The Delocalization Index as an Electronic Aromaticity Criterion: Application to a Series of Planar Polycyclic Aromatic Hydrocarbons

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Abstract: This work introduces a new local aromaticity measure, defined as the mean of Bader's electron delocalization index (DI) of *para*-related carbon atoms in six-membered rings. This new electronic criterion of aromaticity is based on the fact that aromaticity is related to the cyclic delocalized distribution of π-electrons. We have found that this DI and the harmonic oscillator model of aromaticity (HOMA) index are strongly correlated for a series of six-membered rings in eleven planar polycyclic aromatic hydrocarbons. The correlation between the DI and the nucleus-independent chemical shift (NICS) values is less remarkable, although in general six-membered rings with larger DI values also have more negative NICS indices. We have shown that this index can also be applied, with some modifications, to study of the aromaticity in five-membered rings.

Keywords: aromaticity · atoms in molecules theory (AIM) · *para*-delocalization index (PDI) · planar polycyclic aromatic hydrocarbons (PAH) ·

Introduction

Aromaticity is a concept of central importance in physical organic chemistry.[1–6] It has been very useful in the rationalization of the structure, stability, and reactivity of many molecules. Even though this concept was introduced 137 years ago,[7] it has no precise and generally well established definition yet. Aromaticity is not an observable quantity and so, not being directly measurable, it must be defined by convention. According to Schleyer and Jiao,[4] aromatic systems are conjugated cyclic π-electron compounds that exhibit cyclic electron delocalization leading to bond length equalization, abnormal chemical shifts and magnetic anisotropies, and energetic stabilization.

Because of the importance of aromaticity in chemistry, there have been many attempts to rationalize and quantify this property, and to derive a universal quantitative measure of it. However, because of its multiple manifestations, there is not yet any generally accepted single quantitative definition of aromaticity. The evaluation of aromaticity is usually based on the classical aromaticity criteria: structural, magnetic, energetic, and reactivity-based measures.[5, 8]

The structure-based measures of aromaticity rely on the idea that important manifestations of aromaticity are equalization of bond lengths and symmetry.[9] Among the most common structure-based indices of aromaticity, one of the most effective[9] is the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski according to Equation (1) .[10, 11]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_i)^2 \quad (1)$$

Here n is the number of bonds considered, and α is an empirical constant fixed to give HOMA = 0 for a model nonaromatic system and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, assumed to be achieved for fully aromatic systems. R_i stands for a running bond length.

Magnetic indices of aromaticity are based on the π-electron ring current induced when the system is exposed to external magnetic fields. Historically, characteristic proton NMR chemical shifts and the exaltation of magnetic susceptibility (Λ) have been important magnetic criteria for quantification of aromaticity.[8, 9, 12] The exaltation is defined as the difference between the true diamagnetic susceptibility χ_M and the one calculated by an additive scheme by use of atom and bond increments $\chi_{M'}$, according to Equation (2).

$$\Lambda = \chi_M - \chi_{M'} \quad (2)$$

The exaltations are negative (diamagnetic) for aromatic compounds and positive (paramagnetic) for antiaromatic compounds. Ring-current intensities have also been used as a criterion for aromaticity.[13, 14] More recently, a new and widely used aromatic index, the nucleus-independent chemical shift (NICS), has been proposed by Schleyer and co-workers.[4, 15] It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values seem to be indicative of aromatic character. The more negative the NICS values, the more aromatic are the rings.

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Finally, energetic-based indices of aromaticity make use of the fact that conjugated cyclic π-electron compounds are more stable than their chain analogues,[3, 16] while reactivity-based indices exploit the fact that aromatic compounds prefer substitution to addition reactions to retain their π-electron structures.[17] The most commonly used measure among energy-based indices is the aromatic stabilization energy (ASE), calculated as the energetic effect of an imaginary homodesmotic reaction.[18–20]

