ANTIPODAL AND VICINAL SHIFT EFFECTS IN ^{11}B, ^{13}C, AND ^{1}H NMR SPECTRA OF SUBSTITUTED DICARBA-*closo*-DODECABORANES(12)*

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Received April 25th, 1975

Replacement of a hydrogen atom by an electronegative atom in an icosahedral skeleton gives rise to perceptible shielding of the antipodal atom (the antipodal shift effect) and to deshielding of vicinal atoms (the vicinal shift effect). These effects are generally encountered with 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes(12) and can be utilized for assigning the NMR signals of their derivatives. It has been found that the chemical shifts of the skeletal atoms in the icosahedron are considerably affected by the electronegativity of the antipodal atom in the skeleton.

Recently we found that substituent X, bound to the $B_{(8)}$ atom in 3-(η-cyclopentadienyl)-1,2-dicarba-3-cobalta-*closo*-dodecaborane(12), causes distinct shielding (+3 to +10 p.p.m.) of the opposite, *i.e.* the antipodal, $B_{(6)}$ atom and a shift of its signal to higher field (compared with the unsubstituted substance), proportional to the electronegativity of substituent X, expressed on the Sanderson electronegativity scale[1,2]. The existence of this antipodal effect was confirmed by Siedle and coworkers[3] for 9-bromo-, 9,12-dibromo-, 8,9,12-tribromo-1,2-dicarba-*closo*-dodecaborane(12) and 9,12-dibromo-1-carba-2-phospha-*closo*-dodecaborane(11).

In this paper, the effect of the bromine atom, bound at various positions of the 1,2-dicarba-*closo*-dodecaborane skeleton, on the chemical shifts of the individual atoms in the ^{11}B, ^{13}C and ^{1}H-NMR-spectra, is investigated in greater detail.

EXPERIMENTAL

^{11}B-NMR spectra were obtained on an experimental supraconductive NMR spectrometer (University of California, Los Angeles), operating at 80·5 MHz. The spectra were measured in CS_2 and externally related to $BF_3.O(C_2H_5)_2$. ^{13}C-NMR spectra were measured at 22·63 MHz on a Bruker HX-90 NMR spectrometer in CS_2 as a solvent. ^{1}H-NMR spectra were recorded

* Part XXXVII in the series Chemistry of Boranes; Part XXXVI: This Journal *39*, 2363 (1974).

TABLE I

^{11}B, ^{13}C and ^{1}H-NMR Chemical Shifts (p.p.m.) of 1,2-$C_2B_{10}H_{12}$ (*I*) and its 3-, 4-, 8- and 9-Bromo derivatives, *Ia*—*Id* =4 identical with $B_{(4)}$, $\delta^{13}C$ related to CS_2

	Atom	*I*	*Ia*	*Ib*	*Ic*	*Id*
^{11}B	3	15·3	10·7	(12·0)	12·9	13·9
	4	13·9	10·3	8·4	11·5	12·1
	5	=4	11·8	10·0	12·7	=4
	6	=3	12·1	13·2	17·9	=3
	7	=4	=4	(12·8)	=4	12·7
	8	9·1	7·1	7·4	4·0	7·0
	9	2·0	0·5	0·4	−0·3	−1·4
	10	=8	12·1	8·0	8·6	=8
	11	=4	=5	16·3	=5	=5
	12	=9	=9	1·0	=9	−0·2
^{13}C	1	138·1	133·2	136·2	139·6	139·1
	2	=1	=1	137·1	=1	145·6
^{1}H	1-CH	3·54	3·83	3·97	3·62	3·66
	2-CH	=1	=1	3·71	=1	3·66

on a Varian XL-100 NMR spectrometer in $CDCl_3$ as a solvent and were internally related to tetramethylsilane. The superposed signals were separated using a Du Pont 310 Curve Resolver.

The methods described in the literature were employed for the preparation of 3-Br-1,2-$C_2B_{10}H_{11}$ (ref.[4]), 4-Br-1,2-$C_2B_{10}H_{11}$ (ref.[5]), 8-Br-1,2-$C_2B_{10}H_{11}$ (ref.[6]) and 9-Br-1,2-$C_2B_{10}H_{11}$ (ref.[7]).

