is bound to copper(II) primarily through the bidentate nitrogen mode in the chelate plane. Several lines of evidence such as the formation constant comparison also suggest a weaker apical chelation by the carboxylate group.

The 2:1 histidinate complex displays a small negative CD peak which is amplified in the mixed complex with histamine and disappears in the mixed complex with glycine. These results suggest that the conformation of the histidine molecule is dependent upon the other donor atoms bound to copper(II). With histamine as the other ligand, histidine tends to bind more in a glycine-like mode than with glycine the other ligand, for which chelation of histidine through two nitrogen donors in the chelate plane becomes more important.[32] For the latter mode the difference between the logarithms of first and second formation constants is unusually large, as shown by the values for histamine,[15] histidinol, and histidine methyl ester.[19] A consequence of this difference of nearly three log units is that though the first formation constant of copper(II) with all of the above three ligands is greater than that with glycine, the second formation constant for the last ligand is greater than any of those for the first three. A recent X-ray structure of a mixed histidinate–threoninate copper(II) complex shows three nitrogens and one carboxylate oxygen in the chelate plane with the histidinate carboxylate bound weakly with a distorted geometry in an apical position.[33] The absence of observed stereoselectivity in the 1:2 complexes of copper(II) and L,D-histidine as compared with L-histidine suggests that the second histidinate ligand is bound in only a bidenate mode.[34]

The tendency for the histidinate anion to adopt a conformation complementary to that of other donor groups bound to copper(II) is consistent with entirely independent results on binding studies in mixed ligand systems. The formation constant of a mixed copper(II) complex with histamine and serine (which in this pH region chelates like glycine[35]) is 200 times greater than the statistical value of four expected on the basis of unmixed formation constants in this system.[36] Since the histidinate anion contains within a single ligand both the histamine-like and glycine-like binding modes, it is then to be expected that the second ligand will bind in a way complementary to the first. This tendency toward complementarity may be described as the principle of substantial permissivity, which for histidinate implies a multiplicity of bidentate binding modes in addition to tridentate ones.

---

[32] K. M. Wellman and B. K. Wong, *Proc. Nat. Acad. Sci. U. S.*, **64**, 824 (1969).

[33] H. C. Freeman, J. M. Guss, M. J. Healy, R. P. Martin, and C. E. Nockolds, *Chem. Commun.*, 225 (1969).

[34] P. J. Morris and R. B. Martin, *J. Inorg. Nucl. Chem.*, in press.

[35] V. S. Sharma, *Biochim. Biophys. Acta*, **148**, 37 (1967).

[36] D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc.*, 1755 (1967).

An Investigation of the Effects of Substituents on the Hydrogen-1 and Boron-11 Nuclear Magnetic Resonance Chemical Shifts of Boron-Monosubstituted Borazine Derivatives.[1] Evidence for π-Electron Delocalization in the Borazine Ring

O. T. Beachley, Jr.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.
Received March 4, 1970

Abstract: The effects of the substituents CH_3, $N(CH_3)_2$, OCH_3, F, Cl, and Br on the ^{1}H nmr, ^{11}B nmr, and infrared and mass spectral properties of a series B-monosubstituted borazine derivatives ($H_2XB_3N_3H_3$) have been examined in detail. The ^{1}H and ^{11}B chemical shift data are consistent with the hypothesis that the π electrons of borazine are delocalized, at least partially, and the substituents interact with this π system by means of a resonance effect to alter the π-electron density at the *ortho* and *para* positions. This hypothesis is supported by the similarities between analogous borazine and benzene nmr data, as well as excellent correlations between the borazine ^{1}H nmr data and ^{13}C nmr and reactivity parameter, $\sigma_R{}^0$, data. These data are recognized to be related to changes in the π-electron density in the benzene ring. The infrared and mass spectral properties were also compared but no trends in the data, consistent with a change in substituent, were discernible. The new compound $H_2FB_3N_3H_3$ was prepared by allowing $H_2(CH_3)_2NB_3N_3H_3$ to react with $BF_3 \cdot O(C_2H_5)_2$. The synthesis of $H_2CH_3OB_3N_3H_3$ from $H_2ClB_3N_3H_3$, CH_3OH, and $N(CH_3)_3$ in pentane solution also represents a new reaction in borazine chemistry.

