Analysis of Hückel's [4*n* + 2] Rule through Electronic Delocalization Measures[†]

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In the present work, we analyze the π-electronic delocalization in a series of annulenes and their dications and dianions by using electron delocalization indices calculated in the framework of the quantum theory of atoms in molecules. The aim of our study is to discuss the Hückel's $4n + 2$ rule from the viewpoint of π-electronic delocalization. Our results show that there is an important increase of electronic delocalization (of about 1 e) when going from antiaromatic $4n\pi$ systems to aromatic $(4n + 2)\pi$ systems. Less clear is the change in π-electronic delocalization when we move from a $(4n + 2)\pi$-aromatic to a $4n\pi$-antiaromatic species by adding or removing a pair of electrons.

Introduction

Aromaticity is a concept of central importance in physical organic chemistry.[1] It has been very useful in the rationalization of the structure, stability, and reactivity of many molecules. Even though this concept was introduced in 1865 by Kekulé,[2] it has no precise and generally well-established definition yet. Aromaticity is not an observable quantity, and therefore, because it is not directly measurable, it must be defined by convention. There have been many attempts to rationalize and quantify this property and to derive a universal quantitative measure of it.[3] However, because of its multiple manifestations, there is not yet any generally accepted single quantitative measure of aromaticity. Currently widely used indicators of aromaticity involve structural,[4] magnetic,[5] energetic,[6] electronic,[7] and reactivity-based[8] measures.

In 1968, Breslow formulated[9] one of the first energetic criteria of aromaticity by comparing the π energy of a cyclic π-conjugated system to that of the corresponding iso-π-electronic linear compound. A decrease in π energy upon cyclization indicates aromaticity, whereas a decrease points out antiaromaticity. Later, in 1972, Hobey demonstrated[10] that this definition is connected to Hückel's $4n + 2$ rule, derived from the Hückel's molecular orbital (HMO) theory presented in 1931,[11] according to which a monocyclic system with $(4n + 2)\pi$ electrons is aromatic, whereas a system with $4n\pi$ electrons is antiaromatic. The preparation of cycloheptatrienyl cation, $C_7H_7^+$, by Doering in 1954,[12] is considered as the first experimental verification of the Hückel's rule.[13] An extension of the original Hückel's $4n + 2$ rule to polycyclic aromatic hydrocarbons was formulated by Glidewell and Lloyd[14] stating that the total π-electron population tends to form the smallest $4n + 2$ groups and to avoid the formation of the smallest $4n$ groups.

A further development of the Hückel's $4n + 2$ rule came when Baird showed, by using perturbational molecular orbital theory, that annulenes which are aromatic in their singlet ground state are antiaromatic in their lowest-lying triplet state, and vice versa for annulenes that are antiaromatic in the ground state.[15] The identification[16] of the planar triplet ground states of $C_5H_5^+$ and $C_5Cl_5^+$ as well as a recent photoelectron spectroscopic study[17] of the first singlet and triplet states of $C_5H_5^+$ provided experimental support for Baird's extension of the Hückel's $4n + 2$ rule.

From a theoretical point of view, the validity of Hückel's and Baird's rules was proved through nucleus independent chemical shifts and aromatic stabilization energy calculations by Schleyer et al.[18] and also from the study of ring currents.[19] Previous resonance energy and ring current calculations of annulenes provided preliminary evidence for the reliability of the $4n + 2$ Hückel's rule.[20] Moreover, the study of ring currents in $4n\pi$-electron monocycles[21] and a recent theoretical work[22] based on the analysis of the bifurcation in the π contribution to the electron localization function (ELF) for the lowest-lying triplet state of $4n\pi$-electrons monocycles confirmed the validity of the Baird's rule. Let us briefly add here that some of us studied a series of annulenes at the HMO level of theory, with the finding that electron sharing (which corresponds to electron sharing indices (ESI) for an ab initio calculation, *vide infra*) in contiguous atoms is very similar for aromatic and antiaromatic species.[23]

Most aromaticity definitions are invariably linked to the cyclic electronic delocalization of π electrons in classical aromatic organic compounds and of σ-, π-, δ-, or ϕ-electrons in modern aromatic inorganic species.[24] This electronic delocalization is usually studied either by means of the ELF or through the calculation of the so-called delocalization indices (DIs).[7,25] The latter method has been chosen in the present work to get values of the total π-electronic delocalizations (δ_π). By using these quantities, our main aim is to analyze the changes in electronic delocalization and aromaticity when we add or subtract two π electrons to a series of aromatic $(4n + 2)\pi$ and antiaromatic $4n\pi$ organic compounds. We expect that the trends followed by the π-electronic delocalization when adding or removing two π-electrons in annulenes should allow us to discern between aromatic $(4n + 2)$ and antiaromatic $(4n)$ systems. Let us consider a given aromatic system with $(4n + 2)\pi$ electrons. If this system incorporates two electrons, we reach a $4n\pi$-electrons system

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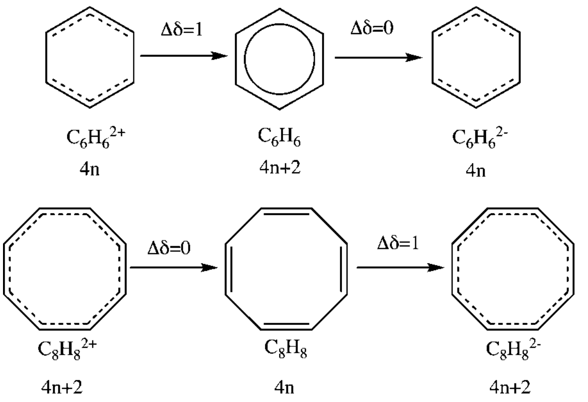
SCHEME 1



which, according to Hückel's rule, should be antiaromatic. Thus, one expects that the added electrons in the molecule will be mainly localized, so that the total π-electron delocalization in the system essentially stays the same when going from $4n + 2$ to $4n\pi$ electrons. If the same system loses two electrons, we have likewise a $4n\pi$-electrons system; one expects that the system breaks its aromatic character, thus losing electron delocalization. In particular, for the addition of two electrons at the aromatic N system, we expect a change in δ_π close to 0, whereas for the addition of two electrons at the $N - 2$ system, the change in total π delocalization index (δ_π) should be positive and around 1 e, depending on the number of C atoms in the ring (*vide infra*). For an antiaromatic species, we expect exactly the opposite trend. Scheme 1 summarizes our hypothesis with respect to an aromatic system (C_6H_6) and an antiaromatic one (C_8H_8) when going from $N - 2$ to N and from N to $N + 2$ systems, where N is the number of π electrons for the neutral species. We anticipate here that our work will show that this hypothesis is only partially fulfilled.

