VIII was dissolved in water and titrated with sodium hydroxide to a phenolphthalein end point (calcd equiv wt, 152; found, 159). The infrared spectrum of VIII (CS_2 solution) exhibited absorptions at λ_{max} 3040 (w), 2595 (vs), 2400 (w), 1140 (m), 1080 (s), 1060 (s), 980 (sh), 970 (s), 931 (m), 895 (m), 875 (m), 846 (m), 745 (sh), 733 (s), and 684 (m) cm^{-1}. The low-voltage mass spectrum cut off sharply at *m/e* 154 corresponding to the $^{11}B_9{}^1H_{11}{}^{12}C^{31}P^+$ parent ion.

1,2-$B_{10}H_9$BrCHP (IX).—To a refluxing solution containing 1,2-$B_{10}H_{10}$CHP (1.0 g, 0.0062 mol) and aluminum chloride (0.9 g, 0.0068 mol) in 50 ml of carbon disulfide was added dropwise over 1–5 hr a solution of bromine (0.94 g, 0.0058 mol) in 25 ml of carbon disulfide. Reflux was continued for 2 hr after addition. The mixture was filtered and the solvent was removed under vacuum. The resulting tan solid was extracted with three 50-ml portions of boiling hexane. Concentration and cooling of the extract gave pure 1,2-$B_{10}H_9$BrCHP, mp 244.5–245.5°. Both tlc and glpc suggested that the product was a single isomer. The mass spectrum of IX at low electron voltage (10 eV) cut off at *m/e* 244 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_{10}{}^{12}C^{31}P^{81}Br^+$. The infrared spectrum (CS_2 solution) included absorptions at λ_{max} 3040 (m), 2590 (s), 1110 (w), 980 (w), 960 (m), 925 (w), 905 (w), 835 (w), 825 (s), and 725 (m) cm^{-1}. The proton nmr spectrum of IX (acetone-d_6) contained a broad peak at τ 5.75.

1,2-$B_{10}H_8Br_2$CHP (X).—The procedure used in this synthesis was the same as for IX. Reaction of 0.0062 mol of 1,2-$B_{10}H_{10}$CHP and 0.0068 mol of aluminum chloride with 0.0117 mol of bromine in carbon disulfide solution gave 1.03 g (52% yield) of 1,2-$B_{10}H_8Br_2$CHP, mp 255–256°. The mass spectrum at low electron voltage (15 eV) cut off at *m/e* 324 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_9{}^{12}C^{31}P^{81}Br_2{}^+$. The infrared spectrum of X (CS_2 solution) included absorptions at λ_{max} 3040 (m), 2605 (s), 1085 (m), 965 (m), 950 (m), 935 (s), 825 (s), and 725 (m) cm^{-1}. The proton nmr spectrum of X (acetone-d_6) contained a broad doublet at τ 5.78.

1,2-$B_{10}H_7Br_3$CHP (XI).—This derivative was prepared by the same procedure described above for IX and X except that 2.9 mol of bromine was used for each mole of 1,2-$B_{10}H_{10}$CHP. The product was recrystallized from *n*-hexane, mp 352–353°. The mass spectrum at low voltage (13 eV) cut off at *m/e* 404 corresponding to a parent ion of composition $^{11}B_{10}{}^1H_8{}^{12}C^{31}P^{81}Br_3{}^+$. The infrared spectrum contained peaks at λ_{max} 3030 (m), 2600 (s), 1125 (m), 1045 (w), 990 (w), 980 (m), 970 (m), 940 (w), 930 (m), 890 (w), 875 (m), 850 (s), 830 (w), 780 (w), 720 (w), 665 (m), 485 (m), 420 (w), and 370 (w) cm^{-1}. The proton nmr spectrum of XI (acetone-d_6) contained a broad doublet at τ 5.6.

1,7-$B_{10}H_9$BrCHP (XII).—This compound was prepared by the same procedure used for IX. The analytical sample was recrystallized from *n*-pentane, mp 226–227.5°. The high-resolution mass spectrum contained a peak at *m/e* 244.0613 (calcd, 244.0613) corresponding to a parent ion of composition $^{11}B_{10}{}^1H_{10}{}^{12}C^{31}P^{81}Br^+$. The infrared spectrum of XII contained absorptions at λ_{max} 3030 (m), 2590 (s), 1140 (w), 1135 (m), 1045 (w), 1000 (w), 975 (w), 925 (m), 827 (w), 810 (s), 780 (w), 737 (m), 730 (w), 665 (w), and 450 (m) cm^{-1}.

1,7-$B_{10}H_8Br_2$CHP (XIII).—This derivative was prepared by the same procedure used for X. The analytical sample was recrystallized from low-boiling (60–68°) petroleum ether, mp 234–235°. Both tlc and glpc suggested that XIII was a single isomer. The mass spectrum at low voltage (10.5 eV) cut off at *m/e* 324 corresponding to a parent composition $^{11}B_{10}{}^1H_9{}^{12}C^{31}P^{81}Br_2{}^+$. The infrared spectrum of XIII included absorptions at λ_{max} 3040 (m), 2600 (s), 1145 (m), 1055 (m), 1015 (s), 940 (s), 915 (m), 880 (m), 845 (m), 825 (s), 795 (m), 750 (m), and 465 (s) cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Nuclear Magnetic Resonance Study of Aminoboranes and Related Nitrogen–Boron Compounds

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Proton and boron magnetic resonance spectroscopy has been applied to the study of a number of aminoboranes in which restriction of rotation about the nitrogen–boron bond is expected to be present. The magnetic anisotropy of the cyclopropyl and vinyl groups has been shown to lead to differential shielding of vicinal substituents when restriction is present. In a number of B-vinyl compounds, the results can be explained by conjugation and restricted rotation about both the N–B and the B–C_{vinyl} bonds with only one isomer present. In (cyclopropylamino)dimethylborane and in (methylphenylamino)-phenylvinylborane, but not in the other B-vinyl compounds, the nonequivalence of the methyl substituents could be removed either by raising the temperature or by using dimethyl sulfoxide as the solvent. The lack of temperature and solvent effects indicates an increased barrier to rotation about the N–B bond contributed by the vinyl substituent. In a number of aminoboranes and related nitrogen–boron compounds, the ^{11}B chemical shifts can be described fairly well in terms of a set of additive substituent contributions. These contributions depend on the mesomeric effect of the substituent rather than on its electronegativity. Steric effects seem to be important insofar as they influence the amount of double-bond character between the boron and the substituents.

Introduction

Restricted rotation about the nitrogen–boron bond in several aminoboranes, resulting from partial double-bond character, was demonstrated previously by nuclear magnetic resonance spectroscopy with a barrier to rotation about the N–B bond of 10–20 kcal/mol. For example, the spectrum of (methylphenylamino)-dimethylborane at room temperature shows two B-methyl peaks, which correspond to the differently shielded boron methyls *cis* and *trans* to the anisotropic phenyl group.[1] As the temperature is raised, these peaks broaden and, at about 100°, merge as the rate of rotation about the N–B bond increases. For each case of boron-substituent nonequivalence, a phenyl or a benzyl group was attached to the nitrogen; nonequivalence of the nitrogen substituents was caused by a phenyl group, a chlorine, a bromine, or a 1-propynyl group on the boron.[2-13]

In the present investigation, aminoboranes with cyclopropyl and vinyl groups have been studied to determine whether these groups cause observable shift differences. By studying aminoboranes with various functional groups, it was hoped that the effect of the substituent could be related to the nature of the N–B bond. Of particular interest were groups such as phenyl and vinyl which could conjugate with the N–B linkage and thus affect the barrier to rotation. The aminoboranes with vinyl on the boron contain the skeleton N=B—C=C, which can be considered a semianalog of the butadiene system. The present investigation was designed to obtain information on the effect of the vinyl group on the N–B bond and, in particular, to establish whether conjugation over the entire system is great enough to restrict the rotation about the $B-C_{vinyl}$ bond.

