Comparison of the Vibration Frequencies of [6] Cyclacene (Zigzag, Armchair and Chiral) Monoring Molecules

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Abstract

The (3N-6) vibration frequencies and IR-absorption intensities of [6] Cyclacene (zig zag, armchair and chiral) monoring molecules were calculated applying Density Functional Theory (DFT) of the type (B3LYP) and a Gaussian basis (6-311G) method. Comparison of the results showed that, similar to the polyaromatic hydrocarbons, the following relations hold:

ν_{sym}. CH str. > $\nu_{asym.}$ CH str.

and,

ν_{sym}. CC str. > $\nu_{asym.}$ CC str. i. e.,

ν_{sym}. CC str.(axial.) > $\nu_{asym.}$ CC str.(axial) > ν_{asym}. CC str.(circumferential) in the zigzag molecule, where axial are the vertical C-C_a bonds (annular bonds) in the rings and circumferential C-C_c are the outer ring bonds. The relation for the C-C str. is reversed in the armchair and the chiral molecules, since the C-Ca bonds are converted to C-Cc bonds in the armchair and chiral cyclacenes. 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 atoms too.

الخلاصة

تمت مقارنة ترددات الاهتزاز وشدد امتصاص الاشعة تحت الحمراء، لجميع الاحداثيات الداخلية لجزيئة (سايكلاسين- 6 بأنواعها الثلاثة Zig-Zag و Chiral و Armchair) و بعددها (3N–6) و مناقشتها تماثليا و تأصريا ، والتي تم حسابها باسلوب نظرية دوال الكثافة DFT (B3LYP/6-311G).

و عند مقارنة نتائج الحسابات للتراكيب الثلاثة، 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 . ويمكن تلخيص هذه العلاقات بالاتي:

$\nu_{sym.}$CH str. > $\nu_{asym.}$ CH str.

وأن

ν_{sym}. CC str. > $\nu_{asym.}$ CC str. i. e.,
ν_{sym}. CC str. (axial.) > $\nu_{asym.}$ CC str. (axial) > ν_{asym}. CC str. (circumferential)

و تمثل $C\text{-}C_a$ في جزيئة zig zag الاواصر العمودية و $C\text{-}C_c$ تمثل الاواصر المحيطية عند الحواف الخارجية لحلقات الجزيئة، وتنعكس العلاقة أعلاه في جزيئتي Chiral و Armchair لتحول الاواصر العمودية الى الاواصر المحيطية.

كما تم و بدقة تعيين جميع ألانماط الاهتزازية العائدة للحركات الانبعاجية و التنفسية والانحنائية باتجاه وعكس اتجاه عقرب الساعة، 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 membered aromatic rings [1]. The hybridization of each carbon atom in the sheet is sp^2 [2]. They are of aromatic character, similar to graphite, and posses conjugated C-C bonds [3]. Their aromaticity is determined by the space distribution of the atoms, the nature of their molecular orbitals, their symmetry and chirality [4]. Various studies appeared in former years for the physical properties of the nanotubes [5-10].

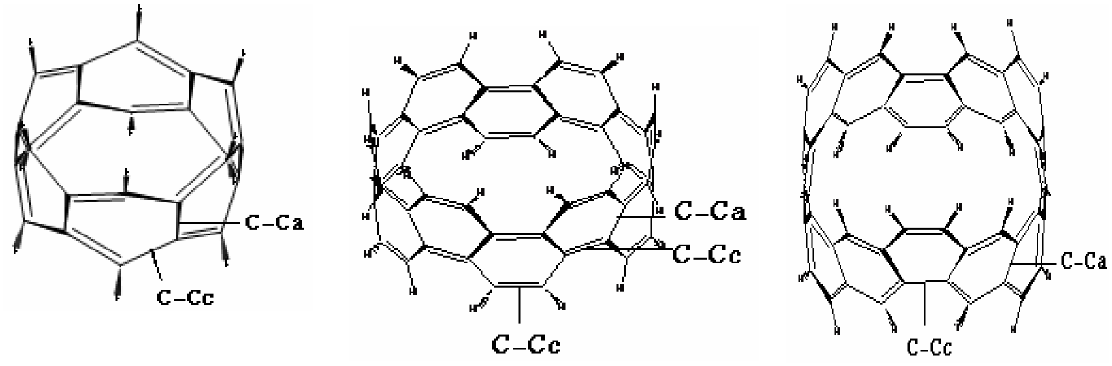
Cyclacenes are monoring segments of carbon nanotubes (CNT), Fig.1. Generally, attempts to synthesize them failed, with the exceptions of few cases [11]. An approach for their chemical stabilization was suggested [12]. It should faciliate their synthesis. For the cyclacene molecules with different ring size, numerous theoretical studies had been published [11]. However, no thorough treatment, including symmetry assignments for their vibration frequencies appeared. Comparison of their vibration frequency values with those of the nanotubes and the planar polyaromatic hydrocarbons should help to estimate the strength of their total force field strength. For this purpose a complete normal coordinate analysis is required. In this work the quantum mechanical Density Functional Theory (DFT) method [13], is applied, in the form of the B3LYP approach [14] and the 6-311G Gaussian bases [15] is utilized.

