

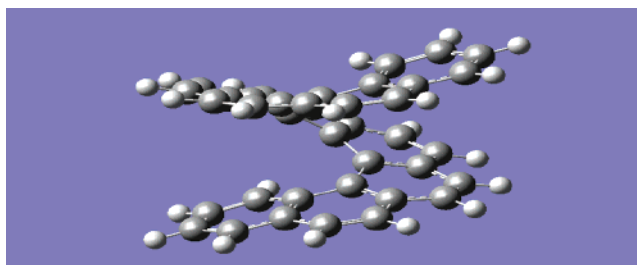
Local Aromaticity of $[n]$ Acenes, $[n]$ Phenacenes, and $[n]$ Helicenes ($n = 1-9$)

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The local aromaticity of the six-membered rings in three series of benzenoid compounds, namely, the $[n]$ acenes, $[n]$ phenacenes, and $[n]$ helicenes for $n = 1-9$, has been assessed by means of three probes of local aromaticity based on structural, magnetic, and electron delocalization properties. For $[n]$ acenes our analysis shows that the more reactive inner rings are more aromatic than the outer rings. For $[n]$ phenacenes, all indicators of aromaticity show that the external rings are the most aromatic. From the external to the central ring, the local aromaticity varies in a damped alternate way. The trends for the $[n]$ helicene series are the same as those found for $[n]$ phenacenes. Despite the departure from planarity in $[n]$ helicenes, only a very slight loss of aromaticity is detected in $[n]$ helicenes as compared to the corresponding $[n]$ phenacenes. Finally, because of magnetic couplings between superimposed six-membered rings in the higher members of the $[n]$ helicenes series, we have demonstrated that the NICS indicator of aromaticity artificially increases the local aromaticity of their most external rings.

Introduction

The concept of aromaticity is fundamental to rationalize and understand the structure and reactivity of about two-thirds of all known chemical species.¹ In the quest for a better understanding of this concept, the study of compounds with condensed benzene rings, the so-called benzenoid hydrocarbons, has occupied many organic and theoretical chemists.

There are at least three series of aligned benzenoid compounds (see Chart 1). A first series corresponds to the $[n]$ acenes, which are planar benzenoid hydrocarbons with linearly annelated benzene rings, such as benzene (**A1**), naphthalene (**A2**), anthracene (**A3**), naphthacene (**A4**), pentacene (**A5**), hexacene (**A6**), and so on. These compounds show increasing reactivity with the number of rings. Indeed, naphthacene, pentacene, and hexacene are reported to be unstable to light and air.² The so-called $[n]$ phenacenes are a second series of these benzenoid compounds. $[n]$ Phenacenes, with a zigzag kind of condensation, are planar angular fused analogues of $[n]$ acenes. The two lower members of these series coincide and they start to differentiate from the third member, phenanthrene (**P3**), and also for chrysene (**P4**), picene (**P5**), and the higher members of the series. Experimental

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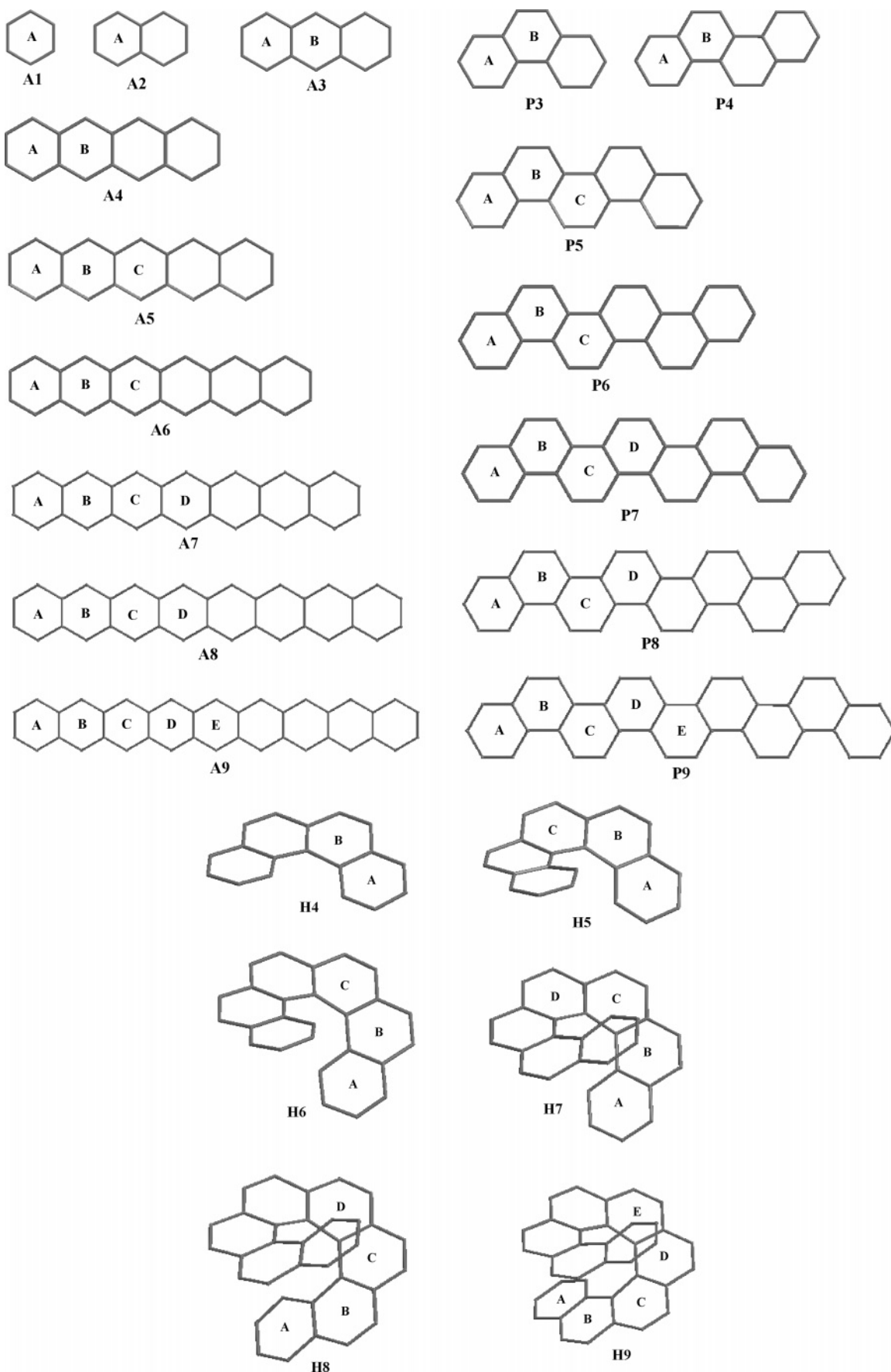
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CHART 1. Labels for the Molecules and Rings^a

^a [n]Acene series; [n]phenacene series; and [n]helicene series.

evidence^{3–5} and resonance energies (REs)^{6–9} reveal that a phenacene is more stable than its isomeric acene. The decrease of stability in acenes as compared to phenacenes has been explained^{5,10} by means of Clar's model of aromaticity^{11,12} in terms of the number of "aromatic π sextets" present in each species. A third nonplanar (except for the first three members) isomeric series of benzenoid compounds are the [n]helicenes. The first different constituent of this set of C_2 -symmetric helical polycyclic benzenoids is benzophenanthrene (**H4**). Ab initio results show that a phenacene is always more stable than its helicene analogue.¹³

The aromaticity of [n]acenes and [n]phenacenes has been discussed using different techniques, such as the study of ring currents,^{14–18} the calculation of REs,^{7–10} and the analysis of several aromaticity indicators such as the nucleus independent chemical shift (NICS),^{10,19} the harmonic oscillator model of aromaticity (HOMA) index,^{10,19} some charge density properties derived from the Atoms-in-Molecules (AIM) theory,²⁰ and graph theory-based descriptors.¹² In general, these studies have shown that the local aromaticity in [n]acenes increases steadily from the peripheral to the central rings. For [n]phenacenes, all indices indicate a zigzag trend in the local aromaticity, the outer rings being the most aromatic whereas the central ones vary commutatively in their aromatic character. On the other hand, the aromaticity of [n]helicenes as compared to [n]phenacenes (for $n = 6–10$ and 16) has been studied by Schulman and Disch using three magnetic criteria, namely, magnetic susceptibilities, NMR chemical shifts, and NICS.¹³ The authors have found that, despite significant deviations from planarity in [n]-helicenes, these species are only slightly less aromatic than [n]phenacenes.

