Electron Delocalization and Aromaticity in Linear Polyacenes: Atoms in Molecules Multicenter Delocalization Index

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Molecular aromaticity in the linear polyacenes is investigated using an atoms in molecules based six center index (SCI-AIM) which measures the electron delocalization. SCI-AIM values for the linear polyacenes indicate decreasing aromaticity going from outer to inner rings in the polyacene series. The SCI-AIM approach is compared to a Mulliken-like approach, and a critical comparison to the PDI index is made.

Introduction

Although there is no exact quantum chemical definition, aromaticity is a widely used concept in chemistry including the theoretical chemistry community. This lack of a proper definition has led to many different perceptions of aromaticity, and many indices for its quantification have been introduced.[1] These include structural indices, including the well-known harmonic oscillator model of aromaticity (HOMA),[2,3] reactivity and conceptual density functional theory (DFT)-based indices,[4,5] indices based on the special magnetic properties of aromatic compounds,[1,6] electronic delocalization indices,[7] and so forth. The concept of aromaticity is also reflected in energetic indices, mainly resonance energies (RE).[8] A thorough discussion of all these different indices is beyond the scope of the present paper, and the reader is referred to refs 9 and 10. Important to note, however, is that not all indices give the same results. Aromaticity measures from different sources may provide divergent results within a series of molecules. This has been ascribed to the so-called multidimensional nature of aromaticity.[11−13] Despite the divergence between different descriptors and the lack of a proper definition for aromaticity, it remains a very often used concept of immense practical importance.[14]

An intriguing situation where different indices give completely opposite results is observed for the local aromaticity of benzenoid rings in the linear polyacenes. According to the numerical values of some indices, the aromatic character of the benzenoid rings in these molecules increases from the outer ring to the inner ring, while for some others, the trend is completely reversed. Table 1 shows a short, nonexhaustive overview of the two sets of indices. Set A comprises those indices that predict an increase of the aromaticity upon going from the outer to the inner benzenoid rings; set B predicts the opposite trend. Clearly, such a contradiction deserves more attention, and our aim in this study is to reveal the possible origin of the existing discrepancies between various types of aromaticity indices. The main focus will be concentrated on the existing inconsistencies among the indices based purely on the electron density and its features.

TABLE 1: Nonexhaustive List of Set A and Set B Indices[a] for the Quantification of Molecular Aromaticity in the Linear Polyacenes

set A	set B
HOMA[2,3]	PPP ring current[18]
NICS[6]	current circuits[19]
PDI[15]	*Polansky index*[20]
ATI[16]	*MQS−NOEL*[21,22]
FHDD[17]	*SCI*[16]
FLU[23]	

[a] Indices based on purely the electron density function features are in italics.

The HOMA index, a structural type index, suggests an increase of the molecular aromaticity from the outer toward the inner rings.[24] This is also the case for the nucleus independent chemical shifts (NICS).[25] Although both indices seemingly yield the same conclusions, there is an important difference in that, according to HOMA, the most aromatic benzenoid ring in the linear polyacene set is benzene. No other benzenoid ring in the larger polyacenes is more aromatic. Benzenoid hydrocarbons of various kinds were also studied geometrically by the use of experimental geometries and modeling ring energies of the carbon skeleton. The result was then found to be in line with the conclusions of the indices belonging to set B.[26] According to NICS, benzenoid rings can certainly grow more aromatic than benzene itself. However, several studies have revealed that in fact NICS cannot be used for quantifying local aromaticity.[27,28] In set B, the recent work of Aihara et al. showed that exactly the opposite trend is observed when bond resonance energies and geometry-independent electron currents are used as a criterion.[19] This result also agrees with the conclusions of Anusooya et al., using ring currents.[18]

Of special importance in the present paper are the indices purely based on the electron density and its features. The Polansky index,[20] proposed in 1967, is the first example of such an approach. This index is based on quantifying molecular aromaticity on the basis of the similarity to benzene. This index