Methods of calculation.

G03 program of Pople et al. [17] was applied throughout the present work.

Results and Discussion.

To study the vibration motions of such molecules, one has to define its geometric parameters, and has to distinguish between the axial CC ($C\text{-}C_{axial}$) and circumferential CC (C-Cc) bonds. Figure 1 shows the two types of bonds in the different cyclacene orings.



Zig-zag Armchair Chiral

Figure 1: Structure of [6] Cyclacene (zigzag, armchair and chiral) monoring molecules, indicating the two types of C-C bonds; C-Caxial ($C-C_a$) and C-$C_{circumferential}$ (C-Cc).

Obviously, the vibration of a nanotube as well as cyclacenes, causes a deformation in its geometry Fig. 2. Structure deformation is expected to change their thermal and electronic properties [18] too.

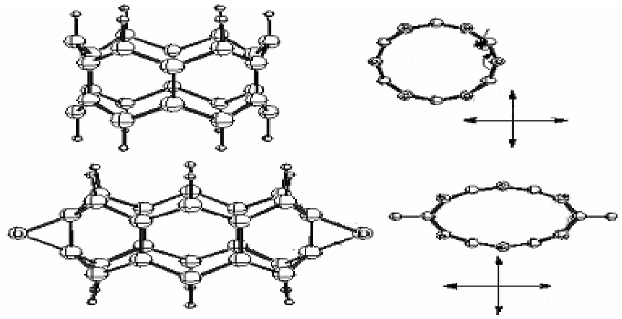


Figure 2: Structure deformation of a [6] Cyclacene (zigzag) monoring molecule as caused by its vibration motion.

Basic vibrations of CNTs were measured and assigned as breathing, puckering and clock-anti-clockwise deformation modes [19]. The frequencies of their IR active vibrations range between (873-1557 cm^{-1}) [20]. They are considered as finger print vibrations for the carbon nanotubes (CNTs) [21]. Measurements were done at 6^oK to study the impact of the puckering distortion on the electronic properties of CNTs [22-23].

[6] cyclacene (zigzag, armchair, chiral) molecules are composed of annulated six membered aromatic rings. Their (DFT) calculated equilibrium geometry shows D_{6h}, D_{6d}, D_{3d} symmetry respectively [24], Figure 3.

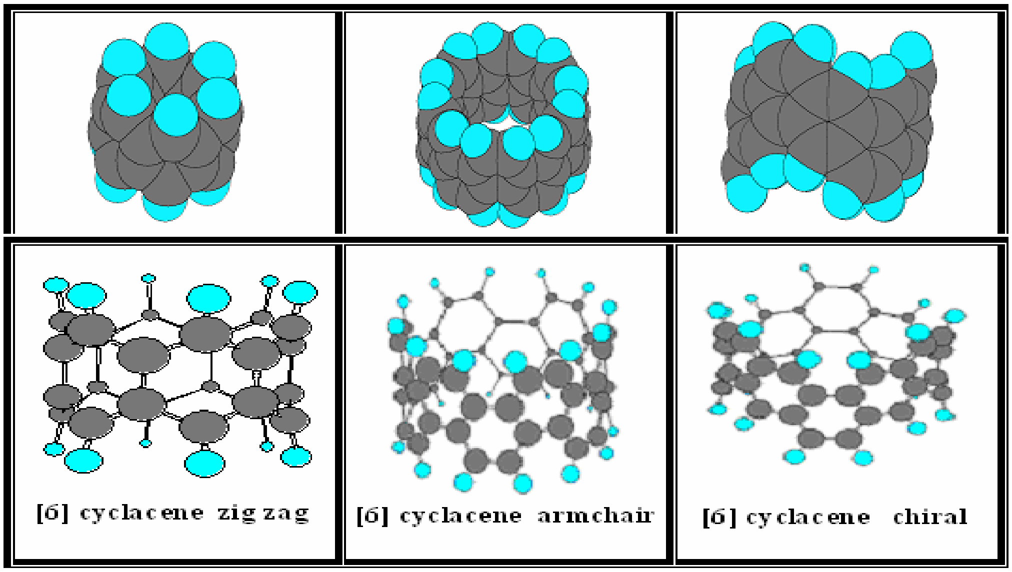
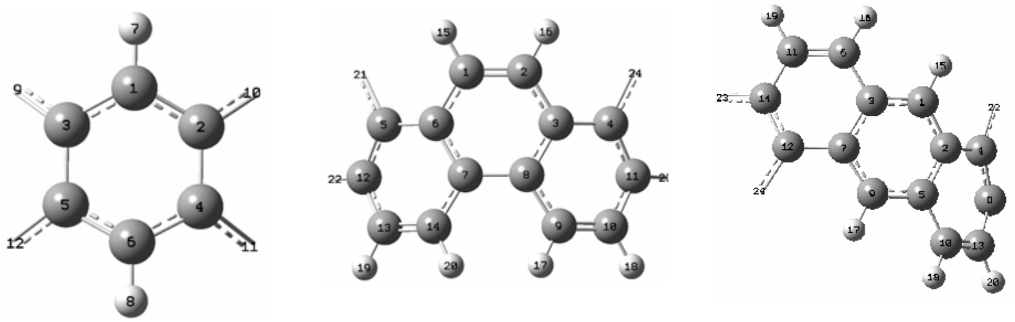


