

Table VII. β -D-Glucosidation Shift Rules for Secondary Alcohols in Pyridine ($\Delta\delta \pm 1$ ppm)^a

	$\Delta\delta_S(C-1')$	$\Delta\delta_A(C-\alpha)$	$\Delta\delta_A[C-\beta-(H)]$	$\Delta\delta_A[C-\beta-(M)]$
Sterically unhindered case ^b	-2.6	+7.2	-2.2 (CH ₂ ,Me)	-4.0 (CH ₂ ,Me)
Sterically hindered case I ^c	-4.2	+5.5 (± 1.5)	$\left\{ \begin{array}{l} -2.2 (CH) \\ -0.5 (C) \end{array} \right.$	-5.1 (CH ₂ ,Me)
Sterically hindered case II	0(± 1.5)	+10.4 (± 1.5)	-1.7 (CH ₂ ,Me)	$\left\{ \begin{array}{l} -1.3 (CH) \\ 0 (C) \end{array} \right.$

^a These rules are also valid for α -L-glucosides, but the $\Delta\delta_A[C-\beta-(H)]$ and $\Delta\delta [C-\beta-(M)]$ as well as sterically hindered cases I and II are exchanged when α -D- or β -L-glucosides are used. ^b A little lower field shift values should be expected when the *sec*-hydroxyl is axial in an aglycone alcohol. ^c Higher and lower field shift values should be applied according as the anomeric configuration is respectively axial and equatorial in the sugar moiety.

dary alcohols, because the usual NMR method using *J* values may not generally be applicable for these compounds. This method should be worth confirming results obtained by other methods¹⁴ which may, in some cases, give ambiguous results. Other cases having substituents on both β carbons or having an sp² or sp- β carbon(s) should be studied in the future.

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Three-Dimensional Aromaticity of Polyhedral Boranes

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Abstract: Resonance energies of typical polyhedral boranes with a general formula of $B_nH_n^{2-}$ have been calculated by means of a graph-theoretical theory of aromaticity previously reported by Aihara. Hückel-type molecular orbitals employed are those of Kettle and Tomlinson with three-center BBB localized orbitals as basis functions. Most polyhedral boranes investigated are predicted to be aromatic with positive resonance energies, in general agreement with their chemistry. The present resonance energy is fairly proportional to the logarithm of the number of valence structures allowed for the polyhedral borane.

The closed polyhedral boranes have long been of great theoretical and experimental interest.^{1,2} Some kinds of three-center bonds have been found to play an important role in molecular orbital (MO) calculations of boranes.^{3,4} Such a three-center bond formalism has also been established in describing their valence structures.^{3,4} Especially, the use of a central three-center BBB bond, in which all the three boron atoms are pairwise neighbors and topologically equivalent, serves as a theoretical basis for the energy consideration of polyhedral boranes.

A spherical network of the central three-center BBB bonds is known to stabilize polyhedral borane ions with a general formula of $B_nH_n^{2-}$ to a considerable extent.¹⁻⁵ In this connection, a graph-theoretical theory of aromaticity has been developed by Aihara,⁶⁻¹¹ and has been remarkably successful in predicting aromaticities of planar conjugated compounds.^{6,9} One of the most important applications of the three-center bond formalism may be the graph-theoretical approach to

aromatic stabilization of these borane dianions. In this paper, we show how it can be used to estimate aromaticity of a three-dimensional network of the central three-center BBB bonds.

Theory

In order to apply the graph-theoretical theory of aromaticity to polyhedral boranes, a Hückel-type MO theory is needed to estimate the ground-state bonding characters. Among the MO theories based on the three-center bond formalism, that of Kettle and Tomlinson^{12,13} is most suitable for the present purpose. They used localized three-center BBB bonding orbitals as basis functions in a Hückel-type MO description of the bonding in polyhedral boranes.

