

Analysis of Electron Delocalization in Aromatic Systems: Individual Molecular Orbital Contributions to Para-Delocalization Indexes (PDI)

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Our research group has recently defined two new aromaticity indexes based on the analysis of electron delocalization in aromatic species using the quantum theory of atoms-in-molecules. One of these indexes is the para-delocalization index (PDI) that measures the electronic delocalization between para-related carbon atoms in six-membered rings. In this paper, we show that this index can be partitioned into individual molecular orbital contributions. We have applied this PDI decomposition to several polycyclic aromatic hydrocarbons showing that this partitioning provides new insight into the origin of aromaticity.

1. Introduction

The concept of aromaticity is of central importance for the interpretation of molecular structure, stability, reactivity, and magnetic properties of many organic and inorganic compounds.^{1,2} Aromaticity is not an observable and consequently it has no precise quantitative definition and is not directly measurable experimentally. The imprecise nature of aromaticity has stimulated the quest for quantitative definitions, although nearly everyone would agree that there is not a well-established method to quantify the aromatic character of molecules yet. The evaluation of aromaticity is usually done indirectly by measuring some physicochemical property that reflects the aromatic character of molecules. Thus, most aromaticity indicators are based on the classical aromaticity criteria, namely, structural, magnetic, energetic, and reactivity-based measures.^{2,3} Undoubtedly, the origin of the aromatic properties is the cyclic delocalized distribution of π -electrons. For this reason, more recently, new ways to quantify the aromaticity based on the measure of electronic delocalization in aromatic molecules have been devised (for a recent review see ref 4). In particular, two new indexes based on the calculation of delocalization indexes (DIs) in the framework of the quantum theory of atoms-in-molecules (QTAIM) have been recently defined by some of us: the para-delocalization index (PDI)⁵ and the aromatic fluctuation index (FLU).⁶ In this context it is worth mentioning the work of Matta et al.⁷ who also attempted to construct an HOMA-like index⁸ from QTAIM by substituting the bond length by the total electron delocalization and also the use by Bultinck et al.⁹ of n -center electron DIs as descriptors of aromaticity.

In the continual drive to reach a wider understanding of aromaticity, some aromaticity measures have been separated into their σ and π contributions in planar species. This goal has been achieved for a series of indicators of aromaticity, namely, ring currents,¹⁰ nucleus-independent chemical shifts (NICS),^{11,12} electron localization function (ELF),¹³ and aromatic stabilization

energies (ASE).¹⁴ Less common is the separation of aromaticity indexes into individual molecular orbital (MO) contributions in MO-based methods, although successful experiences have been reported for NICS^{12,15,16} and ring currents.^{17–20} The aim of the present work is to show that PDI can also be separated into individual MO contributions and, in the particular case of planar systems, into its σ and π contributions. Results for a series of polycyclic aromatic hydrocarbons (PAHs) are presented and compared when possible with results from MO-dissected NICS and ring currents.

2. Theoretical Basis of the Analysis

In 1996, Bader and co-workers²¹ reported in a seminal work that the electron delocalization in benzene was greater for para-related carbon atoms (para-DI) than for *meta*-related ones (meta-DI). Later on, some of us⁵ defined the para-delocalization index (PDI) as the average of para-DI in six-membered rings (6-MRs) and used this index as a measure of local aromaticity. The PDI is a specific measure of local aromaticity for 6-MRs, where three para-related positions exist, namely, (1,4), (2,5), and (3,6). By definition, the PDI of a 6-MR is given by

$$\text{PDI} = \frac{\delta(1,4) + \delta(2,5) + \delta(3,6)}{3} \quad (1)$$

In eq 1, $\delta(A,B)$, the DI, is derived from the double integration of the exchange-correlation density over the atomic basins defined within the QTAIM theory:²²

$$\delta(A,B) = -2 \int_A \int_B \Gamma_{xc}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2)$$

The term $\delta(A,B)$ gives a quantitative measure of the number of electron pairs delocalized or shared between atomic basins A and B.

