

Dimensionality of Aromaticity

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Received August 20, 2007; E-mail: scjaiha@yahoo.co.jp

Aromaticity has been viewed as multidimensional, because different scales of aromaticity sometimes make different predictions as to the aromaticity of a polycyclic π-system. Our graph theory of aromaticity and ring-current diamagnetism enables us to interpret magnetic scales of aromaticity in terms of aromatic stabilization energy (ASE). We have now no reason to regard any magnetic scale of aromaticity as a scale orthogonal to the energetic ones. Aromaticity is one-dimensional in this sense and should in principle be described in terms of ASE. Other scales of aromaticity, such as geometric ones, must likewise reflect ASE to varying extents, although it is not easy to interpret them analytically in energetic terms.

The concept of aromaticity is of central importance to research in organic chemistry. The presently accepted aromaticity criteria can be broadly subdivided into three groups: energetic, geometric, and magnetic ones.[1–3] For a long time, it has been the goal of chemists to develop a simple method to characterize ring compounds, namely, with a single scale of aromaticity. From this viewpoint, Katritzky et al. have reported statistical studies on five- and six-membered heterocyclic compounds.[4–8] In 1989, their principal component analysis (PCA) of 12 proposed aromaticity indices has shown that there are at least two distinct types of aromaticity: "Classical aromaticity" is well described by certain interrelated geometric and energetic indices, whereas the second type, the so-called "magnetic aromaticity," is best measured by anisotropies in the molar magnetic susceptibility. An analogous analysis by Jug and Köster supports the finding by Katritzky et al. that aromaticity is at least a two-dimensional phenomenon.[9]

As pointed out by Dewar and others,[10–13] the term "aromatic" should describe molecules that benefit energetically from the delocalization of mobile electrons in closed circuits. We have discussed aromaticity on the basis of the view that aromaticity itself represents a state of energy.[14,15] Molecules with extra stabilization energy due to cyclic conjugation have been defined as aromatic.[10–15] Our graph theory of aromaticity and ring-current diamagnetism[14–28] has proven to be useful for analyzing the energetic and magnetic properties of cyclic π-systems consistently at the same level of theory. In this theory, a key quantity that connects energetic and magnetic scales of aromaticity is the circuit resonance energy (CRE), which represents a contribution of each cyclic path in a polycyclic π-system to the aromatic stabilization energy (ASE). In this paper, we explicitly show using this theoretical basis that the magnetic scales of aromaticity are not orthogonal (unrelated) to the energetic ones and attempt to solve the problem on the dimensionality of aromaticity.

Theory

First, our theory of ring-current diamagnetism is outlined; it is a graph-theoretical variant[16–28] of Hückel–London theory.[29,30] Our graph theory allows an exact partitioning of the ring-current magnetic susceptibility for a polycyclic π-system into individual circuit contributions. Here, circuits stand for all possible cyclic or closed paths that can be chosen from a cyclic π-system.[31] For example, two six-site circuits and one ten-site circuit can be chosen from the naphthalene π-system. In addition, the topological resonance energy (TRE) can be calculated within the same theoretical framework.[14,15]

Ring-Current Diamagnetic Susceptibility. The key quantity in our theory is the A_i value defined for each circuit in a cyclic π systems, which is needed to formulate graph-theoretically the ring-current diamagnetic susceptibility:[17,25,26]

$$A_i = 4\prod_{m>n}^{r_i} k_{mn} \sum_{j}^{\mathrm{occ}} \frac{P_{\mathrm{G}} - r_i(X_j)}{P'_{\mathrm{G}}(X_j)} \tag{1}$$

where r_i refers to a set of conjugated atoms and π-bonds that constitute the ith circuit, c_i, k_{mn} is the Hückel parameter for the resonance integral between atoms m and n, which run over all π-bonds that belong to r_i, G-r_i is the subsystem of G, obtained by deleting r_i from G, $P_{\mathrm{G}}(X)$ and $P_{\mathrm{G}\text{-}r_i}(X)$ are the characteristic polynomials for G and G-r_i, respectively, X_j is the jth largest zero of $P_{\mathrm{G}}(X)$, to which an added prime indicates a first derivative with respect to X, and j runs over all occupied π molecular orbitals. If there are degenerate π molecular orbitals, Eq. 1 cannot be used.[17,18,21,22]

When an external magnetic field, H, is oriented perpendicular to the plane of G, the ring-current diamagnetic susceptibility, χ_{G}, can then be expressed in the form:[17–23]

$$\chi_{\mathrm{G}} = 4.5\chi_0 \sum_{i}^{\mathrm{G}} A_i \left(\frac{S_i}{S_0}\right)^2 \tag{2}$$

where χ_0 is the ring-current susceptibility of benzene, and 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.[29,30] Thus, χ_{G} can be evaluated additively with respect to individual circuits. The contribution of the ith

