

σ -Aromaticity in Dicationic Halogenated Cycloalkanes

Sladjana Đorđević and Slavko Radenković

sladjana.djordjevic@pmf.kg.ac.rs

University of Kragujevac, Faculty of Science, 34000 Kragujevac, Serbia

Traditionally, aromaticity is associated with π -electron delocalization, while σ -electron delocalization represents a less common form of stability in cyclic systems. This study investigates oxidation-induced σ -aromaticity in inherently non-aromatic halogenated cycloalkanes [1]. By employing different aromaticity descriptors, such as magnetically induced current densities (MICD), the electron density of delocalized bonds (EDDB), and aromatic stabilization energy (ASE), it is demonstrated that oxidation transforms halogenated cycloalkanes into σ -aromatic systems. The resulting σ -electron delocalization in these dications closely mirrors the prototypical double-aromatic $C_{6}I_6^{2+}$ system. Notably, certain deviations from Hückel's rule suggest that the observed aromaticity is better explained by orbital selection rules. These findings provide a unified view of how oxidative processes trigger aromatic character across different molecular architectures.

References:

[1] S. Radenković, S. Đorđević, *Phys. Chem. Chem. Phys.* **27** (2025) 25422-25432.