

OXIDATIVE CYCLODEHYDROGENATION REACTION FOR THE DESIGN OF EXTENDED 2D AND 3D CARBON NANOSTRUCTURES: A THEORETICAL STUDY

Marco Di Stefano^[a], Fabrizia Negri^[a], Paola Carbone^[a], Klaus Müllen^[b]

[a]: Dipartimento di Chimica "G. Ciamician", Università di Bologna,
Via Francesco Selmi 2, 40126 Bologna (Italy)

E-mail: marco@ciam.unibo.it :: fabrizia.negri@unibo.it

[b]: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz (Germany)

Polycyclic aromatic hydrocarbons, or PAHs, are formally regarded as two-dimensional graphite sections and represent one of the most intensively investigated class of compounds since their discovery in coal tar in the middle of last century. They find extensive applications in the area of molecular electronics, besides adding essential contributions to a deeper understanding of the material science of soot, graphite, the spheric fullerenes and nanotubes. Within the class of PAHs, full-benzenoid PAHs, such as the hexa-*peri*-haxabenzocoronene (HBC), C₄₂H₁₈, have a well-defined benzene-like character, as described in Clar's model of the aromatic sextet. Although they possess the greatest chemical stability and the lowest reactivity of all known PAHs, not only do they represent a significant field of research to test π -bond theories but also they can be chemically activated to furnish more reactive species, then utilized in the design and synthesis of much larger systems falling within the range of macromolecules [1].

Large PAHs and full-benzenoid PAHs are readily available by a two-step protocol. It includes the synthesis of nonplanar oligophenylene precursors which are then subjected to an intramolecular cyclodehydrogenation reaction which forces planarization and formation of the polycyclic structures. In literature, the prototype of the cyclodehydrogenation is the successful transformation of the PAH hexaphenylbenzene, C₄₂H₃₀, into HBC and the main purpose of this reaction consists in the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl-aryl bond. In the 1960s Kovacic exploited this reaction to polymerize benzene under relatively mild conditions which were optimized by employing copper(II) chloride as oxydant and aluminium(III) chloride as catalyst [2]. Müllen and co-workers have experimentally investigated the same reaction leading to HBC from hexaphenylbenzene and we schematically represent their results in Figure 1. The transformation of hexaphenylbenzene (also labeled **1**) into HBC, **3**, proceeds via a stepwise mechanism, a conclusion that is supported by the isolation of the intermediate **2** whose detailed NMR-analysis is possible, whilst other intermediate products containing only two new C-C bonds are observed in trace amounts by FD-Mass analysis [3].

In order to rationalize the experimental results and to achieve a general understanding of the main mechanistic aspects of the oxidative cyclodehydrogenation reaction, we implement theoretical calculations on the potential energy surface of interest. Our investigation is carried out by using the DFT hybrid functional B3LYP in conjunction with the split valence 3-21G basis set. In agreement with the experimentalists, we clearly demonstrate that the removal of one electron from the reactant to yield the hexaphenylbenzene radical cation C₄₂H₃₀⁺ is the crucial step. In Figure 2 we draw the optimized geometries at B3LYP/3-21G level of theory of both the neutral, **1**, and the radical cation, **1**⁺, hexaphenylbenzene. The theoretical study of the intermediate species, in both neutral and cationic forms, which contain a growing number of

newly-formed C-C bonds, can aptly support and rationalize the experimental hypothesis concerning a stepwise mechanism for the reaction under study, besides furnishing worthy information on how the new rings can be formed. Finally, B3LYP/3-21G thermochemical calculations are carried out for each step and can give further insights into the reaction mechanism, distinguishing thus between endothermic and exothermic pathways.

References:

- [1]: A.J. Berresheim, M. Müller, K. Müllen, Chem. Rev., **99**, (1999), 1747 (references therein).
 [2]: P. Kovacic, M.B. Jones, Chem. Rev., **87**, (1987), 357.
 [3]: K. Müllen and co-workers, private communication.