Less common is the use of electronically based measures of aromaticity. Among these, we can mention the HOMO–LUMO gap, the absolute and relative hardness, the electrostatic potential, and the polarizability.[12] In addition, the degree of π-delocalization in an aromatic compound is generally considered to provide a measure of its aromaticity. Indeed, several measures of delocalization derived from natural bond orbital analysis of the first-order density have been used to quantify aromaticity in five-membered heteroaromatic compounds.[21, 22] Also noticeable is the work carried out by Moyano and Paniagua,[23, 24] who used local resonance energies obtained from Hückel localized molecular π-orbitals to evaluate local aromaticities. In the framework of Bader's Atoms in Molecules (AIM) theory,[25–27] an aromaticity index that takes account of the topological properties of the electron density at ring-critical points of six-membered rings has been also proposed.[28]

Herein we introduce a new electronically based aromaticity index, the delocalization index (DI), δ(A,B),[29–33] derived from the AIM theory. The term δ(A,B) is obtained by double integration of the exchange-correlation density over the atomic basins, as defined in the AIM theory, of atoms A and B, according to Equation (3).

$$\begin{aligned}\delta(\mathrm{A,B}) &= -\int_A\int_B \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1d\vec{r}_2 - \int_B\int_A \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1d\vec{r}_2 \\ &= -2\int_A\int_B \Gamma_{XC}(\vec{r}_1,\vec{r}_2)d\vec{r}_1d\vec{r}_2\end{aligned} \tag{3}$$

The term δ(A,B) gives a quantitative idea of the number of electrons delocalized or shared between atoms A and B.[29, 31–33] Several reasons prompted us to analyze the validity of the DI as a possible index of aromaticity: first, the basic idea that π-electron delocalization is the central source of aromaticity, second, the fact that this DI, derived from the second-order density, provides an unambiguous way to quantify delocalization, third, the results of a recent paper by Chesnut and Bartolotti,[30] who have applied this index to a series of substituted cyclopentadienyl species, proving that, for a given compound, there is a good correlation between the DI of the formally single C–C bond and the corresponding ASE value, and finally, the finding by Bader and co-workers that the delocalization of the density in benzene is greater between *para*-related carbons—$\delta(\mathrm{C,C'})_p = 0.10$ electrons—than between *meta*-related atoms—$\delta(\mathrm{C,C'})_m = 0.07$ electrons[29, 34]—despite the distance between carbon atoms being shorter in the latter. This result is an indication that, in a valence bond model of benzene, Dewar structures connecting *para*-related carbon atoms are more relevant than those connecting *meta*-related carbon atoms.[34] Thus, we decided to undertake a study of the validity of a new criterion for local aromaticity, defined as the mean of all DIs of *para*-related carbon atoms in a given six-membered ring (PDI). An advantage of the PDI index is that, like the HOMA and NICS indices, it provides a local criterion for each one of the rings in a polycyclic system. A local index of aromaticity is perhaps more useful than a global index for the whole molecule when the aromaticity of large polycyclic aromatic hydrocarbons (PAHs),[28] fullerenes,[17] or nanotubes[35] is being studied.

We must note that, as indicated by Katritzky, Krygowski, and co-workers,[8, 9, 36, 37] aromaticity is a multidimensional property. These authors found that mutual relationships between different aromaticity parameters depend strongly on the selection of molecules in the sample. They therefore recommend the use of more than one aromaticity parameter for comparisons restricted to some regions or groups of relatively similar compounds.[36] Accordingly, Krygowski and co-workers pointed out that fully aromatic systems are those cyclic π-electron species that follow all the main aromatic criteria, while those that do not follow all of them should be considered as partly aromatic.[9, 36] So far, the most widely used indices of aromaticity are based on structural, magnetic, and energetic measures. In this sense, it is very relevant to introduce new aromaticity indices based on other manifestations of aromaticity. The index introduced here is an electronically based index that exploits the key idea of electron delocalization so often found in textbook definitions of aromaticity.

