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Non-Isolated Pentagon Rule Fullerenes: A Review.

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ABSTRACT

Fullerenes were discovered by Curl, Kroto and Smalley in 1985. C₆₀ fullerene molecule composed of 20 hexagons and 12 pentagons has diameter of 0.7 nanometers. Open - shell structures are energetically unfavorable and thus avoided. Structures with isolated pentagons are preferred to those containing adjacent five -membered rings. This happens because the local strain increases with the number of bonds shared by two pentagons (pentalene units), thus affording less – stable molecules. The isolated pentagon rule (IPR) coined by Kroto states that all pentagons must be surrounded by hexagons. A head to tail exclusion rule has been proposed to explain the higher stability of fullerenes obeying the IPR rule. The IPR is a very strong rule of thumb for neutral bare fullerenes, where every adjacent pentagon costs about 100 kJ/mol in stability. However, in order to search for number of expected non – IPR fullerenes whose chemical reactivity and properties should be different from those known for IPR fullerenes , fullerenes violating the pentagon rules have been obtained. The fullerenes violating the pentagon rules have been obtained by increasing the stability by releasing the strain on fused pentagons through endohedral and exohedral derivatization. The endohedral non-IPR cages appeared in the 2000, with the simultaneous discovery of Sc₂@C₆₆ and Sc₃N@C₆₈; the halogenated IPR-violating fullerenes appeared in 2004 with the characterization of the first empty non-IPR cage C₅₀Cl₁₀. From then on, the list of non-IPR cages synthesized with any of the two functionalizations has increased significantly and is reviewed in the present article.

Keywords: Fullerenes, Isolated Pentagon Rule, Endohedral Fullerenes , Exohedral Fullerenes, Non Isolated Pentagon Rule Fullerenes.

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INDRODUCTION

According to Euler's theorem on closed polyhedrons, every fullerene composed of five- and six-membered rings contains $2(10 + M)$ C-atoms, and the resulting cage is made of exactly 12 penta- and M hexagons. The smallest conceivable fullerene accordingly is C₂₀ (M = 0). While this molecule could not be isolated experimentally so far, the related hydrocarbon C₂₀H₂₀ is known. It features the expected pentagon-dodecahedral structure. With M increasing, the number of possible cage structures rises, for example, for the C₇₈-fullerene there are already more than 20000 theoretical isomers. The actual number of isomers observed is much smaller – there is, for instance, exactly one each for C₆₀ and C₇₀. Other fullerenes, like C₆₂–68, do not form at all, even though they are theoretically possible. It is obviously impossible for such carbon cages to adopt a structure exclusively made from hexagons and pentagons with the latter being isolated. From this observation it is clear that open-shell structures are energetically unfavorable and thus avoided. Structures with isolated pentagons are preferred to those containing adjacent five-membered rings [1].

Isolated Pentagon Rule

These intriguing questions were answered by Kroto, who proposed that the local strain increases with the number of bonds shared by two pentagons (pentalene units), thus affording less-stable molecules. This rule was coined as the "isolated pentagon rule" (IPR), stating that all pentagons must be surrounded by hexagons, thus forming the corannulene moiety [2]. The resonance destabilization that results from the adjacent pentagons (8 π electrons which do not satisfy the Hückel rule) and reduction of the π orbital overlapping because of cage curvature explains the lower stability of non-IPR fullerenes [3]. A head-to-tail exclusion rule has been proposed to explain the higher stability of fullerenes obeying the IPR rule [4]. The consequence of the IPR is that the structures best approximating a spherical shape are most stable and the number of double bonds situated in five-membered rings is minimized. As a result, five-membered rings connected via a six-membered one in "meta" position are preferred to the respective "para" variant (Figure 1). "Ortho"-oriented pentagons are already disfavored according to the IPR. The number of possible isomers is drastically reduced by this rule, and it becomes clear why many C_n molecules do not adopt a cage-like structure. The "magic" numbers for stable fullerenes obeying the rules above are $n = 60, 70, 72, 76, 78, 84, \dots$, and really all of them (except for C₇₂) can be affirmed experimentally. Possibly any C₇₂ initially created is transformed *in situ* into the even more stable C₇₀. Higher fullerenes are by far less abundant than the compound C₆₀. The formation of these cage-like compounds is kinetically controlled: among the fullerenes, C₆₀ is by no means the molecule with the least enthalpy per carbon atom. Normally the larger, thermodynamically more stable homologs should be more abundant than C₆₀ with its higher curvature-induced strain.

