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Multicenter bond indices as a new measure of aromaticity in polycyclic aromatic hydrocarbons[†]

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ABSTRACT: This paper reports the application of the recently proposed formalism known as generalized population analysis (GPA) as a new means for the quantitative characterization of the aromaticity of various benzenoid rings in polycyclic aromatic hydrocarbons (PAHs). The quantity which we propose as a new measure of aromaticity is the so-called six-center bond index. The values of this index characterize the extent of delocalized cyclic bonding in individual benzenoid rings of PAHs and it is shown that the scale of the aromaticity represented by this index closely reflects the intuitive idea according to which the aromaticity of individual rings in PAHs can be gauged by the degree of similarity to benzene itself. In addition, the relation of the newly introduced index of aromaticity to other existing aromaticity measures is discussed. Consistent with the presumed orthogonality of classical and magnetic criteria of aromaticity, the classifications based on these two classes of aromaticity measures were found usually to be opposite.

Supplementary electronic material for this paper is available in Wiley Interscience at http://www.interscience.wiley.com/jpages/0894-3230/suppmat/

KEYWORDS: multicenter bond indices; polycyclic aromatic hydrocarbons; aromaticity; generalized population analysis

INTRODUCTION

Concepts are a vital and inescapable part of human thought and their formulation represents one of the most important steps in the buildup of any science. Unfortunately, despite their crucial importance, not all concepts are always strictly defined. Such a situation is often typical of organic chemistry, where a wealth of ill-defined but nevertheless extremely fruitful concepts have been introduced and widely used. An example is the concept of aromaticity. Although it is a very often used concept, the applicability of which has considerably exceeded its originally intended scope,[1–10] the definition or quantification of aromatic character remains a matter of controversy[11] with even proposals to ban the concept from the literature as a whole.[12–14] Nevertheless, despite such rather negative proposals, the interest in the study of aromaticity does not seem to cease and attempts are still being reported in which the authors analyze the very meaning of the concept of aromaticity and propose some new, presumably more general and more universal, aromaticity measures and indices.[15–32] The contemporary situation with the issue of aromaticity has recently been reviewed in a special issue of *Chemical Reviews*.[33]

The main problem which underlies all the existing difficulties and problems with aromaticity is the semantic richness of this term, which evidently covers a much broader scope of properties and situations than can be characterized by any single index. As a consequence, there are many ways to quantify the degree of aromaticity through different aspects of molecular structure and behavior. The existing criteria of aromaticity can be divided into several basic groups according to the molecular property from which they are derived. In this way, it is possible to distinguish between structural criteria based on the tendency of aromatic molecules to equalize the bond lengths in the cyclic systems;[6,17,18,21] energetic criteria, based on the increased stability of aromatic systems;[19,20] and magnetic criteria which reflect the special magnetic properties of aromatic systems.[27,28] Finally, another typical feature of aromatic molecules is their specific chemical reactivity expressed as their tendency to undergo substitution rather than addition reactions. This complexity of the phenomenon of aromaticity has found its reflection in the several previous studies,[34–36] in which the authors concluded that aromaticity is a multi-dimensional phenomenon with at least two basic components. These two components, identified with 'classical' and 'magnetic' aromaticity, were found

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to be essentially divergent so that the correlation with a single aromaticity index can usually be expected only within a class of closely structurally related molecules. This divergence has become known as the orthogonality of the ‘classical’ and ‘magnetic’ aromaticity measures.

Our aim in this study was to follow up the previous efforts in which various aromaticity measures have been introduced and to propose a new index which is close to how the concept of aromaticity is understood by chemists. The basic idea of our approach was inspired by the study by Polansky and Derflinger,[30] who explored the old idea of Clar[37] that individual benzenoid rings in polycyclic aromatic hydrocarbons (PAHs) can be regarded as local benzene-like regions, and proposed to characterize the aromaticity of these rings in PAHs by the ‘similarity’ to benzene itself. This similarity was characterized by the value of a certain index derived from the charge-density bond order matrix. This approach was, however, formulated only at the level of the nowadays outdated HMO theory and its generalization to more sophisticated levels of the theory is not straightforward. In order to remedy this drawback, we propose another, more easily calculatable, index, which we believe characterizes the similarity of benzene-like regions in PAHs to benzene similarly as the original index of Polansky and Derflinger. The quantity we use is the so-called six-center bond index (SCI), whose values characterize the extent of cyclic delocalized conjugation in a given benzene-like region. As will be shown, there is indeed a close correlation between the values of the HMO similarity indices of Polansky and Derflinger and the values of the corresponding six-center bond indices, and we propose them therefore as a new aromaticity index. In addition to demonstrating the applicability of this new index of aromaticity in a broad series of PAHs, we also evaluated the usefulness of this index by comparison with other widely used aromaticity measures such as the well-known structure-based aromaticity index the harmonic oscillator model of aromaticity (HOMA) index[17,18] or with aromaticity measures that rely on the special magnetic properties of aromatic molecules such as nucleus-independent chemical shifts (NICS).[28] In addition, a comparison was also made with another recently proposed aromaticity index, namely the PDI index introduced and used by Poater *et al.*[29]

GENERALIZED POPULATION ANALYSIS

The term generalized population analysis is a generic name for the whole family of approaches based on the partitioning of the identity (1) for various values of k:

$$\frac{Tr(PS)^k}{2^{k-1}} = N = \sum_A \Delta_A^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \cdots \sum_{A<B<C\ldots K} \Delta_{ABC\ldots K}^{(k)} \tag{1}$$

