

Theoretical Study for the Preparation of Sub-Carbon Nano Tubes from the Cyclic Polymerization of Three Molecules from (Corannulene, Coronene and Circulene) Aromatic Compounds

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ABSTRACT

Corannulene, coronene and circulene are polycyclic aromatic hydrocarbons (PAHs) compounds were chosen to study the preparation of carbon tubes with diameters smaller fraction of nano-meter theoretically may achievable using the density function theory (DFT). The results showed that the stability of the molecules are; corannulene molecule is bowl-shaped, coronene molecule is planar, circulene molecule has a unique saddle-shaped structure. Upon to molecular polymerization a tube for three of the molecules selected results a sub-nanotubes formation. The results showed thermodynamic all preparations reactions are spontaneous and exothermic; the tubes prepared have high efficiency in the gap energy, making it potentially useful for solar cell applications.

Keywords: Corannulene, Coronene, Circulene, Dft, Polymerization.

دراسة نظرية لتحضير أنابيب كربون نانوية من البلمرة الحلقية لثلاثة جزيئات من المركبات الأروماتية (الكورانولين والكورونين والسيركولين)

الخلاصة

الكورانولين والكورونين والسيركولين هي مركبات هيدروكربونية أروماتية متعددة الحلقات اختبرت في هذا البحث لدراسة تحضير أنابيب كربونية ذات أقطار أصغر من النانومتر نظرياً باستخدام نظرية دوال الكثافة. أظهرت نتائج الحسابات ان الشكل المستقر للجزيئات المحسوبة هو:

جزيئة الكورانونولين ذات شكل يشبه تقعر الطاسة، وجزيئة الكورونين ذات شكل مستوي، وجزيئة السيركولين ذات شكل يشبه سرج الحصان (محدب). نحصل على الأنابيب نتيجة لتفاعل البلمرة الحلقي لثلاثة جزيئات من الجزيئات المختارة، وأظهرت النتائج الترموديناميكية ان جميع تفاعلات التحضير الانابيب الكربون النانوية هي تلقائية وباعثة للحرارة، وان الأنابيب المحضرة هي ذات كفاءه عالية بالنسبة لطاقة الفجوة مما يجعلها مفيدة في الخلايا الشمسية.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of unique compounds that consist of fused conjugated aromatic rings and do not contain heteroatom or carry substituents [1]. These compounds are one of the most widespread organic pollutants. Some of them are known or suspected carcinogens, and are linked to other health problems. They are primarily formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, or incense [2, 3].

PAHs comprised only of six-membered rings are called alternant PAHs, certain alternant PAHs are called "benzenoid" PAHs. PAHs containing up to six fused aromatic rings are often known as "small" PAHs, and those containing more than six aromatic rings are called "large" PAHs. Due to the availability of samples of various small PAHs, the main research on PAHs has been focused on those of up to six rings [4].

Corannulene ((5) circulene) has the shape of a bowl because it includes a five-membered ring, and is known to invert rapidly. In addition to its nonstandard geometry and dynamic behavior, the molecule attracted a lot of interest since it has been considered as an important building block that should enable the organic chemistry synthesis of C53. Corannulene derivatives also exhibit interesting packing behavior in the solid state [5]. As discussed in detail in Kawase and Kurata review [6] not only bowl-shaped but also ball- and belt-shaped aromatic systems provide an exciting opportunity to explore the concave-convex – interactions by studying their complexation.

Coronene ((6) circulene) is an aromatic planar and very symmetric molecule, it has been studied, synthesized and well characterized [7]. With corannulene, this material has interesting conducting properties due to large electronic resonance. Circulene ((7) circulene), would be the next member of the family, it is conformed by a central cyclooctatetraene fragment fully surrounded by phenyl rings. In spite of the efforts to synthesize it [8], until now this has not been possible. There are a few theoretical studies concerning its structure [9] but no detailed study has been carried out.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1 [10], significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. For instance, nanotubes form a tiny portion of the material(s) in some (primarily carbon fiber) baseball bats, golf clubs,

or car parts [11]. Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) [12] and multi-walled nanotubes (MWNTs) [13]. Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking. In many chemical reactions, fullerenes behave as electron deficient alkenes [14–16]. From its chemical properties, no global aromaticity is expected for C, and computed magnetic properties of closed-shell fullerenes show overall diamagnetic behavior with significant variations in local ring currents [17–23].

