An Assignment of the Hydrogen-1 Magnetic Resonance Spectrum of Decaborane at 220 MHz

By G. M. BODNER and L. G. SNEDDON

Received October 13, 1969

The \(^1\)H nmr spectrum of \(\text{B}_{10}\text{H}_{14}\) has been elucidated through the study of the 2-Br\(\text{B}_{10}\text{H}_{14}\) and 1,2,3,4-\(\text{B}_{10}\text{H}_{13}\text{D}_4\) derivatives. Both solvent studies and dilution studies are reported.

The structure of \(\text{B}_{10}\text{H}_{14}\), given below, is well documented and can be analyzed by symmetry arguments to be composed of four potentially nonequivalent boron environments, the 1,3; 2,4; 5,7,8,10; and 6,9 positions.

The \(^{11}\)B nmr spectrum of \(\text{B}_{10}\text{H}_{14}\) consists of four sets of overlapping doublets which have been assigned \(^2\text{a}\;^3\) (in order of increasing field strength) to the 1,3; 6,9; 5,7,8,10; and 2,4 positions respectively.

The analysis of the \(^1\)H nmr of \(\text{B}_{10}\text{H}_{14}\) is complicated by the nuclear spin of the \(^{11}\)B isotope, which results in a quartet of equal intensity lines for each non-equivalent boron environment. The data obtained from the present normal-coordinate analysis are consistent with the data obtained from the present normal-coordinate analysis. These observations tend to indicate that the borazine molecule is indeed best discussed on the basis of \(D_{\text{th}}\) symmetry.

Acknowledgments.—The authors wish to express their sincere gratitude to Dr. J. R. Scherer, Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif., for his generous advice and assistance in setting up the correct matrix for our calculations. Initial parts of this work were supported by the U. S. Army Research Office (Durham). The authors acknowledge the sizable funds for computing services which were made available by the University of Kentucky Graduate School.

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equivalent proton environment. The spectrum is further complicated by splitting from the \(^{10}\)B isotope (of spin 3) which leads to a septet of equal-intensity lines.

An earlier attempt\(^4\) at the analysis of the \(^1\)H nmr spectrum of \(\text{B}_\text{10} \text{H}_\text{14}\) through the use of computer simulation techniques, led to a tentative but inconclusive assignment.

We wish to report an unambiguous assignment of this spectrum obtained through the use of a 220-MHz spectrometer. This work allows the determination of greater accuracy than by \(^{10}\)B nmr.\(^2,4-6\)

**Experimental Section**

The 220-MHz \(^1\)H nmr spectra were obtained with a Varian Associates HR-220 spectrometer, at a field of 51.680 kG. Spectra were recorded in carbon disulfide, deuteriobenzene, acetone-d\(_6\), acetonitrile-d\(_3\), toluene-d\(_8\), tetrahydrofuran-d\(_6\), and bromobenzene-d\(_6\). Chemical shifts were measured relative to a TMS internal standard, on saturated solutions.

2-Br\(\text{B}_\text{9} \text{H}_\text{14}\) was purified by recrystallization from \(n\)-heptane.

**Results and Discussion**

The spectrum of \(\text{B}_\text{10} \text{H}_\text{14}\) was shown to be substantially solvent dependent and in several instances also concentration dependent (see Table I and Figure 1). The positions most subject to solvent shifts were the bridge hydrogens, which may be related to their acidic nature. In benzenoid solvents the 2,4 positions were shifted downfield but appeared to be unshifted in other solvents. Dilution studies indicate that the chemical shifts of the bridge and 2,4 positions were most susceptible to change, and in all cases where this effect was observed, the 2,4 and bridge positions were shifted in opposite directions. Only minor changes were observed for all other positions, with exception of the spectra run in benzene, where shifts in the 6,9 and 1,3 positions were noted, again in opposite directions.

