

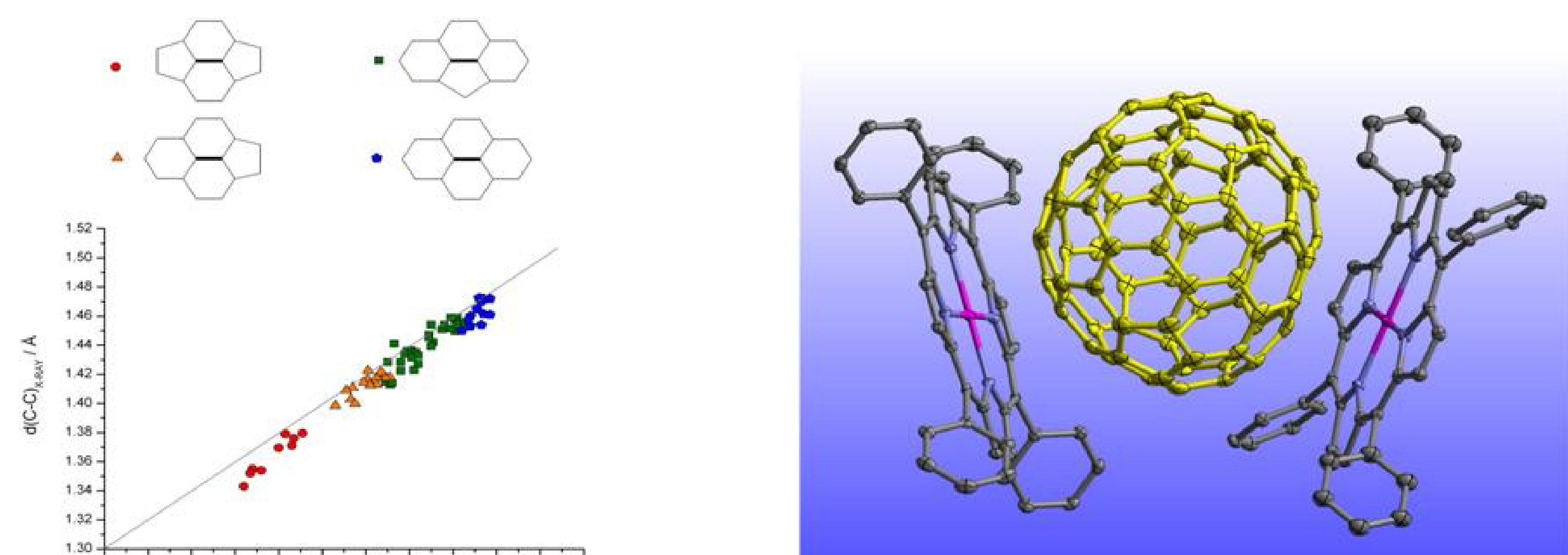


Introduction

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 halogenation pattern appear to be controlled by presence of triple hexagon substructures which trend to generate a new aromatic system during chlorination.

