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Circuit Resonance Energy: A Key Quantity That Links Energetic and Magnetic Criteria of Aromaticity

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Abstract: Energetic and magnetic criteria of aromaticity are different in nature and sometimes make different predictions as to the aromaticity of a polycyclic π-system. Thus, some charged polycyclic π-systems are aromatic but paratropic. We derived the individual circuit contributions to aromaticity from the magnetic response of a polycyclic π-system and named them circuit resonance energies (CREs). Each CRE has the same sign and essentially the same magnitude as the corresponding cyclic conjugation energy (CCE) defined by Bosanac and Gutman. Such CREs were found to play a crucial role in associating the energetic criteria for determining the degree of aromaticity with the magnetic ones. We can now interpret both energetic and magnetic criteria of aromaticity consistently in terms of CREs. Ring-current diamagnetism proved to be the tendency of a cyclic π-system to retain aromatic stabilization energy (ASE) at the level of individual circuits.

1. Introduction

Diatropicity and ring-current diamagnetism have been used widely as conventional measures of aromaticity.[1,2] There indeed is a complicated relationship between these quantities and aromatic stabilization energy (ASE).[3−5] Only for aromatic annulenes, the ring current intensity divided by the ring area was found to be proportional to the ASE.[6,7] In 1996, Schleyer et al. proposed a new magnetic descriptor of aromaticity: a nucleus-independent chemical shift (NICS),[8−10] which is defined as the negative of the magnetic shielding. Negative and positive NICS values at ring or cage centers have since been utilized as indications of local aromatic and antiaromatic character, respectively. Thus, phenomena arising from diatropic and paratropic π-electron currents have been associated with aromaticity and antiaromaticity, respectively. However, NICS proved not to be a general descriptor of aromaticity and does not always represent global or local aromaticity properly; difficulties with NICS have been reported repeatedly.[11−17]

In fact, π-electron currents and related magnetic properties are highly dependent on molecular geometry,[18−27] whereas aromaticity itself represents primarily a state of energy.[28−37] As properly pointed out by Heine et al.,[38] the term 'aromatic' describes molecules that benefit energetically from the delocalization of mobile electrons in closed circuits. Therefore, predictions based on magnetic criteria of aromaticity often deviate appreciably from those based on energetic ones. For example, molecular dianions of anthracene and pyrene are paratropic[39−41] but must be aromatic because the topological resonance energies (TREs) are positive in sign.[42] Like other magnetic indices, NICS suffers from geometry-dependency.

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(1) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley-Interscience: New York, 1994; Chapter 2.
(2) *Chem. Rev.* **2001**, *101* (5), thematic issue on Aromaticity, Schleyer, P. v. R., Guest Editor.
(3) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 558.
(4) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 5704.
(5) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115.
(6) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.
(7) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1163.
(8) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(9) Patchkovskii, S.; Thiel, W. *J. Mol. Model.* **2000**, *6*, 67.
(10) Chen, Z.; Thiel, W. *Chem. Phys. Lett.* **2003**, *367*, 15.
(11) Katritzky, A. R.; Karelson, M.; Slid, S. Krygowski, T. M. *J. Org. Chem.* **1998**, *63*, 5228.
(12) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783.
(13) Aihara, J. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 103.
(14) Aihara, J. *Chem. Phys. Lett.* **2003**, *375*, 571.
(15) Aihara, J.; Oe, S. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1363.
(16) Cuesta, I. G.; Jartín, R. S.; de Merás, A. S.; Lazzeretti, P. *J. Chem. Phys.* **2003**, *119*, 5518.
(17) Aihara, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 101.
(18) London, F. *J. Phys. Radium* **1937**, *8*, 397.
(19) Pullman, B.; Pullman, A. *Les Théories Electroniques de la Chimie Organique*; Masson et Cie: Paris, 1952; Chapitre IX.
(20) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175.
(21) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311.
(22) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 5913.
(23) Aihara, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1245.
(24) Aihara, J. *Chem. Phys. Lett.* **1983**, *95*, 561.
(25) Aihara, J.; Horikawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1853.
(26) Aihara, J. *J. Am. Chem. Soc.* **1985**, *107*, 298.
(27) Aihara, J. *Chem. Phys. Lett.* **2004**, *393*, 7.
(28) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.
(29) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413.
(30) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404.
(31) Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.
(32) Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68.
(33) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.
(34) Randić, M. *Chem. Rev.* **2003**, *103*, 3449.
(35) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.
(36) Aihara, J. *J. Am. Chem. Soc.* **1977**, *99*, 2048.
(37) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.
(38) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber, J. *J. Phys. Chem. A* **2003**, *107*, 6470.
(39) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron Lett.* **1982**, *23*, 5351.
(40) Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 298.
(41) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785.
(42) Aihara, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 651.

