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# Theoretical Study for the Preparation of New Buckyballs from the Cyclic Dimerization Reaction of Two Molecules Corannulene, Coronene and Circulene Aromatic Compounds

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## ABSTRACT

Corannulene, coronene and circulene are polycyclic aromatic hydrocarbons (PAHs) compounds were chosen in this research to study the preparation of new buckyballs with diameters smaller fraction of nano-meter theoretically may achievable using the density function theory (DFT). The results showed that the shapes of stable molecules are; corannulene molecule is bowl-shaped, coronene molecule is planar, circulene molecule has a unique saddle-shaped structure. Upon to cyclic dimerization reaction for two of the molecules selected resulting a new buckyballs formation. The results showed that the new buckyballs prepared have high efficiency in the gap energy, making it potentially useful for solar cell applications.

**Keywords**: Corannulene, Coronene, Circulene, DFT, Buckyballs.

# دراسة نظرية لتحضير بوكيبولات جديدة من تفاعل الدايمر الحلقي لجزيئتين من المركبات الأروماتية (الكوراننولين والكورونين والسيركولين)

## الخلاصة

الكوراننولين والكورونين والسيركولين هي مركبات هيدروكاربونية أروماتية متعددة الحلقات أختيرت في هذا البحث لدراسة تحضير بوكيبولات جديدة ذات أقطار أصغر من النانومتر نظرياً بأستخدام نظرية دوال الكثافة. أظهرت نتائج الحسابات ان الشكل المستقر لجزيئات المحسوبة هو كما يلي: جزيئة الكوراننولين ذات شكل يشبه الطاسة، وجزيئة الكورونين ذات شكل مستوي، وجزيئة السيركولين ذات شكل يشبه سرج الحصان. نحصل على البوكيبولات نتيجة لتفاعل الدايمر الحلقي لجزيئتين من الجزيئات المختارة، وأظهرت النتائج ان البوكيبولات الجديدة 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 heteroatoms or carry substituents [1]. PAHs comprised only of six-membered rings are called alternant PAHs, certain alternant PAHs are called “benzenoid” PAHs. PAHs

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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 [2].

Corannulene 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 $C_{53}$. Corrannulene derivatives also exhibit interesting packing behavior in the solid state [3]. As discussed in detail in Kawase and Kuratare view [4] 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 complication.

Coronene (6-circulene) is an aromatic planar and very symmetric molecule, it has been studied, synthesized and well characterized [5]. With corannulene, this material has interesting conducting properties due to its large electronic resonance. 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 [6], until now this has not been possible. There are a few theoretical studies concerning its structure [7] but no detailed study has been carried out.

## THE CALCULATION METHOD

Gaussian 03, Revision C.01 [8] was used for the calculation of ground-state geometry was optimized to a local minimum without any symmetry restrictions using basis set 6-31G [9,10]. The becke three-parameter hybrid (B3) [11, 12] exchange functional in combination with the Lee-Yang-Parr (LYP) [13] correlation functional (B3LYP) was used for all geometry optimizitions, 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

Previous studies have shown that not all Polycyclic Aromatic Hydrocarbons (PAHs) are flat molecules, aromatic compounds that have been selected in this research known as circulenes. These are 5-circulene (corannulene), 6-circulene (coronene), 7-circulene (circulene). The calculations Density Function Theory (DFT) for these molecules that they are not all of them flats their structure was given in Figure (1). Corannulene molecule is bowl-shaped, coronene molecule is planar and circulene molecule has a unique saddle-shaped structure, these results agree with the literature.

In order to produce buckyballs basic understanding of dimerization of Polycyclic Aromatic Hydrocarbons (PAHs) is important. To prepare buckyballs the dimerization process revealed a production of hydrogen molecules and the formation of new cycles as described in the general reaction in Scheme (1). All buckyballs shapes prepared are spherical compressed from both sides and hollow.