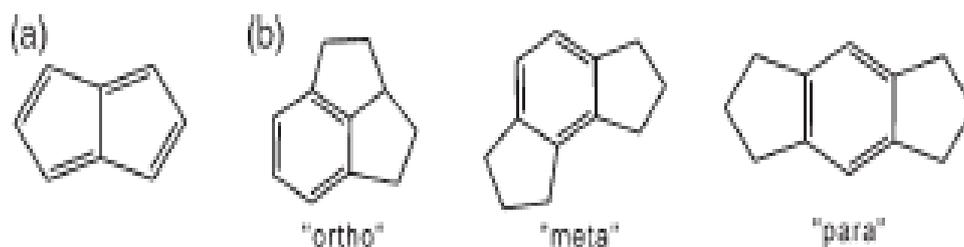


Figure -1: The unfavorable pentalene structure shown here can only be avoided with isolated five-membered rings. (b) The "meta"-arrangement of five-membered rings is preferred for its avoidance of both neighboring pentagons and double bonds within five-membered rings.

For a precise number of carbon atoms forming a cage, number of non-IPR Fullerene isomers is very much larger than the IPR ones. 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 [5]. Therefore there is great interest in the search for number of expected non-IPR fullerenes whose chemical reactivity and properties should be different from those known for IPR fullerenes [6].

The IPR is a very strong rule of thumb for neutral bare fullerenes, where every adjacent pentagon costs about 100 kJ/mol in stability but the rule can be overcome by adjusting the electron count in the structure, either by encapsulating other species, such as metal ions, or functionalising the carbon atoms on the surface [6]. Thus in order to achieve non IPR fullerenes, two different strategies have been developed to increase their stability, namely through endohedral and exohedral derivatization [7]. In both approaches the key issue to stabilize non-IPR fullerenes focuses on how to release the strains on fused pentagons. The first endohedral strategy involves encaging a metal cluster inside the fullerene cage. The bending strain on fused pentagons is significantly decreased because of the strong interactions between the fused pentagons and metal cluster. The second strategy is based on exohedral derivatization, thus changing the carbon bond hybridization and releasing the bending strains

Endohedral Fullerenes

Endohedral fullerenes are a special class of fullerenes that encapsulate other atoms. In certain endohedral fullerenes, the IPR is not obeyed and the carbon cage displays one, two or three locations where two pentagons are fused (called a pentalene fragment). A simple description of the basic geometry of any fullerene cage is based on the spiral algorithm. This principle was originally described by Manolopoulos, May and Down [8]. In order to describe the positions of the pentalene fragments, as well as those of all twelve pentagons present, a standard pentagon starting point is selected and then successive hexagons or pentagons are added in a spiral fashion until the cage is closed. If each hexagon and pentagon is numbered in sequence, the pattern can be simply represented by the numerical order of the twelve pentagons alone. Not only are endohedral fullerenes distinctly different from empty cage fullerenes in their ability to violate the IPR, the metals and clusters that are encapsulated are known to transfer their charge such that the cage acquires a negative charge. In contrast, empty cages are considered to be neutral. Encapsulated group 2 elements such as Ca are divalent, group 3 elements such as Sc and Y are trivalent and group 4 elements are tetravalent. Lanthanide elements are considered to be +3 ions with a few exceptions (Sm, Yb, Eu and Tm are expected to be +2). Trimetallic nitride clusters, M_3N , nearly all +3 M ions, have a net charge of +6. A carbide such as Gd_2C_2 is +4. The number of electrons transferred to the cage dramatically changes the favored cage isomer. As IPR examples, $Ce_2@Ih(7)-C_{80}$ [9] and $Tb_3N@Ih(7)-C_{80}$ [10] represent cases where six electrons are transferred, while in $Sc_2C_2@C_{2v}(5)-C_{80}$ [11], four electrons are transferred, and in $Yb@C_{2v}(3)-C_{80}$ [12], two electrons are transferred. When the potential for non-IPR cages to occur is factored in, the number of cage isomer possibilities is exponentially greater.

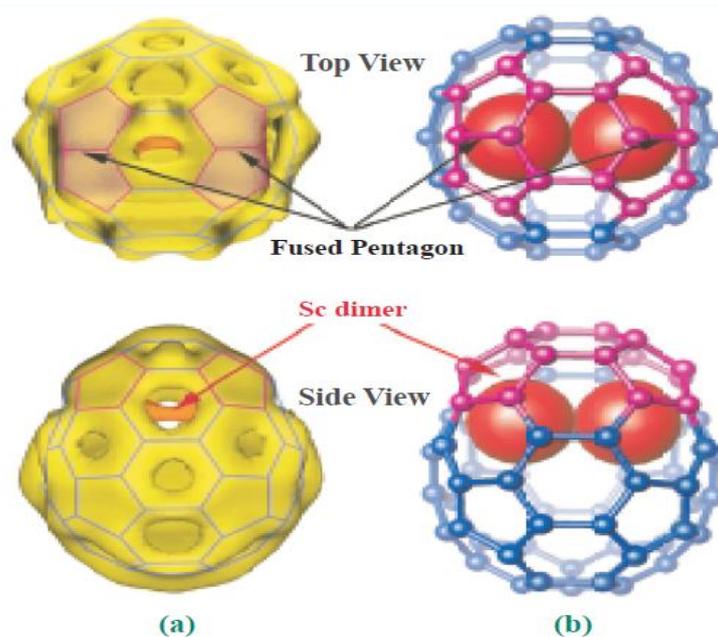


Figure-2 : $Sc_2@C_{66}$ [13,14]

