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Notes

Aromatic Character of Deltahedral Borane Dianions Revisited

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Introduction

Possible three-dimensional aromaticity of *closo*-borane dianions, $B_nH_n^{2-}$, has long been the subject of many theoretical and experimental papers.[1−6] Interestingly, those with $n = 5-12$ have a deltahedral geometry and high kinetic stability.[1−6] The topological resonance energy (TRE), which represents the extra stabilization energy due to cyclic conjugation, can be used as an energetic criterion of aromaticity for $B_nH_n^{2-}$.[7,8] In 1978 we found that those with $n = 6-12$ have a large positive TRE, indicating that they are thermodynamically stable and aromatic.[9] The bonding model employed to describe the skeletal or framework electrons of deltahedral borane dianions was the one devised by Kettle and Tomlinson.[10,11]

Among the magnetic criteria of aromaticity is the nuclear independent chemical shift (NICS) proposed by Schleyer et al.,[12,13] which is defined as the negative of the absolute magnetic shielding computed at the geometric center of a ring or a cage. A negative NICS value indicates diatropicity (i.e., diamagnetism due to cyclic conjugation) or aromaticity. In 1998 they found that the deltahedral borane dianions with $n = 5-12$ have a large negative NICS value.[14−18] The lowest-energy isomers of the unknown *closo*-borane dianions with $n = 13-15$ were also predicted to be deltahedral in shape and proved to have a large negative NICS value.[15]

We have pointed out that the energetic and magnetic criteria of aromaticity must be closely related to each other since both are associated with the same origin of aromaticity.[19−21] Such relationships have indeed been reported for annulenes and other two-dimensional π-electronic systems.[22−26] Schleyer et al. likewise reported that there is a quantitative relationship of the NICS with the aromatic stabilization energy for a set of five-membered rings.[12] Therefore, it seems very instructive to see if there is a qualitative or quantitative relationship between the TRE and the NICS for a series of deltahedral borane dianions.

Theory

The Kettle-Tomlinson bonding model[10,11] is suited for describing the skeletal electronic systems of deltahedral borane dianions. First, a localized central three-center BBB bonding orbital is placed at every triangular face of a borane cage. The skeletal electronic system 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. This bonding model leads to the same pattern of molecular orbital (MO) energy levels as does the LCAO method.[10,11]

The TRE of a deltahedral borane dianion is given as a difference between the total binding energies of the skeletal electronic system and its polyene reference,[7−9] both of which can be calculated readily using the Kettle-Tomlinson bonding model.[10,11] In order to compare the degrees of aromaticity for different borane dianions, the TREs divided by the number of BH units (n) or the TREs/BH were used instead of the TREs themselves. The connectivities of boron atoms predicted by Schleyer et al. were adopted for the dianions with $n = 13-15$.[15]

Results and Discussion

TREs calculated for deltahedral borane dianions with $n = 6-15$ are listed in Table 1. All deltahedral borane dianions, including those with $n = 13-15$, have a positive TRE, indicating that they all are aromatic. The number of skeletal electrons in $B_nH_n^{2-}$ is always the one that attains the highest degree of aromaticity. In other words, $2n + 2$ skeletal electrons are needed to maximize the aromaticity of the deltahedral cage with n BH units. This is fully consistent with the well-known skeletal electron counting rule for cage compounds.[3,4] For example, the energy levels of $B_{12}H_{12}^{2-}$ and its polyene reference are presented in Table 2. The TRE of this ion is maximized when it has 26 skeletal electrons; this ion does indeed have 26 skeletal electrons.[1−4]

It is noteworthy that the highest occupied MOs (HOMOs) are nonbonding for $B_{12}H_{12}^{2-}$ and $B_{14}H_{14}^{2-}$ and antibonding for all other deltahedral borane dianions. This does not matter since

