Are Thermodynamic and Kinetic Stabilities Correlated? A Topological Index of Reactivity toward Electrophiles Used as a Criterion of Aromaticity of Polycyclic Benzenoid Hydrocarbons[⊥]

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A topological index of reactivity (*TIR*) of benzenoid hydrocarbons is defined basing on an approximate value of the bicentric localization energies. *TIR* values correlate with all known (24) Hammett-Streitwieser position constants, based on kinetic data for electrophilic substitution in benzenoid hydrocarbons. The maximum value of the index, denoted by *TIR(max)*, defines the stability of a molecule toward electrophiles. For all 35 nonisoarithmic molecules of benzenoid hydrocarbons for which Hess and Schaad data are known, *TIR(max)* values correlate with classical numerical characteristics of aromaticity: resonance energy per π-electron (*REPE*), HOMO−LUMO gap, and geometry based aromaticity index *HOMA*. Correlation between *TIR(max)* and exaltation of magnetic susceptibility is also found for cata-condensed benzenoid hydrocarbons, whereas if the peri-condensed ones are included, no correlation is observed. This can be ascribed to the presence of both paratropic and diatropic rings in perifusenes.

INTRODUCTION

Aromaticity, electronegativity, ionicity, van der Waals radii of atoms, substituent effects, and many other terms belong to the group of notions named by C. A. Coulson *Primitive Patterns of Understanding*.[1] To some extent they play in chemistry a similar role to that of axioms and postulates in mathematics. They are frequently used in the everyday research language of chemistry and related fields. The common feature of these terms is that in spite of their frequent use, most of them are not uniquely defined. To justify using these imprecise terms, let us quote E. D. Bergmann's opinion:[2] "Classification and theory are not ends in themselves. If they generate new experimental work, new compounds, new processes, new methods - they are good; if they are sterile - they are bad". A substantial number of papers devoted to the problems of how aromaticity is manifested and how to define this notion qualitatively or quantitatively encouraged us to undertake an attempt to present one more view on aromaticity. Most researchers in this field have agreed that classically,[3] aromaticity is characterized by a collection of properties proper for cyclic π-electron systems.[4−8] This is independent whether the cause of aromatic stability is considered as due to the π-electron or σ-electron structure.[9,10] Earlier it was generally accepted that aromaticity was strongly associated with the planarity

of the system.[4] In the last decades it was shown theoretically[11] and experimentally[12] that planarity is not a *conditio sine qua non* for aromatic properties.[13] Benzene itself in crystalline state at 20 K is nonplanar.[14] This has been attributed to intermolecular interactions in the crystal lattice. Recent definitions of aromaticity[15] related this phenomenon to four characteristic features which are components of the whole definition. These are as follows: energy, geometry, magnetism, and "reactivity-based criteria", which are outlined briefly below.

"ENERGY-BASED CRITERIA" OF AROMATICITY

The earliest chemical observation for aromatic systems—first found for benzene—was associated with their resistance to chemical reactions.[16,17] Then it was found that aromatics are thermodynamically more stable than their olefinic analogues, as documented for benzene by pioneer papers by Pauling et al.[18] and Kistiakowsky et al.,[19] and then extended by Wheland for a wider group of π-electron systems.[20] Their concept of resonance energy (*RE*) led to estimations of Aromatic Stabilization Energy (*ASE*), which were based on comparing the energy of a system having cyclic π-electron delocalization to appropriate reference π-electron systems in which no such delocalization is present. This is usually schematically formulated in a form of a reaction. An example for benzenoid hydrocarbons is presented by eq 1:[21]

$$C_{2p}H_{2q} + (3p - 2q)CH_2=CH_2 \rightarrow$$
$$(2p - q)CH_2=CH-CH=CH_2 \quad (1)$$
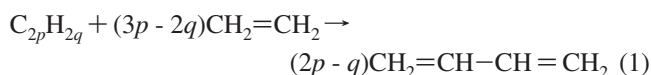
Numerous papers have been published about these kinds of treatments, which differ in details but preserve the general idea of eq 1. For recent reviews see ref 22.

