halogen bonds *cis* to the donor ligands. The intensity would be greater with greater coupling between the halogen stretching and the donor atom stretching.

**Acknowledgment.**—The authors wish to thank Mrs. J. Pluščec and Mrs. A. Benn for assisting with the experimental work. T. C. R. gratefully acknowledges his support by a National Research Council (Canada) Post-doctoral Fellowship.

---

CONTRIBUTION FROM SPACE-GENERAL CORPORATION,
EL MONTE, CALIFORNIA

## Hydrogen Exchange in the $H_2O$–$B_{10}H_{14}$–Cineole System. Suggested Structure for $\mu$-$(C_2H_5O)B_{10}H_{13}$

BY ROBERT E. WILLIAMS

*Received February 22, 1965*

The recent development of higher resolution n.m.r. equipment has made it possible to identify structurally several halogen derivatives of $B_{10}H_{14}$ which eluded interpretation with the older equipment.[1-3] The present note deals with additional chemistry of $B_{10}H_{14}$ as revealed by the $B^{11}$ n.m.r. spectra at 64.2 Mc.

The 12.8-Mc. $B^{11}$ n.m.r. spectrum of $B_{10}H_{14}$ dissolved in 1,8-cineole (an intramolecular ether) differed from the spectrum of $B_{10}H_{14}$ in the common ethers and other solvents[4,5]; in contrast, no differences are apparent in the $B^{11}$ n.m.r. spectra of $B_5H_9$ alone, in cineole or in many other solvents. The $B_{10}H_{14}$ spectrum at 12.8 Mc. (in cineole) resembles partially deuterated decaborane more than $B_{10}H_{14}$. Since rapid hydrogen exchange could also cause such a "partially deuterated appearance," hydrogen exchange was assumed to take place[4] and was later confirmed.[5]

In a reinvestigation of $B_{10}H_{14}$–ether systems we obtained a 32.1-Mc. $B^{11}$ n.m.r. spectrum of $B_{10}H_{14}$ in cineole and found, surprisingly, that it differed only slightly from that of $B_{10}H_{14}$ in other solvents. A more thorough investigation was planned for 32.1 Mc.; however, the Varian 64.2-Mc. experimental instrument,[6] utilizing a cryogenic magnet, became transiently available. Consequently, 64.2-Mc. spectra of $B_{10}H_{14}$ in dry cineole (4 months over calcium hydride) and in cineole saturated with water at room temperature were obtained. The results are shown in Figure 1. In the top spectrum, for comparison purposes, is the complete $B^{11}$ n.m.r. assignment of $B_{10}H_{14}$ as determined by Schaeffer.[7] In the middle spectrum, $B_{10}H_{14}$ in dry cineole, it would seem that the 1,3 and 6,9 positions are less well-resolved than in other solvents, while in the water-saturated $B_{10}H_{14}$–cineole spectrum, the 5, 7, 8, and 10 doublet is collapsed and perhaps lessened in size due to hydrogen exchange.[4] Based on these spectra, several bits of data now fall into place. For one thing, $H_2O$ (or another strong proton donor) must have been present in our original experiments at 12.8 Mc., since the spectrum of $B_{10}H_{14}$ has the appearance of a system undergoing tautomerism or hydrogen exchange. This phenomenon should not occur with $B_5H_9$ in moist cineole, since a water-free environment would automatically be created by the rapid reaction of $B_5H_9$ and $H_2O$.

Hawthorne and Miller carried out the original experiments[8] involving hydrogen exchange between $B_{10}H_{14}$ and $D_2O$ in dioxane; they found that the four bridge hydrogens exchange first[8] (in minutes or seconds). In a subsequent investigation, we found that bridge hydrogen exchange was followed by the exchange of 6,9 terminal hydrogens (0–2 hr.), the 5, 7, 8, and 10 terminal hydrogens (0–2 hr.), and the 2,4 positions (partially) (3 hr.).[9] Alternatively, aging of bridge tetradeuteriodecaborane(14) in dioxane allows the bridge hydrogens and the 5, 7, 8, and 10 hydrogens to scramble (tens of hours).[4]

