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Reactivity Indices for Radical Reactions Involving Polyaromatics

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The reactivity of polyaromatics involved in various radical reactions is studied. The reactions under study are hydrogen abstractions by a methyl radical and additions to double bonds both intra- and intermolecular. The chemical reactivity of the involved molecules is described through different properties, which are calculated within the density functional theory (DFT) framework. The softness reactivity index is tested on its usefulness and reliability to provide information about the reactivity of the global molecule or about chemical selectivity. The applicability of the hard and soft acids and bases (HSAB) principle for bimolecular radical reactions is illustrated by comparing the results of the softness-matching criterion with kinetic and thermodynamic data. For large polyaromatic molecules several magnetic indices, in particular, magnetic susceptibilities, chemical shifts, and nucleus independent chemical shifts (NICS), are computed to quantify the aromatic character of the involved species. The applicability of these magnetic indices in the case of radical reactions is validated by comparing with kinetic results obtained from transition state theory.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most studied chemical compounds during the last years.[1,2] Some PAHs are very carcinogenic substances and are known to be present in more than trace amounts in the earth's atmosphere, soil, and water.[3] PAHs have also been detected in celestial objects such as meteorites and in interstellar space.[3−7] They play an important role during combustion processes of organic substances such as coal, oil, and garbage since they are formed as byproducts due to incomplete combustion.[8−11] Knowledge of their characteristics and their formation processes has attained a lot of theoretical and experimental attention. Several theoretical studies have concentrated on reaction paths that enable the growing of the aromatic species. Usually this is done by classical kinetic studies using an appropriate rate theory and an accurate ab initio method to provide the microscopic ingredients, such as geometries and frequencies. This procedure requires theoretical calculations on the reactants, the transition states, and the products.[9,12] This methodology was followed by some of the authors on radical reactions which are important during coke formation, which is a side process of thermal cracking of hydrocarbons.[13−18]

In this work various of these radical reactions (hydrogen abstraction by a methyl radical and inter- and intramolecular additions) that enable the growth of the PAHs are studied from the point of reactivity indices such as hardness and softness.[19] These were well-known properties within chemistry, although they were mainly defined on a qualitative basis.[20] A theoretical framework to derive reactivity indices from first principles was provided within density functional theory (DFT). For a recent review, we refer to Geerlings et al.[21] Site-selectivity is another important aspect and can be characterized by local descriptors, such as the Fukui function.[22] The concept is a generalization of the frontier molecular orbital reactivity indices (FMO) of Fukui,[23] where all responses to any change of charges, geometry et al. take place in the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), while the core orbitals remain unaffected.

The reactivity indices provide knowledge that can be used to assess the importance of various reaction routes in technologically important processes such as coke formation and can support the elimination of certain reaction paths. The calculations based on reactivity indices are computationally less intensive (but also less detailed) because all information is obtained through study of the reactants only. Consequently, only information about the onset of the chemical reaction should be expected. In this paper we test the reliability of reactivity indices to provide a correct chemical reactivity picture of radical reactions. This approach is compared with earlier reported kinetic results and correlations between the two methods are established. From the concept of reactivity descriptors, it is clear that they can mainly describe kinetically controlled reactions. On the other hand, there might be a correlation between the rate constant and the equilibrium constant, a relation which is incorporated in the noncrossing rule (for further details, we refer to ref 24). In this view, reactivity indices can be expected to provide information about the thermodynamic aspects in some cases.

In our specific case, in which we are dealing with large polycyclic aromatic structures, important information about the reaction mechanism can also be revealed by studying the aromaticity.[25,26] Aromaticity is a complex property, which is usually described by three aspects: high stability, low reactivity, and sustained induced ring current.[27] Many efforts have been made to quantify aromaticity and a number of criteria is

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commonly used to characterize the aromatic behavior of molecules. One distinguishes geometric (bond length alternation and bond order), energetic (stabilization energies), and magnetic (chemical shifts, diamagnetic susceptibility anisotropy, exaltation, nucleus independent chemical shifts (NICS) and ring current effects) criteria.[27] Important contributions within the study of the reactivity of PAHs and their correlation with aromaticity were made by Schleyer and co-workers,[28] and applications on several types of reactions have provided evidence for the utility of these magnetic descriptors, such as NICS.[29−31] Also DFT-based reactivity indices can be used as indicators of aromaticity.[32]

In general, studies on the DFT-based reactivity indices of radical reactions have so far been very limited. Pioneering work on reactions of free radicals has been done by Pearson.[33] Some reactivity indices have been calculated,[34−36] and Chandra et al.[37] have tested the HSAB principle for the addition of free radicals to olefins using the condensed values of the Fukui function and softness. Generally, the attack takes place at the less substituted carbon atom of the double bond, in good agreement with other results. They also found good correlations between the hardness and the activation energy in the case of reactions of the OH radical with halomethanes.[38] The addition mechanism of fluoromethyl radicals to fluoroethylenes has been studied by Korchowiec et al.[39] Hirata et al. studied the electronic excited states of PAH radical ions through use of time-dependent DFT.[40] Very recently, Nguyen et al. performed a critical analysis on the use of reactivity descriptors for rationalizing radical reactions.[41]

In this paper, a detailed investigation about the reactivity indices of several radical systems is provided and furthermore the applicability of the HSAB principle for bimolecular radical reactions is studied. The validity of the HSAB principle for other types of reactions has been discussed earlier,[42−46] and the extension of the principle on its applicability to the time-evolution of chemical reactions has recently been studied.[47] In this paper, we will also investigate possible correlations between kinetic data and results derived from DFT-based indices. Further information about the reactivity of the different radical reactions is provided through the study of the aromatic behavior of the involved molecules.

2. Theoretical background

The **reactivity indices** discussed here are defined as derivatives of the electronic energy $E[N, v(\mathbf{r})]$ with N the total number of electrons and $v(\mathbf{r})$ the external potential due to the nuclei.[19] Three categories are distinguished:[48] global indices, local indices, and kernels, which will be left out of this discussion.

The global indices—chemical potential μ, the hardness η, and the softness S—can be computed applying the finite difference method using the vertical ionization potential and electron affinity.[19]

For our purposes, the local indices, varying from point to point, are of higher importance. They provide direct information about the site-selectivity within a molecule.

