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DENSITY FUNCTIONAL THEORY CALCULATIONS OF THE EFFECT OF OXYGEN ATOMS ON THE ELECTRONIC PROPERTIES OF FULLERENE C_{60} MOLECULE

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ABSTRACT

Present work deals with the electronic properties of fullerene C_{60} cage and it is adducts. B3LYP-DFT hybrid functional was employed with 6-31G basis sets to study the effect of the oxygen atoms added on the electronic properties of fullerene C_{60} cage molecule. The electronic properties are calculated depending on Koopman's method. The results showed that the addition of oxygen atoms reduces the energy gap, but it is independent on the increasing of the added atoms. The new fullerenes have high activity to interact with the surrounding species.

Key words: HOMO, LUMO, Koopman^s theorem, Energy Gap.

INTRODUCTION

A cylindrical fullerene is called either carbon nanotube or Bucky tube while a spherical fullerene is known as a Buckyball[1-4]. Fullerene C_{60} consists of 60 carbon atoms arranged in twenty hexagons and twelve pentagons that form a perfectly symmetrical cage structure of a soccer ball with 1 nm size[5]. C_{60} molecule follows Euler's theorem where each fullerene consists of twelve pentagons and M hexagons containing 2(10+M) carbon atoms[6,7]. Each carbon atom is bonded to three other carbon atoms to form sp^2 hybridization and, consequently, entire C_{60} molecule is surrounded by electron clouds[8]. However, mass production of these carbon based nanoparticles was not possible until Kratchmer et al.[9] succeeded in synthesizing C_{60} by resistive heating method. Fullerene can be used as organic photovoltaic device[10-13]. Currently, the record efficiency for a bulk hetero-junction polymer solar cell is a fullerene-polymer blend. The fullerene acts as the n-type semiconductor (electron acceptor). The n-type is used in conjunction with a p-type polymer (electron donor)[14-17]. The epoxidation of fullerene can proceed readily in the presence of oxidants such as ozone[18], organic peroxide[19], dimethyldioxirane[20], methyltrioxorhenium-hydrogen

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peroxide[21], and cytochrome P450[22]. Under several circumstances, in different oxidations fullerene C_{60} has been shown to give higher oxides ($C_{60}O_n$, $n \geq 2$) that possess only a few regioisomers. For instance, although there are indeed eight possible regioisomers of $C_{60}O_2$ and 43 isomers of $C_{60}O_3$ given the multiple reaction sites available on the C_{60} cage[23], the actual products of most oxidations are only two isomers of $C_{60}O_2$ and three isomers of $C_{60}O_3$. Manoharan showed computationally that multiple epoxidations of C_{60} preferentially proceeds at the adjacent rather than distant double bonds of the existing epoxide group, and predicted that multiple epoxidations should occur on one benzenoid ring of C_{60} to form the $C_{60}O_3$ isomer with C_{3v} symmetry, Feng et al.[24] studied three isomers of $C_{60}O_3$ by using the semiempirical quantum mechanical INDO method, which is used in the previous studied in semiconductor[25] and predicted that the three types of $C_{60}O_3$ isomers with C_{3v}, C_s and C_2 symmetries, respectively, should be very stable, and reported their calculated electronic spectra[28]. Curry et al.[26] predicted that the three lowest-energy isomers (C_{3v}, C_s and C_2) of $C_{60}O_3$ should exist in equilibrium at room temperature by using a modified and extended Hűckel method. In this work, the set of molecules $C_{60}O_n$; $n > 2$ are studied using density functional theory (DFT). DFT is an efficient method to fine-tune the structural stability and electronic properties of some nanostructures[27-29].

Theory

GAUSSIAN 09 package of programs was used to performed the calculations. Full geometry optimizations of fullerene C_{60} and it is adducts were performed with Berny optimization algorithm[30,31]. The gradient corrected density functional methodology was employed Becke's exchange functional (B) and Becke's three-parameters adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee-Yang-Parr correlation functional B3LYP. While the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP contains an admixture of HF exchange. The B3 functional contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange[32]. The standard 6-31G basis set was used for orbital expansion to solve the Kohn–Sham equations in all cases. The computed stationary points for which the structures and force fields are presented correspond to real minima on the molecular potential energy hyper surfaces. The DFT (LUMO-HOMO) energy for the fullerene C_{60} molecule and it is adducts was calculated at the same level of theory[32-34]. The new fullerenes are $C_{60} + O_n$; $n > 2$.

