Aromaticity of ortho and meta 8-Cycloparaphenylene and Their Dications: Induced Magnetic Field Analysis with Localized and Delocalized Orbitals in Strained Nanohoops

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Abstract
Dications of cycloparaphenyles ([n]CPPs) are known to exhibit in-plane global aromaticity, contained in a nanobelt structure. Recently synthesized ortho and meta isomers of [n]CPPs break the radial symmetry of π structure incorporating perpendicular oriented π orbitals. Herein we set to explore the aromaticity of neutral and dicationic ortho and meta isomers of [8]CPP by dissecting the induced magnetic field to contributions of the twofold radial/perpendicular π system using delocalized canonical molecular orbitals (CMO), and introducing the natural localized molecular orbitals (NLMO) analysis with DFT methods. The dications sustain a reduced global aromatic character of the radial π system under a perpendicular orientation of the external field which declines from ortho to meta isomer and reinforces local aromaticity of ortho ring while it destroys aromaticity of meta ring. Aromaticity variations are determined by symmetry governed rotational excitations of frontier π orbitals. The parallel orientation reveals a substantial reduction of local aromaticity verified with NICSπ analysis and electron delocalization indices.

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