The purpose of the present study is to analyze the local aromaticity of the complete series of [n]acenes, [n]phenacenes, and [n]helicenes ($n = 1–9$). For the first time, the changes suffered when going from the linear acenes to the angular phenacenes, and from these to the nonplanar helicenes will be discussed for the three series together (up to the ninth member of the series) at the same level of theory using three probes of local aromaticity based on structure, magnetic properties, and electron delocalization. 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 due to the multidimensional character of aromaticity.^{21–24} The present study, first, includes the results for these series obtained using a new recently defined indicator of aromaticity based on electron delocalization, second, complements the available HOMA and NICS data,^{13,19} which to our knowledge do not exist for the heavier members (beyond $n = 7$), and third, enables a systematic analysis and comparison of trends along the three series.

As a structure-based measure, we have made use of the HOMA index, defined by Kruszewski and Krygowski as^{25,26}

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{opt}} - R_i)^2 \quad (1)$$

where n is the number of bonds considered, and α is an empirical constant (for CC bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system and 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 stands for a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity.^{23,27}

Magnetic indices of aromaticity are based on the π -electron ring current that is induced when the system is exposed to external magnetic fields. In this work we have used the NICS, proposed by Schleyer and co-workers,^{28,29} 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 have used the recently reported para-delocalization index (PDI),^{30,31} which is obtained employing the delocalization index (DI)^{32–34} as defined in the framework of the AIM theory of Bader.^{35–37} The PDI is

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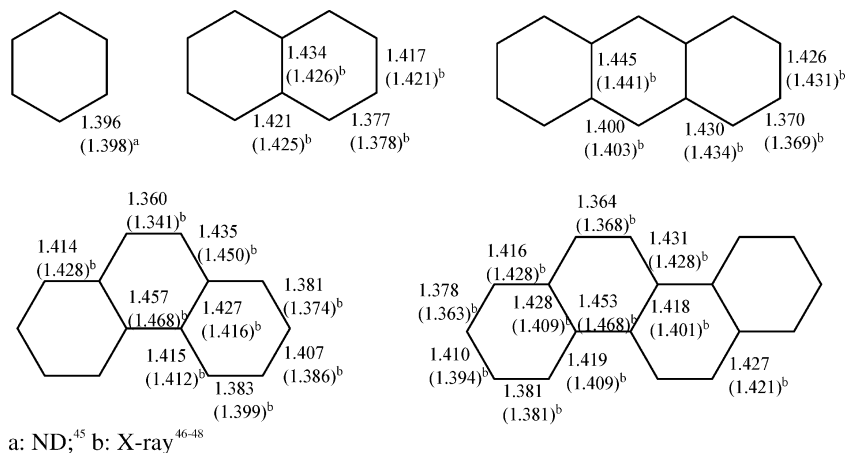


FIGURE 1. B3LYP/6-31G(d) and experimental (in parentheses) bond lengths of benzene, naphthalene, anthracene, phenanthrene, and chrysene.

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 ($\Gamma_{XC}(\vec{r}_1, \vec{r}_2)$) over the basins of atoms A and B, which are defined from the condition of zero-flux gradient in the one-electron density, $\rho(\mathbf{r})$:³⁵⁻³⁷

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

$\delta(A,B)$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B.³²⁻³⁴ Therefore, the PDI is clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity. Previous works^{30,31} have shown that for a series of planar and curved polycyclic aromatic hydrocarbons 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.

Methodology

Molecular geometries of $[n]$ acenes, $[n]$ phenacenes, and $[n]$ helicenes ($n = 1-9$) have been fully optimized with the hybrid density functional theory (DFT) B3LYP method³⁸⁻⁴⁰ using the 6-31G(d) basis set⁴¹⁻⁴³ by means of the Gaussian 98 program.⁴⁴ This method of calculation yields reasonable molecular structures as can be seen from the comparison between B3LYP/6-31G(d) and experimental geometries for benzene, naphthalene, anthracene, phenanthrene, and chrysene (see Figure 1). The calculation of the electronic (PDI), geometric (HOMA),

and magnetic (NICS) aromaticity criteria has been carried out at the same level of theory.

The GIAO method⁴⁹ has been used to perform calculations of NICS at ring centers determined by the non-weighted mean of the heavy atom coordinates. Integrations of DIs were performed by use of the AIMPAC collection of programs.⁵⁰ Calculation of these DIs at the DFT level of theory cannot be performed exactly,⁵¹ 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 HF-like DIs:⁵¹

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

The summations in eq 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 HF values than correlated DIs obtained with a configuration interaction

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TABLE 1. PDI (in electrons), HOMA, and NICS (in ppm) Values for the [*n*]Acene Series with *n* = 1–9^a

parameter	ring	[<i>n</i>]acene system								
		A1	A2	A3	A4	A5	A6	A7	A8	A9
PDI	A	0.1047	0.0756	0.0661	0.0619	0.0599	0.0590	0.0582	0.0579	0.0576
	B			0.0658	0.0620	0.0602	0.0591	0.0585	0.0582	0.0579
	C					0.0608	0.0608	0.0594	0.0592	0.0589
	D							0.0596	0.0595	0.0593
	E									0.0593
HOMA	WA	0.1047	0.0756	0.0660	0.0639	0.0602	0.0596	0.0588	0.0587	0.0585
	A	0.984	0.769	0.619	0.525	0.481	0.453	0.439	0.424	0.414
	B			0.696	0.599	0.540	0.501	0.483	0.463	0.447
	C					0.557	0.507	0.482	0.467	0.445
	D							0.478	0.455	0.427
NICS	E									0.420
	WA	0.984	0.769	0.645	0.562	0.520	0.487	0.469	0.452	0.432
	A	-9.67	-9.98	-8.84	-7.84	-7.06	-6.48	-6.05	-5.71	-5.44
	B			-12.60	-12.59	-12.05	-11.42	-10.85	-10.35	-9.93
	C					-13.48	-13.51	-13.19	-12.77	-13.36
D							-13.95	-13.95	-13.72	
E									-14.16	
WA	-9.67	-9.98	-10.09	-10.22	-10.34	-10.47	-10.59	-10.70	-11.01	

^a The weighted averages (WA) of PDI, HOMA, and NICS have also been included.

method.⁵¹ The numerical accuracy of the AIM calculations has been 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 and (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.³³ 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 0.01 au.

Pyramidalization angles were calculated by the π -orbital axis vector approach (POAV1)⁵² as implemented in the POAV3 program.⁵³ In this method, the local curvature of any carbon atom is defined by constructing a vector that forms equal angles to the three attached σ bonds, assuming that these bonds lie along the internuclear axes. For planar sp^2 centers this angle ($\theta_{\sigma\pi}$) is 90° , while for tetrahedral sp^3 carbons it is 109.47° . The pyramidalization angle is then defined as $\theta_{\sigma\pi} - 90^\circ$. By this definition, the pyramidalization angle is 0° for sp^2 carbon atoms and 19.47° for sp^3 carbon atoms.

Results and Discussion

The present section will be divided into three parts, corresponding to the three series of polyacenes studied in this work: [*n*]acenes (**An**), [*n*]phenacenes (**Pn**), and [*n*]helicenes (**Hn**), with *n* = 1–9 in all cases (see Chart 1). The local aromaticity of each group of polyacenes will be evaluated by means of applying the electronic PDI, the geometric HOMA, and the magnetic NICS aromaticity descriptors to each nonequivalent ring of the molecules composing the three series.

