Aromaticity in Linear Polyacenes: Generalized Population Analysis and Molecular Quantum Similarity Approach

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Abstract: The relative aromaticity of benzenoid rings in the linear polyacenes is investigated using two novel aromaticity approaches. According to the first, the aromaticity of individual benzene rings was gauged by the values of six-center bond indices (SCI) calculated within the so-called Generalized Population Analysis (GPA). In the second approach, the same goal is addressed using the theory of Molecular Quantum Similarity (MQS). Both independent approaches are found to correlate very well, and both point toward decreasing aromaticity in any linear polyacenes upon going from the outer to inner rings.

Key words: polyacenes; aromaticity; density function; quantum similarity; multicenter index

Introduction

Aromaticity is a very widely used concept in chemistry, although not defined from the quantum chemical point of view. This lack of a firm theoretical basis opens the door to the introduction of many different indices to express and quantify molecular aromaticity. An often used classification of aromaticity measures distinguishes the structural, energetic, and magnetic indices based on the properties of the density function. Among the structural indices, especially popular is the HOMA index, based on a harmonic oscillator model of aromaticity. This index uses a sum of two terms, one expressing the spread of the bond lengths between the atoms in the aromatic system and another term aimed at quantifying how much the average bond distance differs from an idealized value. Energetic criteria are among the first recognized as aromaticity indices, and include aromatic stabilization energies, energies from homo- and isodesmotic reactions etc. Magnetic indices reflect the special magnetic properties of aromatic compounds. Among the best-known indices one can mention the nucleus-independent chemical shifts (NICS) based on the diamagnetic shielding at ring centers. Finally, indices have been introduced based on the properties of the electron density. Examples are the works of Matta and co-workers where aromaticity was quantified via the bond critical point properties. Also noteworthy in this context are the Para-Delocalization Indices (PDI) introduced by Poater et al., where the delocalization indices from the Atoms-In-Molecules (AIM) theory between the carbon atoms in para position are used to gauge the degree of aromaticity. Electron delocalization indices have recently been reviewed by Poater et al.

Despite huge efforts, aromaticity remains a lustrous, enigmatic property. Because of the lack of a proper definition, it has even been suggested that the aromaticity concept be banned as a whole. Despite this quite drastic suggestion, the concept of aromaticity is still very often used and plays a key role in chemistry. The enigma of aromaticity is very well illustrated by the observation that in many applications different aromaticity criteria do not correlate at all, and exhibit divergent behavior when comparing different molecules. This behavior finally resulted in the insight that aromaticity is a multidimensional phenomenon. The case of the linear polyacenes is just an example of such a divergence between different aromaticity measures. Despite the apparent structural simplicity of polyacenes, there is already, for a long time, a lot of debate whether the aromaticity increases or decreases from the outer ring.
towards the inner ring. Many different methods have been applied, and many indices have been used supporting any of the two points of view. One of the pioneering studies in the aromaticity of poly-cyclic aromatic hydrocarbons (PAHs) is the work by Polansky and Derflinger. They introduced an index classifying the aromaticity of individual benzenoid rings in PAHs by its similarity to benzene itself. Using their approach they also concluded that the aromaticity decreases from the outer to inner rings. As this “similarity index” was based on relatively simple, but certainly qualitatively correct, HMO theory; their findings remained practically unnoticed. Current day studies on quantifying molecular aromaticity, including local aromaticity, often rely on the use of NICS as a measure. Schleyer et al. stressed that the inner rings of polyacenes are more aromatic than the outer rings since they are characterized by more negative NICS values. This point is certainly debatable given the observed chemical reactivity, which would infer the opposite conclusion. This has led Schleyer et al. to question the use of reactivity as an indicator of molecular aromaticity. The NICS-derived order of aromaticity is, however, inconsistent with the predictions of various other aromaticity measures, such as the Polansky Index (P), the Six-Center Index (SCI), most applications of graph theoretical concepts from graph theory about the relative degrees of aromaticity as an indication of molecular aromaticity. The NICS-derived order of aromaticity is, however, inconsistent with the predictions of various other aromaticity measures, such as the Polansky Index (P), the Six-Center Index (SCI), most applications of graph theory, Valence bond theory calculations etc., for which the trend of aromaticity was found to be completely opposite. This could suggest that there is indeed multidimensional character in aromaticity, and that magnetic properties (like NICS) indeed diverge from other measures of local aromaticity. However, NICS have been criticized on many occasions. One of the most thorough studies was done by Lazzaroni, who argued that the idea of delocalizing all ring current information in a single point is an incorrect approach. Recently, Stanger also showed that local aromaticities of PAHs cannot be assigned by the NICS, because the ring current of each ring is influenced by the neighboring rings. Aihara very recently found that magnetic and energetic criteria of local aromaticity can be unified in Circuit specific Resonance Energies (CRE), which also give the opposite trend for local (benzenoid) aromaticity when compared with NICS.

