in the Pt(bpy)(en)–AMP system was calculated to be 2.95 ± 0.10 ($I$ varies) and 2.19 ± 0.08 ($I$ = 0.1 M $NaClO_4$) at 25 °C from the Benesi–Hildebrand plots (Figure 4). These values are significantly higher than the values for self-stacking of AMP (0.3)[18] and the bpy–AMP stacking (1.41).[19] The $\Delta G$ value for the Pt(bpy)(en)–AMP stacking is calculated to be $-16.8$ kJ mol$^{-1}$ ($I$ varies), which is in contrast with the small value of $-6$ kJ mol$^{-1}$ for the stacking between the benzene rings of phenylalanine.[20] Since the CD spectral magnitude decreases with the increase of the ionic strength (Figure 1), the observed stability difference due to the ionic strength may be indicative of the contribution of the Pt(II)···phosphate interaction.

In conclusion, the Pt(II) complex–nucleotide bonding involves both stacking and the electrostatic interaction, and the latter serves to orient the ribose group near the Pt(II) center. Further studies on the modes and stabilities of the interactions are in progress.

**Acknowledgment.** We thank Dr. Yoshitaka Itatani and Kazuo Toyoda of Kanazawa University for measurements of the $^1H$ NMR spectra and Masahiro Taguchi for assistance with the experiments. Thanks are also due to Dr. Yoshihiro Kuroda of Kyoto University for measurements and discussions of the $^{31}P$ NMR spectra. Financial support from the Ministry of Education, Science, and Culture, Japan, is gratefully acknowledged.

**Registry No.** $Pt(bpy)(en)^{2+}$, 24972-61-0; AMP, 61-19-8; GMP, 58-61-7; adenosine, 58-61-7; CMP, 63-37-6; UMP, 58-97-9.

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# Articles

Contribution from the Departament de Quimica Inorgânica, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain, and Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

## Rules for Predicting the $^{11}B$ NMR Spectra of *closo*-Boranes and *closo*-Heteroboranes

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*Received December 3, 1985*

The $^{11}B$ NMR pattern of *closo*-boranes and *closo*-heteroboranes can be predicted by utilizing five parameters, which we term antipodal, rhomboidal, butterfly, neighbor, and symmetrical neighbor effects. The application of the rules depends on the symmetry of the parent $B_nH_n^{2-}$ borane, and the magnitudes of the various shifts are functions of the coordination number and framework electron contribution of the atoms that cause them. In substituted B–R *closo*-boranes and -heteroboranes, the magnitude of the effects depends primarily on the electronegativity of the R substituent.

### Introduction

Progress in the general area of boron chemistry has depended to a very large extent on information derived from $^{11}B$ NMR spectroscopy. Not only is it possible to determine if new species have been formed by comparison of observed chemical shifts with data in the literature[1,2] but the boron NMR pattern displayed reveals, in many cases, important information about the structure. However, distinctions between possible structures on the basis of NMR results so far have depended to a very great extent on symmetry considerations.

Inasmuch as boron chemical shifts are dominated by the contribution of the paramagnetic term ($\sigma_p$),[3,4] assignment of absorptions in the $^{11}B$ NMR spectrum to specific borons in the molecule is a difficult process. Theoretical predictions require extensive calculations involving a number of approximations. Chemical assignment by deuteration, which to date has been the most reliable method, is time consuming and not always straightforward. Recently, the use of two dimensional (2D) $^{11}B$–$^{11}B$ (COSY) NMR has been shown to be helpful in favorable cases;[5] still, the chemical shift position of some groups of atoms have to be known a priori. Consequently, the availability of rules, even though they may be strictly empirical, that can relate the position of a peak in the $^{11}B$ NMR spectrum to a particular boron in a cluster would be very valuable. Some regularities in NMR spectra that depend on the antipodal effect,[6] the coordination number,[7] and the position of the hydrogen bridges have already been noted.[8]

The paramagnetic term ($\sigma_p$) of the nucleus of interest depends on the molecular orbitals, which in turn are dependent on the symmetry of the molecule. This leads us to believe that by symmetry considerations alone, it should be possible to predict for a specific cluster not only the $^{11}B$ NMR pattern but also the order of its components.[9] In general, the geometry of a closo compound can be predicted once the number of atoms in the cluster is known;[10] however, this is not necessarily true for nido, arachno, and hypho species since they have "extra" hydrogens to be located.[8] For that reason, closo species constitute the most favorable of the four types of clusters that could be used to demonstrate our approach. In this paper, we present some effects we have observed in the closo clusters, which we believe will be valuable in assigning

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[†] Universitat Autònoma de Barcelona.

[‡] The University of Michigan. Deceased, May 11, 1981.

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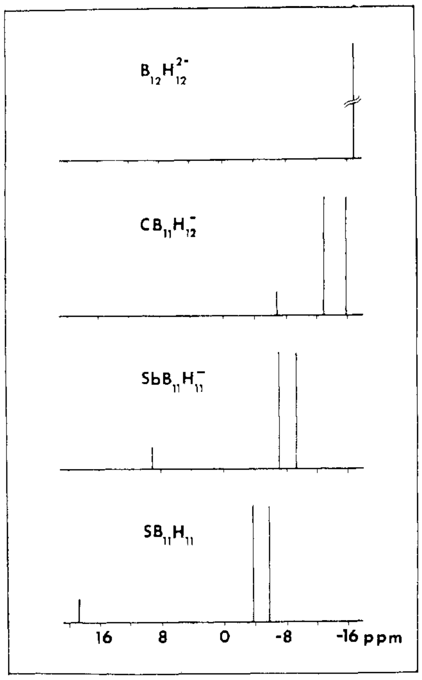

**Figure 1.** Schematic representation of the $^{11}B$ NMR spectra of $B_{12}H_{12}^{2-}$, $CB_{11}H_{12}^{-}$, $SbB_{11}H_{11}^{-}$, and $SB_{11}H_{11}$, showing that all $^{11}B$ NMR absorptions of the heteronuclear clusters are at lower field than the absorption of the parent borane $B_{12}H_{12}^{2-}$.

$^{11}B$ NMR absorptions to specific boron atoms in the molecule. In the first section, only boranes and heteroboranes with B–H bonds are considered. In the second, molecules with B–R groups are considered.

