Quantum Chemical Stuties on Functionalities of π Molecular Systems

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Electrons in π-type molecular orbitals (π orbitals) that conjugate with the adjacent p atomic orbitals can be widely delocalized within the molecule through the orbitals. In addition, the π-type occupied / unoccupied orbitals are generally more unstable / stable, respectively, than those formed by the σ-type molecular orbitals, so these π orbitals often become frontier orbitals. Therefore, molecules with the π orbitals are sometimes more reactive than other stable molecules. In particular, the distributions and energies of the π orbitals in the cyclic molecular systems can be easily changed by the number of ring atoms, the topology and the introduced substituents/heteroatoms as well as the external stimuli. For these reasons, π molecular systems have attracted attention as functional molecules.

In this talk, two examples of functionalities of π molecular systems are presented with the results of the quantum chemical calculations. First, the mechanism of a unique catalytic reaction of the fullerene polymer (Figure 1), which has π orbitals consisting of six- and five-membered rings is discussed. In this system, the charge fluctuations caused by the π-electrons on the polymer surface accelerate the adsorption and structural deformation of CO_2 molecule.[1] It then promotes the reaction with H_2O to form carbonate ions (CO_3^{2-}). As a second topic, the electron conductivity of [18]annulene (Figure 2), which is the aromatic π electron system is also introduced.[2]

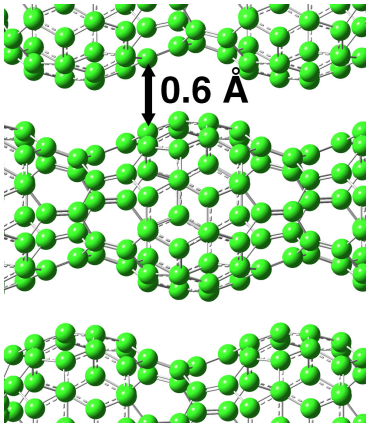

Figure 1 Fullerene polymer

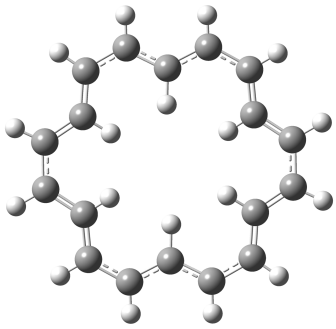

Figure 2 [18]annulene

References

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2. Amamizu, N.; Nishida, M.; Sasaki, K.; Kishi, R.; Kitagawa, Y. *Nanomaterials,* **2024**, *14*, 98.