small and considerably different from those obtained for the hydrolysis.[3] The inductive effect of the butyl group on the negative charge on oxygen can explain the decrease in activation energy as compared with the value for hydrolysis. The activation entropy, −45.3 eu, is one of the largest negative values ever observed and may be attributed to a great deal of "freezing" of solvent into the transition state.

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Photochemistry of Borazine. Preparation and Characterization of Isotopically Substituted B-Monoaminoborazines[1]

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Received December 29, 1967

A photochemical procedure for the preparation of B-monoaminoborazine has been extended to a series of deuterium and ^{15}N isotopically labeled species. Infrared spectra of $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_2$, and $H_3N_3B_3D_2ND_2$ have been obtained and frequencies assigned. Proton magnetic resonance spectra of $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_2$, and $H_3{}^{15}N_3B_3H_2{}^{15}NH_2$ have been obtained and discussed in relation to the analogous benzene derivatives.

Introduction

In the extensive literature on borazine chemistry most of the experimental work has been associated with B-trisubstituted or N-trisubstituted derivatives. Very little is known of the structure or chemical properties of the unsymmetrical mono- or disubstituted compounds. We have recently reported a photochemical procedure for the preparation of some B-monosubstituted borazines.[3] Subsequently, as reported in this paper, the method has been extended to the preparation of deuterium and ^{15}N-labeled B-monoaminoborazines suitable for infrared and nmr studies. It was anticipated that nmr studies on an unsymmetrical borazine derivative would reveal substituent effects, not observable in the symmetrical trisubstituted molecules.

Experimental Section

Borazine was prepared from $LiBH_4$ and NH_4Cl[4] and the impurity, $B_2H_5NH_2$, was removed by adding ammonia and forming a nonvolatile adduct. A mixture of borazine and ammonia each at 10 mm pressure was irradiated for 20 min in a reaction vessel of about 1500 ml.[3] The product, B-monoaminoborazine, was condensed in a trap at −65°, cooled in a slush bath of chloroform. B-Monoamino-^{15}N-borazine was prepared starting with 95% $^{15}NH_3$ and borazine-$^{15}N_3$ prepared from $LiBH_4$ and $^{15}NH_4Cl$ (95%), and B-monoaminoborazine-d_4 was prepared starting with 95% B-trideuterioborazine and 99% ammonia-d_3. Since B-trideuterioborazine was prepared by a photochemical method not previously reported in the literature, the procedure will be described here. A mixture containing 75 mm of deuterium gas and 15 mm of borazine was irradiated for 10 min under the same conditions used for the preparation of aminoborazines. The partially deuterated borazine was then condensed with liquid nitrogen in the reaction vessel and the impure deuterium was pumped off. Pure deuterium was then added to the vessel in a deuterium:borazine ratio of 5:1 and the mixture was again irradiated. This procedure was repeated three times to give a borazine sample over 95% deuterated on the B atom as determined mass spectrometrically. Some borazine is lost in the irradiation process and during the transfer of materials so that usually only about 60% of the original sample of borazine was recovered. Nuclear magnetic resonance spectra indicated the presence of H atoms bound only to nitrogen atoms.

Infrared spectra were obtained on a Perkin-Elmer Model 521 grating spectrophotometer calibrated against indene.[5] The gas spectra were obtained in a 9-cm gas cell fitted with KBr windows and the spectra of solid films were obtained from samples deposited on a KBr window cooled by liquid nitrogen.[3] For the ease of collecting samples for nmr studies, a U-tube trap sealed at the bottom to a long piece of 5-mm o.d. Pyrex tubing was used. Products of the ammonia–borazine reactions were condensed on the lower section of the U tube. When the samples liquefied at room temperature they were then transferred by gravity into the nmr tube. A small amount of a 5:1 CCl_4–TMS mixture was condensed into the tube for the internal standard. The tube was then sealed off at the top and a spectrum was taken at 37° with a Varian Model A-60 analytical nmr spectrometer. The noise level in the spectra obtained in the Pyrex sample tube did not present a serious problem in the analysis.

