Aromatic Character of Large Deltahedral Borane Dianions As Estimated Using the Kettle–Tomlinson Bonding Model

Jun-ichi Aihara

Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422-8529

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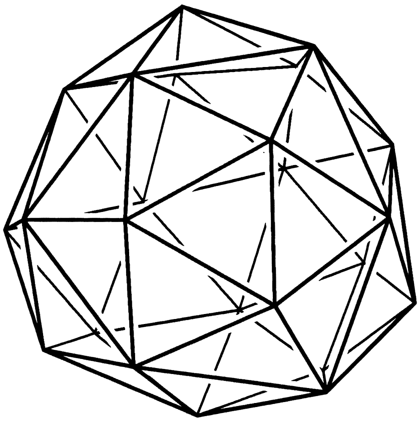
Lipscomb et al. designed the low-energy deltahedral isomers of borane dianions $B_nH_n^{2-}$ for n ranging from 13 to 24. We evaluated the topological resonance energies (TREs) of these dianions by applying the Kettle–Tomlinson (KT) bonding model to them. It was then found that except for $B_{18}H_{18}^{2-}$ (D_{6d}) the TRE per BH unit is highly correlative with the PRDDO binding energy per BH unit. This indicates that the thermodynamic stability of deltahedral borane dianions is determined primarily by aromaticity. $B_{18}H_{18}^{2-}$ (D_{6d}) has a very small TRE per BH unit, strongly reflecting its small HOMO–LUMO energy separation. Thus, the KT model is useful for describing electronic characteristics of large deltahedral borane dianions.

Three-dimensional aromaticity of *closo*-borane dianions, $B_nH_n^{2-}$, has long been the subject of many theoretical and experimental papers.[1–5] Interestingly, the dianions with n = 5–12 are kinetically very stable with a deltahedral geometry, a closed polyhedron with triangular faces.[1–5] The topological resonance energy (TRE) can be used as an energetic criterion of aromaticity for such conjugated systems.[6,7] In 1978 we reported that the $B_nH_n^{2-}$ structures with n = 6–12 are aromatic with a large positive TRE.[8] This was the first explicit suggestion of three-dimensional aromaticity made for deltahedral boranes.[5] The bonding model we employed to depict the skeletal delocalized electrons was a simple Hückel-like one devised by Kettle and Tomlinson.[9,10]

Deltahedral borane dianions with $n > 12$ have not been synthesized yet. In 2000 Schleyer et al. sought the lowest-energy isomers of $B_nH_n^{2-}$ clusters with n = 13–18 using the B3LYP level of theory and found that those with $n > 15$ are no longer in a deltahedral geometry.[11] Deltahedral ones can also be conceivable for large borane dianions. Lipscomb et al. in 1977 predicted the geometries of the low-energy deltahedral $B_nH_n^{2-}$ isomers with n = 13–24 at the PRDDO (partial retention of diatomic differential overlap) level of theory.[12–14] One of the largest species they designed is shown in Fig. 1. We noticed that these structures can be used to further test the applicability of the Kettle–Tomlinson (KT) bonding model to deltahedral borane dianions.

In this paper, we examine the TREs for all the borane dianions designed by Lipscomb et al.[12–14] and show that the KT bonding model, combined with the concept of the TRE, is very useful for characterizing the electronic structure of deltahedral borane dianions in general. Aromaticity and kinetic stability of large deltahedral borane dianions are studied.



$B_{24}H_{24}^{2-}$ (T)

Fig. 1. $B_{24}H_{24}^{2-}$ (T), one of the largest deltahedral borane dianions Lipscomb et al. designed.[12]

Theory

The KT bonding model[9,10] employs localized central three-center BBB bonding orbitals, which are placed at all triangular faces of a borane cage. This bonding orbital is equivalent to the π-electronic system of the cyclopropenium ion, which is highly aromatic with two π electrons. The skeletal conjugated system in a borane cage can then be treated in a Hückel manner, each three-center orbital being assigned a Coulomb integral α and all resonance integrals being set equal to zero, except those between two three-center orbitals which correspond to faces with an edge in common, which are given the value β. The TREs were calculated on the basis of this bonding model.[9,10]

A graph defined by the KT bonding model for a deltahedral borane cage is identical with the dual of the deltahedron.[12,15] The dual of a deltahedron is formed by a one-to-one mapping of faces into vertices and vice versa. Then each of the triangular faces in the deltahedron becomes a three-coordinate vertex and each five- or six-coordinate vertex becomes a pentagonal or hexagonal face in its dual. The dual of a deltahedron with n vertices is identical with a conventional or unconventional

Table 1. The TREs and Related Quantities for Deltahedral Borane Dianions with $n = 6–24$

