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Quantitative Assessment of Substitution NMR Effects in the Model Series of *o*-Carborane Derivatives: α-Shift Correlation Method

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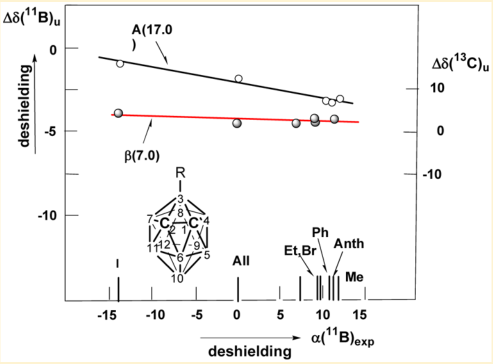
Ⓢ *Supporting Information*

ABSTRACT: The principles of a new α-shift correlation (ASC) NMR method are demonstrated on a model series of substituted derivatives of *o*-carborane for which reliable NMR data are available. This graphical method revealed an acceptable linear correlation between $\alpha(^{11}B)$ or $\alpha(^{13}C)$ shifts and those induced by substituents in unsubstituted (u) positions of the carborane cluster. The linearity holds for all nuclei involved in skeletal bonding: $\Delta\delta(N)_u = g \times \alpha$ (where N = ^{11}B, ^{13}C, and ^{1}H). The factor g (slope of the correlation line × 10^2) becomes an important measure of sensitivity of a given cage position to substituent changes. The β, γ, and δ = A (= antipodal) shifts can be therefore derived from the α-shift, are linearly proportional, and reflect additive character in double substitution. The ASC method appears to be an important tool for quantitative assessment of substituent NMR effects in all *exo*-substituted boron-cluster systems.



■ INTRODUCTION

NMR spectroscopy has become a key method of structural research in the field of B-cluster chemistry that still awaits major development.[1] Despite nearly 2000 publications on *o*-carborane chemistry, contiguous series of specifically substituted derivatives have been rare even in this most studied area of cluster-borane chemistry. Regardless that the [^{11}B—^{11}B]-COSY[2] and ^{1}H-{^{11}B(selective)}[3] techniques have been long known, NMR data are mostly published without assignments; complete ^{1}H NMR data for BH units are almost unavailable. As a result, the number of substituted borane clusters for which all ^{11}B, ^{13}C, and complete ^{1}H NMR parameters have been measured is still incredibly low. For example, even in the most trivial *closo*-$C_2B_{10}H_{11}$-9-X and *closo*-$C_2B_{10}H_{10}$-9,12-X_2 series (where X = halogens and other substituents), chosen for this work as important model compounds for demonstrating substituent effects owing to the broad range of α-shifts, some ^{13}C and detailed ^{1}H NMR data were missing, Therefore, the compounds had to be reprepared to obtain a complete set of reliable values under standard conditions (measured with high resolution on the same equipment and in the same solvent), even though a number of miscellaneous incomplete data have already been reported.[1]

Trends in the ^{11}B NMR shielding effects for some *exo*-substituted borane and carborane derivatives were reviewed by Heřmánek in 1992.[4] These included α (ipso), neighboring (β), and remote (γ and δ = A = antipodal[5−7]) shifts for which effects invoked by various substituents in the skeletal B-positions were reported, but attempts at quantitative assessment of relations among these parameters have not been done to date, except perhaps for nonlinear correlations between chemical shifts and halogen electronegativities.[8−11] In this work we would like to demonstrate graphically on a series of selected *o*-carborane derivatives some new aspects of NMR substituent effects operating within the B-cluster area characterized by delocalized bonding. From the surprisingly poor selection available, we chose a few rare examples of compound series for which reliable and comparable ^{11}B and ^{13}C NMR data have been available.

■ RESULTS AND DISCUSSION

It has been generally established that an arbitrary substituent X attached to any B-cluster[4] molecule induces a considerable NMR shift at the substituted site (α-shift), whose magnitude ($\alpha = \alpha_s - \alpha_p$, where the symbols s and p relate to the substituted and parent compound, respectively) is dependent on the substituent nature and type of the molecule. Moreover, X-substitution also invokes shift changes in all unsubstituted (u) positions, as exemplified by all figures below. It was reasonable to suppose that these changes must be in some way proportional to α-shifts. Indeed, the graphs presented in this work show that this assumption was correct. An important aspect emerging from the figures is that *chemical shift changes in unsubstituted BH and CH positions are, in principle, linearly proportional to α-shifts*. In other words, the α-shifts directly regulate shift changes ($\Delta\delta_u$) in other positisons:

$$\Delta\delta(N)_u = g \times \alpha(^{11}\text{B or } ^{13}\text{C}) + c \qquad (1)$$

where N = ^{11}B, ^{13}C, and ^{1}H; u relates to unsubstituted positions, and c = constant of no relevance for NMR assessments.

