Additivity in Polycyclic Aromatic Systems

Additivity is a cornerstone concept and an integral part of the language of chemistry. It forms the basis of many chemical models and enables prediction of properties of systems that are outside synthetic and/or computational reach.\(^1\,^2\)

Aromaticity is a fundamental property and aromatic compounds are ubiquitous both in nature and in man-made materials, from simple reagents to complex materials. Understanding the nature and extent of their aromaticity is key to both predicting and tailoring the reactivity and properties of such compounds. Thus, both the qualitative and quantitative investigation of aromaticity have received a great deal of attention for many years.

The combination of additivity and aromaticity provides a powerful tool in this regard and opens the door towards utilizing aromaticity as a design element for functional compounds.

Magnetic criteria are the most commonly used to evaluate and compare aromaticity, among which the NICS-based methodologies are the most popular.\(^3\) Several years ago, we introduced the NICS-XY-Scan,\(^4\) which enables identification of local and global ring currents within polycyclic aromatic hydrocarbons. Recently, we showed that the same NICS-XY-Scans can be used in a novel way, as building blocks within an additivity scheme.\(^5\,^6\) This new application sheds new light on aromaticity in large systems, and enables prediction of the aromatic profiles of polycyclic systems at a fraction of the computational cost. The additivity scheme has been shown to be generally applicable to systems comprising carbon-based aromatic moieties as well as heterocyclic components, paving the way for investigation of very large and complex chain-like and graphene-based systems.

The potential of this method is highlighted by our recent work demonstrating a quantitative relationship between the NICS index of aromaticity and the HOMO-LUMO gap and Ionization Potential of a series of aromatic oligomers suitable for organic electronics.\(^7\)
References