In this equation, which holds at the Hartree–Fock (and formally also Kohn–Sham) level of the theory, P and S denote charge-bond order and overlap matrices, respectively. Although this analysis was originally introduced only on an heuristic basis,[38] Carbó-Dorca and co-workers have recently shown that this partitioning can also be obtained directly from higher order electron densities through the use of projection operators.[39–41] The notation $\Delta_{ABC\ldots K}^{(k)}$ refers to the terms holding atoms $ABC\ldots K$. As such, $\Delta_A^{(k)}$ contains the monoatomic terms, $\Delta_{AB}^{(k)}$ diatomic terms, etc. The usefulness of this approach arises from the fact that individual terms resulting from the partitioning (1) for various values of k can be interpreted in terms of quantities and concepts used by chemists to think of molecules and their structures. Thus, for example, the monoatomic terms resulting from the partitioning (1) for $k = 1$ are identical with Mulliken atomic charges.[42] Similarly, the two-center terms resulting from the partitioning (1) for $k = 2$ can be identified with the so-called Wiberg indices,[43] generalized to non-orthogonal basis sets by Giambiagi *et al.*[44] and Mayer,[45,46] which are known to represent the theoretical counterpart of the classical concept of bond multiplicity. The ability to mimic the presence of the bonding interactions within the molecules is also retained for the terms resulting from the partitioning of the identity (1) for higher values of k and, for example, the three-center terms $\Delta_{ABC}^{(3)}$ have been proposed as the so-called three-center bond indices, for the detection of the presence of three-center bonding in molecules.[47–52] In view of the success of these indices for the description of non-classical three-center bonding, we propose to extend the same approach for the description of cyclic delocalized bonding extended over even more centers. In particular, we are interested in cyclic delocalized six-center bonding, which can be expected to be present in individual benzenoid rings in PAHs and in the following part the applicability of the corresponding six-center bond indices as new measures of aromaticity will be discussed. In this connection, it is fair to say, however, that the idea of using the six-center bond indices for the classification of aromaticity was first proposed by Giambiagi and co-workers,[31,53] but our approach is nevertheless slightly different. This difference arises from the definition of the bond index in Eqn (1) which is slightly different from the one proposed originally.[47–50] In order to make this difference clearer, it is useful to refer first to the original definition of multicenter bond index:

$$I_{ABC\ldots K} = \sum_{\alpha\in A}\sum_{\beta\in B}\sum_{\gamma\in C}\cdots\sum_{\kappa\in K}(PS)_{\alpha\beta}(PS)_{\beta\gamma}(PS)_{\gamma\delta}\ldots(PS)_{\kappa\alpha} \tag{2}$$

In this notation, the Greek subscripts refer to the basis functions and summations extend only over the range of basis functions centered on a certain atom A, B, $\ldots K$. The value of this index depends on the order of the labels of individual atoms A, B, C, . . . , etc and the bond indices for different permutations of the labels A, B, C, . . . may generally be different. Giambiagi *et al*. avoided the problem of ambiguity of these bond indices by considering only one term with the numbering of the atoms that reflects the bonding interactions typical for Kekulé structures of individual six-membered rings. As, however, the description of even benzene itself requires one to consider also other types of valence bond (VB) structures, the restriction to only Kekulé structures can be in some respect insufficient. This possible drawback, which ignores the contributions of other VB structures, can be straightforwardly remedied by taking into account all the terms corresponding to different permutations of atomic labels as is the case of indices defined according to Eqn (1). This will be shown to have important consequences on the resulting conclusions of studies on aromaticity.

COMPUTATIONAL METHODS

The molecules used in the present study include benzene and the PAHs shown in Table 1. Roman numbers refer to the different symmetry-unique rings in the molecules. The studied molecules include a fairly large subset of the molecules scrutinized by Polansky and Derflinger.[30] The geometries of all molecules were optimized using the Gaussian 03 program[54] with the B3LYPdensity functional[55,56] and the 6–31G* basis set.

The multicenter bond indices were calculated according to Eqn (1) using our program GMA. This program calculates the overlap matrix over the basis functions and uses the charge and bond order matrix from the Gaussian03 formatted checkpoint file to compute multicenter indices ranging from one up to 10 centers.

RESULTS AND DISCUSSION

The calculated values for the six-center bond indices for individual rings of the studied set of PAHs are summarized in Table 2. The Roman numbers refer to the symmetry-unique rings in the molecules in Table 1.

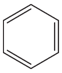
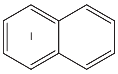
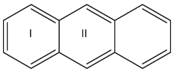
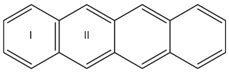
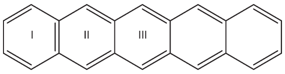
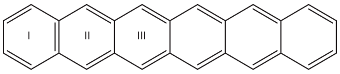
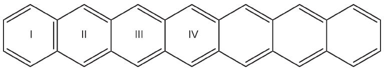
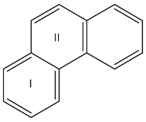
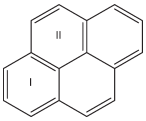
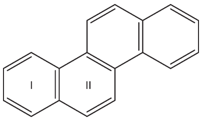
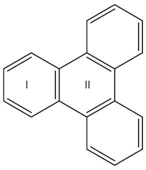
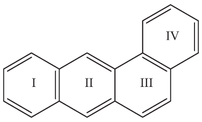
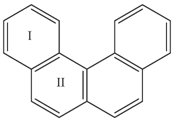
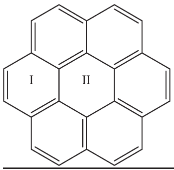
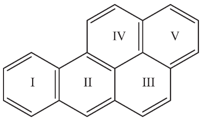
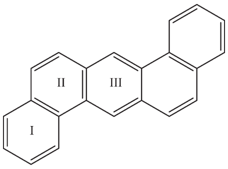
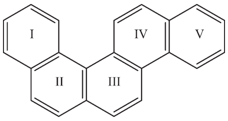
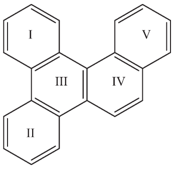
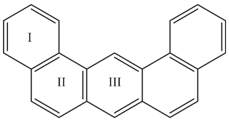
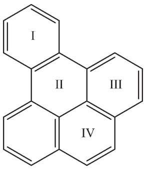
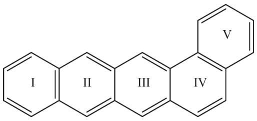
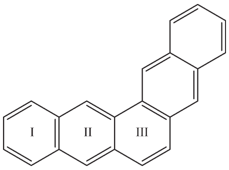
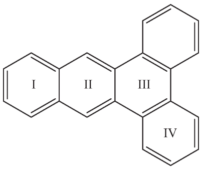
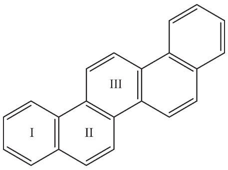
In order to demonstrate the suitability of the calculated multicenter bond indices to characterize the degree of aromaticity of individual rings in the studied set of PAHs, we first compared the calculated values with the set of similarity indices taken for the same set of molecules from the study by Polansky and Derflinger.[30] This set comprises 44 benzenoid rings from 16 molecules. The correlation, based on comparison of Hückel MO (HMO) similarity indices with the six-center bond indices calculated first at the same (HMO) level of theory, is displayed in Fig. 1. This shows that the correlation is extremely tight and although the correlation is not linear, there is in fact strict 1:1 correspondence between both set of indices.

