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Multicenter delocalization indices vs. properties of the electron density at ring critical points: A study on polycyclic aromatic hydrocarbons

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Abstract

Six-center delocalization indices, 6-DI's, computed within Mulliken and QTAIM approaches, and properties of the electron density at ring critical points, RCP's, (electron density and its Laplacian) are studied for a series of 27 polycyclic aromatic hydrocarbons. Both approaches reflect the same trends for the local aromaticity of benzenoid rings. Moreover, there is a linear correlation between the natural logarithm of 6-DI's and RCP properties. The RCP properties calculated at the DFT level indicate the local aromaticity decreases from outer to inner rings in polyacenes. This contradicts previous results obtained at HF level and supports the conclusions of multicenter indices.
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1. Introduction

Ring critical points, RCP's, are associated to ring formation within the framework of the quantum theory of atoms in molecules (QTAIM) [1,2]. A RCP corresponds to a $(3, +1)$ critical point of the electron density, $\rho(\mathbf{r})$, i.e., a minimum of $\rho(\mathbf{r})$ in two space directions and a maximum in the third one [1,2]. The properties calculated at these points r_c, such as $\rho(r_c)$ and the Laplacian $\nabla^2\rho(\mathbf{r}_c)$, are closely related to the stability of the rings. Analogously, the properties calculated at the bond critical point, BCP, are related to the stability of the bond [1,2].

The use of RCP properties as local aromaticity indices was first proposed by Howard and Krygowski [3]. They studied the values of $\rho(\mathbf{r}_c)$, $\nabla^2\rho(\mathbf{r}_c)$ and the eigenvalues of the Hessian matrix of $\rho(\mathbf{r}_c)$ for a series of polycyclic aromatic hydrocarbons at the HF/6-31G(d,p) level of theory. They found that these properties are closely related to the local aromaticity of the benzenoid rings, the smallest values

corresponding to the least aromatic rings. As a remarkable result, according to their calculations, local aromaticity increases from outer to inner rings in polyacenes. However, in this work we show that their results do not hold at higher computational levels.

Multicenter delocalization indices [4,5], obtained from expanding the number of electrons in a single Slater determinant approach in terms of the *n*-order density matrices [6], have been recently applied on several aromaticity studies [6–12]. The results reported in previous works showed that the multicenter indices are a new and powerful tool for studying total and local aromaticity as they also agree with geometrical aromaticity indices like HOMA [6], circuit specific resonance energies (CRE) [12], and indices based on the chemical graph theory [7]. The specific case of the use of 2-center delocalization indices in aromaticity was recently reviewed by Poater et al. [13].

In previous works [7,12], we have shown that local aromaticity based on multicenter indices, without applying any scaling factor, exclusively reflects the local ring currents, and does not include ring currents involving more than one ring. Since the topology of $\rho(\mathbf{r})$ at the RCP

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exclusively depends on the atoms forming the ring, the correlation with the multicenter indices would reinforce the conclusions of previous studies.

2. Computational details

QTAIM 6-center delocalization index, 6-DI, adopts the form of Eq. (1) for restricted calculations on single determinant wave functions. Although the use of Kohn–Sham density functional theory (DFT) wave functions may be questionable, it has been proven repeatedly that very significant chemical information is obtained from them [13].

$$\Delta_6^{\text{QTAIM}} = 4n \sum_R \sum_{i,j,k,l,m,o} \langle i|j\rangle_A \langle j|k\rangle_B \langle k|l\rangle_C \langle l|m\rangle_D \langle m|o\rangle_E \langle o|i\rangle_F$$
(1)

where $i, j, \ldots$, represent occupied spatial orbitals and the space restricted integrals $\langle i|j\rangle$ are computed within the atomic domains of atoms A, B, etc; R represents all the non equivalent permutations (for C_1 symmetry) of atoms included in the summation of (1), and n is the number of centers. The multiplying factor $4n$ includes a factor 2 due to spin and $2n$ accounting for the number of permutations that are always equivalent, even in a cycle of C_1 symmetry (n because of the possibilities to select the starting atom and 2 for clockwise and anticlockwise) [6].

