B_{13}^+ Is Highly Aromatic

Jun-ichi Aihara

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

Received: January 17, 2001; In Final Form: April 2, 2001

As postulated by Fowler and Ugalde [*J. Phys. Chem. A* **2000**, *104*, 397], the lowest-energy B_{13}^+ isomer proved to be highly aromatic. The topological resonance energy of this cationic boron cluster is positive in sign and very large in magnitude. This constitutes the definitive reason B_{13}^+ is kinetically stable and planar or quasiplanar in geometry. The electron-deficient and multivalent character of boron is responsible for the high aromaticity of this cluster. In addition, its minimum bond resonance energy is not too small.

Introduction

In 1988, Anderson and co-workers observed the mass distribution of B_n^+ in the range $n = 1-20$ generated by laser ablation of isotopically pure boron.[1] Cluster dissociation energies and fragmentation patterns revealed that B_{13}^+ is kinetically very stable for a boron cluster.[1] By kinetic stability, we mean reluctance to undergo chemical reaction or decomposition. For example, B_{13}^+ is much less reactive toward O_2 than any other boron cluster.[2] In reacting with D_2O, although no barrier to the reaction exists, the reactivity of B_{13}^+ was 2 orders of magnitude lower than that of similarly sized boron clusters.[3] The anomalous stability of B_{13}^+ has since been the subject of many theoretical studies.

Anderson and co-workers originally postulated the filled icosahedral structure for the B_{13}^+ cation.[1] Many molecular orbital (MO) studies followed it to determine the nuclear arrangements of B_{13}^+ and related species. Boustani predicted a quasiplanar, oval geometry for the B_{13} neutral cluster and its cation.[4−7] Ricca and Bauschlicher reported a rounder, planar geometry for the B_{13}^+ cationic cluster.[8,9] More recently, Gu et al.[10] and Fowler and Ugalde,[11] reexamining the MO calculations so far reported, confirmed that for B_{13}^+ the planar or quasiplanar nuclear arrangements are consistently more stable than any three-dimensional structure.

One should note that MO calculations alone do not give any insight into why the planar or quasiplanar B_{13}^+ cluster is less reactive than the other boron clusters.[8,10,11] Fowler and Ugalde pointed out that planar and quasiplanar structures benefit from π delocalization, suggesting that the stability of the B_{13}^+ cluster might possibly be attributed to its aromaticity.[11] However, they could not present any definitive evidence for it. We show below that this problem can be solved by applying our graph theory of aromaticity[12−14] to the B_{13}^+ cationic cluster or by evaluating its topological resonance energy (TRE).

Theory

Aromatic character of planar and quasiplanar B_{13} isomers and their molecular ions was estimated from their TREs. The TRE is defined within the framework of simple Hückel theory as a difference between the total π-binding energies of a given molecule and its polyene reference.[12−16] It represents extra thermodynamic stabilization because of cyclic conjugation. A matching (or reference) polynomial, i.e., a characteristic polynomial for the polyene reference, must beforehand be constructed for each structure to obtain the total π-binding energy of the polyene reference.

In general, a molecule with a large positive TRE is kinetically stable.[12−16] However, there possibly are exceptions to this trend. Therefore, the kinetic stability of the B_{13}^+ π-bonding systems were analyzed using our bond resonance energy (BRE) model.[15−20] The BRE represents the contribution of a given π bond to the TRE of the molecule. The minimum BRE (min. BRE) signifies the smallest BRE in the molecule. We have presumed that if the min. BRE is less than $-0.100\ |\beta|$ the molecule will be kinetically very unstable with chemically very reactive sites.[15−20] This proved to be the case for many planar polycyclic conjugated hydrocarbons and fullerenes. Here, β represents a resonance integral defined in simple Hückel theory.

Results and Discussion

We consider four of the planar or quasiplanar structures so far proposed for B_{13}, B_{13}^+, and B_{13}^-. Two of them originally proposed by Ricca and Bauschlicher[8,9] and Boustani[4−7] are referred to as Ricca I and Boustani I, respectively. Fowler and Ugalde found that among the low-energy isomers of B_{13}^+ and B_{13}^- are two more planar or quasiplanar ones.[10,11] These two are similar to but slightly different from Ricca I and Boustani I, which are referred to as Ricca II and Boustani II, respectively. All these structures are presented in Figure 1.