When cineole is substituted for dioxane, 6-benzyl-$B_{10}H_{13}$ exchanges the 13 boron-attached hydrogens much more rapidly.[5] When HCl is substituted for $H_2O$ (*i.e.*, dioxane–$B_{10}H_{14}$–HCl), exchange also takes place,[10] but the rates are about 100-fold slower than in the dioxane–$B_{10}H_{14}$–$H_2O$ system. Furthermore, the 1,3 and 2,4 positions are *not attacked* even after 400 hr. at room temperature. Quantitative recovery of $B_{10}H_{14}$ is obtained. Thus, both the substitution of $H_2O$ for HCl and the substitution of cineole for dioxane promote exchange; cineole–$B_{10}H_{14}$–HCl, which may be the most interesting combination, has not been investigated.[11]

The reason why cineole promotes hydrogen exchange better than dioxane is probably related to the fact that cineole is a "ditertiary" intramolecular ether, especially noted for its capacity to add acid protons to form oxonium salts.[12] Perhaps it merely functions as a stronger Lewis base than dioxane (see eq. a in Figure 2) but more likely its activity is due to its greater propensity to form oxonium salts from $H_2O$ and $B_{10}H_{14}$. If so, it would be expected to react reversibly with $B_{10}H_{14}$ to form $C_{10}H_{18}O{:}H^+$ and $B_{10}H_{13}^-$ (eq. b) and with $H_2O$ to form $C_{10}H_{18}O{:}H^+$ and $OH^-$.

---

[1] Specifically 1-$IB_{10}H_{13}$,[2] 1-$ClB_{10}H_{13}$,[3] and 2-$ClB_{10}H_{18}$[3] have been identified.

[2] R. E. Williams and T. P. Onak, *J. Am. Chem. Soc.*, **86**, 3159 (1964).

[3] R. E. Williams and E. Pier, *Inorg. Chem.*, **4**, 1357 (1965).

[4] R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

[5] R. J. F. Palchak, J. H. Norman, and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961).

[6] F. A. Nelson and H. E. Weaver, *Science*, **146**, 223 (1964).

[7] Professor Riley Schaeffer and co-workers have unambiguously assigned the skewed triplet at lowest field as the overlap of two doublets, representing the 1 and 3 boron nuclei (at lowest field) and the 6 and 9 doublet at higher field; private communication.

[8] M. F. Hawthorne and J. J. Miller, *J. Am. Chem. Soc.*, **80**, 754 (1958).

[9] I. Shapiro, M. Lustig, and R. E. Williams, *ibid.*, **81**, 838 (1959).

[10] J. A. DuPont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

[11] An intermediate exchange rate and quantitative recovery of the $B_{10}H_{14}$ may be anticipated. Other boron hydrides would also become candidates for exchange. We have found that both $B_5H_9$ and $B_6H_{10}$ seem to be stable indefinitely in solution with cineole at room temperature.

[12] P. Karrer, "Organic Chemistry," 3rd English Ed., Elsevier Publishing Co., New York, N. Y., 1947, p. 65.