In the Mulliken approach, the integrals within the atomic domains are replaced by products of bond order matrix terms, P, and overlap matrix terms, S, as in Eq. (2), which as Eq. (1) is only valid for single determinant wave functions.

$$\Delta_6^{\text{Mull}} = \frac{4n}{2^n} \sum_R \sum_{i\in A} \sum_{j\in B} \sum_{k\in C} \sum_{l\in D} \sum_{m\in E}$$
$$\times \sum_{o\in F} PS_{ij} PS_{jk} PS_{kl} PS_{lm} PS_{mo} PS_{oi}$$
(2)

It is well known that DI's obtained with single determinant wave functions can provide significant errors in some cases, like in the case of H_2 and other diatomic molecules [14,15]. In this case we are interested in relative values computed for a series of very similar polyatomic systems, not including polar or strongly distorted bonds. Although wave functions obtained from correlated approaches such as CI would be very interesting, it seems currently nearly impossible to obtain these for molecules of the current size, except when using other approximations such as those recently tested by Matito et al. These involve a single-determinant like expression for higher order density matrices in terms of the first order one. Following such an approach, Matito et al. [16] found that the general trend in aromaticity based on 2 center bonding indices remains the same as in the single determinant approach. Correctly computed higher order densities for somewhat larger molecules have been used previously by Cooper and Ponec, showing that large problems can arise in multicenter indices for disputable 3 center 4 electron bonds or strongly distorted mole-

cules [17]. For the present molecules, no such effects are present, however. Therefore, variations of the correlated 6-DI's are expected to be similar to those obtained with the one determinant approximation. One of the aims of the present paper is precisely to confront the density matrices based indices with the electron density computed at certain points. Electron density computed at certain points can very well be used as an aromaticity index, avoiding the use of Hartree–Fock like approaches for computing density matrices.

The properties of the electron density at the RCP's considered in this work are the electron density, $\rho(\mathbf{r}_c)$, its Laplacian, $\nabla^2\rho(\mathbf{r}_c)$, and two of the eigenvalues of the Hessian matrix: λ_3 and λ_2. λ_3 is the eigenvalue associated to the eigenvector perpendicular to the ring plane, so that in the direction of the π density, and λ_2 is associated to an eigenvector lying in the ring plane.

The set of molecules studied is drawn in Fig. 1. All molecules were studied at the B3LYP/6-31G(d) level. Because of computing time reasons only the set comprising molecules **1**–**12**, **22**, **23**, and **27** was studied at the B3LYP/6-311++G(d,p) level. Mulliken 6-DI's were calculated using the smaller basis set for all molecules, whereas QTAIM 6-DI's were calculated with the largest basis set for the reduced set. It can be observed that the increase of computational cost (both in atomic partitioning and in basis set) does not alter any conclusion.

3. Results and discussion

Table 1 collects the QTAIM and Mulliken 6-DI's, together with the values of $\rho(\mathbf{r}_c)$ for all the benzenoid rings drawn in Fig. 1. The values of $\nabla^2\rho(\mathbf{r}_c)$ and λ_3 (see Supplementary Material), provide exactly the same information as $\rho(\mathbf{r}_c)$, as it will be shown later. Both the Mulliken 6-DI's and $\rho(\mathbf{r}_c)$ reflect the same order of aromaticity for benzenoid rings belonging to the same molecule. The only exceptions are the rings A and B in molecule **19**, although both indices reflect very small differences between these rings. The same can be said for QTAIM 6-DI's calculated using the larger basis set, that show the same order of aromaticity as $\rho(\mathbf{r}_c)$.