This result is very interesting since it implies that original Polansky similarity indices, which are difficult to generalize to more sophisticated levels of the theory, can safely be replaced by the six-center indices, whose calculation is much more straightforward. An example of such a correlation which, instead of being based on HMO six-center bond indices, is derived from the same indices calculated at the B3LYP/6–31G* level of theory, is given in Fig. 2. As can be seen, the overall quality of the correlation is slightly worse than in the previous case but the calculated correlation coefficient is still considerably high. The fact that larger deviations between both types of indices is observed in this case can apparently be attributed to the fact that HMO bond indices are in some respects idealized as they are calculated from the HMO density matrix assuming the equivalence of all resonance integrals between neighboring atoms, which, in a sense, is equivalent to assuming the same idealized geometry for individual rings. This, of course, is not true in real molecules and the actual values of more realistic B3LYP/6–31G* indices can be affected by the slight differences in optimized CC bond lengths in individual molecules.

Because of the close relation of our six-center bond indices to bond indices used by Giambiagi *et al*.,[31] it is also interesting to compare the mutual correlation between both types of indices. It should be noted that whereas our indices (SCI) are calculated using all the terms arising from all possible permutations of atomic labels, the Giambiagi *et al*. index takes into account just one term, namely that corresponding to bonding interactions reflected in the Kekulé structures. For this reason, we propose to call this index the Kekulé six-center index (KSCI). We calculated the B3LYP/6–31G* KSCI values for all rings in all molecules and the resulting correlation between the SCI and KSCI indices is shown in Fig. 3.

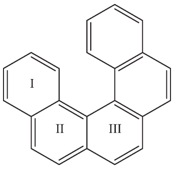
As can be seen, the correlation is very tight, which implies that the dominant contribution to the structure of PAHs indeed comes from the Kekulé structures. In this connection, it is nevertheless necessary to note that such a tight correlation was observed only if the compared SCI and KSCI values were calculated at the same B3LYP/6–31G* level of theory. If, instead, the comparison was made with the original KSCI values calculated by Giambiagi *et al*.,[31] some clear discrepancies are straightforwardly evident. This concerns, for example, the general trend of aromaticity of individual rings in a series of linearly annelated polyacenes (**1**–**7** in Table 1). Hence whereas the decrease in aromaticity on going from outer to inner rings is expected on the basis of both the Polansky index and SCI, the trend in the same series based on semiempirical KSCI values of Giambiagi *et al*. is completely the opposite. Such a discrepancy between the predictions of various approaches is not at all exceptional; in fact, the aromaticity of individual rings in polyacenes is a widely discussed issue, with various methods giving different results. An example of an approach whose conclusions are at variance with the

Table 1. Molecules contained in the studied set of PAHs: Roman numbers refer to the different symmetry-unique rings in the molecules

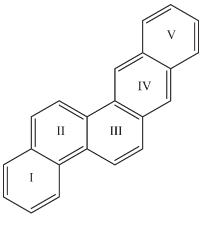
	**1** Benzene
	**2** Naphthalene
	**3** Anthracene
	**4** Tetracene
	**5** Pentacene
	**6** Hexacene
	**7** Heptacene
	**8** Phenanthrene
	**9** Pyrene
	**10** Chrysene
	**11** Triphenylene
	**12** 1,2-Tetraphene
	**13** 3,4-Benzophenanthrene
	**14** Coronene
	**15** 3,4-Benzopyrene
	**16** 1,2,5,6-Dibenzanthracene
	**17** 5,6-Benzochrysene
	**18** 1,2,3,4-Dibenzophenanthrene
	**19** 1,2,7,8-Dibenzanthracene
	**20** 1,2-Benzopyrene
	**21** 1,2-Benzotetracene
	**22** Pentaphene
	**23** 1,2,3,4-Dibenzanthracene
	**24** Picene

(*Continues*)

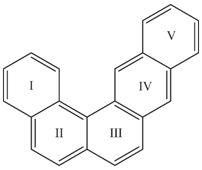
Table 1. (Continued)



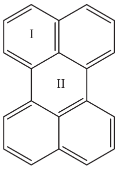
25 3,4,5,6-Dibenzophenanthrene



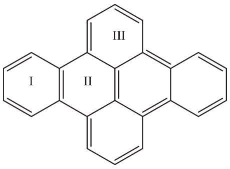
26 2,3,7,8-Dibenzophenanthrene



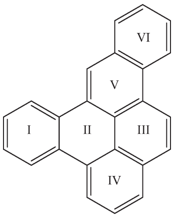
27 2,3,5,6-Dibenzophenanthrene



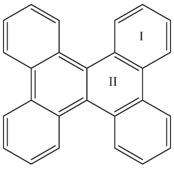
28 Perylene



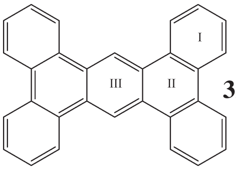
29 1,2-6,7-Dibenzopyrene



30 1,2-4,5-Dibenzopyrene



31 1,2-7,8-Dibenzochrysene



32 1,2-3,4-5,6-7,8-Tetrabenzoanthracene

Table 2. Six-center bond indices calculated for the different rings (Roman numbers, ring numbering as indicated in Table 1) in all molecules (B3LYP/6-31G*)

Compound	I	II	III	IV	V	VI
1	0.0484					
2	0.0263					
3	0.0199	0.0189				
4	0.0172	0.0159				
5	0.0159	0.0143	0.0141			
6	0.0152	0.0135	0.0131			
7	0.0148	0.0131	0.0125	0.0122		
8	0.0314	0.0119				
9	0.0243	0.0123				
10	0.0298	0.0149				
11	0.0348	0.0051				
12	0.0222	0.0205	0.0086	0.0332		
13	0.0298	0.0149				
14	0.0164	0.0078				
15	0.0264	0.0129	0.0094	0.0156	0.0240	
16	0.0324	0.0097	0.0233			
17	0.0304	0.0137	0.0186	0.0142	0.0299	
18	0.0336	0.0336	0.0066	0.0169	0.0291	
19	0.0324	0.0097	0.0230			
20	0.0350	0.0054	0.0265	0.0121		
21	0.0184	0.0169	0.0166	0.0073	0.0338	
22	0.0232	0.0207	0.0063			
23	0.0230	0.0219	0.0037	0.0357		
24	0.0303	0.0139	0.0186			
25	0.0304	0.0133	0.0186			
26	0.0290	0.0161	0.0109	0.0201	0.0214	
27	0.0284	0.0162	0.0108	0.0197	0.0216	
28	0.0237	0.0033				
29	0.0349	0.0053	0.0290			
30	0.0358	0.0041	0.0152	0.0257	0.0138	0.0271
31	0.0329	0.0078				
32	0.0351	0.0043	0.0273			

