Fullerenes

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Synthesis of Long-Sought C_{66} with Exohedral Stabilization**

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Dedicated to Professor Lan-Sun Zheng on the occasion of his 60th birthday

Abstract: *Previously reported fused-pentagon fullerenes stabilized by exohedral derivatization do not share the same cage with those stabilized by endohedral encapsulation. Herein we report the crystallographic identification of* $^{\#4348}C_{66}Cl_{10}$*, which has the same cage as that of previously reported* $Sc_2@C_{66}$*. According to the geometrical data of* $^{\#4348}C_{66}Cl_{10}$*, both strain relief (at the fused pentagons) and local aromaticity (on the remaining* sp^2*-hybrided carbon framework) contribute to the exohedral stabilization of this long-sought 66 carbon atom cage.*

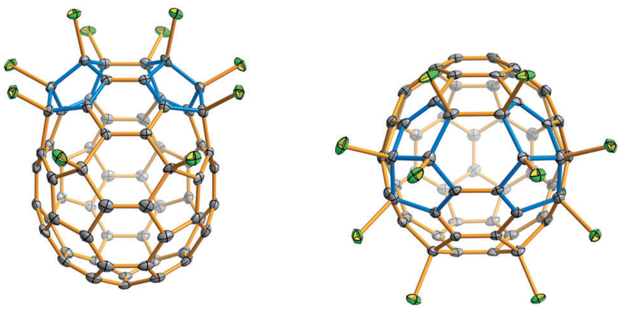

Figure 1. Side (left) and top (right) views of $^{\#4348}C_{66}Cl_{10}$ as ORTEP drawings with thermal ellipsoids at the 50% probability level. The fused pentagons are highlighted in blue.

As an all-carbon cage typically containing a number of hexagons and exactly 12 pentagons, fullerene has numerous isomers.[1,2] Most of them, however, have some of the 12 pentagons fused and are thus elusive according to the well-known isolated pentagon rule (IPR).[3] The labile fused-pentagon fullerenes, however, can be stabilized by exohedral derivatization on the basis of principles of “strain relief” and “local aromaticity”, or by endohedral encapsulation based on electron transfer from *endo* atoms or clusters to the fullerene cage and matching geometries and electronic properties of the involved fullerenes and endoclusters.[4] To date, about 30 fused-pentagon fullerenes, out of thousands geometrically possible all-carbon cages, have been stabilized either endo- or exohedrally.[4] However, previously reported non-IPR fullerenes stabilized by exohedral derivatization do not share the same cage with those stabilized by endohedral encapsulation. Similarly, all known endofullerenes have cages different from the empty fullerenes synthesized so far,[5] thus leading to deeper understanding about available endofullerenes primarily stabilized by electronic transfer from *endo* atoms or clusters to fullerene cages.[6] The gap between endohedral encapsulation and exohedral derivatization should be considered for better understanding of the mechanisms responsible for stabilizing non-IPR fullerenes. Herein, we describe the stabilization of C_{66} (#4348, as specified by the Fowler–Manolopoulos spiral code[2]) by exohedral chlorination (Figure 1) to give the first non-IPR fullerene synthesizable in an exohedral form that corresponds to a previously identified fullerene stabilized by endohedral encapsulation: $Sc_2@C_{66}$ reported by Shinohara and co-workers in 2000.[7] Note that the present case is different from that of previously reported $La@C_{72}(C_6H_3Cl_2)$,[8] for which both an *endo* atom (La) and an *exo* group ($C_6H_3Cl_2$) were simultaneously linked to an individual fullerene cage (C_{72}).

