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Elucidation of the Boron (^{11}B) Nuclear Magnetic Resonance Spectra of Some $B_{10}H_{12}$(ligand)$_2$ Compounds

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An earlier report of the ^{11}B nmr spectra of $B_{10}H_{12}$(ligand)$_2$ compounds has yielded an assignment of the 2,4 positions by specific labeling with bromine.[1]

We have examined the ^{11}B nmr spectra of a series of specifically labeled $B_{10}H_{12}$(ligand)$_2$ compounds with both neutral and negatively charged ligands. This has provided a complete assignment of the ^{11}B nmr of a series of these compounds.

Experimental Section

The 32.1-Mc/sec spectra were obtained with a Varian HR-100 spectrometer. Chemical shifts were measured by interpolation between the external reference, $BF_3 \cdot (C_2H_5)_2O$, and its audio side band. Spectral integrals were measured with a planimeter.

Materials.—2-Bromodecaborane was prepared as described previously and purified by recrystallization from heptane, mp 107–108°.[2,3]

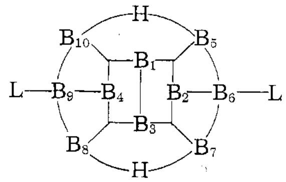
The bis(ligand)decaborane compounds [ligand = CH_3CN and $S(C_2H_5)_2$] and their 2-bromo derivatives were prepared by literature methods.[4,5]

Bis(ethyl isocyanide)decaborane was prepared by a ligand-exchange reaction of bis(diethyl sulfide)decaborane with ethyl isocyanide as recently reported.[6]

The 1,2,3,4-decaborane-d_4 prepared by a literature method[7] was generously supplied to us by J. Dobson, Indiana University. Deuterium analysis on this compound gave 3.98 atoms of deuterium/molecule.[8]

The 5,6,7,8,9,10,bridge decaborane-d_{10} was prepared by the procedure of Dupont and Hawthorne.[7] Deuterium analysis gave 5.96 atoms of deuterium/molecule.

The $Rb_2(2\text{-}BrB_{10}H_{13})$ was prepared from 2-bromodecaborane by the procedure of Muetterties for $Rb_2B_{10}H_{14}$.[9]



Results and Discussion

The previous ^{11}B nmr study of $2\text{-}BrB_{10}H_{11}[S(C_2H_5)]_2$[1] and the results obtained in this study with $2\text{-}BrB_{10}H_{11}(C_2H_5NC)_2$ and $2\text{-}BrB_{10}H_{11}(CH_3CN)_2$ (Table I) clearly indicate that the lowest field doublet (δ = 1–5 ppm) in the spectrum of this type of compound is associated with the 2,4 positions. The equivalent 5,7,8,10 positions are easily assigned by virtue of the integrated area of this doublet (4 B) relative to each of the remaining doublets (2 B). Thus there remains only the assignment of either the 6,9 or 1,3 boron atoms to elucidate completely the ^{11}B nmr spectrum for this type of compound.

Table I

Nmr Data for Some Bis(ligand)decaborane Compounds

Compound	Chemical shifts of boron positions: 2	4	5, 7, 8, 10	6, 9	1, 3
$Rb_2(2\text{-}BrB_{10}H_{13})$	1.73 s[a]	8.5 d[b] (133)	22.4 d (132)	33.6 t	41.2[c]
$B_{10}H_{12}(CH_3CN)_2$	5.7 d (137)	5.7	20.4 d (135)	31.2[c]	42.8 d (152)
$2\text{-}BrB_{10}H_{11}(CH_3CN)_2$	1.45 s	5.74 d	20.8 d (133)	31.8	41.2
$B_{10}H_{12}(C_2H_5NC)_2$	1.27 d (128)	1.27	18.3 d (136)	39.9 d[c]	44.7 d[c]
$2\text{-}BrB_{10}H_{11}(C_2H_5NC)_2$	−0.79 s		20.2 d	40.2 d (144)	
$B_{10}H_{12}[S(C_2H_5)_2]_2$	2.9 d	2.9	19.6[c]		38.7 d (147)
$1,2,3,4\text{-}D_4B_{10}H_8[S(C_2H_5)_2]_2$	4.4 s	4.4 s	20.3[c]	26[d]	39.6 s

[a] Chemical shift values in ppm with an accuracy of ±1.5 ppm unless otherwise indicated: s, singlet; d, doublet; t, triplet. [b] Number in parentheses is BH coupling constant in cps. [c] Approximate value. [d] Approximate value obtained from Figure 1D.

