Relative Stabilities of 2n Framework Electron Clusters. Perhalogenated Neutral *closo*-Boranes

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Synopsis. As in the case of the *closo*-borane dianions, relative stabilities of the title compounds can be elucidated by means of the graph theory of aromaticity.

The perhalogenated neutral *closo*-boranes are of special interest because so little is known about their bonding character.[1,2] In many cluster compounds the geometric shape of the framework is determined by the number of electrons delocalized within the framework molecular orbitals.[3,4] Polyhedral species with $(2n+2)$ framework electrons usually have deltahedral geometries while those with only 2n framework electrons are often found to be capped deltahedra.[3,4] The perhalogenated *closo*-boranes of the general formula B_nX_n (X=Cl, Br), however, appear to be quite a different class of molecules which do not adopt the structures predicted by the framework electron counting rules.[1,2] Each of these boranes has only $2n$ framework electrons, but the structures observed for them are mostly the ones associated with the frameworks containing two additional electrons.[1,2,4,5]

We have been developing the graph theory of aromaticity.[6] I previously applied it to the *closo*-borane dianions,[7] and correctly predicted high stabilities of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$. Therefore, we can fully expect that the same theory might be useful for estimating stabilities of the neutral *closo*-boranes, and that the results might give an important clue to predicting stabilities of the perhalogenated derivatives. In order for this to be seen, the theory was applied to nine neutral *closo*-boranes. All the frameworks were assumed to be deltahedral in shape.[5] The Kettle-Tomlinson bonding model[8] was adopted to describe the framework molecular orbitals. This model uses three-center BBB bonding orbitals, localized at the individual faces of deltahedral borane, as basis functions for the molecular orbital calculation. Resonance energies thus calculated for the neutral *closo*-boranes, *i.e.*, the stabilization energies due to aromaticity, are listed in Table 1. Reference polynomials needed to evaluate the resonance energies can easily be obtained by the use of the computer program reported by Mohar and Trinajstić.[11] The quntity 'resonance energy per face (REPF)' was defined as the resonance energy divided by the number of faces of the deltahedral framework.[7] This can be regarded as a resonance energy normalized with respect to the size of the framework. The REPF values are also listed in Table 1. All the energies are given in units of β or the absolute value of the resonance integral between three-center BBB bonding orbitals which correspond to polyhedron faces with an edge in common.

First, the resonance energies of all B_nH_n species are found to be much smaller than the resonance energy of any *closo*-borane dianion. This implies that the neutral *closo*-boranes are not highly aromatic, and tend to undergo reductions to the dianions. These species should be much less stable. Incidentally none has been observed to date.

Table 1. Resonance energies of neutral *closo*-boranes

Species	$RE^{a)}/\beta$	$REPF^{b)}/\beta$
B_4H_4	0.0000	0.0000
B_5H_5	−0.9806	−0.1634
B_6H_6	−1.0196	−0.1274
B_7H_7	−0.9125	−0.0913
B_8H_8	0.1523	0.0127
B_9H_9	0.4596	0.0328
$B_{10}H_{10}$	0.0723	0.0045
$B_{11}H_{11}$	0.2517	0.0140
$B_{12}H_{12}$	0.1829	0.0091

a) Resonance energy. b) Resonance energy per face.

In sharp contrast, perhalogenated derivatives of these neutral boranes, B_4Cl_4, B_8Cl_8, B_9Cl_9, and B_9Br_9, have been prepared and isolated.[12,13] Massey's group confirmed the formation of the compounds B_nCl_n (n=8—12) in the mass spectra.[13,14] Kutz and Morrison recently prepared B_7Br_7, B_8Br_8, and $B_{10}Br_{10}$ by the thermal decomposition of B_2Br_4.[1] Although these compounds lack the number $(2n+2)$ of framework electrons, they are considered to be deltahedral in shape.[1,2,5] They are not air stable, but thermally stable. The most stable of the compounds, B_9Br_9, survives temperatures of 300 °C for days and 200 °C for weeks.[1] One of the most distinct features of the perhalogenated borane series is that the nine-atom cluster is much more stable than the ten-atom cluster,[1,2,13,14] which is the opposite of the results reported for carboranes and *closo*-borane dianions.[15] The existence and isolation of the neutral B_nX_n species have been postulated as owing to extensive halogen back-donation into the polyhedra.[1,2,4] This explanation may be supported by the limited structural data of some compounds,[2] but it cannot justify the highest stability of B_9X_9. The details of the back-bonding are as yet unknown.

The present REPF values may be only approximations for the perhalogenated species since they do not take the substituents into account. It is, however, noteworthy that these values are quite consistent with the chemistry of perhalogenated *closo*-boranes. The most familiar species B_nCl_n (n=8—12)[13,14] are all derivatives of weakly aromatic neutral *closo*-boranes. The REPF value of B_9H_9 is larger than that of any other *closo*-borane. This compound alone may be classified as aromatic in comparison with the dianions.[7] In harmony with this, B_9X_9 is the most stable perhalogenated species and naturally much more stable than $B_{10}X_{10}$. B_5H_5 and B_6H_6 are predicted to be

the most antiaromatic *closo*-boranes with the largest negative REPF values. Their halogenated derivatives have been neither prepared nor observed in the mass spectra. As mentioned above, B_4Cl_4 and B_7Br_7 have also been isolated.[1,12] B_7Br_7 is the only antiaromatic species so far prepared and identified.[1] $B_{11}H_{11}$ and $B_{12}H_{12}$ are predicted to be as stable as B_8H_8 and $B_{10}H_{10}$. Although $B_{11}X_{11}$ and $B_{12}X_{12}$ have not been isolated yet, the formation of these species has often been observed in the mass spectra.[13,14] These will be isolated in the near future.

The present comparative study showed that although the effect on cluster stabilities of the back bonding between the boron cluster and the halogen substituents may not be negligible, the relative stabilities of perhalogenated *closo*-boranes are primarily determined by the aromatic character of the clusters. This implies that the halogen substituents uniformly modify the Coulomb and resonance integrals in the cluster. Furthermore, bulky halogen substituents and large B–X bond energies possibly enhance the kinetic stability of the B_nX_n series. These all are quite likely to constitute the reason why the B_nX_n species are more stable than the B_nH_n species. Finally, it should be stressed that by means of our graph theory of aromaticity[6,7] stabilities of the neutral *closo*-boranes and their dianions can be explained consistently.

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8) The electronic structure of boranes has in general been rationalized in terms of central three-center BBB bonds,[9] in each of which all three boron atoms are pairwise neighbors and topologically equivalent. Kettle and Tomlinson demonstrated that the localized three-center BBB bonds may be used as basis functions for molecular orbital calculations on *closo*-boranes.[10] They located a localized three-center BBB bonding orbital at every face of a deltahedral borane, and took the individual such orbitals to be non-orthogonal to each other. The framework electrons can then be treated in a Hückel manner, each localized three-center orbital being assigned a Coulomb integral α and all resonance integrals being set equal to zero, except those between orbitals which correspond to polyhedron faces with an edge in common, which are given the value β. This bonding model leads to a delocalized molecular orbital energy level scheme similar to those obtained from more elaborate molecular orbital calculations.[10]

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