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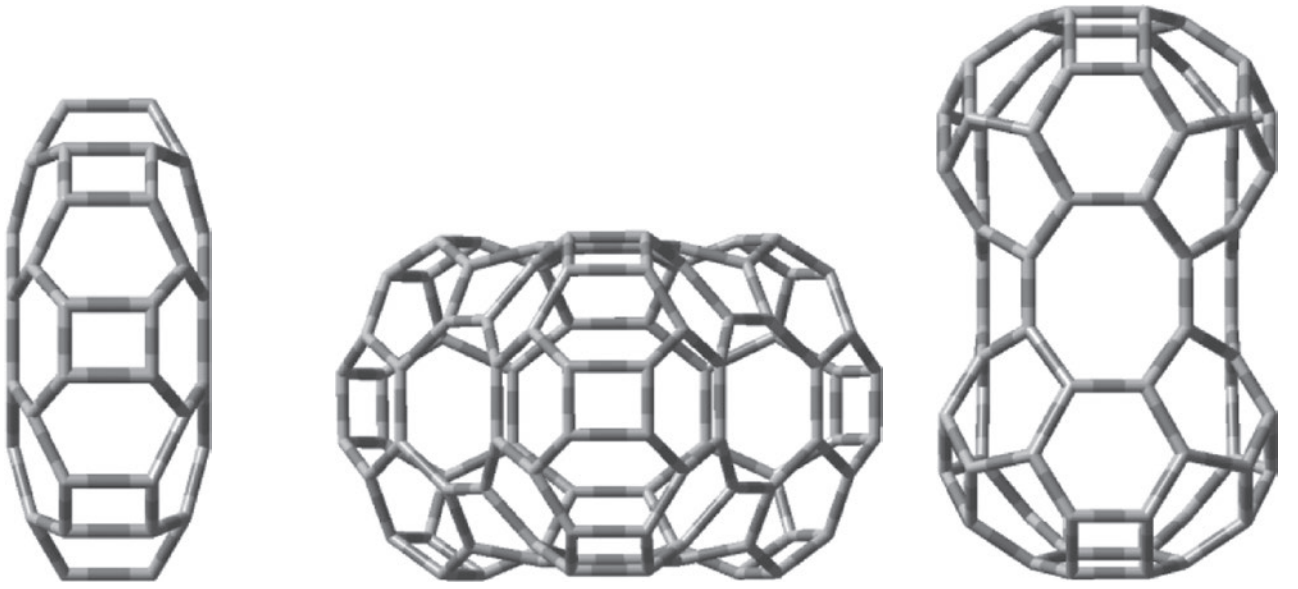

PHYSICAL CHEMISTRY | RESEARCH ARTICLE

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Molecular simulation for novel carbon buckyball materials

Hasan R. Obayes[1], Abdul Hameed Al Obaidy[2], Ghadah H. Alwan[3] and Ahmed A. Al-Amiery[2]*

Abstract: The discovery of buckyballs was unexpected because the researchers were delivering carbon plasmas to reproduce and describe unidentified interstellar matter. Density functional theory was done to study and design the structure of [8]circulene and three new buckyballs with molecular dimensions of less than a nanometer. Cyclic polymerization reactions can be utilized to prepare new buckyballs, and this process also produces molecules of hydrogen. All reactions are spontaneous and exothermic as per the estimations to the values of entropy, Gibbs energy, and enthalpy changes. The results demonstrate that the most symmetric buckyball is the most stable, and the molecular dimensions are less than a nanometer. The new buckyballs are characterized by the high efficiency of their energy gaps, making it potentially useful for solar cell applications.

Subjects: Atomic, Molecular, Physical Chemistry; Computational and Theoretical Chemistry; Materials Chemistry

Keywords: circulene; DFT; solar cells; buckyball; Gibbs energy

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1. Introduction

Previously, just steady bulk types of basic carbon have been accepted to be graphite and diamond. Around 30 years prior, this standard way of thinking has been tested by the discovery of the stable C60 molecule with a circular empty cage (Kroto, Heath, O'Brien, Curl, & Smalley, 1985). This molecule,

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Ahmed A. Al-Amiery is an assistant professor at University of Technology/Environmental Research Center. He has over 80 scientific papers and projects either presented or published and international patent. He is an expert in many areas of applied chemistry. He is the editor for many journals. Recent publications include a paper on the use of novel coumarin derivatives as corrosion inhibitors. He is a visitor professor at Department of Chemical and Process Engineering Universiti Kebangsaan Malaysia. He has postdoctoral degree from the Department of Chemical and Process Engineering Universiti Kebangsaan Malaysia. He was awarded the Medal for scientific excellence (2014), and also holds Science Day Award from the Ministry of Higher Education and Scientific Research for four consecutive years (2010–2011, 2011–2012, 2012–2013, and 2013–2014). He was selected as a member of the Who's Who for International Executives 2015. He is the TWAS young scientist/ TWAS YAs.

