A DFT treatments for studying the vibration frequencies and normal coordinates of cyclacene molecules with different diameters (Unit Construction of ZigZag SWCNTs)

[1]**Rehab M. Kubba, Huda N. Al-Ani**

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq.

E-mail: [1]Rehab_mmr_kb@yahoo.com

Abstract

Semi-empirical methods (MINDO/3, PM3) and Density Functional Theory calculations (DFT/ B3LYP/ 6-311G) were carried out to evaluate the vibration frequencies and Infra-Red (IR) absorption intensities for equilibrium geometries, of 6,7,8,10 and 12 cyclacene's molecules of different diameters for (SWCNTs). The Gaussian 03 and MOPAC computational packages have been employed throughout this study to compute the geometrical Parameters (bond lengths and bond angles) and the energetic properties, (vibration frequency, heat of formation and electronic charge distribution for the modeled 6,7,8,10 and 12 cyclacene's molecules of different diameters nanostructures (zig-zag).   The results include the assignment of all puckering, breathing and clock-anticlockwise bending vibrations. They allow a comparative view of the charge density at the carbon atom too. According to the group theory and character tables all the irreducible representations of the vibration were assigned. The comparison of the calculated models revealed general correlations among the frequencies of (CH and CC) stretching vibration modes, the diameter and chirality.

دراسة ترددات الاهتزاز والاحداثيات الداخلية لجزيئات السايكلاسين (SWCNT) مع اختلاف الاقطار (لوحدات تركيب انابيب النانوكاربون من النوع المتعرج) بطريقة (DFT)

رحاب ماجد كبة، هدى نجم الدين عبد اللطيف العاني

قسم الكيمياء، كلية العلوم، جامعة بغداد

الخلاصة

تم حساب ترددات الاهتزاز و شدد امتصاص طيف الأشعة تحت الحمراء باستخدام حسابات ميكانيك الكم وفق نموذجي الحساب التقريبي MINDO/3 وPM3 و نموذج الحساب التام وفق نظرية دوال الكثافة (B3LYP/6-311G) (DFT)، لجزيئات السايكلاسين باختلاف الاقطار (6 و 7 و 8 و 10 و 12) والتي هي وحدات تركيب أنابيب النانوكاربون نوع zig-zag و مناقشتها تماثليا و تأصريا عند الشكل الهندسي التوازني، وباستخدام برنامجي الحساب MOPAC و Gaussian 03. كما تم استخراج أطوال و زوايا التاصر و بعض الصفات الفيزياوية كحرارة التكوين و توزيع الكثافة الالكترونية.

و عند مقارنة نتائج الحسابات، وجد بأن ترددات الاهتزاز للانماط المتماثلة لحركات المط التآصرية أعلى من تلك غير المتماثلة لاواصر (C-H) والعكس لاواصر (C-C)، و تكون ترددات الاهتزاز غير المتماثلة للحركات الانثنائية (δCH) و (δCC) أعلى من نظائرها المتماثلة وبصورة مماثلة لما هو عليه في الجزيئات العطرية متعددة الحلقات. و تمثل C-Ca في جزيئات zig zag الاواصر العمودية و C-Cc تمثل الاواصر المحيطية عند الحواف الخارجية لحلقات الجزيئة.كما تم و بدقة تعيين جميع ألانماط الاهتزازية العائدة للحركات الانبعاجية و التنفسية والانحنائية باتجاه وعكس اتجاه عقرب الساعة (وفق نظرية المجموعة)، و التي تعود اليها التشوهات الحاصلة من جراء الاهتزاز. أيضا تم حساب و دراسة توزيع الكثافة الالكترونية على ذرات هذه الجزيئات، و كانت النتائج متوافقة مع الصفات الفيزياوية والتوصيلية للانابيب المبنية من امثال هذه الجزيئات.

Introduction

Single wall carbon nanotubes (SWCNTs) are formed from folded sheets of annulated six member aromatic rings [1]. The hybridization of each carbon atom in the sheet is sp^2 [2]. They are of aromatic characters, similar to graphite, and posses' conjugated C-C bonds [3]. Their aromaticity is graded according to the space distribution of the atoms, the nature of their molecular orbitals, the symmetry and chirality [4]. Various quantum mechanical studies were done for the physical properties of the nanotubes [5-9]. To study the vibration motions of such molecules with different diameters, their geometric parameters have to be defining, the vibration of a nanotube causes a change in its geometry Fig. 3. Structure deformation is expected to change their thermal and electronic properties too. Basic vibrations of SWCNTs were measured and assigned as breathing, puckering and clock-anti-clockwise deformation modes [10]. The frequencies of their active vibrations range between (873-1557) cm^{-1} [11], they are considered as finger print vibrations for the carbon nanotubes (CNTs) [12]. Measurements were done to study the impact of the puckering distortion on the electronic properties of CNTs [13-15]. CNTs are of great interest to the industry[16].

The vibration modes of the nanotubes become accessible with the sub-nanometer precision typical of that instrument when tunnelling electrons transfer energy to the carbon lattice, Fig.1.