Published on the web February 12, 2008; doi:10.1246/bcsj.81.241

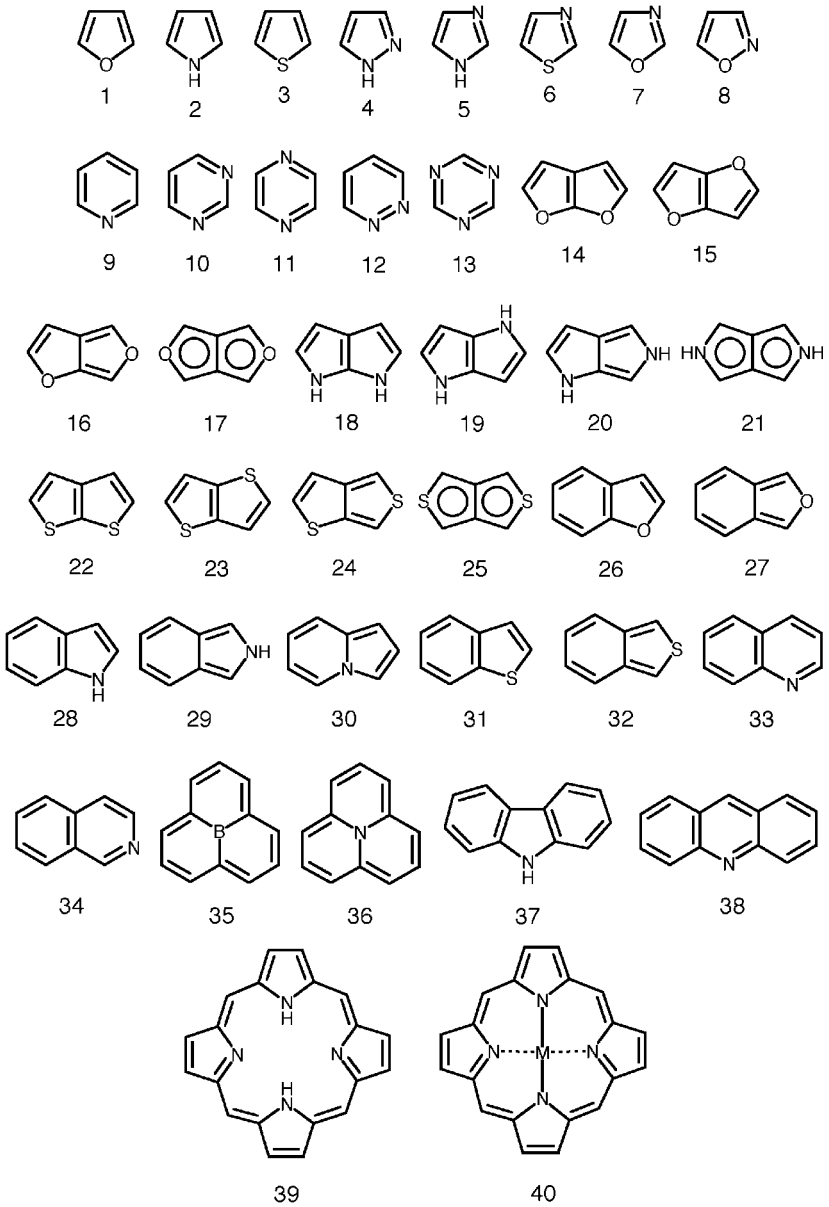

Fig. 1. Typical heterocycles.

circuit to χ_G, i.e., the circuit-current susceptibility, is then given as:[17–22]

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

Circuit Current. A π-electron current induced in each circuit may be called a circuit current. According to general theory of electromagnetism, 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.[32] Since $M = \chi H$, I must be formally equal to $\chi H/S$, and the circuit-current susceptibility for the ith circuit, χ_i, must correspond to the induction of a π-electron current in the circuit whose intensity is given by:[22–24]

$$I_i = 4.5 I_0 A_i \frac{S_i}{S_0} \quad (4)$$

where I_0 is the intensity of a current induced in the benzene ring. Positive and negative A_i values indicate diatropicity and paratropicity, respectively. A π current density map for an entire π system is obtained by superimposing all of the circuit currents.[25–27]

Magnetic Resonance Energy. As stated in a previous paper,[26] the A_i value is interpretable as an energy gain or loss due to cyclic conjugation along the ith circuit and so is termed the ith circuit resonance energy (CRE_i). The sum of the A_i values over all circuits must therefore represent an ASE for an entire π system. This quantity is termed magnetic resonance energy (MRE), which means a TRE-like quantity derived from the magnetic response of the π-system:[25–28]

$$\mathrm{MRE}/|\beta| = \sum_i^{\mathrm{G}} A_i = \sum_i^{\mathrm{G}} \mathrm{CRE}_i/|\beta| \quad (5)$$

