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Studies of Boron-Nitrogen Compounds. VIII.¹ Nuclear Magnetic Resonance Studies of Some μ -Aminodiboranes and Amine Boranes

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The ^{11}B n.m.r. spectra of several amine boranes and μ -aminodiboranes have been investigated. The μ -aminodiboranes undergo intramolecular hydrogen exchange, which is accelerated by ethers. In the limit of rapid exchange, the n.m.r. spectra consist of a symmetrical sextet, indicating that each boron is equally coupled to all five boron hydrogens. The ^{11}B absorptions of the amine boranes and μ -aminodiboranes occur at higher field as hydrogens are successively substituted for methyl groups on nitrogen.

Introduction

In a previous study² it was found that the rate of intramolecular hydrogen exchange in diborane could be observed by examining the temperature dependence of the ^{11}B n.m.r. spectra of solutions of diborane in various ethers. (In pure diborane, the exchange rate is too slow to be observed using n.m.r. techniques.³) In the limit of rapid exchange each boron was found to be equally coupled to all six hydrogens, resulting in a spectrum consisting of a symmetrical septet.

Phillips, Miller, and Muettterties⁴ found that the ^{11}B n.m.r. spectrum of pure μ -dimethylaminodiborane changed as a function of temperature, and they suggested that the observed spectral changes could be due to intramolecular hydrogen exchange.

This paper is concerned with the changes in the ^{11}B n.m.r. spectra of solutions of several μ -aminodiboranes in various ethers as a function of temperature. The ^{11}B chemical shifts vary with degree of N-methyl substitution in μ -aminodiboranes and amine boranes, and this effect is also discussed.

Experimental

μ -Aminodiboranes.—The μ -dimethylamino- and μ -methylaminodiboranes were prepared by the method of Burg and Randolph⁵; μ -aminodiborane was prepared by the method of Schlesinger, Ritter, and Burg.⁶ In a typical experiment, 0.28 ml. of dry ethylene glycol dimethyl ether and 1.15 mmoles of μ -dimethylaminodiborane were condensed into a 5-mm. n.m.r. tube attached to the vacuum line. The tube was then sealed and stored in liquid nitrogen until used. In a similar manner, solutions of μ -dimethylaminodiborane in diethyl ether and tetrahydrofuran were prepared, as well as solutions of μ -methylaminodiborane in ethylene glycol dimethyl ether. Pure liquid samples of each of the μ -aminodiboranes were also prepared. The low stability of liquid samples of μ -aminodiborane prevented extensive investigation and consequently solutions in ethers were not studied.

Amine Boranes.—Ammonia borane,⁷ methylamine borane,⁸ dimethylamine borane,⁹ and trimethylamine borane⁹ were prepared by standard methods. Samples for n.m.r. studies were prepared in a nitrogen-filled drybox using suitable solvents (see Table I).

Boron Exchange in μ -Dimethylaminodiborane.— μ -Dimethylaminodiborane, 0.215 mmole, was mixed with 0.047 mmole of 96% ^{10}B diborane and allowed to stand at 26° for 64 min. in a bulb of 62.7-ml. volume. The diborane was subsequently separated and analyzed mass spectrometrically. The ^{10}B content had changed less than 2%, whereas the data of Rigden and Koski¹⁰

TABLE I

THE ^{11}B CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME AMINE BORANES

Compound	δ , ^a p.p.m.	J , ^b c.p.s.
H_3NBH_3 ^c	23.8	91
$(\text{CH}_3)_2\text{H}_2\text{NBH}_3$ ^d	20.5	93
$(\text{CH}_3)_2\text{HNBH}_3$ ^d	14.2 (14.6) ^e	96 (94)
$(\text{CH}_3)_3\text{NBH}_3$ ^d	8.1 (6.7)	98 (97)

^a With $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as the zero reference; values are in general about ± 0.5 p.p.m. ^b Values of J are in general about ± 3 c.p.s. ^c Solution in water. ^d Solution in chloroform. ^e Values in parentheses from W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

indicate that the hydrogen-deuterium exchange would have proceeded at least 60% under similar conditions.

Spectra.—The ^{11}B n.m.r. spectra were obtained at 19.3 Mc./sec. using a Varian Model 4300B high resolution spectrometer equipped with standard accessories. Chemical shifts (δ) and coupling constants (J) were obtained using the side-band technique and are listed in Tables I and II.

