

Density Functional Theory Calculations of Effects Polycyano Subgroups on the Energies and Thermal Properties of Fullerene C60 Molecule

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Abstract

In this research, we are applying the hybrid functional B3LYP density functional theory to study the effects of the addition of polycyano subgroups on the energies and thermal properties of fullerene C60 cage molecule. The orbital vertical method was used to calculate the ionization energy, electron affinity and electronegativity. The results showed that the location and the subgroups number of cyano in fullerene molecule effect on these energies. So, this addition reduces the energy gap, that an indicates to construct new molecular electronic structures. The thermal energy, specifies heat and entropy of the fullerene is increased with the addition the cyano subgroups in the molecule.

Key words: DFT, Entropy, Enthalpy, Energy Gap, Polarizability.

الخلاصة

تم في هذا البحث تطبيق الدالة المهجنة B3LYP في نظرية دالية الكثافة لدراسة تأثيرات إضافة مجاميع من متعدد السيانيد على الطاقات والخواص الحرارية لجزيئة الفولرين كاريون 60. تم استخدام طريقة المدار المتعامد لحساب طاقة التأين، الالفة الالكترونية والكهروسالبية. تبين النتائج ان موقع وعدد مجاميع السيانيد في جزيئة الفولرين له تأثير على تلك الطاقات. كما أن تلك الاضافة قد خفضت فجوة الطاقة وهذا يدل على أنه تم بناء تراكيب الكترونية جزيئية جديدة. أن الطاقة الحرارية، الحرارة النوعية والانتروبي قد ازدادت مع إضافة مجاميع السيانيد الى الجزيئة.

الكلمات المفتاحية: نظرية دالية الكثافة، الانتروبي، الفجوة الطاقة، الاستقطابية

1- Introduction

Fullerene C60 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[Kroto *et al.*,1985]. C60 molecule follows Euler's theorem where each fullerene consists of twelve pentagons and M hexagons containing $2(10+M)$ carbon atoms[Hirsch and Brett, 2005]. Similarly arranged, other carbon cage structures such as C70, C76, C78, C84, and C90 has been also identified [Died *et al.*,1991]. Each carbon atom is bonded to three other carbon atoms to form sp^2 hybridization and, consequently, entire C60 molecule is surrounded by electron clouds[Buhl; Hirsch, 2001]. C60 has two different types of bonds; 6:6 bond which located in between two hexagon rings and 6:5 bond which located in between a hexagon ring and a pentagon ring and 6:6 bonds are considered as double bonds having shorter bonding length than 6:5 bonds [Buhl; Hirsch, 2001]. C60 molecule was first found in 1985 by Kroto *et al.* [Kroto *et al.*,1985] from the ablation of a graphite with energetic pulsed laser. However, mass production of these carbon based nanoparticles was not possible until Kratchmer *et al.*[Kratchmer *et al.*,1990;Pope *et al.*,1993] succeeded in synthesizing C60 by resistive heating method. Fullerene can be used as organic photovoltaic[Howard *et al.*,1991 ; Lois au, 2006]. Currently, the record efficiency for a bulk heterojunction 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)[Ellis *et al.*, 2000].

2- Theory

All calculations were performed with the GAUSSIAN09 suite of programs. Full geometry optimizations of fullerene C60 and cyano fullerene C60 molecules group

were performed with Berny optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates) [Yu *et al.*, 1998 ; Brabec *et al.*, 2001]. The gradient corrected density functional methodology was employed Becke's exchange functional (B) and Becke's three-parameter 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 one contains an admixture of HF exchange. The B3 functional contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange [Schlegel, 1985]. The standard 6-31G(d,p) basis set of DZP quality 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 poly cyano fullerene C₆₀ molecules group studied in this study was calculated at the same level of theory [Becke , 1988; Lee *et al.*, 1988].

3- Results and Discussion

There are six cyano fullerene C₆₀ molecules group studied in this study and labeled (2-7), and the fullerene is the reference molecule 1. The optimized structures of the mentioned molecules are represented by the optimized coordinates in Angstrom ($\text{\AA}$) for all atoms in these molecules 2-7. The optimized parameters of these molecules included bonds in Angstrom ($\text{\AA}$) and angles in degree calculated from DFT-B3LYP/6-31G(d,p). Figure 1 illustrates the optimized structures of the described molecules under study.

