Patterns of π-electron delocalization in aromatic and antiaromatic organic compounds in the light of Hückel's $4n + 2$ rule†

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The total π-electron delocalization of a series of classical aromatic and antiaromatic organic compounds is separated into *ortho* (1,2), *meta* (1,3), *para* (1,4), and successive contributions (the so-called delocalization crossed terms) and the changes that take place in these crossed terms when two electrons are added or removed are analyzed. Our results show that these changes follow a similar alternation pattern in all cases. The patterns found represent a kind of electronic footprints that makes it possible to discern between aromatic and antiaromatic systems.

Introduction

Hückel's $4n + 2$ rule formulated in 1931[1] represents one of the first and most successful approaches to rationalize aromaticity from a theoretical point of view. Using Hückel's molecular orbital (HMO) theory, the aromatic sextet (introduced some years before by Crocker[2]) was interpreted by Hückel as a closed shell that provides extra stability, similar to the situation found in noble gas elements. Then, according to this rule, a monocyclic system with $(4n + 2)\pi$-electrons is aromatic, whereas a system with $4n\pi$-electrons is antiaromatic. The preparation of the cycloheptatrienyl cation, $C_7H_7^+$, by Doering and Knox in 1954[3] is considered as the first experimental verification of Hückel's rule.[4] Very recently, Mayer has given a theoretical derivation for Hückel's rule.[5] Although the original derivation of Hückel's rule is only strictly valid for monocyclic conjugated systems, this rule was extended to polycyclic aromatic hydrocarbons (PAHs) by Glidewell and Lloyd[6] as follows: in PAHs, the total π-electron population tends to form the smallest $4n + 2$ groups of π-electrons and to avoid formation of the smallest $4n$ groups. A further development of Hückel's $4n + 2$ rule came when Baird showed, 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.[7] The identification[8] of the planar triplet ground states of $C_5H_5^+$ and $C_5Cl_5^+$ as well as a recent photoelectron spectroscopic study[9] of the first singlet and triplet states of $C_5H_5^+$ provided experimental support for Baird's extension of Hückel's $4n + 2$ rule. There is also an analogous to Hückel's rule for magnetic susceptibility.[10] More recently, the $2(n + 1)^2$ rule of aromaticity[11] for spherical compounds has been considered the spherical analog of the $4n + 2$ rule for the cyclic annulenes. Interestingly, the number of conjugated circuits of $4n + 2$ and $4n$ types has been taken by Randić[12] and Trinajstic[13] as a measure of aromaticity. Finally, it is worth noting that Hückel's $4n + 2$ rule is applied nowadays in many studies to discuss multifold aromaticity and antiaromaticity in all-metal clusters.[14]

From a theoretical point of view, resonance energy and ring current calculations of annulenes provided preliminary evidence for the reliability of Hückel's $4n + 2$ rule.[15] Later on the validity of Hückel's and Baird's rules was proved through nucleus independent chemical shifts (NICS) and aromatic stabilization energy (ASE) calculations by Schleyer *et al.*[16] as well as from the study of ring currents.[17] Moreover, the study of ring currents in $4n\pi$-electron monocycles[18] and a recent theoretical work[19] 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.

One of the key features of classical aromatic organic molecules is their π-electron delocalization. This electronic delocalization is a byproduct of geometric constraints imposed by σ-electrons and not a driving force by itself since π-electrons are known to favor localized structures.[20] However, the properties associated with PAHs[21] are in most cases linked to the delocalization of π-electrons.[22] Given the importance of this phenomenon, we decided to analyze in more detail the π-electron delocalization in aromatic compounds in light of Hückel's $4n + 2$ rule through electronic delocalization measures[23] of the π electrons.

In a first paper,[24] we studied the changes in the total π-delocalization index (δ_π) when two electrons have been either added to or removed from a series of aromatic $(4n + 2)\pi$ and antiaromatic $4n\pi$ organic compounds. The aim of the study was to investigate whether the δ_π values are useful for discerning between aromatic and antiaromatic systems. The idea was that when two electrons are added to an aromatic

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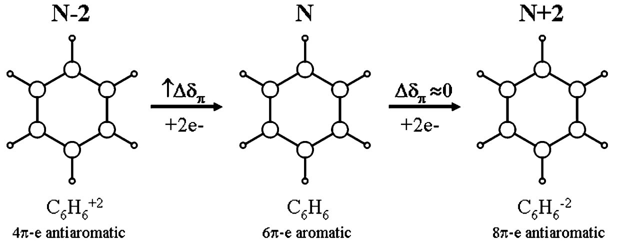


Scheme 1

system ((4n + 2)π electrons), we reach a 4nπ-electron system, which, according to Hückel's rule, should be antiaromatic. Thus, one could expect 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 4nπ electrons. If the same system loses two electrons, we likewise have a 4nπ-electron system, the system breaks its aromatic character, and therefore loss of electron delocalization is expected (see Scheme 1). For an antiaromatic species, one could anticipate exactly the opposite trend when going from $N - 2$ aromatic to N antiaromatic and from N to $N + 2$ aromatic π-electron system, N being the total number of electrons. In our previous study,[24] we found that δ_π perfectly follows the expected trend for aromatic systems, but unexpected trends emerged in antiaromatic systems. So, that analysis did not allow for a clear distinction between aromatic and antiaromatic systems based only on δ_π values.

The present work represents an extension of our previous study.[24] Our aim here is to separate the δ_π values into the *ortho* (1,2), *meta* (1,3), *para* (1,4), and successive contributions (crossed terms, see Fig. 1) and to analyze them in order to derive a series of patterns of changes in π-electron delocalization in aromatic and antiaromatic organic compounds when two electrons are added or removed. We will show that these patterns represent a kind of electronic footprints that makes it possible to discern between aromatic and antiaromatic systems. For such purpose, we have taken under study a series of compounds, the aromaticity or antiaromaticity of which is well-known. Our main goal is neither to develop a new aromaticity criterion nor to discuss the aromaticity of the systems studied, but to investigate the changes undergone by the different components of the π-electronic delocalization after adding or removing two electrons. We expect that such analysis will provide us with a deeper understanding of electronic delocalization in aromatic and antiaromatic compounds.

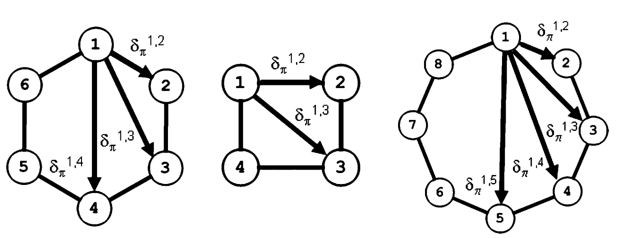


Fig. 1 Decomposition of electron delocalization in crossed-terms $\delta_\pi{}^{1,x}$ for C_6H_6, C_4H_4, and C_8H_8.

Methodology

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

$$\delta(A,B) = -2 \int_A \int_B \gamma_{XC}(\vec{\mathbf{r}_1}, \vec{\mathbf{r}_2}) d\vec{\mathbf{r}_1} d\vec{\mathbf{r}_2}. \qquad (1)$$

For monodeterminantal wave functions one obtains:

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

The summations in eqn (2) run over all occupied molecular spin-orbitals (MSOs). $S_{ij}(A)$ is the overlap between MOs i and j within the molecular space assigned to atom A. $\delta(A,B)$ 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 and successful[25–27] one is that where the partition is carried out in the framework of the quantum theory of atoms-in-molecules (QTAIM) of Bader,[28] by which atoms are defined in 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[29] or the Mulliken scheme,[30] because the QTAIM-ESI produces numbers closer to that which is expected from chemical intuition.[25,26,31]

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

$$\begin{aligned}\delta_{\mathrm{tot}} &= \sum_{A_i, A_j \neq A_i} \delta(A_i, A_j) \\ &= \sum_{A_i, A_j \neq A_i} \delta^{\pi}(A_i, A_j) + \sum_{A_i, A_j \neq A_i} \delta^{\sigma}(A_i, A_j) = \delta_\pi + \delta_\sigma\end{aligned} \qquad (3)$$

In addition, δ_π can be split into the different crossed contributions in the ring. For instance, for any six-membered ring (6-MR) and in particular for benzene, we have *ortho* (1,2), *meta* (1,3), and *para* (1,4) terms. In our study we have considered averaged values for the crossed terms (see Fig. 2). For any 6-MR we have:

$$\delta_\pi = 6\delta_\pi{}^{1,2} + 6\delta_\pi{}^{1,3} + 3\delta_\pi{}^{1,4}$$

$$\delta_\pi^{1,2} = \frac{\delta(1,2) + \delta(2,3) + \delta(3,4) + \delta(4,5) + \delta(5,6) + \delta(1,6)}{6}$$

$$\delta_\pi^{1,3} = \frac{\delta(1,3) + \delta(2,4) + \delta(3,5) + \delta(4,6) + \delta(1,5) + \delta(2,6)}{6}$$

$$\delta_\pi^{1,4} = \frac{\delta(1,4) + \delta(2,5) + \delta(3,6)}{3} \qquad (4)$$

Rings with an even number of atoms follow this previous scheme (see Fig. 2), where the number of farthest crossed

