Background of the Nuclear Magnetic Resonance Antipodal Shift Induced by Substituents; an Analogy of the Mesomeric Effect with Borane Skeletons

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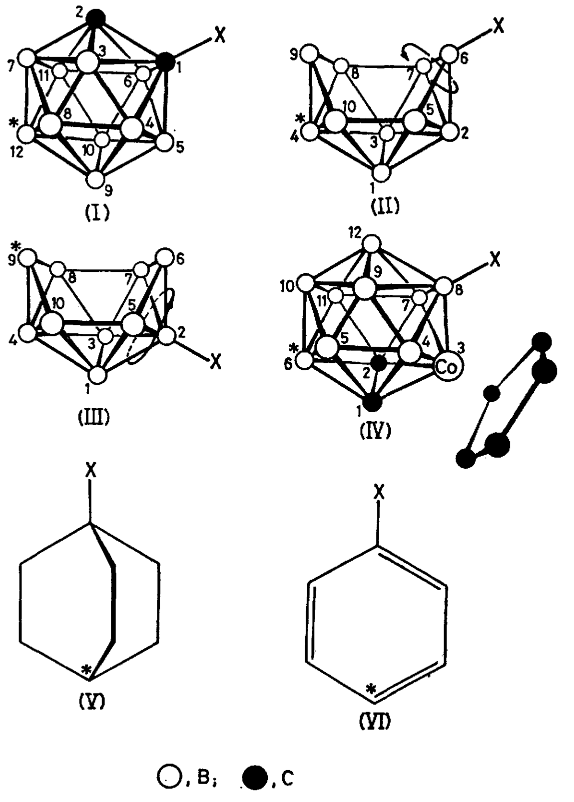
Summary A range of substituents in those boranes or heteroboranes whose molecular structure is based on the icosahedron produce distinct n.m.r. chemical shifts at the cage atom antipodal to the point of substitution; such shifts can be correlated with the ^{13}C chemical shift of the *para*-position in monosubstituted benzenes, and a parallelism, but not an identity, between 'antipodal' and 'mesomeric' effects is suggested.

IN contrast to the common nuclei ^{1}H, ^{13}C, ^{19}F, ^{31}P *etc.*, the n.m.r. behaviour of ^{11}B nuclei located in borane frameworks shows so many irregularities that the ^{11}B chemical shift has not been generally used as an identification tool. Recently we have reported several empirical rules which make it possible to assign particular signals to appropriate boron atoms, and to use ^{11}B chemical shifts for a detailed structural determination of borane derivatives.[1–5] We called one of the n.m.r. regularities the 'antipodal shift',[2–4] and several papers have since substantiated its existence.[6–9] The 'antipodal shift,' δ_A, arises from the presence of a substituent X on a borane framework which causes a shift of the antipodal (*i.e.* opposite) boron atom to higher field, and the shift has been suggested to be proportional to the Sanderson electronegativity of X.[2,3] It was subsequently found that the influence of substituents is transferred, in polyhedral borane frameworks, not only from boron to boron[2–4,6–9] but also to other antipodal atoms such as carbon[3,4,6] or phosphorus,[6] and in the reverse direction from carbon to an antipodal boron.[7,8] Although in all cases the ^{11}B or ^{13}C δ_A values form a mutually comparable series, the nature of the antipodal effect (A-effect) remains obscure. We now report results which indicate that the A-effect is analogous to the well known mesomeric effect found in organic π-electron systems.



For X = Cl, Br, and I, δ^*_A (I): 4·3, 3·4, and 1·2; (II): 3·8, 2·6, and 0·9; and (III): 4·1, 2·6, and 1·1, respectively; for X = F, Cl, Br, and I, δ^*_A (IV): 7·5, 4·8, 3·7, and 1·5, and (VI): 4·4, 2·0, 1·0, and − 1·0, respectively; and for X = F, Cl, and Br, δ^*_A (V): −0·3, 0·6, and 1·2, respectively.

With 1-bromo-1,12-dicarba-*closo*-dodecaborane(12) the antipodal shift is transmitted from carbon to carbon (^{13}C δ_A = 6·8 p.p.m.,[10] and the shift is very similar when the substituent is on a boron atom of the cage, *e.g.* for the C-2 atom in 9-Br-1,2-$C_2B_{10}H_{11}$ ^{13}C δ_A = 6·9 p.p.m.). This led us to compare the n.m.r. characteristics of selected borane frameworks, namely 1-X-1,2-$C_2B_{10}H_{11}$ (I), 2-$XB_{10}H_{13}$ (II), 6-$XB_{10}H_{13}$ (III), and 8-X-1,2-C_2-3-(C_5H_5Co)-B_9H_{10} (IV), with the carbon ring compounds 1-X-bicyclo-octanes (V), and substituted benzenes (VI). The significant point which emerges is that a good linear correlation exists between the ^{11}B δ_A values for (I)—(IV) and the corresponding ^{13}C δ_A values for (VI) while no such correlation exists in the case of (V) [Figure, (a) and (b)]. The following conclusions may also be drawn concerning the A-shift: (i) it is not determined by the dipole moment of the X–B or X–C bonds [*cf.* the character of δ_A in (I)—(IV) differing from δ_A in (V)]; (ii) it is not associated with the 'ring current'[11] since it has practically the same value in 2-$XB_{10}H_{13}$ (II), with the substituent X on the apex of a pentagonal pyramid, as it does in 6-$XB_{10}H_{13}$ (IV), with the substituent on the vertex of an incomplete pyramid, making the presence of any 'ring current' unlikely; (iii) the Figure

