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Giant Fullerenes

# Chlorination of IPR $C_{100}$ Fullerene Affords Unconventional $C_{96}Cl_{20}$ with a Nonclassical Cage Containing Three Heptagons**

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**Abstract:** *Chlorination of $C_{100}$ fullerene with a mixture of $VCl_4$ and $SbCl_5$ afforded $C_{96}Cl_{20}$ with a strongly unconventional structure. In contrast to the classical fullerenes containing only hexagonal and pentagonal rings, the $C_{96}$ cage contains three heptagonal rings and, therefore, should be classified as a fullerene with a nonclassical cage (NCC). There are several types of pentagon fusions in the $C_{96}$ cage including pentagon pairs and pentagon triples. The three-step pathway from isolated-pentagon-rule (IPR) $C_{100}$ to $C_{96}$(NCC-3hp) includes two $C_2$ losses, which create two cage heptagons, and one Stone–Wales rotation under formation of the third heptagon. Structural reconstruction established $C_{100}$ isomer no. 18 from 450 topologically possible IPR isomers as the starting $C_{100}$ fullerene. Until now, no pristine $C_{100}$ isomers have been confirmed based on the experimental results.*

The development of the chemistry of the higher fullerenes is hampered by their low abundance in the fullerene soot (except $C_{84}$) and the existence of many cage isomers. For the higher fullerenes in the range of $C_{76}$–$C_{96}$, it was still possible to isolate individual IPR (isolated pentagon rule) isomers in quantities sufficient for $^{13}$C NMR study ($C_{76}$–$C_{84}$)[1] or for cocrystallization with metal porphyrins ($C_{86}$–$C_{96}$).[2] In the case of even larger (giant) fullerenes, HPLC isolation generally provides much smaller quantities, which sometimes amount to several dozens of micrograms. Therefore, the isolation and structural study of giant empty fullerenes still remain quite challenging. Two recent reports are devoted to the characterization of chlorinated giant empty fullerenes such as two isomers of $C_{104}$[3] and nonclassical, heptagon-containing $C_{102}$ resulting from a chlorination-promoted transformation of IPR $C_{102}$(19)[4] (numbering according to the spiral algorithm[5]). On the other hand, giant endohedral fullerenes such as $Dy_2@C_{100}$,[6] $La_2@C_{100}$(450),[7] and $Sm_2@C_{104}$(822)[8] have been also isolated and characterized.

Up to now, empty fullerene $C_{100}$ has been registered only by mass spectrometry. Theoretical calculations suggested that several of altogether 450 IPR isomers of $C_{100}$ are more stable than others and, therefore, can be present in the fullerene soot. Among them, isomer $D_2$-$C_{100}$(449) was found to be the most stable according to the calculations performed by different methods.[9] The sets of next stable $C_{100}$ isomers found in three theoretical studies[9a–c] are different, most probably due to the use of the selection and cutoffs for subsequent high-level calculations,[9b,c] whereas all 450 IPR isomers have been systematically calculated in Ref. [9a].

Herein we report the isolation and structural characterization of an unprecedented chlorinated $C_{96}$ fullerene with a nonclassical cage (NCC) containing three heptagons, $C_{96}$(NCC-3hp)$Cl_{20}$. The reconstruction of the pathway revealed that $C_{96}$(NCC-3hp) is a result of a three-step transformation, including two $C_2$ losses and one Stone–Wales (SW) rearrangement of the starting IPR $C_{100}$(18), the first isomer of pristine $C_{100}$ evidenced by experimental results.

The fullerene soot was synthesized by the Krätschmer–Huffman DC arc-discharging method with an undoped graphite rod under He pressure of 400 mbar. The extracted fullerene mixture was subjected to HPLC separation in toluene using a preparative 5PYE column. The fraction eluting between 41.4 and 44.6 min was further separated with a semipreparative Buckyprep column and the main subfractions were then subjected to recycling HPLC with a semipreparative Buckyprep-M column. According to mass spectrometric analyses, three subfractions collected after several separation cycles contained mixtures with a prevailing abundance of $C_{100}$ (see the Supporting Information for more details). The most pure $C_{100}$ subfraction was used as the starting material for chlorination.