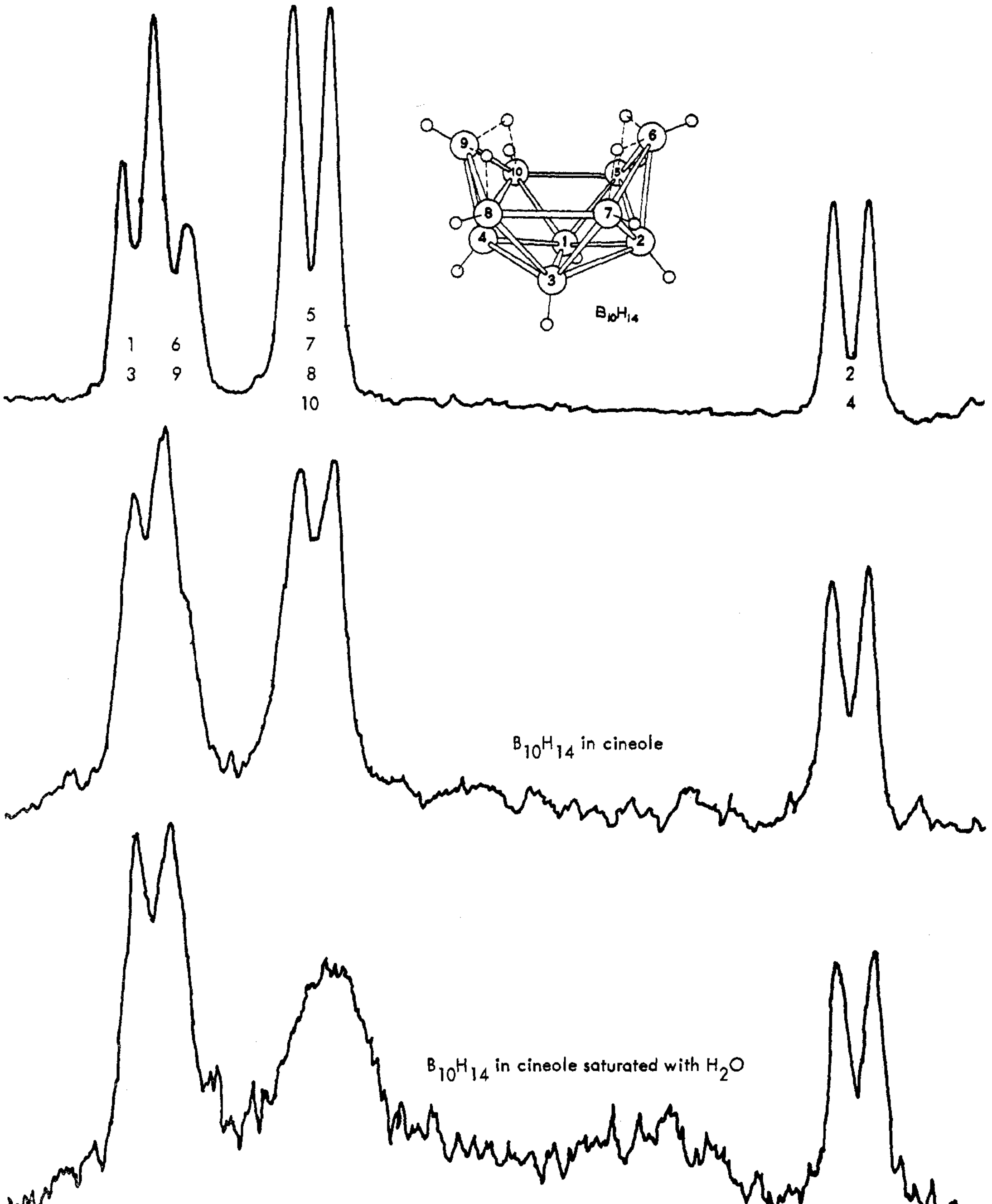


Figure 1.—The 64.2-Mc. $B^{11}$ *n.m.r.* spectra of $B_{10}H_{14}$ in $CS_2$ compared to $B_{10}H_{14}$ in cineole and $B_{10}H_{14}$ in cineole saturated with water.

In the simplest case, aging of $B_{10}H_{14}$ in dioxane,[9] the reversible reaction a would account for bridge-hydrogen exchange with the 5, 7, 8, and 10 hydrogens. When HCl or $H_2O$ is present, reaction b, b and c, or a and d could account for the initial bridge-hydrogen exchange.

Readdition of $H^+$ to IV *via* reaction d or the expected intermolecular rearrangement into V (isoelectronic to the known species (Lewis base)$_2B_{10}H_{12}$, $B_{10}H_{14}^{2-}$) *via* reaction e would account for bridge-hydrogen exchange with the 5, 7, 8, and 10 positions; eq. e additionally would also account for 6,9 hydrogen exchange. We suggest that if $OH^-$ functions as the Lewis base in compound IV, an intramolecular rearrangement would take place wherein the *oxygen rather than hydrogen would occupy a bridge position.* A rationale explaining this possibility in the case of $C_2H_5OB_{10}H_{13}$ will be found in a following section. For the present case it is conceivable that oxygen bridging configurations lead to exchange of the 1, 2, 3, and 4 hydrogens when $OH^-$ is present by virtue of occasional bridging of an OH group between a base boron and a 1, 3, 2, or 4 boron atom.[13]

---

(13) Use of a deuterio alcohol as the $D^+$ donor may eliminate this mechanism.

