Angewandte Chemie International Edition

Fullerenes

DOI: 10.1002/anie.201101323

Fullerene $C_{72}Cl_4$: The Exception that Proves the Rule?**

Nazario Martín*

chlorination reactions · exohedral functionalization · fullerenes · isolated pentagon rule

A most intriguing question in fullerene science is: among the many possible cages that can be formed with carbon atoms, why is that containing 60 atoms the favored one? Furthermore, since all fullerenes C_n are constituted by hexagons ($n \geq 20$ with the exception of $n = 22$) and pentagons (12 for all fullerene cages; these shapes are responsible for the curved geometry), why among the 1812 possible isomers for 60 carbon atoms was only the icosahedral symmetry I_h-C_{60} molecule (the first and most abundant carbon molecular allotrope with a soccer-ball shape) formed?

These fundamental questions were answered by H. Kroto (Nobel laureate together with R. Smalley and R. Curl in 1996) in 1987. Kroto proposed that the local strain increases with the number of bonds shared by two pentagons (pentalene), thus affording less-stable molecules. This basic rule is known as the "isolated pentagon rule" (IPR), which states that all pentagons must be surrounded by hexagons, thus forming the corannulene moiety.[1] The resonance destabilization that results from the adjacent pentagons (8π electrons which do not satisfy the Hückel rule) and reduction of the π-orbital overlap because of cage curvature, account for the known destabilization of non-IPR fullerenes.[2] More recently, a head-to-tail exclusion rule has been proposed to explain the highest stability of the fullerenes that obey the IPR rule.[3]

For a given number of carbon atoms that form a cage, the number of non-IPR fullerene isomers is extraordinarily larger than that of those that obey the IPR. Furthermore, in addition to doubly fused pentagons found in non-IPR fullerenes, triple directly fused pentagons and more recently triple sequentially fused pentagons have been reported.[4] Therefore, there is a lot of interest in the study of this huge number of possible fullerenes whose chemical reactivity and properties are expected to be different from those of IPR fullerenes.

Two different strategies have been followed to stabilize non-IPR fullerenes, namely endohedral and exohedral derivatization.[5] Endohedral fullerenes are known from the earlier stages of fullerene research; these molecules are a singular type of carbon cages able to host atoms, small molecules, or clusters in their inner cavity (Figure 1). Actually, the so-called "endofullerenes" exhibit electronic properties, which are explained by electron transfer from the encapsulated moiety (metals or metallic clusters) to the carbon cage. Thus, it has been possible the encapsulation of unstable clusters that do not exist independently.[6]

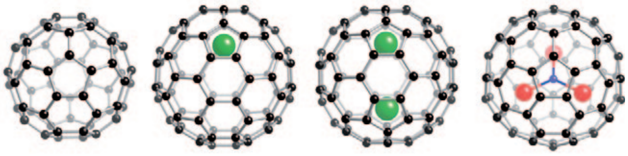

Figure 1. Molecules of IPR hollow fullerene C_{60} and endohedrally stabilized fullerenes $La@C_{82}$, $La_2@C_{80}$, and $Sc_3N@C_{80}$.

Although theoretical studies in the early 1990s proposed that elusive non-IPR fullerenes could be stabilized by the presence of clusters encapsulated in the fullerene cage, the first non-IPR fullerenes, namely $Sc_2@C_{66}$[7] and $Sc_3N@C_{68}$,[8] were obtained in 2000. A most outstanding observation is that the carbon cages in endofullerenes are different from those obtained in empty fullerenes. Therefore, the existing electronic interactions of the encapsulated species with the carbon cage are critical for the stabilization of the resulting endohedral fullerene. In this regard, a simple rule to predict the stability of the formed endohedral has been developed by Poblet and co-workers and is based on the calculated HOMO–LUMO gap for the resulting "ionic" endofullerene. This energy gap can be roughly calculated from the (LUMO-3)-(LUMO-4) gap determined for the neutral cage, thus predicting the most stable IPR and non-IPR endofullerenes.[9]

Interestingly, non-IPR endofullerenes reveal a strong coordination of the metal atoms to the fused pentagons, similar to that observed for a variety of different organometallic species to the inner face of the pentalene unit.[10] This behavior is in sharp contrast to that observed for IPR endofullerenes that show motion for the encapsulated metals or clusters.[11]

