Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 8, No. 4, 657-669, December 2020
DOI: 10.22036/pcr.2020.227279.1759

A DFT Study on Adsorption of Alanine on Pristine, Functionalized and Boron and/or Nitrogen Doped Functionalized C_{60} Fullerenes

H. Dashti Khavidaki* and M. Soleymani
Department of Chemistry, Faculty of Basic Science, Ayatollah Boroujerdi University, Boroujerd, Iran

(Received 16 April 2020, Accepted 2 July 2020)

In this study, the adsorption of alanine on pristine, functionalized, and boron and/or nitrogen doped functionalized C_{60} fullerenes was studied by theoretical methods. The structures of alanine, C_{60} fullerenes derivatives and complexes (C_{60}-alanine) were optimized at the M062X/6-31G* level of theory. Then, the adsorption energies, global DFT reactivity indices, the atomic charges and the global electron density transfer (GEDT) were calculated. The results showed that the maximum adsorption energy occurs for the adsorption of alanine on C_{60}H-OH derivatives in both gaseous and aqueous phases. In addition, the doping of three nitrogen/boron atoms with the functionalized carbon atom in C_{60}H-OH increases the adsorption energy significantly. The results were confirmed by global DFT reactivity indices such as chemical potential and electrophilicity indices. In addition, analysis of the GEDT values showed that the charge transfer occurs from alanine toward C_{60}H-OH fullerene in both phases upon adsorption. The AIM results indicated that the interaction between alanine and C_{60}H-OH in both gaseous and aqueous phases is non-covalent and hydrogen bonding in nature.

Keywords: Alanine, C_{60} fullerene, Functionalized C_{60} fullerenes, Doped functionalized C_{60} fullerenes

INTTRODUCTION

Proteins are the living polymers catalyzing most of the reactions in living cells, and also, they control practically all cellular processes. They have made up of building blocks called amino acids. Amino acids contain both carboxyl and amino groups whose carboxyl group is more acidic than the carboxylic acid. The biological activity of the proteins is determined through the chemical properties of the amino acids [1,2].

Based on the molecular structure, alanine or 2-aminopropanoic acid (Ala or A) is one of the simplest amino acids and is classified as an aliphatic amino acid. Its chemical formula is $HOOCCH(NH_2)CH_3$, with the molar mass of 89.09 g mol^{-1} and the density of 1.424 g cm^{-3}. The non-reactive methyl group in alanine almost never directly participates in protein function. It can be produced by the human body and it is not necessary to enter the body through the diet. Anyway, alanine is found in a wide variety of foods especially meats and it can compensate for its deficiency in the body. It boosts the immune system by producing antibodies, and provides the required energy for muscles tissues, brain, and the central nervous system [1,2].

C_{60} fullerene is an interesting adsorbent that has been used to the adsorption of many compounds. It is the first example of a spherical aromatic molecule, but it is more similar to reactive alkene molecules than aromatic systems with respect to the chemical properties [3]. C_{60} as an electron-deficient alkene exhibits a significant variety of thermal and photochemical reactions [4-7]. The low solubility of fullerenes in common organic solvents restricts the preparation of their derivatives in the solutions. Therefore, it has been explored alternative synthetic methods for fullerene functionalization such as solvent-free mechanochemical reactions [8,9].

The adsorption of some amino acids by pristine fullerenes, C_{60} and C_{80}, has been investigated using a

---

*Corresponding author. E-mail: dashti@abru.ac.ir computer simulation and theoretical calculations [10,11]. Herein, in continuation of our previous theoretical studies on the fullerenes [12-14], adsorption of alanine on pristine C_{60} and its functionalized derivatives as well as boron and/or nitrogen doped OH-functionalized C_{60} fullerene has been studied by using density functional theory (DFT) in both gaseous and aqueous phases.

COMPUTATIONAL METHODS

All calculations were performed by using the Gaussian 09 chemical quantum package [15]. At first, the structures of adsorbents (C_{60} derivatives), adsorbate (alanine) and complex (C_{60}-alanine) were optimized at the M062X/6-31G* level of theory [16]. The geometrical minima were confirmed by the absence of any imaginary frequencies. The conductor-like polarizable continuum model (CPCM) was used to calculate the solvation effects on the studied molecules in the aqueous phase [17].

The adsorption energy (E_{ads}) of alanine on C_{60} was calculated using the following equation:

$$E_{ads} = E_{complex} - (E_{alanine} + E_{fullerene}) + E_{BSSE} \qquad (1)$$

where $E_{alanine}$, $E_{fullerene}$, $E_{complex}$ and E_{BSSE} refer to the energies of alanine, fullerene, complex (alanine + C_{60}) and basis set superposition error, respectively.

The global electrophilicity index (ω) [18] was given by the following expression:

$$\omega = \frac{\mu^2}{2\eta} \qquad (2)$$

where μ is the electronic chemical potential and η is the electronic chemical hardness. The global nucleophilicity index (*N*) [19] is obtained as follows:

$$N = E_{HOMO(Nu)} - E_{HOMO(TCE)} \qquad (3)$$

where *Nu* denotes the given nucleophile. Since tetracyanoethylene (TCE) has the lowest HOMO energy among molecules already investigated in the context of polar organic reactions, it is taken as the reference.

The natural bond orbital (NBO) calculations were performed to analyze the electrical charge of atoms in all structures [20,21].