Figure 3: Equilibrium geometry for [6] Cyclacene (zigzag, armchair and chiral) monoring molecules.

Due to their symmetries D_{6h}, D_{6d} and D_{3d}, figure 4 shows repetitive sections of [6] Cyclacene monoring molecules, and Table 1 shows some of their calculated geometric parameters.



(a) (b) (c)

Figure 4: Repetitive sections of the bonds and angles of [6] Cyclacene ((a) zigzag, (b) armchair and (c) chiral) monoring molecules.

ÅTable 1: DFT calculated bond distances of [6] Cyclacene (zigzag, armchair and chiral) monoring molecules. .

Molecule	Diameter (Å)	Length (A^0)	C---Ca (Å)	C---Ca (Å)	C---Cc (Å)	C=Cc (Å)	C-Cc (Å)	C-H (Å)
[6] Cyclacene zig-zag (D_{6h})	5.183	4.972	1.446	-------	1.413	-------	-------	1.094
[6] Cyclacene armchair (D_{6d})	8.760	5.532	1.435	1.417	-------	1.366	1.452	1.080
[6] Cyclacene chiral (D_{3d})	8.758	6.758	C--C 1.433 C-C 1.449	1.403	1.454	1.356	1.471	=CH 1.082 --CH 1.081

As shown in (Table-1) the C-Ca bonds in the zigzag molecule are single bonds. They are longer than the C-Cc bonds connected to them. The C-Ca bonds in the armchair molecule are essential single bonds, and the C-Cc bonds are either double or single bonds. For the chiral molecule the C-Ca bonds are either single or conjugated and C-Cc bonds are of the three types; double, single and conjugated.

Vibration frequencies of [6] Cyclacene (zigzag, armchair and chiral).

-For zig-zag molecule:

The [6] Cyclacene (zigzag) molecule posses 102 fundamental vibrations. Inspection of its irreducible representations, as defined by the symmetry character table, results in the following modes of vibration;

$$\Gamma_{\text{vibration}} = \Gamma_{\text{total}} - (\Gamma_{\text{rotation}} + \Gamma_{\text{translation}}) = 3N - 6 = 108 - 6 = 102$$

$$= 6A_{1g} + 2A_{2g} + 4B_{1u} + 5B_{2u} + 8E_{1u} + 9E_{2g} + 3A_{1u} + 5A_{2u} + 5B_{1g} + 4B_{2g} + 8E_{1g} + 9E_{2u}$$

Relative to the б_h reflection the vibration modes are classified as symmetric and antisymmetri modes;

a- symmetric modes with respect to б_h (+б_h).

$$\Gamma_{+h\text{б}} = 6A_{1g} + 2A_{2g} + 5B_{1u} + 4B_{2u} + 8E_{1u} + 9E_{2g}$$ **(In-plane σ_h modes of vibrations)**

b- antisymmetric modes with respect to б_h (-б_h)..

$$\Gamma_{-h\text{б}} = 3A_{1u} + 5A_{2u} + 4B_{1g} + 5B_{2g} + 8E_{1g} + 9E_{2u}$$ **(Out of plane σ_h modes of vibrations)**

These are 51 modes of vibration in number, of which 24 are Raman active ($6A_{1g}$ **(polarized)** + $9E_{2g}$ **(depolarized)**), and 18 IR active ($9E_{1u}$).

-For armchair molecule:

$\Gamma_{vibration}$ = 210 = $9A_1$+ $8A_2$ +$9B_1$ +$8B_2$ +$17E_1$ +$18E_2$ +$18E_3$ + $18E_4$+ $17E_5$

These are 79 Raman active (**$9A_1$ (polarized) + $17E_5$, $18E_1$(depolarized)**), and 44 IR active (**$8B_2$, $18E_{1u}$**).