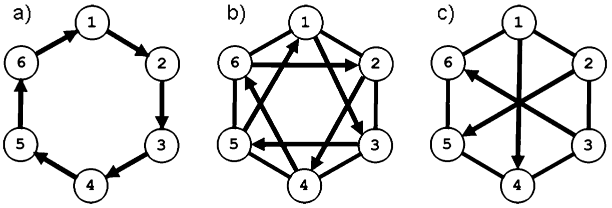


Fig. 2 C_6H_6 crossed contributions $\delta_\pi^{1,x}$ (a) $\delta_\pi^{1,2}$, (b) $\delta_\pi^{1,3}$, and (c) $\delta_\pi^{1,4}$.

terms, *i.e.* $\delta_\pi^{1,3}$ for 4-MRs, $\delta_\pi^{1,4}$ for 6-MRs or $\delta_\pi^{1,5}$ for 8-MRs, that contribute to the average value is half of the members of the ring (*e.g.* C_4H_4 have four $\delta_\pi^{1,2}$ and two $\delta_\pi^{1,3}$). On the other hand, for the rings with an odd number of atoms the number of farthest crossed terms is equal to the number of ring members. For instance, for any 7-MR:

$$\delta_\pi = 7\delta_\pi^{1,2} + 7\delta_\pi^{1,3} + 7\delta_\pi^{1,4}$$

$$\delta_\pi^{1,2} = \frac{\delta(1,2)+\delta(2,3)+\delta(3,4)+\delta(4,5)+\delta(5,6)+\delta(6,7)+\delta(1,7)}{7}$$

$$\delta_\pi^{1,3} = \frac{\delta(1,3)+\delta(2,4)+\delta(3,5)+\delta(4,6)+\delta(5,7)+\delta(1,6)+\delta(2,7)}{7}$$

$$\delta_\pi^{1,4} = \frac{\delta(1,4)+\delta(2,5)+\delta(3,6)+\delta(4,7)+\delta(1,5)+\delta(2,6)+\delta(3,7)}{7} \qquad (5)$$

In our previous work,[24] we proved that when analyzing the changes in the total π-electronic delocalization of a series of neutral systems and the corresponding $N \pm 2$ charged species, the effect of geometry and electron relaxation are small enough to be neglected. As total π-electronic delocalization, crossed-terms are hardly affected by geometry and electron relaxation (see section S1 of the supplementary information†). Therefore, for the present series of compounds under analysis, the geometry optimization is only carried out for the N species; then $N - 2$ and $N + 2$ systems keep the geometry and the MOs of the N system, and thus, the wave function of the N species is used throughout the calculations. Moreover, all systems taken into account in this study have been analyzed in their planar conformation. However, in some compounds, *e.g.* cyclooctatetraene, the planar structure is not a minimum. In order to study how the crossed terms are affected by the planarity of the system, we have analyzed the out-of-plane boat-like deformation of benzene and cyclooctatetraene (see section S2 of the supplementary information for complete results†). The crossed-terms slightly change when the out-of-plane deformation angle increases, but more relevantly, the aromaticity trends are not reversed along the out-of-plane distortion. Thus, the fact that geometry and electron relaxation do not affect the electron delocalization makes the study computationally cheaper and, more importantly, we have checked that the trends derived are not altered when using these approximations.

In addition, multiplicity effects have to be taken into account when two electrons are either added or removed from a D_{nh} compound (degenerated HOMO and LUMO orbitals). Our previous results[24] indicated that, for open-shell systems obtained after adding or removing two electrons, the singlet and triplet electronic states yield similar total π-electronic delocalizations. In the first part of the present work, we focus on the systems that follow Hückel's rule of aromaticity and, thus, electronic delocalization in the N, $N - 2$, and $N + 2$ species is computed at their lowest-lying singlet state. Afterwards multiplicity effects and Baird's rule are analyzed by means of crossed π-delocalization measures and then electronic delocalizations are computed for the lowest-lying triplet states of all monocycles up to 8-MRs.

For the aromaticity analysis we have applied the multicenter index (MCI),[30,32] as it has been recently proven to work correctly for the series of systems under study, especially for the fact that it can be applied to rings of different sizes and with the presence of heteroatoms.[33] MCI is a particular extension of the I_{ring} index.[34]

$$I_{\text{ring}}(\mathscr{A}) = \sum_{i_1,i_2,\ldots i_N} n_{i_1}\ldots n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2)\cdots S_{i_N i_1}(A_N) \qquad (6)$$

n_i being the occupancy of MO i. This expression is used both for closed-shell and open-shell species. In the particular case of a closed-shell monodeterminantal wavefunction we are left with a simpler expression:[35]

$$I_{\text{ring}}(\mathscr{A}) = 2^N \sum_{i_1,i_2,\ldots i_N}^{occ.MO} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2)\cdots S_{i_N i_1}(A_N) \qquad (7)$$

Summing up all the I_{ring} values resulting from the permutations of indices A_1, A_2, …, A_N the mentioned MCI index[30] is defined as:

$$MCI(\mathscr{A}) = \frac{1}{2N}\sum_{P(\mathscr{A})} I_{\text{ring}}(\mathscr{A}) \qquad (8)$$

where $P(\mathscr{A})$ stands for a permutation operator which interchanges the atomic labels A_1, A_2, …, A_N to generate up to the N! permutations of the elements in the string $\mathscr{A}$.[32,36] As a tendency, the more positive the MCI values,[37] the more aromatic the rings. In the same way as π-electron delocalization, the MCI values are hardly affected by the geometry and electron relaxation (see supplementary information†).

In addition and for comparison purposes, the above MCI aromaticity analysis has been complemented with the calculation of the geometry based harmonic oscillator model of aromaticity (HOMA) index,[38] the magnetic based nucleus independent chemical shift (NICS) indicator,[39] and the electronic based fluctuation (FLU) index.[40] HOMA values remain unchanged for $N - 2$ and $N + 2$ species if we use the geometries obtained for the N system. Therefore, to be able to use the HOMA index for the aromaticity analysis, in section D we have used fully optimized geometries with the only restriction that all molecular structures are kept planar. The planarity restriction allows the σ–π separation and the direct comparison with δ_π values. However, as we have already seen for crossed terms, HOMA is hardly affected by the planarity constraint, the HOMA values for fully optimized C_8H_8 and planar C_8H_8 are −0.25 and −0.20, respectively. We have considered closed-shell singlet species for all systems analyzed in sections A and B. Moreover, all monocycles up to 8-MRs studied in section A have been computed also in their triplet states.

All calculations have been performed with the Gaussian 03[41] and AIMPAC[42] packages of programs, at the B3LYP level of theory[43] with the 6-311G(d,p) basis set[44] using Cartesian d and f functions. Calculations of open-shell triplet species have been performed within the unrestricted methodology, while for the singlet molecules we have considered in all cases closed-shell situations and we have used the restricted formalism. We have checked that results obtained considering closed-shell or open-shell singlets do not differ significantly. Calculation of atomic overlap matrices (AOM) and computation of ESIs and MCIs have been performed with the AIMPAC[42] and ESI-3D[45] collection of programs. Calculation of these ESIs with the density functional theory (DFT) cannot be performed exactly because the electron-pair density is not available at this level of theory.[46] As an approximation, we have used the Kohn–Sham orbitals obtained from a DFT calculation to compute Hartree–Fock-like DIs through eqn (2). In particular, this equation does not account for electron correlation effects. In practice the values of the ESIs obtained using this approximation are generally closer to the Hartree–Fock values than correlated ESIs obtained with a configuration interaction method,[25,46] which means that the inclusion of Coulomb correlation increases the electronic localization, but always qualitatively keeping the same trends. The MCI values have also been obtained from the Kohn–Sham orbitals using eqns (6) and (8). The numerical accuracy of the QTAIM calculations has been assessed 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 equal 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 a.u. For all molecules, errors in the calculated number of electrons were always below 0.01 a.u.

Results and discussion

This section is laid out as follows. First, we discuss the crossed δ_π terms in monocyclic aromatic and antiaromatic organic molecules. Second, we study the same contributions in PAHs. Third, we discuss how the change of multiplicity affects these contributions. Finally, we quantify the aromaticity of all studied species by means of different indicators of aromaticity with special emphasis to MCI values.

