Simple Combustion Production and Characterization of Octahydro[60]fullerene with a Non-IPR C60 Cage

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Abstract: For the first time an easier, operable combustion method is employed for the synthesis of non-IPR fullerene, and an octahydro[60]fullerene with a non-IPR C60 cage (C60 isomer #1809C60) produced by combustion is isolated and characterized by MS, UV–vis, IR, and NMR spectroscopies in combination with DFT calculations. This finding shows that, in addition to chlorine, hydrogen can be an ample cataloreactant for the production of non-IPR fullerene derivatives under such conditions as arc-burning and diffusion combustion.

Fullerenes violating the isolated pentagon rule (IPR)1 have caught much attention2 ever since discovery of the first buckyball molecule C60,3 which itself is the smallest IPR-satisfying fullerene. It was believed that non-IPR fullerenes with abutting pentagons play a pivotal role (e.g., as precursors) in the formation of stable IPR-satisfying fullerenes.4,5 However, the inherent instability of non-IPR fullerenes pertaining to their abutting pentagons6 poses difficulties in the synthesis, isolation, and chemical manipulation of pristine non-IPR fullerenes. Nevertheless, recent experimental and theoretical investigations have shown that non-IPR fullerenes can be effectively stabilized by endohedral encapsulation or exohedral functionalization.2 An increasing number of non-IPR fullerenes have been synthesized and characterized as endohedral fullerenes, e.g., Sc3N@C687 and Sc2C2@C68,8 and exohedral derivatives including C50Cl10,9 C58F18,10 C64X4 (X = H11 and Cl12), C52Cl10,12 C60Cl6 (n = 8, 12, 13), C54Cl12,14 C56Cl10, C56Cl12, C60Cl6, and C66Cl10,15 Most of these non-IPR fullerene derivatives were produced by means of graphite arc-discharge. It should be noted that in the macroscopic production of fullerenes, graphite arc-discharge is far less efficient than the combustion method. The latter’s merits are easier operable synthetic device, higher yield of fullerene soot, and consecutive synthesis.16,17 It is stimulating that we recently detected in combustion-produced soot the presence of C60H4,17c which likely has a non-IPR fullerene cage.11 Herein we report the production of a new hydro[60]fullerene C60H8 with a non-IPR cage (C60 isomer #1809 termed by the spiral algorithm18) by the simple combustion method. The structure of this novel fulleride has been characterized by MS, UV/vis, IR, and NMR spectroscopies in combination with density functional theory (DFT) calculations.

Soot containing C60H8 was produced by a modified diffusion combustion approach,19 in which the mixtures of acetylene and benzene with oxygen were burnt at 15–20 Torr in a steel chamber. The optimized gas flow rates are 0.55 L/min for O2, 1.10 L/min for C2H2, and 1.0–1.1 L/min for vaporous benzene. During the process of combustion, hot flow of the gaseous products from the chamber carried soot through a water-cooled conduit onto a filter paper, just outside the combustion furnace for gathering the soot. The soot productivity can be up to 5 g per hour efficiently.

Figure 1. (a) HPLC/APCI-MS chromatogram of toluene-extracted soot products. (b) APCI-MS for C60H8 with isotope distribution (high-resolution MS) inset.

Figure 2. (a) 13C NMR spectrum of C60H8 (150 MHz, C6D6 solvent, room temperature). The asterisk-marked signals are due to residual toluene. (b) DEPT spectrum. (c) 1H NMR spectrum (600 MHz, C6D6 solvent, room temperature).
Separation of C₆₀H₈ from the trapped soot was conducted using a high pressure liquid chromatography (HPLC) (see Supporting Information for the synthetic device and HPLC isolation of C₆₀H₈). Figure 1a shows the HPLC/mass spectra of a prepurified extract solution from the combustion soot; the major products are C₆₀ and C₇₀ with C₆₀H₈ as a minor component. An amount of ~5 mg C₆₀H₈ with purity up to 99% was finally isolated and characterized by means of UV/vis, IR, and NMR spectroscopies. The high-resolution mass spectrum (Figure 1b) of purified C₆₀H₈ sample shows the molecular ion peak of 728 amu, agreeing well with the simulated mass spectrum of C₆₀H₈.