On the other hand, based on the HOMA index, Cyrański et al. conclude that the central rings are more aromatic than the outer rings in linear polyacenes. Despite this apparent agreement in conclusion with NICS, there is a fundamental difference. The HOMA results point out that benzene is the most aromatic molecule and none of the inner rings of the larger polyacenes ever gets more aromatic than benzene itself. According to NICS, inner rings of larger polyacenes can certainly become even more aromatic than benzene itself. In a study by Matta and Hernández-Trujillo, the Atoms-In-Molecules (AIM) theory is used to obtain a new aromaticity index, based on the electron delocalization of the carbon atoms to the other carbon atoms in a benzenoid ring. They obtain results in agreement with the HOMA results. This approach is naturally reminiscent of the work of Kruszewski and Krygowski, who used bond orders between the carbon atoms to obtain an aromaticity index. However, it was recently found by Bultinck et al. that such a two-center delocalization approach does not agree with results of six-center delocalization indices. Because a complete discussion of all previous contributions is out of the scope of the present paper, it is worthwhile to conclude this description of the contradictory results on the aromaticity of benzenoid rings in PAHs by giving a brief account of some very recent findings. In their study based on AIM delocalization index (PDI), Portella et al. concluded, consistent with the trends based on NICS, that aromaticity of individual rings should increase on going from outer to inner rings. This order of aromaticity is, however, questioned in the study by Aihara who showed that exactly the opposite trend is observed when bond resonance energies and geometry-independent electron currents are used as a criterion. This result also agrees with the conclusions of the pioneering study by Polansky and Derflinger and previous work of Anusoye et al., using ring currents. Another interesting result is that by Wu and Jiang. They performed valence bond calculations on many conjugated hydrocarbons, and found that the aromaticity decreases. A very good account of the different conclusions from graph theory about the relative degrees of aromaticity in, among others, polyacene molecules has been given by Randić.

Our aim in the present study is to revive the approach suggested by Polansky in 1967 and to generalize it to the contemporary computational standards. Next, the new approach generalized to contemporary computational standards will be applied to the clarification of the uncertainties concerning the aromaticity of individual benzenoid rings in linear polyacenes. As it will be shown, the conclusions based on this new generalized index are completely consistent with the predictions of the original HMO based study. This result is very important because not only it demonstrates that already the original HMO-like index was reliable enough but also because the same order of aromaticity is also suggested by another recently proposed aromaticity index, namely, the so-called six-center bond index whose values characterize the extent of cyclic delocalization in individual benzenoid rings.

**Theoretical Methods**

From the broad range of various methods for the characterization of the aromaticity we use two relatively recent approaches, which both are in a sense based on extracting the information from the molecular electron density.

The first of them arises from the long recognized fact that one of the typical features of the aromatic molecules is the cyclic delocalization of the electron density over the atoms composing the system. The idea of extended delocalization was ingeniously adopted by Clari, who noticed that the domains of extensive delocalization in PAHs can often be associated with individual benzenoid rings and based on this idea he proposed the now widely recognized concept of the aromatic sextet. Recently, we have attempted to put the qualitative idea of the aromatic sextet on a sounder quantitative theoretical basis. We proposed a new approach allowing to characterize the extent of cyclic delocalization in individual benzenoid rings in PAHs in terms of the so-called six-center bond index (SCI). This index belongs to the broader family of bond indices derived from the formalism of the so-called generalized population analysis (GPA). As the theoretical background underlying the formalism of GPA is sufficiently described in several previous papers, we consider it sufficient to remind here only the basic ideas to the extent necessary for the purpose of this study. For detailed derivations of the GPA expressions the reader is referred to original studies.
Generalized population analysis is a generic name of the procedure coined to the whole family of approaches based on the partitioning of the identity (1) into contributions that can be attributed a certain physical or chemical meaning. This identity is valid at HF and formally also DFT level of the theory and $P$ and $S$ in eq. (1) denote charge density and overlap matrix, respectively.