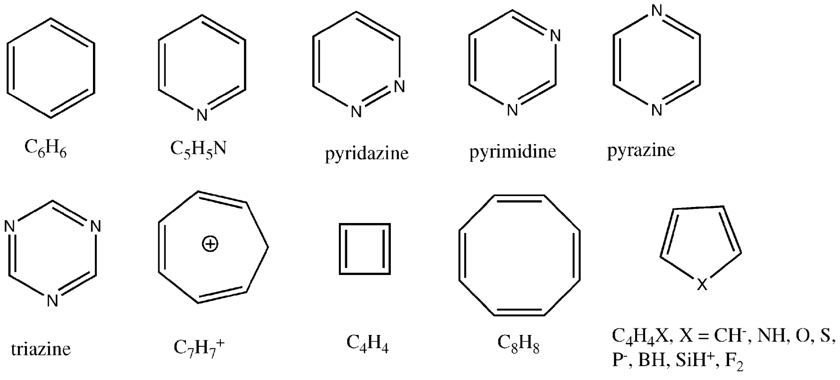
A δ_π crossed contributions in monocyclic systems

First, we focus on a series of aromatic 6- and 7-MRs, going from benzene to heteroaromatic systems (see Scheme 2). Table 1 encloses the corresponding δ_π values together with its decomposition into the different crossed terms. For benzene, it can be seen that from antiaromatic $N-2$ to standard aromatic benzene (N), total δ_π increases from 2.614 e to 3.369 e, whereas from N to $N+2$, δ_π hardly increases to 3.482 e. These trends are the expected ones for an aromatic system, as already discussed.[24] Now, with respect to the crossed terms, the *ortho* $\delta_\pi^{1,2}$ term increases from 0.288 to 0.427 e when two electrons are added to the $N-2$ species to get N aromatic benzene, the *para* $\delta_\pi^{1,4}$ term also increases from 0.059 to 0.094 e. On the other hand the *meta* $\delta_\pi^{1,3}$ term decreases from 0.087 to 0.037 e. Therefore, the increase in total δ_π when going from antiaromatic $N-2$ to aromatic N does not imply an increase in all crossed terms. It is important to notice that, for benzene, the higher electronic delocalization in *para* (0.094 e) than in *meta* (0.037 e)[47,48] was the key factor for the definition of the electronic-based aromaticity criterion named *para*-delocalization index (PDI).[49] This trend is broken for the corresponding antiaromatic ($C_6H_6^{2+}$) system (0.087 *vs.* 0.059 e for *meta* and *para*, respectively). If we now focus on the δ_π values from aromatic C_6H_6 to antiaromatic $C_6H_6^{2-}$, the opposite trends are observed: $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$ decrease from N to $N+2$, whereas $\delta_\pi^{1,3}$ increases. In order to simplify this analysis, the difference between these two steps, $\Delta^2 = [2\delta_N - \delta_{N-2} - \delta_{N+2}]$, is calculated (values in Table 1). This measure represents the sum of the changes on the electron delocalization when going from N to $N-2$ and from N to $N+2$ species and it is proportional to the numerical second derivative of the corresponding crossed term with respect to the number of electrons. A positive value (convex shape) indicates an overall decrease in the electron delocalization with respect to changes in N, while a negative Δ^2 value (concave shape) represents an overall increase (see Fig. 3).

This trend is also reproduced for heteroaromatic systems when one, two or three nitrogen atoms are incorporated to the benzene ring (see Table 1). For pyridine, pyrimidine, pyrazine, pyridazine, and triazine, $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$ increase from $N-2$ to N systems and $\delta_\pi^{1,3}$ decreases, and the opposite trend is found from N to $N+2$ systems. Δ^2 also corroborates this alternate pattern, namely, large positive *ortho*-, negative *meta*-, and positive *para*-values.

The same analysis has been applied to rings of a different size. We have started with $C_7H_7^+$, an aromatic system isoelectronic to benzene that has the same crossed terms. Interestingly, for this system the "*meta*" ($\delta_\pi^{1,3}$) and "*para*" ($\delta_\pi^{1,4}$) contributions are equal (0.05 e). As for the previously analyzed 6-MRs, we observe an increase in $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$, and a decrease in $\delta_\pi^{1,3}$ when going from $N-2$ to N. The same trends are also achieved from N to $N+2$, with the exception of $\delta_\pi^{1,2}$, which shows a slight increase of 0.01 e. Overall, for aromatic 6- and 7-MR systems, we observe alternation among the crossed terms from $N \pm 2$ to N: $\delta_\pi^{1,2}$ increases, $\delta_\pi^{1,3}$ decreases, and $\delta_\pi^{1,4}$ increases.

Next we address antiaromatic systems. We first focus on C_4H_4 (values enclosed in Table 2). In this case, $\delta_\pi^{1,2}$ increases from aromatic $N-2$ to antiaromatic N systems, from 0.243 to 0.477 e, respectively, whereas $\delta_\pi^{1,3}$ decreases from 0.243 to 0.059 e, respectively. Likewise, from N to $N+2$, $\delta_\pi^{1,2}$ decreases and $\delta_\pi^{1,3}$ increases. In the same way, for the bigger antiaromatic C_8H_8 system constrained to be planar, $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$ increase, whereas $\delta_\pi^{1,3}$ and $\delta_\pi^{1,5}$ decrease from $N \pm 2$ to N. Thus, C_8H_8 behaves like C_4H_4, with the only difference that the former presents more crossed terms. We have $\delta_\pi^{1,3} < \delta_\pi^{1,4} > \delta_\pi^{1,5}$ when going from $d_{1,3}$ (2.603 Å) to $d_{1,4}$ (3.400 Å)



Scheme 2

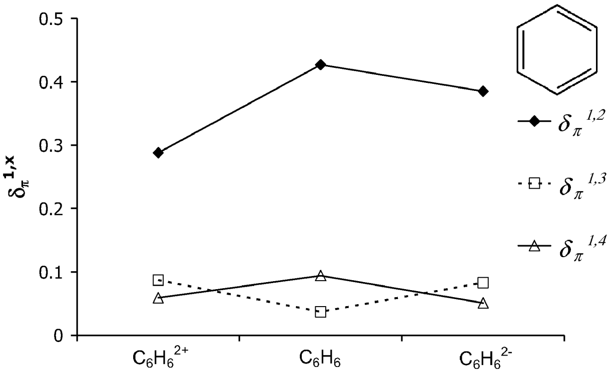


Fig. 3 $\delta_\pi^{1,x}$ measures in $C_6H_6^{2+}$, C_6H_6, and $C_6H_6^{2-}$. Units are electrons.

and to $d_{1,5}$ (3.681 Å) for C_8H_8, while for both aromatic $C_8H_8^{2+}$ and $C_8H_8^{2-}$ we get the opposite, that is $\delta_\pi^{1,3} > \delta_\pi^{1,4} < \delta_\pi^{1,5}$. It is thus noteworthy that, as already proved for benzene,[48–50] there is no connection between the C–C distance and the corresponding crossed terms values, *i.e.*, shorter C–C distances does not always imply larger $\delta_\pi^{1,x}$ values. Recently, Chesnut also recognized the ESIs for non-bonded carbon-carbon interactions reflect the degree of conjugation between the two atoms in question.[51] Fig. 4 shows the changes on the crossed contributions in C_8H_8 system.

Once the patterns of π-crossed terms delocalization have been discussed in 4-, 6-, 7-, and 8-MRs, we focus now our attention to larger rings. Thus, we have computed the π-electron delocalization for the series: C_4H_4, C_6H_6, C_8H_8, $C_{10}H_{10}$, $C_{12}H_{12}$, $C_{14}H_{14}$, and $C_{16}H_{16}$, and charged $C_{11}H_{11}^+$, $C_{11}H_{11}^-$, $C_{13}H_{13}^+$, $C_{13}H_{13}^-$, and $C_{15}H_{15}^+$. As for C_8H_8,

Table 1 Total electronic delocalization (δ_{tot}), total π electronic delocalization (δ_π), and the corresponding crossed contributions to the latter ($\delta_\pi^{1,x}$) for a series of six- and seven-membered monocyclic compounds. Units are electrons

	$N-2$	N	$N+2$	Δ^2		$N-2$	N	$N+2$	Δ^2
C_6H_6					Pyrazine				
δ_{tot}	14.863	15.618	15.731		δ_{tot}	12.161	13.095	12.981	
δ_π	2.614	3.369	3.482		δ_π	2.296	3.230	3.116	
$\delta_\pi^{1,2}$	0.288	0.427	0.385	0.181	$\delta_\pi^{1,2}$	0.283	0.418	0.369	0.184
$\delta_\pi^{1,3}$	0.087	0.037	0.083	−0.096	$\delta_\pi^{1,3}$	0.062	0.042	0.085	−0.063
$\delta_\pi^{1,4}$	0.059	0.094	0.051	0.078	$\delta_\pi^{1,4}$	0.051	0.096	0.044	0.097
C_5H_5N					Triazine				
δ_{tot}	13.518	14.359	14.367		δ_{tot}	11.346	11.87	11.948	
δ_π	2.446	3.287	3.296		δ_π	2.535	3.059	3.137	
$\delta_\pi^{1,2}$	0.284	0.422	0.377	0.183	$\delta_\pi^{1,2}$	0.276	0.410	0.369	0.175
$\delta_\pi^{1,3}$	0.076	0.040	0.084	−0.080	$\delta_\pi^{1,3}$	0.107	0.039	0.091	−0.120
$\delta_\pi^{1,4}$	0.056	0.093	0.047	0.083	$\delta_\pi^{1,4}$	0.055	0.087	0.055	0.064
Pyridazine					$C_7H_7^+$				
δ_{tot}	12.703	13.418	13.27		δ_{tot}	16.434	17.89	18.155	
δ_π	2.533	3.247	3.099		δ_π	2.834	3.677	3.942	
$\delta_\pi^{1,2}$	0.303	0.423	0.364	0.179	$\delta_\pi^{1,2}$	0.244	0.389	0.403	0.131
$\delta_\pi^{1,3}$	0.081	0.041	0.080	−0.079	$\delta_\pi^{1,3}$	0.103	0.050	0.061	−0.064
$\delta_\pi^{1,4}$	0.045	0.094	0.049	0.094	$\delta_\pi^{1,4}$	0.041	0.050	0.042	0.017
Pyrimidine									
δ_{tot}	12.307	13.102	13.034						
δ_π	2.385	3.180	3.113						
$\delta_\pi^{1,2}$	0.291	0.415	0.363	0.176					
$\delta_\pi^{1,3}$	0.074	0.041	0.082	−0.074					
$\delta_\pi^{1,4}$	0.040	0.091	0.052	0.090					