RESALTS AND DISCUSSION

Optimized Structures

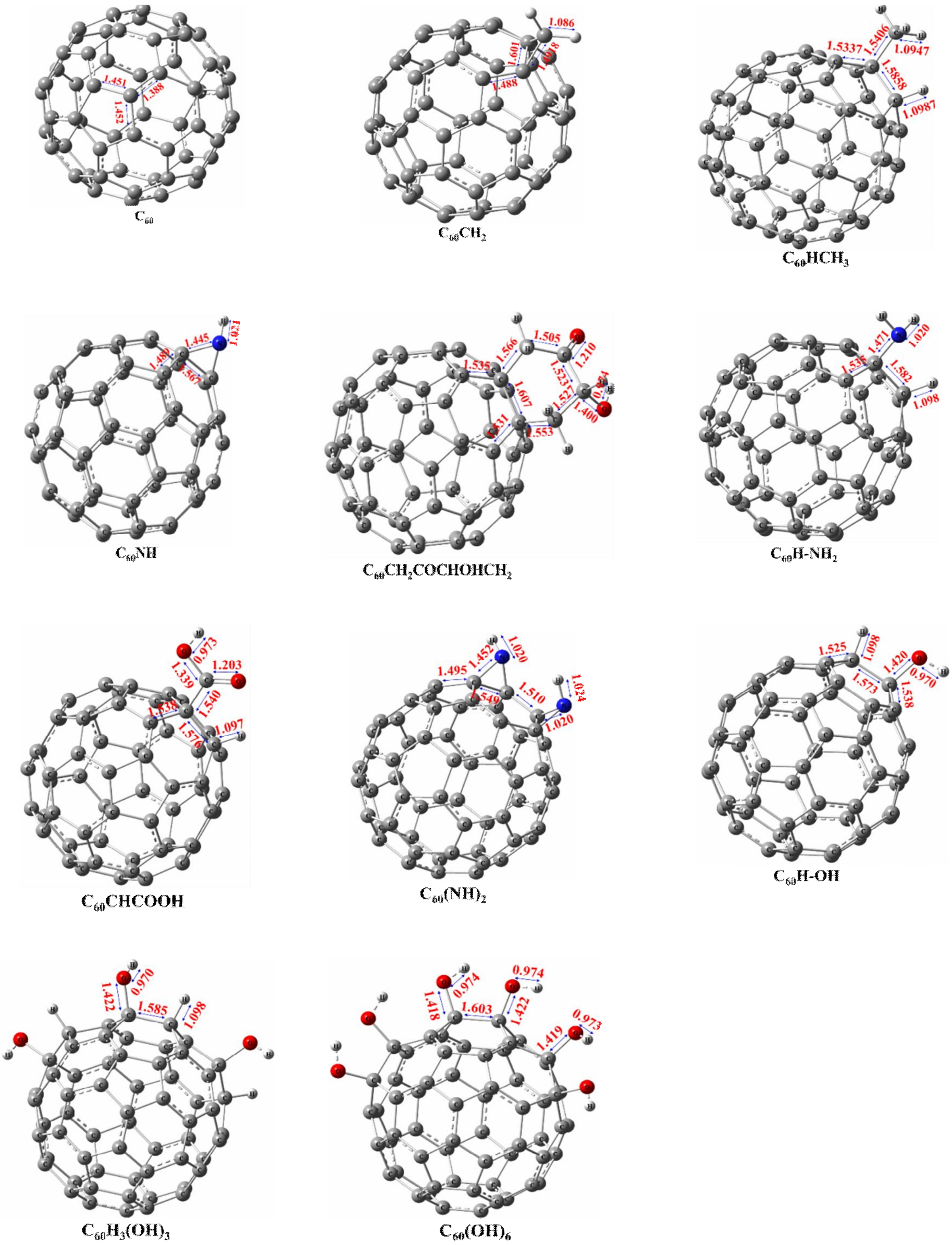
At the first step, the structures of the pristine C_{60} fullerene and some experimentally synthesized functionalized derivatives of the fullerene [22-29] were optimized. Figure 1 shows the optimized structures for pristine C_{60} and its functionalized derivatives. Functional groups on C_{60} contain CH_2, H-CH_3, NH, $CH_2COCHOHCH_2$, H-NH_2, CHCOOH, $(NH)_2$, H-OH, H_3-$(OH)_3$ and $(OH)_6$. In addition, Fig. 2 illustrates the optimized structures for doped C_{60}H-OH (9) functionalized derivatives. In some 9 derivatives, the atom adjacent functionalized carbon atom was replaced with nitrogen or boron atom. In the other 9 derivatives, three atoms adjacent functionalized carbon atom were replaced with three nitrogen or three boron atoms. Also, in two structures, six positions adjacent functionalized carbon atom were replaced with three nitrogen and three boron atoms. Figure 3 shows the optimized structures of fullerene-alanine complexes along with some selected bond lengths and bond orders.

Adsorption Energies

The calculated adsorption energy (E_{ads}) values in gas phase for the complex C_{60}-alanine are given in Tables 1 and 2. The E_{ads} values calculated are found to be negative for all pristine and doped functionalized C_{60} fullerenes.

The E_{ads} value is the least (the weakest adsorption) for adsorption of alanine on pristine C_{60} whereas maximum E_{ads} values (stronger adsorption) are observed for 9, 10 and 11 in both gaseous and aqueous phases. 9 is a one-functionalized C_{60} and 10 and 11 are multi-functionalized C_{60}. If we ignore the effect of many substituents on the adsorption in 10 and 11, the maximum E_{ads} value is related to 9. Thus, we consider this one-functionalized C_{60} for the effect of doping on the adsorption.

When fullerene 9 is doped with nitrogen and boron atoms in the gaseous phase, the E_{ads} value varies. Changes in E_{ads} values are found to be significant in most cases. On doping N atom on OH-functionalized carbon in 9, E_{ads} decreases for 12 in which H atom is bound to C atom but it