Results and Discussion

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra of $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_3$, and $H_3{}^{15}N_3B_3H_2{}^{15}NH_2$ are shown in Figure 1. Chemical shifts based on TMS as internal reference are given in Table I. In general only the resonances associated with the H atom bound to nitrogen atoms were sufficiently intense for identification purposes. Spectra of the compound with the normal N isotopic abundances are very broad due to ^{14}N quadrupole relaxation. Identification of the hydrogen groups was simplified by observing ^{15}N isotopically substituted species. The intense broad peak at about 1.92 ppm in the normal compound, which splits into a doublet (J = 79.1 cps), is attributed to the

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[2] National Science Foundation Undergraduate Research Participant, summer 1967.

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TABLE I

NMR SPECTRA AND SHIFTS FROM TMS[a]

$H_3N_3B_3H_2NH_2$		$H_3N_3B_3H_2{}^{15}NH_2$		$H_3{}^{15}N_3B_3H_2{}^{15}NH_2$	
J, cps	δ, ppm	J, cps	δ, ppm	J, cps	δ, ppm
115	1.92	75	1.25	72	1.20
211	3.52	155	2.58	152	2.53
258	4.30	203	3.38	209	3.48
297	4.95	251	4.18	247	4.12
		294	4.90	285	4.75
				324	5.40

[a] $\delta = (H_{\text{reference}} - H_{\text{sample}})/H_{\text{reference}}$.

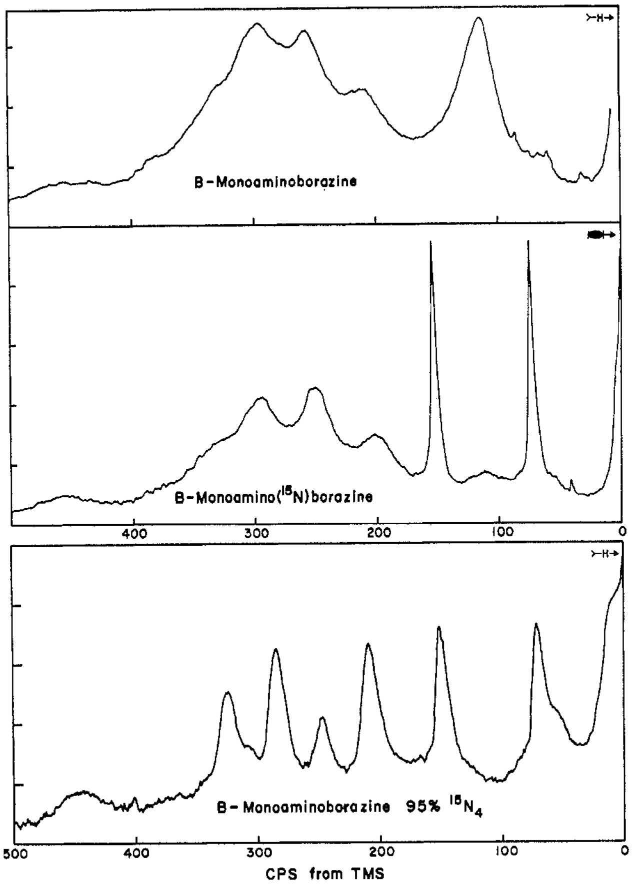


Figure 1.—Nmr spectra (60 Mc) of $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_2$, and $H_3{}^{15}N_3B_3H_2{}^{15}NH_2$.

H atoms on the amino group. Species with ^{14}N in the ring show a very broad unresolved structure at low field. This group splits into two sets of doublets with complete ^{15}N substitution. From the relative intensities of the two groups, the doublets at 4.12 ppm (J = 76.6 cps) and at 4.75 ppm (J = 78.8 cps) are assigned to the o- and p-NH groups, respectively. The ^{15}N–H coupling constants for the three types can be compared with a value of J = 79.4 cps found for ^{15}N-labeled borazine.[6] The J^{15}(NH) value of 79.1 cps for the H atoms on the amino group in aminoborazine is very close to the value of 78.5 cps observed in aniline,[7] suggesting a structural analogy between the two molecules.