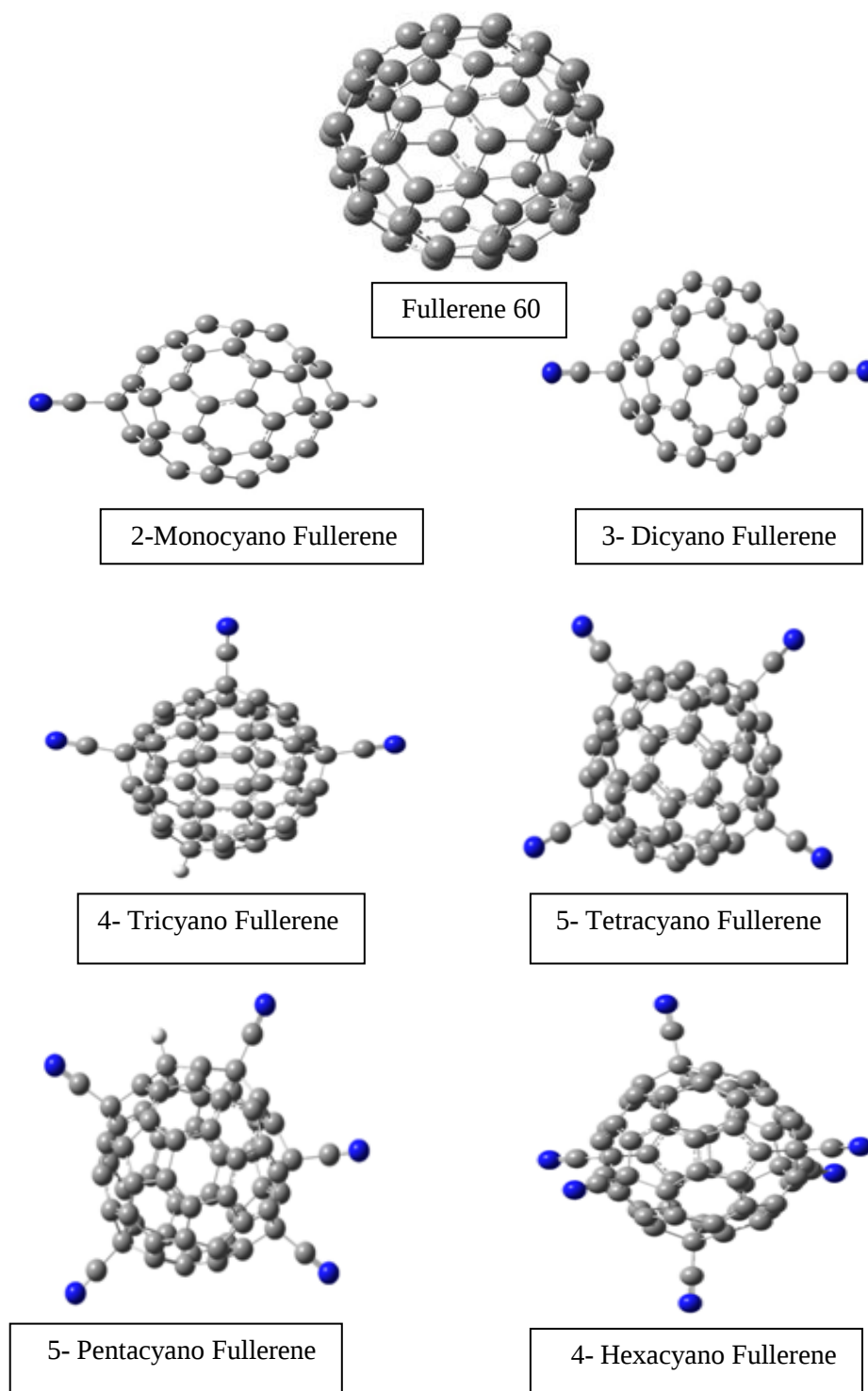


Figure 1: The optimized structures of cyano fullerene molecules group using DFT- B3LYP/6-31G(d, p).

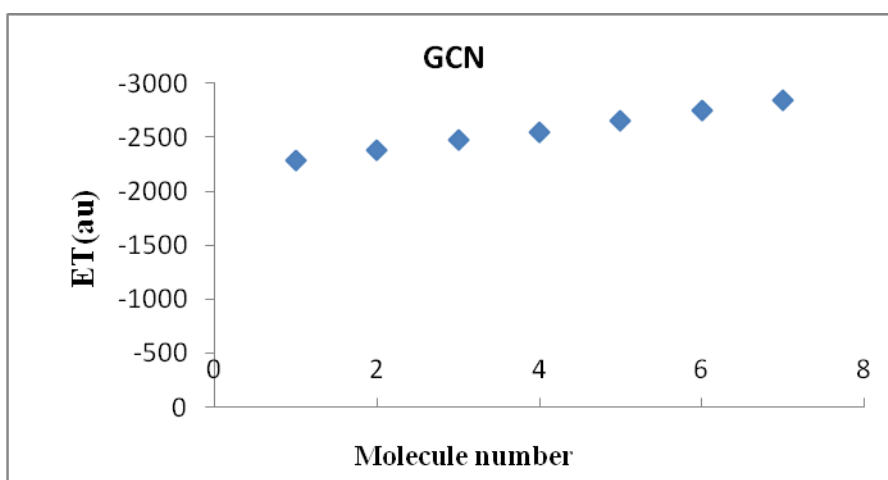
3-1The Computed Energies

Table 1 shows the results of the total energy E_T in a.u , and some computed energies in eV of cyano fullerene moleculesgroup, calculated depending on Koopmen's theorem. included the ionization energy IE , electron affinity EA and electronegativity X.

Table 1 : The calculated energies of cyano fullerene molecules group from DFT-B3YLP/6-31G(d, p).

Molecule	E_T (a.u)	IE(eV)	EA(eV)	X(eV)
1	-2285.5	6.2484	3.3752	4.8118
2	-2378.9	5.1363	4.5752	4.8558
3	-2471.1	5.5088	4.8802	5.1945
4	-2550.9	5.8073	4.8275	5.3172
5	-2656.6	5.9499	4.9839	5.4669
6	-2750.0	6.1632	5.1788	5.6710
7	-2842.2	6.2871	5.3053	5.7962

It is clear from table 1 that the total energy of cyano fullerenemolecules group is less than the total energy of the reference molecule 1 (fullerene C60). The total energy decreased with increase of CN groups number added to fullerene C60 molecule, as figure 2 illustrate this relation . From the linear relation in figure 1, one can found a simple equation associates the E_T of the cyano fullerenemolecules group and the CN groups number (n): $ET = ET(\text{fullerene C60}) + nET(\text{CN})$.

**Figure 1 : The relation between the total energy and CN groups number.**

Figures 2 and 3 show the behavior of ionization energy and electron affinity as a function of CN groups number, respectively. As seen in these figures, the cyano fullerene molecules groups have low values of IE and high values of EA in comparison with the reference molecule 1. Adding the CN group reduced the IE and increased the EA of the fullerene. Molecule 2 has the smallest value of IE, this means that molecule 2 needs a small energy to become cation in comparison with the others. These results are global properties and they are not coming from the frontier molecular electronic states. Molecule 7 has the higher value of EA in comparison with the others, as seen in figure 3, this indicates that, this molecule has high ability to acceptance an electron from the surrounding media.