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  [⊥] This paper is dedicated to Prof. Zbigniew Galus (University of Warsaw) on the occasion of his 70th birthday.
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"GEOMETRY-BASED CRITERIA" OF AROMATICITY

Since the beginning of structural organic chemistry, bond lengths have been considered to be very important parameters related to chemical reactivity.[17] Aromaticity was recognized early as typical for cyclic systems with bonds of intermediate length between those for single and double ones. Quantitatively, Julg et al.[23] were the first who used this view and introduced a quantitative measure of aromaticity, named sometimes as an aromaticity index, A_J. The A_J index was defined as a function of variance of CC bond lengths in the perimeter of molecules. Schematically this approach takes the form of eq 2:

$$A_J = 1 - \frac{225}{m} \sum \left(1 - \frac{R_r}{R}\right)^2 \qquad (2)$$

where m is the number of peripheral bonds with individual bond lengths R_r, and R is their mean value.

Replacement of the mean value in the formula 2 for the variance of bond lengths in a ring or in the whole π-electron system by so-called "optimal bond lengths", R_{opt}, led to the geometry-based index of aromaticity, $HOMA$,[24] which is calculated from geometry by use of formula 3:

$$HOMA = 1 - \frac{1}{m} \sum_{i=1}^{m} \alpha(R_{opt} - R_i)^2 \qquad (3)$$

where m is the number of bonds taken into the summation; α is a normalization constant (for C−C, $R_{C-C} = 257.7$) fixed to give $HOMA = 0$ for a model nonaromatic system, e.g., one cyclohexatrienic Kekulé structure of benzene, and $HOMA = 1$ for the system with all bonds equal to the optimal value R_{opt}. For C−C bonds, $R_{opt,C-C} = 1.388$ Å; R_i stands for a running bond length, whereas the R_{opt} was defined as a bond for fully delocalized π-electron system. For a review on structural aspects of aromaticity see ref 25. The higher the $HOMA$ value, the more "aromatic" the ring in question and, hence, the more delocalized the π-electrons of the system.

"MAGNETISM-BASED CRITERIA" OF AROMATICITY

Measurements of diamagnetic anisotropy and exaltation of the magnetic susceptibility were used[26] at a very early stage for evaluating aromaticity numerically.[27] The exaltation needs additional assumptions (as in the case of RE) on some reference molecules. For critical reviews of these methods see refs 6 and/or 28. Soon afterward, measurements of proton NMR spectra followed, for which the term "aromatic chemical shift" was introduced and applied in many different situations.[29] Along with experimental approaches, in the last decades several theoretical indices of aromaticity have appeared—the best known is the *nucleus independent chemical shift* (*NICS*),[30] which is defined as the absolute value of shielding estimated at a given site of a cyclic π-electron system (most frequently in the center or at 1 Å above it or a perpendicular component of the tensor of *NICS(1)*). The negative values of NICS characterize aromatic systems. The more aromatic system is, the more negative value of NICS is expected.[15b]

For all three criteria mentioned above, there are known numerical parameters, "aromaticity indices", which quantify the "aromatic character" of a given molecule or its particular fragment. Even if they are not equivalent to one another,[5] they allow us to find numerically how much they differ in "measuring" the aromaticity.

Unfortunately, the fourth criterion of aromaticity[15a]—**the reactivity-based one**, cannot be unambiguously defined in a numerical way. If a given system follows the rule of maintaining its π-electron structure after undergoing a chemical reaction (e.g., in an "aromatic electrophilic substitution reaction"),[31] then the criterion is fulfilled, but a more subtle differentiation is very difficult, because of the large variety of possible media, reagents, and reaction conditions used for this purpose. A topological approach for a different type of reactivity, namely a [4 + 2] cycloaddition for benzenoid hydrocarbons with maleic anhydride was suggested for the interpretation of experimental rate constants.[32]

The purpose of this work is to present a topology-based method which allows us to distinguish reactivity in electrophilic substitutions between positions in molecules of benzenoid hydrocarbons, depending on how favorable is it energetically in comparison with all other possible positions. This index of reactivity is then compared with traditional energy-, magnetism-, and geometry-based indices of aromaticity.