-For chiral molecule:

Γ_{vib} = 210 = $18A_{1g}$ + $35E_g$ + $17A_{2u}$ + $35E_u$ + $17A_{2g}$ + $18A_{1u}$

These are 88 Raman active (**$18A_{1g}$ (polarized) + $35E_g$ (depolarized)**), 87 IR active (**$17A_{2u}$ + $35E_u$**) and 35 Raman and IR inactive **($17A_{2g}$, $18A_{1u}$)**. Their assignments are as follows:

CH stretching vibrations

-For the zigzag molecule:

Their frequency values are in the range 3055-3067cm^{-1}, showing the following correlations:

ν_{sym} (CH str. (3067 cm^{-1}) > ν_{asym} (CH str.) (3055cm^{-1})

-For armchair molecule:

Their frequency values are in the range 3083-3046 cm^{-1}. Indicating the following relation:

ν_{sym} (=CH str.) (3083 cm^{-1}) > ν_{asym} (=CH str.) (3046 cm^{-1})
(A_1) (B_1)

-For chiral molecule:

Their frequency values are in the range 3032-3057 cm^{-1}, showing the following correlations:

ν_{sym} (CH str.) (3057 cm^{-1}) > ν_{asym} (CH str.) (3054 cm^{-1})
(A_{1g}) (E_g)

For the three molecules the relation ν_{sym} (CH str.) > ν_{asym} (CH str.) holds

Ring (CC stretching) vibrations

-For zig-zag molecule:

Calculated CC stretching vibration frequencies are in the range 1382-1565 cm^{-1}. Showing the following correlation;

$\nu_{sym.}$ (CC str.) (1531 cm^{-1}) (axial.) > $\nu_{asym.}$ (CC str.) (1457 cm^{-1}) (axial.)
(A_{1g}) (A_{1u})
$\nu_{sym.}$ (CC str.) (1531 cm^{-1}) (axial.) > $\nu_{asym.}$ (CC str.) (1411 cm^{-1}) (circum.)
(A_{1g}) (B_{1g})

In general $\nu_{sym.}$ (CC str.) > $\nu_{asym.}$ (CC str.)

-For armchair molecule:

Calculated vibration frequencies are in the range 1334-1635 cm^{-1}. They show the following relations;

ν_{sym} (C=C str.) (1634 cm^{-1}) < ν_{asym} (C=C str.) (1635 cm^{-1}) circum.
(A_1) (E_1)

ν_{sym} (C--C str.) (1406 cm^{-1}) < ν_{asym} (C--C str.) (1596 cm^{-1}) axial
(A_1) (B_1)
ν_{sym} (C-C str.) (1334 cm^{-1}) < ν_{asym} (C-C str.) (1379 cm^{-1}) circum.
(A_1) (E_2)
In general ν_{sym} (C-C str.) < ν_{asym} (C-C str.)

This relation is reverse to that in zig-zag molecule because the C-Ca bonds become as a C-Cc bonds in armchair molecules.

-For chiral molecule:

Calculated vibration frequencies are in the range 1342-1638 cm^{-1}. They show the following relations;

ν_{sym} (C=C str.) (1637 cm^{-1}) < ν_{asym} (C=C str.) (1642 cm^{-1}) (circum.)
(A_{1g}) (E_g)
ν_{sym} (C--C str.) (1602 cm^{-1}) < ν_{asym} (C--C str.) (1642 cm^{-1}) (axial)
(A_{1g}) (A_{1u})
And generally:
ν (C-C str.) (circum.) < ν (C--C str.) (axial.) < ν (C=C str.) (circum.)

Ring (CCC stretching vibrations)

Unlike the C-C vibration modes, these are not located at definite C atoms as could be seen from the atomic displacement vectors. Their frequencies are lower than those of the C-C vibration modes.

According to the calculating results, the range of these frequencies are 1300-1347cm^{-1} ,for zigzag molecule, 1359-1406 cm^{-1} for armchair molecule, and 1358-1454 cm^{-1} for chiral molecule.

Bending (CCC) vibrations (δCCC)

Of smaller values are the deformation (δCCC) vibrations. According to their assignment, they fall in the range 431-1228 cm^{-1} for zigzag molecule. These modes include the expected clock and anticlockwise vibration motions.

-For armchair molecule:

Their calculated frequencies are in the range 448-1155 cm^{-1}.

-For chiral molecule:

Their calculated frequencies are in the range 833-1102 cm^{-1}.

Generally for the three molecules, the symmetric modes are of higher frequencies than the asymmetric.

Bending CH vibrations (δCH)

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

-For zigzag molecule:

The calculated frequency values are in the range1107-1288 cm^{-1}.

-For armchair molecule:

Their calculated frequencies are in the range 1180-1474 cm^{-1}.

