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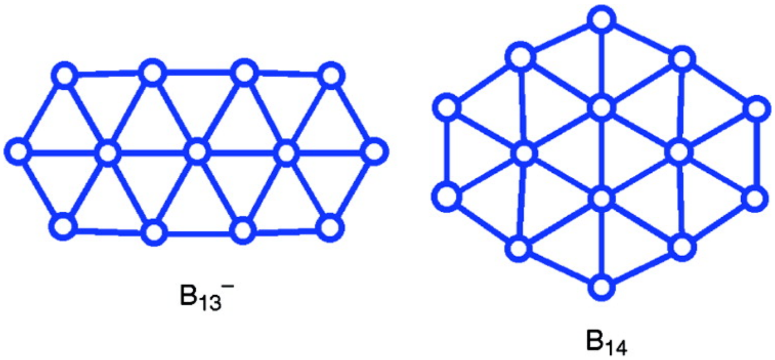

Aromatic boron clusters with eight π electrons

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Aromaticity of Planar Boron Clusters Confirmed

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Abstract: Low-energy boron clusters are characterized by two-dimensional geometry. Aromaticity of these planar boron clusters was established in terms of topological resonance energy (TRE). All planar boron clusters were found to be highly aromatic with large positive TREs even if they have $4n$ π-electrons. Aromaticity must therefore be the origin of unusual planar or quasi-planar geometry. Thus, the aromaticity concept is as useful in boron chemistry as it is in general organic chemistry. It is evident that the Hückel $4n + 2$ rule of aromaticity should not be applied to such polycyclic π-systems. Some of the boron clusters are in the triplet electronic state to attain higher aromaticity. Multivalency and electron deficiency of boron atoms are responsible for lowering the energies of low-lying π molecular orbitals and then for enhancing aromaticity. For polycyclic π-systems, paratropicity does not always indicate antiaromaticity.

Introduction

The structures and energies of elemental boron clusters have been the target of many experimental and theoretical studies. In 1988, Anderson et al. observed the mass distribution of B_n^+ in the range $n = 1-20$ generated by laser ablation of isotopically pure boron.[1−4] They postulated the three-dimensional structures for these elemental boron clusters.[1] Properties and stability of boron clusters have since been of special interest to theoretical and computational chemists.[5−39] Molecular orbital (MO) calculations were repeatedly carried out to determine the nuclear arrangements of boron clusters.[5−39] In 1994, Boustani found that for many boron clusters the planar or quasi-planar nuclear arrangement is consistently more stable than any three-dimensional structure.[11−13] Wang et al. compared experimental detachment energies of B_n^- with those calculated from low-energy B_n^- isomers and determined the planar or quasi-planar geometries of the lowest-energy isomers for B_n^- with $n = 3-15$.[22,24,26−28,34−36] As suggested by Boustani,[11−13] the quasi-planar structures of large clusters are constructed with units consisting of pentagonal, hexagonal, heptagonal, and octagonal pyramids.

Boustani suggested that planar and quasi-planar isomers of boron clusters benefit from π-delocalization.[15,16] This suggestion was a great step forward in the chemistry of elemental boron. Three-dimensional isomers proved to be 1−5 eV higher than planar or convex ones.[13] Fowler and Ugalde pointed out that the marked stability of the B_{13}^+ cluster is attributable to its aromaticity because this cationic cluster has six π-electrons such as benzene.[19] Many others, including Boldyrev's and Wang's groups, have since used the concept of aromaticity to explain

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planarity or quasi-planarity of boron clusters.[22,26−29,34−39] Planar boron clusters have been considered to be aromatic when they have two, six, or 10 π-electrons. Thus, many chemists have applied the Hückel $4n + 2$ rule of aromaticity (hereafter referred to simply as the Hückel rule)[40,41] to such polycyclic π-systems explicitly but without presenting any definitive evidence for the presence or absence of aromaticity. We must note that this rule can be applied safely to monocyclic π-systems but not to polycyclic ones, such as planar boron clusters.[42,43]

Hanley et al. observed that B_{13}^+ has an anomalous stability with little reactivity.[1−4] We previously showed that the degree of aromaticity of such a planar or quasi-planar boron cluster can be estimated using our graph theory of aromaticity.[44−48] B_{13}^+ is highly aromatic with a large positive topological resonance energy (TRE).[48] Some research groups later enumerated π-electrons in a series of planar or quasi-planar boron clusters to apply the Hückel rule to them.[22−37] The objectives of this study are to establish aromatic character of planar and quasi-planar boron clusters and to show decisively that the Hückel rule does not hold for such polycyclic π-systems. The TREs calculated for a series of planar and quasi-planar boron clusters are examined in some detail. Possibility of σ-aromaticity[28] is not considered because it cannot be dealt with analytically at present.

