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Topological resonance energy, bond resonance energy, and circuit resonance energy

Jun-ichi Aihara[a*]

Circuit resonance energy (CRE) is a key quantity that links energetic and magnetic criteria of aromaticity for a polycyclic π-system. Topological resonance energy (TRE) correlates well with the sum of CREs for an entire π-system. We found that bond resonance energy (BRE), so far defined to estimate the degree of kinetic stability for a polycyclic π-system, also correlates very well with the corresponding quantity defined with CREs. These findings justify the view that graph-theoretical quantities, such as TRE and BRE, can be used safely even though they rely on unrealistic reference structures. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: aromaticity; topological resonance energy; bond resonance energy; circuit resonance energy; polycyclic aromatic hydrocarbons

INTRODUCTION

Aromaticity has been defined variously in energetic, magnetic, structural, and other terms.[1–3] However, it has become more and more clear that different quantitative indices of aromaticity do not always vary colinearly.[4–8] Under such circumstances, Cyranski *et al*. asked themselves to what extent aromaticity can be defined uniquely.[9] Our graph-theoretical analysis revealed that energetic and magnetic criteria of aromaticity are quite different by definition.[10–18] In general, aromaticity is a state of energy, whereas ring-current diamagnetism is highly dependent on molecular geometry. Therefore, energetic and magnetic criteria of aromaticity necessarily make different predictions as to the aromaticity of some or many polycyclic π-systems.[19–27]

Our graph theory of ring-current diamagnetism[10–15] was found to provide a new definition of aromatic stabilization energy (ASE).[16–18] According to this theory, ring-current magnetic susceptibility can be resolved into separate circuit contributions. Here, circuits stand for all possible cyclic paths that can be chosen from a cyclic π-system.[28] We derived circuit resonance energies (CREs), a kind of ASE attributable to individual circuits, from the circuit contributions of ring-current magnetic susceptibility.[16–18] The CRE concepts proved to be very useful for consistently describing the energetic and magnetic consequences of cyclic π-electron delocalization. Magnetic resonance energy (MRE), defined by summing up all CREs in the π-system,[16–18,29,30] was found to exhibit a close correlation to topological resonance energy (TRE), a typical energetic descriptor of aromaticity.[13,31–33]

Bond resonance energy (BRE) is also a topological quantity that represents the contribution of a given π-bond to aromaticity,[34,35] The smallest BRE in a molecule has been used successfully as a measure of kinetic stability for polycyclic benzenoid and nonbenzenoid hydrocarbons and fullerenes.[34–41] In this paper, we attempt to interpret the BRE concept in terms of the CREs concerned. As will be seen, CREs can be utilized to estimate not only the magnitude of TRE but also those of BREs for a polycyclic π-system.

THEORY AND DISCUSSION

Our graph theories of aromaticity[31–37] and ring-current diamagnetism[10–18] are the main tools for the present study. The latter theory is a graph-theoretical variant of Hückel–London theory.[42,43] All graph-theoretical calculations were performed on 33 neutral and doubly charged polycyclic aromatic hydrocarbons (PAHs) listed in Table 1; they are benzene (**1**), *p*-polyphenyls (**2–4**), and condensed benzenoid hydrocarbons (**5–33**). Typical energetic and magnetic quantities of each PAH dianion are the same in magnitude as those of the dication because these PAHs are alternant hydrocarbons. Therefore, PAH dianions/dications will be referred to as simply as doubly charged PAHs. For simplicity, all benzenoid hexagons were taken to have the same areas as the benzene ring. We first summarize our graph theory of ring-current diamagnetism.

Circuit resonance energy

The quantity A_i is defined for the ith circuit in a closed-shell polycyclic π-system G as:[13,16–18]