Measures of Electronic Delocalization and Aromaticity

In this work, we will measure the electron delocalization by means of the so-called DIs, or in a more general nomenclature, the ESI. The ESI value between atoms A and B, $\delta(\mathrm{A,B})$ is obtained by double integration of the exchange−correlation density ($\gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)$) over the molecular space regions corresponding to atoms A and B,

$$\delta(\mathrm{A,B}) = -2\int_{\mathrm{A}}\int_{\mathrm{B}} \gamma_{\mathrm{XC}}(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 \qquad (1)$$

For monodeterminantal closed-shell wave functions, one obtains

$$\delta(\mathrm{A,B}) = 4 \sum_{i,j}^{\mathrm{occ.MO}} S_{ij}(\mathrm{A})\, S_{ij}(\mathrm{B}) \qquad (2)$$

The summations in eq 2 run over all occupied molecular orbitals (MOs). $S_{ij}(\mathrm{A})$ is the overlap between MOs i and j within the molecular space assigned to atom A. $\delta(\mathrm{A,B})$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B.

Although several atomic partitions may be used in the ESI definition, the most popular one is that where the partition is carried out in the framework of the quantum theory of atoms in molecules (QTAIM) of Bader,[26] by which atoms are defined from the condition of zero-flux gradient in the one-electron density, $\rho(\mathbf{r})$. In this study, we have preferred this partition over others, such as the fuzzy-atom partition[27] or the Mulliken scheme,[28] because the QTAIM-ESI produces numbers closer to what is expected from chemical intuition.[29,30]

In order to study the delocalization effects upon extraction or addition of two electrons, we will calculate the total delocalization, which can be exactly splitted, because of the planarity ($S_{\sigma\pi}(\mathrm{A}) = 0$) of all systems taken into study, into the σ and π contributions, this latter being responsible for most of the properties associated to aromaticity:

$$\delta_{\mathrm{tot}} = \sum_{\mathrm{A}_i,\mathrm{A}_j\neq \mathrm{A}_i} \delta(\mathrm{A}_i, \mathrm{A}_j) = \sum_{\mathrm{A}_i,\mathrm{A}_j\neq \mathrm{A}_i} \delta^{\pi}(\mathrm{A}_i, \mathrm{A}_j) + \sum_{\mathrm{A}_i,\mathrm{A}_j\neq \mathrm{A}_i} \delta^{\sigma}(\mathrm{A}_i, \mathrm{A}_j) = \delta_\pi + \delta_\sigma \qquad (3)$$

Different aromaticity criteria based on electron delocalization measures have also been employed[7,25] to complement the δ_π values. These indices measure the cyclic electron delocalization of mobile electrons in aromatic rings. First, the para-delocalization index (PDI)[31] is obtained by using the aforementioned DIs.[32] The PDI is calculated as an average of all DIs of para-related carbon atoms in a given six-membered ring. Second, the aromatic fluctuation index (FLU)[33] is constructed by considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, and also by taking into account the similarity of electron sharing between adjacent atoms. Let us consider a ring structure of N atoms represented by the following string $\boldsymbol{A} = \{\mathrm{A}_1, \mathrm{A}_2, ..., \mathrm{A}_N\}$, the elements of which are ordered according to the connectivity of the atoms in the ring. For such ring, the FLU index is defined as

$$\mathrm{FLU}(\boldsymbol{A}) = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\frac{V(\mathrm{A}_i)}{V(\mathrm{A}_{i-1})}\right)^{\alpha}\left(\frac{\delta(\mathrm{A}_i, \mathrm{A}_{i-1}) - \delta_{\mathrm{ref}}(\mathrm{A}_i, \mathrm{A}_{i-1})}{\delta_{\mathrm{ref}}(\mathrm{A}_i, \mathrm{A}_{i-1})}\right)\right]^2 \qquad (4)$$

where $A_0 \equiv A_N$, and half the values of $V(\mathrm{A})$ are recognized by some authors[34] as the atomic valence for a closed-shell system defined as

$$V(\mathrm{A}_i) = \sum_{\mathrm{A}_j\neq \mathrm{A}_i} \delta(\mathrm{A}_i, \mathrm{A}_j) \qquad (5)$$

and α is a simple function to make sure that the first term in eq 4 is always greater or equal to 1, thus taking the values

$$\alpha = \begin{cases} 1 & V(\mathrm{A}_i) > V(\mathrm{A}_{i-1}) \\ -1 & V(\mathrm{A}_i) \leq V(\mathrm{A}_{i-1}) \end{cases} \qquad (6)$$

The $\delta_{\mathrm{ref}}(\mathrm{A}_i,\mathrm{A}_{i-1})$ reference values are $\delta_{\mathrm{ref}}(\mathrm{C,C}) = 1.389$ e, $\delta_{\mathrm{ref}}(\mathrm{C,N}) = 1.318$ e, $\delta_{\mathrm{ref}}(\mathrm{C,S}) = 1.270$ e, and $\delta_{\mathrm{ref}}(\mathrm{C,O}) = 0.970$ e (the $\delta(\mathrm{C,C})$, $\delta(\mathrm{C,N})$, $\delta(\mathrm{C,S})$, and $\delta(\mathrm{C,O})$ values in benzene, pyridine, tiophene, and furan, respectively, at the B3LYP/6-311++G(d,p) level). FLU is close to 0 in aromatic species and differs from it in nonaromatic ones. Third, we have employed the multicenter index of Giambiagi et al. (I_{ring}) used by the same authors to account for simultaneous electron sharing of various centers:[35]

$$I_{\mathrm{ring}}(\boldsymbol{A}) = \sum_{i_1,i_2,\ldots,i_N} n_{i_1} \ldots n_{i_N} S_{i_1 i_2}(\mathrm{A}_1)\, S_{i_2 i_3}(\mathrm{A}_2) \ldots S_{i_N i_1}(\mathrm{A}_N) \qquad (7)$$

n_i is the occupancy of orbital i. This expression is used both for closed-shell and open-shell species. In the particular case of a closed-shell monodeterminantal wave function, we are left with a simpler expression:[36]

$$I_{\mathrm{ring}}(\boldsymbol{A}) = 2^N \sum_{i_1,i_2,\ldots,i_N}^{\mathrm{occ.MO}} S_{i_1i_2}(\mathrm{A}_1)\, S_{i_2i_3}(\mathrm{A}_2)\, \ldots\, S_{i_Ni_1}(\mathrm{A}_N) \qquad (8)$$