RESULTS AND DISCUSSION

Fig. 1 illustrates the relax structures of the fullerene molecule and it is adducts under study in this work. DFT-B3YLP/6-31G (d, p) was used to investigate the electronic properties of the molecules after the relaxation. Fullerene C_{60} is the base molecule labeled 1, and the others six molecules are labeled (Molecules 2-7) due to addition the oxygen atoms to the fullerene molecule.

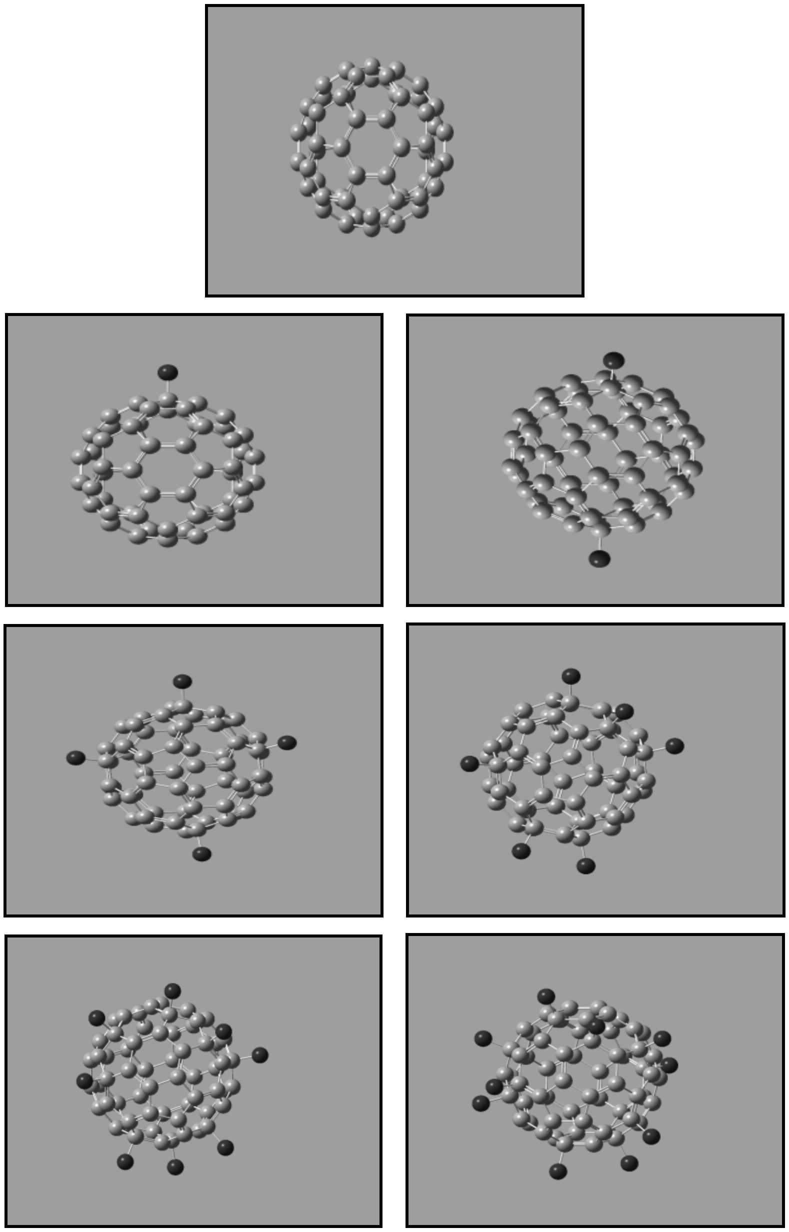

Fig. 1: The relaxed structures of fullerene C_{60} and it is adducts from DFT

The results of the relaxation of the studied structures are shown in Table 1. The investigated electronic properties are carried out by performing the three parameters

Lee-Yang-Parr B3LYP at 6-31G level of density functional theory. These properties are included the total energy ET in a. u, ionization energy IE, electron affinity EA, electrochemical hardness H and electrophilic index Win eV calculated according to Koopmans's theorem.