Around 0.02 mg of $C_{100}$ was placed into a glass ampoule and approximately 0.4 mL of $VCl_4$ and a drop of $SbCl_5$ were added. The ampoule was evacuated, sealed off, and heated at 350–360 °C for roughly four weeks. After the ampoule was cooled and opened, the reaction product was washed with conc. HCl and water to remove excess $SbCl_5$ and $VCl_4$ leaving small orange-colored crystals. Single-crystal X-ray diffraction

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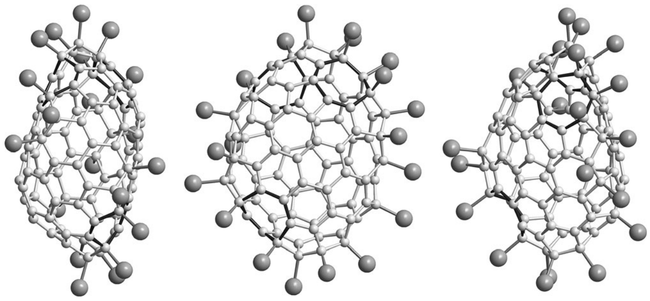

***Figure 1.*** Three projections of the $C_1$-$C_{96}$(NCC-3hp)$Cl_{20}$ molecule with heptagon rings highlighted in black. The left projection is along the former $C_2$ axis of the starting $C_{100}$, the middle one shows the relative positions of three cage heptagons, whereas the third one demonstrates a concave cage region due to the removal of a $C_2$ unit.

using synchrotron radiation revealed the formation of $C_{96}$ fullerene chloride.[10]

The crystallographic results revealed that the obtained $C_{96}$ chloride, $C_{96}Cl_{20}$, possesses a very unusual molecular structure featuring the presence of three heptagonal rings (hp) in its carbon cage (Figure 1) and, therefore should be designated as a "nonclassical carbon cage" (NCC) in contrast to "classical" fullerenes containing only five- and six-membered rings. Significantly, although the possible role of heptagons in high-temperature fullerene synthesis and their formation by the loss of $C_2$ moieties have been intensely discussed in the literature,[11,12] so far the experimentally confirmed NCC fullerene derivatives including $C_{58}F_{18}$ and $C_{58}F_{17}(CF_3)$,[13] $C_{68}Cl_6$,[12] $C_{84}Cl_{32}$,[14] and $C_{88}Cl_{22/24}$[15] all contain only one heptagon in the carbon cage.

As a consequence of the Euler theorem, the carbon cage of $C_{96}$(NCC-3hp)$Cl_{20}$ contains 15 pentagons (versus 12 pentagons in all classical fullerenes), most of which are fused forming three pentagon pairs, one sequentially fused triple, and one directly fused triple (see the top right Schlegel diagram in Figure 2). As a result, the $C_{96}$(NCC-3hp)$Cl_{20}$ molecule as a whole has a rather irregular shape because the areas of pentagon fusion are protruding, whereas the regions with heptagons are concave (see Figure 1).

The attachment of 20 Cl atoms on the $C_{96}$(NCC-3hp) cage is quite nonuniform; the structure features a long nine-membered chain of adjacent additions together with shorter, three- and four-membered chains (Figure 2). It is known that a pentagon fusion in fullerene cages results in additional strain which can be relieved by exohedral chlorination.[16] Indeed, all common edges of fused pentagon pairs are chlorinated. In the sequentially fused triple of pentagons three vertices of two common edges are chlorinated in accordance with the rule formulated previously for such pentagon arrangements.[17] Finally, in the directly fused pentagon triple only three of four vertices of fusion are chlorinated in contrast to the only known example for lower non-IPR fullerene, $C_{64}Cl_4$[18] (see discussion below). Noteworthy, in spite of the involvement of Cl atoms in adjacent attachments, two cage pentagons are not chlorinated. Similarly, two unoccupied pentagons in chlorinated higher fullerenes with more than 12 attached Cl atoms have been reported for $C_{88}(17)Cl_{16}$[19] and $C_{104}(258)Cl_{16}$.[3]

