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Headline Articles

Magnetic Resonance Energy and Aromaticity of Polycyclic Aromatic Hydrocarbon Dianions/Dications

Jun-ichi Aihara

Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422-8529

Received September 8, 2003; E-mail: scjaiha@ipc.shizuoka.ac.jp

Molecular dianions/dications of many polycyclic aromatic hydrocarbons (PAHs) have long been regarded as antiaromatics because of their global paratropic π-electron current. However, many of them are supposed to be aromatic due to their positive topological resonance energies (TREs). In order to reconcile such energetic and magnetic criteria of aromaticity, we derived a new TRE-like energetic quantity from the magnetic response of the π-system and called it a magnetic resonance energy (MRE). MRE was found to be highly correlative with TRE for a variety of PAHs and their molecular dianions/dications. We can now discuss energetic and magnetic criteria of aromaticity unambiguously on this theoretical basis. Many PAH dianions/dications indeed turned out to be aromatic with positive MREs even if they exhibit paratropic currents along the periphery of the π-system.

A ring current and ring-current magnetic susceptibility have been used widely as conventional measures of aromaticity.[1] There indeed is a close but rather complicated relationship between these quantities and the aromatic stabilization energy (ASE).[2–5] In 1996, Schleyer et al. proposed a new magnetic descriptor of aromaticity: a nucleus-independent chemical shift (NICS),[6–10] which is defined as the negative of the magnetic shielding. NICS values are usually computed at the ring centers. Negative and positive NICS values at ring centers have since been utilized as indicators of local aromatic and antiaromatic character, respectively. Thus, diatropic and paratropic π-electron currents were tacitly associated with aromaticity and antiaromaticity, respectively. Schleyer prefers to regard aromaticity as a manifestation of a π-electron current arising from the cyclic π-electron delocalization.[9,11]

When dealing with polycyclic aromatic hydrocarbons (PAHs), organic chemists used to refer to Platt's so-called periphery (or perimeter) model,[12] which emphasizes the contribution of the peripheral π-conjugation to aromaticity, with the inner bonds if any being considered as a bridging perturbation to the annulene skeleton. For example, dianions of anthracene and phenanthrene have been considered antiaromatic because they have $4n$ π-electrons along the periphery of the π-system and can sustain paratropic currents along the periphery.[13–15] In monocyclic π-systems, paramagnetic circulation of π-electrons is really associated with $4n$ π electrons.[16,17] However, no one has proved that the Hückel $(4n+2)$ rule and the periphery model can be applied to polycyclic π-systems. At least, the original form of the Hückel rule should be confined to monocyclic π-systems.[1]

In general, a π-electron current and related magnetic properties are highly dependent on molecular geometry,[2–5,18] whereas aromaticity itself represents primarily a state of energy. Within Hückel molecular orbital (HMO) theory, aromatic stabilization energy (ASE) or stabilization energy due to cyclic conjugation is dependent solely on the connectivity of conjugated atoms.[5,19–21] Therefore, there is a large possibility that a current induced along the periphery of a polycyclic π-system does not reflect the aromatic or antiaromatic character of the entire π-system.[4,5,22] We show below that our graph-theoretical approach is very useful for reconciling typical energetic and magnetic indicators of aromaticity for polycyclic π-systems. We propose the concept of magnetic resonance energy (MRE) as an index directly linking energetic and magnetic criteria of aromaticity. The same quantity has previously been proposed as an approximate topological resonance energy (TRE).[4,5]

Theory

Our graph-theoretical variant[23,24] of the venerable Hückel–London ring current model[25] is applied to PAHs in Figs. 1 and 2. At the limit of zero magnetic field a π-electron current induced in a polycyclic π-system is given exactly as a superposition of currents induced independently in all possible circuits.[23,24] Here all possible circuits mean all possible cyclic paths in a π-system. A PAH π system is denoted by G. We first evaluate the value of A_i defined for each circuit as:

$$A_i = 4\sum_{j}^{\text{occ}} \frac{P_{\text{G}-\text{r}_i}(X_j)}{P'_{\text{G}}(X_j)} \tag{1}$$

where r_i is the ith circuit; $\text{G}-\text{r}_i$ is the subsystem of G, obtained