Table 1: The calculated energies of fullerene C_{60} and it is adducts from DFT

Molecule	ET (a.u)	IE (eV)	EA (eV)	H (eV)	W (eV)
1	-2285.5	6.2484	3.3752	1.4366	16.6311
2	-2360.732	6.2294	3.5088	1.3603	16.1250
3	-2435.883	6.252	3.5907	1.3306	16.1139
4	-2586.167	6.3173	3.8117	1.2528	16.0666
5	-2736.445	6.7551	3.7575	1.4988	20.7049
6	-2886.766	6.7151	4.5066	1.1042	17.3818
7	-3037.059	6.7570	4.7711	0.9929	16.4950

The behavior of the total energy ET as a function of the number of oxygen atoms added to the fullerene C_{60} molecule was shown in Fig. 2. The total energy of new fullerene molecules group is less than the total energy of the base fullerene C_{60} cage molecule. The total energy is linearly decreased with increase the number of oxygen atoms added to fullerene C_{60} cage molecule. From the linear relation in Figure 2, we can found that the total energy ET of the fullerene molecules group is approximately the summation of ET of fullerene C_{60} and ET of the number (n) of oxygen atoms added to the fullerene, means:

$$ET = Et\ (\text{Fullerene } C_{60}) + nET\ (\text{Oxygen atom})$$

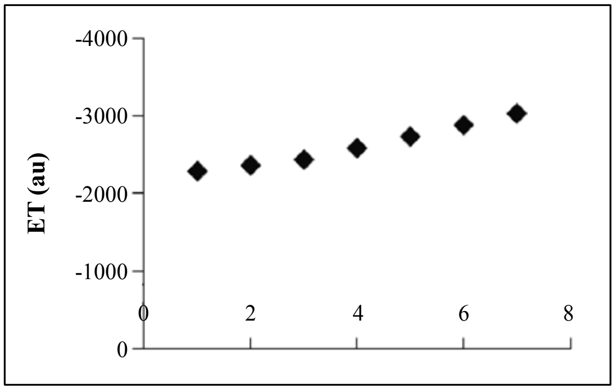

Fig. 2: The total energy of fullerene C_{60} and it is adducts

The results of the ionization energy IE and electron affinity EA as functions of the number of oxygen atoms added to fullerene C_{60} cage molecule are illustrated in Figs. 3 and 4, respectively. The results showed that the IE is independent on the increase of added atoms to fullerene, molecule 2 has IE lower than that for fullerene C_{60}, molecule 2 has the lowest value of IE (6.229 eV), while all the others have high value of IE in comparison with fullerene C_{60}. Molecule 2 needs small energy to donating electron and becomes anion. Figure 4 showed that the new fullerene molecules group have high value of EA in comparison with the base fullerene C0 molecule. Molecule 7 has the highest, means small energy is required to this molecule to acceptance electron. The results of IE and EA are global electronic properties, they are not coming from the frontier molecular electronic states.