order of aromaticity based on the KSCI values of Giambiagi *et al*. is, e.g., the study by Anusooya *et al*.,[57] who also found that the aromaticity of individual rings should decrease on going from outer to inner rings. In order to reveal the origin of this variance between predictions of various methods, we also calculated the SCI and KSCI indices using semiempirical methods as in the study of Giambiagi *et al*.[31] The indices were calculated using the PM3 density matrix for both B3LYP/6–31G* and PM3 optimized geometries. Table 3 shows as an example the indices calculated at different levels of theory and different geometries for pentacene.

Let us attempt now to discuss the conclusions that can be deduced from Table 3. First, what can be seen from the calculated values is that although the table reflects the effect of the variation of two different factors, namely of the molecular geometry and the quality of the density matrix, the general trend in the aromaticity of individual rings is predominantly determined only by the level of the theory used to generate the density matrix. Thus, for example, whereas both SCI and KSCI values calculated at the B3LYP/6–31* level clearly suggest a decrease in aromaticity on going from outer to inner rings, the trend

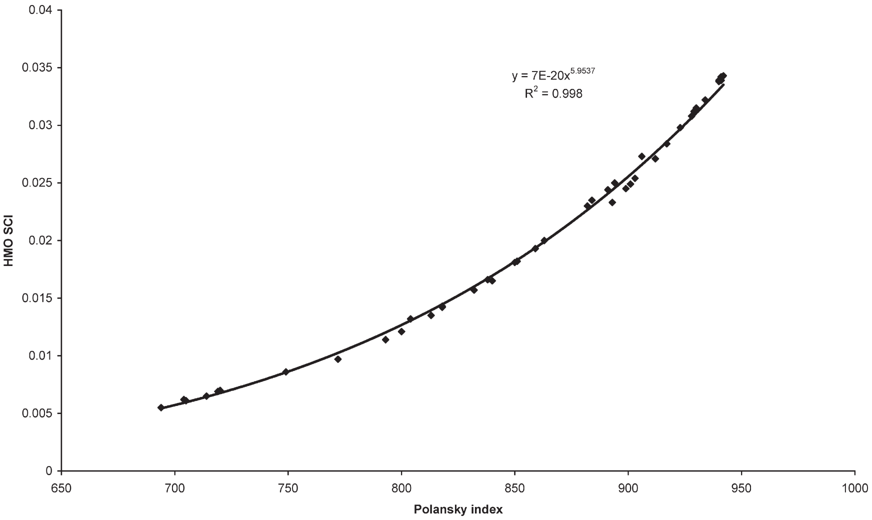


Figure 1. Correlation between HMO-based six-center index (HMO SCI) and the Polansky HMO-based similarity index of individual benzenoid rings to benzene

of the aromaticity in the same series calculated at the PM3 level is completely the opposite irrespective of the actual molecular geometry used. This result is very interesting and important since it suggests that one must be very careful when comparing various aromaticity measures and indices, especially if they have not been determined at the same or a comparable level of the theory.

Correlation between aromaticity indices

After having demonstrated that the scale of aromaticity characterized by the extent of the cyclic delocalization as gauged by the values of six-center bond indices is closely related to Polansky similarity indices, let us attempt now to compare the new proposed aromaticity index with some other previously reported aromaticity measures.

One of the most often used approaches to introduce the scale of aromaticity is the structural criterion based on the equalization of bond lengths in the aromatic system. The most widespread approach of this type is known as the harmonic oscillator model of aromaticity (HOMA).[17,18] HOMA values can be easily calculated from the optimized molecular geometries using the equation

$$\mathrm{HOMA} = 1 - \frac{\alpha}{N}\sum_{i=1}^{N}(R_0 - R_i)^2 \tag{3}$$

where $\alpha = 257.7$ and is constant for the type of chemical bond involved, N is the number of bonds (six in the present case) and R_0 is the ideal bond length. R_0 is set equal to 1.388 Å. For all molecules in the present set, HOMA values were calculated. The correlation between the SCI and HOMA data reveals that the agreement is best for a linear relationship between the HOMA values

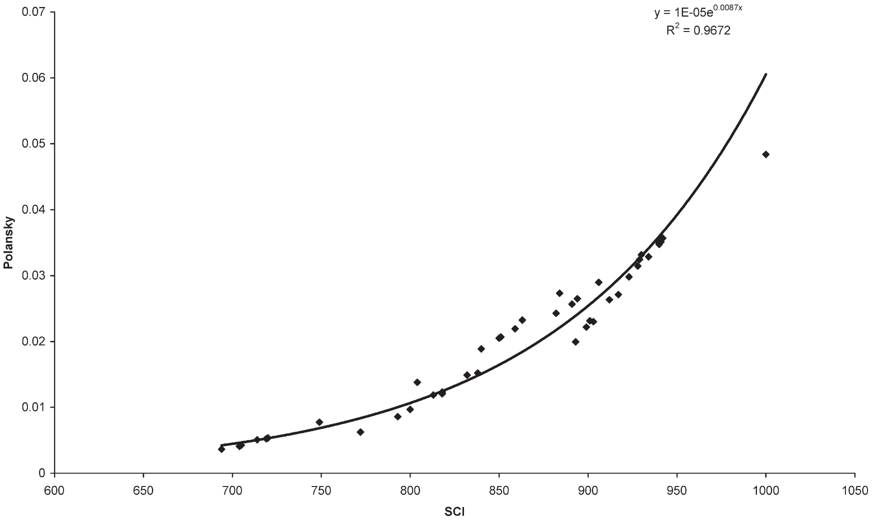


Figure 2. Correlation between B3LYP/6–31G* six-center index (SCI) and the Polansky HMO-based similarity index