Table 1. TREs, MREs, Intensities of Ring Currents, and Ring-Current Diamagnetic Susceptibilities for Five-Membered Heterocycles

Species	TRE/$\|\beta\|$	MRE/$\|\beta\|$	I_π/I_0	χ_G/χ_0
Furan (**1**)	0.1360	0.1238	0.369	0.244
Pyrrole (**2**)	0.2462	0.2094	0.624	0.413
Thiophene (**3**)	0.1965	0.1710	0.509	0.337
Pyrazole (**4**)	0.2664	0.2241	0.668	0.442
Imidazole (**5**)	0.2431	0.2077	0.619	0.410
Thiazole (**6**)	0.1961	0.1710	0.509	0.337
Oxazole (**7**)	0.1360	0.1240	0.369	0.245
Isoxazole (**8**)	0.1608	0.1441	0.430	0.284
1,2,4-Triazole	0.2585	0.2195	0.654	0.433
4*H*-1,2,4-Triazole	0.2466	0.2110	0.629	0.416
1*H*-1,2,3-Triazole	0.2745	0.2304	0.686	0.455
2*H*-1,2,3-Triazole	0.2914	0.2417	0.720	0.477
1*H*-1,2,3,4-Tetrazole	0.2738	0.2312	0.689	0.456
2*H*-1,2,3,5-Tetrazole	0.2940	0.2447	0.729	0.483
Pentazole	0.3058	0.2543	0.758	0.502
1,3,4-Oxadiazole	0.1392	0.1269	0.378	0.250
1,2,5-Oxadiazole	0.1945	0.1707	0.509	0.337
1,2,4-Oxadiazole	0.1566	0.1412	0.421	0.279
1,2,3-Oxadiazole	0.1697	0.1513	0.451	0.299
1,2,3,5-Oxatriazole	0.1993	0.1749	0.521	0.345
1,2,3,4-Oxatriazole	0.1689	0.1514	0.451	0.299
Isothiazole	0.2182	0.1872	0.558	0.369
1,3,4-Thiadiazole	0.2006	0.1749	0.521	0.345
1,2,3-Thiadiazole	0.2281	0.1947	0.580	0.384
1,2,5-Thiadiazole	0.2461	0.2072	0.617	0.409
1,2,4-Thiadiazole	0.2129	0.1840	0.548	0.363
1,2,3,4-Thiatriazole	0.2283	0.1958	0.584	0.386
1,2,3,5-Thiatriazole	0.2506	0.2113	0.630	0.417

where i runs over all circuits in G. For polycyclic aromatic hydrocarbons and heterocycles, MRE highly correlates with TRE.[25–28]

Van-Catledge's set of Hückel parameters for heteroatoms[33] is employed to evaluate the aromaticity scales. Our theory uses no other empirical parameters. For the sake of simplicity, all rings but those in porphines (**39** and **40** in Fig. 1) are assumed to be regular polygons with the lengths of edges being equal to that of the benzene CC bond. The geometries of **39** and **40** are those obtained by Jusélius and Sundholm[34,35] using the resolution-of-the-identity density-functional theory (RI-DFT)[36] with the Becke–Perdew (B–P) parametrization.[37–39] We assume that the metal ion (e.g., the magnesium ion) in **40** is not included in the π-system and that all nitrogen atoms coordinated to the metal ion are of imine (=N–) type.

Results and Discussion

We tackled the problem on the orthogonality of classical and magnetic aromaticity by exploring possible relationships between energetic and magnetic scales of aromaticity. TRE and χ_G were adopted as primary energetic and magnetic scales of aromaticity, respectively, because they can be formulated analytically and evaluated accurately within the same theoretical framework. Tables 1 and 2 contain the relevant data for a variety of five- and six-membered heterocycles, respectively. Structural formulae of representative heterocycles and hydrocarbons studied are given in Figs. 1 and 2, respectively.