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The parameter g (gradient = the slope of the correlation line $\times 10^2$ quoted in parentheses) varies for β, γ, and A positions and becomes one of the specific NMR characteristics for a given type of cluster and site of substitution that can be taken as a *measure of sensitivity in specific positions of a given structure to substituent changes*. We suggest that positive g factors indicate the prevailing trend for shielding (on going from X = I to X = F); negative values stand for deshielding.

Figures 1−4 illustrate the acceptable accuracy of the ASC method when the measurements were performed under equal conditions with high resolution (500 and 600 MHz for ^{1}H). It was also verified that the linear behavior holds even for ^{13}C and ^{1}H nuclei involved in the skeletal bonding (experimental NMR shifts for haloderivatives are in Figure S1; for selection of authentic NMR spectra see Figures S2−S19). To recognize the subtle changes in the ^{1}H NMR shifts and their assignments to individual BH vertexes, the use of high-resolution [^{11}B−^{1}H] correlation techniques seems necessary. The elusive 9,12-F_2 derivative has not yet been isolated (the reported ^{11}B data[14] with two 1:1 singlets are incompatible with the 9,12-F_2 structure).

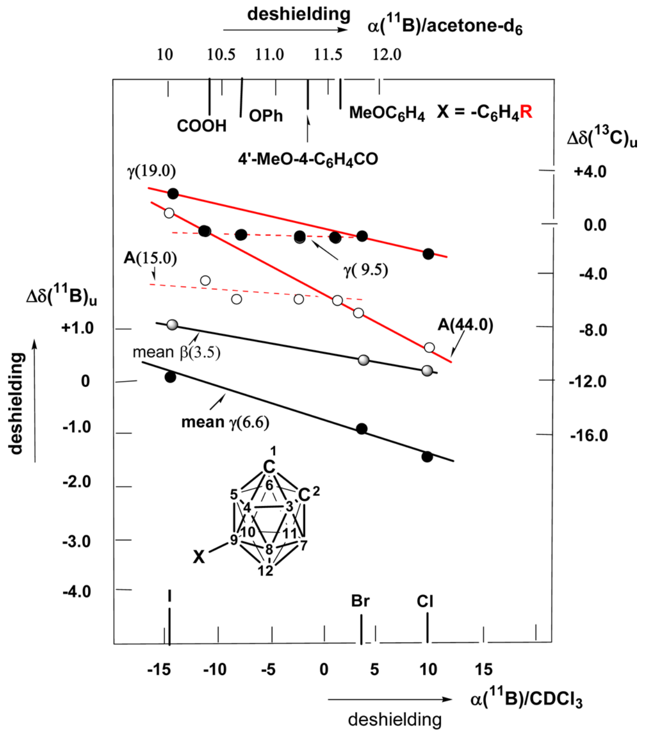

Figure 1. A plot of $\Delta\delta(^{11}B)_u$ (black lines) and $\Delta\delta(^{13}C)_u$ (red lines) shift changes vs $\alpha(^{11}B)$ shifts for unsubstituted (u) cluster positions in 9-X-substituted *o*-carboranes (X = halogens, bottom scale, this work). Data for X = RC_6H_4 derivatives (upper scale, dotted lines) from ref 12 (mean $g \times 10^2$ values in parentheses).

Inspection of Figure 2 shows considerably steeper correlation lines for a group of electron-withdrawing group (EWG) substituents (RNH, OH, and F)[4,13] exhibiting higher g values than those for halogen and phenylene functions. Both figures also reveal relatively high g values for antipodal (A) shieldings, enhanced in the 9,12-substituted series by cumulative effects due to disubstitution that also leads to remarkable shielding of all positions, when compared to the monosubstituted counterpart. The linearity is preserved even when a much more detailed α-scale is used to outline shieldings for a group of phenylene substituents.[12] The graphs suggest, too, that different substituent groups exhibit different shielding behavior and correlation lines.