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Table 1. Ring-Current Diamagnetic Susceptibilities for Typical PAHs

species	χ_G/χ_0 this work	χ_G/χ_0 PPP-MO[a]
benzene **(1)**	1.000	1.00
naphthalene **(2)**	2.185	2.17
anthracene **(3)**	3.448	3.41
phenanthrene **(4)**	3.248	3.22
naphthacene **(5)**	4.747	4.69
chrysene **(6)**	4.440	4.41
triphenylene **(7)**	4.076	4.06
pyrene **(8)**	4.580	4.57
perylene **(9)**	4.120	4.36
coronene **(10)**	9.794	9.53

[a] ref 47.

Krygowski et al. recommended the use of NICS as an index of local aromaticity but not as that of global aromaticity.[12]

To what extent can aromaticity be defined uniquely? This is the question asked by Cyranski, Krygowski, Katritzky, and Schleyer.[43] We recently found that our graph-theoretical approach is very promising for consistently interpreting typical energetic and magnetic indicators of aromaticity for polycyclic π-systems.[42] A key quantity that connects energetic and magnetic criteria of aromaticity may be what is called circuit resonance energy (CRE), which is defined as a contribution of each cyclic path in a polycyclic π-system to the ASE. As will be seen, both energetic and magnetic criteria can be formulated consistently in terms of CREs. Essentially, the same quantity has been proposed by Bosanac and Gutman.[44−46] Their idea of cyclic conjugation energy (CCE) gave us an important clue to the critical evaluation of our CRE concept. In this paper, we definitely demonstrate that energetic and magnetic criteria of aromaticity are closely related to each other even if the magnetic ones should not be used without reservations to estimate the aromaticity of polycyclic π-systems.

2. Theory and Discussion

We have long been developing a graph theory of aromaticity and diatropicity. Our graph-theoretical variant[5,22−27] of Hückel−London theory[18,19] is utilized to calculate the ring-current magnetic susceptibilities and related quantities of polycyclic aromatic hydrocarbons (PAHs). Hückel molecular orbital (HMO) theory is used throughout this paper. For simplicity, ideal molecular structures are adopted in which all carbon−carbon bond lengths are equal to those in benzene. All calculations were performed on 10 typical PAHs listed in Table 1.

Ring-Current Magnetic Susceptibility. According to our graph theory, ring-current magnetic susceptibility for a polycyclic π-system can be partitioned exactly among the circuits. Here, circuits stand for all possible cyclic paths that can be chosen from a cyclic π-system. For example, two six-membered circuits and one ten-membered one can be chosen from the naphthalene π-system.[2] In this context, r_i denotes a set of carbon atoms that constitute the ith circuit c_i. All nonidentical circuits in the 10 PAHs are presented in Figure 1.

Before presenting the graph-theoretical formula for ring-current magnetic susceptibility, the quantity A_i for the ith circuit in a closed-shell polycyclic π-system G is defined as follows:[22]

$$A_i = 4\sum_j^{\text{occ}} \frac{P_{G-r_i}(X_j)}{P'_G(X_j)} \tag{1}$$

where $G-r_i$ is the subsystem of G, obtained by deleting from G all carbon atoms that constitute the ith circuit; $P_G(X)$ and $P_{G-r_i}(X)$ are the characteristic polynomials for G and $G-r_i$, respectively; and X_j is the jth largest root of the equation $P_G(X) = 0$; and j runs over all occupied π orbitals. If degenerate π orbitals are occupied, this formula must be replaced by others.[5,22,24] The A_i value for a single circuit in benzene **(1)** is 1/4.5. A_i values for all nonidentical circuits in the ten PAHs are listed as CREs in Table 2.

Ring-current magnetic susceptibility is defined as the second derivative of total π-electron energy with respect to the intensity of the magnetic field and at the limit of zero magnetic field. When an external magnetic field, H, is oriented perpendicular to the plane of G, the ring-current magnetic susceptibility is expressed in the form:[5,22]

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

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 A_i values represent diamagnetic and paramagnetic contributions, respectively. χ_G agrees exactly with the value calculated using conventional Hückel−London theory.[47] Table 1 and Figure 2 show that χ_G is highly correlative with the value calculated with semiempirical Pariser−Parr−Pople molecular orbital (PPP-MO) methods.[47,48] For typical PAHs, χ_G is also highly correlative with diamagnetic susceptibility exaltation (Λ_G).[49,50] These excellent correlations justify the use of HMO theory in predicting magnetic properties of PAH molecules.

