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Local Aromaticity in Polycyclic Aromatic Hydrocarbons: Electron Delocalization versus Magnetic Indices

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Abstract: The local aromaticity of benzenoid rings is examined by means of the Polansky index (P) and generalized population analysis (GPA). The results are found to agree very well with recently published circuit-condensed ring currents and magnetic-energetic aromaticity indices, but no correlation is found with nucleus independent chemical shifts (NICS). This is usually seen as a manifestation of the more general multidimensional nature of aromaticity. This paper examines the sources for the observed correlations, showing that some indices give conflicting results because they inherently reflect different phenomena.

Keywords: aromaticity · bond theory · generalized population analysis · NICS · ring currents

Introduction

Aromaticity remains a controversial and enigmatic property. Due to the fuzzy nature or even lack of a proper definition of aromaticity, many different approaches have been used to identify and quantify the aromaticity degree of molecules, or parts thereof. A thorough discussion of all different classes of aromaticity indices is outside the scope of this paper, and the reader is referred to recent special issues of Chemical Reviews on the topic.[1–2] Despite the lack of a conclusive definition, organic chemists use a spectrum of properties to conclude aromatic character.[3]

The existence of many different indices or measures to quantify molecular aromaticity has resulted in sometimes contradictory claims regarding the aromaticity of some molecules. This has given rise to the often cited multidimensional character of aromaticity,[4–7] exemplified in what is called the orthogonality between classical (structural and energetic) and magnetic criteria of aromaticity.

The importance of magnetic criteria of aromaticity has recently been stressed by Lazzeretti who raised the question as to whether it would be possible to find a quantitative theory of aromaticity by using only measurable properties.[8] The conclusion of his paper was that the most advisable approach could be by some specific magnetic molecular features, as they are related immediately to experimentally observable properties which could, in principle, be subjected to experimental verification. On the other hand, the question has also been raised recently as to whether magnetic criteria are sufficient to determine aromatic character.[9]

Naturally, the problematic character of the aromaticity concept is even more acute for so-called local aromaticity. Local aromaticity is considered to be the retention of aromatic character in a molecular fragment compared to the same fragment in an archetypical molecule. The most common example is the local aromaticity of benzenoid rings in a polyaromatic aromatic hydrocarbon or substituted benzene, meaning that one examines how much of the aromatic character of a benzenoid ring in a molecule is retained in comparison to the benzenoid ring in benzene. Quantifying local aromaticity requires that one is able to develop indices that allow relating in a strict fashion the index with a specific group of atoms, for example, the benzenoid ring. Such a partitioning into local contributions can quite straightforwardly be applied to molecular electron densities and in the past few years several density-function-based local aromaticity measures were proposed.[10] Examples in this respect are the multicenter bond indices introduced for aromaticity[11–17] within the framework of generalized population analysis (GPA)[18–20] or the Polansky similarity index,[21] recently gen-

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eralized to the ab initio level of the theory.[15,16] Unfortunately, when applied to the classification of aromaticity of individual benzenoid rings in linear polyacenes both these inherently local structural aromaticity measure indices strongly disagree with the classification, based on the presumed local magnetic aromaticity index, namely NICS.[22] The discussion of the existing discrepancies in the predictions of these aromaticity measures was given a new impetus in the study by Stanger who seriously questioned the use of NICS as a local aromaticity measure and attributed its failure to the contamination of NICS values for any particular ring by the contributions from neighboring rings.[23] The computational and conceptual framework of NICS has been revised on several occasions to answer criticism, giving rise to several new versions like NICS$_{\pi,zz}$.[24] Yet, taking anthracene as an example, the new NICS indices still point out that the inner ring is apparently more aromatic than the outer ring.[23]