The proton spectra of those aminoboranes which have not been studied previously and which contain nonequivalent methyl groups have been investigated in detail. The temperature dependence of the separation between the nonequivalent methyl resonances was determined. The effects of solvents such as dimethyl sulfoxide and chloroform which may reduce the N–B double-bond character either by donating an electron pair to the boron or by accepting an electron pair from the nitrogen have also been investigated. Careful determinations have been made of the substituent proton shifts and of their temperature and solvent dependences in order to correlate these with bonding and configuration in the aminoboranes. However, since the shifts were independent of temperature and solvent, the results of these studies are not tabulated in detail. In addition, the ^{11}B shifts of a number of aminoboranes and related nitrogen–boron compounds were determined in order to relate these shifts to substituent effects.

Experimental Section

The nuclear magnetic resonance spectra were obtained on a Varian DP-60 spectrometer, the proton spectra at 60 Mc/sec and the boron spectra at 19.3 Mc/sec. Normal sample temperature in the instrument was 32 ± 2°. For temperature-dependence runs, the Varian variable-temperature accessory was employed, and the sample equilibrated at the desired temperature at least 0.5 hr before measurements were begun. The sample temperature was monitored with a copper–constantan thermocouple. The thermocouple and the probe had previously been calibrated using the known temperature dependence of the chemical shifts of methanol and of ethylene glycol. The temperatures reported are believed to be accurate to ±2°.

The samples of (methylcyclohexylamino)dimethylborane, (methylphenylamino)dimethylborane, (methylcyclohexylamino)dichloroborane, (diethylamino)dichloroborane, and (methylphenylamino)dichloroborane were prepared by Dr. G. E. Ryschkewitsch of this department. All the other samples were supplied by Dr. K. Niedenzu and Dr. P. Fritz of Duke University. Methods of preparation for each of the compounds are given in Tables II and IV. The samples were pure except for some small impurity peaks, area ratio corresponding to 0.1 hydrogen or less, in (cyclopropylamino)dimethylborane, (dimethylamino)methylvinylborane, (methylphenylamino)phenylvinylborane, and (dimethylamino)methylchloroborane.

Solutions of the samples were prepared in a DriLab Vacuum Atmospheres, Inc., drybox. Only solvents thoroughly dried over molecular sieve were used. Careful inspection of the spectra shows that, unless specifically otherwise stated, the aminoboranes were not decomposed by the solvents used. Unless otherwise indicated, the solutions were made up as approximate volume-to-volume solutions. The neat liquid samples or the solutions were degassed and sealed into an nmr tube. The lower temperature limit of the investigations was set by the temperature of freezing or of loss of resolution of the given sample. The upper temperature limit was approximately 10° below the boiling point of the sample at atmospheric pressure. For those samples which were liquids at room temperature, the temperature dependence of the nonequivalent groups was first investigated in the neat liquid since the temperature range for a neat liquid aminoborane was considerably greater than for either a carbon tetrachloride or a chloroform solution of the same compound. The range of the temperature studies was generally from -10 to $+70°$ for the carbon tetrachloride solutions and from -50 to $+32°$ for the deuterated chloroform solutions.

The spectra were calibrated using audio side bands. All the values reported for the chemical shifts and the peak separations are the average of five to ten independent determinations. The indicated scatter in these values is the average deviation from the mean of these determinations. Since the chemical shifts showed such small temperature dependence, whenever possible the shifts have been determined and reported to 0.001 ppm although, in many cases, the experimental scatter was somewhat larger than 0.001 ppm.

In the aminoboranes containing phenyl groups, the phenyl spectrum usually consists of a large central peak and several small lines. No attempt has been made to analyze the spectra of the phenyl, the *n*-butyl, or the cyclopropyl groups, and estimates as to their chemical shifts are not included in the chemical shift tables. For the perdeuteriodimethyl sulfoxide solutions, the residual hydrogen peak of the solvent was used as the reference because of the low solubility of tetramethylsilane in this solvent. The chemical shift of the residual hydrogen peak in a 1:1 perdeuteriodimethyl sulfoxide–deuterated chloroform solution with tetramethylsilane internal reference has been found to be τ 7.458 ± 0.007. In all the other solvents and in neat (cyclopropylamino)dimethylborane, tetramethylsilane was used as an internal reference.

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TABLE I

METHYL PROTON CHEMICAL SHIFTS AND PEAK SEPARATIONS OF (CYCLOPROPYLAMINO)DIMETHYLBORANE IN VARIOUS SOLUTIONS

Soln[a]	BCH_3 τ, ppm		BCH_3 peak sepn, ppm
Neat	9.630 ± 0.007	9.827 ± 0.007	0.197 ± 0.002
1:1 benzene	9.544 ± 0.014	9.760 ± 0.008	0.208 ± 0.005
1:7 benzene	9.473 ± 0.017	9.695 ± 0.017	0.205 ± 0.008
1:1 *m*-xylene	9.586 ± 0.011	9.808 ± 0.006	0.222 ± 0.007
1:7 *m*-xylene	9.568 ± 0.008	9.747 ± 0.010[b]	0.180 ± 0.003[b]
1:7 *m*-xylene	. . .	9.762 ± 0.008[b]	0.195 ± 0.003[b]
1:15 *m*-xylene	9.575 ± 0.002	9.745 ± 0.002	0.167 ± 0.005

[a] Concentrations are given in ratios of sample volume to solvent volume. [b] Alternate peak assignments.

TABLE II

METHYL PROTON CHEMICAL SHIFTS AND PEAK SEPARATIONS OF SOME AMINOBORANES IN VARIOUS SOLUTIONS

Compd and soln[a]	NCH_3 τ, ppm		NCH_3 peak sepn, ppm	BCH_3 τ, ppm
$(CH_3)_2NB(CH_3)CH{=}CH_2$				
Neat	. . .	. . .	0.047 ± 0.002	. . .
1:2 CCl_4	7.19 ± 0.01	7.23 ± 0.01	0.045 ± 0.003	9.68 ± 0.01
1:1 $CDCl_3$	7.193 ± 0.006	7.245 ± 0.006	0.052 ± 0.001	9.647 ± 0.005
Satd, DMSO-d_6	7.20 ± 0.01	7.25 ± 0.01	0.048 ± 0.002	9.68 ± 0.02
$(CH_3)_2NB(C_6H_5)CH{=}CH_2$				
Neat	. . .	. . .	0.198 ± 0.005	. . .
Dilute CCl_4	7.058 ± 0.006	7.286 ± 0.006	0.228 ± 0.002	. . .
1:3 $CDCl_3$	7.079 ± 0.026	7.314 ± 0.026	0.235 ± 0.003	. . .
$CH_3(n\text{-}C_4H_9)NB(C_6H_5)CH{=}CH_2$				
Neat	. . .	. . .	0.212 ± 0.005	. . .
1:2 CCl_4	7.052 ± 0.014	7.282 ± 0.014	0.230 ± 0.007	. . .
1:1 $CDCl_3$	7.044 ± 0.016	7.271 ± 0.016	0.227 ± 0.005	. . .
Satd, DMSO-d_6	7.046 ± 0.001	7.306 ± 0.001	0.260 ± 0.005	. . .
$CH_3(C_6H_5)NB(C_6H_5)CH{=}CH_2$[b]				
Satd, CCl_4	6.91 ± 0.01		. . .	. . .
CCl_4[c]	6.86 ± 0.01		. . .	. . .
CCl_4, DMSO-d_6[d]	7.01 ± 0.02		. . .	. . .
$(CH_3)_2NB(n\text{-}C_4H_9)Cl$				
Neat	. . .	. . .	0.065 ± 0.002	. . .
1:2 CCl_4	6.908 ± 0.015	6.967 ± 0.015	0.059 ± 0.005	. . .
1:1 $CDCl_3$	6.933 ± 0.014	7.000 ± 0.014	0.067 ± 0.004	. . .
$(CH_3)_2NB(CH_3)Cl$[e]				
Satd, CCl_4	7.115 ± 0.007	7.175 ± 0.007	0.060 ± 0.002	9.414 ± 0.010