In this study, two different series of compounds have been taken into consideration to test the delocalization index (DI) as an aromaticity criterion. The first is a series of PAHs containing six-membered rings, and the second a series of substituted cyclopentadienyl compounds with five-membered rings, widely used in previous aromaticity studies.[15, 30, 38, 39]

Abstract in Catalan: *En aquest treball introduïm una nova mesura local d'aromaticitat, definida com la mitjana dels índexos de deslocalització de Bader (DI) entre carbonis en posició para en anells de sis membres. Aquest nou criteri d'aromaticitat es basa en el fet que aquesta propietat està relacionada amb la deslocalització cíclica dels electrons π. Hem trobat que aquest DI i l'índex del model de l'oscillador harmònic d'aromaticitat (HOMA) presenten una bona correlació pels anells de sis membres per a una sèrie d'onze hidrocarburs policíclics aromàtics plans. La correlació entre els DI i els valors del desplaçament químic independent del nucli (NICS) no és tan bona, encara que, en general, els anells de sis membres amb majors valors de DI també presenten NICS més negatius. Hem demostrat que, amb algunes modificacions, aquest índex també es pot aplicar a l'estudi de l'aromaticitat en anells de cinc membres.*

Computational Methods

All calculations were performed with the Gaussian 98[40] and AIMPAC[41] packages of programs. For the series of planar PAHs,[15] DIs have been

obtained at the B3LYP/6-31G* optimized geometries, and for the series of substituted cyclopentadienyl systems,[15, 30, 38, 39] at the MP2/6-31G* optimized geometries. The GIAO method[42] has been used to perform HF/6-31+G* calculations of NICS at ring centers determined by the non-weighted mean of the heavy atom coordinates.[15] It is also possible to calculate the NICS at 1 Å above the molecular plane—NICS(1)—which should in principle better reflect the π-electron effects. However, previous works[36, 43] have shown NICS(1) to be qualitatively very close to NICS, which is more widely applied.

DIs have been calculated by the HF/6-31G* method. The DIs have not been calculated at the DFT level of theory because it is not possible to obtain correlated second-order densities for this methodology. In a recent work, we have shown that Hartree–Fock DIs are generally quite accurate in comparison to correlated DIs.[44] Moreover, because of computational limitations, it has not been possible to calculate the DIs at the configuration interaction (CI) level of theory, although values for the benzene molecule are included here for comparison (Table 1). In agreement with previous results,[29, 31, 32] we have found that correlated DIs are always somewhat smaller than the HF ones, although the qualitative trends are preserved when going from HF to CI. In particular, both levels of theory yield a larger value for $\delta(C,C')_p$ than for $\delta(C,C')_m$.

Table 1. HF/3–21G* and CISD/3–21G*//HF/3–21G* calculated delocalization indices (DIs) for the benzene molecule.[a]

	HF	CI
$\delta(C,C)_{ortho}$	1.398	1.162
$\delta(C,C)_{meta}$	0.068	0.048
$\delta(C,C)_{para}$	0.106	0.071
$\delta(C,H)$	0.963	0.836

[a] Units are electrons.

Results and Discussion

Planar polycyclic aromatic hydrocarbons: The PDI electronic measure of aromaticity is applied in this section to a series of eleven planar PAHs, including benzene, used as the reference compound. Schleyer and co-workers[15] have already calculated the NICSs and $\mathcal{A}$s for part of this series, showing that there is some correlation between these two aromaticity measures (see Table 2). Nevertheless, NICS and $\mathcal{A}$ being a local and a global measure of aromaticity, respectively, they cannot be unambiguously compared when various rings are present. This, together with the multidimensional character of aromaticity,[36] makes it necessary to include other measures of aromaticity. Apart from these two magnetic criteria (NICS and $\mathcal{A}$), we have therefore calculated the HOMA and the PDI indices as geometric and electronic criteria of aromaticity, respectively. Comparison between the NICS, HOMA, and PDI indices should give an indication of the usefulness of the PDI as a measure of aromaticity.