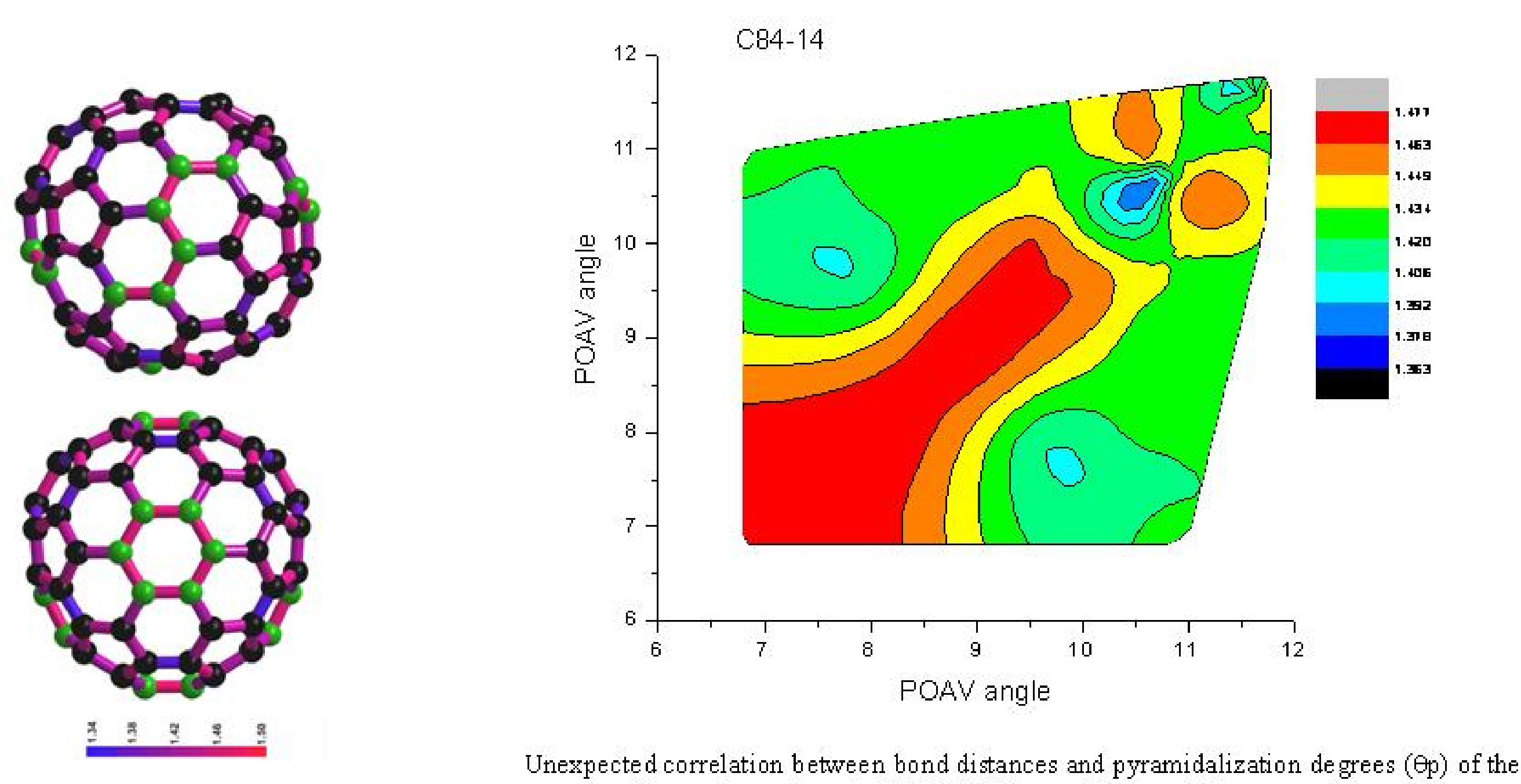
Strain in higher fullerenes

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 analyses 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 ($\theta_p = 6-8^\circ$) should result in better conjugation of the corresponding atoms due to a more efficient overlapping of the respective π -orbitals. However, surprisingly enough, exactly the opposite tendency have been experimentally found in $C_{84}(14)$ fullerene – 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 pyraclyene fragments, whereas the longest ones (1.46–1.48 Å) are involved in pyrene fragments.



Left: Correlation between the experimentally obtained and the DFT calculated C-C bond distances in $C_{84}(14)$. Correlation between the C-C bond length and the type of fragment in which the corresponding bonds are involved (the bonds under consideration are bold labeled). Right: ORTEP projection of the molecular structure of $C_{84}(14)$ in the crystal. Thermal ellipsoids are drawn at 50% probability level.

