Rings-in-Molecules: Aromaticity as a Similarity Distance to the Localization-Delocalization Matrix (LDM) of Benzene

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Aromaticity eludes unique precise definition [1]. There exists a large number of aromaticity indices each designed to capture primarily one facet of this multidimensional property, *e.g.*, structural, magnetic, energetic, or electronic. It is not surprising, then, that the various aromaticity measures not infrequently disagree with one another in ranking rings in molecules in terms of their overall aromatic character. The recently defined electron localization-delocalization matrices (LDMs) [2-4] code for more than one aspect of the electron distribution in the molecule (including information derived from the one-electron and the pair densities). It is proposed to quantify aromatic character in terms of the similarity of a given 6-membered ring in a condensed aromatic system to benzene, instead of attempting to quantify aromaticity through the choice of only one of its facets [5]. In a second approach, the eigenvalues of the LDM of a "ring-in-a-molecule (RIM)" are taken as predictors of the local aromatic character of that ring [6]. A comparison with well-known aromaticity criteria such as HOMA (structural), NICS (magnetic), and FLU and PDI (electron delocalization) with the Frobenius distance of local rings from benzene reveals strong correlations. The eigenvalues of the LDMs taken as absolute predictors of aromaticity (not compared with benzene) are also highly correlated with these aromaticity measures as well.

Some of these correlations are depicted in Fig. 1 and will be reported in detail elsewhere [5,6].

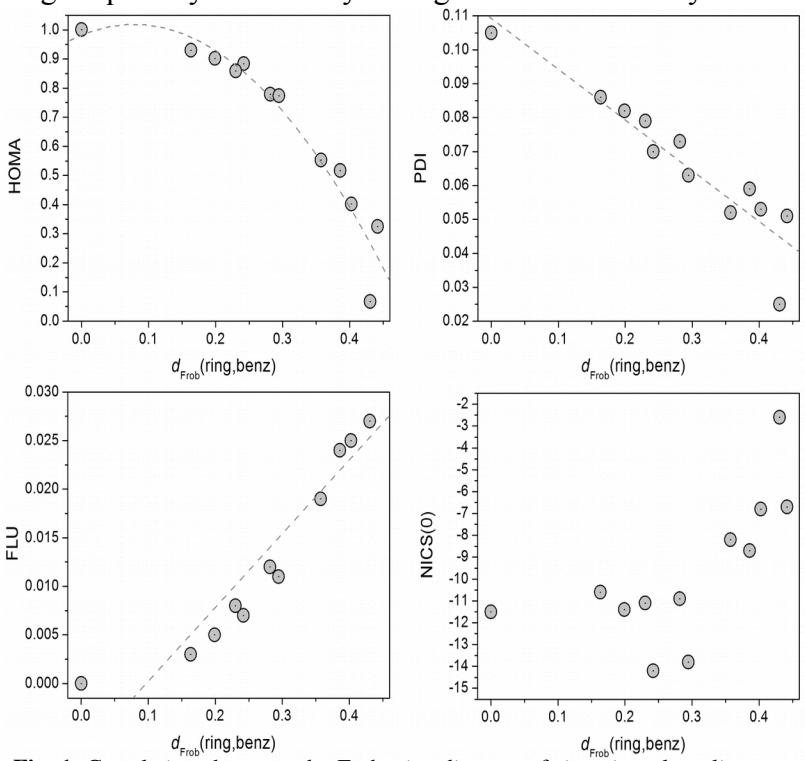

Fig. 1. Correlations between the Frobenius distance of rings-in-polycyclic aromatic benzenoids from benzene and aromaticity indices (HOMA, PDI, FLU, & NICS(0)).

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