

The interaction of H with coronene: a quantum chemist's view

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Motivated by recent laboratory studies of the hydrogenation process of coronene (C₂₄H₁₂)^{1,2} we undertook a detailed density-functional-theory investigation of the addition reactions that lead to its fully superhydrogenated form. We carefully choose a high-level density functional to compute accurate binding and barrier energies for hydrogen atom attachment, using simple guiding principles to find the most reasonable pathways to the final C₂₄H₃₆ structure. More than 100 structures were scrutinized for binding and the main hydrogenation pathways identified. Our results agree well with the experimental findings that indicate that some structures with 10,14,18 and 24 extra hydrogens accumulate during the exposure to a hydrogen atom source^{1,2}.

In this contribution we report the results of this theoretical investigation and show that they can be rationalized with the help of simple concepts developed for π -carbon substrates^{3,4}. These comprise the “ π -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. In addition, the present findings uncover an extra-stabilization effect that occurs when preserving one or more aromatic sextets. Such effect makes the structures of Fig. 1a-c the most likely candidates for the species that accumulate in the experiments.

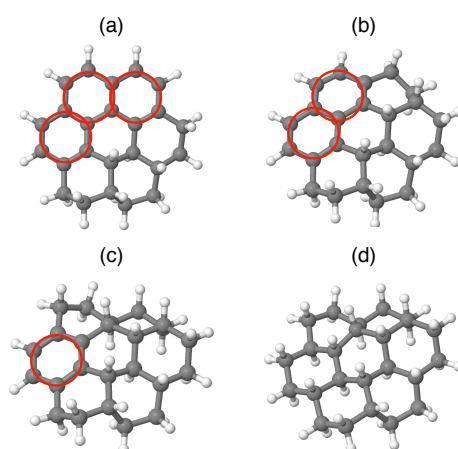


Figure 1: Superhydrogenated coronene molecule with 10, 14, 18 and 24 extra hydrogen atoms along the “main” hydrogenation sequence (panels a-d, respectively)

References

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