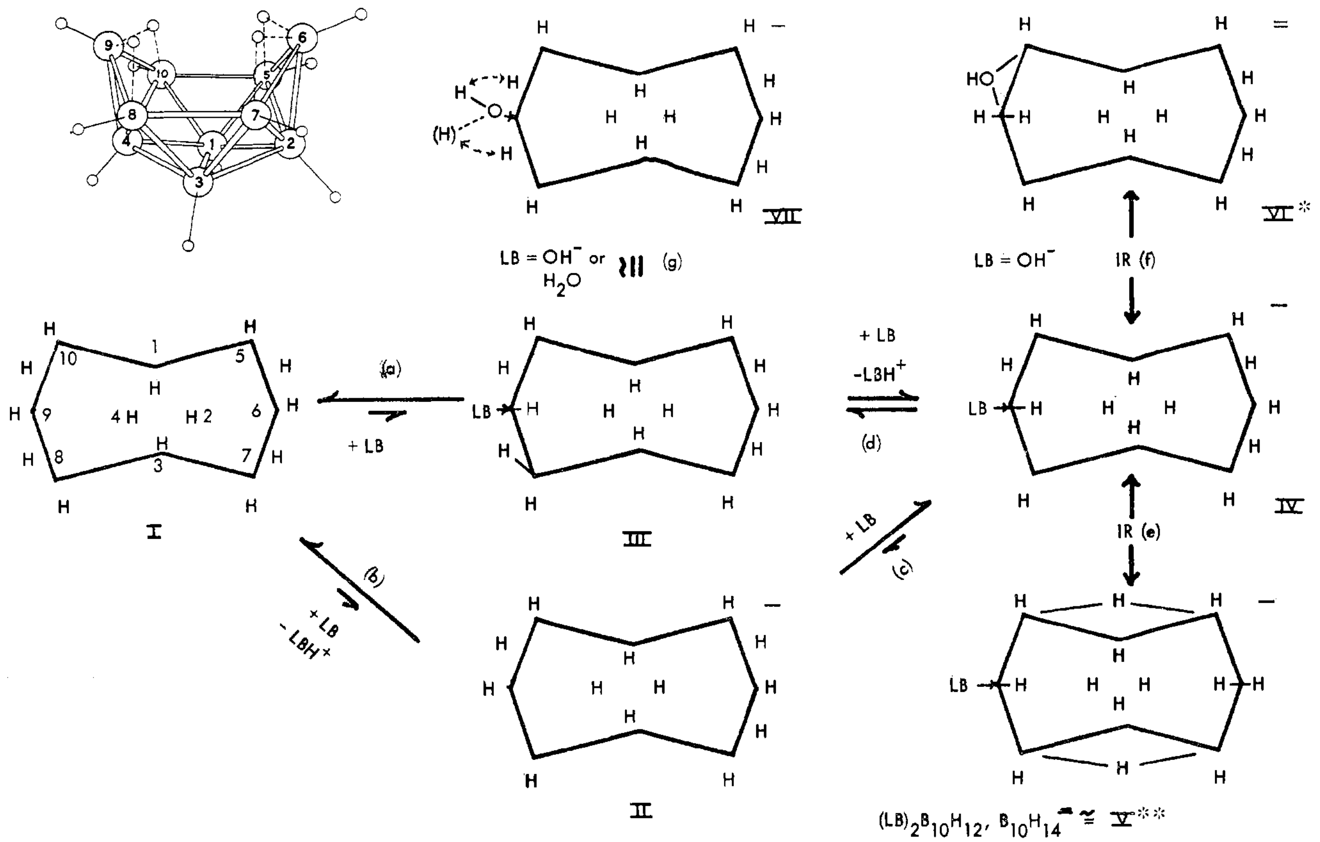


Figure 2.—Candidate reactions of $B_{10}H_{14}$ with Lewis Bases: IR, intramolecular rearrangement; LB, dioxane, cineole, $H_2O$, or other Lewis bases. * L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Am. Chem. Soc.*, **85**, 2674 (1963). ** B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, 1, 623 (1962).