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clearly showed the aromaticity to decrease when going from the outermost benzenoid ring toward the inner rings. This index was, however, based on the nowadays often considered outdated Hückel molecular orbital (MO) theory. Recently, Bultinck et al.[21,22] generalized this index for molecular aromaticity using the molecular quantum similarity theory (MQS),[29] applying the NOEL index by Cioslowski et al.,[30,31] and found that the same conclusions are obtained using contemporary methodologies. The essence of the NOEL index is that one directly compares the electron density of a benzenoid ring in a molecule with the electron density of benzene itself. Bultinck et al. also introduced the so-called six-center delocalization Index (SCI), which measures directly the delocalization of the electron density over all six atoms in the benzenoid ring.[16] Using a Mulliken-like approach, these SCI indices could be computed very efficiently and were found to correlate nearly perfectly with the results of the Polansky[20] and MQS−NOEL indices.[21] All these indices only employ the electron density to show that the aromaticity decreases from the outer to the inner benzenoid rings in the linear polyacenes.

Set A, however, also contains several indices based on the electron density or its features. One of them is the Fermi hole density delocalization index (FHDD) introduced by Matta et al.[17] The FHDD measures the delocalization and thus aromaticity by computing the alternation of the delocalization indices. The values reported by Matta et al. in their study suggest an increase of local aromaticity on going from outer to inner rings. This trend was, however, questioned by our independent calculations of this index.[22] Finally, the FLU index of Matito et al.[23] is based also on using benzene as a reference and computes the deviation between the individual bond orders within the ring and those in benzene. The reversed trend of aromaticity is mainly advocated by the values of the para delocalization index (PDI) index, which is defined as the average of delocalization indices[32] from the atoms in molecules (AIM) theory,[33−35] calculated between each set of two carbon atoms in para position. This index was reported in the study of Poater et al.[15] for the first four members of the polyacene series, and the calculated values do indeed suggest the increase of aromaticity on going from the outer to inner rings for both anthracene and tetracene. The relevance of this trend was corroborated by referring to the coincidence of the PDI trends with those based on the NICS and HOMA indices. As it will be shown, however, the situation with the PDI is a bit more complicated, as in subsequent studies using the same index, the trend of higher local aromaticity for the inner rings was confirmed only for tetracene and pentacene, while for anthracene, the index suggests the aromaticity of the central ring to be lower than that of the outer rings.[36] Moreover, NICS indices are being criticized as local aromaticity descriptors. Most recently, it has been shown by Stanger that none of the alternative NICS indices, such as (NICS(0), NICS(1), ...) are useful to quantify local aromaticities in polycyclic systems.[28]

In a recent study, it was furthermore found that, according to the PDI, for larger polyacenes the order of aromaticity of individual benzenoid rings depends on the electronic state considered.[37] It has been suggested that, for the larger polyacenes, the lowest-energy state could possibly correspond to a diradical singlet state rather than the closed-shell singlet state.[38,39] Poater et al.[37] performed UB3LYP/6-31G* calculations and investigated the effect of the change in state compared to the RB3LYP/6-31G* level of theory used originally to find quite dramatic changes in ordering of local aromaticities as measured by the PDI. Whereas the PDI for the closed-shell singlet case points toward an increase of the aromaticity toward the more inner rings, the opposite is found in the diradical state. This infers that no general claim on local aromaticity in polyacenes could be made, since the results would depend strongly on the length of the polyacene. It should be noted that the scope of the present paper is not to settle which state is the lowest in energy, since this will require extensive higher-level calculations. Rather, we wish to examine the behavior of our aromaticity indices when going from one state to the other.

In view of all the above uncertainties, we decided to address the problem of the aromaticity of linear polyacenes in more detail with special emphasis on the comparison of the PDI and SCI indices with the AIM generalized counterpart AIM-SCI. The reason is that all these indices are in a sense closely related and can be derived from the same theoretical framework, and still, the predictions to which they lead are considerably different.