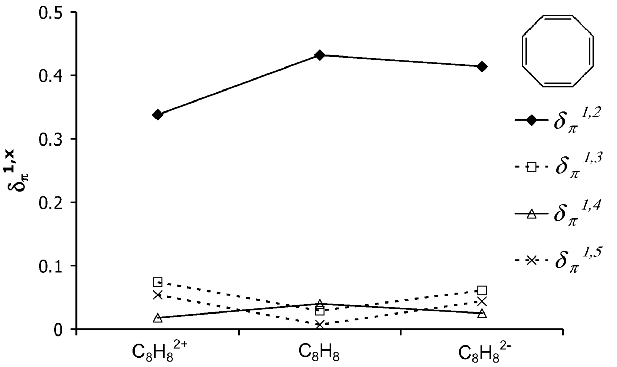


Fig. 4 $\delta_\pi^{1,x}$ measures in $C_8H_8^{2+}$, C_8H_8, and $C_8H_8^{2-}$. Units are electrons.

some systems are not minima because they are forced to be planar. We kept them planar as this way the separation between the σ- and π-electron delocalization is exact. Our analysis is qualitative in the sense that we just want to see whether the alternation pattern for the crossed terms in aromatic and antiaromatic systems is maintained when going to larger rings. To analyze the trends very precise numbers are not necessary and, therefore, instead of tabulating the δ_π values, we have depicted the corresponding values for the most representative systems in Fig. 5. In addition, in this set of rings we have concentrated our analysis in the $N - 2$ and N species. In all cases, $N - 2$ and $N + 2$ follow the same trends and, in order to simplify the analysis and make the trends in the plots more visible, $N + 2$ values are not included in Fig. 5 (complete results can be found in Fig. S3 of the supplementary information†). Thus, Fig. 5a shows how for antiaromatic C_4H_4, $\delta_\pi^{1,2}$ increases from $N - 2$ to N, whereas $\delta_\pi^{1,3}$ decreases, as above mentioned. For aromatic benzene (see Fig. 5b), $\delta_\pi^{1,2}$ increases, $\delta_\pi^{1,3}$ decreases and $\delta_\pi^{1,4}$ increases, and for the other larger systems the alternation is kept for both aromatic ($C_{14}H_{14}$) and antiaromatic (C_8H_8 and $C_{16}H_{16}$) systems. It must be noticed that the larger the x value in the δ_π^{1x} crossed term, the smaller the alternation. This is especially visible in Fig. 5e for $C_{16}H_{16}$. The same conclusions are extracted from the systems in the series not enclosed in Fig. 5 but included as supplementary information (see Fig. S4†). The alternation between even ($\delta_\pi^{1,2}$ $\delta_\pi^{1,4}$ ...) and odd ($\delta_\pi^{1,3}$ $\delta_\pi^{1,5}$ ...) crossed terms is kept.

Table 2 Total electronic delocalization (δ_{tot}), total π electronic delocalization (δ_π), and the corresponding crossed contributions to this latter ($\delta_\pi^{1,x}$) for C_4H_4 and C_8H_8 antiaromatic compounds. Units are electrons

	$N - 2$	N	$N + 2$	Δ^2
	C_4H_4			
δ_{tot}	9.562	10.26	10.382	
δ_π	1.519	2.217	2.339	
$\delta_\pi^{1,2}$	0.243	0.477	0.375	0.336
$\delta_\pi^{1,3}$	0.243	0.059	0.233	−0.358
	C_8H_8			
δ_{tot}	20.344	20.866	21.172	
δ_π	3.955	4.477	4.783	
$\delta_\pi^{1,2}$	0.338	0.432	0.414	0.112
$\delta_\pi^{1,3}$	0.074	0.029	0.061	−0.077
$\delta_\pi^{1,4}$	0.018	0.040	0.025	0.037
$\delta_\pi^{1,5}$	0.054	0.007	0.044	−0.084

The observed trends have been schematically represented in Table 3 for the different rings analyzed (except for 5-MRs) and from antiaromatic N to aromatic $N \pm 2$ and *vice versa*. It is clear that the patterns of changes found help to distinguish between aromatic and antiaromatic rings. Thus, for instance, for an aromatic 6-MR, $\delta_\pi^{1,4}$ decreases when adding or removing two electrons, while the opposite is observed in antiaromatic systems. Moreover, the crossed term corresponding to the two farthest atoms in the ring (*i.e.*, $\delta_\pi^{1,4}$ in 6-MRs or $\delta_\pi^{1,5}$ in 8-MRs) decreases in aromatic species when two electrons are added or removed, whereas the opposite is true for antiaromatic species. These patterns of π-electron delocalization allow for a clear differentiation between aromatic and antiaromatic rings. It is important to mention that by just focusing on the total δ_π, we cannot appreciate any difference between C_6H_6 and C_4H_4, as in the latter δ_π increases in 0.70 and 0.12 e from $N - 2$ to N and from N to $N + 2$, respectively, values very close to those of C_6H_6 (0.76 and 0.11 e, respectively).

Let us finally discuss the particular case of heteroaromatic 5-MRs (C_4H_4X) that, depending on the heteroatom X (see Scheme 2) can be either aromatic (X = CH^-, NH, O, S, P^-) or antiaromatic (X = BH, SiH^+, F_2). The corresponding δ_π values for these species are enclosed in Table 4. For aromatic C_4H_4X systems, from antiaromatic $N - 2$ to aromatic N we would expect an increase in $\delta_\pi^{1,3}$ since 1 and 3 are the two C atoms furthest separated in the ring. However, the opposite trend is obtained. Thus, $\delta_\pi^{1,2}$ increases from 0.337 to 0.436 e from $N - 2$ to N in $C_5H_5^-$ and $\delta_\pi^{1,3}$ decreases from 0.104 to 0.085 e. And the same tendency is observed for the rest of the aromatic species (X = NH, O, S, P^-). On the other hand, for the antiaromatic species, the expected tendency would be an increase in $\delta_\pi^{1,2}$ from aromatic $N - 2$ to antiaromatic N, and a decrease of $\delta_\pi^{1,3}$. From the values in Table 4 it is shown that all three antiaromatic C_4H_4X (X = BH, SiH^+, F_2) compounds follow this trend. Thus, for aromatic species the 5-MRs do not follow the expected trend. Our hypothesis is that $\delta_\pi^{1,3}$ could also be considered $\delta_\pi^{1,4}$ (depending whether one follows clockwise or anticlockwise directions in the ring when going from one atom to the farthest one in the ring), which means that this particular crossed term can be considered between the equivalent *meta* and *para* in benzene. For this reason, big differences are not generally observed in $\delta_\pi^{1,3}$ for 5-MRs when going from $N - 2$ to N and from N to $N + 2$, and the main change takes place on $\delta_\pi^{1,2}$. This makes the series of 5-MRs a particular case for which the patterns of changes in crossed term delocalizations do not allow for a clear separation between aromatic and antiaromatic species. Notwithstanding, it is worth mentioning that the smallest unsigned Δ^2 values for the $\delta_\pi^{1,3}$ crossed term when going from N to $N \pm 2$ are found for aromatic species, whereas the largest ones correspond to antiaromatic ones. In addition, the aforementioned alternation pattern is retained in higher crossed terms of larger rings with odd number of members. Thus, for $C_7H_7^+$, even though it follows the expected alternation, the *para* Δ^2 value is only 0.017 as compared to 0.078 or −0.084 in C_6H_6 or C_8H_8, respectively, while the rest

