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Local Aromaticity of the Lowest-Lying Singlet States of [*n*]Acenes (*n* = 6−9)

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The local aromaticities of the six-membered rings in the two lowest-lying singlet states of [*n*]acenes (*n* = 6−9) have been assessed by means of three probes of local aromaticity based on structural, magnetic, and electron delocalization properties. Important differences between the local aromaticities of the closed-shell and diradical singlet electronic states are found. Thus, while the inner rings have the largest aromatic character in the closed-shell singlet states, the outer rings become the most aromatic for the diradical singlet states.

In a recent article,[1] we analyzed the local aromaticities of the six-membered rings (6-MRs) in a series of [*n*]acenes, [*n*]-phenacenes, and [*n*]helicenes with *n* = 1−9 by means of *para*-delocalization index (PDI),[2] harmonic oscillator model of aromaticity (HOMA),[3,4] and nucleus-independent chemical shift (NICS)[5,6] aromaticity criteria at the B3LYP/6-31G(d) level of theory. All systems were studied at their corresponding closed-shell singlet states, which are expected to be the ground states. Nevertheless, shortly after the publication we became aware of the existence of a recent communication by Bendikov and co-workers,[7] in which the lowest-lying singlet electronic states of [*n*]acenes are described. Bendikov et al.[7] reported that the restricted RB3LYP/6-31G(d) level of theory of polyacenes that are longer than pentacene becomes unstable. For these species, a diradical singlet state obtained using the unrestricted broken symmetry UB3LYP/6-31G(d) method is found to be more stable than the closed-shell singlet state. Their conclusion was supported by a preliminary complete active space self-consistent field (CASSCF) investigation.

Our present calculations confirm that the UB3LYP/6-31G(d) diradical singlet state for [*n*]acenes with *n* = 6−9 is more stable than the RB3LYP/6-31G(d) closed-shell singlet state (see Table 1). For these systems, the triplet state is found to be slightly higher in energy than is the open-shell diradical singlet state, and the energy difference between these two states decreases when *n* increases.[7] We have verified that neither the [*n*]phenacene nor the [*n*]helicene members of the series with *n* = 1−9 studied in our previous work[1] present an open-shell singlet diradical state more stable than the closed-shell singlet ground state. Hence, with the aim to complement the former manuscript, in this work we analyze the local aromaticity of hexacene (**A6**), heptacene (**A7**), octacene (**A8**), and nonacene (**A9**) in their diradical singlet states. For this purpose, the structure-based HOMA,[3,4] the magnetic-based NICS,[5,6] and the electronic-based PDI[2] aromaticity indices have been calculated. Geometry optimizations and HOMA, NICS, and PDI calculations have been carried out at the same B3LYP/6-31G(d) level used in our previous study[1] by means of the Gaussian03[8] and AIMPAC[9] software packages.

TABLE 1: Relative Energy (in kcal·mol^{-1}) of the Diradical Singlet State (OS) with Respect to the Corresponding Closed-Shell Singlet State (CS) and Spin Contamination for the Diradical Singlet State

system	ΔE (OS−CS)[a]	$\langle S^2 \rangle$
A6	−0.12	0.26
A7	−1.70	0.80
A8	−4.05	1.08
A9	−6.58	1.26

[a] ΔE values are slightly different from those of ref 7 because zero-point vibrational energies were not included in this paper.

Before going into the aromaticity analysis, it is worth noting that the UB3LYP/6-31G(d) diradical singlet states are found to be largely contaminated by higher spin states ($\langle S^2 \rangle$ values in Table 1 different from 0 (pure singlet) or 2 (pure triplet)). The spin contamination of the diradical singlet state grows from *n* = 6 to *n* = 9, and this may be likely the result of the energy gap between the diradical singlet and the triplet states becoming smaller as the size of the [*n*]acene increases. Although $\langle S^2 \rangle$ is not rigorously defined in density functional theory (DFT),[10] spin contamination makes the larger stability of the diradical relative to the closed-shell singlet states questionable.[11] In addition, the fact that the experimental vertical π ionization potentials of **A6** are not much different from those of pentacene and tetracene[13] suggests that, at least, the ground state of **A6** may have the