Scheme 1 shows the molecular structures of the eleven planar PAHs together with the labels given to each ring. The values of the NICS, $\mathcal{A}$, HOMA, and PDI for each PAH are collected in Table 2. As already mentioned, because NICS and $\mathcal{A}$ are based on different properties, good correlation is not completely achieved for this series. In general, however, systems with more negative values of $\mathcal{A}$ also have more negative values of NICS. Table 2 shows that in most cases there is a good correspondence between the different indices, compounds with more negative NICS values also having larger HOMA and PDI measures. This can be clearly seen in Figure 1 and Figure 2, which plot PDI versus HOMA and PDI versus NICS, respectively. In particular, electronic PDI and structural HOMA indices give almost the same order of aromaticity for the different six-membered rings in the PAHs analyzed, with a few exceptions. One of these is the six-membered ring in benzocyclobutadiene, which is quite aromatic according to the PDI index and only moderately aromatic as indicated by the HOMA index. Note that benzene (C1) is the most aromatic six-membered ring of the series according to both HOMA and PDI indices.

Table 2. HF/6–31+G* calculated NICS (ppm) and magnetic susceptibility exaltations $\mathcal{A}$ (ppm cgs), together with HF/6–31G* HOMA, PDI delocalization indices (electrons) and the π contribution to PDI (electrons). All of these parameters have been obtained at the B3LYP/6–31G* geometry.

Molecule	Ring	NICS	$\mathcal{A}$[a]	HOMA[b]	PDI	PDI_π
C1	6A	−9.7[a]	−13.4	0.981	0.101	0.093
C2	6A	−9.9[a]	−28.2	0.769	0.073	0.066
C3	6A	−10.2[a]	−47.9	0.854	0.082	0.074
	6B	−6.5[a]		0.433	0.044	0.037
C4	6A	−9.3	−57.6	0.889	0.086	0.079
	6B	−2.2		0.047	0.025	0.019
C5	6A	−8.2[a]	−49.8	0.616	0.061	0.054
	6B	−13.3[a]		0.692	0.067	0.060
C6	6A	−10.1		0.804	0.079	0.071
	6B	−7.6		0.541	0.052	0.045
C7	6A	−6.8		0.456	0.055	0.048
	6B	−13.1		0.602	0.062	0.055
C8	6A	−2.5[a]	9.0	0.664	0.083	0.074
	4B	22.5[a]		−1.570		
C9	6A	−5.1[a]	−7.9	0.835	0.089	0.081
	4B	19.0[a]		−1.044		
C10	6A	−8.6[a]	−32.5	0.834	0.070	0.062
	5B	2.9[a]		0.142		
C11	6A	−0.1[a]	−8.4	0.755	0.067	0.059
	5B	12.8[a]		−0.164		

[a] From ref. [15]. [b] Equation (1) with $\alpha = 257.7$ and $R_{opt} = 1.388$ Å according to ref. [9].

There is also some correlation between PDI and NICS values, with five exceptions. Two of these five uncorrelated cases are the 6B inner rings of C5 and C7, which have similar structural environments. These rings show a quite large negative value of NICS (≈ −13.2), denoting substantial aromaticity, while the PDI (≈0.06) and HOMA (≈0.6) indices indicate that these rings have intermediate aromatic character. Remarkably, all indices agree in attributing a greater aromaticity to the inner rings of C5 and C7 than to their outer rings. Other uncorrelated examples correspond to compounds C8 and C9, with fused four- and six-membered rings. In these systems, the NICS values suggest a rather small aromatic character for the six-membered rings, while PDI and HOMA indices indicate that these rings are quite aromatic, especially the 6A ring of C9. The last case to mention is the 6A ring of C11, which has nonaromatic character according to its NICS value of close to zero, while both PDI and HOMA indices favor a partial aromatic character for this ring. It is worth noting that Diogo and co-workers,[45] using thermochemical, structural, and NMR data, have also not reached a clear-cut answer regarding the aromatic or antiaromatic character of C11.