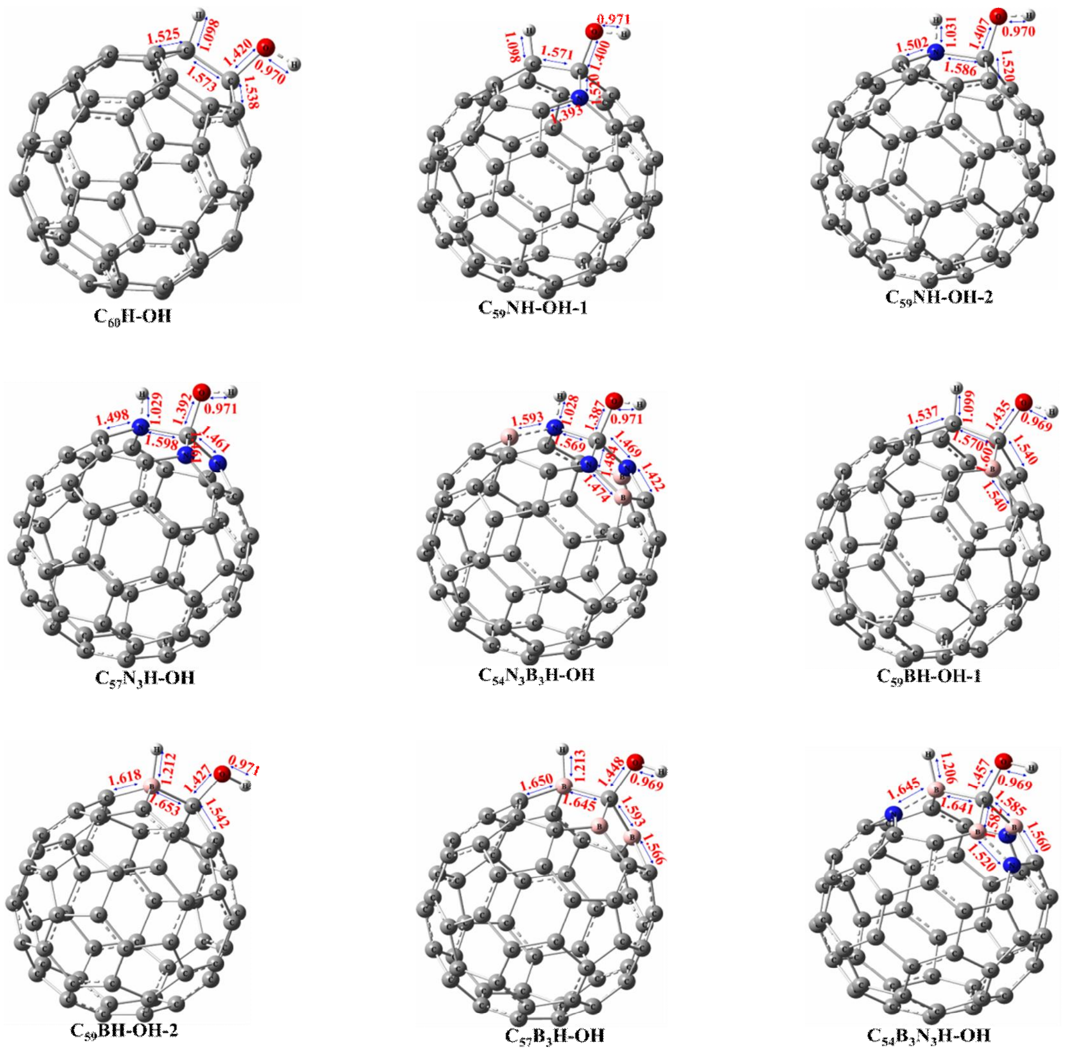
C_{60} $C_{60}CH_2$ $C_{60}HCH_3$

$C_{60}NH$ $C_{60}CH_2COCHOHCH_2$ $C_{60}H\text{-}NH_2$

$C_{60}CHCOOH$ $C_{60}(NH)_2$ $C_{60}H\text{-}OH$

$C_{60}H_3(OH)_3$ $C_{60}(OH)_6$

Fig. 1. The optimized structures of pristine and functionalized C_{60} fullerene along with some selected bond lengths (in Å).



$C_{60}H$-OH $C_{59}NH$-OH-1 $C_{59}NH$-OH-2

$C_{57}N_3H$-OH $C_{54}N_3B_3H$-OH $C_{59}BH$-OH-1

$C_{59}BH$-OH-2 $C_{57}B_3H$-OH $C_{54}B_3N_3H$-OH

Fig. 2. The optimized structures of $C_{60}H$-OH fullerene and doped with one, two or three nitrogen or boron atoms as well as six atoms (three nitrogens and three borons) along with some selected bond lengths (in Å).

increases for 13 in which H atom is bound to N atom significantly. In 13, the adsorption of alanine can be taken place by two interactions with hydrogen atoms attached to oxygen and nitrogen of the fullerene through formation of hydrogen bonding. On the other hand, in 12, alanine can interact only with one hydrogen atom attached to oxygen. In the solution phase, the interaction of the water molecules with the polar functionalized fullerene can compete with adsorption of alanine and thus, it can decrease the adsorption energies, proportionally.

On doping three N atoms in 14, E_{ads} increases vigorously (from -44.62 to -67.46). There is a weaker effect for similar doping in the aqueous phase. On doping one B atom, E_{ads} increases for both 16 and 17, but the effect is stronger for 17. On doping three B atoms in 18, E_{ads} increases vigorously (from -44.62 to -65.45). Also, it can be doped every six positions around functionalized carbon in 9 (15 and 19). In the case, E_{ads} decreases if there are three N atoms in the position nearer to functionalized carbon (15), but in the presence of three B atoms in the position nearer