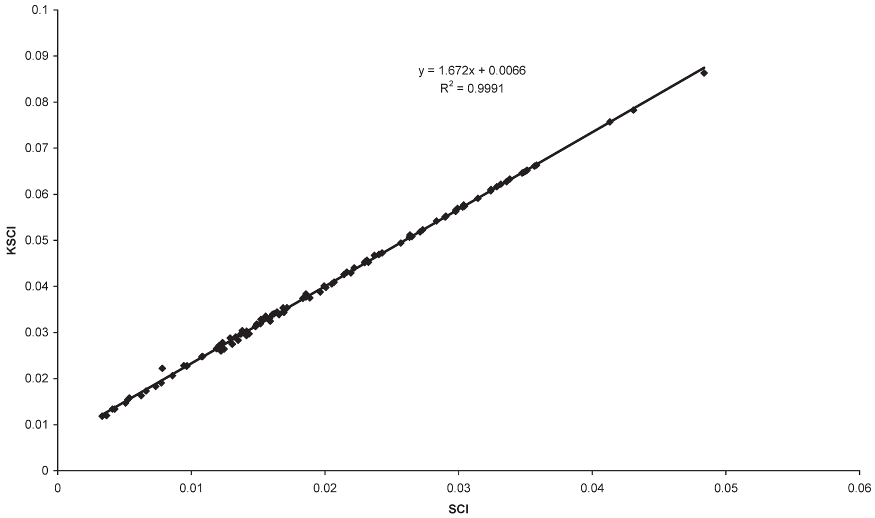


Figure 3. Correlation between SCI and KSCI values calculated at the B3LYP/6–31G* level

Table 3. SCI and KSCI values calculated for pentacene at different levels of theory for different charge and bond order matrices and different geometries

Index	Density matrix	Geometry	Ring I	Ring II	Ring III
SCI	B3LYP/6–31G*	B3LYP/6–31G*	0.01585	0.01433	0.01413
KSCI	B3LYP/6–31G*	B3LYP/6–31G*	0.03310	0.02975	0.02937
SCI	PM3	B3LYP/6–31G*	0.00426	0.00564	0.00625
KSCI	PM3	B3LYP/6–31G*	0.00110	0.01547	0.01749
SCI	PM3	PM3	0.00369	0.00567	0.00694
KSCI	PM3	PM3	0.00932	0.01547	0.01956

and the logarithm SCI. Graphical inspection of the correlation shown in Fig. 4 reveals again that in general there is fair agreement but that there are nevertheless several outliers that strongly affect the quality of the correlations.

The three most notable outliers, with negative HOMA values and SCI values of 0.00776, 0.01333 and 0.01858, correspond to molecule **31**, ring II, and molecule **25**, rings II and III, respectively. In order to elucidate the factors responsible for the existence of these outliers, it is

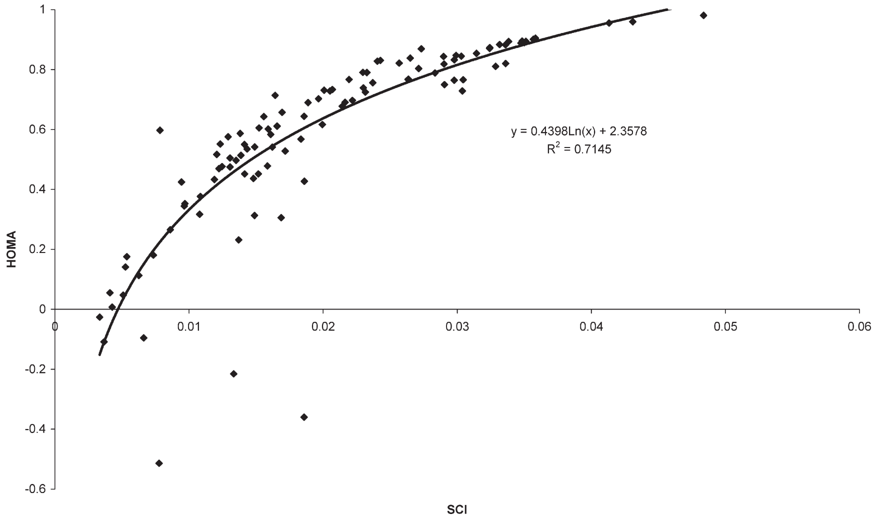


Figure 4. Correlation between HOMA indices and six-center bond indices for all benzenoid rings in the studied molecules (B3LYP/6–31G*)

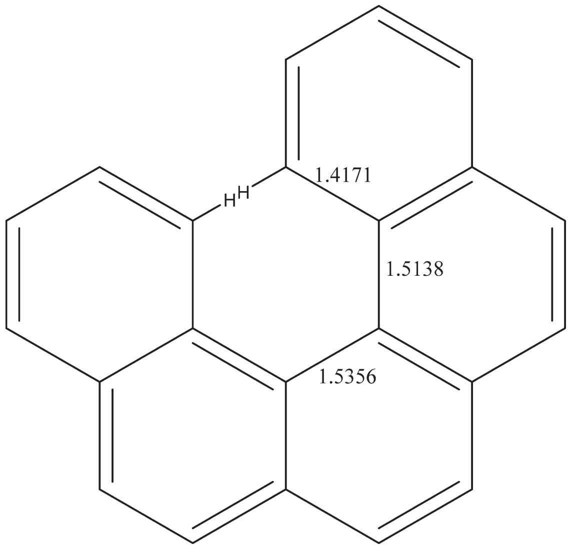


Figure 5. Structure of molecule **25** with bond lengths for different deviating C—C bonds. Hydrogen atoms responsible for steric hindrance are also shown

useful to look in closer detail at the geometric structure of the corresponding molecules. Such an inspection shows these outliers really possess some C—C bonds with lengths that deviate strongly from the reference value of 1.388 Å. An example of such system is molecule **25**, in which the dramatic increase in the bond lengths of two particular C—C bonds evidently comes from the strong steric strain from the closeness of two H atoms (Fig. 5).

Closely related to the HOMA index is the approach which relies on the supposed existence of a linear relationship between bond lengths and bond orders.[58] Such a type of index has also been proposed in the literature,[59,60] but systematic applications to broader set of PAHs are scarce.[61,62] For this reason, we also made a comparison with a new index of this type which we propose to call BOIA (bond order index of aromaticity). This index, defined by Eqn (4), requires the calculation of the sum of the quadratic differences between the bond order between each pair of adjacent atoms in the considered ring (B_i) and that in benzene $B_{C_6H_6}$.

$$\mathrm{BOIA} = 1 - \frac{1}{6}\sum_{i=1}^{6}\left(B_{C_6H_6} - B_i\right)^2 \qquad (4)$$

The B3LYP/6–31G* bond orders (two-center bond indices) for benzene and all other benzenoid rings in the studied molecules were calculated from Eqn (1) and the BOIA values were subsequently calculated according to Eqn (4). Intuitively, one can suppose that there should be a linear correlation between the HOMA values and BOIA values and the existence of such a relationship is indeed demonstrated in Fig. 6.