## THE CYCLIC DIMERIZATION FOR TWO MOLECULES OF CORANNULENE

Scheme (2) shows the cyclic dimerization for two molecules of corannulene: reaction (1) produced a buckyball $C_{40}$ (I) and this means a formation of ten pentagon cycles, reaction (2) produced a buckyball $C_{40}$ (II) and this means a formation five butagon and five hexagon cycles. Both reactions are spontaneous and exothermic according to the values of $\Delta S_r$ (the change of entropy), $\Delta G_r$ (the change of Gibbs energy) and $\Delta H_r$ (the change of enthalpy) for each 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 buckyball $C_{40}$ (I) is more stable than buckyball $C_{40}$ (II) and the increase in amount of $E_{HOMO}$ is (-0.6182 eV). Also the increases of amount in total energy is (-0.2862 a.u.) or equivalent (-179.5932 $KCal.mol^{-1}$). The structure for the product buckyball $C_{40}$ (I) and buckyball $C_{40}$ (II) were shown in Figure (2). The diameter of buckyball $C_{40}$ (I) is (0.46, 0.57)nm and buckyball $C_{40}$ (II) is (0.43 , 0.62)nm.

## THE CYCLIC DIMERIZATION FOR TWO MOLECULES OF CORONENE

Scheme (3) shows the cyclic dimerization for two molecules of coronene. The scheme contains two reactions: reaction (1) produced buckyball $C_{48}$ (I) indicating the formation twelve of pentagon cycles, reaction (2) produced buckyball $C_{48}$ (II) indicating the formation of six butagon and six hexagon cycles. Both reactions are spontaneous and exothermic according to the values of $\Delta H_r$, $\Delta S_r$ and $\Delta G_r$ for each reaction. But from the $E_{HOMO}$ and total energy for the products of the two reactions in Table (1), one can observe the product that has more stability. In this state the product buckyball $C_{48}$ (I) is more stable than buckyball $C_{48}$ (II) and the increase of amount in $E_{HOMO}$ is (-0.625 eV), and the increase of amount in total energy is (-0.3114 a.u.) or equivalent (-195.4064 $KCal.mol^{-1}$). The structure of all products buckyball $C_{48}$ (I) and buckyball $C_{48}$ (II) were given in Figure (3). The diameter of buckyball $C_{48}$ (I) is (0.42 , 0.71)nm and buckyball $C_{48}$ (II) is (0.40 , 0.72)nm.

## THE CYCLIC DIMERIZATION FOR TWO MOLECULES OF CIRCULENE

Scheme (4) shows the cyclic dimerization for two molecules of circulene, we find in the scheme two reactions: reaction (1) produced buckyball $C_{56}$ (I) and this means the formation fourteen pentagon cycles, reaction (2) produced buckyball $C_{56}$ (II) and this means the formation seven butagon and seven hexagon cycles. All two reactions are spontaneous and exothermic according to the values of $\Delta S_r$ (the change of entropy), $\Delta G_r$ (the change of Gibbs energy) and $\Delta H_r$ (the change of enthalpy) for each reaction. But from that $E_{HOMO}$ and total energy for the products of the two reaction in table (1) can find the product the more stability, in this state the product buckyball $C_{56}$ (I) is more stable than buckyball $C_{56}$ (II) and the increase of amount in $E_{HOMO}$ is (-0.5788 eV). Also the increase of amount in total energy is (-0.3748 a.u.) or equivalent (-235.1905 $KCal.mol^{-1}$). The structure for all products buckyball $C_{56}$ (I) and buckyball $C_{56}$ (II) were shown in Figure (4). The diameter of buckyball $C_{56}$ (I) is (0.38 , 0.80)nm and buckyball $C_{56}$ (II) is (0.37 , 0.80)nm.

## ENERGY GAP

In solid state physics, a band gap, also called an energy 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 shellelectron 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 conducting 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 buckyballs in the range of (1.2278 – 2.3056) eV, arranged by the increases in energy efficiency gap as follows:

Buckyball $C_{56}$ (I) < Buckyball $C_{40}$ (I) < Buckyball $C_{48}$ (I) < Buckyball $C_{56}$ (II)
< Buckyball $C_{40}$ (II) < Buckyball $C_{48}$ (II)

## CONCLUSIONS

A quantum chemistry calculation is carried out using the Density Function Theory (DFT) method to study optimized and frequencies for three of Polycyclic Aromatic Hydrocarbons (PAHs) namely corannulene, coroneneand 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 dimerization reactions lead to the formation of a buckyballs with a diameter smaller than a nanometer, as characterized by high efficiency in the energy gap.