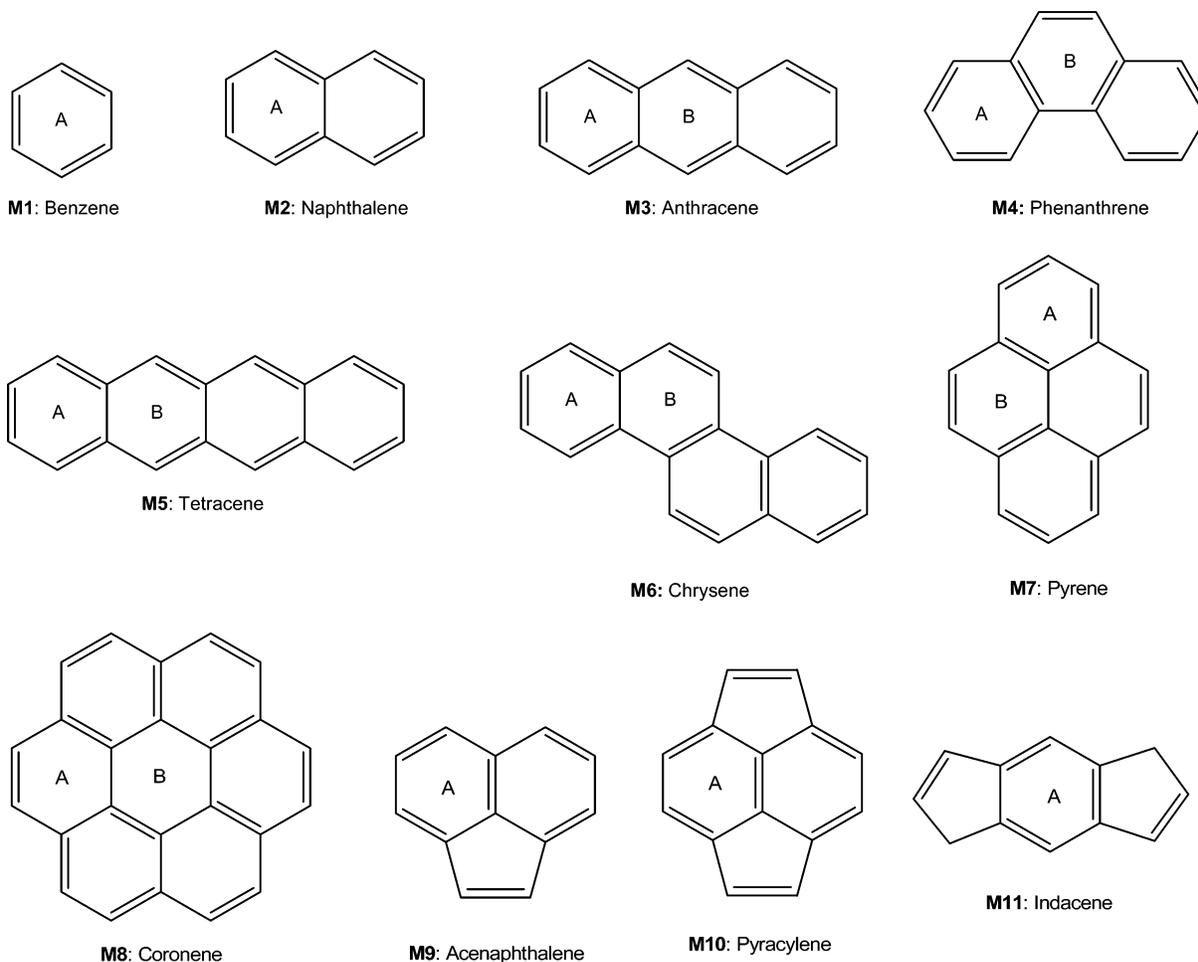
For closed-shell molecules and for single determinant wave functions, eq 2 is simplified to²²

$$\delta(A,B) = 2 \sum_{i,j} S_{ij}(A) S_{ij}(B) \quad (3)$$

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CHART 1: Schematic Representations of the Molecules Studied Together with Ring Labels

where the summations run over all the occupied molecular spin-orbitals and $S_{ij}(A)$ is the overlap between occupied molecular spin-orbitals i and j over the basin of atom A.