CONCEPT AND METHODOLOGY

Consider a benzenoid hydrocarbon in which one of carbon atoms, say C_i, is a potential site of reaction, whereas all other carbons are labeled C_k. When the C_i atom is already involved in the reaction (i.e., it is excluded from the π-electron distribution), the rest of the molecule has a different π-electron structure compared to the initial state. In order to assign a canonical structure for the remaining part of the molecule another carbon C_j (alternant in respect to C_i) has to be excluded from the distribution. Then the remaining part of the molecule (i.e., the carbon atoms C_k; $k \neq i, j$) may be described by different sets of canonical structures.[33] For each position i we have n independent sets of canonical structures in which bicentric π-electron localization occurs that for the i-th carbon atom corresponds to the number of so-called Pauling bond orders generalized to long bonds.[34] Consider anthracene as an illustrative example. First we divide the carbon atoms into two sets of n atoms as starred and unstarred (see Figure 1a). We localize first one electron in a starred position $i = 1$, and then we obtain 7 sets of canonical structures in which the second localization j is in unstarred positions 2, 4, 5, 7, 10, 12, and 13. Thus we have 7 sets of canonical structures for each of $n = 7$ sets of bicentric reactions involving the i-th carbon atom (see Figure 1c). The n value is always equal the half of the number N of π-electrons of the system: $n = N/2$.

Each of these sets represents a bicentric reaction. Each of these canonical structures is a realization of a virtual state in which electrons are localized in positions i and j, whereas the remainder of the molecule is described by a collection of single and double CC bonds. It is well-known that the larger the number of canonical structures, the more stable the π-electron system.[17] This is represented by formula $RE \sim \ln K$, where K is the number of canonical structures.[35] On the other hand, K may be considered as a number of states characterized by different π-electron distributions, i.e. canonical structures. This quantity in the case of anthracene is $K = 4$ (see Figure 1b). By analogy, this notion may be compared to Boltzmann's definition of entropy S in which

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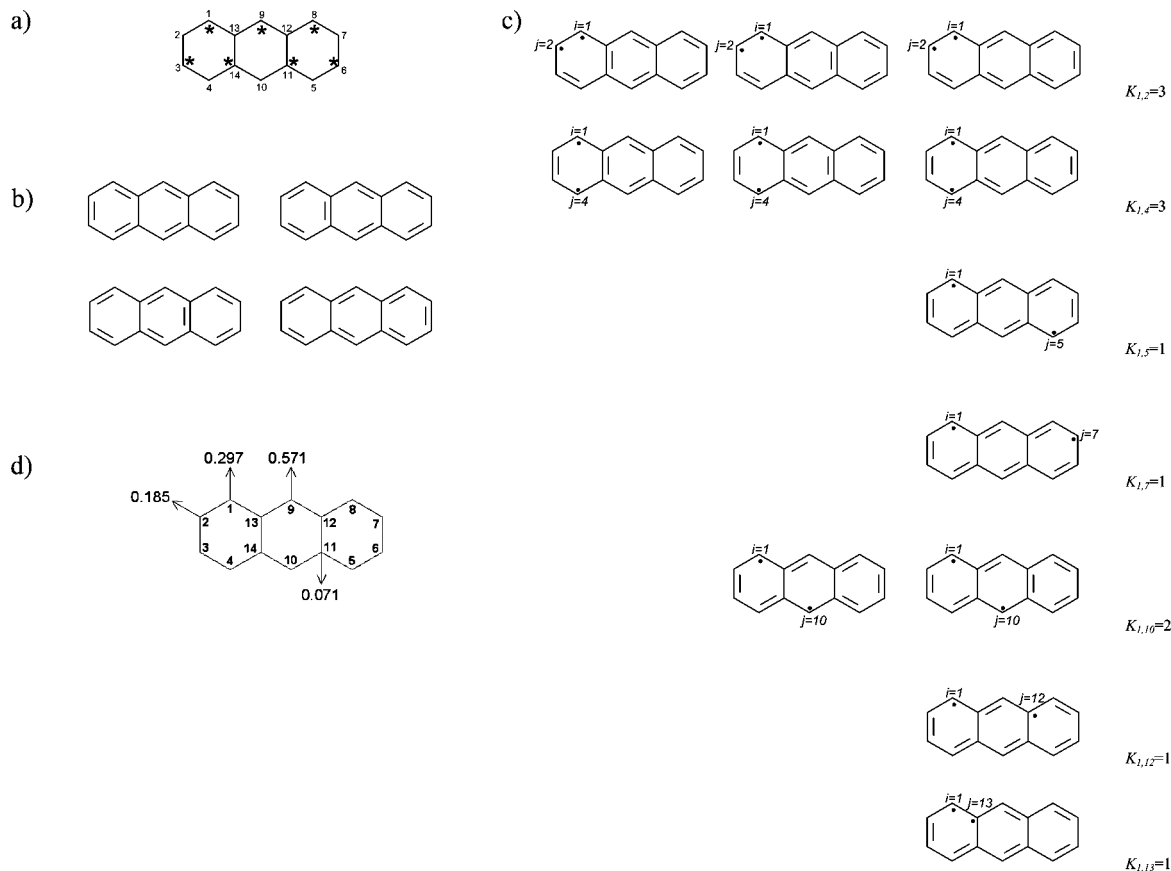*J. Chem. Inf. Model., Vol. 49, No. 2, 2009* **371**