A. [*n*]Acene Series. Benzene (C_6H_6) and naphthalene ($C_{10}H_8$) are the first two benzenoid compounds common in all three series. So, they will be discussed now and will not be included in the next two parts of this section (see Table 1). Benzene presents a higher PDI value (0.105 e) than naphthalene (0.076 e), thus showing a greater

local aromatic character. As already observed in previous works focused on polycyclic aromatic hydrocarbons,³⁰ the 6-MR in benzene presents the highest PDI value, behaving as the most aromatic with respect to the PDI value. HOMA values follow the same trend: 0.984 and 0.769 for the 6-MRs of benzene and naphthalene, respectively. The HOMA for benzene is not 1.000 as we have optimized this structure at the B3LYP/6-31G(d) level of theory, and the C–C distance obtained is slightly different than that taken as a reference in eq 1. On the other hand, NICS values do not follow the same trend, being the 6-MRs in naphthalene (-10.0 ppm) slightly more aromatic than that of benzene (-9.7 ppm). The larger NICS value of naphthalene as compared to benzene is consistent with the 1H NMR chemical shifts of these two species¹⁴ as well as with the ring currents calculated by Steiner et al.^{14,16} This notwithstanding, electronic (PDI), geometric (HOMA), and also energetic (REs)⁸ descriptors of aromaticity find the aromatic character of the 6-MR of benzene larger than that of naphthalene. To find indicators of aromaticity that afford different orderings for relatively similar 6-MRs is not completely unexpected⁵⁴ and it is considered a manifestation of the multidimensional character of aromaticity. In such a case, it is not possible to reach a definite conclusion on the relative local aromatic character of the compared 6-MRs,⁵⁴ although one may argue that there are more indicators pointing out the higher aromatic character of benzene than the other way round. So, in principle, the 6-MR of benzene should be considered more aromatic than that of naphthalene.

Table 1 also contains the PDI, HOMA, and NICS values for all nonequivalent rings of the [*n*]acenes with *n* = 3–9. Figure 2 schematically summarizes the results listed in Table 1. PDI values in Table 1 are enclosed into a short range of values, from 0.066 (**A3**) to 0.058 e (**A9**). Thus, all 6-MRs present a similar aromaticity from an electronic delocalization point of view. PDI values indicate that terminal 6-MRs are less aromatic than inner ones, with the only exception of **A3** for which rings A and B have almost the same PDI value. As a general trend, the local aromaticities of the outer and inner 6-MRs

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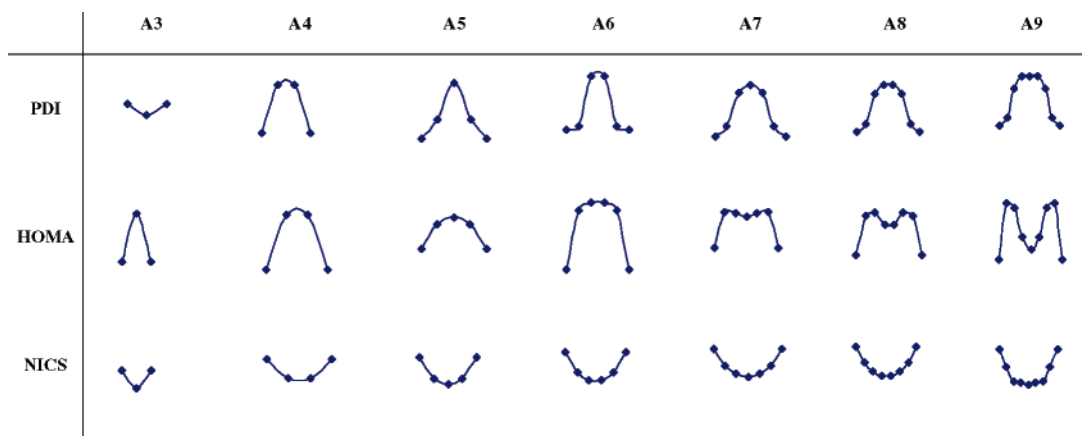


FIGURE 2. Schematic representation of trends in $[n]$ acenes ($n = 3-9$) according to PDI, HOMA, and NICS results.

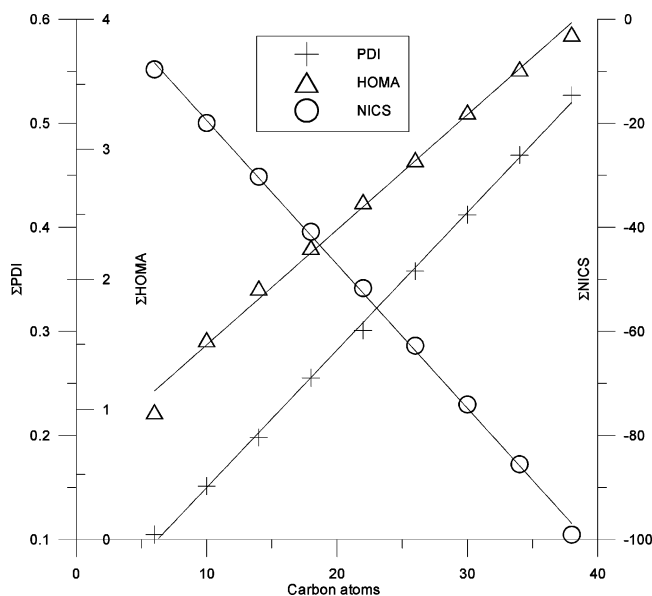


FIGURE 3. Plot of accumulative PDI, HOMA, and NICS values versus number of carbon atoms for the $[n]$ acene series.

decrease with increasing number of rings. The reduction of aromaticity in the central 6-MR is more important than in the peripheral ring, the largest difference between the most and least aromatic ring being reduced with increasing number of carbon atoms. Indeed, for **A4** with PDI values of 0.062 and 0.066 e for rings A and B, respectively, the difference is the largest, while the smallest correspond to the **A9** species with PDI values of 0.058 e for ring A and 0.059 e for ring E. Thus, there is a clear convergence of the PDI value for 6-MRs of the heavier members of the acenes analyzed. Figure 3 represents the sum of the PDI (Σ PDI), HOMA (Σ HOMA), and NICS (Σ NICS) values in front of the number of carbon atoms of the $[n]$ acene series for $n = 1-9$. For example, for **A3** with 14 carbon atoms (x -axis value) the Σ PDI value is $0.0661 + 0.0658 + 0.0661 = 0.1980$ e (y -axis value). Figure 3 shows how the accumulative local aromaticity linearly increases with the number of carbon atoms that form the molecule. Finally, the local aromaticity per ring slightly decreases with the size of the system (from 0.066 e in **A3** to a virtually converged 0.059 e value in **A9**) according to the weighted average PDI values given in Table 1. This observed reduction of aromaticity per

ring is consistent with REs reported by Behrens and co-workers⁷ and Moyano and Paniagua.⁸

With respect to the HOMA values (see Table 1), inner rings present higher HOMA values than terminal ones from **A3** to **A6**, following the same trend as that found from the PDI values, i.e., first, the local aromaticity in a given acene increases from the edge to the center, and second, the local aromaticity of the peripheral and central rings decreases as n increases. This tendency was already observed by Cyrański and co-workers¹⁹ and by Schleyer et al.¹⁰ for the **A1–A6** systems. However, there is a reduction of aromaticity from ring C to D for the **A7–A8** acenes and from C to E in **A9**, although they remain more aromatic than ring A in each case. This unexpected reduction (already detected by Cyrański et al.¹⁹ and by Schleyer and co-workers¹⁰ for **A7**, although not discussed in their papers) can be further analyzed by splitting the HOMA formula (eq 1) into the energetic (EN) and geometric (GEO) contributions according to the relation $\text{HOMA} = 1 - \text{EN} - \text{GEO}$ as proposed by Krygowski and Cyrański.^{19,23,55,56} These authors have shown that a reduction in the HOMA value can be due either to an increase in bond length alternation (GEO) or to the lengthening/shortening of the mean bond lengths of the ring (EN). Table 2 contains the HOMA, EN, and GEO terms for **A6–A9**. It can be seen how, for each system, there is an increase of the energetic contribution when going from the outer to the inner rings, as well as a decrease of the geometric term in the same direction. This latter effect is responsible for the largest HOMA values for the central ring of **A3–A6** species. Interestingly, the reduction of aromaticity observed for rings C to E in **A7–A9** can be attributed to the fact that while the EN term continues to grow from the outer to the inner rings, the GEO term remains almost constant in these 6-MRs. This implies that the observed reduction of aromaticity for rings C to E in **A7–A9** has to be attributed to an increase of the C–C bond lengths of the central ring as more rings are added (EN term), which is not compensated by a reduction in bond length alternation (GEO term). Neither PDI nor NICS (vide infra) are affected by these geometrical variations. As for the PDI values, from Figure 3 it can be seen that HOMA also linearly increases with the number of carbon atoms, with a good correlation. It