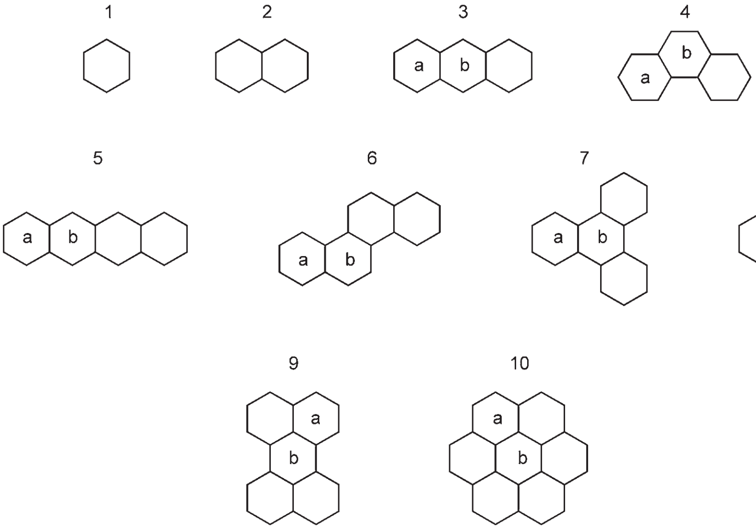

Figure 1. Molecules included in the present study with ring labeling. For clarity, only the σ-bond framework is shown.

Our aim in this study is to address the problem of the above inconsistencies in detail and to demonstrate that rather than reflecting the often invoked divergence between classical and magnetic aromaticity measures, the inconsistencies result from the fact that different indices are inherently incomparable. To corroborate our claim, we are going to demonstrate that no discrepancies between classical and magnetic aromaticity measures exists, provided the comparison is based on the indices of inherently and strictly local nature, such as, for example, the case for the correlation of the Polansky and SCI indices as the representatives of classical local aromaticity indices and local ring currents by Annusooya et al.[25] as representatives of presumably orthogonal local magnetic aromaticity measures. The predictions based on these aromaticity measures are completely consistent with each other, but all of them completely refute the NICS-based conclusions. The same situation also exists in the case of another local index, based on circuit-specific ring currents, namely, the circuit-specific resonance energies recently introduced by Aihara.[26]

Computational Methods

The present study focuses on the comparison of several local aromaticity measures and indices for the series of polycyclic aromatic hydrocarbons depicted in Figure 1 and demonstrates that there is in fact no disagreement between the predictions of different aromaticity measures provided that the corresponding indices do indeed reflect the local contributions of individual benzenoid rings without interference from the contributions of other rings.

The indices considered for the comparison involve the ring-specific six-center index (SCI)[11–13,15–17] from GPA[18–20] and the Polansky similarity index (P)[21] as representatives of local, electron density-based aromaticity measures, recently introduced circuit resonance energies (CRE)[26] as representatives of local magnetic-energetic aromaticity measures, and circuit-specific ring currents as representatives of magnetic aromaticity measures.[25] The values of the two latter types of indices were taken from the studies by Aihara[26] and Anusooya et al.,[25] respectively. The values of the SCI and P index were calculated by using the simple Hückel method (HMO). Both latter indices were introduced as quantities to characterize the local aromaticity of a particular benzenoid ring in a given polycyclic aromatic hydrocarbon. The Polansky approach relies on the idea that the degree of aromaticity of any local benzenoid ring L within a given polyaromatic hydrocarbon (PAH) can be gauged by the similarity of the electronic structure of this fragment to benzene itself. This similarity is quantitatively measured by the value of the index

$$P_{L,B} = \frac{2}{N_L} \sum_{\mu \in L} \sum_{\nu > \mu;\, \nu \in L} p^{L}_{\mu\nu} p^{B}_{\mu\nu} \qquad (1)$$

in which N_L is the number of electrons contained in the fragment, Greek symbols refer to atoms, and $p^{L}_{\mu\nu}$ and $p^{B}_{\mu\nu}$ are the HMO bond orders between the atoms μ and ν in the fragment L and benzene (B), respectively. The value of the index always varies between 0–1. The limiting value 1 implies ideal aromatic character typical for benzene itself and the smaller the index becomes, the smaller the local aromaticity of the fragment L.

Slightly different but still intuitively straightforward is the classification of aromaticity by using the SCI. The philosophy underlying the introduction of this index arises from Clar's idea of the aromatic sextet as a region in the molecule characteristic of extended delocalized bonding.[27] This extended cyclic delocalization is characterized within GPA by the value of the six-center-bond index SCI defined at the HMO level of the theory as:

$$SCI_L = \frac{6}{32} \sum_i \Gamma_i [P_{AB} P_{BC} P_{CD} P_{DE} P_{EF} P_{FA}] \qquad (2)$$

The summation runs over the atoms A–F involved in a given benzenoid fragment and Γ is the appropriate permutation operator required to take into account all possible permutations of the atomic labels.[12] The term 6/32 is a scaling factor for the SCI.