Structure[a)]	(E_{PRDDO}/BH)/au[b)]	TRE/$\|\beta\|$	(TRE/BH)/$\|\beta\|$	(Energy of the HOMO-α)/β [c)]	(Energy of the LUMO-α)/β [d)]	HOMO–LUMO energy gap/$\|\beta\|$
6 (O_h)	25.215	0.844	0.1407	−1.000(3)	−3.000(1)	2.000
7 (D_{5h})	25.232	0.938	0.1340	−0.618(2)	−2.618(2)	2.000
8 (D_{2d})	25.238	0.798	0.0998	−1.000(1)	−2.000(1)	1.000
9 (D_{3h})	25.249	0.813	0.0903	−1.000(1)	−1.732(1)	0.732
10 (D_{4d})	25.259	1.145	0.1145	−0.518(2)	−1.932(2)	1.414
11 (C_{2v})	25.257	1.000	0.0909	−0.555(1)	−1.379(1)	0.824
12 (I_h)	25.276	1.763	0.1469	0.000(4)	−2.000(4)	2.000
13 (C_{2v}; I)	25.260	1.349	0.1038	−0.375(1)	−1.233(1)	0.858
14 (D_{6d}; IIa)	25.266	1.807	0.1291	0.000(2)	−1.414(2)	1.414
15 (D_{3h}; III)	25.260	1.688	0.1125	−0.311(1)	−1.000(1)	0.689
16 (D_2; IV)	25.262	1.770	0.1107	−0.132(1)	−1.000(1)	0.868
17 (D_{5h}; Vb)	25.267	1.881	0.1107	+0.132(2)	−1.122(2)	1.253
18 (D_{3d}; VIc)	25.262	1.451	0.0806	−0.382(1)	−0.524(1)	0.142
19 (C_s; VIIc)	25.261	1.814	0.0955	−0.177(1)	−0.787(1)	0.610
20 (D_{3h}; VIIIb)	25.262	1.952	0.0976	0.000(2)	−1.000(3)	1.000
21 (D_3; IXa)	25.261	2.037	0.0970	+0.123(2)	−0.846(1)	0.969
22 (D_{5d}; Xb)	25.261	2.090	0.0950	+0.189(2)	−0.855(2)	1.044
23 (C_{2v}; XIb)	25.255	2.069	0.0899	−0.093(1)	−0.714(1)	0.622
24 (T; XIIa)	25.257	2.223	0.0926	+0.134(3)	−0.860(3)	0.993

a) Notation: n (symmetry, label in Refs. 12 and 14 where applicable).
b) Ref. 14.
c) The number in parentheses represents the degeneracy of the HOMOs.
d) The number in parentheses represents the degeneracy of the LUMOs.

fullerene molecule with $2n$–4 vertices.

Results and Discussion

TREs for Deltahedral Borane Dianions. The TREs for deltahedral borane dianions $B_nH_n^{2-}$ with n ranging from 6 to 24 are presented in Table 1 along with related quantities. For geometries of the dianions see Refs. 12–14 and 16. The TRE divided by the number of BH units (n) or the TRE/BH enables one to compare the degrees of aromaticity for different dianions. All deltahedral borane dianions, including the hypothetical ones with $n = 13–24$, have a positive TRE/BH, indicating that they all are aromatic. This corresponds to the fact that conventional and unconventional fullerene molecular hexaanions made of 8–44 carbon atoms are generally aromatic.[17,18]

It is not easy to estimate relative thermodynamic stabilities of charged species. For deltahedral borane dianions, the PRDDO binding energy per BH unit (E_{PRDDO}/BH) increases as n becomes larger since the Coulomb repulsion in the dianions decreases and there is a greater number of favorable multicenter bonding interactions.[12,13,17] When n is small, E_{PRDDO}/BH varies markedly. However, when we are concerned with sufficiently large dianions only, E_{PRDDO}/BH can be used as a rough measure of relative thermodynamic stability. The patterns of the TRE/BH and E_{PRDDO}/BH values are compared in Fig. 2.

One observation can immediately be made from this figure; the trend in the TRE/BH values is similar to that in the E_{PRDDO}/BH values. In general, a borane dianion with a relatively large E_{PRDDO}/BH value has a relatively large TRE/BH value. Thus, the dianions with $n = 6$, 10, 12, 14, and 17 have not only a large TRE/BH value but also a large E_{PRDDO}/BH value. This clearly shows that the thermodynamic stability of a deltahedral borane dianion is determined primarily by aromaticity or cyclic conjugation of skeletal electrons. Only $B_{18}H_{18}^{2-}$ (D_{3d}) appears to be exceptional, in that it has a very small TRE/BH although E_{PRDDO}/BH is not very small.