Deuteration of 1,7-$C_2B_{10}H_{12}$

To a solution of 1 g 1,7-$C_2B_{10}H_{12}$ in 50 ml CS_2, a catalytic amount (0·1 g) of anhydrous aluminium trichloride was added; the flask containing this mixture was evacuated and cooled in a dry ice–ethanol bath. The mixture was saturated with gaseous DCl, stirred for 2 h, evacuated, cooled

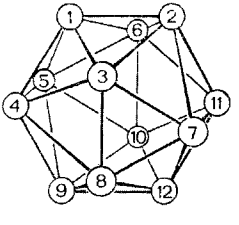


FIG. 1
Numbering of Positions in Icosahedron

and again saturated with gaseous DCl. This procedure was repeated three more times. After the overall deuteration time, 12 hours, the carbon disulphide was distilled off, the residue was extracted with hexane, the hexane extract was evaporated and the residue was sublimed at 80°C and 10^{-2} Torr. According to the ^{11}B spectrum, the 1,7-dicarbadodecaborane(12) (1·0 g) contained more than 80% deuterium in the 9 and 10 positions.

RESULTS AND DISCUSSION

Antipodal and Vicinal Shift Effects Caused by the Presence of a Substituent on an Icosahedral Skeleton

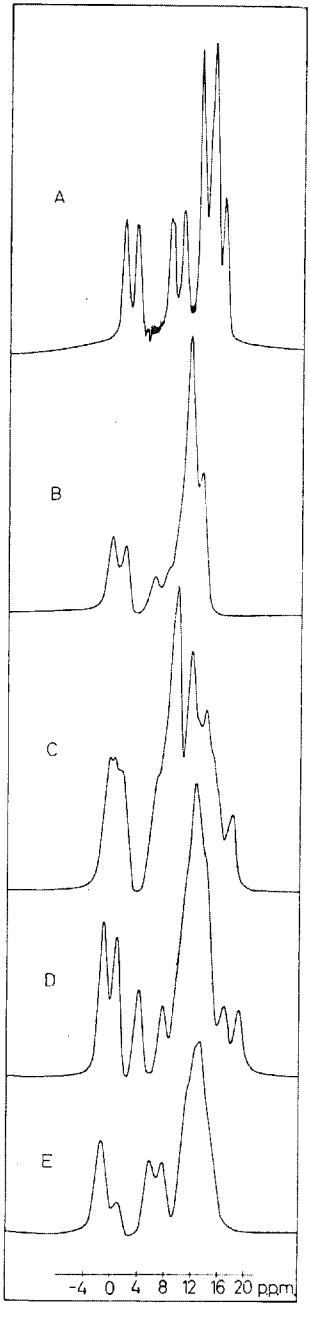
The ^{11}B-NMR spectra of 1,2-dicarba-*closo*-dodecaborane(12) (*I*) (Fig. 1) and its 3-bromo- (*Ia*), 4-bromo- (*Ib*), 8-bromo- (*Ic*) and 9-bromo derivatives (*Id*), measured at 80·5 MHz, are given in Figs 2*A*–2*E*. The positions of the individual signals and their intensities were determined using a "curve resolver" in the regions of superposition and are given in Table I.

When chemical shifts of the B atoms in the parent carborane, *I*, are graphically compared with the chemical shifts and signal intensities for 8-bromo-1,2-dicarba-*closo*-dodecaborane(12) (Fig. 3*A*), it can be seen that introduction of the substituent into position $B_{(8)}$ led to the loss of one plane of symmetry and thus to the loss of identity of atoms $8 \neq 10$, $4 = 7 \neq 5 = 11$ and $3 \neq 6$. The singlet at 4·0 p.p.m. corresponds quite unambiguously to atom $B_{(8)}$. The doublet of intensity (1) in the highest field (17·9 p.p.m.) is assigned to atom $B_{(6)}$ on the basis of the antipodal shift effect observed previously[1,2]. Of the two remaining doublets of intensity (1), the signal at 8·6 p.p.m. is assigned to atom $B_{(10)}$ and the other, located at 12·9 p.p.m., to atom $B_{(3)}$. It is evident from the graphical comparison (Fig. 3A) that substitution by bromine in position $B_{(8)}$ gives rise to a perceptible shift of the signals of vicinal $B_{(9,12)}$ and $B_{(3)}$ atoms to a lower field (compared with the unsubstituted *ortho*-carborane) and has only a small effect on the position of the signal of atom $B_{(10)}$, located in the *meta* position. Consequently, vicinal atoms $B_{(4,7)}$ are assigned to the doublet at 11·5 p.p.m. and *meta* atoms $B_{(5,11)}$, to the doublet at 12·7 p.p.m.