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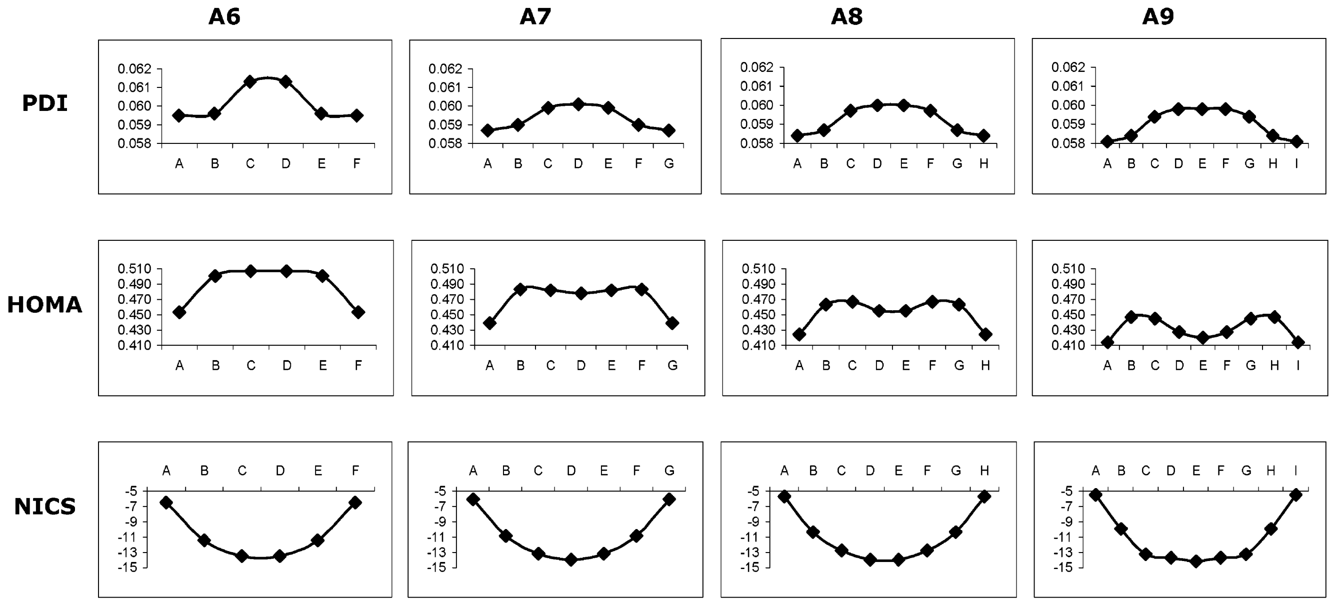

Figure 1. Schematic quantitative representation of trends in closed-shell singlet [*n*]acenes ($n = 6-9$) according to PDI, HOMA, and NICS results. The *x*-axis contains the labels of the different rings. The outer ring is considered ring A, and the rest are labeled in alphabetical order.