In any event the preceding observations focused our attention on substituted boron hydrides in general and the possible *capacities of various substituents to form bridge configurations.* Particularly interesting are the alkoxyl-substituted boron hydrides. In order to consider the probable disposition of an alkoxyl group in a substituted boron hydride, a clear distinction must first be made between the alkoxyl group (RO) and the related Lewis base (ROR). Elements in the first row of the periodic table generate Lewis bases in the order of decreasing strength $R_3N > R_2O > RF$ (R = alkyl). For example, many boron hydride adducts have been made of $R_3N$ and $R_2O$, and in such adducts the Lewis base may be considered to occupy a terminal position substituting for hydride ion ($H^-$). In (Lewis base): $BH_3$, which is isoelectronic with $BH_4^-$, the Lewis base donates one pair of electrons. Functional groups with one less R group, namely $R_2N$, RO, and F, may be potential substituents in *bridge-hydrogen-containing boron hydrides* in place of terminal hydrogens (H), but to our knowledge *not one such compound has been identified.* Many other groups, *e.g.*, Cl, Br, and I, are found as terminal substituents in the bridge-hydrogen-containing species $B_2H_6$, $B_4H_{10}$, and $B_{10}H_{14}$. $R_2N$ and F derivatives of borazine,[14,15] $B_{10}H_{10}^{2-}$,[16] and $B_{12}H_{12}^{2-}$,[17] have been reported, *but no bridge hydrogens are present in these compounds.*

The bulk of the literature suggests that there is an order of bridging which overrides considerations of the type of bridge in the boron hydrides and related electron-deficient compounds, *i.e.*, three-center bond for H and alkyl bridges (two electrons) *vs.* coordinate covalent bridges for $R_2N$ and RO groups (four electrons). In the order of decreasing "bridging" capacity, $R_2N > H > Cl > R$.[18-21] It follows that when a bridge position is available in a boron hydride and if it has a choice between a bridge hydrogen and a substituent with better bridging potentialities, the latter group will pre-empt the bridge position. Thus, $\mu$-dimethylaminodiborane rather than $1\text{-}(CH_3)_2NB_2H_5$ exists.[19] A similar situation is found in $R_3N{:}B_8H_{11}NR_2$, where the $R_2N$ group occupies a bridge position.[19] In this compound, the $R_3N$ substituent may be considered as

---

[14] R. H. Toeniskoetter and F. R. Hall, *Inorg. Chem.*, **2**, 29 (1963).

[15] A. W. Laubengayer, *et al.*, *ibid.*, **2**, 519 (1963).

[16] W. R. Hertler and M. S. Raasch, *J. Am. Chem. Soc.*, **86**, 3661 (1964).

[17] (a) W. H. Knoth, *et al.*, *ibid.*, **84**, 1056 (1962); (b) *ibid.*, **86**, 3973 (1964); (c) *Inorg. Chem.*, **3**, 159 (1964).

[18] This listing follows from the knowledge that the $(CH_3)_2N$ group occupies a bridge position[14] in dimethylaminodiborane while the Cl and R groups occupy terminal positions in their substituted diboranes. Chlorine occupies bridge situations in the dimeric alkylaluminum chlorides. A more comprehensive, but tentative list would be $R_2N > RO > H \cong F > Cl > CH_3 > C_2H_5 > i\text{-}C_4H_9$. The order of the alkyl groups is taken from the known degree of association of the various $R_3Al$ species.[20] F is considered to be a better bridging group than Cl, based on the degree of association of the halogen-bridged $(CH_3)_2AlF$ and $(CH_3)_2AlCl$ species.[21] RO is placed above F because of the oxygen bridging of $(CH_3OBF_2)_3$.

[19] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

[20] K. Ziegler, "Organo-Metallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 208.

[21] G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 141.