PUBLIC INTEREST STATEMENT

Density functional theory was applied to design and investigate the structure of [8]circulene and three new buckyballs with molecular dimensions of less than a nanometer. [8]circulene molecule has a unique saddle-shaped structure. The cyclic polymerization reactions of [8]circulene molecules can be used to prepare new buckyballs, and this process also produces molecules of hydrogen. All of these reactions are spontaneous and exothermic according to the values of entropy change $\Delta_r S$ (positive value), Gibbs energy change $\Delta_r G$ (negative value) thermodynamically favored, and enthalpy change $\Delta_r H$ (negative value). Our new buckyballs show that the most symmetric buckyball is the most stable, depending on the values of EHOMO [high occupied molecular orbital (HOMO)]. The molecular dimensions of all the new buckyballs are less than a nanometer, and the new buckyballs are characterized by the high efficiency of their energy gaps, making it potentially useful for solar cell applications.

called "buckyball," ended up being just a specific illustrative of the group of "fullerene" molecules. Later on, it has been observed that C60 molecules can total to structure a molecular crystal. The interest in C60 rose dramatically following the effective advancement of a mass production method for this system (Krätschmer, Lamb, Fostiropoulos, & Huffman, 1990). Fullerenes are molecules that comprise precisely 12 pentagons and a fluctuating number of hexagons. The most acclaimed fullerene atom is C60 with 12 pentagons and 20 hexagons (ordinarily alluded to as "Buckyballs," another way to say "Buckminsterfullerene"), which was found in 1985. Smalley, Curl, and Kroto were awarded the 1996 Nobel Prize in Chemistry for their disclosure, which not just permitted the investigation of the entrancing properties of C60 molecules and solids, for example, superconductivity in alkali metal-doped C60 robust (Hebard et al., 1991; Kroto, 1982). Interestingly, in his Nobel lecture, he underlines the pentagon separation guideline (Kroto, 1987, 1997) foreseeing the most stable fullerenes to have the 12 pentagons as far apart as would be prudent. In light of this rule, the C20 fullerene cage ought to be exceedingly unsteady, and by defying this tenet C20 is once in a while alluded to as an "unconventional fullerene" (Jon Seiders, Baldridge, & Siegel, 2001; Wang et al., 2006). A standout amongst the most confusing parts of fullerenes (C60, C70, etc.) is the way such confused symmetric molecules are structured from a gas of atomic carbons, namely, the atomistic (Hua, Çagin, Che, & Goddard, 2000). The smallest illustrations of these graphitic structures are the [n]circulenes, wherein a focal n-sided polygon is surrounded by n-fused benzenoid rings (Bhola et al., 2010). [7]circulene, initially synthesized by Yamamoto, Nakazaki, and collaborators in 1983, is saddle formed (Yamamoto et al., 1983). [6]circulene, or is the trifling, planar case, and it was initially prepared by Scholl and Meyer in 1932 (Ivasenko et al., 2009) additionally happens commonly. [5]circulene, embodies one-third of the C60 skeleton and has been seriously studied, (Wu & Siegel, 2006) and it was initially arranged by Lawton and Barth (1971). While a couple of spearheading endeavors have been reported (Christoph et al., 2008), [4]circulene has never been incorporated previously. Attempts to get [8]circulene through the oxidative photochemical cyclization of [2.2](3,6)phenanthrenophane-diene have been unsuccessful. This domino reaction should structure the focal eight-membered ring and two fringe benzenoids from a planar starting beginning in one prepared step; however, it is unsuitable for the creation of a profoundly strained molecule. In light of this data, the manufactured strategy displayed thus is to first construct the central eight-membered ring, and then after that to produce the peripheral benzenoids (Thulin & Wennerström, 1983). A density function theory (DFT) estimation introduces an additional step to each major phase of a Hartree–Fock calculation. The aim of this study was to synthesize and investigate new buckyballs with molecular dimensions of less than a nanometer using DFT.