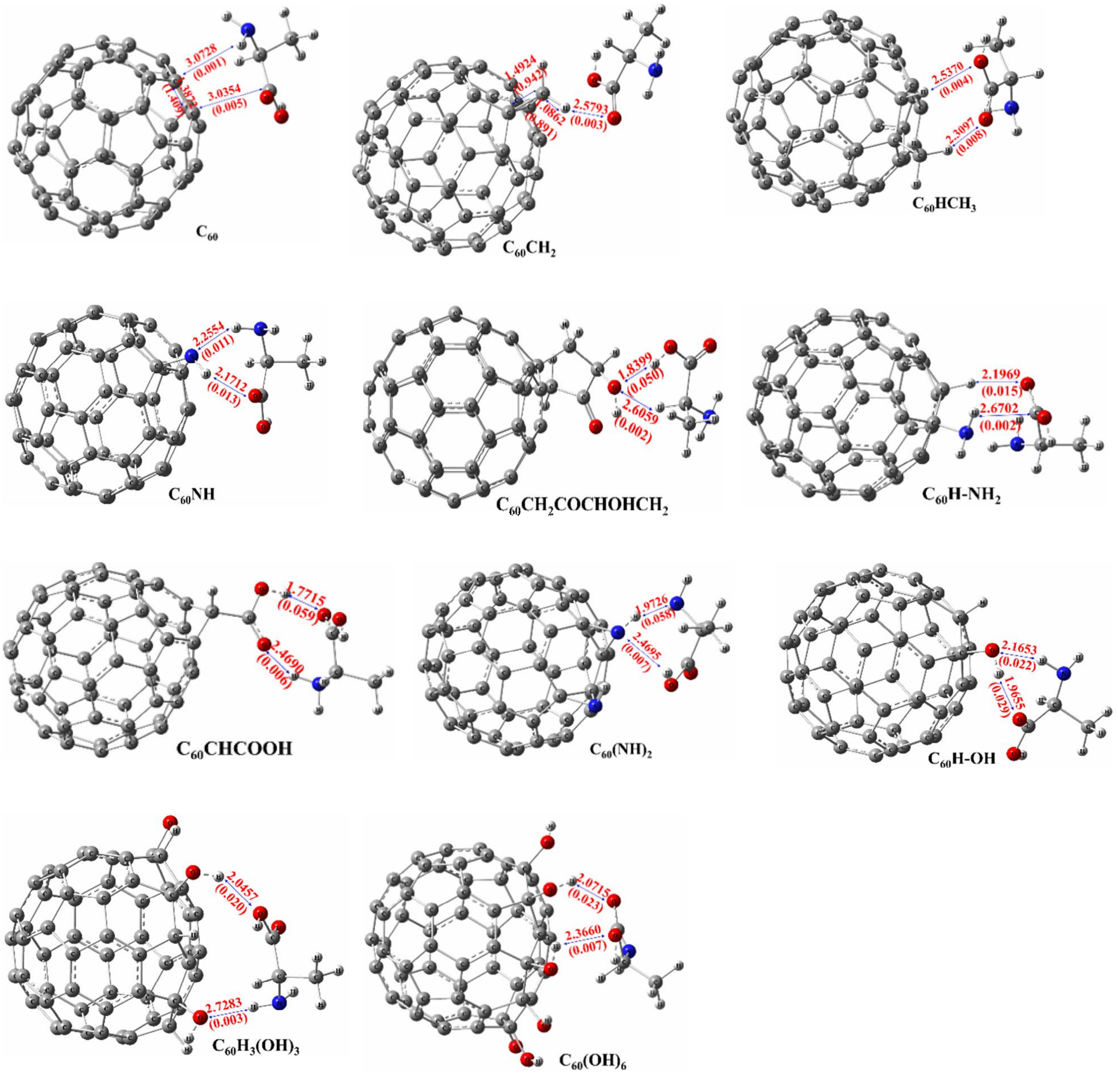


Fig. 3. The optimized structures of fullerene-alanine complexes along with some selected bond lengths (in Å) and bond orders given in parenthesis.

to functionalized carbon (19), E_{ads} increases vigorously (from -44.62 to -59.15). Again, the effect of similar doping in the aqueous phase is weaker.

Figures 4 and 5 show the effect of the functionalized C_{60} and the doped fullerenes 9 on the adsorption of alanine on them in both gaseous and aqueous phases, respectively. As can be seen in the figures, the E_{ads} values are larger in gaseous phase than those in aqueous phase. Probably, in the aqueous phase, alanine can be hydrated and can form hydrogen bond with the water molecules. Thus, it decreases its tendency to adsorb on fullerene.

Table 1. Calculated Energies (in kJ mol^{-1}) for Adsorption of Alanine on Pristine Fullerenes in both Gaseous and Aqueous Phases

Complex No.	Fullerene derivative	Gas phase	Aqueous phase
1	C_{60}	-5.63	-6.50
2	$C_{60}CH_2$	-6.45	-6.67
3	$C_{60}HCH_3$	-20.23	-6.58
4	$C_{60}NH$	-39.55	-36.27
5	$C_{60}CH_2COCHOHCH_2$	-33.86	-28.26
6	$C_{60}H\text{-}NH_2$	-39.25	-27.03
7	$C_{60}CHCOOH$	-41.98	-27.87
8	$C_{60}(NH)_2$	-43.42	-34.36
9	$C_{60}H\text{-}OH$	-44.62	-38.70
10	$C_{60}H_3(OH)_3$	-52.49	-39.21
11	$C_{60}(OH)_6$	-61.23	-47.39

Table 2. Calculated Energies (in kJ mol^{-1}) for Adsorption of Alanine on Doped Fullerenes in both Gaseous and Aqueous Phases

Complex No.	Fullerene derivative	Gas phase	Aqueous phase
9	$C_{60}H\text{-}OH$	-44.62	-38.70
12	$C_{59}NH\text{-}OH\text{-}1$	-33.64	-30.89
13	$C_{59}NH\text{-}OH\text{-}2$	-47.67	-34.48
14	$C_{57}N_3H\text{-}OH$	-67.46	-43.03
15	$C_{54}N_3B_3H\text{-}OH$	-35.64	-20.65
16	$C_{59}BH\text{-}OH\text{-}1$	-45.09	-42.87
17	$C_{59}BH\text{-}OH\text{-}2$	-54.96	-44.92
18	$C_{57}B_3H\text{-}OH$	-65.45	-55.10
19	$C_{54}B_3N_3H\text{-}OH$	-59.15	-54.17

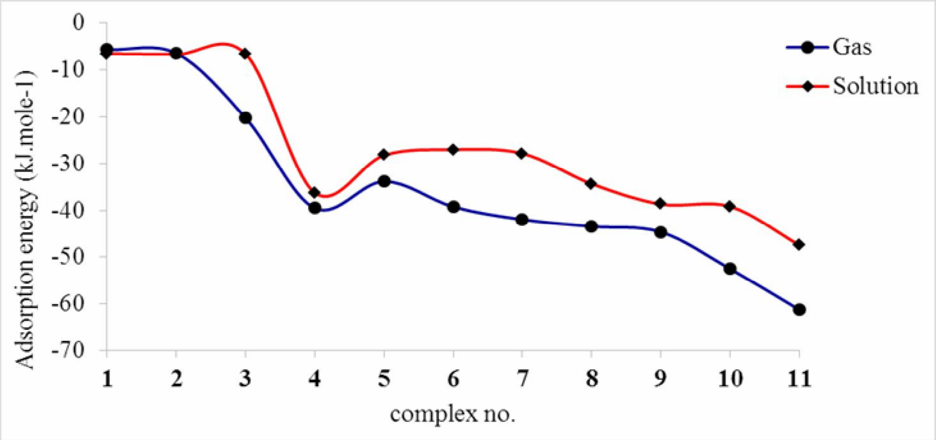


Fig. 4. The effect of the functionalized C_{60} fullerenes on the adsorption of alanine in both gaseous and aqueous phases.

