Origin of Stacked-Ring Aromaticity

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Although strong diatropic currents run in the π-stacked dimers of 4nπ annulenes, they are still antiaromatic with negative topological resonance energies (TREs). The TRE difference between two annulene molecules and the π-stacked annulene dimer can be used as a practical measure of stacked-ring aromaticity. As predicted by Corminboeuf et al., all π-stacked 4nπ annulene dimers exhibit marked stacked-ring aromaticity. In contrast, the TRE for the entire conjugated system of a π-stacked benzene dimer is much smaller than twice the TRE for benzene. The analysis of circuit contributions to energetic and magnetic properties shows that such stacked-ring aromaticity and diatropicity arise from many $(4n + 2)$-site circuits created by the stacking of two antiaromatic rings. Tetragonal faces formed in the dimers are responsible for the creation of these $(4n + 2)$-site circuits.

Introduction

Weakly bound dimers of benzene and polycyclic aromatic hydrocarbons have been studied extensively to explore the fundamental nature of $\pi-\pi$ interactions.[1−5] Corminboeuf et al.[6] and Bean and Fowler[7] then found that the stacking of antiaromatic annulene rings into superphane (i.e., multibridged cyclophane[8]) can reverse their antiaromaticity by through-space electron delocalization. The evidence comes from molecular orbital calculations on methano-bridged cyclophanes that display equalized CC bond lengths and negative nucleus-independent chemical shift (NICS) values at the centers of component rings.[6,7,9] They pointed out that π-stacking, along with triplet[10] and Möbius[11,12] strategies, is the third way to render $4n$-π-electron systems aromatic. In their discussions,[6,7] diatropicity and negative NICS values represent aromaticity. According to Li and Houk,[13] a kind of π-stacked cyclobutadiene dimer occurs as a second-order saddle point in the course of syn dimerization of cyclobutadiene.[9]

In conjunction with the aromatic character of superphanes, stacked-ring aromaticity may be defined as extra aromaticity due to π-stacking of two or more π-electron rings. However, there have been no studies on the energetic aspects of this phenomenon. In our view,[14−21] "aromatic" describes molecules that benefit energetically from cyclic delocalization of π-electrons. For polycyclic π-systems, energetic and magnetic scales of aromaticity sometimes make different predictions.[22−24] To establish the concept of stacked-ring aromaticity firmly, the analysis based on energetic criteria of aromaticity is indispensable. In this article, we make a graph-theoretical analysis of stacked-ring aromaticity and explain this phenomenon consistently in energetic, magnetic, and geometric terms. Diatropicity and paratropicity will be referred to collectively as magnetotropicity.

Theory

In our graph theory,[19,20,25−33] formulation of aromaticity and magnetotropicity is made within the simple Hückel framework. We use topological resonance energy (TRE) as an indicator of global aromaticity.[19,20,25] Our theory of ring-current diamagnetism,[25,26] which is outlined below, is nothing other than an analytical reformulation of Hückel−London theory.[34,35] Both theories give exactly the same numerical values for the intensity of a ring current and ring-current diamagnetic susceptibility. In addition, our theory[19,20,25−33] has as its main advantage the ability to decompose the ring currents and ring-current diamagnetic susceptibility into circuit contributions. For simplicity, all component rings in **1**−**6** are assumed to be regular polygons in shape.

First, the quantity A_i is defined for each circuit in a π-system G in the following manner[23,26,31−33]

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

where k_{mn} is the Hückel parameter for the resonance integral between carbon atoms m and n; m and n run over all π-bonds that lie along the ith circuit c_i; r_i stands for a set of carbon atoms that lie along c_i; $G-r_i$ is the subsystem of G, obtained 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 jth 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, then this formula must be replaced by others.[26−28]

Every circuit is supposed to sustain a π-electron current (i.e., circuit current) in the magnetic field, the intensity of which is given by[27−29]

$$I_i = 4.5 I_0 A_i \frac{S_i}{S_0} \tag{2}$$

where I_0 is the intensity of a π-electron current induced in benzene and S_i and S_0 are the areas of the ith circuit and the benzene ring, respectively. For 3D conjugated systems, S_i must be the "line-of-sight" area, that is, the area of the polygon obtained by projecting the circuit onto the plane perpendicular to the magnetic field. Positive and negative A_i values are indicative of diatropicity and paratropicity, respectively. A total

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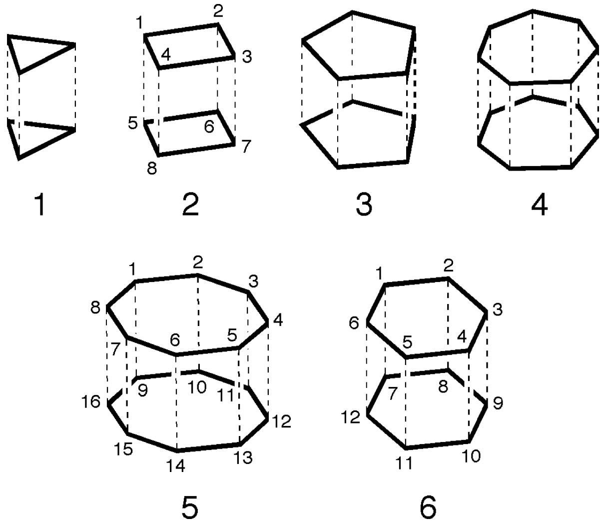

Figure 1. Polygonal prismatic conjugated systems as found in π-stacked annulene dimers and superphanes constructed from annulene rings linked by methano bridges.

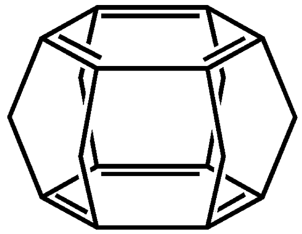

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Figure 2. Benzenoid superphane, in which two benzene rings are linked by six methano bridges.

