rial in the other. The greater shift (than in (b)) appears related to the ring-oxygen since it has been detected for the axial and equatorial hydrogens of the methylene group of β-D-xylopyranose tetraacetate.

Because of spin coupling between the hydrogens on neighboring carbons, the shifts mentioned in (b) often are obscured by inadequate resolution of the complex spectrum. The configurational effects on the signals produced by the acetoxy groups are not obscured by spin coupling and will perhaps prove the most generally useful in configurational and conformational studies. These facts are illustrated by the spectra for *myo*- and *levo*-inositol hexaacetates[3] shown in Fig. 1. It is seen that the

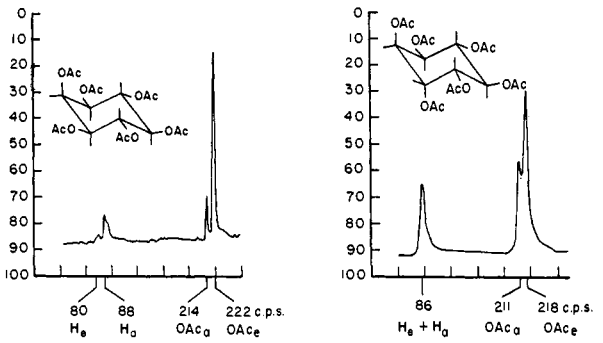


Fig. 1.—Proton magnetic resonance spectra of the *myo*- and *levo*-inositol hexaacetates, respectively.

equatorial hydrogen in the *myo*-isomer is identified readily from its relative intensity. The signals for the equatorial and axial hydrogens are blended into one broad band in the case of the *levo*-isomer. The relative intensities of the signals for the acetoxy groups clearly demonstrate the ratio of axial to equatorial acetoxy groups in both cases. It must be noted, however, that the spectra in the acetoxy group region are not always simple and readily interpreted. This is seen in the spectra D, E and F of Fig. 2. In the case of β-L-arabinopyranose tetraacetate we were not able to resolve the signal for the axial acetoxy group.

The assignments of the signals were made through a comparison of the NMR spectra of a variety of acetylated aldoses, ketoses, glucosides and sugar alcohols and appear unequivocal. The spectra of the anomeric xylopyranose and arabinopyranose tetraacetates provided evidence in support of the conformations shown in Figs. 1 and 2.

It is of considerable interest to note that the NMR spectra have yielded a convincing confirmation of the configurations at the anomeric center of sugar acetates which previously in most cases were assigned[4] entirely on the basis of Hudson's rule of isorotation.[5]

It was also observed that configuration has an effect on spin-coupling constants as well as on chemical shift. Analysis of the spectra for the acetyl derivatives of glucose, galactose, xylose and arabinose showed that the spin coupling between

(3) We are indebted to Dr. E. C. Horswill for providing us with the levo compound.

(4) R. U. Lemieux, *Can. J. Chem.*, **29**, 1079 (1951).

(5) C. S. Hudson, *Advances in Carbohydrate Chem.*, **3**, 15 (1948).