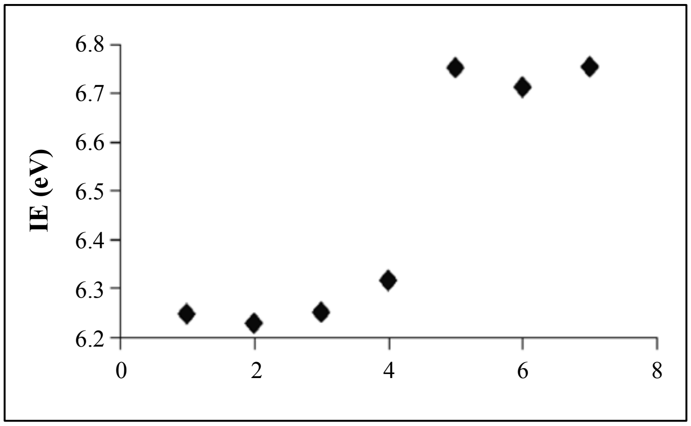

Fig. 3: The IE of fullerene C_{60} and it is adducts

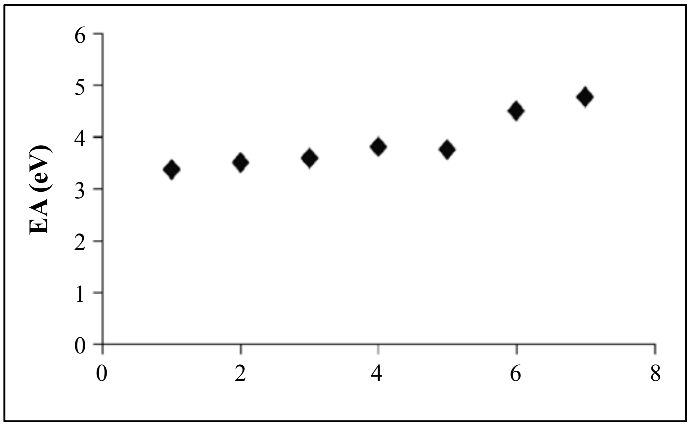

Fig. 4: The EA of fullerene C_{60} and it is adducts

The results of electrochemical hardness H and electrophilic index W of the fullerene C_{60} cage molecule and it is adducts are illustrated in Figs. 5 and 6, respectively. From Fig. 5, all new fullerene molecules group have electrochemical hardness less than that for fullerene C_{60} molecule, they are more soft than the base fullerene C_{60} cage molecule except molecule 5, it has large value of Hin comparison with fullerene C_{60}. The decreasing of electrochemical hardness is the main future and refers to that band gap goes to be rather soft and lowering the resistance of these structures to lose an electron. The electrophilic index in figure 6 showed that molecules 5 and 6 have the larger value of W. They are more active for interacting with other species than the base fullerene C_{60}.

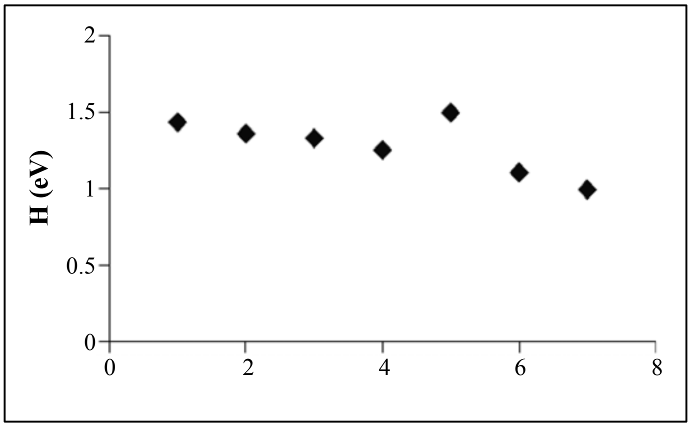

Fig. 5: The H of fullerene C_{60} and it is adducts

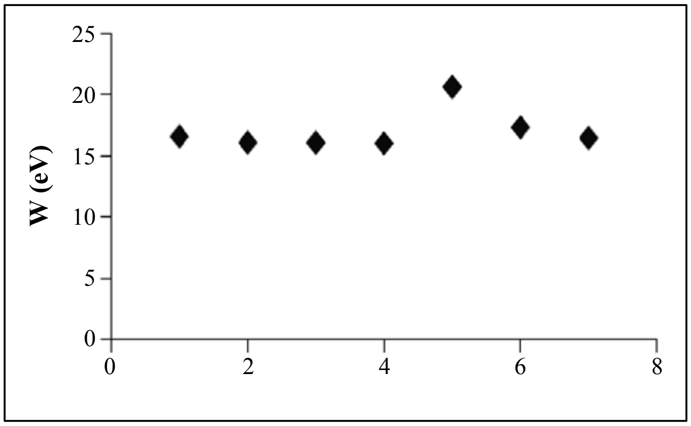

Fig. 6: The W of fullerene C_{60} and it is adducts

The calculated values of the electronic states (high occupied molecular orbital energy E_{HOMO} and lower unoccupied molecular orbital energy E_{LUMO}) and the energy gap E_g of fullerene molecules group are listed in Table 2. The influence of added oxygen atoms to the fullerene C_{60} on the energies of HOMO and LUMO showed that the effect on LUMO energy is more than on HOMO energy. The results of HOMO and LUMO effect on the calculated value of energy gap for each molecule. The energy gap was decrease from (2.873 eV) for fullerene C_{60} to (1.985 eV) for molecule 7. The mode of variation of the energy gap refers to that the energy gap of fullerene will be soft depends on the number of oxygen atoms added to fullerene C_{60} cage molecule, as we see in Fig. 7.