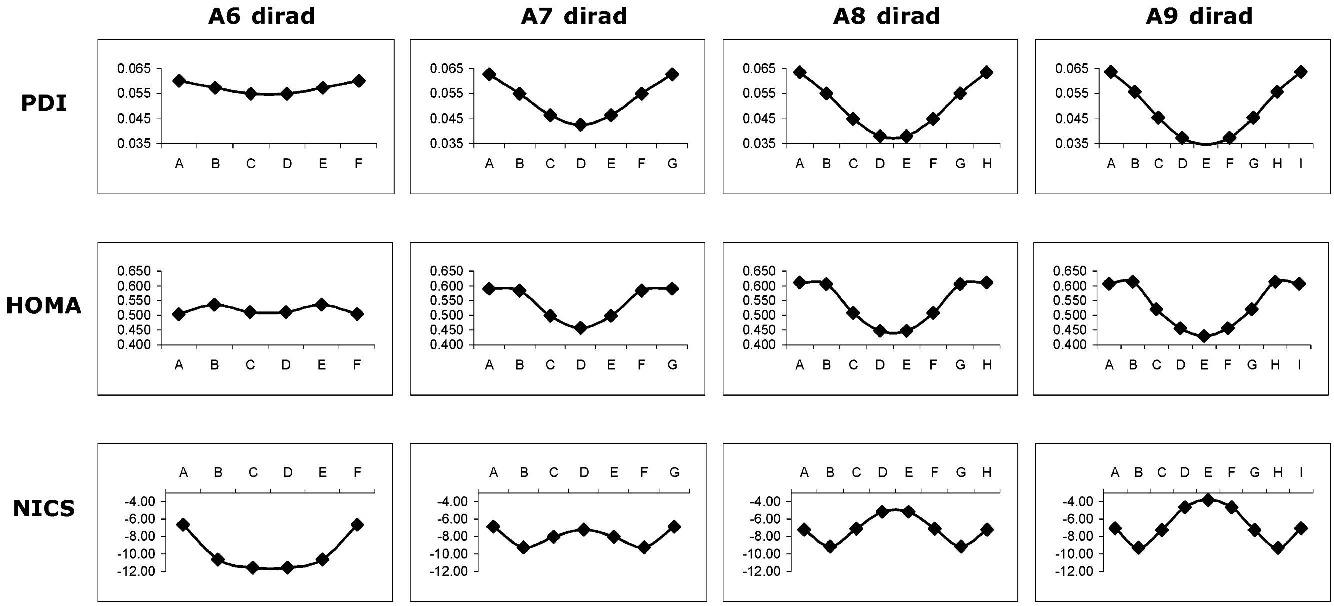

Figure 2. Schematic quantitative representation of trends in open-shell diradical singlet [*n*]acenes ($n = 6-9$) according to PDI, HOMA, and NICS results. The *x*-axis contains the labels of the different rings. The outer ring is considered ring A, and the rest are labeled in alphabetical order.

same closed-shell nature as those of pentacene and tetracene. Further, the sharp ^{1}H NMR signals obtained for two functionalized **A7** compounds, combined with electron paramagnetic resonance (EPR) spectroscopy, confirm the closed-shell nature of these compounds.[14] Finally, it is worth noting that the full π system was not included in the active space of the CASSCF calculations carried out by Bendikov and co-workers,[7] who limited the active space to 10 π electrons (CASSCF(10,10)). Broken symmetry UHF/6-31G(d)//UB3LYP/6-31G(d) calculations indicate that meaningful CASSCF calculations for **A6** should include at least all 26 π electrons according to the criterion established by Bofill and Pulay.[15] So, the preliminary CASSCF/6-31G(d) results indicating the higher stability of the open-shell diradical singlet state for the **A6**−**A9** species are not fully conclusive either. Be as it may, to complete our previous study done on closed-shell singlet states, we have studied the aromaticity of the open-shell diradical singlet states of the **A6**−**A9** species. The whole series of results allows for a discussion of the change in the local aromaticity trends when going from the closed-shell to the open-shell singlet states.

As a summary of our previous results,[1] Figure 1 shows the quantitative tendencies given by the three aromaticity criteria for the closed-shell singlet states. PDI and NICS predict a higher aromaticity for the inner rings than for the outer ones. The above tendency for [*n*]acenes is also supported by other techniques (i.e., ring currents, resonance energies, and charge density properties derived from the atoms in molecules (AIM) theory),[16] although not in all cases.[17] This tendency is also not kept by HOMA, except for **A6**. HOMA shows a reduction of aromaticity from ring C to D for **A7**[1,18] and **A8**, and from C to E in **A9**, although they remain more aromatic than the outer ring in all cases. This particular behavior of HOMA for **A7**−**A9** was explained by the increase of the C−C bond lengths of the central rings as more rings were added.[1] Both PDI and HOMA show that the aromaticity of each ring decreases from **A6** to **A9**, whereas NICS indicates an almost constant aromaticity for each kind of ring when going from **A6** to **A9**. At this point, it is worth noting that each descriptor of aromaticity is based on different physical properties and, for this reason, the trends yielded by each descriptor are not necessarily always the same. For this reason, it is strongly recommended that one uses differently based aromaticity parameters for comparison of local aromaticity in a given series of compounds.[19]