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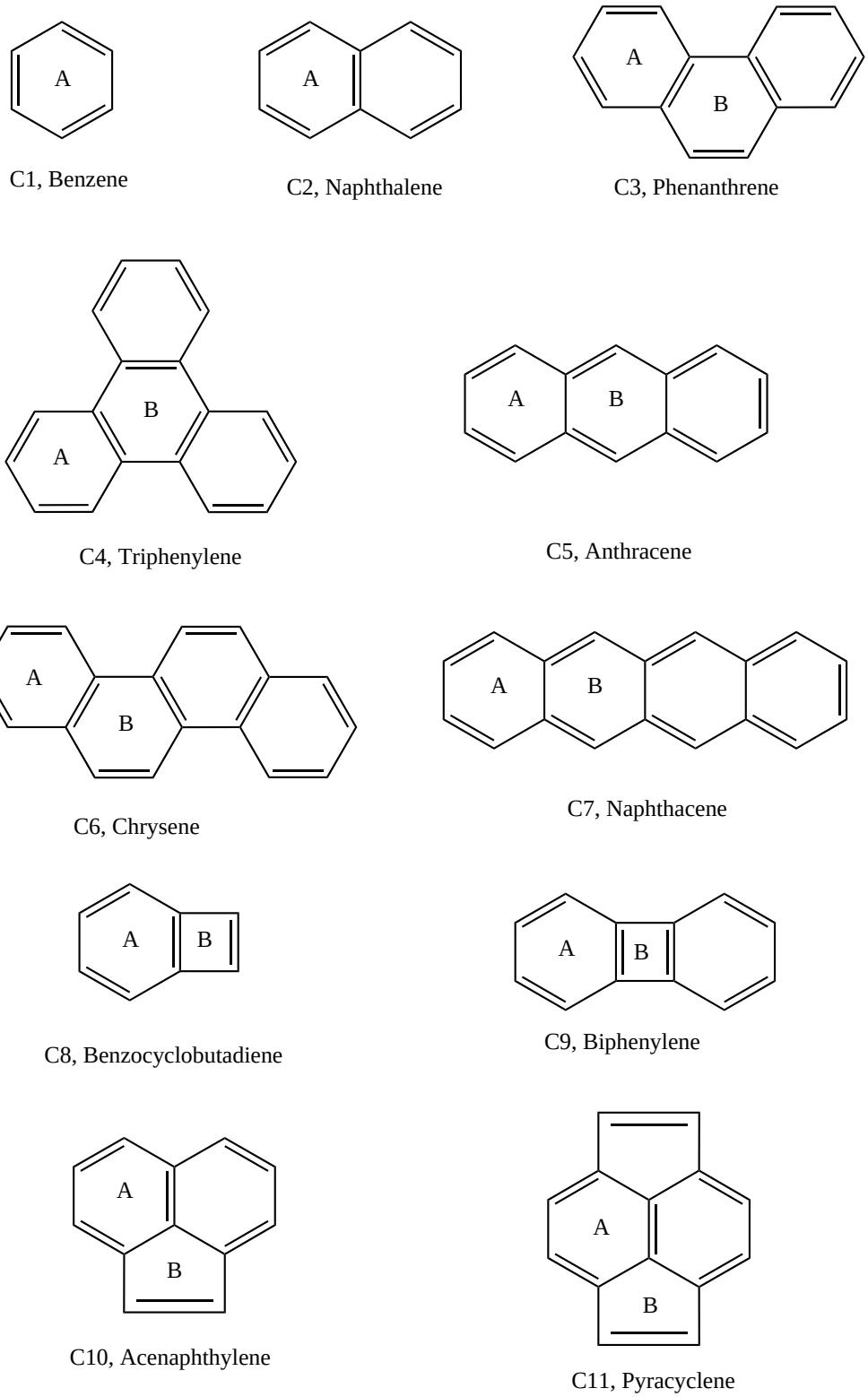

Scheme 1. Labels for the molecules and rings listed in Table 2, corresponding to the planar polycyclic aromatic hydrocarbons studied.