## Closo Molecules: Boranes and Heteroboranes. Rules and Effects

To begin with, we have observed interesting regularities in the $^{11}B$ NMR spectra of *n*-atom polyhedral boranes and heteroboranes with a framework electron count of $2n + 2$ (closo molecules). These suggested to us that the boron spectrum of a closo molecule could be predicted reasonably well by considering just the geometry of the cluster. As can be seen in Figure 1, the spectra of $CB_{11}H_{12}^{-}$, $SbB_{11}H_{11}^{-}$, and $SB_{11}H_{11}$ all exhibit the same type of pattern, but with all their absorptions at lower field than those of $B_{12}H_{12}^{2-}$.

This trend seems to be common to every series of heteroborane with a given value of *n*, where *n* is the number of atoms in the cluster. Therefore, it was inferred that the spectrum of a heteroborane could be considered to be derived from that of a borane of the type $B_nH_n^{2-}$, altered by the substitution of one or more heteroatoms for boron atoms. Such considerations have led us to the following empirical rules, which we have found to be useful for all compounds we have tested so far. They have proved to be particularly helpful in assigning a spectrum to one of several possible isomers.

**Rule I.** The position of an absorption attributed to a given boron atom in a $B_nH_n^{2-}$ species will depend on the coordination number of the atom.[11] The lower the coordination number, the more positive the chemical shift, and the higher the coordination number, the more negative the shift.[12] Although only coordination numbers four, five, and six have been considered, it is likely that the same trend will extend to coordination number three.

**Rule II.** The $^{11}B$ NMR spectrum of an *n*-atom *closo*-heteroborane cluster with $2n + 2$ framework electrons and a single heteroatom can be predicted from the spectrum of the parent $B_nH_n^{2-}$ by considering specific effects caused by the substitution of the new atom. In turn, the spectrum of an *n*-atom *closo*-heteroborane cluster with two heteroatoms may be derived from the spectrum of a one-heteroatom *closo*-borane by considering the effect of the second substitution.

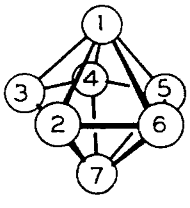

**Figure 2.** Idealized geometry of $B_7H_7^{2-}$ ($D_{5h}$).

In the application of Rule II, the initial idealized geometry and point group of the parent borane, $B_nH_n^{2-}$, are retained as the reference basis in the substituted compounds. The substitution effects that then must be considered are classified as follows:

**Antipodal Effects (AE).** The effect[6] is produced by an atom on a second atom placed opposite to the first. Both atoms must lie on a symmetry axis of the reference structure.

**Rhomboidal Effect (RE).** The effect is produced by an atom on a second atom located at the opposite vertex of a rhombus.

**Butterfly Effect (BE).** The effect is caused by one atom on another located two bonds away, with each atom occupying an unshared vertix of two triangular faces sharing a common side. Both atoms must lie on a symmetry plane of the reference structure.

**Neighbor Effect (NE).** The effect is caused by an atom on a neighbor, providing that the bond defined by the two atoms lies in a symmetry plane of the reference structure; however, this effect is always considered when the heteroatom is in a tetracoordinated position.

**Rule III.** The substitution of a boron atom in a cage structure by a heteroatom located in a column of the periodic table to its right will result in the previous effects shifting signals downfield. The effect of an atom in a given family of the periodic table will increase as the atomic number increases.[13] The magnitude of the effect will depend on the coordination number of the perturbing atom. If the perturbing atom is tetracoordinate, the magnitudes of the effects fall in the order AE > NE > BE. For a pentacoordinate atom, the order is AE > RE > BE > NE.

## Application of the Rules

In order to clarify the preceding rules and to illustrate their utility, a number of examples are shown below.

**Spectra of $2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_5H_5$ and $2,4\text{-}(CH_3)_2\text{-}2,4\text{-}C_2B_5H_5$.** The idealized geometry and numbering of the borane $B_7H_7^{2-}$ ($D_{5h}$) is represented in Figure 2. As indicated in rule II, the spectrum of both the 2,3- and 2,4-isomers may be predicted from the spectrum of the parent $B_7H_7^{2-}$ after considering the effects caused by substituting the 2,3- and 2,4-borons by methyl-substituted carbons.[14]

**(a) Predicted and Observed $^{11}B$ NMR Spectrum of $B_7H_7^{2-}$.** Two peaks with relative intensities of 5:2 are expected from symmetry considerations. Rule I predicts that the absorptions of B(2,3,4,5,6), which are tetracoordinate, will appear on the low-field part of the spectrum and those due to B(1,2), which are pentacoordinate atoms, will appear at the high field side.

Predicted spectrum: two peaks with intensities 5:2, low to high field.

Observed spectrum:[15] −0.2 (5 B) and −22.6 (2 B) ppm.

**(b) Predicted Spectrum of $2\text{-}CH_3\text{-}2\text{-}CB_6H_6^{-}$.** The substituted C(2) occupies a tetracoordinate position in $2\text{-}CH_3\text{-}2\text{-}CB_6H_6^{-}$. The only effect allowed by symmetry considerations is the neighbor effect (NE) on B(1,3,6,7). As can be seen in Figure 3,[16] ab-

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(11) Throughout the paper the exocluster bonds are not counted for the coordination number.

(12) We have adopted the sign convention of the Third International Meeting on Boron Chemistry. A positive sign indicates a shift at lower field than the standard trifluoroborane etherate.

(13) This assumption is valid for the second, third, and/or fourth periods.

(14) A substituted carbon $CH_3$–C can be considered as a heteratom. Their effects will be slightly different from those of a C bonded to a hydrogen.

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(16) The distances between the different sets of equivalent borons are not proportional to their differences in chemical shifts, but equal distances are used to indicate a particular effect.

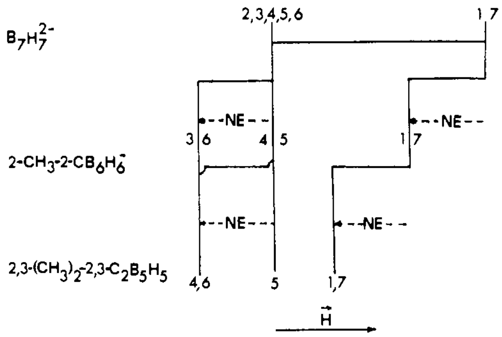

Figure 3. Schematic representation of the $^{11}$B NMR spectra of $B_7H_7^{2-}$, 2-$CH_3$-2-$CB_6H_6^-$ and 2,3-$(CH_3)_2$-2,3-$C_2B_5H_5$. In all figures, the magnetic field increases from left to right. The numbers indicate the boron atoms; e.g., 1,7 means B(1,7).