Figure 1. a) The molecule of anthracene with starred and unstarred carbon atoms. b) All unexcited canonical resonance structures of anthracene. c) Canonical resonance structures for all seven positions for $i = 1$ carbon atom for anthracene (in which the bicentric reaction occurs). K_{ij} stands for the number of canonical structures of the remaining part of the molecule. d) The *TIR* values for four independent positions in anthracene.

$S \sim \ln W$, where W denotes a thermodynamic probability associated with a number of ways in which a given system may be realized. Hence for a given benzenoid hydrocarbon we can define a "π-electron delocalization entropy" in the meaning presented above: $S = \ln K$.

In our case, for each molecule of benzenoid hydrocarbon there are defined bicentric reactions in which for a fixed i-th atom there is a set of localizations labeled by j. For each set we can describe a "partial entropy" denoted as $S_{ij} = \ln K_{ij}$.

Now we define a topological index of reactivity, TIR_i of the i-th carbon atom, as a ratio of the mean partial entropy of the system (in which the bicentric reaction occurs) to the entropy of an initial state.

$$TIR_i = \frac{\bar{S}_{ij}}{S} \qquad (4)$$

Hence

$$TIR_i = \frac{\frac{1}{n}\sum_{j=1}^{n} S_{ij}}{S} = \frac{\frac{1}{n}\sum_{j=1}^{n} \ln K_{ij}}{\ln K} \qquad (5)$$

The summation is over n, which is the number of sets of bicentric reactions $n = N/2$, where N is total number of π-electrons

Thus

$$TIR_i = \frac{\sum_{j}^{N/2} \ln K_{ij}}{\frac{N}{2}\ln K} \qquad (6)$$

For the archetypal aromatic compound, benzene, $TIR_i = 0$, since each bicentric reaction leads to a fully localized π-electron structure, with $K_{ij} = 1$ and hence $\ln K_{ij} = 0$. In this way the reactivity of benzene is the lowest possible among polycyclic benzenoid hydrocarbons, in line with chemical experience.

Let us consider the example for anthracene in position $i = 1$. Application of (6) leads to

$$TIR_1 = \frac{(\ln K_{1,2} + \ln K_{1,4} + \ln K_{1,5} + \ln K_{1,7} + \ln K_{1,10} + \ln K_{1,12} + \ln K_{1,13})}{7 \cdot \ln K}$$

$$TIR_1 = \frac{(1.099 + 1.099 + 0 + 0 + 0.693 + 0 + 0)}{7 \cdot 1.386} = 0.297$$

The *TIR* values of four independent positions for anthracene are presented in Figure 1d. As a consequence of much higher *TIR* values for C_1, C_2, and C_9 the reaction should be most effective for position 9; therefore, position 9 is decisive about reactivity of a system in question. The *TIR* value for C_{11} and all equivalent positions (C_{12}, C_{13}, C_{14}) is dramatically lower than for other ones. For this reason the

Table 1. Values of *TIR(max)*, *HOMA*, *REPE* ($\times 10^3$ [β]), Exaltation of Magnetic Susceptibility, Λ [cgs-ppm], and the Values of the HOMO−LUMO Gap $\Delta\varepsilon$ in au[a]