In general, despite being based on different physical manifestations of aromaticity, the NICS, HOMA, and PDI parameters yield similar results, with some exceptions. Thus, all methods classify the 6A rings of C1, C2, C3, C4, C6, and C10 as manifestly aromatic, while the 6B rings of C3, C4, and C6 and ring 6A of C7 are classified as being only moderately aromatic. When different aromaticity criteria provide the same answer, then one can be quite sure about the aromaticity of a given ring. However, in some cases (rings 6A of C5, C8, C9, and C11 or rings 6B of C5 and C7), different indices afford divergent answers. Since the different available measures of aromaticity are based on different manifestations of

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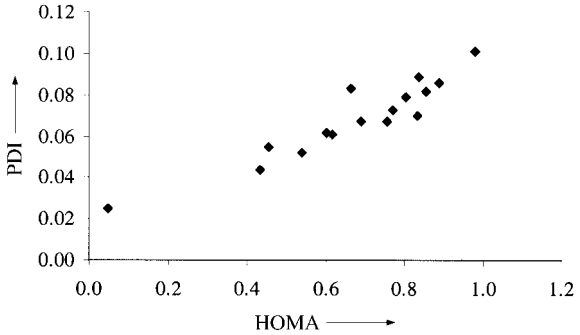


Figure 1. Plot of PDI versus HOMA for the series of planar polycyclic aromatic hydrocarbons studied.

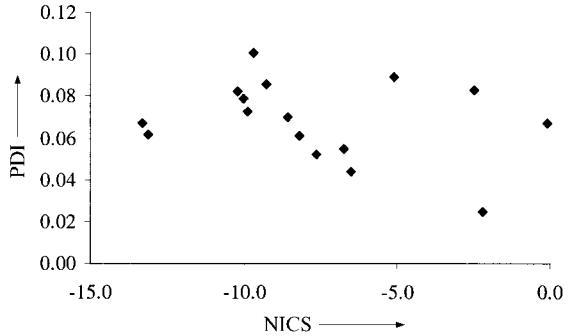


Figure 2. Plot of PDI versus NICS for the series of planar polycyclic aromatic hydrocarbons studied.

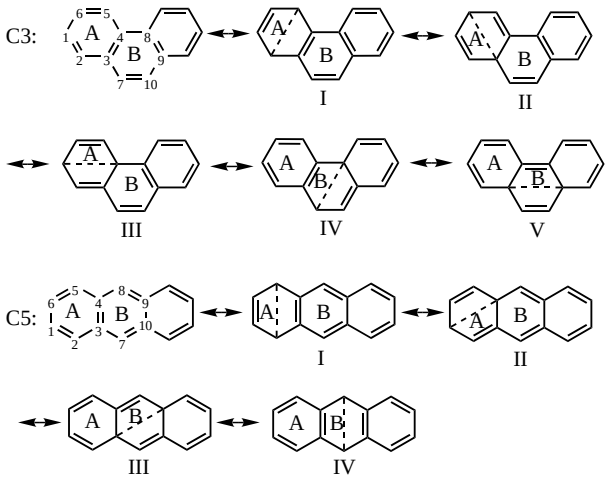
this phenomenon, it is not surprising that distinct aromaticity indices may yield different results.[36] Thus, for instance, the addition of a five-membered ring to C10 to give C11 substantially reduces the NICS of the six-membered rings in C11 as compared to C10, while at the same time hardly affecting the PDI and HOMA indices. In this sense, when quantifying the aromaticity of certain species, the safer method is to use different measures of aromaticity. This is in line with the suggestion of Schleyer and Jiao[4] that bond length equalization alone should not be used as a criterion for aromaticity, as some bond-equalized systems are not aromatic.

If we now just focus on the systems containing outer and inner six-membered rings (C3 – C7), all aromaticity indices in Table 2 show the inner rings of "linear" C5 and C7 as more aromatic than the outer rings, while the reverse is true for C3, C4, and C6 systems with six-membered rings fused in angular arrangements. Analysis of the components of the PDI index provides further insight into the differences between "linear" and "nonlinear" systems. In particular, we have collected all the delocalization indices of *para*-related carbons for the outer (A) and inner (B) rings of the simplest "linear" and "nonlinear" systems (C5 and C3, respectively) in Table 3. These values provide an indication of the most probable Dewar resonance structures for each system in a valence bond picture (Scheme 2). From the DIs obtained we can state, for C3 for instance, that the π-electron delocalization is more important in ring A than in ring B. We can also anticipate that the Dewar structure I should be more significant ($\delta(C_2,C_5) = 0.097$) than structures II and III, which should in turn be more relevant than IV and V. For C5, on the other hand, we find the opposite behavior, the electron delocalization in ring B being