X-ray crystallography revealed two C_s-symmetric $^{\#4348}C_{66}Cl_{10}$ molecules and two cocrystallized CS_2 molecules in the asymmetric unit.[9] The $^{\#4348}C_{66}$ cage with C_{2v} symmetry contains two pairs of fused pentagons (Figure 1), and is thus exactly the same as the parent cage of the previously reported endofullerene $Sc_2@C_{66}$.[7]

Unlike endofullerene $Sc_2@C_{66}$, in which the non-IPR cage is stabilized mainly by electron transfer from *endo* atoms (Sc_2) to the fullerene cage (C_{66}),[7] as expected, the C_{66} chloride releases its strain at the pentagon fusion sites by bonding with external chlorine atoms. An additional six chlorine atoms are bonded at the sites of pentagon–hexagon–hexagon vertices to divide the $^{\#4348}C_{66}Cl_{10}$ molecule into a hemispherical C_{50} fragment and a C_6 ring fragment with sp^2 hybridization (see the yellow portions of the molecule in Figure 2). The C_6 unit has smaller pyramidalization angles (θ_p:[10] 5.1, 3.2, 4.1, 4.8, 4.8, 4.7°) and balanced bond lengths (1.367–1.408 Å), thus clearly showing a geometric structure comparable with that of aromatic benzene. Interestingly, the hemispherical C_{50} fragment is exactly the end-cap framework of a [5,5] carbon

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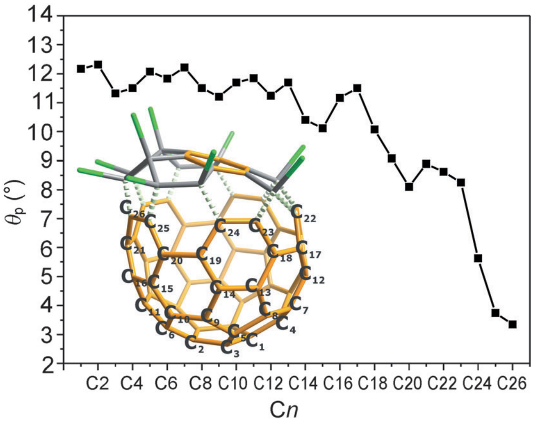

Figure 2. Pyramidalization angles (θ_p) of the carbon atoms of the C_{50} fragment from the bottom to the rim at the top in the top view. Carbon atoms C*n* ($n = 1$–26) are labeled in the structure, in which the sp^2-hybrided C_6 and C_{50} fragments are highlighted in yellow. A top view showing the mirror symmetry plane of the C_{50} fragment of the chlorofullerene with the corresponding carbon-atom numbering is also presented in Figure S1 of the Supporting Information.

nanotube with elegant C_{5v} symmetry. Among the alternative C−C/C=C bonds in the C_{50} framework, the C−C bonds in pentagons have lengths of 1.415–1.499 Å, and the C=C bonds in hexagons have lengths in the range from 1.366 to 1.409 Å. The pyramidalization angles of carbon atoms at the opening rim of the cap-like C_{50} fragment are significantly smaller than those at the bottom end. Figure 2 shows the pyramidalization angles as a function of the carbon-atom position (in the side view), from the bottom end to the opening rim. It is clear that the exohedral chlorination influences the distribution of the pyramidalization angles of the remaining sp^2-hybrided carbon atoms. The pyramidalization angles of 35 carbon atoms in the C_{50} fragment are smaller those in I_h-symmetric C_{60} ($\theta_p = 11.6°$),[11] and some of them are as small as 3–4°. The significant reduction of the pyramidalization angles in the C_{50} fragment indicates that the exohedral chlorination contributes to strain relief not only in the pentagon–pentagon fusions but also in the remaining sp^2-hybrided C_{50} fragment, and further aids the stabilization of the whole cage.

Interestingly, the distribution patterns of C−C/C=C bonds and pyramidalization angles in the hemispherical C_{50} fragment are consistent with those of $C_{50}H_{10}$, which was synthesized by organic chemical methods by Scott et al.[12] (see Figures S2 and S3 in the Supporting Information). Scrutiny of the crystallographic geometrics of both C_{50} frameworks indicated that the pyramidalization angles of the C_{50} fragment are slightly bigger than those of $C_{50}H_{10}$ (see Figure S3), and the diameter of the opening rim of the C_{50} fragment, at 6.6 Å, is about 0.5 Å smaller than that of $C_{50}H_{10}$ containing a carbon disulfide molecule (see the Supporting Information).