TABLE 1: TREs for Neutral and Charged Annulenes Concerned

species	TRE/|β|
cyclopropenide ion ($C_3H_3^-$)	−1.4641
cyclobutadiene (C_4H_4)	−1.2263
cyclopropenium ion ($C_5H_5^+$)	−0.9193
cycloheptatienide ion ($C_7H_7^-$)	−0.6647
cyclooctatetraene (C_8H_8)	−0.5948
benzene (C_6H_6)	0.2726

TABLE 2: TREs for the π-Stacked Annulene Dimers[a]

	TRE/|β|	
species	$k_{R\text{-}R}$ = 0.20	$k_{R\text{-}R}$ = 0.50
$(C_3H_3^-)_2$ (**1**)	–2.1747 (0.7535)	–1.2271 (1.7011)
$(C_4H_4)_2$ (**2**)	–1.7206 (0.7320)	–0.8950 (1.5576)
$(C_5H_5^+)_2$ (**3**)	–1.1260 (0.7126)	–0.3993 (1.4393)
$(C_7H_7^-)_2$ (**4**)	–0.6574 (0.6720)	–0.1492 (1.1802)
$(C_8H_8)_2$ (**5**)	–0.5803 (0.6093)	–0.1558 (1.0338)
$(C_6H_6)_2$ (**6**)	0.4369 (–0.1083)	–0.1589 (–0.7041)

[a] Values in parentheses are IRREs.

ring-current pattern for G can be obtained by superposing all circuit currents on the molecular graph.

Let the ring-current diamagnetic susceptibility for an entire π-system be denoted by χ_G, and the contribution of the ith circuit to χ_G (i.e., circuit-current susceptibility) can be expressed in the same manner[25,26]

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

where χ_0 is the ring-current susceptibility of benzene. Positive and negative A_i values now represent diamagnetic and paramagnetic contributions, respectively. Then, χ_G is given by summing all circuit-current susceptibilities. Therefore, not only ring currents but also χ_G can be evaluated additively with respect to individual circuits. This approach provides an independent numerical check on the calculation based on the original Hückel–London theory.[34,35]

In fact, the A_i value can be interpreted theoretically as an energy gain or loss due to cyclic conjugation along the ith circuit.[31−33] It is a TRE-like quantity derived from the magnetic response of the circuit and so was termed circuit resonance energy (CRE). Positive and negative CREs indicate aromaticity and antiaromaticity, respectively, at the level of individual circuits. The sum of A_i values or CREs over all circuits represents a kind of aromatic stabilization energy for an entire π-system. We reported that this sum, termed magnetic resonance energy (MRE), highly correlates with TRE, at least for aromatic benzenoid hydrocarbons and heterocycles.[24−26] On this theoretical ground, eqs 2 and 3 can be interpreted in the following manner. The intensity of a circuit current is proportional to the CRE multiplied by the area of the circuit, whereas circuit-current diamagnetic susceptibility is proportional to the CRE multiplied by the area of the circuit squared. Therefore, CRE is the origin of ring-current diamagnetism.

Results and Discussion

Polygonal prisms **1**–**6** in Figure 1 represent 3D conjugated systems in π-stacked annulene dimers. In this Figure, inter-ring interactions are denoted by dotted lines. Cyclopropenide ion, cyclobutadiene, cyclopentadienium ion, cycloheptatrienide ion, and cyclooctatetraene are component annulenes of the dimers **1**, **2**, **3**, **4**, and **5**, respectively; the first three are 4π annulenes, and the rest 8π annulenes. Dimer **6** consists of two aromatic benzene rings. Li and Houk's second-order saddle point

TABLE 3: Inter-Ring π-Bond Orders for the π-Stacked Annulene Dimers[a]

	inter-ring π-bond orders	
species	$k_{R\text{-}R}$ = 0.20	$k_{R\text{-}R}$ = 0.50
1	0.6667 (0.3333)	0.6667 (0.3333)
2	0.5000 (0.5000)	0.5000 (0.5000)
3	0.4000 (0.5236)	0.4000 (0.5236)
4	0.2857 (0.5784)	0.2857 (0.5784)
5	0.2500 (0.6036)	0.2500 (0.6036)
6	0.0000 (0.6667)	0.0000 (0.6667)

[a] Values in parentheses are π-bond orders for the intra-ring CC bonds.

TABLE 4: Induced Ring Currents and the z Components of Ring-Current Diamagnetic Susceptibilities for the π-Stacked Annulene Dimers

	I_R/I_0		
species	$k_{R\text{-}R}$ = 0.20	$k_{R\text{-}R}$ = 0.50	χ_z/χ_0
1	0.1667	0.1667	0.056
2	0.4330	0.4330	0.333
3	0.6241	0.6241	0.827
4	1.0402	1.0402	2.910
5	1.2619	1.2619	4.690
6	1.0000	1.0000	2.000

TABLE 5: Circuit Resonance Energies and Circuit Currents for the π-Stacked Cyclobutadiene Dimer (2)[a]

circuit type	number of sites	area/S_0	multiplicity	CRE/|β|	CC/I_0
		π-stacked cyclobutadiene dimer with $k_{\text{R-R}} = 0.20$			
2a	4	0.38400	2	−1.04948	−1.8178
2b	4	0	4	−0.31274	0
2c	6	0.38490	8	0.32323	0.5599
2d	6	0	4	0.02210	0
2e*	6	0.38490	4	0.00955	0.0165
2f	8	0	4	−0.31368	0
2g	8	0.38490	2	−0.01255	−0.0217
		π-stacked cyclobutadiene dimer with $k_{\text{R-R}} = 0.50$			
2a	4	0.38400	2	−0.34375	−0.5954
2b	4	0	4	−0.13333	0
2c	6	0.38490	8	0.14792	0.2562
2d	6	0	4	0.05000	0
2e*	6	0.38490	4	0.01736	0.0301
2f	8	0	4	−0.13056	0
2g	8	0.38490	2	−0.03264	−0.0565