2. Methodology

Molecular geometries of the all molecules were completely optimized with the hybrid DFT B3LYP method (Becke, 1993; Lee, Yang, & Parr, 1988; Pietro et al., 1982) using the 6-31G basis set (Al-Amiery et al., 2012; Frisch et al., 2004) by means of the Gaussian 09, revision A.02 (Baryshnikov, Minaev, Pittelkow, Nielsen, & Salcedo, 2013) utilizing for all geometry optimizations, thermodynamic functions at conditions (temperature = 298 K, and pressure = 1.0 atm), high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) distribution, and some physical properties for all molecules addressed in this study.

3. Results and discussion

Previous studies have shown that not all polycyclic aromatic hydrocarbons (PAHs) are flat molecules. [n]circulene is a macrocyclic arene in which there is a central n-sided polygon, these are [5]circulene (corannulene), [6]circulene (coronene), and [7]circulene (circulene or pleiadannulene) prepared in previous studies. The shapes of these circulenes change from a bowl ([5]circulene) through a plane ([6]circulene) to a saddle ([7]circulene). [8]circulene has not yet been synthesized in the laboratory, presumably because of its highly strained structure and instability (Hebard et al., 1991). In contrast, its various planar analogs, such as tetraoxo[8]circulene, (Baryshnikov, Minaev, Karaush, & Minaeva, 2014; Baryshnikov, Minaev, Minaeva, Nenajdenko, 2013; Radenković, Gutman, & Bultinck, 2012) octathio[8]circulene, (Fujimoto, Suizu, Yoshikawa, & Awaga, 2008; Gahungu & Zhang, 2008; Miller, Duncan, Schneebeli, Gray, & Whalley, 2014; Sakamoto & Suzuki, 2013), and tetrabenzo[8]circulene (Naama et al., 2013; Obayes, Alwan, Al-Amiery, Kadhum, & Mohamad, 2013) have been successfully

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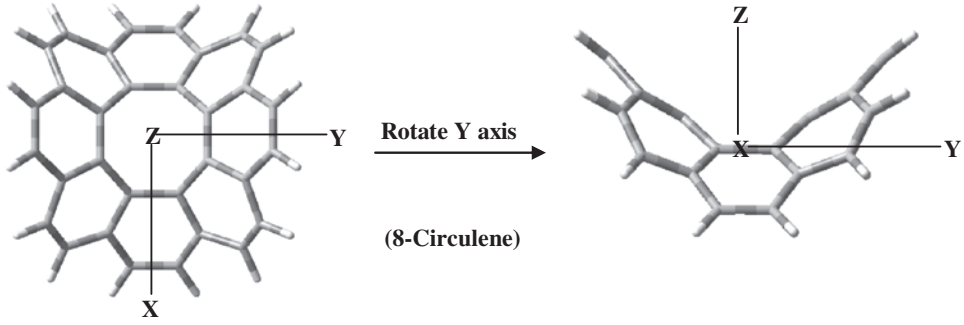

Figure 1. B3LYP/6-31G optimized structures of [8] circulene.

generated. The calculation of DFT for [8]circulene has been predicted to have a saddle-shaped structure was given in Figure 1. These results agree with the literatures. The cyclic polymerization of PAHs was used to design new carbon buckyball. The important about this process was released hydrogen molecules and the formation of new butagon and hexagon cycles as described in the general reaction shown below in Equation 1:

$$x(C_{32}H_{16}) \qquad \text{Buckyball } [C_{(32)x}] + (8)xH_2 \tag{1}$$

where x is the molecules number of [8]circulene.

3.1. The cyclic polymerization of [8]circulene molecules

Scheme 1 shows the design of buckyballs from cyclic polymerization reactions of two, three, and four [8]circulene molecules. Reaction (1) produced a new buckyball C_{64} by forming eight butagons, and eight hexagons cycles from two [8]circulene molecules. Reaction (2) produced a new buckyball C_{96} by forming nine butagons, and 14 hexagons cycles from three [8]circulene molecules. Reaction (3) produced a new buckyball C_{128} by forming 12 butagons, 16 hexagons, and two octagons cycles from four [8]circulene molecules. All of these reactions are spontaneous and exothermic according to the values of entropy change $\Delta_r S$ (positive value), Gibbs energy change $\Delta_r G$ (negative value) thermodynamically favored, and enthalpy change $\Delta_r H$ (negative value) (Baryshnikov, Minaev, Minaeva, et al., 2013; Radenković et al., 2012). E_{HOMO} (the energy of HOMO) of the three reaction products is shown in Table 1. Revealed that the products are stable, (Obayes, Al-Amiery, et al., 2013a; Obayes et al., 2014) buckyball C_{64} was the most stable of these, the increase in E_{HOMO} for buckyball C_{64} was (−0.2068 eV) and −0.03456 eV) relative to buckyball C_{96} and buckyball C_{128}, respectively. The structures of the three buckyballs are shown in Figure 2. The diameters of these buckyballs are: buckyball C_{64} is (0.875 nm *x*-axis, 0.355 nm *y*-axis, 0.875 nm *z*-axis), buckyball C_{96} is (0.900 nm *x*-axis, 0.642 nm *y*-axis, 0.625 nm *z*-axis), and buckyball C_{128} is (1.355 nm *x*-axis, 0.472 nm *y*-axis, 1.355 nm *z*-axis).