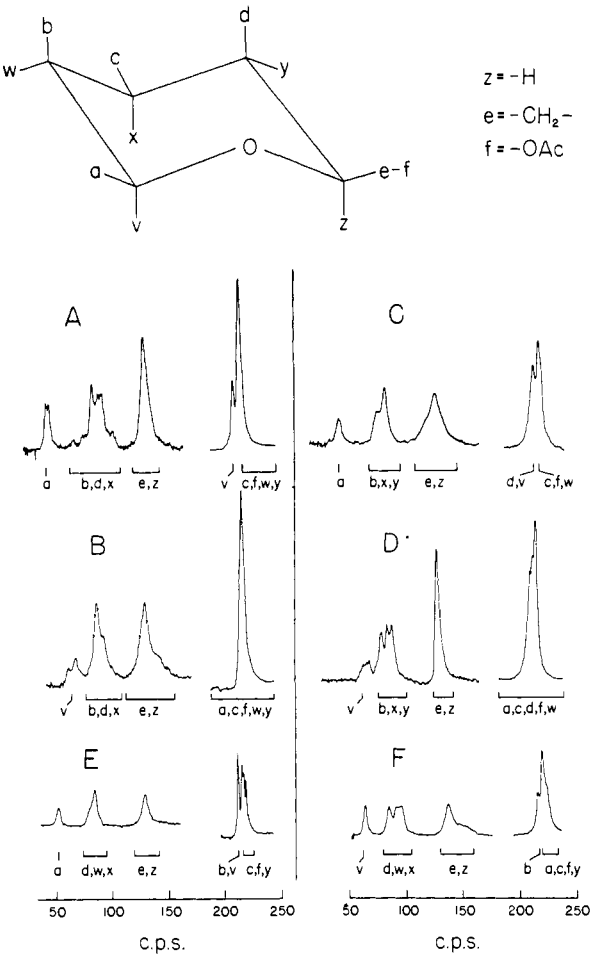


Fig. 2.—Proton magnetic resonance spectra of acetylated sugars: A, α-D-glucopyranose pentaacetate (a, b, x, d = — H, v, w, c, y = — OAc); B, β-D-glucopyranose pentaacetate (v, b, x, d = — H, a, w, c, y = — OAc); C, α-D-galactopyranose pentaacetate (a, b, x, y = — H, v, w, c, d = — OAc); D, β-D-galactopyranose pentaacetate (v, b, x, y = — H, a, w, c, d = — OAc); E, α-D-mannopyranose pentaacetate (a, w, x, d = — H, v, b, c, y = — OAc); F, β-D-mannopyranose pentaacetate (v, w, x, d = — H, a, b, c, y = — OAc).

hydrogens on neighboring carbon atoms is 2 to 3 times greater when both the hydrogens are in axial orientation than when one or both of the hydrogens are in equatorial orientation.

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RECEIVED NOVEMBER 23, 1956

## A NEW TYPE OF SUBSTITUTED BORANE

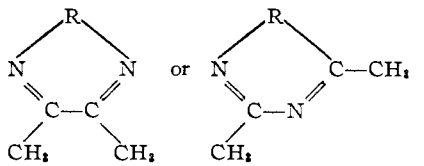
*Sir:*

We wish to report the discovery of a new class of borane derivatives formed by the reaction of a nitrile with a boron hydride. When a decaborane solution in acetonitrile is heated to reflux, the solution slowly becomes light yellow and evolves hydrogen. On cooling after one hour at reflux, a

white precipitate consisting of well-formed, needle-shaped crystals deposits from the solution and may be washed free of the slightly colored, supernatant liquid with a small amount of the nitrile. The amount of hydrogen evolved corresponds closely to one mole per mole of $B_{10}H_{14}$ used, and the analysis of the material confirms the fact that two hydrogens have been replaced by two acetonitrile groups. (Calculated for $B_{10}H_{12}\cdot 2CH_3CN$: B, 53.5; C, 23.7; H, 8.9; N, 13.8. Observed: B, 53.2; C, 22.9, 22.6; H, 8.6, 8.4; N, 13.2. Empirical formula: $B_{10.4}H_{17.9}N_{2.0}C_{4.0}$.)

The new compound is non-volatile, apparently indefinitely stable in air, melts over 200° with decomposition, and is insoluble in most organic solvents except acetonitrile. The material is diamagnetic.

