

THE CLOSE RELATION BETWEEN CYCLIC DELOCALIZATION, ENERGY EFFECTS OF CYCLES AND AROMATICITY

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Dedicated to the memory of Professor Otto Exner.

New evidence questioning the multidimensionality of the aromaticity phenomenon exemplified in what is called orthogonality between the classical (structural and energetic) and magnetic aromaticity indices and measures is reported. For this purpose, the recently proposed methodologies for the quantitative characterization of the energy benefits associated with the cyclic arrangement of mobile π -electrons in polycyclic aromatic hydrocarbons are compared with the indices characterizing the extent of cyclic delocalization in the corresponding conjugated circuits. The reported close correlation between both types of indices implies that no discrepancies between classical and magnetic aromaticity measures exist provided the comparison is based on the indices of inherently local nature and/or the interfering contributions of contaminating conjugated circuits is properly taken into account in the description of aromaticity measures like topological resonance energy (TRE) or nucleus independent chemical shift (NICS).

Keywords: Aromaticity; Arenes; Electron delocalization; Topological resonance energy; Polycyclic aromatic hydrocarbons; Chemical theory.

There is probably no other concept that contributed to the development of chemistry so remarkably as the qualitative, ill-defined concept of aromaticity¹⁻⁸. Although every chemist has some appreciation and intuitive understanding of what molecular properties aromaticity should be associated with, the situation becomes much more difficult when it comes to quanti-

tative comparison of the degree of aromaticity of individual molecules⁹⁻¹¹. The main problem, which makes the concept of aromaticity so inspiring and at the same time controversial, is that predictions of various aromaticity criteria often contradict each other. The existence of such contradictions is usually attributed to the multidimensional character of aromaticity, exemplified in what is called the orthogonality between classical (structural and energetic) and magnetic criteria of aromaticity¹¹⁻¹³. Although such an explanation has received wide acceptance, the detailed insights provided by recent theoretical analyses clearly demonstrated that no inconsistencies between the classical and magnetic aromaticity measures are observed provided the comparison involves inherently local aromaticity indices associated with individual rings within polycyclic aromatic hydrocarbons (PAH)¹⁴⁻¹⁸. This is, e.g., the case of the Polansky similarity index and its recent generalization^{19,20}, circuit-specific magnetic indices of Aihara and Anusooya^{16,21} and the so-called multicenter bond indices²²⁻²⁴, which all were found to correlate with each other.

Our aim in this study is to follow up with the results of the above recent theoretical analyses and to demonstrate that a similar close parallel also involves the indices characterizing the energetic benefits associated with cyclic arrangement of mobile π -electrons. An example of such an index, specifically focused on the evaluation of energetic effects of the cyclic conjugation in PAH, is represented by the so-called *ef*-values²⁵⁻²⁷. The main goal of this study is to demonstrate the close link between this particular type of local index and the extent of cyclic delocalization of mobile π -electrons in individual rings of the PAH, quantitatively gauged by the values of the multicenter bond indices.

THEORETICAL

Multicenter Bond Indices

The multicenter bond indices (MCI) are quantities specifically designed to detect the possible presence of delocalized multicenter bonding in molecules like non-classical carbocations, electron-deficient boranes, lithiated hydrocarbons, etc.^{22,23,28-33}. In view of the success of these indices in the description of non-classical three-center bonding, the idea of the multicenter bond index was recently generalized so as to be applicable also for the description of cyclic delocalized bonding extended over even more centers^{24,34,35}. In the general case of *k*-center bonding, the corresponding index was defined as the permutation unique *k*-center term resulting from the

partitioning of the identity (1), where (PS) denotes the product of charge-density bond order matrix P and the overlap matrix S , respectively, and A, B, C...K label individual atoms in the molecule.