One should emphasize that eq 2 is an exact expression for ring-current susceptibility within the framework of Hückel−London theory.[5,22] This expression has no terms containing the areas of two or more circuits. Thus, at the limit of a vanishingly small magnetic field, ring-current susceptibility can be evaluated additively with respect to individual circuits. This indicates that a π-electron current induced in a polycyclic π system can be partitioned among all possible circuits in it. On this theoretical basis, we can naturally formulate the contribution of the ith circuit to χ_G as[5,22]

$$\chi_i = 4.5\chi_0 A_i \left(\frac{S_i}{S_0}\right)^2 \tag{3}$$

Circuit Current. The ring-current magnetic susceptibility of a polycyclic π-system arises because of currents circulating along the circuits as a result of the application of an external magnetic field. According to electromagnetism, the magnetization, M, due to a loop current, I, induced by a magnetic field,

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(43) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem*. **2002**, *67*, 1333.
(44) Bosanac, S.; Gutman, I. *Z. Naturforsch*. **1977**, *32*a, 10.
(45) Gutman, I.; Bosanac, S. *Tetrahedron* **1977**, *33*, 1809.
(46) Gutman, I. *Monatsh. Chem*. **2005**, *136*, 1055.
(47) Lazzeretti, P.; Taddei, F. *J. Chem. Soc*., *Faraday Trans. 2* **1972**, *68*, 1825.
(48) Long, E. R., Jr.; Memory, J. D. *J. Chem. Phys*. **1976**, *65*, 2918.
(49) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc*. **1968**, *90*, 811.
(50) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc*. **1969**, *91*, 1991.

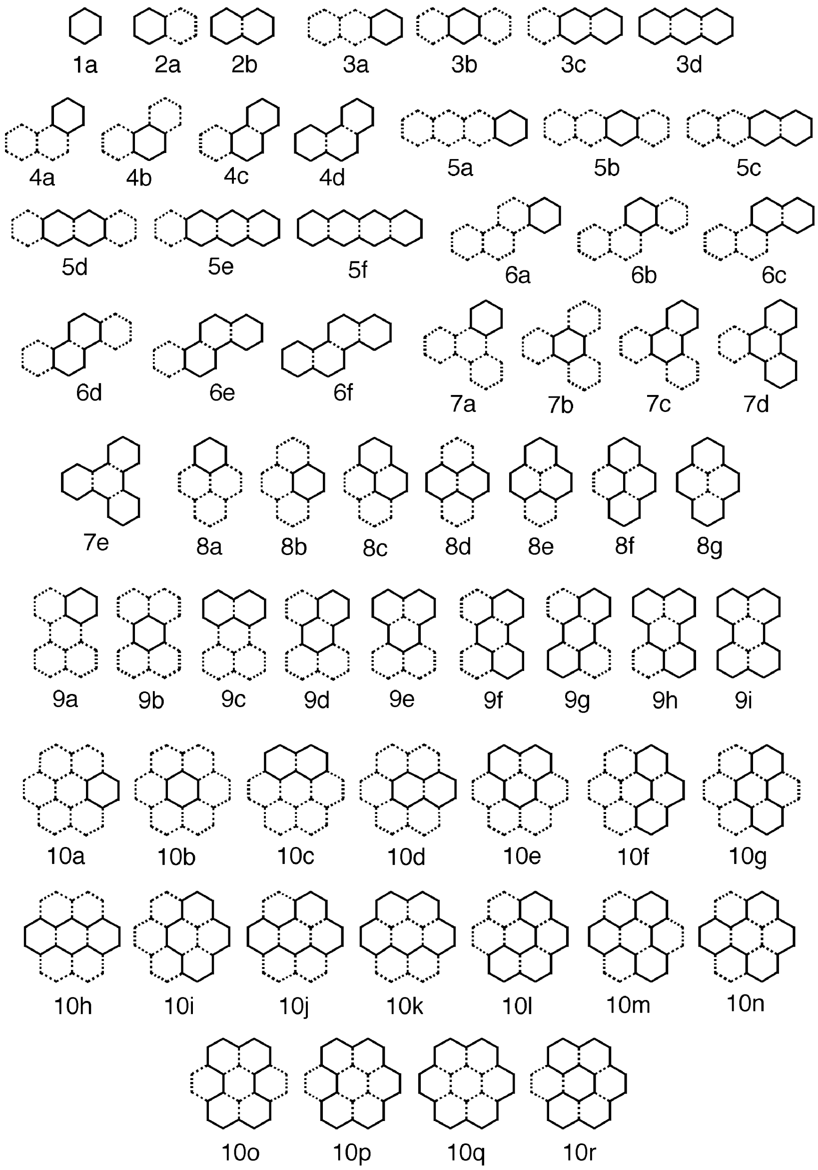

Figure 1. Nonidentical circuits in 10 PAHs.