Matching polynomials for the four geometric structures of B_{13}^+ are given below:

(a) Ricca I:

$$R(X) = X^{13} - 25X^{11} + 219X^9 - 840X^7 + 1429X^5 - 957X^3 + 170X$$

(b) Ricca II:

$$R(X) = X^{13} - 24X^{11} + 203X^9 - 757X^7 + 1258X^5 - 826X^3 + 145X$$

(c) Boustani I:

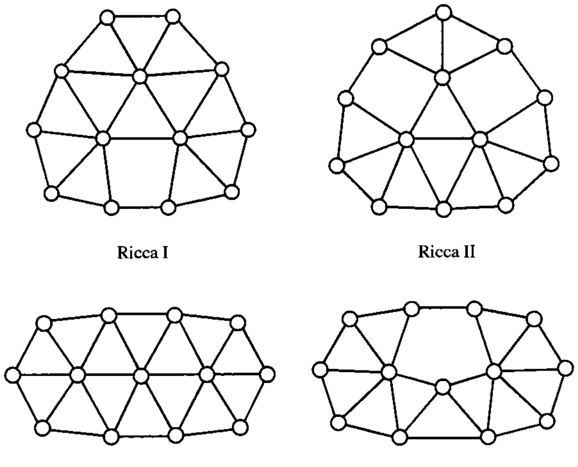
$$R(X) = X^{13} - 26X^{11} + 238X^9 - 950X^7 + 1674X^5 - 1158X^3 + 207X$$

(d) Boustani II:

$$R(X) = X^{13} - 24X^{11} + 204X^9 - 756X^7 + 1244X^5 - 808X^3 + 137X$$

Energies of the π-type molecular orbitals (π-MOs) calculated for the four structures of B_{13}^+ and their polyene references are

10.1021/jp010190f CCC: $20.00



Ricca I

Ricca II

Boustani I

Boustani II

Figure 1. π-Bonding systems of four B_{13} isomers.

TABLE 1: Energies of π-MOs and TREs for the Ricca I Molecular Ions

	(energy − α_B)/β_{BB}		
π-MO	actual system	polyene reference	TRE[a]/$\lvert\beta_{BB}\rvert$
1	4.255	3.157	2.198
2	2.615	2.666	2.096
3	2.322	1.891	2.959
4	0.744	1.443	1.562
5	0.646	1.009	0.836
6	0.000	0.505	−0.175
7	−0.576	0.000	−1.327
8	−0.808	−0.505	−1.933
9	−1.283	−1.009	−2.482
10	−1.514	−1.443	−2.623
11	−2.000	−1.891	−2.842
12	−2.000	−2.666	−1.511
13	−2.401	−3.157	0.000

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

TABLE 2: Energies of π-MOs and TREs for the Ricca II Molecular Ions

	(energy-α_B)/β_{BB}		
π-MO	actual system	polyene reference	TRE[a]/$\lvert\beta_{BB}\rvert$
1	4.070	3.251	1.638
2	2.438	2.466	1.582
3	2.403	1.992	2.404
4	0.794	1.452	1.087
5	0.702	1.000	0.491
6	0.000	0.519	−0.548
7	−0.579	0.000	−1.707
8	−0.606	−0.519	−1.880
9	−1.331	−1.000	−2.542
10	−1.398	−1.452	−2.435
11	−1.967	−1.992	−2.384
12	−2.100	−2.466	−1.652
13	−2.425	−3.251	0.000

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

TABLE 3: Energies of π-MOs and TREs for the Boustani I Molecular Ions

	(energy-α_B)/β_{BB}		
π-MO	actual system	polyene reference	TRE[a]/$\lvert\beta_{BB}\rvert$
1	4.335	3.351	2.009
2	3.077	2.676	2.810
3	1.618	2.022	2.001
4	1.369	1.473	1.793
5	0.618	1.041	0.946
6	−0.280	0.517	−0.649
7	−0.618	0.000	−1.885
8	−1.000	−0.517	−2.850
9	−1.527	−1.041	−3.822
10	−1.545	−1.473	−3.964
11	−1.618	−2.022	−3.155
12	−2.197	−2.676	−2.198
13	−2.252	−3.351	0.000