The Fukui function $f(\mathbf{r})$ is the normalized local softness $s(\mathbf{r})$:[20]

$$s(\mathbf{r}) = f(\mathbf{r})S \tag{1}$$

As N does not represent a continuous variable but only takes integer values,[49] three distinct classes of indices appear, respectively, for (i) nucleophilic attack, where the molecule gains an electron, (ii) electrophilic attack, where the molecule loses an electron, and (iii) radical attack, where the total electron number remains unchanged. The condensed Fukui functions give an approximate value for the local Fukui function at the position of an atomic center and are obtained by integration of the Fukui function over an atomic region:[50]

$$f_k^+ = q_k(N+1) - q_k(N)$$

$$f_k^{\,-} = q_k(N) - q_k(N-1)$$

$$f_k^{\,0} = \frac{1}{2}(q_k(N+1) - q_k(N-1))$$

with $q_k(N)$ the electron population on the kth atom of the molecule with N electrons. To calculate the density in an atomic region, different population analysis methods can be used. Geerlings et al. have studied the sensibility of the Fukui function in terms of the population analysis method.[51]

The above-mentioned indices are applied in the hard and soft acids and bases (HSAB) principle, which was originally suggested in 1963 by Pearson:[20]

"Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties."

Several attempts to prove the HSAB principle were suggested in the literature; for a review, see ref 21. The principle states that the interaction between a system A and a system B will be favored in the case of global softnesses which are close to each other, the optimum being reached when $S_A = S_B$ (in terms of global indices).[52] The local version of the principle states that the optimal interaction sites may be characterized by the condition $s_{Ai} = s_{Bj}$ in case the ith atom of system A interacts with the jth atom of system B.[53] This softness-matching criterion provides the working equations for testing the validity of the HSAB principle and therefore we introduce the variable $\Delta s_{i,j}$:

$$\Delta s_{i,j} = s_i - s_j \tag{2}$$

which defines the difference between the condensed softness of the ith atom of the first molecule and the jth atom of the second molecule. The minimal $\Delta s_{i,j}$ indicates the preferred reaction sites i and j in the reactants.

It has been shown by Parr et al. that reactivity indices (and in particular the hardness) can also be used as indicators of aromaticity,[27] based on the fact that both hardness and aromaticity are measures of high stability and low reactivity. Another important characteristic of aromaticity is the possibility to sustain induced ring currents. On the basis of these three aspects, different criteria to describe the aromatic character of molecules are used.[26,32] The most important magnetic descriptors are based on NMR theory,[54] and according to Jiao et al.[29] "the magnetic criterion is the most specific and unambiguous manifestation of aromaticity". Another important factor is the geometry, as reflected in the planarity of the molecule and the equalization of bond lengths.

The magnetic probes used in this work are the diamagnetic susceptibility anisotropy $\Delta\chi$, the chemical shift δ, and the nucleus independent chemical shift (NICS). The first descriptor is defined as the difference between the out-of-plane component χ_3 and the average of the in-plane components χ_1 and χ_2:

$$\Delta\chi = \chi_3 - \frac{1}{2}(\chi_1 + \chi_2) \tag{3}$$

This quantity is however size dependent.[55] The chemical shift δ is defined as

$$\delta = \sigma_{\mathrm{TMS}} - \sigma \tag{4}$$

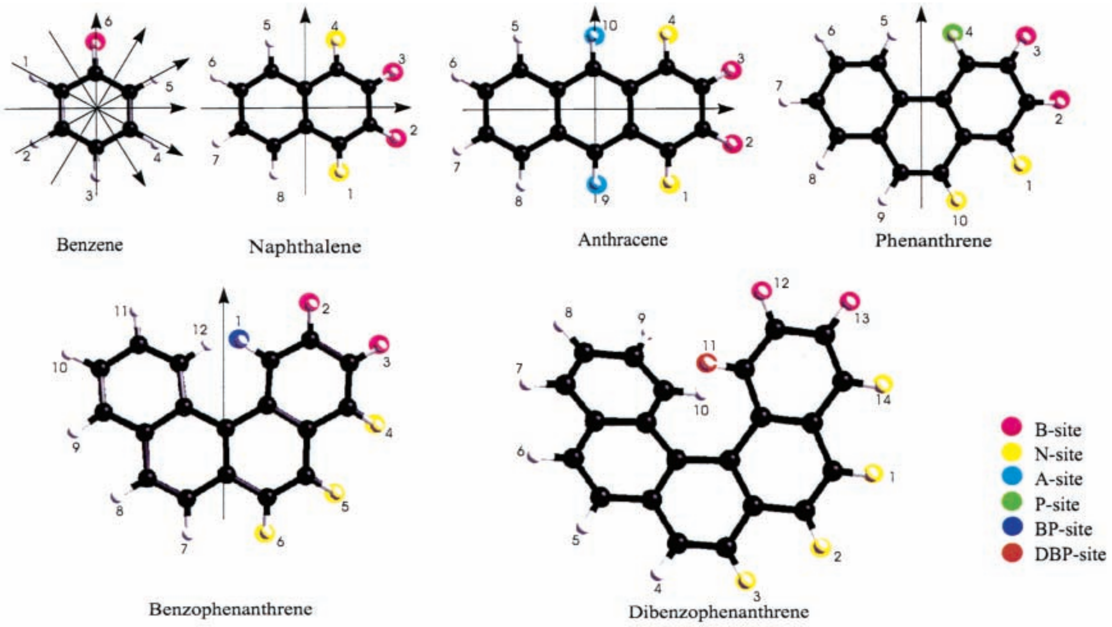

Figure 1. Benzene and some polycyclic aromatic molecules (PAHs) studied in the hydrogen abstraction reactions. The symmetry axes lying inside the molecular plane are shown. The different sites are indicated.

with σ the isotropic part of the shielding tensor. The reference molecule used in NMR experiences is tetramethylsilane (TMS). The chemical shifts are less obvious indicators of aromaticity because they mainly monitor local effects and to a much lesser extent global ones (like ring currents).[56] The NICS, as defined by Schleyer et al.,[57] is the absolute magnetic shielding in the center of a ring and consist of a diamagnetic and a paramagnetic contribution.[58] Schleyer et al. recommended the use of the NICS values calculated at 1 Å above the ring centers as aromaticity index, rather than the NICS values computed in the ring centers.[58] The main advantage of the NICS values is that they are less dependent on the ring size and that they do not require a reference system. The disadvantage is that NICS gives only a reliable absolute indication in the case of large ring sizes, where local shielding effects can be ignored.