Recently, Bultinck and co-workers have worked on a particular extension of the I_{ring} index. According to these authors, summing up all the I_{ring} values resulting from the permutations of indices $\mathrm{A}_1, \mathrm{A}_2, \ldots, \mathrm{A}_N$ defines a new index of aromaticity, the so-called multicenter index (MCI),[28] the formula of which reads

$$\mathrm{MCI}(\boldsymbol{A}) = \frac{1}{2N} \sum_{P(\boldsymbol{A})} I_{\mathrm{ring}}(\boldsymbol{A}) \qquad (9)$$

where $P(\boldsymbol{A})$ stands for a permutation operator which interchanges the atomic labels $\mathrm{A}_1, \mathrm{A}_2, \ldots, \mathrm{A}_N$ to generate up to the $N!$ permutations of the elements in the string $\boldsymbol{A}$. Generally, the values of MCI and I_{ring} are in tight correlation because the dominant contribution to MCI comes usually from the Kekulé structure;[37] nonetheless, some exceptions may arise.[38] Some of us have recently found that these indices should not be applied to systems of different size and proposed the normalized version of I_{ring} and MCI.[38] However, the qualitative conclusions drawn in this paper are the same as those achieved when using the normalized version of the multicenter indices, and thus, here, we only present the original values for these indices.

For the series of indices used, we have that the lower the FLU index, the higher the PDI, and the more positive the MCI values,[39] the more aromatic the rings.

Computational Details

All calculations have been performed with the Gaussian 03[40] and AIMPAC[41] packages of programs, at the B3LYP level of theory[42] with the 6-311G(d,p) basis set (Cartesian *d* and *f* functions).[43]

Calculation of atomic overlap matrices and computation of ESI and MCI have been performed with the AIMPAC[41] and ESI-3D[44] collection of programs. Calculation of these ESIs with the density functional theory (DFT) can not be performed exactly because the electron-pair density is not available at this level of theory.[45] As an approximation, we have used the Kohn−Sham orbitals obtained from a DFT calculation to compute Hartree−Fock (HF)-like DIs through eq 2 that do not account for electron-correlation effects. In practice, the values of the ESIs obtained by using this approximation are generally closer to the HF values than correlated ESIs obtained with a configuration interaction method.[30,45]

The numerical accuracy of the QTAIM calculations has been assessed by using two criteria: (i) the integration of the Laplacian of the electron density ($\nabla^2\rho(r)$) within an atomic basin must be close to zero, and (ii) the number of electrons in a molecule must be equal to the sum of all the electron populations of the molecule and also to the sum of all the localization indices and half of the DIs in the molecule. For all atomic calculations, integrated absolute values of $\nabla^2\rho(r)$ were always less than 0.001 au. For all molecules, errors in the calculated number of electrons were always below 0.01 au.

Preliminary Considerations

Before starting the analysis of the results, we should question what happens to the total electronic delocalization when an electron is added (or removed) from a reference species. Is it always the case that the total electronic delocalization raises when the number of the electrons in a given system increases? A paradigmatic example that can help us answer this question is the H_2 molecule.[46,47] This molecule in the ground state has the σ_g^2 electronic configuration. In this paragraph, we use A and B to refer to the two H atoms of H_2 and H_2^-, while *a* and *b* are used to refer to the bonding σ_g and antibonding σ_u* MOs of H_2, respectively. The ground-state wave function can be written as

$$^1\Psi = \frac{1}{\sqrt{2}} a(1)\, a(2)[\alpha(1)\, \beta(2) - \alpha(2)\, \beta(1)] \qquad (10)$$

By taking into account the restrictions derived from the $D_{\infty h}$ symmetry, the MO overlaps and the corresponding DI derived from eq 2 are

$$S_{aa}(\mathrm{A}) = S_{aa}(\mathrm{B}) = S_{bb}(\mathrm{A}) = S_{bb}(\mathrm{B}) = \frac{1}{2} \qquad (11)$$

$$\delta(\mathrm{A}, \mathrm{B}) = 4S_{aa}(\mathrm{A})\, S_{aa}(\mathrm{B}) = 1 \qquad (12)$$

Thus, the DI in the ground state of the H_2 molecule is exactly 1 at the restricted HF or DFT (in the HF-like approximation) levels, irrespectively of the basis set or internuclear distance. Therefore, one electron is localized (half in each H atom), and the other is delocalized between the two H atoms. The inclusion of Coulomb correlation in the wave function results in a reduction of the DI of H_2.[47] Now, we add an electron to the H_2 molecule to form H_2^-. For this system, the overlaps between MOs are those of eq 11, and the DI is given by

$$\delta(\mathrm{A}, B) = 2[2S_{aa}(\mathrm{A})\, S_{aa}(\mathrm{B}) + S_{bb}(\mathrm{A})\, S_{bb}(\mathrm{B}) + \\ S_{ab}(\mathrm{A})\, S_{ab}(\mathrm{B}) + S_{ba}(\mathrm{A})\, S_{ba}(\mathrm{B})]\ \delta \\ \delta(\mathrm{A}, \mathrm{B}) = 1.5 - 4(S_{ab})^2 \qquad (13)$$

The extra electron in H_2^-, compared to H_2, has two different effects on δ(A,B). In one hand, one electron in the σ_u* orbital, on its own, contributes 0.5 to δ(A,B), as each of the two electrons of H_2. On the other hand, the extra electron correlates with the same-spin electron in the σ_g orbital and reduces δ(A,B) by $-4S_{ab}(\mathrm{A})^2$. Therefore, the answer to our question is that depending on the overlap between σ_g and σ_u* orbitals (and, in general, between the involved MOs), there could be an increase or a reduction of the electronic delocalization. For more details about electron delocalization in H_2 and H_2^-, see ref 46.