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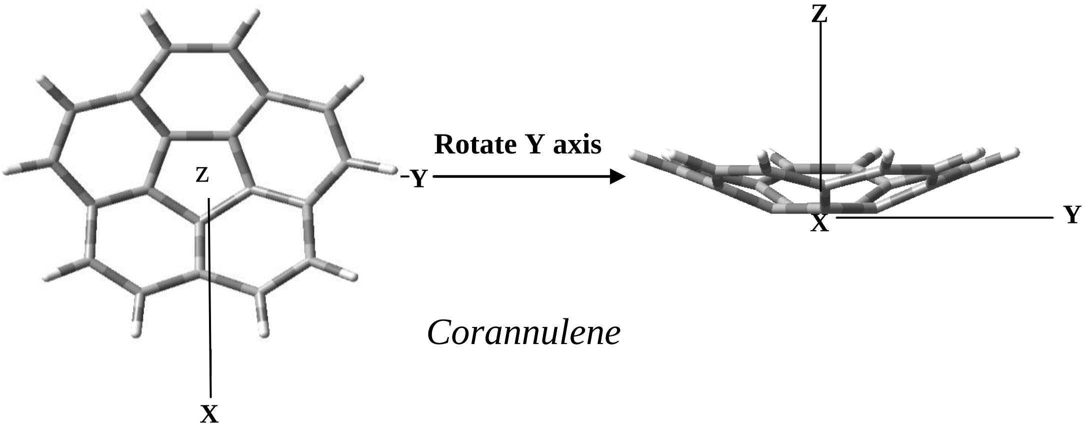
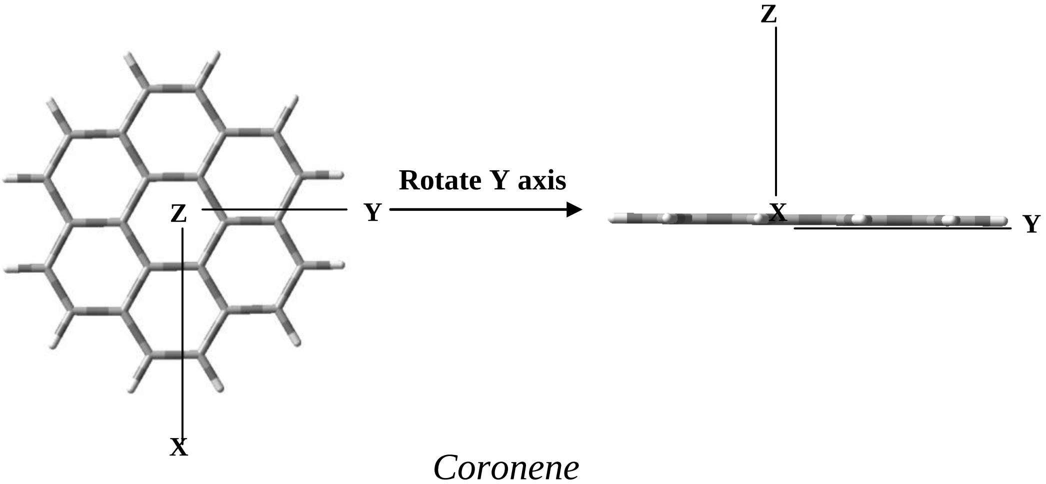
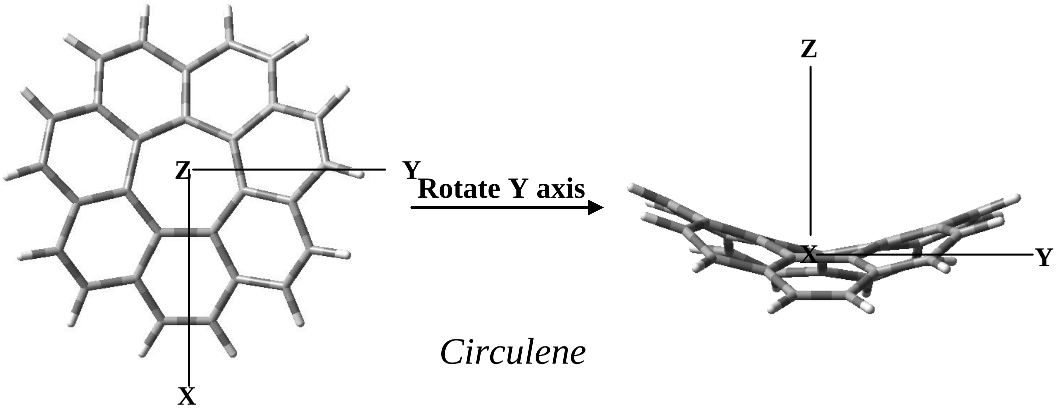