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

TABLE 4: Energies of π-MOs and TREs for the Boustani II Molecular Ions

	(energy-α_B)/β_{BB}		
π-MO	actual system	polyene reference	TRE[a]/$\lvert\beta_{BB}\rvert$
1	3.963	3.157	1.612
2	3.077	2.666	2.434
3	1.932	1.891	2.516
4	0.880	1.443	1.391
5	0.618	1.009	0.609
6	−0.204	0.505	−0.810
7	−0.280	0.000	−1.371
8	−0.862	−0.505	−2.084
9	−1.545	−1.009	−3.156
10	−1.600	−1.443	−3.469
11	−1.618	−1.891	−2.924
12	−2.109	−2.666	−1.810
13	−2.252	−3.157	0.000

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

TABLE 5: TREs and min. BREs for Four B_{13}^+ Isomers

isomer	TRE/$\lvert\beta_{BB}\rvert$	min. BRE/$\lvert\beta_{BB}\rvert$
Ricca I[a]	2.959	−0.0478
Ricca II	2.404	−0.0270
Boustani I	2.001	−0.1377
Boustani II[b]	2.516	0.0890

[a] The lowest-energy isomer. [b] The second-lowest-energy isomer.

listed in Tables1−4. All of the TREs are given in units of $\lvert\beta_{BB}\rvert$, where β_{BB} is the resonance integral between two bonded boron $2p_z$ orbitals. Fowler and Ugalde showed that both of the Boustani and Ricca cationic clusters have six π electrons.[11] The TREs of Ricca I, Ricca II, and Boustani II are maximized when they have six π electrons. Boustani I is slightly different from them in that it has the largest TRE when it has four π electrons. In any case, all structures have large positive TREs when they bear one formal positive charge. The TREs for the four B_{13}^+ cationic clusters are summarized in Table 5.

According to Gu et al.[10] and Fowler and Ugalde,[11] Ricca I represents the π-electronic system of the lowest-energy B_{13}^+ cationic cluster. Boustani II, which is the second-lowest-energy isomer, lies 27.6 kcal/mol above Ricca I.[11] The lowest-energy species, Ricca I, was found to be the most highly aromatic one with the largest TRE (2.959 $\lvert\beta_{BB}\rvert$). The other three isomers likewise have a TRE $>$ 2.000 $\lvert\beta_{BB}\rvert$. For reference, the TREs of the phenalenium ($C_{13}H_9^+$) and phenalenide ($C_{13}H_9^-$) ions, anthracene ($C_{14}H_{10}$), and phenanthrene ($C_{14}H_{10}$) are 0.410, 0.410, 0.475, and 0.546 $\lvert\beta_{CC}\rvert$, respectively,[12−14] where β_{CC} is the resonance integral between two bonded carbon $2p_z$ orbitals. It seems that B_{13}^+ is much more aromatic than polycyclic aromatic hydrocarbons of a similar size.

Van-Catledge evaluated Hückel parameters consistently for many heteroatoms.[21] The Coulomb and resonance integrals he determined for boron-containing π-bonding systems are

$$\alpha_B = \alpha_C - 0.45\,\beta_{CC}$$

$$\beta_{BB} = 0.87\,\beta_{CC}$$

Here, α_B and α_C are the Coulomb integrals for boron and carbon $2p_z$ orbitals, respectively. Thus, β_{BB} is 0.87 times as large as β_{CC}. Even if we take this into account, we can still say that the TREs of four B_{13}^+ isomers are very large.

Unusually large TREs of the planar or quasiplanar B_{13}^+ clusters might be explained by remembering that boron is an electron-deficient, multivalent atom. Note that there are only six π electrons in B_{13}^+.[11] Each boron atom in B_{13}^+ is bonded to 3−6 adjacent boron atoms, which markedly lowers the energy of the lowest-lying π-MO. As can be seen from Figure 2, the lowest π-MO in the Ricca I π-bonding system is much lower than the corresponding one in the polyene reference. Such a trend in the lowest π-MO is common to all of the four planar or quasiplanar structures studied. This is the main origin of aromaticity.

A complete graph of degree 13, K_{13}, may be considered as a limiting π-bonding system consisting of thirteen multivalent boron atoms.[22,23] In K_{13}, each boron atom is hypothetically bonded to all other atoms, forming a single π-bonding system. As listed in Table 6, K_{13} has only one bonding π-MO. This lowest π-MO has an energy of $\alpha_B + 12.000\,\beta_{BB}$, which is by far lower than the corresponding one with an energy of $\alpha_B + 5.800\,\beta_{BB}$ in the polyene reference. All complete graphs have the largest TRE when they contain only two π electrons.[23]

The B_{13} π-bonding systems need more than two π electrons to attain the highest degree of aromaticity. In this sense, they may be regarded as "incomplete" complete graphs of degree13. The B_{13} π-bonding system has the largest TRE when it bears four or six π electrons. The most realistic Ricca I cation has six π electrons.[11] If the number of π electrons were close to that of conjugated boron atoms, the entire π-bonding system would be antiaromatic with a negative TRE. This is in marked contrast to commonplace polycyclic aromatic hydrocarbons. Their degrees of aromaticity are maximized when the number of π electrons is equal to that of conjugated carbon atoms.

