Theoretical Investigation of Inner and Outer Surface Interaction of H₂ and Cl₂ Adsorption with C20 (cage) Fullerene

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In this research, the structure of C20 cage fullerene which has carbon-bound to H2 atoms is designed and quantum computations is conducted through using density function theory (DFT) at the level of B3LYP and basis set of 6-31G. By modeling the structure of H2@ C20, H2 adsorption on the H2@C20 surface at angles of 90 and 180 degrees is the appropriate optimized location for adsorption. To study the type of gas interaction with surface, and changes of electronic properties of fullerenes, the AIM calculations are performed. Therefore, the results show that the binding power of exterior hydrogen (H23-H24) is stronger than interior hydrogen (H21-H22) in H2@C20, H2@C20-H2-90°, H2@C20 -H2-180° molecules. Also, the results are obtained from the chlorine adsorption in the surface structure of H2@C20-H2-180° molecules. Also, the compared with H2. The results about chlorine show that the joint power of exterior chlorine is stronger than interior hydrogen in the H2@C20-H2-90° and H2@C20-H2-180° molecules. Also, the comparison of the joint power of exterior chlorine for these molecules shows that the binding power of H2@C20-H2-90° is stronger than H2@C20-H2-180° molecules.

Keywords: Fullerene, Adsorption, Density Function Theory, Hydrogen Storage, AIM Calculations. .

In recent years, many studies have been done under the umbrella of nanotechnology and its applications especially in storing gases which deal with much attention over the nanostructures. At first, nanostructures were the center of focus such as carbon nano-tubes, carbon fullerene and etc¹⁻⁶. In this regard, this study has been done based on the consideration of specific specifications of fullerene such as high temperature resistance, non-conductive, structural stability, and nanocage combinations. C20 can form the basic cage fullerene. This fullerene is ranged more and consists of compact and unsaturated pentagons, so it is very reactive. Due to small size of C20, its ratio of surface is larger than its volume. As a result, formation of C20 (cage) has a larger density in contrast to C60⁷. H2 as a fuel resource of cars is one of the discussing issues on the table. In this case, to find a carrier and storage for H2 seems important. Compactness and lightweight volume is one of carrier's major features.

Today, many researchers have thought of the applications of H2 because it becomes more replacement source for conventional fuels. H2 is a promising source for providing energy in future fuels because it can be used in fuel cells. Tiny molecules of H2 are leaking from apertures, gaps, links and valves so fast and can become vapor so soon. Overcoming this problem plays an important

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role in maintaining the safety of a device because the droplets of H2 evaporate soon and distribute in the environment so that the device's safety is in danger. Although H2 is a denser liquid and the storage seems easy in there, this storage can carry some difficulties. Some developed systems for H2 storing are such as compressed H2, liquid H2, and chemical bonds between H2 and a storage substance (e.g. metal hydrides). As no appropriate transportation and distribution system exists for H2 up to now, its capability in re-producing from various sets of sources and its clean-burning make it be a proper substitute replacement.

The first theoretical study in the case of C60 formation is done by Hokel⁸. These results have been revised 9. In 1980, an article has been published talking about a graph theory for finding a simplified algebraic solution in order to calculate molecules orbital of C6010 and suggested consequently this molecule and processes like 3-D aromaticity. Some similar results are also obtained 11. About fullerenes, an interesting aspect is that they can put various atoms and molecules inside their interior area. There are two kinds of endohedral fullerene. In the first case, the guest atom is in the center of carbon hole. The resistance factor in there is electrostatic interactions. In the second case, the resistance of fullerene endohedral takes its shape from the guest atom's covalence bond linking with carbon skeleton.

Fullerene power is distinguish in trapping the atoms of lanthanides and isolated mass spectrums of endohedral complexes of La@C60 and La2@C60 are emerged ¹². To form fullerenes and endohedrals is a so hard process and they can just become isolated from little values than milligrams. Therefore, theoretical studies seem essential on these combinations. At first, most of the works are focused on heavy metal fullerene complexes ¹³⁻²⁰.

