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Skeletal Transformation of Isolated Pentagon Rule (IPR) Fullerene C_{82} into Non-IPR $C_{82}Cl_{28}$ with Notably Low Activation Barriers

Ilya N. Ioffe,*[†] Olga N. Mazaleva,[†] Lev N. Sidorov,[†] Shangfeng Yang,[‡] Tao Wei,[‡] Erhard Kemnitz,[§] and Sergey I. Troyanov*[†]

[†]Chemistry Department, Moscow State University, Leninskie Gory, 119991 Moscow, Russia
[‡]Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China
[§]Institute of Chemistry, Humboldt University of Berlin, Brook-Taylor Strasse 2, 12489 Berlin, Germany

Ⓢ *Supporting Information*

ABSTRACT: A novel case of chlorination-promoted skeletal transformation in higher fullerenes is reported. Chlorination of C_{82} [isolated pentagon rule (IPR) isomer no. 3] with $SbCl_5$ results in two consecutive Stone–Wales rearrangements into non-IPR $C_{82}Cl_{28}$ with one pair of fused pentagons. An extensive theoretical study of the transformation pathways in C_{82} revealed that the thermodynamically favorable rearrangement into non-IPR $C_{82}Cl_{28}$ needs a comparatively low activation energy.

Fullerene chemistry saw extensive development in the past 2 decades and still remains a hot field. However, most research is concerned with exohedral derivatization without affecting the connectivity/topology of the carbon skeleton. The rare exclusions to be mentioned, apart from in situ formation of endohedrally or exohedrally functionalized non-IPR (IPR = isolated pentagon rule) cages[1] or destruction under harsh conditions,[2] encompassed the insertion of functionalized C_2 fragments to form four-membered rings[3] and cage-opening fullerene surgery[4] with a remarkable possibility of reversion.[5] Recently, we discovered a totally new type of cage transformation in fullerenes, namely, chlorination-assisted skeletal transformation. These findings include the thermodynamically driven formation of strong non-IPR $^{\#18917}C_{76}Cl_{24}$ via multistep Stone–Wales (SW) rearrangements[6] and heptagon formations via the abstraction of a C_2 unit.[7] Possible mechanisms of these transformations have been discussed theoretically, but their experimental confirmation/elucidation remains problematic because of diverse experimental complications, in particular, the lack of isolable intermediate compounds. Nevertheless, skeletal transformations in fullerenes are of a great importance, both practically and theoretically, because they open a road to the entirely new chemistry of fullerenes.

Herein, we report a new case of skeletal transformation in higher fullerenes. We present a non-IPR $C_{82}Cl_{28}$ structure that has, unlike $^{\#18917}C_{76}Cl_{24}$, only one pair of fused pentagons. The relative simplicity of the newly discovered transformation allowed for a detailed study of its pathway and driving forces.

A fraction containing mostly C_{84} and ca. 10% of C_{82} was isolated by high-performace liquid chromatography from the fullerene soot obtained from a standard arc-discharge process with undoped graphite rods [see the Supporting Information (SI) for details]. To carry out the chlorination, 2 mg of a C_{82}–C_{84} mixture was placed in a thick-walled glass ampule and 0.4 mL of $SbCl_5$ was added. The ampule was cooled, evacuated, and sealed off. Heating the ampule at 300–350 °C for 30 days gave small yellow-orange crystals, which were isolated after washing $SbCl_5$ with, successively, concentrated HCl, dilute HCl, and water. An X-ray study of the crystals using synchrotron radiation revealed the formation of $C_{82}Cl_{28}$ with a non-IPR carbon cage.[8] Interestingly, no crystalline C_{84} chlorides were obtained.