The results are fundamental for understanding the flow of heat and electrical charge in carbon nanostructures, the vibration motion of carbon nanotubes reflects mechanical strength or softness and depends critically on the perfection of the carbon structure on the atomic scale.
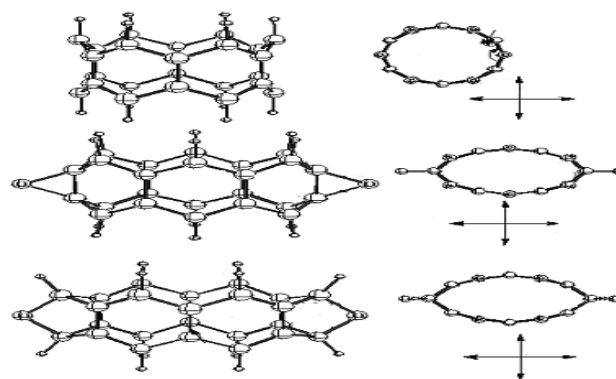

Fig. 1: Structure deformation of a [6] Cyclacene (zig zag) molecule as caused by its vibration motion (SWCNTs).

Vibration motion of atoms decreases the electrical conductivity of nanotubes and limits the performance of nanotransistors and other electronic devices based on them similarly [17], the stiffness of a nanotube and its capability for transporting heat is reduced with increasing defect density [18, 19]. A nanotube's thermal conductivity is predicted to be 10 times higher than silver [20]. Unlike metals, which conduct heat by moving electrons [21], CNTs conduct heat by wiggling the bonds between the carbon atoms themselves [22-24]. However no study could be found in the literatures for a complete normal coordinate analysis of the simplest type of nanotube i.e, the cyclacene nanoring molecules.

Results and Discussion

SWNCs are composed of (6,7,8,10 and 12) cyclacene's molecule of variable diameter interconnected by various linker compounds. Cyclacenes map directly onto and can be viewed as the shortest segments of (n,0) zig zag carbon nanotubes, Fig.2. Depending upon the nature and the orientation of the linkers molecule which composed of annulated 6, 7,8,10 and12 member aromatic rings.
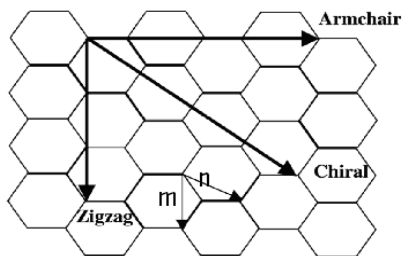
Fig. 2: Schematic diagram showing how a hexagonal sheet of graphite is 'rolled' to form a carbon nanotube.

Geometry optimizations have been performed at the semi-empirical methods (MINDO/3, PM3) and density functional theory calculations (DFT/B3LYP) were carried out to evaluate the vibration frequencies and Infra-Red (IR) absorption intensities for equilibrium geometries, of [6] cyclacene, [7] cyclacene, [8] cyclacene, [10] cyclacene and [12] cyclacene, Fig.3.

The Gaussian 03 [25] and MOPAC computational packages [26] have been employed throughout this study to compute the geometrical Parameters (bond lengths and bond angle) and the energetic properties, (vibration frequency, heat of formation and electronic charge distribution for the modeled (n= 6,7,8,10,12) Cyclacene, molecules of different diameters nanostructures (zig-zag). According to the group theory and character tables all the irreducible representations of the vibration were assigned [27, 28].

Generally the calculated frequencies applying MINDO/3 program were acceptable. Scaling factors have been applied for MINDO/3 outputs to improve the frequency values, in such away to accord with the experimental values and the ab initio results. The comparison of the calculated models revealed general correlations among the frequencies of (CH, CC) stretching vibration modes, with different diameter [29], by using Gaussian 03 and MOPAC computational packages.

Zig Zag Cyclacene Molecules

The (zig zag) molecules in our research contain (6,7,8,10 and 12) benzen rings fuized together, calculations (DFT/B3LYP) were carried out to evaluate for equilibrium geometries, of Cyclacene molecules. They showe (D_{6h}),(C_{2V}), (D_{4h}), (D_{5d}) and (D_{3h}) point group [30,32]. Figure 4 show the structure of [6] Cyclacene (zig zag) molecule, indicating the two types of C-C bonds; C-Caxial (C-Ca) and CCcircumferential as an example.

Equilibrium geometry of the [6] Cyclacene's molecule applying Mindo/3, PM3 and DFT. Due to its symmetry (D_{6h}) it undergoes the following symmetry operations (E, $2C_6$, $2C_3$, C_2 , $3C`_2$, $3C``_2$, i , $2S_3$, $2S_6$, σ_h , $3\sigma_d$, $3\sigma_v$). Fig. 5 shows a repeated section of [6]