[a] Concentrations are given as ratios of sample volume to solvent volume. [b] K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3**, 778 (1964). [c] One volume of saturated carbon tetrachloride solution to three volumes of carbon tetrachloride. [d] One volume of saturated carbon tetrachloride solution to one volume of perdeuteriodimethyl sulfoxide. [e] K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press, Inc., New York, N. Y., 1965, pp 59–60.

The boron chemical shifts have been obtained relative to external trimethyl borate. Liquid samples were run neat and solids in carbon disulfide or benzene solution.

Results

For aminoboranes with nonequivalent methyl groups, which have not previously been investigated, the room-temperature methyl proton chemical shifts and peak separations in various solutions are summarized in Tables I and II.

The vinyl parts of the spectra are ABC patterns, such that computer analysis was necessary to extract the coupling constants and the chemical shifts. The Frequint IV and the LAOCN3 programs[14] on the IBM 709 and the IBM 360 computers of the University of Florida Computing Center were used for this purpose. In the Frequint IV program, the input trial parameters are manually adjusted until the calculated and experimentally observed spectral line positions and line intensities agree within experimental error. The LAOCN3 program uses an iterative method for adjusting the trial parameters until the best least-squares fit is obtained between calculated and observed spectral line positions. For (dimethylamino)methylvinylborane there are two combination lines of appreciable intensity in the methine part of the spectrum. The LAOCN3 program gave the corrected calculated line intensities for these combination lines only if the *trans* and *cis* coupling constants were held constant during the iterative process. For the other vinyl-containing compounds, all of the vinyl spectral parameters were allowed to vary during the iterative process. The vinyl spectral parameters obtained by the Frequint IV and the LAOCN3 programs agree within experimental error and have been summarized in Table III.

The boron shifts for the aminoboranes and for the related nitrogen–boron compounds are contained in Table IV. Some of these shifts have been reported

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(14) The Frequint IV and the LAOCN3 programs have been kindly supplied by Drs. A. A. Bothner-By and S. Castellano, Mellon Institute, Pittsburgh, Pa.

TABLE III

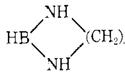
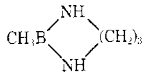
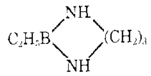
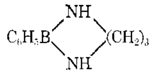
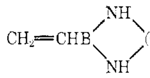
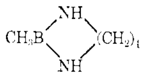
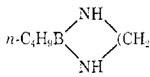
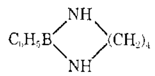
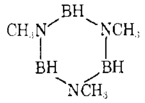
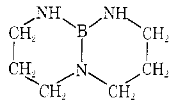
VINYL PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS[a]

Compound	Chemical shifts (τ), ppm			Coupling constants, cps		
	H_A[b]	H_B[b]	H_C[b]	J_{AB}[b]	J_{AC}[b]	J_{BC}[b]
$(CH_3)_2NB(CH_3)CH{=}CH_2$	4.330 ± 0.017	4.302 ± 0.017	3.710 ± 0.017	4.2	13.0	19.5
$(CH_3)_2NB(C_6H_5)CH{=}CH_2$	4.129 ± 0.009	4.617 ± 0.009	3.537 ± 0.009	4.0	13.3	19.1
$CH_3(n\text{-}C_4H_9)NB(C_6H_5)CH{=}CH_2$	4.109 ± 0.012	4.600 ± 0.012	3.495 ± 0.012	4.2	13.1	19.0
$CH_3(C_6H_5)NB(C_6H_5)CH{=}CH_2$	4.224 ± 0.017[c]	4.530 ± 0.017[c]	4.003 ± 0.017[c]	4.5[c]	13.0[c]	19.0[c]
	4.171 ± 0.035[d]	4.477 ± 0.035[d]	3.790 ± 0.035[d]	4.3[d]	13.3[d]	19.4[d]

[a] The sample temperature was +32° unless otherwise noted. The most concentrated carbon tetrachloride solutions given in Table II were used. [b] Designation of protons as in Figures 2–4. [c] Sample temperature −20°. [d] Sample temperature +70°.

TABLE IV

THE ^{11}B CHEMICAL SHIFTS OF SOME NITROGEN–BORON COMPOUNDS

Compd no.	Formula	Method of prepn	Solvent	Chemical shift, ppm (from trimethyl borate)	
				Obsd	Calcd[h]
1	$CH_3(C_6H_{11})NB(CH_3)_2$	*a*	None	−26.3 ± 0.06	−26.3
2	$C_3H_5NHB(CH_3)_2$	*b*	None	−28.8 ± 0.04	. . .
3	$CH_3(C_6H_5)NB(CH_3)_2$	*a*	None	−27.8 ± 0.2	−27.3
4	$CH_3(C_6H_5)NB(CH_3)C_6H_5$	*c*	CS_2	−26.3 ± 0.1	−25.7
5	$(CH_3)_2NB(CH_3)CH{=}CH_2$	*d*	None	−21.4 ± 0.05	−22.6
6	$(CH_3)_2NB(C_6H_5)CH{=}CH_2$	*d*	None	−21.9 ± 0.2	−21.0
7	$CH_3(n\text{-}C_4H_9)NB(C_6H_5)CH{=}CH_2$	*d*	None	−20.8 ± 0.1	−21.0
8	$(CH_3)_2NB(n\text{-}C_4H_9)Cl$	*e*	None	−20.7 ± 0.03	−20.2
9	$CH_3(C_6H_{11})NBCl_2$	*a*	None	−12.0 ± 0.2	−12.1
10	$(C_2H_5)_2NBCl_2$	*a*	None	−12.0 ± 0.05	−12.1
11	$CH_3(C_6H_5)NBCl_2$	*a*	None	−12.7 ± 0.1	−13.1
12		*f*	None	−7.1 ± 0.4	. . .
13		*f*	None	−11.8 ± 0.1	−11.9
14		*f*	None	−12.0 ± 0.02	−11.9
15		*f*	Benzene	−9.0 ± 0.01	−10.3
16		*f*	None	−8.9 ± 0.1	−8.2
17		*f*	Benzene	−11.8 ± 0.1	−11.9
18		*f*	Benzene	−12.5 ± 0.1	−12.9
19		*f*	Benzene	−10.4 ± 0.05	−10.3
20		*g*	None	−14.0 ± 0.2	. . .
21		*f*	Benzene	−3.8 ± 0.02	−3.9

[a] J. F. Brown, *J. Am. Chem. Soc.*, **74,** 1219 (1952); K. Niedenzu and J. W. Dawson, *ibid.*, **81,** 5553 (1959); **82,** 4223 (1960). [b] Transamination of (dimethylamino)dimethylborane with cyclopropylamine. [c] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81,** 5553 (1959); **82,** 4223 (1960). [d] K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3,** 778 (1964). [e] H. Nöth and P. Fritz, *Z. Anorg. Allgem. Chem.*, **322,** 297 (1963). [f] K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, **3,** 1077 (1964). [g] K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press, Inc., New York, N. Y., 1965, p 93. [h] Using substituent contributions from Table VI.

previously[15] but are included for completeness. (Dimethylamino)methylchloroborane and (methylphenylamino)phenylvinylborane were insufficiently soluble in carbon tetrachloride to obtain boron shifts.