The new $C_{82}Cl_{28}$ molecule is characterized by the rather unsymmetrical shape of its carbon cage (Figure 1), which contains one pair of fused pentagon and thus constitutes the first available representative of the potentially broad family of empty non-IPR C_{82} fullerenes. Within the set of 39718 IPR and non-IPR isomers, the non-IPR cage of $C_{82}Cl_{28}$ has the number 39173 according to its spiral code.[9] The chlorination pattern of $^{\#39173}C_{82}Cl_{28}$, similar to many other higher chlorides of fullerenes,[10] is based on two long chains of adjacently attached Cl atoms and additionally includes one pair of adjacent addends and six attached more remotely with respect to the others. Chlorination cuts the three-dimensional π system of pristine C_{82} into one pyrene fragment, one vinylpyrene fragment, two isolated benzenoid rings, and three isolated double C–C bonds (Figure 2).

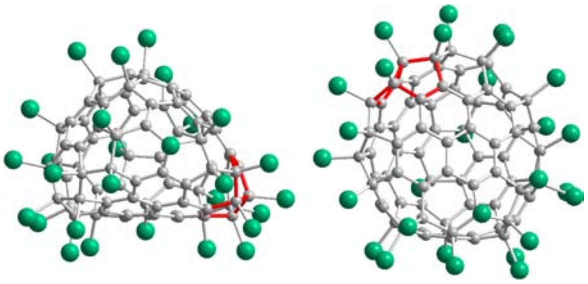

Figure 1. Two projections of the $^{\#39173}C_{82}Cl_{28}$ molecule. Color code: C, gray; Cl, green; fused pentagonal rings, red.

The initial precursor of $^{\#39173}C_{82}Cl_{28}$ is apparent: all previous ^{13}C NMR characterizations of the C_{82} fractions from an arc-

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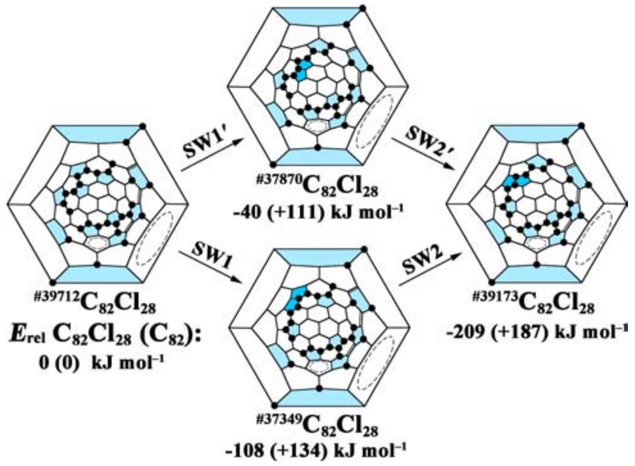

Figure 2. Skeletal transformation of the IPR $^{\#39712}C_{82}Cl_{28}$ into the non-IPR $^{\#39173}C_{82}Cl_{28}$ via two alternative intermediates, $^{\#37870}C_{82}Cl_{28}$ and $^{\#37349}C_{82}Cl_{28}$, a Schlegel diagram presentation. Cage pentagons are filled with blue; benzenoid rings and isolated C=C bonds are also indicated. The relative energy values are given for chlorinated and pristine cages.

discharge procedure reported C_2-symmetric IPR isomer no. 3 ($^{\#39712}C_{82}$ in the full list) as either the only or predominant component.[11] Moreover, theoretical studies pointed to the higher stability of $^{\#39712}C_{82}$ compared to that of the eight other IPR isomers.[12] Besides, it was $^{\#39712}C_{82}$ whose derivatives were found in the recent X-ray diffraction studies of the $C_{82}(CF_3)_n$ (n = 12, 16, and 18) trifluoromethylation products of the same C_{82}−C_{84} mixture.[13] Under a natural assumption that skeletal transformations proceed via SW rearrangements, we found pathways between $^{\#39712}C_{82}$ and $^{\#39173}C_{82}$ of only two permutable SW steps. These two sequences are shown in Figure 2. Depending on the order of the rearrangement steps, the intermediate non-IPR cage can be either #37870 or #37349. These findings made it possible to exclude the potential precursory role of C_{84} via C_2 abstraction because of the lack of comparably close topological relations with our product. According to our density functional theory (PBE[14]/TZ2P) calculations with the use of the *PRIRODA* software,[15] pristine non-IPR cages turn out to be much less stable than the parent $^{\#39712}C_{82}$. The final $^{\#39173}C_{82}$ is 187 kJ mol^{-1} higher, while the two possible intermediate cages can be found in between. This finding clearly suggested that the skeletal transformations cannot occur in pristine $^{\#39712}C_{82}$ but, similar to the $C_{76}Cl_{24}$ case, are driven by chlorination, in particular, by the increase of the C−Cl bond energy at the sites that belong to emerging contacts of fused pentagons. Therefore, to analyze the transformation pathway, one has to find the possible starting chloride of $^{\#39712}C_{82}$ in which the first transformation is triggered.