On the basis of these conclusions it can be assumed that introduction of a bromine atom on an arbitrary skeletal atom in icosahedron: *1*) shifts the signal of the antipodal B atom to a higher field by +2·5 p.p.m. on average (the antipodal shift effect); *2*) shifts the signal of the vicinal B atoms to a lower field by −2·5 p.p.m. on an average (the vicinal shift effect); *3*) usually has only a small effect on atoms in the *meta* position.

These empirical rules were verified on the 9-bromo derivative (*Id*), where it was found that the changes due to the presence of the substituent have the same character and magnitude (Fig. 3*B*, Table I).

A somewhat more complicated situation arises with the 3-bromo derivative, whose spectrum contains a multiplet in the region, 8 – 14 p.p.m. with a total relative



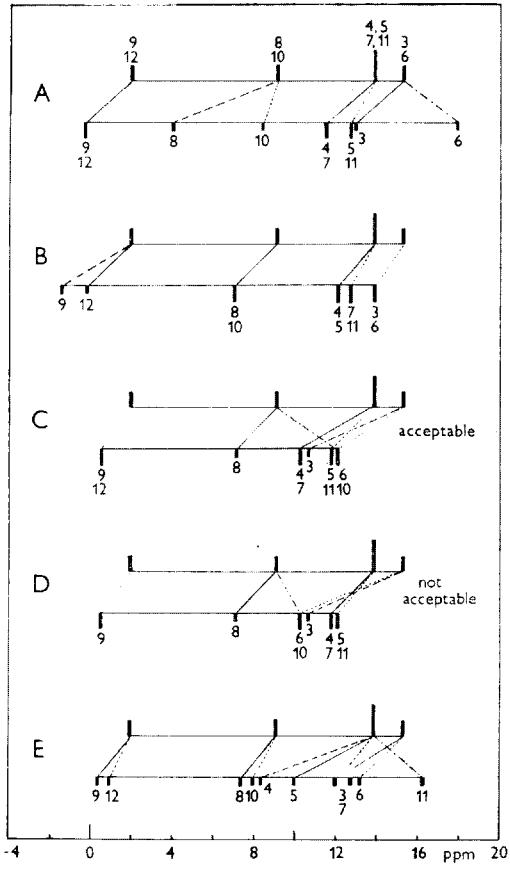


FIG. 3

Correlation of Chemical Shifts of Individual B Atoms in 1,2-Dicarba-*closo*-dodecaborane(12) and its 8-Bromo *A*, 9-Bromo *B*, 3-Bromo *C* and *D* and 4-Bromo *E* Derivatives

Changes caused by substitution ———, by a Br atom in the vicinal ———, antipodal –·–·– and *meta* position · · · · ·.

FIG. 2

The 80·5 MHz ^{11}B-NMR Spectra of 1,2-$C_2B_{10}H_{12}$ *A* and its 3-Bromo *B*, 4-Bromo *C*, 8-Bromo *D* and 9-Bromo *E* Derivatives in CS_2 Solution

intensity of 7, which should consist of five signals with relative intensities 1 : 1 : 1 : 2 : 2. However, only four signals were found during the analysis of the multiplet, at 10·3 d (2), 10·7 s (1), 11·8 d (2) and 12·1 d (2) p.p.m., among which one doublet of intensity (2) is formed by superposition of two doublets of intensity (1). From the graphical comparison (Figs 3C, 3D) it follows that variant 3D, *i.e.* the spectrum in which two doublets of intensity (1) overlap at position 10·3 p.p.m., is less probable, as anomalous magnitudes of the individual effects would have to be assumed here. A majority of the signals for 4-bromo derivative (Fig. 3E) were assigned using an analogous elimination method; then only signals in the region, 11 – 14 p.p.m., corresponding to atoms $B_{(3)}$, $B_{(6)}$ and $B_{(7)}$, are assignable with difficulty.