The reason for our choice of the HMO method is that circuit-specific ring currents of Anusooya et al. and the circuit-specific resonance energies of Aihara were derived from simple PPP or graph theoretical models which all are closely related to the HMO description. Our use of the HMO theory thus only ensures the maximum compatibility of the compared indices. In this connection it is, however, important to realize that both the P and SCI indices can be generalized to more sophisticated levels of theory and both these generalized indices exhibit close correlations with the corresponding HMO counterparts.[13–17] The HMO method implicitly assumes ideal geometries for all benzenoid rings. This is another approximation; however, it was shown previously that geometry optimization causes only very minor differences.[16] Furthermore, it is very well-known that, for example, the benzene molecule retains its aromaticity, even under severe geometrical distortions.[28] So, the HMO method is certainly an acceptable level of theory to study aromaticity in the PAH considered here.

NICS(0) values were computed by using the Gaussian 03 program[29] on the B3LYP/6-31G*[30–32] level by using idealized benzenoid geometries.

Results and Discussion

Table 1 reports the values for the different indices for the benzenoid fragments in each of the molecules in Figure 1. Next to the benzenoid Polansky index (P_B) of Equation (1) and the HMO SCI, the benzenoid ring-specific ring current (B-RC) of Anusooya is given as well as the benzenoid ring resonance energy (B-CRE) of Aihara and NICS evaluated in the center of each benzenoid ring.

Table 1. Polansky similarity index (P_B), SCI index, benzenoid ring current (B-RC), benzenoid circuit resonance energy (B-CRE), and NICS values evaluated at the ring centers for the molecules of Figure 1. NA means data not reported in the original study.

Molecule	Ring	P_B	SCI	B-RC[25]	B−CRE[26]	NICS
1		1.000	0.0494	1.00	0.2222	−9.67
2		0.912	0.0271	0.79	0.1120	−10.13
3	a	0.893	0.0233	0.71	0.0902	−9.45
	b	0.840	0.0165	0.70	0.0628	−12.20
4	a	0.928	0.0308	0.86	0.1414	−9.88
	b	0.813	0.0135	0.53	0.0520	−7.42
5	a	0.888	0.0223	0.70	0.0857	−8.87
	b	0.825	0.0146	0.64	0.0520	−12.27
6	a	0.923	0.0298	NA	0.1324	−9.85
	b	0.832	0.0157	NA	0.0662	−7.87
7	a	0.940	0.0339	NA	0.1648	−8.68
	b	0.714	0.0065	NA	0.0240	−0.70
8	a	0.882	0.0230	NA	0.0988	−12.60
	b	0.818	0.0143	NA	0.0514	−5.39
9	a	0.885	0.0232	NA	0.1015	−6.17
	b	0.699	0.0059	NA	0.0216	7.26
10	a	0.837	0.0166	NA	0.0674	−11.00
	b	0.753	0.0095	NA	0.0295	−1.21

Table 1 clearly reveals that P_B, SCI, B-RC, and B-CRE all indicate that the benzenoid ring in benzene has the highest extent of electron delocalization. Only in case of the NICS, one finds benzenoid rings that have a larger local aromaticity than the ring in benzene.

Table 2 shows the linear regression correlation coefficients between each pair of indices; it also shows that there is a very good correlation between the P_B and SCI indices. A linear model already gives a value of R^2 of 90%. However, the correlation between the P_B and log(SCI) index is even such that a one-to-one correlation exists between both indices.[15] Figure 2 shows the correlation obtained between the P_B and log(SCI) index. The reason why the logarithmic plot is better is related to the fact that the P_B uses the density matrix of the molecule considered only to the first power, whereas the SCI uses the sixth power.

Table 2. Regression coefficients (R^2) between each pair of indices in Table 1.