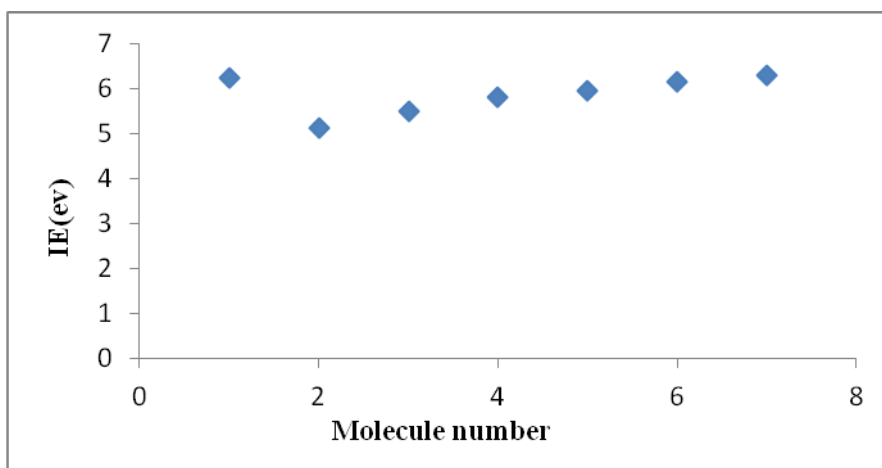


Figure 2 : The relation between the ionization energy and CN groups number.

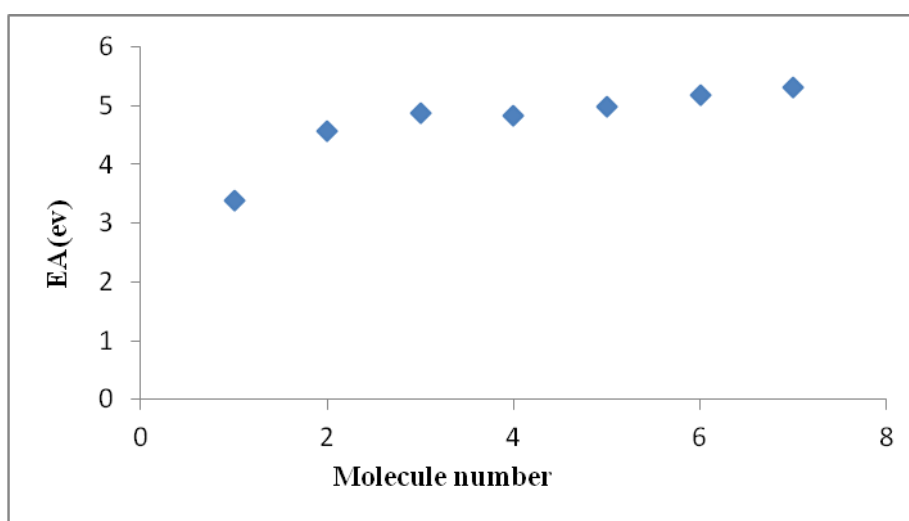


Figure 3 : The relation between the electron affinity and CN groups number.

Figure 4 illustrates the electronegativity X of the studied molecules 2-7 with the reference fullerene. It is obvious from this figure that all cyano fullerene molecules group have electronegativity more than that for fullerene molecule, that means these molecules have a large escaping tendency comes from the presence of cyano groups in the molecule, it is clear from this figure that the electro chemical hardness of all studied molecules is smaller than the original.

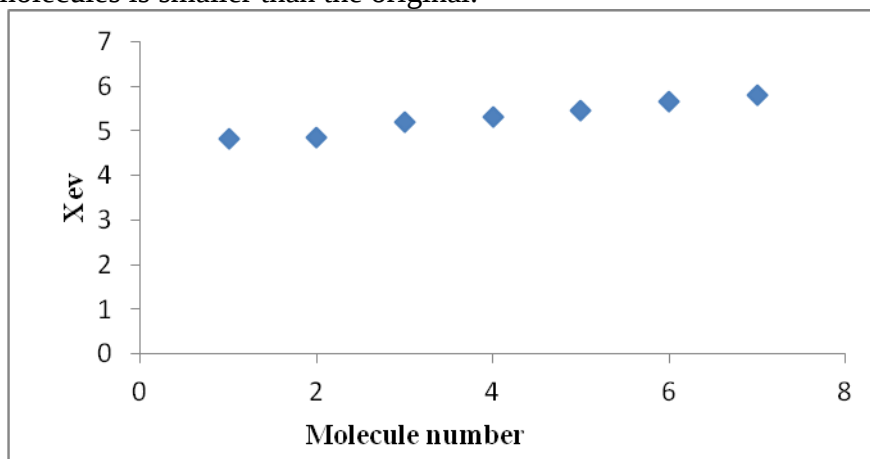


Figure 4 : The relation between the electronegativity and CN groups number.

3-2 Electronic States and Energy Gap

Table 2 illustrates the high occupied molecular orbital energy E_{HOMO} , lower unoccupied molecular orbital energy E_{LUMO} and the energy gap of cyano fullerene molecules group. Figures 5 and 6 show the effect of adding the CN groups on HOMO and LUMO energies, respectively. From these figures, the addition of cyano groups has effect on both HOMO and LUMO energies, but its effect on HOMO energy is more than on LUMO energy. Generally, the main change occurs at HOMO level and depends on CN groups number in the fullerene. The results showed that the energy gap of fullerene C60 cage molecule decreases with the addition of CN groups, but the least is at (hydroxyl fullerene). Figure 7 shows the variation mode of the energy gap, this variation indicates that the energy gap of fullerene will be soft depends on the number of cyano groups in the molecule.

Table 2 : The E_{HOMO} , E_{LUMO} and E_g of cyano fullerene molecules group from DFT-B3YLP/6-31G(d, p).