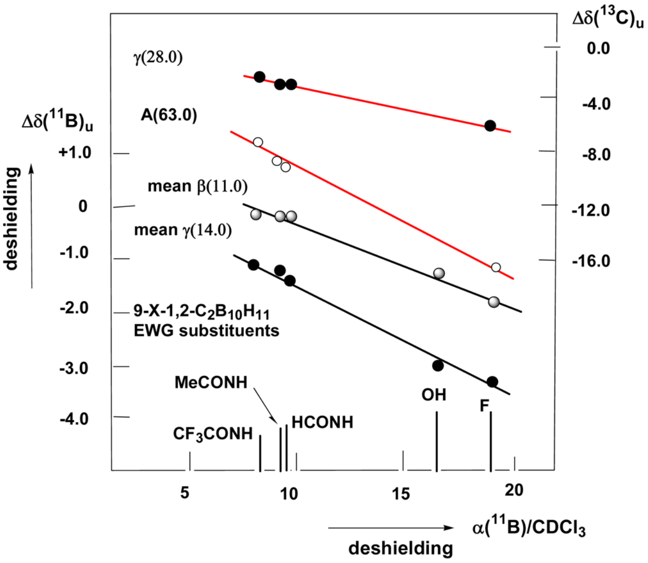

Figure 2. A plot of $\Delta\delta(^{11}B)_u$ (black lines) and $\Delta\delta(^{13}C)_u$ (red lines) shift changes vs $\alpha(^{11}B)$ shifts for unsubstituted (u) cluster positions in 9-X-*o*-carboranes (X = EWG substituents, $g \times 10^2$ values in parentheses). Data from refs 4 and 13.

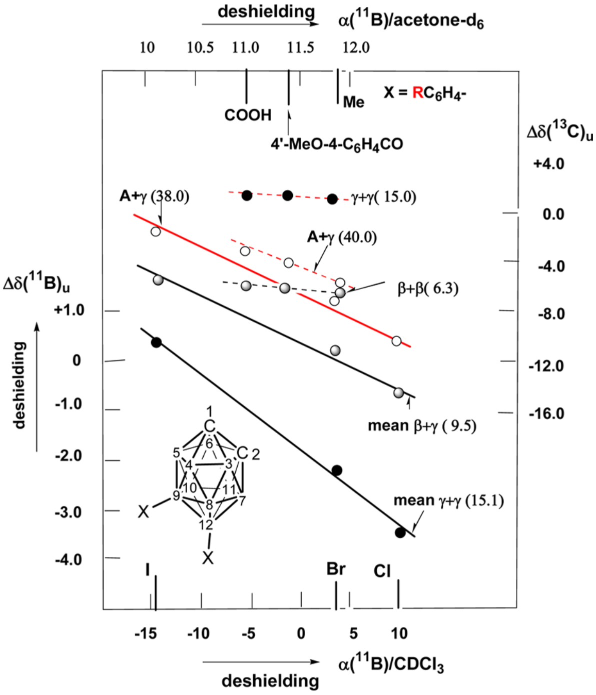

Figure 3. A plot of $\Delta\delta(^{11}B)_u$ (black lines) and $\Delta\delta(^{13}C)_u$ (red lines) shift changes vs $\alpha(^{11}B)$ shifts for unsubstituted (u) cluster positions in 9,12-dihalo *o*-carboranes (mean $\Delta\delta/g \times 10^2$ values in parentheses). Data for substituted RC_6H_4-groups (upper scale, dotted lines) from ref 12.

The next Figure 5 shows another interesting feature: the $\alpha(^{11}B)$ scale can be replaced by the "alkane" $\alpha(^{13}C)$ scale,[15] which is then used quite conveniently as a fixed reference scale (α_{ref}) for ASC purposes, as it eliminates the sudden break in the continuity of the correlation line for EWG substituents, so that

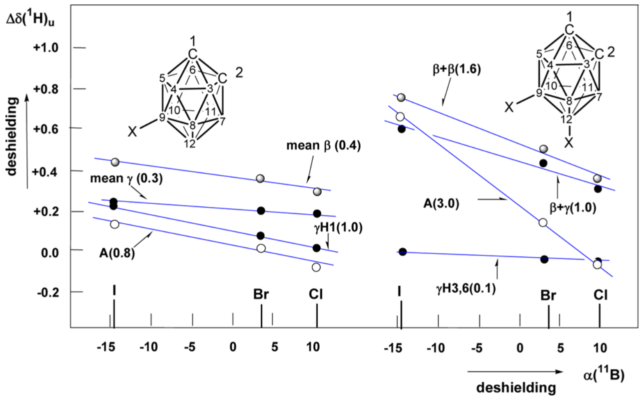

Figure 4. A plot of $\Delta\delta(^{1}H)_u$ (600 MHz) shift changes (blue lines) vs $\alpha(^{11}B)$ shifts for unsubstituted (u) cluster positions in 9-X- and 9,12-X_2-*o*-carboranes ($g \times 10^2$ values in parentheses).