H, is given by *IS*, where *S* is the area enclosed by the loop.[51] Since $M = \chi H$, *I* must be equal formally to $\chi H/S$, the ith circuit-current susceptibility, χ_i, must correspond to the induction of a π-electron current in the *i*th circuit the intensity of which is given by:[25−27]

$$I_i = 4.5 I_0 A_i \frac{S_i}{S_0} \tag{4}$$

where I_0 is the intensity of a π-electron current induced in the benzene ring, respectively. Positive and negative A_i values indicate diatropic and paratropic currents, respectively. A current density map for *G* can be obtained by superposing all such circuit currents because the ring-current susceptibility can be obtained additively with respect to individual circuits. This does not imply that all circuit currents flow independently; their intensities are indeed interdependent through the values for A_i. Such a graph-theoretical 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. Current density patterns thus obtained for PAHs are shown in Figure 3, in which counterclockwise currents indicate diatropicity. These patterns are exactly the same as those obtained using conventional Hückel−London methods,[52−55] so that there must be no problem in the above derivation of current intensities.

Although PAHs are well-known to exhibit diatropic overall currents, circuit-current analyses revealed that some of the circuits are paratropic. As far as neutral PAH molecules are concerned, calculated circuit currents are consistent with the extended Hückel rule proposed by Hosoya et al.[56,57] For such π-systems, I_i values are positive and negative in sign for all $(4n+2)$- and $4n$-membered circuits, respectively.[4,5,25−27] This indicates that $(4n+2)$- and $4n$-membered circuits are diatropic and paratropic, respectively. This aspect of circuit currents is fully consistent with the chemistry of annulenes[1] and justifies

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(51) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811.

(52) Maddox, I. J.; McWeeny, R. *J. Chem. Phys.* **1962**, *36*, 2353.

(53) Jonathan, N.; Gordon, S.; Dailey, B. P. *J. Chem. Phys.* **1962**, *36*, 2443.

(54) Memory, J. D. *J. Chem. Phys.* **1963**, *38*, 1341.

(55) Haigh, C. W.; Mallion, R. B. *J. Chem. Phys.* **1982**, *76*, 4063.

(56) Hosoya, H.; Hosoi, K.; Gutman, I. *Theor. Chim. Acta* **1975**, *38*, 37.

(57) Hosoya, H. *Monatsh. Chem.* **2005**, *136*, 1037.

Table 2. Two Types of Circuit Resonance Energies for All Nonidentical Circuits in Typical PAHs

species	circuit[a]	no. of identical circuits	CRE/|β|	CCE/|β|
benzene **(1)**	1a	1	0.2222	0.2726
naphthalene **(2)**	2a	2	0.1120	0.1211
	2b	1	0.0654	0.0709
anthracene **(3)**	3a	2	0.0902	0.0951
	3b	1	0.0628	0.0652
	3c	2	0.0354	0.0369
	3d	1	0.0267	0.0279
phenanthrene **(4)**	4a	2	0.1414	0.1586
	4b	1	0.0520	0.0534
	4c	2	0.0267	0.0275
	4d	1	0.0193	0.0198
naphthacene **(5)**	5a	2	0.0857	0.0900
	5b	2	0.0520	0.0535
	5c	2	0.0268	0.0275
	5d	1	0.0201	0.0206
	5e	2	0.0154	0.0158
	5f	1	0.0130	0.0134
chrysene **(6)**	6a	2	0.1324	0.1464
	6b	2	0.0662	0.0689
	6c	2	0.0371	0.0387
	6d	1	0.0117	0.0118
	6e	2	0.0080	0.0081
	6f	1	0.0064	0.0064
triphenylene **(7)**	7a	3	0.1648	0.1909
	7b	1	0.0240	0.0242
	7c	3	0.0101	0.0102
	7d	3	0.0067	0.0068
	7e	1	0.0053	0.0053
pyrene **(8)**	8a	2	0.0988	0.1063
	8b	2	0.0514	0.0528
	8c	4	0.0194	0.0198
	8d	1	0.0056	0.0056
	8e*	2	−0.0023	−0.0023
	8f	2	0.0125	0.0128
	8 g	1	0.0125	0.0128
perylene **(9)**	9a	4	0.1015	0.1093
	9b*	1	0.0216	0.0218
	9c	2	0.0543	0.0586
	9d*	4	0.0043	0.0044
	9e*	2	−0.0018	−0.0018
	9f*	2	0.0013	0.0013
	9 g*	2	0.0013	0.0013
	9h*	4	−0.0006	−0.0006
	9i*	1	0.0003	0.0003
coronene **(10)**	10a	6	0.0674	0.0703
	10b	1	0.0295	0.0298
	10c	6	0.0154	0.0156
	10d	6	0.0046	0.0047
	10e*	6	−0.0009	−0.0009
	10f	6	0.0051	0.0051
	10g	6	0.0017	0.0017
	10h*	3	0.0007	0.0007
	10i	6	0.0017	0.0017
	10j*	12	−0.0002	−0.0002
	10k*	6	−0.0004	−0.0004
	10l	6	0.0011	0.0011
	10m	2	0.0010	0.0010
	10n	6	0.0010	0.0010
	10o*	3	0.0001	0.0001
	10p	6	0.0011	0.0011
	10q	1	0.0039	0.0039
	10r	6	0.0009	0.0009

[a] Nonconjugated circuits are denoted by asterisks.