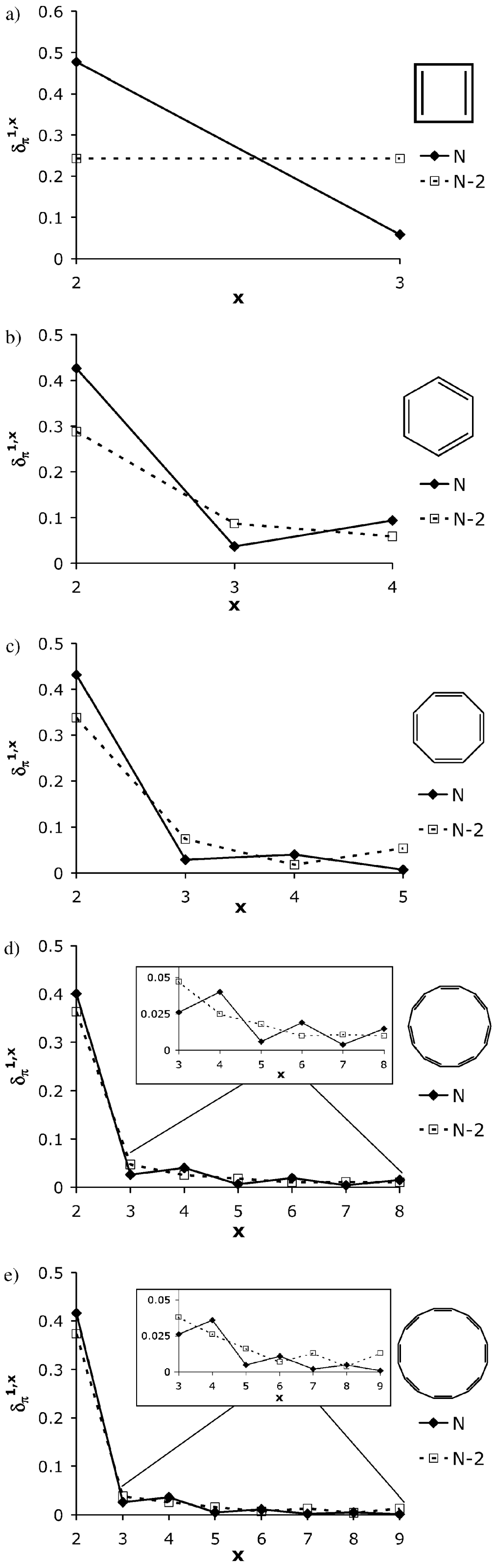


Fig. 5 Evolution of $\delta_\pi^{1,x}$ (in electrons) in N and $N-2$ species for (a) C_4H_4, (b) C_6H_6, (c) C_8H_8, (d) $C_{14}H_{14}$, and (e) $C_{16}H_{16}$.

of Δ^2 values are relatively similar for either even or odd membered rings. And the same behavior is observed when comparing $C_9H_9^-$ to $C_{10}H_{10}$.

Table 3 Schematic representation of the behavior of the crossed contributions to the total π-electronic delocalization in antiaromatic and aromatic compounds of different ring sizes. ⇑ and ⇓ refer to increase and decrease, respectively

	Antiaromatic $N \rightarrow N \pm 2$			Aromatic $N \rightarrow N \pm 2$		
	4-MR	6-,7-MR	8-,9-MR	4-MR	6-,7-MR	8-,9-MR
$\delta_\pi^{1,2}$	⇓	⇑	⇓	⇑	⇓	⇑
$\delta_\pi^{1,3}$	⇑	⇓	⇑	⇓	⇑	⇓
$\delta_\pi^{1,4}$		⇑	⇓		⇓	⇑
$\delta_\pi^{1,5}$			⇑			⇓

B δ_π crossed contributions in polycyclic aromatic hydrocarbons

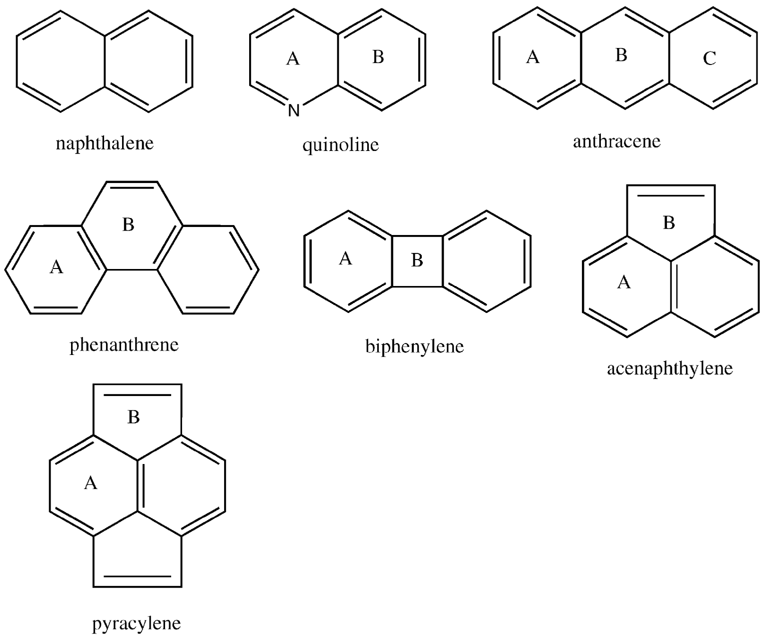
The above analysis has been performed on monocyclic systems for which Hückel's rule holds. The next step is to see if the above patterns of π-electron delocalization are kept for PAHs. For this purpose, we analyze in this section the following series of PAHs: naphthalene, quinoline, anthracene, phenanthrene, biphenylene, acenaphthylene, and pyracylene (see Scheme 3). Table 5 encloses the δ_π values for this series and the corresponding crossed terms (in the calculation of the crossed terms C atoms from different rings can be involved). For naphthalene, the trends observed for benzene are kept. By comparison of the values, from benzene (see Table 1) to naphthalene, it is observed how all differences in δ_π from $N-2$ to N decrease. For benzene, the differences in δ_π are 0.14, −0.05, and 0.11 for $\delta_\pi^{1,2}$, $\delta_\pi^{1,3}$ and $\delta_\pi^{1,4}$, respectively, whereas for naphthalene they are 0.07, −0.01, and 0.03, respectively, thus showing the decrease in electron delocalization changes in the rings when going from benzene to the 6-MRs of naphthalene, which have a lower aromaticity, as previously observed.[52] This trend is even more pronounced for the external ring of anthracene, even though for both rings the expected pattern of electron delocalization for an aromatic ring is observed. This conclusion can be extrapolated to the rest of the systems in this series. The 4-MR in biphenylene also behaves like C_4H_4, but also with much lower differences between the values for the $N-2$ and N species. 5-MRs in acenaphthylene and pyracylene also present the expected trend for antiaromatic 5-MRs. Analogous conclusions might be drawn by checking the $N+2$ to N crossed terms, and therefore, by Δ^2 values.

C Multiplicity

In this section, the patterns of crossed π-delocalization measures are studied for the lowest-lying triplet states of all monocycles analyzed in Tables 1, 2, and 4. In a previous work, we showed that in dicationic or dianionic D_{nh} annulenes, the lowest-lying singlet and triplet states present similar *total* π-electronic delocalization values. Consequently, total δ_π cannot discern between singlet and triplet states. However, as we can see in Fig. 6 and 7, the crossed terms can clearly reproduce the multiplicity effects and show opposite trends according to Hückel's and Baird's rules. While the lowest-lying triplet state of C_6H_6 is antiaromatic, $C_6H_6^{2+}$ and $C_6H_6^{2-}$ are aromatic. Thus, for the antiaromatic C_6H_6 triplet state, lower $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$ and higher $\delta_\pi^{1,3}$ are observed in comparison to the aromatic lowest-lying singlet state (see Fig. 6). In the antiaromatic C_6H_6 triplet state, $\delta_\pi^{1,2}$ and $\delta_\pi^{1,4}$ decrease from aromatic

Table 4 Total electronic delocalization (δ_{tot}), total π electronic delocalization (δ_π), and the corresponding crossed contributions to this latter ($\delta_\pi{}^{1,x}$) for a series of five-membered monocyclic compounds. Units are electrons

	$N-2$	N	$N+2$	Δ^2		$N-2$	N	$N+2$	Δ^2
$C_5H_5{}^-$					$C_4H_4P^-$				
δ_{tot}	12.634	13.177	13.056		δ_{tot}	11.308	11.908	11.676	
δ_π	2.430	2.973	2.852		δ_π	2.330	2.930	2.698	
$\delta_\pi{}^{1,2}$	0.337	0.436	0.338	0.197	$\delta_\pi{}^{1,2}$	0.341	0.440	0.361	0.178
$\delta_\pi{}^{1,3}$	0.104	0.085	0.091	−0.025	$\delta_\pi{}^{1,3}$	0.083	0.088	0.092	0.001
C_4H_4NH					C_4H_4BH				
δ_{tot}	11.688	12.383	12.186		δ_{tot}	10.972	11.702	12.39	
δ_π	2.074	2.769	2.572		δ_π	1.550	2.281	2.969	
$\delta_\pi{}^{1,2}$	0.281	0.417	0.329	0.224	$\delta_\pi{}^{1,2}$	0.158	0.361	0.404	0.160
$\delta_\pi{}^{1,3}$	0.106	0.086	0.091	−0.025	$\delta_\pi{}^{1,3}$	0.135	0.053	0.093	−0.122
C_4H_4O					$C_4H_4SiH^+$				
δ_{tot}	10.572	11.278	11.117		δ_{tot}	10.915	11.632	12.369	
δ_π	1.931	2.638	2.477		δ_π	1.577	2.294	3.031	
$\delta_\pi{}^{1,2}$	0.256	0.407	0.322	0.236	$\delta_\pi{}^{1,2}$	0.157	0.359	0.440	0.121
$\delta_\pi{}^{1,3}$	0.112	0.081	0.095	−0.045	$\delta_\pi{}^{1,3}$	0.144	0.065	0.085	−0.099
C_4H_4S					$C_4H_4F_2$				
δ_{tot}	11.244	11.889	11.665		δ_{tot}	12.619	13.282	13.472	
δ_π	2.059	2.704	2.480		δ_π	2.447	3.129	3.363	
$\delta_\pi{}^{1,2}$	0.269	0.417	0.335	0.230	$\delta_\pi{}^{1,2}$	0.167	0.358	0.316	0.233
$\delta_\pi{}^{1,3}$	0.123	0.082	0.087	−0.046	$\delta_\pi{}^{1,3}$	0.113	0.043	0.090	−0.117



Scheme 3

$N-2$(t) to antiaromatic N(t), whereas $\delta_\pi{}^{1,3}$ increases (see Table 6). The opposite trend has been already shown for the singlet ground state. The Δ^2 measures contained in Table 6 show opposite patterns for the lowest-lying singlet and triplet states in line with Baird's rule.