Molecule	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_g(\text{eV})$
2	-5.1363	-4.5752	0.5610
3	-5.5088	-4.8802	0.6285
4	-5.8073	-4.8275	0.9798
5	-5.9499	-4.9839	0.9659
6	-6.1632	-5.1788	0.9844
7	-6.2871	-5.3053	0.9817

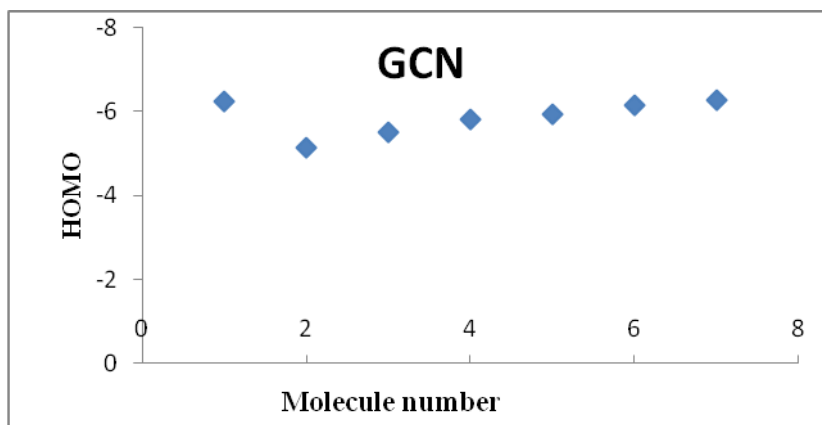


Figure 5 : The relation between the E_{HOMO} and CN groups number.

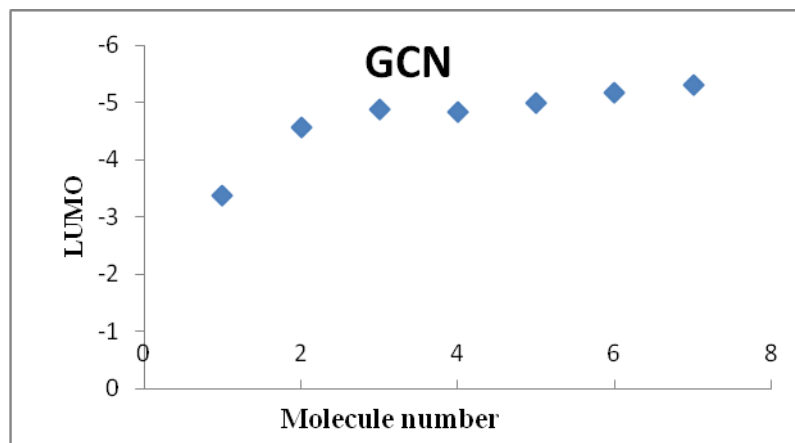


Figure 6 : The relation between the E_{LUMO} and CN groups number.

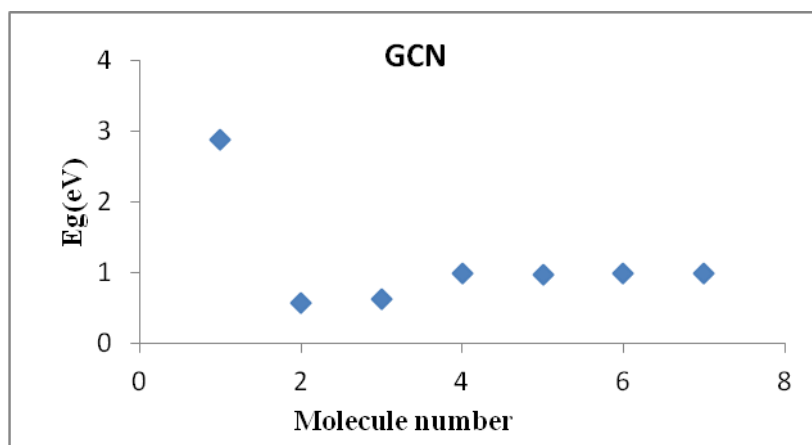


Figure 7 : The relation between the E_g and CN groups number.

The results in figures 5-7 mean the adding of the cyano subgroups effects on the density of states of the fullerene molecule. Poly cyano fullerene molecules has lower number of degenerate states in comparison with the original fullerene C60 molecule. Also, increasing number of cyano subgroups added to fullerene leads to lowering the degeneracy, this lowering of the degeneracy caused by the existence of the new types of atoms, and leads to varying the bond lengths and angles or changing the geometry of the structure.

3- 3 Total Dipole Moment and Polarizability

Table 3 illustrates the total dipole moment in Debye and Polarizability in a.u for cyno fullerene molecules group. This table showed that the addition of cyano groups to the fullerene C60 molecule changes the symmetric charge distribution and, therefore, changes the dipole moment of the molecule. This effect depends on the number of cyano groups in the fullerene molecule and corresponds to the symmetry point group for each molecule .

The calculated average polarizability and its componentes in table 3 declare that all cyano fullerene molecules group has a large values of polarizability in comparison with the reference fullerene C60 molecule and that an indicates to these molecules are more reactive in charge transfer with the surrounding media. This may a result of the presence of CN groups in the molecule. In which , they are in order of $azz > ayy > axx$ for all molecules .

Table 3: The calculated total dipole moment and Polarizability of cyano fullerene molecules group .

Molecule	Total D.M (Debye)	Polarizability(a.u)			
		xx (a.u) α	yy (a.u) α	zz (a.u) α	$\langle\alpha\rangle$ (a.u)
1	0.00	460.664	460.693	460.719	460.692
2	7.1574	479.942	515.146	697.296	564.128
3	0.0042	482.434	512.500	753.578	582.837
4	5.8815	478.839	587.592	615.544	560.658
5	2.5855	512.059	646.812	708.379	622.416
6	3.2658	490.560	708.114	731.489	643.387
7	2.4754	658.622	662.873	670.750	664.081

3- 4 Thermal Properties

Table 4 declares the thermal corrections values calculated for the cyano fullerene molecules group, included the corrections to energy, enthalpy and Gibbs free

energy with the zero-point energy ZPE. To calculate the total energies, enthalpies and Gibbs free energies, the total electronic energies of the studied structures are added to the thermal corrections. Table 5 shows this summation of thermal corrections. As seen in table 5, the summation of electronic energy and thermal correction for each terms was increased with increasing the number of cyano subgroups added to fullerene C60, that means these thermal energies depend on the molecular mass or on the number of atoms in the molecule. Figures 8-11 illustrate this dependence .