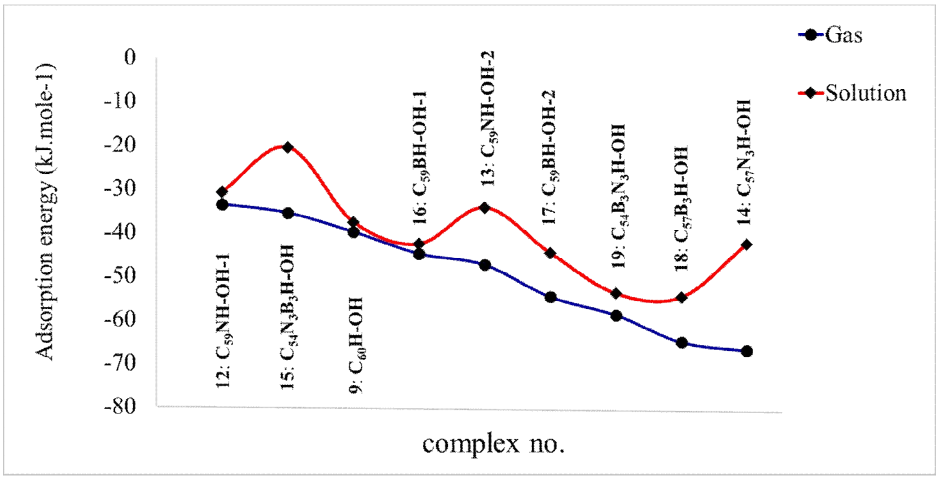


Fig. 5. The effect of the doped C_{60}H-OH fullerenes on the adsorption of alanine in both gaseous and aqueous phases.

Analysis of the Global DFT Reactivity Indices

Global DFT reactivity indices containing chemical potential (μ), chemical hardness (η), electrophilicity index (ω) and nucleophilicity index (N) are the useful tools for studying the reactivity of the reactants [30]. Therefore, the global DFT reactivity indices were calculated for the structures in both gaseous and aqueous phases. The results given in Table 3, show that chemical potential of pristine C_{60} and functionalized C_{60} fullerenes are more negative than that of alanine. Thus, pristine C_{60} and functionalized C_{60} fullerenes accept the electron and act as the electron acceptor and alanine donates the electron and acts as an electron donor. The considerable increasing electrophilicity index for pristine C_{60} and functionalized C_{60} fullerenes relative to alanine confirms the results and shows that pristine C_{60} and functionalized C_{60} fullerenes are the strong electrophile against alanine. Since there is a higher electrophilicity difference between C_{60} fullerenes and alanine compared to their nucleophilicity difference, the former is a more important factor, thus, pristine C_{60}

Table 3. The Electronic Chemical Potential (μ), Chemical Hardness (η), Electrophilicity Index (ω) and Global Nucleophilicity (N), in *eV*, for Alanine, Pristine and Various Functionalized C_{60} Fullerenes in both Gas and Aqueous Phases, Computed at the M062X/6-31G* Level

Species	Gas phase				Aqueous phase			
	μ	η	N	ω	μ	η	N	ω
Alanine	-3.44	5.32	1.84	1.11	-3.54	5.26	1.43	1.19
C_{60}	-4.97	2.27	3.35	5.44	-4.86	2.27	3.09	5.20
$C_{60}CH_2$	-4.77	2.16	3.66	5.27	-4.71	2.15	3.37	5.14
$C_{60}HCH_3$	-4.66	2.13	3.44	5.10	-4.73	2.14	3.73	5.22
$C_{60}NH$	-4.89	2.18	3.53	5.48	-4.78	2.18	3.27	5.25
$C_{60}CH_2COCHOHCH_2$	-4.79	2.14	3.67	5.36	-4.70	2.13	3.39	5.19
$C_{60}H\text{-}NH_2$	-4.77	2.15	3.68	5.29	-4.69	2.14	3.40	5.14
$C_{60}CHCOOH$	-4.89	2.25	3.45	5.33	-4.83	2.25	3.15	5.19
$C_{60}(NH)_2$	-4.88	2.18	3.53	5.47	-4.79	2.18	3.26	5.25
$C_{60}H\text{-}OH$	-4.82	2.15	3.62	5.41	-4.73	2.15	3.36	5.19
$C_{60}H_3(OH)_3$	-4.58	2.14	3.87	4.89	-4.51	2.14	3.58	4.74
$C_{60}(OH)_6$	-4.75	2.10	3.74	5.37	-4.67	2.10	3.46	5.18

fullerenes and alanine act as the electron acceptor and the electron donor, respectively, while alanine is a moderate nucleophile.

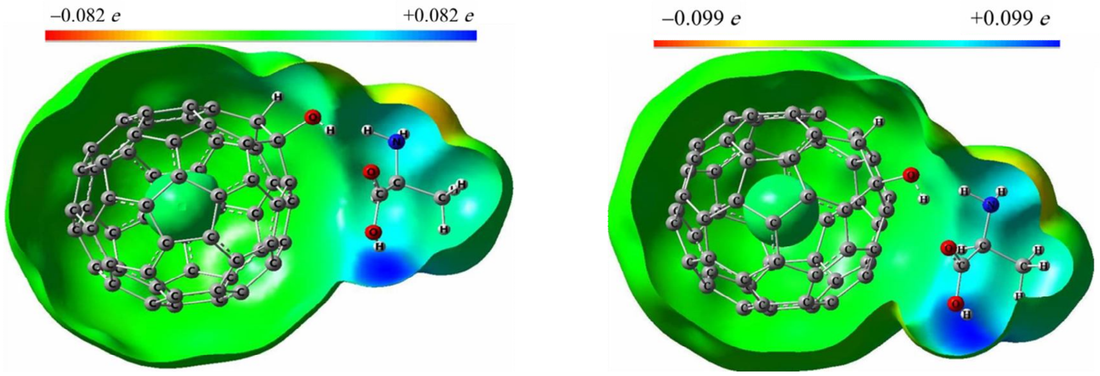
As can be seen in Table 4, in 9 doped functionalized derivatives, chemical potential of 17, 18 and 19 are more negative than the other functionalized C_{60} fullerenes, thus, they accept the electron more than the other functionalized C_{60} fullerenes in both gaseous and aqueous phases. The electrophilicity index for the derivatives is high, too. The E_{ads} values confirm the present results.