**Table I**

<table>
<thead>
<tr>
<th></th>
<th>Bridge</th>
<th>2,4</th>
<th>5,7,8,10</th>
<th>1,3</th>
<th>6,9</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)D(_4)</td>
<td>2.77</td>
<td>-0.56</td>
<td>-3.09</td>
<td>-3.44</td>
<td>-4.04</td>
</tr>
<tr>
<td>C(_2)D(_3)C(_2)</td>
<td>2.75</td>
<td>-0.87</td>
<td>-3.03</td>
<td>-3.49</td>
<td>-3.76</td>
</tr>
<tr>
<td>BrC(_2)D(_4)</td>
<td>2.44</td>
<td>-0.81</td>
<td>-3.01</td>
<td>-3.67</td>
<td></td>
</tr>
<tr>
<td>C(_8)</td>
<td>2.38</td>
<td>-0.55</td>
<td>-3.01</td>
<td>-3.50</td>
<td>-3.60</td>
</tr>
<tr>
<td>THF-d(_4)</td>
<td>1.85</td>
<td>-0.59</td>
<td>-3.00</td>
<td>-3.44</td>
<td>-3.78</td>
</tr>
<tr>
<td>C(_2)D(_2)CN</td>
<td>1.79</td>
<td>-0.65</td>
<td>-3.11</td>
<td>-3.84</td>
<td>-3.95</td>
</tr>
<tr>
<td>(C(_8)H(_2))(_2)CO</td>
<td>1.67</td>
<td>-0.56</td>
<td>-3.01</td>
<td>-3.45</td>
<td>-3.84</td>
</tr>
</tbody>
</table>

\(^1\)H (220 MHz) ... 156 ± 2 158 ± 2 102 ± 5 145 ± 5
\(^3\)B (32.1 MHz) ... 156 ± 5 160 ± 5 151 ± 10 150 ± 15

\(^6\) Deviation ±0.05 ppm. \(^5\) Deviation ±0.1 ppm. \(^4\) As measured on a carbon disulfide solution of \(\text{B}_\text{10} \text{H}_\text{14}\).

The \(^1\)H nmr spectrum of \(\text{B}_\text{10} \text{H}_\text{14}\) is composed of four overlapping quartets of intensity 2:2:4:2 and a broad upfield singlet of intensity 4. There is evidently some resolvable \(^{10}\)B-\(^1\)H coupling, which can be seen under the quartet centered at -0.55 ppm.

The broad singlet at 2.38 ppm can be assigned to the bridge hydrogens, both by analogy with the chemical shift of other known bridge positions\(^1\) and due to the nonexistence of a quartet structure.\(^11\)

The partial splitting of the bridge resonance in the 2-Br\(\text{B}_\text{9} \text{H}_\text{14}\) derivative is evidence of the loss of degeneracy of the bridge protons. There are two bridge protons which are deshielded by the effect of the bromine substituent.

The disappearance of the quartets centered at -0.55 ppm is an indication of the rate of deuteration of the bridge. The spectrum obtained through the use of a 220-MHz spectrometer designed by A. O. Clouse of this department. Studies on samples of incomplete deuteration have demonstrated for the first time that deuteration occurs with preference for the 2,4 positions, as predicted by Moore and Lipscomb.\(^9\)

**Figure 1.**—The 220-MHz \(^1\)H nmr spectra of (A) 1,2,3,4-\(\text{B}_\text{9} \text{H}_\text{14}\)D\(_4\) in \(\text{CS}_\text{2}\), (B) 2-Br\(\text{B}_\text{9} \text{H}_\text{14}\) in \(\text{CS}_\text{2}\), (C) \(\text{B}_\text{10} \text{H}_\text{14}\) in \(\text{CS}_\text{2}\), and (D) \(\text{B}_\text{9} \text{H}_\text{14}\) in \(\text{CD}_\text{2}\).


and −3.50 ppm in the spectrum of 1,2,3,4-B$_2$H$_8$D$_4$ and the collapse to area 1 of the quartet at −0.55 ppm in the spectrum of 2-BrB$_2$H$_8$ allow the unambiguous assignment of the 1,3 and 2,4 positions in the spectrum of B$_2$H$_8$. The quartet of area 4 must arise from the 5,7,8,10 positions. The remaining quartet at −3.6 ppm may now be assigned to the 6,9 positions.