Theoretical Methods

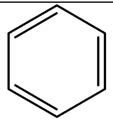
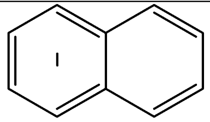
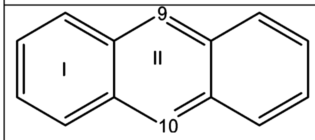
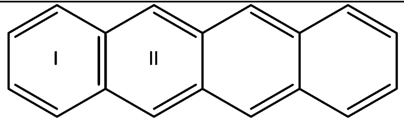
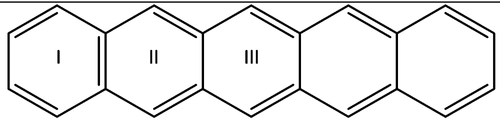
Some time ago, Bultinck et al., following suggestions in previous work of Giambiagi et al.,[40] pursued a new approach to the quantitative characterization of aromaticity.[16] The approach characterizes the extended delocalized bonding, which is generally considered one of the typical manifestations of aromaticity, by the values of the so-called multicenter bond indices defined as

$$\mathrm{MCI}_{ABC...K} = \eta \sum_{\mu\in A} \sum_{\nu\in B} \cdots \sum_{\kappa\in K} \sum_{i} \Gamma_i[(PS)_{\mu\nu}(PS)_{\nu\rho}\cdots(PS)_{\kappa\mu}] \quad (1)$$

where P and S represent charge density and bond order and overlap matrices respectively, η is an appropriate normalization constant, and Γ_i the permutation operator that interchanges the Greek basis function labels so as to ensure that the index includes all the terms required by the formalism of generalized population analysis (GPA).[41−43]

In the particular case of aromaticity of polycyclic aromatic hydrocarbons, such extended delocalized bonding is often associated with individual benzenoid rings, and the corresponding six-center index (SCI) attempts to quantitatively characterize the old Clar concept of the aromatic sextet.[44] Although the reported applications of this approach clearly demonstrate the usefulness of multicenter bond indices as a new universal aromaticity measures, in the particular case of linear polyacenes the values of SCI contradict the classification on the basis of other aromaticity measures such as PDI. This result by itself would not be too surprising, since the inconsistencies between various aromaticity measures are quite common, but what makes the situation with these two indices puzzling is that they are in fact closely related. Both of them can be, namely, derived from the general framework of GPA, but while SCI represents the index which characterizes the aromatic sextet by a genuine six-center term corresponding to the special case of the index (eq 1) for $k = 6$, the PDI projects the same phenomenon into two-center contributions only. The question thus naturally arises whether the reported discrepancies in the prediction of aromaticity in linear polyacenes could not be due to the fact that the projection of the cyclic delocalization into two-center contributions only is in a sense restrictive and emphasizes only certain aspects of the complex phenomenon of aromaticity while neglecting some others. One of the primary aims of this study is to attempt the elucidation of the factors responsible for the existence of the discrepancies in the predictions based on two- and multicenter bond indices. To be able to address this problem reliably enough, we report in this study the extension of the original formalism of multicenter bond indices into the frame-

TABLE 2: Molecules Included in the Present Study with Benzenoid Ring Numbering

	**1** **Benzene**
	**2** **Naphthalene**
	**3** **Anthracene**
	**4** **Tetracene**
	**5** **Pentacene**

work of AIM theory so as to be put on the same theoretical footing as the approach using the PDI indices. Although there have been previous studies where GPA was combined with AIM theory,[45] the present study introduces for the first time GPA-based aromaticity descriptors involving all participating atoms in the delocalized system. Within the framework of AIM approach, the original definition (eq 1) reduces in the case of six-center index to the form

$$\mathrm{AIM}-\mathrm{MCI}_{ABCDEF}=\Delta^{(6)}_{ABCDEF}=\eta\sum_i\sum_j\sum_k\sum_{\ldots}\sum_x\sum_y\sum_\alpha\Gamma_\alpha[(S)^A_{ij}(S)^B_{jk}\cdots(S)^E_{xy}(S)^F_{yi}]\quad(2)$$

where $(S)^A_{ij}$ means the overlap integral between occupied MOs i and j is computed over the basin of atom A (Ω_A)

$$(S)^A_{ij}=\int_{\Omega_A}\psi_i^*\psi_j\,\mathrm{d}\tau\quad(3)$$

and the meaning of the projection operator Γ_α is analoguous to the one in the original formula (eq 1). Within the same approach, the PDI is then defined as a mean of two-center bond indices (eq 4) calculated for the pairs of atoms located in each particular benzenoid ring in para positions.

$$\delta_{AB}=\sum_i\sum_j(S)^A_{ij}(S)^B_{ji}\quad(4)$$

The above indices are commonly known as delocalization indices,[32] but other terms such as shared-electron distribution index (SEDI)[46] were also proposed.