It must be noticed that the RCP properties display very small changes along the series of benzenoid rings here studied, whereas changes on the 6-DI's are much larger. As remarked in a previous work, [6] the contribution of the σ electrons to the 6-DI is very small. On the contrary, the σ density is expected to play an important role in the value of the RCP properties. Thus, aromaticity, which is related to the π electrons, can be considered as a small contribution to the RCP properties. However, in the absence of significant differences on the σ density, such as the series of benzenoid rings here studied, aromaticity becomes the main factor and its relative value can be estimated by $\rho(\mathbf{r}_c)$ and $\nabla^2\rho(\mathbf{r}_c)$. On the contrary, they are useless for comparing the aromaticity in cycles such as pyridine and benzene, due to the very different σ densities.
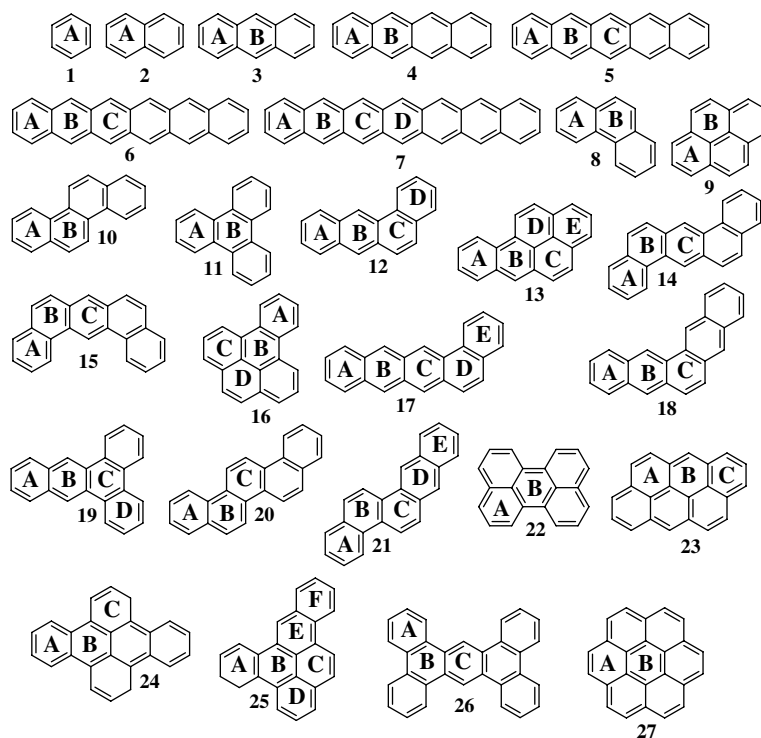
Fig. 1. Molecules studied and nomenclature employed.

Table 1
Mulliken and QTAIM 6-center electron delocalization indices, Δ_6^{Mull} and Δ_6^{QTAIM}, calculated at B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels respectively, and the electron density at the RCP's, $\rho(\mathbf{r}_c)$, calculated at the same levels