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Table 1. TREs and NICSs for the Deltahedral Borane Dianions $B_nH_n^{2-}$

n	TRE/ $\lvert\beta\rvert$	(TRE/BH)/ $\lvert\beta\rvert$	HOMO−LUMO gap[a]/$\lvert\beta\rvert$	NICS[b]/ ppm	LBLD[c]/ pm
6 (O_h)	0.844	0.1407	2.000 (3)	−34.26	0.0
7 (D_{5h})	0.938	0.1340	2.000 (2)	−27.52	17.2
8 (D_{2d})	0.798	0.0998	1.000 (1)	−24.22	29.1
9 (D_{3h})	0.813	0.0903	0.732 (1)	−27.38	27.5
10 (D_{4d})	1.145	0.1145	1.414 (2)	−33.47	13.8
11 (C_{2v})	1.000	0.0909	0.824 (1)	−32.47	35.6
12 (I_h)	1.763	0.1469	2.000 (4)	−35.82	0.0
13 (C_{2v})	1.349	0.1038	0.858 (1)	−30.93	37.6
14 (D_{6d})	1.807	0.1291	1.414 (2)	−32.25	18.4
15 (D_{3h})	1.688	0.1125	0.689 (1)	−31.59	26.6

[a] The number in parentheses represents the degeneracy of the HOMOs. [b] Taken from ref 15. [c] Largest bond length differences taken from ref 15.

Table 2. MO Energies and TREs for Icosahedral $B_{12}H_{12}$ Molecular Ions

MO	(MO energy − α)/β actual system	polyene reference	TRE[a]/$\lvert\beta\rvert$
1	3.000	2.706	0.590
2	2.236	2.507	0.048
3	2.236	2.251	0.018
4	2.236	1.985	0.520
5	1.000	1.713	−0.906
6	1.000	1.467	−1.839
7	1.000	1.199	−2.237
8	1.000	0.790	−1.817
9	1.000	0.458	−0.733
10	0.000	0.182	−1.096
11	0.000	−0.182	−0.733
12	0.000	−0.458	0.183
13	0.000	−0.790	1.763
14	−2.000	−1.199	0.161
15	−2.000	−1.467	−0.906
16	−2.000	−1.713	−1.480
17	−2.000	−1.985	−1.510
18	−2.236	−2.251	−1.480
19	−2.236	−2.507	−0.939
20	−2.236	−2.706	0.000

[a] The value corresponding to the *m*th MO represents the TRE for the system with 2*m* skeletal electrons.

the basis functions themselves, i.e., the central three-center BBB bonding orbitals, are highly bonding in nature. This interpretation is supported by the fact that the NICS value computed for the points 1.0 Å above every triangular face is negative in sign.[16] Each central three-center BBB bond is equivalent to the π-electronic system in the cyclopropenium ion, which is aromatic with two π electrons. All lowest unoccupied MOs (LUMOs) are necessarily antibonding.

As can be seen from Table 1, deltahedral borane dianions with $n = 6$, 10, 12, and 14 are more aromatic than their respective neighbors. Their HOMOs are all multiply degenerate. In general, π-electronic systems with degenerate HOMOs are highly aromatic when they are fully occupied.[7,27] It seems likely that borane dianions are not exceptional. Degenerate HOMOs in deltahedral borane dianions with $n = 6$, 10, 12, and 14 are completely occupied, which makes the dianions highly aromatic. $B_{12}H_{12}^{2-}$ with quadruply degenerate HOMOs is the most aromatic dianion with the largest TRE/BH. This dianion is also presumed to be kinetically very stable since it has the largest HOMO−LUMO energy separation.

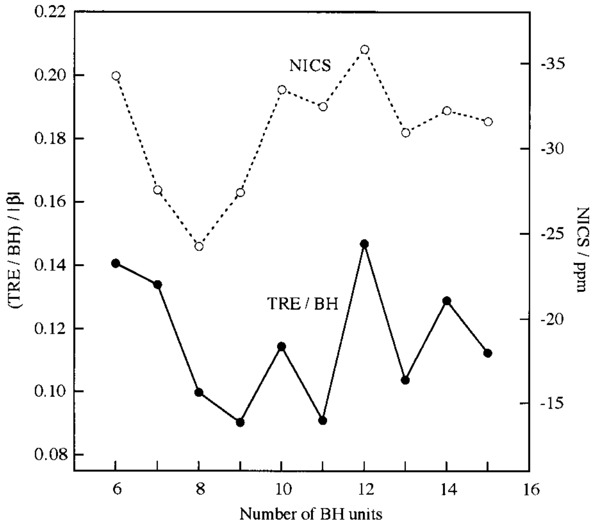

Figure 1. Plots of the TRE/BH and the NICS computed at the center of the borane cage against the number of BH units for the deltahedral borane dianions $B_nH_n^{2-}$ ($n = 6-15$). The NICS values were taken from ref 15.

