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Synthesis of $C_{3v}\text{-}\#^{1911}C_{64}H_4$ using a low-pressure benzene/oxygen diffusion flame: Another pathway toward non-IPR fullerenes

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ABSTRACT

In addition to the traditional Krätschmer–Huffman graphite arc-discharge method, a combustion method has been developed to synthesize fullerenes that defy the isolated pentagon rule (IPR). The C_{3v} -symmetric $\#^{1911}C_{64}H_4$, as well as other non-IPR fullerenes such as the possible non-IPR C_{60} isomer, have been synthesized as fullerene hydrides in a low-pressure benzene/oxygen diffusion flame. The non-IPR structure of the chromatographically isolated C_{64} species was unambiguously identified by its HPLC retention time, UV absorption and mass spectrum by comparison with the reference material $C_{3v}\text{-}\#^{1911}C_{64}H_4$. The synthesis, isolation and identification of $C_{3v}\text{-}\#^{1911}C_{64}H_4$, as described in this work, show that this combustion method is successful, is energy efficient and is a promising candidate for the macroscopic synthesis of non-IPR fullerenes.

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1. Introduction

The stability of fullerenes is governed by the isolated pentagon rule (IPR) [1,2], which states that in a stable fullerene cage no pentagon is connected to another, i.e., each of the 12 pentagons is surrounded by five hexagons. The most notable IPR-satisfying fullerenes include the I_h -symmetric C_{60} and D_{5h} -symmetric C_{70} , both of which have been extensively studied in the fullerene world. The number of non-IPR fullerenes is considerable greater than IPR fullerenes. Because of their diversity and special structures, compared with IPR fullerenes, non-IPR fullerenes should present more diverse physical and chemical properties, which may be applied to semiconductor materials, fuel cells, solar cells, etc. In addition, the non-IPR fullerenes may provide valuable information about the formation mechanism of fullerenes. Therefore the non-IPR fullerenes are of significance in the field of fullerene studies.

However, IPR-violating fullerenes, typically having higher geometrical strain and resonance destabilization by virtue of the fused pentagons, are too reactive to be synthesized as all-carbon molecules. It has been a challenge for chemists to synthesize non-IPR fullerenes since these have numerous topological possibilities and unusual properties.

In principle, non-IPR fullerenes can be stabilized by endohedral [3–7] or exohedral derivatization [8–11]. Surprisingly, all the

previously reported non-IPR fullerenes were synthesized via the traditional Krätschmer–Huffman graphite arc-discharge method, with normal metals (or their carbides and oxides) filling the graphite rods to produce endofullerenes or by adding reactant gas into the generator to make exofullerenes. For example, in addition to the non-IPR fullerenes stabilized by the endohedral method, Wang et al. [10] reported the synthesis and structural characterization of a stable non-IPR fullerene derivative of C_{64} (No. 1911) [11], $C_{3v}\text{-}\#^{1911}C_{64}H_4$, using a carbon arc. This non-IPR structure with a triplet of directly fused-pentagons was later confirmed by X-ray crystallography [12].

However, the Krätschmer–Huffman synthesis is unavoidably a discontinuous process, largely due to the limitation in length of the graphite-rod for the graphite arc-discharge. In contrast, flame methods are an alternative way to synthesize fullerenes with an uninterrupted procedure [13–15] and has been developed as a commercial method to produce fullerenes by successive combustion of organic fuels such as benzene and toluene in a low pressure of oxygen gas or other oxidizing gas. In addition, the heat from combustion can provide the energy needed for the formation of the fullerenes. Consequently, the combustion method, thanks to its success and energy-efficiency, has great value for industrial applications and has been adopted by MITSUBISHI Co. for thousand-ton-scale production of fullerene $I_h\text{-}C_{60}$. The new combustion technique devised by Nano-C Co. enables the production of IPR-satisfying fullerene species with high purity. IPR-violating fullerenes, however, have never previously been retrieved from flame soot.

In this work we show that the non-IPR fullerene derivative $C_{3v}\text{-}\#^{1911}C_{64}H_4$ can be extracted and separated from the soot of a

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low-pressure benzene/oxygen diffusion flame. The molecular structure has been established by comparing the analytical data (HPLC retention time, UV absorption and mass spectrum) with a reference sample. These results demonstrate that, for the first time, non-IPR fullerenes can be generated and survive in a flame. Meanwhile, some other possible non-IPR fullerenes such as $C_{60}H_8$ were also detected in our combustion experiments. It is confidently expected that combustion can be developed as a routine industrial method for the macroscopic synthesis of non-IPR fullerenes or their derivatives.

