



Molecular properties of nanoscale fullerene based systems as a corrosion inhibitors

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ABSTRACT

The nanoscale C₆₀ and some of its doped derivatives with some elements of group III and V was performed by Density Functional Theory. EHOMO, ELUMO, energy gap (ΔE), and those parameters that give valuable information about the reactive behavior: the ionization potential (IP), electron affinities (EA), chemical potential (μ), electronegativity (χ), global hardness (η), softness (S), electrophilic index (ω), the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation ($\Delta E_{\text{Back-donation}}$) have been calculated using the DFT/B3LYP methods with the 3-21G** basis set. The outcomes have shown that the (C₆₀) could experience more honest functioning as a corrosion inhibitor by the substitution with heavier elements ongoing from B to In and from N to Sb.

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KEYWORDS

Computational study;
Nano materials;
DFT;
Molecular properties;
Fullerene based systems;
Corrosion inhibition;
Gaussian model.

INTRODUCTION

Molecular (nanoscale) electronics are attracting great attention due to potential applications in future sensor devices, computing engineering and related fields^[1]. Theoretical and observational studies aimed at inferring the fundamental physics of molecular and nanoelectronic devices have started to throw light on electron transfer mechanisms through molecules and engineered nanomaterials and help identify appropriate molecular and nanoscale architectures for effective functional elements in electronic devices^[2,3]. The discovery^[4] and large scale synthesis^[5] of C₆₀ fullerenes have stimulated much interest in the existence of similar type of clusters constructed with different species. Among others, carbon fullerene is one of the most stable and a

well-known nano-scale molecular structure; C₆₀ often acts as a semiconductor quantum dot.

Since C₆₀ is a true nanoscale single molecule, its electronic structure and energy levels can be considerably affected by modifying a single atom in its structure. Thus, doping of fullerenes can be generally looked to change their electronic conductivity due to alteration in the density of states near the Fermi surface. Many physicists have gone for the interaction of the fullerene cage with foreign particles. Several groups^[6,7] produced dopant substituted fullerenes C₅₉X (X = B, N, Si, Fe, Co, Rh, and so on). Theoretically, Andreoni *et al.*^[8] and Kurita *et al.*^[9] studied the properties of C₅₉B and C₅₉N molecules.

Indeed, an experimental study has shown that the C₅₉N molecule acts as a molecular rectifier in a double

barrier tunnel junction via the single electron tunneling effect^[10].

The study of corrosion processes and their inhibition by organic compounds is a very active field of research. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media^[11-12]. It has been commonly recognized that organic inhibitor usually promotes formation of a clot on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process^[13].

The inhibition efficiency has been closely related to the inhibitory adsorption abilities and the molecular properties of different kinds of organic compounds^[14-15].

Recently, density functional theory, DFT, was found to be quite well suited for addressing and describing such physical processes of internal rotation because it provides appropriate theoretical parameters like electronic, chemical potential and molecular hardness to study such processes^[15,17,18]. The hardness profile is found to be a faithful description of the dynamics of internal rotation of molecules^[15,17,18]. The origin of the barrier to internal rotation is an ever-enticing problem of theoretical chemistry. Schleyer *et al.*^[19] has pointed out that while quite accurate barrier heights can be calculated, even at relatively modest levels of theory, the origin of barrier is still debatable. However, Ghosh *et al.*^[20,21] have observed that the determination of the origin of barrier to the physical process of inversion in terms of energy partitioning analysis of Fischer and Kollmar^[22] is a meaningful venture.

The vast majority of these studies has been done on C₆₀ molecule. The electronic properties of such systems have been studied theoretically by performing the semi-empirical and DFT calculations to understand the doping influences^[23,24].

In this report, we are going on the DFT using the standard 3-21G** basis set at the level of B3LYP of theory calculations to predict the molecular properties, corrosion inhibition performance and conduct of some doped fullerenes.

COMPUTATIONAL DETAILS

All the computational studies were carried out us-

ing the density functional theory (DFT) methods implemented in the Gaussian 03 suite of programs^[25]. By aggregating the effects of the GaussView^[26] program. The molecular properties of the C₆₀ and some of its doped derivatives with some elements of group III and V had been computed by DFT using the 3-21G** basis set. In the DFT calculations, Lee, Yang and Parr correlation functions are employed together with Becke's three parameters^[20] exchange functional B3LYP.

