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Assessment of Clar's aromatic π-sextet rule by means of PDI, NICS and HOMA indicators of local aromaticity‡

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ABSTRACT: The local aromaticity of a series of benzenoid systems was determined through the use of structurally (HOMA) and magnetically (NICS) based measures, and also by using a new electronically based indicator of aromaticity, the *para*-delocalization index (PDI). The results were compared with the predictions of Clar's aromatic π-sextet rule. It is found that, for all analyzed benzenoid hydrocarbons having a single Clar structure, local aromaticity orderings of the different six-membered rings given by all descriptors of aromaticity tested are identical and in agreement with Clar's aromatic π-sextet rule. For benzenoid species that are described by a superposition of Clar structures, HOMA and PDI indices provide local aromaticity values that are totally consistent with Clar's rule, whereas NICS results deviate somewhat from the estimations based on this model. Copyright © 2005 John Wiley & Sons, Ltd.
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KEYWORDS: Clar's aromatic π-sextet rule; local aromaticity; *para*-delocalization index (PDI); harmonic oscillator model of aromaticity (HOMA); nucleus independent chemical shift (NICS); polycyclic aromatic hydrocarbons (PAHs)

INTRODUCTION

Even though the concept of aromaticity was introduced in 1865,[1] it still continues to be of central importance in physical organic chemistry for the rationalization of the structure, stability and reactivity of many molecules.[2–7] The Hückel $4n+2$ rule represented an important step forward in the comprehension of aromaticity.[8–11] Since this rule is strictly valid only for monocyclic conjugated systems, numerous attempts have been made to extend this rule to polycyclic systems. Among them, one of the most successful was Clar's model of the extra stability of $6n$ π-electron benzenoid species.[12–14] According to Clar's rule, the Kekulé resonance structure with the largest number of disjoint aromatic π-sextets, i.e. benzene-like moieties, is the most important for the characterization of the properties of polycyclic aromatic hydrocarbons (PAHs). Aromatic π-sextets are defined as six π-electrons localized in a single benzene-like ring separated from adjacent rings by formal CC single bonds. For instance, application of this rule to phenanthrene indicates that the resonance structure **2** (Scheme 1) is more important than resonance structure **1**. Therefore, outer rings in phenanthrene are expected to have a larger local aromaticity than the central ring. This result has been confirmed by several measures of local aromaticity.[15–17] Moreover, recent experimental results on the distribution of π-electrons in large PAHs,[18] valence bond calculations[19] and nucleus independent chemical shift (NICS) studies on pericondensed benzenoid PAHs[20] have provided extensive support for Clar's rule.

The Clar structure (see Scheme 1) of a given PAH is the resonance structure having the maximum number of isolated and localized aromatic π-sextets, with a minimum number of localized double bonds. In general, a PAH with a given number of aromatic π-sextets is kinetically more stable than its isomers with fewer aromatic π-sextets.[12–14,20] Moreover, aromatic π-sextet rings are considered to be the most aromatic centers in the PAH. The other rings are less aromatic and are chemically more reactive.[21] There are PAHs that present a

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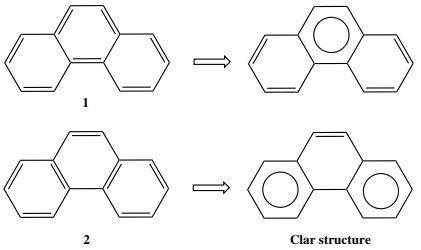


Scheme 1. Two of the five Kekulé resonance structures of phenanthrene and their corresponding Clar aromatic π-sextets indicated with a circle. The structure with the largest number of aromatic π-sextets is the so-called Clar structure

unique Clar structure (e.g. phenanthrene), whereas several Clar structures are possible for other PAHs.[14] For these latter, Clar's rule cannot differentiate which of the corresponding resonance structures is mainly responsible for the aromaticity of the system. Different attempts have been made in order to solve this limitation,[14,22–26] the most recent being the Y-rule by Ruiz-Morales.[20,27] In addition, we can briefly mention that an extension of Clar's model to non-benzenoid systems was also proposed some years ago by Glidewell and Lloyd.[28]