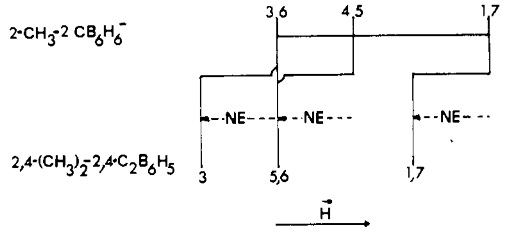

Figure 4. Schematic representation of the $^{11}$B NMR spectra of 2-$CH_3$-2-$CB_6H_6^-$ and 2,4-$(CH_3)_2$-2,4-$C_2B_5H_5$.

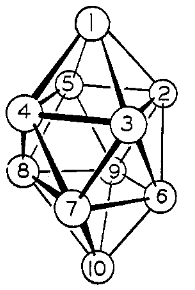

Figure 5. Idealized geometry of $B_{10}H_{10}^{2-}$ ($C_{4v}$).

sorptions of these borons are expected to shift to low field with respect to the signals of the corresponding boron in $B_7H_7^{2-}$.

Predicted spectrum: three signals with intensities 2:2:2 from low to high field.

**(c) Predicted and Experimental Spectrum of 2,3-$(CH_3)_2$-2,3-$C_2B_5H_5$.** The substituted C(3) occupies a tetracoordinate position in 2,3-$(CH_3)_2$-2,3-$C_2B_5H_5$, and as in the previous case, its only allowed effect is the neighbor effect (NE) on B(1,4,7), causing a shift of their absorptions to lower field. (See Figure 3.)

Predicted spectrum: three signals with intensities 2:1:2 from low to high field.

Experimental spectrum:[17] 10.6 (2 B), 5.2 (1 B), and −12.1 (2 B) ppm.

**(d) Predicted and Experimental Spectrum of 2,4-$(CH_3)_2$-2,4-$C_2B_5H_5$.** The substituted C(4) occupies a tetracoordinate position in 2,4-$(CH_3)_2$-2,4-$C_2B_5H_5$. As before, the only allowed effect is NE on B(1,3,5,7). Consequently, these borons will absorb at lower field than the corresponding ones in 2-$CH_3$-2-$CB_6H_6$. See Figure 4.

Predicted spectrum: three signals with intensities 1:2:2 from low to high field.

Experimental spectrum:[18] 7.6 (1 B), 5.4 (2 B), and −18.0 (2 B) ppm.

**Spectra of 1,2-$C_2B_8H_{10}$ and 1,6-$C_2B_8H_{10}$.** The idealized geometry and numbering of the borane $B_{10}H_{10}^{2-}$ ($C_{4v}$) is indicated in Figure 5. The spectra of 1,2-$C_2B_8H_{10}$ and 1,6-$C_2B_8H_{10}$ are derived from the one of $B_{10}H_{10}^{2-}$.

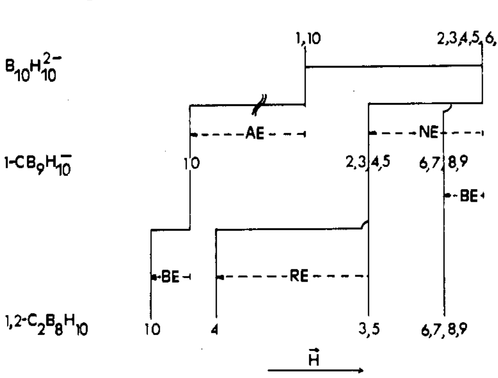

Figure 6. Schematic representation of the $^{11}$B NMR spectra of $B_{10}H_{10}^{2-}$, 1-$CB_9H_{10}^-$, and 1,2-$C_2B_8H_{10}$.

Table I. Chemical Shifts of One-Heteroatom Ten-Atom Clusters[a]

| compd | chem shift B(10) | B(2,3,4,5) | B(6,7,8,9) | ref |
|---|---|---|---|---|
| $CB_9H_{10}^-$ | 28.4 | −20 | −25.1 | 20 |
| $B_9H_9CN(CH_3)_3$ | 31.8 | −17.3 | −26.0 | 21 |
| $SB_9H_9$ | 74.5 | −4.8 | −17.6 | 22, 23 |

[a] Chemical shifts in ppm, referred to $BF_3 \cdot Et_2O$.

**(a) Predicted and Experimental Spectra of $B_{10}H_{10}^{2-}$.** By symmetry there are two different sets of equivalent borons: B(1,10) tetracoordinate and B(2,3,4,5,6,7,8,9) pentacoordinate.

Predicted spectrum: two signals with intensity 2:8 from low to high field.

Experimental spectrum:[19] −1 (2 B) and −28 (8 B) ppm.

**(b) Predicted and Experimental Spectra of 1-$CB_9H_{10}^-$.** C(1) occupies a tetracoordinate position in 1-$CB_9H_{10}^-$. The symmetry allows C(1) to cause AE on B(10), NE on B(2,3,4,5), and BE on B(6,7,8,9), decreasing in this order. Therefore, the absorptions of these borons will be shifted inequally to lower field with respect to the same ones in $B_{10}H_{10}^{2-}$. Figure 6 represents these shifts.

Predicted spectrum: three signals with intensities 1:4:4 from low to high field.

Experimental spectrum:[22-27] 28.4 (B(10)), −20.0 (B(2,3,4,5)), and −24.1 (B(6,7,8,9)) ppm.

The spectral absorptions of other 10-atom clusters with one heteroatom in position 1 are indicated in Table I. According to the aforementioned rules the pattern is the same as 1-$CB_9H_{10}^-$.

**(c) Predicted and Experimental Spectra of 1,2-$C_2B_8H_{10}$.** C(2) occupies a pentacoordinate position in 1,2-$C_2B_8H_{10}$. The symmetry of the parent borane allows C(2) to have an RE on B(4) and a BE on B(10), RE being larger than BE. See Figure 6 for changes of the absorption of these borons with respect to the ones in 1-$CB_9H_{10}^-$.

