Aromaticity patterns in graphene nanoribbons

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We analyse the geometry, electronic structure and aromaticity of graphene nanoribbons (GNRs) and carbon nanotubes (CNTs) through a series of delocalisation and geometry analysis methods.[1] In particular, the Six Centre Index (SCI) [2-3] is found to be in good agreement with the Mean Bond Length (MBL) and Ring Bond Dispersion (RBD) geometry descriptors. Based on Density Functional Theory (DFT) periodic calculations, the type of edge and the width of the GNRs are found to be the factors determining the aromaticity pattern. Unlike zigzag GNRs, which are geometrically uniform, armchair GNRs present distinct geometrical patterns depending on their width. For this last class of GNRs, three distinct classes of aromaticity patterns have been found, the so-called incomplete-Clar (i-C), Clar (C) and Kekulé (K) class, appearing periodically as the width of the ribbon is increased. The appearance of such distinct aromaticity distribution is explained within the framework of the Clar's Sextet Theory. The SCI is found to be very useful tools for easily analysing the aromaticity in graphite-like structures such as GNRs and CNTs. It has been shown that delocalisation indices like the SCI and the bond order are able to probe the aromaticity distribution starting from uniform geometries without any optimisation procedure. In this way, these delocalisation indices are able to predict the bond length distribution throughout the nanosystem without the burden of a geometry optimization. In this way, the delocalisation analysis methods are shown to be very fast and reliable tools for easily analysing the aromaticity in carbon nanosystems.

References

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Figures
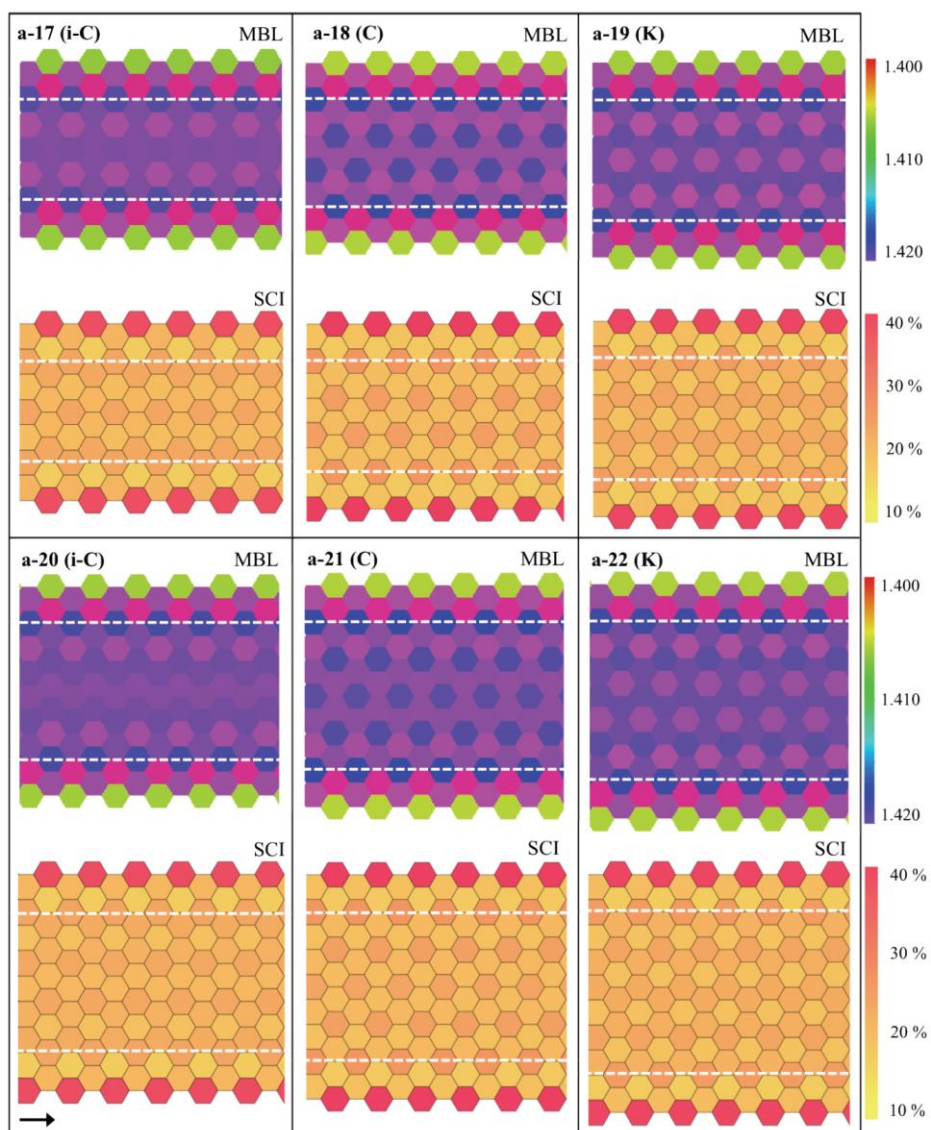
MBL and SCI representations for the three classes of armchair GNRs. Percentages in SCI are related to benzene (100%). Arrow in the left bottom part of the figure indicates the periodic direction.