As can be seen, the correlation is in general satisfactory, but nevertheless one can again observe several outliers and closer inspection shows that they are the same outliers as reported above in the discussion of the correlation between the HOMA index and SCI. In these molecules the bond order–HOMA linear relationship breaks down, whereas on the whole this supposed relationship seems to be justified.

When considering the six-center bond index, there is a fair correlation between the SCI and BOIA values with a

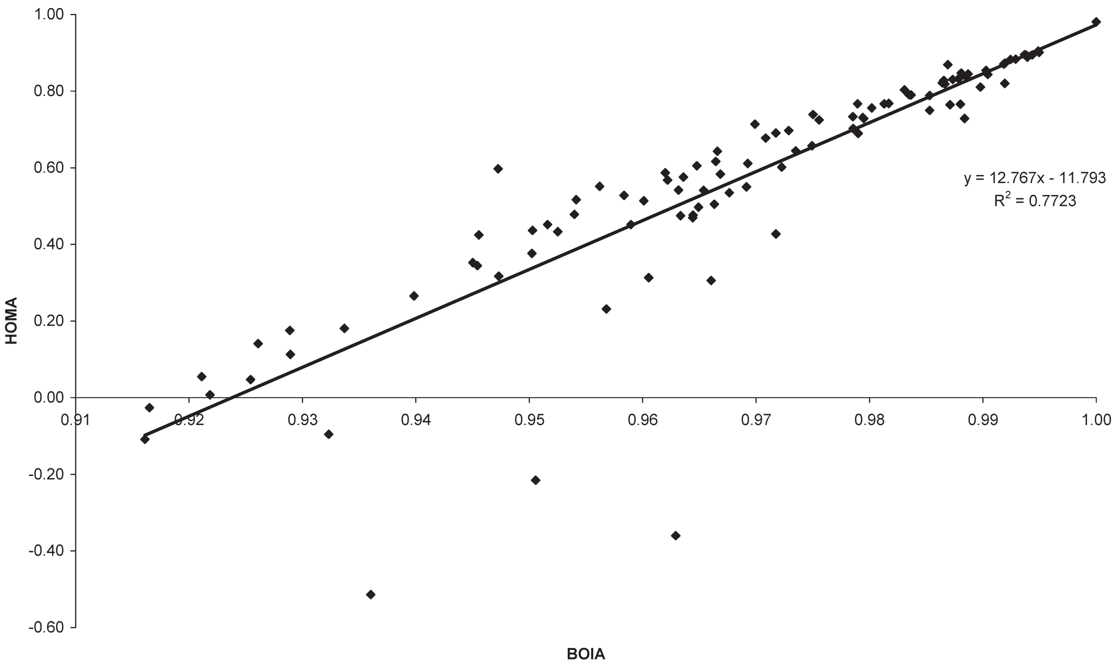


Figure 6. Correlation between HOMA and BOIA values over all benzenoid rings in the molecular set

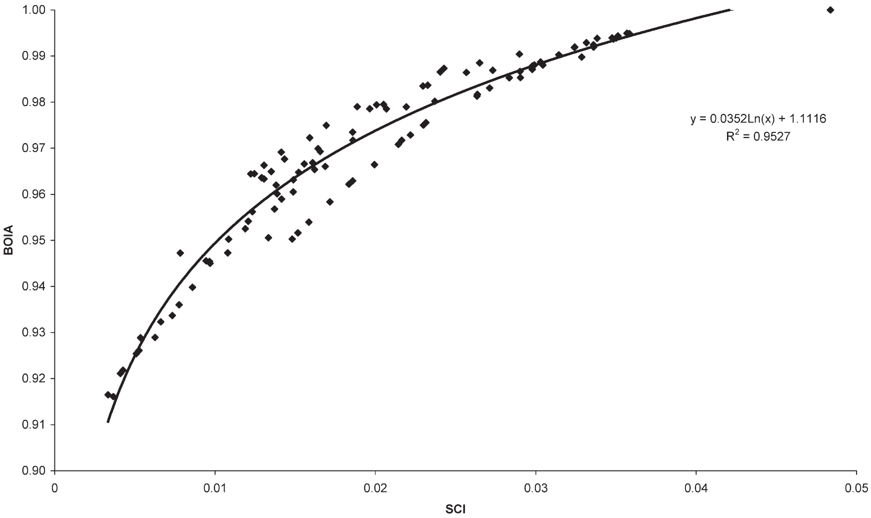


Figure 7. Regression between GPA six-center bond indices and BOIA values for the molecular set, calculated using B3LYP/6–31G*

correlation coefficient of 95% for the regression equation $\mathrm{BOIA} = 0.0351\ln(\mathrm{SCI}) + 1.1113$. The regression between SCI and BOIA values is shown in Fig. 7.

It is interesting that the existence of the outliers detected in the correlation of HOMA and BOIA values is not so dramatic in this case and, although clear deviations from the regression line can be seen also in Fig. 7, their importance is considerably reduced.

Another relatively recent aromaticity scale was introduced by Poater *et al.*,[29] who proposed the so-called PDI values defined as the average of *para*-delocalization indices introduced some time ago by Bader *et al.*[63] within the framework of AIM theory.[64] Delocalization indices δ_{AB} between two atoms A and B are defined as

$$\delta_{AB} = F_{AB} + F_{BA} \tag{5}$$

with

$$F_{AB} = 2\sum_{i}^{occ}\sum_{j}^{occ}\langle i|j\rangle_A\langle j|i\rangle_B \tag{6}$$

where the overlap integrals are calculated over Bader's atomic domains of atoms A and B involved. PDIs are then calculated as the average of the delocalization indices between every set of two carbon atoms in the *para* position. Poater *et al.* reported values for different PAHs, but unfortunately the set of molecules used in their study is too small to assess the correlation with aromaticity indices for wider sets of data. In order to remedy this drawback, we propose to introduce an approximation for the calculation of PDI indices which is based on replacing the original delocalization indices by their counterparts calculated using the philosophy of GPA. Within this approach, the calculated delocalization indices are identical with two-center bond indices derived from the partitioning of Eqn (1) for $k = 2$:

$$F_{AB} = 2\sum_{\alpha\in A}\sum_{\beta\in B}(PS)_{\alpha\beta}(PS)_{\beta\alpha} \tag{7}$$

These indices can be calculated very quickly for any pair of *para*-positioned carbon atoms, and by taking the average of these three indices, it was possible to calculate the 'approximate' PDI values for the whole set of molecules studied here. These indices will henceforth be called the average two-center indices (ATI). For the set of PDI data available in the paper by Poater *et al.*,[29] we examined the agreement between ATI and PDI values, and found that the trends are the same, so it is safe to consider ATI values as a proper alternative to PDI values. In view of this result, we subsequently tried to correlate the ATI values, which could easily be calculated for the whole wide series of molecules studied in this study, with the corresponding SCI values. The resulting correlation is shown in Fig. 8.