[a] A circuit marked with an asterisk is a so-called nonconjugated circuit. Multiplicity represents the number of identical circuits.

may possibly be the best realistic example of π-stacked annulene dimers.[13] Model systems **1**−**6** can also be viewed as simplified conjugated systems in methano-bridged superphane singlets. As a concrete example of methano-bridged superphanes, the benzenoid species is shown in Figure 2; small bridges maximize the inter-ring interaction by forcing the rings to lie close together.[6,7]

Inter-ring interactions in **1**−**6** are associated with through-space delocalization of π-electrons.[6,7] As shown in Figure 1, the resulting conjugated systems are polygonal prismatic in shape. Such inter-ring interactions can therefore be described with resonance integrals between two 2p$_z$ carbon atoms on different rings, $k_{\text{R-R}}\beta$. Here $k_{\text{R-R}}$ is the variable parameter, with β being the standard value for the resonance integral between two bonded carbon 2p$_z$ orbitals. In this study, we choose two relatively small values for $k_{\text{R-R}}$: 0.20 and 0.50. Here we took into account the fact that the high-symmetry approach to two stacked cyclobutadiene molecules to form cubane is symmetry forbidden.[36] This simplified π-bonding model reproduces well the MO interaction diagram of the π-stacked cyclobutadiene dimer,[6,7] in which the unfavorable individual HOMOs of the monomeric units relate to the favorable doubly degenerate HOMOs of the dimer.

TREs for component annulenes and the π-stacked dimers are listed in Tables 1 and 2, respectively. TREs for the component annulenes in **1**−**5** are all negative in sign simply because these monocycles have 4n π-electrons.[19,20,25] In disagreement with the predictions by Corminboeuf et al.[6] and Bean and Fowler,[7] π-stacked dimers of these antiaromatic annulenes (**1**−**5**) still proved to be antiaromatic with negative TREs. This discrepancy is due to the use of different criteria of aromaticity. Their predictions are based on the magnetic criteria of aromaticity, such as the direction of a ring current and the sign of the NICS value,[6,7] whereas our assessment of aromaticity is based on TRE, a kind of energetic criterion of aromaticity. π-Stacked dimers of antiaromatic annulenes have smaller negative TREs when $k_{\text{R-R}}$ becomes larger. TRE for a π-stacked benzene dimer (**6**) is positive as far as $k_{\text{R-R}}$ is relatively small but becomes negative when $k_{\text{R-R}}$ becomes larger.

We then compare the TREs for **1**−**6** with twice the TREs for the component annulenes. The TRE difference between a π-stacked dimer and two component rings can be used as a simple indicator of stacked-ring aromaticity, which is termed inter-ring resonance energy (IRRE). Table 2 contains IRREs calculated for **1**−**6**. Interestingly, the π-stacked dimers of antiaromatic annulenes (**1**−**5**) all have large positive IRREs, which indicate that antiaromatic annulenes are stabilized by dimerization or through-space interaction. This part of our interpretation is formally consistent with the one made by Corminboeuf et al.[6] and Bean and Fowler.[7] Li and Houk also presumed that the antiaromaticity of the cyclobutadiene might diminish in the π-stacked cyclobutadiene dimer-like saddle point.[13] In contrast, the π-stacked benzene dimer has a large negative IRRE, irrespective of the magnitude of the $k_{\text{R-R}}$ value.

We found that the inter-ring separations in the methano-bridged superphanes, calculated at the B3LYP/6-311+G** level of theory,[6] are quite consistent with the IRRE values. The inter-ring distance in the benzenoid superphane (**6**) is 2.305 Å.[6] All antiaromatic superphanes but **1** have shorter distances in the range of 2.002 to 2.202 Å.[6] Short inter-ring distances for the antiaromatic superphanes suggest stabilizing interactions between the rings, as implicated by the IRREs. The cyclopropenide-based superphane (**1**) has an exceptionally large inter-ring distance (2.365 Å) due to large inter-ring Coulomb repulsions.[6] The cyclobutadiene-based superphane has a much shorter inter-ring distance (2.055 Å),[6] which is smaller than the CASSCF/6-31G* optimized distance in the Houk and Li second-order saddle point (2.450 Å).[13] These short distances for the antiaromatic superphanes support not only stabilizing interactions between the rings but also positive IRREs.

Hückel π-bond orders are also consistent with the IRREs. As can be seen from Table 3, inter-ring π-bond orders for **1**−**5** are all positive in sign, whereas those for **6** vanish. Therefore, inter-ring interaction is attractive in antiaromatic annulene dimers but not in the benzene dimer. In this context, no attractive interaction has been recognized explicitly between rings in [2.2]paracyclophane.[37−39] It is noteworthy that inter-ring π-bond orders in **1**−**6** remain constant even if the $k_{\text{R-R}}$ value is widely varied. For **1**−**5**, the intra-ring π-bond orders are exactly the same as those for the component annulene in the triplet state. The intra-ring π-bond orders in **6** are exactly the same as those for isolated singlet-state benzene. It follows that all π-bond orders are independent of the magnitude of through-space interaction. As has been seen above, inter-ring distances in the annulene-based superphanes reflect this aspect of π-bond orders. As for **1**−**5**, the loss of bond-length alternation in the component annulenes[6,7,13] is also consistent with a stabilizing diminution of antiaromaticity.