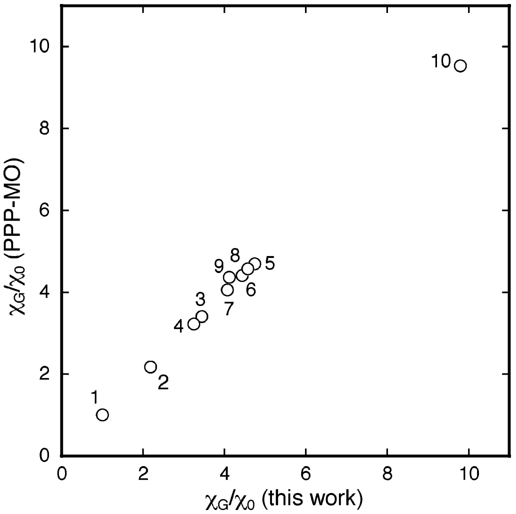

Figure 2. Correlation between χ_G/χ_0(this work) and χ_G/χ_0 (PPP-MO) for 10 PAHs.

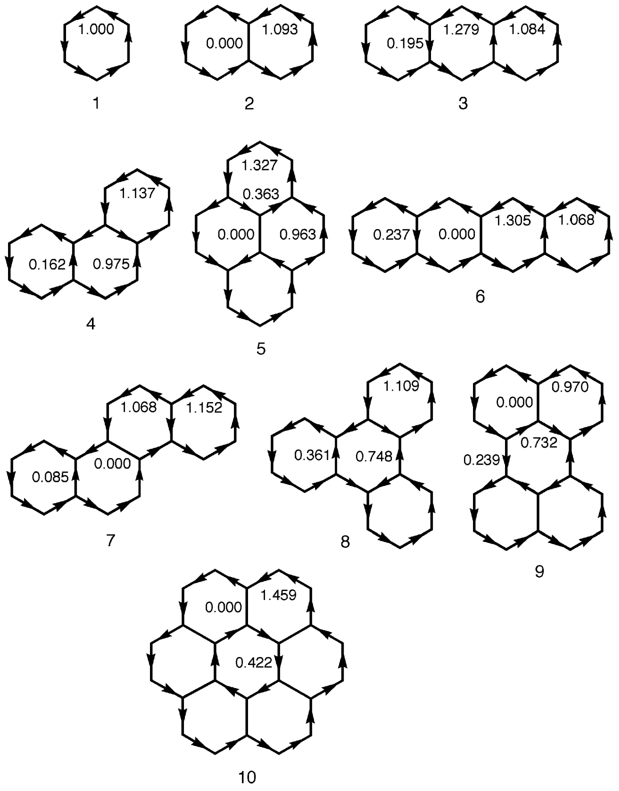

Figure 3. Current density maps of 10 PAHs. All currents are given in units of that in benzene. Counterclockwise currents indicate diatropicity.

the partition of an overall π-electron current in the form of eq 4. The Hückel-like rule of superaromaticity for charged paracyclophanes[58] and the counter-rotating rim and hub currents in coronene[27] can be rationalized successfully in terms of circuit currents. An apparently paratropic current induced in the central benzene ring of coronene **(10)** turned out to arise from the superposition of many diatropic circuit currents.[27] These facts also support our derivation or definition of circuit currents.

It may be mentioned in passing that there has been the idea of breaking down the overall ring-current effect in a polycyclic π-system into contributions attributable to each of its constituent rings.[59] For example, coronene **(10)** consists of seven benzene rings. Figure 4 illustrates the formal partition of an overall π-electron current in **10** among the seven rings. One may see from this figure that a diamagnetic current may also be induced

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(58) Aihara, J. *Chem. Phys. Lett.* **2003**, *381*, 147.

(59) Aihara, J. *J. Phys. Chem. A* **2003**, *107*, 11553.

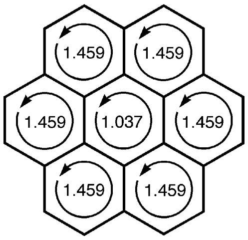

Figure 4. Formal partion of the overall π-electron currents in coronene **(10)** among the constituent rings. Counterclockwise currents indicate diatropicity.

in the central benzene ring even if the current density pattern in Figure 3 indicates that a paramagnetic current is apparently induced along the inner benzene ring. However, such a way of partitioning π-electron currents cannot be rationalized theoretically, because ring-current susceptibility is never additive with respect to constituent rings.