3. Computational Details

All ab initio calculations are performed within the Gaussian 98 software package,[59] using Becke's three-parameter hybrid B3LYP functional.[60] The molecular orbitals are expanded in a triple-ζ 6-311G basis augmented with a set of single d and p polarization functions. The B3LYP functional is known to give a reliable and quantitatively good description of geometries, frequencies and reaction barriers for radical reactions.[61] Several studies have also indicated that B3LYP, and even Hartree–Fock, methods are sufficiently accurate for estimating the relative stabilities of different conformers, especially when large basis sets including polarization functions are used.[61d,62] According to a specific study on the activation energies of radical addition and abstraction reactions,[63] it was found that DFT/B3LYP methods are able to reproduce qualitative trends in the activation energies when compared to CBS-QB3 methods. When comparing with experimental activation energies the resemblence is even more striking. Only hydrogen abstractions in which a hydrogen radical is involved may be less accurate.

The condensed Fukui functions and softnesses are systematically calculated using the natural population analysis (NPA). This population analysis is known to give reliable results,[64] especially for molecules with low polarizibility which are subject of this study. Therefore, other population schemes such as CHELP[65] and MK (Merz–Singh–Kollman),[66] which are based on the electrostatic potential, are not taken into consideration. The Mulliken scheme is known to be less accurate, since it is strongly dependent on the basis set.

The NMR quantities are calculated using the CSGT method. The CSGT (continuous set of gauge transformations) method, developed by Keith and Bader,[67] achieves gauge-invariance by performing a continuous set of gauge transformations, one for each point in real space. An accurate three-dimensional description of the first-order electronic current density is obtained, from which the shielding tensors and magnetic susceptibility can be determined. For a review of CSGT and other DFT methods for calculating NMR properties, we refer to Helgaker et al.[68] Studies on a large number of molecules reveal that the CSGT method is computationally very efficient and accurate.[69] This method demands the use of a large basis to obtain reliable results.[67,70]

4. Results and Discussion

4.1. Applicability of HSAB Principle. Hydrogen Abstraction. Figure 1 shows benzene (B) and the polycyclic aromatic molecules (PAHs) naphthalene (N), anthracene (A), phenanthrene (P), benzophenanthrene (BP), and dibenzophenanthrene (DBP). The molecules BP and DBP are characterized by a nonplanar geometry, due to steric interactions between adjacent hydrogens. Hydrogen abstraction reactions by an approaching methyl radical on each of these molecules are studied. This leads to the formation of a variety of organic radicals (aryl radicals) and methane. Within a specific molecule abstraction can occur at different places, resulting in different radicals which cannot be related to each other by symmetry operations. For example if one looks at naphthalene, there are two possibilities: abstraction of hydrogen number 1 (and equally 4, 5, and 8) or abstraction of hydrogen number 2 (and equally 3, 6, and 7). Within the field of polyaromatics it may be convenient to introduce a specific nomenclature to identify the various positions.[15,71] One distinguishes between benzene-, naphthalene-, anthracene-, phenanthrene-, benzophenanthrene- and dibenzophenanthrene-like sites. This nomenclature is clarified in Figure 1, where all hydrogens are assigned to a specific site. The different sites X are characterized in the following way:

TABLE 1: Hardness η and Condensed Softness Differences $\Delta s_{C,Hi}$ Calculated at the B3LYP/6-311g Level in the Case of Hydrogen Abstraction Reactions, Where Experimental Results Are Given in Italics in Parentheses**[75]

η (eV)					
B	N	A	P	BP	DBP
5.556 (*5.3*)	4.237 (*4.2*)	3.396 (*3.3*)	3.998 (*3.8*)	3.581	3.485

	$\Delta s_{C,Hi}$					
i	B	N	A	P	BP	DBP
1	1.951	2.089	2.090	2.105	2.152	2.098
2	1.951	2.072	2.069	2.086	2.094	2.096
3	1.951	2.072	2.069	2.092	2.089	2.102
4	1.951	2.089	2.090	2.122	2.102	2.102
5	1.951	2.089	2.090	2.122	2.097	2.096
6	1.951	2.072	2.069	2.092	2.093	2.098
7		2.072	2.069	2.086	2.093	2.116
8		2.089	2.090	2.105	2.097	2.101
9			2.087	2.087	2.102	2.115
10			2.087	2.087	2.089	2.169
11					2.094	2.169
12					2.152	2.115
13						2.101
14						2.116

we count the number of intermediate carbon atoms at both sides between the specific hydrogen center and the adjacent hydrogen atoms. The thus obtained numbers *A* and *A′* are used to classify the X-like sites according to *A*/*A′*. As such the α- and β- protons in naphthalene[72] are identified as $^2/_2$ and $^3/_2$ sites, respectively. Applying this procedure for all the hydrogens, we obtain $^2/_2$ in the case of X = B, $^3/_2$ in the case of X = N, $^3/_3$ in the case of X = A, $^4/_2$ in the case of X = P, $^5/_2$ in the case of X = BP, and $^6/_2$ in the case of X = DBP.