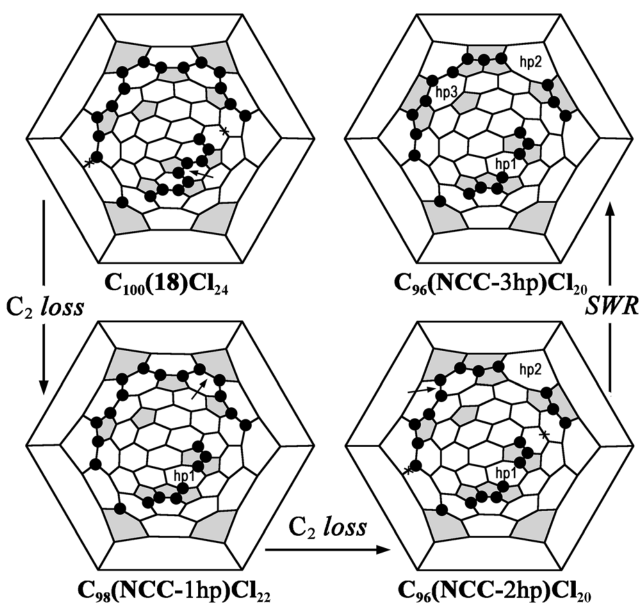


***Figure 2.*** Schlegel diagram representation of a three-step pathway from IPR $C_{100}(18)Cl_{24}$ via $C_{98}$(NCC-1hp)$Cl_{22}$ and $C_{96}$(NCC-2hp)$Cl_{20}$ to the experimentally determined $C_{96}$(NCC-3hp)$Cl_{20}$. Pentagons are shown in gray, and heptagons are labeled hp1, hp2, and hp3. Small arrows show the position of the bonds that are removed or rotated in the next step. The positions of the twofold axes of the carbon cages in $C_{100}(18)Cl_{24}$ and $C_{96}$(NCC-2hp)$Cl_{20}$ are marked with +. SWR = Stone–Wales rearrangement.

The most interesting question arises about the origin of the $C_{96}$(NCC-3hp) cage because neither non-IPR nor non-classical empty fullerenes can be present in the starting material. Because the starting fraction of $C_{100}$ was compositionally rather pure (see the Supporting Information), the pathway from IPR $C_{100}$ to $C_{96}$(NCC-3hp) cage should be sought. It follows from the previous cases of IPR fullerene shrinkage that heptagonal rings can be formed by the elimination of 5:6 C−C bonds from the cage.[13–15] Obviously, two such eliminations are responsible for the formation of two heptagons, whereas the third heptagon should be created by a different way. It can be assumed that the third heptagon is obtained by a Stone–Wales rotation of a 6:6 C−C bond, which connects a pentagon with a hexagon. Such transformations have never been reported for fullerenes, but a similar rotation of a 6:6 bond in a pyrene-like fragment (four hexagons) is widely discussed as a mechanism creating so-called Stone–Wales defects in nanotubes and graphene (two pentagons and two heptagons).[20] A reconstruction of a possible pathway from $C_{100}$ to $C_{96}$(NCC-3hp) revealed that only three transformation steps (in any order) are necessary, including two $C_2$ losses and one SW rotation of the type discussed above.

Figure 2 shows a possible three-step pathway with $C_2$ losses occurring first, followed by the SW rotation. The starting IPR $C_{100}$ cage corresponds to isomer 18,[5] whereas the final and intermediate NCC cages can be properly designated with their spiral codes (see the Supporting Information).

It should be noted that the attachment positions in the starting and intermediate chlorinated fullerenes in Figure 2 are given somewhat arbitrarily. In fact, some positions, especially those in triple hexagon junctions (THJs) could be chlorinated in next steps, where THJs change to junctions of two hexagons and one pentagon (HHP). Most probably, a $C_2$ moiety is removed from the cage as a chlorinated species ($C_2Cl_n$).[14,15] The driving force of the $C_2$ losses and heptagon generation is the simultaneous formation of chlorinated sites at pentagon–pentagon adjacencies of fused pentagon pairs and within pentagon triples. The two $C_2$ losses from the $C_2$-$C_{100}$(18) cage are symmetrically related and that produces $C_{96}$(NCC-2hp)$Cl_{20}$ containing the carbon cage with twofold symmetry.

Apparently, the SW rotation of a chlorinated C–C bond in the third step accompanied by the creation of the third heptagon (hp3) is driven by the formation of additional chlorinated pentagon–pentagon junctions, in particular, the directly fused pentagon triple. DFT calculations revealed this transformation to be strongly (103 kJ $mol^{-1}$) exothermic.[21] The SW rotation proceeds without formation of new chlorinated sites, so that one vertex of the resulting directly fused pentagon triple remains nonchlorinated. Interestingly, the cage regions of heptagons 1 and 2, which were formed by $C_2$ abstraction, are pronouncedly concave (see Figure 1), whereas heptagon 3, which resulted from the SW rotation, is only slightly twisted. Average pyramidalization angles at $sp^3$ sites (defined as the average Cl-C-C angle minus 109.5°)[17] are $-0.7°$ (THJ), $+0.2°$ (HHP), $+2.8°$ (PPH), and 4.2° (PPHp and PPP), where HHP, PPH, PPHp, and PPP designate the junctions of pentagons (P), hexagons (H), and heptagons (Hp).