For the C_8H_8 species, the aromatic lowest-lying triplet, N(t), presents higher $\delta_\pi{}^{1,3}$ and $\delta_\pi{}^{1,5}$ and lower $\delta_\pi{}^{1,2}$ and $\delta_\pi{}^{1,4}$ than the antiaromatic lowest-lying singlet, N(s). Thus, alternation of the crossed terms between antiaromatic N(s) and aromatic N(t) is confirmed (see Fig. 7) showing opposite patterns according to Baird's rule. As we previously showed, it is especially interesting to analyze the relationship between distance and electron delocalization. In the constrained planar optimized C_8H_8 molecule, the distance between the farthest positions (*i.e.* $d_{1,5}$) is practically the same for the singlet and triplet states (3.680 *vs.* 3.665 Å). However, the behavior of the electron delocalization is completely different, because in antiaromatic N(s), $\delta_\pi{}^{1,5}$ is only 0.007 e, while it increases to 0.049 e in aromatic N(t). Moreover, the rest of the monocycles from Tables 1, 2, and 4 have been analyzed by means of electron delocalization patterns for N(s) and N(t) species (see Tables S5 and S6 of the supplementary information†). All systems studied follow the expected trends and the alternation between N(s) and N(t) crossed terms is observed. Again, the aromatic 5-MRs represent the only exception, in this particular case, $\delta_\pi{}^{1,2}$ decreases while $\delta_\pi{}^{1,3}$ is hardly affected and the alternation is not observed when going from aromatic N(s) to antiaromatic N(t).

Table 5 Total electronic delocalization (δ_{tot}), total π electronic delocalization (δ_π), and the corresponding crossed contributions to this latter ($\delta_\pi^{1,x}$) for a series of planar polycyclic aromatic hydrocarbons. Units are electrons. *A* and *B* refer to the different rings in the PAH (see Scheme 3)

	$N-2$	N	$N+2$	Δ^2
Naphthalene				
δ_{tot}	24.554	25.079	25.318	
δ_π	5.113	5.639	5.877	
$\delta_\pi^{1,2}$	0.308	0.376	0.356	0.088
$\delta_\pi^{1,3}$	0.039	0.029	0.038	−0.019
$\delta_\pi^{1,4}$	0.039	0.066	0.038	0.055
Quinoline				
δ_{tot}	23.309	23.826	23.999	
δ_π	5.033	5.550	5.722	
$\delta_\pi^{1,2\mathrm{A}}$	0.343	0.373	0.338	0.065
$\delta_\pi^{1,3\mathrm{A}}$	0.037	0.031	0.042	−0.017
$\delta_\pi^{1,4\mathrm{A}}$	0.052	0.065	0.031	0.047
$\delta_\pi^{1,2\mathrm{B}}$	0.268	0.372	0.366	0.110
$\delta_\pi^{1,3\mathrm{B}}$	0.048	0.029	0.036	−0.026
$\delta_\pi^{1,4\mathrm{B}}$	0.034	0.065	0.046	0.050
Anthracene				
δ_{tot}	34.626	35.086	35.348	
δ_π	7.357	7.816	8.078	
$\delta_\pi^{1,2A}$	0.335	0.363	0.364	0.027
$\delta_\pi^{1,3A}$	0.030	0.024	0.030	−0.012
$\delta_\pi^{1,4A}$	0.048	0.058	0.049	0.019
$\delta_\pi^{1,2B}$	0.272	0.333	0.309	0.085
$\delta_\pi^{1,3B}$	0.022	0.022	0.023	−0.001
$\delta_\pi^{1,4B}$	0.021	0.058	0.021	0.074
Phenanthrene				
δ_{tot}	34.078	34.56	34.843	
δ_π	7.427	7.910	8.192	
$\delta_\pi^{1,2A}$	0.336	0.386	0.369	0.067
$\delta_\pi^{1,3A}$	0.038	0.031	0.035	−0.011
$\delta_\pi^{1,4A}$	0.042	0.072	0.044	0.058
$\delta_\pi^{1,2B}$	0.265	0.321	0.306	0.071
$\delta_\pi^{1,3B}$	0.034	0.022	0.033	−0.023
$\delta_\pi^{1,4B}$	0.024	0.038	0.022	0.030
Biphenylene				
δ_{tot}	28.755	29.249	29.554	
δ_π	6.281	6.774	7.079	
$\delta_\pi^{1,2\mathrm{A}}$	0.328	0.409	0.369	0.121
$\delta_\pi^{1,3\mathrm{A}}$	0.049	0.033	0.039	−0.022
$\delta_\pi^{1,4\mathrm{A}}$	0.041	0.079	0.038	0.079
$\delta_\pi^{1,2\mathrm{B}}$	0.171	0.201	0.229	0.001
$\delta_\pi^{1,3\mathrm{B}}$	0.092	0.036	0.064	−0.084
Acenaphthylene				
δ_{tot}	29.112	29.632	29.848	
δ_π	6.148	6.668	6.884	
$\delta_\pi^{1,2\mathrm{A}}$	0.313	0.365	0.347	0.070
$\delta_\pi^{1,3\mathrm{A}}$	0.029	0.025	0.032	−0.011
$\delta_\pi^{1,4\mathrm{A}}$	0.034	0.063	0.040	0.052
$\delta_\pi^{1,2\mathrm{B}}$	0.197	0.309	0.332	0.089
$\delta_\pi^{1,3\mathrm{B}}$	0.065	0.026	0.050	−0.063
Pyracylene				
δ_{tot}	33.017	33.466	33.773	
δ_π	7.464	7.914	8.221	
$\delta_\pi^{1,2\mathrm{A}}$	0.319	0.358	0.344	0.053
$\delta_\pi^{1,3\mathrm{A}}$	0.031	0.027	0.031	−0.008
$\delta_\pi^{1,4\mathrm{A}}$	0.026	0.058	0.039	0.051
$\delta_\pi^{1,2\mathrm{B}}$	0.236	0.301	0.326	0.040
$\delta_\pi^{1,3\mathrm{B}}$	0.033	0.029	0.045	−0.020

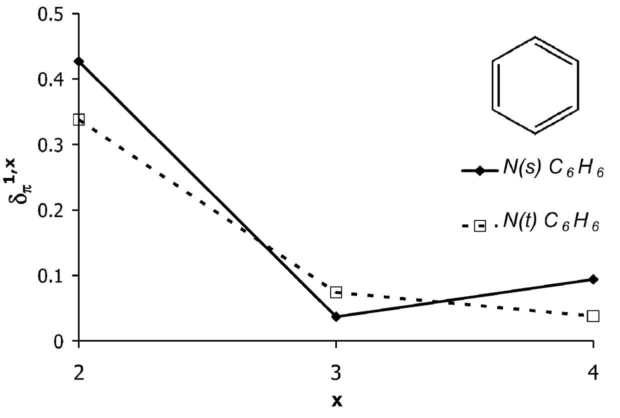


Fig. 6 $\delta_\pi^{1,x}$ measures in aromatic C_6H_6 (s) and antiaromatic C_6H_6 (t). Units are electrons.

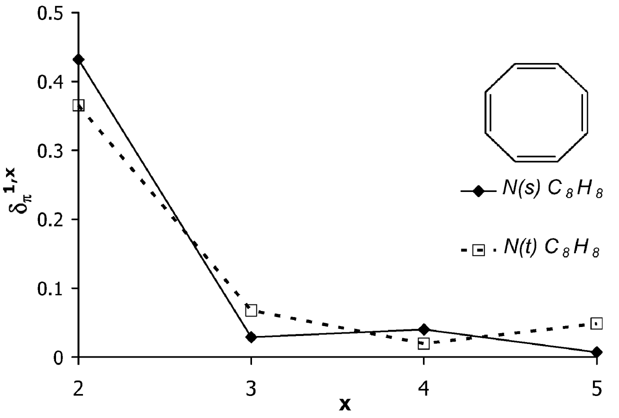


Fig. 7 $\delta_\pi^{1,x}$ measures in antiaromatic C_8H_8 (s) and aromatic C_8H_8 (t). Units are electrons.