-For chiral molecule:

The calculated frequencies are in the range 1164-1484 cm^{-1}, with the following correlation:

$\nu_{sym.}$ δ(--CH) (rock.) > $\nu_{sym.}$ δ(--CH) (sciss.)
$\nu_{sym.}$ δ(--CH) (sciss.) > $\nu_{sym.}$ δ(=CH) (sciss.)
$\nu_{asym.}$ δ(=CH) (rock.) > $\nu_{asym.}$ δ(=CH) (sciss.)

Out of plane vibration frequencies (γCH)

-For the zigzag molecule:

The (γCH) out of plane vibration frequencies are in the range 817-956 cm^{-1}. The following relations hold too;

ν_{sym} (γCH) (wag.) (956 cm^{-1}) > ν_{asym} (γCH) (twist.) (860 cm^{-1})
(A_{1g}) (B_{1g})
ν_{asym} (γCH) (wag.) (936 cm^{-1}) > ν_{asym} (γCH) (twist.) (904 cm^{-1})
(E_{1g}) (E_{2g})

-For armchair molecule:

The (γCH) out of plane vibration frequencies are in the range 706-993 cm^{-1}.

-For chiral molecule:

The calculated frequencies are in the range 682-997cm^{-1}, with the following relations:

$\nu_{asym.}$ γ(=CH) (twist.) circum. > $\nu_{asym.}$ γ(--CH) (twist.) (axial.)
$\nu_{sym.}$ γ(=CH) (wag.) circum. < $\nu_{asym.}$ γ(--CH) (twist.) (axial.)
$\nu_{sym.}$ γ(=CH) (wag.) circum. < $\nu_{sym.}$ γ(--CH) (wag.) (axial.)

Ring out of plane vibrations (γCCC)

The ring out of plane vibrations (γCCC), show frequencies values of which the range is 133-768 cm^{-1}. The modes include puckering, deformations, as well as breathing vibrations of the whole ring. The relation of the sym. to the asym. modes for zigzag molecule is viewed in the following scheme;

$\nu_{sym.}$ (γCCC) (axial.) (537 cm^{-1}) > $\nu_{sym.}$ (γCCC) (circum.) (462 cm^{-1})
(A_{1g})
(A_{1g})
$\nu_{asym.}$ (γCCC) (axial.) (768 cm^{-1}) > $\nu_{asym.}$ (γCCC) (circum.) (658 cm^{-1})
(E_{1g})
(E_{1g})
$\nu_{sym.}$ (γCCC) (axial.) (537 cm^{-1}) > $\nu_{asym.}$ (γCCC) (axial.) (324 cm^{-1})
(A_{1g})
(B_{1u})
$\nu_{sym.}$ (γCCC) (circum.) (462 cm^{-1}) > $\nu_{asym.}$ (γCCC) (circum.) (331 cm^{-1})
(A_{1g})
(B_{1g})

-For armchair molecule:

The calculated frequencies range is (187-865 cm^{-1}).

-For chiral molecule:

The calculated frequencies range is (64-765 cm^{-1}), with the following relations:

$$\underset{(A_{1g})}{\nu_{sym.}\,(\gamma CCC)\,(616\ cm^{-1})} < \underset{(A_{1u})}{\nu_{asym.}\,(\gamma CCC)\,(765\ cm^{-1})}$$

Table 2 includes the calculated frequencies and IR absorption intensities of the vibration modes of the zigzag molecule as a sample of the calculation and assignment results. Commonly known, the vibrations with (intensity= 0.0) are IR forbidden, those with (intensity≠ 0.0) are IR allowed. The vibration modes in the table are classified according to the Herzberg scheme [25].

Figure 5 shows the vibration pictures for some modes of the [6] Cyclacene (zig zag) molecule, as calculated applying the DFT method.

Table (2): Calculated vibration frequencies and IR absorption intensities for [6] Cyclacene (zig zag) molecule.