From the knowledge of the reactivity indices, defined in section 2, and the HSAB principle, one should be able to predict which hydrogen atom is preferred for abstraction. The availability of an extended database of ab initio kinetic studies on these hydrogen abstraction reactions, performed by the authors,[17,73] can be used to validate the concept of reactivity indices within the context of the HSAB principle. The HSAB predictions can be done on the basis of properties of the reactants only, indicating the advantage of reactivity indices compared to more elusive, reaction path type kinetic studies. The computed global hardnesses of the studied molecules are given in Table 1, and it is seen that most molecules can be considered as soft (except for B which one could consider to be intermediately hard). Consequently, hard−hard effects are of less importance.[74] Note that the experimental hardnesses are quite well reproduced. The global hardness of the attacking methyl radical is 5.478 eV, indicating the intermediate hard character of this radical. Because of the above considerations the soft−soft model should provide an adequate description for the studied reactions. The condensed local softness of the carbon atom of the methyl radical amounts to 2.192 1/au. According to the softness-matching criterion the attack of the methyl radical will take place at the hydrogen atom of the hydrocarbon whose condensed softness is closest to the value of the methyl radical. For that purpose it is instructive to analyze the condensed softnesses of the various hydrogen atoms *i* of the polyaromatic with reference to the value 2.192. These $\Delta s_{C,Hi}$ values are given in Table 1 (the numbers in the first column refer to the labeling of the hydrogen atoms as given in Figure 1 and are in accordance with the IUPAC convention). It should be stressed that hydrogen atoms belonging to the same X-site do not necessarily have the same $\Delta s_{C,Hi}$ value, as these sites cannot be transformed into one another by a symmetry operator belonging to the molecular point group. With the exception of DBP, the lowest $\Delta s_{C,Hi}$ values are found at a benzene-like site of the molecules. According to the HSAB principle, abstraction of the hydrogen atom at these sites should be less activated. This rule does not hold for DBP where the lowest $\Delta s_{C,Hi}$ values are found at naphthalene-like sites (Table 1). This is probably due to the nonplanarity of the DBP-radical.

The validity of the HSAB conclusions is now tested by comparing with kinetic and thermodynamic quantities for the hydrogen reactions under study. Is there any correlation between the local softness and some specific kinetic parameters and/or thermodynamic quantities (activation energy, reaction enthalpy, ...)? First, comparison is made with the kinetic parameters of the abstraction reaction: the activation energy and the pre-exponential factor defining the reaction rate. These quantities were calculated within the framework of transition state theory (TST)[17] and are determined by microscopic quantities, such as the reaction barrier at 0 K (ΔE_0: this is the energy difference between the reactant and the transition state, including the zero-point energy difference) and the partition functions belonging to the reactants and transition states. Since the various reactivity indices playing a role in the HSAB principle are systematically determined at 0 K, it is more plausible to use the reaction barrier ΔE_0 at 0 K as comparative material instead of the activation energy. They are given in Figure 2. The reaction $B \rightarrow B_R$ and abstraction at other benzene-like sites turns out to yield the lowest reaction barrier (62.33 kJ/mol for N, 62.23 kJ/mol for A, and 62.82 kJ/mol for P), supporting a preference for abstraction of a hydrogen atom bound to a benzene-like site. Thus, the HSAB principle is a good prediction model for the kinetics of abstraction of H atoms by methyl radicals on polyaromatics.

At the next stage, one can look at the stability of the formed radicals after abstraction at various positions. The most stable radicals are depicted in Figure 2 (the ground state energies of all possible radicals are given in Table S1 of the Supporting Information). The radicals which are predicted to be formed by the HSAB principle are not the most stable ones. This clearly illustrates that the HSAB principle correlates nicely with kinetics but not necessarily with thermodynamic properties. This could be expected since reactivity indices only give information on the onset of a chemical reaction.[24] Following this discussion an Evans−Polanyi relation which establishes a correlation between the reaction barrier and the reaction enthalpy[76] should not be valid for the studied reactions. The validity of such correlation on hydrogen abstractions was thoroughly discussed in a recent work by some of the presenting authors.[73] It was found that Evans−Polanyi holds for abstractions at a substituted benzene ring with a methyl radical leading to phenylic, alkylic, allylic and benzylic radicals. This is illustrated in Figure 3 where the reaction barrier is plotted vs the reaction enthalpy at 0 K. At the same figure, the results of the hydrogen abstractions at the polyaromatics are shown (indicated by B, N, A, P, BP, and DBP). The quasi-linear correlation between the reaction barrier and the stability of the formed radicals is no longer valid. Some nonlinear clustering is observed for the hydrogen abstractions discussed in this work. This clustering within the subcategory of reactions leading to aryl radicals indicates that the reaction enthalpy cannot be regarded as a suitable reactivity index for hydrogen abstraction reactions. This is not too surprising, since it concerns subtle differences within a subset of reactions. For further information about reaction enthalpies and bond energies of benzene and several polyaromatics, we refer to ref 77. We stress that the HSAB principle apparently succeeds in predicting

