Halogenated Fullerenes

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Fusing Pentagons in a Fullerene Cage by Chlorination: IPR D_2-C_{76} Rearranges into non-IPR $C_{76}Cl_{24}$**

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As is well known, fullerenes obtained by conventional arc-discharge synthesis obey the isolated pentagon rule (IPR).[1,2] Unless fullerene molecules are directly subjected to "fullerene surgery",[3] exohedral functionalization does not affect the connectivity of their carbon networks. Non-IPR fullerene isomers have been available through appropriate modifications of the arc-discharge methodology to synthesize an already chemically derivatized molecule in which the derivatization stabilizes the pentagon–pentagon junctions. In particular, non-IPR cages are quite common in endohedral metallofullerenes, as encapsulated metal atoms are likely to stabilize the fused pentagon fragments by charge-transfer binding to them.[4] More recently, a number of unconventional exohedral fullerene derivatives, including $C_{50}Cl_{10}$,[5,6] $C_{56}Cl_{10}$,[7] $C_{66}H_4$,[8] $C_{68}Cl_4$,[6] and non-IPR $C_{60}Cl_8$ and $C_{60}Cl_{12}$,[9] have been obtained by means of an arc-discharge process in presence of additives such as CCl_4, Cl_2, and CH_4. Rare examples of more classical chemical approaches to non-IPR fullerenes are indirectly confirmed transformation of dodecahedrane into C_{20}[10] and synthesis of a C_{62} derivative with four-membered cycle in its carbon cage from C_{60}.[11]

Herein we report a new, completely different, and quite unexpected synthesis of a derivatized non-IPR fullerene molecule from a pre-formed IPR fullerene cage. The reaction of D_2-C_{76} (IPR) with $SbCl_5$ affords the chlorinated product $C_{76}Cl_{24}$ with a deeply rearranged, strongly non-IPR carbon cage. The formation of $C_{76}Cl_{24}$ is the first discovered case of IPR to non-IPR rearrangement of a fullerene cage in the course of a chemical reaction.

C_{76} was isolated from fullerene soot by HPLC (10 × 250 mm Buckyprep column, elution with toluene, 4.6 mL min^{-1}, 290 nm). The fraction eluted at 19.1 min contained D_2-C_{76}, as proven by UV/Vis and ^{13}C NMR spectroscopy on the basis of reference data available.[12] D_2-C_{76} (0.2 mg) was treated with excess $SbCl_5$ (0.3 mL) in a sealed glass ampoule at 340 °C for 4–5 days. After subsequent cooling, the ampoule was opened and $SbCl_5$ was washed out by treatment with several portions of concentrated HCl and water. The reaction product contained plate-like orange crystals. Their composition ($C_{76}Cl_{24}$) and crystal structure were determined by single-crystal X-ray diffraction with the use of synchrotron radiation.[13] The same crystals $C_{76}Cl_{24}$ were also obtained, among others, by applying the same chlorination protocol to a higher fullerene mixture (MER Corp.) containing the C_{76}–C_{96} range plus small amounts of C_{60} and C_{70}.

The structurally characterized $C_{76}Cl_{24}$ molecule (Figure 1) appeared to be a chlorinated derivative of a non-IPR, C_2-symmetric isomer 18917 of C_{76} (numbering according to the

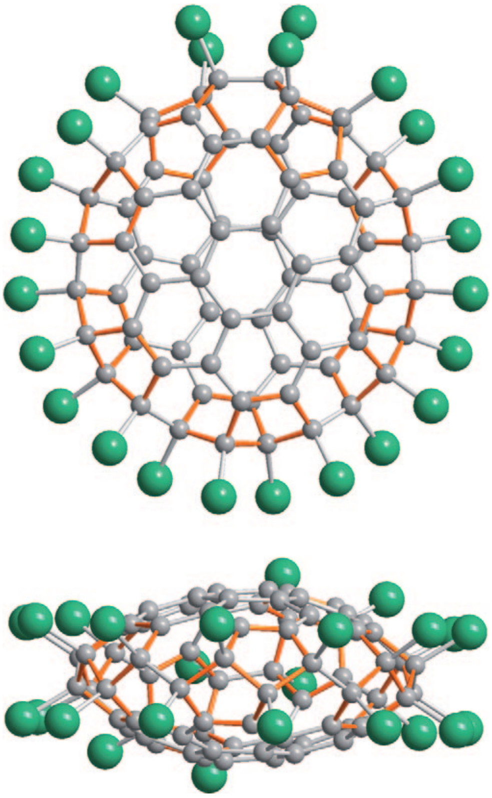

Figure 1. Molecular XRD structure of 18917-$C_{76}Cl_{24}$ presented in two projections with Cl atoms shown as larger green spheres. The pentagons are highlighted in orange.