Table 4 : The summation of electronic energy and thermal corrections of cyanofullerene molecules group .

Molecule	Thermal corrections(Hartree/Particle)			
	Zero-point	Energy	Enthalpy	Gibbs Free energy
2	0.3963	0.4192	0.4202	0.3508
3	0.3941	0.4191	0.4200	0.3462
4	0.4058	0.4342	0.4351	0.3551
5	0.4118	0.4415	0.4424	0.3590
6	0.4315	0.4638	0.4647	0.3759
7	0.4290	0.4634	0.4643	0.3711

Table 5 : The summation of electronic energy and thermal corrections of cyanofullerene molecules group .

Molecule	Sum of thermal corrections(Hartree/Particle)			
	Zero-point energy	Thermal Energies	Thermal Enthalpies	Free Energies
1	-2285.210	-2285.189	-2285.188	-2285.252
2	-2378.516	-2378.493	-2378.492	-2378.562
3	-2470.713	-2470.688	-2470.687	-2470.761
4	-2550.588	-2550.560	-2550.559	-2550.639
5	-2656.262	-2656.233	-2656.232	-2656.315
6	-2749.593	-2749.561	-2749.560	-2749.649
7	-2841.798	-2841.764	-2841.763	-2841.856

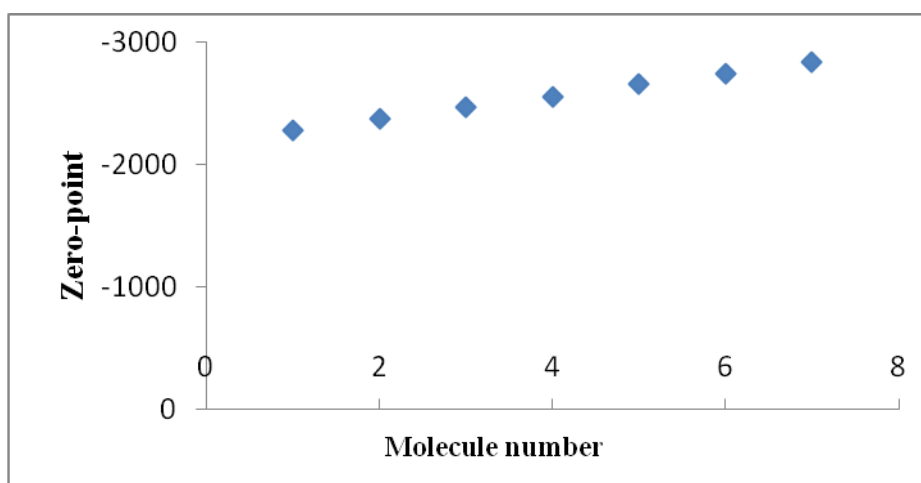


Figure 8 : The summation of electronic and Zero-Point energies as a function of cyano subgroups number.

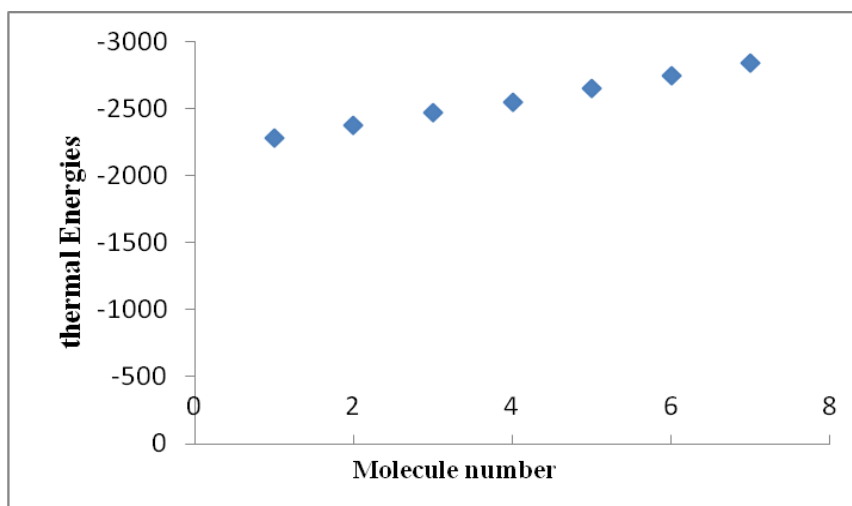


Figure 9: The summation of electronic and thermal energies as a function of cyano subgroups number.

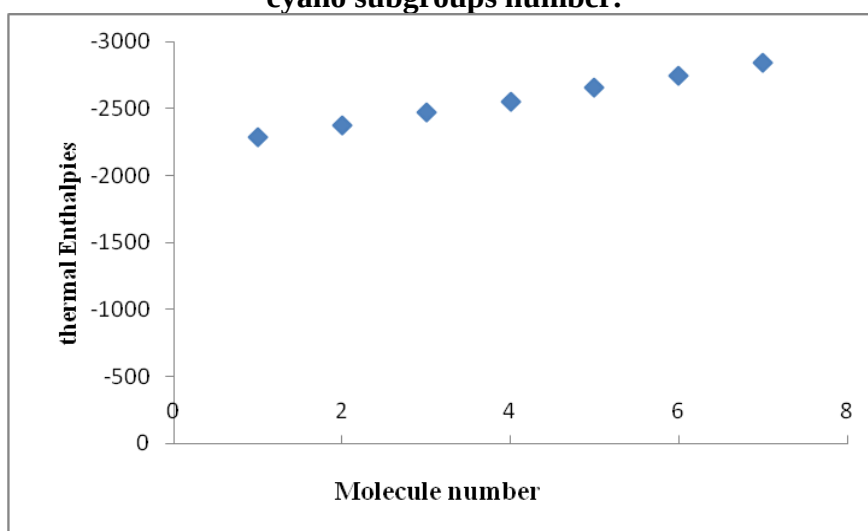


Figure 10 : The summation of electronic and thermal enthalpies as a function of cyano subgroups number.

