Chlorinated Fullerenes

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Chlorination of C_{86} to $C_{84}Cl_{32}$ with Nonclassical Heptagon-Containing Fullerene Cage Formed by Cage Shrinkage**

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Interconversion of fullerene isomers is thought to play an important role in the course of fullerene synthesis by arc-discharge processes.[1,2] Key steps of such transformations in closed 3D carbon cages are believed to include loss or insertion of C_2 units and Stone–Wales rearrangements, that is, 90° rotations of the C_2 units within the cage.[2] However, direct experimental evidence of fullerene cage transformations are quite scarce. For pristine carbon cages, it was observed that some higher fullerenes (C_{76}, C_{78}, C_{84}) may degrade to C_{60} and C_{70} on heating above 1000 °C.[3] More versatile, albeit still very limited, means of cage transformation are provided by chemical reactions. For instance, a multistep organic protocol yields a derivative of C_{62} from C_{60} as a result of cage expansion.[4] On the contrary, cage shrinkage can be achieved by fluorination of C_{60} giving C_{58} fluorides as isolable byproducts.[5] Recently, we found that chlorination of C_{76} with $SbCl_5$ provides an environment suitable for initiating Stone–Wales rearrangements: the D_2-C_{76} isomer, which fulfils the isolated-pentagon rule (IPR) was surprisingly transformed into $C_{76}Cl_{24}$ with a non-IPR cage containing five pairs of fused pentagons.[6]

Whereas most fullerene cages comprise exclusively pentagons and hexagons, some other, nonclassical fullerenes may contain other polygons. The role of heptagons in fullerene chemistry has been widely discussed.[1,7] In accordance with Euler's theorem, introduction of a heptagon instantly causes an additional, thirteenth pentagon to emerge (if only five-, six-, and seven-membered rings are considered). Some highly strained lower fullerenes were theoretically predicted to have a heptagon-containing lowest energy isomer.[7] Theoretical calculations also revealed that one-heptagon structures may play an important role in fullerene growth mechanisms.[7c] However, experimental observation of heptagons in fullerenes is limited to the case of $C_{58}F_{18}$ and $C_{58}F_{17}(CF_3)$ as the products of a destructive side pathway of fluorination of C_{60}, for which the probable structures were only deduced from ^{19}F NMR spectra.[5] Herein we report the first direct X-ray structural evidence of heptagon formation in a fullerene cage upon C_2 loss under relatively mild conditions: chlorination of C_{86} to $C_{84}Cl_{32}$, a derivative with a shrunken carbon cage containing a heptagon.

C_{86} fullerene was separated from the toluene extract of fullerene soot by three-stage HPLC. In the first stage, the C_{86} fraction contaminated with C_{84} was collected with retention times ranging from 21 to 23 min by using a Cosmosil preparative 5PYE column (20 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as eluent (15.0 mL min^{-1} flow rate, monitored at 320 nm). In the second and third stages, this fraction was subjected to recycling HPLC with the same 5PYE column and toluene as eluent, and collecting the subfraction after five and four cycles, respectively, resulted in the isolation of pure C_{86}, as confirmed by MALDI-TOF MS analysis (see Supporting Information). The UV/Vis/NIR spectrum of the isolated C_{86} fullerene in toluene solution, recorded on a UV-Vis-NIR 3600 spectrometer (Shimadzu, Japan), and showed close coincidence with that reported in reference [8] for isomerically pure C_{86} (isomer 16) and thus indicated prevailing content of this isomer.

To carry out the chlorination, about 0.2 mg of C_{86} was placed in a glass ampoule and 0.3 mL of VCl_4 was added. The ampoule was cooled, evacuated, and sealed. Heating the ampoule at 250 °C for 4–5 d gave yellow crystals, which were isolated by discarding VCl_4 and further washing with water. Close examination revealed crystals of two different shapes (hexagonal and rectangular plates). X-ray diffraction with synchrotron radiation demonstrated that the hexagonal plates represent $C_{86}(16)Cl_{28}$, while the rectangular crystals contain $C_{84}Cl_{32}$ with a nonclassical heptagon-containing cage.[9]