In planar molecules the orbitals can be classified as σ or π , depending on their symmetric or antisymmetric behavior with respect to reflection in the plane. In these molecules and because the QTAIM partition of space preserves the symmetry of the system, the overlap integrals $S_{ij}(A)$ vanish when i and j belong to different sets, and consequently, the contributions of σ and π electrons to the DIs can be separated exactly. In this case, it is possible to define the π contribution to the PDI using the π component of the DIs between para-related carbon atoms in 6-MRs as

$$\text{PDI}_{\pi} = \frac{\delta_{\pi}(1,4) + \delta_{\pi}(2,5) + \delta_{\pi}(3,6)}{3} \quad (4)$$

Finally, eq 3 can also be written as

$$\delta(A,B) = \sum_i 2 \sum_j S_{ij}(A) S_{ij}(B) = \sum_i \delta_i(A,B) \quad (5)$$

where $\delta_i(A,B)$ gives the contribution of the i orbital to the total $\delta(A,B)$. Thus, for monodeterminantal wave functions, the DI can be separated into its individual MO contributions and, in particular, the PDI can also be split into MO components as

$$\text{PDI}_i = \frac{\delta_i(1,4) + \delta_i(2,5) + \delta_i(3,6)}{3} \quad (6)$$

with

$$\text{PDI} = \sum_i \text{PDI}_i = \sum_i \frac{\delta_i(1,4) + \delta_i(2,5) + \delta_i(3,6)}{3} \quad (7)$$

For planar species, one can also define analogously the $\text{PDI}_{\pi,i}$ as the contribution of the i π -orbital to the PDI_{π} . Although total $\delta(A,B)$ or $\delta_{\pi}(A,B)$ are always positive, the components $\delta_i(A,B)$ or $\delta_{\pi,i}(A,B)$ can be positive or negative depending on the overlaps between i and j orbitals in the basins of atoms A and B. $\delta_i(A,B)$ is negative when the two electrons occupying orbital i cause a localization of the rest of the electrons in the molecule and, therefore produce a reduction in the total electronic delocalization.

3. Computational Details

Geometries of all PAHs in their ground states have been fully optimized with the hybrid density functional theory (DFT) B3LYP method²³ using the 6-311G(d,p) basis set by means of the Gaussian 03 program.²⁴ Integrations of DIs needed to calculate the PDIs have been performed using the AIMPAC collection of programs.²⁵ Calculation of these DIs at the DFT level of theory cannot be performed exactly²⁶ because the electron-pair density is not available at this level of theory. As an approximation, we have used the Kohn–Sham orbitals obtained from DFT to calculate Hartree–Fock-like DIs using eq 5.²⁶ The numerical accuracy of the AIM calculations has been assessed using two criteria: (i) The integration of the

TABLE 1: PDI and PDI_π for All Studied Rings as Well as All Individual Molecular Orbital Contributions to PDI_π (Units Are Electrons)