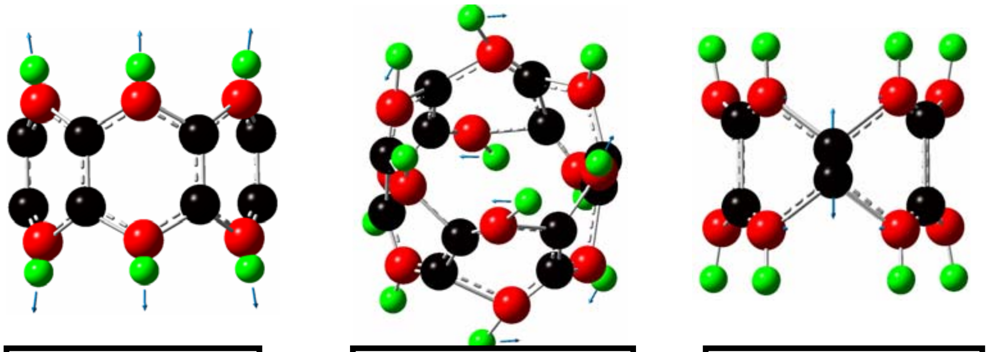
Symmetry & description		PM3 Freq. cm^{-1}	(DFT) B3LYP/ 6-311G Freq. cm^{-1}	Intensity km/mol
A_{1g}				
ν_1	CH **str**.	3073	3067	0.000
ν_2	ring (CC **str**.) (**axial b.**)	1644	1531	0.000
ν_3	γCH (**wag.**)	950	956	0.000
ν_4	δring (δCCC) (**elongation**)	890	775	0.000
ν_5	γring (γCCC) (**axial b.**) (**breath.**)	538	537	0.000
ν_6	γring (γCCC) **(circum. b.)** (**breath.**)	452	462	0.000
B_{1g}				
ν_7	CH **str.**	3072	3055	0.000
ν_8	ring (CC **str**.) (**cercum. b**)	1600	1411	0.000
ν_9	γCH (**twist**.)	867	860	0.000
ν_{10}	γCH (**twist**.) + γring (γCCC)	782	817	0.000
ν_{11}	γring (γCCC) (**cercum. b**.) (**puck.**)	330	331	0.000
A_{1u}				
ν_{12}	ring (CC **str**.) (**cercum. b**.) + δCH **rock**.)	1717	1388	0.000
ν_{13}	δCH (**rock.**)+δring(δCCC)(**axial. b**.)	1119	1107	0.000
ν_{14}	δring (δCCC)**(clock & anticlock wise)**	453	431	0.000

B_{1u}				
ν_{15}	ring (CC **str.**) (**axial b**.)+ δCH (**sciss**.)	1583	1457	0.000
ν_{16}	ring (CCC **str.**) (**axial b**.)	1377	1363	0.000
ν_{17}	ring (δCCC) + δCH (**sciss**.)	979	903	0.000
ν_{18}	γring (γCCC) (**axial b**.) (**puck.**)	358	324	0.000
E_{1g}				
ν_{19}	CH **str.**	3071	3061	0.000
ν_{20}	CH **str.**	3071	3061	0.000
ν_{21}	ring (CC **str**.) (**cercum. b**)	1694	1565	0.000
ν_{22}	ring (CC **str**.) (**cercum. b**)	1694	1565	0.000
ν_{23}	δCH + δring (δCCC)	1384	1288	0.000
ν_{24}	δCH + δring (δCCC)	1384	1288	0.000
ν_{25}	δCH + δring (δCCC)	1145	1207	0.000
ν_{26}	δCH + δring (δCCC)	1145	1207	0.000
ν_{27}	γCH (**wag**.)	925	936	0.000
ν_{28}	γCH (**wag**.)	925	936	0.000
ν_{29}	γring (γCCC) (**axial. b**.) (**puck.**)	827	768	0.000
ν_{30}	γring (γCCC) (**axial. b**.) (**puck.**)	827	768	0.000
ν_{31}	γring (γCCC) (**cercum. b**.) (**puck.**)	638	658	0.000
ν_{32}	γring (γCCC) (**cercum. b**.) (**puck.**)	638	658	0.000
ν_{33}	γring (γCCC) (**puck.**)	329	333	0.000
ν_{34}	γring (γCCC) (**puck.**)	329	333	0.000
E_{1u}				
ν_{35}	CH **str.**	3073	3062	20.066
ν_{36}	CH **str.**	3073	3062	20.066
ν_{37}	ring (CC **str.**) (**axial b**.) + δCH **(rock.)**	1632	1516	3.559
ν_{38}	ring (CC **str.**) (**axial b**.) + δCH **(rock.)**	1632	1516	3.559
ν_{39}	ring (CCC **str**.) (**axial b**.)	1479	1347	32.422
ν_{40}	ring (CCC **str**.) (**axial b**.)	1479	1347	32.422
ν_{41}	δCH (**rock**.) + ring (CCC **str**.)	1156	1201	0.117
ν_{42}	δCH (**rock**.) + ring (CCC **str**.)	1156	1201	0.117
ν_{43}	γCH (**twist**.)	927	910	557.652
ν_{44}	γCH (**twist**.)	927	910	557.652
ν_{45}	δring (δCCC) (**axial b**.) (**elongation**)	894	762	5.054
ν_{46}	δring (δCCC) (**axial b**.) (**elongation**)	894	762	5.054