B(6,7,8,9) belong to two different sets of equivalent borons, B(6,9) and B(7,8). In these cases where the rules do not predict a splitting but the symmetry does, the use of eq 1 is helpful, where

$$xn = x_a n_a + x_b n_b \qquad (1)$$

$x$ = predicted chemical shift based on the rules, $n$ = number of boron atoms, $x_a$ = observed chemical shift for $n_a$ equivalent borons, $x_b$ = observed chemical shift for $n_b$ equivalent borons.

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(20) The values given by these authors are referred to $B(OCH_3)_3$. It has been considered that $B(OCH_3)_3$ is at +18.1 ppm with respect to $BF_3 \cdot Et_2O$.

(21) The assignments have been done in comparison with those of $SB_9H_9$. See ref 23.

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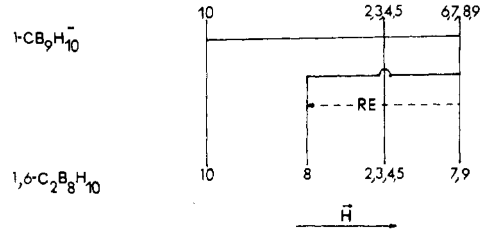

**Figure 7.** Schematic representation of the $^{11}B$ NMR spectra of 1-$CB_9H_{10}^-$ and 1,6-$C_2B_8H_{10}$.

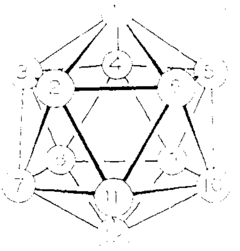

**Figure 8.** Idealized geometry of $B_{12}H_{12}^{2-}$ ($I_h$).

Predicted spectrum of 1,2-$C_2B_8H_{10}$: four signals with intensities 1:1:2:4 from low to high field.

Experimental spectrum:[24] 38.4 (1 B), −8.5 (1 B), −19.3 (2 B), −25.4 (4 B) ppm.

**(d) Predicted and Experimental Spectra of 1,6-$C_2B_8H_{10}$.** C(6) occupies a pentacoordinate position in 1,6-$C_2B_8H_{10}$. The symmetry of the borane allows C(6) to have an RE on B(8), shifting the $^{11}B$ NMR position of this boron to lower field with respect to B(8) in 1-$CB_9H_{10}^-$. Since RE in the previous case was 11.5 ppm, a close value is expected now. Because the $\Delta\delta_i$ between B(2,3,4,5) and B(6,7,8,9) is 5.1 in $CB_9H_{10}^-$ the expected spectrum is resolved as indicated in Figure 7.

Predicted spectrum: four signals with intensities 1:1:4:2 from low to high field. The signal of intensity 4 is split by symmetry, displaying a 1:1:2:2:2 pattern.

Experimental spectrum:[25] 23.8 (1 B), −17.8 (1 B), −19.6 (2 B), −21.6 (2 B), −26.6 (2 B) ppm.

Equation 1 can be used to ascertain which signals belong to B(2,3,4,5). According to the rules, the unsplit $^{11}B$ NMR signal for B(2,3,4,5) is −20 ppm (see Table I). If the absorption at −19.6 ppm is attributed to either B(2,3) or B(4,5), eq 1 predicts the chemical shift of the other boron couple close to −20 ppm. It may be concluded that the absorptions at −19.6 and −21.6 ppm belong to B(2,3,4,5).[28]

**Spectra of 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$.** The idealized geometry and numbering of the borane $B_{12}H_{12}^{2-}$ ($I_h$) is indicated in Figure 8. The $^{11}B$ NMR spectra of 1,2- and 1,7-$C_2B_{10}H_{12}$ are considered derivatives of the spectrum of $B_{12}H_{12}^{2-}$.

**(a) Predicted and Experimental Spectrum of $B_{12}H_{12}^{2-}$.** By symmetry considerations there is only one type of boron that is pentacoordinate.

Predicted spectrum: one signal.

Experimental spectrum:[26] −16.9 ppm.

**(b) Predicted and Experimental Spectrum of 1-$CB_{11}H_{12}^-$.** C(1) occupies a pentacoordinate position in 1-$CB_{11}H_{12}^-$. The symmetry of the polyhedron permits C(1) to cause AE on B(12), BE on B(7,8,9,10,11), and NE on B(2,3,4,5,6), the effects decreasing in this order. The $^{11}B$ NMR signals of these borons will be shifted to lower field with respect to the $^{11}B$ NMR signals of $B_{12}H_{12}^{2-}$, as indicated in Figure 9.

Predicted spectrum: three signals with intensities 1:5:5 from low to high field.

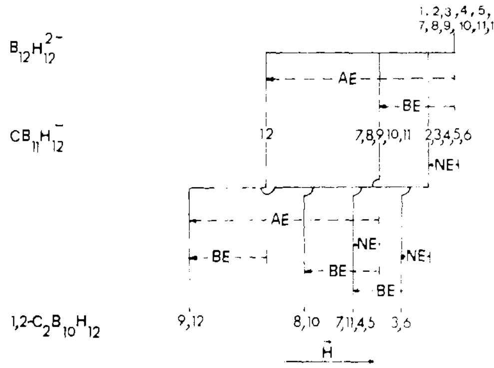

**Figure 9.** Schematic representation of the $^{11}B$ NMR spectra of $B_{12}H_{12}^{2-}$, $CB_{11}H_{12}^-$, and 1,2-$C_2B_{10}H_{12}$.

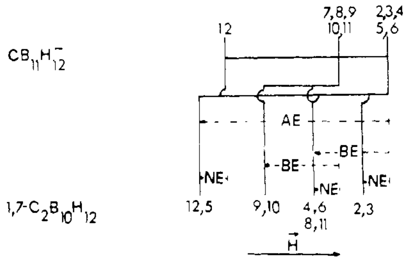

**Figure 10.** Schematic representation of the $^{11}B$ NMR spectra of $CB_{11}H_{12}^-$ and 1,7-$C_2B_{10}H_{12}$.

**Table II.**[29] Chemical Shifts of One-Heteroatom Twelve-Atom Clusters[a]

| compd | chem shift B(12) | chem shift B(7,8,9,10,11) | chem shift B(2,3,4,5,6) | ref |
|---|---|---|---|---|
| $CB_{11}H_{12}^-$ | −7.0 | −13.1 | −16.0 | 27 |
| $SbB_{11}H_{11}^-$ | 9.4 | −6.9 | −9.3 | 30 |
| $SB_{11}H_{11}$ | 18.7 | −3.7 | −5.7 | 31 |

[a] Chemical shifts in ppm referred to $BF_3 \cdot Et_2O$.