Borazine is isoelectronic with benzene. All of the chemistry of benzene is consistent with the hypothesis that the π electrons are completely delocalized. However, the situation is very different in the case of borazine. Molecular orbital calculations[2] suggest that the π electrons are partially delocalized, but there are no experimental data which can be conclusively interpreted in terms of either the existence of, or the

---

[1] Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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

lack of, π-electron delocalization. Even so, some authors claim borazine to be aromatic like benzene, whereas others claim that the delocalization of π electrons has been overemphasized.[3]

The purpose of this investigation was to gather experimental data which might be used to demonstrate the nature of the π electrons in borazine chemistry. We have prepared a series of **B**-monosubstituted borazine derivatives and have studied the influence of the single substituent on those properties which might be a measure of the relative electron density at the various positions of the ring. A change in electron density at the position *para* to the substituent would be consistent with a resonance effect and π-electron delocalization. The effects of the substituents CH_3, $N(CH_3)_2$, OCH_3, F, Cl, and Br on the infrared, mass, and proton and boron-11 nmr spectral properties have been examined in detail.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. The 2,4,6-trichloroborazine[4] was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200°. Borazine was prepared by the $NaBH_4$ reduction[5] of $Cl_3B_3N_3H_3$ in a glycol ether. The unsymmetrically substituted borazine, $H_2ClB_3N_3H_3$, was prepared by the lithium borohydride reduction[6] of a pyridine complex of $Cl_3B_3N_3H_3$. The compound $H_2CH_3B_3N_3H_3$[6] was prepared by allowing $H_2ClB_3N_3H_3$ to react with methylmagnesium iodide in ether. The preparation[7] of $H_2(CH_3)_2NB_3N_3H_3$ has also been previously described.

Preparation of $H_2FB_3N_3H_3$. The new compound 2-fluoroborazine was prepared by allowing $H_2(CH_3)_2NB_3N_3H_3$ to react with $BF_3 \cdot O(C_2H_5)_2$. In a typical experiment, 0.4340 g (3.50 mmol) of $H_2(CH_3)_2NB_3N_3H_3$ was condensed onto the walls of a 100-ml flask which was attached to the vacuum system. On top of the borazine was condensed 0.5730 g (4.03 mmol) of $BF_3 \cdot O(C_2H_5)_2$ by use of a −196° bath. The mixture was slowly warmed to room temperature over a period of about 15 min, and then allowed to stand for only 1 hr. The reaction products appeared as a mixture of solid and liquid phases. The volatile material was fractionated by using trap temperatures of −46, −78 and −196°. The −196° trap contained 0.310 g of a mixture of diethyl ether and a small amount of $H_3B_3N_3H_3$. The stoichiometry of the reaction, 4.03 mmol of $BF_3 \cdot O(C_2H_5)_2$, requires 0.298 g of $O(C_2H_5)_2$. The −78° trap contained 0.1720 g (1.74 mmol, a 43.2% yield based on $H_2(CH_3)_2NB_3N_3H_3$) of $H_2FB_3N_3H_3$ and the −46° trap contained 0.0460 g (0.393 mmol, 9.75% yield) of $HF_2B_3N_3H_3$. Mass spectral data also indicated the presence of $F_2BN(CH_3)_2$ as a reaction product. The compound $H_2FB_3N_3H_3$ had a melting point of +3–4° and a vapor pressure of 35.6 mm at 0° and 116 mm at 24°. The difluoro derivative $HF_2B_3N_3H_3$ had a melting point of 44–45° (rapid heating) and a vapor pressure of 4.0 mm at 0° and 18 mm at 24°. Both $H_2FB_3N_3H_3$ and $HF_2B_3N_3H_3$ disproportionate and/or decompose at room temperature. It should be noted that we have not observed $F_3B_3N_3H_3$ among any reaction or decomposition products.

Anal. Calcd for $H_2FB_3N_3H_3$: N, 42.4; hydrolyzable H, 2.02. Found: N, 42.0; hydrolyzable H, 1.95. Calcd for $HF_2B_3N_3H_3$: N, 36.6; hydrolyzable H, 0.848. Found: N, 36.8; hydrolyzable H, 0.850.

The mass spectra also demonstrated the compounds to be pure. There was no $H_3B_3N_3H_3$, $O(C_2H_5)_2$, or other fluoroborazines present in a given sample.