We then examine the ring-current maps for **1**−**6** in some detail. When a magnetic field is directed perpendicular to the

TABLE 6: Circuit Resonance Energies and Circuit Currents for the π-Stacked Cyclooctatetraene Dimer (5)[a]

circuit type	number of sites	area/S_0	multiplicity	CRE/|β|	CC/I_0
π-stacked cyclooctatetraene dimer with $k_{\text{R-R}} = 0.20$					
5a	4	0	8	−0.02479	0
5b	6	0	8	0.01306	0
5c	8	1.85846	2	−0.21564	−1.8034
5d	8	0	8	−0.01937	0
5e	10	1.85846	16	0.02320	0.1940
5f*	10	1.85846	16	0.00161	0.0135
5g	10	0	8	0.00517	0
5h	10	1.85846	16	0.02225	0.1861
5i*	10	1.85846	8	0.00206	0.0172
5j	12	1.85846	16	−0.00086	−0.0072
5k*	12	1.85846	16	−0.00004	−0.0003
5L	12	1.85846	8	−0.00085	−0.0071
5m*	12	1.85846	32	−0.00004	−0.0003
5n*	12	1.85846	32	−0.00002	−0.0002
5o	12	0	8	−0.01960	0
5p*	12	1.85846	4	−0.00000	−0.0000
5q	12	1.85846	16	−0.00085	−0.0071
5r*	12	1.85846	16	−0.00002	−0.0002
5s	14	1.85846	16	0.00003	0.0003
5t*	14	1.85846	16	0.00000	0.0000
5u*	14	1.85846	16	0.00000	0.0000
5v*	14	1.85846	8	0.00000	0.0000
5w	14	0	8	0.00125	0
5x	16	1.85846	2	−0.00000	−0.0000
5y	16	0	8	−0.02019	0
π-stacked cyclooctatetraene dimer with $k_{\text{R-R}} = 0.50$					
5a	4	0	8	−0.04621	0
5b	6	0	8	0.02983	0
5c	8	1.85846	2	−0.06660	−0.5570
5d	8	0	8	−0.00983	0
5e	10	1.85846	16	0.01655	0.1384
5f*	10	1.85846	16	0.00308	0.0257
5g	10	0	8	0.01259	0
5h	10	1.85846	16	0.01491	0.1247
5i*	10	1.85846	8	0.00380	0.0318
5j	12	1.85846	16	−0.00337	−0.0282
5k*	12	1.85846	16	−0.00041	−0.0034
5L	12	1.85846	8	−0.00319	−0.0267
5m*	12	1.85846	32	−0.00041	−0.0034
5n*	12	1.85846	32	−0.00023	−0.0019
5o	12	0	8	−0.00825	0
5p*	12	1.85846	4	−0.00005	−0.0004
5q	12	1.85846	16	−0.00319	−0.0267
5r*	12	1.85846	16	−0.00023	−0.0019
5s	14	1.85846	16	0.00074	0.0062
5t*	14	1.85846	16	0.00005	0.0004
5u*	14	1.85846	16	0.00005	0.0004
5v*	14	1.85846	8	0.00005	0.0004
5w	14	0	8	0.00350	0
5x	16	1.85846	2	−0.00017	−0.0015
5y	16	0	8	−0.01111	0

[a] Circuits marked with asterisks are so-called nonconjugated circuits. Multiplicity represents the number of identical circuits.

component rings, a diamagnetic current runs around each ring. The intensities of ring currents induced in **1**−**6** are summarized in Table 4, where the plus sign indicates diatropicity. As noted by Corminboeuf et al.,[6] all six superphanes constructed from antiaromatic or aromatic rings linked by methano bridges have rings that have negative values of NICS. Note that paramagnetic currents run around isolated 4n-π-electron annulenes when they are in the bond-alternate ground-state configuration.[10,40] Dimerization makes antiaromatic annulene rings diatropic, although it does not make the resulting conjugated system aromatic. Therefore, our simple π-bonding model reproduces very well stacked-ring diatropicity predicted by Corminboeuf et al.[6] and Bean and Fowler.[7]

As Table 4 indicates, the intensities of ring currents induced in **1**−**6** remain constant, even if the $k_{\text{R-R}}$ value is widely varied. In fact, those induced in **1**−**5** remain unchanged at least for $0.01 \le k_{\text{R-R}} \le 1.00$. Therefore, a trace of through-space interaction is enough to make paratropic annulenes highly diatropic. Likewise, the intensity of a ring current induced in **6** remains unchanged at least for $0.00 \le k_{\text{R-R}} \le 0.99$. In marked contrast, TRE widely varies if $k_{\text{R-R}}$ widely varies. For example, when $k_{\text{R-R}}$ varies from 1.00 to 0.01, TRE for the π-stacked cyclobutadiene dimer (**2**) varies markedly from −0.3323 to −2.4127 |β|; the latter value is necessarily very close to twice the TRE for highly antiaromatic cyclobutadiene (−2.4525 |β|). The same is true for **1**, **3**, **4**, and **5**. Therefore, there surely exists

TABLE 7: Circuit Resonance Energies and Circuit Currents for the π-Stacked Benzene Dimer (6)[a]

circuit type	number of sites	area/S_0	multiplicity	CRE/$\lvert\beta\rvert$	CC/I_0
π-stacked benzene dimer with $k_{R\text{-}R} = 0.20$					
6a	4	0	6	−0.00671	0
6b	6	1.00000	2	0.24748	1.1137
6c	6	0	6	0.00205	0
6d	8	1.00000	12	−0.00253	−0.0114
6e	8	0	6	−0.00217	0
6f*	8	1.00000	12	−0.00063	−0.0028
6g	8	1.00000	6	−0.00228	−0.0103
6h	10	1.00000	12	0.00008	0.0003
6i*	10	1.00000	6	0.00001	0.0000
6j	10	0	6	0.00031	0
6k*	10	1.00000	12	0.00001	0.0000
6L	12	1.00000	2	−0.00000	−0.0000
6m	12	0	6	−0.00165	0
π-stacked benzene dimer with $k_{R\text{-}R} = 0.50$					
6a	4	0	6	−0.04639	0
6b	6	1.00000	2	0.48842	2.1979
6c	6	0	6	0.03372	0
6d	8	1.00000	12	−0.03135	−0.1411
6e	8	0	6	−0.01991	0
6f*	8	1.00000	12	−0.00552	−0.0248
6g	8	1.00000	6	−0.02911	−0.1310
6h	10	1.00000	12	0.00646	0.0291
6i*	10	1.00000	6	0.00056	0.0025
6j	10	0	6	0.00814	0
6k*	10	1.00000	12	0.00056	0.0025
6L	12	1.00000	2	−0.00147	−0.0066
6m	12	0	6	−0.02359	0

[a] Circuits marked with asterisks are so-called nonconjugated circuits. Multiplicity represents the number of identical circuits.