Table 2. TREs, MREs, Intensities of Ring Currents, and Ring-Current Diamagnetic Susceptibilities for Six-Membered Heterocycles

Species	TRE/$\|\beta\|$	MRE/$\|\beta\|$	I_π/I_0	χ_G/χ_0
Pyridine (**9**)	0.2685	0.2198	0.989	0.989
Pyrimidine (**10**)	0.2576	0.2133	0.960	0.960
Pyrazine (**11**)	0.2716	0.2217	0.998	0.998
Pyridazine (**12**)	0.2757	0.2249	1.012	1.012
1,3,5-Triazine (**13**)	0.2411	0.2030	0.914	0.914
1,2,4-Triazine	0.2716	0.2225	1.001	1.001
1,2,3-Triazine	0.2758	0.2257	1.016	1.016
1,2,4,5-Tetrazine	0.2795	0.2281	1.027	1.027
1,2,3,4-Tetrazine	0.2834	0.2312	1.040	1.040
Phosphabenzene	0.2456	0.2006	0.903	0.903

In Fig. 3, TREs are plotted against the χ_G values for 28 five-membered heterocycles and 10 six-membered ones, all with six π-electrons. As can be seen, for the set of five-membered heterocycles, there was a linear correlation between these two quantities. The same is true for a set of six-membered ring compounds. However, such a linear relationship disappeared when five- and six-membered heterocycles were considered together. The lack of common correlation is obviously related to the fact that, unlike energetic scales of aromaticity, the magnetic scales are dependent on molecular geometry, i.e., the ring area. Therefore, it seems that χ_G cannot be used as a reliable scale of aromaticity. Figure 4 shows a plot of MREs against TREs for the same mixture of five- or six-membered species. In marked contrast to Fig. 3, there was an excellent linear relationship between the two quantities.

We next examined the aromaticity and ring-current diamagnetism of polycyclic π-systems. Tables 3 and 4 contain the relevant data for 40 mono- and poly-cyclic heterocycles and 30 benzenoid hydrocarbons, respectively. Figure 5 shows a plot of χ_G values against TREs for a total of 70 species. Not surprisingly, for polycyclic π-systems no meaningful correlation between TRE and χ_G was observed; the correlation coefficient R was only 0.789. Even if only polycyclic benzenoid hydrocarbons **41–70** are considered, χ_G is still out of proportion to TRE. For example, the TRE for coronene (**63**) is 4.5 times larger than that for benzene (**41**), whereas χ_G for **63** is 9.8 times larger than that for **41**. Porphines (**39** and **40**), likewise, exhibited much larger susceptibilities than expected from their TREs. 9b-Boraphenalene (**35**) and 9b-azaphenalene (**36**) had ring-current paramagnetic susceptibilities, although they are aromatic with positive TREs. We previously reported that dianions/dications of anthracene (**43**), pyrene (**45**), and chrysene (**48**) are paratropic, although they have positive TREs.[25] These facts convinced us that χ_G and the associated diamagnetic susceptibility exaltation are unreliable as scales of aromaticity.

We then examined the relationship between TRE and MRE for polycyclic π-systems. In general, MRE is more or less smaller than TRE;[25–28] the only exception is 9b-boraphenalene (**35**). In Fig. 6, MREs are plotted against TREs for the same set of 70 mono- and poly-cyclic π-systems. This figure demonstrates numerically that, even for a wide variety of carbocyclic and heterocyclic π-systems, MRE correlates well with TRE ($R = 0.996$). Both types of resonance energies are almost