---

[*] Prof. Dr. N. Martín
Departamento de Química Orgánica I
Facultad de Ciencias Químicas
Ciudad Universitaria s/n, 28040 Madrid (Spain)
Fax: (+34) 91-394-4103
and
IMDEA-Nanociencia
Campus de Cantoblanco, 28049 Madrid (Spain)
E-mail: nazmar@quim.ucm.es
Homepage: http://www.ucm.es/info/fullerene

[**] Financial support by the Ministerio de Ciencia e Innovación (MICINN) of Spain (projects CTQ2008-00559/BQU, consolider-Ingenio CSD2007-00010), and the Comunidad Autónoma de Madrid (project MADRISOLAR-2, S2009/PPQ1533) is acknowledged.

Exohedral derivatization, on the other hand, has allowed the preparation of a variety of non-IPR derivatives based on the remarkable reactivity of the fused pentagons. Many other examples have been reported since the first small fullerene $^{\#271}C_{50}$ (the Fowler–Manolopoulos nomenclature to differentiate isomers is specified by symmetry and/or by spiral algorithm) was trapped and stabilized by chlorine atoms as $^{\#271}C_{50}Cl_{10}$ in 2004.[12] This stabilization of the resulting non-IPR fullerene derivatives has been accounted for by the "strain-relief principle" resulting from the rehybridization from sp^2 to sp^3 carbon atoms, as well as by the "local aromaticity principle", which involves maintaining the local aromaticity of the un-derivatized sp^2 carbon skeleton that remains after the derivatization process. Based on both principles, it has been possible to predict the stability of a variety of exohedrically functionalized non-IPR fullerenes.

Since the preparation of the C_{60} molecule, a series of soccer-ball-shaped molecules have been synthesized and characterized, namely from C_{70} to C_{96}, all of them having representative empty IPR isomers. The only exception known to date is for the cluster that has 72 carbon atoms, whose empty fullerene C_{72} has never been isolated and characterized, despite that the D_{6d}-C_{72} isomer obeys the IPR rule. However, what makes this D_{6d}-C_{72} isomer ($^{\#11190}C_{72}$) singular is that it is not the most stable isomer found for the C_{72} family of isomers. Actually, D_{6d}-C_{72} is 11–15 kcal mol^{-1} higher than the non-IPR isomer $^{\#11188}C_{72}$. Although this theoretical prediction was made fourteen years ago,[13] no experimental evidence was reported. Last year, the first and unambiguous experimental evidence became reality. This is an outstanding finding in fullerene science that has been simultaneously and independently reported by the research groups of Xie[14] and Jansen.[15] This is the only example reported to date in which a non-IPR hollow fullerene is more stable than its IPR isomer.

Previous attempts to stabilize the C_{72} fullerene by means of endohedral functionalization have afforded chemically modified endofullerenes with less-stable cages, namely $La_2@^{\#10611}C_{72}$, $La_2@^{\#10612}C_{72}$, and $Ce_2@^{\#10611}C_{72}$, in which stabilization occurs by the electron transfer from the metal atoms located at the inner cavity to the fullerene cage.[16] As a result, endofullerenes show highly reactive fused-pentagon sites but those carbon atoms that form the [5,5] junctions are less reactive than the adjacent atoms. This difference can be explained as the fused-pentagon double bond interacts with the stabilizing metals, and is thus less reactive for further exohedral functionalization.

The reason for this behavior stems from the fact that the stabilization of the resulting endofullerene is mainly related to the stability of the negatively charged sphere, regardless of the stability of the neutral cage.[9b] Therefore, the proposal from the Xie and Jansen research groups to trap the elusive $^{\#11188}C_{72}$ isomer (Figure 2) has been to skillfully use the exohedral stabilization, where the stability of the pristine hollow fullerene is a key issue. Thus, both research groups have been able to isolate and unambiguously characterize by X-ray analyses the C_{2v}-C_{72} fullerene cage by means of exohedral chlorination reaction.[14,15]