TABLE II

THE ^{11}B CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME μ -AMINODIBORANES

Compound	δ , ^a p.p.m.	J , ^b c.p.s.		
		BH_2	BHB	Multi-plet
$\text{H}_2\text{NB}_2\text{H}_5$	26.7	130	30	
$(\text{CH}_3)\text{HNB}_2\text{H}_5$	22.7	130	30	58 ^c
$(\text{CH}_3)_2\text{NB}_2\text{H}_5$	17.0 (18.5) ^d	130 (130)	30 (29)	58 ^e

^a With $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as the zero reference; values are in general about ± 0.5 p.p.m. ^b Values of J are in general about ± 2 c.p.s. ^c In ethylene glycol dimethyl ether solution. ^d Values in parentheses from W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). ^e In tetrahydrofuran solution.

Results

The ^{11}B n.m.r. spectrum of pure μ -dimethylaminodiborane indicates only relatively slow intramolecular hydrogen exchange at room temperature,⁴ but in ether solutions the exchange rates increase with the base strength of the ethers in the order diethyl ether < ethylene glycol dimethyl ether << tetrahydrofuran. The temperature dependence of the spectrum of μ -dimethylaminodiborane in ethylene glycol dimethyl ether solution is shown in Fig. 1. It is interesting to note that the two outermost peaks are present at all temperatures, and that the spacing between them is always the same (290 c.p.s.). A similar temperature dependence is observed for μ -methylaminodiborane in ethylene glycol dimethyl ether solution, except that each change occurs about 15° lower. It appears that the ease of intramolecular hydrogen exchange increases in the order μ -dimethylamino- < μ -methylamino- < μ -aminodiborane.

(10) J. S. Rigden and W. S. Koski, *ibid.*, **83**, 552 (1961).

(1) Part VII: G. A. Hahn and R. Schaeffer, *J. Am. Chem. Soc.*, **86**, 1503 (1964).

(2) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

(3) R. Schaeffer and F. Tebbe, *ibid.*, in press.

(4) W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(5) A. B. Burg and C. L. Randolph, *ibid.*, **71**, 3451 (1949).

(6) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 2297 (1938).

(7) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

(8) D. F. Gaines and R. Schaeffer, *ibid.*, **85**, 395 (1963).

(9) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

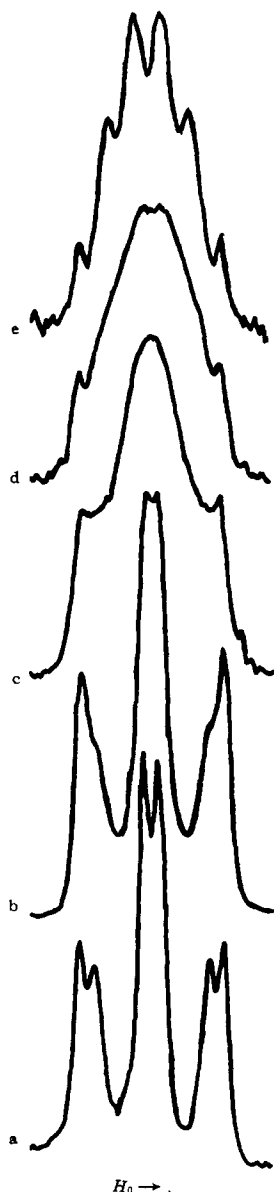


Fig. 1.—The temperature dependence of the ^{11}B n.m.r. spectra of μ -dimethylaminodiborane in ethylene glycol dimethyl ether solution: a, -39° ; b, -6° ; c, 42° ; d, 63° ; e, 83° .

The average lifetimes, τ , were estimated for the spectra of μ -dimethylaminodiborane in ethylene glycol dimethyl ether solution at various temperatures by the method previously described.² An Arrhenius plot of $\log 1/\tau$ vs. $1/T$ gives a line the slope of which corresponds to an activation energy for the exchange of about 3.7 kcal./mole. The value for diborane in diethyl ether solution is 4.8 kcal./mole.²

The spectrum of μ -dimethylaminodiborane in tetrahydrofuran solution at 63° is shown in Fig. 2. Integration of this spectrum gives the values 1.25:5.17:10.00 . . . , theoretical values for a sextet are 1.00:5.00:10.00 . . .

Discussion

The ^{11}B chemical shifts of the amine boranes and μ -aminodiboranes (Tables I and II) occur at a higher field as hydrogens are successively substituted for methyl groups on nitrogen. Similar trends have been observed in the cycloborazanes.¹¹ If one assumes without justi-

(11) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3592 (1963).