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

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* Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422-8529, Japan.
E-mail: scjaiha@yahoo.co.jp

a J. Aihara
Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422-8529, Japan

Table 1. TREs and MREs for neutral and doubly charged PAHs

Species	Neutral molecule		Doubly charged ion	
	TRE/$\vert\beta\vert$	MRE/$\vert\beta\vert$	TRE/$\vert\beta\vert$	MRE/$\vert\beta\vert$
benzene (**1**)	0.273	0.222	−0.692	—
biphenyl (**2**)	0.502	0.415	−0.178	−0.694
p-terphenyl (**3**)	0.727	0.607	0.127	−0.203
p-quaterphenyl (**4**)	0.950	0.797	0.384	0.081
naphthalene (**5**)	0.389	0.289	−0.140	−0.072
anthracene (**6**)	0.475	0.341	0.173	0.261
phenanthrene (**7**)	0.546	0.407	−0.083	−0.129
pyrene (**8**)	0.598	0.417	0.199	0.248
naphthacene (**9**)	0.553	0.393	0.377	0.393
benz[*a*]anthracene (**10**)	0.643	0.472	0.217	0.276
chrysene (**11**)	0.688	0.505	0.144	0.216
triphenylene (**12**)	0.739	0.574	−0.109	—
perylene (**13**)	0.740	0.553	0.470	0.370
benzo[*a*]pyrene (**14**)	0.725	0.509	0.398	0.418
benzo[*e*]pyrene (**15**)	0.791	0.580	0.256	0.211
pentacene (**16**)	0.630	0.448	0.527	0.477
dibenz[*a*,*h*]anthracene (**17**)	0.807	0.595	0.296	0.308
picene (**18**)	0.835	0.611	0.276	0.304
dibenz[*a*,*c*]anthracene (**19**)	0.845	0.647	0.299	0.271
benzo[*g*]chrysene (**20**)	0.869	0.655	0.257	0.271
dibenzo[*def*,*mno*]chrysene (**21**)	0.766	0.522	0.548	0.492
benzo[*ghi*]perylene (**22**)	0.853	0.596	0.380	0.344
dibenzo[*de*,*mn*]naphthacene (**23**)	0.780	0.585	0.697	0.540
dibenzo[*fg*,*op*]naphthacene (**24**)	0.983	0.743	0.315	−0.026
dibenzo[*a*,*h*]pyrene (**25**)	0.844	0.593	0.594	0.568
coronene (**26**)	0.947	0.628	0.242	—
hexacene (**27**)	0.706	0.504	0.648	0.545
fulminene (**28**)	0.980	0.713	0.444	0.460
dibenzo[*a*,*c*]naphthacene (**29**)	0.929	0.702	0.604	0.587
tribenz[*a*,*c*,*h*]anthracene (**30**)	1.004	0.765	0.375	0.241
dibenzo[*b*,*g*]chrysene (**31**)	0.958	0.709	0.560	0.593
dibenzo[*g*,*p*]chrysene (**32**)	1.041	0.790	0.431	0.416
peropyrene (**33**)	0.942	0.645	0.697	0.606

where r_i is a set of carbon atoms that constitute the *i*th circuit; G-r_i is the subsystem of G and is obtained when all carbon atoms that constitute the ith circuit are deleted from G; $P_G(X)$ and $P_{G-r_i}(X)$ are the characteristic polynomials for G and G-r_i, respectively; and X_j is the *j*th largest root of the equation $P_G(X) = 0$; and j runs over all occupied π molecular orbitals. If some occupied molecular orbitals have the same energies, this formula must be replaced by others.[11,14,44,45]

We previously showed that the A_i value represents the energy gain or loss due to cyclic conjugation along the *i*th circuit.[16–18] It has hence been called circuit resonance energy (CRE). In fact, CRE correlates very well with the corresponding cyclic conjugation energy (CCE) defined by Gutman and Bosanac.[46–48] As numerical examples, the A_i values for all non-identical circuits in perylene (**13**) and its doubly charged ion are presented in Figure 1. For neutral PAH species, such as neutral **13**, the signs of A_i values obey the extended Hückel rule proposed by Hosoya *et al.*;[49,50] all $(4n + 2)$-site circuits are aromatic with positive CREs, whereas all 4n-site ones are antiaromatic with negative CREs. In accord with Randić's way of reasoning,[51,52] conjugated circuits have much larger CREs than non-conjugated ones. These rules do not hold for the circuits in charged species.

