Structures and cage transformations of higher fullerenes

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Since the discovery of fullerenes, rapid development of their chemistry was mostly restricted to C_{60} and C_{70}. The chemistry of higher fullerenes of more than 70 carbon atoms remains largely unexplored due to much lower abundance and difficulties in isolation thereof. Moreover, these complications grow more severe with molecular size due to increasing isomeric complexity even under the restrictions of the Isolated Pentagon Rule (IPR). Separation of higher fullerenes is usually achieved by chromatographic methods (HPLC) augmented by ^{13}C NMR characterization, which is, however, not fully reliable in some cases. An efficient alternative is constituted by chemical derivatization of higher fullerenes followed by separation and direct structural characterization of the derivatives thus obtained, as illustrated by several examples within the C_{76} - C_{96} range [1].

Reactions of mixtures of higher fullerenes with CF_3I or C_2F_5I followed by HPLC separation of the resulting perfluoroalkylated derivatives and their X-ray diffraction study enabled determination of cage connectivity in C_{76}, C_{78} (two isomers), C_{82}, C_{84} (six isomers), C_{86}, C_{88}, C_{92}, C_{94}, and C_{96}. Further, chlorination with inorganic chlorides ($SbCl_5$, VCl_4, etc.) afforded isolation and crystallographic characterization of chlorinated derivatives of C_{76}, C_{78}, and C_{90} [2].

An entirely new phenomenon, chlorination-promoted skeletal transformations, has been discovered in several higher fullerenes including C_{76}, C_{82}, C_{86}, and C_{88}. Chlorination of IPR D_2-C_{76} fullerene with $SbCl_5$ is accompanied by a 7-step Stone-Wales skeletal rearrangement to non-IPR $^{\#18917}C_{76}Cl_{24}$ containing five pairs of fused pentagons in the carbon cage [3]. Chlorination of C_{86} (isomer 16) accompanied by the loss of a C_2 unit resulted in $C_{84}Cl_{32}$ with a non-classical heptagon-containing cage [4]. Also, very recent results on skeletal rearrangements in C_{82} and C_{88} will be presented. The driving forces and possible pathways of the skeletal rearrangements will be discussed in more detail.

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