As already stated, the min. BRE has been a useful index for predicting the kinetic stability of a π-bonding system. Those for four B_{13}^+ structures are added in Table 5. Three structures other than Boustani I have a min. BRE > $-0.100\,|\beta_{BB}|$. It then follows that the π-bonding system of the Ricca I cation with the highest thermodynamic stability is kinetically fairly stable. The π-bonding system of the second-lowest-energy isomer, Boustani II, is also presumed to be kinetically stable. This is consistent with the experimental fact that B_{13}^+ is not only thermodynamically but also kinetically stable.[1−3] Boustani I must be very reactive because the min. BRE is less than $-0.100\,|\beta_{BB}|$.

The aromaticity of B_{13}^- can be considered in a similar way. It is interesting to see that throughout the various charge states planar or quasiplanar structures are preferred for B_{13}.[4−11] All of the four structures in Figure 1 have large positive TREs even if they bear one formal negative charge or eight π electrons. The TREs for the four B_{13}^- anionic clusters are summarized in Table 7. The Boustani I anion is the lowest-energy isomer of B_{13}^- with the largest TRE ($1.793\,|\beta_{BB}|$).[11] Next comes the Ricca II anion, which lies 12.6 kcal/mol above the lowest-energy isomer. For all B_{13}^- isomers, the anion has a less TRE than the cation because the anion has a bit too many π electrons.

As seen from Table 7, the min. BRE of the Boustani I anion is very small but positive in sign, indicating that all π bonds contributes to aromaticity. By contrast, all of the other three isomers with one formal negative charge are predicted to be extremely reactive with a min. BRE less than $-0.100\,|\beta_{BB}|$. Thus, the Boustani I anion alone appears to be not only thermodynamically but also kinetically stable. The degrees of aromaticity and kinetic stability drastically decrease as the B_{13}^- cluster acquires more π electrons.

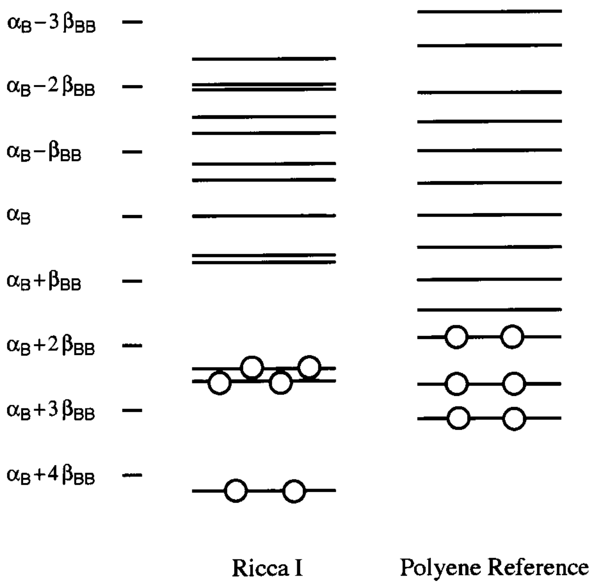


Figure 2. Energies of π-MOs in Ricca I and its polyene reference, both with six π electrons.

TABLE 6: Energies of π-MOs and TREs for the Complete Graph of Degree 13, K_{13}

	(energy − α_B) /β_{BB}		
π-MO	actual system	polyene reference	TRE[a]/$\|\beta_{BB}\|$
1	12.000	5.800	12.400
2	−1.000	4.591	1.217
3	−1.000	3.563	−7.910
4	−1.000	2.621	−15.151
5	−1.000	1.725	−20.602
6	−1.000	0.857	−24.316
7	−1.000	0.000	−26.316
8	−1.000	−0.857	−26.602
9	−1.000	−1.725	−25.151
10	−1.000	−2.621	−21.910
11	−1.000	−3.563	−16.783
12	−1.000	−4.591	−9.600
13	−1.000	−5.800	0.000

[a] The value corresponding to the mth π-MO represents the TRE for the system with $2m$ π electrons.