	P_B	SCI	B-RC[25]	B−CRE[26]	NICS
P_B	1.00				
SCI	0.90	1.00			
B-RC	0.91	0.90	1.00		
B-CRE	0.87	0.99	0.91	1.00	
NICS	0.52	0.29	0.01	0.25	1.00

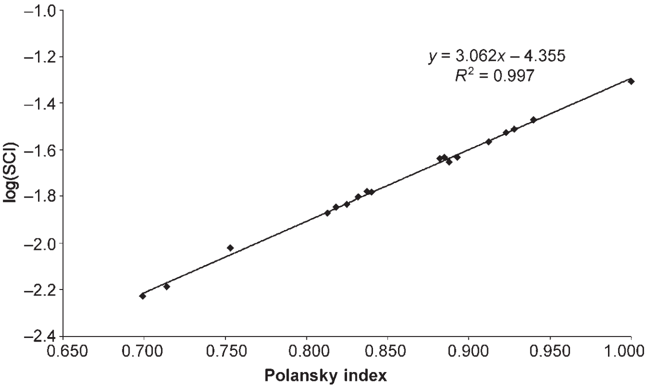

Figure 2. Correlation between the Polansky index and log(SCI) for the set molecules in Figure 1.

The correlation reported in Table 2 and Figure 2 shows that both indices sample the same information. The results clearly show that both indices reveal benzene as the most aromatic benzenoid ring over all molecules. This corresponds to the classical view of Clar's dilution of the aromatic sextet in PAHs.

Another interesting result that can be seen from Table 2, lies in the fact that the circuit-specific magnetic indices of Anusooya et al.[25] and Aihara[26] also correlate very well with the P_B and SCI indices. This is a very noteworthy result because the B-RC is a magnetic index and the B-CRE can be considered as an index that relates magnetic and energetic criteria.[26] This means that there is, for these indices, no need to introduce any multidimensional character to explain different behavior of density-based and magnetic/energetic indices. Figure 3 shows as an example the correlation between the B-CRE of Aihara and SCI. It is worth noting that such good correlations are not only present for the benzenoid circuits. The correlation is of the same quality for the larger circuits as the perimeter circuit in naphthalenic fragments when using an extended Polansky index and a GPA

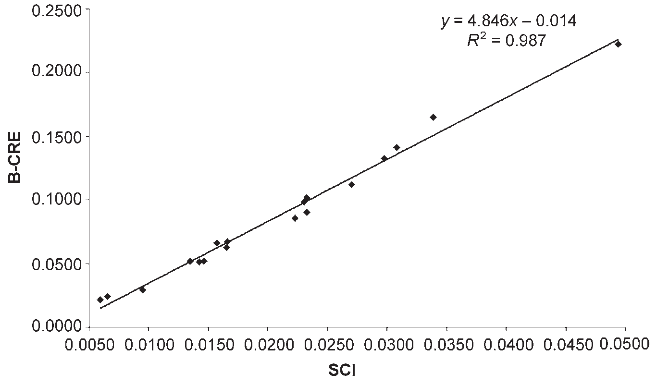

Figure 3. Correlation between B-CRE and SCI for the molecules in Figure 1.

index involving all 10 atoms of the circuit (Supporting Information).

Aihara and Anusooya et al. procedures for magnetic indices very explicitly project out different circuit-specific contributions from the total ring current. This means that an aromaticity index I can be written as a sum of contributions from different circuits. The case of anthracene is a good example. As Figure 4 shows, one can distinguish six circuits.

The projection procedure of Aihara and Anusooya et al. infers that a global molecular response can be written as the sum of contributions from the different circuits. A molecular response index I for a ring x, such as the ring current intensities, can be written as a sum of contributions over the different circuits:

$$\mathrm{I}(x) = \mathrm{I}_X(x) + \sum_{Z\neq X} \mathrm{I}_Z(x) \tag{3}$$

$\mathrm{I}_X(x)$ corresponds to the ring-current intensity for the benzenoid ring current X containing the benzenoid ring x. An example is $\mathrm{I}_\mathrm{A}(\mathrm{a})$ in Figure 4. The summation appearing in Equation (3) can in turn be split in two parts as:

$$\sum_{Z\neq X} \mathrm{I}_Z(x) = \sum_{Z\neq X;\, x\in Z} \mathrm{I}_Z(x) + \sum_{Z\neq X;\, x\notin Z} \mathrm{I}_Z(\chi) \tag{4}$$

The first summation on the right-hand side means that ring x is contained in the circuit $Z\neq X$, in the sense that in Figure 4, ring a is contained in circuits D and F. The second summation is identified as the so-called spill-over effect, meaning the remote effect of a circuit Z on ring x, although ring x is not contained in the circuit Z.