Table 2: The E_{HOMO}, E_{LUMO} and E_g of fullerene C_{60} and it is adducts

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg (eV)
1	-6.2484	-3.3752	2.8732
2	-6.2294	-3.5088	2.7205
3	-6.252	-3.5907	2.6613
4	-6.3173	-3.8117	2.5056
5	-6.7551	-3.7575	2.9976
6	-6.7151	-4.5066	2.9575
7	-6.7570	-4.7711	1.9859

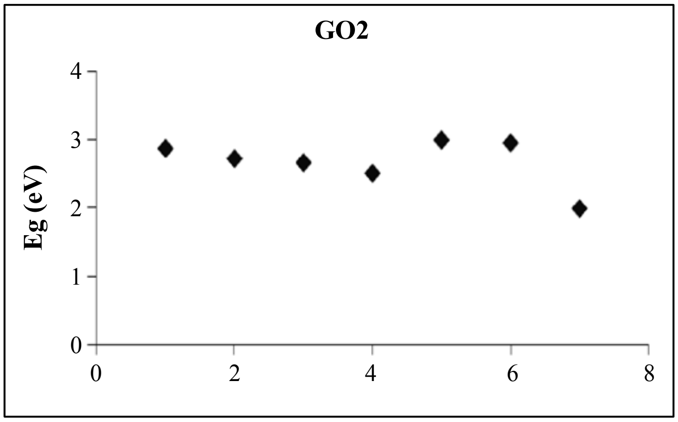

Fig. 7: The E_g of fullerene C_{60} and it is adducts

Table 3 shows the calculated values of total dipole moment in Debye and Polarizability in a. u for the fullerene C_{60} and it is adducts using density functional theory.

The results showed that the base fullerene molecule is high symmetry molecule, it has not dipole moment. Adding oxygen atoms to the fullerene gave the molecule to become dipolar molecule and the polarity was increased with increasing the added atoms to the fullerene. The average Polarizability was increased from (460.664 a. u) for fullerene C_{60} molecule to (542.785 a. u) for the last molecule 7. This result refers to that the new fullerenes have high activity to interact with the surrounding species.

Table 3: The dipole moment and polarizability of fullerene C_{60} and it is adducts

Molecule	Dipole moment D.M. (Debye)	Polarizability (a. u)			
		$_{xx}\alpha$	$_{yy}\alpha$	$_{zz}\alpha$	$<\alpha>$
1	0.000	460.692	460.719	460.693	460.664
2	1.8284	455.338	459.467	483.483	466.096
3	0.6398	454.556	460.111	505.947	473.538
4	0.8366	449.674	494.701	504.702	483.025
5	2.5282	455.102	485.454	524.918	488.491
6	3.6946	440.258	557.396	574.229	523.961
7	4.4813	435.406	584.274	608.675	542.785

CONCLUSION

From the above results, we concluded that total energy was decreased linearly with increasing the number of oxygen atoms added to the fullerene C_{60} cage molecule. The ionization potential of the fullerene is independent on the increase of added oxygen atoms to fullerene, molecule 2 has IE lower than that for fullerene C_{60}, molecule 2 has the lowest value of IE, while all the others have high value of IE in comparison with fullerene C_{60}. The new fullerene molecules group have high value of EA in comparison with the base fullerene C_{60} molecule. Molecule 7 has the highest, means small energy is required to this molecule to acceptance electron. All new fullerene molecules group have electrochemical hardness less than that for fullerene C_{60} molecule, they are more soft than the base fullerene C_{60} cage molecule except molecule 5, it has large value of H in comparison with fullerene C_{60}. Adding the oxygen atoms to the fullerene molecule leads to change both the HOMO and LUMO energies, the effect on LUMO energy is more than on HOMO energy. The mode of variation of the energy gap refers to that the energy gap of fullerene will be soft depends on the number of oxygen atoms added to fullerene C_{60} cage molecule. the new constructing fullerene molecules have high reactivity to interact with the surrounding media in compared with the base fullerene C_{60} cage molecule.

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