Theory

Boron has three valence electrons and a short covalent radius, undergoing sp^2 hybridization in many boron clusters. That leaves one empty $2p_z$ atomic orbital (AO) and renders boron electron-deficient. Unlike a single boron atom, Mulliken population analysis showed partial population of such AOs in boron clusters,[15,16] which occurs through sp-promotion. Consequently, planar boron clusters contain delocalized π systems consisting of such $2p_z$ orbitals. Aromatic character of planar and quasi-planar boron clusters and their molecular ions can be estimated from their TREs.[44−48] The TRE is defined within the framework of Hückel theory as a difference between the total π-binding energies of a given molecule and the graph theoretical polyene reference. It represents extra thermodynamic stabilization due to cyclic conjugation. For simplicity, all quasi-planar or convex boron clusters studied are assumed to be planar with all bond lengths being equal to each other.

A matching (or reference) polynomial (i.e., a characteristic polynomial for the polyene reference) must beforehand be constructed for each planar species to obtain the total π-binding energy of the polyene reference. A matching polynomial for a planar cluster with n boron atoms, G, is expressed as[44,45]

$$R_G(X) = X^n + \sum_{k=1}^{[n/2]} (-1)^k p_G(k) X^{n-2k} \tag{1}$$

Here, $p_G(k)$ is the number of ways in which k disjoint BB bonds are chosen from G, and $[n/2]$ is the largest integer not exceeding $n/2$. Let the energy of the mth largest root of the equation $R_G(X) = 0$ be denoted by X_m^0, and the energy of the mth π-MO in the polyene reference is given as $\alpha_B + X_m^0 \beta_{BB}$, where α_B and β_{BB} are the Coulombic integrals for boron $2p_z$ AOs and the resonance integral between two bonded boron $2p_z$ AOs, respectively.

Van-Catledge determined Hückel parameters consistently for many heteroatoms and heterobonds.[49] In this Van-Catledge system, Coulombic and resonance integrals for boron-containing π-systems are:

$$\alpha_B = \alpha_C - 0.45\beta_{CC} \tag{2}$$

$$\beta_{BB} = 0.87\beta_{CC} \tag{3}$$

Here, α_C is the Coulombic integrals for carbon $2p_z$ orbitals, and β_{CC} is the resonance integral between two bonded carbon $2p_z$ orbitals. Thus, β_{BB} is 0.87 times as large as β_{CC}, which is large enough to give rise to a large positive or large negative TRE.

A graph theoretical variant[50−53] of Hückel−London theory[54] is utilized to calculate the intensities of π-electron currents magnetically induced in some planar boron clusters. According to this theory, a π-electron current induced in a polycyclic π-system can be partitioned formally among all possible circuits in it. Here, all possible circuits stand for all possible cyclic paths that can be chosen from a π-system.[55] This does not imply that all circuit currents flow independently because their intensities are interdependent.[25] A current intensity assignable to the ith circuit, I_i, in G is expressed in the form:[50−53]

$$I_i = 18 I_0 \frac{\beta_{BB}}{\beta_{CC}} \frac{S_i}{S_0} \sum_{j}^{occ} \frac{P_{G-r_i}(X_j)}{P'_G(X_j)} \tag{4}$$

where I_0 is the intensity of a current induced in the benzene ring; S_i and S_0 are the areas of r_i and the benzene ring, respectively; $G - r_i$ 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 orbitals. If there are degenerate π-orbitals, this formula must be replaced by others.[50] Positive and negative values for I_i signify diatropicity and paratropicity, respectively.

In fact, circuit currents thus defined are consistent with the extended Hückel rule proposed by Hosoya et al.,[56] in the sense that, for neutral π-systems, I_i values are positive and negative in sign for $(4n + 2)$- and $4n$-membered circuits, respectively.[47,50,51,57,58] This indicates that $(4n + 2)$- and $4n$-membered circuits are diatropic and paratropic, respectively. This aspect of magnetotropicity fully justifies the partition of a total π-electron current in the form of eq 4. The Hückel-like rule of superaromaticity for charged paracyclophanes and the counter-

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Table 1. Number of π-Electrons, N_π, in the Possible Lowest-Energy Isomers of Elemental Boron Clusters[a]

species[a]	N_π	refs	species	N_π	refs
B_3^-	2	25,33	B_8*	4	38
B_4^+	2	29	B_8^{2-}	6	26,34
B_4	2	29,33	B_9^-	6	26
B_4^-	2	29,33	B_{10}	6	27
B_5	2	23	B_{11}^-	6	27
B_5^-	2	23,31	B_{12}	6	27
$B_6(II)^+$	2	28	$B_{13}(I)^+$	6	19
$B_6(I)$*	3	25,28	$B_{13}(III)^-$	8	19,27
$B_6(II)^-$	3	25,28	$B_{14}(II)$	8	27
$B_6(II)^{2-}$	4	25,28	$B_{15}(I)^-$	10	27
B_7^-*	4	35			

[a] For molecular geometries, see Figure. 1. Triplet-state species are denoted by asterisks; all others are in the singlet electronic state.

rotating rim and hub currents in coronene can be rationalized successfully in terms of circuit currents.[52,59] These facts also support the utility of eq 4. Bifurcation of π-electron currents in a polycyclic system[60] can also be explained reasonably and quantitatively in terms of circuit currents.