ν_{47}	δring (δCCC) (**cercum. b**.)	594	585	19.554
ν_{48}	δring (δCCC) (**cercum. b**.)	594	585	19.554
ν_{49}	γring (γCCC) (**cercum. b**.) (**puck.**)	443	403	8.433
ν_{50}	γring (γCCC) (**cercum. b**.) (**puck.**)	443	403	8.433
A_{2g}				
ν_{51}	ring (CC **str.**) **(circum. b., clock & anti clockwise)** + δCH	1248	1504	0.000
ν_{52}	δCH (**rock.**) **(clock & anticlockwise)**	1090	1227	0.000
A_{2u}				
ν_{53}	CH **str.**	3072	3064	58.588
ν_{54}	ring (CCC **str**.) (**cercum. b**.) + δCH	1404	1300	90.410
ν_{55}	γCH (**wag**.)	928	922	378.955
ν_{56}	γring (γCCC) (**axial. b**.) (**puck.**)	809	735	131.157
ν_{57}	γring (γCCC) (**cercum. b**.) (**puck.**)	418	382	76.438
B_{2g}				
ν_{58}	ring (CC **str**.) (**cercum. b**)	1556	1432	0.000
ν_{59}	δCH **(sciss.)** + ring (δCCC)	1207	1274	0.000
ν_{60}	γring (γCCC) (**axial. b**.) (**puck.**)	678	665	0.000
ν_{61}	ring (δCCC) (**cercum. b**.)	475	466	0.000
B_{2u}				
ν_{62}	CH **str.**	3073	3056	0.000
ν_{63}	ring (CCC **str**.) + δCH (**sciss**.)	1573	1320	0.000
ν_{64}	γCH (**twist**.)	832	876	0.000
ν_{65}	ring (δCCC) + δCH (**sciss**.)	598	599	0.000
ν_{66}	γring (γCCC) (**axial b**.) (**puck.**)	281	255	0.000
E_{2g}				
ν_{67}	CH **str**.	3073	3058	0.000
ν_{68}	CH **str.**	3073	3058	0.000
ν_{69}	ring (CC **str**.)(**axial b**.) + δCH (**sciss**.)	1608	1497	0.000
ν_{70}	ring (CC **str**.)(**axial b**.) + δCH (**sciss**.)	1608	1497	0.000
ν_{71}	ring (CC **str**.) (**axial b**. + **cercum. b**.)	1576	1382	0.000
ν_{72}	ring (CC **str**.) (**axial b**.+ **cercum. b**.)	1576	1382	0.000
ν_{73}	δCH + (δCCC)	1280	1271	0.000
ν_{74}	δCH + (δCCC)	1280	1271	0.000
ν_{75}	γCH (**twist**.)	961	904	0.000
ν_{76}	γCH (**twist**.)	961	904	0.000

ν_{77}	γCH (**twist**.) + γring (γCCC)	864	845	0.000
ν_{78}	γCH (**twist**.) + γring (γCCC)	864	845	0.000
ν_{79}	δring (δCCC) (**circum b**.) (**elongation**)	627	619	0.000
ν_{80}	δring (δCCC) (**circum b**.) (**elongation**)	627	619	0.000
ν_{81}	γring (γCCC) (**cercum. b**.) (**puck.**)	405	387	0.000
ν_{82}	γring (γCCC) (**cercum. b**.) (**puck.**)	405	387	0.000
ν_{83}	γring (γCCC) (**axial b**.) (**puck.**)	147	133	0.000
ν_{84}	γring (γCCC) (**axial b**.) (**puck.**)	147	133	0.000
E_{2u}				
ν_{85}	CH **str.**	3072	3056	0.000
ν_{86}	CH **str.**	3072	3056	0.000
ν_{87}	ring (CC **str**.) (**cercum. b**)	1685	1547	0.000
ν_{88}	ring (CC **str.**) (**cercum. b**)	1685	1547	0.000
ν_{89}	ring (CCC **str**.) + δCH (**sciss**.)	1428	1308	0.000
ν_{90}	ring (CCC **str**.) + δCH (**sciss**.)	1428	1308	0.000
ν_{91}	δring (δCCC) (**cercum. b**)	1196	1228	0.000
ν_{92}	δring (δCCC) (**cercum. b**)	1196	1228	0.000
ν_{93}	γCH **(twist.)**	885	892	0.000
ν_{94}	γCH **(twist.)**	885	892	0.000
ν_{95}	γCH (**twist**.) + γring (γCCC)	846	839	0.000
ν_{96}	γCH (**twist**.) + γring (γCCC)	846	839	0.000
ν_{97}	γring (γCCC) (**axial. b**.) (**puck.**)	672	670	0.000
ν_{98}	γring (γCCC) (**axial. b**.) (**puck.**)	672	670	0.000
ν_{99}	γring (γCCC) (**cercum. b**) (**puck.**)	430	429	0.000
ν_{100}	γring (γCCC) (**cercum. b**) (**puck.**)	430	429	0.000
ν_{101}	γring (γCCC) (**cercum. b**) (**puck.**)	181	185	0.000
ν_{102}	γring (γCCC) (**cercum. b**) (**puck.**)	181	185	0.000