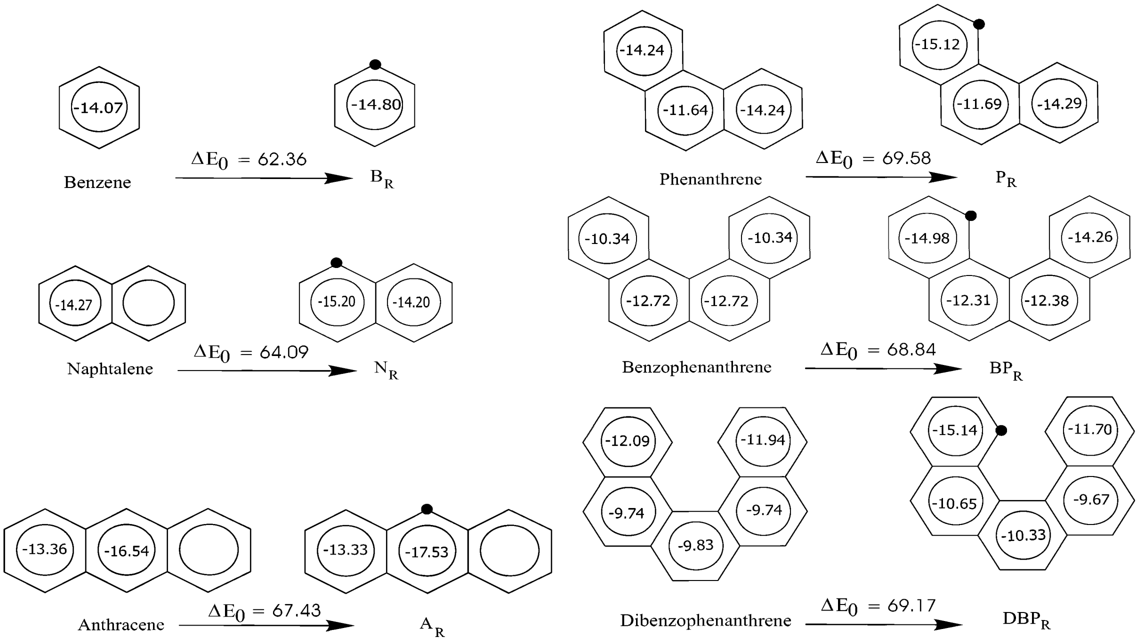

Figure 2. NICS values of molecules involved in hydrogen abstractions. NICS values of the planar molecules are calculated 1 Å above the plane of the ring; NICS values of the nonplanar molecules are calculated in the plane of the ring. The reaction barriers ΔE_0 at 0 K are given (in kJ/mol).

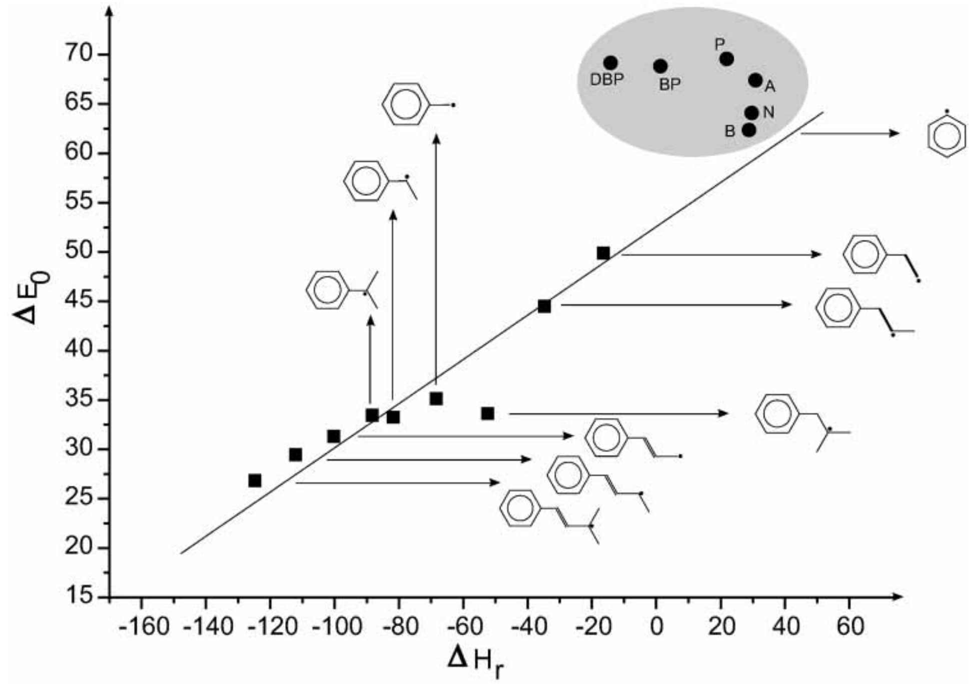

Figure 3. Correlation between ΔE_0 (in kJ/mol) and ΔH_r (at 0 K, in kJ/mol) for all types of hydrogen abstraction reactions (most of the values were taken from ref 73). Clustering is observed within the subcategory of phenylic radicals as discussed in this paper.

correctly the subtle differences in activation energies. This is in line with previous observations where the DFT-based reactivity indices were found to probe mainly the kinetic aspects of a reaction.[21] We would like to emphasize again that a correlation between HSAB results and thermodynamic properties can be expected in the case of noncrossing reactions. For the hydrogen abstraction reactions studied in this work, no such correlation was however found.

Addition Reactions. As a second class of bimolecular radical reactions, we consider addition reactions of radicals to several gas-phase components, such as ethene, propene, ethyne, and propyne. These reactions are of fundamental importance in this field of hydrocarbon chemistry as they lie on the basis of the growth of surface radicals toward larger polyaromatics.[13] We make some particular selection of addition reactions figuring in polyaromatic growth and for which ab initio results are available as comparative material for the analysis with the softness differences Δs. The kinetics of additional reactions were calculated by analogous procedures as outlined in ref 13. The studied radicals are the ethylbenzene radical (R1), phenylacetylene radical (R2), butylbenzene radical (R3) and 1-phenyl-1,3-butadiene-4-yl radical (R4) (Figure 4). The possible reaction paths are illustrated in Figure 4. A relevant question is which olefins are the most reactive for addition reactions.

In the case of an electrophilic addition to alkenes and alkynes the regioselectivity is usually described by applying the Mark-