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spiral algorithm[2]), which contains five pairs of fused pentagons and thus exhibits dramatic structural difference to the starting D_2 IPR cage of C_{76},[12] as illustrated by the Schlegel diagrams in Figure 2. The pristine carbon cage of isomer 18917 exhibits, according to our DFT calculations (see the Supporting Information), a strongly flattened lens-like shape, which results from the concentration of both fused and isolated pentagons in the highly curved equatorial belt that surrounds coronene-like hexagon arrangements in the flattened regions. The XRD structure of $^{\#18917}C_{76}Cl_{24}$ reveals that the chloride has the same C_2 symmetry as pristine $^{\#18917}C_{76}$ but shows even greater degree of cage flattening owing to the addition of all chlorine atoms to the said equatorial belt, including, in particular, all 10 strongly pyramidalized pentagon–pentagon junctions (see Table S1 in the Supporting Information).

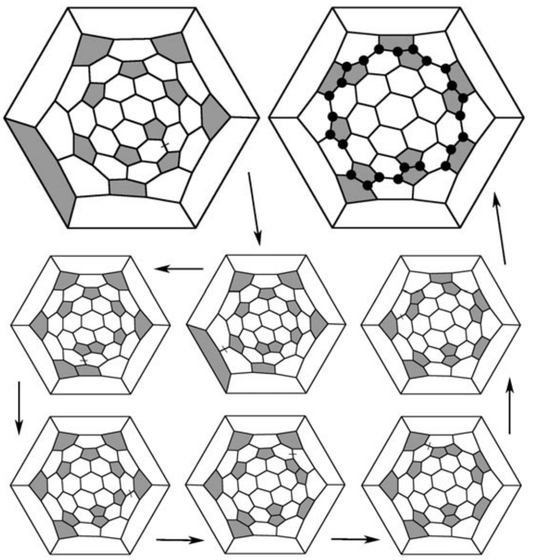


Figure 2. Schlegel diagrams of IPR D_2-19150-C_{76} (top left) and C_2-18917-$C_{76}Cl_{24}$ (top right) as well as Stone–Wales pathway connecting these two carbon cages (pentagons are shown in gray, rotating bonds are marked with dashes).

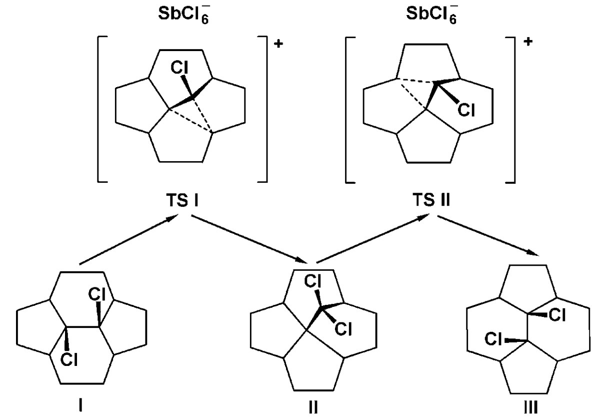
Such a deep transformation of the carbon skeleton under the conditions described can be possible only if it is thermodynamically favorable. In other words, similarly to the above cited cases of arc-discharge synthesis in presence of additives,[5–9] a considerably energetically unfavorable pristine non-IPR carbon cage becomes stabilized by chemical modification. However, whereas arc-discharge syntheses are a sort of black box and usually afford complicated mixtures of compounds, the transformation reported herein involves a known starting molecule that determines the final product.

To analyze the thermodynamic aspects of the formation of $^{\#18917}C_{76}Cl_{24}$, we carried out DFT calculations on pristine and chlorinated C_{76} cages. The pristine $^{\#18917}C_{76}$ fullerene appeared to be as much as 8.1 eV less stable than the IPR D_2 isomer $^{\#19150}C_{76}$. However, chlorination completely inverts this order of stability. As we could not consider all possible isomers of $^{\#19150}C_{76}Cl_{24}$, we reviewed a number of structures that contained, in analogy to $^{\#18917}C_{76}Cl_{24}$, two large conjugated aromatic fragments separated by a belt of chlorinated atoms (the assumption of high stability of such structures was based on the already somewhat flattened shape of $^{\#19150}C_{76}$). It was found that all the said hypothetical isomers of $^{\#19150}C_{76}Cl_{24}$ are at least 4.3 eV less stable than the reported $^{\#18917}C_{76}Cl_{24}$ isomer. If one considers $^{\#19150}C_{76}Cl_{18}$, the recently characterized chloride compound of IPR C_{76},[14] and projects its calculated average C−Cl bond energy to a $C_{76}Cl_{24}$ composition, this energy difference decreases but still exceeds 3.5 eV in favor of the non-IPR structure. Thus, the average binding energy of chlorine in $^{\#18917}C_{76}Cl_{24}$ is much higher than in the known IPR chlorides of C_{60} ($C_{60}Cl_6$, $C_{60}Cl_{24}$, $C_{60}Cl_{30}$—by 0.55–0.6 eV per Cl atom) as well is in $^{\#19150}C_{76}Cl_{18}$ (by ca. 0.5 eV per Cl atom). Interestingly, it is only 0.05 eV lower than in D_{5h}-$C_{50}Cl_{10}$,[6,7] in which all chlorine atoms are attached to pentagon–pentagon junctions.

