Computational Study of 13C NMR Chemical Shift Anisotropy Patterns in C20H10 and [C20H10]4-. Insights into Their Variation upon Planarization and Formation of Concentric Aromatic Species in the Smaller Isolated-Pentagon Structural Motif

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Corannulene, C20H10, exhibits a concave surface in the ground state that is able to experience a bowl-to-bowl inversion through a planar conformation. Such a structure is the smaller example resembling an isolated-pentagon motif, as a relevant fragment in fullerene chemistry. Here, we explored the differences between bowl and planar conformations involving both energetic and 13C NMR properties, for the neutral and tetraanionic species by using density functional theory (DFT) methods. This allows us to understand the variation of the chemical environment at the carbon atoms upon planarization of this representive motif. Our results reveal that the variation of the chemical shift comes about from the variation of different main components of the shielding tensor, according to the relative position of the carbon atoms in the structure (i.e., rim, hub, and protonated), which is more relevant for both hub and protonated sites, in contrast to the rim carbon remaining almost unshifted. Interestingly, the planar transition state exhibits a more favorable bonding situation than the bowl-shaped conformation; however, the higher strain is enough to overcome this extra stabilization. Upon reduction to the tetraanionic counterpart (C20H104-), a lesser strain in the planar conformation is observed, decreasing the inversion barrier. In addition, the formation of the concentric aromatic ring systems in C20H104-, results in a more axially symmetric chemical shift anisotropy (CSA) tensor for the hub carbons, accounting in a local manner, for the concentric aromatic behavior in such structure in contrast to the neutral parent. These observations can be useful to evaluate the aromatic behavior of teh isolated-pentagon rule (IPR) motif in fullerene cages.