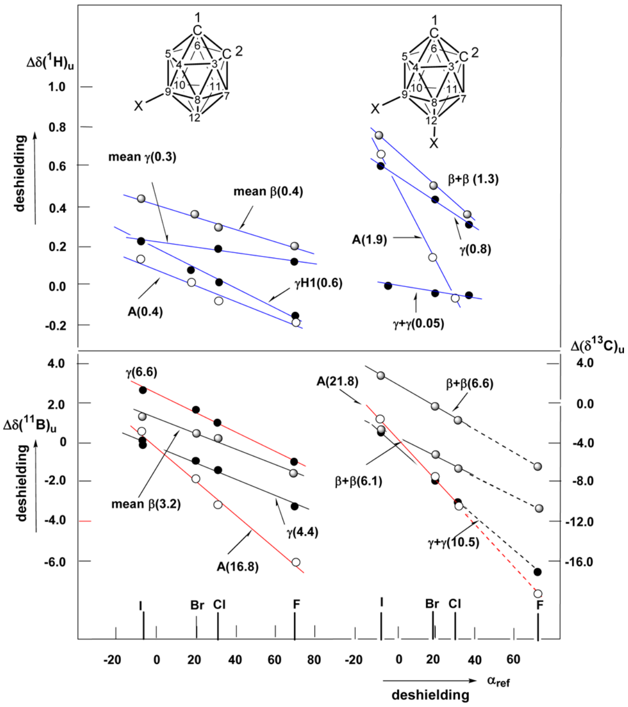

Figure 5. A plot of $\Delta\delta(^{11}B)_u$ (192.6 MHz, black lines), $\Delta\delta(^{13}C)_u$ (150.9 MHz, red lines), and $\Delta\delta(^{1}H)_u$ (600.2 MHz, blue lines) shift changes vs α_{ref} shifts for unsubstituted (u) cluster positions for halogenated *closo*-1,2-$C_2B_{11}H_{11}$-9-X and 1,2-$C_2B_{11}H_{10}$-9,12-X_2 compounds ($g \times 10^2$ values in parentheses). Measured in $CDCl_3$; for $\Delta\delta$ values see Supporting Information, Figure S1.

all data points, inclusive of those for F, lie on the line. The reason is that the α_{ref} scale reflects only electron-withdrawing effects at the substituted site and thus removes the variances that $\alpha(^{11}B)$ shifts exhibit for individual B cages and sites of substitution[4] due to back-donation of substituent nonbonding electrons to the cluster. As a result, both experimental $\alpha(^{11}B)$ or $\alpha(^{13}C)$ and α_{ref} scales can be used for the ASC assessment of substituent effects.

Furthermore, comparison of the *g* factors for mono- and disubstituted compounds in Figure 5 clearly suggests that the sensitivity in all unsubstituted sites of the *o*-carborane cage approximately doubles after introducing one more substituent, in agreement with earlier proposed shift additivity rules.[4,16−22] It is also obvious that the resulting A(^{13}C and ^{1}H) effects in the disubstituted series derive from the combined A + *β* effect in the C1,2 vertexes. In addition, the shift diagrams can be used for accurate predictions of NMR shifts for all nuclei involved (see the dotted lines for the elusive 9,12-F_2 derivative and the predicted spectrum in Figures 5 and S1).

The disubstituted *o*-carborane series was supplemented in this work by the preparation of new 9,12-Cl,X *o*-carborane derivatives (where X = Br and I) that contain two different halogens in antipodal sites with respect to CH1,2. The diagrams in Figure 6 reflect shift accumulation effects invoked by the two different halogens at unsubstituted positions.

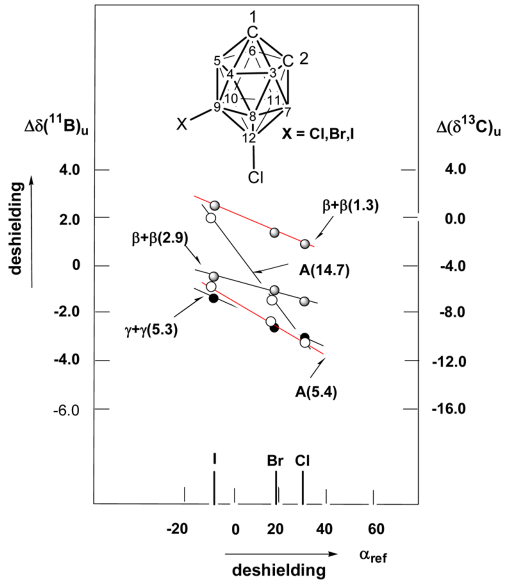

Figure 6. A plot of $\Delta\delta(^{11}B)_u$ (black lines) and $\Delta\delta(^{13}C)_u$ (red lines)shift changes vs α_{ref} shifts for unsubstituted cluster positions in *closo*-1,2-$C_2B_{10}H_{10}$-9,12-ClX compounds; $g \times 10^2$ values in parentheses. Measured in $CDCl_3$; for $\Delta\delta$ values see Supporting Information, Figure S1.