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

Although the bond indices (1) can in principle be used for the description of delocalized multicenter bonding extended over an arbitrary number of centers, the practical applicability of such indices is to a certain extent restricted due to the presence of the normalization factor $(1/2)^{(k-1)}$ owing to which the values of the indices rapidly decrease with increasing k . For that reason, most of the reported applications have so far been restricted to the detection of three-center two-electron (3c-2e) bonding^{23,29,31,32,36}. In order to remedy the above disadvantage, and to make the approach more suitable also for multicenter bonding extended over more centers, it is useful to return to the original proposal by Sannigrahi and Kar²⁹ and to define general k -center bond index as permutation-unique term from the partitioning of Eq. (2).

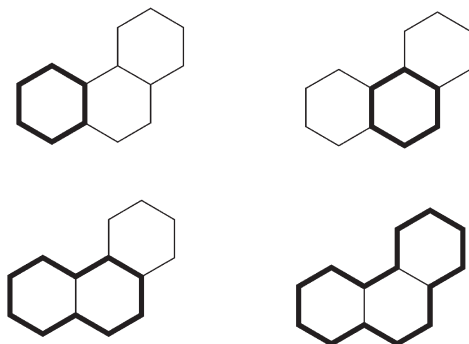
$$\text{Tr}(PS)^{(k)} = 2^{(k-1)} N = \sum_A \text{MCI}_A^{(k)} + \sum_{A<B} \text{MCI}_{AB}^{(k)} + \dots + \sum_{A<B\dots<K} \text{MCI}_{ABC\dots K}^{(k)} \quad (2)$$

Of special importance is, of course, the delocalized 6-center bonding, whose presence can to some extent be expected in individual benzenoid rings of aromatic hydrocarbons. The 6-center bond index (SCI) characterizing the extent of the cyclic delocalization within the particular benzene ring involving the atoms A-F is then defined as

$$\text{SCI} = 2^5 \Delta_{ACBC\dots F}^{(6)} = \sum_{\mu \in A} \sum_{\nu \in B} \dots \sum_{\xi \in F} \sum_I \Gamma_I [(PS)_{\mu\nu} (PS)_{\nu\xi} \dots (PS)_{\xi\mu}] \quad (3)$$

where μ, ν, \dots, ξ refer to atomic basis functions and Γ is the permutation operator that takes into account all possible 6! permutations of the atomic labels. Of course, the above generalization of the multicenter index is not restricted only to the delocalization over 6-centers, but similar indices can also be calculated for bigger fragments involving 10, 14, etc. centers corre-

sponding to naphthalene, anthracene, phenanthrene, pyrene and other circuits in a given PAH (Scheme 1).



SCHEME 1

Energy Effects of Cycles

The dependence of the total π -electron energy E (as computed within the HMO approximation, and expressed in the units of the HMO carbon-carbon resonance integral β) was much studied in the past and is relatively well understood; for details see the book³⁷ and reviews^{38,39} and the references cited therein. Applying the Sachs theorem⁴⁰ to the Coulson integral formula⁴¹ for E , one can envisage the dependence of E on the cycles present in the underlying polycyclic conjugated molecule^{42,43}. By means of appropriate mathematical arguments, it was possible to express the energy effect (on total π -electron energy) caused by an individual cycle Z . The formula reads^{26,27}

$$ef(G, Z) = \frac{2}{\pi} \int_0^{\infty} \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z, ix)} \right| dx \quad (4)$$

where $\pi = 3, 4, \dots$, $i = \sqrt{-1}$, G is the underlying molecular graph^{42,43}, $G - Z$ is the subgraph obtained by deleting the cycle Z from G , and where $\phi(H, x)$ is the characteristic polynomial of the graph H ^{44,45}. Details of the theory on which Eq. (3) is based, as well as numerous examples of its applications can be found in a recent review²⁵.