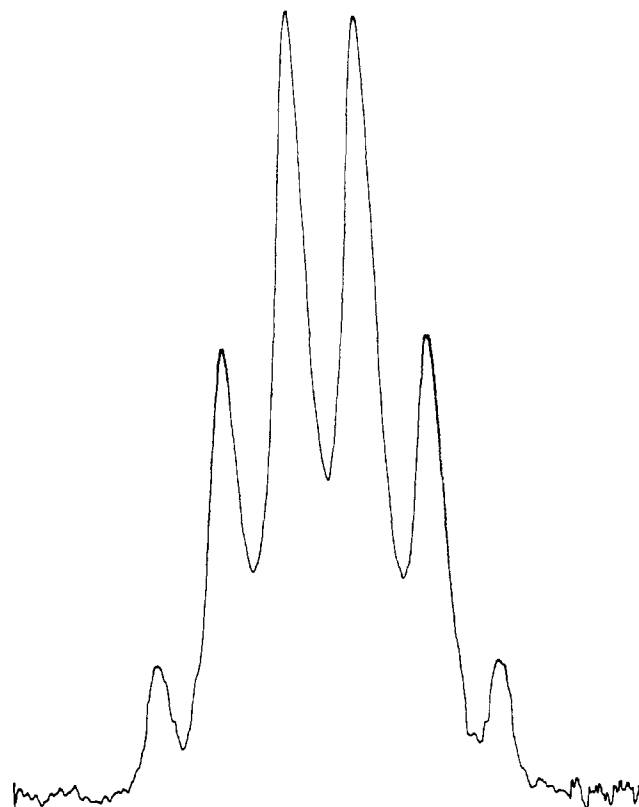


Fig. 2.—The ^{11}B n.m.r. spectrum of μ -dimethylaminodiborane in tetrahydrofuran solution at 63° .

fication that boron chemical shifts will be sensitive to electron density about the boron atom, the observed shifts can be correlated, using the conclusions of Hoffmann¹² that in boron-nitrogen compounds the nitrogen receives more charge from a hydrogen than from a methyl group. Thus, as the number of hydrogens on nitrogen increases, the electron density at the boron increases and the absorption occurs at higher field.

Phillips, Miller, and Muettterties⁴ observed the temperature dependence of the ^{11}B n.m.r. spectra of pure μ -dimethylaminodiborane up to a point corresponding to about half-way between b and c in Fig. 1. They suggested that a probable mechanism to explain the collapse of bridge hydrogen coupling might consist of rupture of half the bridge hydrogen bond followed by rotation about the boron-nitrogen bond and re-formation of the hydrogen bridge using a different hydrogen. Williams,¹³ however, favored an intermediate containing a hydrogen bridge between boron and nitrogen. The absence of boron exchange between μ -dimethylaminodiborane and ^{10}B diborane indicates that Williams'^{1,7} intermediate is less probable than that of Phillips, Miller, and Muettterties. The model suggested by Rigden and Koski¹⁰ for the deuterium exchange between diborane- d_6 and μ -dimethylaminodiborane is consistent with this result although rupture of the boron-nitrogen bond is negligible under the conditions of the exchange reaction.

It appears as though the collapse observed by Phillips, Miller, and Muettterties⁴ constitutes the first stages of a complex and only partially understood intramolecular exchange mechanism. In the limit of rapid ex-

(12) R. Hoffmann, Preprints of Papers, International Boron-Nitrogen Symposium, Durham, N. C., April 23-25, 1963.

(13) R. E. Williams, *Inorg. Chem.*, **1**, 971 (1962).

change each boron is equally coupled to all five boron hydrogens (Fig. 1 (curve e) and Fig. 2), and the suggested mechanism is probably a correct representation of the over-all process. The acceleration of the rate of intramolecular hydrogen exchange in the μ -aminodiboranes by the presence of ethers may well occur in the same way as suggested for diborane.² Nucleophilic attack by ether with bridge opening, rotation of the BH_3 group,

and subsequent nucleophilic displacement of ether by hydride to re-form the bridge would produce the observed spectral collapse provided the reactions were sufficiently rapid.

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The ρ - ρ Relation and the Reaction of *trans*-Cinnamic Acids with Diphenyldiazomethane The Basis of the Hammett Equation¹

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Rate data for the reactions of 15 *trans*-cinnamic acids (*m*- CH_3CO_2 , *m*-Cl, *p*-Cl, H, *m*-F, *p*-F, *p*-OH, *p*-(CH_3) $_2\text{CH}$, *m*- CH_3O , *p*- CH_3O , *p*- CH_3 , *m*- NO_2 , *p*- NO_2 , *p*-(CH_3) $_2\text{N}$, and 2,4-(CH_3O) $_2$) with diphenyldiazomethane (DDM) in ethanol have been obtained. The entropies of activation ($-\Delta S^* = 8$ –21 e.u.) are proportional to the activation energies ($E_{\text{act}} = 12$ –17 kcal. mole⁻¹) in this series with a slope of ca. 298°. Satisfactory Hammett lines for 12 substituents have been obtained: at 25° with k in l. mole⁻¹ min.⁻¹, $\log k = 0.41\sigma - 0.1705$; at 35°, $\log k = 0.43\sigma + 0.1757$. The ρ -value for the cinnamic acids follows the relation, $\rho_{\text{RGC00H}}/\rho_{\text{RGCOS}} = \text{constant}$, suggesting that the factors affecting the transmission of electronic effects in acid dissociation parallel those in the reactions of the acids with DDM. For systems of the type RGC00H , the link between ρ and the distance across G, the polarizability of G, or σ -values involving G are discussed. In some cases, field and mesomeric-inductive effects as embodied in the Kirkwood–Westheimer and Dewar–Grisdale theories can generate observed rate or equilibrium properties.