Ring-current magnetic susceptibility

When an external magnetic field, H, is oriented perpendicular to the plane of G, the ring-current magnetic susceptibility is given in the exact form[11,13]

$$\chi_\pi = 4.5\chi_0 \sum_i^G A_i \left(\frac{S_i}{S_0}\right)^2 \qquad (2)$$

where χ_0 is the ring-current susceptibility of benzene; S_i and S_0 are the areas of the *i*th circuit in G and the benzene (**1**) ring, respectively; and the summation is made over all circuits in G. In fact, the definition of the A_i value stems from this equation; positive and negative A_i values represent diamagnetic and para-

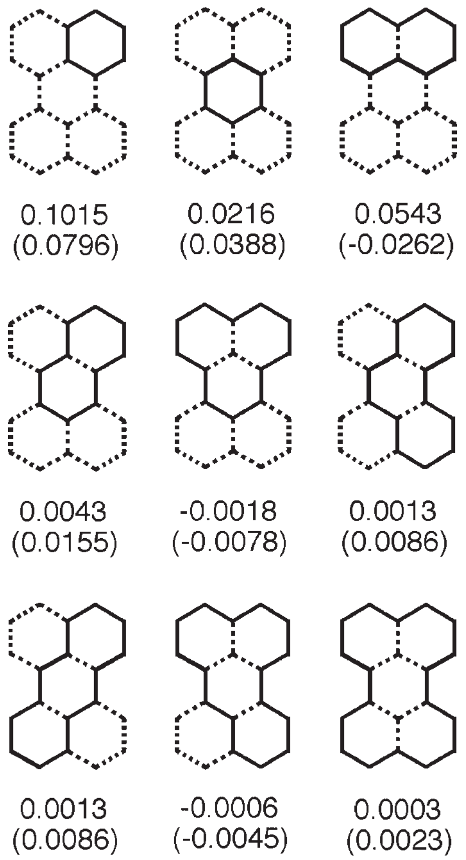

Figure 1. All non-identical circuits in perylene (**13**). Upper and lower values are the A_i values for the circuits in the neutral and doubly charged species, respectively

magnetic contributions, respectively. Thus, ring-current magnetic susceptibility is additive with respect to individual circuits.

Circuit current

According to Eqn 2, the contribution of the *i*th circuit to χ_π, that is, the *i*th circuit-current susceptibility, is given simply as[11,13]

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

This equation shows that circuit-current susceptibility, that is, the tendency of a given circuit to escape from the external magnetic field, is proportional to the CRE multiplied by the circuit area squared. Thus, ring-current diamagnetism represents the tendency of a cyclic π-system to retain ASE at the level of individual circuits.

Magnetization, *M*, due to a loop current, *I*, induced by a magnetic field, *H*, is given by *IS*, where *S* is the area enclosed by the loop.[53] Since $M = \chi H$, *I* can be equated formally to $\chi H/S$. Hence, χ_i must correspond to the induction of a π-electron current in the *i*th circuit the intensity of which is expressed as[14,15]

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

where I_0 is the intensity of a π-electron current induced in the benzene (**1**) ring. Positive and negative A_i values indicate diatropicity and paratropicity, respectively. A current density map for *G* can be obtained by superposing all circuit currents induced in *G*.

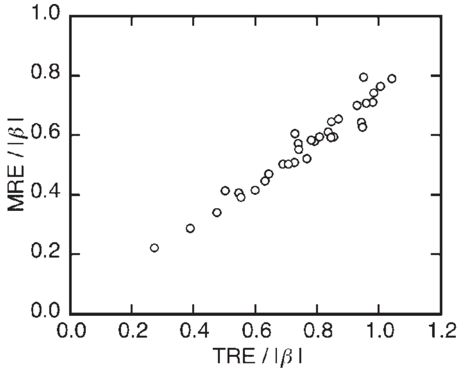

Figure 2. Excellent correlation found between MRE and TRE for 33 neutral PAHs

Magnetic resonance energy

Since the A_i value can be interpreted as CRE_i, the sum of A_i values over all circuits must represent the ASE for an entire π-system. This sum is nothing other than magnetic resonance energy (MRE)[16–18,29,30]

$$\mathrm{MRE}/|\beta| = \sum_i^G A_i \tag{5}$$

Not requiring hypothetical reference standards for their qualification, CRE and MRE can be regarded as absolute measures of aromatic stabilization. MRE has a unique advantage in that it is additive with respect to individual circuits.