Because it is not an observable quantity, there is not yet any generally established definition of aromaticity. Probably the most widely accepted definition was that given by Schleyer and Jiao,[5] who defined aromatic systems as conjugated cyclic π-electron compounds that exhibit cyclic electron delocalization leading to bond length equalization, abnormal chemical shifts, enhanced diamagnetic susceptibility and magnetic anisotropies and energetic stabilization. Accordingly, the evaluation of aromaticity is usually based on the classical aromaticity criteria: structural, magnetic, energetic and reactivity-based measures.[1,6,7,29] In addition, measures of local aromaticity based on the analysis of electron delocalization have recently been proposed.[30,31] It is worth noting that the use of differently based aromaticity criteria is recommended for comparisons restricted to some regions or groups of relatively similar compounds owing to the multi-dimensional character of aromaticity.[29,32–34] In the present work, we used three quantitative local aromaticity criteria, the *para*-delocalization index (PDI),[30] the harmonic oscillator model of aromaticity (HOMA)[35,36] and NICS,[37] with the aim of investigating whether these three widely used methods for quantifying local aromaticity give results consistent with the qualitative original Clar's π-sextet model.[12,13]

Thus, as a structure-based measure, we employ the HOMA index, defined by Kruszewski and Krygowski as[35,36]

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

where n is the number of bonds considered and α is an empirical constant (for CC bonds $\alpha = 257.7$) fixed to give $\mathrm{HOMA} = 0$ for a model non-aromatic system, and $\mathrm{HOMA} = 1$ for a system with all bonds equal to an optimal value R_{opt}, which is 1.388 Å for CC bonds, assumed to be achieved for fully aromatic systems; R_i represents a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity.[2,33]

Magnetic indices of aromaticity are based on the π-electron ring current that is induced when the system is exposed to external magnetic fields. Here we use the NICS, proposed by Schleyer *et al.*,[37] as a magnetic index of aromaticity. This is one of the most widely employed indicators of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS values, the more aromatic the rings are.

Finally, as an aromaticity criterion based on electron delocalization, we calculate the recently reported PDI,[30,38] which is obtained employing the delocalization index (DI)[39–41] as defined in the framework of the AIM theory of Bader.[42–44] The PDI is an average of all DI of *para*-related carbon atoms in a given six-membered ring (6-MR). The DI value between atoms A and B, $\delta(A,B)$, is obtained by double integration of the exchange-correlation density $[\Gamma_{\mathrm{XC}}(\vec{\mathbf{r}}_1,\vec{\mathbf{r}}_2)]$ over the basins of atoms A and B, which are defined from the condition of zero-flux gradient in the one-electron density, $\rho(\mathbf{r})$:

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

$\delta(A,B)$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B. Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous work[30,38] has shown that for a series of planar and curved PAHs there is a satisfactory correlation between NICS, HOMA and PDI. In general, larger PDIs go with larger absolute values of NICS and larger HOMA values.

COMPUTATIONAL METHODS

Molecular geometries of the series of PAHs were fully optimized with the hybrid density functional theory (DFT) B3LYP method[45–47] using the 6–31G(d) basis set[48–50] by means of the Gaussian 98 program.[51] It has been demonstrated previously that the B3LYP/6–31G(d) method of calculation yields reasonable molecular structures of PAHs as compared with experiment.[17] The

calculation of the electronic (PDI), geometric (HOMA) and magnetic (NICS) aromaticity criteria was carried out at the same level of theory.

The GIAO method[52] was used to perform calculations of NICS at ring centers [NICS(0)] determined by the non-weighted mean of the heavy atom coordinates. To complement the NICS analysis, we also calculated the NICS(1) values, which are NICS measured at 1 Å above or below the center of the ring taken into analysis. Integrations of DIs were performed by use of the AIMPAC collection of programs.[53] Calculation of these DIs at the DFT level of theory cannot be performed exactly,[54] because the electron-pair density is not available at this level of theory. As an approximation, we used the Kohn–Sham orbitals obtained from DFT to calculate Hartree–Fock-like DIs:[54]