THE CALCULATION METHOD

Gaussian 03, Revision C.01 [24] used for the calculation of ground-state geometry was optimized to a local minimum without any symmetry restrictions using basis set 6-31G [25, 26]. The Becke three-parameter hybrid (B3) [27, 28] exchange functional in combination with the Lee-Yang-Parr (LYP) [29] correlation functional (B3LYP) [30, 31] was used for all geometry optimizations, thermodynamic Functions at conditions of (Temperature= 298.150 Kelvin, and Pressure = 1.0 Atm), High Occupied Molecular Orbital Energy (E_{HOMO}) and Low Unoccupied Molecular Orbital Energy (E_{LUMO}), and some physical properties for all molecules are addressed in this study.

RESULTS AND DISCUSSION

The calculations density function theory (DFT) for these molecules indicated that they are not all of them are flats as their structure were given in Figure (1). Corannulene [Cora] molecule is bowl-shaped, coronene [Coro] molecule is planar and circulene [Circ] molecule has a unique saddle-shaped structure, these results agree with the literature. In order to preparation of sub-nanotube the basic understanding of polymerization of Polycyclic Aromatic Hydrocarbons (PAHs) is important. To prepare carbon with sub-nanotubes the polymerization process revealed a production of hydrogen molecules and the formation of new cycles as described in the general reaction in scheme (1) symbolized for the shortcut for butagon cycle formed number (4) and pentagon cycle formed number (5) and hexagon cycle formed number (6).

THE CYCLIC POLYMERIZATION FOR THREE MOLECULES OF CORANNULENE

The scheme (2) shows the cyclic polymerization for three molecules of corannulene: reaction (1) produced a tube [Cora-4-Cora-5-Cora-6] and this means a formation of three different cycles (butagon, pentagon and hexagon cycles), reaction (2) produced a tube [Cora-5-Cora-5-Cora-5] and this means a formation three pentagon cycles. Both reactions are spontaneous and exothermic according to the values of ΔS_r (the entropy change of reaction), ΔH_r (the enthalpy change of reaction) and ΔG_r (the gibbs energy change of reaction). But from the E_{HOMO} (the

Energy of High Occupied Molecular Orbital) and total energy for the products of the two reactions in Table (1) reveals that the product has more stability, in this state the product [Cora-5-Cora-5-Cora-5] is more stable than [Cora-4-Cora-5-Cora-6] and the increase in amount of E_{HOMO} is (-0.2710 eV), also the increases of amount in total energy is (-0.0502 a.u.) or equivalent (-31.5009 KCal.mol⁻¹). The structure for the product [Cora-4-Cora-5-Cora-6] and [Cora-5-Cora-5-Cora-6] were shown in Figure (2). The shapes the prepared tubes were void and inflation from the middle. The diameters of these tubes are ranges (0.76-0.84) nm.

The cyclic polymerization for three molecules of coronene

The scheme (3) shows the cyclic polymerization for three molecules of coronene, the scheme contains four reactions: reaction (1) produced tube of [Coro-4-Coro-4-Coro-4] indicating the formation three of butagon cycles, reaction (2) produced tube of [Coro-4-Coro-5-Coro-5] indicating the formation of one butagon and two pentagon cycles, reaction (3) produced tube of [Coro-5-Coro-5-Coro-6] indicating the formation of two pentagon and one hexagon cycles, reaction (4) produced tube of [Coro-6-Coro-6-Coro-6] indicating the formation of three hexagon cycles. All these four reactions are spontaneous and exothermic according to the values of ΔS_r , ΔH_r and ΔG_r . But from the E_{HOMO} and total energy for the products of the four reactions in Table (1), one can observe the product that has more stability. In this state the product [Coro-5-Coro-5-Coro-6] is more stable than [Coro-4-Coro-4-Coro-4] the increase of amount in E_{HOMO} is (-0.1415 eV), and the increase of amount in total energy is (-0.1981 a.u.) or equivalent (-124.3096 KCal.mol⁻¹) supporting the molecular polymerization stability. Also the product [Coro-5-Coro-5-Coro-6] is more stable than [Coro-4-Coro-5-Coro-5] the increase of amount in E_{HOMO} is (-0.0378 eV), and the increase of amount in total energy is (-0.0636 a.u.) or equivalent (-39.9096 KCal.mol⁻¹). Also the product [Coro-5-Coro-5-Coro-6] is more stable than [Coro-6-Coro-6-Coro-6] the increase of amount in E_{HOMO} is (-0.5051 eV), and the increase of amount in total energy is (-0.0001 a.u.) or equivalent (-0.0628 KCal.mol⁻¹). The structure of all products [Coro-4-Coro-4-Coro-4], [Coro-4-Coro-5-Coro-5], [Coro-5-Coro-5-Coro-6] and [Coro-6-Coro-6-Coro-6] were given in Figure (3) showing tubes shapes. The diameters of these tubes are ranges (0.80-0.89) nm.