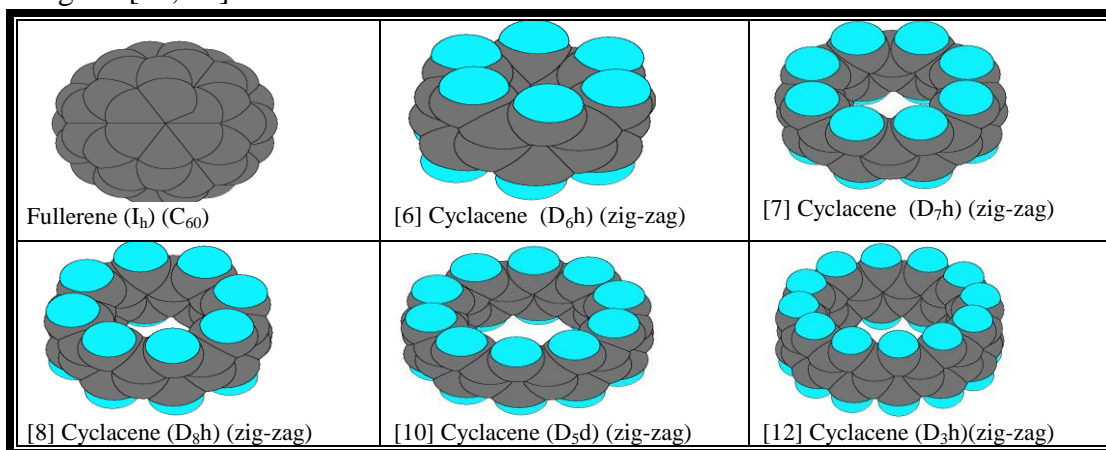|		
Fullerene (I_h) (C_{60})	[6] Cyclacene (D_6h) (zig-zag)	[7] Cyclacene (D_7h) (zig-zag)
[8] Cyclacene (D_8h) (zig-zag)	[10] Cyclacene (D_5d) (zig-zag)	[12] Cyclacene (D_3h)(zig-zag)

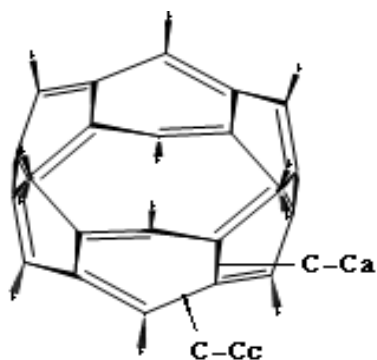*Fig.3: Equilibrium geometry for (6, 7,8,10 and 12) Cyclacene (zig zag) with Fullarene molecules.*

Fig .4: Structure of [6] Cyclacene (zig zag) molecule, indicating the two types of C-C bonds; C-C$_{axial}$ (C-C$_a$) and CC$_{circumferential}$.
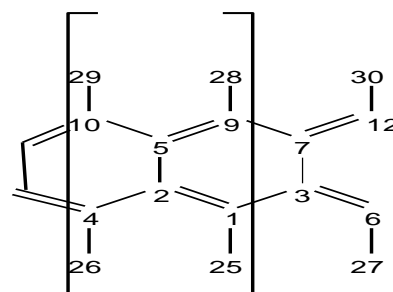

Fig. 5: Repeated section of the bonds and angles according to the symmetry of the [6] Cyclacene (Zig-Zag) molecule.

Table 1: Calculated geometries and some of physical properties for [6] Cyclacene by MINDO/3, PM3 and DFT calculations.

Bond length (Å) And Bond angles (deg.)	MOPAC (MINDO/3)	MOPAC (PM3)	Gaussian (DFT) B3LYP/ 6-311G
C_1C_2	1.394	1.386	1.413
C_1H_{25}	1.108	1.095	1.083
C_2C_4	1.476	1.441	1.421
C_2C_5	1.510	1.446	1.455
C_4H_{26}	1.108	1.095	1.083
C_5C_9	1.394	1.386	1.413
C_5C_{10}	1.476	1.441	1.421
C_9H_{28}	1.108	1.095	1.083
$< C_1C_2 C_4$	118.512	116.821	117.184
$< C_1C_2C_5$	116.541	119.573	118.317
$< C_1C_3C_6$	118.510	116.812	118.317
$< C_1C_3C_7$	118.228	119.566	118.317
$< C_2 C_1C_3$	117.727	113.829	115.779
$< C_2C_1H_{25}$	117.667	120.300	118.179
$< C_2C_5C_{10}$	118.223	119.564	118.179
$< C_5C_9C_7$	117.741	113.841	115.779
$< C_5C_9H_{28}$	117.665	120.300	118.179

cyclacene's molecule, and (Table 1) shows its calculated geometric parameters.

 The vibration frequencies were calculated. Totally 102 modes of vibrations are expected for the molecule. They are classified according to the following representations [30]:

$\Gamma_{vib} = \Gamma_{tot} - (\Gamma_{rot} + \Gamma_{tran}) = 3N - 6 = 108 - 6 = 102 = 6A_{1g} + 2A_{2g} + 4B_{1u} + 5B_{2u} + 8E_{1u} + 9E_{2g} + 3A_{1u} + 5A_{2u} + 5B_{1g} + 4B_{2g} + 8E_{1g} + 9E_{2u}$

Relative to the Ϭ$_h$ reflection plane the vibration modes are classified as symmetric and antisymmetrical modes.

a- Symmetric modes with respect to Ϭ$_h$ (+Ϭ$_h$).