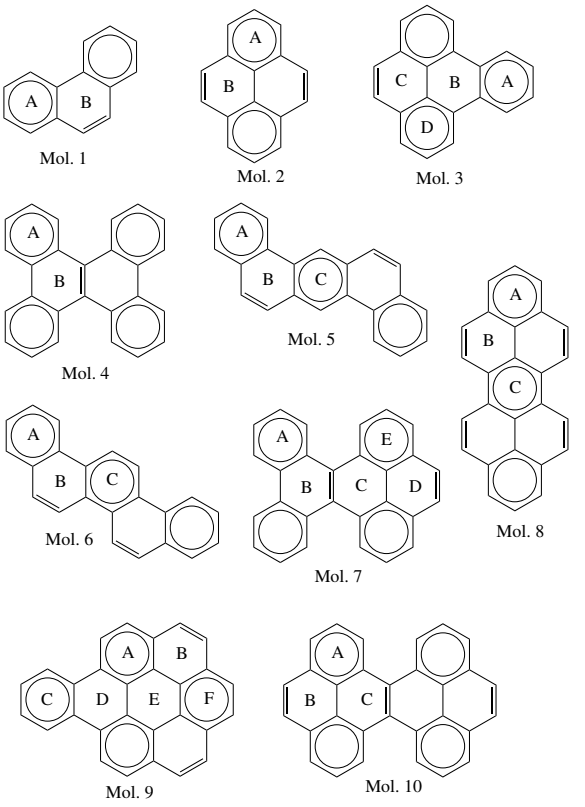
$$\delta(A,B) = 4\sum_{i,j}^{N/2} S_{ij}(A)S_{ij}(B) \qquad (3)$$

The summations in Eqn (3) run over all the $N/2$ occupied molecular orbitals. $S_{ij}(A)$ is the overlap of the molecular orbitals i and j within the basin of atom A. Equation (3) does not account for electron correlation effects. In practice, the values of the DIs obtained using this approximation are generally closer to the Hartree–Fock values than correlated DIs obtained with a configuration interaction method.[54] The numerical accuracy of the AIM calculations was assessed using two criteria: (i) the integration of the Laplacian of the electron density $[\nabla^2\rho(\mathbf{r})]$ within an atomic basin must be close to zero; (ii) the number of electrons in a molecule must be equal to the sum of all the electron populations of a molecule, and also equal to the sum of all the localization indices and half of the delocalization indices in the molecule.[40,41] For all atomic calculations, integrated absolute values of $\nabla^2\rho(\mathbf{r})$ were always <0.001 a.u. For all molecules, errors in the calculated number of electrons were always <0.01 a.u.

RESULTS AND DISCUSSION

Scheme 2 represents the series of 10 PAHs considered in the present work. All of them are small benzenoid hydrocarbons that have a single Clar structure. Table 1 gives the corresponding PDI, HOMA, and NICS values for this series of molecules.

All Kekulé valence structures depicted in Scheme 2 are the Clar structures of the 10 PAHs considered, as in all cases they have the maximum number of non-adjacent aromatic π-sextets (circles).[14] These π-sextets represent rings where six π-electrons tend to be localized. From a local aromaticity point of view, the rings enclosing a π-sextet are expected to present higher local aromaticity. We discuss the reliability of Clar's π-sextet rule by analyzing the local aromaticity of the rings through three



Scheme 2. Representation of the series of PAHs having a single Clar structure that were analyzed, with the corresponding ring labels.[14] Clar's aromatic π-sextets are indicated with circles

widely validated aromaticity criteria: PDI, HOMA and NICS.

With respect to the electronic-based measure, PDI, it can be seen how the largest PDI values in each PAH correspond to the π-sextets. The PDIs for aromatic π-sextets are within the range 0.09–0.06 e, with the only exception of ring 8C (0.045 e). On the other hand, non-π-sextet rings present lower PDI values ranging from 0.03 to 0.05 e. It must be noted that in all cases PDI can clearly differentiate the aromatic π-sextets, except for system 8, in which rings B and C present almost the same aromaticity. Hence PDI is shown to correlate perfectly with Clar's π-sextet rule.

Regarding the geometry-based aromaticity criterion, HOMA, the results in Table 1 indicate the same qualitative behavior for the HOMA and PDI values. In this case, the range of HOMA values for the aromatic π-sextets is 0.89–0.64, except for ring 8C (0.570). Lower HOMA values correspond to non-aromatic 6-MRs, which in some cases (rings 3B, 7B, 7C and 10C) even reach negative values. Hence the HOMA criterion also validates Clar's π-sextet rule.