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TABLE 2. Separation of the Aromaticity Index HOMA into Energetic (EN) and Geometric Contributions (GEO) for Systems A6–A9

system	ring	EN	GEO	HOMA
A6	A	0.200	0.347	0.453
	B	0.278	0.222	0.501
	C	0.301	0.192	0.507
A7	A	0.200	0.361	0.439
	B	0.283	0.234	0.483
	C	0.310	0.208	0.482
	D	0.316	0.206	0.478
A8	A	0.207	0.369	0.424
	B	0.298	0.239	0.463
	C	0.316	0.217	0.467
	D	0.331	0.214	0.455
A9	A	0.212	0.374	0.414
	B	0.301	0.252	0.447
	C	0.325	0.231	0.445
	D	0.343	0.229	0.427
	E	0.353	0.227	0.420

is also found from the weighted average HOMA values in Table 1 that the aromaticity per ring decreases along the **A1** to **A9** series.

NICS, the third aromaticity criterion used in this study, is a magnetic-based measure. For each nonequivalent 6-MR, the NICS values are also listed in Table 1. The trend yielded by NICS perfectly fits with that provided by PDI (except for **A3**). Thus, according to NICS, aromaticity increases when going from the terminal to the inner rings with no exception.^{10,19} The fact that NICS gives a higher aromaticity to the center of the molecule is not unexpected from the stronger ring currents observed around the inner rings of acenes in the corresponding current density maps, as previously shown by Steiner et al.^{14,16} Conversely, at variance with PDI, the difference between the less aromatic terminal ring (A) and the most aromatic inner ring gets larger when going from **A3** (−8.8 and −12.6 ppm for A and B, respectively) to **A9** (−5.4 and −14.2 ppm for A and E, respectively). For all three criteria, the aromaticity of the terminal ring decreases with the addition of rings; however, for the inner ring, while both PDI and HOMA agree indicating that its aromaticity decreases, NICS shows exactly the opposite trend. These two latter findings give support to the claimed overestimation by NICS of the local aromaticity of the central rings in polyacenes.^{57,58} It must be noticed that the correlation of the NICS values in front of either the PDI or the HOMA ones is not very good, although the observed tendencies are in general similar. As for PDI and HOMA, NICS linearly decreases (so aromaticity increases) with the increase of the number of carbon atoms in acenes (see Figure 3). However, according to weighted average NICS values, the aromaticity per ring increases with the size of the acenes, in contrast to the trend found with the PDI and HOMA indices. This difference is also in line with the believed overestimation by NICS of the aromaticity of central rings.

Finally, it is worth noting that central rings in the [*n*]-acenes series are not only the most aromatic according to the local aromaticity descriptors analyzed here, but

also they are the most reactive.^{5,8,59} Although this result is apparently contradictory, it can be explained by noticing that there is a larger gain of aromaticity when going from reactants to products if the reaction is the addition type and takes place in the central rather than in the outer rings of acenes.⁵

B. [*n*]Phenacene Series. The [*n*]phenacene compounds (**P3–P9**) are angular fused isomers of the [*n*]-acenes. [*n*]Phenacenes present a zigzag conformation which, as compared to linear [*n*]acenes, changes the connectivity of the joined 6-MRs in such a way that, for each inner ring of a given [*n*]phenacene, the carbons bound to an H atom are in the ortho position instead of being in the para position. With respect to the aromaticity measured from PDI values (see Table 3), it is worth noting that the range of values is larger (0.039–0.080 e) than that for the previous series and the trends followed by the different rings change. Thus, the most aromatic rings are now the terminal ones (A) in all cases, largely differing from the rest. Interestingly, the PDI value for ring A is almost kept fixed for this whole series (0.080 e). In addition, not only the PDI values for ring A are unaltered, but also the PDI for a specific inner ring is quite constant (for instance, the PDI value for all C rings is ca. 0.058 e). The PDI values indicate a zigzag trend in the local aromaticity. Thus starting from the most aromatic ring A, the aromaticity of the central rings varies in a damped alternate way. For instance, for **P7** the PDI values are 0.080 e (A) > 0.051 e (B) < 0.058 e (C) > 0.055 e (D) < ... (symmetric), and the same happens for the rest. The difference of aromaticity between the central ring and its adjacent ring decreases along the **P3** to **P9** series, being close to zero for **P9**. The aromaticity for the terminal rings is larger for this series than for the [*n*]acene one, but for the inner rings it is lower. As a consequence, the weighted averaged PDI value is similar for the isomeric members of the two series, yet somewhat larger for [*n*]phenacenes. So, in line with the results reported by Cyrański et al.¹⁹ using aromatic stabilization energies (ASE), NICS, and HOMA, as indicators of aromaticity, the PDI also shows that the aromaticity of [*n*]acenes is smaller than that of the corresponding [*n*]phenacenes. As in [*n*]acenes, the local aromaticity per ring decreases with an increase in the size of the system, although the reduction in [*n*]phenacenes is slower.

Table 3 also contains the HOMA values for the [*n*]phenacene series. For *n* = 1–7, our HOMA results do not differ very much from those of Cyrański et al.,¹⁹ the trends being qualitatively the same. Thus, as for the PDI measure, HOMA values indicate that the terminal ring in [*n*]phenacenes is the most aromatic with a quite constant value (0.84). When moving from the external ring to the inner rings, an alternation of local aromaticities is found. The alternation of HOMA values is especially important when going from the outer ring to the ring closest to it and then it is attenuated until apparently it finally converges (for **P9**, the difference between rings D and E is only 0.017). The weighted averaged HOMA values also show a slight decrease in the local aromaticity per ring along the **P1–P9** series. As no “strange” behavior is observed for the HOMA values of this series, like the decrease of aromaticity in the central

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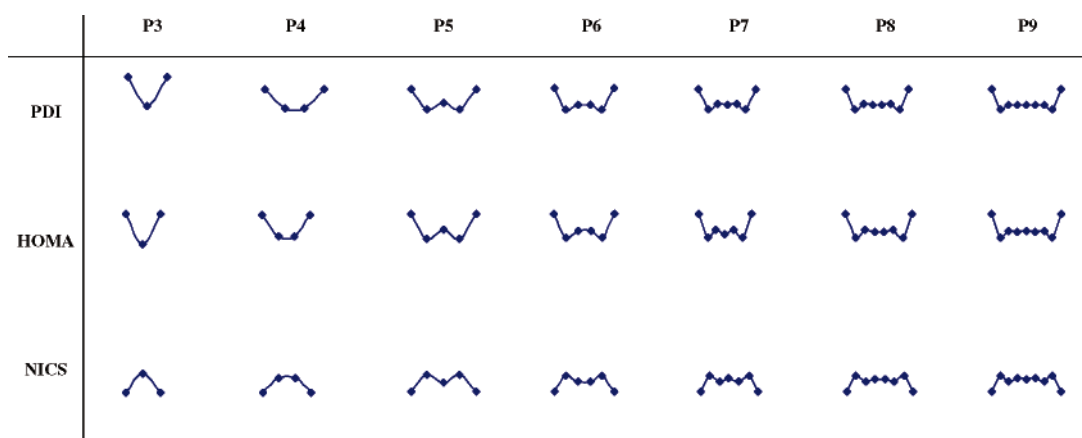
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TABLE 3. PDI (in electrons), HOMA, and NICS (in ppm) Values for the [*n*]Phenacene Series with $n = 3-9^a$