Endohedral fullerenes have been known from the earliest times of fullerenes but the first non IPR fullerene, [namely $\text{Sc}_2\text{@C}_{66}$ [13] [Figure- 2] and $\text{Sc}_3\text{N@C}_{68}$ [14, 15], were obtained in 2000. It is important to note that carbon cages in endohedral fullerenes are different from those observed in empty fullerenes. Therefore, favorable electronic interactions between the encapsulated species with the carbon cage are required for stabilization of the resulting endohedral fullerenes. The case of the C84 endohedrals is illustrative. In 2006, the first structure of a non-IPR cage of C84 in the compound $\text{Tb}_3\text{N@C}_{84}$ with a single instance of fused pentagons [16] was reported. The compound formed a cocrystal with NiII(OEP) and two benzenes. Subsequently, the isostructural compounds involving Tm and Gd [17], and Y [18] were reported. Figure 3 shows the Gd fullerene together with the nearest molecule of NiII(OEP) [19].

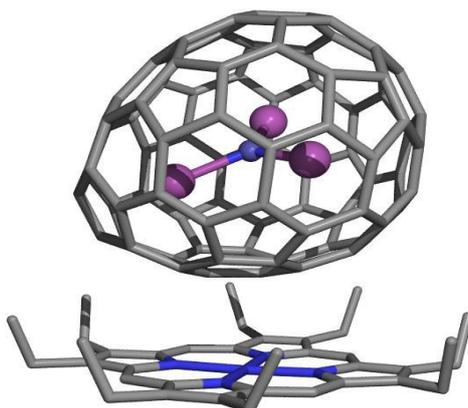


Figure- 3 : The compound $\text{Tb}_3\text{N@C}_{84}$ with a single instance of fused pentagons: cocrystal with NiII(OEP) and two benzenes [19]

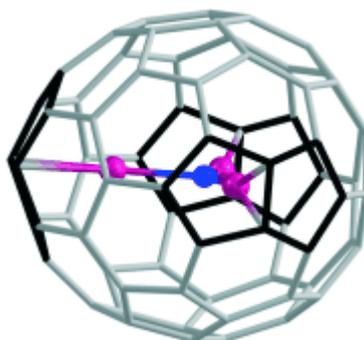


Figure-4 : $\text{C}_{70} (\text{Sc}_3\text{N@C}_{70})$ [20]

Following other metal nitride $\text{Sc}_3\text{N@C}_{70}$ [20] [Figure-4] and $\text{Y}_3\text{N@C}_{78}$ [21] etc. metal carbide containing endofullerene $\text{Sc}_2\text{C}_2\text{@C}_{68}$ [22] and metal cyanide endofullerene $\text{Sc}_3\text{NC@C}_{78}$ [23] have been prepared. A simple and qualitative rule to predict the stability of a hedral is based on the calculated HOMO-LUMO gap for the resulting “ionic “ endofullerene. This energy gap can be calculated from the (LUMO-3)-(LUMO-4) gap determined for the neutral cage, thus predicting the metal stable IPR and non – IPR endofullerenes [24].

Remarkably, non –IPR endohedral metallofullerenes (fullerenes containing one or more metal atoms in the inner cavity) show a strong coordination of the metal atoms to the fused pentagons, similar to that observed for a variety of organometallic species in which the concave face of the pentalene unit is coordinated to the metal atom [25]. In contrast, IPR endofullerenes show a motion for the encapsulated metals or cluster in the inner cavity. In some cases involving endofullerene endowed with only one atom, the metal generally co-ordinates with the cage and motion is difficult. Particular attention has been devoted to the structure of fullerene C72, a so called “missing fullerene “ because empty C72, IPR or non – IPR isomer, had never been

isolated . However, along with further studies , recently several C_{72} –based species have been successfully prepared and characterized , namely $La_2@D2(10611) - C_{72}$ [26, 27] [Figure-5], $Ce_2@D2(10611) - C_{72}$ [28], $La@C2(10612)-C_{12}$ [29], and $Sc_2S@Cs(10528)-C_{72}$ [30].