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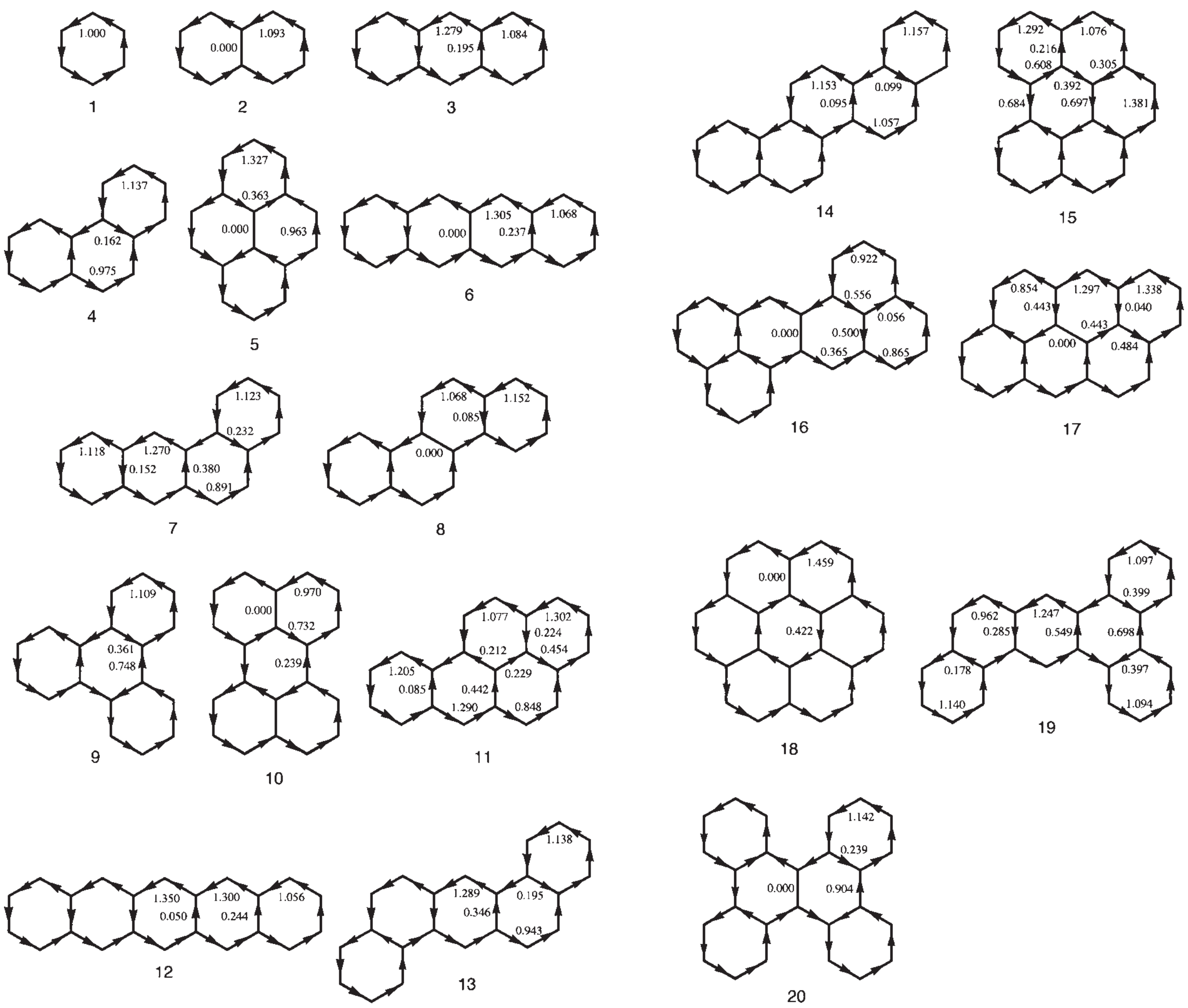


Fig. 1. Benzene and nineteen PAHs and the induced π-electron currents. All currents are given in units of that for benzene.

by deleting r_i from G; $P_G(X)$ and $P_{G-r_i}(X)$ are the characteristic polynomials for G and $G - r_i$, respectively; X_j is the *j*th largest zero of $P_G(X)$; a prime added to $P_G(X)$ indicates the first derivative with respect to X; *j* runs over all occupied π molecular orbitals (MOs); and all π-bonds are assumed to have equal resonance integrals. If there are degenerate π MOs, Eq. 1 must be replaced by others.[23,26] A_i is a function of molecular topology alone, in the sense that it is determined solely by the connectivity of conjugated atoms.

The *i*th circuit-current susceptibility, χ_i, i.e., the contribution of the *i*th circuit to the ring-current magnetic susceptibility of the entire π-system, can be expressed in the form:[3]

$$\frac{\chi_i}{\chi_0} = 4.5A_i\left(\frac{S_i}{S_0}\right)^2 \tag{2}$$

where χ_0 is the ring-current susceptibility of benzene; S_i and S_0 are the areas of r_i and the benzene ring, respectively. Positive and negative values for χ_i/χ_0 denote diamagnetic and paramagnetic susceptibilities, respectively. Ring-current susceptibility for a polycyclic π-system is obtained by summing up all circuit-current susceptibilities.

In this context, a current responsible for χ_i is the one induced in the *i*th circuit, I_i, which is called the *i*th circuit current and is expressed as:[23,24]

$$\frac{I_i}{I_0} = 4.5A_i\frac{S_i}{S_0} \tag{3}$$

where I_0 is the current intensity induced in the benzene ring; positive and negative values for I_i/I_0 denote diamagnetic and paramagnetic currents, respectively. As suggested above, a current density map for G is obtained by superposing all circuit currents. Such a formulation of Hückel–London theory is the only one that can prove explicitly the additivity of a π-electron current with respect to all possible circuits.[3,23,24] Possible computational errors in the circuit currents can be checked by examining if they reproduce the current density patterns obtained with conventional π-electron current calculations.[28–34] Both circuit-current susceptibility and circuit currents are functions of molecular topology and molecular geometry.