Ring	Δ_6^{Mull}	$\rho(\mathbf{r}_c)^a$	Δ_6^{QTAIM}	$\rho(\mathbf{r}_c)^b$	Ring	Δ_6^{Mull}	$\rho(\mathbf{r}_c)^a$	Ring	Δ_6^{Mull}	$\rho(\mathbf{r}_c)^a$	Δ_6^{QTAIM}	$\rho(\mathbf{r}_c)^b$
1A	0.0484	0.0200	0.0267	0.0217	13A	0.0264	0.0195	20A	0.0303	0.0197		
2A	0.0263	0.0194	0.0143	0.0209	13B	0.0129	0.0186	20B	0.0139	0.0187		
3A	0.0199	0.0191	0.0107	0.0206	13C	0.0095	0.0186	20C	0.0186	0.0190		
3B	0.0189	0.0190	0.0098	0.0204	13D	0.0156	0.0191	21A	0.0290	0.0196		
4A	0.0172	0.0190	0.0092	0.0205	13E	0.0240	0.0195	21B	0.0161	0.0188		
4B	0.0159	0.0188	0.0081	0.0202	14A	0.0324	0.0198	21C	0.0109	0.0184		
5A	0.0159	0.0189	0.0084	0.0204	14B	0.0097	0.0183	21D	0.0201	0.0192		
5B	0.0143	0.0187	0.0072	0.0201	14C	0.0233	0.0195	21E	0.0214	0.0193		
5C	0.0141	0.0187	0.0071	0.0201	15A	0.0324	0.0198	22A	0.0237	0.0194	0.0129	0.0208
6A	0.0152	0.0189	0.0080	0.0203	15B	0.0097	0.0183	22B	0.0033	0.0171	0.0021	0.0182
6B	0.0135	0.0187	0.0068	0.0200	15C	0.0230	0.0195	23A	0.0097	0.0186	0.0053	0.0199
6C	0.0131	0.0186	0.0065	0.0200	16A	0.0350	0.0200	23B	0.0131	0.0189	0.0073	0.0202
7A	0.0148	0.0189	0.0076	0.0203	16B	0.0054	0.0175	23C	0.0215	0.0193	0.0117	0.0207
7B	0.0131	0.0186	0.0067	0.0200	16C	0.0265	0.0196	24A	0.0348	0.0200		
7C	0.0125	0.0186	0.0063	0.0200	16D	0.0121	0.0187	24B	0.0053	0.0174		
7D	0.0122	0.0185	0.0061	0.0198	17A	0.0184	0.0191	24C	0.0290	0.0197		
8A	0.0314	0.0197	0.0172	0.0212	17B	0.0169	0.0190	25A	0.0358	0.0200		
8B	0.0119	0.0184	0.0065	0.0198	17C	0.0166	0.0190	25B	0.0041	0.0172		
9A	0.0243	0.0194	0.0133	0.0209	17D	0.0073	0.0180	25C	0.0152	0.0190		
9B	0.0123	0.0188	0.0067	0.0201	17E	0.0338	0.0198	25D	0.0257	0.0196		
10A	0.0298	0.0197	0.0163	0.0212	18A	0.0232	0.0193	25E	0.0138	0.0187		
10B	0.0149	0.0187	0.0082	0.0200	18B	0.0207	0.0193	25F	0.0271	0.0196		
11A	0.0347	0.0200	0.0189	0.0214	18C	0.0063	0.0179	26A	0.0351	0.0200		
11B	0.0051	0.0171	0.0030	0.0183	19A	0.0230	0.0194	26B	0.0043	0.0171		
12A	0.0222	0.0193	0.0119	0.0208	19B	0.0219	0.0195	26C	0.0273	0.0200		
12B	0.0205	0.0192	0.0107	0.0207	19C	0.0037	0.0169	27A	0.0164	0.0191	0.0089	0.0204
12C	0.0086	0.0181	0.0047	0.0194	19D	0.0357	0.0200	27B	0.0079	0.0185	0.0047	0.0196
12D	0.0332	0.0198	0.0181	0.0213								

[a] Values calculated at the B3LYP/6-31G(d) level.
[b] Values calculated at the B3LYP/6-311++G(d,p) level.

As a remarkable finding, the B3LYP values of $\rho(\mathbf{r}_c)$ and $\nabla^2\rho(\mathbf{r}_c)$ for polyacenes (molecules **1**–**7**) agree with the values of Mulliken and QTAIM 6-DI's. Thus, the outer rings display larger aromaticity than the inner ones. Since the RCP properties exclusively depend on the electron density of atoms forming the ring, the correlation with 6-DI's supports the conclusion that the multicenter indices only reflect the local ring currents and are slightly influenced by ring currents involving more than one ring [7,12]. The previous work by Howard and Krygowski [3] reached the opposite conclusion concerning local aromaticity gauged by the RCP properties, despite using a very similar basis set as our smaller basis. The main difference between their study and the present one lies in the use of Hartree–Fock calculations in the previous study versus DFT in the current one. Similar differences have also been found using the PDI when comparing relative aromaticities between the benzenoid rings of anthracene [8,18]. Given the fact that the DFT density apparently also yields geometries in better agreement with experiment, we trust more the DFT results [8,18]. In order to support the DFT conclusions, it is worth referring to the recent finding that RCP densities computed for a subset of the present molecule set at the CCSD/6-31G//B3LYP/6-31G* level confirm the DFT results and disagree with the Hartree–Fock results

[19]. This is also the case for the relative aromaticity of benzenoid rings in anthracene.

Fig. 2 shows the good linear correlation found between the natural logarithm of the Mulliken 6-DI's and $\rho(\mathbf{r}_c)$ and $\nabla^2\rho(\mathbf{r}_c)$ calculated at the lower level for all the benzenoid rings. This good correlation is not exclusively found for the Mulliken indices and Fig. 3 shows equivalent plots for the QTAIM indices calculated using the larger basis set. Figs. 2 and 3 also reflect the straight relation between the multicenter electron delocalization and the stability of the ring, the former accounting for the aromatic stabilization and the latter related to RCP properties.