The order of chemical shifts in the $^1$H nmr parallels that of the $^{11}$B nmr, with the exception of a small inversion of the 1,3 and 6,9 positions, and is in agreement with the order postulated by Williams, et al.4

Acknowledgments.—We wish to express appreciation for the discussions with Drs. L. J. Todd and R. O. Schaeffer. We gratefully acknowledge the support of the National Science Foundation for G. M. B. and the support of the Office of Naval Research. We also wish to acknowledge the gift of 2-BrB$_2$H$_8$ by J. T. Moran.

The Kinetics and Mechanism of Trimethylamine-Haloborane Hydrolysis

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Received December 31, 1969

The rates of solvolysis of trimethylamine–mono- and dihaloboranes in aqueous dioxane at 25° increase in the series (CH$_3$)$_3$NBHCl < (CH$_3$)$_3$NBHBr < (CH$_3$)$_3$NBH$_2$I. The diiodoborane adduct reacts more slowly than the monoiodo compound but faster than trimethylamine–borane. Only a very slight retardation in rate is observed on substitution of deuterium for hydrogen on boron in the diiodo derivative (k$_D$/k$_H$ = 1.1); however, a noticeable solvent isotope effect (k$_H$/k$_D$ = 1.8) is observed for hydrolysis of both the mono- and diiodoborane adducts in 67% aqueous dioxane at 25°. Rates increase with increasing water content of the aqueous dioxane solvent system. No significant effect on rate of acidity is seen for hydrogen ion concentrations as high as 0.3 M or hydroxide ion concentrations up to 0.1 M, nor is the rate appreciably affected by the addition of potassium chloride or potassium iodide up to 0.3 M. The results indicate a mechanism for hydrolysis of the halo compounds quite different from that postulated for amine–BH$_n$ adducts. It is proposed that a rate-determining cleavage of a boron–halogen bond is followed by rapid collapse of an incipient boron(1+) ion. An analogy to nucleophilic substitution reactions in haloborane–amines leading to kinetically stable boronium ions is suggested.

Introduction

Various effects of B and N substitution on the rates and mechanism of hydrolysis of amine–boranes have been reported.4–9 Reaction paths proposed include rate-determining cleavage of a boron–hydrogen bond for solvolysis of certain B-phenyl-substituted boranes,4–6 the boron–nitrogen bond for solvolysis of BH$_n$ adducts of amines,7,8 and a boron–halogen bond for the decomposition of tertiary amine–trichloroboranes in aqueous ethanol.9 The development, in recent years, of convenient routes to the synthesis of mono- and dihaloborane adducts of amines10–13 now allows the study of these substrates as a means of elucidating specific effects of B-halo substitution on the mechanism of reactions of hydride-containing amine–borane addition compounds.

Experimental Section

Materials.—Sources of chemicals were as follows: trimethylamine–borane (99.1%) and boron trichloride, Matheson Coleman and Bell; deuterium oxide (99.8% isotopic purity), New England Nuclear Corp.; lithium tetrahydroaluminate and boron tribromide, Alfa Inorganics. Tetrahydrofuran (MCB) was distilled from LiAlH$_4$ prior to use (caution should be exercised in the distillation of tetrahydrofuran).14 The p-dioxane was obtained from Eastman and was treated according to the procedure described by Vogel15 and then boiled under reflux with LiAlH$_4$ and distilled. Benzene (MCB) was distilled from sodium.

Spectra and Analysis.—Infrared spectra were obtained on samples contained in KBr wafers using a Perkin-Elmer Model 237 infrared spectrophotometer. Proton nmr were obtained using a Varian A-60A spectrometer and are referred to trimethylsilylane as external standard. The $^1$B nmr were obtained using a Varian Model HA100 spectrometer with a $^1$B probe (32.1 Mc) and are referred to trimethyl borate as external standard. Chemical analyses for C, H, N, and halogen as well as molecular weight data were obtained by M-H-W Laboratories, Garden City, Mich. Hydridic hydrogen was determined by measurement of the hydrogen evolved on acid hydrolysis of known