Quantity A_i, defined by Eq. 1, has been interpreted as an approximate contribution of the *i*th circuit to the TRE.[4,5] Therefore, the sum of A_i values for all circuits represents the approximate TRE. For reasons given below, we propose to call this a magnetic resonance energy (MRE), which means a TRE-like quantity associated with the magnetic response of the π-system:

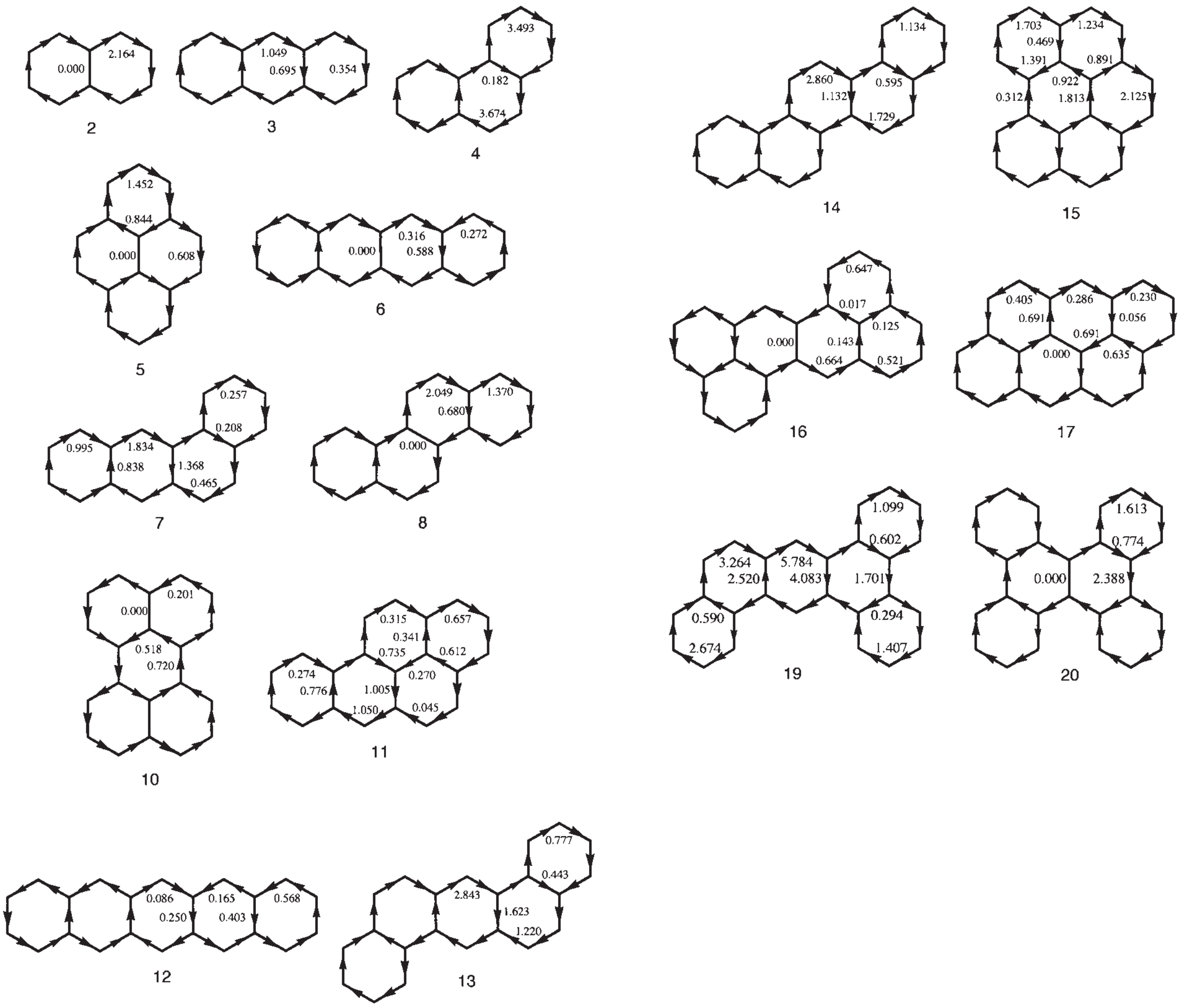


Fig. 2. Closed-shell molecular dianions/dications of seventeen PAHs and the induced π-electron currents. All currents are given in units of that for benzene.

$$\mathrm{MRE} = \sum_{i}^{\mathrm{G}} A_i \tag{4}$$

where i runs over all circuits in G. Like TRE, MRE is a function of molecular topology only.

In general, an aromatic monocyclic molecule is thermodynamically stable, in the sense that the external magnetic field destabilizes it energetically. The NICS value at the ring center must be proportional to the intensity of the current induced in the sole ring. There indeed is an excellent correlation between NICS and aromatic stabilization energy (ASE) for a range of five-membered heterocycles.[6,9] Schleyer et al. employed heats of homodesmotic reaction as ASEs.[6,9,35] The ASEs of the five-membered heterocycles likewise correlate with their diamagnetic susceptibility exaltations.[35] We have shown that for $[4n+2]$annulenes the ring current intensity divided by the ring area is proportional to the TRE.[16,17] Thus, for a set of monocyclic π-systems with similar ring areas, the NICS value is roughly proportional to ASE. Considering that A_1 represents an approximate TRE, a kind of ASE, the A_1 value itself can be interpreted as a kind of ASE. Here A_1 is the A_i value for the only circuit in a monocyclic π-system.

We extend this way of reasoning to polycyclic π-systems. All circuits in a polycyclic π-system are the source of aromatic stabilization or antiaromatic destabilization. By analogy with monocyclic π-systems, we presume that the intensity of the current induced in the ith circuit is proportional not only to the area of the circuit but also to the ASE arising from the circuit. The A_i value is then supposed to represent an ASE due to the ith circuit and is called the ith circuit resonance energy. If such a presumption is reasonable or acceptable, the energetic quantity defined by Eq. 4 can be interpreted as an ASE of the entire π-system as experienced by the external magnetic field. As will be seen, this interpretation of MRE is fully supported by its excellent numerical correlation with TRE.