As can be seen from eq 4, the intensity of the circuit current is proportional to the following quantity:

$$A_i = 4\frac{\beta_{\mathrm{BB}}}{\beta_{\mathrm{CC}}}\sum_{j}^{\mathrm{occ}}\frac{P_{G-r_i}(X_j)}{P'_G(X_j)} \qquad (5)$$

Equations 4 and 5 apply only to the π-systems of planar boron clusters. We found in 1981 that A_i can be interpreted as an approximate contribution of the ith circuit to the TRE.[57] In other words, the intensity of each circuit current reflects the contribution of the circuit to aromatic stabilization energy. It follows that the sum of A_i values over all circuits must represent the approximate TRE. For the reasons given previously,[58] we call the sum a magnetic resonance energy (MRE), which means a TRE-like quantity derived from the magnetic response of the π-system. Like TRE, MRE is a function of molecular topology only. MRE is highly correlative in magnitude with TRE.[58,61]

Results and Discussion

Aromaticity. Possible lowest-energy isomers of neutral and charged boron clusters are listed in Table 1. Nuclear arrangements of these boron clusters, which were taken from the references cited in Table 1, are presented in Figure 1. Hereafter, chemical formulas, such as B_4 and B_{13}(I), represent not only molecular formulas but also the corresponding topologies or nuclear arrangements in Figure 1. In fact, most of these structures were first predicted by Boustani and others.[11−16] Most neutral boron clusters are similar in structure to the cationic ones.[11,13] However, topologies of some clusters depend on the charge they carry. For example, B_6(I) represents the topology of neutral B_6, whereas B_6(II) indicates those of B_6^+, B_6^-, and B_6^{2-}.[25,28] B_{9-12} and B_{15}(I) represent the common global minimum topologies of the corresponding neutral and anionic species.[19,26,27] B_{12} is also the topology of the lowest-energy cation. B_{13}(I) represents the global minima of B_{13} and B_{13}^+.[19] B_{13}(II) is the second lowest-energy topology of B_{13} and B_{13}^-.[19,27] B_{13}(III) indicates the topology of the lowest-energy B_{13}^-.[19,27]

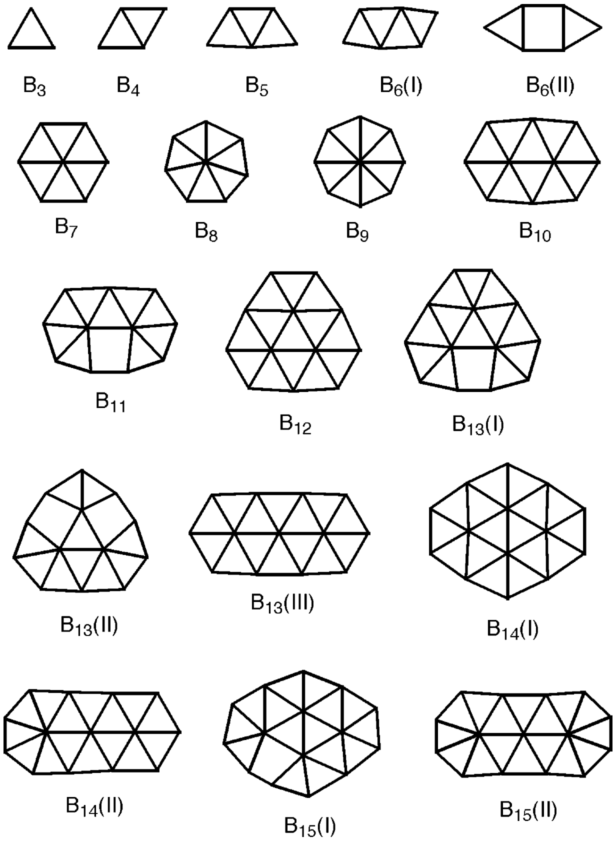

Figure 1. Geometries of low-energy isomers of planar or quasi-planar boron clusters.