2. Experimental

Fig. 1 shows the setup of our home-made generator. This features a glass chamber and a burner. The steel burner (Fig. 1b) is composed of two concentric tubes, with the length of the inner tube 25 mm shorter than the outer one, so that the zone at the ends of the tubes allow mixing of the reaction gases. The oxygen flow from the inner tube and benzene vapor from the outer tube are mixed in the zone and burned in a glass flask of about 5 L capacity to generate flame soot. The flask was pumped to vacuum by a rotary pump through a filter. The benzene vapor flow was maintained by heating liquid benzene in a container to a constant temperature of 318 K. In a typical operation, the flow rates of benzene vapor and oxygen gas were controlled at 200 mL/min and 270 mL/min, respectively, using two mass flow controllers. The pressure was kept in the range of 15–20 Torr, so that a stable flame could be maintained. The product soot was collected mainly from the upper inner surface of the flask and the filter. About 100 g soot could be obtained by the consumption of 8 L benzene.

About 25% of soluble component was ultrasonically extracted from the soot with toluene. The extract was separated using four cycles of high-performance liquid chromatography (HPLC). A Buckyprep column (10 mm \times 250 mm) was used in the first two HPLC cycles with toluene as eluent, in order to enrich the $C_{64}H_4$ -containing fractions and remove majority components such as PAHs and fullerene C_{60} (about 0.4% of the soluble components). By comparison with the abundance of C_{60} in HPLC, it was estimated that about 10 ppm of the desired sample was present in the soluble component. To further enrich the $C_{64}H_4$ and remove impurities, a C18 column (10 \times 250 mm, SUPELCO) was used in the next two cycles with methanol/cyclohexane (4:1) as eluent. A brown yellow toluene solution of the obtained sample was LC–MS analyzed by a discovery C18 analytical column (SUPELCO 4.6 \times 250 mm 5 μ m particle size), eluted with a mixture of the ternary mobile phase of methanol, ethanol and cyclohexane in gradient elute mode. Since methanol will not completely dissolve more than 35% of

cyclohexane, a mixed solvent of methanol/ethanol (11:2) was used to increase the proportion of cyclohexane in the eluent. The 200-min gradient program consisted of a linear increase of cyclohexane from 0% to 5% in the first 50 min, from 5% to 35% in the next 120 min, then holding this at 35% for the last 30 min. Methanol was linearly decreased from 84.6% to 80.4% in the first 50 min, from 80.4% to 55% in the next 120 min, and subsequently held at 55% for the last 30 min. The proportion of ethanol was changed accordingly. The eluent flow rate was 0.8 mL/min.

The LC–MS analysis was performed with an Agilent 1200 LC system combined with a Bruker HCT esquire 5.3 mass spectrometer. The operating conditions for the MS measurements were as follows: APCI (Bruker, US) ion source, negative ion detection mode, dry gas temperature 350 $^{\circ}$ C, dry gas flow rate 4 L/min, nebular gas pressure 45 psi, vaporizer temperature 250 $^{\circ}$ C, capillary voltage 1000 V. The reference sample of $C_{3v}-^{1911}C_{64}H_4$ was synthesized in a graphite arc-discharge and isolated with HPLC and was provided by Wang et al. [10]. The authentic structure of $C_{64}H_4$ isolated in the present work was identified by comparisons of the HPLC retention time and UV absorption with the reference sample.

3. Results and discussion

3.1. Combustion synthesis

In our home-made diffusion flame setup, benzene vapor and oxygen gas are fed into the burner through two separated tubes, and diffuse to form a mixed gas at the combustion zone at the ends of the tube. The degree of diffusion determines the effect of the combustion reaction, for the diffusion speeds of benzene vapor and oxygen are much slower than the combustion reaction itself. This is in contrast to the premixed combustion mode that is widely used for producing fullerenes on the industrial scale, in which the reactants are uniform mixtures of fuels and oxygen. The diffused combustion mode gives a more complicated flame configuration because of the concentration gradient caused by the inhomogeneous mixing of fuel and oxygen in the flame zone. The combustion products from the diffused flame are more abundant than those from the premixed flame, which favours the exploration of new flame species. Lower pressure in the reactor facilitates diffusion of the gases. The combustion efficiency and flame temperature can be increased by accelerating diffusion of the gases. For example, no fullerene was extracted from the soot produced at a pressure of 40 Torr, though the yield of soot containing polycyclic aromatic hydrocarbons (PAHs) is higher. The absence of fullerene in the soot can be rationalized by the lower flame temperature due to poor diffusion of benzene and oxygen. If the pressure of

