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The Unsymmetrically Substituted N- and B-Methylborazines

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The compounds $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_2CH_3B_3N_3H_3$, and $H(CH_3)_2B_3N_3H_3$ have been prepared by new synthetic procedures and compared with $H_3B_3N_3H_3$ with regard to their ^1H and ^{11}B nmr, infrared, and mass spectra. The ^1H nmr data are consistent with the methyl group acting as an electron-releasing substituent, especially for the B-methylborazine derivatives. The ^{11}B nmr, infrared, and mass spectral data are also discussed.

The bonding in the borazine ring has been the subject of many discussions. Molecular orbital calculations[1–3] suggest that some π-electron density is transferred from nitrogen to boron, but the higher electronegativity of the nitrogen atom, acting through the σ system, maintains a partial negative charge on nitrogen and a partial positive charge on boron. These differences in the charges and electronegativities of the boron and nitrogen atoms should also lead to different substituent effects, depending on whether a group is bound to boron or nitrogen. We have investigated the effect of a methyl group on the borazine ring by studying the properties of the unsymmetrically substituted B- and N-methylborazine derivatives. The unsymmetrically substituted derivatives, especially the monosubstituted compound, were chosen as model compounds in order to minimize steric interactions and other effects not related to the bonding in the ring and to distinguish the *ortho, meta,* and *para* positions. The proton and boron-11 nmr, infrared, and mass spectral data have been used to monitor the effect of the methyl group.

Experimental Section

All of the compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents were dried by conventional means. All of the unsymmetrically substituted borazines were identified by their mass spectra and vapor pressures.

Preparation of 1-Methyl- and 1,3-Dimethylborazine.—Preliminary experiments[4] on the intermediates in the formation of the borazine ring have demonstrated that ethylamine hydrochloride reacts with the N-methylaminoborane trimer, $(H_2BNHCH_3)_3$, to form all of the possible unsymmetrically substituted N-methylethylborazines. Further experiments have shown that NH_4Cl also reacts with $(H_2BNHCH_3)_3$ at 125–150° to form all of the possible N-methylborazines. The yields of $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_3B_3N_3(CH_3)_3$, and $H_3B_3N_3H_3$ are influenced by the pyrolysis temperature and ratio of NH_4Cl to $(H_2BNHCH_3)_3$. As the temperature and $NH_4Cl:(H_2BNHCH_3)_3$ ratio are increased, less of the unsymmetrically substituted borazines are obtained.

TABLE I
REACTION OF $NaBH_4$ WITH MIXTURES OF NH_4Cl AND CH_3NH_3Cl

Reactants, mol			Products, mmol			
$NaBH_4$	NH_4Cl	CH_3-NH_3Cl	H_3B_3-N_3H_3	$H_3B_3N_3$-H_2CH_3	$H_3B_3N_3$-$H(CH_3)_2$	$H_3B_3N_3$-$(CH_3)_3$
0.50	0.30	0.30	17.0	12.8	16.7	5.30
0.50	0.20	0.40	12.5	8.77	17.8	6.72
0.50	0.40	0.20	11.8	3.16	0.713	0.613

The exploratory reactions between $(H_2BNHCH_3)_3$ and NH_4Cl required the prerequisite preparation[5] of $(H_2BNHCH_3)_3$, a time-consuming step. In order to prepare gram quantities of the unsymmetrically substituted borazines, the normal reagents and conditions for the preparation of $(H_2BNHCH_3)_3$ were employed but $NaBH_4$ was allowed to react, instead, with a mixture of CH_3NH_3Cl and NH_4Cl. The product of this reaction was not isolated but pyrolyzed without any purification. The results of these experiments are given in Table I. In a typical experiment, 25 ml of dry dimethoxyethane cooled to 0° was slowly added with vigorous stirring to a 0° mixture of $NaBH_4$, CH_3NH_3Cl, and NH_4Cl. After the H_2 evolution was complete, the dimethoxyethane was removed by a vacuum distillation to leave a white pasty material. This material was then pyrolyzed in a N_2 atmosphere. The volatile products were collected in two −196° traps connected to the pyrolysis flask. The H_2 escaped through a mercury bubbler. Hydrogen evolution began at 75° and was vigorous and rapid at 100–110°. The reaction was essentially complete in about 15 min. but the heating was continued for 1 hr more and the temperature was raised to 150°. The volatile material was then transferred to a vacuum system and fractionated using trap temperatures of −196, −78, −63, and −46° which separated $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$ (vapor pressure, 27.0 mm at 0°; lit.[6] 23.5 mm), $H_3B_3N_3H(CH_3)_2$ (vapor pressure 8.2 mm at 0°; lit.[6] 8.2 mm), and $H_3B_3N_3(CH_3)_3$, respectively. Small quantities of $H_3B_3N_3H_2CH_3$ pass through a −78° trap. However, $H_3B_3N_3H_3$ and $H_3B_3N_3H_2CH_3$ can be separated with a −96° trap and extended pumping. All samples of the N-methylborazines were demonstrated to be pure by their mass spectra.