THE CYCLIC POLYMERIZATION FOR THREE MOLECULES OF CIRCULENE

The scheme (4) shows the cyclic polymerization for three molecules of circulene, we find in the scheme two reactions: reaction (1) produced to the tube [Circ-4-Circ-5-Citic-6] and this means the formation three different cycles (butagon, pentagon and hexagon cycles), reaction (2) produced to the tube [Circ-5-Circ-5-Circ-5] and this means the formation three pentagon cycles. All two reactions are spontaneous and exothermic according to the values of ΔS_r , ΔH_r and ΔG_r . But from that E_{HOMO} and total energy for the products of the two reaction shows in Table (1) can find the product the more stability, in this state the product [Circ-5-Circ-5-Circ-5] is more stable than [Circ-4-Circ-5-Citic-6] and the increase of amount in E_{HOMO} is (-0.5295 eV). Also the increase of amount in total energy is (-0.0822 a.u.) or equivalent (-51.5813 KCal.mol⁻¹). The structure for all products [Circ-4-Circ-5-Citic-6] and [Circ-5-Circ-5-Circ-5] were shown in Figure (4) show

that tubes and compressed in the middle. The diameter of these tubes are ranges (0.82 -0.95) nm.

ENERGY GAP

The energy gap is also called band gap, is an energy range in a solid where no electron states can exist, the gap energy generally refers to the energy difference (in electron volts) between the Low Unoccupied Molecular Orbital (LUMO) and the High Occupied Molecular Orbital (HOMO) in insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material. In fact, the band gap has a major factor determining the electrical conductivity of a solid. Substances with large gaps energies are generally insulators, those with smaller gaps energies are semiconductors, while conductance materials either have very small gaps energies or none. The Shockley–Queisser limit gives the maximum possible efficiency of single junction solar cells under un-concentrated sunlight, as a function of the semiconductor band gap. If the band gap is too high, most daylight photons cannot be absorbed; if it is too low, then most photons have much more energy than necessary to excite electrons across the band gap, and the rest is wasted. The semiconductors commonly used in commercial solar cells have band gaps near the peak of this curve shown in Figure (5). In Table (1) the values of energy gap for all tubes in the range of (1.4607 – 3.0175) eV, arranged by the increases in energy gap as follows:

[Coro-6-Coro-6-Coro-6] < [Cora-4-Cora-5-Cora-6] < [Coro-5-Coro-5-Coro-6] < [Coro-4-Coro-4-Coro-4] < [Coro-4-Coro-5-Coro-5] < [Cora-5-Cora-5-Cora-5] < [Circ-4-Circ-5-Circ-6] < [Circ-5-Circ-5-Circ-5]

And reverse this order of increase for maximum efficiency, as follows:

[Circ-5-Circ-5-Circ-5] < [Circ-4-Circ-5-Circ-6] < [Cora-5-Cora-5-Cora-5] < [Coro-4-Coro-5-Coro-5] < [Coro-4-Coro-4-Coro-4] < [Coro-5-Coro-5-Coro-6] < [Cora-4-Cora-5-Cora-6] < [Coro-6-Coro-6-Coro-6].

CONCLUSIONS

A quantum chemistry calculation is carried out using the Density Function Theory (DFT) method to study the optimization and frequencies for three of Polycyclic Aromatic Hydrocarbons (PAHs) namely corannulene, coronene and circulene. The results obtained for these molecules shows that not all of them are flat, corannulene molecule is bowl-shaped, coronene molecule is planar and circulene molecule has a unique saddle-shaped structure. The cyclic polymerization reaction leads to the formation of a tube with a diameter smaller than a nanometer, the results showed thermodynamic all preparations reactions are spontaneous and exothermic; these tubes prepared are characterized by high efficiency in the energy gap.