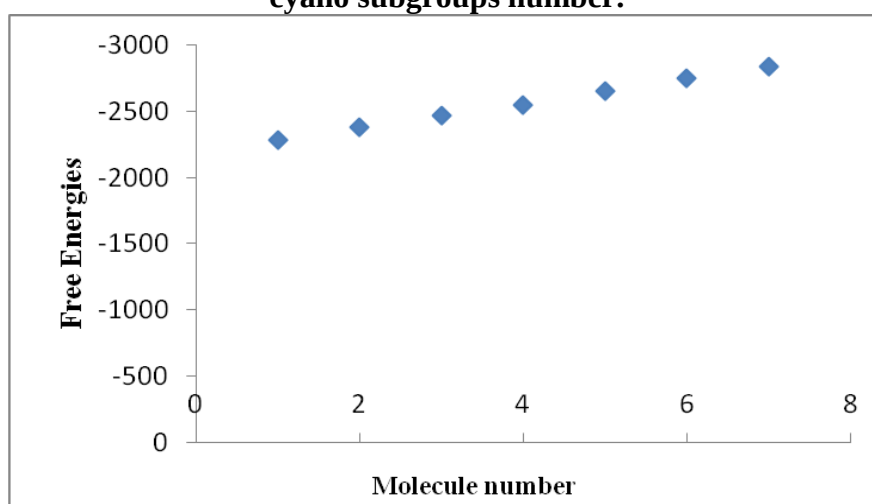


Figure 11 : The summation of electronic and free energies as a function of cyano subgroups number.

Table 6 declares the results of thermal properties of the cyano fullerene molecules group, included the translational and rotational energies with their components (thermal energy E_{th} , specific heat C_v and thermal entropy S_{th}). This table showed that the components of translation and rotation for E_{th} and C_v are not changed with the number of cyano subgroups added to the fullerene C60 molecule, they are independent of the number of atoms in the molecule. While the S_{th} components of translation and rotation energies are change due to the charge distribution according to the number and position of the cyano subgroups in the fullerene molecule, S_{th} was increased with increasing the number of electrons in the molecule. Figures 12 and 13 illustrate the S_{th} component of translational energy and rotational energy of cyano fullerene molecules group, respectively.

Table 6 : The components E_{th} , C_v and S_{th} of translational and rotational energies of cyano fullerene molecules group.

Molecule	Translational energy			Rotational energy		
	$E_{th}(\text{KCal/Mol})$	$C_v(\text{Cal/Mol-Kelvin})$	$S_{th}(\text{Cal/Mol-Kelvin})$	$E_{th}(\text{KCal/Mol})$	$C_v(\text{Cal/Mol-Kelvin})$	$S_{th}(\text{Cal/Mol-Kelvin})$
1	0.889	2.981	45.602	0.889	2.981	37.572
2	0.889	2.981	45.712	0.889	2.981	37.870
3	0.889	2.981	45.810	0.889	2.981	38.119
4	0.889	2.981	45.913	0.889	2.981	38.354
5	0.889	2.981	46.005	0.889	2.981	38.596
6	0.889	2.981	46.101	0.889	2.981	38.816
7	0.889	2.981	46.187	0.889	2.981	39.023

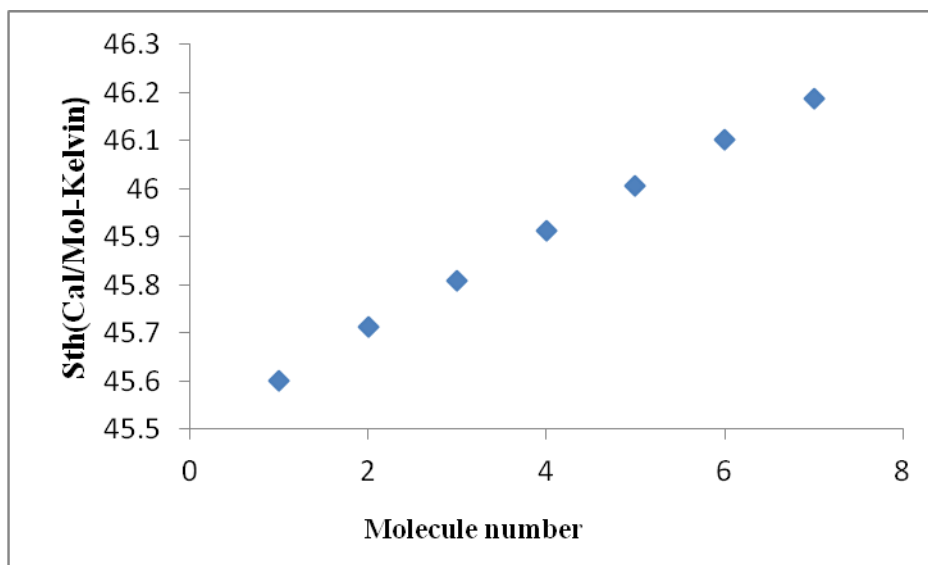


Figure 12 : S_{th} of translation energy as a function of cyano subgroups number .