The structure of the new compound has not been determined, but several limitations can be imposed on likely structures. Thus, the infrared spectrum shows no evidence of N—H or C=N groups, nor of the original C≡N group. Prolonged reflux with methanol does not completely degrade the compound, but produces a new material showing a strong C=N absorption. The $B^{11}$ nuclear magnetic resonance spectrum is complex but does show that attack has not occurred at the 2,2′ positions. The diamagnetism seems to necessitate a cyclic structure involving linkage of the two nitrile groups. It then seems most probable that the structure involves a carbon–nitrogen "bridge" linking two equivalent borons through utilization of B–N bonds. Two possible structures migh ɔe

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where the R group represents the decaborane cage. Alcoholysis of such a compound could easily produce residues showing free C=N, whereas the electron withdrawing decaborane group would probably cause substantial shifts in the original material making the characteristic frequency difficult to identify. The structure is currently being sought by X-ray diffraction studies in Professor Lipscomb's laboratory.

Preliminary studies show that pentaborane-9 behaves in a similar fashion and that other nitriles may be substituted for acetonitrile, although in no case is the reaction as clean as that reported above. Complete studies will be reported at a later date.

DEPARTMENT OF CHEMISTRY
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RECEIVED JANUARY 2, 1957

## THE DIAMMONIATE OF TETRABORANE

*Sir:*

Stock, Wiberg, Martini, and Nicklas[1] reported that ammonia in excess added to tetraborane ($B_4H_{10}$) at −75° in a 4 to 1 ratio to give a product which decomposed when warmed to room temperature. A variety of products including $H_2$ and $NH_3$ was recovered from the decomposition process.

Recent work in this laboratory has failed to confirm the existence of a tetraammoniate under a wide variety of conditions; however, a *stable crystalline* diammoniate ($B_4H_{10}\cdot 2NH_3$) has been isolated. The slow addition of ammonia to a cold (−78°) ether solution of $B_4H_{10}$ gave complete ammonia absorption. An excess of $B_4H_{10}$ was always used. After ammonia addition the system was aged for four days at −78° and for twelve hours at −45°. The solution was filtered on a vacuum line filter at −45° to remove a slight turbidity; then the ether was removed at −45° from the clear filtrate. The white solid which was left after removal of the ether was washed with cold dry benzene and transferred to a filter disc. It was then washed through the filter disc with dry ether. Removal of the solvent left a white, dry microcrystalline solid which was characterized as follows. *Anal.* N, 32.3; B, 49.4; $H_2$ 124.3 mmoles/g. Theory for $B_4H_{10}\cdot 2NH_3$: N, 32.1; B, 49.5; $H_2$, 125.8 mmoles/g. based on the hydrolysis equation

$$B_4H_{10}\cdot 2NH_3 + 8H_2O + 2H^+ \longrightarrow 4HBO_2 + 2NH_4^+ + 11H_2$$

The molecular weight as determined by vapor pressure depression in liquid ammonia was 81. Theoretical for $B_4H_{10}\cdot 2NH_3$ is 87. Yields ran as high as 86% based on the $NH_3$ used or 78% based on the $B_4H_{10}$ (slight excess used.)

The compound is stable in air and dissolves in cold water with only very slow hydrogen evolution. Acid or platinized platinum accelerates gas liberation. It is soluble in and can be recovered unchanged from perfectly dry ether but, if the compound has been exposed to moist air before solution, a precipitate slowly forms. It can be dissolved in and recovered unchanged from liquid ammonia.

A liquid ammonia solution of the compound reacts at −78° with sodium dissolved in liquid ammonia to give one half mole of $H_2$ per mole of $B_4H_{10}\cdot 2NH_3$ in less than 20 minutes. A significant yield of the recently described[2] compound $NaB_3H_8$ was recovered from the residue by leaching with diethyl ether. Identification was by X-ray powder pattern.

The diammoniate of tetraborane gives a definite X-ray powder pattern. Attempts to index it are being made in this laboratory. Additional chemical data on structure will be presented in a subsequent publication.

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(1) A. Stock, E. Wiberg and H. Martini, *Ber.*, **63**, 2927 (1930); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **65B**, 1711 (1932).

(2) W. Hough, S. J. Edwards and A. D. McElroy, THIS JOURNAL, **78**, 689 (1956).