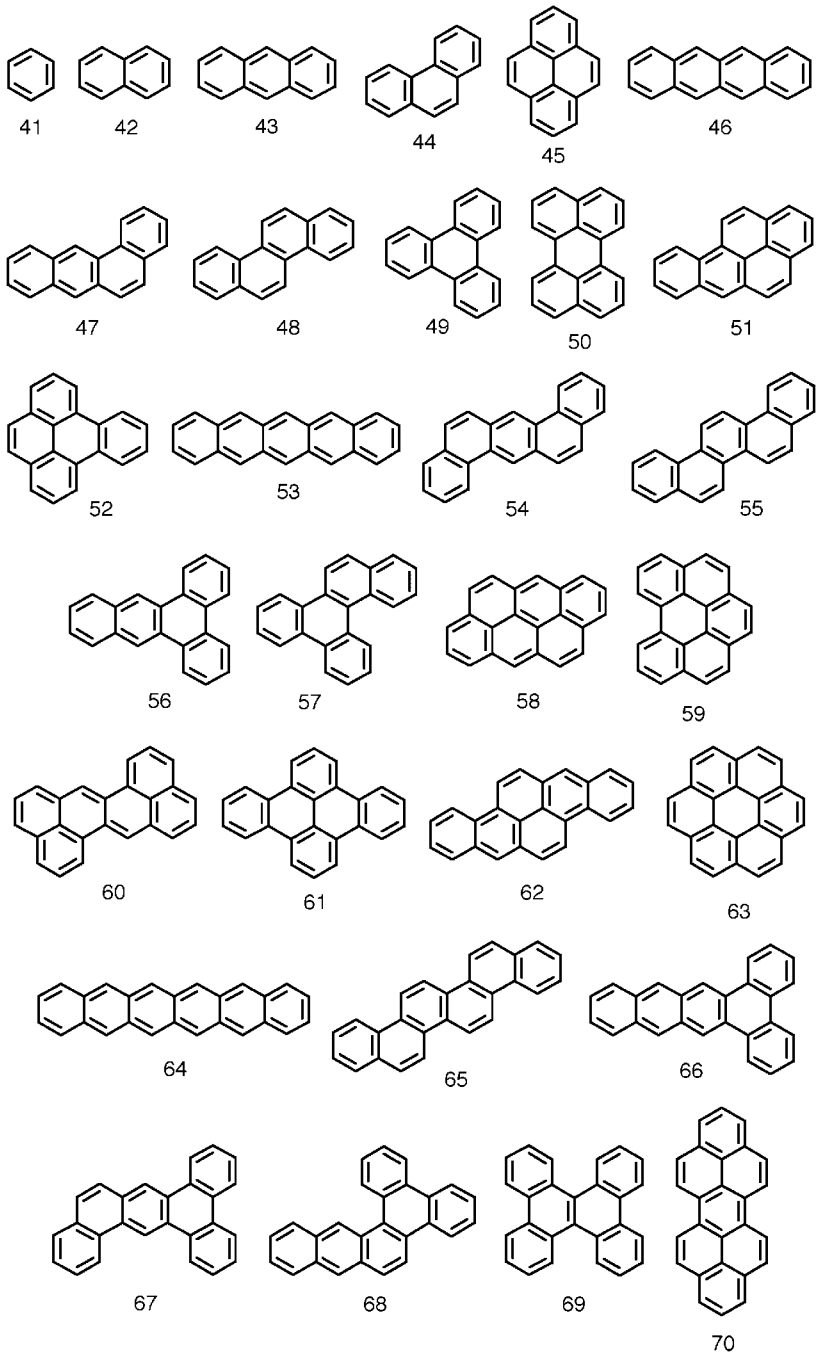

Fig. 2. Typical polycyclic benzenoid hydrocarbons.

tantamount to each other. This aspect of MRE means that χ_G is not independent of ASE. Thus, ASE should be considered as a primary scale of aromaticity. Not only TRE but also MRE can be used as a common scale of aromaticity, applicable to a wide variety of cyclic π-systems. ASEs calculated using homodesmotic reactions may be useful for the same purpose, although the ASE values obtained in this manner are very sensitive to the choice of reaction type and the level of theory.[40]

As can be seen from Eq. 3, circuit-current susceptibility (χ_i), i.e., the tendency of a given circuit to escape from the magnetic field, is proportional to the CRE multiplied by the circuit area squared.[26] Thus, the ring-current diamagnetism represents the tendency of a π system to retain ASE at the level of individual circuits. In general, magnetic scales of aromaticity are the energetic ones disturbed by the areas of the individual circuits. If one calculates χ_G by using Eq. 2 and on the assumption that $S_i = S_0$ for all circuits, a kind of geometry-independent diamagnetic susceptibility is obtained, which is necessarily proportional to MRE. Apart from this, MRE can be interpreted as an approximation of TRE.[19,26] Therefore, MRE can be viewed reasonably as a kind of magnetic scale of aromaticity, although it is energetic in appearance. We can safely say that energetic and magnetic scales can be unified by using MRE as a new aromaticity scale. Other magnetic scales, associated with ring-current diamagnetism, cannot be

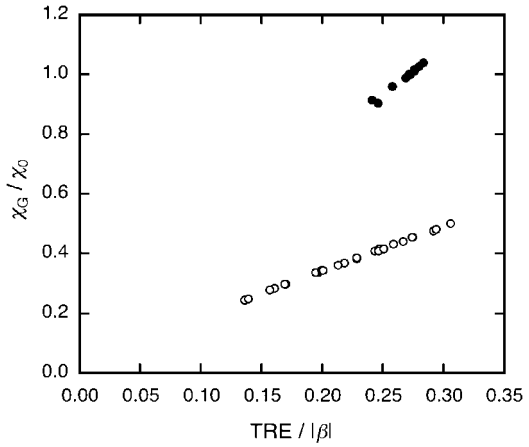

Fig. 3. Correlation between TRE and ring-current diamagnetic susceptibility for 28 five-membered heterocycles (○) and 10 six-membered heterocycles, including benzene (●).