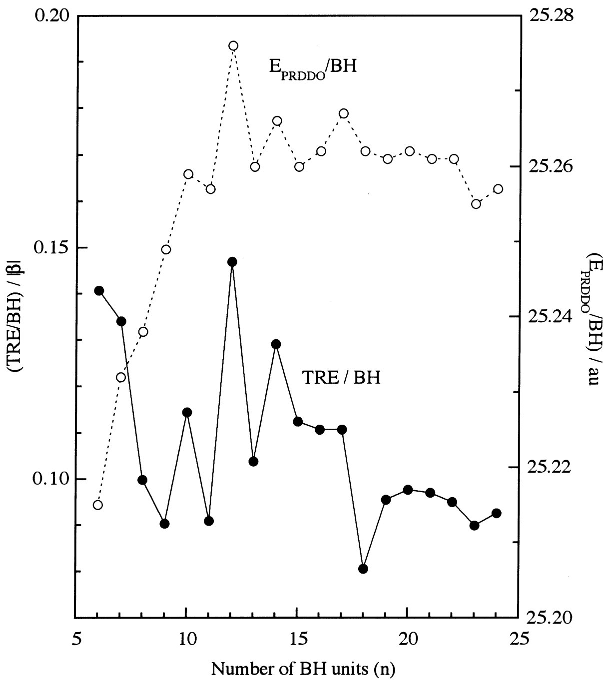


Fig. 2. Plots of TRE/BH and E_{PRDDO}/BH vs the number of BH units for deltahedral borane dianions.

For all deltahedral borane dianions but $B_{18}H_{18}^{2-}$ (D_{3d}), the number of skeletal electrons is equal to the one that attains the highest degree of aromaticity. $B_nH_n^{2-}$ has $2n + 2$ skeletal electrons in general; these are necessary to maximize the TRE. For example, $B_{20}H_{20}^{2-}$ (D_{3h}) has a larger TRE than $B_{20}H_{20}$ (D_{3h}) and $B_{20}H_{20}^{4-}$ (D_{3h}). The TREs/BH of $B_{20}H_{20}$ (D_{3h}), $B_{20}H_{20}^{2-}$ (D_{3h}), and $B_{20}H_{20}^{4-}$ (D_{3h}) are 0.0533, 0.0976, and 0.0622 $|\beta|$, respectively. Such an aspect of deltahedral borane dianions is fully consistent with the well-known skeletal electron counting rule for cage compounds.[3–5] Peculiar electronic features of $B_{18}H_{18}^{2-}$ (D_{3d}) will be mentioned later in some detail.

Lipscomb et al. suggested that no deltahedral borane dianions with great thermodynamic stability would be found for $n > 22$.[13,14] Although they examined many structures with $n = 23$ and $n = 24$, none was found to be energetically competitive with those for $n < 23$. The TRE/BH values obviously reflect such a trend in the E_{PRDDO}/BH values. As can be seen from Fig. 1, there are no highly aromatic species among the borane dianions with $n > 17$. However, the skeletal electron counting rule[3–5] holds for them regardless of their relative thermodynamic stabilities.

Highly Aromatic Borane Dianions. Borane dianions with $n = 6$, 10, 12, 14, and 17 are predicted to be highly aromatic with large TRE/BH values. Schleyer et al. computed the nuclear independent chemical shift (NICS) values at the cage centers of deltahedral borane dianions with $n < 16$.[11] Dianions with $n = 6$, 10, 12 and 14, which have a large TRE/BH value, have a NICS value less than -32 and are predicted to be more diatropic than their respective neighbors. Thus, the trend in NICS values is very similar to that in the TRE/BH values. We can naturally say that both the TRE and the NICS arise from the same cyclic conjugation of skeletal electrons. As has been reported previously,[21–23] the energetic criterion of aromaticity must in principle be closely related to the magnetic one. This proved to be the case for deltahedral borane dianions.

As shown in Table 1, highly aromatic dianions with $n = 6$, 10, 12, 14, and 17 have multiply degenerate highest occupied molecular orbitals (HOMOs) in the framework of the KT model. In general, conjugated systems with degenerate HOMOs are highly aromatic when they are fully occupied.[6,19] Most deltahedral borane dianions conform to this rule. Degenerate HOMOs in the dianions with $n = 6$, 10, 12, 14, and 17, are completely occupied. These dianions happen to have multiply degenerate lowest unoccupied molecular orbitals (LUMOs). Thus, in the case of polyhedral conjugated systems, high aromaticity is often associated with high molecular symmetry.