*Corannulene*



*Coronene*



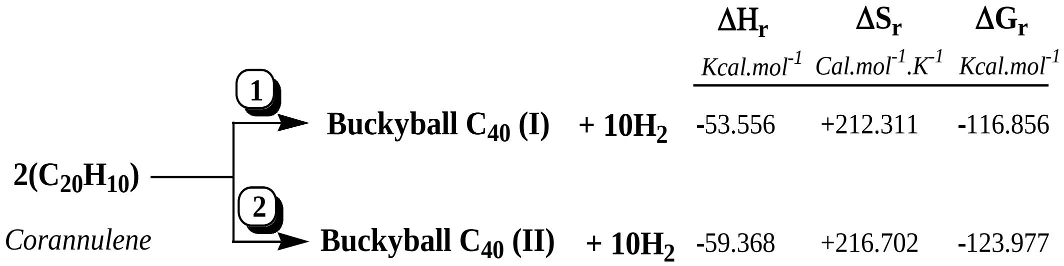
*Circulene*

**Figure (1) B3LYP/6-31G optimized structures of Corannulene , Coronene, and Circulene.**

$$2\begin{bmatrix}\textbf{Polycyclic aromatic}\\ \textbf{hydrocarbons}\\ (C_nH_{\frac{1}{2}n})\end{bmatrix} \longrightarrow \textbf{Buckyball } [C_{2n}] + \tfrac{1}{2}\,nH_2$$

$$[PAHs] \qquad n = \text{number of carbon atoms.}$$

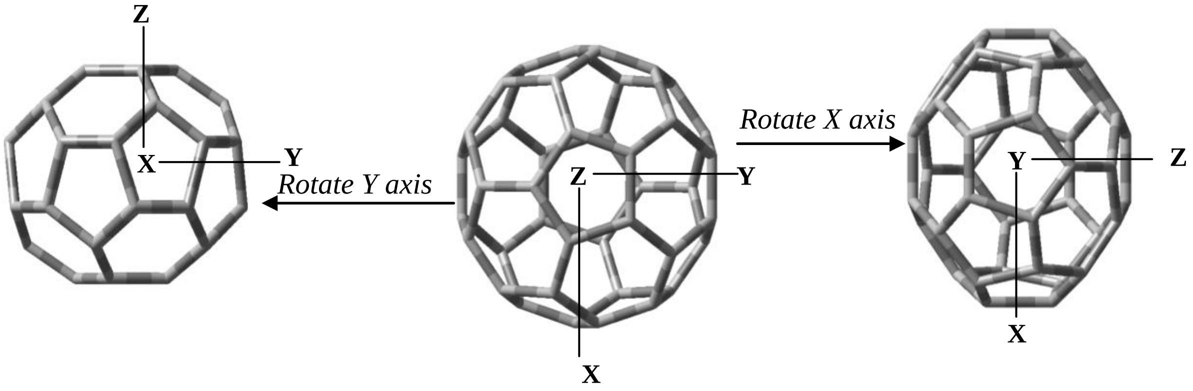
**Scheme (1)** the general reaction of formation new buckyballs from two molecules of Polycyclic Aromatic Hydrocarbons (PAHs).