Thermal Stability of $H_3B_3N_3H_2CH_3$ and $H_3B_3N_3H(CH_3)_2$.—The compounds $H_3B_3N_3H_2CH_3$ and $H_3B_3N_3H(CH_3)_2$ are the most stable unsymmetrically substituted derivatives yet characterized. There was no significant change in the mass spectrum after heating samples at 100° for 3 hr or in the proton nmr spectrum after standing for 3 months. However, slight decomposition did occur when samples were allowed to stand for 3 months because a nonvolatile solid remained in the tube after the sample was removed.

Preparation of 2-Methyl- and 2,4-Dimethylborazine.— The unsymmetrically substituted B-methylborazines were prepared

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[1] P. M. Kuznesof and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 1683 (1968).

[2] P. G. Perkins and D. H. Wall, *J. Chem. Soc., A*, 235 (1966).

[3] O. Chalvet, R. Daudel, and J. Kaufman, *J. Am. Chem. Soc.*, **87**, 399 (1965).

[4] O. T. Beachley, Jr., *Inorg. Chem.*, **7**, 701 (1968).

[5] D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

[6] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 1296 (1938).

by allowing $H_3B_3N_3H_3$ to react with a deficient amount of methylmagnesium iodide. In a typical experiment 15.0 ml of a 1.13 *M* ether solution of methylmagnesium iodide was slowly added to 1.5 g (19 mmol) $H_3B_3N_3H_3$ dissolved in 25 ml of dry diethyl ether. The reaction mixture was allowed to stand overnight and then the ether was removed by distillation at atmospheric pressure. The borazines were then fractionated in a vacuum system. The initial trap temperatures of −46, −63, −78, and −196° separated $(CH_3)_3B_3N_3H_3$, $H(CH_3)_2B_3N_3H_3$, a mixture of $H(CH_3)_2B_3N_3H_3$ and $H_2CH_3B_3N_3H_3$, and a mixture of $H_2CH_3B_3N_3H_3$, $H_3B_3N_3H_3$, and ether. These components were identified by mass spectroscopy. Each of the fractions containing unsymmetrically substituted borazines was refractionated. The original −63 and −78° fractions (0.284 g total) were combined and further fractionated using −63, −78, −96, and −196° traps. After several further fractionations, the −63° trap contained 0.132 g of $H(CH_3)_2B_3N_3H_3$ (vapor pressure, 6.4 mm at 0°; lit.[7] 6.5 mm) which was shown to be pure and free of $(CH_3)_3B_3N_3H_3$ and $H_2CH_3B_3N_3H_3$ by its mass spectrum. The original −196° fraction (0.134 g) was refractionated by using trap temperatures of −78, −96, and −196°. After several refractionations of the material collected in the −96° trap, the mass spectrum showed the material to be a mixture of $H_2CH_3B_3N_3H_3$ and ether. After extended pumping on the material in the −96° trap, 0.076 g of pure $H_2CH_3B_3N_3H_3$ (vapor pressure 18.6 mm at 0°; lit.[7] 19.5 mm) was obtained. The purification of $H_2CH_3B_3N_3H_3$ and $H(CH_3)_2B_3N_3H_3$ was extremely tedious and difficult. Many, many hours of fractionation were required.