Table 1 compares MREs with TREs for 33 neutral and doubly charged PAHs. As shown in Fig. 2, MRE and TRE vary almost colinearly with a correlation coefficient (cc) of 0.974. It is noteworthy that such a TRE-like ASE can be extracted from the magnetic properties of a cyclic π-system. Conversely, an excellent correlation between TRE and MRE justifies the utility of TRE even though the TRE relies on the hypothetical polyene reference. Ring-current diamagnetism can now be interpreted as the tendency of the π-system to retain CREs at the level of individual circuits.

Figure 3 shows that a correlation between MRE and TRE is a little worse for the doubly charged ions ($\mathrm{cc} = 0.870$). Thus, MRE

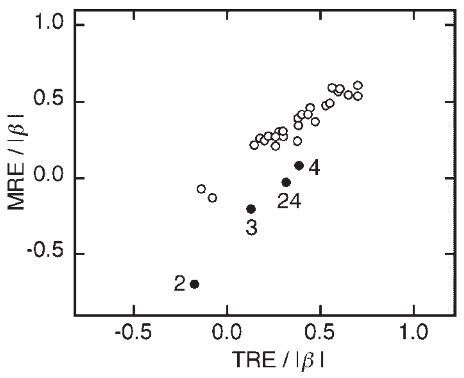

Figure 3. Plot of MRE against TRE for 30 doubly charged PAHs. Closed circles indicate species that deviate from colinearity