Substitution in a molecule alters its reactivity. How does a substituent which is fairly remote from the site of reaction do this? The Hammett equation

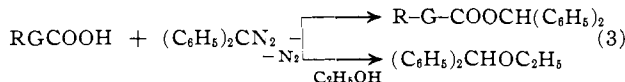
$$\log k = \rho\sigma + \text{constant} \quad (1)$$

seemed to answer this question for aryl systems. One could obtain a ρ -value which characterized the reaction, the reaction conditions (solvent, ionic strength, temperature, etc.), as well as the group G_i (often but not always equivalent to $-\text{C}_6\text{H}_4\text{T}_i-$) through which the electronic effect was relayed to the reaction site.² But after one calculated ρ appropriate to the experimental system, what did it mean?

In a previous paper it was shown that

$$\rho_{\text{RGC00H}}/\rho_{\text{RGCOS}} = \pi = \text{constant} \quad (2)$$

might be helpful in discussing ρ .³ Here the electronic effects are relayed through various groups G_i ; the reaction site in a given reaction, $-\text{COS}$, is being compared with $-\text{COOH}$ in acid dissociation. To date, line A of Fig. 1 for the hydrolysis of families of ethyl esters provided the only adequate test of eq. 2. Line B of Fig. 1 gives the available data for a second system.



In this work, rate studies are reported for the *trans*-cinnamic acids in process 3.

Results and Discussion

The kinetics and mechanism of the reaction of acids with diphenyldiazomethane (DDM) have been discussed.⁴ Suffice it to remark here that the comparison of

the slow proton-transfer process of eq. 3 with acid dissociation appears to be highly suitable for a test of the ρ - ρ relation (eq. 2).³

Rate data for the *trans*-cinnamic acids are given in Table I. For a wide range of substituents, the rate constants vary by a factor of only 3 to 4. The rate constants were determined at two temperatures chiefly

TABLE I
RATE CONSTANTS AND ACTIVATION PARAMETERS
FOR THE REACTION^a

R	k , l. mole ⁻¹ min. ⁻¹ ^b		$-\Delta H^*$ ± 1.0, kcal. mole ⁻¹	$-\Delta S^*$ ± 3.0, cal. deg. ⁻¹ mole ⁻¹
	(25.0 ± 0.1)°	(35.0 ± 0.1)°		
<i>p</i> -(CH_3) $_2\text{N}$	0.392 ± 0.024 ^c	1.01 ^d	16.6	8
2,4-(CH_3O) $_2$.346 ± 0.007 ^d			
<i>p</i> -OH	.679 ± 0.023	1.60 ± 0.02	15.1	12
<i>p</i> - CH_3O	.511 ± 0.019	1.20 ± 0.02	14.9	13
<i>p</i> - CH_3	.622 ± 0.003	1.34 ± 0.06 ^c	13.4	18
<i>p</i> - <i>i</i> -(CH_3) $_2\text{CH}$.645 ± 0.006	1.33 ± 0.08 ^c	12.6	21
H	.695 ± 0.041	1.52 ± 0.004 ^c	13.7	17
<i>p</i> -F	.693 ± 0.019	1.69 ± 0.023	15.6	10
<i>m</i> - CH_3O	.708 ± 0.017	1.48 ± 0.04	12.9	20
<i>p</i> -Cl	.785 ± 0.031	1.91 ± 0.04	15.6	10
<i>m</i> -F	.935 ± 0.017 ^c	1.96 ± 0.06	12.9	19
<i>m</i> -Cl	.891 ± 0.008	2.19 ± 0.08	15.8	9
<i>m</i> - CH_3COO	.873 ± 0.020	1.75 ± 0.10 ^c	12.1	22
<i>m</i> - NO_2	1.54 ± 0.02	3.62 ± 0.12	15.0	12
<i>p</i> - NO_2	1.42 ± 0.01 ^d	3.36 ± 0.15	15.1	11

^a For internal consistency, three significant figures have been retained; however see average deviations and uncertainties listed for each entry. ^b Average of 4 runs, except as indicated. ^c Average of 6–9 runs. ^d Average of 2–3 runs.

(1) Supported by the U. S. Army Research Office (Durham).

(2) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(3) R. A. M. O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963).

(4) J. D. Roberts and C. M. Regan, *ibid.*, **76**, 939 (1954), and previous papers.