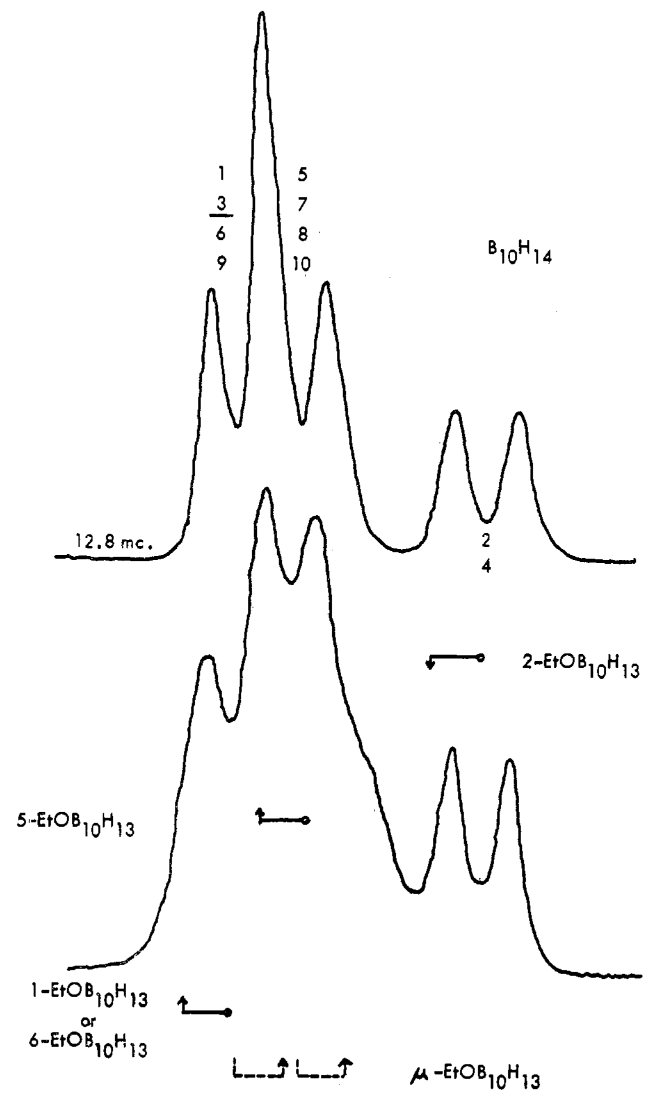


Figure 3.—$B^{11}$ n.m.r. spectra of $B_{10}H_{14}$ and $C_2H_5OB_{10}H_{13}$.

isoelectronic with a terminal hydrogen (two-electron bond), whereas $R_2N$ as a bridge group( four electrons—two bonds) is not isoelectronic with a bridge hydrogen (two electrons—one three-center bond).

In our judgment the literature suggests that an RO group would also be equivalent to or better than hydrogen in bridging capabilities, barring steric complications. A μ-alkoxydiborane has not been reported, but alkoxyl occupation of the bridge position would seem to be a prerequisite to the observed disproportionation of $(RO)_2BH$ into $(RO)_3B$ and $B_2H_6$.[22] Similarly, oxygen occupies bridge positions in the trimer $(CH_3OBF_2)_3$,[23] and the related sulfur compound $(RSBH_2)_3$[24] utilizes sulfur bridge bonds, not hydrogen. Fluorine, perhaps, is similar in bridging affinity to hydrogen; B–F–B bridges, for example, have long been known to be present when $BF_3$ dimerizes at low temperature.[25]

As far as we are aware, only one confirmed alkoxyl boron hydride has been reported, *viz.*, $C_2H_5OB_{10}H_{13}$ by Hawthorne and Miller.[26] Unfortunately the $B^{11}$ n.m.r. spectrum was not published, and it only recently appeared in a book authored by Lipscomb[19] (reproduced in Figure 3).

In interpreting the $B^{11}$ n.m.r. spectrum of $C_2H_5OB_{10}H_{13}$, it is noteworthy that in every observable case the substitution of a single terminal hydrogen in a boron hydride by another terminal group chemically shifts the substituted boron in the direction that the tetrasubstituted analog $(BX_4^-)$ is shifted from $BH_4^-$. No deviations from this empirical "rule" are known.[27] In the order of increasing field for the chemical shift values are $BCl_4^- < BF_4^- \cong B(OR)_4^- < B(C_6H_5)_4^- < BR_4^- < BBr_4^- < BH_4^- < BI_4^-$. In the boron hydrides, substitution of a single terminal hydrogen by all groups (except iodine) causes a shift to lower field in all cases thus far reported.[23] The substituted borons in 1-$CH_3B_2H_5$,[29] 1-$ClB_2H_5$,[27] and 1-$BrB_2H_5$[30] are shifted to lower field as are those in 1-$BrB_5H_8$,[31] 2-$ClB_5H_8$,[32] 1-$ClB_{10}H_{13}$,[3] 2-$ClB_{10}H_{13}$,[3] and 1-$BrB_{10}H_{13}$.[31] This body of circumstantial evidence leads us to expect that the substitution of a *terminal $C_2H_5O$ group* for a terminal hydrogen on a boron hydride would chemically shift the involved boron to lower field. Experimental evidence that substitution of a terminal alkoxyl group for a terminal hydrogen would result in a shift to lower field is revealed in the $B^{11}$ n.m.r. spectra of $B_{12}H_{11}OH^{2-}$, $B_{12}H_{10}(OH)_2{}^{2-}$, and $B_{10}H_9OH^{2-}$. Here the OH-substituted boron nuclei are shifted to lower field[17b,33] $(B(OR)_4^-$ and $B(OH)_4^-$ have identical chemical shift values within experimental error). Of course these species have no bridge positions for either oxygen or hydrogen.