3.2. Energy gap

The energy gap, which is also called the band gap, the gap energy generally refers to the energy difference (in electron volts) between the LUMO and the HOMO in insulators and semiconductors. This gap energy is equivalent to the energy required to free an outer shell electron from its orbit

Table 1. Some physical values for all new buckyballs were calculated in B3LYP/6-31G optimized and frequencies

Molecules	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)	7.847	31.132	−11.8086	+2.7235	14.5321
[8]Circulene	247.095	140.065	−4.9527	−1.8866	3.0661
Buckyball C_{64}	255.729	175.973	−5.37044	−4.12171	1.24873
Buckyball C_{96}	405.023	201.496	−5.16364	−4.07164	1.09200
Buckyball C_{128}	559.590	230.855	−5.33588	−4.16035	1.17553

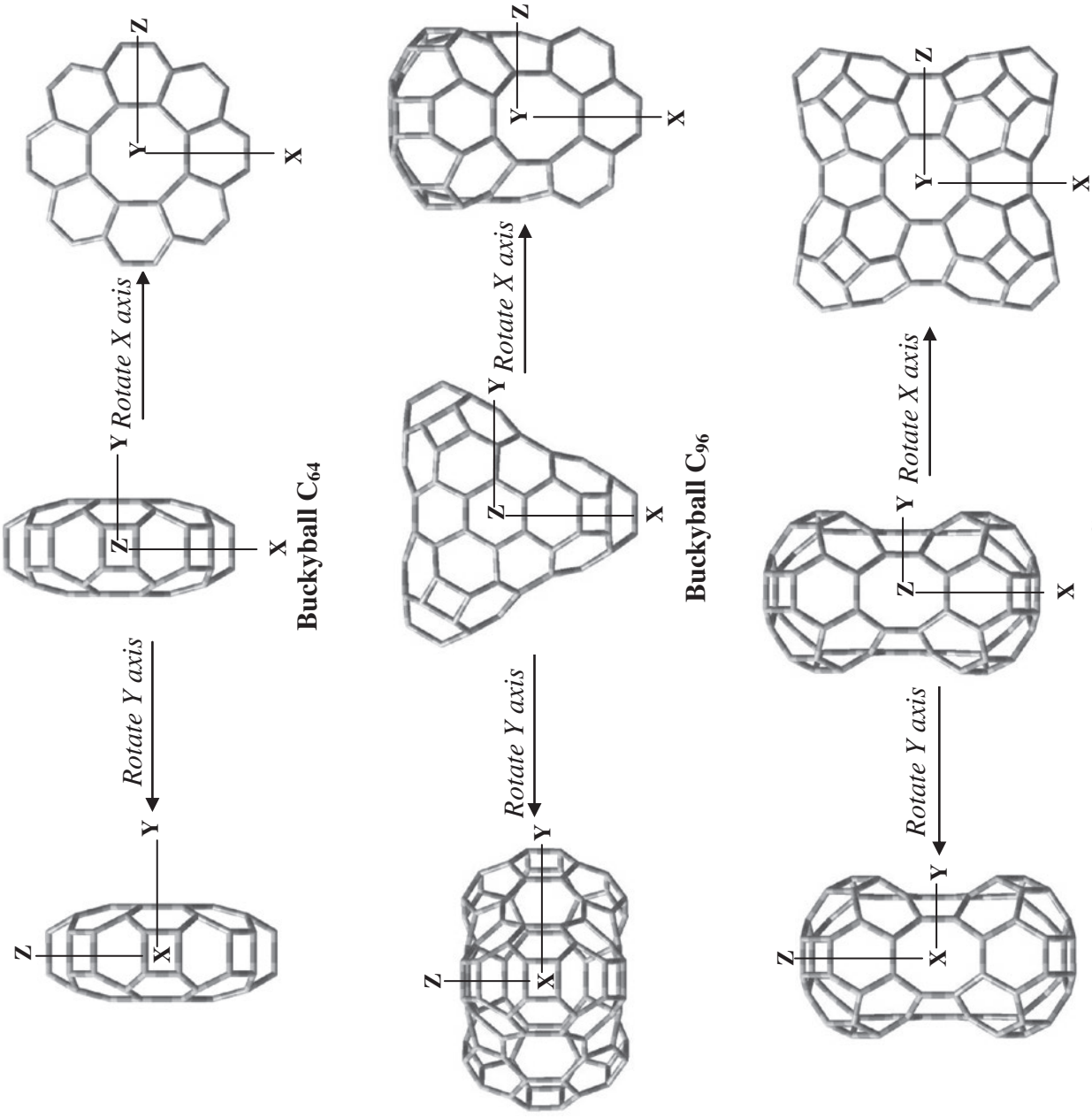

Figure 2. B3LYP/6-31G optimized structures of new buckyball C_{64}, buckyball C_{96}, and buckyball C_{128}.

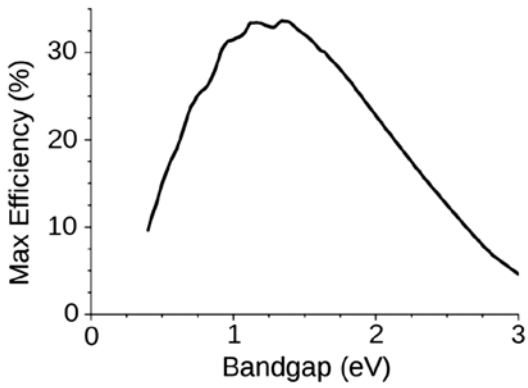

Figure 3. The Shockley–Queisser limit for energy efficiency gap.

Scheme 1. The reactions of design buckyballs (C_{64}, C_{96}, and C_{128}) based on [8]circulene and values of $\Delta_r H$ (the change of enthalpy), $\Delta_r S$ (the change of entropy), and $\Delta_r G$ (the change of Gibbs energy).

			$\Delta_r H$	$\Delta_r S$	$\Delta_r G$
			Kcal.mol^{-1}	*Cal.mol*$^{-1}$.*K*$^{-1}$	*Kcal.mol*$^{-1}$
$2(C_{32}H_{16})$ *[8]Circulene*	1 →	**Buckyball C_{64}** + **$16H_2$**	-112.909	+393.955	-230.367
$3(C_{32}H_{16})$ *[8]Circulene*	2 →	**Buckyball C_{96}** + **$24H_2$**	-147.934	+528.469	-305.497
$4(C_{32}H_{16})$ *[8]Circulene*	3 →	**Buckyball C_{128}** + **$32H_2$**	-177.686	+666.819	-376.498

