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Electronic properties of substituted $C_{59}X$ (X= C,B, Al,Ga, In) fullerene

Abdel-Baset H.Mekky[1]*, Hanan Elhaes[2], Mohamed M.El-Oker[3], Medhat A.Ibrahim[4]

[1]Buraydah Colleges, Al-Qassim, Buraydah King Abdulazziz Road East Qassim University,
P.O.Box 31717, (KING OF SAUDI ARABIA)
[2]Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757 Cairo, (EGYPT)
[3]Physics Department, Faculty Science, El Azhar University, Cairo, (EGYPT)
[4]Spectroscopy Department, National Research Centre, 12311, Dokki, Cairo, (EGYPT)
E-mail: hofny_a@yahoo.com

ABSTRACT

Hartree Fock (HF) and Density Functional Theory (DFT/B3LYP) were employed to study fullerene C_{60} and specific substitutions $C_{59}X$ (X= B, Al, Ga, In). HF and B3LYP with different basis sets were used to investigate the structure and electronic properties for fullerene and substituted fullerene molecules. Molecular point group for C_{60} and $C_{59}X$ is corresponding to C1 point group. The calculated C-C bond lengths for C_{60} decreased as the polarization function of the basis set increased. C-X bonds are in the range of 1.381–2.176Å. The bond angles C-C-C and C-X-C decrease monotonically down ongoing from B to In. The calculated energy gaps were 3.00 eV, 1.63eV, 1.45 eV, 1.44 eV and 1.42eV respectively for C_{60}, $C_{59}B$, $C_{59}Al$, $C_{59}Ga$ and $C_{59}In$. Generally substituted fullerene show a unique chemical site on its surface, which modify the electronic properties, then could be used as a reactive center. So that substituted fullerenes are possibility utilized as atom-like building units. This substitution allows the tuning of the physical and chemical properties of original molecule.

KEYWORDS

INTRODUCTION

Fullerenes (buckminsterfullerene) are discovered allotropes of carbon named after the scientist and architect Richard Buckminster Fuller, but were discovered in 1985 by a team of scientists from Rice University and the University of Sussex, three of whom were awarded the 1996 Nobel Prize in Chemistry[19].

Doped fullerenes have attracted a great deal of interest due to their remarkable structural, electronic, optical, and magnetic properties[3, 9]. The dopant atoms may be located (a) outside the cage, producing fulleride salts; (b) inside the cage, producing a sort of superatom; or (c) as part of the cage itself, replacing one or more of the carbon atoms in the cage network. Molecular nanoscale electronic devices have attracted a great deal of attention in recent years[23]. Carbon fullerene is one of the most stable and a well known nano-scale molecular structure; C_{60} often acts as a semiconductor. For electronic uses one of the main objectives in the

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doping of fullerenes is the production of p-type and n-type semiconductors materials. Fullerenes are known as excellent electron acceptors and can be chemically modified to improve solubility in organic solvents. Such soluble fullerene derivatives are known as some of the best n-type organic semiconductors[22].

Modeling techniques help to pave the way toward understanding the physical and chemical properties of fullerene derivatives as well as other materials[5,10]. Over the last few decades, there has been a major interest into development of computational programs to aid in solving real world chemical problems (e.g., for molecular geometries, spectroscopic values, transition states, and various thermodynamic properties). In the beginning, attempts to solve the time-independent Schrödinger equation for the electronic structure of a system were carried out through approximation techniques. One of the first methods used was called ab initio, "from the beginning," calculations. This method starts with the Schrödinger equation and makes approximations to construct Hamiltonians that can be solved. This gives approximate values from the selected wave functions when the Schrödinger equation has too many variables to be solved exactly (i.e., for any system more complex than the hydrogen atom)[1]. Another method proposed early in the 1960's was Density Functional Theory, DFT. This method states that a good approximation for the wave functions can be found by using a function that defines the electron density about the nucleus or nuclei of the system[16, 18]. DFT was first used in the physics community and did not see much popularity with chemists until the late 1980's and early 1990's when computers became more powerful and easier to use and when "user friendly" computational software packages (i.e., Gaussian, Spartan, etc.) became more readily available[6].

In this paper, the electronic properties of C_{60} and some of its substitutions with some elements of group III (B, Al, Ga, In) will be studied. Accordingly both HF and B3LYP will be performed with the help of different bases sets.

COMPUTATIONAL DETAILS

As seen in Figure 1 the carbon atom number 60 is replaced separately with B, Al, Ga and In respectively. Accordingly the system under study is $C_{59}X$ where X is C, B, Al, Ga and In.