Finally, the magnetic-based measure, NICS, also shows the same tendency as PDI and HOMA, aromatic π-sextets displaying the most negative NICS values. In particular, for this series, NICS gives larger differences between aromatic π-sextets and non-aromatic 6-MRs

Table 1. PDI (in electrons), HOMA and NICS (in ppm) values for the first series of PAHs studied (see the corresponding numbering in Scheme 2)

		Molecule									
Measure	Ring	1	2	3	4	5	6	7	8	9	10
PDI	A	0.080	0.069	0.086	0.084	0.083	0.080	0.084	0.068	0.058	0.071
	B	0.047	0.043	0.026	0.034	0.041	0.051	0.034	0.044	0.051	0.045
	C			0.044		0.068	0.059	0.031	0.045	0.082	0.031
	D			0.073				0.045		0.033	
	E							0.071		0.029	
	F									0.055	
HOMA	A	0.856	0.834	0.889	0.811	0.872	0.847	0.807	0.840	0.749	0.721
	B	0.435	0.553	−0.030	0.383	0.356	0.520	−0.518	0.550	0.686	0.477
	C			0.518		0.788	0.640	−0.496	0.570	0.853	−0.511
	D			0.838				0.479		0.341	
	E							0.723		0.510	
	F									0.732	
NICS	A	−10.06	−12.74	−8.63	−9.44	−9.93	−9.80	−9.30	−12.63	−10.97	−12.22
	B	−6.82	−5.07	−1.18	−4.13	−5.38	−7.15	−3.74	−4.82	−9.33	−5.88
	C			−5.47		−11.27	−8.35	−2.29	−13.04	−9.77	−1.83
	D			−11.58				−6.04		−5.86	
	E							−12.38		0.05	
	F									−11.39	

than PDI or HOMA, thus facilitating the distinction. NICS values for aromatic π-sextets are within the range −13.4 to −8.4 ppm, and for non-aromatic 6-MRs −7.2 to +0.1 ppm, with the only exception of ring 9B (−9.33 ppm). In contrast to PDI and HOMA, NICS clearly attributes a higher aromaticity to ring 8C (−13.04 ppm) than 8B (−4.82 ppm). By comparison with PDI and HOMA, it is worth noting that for compounds with more than one aromatic π-sextet NICS provides a different ordering of aromaticity of these π-sextets (i.e. molecules 3, 5, 7, 8 and 9). A complete analysis of the origin of these differences is beyond the scope of the present work. However, we think that the different ordering given by NICS results may be attributed to the well-known effect of the adjacent ring currents on the NICS measures.[17,55–57] The perpendicular component of NICS ($NICS_{zz}$),[58] recently presented as a better aromaticity measure than NICS, and NICS calculated at 1 Å above the molecular plane [NICS(1)],[59] considered to reflect better the π-electron effects, present the same tendency as NICS (see Supplementary material).

Figure 1 shows the correlations between the three aromaticity criteria for the 10 PAHs depicted in Scheme 2. From the graphics it is seen that, in general, some trends emerge. In PDI vs HOMA ($r^2 = 0.59$), the correlation would be largely improved ($r^2 = 0.84$) by removing negative HOMA values. Indeed, negative HOMA values are probably not as meaningful as positive values since it is considered that HOMA = 0 corresponds to a typical conjugated non-aromatic species such as 1,3-butadiene. In PDI vs NICS ($r^2 = 0.58$) and HOMA vs NICS ($r^2 = 0.55$), the correlations are even worsened after removal of the rings with negative HOMA values ($r^2 = 0.45$ and 0.51, respectively). This poorer correlation is due to the different