In the theoretical study of endohedral fullerenes, a significant point is to predict them with the noble gases before initial empirical discovering ²³⁻²¹. According to calculations, the guest atoms in Ne@C60, the complex is located in the center of the cage carbon, and complex is unstable than some isolated compounds. They proposed the most probable mechanism of cage trapping atoms involved in the reversible dissociation of one or a number of carbon-carbon bonds against guest

atoms of the cage fullerene ²⁴. The molecular mechanisms are used in the study of molecular interactions between fullerene C70 and noble gas atoms ²⁵. The study of construction of some small fullerenes (C50, C40, C36, C32, C28, C24, C20) and He's complexes are performed with the method of ((B3LYP/6-31G (d)) ²⁶. Therefore, to detect spherical- based electron, independent nucleus chemical shifts (NICS) are calculated at the center of the cage carbon. The possibility of fixing the complexes of small endohedral fullerenes (C60, C50, C40, C32, C30, C24, and C20) has been studied with noble gases Ar, Ne, He ²⁷.

As storage of hydrogen is important, and chlorine is a pollutant, toxic and dangerous gas, in this respect the adsorption of these two gases is studied.

Quantum Computing

Recently, density function theory (DFT) is used to study the interaction of gases and fullerene ²⁸. In this paper, all calculations are conducted by the software set of GAUSSIAN03W ²⁹. The geometry structure optimization for all compounds in the gas phase has been performed at the B3LYP computational level, and also at the 6-31G standard basis set³⁰.

After obtaining the most stable geometry compounds, to investigate adsorption and storage properties of the gas, we analyze the appropriate location for hydrogen and chlorine adsorption in the 90° and 180° degree angles. We have analyzed the structures of H2@C20, H2@C20-H2-90°, H2@C20-H2-180°, H2@C20-Cl2-90° and H2@ C20-Cl2-180° in the gas phase. Also, to study the type of gas interaction with level and with changes in the electronic properties of fullerene, atoms in molecules computations (AIM) is performed on each of the structures. The AIM theory calculations were performed by AIM2000, software package ³¹.

RESULTS AND DISCUSSION

Structure optimization

The structures of optimized geometry are given for H2@C20, H2@C20-H2-90°, H2@C20-H2-180°, H2@C20-C12-90° and H2@C20-C12-180° by using B3LYP/6-31G method, respectively in figures 1 to 5. For all the interactions, the total energy values are given in Table 1. Negative value of energy indicates the occurrence of absorption in the range of physical adsorption. In each of the five structures (Figs.1 -5), the most stable location for H2 and Cl2 is shown relative to the adsorbing species. The most energy is released in adsorbed angle of 180° . While the angle is 90° , the energy released is lower. Based on the values in Table 1, it can be claimed that the angle of half-page interaction causes increase in the stability in that the structure of H2@C20-H2-180 is 0.317 kcal/mol

times more stable than H2@C20-H2-90°. Similarly, for the Cl2 adsorption, the structure of H2@C20-Cl2-180° is 68.347 kcal/mol times more stable than H2@C20-Cl2-90°. Table 1 shows the value of relative energy in which chlorine adsorption is highly desirable than hydrogen adsorption.

Table 2 shows that after optimizing the energy, H2 bond length is reduced. Table 3 has completely shows the comparison of the effective

Structure	E/a.u.	E/Kcal.mol-1	E. rel / Kcal.mol-1
$\begin{array}{c} H_2@C_{20} \\ H_2@C_{20}-H_2-90^{\circ} \\ H_2@C_{20}-H_2-180^{\circ} \\ H_2@C_{20}-CI_2-90^{\circ} \\ H_2@C_{20}-CI_2-90^{\circ} \\ H_2@C_{20}-CI_2-180^{\circ} \end{array}$	-762.1781167 -763.3537607 -763.3542664 -1682.418998 -1682.527915	-478274.0089 -479011.7367 -479012.054 -1055733.904 -1055802.25	0 737.727779 738.04511 577459.895 577528.242