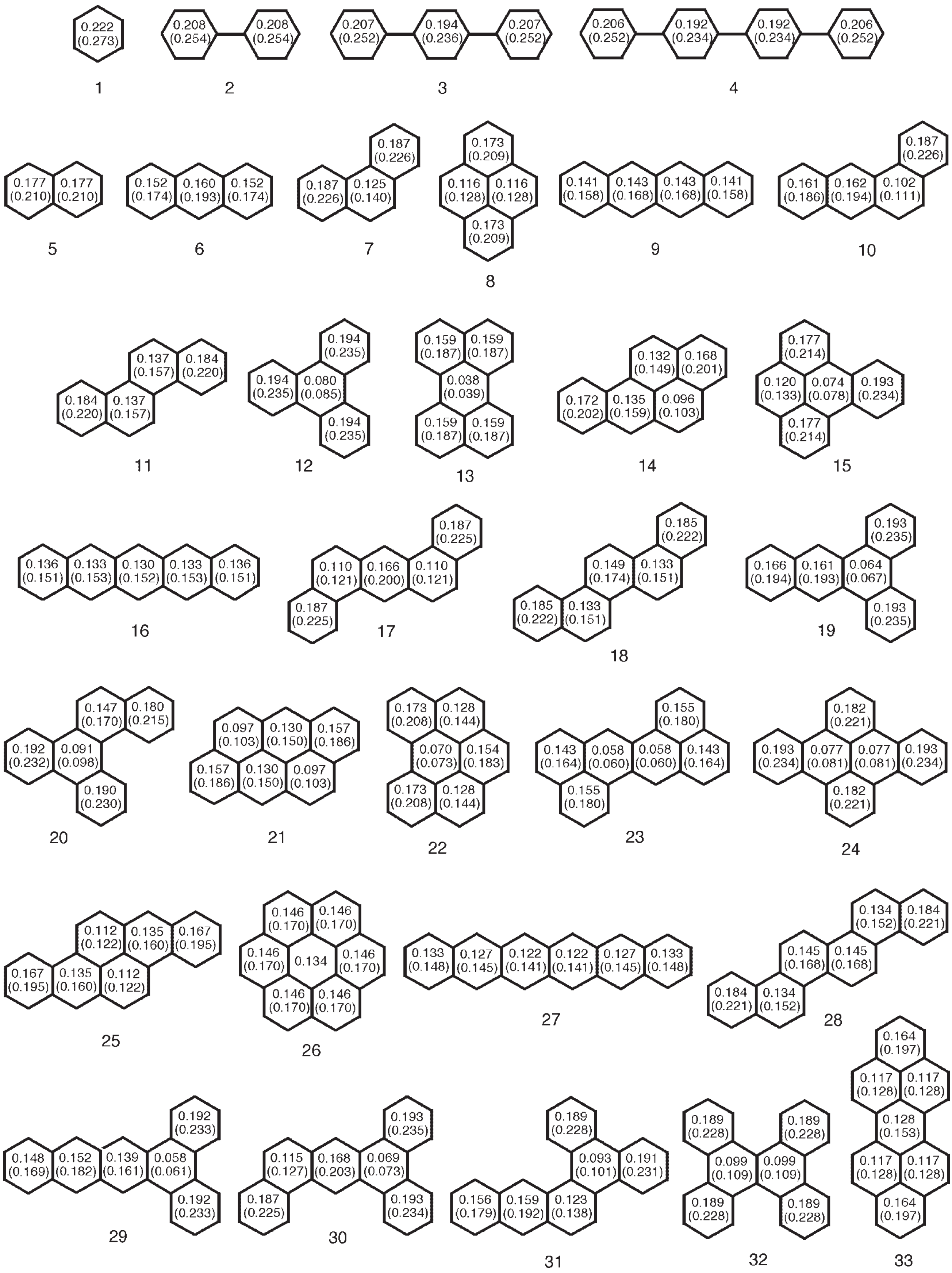

Figure 4. *m*-BREs in units of $|\beta|$ for the peripheral π-bonds in neutral PAHs. Values in parentheses are the corresponding *t*-BREs in units of $|\beta|$