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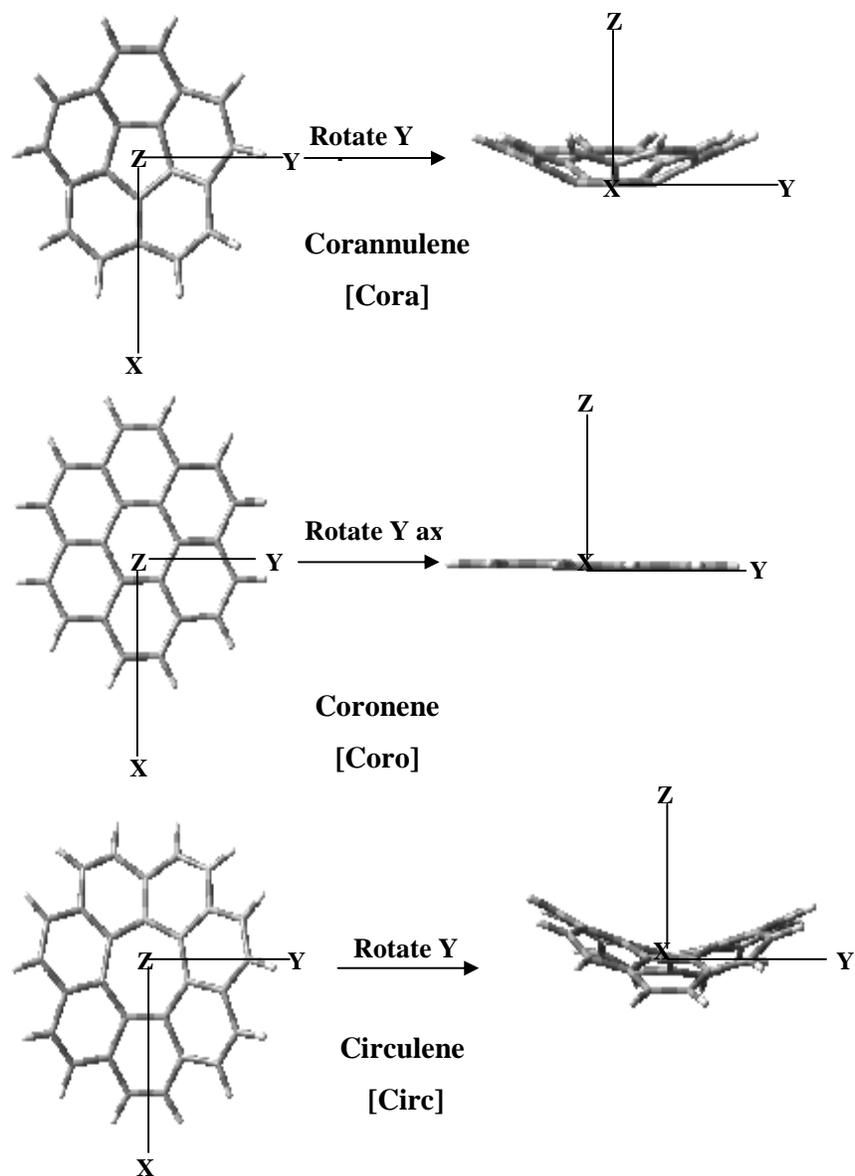
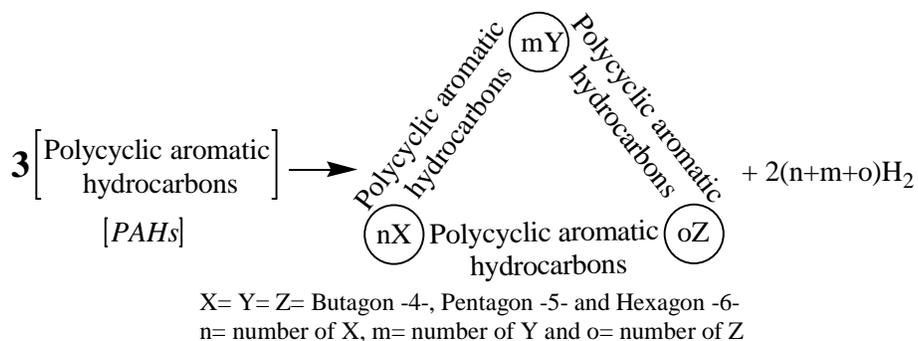
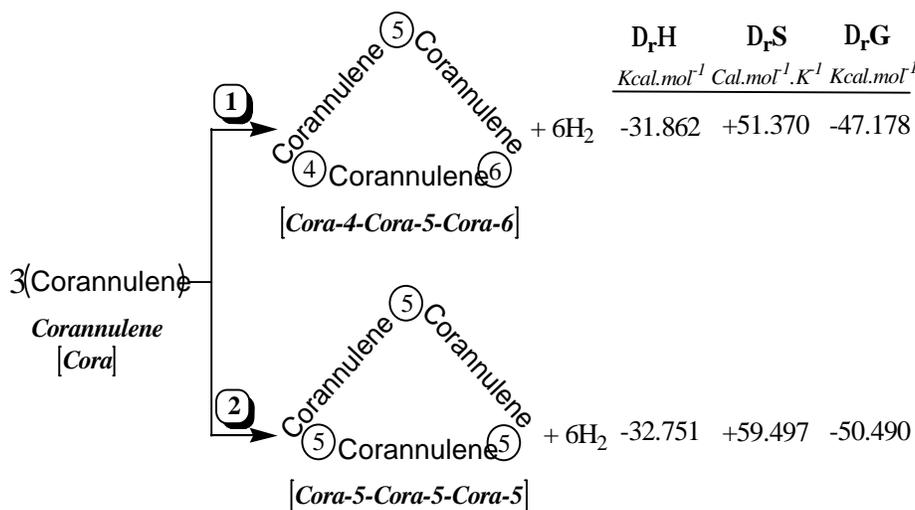