Table 1. Values of total energy for all interactions

 Table 2. Comparison of Bond Length

 before and after Interaction for H2@C20

H2AC20	H21-H22 before Opt	H21-H22 after Opt
Length bond	0.744	0.665

Table 3. Comparison of Bond Length before and after Interaction at 90° and 180°

H ₂ @C ₂₀ -H ₂ -90°	H ₂₁ -H ₂₂ B.O	H ₂₁ -H ₂₂ A.O	H ₂₃ -H ₂₄ B.O	H ₂₃ -H ₂₄ A.O	H ₂₃ -C ₈ B.O	H ₂₃ -C ₈ A.O
	0.744	0.665	0.6	0.742	3.059	3.896
H ₂ @C ₂₀ -H ₂ -180°	H ₂₁ -H ₂₂ B.O	H ₂₁ -H ₂₂ A.O	H ₂₃ -H ₂₄ B.O	H ₂₃ -H ₂₄ A.O	H ₂₃ -C ₁₄ B.O	H ₂₃ -C ₁₄ A.O
2 20 2	0.744	0.665	0.743	0.742	2.976	3.635
H ₂ @C ₂₀ -Cl ₂ -90°	H ₂₁ -H ₂₂ B.O	H ₂₁ -H ₂₂ A.O	Cl ₂₃ -Cl ₂₄ B.O	Cl ₂₃ -Cl ₂₄ A.O	Cl ₂₄ -C ₃ B.O	Cl ₂₄ -C ₃ A.O
2 20 2	0.744	0.744	2.2	2.2	2.826	2.826
$H_{2}@C_{20}-Cl_{2}-180^{\circ}$	H ₂₁ -H ₂₂ B.O	H ₂₁ -H ₂₂ A.O	Cl ₂₂ -Cl ₂₄ B.O	Cl ₂₂ -Cl ₂₄ A.O	Cl ₂₄ -C ₁₇ B.O	$Cl_{24}-C_{17}A.O$
2 - 20 2	0.744	0.668	1.953	2.701	2.865	1.948

Table 4. Output I diameters of Anyi Calculations for 112(0,02	Table 4.	Output	Parameters	of AIM	Calculations	for	H2(a)C2(
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BCP	Atoms	Rho	DelSqRho	Bond Ellipticity	G	V	Hb
1	H ₂₁ -H ₂₂	0.349	-1.92	0.002	0.018	-0.517	-0.499
2	$C_{16}^{21}-H_{21}^{22}$	0.039	0.182	1.85	0.046	-0.047	-0.001
3	$C_{18}^{10}-H_{21}^{21}$	0.055	0.194	0.432	0.059	-0.069	-0.01
4	$C_{0}^{10}-H_{21}^{21}$	0.042	0.186	15.671	0.049	-0.051	-0.002
5	$C_{7} - H_{21}^{21}$	0.039	0.182	1.022	0.046	-0.047	-0.001
6	$C_{6}^{'}-H_{22}^{21}$	0.039	0.181	0.699	0.046	-0.046	0
7	$C_{1}^{0}-H_{22}^{22}$	0.055	0.193	0.508	0.058	-0.068	-0.01
8	$C_{4}^{1}-H_{22}^{22}$	0.051	0.193	9.771	0.055	-0.062	-0.007
9	$C_{15}^{4}-H_{22}^{22}$	0.039	0.181	0.539	0.046	-0.047	-0.001
10	$C_{20}^{13}-H_{22}^{22}$	0.043	0.188	9.333	0.05	-0.052	-0.002

bond lengths within and outside the C20 (cage) fullerene before and after optimization in that the bond length is reduced after optimization. For $H2@C20-90^\circ$, bond length of interior hydrogen

decreases after optimization, bond length of exterior hydrogen increases, and the distance of exterior hydrogen from fullerene surface increased, whereas through same interaction for H2@C20-