$\Gamma_{+Ϭh} = 6A_{1g} + 2A_{2g} + 5B_{1u} + 4B_{2u} + 8E_{1u} + 9E_{2g}$ (In-plane σ$_h$ modes of vibrations)

b- Antisymmetric modes with respect to Ϭ$_h$ (-Ϭ$_h$).

$\Gamma_{-Ϭh} = 3A_{1u} + 5A_{2u} + 4B_{1g} + 5B_{2g} + 8E_{1g} + 9E_{2u}$ (Out of plane σ$_h$ modes of vibrations)

Table 2: Calculated vibration frequencies and IR absorption intensities of [6] Cyclacene (Zig-Zag) molecule.

Symmetry & description	Scaled MINDO/3 Freq. cm^{-1}	PM3 Freq. cm^{-1}	(DFT) B3LYP/ 6-311G Freq. cm^{-1}	Intensity km/mol
E$_{1u}$				
ν_{35} **CH str.**	**3062**	**3073**	**3062**	**20.066**
ν_{36} **CH str.**	**3062**	**3073**	**3062**	**20.066**
ν_{37} **ring (CC str.)(axial b.)+ δCH(rock.)**	**1596**	**1632**	**1516**	**3.559**
ν_{38} **ring (CC str.)(axial b.)+ δCH(rock.)**	**1596**	**1632**	**1516**	**3.559**
ν_{39} **ring(CC str.) (axial b.)**	**1391**	**1479**	**1347**	**32.422**
ν_{40} **ring (CC str.) (axial b.)**	**1391**	**1479**	**1347**	**32.422**
ν_{41} **δCH (rock.) + ring (CCC str.)**	**1147**	**1156**	**1201**	**0.117**
ν_{42} **δCH (rock.) + ring (CCC str.)**	**1147**	**1156**	**1201**	**0.117**
ν_{43} **γCH (twist.)**	**932**	**927**	**910**	**557.652**
ν_{44} **γCH (twist.)**	**932**	**927**	**910**	**557.652**
ν_{45} **δring(δCCC)(axial b.) (elongation)**	**781**	**894**	**762**	**5.054**
ν_{46} **δring(δCCC)(axial b.) (elongation)**	**781**	**894**	**762**	**5.054**
ν_{47} **δring (δCCC) (cercum. b.)**	**586**	**594**	**585**	**19.554**
ν_{48} **δring (δCCC) (cercum. b.)**	**586**	**594**	**585**	**19.554**
ν_{49} **γring (γCCC) (cercum. b.) (puck.)**	**436**	**443**	**403**	**8.433**
ν_{50} **γring (γCCC) (cercum. b.) (puck.)**	**436**	**443**	**403**	**8.433**
A$_{2u}$				
ν_{53} **CH str.**	**3057**	**3072**	**3064**	**58.588**
ν_{54} **ring (CC str.) (cercum. b.) + δCH (rock.)**	**1385**	**1404**	**1300**	**90.410**
ν_{55} **γCH (wag.)**	**891**	**928**	**922**	**378.955**
ν_{56} **γring (γCCC) (axial. b.) (puck.)**	**730**	**809**	**735**	**131.157**
ν_{57} **γring (γCCC) (cercum. b.) (puck.)**	**364**	**418**	**382**	**76.438**

Scaling factors for Mindo/3 calculation: 0.885 (CH str.); 0.98 (ring CC str.); 1.07 (ring (CCC str.)); 1.03 (δCH); 1.09 (γCH).

Special scaling factors were used for vibration modes with overlaps of different types of motion; 1.09 (δCH + δCCC) or (γCCC+ γCH) or (γCC + γCH) or (γCH + γCC); 1.10 (δCC + δCH); no scaling factors for other modes [19].

Scaling factors: 0.96 (CH str.) for all DFT (B3LYP/6-311G) frequencies, [23].

γ: Out of plane of the molecule.   δ: In- plane of the molecule. ,   (breath.): ring breathing mode., (puck.): ring puckering mode. , (rock.): CH rocking mode. (sciss.): CH scissoring mode., (twist.): CH twisting mode.,   (wag.): CH wagging mode.

1- Frequencies of the symmetric modes of vibration (+б$_h$)

CH stretching vibrations

The displacement vectors of which are located at the H atoms Fig.6. Their frequency values in Table 4 detect the following correlations:

ν_{sym}C-Hstr. (Cyclacene 6) > ν_{sym}C-H str. (Cyclacene 7) > ν_{sym}C-H str. (Cyclacene8) > ν_{sym}C-H str. (Cyclacene 12) (PM3)

ν_{sym}C-Hstr. (Cyclacene 6) > ν_{sym}C-H str. (Cyclacene 7) > ν_{sym}C-H str. (Cyclacene 8) (DFT)

ν_{asym}C-H str. (Cyclacene 6) > ν_{asym}C-H str. (Cyclacene 7) > ν_{asym}C-H str. (Cyclacene 8). > ν_{asym} C-H str. (Cyclacene 12). (PM3)

Ring (CC stretching) vibrations

Their displacement vectors are mainly located at the carbon atoms of the related bonds Fig.6. Their calculated vibration frequencies show the following relations Table 4.