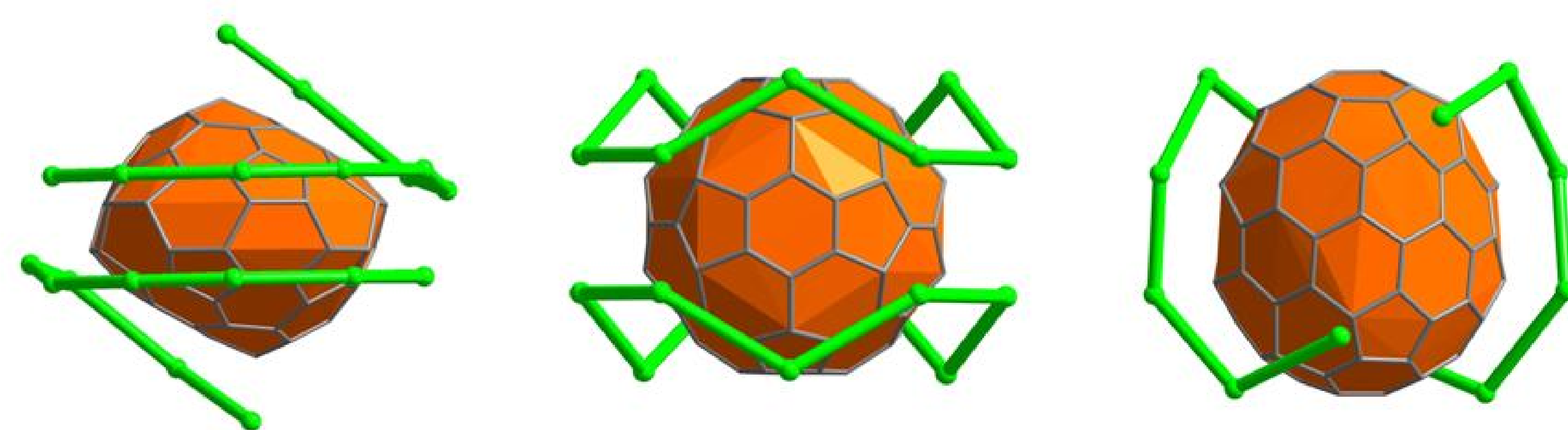
POAV analysis shows as well an unexpected correlation between bond distances and pyramidalization of the corresponding carbon atoms. The highly pyramidalized carbon atoms ($\theta_p \approx 11$) form the shortest bonds with lengths of about of 1.34 Å – a length typical for a "classical" double bond. The less pyramidalized THJ atoms ($\theta_p < 8$) form bonds of about of 1.48 Å, which are closer to a single carbon-carbon bond



Unexpected correlation between bond distances and pyramidalization degrees (θ_p) of the corresponding carbon atoms in $C_{84}(14)$ fullerene (X-Ray data)