However, in theory, the discovered isomerization of chlorinated C_{76} is not the only thermodynamically favorable process of such kind. For example, theoretical calculations for non-IPR $C_{60}Cl_8$ predict it to be 1.4 eV lower in energy than the most stable octachloride of I_h-C_{60}.[8] Nevertheless, chlorination of C_{60} with $SbCl_5$ under the similar conditions as reported is known to yield only IPR $C_{60}Cl_{24}$ and $C_{60}Cl_{30}$ molecules.[15] Chlorination of C_{70},[16] C_{78},[17] and C_{90}[18] also leaves the σ networks of their carbon cages intact; the same applies to a different technique of chlorination of C_{76}[14] and C_{80}[19] at lower temperatures. Therefore, one can suppose that the reported rearrangement of chlorinated C_{76}, an apparently multistep process, must be favorable not only globally but also stepwise and, moreover, must be characterized by reasonably low activation energies.

Unfortunately, no intermediate products of chlorination of C_{76} were isolated in our experiment, so there is no evidence with regard to the formation pathway of $^{\#18917}C_{76}Cl_{24}$. Nevertheless, one can hypothesize that the most readily conceivable step of the process in question can be the well known Stone–Wales rearrangement[20] and, in addition, rearrangements of the chlorine shell of the molecule. We have found several pathways that arbitrarily start from the most stable calculated isomers of the IPR $^{\#19150}C_{76}Cl_{24}$ and reaches $^{\#18917}C_{76}Cl_{24}$ through a sequence of exothermic steps including seven Stone–Wales rearrangements shown in Figure 2. The general thermodynamic driving force behind this sequence is not only high binding energy of chlorine to the pentagon–pentagon junctions but also formation of larger conjugated assemblies of hexagons in the initial stages and further advantageous flattening of these planar aromatic substructures in the later steps.

Under the conditions of interest, the migration of chlorine addends has already been demonstrated to be a facile process that enables interconversion of more stable isomers via less stable ones by multiple chlorine shifts.[21] In contrast, DFT calculations of the barrier of Stone–Wales rearrangement in C_{60} yield a value of approximately 6 eV.[22] However, it appears that the presence of chlorine addends and their ability to migrate between the carbon cage sites may lower this value dramatically. In Scheme 1 we suggest a mechanism



Scheme 1. Possible mechanism for the Stone–Wales rearrangement on a chlorinated cage fragment. TS denotes a transition state.

that follows from our DFT survey of possible processes in the fullerene chloride–SbCl$_5$ system. This mechanism is somewhat similar to that suggested for pristine C$_{60}$;[22] however, there is a key difference in chlorine atoms carried by the rotating C$_2$ unit. In absence of chlorine atoms, the analogue of state II in Scheme 1 is, as shown in reference [22], a transition state corresponding to the above mentioned 6 eV barrier. In our case, migration of chlorine atoms makes this state II an intermediate valence-saturated stable structure, whereas the actual transition states are ion pairs in which the migrating chlorine atom joins an SbCl$_5$ molecule to form an SbCl$_6^-$ anion. Our DFT calculations for the last Stone–Wales transformation on the pathway to $^{\#18917}$C$_{76}$Cl$_{24}$ (with chlorine atoms in the precursory structure attached to the same sites as in the final product; see Figure 2) predict state II to be only 0.5 eV above the initial state I, and the activation barriers for transitions of I to II and II to III accordingly decrease to 2.1 and 1.3 eV. Perhaps, the solvation effects may favor the polar transition states even further.

Thus, chlorination manifests itself as a simple but efficient tool for structural transformation of carbon cages. Moreover, chlorine may be the most convenient addend to effect such transformations, as its moderate binding energy provides a good balance between thermal stability and capability of migrating over the fullerene cage. The role of SbCl$_5$ as a medium is also quite important since its molecules may be involved in the said migration.

It has to be pointed out that the molecules such as $^{\#18917}$C$_{76}$ can prove to be more than a point of merely theoretical interest. Our DFT calculations have provided an adiabatic EA value of 3.4 eV for $^{\#18917}$C$_{76}$, which is 0.5 eV higher than in D_2-C$_{76}$; of the same order (3.5 eV) is the adiabatic EA value of the D_{5h}-C$_{50}$ cage with fused pentagons.[23] The calculated EA value of $^{\#18917}$C$_{76}$Cl$_{24}$ itself appears to be of the same order (3.5 eV). Thus, $^{\#18917}$C$_{76}$Cl$_{24}$ combines desirable electron-withdrawing properties with potential capability of further chemical functionalization by substitution of comparatively labile chlorine atoms. Such benefits may give a new impulse to studies of fullerene-based photovoltaic devices and sensors.

To conclude, the discovered IPR to non-IPR fullerene transformation can open novel possibilities in fullerene chemistry and enhance the diversity of available compounds. It is particularly important that this transformation can, in principle, be attempted selectively on any isolated fullerene isomer. However, to rationalize the generality of this rearrangement phenomenon, it would be helpful to obtain experimental insights into its pathway by isolating intermediate compounds.

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