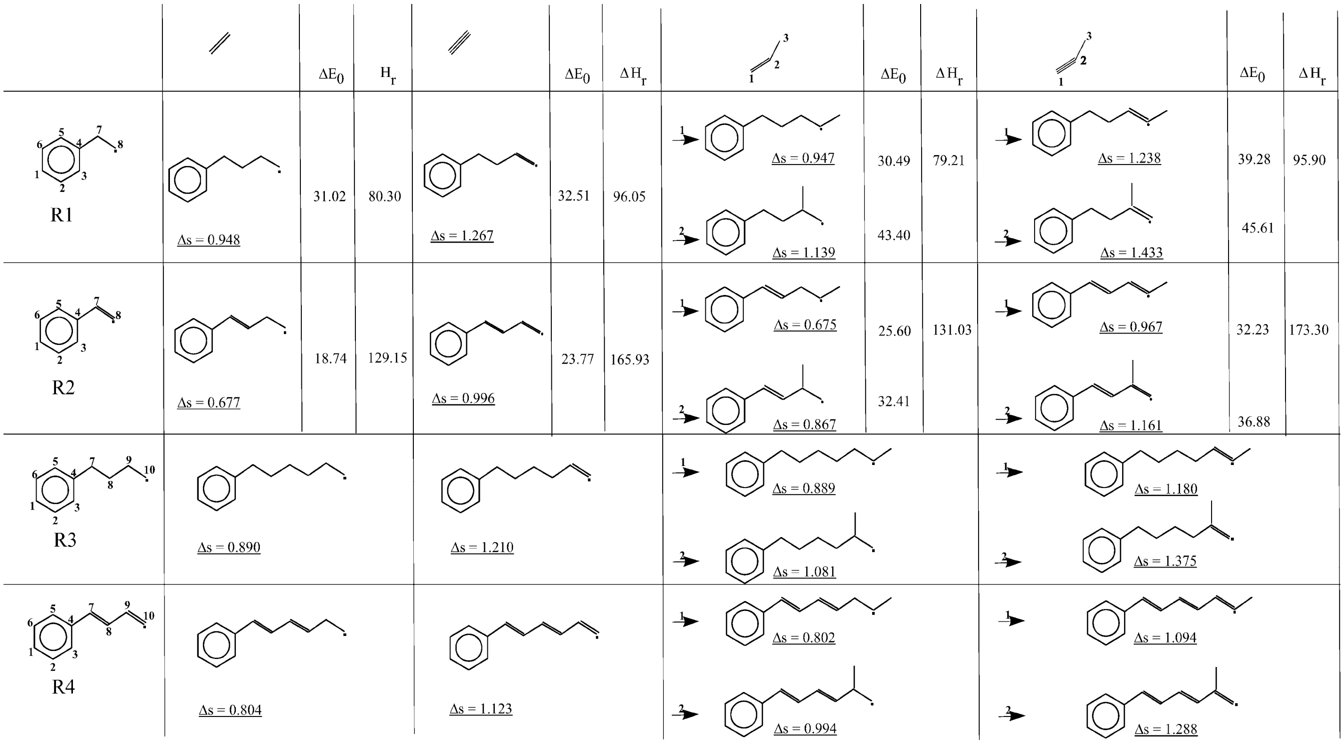

Figure 4. Schematic representation of the addition reactions. Minimal softness diferrences Δ*s* according the softness matching criterion and reaction barriers ΔE_0 (in kJ/mol) and reaction enthalpy values (in kJ/mol) are included.

ovnikov rule, which states that the least electronegative part of the reagent attaches itself to the carbon atom that has the most hydrogens already attached to it (least substituted carbon atom). During this addition reaction, an intermediate carbocation is formed and the positive charge is spread out over the neighboring carbon atoms, increasing the stability of the total system. Aizman et al. have recently studied the Markovnikov rule in the light of site activation models and found good correlations with variations in the Fukui function.[78] In the case of a radical addition reaction the regioselectivity of the reaction can analogously be described, using hyperconjugation arguments.

The condensed softness values are taken up in Table S2 of the Supporting Information. The maximum value of the local softness usually indicates the most reactive part of the molecule. For the radicals, this reactive part is always located at the radical center, as could be expected. As in the previous section, the validity of the HSAB-principle is shown by comparing the softness-matching criterion with the reaction barrier ΔE_0. The kinetic results and the softness differences Δ*s* are given in Figure 4. The Δ*s* values are the minimal differences between the condensed softnesses of the carbon atom of the radical center on one hand and the carbon atoms of the olefin on the other hand.

Several conclusions can be made.

1. The site-reactivity of the nonsymmetric molecules propene and propyne is in accordance with the Markovnikov rule: the addition of the radical will preferentially occur at the least substituted carbon atom involved in the double, respectively triple bond. The minimal softness Δ*s* shows a lower value for reaction path 1 compared with reaction path 2 (see Figure 4). This preference for reaction path 1 is also supported by the reaction barriers reporting large differences between the two paths (average difference of 7.67 kJ/mol). The first reaction path gives rise to a secondary radical which is more stable than a primary radical.

2. Minimal softness differences may serve as a measure for the reactivity of the different precursors. The lowest Δ*s* values are observed in the addition reactions to propene and ethene, and following the HSAB principle they are assigned as the most reactive precursors. The softness differences are distinctly larger for the two other remaining precursors ethyne and propyne. The deviations between the Δ*s* values of the reactions with ethene (ethyne) and reactions with propene (propyne) are small. This is due to the fact that condensed reactivity indices only provide information concerning a limited molecular region. The chain length is of little importance here, and the methyl substituent in the chain does not substantially influence the reactivity index of the carbon atom number 1 (see Figure 4). This carbon atom is mainly influenced by the double and triple bonds, respectively.

The Δs values are in agreement with the ΔE_0 values and support the observation that addition to precursors exhibiting a double bond is favored with regard to triple bonds.

As discussed in the previous section, no correlation can be found between the HSAB predictions and thermodynamics. The reaction enthalpies ΔH_r are depicted in Figure 4. It is also seen that no linear correlation can be found between the ΔH_r values and the ΔE_0 values. We will not go into detail about this problem, but refer to the review of Fischer and Radom about radical addition reactions, where the validity of the linear Evans–Polanyi relation is thoroughly discussed for this class of reactions.[79]

3. On basis of the Δ*s* values, we conclude that R2 is more reactive than R4, followed by R3 and R1. This is in line with chemical intuition since R2 and R4 are both vinylic radicals and are more reactive than the primary radicals R1 and R3. This is completely confirmed by the trend of the energy barrier ΔE_0 predicting much lower values for R2, emphasizing the large reactive character of this radical.