In addition to reporting the extension of the formalism of the generalized population analysis into the framework of AIM theory, the focus of this study will also be concentrated on the following problems and questions.

(i) Is the order of aromaticity in linear polyacenes as reflected in the values of both two- and multicenter bond indices in a series of linear polyacenes sensitive to the particular approximation used for their calculation?

(ii) Why do the predictions of aromaticity based on AIM-SCI and PDI diverge for the linear polyacenes, whereas for most other hydrocarbons, a relatively good agreement is found?

(iii) To what extent does the aromaticity of individual benzenoid rings of linear polyacenes depend on the actual electronic state of these species?

Computational Methods

To investigate the local aromaticity of the different benzenoid rings based on the PDI and AIM-SCI indices, a set of five linear polyacenes was chosen. Molecules included in the set are shown in Table 2 with Roman numerals identifying the different rings.

All molecules were optimized at the B3LYP/6-31G*[47−49] level using the *Gaussian 03* program.[50] Hessians were computed to confirm the stationary points as minima. All molecules have a D_{2h} symmetry, except benzene with a D_{6h} symmetry. Wave function stability was checked for each molecule, and for all molecules, the ground state was found to correspond to a closed-shell singlet state. This agrees with previous findings that diradical singlet states become ground states only for longer polyacene chains.[37]

In connection with the particular level of theory, which belongs to the category of DFT approaches, it is necessary to realize that the use of Kohn−Sham orbitals for the calculation of delocalization indices is an approximation. The calculation of such indices requires, namely, the knowledge of the first-order density matrix. Such a matrix is for single determinant methods, however, available only within the Hartree−Fock approximation. The DFT theory provides, however, only the first-order density so that the application of GPA to this level of the theory is, strictly speaking, not exactly justified. Yet, it has become common practice to use the same expressions for the calculation of bond indices as in the Hartree−Fock case,[7] and ample numerical data show that this approximation is a very good one.[7] The most important advantage of using DFT calculations in this work is that B3LYP calculations usually give better geometries,[51] and the tests for benzene, naphthalene, and anthracene, optimized using Hartree−Fock and B3LYP approaches, did indeed reveal that the agreement between experiment and theory is substantially better with B3LYP.[36,52]

After having discussed the choice of the computational methods used, let us discuss, in the following part, other technical aspects of the calculations. First of them concerns the accuracy of aromaticity indices calculated within the AIM approach. The computation of the AIM theory-based indices requires the determination of atomic basins and subsequent computation of the MO overlap integrals over these individual basins. The resulting atomic overlap matrix (AOM) elements are then used to compute all the required multicenter indices. As the accuracy of the calculated bond indices primarily depends on the accuracy of the necessary AOM integrals, we have focused on the accuracy of the numerical integration procedures used, and the following criteria were used. For all atoms, the integration of the Laplacian of the electron density within the basin had to be lower than 10^{-3}. A novel integration technique, based on finite elements, is able to reduce this error, even for trigonally shaped atoms with thin tails.[53] A second, often used criterion concentrates on the sum of the atomic populations which should be equal to the number of electrons in the molecule. Since AIM programs use numerical integration techniques, an exact equality is usually not obtained, and so, only the minimal difference is usually required. Nevertheless, we found during the present study that that this criterion represents only a necessary but not sufficient condition for the AOM matrices to be accurate enough. The computation of the delocalization and multicenter indices requires, namely, all the elements of the MO overlap matrix, and even if the normalization to the total number of electrons is satisfied with reasonable accuracy, noticeable errors can still persist in off-diagonal elements. To check the accuracy of the whole AOM matrices, we have used a criterion which requires the sum of overlap integrals over the domains of all atoms to be equal to the unit matrix. We required the maximum deviation in any element to be below 10^{-5}. In case any values would be larger than this threshold, a new integration is performed with a denser integration grid. Another requirement that we imposed on AOM matrices was that their values should correctly reflect the symmetry of the molecule. All AIM calculations were performed using the Morphy program[54−56] in a modified version that allows the computation of atomic basin basis function overlap integrals. From these integrals and the MO coefficients, the MO overlap matrix is constructed.