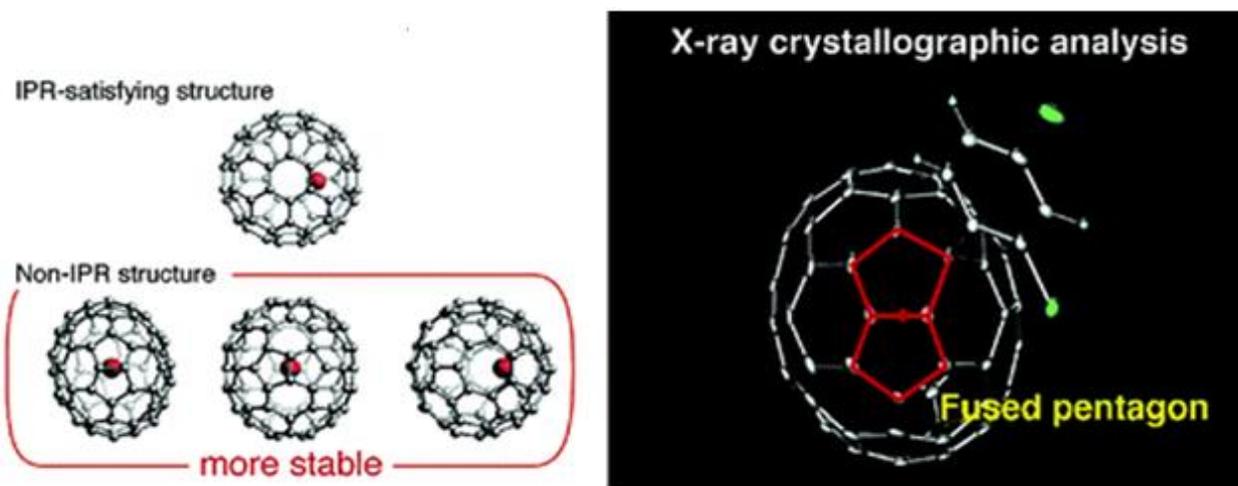


Figure-5 : $La@C_{72}$ with a non-IPR cage [27]

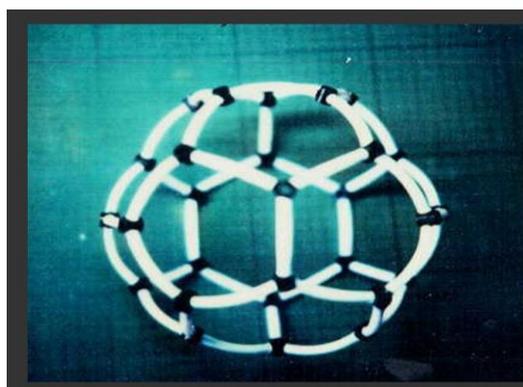


Figure-6 : $C_{28}H_4$ [31]

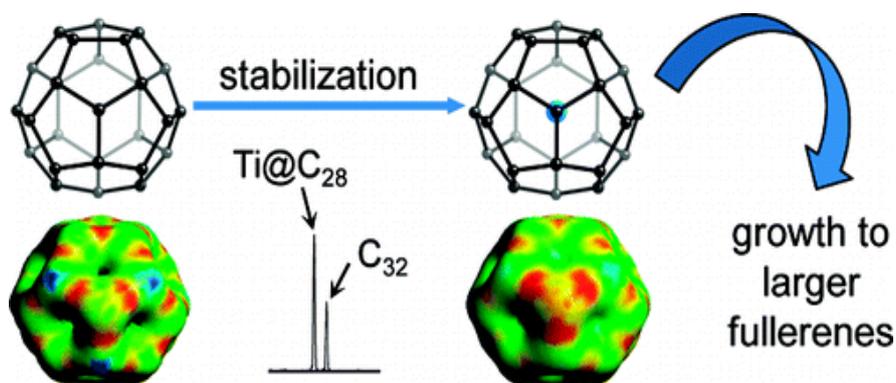


Figure-7 : C_{28} fullerene stabilized by encapsulation with a metal [32]

Kroto after coining the “isolated pentagon rule “ (IPR), stating that all pentagons must be surrounded by hexagons, thus forming the corannulene moiety , proposed that C_{28} fullerene can be stabilized by the combination of four atom of hydrogen. The $C_{28}H_4$ can be stable smallest fullerene. From a model of C_{28} molecule it was realised that C_{28} is a special in that it is tetrahedral and if it added four hydrogen atoms to

the four tetrahedral C corner atoms then it still retained four aromatic six-membered rings and the corner atoms become sp^3 and would be relaxed. This suggests that C_{28} might be a cluster super atom tetravalent analogue of the carbon atom [31] [Figure-6]. Kroto group has confirmed these observations and showed indeed C_{28} is very special indeed and can satisfy its tetravalency by trapping a tetravalent individual atom such as Ti, Zr, U [Figure-7]. Thus C_{28} has special nature and does not follow isolated pentagon rule [32]. Recently it has been shown that $U@C_{28}$ 34 valence electrons preferentially obey the 32-electron principle which fills all the s-, p-, d-, and f-type valence shells of the uranium atom. The remaining two valence electrons cannot break the electronic configuration and thus are located on the cage [33].