All calculations were carried out using Gaussian 98 suite of program[6] without imposing any external constraints. HF and B3LYP methods were utilized using different basis sets namely STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G** respectively. In the first step, geometry optimizations were performed for C_{60} using the basis sets, STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G** respectively. Then geometries of substituted fullerenes were further optimized using B3LYP with 3-21G** basis set. The results of a (B, Al, Ga, In) (p-type) substitution in C_{60} are reported. Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated at the same level of theory.

RESULTS AND DISCUSSION

First, the geometries were fully optimized for C_{60} with HF and B3LYP. The effects of basis sets were regarded by considering STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G** respectively. Then one level of theory is chosen to discuss the effect of substitutions.

Optimized bond lengths and bond angles of C_{60}

TABLE 1 shows the calculated bond lengths and bond angles for C_{60}, which calculated by HF and B3LYP methods with different basis sets. The obtained results were compared with those available in the literature. C_{60} has only one unique atom and two different bond distances. The calculated data by HF and B3LYP of minimal value of bond lengths, minimal value of bond angles and maximal value of bond angles between carbon atoms) are in agreement with previous investigations[2]. So that HF and B3LYP methods are accurate enough for the geometry optimization of C_{60} molecule. The basis sets by considering STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G** are used to test its influence on the geometrical parameters. In comparison between these different basis sets as shown in TABLE 1, the calculated C-C bond lengths for C_{60} decreased as the basis size or as the polarization function included. This took place on going from

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STO-3G to 6-31G**. Generally the bond lengths obtained with basis sets in combination with B3LYP are in most cases in good agreement with previous investiga-

tions[7, 25]. The angles of C-C-C are varied from 108°-120° and it is in a good agreement with the results reported in the literature[20, 28].

TABLE 1 : Calculated bond lengths (Å) and bond angles (°) for C$_{60}$, which calculated by HF and B3LYP methods with different basis sets

Basis set	HF				B3LYP				Reference			
	CC^a	CC^b	CCC^c	CCC^d	CC^a	CC^b	CCC^c	CCC^d	CC^a	CC^b	CCC^a	CCC^b
STO-3G	1.376	1.463	108	120	1.412	1.478	108	120	1.391[2]	1.455[2]	108[20.28]	120[20.28]
3-21G	1.367	1.453	108	120	1.390	1.460	108	120				
3-21G*	1.367	1.453	108	120	1.390	1.460	108	120				
3-21G**	1.367	1.453	108	120	1.385	1.464	108	120				
6-31G	1.375	1.452	108	120	1.398	1.459	108	120				
6-31G*	1.373	1.449	108	120	1.392	1.455	108	120				
6-31G**	1.373	1.449	108	120	1.396	1.454	108	120				

(a) Minimal value of bond length between carbon atoms; (b) Maximal value of bond length between carbon atoms (c) Minimal value of bond angle between carbon atoms; (d) Maximal value of bond angle between carbon atoms

Optimized bond lengths and bond angles substituted fullerenes

In order to make a comparison between C$_{60}$ and C$_{59}$X (where, X= B, Al, Ga, In), C$_{60}$ cluster was first studied. When a carbon atom of C$_{60}$ is replaced by a dopant atom, this dopant atom can occupy carbon site, and they are designated as C$_{59}$X.

TABLE 2, shows the optimized geometrical parameters for C$_{59}$B, C$_{59}$Al, C$_{59}$Ga, and C$_{59}$In, which obtained with DFT level calculations at B3LYP/3-21g** and compared them with C$_{60}$.

The various calculated C-X bonds are in the range of 1.381 to 2.176Å. The bond lengths for the larger atoms increased significantly. For example, C-X (min) bond lengths of C$_{59}$-B, C$_{59}$-Al, C$_{59}$-Ga and C$_{59}$-In amount to 1.52, 1.879, 1.896 and 2.144 Å respectively. As it can be expected, bond lengths increase monotonically down the groups on going from B to In. The average bond length between C and its nearest-neighbor In atom C-In is larger than that between C and Ga atom (C-Ga), indicating the interaction between C and In atom (C$_{59}$-In) is the weakest. Similarly, (C$_{59}$-Ga) is weaker than (C$_{59}$-Al), and (C$_{59}$-Al) is weaker than (C$_{59}$-B). From these results, one can say that, the stability for the group is decreased by the substitution with the heavier elements. C$_{60}$ and C$_{59}$-B found to be the most stable for the group. As shown from TABLE 2, these values of average bond lengths are close to the