Circuit Resonance Energy. We have seen that the plus and minus signs of the A_i values represent diatropicity and paratropicity, respectively. The numerical values for A_i in Table 2 further support this view. *cata*-Condensed hydrocarbons, such as **1**−**7**, have $(4n+2)$-membered conjugated circuits only, whereas *peri*-condensed hydrocarbons such as **8**−**10** have not only conjugated but also nonconjugated circuits. These PAHs have no $4n$-membered conjugated circuits. For all PAHs, A_i is positive in sign for all $(4n+2)$-membered circuits and negative for all $4n$-membered ones. Conjugated circuits exhibit much larger A_i values than nonconjugated ones of similar size. Smaller conjugated circuits exhibit larger A_i values than larger conjugated ones. These aspects of A_i values are fully consistent with the Herndon−Randić conjugated circuit theory.[30−34] They neglected nonconjugated circuits in their theory because they were supposed to contribute little to aromaticity. Therefore, we might presume that A_i represents well the circuit contribution to the ASE of the entire π-system. We proposed to call the A_i value the ith circuit resonance energy (CRE$_i$).[42]

We next show definite evidence for the reasonableness of the CRE$_i$ values. In 1977 Bosanac and Gutman proposed a definition of a kind of CRE for polycyclic π-systems.[44−46] First, a new characteristic polynomial $P_{G-c_i}(X)$ is defined for a hypothetical π-system $G-c_i$. Here, $G-c_i$ has the same topology as G but is assumed to have no ith circuit (i.e., no cyclic motion of π-electrons around the ith circuit). In other words, we enumerate the coefficients of $P_{G-c_i}(X)$ using the Sachs theorem, neglecting the contribution of the ith circuit to the coefficients.[60,61] By definition, $P_{G-c_i}(X)$ has the same order as $P_G(X)$, being identical with the following expression:

$$P_{G-c_i}(X) = P_G(X) + 2P_{G-r_i}(X) \tag{5}$$

The roots of the equation $P_{G-r_i}(X) = 0$ are supposed to represent the π-orbital energies of $G-c_i$. Bosanac and Gutman defined the cyclic conjugation energy (CCE) arising from the ith circuit as the difference in total π-electron energy between G and $G-c_i$.[44−46] This energy difference is attributable to the energy gain or loss due to cyclic conjugation along the ith circuit.

Therefore, there is a large possibility that CCE is comparable in magnitude to our CRE. We then calculated CREs and CCEs for all circuits in 10 PAHs and presented them in Table 2 and Figure 5. It is very impressive that CRE and CCE have not only the same sign but also essentially the same magnitude for all circuits investigated. Such an excellent correlation must never be a coincidence but a necessity, which can be shown mathematically in the following manner. If a numerical value of $2P_{G-r_i}(X)$ in eq 5 is sufficiently small, the jth root of the equation $P_{G-c_i}(X) = 0$ can be approximated using Newton's method as

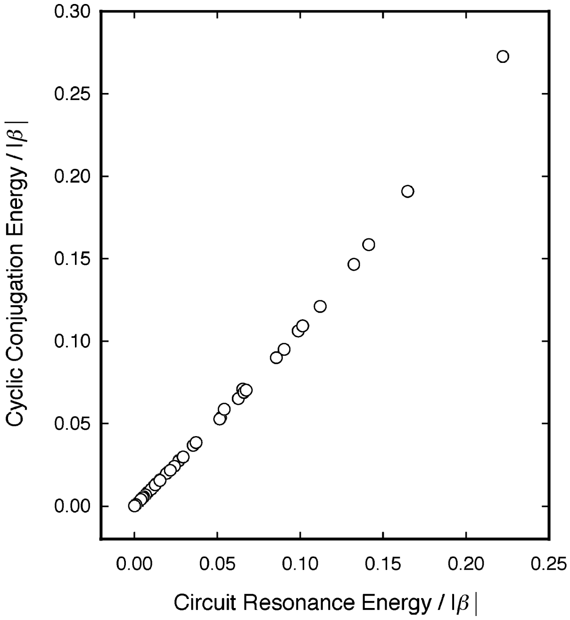

Figure 5. Correlation between CREs and CCEs for all nonidentical circuits in 10 PAHs.

$$X_j^* \approx X_j - 2\frac{P_{G-r_i}(X_j)}{P'_G(X_j)} \tag{6}$$

where X_j and X_j^* are the jth roots of the equations $P_G(X) = 0$ and $P_{G-c_i}(X) = 0$, respectively. Therefore, the following approximation generally holds:

$$\mathrm{CCE}_i/|\beta| = 2\sum_{j}^{\mathrm{occ}}(X_j - X_j^*) \approx A_i = \mathrm{CRE}_i/|\beta| \tag{7}$$