Experimental spectrum:[27] −7.0 (1 B), −13.1 (5 B), and −16.0 (5 B) ppm.

Table II[29] shows the effects on the chemical shifts caused by different heteroatoms.

**(c) Predicted and Experimental Spectra of 1,2-$C_2B_{10}H_{12}$.** C(2) occupies a pentacoordinate position in 1,2-$C_2B_{10}H_{12}$. The symmetry of the borane $B_{12}H_{12}^{2-}$ allows C(2) to effect AE on B(9), BE on B(4,5,8,10,12), and NE on B(3,6,7,11), the magnitude of the effects decreasing in this order. Figure 9 represents the changes of the $^{11}B$ NMR absorptions of these borons with respect to the same ones in 1-$CB_{11}H_{12}^-$.

Predicted spectrum: four signals with intensities 2:2:4:2 from low to high field.

Experimental spectrum:[32] −2.8 (B(9,12)), −9.8 (B(8,10)), −14.3 (B(4,5,7,11)) , and −15.1 (B(3,6)) ppm. Table III shows the effects on the chemical shifts caused by different heteroatoms.

**(d) Predicted and Experimental Spectra of 1,7-$C_2B_{10}H_{12}$.** C(7) occupies a pentacoordinate position in 1,7-$C_2B_{10}H_{12}$. It causes AE on B(5), BE on B(4,6,9,10), and NE on B(2,3,8,11,12), the magnitude of the effect decreasing in this order. Figure 10 represents the expected spectrum.

Predicted spectrum: four signals with intensities 2:2:4:2 from low to high field.

Experimental spectrum:[33] −6.9 (B(12,5)), −10.9 (B(9,10)), −13.5 (B(4,6,8,11)), and −17.2 (B(2.3)).

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(29) The assignments have been made on the basis of the rules presented in this paper.

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**Table III.** Chemical Shifts of Two-Heteroatom Twelve-Atom Clusters[a]

| | chem shift | | | | |
|---|---|---|---|---|---|
| compd | B(9,12) | B(8,10) | B(4,5,7,11) | B(3,6) | ref |
| 1,2-$C_2B_{10}H_{12}$ | −2.8 | −9.8 | −14.3 | −15.1 | 32 |
| 1,2-$B_{10}H_{10}$CHP | 2.4 (9.3) | −0.85 | −6.7 | −10.8 | 33 |
| 1,2-$P_2B_{10}H_{10}$ | 17.7 | 4.6 | 0.8 | −1.2 | 34 |
| 1,2-$As_2B_{10}H_{10}$ | 15.5 | 3.8 | 0.9 | −0.8 | 35 |
| 1,2-$Sb_2B_{10}H_{10}$ | 13.9 | 3.9 | −1.7 | −4.6 | 30 |
| 1,2-AsSb$B_{10}H_{10}$ | 14.2 (1), 12.3 (1) | 3.0 (2) | −0.1 (2), −2.0 (2) | −3.5 (2) | 30 |

[a] Chemical shifts in ppm referred to $BF_3{\cdot}Et_2O$.

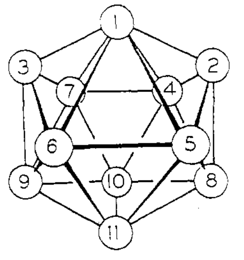

**Figure 11.** Idealized geometry of $B_{11}H_{11}^{2-}$ ($C_{2v}$).

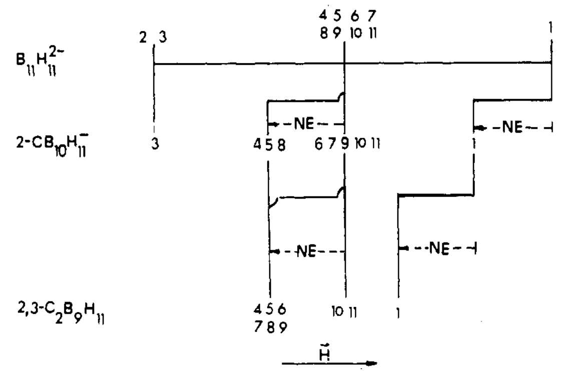

**Figure 12.** Schematic representation of the $^{11}$B NMR spectra of $B_{11}H_{11}^{2-}$, 2-$CB_{10}H_{11}^-$, and 2,3-$C_2B_9H_{11}$.

**$^{11}$B NMR Spectra of Eight- and Eleven-Atom Clusters.** The eight-atom dodecahedral ($D_{2d}$) and eleven-atom ($C_{2v}$) clusters have the lowest symmetry of the closo molecules from four to twelve atoms, but even in these cases the rules' predictions do not contradict the experimental results.

**Spectrum of $C_2B_9H_{11}$.** The carborane $C_2B_9H_{11}$ has the octadecahedron geometry, $C_{2v}$. This is the only geometry for which rule I is not sufficient to predict the spectrum of the hypothetical nonfluxional parent borane $B_{11}H_{11}^{2-}$.[37] Figure 11 shows the proposed structure and numbering of $C_2B_9H_{11}$.

To predict the $^{11}$B NMR spectrum of $C_2B_9H_{11}$, it has been assumed that all the pentacoordinated borons in nonfluxional $B_{11}H_{11}^{2-}$ have identical chemical shifts. If this supposition is true, three absorptions with intensities 2:8:1 would be expected for $B_{11}H_{11}^{2-}$.

**(a) Predicted Spectrum of Nonfluxional 2-$CB_{10}H_{11}^-$.** Upon substitution of B(2) by C(2) in $B_{11}H_{11}^{2-}$ a NE is expected on B(1,4,5,8), causing their absorptions to shift to lower field than the corresponding ones in $B_{11}H_{11}^{2-}$. See Figure 12.