TABLE 7: TREs and min. BREs for Four B_{13}^- Isomers

isomer	TRE/$\|\beta_{BB}\|$	min. BRE/$\|\beta_{BB}\|$
Ricca I	1.562	−0.5100
Ricca II[b]	1.087	−0.4930
Boustani I[a]	1.793	0.0008
Boustani II	1.391	−0.2251

[a] The lowest-energy isomer. [b] The second-lowest-energy isomer.

Concluding Remarks

The present study clarified that the lowest-energy B_{13}^+ isomer can attain the highest degree of aromaticity through π delocalization. It contains the optimum number of π electrons for this purpose. Such aromatic character of the cluster is nothing other than what Fowler and Ugalde expected for B_{13}^+.[11] In addition, the π-bonding system of the lowest-energy B_{13}^+ isomer is predicted to be kinetically stable. Essentially the same thing can be predicted for the lowest-energy B_{13}^- isomer.

We have focused on the aromaticity of 13-boron clusters because their structural and electronic structures have been studied extensively.[4−11] The number of π electrons was recently reported only for them.[11] Many other B_n^+ clusters must likewise be more or less aromatic as far as they have planar or quasiplanar nuclear arrangements with a fairly small number of π electrons. For example, anther stable cationic cluster, B_5^+, has been predicted to be pentagonal in geometry.[4,8] This ion must have a TRE of 0.196 $|\beta_{BB}|$ with two π electrons. Otherwise, it would be antiaromatic with high kinetic instability. All such boron clusters will constitute a group of novel aromatic molecules.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (A) “Creation of Delocalized Systems” (No. 10146101) from the Ministry of Education, Science, Sports, and Culture, Japan. Computation was performed at the Information Processing Center, Shizuoka University.

References and Notes

(1) Hanley, L.; Whitten, J. L.; Anderson, S. L. *J. Phys. Chem*. **1988**, *92*, 5803.
(2) Hanley, L.; Anderson, S. L. *J. Chem. Phys*. **1988**, *89*, 2848.
(3) Hintz, P. A.; Sowa, M. B.; Ruatta, S. A.; Anderson, S. L. *J. Chem. Phys*. **1990**, *92*, 292.
(4) Boustani, I. *Int. J. Quantum Chem*. **1994**, *52*, 1081.
(5) Boustani, I. *Chem. Phys. Lett*. **1995**, *233*, 273.
(6) Boustani, I. *Surf. Sci*. **1997**, *370*, 355.
(7) Boustani, I. *Phys. Rev. B* **1997**, *55*, 16426.
(8) Ricca, A.; Bauschlicher, C. W., Jr. *Chem. Phys*. **1996**, *208*, 233.
(9) Ricca, A.; Bauschlicher, C. W., Jr. *J. Chem. Phys*. **1997**, *106*, 2317.
(10) Gu, F. L.; Yang, X.; Tang, A.-C.; Jiao, H.; Schleyer, P. v. R. *J. Comput. Chem*. **1998**, *19*, 203.
(11) Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **2000**, *104*, 397.
(12) Aihara, J. *J. Am. Chem. Soc*. 1976, **98**, 2750.
(13) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc*. **1977**, *99*, 1692.
(14) Aihara, J. *J. Am. Chem. Soc*. **1977**, *99*, 2048.
(15) Aihara, J. *Pure Appl. Chem*. **1982**, *54*, 1115.
(16) Aihara, J. *J. Mol. Struct. (THEOCHEM)* **1994**, *311*, 1.
(17) Aihara, J. *J. Am. Chem. Soc*. **1995**, *117*, 4130.
(18) Aihara, J. *J. Phys. Chem*. **1995**, *99*, 12739.
(19) Aihara, J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2185.
(20) Aihara, J. *J. Chem. Soc., Faraday Trans*. **1998**, *94*, 3537.
(21) Aihara, J. *Bull. Chem. Soc. Jpn*. **1999**, *72*, 7.
(22) Aihara, J. *Phys. Chem. Chem. Phys*. **2000**, *2*, 3121.
(23) Van-Catledge, F. A. *J. Org. Chem*. **1980**, *45*, 4801.
(24) Gutman, I.; Hosoya, H. *Theor. Chim. Acta* **1978**, *48*, 279.
(25) Aihara, J. *Bull. Chem. Soc. Jpn*. **1979**, *52*, 2202.