The correlation seems to be fairly good, but again some caution is necessary. Thus, e.g., if we consider again the linear polyacenes as an example, both PDI and ATI values suggest an increase in aromaticity on going from outer to inner rings. This order is, however, opposite to what is suggested by the SCI values (and also the Polansky similarity index), so that the predictions of both methods are in this case evidently incompatible. As an example, HF/6–31G* PDI[29] and B3LYP/6–31G* ATI and SCI values for the tetracene molecule are reported in Table 4.

The existence of such a serious discrepancy between the predictions of these two approaches is very important since it suggests that one of them is apparently less reliable than the other, and because the trend of SCI

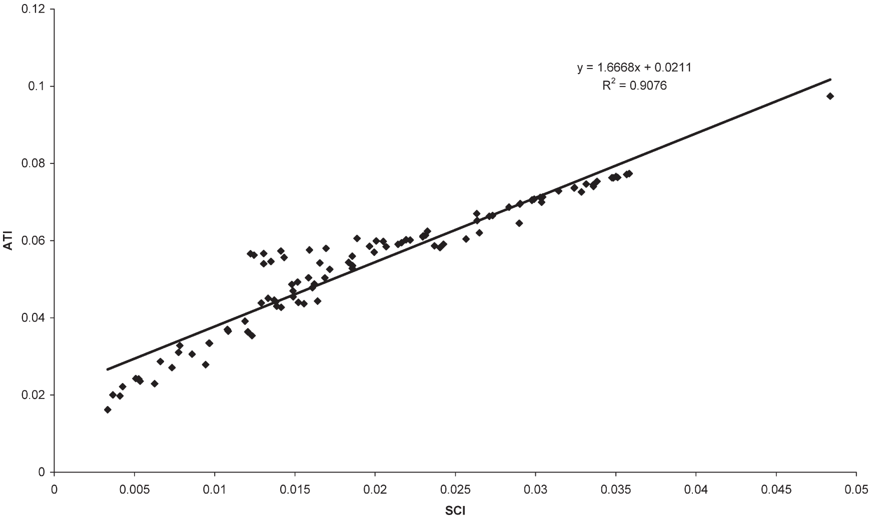


Figure 8. Correlation between B3LYP/6–31G* SCI and ATI values for the entire molecular set

Table 4. SCI, ATI and PDI[29] values for rings I and II in tetracene

Index	Ring I	Ring II
SCI	0.0172	0.0159
ATI	0.0526	0.0576
PDI	0.055	0.062

values corresponds to the chemically justified order of aromaticity measured by the Polansky index, we prefer the SCI as more reliable. Another aspect which independently questions the applicability of PDI as a universal aromaticity measure concerns the extension of this approach to five-membered rings. In this case, there is only one pair of atoms between which the PDI (or ATI) can be calculated and averaging, which could reflect the cyclic delocalized bonding in the ring, is not possible.

As most of the above correlations involved only the indices that belong to the family of structure-based aromaticity measures, it was of interest to see how the quality of the correlations will be affected when other, magnetic criteria of aromaticity are considered. As an example of such a magnetic-based aromaticity index, we chose the so-called NICS index introduced by Schleyer *et al.*[28] In order to be able to include the whole set of studied molecules and to maintain the maximum compatibility with the other correlations, all NICS values were recalculated at the B3LYP/6–31G* level of theory. The results of the correlations of NICS with the whole set of scrutinized aromaticity indices and also of all other crossed correlations are summarized in Table 5. All calculated data for the entire molecular sets are available as Supplementary material in Wiley Interscience.

As can be seen from Table 5, whereas all the cross-correlations between individual structure-based aromaticity indices are generally fairly satisfactory, the correlation with NICS values is in all cases much worse and in fact in some cases there is no correlation at all. This result is very important since it nicely corresponds with the results of previous studies,[34–36] in which the statistical analysis of a wide range of various aromaticity indices resulted in the conclusion that aromaticity is a multidimensional phenomenon with at least two mutually orthogonal principal components. One of these

Table 5. Linear correlation coefficients (R^2) for the correlation of six-centered bond indices with different other aromaticity indices[a]

	SCI	KSCI	ATI	HOMA	BOIA	NICS	Polansky
SCI	1.00	0.99	0.91	0.65 (0.71)	0.86 (0.95)	0.31	0.93
KSCI		1.00	0.90	0.66	0.86	0.30	0.93
ATI			1.00	0.66	0.92	0.55	0.94
HOMA				1.00	0.77	0.39	0.83
BOIA					1.00	0.60	0.92
NICS						1.00	0.64
Polansky							1.00

[a] SCI = six-center bond index from GPA, KSCI are ring indices, ATI are *para*-delocalization indices using two-center bond indices, HOMA are harmonic oscillator model of aromaticity values, BOIA are bond order indices of aromaticity, NICS are nucleus-independent chemical shifts and Polansky are the HMO similarity indices. Values in parentheses refer to correlations of the type $y = a \ln x + b$, where a and b are regression constants and y and x are the two sets of aromaticity indices involved.

