Title

New Perspectives on Delocalization Pathways in Aromatic Molecular Chameleons

Abstract

This study comprehensively analyzes the magnetically induced current density of polycyclic compounds labeled as “aromatic chameleons” since they can arrange their π-electrons to exhibit aromaticity in both the ground and the lowest triplet state. These compounds comprise benzenoid moieties fused to a central skeleton with 4n π-electrons and traditional magnetic descriptors are biased due to the superposition of local magnetic responses. In the S0 state, our analysis reveals that the molecular constituent fragments preserve their (anti)aromatic features in agreement with two types of resonant structures: one associated with aromatic benzenoids and the other with a central antiaromatic ring. Regarding the T1 state, a global and diatropic ring current is revealed. Our aromaticity study is complemented with advanced electronic and geometric descriptors to consider different aspects of aromaticity, particularly important in the evaluation of excited state aromaticity. Remarkably, these descriptors consistently align with the general features on the main delocalization pathways in polycyclic hydrocarbons consisting of fused 4n π-electron rings. Moreover, our study demonstrates an inverse correlation between the singlet-triplet energy difference and the antiaromatic character of the central ring in S0.

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