$$\frac{1}{2^{N}} Tr(PS)^{k} = N = \sum_{A} \Delta_{A}^{(k)} + \sum_{A< B} \Delta_{AB}^{(k)} + \sum_{A< B< C} \Delta_{ABC}^{(k)} + \ldots \sum_{A< B< C< \ldots K} \Delta_{ABC \ldots K}^{(k)}.$$  \hspace{1cm} (1)

The simplest situation is for the indices derived from the partitioning of (1) for $k = 1$ since the mono-atomic terms correspond to Mulliken populations on individual atoms. Similarly simple and straightforward interpretation holds also for diatomic indices resulting from the partitioning of the identity (1) for $k = 2$; these indices are identical to the well known Wiberg or Wiberg–Giambiagi–Mayer indices, whose values are often known to coincide with the classical bond multiplicities. The family of bond indices is not exhausted by these two simplest examples but similarly useful multicenter bond indices can be obtained also from the partitioning (1) for higher values of $k$. Thus, for instance the triatomic terms resulting from $k = 3$ are known as three-center bond indices and their values can advantageously be used for the interpretation of the electronic structure of molecules such as electron deficient boranes for which the existence of three-center bonding was corroborated. In the same way it is then possible to introduce the multicenter bond indices as the indicators of the delocalized bonding extended over even more centers. A typical example in this respect is the concept of the aromatic sextet and the six center bond indices (SCI), defined as the six-center terms from the partitioning of (1) for $k = 6$. The SCI characterize the extent of the cyclic delocalization over individual benzenoid rings in PAH. In this connection it is fair to note that the idea of using multicenter bond indices for the characterization of aromaticity is due to Giambiagi et al., but the index they considered is slightly different from the one we use here. As it was stressed in the previous study, our index for a benzenoid ring with atoms A–F, through the permutation operator $\Gamma_i$, takes into account all the contributions corresponding to all possible permutations of the atomic labels in eq. (2)

$$SCI_L = \frac{6!}{32} \sum_{L} \sum_{\mu} \sum_{\sigma} \sum_{\nu} \sum_{\delta} \sum_{\lambda} \sum_{\gamma} \sum_{\pi} \sum_{\sigma'} \Gamma_i \times (PS)_{\mu\nu} (PS)_{\nu\lambda} (PS)_{\lambda\gamma} (PS)_{\gamma\pi} (PS)_{\pi\sigma} (PS)_{\sigma'}$$ \hspace{1cm} (2)

where the index by Giambiagi et al. takes into account just one term, namely the one in which the ordering of labels A,B,C,... corresponds to bond pairing characteristics for the Kekulé structure. Also, their study used the PM3 Hamiltonian, which is nowadays considered somewhat outdated for the size of molecules considered in the present study.

It is important to emphasize that, as in e.g. the PDI index and the approach by Matta et al., electron delocalization is used to quantify the aromaticity. However, there is an important difference. In GPA one is able to consider truly the delocalization of the entire ring, and does not have to rely on lower dimensionality quantities such as diatomic delocalization indices. The advantage is then that GPA allows us to also compute in an efficient and unambiguous way the aromaticity of rings of any size. GPA can equally well be used for the quantification of homoaromaticity and for the study of nonplanar molecules, where NICS can be ambiguous. Moreover, Bultinck et al. already showed in a Mulliken like approach that averaged diatomic bond order indices can yield opposite conclusions when compared with their GPA based index, which considers the entire delocalization over the cyclic structure.

The second approach we are going to use for the same goal of characterizing the aromaticity of individual benzenoid rings in PAH is based on the pioneering study by Polansky and Derflinger which can be regarded as the first attempt to address the problem of the quantitative characterization of molecular aromaticity, quantified through comparison with benzene as reference. Later, in 1980 Carbo et al. introduced the field, now known as Molecular Quantum Similarity (MQS). Inspired by the suggestion of Giambiagi et al., we use this theory to construct a modern day quantification of molecular aromaticity through considering the similarity of a molecule to benzene.