Let us now consider 2π-electron cyclic systems. These two electrons populate the same orbital, and at the HF level, because Coulomb correlation is not taken into account, these α and β electrons present no interaction. For instance, for $C_4H_4^{2+}$, with D_{4h} symmetry, four carbon atoms (A,B,C,D), and *a* as the occupied π-MO, the wave function can be written again as eq 10, and the π-MO overlaps and the corresponding DI, when taking into account the restrictions derived from the D_{4h} symmetry, are

$$S_{aa}(\mathrm{A}) = S_{aa}(\mathrm{B}) = S_{aa}(\mathrm{C}) = S_{aa}(\mathrm{D}) = \frac{1}{4} \qquad (14)$$

$$\delta(\mathrm{A}, \mathrm{B}) = 4S_{aa}(\mathrm{A})\, S_{aa}(\mathrm{B}) = \frac{1}{4} \qquad (15)$$

The total number of combinations between atom pairs in one ring can be calculated as

$$N_{\mathrm{DI}} = \binom{n}{2} \qquad (16)$$

where *n* is the number of atoms of the ring. Thus, for a four-membered ring, we have six possible combinations ($N_{\mathrm{DI}} = 6$):

$$\delta(\mathrm{A,B}) = \delta(\mathrm{A,C}) = \delta(\mathrm{A,D}) = \delta(\mathrm{B,C}) = \delta(\mathrm{B,D}) = \delta(\mathrm{C,D}) = \frac{1}{4} \quad (17)$$

Therefore, the total π-electron delocalization is

$$\delta_\pi = \sum_i \delta_i = 6\frac{1}{4} = 1.5 \quad (18)$$

By following similar reasoning, the total π-electron delocalization in $C_6H_6^{4+}$ is 5/3. In general, for a D_{nh} $C_nH_n^{(n-2)+}$ annulene with n edges, it is $2(n-1)/n$, and this means that, for $n = \infty$, the two electrons are totally delocalized. As before, these results are independent of the basis set and internuclear distances insofar as the D_{nh} symmetry is preserved. Thus, when a pair of independent electrons is added to an annulene, the increase in the electron delocalization ranges from 1 to 2 e, the exact change depending on the size of the annulene. Obviously, the added electrons are usually not independent and interact with the rest of the π system. Consequently, these values have to be taken as an upper-bound to the actual change in total π-electron delocalization.

Results and Discussion

This section is organized as follows. First, we prove that the total electronic delocalization of a given annulene does not change significantly whether or not one takes into account the nuclear and electronic relaxation due to the change in the number of electrons in the system. Second, we show that, for open-shell systems obtained after adding or removing two electrons, the singlet and triplet electronic states yield similar total electronic delocalizations. Finally, we analyze the changes in total electronic delocalization in a series of aromatic and antiaromatic systems and their dications and dianions.

A. Effect of the Nuclear and Electronic Relaxation. In this first subsection, we analyze to which extent the electron and the geometry relaxation affect the electron delocalization upon addition/extraction of two electrons. For such purpose, we have first calculated the total delocalization (δ_{tot}) with the corresponding σ and π contributions for a series of four planar monocycle molecules (C_6H_6, planar C_8H_8, C_4H_4, and $C_5H_5^-$) by means of three different schemes: (a) full geometry and MO relaxation of all N, $N-2$, and $N+2$ species (OPT); (b) geometry optimization only for N species; $N-2$ and $N+2$ keep the geometry of N, but the MOs are fully relaxed (GEO); and (c) geometry optimization only for N species; $N-2$ and $N+2$ keep the geometry and the MOs of the N system, and thus, the wave function of N species is used throughout the calculations (ONLY).

Before going into detail with the results, it is convenient to mention that C_6H_6 and $C_5H_5^-$ present degenerated HOMO and LUMO states (see Figure 1); however, we have checked that the effect of either populating with two electrons any of the LUMO orbitals or removing two electrons from any of the HOMO orbitals is negligible.

Table 1 encloses the DIs obtained for benzene through the three schemes. It is observed how, for C_6H_6, the OPT approach gives $\delta_{\mathrm{tot}} = 15.65$ e, from which $\delta_\sigma = 12.26$ e and $\delta_\pi = 3.39$ e. As aforementioned, we are going to focus on this last δ_π value, because our goal is to analyze the $4n + 2$ rule, which concerns π electrons. Moreover, when adding or removing π electrons, δ_σ remains approximately constant in all cases. From $C_6H_6^{2+}$ to C_6H_6, δ_π increases by 0.70 e (Δ_1), whereas from C_6H_6 to $C_6H_6^{2-}$, δ_π increases by 0.09 e (Δ_2), in line with our hypothesis that going from $4n$ ($C_6H_6^{2+}$) to ($4n + 2$) (C_6H_6) system, the incoming electrons are largely delocalized, whereas from $4n + 2$ to $4n$ ($C_6H_6^{2-}$) system, the added electrons are mostly localized. Let us note in passing that the electronic spectra of $C_6H_6^{2+}$ has been recently reported.[48] Now, going down in Table 1, it is seen how δ_π values obtained from the GEO approach are almost the same as those from OPT. In particular, Δ_1 and Δ_2 are 0.69 and 0.10 e, respectively. And, more importantly, δ_π values from the ONLY approach are also very close, with $\Delta_1 = 0.76$ e and $\Delta_2 = 0.11$ e. This observation is really important because it shows that the wave function obtained without relaxing neither the geometry nor the MOs is good enough to describe the electron delocalization upon extraction/addition of two electrons. Obviously, by no means, we state here that the wave function should be close enough. For the OPT approach, a smaller different basis set, 6-31G(d), has been used for comparison to assess the influence of the basis set, which is proven to be small (see Table 1).

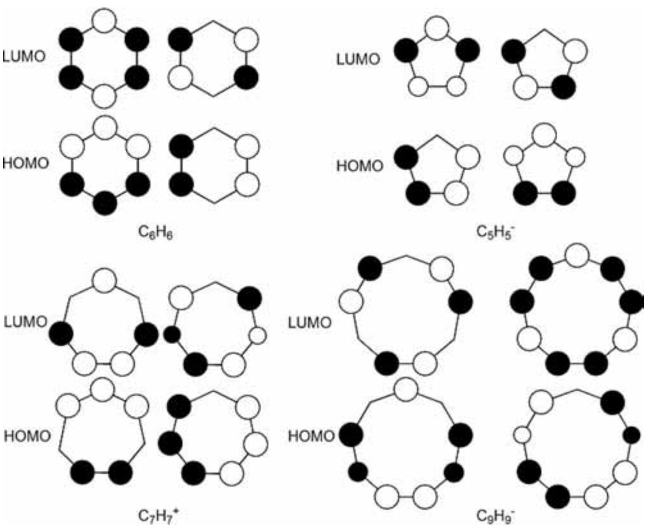


Figure 1. HOMO and LUMO orbital diagrams of C_6H_6, $C_5H_5^-$, $C_7H_7^+$, and $C_9H_9^-$.