The Proton Resonances. (a) **(Cyclopropylamino)-dimethylborane.**—The room-temperature spectrum of neat liquid (cyclopropylamino)dimethylborane consists of a broad NH peak at τ 5.7, an unsymmetrical group of seven lines centered at τ 7.55, attributed to the CH proton α to the nitrogen, and a complex group of lines above τ 9, belonging to the methylene and B-methyl protons. As the temperature of the sample was lowered, its nmr spectrum changed markedly. At about 0°, two tall, fairly broad peaks began to emerge in the upfield portion of the complex of lines belonging to the methylene and B-methyl protons. As the temperature was further lowered, the peaks attributed to the nonequivalent boron methyl groups became narrower and more prominent.

The temperature dependence of neat liquid (cyclopropylamino)dimethylborane was investigated from -100 to $+70°$. Because of the overlap of the methylene peaks with the B-methyl peaks, the activation energy could not be determined. Dilution and temperature-dependence studies have been made of this compound in benzene and in *m*-xylene, in an attempt to alter the relative shielding of the protons of the sample. The range of the temperature study was from -11 to 32° for benzene and from -52 to 60° for *m*-xylene. While the B-methyl peaks are appreciably deshielded in these aromatic solvents (see Table I), the overlap with the methylene peaks is still too large to permit quantitative measurements.

In perdeuteriodimethyl sulfoxide solution, the B-methyl protons show up as a single, large, fairly narrow peak which is superimposed on the cyclopropyl methylene peaks. Apparently, the dimethyl sulfoxide reduces the N–B double-bond character to such an extent that the B-methyl peaks become equivalent. The large B-methyl peak in this solution did not broaden as the temperature was lowered as far as $+10°$.

Figure 1 provides a comparison of the methylene and B-methyl region of the spectrum of (cyclopropylamino)dimethylborane as a neat liquid at -90 and $+32°$ and in dimethyl sulfoxide solution at $+32°$.

(b) **(Dimethylamino)methylvinylborane.**—The N-methyl peaks in the spectrum of this compound show up as two separate peaks of equal intensity over the entire temperature range of the investigation (-90 to $+70°$). Thus the N-methyls are nonequivalent although no phenyl, chlorine, or 1-propynyl group is attached to the boron. The separation between the two N-methyl peaks changes very little as the temperature is raised. Even at $+70°$ there is no indication of peak merging or broadening. The sample was also run as a saturated solution in perdeuteriodimethyl sulfoxide, but the N-methyl nonequivalence was not removed by this solvent.

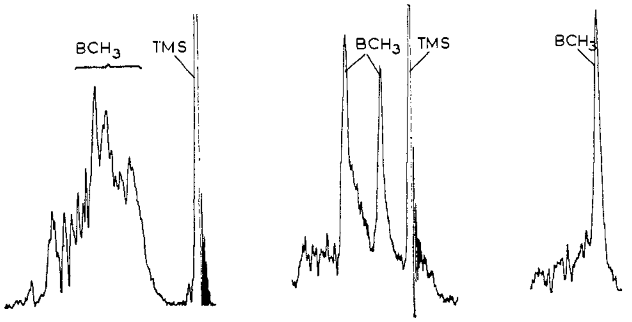


Figure 1.—The methylene and B-methyl region of (cyclopropylamino)dimethylborane. From left to right: neat liquid at $+32°$, neat liquid at $-90°$, and dimethyl sulfoxide solution at $+32°$.

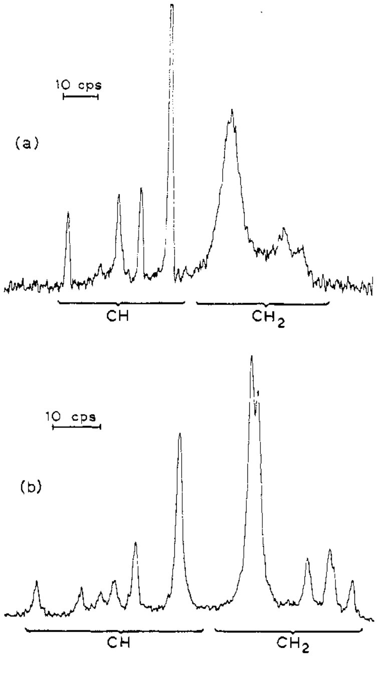


Figure 2.—The vinyl part of the spectrum of neat (dimethylamino)methylvinylborane: (a) $+32°$, the third peak from the left is the superposition of the two combination lines; (b) $-90°$, the third and fourth peaks from the left are the combination lines.

The vinyl spectrum of this compound is a moderately collapsed ABC pattern since the two methylene protons have nearly the same chemical shifts with only 0.03-ppm shift difference between them at 32°. The methine part of the spectrum contains, besides the four fundamental lines, two fairly intense combination lines. As the temperature of the sample was lowered, the line positions and the line intensities in the methine part of the spectrum changed markedly. Figure 2 illustrates these changes. Computer analysis of the spectra has shown that the observed changes were not caused by any temperature dependence of coupling constants, but rather by changes in the relative chemical shifts of the two methylene protons. At lower temperatures the methylene protons beome even more nearly equivalent, having no shielding difference at $-90°$. Such parallel changes in the appearance in the methine part of the spectrum and the chemical shifts of the methylene pro-

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[15] M. R. Chakrabarty, C. C. Thompson, Jr., and W. S. Brey, Jr., *Inorg. Chem.*, **6**, 518 (1967).

tons had previously been observed in vinyl bromide by Schaefer and Schneider[16] as the solvent was varied, and in vinyl chloride by Brey, Scott, and Whitman[17] as the temperature was varied.

(c) (Dimethylamino)phenylvinylborane and (Methyl-*n*-butylamino)phenylvinylborane.—As expected, the temperature dependences of these two compounds were very similar. The N-methyl resonances in both compounds appear as two separate peaks over the entire temperature range from −10 to +120° with no sign of merging or line broadening even at +120°.

Spectra were also obtained of (methyl-*n*-butylamino)phenylvinylborane as a saturated solution in perdeuteriodimethyl sulfoxide. Again, as was found for (dimethylamino)methylvinylborane, this solvent did not remove the nonequivalence of the N-methyls. (Dimethylamino)phenylvinylborane decomposed in perdeuteriodimethyl sulfoxide. Since none of the other aminoboranes with vinyl on the boron has been decomposed by perdeuteriodimethyl sulfoxide, such behavior is rather peculiar, and trace impurities may have catalyzed the decomposition.

Next, a less potent reagent, deuterated chloroform, was tried. Whereas neither of the samples was decomposed in deuterated chloroform, the N-methyl nonequivalence was neither removed nor reduced. Both the chemical shifts and the N-methyl peak separation are nearly the same in deuterated chloroform as in carbon tetrachloride. The temperature dependences of the shifts and peak separations are also comparable in the two solvents.