Results and Discussion

First, the AIM-SCI values computed using the B3LYP/6-31G* optimized geometries will be discussed and compared to previously introduced six-center bond indices that represent the Mulliken-like counterparts of the present AIM generalized indices. Table 3 shows the comparison of original Mulliken-like SCI and AIM-SCI indices for the different benzenoid rings in the linear polyacenes.

Several trends can be deduced from Table 3. First of all, it is seen that, although the values of original SCI indices are slightly smaller, the trends in both sets of indices are the same. The largest index is in both cases found for benzene, and the values systematically decrease on increasing the number of fused rings. The decrease is observed not only on going from outer to inner rings, but a similar reduction of the cyclic delocalization is also evident from the values of SCI of the outermost ring on going from benzene to pentacene. This general trend is displayed in Figure 1 from which it is also evident that the value of the AIM-SCI index converges to a limit close to 0.02.

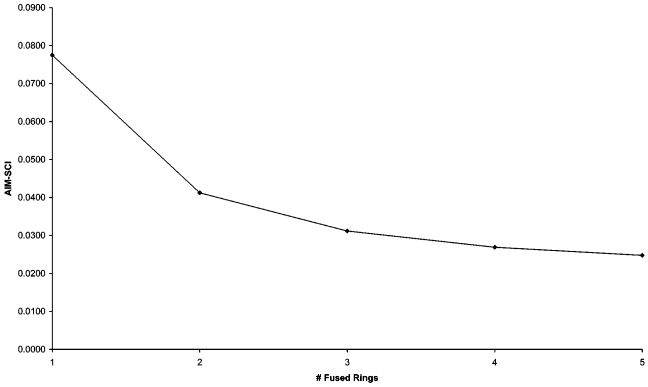


Figure 1. B3LYP/6-31G* AIM-SCI values for the outer benzenoid ring versus the number of fused polyacene rings in the linear polyacenes.

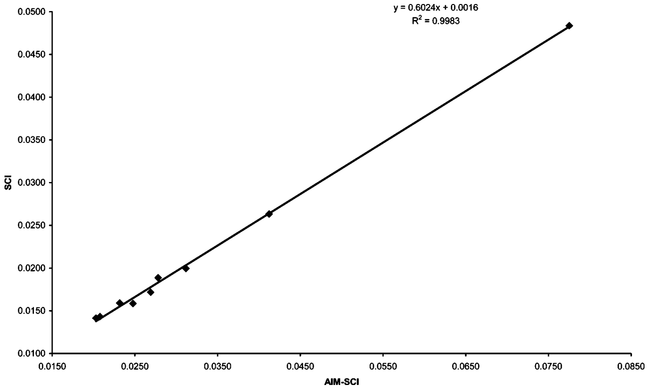


Figure 2. Correlation between B3LYP/6-31G* SCI and AIM-SCI indices for the symmetry-unique benzenoid rings in the set of linear polyacenes.

TABLE 3: Calculated Values of B3LYP/6-31G* AIM-SCI (first number) and SCI (Mulliken-type index, second number) Indices for the Linear Polyacenes

molecule	ring	AIM-SCI/SCI
1 benzene	I	0.0775 0.0484
2 naphthalene	I	0.0412 0.0263
3 anthracene	I	0.0312 0.0199
	II	0.0278 0.0189
4 tetracene	I	0.0269 0.0172
	II	0.0232 0.0159
5 pentacene	I	0.0248 0.0159
	II	0.0208 0.0143
	III	0.0203 0.0141

These results are very interesting since both indices thus exactly reproduce the trends of aromaticity as in the Polansky indices and its recent ab initio generalization.[21,22] The close parallel between the SCI and AIM-SCI indices is also reflected in the existence of the correlation between both types of indices. This correlation is depicted in Figure 2.