The ground-breaking synthesis of $Sc_2@C_{66}$ as well as $Sc_3N@C_{68}$[13] in a carbon arc was a milestone in experimental studies on non-IPR fullerenes. The structural determination of $Sc_2@C_{66}$, however, has suffered from lack of crystallographic data in the past decade. In the initial report by Shinohara and co-workers,[7] ^{13}C NMR spectroscopic and synchrotron radiation powder data suggested that $Sc_2@C_{66}$ should have a Sc dimer encapsulated in $^{\#4348}C_{66}$ with two pairs of fused pentagons. However, density functional calculations by Kobayashi and Nagase[14] revealed that $Sc_2@^{\#4348}C_{66}$ disobeyed an energy minimum, and that instead, isomeric $Sc_2@^{\#4059}C_{66}$ with two triple sequentially fused pentagons was the most probable candidate in view of the available evidence. Owing to this controversy, more detailed structural analyses of $Sc_2@C_{66}$, still based on synchrotron X-ray power diffraction experiments and theoretical computation, were performed by Takata et al.,[15] who established that $^{\#4348}C_{66}$ had the best reliability factor and thus could be the best fitting C_{66} isomer among numerous isomers of 66 carbon atom fullerenes with C_{2v} symmetry. Clearly, it is essential to determine the crystallographic structure of the C_{66} isomer (especially in the form of $Sc_2@C_{66}$) to quell this long-standing controversy.

Long-sought C_{66}, however, is elusive as a result of its violation of the IPR. According to equilibrium statistical thermodynamic analysis,[16] the relative concentration of $^{\#4348}C_{66}$ increases with temperature and reaches 30 % among the family of C_{66} isomers at approximately 2000 K. In

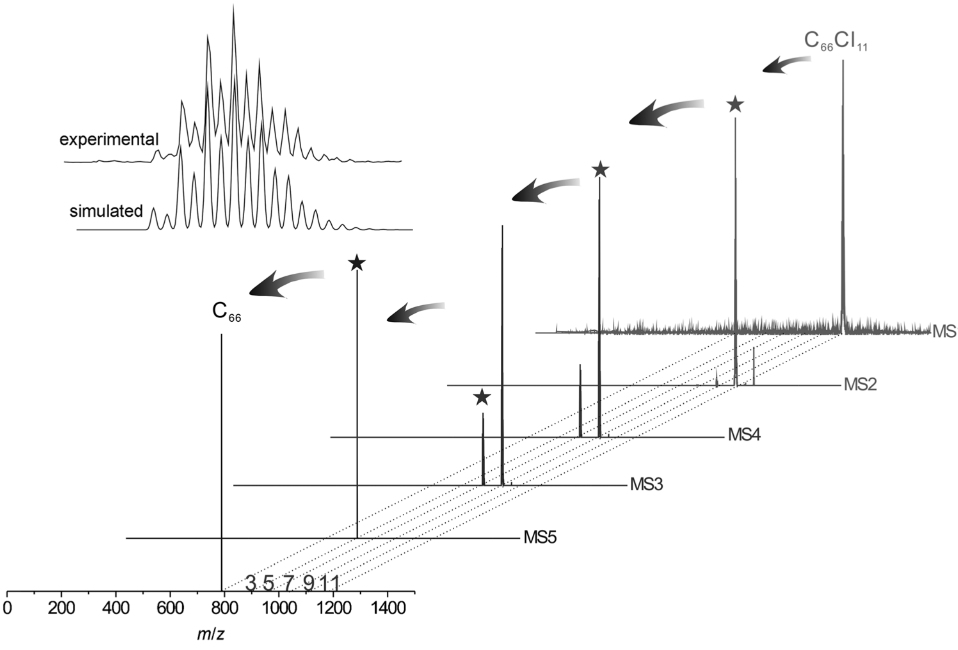

Figure 3. Multistage mass spectra (MS^n, $n = 1$–5). The arrows indicate the dechlorination of $C_{66}Cl_x$ (x is indicated on the bottom line, and the $C_{66}Cl_x$ peaks marked by stars are the mother ions for the next stage of fragmentation). The insets are the experimental and simulated mass distributions of $C_{66}Cl_{11}$.