We have also checked the existence of correlations between 6-DI's and the eigenvalues of the Hessian matrix. Howard and Krygowski [3] pointed out that the best fit between RCP properties and other aromaticity indices such as HOMA (harmonic oscillator model of aromaticity) was shown by λ_3. Fig. 4 shows the linear fittings of ln(QTAIM 6-DI's) with λ_3 and λ_2. As it can be seen the correlation is good for λ_3 in agreement with the Howard and Krygowski's results, but it clearly worsens for λ_2. Since λ_2 is placed in a nodal plane of the π density, it mainly depends on the σ density. Therefore, λ_2 is not expected to display good correlation with the natural log-
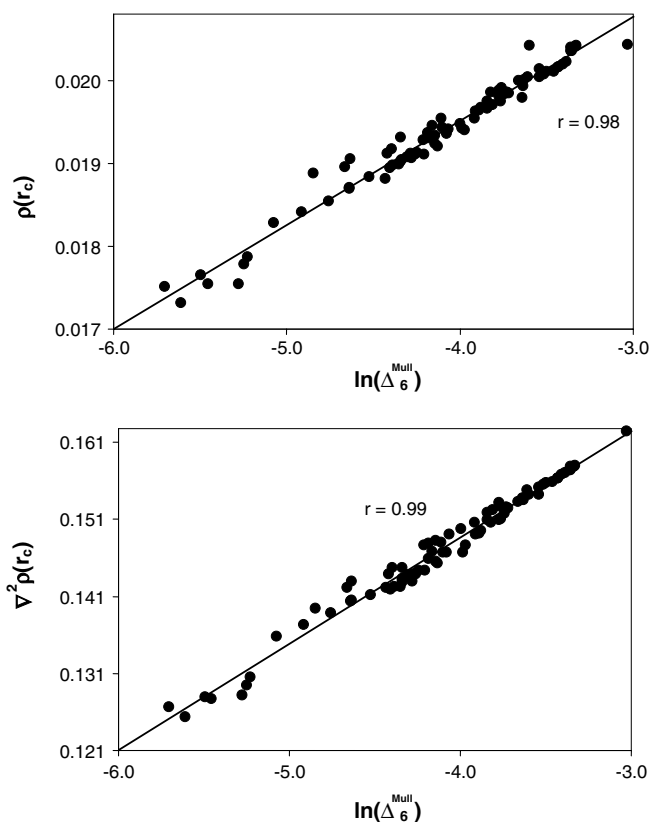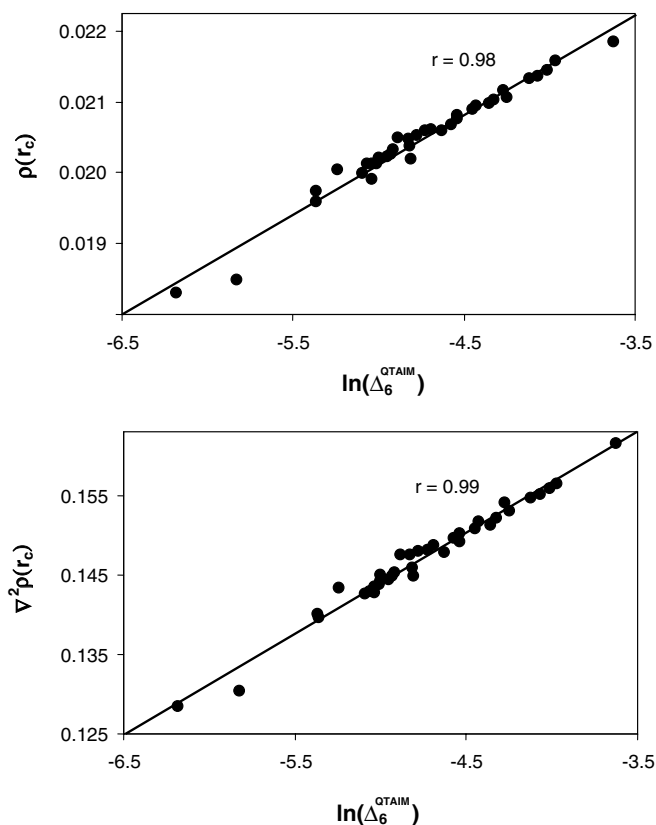