No	Structure	TIR(max)	HOMA	REPE	Λ	$\Delta\varepsilon$	No	Structure	TIR(max)	HOMA	REPE	Λ	$\Delta\varepsilon$
1	benzene	0.000	0.991	65	14.5	0.247	20	naphtho[2,1,8-qra]naphthacene	0.707	0.665	45	85.7	0.105
2	naphthalene	0.252	0.811	55	29.6	0.176	21	benzo[a]perylene	0.761	0.639	45	62.3	0.094
3	anthracene	0.571	0.718	47	45.5	0.132	22	benzo[b]perylene	0.656	0.642	49	56.0	0.113
4	phenanthrene	0.318	0.742	55	41.4	0.173	23	coronene	0.557	0.742	53	123.9	0.148
5	pyrene	0.585	0.742	51	59.2	0.141	24	zethrene	0.759	0.623	41	45.5	0.082
6	naphthacene	0.638	0.670	42	62.2	0.102	25	benzo[a]pentacene	0.716	0.638	42	86.7	0.086
7	benz[a]anthracene	0.568	0.696	50	55.2	0.138	26	dibenzo[b,k]chrysene	0.579	0.661	46	85.9	0.115
8	chrysene	0.466	0.709	53	55.5	0.156	27	naphtho[2,3-g]chrysene	0.616	0.657	51	76.2	0.131
9	triphenylene	0.338	0.691	56	49.3	0.180	28	naphtho[8,1,2-bcd]perylene	0.702	0.661	47	71.9	0.101
10	perylene	0.636	0.656	48	42.8	0.111	29	dibenzo[cd,lm]perylene	0.720	0.690	48	105.1	0.104
11	benzo[e]pyrene	0.589	0.690	53	66.9	0.147	30	dibenzo[a,f]perylene	0.837	0.630	43	81.1	0.076
12	benzo[a]pyrene	0.702	0.700	49	72.2	0.124	31	phenanthro[1,10,9,8-opqra]perylene	0.879	0.600	42	58.2	0.067
13	pentacene	0.739	0.644	38	79.9	0.081	32	dibenzo[de,op]pentacene	0.856	0.620	38	48.4	0.066
14	benzo[a]naphthacene	0.631	0.660	45	70.3	0.108	33	dibenzo[a,l]pentacene	0.699	0.637	44	94.5	0.092
15	dibenz[a,h]anthracene	0.558	0.683	51	66.6	0.142	34	benzo[2,1-a:3,4-a']dianthracene	0.563	0.618	47	88.6	0.125
16	benzo[b]chrysene	0.590	0.680	49	70.5	0.128	35	naphtho[2,1,8-yza]hexacene	0.790	0.636	40	116.5	0.073
17	picene	0.497	0.697	53	68.6	0.155							
18	benzo[ghi]perylene	0.629	0.707	51	79.8	0.129							
19	anthanthrene	0.712	0.691	45	89.3	0.106							

[a] Dots represent carbon atoms with the maximal values of *TIR$_r$*.

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Table 2. Juxtaposition of Experimental Position Constants σ_r^{+56} and TIR_r Values for 24 Positions of 14 Benzenoid Hydrocarbons[a]

	σ_r^+	TIR_r
benzene	0.00	0.000*
1-naphthalene	0.35	0.252*
2-naphthalene	0.25	0.126
1-anthracene	0.41	0.297
2-anthracene	0.36	0.185
9-anthracene	0.72	0.571*
5-naphtacene	0.80	0.638*
3-perylene	0.74	0.636*
1-pyrene	0.67	0.585*
2-pyrene	0.22	0.202
4-pyrene	0.36	0.314
7,12-benz[a]anthracene	0.64	0.568*
coronene	0.44	0.557*
1-triphenylene	0.32	0.338*
2-triphenylene	0.26	0.327
6-anthanthrene	0.81	0.712*
1-phenanthrene	0.34	0.318*
2-phenanthrene	0.25	0.221
3-phenanthrene	0.29	0.282
4-phenanthrene	0.33	0.257
9-phenanthrene	0.365	0.308
6-chrysene	0.46	0.466*
6-benzo[a]pyrene	0.86	0.702*
7-dibenz[a,h]anthracene	0.65	0.429*