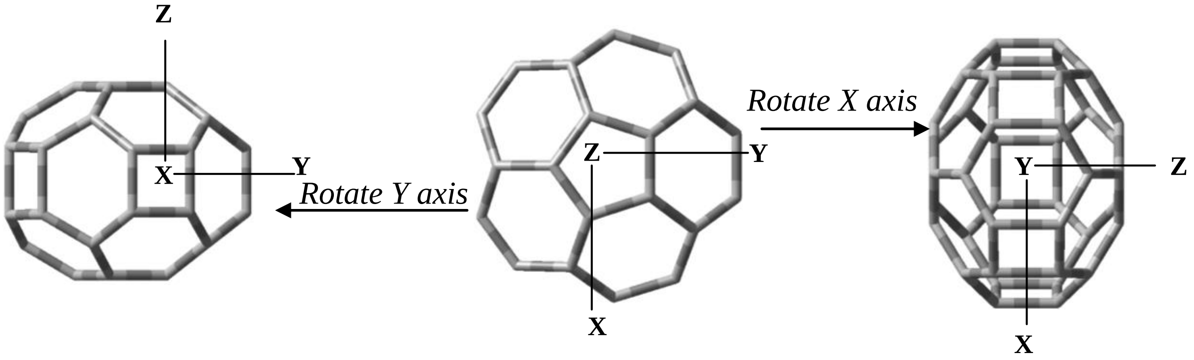
**Scheme (2)** the reaction of formation buckyball $C_{40}$ from two molecules of corannulene and values of $\Delta H_r$ (the change of enthalpy), $\Delta S_r$ (the change of entropy) and $\Delta G_r$ (the change of Gibbs energy).

**Table (1) some physical values for all new buckyballs 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 |
|---|---|---|---|---|---|---|
| **$H_2$** | -1.1755 | 7.847 | 31.132 | -11.8086 | +2.7235 | 14.5321 |
| **Corannulene** | -767.9696 | 154.105 | 103.100 | -6.0170 | -1.5783 | 4.4387 |
| **Buckyball $C_{40}$ (I)** | -1523.2980 | 176.184 | 107.191 | -6.1563 | -3.9152 | 2.2411 |
| **Buckyball $C_{40}$ (II)** | -1523.0118 | 170.372 | 111.582 | -5.5381 | -4.1976 | 1.3405 |
| **Coronene** | -921.6885 | 185.772 | 115.845 | -5.4880 | -1.4049 | 4.0831 |
| **Buckyball $C_{48}$ (I)** | -1827.8360 | 209.165 | 118.599 | -5.9514 | -3.9767 | 1.9747 |
| **Buckyball $C_{48}$ (II)** | -1827.5246 | 202.120 | 128.874 | -5.3264 | -4.0986 | 1.2278 |
| **Circulene** | -1075.2072 | 216.027 | 132.547 | -5.1430 | -1.4348 | 3.7082 |
| **Buckyball $C_{56}$ (I)** | -2132.0617 | 239.494 | 133.574 | -6.0853 | -3.7797 | 2.3056 |
| **Buckyball $C_{56}$ (II)** | -2131.6869 | 230.191 | 142.131 | -5.5065 | -3.7884 | 1.7181 |