Table 2. Coefficients of Matching Polynomials for Planar Boron Clusters

species	$p_G(1)$	$p_G(2)$	$p_G(3)$	$p_G(4)$	$p_G(5)$	$p_G(6)$	$p_G(7)$
B_3	3						
B_4	5	2					
B_5	7	7					
B_6(I)	9	16	3				
B_6(II)	8	14	2				
B_7	12	33	20				
B_8	14	49	49	7			
B_9	16	68	96	34			
B_{10}	19	111	232	152	14		
B_{11}	20	130	330	311	75		
B_{12}	24	195	658	903	411	28	
B_{13}(I)	25	219	840	1429	957	170	
B_{13}(II)	24	203	757	1258	826	145	
B_{13}(III)	26	238	950	1674	1158	207	
B_{14}(I)	28	282	1282	2734	2561	832	41
B_{14}(II)	29	304	1449	3240	3143	1041	52
B_{15}(I)	30	333	1740	4496	5500	2740	366
B_{15}(II)	30	330	1686	4233	5058	2486	334

Likewise, B_{14}(I) is the lowest-energy isomer of B_{14}, whereas B_{14}(II) represents the topology of the lowest-energy B_{14}^-.[27] B_{15}(II) represents their second lowest-energy B_{15} isomers.[27]

Coefficients of the matching polynomials for the π-systems of all boron clusters studied are listed in Table 2. The numbers of π-electrons (N_π) in the lowest-energy isomers of neutral and charged boron clusters are given in Table 1. In all boron clusters, π-electrons are relatively few. All boron clusters with N_π = even number are in either the singlet or triplet electronic state.[5−39] The TREs calculated for the singlet-state species using characteristic and matching polynomials are given in Table 3 as functions of N_π. Therefore, the TRE for π-system G with N_π

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Table 3. TREs for Planar Boron Clusters and Their Molecular Ions in the Singlet Electronic State

	TRE/$\lvert\beta_{BB}\rvert$						
species	$N_\pi = 2$	$N_\pi = 4$	$N_\pi = 6$	$N_\pi = 8$	$N_\pi = 10$	$N_\pi = 12$	$N_\pi = 14$
B_3	0.536	−1.464					
B_4	0.852	−0.473					
B_5	1.058	0.095	−0.830				
B_6(I)	1.199	0.781	−1.030				
B_6(II)	0.758	0.549	−0.243				
B_7	1.521	0.159	0.315	−1.685			
B_8	1.564	0.513	0.634	−1.082			
B_9	1.598	0.767	0.855	−0.598			
B_{10}	1.839	1.854	1.568	−0.019			
B_{11}	1.593	2.017	1.798	0.225	−0.274		
B_{12}	2.027	1.698	2.605	0.649	−0.279		
B_{13}(I)	2.198	2.096	2.959	1.562	0.836	−0.175	
B_{13}(II)	1.638	1.582	2.404	1.087	0.491	−0.548	
B_{13}(III)	2.009	2.810	2.001	1.793	0.946	−0.649	
B_{14}(I)	2.012	2.919	2.140	2.055	1.342	−0.067	
B_{14}(II)	2.158	2.539	3.069	2.050	1.111	−0.142	
B_{15}(I)	2.008	2.518	2.987	2.477	1.631	0.250	−1.070
B_{15}(II)	2.021	3.012	2.232	2.323	1.691	0.328	−0.586

π-electrons is expressible as TRE(G,N_π). All TREs in this table are given in units of $\lvert\beta_{BB}\rvert$. TREs for doublet- or triplet-state species can be calculated easily from this table. The TRE for a species with N_π = odd number is equal to [TRE(G,$N_\pi + 1$) + TRE(G,$N_\pi - 1$)]/2. Such an electronic state appears when the cluster takes a doublet- or triplet-state electronic configuration. The TRE for a triplet-state π-system with N_π = even number is equal to [TRE(G,$N_\pi + 2$) + TRE(G,$N_\pi - 2$)]/2.

As shown in Table 3, all realistic neutral and charged boron clusters turned out to be highly aromatic with large positive TREs. For example, B_{10}, B_{11}^-, B_{12}, $B_{13}(III)^-$, B_{14}(II), and $B_{15}(I)^-$ have TREs of 1.568, 1.798, 2.605, 1.793, 2.050, and 1.631 $\lvert\beta_{BB}\rvert$, respectively. These clusters are much more aromatic than typical polycyclic aromatic hydrocarbons (PAHs) even if we take into account that $\lvert\beta_{BB}\rvert$ is slightly smaller than $\lvert\beta_{CC}\rvert$. For reference, the TREs are 0.273 for benzene (C_6H_6), 0.389 for naphthalene ($C_{10}H_8$), 0.475 for anthracene ($C_{14}H_{10}$), and 0.598 for pyrene ($C_{16}H_{10}$), respectively, all in units of $\lvert\beta_{CC}\rvert$.[44−47] High aromaticity of planar boron clusters fully supports Boustani's view that the optimal overlap of boron 2p$_z$ AOs causes a high cluster stability although it represents sp-promotion (i.e., an increase in the population of higher-energy 2p$_z$ AOs).[15,16]