[a] The *r*-value precedes the hydrocarbon name. An asterisk indicates *TIR(max)*.
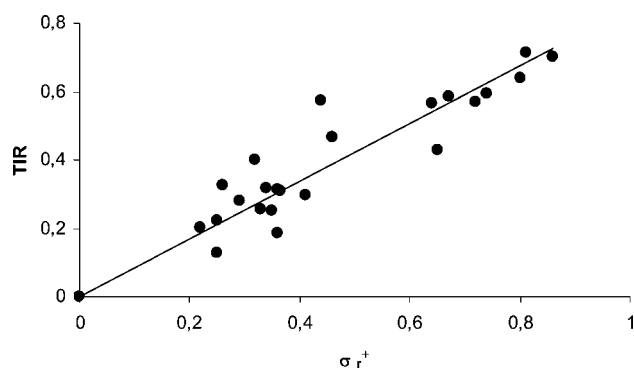
**Figure 2.** Scatter plot of position constants σ_r^+ and *TIR* values for 24 positions of 14 benzenoid hydrocarbons. Correlation coefficients R = 0.95 (for all points) and R = 0.94 (benzene not included).
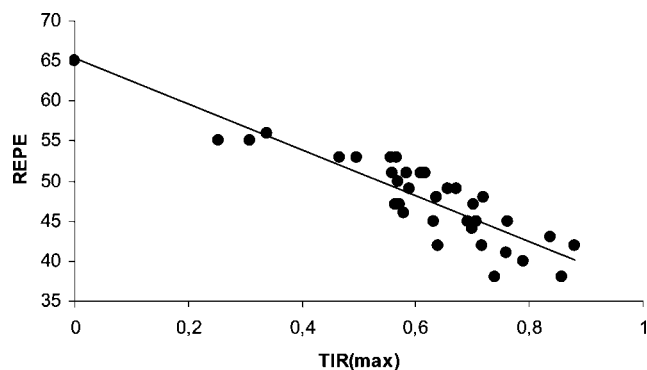
Figure 3. The scatter plot of $REPE^{51}$ on *TIR(max)*. Correlation coefficients R = −0.88 (for all points) and R = −0.83 (benzene not included).

maximal *TIR* value (*TIR_max*) may be used as a reactivity-based descriptor of aromaticity. Importantly the minimal value of *TIR* (*TIR_min*) characterizes the inner carbon atoms of anthracene (i.e., atoms not bound to hydrogen, for which
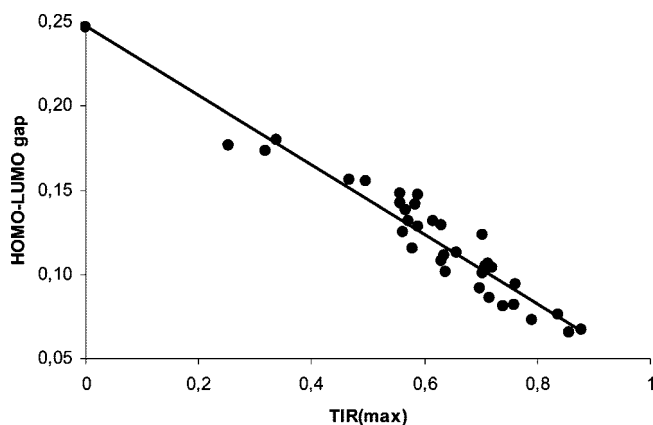
Figure 4. The scatter plot of the HOMO−LUMO gap in au on *TIR(max)*. Correlation coefficients R = −0.96 (for all points) and R = −0.94 (benzene not included).
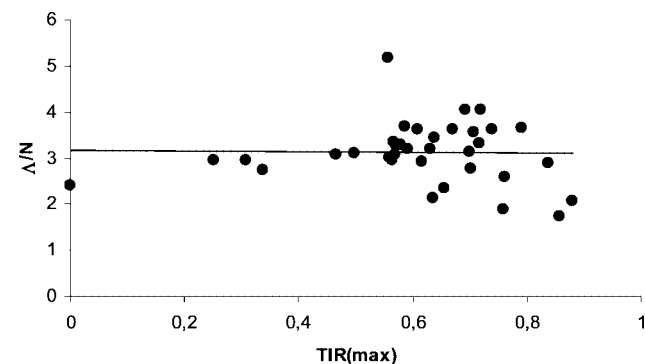
Figure 5. The scatter plot between Λ per number of π-electrons vs *TIR(max)*. Correlation coefficient R = 0.00.
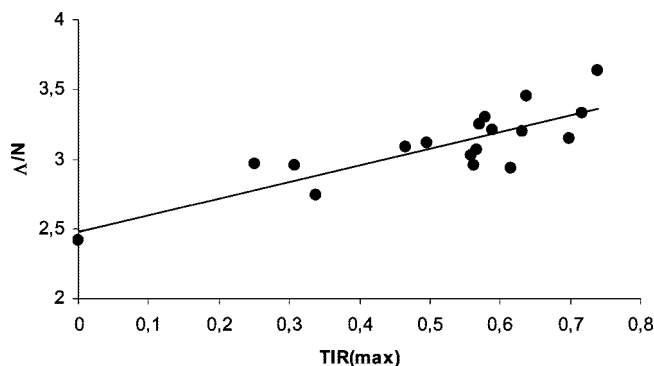
Figure 6. The scatter plot between Λ per number of π-electrons vs *TIR(max)* for cata-condensed benzenoids. Correlation coefficients R = 0.83 (for all points) and R = 0.70 (benzene not included).