Interpretation of MRE as a kind of ASE is very advantageous, in that any hypothetical polyene reference, homodesmotic reaction, or a π-energy increment system for the structure components is not required to evaluate ASE. MRE depends solely on an intrinsic magnetic property of a π-system, which can be observed directly or indirectly by experiment. Note that a matching polynomial must beforehand be constructed to evaluate the energy of a hypothetical reference structure needed to calculate TRE.[20,21] It is extremely difficult to enumerate the coefficients in the matching polynomial for large π-systems. The reference energy tacitly used to obtain MRE is the field-free π-binding energy of a real π-system. This fact never indicates that the polyene reference used to obtain TRE is meaningless.

The π-electron current distribution in a PAH molecular dianion is exactly the same as that in the molecular dication of the same PAH since all PAHs are alternant hydrocarbons. Therefore, we use the term ‘dianion/dication’ collectively for divalent PAH ions. MRE cannot be defined for open-shell species, such as dianions/dications of benzene (**1**), triphenylene (**9**), and coronene (**18**). These ions have two π-electrons in doubly degenerate highest occupied MOs (HOMOs) or lowest unoccupied MOs (LUMOs). These open-shell species must be very reactive even if they have large positive TREs.

Results and Discussion

We evaluated bond currents in benzene (**1**) and nineteen PAHs (**2**–**20**) and their doubly charged molecular ions, which are graphically summarized in Figs. 1 and 2. By bond currents we mean π-electron currents flowing through individual π bonds. Such current density maps for PAHs can be reproduced well by ab initio molecular orbital calculations.[36–38] It is assumed in these figures that the external magnetic field is perpendicular to the molecular plane, so that counterclockwise and clockwise currents indicate diatropicity and paratropicity, respectively. Like electrical circuits, π-electron currents obey Kirchhoff’s law. The MREs for **1**–**20** and their dianions/dications were obtained as byproducts of circuit-current calculations and are listed together with the TREs in Table 1.

It is instructive to compare the magnitude of MRE with that of TRE for a variety of PAHs. All neutral PAH molecules are highly aromatic with large positive TREs.[39,40] As opposed to the prediction based on magnetotropicity,[13–15] most PAH dianions/dications were found to be still aromatic with positive TREs. Figures 3 and 4 show that there is an excellent linear cor-

Table 1. TREs and MREs for Benzene and Nineteen PAHs and Their Molecular Ions

Species	Neutral molecule		Dianion/Dication	
	TRE/$\lvert\beta\rvert$	MRE/$\lvert\beta\rvert$	TRE/$\lvert\beta\rvert$	MRE/$\lvert\beta\rvert$
Benzene (**1**)	0.273	0.222	−0.692	—
Naphthalene (**2**)	0.389	0.289	−0.140	−0.072
Anthracene (**3**)	0.475	0.341	0.173	0.261
Phenanthrene (**4**)	0.546	0.407	−0.083	−0.129
Pyrene (**5**)	0.598	0.417	0.199	0.248
Naphthacene (**6**)	0.553	0.393	0.377	0.393
Benz[*a*]anthracene (**7**)	0.643	0.472	0.217	0.276
Chrysene (**8**)	0.688	0.505	0.144	0.216
Triphenylene (**9**)	0.739	0.574	−0.109	—
Perylene (**10**)	0.740	0.553	0.470	0.370
Benzo[*a*]pyrene (**11**)	0.725	0.509	0.398	0.418
Pentacene (**12**)	0.630	0.448	0.527	0.477
Dibenz[*a*,*h*]anthacene (**13**)	0.807	0.595	0.296	0.308
Picene (**14**)	0.835	0.611	0.276	0.304
Benzo[*ghi*]perylene (**15**)	0.853	0.596	0.380	0.344
Dibenzo[*de*,*mn*]naphthacene (**16**)	0.780	0.585	0.697	0.540
Dibenzo[*def*,*mno*]chrysene (**17**)	0.766	0.552	0.548	0.492
Coronene (**18**)	0.947	0.628	0.242	—
Tribenz[*a*,*c*,*h*]anthracene (**19**)	1.004	0.765	0.375	0.241
Dibenzo[*g*,*p*]chrysene (**20**)	1.041	0.790	0.431	0.416

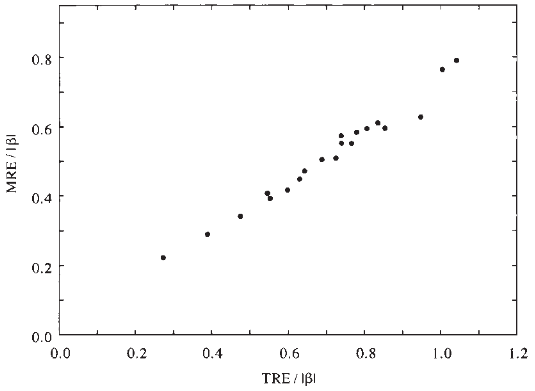


Fig. 3. Correlation between MRE and TRE for neutral PAH molecules.