As mentioned, the Hückel rule has been applied to planar polycyclic boron clusters. Many boron clusters are really aromatic with two or six π-electrons and apparently conform to this rule. If the Hückel rule holds true without reservations, $B_6(II)^{2-}$, three B_{13}^- isomers, and two B_{14} isomers must be antiaromatic with four or eight π-electrons.[25,27,28] However, these clusters proved to have large positive TREs. It then is clear that the Hückel rule does not hold at least for these boron clusters. When N_π is relatively small, a planar boron cluster is always aromatic. Larger clusters have a larger range in N_π that keeps them aromatic. For example, six-boron clusters are aromatic with positive TREs if they have two to four π-electrons. In contrast, 15-boron clusters are aromatic as long as they have two to 12 π-electrons.

Zhai et al. stated like others that the number of π-electrons in the planar boron cluster renders the system aromatic or antiaromatic according to the Hückel rule.[23,25−27,33−35] They discussed preferable geometric shapes and spin multiplicity of presumed "antiaromatic" species.[27] For example, B_{13}^- has eight π-electrons, and therefore they considered it antiaromatic. This anion prefers an elongated shape, $B_{13}(III)^-$, to a round one, $B_{13}(I)^-$. For such clusters with 4n π-electrons, there are not enough π-electrons to completely fill a near-degenerate π-MO pair of a given node. They presumed that in this case there are two possibilities.[27] If each component of the π-MO pair is occupied with one electron, resulting in a triplet state, the system might be again aromatic[62,63] and should be circular in shape. Alternatively, if only one component of the π-MO pair is doubly occupied, a structural elongation ensues. In our view, such a structural modification in principle could occur even if the Hückel rule does not hold. In fact, all B_{13}^- are aromatic with large positive TREs. Note that not only many PAH molecules but also their molecular dianions and dications are aromatic with positive TREs.[58] This indicates that 4n π-electron systems can often be aromatic.

The inapplicability of the Hückel rule to polycyclic π-systems never means that all low-lying π-MOs contribute to aromaticity. For small clusters with five to nine boron atoms, TRE(G,4) is smaller than TRE(G,2). This indicates that the second π-MO is antiaromatic in nature even if TRE(G,4) is positive in sign. This is apparently consistent with the Hückel rule.[42] However, the same thing is not true for B_{10} and larger boron clusters. For these clusters, the first two π-MOs are aromatic, both contributing to the increase in TRE. For B_{15}(II), the first three π-MOs are aromatic, whereas the next four π-MOs are antiaromatic. Therefore, $B_{15}(I)^+$ ($N_\pi = 6$) has a larger TRE than $B_{15}(I)^-$ ($N_\pi = 8$). Such an arrangement of aromatic and antiaromatic π-MOs is not compatible with the original Hückel rule.[42] For the Hückel rule to hold, the highest occupied molecular orbital (HOMO) must determine the sign of the TRE. At least, aromatic and antiaromatic π-MOs must alternate without exceptions.

It is noteworthy that, as suggested by Zhai et al.,[27] some boron clusters are in the triplet electronic state. B_6(I) and B_6(II) are in the triplet state with three π-electrons, in which one electron to reside in the second π-MO is promoted to the σ-system.[25,28] This is due in part to the highly antiaromatic nature of the second π-MO. The TREs for B_6(I) and B_6(II) are 0.990 and 0.654 $\lvert\beta_{BB}\rvert$, respectively. If these neutral clusters are in the singlet state with four π-electrons, the TREs would be more or less smaller. For essentially the same reason, B_7^- and B_8 are triplet-state species with four π-electrons.[26,35] $B_{13}(II)^-$ was also predicted to be in the triplet electronic state with eight π-electrons.[27] The highly antiaromatic nature of the fourth π-MO in this anion must be responsible at least in part for the triplet-state configuration, in which one electron in the fourth π-MO is promoted to the fifth one. The TRE for the resulting triplet-state species is 1.448 $\lvert\beta_{BB}\rvert$, which is 0.361 $\lvert\beta_{BB}\rvert$ larger than that for the singlet-state species (1.087 $\lvert\beta_{BB}\rvert$).