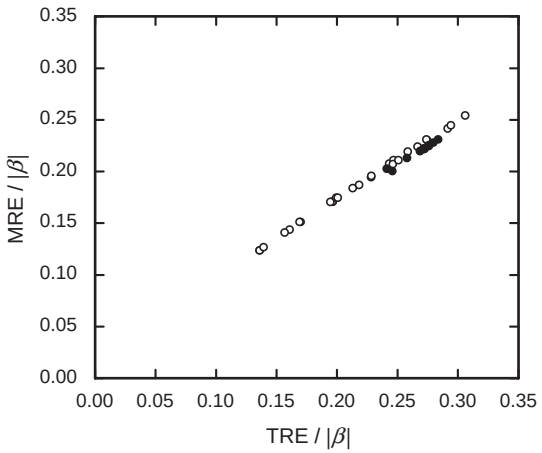

Fig. 4. Correlation between TRE and MRE for 28 five-membered heterocycles (○) and 10 six-membered heterocycles, including benzene (●).

used as reliable scales of global aromaticity, because they also are strongly geometry-dependent. In general, larger circuits contribute more to the magnetic scales of aromaticity because of their large areas, whereas smaller circuits contribute more to TRE and MRE.

Katritzky et al. have noted that two difficulties are encountered in theoretically assessing the aromaticity of a variety of compounds.[4] First, the parameters for heteroatoms used for theoretical molecular orbital methods have been in the past, and in some cases are still controversial. Secondly, there is a particular uncertainty when comparing aromatic compounds with nonaromatic models, and the precise definition of these models is not easy. Our non-parametric approach overcomes these difficulties. We used Van-Catledge's heteroatom parameters,[33] which have been determined consistently for many heteroatoms. Our approach is an analytical and exact one, although it is based on rather crude Hückel–London theory. Therefore, nonaromatic models can be defined without theoretical and numerical ambiguities. Total π-binding energy of a heterocycle may indeed depend on the choice of heteroatom parameters. However, the dependence of TRE on the heteroatom parameters is relatively small, because it is an energy difference between an actual π-system and the polyene reference. Neither hypothetical polyene references nor homodesmotic reactions are needed to evaluate MRE.

In 1978, Haddon has pointed out that, for aromatic annulenes, ASE is proportional to the ring-current intensity, divided by the area enclosed by the ring.[41] The ASE employed by him is a so-called A-I resonance energy, defined by us.[14] We then derived an analogous relationship using TRE as an ASE.[42] If we replace A_i in Eq. 4 with MRE, essentially the same relationship is obtained for all monocyclic π-systems, including aromatic annulenes, that is, MRE is proportional to the ring-current intensity, divided by the ring area. For monocyclic π-systems with the same ring areas, the intensity of an induced

Table 3. TREs, MREs, and Ring-Current Diamagnetic Susceptibilities for Typical Mono- and Poly-cyclic Heterocycles

Species	TRE/$\|\beta\|$	MRE/$\|\beta\|$	χ_G/χ_0
Furan (**1**)	0.1360	0.1238	0.244
Pyrrole (**2**)	0.2462	0.2094	0.413
Thiophene (**3**)	0.1965	0.1710	0.337
Pyrazole (**4**)	0.2664	0.2241	0.442
Imidazole (**5**)	0.2431	0.2077	0.410
Thiazole (**6**)	0.1961	0.1710	0.337
Oxazole (**7**)	0.1360	0.1240	0.245
Isoxazole (**8**)	0.1608	0.1441	0.284
Pyridine (**9**)	0.2685	0.2198	0.989
Pyrimidine (**10**)	0.2576	0.2133	0.960
Pyrazine (**11**)	0.2716	0.2217	0.998
Pyridazine (**12**)	0.2757	0.2249	1.012
1,3,5-Triazine (**13**)	0.2411	0.2030	0.914
Furo[2,3-*b*]furan (**14**)	0.2279	0.1945	0.457
Furo[3,2-*b*]furan (**15**)	0.2240	0.1908	0.449
Furo[3,4-*b*]furan (**16**)	0.1650	0.1484	0.381
Furo[3,4-*c*]furan (**17**)	0.1871	0.1575	0.665
Pyrrolo[2,3-*b*]pyrrole (**18**)	0.3795	0.2973	0.811
Pyrrolo[3,2-*b*]pyrrole (**19**)	0.3849	0.2989	0.816
Pyrrolo[3,4-*b*]pyrrole (**20**)	0.3319	0.2686	0.809
Pyrrolo[3,4-*c*]pyrrole (**21**)	0.3419	0.2685	1.023
Thieno[2,3-*b*]thiophene (**22**)	0.3093	0.2491	0.639
Thieno[3,2-*b*]thiophene (**23**)	0.3107	0.2485	0.639
Thieno[3,4-*b*]thiophene (**24**)	0.2508	0.2114	0.603
Thieno[3,4-*c*]thiophene (**25**)	0.2671	0.2147	0.856
Benzo[*b*]furan (**26**)	0.3216	0.2527	1.226
Benzo[*c*]furan (**27**)	0.2196	0.1878	1.051
Indole (**28**)	0.3763	0.2858	1.476
Isoindole (**29**)	0.3266	0.2567	1.466
Indolizine (**30**)	0.3088	0.2418	1.405
Benzo[*b*]thiophene (**31**)	0.3485	0.2673	1.361
Benzo[*c*]thiophene (**32**)	0.2843	0.2286	1.313
Quinoline (**33**)	0.3844	0.2871	2.161
Isoquinoline (**34**)	0.3846	0.2873	2.167
9b-Boraphenalene (**35**)	0.2501	0.2220	−0.069
9b-Azaphenalene (**36**)	0.1606	0.1743	−1.744
Carbazole (**37**)	0.5515	0.4228	2.480
Acridine (**38**)	0.4714	0.3402	3.380
Free-base porphine (**39**)	0.4322	0.3390	13.492
Metal(II) porphine (**40**)	0.4744	0.3718	11.593