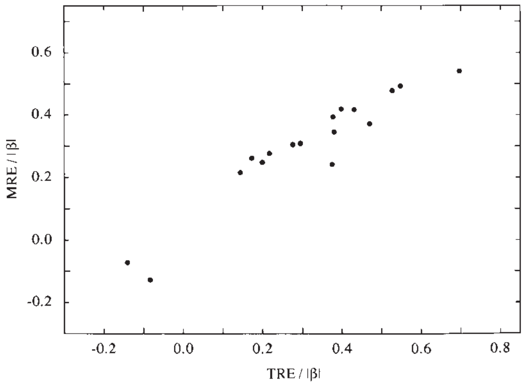


Fig. 4. Correlation between MRE and TRE for PAH dianions/dications.

relation between TRE and MRE for neutral PAHs and their molecular dianions/dications. This definitely supports our view that MRE can be interpreted as a kind of ASE due to cyclic π-electron conjugation. It follows that, at the level of individual circuits, a π-electron current is proportional to ASE. We can safely say that MRE, straightforwardly associated with magnetotropicity, can indeed be used as an energetic criterion for determining the degree of aromaticity. As far as neutral PAHs are concerned, MRE is somewhat smaller than TRE.

It is true that the dianions/dications of most PAHs are less aromatic than their respective parent hydrocarbons. Dianions/dications of all PAHs but benzene (**1**), naphthalene (**2**), phenanthrene (**4**), and triphenylene (**9**) are still moderately aromatic with positive TREs and positive MREs. Such aromatic character of these ions is fully consistent with their synthetic accessibility.[13–15] Interestingly, the dianion/dication of pentacene (**12**) is as aromatic as the parent molecule. This is due to the fact that high-lying HOMOs in higher polyacenes make little or slightly negative contributions to ASE.[41] Dianions/dications of **1**, **2**, **4**, and **9** are antiaromatic with negative MREs and/or negative TREs. Neutral molecules of these PAHs are highly aromatic with low-lying HOMOs and high-lying LUMOs. Therefore, they are made antiaromatic either by gaining two more electrons or by losing two π-electrons.

Peripheral currents in all neutral PAH molecules studied flow counterclockwise as shown in Fig. 1. For all PAHs but perylene (**10**), strong diatropic currents are induced along the periphery of the π-system. These diatropic currents have often been regarded as experimental evidence for aromaticity.[13–15] Neutral perylene appears to consist of two weakly interacting naphthalene nuclei. Diatropic currents flow primarily around the individual naphthalene nuclei. The central ring in it is a so-called empty one,[42,43] which sustains a very small diatropic current. Three central rings in dibenzo[*de*,*mn*]naphthacene (zethrene, **16**) are also empty, but the π-system sustains a fairly large diatropic current along the periphery. Some inner bonds of pericondensed hydrocarbons such as benzo[*a*]pyrene (**11**), benzo[*ghi*]perylene (**15**), dibenzo[*def*,*mno*]chrysene (anthanthrene, **17**), and coronene (**18**) sustain strong currents, which implies that the periphery model is not operative at least in these PAHs.

Many PAHs undergo a facile reduction process with electropositive alkali metals to yield the corresponding dianions.[13–15] ^{1}H NMR spectra of many doubly charged PAH ions exhibit characteristic high-field chemical shifts, which appear to reflect the existence of an enhanced antiaromatic-paratropic π-electron current. Close examination of Fig. 2 reveals that, in line with their proton chemical shifts, many dianions/dications are totally or partially paratropic. Peripheral paratropic currents are induced in PAH dianions/dications except for those of naphthacene (tetracene, **6**), perylene (**10**), pentacene (**12**), dibenzo[*de*,*mn*]naphthacene (**16**), and dibenzo[*def*,*mno*]chrysene (**17**). Thus, paratropicity and aromaticity coexist in many PAH dianions/dications. Considering that all neutral PAH molecules are diatropic in nature, the paratropicity of many PAH dianions/dications decisively indicates that the HOMOs contribute much to the π-electron currents induced in PAH molecules and their dianions/dications. In accord with this finding, Steiner and Fowler pointed out that only a few subsets of the high-lying π electrons dominate the current-density patterns of polycyclic π-systems.[37]

In 1985 Rabinovitz et al. estimated the net paratropic shifts due to π-electron currents for the dianions and/or dications of **3–8**, **10–13**, **15**, **19**, and **20** by subtracting the charge effect from the ^{1}H chemical shifts.[15] They then inferred from the results that polycyclic π-systems in which an efficient delocalization of 4*n* π-electrons exists possess an antiaromatic character.[15] According to their analysis, the ^{1}H paramagnetic shifts in dianions and/or dications of **10**, **12**, and **6** are relatively small, suggesting that paratropic currents must be weak along the peripheries of these π-systems.[15] Figure 2 indicates that the divalent ions of these three PAHs have one or more diatropic rings, which must be the main origin of 'reduced paratropicity' estimated by Rabinovitz et al.[15] It seems very likely that they misinterpreted reduced diatropicity as reduced paratropicity.

The inapplicability of the periphery model to polycyclic π-systems is further supported by the fact that it is compatible neither with the conjugated circuit model[44,45] nor with the extended Hückel rule proposed by Hosoya et al.,[46] both of which emphasize the local origin of aromaticity. These theories have been employed to rationalize the larger contribution of smaller conjugated circuits to the ASE of a PAH. A peripheral circuit is at most the largest conjugated circuit that contributes modestly to ASE. This energetic aspect of circuits supports our view that magnetic properties are associated straightforwardly with all circuits in a π-systems, including a peripheral circuit as one of them. Gutman et al. pointed out that for PAHs Dewar resonance energy is proportional to the logarithm of the Kekulé structure count.[47] This also is in accord with the view that the peripheral π-conjugation is not so important.