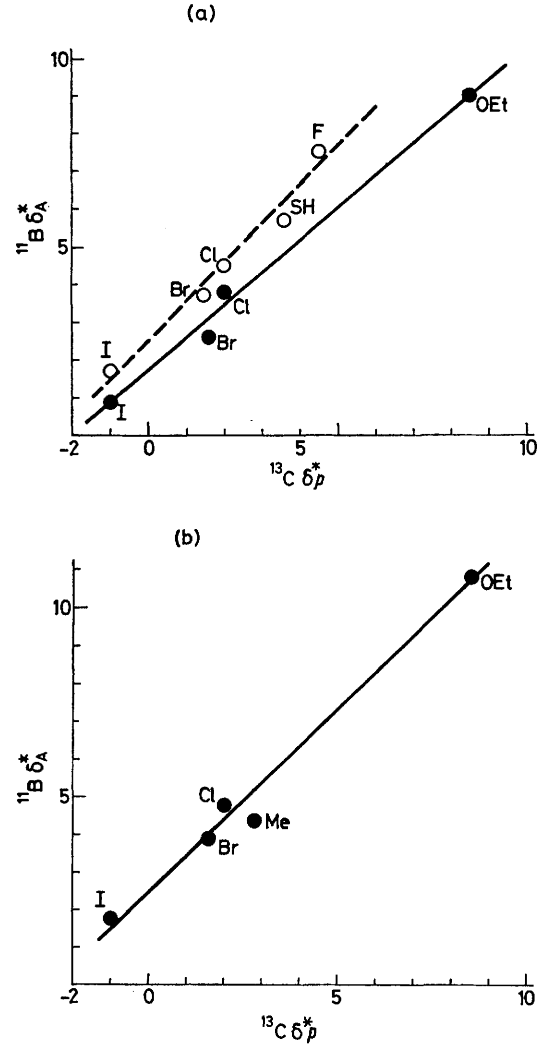


FIGURE. (a) Plot of antipodal shift ^{11}B δ_A at 6-$XB_{10}H_{13}$ (●) (R. F. Sprecher, B. E. Aufderheide, G. W. Luther III, and J. C. Carter, *J. Amer. Chem. Soc.*, 1974, **96**, 4404) and 8-X-1,2-C_2-3-C_5H_5Co-B_9H_{10} (○) (refs. 2, 3) *vs.* *para*-shift ^{13}C δ_p at X-Ph. (b) Plot of ^{11}B δ_A at 1-X-1,2-$C_2B_{10}H_{11}$ (ref. 11) *vs.* ^{13}C δ_p at X-Ph.

[(a) and (b)] indicates that it is analogous to the *para*-effect in (VI) which arises mainly as a result of the mesomeric effect. The fact that the A-effect increases generally in the order $\mathrm{I} < \mathrm{Br} < \mathrm{Cl} < \mathrm{SH} < \mathrm{F} < \mathrm{OR}$, *i.e.* in accord with the rising electron donation,[12] indicates that this property is the dominating factor and not the electronegativity[2,3] which increases in the order $\mathrm{SH} < \mathrm{I} < \mathrm{Br} < \mathrm{Cl} < \mathrm{OR} < \mathrm{F}$.[13]

A parallelism of the mesomeric (M) effect in organic π-systems with the A-effect in borane frameworks possessing no π-electrons is surprising, but may be rationalised as being the result of the transfer of several single competing effects through a system possessing a very high degree of electron delocalisation, and is supported by the following further facts: (a) the value of the A-shift is dependent upon the location of the substituent X, and decreases with increasing angle between the B–X (or C–X) bond and a dipole (or main polarisability) axis of the given molecule (*cf.* decreasing A-effect in 1-, 3-, 4-, and 8-bromo-*o*-carbaboranes of δ_A 4·2, 3·0, 2·4, and 2·6 p.p.m., respectively; (b) the presence of F or RO groups shifts most signals of a given borane framework to higher field (compared with the parent compound) corresponding to an increased electron density on these atoms[10]); (c) In a series of 1-X-*p*-carbaboranes, an increased shielding of the proton bound to the antipodal C-atom in the order $\mathrm{I} < \mathrm{Br} < \mathrm{H} < \mathrm{Cl} < \mathrm{Me}$ was observed[8] showing that in Cl and Me derivatives an electron donation from X dominates over the electron attraction.

Both the above measurements and those made on a wider range of compounds,[10] imply that, in spite of a mutual similarity, the M- and A-effects are not identical because the π-aromaticity is not identical with the 'pseudoaromaticity' of boranes which is produced by the delocalisation of electrons in an electron-deficient skeleton. However, the presence of the +M type of substituent, with the free electron pair on the atom bound to the borane framework, would allow the back-donation of the negative charge from X^- to the X^-–B bond (analogous to the +M effect) and a transfer of the electron density along a polarisability axis to the antipodal position. An effect analogous to the −M effect is impossible since the 'pseudoaromatic' borane framework has no π-electrons, and in accord with these ideas a distinct A-shift was observed with all the derivatives studied having substituents of the +M type (HO, RO, $\mathrm{Me_3SiO}$, AcO, F, Cl, Br, I, HS, RS, NCS, R, or Ph), while the presence of substituents of the −M type ($\mathrm{CO_2H}$, $\mathrm{CO_2R}$, COCl, or CN) produced no A-shift. The detailed mechanism of the A-effect is under investigation.

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