Mass Spectra.—The mass spectra of $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_2CH_3B_3N_3H_3$, and $H(CH_3)_2B_3N_3H_3$ were recorded with a Consolidated Electrodynamics Corp. Model 21-130 mass spectrometer. The spectra (Table II) all have the correct *m/e* cutoff values expected for the parent and agree very closely with the spectra calculated[8] on the basis of the natural abundance of the boron isotopes.

Infrared Spectra.—The infrared spectra of the unsymmetrically substituted borazines were recorded in the range 5000–630 cm^{-1} with a Beckman IR-5A spectrophotometer. All spectra were taken on samples in the gas phase at a variety of pressures in a 10-cm cell. The infrared frequencies are given in Table III.

Nuclear Magnetic Resonance Spectra.—The proton nmr spectra were recorded at 60 Mc/sec with a Varian Model A-60 spectrometer. The boron-11 nmr spectra were recorded at 15.1 Mc/sec with a Varian Model DA-60-IL spectrometer. The reference compounds were tetramethylsilane and boron trifluoride–diethyl-etherate. The chemical shifts of the ^{11}B spectra were determined using the side-band technique. Borazine and the N-methylborazines were run neat. The B-methylborazines were run in CCl_4 solutions at two different concentrations. There was no dependence of the spectra on concentration. The chemical shifts and coupling constants are given in Table IV.

Results and Discussion

The unsymmetrically substituted N- and B-methylborazine derivatives have been prepared by new synthetic procedures, but the previous characterizations[6,7] have been confirmed. Considering the difficulties encountered in the separation and purification of these compounds and the fact that mass spectroscopy is a very sensitive measure of purity, the earlier workers[6,7] should be recognized for the competence demonstrated in their investigations.

The proton and boron-11 nmr data are given in

Table II

Mass Spectra

	Relative peak heights			
m/e	$H_2CH_3B_3N_3H_3$	$H_3B_3N_3H_2CH_3$	$H(CH_3)_2B_3N_3H_3$	$H_3B_3N_3H(CH_3)_2$
110			1	1
109			36	35
108			34	100
107			14	82
106			2	24
105			1	5
104				1
96	2	1		
95	47	27	3	1
94	69	100	100	3.5
93	35	67	76	2.5
92	10	21	24	3.5
91	5	5	10	2.5
90	3	1	6	3
89	1		3	
88			2	
81	2	<1	2	23
80	100	<1	2	12
79	73	<1	2	9
78	25	2	4.5	6
77	14	3	14	4
76	10	2.5	11	3
75	3	1	5	1
74	3		1	
73	1			
68	2	1	2	1
67	38	30	55	23
66	28	17	43	13
65	10	13	16	13
64	4	7.5	2	7
63	10	10	2.5	10
62	9	8	2.5	8
61	4	4	2	4
60	2	2	1	6.5
59	6			2
58				3
55			1.5	
54			2	8
53.5			2	
53	27	8	13	11.5
52.5			1	
52	23	7.5	18	15
51	11	3	13	10
50	4	1	6	3
49			2	1
48			1	
47	2		2	
46.5	7	6	8	
46	6	4	6.5	1
45.5	3	5	2	
45	7	3.5	1	14
44.5	1	2		
44	1	1		1
43	3			3
42	3		4	2
41	4		4	1
40	5	14	6	25
39.5	2			
39	6	6	5	11
38.5	3			
38	14	27.5	14	46
37	10	18	10	26
36	3	4	2	6
35	1	1	1	

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(7) H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Am. Chem. Soc.*, **58**, 409 (1936).

(8) R. E. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).