Aromatic character of planar or quasi-planar boron clusters might be rationalized qualitatively in terms of multivalency of boron atoms.[48,62] As can be seen from Figure 1, each boron atom is bonded to two to eight adjacent ones. We previously pointed out that the π-systems of large planar boron clusters somewhat resemble complete graphs,[48] in which each vertex is connected to all other vertexes. Such nuclear arrangements

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markedly lower the energy of the lowest π-MO. For example, the energies of the lowest π-MOs in B_{13}(I), B_{14}(I), and B_{15}(I) are $\alpha_B + 4.355\ \beta_{BB}$, $\alpha_B + 4.415\ \beta_{BB}$, and $\alpha_B + 4.453\ \beta_{BB}$, respectively. Consequently, the lowest π-MO in each boron cluster is much lower than the corresponding one in the polyene reference, contributing much to the aromaticity. These lowest π-MOs with two π-electrons contribute as much as 2.198, 2.012, and 2.008 $|\beta_{BB}|$ to the TREs of B_{13}(I), B_{14}(I), and B_{15}(I), respectively. Such a trend in the lowest π-MO is common to all planar or quasi-planar structures studied.

For any planar boron cluster, the maximum TRE is attained when it has two to six π-electrons, which obviously reflects the lowering of the lowest π-MO due to the multivalency of boron atoms. For all boron clusters studied, the number of bonding π-MOs is always smaller than that of antibonding ones. In case the π-system represents a complete graph, there is only one bonding π-MO. All bonding π-MOs are not filled at least in large boron clusters. For the polyene reference of any planar boron cluster, the number of bonding π-MOs is always equal to that of antibonding π-MOs. Such a difference in the number of bonding π-MOs between a planar boron cluster and the polyene reference is the main origin of high aromaticity in the cluster. If N_π were close to that of conjugated boron atoms, most planar boron clusters would be antiaromatic with negative TREs. This is in marked contrast to commonplace PAHs. Their degrees of aromaticity are maximized when the number of π-electrons is equal to that of conjugated carbon atoms.

Magnetotropicity. Diatropicity and paratropicity are referred to collectively as magnetotropicity. Magnetotropicity[43] and nucleus-independent chemical shift (NICS)[63] have often been used as magnetic criteria of aromaticity. Local aromaticity has been identified by diatropicity and a negative NICS value, and local antiaromaticity by paratropicity and a positive NICS value. These magnetic criteria have often led organic chemists to classify many aromatic PAH dianions, such as dianions of anthracene, phenanthrene, and pyrene, as antiaromatics.[64] For example, the pyrene dianion is still considered antiaromatic because it is paratropic.[65] In fact, these dianions are aromatic with positive TREs and positive MREs.[58] Essentially the same situation is encountered when the intensities of ring currents induced in planar boron clusters are evaluated.

Current density distributions induced in $B_6(II)^{2-}$, B_7^-, and B_8 are presented in Figure 2, in which all currents are given in units of that induced in benzene. Clockwise and counterclockwise currents indicate paratropicity and diatropicity, respectively. Planar geometries utilized for $B_6(II)^{2-}$ and B_8 are those obtained by Fowler et al.[66] and Zhai et al.,[26] respectively. We assumed somewhat pyramidal B_7^- to be planar and set the lengths of the peripheral BB bonds equal to those calculated by Alexandrova et al. (1.633 Å).[35] As already mentioned, a ring current induced in a polycyclic π-system can be partitioned formally among all possible circuits. All nonidentical circuits that can be chosen from the B_6(II), B_7, and B_8 π-systems are presented in Figure 3. Current intensities assigned to these circuits are summarized in Table 4, where the positive and negative values indicate diatropicity and paratropicity, respectively.

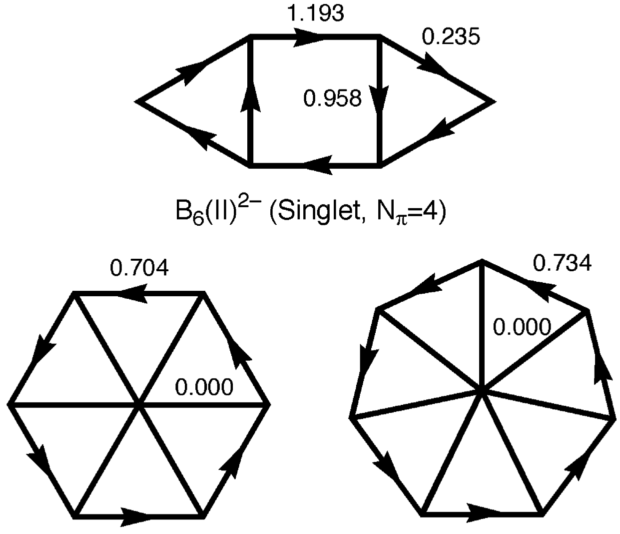

Figure 2. π-Electron currents induced in $B_6(II)^{2-}$, B_7^-, and B_8. All current intensities are given in units of that for benzene. Clockwise and counterclockwise currents are indicative of paratropicity and diatropicity, respectively.