It is noteworthy that the HOMOs of $B_8H_8^{2-}$ (D_{2d}) and $B_9H_9^{2-}$ (D_{3h}) have an energy of α-β, which are apparently antibonding. However, they can still be considered as a kind of bonding orbitals since the basis functions themselves, i.e., the central three-center BBB bonding orbitals, are highly bonding in nature. This view is further supported by the fact that the NICS value computed for the points 1.0 Å above every triangular face is negative in sign.[20] Therefore, the LUMOs with the energy lower than α-β must now be the origin of kinetic instability and are possibly responsible for the failure to isolate the dianions with $n > 12$.

Kinetically Unstable $B_{18}H_{18}^{2-}$ Isomers. We now examine peculiar electronic features of $B_{18}H_{18}^{2-}$ in some detail. Its doubly negative charge does not maximize the degree of aromaticity. Adding two more electrons to $B_{18}H_{18}^{2-}$ (D_{3d}) increases the TRE. The resulting tetraanion has the maximum TRE/BH of 0.100 $|\beta|$. In this sense, $B_{18}H_{18}^{2-}$ (D_{3d}) is incompatible with the skeletal electron counting rule for *closo*-boranes. This dianion has a very low-lying LUMO so must be kinetically very unstable. As pointed out by Lipscomb et al.,[14] $B_{18}H_{18}^{2-}$ (D_{3d}) has the smallest HOMO–LUMO energy separation among the borane dianions studied. $B_{18}H_{18}^{2-}$ (D_{3d}) is likely to be one of the rare examples that are thermodynamically stable but kinetically very unstable. In this context, some boranes are presumed to adopt a fully deltahedral geometry only if they contain merely $2n$ framework electrons.[13,14]

Lipscomb proposed three more deltahedral isomers of the $B_{18}H_{18}^{2-}$ cluster.[12,14] The TRE/BH and related quantities for all the four $B_{18}H_{18}^{2-}$ isomers are summarized in Table 2. $B_{18}H_{18}^{2-}$ (D_3) and $B_{18}H_{18}^{2-}$ (D_{3h}) are more aromatic than $B_{18}H_{18}^{2-}$ (D_{3d}) but are still slightly less aromatic than $B_{17}H_{17}^{2-}$ (D_{5h}). In contrast, the isomer in O_h symmetry is antiaromatic with a negative TRE/BH value although it has completely filled sextuply degenerate HOMOs. It is interesting to see that deltahedral borane dianions are not always aromatic with a positive TRE/BH value. Such an antiaromatic isomer is again exceptional to the skeletal electron counting rule.

Concluding Remarks

The KT bonding model[9,10] proved to give a practical or qualitatively acceptable picture for explaining the electronic structure and three-dimensional aromaticity of deltahedral $B_nH_n^{2-}$ species with $n = 6$–24. The TRE/BH is highly correlative with the E_{PRDDO}/BH for most deltahedral borane dianions. Thus, we confirmed that aromaticity is an important factor for determining the relative thermodynamic stabilities of doubly negative deltahedral borane ions. The value of β may vary, depending

Table 2. The TREs and Related Quantities for Four Deltahedral $B_{18}H_{18}^{2-}$ Isomers

Structure[a)]	(EPRDDO/BH)/au[b)]	TRE/$\lvert\beta\rvert$	(TRE/BH)/$\lvert\beta\rvert$	(Energy of the HOMO-α)/β [c)]	(Energy of the LUMO-α)/β [d)]	HOMO-LUMO energy gap/$\lvert\beta\rvert$
18 (D_3; VIa)	25.256	1.757	0.0976	−0.104(2)	−0.944(2)	0.840
18 (D_{3h}; VIb)	25.253	1.881	0.1045	0.000(1)	−1.000(1)	1.000
18 (D_{3d}; VIc)	25.262	1.451	0.0806	−0.382(1)	−0.524(1)	0.142
18 (O_h; VId)	25.242	−0.159	−0.0088	−0.000(6)	−1.000(4)	1.000

a) Notation: *n* (symmetry, label in Refs. 12 and 14).

b) Ref. 14.

c) The number in parentheses represents the degeneracy of the HOMOs.

d) The number in parentheses represents the degeneracy of the LUMOs.

on the curvature of the cage,[8] so it is not easy to discuss the difference in the TREs/BH of very large and very small borane cages.

Schleyer et al. noted that borane dianions with n = 13–15 will adopt the same deltahedral geometry as predicted by Lipscomb et al.[11] Nevertheless, it seems that deltahedral structures become less favorable for larger dianions since the degree of three-dimensional aromaticity tends to decrease.[11] For the present purpose, however, it doesn't matter whether deltahedral isomers predicted by Lipscomb et al.[12,14] are really the lowest-energy ones or not. These hypothetical isomers proved to be very useful for testing the validity of the TRE concept and the KT bonding model.

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