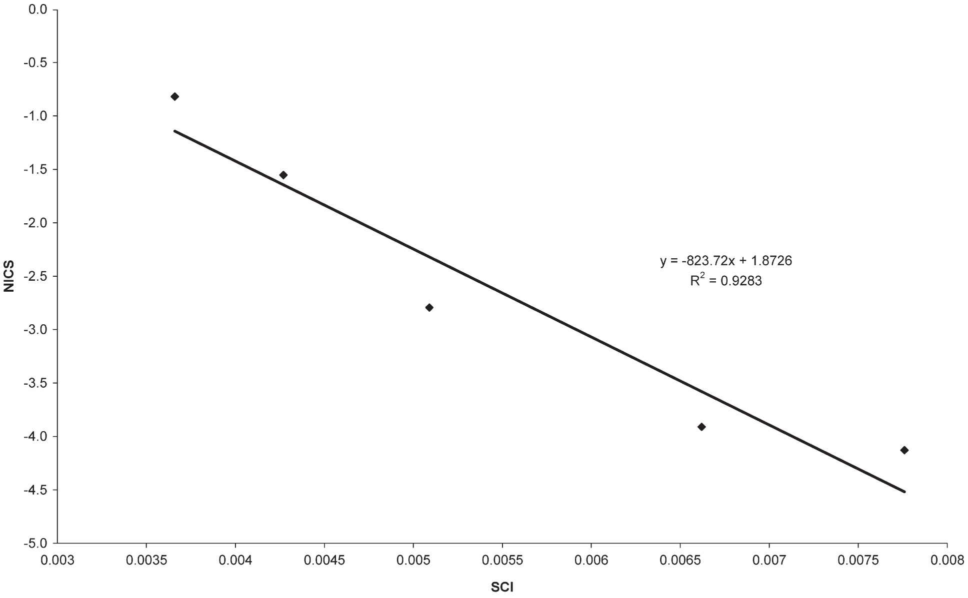


Figure 9. Correlation between NICS and SCI values for a set of five benzenoid rings of triphenylene-like molecules

components was identified with 'classical' aromaticity, which is well characterized by various energetic and structural criteria, and the other by magnetic criteria. The absence of reasonable correlations between these two types of indices as reported in Table 5 thus straightforwardly confirms the assumed orthogonality of these two types of aromaticity measures. The apparent incompatibility of magnetic and structural aromaticity measures, anticipated on the basis of orthogonality of the corresponding aromaticity measures, can again be demonstrated by the discrepancy between the general trends in the aromaticity of individual benzenoid rings in linear polyacenes. Thus, for example, whereas the SCI and Polansky values suggest a decrease in aromaticity on going from outer to inner rings, the classification based on the NICS values is just the opposite. The same opposite order of aromaticity was also reported by Steiner and Fowler[65,66] using another magnetic criterion, namely the paramagnetic ring currents, but in view of the anticipated orthogonality of structural and magnetic criteria of aromaticity this result is not surprising.

In this connection it is necessary to mention, however, studies[67,68] in which the authors reported the existence of a linear correlation between structural and magnetic aromaticity indices so that the orthogonality of these indices was questioned. This would certainly be a very

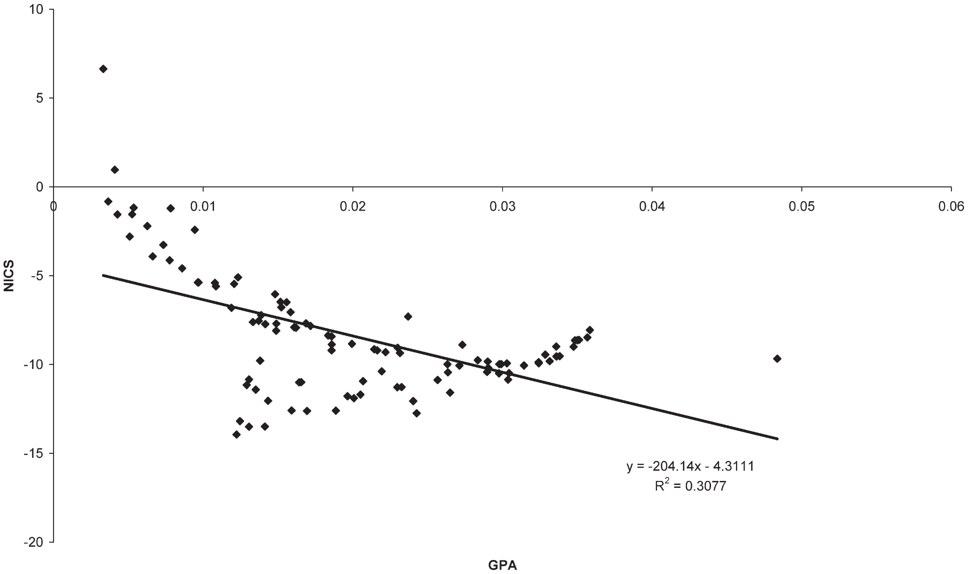


Figure 10. Correlation between B3LYP/6–31G* NICS and SCI values for the set of molecules in Table 1

serious result but we would like to show here that similar claims are not apparently completely general and such correlations, if they exist, are usually confined to only relatively narrow sets of data. When wider sets of systems are considered, such correlations cease to exist. In order to corroborate this claim, we subjected the whole set of our data to thorough statistical analysis aiming at the detection of the eventual correlations between SCI and NICS values for smaller subsets of the molecules, and we found that such 'restricted' correlations are in fact fairly abundant. An example of such a correlation which also violates the assumed orhogonality of structural and magnetic criteria of aromaticity is given in Fig. 9, which correlates the aromaticity of the central benzenoid ring in a series of triphenylene-like molecules, **11**, **18**, **23**, **31** and **32**.

Similarly, it was possible to find several dozen very good correlations (with $R^2 > 0.99$) between SCI and NICS values for the restricted subsets involving 10 benzenoid rings, but all these correlations can again be observed only if the studied subset involves a relatively narrow series of closely structurally related molecules. If, instead, the whole set of 101 benzenoid rings in all 32 molecules studied is considered, the correlation between SCI and NICS values disappears (Fig. 10). This result is very important since it clearly demonstrates that previous claims questioning the orthogonality between structural and magnetic criteria are evidently only of limited relevance and their existence is only possible for relatively narrow classes of closely structurally related molecules, as was the case in the study by Schleyer *et al.*[68]

CONCLUSIONS

This paper reports the application of the so-called six-center bond index as a new structural index of aromaticity of individual benzenoid rings in a wide series of PAHs. It has been shown that this index, which quantitatively measures the extent of cyclic delocalized bonding in these systems, correlates with Polansky similarity index and also with other structural aromaticity indices. On the other hand, the correlations between SCI and magnetic similarity measures such as NICS can be observed only within relatively narrow series of closely structurally related molecules. For wider series of data no such correlations exist and the results are consistent with the orthogonality of structural and magnetic criteria of aromaticity.

Supplementary material

Lists with all values of the different aromaticity indices for the molecules considered in this work are available in Wiley Interscience.

Acknowledgments

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