molecule	symmetry	label	orbitals	PDI contributions		molecule	symmetry	label	orbitals	PDI contributions				
				A	B					A	B			
benzene	<i>D</i> _{6h}	M1	a _{2u} (17)	-0.088		chrysene	<i>C</i> _{2h}	M6	a _u (60)	0.011	0.017			
			e _{1g} (20,21)	0.181					PDI _π	0.070	0.044			
			PDI _π	0.093					PDI	0.079	0.052			
			PDI	0.103										
naphthalene	<i>D</i> _{2h}	M2	b _{1u} (27)	-0.045		pyrene	<i>D</i> _{2h}	M7	b _{1u} (39)	-0.024	-0.025			
			b _{2g} (31)	-0.012					b _{2g} (45)	-0.033	0.011			
			b _{3g} (32)	0.046					b _{3g} (46)	0.013	-0.006			
			b _{1u} (33)	0.045					b _{1u} (49)	0.016	-0.008			
			a _u (34)	0.031					a _u (50)	0.034	0.011			
			PDI _π	0.066					b _{1u} (51)	0.005	0.039			
			PDI	0.075					b _{2g} (52)	0.029	0.016			
									b _{3g} (53)	0.020	-0.003			
anthracene	<i>D</i> _{2h}	M3	b _{1u} (36)	-0.021	-0.045	coronene	<i>D</i> _{6h}	M8	a _{2u} (55)	-0.014	-0.023			
			b _{2g} (39)	-0.033	0.015				e _{1g} (61,62)	0.020	0.022			
			b _{1u} (43)	0.010	-0.018				e _{2u} (68,69)	0.006	-0.005			
			b _{3g} (44)	0.021	0.048				a _{2u} (72)	0.013	-0.015			
			a _u (45)	0.039	-0.009				b _{1g} (73)	0.000	0.000			
			b _{2g} (46)	0.027	0.029				b _{2g} (74)	0.016	0.003			
			b _{3g} (47)	0.011	0.035				e _{1g} (75,76)	0.026	0.051			
			PDI _π	0.056	0.055				e _{2u} (77,78)	0.018	-0.009			
phenanthrene	<i>C</i> _{2v}	M4	b ₁ (36)	-0.027	-0.035	acenaphthalene	<i>C</i> _{2v}	M9	b ₁ (30)	-0.036				
			a ₂ (40)	-0.035	0.013				a ₂ (35)	-0.011				
			b ₁ (43)	0.007	0.005				b ₁ (37)	0.019				
			b ₁ (44)	0.035	0.011				b ₁ (38)	0.041				
			a ₂ (45)	0.037	0.014				a ₂ (39)	0.028				
			a ₂ (46)	0.035	0.013				b ₁ (40)	0.020				
			b ₁ (47)	0.021	0.016				PDI _π	0.060				
			PDI _π	0.072	0.037				PDI	0.070				
tetracene	<i>D</i> _{2h}	M5	b _{1u} (46)	-0.011	-0.032	pyracylene	<i>D</i> _{2h}	M10	b _{1u} (34)	-0.035				
			b _{2g} (48)	-0.026	-0.004				b _{2g} (38)	0.023				
			b _{1u} (51)	-0.015	0.002				b _{3g} (41)	-0.011				
			b _{3g} (55)	0.011	0.034				b _{1u} (43)	-0.006				
			b _{2g} (56)	0.015	-0.008				a _u (44)	0.026				
			a _u (57)	0.029	0.009				b _{1u} (45)	0.041				
			b _{1u} (58)	0.019	0.021				b _{2g} (46)	0.021				
			b _{3g} (59)	0.025	0.005				PDI _π	0.058				
			a _u (60)	0.004	0.025				PDI	0.068				
			PDI _π	0.052	0.053				indacene	<i>D</i> _{2h}	M11	b _{1u} (29)	-0.027	
			PDI	0.061	0.061							b _{2g} (35)	0.017	
chrysene	<i>C</i> _{2h}	M6	a _u (45)	-0.016	-0.030	b _{3g} (37)	0.025							
			b _g (48)	-0.033	-0.001	b _{1u} (38)	-0.007							
			a _u (52)	-0.013	-0.001	a _u (39)	-0.012							
			b _g (55)	0.006	0.012	b _{2g} (40)	0.025							
			a _u (56)	0.027	0.018	PDI _π	0.021							
			b _g (57)	0.031	0.007	PDI	0.030							
			b _g (58)	0.031	0.004									
			a _u (59)	0.026	0.017									

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.²⁷ For all atomic calculations, integrated absolute values of $\nabla^2\rho(\mathbf{r})$ were always less than 0.001 au. For all molecules, errors in the calculated number of electrons were always less than 0.001 au.