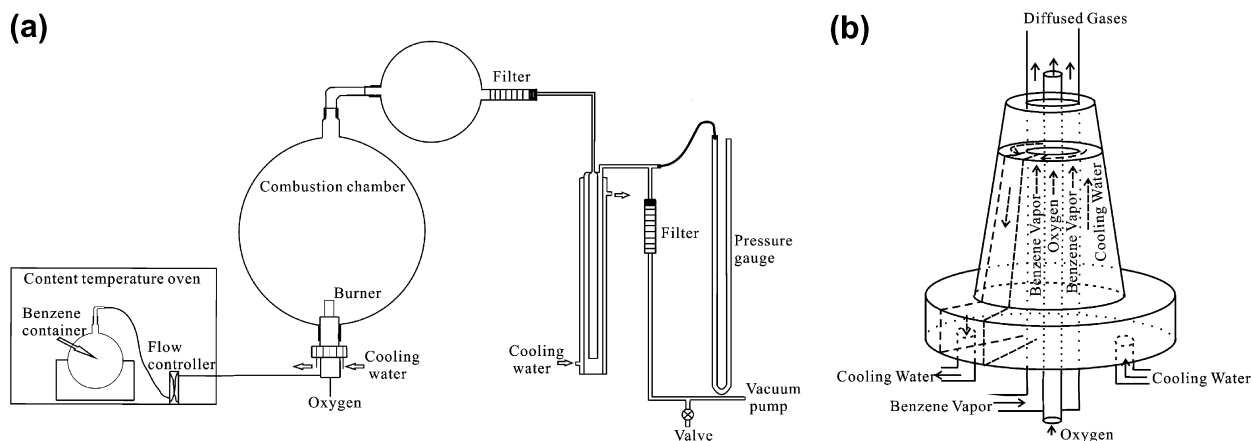


Fig. 1. (a) The glass combustion generator and (b) configuration of the burner.

the combustion chamber is reduced to 20 Torr or lower, the content of fullerenes in the soot, such as I_h -C₆₀ and D_{5h} -C₇₀, is much greater. Further reducing the chamber pressure will cause an apparent drop in soot yield.

3.2. Identification of C_{3v} -^{#1911}C₆₄H₄ and related species

The mass spectrum (Fig. 2) recorded by HPLC–APCI–MS at a retention time of 136 min (Fig. 4a) is a good match with the molecular mass of C₆₄H₄. At the position 788 *m/z* in the corresponding mass spectrum (Fig. 3), the weak peak at 126 min in HPLC chro-

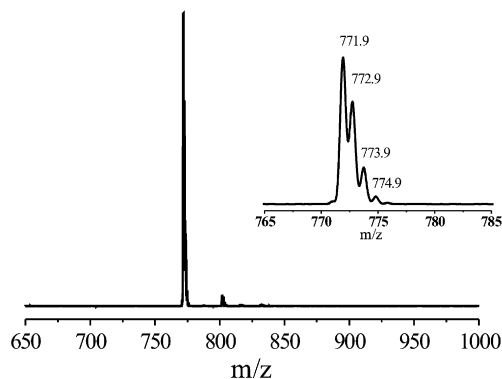


Fig. 2. Mass spectrum of C_{3v} -^{#1911}C₆₄H₄ at a HPLC retention time of 136 min.

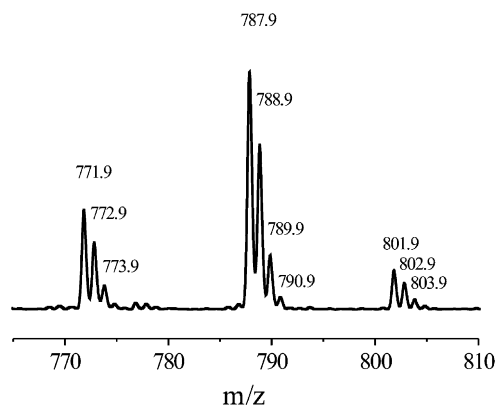


Fig. 3. Mass spectrum of the monoxide of C_{3v} -^{#1911}C₆₄H₄ at a retention time of 126 min.