The ABC patterns of the vinyl group of (dimethylamino)phenylvinylborane and of (methyl-*n*-butylamino)phenylvinylborane are not nearly as collapsed as that of (dimethylamino)methylvinylborane since the shifts of the two methylene protons are quite different when there is a phenyl on the boron.

For (methyl-*n*-butylamino)phenylvinylborane the lines belonging to the methine proton and the methylene proton *cis* to the boron are doubled in both the carbon tetrachloride and the deuterated chloroform solutions. The splitting of the peaks is proportional to the applied field as was shown by obtaining spectra at 60 and 100 Mc. The two sets of peaks are attributed to differently shielded isomeric species about the N–B partial double bond. The two sets of peaks are of approximately equal area. Within experimental error, neither the area ratio nor the peak separations changed over the temperature range of investigation.

The splitting of the methine proton peaks is markedly concentration dependent. No splitting could be observed in the neat liquid. In the solution containing one volume of sample to one volume of deuterated chloroform and in the solution containing one volume of sample to approximately five volumes of deuterated chloroform the splitting was 0.015 and 0.025 ppm, respectively. The splitting of the methylene proton *cis* to the boron is less concentration dependent. At 100 Mc the neat liquid sample showed a splitting of less than 1 cycle; this splitting increased to only 1.3 cps in the more dilute deuterated chloroform solution. Splitting could not be observed in the lines belonging to the methylene proton *trans* to the boron in any of the samples.

In the more dilute deuterated chloroform solution, the two sets of methine proton peaks are far enough separated so that the peak widths could be measured. The full widths at half-maximum peak intensity were 0.55 ± 0.05 and 0.75 ± 0.05 cps for the low-field set and the high-field set, respectively. The difference in line shape of the two sets of peaks is attributed to different relaxation times in the two isomers.

(d) (Methylphenylamino)phenylvinylborane.—The N-methyl and the vinyl peaks of this compound in the carbon tetrachloride solution are narrow at low temperatures. As the temperature of the sample is raised, these peaks show a marked broadening around room temperature. As the temperature is further increased, the peaks narrow again. The temperature dependence of the N-methyl peak width is shown in Table V. The slight broadening of the N-methyl peak at −20° can be attributed to the increased viscosity of the solution near the freezing point. Figure 3 shows the well-resolved vinyl spectrum at −20 and +70° and the broadened vinyl spectrum at +10°. These results have been found to be quite reproducible, and the broadening was not due to field inhomogeneity since, for the tetramethylsilane peak, the full width at half-maximum peak intensity was 1.2 cps or less at all temperatures. Neither was the broadening caused by intermolecular dipole–dipole interaction of the solute molecules since the peak widths remained unaltered on dilution with three volumes of carbon tetrachloride to one volume of saturated carbon tetrachloride solution.

TABLE V

TEMPERATURE DEPENDENCE OF THE N-METHYL PEAK WIDTH OF (METHYLPHENYLAMINO)PHENYLVINYLBORANE IN SATURATED CARBON TETRACHLORIDE SOLUTION

Temp, °C	Full width at half-maximum intensity, cps	Temp, °C	Full width at half-maximum intensity, cps
+70	1.5 ± 0.1	+32	4.5 ± 0.2
+61	2.0 ± 0.2	+20	5.6 ± 0.3
+50	2.2 ± 0.1	+10	4.4 ± 0.2
+41	3.3 ± 0.2	0	3.1 ± 0.3
+37	3.5 ± 0.2	−10	2.0 ± 0.1
+34	3.5 ± 0.2	−20	2.8 ± 0.3

Broadening of the peaks might be caused by a relaxation mechanism resulting from quadrupolar interaction of the N and B nuclei with the electric field gradient within the molecule. Since about the same broadening of the methyl and the vinyl protons in the same temperature range has been observed, this would require comparable magnitude and temperature dependence of the relaxation mechanism caused by the two rather different quadrupolar nuclei. This seems rather unlikely unless the nitrogen and boron are strongly coupled together and act as a unit. It is also quite unlikely

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[16] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **38**, 2066 (1960).

[17] W. S. Brey, Jr., K. N. Scott, and D. R. Whitman, *J. Phys. Chem.*, **72**, 4351 (1968).

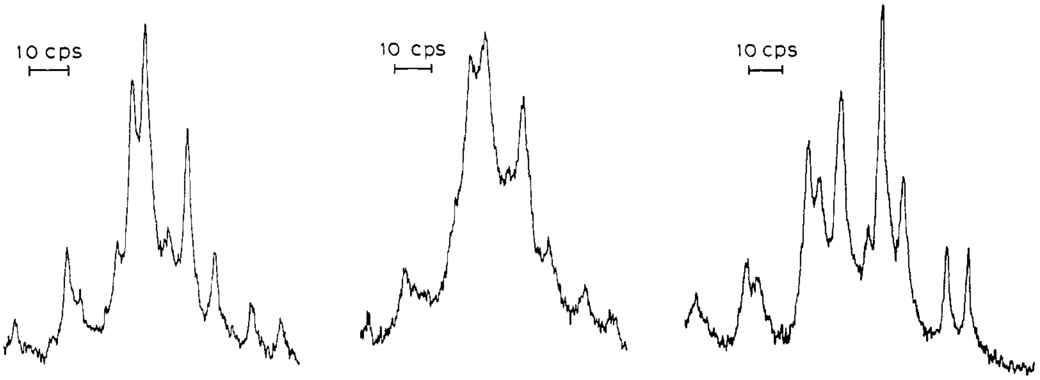

Figure 3.—The vinyl part of the spectrum of (methylphenylamino)phenylvinylborane, saturated solution in carbon tetrachloride. From left to right: −20°, +10°, and +70°.

that the various protons at different distances would be equally affected by the quadrupolar nuclei.

Alternatively, the broadening of the N-methyl and vinyl proton peaks around room temperature may be explained by a slow interconversion, such as restricted rotation about a bond, between two magnetically nonequivalent states, the chemical shifts of which are close enough together so that separate peaks cannot be resolved and only broadening is observed. As the temperature is raised, interconversion between the states becomes more rapid and an average shift accompanied by a narrowing of lines is observed. Thus the temperature dependence of (methylphenylamino)-phenylvinylborane above room temperature is analogous to the behavior of other aminoboranes above the coalescence temperature.

The narrowing of the lines below 20° can be explained by a rapid decrease in the population of the less favored isomer, so that at low temperatures essentially the spectrum of the favored isomer is seen. Such a steep temperature dependence implies a fairly large enthalpy difference between the two states. For a similar compound, (methylphenylamino)methylphenylborane, which also has unequal population of the two isomers at room temperature, Chakrabarty[18] has found a threefold decrease in the equilibrium constant between +55 and +22°.

(e) **(Dimethylamino)-*n*-butylchloroborane and (Dimethylamino)methylchloroborane.**—Nonequivalence of the N-methyl protons was observed in both of these compounds. The N-methyl peak separation in both of these compounds changes very little over the entire temperature range. For the neat liquid, the N-methyl peak separation decreases by only 0.07 ppm over the range of the temperature study from −90 to +80°. Such a small change is probably due to chemical shift changes of the N-methyl protons rather than to an increased rate of rotation.

Both (dimethylamino)methylchloroborane and (dimethylamino)-*n*-butylchloroborane were also run in carbon tetrachloride solution. The temperature dependence of (dimethylamino)-*n*-butylchloroborane in this solvent is almost identical with that of the neat liquid. For (dimethylamino)methylchloroborane the N-methyl peak separation increases only by 0.01 ppm as the temperature is raised by 80°. Again this change is attributed to change in the shielding of the N-methyl protons with temperature.