BCP	Atoms	Rho	DelSqRho	Bond Ellipticity	G G	V	Hb
1	C ₇ -H ₂₁	0.039	0.181	1.636	0.045	-0.046	-0.001
2	C18-H21	0.053	0.191	0.611	0.057	-0.066	-0.009
3	$C_{10}^{10}-H_{21}^{21}$	0.052	0.191	1.978	0.056	-0.064	-0.008
4	$C_{14}^{10}-H_{21}^{21}$	0.051	0.192	2.657	0.055	-0.063	-0.008
5	$C_{16}^{14}-H_{21}^{21}$	0.039	0.182	1.168	0.046	-0.047	-0.001
6	$C_4 - H_{22}^{21}$	0.051	0.193	2.843	0.056	-0.063	-0.007
7	$C_{5}^{-}-H_{22}^{22}$	0.052	0.193	2.191	0.056	-0.064	-0.008
8	C1-H22	0.053	0.193	0.608	0.057	-0.066	-0.009
9	$C_{4}^{1}-H_{22}^{22}$	0.039	0.182	1.62	0.046	-0.046	0
10	$C_{15}^{0}-H_{22}^{22}$	0.039	0.182	1.7	0.046	-0.046	0
11	H ₂₁ -H ₂₂	0.349	-1.92	0.002	0.018	-0.517	-0.499
12	H ₂₂ -H ₂₄	0.246	-1.066	0.000006	0.000004	-0.266	-0.265996
13	$C_{8}^{23}-H_{23}^{24}$	0.0009	0.003	2.169	0.0006	-0.0003	0.0003

 Table 5. Output Parameters of AIM Calculations for H2@C20-H2-90°

Table 6. Output Parameters of AIM Calculations for H2@C20-H2-180°

BCP	Atoms	Rho	DelSqRho	Bond Ellipticit	y G	V	Hb
1	H ₂₁ -H ₂₂	0.349	1.918	0.002	0.018	-0.0517	-0.499
2	H ₂₃ -H ₂₄	0.246	1.065	0.000001	0.000003	-0.0266	-0.26597
3	$C_{17}^{23}-H_{23}^{23}$	0.001	0.005	0.493	0.0009	-0.0005	-0.0004
4	$C_{10}^{1}-H_{21}^{2}$	0.052	0.192	1.516	0.056	-0.064	-0.008
5	C ₁₄ -H ₂₁	0.052	0.191	1.174	0.056	-0.064	-0.008
6	C ₁₈ -H ₂₁	0.051	0191	0.724	0.056	-0.064	-0.008
7	C ₇ -H ₂₁	0.039	0.182	2.144	0.046	-0.046	0
8	$C_{19} - H_{21}$	0.043	0.2	1.555	0.052	-0.054	-0.002
9	C4-H22	0.052	0.193	1.125	0.056	-0.065	-0.009
10	C ₅ -H ₂₂	0.053	0.193	1.376	0.056	-0.065	-0.009
11	C ₁ -H ₂₂	0.052	0.192	0.803	0.056	-0.064	-0.008
12	C ₆ -H ₂₂	0.039	0.182	8.56	0.045	-0.046	-0.001
13	$C_{15} - H_{22}$	0.039	0.182	1.355	0.046	-0.0467	-0.0007

Table 7. Output Parameters of AIM Calculations for H2@C20-Cl2-90°

ВСР	Atoms	Rho	DelSqRho	Bond Ellipticity	G	V	Hb
1	H ₂₁ -H ₂₂	0.293	-0.833	0.004	0.027	-0.263	-0.236
2	$Cl_{23}^{2}-Cl_{24}^{2}$	0.082	0.084	0.005	0.039	-0.056	-0.017
3	$C_{18}^{25}-H_{21}^{24}$	0.044	0.174	0.639	0.05	-0.056	-0.006
4	$C_{19}^{10}-H_{21}^{21}$	0.045	0.173	0.03	0.048	-0.052	-0.004
5	C ₁₃ -H ₂₁	0.057	0.234	4.10009	0.066	-0.074	-0.008
6	$C_{7}^{-}H_{21}^{-}$	0.043	0.167	2.603	0.046	-0.05	-0.004
7	$C_3 - Cl_{23}$	0.018	0.064	3.585	0.015	-0.014	-0.001
8	$C_{3} - Cl_{24}$	0.02	0.066	0.26	0.015	-0.014	-0.001
9	C ₁ -H ₂₂	0.113	0.197	0.347	0.11	-0.17	-0.06