parameter	ring	[<i>n</i>]phenacene system						
		P3	P4	P5	P6	P7	P8	P9
PDI	A	0.0797	0.0797	0.0804	0.0802	0.0803	0.0802	0.0802
	B	0.0465	0.0528	0.0505	0.0512	0.0510	0.0511	0.0510
	C			0.0593	0.0570	0.0577	0.0574	0.0575
	D					0.0547	0.0554	0.0552
	E							0.0561
HOMA	WA	0.0686	0.0663	0.0642	0.0628	0.0618	0.0610	0.0604
	A	0.856	0.829	0.847	0.841	0.841	0.842	0.841
	B	0.435	0.542	0.520	0.529	0.524	0.527	0.524
	C			0.640	0.621	0.635	0.632	0.627
	D					0.581	0.606	0.604
NICS	E							0.621
	WA	0.716	0.686	0.675	0.664	0.654	0.652	0.646
	A	-10.06	-9.94	-9.80	-9.91	-9.88	-9.90	-9.86
	B	-6.82	-7.69	-7.15	-7.35	-7.28	-7.28	-7.27
	C			-8.35	-8.10	-8.14	-8.11	-8.09
D					-7.69	-7.76	-7.70	
E							-7.82	
WA	-8.98	-8.82	-8.45	-8.45	-8.33	-8.26	-8.18	

^a The weighted averages (WA) of PDI, HOMA, and NICS have also been included.

**FIGURE 4.** Schematic representation of trends in [*n*]phenacenes ($n = 3-9$) according to PDI, HOMA, and NICS results.

rings of **A7–A9**, we have not included a table with the energetic and geometric contributions to HOMA for this series. Furthermore, the decomposition of HOMA into its GEO and EN components for this series (up to $n = 7$) has been reported already by Cyrański et al.¹⁹

Finally, the NICS values in Table 3 present the same behavior as the electronic PDI and the geometric HOMA aromaticity criteria. Thus, NICS results show that both the external rings are the most aromatic and the aromaticity for the inner rings alternates and eventually converges for $n > 9$. NICS results also point out the quite constant values of local aromaticity especially for the terminal rings (-9.9 ppm), but also for the inner rings. The same trends of NICS values were found for [16]-phenacene.¹³ The different behavior of NICS in [*n*]phenacenes as compared to their isomeric [*n*]acenes agrees with previously reported current density maps. For instance, Zanasi et al.¹⁸ calculated them for anthracene (**A3**) and phenanthrene (**P3**) finding an intense circulation mainly localized on the central hexagon of anthracene and on the external 6-MRs of phenanthrene. As found for the PDI and HOMA indices, the weighted averaged NICS values show a reduction of the local aromaticity per ring when increasing the size of the system. Figure 4 schematically represents the results for the [*n*]phenacene series. Finally, it must be said that for

all three aromaticity criteria we found again a linear correlation between the sum of indices (as a measure of global aromaticity) and the number of carbon atoms (figure not included).

At variance with [*n*]acenes where some divergences between indices were found, for [*n*]phenacenes all three aromaticity criteria (including ring REs⁸) fully coincide in the trends (see Figure 4). Therefore, the main conclusions drawn for [*n*]phenacenes, i.e., the most aromatic 6-MR is the external one and there is a damped alternation of the local aromaticity from the external to the central ring, are conclusive and well supported. Moreover, the alternate character of the local aromaticity in such benzenoid compounds is already predicted by simple models such as the Clar's aromatic π sextets model.^{11,12} Thus, [*n*]phenacenes with $n =$ odd number, like **P3** (two terminal rings A are Clar aromatic π sextets) or **P5** (terminal rings A and central ring C are Clar aromatic π sextets), have a single Clar structure in which the A, C, E, ... 6-MRs have an aromatic π sextet and are predicted to be more aromatic than the B, D, F, ... rings. Although the number of Clar structures for [*n*]phenacenes ($n =$ even number) increases, the conclusion about the alternation of aromaticity remains unaltered.

C. [*n*]Helicene Series. The last group of molecules to be discussed is the [*n*]helicene series (**Hn**). This series

TABLE 4. PDI (in electrons), HOMA, and NICS (in ppm) Values for the [*n*]Helicene Series with *n* = 3–9^a

parameter	ring	[<i>n</i>]helicene system						
		H3	H4	H5	H6	H7	H8	H9
PDI	A	0.0797	0.0792	0.0792	0.0791	0.0789	0.0789	0.0789
	B	0.0465	0.0538	0.0517	0.0514	0.0517	0.0515	0.0514
	C			0.0606	0.0583	0.0585	0.0584	0.0581
	D					0.0569	0.0568	0.0569
	E							0.0569
HOMA	WA	0.0686	0.0665	0.0645	0.0629	0.0622	0.0614	0.0608
	A	0.856	0.806	0.818	0.825	0.813	0.824	0.825
	B	0.435	0.503	0.453	0.464	0.484	0.483	0.477
	C			0.584	0.543	0.549	0.572	0.570
	D					0.497	0.513	0.538
NICS	E							0.527
	WA	0.716	0.655	0.625	0.611	0.598	0.598	0.594
	A	-10.06	-9.99	-9.48	-10.20	-10.78	-10.94	-11.08
	B	-6.82	-7.62	-7.13	-6.82	-7.48	-8.02	-8.19
	C			-7.32	-7.09	-6.33	-7.19	-7.78
D					-6.63	-5.85	-6.60	
E							-5.02	
WA	-8.98	-8.81	-8.11	-8.04	-7.97	-8.00	-8.04	

^a The weighted averages (WA) of PDI, HOMA, and NICS have also been included.

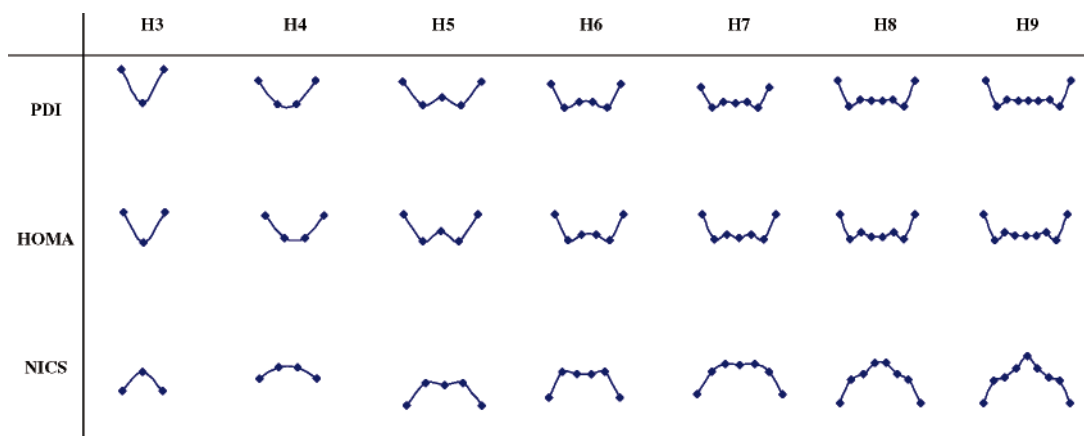


FIGURE 5. Schematic representation of trends in [*n*]helicenes (*n* = 3–9) according to PDI, HOMA, and NICS results.

presents a very similar connectivity to the [*n*]phenacene series (the two carbons bound to H are in the ortho position), but without the zigzag conformation, which makes these compounds nonplanar C_2 -symmetric helical polycyclic benzenoids. Helicene **H3** and phenacene **P3** are equivalent and the first different member of the series is benzophenanthrene (**H4**). As pointed out by Schulman and Disch,¹³ [*n*]helicenes and [*n*]phenacenes share identical local connectivities, Kekulé counts, conjugated circuits, and other graph theoretical descriptors.¹² From this point of view one may predict a similar aromaticity for the two series. On the other hand, and because the planarity in [*n*]helicenes (for *n* > 3) is lost, one may also expect a reduction of local aromaticity for the [*n*]helicenes series.

