Mechanism of the Antipodal Effect with Borane Cages

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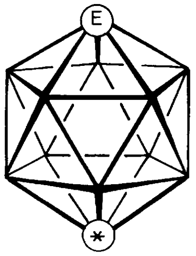
With the $EB_{11}H_{11}$ (**1**) and EB_9H_9 (**2**) series, CNDO/2 and extended Hückel type calculations show that with decreasing electron density on the vertex E: $AlR^{2-} > BH^{2-} > CH^- > NH > S$ the electron density on the antipodal skeletal atom decreases proportionally in the tangential p_x and p_y (π) atomic orbitals and increases in the radial p_z orbital through both series; this explains contradictory information about the electron density on the antipodal atom, a low electron density being indicated by the ^{11}B NMR chemical shift and a high one being deduced from chemical behaviour.

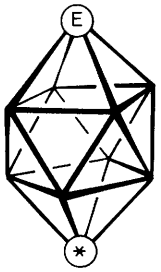
Transfer of electrons or electronic perturbations through classical π systems ($C=C$, $C=N$, $N=N$, aromatic systems, *etc.*) is well understood. In contrast the situation is much less well understood with compounds composed of electron-deficient atoms (B, transition metals, *etc.*) whose structure consists of polyhedra (*closo*, $2n + 2$ electrons) or their fragments (*nido*, $2n + 4$, *arachno* $2n + 6$ electrons).

The most straightforward indicator of the electronic changes in boron cage molecules of type (**1**) and (**2**) is the NMR antipodal (*A*) effect both of the $+M$ type substituent X[1] and of the heterovertex E.[2—4] The first shifts the NMR signal of the antipodal skeletal atom to higher field by 1—15 p.p.m. for X = I, Br, Cl, SR, F, or OR [I in (**1**)][1,2,5,6] while the second shifts the antipodal atom signal to lower or higher field (compared with E = BH) in proportion to the change in electron density on E,[3] namely by 34.0,[7] 8.4,[8] 0, and −10.2[9] p.p.m. for S, CH^-, BH^{2-}, and $AlMe^{2-}$, respectively [II in (**1**)], and by 73.5, 61,[10] 31.8, and 0 p.p.m. for S, NH, CH^-, and BH^{2-}, respectively [II in (**2**)]. From a few comparable compounds it follows that the *A* effect in (**2**) is more than twice as great as that in (**1**).[3] The sign of the *A* shift thus implies an increase in electron density on the atom caused by the $+M$ substituent and a decrease caused by the positive vertex E. In fact, reverse effects were observed chemically; a decrease in electron density at the 12-position was found in the halogenation of the anions $XB_{12}H_{11}^{2-}$ (X = Cl, Br, or I)[11] affording largely 1,7- and no 1,12- dihalogen substituted isomers, while an increase was observed in the deuteriation of the anion $CB_{11}H_{12}^-$ proceeding preferentially in the antipodal position.[12]

In this communication we focus on the most marked effect, the antipodal effect of a heterovertex E in both skeletons (**1**) and (**2**). Using CNDO/2 and extended Hückel type (EHT)



(**1**)



(**2**)

Ⓔ I $E = (B{-}X)^{2-}$; X = I, Br, Cl, SR, F, OR
II $E = AlR^{2-}$, BH^{2-}, CH^-, NH, S

⊛ antipodal atom

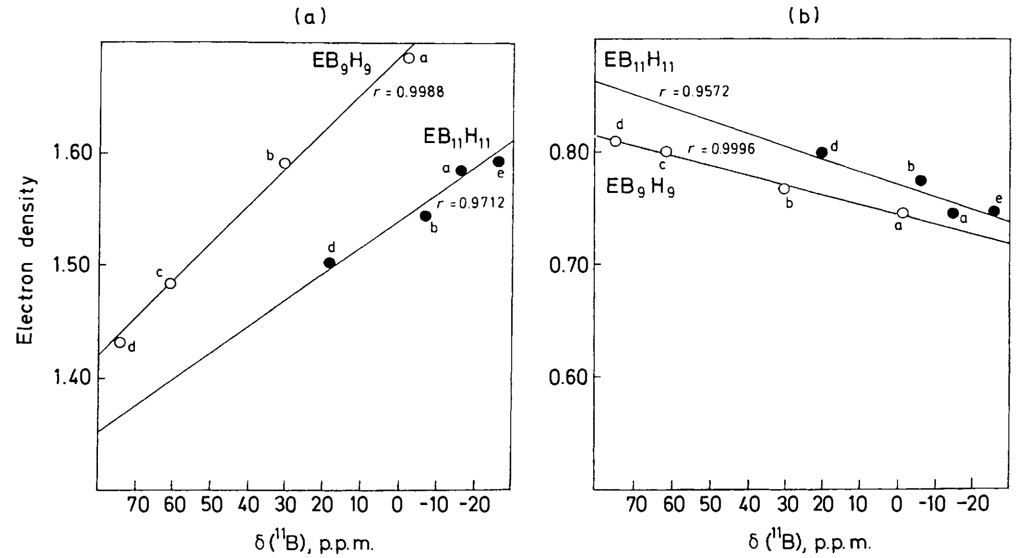
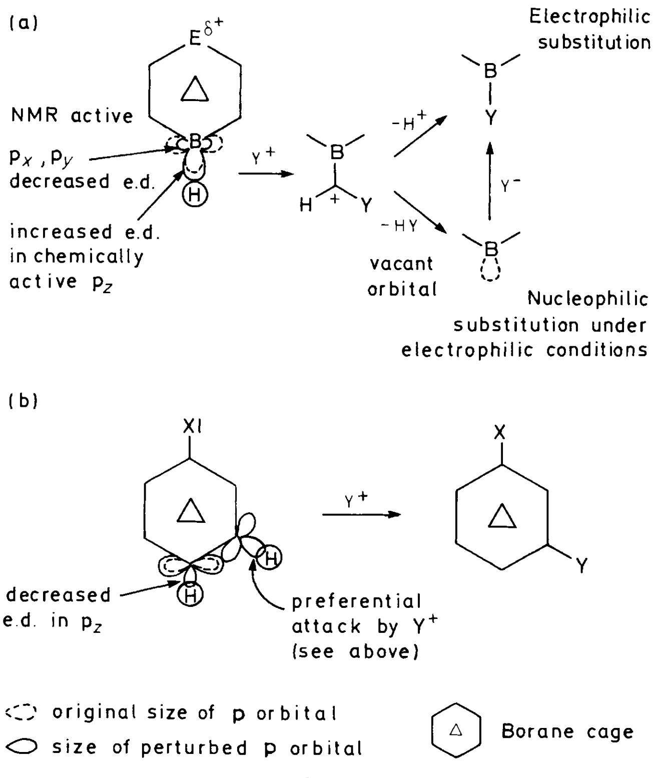