Figure (1) B3LYP/6-31G optimized structures of corannulene, coronene, and circulene.



Scheme (1) The general reaction for the cyclic polymerization reactions of three molecules of polycyclic aromatic hydrocarbons (PAHs).



Scheme (2) The cyclic polymerization reactions of three molecules of corannulene and values of ΔH (the change of enthalpy), ΔS (the change of entropy) and ΔG (the change of Gibbs energy).

Table (1) Some physical values for all molecules and tubes were calculated (in B3LYP/6-31G optimized and frequencies).

Molecules	Total Energy a.u.	Enthalpy (H) KCal.mol ⁻¹	Entropy (S) Cal.mol ⁻¹ .K ⁻¹	E _{HOMO} eV	E _{LUMO} eV	Gap energy (E _{LUMO} - E _{HOMO}) eV
Hydrogen molecule [H ₂]	-1.1755	7.847	31.132	-11.8086	+2.7235	14.5321
Corannulene [Cora]	-767.9696	154.105	103.100	-6.0170	-1.5783	4.4387
[Cora-4-Cora-5-Cora-6]	-2296.4817	383.371	173.878	-4.7538	-2.7663	1.9875
[Cora-5-Cora-5-Cora-5]	-2296.5319	382.482	182.005	-5.0248	-2.7470	2.2778
Coronene [Coro]	-921.6885	185.772	115.845	-5.4880	-1.4049	4.0831
[Coro-4-Coro-4-Coro-4]	-2757.3946	476.637	218.744	-4.6031	-2.6049	1.9982
[Coro-4-Coro-5-Coro-5]	-2757.5291	478.640	213.899	-4.7068	-2.6803	2.0265
[Coro-5-Coro-5-Coro-6]	-2757.5927	479.221	211.299	-4.7446	-2.7570	1.9876
[Coro-6-Coro-6-Coro-6]	-2757.5926	478.454	210.283	-4.2395	-2.7788	1.4607
Circulene [Circ]	-1075.2072	216.027	132.547	-5.1430	-1.4348	3.7082
[Circ-4-Circ-5-Circ-6]	-3218.2315	571.489	249.274	-4.4850	-1.9734	2.5116
[Circ-5-Circ-5-Circ-5]	-3218.3137	572.909	247.261	-5.0145	-1.9970	3.0175