An attempt was made to run both samples in perdeuteriodimethyl sulfoxide solution, but not surprisingly both samples decompose very rapidly in this solvent. In deuterated chloroform neither of the compounds decomposed, but (dimethylamino)methylchloroborane was insufficiently soluble to obtain a usable spectrum. The temperature dependence of (dimethylamino)-*n*-butylchloroborane in deuterated chloroform is almost identical with that for the carbon tetrachloride solution.

The Boron Resonances.—As expected, all of the boron resonances were broad because of the quadrupolar broadening of the boron nucleus. The resonances for the phenyl-containing compounds were particularly broad: 80–400 cps full width at half-maximum peak intensity. Apparently, the magnetic anisotropy of the phenyl ring contributes to relaxation and broadening. The widths of the boron resonances in samples containing no phenyl group ranged from 35 to 75 cps full width at half-maximum peak intensity.

With the exception of the samples containing hydrogen directly on the boron, no fine structure could be resolved in any of the boron resonances. The B–H coupling constant was found to be 99 ± 10 cps for trimethylborazine and 111 ± 10 cps for 1,3-diaza-2-boracyclohexane.

Hawthorne[19] has shown that the boron resonances for monomeric dialkylaminoboranes are downfield from trimethyl borate, while those for dimeric dialkylaminoboranes are upfield from trimethyl borate. The ^{11}B chemical shifts of all of the compounds in the present investigation are downfield from trimethyl borate. Therefore, all of the aminoboranes in the present series are in the monomeric form. Thus any nonequivalence of alkyl groups on boron or nitrogen cannot be due to dimer formation.

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[18] M. R. Chakrabarty, private communication, Marshall University, Huntington, W. Va.

[19] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2671 (1961).

Discussion

The Proton Resonances. (a) Anisotropy of the Substituents.—(Cyclopropylamino)dimethylborane is the first compound for which boron substituent nonequivalence has been observed when there was neither phenyl nor benzyl substituent on the nitrogen. Apparently the cyclopropyl group is sufficiently anisotropic to contribute appreciably to the shielding of one of the two B-methyl groups.

By comparing the B-methyl τ values of 9.63 and 9.83 obtained for neat (cyclopropylamino)dimethylborane with the τ values of 9.51 and 9.80 obtained by Becher and Baechle[11] for neat (methylphenylamino)dimethylborane, it is seen that the two sets of shifts are very similar although the shielding difference for (methylphenylamino)dimethylborane is somewhat larger. For aminoboranes of the type $R(C_6H_5)NB(CH_3)_2$, the shielding difference between the B-methyls was found to be 0.33 ppm for $R = CH_3$ and 0.42 ppm for $R = CH_2CH_3$.[8] The increased shielding difference is attributed to the increased skew angle between the molecular plane and the plane of the phenyl ring as a result of the bulkier ethyl group. So if the difference in size of the hydrogen and the methyl substituents is taken into account, the shielding difference of the B-methyls in (cyclopropylamino)dimethylborane compares with that in (methylphenylamino)dimethylborane. This suggests that the neighbor anisotropy effect of the cyclopropyl group is of a magnitude comparable with that of the phenyl group.

(Dimethylamino)methylvinylborane is the first compound for which nitrogen substituent nonequivalence has been observed when neither phenyl, chlorine, bromine, nor 1-propynyl substituent was attached to the boron. Apparently the vinyl group is sufficiently anisotropic to cause different shielding of the N-methyl group *cis* and *trans* to the vinyl. The shielding difference of 0.05 ppm for the two N-methyls in (dimethylamino)methylvinylborane, as compared to the shielding difference of 0.11 ppm obtained for (dimethylamino)methylphenylborane,[8] suggests that the vinyl group has a smaller neighbor anisotropy effect than the phenyl group.

(b) Effect of the Substituent on the Barrier to Rotation.—The increase in the barrier to rotation about the N–B double bond by a chlorine substituent[4,6,9,10] has been confirmed by this investigation since neither merging nor broadening of the nonequivalent N-methyl peaks for (dimethylamino)methylchloroborane or (dimethylamino)-*n*-butylchloroborane was observed. Stabilization of the N–B double bond for aminoboranes with vinyl on the boron is indicated since merging or broadening of the nonequivalent N-methyl peaks or vinyl peaks was not observed for (dimethylamino)methylvinylborane, (dimethylamino)phenylvinylborane, and (methyl-*n*-butylamino)phenylvinylborane.

Nonequivalence of the nitrogen substituents in aminoboranes with vinyl on the boron may arise in either of two ways. The first is a restriction of rotation about the N–B bond, but a high barrier to rotation seems peculiar to the boron–vinyl system. If restricted rotation about the N–B bond is the sole cause of the nonequivalence, the increased barrier to rotation when vinyl is on the boron is unexpected, for the vinyl group itself should form a partial double bond with the boron, competing with a potential nitrogen–boron double bond, and the N–B order might be decreased. Indeed, the molecular orbital calculations of Chakrabarty, Thompson, and Brey[15] indicate that the π-bond order of the B–N bond in (dimethylamino)methylvinylborane is 0.516, which is slightly lower than the π-bond order of 0.538 found for (dimethylamino)dimethylborane.

The second source of the nitrogen substituent nonequivalence may be a simultaneous restriction of rotation about both the N–B and the $B-C_{vinyl}$ bonds, associated with conjugation of the entire four-atom system of the N–B–C–C grouping in analogy with the butadiene system. By this analogy, delocalization of the π electrons to give a certain degree of boron–carbon double bonding is probable. Thus, Niedenzu and Sawodny[20] found from the analysis of the vibrational spectra of vinylboranes that the boron–carbon valence force constant in these compounds is substantially increased when compared with that of trimethylborane.

If there is significant restriction of rotation about the boron–carbon bond, *cis–trans* isomers about this bond are possible. This would yield two isomers for (dimethylamino)phenylvinylborane and (dimethylamino)methylvinylborane and a total of four isomers for (methyl-*n*-butylamino)phenylvinylborane and (methylphenylamino)phenylvinylborane. The vinyl protons of the isomers are expected to be nonequivalent although the shielding may not be very different when all of the substituents are methyl groups. Only one set of peaks has been observed for the vinyl protons of (dimethylamino)methylvinylborane and (dimethylamino)phenylvinylborane, and only two sets of peaks have been observed for the vinyl protons of (methyl-*n*-butylamino)phenylvinylborane. For (methylphenylamino)phenylvinylborane separate sets of peaks for the vinyl protons were not resolved, and only broadening was observed. Actually, for such a conjugated system, the *s-trans* isomer is expected to be energetically favored to a considerable degree.[21,22]

Conjugation and restricted rotation throughout the four-atom system with only the *s-trans* isomer present will account for all of the observed nmr facts: (1) N-methyl nonequivalence; (2) only one set of vinyl peaks for (dimethylamino)methylvinylborane and (dimethylamino)phenylvinylborane, two sets for (methyl-*n*-butylamino)phenylvinylborane, and an unresolved but broadened set for (methylphenylamino)phenylvinylborane; and (3) a high barrier to rotation about the N–B bond, which now can be explained by conjugation and delocalization throughout the four-atom sys-

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[20] K. Niedenzu and W. Sawodny, *Z. Anorg. Allgem. Chem.*, **344**, 179 (1966).