a Krätschmer–Huffman graphite-arc-discharge process involving chlorine,[17] our ^{13}C-labeling experiments established the growth of pristine fullerenes in the arc zone at 2000–2500 K and their subsequent capture/stabilization by chlorination beyond the arc zone.[18] Therefore, the capture of $^{\#4348}C_{66}$ as a chlorofullerene is reasonable in the present synthesis in a carbon arc in the presence of carbon tetrachloride.

Our mass spectrometric evidence supports the specificity of $^{\#4348}C_{66}$. For example, the molecular ions of $^{\#4348}C_{66}Cl_{10}$ are missing in the mass spectra of the purified $^{\#4348}C_{66}Cl_{10}$ (Figure 3). Instead, the dominant isotopic pattern of the peak at m/z 1182.7 is a good match with the simulated $C_{66}Cl_{11}$ anion ($C_{66}Cl_{10}$+Cl^{-1}). The addition of a chlorine anion in the mass spectrum is rarely seen for other chlorofullerenes[19] and implies that $^{\#4348}C_{66}Cl_{10}$ shows electrophilic properties, which may be critical for its stabilization by exohedral derivatization and its accessibility by endohedral encapsulation. However, further study is necessary to understand the implicit mass spectra.

Progressive dechlorination in the multistage mass spectrometric experiment showed a regular 1,2- or 1,4-elimination of chlorine atoms.[20] $^{\#4348}C_{66}Cl_{10}$ was dissociated into $C_{66}Cl_x$ ($x = 9$, 7, 5, 3, 1), and a 66 carbon atom cluster eventually resulted. It was hard to further fragment the C_{66} anion under the mass spectrometric conditions, thus indicating that pristine $^{\#4348}C_{66}$ has a nonnegligible lifetime in the gas phase and is available for capture by chemical manipulation in the solid state.[21]

In conclusion, the present study verifies that long-sought $^{\#4348}C_{66}$ exists and is obtainable by exohedral chlorination in a carbon arc. The geometric structure of $^{\#4348}C_{66}Cl_{10}$, as identified by crystallographic data, indicates that the exohedral stabilization of $^{\#4348}C_{66}$ is attributable to both the relief of strain on the two pairs of fused pentagons and the retention of local aromaticity on the hemispherical C_{50} and benzene-like C_6 fragments. Mass spectrometric evidence supports the specificity of $^{\#4348}C_{66}$, but the detailed mechanism remains to be explored. These results may stimulate future theoretical and experimental studies into the mechanism responsible for the formation of such non-IPR fullerenes stabilized by both endo- and exohedral methods.

Experimental Section

Pure $^{\#4348}C_{66}Cl_{10}$ was separated from a toluene extract of the fullerene-containing soot generated by graphite-arc discharge under CCl_4 (0.0395 atm) and helium (0.1974 atm; see Figure S4 for the detailed chromatograms).[17] Mass spectra were acquired on a Bruker Esquire HCT mass spectrometer with an ion source of atmospheric pressure chemical ionization (APCI) in the negative-ion mode. Single crystals of $^{\#4348}C_{66}Cl_{10}$ were obtained by the evaporation of a solution in carbon disulfide. X-ray diffraction data were collected at 173 K on an Agilent SuperNova X-ray single-crystal diffractometer with a $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å) microfocus X-ray source. The data were processed by using the software CrysAlis^{Pro}.[22] The structure was solved and refined by using full-matrix least-squares based on F^2 with the programs SHELXS-97 and SHELXL-97[23] within OLEX2[24].

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