

# Stable Structures and Alternative Paths on the Road to SuperHydrogenated Coronene

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With a ~0.5% (mass) abundance, Carbon is ranked fourth in the elemental composition of the baryonic matter of the Universe and is responsible of much of its molecular complexity. It is ubiquitous in the interstellar medium and shows up in an extraordinary variety of molecular forms that range from simple species, to linear and cyclic molecules up to condensed molecules (polycyclic aromatic hydrocarbons, PAHs), fullerenes and nanodiamonds[1]. Among these species, PAHs lock ca. 5-15% of the whole Carbon and bridge the scale gap between small molecular species and the carbonaceous (graphitic-like) mantles of the interstellar dust grains. Though no single PAH has been yet identified, it is now generally accepted that PAHs are the most abundant polyatomic species in space and that they are involved in most of the physical and chemical processes of the interstellar medium. Hydrogen is a likely reaction partner to consider and this motivated a number of terrestrial experiments on superhydrogenated forms of PAHs[2].

Here, we present a detailed density-functional-theory investigation of the addition reactions that starting from coronene (C<sub>24</sub>H<sub>12</sub>) lead to its fully superhydrogenated form. We adopted a high-level density functional to compute binding and barrier energies for hydrogen atom attachment, and used simple guiding principles to follow the hydrogenation process from the very first adsorption event to the final C<sub>24</sub>H<sub>36</sub> structure. Binding energies for hydrogen addition to more than 150 sites were computed (along with energy barriers in the most important cases) and the main hydrogenation pathways were identified. In particular, the stable structures with 10,12,18 and 24 extra hydrogens that are found to accumulate during the hydrogen exposure[3] were identified along the investigated pathways.

We show how the results can be rationalized with the help of simple concepts[4] that apply equally well to different PAHs. These comprise the “ $\pi$  coordination” that determines the edge localization of the frontier orbitals, the “hyperconjugation” that makes some edge sites more reactive than others and the “sublattice localization” that operates when unpaired electrons are present.

## References:

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