When three boron atoms are triangularly bound to each other, a localized three-center BBB bonding orbital is often stabilized with respect to the zeroth-order energies of the valence shell atomic orbitals of which it is a linear combination.¹

Such a localized orbital can be imagined to exist in every triangular face of $B_nH_n^{2-}$. In the present approach, the adjacent localized orbitals in the same $B_nH_n^{2-}$ ion are assumed to interact with each other, as in the case of p_π orbitals of carbon atoms in an unsaturated hydrocarbon. This assumption leads to a delocalized MO energy scheme of the $B_nH_n^{2-}$ ion. Each MO of $B_nH_n^{2-}$ can hence be expressed as a linear combination of the three-center BBB bonding orbitals. This three-center bond formalism actually leads to the same pattern of MO energy levels as does the LCAO method.¹²

On this basis, the MO calculation can be carried out in a manner entirely analogous to the original Hückel method for treating conjugated hydrocarbons, setting up an $N \times N$ matrix A , where N is the number of triangular faces of a polyhedral borane considered. The n th column and n th row of the matrix are each put into a 1:1 correspondence with the n th face of the polyhedron. Diagonal matrix elements are given the value α (Hückel Coulomb integral), and off-diagonal matrix elements, which correspond to faces with an edge in common, the value β (Hückel resonance integral). All other matrix elements are set equal to zero.

A secular equation of this polyhedral borane is then expressed as

$$P(X) = \det |A + EX| = 0 \quad (1)$$

where E is a unit $N \times N$ matrix. The total energy of $B_nH_n^{2-}$ in the ground state is given as twice the sum of the larger ($n + 1$) roots of eq 1. On the other hand, the reference energy of $B_nH_n^{2-}$, relative to which aromatic stabilization is calculated, can be estimated from the following equation:^{6,7}

$$R(X) = \sum_{k=0}^{[N/2]} (-1)^k p(k) X^{N-2k} = 0 \quad (2)$$

where $[N/2]$ signifies the maximum integer not exceeding $N/2$, and $p(k)$ is the number of ways in which k pairs of triangular faces are chosen, on condition that each pair of faces has an edge in common and that any pair of faces chosen does not have edges in common with the other pairs chosen. This is nothing other than a nonadjacent number,¹⁴ defined for a network of three-center BBB bonding orbitals. The reference energy of $B_nH_n^{2-}$ is given as twice the sum of the larger ($n + 1$) roots of this equation.

As shown in previous papers,⁶⁻¹⁰ the resonance energy is defined as the difference between the total energy of a polyhedral borane and its reference energy. This type of resonance energy can be interpreted as the extra stabilization energy gained by a circular migration of bonding electrons from face to face through successive resonance integrals.⁷ It should hence be aromatic stabilization energy if it has a positive value.

Results

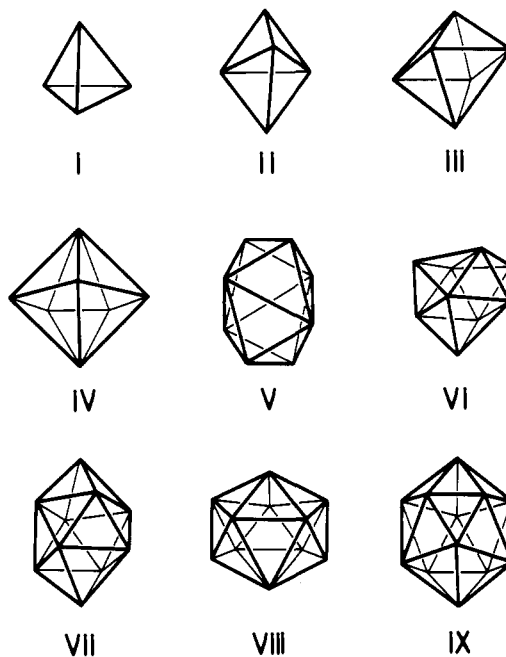
Resonance energies thus calculated for a series of $B_nH_n^{2-}$ ions are presented in Table I. It was fortunate that the geometries of these boranes are all closely approximated by regular deltahedra (i.e., polyhedra whose faces are equilateral triangles).^{2,15} Otherwise, the above theory must have been modified to reflect bonding characters other than the three-center BBB bonds.

First, resonance energies of B_4H_4 and $B_5H_5^{2-}$ are zero, suggesting that these are nonaromatic. This nonaromaticity is a result of filling with electrons all the MOs formed by the localized three-center BBB bonding orbitals. Resonance energies of the $B_nH_n^{2-}$ ions with $n \geq 6$ are all positive, indicating that these ions should be aromatic. In accord with this, these species have so far been prepared, and exhibited considerable thermal stability and trends toward substitution reactions.^{2,5} Contrary to them, B_4H_4 and $B_5H_5^{2-}$ have never been prepared. This gives a gross support to the present resonance energies.