Table 4 contains the PDI, HOMA, and NICS values for the present series. These results are graphically represented in Figure 5. First, with respect to the PDI electronic aromaticity measure, we find that the rings of the helicenes are almost equally delocalized as those of the phenacenes. The PDI for the terminal ring is invariant for all the systems (0.079), only slightly inferior to that of phenacenes (0.080). For the same group of rings, PDI values are also quite invariant and very close to the values reported for [*n*]phenacenes, yet somewhat larger (except for the outer ring). Both the local aromaticity

alternation when going from the terminal to the inner rings and the convergence for the central rings of the higher members of the series are present too. Thus, according to this electronic delocalization point of view, going from a planar [*n*]phenacene to its pyramidalized [*n*]helicene isomer system almost does not affect its aromaticity. At first sight, the fact that loss of planarity in [*n*]helicenes does not go with a substantial loss of aromaticity may seem surprising. However, there are two reasons that justify this result. First, loss of planarity when going from [*n*]phenacenes to [*n*]helicenes series is not dramatic, as can be inferred by analyzing the degree of pyramidalization of [*n*]helicenes. For instance, when the π -orbital axis vector approach (POAV1)⁵² has been applied to the **H9** molecule we have found that the averaged pyramidalization angles of each ring are 0.83°, 1.18°, 0.88°, 0.53°, and 0.53° for rings A, B, C, D, and E, respectively. As a reference, the pyramidalization angle for the carbon atoms of C_{60} is 11.64°.⁵² Clearly the departure from planarity for each ring in [*n*]helicenes is very small. Second, this result is in agreement with the theoretical finding that benzene can experience deviations from planarity up to 25° without a substantial loss of electron conjugation^{60,61} and also with the high conformational out-of-plane flexibility of aromatic systems,⁵⁸ as well as with the experimental and theoretical observa-

tion that chemical shifts of aromatic protons, magnetic anisotropies, and X-ray molecular structures of meta and paracyclophanes support an essentially unperturbed aromaticity as a result of the distortion suffered by the planar aromatic ring.^{62–67}

With respect to the HOMA geometric aromaticity criterion, something similar happens. The terminal rings present the same HOMA value for the whole series (0.81–0.82), slightly inferior to that for the phenacenes (0.84). The HOMA values for the inner rings are also kept quite constant, but in this case a slight decrease in local aromaticity of all rings with respect to the $[n]$ phenacene series is found.

The aromatic character of the 6-MRs changes only slightly when going from phenacenes to helicenes, according to NICS, for $n = 3$ to 7. However, for **H8** and **H9** the trends in local aromaticity are completely changed. The damped alternation of local aromaticity observed in **P8** and **P9** is not present in **H8** and **H9**, for which the local aromaticity decreases continuously from the peripheral to the central rings. A similar lack of convergence was also observed for [16]helicene.¹³ Moreover, while for phenacenes the NICS values of the most external ring are rather constant for the full series, in helicenes NICS indicates a steady increase of aromaticity of the outer ring starting from **H5**. This increase is also observed for rings B along the **H6** to **H9** series, for the rings C of **H7**, **H8** and **H9**, and for rings D of **H8** and **H9**, in contrast to what is found in phenacenes. Finally, for the most inner and planar D and E rings of **H8** and **H9**, NICS shows a clear reduction of aromaticity as compared to the analogous rings in **P8** and **P9** species.

For all indices the weighted averaged values indicate a virtually identical or somewhat lower aromatic character of helicenes as compared to phenacenes, which agrees with the aforementioned small reduction of aromaticity due to loss of planarity. Loss of aromatic character according to isotropic magnetic susceptibilities also was found to be small when going from phenacenes to helicenes.¹³ In addition, as for the previous two series, it must be said that the linear correlation between the sum of indices (as a measure of global aromaticity) given by each aromaticity measure and the number of carbon atoms is also kept constant for this $[n]$ helicene series (figure not included).

According to PDI and HOMA the aromatic character of all equivalent 6-MRs of $[n]$ phenacenes and $[n]$ helicenes is basically identical. With respect to NICS, the same conclusion can be drawn from the results up to **H5**, but

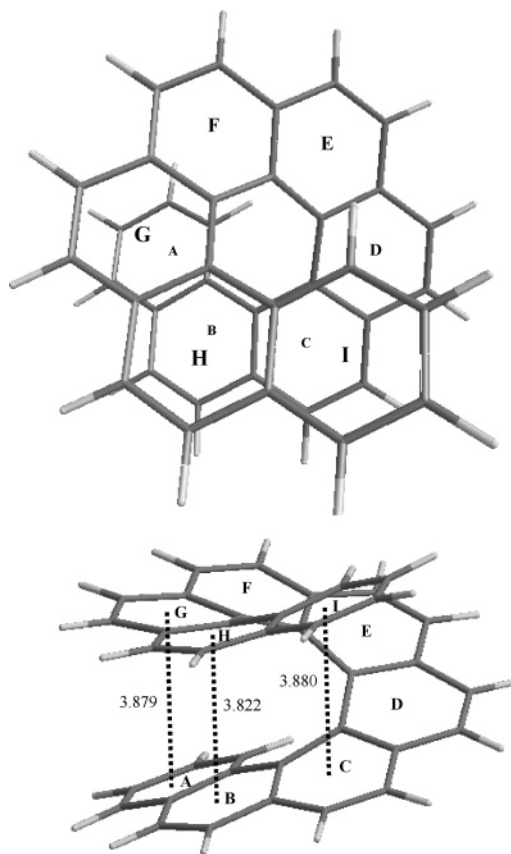


FIGURE 6. Two molecular representations of **H9** that show its helix structure and ring-to-ring distances (in Å).

not for the higher members of the series. As can be clearly seen in Figure 5, the aromaticity of $[n]$ helicenes evaluated with NICS changes with respect to that of $[n]$ phenacenes for **H6–H9**. In these $[n]$ helicenes ($n = 6–9$) species, there are some 6-MRs placed one over the other. For this reason, we suspect that the particular behavior of NICS in **H6** to **H9** species must be attributed to the magnetic couplings between superimposed 6-MRs along the helix structure. Our hypothesis is, therefore, that there is an artificial increase of the absolute NICS values for the most external rings of the **H6–H9** helicenes because of these magnetic couplings. In fact, since the distance between rings A and G in **H9** (see Figure 6) is about 4 Å the effect of this coupling can be predicted to be about 1 ppm in the center of the A and G rings according to the empirical model for benzene determined by Johnson and Bovey using a current loop model.⁶⁸ This is approximately the increase in NICS observed for rings A and B in **H9** as compared to **P9**.

This plausible effect can be further analyzed by calculating the NICS values for ring A of **P9** and **H9** along the axis defined by the vector perpendicular to the plane of ring A starting from its center up to 2 Å above and below the ring by making steps of 0.5 Å (see Figure 7 for **H9**). Table 5 contains the NICS values obtained for **P9** and **H9**. It can be seen from it that, as happens for the NICS values corresponding to the center of the ring, **H9** presents higher negative values of NICS from 2 to –2 Å than **P9**. Obviously, **P9** presents symmetric NICS values

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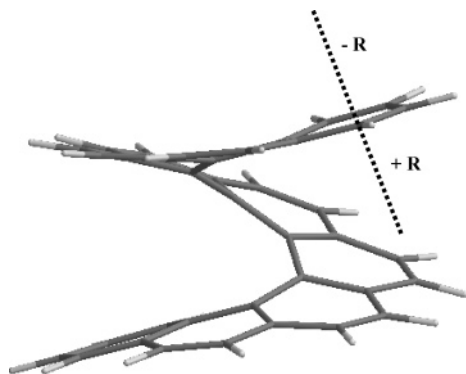


FIGURE 7. Molecular representation of **H9** including the perpendicular vector to the plane of ring A along which NICS calculations have been carried out at different distances above and below the center of the ring (R values range from 2.0 to -2.0 Å).