Exohedral Fullerenes

The second strategy based on exohedral derivatization has afforded a variety of non IPR derivatives based on the remarkable reactivity of the fused pentagons, thus changing the carbon bond hybridization and releasing the bending strains. The first fullerene C_{50} was trapped and stabilized by chlorine atoms as $C_{50}Cl_{10}$ in 2004 [34-36]. Since then the fullerene cage has been exohedrally functionalized by introducing hydrogen or chloride atoms on the cage surface, to produce a variety of non-IPR fullerene derivatives, such as $C_{64}H_4$ [17], $C_{71}H_2$ [36], $C_{78}Cl_8$ [37] etc. The stabilization of the resulting non-IPR fullerene derivatives has been accounted for by the "strain-relief principle" resulting from the rehybridization from sp^2 and sp^3 carbon atoms as well as by the local aromaticity principle which involves maintaining the local aromaticity of underivatized sp^2 carbon skeleton that remains after the derivatization process.

Chinese researchers have made an exotic new family of fullerenes that contain three pentagons fused sequentially in their structure. Unlike classical fullerenes, such as the soccer ball-shaped buckminsterfullerene (C_{60}) - the new compounds bulge out in unusual egg-shapes. It is hoped that these new structures might help reveal some of fullerenes' mysteries. The researchers at Xiamen University, China, [38] vapourised graphite in an arc-discharge reactor in the presence of carbon tetrachloride (CCl_4), which produced 3g of fullerene-rich soot every hour. This was then purified and separated by several stages of high performance liquid chromatography. Four new fullerenes were identified: $C_{54}Cl_8$, which contains two sets of triple sequentially-fused pentagons; $C_{56}Cl_{12}$, which has one set of triple sequentially-fused pentagons and two sets of double-fused pentagons; and two larger fullerenes, $C_{66}Cl_6$ and $C_{66}Cl_{10}$, which each contain a single set of triple sequentially-fused pentagons [Figure-8 &9].

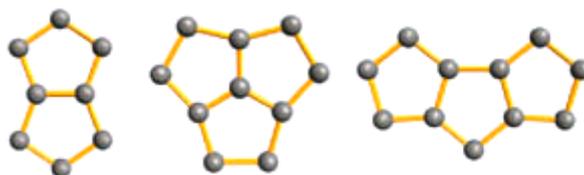


Figure-8 : Double-fused and triple directly fused pentagons have been seen in fullerenes before, triple sequentially-fused pentagons have not (left to right) [38]

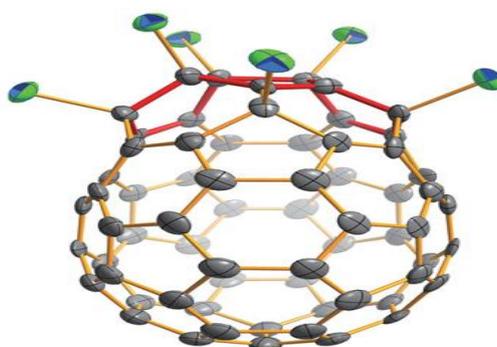


Figure-9 The strain caused by three sequentially-fused pentagons causes the fullerenes to bulge into unusual shapes, shown here in $C_{66}Cl_6$ [38]

Experimental results have recently reported, for the first time, the higher stability of non-IPR fullerene compared to its related IPR isomer for $C_{72}C_{14}$ [39, 40] (Figure 10). *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* [41]. The IPR rule is therefore valid for pristine fullerenes, whereas for fullerene derivatives additional factors emerge that could eventually force a non-IPR cage to be the most stable one. These new results pave the way to the advent of a huge family of, so far unknown non-IPR fullerenes whose number would be almost infinite. These thermodynamically less stable carbon cages should exhibit significant differences compared to those IPR obeying fullerenes, thus enhancing the properties and applications of those molecular allotropes of carbon.