TABLE III
INFRARED SPECTRA (CM^{-1})[a]

$H_3B_3N_3H_3$		$H_2CH_3B_3N_3H_3$		$H(CH_3)_2B_3N_3H_3$		$H_3B_3N_3H_2CH_3$		$H_3B_3N_3H(CH_3)_2$		Assignment
3486	m	3481	m	3490	m	3485	m	3478	m	N–H str
		2993	w	3006	w	3038	sh	3032	sh	C–H str
						2987	w	2980	w	
						2935	sh	2925	sh	
								2850	sh	
2520	m	2522	m	2531	m	2529	m	2518	m	B–H str
						2516	m	2479	m	
						1483	sh	1470	sh	
1465	vs	1477	vs	1479	vs	1463	vs	1464	vs	B–N str
1406	m	1458	sh	1457	sh	1441	sh	1454	sh	
1398	sh	1393	m	1382	m	1388	m	1380	m	
1378	w									
1362	w									
						1409	w	1428	s	N–C str
		1355	sh							B–C str
		1350	w	1364	w					
		1339	sh							
		1319	sh	1317	w					
								1149	sh	
								1137	w	
								1129	sh	
						1071	w	1078	sh	
						1051	w	1068	w	
934	sh									B–H bend
923	s	927	s	927	s	925	m			
						919	sh			
917	s	913	s	912	s	913	s	914	s	
904	m	904	sh	904	sh			902	sh	
897	sh					899	m	899	m	
								891	m	
729	m	727	sh	725	sh			709	sh	N–H bend
719	s	716	m	716	m	710	m	698	m	
704	m	706	sh	705	sh			686	sh	
699	sh									

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

TABLE IV
NUCLEAR MAGNETIC RESONANCE DATA

	$H_3B_3N_3H_3$	$H_2CH_3B_3N_3H_3$	$H(CH_3)_2B_3N_3H_3$	$(CH_3)_3B_3N_3H_3$	$H_3B_3N_3H_2CH_3$	$H_3B_3N_3H(CH_3)_2$	$H_3B_3N_3(CH_3)_3$
			Proton Spectra				
δ(NH), ppm	−5.45	−5.10	−5.04	−4.63	−5.38	−5.35	....
J, cps	55	52	(45)[a]	....	56	55	....
δ(BH), ppm	−4.47	(−4.37)[b]	(−4.39)[b]	....	−4.49	−4.49	−4.45[d]
J, cps	137			....	137	137	125[d]
δ(CH), ppm	....	−0.292	−0.300	−0.266	−3.03	−2.97	−3.00[d]
			Boron-11 Spectra				
δ(BH), ppm	−29.2 −30.4[c]	−30.5	−30.9	....	−32.1	−32.1	−31.7 −32.4[c]
J, cps	139 136[c]	137	137	....	140	140	130 134[c]
δ(BCH_3), ppm	....	−35.0	−34.9	−34.8			

[a] The two side bands were not well defined; therefore the coupling constant is only an estimate. [b] Estimated from spectra from the lowest field resonance and the boron-11 coupling constant (see text). [c] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [d] K. Ito, H. Watanabe, and M. Kubo, *J. Chem. Phys.*, **34**, 1043 (1961).

Table IV. The data for the N-methylborazine derivatives agree very closely with those obtained by another.[9] The proton spectra of the N-methylborazines were comprised of a single sharp resonance due to the methyl group, a well-defined symmetrical triplet with the center band more intense than the outer bands due to the protons on nitrogen, and a symmetrical quartet due to the protons on boron. These assignments are based on the reported spectra of borazine and related compounds.[10] All of the resonances were clearly recognizable but they were slightly broader than the corresponding resonances of borazine. The spectra of the B-methylborazines were similar to the spectra of the N-methyl compounds except that the NH and BH

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(9) A. D. Norman, Thesis, Indiana University, 1963.

(10) K. Ito, H. Watanabe, and M. Kubo, *J. Chem. Phys.*, **34**, 1043 (1961).

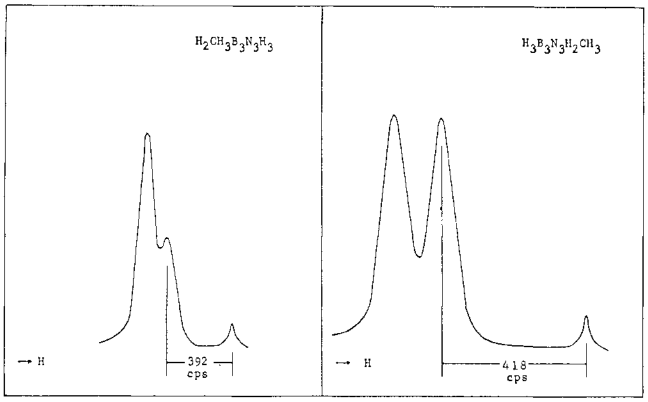

Figure 1.—Boron-11 nuclear magnetic resonance spectra.