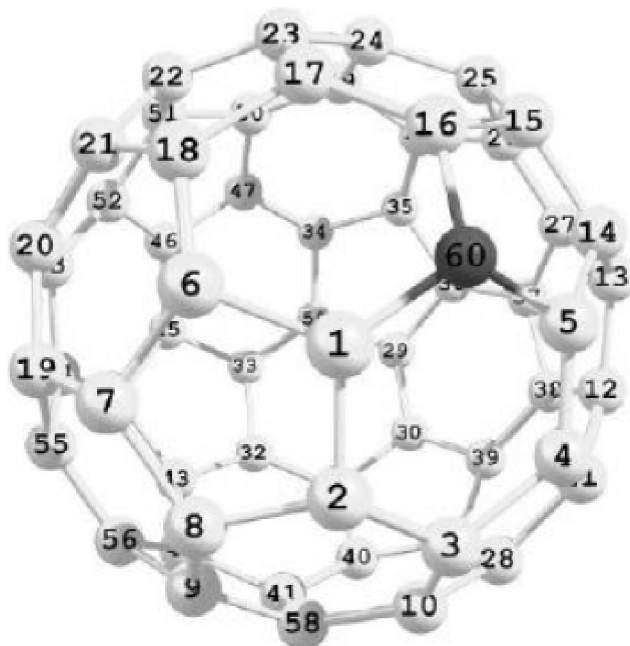


Figure 1 : Optimized DFT structure of C₆₀. Observe that the dopant is replaced with a carbon atom number 60

Figure 1. Demonstrates the structure of C₆₀, which doped with some elements of group III and V. We have picked out some elements of group II and V to be superseded with the carbon atom number 60 in the fullerene-C₆₀ cage.

During this investigation, the objective is to study the analyzing of some properties of C₆₀, which doped with some elements of group III and V is using DFT calculations. These properties are: the molecular structure, EHOMO, ELUMO, energy gap (ΔE), and those parameters that give valuable data around the reactive behavior: the ionization potential (IP), electron affinities (EA), chemical potential (μ), electronegativity (χ), global hardness (η), softness (S), electrophilic index (ω), the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation (ΔE Back-donation).

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The ionization potential is computed as the energy difference between the energy of the molecule derived from electron-transfer and the respective neutral molecule; $IP = E_{\text{cation}} - E_{\text{n}}$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_{\text{n}} - E_{\text{anion}}$ [27].

Koopman's theorem states that if the single particle energies are not moved by adding or taking away a single electron, then the ionization energy is the energy of the highest occupied, single particle molecular orbital (the HOMO) and the electron affinity is the vigor of the lowest unoccupied molecular orbital (the LUMO) with the negative sign as [25], $IP = -E_{\text{HOMO}}$, $EA = -E_{\text{LUMO}}$, Where IP: ionization potential, EA: electronic affinity, EHOMO: energy of the highest occupied molecular orbital and ELUMO: energy of the lowest unoccupied molecular orbital.

Koopman's theorem is extremely useful in predicting ionization energies and spectra [28]. Energy gap generally refers to the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) according to the Koopmans theorem [29,30], $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$.

Ionization energy (IP) sets as the minimum energy needed to get rid of an electron from the particle in a gaseous form. Ionization energy is expressed in units of electron volt (eV) [30]. Electron affinity can be determined as the energy released upon attachment of an electron to a particle or molecule resulting in the formation of the negative ion [30].

Chemical hardness is the impedance of a species to lose electrons [31], for insulator and semiconductor, hardness is half of the energy gap [32]. We can estimate the chemical hardness (η) as $\eta = (IP - EA) / 2$. The softness can be specified as the opposite of the hardness [31], $S = 1 / \eta$. The chemical potential, μ as $\mu = -(IP + EA) / 2$. On further approximation, the above equations take the form: $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2$ and $\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2$. The electronegativity (χ), as:

$$\chi = (IP + EA) / 2.$$

Electrophilicity is defined as the index (ω) measures the stabilization in energy when the system gets an additional electronic charge from the surroundings. In the other word, it can be determined as a standard of energy, lowering due to maximal electron flow between

donor and acceptor [33], $\omega = \mu^2 / 2\eta$.

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. When two systems, Fe (iron) and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. The number of transferring electrons (ΔN) was also calculated [34] by using the equation below.

$$\Delta N = \frac{(\chi_{\text{Fe}} - \chi_{\text{inh}})}{[2(\eta_{\text{Fe}} + \eta_{\text{inh}})]}$$

Where (χ_{Fe}) and (χ_{inh}) denote the absolute electronegativity of iron and inhibitor molecule respectively (η_{Fe}) and (η_{inh}) denote the absolute hardness of iron and the inhibitor molecule, respectively. In this work, we utilize the theoretical value of (χ_{Fe}) = 7.0 eV and (η_{Fe}) = 0 for the computation of number of transferred electrons [34]. The difference in electronegativity drives the electron transfer, and the essence of the hardness parameters acts as a resistance [35].