calculated values in substituted fullerenes[2, 24, 28]. The bond angles between C-C-C and C-X-C are also listed in TABLE 2 for fullerene and substituted fullerene. From the table it is found that the bond angles CCC and CXC decrease monotonically down the groups. The calculated bond angles for fullerene and boron substituted fullerene are in a good agreement with the calculated results from the literatures[20, 28]. Regarding C$_{59}$Al, C$_{59}$Ga, and C$_{59}$In the bond angles are a little bit smaller than those listed in the literatures[28]. This insures that C$_{60}$ and C$_{59}$B are more stable as compared with C$_{59}$Al, C$_{59}$Ga, and C$_{59}$In.

TABLE 2 : Calculated bond lengths (Å) and bond angles (°) for C$_{60}$ and substituted fullerenes, which calculated at B3LYP/3-21g** level of theory

	C$_{60}$	C$_{59}$-B	C$_{59}$-Al	C$_{59}$-Ga	C$_{59}$-In
CC (min)	1.385	1.387	1.383	1.382	1.381
CC (max)	1.464	1.496	1.528	1.527	1.518
CX (min)	------	1.520	1.879	1.896	2.144
CX (max)	------	1.548	1.899	1.926	2.176
Reference	1.391-1455[2]	1.43-1.54[2]	1.872-1.933[28]	1.875-1.943[28]	2.069-2.138[28]
CCC(min)	108	107.3	105.9	105.8	106.2
CCC(max)	120	122.1	125.6	126.2	126.3
CXC(min)	------	106.1	94	93.1	79.73
CXC(max)	------	118.7	117.6	116.6	115.1
Reference	108-120[20,28]	105.58-118.2[28]	90.03-101.96[28]	90.62-103.99[28]	80.85-90.244[28]

X=B, Al,Ga, and In

TABLE 3 : Calculated bond lengths (Å), molecular point group for C_{60} as well as substituted C_{60}, which calculated at B3LYP/3-21g**

Bond length, Å	C_{60}	$C_{59}B$	$C_{59}Al$	$C_{59}Ga$	$C_{59}In$
$D_{60} C_1$	1.385	1.52	1.879	1.896	2.144
$D_{60} C_5$	1.464	1.548	1.899	1.926	2.176
$D_{60} C_{16}$	1.464	1.548	1.899	1.926	2.176
Molecular point Group	C_1	C_1	C_1	C_1	C_1

D = C, B, Al, Ga and In respectively

From TABLE 3 it is noticed that in fullerenes every atom makes three bonds with its neighboring carbon atoms. There are two types of bond lengths (two hexagons and one pentagons), as example, for $C_{59}B$ the boron atom makes three bonds with carbon atoms number 1, 5 and 16 respectively. B_{60}-C1=1.520 Å, B_{60}-C5 = 1.548 Å and B_{60}-C16 =1.548 Å. Molecular point group for C_{60}, $C_{59}B$, $C_{59}Al$, $C_{59}Ga$ and $C_{59}In$ is corresponding to C1 point group which means rotation by 2π angle. Figure 1 shows the fragment of substituted buckminsterfullerene C_{60} structure and the bonds between carbon atom and the other neighboring atoms.
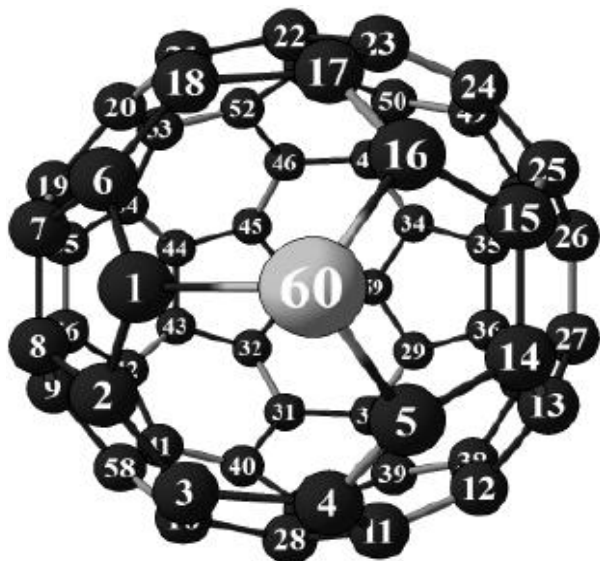

Figure 1 : Buckminsterfullerene C_{60} structure indicating the atom which is substituted with B, Al, Ga and In respectively

Calculated energy gap for C_{60}

Energy gap in this work is calculated as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the unit of eV. TABLE 4 shows the calculated energy gap for C_{60} which calculated by HF and B3LYP methods with different basis sets.