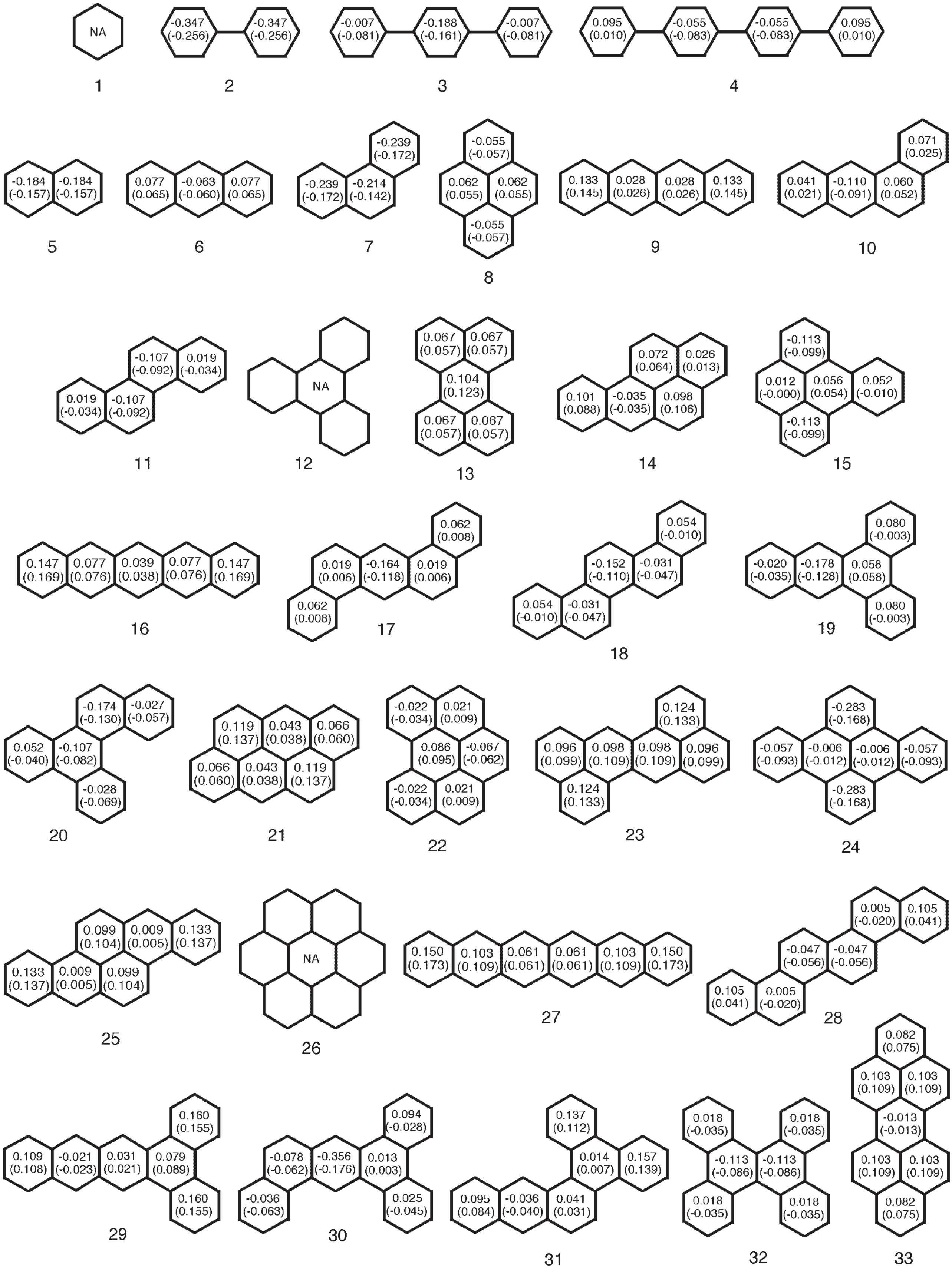

Figure 5. *m*-BREs in units of $|\beta|$ for the peripheral π-bonds in doubly charged PAHs. Values in parentheses are the corresponding *t*-BREs in units of $|\beta|$. NA indicates "Not Available"

reproduces the relative magnitude of TRE better for neutral PAHs than for their doubly charged ions. A bit smaller correlation coefficient for the charged species is presumably associated with Mallion's finding that the calculated magnetic properties of polycyclic π-systems other than typical aromatics are very sensitive to the molecular geometry and the molecular orbital method employed.[54–56] In general, a doubly charged PAH ion is much less aromatic than the neutral species.[16]

Four of the doubly charged species, denoted by filled circles in Fig. 3, deviate appreciably from colinearity. They are doubly charged ions of biphenyl (**2**), *p*-terphenyl (**3**), *p*-quaterphenyl (**4**), and dibenzo[*fg*,*op*]naphthacene (**24**). If these four species are disregarded, the correlation between TRE and MRE is improved up to cc = 0.959. These four exceptions happen to be fully benzenoid hydrocarbons in Clar's terminology.[57] There are no formal double bonds in the Clar structural formulae of these highly aromatic PAHs. Benzene (**1**) and triphenylene (**12**) are also fully benzenoid hydrocarbons. MRE cannot be evaluated for the open-shell dianions/dications of **1**, **12**, and coronene (**26**).

Bond resonance energy

Let β be the standard resonance integral between two adjacent carbon p_z orbitals and a hypothetical π-system in which a given π-bond, for example, the C_p—C_q bond, blocks cyclic conjugation through the π-bond is designed by assuming that $\beta_{pq} = i\beta$ and $\beta_{qp} = -i\beta$, where i is the square root of -1. In this π-system no circulation of π-electrons is expected along the circuits that share the C_p—C_q bond in common.[34–41] The BRE for the C_p—C_q bond is then defined as the destabilization energy of this hypothetical π-system relative to the actual one. BRE defined in this manner will hereafter be referred to as *t*-BRE because another definition of BRE will be introduced later. Here, letter "*t*" means a topologically defined quantity. The smallest *t*-BRE in a π-system represents well the degree of kinetic stability for the π-system.[34–41] In general, a cyclic π-system is kinetically very unstable, if the smallest *t*-BRE is smaller than $-0.100\ |\beta|$.

Magnetic definition of bond resonance energy

We now derive a *t*-BRE-like quantity from a subset of A_i values. Since A_i can be interpreted as an ASE at the level of individual circuits, the sum of A_i values over all circuits that share a given π-bond in common must be close to the *t*-BRE for the π-bond. This value will be referred to as *m*-BRE because it is a magnetically derived *t*-BRE-like quantity. In fact, *m*-BRE is mathematically an approximation of *t*-BRE like CRE is an approximation of CCE.[17] *m*-BREs thus obtained for all peripheral π-bonds in 33 neutral and doubly charged PAHs are graphically shown in Figs 4 and 5, respectively; the values in parentheses are the corresponding *t*-BREs.