TABLE 8: Ring Currents Induced in Some π-Stacked Annulene Trimers and Tetramers[a]

species	$k_{R\text{-}R}$	I_R/I_0 outer rings	I_R/I_0 inner ring(s)
$(C_4H_4)_3$ (**7***)	0.200	0.4330	0.4330
	0.500	0.4330	0.4330
$(C_4H_4)_4$ (**8**)	0.200	0.4330	0.4330
	0.500	0.4330	0.4330
$(C_8H_8)_3$ (**9***)	0.200	1.2619	1.2619
	0.500	1.2619	1.2619
$(C_8H_8)_4$ (**10**)	0.200	1.2619	1.2619
	0.500	1.2619	1.2619
$(C_6H_6)_3$ (**11**)	0.200	1.0000	1.0000
	0.500	1.0000	1.0000
$(C_6H_6)_4$ (**12**)	0.200	1.0000	1.0000
	0.500	1.0000	1.0000

[a] Triplet-state species are denoted by asterisks.

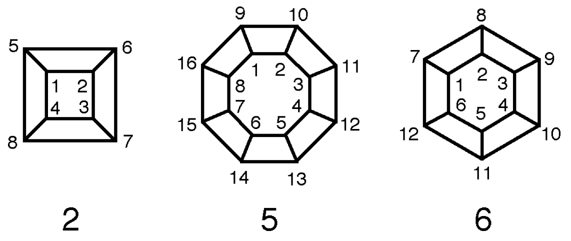

Figure 3. Molecular graphs for polygonal prismatic conjugated systems in **2**, **5**, and **6**.

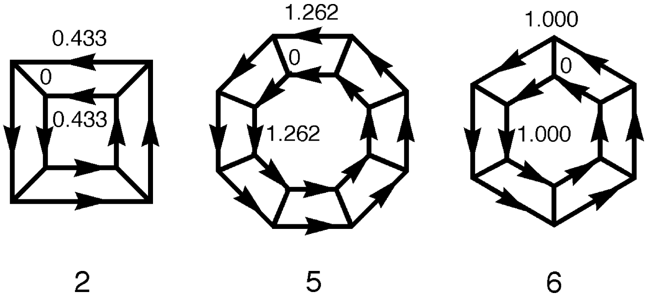

Figure 4. Ring currents induced in **2**, **5**, and **6**.

diatropic but antiaromatic conjugated systems. In the case of polycyclic conjugated systems, diatropicity is not always a synonym for aromaticity.[22−25]

The z components of ring-current diamagnetic susceptibilities (χ_z) for **1**−**6** are added in Table 4. Here the direction of the external magnetic field is taken as the z-axis. For these annulene dimers, χ_z is always positive in sign (i.e., diamagnetic) although **1**−**5** are antiaromatic in nature. For **6**, χ_z is exactly twice as large as that for isolated benzene. As in the case of ring currents, this quantity is independent of the $k_{R\text{-}R}$ value. It is clear that not only diamagnetic ring currents but also ring-current diamagnetic susceptibility cannot be used safely as indicators of aromaticity. Note that diamagnetic susceptibility exaltation, which represents experimentally estimated ring-current diamagnetic susceptibility, had long been used as the most reliable indicator of aromaticity.[14]

In what follows, we explore the origin of ring currents induced in three typical π-stacked annulene dimers **2**, **5**, and **6** in some detail. These dimers consist of neutral annulene molecules and thus can be easily examined graph-theoretically. Planarized molecular graphs of the three dimers are drawn in Figure 3, where the conjugated atoms are taken as vertices, and the bonds between them are taken as edges. Conjugated carbon atoms in these graphs are numbered as in the corresponding prismatic structures in Figure 1. The ring-current maps for these annulene dimers are presented in Figure 4. Here diamagnetic (diatropic) circulation is shown counterclockwise. As can be seen from eq 2, such ring-current maps can be obtained exactly by superpos-

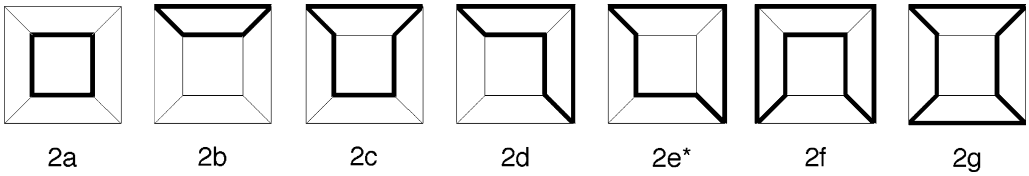

Figure 5. Nonidentical circuits in **2**. A circuit marked with an asterisk is a so-called nonconjugated circuit.