4.2. Effect of Aromaticity on the Reactivity of PAHs. The relation between aromaticity and reactivity can be studied through several indices.[27,32] In this paper, we focus on the magnetic indices originated from NMR theory. Furthermore, it is instructive to study the evolution of the aromaticity descriptors along the reaction path. In the following section, we try to

TABLE 2: Magnetic Properties of Hydrogen Abstraction and Cyclization Reactions[a]

molecule	$\Delta\chi$ (ppm cgs)	δ (ppm)	NICS(0) (ppm)	NICS(1) (ppm)
benzene[b]	−65.65 (*−62.9*)[d]	6.34	−12.80 (*−11.5*)[e]	−14.07
B$_R$[b]	−59.39	6.16	−16.16	−14.80
naphthalene[b]	−127.36 (*−130.3*)[d]	6.67	−13.03 (*−11.4*)[e]	−14.27
N$_R$[b]	−119.82	6.55	−14.87	−14.66
anthracene[b]	−191.55 (*−204.8*)[d]	6.93	−13.16 (*−11.2*)[e]	−14.42
A$_R$[b]	−183.99	6.85	−14.60	−14.73
phenanthrene[b]	−178.80	6.88	−11.89(*−10.0*)[e]	−13.37
P$_R$[b]	−171.55	6.73	−13.35	−13.70
benzophenanthrene[c]	−226.58	7.02	−11.53	
BP$_R$[b]	−243.67	7.00	−12.81	−10.73
dibenzophenanthrene[c]	−247.12	6.88	−10.67	
DBP$_R$[c]	−252.23	6.84	−11.50	

molecule	ΔE_0 (kJ/mol)	$\Delta\chi$ (ppm cgs)	R	δ (ppm)	T	NICS^{av} (ppm)
B$_{RE}$	51.79	−65.38	−16.34E−2	6.29	−0.0768	−12.30
B$_{TS}$		−54.70		5.81		−6.84
N$_{RE}$	49.11	−131.13	−15.19E−2	6.70	−0.0730	−12.53
N$_{TS}$		−111.22		6.21		−8.95
A$_{RE}$	41.39	−191.38	−7.51E−2	6.97	−0.0596	−12.74
A$_{TS}$		−177.01		6.56		−10.19
P$_{RE}$	33.43	−174.55	−5.18E−2	6.80	−0.0210	−11.77
P$_{TS}$		−165.51		6.66		−11.11
BP$_{RE}$	50.03	−201.19	2.99E−2	6.60	0.0088	−9.63
BP$_{TS}$		−207.23		6.65		−9.89

[a] These values were calculated using the CSGT method at B3LYP/6-311 g** level. Other computed values are in italics. [b] Planar molecule. [c] Nonplanar molecule. [d] Reference 29c. [e] GIAO−SCF/6-31g*//B3LYP/6-31g*.[57]

establish a correlation between the magnetic indices—calculated at reactants, transition states and products—and the reaction kinetics.

Hydrogen Abstraction. The results of the magnetic susceptibility anisotropy, the average proton chemical shift and the average NICS value calculated on the aromatics and the subsequent formed radicals after hydrogen abstraction (computed at B3LYP/6-311g** level), are reported in Table 2. For this discussion we retained the most stable aryl radicals (see previous discussion) as displayed in Figure 2. For comparison also other computed values reported in the literature are included. Although the calculations have not been performed on the same computational levels, a qualitative agreement is found. The homologous series of linear acenes (with B, N, and A as the first three components) has been intensively studied[28] and the NICS values have also been subject of elaborated study, from semiempirical to ab initio studies.[80]

The differences between the magnetic indices of the reactants and the product species appear to be small, indicating that the change of aromaticity is not the driving force behind this type of reactions and thus no clear correlation between ΔE_0 (see also Figure 2) and the magnetic descriptors can be found. Furthermore, the magnetic susceptibility anisotropy $\Delta\chi$ and the average proton chemical shift δ show that the radicals are less aromatic than the reactants in the case of B, N, A, and P. The abstraction of a σ-electron indeed results in less shielding of the nuclei by the electron cloud and a decrease in aromaticity. The magnetic susceptibility anisotropy of BP and DBP suggests just the contrary since the anisotropy value of the radical is larger than the value of the reactant, whereas the average proton chemical shift remains almost constant. Both BP and DBP molecules are nonplanar, and by abstracting a hydrogen, the planarity of the substrate increases (in the case of BP$_R$ this leads to a perfect planar molecule) and thus the aromaticity increases, which is reflected in the values for the magnetic susceptibility anisotropy. As $\Delta\chi$ is a size-dependent quantity, a comparative study of magnetic indices can be instructive if limited to the same family of molecules but with different types of sites, such as A and P. Because of the geometric structure A (A$_R$) is more aromatic than P (P_R): electronic currents experience less resistance in a fully stretched geometry.[81]

For the sake of completeness, the averages of the computed NICS values of all rings of the involved polycyclic molecule are included in Table 2. Schleyer et al. recommended the use of the NICS values computed 1 Å above the ring center (NICS(1)) for planar molecules;[58] for nonplanar molecules the NICS values are computed at the ring centers (NICS(0)). All calculated NICS values are also given in Figure 2. The increase of NICS going from reactants to transition states is no effect of aromaticity, and will not further be treated here. Within this context, the influence of a biradical electron pair on the aromaticity for biradical benzynes has been studied earlier,[82] where more detailed information based on the dissected NICS values is presented.

Cyclization. In this section we focus on unimolecular radical cyclization reactions that eventually lead to a further growing of the polycyclic aromatic molecule. The reactants consist of an aromatic nucleus of conjugated benzene rings and an attached alkyl chain with the appropriate number of carbons to allow cyclization. After the reaction, an extra ring is formed as schematically shown in Figure 5. On the basis of geometrical considerations one distinguishes two classes: a first class wherein the aromatic nucleus is flat (B$_{RE}$, N$_{RE}$, and A$_{RE}$) and a second class where the clusters are folded due to large steric hindrance between the attached alkyl chain and the aromatic nucleus (P$_{RE}$ and BP$_{RE}$). To test the influence of the aromatic character of the involved species on the reactivity various magnetic indices of reactants and transition states are computed. For more details we refer to refs 17 and 18.