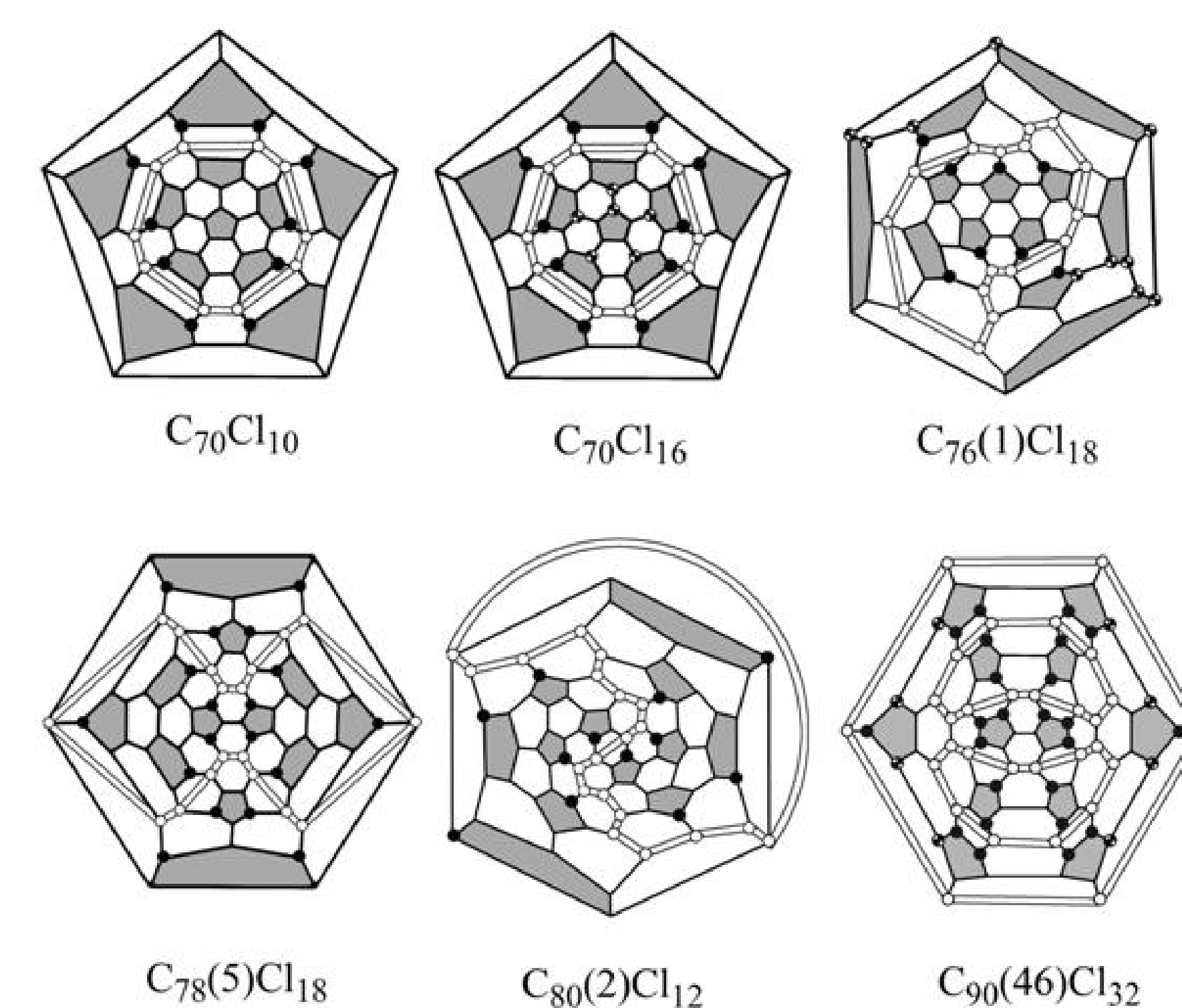
Chlorination pattern of higher fullerenes

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, $C_{76}(1)Cl_{18}$ [2], $C_{78}(2)Cl_{18}$ [3], $C_{78}(3)Cl_{18}$ [3], $C_{78}(5)Cl_{18}$ [4] and $C_{80}(2)Cl_{12}$ [5], were obtained in our group using the Br_2-TiCl_4 mixture 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.



Belts of chlorine atoms in chlorinated higher fullerenes $C_{76}(1)Cl_{18}$, $C_{78}(5)Cl_{18}$ and $C_{80}(2)Cl_{12}$. The chlorine atoms are linked together for clarity.

The addition sites (black circles) separate THJ carbon atoms (white circles) which formally constitute "graphitic" substructures, striving to be planar, from the ICCB carbon atoms, which are fragments of the curved C_{60} fullerene surface. Such a separation enables the strained THJ regions to relax and leads to better conjugation. After addition of chlorine in such a way the molecule contains formally the fragments of C_{60} fullerene and the "constructed" from THJ carbon atoms conjugated regions – "islands" of aromaticity.



After "aromatization" of the THJ substructures these regions become completely inert, whereas the C_{60} substructures left are able to undergo further addition. The existence of a whole homologous series of halogen derivatives of C_{60} demonstrates the "availability" of the ICCB carbon atoms for chlorine addition.

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.

References

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