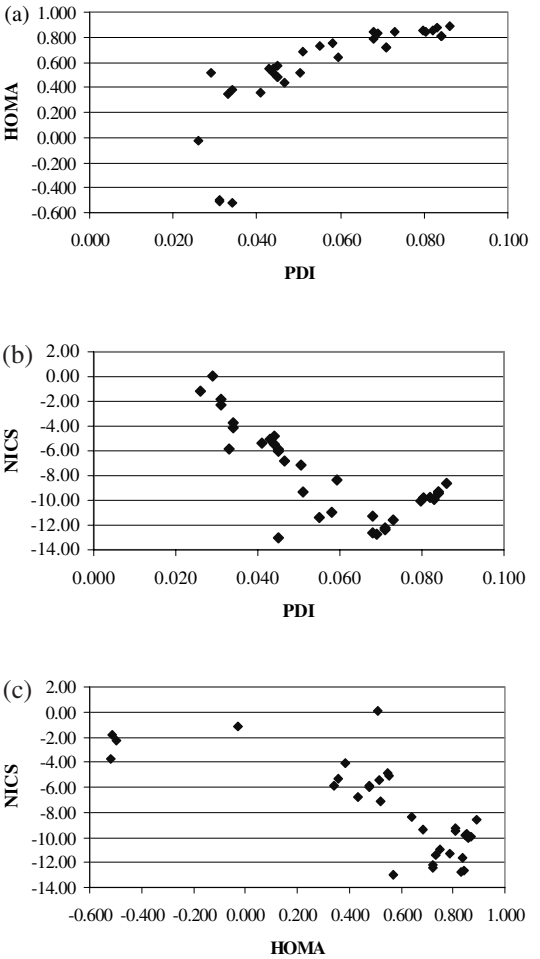
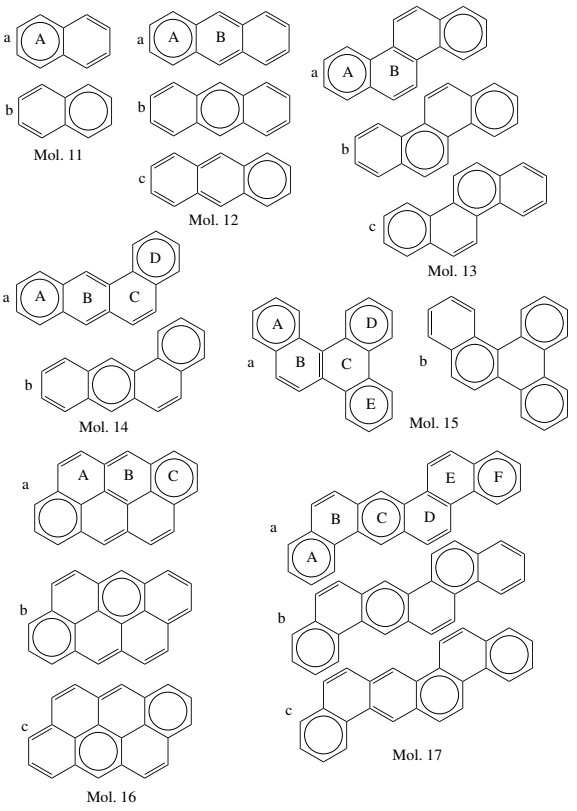


Figure 1. (a) Plot of PDI versus HOMA, (b) plot of PDI versus NICS and (c) plot of HOMA versus NICS for the series of PAHs studied



Scheme 3. Representation of seven PAHs having several Clar valence structures that were analyzed, with the corresponding ring labels. Clar's aromatic π-sextets are indicated with circles

orderings of aromaticity given by NICS in several molecules as commented on above.

So far we have shown that all three aromaticity criteria applied agree perfectly with the qualitative description given by Clar's π-sextet rule for PAHs having a single Clar structure. To complement this work, another series of PAHs having several Clar valence structures were studied.[14,17] Scheme 3 shows the additional systems considered with their Clar structures and Table 2 lists the corresponding PDI, HOMA and NICS measures. For molecule 11, it is worth noting that all three criteria attribute to ring A a lower aromaticity compared with molecule 1, whose ring A presents a similar environment. This reduction is attributed to the non-localizability of the π-sextet in molecule 11. This fact can be better seen in molecule 12, for which the lack of localizability of the π-sextets is evident. In this case, PDI and HOMA measures attribute very similar aromaticity to rings A and B, whereas according to NICS values a much larger aromatic character is attributable to ring B than ring A. The opposite behavior of NICS compared with PDI and HOMA supports the claimed overestimation by NICS of the local aromaticity of the central rings in polyacenes.[6,17,60] However, it is also worth noting that the higher aromaticity of the central ring of the molecule as indicated by NICS agrees with the stronger ring currents around the inner rings of acenes observed by Steiner and co-workers.[55,61]