The basic idea of the Polansky approach is close to the traditional chemical understanding of aromaticity according to which the ideal aromatic sextet exists just in the benzene molecule and any fusion of benzenoid rings leading to PAHs results in the deterioration of the cyclic conjugation within the individual benzenoid rings and, consequently, to the reduction of their aromaticity. To characterize this deterioration quantitatively Polansky et al. introduced the index (3) whose values characterize the similarity of the electron density within any particular benzenoid ring of the PAH to the electron density of the benzene itself and proposed to use this index as a measure of the aromaticity of individual benzenoid rings.

$$P_{L,B} = \frac{1}{2N_{L}} \sum_{\mu \neq L} \sum_{\nu \neq L} P_{\mu \nu} P_{\nu \mu}.$$  \hspace{1cm} (3)

Equation (3) shows how the quantification of the aromaticity of a benzenoid ring L is based on the comparison of the fragment density matrix of L, with the density matrix of benzene. $N_{L}$ is the number of $\pi$ electrons involved in the ring considered (6) in the case of benzenoid ring. The reason for including this parameter is to ensure the normalization of the index so as to give the maximum similarity (identity) for the comparison of benzene with itself. In all other cases the values will be smaller than 1 and the more the index deviates from its idealized value 1, the less similar is a given ring L to benzene and, consequently, the smaller will be its aromaticity. This way, a simple Huckel Molecular Orbital program can be used to compute very quickly the necessary similarity measures for all benzenoid rings that will be considered in the present work.

Although the idea of gauging the aromaticity of individual benzenoid rings by the similarity to ideally aromatic benzene is certainly very attractive, the original approach suffers from the fact that it was introduced only at the simple and nowadays outdated HMO level of the theory. It was therefore of interest to attempt at
the generalization of the formula (3) so as to correspond to contemporary computational standards. Such a generalization was proposed in our previous study,

\[ Z_{AB} = \int \rho_A(x,y)\rho_B(x,y) \, dx \, dy. \]  

(4)

The extension of this original index to approach as much as possible the original index by Polansky is relatively straightforward and only requires the detailed specification of two density matrices entering in the formula (4).

Since our aim is to quantify the aromaticity of individual parts (benzenoid rings) in a molecule, we use projected out density matrices for these parts. In the present study, the projection operator for a fragment \( L \) within a molecule is given by:

\[ \Pi_L = \sum_{\nu} \sum_{\mu} S_{\nu \mu} \langle \nu | \mu \rangle \]  

(5)

where \( \nu \) and \( \mu \) are basis functions and \( S \) is the overlap matrix over the basis functions. Application of this projection operator for a fragment \( L \) in molecule A and a fragment \( L' \) in molecule B gives after some manipulation

\[ Z_{LL'} = \sum_{\nu} \sum_{\mu} \langle \Pi_L | \chi_A \rangle \langle \Pi_{L'} | \chi_B \rangle \langle \chi_A | \chi_B \rangle. \]  

(6)

To keep the analogy with the Polansky approach, it is clear that one fragment refers to the benzenoid ring in the PAH, whereas \( L' \) is then the benzenoid fragment (i.e. the \( C_6 \) ring) in isolated benzene. Integrating out the spin in (6) and obtaining the SCF formulae to be computed is then a matter of simple algebra. Although this generalization can indeed be regarded as the close counterpart of the original approach by Polansky et al., the resemblance of the two approaches can be even more emphasized if, instead of comparing the total electron densities of the benzene and the corresponding fragment, one concentrates just on \( \pi \) electrons. In connection with this new approach it is, however, necessary to remind one important aspect. This aspect concerns the fact that the calculation of the NOEL index relies on the molecular alignment since the values of the overlap integrals in equation (6) naturally depend on the mutual position of the molecules or fragments whose electron densities are being compared. Such dependence can sometimes be quite strong, and in order to avoid problems with the optimization of the mutual position and, also, in order to keep as much as possible the parallel with the original Polansky approach, we opt for idealized geometries of the PAHs for which the perfect alignment of the benzenoid rings is possible. This approximation, together with the already mentioned consideration of \( \pi \) electrons only leads to the index which indeed resembles (except for the normalization factor) the original Polansky index.