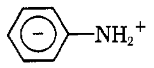
Following the procedure of Binsch, *et al.*,[8] we have estimated from the ^{15}N–H coupling constants the amount of s character and the HN< angles for each of the three types of N atoms (Table II). Without a further theoretical interpretation of the results, departure from sp^2 hybridization in all three positions is indicated with little distinction between the nitrogen atoms in the amino group and those in the ring.

TABLE II

PROTON RESONANCES IN ISOTOPIC SPECIES OF B-MONOAMINOBORAZINE

Proton	Shifts, cps (from TMS) $H_3N_3B_3H_2NH_2$	$H_3N\ B_3H_2{}^{15}NH_2$	$H_3{}^{15}N_3B_3H_2{}^{15}NH_2$	$J_{^{15}NH}$, cps	Estd s character on N atom, %	Estd HN< bond angle, d.g
$-NH_2$	115	75	72	79.1	27.7	112.5
		155	152			
o-NH	211	203	209	76.6	26.9	111.5
	258	251	285			
	297	294				
p-NH	Masked	Masked	247	78.8	27.7	112.5

In Table III we compare the chemical shifts for all H atoms bonded to nitrogens in aminoborazine (relative to borazine) with those for H atoms in equivalent structural positions in aniline (relative to benzene).[9] The results indicate, as in aniline, the *ortho* position is affected to a greater extent than the *para* position. The shift to higher field is as expected from the electron-donating substitutent ($-NH_2$) to form the mesomeric form



increasing the shielding of the protons.[10]

TABLE III

CHEMICAL SHIFTS (δ, PPM) FROM THE POSITIONS OF THE UNSUBSTITUTED COMPOUNDS

Proton	B-Monoamino-borazine	Aniline[a]
ortho	−1.31	−0.77
para	−0.67	−0.40
ortho/*para*	1.95	1.93

[a] Data from ref 9.

Infrared Spectra.—Infrared spectra of gaseous B-monoaminoborazine with isotopic compositions $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_2$, and $H_3N_3B_3D_2ND_2$ are shown in Figure 2. Solid-film spectra of $H_3N_3B_3H_2NH_2$ and $H_3N_3B_3H_2{}^{15}NH_2$ are shown in Figure 3. In

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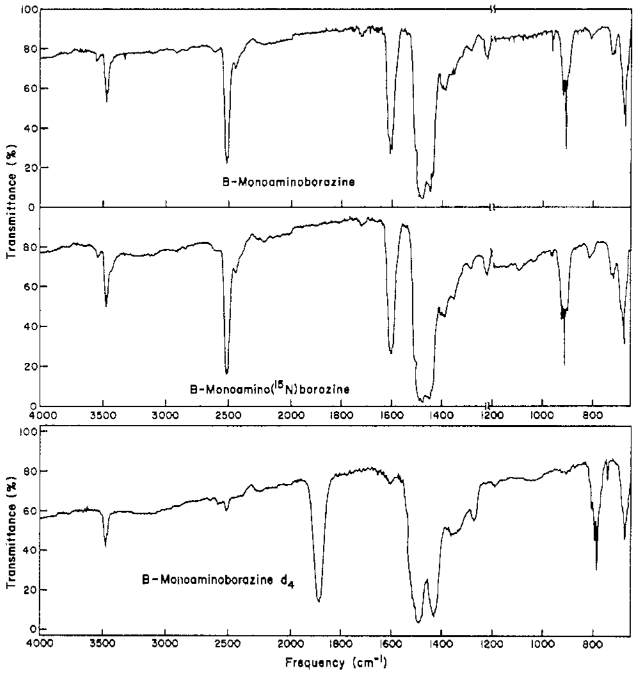

Figure 2.—Infrared spectra of gaseous $H_3N_3B_3H_2NH_2$, $H_3N_3B_3H_2{}^{15}NH_2$, and $H_3N_3B_3D_2ND_2$.