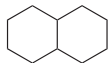
COMPUTATIONAL METHODS

The calculations of multicenter bond indices and ef -values were performed for the set of the PAHs specified in Table I. Based on the numbering of indi-

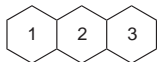
TABLE I
Studied set of polycyclic aromatic hydrocarbons



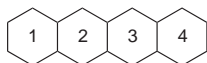
1 Benzene



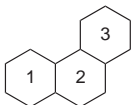
2 Naphthalene



3 Anthracene



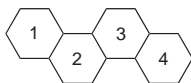
4 Tetracene



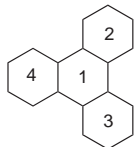
5 Phenanthrene



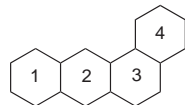
6 Pyrene



7 Chrysene



8 Triphenylene



9 Benzo[a]anthracene

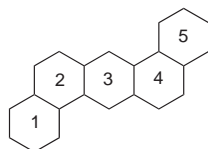
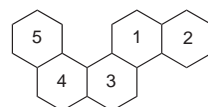
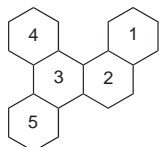
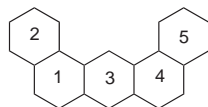
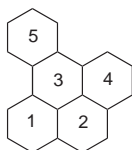
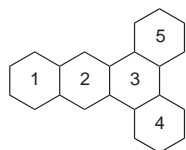
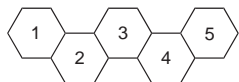
TABLE I
(Continued)**10** Benzo[a]phenanthrene**11** Benzo[a]pyrene**12** Dibenzo[a,h]anthracene**13** Benzo[c]chrysene**14** Dibenzo[a,c]phenanthrene**15** Dibenzo[a,j]anthracene**16** Benzo[e]pyrene

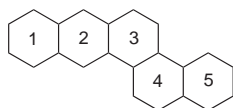
TABLE I
(Continued)



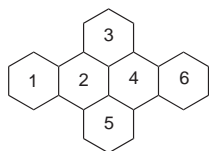
17 Dibenzo[a,c]anthracene



18 Picene



19 Dibenzo[a,h]phenanthrene



20 Dibenzo[e,l]pyrene

vidual symmetry unique benzene rings specified in the Table, the following types of indices were calculated

1) 6-center bond indices (SCI) and the corresponding ef -values for all symmetry unique benzene circuits in PAHs

2) 10-center bond indices (TCI) and the corresponding ef -values for all symmetry-unique naphthalene circuits in the PAHs

3) 14-center bond indices (FCI) and the corresponding ef -values for all symmetry-unique 14-membered circuits in the PAHs. There are three different types of such circuits, corresponding to anthracene, phenanthrene and pyrene fragments.

For the sake of straightforward comparability with the ef -values, the multicenter bond indices were calculated using the so-called pseudo- π approach⁴⁶⁻⁵⁰ for the idealized geometries formed in each particular case by formal fusion of clamped benzene rings with the C-C bond length 140 pm. Within this approach each of the carbon atoms is represented just by one

singly occupied orbital like in the Hückel method, and the only difference compared to HMO theory is that the bond indices are calculated using the formula (2) that takes into account actual overlap matrix S which in HMO theory is set to unit matrix. The calculated values of the above multicenter bond indices and the corresponding ef -values for 6-, 10- and 14-center rings are summarized in Tables II-IV. For the sake of comparison of both approaches we also present the values of HMO 6-center indices in the Table II.

RESULTS AND DISCUSSION

The existence of the link between the energetic benefits resulting from the cyclic conjugation of mobile π -electrons and the extent of the cyclic delocalization in individual conjugated circuits can most straightforwardly be demonstrated by looking for the possible relation between the ef -values and multicenter bond indices for individual types of the conjugated circuits. Because of the fact that the stabilizing energy contributions due to the cyclic delocalization rapidly decrease with the size of the cycle, we first focus on the relation between the ef -values and the 6-center bond index (SCI). This dependence is displayed in Fig. 1, from which the tight correlation of both indices is straightforwardly evident.