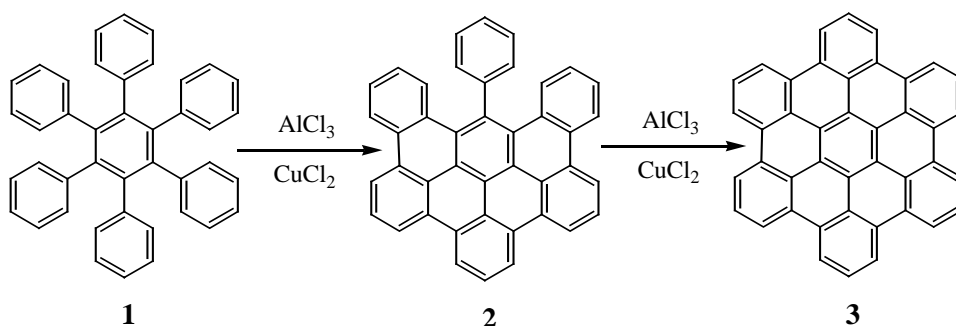


Figure 1. Schematic representation of the oxidative cyclodehydrogenation reaction of hexaphenylbenzene, **1**, leading to hexa-*peri*-hexabenzocoronene, **3**.

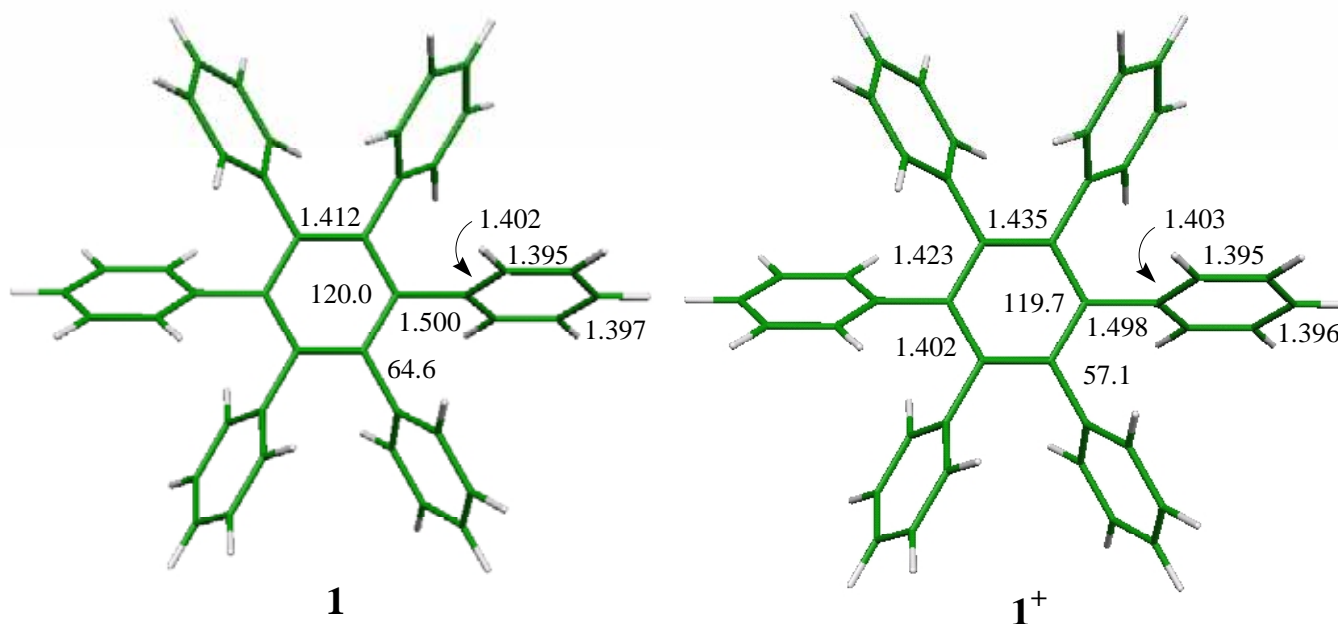


Figure 2. Optimized geometries at B3LYP/3-21G level of theory of the neutral, **1**, and radical

cationic, **1**⁺hexaphenylbenzene. Bond lengths are in Å and angles in degrees.