4. Results and Discussion

Chart 1 depicts the eleven PAHs analyzed together with the labels assigned to each different ring. Table 1 contains the values of the PDI and PDI_π for all studied rings as well as all individual MO contributions to PDI_π, which are certainly the most important contributions to the total PDI. The PDI_π contribution to the total PDI ranges from 90% in the most aromatic 6-MR (benzene) to 70% for the least aromatic 6-MR of indacene. The

PDI_σ obtained as the difference between the total PDI and PDI_π has values that go from 0.010 e in benzene, pyracylene, and acenaphthalene to 0.008 e in ring B of chrysene. So, the σ contribution to PDI is relatively small and, more importantly, it is quite constant for all PAHs studied; therefore, the differences between PDI values come mainly from the PDI_π contribution. For this reason, the decomposition into individual MO contributions in Table 1 is only done for the PDI_π part of the PDI. The occupied π-orbitals of the eleven PAHs studied are depicted in Figure 1.

For the archetypical aromatic molecule, benzene, it is found that the doubly degenerated e_{1g}(HOMO) orbitals are those that have a greater contribution to the PDI. The a_{2u} π-orbital has a negative contribution of -0.088 e. This means that the two electrons in a_{2u} MO reduce the delocalization between para-

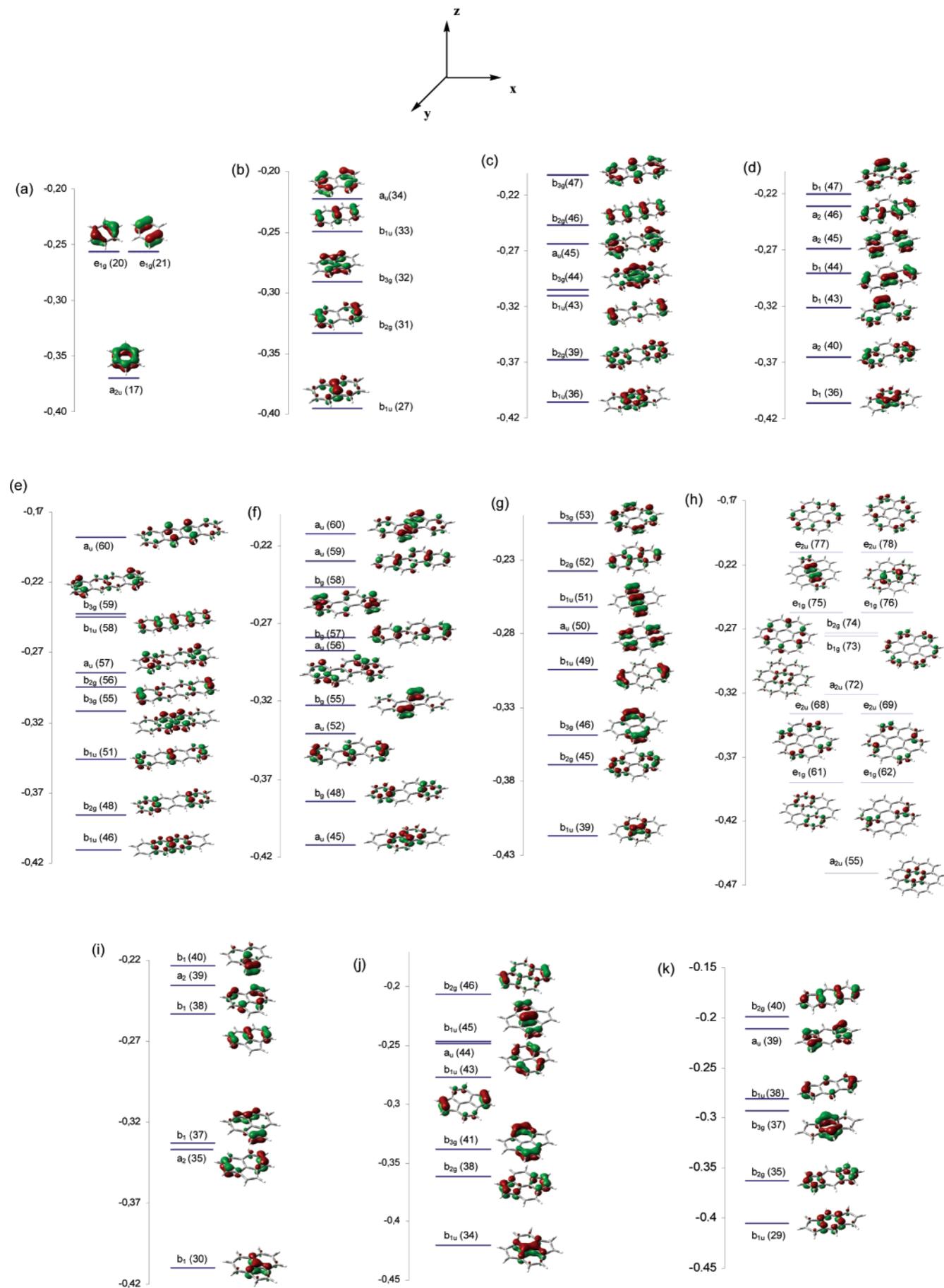


Figure 1. Occupied π molecular orbitals of (a) benzene, (b) naphthalene, (c) anthracene, (d) phenanthrene, (e) tetracene, (f) chrysenes, (g) pyrene, (h) coronene, (i) acenaphthalene, (j) pyracylene, and (k) indacene. Isosurface values are -0.05 and 0.05 au. The z -axis contains energies in hartrees.

related carbon atoms in benzene. This can be understood by simple inspection of the a_{2u} and e_{1g} π -orbitals, which shows that the products $S_{a_{2u}e_{1g}}(C_1) S_{a_{2u}e_{1g}}(C_4)$, $S_{a_{2u}e_{1g}}(C_2) S_{a_{2u}e_{1g}}(C_5)$, and $S_{a_{2u}e_{1g}}(C_3) S_{a_{2u}e_{1g}}(C_6)$ involved in the $PDI_{\pi,a_{2u}}$ calculation are always negative or zero. Indeed, the product $S_{ij}(A) S_{ij}(B)$, being A and B para related carbon atoms in a 6-MR, is always