The close parallel between the ef -values and multicenter bond indices is not, however, restricted only to 6-center contributions of the benzene

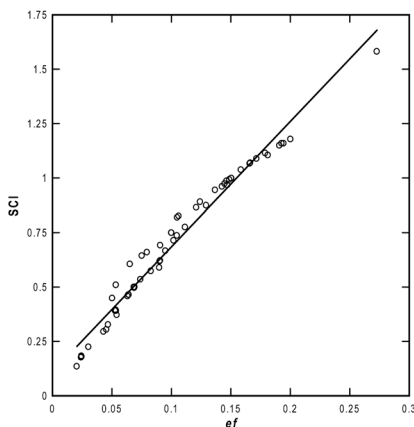


FIG. 1

Correlation of 6-center bond indices (SCI) with the ef -values for individual symmetry-unique benzenoid rings in the studied set of molecules (correlation coefficient $R = 0.986$)

TABLE II
 Calculated 6-center bond indices (SCI) and ef -values for individual symmetry-unique benzene circuits in the studied PAHs

Molecule	Ring label	$ef(6)$ (β -units)	SCI(pseudo- π)	SCI(HMO)
1	1	0.2729	1.5808	1.5802
2	1	0.1211	0.8640	0.866
3	1	0.0951	0.6656	0.7449
	2	0.0653	0.6048	0.5294
4	1	0.0900	0.5888	0.7124
	2	0.0535	0.5088	0.4679
5	1	0.1586	1.0368	0.9862
	2	0.0534	0.3936	0.4312
6	1	0.1063	0.8256	0.7367
	2	0.0528	0.3904	0.4564
7	1	0.1465	0.9856	0.9534
	2	0.0689	0.4960	0.5034
8	1	0.0242	0.1760	0.2083
	2	0.1910	1.1488	1.0830
9	1	0.1048	0.7360	0.7852
	2	0.0796	0.6592	0.5778
	3	0.0431	0.2944	0.3626
	4	0.1717	1.0880	1.0084
10	1	0.1449	0.9728	0.9430
	2	0.0693	0.4992	0.5043
11	1	0.0504	0.4480	0.3975
	2	0.1294	0.8736	0.8839
	3	0.0455	0.3040	0.4019
	4	0.0686	0.4992	0.5345
	5	0.1050	0.8192	0.7257
12	1	0.1665	1.0688	0.9989
	2	0.0469	0.3264	0.3872
	3	0.1001	0.7488	0.6408

TABLE II
(Continued)

Molecule	Ring label	$ef(6)$ (β -units)	SCI(pseudo- π)	SCI(HMO)
13	1	0.0633	0.4576	0.4833
	2	0.1506	0.9984	0.9531
	3	0.0907	0.6208	0.5851
	4	0.0643	0.4640	0.4771
	5	0.1489	0.9920	0.9627
14	1	0.1369	0.9440	0.9213
	2	0.0829	0.5728	0.5656
	3	0.0304	0.2240	0.2445
	4	0.1790	1.1136	1.0459
	5	0.1813	1.1040	1.0606
15	1	0.0469	0.3264	0.3873
	2	0.1660	1.0656	0.9969
	3	0.1002	0.7488	0.6416
16	1	0.1243	0.8896	0.7995
	2	0.0537	0.3904	0.4545
	3	0.0245	0.1824	0.2244
	5	0.1945	1.1584	1.0843
17	1	0.1116	0.7744	0.8124
	2	0.0908	0.6912	0.6270
	3	0.0206	0.1344	0.1773
	4	0.2003	1.1776	1.0962
18	1	0.1505	0.9984	0.9633
	2	0.0640	0.4640	0.4825
	3	0.0903	0.6176	0.5840
19	1	0.1020	0.7136	0.7738
	2	0.0753	0.6432	0.5656
	3	0.0542	0.3712	0.4276
	4	0.0741	0.5344	0.5195
	5	0.1427	0.9600	0.9420
20	1	0.1928	1.1584	1.0832
	2	0.0247	0.1792	0.2221
	3	0.1472	0.9664	0.8720