TABLE 5. NICS Values (in ppm) at Different Distances from the Center of the Ring (in Å) Following a Vector Perpendicular to the Plane of Ring A for Systems **P9** and **H9**^a

NICS	distance to ring center								
	2.0	1.5	1.0	0.5	0.0	-0.5	-1.0	-1.5	-2.0
P9	-5.1	-8.2	-11.5	-11.7	-9.9	-11.7	-11.5	-8.2	-5.1
H9	-7.4	-9.4	-12.1	-12.1	-11.1	-13.6	-13.4	-9.7	-6.4

^a For **H9**, positive distances are toward the helicene structure.

above and below the ring, while this symmetry is lost in **H9** due to the magnetic couplings with the other rings placed in front of ring A. The larger NICS values for **H9** as compared to **P9** can be understood on the basis of the Johnson–Bovey model.⁶⁸ However, we found that the magnetic couplings are more important for $R = -0.5$ to -1.5 (thus getting farther from the helicene structure) than for $R = 0.5$ to 1.5 (thus moving toward the center of the helix), which is exactly the reverse trend expected from the Johnson–Bovey model. In principle, when getting closer to the opposite ring, the larger the magnetic coupling should be. Next, we will try to provide an explanation for these two unexpected results of NICS, i.e., the increase of aromaticity for the external 6-MRs of the higher members of the [*n*]helicenes series as compared to the corresponding phenacenes and the higher increase of aromaticity in ring A of **H9** when moving away from the helicene structure than when moving toward it.

To provide evidence for the origin of the observed increase by NICS of local aromaticity for the outer rings of **H6–H9**, which we attribute to magnetic couplings between superimposed rings, we have simulated this effect by means of two benzene rings (at the optimized B3LYP/6-31G(d) geometry of the free benzene molecule) placed parallel one over the other (see Figure 8a) separated by a distance of 4 Å (similar to rings A and G in **H9**). The NICS values are listed in Table 6. As found for **H9** (Table 5), there is an increase of the absolute NICS value of about 0.7 ppm in the center of the benzene ring due to the magnetic field created by the opposite benzene molecule. This value is close to the result predicted by the empirical Johnson–Bovey model.⁶⁸ Therefore, even though the rings are separated by 4 Å, the influence on the shielding is relevant. It is worth noting that the PDI

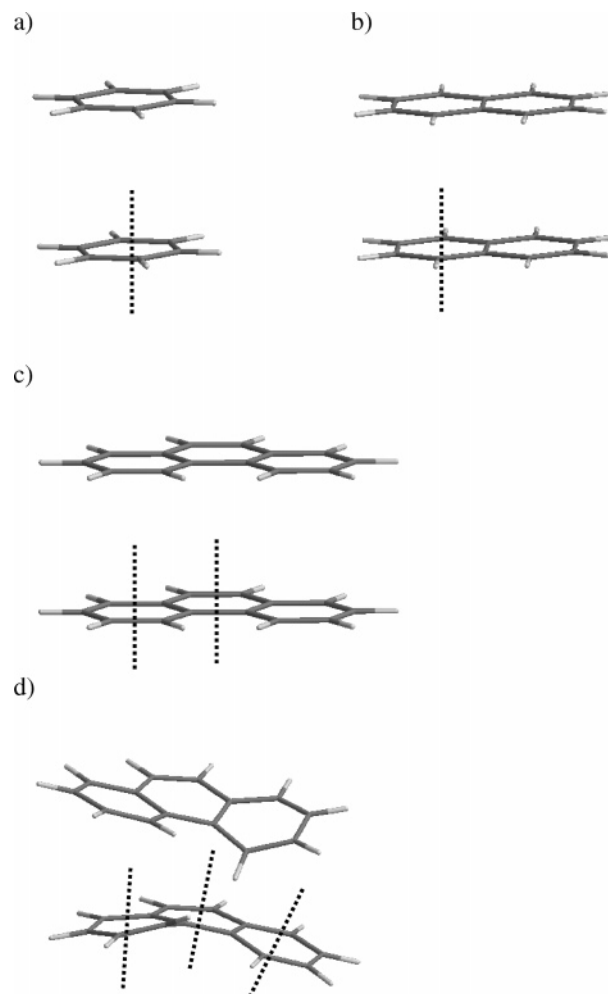


FIGURE 8. Molecular representation of (a) two parallel benzene rings, (b) two parallel naphthalenes, (c) two parallel phenantrenes, and (d) two phenantrenes in the **H9** geometry (rings A, B, C, G, H, I), situated one above the other, together with the perpendicular vector to the plane of one ring in which NICS calculations have been carried out at different distances above and below the center of the ring (R values range from 2.0 to -2.0 Å).

value for either the “benzene sandwich” or the free benzene molecule is exactly the same (0.104 e), showing that the effect of having another ring at 4 Å above or below has almost no influence on the electronic delocalization. The same conclusions can be achieved when going to larger models such as the “naphthalene sandwich” and the “phenanthrene sandwich” at 4 Å (again using the optimized B3LYP/6-31G(d) geometry of the free molecules). So, these small models already show that placing a benzenoid ring over a given aromatic 6-MR modifies the calculated NICS and therefore the predicted local aromaticity, which is artificially augmented by a quantity that depends on the distance between the two 6-MRs.

It can be seen from the above “sandwich” calculations for benzene, naphthalene, and phenanthrene that the presence of another system above causes a decrease of the NICS values, and as a consequence a false increase of aromaticity of rings A and B in **H9**. However, in these small models, at variance with the **H9** system (Table 5), the effect of having another ring above causes a larger

TABLE 6. NICS Values (in ppm) at Different Distances from the Center of the Ring (in Å) Following a Vector Perpendicular to the Plane of a Given Ring for a System Corresponding to Two Benzenes (C_6H_6), Two Naphthalenes ($C_{10}H_8$), and Two Phenanthrenes ($C_{14}H_{10}$) Placed Parallel One over the Other at a Distance of 4 Å (see Figure 6) and Together with Two Phenanthrenes at the Same Geometry as for the H9 System ($C_{14}H_{10}^{H9}$)^a

system	"sandwich" structure										free molecule		
	NICS at different distances										PDI	NICS	PDI
	2.0	1.5	1.0	0.5	0.0	-0.5	-1.0	-1.5	-2.0				
C_6H_6	-8.9	-10.1	-12.5	-12.3	-10.4	-12.0	-11.7	-8.2	-5.1	0.104	-9.7	0.104	
$C_{10}H_8$	-9.9	-11.1	-13.4	-13.1	-11.0	-12.6	-12.3	-8.9	-5.7	0.075	-9.9	0.075	
$C_{14}H_{10}$													
ext	-9.8	-11.0	-13.4	-13.2	-11.1	-12.8	-12.3	-8.9	-5.7	0.081	-10.1	0.080	
cent	-8.9	-9.7	-11.1	-10.1	-8.0	-9.7	-10.0	-7.7	-5.3	0.046	-6.8	0.047	
$C_{14}H_{10}^{H9}$													
ext	-7.9	-9.7	-12.3	-12.3	-11.2	-13.6	-13.3	-9.6	-6.2	0.081	-10.3	0.081	
cent	-9.3	-9.6	-10.7	-9.6	-8.3	-10.8	-11.2	-8.6	-6.0	0.049	-6.8	0.049	
int	-10.6	-11.1	-12.1	-12.5	-10.4	-12.2	-12.1	-8.9	-5.9	0.082	-9.0	0.082	

^a PDI (in e) for the different "sandwich" structures have also been included, together with the corresponding NICS and PDI for the structures alone. For $C_{14}H_{10}^{H9}$, ext, cent, and int denote the external, central, and internal rings, respectively.

increase of aromaticity when moving toward the other ring (positive values of distances to the ring center) than when moving away from it. Thus, it seems that in order to get the complete picture, we should take into consideration other effects. The above model calculations have been carried out on completely planar and parallel structures separated by a distance of 4 Å. In our last attempt to reproduce by a simple model the NICS changes along a perpendicular axes in ring A of **H9** we have removed rings D, E, and F of **H9** structure⁶⁹ (see Figures 6 and 8d), and we have calculated the NICS values at different distances from the center of rings A (external), B (central), and C (internal). The corresponding values can be found in Table 6. At difference with the "phenanthrene sandwich", now the NICS calculations reproduce those found for **H9**. Therefore, the unexpected decrease of aromaticity when getting closer to the ring above may be attributed to the distortion from a completely planar and parallel "sandwich" structure. This trend is observed for the external and the central rings, those in **H9** that have been shown to be the most affected from the NICS point of view due to the presence of other rings above.