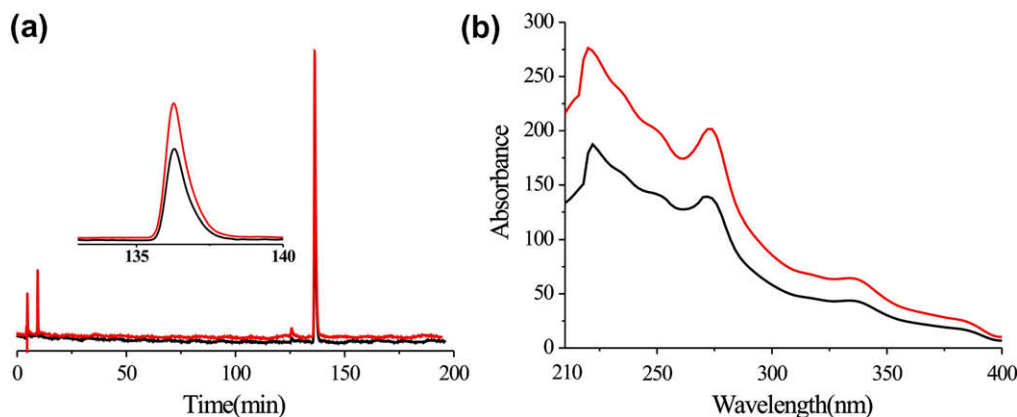


Fig. 4. (a) HPLC chromatograms and (b) UV spectra, of the samples without (black) and with (red) the addition of the reference sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

matogram (Fig. 4a) can be assigned to a monoxide of C₆₄H₄. The mass signal at 802 *m/z* may be due to a methoxy derivation of C₆₄H₄, which can be produced by reaction with methanol solvent in the HPLC–APCI–MS process. Such methoxy derivatization is common for non-IPR fullerenes previously reported [8,12]. These additional exohedral derivatizations involving monoxide and methoxy indicate that the isolated C_{3v} -^{#1911}C₆₄H₄ is ready for further chemical modification.

Fig. 4 shows a comparative chromatogram and UV spectrum of the purified sample with and without the addition of the reference sample. In general, different organic substances should have different retention behavior in the HPLC. For the chromatograms (Fig. 4a) recorded at 300 nm, the retention times for both the sample and the reference C_{3v} -^{#1911}C₆₄H₄ are the same (136 min), implying that identical C_{3v} -^{#1911}C₆₄H₄ is produced from the flame. The UV spectra (Fig. 4b) of both samples show the same absorbances at 220, 254, 274, 330, and 384 nm, further confirming that the sample isolated from the flame soot is the non-IPR fullerene C_{3v} -^{#1911}C₆₄H₄.

3.3. Stabilization of non-IPR fullerenes in combustion

Comparisons between the HPLC, UV and mass spectra have confirmed the existence of C_{3v} -^{#1911}C₆₄H₄ in the flame soot. Do any other non-IPR fullerene derivatives co-exist in the flame soot? Another component, with *m/z* 728, was observed in mass spectra from the HPLC–APCI–MS analysis of the flame soot. As shown in the corresponding mass spectrum (Fig. 5), the parent molecular ions with *m/z* = 728 produce a C₆₀ fragment with 720 *m/z*. Therefore, the composition of the detected molecule can be assigned as C₆₀H₈. Of interest is the unusual abundance of this C₆₀H₈ species in the flame soot. Among the C₆₀ hydrides produced in the combustion, C₆₀H₈ predominates over the other C₆₀ hydrides such as C₆₀H₂, C₆₀H₄, and C₆₀H₆. In previous literature, however, reaction of I_h -symmetric ^{#1812}C₆₀ with reductant has been shown to result in minor amounts of ^{#1812}C₆₀H₈ [16]. Due to its unusual abundance, the C₆₀H₈ isolated from flame soot is obviously different from classical ^{#1812}C₆₀H₈ and is very likely to be a non-IPR species. Recently we have been able to isolate and characterize two chlorides of isomeric C₆₀, C_{2v} -^{#1809}C₆₀C₁₈ and C_s -^{#1804}C₆₀C₁₂ [17]. An unusual abundance of C_{2v} -^{#1809}C₆₀C₁₈ was also observed for the graphite arc-discharge soot, probably because ^{#1809}C₆₀C₁₈ is theoretically calculated to be 33.1 kcal mol^{−1} more stable than ^{#1812}C₆₀C₁₈ [17]. Very recently, experimental evidence has shown that non-IPR fullerene exohedral derivatives are stable [8,12,17–19]. So it is reasonable to suppose that the flame-synthesized C₆₀H₈ has a non-IPR cage structure.

