Substitution Effect of a Single Nitrogen Atom on Linear Polycyclic Aromatic Hydrocarbons (PAHs) and Integrated Multiple π-Electron Conjugation

Sung Cho

Chonnam National University

We investigated the substitution effect of a single nitrogen atom on the molecular structure and π-electron delocalization in linear nitrogen-substituted polycyclic aromatic hydrocarbons (N-PAHs). Out study identified three types of substituted N atoms, distinguished by the shape of polygons and the number of covalent bonds at N atoms; pyridic, pyrrolic, and graphitic N atoms. On the basis of the optimized molecular structures and magnetic-field induced properties of linear N-PAHs, we discovered that the local π-electron delocalization of sub-polycycles (e.g., mono- and bi-cyclic constituent moieties) in linear N-PAHs is preserved, despite deviation from ideal structures of parent monocycles and resulting in less effective π-electron delocalization at sub-polycycles. Notely, the introduction of a fused five-membered ring with a N atom (N-5MR) in linear N-PAHs significantly perturbs the π-electronic condition of the neighboring fused six-membered ring (6MR). The monocyclic pyrrole, which represents the most optimized structure of N-5MR with six π-electrons, exhibits substantial bond length alternations, thereby strongly influencing the π-electron conditions of both the fused N-5MR and 6MR, depending on the location of shared covalent bond. Additionally, the N-6MR with a graphitic N atom cannot generate monocyclic π-electron delocalization, but instead contributes the formation of polycyclic π-electron delocalization, as evidenced by bifurcated diatropic ring currents induced by a magnetic field orthogonal to the molecular plane. In conclusion, we propose that the satisfaction of Hückel 4n+2 rule for both sub- and macro-polycycles is curial for comprehending the overall π-electron delocalization, as well as the energetic benefit and spatial distribution of π-electrons in linear N-PAHs.