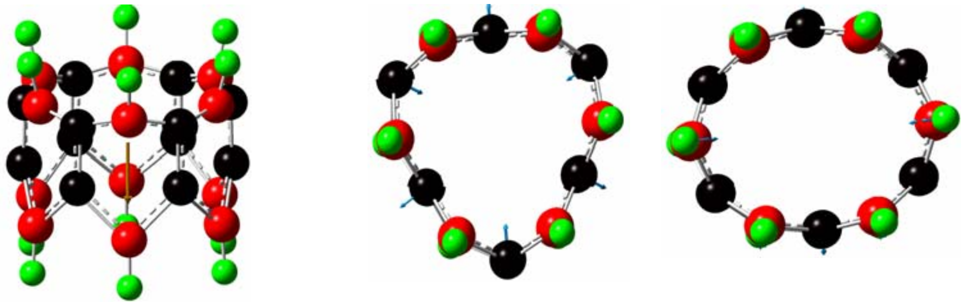
γ: Out of plane of the molecule., δ: In- plane of the molecule.
(breath.): ring breathing mode., **(puck.)**: ring puckering mode. , **(sciss.)**: CH scissoring mode.
(twist.): CH twisting mode., **(wag.)**: CH wagging mode.



sym. CH str.
(ν_1, A_{1g}, 3067)

sym.CC **str.(cercum. b)**
(ν_{87}, E_{2u}, 1547)

sym. CC**str. (axial b.)**
(ν_{71}, E_{2g}, 1382)



asym CCC **str.(cercum. b.)**
(ν_{54}, A_{2u}, 1300)

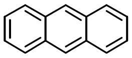
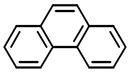
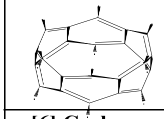
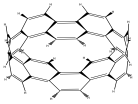
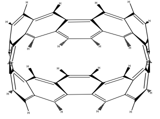
sym. γring **(cercum. b.)**
(ν_{81}, B_{1u}, 324)

sym. γring **(axial b.)**
(ν_{84}, E_{2g}, 133)

Figure 5. The graphical pictures of some vibration modes for [6] Cyclacene (zigzag) molecule as calculated applying the DFT method.

Table 3 shows comparison of the calculated vibration frequencies of [6] cyclacenes molecules with the frequencies of anthracene and phenanthrene molecules by using the same level of DFT theory, the frequency values of [6] cyclacenes are lower. The comparison shows that the force field for cyclacene is weaker than that of the coplanar polyaromatic molecule. It indicates the influence of folding in diminishing the C-C bond strength of the aromatic molecule too.

Table 3: Comparison of the calculated vibration frequencies of [6] cyclacene molecules with those of coplanar anthracene and phenanthrene molecules using B3LYP/6-311G .

Molecule	C-H sym.	C-H asym.	C-Ca sym.	C-Ca asym.	C-Cc sym.	C-Cc asym.	δCH sym.	δCH asym	γCH sym.	γCH asym.
Anthracene (D_{2h}) 	**3156** **A_g**	**3153** **B_{1u}**	**1592** **A_g**	**1582** **B_{2u}**	-------	**1670** **B_{1u}**	**1302A** **g-**	**1320** **B_{3g}**	------	**992** **B_{1g}**
Phenanthrene (C_{2v}) 	**3209** **A_1**	**3198** **B_2**	**1644** **A_1**	**1656** **B_1**	**1662** **A_1**	-------	**1341** **A_1**	**1328** **B_2**	**1005** **A_2**	**1021** **B_1**
[6] Cyclacene zig-zag (D_{6h}) 	**3067** **A_{1g}**	**3055** **B_{1g}**	**1531** **A_{1g}**	**1457** **B_{1u}**	-------	**1411** **B_{1g}**	**1222** **A_{1g}**	**1274** **B_{2g}**	------	**992** **B_{1g}**
[6] Cyclacene armchair(D_{6d}) 	**3083** **A_1**	**3046B** **1**	**1406** **A_1**	**1496** **B_1**	**1634** **A_1**	**1635** **E_1**	**1222** **A_1**	**1214** **E_1**	**810** **A_1**	**963** **B_1**
[6] Cyclacene chiral (D_{3d}) 	**3057** **A_{1g}**	**3042** **A_{1u}**	**1602** **A_{1g}**	**1642** **A_{1u}**	**1637** **A_{1g}**	**1641** **E_g**	**1224** **A_{1g}**	**1244** **A_{1u}**	**933** **A_{1g}**	**915** **E_g**

The result parallels that of Turker [26] who showed, on the basis of the Hückel treatment, that the electronic binding energy of the planar polyaromatic hydrocarbon are bigger in value than those of the cyclacene molecule with similar number of benzene rings.

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