Predicted spectrum: four signals with intensities 1:3:5:1 from low to high field.

**(b) Predicted and Experimental Spectrum of 2,3-$C_2B_9H_{11}$.** C(3) occupies a tetracoordinate position in 2,3-$C_2B_9H_{11}$. As in the previous case only NE is expected on B(1,6,7,9). Figure 12 shows the shifts of these absorptions with respect to the ones in 2-$CB_{10}H_{11}^-$.

Predicted spectrum: three signals with intensities 6:2:1 from low to high field. If the symmetry is considered, the signal of intensity 6 must be split in two. Consequently, the expected pattern is 4:2:2:1 or 2:4:2:1.

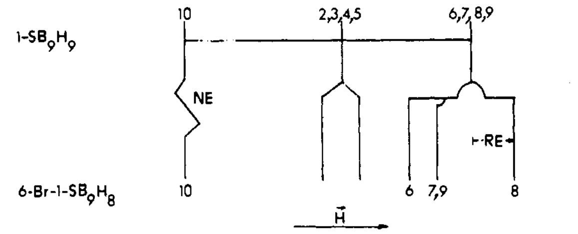

**Figure 13.** Schematic representation of the $^{11}$B NMR spectra of 1-$SB_9H_9$ and 6-Br-1-$SB_9H_8$.

Experimental spectrum:[39] −1.2 (B(4,5,6,7)), −7.3 (B(8,9)), −10.5 (B(10,11)), and −17.3 (B(1)) ppm.

**Substituted B–R Closo Molecules. Rules and Effects**

The $^{11}$B chemical shift predictions are more difficult for substituted closo molecules than for nonsubstituted molecules. Nevertheless, we have found some trends that allow, in most of the cases, either directly or by exclusion, the correct assignment of the $^{11}$B NMR chemical shifts to specific borons in the cluster. These trends have been summarized in the following rules.

**Rule IV.** The effects created by a substituted boron on the $^{11}$B NMR chemical shifts of other borons in the cluster are the same effects that occur in molecules without substituents. Another effect, the symmetrical neighbor effect (SNE) is defined as the effect created by two equivalent substituted borons on the common neighbor.

**Rule V.** In the absence of other effects, the $^{11}$B NMR chemical shift of a boron atom experiencing either AE or RE caused by a substituted boron is always upfield. The chemical shift of a boron experiencing two BE's always moves upfield. The value of the shift depends upon the substituent, but in general the more electronegative the substituent is, the larger the effect. It is more difficult to make predictions about BE, NE, and SNE. In general, a boron experiencing BE either does not move or moves upfield. Iodine is usually an exception. In most of the cases the shift created by BE and NE is small and does not create any problem in making the assignment. The SNE is larger, and its sign depends upon the position of the atom experiencing the effect with respect to the cluster heteroatoms.

**Rule VI.** When a substituted boron causes a rhomboidal effect, RE, the chemical shifts of the other borons in the rhombus follow eq 2, where $i$ = 1 stands for the substituted boron, o denotes the

$$[\sum_{i=2}^{4}\delta_i]_o = [\sum_{i=2}^{4}\delta_i]_f \qquad (2)$$

situation where the substituent is H, and f denotes the situation when the substituent is a non-hydrogen atom.

**Rule VII.** The chemical shift of the boron holding the substituent moves downfield with respect to the case when X = H, except when X = I. It has been proven that this depends on the electronegativity of X. Nevertheless, exceptions to this rule have been noticed when the substituent is in a tetracoordinate site

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(37) See: Muetterties, E. L.; Hoel, E. L.; Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 950.

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(39) Schoeler, F. R.; Brown, R.; Gladkowski, D.; Wright, W. F.; Todd, L. J. *Inorg. Chem.* **1979**, *18*, 921.

(40) See the example of 6-Br-1-$SB_9H_8$.

**Table IV.** Rhomboidal and Antipodal Effects as a Function of Electronegativity[a]

| compd | $\chi_X$ | RE[b] | ref | compd | $\chi_X$ | AE[b] | ref |
|---|---|---|---|---|---|---|---|
| 6-I-1-$SB_9H_8$ | 2.21 | -2.3 | 38 | 9,10-$I_2$-1,7-$C_2B_{10}H_{10}$ | 2.21 | -1.6 | 44 |
| 6-Me-1-$SB_9H_8$ | 2.50 | -3.1 | 43 | 9,10-$Br_2$-1,7-$C_2B_{10}H_{10}$ | 2.74 | -5.8 | 1 |
| 6-Et-1-$SB_9H_8$ | 2.50 | -3.4 | 43 | 9,10-$Cl_2$-1,7-$C_2B_{10}H_{10}$ | 2.83 | -4.2 | 33 |
| 6-Br-1-$SB_9H_8$ | 2.74 | -3.7 | 38 | | | | |
| 6-Cl-1-$SB_9H_8$ | 2.83 | -5.6 | 38 | | | | |

[a] Allred–Rochow electronegativity values. [b] Values in ppm.

experiencing a very strong AE, for instance $SB_9H_9$.

**Application of the Rules. Spectrum of 6-Br-1-$SB_9H_8$.** The idealized geometry and numbering of the borane $B_{10}H_{10}^{2-}$ is represented in Figure 5. The spectrum of $SB_9H_9$ has already been indicated and displays three signals at 74.5 (B(10)), -4.8 (B(2,3,4,5)), and -17.6 (B(6,7,8,9)). The substitution of a hydrogen atom at B(6) by a bromine causes B(6) to go downfield (rule VII); B(8) experiences RE and moves upfield (rule V), and B(7,9) moves a downfield (rule VI). No effect is expected on B(2,3,4,5), but due to the symmetry, they will be split and will follow eq 1. NE is expected on B(10) (rule V). Figure 13 represents these changes all referred to $SB_9H_9$.

Predicted spectrum of 6-Br-1-$SB_9H_8$: six signals with intensities 1:2:2:1:2:1 from low to high field.

Observed spectrum of 6-Br-1-$SB_9H_8$:[38] 69.3(1 B), -3.0(2 B), -6.9(2 B), -10(1 B, s), -15.4(2 B), and -21.3(1 B) ppm.