TABLE 4: B3LYP/6-31G* PDI Values for All Symmetry Unique Benzenoid Rings in the Linear Polyacenes

molecule	ring	PDI
1 benzene	I	0.1046
2 naphthalene	I	0.0756
3 anthracene	I	0.0661
	II	0.0658
4 tetracene	I	0.0619
	II	0.0621
5 pentacene	I	0.0599
	II	0.0601
	III	0.0608

Clearly, the correlation is nearly perfect, and its existence thus clearly demonstrates that both approaches are nearly interchangeable and, also, that our AIM integration procedure can be trusted. This result is very important since the calculation of Mulliken-like SCI indices is numerically much less demanding than the calculation of the analogous AIM generalized quantities, and their values could thus safely be used as a measure of aromaticity in wider series of polycyclic aromatic hydrocarbons (PAHs). On the other hand, the Mulliken approach is known to have several shortcomings,[57] and in such cases, the AIM-SCI approach can be safely used.

After having demonstrated the equivalence of the SCI and AIM-SCI indices for the present basis set, let us address now the problem of the discrepancies between the trends of aromaticity based on the AIM-SCI and the PDI. As was already stressed above, the PDI indices reported by Poater et al.[15] for the first four members of the polyacene series suggested an increase of aromaticity on going from the outer to inner rings for both anthracene and tetracene. This general trend was, however, slightly questioned in the subsequent study by Portella et al.[36] who extended the study to higher polyacenes and confirmed the trend of increasing aromaticity for inner rings only for tetracene and pentacene, while for anthracene, the PDI index suggests the aromaticity of the central ring to be lower than that of the outer rings. Because of these discrepancies, we opted to recalculate the PDI indices in the same series of polyacenes, and the resulting values are summarized in Table 4.

The level of the theory used presently is the same as in the study by Portella et al., and the calculated values very closely agree with those reported in the latter study.[36] To elucidate the origin of the disagreement with the earlier study of Poater et al.,[15] we decided to check whether it could not be due to slight differences in the AIM integration thresholds. This proved not to be the case, and the most probable reason for the inconsistency of the PDI trends for anthracene is that, in the study by Poater et al.,[15] the indices were calculated at the HF/6-31G* level of the theory, while in the present study and in the study by Portella et al.,[36] the B3LYP/6-31G* level was used.

Given the discrepancy between the PDI and AIM-SCI indices, it is well worth examining in more detail the reasons for this difference. The discrepancy in the aromaticity of the central ring of anthracene can apparently be attributed to the difference in the optimized geometries yielded by the HF and B3LYP methods. The comparison of calculated geometrical parameters shows that better agreement with experiment is obtained with the B3LYP procedure, and for this reason, we believe that the aromaticity of the central ring of anthracene is better reflected in the values of the PDI calculated by Portella et al.,[36] which imply that the central ring is less aromatic then the terminal ones. The anomalous classification of the anthracene local aromaticities reported previously[15] reflects the fact that the most important difference between HF and B3LYP optimized geometries in the case of anthracene is the distortion of the central ring, which, at HF level of the theory, results in the shortening of the interatomic distance between atoms 9 and 10 by roughly 0.025 Å compared to B3LYP (see Table 2 for atom numbering). Although the difference is at first sight not dramatic, the above difference in geometry can have far-reaching consequences for the classification of aromaticity of the central anthracene ring. The PDI is defined as the average of two-center diatomic delocalization indices between the pairs of atoms in para position, and the shortening of the bond distance between atoms 9 and 10 can very well be expected to result in a stronger interaction and thus bond index. This explains why a change in geometry between the two methods can alter the conclusions on aromaticity.

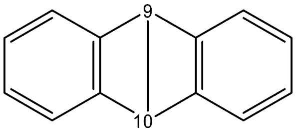


Figure 3. Example of a Dewar resonance structure for anthracene.

A more fundamental issue about the PDI is that it is biased to the interactions reflected in the Dewar resonance formulas. These structures, of course, contribute to aromaticity, but the fact that the PDI overemphasizes the role of these structures while not properly accounting for the role of Kekulé and other structures means that the classification of the aromaticity based on these indices is, in a sense, biased. The structure of anthracene can be described as a resonance hybrid of several Kekulé and Dewar structures.