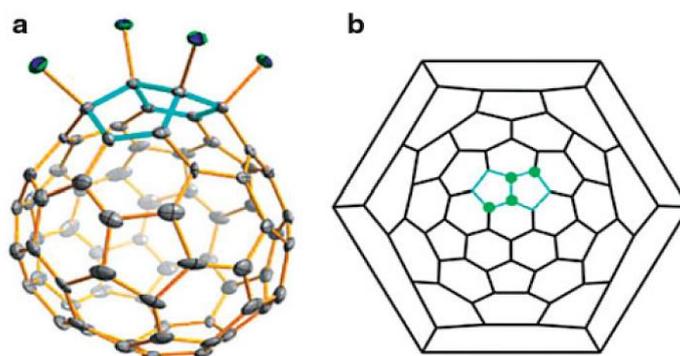


Figure -10: X-ray structure of non-IPR $C_{72}C_{14}$ (a) Fused pentagons are shown in blue (b) Schlegel diagram showing the position of four chlorine atoms [39,40]

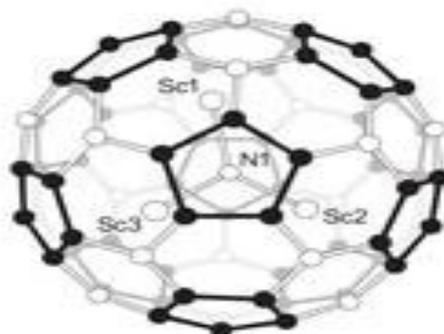


Figure-11 : $Sc_3N@I_hC_{60}$ showing maximum separation of pentagon [42]

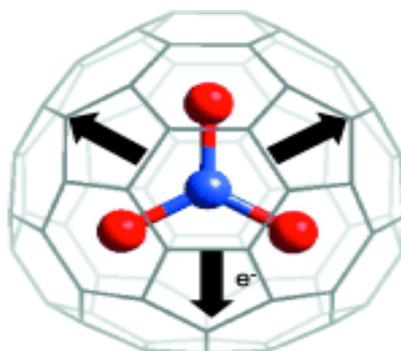


Figure-12: $Sc_3N^{6+}@C_k^{6-}$ showing ability of fullerenes to accept six electrons[43]

From then on, the list of non-IPR cages synthesized with any of the two functionalizations has increased significantly. It is important to note that there exists no IPR-violating isomer obtained both as

metallo-endohedral and chlorinated fullerene, suggesting that isomers encapsulating metals are not suitable to be obtained with halogen derivatization. The rules that govern the formation of stable non IPR metalloendohedral fullerenes have been proposed [42, 43]. A maximum pentagon separation rule is proposed, which predicts that the most stable cages are those with pentagons having the largest separation [42]. Figure-11 shows maximum separation of pentagons in $Sc_3N@I_h C_{60}$ [42]. The bonding in trimetallic nitride template (TNT) endohedral metallofullerenes is widely described by the ionic model $Sc_3N^{6+}@C_k^{6-}$. The ability of the fullerene cage to accept six electrons determines its capacity to encapsulate the TNT unit, Figure-12.