resonances were much, much broader. In a typical spectrum of 2-methylborazine, if the CH resonance was on scale, the NH resonance was barely discernible and the BH resonance was not even detectable. However, at spectrum amplitudes which put the CH resonance completely off scale, the NH resonance was clearly distinguishable and appeared symmetrical. At these high amplitudes, the expected quartet due to the protons on boron could still be only partially observed. The lowest field BH resonance was clearly recognizable but the others were either partially or completely masked by the NH and CH resonances.

The boron-11 nmr spectra were extremely simple; examples are shown in Figure 1. The N-methylborazine spectra were symmetrical doublets. The B-methylborazines also exhibited doublets but they were unsymmetrical. The lower field resonance was more intense than the other but each resonance was symmetrical. The boron bound to hydrogen should give a doublet whereas the boron bound to the methyl group should exhibit a singlet. Therefore, the lower field resonance is due to the superposition of the BCH_3 resonance and one part of the BH doublet. The higher field resonance is due to the other part of the BH doublet. The ratios of the lower to higher field resonances were 2:1 and 3 : 1 for 2-methyl- and 2,4-dimethylborazine, respectively. The spectrum of 2,4,6-trimethylborazine consisted of only a singlet which was similar to the low-field resonance of the unsymmetrically substituted B-methylborazines.

The chemical shifts of the proton and boron-11 resonances of the B- and N-methylborazines relative to $H_3B_3N_3H_3$ are given in Table V. These calculations are based on the data for $H_3B_3N_3H_3$ obtained in this investigation. If the proton chemical shift data are a measure of the change in the apparent electron density around the nucleus, the methyl group is electron releasing and acting normally. The data are especially clear for the B-methylborazine derivatives. The molecular orbital calculations[1] also indicate that the methyl group is more electron releasing if it is bound to boron than to nitrogen. The very small downfield shifts for the protons on boron of the N-methyl derivatives relative to $H_3B_3N_3H_3$ might not be due to a decrease in electron density. These shifts are almost within the error of the experimental measurement, considering the broadness of the resonances. If these shifts are real, other interpretations based on the relative electronegativities of boron and nitrogen are possible. It is of interest to note that the *ortho* and *para* positions are identical, in terms of the nmr data. It has been previously observed that the *ortho* and *para* protons in 2-aminoborazine[11] have different chemical shifts. For comparison the *ortho* and *para* protons of toluene are identical, according to the nmr spectrum,[12] but distinguished in aniline.

All the boron-11 nmr resonances are shifted downfield relative to $H_3B_3N_3H_3$. There is a larger shift of the resonances assigned to boron atoms bound to a hydrogen of the N-methyl than the B-methyl derivatives. These shifts might be due to magnetic effects, instead of a decrease in electron density. The molecular orbital calculations[1] suggest the boron atoms of $H_3B_3N_3(CH_3)_3$ have the same charge as $H_3B_3N_3H_3$, not less. The relative chemical shifts of the borazine derivatives are similar to the carbon-13 chemical shifts[13] for aromatic hydrocarbons relative to benzene. The *ortho* carbon atoms are shifted downfield more than the *meta* carbon atoms of a derivative with an electron-releasing substituent. However, the significance of these shifts is not fully understood and cannot be correlated with changes in electron density. Only the shift of the *para* carbon atom is related to a change in electron density. The resonances of the *para* boron atom in $H_3B_3N_3H_2CH_3$ are probably not observed but buried under the more intense and extremely broad resonances of the *ortho* boron atoms. The resonance of the boron atom bound to the methyl group is also shifted downfield, -5.7 ppm. The molecular orbital calculations[1] predict this boron atom to be more negative than a boron atom in $H_3B_3N_3H_3$. Similarly, the carbon atom bound to the methyl group in toluene is shifted downfield (-9.1 ppm) relative to benzene. The reason for this downfield shift is not understood[14] either and it is not considered to indicate that this carbon atom has a lower electron density than a carbon atom of benzene. Similarly, on the basis of the ^{11}B nmr data the boron atom bound to the methyl group should probably not be considered to have a lower electron density than a boron atom in borazine. It should be emphasized that none of these ^{11}B nmr shifts is fully understood.