The $C_2$-$C_{100}$(18) isomer can be confidently considered to be the starting IPR cage because 1) it is achievable by the shortest reconstruction path from the experimentally determined $C_{96}$(NCC-3hp) cage and 2) IPR–IPR transformations do not occur at the relatively low reaction temperatures of 350–360 °C used in the present study. Furthermore, $C_2$-$C_{100}$(18) isomer ranks second in stability among all 450 IPR $C_{100}$ isomers and possesses a large HOMO–LUMO gap according to theoretical calculations.[9a] A high probability of the presence of $C_{100}$(18) in the fullerene soot is additionally supported by the fact that its relative content in the equilibrium mixture of $C_{100}$ isomers is rather high over a wide temperature range as revealed by the calculation of Gibbs energies.[9a] The absence of $C_{100}$(18) among the most stable $C_{100}$ isomers in other theoretical studies[9b,c] might be due to the incompleteness of the isomer sets used in the calculations.

DFT calculations of the formation energies of IPR and NCC $C_{96}$ fullerenes and $C_{96}$(NCC-3hp)$Cl_{20}$ allowed us to estimate the average energy of C–Cl bonds (chlorination enthalpy of the parent fullerene per one Cl atom).[21] As expected, the $C_{96}$(NCC-3hp) fullerene is energetically extremely unfavorable being 696 kJ $mol^{-1}$ less stable than the most stable IPR $D_2$-$C_{96}$(183). However, the $C_{96}$(NCC-3hp)$Cl_{20}$ molecule is very stable; its C–Cl bond energy is 42 kJ $mol^{-1}$ higher than that in $D_{3d}$-$C_{60}Cl_{30}$,[22] apparently, due to the contribution from chlorinated pentagon–pentagon adjacencies, in particular, the triply fused pentagons. For comparison, the value for the non-IPR $^{\#18917}C_{76}Cl_{24}$ containing five pairs of fused pentagons is still higher (55 kJ $mol^{-1}$) because of additional stabilization due to the presence of the flattened coronene fragments on the unfunctionalized part of the $C_{76}$ cage.[23] In contrast, the average C–Cl bond energy in the IPR $C_{96}$(183)$Cl_{24}$ molecule[24] is only 1.8 kJ $mol^{-1}$ higher than that in $D_{3d}$-$C_{60}Cl_{30}$; this is in accord with the empirical rule that the C–Cl bond energy slightly decreases with the increasing number of Cl attachments.[19,24]

In contrast to the empty $C_{100}$ fullerenes, of which the lowest-energy isomers possess numbers 449 and 18, the endohedral $C_{100}$ fullerenes have a fully different stability order. Thus, IPR isomer $D_5$-$C_{100}$(450) was theoretically predicted to be the most favorable $C_{100}$ cage for the endohedral fullerenes incorporating two lanthanide atoms, which are able to donate up to six electrons to the carbon cage.[25] This assumption was later confirmed by the isolation and structure determination of $La_2@C_{100}$(450).[7] Note that empty $C_{100}$(450) is 395th in the stability row ranking and possesses a virtually zero HOMO–LUMO gap according to theoretical calculations.[9a]

In summary, the significance of the findings of this work for the fundamental fullerene chemistry is threefold. First, a chlorinated nonclassical $C_{96}$ fullerene featuring, for the first time, three heptagons and sequentially/directly fused pentagon triples has been isolated and structurally characterized. Second, a new transformation path to heptagons, a Stone–Wales rearrangement, has been shown to proceed in the course of chlorination under relatively mild conditions. Third, the presence of the first IPR isomer of empty $C_{100}$ fullerene, $C_2$-$C_{100}$(18), in the arc-discharge fullerene soot has been proposed on the basis of the experimental structural data. Thus, chlorination followed by a single-crystal X-ray diffraction study proved to be a powerful means of investigating higher fullerenes available only in extremely small quantities. Structural studies on the derivatives of other $C_{100}$ isomers are underway in our laboratories.

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