We then examine in some detail the circuit contributions to the global magnetotropicity and MRE of a polycyclic π-system. For this purpose we choose two PAHs, anthracene (**3**) and pyrene (**5**). Their dianions/dications have long been believed to be typically antiaromatic because of the paratropic π-electron current. Very recently Arpahamian et al. repeated that the two-electron reduction of **5** with alkali metals converts it into an antiaromatic system.[48]

Anthracene and Its Dianion/Dication. As explicitly shown in Fig. 5, there are two types of benzene rings in anthracene (**3**) and pyrene (**5**). The current density map of **3** in Fig. 1 shows that bond currents are slightly stronger around ring B ($1.279\ I_0$) than around ring A ($1.084\ I_0$). In harmony with these current intensities, NICS values are -5.6 and -11.3 at the centers of rings A and B, respectively, indicating that ring B is more diatropic.[6,7] As can be seen from Fig. 2, the dianion/dication π-system of **3** carries an induced paratropic current along the periphery. Paratropic bond currents are much stronger around ring B ($-1.049\ I_0$) than around ring A ($-0.354\ I_0$). Such a non-uniform distribution of the peripheral π-electron current is incompatible with the periphery model.

All circuits that can be chosen from the anthracene π-system are presented in Fig. 5. This π-system has four non-identical circuits and six circuits in all. In general, circuit currents induced in neutral PAHs formally obey Hückel's $4n+2$ rule.[23,24] That is, $(4n+2)$- and $4n$-membered circuits sustain diatropic and paratropic currents, respectively. All circuits in **3** are diatropic in the neutral electronic state since they are $(4n+2)$-membered conjugated ones. High diatropicity of **3** is associated with the absence of paratropic $4n$-membered circuits. There are no non-conjugated circuits in **3**. Intensities of currents induced in individual circuits are listed in Table 2, in which positive and negative values indicate diamagnetic and paramagnetic currents, respectively. By superposing all these circuit currents, we can reproduce the bond current pattern in Fig. 1.

Table 2 indicates that the Hückel rule no longer applies to charged PAHs. The global magnetotropicity of **3** and its dianion/dication is determined largely by the ten- and fourteen-membered circuits, which are diatropic in the neutral species but become paratropic in the dianion/dication. This reflects the large negative charge that resides along the long circumferences of these circuits. Six-membered circuits **a1** and **a2** are still diatropic in the dianion/dication because the number of π electrons that reside on these circuits does not deviate far from six. It is interesting to note that diamagnetic currents induced in two edge six-membered circuits (**a1**) are intensified in the dianion/dication. Such a phenomenon often occurs when highly paratropic circuits appear. Large circuits tend to become paratropic when the π-system acquires or loses two electrons. Circuit **a4** is a peripheral fourteen-membered circuit with the largest area. This circuit makes a large paratropic contribution to the π-electron current but contributes modestly to the MRE. In general, both small and larger circuits make comparable contributions to a π-electron current.

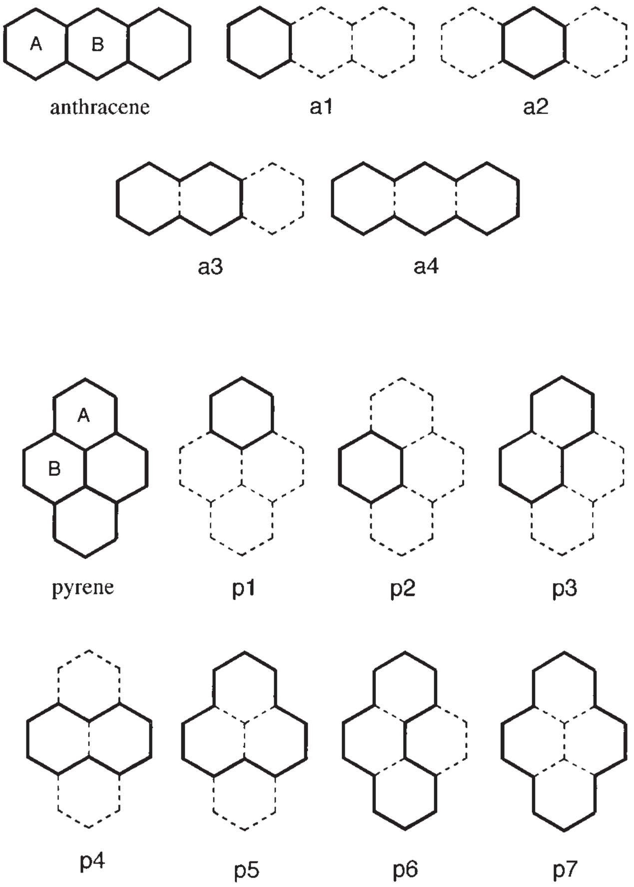


Fig. 5. Circuits in anthracene (**3**) and pyrene (**5**).

In 2001 Schleyer et al. made a comprehensive study on the magnetic properties of polyacenes.[7] They presumed that the NICS values are due to the π contribution of the ring concerned as well as the π contributions of the more remote rings, with the latter contributions being small (10% or less). They then concluded that each benzenoid ring in the polyacenes behaves as a rather separate or localized entity in this respect. We, however, have seen that bond currents induced around each ring consist of two or more circuit currents, so these currents are never of local origin. For example, peripheral bonds around the central ring of **3** carry circuit currents induced in **a2**, **a3**, and **a4**. It is clear that all bond currents and then all NICS values are global, in the sense that they are closely associated with the entire π-system. Such a global nature of magnetic properties is shared by all PAHs and their molecular ions.