Similar effects caused by a substituent can also be observed in the ^{11}B-NMR spectra of 9-halogeno-[8] (Figs 4A – 4C) and 9,10-dihalogeno-1,7-dicarba-*closo*-dodecaboranes(12) (ref.[9]) (Figs 4D – 4F), of course, only assuming that the signal order for *m*-carborane is 5,12 ≪ 9,10 < 4,6,8,11 ≪ 2,3 and not 9,10 ≪ 5,12 < 4,6,8,11 ≪ ≪ 2,3 as was erroneously assumed by both the authors in the spectra of the cited bromo-*m*-carboranes[8,9] and of the parent *m*-carborane[10,11]. The correct order, identical with the former series, was indicated earlier[12,13] and verified here by deuteration of 1,7-$C_2B_{10}H_{12}$ under electrophilic conditions, during which the signal at 11·2 p.p.m. changed, indicating that it corresponds to atoms $B_{(9)}$ and $B_{(10)}$.

A perceptible effect of a substituent on the skeletal atoms can also be observed in the ^{11}B-NMR spectra of 2-halogeno-1,12-dicarbadodecaboranes[8], where the signal of the antipodal $B_{(9)}$ atom is shifted by 3 – 6·5 p.p.m. to a higher field compared with the parent carborane. The general character of the above observations is also confirmed by the ^{13}C-NMR spectra of substances *I* and *Ia – Id*, for which both the antipodal[2,3] (+7·5 p.p.m.) and the vicinal shift effect (−1·8 to −4·9 p.p.m.) were observed, which permitted assignment of all the ^{13}C signals (Table I).

The examples summarized indicate that the observed effects, caused by the presence of a substituent, have a more general character and that these effects could be caused by long range shielding combined with vicinal deshielding due to the substituent induction effect. A mechanism of both effects is under investigation.

While introduction of a halogen on a skeletal atom of an icosahedron gives rise to both long range shielding (the antipodal shift effect) and deshielding (the vicinal shift effect), only deshielding of the CH protons was observed in the ^{1}H-NMR spectra, which is the stronger, the closer the halogen atom is to the particular CH group. This indicates that the chief factor here is a change in the electronic density at the CH group, caused by the halogen induction effect. However, this is not the only effect, as the chemical shift of the CH signal of some halogeno-dicarba-*closo*-dodecaboranes(12) (*cf.* the δCH values in ref.[14]) indicates increased shielding of this proton.