ν_{sym}C-C str. (Cyclacene 6) < ν_{sym}C-C str. (Cyclacene 7) < ν_{sym}C-C str. (Cyclacene 8) < ν_{sym} C-C str. (Cyclacene 12) (PM3)

ν_{sym}C-C str. (Cyclacene 6) < ν_{sym}C-C str. (Cyclacene 8) < ν_{sym}C-C str. (Cyclacene10) DFT

ν_{asym}C-C str. (Cyclacene 6) < ν_{asym}C-C str. (Cyclacene 7) < ν_{asym}C-C str. (Cyclacene 12) (PM3)

Bending (CCC) vibrations (δCCC)

Of smaller values are the deformation (δCCC) vibrations. According to their assignment, these modes include the expected clock and anticlockwise vibration motion.

Their symmetric modes are of higher frequency than the asymmetric Fig.6.

Bending CH vibrations (δCH)

Their displacement vectors are mainly located at the corresponding H atoms Fig.6.

2- Frequencies of the asymmetric modes of vibration (-6$_h$).

The (γCH) out of plane vibration frequencies, The ring out of plane vibrations (γCCC), The modes include puckering deformations, as well as breathing vibrations of the whole ring Fig.6.

Table 4: PM3 and DFT calculations for vibration frequencies (cm^{-1}) of (6,7,8,10 and 12) Cyclacene (Zig-Zag) molecules.

Molecule	νCH str.	νCC str.	νCCC str.	νδCH
Cycla. 6 (PM3) D$_{6h}$	3073-3071	1697-1479	1717-864	1428-832
Cycla. 6 (DFT) D$_{6h}$	3067-3055	1565-1347	1531-845	1363-892
Cycla. 7 (PM3) D$_{7h}$	3067-3066	1681-1445	1661-1402	1246-821
Cycla. 7 (DFT) C$_{2v}$	3068-3065	1762-1563	----------	1397-625
Cycla. 8 (PM3) D$_{8h}$	3004-2999	1708-1449	1700-1256	1402-298
Cycla. 8 (DFT) D$_{4h}$	3182-3170	1632-1377	1542-1281	1132-875
Cycla. 10 (PM3) D$_{5d}$	3065-3055	1731-1602	1662-1349	1399-421
Cycla. 10 (DFT) D$_{5d}$	3110-3099	1604-1406	1591-1349	1393-90
Cycla. 12 (PM3) D$_{3h}$	2994-2989	1738-1551	1624-1369	1235-619

sym. CH str. **(v1, A1g, 3067)**	**asym. CH str.** **(v53. A2u, 3064)**	**sym.CC str.(cercum. b)** **(v87, E2u, 1547)**
sym. CCstr. (axial b.) **(v71, E2g, 1382)**	**asym CC str.(cercum. b.)** **(v54, A2u, 1300)**	**Sym. γring (axial. b.)** **(v60, B2g, 665)**
asym γring (cercum. b.)	**sym. γring (cercum. b.)** **(v81, B1u, 324)**	**sym. γring (axial b.)** **(v84, E2g, 133)**
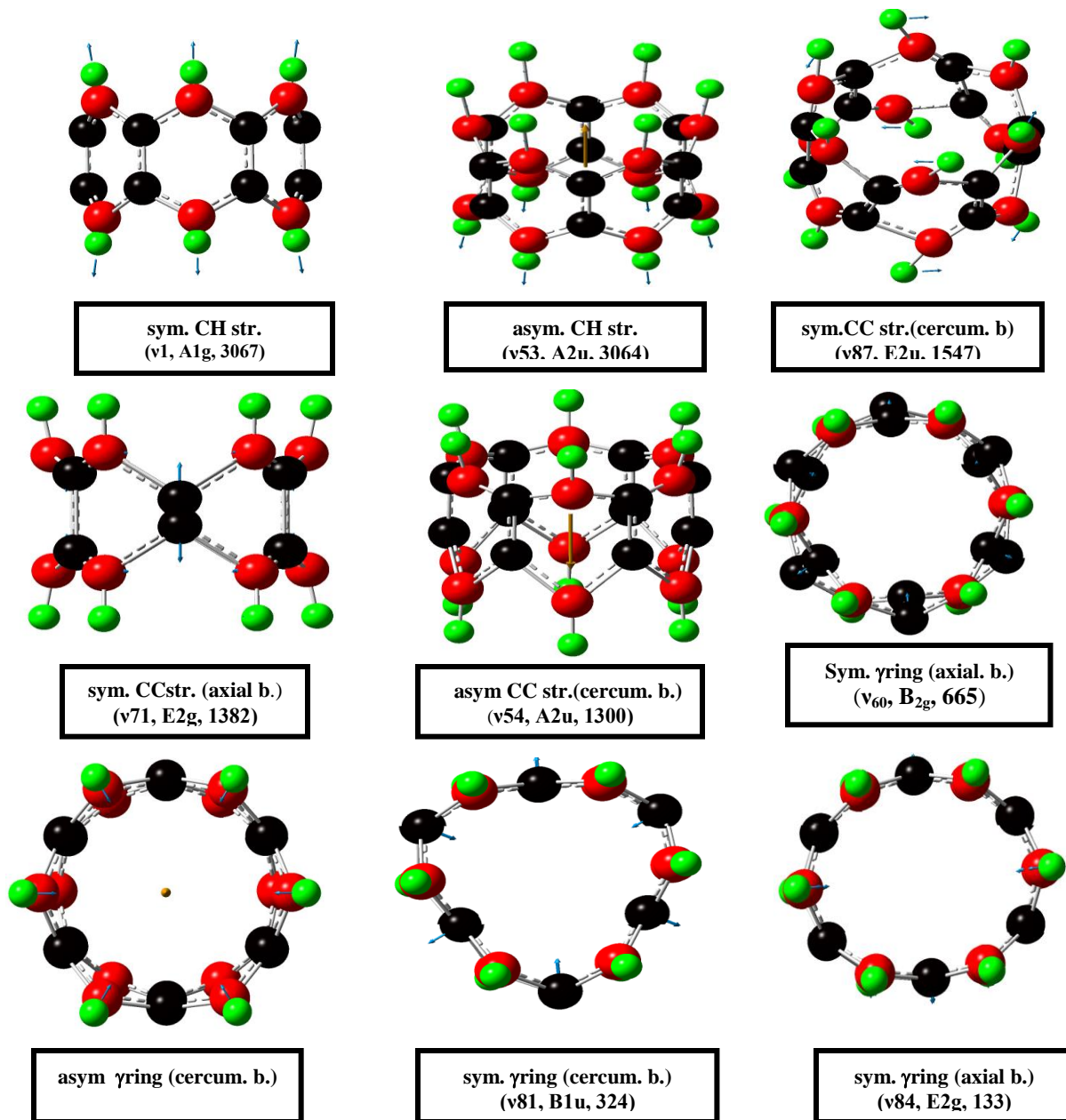
Fig.6. The graphical pictures of some vibration modes for [6] Cyclacene (zig zag) molecule as calculated applying DFT method.