Figure 3 displays the $B^{11}$ n.m.r. spectrum of $C_2H_5OB_{10}H_{13}$ at 12.8 Mc. The predicted influence of a $C_2H_5O$ group as a terminal substituent at the various positions is graphically shown (solid arrows) as a partial collapse of the indicated doublet and a concomitant shift to lower field. There appears to be no indication of a terminal $C_2H_5O$ group on $B_{10}H_{14}$ in the observed spectrum. Based on the idea that a $C_2H_5O$ group would pre-empt a bridge position and that the $B^{11}$ n.m.r. spectrum appears to be incompatible with terminal alkoxyl substitution, we are led to the conclusion that a structure with a bridge oxygen group (*e.g.*, 5,6-μ-$C_5H_5OB_{10}H_{13}$) is the most promising candidate. We have only limited experience with bridge-substituted boron hydrides, but the observed n.m.r. spectrum seems to be compatible with such a structure.

---

(22) M. F. Lappert, *Chem. Rev.*, **56**, 984 (1956).

(23) H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 2663 (1961).

(24) E. L. Muetterties, N. E. Miller, K. J. Packer, and H. C. Miller, *Inorg. Chem.*, **3**, 870 (1964).

(25) Possibly the *lack of compounds containing terminal fluorine in combination with a bridge hydrogen* is coupled to the capacity of fluorine to occupy bridge positions which may facilitate disproportionation and destruction of the parent molecule.

(26) M. F. Hawthorne and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 500 (1960).

(27) R. E. Williams, K. M. Harmon, and J. R. Spielman, *ibid.*, submitted.

(28) This rule does not obtain when grossly different species are compared, *e.g.*, the apex boron nuclei in both $B_{10}Cl_{10}^{2-}$ and $B_{10}Br_{10}^{2-}$ are found at higher field than the equivalent nuclei in $B_{10}H_{10}^{2-}$.[17c]

(29) R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960).

(30) D. F. Gaines and R. Schaeffer, *ibid.*, **68**, 955 (1964).

(31) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **80**, 2670 (1958).

(32) T. P. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(33) Referee I brought this experimental evidence to our attention.

The $B^{11}$ n.m.r. spectrum of $\mu$-$(CH_3)_2NB_2H_5$, for example, is found at *higher field* than that of $B_2H_6$.[34,35] Note that when a nitrogen bridge is formed four electrons are utilized as compared with a two-electron three-centered bridge hydrogen situation. In contrast, when an $R_3N$ group occupies a terminal position, as in $B_{12}H_{11}N(CH_3)_3^-$,[16] the boron resonance is shifted to lower field (the boron resonance of $B(NR_2)_4^-$ is predicted[27] to be at considerably lower field than that of $BH_4^-$). In this case the number of bonding electrons remains constant; thus nitrogen and hydrogen as bridges differ in kind while nitrogen and hydrogen as terminal substituents differ only in degree.

The substitution of a bridge oxygen for a bridge hydrogen would also feed more bonding electrons into the neighboring boron environments, which in turn would be expected to lead to increased shielding and a shift to higher field. The shift to higher field of two boron nuclei[36] (dotted arrows in Figure 3) fits well with the observed spectrum. We conclude that Hawthorne and Miller prepared $C_2H_5OB_{10}H_{13}$, wherein the $C_2H_5O$ group occupies a bridge position; a single pair of optical isomers is quite likely and an X-ray study would be most useful.

**Acknowledgment.**—This investigation was supported by the Office of Naval Research. Thanks are also extended to Varian Associates (*i.e.*, Mr. E. Pier, Mr. F. Nelson, and Dr. Harry Weaver) for obtaining the 64.2-Mc. $B^{11}$ n.m.r. spectra.