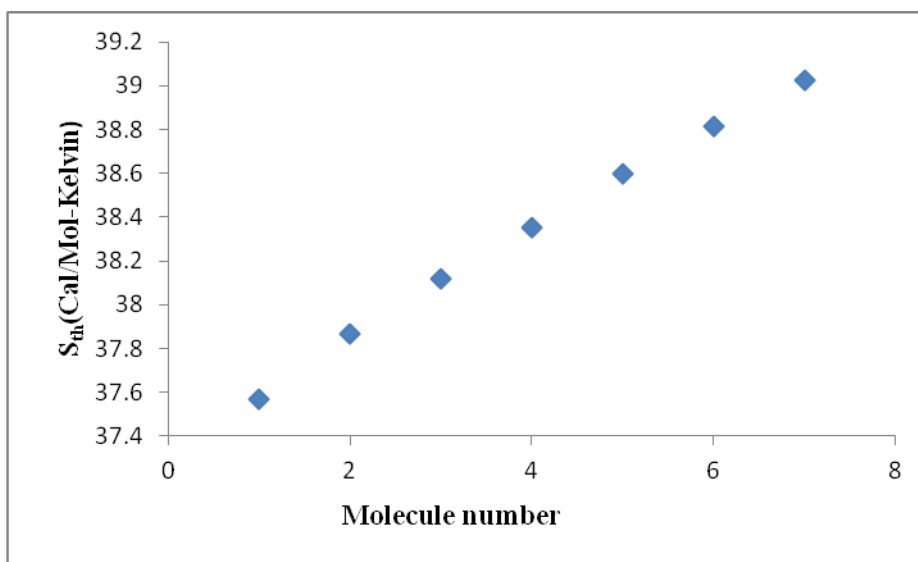


Figure 13 : S_{th} of rotation energy as a function of cyano subgroups number.

Table 7 illustrates the components E_{th} , C_v and S_{th} of vibrational energy. The results showed that, all the components E_{th} , C_v and S_{th} of vibrational energy are slightly increased with increasing the number of cyano subgroups added to fullerene, as seen in figures 14-16. This indicates that the vibrational energy depends on the number of vibrational modes, in which they are increase as the number of atoms increased. More therefore, the vibrational energy depends on the total number of electrons in the molecule. The increase of the vibrational energy as a function of cyano subgroups number leads to change the total energy of the molecule, the components E_{th} , C_v and S_{th} of total energy are increase with increasing the number of cyano subgroups, as seen in figures 14-16.

Table 7 : The components E_{th} , C_v and S_{th} of total energy and vibrational energy and of cyano fullerene molecules group.

Molecule	Totalenergy			Vibrationalenergy		
	E_{th} (KCal/Mol)	C_v (Cal/Mol-Kelvin)	S_{th} (Cal/Mol-Kelvin)	E_{th} (KCal/Mol)	C_v (Cal/Mol-Kelvin)	S_{th} (Cal/Mol-Kelvin)
1	250.428	112.272	134.130	248.650	106.310	50.955
2	263.110	122.257	146.018	261.332	116.295	62.436
3	263.004	128.890	155.374	261.226	122.928	71.444
4	272.498	142.318	168.544	270.721	136.356	84.277
5	277.075	144.454	175.704	275.298	138.492	91.103
6	291.044	153.716	186.972	289.266	147.754	102.055
7	290.810	160.229	196.313	289.032	154.267	111.103

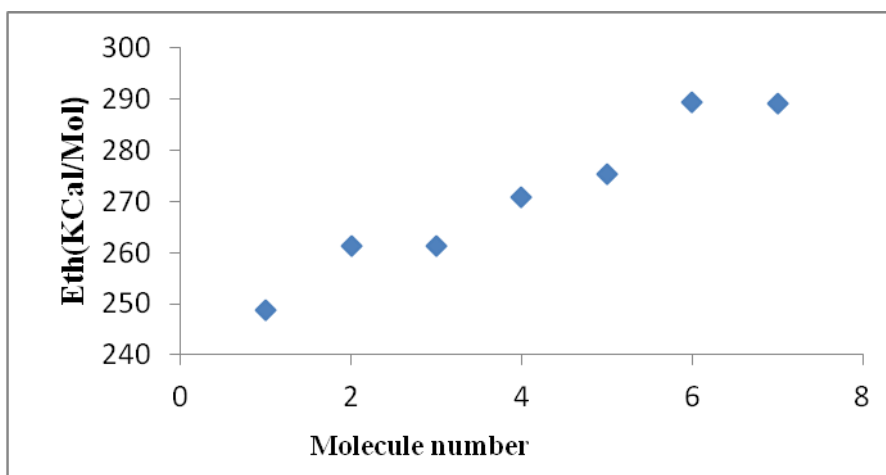


Figure 14 : E_{th} of vibrational energy as a function of cyano subgroups number.

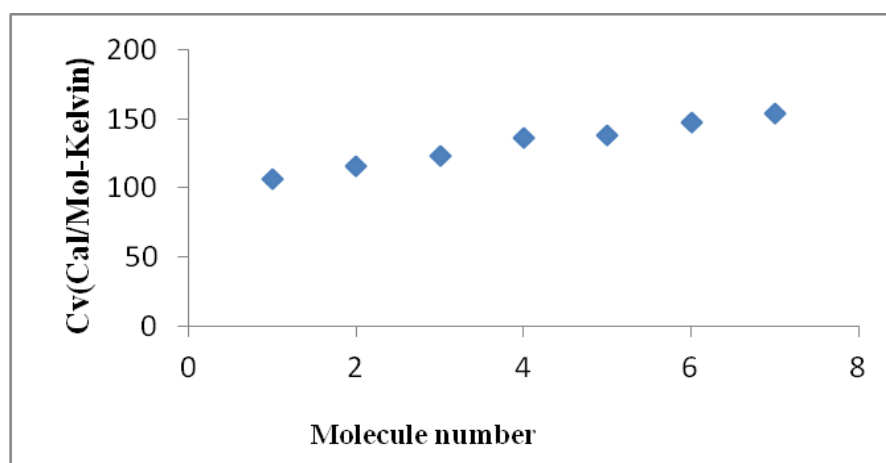


Figure 15 : Cv of vibrational energy as a function of cyano subgroups number.