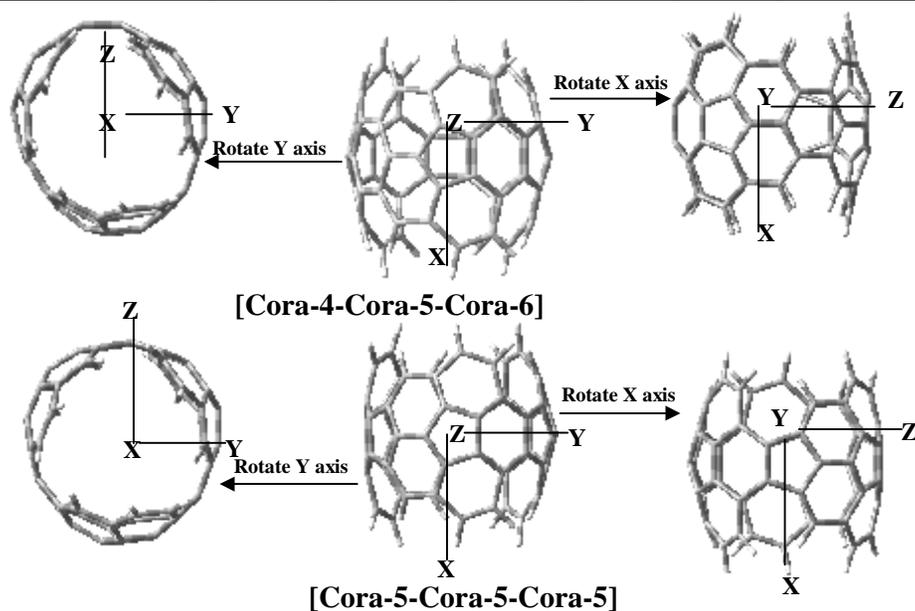
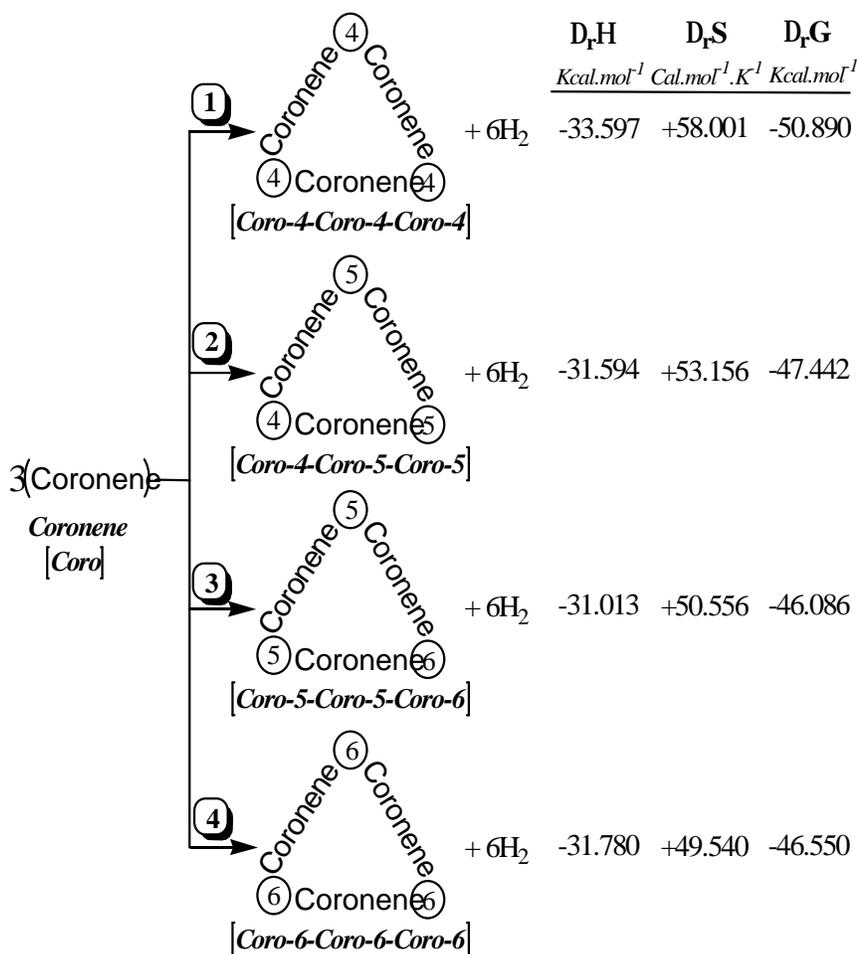


Figure (2) B3LYP/6-31G optimized structures of products for the cyclic polymerization for three molecules of corannulene.