Preparation of $H_2CH_3OB_3N_3H_3$. In a typical experiment, 0.4280 g (3.72 mmol) of $H_2ClB_3N_3H_3$ was dissolved in 20 ml of dry *n*-pentane. A room temperature solution of 0.2220 g (3.76 mmol) of $N(CH_3)_3$, 0.1240 g (3.88 mmol) of CH_3OH, and 5 ml of pentane was then added to the stirred $H_2ClB_3N_3H_3$ solution at 25°. (It is important for both solutions to be at room temperature before mixing.) A precipitate formed immediately. The mixture was stirred for an hour and then fractionated by using traps at −46, −63 and −196°. The −196° trap contained pentane and unreacted $N(CH_3)_3$ (0.61 mmol), the −63° trap was empty, and the −46° trap contained 0.2000 g (1.82 mmol, 48.8% yield) of $H_2CH_3OB_3N_3H_3$. This compound was identified by its vapor pressure, 4.6 mm at 20.5° (lit.[8] ~6 mm at 25°), infrared spectrum,[8] and mass spectrum.[8] The mass spectrum demonstrated that the sample was pure and did not contain $B(OCH_3)_3$[8] or starting materials.

Preparation of $H_2BrB_3N_3H_3$. The compound $H_2BrB_3N_3H_3$ was prepared according to a previously reported method,[9] but with one major modification. The products were fractionated 1 hr after the reagents were mixed instead of the previously suggested 4 days.[9] When we waited 4 days, no bromoborazines were isolated. In a typical experiment, 2.47 mmol of BBr_3 was allowed to react with 8.30 mmol of $H_3B_3N_3H_3$ for 1 hr. One reagent was condensed onto the walls of a 100-ml flask and then the other on top of it by using a −196° bath. After slow warming to 25°, a white solid formed and bubbling occurred. Fractionation of the components was accomplished by using −46, −63, −78, and −196° traps. The products of the reaction included 0.568 mmol of H_2, 1.25 mmol of B_2H_6, 0.905 mmol of $H_2BrB_3N_3H_3$ (−63° trap), a 13.1% yield based on the $H_3B_3N_3H_3$ consumed, and 0.289 mmol of $HBr_2B_3N_3H_3$ (−46° trap), a 4.2% yield. Unreacted $H_3B_3N_3H_3$ (1.40 mmol) was also recovered from the −196° trap. The vapor pressure of $H_2BrB_3N_3H_3$ (10.0 mm at 23°, lit.[9] 13.3 mm at 26.4°) and its mass spectrum were used for identification.

Mass Spectra. The mass spectra of $H_2CH_3OB_3N_3H_3$, $H_2FB_3N_3H_3$, $HF_2B_3N_3H_3$, $H_2BrB_3N_3H_3$, and $HBr_2B_3N_3H_3$ were recorded by using a Perkin-Elmer Hitachi Model RMU6-E mass spectrometer and are given below. The spectra of the other (CH_3, $N(CH_3)_2$, Cl) derivatives have been previously reported.[6,7] All spectra had the correct *m/e* cutoff values expected for the parent and agree very closely with the spectra calculated on the basis of the natural abundance of the various isotopes. The spectra of all the monosubstituted derivatives can be readily interpreted in terms of the following species: $B_3N_3H_5X$, B_3N_2HX, $B_2N_3H_4X$, $B_2N_2H_2X$, B_2NHX, BNH_2X, $B_3N_3H_5$, $B_2N_3H_5$, $B_3N_2H_2$, $B_2N_2H_3$, B_2NH_2, and BNH_3. There does not appear to be any trend between the intensity of the various species and the substituent. The spectra of the disubstituted derivatives are less straightforward. For example, the spectrum of $HF_2B_3N_3H_3$ has a series of peaks, *m/e* 99–93. These could be due to an impurity of $H_2FB_3N_3H_3$, as well as the species $B_3N_2F_2$ which also has a mass of 99. The analogous species in the spectrum of $H_2FB_3N_3H_3$, B_3N_2HF (*m/e* 81), is also reasonably intense, just as the species $B_3N_2H_2$ (*m/e* 63) is in the spectrum of $H_3B_3N_3H_3$.