Table 4. TREs, MREs, and Ring-Current Diamagnetic Susceptibilities for Benzene and Polycyclic Benzenoid Hydrocarbons

Species	TRE/$\|\beta\|$	MRE/$\|\beta\|$	χ_G/χ_0
Benzene (**41**)	0.2726	0.2222	1.000
Naphthalene (**42**)	0.3888	0.2894	2.185
Anthracene (**43**)	0.4746	0.3405	3.448
Phenanthrene (**44**)	0.5459	0.4074	3.248
Pyrene (**45**)	0.5978	0.4167	4.580
Naphthacene (**46**)	0.5531	0.3928	4.747
Benz[*a*]anthracene (**47**)	0.6433	0.4717	4.402
Chrysene (**48**)	0.6884	0.5053	4.440
Triphenylene (**49**)	0.7391	0.5741	4.076
Perylene (**50**)	0.7396	0.5532	4.120
Benzo[*a*]pyrene (**51**)	0.7247	0.5089	5.722
Benzo[*e*]pyrene (**52**)	0.7910	0.5799	5.395
Pentacene (**53**)	0.6298	0.4476	6.062
Dibenz[*a*,*h*]anthracene (**54**)	0.8066	0.5949	5.451
Picene (**55**)	0.8348	0.6105	5.580
Dibenz[*a*,*c*]anthracene (**56**)	0.8450	0.6466	5.133
Benzo[*g*]chrysene (**57**)	0.8689	0.6548	5.359
Dibenzo[*def*,*mno*]chrysene (**58**)	0.7657	0.5217	6.978
Benzo[*ghi*]perylene (**59**)	0.8534	0.5963	6.801
Dibenzo[*de*,*mn*]naphthacene (**60**)	0.7804	0.5849	4.305
Dibenzo[*fg*,*op*]naphthacene (**61**)	0.9830	0.7430	6.244
Dibenzo[*a*,*h*]pyrene (**62**)	0.8442	0.5933	6.973
Coronene (**63**)	0.9474	0.6277	9.794
Hexacene (**64**)	0.7063	0.5040	7.385
Fulminene (**65**)	0.9795	0.7129	6.750
Dibenzo[*a*,*c*]naphthacene (**66**)	0.9287	0.7023	6.327
Tribenz[*a*,*c*,*h*]anthracene (**67**)	1.0043	0.7648	6.237
Dibenzo[*b*,*g*]chrysene (**68**)	0.9583	0.7095	6.607
Dibenzo[*g*,*p*]chrysene (**69**)	1.0413	0.7905	6.376
Peropyrene (**70**)	0.9425	0.6449	8.226

ring current is proportional to χ_G. Unfortunately, these relationships cannot be applied to polycyclic π-systems.

In 1995, Schleyer et al. have reported an excellent linear correlation between theoretically obtained diamagnetic susceptibility exaltations and ASEs for a series of five-membered C_4H_4X ring systems.[43] Such a linear correlation is essentially the same as that observed in Fig. 3. Schleyer et al. have also found a colinearity between nucleus-independent chemical shift (NICS) and ASE for five-membered heterocycles.[44] This colinearity is justifiable considering that the NICS value at the center of the five-membered ring is proportional to the intensity of the induced ring current (Eq. 4). If the ring area is kept constant for a series of monocyclic systems, not only the intensity of the induced ring current but also χ_G is proportional to MRE. Such linear relationships do not hold for polycyclic π-systems. Note that furan (**1**) and thiophene (**3**) have larger negative NICS values than benzene (**41**).[45] This is due primarily to the smaller radii of the five-membered rings.