REFERENCES

- [1] Krueger A., Carbon Materials and Nanotechnology. Copyright © 2WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-31803-2 (2010)
- [2] Kroto H.W., The stability of the fullerenes C_n , with $n = 24, 28, 32, 36, 50, 60$ and 70 . *Nature* 329:529–531 (1987)
- [3] Wessendorf F., Grimm B., Guldi D.M. Pairing fullerenes and porphyrins: supramolecular wires that exhibit charge transfer activity. *J Am Chem Soc.*,132:10786–10795 (2010)
- [4] Schmalz T.G., Seitz W.A., Klein D.J., C_{60} carbon cages. *Chem Phys Lett.* 130:203–207 (1986)
- [5] Schein S. and Friedrich T.A., A geometric constraint, the head-to-tail exclusion rule, may be the basis for the isolated-pentagon rule in fullerenes with more than 60 vertices. *Proc Natl Acad Sci USA* 105,19142–19147 (2008)
- [6] Patrick F., Fullerene stability: One rule for the electron-rich...,*Nature Chemistry* 7, 857–858(2015)
- [7] Martín N., Fullerene $C_{72}Cl_4$: the exception that proves the rule? *Angew Chem Int Ed.*, 50,5431–5433(2011)
- [8] Manolopoulos D.E., May J.D. and Down S.E., Theoretical studies of the fullerenes: C_{34} to C_{70} . *Chem. Phys. Lett.*,181,105 (1991)
- [9] Feng,L., Suzuki M., Mizorogi N., Lu,X., Yamada, M., Akasaka T and Nagase S., Mapping the Metal Positions inside Spherical C_{80} Cages: Crystallographic and Theoretical Studies of $Ce_2@D_{5h}C_{80}$ and $Ce_2@I_hC_{80}$, *Chem. Eur. J.*, 19, 988 (2013)
- [10] Zuo, T., Beavers, C.M., Duchamp, J.C., Campbell, A., Dorn H.C., Olmstead M.M. and Balch, A.L. Isolation and Structural Characterization of a Family of Endohedral Fullerenes Including the Large, Chiral Cage Fullerenes $Tb_3N@C_{88}$ and $Tb_3N@C_{86}$ as well as the I_h and D_{5h} Isomers of $Tb_3N@C_{80}$. *J. Am. Chem. Soc.*,129, 2035 (2007)
- [11] Kurihara, H., Lu, X., Iiduka, Y., Nikawa H., Mizorogi N., Slanina Z., Tsuchiya T., Nagase S. and Akasaka T. Chemical Understanding of Carbide Cluster Metallofullerenes: A Case Study on $Sc_2C_2@C_{2v}(5)-C_{80}$ with Complete X-ray Crystallographic Characterizations. *J. Am. Chem. Soc.*, 134,3139 (2012)
- [12] Xie, Y., Suzuki, M., Cai, W., Mizorogi, N., Nagase, S., Akasaka T. and Lu X., Highly Regioselective Addition of Adamantylidene Carbene to $Yb@C_{2v}(3)-C_{80}$ to Afford the First Derivative of Divalent Metallofullerenes, *Angew Chem Int Ed Engl* 52(19),5142-5(2013)
- [13] Tan Y-Z., Xie S-Y., Huang R-B., The stabilization of fused-pentagon fullerene molecules. *Nat Chem.* 1, 450–460 (2009)
- [14] Wang C.R., Kai T., Tomiyama T., Materials science - C_{66} fullerene encaging a scandium dimer., *Nature* 408,426–427 (2000)
- [15] Stevenson S., Fowler P.W., Heine, T., Duchamp J.C., Rice, G., Glass, T., Harich K. Hajdu E., Bible R. and Dorn H.C., Materials science: A stable non-classical metallofullerene family, *Nature* 408, 427-428 (2000)
- [16] Beavers, C.M., Zuo T., Duchamp J.C., Harich, K., Dorn, H.C., Olmstead M.M. and Balch A.L., $Tb_3N@C_{84}$: An Improbable, Egg-Shaped Endohedral Fullerene that Violates the Isolated Pentagon Rule, *J. Am. Chem. Soc.*, 128, 11352 (2006)
- [17] Zuo, T., Walker, K., Olmstead, M.M., Melin, F., Holloway, B.C., Echegoyen, L., Dorn, H.C., Chaur, M.N., Chancellor, C.J., Beavers, C.M., Balch A.L. and Athans, A.J., New egg-shaped fullerenes: non-isolated pentagon structures of $Tm_3N@C_{51}365-C_{84}$ and $Gd_3N@C_{51}365-C_{84}$, *Chem. Commun.*, 1067 (2008)
- [18] Fu, W., Xu, L., Azurmendi, H., Ge, J., Fuhrer, T., Zuo, T., Reid J., Shu, C., Harich K. and Dorn H.C., ^{89}Y and ^{13}C NMR Cluster and Carbon Cage Studies of an Yttrium Metallofullerene Family, $Y_3N@C_{2n}$ ($n = 40-43$). *J. Am. Chem Soc.*,131,11762. (2009)
- [19] Olmstead, M.M., Balch, A.L., Bowles, F.L., Beavers C.M., Zhang J. and Dorn, H.C., Structure of surprising non-isolated pentagon rule endohedral metal carbide made possible by synchrotron radiation www.amerocrystalassn.org/documents/2013%20Transactions/10-Olmstead.pdf