On the other hand, for planar C_8H_8, example of an antiaromatic system, it is observed in Table 2 that for all approaches, both Δ_1 and Δ_2 values are similar and opposite to our hypothesis of Δ_1 close to 0 and Δ_2 close to 1, thus not following exactly the expected trend from Hückel's rule. However, as for benzene, we also obtain close results between the OPT and ONLY approaches (see Table 2). Thus, the ONLY approach for this system causes small differences in Δ_1 and Δ_2 of 0.04 and 0.09 e, respectively, with respect to the fully optimized values. Finally, $C_5H_5^-$ and C_4H_4 systems also corroborate the suitable use of the ONLY approach (see Tables S1 and S2 of the Supporting Information).

In addition, Table 1 also encloses the values of three electronic aromaticity indices (PDI, FLU, and MCI), calculated at the three analyzed schemes for benzene. Again, it is observed that the values obtained by means of the ONLY approach are very close to those of OPT, thus confirming the suitability of this methodology. As expected, the three approaches consider an increase of aromaticity from $N-2$ to N and a decrease from N to $N+2$, and the values just differ in the third decimal place. Table 2 encloses the FLU and MCI values for C_8H_8 (PDI can only be applied to 6-MRs), and in this case, a decrease from $N-2$ to N and an increase from N to $N+2$ are observed. Again, the adequacy of the ONLY approach is proven.

B. Effect of Multiplicity on the Electronic Delocalization. Most aromatic molecules studied present D_{nh} symmetry, and they have two HOMO and two LUMO orbitals energetically

TABLE 1: Total DI (δ_{tot} in e) for Benzene System with N, $N - 2$, and $N + 2$ electrons[a]

	C_6H_6					
	$N - 2$	N	$N + 2$	Δ_1	Δ_2	*diff*
			OPT B3LYP/6-311G**			
δ_{tot}	14.524	15.650	15.718	1.125	0.069	
δ_σ	11.834	12.264	12.244	0.429	−0.020	
δ_π	2.690	3.386	3.474	0.696	0.088	−0.608
PDI	0.050	0.103	0.062	0.054	−0.042	−0.095
FLU	0.029	0.000	0.015	−0.029	0.015	0.044
MCI	−0.013	0.073	0.002	0.085	−0.071	−0.156
			GEO B3LYP/6-311G**			
δ_{tot}	14.600	15.650	15.731	1.049	0.082	
δ_σ	11.904	12.264	12.249	0.360	−0.015	
δ_π	2.697	3.386	3.482	0.690	0.096	−0.594
PDI	0.069	0.103	0.061	0.035	−0.043	−0.078
FLU	0.023	0.000	0.021	−0.023	0.021	0.044
MCI	−0.020	0.073	0.003	0.093	−0.069	−0.162
			ONLY B3LYP/6-311G**			
δ_{tot}	14.863	15.618	15.731	0.755	0.113	
δ_σ	12.249	12.249	12.249	0.000	0.000	
δ_π	2.614	3.369	3.482	0.755	0.113	−0.642
PDI	0.069	0.104	0.061	0.035	−0.044	−0.079
FLU	0.028	0.000	0.021	−0.028	0.021	0.049
MCI	−0.012	0.073	0.003	0.086	−0.070	−0.156
			OPT B3LYP/6-31G*			
δ_{tot}	14.446	15.558	15.562	1.112	0.004	
δ_σ	11.768	12.223	12.154	0.455	−0.069	
δ_π	2.678	3.335	3.407	0.657	0.072	−0.585
PDI	0.050	0.105	0.059	0.055	−0.046	−0.101
FLU	0.029	0.000	0.034	−0.029	0.034	0.063
MCI	−0.013	0.078	0.001	0.091	−0.076	−0.167
			OPT UB3LYP/6-311G**, $N - 2$ Triplet, $N + 2$ Triplet			
δ_{tot}	14.370	15.650	16.333	1.248	0.715	
δ_σ	11.880	12.264	12.875	0.369	0.626	
δ_π	2.490	3.386	3.458	0.879	0.089	−0.791
PDI	0.112	0.103	0.080	−0.007	−0.025	−0.017
FLU	0.011	0.000	0.006	−0.011	0.006	0.017
MCI	0.157	0.073	0.071	−0.084	−0.002	0.081
			GEO UB3LYP/6-311G**, $N - 2$ Triplet, $N - 2$ Triplet			
δ_{tot}	14.433	15.650	16.433	1.185	0.815	
δ_σ	11.940	12.264	12.933	0.309	0.684	
δ_π	2.494	3.386	3.500	0.876	0.131	−0.745
PDI	0.112	0.103	0.083	−0.008	−0.021	−0.013
FLU	0.010	0.000	0.004	−0.010	0.004	0.014
MCI	0.156	0.073	0.070	−0.083	−0.003	0.080
			ONLY UB3LYP/6-311G**, $N - 2$ Triplet, $N + 2$ Triplet			
δ_{tot}	14.816	15.618	15.700	0.802	0.082	
δ_σ	12.273	12.249	12.249	−0.024	0.000	
δ_π	2.542	3.369	3.451	0.827	0.082	−0.745
PDI	0.109	0.104	0.092	−0.005	−0.012	−0.007
FLU	0.015	0.000	0.002	−0.015	0.001	0.016
MCI	0.143	0.073	0.090	−0.069	0.017	0.086

[a] δ_σ and δ_π stand for total σ and π DIs (in e), respectively. $\Delta_1 = [N] - [N - 2]$, $\Delta_2 = [N + 2] - [N]$, and *diff* $= \Delta_2 - \Delta_1$, in e, for any of the properties. PDI, FLU, and MCI aromaticity indices are also enclosed.

