Fullerenes

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New Isolated-Pentagon-Rule and Skeletally Transformed Isomers of C_{100} Fullerene Identified by Structure Elucidation of their Chloro Derivatives

Song Wang, Shangfeng Yang, Erhard Kemnitz,* and Sergey I. Troyanov**

Abstract: *High-temperature chlorination of C_{100} fullerene followed by X-ray structure determination of the chloro derivatives enabled the identification of three isomers of C_{100} from the fullerene soot, specifically numbers 18, 425, and 417, which obey the isolated pentagon rule (IPR). Among them, isomers C_1-$C_{100}(425)$ and C_2-$C_{100}(18)$ afforded C_1-$C_{100}(425)Cl_{22}$ and C_2-$C_{100}(18)Cl_{28/30}$ compounds, respectively, which retain their IPR cage connectivities. In contrast, isomer C_{2v}-$C_{100}(417)$ gives C_s-$C_{100}(417)Cl_{28}$ which undergoes a skeletal transformation by the loss of a C_2 fragment, resulting in the formation of a nonclassical (NC) C_1-$C_{98}(NC)Cl_{26}$ with a heptagon in the carbon cage. Most probably, two nonclassical C_1-$C_{100}(NC)$-$Cl_{18/22}$ chloro derivatives originate from the IPR isomer C_1-$C_{100}(382)$, although both C_1-$C_{100}(344)$ and even nonclassical C_1-$C_{100}(NC)$ can be also considered as the starting isomers.*

The investigation and structural identification of higher fullerenes is made difficult by their very low abundance in the fullerene soot and the existence of many cage isomers.[1] ^{13}C NMR spectroscopy can be used as an effective identification tool only up to C_{88}.[2] When only point-symmetry information is available from the ^{13}C NMR study of isomer mixtures, theoretical calculations of the relative energetic stabilities are helpful in the prediction of more probable isomers, as in the cases of C_{90}[3] and C_{96}.[4] Alternatively, some isomers of higher pristine fullerenes C_{90}–C_{96} could be unambiguously identified by crystallographic studies of either co-crystals with metal porphyrins[5] or exohedral derivatives.[6]

The investigation of giant fullerenes beginning symbolically with C_{100} is quite challenging because their abundance in the fullerene soot is extremely low, and, at the same time, there are several hundred topologically possible isomers which obey the isolated pentagon rule (IPR). Nevertheless, a few isomers of some giant pristine fullerenes have been identified by isolation of their chloro derivatives followed by X-ray crystallographic analysis. In this way, the most stable IPR isomers of C_{102} and C_{104} have been confirmed as $C_{102}(234)Cl_{16\text{-}22}$ and $C_{104}(603)Cl_{18/20}$, respectively[7] (isomer numbering according to the spiral algorithm[1]). Additionally, two less stable C_{104} isomers (numbers 258 and 812) have been captured as chlorides,[8a] and the existence of the IPR isomer $C_{102}(19)$ was deduced from a structural study of a non-IPR chloride $C_{102}Cl_{20}$, formed as a result of chlorination-promoted cage transformation.[8b]

The giant fullerene C_{100} has 450 topologically possible IPR isomers. According to theoretical calculations of relative formation energies, isomer $C_{100}(449)$ is the most stable followed by isomer numbers 18, 425, 440, and 442, in different orders depending on the calculation method used.[9] Therefore, it is highly surprising that the first experimentally confirmed isomer of C_{100} fullerene was an extremely unstable isomer, D_{5d}-$C_{100}(1)$, which was isolated as a chloride, $C_{100}(1)Cl_{12}$, with a remarkable carbon cage of nanotubular shape.[10] Another rather stable isomer $C_{100}(18)$ was indirectly confirmed as the most probable starting fullerene of the skeletal transformations to the nonclassical (*NC*) chlorides $C_{96}(NC3)Cl_{20}$ and $C_{94}(NC1)Cl_{22}$ (the numeral after *NC* indicates the number of heptagons in the carbon cage).[11]

Herein we report the first isolation and structural characterization of several chlorides of C_{100} fullerene containing IPR isomers C_2-$C_{100}(18)$, C_1-$C_{100}(425)$, and C_{2v}-$C_{100}(417)$. The product of the chlorination-promoted skeletal transformation of $C_{100}(417)Cl_{28}$ to $C_{98}(NC)Cl_{26}$ has been also structurally characterized. Additionally, another new isomer, C_1-$C_{100}(382)$, is proposed as the starting C_{100} isomer of two isolated nonclassical $C_{100}(NC)Cl_{18/22}$ chlorides containing one heptagon in the carbon cage.