### Computational Details

The approaches used in this study for addressing the widely discussed issue of the aromaticity of individual benzenoid rings in linear polyacenes from benzene up to heptacene require two kinds of calculations. The first one, used for the calculation of six-center bond indices (SCI) requires first the optimization of the geometries of all studied polyacenes. These calculations were performed using Gaussian 03\(^{*}\) at the B3LYP/6-31G* level of theory. All wavefunctions used correspond to closed shell singlets, including for the larger polyacenes. There have been discussions on the true ground state of the longer polyacenes, yielding different conclusions on whether the true ground state is the closed shell singlet state or a diradical singlet state. For the diradical state results, the SCI results will be reported elsewhere. The resulting wave functions were then used to construct the corresponding density matrices from which the values of multicenter bond indices were calculated and the order of the aromaticity of individual rings established. The numbering of individual rings in the polyacene series is given in Table 1.

As the planar geometry of all the studied molecules allows strict \( \pi-\pi \) separability, the corresponding multicenter bond indices could be calculated not only from total electron densities but also from the \( \pi \) component of the density only.

The second approach we used in this study for the classification of the aromaticity is the one based on the generalization of the original Polansky similarity index to contemporary computational standards. This type of analysis required to run the quantum chemical calculations on the polyacene series for the idealized geometries constructed as simple fused benzenoid rings with the same geometry as that of the benzenoid ring in the optimized benzene molecule. Hydrogen atoms were added with the same C–H bond lengths and angles as in benzene. These calculations were also run at B3LYP/6-31G* level of the theory.

### Results and Discussion

After having specified the necessary technical details of the calculations let us discuss now the conclusions resulting from the calculated indices and let us start first with the scrutiny of the SCI. Table 2 gives the SCI values computed for all benzenoid rings in the set of PAHs, both considering the total density as well as considering only the \( \pi \) component. It is immediately clear from the idempotency relation in eq. (1) that larger values for \( k \) will result in smaller individual terms. As a consequence multicenter bond indices tend to grow smaller for larger \( k \). The results reported in Table 2, however, were obtained in such a way that they can be trusted completely within the number of digits given, and that trends apparent from these numbers are not artifacts. Given the idempotency in eq. (1), there is a simple check to see whether the integrations are still sufficiently accurate. For any \( k \) in eq. (1) the sum of all terms should equal N. If the result is no longer sufficiently close to N, the results should be considered insufficiently accurate.

The first observation from Table 2 is that the values based on solely the \( \pi \) density contribution are very close to the total values. This clearly suggests that the extended cyclic delocalization,
which is assumed to be responsible for the aromaticity, is indeed due mainly to the \( \pi \) electrons. The contribution of the \( \sigma \) backbone is only of marginal importance. Another conclusion which straightforwardly confirms the idea that the ideal conditions for the cyclic delocalization are found in the benzene molecule is also clearly evident from Table 2. The calculated SCI is indeed the highest for the parent benzene molecule, whereas for any of the other rings the SCI value is smaller. This allows one to gauge the aromaticity of individual rings by the deviations of the actual index from the one for the benzene standard. Furthermore, it is clear that the aromaticity in the PAHs decreases on going from outer to inner rings. This order of aromaticity is opposite to what is predicted on the basis of NICS and PDI values but on the other hand agrees completely with the order suggested by the values of the original Polansky similarity index and also with the results of the recent study by Aihara and Hideaki who even claimed that

Table 1. Ring Numbering Used for the Linear Polyacenes.

<table>
<thead>
<tr>
<th>Number</th>
<th>Ring Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
</tr>
<tr>
<td>2</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>3</td>
<td>Anthracene</td>
</tr>
<tr>
<td>4</td>
<td>Tetracene</td>
</tr>
<tr>
<td>5</td>
<td>Pentacene</td>
</tr>
<tr>
<td>6</td>
<td>Hexacene</td>
</tr>
<tr>
<td>7</td>
<td>Heptacene</td>
</tr>
</tbody>
</table>

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NICS are not appropriate indicators of aromaticity in the polyacene series. More extensive comparisons and correlations between the SCI and different aromaticity descriptors were previously reported by Bultinck et al. In order to settle the above discrepancy of various approaches we decided to complement the approach based on the SCI by the second approach in this study, namely the generalized Polansky similarity index. This way it is also possible to see whether the correspondence between our SCI based conclusions and the original conclusions by Polansky et al. could not be due to deficiency of their original HMO-like approach. In the following part the conclusions resulting from the NOEL indices will be discussed.