TABLE III
 Calculated 10-center bond indices (TCI) and ef -values for individual symmetry-unique naphthalene circuits in the studied PAHs

Molecule	$ef(10)$ (β -units)	TCI	Circuit label
2	0.0709	0.5567	
3	0.0369	0.3612	
4	0.0275	0.2940	1+2
	0.0206	0.2684	2+3
5	0.0275	0.2568	
6	0.0198	0.1996	1+2
	0.0056	0.0469	2+3
7	0.0387	0.3254	1+2
	0.0118	0.1267	2+3
8	0.0102	0.1104	
9	0.0471	0.4086	1+2
	0.0139	0.1530	2+3
	0.0193	0.1858	3+4
10	0.0389	0.3244	1+2
	0.0118	0.1270	2+3
11	0.0281	0.2868	1+2
	0.0091	0.1073	1+3
	0.0091	0.1085	1+4
	0.0068	0.0490	3+4
	0.0139	0.1421	3+5
	0.0294	0.2595	4+5
12	0.0223	0.2102	1+2
	0.0178	0.1788	2+3

TABLE III
 (Continued)

Molecule	$ef(10)$ (β -units)	TCI	Circuit label
13	0.0344	0.3000	1+2
	0.0160	0.1573	1+3
	0.0160	0.1578	3+4
	0.0349	0.3210	4+5
14	0.0488	0.3737	1+2
	0.0047	0.0553	2+3
	0.0144	0.1420	3+4
15	0.0224	0.2102	1+2
	0.0179	0.1788	1+3
16	0.0229	0.2148	1+2
	0.0074	0.0870	1+3
	0.0025	0.0262	2+3
	0.0095	0.1105	3+5
17	0.0549	0.4361	1+2
	0.0051	0.0655	2+3
	0.0073	0.0805	3+4
18	0.0348	0.3033	1+2
	0.0159	0.1576	2+3
19	0.0437	0.3955	1+2
	0.0198	0.1978	2+3
	0.0087	0.0933	3+4
	0.0431	0.3498	4+5
20	0.0099	0.1096	1+2
	0.0085	0.0931	2+3
	0.0012	0.0148	2+4

TABLE IV
 Calculated 14-center bond indices (FCI) and ef -values for individual symmetry-unique anthracene, phenanthrene and pyrene circuits in the studied PAHs

Molecule	$ef(14)$ (β -units)	FCI	Circuit label
3	0.02790	0.17808	
4	0.01580	0.12852	
5	0.01980	0.15778	
6	0.01280	0.13342	1+2+4
	0.01280	0.08456	1+2+3+4
7	0.00810	0.07714	
8	0.00680	0.06566	
9	0.00990	0.07686	1+2+3
	0.00990	0.09422	2+3+4
10	0.00810	0.07728	
11	0.00620	0.05600	1+2+3
	0.00620	0.06230	1+2+4
	0.00570	0.07070	1+3+5
	0.00570	0.07252	1+4+5
	0.00570	0.04648	1+3+4+5
12	0.00370	0.03416	2+3+4
	0.01300	0.11046	1+2+3
13	0.01150	0.09618	1+2+3
	0.00330	0.03696	1+3+4
	0.001150	0.09688	3+4+5

TABLE IV
(Continued)