D Aromaticity analysis

In this last subsection we quantify the aromaticity of the rings studied to corroborate their aromatic or antiaromatic character. For this purpose the electronic aromaticity criterion called multicenter index (MCI) has been applied, as we have recently demonstrated it performs very well for different aromatic series of compounds[33] and, in addition, it can be applied to any ring. Despite the good performance of MCI, for the aim of comparison, HOMA, NICS(0), $\mathrm{NICS}(0)_{zz}$, NICS(1) and $\mathrm{NICS}(1)_{zz}$, and FLU aromaticity criteria have been also calculated. All aromaticity indices reported in this section have been calculated at the fully relaxed geometries of all species (N, N−2, and N + 2) with the only constrain that all molecular structures are kept planar, at variance with the above analysis (values enclosed in the supplementary information). It is worth

Table 6 Crossed terms measures in C_6H_6 and C_8H_8 for $N-2$, N, and $N+2$ triplet states. Units are electrons

	$N-2(t)$	$N(t)$	$N+2(t)$	Δ^2(triplet)	Δ^2(singlet)[a]
C_6H_6					
$\delta_{\pi}^{1,2}$	0.275	0.338	0.405	−0.004	0.181
$\delta_{\pi}^{1,3}$	0.070	0.074	0.057	0.021	−0.096
$\delta_{\pi}^{1,4}$	0.103	0.038	0.068	−0.095	0.078
C_8H_8					
$\delta_{\pi}^{1,2}$	0.316	0.365	0.417	−0.002	0.112
$\delta_{\pi}^{1,3}$	0.061	0.068	0.046	0.029	−0.077
$\delta_{\pi}^{1,4}$	0.041	0.020	0.036	−0.038	0.037
$\delta_{\pi}^{1,5}$	0.015	0.049	0.026	0.056	−0.084

[a] Results from Table 1.

noting that the geometry-based HOMA indicator of aromaticity does not denote changes of aromaticity if the same geometry is used for the N, N−2, and N + 2 species.

The MCI values for the whole series of compounds analyzed are enclosed in Table 7. First, for 6-MR systems, in all cases the N ring appears to be the most aromatic, with the corresponding increase in aromaticity from N−2 to N and the decrease from N to N + 2 as expected from the above $\delta_{\pi}^{1,4}$ values, that increases in *para* positions from antiaromatic N−2 to aromatic N, and decreases from N to antiaromatic N + 2. The same behavior is observed for $C_7H_7^+$, and completely opposite for both antiaromatic C_4H_4 and C_8H_8, in which N−2 and N + 2 present higher aromaticities than N, again in line with δ_{π} trends.

For the series of five-membered rings (C_4H_4X), it is important to notice that while the crossed contributions to δ_{π} do not give the expected trends for the aromatic systems, the aromaticity analysis clearly confirms the higher aromaticity of N *vs* $N-2$ and $N+2$ for the aromatic X = CH^-, NH, O, S, and P^-, whereas the N ring is the least aromatic for X = BH, SiH^+, and F_2. The aromaticity analysis carried out for the PAHs also shows the expected trends derived from the δ_{π} values. It is important to notice the decrease of MCI of these polycyclic systems as compared to benzene, as well as the smaller differences between antiaromatic $N-2$ and aromatic N systems. Moreover, when the effects of multiplicity are taken into account, the MCI values show opposite trends between lowest-lying singlet and triplet states according to Baird's rule.

Finally, Table S7 (see supplementary information†) encloses the values corresponding to HOMA, FLU, and NICS aromaticity criteria. There is a very good correspondence of these indices with MCI, thus corroborating the trends obtained with this electronic indicator of aromaticity. The only exceptions have been found for the $N-2$ species of C_4H_4, C_4H_4BH, $C_4H_4SiH^+$ and $C_4H_4F_2$, where NICS(0) and NICS(0)$_{zz}$ predict antiaromatic behavior whereas the opposite trend is found for the rest of the indices. In particular and in contrast to NICS(0), NICS(1) and NICS(1)$_{zz}$ show aromatic character for these $N-2$ species and predict the correct trends for all the systems analyzed. For aromatic organic compounds, NICS(1) is considered to better reflect the π-electron effects than NICS(0).[53] Moreover, MCI, HOMA, FLU and NICS indices agree with the Baird's rule and predict a reduction of aromaticity for the lowest-lying triplet state when the lowest-lying singlet state is aromatic and *viceversa*. Just to conclude, even though we have calculated NICS for all systems (see Table S7 of the supplementary information†), it should be mentioned that the manner in which we compute the open-shell NICS values is somewhat lacking in rigour.[54]

Table 7 MCI measures of the series of compounds. *A* and *B* refer to the different rings in the PAH (see Scheme 3). Units are electrons

	$N-2$	N	$N+2$
C_6H_6	−0.020	0.073	0.002
C_5H_5N	−0.010	0.069	0.004
Pyridazine	0.000	0.070	0.002
Pyrimidine	0.001	0.066	0.002
Pyrazine	0.006	0.066	0.003
Triazine	−0.016	0.064	0.002
$C_7H_7^+$	−0.005	0.058	−0.017
C_4H_4	0.183	0.009	0.064
C_8H_8	0.040	−0.001	0.014
$C_5H_5^-$	−0.028	0.072	0.010
C_4H_4NH	−0.014	0.050	0.011
C_4H_4O	−0.010	0.029	0.013
C_4H_4S	−0.021	0.041	0.014
$C_4H_4P^-$	−0.019	0.068	0.014
C_4H_4BH	0.022	−0.003	0.040
$C_4H_4SiH^+$	0.037	−0.006	0.057
$C_4H_4F_2$	0.017	−0.005	0.023
Naphthalene	0.020	0.039	0.018
Quinoline^A	0.021	0.037	0.016
Quinoline^B	0.008	0.038	0.020
Anthracene^A	0.028	0.029	0.025
Anthracene^B	0.013	0.027	0.012
Phenanthrene^A	0.019	0.047	0.020
Phenanthrene^B	0.010	0.018	0.008
Biphenylene^A	0.008	0.056	0.010
Biphenylene^B	0.054	0.021	0.016
Acenaphthylene^A	0.014	0.038	0.019
Acenaphthylene^B	0.005	0.011	0.034
Pyracylene^A	0.015	0.032	0.019
Pyracylene^B	0.017	0.012	0.030
C_6H_6 (t)	0.079	−0.002	0.036
C_8H_8 (t)	−0.002	0.028	0.007

Conclusions

In the present work, we have analyzed the changes in the crossed contributions to the total π electronic delocalization (δ_{π}) when two electrons are added or removed for a given species and we have shown that the patterns derived can be used to distinguish between aromatic and antiaromatic systems. Remarkably, all crossed terms contribute to the description of the aromaticity and antiaromaticiy of the system. For aromatic benzene, *ortho* ($\delta_{\pi}^{1,2}$) and *para* ($\delta_{\pi}^{1,4}$) contributions increase and *meta* ($\delta_{\pi}^{1,3}$) decrease from antiaromatic $C_6H_6^{2+}$ or $C_6H_6^{2-}$ to aromatic C_6H_6. Likewise, for the antiaromatic cyclobutadiene, from aromatic $C_4H_4^{2+}$ to antiaromatic C_4H_4 $\delta_{\pi}^{1,2}$ increases and $\delta_{\pi}^{1,3}$ decreases. Both of the alternation patterns are kept for larger aromatic and antiaromatic rings. Aromatic 5-MR systems are the only exception to the general behavior found and this may be attributed to the fact that for such small ring size, $\delta_{\pi}^{1,3}$ could also be considered $\delta_{\pi}^{1,4}$ depending whether one follows clockwise or anticlockwise directions in the ring when going from one atom to the farthest one in the ring. It has been proven that the expected alternation pattern is kept for large annulenes like $C_{16}H_{16}$, although becomes smaller when the separation between the atoms involved increases. The rules presented are also perfectly valid for planar polycyclic aromatic hydrocarbons. In addition, crossed terms show opposite trends between lowest-lying singlet and triplet states in line with the Baird's rule. Finally, the aromaticity of the rings has been corroborated by means of the MCI, HOMA, NICS, and FLU indices of aromaticity.

As a whole, the present analysis based on crossed terms of the delocalization index represents a step forward towards a better comprehension of the electronic delocalization behavior of aromatic or antiaromatic systems. We consider that this analysis can be extended to the analysis of aromaticity/antiaromaticity in pure metal and semi-metal aromatic clusters or to evaluate the strength of the conjugation and hyperconjugation effects in conjugated systems. More research is underway in our laboratory concerning these particular issues.