Table I. Resonance Energies of Polyhedral Boranes

Species	Molecular shape	Number of faces	Resonance energy (β)	Number of valence structures ^a
B_4H_4	I	4	0.000	1
$B_5H_5^{2-}$	II	6	0.000	2
$B_6H_6^{2-}$	III ^b	8	0.844	32
$B_7H_7^{2-}$	IV ^c	10	0.938	20
$B_8H_8^{2-}$	V ^c	12	0.798	8 ^h
$B_9H_9^{2-}$	VI ^d	14	0.813	16
$B_{10}H_{10}^{2-}$	VII ^e	16	1.145	72
$B_{11}H_{11}^{2-}$	VIII ^f	18	1.000	16 ^h
$B_{12}H_{12}^{2-}$	IX ^g	20	1.763	132 ^h

^a Reference 18. ^b R. Schaeffer, D. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965). ^c F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *ibid.*, **6**, 1271 (1967). ^d L. J. Guggenberger, *ibid.*, **7**, 2260 (1968). ^e R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962). ^f F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966). ^g J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960). ^h R. N. Camp, I. R. Epstein, and W. N. Lipscomb, unpublished work.



A quantity defined as the resonance energy per π electron (REPE) has been acknowledged as an excellent index for relative stability of a planar conjugated system.¹⁶ In polyhedral boranes, every three-center BBB bonding orbital is two dimensional, in the sense that it spreads within a triangular plane formed by the three boron atoms. Considering that the resonance energy is used to sustain a polyhedron covered with these bonds, the degree of aromatic stabilization should be proportional to the resonance energy divided by the surface area of the polyhedron. For simplicity, the surface area can be represented by the number of triangular faces (NF) of the polyhedron. The REPE-like index can hence be defined for polyhedral boranes as the resonance energy per face, and is termed REPF for short. REPF values are listed in Table II.

It has generally been accepted that $B_{12}H_{12}^{2-}$ is the most stable followed by $B_{10}H_{10}^{2-}$. These two ions have been seen as typical examples of inorganic aromatics.^{2,5} In considerations of such stability, many factors necessarily come into play, both thermodynamic and kinetic in nature. However, it has been said that a molecular symmetry may be an approximate re-

Table II. Relative Stability Indexes for Polyhedral Boranes

Species	REPF ^a	VSI ^b	ΔE^c
B ₄ H ₄	0.0000	0.0000	
B ₅ H ₅ ²⁻	0.0000	0.0502	
B ₆ H ₆ ²⁻	0.1055	0.1881	2.000
B ₇ H ₇ ²⁻	0.0938	0.1301	2.000
B ₈ H ₈ ²⁻	0.0665	0.0753	1.000
B ₉ H ₉ ²⁻	0.0580	0.0860	0.732
B ₁₀ H ₁₀ ²⁻	0.0716	0.1161	1.414
B ₁₁ H ₁₁ ²⁻	0.0555	0.0669	0.824
B ₁₂ H ₁₂ ²⁻	0.0881	0.1060	2.000

^a Resonance energy per face in β . ^b Valence structure index. ^c LUMO-HOMO separation in β .

flection of resonance stabilization.^{1,2} In this context, the most symmetric anion, B₁₂H₁₂²⁻, should have the greatest resonance stabilization. This geometrical aspect appears in line with the B₁₂H₁₂²⁻ chemistry.

Accordingly, in order to further justify the theory of aromaticity, it is desirable to examine a correlation between the obtained REPF values and the above situation. As seen from Table II, this kind of correlation actually holds well for the polyhedral borane series. The B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ ions obviously have larger REPF values than the neighboring members of the same series (i.e., B₁₁H₁₁²⁻, B₉H₉²⁻, and B₈H₈²⁻). It is noteworthy that, among low REPF ions, B₈H₈²⁻ and B₁₁H₁₁²⁻ show intramolecular rearrangements with facility in solution.^{2,17} The ground-state forms of these ions are very sensitive to environment. Such stereochemical nonrigidity may be considered as an indication of being relatively less stable (or less aromatic), although a possibility cannot be precluded that every solution form is equally highly aromatic.