TABLE 4 : Calculated HOMO/LUMO energy gap as (eV) for C_{60} which calculated with HF and B3LYP methods with different basis sets

Basis set	HF	B3LYP	Reference[31]
STO-3G	8.66	3.23	2.2553
3-21G	7.70	2.94	
3-21G*	7.70	2.94	
3-21G**	7.70	3.01	
6-31G	7.54	2.87	
6-31G*	7.42	2.89	
6-31G**	7.65	5.99	

The energy gap is found for C_{60} to be around 3.00 eV. This slightly large energy gap indicates that C_{60} is thermally stable. By comparing the calculated energy gap for C_{60} which shown in TABLE 4 with different basis sets, it is found that the energy gap which obtained by B3LYP are in most cases in a good agreement with previous investigations[31]. The value of energy gap calculated by HF was found to be larger than that listed in the previous investigations.

Calculated energy gap for substituted fullerenes

TABLE 5 shows the calculated energy gap for C_{60} and substituted fullerene, which calculated at B3LYP/3-21g** level of theory.

TABLE 5 : Calculated HOMO/LUMO energy gap as (eV) for C_{60} and specific fullerene derivatives, which calculated at B3LYP/3-21g** level of theory

	C_{60}	$C_{59}B$	$C_{59}Al$	$C_{59}Ga$	$C_{59}In$
Energy gap	3.01	1.63	1.45	1.44	1.42
Reference	2.26[31]	2.04[28]	1.82[28]	1.80[28]	1.47[28]

(a) Tomekia et al., 2005; (b) Zou Y. et al., 1998

The energy gaps are found to be 1.63 eV, 1.45 eV, 1.44 eV and 1.42 eV for $C_{59}B$, $C_{59}Al$, C_{59} Ga and $C_{59}In$ respectively. These values are much smaller than that (3.01 eV) of C_{60}. Accordingly the energy gaps of all the studied $C_{59}X$ clusters are associated with the chemical stabilities against electronic excitation, are smaller than C_{60}. These results are nearly in agree with the values mentioned before[28, 31]. From the results one can say that electrons in all $C_{59}X$ clusters are easier to excite from the HOMO to the LUMO than in the case

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of C$_{60}$. Furthermore the stability for the group is decreased by the substitution with heavier elements ongoing from B to In.

Replacing one C by B atom, one hole is doped in the HOMO of C$_{60}$. Obviously, these substituted doping destroy the special symmetry of the C$_{60}$ molecule and make the energy degeneracy much reduced. Thus, there exist a possibility to produce a semiconductor components C$_{59}$X (where, X "dopant"= B, Al, Ga and In) with various band gaps[17, 24].

CONCLUSION

The geometries and electronic properties of C$_{60}$ and substituted fullerene were fully optimized by using both HF and B3LYP methods. C$_{60}$ has only one unique atom and two different bond distances. The calculated bond lengths and bond angles are in agreement with previous investigations. Also the effects of basis sets for both HF and B3LYP methods by considering STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G**were discussed. The B3LYP method and the accuracy of the applied calculations are good enough for the geometry optimization of C$_{60}$ molecule. And also for C$_{60}$ with different basis sets, it is found that the bond length decreases as basis size or including the polarization function.

For the various calculated CX bonds where X =B, Al, Ga, and In, the bond lengths for the larger atoms increased significantly. The stability of group III is decreased by the substitution with heavier elements on going from B to In.

The large energy gap (3.01 eV) indicates that C$_{60}$ is thermally stable. The energy gap obtained with the basis sets STO-3G, 3-21G, 3-21G*, 3-21G**, 6-31G, 6-31G*, and 6-31G** in combination with B3LYP methods are in most cases in good agreement with previous investigations. The energy gaps of C$_{59}$X clusters, which are associated with the chemical stabilities against electronic excitation, are smaller than in the case of C$_{60}$. It suggests that electrons in all C$_{59}$X clusters are easier to excite from the HOMO to the LUMO than in the case of C$_{60}$. Finally, the stability for the group is decreased by substitution with heavier elements. Accordingly there exists a possibility to produce semiconduct-

ing components from C$_{60}$X with various band gaps.

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