Table 3 gives the NOEL values for the set of polyacene molecules, including the NOEL index based on the \( \pi \) density alone. One of the advantages of the NOEL approach, as well as the SCI approach, comparing to the HMO approach is that the framework can be included as well.

Inspection of the values summarized in the Table 3 clearly confirms the conclusions resulting from the previous scrutiny of SCI. Both approaches consistently predict the decrease of aromaticity on going from outer to inner rings. This implies that the scale of aromaticity represented by the original Polansky similarity index was indeed realistic and that its generalization to contemporary computational standards does not change the final picture qualitatively. This result is very important since it provides an independent additional evidence for the correctness of the claims of various studies questioning the order of aromaticity based on NICS and PDI values. In this context it is worth mentioning that recent results by the present authors reveal some debatable aspects of the use of PDI indices as aromaticity indices (The SCI index was generalized to the AIM level of theory and corresponding SCI(AIM) values yield the same aromaticity ordering as the SCI and NOEL based ordering obtained in the present study). Results of AIM theory based multicenter aromaticity indices will be reported elsewhere, but they confirm the present SCI findings.

In addition to this primary result, the comparison of both approaches allows one to address also some additional questions related to the issue of benzenoid aromaticity. An example in this respect can be, e.g., the evaluation of the effect of slight variations in the geometry of the individual rings on their aromaticity and to what extent the aromaticity of individual rings is affected by the fusion with one or more benzene ring(s). Such an evaluation can be straightforwardly made by comparing the values of the SCI calculated at the optimized molecular geometries with the same values determined for the idealized geometries used for the calculation of NOEL indices. The corresponding “idealized” values are summarized, again for both \( \sigma \) and \( \pi \) components in Table 4.

From comparison of Tables 2 and 4 we see that the SCI show only minor changes upon geometry optimization. Two effects may be discerned. On the one hand, the outermost rings grow clearly less aromatic upon geometry optimization. This is clear from e.g., the outer ring in pentacene, where the SCI decreases from 0.019 to 0.016. On the other hand, the SCI in the innermost rings show a tendency to loose less in SCI, or to even slightly increase. Again in pentacene this effect is clearly seen for ring III where the SCI grows from 0.013 to 0.014. These results are not very surprising since they correspond to what could be anticipated on the basis of naïve intuitive considerations. Still, the possibility to evaluate the effect of slight geometry variations on the aroma-

### Table 2. B3LYP/6-31G* SCI for each Symmetry Unique Ring in the Polyacenes in Optimized Geometry.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.048 (0.047)</td>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.026 (0.025)</td>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.020 (0.019)</td>
<td>Anthracene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.017 (0.016)</td>
<td>Tetracene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.016 (0.015)</td>
<td>Pentacene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015 (0.014)</td>
<td>Hexacene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015 (0.014)</td>
<td>Heptacene</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Values in brackets are the \( \pi \) contributions to the SCI.

### Table 3. NOEL Values for the PAHs with the Benzenoid Ring of Benzene as Reference.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.082 (6.000)</td>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.404 (5.712)</td>
<td>Naphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.339 (5.644)</td>
<td>Anthracene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.314 (5.617)</td>
<td>Tetracene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.302 (5.605)</td>
<td>Pentacene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.297 (5.600)</td>
<td>Hexacene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.295 (5.598)</td>
<td>Heptacene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in brackets refer to NOEL \( \pi \) components.
ticity of individual benzenoid rings can be useful. It allows one to address some other problems related to the reliability of the proposed aromaticity measures. One of them is, e.g., the mutual compatibility of both SCI and NOEL indices. For this purpose Figure 1 shows the correlation of both indices calculated for idealized molecular geometries and π electrons only.

As it is possible to see, although the correlation is not linear between the SCI and the NOEL index directly, it is indeed extremely tight between log(SCI) and the NOEL index. This implies that they are more or less interchangeable. This establishes that both new indices introduced in the present study, independently of each other yield the same conclusions, using no other information than the density matrices of the involved molecules.