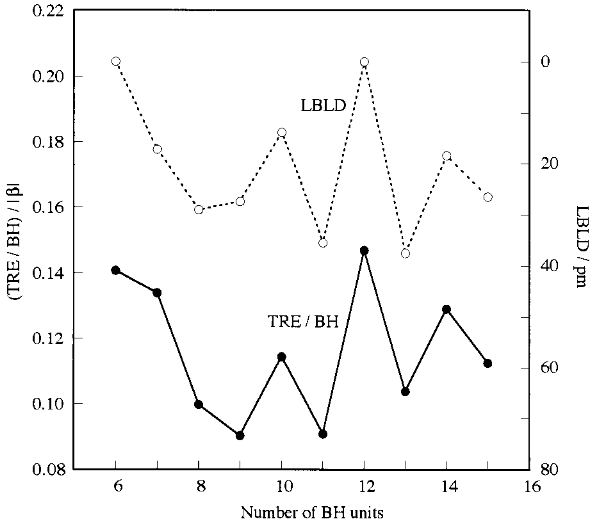

Figure 2. Plots of the TRE/BH and the largest bond length difference (LBLD) against the number of BH units for the deltahedral borane dianions $B_nH_n^{2-}$ ($n = 6-15$). The LBLDs were taken from ref 15.

The NICS values computed at GIAO-HF/6-31+G*//B3LYP/6-31G* at the cage centers[14−16] are added in Table 1. Those with $n = 6$, 10, 12, and 14 have a NICS value less than −32 ppm and are predicted to be more diatropic than their respective neighbors. Figure 1 shows that the NICS values are highly correlative with the TREs/BH. The two curves track each other closely. Thus, the trend in NICS values is very similar to that in the TRE/BH values. This clearly shows that for the 10 borane dianions studied the energetic criterion of aromaticity is closely related to the magnetic one, witnessing that both TRE and NICS arise from the same origin, i.e., cyclic conjugation of skeletal electrons.

It might also be interesting to see if there is a relationship between the TREs/BH and some geometric aspect of the borane dianions. Schleyer et al. found that the trend in the NICS values is similar to that in the largest bond length differences (LBLDs).[15] Here, the LBLD represents the difference between the longest and shortest BB bond lengths in each boron cage. We compared the patterns of the TRE/BH and the largest bond length difference in Figure 2. Both were found to be remarkably similar, which shows that the LBLD reflects the extent of delocalization, i.e., the degree of aromaticity in the cage.

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Concluding Remarks

As has been seen, the TRE/BH was found to be highly correlative with the NICS value for deltahedral borane dianions. Thus, the qualitative relationship between energetic and magnetic criteria of aromaticity found earlier for monocyclic planar π-electronic systems[22−24] can be extend to deltahedral borane dianions. In this sense, the present work constitutes one of the most successful attempts to investigate the theoretical basis for three-dimensional aromaticity. Schleyer et al. noted that our previous discussion of the aromaticity of kekulene[25] and oxocarbon dianions[26] based on the TREs is consonant with the magnitudes of the NICS values.[28,29]

Unfortunately, the Kettle−Tomlinson bonding model[10,11] is not applicable to borane dianions with $n = 5$ or $n > 15$ as they are no longer deltahedral in geometry.[15] This model cannot reproduce the electronic structure of such capped deltahedrons well.[10] The value of β must vary depending on the curvature of the cage,[10] so it must be difficult to discuss the difference in the TREs/BH of very large and very small borane cages.

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