Here, an apparent difficulty in the present resonance energies is that the REPF values for B₇H₇²⁻ and B₆H₆²⁻ are somewhat larger than that for the supposedly most stable B₁₂H₁₂²⁻ ion. This is inconsistent with the fact that the two ions are less stable than the B₁₂H₁₂²⁻ ion.² Every chemical aspect suggests that B₇H₇²⁻ is the least stable of all the known species.² A discussion on this point will be made later.

On the contrary, there is encouraging evidence to support the present results. Since 1957, Lipscomb's group has been developing a topological theory of borane three-center valence structures.¹ In 1971, Epstein and Lipscomb formulated resonance stabilization of boranes, suggesting modestly that the existence of many valence structures is a prerequisite to the existence of a molecule with that topology.¹⁸ In order to see a correlation between their theory and ours, their number of allowed valence structures (NVS) for each borane must beforehand be processed mathematically.

Let the number of valence structures allowed for borane I be n_1 and that for borane II be n_{11} . If the two boranes are connected by an essential two-center BB bond, the number of valence structures allowed for the entire borane is given as a product of n_1 and n_{11} . When resonance energies of boranes I and II are respectively RE_I and RE_{II}, the resonance energy of the combined system should be roughly RE_I + RE_{II}. On this basis, we can infer that if the number of allowed valence structures reflects the stabilization energy of a conjugated system, the latter value should be proportional to the logarithm of the former value.¹⁹

For this reason, we introduce a new quantity based on the number of borane valence structures. It is defined as the logarithm of the number of allowed valence structures, divided by the number of triangular faces of the polyhedron. This quantity is termed a valence structure index or VSI for short. As in the case of benzenoid hydrocarbons,^{9,10,19} this VSI may

be compared to the REPF. The VSI values are added for comparison in Table II.

As may be seen from this table, a general correlation is actually found between the REPF and VSI values. The VSI values for B₆H₆²⁻ and B₇H₇²⁻ are larger than those for B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻. The VSI values for these four ions are larger than those for B₈H₈²⁻, B₉H₉²⁻, and B₁₁H₁₁²⁻, and much larger than those for B₅H₅²⁻ and B₄H₄. Such an orderliness of magnitude is in nice agreement with that for the REPF values. This gives a mutual support to the congruence of both the valence structure theory and our aromaticity theory.

Another support for our resonance energies comes from a fairly good correlation between the REPF value and the energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy of the LUMO is linearly related to the electron affinity, while the energy of the HOMO is linearly related to the ionization potential. In other words, the LUMO energy represents a trend toward a reduction reaction, whereas the HOMO energy represents a trend toward an oxidation reaction. Accordingly, when a given compound has a large LUMO-HOMO energy separation, we might say that this compound is rather resistant to oxidation and/or reduction. The energy separation can hence be regarded as a kind of stability index for a conjugated compound. For benzenoid hydrocarbons, this is the case.^{9,20} The LUMO-HOMO energy separation for these compounds is linearly related to the REPE.

In this sense, it is gratifying to see that the LUMO-HOMO separations (ΔE) for B₆H₆²⁻ and B₇H₇²⁻ are similar to that for B₁₂H₁₂²⁻ (see Table II). The other ions have smaller LUMO-HOMO energy separations than these three ions. This fact is also favorable to the relatively large resonance energies of B₆H₆²⁻ and B₇H₇²⁻.

From the above viewpoints of aromaticity, we might conclude that B₁₂H₁₂²⁻ and B₆H₆²⁻ represent two of the most aromatic species of all. Large resonance energies of these ions remind us of the very rigid crystal structures of elemental boron and many metal hexaborides.

There are several allotropic forms of elemental boron.²¹ The crystals are extremely hard, chemically very inert, and thermally stable. Each allotrope is built of icosahedral B₁₂ clusters and (sometimes) additional interstitial boron atoms. In any of boron allotropes, 26 electrons are left for the intraicosahedral bonding of each B₁₂ cluster.^{22,23} These 26 electrons just fill the bonding intraicosahedral MOs. Considering that the icosahedral boron cluster is isoelectronic with B₁₂H₁₂²⁻, a large part of the stability of boron crystals should be attributed to the aromaticity of B₁₂ clusters in them.