The correlations.

1- Relation is found between the verity radiuses increased with the increase number of rings (n) for cyclacene molecules of different diameters, Fig.7.
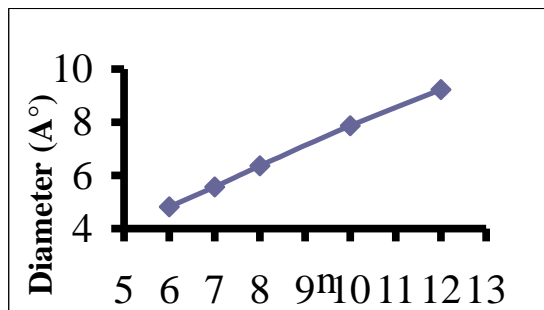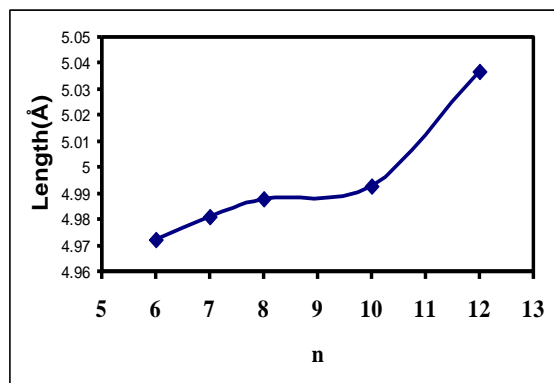

Fig.7: Relation between the diameters length and number of rings (n) for cyclacene molecules of different diameters applying DFT and PM3 methods.

2. Relation is found between the verity lengths increased with the increase of number of rings (n) for cyclacene molecules of different diameters, Fig.8.

Fig.8: Relation between the length and number of rings (n) for cyclacene molecules of different diameters applying DFT and PM3 methods.

3. Relation is found between the heats of formation ΔH increased with the number of rings (n) for cyclacene molecules of different diameters, Fig.9.
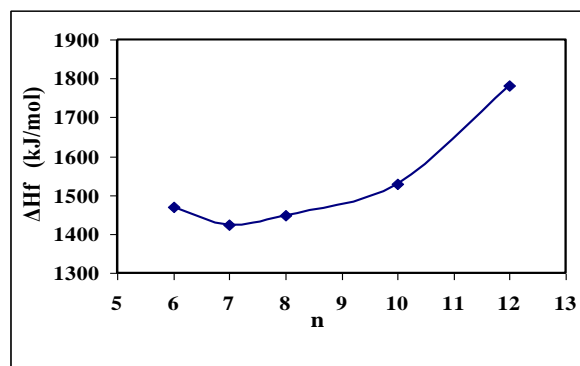

Fig.9: Relation between the heat of formation ΔH and number of rings (n) for cyclacene molecules of different diameters applying PM3 method.