What thus remains to be done is the discussion of the observed discrepancies between the predictions of SCI and NOEL on one side and NICS, PDI and HOMA on the other. Although we do not claim that the origin of these discrepancies is completely clear, some possible reasons can nevertheless be mentioned. For example, in the case of NICS, one possible complication may be due to the fact that the NICS values in the middle of the ring or above a ring center need not be entirely attributed to this specific ring. In other words, the neighboring rings may also have an influence and artificially increase NICS values for inner rings. This phenomenon was in fact also considered by Schleyer et al. who argued, however, that this effect would be rather small and below 10%.20 The same effect was considered also in a recent study by Portella et al., however, who found that in some molecules, the effect of the neighboring rings can be relatively large.29 In the specific case of NICS, for larger polycycles one will always find an increase of aromaticity toward the center of the molecule since NICS reflect the number of ring currents of different size the ring is involved in.59 Another index which partly contradicts the conclusions of this study is the HOMA index. The applicability of this index in the polycyclic series was discussed by Aihara and Hideaki who also suggested that the agreement between HOMA and NICS should be treated with some care.30 The reason for this is that according to NICS, the innermost ring in the polycycles grows more aromatic with growing molecular size, whereas the opposite is found for the HOMA. As a consequence, according to NICS, steadily more aromatic benzenoid rings will be found in the inner rings of a steadily longer polycycl. HOMA as well as the present NOEL and SCI results identify the benzenoid ring in pure benzene as the most aro-

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Correlation between NOEL π and SCI π indices for the different benzenoid rings in the linear polycycles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
matic ring. The PDI index also yield an increase in aromaticity upon going from the outer to the inner ring in a linear polyacene. The present authors have found, however, that an AIM generalization of the SCI index also indicates a decrease in aromaticity upon going from the outer to inner ring in PAH molecules. Detailed results of this study will be published separately. In this context it is worth pointing out that a Mulliken analogue of the PDI index was previously introduced and it was found that for the linear polyacenes, this Mulliken analogue yielded exactly the opposite conclusions than the SCI. We believe that to assess the electron delocalization in a six-membered ring, it is more appropriate to consider the true six center delocalization, rather than an average of two center delocalization indices. An especially intriguing question concerns the different conclusion obtained from the present SCI results with respect to the PM3 results of Giambiagi et al. These authors used a similar methodology to obtain multicenter indices, although considering only one exchange term whereas here all exchange terms are used to derive the multicenter bond expressions. It was, however, found by Bulitnc et al. that the reason for the mentioned discrepancy in the conclusions is due to the use of the PM3 Hamiltonian. This was established from the fact that if the same expressions are used for the multicenter index and the same molecular geometries are used, the PM3 and B3LYP/6-31G* results still point to opposite directions concerning the trend in aromaticity in the linear polyacenes. Clearly, the B3LYP/6-31G* level of calculation supercedes the PM3 level.

Concerning the further comparison between the NOEL and SCI indices on the one hand, and other aromaticity indices like NICS, HOMA etc. it is interesting to note that if one considers the angular polyacenes, starting e.g. with chrysene, the different indices point in the same direction, pointing out the special nature of the linear polyacenes and the difficulties to quantify the aromaticity of the individual benzenoid rings in these molecules. For the linear polyacenes, the NOEL and SCI indices clearly agree in their conclusions with the recent findings of Aihara who convincingly showed that energetic and magnetic indices can be united in the CRE descriptor. NICS have furthermore been shown to be unreliable in quantifying local aromaticity. The HOMA index agrees with the NOEL and SCI indices in that benzene is the most aromatic six-membered ring over all linear polyacenes. HOMA should be treated with care, however, since it is not so easy to link geometry with the \( \pi \) electronic structure since it will also be largely controlled by the \( \sigma \) density. In fact, the D\( \text{ab} \) geometry of benzene is commonly perceived to be mainly a consequence of the \( \sigma \) density rather than the \( \pi \) density. It therefore remains important to continue examining carefully the different local aromaticity descriptors and to know their limitations.

Conclusions

The aromaticity in the linear polyacenes was re-examined using two different techniques. First the polycene structures are composed from benzene fragments in their ideal geometries. For these structures, both a quantum similarity based measure (NOEL) of aromaticity is computed as well as a Generalized Population Analysis based measure (SCI). Both indices point toward a decreasing aromaticity of the benzenoid rings from the outer to the inner rings.