Unfortunately, there is no evidence regarding the degree of chlorination in the precursory IPR chlorides (possibly different from that of the resulting product), while computational predictions for low-symmetric higher fullerene chlorides are prohibitively expensive. However, there is a key criterion to distinguish between likely and unlikely isomers: the average C−Cl bond energy. This quantity demonstrates very small variations over the whole set of presently available IPR fullerene chlorides and tends to slightly decrease in higher chlorinated molecules. Initially, we considered a hypothetical $^{\#39712}C_{82}Cl_{28}$ with the same chlorination pattern as that in the isolated non-IPR product (Figure 2) and found its calculated average C−Cl bond energy to fall just between those of IPR-$C_{76}Cl_{28}$ and IPR-$C_{76}Cl_{34}$,[6b] within only 2−3 kJ mol^{-1} from both of them from, e.g., IPR-D_{3d}-$C_{60}Cl_{30}$.[16] Because one may further expect the binding energy to slightly decrease with the carbon cage size for steric reasons, our hypothetical $^{\#39712}C_{82}Cl_{28}$ must be among the most stable chlorides of the starting $^{\#39712}C_{82}Cl_{28}$ with appreciable abundance in the high-temperature equilibrium mixture. This justified limiting our consideration to the structures with the same chlorination pattern as that in the $^{\#39173}C_{82}Cl_{28}$. As shown in Figure 2, both alternative pathways are thermodynamically favorable, showing a monotonic decrease in energy. The initial rotation stabilizes the molecule because of energetically favorable attachment of one chlorine addend to an emerging junction of fused pentagons; however, the second site of the junction remains unoccupied at this stage. This is cured by the second rotation, which relocates the junction in such a way that both of its sites become chlorinated. Compared to the initial $^{\#39712}C_{82}Cl_{28}$, there is a decrease in the relative energy by 209 kJ mol^{-1}, which corresponds to an increase in the average C−Cl binding energy by ca. 14 kJ mol^{-1}.

The general pathway of SW transformation in chlorinated fullerenes has been described previously.[6] It involves chlorine transfer through a $SbCl_6^-$ anion to stabilize an intermediate structure where one of the C atoms of the rotating bond forms a CCl_2 bridge, while the other C atom develops a fourth C−C bond. It is required that, for the atom to form a bridge, the initial compound should already bear chlorine. To find out whether the experimentally observed transformation is unique or, on the contrary, constitutes only one of the possible alternatives, we considered all conceivable SW rotations that satisfied this requirement. It turned out that the intermediates shown in Figure 2 are the most energetically favorable ones, while all other hypothetical products of SW rotation in IPR-$^{\#39712}C_{82}Cl_{28}$ but one are even less stable than the starting compound (see the SI for more details). It is worth noting that, setting aside the chlorination pattern, some of the unfavorable SW rotations are precisely coupled to the exothermic ones by the C_2 axis of the initial $^{\#39712}C_{82}Cl_{28}$ cage: the seemingly not very important asymmetry of the chlorination pattern appears to impart major distinctions in SW energetics.