On the other hand, for the open-shell diradical singlet state of [*n*]acenes ($n = 6-9$), completely different trends are observed (see Figure 2). First, the PDI for these diradical species shows that inner rings present lower aromaticities than do terminal ones. In addition, while the aromaticity of the terminal rings is kept almost constant from **A6** to **A9**, the aromaticity of inner rings strongly decreases with the addition of more rings. It is also worth noting that, while there is a convergence of the PDI value for 6-MRs of the heavier members of the closed-shell acenes analyzed, for the diradicals the local aromaticity of the inner rings gradually decreases from **A6** to **A9**. In addition, Figure 2 shows that HOMA and NICS follow parallel tendencies for this series of diradical systems. Thus, both criteria attribute a higher aromaticity to the external rings compared to that of the central rings, like PDI. But, unlike PDI, HOMA and NICS give an almost equivalent or even higher aromaticity to ring B compared to that of ring A for diradical **A7**−**A9** systems. The diradical **A6** does not follow the same tendency; thus, for HOMA, the aromaticity is almost constant for all 6-MRs, whereas NICS shows a higher aromaticity for the inner rings compared to that of the terminal ones. It is also noticeable that, while HOMA values for the central rings are kept quite constant from **A7** to **A9**, NICS indicates an important decrease in the local aromaticity of these rings. The global aromaticity of each species can be discussed through the weighted average (WA)[1] values of PDI, HOMA, and NICS, which are listed in Table S1 of the Supporting Information. According to the WA values of NICS, there is a clear reduction on the global aromaticity when going from the closed-shell to the diradical singlet state. In contrast, the WA values of PDI and HOMA indicate that, despite the important local aromaticity changes, the global aromaticity of the closed-shell and diradical states remains almost the same (or even increases, as indicated by HOMA).

To find a reason for the change in local aromaticity when going from the closed-shell singlet to the diradical singlet, we have analyzed the shape of the highest occupied molecular orbital (HOMO) of the closed-shell singlet and compared it with that of the α and β singly occupied molecular orbitals (SOMOs) of the diradical singlet state. These three orbitals are depicted in Figure 3 for **A6** and **A9** (for **A7** and **A8**, these orbitals can be found in the Supporting Information).

It is clearly seen that the difference between the HOMO and the SOMOs is small for **A6** and increases up to **A9**. In the latter, as reported by Bendikov and co-workers for decacene,[7] the excess of α and β electrons in the diradical singlet species is mostly localized along the superior and inferior ribbons of the acene structure. Interestingly, the localization is larger for the central rings and becomes less pronounced for the most outer rings. This behavior offers an explanation to the change in local aromaticity when going from the closed-shell to the diradical singlet state. The most aromatic central rings in the closed-shell species become the less aromatic in the diradical singlet state because of the high localization of the unpaired α and β electrons. Moreover, since the localization of the SOMOs in the diradical states increases when going from **A6** to **A9**, the loss in aromaticity of the central ring is small in **A6**, and it is particularly important for the highest member of the [*n*]acenes series analyzed. On the contrary, electronic localization of the SOMOs in the outer rings is not so pronounced, and, as a result, these rings become the most aromatic in the diradical singlet state. These trends are reflected by the three aromaticity indices used.