Anthracene (**3**) and its dianion/dication have TREs of 0.475 and 0.173 $|\beta|$, respectively.[20,21,39,40] MREs of these species can be obtained by summing up the circuit resonance energies (A_i) in Table 2. The MREs thus obtained are 0.341 $|\beta|$ for **3** and 0.261 $|\beta|$ for its dianion/dication. Thus, the reduced degree of aromaticity and a peripheral paratropic current occur simultaneously in the dianion/dication. We can safely say that the anthracene dianion/dication is still aromatic, although it sustains a strong paratropic current.

Table 2. Circuit Currents and Circuit-Current Susceptibilities for Anthracene and Its Molecular Dianin/Dication

Circuit	Number of carbon atoms	Area $/S_0$	Circuit current$/I_0$	Circuit-current susceptibility$/\chi_0$	Circuit resonance energy$/|\beta|$	Number of identical circuits
A. Neutral molecule						
a1	6	1	0.406	0.406	0.090	2
a2	6	1	0.282	0.282	0.063	1
a3	10	2	0.318	0.637	0.035	2
a4	14	3	0.360	1.081	0.027	1
B. Dianion/dication						
a1	6	1	0.729	0.729	0.162	2
a2	6	1	0.167	0.167	0.037	1
a3	10	2	−0.132	−0.264	−0.015	2
a4	14	3	−0.952	−2.855	−0.070	1

Table 3. Circuit Currents and Circuit-Current Susceptibilities for Pyrene and Its Molecular Dianion/Dication

Circuit	Number of carbon atoms	Area $/S_0$	Circuit current$/I_0$	Circuit-current susceptibility$/\chi_0$	Circuit resonance energy$/\lvert\beta\rvert$	Number of identical circuits
A. Neutral molecule						
p1	6	1	0.445	0.445	0.099	2
p2	6	1	0.231	0.231	0.051	2
p3	10	2	0.175	0.350	0.019	4
p4	10	2	0.050	0.100	0.006	1
p5	12	3	−0.031	−0.094	−0.002	2
p6	14	3	0.169	0.507	0.013	2
p7	14	4	0.225	0.902	0.013	1
B. Dianion/dication						
p1	6	1	0.187	0.187	0.042	2
p2	6	1	0.454	0.454	0.101	2
p3	10	2	0.175	0.350	0.019	4
p4	10	2	0.407	0.814	0.045	1
p5	12	3	−0.328	−0.984	−0.024	2
p6	14	3	−0.498	−1.495	−0.037	2
p7	14	4	−0.664	−2.657	−0.037	1

Pyrene and Its Dianion/Dication. The diatropic π-electron current in pyrene (**5**) is strong around ring A (1.327 I_0) but is weak around ring B (0.963 I_0). In harmony with this, NICS values are −11.3 and −5.6 at the centers of rings A and B, respectively.[8] In contrast, the dianion/dication carries a paratropic current induced along the periphery of the π-system. Paratropic bond currents in the dianion/dication are much stronger around ring A (−1.452 I_0) than around ring B (−0.608 I_0). Therefore, we cannot say that the π-electron current is induced primarily along the periphery of the π-system.

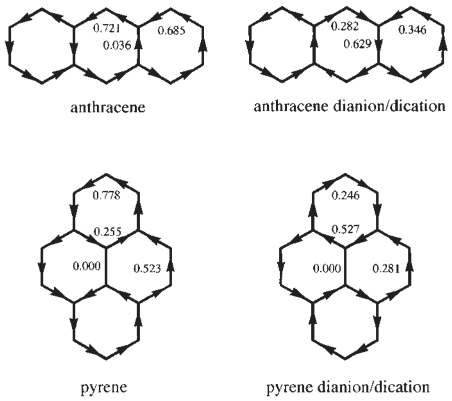
This molecule has seven non-identical circuits and fourteen circuits in all. All circuits but **p5** are $(4n+2)$-membered ones. Circuit **p5** is a twelve-membered circuit. In the neutral species, $(4n+2)$- and $4n$-membered circuits are diatropic and paratropic, respectively, without exceptions. All but circuits **p4** and **p5** are conjugated circuits. Intensities of currents induced in all circuits are listed in Table 3. Circuit **p7** is a peripheral fourteen-membered circuit with the largest area. This circuit, together with other conjugated circuits, makes a large contribution to the π-electron current in the neutral electronic state. Non-conjugated circuits in general sustain much smaller currents. High diatropicity of **5** is associated with the fact that there are no paratropic conjugated circuits. The only paratropic circuit, **p5**, is not a conjugated circuit.

Like the anthracene dianion/dication, the pyrene dianion/dication sustains a strong paramagnetic current along the periphery of the π-system. All fourteen-membered circuits **p6** and **p7** become highly paratropic in the dianion/dication. Interestingly, diatropic currents in **p2** and **p4** are intensified in the dianion/dication. Large currents induced in these currents determine the paratropicity of the periphery of the π-system. Paratropicity of the twelve-membered circuit **p5** is also intensified in the dianion/dication. Even non-conjugated circuits, **p4** and **p5**, sustain large currents in the charged species. In this context, the conjugated circuit model no longer applies to charged π-systems, such as PAH dianions/dications.