the electrophilic substitution does not occur). This is general for all benzenoids hydrocarbons considered (data not shown). Therefore *TIR_min* should not be taken into consideration as a descriptor of reactivity.

CALCULATIONS

The magnetic susceptibility exaltations (Λ) for systems (**1**)-(**35**), see Table 1, were evaluated by using eq 1. The magnetic susceptibility computations were made at the CSGT/B3LYP/6−311G** level of theory[36] by using optimized geometries at the B3LYP/6−311G** DFT level.[37] All molecules in eq 1 corresponded to real minima on the potential energy surface, with no imaginary vibrational frequencies. This method reproduces reasonably well the

Figure 7. The scatter plot of *HOMA* vs *TIR(max)*. Correlation coefficients R = −0.86 (for all points) and R = −0.78 (benzene not included).

experimental data of magnetic susceptibilities for benzenoid hydrocarbons. For example the calculated and experimental values are as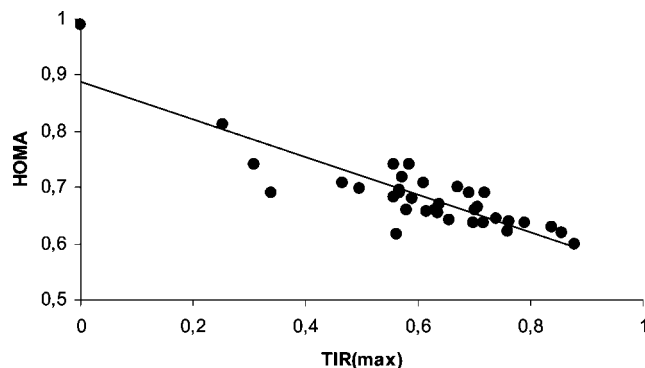 follows: benzene: −53.0 cgs-ppm (calc.) and −54.8 cgs-ppm[38,39] (exp.); naphthalene: −90.3 (calc.) and −89.8 cgs-ppm,[39,40] or −91.6 cgs-ppm,[39,41−43] or −93.6 cgs-ppm[39,44] (exp.); anthracene: −128.4 cgs-ppm (calc.) and −123.7[39,40,45] cgs-ppm (exp.); pyrene: −151.5 cgs-ppm (calc.) and −149.4[39,41,46] or −154.9[39,46,47] (exp.); chrysene: −160.7 (calc.) and −160.7 cgs-ppm[39,44,47,48] (exp.); perylene: −157.4 cgs-ppm (calc.) and −159.6 cgs-ppm[39,49] (exp.). The calculations were performed using the Gaussian 03 program.[50]

The values of *HOMA*, the HOMO−LUMO gap, and exaltation of magnetic susceptibility, Λ (Table 1), were calculated from optimized structures at the same (B3LYP/6−311G**) level of theory. The values of *REPE* were taken from the paper by Hess and Schaad.[51] They are given in Table 1.