- [20] Beavers C.M., Zuo T.M., Duchamp J.C., Tb3N@C84: an improbable, egg-shaped endohedral fullerene that violates the isolated pentagon rule. *J Am Chem Soc.*, 128,11352–11353(2006)
- [21] Yang S.F., Popov A.A. and Dunsch L., Violating the isolated pentagon rule (IPR): the endohedral non-IPR C70 cage of Sc3N@C70. *Angew Chem Int Ed.*, 46,1256–1259(2007)
- [22] Ma Y.H., Wang T.S., Wu J.Y., Size effect of endohedral cluster on fullerene cage: preparation and structural studies of Y3N@C78-C2. *Nanoscale* 3, 4955–4957 (2011)
- [23] Shi Z.Q., Wu X., Wang C.R., Isolation and characterization of Sc2C2@C68: a metal-carbide endofullerene with a non-IPR carbon cage. *Angew Chem Int Ed.*, 45,2107–2111 (2006)
- [24] Wu J.Y., Wang T.S., Ma Y.H., Synthesis, isolation, characterization, and the theoretical studies of Sc3NC@C78-C2. *J Phys Chem C* 115,23755–23759 (2011)
- [25] Campanera J.M., Bo C., Poblet J.M., General rule for the stabilization of fullerene cages encapsulating trimetallic nitride templates. *Angew Chem Int Ed.*, 44,7230–7233 (2005)
- [26] Tan Y.Z., Li J., Zhou T., Feng Y.Q., Pentagon-fused hollow fullerene in C78 family retrieved by chlorination. *J Am Chem Soc.* 132,12648–12652 (2010)
- [27] Wakahara T., Nikawa H., Kikuchi T., Nakahodo T., Aminur Rahman G.M., Tsuchiya T., Maeda Y., Akasaka T., Yoza K., Horn E., Yamamoto K., Mizorogi N., Slanina Z., and Nagase S., La@C72- Having a Non IPR Carbon Cage, *J. Am. Chem. Soc.* 128 (44),14228–14229 (2006)
- [28] Kato H., Taninaka A., Sugai T., Structure of a missing-caged metallofullerene: La2@C72. *J Am Chem Soc.*, 125,7782–7783 (2003)
- [29] Yamada M., Wakahara T., Tsuchiya T., Spectroscopic and theoretical study of endohedral dimetallofullerene having a non-IPR fullerene cage: Ce2@C72. *J Phys Chem A* 112,7627–7631 (2008)
- [30] Wakahara T., Nikawa H., Kikuchi T., La@C72 having a non-IPR carbon cage. *J Am Chem Soc.* 128,14228–14229 (2006)
- [31] Kroto H.W., The stability of fullerene C_n, with n= 24, 28, 32, 36, , 50, 60 and 70 , *Nature* 329, 529-531 (1987)
- [32] Dunk ,P.W., Kaiser N.K, Mulet-GasM. , Rodríguez-ForteA., Poblet J.M., Shinohara H., Hendrickson C.L. , Marshall,A.G. and Kroto,H.W., The Smallest Stable Fullerene, M@C₂₈ (M = Ti, Zr, U): Stabilization and Growth from Carbon Vapor, *J. Am. Chem. Soc.* 134 (22), 9380–9389(2012)
- [33] Dai,X., Gao Y., Jiang W., Lei Y. and Wang Z. , U@C₂₈: the electronic structure induced by the 32-electron principle, *Phys. Chem. Chem. Phys.* 17, 23308-23311(2015)
- [34] Summerscales O.T. and Cloke F.G.N., The organometallic chemistry of pentalene. *Coord Chem Rev.*, 250:1122–1140 (2006)
- [35] Xie S.Y. Gao F., Lu X., Capturing the labile fullerene[50] as C50Cl10., *Science* 304,699–699 (2004)
- [36] Wang C.R., Shi Z.Q., Wan L.J., C64H4: Production, isolation, and structural characterizations of a stable unconventional fulleride. *J Am Chem Soc.* 128,6605–6610 (2006)
- [37] Li B., Shu C.Y., Lu X., Addition of carbene to the equator of C(70) to produce the most stable C(71)H(2) isomer: 2 aH-2(12)a-homo(C(70)-D(5h(6)))[5,6]fullerene. *Angew Chem Int Ed.*, 49,962–966 (2010)
- [38] Tan,Y-Z., Li J., Zhu F., Han X., Jiang W., Huang R., Zheng Z., Qian Z., Chen R., Liao Z., Xie,S., Lu X. and ZhengL., Chlorofullerenes featuring triple sequentially fused pentagons. *Nat Chem.* 2,269–273(2010)
- [39] Chen N., Beavers C.M., Mulet-Gas M., Sc2S@C(s)(10528)-C72: a dimetallic sulfide endohedral fullerene with a non isolated pentagon rule cage. *J Am Chem Soc.* 134,7851–7860 (2012)
- [40] Tan Y-Z., Zhou T., Bao J., Shan G-J., Xie S-Y., Huang R-B. and Zheng L-S., C72Cl4: A pristine fullerene with favorable pentagon-adjacent structure. *J Am Chem Soc.* 132,17102–17104 (2010)
- [41] TanY-Z., Xie S-Y., HuangR-B. and Zheng L-S. , The stabilization of fused-pentagon fullerene molecules, *Nature Chemistry* 1, 450 - 460(2009)
- [42] Rodriguez-ForteA., Alegret N., Balch A. L. and Poblet J. M., The maximum pentagon separation rule provides a guideline for the structures of endohedral metallofullerenes *Nature Chem.* 2, 955 (2010)
- [43] Campanera, J. M., Bo C. and Poblet J. M., General Rule for the Stabilization of Fullerene Cages Encapsulating Trimetallic Nitride *Angew.Chem., Int. Ed.* 44, 7230-7233 (2005)