negative or zero if the sum of total nodal planes in orbitals i and j gives an odd number and positive or zero otherwise. Interestingly, when the two electrons from orbital a_{2u} are removed without reoptimizing the wave function, the PDI_{π} value becomes 0.375 e, which means that the aromaticity of benzene increases by removing these two electrons in the a_{2u} orbital according to PDI values.

Our result for benzene is totally in agreement with those derived from the analysis of the individual MO contributions to ring currents and dissected-MO NICS. As shown by Steiner and Fowler, an occupied-to-unoccupied $e_{1g}(\text{HOMO}) \rightarrow e_{2u}(\text{LUMO})$ translationally allowed transition gives the main diamagnetic contribution to the diatropic ring of benzene.^{18–20} According to this result only the four electrons of the two e_{1g} π -orbitals contribute significantly to the ring current.^{18,19} As to the NICS studies, although the NICS(0) value of the a_{2u} MO is more negative than that of the two e_{1g} π -orbitals,¹² the opposite is true for NICS_{zz}(0) (the zz tensor component of the isotropic NICS(0)).¹⁶ Because the ring current density in aromatic compounds is more related to NICS_{zz}(0) than to NICS(0) itself,²⁸ the conclusion from NICS studies is also that the e_{1g} π -orbitals are the main responsible of the aromatic behavior in benzene.¹⁶

In the naphthalene π -system again only the four electrons in the two highest-lying $a_u(\text{HOMO})$ and $b_{1u}(\text{HOMO}-1)$ make significant contributions to the total diamagnetic ring current.¹⁹ These two orbitals also give important individual MOs contributions to PDI, but in our case the orbital that contributes the most to the PDI is the $b_{3g}(\text{HOMO}-2)$ owing to the large and positive $S_{a_u b_{3g}}(C_1) S_{a_u b_{3g}}(C_4)$ term. Thus, the three highest-lying MOs of naphthalene contribute positively to the PDI, and the two lowest-lying π -orbitals have negative contributions, especially the $b_{1u}(\text{HOMO}-7)$. Thus, like in benzene, the π -orbital with a unique nodal plane (the molecular plane) is the one that reduces more significantly the PDI value.