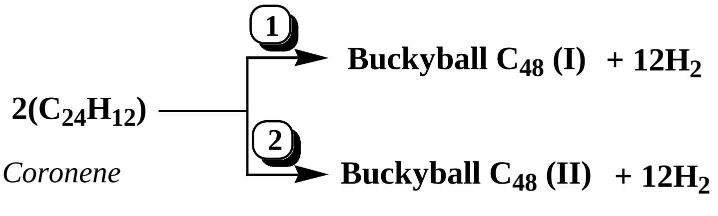


**Buckyball $C_{40}$ (I)**



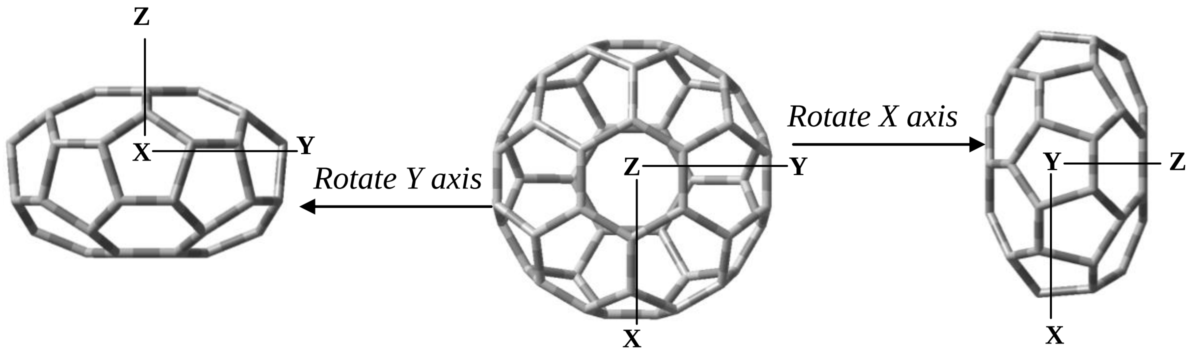
**Buckyball $C_{40}$ (II)**

Figure (2) B3LYP/6-31G optimized structures of buckyball $C_{40}$ (I) and buckyball $C_{40}$ (II).

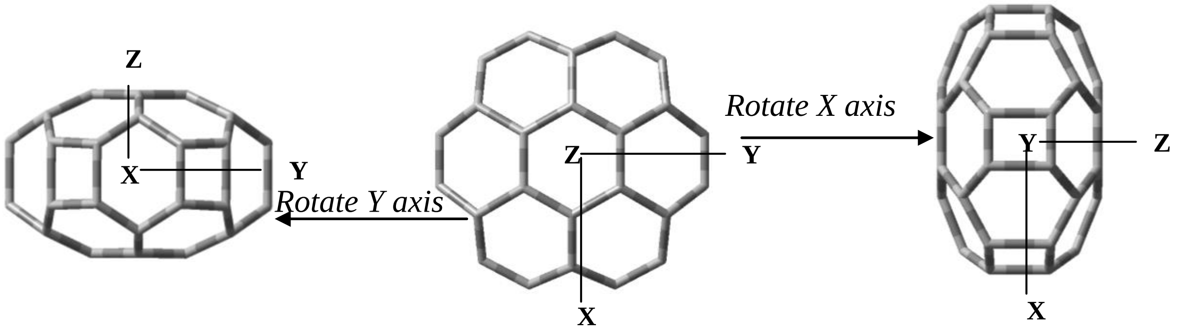


| | $\Delta H_r$ *Kcal.mol$^{-1}$* | $\Delta S_r$ *Cal.mol$^{-1}$.K$^{-1}$* | $\Delta G_r$ *Kcal.mol$^{-1}$* |
|---|---|---|---|
| ① Buckyball $C_{48}$ (I) + 12$H_2$ | -68.215 | +260.493 | -145.880 |
| ② Buckyball $C_{48}$ (II) + 12$H_2$ | -75.260 | +270.768 | -155.989 |

Scheme (3) the reaction of formation buckyball $C_{48}$ from two molecules of coronene and values of $\Delta H_r$, $\Delta S_r$ and $\Delta G_r$.