BCP	Atoms	Rho	DelSqRho	Bond Ellipticity	G	V	Hb
1	H ₂₁ -H ₂₂	0.337	-0.169	0.001	0.016	-0.324	-0.308
2	$Cl_{22}^{21}-Cl_{24}^{22}$	0.033	0.095	0.008	0.023	-0.022	-0.001
3	C_{17}^{25} - Cl_{24}^{24}	0.118	0.058	0.002	0.059	-0.104	-0.045
4	$C_{18}^{17}-H_{21}^{24}$	0.057	0.185	0.407	0.059	-0.072	-0.013
5	$C_{16}^{10}-H_{21}^{21}$	0.049	0.18	0.288	0.052	-0.06	-0.008
6	$C_{14}^{10}-H_{21}^{21}$	0.055	0.183	0.45	0.057	-0.068	-0.011
7	$C_{6}^{14}-H_{22}^{21}$	0.05	0.187	3.714	0.054	-0.063	-0.009
8	C ₉ -H ₂₂	0.046	0.194	2.611	0.052	-0.055	-0.003
9	C1-H22	0.057	0.19	0.484	0.06	-0.073	-0.013
10	C ₃ -H ₂₂	0.056	0.203	0.748	0.063	-0.075	-0.012
11	$C_{5}^{3}-H_{22}^{22}$	0.051	0.192	0.714	0.055	-0.063	-0.008
12	$C_4 - H_{22}^{22}$	0.054	0.196	0.169	0.06	-0.071	-0.011

 Table 8. Output Parameters of AIM Calculations for H2@C20-Cl2-180°

180°, bond length of interior hydrogen increases after optimization, bond length of exterior H2 does not change, and the distance of exterior hydrogen from fullerene surface increased. When Cl2 adsorption is issue, for 90° the bond length of interior H2 after optimization, bond length of exterior Cl2, and distance of Cl2 from fullerene surface all become constant. For 180°, bond length of interior hydrogen decreases after optimization, bond length of exterior hydrogen increases, and the distance of exterior hydrogen from fullerene surface decreased. After comparison of H2@ C20-H2-180° with H2@C20-Cl2-180°, we can observe the effect of adsorbed chlorine (in outside of cage) on the bond between interior hydrogen. Bond length in interior H2 becomes longer in the presence of Cl2 because fullerene electron density becomes involved in electronegative chlorine groups.

AIM Analysis

AIM model is the only known model which does not depend on the solution of Schrödinger equation and can represent the molecular structure independently with the assistance of electron charge distribution. Symbolically, the main concepts of the AIM are given in Figure 6 such as bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP).

AIM analysis of the optimized geometry by B3LYP/6-31G method is given in figures 7 to 10 for H2@C20, H2@C20-H2-90°, H2@C20-H2-180°, H2@C20-Cl2-90° and H2@C20-Cl2-180°, respectively. The total energy values are given in Tables 4 to 8 for all of these interactions.

Since BCP indicates that there is a chemical bond

between each pair of nucleuses, we classify the types of chemical bonds due to the mathematical properties of this particular point.

Overall, ρb , $\nabla^2 \rho b$ and \pounds are mathematic coordinates of BCP

BCP values which show the charge focus on electron density is negative in (shared) covalence joints, i.e. electron charge is located in the area of two nucleuses and is shared the electron charge between these nucleuses. In covalence joints the value of Áb is about 1-10 a.u. the quantity in closed shell joints which are related to the ionic bonding, hydrogen bonding, Van-der-Waals binding and link of ideal gases in gas clusters is positive and the numerical value for Áb is about 2-10 a.u. Therefore, the results for the structure of H2@C20 is Van-der-Waals for C16-H21, C18-H21, C9-H21, C7-H21, C6-H22, C1-H22, C4-H22, C15-H22, C20-H22 joints, and covalence for H21-H22.

For H2@C20-H2-90°, the results are Van-der-Waals for joints of C7-H21, C18-H21, C10-H21, C14-H21, C16-H21, C4-H22, C5-H22, C1-H22, C6-H22, C15-H22, C8-H23, and nonpolar covalent bonding for H21-H22, H23-H24.