The supplementary Figure 7 demonstrates the validity of linear behavior for 9-R substituted *o*-carborane derivatives (R =

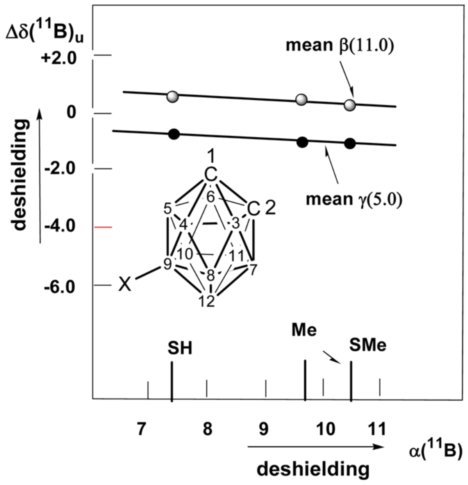

Figure 7. A plot of $\Delta\delta(^{11}B)_u$ shift changes vs $\alpha(^{11}B)$ shifts for unsubstituted (u) cluster positions in *closo*-1,2-$C_2B_{11}H_{11}$-9-R compounds ($g \times 10^2$ values in parentheses). Measured in $CDCl_3$; 64.18 MHz ^{11}B data from ref 4.

Me, SH, and SMe) bearing other than halogen substituents on the cage.[4] Unfortunately, ^{13}C and complete ^{1}H parameters still remain unknown, and it is therefore impossible to define the A(^{13}C) shift and ^{1}H behavior.

A linear trend can be also traced in the NMR spectra of C-substituted 1-R-*closo*-1,2-$C_2B_{10}H_{11}$ compounds, which is certainly the most studied field of *o*-carborane chemistry. However, key derivatives were prepared in early stages of B chemistry, and the data could not be considered. It was really difficult to find a suitable set of structurally similar compounds the NMR data of which have been collected under comparable conditions; results from different laboratories cannot be often compared, too. Among the plethora of various derivatives we found two sufficiently long series of diverse simple substitution on the carbon vertex. The ASC correlation picture is illustrated in Figure 8. The lower diagram shows the A-shift/α_{ref} correlation for compounds equipped with functionalities of broadly different character, which may perhaps account for the apparent dispersity (max ≈ 2 ppm) around the correlation line. No ^{13}C or ^{1}H measurements in this series have been reported by the author.[4] The upper diagram (note the fine ^{13}C scale) relates to the derivatives of 1-Me *o*-carborane[23] that exhibit a narrow span of α values and a good linear behavior on correlation with the experimental $\alpha(^{13}C)$ shifts. An unusual feature is the $\beta(^{13}C)$ deshielding trend ($g = -180$, relative to $CDCl_3$ standard) for C2 vertexes neighboring the substituted C1 atom, which must be taken with caution, as the authors did not quote the $\Delta\delta$ shifts in acetone-d_6.