Let us now consider the case of really ring-specific indices, such as P and SCI. In this case one very specifically concentrates solely on a specific ring or circuit. Equations (1) and (2) illustrate this very well. There is no contribution from any other ring. This does not mean that SCI and P are independent of the chemical surroundings of the ring, but this dependence is implicit in the matrix P used for both indices.

In case of B-RC and B-CRE, the values of $\mathrm{I}_X(x)$ and $\sum_{Z\neq X;\, x\in Z} \mathrm{I}_Z(x)$ are available and $\sum_{Z\neq X;\, x\notin Z} \mathrm{I}_Z(x)$ is zero. $I_X(x)$ can be seen as the ring-current intensity of the benzenoid circuit X containing (only) ring x, so this is the most natural way to compare a benzenoid ring with benzene itself by magnetic or magnetism-derived properties, such as B-RC and B-CRE. As a consequence, it is also the most natural index to seek for correlation with the index P_B or SCI for the same benzenoid ring. As Table 2 and Figure 3 have clearly shown, when such values $I_X(\chi)$ are available, as is the case for B-RC and B-CRE, very good correlations are obtained with the indices P_B and SCI.

In clear contrast to the very good correlations reported above, Table 2 reveals that NICS do not correlate in any significant way with any of the other indices. This is quite surprising, as it is commonly considered a de facto standard magnetic aromaticity index. Also noteworthy is that this index makes the central ring of anthracene the most aromatic ring. This observation has led to quite a lot of criticism on NICS as a local aromaticity criterion, although it was argued by Schleyer et al. that experimental chemical reactivity is not an aromaticity criterion.[33] Yet, in the recent study by Stanger,[23] it is inferred that this observation is an emblematic failure of NICS. This agrees with the conclusions of Aihara et al.[34] Another strange observation is that the aromaticity in the naphthalene rings is larger than in pure benzene, again in clear disagreement with experiment. In

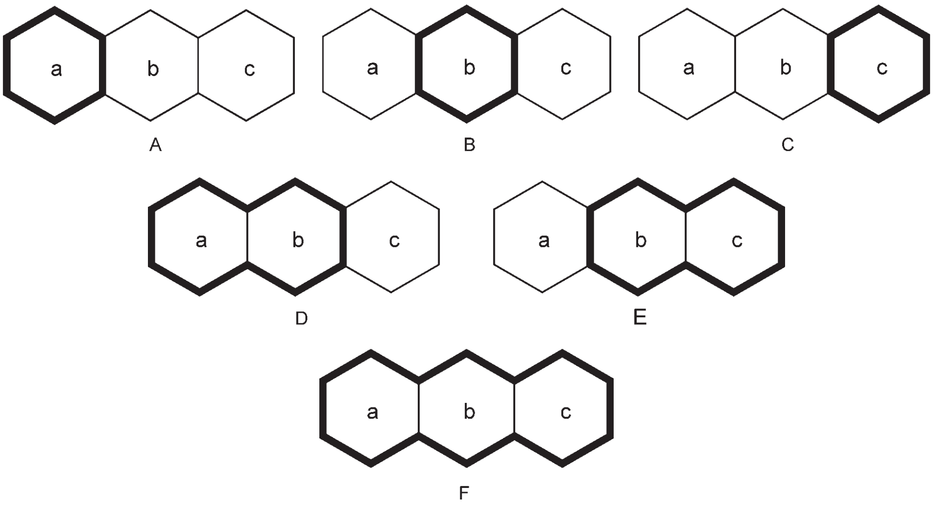

Figure 4. The six different circuits in anthracene. Lowercase labels refer to benzenoid rings, uppercase letters are used to denote the individual circuits.

the case of NICS, neglecting any remote contribution,[33] Equations (3) and (4) should be rewritten as:

$$\mathrm{NICS}(x) = \mathrm{NICS}_X(x) + \sum_{Z \neq X;\, x \in Z} \mathrm{NICS}_Z(x) \tag{5}$$

To compute NICS values, a point is placed in the center of the ring x considered or above the plane of the ring. The value obtained is equivalent to NICS(x) in Equation (5). This value thus is a sum of contributions of all circuits containing the ring x. If one then wishes to compare the local aromaticity between, for example, ring a and b in anthracene, one needs the value $\mathrm{NICS_A(a)}-\mathrm{NICS_B(b)}$. Unfortunately, the circuit specific contributions of NICS are not available. The difference NICS(a)−NICS(b) cannot be used, as this means that one includes all other circuits and these could have a large effect on the final result. This is clear, for example, for anthracene in which the summation $\sum_{Z \neq X;\, x \in Z} \mathrm{NICS}_Z(x)$ runs over two circuits for ring a and three circuits for ring b in Figure 4.