The following give the spectra down to *m/e* 50 of the unsymmetrically substituted borazines [*m/e* (relative intensity)].

$H_2CH_3OB_3N_3H_3$: 112 (2), 111 (54), 110 (100), 109 (58), 108 (15), 107 (4), 106 (1), 98 (1), 97 (1), 96 (5), 95 (4), 94 (4), 93 (10), 92 (8), 91 (3), 90 (1), 84 (2), 83 (46), 82 (25), 81 (8), 80 (15), 79 (14), 78 (15), 77 (12), 76 (7), 75 (3), 74 (1), 73 (2), 69 (4), 68 (8), 67 (7), 66 (4), 65 (2), 63 (4), 62 (4), 61 (3), 60 (1), 59 (1), 58 (3), 57 (1), 56 (1), 55 (4), 54 (8), 53 (20), 52 (15), 51 (11), 50 (1).

$H_2FB_3N_3H_3$: 100 (2), 99 (37), 98 (100), 97 (62), 96 (21), 95 (9), 94 (4), 93 (1), 81 (24), 80 (18), 79 (7), 78 (4), 77 (3), 76 (2), 75 (1), 74 (1), 72 (1), 71 (19), 70 (14), 69 (4), 68 (1), 67 (1), 66 (1), 63 (.5), 62 (1), 61 (1), 60 (1), 59 (1), 56 (5), 55 (4), 54 (1), 53 (16), 52 (13), 51 (5), 50 (1).

$HF_2B_3N_3H_3$: 117 (35), 116 (100), 115 (61), 114 (15), 113 (1), 99 (59), 98 (83), 97 (49), 96 (24), 95 (15), 94 (6), 93 (2), 81 (18), 80 (16), 79 (6), 78 (3), 77 (2), 76 (1), 75 (1) 74 (12), 73 (8), 72 (1), 71 (41), 70 (32), 69 (14), 68 (1), 67 (1), 66 (1), 56 (11), 55 (10), 54 (3), 53 (12), 52 (10), 51 (5), 50 (1).

$H_2BrB_3N_3H_3$: 161 (19), 160 (19), 159 (28), 158 (22), 157 (9), 156 (3), 155 (2), 154 (1), 143 (2), 142 (2), 141 (3), 140 (2), 139 (1), 133 (8), 132 (6), 131 (10), 130 (6), 129 (2), 128 (1), 118 (2), 117 (3), 116 (5), 115 (6), 114 (10), 113 (6), 112 (2), 111 (1), 89 (1), 88 (1),

---

(3) The most recent review of borazine chemistry is by K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Academic Press, New York, N. Y., 1965.

(4) G. L. Brennan, G. H. Dahl, and R. Schaeffer, *J. Amer. Chem. Soc.*, **82**, 6248 (1960).

(5) L. F. Hohnstedt and D. T. Haworth, *ibid.*, **82**, 89 (1960).

(6) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 2665 (1969).

(7) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *ibid.*, **6**, 575 (1967).

(8) M. Nadler and R. F. Porter, *ibid.*, **6**, 1739 (1967).

(9) G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 1612 (1951).

Table I. Nuclear Magnetic Resonance Data for 2-Substituted Borazines[a]

	$H_2CH_3B_3N_3H_3$	$H_2(CH_3)_2N$-$B_3N_3H_3$	H_2CH_3O-$B_3N_3H_3$	$H_2FB_3N_3H_3$	$H_2ClB_3N_3H_3$	$H_2BrB_3N_3H_3$
			Proton Data			
δ(*ortho* NH), ppm	−5.10	−4.28	−4.62	−4.65	−5.33	−5.52
J, Hz	52	*b*	*b*	55	55	55
δ(*para* NH), ppm	−5.10	−4.80	−5.10	−5.21	−5.33	−5.52
J, Hz	52	*b*	*b*	56	55	55
δ(*meta* BH), ppm	−4.37	(−4.41)[c]	(−4.41)[c]	−4.43	−4.38	−4.30
J, Hz	137	(130)	(130)	138	135	130
δ(CH), ppm	−0.29	−2.52	−3.48			
			Boron-11 Data			
More intense line	−35.0	−24.5	−25.7	−26.7	−27.4	−28.4
Less intense line	−25.9	−33.5	−35.4	−37.0	−35.8	−36.5

[a] For comparison, $H_3B_3N_3H_3$: δ(NH) −5.45 ppm, *J*(NH) = 55 Hz; δ(BH) −4.47 ppm, *J* = 138 Hz; δ(B^{11}) −29.2 ppm, *J* = 138 Hz. [b] Broad singlet (see Figure 1). [c] Estimated from spectra from the lowest field resonance.