Granting to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez et al., [36] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept proves that if both operations take place, namely charge transfer to the molecule and back-donation from the atom, the energy change is immediately linked to the severity of the atom, as suggested in the following formulation. $\Delta E_{\text{Back-donation}} = -\eta/4$,

The $\Delta E_{\text{Back-donation}}$ implies that one $\eta > 0$ and $\Delta E_{\text{Back-donation}} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, therefore, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then it is expected that it will decrease as the hardness increases.

RESULTS AND DISCUSSION

In lodge to draw a comparison between C60 and C59X (where, X= B, Al, Ga, In, N, P, As and Sb), C60 cluster was first considered. When a C atom of C60 is replaced by a dopant atom, this dopant atom

TABLE 1 : The changes in HOMO, LUMO, HOMO-LUMO gap [ΔE (eV)] and total energy (a.u) of C60 and C59X (X=B, Al, Ga and In), which calculated at B3LYP/3-21G** level of theory

Molecule	Electronic States (eV)		ΔE (eV)	Total Energy (a.u)
	E LUMO	E HOMO		
C60	-3.5	-6.51	3.01	-2273.521324
C59B	-4.52	-6.15	1.63	-2281.328226
C59Al	-4.35	-5.8	1.45	-2476.72808
C59Ga	-4.43	-5.87	1.44	-4151.210291
C59In	-4.37	-5.79	1.42	-7953.20446

can occupy carbon site, and they are designated as C59X.

TABLE 1, shows the changes in HOMO, LUMO, HOMO-LUMO gap (eV) and total energy (a.u) parameters for C59B, C59Al, C59Ga, and C59In, which obtained with DFT level calculations at B3LYP/3-21G** and compared them with C60.

Calculated HOMO, LUMO, HOMO-LUMO gap (eV) and total energy (a.u) of C60 and C59X (X=N, P, As and Sb), at DFT-B3LYP/3-21G** level of theory, presented in TABLE 2.

The presence of substituent decreases the energy gaps improves the conductivities and also raises the solubility of these molecules. The LUMO-HOMO energy gaps of C59X (X=B, Al, Ga, In, N, P, As and Sb), molecules is less than that of C60 molecule, with decreasing energy gap, electrons can be easily excited from the ground state. An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap.

As ΔE decreases the reactivity of the molecule leading to increase in the inhibition efficiency (%IE) of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to transfer an electron from the last occupied orbital will be low^[37]. A molecule with a low energy gap is more polarizable and is mostly affiliated with the high chemical activity and low kinetic stability and is termed soft molecule^[38]. The consequences as indicated in TABLE 1 and TABLE 2 show that all C59X have the low energy gap, this implies that the molecule (C60) could experience more honest functioning as a corrosion inhibitor by the substitution with heavier elements ongoing from B to In and from N to Sb. The total energy of the best inhibitors C59In and C59Sb are equal to -

TABLE 2 : The changes in HOMO, LUMO, HOMO-LUMO gap [ΔE (eV)] and total energy (a.u) of C60 and C59X (X=N, P, As and Sb), which calculated at B3LYP/3-21G** level of theory

Molecule	Electronic States (eV)		ΔE (eV)	Total Energy (a.u)
	E LUMO	E HOMO		
C60	-3.5	-6.51	3.01	-2273.521324
C59N	-3.8	-4.94	1.14	-2290.048084
C59P	-3.85	-4.59	0.74	-2575.328175
C59As	-3.97	-4.66	0.69	-4460.994627
C59Sb	-4.564	-4.65	0.086	-8524.419827

7953.20446 a.u. and -8524.419827 a.u., respectively.

Quantum chemical parameters are held from the computations which are responsible for the inhibition efficiency of inhibitors such as the electronic, chemical potential (μ), electronegativity (χ), electron affinity (EA), global hardness (η), softness (S), ionization potential (IP) and global electrophilicity index (ω) are collected in TABLE 3 and TABLE 4.

We recognize that the HOMO-LUMO gap and the global hardness are the index of chemical reactivity and the chemical potential measures the electron-escaping tendency from a molecule. From TABLES 3 and 4 we can see that, the molecule of the larger HOMO/LUMO energy gap, the harder the molecule. The hardness is a measure of the resistance of a chemical system species to changes in its electronic configuration, and it is thought to be an indicator of stability^[39].

The larger the hardness, the more stable the compound. The global electrophilicity index, ω is also calculated and listed in TABLES 3 and 4.

The results showed that the ionization potential of the C60 molecule is greater than that for the C59X molecules (X=B, Al, Ga and In), this indicates that when the doped C60 molecule with X=B, Al, Ga and In, needs low energy to become cation comparing with the C60. Likewise, for the C59X molecules (X= N, P, As and Sb).