The fullerene soot was synthesized by a Krätschmer–Huffman DC arc-discharging method with an undoped graphite rod under a He pressure of 400 mbar. The extracted fullerene mixture was subjected to HPLC separation in toluene using a preparative 5PYE column. The fraction eluted between 41.4 and 44.6 min was further separated with a semi-preparative Buckyprep column and the main subfractions were then subjected to recycling HPLC with a semi-preparative Buckyprep-M column. One of the subfractions collected after several separation cycles contained compositionally pure C_{100}, whereas three others were admixtures of C_{100} with C_{96}, C_{98}, or C_{102} (see the Supporting Information for

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[*] S. Wang, Prof. Dr. S.-F. Yang
Hefei National Laboratory for Physical Sciences at Microscale
CAS Key Laboratory of Materials for Energy Conversion
Department of Materials Science and Engineering
University of Science and Technology of China
Hefei 230026 (China)
E-mail: sfyang@ustc.edu.cn

Prof. Dr. E. Kemnitz
Institute of Chemistry, Humboldt University Berlin
Brook-Taylor.-Str.2, 12489 Berlin (Germany)
E-mail: erhard.kemnitz@chemie.hu-berlin.de

Prof. Dr. S. I. Troyanov
Department of Chemistry, Moscow State University
119991 Moscow, Leninskie gory (Russia)
E-mail: stroyano@thermo.chem.msu.ru

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more details). Subfractions obtained were used as the starting material for chlorination.

In each chlorination experiment, circa 0.02 mg of the C_{100} subfraction was placed into a glass ampoule and circa 0.4 mL VCl_4 and a drop of $SbCl_5$ were added. The ampoule was evacuated, sealed off, and heated at 350–360 °C for 1–12 weeks until crystals had formed. Rather long reaction times are needed because of the low fullerene concentration in the reaction system, high activation barriers for skeletal transformations, and the very slow crystal-growth process. After the ampoule was cooled and opened, the reaction product was washed with HCl and water to remove excess $SbCl_5$ and VCl_4, leaving small red- or orange-colored crystals. Single-crystal X-ray diffraction studies, using synchrotron radiation, of crystals from different chlorination experiments revealed the formation of $C_{100}(18)Cl_{28/30}$, $C_{100}(425)Cl_{22}$, $C_{100}(417)Cl_{28}/C_{98}(NC)Cl_{26}$ (both in the same crystal), and $C_{100}(NC)Cl_{18/22}$ (see Table S1 in the Supporting Information).[17]

Projections of the structurally characterized molecules are shown in Figure 1. Most molecules show rather irregular shapes because of the non-uniform distribution of pentagons, aromatic substructures, and chloride attachments on fullerene cages. Noteworthily, the isolation of C_2-$C_{100}(18)Cl_{28/30}$ in the present work confirms our previous supposition concerning the presence of $C_{100}(18)$ in the fullerene soot based on the structural reconstruction of pathways to chlorides of C_{94} and C_{96} with nonclassical carbon cages.[11]