As said previously, NICS also shows a loss of aromaticity for the most inner D and E rings of **H8** and **H9** as compared to the equivalent rings in the $[n]$ phenacene series. The decrease in the aromatic character of the E ring (-5.02 ppm in **H9** as compared to -7.82 ppm in **P9**) can be analyzed by computing the NICS for this ring in a phenanthrene-like system formed by rings DED at the geometry of the **H9** species.⁷⁰ The NICS value for the E ring in this model is -6.22 ppm, which is 0.6 ppm lower than the same ring in phenanthrene (-6.82 ppm, see **P3** in Table 3). This means that the reduction of aromaticity due to loss of planarity is minor and the largest contribution to the reduction of aromaticity in ring E of **H9** as compared to **P9** has to be attributed to magnetic couplings with rings A, B, and C.

In summary, PDI and HOMA values indicate that the change in aromaticity when going from $[n]$ phenacenes

to $[n]$ helicenes is very small. The same conclusion can be drawn from the NICS values of **H4** and **H5**. However, for $n > 5$, NICS finds that the external rings in $[n]$ -helicenes are clearly more aromatic than those of $[n]$ -phenacenes. We have demonstrated that the special behavior of NICS in the outer rings of **H6**–**H9** species and the inner rings of **H8** and **H9** is due to magnetic couplings with neighboring rings placed above that completely modify the trends in local aromaticities. We think that this provides another example of the limits of the NICS concept as a measure of aromaticity.^{71,72} It is not only that the NICS indicator of aromaticity can potentially incorporate some spurious information arising from the electron flow perpendicular to the molecular plane,^{71,72} but also that paratropic (or diatropic) ring currents in neighboring rings can produce a large effect on the NICS values of the studied ring. In our opinion, this proves that, for some systems, the assessment of local aromaticities based on NICS values only must be made with great care.⁷³ For this reason, we recommend to use several differently based aromaticity parameters for comparisons of local aromaticity in a given series of compounds.⁵⁴

Just to conclude the present section, it would be convenient to carry out an overall comparison of the three aromaticity criteria used in this study by taking into account all the values for the three series of results. Figure 9 contains the plot of PDI in front of HOMA values. It is seen how a relatively good correlation is achieved, as it had been previously seen for bowl shaped polycyclic aromatic hydrocarbons.³¹ The group of central values corresponds to acenes and inner rings of phenacenes and helicenes, while those with higher values of both aromaticity measures correspond to terminal rings of phenacenes and helicenes. Figure 10 depicts the PDI versus NICS graph. The correlation is not good, although points are localized in three well-defined groups. It is noticeable that the group corresponding to the terminal rings of helicenes **H6**–**H9** presents an important change of NICS, while PDI remains almost invariant. And finally, Figure 11 plots HOMA versus NICS values. As

(69) We have started from the B3LYP/6-31G(d) optimized geometry of **H9**. To fill the free valences that appeared in rings adjacent to rings D and F, we have placed hydrogen atoms with a C-H bond length of 1.07 Å. No further reoptimization has been carried out.

(70) As before the unfilled valences produced by the removal of rings A, B, and C in **H9** have been covered with H atoms using C-H bond lengths of 1.07 Å.

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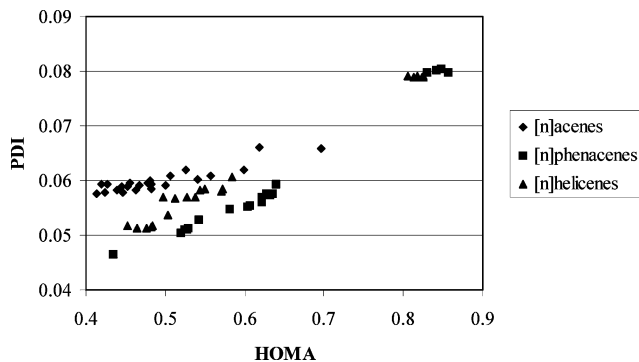


FIGURE 9. Plot of PDI versus HOMA for the values of the three series.

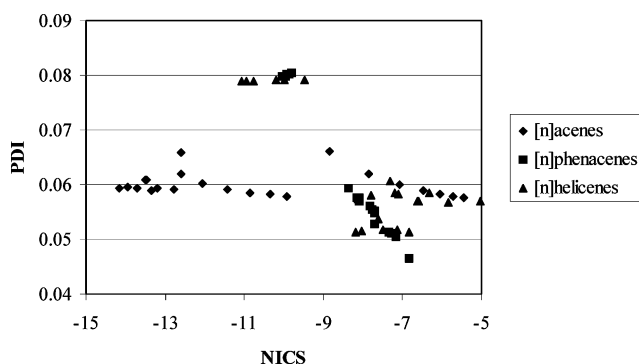


FIGURE 10. Plot of PDI versus NICS for the values of the three series.

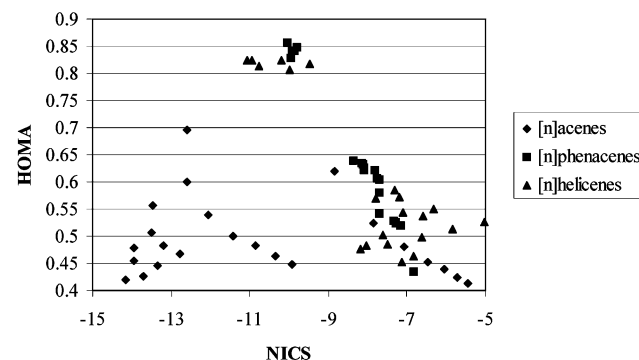


FIGURE 11. Plot of HOMA versus NICS for the values of the three series.

for the previous plot, three well-defined groups are obtained. There is a group that presents an important variation of NICS while HOMA keeps invariable. Again, the highly negative NICS values correspond to the terminal rings of helicenes.

Conclusions

In the present study, we have quantified the local aromaticity of six-membered rings in the series of [*n*]acenes, [*n*]phenacenes, and [*n*]helicenes ($n = 1-9$) by means of NICS, HOMA, and PDI aromaticity descriptors. We have discussed the trends along the series and the variations observed when going from the linear acenes

to the angular phenacenes, and from these to the non-planar angular helicenes.

For the [*n*]acene series, it is found that inner rings are more aromatic than outer rings, even though the former are more reactive. According to PDI and HOMA, the aromaticity per ring decreases with the size of [*n*]acenes, whereas NICS values yield the opposite behavior. This different trend has been attributed to the overestimation by NICS of the local aromaticity of the central rings in [*n*]acenes. All indicators of aromaticity used agree pointing out that the most external ring in the [*n*]phenacene series is the most aromatic, and that there is a damped alternation of the local aromaticity from the outer to the inner rings. Finally, HOMA and PDI indices indicate a small change in aromaticity when going from [*n*]phenacenes to [*n*]helicenes, despite the loss of planarity in the latter species. NICS results show the same behavior for systems with $n \leq 5$; however, for larger systems NICS considers the terminal rings of [*n*]helicenes clearly more aromatic than those of [*n*]phenacenes. We have shown that the increase of local aromaticity in terminal rings of [*n*]helicenes ($n = 6-9$) according to NICS has to be attributed to magnetic couplings with neighboring rings placed above that alter the expected trend in the local aromaticities of these compounds.

The special behavior of the NICS index for the higher members of the [*n*]helicenes series represents a clear example of the limitations of the NICS concept as a measure of aromaticity.^{71,72,74} Thus, NICS values should be used carefully when a nearby portion of the system may influence the chemical shift on the dummy atom. In the same way, the calculation of HOMA in rings exhibiting a lengthening/shortening of the mean bond lengths may also become problematic. What is more, not only NICS or HOMA, but any criterion of aromaticity has its own limitations. In this sense, we recommend to use several differently based aromaticity parameters for comparisons of local aromaticities in a given series of compounds.

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Supporting Information Available: Cartesian coordinates of all compounds treated in the present work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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