Figures 6 and 7 show the plots of *m*-BRE against *t*-BRE for all peripheral π-bonds in neutral and doubly charged PAHs, respectively. We see from these figures that *m*-BRE highly correlates with *t*-BRE although the former value is slightly smaller than the latter one; the correlation coefficients are as large as 0.998 for neutral PAH molecules and 0.933 for the doubly charged species. A slightly worse correlation for the doubly charged species must again be due to the greater ambiguity inherent in the calculated magnetic properties of charged species.[54–56] In both figures, it seems that the correlation line passes through the origin. Such an excellent correlation supports not only our definition of *m*-BRE but also our interpretation of the A_i value as a CRE.

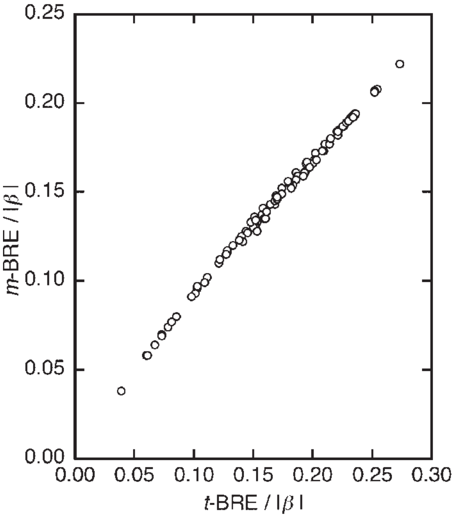

Figure 6. Excellent correlation between *m*-BRE and *t*-BRE for all peripheral π-bonds in 33 neutral PAHs

As reported previously,[37] the geometric distribution of *t*-BRE values in a PAH molecule conforms well to Clar's sextet formula,[57] suggesting that both types of BREs for peripheral π-bonds can be used as local aromaticity indices. Peripheral π-bonds that belong to sextet rings in fully benzenoid hydrocarbons have *t*-BREs > 0.221 $|\beta|$ and *m*-BREs > 0.182 $|\beta|$. On the contrary, central "empty" rings in perylene (**13**) and dibenzo[*de*,*mn*]naphthacene (**23**) are least aromatic with the peripheral π-bonds having very small BREs. Here, empty rings stand for the rings on which aromatic sextets can never be placed.[57] Presumably, benzene (**1**) is the most aromatic hydrocarbon with the largest *t*-BRE and the largest *m*-BRE.

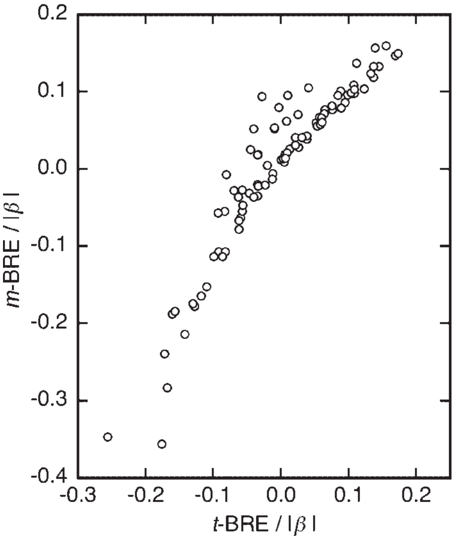

Figure 7. Plot of *m*-BRE against *t*-BRE for all peripheral π-bonds in 30 doubly charged PAHs

CONCLUDING REMARKS

Aromaticity and diatropicity are deeply rooted in each other. Major aspects of polycyclic π-systems can be explained consistently in terms of CREs. Circuit-current susceptibility, that is, the tendency of a given circuit to escape from the external magnetic field, is proportional to the CRE multiplied by the circuit area squared. We have seen that general trends in the TRE and *t*-BRE values can also be reproduced properly using the same set of CREs. This fact supports our view that TRE and *t*-BRE are still very meaningful for analyzing electronic features of aromatic and antiaromatic molecules even though they are based on virtual reference structures.

In order to avoid complexity and confusion, we have not discussed the *t*-BREs and *m*-BREs for the inner π-bonds shared by two rings. Two types of BREs can likewise be calculated for these π-bonds. For PAH molecules, BREs for peripheral π-bonds are appreciably smaller than those for inner π-bonds, because the latter π-bonds are shared by two six-site circuits.[37] Thus, there is little doubt that at least for such polycyclic benzenoid hydrocarbons, kinetic stability and local aromaticity are determined primarily by the BREs for peripheral π-bonds.

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