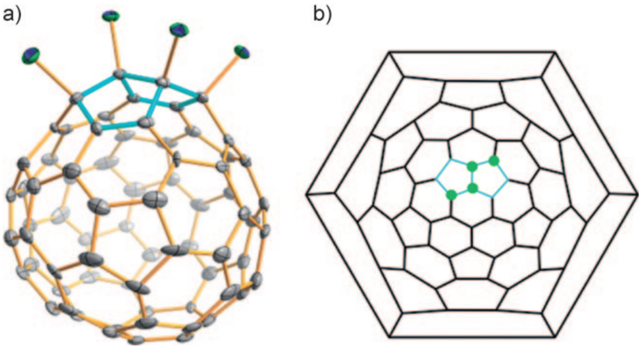

Figure 2. X-ray structure of $^{\#11188}C_{72}Cl_4$. a) Fused pentagons are shown in blue. b) Schlegel diagram showing the position of the four chlorine atoms (from reference [14]).

The new compound $^{\#11188}C_{72}Cl_4$ has been produced by both research groups in milligram quantities by following similar experimental procedures. Thus, by using a Krätschmer–Huffman carbon arc reactor[14] or a high-frequency furnace technique[15] in the presence of CCl_4 as chlorinating reagent, a soot was obtained from which the $^{\#11188}C_{72}Cl_4$ was separated in high purity by means of HPLC.

The new fullerene derivative was found to be stable in toluene solution (with a vivid dark red color) as well as in the solid state under ambient conditions without observing any degradation by HPLC. The electronic spectrum reveals absorption along the visible region up to around 800 nm. However, when the sample was subjected to laser desorption ionization (LDI) mass analysis, the typical loss of chlorine atoms observed in related chlorinated fullerenes occurred, thus forming the unprecedented C_{72} fullerene at m/z 864.0.

Interestingly, the X-ray analyses of a suitable single crystal of the $^{\#11188}C_{72}Cl_4$ molecule has been performed by both research groups and reveal that the $^{\#11188}C_{72}$ cage is stabilized by four chlorine atoms that are covalently attached to the pentalene moiety (Figure 2). This addition pattern reduces the symmetry of the parent C_{72} molecule from C_{2v} to C_2, thus giving rise to the formation of two stereoisomers for the $C_{72}Cl_4$ molecule. This chlorination pattern can be rationalized in terms of the above "strain-release" and "local aromaticity" principles, as the relaxation that results from the addition of chlorine to the fused carbon atoms of the adjacent pentagons (pentagon–pentagon junction) significantly reduces the local strain. The other two chlorine atoms are responsible for the rehybridization of the carbon atoms from sp^2 to sp^3, thus affording a structure that fulfils the "local aromaticity" principle.

In summary, the outstanding experimental result on the higher stability of a non-IPR fullerene than its related IPR isomer is, to date, the exception that proves the rule within the fullerene scenario. Interestingly, these new results violate the "universal" IPR rule for fullerenes, but confirm the valuable "strain-release" and "local aromaticity" principles that have been so useful to predict the stability of a wide variety of fullerene derivatives. The IPR rule is strong and valid for parent fullerenes, whereas for fullerene derivatives, additional factors come into play that can eventually force a non-IPR cage to be the most stable one.

On the other hand, the ease of access, relative availability (in milligram quantities), and low degree of chlorination, makes this new $C_{72}Cl_4$ fullerene suitable for further chemical derivatization. These new results open a new avenue for the study of the chemical reactivity, optical and electronic properties, and practical applications[17] of the most unusual non-IPR fullerenes. It is important to note, however, that pristine C_{2v}-C_{72} fullerene has not been isolated to date and, therefore, catching this elusive molecule should stimulate future calculations and experiments in this field.

Received: February 22, 2011
Revised: March 17, 2011

---

[1] H. W. Kroto, *Nature* **1987**, *329*, 529–531.

[2] T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite, *Chem. Phys. Lett.* **1986**, *130*, 203–207.

[3] S. Schein, T. A. Friedrich, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 19142–19147.

[4] T.-Z. Tan, J. Li, F. Zhu, X. Han, W.-S. Jiang, R.-B. Huang, Z. Zheng, Z.-Z. Qian, R.-T. Chen, Z.-J. Liao, S.-Y. Xie, X. Lu, L.-S. Zheng, *Nat. Chem.* **2010**, *2*, 269–273, and references therein.