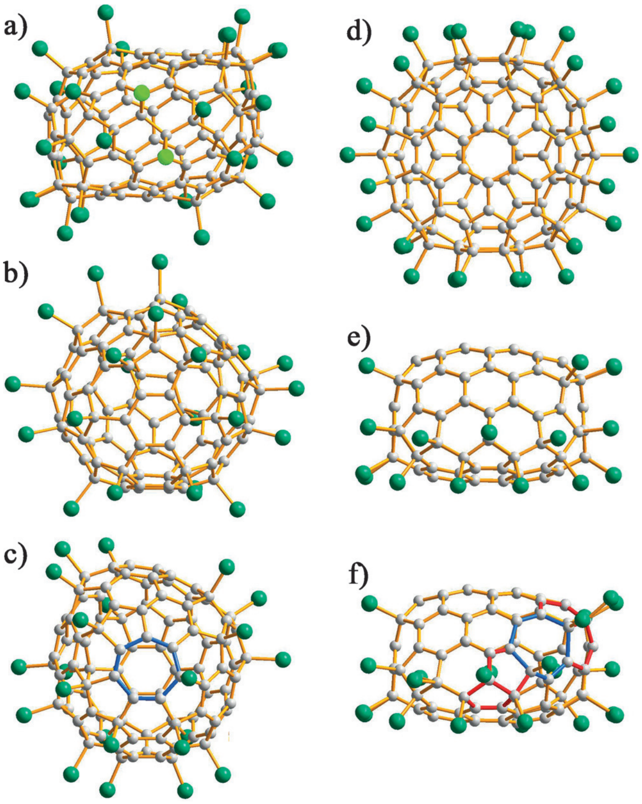

Figure 1. Projections of molecules a) C_2-$C_{100}(18)Cl_{28/30}$, b) C_1-$C_{100}(425)Cl_{22}$, c) C_1-$C_{100}(NC)Cl_{22}$, d, e) C_s-$C_{100}(417)Cl_{28}$, and f) C_1-$C_{98}(NC)Cl_{26}$.[17] Two additional Cl atoms in the C_2-$C_{100}(18)Cl_{30}$ molecule (a) are shown as light green. Projections (a) and (d) are given along the two-fold axis and parallel to the mirror plane, respectively. Cage heptagons are shown in blue (c, f) and fused pentagons are drawn in red (f).

In fact, overlapping molecules of $C_{100}(18)Cl_{28}$ and $C_{100}(18)Cl_{30}$ (Figure 1 a) are present in two investigated crystals (with occupancy ratios of 65/35 and 30/70, respectively) obtained in different chlorination experiments. Noteworthily, the $C_{100}(18)Cl_{28/30}$ chlorides formed in a relatively short reaction time of circa one week, whereas the products of the $C_{100}(18)$ cage transformation were isolated after a four-week reaction at the same temperature.[11b] The chlorination patterns of C_2-$C_{100}(18)Cl_{28}$ contain relatively long chains of adjacent (*ortho*) additions of Cl atoms in regions of two closely arranged groups of four pentagons (Figure 2, left). Two ethenylbenzene-like substructures and four isolated and nearly isolated C=C bonds contribute to the stabilization of the structure. Note that $C_{100}(18)Cl_{30}$ contains a longer *ortho* chain of Cl atoms as a result of the attachment of two Cl atoms at triple hexagon junctions (THJs) which are generally unfavorable for addition to fullerenes. The flattened overall shape of the carbon cage of the $C_{100}(18)Cl_{28/30}$ molecules is due to the presence of oppositely arranged coronene substructures in the $C_{100}(18)$ isomer.

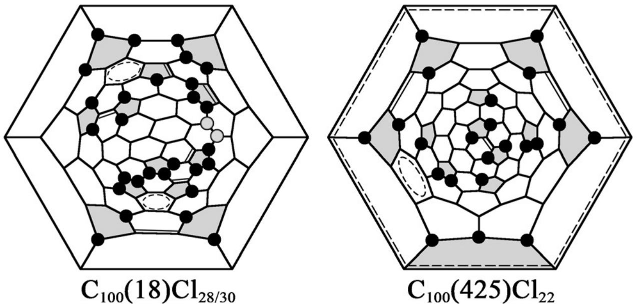

Figure 2. Schlegel diagrams of C_2-$C_{100}(18)Cl_{28/30}$ and C_1-$C_{100}(425)Cl_{22}$. Black circles show the positions of the Cl atoms. Two additional Cl atoms in the structure of C_2-$C_{100}(18)Cl_{30}$ are shown in gray. Isolated and nearly isolated benzenoid rings and double C=C bonds are shown.

It should be noted that the chlorination patterns of C_2-$C_{100}(18)Cl_{28/30}$ differ significantly from that proposed previously for C_2-$C_{100}(18)Cl_{24}$ as the starting structure of the cage transformations to $C_{96}(NC3)Cl_{20}$ and $C_{94}(NC1)Cl_{22}$.[11] This discrepancy suggests that the stable chloride derivatives isolated and characterized in this work change their chlorination pattern in the course of further reaction (including the "chlorine dance") to the structures which are prone to skeletal transformations.

Two crystalline modifications of $C_{100}(425)Cl_{22}$ were obtained in the same chlorination experiment. They contain the carbon cage of a new C_1-$C_{100}(425)$ isomer, while their crystal structures differ by packing motifs only. The $C_{100}(425)Cl_{22}$ molecule has a rather spherical shape as a result of the absence of coronene substructures in the cage (Figure 1 b). In contrast to $C_{100}(18)Cl_{28/30}$, the chlorination pattern of $C_{100}(425)Cl_{22}$ contains only two sets of attachments of

Cl atoms in adjacent positions (Figure 2, right). Three isolated double C=C bonds and two benzenoid rings stabilize the chlorination pattern.