Numerical agreement between CCE and CRE clearly show that eq 7 holds for all or most circuits in PAHs. In this context, we noted in 1981 that A_i can be interpreted as an approximate contribution of the ith circuit to the TRE.[4]

The NICS value at the center of a monocyclic π-system must be proportional to the intensity of the current induced in the sole circuit if the circuit area remains almost unchanged. In this case, the current intensity is proportional to ASE. There indeed is an excellent correlation between NICS and ASE for a range of five-membered heterocycles.[8,43] Schleyer et al. employed energies of homodesmotic reactions as ASEs.[8,43] Haddon and we have shown that for [4n+2]annulenes the ring current intensity divided by the ring area is proportional to the ASE.[6,7] Thus, for a set of monocyclic π-systems with similar ring areas, the NICS value is roughly proportional to ASE. Therefore, we might safely say that at least for monocyclic π-systems, the current intensity is proportional to the sole CRE multiplied by the area enclosed by the ring. Equation 4 definitely shows that

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(60) Hosoya, H. *Theor. Chim. Acta* **1972**, *25*, 215.
(61) Graovac, A.; Gutman, I.; Trinajstić, N.; Zivković, T. *Theor. Chim. Acta* **1972**, *26*, 67.

Table 3. Two Type of Aromatic Stabilization Energies for Typical PAHs

species	TRE/$|\beta|$	MRE/$|\beta|$
benzene **(1)**	0.273	0.222
naphthalene **(2)**	0.389	0.289
anthracene **(3)**	0.475	0.341
phenanthrene **(4)**	0.546	0.407
naphthacene **(5)**	0.553	0.393
chrysene **(6)**	0.688	0.505
triphenylene **(7)**	0.739	0.574
pyrene **(8)**	0.598	0.417
perylene **(9)**	0.740	0.553
coronene **(10)**	0.947	0.628

the same idea can be applied to all circuits in polycyclic π-systems. The intensity of each circuit current is proportional not only to the circuit area but also to the CRE concerned.

We must here note that neither the CRE nor CCE concept is perfect. CRE cannot be evaluated for mono- and poly-cyclic π-systems with incompletely filled degenerate HOMOs, such as molecular dianions of benzene **(1)**, triphenylene **(5)**, and coronene **(10)**. However, this does not seem to be a serious problem because such open-shell species are always reactive and unstable. On the other hand, CCE may have an imaginary part for some charged π-systems because zeroes of $P_{G-r_i}(X)$ are not always real. This is also a minor problem because the imaginary part, if any, is very small.

Magnetic Resonance Energy. We have seen that the A_i value can be interpreted reasonably as CRE$_i$, i.e., the contribution of the ith circuit to global aromaticity. Therefore, the sum of A_i values over all circuits must represent the approximate TRE. The sum is here considered not as approximate TRE but as (exact) magnetic resonance energy (MRE), which means a TRE-like quantity derived from the magnetic response of the π-system:[42,62,63]

$$\mathrm{MRE}/|\beta| = \sum_i^G A_i$$

$$= \sum_i^G \mathrm{CRE}_i/|\beta| \qquad (8)$$

where i runs over all circuits in G. Like TRE and other ASEs, MRE depends on molecular topology but not on molecular geometry. As can be seen from Table 3 and Figure 6, MRE is highly correlative in magnitude with TRE although the former is always slightly smaller than the latter.[42,62,63] This fact supports the view that MRE can really be used as a kind of ASE. Excellent correlation between TRE and MRE also supports the reasonableness of CRE as a circuit resonance energy. Thus, we have succeeded in extracting a TRE-like energy quantity, MRE, from the magnetic response of the π-system.

Being based directly on cyclic π-electron delocalization, CRE and MRE can be regarded as absolute measures of aromatic stabilization, in the sense of not requiring reference standards for their qualification. Note that hypothetical polyene references are necessary to evaluate Hess-Schaad and topological resonance energies.[28,29,36,37] We do not need to construct a matching (or reference) polynomial or the like to calculate CRE and MRE. Thus, CRE and MRE are very realistic quantities as compared to these ASEs. MRE has a further advantage in that it can be evaluated additively with respect to individual circuits. Although nonadditive terms that may contribute to TRE are truncated in the present approach, there are essentially no problems in analyzing the topological relationship between TRE and the geometry of the π-system.

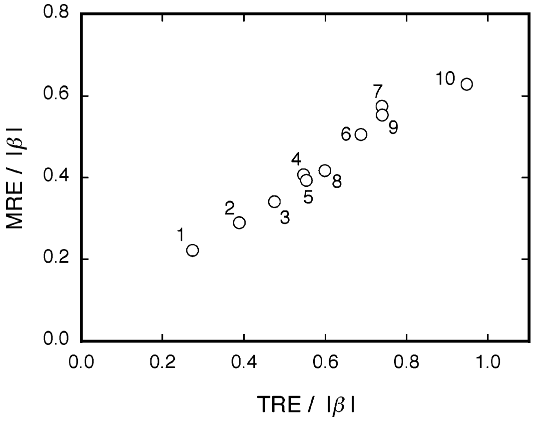

Figure 6. Correlation between TREs and MREs for 10 PAHs.