Molecule	$ef(14)$ (β -units)	FCI	Circuit label
14	0.00300	0.03332	1+2+3
	0.00300	0.03304	2+3+4
	0.01020	0.08554	3+4+5
	0.00300	0.03304	2+3+5
15	0.00370	0.03416	1+3+4
	0.01300	0.11046	1+2+3
16	0.00110	0.01218	2+3+5
	0.01530	0.13650	1+2+4
	0.00430	0.05614	1+3+4
	0.00480	0.05236	1+3+5
	0.00430	0.04102	1+2+3+4
17	0.00330	0.03290	1+2+3
	0.00330	0.03822	2+3+4
	0.00440	0.04606	3+4+5
18	0.01140	0.09646	1+2+3
	0.00330	0.03696	2+3+4
19	0.01470	0.09912	1+2+3
	0.00420	0.04732	2+3+4
	0.00550	0.05642	3+4+5
20	0.00050	0.00686	1+2+4
	0.00560	0.05586	1+2+3
	0.00520	0.05726	2+3+5
	0.00150	0.01988	2+3+4+5

rings, but similar correlations are observed also for 10- and 14-center rings and it is interesting that the indices even for these more extended delocalized systems fit the same correlation line as in the case of benzene (Fig. 2).

Both indices, of which one reflects the local energetic contribution of an individual conjugated circuit and the other reflects the extent of cyclic conjugation in the same circuit, are seen to correlate very well thereby showing that both approaches to the concept of aromaticity yield the same conclusions. Moreover, the multicenter indices were recently successfully shown to allow the reconstruction of ring current density maps in PAHs¹⁷. The presently shown correlation in Fig. 2 and the latter fact imply that energetic and magnetic manifestations of aromaticity are also closely related and, moreover, that no discrepancies between both types of indices exist provided the comparison involves strictly local contributions of individual rings. This result is very interesting because of its possible implications for the often observed inconsistencies between the classical and magnetic aromaticity measures. It implies, namely, that such inconsistencies, if observed, do not in fact reflect the “orthogonality” of the corresponding measures, but they stem from the fact that comparison is made between indices that are inherently incomparable. The importance of the requirement of comparability can be best demonstrated by the example of the widely

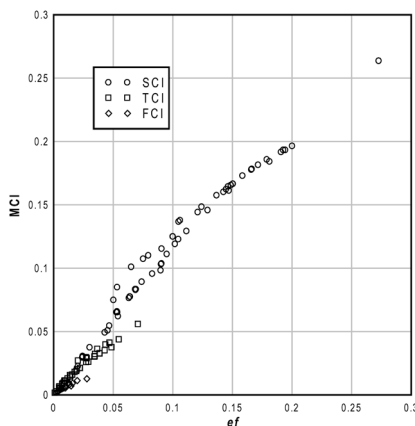


FIG. 2

Joint correlation of multicenter (6-, 10- and 14-center) bond indices (MCI) with ef -values for the studied set of molecules

used magnetic aromaticity index NICS⁵¹⁻⁵⁴. Although this index is calculated in a fixed point associated with a particular ring, and as such seems to represent a local aromaticity measure of a given ring, its correlations with other inherently local aromaticity measures like the Polansky index¹⁹, Aihara's circuit resonance energy¹⁶, multicenter bond indices²⁴, etc., dramatically fail. However, the traditional interpretation of such discrepancies in terms of multidimensionality of the aromaticity phenomenon was seriously questioned in recent theoretical studies^{14,15,24,55,56}, in which it was demonstrated that the observed lack of correlations is due to the fact that the values of NICS are in fact contaminated by the contributions of the ring currents of all conjugated circuits in the molecule. Provided proper account is taken of the contributions of the contaminating circuits, no inconsistencies between NICS and local aromaticity measures exists. Another example demonstrating the importance of the interference of contaminating conjugated circuits can be found in a recent graph theoretical study⁵⁷, in which the correlation of the topological resonance energy (TRE), as global aromaticity measure, with the local energy contributions (*ef*-values) of individual rings was reported. Based on that study, and in view of the correlation between the *ef*-values and multicenter bond indices, it can be expected that similar correlations will also exist between TRE and the multicenter bond indices. Because of dominance of the contributions from 6-center benzenoid cycles, the correlation of TRE with multicenter bond indices can, in a first approximation, be written in the form of the following Eq. (5)

$$\text{TRE} = a \sum_i \text{SCI}_i + b \quad (5)$$

which can also be regarded as the counterpart of a similar relationship between TRE and magnetic resonance energy (MRE) reported in the graph theoretical study of Aihara¹⁶. In order to demonstrate the difference between the bond indices calculated at pseudo- π and HMO level of the theory, the parameters of the correlation equation (5) were calculated for both types of indices. The resulting values, together with the corresponding correlation coefficients are given bellow (Eq. (6)).