**Spectrum of 4,7-$(OH)_2$-2,3-$(CH_3C)_2B_9H_7$.** The experimental $^{11}B$ NMR spectrum of $(CH_3C)_2B_9H_7(OH)_2$ displays six absorptions at +18.6 (2 B), -0.9 (1 B), -3.4 (2 B), -9.4 (1 B), -21.3 (2 B), and -22.6 (1 B) ppm whereas the $^{11}B$ NMR spectrum of the parent carborane $(CH_3C)_2B_9H_9$ displays four at -2.9 (B(4,5,6,7)), -6.8 (B(8,9)), -10.5 (B(10,11)), and -11.0 (B(1)).[41] It is clear that a comparison of both sets of data does not permit the assignment of the absorptions in the hydroxy compound. Therefore, it was a good example to test the validity of the rules.

The idealized geometry and numbering of the nonfluxional borane $B_{11}H_{11}^{2-}$ is represented in Figure 11. B(1,7,6,9) and B(1,4,5,8) form two rhombus, and consequently eq 2 can be used. The absorption at +18.6 (2 B, s) is attributed to B(4,7). It is expected that the resonances of B(5) and B(6) will shift upfield[40] since these atoms are experiencing RE from atoms B(4) and B(7), respectively. The absorption at -21.3 ppm is then attributed to B(5,6). The only other possibility for a peak of intensity 2 was the absorption at -3.4 (2 B) ppm, but this is inconsistent with the existence of RE on these borons. As a result of this assignment the signal of intensity 2 at -3.4 ppm is attributed to B(9,8). These assignments are further proved since it was expected that atoms B(9), B(8), and B(1) would shift downfield as a consequence of RE on B(6) and B(5) (eq 2). Once the chemical shifts of B(6) and B(9) are known, it is possible to calculate approximately (using eq 2) the expected position for B(1). $[\delta(B(1)) + \delta(B(6)) + \delta(B(9))]_o \simeq [\delta(B(1)) + \delta(B(6)) + \delta(B(9))]_f$ giving $\delta(B(1))_f \simeq$ 4 ppm.

The chemical shift of B(1) is expected to be at a lower field than that in $(CH_3C)_2B_9H_9$, and consequently the signal at -22.6 ppm is not B(1). Of the two remaining, the closest one to the calculated value is the absorption at -0.9 ppm and tentatively it can be assigned to B(1).

The absorption at -22.6 ppm is assigned to B(10) since this one is experiencing SNE.[41] These two assignments are further corroborated by the assignment of the absorption at -9.4 ppm to B(11). This boron atom does not experience any mentioned effect, so its position in the hydroxy derivative must be close to the position it had in $(CH_3C)_2B_8H_9$, which was -10.5 ppm.

Our conclusions agree completely with the work of Todd and co-workers,[39] who made the assignments experimentally.

## Discussion

With only symmetry considerations and the effects described in this paper, the $^{11}B$ NMR spectrum of a nonfluxional *closo*-heteroborane $X_yB_{n-y}H_z^{m-}$ can be predicted from the $^{11}B$ NMR spectrum of nonfluxional *closo*-borane $B_nH_n^{2-}$. As a part of the general case, only the 12- and 10-atom clusters are used to discuss the differences in chemical shifts between the parent borane and its derivatives. As can be observed in Figure 1, the $^{11}B$ NMR spectra of $CB_{11}H_{12}^-$, $SbB_{11}H_{11}^-$, and $SB_{11}H_{11}$, all closo species with 26 framework electrons, have the same type of pattern. Nevertheless, all the resonances in these spectra appear at lower field than the equivalent resonances in the parent borane $B_{12}H_{12}^{2-}$, being in the order $SB_{11}H_{11} > SbB_{11}H_{11}^- > CB_{11}H_{12}^- > B_{12}H_{12}^{2-}$.

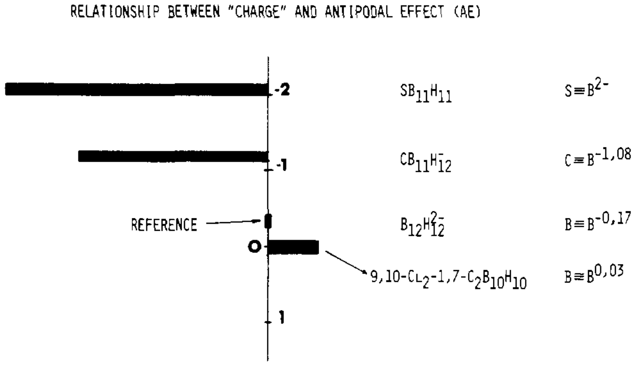

**Figure 14.** Graphical representation of the antipodal effect as a function of the "charge" of the perturbing atom.

All the species considered in Figure 1 have an icosahedron type of structure, but they have neither the same cluster composition nor the same charge. In order to achieve 26 framework electrons, or a closed-shell system, the sulfur atom should contribute four electrons to the framework, the antimony and carbon atoms three, and the boron atom two.[10] Consequently, there is a parallel relationship between the shift to lower field and the framework electron contributions of the atoms in the cluster. Tables I–III show clearly this relationship. In general, for perturbing atoms with the same framework electron contributions, the magnitude of the shifts increase considerably as the atomic number $Z$ of the perturbing atom increases and, after a certain value of $Z$, decrease smoothly.

The species $B_{12}H_{12}$ needs two extra electrons to achieve a closed shell, and they can be considered delocalized throughout the molecule giving a charge of 0.17 e to each boron.[42] Upon substitution of one boron atom by a carbon in $B_{12}H_{12}^{2-}$, the cluster $CB_{11}H_{12}^-$ is obtained. In terms of the framework electron contribution a carbon can be considered a negatively charged boron $B^-$, in which case the charge of this particular "boron" would be $\simeq$1.08 e instead of the initial 0.17 e. Substitution of a boron atom by a sulfur in $B_{12}H_{12}^{2-}$ gives $SB_{11}H_{11}$, equivalent to having a doubly charged boron $B^{2-}$. In other words, the substitution of a boron atom by another atom with a larger framework electron contribution can be viewed as a way of increasing the valence electronic

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(41) It can be observed that B(1) also experiences SNE. This would explain the discrepancy between the calculated and observed position for B(1).