The structure of C_s-$C_{86}(16)Cl_{28}$ provides the first confirmation of the cage connectivity in C_s-$C_{86}(16)$. According to an earlier ^{13}C NMR study on C_{86}, two isomers with C_s and C_2 molecular symmetries form in the mixtures produced by the conventional arc-discharge process.[10] Theoretical calculations of relative stability and NMR patterns of all 19 IPR C_{86} cages suggest that these isomers are C_s-$C_{86}(16)$ and C_2-$C_{86}(17)$,[11] and XRD confirmation of the latter cage was obtained recently.[12]

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The C_s-$C_{86}(16)Cl_{28}$ molecule retains the mirror symmetry of the C_s-C_{86} (16) cage (Figure 1). There are three long continuous chains of chlorinated carbon atoms isolating two C=C bonds and three large aromatic systems represented by pyrene-, anthracene-, and corranulene-like fragments. Such a combination of long chains of *ortho* Cl···Cl contacts and isolated aromatic systems is a common feature of higher fullerene chlorides like $C_{60}Cl_{28}$, $C_{60}Cl_{30}$, $C_{70}Cl_{28}$, $C_{78}Cl_{30}$, and $C_{90}Cl_{32}$.[13]

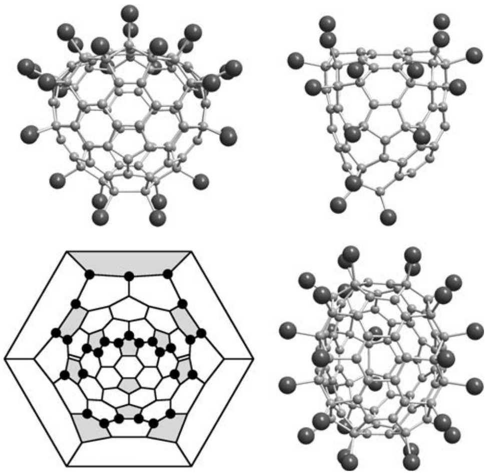

Figure 1. Three projections of the C_s-$C_{86}(16)Cl_{28}$ molecule and its Schlegel diagram. Cage pentagons are shaded gray.

It is, however, the second product, $C_{84}Cl_{32}$, which is more interesting, as it has a heptagon in its carbon cage (Figure 2). Accordingly, there are 13 pentagons in the C_{84} cage, all of which are isolated from each other. The molecular structure of $C_{84}Cl_{32}$ is closely related to that of C_s-$C_{86}(16)Cl_{28}$. As shown in Figure 2, formation of the C_{84} cage only requires withdrawal of a 5:6 C_2 unit from the corranulene fragment of C_s-$C_{86}(16)Cl_{28}$. The general principles of the arrangement of the chlorine shell are also retained, as well as the aromatic substructures on the carbon cage: apart from C_2 abstraction, only two chlorine atoms need to be relocated and four more added to transform C_s-$C_{86}(16)Cl_{28}$ into $C_{84}Cl_{32}$. Most affected by these changes is the original 24-electron bis-ethenylated corranulene fragment of C_s-$C_{86}(16)Cl_{28}$, which transforms into the more aromatic and planar 18-electron system with one heptagon, two pentagons, and two hexagons.

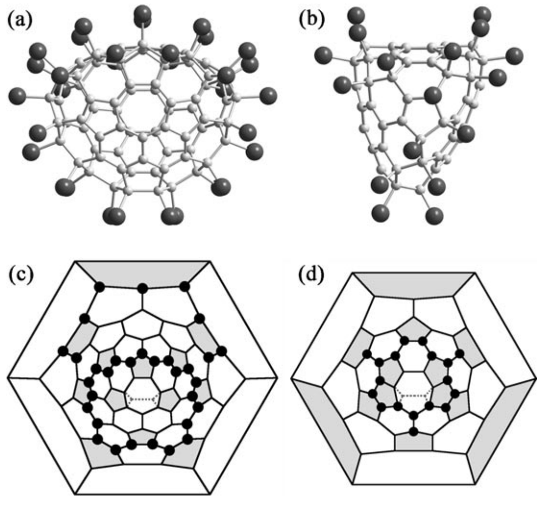

Figure 2. Top and side projections of the $C_{84}Cl_{32}$ molecule (a, b), its Schlegel diagram (c), and Schlegel diagram of $C_{58}F_{18}$ suggested in ref. [5] (d). Cage pentagons are shown in gray. Dotted lines indicate C–C bonds abstracted from the parent C_s-C_{86} (16) and I_h-C_{60} cages.