In the most accurately determined crystal structure of giant fullerene chlorides, $C_{100}(425)Cl_{22}$-II, the isolated C=C bonds are the shortest, with a typical averaged length of 1.319 Å. The average C−C bond length of benzenoid rings is 1.398 Å, whereas the longest C−C bonds (1.557–1.592 Å) are of the sp^3–sp^3 type. Similar elongation (up to 1.71 Å) was reported previously in the structures of polychlorinated fullerenes.[6b–d,7,8a,11b,12] The C−Cl bonds have a typical average length of 1.816 Å.

Isomer C_{2v}-$C_{100}(417)$ was captured as C_s-$C_{100}(417)Cl_{28}$ in two crystal structures. One structure is built of mirror-symmetrical molecules which are markedly flattened owing to two coronene substructures on opposite sides of the carbon cage (Figure 1 d,e). 26 attached Cl atoms are arranged according to C_{2v} symmetry of the cage, whereas two attached Cl atoms reduce the symmetry of the whole chlorination pattern to C_s (Figure 3). The carbon cage of $C_{100}(417)Cl_{22}$ contains two butadiene-like units and two aromatic systems within coronene substructures.

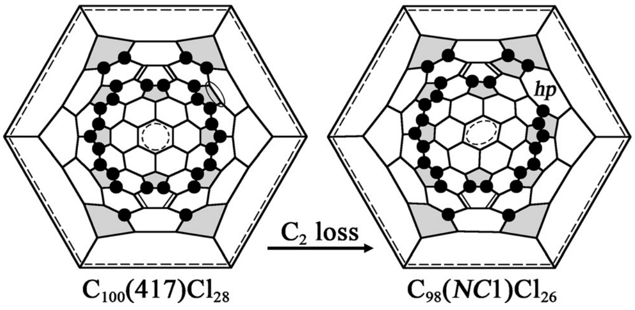

Figure 3. Schlegel diagrams of C_s-$C_{100}(417)Cl_{28}$ and C_1-$C_{98}(NC)Cl_{26}$, with C_1-$C_{98}(NC)Cl_{26}$ being obtained by loss of a C_2 fragment from C_s-$C_{100}(417)Cl_{28}$. Black circles denote the positions of Cl atoms. Delocalized aromatic substructures and butadiene-like fragments are marked. The C−C bond to be removed from $C_{100}(417)Cl_{28}$ is marked with a small oval, whereas the created heptagon in $C_{98}(NC)Cl_{26}$ is indicated by *hp*.

In the second crystal structure, there are two different molecules, $C_{100}(417)Cl_{28}$ and $C_{98}(NC)Cl_{26}$ (Figure 1 f), in the same crystallographic site with 0.471/0.529 occupancies. A comparison of Schlegel diagrams for the two structures demonstrates clearly that the chloride of C_{98} with a heptagon in the carbon cage originates from $C_{100}(417)Cl_{28}$ by the loss of a 5:6 C−C bond (Figure 3). This type of C_2 loss is denoted as type C2L2 in the topological classification of skeletal transformations in fullerenes (presented in Ref. [11b]). A similar type of cage shrinkage was observed previously in isomers of C_{96} fullerene.[13] Since C_2 losses are generally associated with chlorinated C−C bonds, it can be assumed that two Cl atoms migrate to the C−C bond (in the same pentagon) to be removed. Importantly, two pentagon–pentagon fusions in the transformed cage are chlorinated in the resulting $C_{98}(NC)Cl_{26}$, substantially contributing to its enhanced stability.

Both C_1-$C_{100}(NC)Cl_{18}$ and C_1-$C_{100}(NC)Cl_{22}$ molecules (Figure 1 c) were found in the same crystal structure. They both contain the same nonclassical C_{100} cage with one heptagon, whereas the chlorination patterns contain 17 common attachment positions including one THJ (Figure 4). There are three and four isolated and nearly isolated C=C bonds on the carbon cage of $C_{100}(NC)Cl_{18}$ and $C_{100}(NC)Cl_{22}$, whereas the number of isolated and nearly isolated benzenoid rings is three and five, respectively.