87 (2), 86 (1), 82 (3), 81 (3), 80 (100), 79 (83), 78 (51), 77 (34), 76 (22), 75 (10), 74 (2), 69 (1), 68 (1), 67 (1), 66 (1), 63 (7), 62 (10), 61 (8), 60 (3), 59 (1), 53 (38), 52 (36), 51 (16), 50 (4).

$HBr_2B_3N_3H_3$: 241 (5), 240 (4), 239 (11), 238 (7), 237 (6), 236 (5), 235 (2), 234 (1), 197 (5), 196 (4), 195 (19), 194 (15), 193 (19), 192 (12), 191 (5), 190 (2), 189 (1), 179 (1), 178 (1), 177 (3), 176 (3), 175 (3), 174 (2), 173 (1), 161 (7), 160 (20), 159 (20), 158 (26), 157 (15), 156 (8), 155 (3), 154 (3), 153 (2), 152 (3), 151 (8), 150 (13), 149 (18), 148 (22), 147 (14), 146 (4), 145 (1), 143 (2), 142 (2), 141 (2), 140 (2), 139 (5), 138 (1), 137 (4), 136 (1), 135 (2), 134 (2), 133 (16), 132 (10), 131 (16), 130 (10), 129 (4), 128 (4), 127 (2), 126 (1), 120 (1), 119 (1), 118 (2), 117 (4), 116 (24), 115 (25), 114 (80), 113 (58), 112 (34), 111 (18), 110 (8), 109 (6), 108 (2), 107 (6), 106 (2), 105 (2), 104 (1), 103 (2), 99 (2), 98 (8), 97 (11), 96 (13), 95 (9), 94 (6), 93 (5), 92 (3), 91 (2), 90 (1), 89 (9), 88 (9), 87 (35), 86 (21), 85 (7), 84 (2), 83 (2), 82 (40), 81 (20), 80 (55), 79 (46), 78 (45), 77 (40), 76 (30), 75 (17), 74 (10), 73 (62), 72 (7), 71 (8), 70 (5), 69 (9), 68 (10), 67 (8), 66 (4), 65 (1), 64 (1), 63 (6), 62 (11), 61 (12), 60 (5), 59 (5), 58 (1), 57 (5), 56 (9), 55 (5), 54 (2), 53 (36), 52 (39), 51 (20), 50 (5).

Infrared Spectra. The infrared spectra were recorded in the range 4000–630 cm^{-1} by means of a Beckman IR-5A spectrometer. All spectra were taken on samples in the gas phase at a variety of pressures in a 10-cm cell. There are no apparent trends between the frequencies of the BH, NH, and BN stretching vibrations and the substituents.

The following give the spectra [frequency, cm^{-1} (intensity, s = strong, m = medium, w = weak, sh = shoulder)].

$H_2CH_3OB_3N_3H_3$: 3498 (m), 3008 (w), 2963 (sh), 2530 (s), 1530 (sh), 1496 (vs), 1460 (sh), 1449 (vs), 1400 (w), 1373 (m), 1358 (m), 1293 (w), 1279 (sh), 1264 (w), 1044 (w), 1035 (w), 1031 (w), 926 (m), 912 (m), 905 (sh), 714 (sh), 704 (sh), 698 (m).

$H_2FB_3N_3H_3$. 3496 (m), 2646 (w), 2540 (s), 1518 (sh), 1496 (vs), 1481 (vs), 1469 (vs), 1395 (w), 1226 (m), 934 (m), 910 (s), 905 (w), 726 (sh), 714 (m), 704 (m), 694 (m).

$HF_2B_3N_3H_3$. 3479 (m), 2634 (w), 2541 (m), 1527 (sh), 1512 (sh), 1493 (vs), 1478 (sh), 1400 (m), 1288 (m), 1150 (m), 1142 (m), 929 (m), 915 (m), 909 (w), 873 (w), 733 (sh), 725 (m), 714 (s), 704 (m), 697 (sh), 684 (w).