The resonance structure depicted in Figure 3 is traditionally invoked by organic chemists to explain the high reactivity (and consequently low aromaticity) of the central ring of anthracene. This structure will contribute a lot to the PDI, and thereby artificially increase the aromaticity of this ring. The bias of the PDI toward Dewar structures does not always need to be expressed so dramatically as in the present case, and indeed, many examples of successful applications of the PDI have been reported.[7] This is further corroborated by the fact that a fairly good correlation has been reported between the SCI and the average two-center index (ATI), which corresponds to a Mulliken-based version of the PDI, except when Dewar structures play a more significant role.[16] However, the inherent tendency of this index to emphasize the delocalization reflected in the Dewar structures requires one to be careful in generalizing the conclusions based on this index. The importance of including different and not just selected resonance structures for the classification of aromaticity was also demonstrated by Wu et al.[58] who performed extensive VB calculations on many polyaromatic benzenoid hydrocarbons and computed relative local hexagon energies (RLHE) defined by Herndon and Ellzey.[59,60] It was found that these RLHE for the set of molecules from benzene to pentacene confirm the decreasing trend in aromaticity in the linear polyacenes going from the outer to the inner ring. This is also the case using the circuit specific ring currents of Anusooya et al. where it was also found that the aromaticity decreases.[18] In the context of the reported Dewar bias of the PDI and the necessity to include all resonance forms for a benzenoid ring, it is important to note that all are accounted for in the SCI, as described by Bollini et al.[61]

The bias of the PDI in the particular case of linear polyacenes can also be demonstrated by the closely related FHDD index of Matta et al.[17] Like the PDI, the FHDD is also based on diatomic delocalization indices only. But in contrast to the PDI, which takes into account only the diatomic delocalization

TABLE 5: B3LYP/6-31G* FHDD Indices for the Set of Polyacenes

molecule	ring	FHDD
1 benzene	I	1.000
2 naphthalene	I	0.768
3 anthracene	I	0.709
	II	0.683
4 tetracene	I	0.683
	II	0.650
5 pentacene	I	0.672
	II	0.633
	III	0.627

between two carbon atoms in para position, the FHDD index measures the aromaticity by computing the alternation of the delocalization indices as described in eq 5

$$\vartheta = 1 - \frac{c}{6}\sqrt{\sum_{i=1}^{6}\left(\kappa - \sum_{j=1}^{6}\delta_{ij}\right)^2} \qquad (5)$$

κ is a constant and reflects an idealized sum of the delocalization indices between a carbon atom in benzene and all other carbon atoms. In a general benzenoid ring, $\sum_{j=1}^{6}\delta_{ij}$ stands for the sum of delocalization indices between carbon atom i and all other carbon atoms in the ring; c is a constant. The FHDD values at the current B3LYP/6-31G* level are given in Table 5, using the corrected constant $c = 2.4312$.[62]

Table 5 shows that the trend of the local aromaticity is in this case again completely identical to the trend based on SCI and AIM-SCI, so that despite original claims[17] the FHDD corroborates the decrease of aromaticity on going from outer to inner rings.

In addition to all these results which contradict the trends of aromaticity reflected in the PDI values for linear polyacenes, there is yet another important aspect which casts some doubts on the reliability of this index in this particular case. This aspect is related to the recent findings, according to which the lowest-energy state of higher polyacenes could possibly correspond to a diradical singlet state rather than the closed-shell singlet state.[38,39] This dichotomy was recently addressed Poater et al.[37] who calculated the PDI indices for both lowest-lying electronic states and found that the trends of aromaticity for each of these states are completely different. Whereas the PDI for the closed-shell singlet case points toward an increase of the aromaticity toward the more inner rings, the opposite is found in the diradical state. This infers that no general claim on local aromaticity in polyacenes could be made, since results would depend strongly on the length of the polyacene. This, however, would be quite unpleasant, since abrupt changes in the properties of polyacenes could be expected after exceeding the critical number of fused benzene rings. Fortunately, this is not observed. To clarify the situation, we also computed SCI indices for the UB3LYP/6-31G* diradical singlet states using optimized geometries at that level and compared them with the previously calculated values for the closed-shell singlet states. The results are quite interesting, since in contrast to the divergent behavior of PDI indices, the SCI does not infer any drastic change in the local aromaticity trend, and it remains that the outermost ring is always the most aromatic irrespective of the electronic state of the polyacene. As an example, Figure 4 shows the trend in PDI and SCI values for hexacene. This trend was also confirmed for heptacene in both states (data not shown).