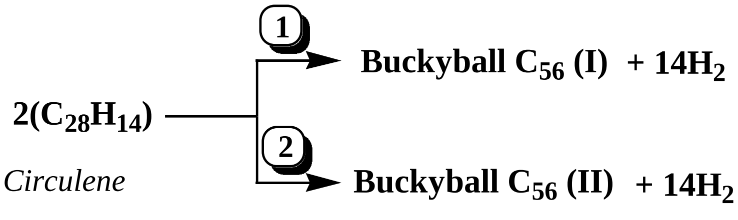


**Buckyball $C_{48}$ (I)**



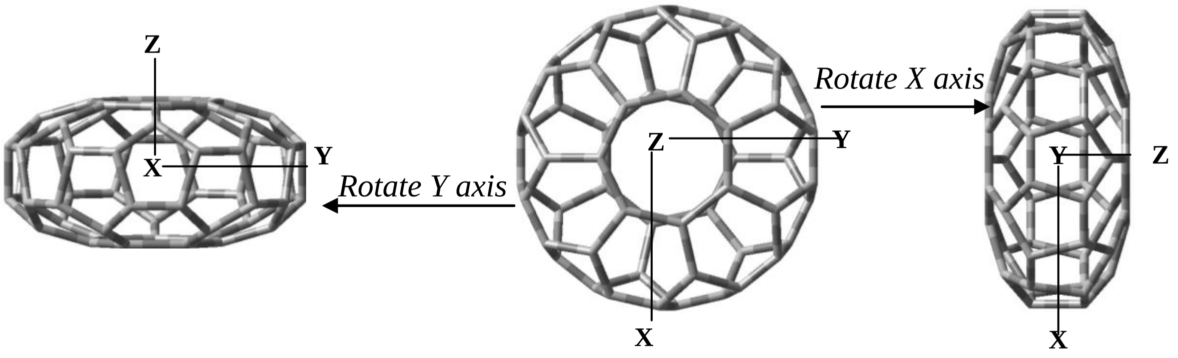
**Buckyball $C_{48}$ (II)**

**Figure (3) B3LYP/6-31G optimized structures of buckyball $C_{48}$ (I) and buckyball $C_{48}$ (II).**

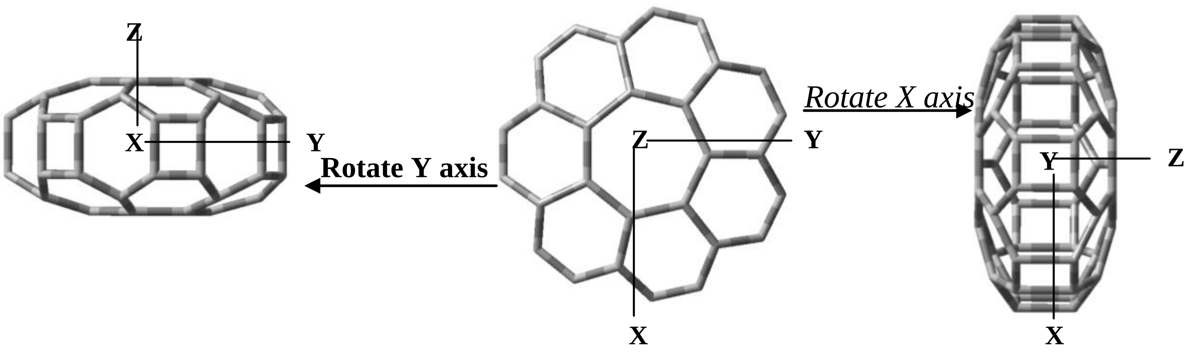


| | $\Delta H_r$ *Kcal.mol$^{-1}$* | $\Delta S_r$ *Cal.mol$^{-1}$.K$^{-1}$* | $\Delta G_r$ *Kcal.mol$^{-1}$* |
|---|---|---|---|
| Buckyball $C_{56}$ (I) + $14H_2$ | -82.702 | +304.328 | -173.437 |
| Buckyball $C_{56}$ (II) + $14H_2$ | -92.005 | +312.885 | -185.291 |

**Scheme (4)** the reaction of formation buckyball $C_{56}$ from two molecules of circulene and values of $\Delta H_r$, $\Delta S_r$ and $\Delta G_r$.



**Buckyball $C_{56}$ (I)**



**Buckyball $C_{56}$ (II)**

**Figure (4) B3LYP/6-31G optimized structures of buckyball $C_{56}$ (I) and buckyball $C_{56}$ (II).**

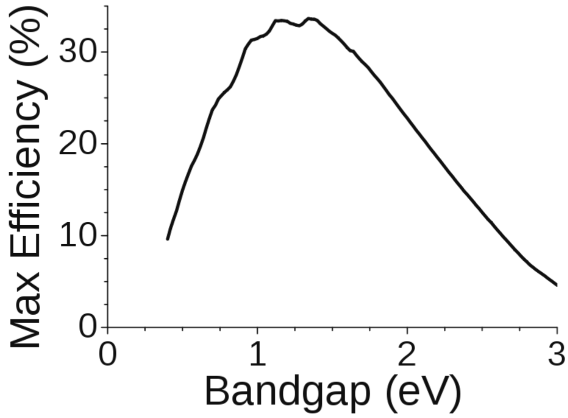


**Figure (5) The Shockley–Queisser limit for energy efficiency gap.**