about the nucleus to become a mobile charge carrier that moves freely within the solid material. The band gap is a major factor that determines the electrical conductivity of a solid. Substances with large gap energies are generally insulators, materials with smaller gap energies are semiconductors, and conducting materials have very small or no gap energies. The Shockley–Queisser limit gives the maximum possible efficiency of single-junction solar cells under unconcentrated sunlight as a function of the semiconductor band gap. If the band gap is too high, then the material cannot absorb most daylight photons; if the band gap is too low, then most photons have much more energy than is necessary to excite electrons across the band gap, and the rest is wasted. The semiconductors that are used commonly in commercial solar cells have band gaps near the peak of this curve shown in Figure 3. In Table 1, the values of the energy gaps for all buckyballs in the (1.09200–1.24873) eV range, arranged by the increases in energy gap, are as follows as in Equation 2:

$$\text{Buckyball } \mathbf{C_{96}} < \text{Buckyball } \mathbf{C_{128}} < \text{Buckyball } \mathbf{C_{64}} \quad (2)$$

4. Conclusions

DFT was used for synthesis and investigate of three new buckyballs from the cyclic polymerization reactions of [8]circulene molecules, this reaction also produces molecules of hydrogen. The results obtained for the new buckyballs show that the most symmetric buckyball is the most stable, depending on the values of E_{HOMO}. The molecular dimensions of all the new buckyballs are less than a nanometer, and the new buckyballs are characterized by the high efficiency of their energy gaps.

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