Study of Charge Transfer in the Adsorption Process

Global electron density transfer (GEDT) is an important factor for charge transfer in the adsorption process and can show the path of electron transfer [31]. Therefore, to study the charge transfer in the adsorption of alanine on fullerene 9, the GEDT value was calculated in both gaseous and aqueous phases. Figure 6 depicts the calculated values of GEDTs along with its molecular electrostatic potential map (MESP). In the MESP map, the greenish regions are more negative (relatively high electron density) and the bluish ones are more positive (relatively low electron density). Thus, analysis of the GEDT values reveals that the electron transfer takes place from alanine toward fullerene 9 in both gaseous and aqueous phases upon adsorption. Meanwhile, it was found that less electron transfer in the aqueous phase (0.020 e against 0.023 e) is due to the hydration of alanine

Table 4. The Electronic Chemical Potential (μ), Chemical Hardness (η), Electrophilicity Index (ω) and Global Nucleophilicity (N), in *eV*, for Alanine and Doped $C_{60}H$-OH Fullerene in both Gas and Aqueous Phases, Computed at the M062X/6-31G* Level

Species	Gas phase				Aqueous phase			
	μ	η	N	ω	μ	η	N	ω
Alanine	-3.44	5.32	1.84	1.11	-3.54	5.26	1.43	1.19
$C_{60}H$-OH	-4.82	2.15	3.62	5.41	-4.73	2.15	3.36	5.19
$C_{59}NH$-OH-1	-4.07	1.40	5.13	5.90	-3.95	1.38	4.90	5.64
$C_{59}NH$-OH-2	-3.61	1.01	5.98	6.47	-3.53	1.04	5.66	5.99
$C_{57}N_3H$-OH	-4.09	1.54	4.96	5.42	-3.96	1.50	4.78	5.23
$C_{54}N_3B_3H$-OH	-4.44	1.92	4.23	5.15	-4.39	1.93	3.92	4.99
$C_{59}BH$-OH-1	-4.69	2.01	3.90	5.48	-4.58	2.00	3.65	5.25
$C_{59}BH$-OH-2	-4.95	2.03	3.62	6.04	-4.82	2.05	3.37	5.67
$C_{57}B_3H$-OH	-5.19	1.27	4.14	10.61	-6.06	1.29	3.88	9.94
$C_{54}B_3N_3H$-OH	-4.97	1.94	3.68	6.36	-4.80	1.96	3.47	5.89



Gas Phase, GEDT=0.023 e

Aqueous Phase, GEDT= 0.020 e

Fig. 6. The molecular electrostatic potential maps and the global electron density transfer (GEDT) values obtained for the adsorption of alanine on $C_{60}H$-OH in both gaseous and aqueous phases.

and its stability. Figures S1 and S2 in the Supplementary Information file show the molecular electrostatic potential maps for the adsorption of alanine on the C_{60} fullerene and its functionalized forms and the doped C_{60} fullerenes, respectively.

AIM Study in the Adsorption Process

The theory of atoms in molecules (AIM) has been widely applied to study the atom-atom interactions in covalent and non-covalent interactions in molecules. In the theory, the electron density of molecules is used to determine the nature of bonding in molecular systems. The topological properties of electron density and its derivatives are found to be useful in determining the concept of the bonding through bond paths and bond critical points (BCPs). The topological parameters in BCPs contain electron density (ρ_{BCP}), laplacian of electron density ($\nabla^2\rho_{BCP}$), electronic kinetic energy density (G_{BCP}), electronic potential energy density (V_{BCP}), electronic energy density (H_{BCP}) and estimated interaction energy (E_{int}) [32-35].

The molecular graph for the adsorption of alanine on 9 obtained from AIM calculations is shown in Fig. 7 and the topological parameters in BCPs are given in Table 5. As seen, there are two bond critical points (A and B) between the fullerene and alanine molecules, with BCPs higher than those of the other points. In these points, the interatomic distances between the interacting atoms (d) are found to be 2.17, and 1.97 Å, respectively. Since these distances are smaller than summation of the van der Waals radii for interacting atoms (2.72 Å), it can be concluded that the hydrogen bonding can be formed between alanine and 9.

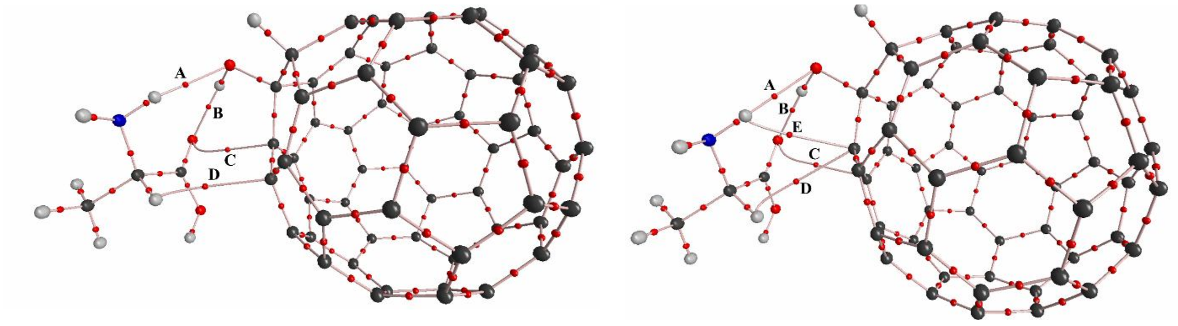
In the bond critical point A, hydrogen atom attached to amine nitrogen interacts with oxygen atom of hydroxyl group in Fullerene by hydrogen bonding. The interaction decreases in aqueous phase probably due to interaction with water molecules.