Table 3. *Para*-delocalization indices and PDI for the outer and inner rings of C3 and C5.[a]

		C3	C5
A	$\delta(C_1,C_4)$	0.075	0.045
	$\delta(C_2,C_5)$	0.097	0.093
	$\delta(C_3,C_6)$	0.074	0.045
	PDI	0.082	0.061
B	$\delta(C_3,C_9)$	0.033	0.049
	$\delta(C_4,C_{10})$	0.049	0.049
	$\delta(C_7,C_8)$	0.049	0.105
	PDI	0.044	0.067

[a] See Scheme 2 for atom numbering. Units are electrons.



Scheme 2. Dewar resonance structures for phenanthrene (C3) and anthracene (C5).

slightly more important than in ring A. Thus, in this case we may also conclude that structure IV ($\delta(C_7,C_8) = 0.105$) is the most important of the Dewar structures, followed successively by I, III, and II. Finally, it is worth noting that *para*-DIs connecting two carbon atoms located in a ring fusion are always smaller than those possessing only one carbon atom in a bridge, which are in turn smaller than *para*-DIs linking C atoms not located in ring fusions. Therefore, the low aromaticity in ring B of "nonlinear" systems can be attributed to the fact that in this ring at least one C atom is located in a ring fusion for all *para*-related carbon atoms.

For planar PAHs, PDI values, like NICS indices, can be separated into σ and π contributions. Values for the π contributions (PDI_π) are tabulated in Table 2, while values for the σ contributions, obtained as the difference between PDI and PDI_π values, have been omitted because they are quite constant along the series ($PDI_\sigma \approx 0.008$ electrons). Owing to the constancy of the σ contribution, the trends obtained from the PDI_π values are the same as those derived from the PDI measures.

In this first section, we have shown that the PDI index is a simple and efficient probe for local aromaticity in six-membered rings. The PDI index cannot be used to quantify the aromaticity in pentagonal rings, because five-membered rings do not have *para*-related carbon atoms. However, we show in the next section that a related index based on DIs also allows the aromaticity of five-membered rings to be quantified.

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Substituted cyclopentadienyl compounds: The series of substituted cyclopentadienyl compounds chosen is the same as that used by Schleyer and co-workers previously[15] to show that the NICS parameter correlates well with the aromatic stabilization energies and the magnetic susceptibility exaltations. This series presents a wide range of five-membered ring heterocyclic compounds going from the fully aromatic cyclopentadienyl anion to antiaromatic species such as borol. Table 4 lists the NICS, ASE, and Λ values for the eleven systems studied. One can easily see that the more aromatic a compound is, the more negative are its NICS and Λ and the more positive its ASE.[15, 38]

Table 4. GIAO-SCF calculated NICS (ppm), magnetic susceptibility exaltations Λ (ppm cgs), aromatic stabilization energies ASE (kcal mol^{-1}), HF/6–31G* delocalization indices δ (electrons), differences between δ(C=C) and δ(C–C), ΔDI (electrons), and differences between r(C=C) and r(C–C), Δr (Å). All of these parameters have been obtained at the MP2/6–31G* geometry.

C_4H_4-X	NICS[a]	ASE[a]	Λ[a]	δ(C=C)	δ(C–C)	ΔDI	Δr
CH^-	–19.4	28.8	–17.2	1.388	1.388	0.000	0.000
NH	–17.3	25.5	–12.1	1.488	1.273	0.214	0.036
S	–14.7	22.4	–10.0	1.597	1.221	0.376	0.043
O	–13.9	19.8	–9.1	1.576	1.200	0.376	0.062
SiH^-	–8.0	13.8	–7.7	1.684	1.179	0.505	0.054
PH	–5.9	7.0	–3.3	1.752	1.121	0.631	0.088
CH2	–4.2	3.7	–2.4	1.746	1.100	0.647	0.111
AlH	6.9	–6.8	11.2	1.892	1.044	0.848	0.144
SiH^+	13.4	–24.1	13.2	1.860	1.009	0.851	0.161
BH	17.2	–19.3	12.8	1.873	1.018	0.855	0.160
CH^+	54.2	–56.7	32.6	1.674	0.970	0.704	0.209

[a] From refs. [15, 38].