$$\text{pseudo-}\pi: \quad a = 0.2264, \quad b = 0.0029, \quad R = 0.973 \quad (6a)$$

$$\text{HMO:} \quad a = 0.2304, \quad b = 0.025, \quad R = 0.915 \quad (6b)$$

As it is possible to see, the description based on the indices calculated using pseudo- π approach is noticeably better than the one based on the correlation with HMO 6-center indices. This clearly implies the superiority of the pseudo- π approach used in this study and this is why only this particular approach was considered in the extension of the model based on taking into account the contributions of other contaminating conjugated circuits. The inclusion of these circuits resulted for the studied set of 20 PAHs, in the multilinear correlation equation

$$\text{TRE} = 0.1946 \sum_{\alpha} \text{SCI}_{\alpha} + 0.1784 \sum_{\beta} \text{TCI}_{\beta} + 0.049 \sum_{\gamma} \text{FCI}_{\gamma} - 0.038, \quad R = 0.999 \quad (7)$$

whose statistical analysis⁵⁸ confirms that inclusion of additional parameters does indeed increase the statistical importance of the correlation (Eq. (7)) compared to Eq. (6a). The internal predictivity of the Eq. (7) was tested using the leave-10%-out procedure which resulted in q^2 value 0.9985. The excellent quality of the correlation equation can also be demonstrated by the simple correlation of theoretical versus predicted TRE values whose plot is displayed in Fig. 3. The slope of the correlation line is 1.00, the intercept is 0.00 and the correlation coefficient $R = 0.999$.

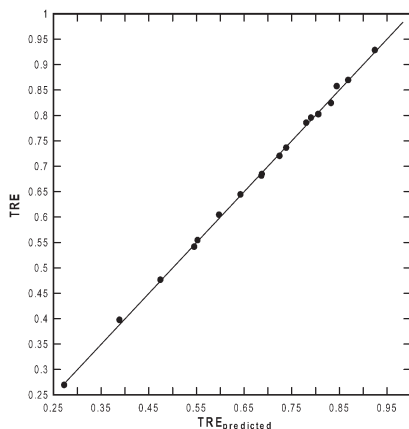


FIG. 3

Correlation between the topological resonance energy (TRE) and TRE predicted from the correlation equation (6) (slope 1.00, intercept 0.00, correlation coefficient $R = 0.999$)

This result is very important because the form of the correlation equation (Eq. (7)) closely resembles the relations recently used to reveal the interfering contributions of contaminating conjugated circuits to the traditional magnetic aromaticity index NICS⁵⁵. The close similarity of both types of the correlation equations thus implies that the parallels between energetic and magnetic criteria of aromaticity are not restricted only to the comparison of the measures of strictly local nature (*ef*-values vs MCI) but, provided proper care is taken of the interfering contribution of all participating conjugated circuits, there is also no inconsistency between the local and global aromaticity measures.

CONCLUSIONS

The paper reports new evidence questioning the often invoked phenomenon of multidimensionality of the aromaticity exemplified in what is called orthogonality between the classical (structural and energetic) and magnetic aromaticity measures. The reported approach, that is based on the quantitative comparison of energy benefits associated with the cyclic arrangement of mobile π -electrons in polycyclic aromatic hydrocarbons and the extent of the cyclic delocalization in the corresponding conjugated circuits shows that no discrepancy between both types of indices exist provided the comparison involves local contributions of individual rings and conjugated circuits. In addition we also show that provided the interfering contributions of contaminating conjugated circuits are properly taken into account, the same close parallel can be observed also for global aromaticity measures like TRE and NICS.

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