For H2@C20-H2-180°, the results are Van-der-Waals for joints of C17-H23, C10-H21, C14H21, C18-H21, C7-H21, C19-H21, C4-H22, C5-H22, C1-H22, C6-H22, C15-H22, and covalence for H21-H22, H23-H24 joints. For H2@C20-Cl2-90°, results are Van-der-Waals for Cl23-Cl24, C18-H21, C19-H21, C13-H21, C7-H21, C3-Cl23, C3-Cl24, C1-H22 joints, and covalence for H21-H22 binding. Finally, the results are Van-der-Waals for H2@C20-Cl2-180° in the joints



Fig. 1. The structures of optimized geometry of H2@C20 by Method of B3LYP/3-31G



Fig. 3. The structures of optimized geometry of H2@ C20-H2-180° by Method of B3LYP/6-31G



Fig. 5. The structures of optimized geometry of H2@ C20-Cl2-180° by Method of B3LYP/6-31G

Fig. 2. The structures of optimized geometry of H2@ C20-H2-90° by Method of B3LYP/6-31G



Fig. 4. The structures of optimized geometry of H2@ C20-Cl2-90° by Method of B3LYP/6-31G



Fig. 6. Schematic Interaction in AIM Model

of Cl23-Cl24, C17-Cl24, C18-H21, C16-H21, C14-H21, C6-H22, C9-H22, C1-H22, C3-H22, C5-H22, C4-H22, and covalence for H21-H22 joint.

For H2@ 20, the average of G and V is equal for inter bindings H21 and H22 from carbon fullerenes, so the power of connections is the same for interior fullerene with interior



Fig. 7. AIM Analysis of H2@C20 by B3LYP/6-31G Method



Fig. 8. AIM Analysis of H2@C20-H2-90° by B3LYP/6-31G Method



Fig. 9. AIM Analysis of H2@C20-H2-180° by B3LYP/6-31G Method



Fig. 11. AIM Analysis of H2@C20-Cl2-180° by B3LYP/6-31G Method



Fig. 10. AIM Analysis of H2@C20-Cl2-90° by B3LYP/6-31G Method

hydrogen. For H2@C20-H2-90°, the numerical V-value in the joint of C8-H23 is more negative than C-H interior joints, and the power of interior H2 is weaker than of exterior H2. The G-value for exterior fullerene is the smallest with 0.0006, therefore we can overlook the G minimum-value effect for C8-H23 joint. For H2@C20-H2-180°, numerical value of V in C17-H23 joints is more negative than interior C-H, therefore the binding power of interior H2 is weaker than of exterior H2. The G-value is the smallest value for C3-Cl24 joint. For H2@C20-Cl2-90°, the values of G and V in c3-Cl24 joint for exterior fullerene are smaller and more negative than interior joints, therefore joint power of C3-Cl24 is stronger than interior joints. For H2@C20-Cl2-180°, the values of G and V in interior joints are smaller and more negative than Cl7-Cl24 exterior joint, therefore interior joint power is stronger than this molecule.

Bond Ellipticity results show the elliptical condensation of super electron in central bond of atomic joints (indicating the condensation of electron density in single, double and triple bonds). The elliptical value of interior H-H joints in H2@ C20 is 0.002, of interior H-H joints in H2@C20-H2-90° is 0.002, of interior H-H joints in H2@C20-H2-180° is 0.002, of exterior H-H is 0.000, of interior H-H joints in H2@C20-C12-90° is 0.004, and of interior H-H joints in H2@C20-C12 is 0.001. The elliptical value of C-H bond in H2@C20-H2-180° is 0.493, of Cl-Cl and Cl-C in H2@C20-C12-90° are respectively 0.005 and 0.260, and in H2@C20-C12-180° are respectively 0.008 and 0.002 in computational B3LYP/6-31G.

CONCLUSION

Using computational chemistry, adsorption and storage of hydrogen and chlorine gases are investigated on adsorbent bed and fullerene nanostructures. Indexes such as bond length, the structure's total energy, bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP) are calculated. Since the aim in adsorbing hydrogen on the surface of various adsorbents is to use it as fuel, therefore desorption process should be easily and efficiently done in that the amount of energy has to be little. In general, the adsorption of chloride is higher than of hydrogen over fullerene. The comparison of joint power of exterior chlorines shows that the binding power of H2@C20-Cl2-180° is stronger than the joint power of H2@C20-Cl2-90°.

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