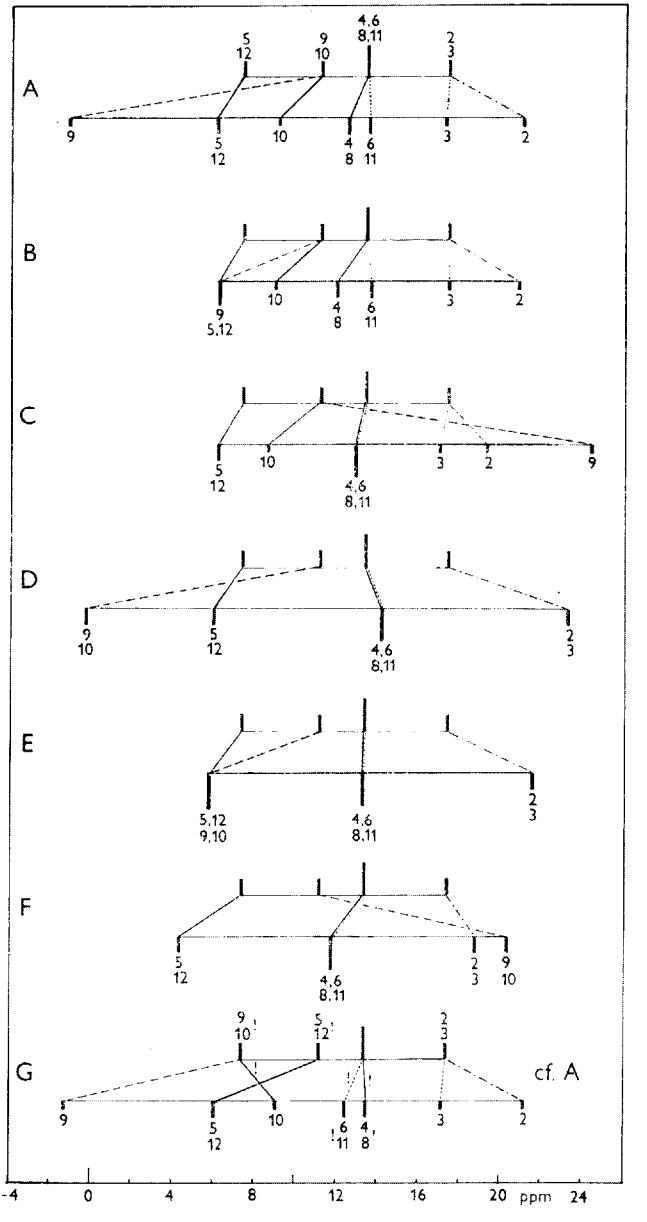


FIG. 4

Correlation of Chemical Shifts of Individual B Atoms in 1,7-Dicarba-*closo*-dodecaborane(12) and its 9-Chloro *A*, 9-Bromo *B*, 9-Iodo *C*, 9,10-Dichloro *D*, 9,10-Dibromo *E* and 9,10-Diiodo *F* Derivatives

Compare A with G where irregularities (denoted!) in the "vicinal shift effect" are caused by improper assignment of signals in ref.[8].

Antipodal Shift Effect Caused by the Presence of a Charge on a Skeletal Atom

The assignment of the individual signals for 1,2-$C_2B_{10}H_{12}$ showed that chemical shielding of the B atoms increases with decreasing electronegativity of the given atom[10]. This finding was applied[10] in assignment of the signals for 1,7-$C_2B_{10}H_{12}$ and was mathematically substantiated by Lipscomb and coworkers[11], who explained the ^{11}B chemical shifts as the result of different paramagnetic shielding of atoms in different chemical environments and obtained agreement in the signal order not only for 1,2-$C_2B_{10}H_{12}$, but also for 1,7-$C_2B_{10}H_{12}$. However, the assumed signal order for the 1,7-isomer (9,10 $\ll$ 5,12 $<$ 4,6,8,11 $\ll$ 2,3) was found, on the basis of refs[12,13] and of the present study, to be at variance with reality (5,12 $\ll$ 9,10 $<$ $<$ 4,6,8,11 $\ll$ 2,3), thus indicating that other factors also play a role here.

Recently, we formed a hypothesis[1,2,15] that the chemical shift of the signals of the skeletal atoms is significantly affected by the sign and the magnitude of the charge on the antipodal atom. This effect also plays a role in isomeric dicarbadodecaboranes(12), as the correlation of the electronegativity order for the individual skeletal atoms with the ^{11}B chemical shift for the antipodal atoms (Table II) is in full agreement with the experimental signal order, not only for 1,2-$C_2B_{10}H_{12}$, but also for the 1,7-isomer, for which the correlation of the chemical shifts with the electronegativities of the particular atoms gave an incorrect order[11]. However, the real cause of this effect is still not clear and more experimental material will be needed for its explanation.

We thank Professor F. A. L. Anet, Dr R. J. Wiersem and Dr R. R. Rietz for the measurement of the ^{11}B-NMR spectra on the experimental supraconductive NMR spectrometer at the University of California, Los Angeles.

Table II

Relationships of ^{11}B Chemical Shifts to Electronegativities of Antipodal Atoms

E atoms ordered according to increasing electronegativity; A atoms antipodal to those in the above line; S B atoms ordered according to increasing shielding.

1,2-$C_2B_{10}H_{12}$	E	C1	C2	3	6	4	5	7	11	8	10	9	12
	A	9	12	8	10	4	5	7	11	3	6	C1	C2
	S	9	12	8	10	4	5	7	11	3	6	—	—
1,7-$C_2B_{10}H_{12}$	E	C1	C7	2	3	4	6	8	11	5	12	9	10
	A	5	12	9	10	4	6	8	11	C1	C7	2	3
	S	5	12	9	10	4	6	8	11	—	—	2	3

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Translated by M. Štulíková.