Similarly, for the A ring of anthracene and phenanthrene, the four highest-lying occupied π -orbitals are those that contribute more to the PDI, whereas involvement of the three lowest-lying π -orbitals is negative or close to zero. Contributions of the four highest-lying occupied π -orbitals to the PDI of phenanthrene are larger, in general, than those to anthracene as expected from the large aromatic character of ring A in phenanthrene.²⁹ For the B ring of anthracene the $a_u(\text{HOMO}-2)$ has a negative contribution, whereas the $b_{2g}(\text{HOMO}-8)$ has a positive nonnegligible role in the π -para electronic delocalization. For tetracene and chrysene, the six highest-lying MOs are those that contribute more to the PDI of both rings A and B, whereas the three lowest-lying π -orbitals have a negative contribution, with the only exception of the $b_{2g}(\text{HOMO}-4)$ and $b_{1u}(\text{HOMO}-9)$ orbitals for the ring B of tetracene that have small negative and positive contributions to PDI, respectively.

As indicated by other aromaticity indexes,³⁰ PDI gives also the largest aromaticity to the most external rings A of pyrene and coronene. For these A rings, the largest contributions to PDI come from the six and seven highest-lying occupied π -orbitals, respectively. In particular, for the ring A of pyrene, the large value assigned to the $a_u(\text{HOMO}-3)$ π -orbital comes mainly from its interaction with the $b_{3g}(\text{HOMO})$. Interestingly, for the less aromatic ring B of pyrene and coronene, the

contributions from the b_{3g} and $e_{2u}(\text{HOMO})$ orbitals, respectively, to the PDI values are negative. Indeed, for coronene, we find, unexpectedly, that the pair of degenerate $e_{2u}(\text{HOMO})$ s does not have an important participation to the PDIs of rings A and B. This result is not in line with the orbital contributions to the current density analysis carried out by Steiner and Fowler in coronene. These authors found that both the inner and outer circulations in coronene come mainly from the four electrons in the degenerate $e_{2u}(\text{HOMO})$.¹⁹

Acenaphthalene results from the addition of a fused 5-MR to naphthalene, whereas a further addition of a 5-MR leads to pyracylene. 5-MR addition decreases the aromaticity of the 6-MRs when going from naphthalene to acenaphthalene, and from this to pyracylene.³¹ Similarly to that found for most 6-MRs, the main contributions to the PDI of the 6-MRs in acenaphthalene originate from the highest-lying π -orbitals ($b_{1u}(\text{HOMO}, \text{HOMO}-2, \text{HOMO}-3)$ and $a_2(\text{HOMO}-1)$). For pyracylene, the most important individual MO contributors to PDI are the $b_{2g}(\text{HOMO}$ and $\text{HOMO}-8)$ π -orbitals and especially the near-degenerate $b_{1u}(\text{HOMO}-1)$ and $a_u(\text{HOMO}-2)$ π -MOs. This is consistent with the fact that the electrons placed in these two latter orbitals are the main responsible for the diamagnetic electronic circulation around the perimeter of the naphthalenic unit, according to Steiner and Fowler.¹⁹ Finally, for indacene, with two 5-MRs and only one 6-MR, the aromaticity of the 6-MR is rather low and the main contributions to PDI come from the b_{2g} orbitals, specially owing to the positive overlap between orbitals $b_{3g}(\text{HOMO}-3)$ and $b_{2g}(\text{HOMO})$. MO-dissected ring currents also show that the origin of the paratropic ring current of the 6-MR in indacene lies basically in the $b_{2g}(\text{HOMO}) \rightarrow b_{1g}(\text{LUMO})$ transition.

4. Conclusions

In this work, we have decomposed the para-delocalization index of local aromaticity into its individual molecular orbital components for a series of PAHs. In general, we have found the lowest-lying π -MOs contribute negatively to the PDI_{π} and the total PDI, whereas the highest-lying π -MOs are those that increase more the π -electronic delocalization between para-related C atoms. In this sense, those orbitals with a larger number of nodal planes usually have a larger contribution to the para-electronic delocalization than those with a few nodal planes. Indeed, for all systems studied, the π -orbital with a unique nodal plane (the molecular plane) negatively contributes to the PDI, and in most cases this π -orbital is the one that reduces more significantly the PDI value.

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