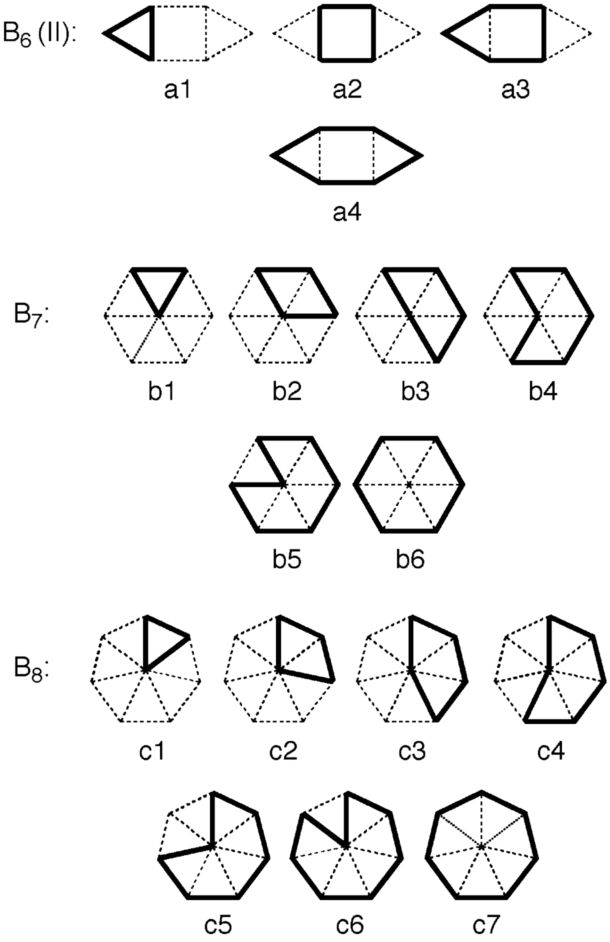

Figure 3. Nonidentical circuits in B_6(II), B_7, and B_8.

$B_6(II)^{2-}$ is in the singlet electronic state with four π-electrons.[25,28] As shown in Figure 2, this dianion sustains a large paramagnetic ring current. The gross feature of this current density pattern is similar to that obtained by Fowler et al.; a strong π-electron current flows along the inner four-membered

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Table 4. Circuit Currents and Circuit Resonance Energies for $B_6(II)^{2-}$, B_7^-, and B_8

a. $B_6(II)^{2-}$ in the singlet electronic state with four π-electrons

circuit	number of identical circuits	circuit current/I_0	$A_i/|\beta_{CC}|$
a1	2	0.437	0.453
a2	1	−0.198	−0.074
a3	2	−0.323	−0.089
a4	1	−0.350	−0.076

b. B_7^- in the triplet electronic state with four π-electrons

circuit	number of identical circuits	circuit current/I_0	$A_i/|\beta_{CC}|$
b1	6	0.123	0.120
b2	6	−0.034	−0.017
b3	6	−0.098	−0.032
b4	6	0.040	0.010
b5	6	0.145	0.028
b6	1	0.059	0.010

c. B_8 in the triplet electronic state with four π-electrons

circuit	number of identical circuits	circuit current/I_0	$A_i/|\beta_{CC}|$
c1	7	0.127	0.112
c2	7	0.016	0.007
c3	7	−0.076	−0.022
c4	7	−0.046	−0.010
c5	7	0.060	0.011
c6	7	0.100	0.015
c7	1	0.084	0.011

ring.[66] They predicted this dianion to be antiaromatic on this magnetic criterion. However, we have noted that $B_6(II)^{2-}$ is aromatic with a positive TRE of 0.549 $|\beta_{BB}|$ even if it has four π-electrons. Four nonidentical circuits, a1−a4, can be chosen from the $B_6(II)$ π-system. Paratropicity of this dianion is determined by the paramagnetic circuit currents induced in a2−a4. In contrast, the largest aromatic contribution to MRE (0.578 $|\beta_{CC}|$) comes from a1, which overwhelms the antiaromatic contribution of a2−a4. However, circuit a1 makes a modest contribution to the ring current because this circuit has the smallest area. This constitutes the very reason this dianion is aromatic but paratropic. Thus, it is clear that the magnetotropicity of a polycyclic π-system does not always represent aromaticity. For $B_6(II)^{2-}$, the TRE is 0.549 $|\beta_{BB}|$, which is equal to 0.478 $|\beta_{CC}|$.