Solution of C₆₀H₈ in cyclohexane or benzene is light yellow. The ¹³C NMR spectrum of C₆₀H₈ in CD₃ solvent (Figure 2a) shows four upfield signals (4 × 2, 47.8, 48.7, 51.3, and 55.7 ppm) arising from sp³-hybridized carbon atoms, and about 27 downfield signals ranging from 132.3 ppm to 152.0 ppm pertaining to sp²-hybridized carbon atoms. DEPT spectrum (Figure 2b) further indicates that C₆₀H₈ has in total four types of sp³-hybridized carbon atoms attached by H atoms, suggesting this molecule belongs to C₁, C₂, or C₃ point group of symmetry.

The ¹H NMR spectrum of C₆₀H₈ in CD₃ solvent (Figure 2c) comprises four parts (Hₐ, Hₐ, Hₙ, and Hₙ) with the peak-area integral ratio 2:2:2:2. The doublet peak at 4.95 ppm (Hₐ) is clearly discerned from the multiplet peaks around 4.2 ppm for Hₐ, Hₙ, and Hₙ. With the aid of 2D ¹H–¹H COSY spectrum (Figure 3), the multiplet peaks could be disassembled clearly: Hₐ (doublet, 4.19 ppm, 2H), Hₐ (triplet, 4.22 ppm, 2H) and Hₙ (quadruplet, 4.26 ppm, 2H). The COSY spectrum also indicates the following spin–spin coupling correlations. First, Hₐ is weakly correlated to Hₐ with a coupling constant (Jₐₐ) of 2.4 Hz. Second, Hₐ is strongly correlated to Hₙ (Jₐₙ = 10.3 Hz). Third, Hₐ is strongly correlated to Hₐ and Hₙ. Based on Jₐ₉ and Jₐ₉, the coupling constant Jₐ₉ for the spin–spin coupling between Hₐ and Hₙ is estimated to be ~7.0 Hz. Thus, the C₆₀H₈ has four types of H atoms; among them, Hₐ, Hₐ, Hₙ, and Hₙ are linked to three sequentially neighboring carbon atoms, whereas the Hₐ- linked carbon atom is by one or two sp²-hybridized carbon atoms away from the Hₐ-linked carbon atom.

Yet, the aforementioned NMR spectra are not enough to afford a clear-cut determination of the C₆₀H₈ structure. On account of the harsh synthetic conditions, final products surviving from the combustion process are likely thermodynamically favored. Hence, we performed semiempirical PM3 calculations and DFT calculations at the PBE/DNP level of theory to search for the lowest-energy structure of C₆₀H₈, in which the C₆₀ cage may be the IPR-satisfying one, i.e., #1812C₆₀, or a non-IPR one, e.g., #1809C₆₀. Figure 4 shows three low-energy isomers of C₆₀H₈ from PBE/DNP calculations. Both isomers 1 and 2 contain the same non-IPR #1812C₆₀ cage with two pentagon–pentagon fusions, while isomer 3 has the #1812C₆₀ cage. Among them, the C₃-symmetric isomer 1 is the lowest-energy isomer of C₆₀H₈; isomer 2, isostructural to the previously synthesized #1809C₆₀Cl₈, is by 4.6 kcal mol⁻¹ less stable than 1; isomer 3 is by 15.8 kcal mol⁻¹ higher in energy than 1. Noteworthy, the lowest-energy isomer 1 has the structural features (symmetry and H positions) deduced from the NMR spectra.

We then computed the NMR chemical shifts and ¹H–¹H spin–spin coupling constants of C₆₀H₈ 1 at the GIAO-B3LYP/6-31G** level of theory. The DFT-predicted ¹H–¹H spin–spin coupling constants (Jₛₛ ≈ 10.5, Jₐₐ ≈ 7.5, Jₐ₉ ≈ 4.2 Hz) agree well with the experimental ones (Jₛₛ ≈ 10.3, Jₐₐ ≈ 7.0, Jₐ₉ ≈ 2.4 Hz). The predicted ¹H chemical shifts for the four types of H atoms (Hₐ ≈ 4.7, Hₐ ≈ 4.5, Hₙ ≈ 4.7, and Hₙ ≈ 5.4 ppm) are comparable to the experimental ones (4.2, 4.2, 4.3, 4.9 ppm). For the four types of sp³-hybridized carbon atoms, the DFT-calculated ¹³C chemical shifts are 52.9 (Cₐ), 52.5(Cₐ), 55.7 (Cₙ), and 59.4 (C₉) ppm, corresponding to the measured ones, 48.7, 47.8, 51.3, and 55.7 ppm. The computed ¹³C chemical shifts for 27 types of sp²- hybridized carbon atoms (25 × 2, 2 × 1) range from 132.1 to 150.7 ppm, in accordance with the measured ones ranging from 132.3 to 152.0 ppm (see Supporting Information for details). These computational data clearly show that the synthesized C₆₀H₈ is isomer 1 with a non-IPR C₆₀ cage.