Figure 1. Correlation between the ^{11}B chemical shift of the antipodal B atoms [δ(^{11}B) in p.p.m.] with compounds (**1**), II (●) and (**2**), II (○) for E = (a) BH^{2-}, (b) CH^-, (c) NH, (d) S, and (e) $AlMe^{2-}$, and CNDO/2 electron densities (e.d.) in (a) p_x + p_y and (b) p_z orbitals.



Scheme 1

methods we have found that the electron density decreases in the tangential p_x, p_y (π) orbitals and increases in the axial p_z orbital of the antipodal atom with a decrease in electron density on the vertex E in the order: $AlMe^{2+} > BH^{2-} > CH^- > NH > S$. A significant feature is a straight line correlation between the ^{11}B chemical shift of the antipodal atom and its p_x + p_y electron density [Figure 1(a)]. A good correlation but of inverse slope was found between the δ(^{11}B) value and electron density of the orbital p_z [Figure 1(b)]. This is the first example of an acceptable δ(^{11}B) electron density correlation to our knowledge.

The results obtained can be explained as follows: the ^{11}B NMR chemical shift of individual nuclei is dominated mainly by the paramagnetic shielding σ_p which is caused by three main factors: the orbital expansion term corresponding to the electron density $<r^{-3}>_{2p}$, the p-electron 'imbalance' P_u, and the mean electronic excitation energy ΔE.[13] Of these, only the first is expected to play a decisive role in changes produced by the vertex E in the series (**1**) and (**2**).

As already stated, a consecutive shift of the ^{11}B signals of the antipodal atoms to lower magnetic field with decreasing electron density on the vertices E indicates a decrease in electron density on the antipodal atoms in the series (**1**) and (**2**). The quantum chemical calculations (CNDO/2, EHT) indicate, however, that such an effect is reflected only with the tangential p_x, p_y orbitals which can be therefore considered as the NMR-active ones. In contrast, the radial p_z orbitals directed to the exo hydrogen atoms on antipodal atoms show an increased electron density with species (**1**), II and (**2**), II. This documents a transfer of a part of the electrons from the π to the exo p_z orbitals of the antipodal atoms, and thus substantiates preferential electrophilic deuteriation of the anion $CB_{11}H_{12}^-$ in the antipodal position[12] (Scheme 1, $Y^+ = D^+$). Hence, we can consider such p_z orbitals as the chemically active ones, and propose the probable mechanism of electrophilic substitution as shown in Scheme 1a.

Vice versa, we can assume that an increase in electron density in π orbitals, stemming from the introduction of a negative vertex (*e.g.* E = $AlMe^{2-}$) or, predominantly, from an introduction of a $+M$ type substituent X into the E position [E = BX^{2-} in (**1**), I and (**2**), I] causes at the antipodal atom an increase in electron density in π orbitals (*i.e.* an *A* shift to higher magnetic field) and a decrease in electron density in the exo p_z orbitals (Scheme 1b). This could explain the unexpected dominant electrophilic substitution of the halogen-substituted $B_{12}H_{11}^{2-}$ in the '*m*'-position[11] (Scheme 1b) and not in the antipodal position, as follows from NMR considerations, or in the '*o*'-position as predicted by calculations[14] and seemingly corroborated by NMR data.[15] A confirmation of this assumption will need a more efficient quantum chemical method of calculation, as CNDO/2 and EHT showed only insignificant change caused even by the very efficient F substituent.

The results fully confirm our hypothesis presented recently[7] and give a deeper insight into the mechanism of the antipodal effect discussed in 1977.[1]

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