In addition, molecule 13 contains two π-sextets in each of the three existing Clar structures. All three criteria coincide in attributing a higher local aromaticity to ring A than ring B. With respect to ring B, by comparison to the ranges of values for PDI, HOMA and NICS attributed to localized π-sextet rings for the above series of compounds (1–10), its values are between those found for aromatic π-sextet rings and non-aromatic 6-MRs. This description agrees perfectly with that considering the overall aromaticity of this system as the superposition of the three Clar structures of molecule 13, with ring A

Table 2. PDI (in electrons), HOMA and NICS (in ppm) values for the second series of PAHs studied (see the corresponding numbering in Scheme 3)

		Molecule						
Measure	Ring	11	12	13	14	15	16	17
PDI	A	0.076	0.066	0.080	0.069	0.079	0.036	0.083
	B		0.066	0.053	0.066	0.057	0.048	0.040
	C				0.038	0.031	0.064	0.067
	D				0.084	0.085		0.047
	E					0.085		0.054
	F							0.079
HOMA	A	0.769	0.619	0.829	0.697	0.749	0.447	0.877
	B		0.696	0.542	0.730	0.305	0.666	0.333
	C				0.266	−0.097	0.783	0.783
	D				0.883	0.820		0.464
	E					0.883		0.568
	F							0.824
NICS	A	−9.98	−8.84	−9.94	−9.30	−10.19	−1.90	−9.83
	B		−12.60	−7.69	−11.69	−7.68	−10.06	−5.06
	C				− 4.58	−3.91	−12.70	−11.36
	D				−9.81	−9.55		−6.42
	E					−8.99		−7.81
	F							−9.84

presenting an aromatic π-sextet in two Clar structures, and with ring B with just a π-sextet in a single Clar structure. This explains the higher aromaticity of ring A. With respect to molecule 14, a similar behavior to the two previous systems is found, as both possible Clar structures give a similar contribution. PDI and HOMA give the largest aromatic character to ring D, a lower equivalent aromaticity to rings A and B and consider ring C almost non-aromatic. This description agrees perfectly with considering the overall aromaticity of this system as the superposition of the two Clar structures, with ring D presenting a π-sextet in both cases, rings A and B with just one π-sextet and ring C with none. The NICS criterion also considers rings A, B and D to be more aromatic than C, but with a different ordering, hence not meeting Clar's rules' description in a precise way. This does not necessarily mean that NICS is failing in these systems because, when several Clar valence structures are possible, one of them may have a dominant character. However, it is also true that the different results obtained with NICS compared with HOMA and PDI in PAH molecule 14 may be caused by the magnetic influence of adjacent rings. For molecules 15, 16 and 17, we find analogous results to those found for molecule 14, and therefore for the sake of conciseness they will not be commented on further.

CONCLUSIONS

A series of PAHs were studied to assess the validity of the qualitative Clar's π-sextet rule by means of three widely applied quantitative criteria of local aromaticity: PDI, HOMA and NICS. For the series of PAHs having a single Clar structure, all local aromaticity criteria employed verify the validity of Clar's rule. The PDI, HOMA and NICS results justify the location of the π-sextets in the corresponding rings according to Clar's rule. The results are less clear for systems having several Clar structures. The HOMA and PDI results are in agreement with Clar's rule if one assigns the same weight to all possible Clar structures. On the other hand, the NICS values in some cases deviate from the estimates of local aromaticity based on Clar's rule. This does not necessarily mean that NICS values fail for these systems because, when several Clar valence structures are possible, one of them may have a dominant character. However, the possibility that the different qualitative results obtained with NICS compared with HOMA and PDI in certain PAHs with several Clar structures may be caused by the magnetic influence of adjacent rings also cannot be ruled out.

Supplementary material

$NICS_{zz}$ and NICS(1) values for all compounds are available in Wiley Interscience.

Note: It is worth noting that the validity of the Clar's model was also discussed by Schleyer and coworkers (Moran D, Stahl F, Bettinger HF, Schaefer III HF, Schleyer PvR. *J. Am. Chem. Soc.* 2003; **125**: 6746–6752) for D_{6h}-symmetric polybenzenoid hydrocarbons using NICS as a measure of aromaticity.

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