In reference [5], which is the only report on C_2 loss under chemically accessible and mostly nondestructive conditions, a somewhat similar case of heptagon formation was postulated on the basis of ^{19}F NMR data: the C_{58} cages of $C_{58}F_{18}$ and $C_{58}F_{17}(CF_3)$ were suggested to contain a heptagon flanked by two sets of three sequentially fused pentagons (Figure 2).[5] The synthetic conditions in reference [5] were quite harsh (550 °C), additionally aggravated by the high exothermicity of fluorination. It is not surprising that fluorination under such conditions brought the carbon cage to the edge of destruction and thus resulted in a loss of two carbon atoms even from a highly sterically favorable benzenoid fragment of $C_{60}F_{18}$. This was believed to occur via sequential fluorine addition to a C–C single bond and an adjacent C=C bond, followed by loss of $:CF_2$ carbene fragments.[5] The transformation of C_s-$C_{86}(16)Cl_{28}$ into $C_{84}Cl_{32}$ reported here differs from the case in ref. [5] in much milder temperature conditions and lower heats of chlorination. Its driving force, inaccessible for the C_{58} case, seems to be rather of a "cage-improving" nature, that is, formation of more aromatic and planar $4n+2$ 18-electron fragment. As highly endothermic elimination of $:CCl_2$ has not been observed before, even in higher temperature chlorinations of other carbon cages, we discuss alternative mechanisms of C_2 loss on the basis of the DFT calculations.[14]

Comparison of the DFT C–Cl bond energy in $C_{86}(16)Cl_{28}$ and the hypothetical $C_{86}(16)Cl_{32}$ analogue of $C_{84}Cl_{32}$ reveals that the average value in $C_{86}(16)Cl_{32}$ decreases by 4.2 kJ mol^{-1}, which translates into a more significant value of 33.6 kJ mol^{-1} for the four extra chlorine atoms (see Supporting Information). On the contrary, in $C_{84}Cl_{32}$ the average C–Cl bond energy is 1.8 kJ mol^{-1} higher than in $C_{86}Cl_{28}$, and both values almost coincide with those observed in other higher chlorides of IPR fullerenes like $C_{60}Cl_{30}$.[13b] Thus, it may be more likely that C_2 elimination takes place in $C_{86}Cl_{28}$ preceding further chlorination. On the other hand, our calculations demonstrate that the possible pathways discussed below have somewhat lower activation energies in the case of $C_{86}Cl_{32}$. Anyway, rationalization of the detailed pathway of this elimination appears to be very complicated.

Removal of a bare C_2 fragment is hugely endothermic, and this effect can be even overestimated in calculations.[15] Apparently, C_2 must leave as a "good" leaving group, that is, chlorinated, complexed by vanadium chloride (e.g., VCl_3), or both (to our knowledge, such "assisted" elimination from fullerenes has not been yet addressed in the literature). Still, in agreement with the well-known high stability of fullerene cages, we found no pathway characterized by an activation barrier below 3.4 eV without involving vanadium chlorides. Therefore, we believe that C_2 abstraction is a vanadium-catalyzed process. Unfortunately, consideration of chlorofullerene–vanadium chloride complexes posed its own problems stemming from the gas-phase nature of the calculations, since the high VCl_3–Cl binding energy in the gas phase (ca. 3 eV[16]) far exceeds the C–Cl bond strengths in chlorofullerenes and thus makes it difficult to avoid chlorine withdrawal by vanadium.