[34] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 1496 (1959).

[35] T P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[36] Substitution of a hydrogen bridge by an oxygen bridge introduces two additional electrons; greater shielding and a shift to higher field results.

---

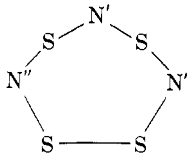
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS
RESEARCH DIVISION OF THE LAWRENCE RADIATION
LABORATORY, BERKELEY, CALIFORNIA 94720

# The Nitrogen-15 Nuclear Magnetic Resonance Spectrum of the $S_4N_3^+$ Ion

BY NORMAN LOGAN[1] AND WILLIAM L. JOLLY

*Received April 5, 1965*

Nitrogen-15 nuclear magnetic resonance spectra have recently been observed for compounds containing the $^{15}N$ isotope at natural abundance (0.36%) and also for $^{15}N$-enriched samples.[2-4] However, the utility of $^{15}N$ n.m.r. as a structural tool for the detection of nitrogen atoms in nonequivalent environments has not been demonstrated previously for inorganic systems. We have obtained the $^{15}N$ spectrum of the thiotrithiazyl cation $S_4N_3^+$ (97.2% $^{15}N$) and find it to be consistent with the structure



which has recently been determined by X-ray analysis.[5]

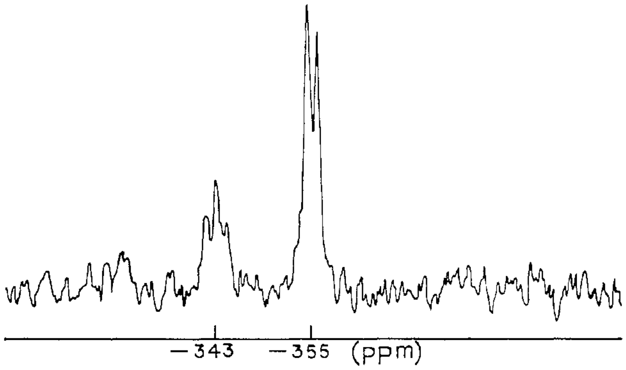


Figure 1.—The $^{15}N$ n.m.r. spectrum of $S_4N_3^+$ in 70% nitric acid. Chemical shifts relative to $^{15}NH_4^-$.

The relatively stable chloride, $S_4N_3Cl$, was used in the present work. This compound was synthesized from ammonium chloride (97.2% enriched in $^{15}N$) and disulfur dichloride. Because of the inherently low sensitivity of nitrogen resonances ($1 \times 10^{-3}$ that of $^1H$ at constant field) it was necessary to use a solution more concentrated than 1 *M* in $S_4{}^{15}N_3^+$ in order to obtain a favorable signal-to-noise ratio. The salt undergoes rapid decomposition in water and is insoluble in most organic solvents. However, $S_4N_3Cl$ dissolves in 70% $HNO_3$ to the extent of 3–4 *M*, forming a solution which is stable for at least 1 day at room temperature.

The $^{15}N$ spectrum of a 3.1 *M* solution of $S_4N_3Cl$ (97.2% $^{15}N$) in 70% $HNO_3$ is shown in Figure 1. The two resonances have an over-all intensity ratio of 1:2, corresponding to the N′ atom and the two equivalent N″ atoms shown in the structure. Both resonances exhibit spin–spin splitting. The weaker resonance, due to N′, is a 1:2:1 triplet, and the stronger resonance, due to the N″ atoms, is a 1:1 doublet. The triplet and doublet occur at 343 and 355 ± 1 p.p.m., respectively, downfield from the $^{15}NH_4^+$ resonance. The $^{15}N$–$^{15}N$ coupling constant is 7 ± 1 c.p.s. and the half-width of individual components of the multiplets is approximately 7 c.p.s.

No particular significance can be attached to the magnitude of the chemical shifts; however, some qualitative observations can be made. Paramagnetic effects associated with electronic asymmetry are considered to provide the dominant contribution to

---

[1] Miller Research Fellow, University of California, Berkeley, 1964–1965.

[2] J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **51**, 735 (1964).

[3] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964).

[4] J. D. Ray, *J. Chem. Phys.*, **40**, 3440 (1964).

[5] J. Weiss, *Z. anorg. allgem. Chem.*, **333**, 314 (1964); A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).