The theoretical values for the magnetic susceptibility anisotropy, the average proton chemical shift of the protons attached to the aromatic nucleus, and the average NICS values computed at the ring center are given in the lower part of Table 2. The last two magnetic properties include mainly information about the aromatic nucleus whereas the magnetic susceptibility anisotropy includes also effects of the attached alkyl chain. All indices lead to the following general conclusion: the transition states B$_{TS}$, N$_{TS}$, A$_{TS}$, and P$_{TS}$ are less aromatic than the

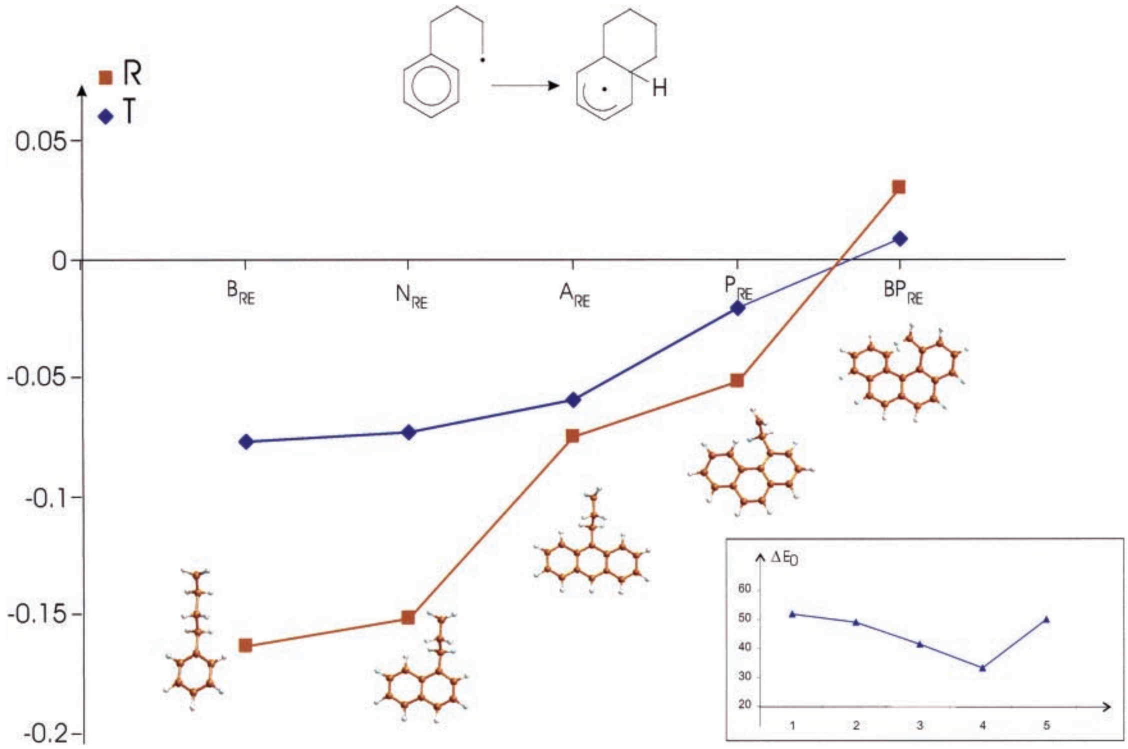

Figure 5. Relative dimensionless parameters *R* and *T* for the cyclization of the benzene, naphthalene, anthracene, phenanthrene, and benzophenanthrene reactant. The reaction barrier ΔE_0 is shown in the inset.

corresponding reactants. For these cyclization reactions, the transition states are less planar than the reactants due to the formation of the extra ring which prohibits the flowing of ring currents. Benzophenanthrene forms an exception: the transition state is more aromatic than the reactant. In this case, the reactant is strongly folded due to steric hindrance between the attached alkyl chain and the aromatic nucleus. During cyclization the deviations from planarity decrease.

It is now instructive to compare the magnetic indices with the kinetics calculated with TST. We only report reaction barriers at 0 K, in analogy with discussions in previous sections. The results are reported in Table 2 and are taken from ref 15. To compare various reactions, a suitable normalization is required for the magnetic susceptibility anisotropy since this property is size-dependent. We therefore introduce the relative dimensionless parameter *R*:

$$R = \frac{\Delta\chi(\mathrm{TS}) - \Delta\chi(\mathrm{RE})}{\Delta\chi(\mathrm{RE})} \tag{5}$$

Similarly, for the proton chemical shifts, we define *T*:

$$T = \frac{\delta(\mathrm{TS}) - \delta(\mathrm{RE})}{\delta(\mathrm{RE})} \tag{6}$$

δ represents the average chemical proton shift of the protons attached to the aromatic nucleus. The resulting values are given in Table 2 and their evolution in function of the type of the site is depicted in Figure 5. For the interpretation of these data it is important to stress that the properties *R* and *T* are mainly determined by the aromatic nucleus. A lower absolute value for *R* and *T* indicates a smaller aromaticity difference between reactant and transition state. Comparison between these magnetic parameters and the reaction barriers at 0 K indicates that the smaller the aromaticity difference between the aromatic nucleus in the transition state and reactant the lower the reaction barrier for cyclization. The sign of the parameters *R* and *T* indicates whether the aromaticity increases (positive sign) or decreases (negative sign) when going to the transition state. Only for BP does the aromaticity increase when going to the transition state. During this cyclization reaction, the molecule becomes more planar due to the presence of the benzylic type of radical. One can correlate this result with the highest barrier for cyclization. Both relative indices show a similar behavior and are in agreement with the kinetic results ΔE_0, as presented in Figure 5.

5. Conclusions

In this work, we studied the reactivity of various PAHs which are involved in radical reactions. The studied reactions are hydrogen abstractions, addition reactions, and cyclization reactions which play a significant role in several technologically important processes such as thermal cracking and soot formation. The reactivity is investigated by means of the HSAB principle, using the softness-matching criterion. The validity of the latter principle for the bimolecular radical reactions was shown, since the predictions of the HSAB principle are confirmed by kinetic results, such as reaction barriers. A correlation between the thermodynamic properties of the reactions (reaction enthalpy) is not always valid, which can be expected since DFT-based reactivity indices only give information on the onset of chemical reactions. Concerning various magnetic indices describing aromaticity, it was found that they give a consistent prediction of aromaticity which is in accordance with our chemical intuition. For hydrogen abstractions at PAHs, no correlation between the reaction barriers and the magnetic descriptors could be established, since aromaticity is not the driving force for these reactions. In the case of cyclization reactions of alkyl chains at an aromatic nucleus, the aromaticity change of the aromatic nucleus during the reaction is the determining reactivity factor and thus the magnetic indices are in good agreement with the reaction barriers at 0 K.

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Supporting Information Available: Tables of absolute energies of radicals induced by hydrogen abstraction (Table S1) and of condensed softness values for the molecules involved in the addition reactions (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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