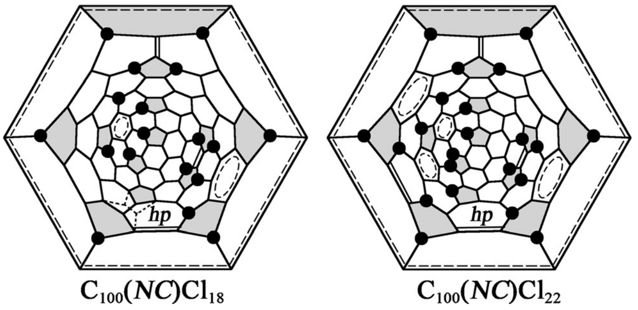

Figure 4. Schlegel diagrams of C_s-$C_{100}(NC)Cl_{18/22}$ with nonclassical carbon cages. Black circles denote the positions of Cl atoms. Isolated aromatic substructures and C=C bonds as well as positions of heptagons (*hp*) are shown. The location of SWR2 in the suggested transformation starting from IPR isomer $C_{100}(382)$ is indicated by dotted lines on the Schlegel diagram of $C_{100}(NC)Cl_{18}$.

The most intriguing question arises about the origin of the $C_{100}(NC)$ cage of both chloro derivatives. A transformation from even higher fullerenes should be excluded because the starting fullerene mixture contained no fullerene beyond C_{100} (see Figure S2). Topologically, two IPR C_{100} cages, $C_{100}(382)$ or $C_{100}(344)$, can be converted into $C_{100}(NC)$ by a single Stone–Wales rearrangement of the type SWR2[11b] (that is, a rotation of a 6:6 C−C bond which connects a pentagon with a hexagon) as shown in Figure 4. From two possible starting IPR cages, we choose isomer $C_{100}(382)$ because its relative formation energy is circa 13 kJ mol^{-1} lower than that of $C_{100}(344)$.[9b] Indeed, according to the estimations of relative abundance in the equilibrium mixture of C_{100} fullerenes, at temperatures above 1500 K a content of $C_{100}(382)$ of several percent is achieved.[9b]

A serious problem of considering SWR2 as a possible formation mechanism of $C_{100}(NC)$ from IPR $C_{100}(382)$ or $C_{100}(344)$ is the lack of an obvious driving force for both transformations seeing as the final cage does not contain fused pentagons. Previously, SWR2 was suggested to occur at the formation of $C_{96}(NC3)Cl_{20}$, accompanied by the formation of chlorinated edges of fused pentagons as the main driving force for the transformation.[11] Therefore, one more option should be considered, specifically that the nonclassical C_{100}-(NC) could be present as such in the starting fullerene mixture used for chlorination. In fact, this isomer is only 21 kJ mol^{-1} less stable than $C_{100}(449)$ according to our DFT calculations,[14] so its presence in the fullerene soot cannot be ruled out. Nonclassical pristine fullerenes have never been found experimentally in the fullerene soot though their role in the fullerene synthesis has been widely discussed in the literature.[15] However, the recently reported endohedral metallofullerene $LaSc_2N@C_{80}$ contains one heptagon in the C_{80} cage.[16]

In summary, we successfully identified several new isomers of giant fullerenes, including C_2-C_{100}(18), C_1-C_{100}(425), and C_{2v}-C_{100}(417), significantly enlarging the number of experimentally confirmed isomers of pristine C_{100} fullerene. Noticeably, the stability of the established isomers of C_{100} varies considerably. Both C_{100}(18) and C_{100}(425) are isomers of high relative stability, whereas isomer C_{100}(417,) as well as the previously reported C_{100}(1), have very low relative stabilities according to theoretical calculations. Remarkably, the presence of the most stable isomer C_{100}(449) still remains unproven. Although the existence of the moderately stable isomer C_{100}(382) has been tentatively proposed, an alternative nonclassical isomer of C_{100} cannot be excluded. However, the question concerning the presence of nonclassical fullerenes in the fullerene soot requires further theoretical work and experimental confirmation which will constitute the next task in our studies.

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[17] CCDC 1443372 (C_{100}(18)Cl_{28}), 1443373 (C_{100}(18)Cl_{30}), 1443374 (C_{100}(425)Cl_{22}-I), 1443375 (C_{100}(425)Cl_{22}-II), 1443376 (C_{100}(417)Cl_{28}), 1443377 ($C_{100}Cl_{28}/C_{98}Cl_{26}$), and 1443378 ($C_{100}$-(*NC*)$Cl_{18/22}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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