The effectiveness of an acceptor molecule is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO^[40]. An acceptor must have a high EA, adding the dopant X (X=B, Al, Ga and In), to C60 leads to increasing the power of the electron affinity for the particle, as demonstrated in TABLES 3 and 4.

The behavior of electronegativity, softness and

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TABLE 3 : Comparison of some molecular properties of C60 and C59X (X=B, Al, Ga and In), by performing the DFT using the standard 3-21G** basis set at the level of B3LYP of theory

Molecule	IP (eV)	EA (eV)	η (eV)	μ (eV)	χ (eV)	S	ω
C60	6.51	3.5	1.505	-5.005	5.005	0.664451827	8.322267442
C59B	6.15	4.52	0.815	-5.335	5.335	1.226993865	17.46148773
C59Al	5.8	4.35	0.725	-5.075	5.075	1.379310345	17.7625
C59Ga	5.87	4.43	0.72	-5.15	5.15	1.388888889	18.41840278
C59In	5.79	4.37	0.71	-5.08	5.08	1.408450704	18.17352113

TABLE 4 : Comparison of some molecular properties of C60 and C59X (X=N, P, As and Sb), by performing the DFT using the standard 3-21G** basis set at the level of B3LYP of theory

Molecule	IP (eV)	EA (eV)	η (eV)	μ (eV)	χ (eV)	S	ω
C60	6.51	3.5	1.505	-5.005	5.005	0.664451827	8.322267442
C59N	4.94	3.8	0.57	-4.37	4.37	1.754385965	16.75166667
C59P	4.59	3.85	0.37	-4.22	4.22	2.702702703	24.06540541
C59As	4.66	3.97	0.345	-4.315	4.315	2.898550725	26.98438406
C59Sb	4.65	4.564	0.043	-4.607	4.607	23.25581395	246.7959186

TABLE 5 : Calculated the number of electrons transferred (ΔN) and the back-donation (ΔE Back-donation) of C60 and C59X (X= B, Al, Ga and In), by performing the DFT using the standard 3-21G** basis set at the level of B3LYP of theory

Molecule	ΔN	ΔE back-donation (eV)
C60	-0.199300699	-0.37625
C59N	-0.156044986	-0.20375
C59P	-0.189655172	-0.18125
C59As	-0.17961165	-0.18
C59Sb	-0.188976378	-0.1775

TABLE 6 : Calculated the number of electrons transferred (ΔN) and the back-donation (ΔE Back-donation) of C60 and C59X (X=N, P, As and Sb), by performing the DFT using the standard 3-21G** basis set at the level of B3LYP of theory

Molecule	ΔN	ΔE back-donation (eV)
C60	-0.199300699	-0.37625
C59N	-0.300915332	-0.1425
C59P	-0.329383886	-0.0925
C59As	-0.311123986	-0.08625
C59Sb	-0.259713479	-0.01075

electrophilic index for the studied molecules shows the magnitude larger than those for the original molecules C60, adding the dopants give the molecule more softness.

The number of electrons transferred (ΔN) was too calculated and tabulated in TABLES 5 and 6. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface^[41]. Therefore, the highest fraction of electrons transferred is associated with the best inhibitor, while the least fraction is associated with the inhibitor that holds the least inhibition efficiency.

In TABLE 5, the calculated ΔE back-donation values for C60 and C59X (X= B, Al, Ga and In), are heeled. The order followed is: C59X (X= B, Al, Ga and In) > C60, which indicates that back-donation is favored for the C59X (X= B, Al, Ga and In), which is the best inhibitor.

Also, in TABLE 6, the calculated ΔE back-donation values for C60 and C59X (X= N, P, As and Sb), are listed. The order followed is: C59X (X= N, P, As and Sb) > C60, which indicates that back-donation is preferred for the C59X (X= N, P, As and Sb), which is the best inhibitor.

The substitution of C60 with heavier elements ongoing from B to In and from N to Sb has the highest inhibition efficiency because it received the highest (ΔE Back-donation) values and lowest energy gap it was the most capable of offering electrons and it could bear a more serious performance as corrosion inhibitor.

CONCLUSIONS

Quantum chemical parameters are obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the electronic, chemical potential (μ), electronegativity (χ), electron affinity (EA),

global hardness (η), softness (S), ionization potential (IP), global electrophilicity index (ω), the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation ($\Delta E_{\text{Back-donation}}$) are have been predicted here. C60 could have more honest functioning as a corrosion inhibitor by the substitution with heavier elements ongoing from B to In and from N to Sb.

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