In conclusion, caution must be exercised when attempting to interpret the nmr data for borazine compounds. Many more examples must be studied before it will be possible to understand fully the nmr spectra and the effect of a substituent.

The infrared spectral data are given in Table III. The probable assignments of the various bands are based on previous assignments of the spectrum of borazine.[15] The most notable feature of these spectra is the

[11] R. F. Porter and E. S. Yeung, *Inorg. Chem.*, **7**, 1306 (1968).
[12] P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).
[13] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
[14] J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965).

TABLE V

CHEMICAL SHIFTS (PPM) FROM $H_3B_3N_3H_3$

	$H_2CH_3B_3N_3H_3$	$H(CH_3)_2B_3N_3H_3$	$(CH_3)_3B_3N_3H_3$	$H_3B_3N_3H_2CH_3$	$H_3B_3N_3H(CH_3)_2$	$H_3B_3N_3(CH_3)_3$
NH	+0.35	+0.41	+0.82	+0.07	+0.10	...
BH	(+0.10)	(+0.08)	...	−0.02	−0.02	+0.02
^{11}B (H)	−1.3	−1.7	...	−2.9	−2.9	−2.5
^{11}B (CH_3)	−5.8	−5.7	−5.6	...	...	...

doublet in the BH stretching frequency region (2500 cm^{-1}) for the N-methylborazines. This splitting might be due to symmetry. However, one might expect a similar situation in the NH region (3500 cm^{-1}) of the B-methylborazines but it is not observed. There should also be symmetric and antisymmetric stretching vibrations active in the infrared region which might only be visible in a high-resolution spectrum. Another possibility is that one of the bands is a combination band. Many combination bands[16] are observed in the CH stretching region for monosubstituted benzene derivatives.

A change in the frequency of the NH and BH stretching vibrations might reflect changes in electron density. These vibrations are independent[17] of the substituent masses and force constants. The methyl group, on either boron or nitrogen, does not significantly alter the NH or BH vibrational frequencies. It has been previously observed that the NH stretching frequency is essentially the same in the 2,4,6-trihaloborazines.[17] For comparison, the CH vibrational frequencies in aromatic compounds[16] are altered by the substituent but the changes cannot be correlated with substituent effects.

The frequencies assigned to the B–N ring vibrations are at a higher frequency for the B-methyl compounds than for the N-methyl derivatives, Table III. Therefore, one might conclude that the boron–nitrogen bond is stronger when a methyl group is bound to boron. If an electron-releasing substituent, such as a methyl group, is bonded to boron, the boron–nitrogen bond should become weaker. If the methyl group is on nitrogen, the bond should be stronger. The high-field shift of the proton nmr data would indicate that the BN bond is stronger in $H_3B_3N_3H_2CH_3$ than $H_2CH_3B_3N_3H_3$. Either the proton nmr data are not a measure of relative electron density or, more probably, the infrared data are not a measure of the strength of the boron–nitrogen bond. The change in this frequency probably reflects changes in the boron–nitrogen vibrational force constant as well as changes in the ring substituent force constants.

The mass spectra of the B- and N-methylborazines are significantly different in the range of the higher masses. The most abundant species in the spectrum of 1-methylborazine is due to the parent minus a hydrogen, $B_3N_3CH_7^+$ (94). Whereas for 2-methylborazine, the species, $B_3N_3H_5^+$ (80), due to the loss of the methyl group, is the most abundant. These differences are also evident in the spectra of the disubstituted derivatives. The low-mass ranges of the spectra are similar. Some of the other more abundant species are $B_2N_2CH_5^+$ (67), $B_3N_2H_2^+$ (63) and $B_2N_2H_3^+$ (53).

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(17) R. E. Hester and C. W. J. Scaife, *Spectrochim. Acta*, **22**, 455 (1966).