	C ₁₄ -H ₃₁	0.00006	+0.0002	C ₁₄ = -0.00062	C ₁₄ = -0.0014
	H ₃₁ -H ₃₂	0.26717	-1.33484		
C ₂₀ , H ₂ bowl, hexa, two-fold	C ₁₈ -H ₃₂	0.00176	+0.00548	C ₁₈ = -0.00112	C ₁₈ = -0.0040
	H ₃₁ -H ₃₂	0.26749	-1.337745		
C ₁₉ Si cage, H ₂	Si ₂₀ -H ₂₂	0.02642	+0.014	Si ₂₀ = -0.00332	Si ₂₀ = -0.0216
	H ₂₁ -H ₂₂	0.26977	-1.47908		
C ₁₉ Si, H ₂ penta	Si ₃₀ -H ₃₁	0.00723	+0.01824	Si ₃₀ = 0.02738	Si ₃₀ = -0.0080
	H ₃₁ -H ₃₂	0.26891	-1.35104		
C ₁₉ Si, H ₂ hexa, two- fold	Si ₃₀ -H ₃₁	0.0071659	+0.0182	Si ₃₀ = -0.13132	Si ₃₀ = -1.2577
	H ₃₁ -H ₃₂	0.265399	-1.30429		

¹: $\Delta q = q$ atom after adsorption - q atom before adsorption

²: $\Delta k = k$ atom after adsorption - k atom before adsorption

CONCLUSIONS

In this research, we compared the effect of H₂ molecule adsorption on the electronic properties of the different structures of C₂₀ (cage), C₂₀ (bowl), C₁₉Si (bowl, penta), C₁₉Si (bowl, hexa three- fold) and C₁₉Si (bowl, hexa two- fold) at the level of B3LYP/6-31++G** DFT calculations by Gaussian 03. Our results show that C₂₀ (bowl), with H₂ system is more stable than the cage form by 6.7 a.u. in total energy. The (C₁₉Si hexa two- fold, with H₂) system is more stable than (C₂₀_{cage}, with H₂), (C₂₀, (bowl), with H₂) and (C₁₉ Si (penta), with H₂) systems by 258.09, 251.39 and 0.1 a.u., respectively. In order to obtain the effects of the Hydrogen on the structures, NBO analysis was operated. By NBO analysis, HOMO-LUMO gaps, electronic chemical potential and hardness are obtained. NBO calculations essentially show significant change in the properties of C₁₉Si (hexa two- fold) when H₂ molecule approach to this structure. In addition, the topological analysis of electronic density distribution in the theory of AIMs was used to compute some other molecular properties. The results of ΔHLG , $\Delta\mu$, $\Delta\eta$ and energy densities at the BCP indicate that hydrogen molecule binds molecularly to structures with a Van der Waals interaction and Si atom substitution in hexa two- fold position provides suitable condition for hydrogen molecule adsorption.

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