RESULTS AND DISCUSSION

Reactivity is associated with a particular site in a molecule—the reaction site. Hence, in cases when there are a few possible reaction sites—positions in benzenoid hydrocarbons—it has to be decided which position should be taken as a criterion of aromaticity. The most reactive position should be decisive about the overall (kinetic) stability of a molecule. Thus, the problem is to find this kind of position in polycyclic benzenoid hydrocarbons. The classical works on electrophilic aromatic substitution in benzenoid hydrocarbons came from the mid-twentieth century,[52] was summarized in a monograph by Streitwieser,[53] and then reviewed extensively several decades ago.[31] Streitwieser defined reactivity constants for aromatic substitution (mostly the rate constants of nitration in acetic anhydride), σ_r^+, where *r* is the position in the benzenoid hydrocarbon molecule.[54] These constants described well various kinds of reactivity of a given position.[54] It was also shown that physicochemical properties of the functional groups attached to position *r* in a hydrocarbon follow in a regular way the changes in σ_r^+ values.[55,56]

The following question arises: do the topological indices TIR_r of reactivity follow any relationship with the experimental indices σ_r^+. The data of Table 2 and Figure 2 answer this question.

The scatter plot in Figure 2 illustrates the fact that the purely topological index of reactivity for given positions,

TIR_r, correlates with the experimentally described reactivity in these positions given by σ_r^+. Thus, at least approximately, the maximum values, *TIR(max)*, of TIR_r for a given position in a given molecule of a benzenoid hydrocarbon can be used as a reactivity-based index of aromaticity. Figures 3 and 4 show how this approach works in comparison with global aromaticity indices such as *REPE*[51] and the HOMO−LUMO gap computed by use of Gaussian 03 at the B3LYP/6−311G** DFT level of theory,[50] which are also considered as measures of stability.[57] Figures 3 and 4 present scatter plots of *REPE* and the HOMO−LUMO gap versus *TIR(max)*. Taking into account the very approximate way of estimation the reactivity index *TIR* as well as values of *REPE* and the HOMO−LUMO gap, the observed correlation should be taken as a convincing argument that there is some equivalency between the maximal reactivity of a given benzenoid hydrocarbon and its energetic characteristic.

A completely different picture results from a correlation of the exaltation of magnetic susceptibility data divided by the number of π-electrons with the *TIR(max)* values for the whole data set of all molecules of benzenoid hydrocarbons for which data are available (35 nonisoarithmic[58,59] molecules listed by Hess and Schaad).[51] As is apparent from Figure 5, there is no correlation at all. However, if only molecules of cata-condensed benzenoid hydrocarbons (catafusenes) are taken into account, as in Figure 6, a correlation becomes evident, qualitatively even acceptable.

The disagreement between scatter plots in Figures 5 and 6 may result from the fact that, in peri-condensed benzenoid hydrocarbons (perifusenes), the overall magnetic susceptibility is a sum of ring currents, which for some rings are clockwise and for other ones are anticlockwise. Coronene is the best illustration.[60] Moreover, some support comes also from recent studies showing that there is no direct relationship between resonance energy and magnetic response properties.[61] Since *TIR(max)* is related to *REPE* (Figure 3), the lack of correlation observed in Figure 5 seems to be understandable.

Finally, the relationship between *HOMA* and *TIR(max)* shown by Figure 7 illustrates also an acceptable dependence between these indices. Again the correlation is not as good as for the previous relationships (Figures 2 and 3), but note that (when taking all points into account) $100 \times R^2 = 74.0$ means that 74.0% of the total variance of *HOMA* values is explained by the linear regression presented in Figure 7.

In conclusion it may be said that for a homogeneous set of 35 benzenoid hydrocarbons, all four criteria of aromaticity, represented by numerical indices describing energetic, magnetic (for catafusenes), geometric, and reactivity properties, of the whole molecule are in a qualitative agreement. It is important to mention that all compared quantities are intensive in nature, whereas the extensive quantities such as exaltation of magnetic susceptibilities and resonance energies are calculated per π-electron.

Supporting Information Available: Cartesian coordinates, absolute electronic energies at B3LYP/6−311G** zero

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point vibrational energies (ZPE) at B3LYP/6−311G** and magnetic susceptibilities calculated at CSGT/B3LYP/6−311G** for molecules presented in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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