Ring-Current Magnetic Susceptibility Again. In general, an aromatic molecule is thermodynamically stable, in the sense that an external magnetic field destabilizes it energetically.[3−5] Therefore, an aromatic π-system is diamagnetic and enjoys the lowest energy when there is no magnetic field. As pointed out in 1979,[3] any magnetic field diminishes the contribution of cyclic conjugation to TRE in rather a complicated way. The present study clarified that ring-current diamagnetism is operative at the level of individual circuits. Circuit-current susceptibility, i.e., the tendency of a given circuit to escape from the magnetic field, is proportional to the CRE multiplied by the circuit area. In other words, the sum of all CREs is equal to MRE or close to TRE. Thus, ASE is fully responsible for ring-current diamagnetism. An external magnetic field decreases the total π-electron energy and TRE of an aromatic π-system. This is the origin of circuit currents and ring-current diamagnetism. Ring-current diamagnetism represents the tendency of the π-system to retain aromatic stabilization energy at the level of individual circuits.

As has been seen, magnetic criteria of aromaticity are more or less obscure due to their geometry dependencies. This can be readily seen by comparing eqs 3, 4, and 8. MRE, a kind of ASE, is obtained simply by adding up the A_i values over all circuits. In contrast, the current density pattern and ring-current susceptibility are obtained by adding up the A_i value with weights of the area and the area squared, respectively. These weights impair the reliability of these magnetic quantities as criteria of aromaticity. In general, larger circuits contribute less to MRE but much more to magnetic properties because of their large areas. It is for this reason that χ_G decreases in the order naphthacene **(5)** $>$ chrysene **(6)** $>$ triphenylene **(7)** although TRE- or MRE-based aromaticity order of these tetracyclic PAHs is **7** $>$ **6** $>$ **5**. It is for the same reason that some charged polycyclic π-systems are paratropic but aromatic.[42]

Concluding Remarks

Energetic and magnetic criteria of aromaticity are different by definition. Therefore, they might possibly make different

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(62) Aihara, J.; Kanno, H. *J. Phys. Chem. A* **2005**, *109*, 3717.
(63) Aihara, J.; Kanno, H.; Ishida, T. *J. Am. Chem. Soc.* **2005**, *127*, 13324.

predictions as to the aromaticity of a given π-system. In this study, we unveiled the graph-theoretical features that underlie induced π-electron currents and then firmly established the CRE/MRE concept, which proved to be very useful for linking energetic criteria of aromaticity with magnetic ones. In this sense, MRE is an excellent indicator of aromaticity that reflects both energetic and magnetic criteria of aromaticity. Note that MRE is a kind of energetic criterion of aromaticity derived from a magnetic criterion of aromaticity.

In 2000, Jusélius and Sundholm predicted the existence of two or more aromatic pathways in porphine and magnesium porphyrins.[64,65] They claimed that the total aromatic pathway of these species must be considered as a superposition of several pathways. These aromatic pathways in principle must be identical with aromatic circuits as defined in this study. Steiner and Fowler analyzed the current density pattern in porphyrin and presumed that, in addition to a current along the porphyrin macrocycle, local circulation of π-electrons is induced within each pyrrole ring.[66] Bifurcation of current flow in polycyclic π-systems can anyways be accounted for in terms of circuit currents.

Other recent studies of magnetic properties include analyses of individual molecular orbital contributions to current density patterns by Fowler et al.[66−68] and Heine et al.[38] The latter research group critically compared these two studies.[38] Their methodologies and our graph-theoretical one yield quite different types of information on π-electron currents, which must be complimentary to each other. In aromatic chemistry, discussion is often focused on possible relationships between ring structure and energy (or magnetism). Ring-current magnetic susceptibility, π-electron currents, and MRE can all be partitioned not only among the circuits but also among the occupied π-electron molecular orbitals. We believe that our approach is very useful in these senses.

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(64) Jusélius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2145.
(65) Jusélius, J.; Sundholm, D. *J. Org. Chem.* **2000**, *65*, 5233.
(66) Steiner, E.; Fowler, P. W. *Org. Biomol. Chem.* **2003**, *1*, 1785.
(67) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **2001**, *105*, 9553.
(68) Fowler, P. W.; Steiner, E.; Havenith, R. W. A.; Jenneskens, L. W. *Magn. Reson. Chem.* **2004**, *42*, S68.