[21] L. M. Sverdlov and E. N. Bolotina, *Russ. J. Phys. Chem.*, **36**, 1502 (1962).

[22] A. A. Brothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3451 (1965), and references listed therein.

tem. This delocalization would be lost if there were rotation about the N–B bond. It is noteworthy that, due to delocalization of electrons, a higher barrier to rotation about any bond in the conjugated system may be present, although the N–B bond itself is of lower order. Apparently the slight decrease in the bond order of the N–B bond is more than compensated for by the gain in delocalization energy.

The two N-attached alkyl groups in (methyl-*n*-butylamino)phenylvinylborane might not have a sufficiently different shielding effect on the vinyl hydrogens to explain the observed results. However, they are expected to cause a different skew angle between the phenyl plane and the molecular plane, which in turn produces different shielding of the vinyl hydrogens by the phenyl.

For (methylphenylamino)phenylvinylborane, the N-methyl peak width is 1.3 cps in a solution containing one volume of saturated carbon tetrachloride solution to one volume of perdeuteriodimethyl sulfoxide as compared to 4.5 cps in the saturated carbon tetrachloride solution. This indicates that restricted rotation about a boron bond is involved in causing the peak broadening, because the partial double-bond character of any boron bond is greatly reduced by dimethyl sulfoxide and rapid rotation about the bond is observed. Both the N–B and the $B-C_{vinyl}$ bonds may be involved.

The Stuart–Briegleb model of (methylphenylamino)phenylvinylborane shows considerable steric hindrance to rotation about the $B-C_{vinyl}$ bond. The temperature dependence of the proton chemical shifts seems to indicate that restriction of rotation about both the N–B and $B-C_{vinyl}$ bonds is involved. The chemical shift of the methine proton decreases as the temperature is raised whereas, within experimental error, the chemical shifts of the other vinyl protons and of the methyl protons do not change. This is precisely the expected temperature dependence of the vinyl chemical shifts if there is restricted rotation about the B–C vinyl bond but increasingly free rotation about the N–B bond as the temperature is raised. One cannot as readily predict the expected temperature dependence of the N-methyl proton chemical shift since shielding by both the phenyl and the vinyl substituents contributes to this shift. However, the B-vinyl and the B-phenyl groups may have opposing effects on the N-methyl shifts with increasingly free rotation about the N–B bond and the fortuitous cancellation of these effects can lead to the observed lack of temperature dependence of the N-methyl chemical shifts.

That the phenyl group lowers the N–B double-bond character[4,10] seems to be borne out by the temperature dependence of the spectrum of (methylphenylamino)phenylvinylborane. This is the only compound with vinyl on the boron where rapid interconversion of isomers was attained as indicated by the narrowing of the broad methyl and vinyl peaks at elevated temperatures. The different behavior of this vinyl on boron compound is attributed to the presence of the two phenyl groups.

Whereas the activation energy could not be determined for (cyclopropylamino)dimethylborane because of the peak overlap, the barrier to rotation appears not to be unusually high since nonequivalence could be removed either by raising the temperature or by using dimethyl sulfoxide as the solvent.

(c) **Solvent Effects on the Barrier to Rotation.**—For the two compounds, (cyclopropylamino)dimethylborane and (methylphenylamino)phenylvinylborane, for which the barrier to rotation was low enough to see changes in the spectra at elevated temperatures, the solvent perdeuteriodimethyl sulfoxide removed the nonequivalence at room temperature. Presumably the oxygen of the dimethyl sulfoxide forms a strong enough dative bond with boron so that the barrier to rotation about the N–B bond is lowered and nonequivalence is removed at a lower temperature than when no dimethyl sulfoxide is used.

For the other two compounds of the series which did not decompose in perdeuteriodimethyl sulfoxide—(dimethylamino)methylvinylborane and (methyl-*n*-butylamino)phenylvinylborane—dimethyl sulfoxide did not remove the nonequivalence. Since both of these compounds contain vinyl on the boron, the lack of solvent effect in dimethyl sulfoxide is further proof for the increased barrier of rotation about the N–B bond by a vinyl group.

The mildly hydrogen-donating solvent, deuterated chloroform, did not affect the barrier to rotation in any of the aminoboranes that were studied in this solvent.

(d) **The Vinyl Spectra.**—The vinyl parameters determined in this work are the first to be reported for a vinyl group attached to boron. In other vinylic systems each of the proton coupling constants has been found to increase with decreasing electronegativity of the substituent.[23–28] Using the electronegativity value of 2.0 for boron, the coupling constants obtained in the present work fit the coupling constant *vs.* electronegativity relationship for vinylic systems[23–28] very nicely. In particular, the large positive value of $+4.3 \pm 0.3$ cps obtained for the *gem* coupling constant is well in line with expectations. Only when a more electropositive metal, such as lithium or aluminum, is the substituent has the observed *gem* coupling constant been a larger positive number.[28]

The τ values in Table III show that replacing a methyl on boron by a phenyl deshields the methine proton and the methylene proton *trans* to the boron, each by about 0.2 ppm. The methylene proton *cis* to the boron, however, is shielded by 0.3 ppm. The deshielding of the protons could be caused by the different inductive effect of the phenyl group. The shielding of the methylene proton *cis* to the boron is attributed to the neighbor anisotropy effect of the phenyl group and indicates that the phenyl ring is tilted[8,11] out of the molecular plane.

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(23) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(24) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **35**, 380 (1961).

(25) J. S. Waugh and S. Castellano, *ibid.*, **35**, 1900 (1961).

(26) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(27) J. Feeney, A. Ledwith, and H. L. Sutcliffe, *J. Chem. Soc.*, 2021 (1962).

(28) F. Hruska, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **43**, 2827 (1965).

Broadening of the methylene proton lines in the vinyl spectra of (dimethylamino)methylvinylborane, (dimethylamino)phenylvinylborane, and (methyl-*n*-butylamino)phenylvinylborane was observed as the temperature was raised, as illustrated by Figure 4. This broadening was particularly marked for the proton *trans* to the boron. In (dimethylamino)methylvinylborane broadening of the lines began below −20°, whereas in the other two compounds comparable broadening did not start until about +50°.

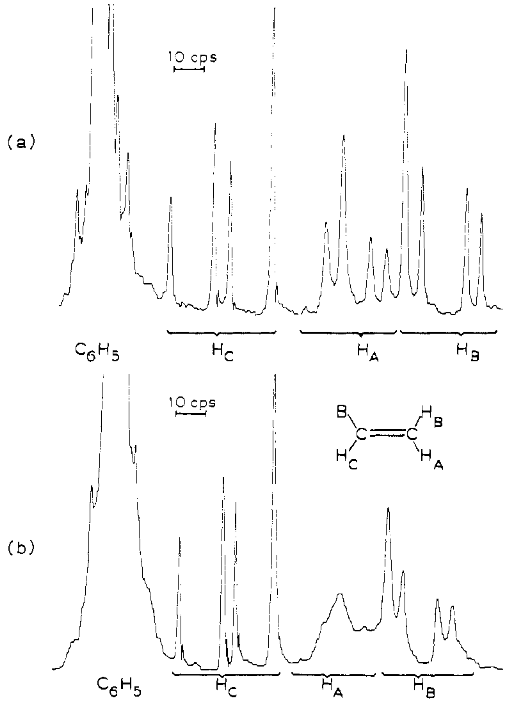

Figure 4.—The phenyl and vinyl regions of neat (dimethylamino)-phenylvinylborane: (a) +32°; (b) +120°.