Pyrene (**5**) is highly aromatic with a TRE of 0.598 $|\beta|$.[20,21,39,40] The dianion/dication is moderately aromatic with a TRE of 0.199 $|\beta|$. The MREs are 0.417 $|\beta|$ for **5** and 0.248 $|\beta|$ for its dianion/dication. There is no doubt that the pyrene dianion/dication is aromatic, although it sustains a strong paratropic current along the periphery. Thus, the reduced degree of aromaticity and the induced peripheral paratropic current in many PAH anions/cations can be predicted consistently within the same theoretical framework. Both quantities can be attributed to the same set of circuits in the π-system. When a polycyclic π-system is very large or fairly large, two more or two less π-electrons are not enough to make small conjugated circuits paratropic.

Geometry-Independent Current Density Maps. Equation 3 indicates that the bond current distribution in a polycyclic π-system is strongly dependent on molecular geometry. If a molecule is artificially deformed to reduce the areas of all rings or all circuits, the entire π-electron current will be greatly decreased. In order to visualize such a geometric feature of π-electron currents, hypothetical bond currents in anthracene (**3**) and its dianion/dication were evaluated by assuming that all circuit areas are equal to that of the benzene ring (i.e., $S_i = S_0$ for all circuits). Of course it is really impossible to deform a polycyclic π-system in this manner because all circuit areas are interdependent. The geometry-independent current density maps thus obtained for anthracene (**3**), pyrene (**5**), and their dianions/dications are shown in Fig. 6.

We see from this figure that the peripheral diatropic current in **3** is reduced to some extent but that the peripheral paratropic current in its dianion/dication is greatly reduced. As a result, bond currents in ring B are made diatropic in the doubly charged state. These current density maps clearly indicate that large circuits contribute much to the peripheral currents in actual π-systems, even if their contribution to MRE is fairly small. The peripheral paratropic current in the dianion/dication of **5** is also greatly reduced in the hypothetical structure. It is noteworthy



anthracene

anthracene dianion/dication

pyrene

pyrene dianion/dication

Fig. 6. Hypothetical current density maps of anthracene (**3**), pyrene (**5**), and their dianions/dications as calculated assuming that all circuit areas are equal to that of the benzene ring. All currents are given in units of that for benzene.

that ring B became slightly diatropic, indicating that the strong patatropicity in the actual π-system reflects the areas of large circuits but not their aromaticity. It is again evident that a paratropic peripheral current cannot always be regarded as an indication of antiaromaticity.

Ring-Current Susceptibilities. Ring-current susceptibility can also be partitioned among all circuits.[2–5] It is equal to the sum of all circuit-current susceptibilities defined by Eq. 2. Circuit-current susceptibilities for **3**, **5**, and their dianions/dications are added in Tables 2 and 3, in which all susceptibility values are given in units of the ring-current susceptibility for benzene (χ_0). Therefore, positive and negative values indicate diamagnetism and paramagnetism, respectively. Since the circuit-current susceptibility is a product of the A_i value and the circuit area squared, both small circuits and some large ones contribute significantly to the entire ring-current susceptibility. In general, larger circuits contribute much more to the ring-current susceptibility than to the π-electron current.

Overall ring-current susceptibilities are 3.448 for **3**, -1.756 for its dianion/dication, 4.580 for **5**, and -4.122 for its dianion/dication, all in units of that for benzene. Values for neutral species agree exactly with those reported by Pullman and Pullman.[49] It goes without saying that the negative ring-current diamagnetic susceptibilities for the two dianions/dications never indicate that these molecular ions are antiaromatic. Contributions of large circuits are exaggerated not only in the π-electron current but also in the ring-current susceptibility although they contribute modestly to MRE. For this reason, it is obvious that ring-current susceptibility is not always a reliable index of aromaticity.

Concluding Remarks

The conventional interpretation of π-electron currents and related magnetic properties gives a misleading picture on the aromatic character of PAH molecular ions. We long ago suggested that some non-alternant hydrocarbons, such as butalene and bicyclo[6.2.0]decapentaene, might be diatropic, although they are antiaromatic with negative TREs.[4,5] According to Wilcox and Farley,[22] Aihara has shown how relative circuit areas can lead to situations where TRE and ring-current susceptibility have the same sign (diatropic antiaromatics) as opposed to the normal negative proportionality. Krygowski et al. pointed out that all magnetic criteria of aromaticity suffer from geometry-dependence.[18] Therefore, magnetic criteria of aromaticity are intrinsically very obscure as compared to energetic ones.

In this study, we pointed out that, at the level of individual circuits, a π-electron current is proportional to the ASE. On this theoretical basis, we derived a new energetic index of aromaticity (i.e., MRE). It is an energetic quantity that is closely associated with observable magnetic properties, such as diamagnetic susceptibility exaltation, ^{1}H chemical shift, and NICS. In this sense, MRE can be regarded as a physically sound index of aromaticity that straightforwardly links energetic and magnetic criteria of aromaticity. Using such an indicator of aromatic stabilization based on magnetotropicity, we were able to show that there indeed are paratropic but aromatic polycyclic π-systems. Among them are many PAH dianions/dications. We repeatedly demonstrated that the periphery model in principle is inapplicable to polycyclic π-systems, such as PAH dianions/dications.

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