B_7^- is a triplet-state species with four π-electrons.[35] The second and the third π-MO in this anion are degenerate as in the case of benzene, so that the singlet configuration is energetically unstable. As can be seen from Figure 2, a strong diamagnetic current is induced along the perimeter of this anion, which is apparently consistent with its large positive TRE of 0.918 $|\beta_{BB}|$ or 0.799 $|\beta_{CC}|$. B_7^- has six nonidentical circuits, b1−b6. However, its diatropicity primarily arises not from b6 located along the perimeter but from six b1-type three-membered circuits, which make a large aromatic contribution to the MRE (0.667 $|\beta_{CC}|$). The singlet-state B_7^- species has a much lower TRE of 0.159 $|\beta_{BB}|$ although it is still positive in sign.

B_8 is also a triplet-state species with four π-electrons,[26] being nearly iso-π-electronic with B_7^-. The current density distribution in Figure 2 suggests that diamagnetic current is induced along the periphery of the π-system. It is associated straightforwardly with the fact that this cluster is diatropic when it has two or six π-electrons. A large negative NICS(1) value of −22.9 ppm for B_8 is apparently consistent with the positive TRE.[26] This eight-atom cluster has seven nonidentical circuits, c1−c7. As in the case of B_7^-, its diatropicity primarily arises from c1-type three-membered and c6-type eight-membered circuits, which make a large aromatic contribution to the MRE (0.792 $|\beta_{CC}|$). Thus, the evaluation of circuit currents is very useful for looking for the aromatic substructures in a polycyclic π-system. The corresponding TRE is 1.099 $|\beta_{BB}|$ or 0.956 $|\beta_{CC}|$.

We have reported that the MRE concept is very useful for reconciling the energetic and magnetic crietria of aromaticity.[58,61] For the three boron clusters, MRE has the same sign as TRE, the former being slightly smaller in magnitude than the latter. It is noteworthy that, although it seems that strong currents are induced along the molecular perimeters of $B_6(II)^{2-}$, B_7^-, and B_8, their perimeter circuits (i.e., a4, b6, and c7) contribute modestly to the MREs. It is therefore evident that a so-called perimeter model[67] should not be applied to polycyclic π-systems.

Concluding Remarks

As noted by Alexandrova et al.,[25] the concept of aromaticity in deltahedral boranes was already advanced by us[68,69] and by King and Rouvray.[70,71] The present study firmly established aromatic character of planar boron clusters. Aromaticity is presumably responsible at least in part for planar geometry of these boron clusters. All of the scanty valence electrons in these boron clusters are not used for σ-bonding but some of them are used to aromatize the clusters. These planar boron clusters indeed constitute a group of novel aromatic molecules. Participation of the pentagonal, hexagonal, or heptagonal pyramids in the cluster geometries seems to be energetically favorable. In particular, such substructures markedly lower the lowest π-MO.

We definitely showed that the Hückel $4n + 2$ rule of aromaticity cannot be applied to polycyclic π-systems.[42] As pointed out by Minkin et al.,[43] the Hückel rule should be confined to monocyclic π-systems. Nevertheless, most chemists still use this rule to explain the aromaticity of polycyclic π-systems.[23,25−27,33−35,65,72,73] According to the extended Hückel rule,[56] the aromaticity of neutral polycyclic benzenoid and nonbenzenoid hydrocarbons is related not to the total number of π-electrons but to the presence of $(4n + 2)$-membered circuits. Unfortunately, this rule cannot be applied to charged PAHs and planar boron clusters because N_π is not equal to the number of conjugated atoms. However, this rule strongly suggests that, even for planar polycyclic boron clusters, aromaticity is never related to the total number of π-electrons. The conjugated circuits model proposed by Herndon[74] and Randić[75] also insists that the presence of particular circuits but not the total number of π-electrons is the determinant of aromaticity for polycyclic π-systems.

In 1978, we proposed the concept of excited-state aromaticity to elucidate the allowedness of photochemical pericyclic reactions.[76] It was found that the aromaticity of the transition-state species is a determinant of allowedness and that the reverse of

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the Hückel rule holds true for excited-state annulenes; [4*n* + 2]- and [4*n*]annulenes have negative and positive TREs, respectively, in the first excited state. The idea that triplet-state [4*n*]annulenes may be regarded as being aromatic was suggested in 1972 by Baird, who concluded that the Hückel rule is exactly reversed in the lowest triplet state of annulenes.[77−79] Gogonea et al. recently supported this idea by obtaining the negative NICS values at the centers of triplet-state [4*n*]annulenes.[78] We have seen earlier in this article that some polycyclic π-systems, such as B_7^- and B_8, are aromatized to a higher degree by taking a triplet-state configuration. These two species are aromatic even in the singlet state. Thus, the lowest triplet state is sometimes favored to partly suppress antiaromaticity due to an antiaromatic π-MO and then to enhance the aromaticity of the entire π-system.

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