The Principles of Higher Fullerenes Reactivity

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Introduction

A characteristic feature of all fullerenes which makes them interesting and defines their unique chemical and physical properties is the steric strain induced by the curvature of the fullerene “surface”. The strain as caused by nonplanarity, has been addressed in term of the degree of carbon rehybridization. Detailed analysis of chlorinated higher fullerenes has revealed basic principles of halogen addition to fullerenes. The number of halogen atoms added and the resulting halogeneration pattern appear to be controlled by presence of triple hexagon substructures which tend to generate a new aromatic system during chlorination.

Strain in higher fullerenes

The presence of triple hexagon junctions (THJ) is a characteristic feature of higher fullerenes. In contrast to higher fullerenes, in C_{60}, each carbon atom constitutes a junction of a pentagon and two hexagons (pentagon-hexagon junction – PHJ). POAV analysis of higher fullerenes show that the pyramidalization of THJ carbon atoms are indeed significantly lower in comparison to PHJ atoms in C_{60}. According to POAV theory, the low pyramidalization of THJ carbon atoms (θp = 6–8°) should result in better conjugation of the corresponding atoms due to a more efficient overlapping of the respective σ-orbitals. However, surprisingly enough, exactly the opposite tendency has been experimentally found in C_{60}(14) fullerenes — the one and only example of a fully ordered pristine higher fullerene crystal [1]. It has been shown that decreasing the number of pentagons in the fragments leads to elongation of the corresponding bonds, despite the geometry in these fragments being more suitable for effective conjugation. Thus, the shortest bonds (1.34–1.38 Å) are found between two pentagons in the pyracene fragments, whereas the longest ones (1.46–1.48 Å) are involved in pyrene fragments.

Chlorination pattern of higher fullerenes

Chlorination has emerged as a powerful tool for obtaining well crystallized higher fullerene derivatives. Recently, a number of high quality crystals containing chlorinated higher fullerenes, C_{60}(Cl)_{12}, C_{60}(Cl)_{16}, C_{60}(Br)_{12}, C_{60}(Br)_{16}, C_{60}(ClBr)_{12} and C_{60}(ClBr)_{16}, were obtained in our group using the Br_{2}/TCE mixtures as a selective chlorinating agent. In all reported halogenated higher fullerenes, the halogen atoms bind to carbon atoms preferentially at 1,4-positions in the hexagons in such a way that contiguous ribbons of halogen atoms form.

References


Conclusion

1. Despite the low pyramidalization of THJ carbons, they introduce essential strain in the molecule and determine reactivity of higher fullerenes.

2. The driving force of chlorine addition is the formation of “islands” of aromaticity via “separation” of THJ substructures from curved regions preferring 1,4 addition.

3. The formation of chlorine belts conditioned by the direction of THJ chain, which always forms close loops around the fullerene molecule.

4. After “separation” of THJ the C_{60} substructures left are able to undergo further addition likewise C_{60} itself.