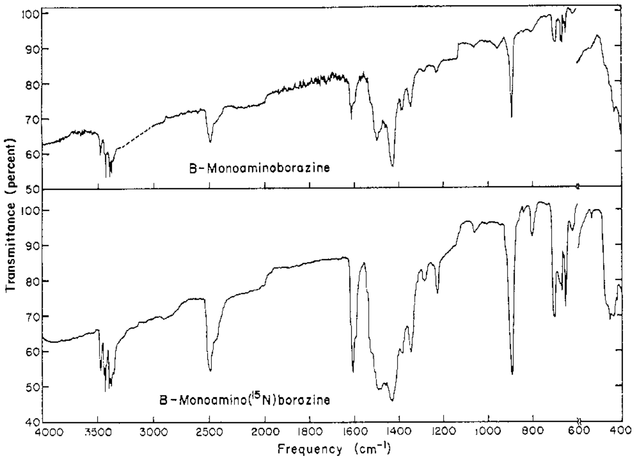

Figure 3.—Infrared spectra of solid films (−196°) of $H_3N_3B_3H_2NH_2$ and $H_3N_3B_3H_2{}^{15}NH_2$.

Table IV

Infrared Spectra of Isotopically Labeled B-Monoaminoborazine[a] (cm^{-1})

$H_3N_3B_3H_2NH_2$		$H_3N_3B_3H_2{}^{15}NH_2$		$H_3N_3B_3D_2ND_2$
Gas	Solid	Gas	Solid	Gas
3561 w	3490 m	3552 w	3483 m	3483 m
3482 m	3440 m	3482 m	3440 m	
	3405 m		3403 m	
	3386 m		3386 m	
2521 s	2500 s	2521 s	2500 s	2578 w
2452 w		2452 w		2519 w
				1884 s
1612 s	1616 s	1604 s	1605 s	
1482 s	1502 s	1483 s	1494 s	1492 s
1451 s	1435 s	1450 s	1434 s	1431 s
1395 m	1386 m	1393 m	1384 m	1366 m
	1351 m		1346 m	
1292 w	1288 w	1291 w	1286 w	
				1275 m
1228 w	1236 w	1227 w	1233 w	1188 vw
	1062 w		1066 w	
926 m	897 s	926 m	897 s	796 m
913 s		913 s		787 s
817 w	809 vw	814 w	806 w	(744 w)
725 m	702 m	719 m	704 m	
677 s	669 m	677 s	669 m	673 m
	654 m		653 m	
	436 w		456 w	
			436 w	

[a] s, strong; m, medium; w, weak; vw, very weak.

Table IV frequencies are listed only for the bands that were sufficiently strong to be attributed confidently to the aminoborazine species. A partial vibrational assignment is given in Table V. In the vibrational analysis it was assumed that aminoborazine is structurally similar to aniline[11] and methylamine[12] with C_s symmetry. However, without the additional evidence from the nmr spectra, we cannot rule out a totally planar structure with C_{2v} symmetry. From the isotopic shifts observed on deuterium substitution, it was possible to distinguish the bands most closely associated with the ring proper. The high-frequency out-of-phase N–H stretch (amino group) at 3561 cm^{-1} corresponds to the band at 3573 cm^{-1} in aniline.[13] The strong band at 1612 cm^{-1}, which shifts and becomes a weak band at 1275 cm^{-1} on deuterium substitution, is close to the $-NH_2$ deformation frequency (1623 cm^{-1}) in methylamine.[12] This band is important for purposes of identification. The band at 725 cm^{-1} is shifted on deuterium substitution but is either masked or too low in intensity for observation. This band probably corresponds to the NH_2 wagging vibration at 780 cm^{-1} in methylamine.[12] There is apparently no simple molecule for comparison in the case of the $B-NH_2$ stretch assigned to the band at 1228 cm^{-1}. The isotopic shift on ^{15}N substitution (NH_2 group) is not very large but the shift on deuterium substitution (ND_2 group) is quite large, indicating participation of the H atom in the vibration. Two strong bands at 913 and 677 cm^{-1} in B-monoaminoborazine are closely related to the out-of-plane B–H bend (917.5 cm^{-1}) and the out-of-plane N–H bend (719 cm^{-1}), respectively, in borazine.[14] In borazine two ring stretching vibrations of type E (based on D_{3h} symmetry) are infrared active. In aminoborazine they split into four bands of type A′ and A″. The two strong bands at 1483 and 1451 cm^{-1} and the weaker band at 1395 cm^{-1} are attributed to ring vibrations, although their symmetry types have not been assigned.