TABLE 2: Total DI (δ_{tot} in e) for C_8H_8 system with N, $N - 2$, and $N + 2$ electrons[a]

	C_8H_8					
	$N - 2$	N	$N + 2$	Δ_1	Δ_2	*diff*
			OPT B3LYP/6-311G**			
δ_{tot}	20.057	20.892	21.281	0.836	0.389	
δ_σ	16.124	16.400	16.387	0.276	−0.013	
δ_π	3.932	4.492	4.894	0.560	0.401	−0.159
FLU	0.002	0.052	0.001	0.049	−0.051	−0.100
MCI	0.041	−0.001	0.015	−0.042	0.016	0.057
			GEO B3LYP/6-311G**			
δ_{tot}	20.060	20.892	21.321	0.832	0.429	
δ_σ	16.130	16.400	16.407	0.270	0.008	
δ_π	3.930	4.492	4.914	0.562	0.422	−0.141
FLU	0.005	0.052	0.004	0.047	−0.048	−0.095
MCI	0.040	−0.001	0.014	−0.040	0.015	0.055
			ONLY B3LYP/6-311G**			
δ_{tot}	20.344	20.866	21.172	0.522	0.307	
δ_σ	16.389	16.389	16.389	0.000	0.000	
δ_π	3.955	4.477	4.783	0.522	0.307	−0.215
FLU	0.007	0.052	0.004	0.045	−0.048	−0.093
MCI	0.038	−0.001	0.015	−0.038	0.016	0.054
			OPT UB3LYP/6-311G**, N Triplet			
δ_{tot}	20.057	20.782	21.281	0.726	0.498	
δ_σ	16.124	16.405	16.387	0.281	−0.018	
δ_π	3.932	4.376	4.894	0.443	0.518	0.074
FLU	0.002	0.001	0.001	−0.001	−0.001	0.000
MCI	0.041	0.055	0.015	0.014	−0.040	−0.054

[a] δ_σ and δ_π stand for total σ and π DIs (in e), respectively. $\Delta_1 = [N] - [N - 2]$, $\Delta_2 = [N + 2] - [N]$, and *diff* $= \Delta_2 - \Delta_1$, in e, for any of the properties. PDI, FLU, and MCI aromaticity indices are also enclosed.

degenerated. Therefore, when two electrons are either removed or added, the dilemma between treating the charged system as a singlet or a triplet state emerges. Hückel's rule considers $(4n + 2)\pi$ systems aromatic and $4n\pi$ systems antiaromatic at their singlet state, whereas the opposite trend is predicted when we consider the lowest-lying triplet state (Baird's rule). Because Hückel's rule is different for singlet and triplet states, electronic delocalizations in the N, $N - 2$, and $N + 2$ systems will be computed at their lowest-lying singlet state.

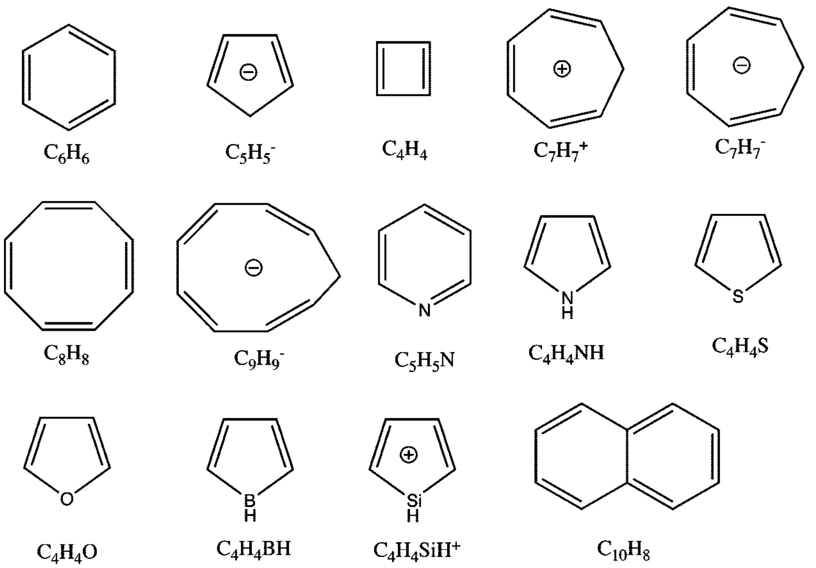
However, it is interesting to analyze the effect of changing the multiplicity on the electronic delocalization of the $N - 2$ and $N + 2$ systems. Table 1 encloses the calculation of δ_π by means of the same three approaches at the triplet state for $C_6H_6^{2+}$ and $C_6H_6^{2-}$ systems. By comparison to the above values obtained at the corresponding singlet state, it is seen how close the δ_π values are, thus proving that the fact of analyzing the electronic distribution for $C_6H_6^{2+}$ and $C_6H_6^{2-}$ at either the singlet or triplet state does almost not affect the total π-electron delocalization values. For instance, for the ONLY approach, the differences in Δ_1 and Δ_2 from both electronic states are only 0.07 and 0.03 e, respectively.

On the other hand, the three aromaticity measures calculated for this triplet state largely differ from those calculated at the corresponding singlet state, but this is because they correctly reproduce the expected trend for the Hückel's rule for triplets; that is, $4n$ systems are aromatic, and $4n + 2$ are antiaromatic. Therefore, the aromatic indices give $C_6H_6^{2-}$ and $C_6H_6^{2+}$ in their lowest-lying triplet state as aromatic systems. Thus, although the total and the π-electronic delocalization do not differentiate between the aromatic triplet and the antiaromatic singlet states of $C_6H_6^{2-}$ or $C_6H_6^{2+}$, the electronic indices of aromaticity allow for such distinction.

Finally, for antiaromatic systems, we do not have degenerated states, because the antiaromatic C_4H_4 has D_{2h} symmetry instead of D_{4h} or C_8H_8 has D_{4h} symmetry instead of D_{8h} because of the Jahn−Teller distortion. In spite of that, we have calculated the values for C_8H_8 for its triplet state (see Table 2). It is seen how Δ_1 and Δ_2 for δ_π differ by just 0.12 e compared to the equivalent values for the singlet state calculated with the OPT approach. Finally, it is worth noticing that, with respect to the aromaticity indices, C_8H_8 singlet is antiaromatic, whereas at the triplet state, it becomes aromatic.

C. Aromaticity Analysis under Electronic Measures. In the present subsection, a series of aromatic and antiaromatic systems (see Scheme 2) will be analyzed by means of electronic delocalization measures, with the aim to discuss the behavior of Hückel's rule when either adding or removing two electrons

SCHEME 2



from a certain system. The ONLY approach is the one chosen because of its low computational cost, as previously discussed.