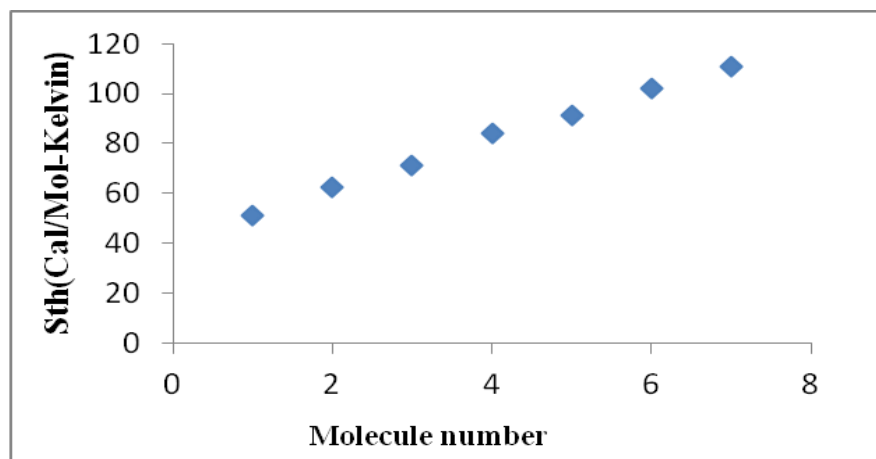


Figure 16 : Sth of vibrational energy as a function of cyano subgroups number.

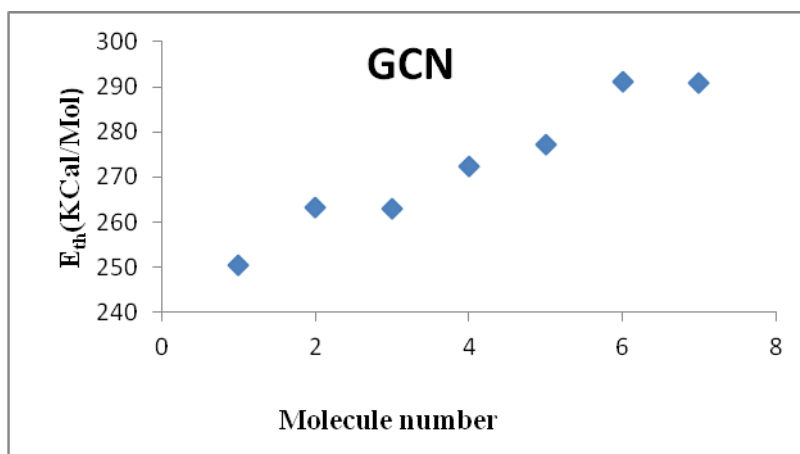


Figure 17 : E_a of total energy as a function of cyano subgroups number.

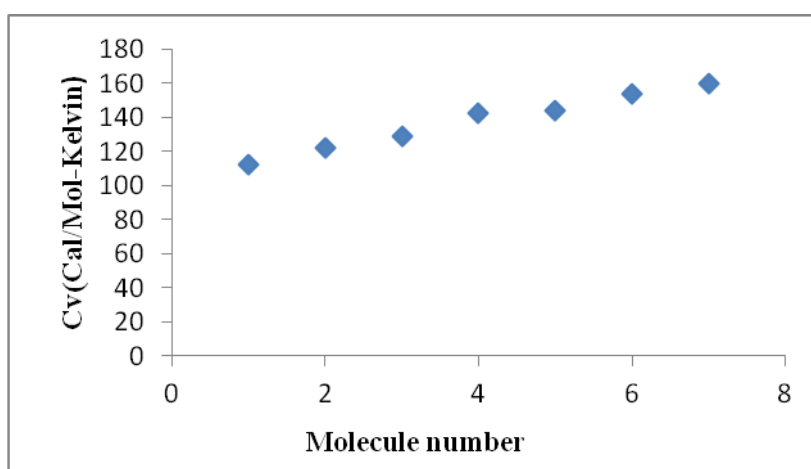


Figure 18: C_v of total energy as a function of cyano subgroups number.

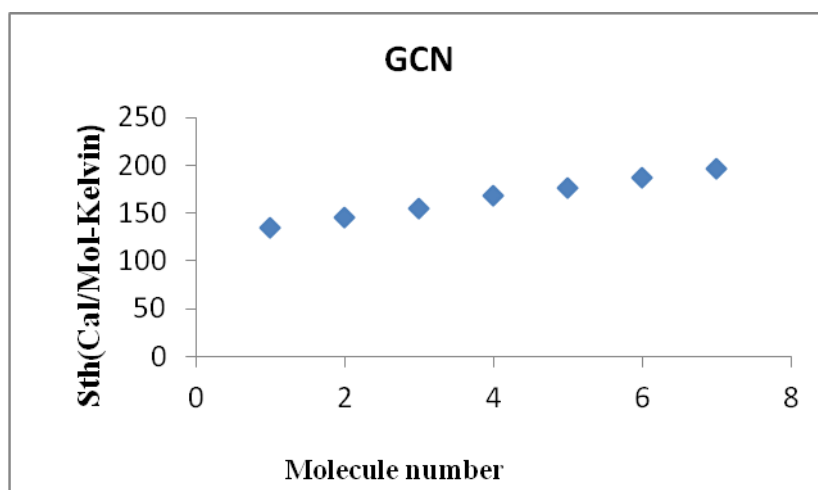


Figure 19 : S_{th} of total energy as a function of cyano subgroups number.

4- Conclusions

From the results obtained in this study, we can conclude:

- 1- The total energy of the cyano fullerene C60 molecules group is a linear function of cyano subgroups added to the molecule, the total energy was linearly decreased with increasing the number of cyano subgroups in the molecule.
- 2- Adding the cyano subgroups to the fullerene C60 molecule leads to change both the HOMO and LUMO energies, therefore reduced the energy gap of the molecule, but this decrease of energy gap depends on the number and the location of cyano subgroups in the molecule. This result is a sign of constructing new molecular structures which have new molecular electronic properties.
- 3- The molecular polarizability was increase with increasing the number of cyano subgroups in the molecule, this is an indicate to that the new constructing molecules have high reactivity to interacts with the surrounding.
- 4- The thermal properties of the molecule changes due to adding the cyano subgroups in the molecule, the entropy of the molecule increased linearly with increasing the subgroups in the molecule.

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