This result is very important since the fact that the SCI index predicts the same order of aromaticity irrespective of the eventual change in the nature of the lowest electronic state makes the classification of aromaticity less ambiguous and, also, more consistent with observed chemistry. One can thus conclude that the AIM-SCI gives a coherent picture for both the closed-shell and diradical singlet states without drastic inversions of aromaticity sequences within the molecules. Independent of the question of what is the exact ground state of the polyacenes, the AIM-SCI points toward a decrease of the aromaticity.

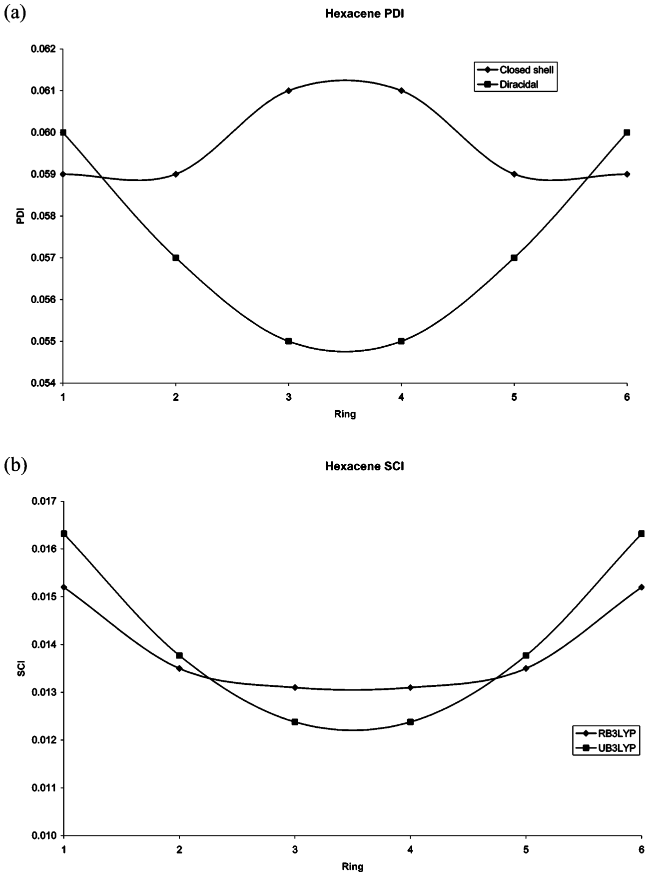


Figure 4. PDI (a) and SCI (b) aromaticity indices for the different benzenoid rings in hexacene in the singlet (RB3LYP) and diradical (UB3LYP) states. Rings are numbered starting from the left, outermost ring 1 and then numbered consecutively.

Conclusions

It has been shown that the electron delocalization, measured via six-center indices, can be computed from the atoms in molecules theory. Several trends could be discerned, such as a continuous decrease in six-center delocalization for the outer ring when studying linear polyacenes with increasing number of fused rings. Within each of the polyacenes, the six-center delocalization decreases when going to the inner rings in a uniform way. This confirms previously found trends from Mulliken-like six-center indices and molecular quantum similarity. So, when electron delocalization over all six centers is considered an aromaticity descriptor, the present study unequivocally shows that the aromaticity decreases from the outer to the inner rings. Still, not all indices are found to agree with the present findings, including, for example, NICS. In case of electron delocalization indices, the presently introduced indices as well as the current calculations of the FHDD index all agree. For the PDI, an explanation is offered for the divergent results compared to the SCI and FHDD indices.

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