4. Relation is found between the $\Delta E_{HOMO-LUMO}$ and number of rings (n) for cyclacene molecules of different diameters, Fig.10.
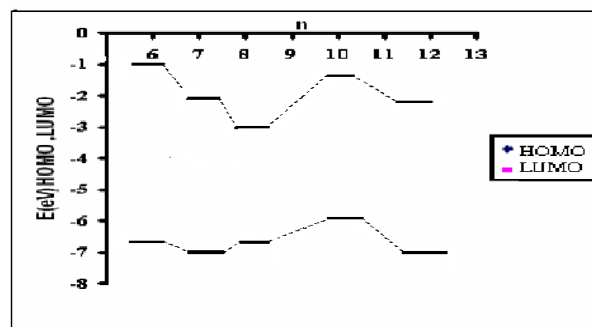

Fig.10: Relation between the E_{HOMO}, E_{LUMO} and number of rings (n) for cyclacene molecules of different diameters applying PM3 method.
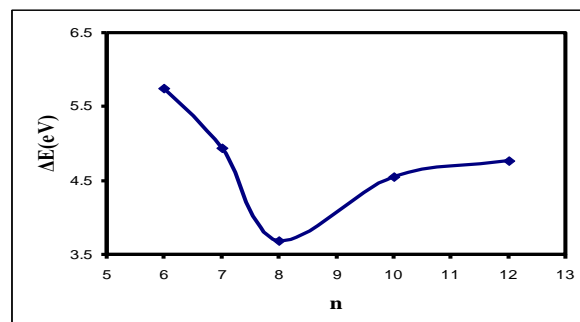

Fig.11: Relation between the $\Delta E_{HOMO-LUMO}$ and number of rings (n) for cyclacene molecules of different diameters applying PM3 method.

5- The relation is found for zig zag cyclacene [n] vibration frequencies calculated with different diameters by DFT, PM3 treatment:

1- Comparing all the C-H modes, the following correlation is detected

ν_{sym}CHstr. (Cyclacene- 6) > ν_{sym}CH$_{str}$ (Cyclacene -7) > ν_{sym}CHstr. (Cyclacene-8) > ν_{sym}CH str. (Cyclacene-12) MOPAC (PM3)

ν_{sym}CHstr. (Cyclacene- 6) > ν_{sym}CH$_{str}$(Cyclacene -7) > ν_{sym}CHstr. (Cyclacene-8) Gaussian (DFT)

2- Comparing all the CC stretching vibrations modes, the following correlation is detected

ν_{sym}CC$_{str.}$ (Cyclacene-6) < ν_{sym}CCstr. (Cyclacene-7) < ν_{sym}CCstr.(Cyclacene-8) < ν_{sym}CC $_{str.}$ (Cyclacene 12) (PM3).

ν_{sym}CC$_{str}$ (Cyclacene-6) < ν_{sym}CCstr (Cyclacene-8) < ν_{sym}CC$_{str}$ (Cyclacene10) Gaussian (DFT)

ν_{asym}CC$_{str}$ (Cyclacene 6) < ν_{asym}CC$_{str.}$(Cyclacene 7) < ν_{asym}CC$_{str}$ (Cyclacene. 12) (PM3)
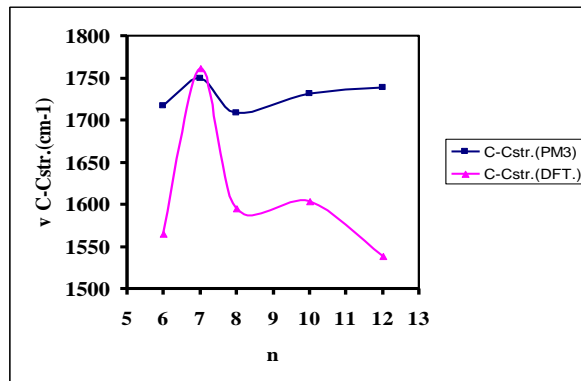

Fig. 12: Graphical correlation between the number of rings (n) at different diameters with the C-C stretching vibration frequencies applying DFT and PM3 methods.

Conclusions

The Gaussian03 and MOPAC Computational Packages have been employed through out this study to compute the geometrical Parameters (bond lengths and bond angle) and the energetic properties of different diameters Cyclacene (6,7,8,10,12) (zig-zag) molecules. The importance of these nano sized molecules based on their extensive applications in various technological and industrial fields. Obviously, the vibration of a nanotube causes a change in its geometry structure deformation is expected to change their thermal and electronic properties too.

Table 3: DFT Calculations for geometries, and some physical properties of (Cyclacene 6,7,8,10 and 12) (Zig-Zag)) molecules.

Molucule	Diameter (A^0)	Length (A^0)	a- bond length (A^0)	b- bond length (A^0)	c- bond length^0) (A^0)	vCCstr. (cm^{-1})	Terminal C Electronic Charge.
Cyclacene 6 (D_6h)	4.816	4.972	1.413	1.412	1.446	1565	-0.165
Cyclacene 7 (D_7h)	5.572	4.982	1.408	1.391	1.449	1762	-0.168
Cyclacene 8 (D_8h)	6.331	4.988	1.411	1.410	1.459	1595	-0.184
Cyclacene 10 (D_5d)	7.801	4.992	1.405	1.405	1.441	1604	-0.195
Cyclacene 12 (D_3h)	9.226	5.037	1.413	1.413	1.441	1539	-0.171

*(a) CC circumferential bond. ، *(b) C=C bond, ، * (c) C-C axil bond , ، * (d) bond C-H*

Measurements were done to study the comparison of the calculated models revealed general correlations among the frequencies of (CH, CC, ring) stretching vibration modes, the impact of the puckering distortion on the electronic properties of CNTs [32,33] with different diameters molecules.