The spectrum of $1,2,3,4\text{-}D_4B_{10}H_8[S(C_2H_5)_2]_2$ shown in Figure 1B contains a singlet at low field attributed to the 2,4 positions and a singlet at high field which therefore must be associated with the 1,3 positions. Further confirmation of this assignment is found in the spectrum of $B_{10}H_{12}[S(C_2H_5)_2]_2$ partially deuterated in the 5,6,7,8,9,10,bridge positions (Figure 1D). This shows a partial collapse of the central peaks but no effect on the high- and low-field doublets. It had been observed previously that the high-field doublet of the $B_{10}H_{12}[S(C_2H_5)_2]_2$ spectrum was unusually sharp. One would expect a decrease in quadrupole broadening as the electric field gradient became more symmetrical. Thus it was suggested[1] that the sharp high-field doublet was associated with the higher symmetry 1,3 boron atoms as this study indicates.

In the spectrum of $B_{10}H_{12}(C_2H_5NC)_2$ (Figure 1C) the 6,9 and 1,3 positions appear as two overlapping doublets (apparent triplet) at high field. We have observed that in the spectra of all $2\text{-}BrB_{10}H_{11}$(ligand)$_2$ compounds the 1,3 doublet was broader than that found for the unsubstituted derivative. In the spectrum of $2\text{-}BrB_{10}H_{11}(C_2H_5NC)_2$ the high-field portion of the apparent triplet was considerably broadened. On this basis we suggest the assignments indicated in Figure 1C.

In the case of negative ligand derivatives such as $Rb_2B_{10}H_{14}$, the 6,9 positions had been located previously as a triplet at 38.8 ppm by proton spin decoupling.[9] However there existed an uncertainty about the assignment of the 1,3 and 2,4 positions. The spectrum of $Rb_2(2\text{-}BrB_{10}H_{13})$ shown in Figure 1A clearly indicates that the low-field doublet is associated with the 2,4 boron atoms.

Comparison of the chemical shifts of different

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(1) C. Naar-Colin and T. L. Heying, *Inorg. Chem.*, **2**, 659 (1963).

(2) M. S. Cohen and C. E. Pearl, U. S. Patent 2,990,239 (1961).

(3) The purity of all compounds was determined by satisfactory carbon, hydrogen, nitrogen, or bromine analyses obtained by J. Nemeth and associates of this department.

(4) T. L. Heying and C. Naar-Colin, *Inorg. Chem.*, **3**, 282 (1964).

(5) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).

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(7) J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 1804 (1962).

(8) Deuterium analyses were performed by J. Nemeth of this department by the combustion and falling-drop method.