Comparison of solid-film and gaseous spectra (Table IV) reveals a number of obvious similarities. Some differences are noted in the high-frequency region between 3300 and 3600 cm^{-1}. In this region, the solid-

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TABLE V

FUNDAMENTAL VIBRATIONS (CM^{-1}) IN B-MONAMINOBORAZINE

$H_3N_3B_3H_2NH_2$	$H_3N_3B_3H_2{}^{15}NH_2$	$H_3N_3B_3D_2ND_2$	Vibration species	Description
1612	1604	1275	A′	NH_2 def
1228	1227	1188		B–(NH_2) str
926	926	796		B–H bend
913	913	787		
725	719			NH_2 wag
677	677	673		N–H (ring) bend
3561	3552	2578	A″	NH_2 str
3482	3482	3483		N–H (ring) str
2521	2521	1884		B–H str
1483	1483	1492	Unassigned	B–N ring str
1451	1450	1431		B–N ring str
1395	1393	1366		B–N ring str

film spectra are shifted toward lower frequencies and features appear that are not observed in the gas spectra. The doublet at 3440 and 3405 cm^{-1} in the solid film spectrum probably results from an intermolecular splitting of the N–H (ring) vibrations, and the band at 3386 cm^{-1} is probably the counterpart of the in-phase N–H (NH_2 group) stretch in the gaseous molecule.

Acknowledgment.—The authors wish to thank Professor J. J. Zuckerman and Dr. D. E. Fenton for their valuable suggestions on the nmr studies.

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A Vibrational Analysis of Gaseous Boroxine[1-3]

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Received December 20, 1967

With an improved method for the preparation of boroxine it has been possible to obtain infrared spectra of the gaseous compound at pressures up to 20 mm. Infrared spectra have been obtained for the isotopic species $H_3{}^{11}B_3{}^{16}O_3$, $H_3{}^{10}B_3{}^{16}O_3$, $H_3{}^{11}B_3{}^{18}O_3$, $D_3{}^{11}B_3{}^{16}O_3$, and $D_3{}^{11}B_3{}^{18}O_3$. The spectra are discussed in relation to two possible molecular structures: a planar model (D_{3h} configuration) and a nonplanar model (C_{3v} configuration). Spectral evidence from the partially deuterated species $H_2DB_3O_3$ and $HD_2B_3O_3$ support the nonplanar model and similarities between the spectra of boroxine and borazine are discussed. A normal-coordinate analysis based on several isotopic species yielded a set of simple valence force constants including one interaction constant, which could predict most of the observed vibrational frequencies to within 3%.

Introduction

Boroxine is a high-temperature molecule and at room temperature decomposes to B_2H_6 and B_2O_3 with a lifetime of from 10 min to 4 hr depending upon the surface condition of the vessel.[4,5] If the gas is condensed at liquid nitrogen temperature and then allowed to warm to room temperature, it decomposes to form diborane and boron oxide. Definite evidence for its existence was obtained by Sholette and Porter[6] from studies of the high-temperature reaction of H_2 and B–B_2O_3 in the mass spectrometer. Experiments by Lee, Bauer, and Wiberley[7] showed it to be an intermediate in the oxidation of pentaborane-9. The infrared spectrum of the solid was observed by Gupta and Porter in 1963.[8] Since then, two other independent investigations have reported a gas-phase infrared spectrum of low-pressure samples.[5,9] By the above procedures it was not possible to obtain pressures of boroxine above approximately 5 mm. Barton, Grimm, and Porter[10] found that much higher pressures of boroxine could be obtained by applying an electrical discharge to low-pressure diborane–oxygen mixtures. Using this technique we have obtained much stronger spectra, making it possible to reinvestigate the infrared spectrum for new absorption bands. From the observed frequencies a

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency, Cornell University, Ithaca, N. Y.

[2] Taken in part from a thesis submitted by F. A. Grimm in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School, Cornell University, Jan 1968.

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