The IR spectrum of C₆₀H₈ (Supporting Information) shows intense absorptions around 2900 cm⁻¹, a fingerprint of tertiary CH moieties. The UV/vis spectrum (Supporting Information) of C₆₀H₈ in cyclohexane solution shows absorptions at 215, 254, 280, 342, and 393 nm, differing slightly from those of #1812C₆₀ (absorptions at 210, 256, 328, 405 nm). The PBE/DNP-predicted HOMO–LUMO gap of #1809C₆₀H₈ is 1.67 eV, equal to that of #1812C₆₀. Both UV/vis spectrum and DFT calculations show #1809C₆₀H₈ is a wide band gap fulleride.

It is interesting to note that the newly synthesized #1809C₆₀H₈ isomer 1 (Figure 4) differs in structure from the previously reported #1812C₆₀Cl₈ isomer 2, despite both compounds sharing the same non-IPR #1809C₆₀ cage and having the same number of exohedral addends. In accordance with such experimental observations, PBE/DNP computations revealed that for the octa-chlorinated case #1809C₆₀Cl₈ 2 is by 3.0 kcal mol⁻¹ more stable than #1812C₆₀Cl₈ 1.
while for the octa-hydrogenated case, \(^{1809}\text{C}_{60}\text{H}_8\) is by 4.6 kcal mol\(^{-1}\) more stable than isomer 2. Thus, the exohedral addition pattern of \(^{1809}\text{C}_{60}\) depends on the nature of addends. A similar trend could be found for the different hydrogenation/chlorination patterns of \(^{1812}\text{C}_{60}\). That is, chlorine atoms are more spatial and more sterically repulsive than hydrogen atoms, and as a result, addends tend to lie together in \(\text{C}_{60}\) and to be separated apart in \(\text{C}_{60}\text{Cl}_x\). Note that \(^{1809}\text{C}_{60}\) isomer 1 and \(^{1810}\text{C}_{60}\text{Cl}_8\) isomer 2 share the common features that the active pentagon–pentagon fusions of the non-IPR carbon cage are completely saturated by H or Cl atoms and their small sp\(^2\)-hybridized carbon fragments, i.e. a benzene-like \(\text{C}_6\) ring in \(^{1810}\text{C}_{60}\text{Cl}_8\) isomer 2, fulfill the Hückel rule of aromaticity. These two special addition patterns of H/Cl addends improve the planarity of the sp\(^2\)-hybridized carbon fragments and, hence, enhance their \(\pi\)-electron conjugation and delocalization. These features account for the stability of both non-IPR \(^{1808}\text{C}_{60}\) derivatives. In addition, the very small energy gap between isomers 1 and 2 for both the chlorinated and hydrogenated cases suggests that \(^{1809}\text{C}_{60}\text{H}_8\) isomer 2 and \(^{1810}\text{C}_{60}\text{Cl}_8\) isomer 1 also could be synthetically viable and deserve further experiments.

In conclusion, we have synthesized a non-IPR fullerene derivative via simple combustion of gaseous acetylene/benzene mixture. The synthesized crown-shaped octahydro[60]fullerene, though sharing the same non-IPR \(^{1809}\text{C}_{60}\) cage with \(^{1809}\text{C}_{60}\text{Cl}_8\), is the first hydrogenated fulleride of non-IPR \(\text{C}_{60}\). Moreover, the successful synthesis of this non-IPR hydro[60]fullerene shows that in addition to chlorine, hydrogen can be an ample cataloreactant for the production of non-IPR fullerene derivatives under such conditions as arc-burning and combustion. Further experiments are in progress in our laboratory to synthesize other non-IPR fullerenes by the same method of arc-burning and combustion.

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Supporting Information Available: Scheme of synthesis apparatus, chromatograms of isolation of \(\text{C}_{60}\)Ir and UV/vis spectra of \(\text{C}_{60}\text{H}_x\), thermostability of \(\text{C}_{60}\text{H}_x\), PM3- and PBE/DNP-computed relative energies of \(\text{C}_{60}\text{H}_x\) isomers, details of GIAO-B3LYP NMR calculations of \(\text{C}_{60}\text{H}_x\), Cartesian coordinates of \(\text{C}_{60}\text{H}_x\) isomers, and complete ref 23d. This material is available free of charge via the Internet at http://pubs.acs.org.

References