Table 3 encloses the 13 monocycle systems studied, plus naphthalene as a bicyclic one. In addition to the total, σ- and π-total delocalizations, the electronic-based PDI, FLU, and MCI aromaticity indices have also been calculated for each molecule.

In the case of benzene, starting from $C_6H_6^{4+}$, we have a total π-electron delocalization of 1.667 e, a value that can be readily obtained by simple symmetry considerations for a 2π-electron system (*vide supra*). Adding two electrons to obtain the $C_6H_6^{2+}$ dication has the effect of increasing the total π-electron delocalization by 0.947 e, a quite important increase, although far from the expected 1.667 e if the two added electrons were completely independent. Because we are moving from a 2π-aromatic to a 4π-antiaromatic species, we did not expect such a large increase in the total π-electron delocalization. Going from 2π- to 4π-electron species leads invariably to an important increase of π-electronic delocalization, the reason being that when having initially only 2π electrons, the interaction of these two electrons with the incoming ones is not strong enough to avoid the increase in the π-electronic delocalization. The two added electrons occupy the e_{1g} degenerated orbitals of benzene. By just looking at the shapes of these orbitals and that of the already doubly occupied a_{2u} orbital, one can see that there are more $S_{a_{2u}e_{1g}}(A)\ S_{a_{2u}e_{1g}}(B)$ overlap products contributing positively than negatively to the total π-electron delocalization, which explains the increase in the delocalization.[49] By adding two more electrons, we reach benzene with an increase in the total π-electron delocalization of 0.755 e. Finally, adding two more electrons has a minor effect in the π-electronic delocalization that increases by merely 0.113 e, as expected for an aromatic system that increases by 2 e its π-electronic population.

From Table 3, it is seen that Δ_1 is larger than Δ_2 in aromatic systems, Δ_1 being in general closer to 1 and Δ_2 closer to 0. In some cases, a negative value for Δ_2 is observed, that is, a decrease of the total π-electron delocalization. This is caused by the overlaps between the MOs already occupied and those of the two additional electrons, which give an overall effect that localizes not only the two electrons added but also those already existing electrons in the molecule.

Among antiaromatic compounds, C_4H_4, C_4H_5B, $C_4H_5Si^+$, $C_7H_7^-$, and planar C_8H_8, none exhibits a behavior somewhat close to the expected trend of Δ_1 close to 0 and Δ_2 close to 1. First of all, special attention must be paid to those systems containing 4π electrons, C_4H_4, C_4H_5B, and $C_4H_5Si^+$, which suffer from the problem that their $N - 2$ counterparts are left only with 2π electrons. As seen before, these two electrons are fully delocalized, the electron delocalization being $2(n - 1)/n$ e. In the particular case of a four-membered ring with D_{4h} symmetry, this value is 1.5, quite close to the π-electron delocalization value for D_{2h} $C_4H_4^{2+}$ species in Table 3. For a D_{5h} five-membered ring (C_4H_4BH or $C_4H_4SiH^+$), δ_π would be 1.6, also in agreement with Table 3, the difference being attributed to the actual C_{2v} symmetry instead of D_{5h}.

Furthermore, the fact that 8π-electrons species, $C_7H_7^-$ and C_8H_8 exhibit larger delocalization in their $N - 2$ analogues, thus reducing the value of Δ_1, gives support to this argument. Notwithstanding, Δ_1 and Δ_2 values for antiaromatic do not follow the expected trends. The results obtained in these cases cannot be easily related with the Hückel's rule. Therefore, the value of electron delocalization does not help assign a clear frontier value between the aromatic and antiaromatic compounds and should be rejected as a possible measure of aromaticity.

In addition to total delocalization values, Table 3 also encloses the electronic-based aromaticity indices, together with the corresponding differences from $N - 2$ to N and from N to $N + 2$. For an aromatic system, we expect larger PDI and MCI values and smaller FLU values when going from $N - 2$ to N, whereas we expect smaller PDI and MCI values and larger FLU values from N to $N + 2$. The opposite trend is expected for antiaromatic systems. This is accomplished for all systems. As we can observe in Table 3, aromatic systems present negative differences between Δ_2 and Δ_1 (*diff*) for PDI and MCI and positive diff for FLU, and all antiaromatic systems present negative *diff* for FLU and positive *diff* for MCI. Therefore, the differences between the aromaticity indices do allow a clear distinction between aromatic and antiaromatic systems, which perfectly complements the above π-delocalization analysis.

Just to conclude, naphthalene has been included as an example of a polycyclic system, which also behaves as an aromatic system with respect to changes in δ_π from $N - 2$ to N and from N to $N + 2$. In this case, the PDI, FLU, and MCI for one of the two six-membered rings of naphthalene also exhibit the expected trend when going from a $4n$ (positively or negatively charged naphthalene) system to $4n + 2$ (neutral naphthalene).

TABLE 3: Total DI (δ_{tot} in e) for a series of moncycles with N, $N - 2$, and $N + 2$ electrons at B3LYP/6-311G** level with ONLY approach[a]