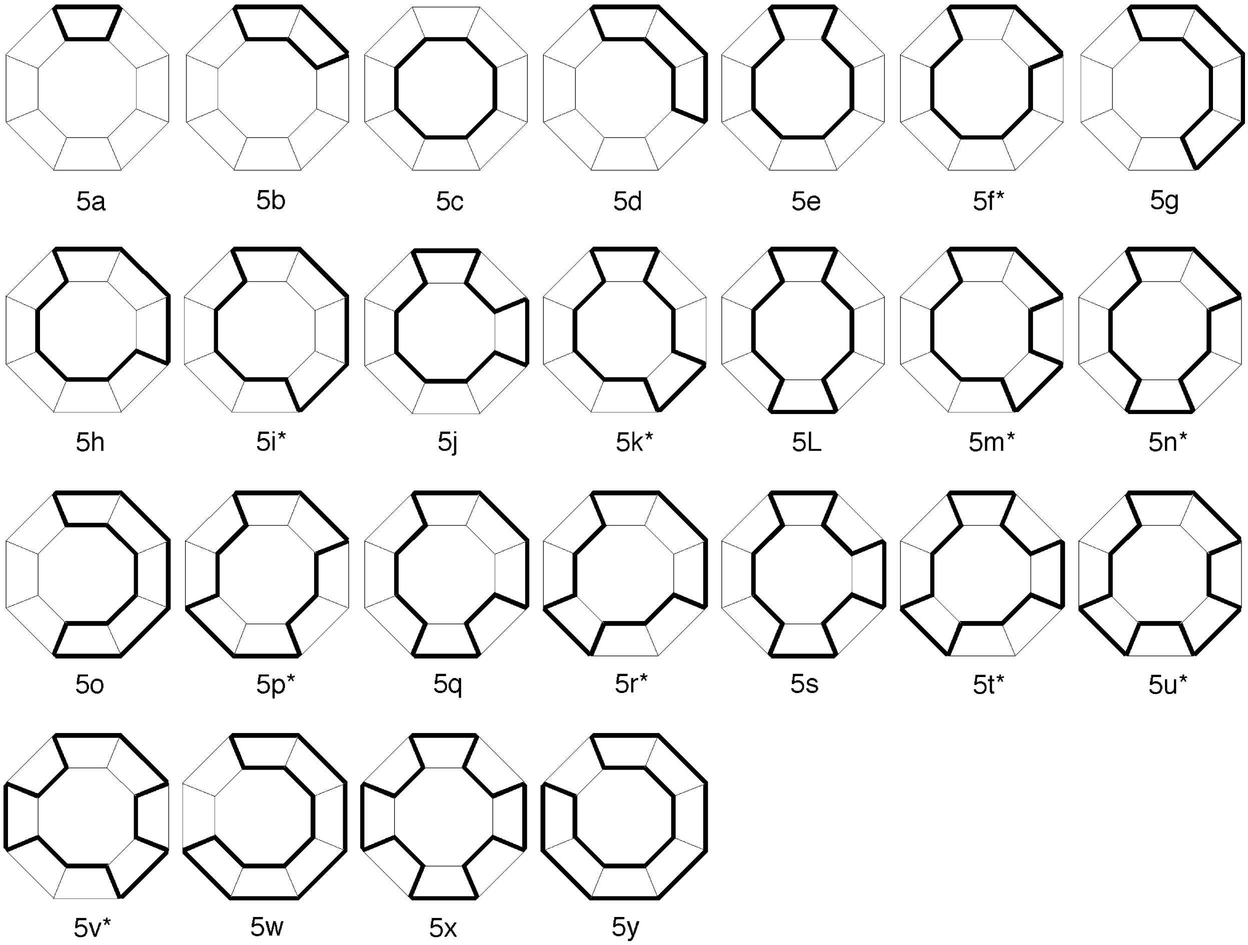

Figure 6. Nonidentical circuits in **5**. Circuits marked with asterisks are so-called nonconjugated circuits.

ing all circuit currents, that is, all currents induced in individual circuits, on the molecular graph. All nonidentical circuits in **2**, **5**, and **6** are depicted in Figures 5, 6, and 7, respectively.

Let us survey types of circuits in **2**, **5**, and **6**. As shown in Figure 5, there are seven nonidentical circuits and a total of 28 circuits in the square prismatic cyclobutadiene dimer (**2**). A total of 312 circuits can be chosen from the π-stacked cyclooctatetraene dimer (**5**); 25 nonidentical circuits in this dimer are presented in Figure 6. Here chiral circuits are enumerated as identical ones. A total of 94 circuits can be chosen from the π-stacked benzene dimer (**6**). They are classified into 13 nonidentical circuits in Figure 7. Isolated [4*n*]annulenes have no ($4n + 2$)-site circuits; however, not only many $4n$-sites but also many ($4n + 2$)-site circuits are created in the π-stacked dimers. Tetragonal faces formed in the dimers are responsible for the creation of these ($4n + 2$)-site circuits. In the case of the π-stacked cyclobutadiene dimer (**2**), a total of 28 circuits consist of 12 $4n$-site circuits and 16 ($4n + 2$)-site circuits.

Circuit resonance energies (CREs) and intensities of the circuit currents (CCs) induced in **2**, **5**, and **6** are listed in Tables 5−7, respectively. One should note that all circuits in these dimers formally obey the Hückel's $4n + 2$ rule of aromaticity without regard to the magnitude of the $k_{\text{R-R}}$ value. That is, all $4n$-site circuits are antiaromatic with negative CREs, whereas ($4n + 2$)-site circuits are always aromatic with positive CREs. In principle, this type of rule holds for neutral conjugated hydrocarbons, such as **2**, **5**, and **6**.[41,42] Nonconjugated circuits, such as those marked with asterisks in Figures 5−7, exhibit much smaller CREs as compared with conjugated circuits of similar sizes.[18] It is evident that positive IRREs for π-stacked [4*n*]annulene dimers arise from the larger contribution of ($4n + 2$)-site circuits to aromaticity. It is 12 six-site and 30 ten-site conjugated circuits that contribute much to the positive IRRE values for **2** and **5**, respectively. In the case of the π-stacked benzene dimer, $4n$-site circuits are predicted to contribute more to IRRE than ($4n + 2$)-site circuits do. This is the primary reason why benzene is destabilized by dimerization.