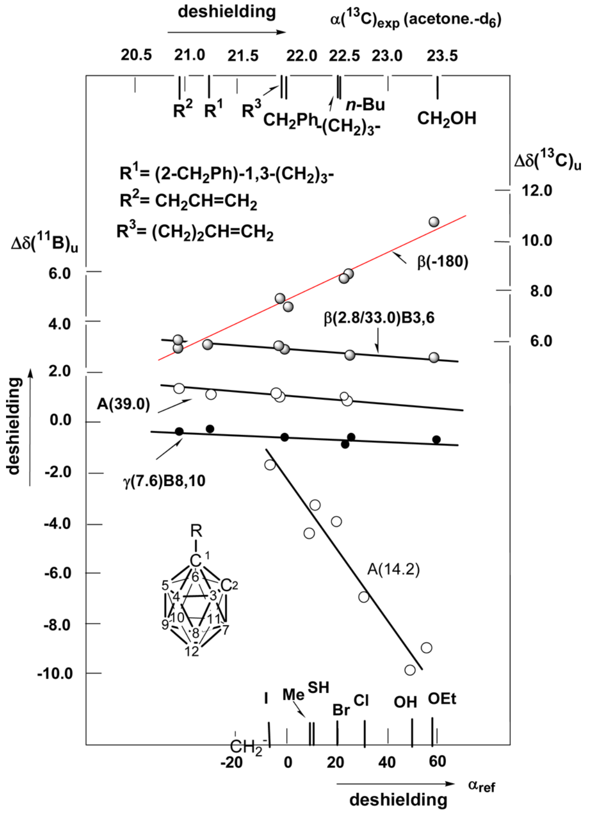

Figure 8. (upper) A plot of $\Delta\delta(^{11}B)_u$ (163.5 MHz, black lines) and $\Delta\delta(^{13}C)_u$ (125.75 MHz, red line) shift changes vs $\alpha(^{13}C)_{exp}$-shifts (acetone-d_6) for unsubstituted cluster positions in 1-R-*closo*-1,2-$C_2B_{10}H_{11}$ compounds[23] ($g \times 10_2$ values in parentheses). (bottom) A plot of $\Delta\delta(^{11}B)_u$ (64.18 MHz, $CDCl_3$, black line) shift changes[4] vs α_{ref} shifts for A-positions for various 1-R substituents.

The ASC correlation diagrams for the less-explored 3-R derivatives (R = I, Br, alkyls, and aryls[24−26]) are illustrated in Figure 9. Except for the 3-I derivative,[25] no ^{11}B assignments were reported, and therefore we dared to assign tentatively only some of the resonances. The ^{11}B spectra for halogen and alkyl/aryl-substituted compounds exhibit a standard A-shift behavior (g = 17.0), but there is a different diagram for EWG-substitution[13] (F and amino derivatives; see the more detailed view in the bottom diagram). Of interest is the exceptionally low sensitivity and the unusualy mild trend for deshielding in the otherwise strongly shielded antipodal B10 sites for EWG (g = −4.8) together with a strong γ-shielding trend for B6 atoms (g = 44.0) and a strong β-deshielding at B8 vertexes (g = −12.7). The diagram also allows for predicting the $\delta(^{13}C)$ shift = 57.0 ppm for the 3-F compound. Nevertheless, a more reliable insight into the 3-substituted family would be provided if the ^{11}B spectra were definitely assigned.

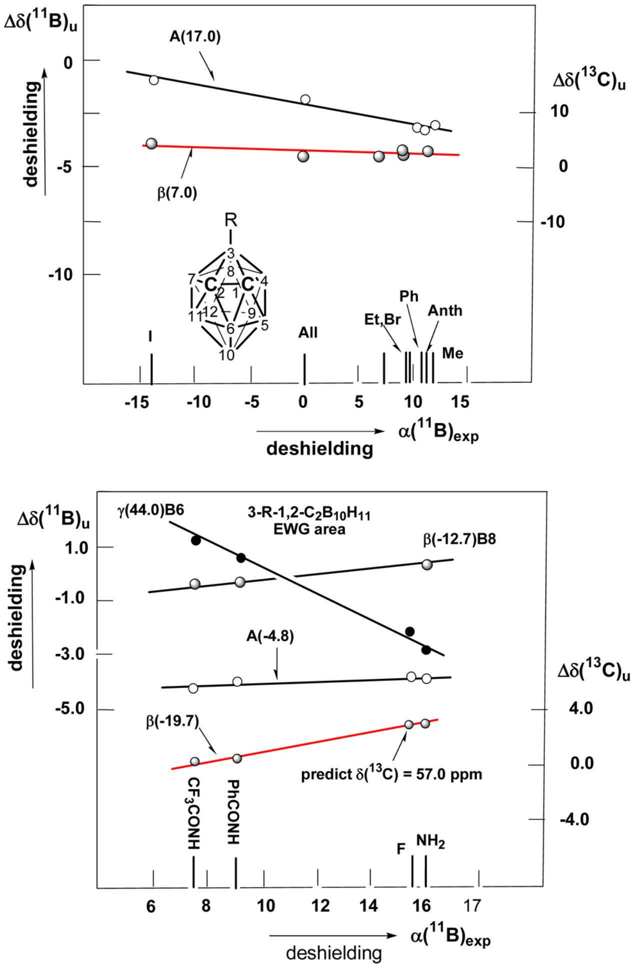

Figure 9. (upper) A plot of $\Delta\delta(^{11}B)_u$ (black line) and $\Delta\delta(^{13}C)_u$ (red line) shift changes vs $\alpha(^{11}B)_{exp}$-shifts ($CDCl_3$) for unsubstituted (u) cluster positions in *closo*-1,2-$C_2B_{10}H_{11}$-3-R-compounds (mean $\Delta\delta/g \times 10^2$ values in parentheses). (bottom) Diagrams for a group of EWG substituents.

The 4-substituted *o*-carborane derivatives have so far been very rare,[27] and a contiguous series suitable for ASC treatment has not been available.