	$N - 2$	N	$N + 2$	Δ_1	Δ_2	*diff*
C_6H_6						
δ_{tot}	14.863	15.618	15.731	0.755	0.113	
δ_σ	12.249	12.249	12.249	0.000	0.000	
δ_π	2.614	3.369	3.482	0.755	0.113	−0.642
PDI	0.069	0.104	0.061	0.035	−0.044	−0.079
FLU	0.028	0.000	0.021	−0.028	0.021	0.049
MCI	−0.012	0.073	0.003	0.086	−0.070	−0.156
$C_5H_5^-$						
δ_{tot}	12.634	13.177	13.056	0.543	−0.121	
δ_σ	10.204	10.204	10.204	0.000	0.000	
δ_π	2.430	2.973	2.852	0.543	−0.121	−0.664
FLU	0.055	0.000	0.015	−0.054	0.015	0.069
MCI	−0.023	0.073	0.010	0.097	−0.063	−0.160
C_4H_4						
δ_{tot}	9.562	10.259	10.382	0.697	0.123	
δ_σ	8.043	8.043	8.043	0.000	0.000	
δ_π	1.519	2.217	2.339	0.698	0.122	−0.575
FLU	0.024	0.105	0.006	0.082	−0.099	−0.181
MCI	0.181	0.010	0.071	−0.171	0.062	0.233
$C_7H_7^+$						
δ_{tot}	17.026	17.890	18.155	0.864	0.265	
δ_σ	14.214	14.214	14.214	0.000	0.000	
δ_π	2.813	3.677	3.942	0.864	0.265	−0.599
FLU	0.041	0.001	0.017	−0.040	0.017	0.057
MCI	−0.009	0.058	−0.006	0.067	−0.064	−0.131
$C_7H_7^-$						
δ_{tot}	18.000	18.414	18.600	0.414	0.185	
δ_σ	14.317	14.317	14.317	0.000	0.000	
δ_π	3.683	4.097	4.282	0.414	0.185	−0.229
FLU	0.010	0.036	0.003	0.026	−0.033	−0.060
MCI	0.047	−0.004	0.010	−0.051	0.014	0.065
C_8H_8						
δ_{tot}	20.344	20.866	21.172	0.522	0.307	
δ_σ	16.389	16.389	16.389	0.000	0.000	
δ_π	3.955	4.477	4.783	0.522	0.307	−0.215
FLU	0.007	0.052	0.004	0.045	−0.048	−0.093
MCI	0.038	−0.001	0.015	−0.038	0.016	0.054
$C_9H_9^-$						
δ_{tot}	23.318	23.802	24.590	0.484	0.787	
δ_σ	18.516	18.516	18.516	0.000	0.000	
δ_π	4.802	5.287	5.374	0.485	0.087	−0.397
FLU	0.018	0.000	0.007	−0.018	0.007	0.025
MCI	−0.007	0.016	−0.001	0.022	−0.017	−0.039
C_5H_5N						
δ_{tot}	13.518	14.359	14.367	0.841	0.008	
δ_σ	11.071	11.071	11.071	0.000	0.000	
δ_π	2.446	3.287	3.296	0.841	0.008	−0.833
PDI	0.067	0.104	0.058	0.037	−0.047	−0.084
FLU	0.036	0.004	0.018	−0.031	0.013	0.044
MCI	−0.005	0.070	0.005	0.074	−0.065	−0.139
C_4H_4NH						
δ_{tot}	11.688	12.383	12.186	0.694	−0.197	
δ_σ	9.614	9.614	9.614	0.000	0.000	
δ_π	2.074	2.769	2.572	0.695	−0.197	−0.891
FLU	0.042	0.004	0.016	−0.038	0.012	0.050
MCI	−0.014	0.049	0.011	0.062	−0.037	−0.099
C_4H_4S						
δ_{tot}	11.244	11.889	11.665	0.645	−0.224	
δ_σ	9.185	9.185	9.185	0.000	0.000	
δ_π	2.059	2.704	2.480	0.645	−0.224	−0.869
FLU	0.025	0.011	0.025	−0.014	0.014	0.028
MCI	0.014	0.041	0.014	0.027	−0.027	−0.054
C_4H_4O						
δ_{tot}	10.572	11.278	11.117	0.707	−0.161	
δ_σ	8.640	8.640	8.640	0.000	0.000	
δ_π	2.031	2.638	2.477	0.607	−0.161	−0.768
FLU	0.040	0.087	0.119	0.046	0.033	−0.014
MCI	−0.021	0.034	0.013	0.054	−0.020	−0.075
C_4H_4BH						
δ_{tot}	10.972	11.702	12.390	0.730	0.688	
δ_σ	9.421	9.421	9.421	0.000	0.000	
δ_π	1.550	2.281	2.969	0.731	0.688	−0.042
MCI	0.022	−0.003	0.040	−0.026	0.043	0.069
$C_4H_4SiH^+$						
δ_{tot}	10.915	11.632	12.369	0.717	0.737	
δ_σ	9.338	9.338	9.338	0.000	0.000	
δ_π	1.577	2.294	3.031	0.717	0.737	0.019
MCI	0.077	−0.012	0.058	−0.089	0.070	0.159
$C_{10}H_8$						
δ_{tot}	24.554	25.079	25.318	0.526	0.238	
δ_σ	19.441	19.441	19.441	0.000	0.000	
δ_π	5.113	5.639	5.877	0.526	0.238	−0.287
PDI	0.048	0.075	0.047	0.031	−0.033	−0.064
FLU	0.014	0.010	0.014	−0.006	0.004	0.010
MCI	0.020	0.039	0.020	0.019	−0.019	−0.038

[a] δ_σ and δ_π stand for total σ and π DIs (in e), respectively. $\Delta_1 = [N] - [N - 2]$, $\Delta_2 = [N + 2] - [N]$, and $diff = \Delta_2 - \Delta_1$, in e, for any of the properties. PDI, FLU, and MCI aromaticity indices are also enclosed.

These results show that the existing electronic aromaticity indices behave correctly with respect to the Hückel's rule.

Conclusions

In this study, the Hückel's $4n + 2$ rule has been analyzed in detail by means of electronic delocalization measures of the π electrons. In particular, the total π-delocalization index (δ_π) has been proposed for the study of a series of systems in which two electrons have been either added or removed. For an aromatic system, from $N - 2$ to N, we expect the two added electrons to delocalize, whereas from N to $N + 2$, the added electrons should localize. For an antiaromatic system, the opposite behavior is expected. It has been shown how δ_π perfectly follows the expected trend for aromatic systems, but unexpected trends emerge in antiaromatic systems, especially for the $N - 2$ species in those cases where only 2π electrons are left in the system. This kind of analysis does not allow assigning a clear frontier between aromatic and antiaromatic systems. However, the same analysis done by means of three electronic-based aromaticity measures (PDI, FLU, and MCI) can clearly assign an aromatic or antiaromatic character to each system by taking the differences from $N - 2$ to N and from N to $N + 2$, thus proving the validity of these electronic aromaticity indices to explain the Hückel's rule.

On the other hand, we have found that when analyzing the total π-electronic delocalization of this series of neutral systems and the corresponding charged species, the effect of geometry and electron relaxation are small enough to be neglected. In addition, we have shown that in dicationic or dianionic D_{nh} annulenes, the lowest-lying singlet and triplet states present similar delocalization values.

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Supporting Information Available: Total DIs for $C_5H_5^-$ and C_4H_4 obtained by using the three possible approaches and for both singlet and triplet states. This material is available free of charge via the Internet at http://pubs.acs.org.

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