In addition, in the bond critical point B, oxygen atom of carboxyl group in alanine has interacted with hydrogen atom of hydroxyl group in Fullerene by hydrogen bonding. The interaction increases in aqueous phase probably due to creation of zwitterionic form through acid dissociation. In the zwitterionic form, oxygen atom of carboxyl group has more negative charge and it establishes the stronger interaction with hydrogen atom of hydroxyl group in Fullerene. The NBO charges support this trend because the charge of oxygen atom in carboxyl group in gaseous phase, -0.619, is less than that in aqueous phase, -0.662. There are also some other interactions between alanine and fullerene whose energies are less than the hydrogen bonding energy (the bond critical points C, D and E).

The ratio of V_{BCP} to G_{BCP} can be considered as a criterion for the nature of interaction. The value close to the unit for the ratio shows that the interaction is non-covalent (such as hydrogen bonding) [36]. Here, the ratio is close to the unit for the whole interactions, and therefore, they are non-covalent and hydrogen bonding in nature. The results of AIM calculations for all compounds are given in Supplementary Information. In agreement with the adsorption energies presented in Tables 1 and 2, these results show that the weakest and strongest adsorptions take place for compounds 1 and 14 (as well as 18), respectively.

CONCLUSIONS

The computational methods at B3LYP/6-311G** and M062X/6-311G** levels of theory were used to study the adsorption of alanine on pristine and boron and/or nitrogen doped functionalized C_{60} fullerenes. The structures of adsorbent (C_{60} derivatives), adsorbate (alanine) and complex were optimized and their frequencies were calculated. The adsorption energies for the adsorption of alanine on the pristine, functionalized and the doped functionalized C_{60} fullerenes were also calculated. The least adsorption energy was found for the adsorption of alanine on pristine C_{60}, and the maximum adsorption was found for the derivative 9 in both gaseous and aqueous phases, among one-functionalized derivatives of C_{60}. In addition, the doping nitrogen/boron atoms with the functionalized carbon atom in 9 affect the adsorption energy. On doping N and B atoms on OH-functionalized carbon in 9, the adsorption energy increases for 13 and 17 significantly, respectively. On doping three N atoms in 14 or three B atoms in 18, the adsorption energy increases vigorously. Also, the adsorption energy increases on doping every six positions around functionalized carbon in 9, so that there are three B atoms in the position nearer to functionalized carbon. The results are confirmed by the global DFT reactivity indices such as chemical potential and electrophilicity index. Therefore,



Gas Phase

Aqueous Phase

Fig. 7. Molecular graphs for the adsorption of alanine on C_{60}H-OH in both gaseous and aqueous phases obtained by AIM calculations. The bond critical points and bond paths are presented by red spheres and pink lines, respectively.

Table 5. Topological Parameters in the Bond Critical Points between Alanine and C_{60}H-OH in both Gaseous and Aqueous Phases Obtained by AIM Calculations[a]

Phase	Gas phase				Aqueous phase				
Critical point	A	B	C	D	A	B	C	D	E
ρ_{BCP}	0.018	0.024	0.011	0.008	0.015	0.031	0.009	0.007	0.007
$\nabla^2\rho_{BCP}$	0.056	0.083	0.037	0.023	0.050	0.107	0.031	0.022	0.025
G_{BCP}	0.015	0.021	0.008	0.005	0.012	0.027	0.006	0.004	0.005
V_{BCP}	0.015	0.021	0.006	0.004	0.012	0.028	0.005	0.003	0.004
H_{BCP}	0.030	0.042	0.014	0.009	0.024	0.055	0.011	0.007	0.009
E_{int}	19.69	27.57	7.88	5.25	15.75	36.76	6.56	3.94	5.25
d^b	2.17	1.97	3.01	2.76	2.26	1.85	3.12	2.91	2.71

[a] ρ_{BCP}, $\nabla^2\rho_{BCP}$, G_{BCP}, V_{BCP}, H_{BCP} in a.u. and E_{int} in kJ mol^{-1}. [b] The distance between interacting atoms in Angstrom.

among the studied C_{60} fullerene derivatives, 14 and 18 are the most appropriate adsorbents for the adsorption of alanine. In addition, analysis of the GEDT values reveals that the electron transfer takes place from alanine toward fullerene 9 in both phases upon adsorption, and also, less electron transfer occurs in the aqueous phase due to hydration of alanine and its stability. Finally, topological parameters in AIM show that the interaction between alanine and 9 in the bond critical points A and B, in both gaseous and aqueous phases, is non-covalent and hydrogen bonding in nature.

REFERENCES

[1] Berg, J. M.; Tymoczko, J. L.; Gatto, J. J.; Stryer, J., Biochemistry. W. H. Freeman and Company, New

York, 2015.

[2] Hames, B. D.; Hooper, N. M., Biochemistry. Taylor & Francis, New York, 2005.

[3] Taylor, R., Lecture Notes on Fullerene Chemistry: A Handbook for Chemists. Imperial College Press, London, 1999.

[4] Taylor, R.; Walton, D. R. M., The chemistry of fullerenes. *Nature.* **1993**, *363*, 685-693, DOI: 10.1038/363685a0.

[5] Hirsch, A., The Chemistry of the Fullerenes: An Overview. *Angew. Chem.* **1993**, *32*, 1138-1141, DOI: 10.1002/anie.199311381.

[6] Hirsch, A., The Chemistry of Fullerenes. Georg Thieme Verlag Stuttgart, New York, 1994.

[7] Yurovskaya. M. A.; Trushkov, I. V., Cycloaddition to buckminsterfullerene C60: advancements and future prospects. *Russ. Chem. Bull.* **2002**, *51*, 367-443, DOI: 10.1023/A:1015565600068.

[8] Braun, T., Mechanochemical approaches to fullerene chemistry. *Fullerene Sci. Technol.* **1997**, *5*, 1291-1311, DOI: 10.1080/15363839708013321.

[9] Komatsu, K.; Murata, Y.; Wang, G. W.; Tanaka, T.; Kato, N.; Fujiwara, K., The solid-state mechanochemical reaction of fullerene C60. *Fullerene Sci. Technol.* **1999**, *7*, 609-620, DOI: 10.1080/10641229909351365.

[10] De Leon, A.; Jalbout, A. F.; Basiuk, V. A., Fullerene-amino acid interactions. A theoretical study. *Chem. Phys. Lett.* **2008**, *452*, 306-314, DOI: 10.1016/j.cplett.2007.12.065.