On the other hand, metal borides of the type MB₆ provide the rare systems, apart from the elemental boron and the boron hydrides, in which extensive clustering of boron atoms occurs.²⁴ They are also chemically very stable. In each metal hexaboride, the boron atoms form octahedral B₆ clusters which are linked together in three dimensions to give a cubic lattice. The metal atoms are accommodated in the holes between eight octahedra. Supposedly, the metal atoms are unimportant to the stability of the lattice, a view which is supported by the similarity of the lattice constants for the entire MB₆ isostructural series.²⁴

In an MB₆ crystal, two electrons are transferred from each metal atom to the boron framework.^{23,25} Then 14 electrons are used to fill all the seven bonding intraoctahedral MOs. This electronic structure can be understood by analogy with B₆H₆²⁻. Therefore, it seems quite natural to ascribe a large part of the stability of the MB₆ crystal to the aromatic character of each octahedral B₆ cluster in it. Conversely, the rigid crystal structures of the elemental boron and the metal hexaborides favor the proposed aromaticities of the icosahedral

$B_{12}H_{12}^{2-}$ and octahedral $B_6H_6^{2-}$ ions. The applicability of our aromaticity theory to polyhedral boranes has thus been justified in several ways. Therefore, a significant discrepancy found between the REPF values and the chemistry of $B_6H_6^{2-}$ and $B_7H_7^{2-}$ should be ascribed to some effect other than the aromatic character.

Discussion

In considering the net stability of the $B_nH_n^{2-}$ ions, a precise composition of the basis orbitals employed must of course be examined for every ion. To be exact, it must differ from borane to borane; so too must the values of α and β .¹² It follows that the parameter transferability does not exist. The decrease in the absolute value of β leads to the decrease in the resonance energy calculated. In principle, one should determine the values of α and β from thermochemical data of each polyhedral borane, as in the case of organic compounds,¹⁶ and thus test the transferability of these Hückel parameters. Unfortunately, the necessary data are not available in the literature.

Next, a strain energy term must be taken into consideration. There is no contribution of this term to the calculated resonance energies because we tacitly assumed that every borane and its reference structure are equally strained. Considering that many basket-shaped boranes¹³ are fragments of either an icosahedral $B_{12}H_{12}^{2-}$ or octahedral $B_6H_6^{2-}$ ion, the other less symmetric $B_nH_n^{2-}$ ions must be more or less strained. The strain diminishes the stability of a borane even if it has large resonance energy.

In addition to the strain energy, an asymmetry in the molecular geometry, if any, should significantly relate to reactivity.^{2,5} The existence of unequivalent boron atoms possibly reduces the stability of the conjugated system. The least stable $B_7H_7^{2-}$ ion typically has unequivalent boron atoms with a different coordination number. The unequivalent boron atoms break a uniformity of aromaticity on the surface of the polyhedron. The less aromatic sites are generally reactive,⁹ and may be responsible for relative instability of $B_7H_7^{2-}$. In contrast to this ion, the framework of the most stable $B_{12}H_{12}^{2-}$ ion is a regular icosahedron. Since that of $B_6H_6^{2-}$ is a regular octahedron, it is also free from this effect.

One of the most probable factors which make $B_6H_6^{2-}$ less stable than $B_{12}H_{12}^{2-}$ might be the surface curvature of its polyhedral structure. Because of a smaller radius of $B_6H_6^{2-}$, the six BH bonds in it are evidently more exposed to the outer space than those in $B_{12}H_{12}^{2-}$. Any chemical reagent can attack the BH bonds of the former ion from a wider solid angle. This might explain why the stability of $B_6H_6^{2-}$ does not reflect its high aromaticity. Such a stereochemical aspect is common to the other small members of the $B_nH_n^{2-}$ series.

As seen above, there are several factors which might influence the stability of polyhedral boranes. If these factors could be disregarded, the stability of polyhedral boranes would reflect the aromaticity more frankly.

Concluding Remarks

The present approach presents a theoretical basis for the concept of three-dimensional aromaticity of deltahedral boranes. Although the subject of structure-aromaticity relationships is in a primitive stage, we might safely say that the primary origin of stability is aromatic in nature rather than kinetic. Especially, $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$ are markedly aromatic. The stability of each three-center BBB bond itself¹² should be examined separately. Our results are of course in harmony with some topological rules,^{15,26} each of which says that the $B_nH_n^{2-}$ ion is stable when it is a dianion. It is hoped that there will soon be much more detailed intercomparison of various polyhedral boranes and carboranes with regard to stability and aromaticity considerations.

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