(9) E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

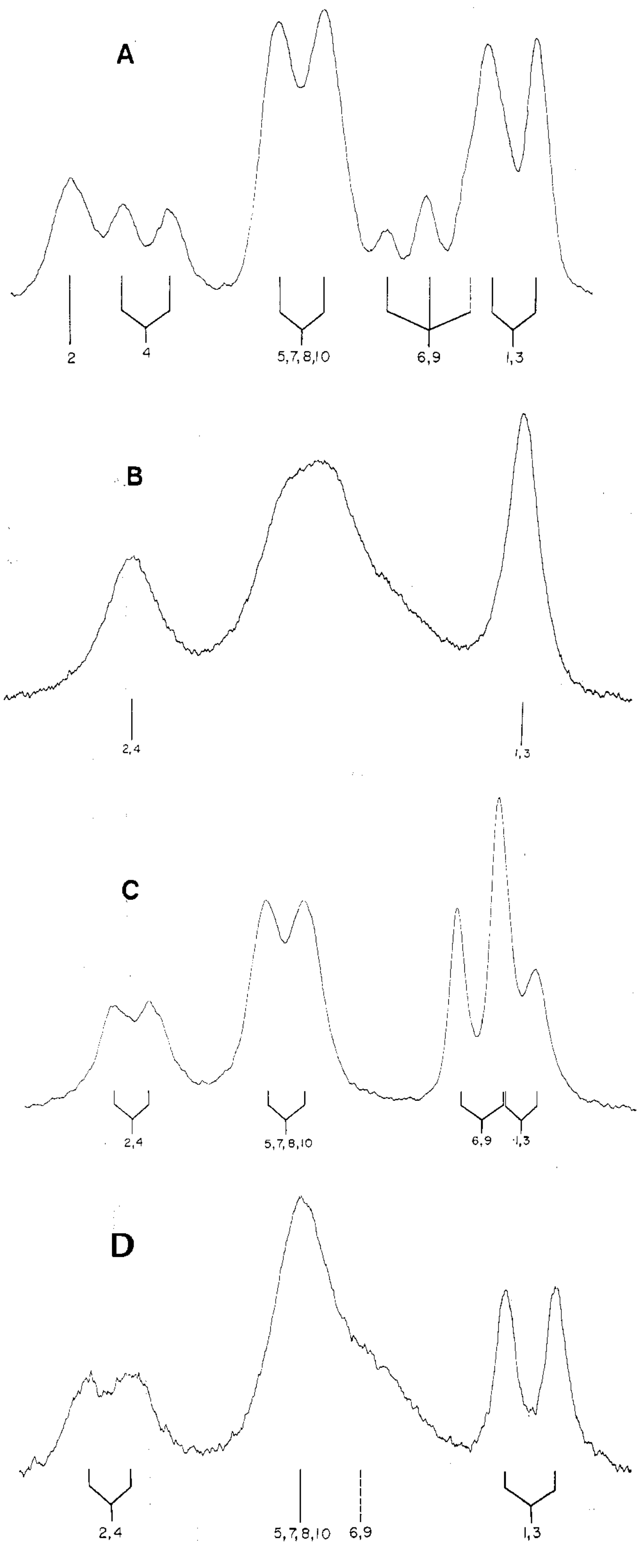

Figure 1.—^{11}B nmr spectra (32.1 Mc) of (A) $Rb_2(2\text{-}BrB_{10}H_{12}CN)$, (B) $1,2,3,4\text{-}D_4B_{10}H_8[S(C_2H_5)_2]_2$, (C) $B_{10}H_{12}(C_2H_5NC)_2$, and (D) $5,6,7,8,9,10,\text{bridge-}D_8B_{10}H_4[S(C_2H_5)_2]_2$ (partially deuterated).

$B_{10}H_{12}$(ligand)$_2$ compounds (see Table I) indicates that the variance of the 2,4 (4.5 ppm), 5,7,8,10 (4.1 ppm), and 1,3 (6 ppm) positions is far less than that observed for the 6,9 (14 ppm) positions. All other factors being equal, the 6,9 doublet appears to move to higher field as the base strength of the attached ligand increases. Further studies may indicate that these general trends are applicable to all compounds of the 2632, $B_{10}H_{14}^{2-}$ type.

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CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY,
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Calcium Indate, an Isotype of Calcium Ferrite and Sodium Scandium Titanate

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The calcium ferrite structure type,[1,2] characterized by an orthorhombic unit cell and a short (3 A) *b* axis, has been established for a number of AB_2O_4 compounds including $SrFe_2O_4$,[1] CaV_2O_4,[2] β-$CaCr_2O_4$,[2] Eu_3O_4,[3] $CaSc_2O_4$,[4] and $MgSc_2O_4$,[5] and powder patterns also indicate isomorphism for a series of compounds where atom A is Ba or Sr and atom B is a rare earth.[6-8]

The calcium ferrite structure is built up of double blocks of edge-shared octahedra, extending infinitely in the *b*-axis direction, with each double string joined by octahedral corners to other double strings in such a way as to produce tunnels large enough to accommodate the calcium atoms. An alternative arrangement of double blocks is found in the calcium titanate ($CaTi_2O_4$) structure[9-11] which has similar tunnels but a different edge-sharing arrangement fitted within an orthorhombic unit cell with axes very similar to those of $CaFe_2O_4$.

In the course of our work on the reasons for variations in double-block arrangements we have reexamined calcium indate, $CaIn_2O_4$, variously reported to have space group either $Pca2_1$ or Pbcm[12] or, on the basis of powder pattern and density, to be of calcium ferrite type.[6] Structure factor calculations show it in fact to be of calcium ferrite structure type, space group Pnma, isomorphous with calcium scandate[4] and with sodium scandium titanate.[13]

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