[11] De Leon, A.; Jalbout, A. F.; Basiuk, V. A., Fullerene-amino acid interactions: theoretical insights. *Int. J. Quant. Chem.* **2010**, *110*, 953-959, DOI: 10.1002/qua.21780.

[12] Soleymani, M.; Dashti Khavidaki, H., Functionalization of the C20 fullerene by pyridine and pyrimidine: A theoretical study. *Iran. Chem. Commun.* **2020**, *8*, 111-122, DOI: 10.33945/SAMI/ECC.2020.2.13.

[13] Soleymani, M.; Dashti Khavidaki, H., Inactivation possibility of pyrene by C20 fullerene *via* cycloaddition reactions: A theoretical study. *Comp. Theor. Chem.* **2017**, *1112*, 37-45, DOI: 10.1016/ j.comptc.2017.04.014.

[14] Soleymani, M., Theoretical study of the possibility of functionalization of C20 fullerene with the simplest ketene CH_2CO. *J. Struct. Chem.* **2019**, *60*, 524-535, DOI: 10.1134/S0022476619040036.

[15] Frisch, M. J.; Trucks, G. W.; Schlegal, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malich, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., 2004 Gaussian (Wallingford CT: Gaussian Inc.).

[16] Zhao, Y.; Truhlar, D. G., Comparative DFT study of van der Waals complexes: Rare-gas dimers, alkaline-earth dimers, zinc dimer, and zinc-rare-gas dimers. *J. Phys. Chem. A.* **2006**, *110*, 5121-5129, DOI: 10.1021/jp060231d.

[17] Barone, V.; Cossi, M., Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A.* **1998**, *102*, 1995-2001, DOI: 10.1021/jp9716997.

[18] Parr, R. G.; Szentpaly, L. V.; Liu, S., Electrophilicity index. *J. Am. Chem. Soc.* **1999**, *121*, 1922-1924, DOI: 10.1021/ja983494x.

[19] Domingo, L. R.; Perez, P.; Ortega, D. E., Why do five-membered heterocyclic compounds Sometimes not participate in polar diels-alder reactions? *J. Org. Chem.* **2013**, *78*, 2462-2471, DOI: 10.1021/

jo3027017.

[20] Reed, A. E.; Curtiss, L. A.; Weinhold, F., Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, *88*, 899-926, DOI: 10.1021/cr00088a005.

[21] Carpenter, J. E.; Weinhold, F. J., Analysis of the geometry of the hydroxymethyl radical by the ‘‘different hybrids for different spins” natural bond orbital procedure. *J. Mol. Struct.* **1988**, *139*, 41-62, DOI: 10.1016/0166-1280(88)80248-3.

[22] Schneider, N. S.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M., Formation of fullerols *via* hydroboration of fullerene-C60. *J. Chem. Soc., Chem. Commun.* **1994**, *4*, 463-464, DOI: 10.1039/C39940000463.

[23] Hirsch, A.; Soi, A.; Karfunkel, H. R., Titration of C60: A method for the synthesis of organofullerenes. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766-768, DOI: 10.1002/anie.199207661.

[24] Hirsch, A.; Grosser, T.; Skiebe, A.; Soi, A., Synthesis of isomerically pure organodihydrofullerenes. *Chem. Ber.* **1993**, *126*, 1061-1067, DOI: 10.1002/cber.19931260428.

[25] Seshadri, R.; Govindaraj, A.; Nagarajan, R.; Pradeep, T.; Rao, C. N. R., Addition of amines and halogens to fullerene C60 and C70. *Tetrahedron Lett.* **1992**, *33*, 2069-2070, DOI: 10.1016/0040-4039(92)88144-T.

[26] Torres-Garcia, G.; Mattay, J., Exohedral functionalization of [60]fullerene by [4+2] cycloadditions. Diels-alder reactions of [60]fullerene with electron rich 2,3-dioxysubstituted-l,3-butadienes. *Tetrahedron.* **1996,** *52*, 5421-5426, DOI: 10.1016/0040-4020(96)00172-X.

[27] Miller, G. P., Reactions between aliphatic amines and [60]fullerene: a review. *C. R. Chim.* **2006**, *9*, 952-959, DOI: 10.1016/j.crci.2005.11.020.

[28] Afreen, S.; Kokubo, K.; Muthoosamy, K.; Manickam, S., Hydration or hydroxylation: direct synthesis of fullerenol from pristine fullerene [C60] via acoustic cavitation in the presence of hydrogen peroxide. *RSC Adv.* **2017**, *7*, 31930-31939, DOI: 10.1039/C7RA03799F.

[29] Saha, B.; Bhattacharyya P. Kr. Adsorption of amino acids on boron and/or nitrogen doped functionalized graghene: A density functional study. *Comput. Theor. Chem.* **2016**, *1086*, 45-51, DOI: 10.1016/j.comptc. 2016.04.017.

[30] Geerlings, P.; De Proft, F.; Langenaeker, W., Conceptual density functional theory. *Chem. Rev.* **2003**, *103*, 1793-1874, DOI: 10.1021/cr990029p.

[31] Domingo, L. R., A new C-C bond formation model based on the quantum chemical topology of electron density. *RSC Adv.* **2014**, *4*, 32415-32428, DOI: 10.1039/C4RA04280H.

[32] Bader, R. F. W., Atoms in Molecules: A Quantum Theory. Clarendon Press, Oxford, 1990.

[33] Bader, R. F. W.; Johnson, S.; Tang, T. H.; Popelier, P. L. A., The electron pair. *J. Phys. Chem.* **1996**, *100*, 15398-15415, DOI: 10.1021/jp961297j.

[34] Fradera, X.; Austen, M. A.; Bader, R. F. W., The lewis model and beyond. *Phys. Chem. A.* **1999**, *103*, 304-314, DOI: 10.1021/jp983362q.

[35] Grabowski, S. J., What is the covalency of hydrogen bonding? *Chem. Rev.* **2011**, *111*, 2597-2625, DOI: 10.1021/cr800346f.

[36] Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E., From weak to strong interactions: A comprehensive analysis of the topological and energetic properties of the electron density distribution involving X-H-F-Y systems. *J. Chem. Phys.* **2002**, *117*, 5529-5542, DOI: 10.1063/1.1501133.