Delocalization indices (DIs) for the formally single C–C bond (δ(C–C)) and the formal double C=C bond (δ(C=C)) have been calculated by using Equation (3), and values are listed in Table 4. In agreement with the results reported by Chesnut and Bartolotti,[30] the more aromatic the compound is, the more negative is the NICS value, the smaller the δ(C=C) value and the larger the δ(C–C) value. A maximum of aromaticity is obtained for the cyclopentadienyl anion, which has five equivalent bonds and a totally delocalized five-membered ring. In other words, the more aromatic the compound, the smaller the difference between the DIs of the single and double bonds. To describe this situation, we have defined ΔDI as the difference between δ(C=C) and δ(C–C) delocalization indices. This is a measure of the deviation with respect to a totally bond equivalent system, such as the cyclopentadienyl anion. This measure correlates better with NICS, ASE, and Λ values than either δ(C–C) or δ(C=C), increasing when the aromaticity is reduced. This can be clearly observed in Figure 3, which shows a good correlation between the ΔDIs and the NICS values, with the sole exception of the cyclopentadienyl cation.

Finally, Table 4 also contains the parameter Δr: the difference between the single C–C and the double C=C bond lengths. As can be seen from these values, ΔDI and Δr are clearly related: the larger the ΔDI, the larger the Δr. Thus, as mentioned above, larger bond length alternations are associated with lower aromaticities.

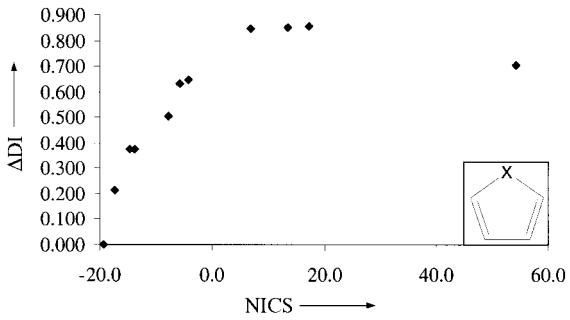

Figure 3. Plot of the difference between δ(C=C) and δ(C–C)—ΔDI—versus nucleus-independent chemical shifts (NICS) for the series of substituted cyclopentadienyl compounds.

From the above two applications, we have demonstrated the validity of the DI as an electronic local aromaticity criterion in five- and six-membered rings. Nevertheless, there are other conjugated rings that are also interesting from the point of view of their aromaticity. For instance, this is the case in 4π-electron systems such as cyclobutadiene, for which the difference of DIs between the single and double bonds should also give a measure of antiaromatic character. However, more studies need to be carried out to corroborate the validity of the DI for quantification of local aromaticity in conjugated rings other than five- and six-membered ones.

Conclusion

In this work we have introduced the delocalization index, an electron-pair property, as a new electronically based measure of aromaticity. We have demonstrated that the PDI for six-membered rings and the ΔDI for five-membered rings are simple and efficient probes for local aromaticity. This is not completely surprising, since aromaticity has always been associated with the cyclic delocalization of electrons. We have shown that these DIs, with some exceptions, correlate well with other already existing independent local aromaticity parameters, such as the magnetic-based NICS criterion or the geometry-based HOMA, which are commonly in use nowadays. The different behavior of the PDI, HOMA, and NICS aromaticity indices has been attributed to the multidimensional character of aromaticity. We have also shown that these DIs can be easily associated with valence bond-like structures, derived from the Lewis model. Thus, DIs appear to be useful tools that can help chemists to classify five- and six-membered rings with respect to their local aromaticity. In particular, these indices can be used to discuss local aromaticity in fullerenes, buckybowls, and nanotubes, most of these consisting of fused five- and six-membered rings. Research in this direction is currently under way in our laboratory.

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