Scheme (3) The cyclic polymerization reactions of three molecules of coronene and values of ΔH (the change of enthalpy), ΔS (the change of entropy) and ΔG (the change of Gibbs energy).

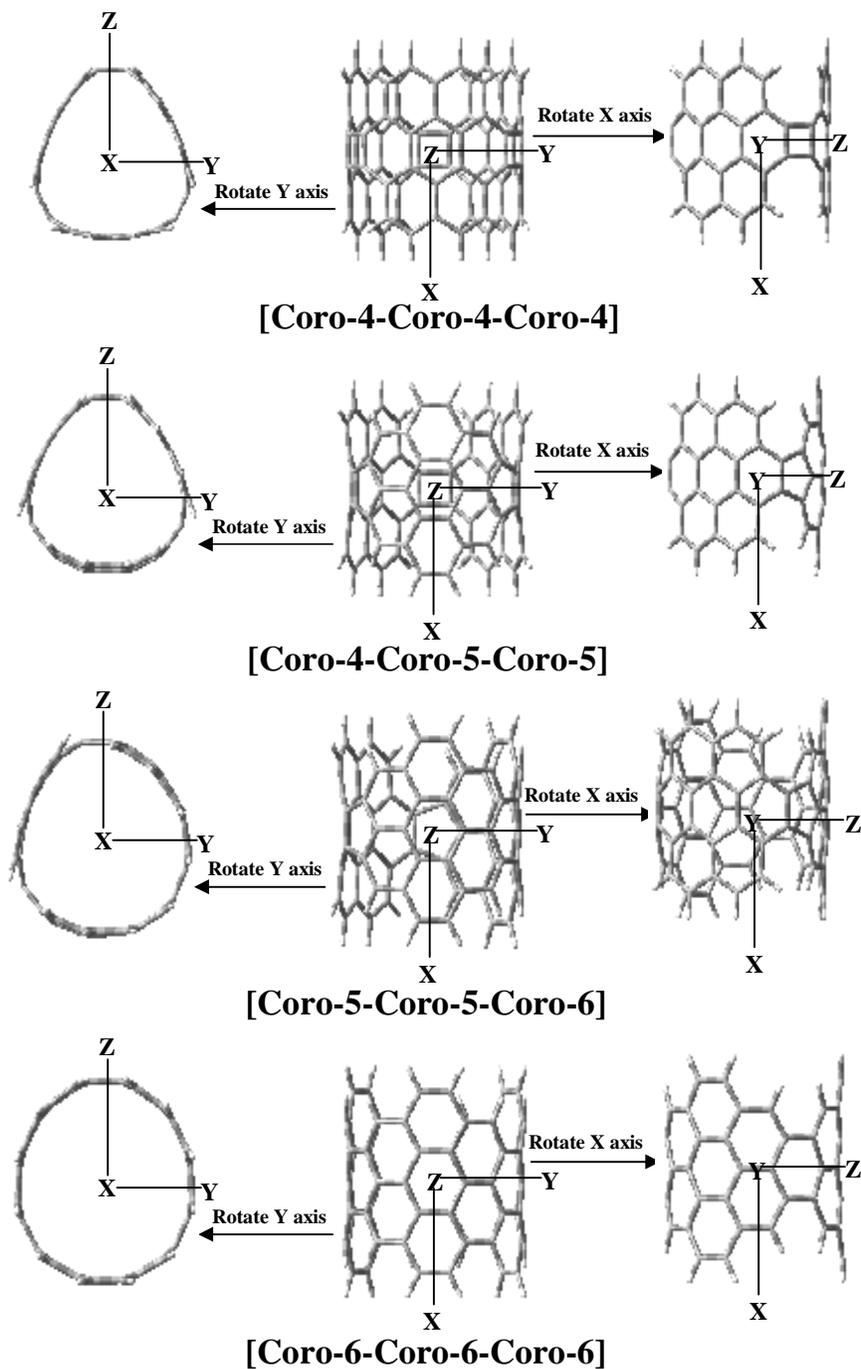
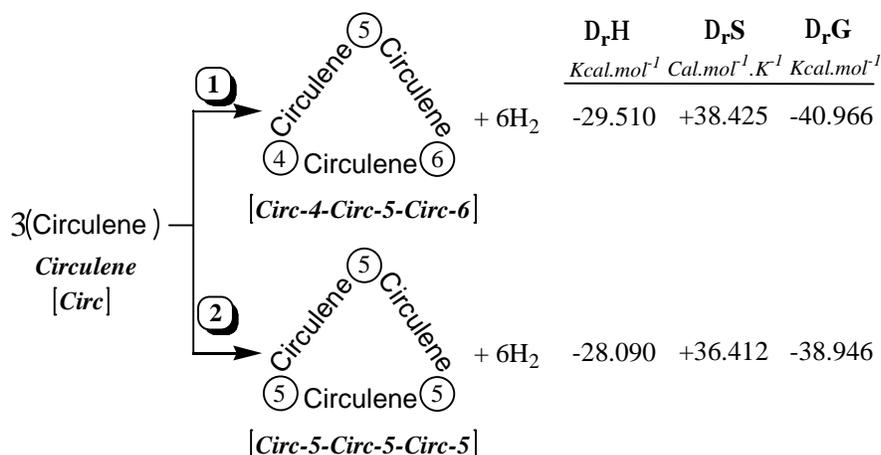