(42) (a) This is a rough approximation but is useful as a qualitative explanation. Amstrong and co-workers[42b] and Lipscomb and co-workers,[42c] using two different methods, assign charges to the hydrogen atoms which amount to -0.05 and -0.15e, respectively. The difference between these values and -0.17e is attributed to the boron atom. (b) Amstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 627. (c) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226.

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**Table V.** Splitting of B(2,3,4,5) in 6-X-$SB_9H_8$ as a Function of the Electronegativity of X[a]

| compd | δ(B(2,3)) − δ(B(4,5)) | $X_X$ | [δ(B(2,3)) + δ(B(4,5))]/2 | ref |
|---|---|---|---|---|
| 1-$SB_9H_9$ | 0 | 2.20 | −4.8 | 22 |
| 6-I-1-$SB_9H_8$ | 0 | 2.21 | −5.1 | 38 |
| 6-Me-1-$SB_9H_8$ | 2.6 | 2.50 | −4.9 | 43 |
| 6-Br-1-$SB_9H_8$ | 3.9 | 2.74 | −5.0 | 38 |
| 6-Cl-1-$SB_9H_8$ | 5.0 | 2.83 | −4.5 | 38 |

[a] Allred–Rochow electronegativity values.

density in a particular spot of the cluster, and the larger this is the larger is the antipodal, rhomboidal, butterfly, or neighbor effect.

In all the previous considerations the reference point was the initial charge of the boron in $B_{12}H_{12}^{2-}$, i.e. 0.17 e. Any charge larger than this causes effects that shift the resonances of the other borons to lower field. Now, what will happen when the charge of this boron is lowered, as when its hydrogen is substituted by a more electronegative atom such as carbon, bromine, chlorine, etc.? If only the electronegativity is considered, it should be concluded that the boron atom has become more positive. According to Amstrong and co-workers[42b] there is a +0.20 e change of charge from $B_{12}H_{12}^{2-}$ to $B_{12}Cl_{12}^{2-}$ for each boron atom. Then, the substitution of one hydrogen by chloride should lead to upfield shifts. Figure 14 describes graphically the antipodal effects as a function of the "charge" of the perturbing atom.

In Table IV are indicated some rhomboidal and antipodal effects created by substitution of one hydrogen atom by a more electronegative element. The negative sign implies an upfield shift. From the data the parallelism between electronegativity and RE/AE seems to be obvious.

In substituted *closo*-heteroboranes not only the effect of the substituted boron on the chemical shifts of the remaining borons but also the effect of it on the heteroatom must be considered. The substituted boron has an increased electronegativity value due to its positive charge, polarizing the valence electrons of the heteroatom and, consequently, modifying its effects. The $^{11}$B NMR spectra of 6-X-1-$SB_9H_8$ present an example of the interaction between substituted borons and the heteroatom. According to the rules no effect created by B(6) would be expected on the chemical shifts of the upper belt borons in 6-X-1-$SB_9H_8$. Nevertheless, B(2,3,4,5) atoms are split into two groups, B(2,3) and B(4,5), as would be expected by symmetry considerations alone. Two relevant features need to be mentioned: first, the magnitude of the splitting is a function of the electronegativity of the substituent; second, the chemical shift average of B(2,3) and B(4,5) remains the same within ±0.3 ppm of its value in $SB_9H_9$.

The magnitude of the splitting and the observed chemical shifts can be interpreted in terms of the effect of B(6) on the apical sulfur. An increase of the positive charge in B(6) disturbs the heteroatom's valence electrons resulting in an increase of density toward B(2,3) and a decrease toward B(4,5), both changes being of the same absolute value but of opposite sign.

Some cases dealing with Br and Cl, of which Table IV gives one example, indicate that other factors besides electronegativity must be considered to get a more precise description of the chemical shifts for molecules of this type. These other factors become more important in the case of the smaller effects, NE and BE.

The symmetrical neighbor effect, SNE, was introduced in the case of di- or polysubstituted *closo*-boranes and -heteroboranes. It is a short range effect, but strong, and its consideration was necessary to interpret the chemical shift represented by a boron atom equivalently bonded to two substituted borons. The chemical shift of the substituted boron is better understood and correlates fairly well with the electronegativity of the substituent.[45]

The order of the effects has been established by a process of trial and error, and no theoretical considerations have been made. Nevertheless, it was expected that the same perturbing atom placed in two positions differing in the skeletal coordination number would behave differently. The reason, again, is that atoms of lower coordination number have a greater share of the available skeletal electrons.[28]

Unlike this work, Hermâneck and co-workers[28] have proposed that the antipodal effect increases with the rising electron donation of the substituent. On the basis of what has been indicated in this paper, our idea of different valence electronic density in one particular position of the cluster gives a logical explanation for the chemical shifts observed in closo molecules, and permits a smooth transition from nonsubstituted to substituted boranes and heteroboranes.

## Conclusions

It has been shown that a relationship exists between $^{11}$B NMR chemical shifts and geometrical structure in closo molecules. Substitution of a heteroatom for a boron in an *n*-atom closo molecule disturbs the cluster's original molecular orbitals and therefore affects the paramagnetic term ($\sigma_p$) of the screening constants ($\sigma$). As a result of the perturbation, the $^{11}$B NMR absorptions are shifted with respect to the positions they had in the unperturbed *closo*-borane. The effects on the boron chemical shifts caused by that perturbation have been classified in the following manner: antipodal effect (AE), rhomboidal effect (RE), butterfly effect (BE), and neighbor effect (NE). These effects depend on the position of the perturbing atom in the cluster and the symmetry of the unperturbed cluster. The finding of these effects is very useful for the assignment of $^{11}$B NMR absorptions to specific borons in the cluster. Thus, it is possible to determine, in favorable cases, which isomer among different isomers is responsible for a specific pattern in the $^{11}$B NMR spectrum.

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**Registry No.** 2,3-$(CH_3)_2$-2,3-$C_2B_5H_5$, 31566-10-6; 2,4-$(CH_3)_2$-2,4-$C_2B_5H_5$, 21687-53-6; 1,2-$C_2B_8H_{10}$, 41655-27-0; 1,6-$C_2B_8H_{10}$, 23704-81-6; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; 2,3-$C_2B_9H_{11}$, 17764-84-0; 6-Br-1-$SB_9H_8$, 58575-43-2; 4,7-$(OH)_2$-2,3-$(CH_3C)_2B_9H_7$, 40618-03-9.

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