The electronic Charge density at the carbon atoms have also been calculated, Fig.13, the charge densities are mainly concentrated at the circumferential carbon and hydrogen atoms of cyclacene. The axial carbon atoms have diminishing charges. And whereas the H atoms are positively charged, the C atoms are of the negative charge.

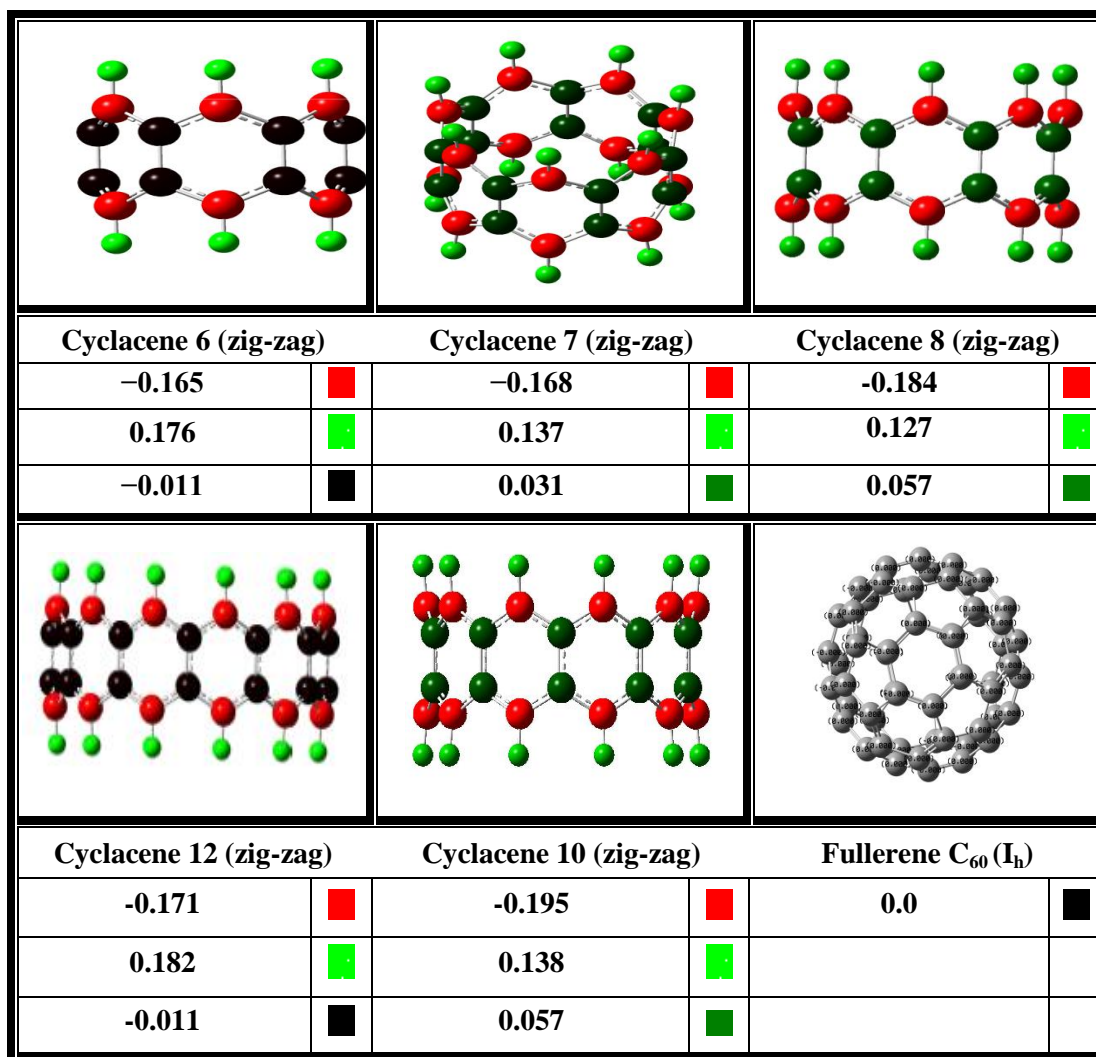| Cyclacene 6 (zig-zag)		Cyclacene 7 (zig-zag)		Cyclacene 8 (zig-zag)	
−0.165	🟥	−0.168	🟥	-0.184	🟥
0.176	🟩	0.137	🟩	0.127	🟩
−0.011	⬛	0.031	🟩	0.057	🟩
Cyclacene 12 (zig-zag)		Cyclacene 10 (zig-zag)		Fullerene C_{60} (I_h)	
-0.171	🟥	-0.195	🟥	0.0	⬛
0.182	🟩	0.138	🟩		
-0.011	⬛	0.057	🟩		

Fig.13: Distribution of charge density at the atoms of Cyclacene (6,7,8,10 and 12) (zig-zag) molecules and Fullerene as calculated applying DFT (B3LYP/6-311G).

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