Naturally, a critical test for the reasoning above would exist in the existence of a good correlation between multicenter indices and NICS for molecules containing only one ring. In that case one obviously finds that $\mathrm{NICS}(x) = \mathrm{NICS}_X(x)$. We have previously studied[14] the difficult case of aromaticity in a number of five-membered rings and homoaromaticity in a number of systems from Freeman[35] by using the five center index. This set of 17 molecules certainly is a good test case, as it contains not only systems like furane, thiophene, etc., but also homoaromatic species derived from bicyclo[3.2.1]octane skeletons with a single five-center homoaromatic system. It was found that in this diverse set of molecules, there is a good correlation between NICS and the multicenter index ($R^2 = 0.96$) and that all molecules are correctly classified as either anti-(homo)aromatic, non(homo)aromatic, or (homo)aromatic.[14] Both the homoaromatic cases and the aromatic cases were found to lie on the same regression line. So it is fair to conclude that the multicenter index is a good aromaticity index that, in the case of single rings, correlates with NICS. It also supports the explanation above that when multiple circuits are present, there is a large mutual influence between the different circuits, making it impossible to use NICS as local aromaticity criteria to compare benzenoid rings in different PAH.

It is sometimes claimed that ring-current pictures for polyacenes demonstrate larger aromaticity for the inner benzenoid rings compared to the outer. However, the results of Steiner et al.[36,37] can be perfectly rationalized in the sense that for the inner rings one has simply a concentration of ring-current density towards the center of the molecule, as there, simply more circuits meet. It is worth noting in this context that Aihara et al. have shown previously how the superposition of the different individual circuits intensities in, for example, pentacene results in a ring-current picture that looks exactly like the one obtained for the global ring current.[34] It is worth mentioning the work by Sola and coworkers on PAH, including the linear polyacenes. They used mainly the para delocalization index (PDI) and found for the linear polyacenes that the aromaticity increases towards the center of the molecule.[38–41] We have, however, recently shown that the PDI index should be used with caution, and that restricting oneself to delocalization indices across the benzenoid ring overemphasizes the contributions of Dewar resonance structures and does not correctly account for all resonance structures.[17] Similar conclusions were reported also by Mandado et al.[42]

All this also casts some new light on the multidimensional nature of aromaticity. The P_B and SCI indices reflect strictly the aromaticity in the benzenoid circuits. The above discussion shows that NICS and differences in NICS values for different rings in a PAH molecule do not reflect solely the change in local aromaticity of the benzenoid circuits. So it is not surprising that there is no good correlation at all between the P_B and SCI indices on the one hand and NICS on the other. However, if ring currents are analyzed in circuit specific quantities like in B-RC and B-CRE, which also strictly reflect only a specific benzenoid current, there is an excellent agreement with the P_B and SCI indices. This means that magnetic criteria, or in the case of B-CRE a magnetic/energetic criterion, do not have to be orthogonal to other criteria as long as one strictly compares only truly comparable quantities. Ring-specific NICS values would certainly be very powerful quantities for comparison of local aromaticity, but the projection operators or other techniques to do so still remain unknown.

Conclusion

It has been shown that the Polansky measure of benzenoid character, the GPA-based SCI, the circuit-specific ring current reported by Anusooya et al., and circuit resonance energies of Aihara et al. all mutually correlate very well and all point out the same trends in relative aromaticity for a set of polyaromatic hydrocarbons. Nucleus independent chemical shifts (NICS) on the other hand do not show any correlation with these measures. This is found to be due to the basic character of NICS which are influenced by all circuits rather than allowing NICS to describe local (benzenoid) aromaticity. The apparent divergence between magnetic and electron delocalization indices does not exist when comparisons are based on indices of inherently and strictly local nature.

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