Fig. 2. Plots of the electron density, $\rho(\mathbf{r}_c)$, and its Laplacian, $\nabla^2\rho(\mathbf{r}_c)$, (both in au) at the RCP's of benzene rings drawn in Fig. 1 vs. the natural logarithm of Mulliken 6-center electron delocalization indices, $\ln(\Delta_6^{\mathrm{Mull}})$. All properties were computed at B3LYP/6-31G(d) level.

Fig. 3. Plots of the electron density, $\rho(\mathbf{r}_c)$, and its Laplacian, $\nabla^2\rho(\mathbf{r}_c)$, (both in au) at the RCP of some benzene rings drawn in Fig. 1 (see text for details) vs. the natural logarithm of QTAIM 6-center electron delocalization indices, $\ln(\Delta_6^{\mathrm{QTAIM}})$. All properties were computed at B3LYP/6-311++G(d,p) level.
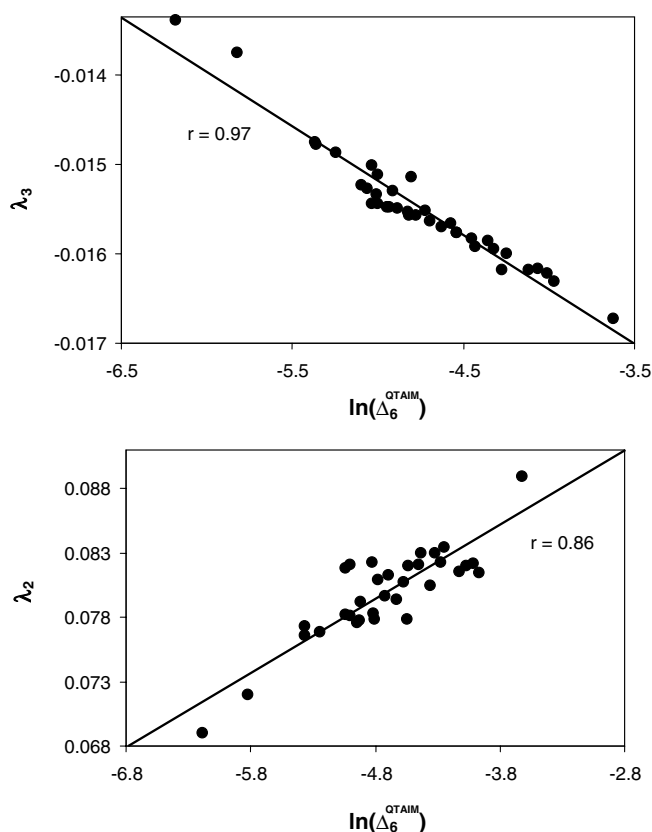
Fig. 4. Plots of the λ_3 and λ_2 eigenvalues of the Hessian matrix of the electron density, $\rho(\mathbf{r})$, at the RCP's of some benzene rings drawn in Fig. 1 (see text for details) vs. the natural logarithm of QTAIM 6-center electron delocalization indices, $\ln(\Delta_6^{QTAIM})$. All properties were computed at B3LYP/6-311++G(d,p) level.

arithm of the 6-DI, which, as explained above, mainly accounts for π electron delocalization.

4. Conclusions

The results obtained for 27 polycyclic aromatic hydrocarbons reflect that RCP properties and 6-DI's obtained with a monodeterminant approach are in complete agreement, providing the same order of aromaticity. Moreover, a logarithmic relation between both kinds of properties was shown.

The DFT calculations here presented contradict the previously reported HF calculations of the RCP properties for polyacenes. Thus, according to DFT calculations the local aromaticity decreases from outer to inner rings in polyacenes, both using the RCP properties and the approximated 6-DI's as aromaticity indicators. The DFT densities at RCP's are in line with those obtained from recent CCSD calculations, contradicting earlier HF results.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2006.11.009.

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