The two most obvious possibilities that can be conceived without implicating vanadium, symmetric and asymmetric, are shown in Figure 3. Their quantitative discussion below is based on the hypothetical $C_{86}Cl_{34}$ (Figure S4 in Supporting Information). We start from intermediate compound **a**, in which two additional chlorine atoms are attached to the C_2 unit to be removed; we do not consider radical structures with only one chlorine atom because of its very low binding energy, whereas two added chlorine atoms in a closed-shell molecule stabilize each other. The DFT calculations show that structure **b1** is a transition state on the way from **a** to **b2** with an activation barrier of 3.4 eV, while **b2** is less stable than **a** by 0.7 eV. Species **b1** is quite asymmetric, and some of the indicated bonds are considerably elongated (Figure S6 in Supporting Information). Elimination of C_2Cl_2 from **b2** has a barrier of 1.2 eV and is exothermic by 0.4 eV. Thus, the overall process is not energetically favorable and must be favored by entropic factors. Chlorination of **b2** to **b3** and subsequent abstraction of C_2Cl_4 seems more preferable: the high heat of chlorination stabilizes the C_2Cl_4 bridge, and its abstraction requires only 0.4 eV of activation energy and is exothermic by 2.5 eV.

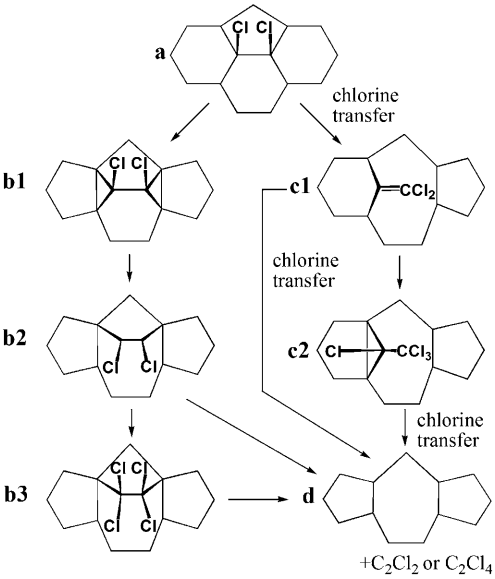

Figure 3. Schematic representation of conceivable pathways for removal of a C_2 unit from the C_{86} cage.

The alternative asymmetrical possibility involves a more stable intermediate **c1**, which lies only 0.2 eV higher in energy than **a**. However, this advantage is likely to be outweighed by the higher activation energy (≥ 3.5 eV) of the transformations that yield **c1**. Furthermore, ultimate abstraction of C_2 would require transfer of chlorine atoms, which seems to be less easy than in our recent study of rearrangements in $C_{76}Cl_{24}$ mediated by $SbCl_5$.[6] Therefore, we stress again that vanadium is likely to be heavily involved in the C_2-abstraction process, whatever its actual pathway is.

In conclusion, the chemistry of fullerenes may get a second wind with the discovery of a simple chemical approach to transformations of carbon cages, which was thought unlikely to exist. The Stone–Wales rearrangements found in C_{76} are now followed by C_2 loss from C_{86}. Most importantly, both cases provide highly unconventional fullerene structures with multiple pentagon adjacency (C_{76}) or heptagon formation (C_{86}), which are not present in pristine fullerene soot. Though such phenomena may prove to be highly cage specific, this research is still in its infancy, and therefore the search for a chlorination protocol to expand the cage-transformation processes to further fullerene isomers is an important task.

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[9] Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF at the Free University of Berlin, Germany) with a MAR225 CCD detector at $\lambda = 0.9050$ Å. Structures were solved by direct methods with SHELXS and refined with SHELXL. $C_{86}(16)Cl_{28}$: monoclinic, $P2_1/c$, $a = 20.941(2)$, $b = 12.853(1)$, $c = 29.303(3)$ Å, $\beta = 110.237(9)°$, $V = 7400(1)$ Å^3, $Z = 4$. Anisotropic refinement with 14644 reflections and 1027 parameters to $wR_2 = 0.393$ and $R_1 = 0.158$ for 8298 reflections with $I > 2\sigma(I)$. $C_{84}Cl_{32}\cdot 1.73\,Cl_2$: triclinic, $P\bar{1}$, $a = 14.780(1)$, $b = 15.175(1)$, $c = 18.347(1)$ Å, $\alpha = 68.029(4)$, $\beta = 78.323(4)$, $\gamma = 79{,}463(5)°$, $V = 3711.0(4)$ Å^3, $Z = 2$. Anisotropic refinement with 13386 reflections and 1162 parameters yielded a conventional $R_1 = 0.069$ for 8546 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.179$ for all reflections. Cl_2 molecules of solvation are strongly disordered over several positions. CCDC 764243 and 764244 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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