Assuming that the activation barriers for SW rotations must correlate with the heat of the process, clearly favorable is the pathway via $^{\#37349}C_{82}Cl_{28}$, which is characterized by more exothermic first stage (108 vs 40 kJ mol^{-1}). To rationalize why the two-step transformation has no development, we additionally considered potential SW rotations in the isolated $^{\#39173}C_{82}Cl_{28}$ and found that none of them provides a decrease in energy. Thus, the SW pathway observed is fully determined by the chlorination pattern, which governs the energetics of the chlorinated cages and, correspondingly, the thermodynamic feasibility of each SW stage. However, it is the starting IPR cage that, in turn, determines the initial chlorination motif. As one can see, unlike the case of C_{76}, $^{\#39712}C_{82}$ does not seem to provide the possibility of a really deep skeletal transformation: additional SW rotations do not lead to the formation of new advantageous aromatic substructures that could stimulate further rearrangements around them.

In $C_{76}Cl_{24}$, we calculated an activation energy of 240 kJ mol^{-1} for the first, nearly thermoneutral, SW stage and 200 kJ mol^{-1} for the much more favorable last stage.[6b] In the present case, the exothermicity of transformations that proceed via $^{\#37349}C_{82}Cl_{28}$ is even higher: 100+ kJ mol^{-1} per stage compared

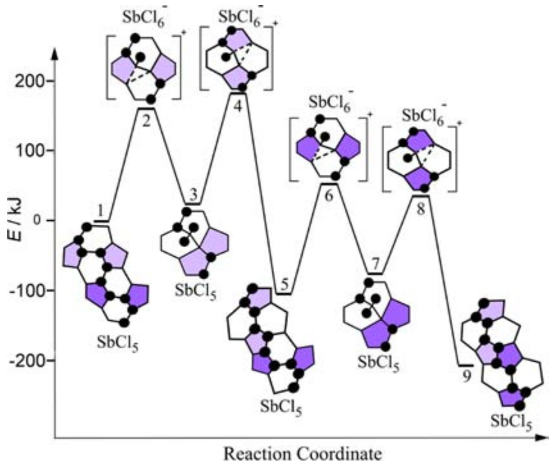

Figure 3. Reaction profile for the transformation of $^{\#39712}C_{82}Cl_{28}$ (1) into $^{\#39173}C_{82}Cl_{28}$ (9) via $^{\#37349}C_{82}Cl_{28}$ (5). States 3 and 7 are intermediate structures with CCl_2 bridges, while states 2, 4, 6, and 8 are ion-pair transition states.

to ca. 60−70 kJ mol^{-1} in $C_{76}Cl_{24}$, which made it possible to expect certain reductions in the activation barriers. Indeed, the results of our calculations presented in Figure 3 demonstrate that in the present case the activation barriers do not exceed 180 kJ mol^{-1} with respect to the starting structure, both at the PBE/TZ2P level and after single-point PBE0[17]/Def2-SVP[18] recalculation with D-PCM correction[19] for the effects of the $SbCl_5$ environment (*Firefly* QC package[20]). Thus, remarkably, the transformations in C_{82} can proceed even easier than those in C_{76}.

On the basis of our previous studies of $C_{76}Cl_{24}$ and the present C_{82} case, a general conclusion can be made that multistep SW pathways are governed by thermodynamic driving forces. In the typical range of 300−350 °C, quite high but surmountable activation barriers allow for exothermic (or nearly so) SW rotations; however, when only endothermic SW options remain, the skeletal transformation terminates.

In summary, the discovery of the second instance of chlorination-promoted SW rearrangements in C_{82} confirms that such transformations are likely common to many higher fullerenes. In fact, while preparing this manuscript, we observed further examples of such kinds, which will be published in due course. Together with the processes of heptagon formation upon C_2 abstraction, as exemplified by the formation of $C_{84}Cl_{32}$ from C_{86},[7] they may prove a powerful tool for fullerene cage engineering. However, these skeletal transformations cannot be carried out in a direct way so far; therefore, much theoretical work is required in this direction. Also, there remains a challenging experimental task of recovery and investigation of pristine non-IPR cages that requires synthetic effort on larger scales.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of quantum-chemical calculations, Schlegel diagrams of the transformation steps, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ioffe@thermo.chem.msu.ru (I.N.I.), stroyano@thermo.chem.msu.ru (S.I.T.). Tel: +007 495 9395396. Fax: +007 495 9391240.

Notes

The authors declare no competing financial interest.

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