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References

1 P. Hückel, *Z. Phys.*, 1931, **70**, 204; P. Hückel, *Z. Phys.*, 1932, **76**, 628.
2 E. C. Crocker, *J. Am. Chem. Soc.*, 1922, **44**, 1618.
3 W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1954, **76**, 3203.
4 S. Kikuchi, *J. Chem. Educ.*, 1997, **74**, 194.
5 I. Mayer, *Theor. Chem. Acc.*, 2010, **125**, 203.
6 C. Glidewell and D. Lloyd, *Tetrahedron*, 1984, **40**, 4455.
7 N. C. Baird, *J. Am. Chem. Soc.*, 1972, **94**, 4941.
8 R. Breslow, H. W. Chang, R. Hill and E. Wasserman, *J. Am. Chem. Soc.*, 1967, **89**, 1112; M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffmann Jr., C. Perchonock, E. Wasserman, R. S. Hutton and V. J. Huck, *J. Am. Chem. Soc.*, 1973, **95**, 3017.
9 H. J. Worner and F. Merkt, *Angew. Chem., Int. Ed.*, 2006, **45**, 293.
10 N. Mizoguchi, *Chem. Phys. Lett.*, 1984, **106**, 451.
11 A. Hirsch, Z. Chen and H. Jiao, *Angew. Chem., Int. Ed.*, 2000, **39**, 3915; Z. H. Chen, H. J. Jiao, A. Hirsch and W. Thiel, . *Mol. Model.*, 2001, **7**, 161; Z. F. Chen, A. Hirsch, S. Nagase, W. Thiel and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 2003, **125**, 15507.
12 M. Randić, *Chem. Rev.*, 2003, **103**, 3449.
13 D. Plavsic, S. Nikolic and N. Trinajstic, *J. Math. Chem.*, 1991, **8**, 113.
14 A. I. Boldyrev and L. S. Wang, *Chem. Rev.*, 2005, **105**, 3716; C. A. Tsipis, *Coord. Chem. Rev.*, 2005, **249**, 2740; H.-J. Zhai, A. E. Kuznetsov, A. Boldyrev and L.-S. Wang, *ChemPhysChem*, 2004, **5**, 1885; F. De Proft, P. W. Fowler, R. W. A. Havenith, P. v. R. Schleyer, G. Van Lier and P. Geerlings, *Chem.–Eur. J.*, 2004, **10**, 940; A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai and L.-S. Wang, *J. Phys. Chem. A*, 2004, **108**, 3509; Y. Jung, T. Heine, P. v. R. Schleyer and M. Head-Gordon, *J. Am. Chem. Soc.*, 2004, **126**, 3132.
15 R. C. Haddon, *J. Am. Chem. Soc.*, 1979, **101**, 1722; I. Gutman, M. Milun and N. Trinajstic, *J. Am. Chem. Soc.*, 1977, **99**, 1692.
16 H. J. Jiao, P. v. R. Schleyer, Y. Mo, M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc.*, 1997, **119**, 7075.
17 E. Steiner and P. W. Fowler, *Chem. Commun.*, 2001, 2220; E. Steiner and P. W. Fowler, *J. Phys. Chem. A*, 2001, **105**, 9553; A. Soncini, P. W. Fowler and F. Zerbetto, *Chem. Phys. Lett.*, 2005, **405**, 136.
18 P. W. Fowler, E. Steiner and L. W. Jenneskens, *Chem. Phys. Lett.*, 2003, **371**, 719.
19 S. Villaume, H. A. Fogarty and H. Ottosson, *ChemPhysChem*, 2008, **9**, 257.
20 P. C. Hiberty, D. Danovich, A. Shurki and S. Shaik, *J. Am. Chem. Soc.*, 1995, **117** 7760; P. C. Hiberty and S. Shaik, *Theor. Chem. Acc.*, 2005, **114**, 169; P. C. Hiberty and S. S. Shaik, *Phys. Chem. Chem. Phys.*, 2004, **6**, 224; S. Shaik, S. Zilberg and Y. Haas, *Acc. Chem. Res.*, 1996, **29**, 211; S. S. Shaik and P. C. Hiberty, *J. Am. Chem. Soc.*, 1985, **107**, 3089; S. S. Shaik, P. C. Hiberty, J.-M. Le Four and G. Ohanessian, *J. Am. Chem. Soc.*, 1987, **109**, 363; S. S. Shaik, A. Shurki, D. Danovich and P. C. Hiberty, *Chem. Rev.*, 2001, **101**, 1501; S. C. A. H. Pierrefixe and F. M. Bickelhaupt, *Chem.–Eur. J.*, 2007, **13**, 6321; A. Gobbi, Y. Yamaguchi, G. Frenking and H. F. Schaefer III, *Chem. Phys. Lett.*, 1995, **244**, 27; A. Rehaman, A. Datta, S. S. Mallajosyula and S. K. Pati, *J. Chem. Theory Comput.*, 2006, **2**, 30; K. Jug and A. M. Koster, *J. Am. Chem. Soc.*, 1990, **112**, 6772; N. D. Epiotis, *Pure Appl. Chem.*, 1983, **55**, 229.
21 R. Dabestani and I. N. Ivanov, *Photochem. & Photobiol.*, 1999, **70**, 10.
22 N. Sadlej-Sosnowska, *J. Org. Chem.*, 2001, **66**, 8737.
23 J. Poater, M. Duran, M. Solà and B. Silvi, *Chem. Rev.*, 2005, **105**, 3911; G. Merino, A. Vela and T. Heine, *Chem. Rev.*, 2005, **105**, 3812.
24 F. Feixas, E. Matito, M. Solà and J. Poater, *J. Phys. Chem. A*, 2008, **112**, 13231.
25 E. Matito, M. Solà, P. Salvador and M. Duran, *Faraday Discuss.*, 2007, **135**, 325.
26 E. Matito, J. Poater, M. Solà, M. Duran and P. Salvador, *J. Phys. Chem. A*, 2005, **109**, 9904.
27 P. Bultinck, D. L. Cooper and R. Ponec, *J. Phys. Chem. A*, 2010, DOI: 10.1021/jp101707w.
28 R. F. W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9; R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon, Oxford, 1990; R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893.
29 I. Mayer and P. Salvador, *Chem. Phys. Lett.*, 2004, **383**, 368.
30 P. Bultinck, M. Rafat, R. Ponec, B. van Gheluwe, R. Carbó-Dorca and P. Popelier, *J. Phys. Chem. A*, 2006, **110**, 7642.
31 E. Matito, P. Salvador, M. Duran and M. Solà, *J. Phys. Chem. A*, 2006, **110**, 5108.
32 P. Bultinck, R. Ponec and S. Van Damme, *J. Phys. Org. Chem.*, 2005, **18**, 706.
33 F. Feixas, E. Matito, J. Poater and M. Solà, *J. Comput. Chem.*, 2008, **29**, 1543.
34 M. Giambiagi, M. S. de Giambiagi, C. D. dos Santos and A. P. de Figueiredo, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3381.
35 L. Lain, A. Torre, R. C. Bochicchio and R. Ponec, *Chem. Phys. Lett.*, 2001, **346**, 283.
36 J. Cioslowski, E. Matito and M. Solà, *J. Phys. Chem. A*, 2007, **111**, 6521.
37 P. Bultinck, R. Ponec, A. Gallegos, S. Fias, S. Van Damme and R. Carbó-Dorca, *Croat. Chem. Acta*, 2006, **79**, 363; M. Mandado, M. J. González-Moa and R. A. Mosquera, *J. Comput. Chem.*, 2007, **28**, 127; M. Mandado, M. J. González-Moa and R. A. Mosquera, *J. Comput. Chem.*, 2007, **28**, 1625.
38 J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.*, 1972, **13**, 3839; T. M. Krygowski and M. K. Cyranski, *Chem. Rev.*, 2001, **101**, 1385.
39 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317; Z. F. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842.

40 E. Matito, M. Duran and M. Solà, *J. Chem. Phys.*, 2005, **122**, 014109; Erratum: E. Matito, M. Duran and M. Solà, *J. Chem. Phys.*, 2006, **125**, 059901.

41 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03*, Revision C.01 edn, Gaussian Inc., Pittsburgh, PA, 2003.

42 F. W. Biegler-König, R. F. W. Bader and T.-H. Tang, *J. Comput. Chem.*, 1982, **3**, 317.

43 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

44 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

45 E. Matito, *ESI-3D: Electron Sharing Indices Program for 3D Molecular Space Partitioning (http: //iqc.udg.edu/~eduard/ESI)*, Institute of Computational Chemistry, Girona, 2006.

46 J. Poater, M. Solà, M. Duran and X. Fradera, *Theor. Chem. Acc.*, 2002, **107**, 362.

47 R. L. Fulton, *J. Phys. Chem.*, 1993, **97**, 7516.

48 R. F. W. Bader, A. Streitwieser, A. Neuhaus, K. E. Laidig and P. Speers, *J. Am. Chem. Soc.*, 1996, **118**, 4959.

49 J. Poater, X. Fradera, M. Duran and M. Solà, *Chem.–Eur. J.*, 2003, **9**, 400.

50 R. L. Fulton and S. T. Mixon, *J. Phys. Chem.*, 1993, **97**, 7530.

51 D. B. Chesnut, *Chem. Phys.*, 2009, **358**, 75.

52 G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solà, *J. Org. Chem.*, 2005, **70**, 2509; Erratum: G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solà, *J. Org. Chem.*, 2005, **70**, 4560.

53 C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer and J. Weber, *Phys. Chem. Chem. Phys.*, 2004, **6**, 273; P. v. R. Schleyer, M. Manoharan, H. J. Jiao and F. Stahl, *Org. Lett.*, 2001, **3**, 3643.

54 V. Gogonea, P. v. R. Schleyer and P. R. Schreiner, *Angew. Chem., Int. Ed.*, 1998, **37**, 1945; E. D. Becker, C. L. Fisk and C. L. Khetrapal, in *Encyclopedia of Nuclear Magnetic Resonance*, ed. D. M. Grant and R. K. Harris, Wiley, Chichester, 1996, vol. 1, p. 41.