There is no doubt that other aromaticity scales, such as geometric ones, reflect the degree of aromaticity to varying extents.[4–8,46,47] However, it is not easy to associate the geometric scales of aromaticity straightforwardly with ASE, etc. π-Electrons in a neutral closed-shell π-system are subject to distortion along a bond alternation mode and at the same time tend to delocalize by resonance relative to a localized reference

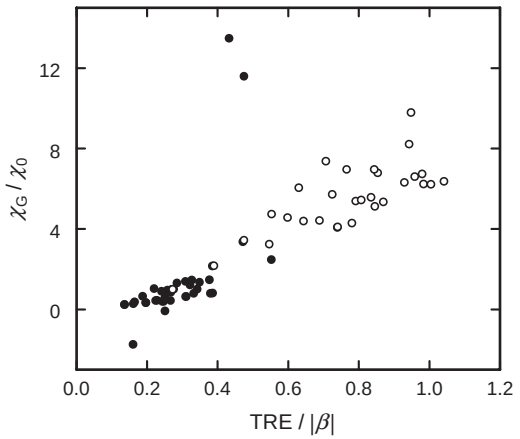

Fig. 5. Correlation between TRE and ring-current diamagnetic susceptibility for 40 mono- and poly-cyclic heterocycles (●) and 30 polycyclic benzenoid hydrocarbons, including benzene (○).

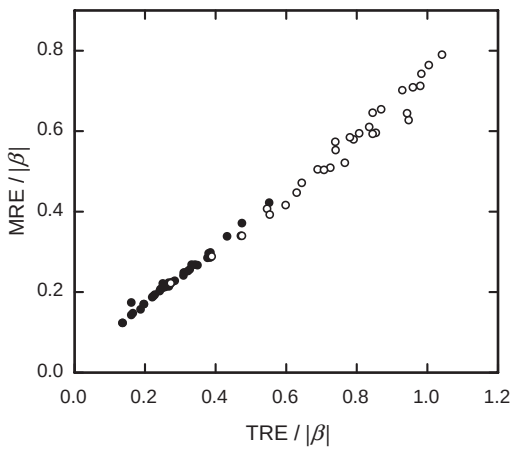

Fig. 6. Correlation between TRE and MRE for 40 mono- and poly-cyclic heterocycles (●) and 30 polycyclic benzenoid hydrocarbons, including benzene (○).

structure, if the π-system is aromatic with a sufficiently large positive ASE.[48] Molecular structure is determined as a compromise between these two competing tendencies. It is in this sense that geometric scales of aromaticity reflect the degree of aromaticity to varying extents.

On the other hand, a quantitative interpretation of aromaticity in terms of chemical reactivity is very difficult and is especially complicated due to the interplay between thermodynamic and kinetic factors.[6,8] In fact, there are many aromatic molecules with chemically reactive sites. For example, large fullerene molecules that violate the isolated pentagon rule are aromatic with positive TREs, but the carbon–carbon bonds shared by two five-membered rings are very reactive with large negative bond resonance energies.[49,50] Thus, for polycyclic π-systems, thermodynamic stability is compatible with kinetic instability, both of which arise from the same cyclic conjugation of π-electrons. It follows that chemical reactivity cannot serve satisfactorily as a general criterion of aromaticity.

Concluding Remarks

All accepted scales of aromaticity are approximations,

which employ either theoretical or experimental methods for generating data.[1–3] Therefore, a given set of data can be compared meaningfully with another one, only if both sets of data are obtained by the same reliable method. Katritzky et al. have stressed on the basis of the PCA analysis that classical concepts of aromaticity are almost completely orthogonal to magnetic ones.[4] However, it should be noted that the results of the PCA analysis depend on the aromaticity scales employed and the compounds included.[6,9] Therefore, orthogonality does not have an absolute meaning, only a relative one. To make matters worse, principal components derived from a PCA analysis do not always represent physically meaningful quantities or concepts.[51]

Our graph theory of aromaticity and ring-current diamagnetism enables us to analyze ASE and χ_G consistently. We showed analytically and numerically that energetic and magnetic scales of aromaticity are closely linked to each other.[25,26] MRE, a kind of ASE like TRE, is a sum of all CREs, whereas χ_G is proportional to the weighted sum of all CREs, of which the weight is equal to the circuit area squared. Both MRE and TRE are dependent on molecular topology, but independent of molecular geometry. These facts strongly support the view that ASE is a fundamental or primary quantity that characterizes aromaticity. At least, there is no reason to regard any magnetic scale of aromaticity as a scale orthogonal to energetic ones. Aromaticity is one-dimensional in this sense. The apparent orthogonality of classical and magnetic aromaticity[4] arises from the failure of the numerical and PCA analyses to recognize the similarity in formalism of ring-current diamagnetism (Eq. 2) and MRE (Eq. 5).

This work was supported by a Grant-in-Aid for Scientific Research (No. 16550016) from the Japan Society for the Promotion of Science. Computations were carried out at the Information Processing Center, Shizuoka University.

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