For all cyclic conjugated systems including **1**−**6**, all circuits have nonzero CREs contributing more or less to the increase or decrease in TRE. However, some circuits do not contribute to stacked-ring magnetotropicity because the line-of-sight areas vanish. Remember that the line-of-sight area of each circuit used to calculate magnetic quantities (S_i) is that of the polygon obtained by projecting the circuit onto the plane perpendicular

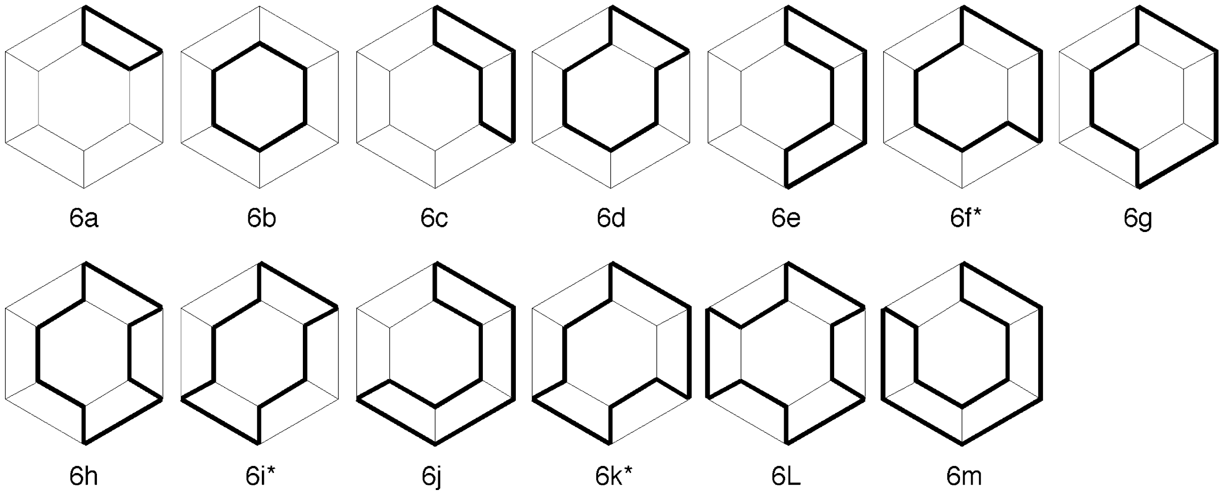

Figure 7. Nonidentical circuits in **6**. Circuits marked with asterisks are so-called nonconjugated circuits.

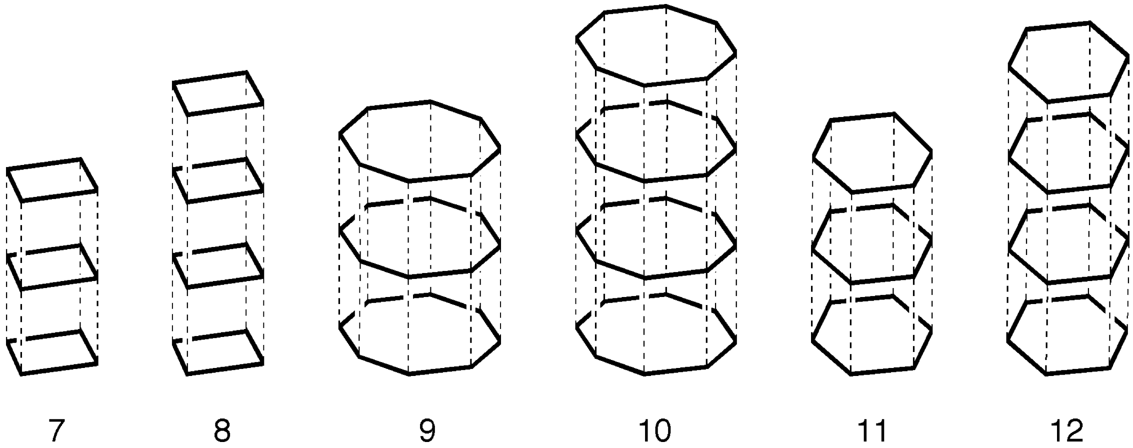

Figure 8. Typical π-stacked annulene trimers and tetramers.

to the magnetic field. In the present case, tetragonal faces on all sides of a polygonal prismatic conjugated system are parallel to the magnetic field and do not contribute to the line-of-sight areas of circuits that enclose one or more tetragonal faces. Therefore, the line-of-sight area of each circuit either vanishes or equals the area of the component annulene ring.

Among the circuits in the π-stacked cyclobutadiene dimer (**2**), **2b**-, **2d**-, and **2f**-type circuits have no such areas. They then contribute neither to the ring-current map nor to the z component of ring-current susceptibility. Apart from type-**2a** circuits that can be chosen from the component cyclobutadiene rings, four **2b**- and four **2f**-type circuits are major antiaromatic circuits in **2**. Because these circuits have no line-of-sight areas, they do not make any contribution to the ring-current map. Paratropic currents induced in type-**2a** and -**2g** antiaromatic circuits are then swept away by strong diatropic currents induced in eight type-**2c** circuits. Note that if the dimer molecule is tilted to some extent all circuits will make nonzero diamagnetic or paramagnetic contributions to the ring-current distribution.

Likewise, the π-stacked cyclooctatetraene dimer (**5**) is diatropic as a whole. Paratropic currents induced mainly in two type-**5c** circuits are overwhelmed by diatropic currents induced in 16 type-**5e** and 16 type-**5h** circuits. Such a magnetotropic situation in **2** and **5** remains unchanged even if $k_{\mathrm{R\text{-}R}}$ is very small. In the π-stacked benzene dimer (**6**), paramagnetic circuit currents are also swept away by diamagnetic ones. As a result, a net diamagnetic current, the intensity of which is equal to that induced in the isolated benzene molecule, is induced in each benzene ring. Of course, this does not mean that the diamagnetic current as large as that in isolated benzene is induced in each type-**6b** circuit.