Figure (3) B3LYP/6-31G optimized structures of products for the cyclic polymerization for three molecules of coronene.



Scheme (4) The cyclic polymerization reactions of three molecules of circulene and values of ΔH (the change of enthalpy), ΔS (the change of entropy) and ΔG (the change of Gibbs energy).

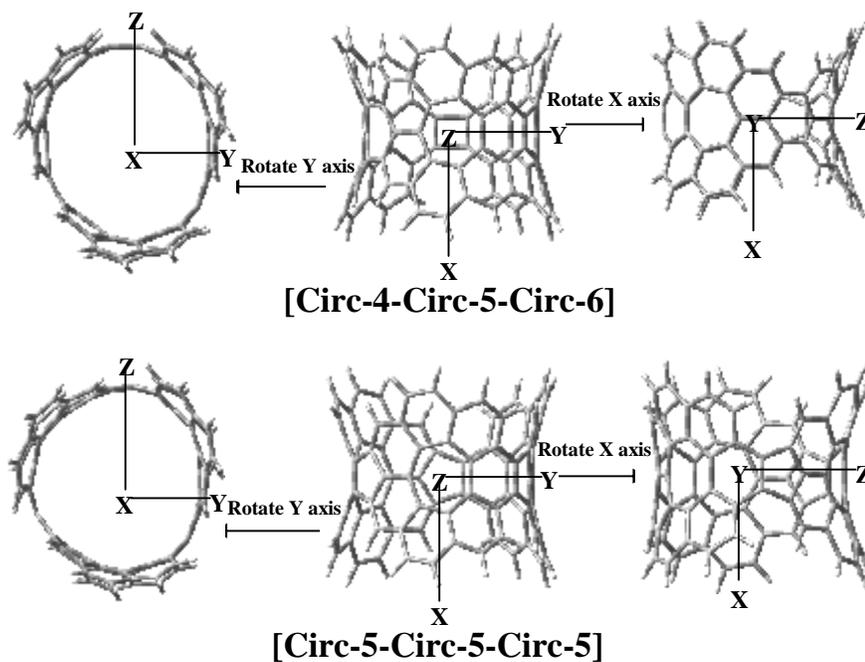


Figure (4) B3LYP/6-31G optimized structures of products for the cyclic polymerization for three molecules of circulene.

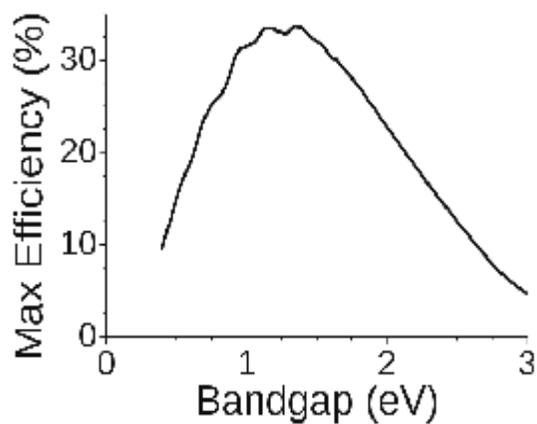


Figure (5) The Shockley – Queisser limit for energy efficiency gap.