Table 1. Mean Shift ($\Delta\delta$)/Sensitivity (g)/Max Deviation (ppm) Values for Unsubstituted Positions for Groups of Specifically Substituted *o*-Carborane Derivatives

series	β-shift	γ-shift	A-shift
1-R alkyls	2.8/33.0/0.2[a] 8.3/−180.0/0.3[b]	−0.08/7.6/0.2[a]	0.9/39.0/0.2[a]
1-R others			−6.0/14.2/2.0[a]
3-R	4.0/7.0/0.3[b]		−2.0/17.0/0.3[a]
3-R EWG	0.0/−12.7/0.2[a] 1.8/−19.7/0.2[b]	−0.5/44.0/0.3[a]	−3.8/−4.8/0.3[a]
9-X halogens	0.5/3.5/0.1[a] 0.35/0.4/0.02[c]	−0.9/6.6/0.1[a] 0.0/19.0/0.0[b] 0.22/0.3/0.01[c] 0.10/1.0/0.02[c]	−4.0/44.0/0.1[b] 0.05/0.8/0.01[c]
9-R aryls		−1.5/9.5/0.1[b]	−5.5/15.0/0.1[b]
9-R others	0.5/11.0[a]	−1.0/5.0[a]	
9-R EWG	−0.7/11.0/0.1[a] −4.0//28/0.2[b]	−2.3/14.0/0.1[a]	−12.0/63.0/0.3[b]
9,12-X_2 halogens	1.5/9.5/0.2[a] 0.55/1.6/0.02[c]	−1.5/15.1/0.1[a] 0.45/1.0/0.02[c] −0.05/0.1/0.0[c]	−5.0/38.0/0.2[b] 0.3/3.0/0.01[c]
9,12-X_2 aryls	1.5/6.0/0.1[a]	−1.5/15.0/0.1[b]	−4.5/40.0/0.0[b]

[a] ^{11}B-shift. [b] ^{13}C-shift. [c] ^{1}H-shift.

Table 1 shows that mean $\Delta\delta$ shifts (defined by positioning of the center of the correlation line) usually exhibit shielding growing in the series $\beta < \gamma <$ A, depending on the substitution site and type of the substituent. Maximum deviations from the correlation line are in most cases within the ranges of ±0.3 ppm for ^{11}B and ^{13}C and of ±0.02 ppm for ^{1}H nuclei. Comparison of absolute g values in Table 1 is in accord with the prevailing hierarchy of sensitivity of substituent shifts toward substituent changes: A $\gg \beta \geq \gamma$. The A-effect is thus the most important feature of the unsubstituted sphere, being typically of similar magnitude for comparable derivatives discussed in this work ($g \approx$ 15−40 for ^{11}B; 40−80 for ^{13}C), though there are exceptions for EWG substitution. Moreover, the shielding trends invoked in unsubstituted positions are in most cases inversed to those observed at substituted sites. For example, in the 3- and 9-substituted series the shielding order in A- and γ-positioned vertexes is inversed to that observed in α-positions.

The concept behind the ASC phenomenon may consist in synergic activation of the + I and the + R resonance effects,[4] which is in some respects analogical to substituent effects on the benzene ring. The + I effect seems to operate mostly at the α-site, while the + R effect is associated with electron donation from the substituent electron pair to the substituted atom and afterward to the skeleton as a whole, the + R effect being enhanced by electrodeficiency at the cage α-vertex. Both of these effects seem to be transmitted via cluster B−B, C−B, and C−C bonds on the surface of the electron-deficient pseudoaromatic carborane core.[28]

CONCLUSIONS

The ASC method provides best results when NMR experiments are done under identical, standard conditions, with highest possible resolution. Evidently, the ASC parameters differ for individual cluster shapes and sites, in particular, for specific substituent groups (halogens, alkyls, aryls, amines, etc). As demonstrated on a selected series of simple *o*-carborane derivatives, the ASC approach has unambiguously revealed inter-relations among chemical shifts operating within the cluster space that hold for all nuclei involved in the skeletal bonding. The main feature of the method is the trend for linear correlation between α-shifts (α_{ref}, $\alpha(^{13}\mathrm{C})_{\mathrm{exp}}$ or $\alpha(^{11}\mathrm{B})_{\mathrm{exp}}$) and those induced in unsubstituted positions. Simply, all $\Delta\delta$ changes in all cluster sites derive from the α-shift and can be, for the first time, assessed quantitatively (see Table 1). The easily obtainable g factors resulting from the method reflect the measure of sensitivity of a given cage position to substituent changes, apart from the fact that they take shift additivity effects into account, too.