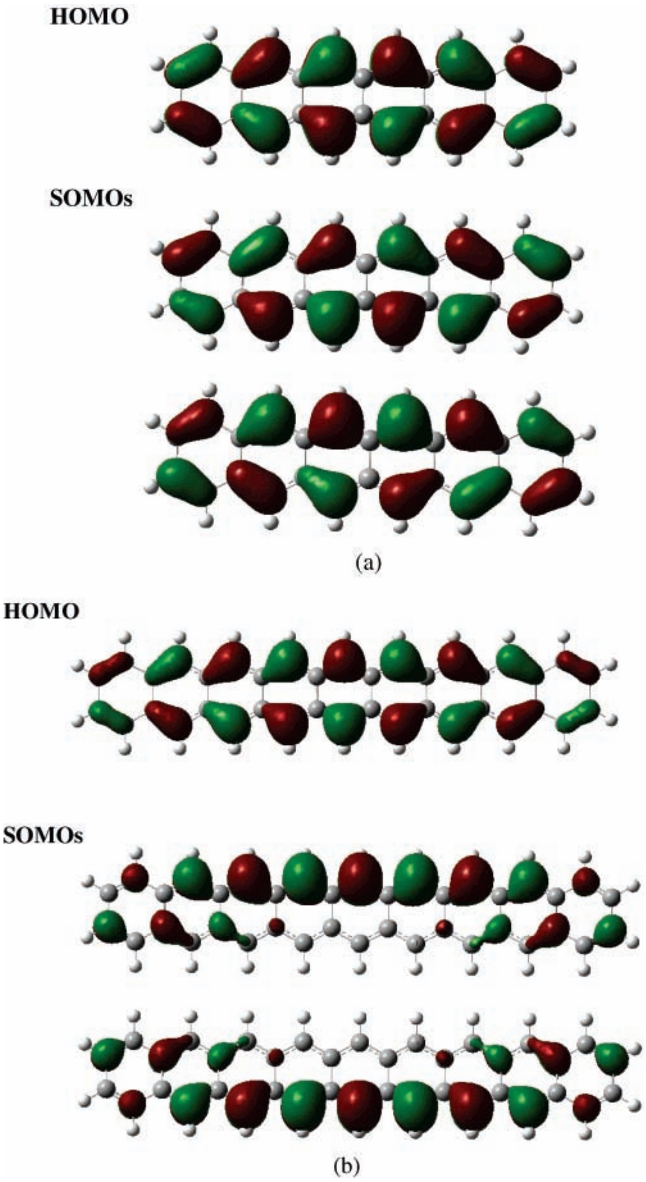

Figure 3. HOMO and SOMOs of (a) hexacene (**A6**) and (b) nonacene (**A9**).

As a whole, in this manuscript we have analyzed the local aromaticity of the lowest-lying singlet states of [*n*]acenes ($n = 6-9$), which present, at the B3LYP/6-31G(d) level of theory, a more stable open-shell diradical singlet state than does the closed-shell singlet one. The electronic changes when going from closed-shell to diradical states lead to important consequences in local aromaticity trends along the series. Closed-shell singlet state [*n*]acenes ($n = 1-9$) show a higher aromaticity of the inner rings than do the terminal ones,[1] whereas open-shell singlet state [*n*]acenes ($n = 6-9$) present, in general, an opposite behavior. Thus, not unexpectedly, we have found that local aromaticities in polyacenes may largely depend on the electronic state taken into account. Besides the aromatic aspects discussed so far, we would like to finish by remarking that, even though recent experimental results have confirmed the closed-shell singlet as the ground state of **A6** and **A7** derivatives,[14] the question of whether the ground state of **A8** and **A9** is the closed-shell or the open-shell diradical singlet state has not been solved yet, despite recent efforts in this direction.[7] In our opinion, high-level ab initio calculations are still needed to definitely determine the electronic ground state of the higher members of the [*n*]acenes series.

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Supporting Information Available: B3LYP/6-31G(d)-optimized Cartesian *xyz* coordinates for the open-shell singlet states of [*n*]acenes ($n = 6-9$). A table with PDI (in electrons), HOMA, and NICS (in ppm) values for the closed-shell and open-shell singlet states of the [*n*]acene series with $n = 6-9$. A figure with the plot of the HOMO and SOMOs of **A7** and **A8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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