The broadening of the methylene lines is probably not caused by intermolecular interactions since about the same degree of broadening was observed in the carbon tetrachloride solutions as in the neat liquid samples. Also, since the broadening appears at elevated temperatures where intermolecular interactions are expected to be diminishing, intramolecular interactions appear to be the more likely explanation for the observed broadening.

Intramolecular interactions which may cause broadening are anisotropic shielding, internal dipole–dipole interactions, quadrupolar interactions, and spin–rotation interactions. While for fluorine the anisotropic shielding may contribute to relaxation, for protons the much smaller magnitude of the shielding makes it possible to neglect the effect of anisotropic shielding.[29] Dipole–dipole interactions have the wrong temperature dependence since they would cause broadening with decreasing temperature.[30,31] Both quadrupolar interactions and spin–rotation interactions cause increased broadening with increasing temperature; moreover, both of these interactions cause broadening which is independent of the magnetic field strength. At a given temperature the broadening observed in the methylene lines was found to be comparable at 60 and 100 Mc. Thus both quadrupolar interactions and spin–rotation interactions are consistent with the experimental data. It is difficult to see how over-all rotation of the molecule can cause relaxation that would result in the observed highly specific broadening, but spin–internal rotation[32] interactions may be involved. To see whether the broadening was caused by spin–rotation interaction, a close hydrocarbon analog of (dimethylamino)methylvinylborane, 3-methyl-1,3-pentadiene, was studied. 3-Methyl-1,3-pentadiene is expected to have spin–rotation characteristics similar to (dimethylamino)methylvinylborane, but no quadrupolar relaxation mechanism. Neither 3-methyl-1-*trans*-3-pentadiene nor 3-methyl-1-*cis*-3-pentadiene has shown any broadening of the vinyl lines in the available temperature range of −90 to +70°. This implies that the line broadening observed in compounds with vinyl on boron is caused by the anisotropy of the boron quadrupolar coupling rather than by spin–rotation interactions.

The Boron Resonances. (a) Additivity of Substituent Effects.—The ^{11}B chemical shifts of the aminoboranes show a definite pattern which appears to be closely related to the substituents directly attached to the boron. To test the additivity of the shift effects, a set of shift contributions has been obtained. For example, the effect of replacing a methyl group attached to boron by a phenyl group may be obtained by comparison of compounds **3** and **4** in Table IV, by comparison of **13** and **15**, or by comparison of **17** and **19**.

The substituent contribution values which fit the results best are listed in Table VI. The basic compound is taken as that in which two methyl groups are attached to the boron and the nitrogen bears two alkyl or cycloalkyl groups. A phenyl on the nitrogen produces a small downfield boron shift, for which a correction of 1.0 ppm is made. Those compounds, including **12–19** and **21**, which have the boron attached to two NH groups are treated in the following way: one of the attached nitrogens is considered as part of the basic unit, but with one of its alkyls replaced by hydrogen, for which a correction of +3.2 ppm is made. Because all of these compounds are cyclic, this correction may include an effect of the presence of the ring as well as of the hydrogen substitution. The second nitrogen unit is considered to be an RHN substituent on the boron, replacing an alkyl group in the reference molecule.

The ^{11}B chemical shifts predicted on the basis of the entries in Table VI are listed in the last column of Table IV. Agreement with the observed values is fairly satisfactory, although there are several devia-

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TABLE VI

THE ^{11}B CHEMICAL SHIFT CONTRIBUTIONS OF SUBSTITUENTS RELATIVE TO $R_2NB(CH_3)_2$

Substituent	Shift contribution, ppm
On boron atom	
C_2H_5	0.0
n-C_4H_9	−1.0
C_6H_5	+1.6
$CH_2{=}CH$	+3.7
Cl	+7.1
RHN	+11.2
On nitrogen atom	
H	+3.2
C_6H_5	−1.0

tions larger than the experimental error. These occur particularly when a vinyl group is present.

(b) **The ^{11}B Shift and Inductive–Mesomeric Effects of the Substituents.**—Inspection of Table VI shows that the relative shift contribution of the substituents gives an order opposite from that expected from electronegativity–inductivity considerations. Similarly, only a rough relationship exists between the shifts and the sum of the electronegativities of the first atom in the substituent, as illustrated by Figure 5. For a given electronegativity, the compounds with two or three nitrogens are more shielded than the ones with only one nitrogen. This indicates that increased π bonding between the boron and the substituent is rather effective in shielding the boron since more double bonding is expected between boron and nitrogen than between boron and either chlorine or a phenyl or a vinyl substituent.

For the group of compounds with two or three nitrogen substituents, there are too few data points to be able to say whether the shielding increases or decreases with increasing electronegativity of the substituents. For the compounds with only one nitrogen, there are enough data points to indicate that the shielding increases with increasing electronegativity of the substituents. By inspecting the substituents, we see that the ease with which they form a double bond with boron Cl > C, predicts the correct direction for the observed shielding. Thus for the aminoboranes studied, any ^{11}B shift and substituent electronegativity correlation that may exist is overshadowed by the mesomeric effect of the substituents. These observations substantiate previous results[33] obtained for trisubstituted boron compounds.

(c) **Importance of Steric Effect.**—The vinyl group causes greater shielding of ^{11}B than does the phenyl group as shown by comparing the shift of (dimethylamino)methylvinylborane with that of (methylphenylamino)methylphenylborane. Apparently the vinyl group is more effective in its mesomeric contribution than is the phenyl group. For most effective conjugation, the plane of the phenyl ring or the plane of the vinyl carbon–carbon bond has to lie in the plane of the N–B bond. Now it is easier for the vinyl group to attain this desired configuration than it is for the bulky phenyl group to do so, as can be seen from Stuart–Briegleb models of (dimethylamino)methylphenylborane and (dimethylamino)methylvinylborane.

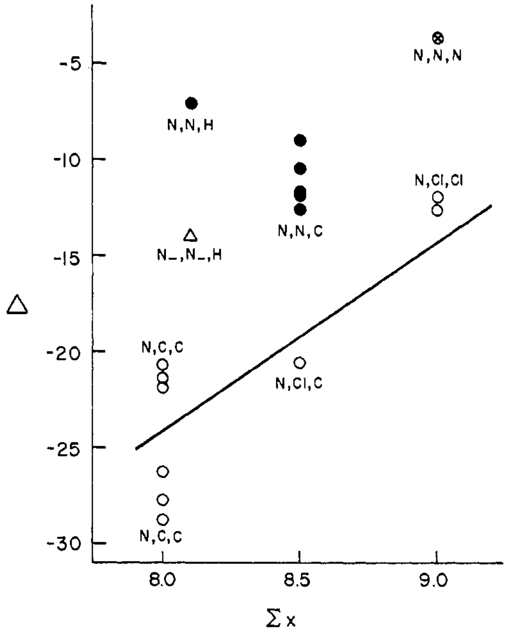

Figure 5.—Boron shift dependence on substituent electronegativities. Δ is the boron chemical shift in ppm from trimethyl borate. Σ_X is the sum of the Pauling electronegativities of the first atom in the substituents. The first atom in the substituent is indicated next to each point: ○, one N substituent; ●, two N substituents; ⊗, three N substituents; △, N-trimethylborazine, where N– indicates a nitrogen which is also bonded to a second boron.

Steric effects must be negligible in going from a six-membered to a seven-membered ring as can be seen from the shifts of the 1,3-diaza-2-boracyclohexanes, which are almost identical with the shifts of the comparably substituted 1,3-diaza-2-boracycloheptanes.

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