The ASC method becomes an important tool for quantitative (numerical) assessment of substituent NMR effects that is generally applicable to all *exo*-substituted boron-cluster systems. Nowadays, when substitution reactions dominate B-cluster area and NMR methods have become absolutely necessary for structural investigations, any contribution to the recognition of substitution phenomena might be helpful; extensions of the ASC approach to other B-clusters are in progress in our laboratories. Insights into the background of the ASC phenomenon might perhaps call attention of theoretical chemists as well.

EXPERIMENTAL SECTION

Materials and Methods. All the reactions associated with the synthesis of the haloderivatives of *o*-carborane were performed under argon atmosphere. Dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other conventional chemicals were of reagent or analytical grade and were used as purchased. High-resolution NMR spectroscopy was performed in the $CDCl_3$ solvent (296 K) at field strength of 14.1 T (600 Mz for ^{1}H, 192.6 Hz for ^{11}B, and 150.9 Mz for ^{13}C), inclusive of ^{11}B HMQC and [^{11}B−^{11}B] COSY[2] pulse sequences, which led to complete assignments of all resonances to individual cage BH units. Chemical shifts in Figure S1 are given in parts per million to high-frequency (low field) of Ξ = 32.083 971 MHz (nominally $F_3B \times OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), Ξ = 25.144 MHz for ^{13}C (quoted ±0.5 ppm), and Ξ = 100 MHz for ^{1}H (quoted ±0.05 ppm), Ξ is defined as in ref 29, and the solvent resonances were used as internal secondary standards. The g factors relating to individual cluster sites were determined either graphically or calculated on the basis of $\Delta\delta$ values given in Figure S1 (for haloderivatives) and those calculated on the basis of literature data. The synthesis of haloderivatives outlined below is based on modification of previously reported procedures.[14,30]

***closo*-1,2-$C_2B_{10}H_{11}$-9-X and *closo*-1,2-$C_2B_{10}H_{10}$-9,12-X_2 Derivatives.** A solution of *o*-carborane (150 mg, 1.04 mmol) in CCl_4 (10 mL) was treated with anhydrous $AlCl_3$ (~10 mg), and the mixture was stirred for 24 h at room temperature. After this time, monitoring by ^{11}B NMR revealed complete disappearance of the B9 doublet signal of **1** and indicated a formation of a mixture of 9-Cl and 9,12-Cl_2 derivatives. The mixture was carefully treated with water (5 mL) and CH_2Cl_2 (20 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated with ~5 g of silica gel. The material remaining after evaporation of the solvent was mounted onto the top of a silica gel packed liquid chromatography (LC) column (~2.5 × 30 cm), which was developed with 15% CH_2Cl_2−hexane to collect several fractions. These were checked by ^{11}B NMR for purity. Fractions containing pure products were combined, evaporated to dryness, and subjected to vacuum sublimation at ~100−120 °C (bath) to isolate

~60% and 15% of 9-Cl and 9,12-Cl_2. The 9-Br and 9,12-Br_2 compounds were isolated in a similar manner from the room-temperature bromination with Br_2 (~1.5 molar excess) in CS_2 (yields ~52 and 17%, respectively) in the presence of $AlCl_3$. The 9-I and 9,12-I_2 compounds were obtained in a similar way from the $AlCl_3$-catalyzed reaction with elemental I_2 in refluxing benzene. All the compounds were characterized by NMR (see Supporting Information, Figure S1; for selected NMR measurements see Figures S2−S19).

***closo*-1,2-$C_2B_{10}H_{11}$-9-F.** The literature procedure was employed, except that *n*-hexane was used as a solvent (yield ≈ 35%).

***closo*-1,2-$C_2B_{10}H_{10}$-9,12-ClX (where X = Br and I) Derivatives.** To the solution of 9-halocarboranes *closo*-1,2-$C_2B_{10}H_{10}$-9-X (X = Br and I, reaction scale ~1 mmol) in dried CCl_4 was added anhydrous $AlCl_3$ (~0.1 mmol), and the mixture was stirred overnight at ambient temperature. The colorless solution was decanted from the brown oil, CCl_4 was removed in vacuo, and the rest was purified by flash chromatography on a silica gel substrate, using a benzene−hexane (1:3) mixture as the mobile phase. The corresponding 9,12-ClX dihalocarboranes were isolated as white crystalline solids in 85−90% yields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01023.

> Graphical representation of ^{11}B, ^{13}C, and ^{1}H NMR spectra for 9-X, 9,12-X_2, and 9,12-ClX-substituted *o*-carboranes with numerical chemical shift values. Examples of authentic NMR measurements on *closo*-1,2-$C_2B_{10}H_{10}$-9,-X (where X = Cl and F) and *closo*-1,2-$C_2B_{10}H_{10}$-9,12-ClBr dicarbaboranes (PDF)

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Notes

The authors declare no competing financial interest.

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