Finally, magnetotropicity of π-stacked annulene trimers and tetramers[7] is briefly surveyed. Typical such hydrocarbons are the trimers of cyclobutadiene (**7**), cyclooctatetraene (**9**), and benzene (**11**) and the tetramers of cyclobutadiene (**8**), cycooctatetraene (**10**), and benzene (**12**), the 3D conjugated systems of which are depicted in Figure 8. Among them, singlet-state species of **7** and **9** are extremely paratropic with no HOMO−LUMO energy gaps. Therefore, intensities of the ring currents induced in the triplet state were calculated for these two trimers. The benzene trimer **11** remains diatropic with nonzero HOMO−LUMO energy separation. π-Current intensities calculated for **7**−**12** are listed in Table 8. Interestingly, all of these trimers and tetramers, including two triplet-state species, sustain diamagnetic ring currents of the same intensities as those induced in the dimers. Ring-current distributions in **7**−**12** remain unchanged on going from $k_{\mathrm{R\text{-}R}} = 0.20$ to 0.50; outer and inner rings sustain diamagnetic currents of the same intensity.[7] It is noteworthy that aromatization by face-to-face stacking works not only in π-stacked annulene dimers but also in π-stacked annulene trimers and tetramers. Ring-current patterns for **10** and **11** are essentially the same as those reported by Bean and Fowler.[7]

Concluding Remarks

The anomalous magnetotropic character of π-stacked annulene dimers, trimers, and tetramers[6,7] has been explored using our unified theory of aromaticity and ring-current diamagnetism.[19,20,25−33] This theory is very useful for consistently interpreting aromaticity and magnetotropicity in polycyclic conjugated systems. We then noted that dimerization of antiaromatic annulenes creates many aromatic $(4n + 2)$-site circuits, which significantly contribute to stacked-ring aromaticity and diatropicity.

π-Stacked $4n\pi$ annulene dimers, trimers, and tetramers have tetragonal faces on all sides of the polygonal prismatic conjugated systems. These four-center conjugation pathways do not make any paratropic contribution to the magnetotropicity of the entire conjugated system, but they are fully responsible for the creation of many aromatic $(4n + 2)$-site circuits. These aromatic circuits contribute decisively to stacked-ring aromaticity and diatropicity in the π-stacked $4n\pi$-annulene dimers. It is now clear that the paratropicity of $4n\pi$-annulenes is no longer a determinant of magnetotropicity in the π-stacked dimers. As pointed out by Corminboeuf et al.,[6] π-stacking is indeed a novel way to design less antiaromatic ring systems from highly antiaromatic annulenes, even if the resulting conjugated system is not aromatic with a positive TRE.

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References and Notes

(1) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, T. *J. Am. Chem. Soc.* **2002**, *124*, 104.

(2) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887.

(3) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. *J. Chem. Phys.* **2004**, *120*, 647.

(4) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656.

(5) Yurtsever, E. *J. Phys. Chem. A* **2009**, *113*, 924.

(6) Corminboeuf, C.; Schleyer, P. v. R.; Warner, P. *Org. Lett.* **2007**, *9*, 3263.

(7) Bean, D. E.; Fowler, P. W. *Org. Lett.* **2008**, *10*, 5573.

(8) Gleiter, R.; Kratz, D. *Acc. Chem. Res.* **1993**, *26*, 311.

(9) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(10) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed* **1998**, *37*, 1945.

(11) Heilbronner, E. *Tetrahedron Lett.* **1964**, *29*, 1923.

(12) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2395.

(13) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 880.

(14) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. Chapter 2. In *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley-Interscience: New York, 1994.

(15) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(16) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.

(17) Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.

(18) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.

(19) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.

(20) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

(21) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber, J. *J. Phys. Chem. A* **2003**, *107*, 6470.

(22) Aihara, J. *J. Am. Chem. Soc.* **1981**, *103*, 5704.

(23) Wilcox, C. W., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195.

(24) Aihara, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 101.

(25) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115.

(26) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 5913.

(27) Aihara, J.; Horikawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1853.

(28) Aihara, J.; Horikawa, T. *Chem. Phys. Lett.* **1983**, *95*, 561.

(29) Aihara, J. *J. Am. Chem. Soc.* **1985**, *107*, 298.

(30) Aihara, J.; Ishida, T.; Kanno, H. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1518.

(31) Aihara, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 651.

(32) Aihara, J.; Kanno, H. *J. Phys. Chem. A* **2005**, *109*, 3717.

(33) Aihara, J. *J. Am. Chem. Soc.* **2006**, *128*, 2873.

(34) London, F. *J. Phys. Radium* **1937**, *8*, 397.

(35) Pullman, B.; Pullman, A. Chapitre IX. In *Les Théories Electroniques de la Chimie Organique*; Masson et Cie: Paris, 1952.

(36) Halevi, E. A. *Orbital Symmetry and Reaction Mechanism: The OCAMS View*; Springer-Verlag: New York, 1992; pp 171−177.

(37) Lyssenko, K. A.; Antipin, M. Yu.; Antonov, D. Yu. *ChemPhysChem* **2003**, *4*, 817.

(38) Caramori, G. F.; Galembeck, S. E.; Laali, K. K. *J. Org. Chem.* **2005**, *70*, 3242.

(39) Poater, J.; Bofill, J. M.; Alemany, P.; Solà, M. *J. Org. Chem.* **2006**, *71*, 1700.

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

(41) Hosoya, H.; Hosoi, K.; Gutman, I. *Theor. Chim. Acta* **1972**, *38*, 37.

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

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