[5] For a recent review, see: Y.-Z. Tan, S.-Y. Xie, R.-B. Huang, L.-S. Zheng, *Nat. Chem.* **2009**, *1*, 450–460.

[6] *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluwer Academic Publishers, Dordrecht, **2002**. For recent reviews on endohedral fullerenes, see: a) L. Dunsch, S. Yang, *Small* **2007**, *3*, 1298–1320; b) M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen, *Angew. Chem.* **2009**, *121*, 7650–7675; *Angew. Chem. Int. Ed.* **2009**, *48*, 7514–7538; c) M. Yamada, T. Akasaka, S. Nagase, *Acc. Chem. Res.* **2010**, *43*, 92–102; d) S. Osuna, M. Swart, M. Solà, *Phys. Chem. Chem. Phys.* **2011**, *13*, 3585–3603.

[7] C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2000**, *408*, 426–427.

[8] S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2000**, *408*, 427–428.

[9] a) J. M. Campanera, C. Bo, J. M. Poblet, *Angew. Chem.* **2005**, *117*, 7396–7399; *Angew. Chem. Int. Ed.* **2005**, *44*, 7230–7233; b) A. Rodríguez-Fortea, N. Alegret, A. Balch, J. M. Poblet, *Nat. Chem.* **2010**, *2*, 955–961.

[10] O. T. Summerscales, F. G. N. Cloke, *Coord. Chem. Rev.* **2006**, *250*, 1122–1140.

[11] For endofullerenes endowed with only one metal atom, the metal generally coordinates with the cage and shows no obvious motion.

[12] S. Y. Xie, F. Gao, X. Lu, R.-B. Huang, C.-R. Wang, X. Zhang, M.-L. Liu, S.-L. Deng, L.-S. Zheng, *Science* **2004**, *304*, 699–699.

[13] K. Kobayashi, S. Nagase, M. Yoshida, E. Osawa, *J. Am. Chem. Soc.* **1997**, *119*, 12693–12694.

[14] Y.-Z. Tan, T. Zhou, J. Bao, G.-J. Shan, S.-Y. Xie, R.-B. Huang, L.-S. Zheng, *J. Am. Chem. Soc.* **2010**, *132*, 17102–17104.

[15] K. Ziegler, A. Mueller, K. Y. Amsharov, M. Jansen, *J. Am. Chem. Soc.* **2010**, *132*, 17099–17101.

[16] a) T. Wakahara, H. Nikawa, T. Kikuchi, T. Nakahodo, G. M. A. Rahman, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase, *J. Am. Chem. Soc.* **2006**, *128*, 14228–14229; b) X. Lu, H. Nikawa, T. Nakahodo, T. Tsuchiya, M. O. Ishitsuka, Y. Maeda, T. Akasaka, M. Toki, H. Sawa, Z. Slanina, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 9129–9136; c) X. Lu, H. Nikawa, T. Tsuchiya, Y. Maeda, M. O. Ishitsuka, T. Akasaka, M. Toki, H. Sawa, Z. Slanina, N. Mizorogi, S. Nagase, *Angew. Chem.* **2008**, *120*, 8770–8773; *Angew. Chem. Int. Ed.* **2008**, *47*, 8642–8645.

[17] Some endofullerenes have recently attracted interest in photovoltaic applications, see: a) R. B. Ross, C. M. Cardona, D. M. Guldi, S. S. Gayathri, M. O. Reese, N. Kopidakis, J. Peet, B. Walker, G. C. Bazan, E. Van Keuren, B. C. Holloway, M. Drees, *Nat. Mater.* **2009**, *8*, 208–212; b) J. R. Pinzón, M. E. Plonska-Brzezinska, C. M. Cardona, A. J. Athans, S. S. Gayathri, D. M. Guldi, M. A. Herranz, N. Martín, T. Torres, L. Echegoyen, *Angew. Chem.* **2008**, *120*, 4241–4244; *Angew. Chem. Int. Ed.* **2008**, *47*, 4173–4176.