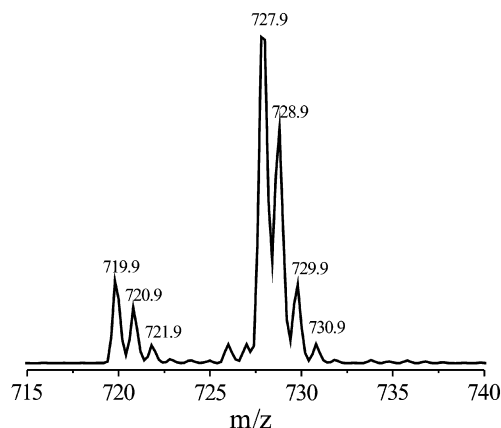


Fig. 5. Mass spectrum of $C_{60}H_8$ in the flame soot.

3.4. Mechanism for stabilization of non-IPR fullerenes

The formation of fullerenes in flames is due to a bimolecular aggregation reaction of smaller PAHs and a unimolecular rearrangement reaction of certain aromatic oligomers governed respectively by dynamics and thermodynamics [20,21]. This differs from the proposed mechanism for the formation of fullerenes involving carbon clustering in plasma conditions [22]. In Homann's [21] scenario for fullerene formation in flames, there are two zones for fullerene growth: (1) In the relatively low temperature zone of the flame, the dynamics favours the bimolecular aggregation of smaller PAHs to form larger molecules (aromatic oligomers, including a small amount of fullerenes); (2) In the higher temperature zone, unimolecular bonding and rearrangement as well as dehydrogenization of larger oligomers is controlled by thermodynamics to give stable fullerenes or related derivatives. Such a pathway allows the occurrence of non-IPR fullerenes or their derivatives such as $C_{3v}\text{-}\#^{1911}C_{64}H_4$ to survive the final stage of dehydrogenization and rearrangement. To some extent, the unambiguous identification of non-IPR $C_{3v}\text{-}\#^{1911}C_{64}H_4$ and the possible non-IPR $\#^{1809}C_{60}H_8$ ratifies Homann's scenario for fullerene formation in flames. According to this, other non-IPR fullerenes might also grow in the flame, and the possibility of large scale production of non-IPR fullerenes through combustion is very high.

For the point of view of its topological structure, the cage skeleton of $C_{3v}\text{-}\#^{1911}C_{64}H_4$ is special because it is a non-IPR fullerene with a triply-fused-pentagon (TFP) [10]. The naked $C_{3v}\text{-}\#^{1911}C_{64}H_4$ cage is not the most stable among the C_{64} isomers. Curvature in this TFP is larger than other parts of the cage skeleton, making the $C_{3v}\text{-}\#^{1911}C_{64}H_4$ highly reactive. The four carbon atoms at the vertices of the pentagon-abutting sites (three pairs of adjacent pentagons and one triplet fused-pentagon) are thus readily bonded to hydrogen atoms. Subsequently, the hybrid states of the skeleton carbon atoms in the TFP are changed from sp^2 to sp^3 , to reduce the bending energy and to stabilize the carbon skeleton containing the TFP.

4. Conclusion

Comparisons of HPLC, UV and mass spectra have demonstrated that the non-IPR fullerene derivative $C_{3v}\text{-}\#^{1911}C_{64}H_4$ indeed exists in the soot from the low pressure diffusion flame of benzene-oxygen. In addition, other non-IPR fullerenes such as the tentatively

identified $\#^{1809}C_{60}H_8$ may also be produced in the flame. The present results demonstrate that the traditional Krätschmer–Hoffman method is no longer the exclusive pathway for the synthesis of non-IPR fullerenes. This combustion method may be more promising for commercial non-IPR fullerene synthesis in macroscopic quantities, being more likely to be successful and more energy-efficient.

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