$H_2BrB_3N_3H_3$. 3495 (m), 2615 (w), 2554 (s), 1479 (sh), 1462 (vs), 1445 (vs), 1418 (sh), 1385 (w), 1370 (w), 1300 (vw), 1240 (vw), 1071 (m), 1029 (sh), 1004 (s), 923 (m), 913 (s), 722 (sh), 711 (s), 700 (sh).

$HBr_2B_3N_3H_3$. 3451 (m), 2603 (w), 2554 (w), 1463 (sh), 1448 (vs), 1438 (vs), 1425 (vs), 1245 (w), 1062 (w), 1043 (vw), 980 (m), 917 (w), 911 (m), 863 (m), 705 (m), 648 (w).

Nuclear Magnetic Resonance Spectra. The proton nmr spectra were recorded at 100 MHz by means of a Varian Model HA-100 spectrometer. The boron-11 nmr spectra were recorded at 15.871 MHz with a Varian Model HR-60 spectrometer. The reference compounds were tetramethylsilane and boron trifluoride diethyl etherate. The chemical shifts of the boron-11 spectra were determined by using the side-band technique. All compounds were run as 5% solutions in CCl_4. There was no apparent dependence of the spectra on concentration. The chemical shifts and coupling constants for the monosubstituted derivatives are given in Table I. The ^1H spectrum of $HF_2B_3N_3H_3$ consisted of an NH triplet (δ −4.62 ppm, *J* = 52 Hz) and a BH quartet which was broad and weak. The compound $HBr_2B_3N_3H_3$ exhibited a poorly resolved NH triplet, δ −5.56 ppm, and a broad and weak BH quartet. The boron-11 spectrum of $HBr_2B_3N_3H_3$ was identical with that of $H_2BrB_3N_3H_3$.

Results and Discussion

Significant advancements have been made in the syntheses of unsymmetrically substituted borazines. All of the members of the series, $H_2CH_3B_3N_3H_3$, $H_2(CH_3)_2NB_3N_3H_3$, $H_2CH_3OB_3N_3H_3$, $H_2FB_3N_3H_3$, $H_2ClB_3N_3H_3$, and $H_2BrB_3N_3H_3$, have been prepared by a convenient procedure and fully characterized. The previously unknown compound, 2-fluoroborazine ($H_2FB_3N_3H_3$), has been prepared by allowing $H_2(CH_3)_2NB_3N_3H_3$ to react with $BF_3{\cdot}O(C_2H_5)_2$ according to the following idealized equation. A possible intermediate in this reaction could be the adduct $H_2(F_3BN(CH_3)_2)B_3N_3H_3$, which could then rearrange by a fluorine transfer reaction to give the products. It is apparent that the dimethylamino group is a stronger base than the oxygen in ether. Other cleavage reactions[10] of exocyclic boron–nitrogen bonds have been previously used for the preparation of various trisubstituted derivatives. However, BF_3 reacts with 2-aminoborazine[11] to give diborazinylamine, $HN(H_2B_3N_3H_3)_2$, and F_3BNH_3, not $H_2FB_3N_3H_3$. The preparation of $H_2CH_3OB_3N_3H_3$ from the reaction of $H_2ClB_3N_3H_3$, CH_3OH, and $N(CH_3)_3$ according to the following idealized equation also represents a new synthetic procedure in borazine chemistry. It is of interest to note that there is a distinct difference between the chemistry of $H_2ClB_3N_3H_3$ and $H_3B_3N_3H_3$ toward CH_3OH. Methanol[12] adds to $H_3B_3N_3H_3$ to form $H_3B_3N_3H_3{\cdot}3CH_3OH$ instead of substituting the boron atoms.

$$H_2(CH_3)_2NB_3N_3H_3 + F_3B{\cdot}O(C_2H_5)_2 \longrightarrow H_2FB_3N_3H_3 + F_2BN(CH_3)_2 + O(C_2H_5)_2$$

$$H_2ClB_3N_3H_3 + CH_3OH + N(CH_3)_3 \longrightarrow H_2CH_3OB_3N_3H_3 + N(CH_3)_3HCl$$

The various members of this series of B-monosubstituted borazine derivatives have been compared to $H_3B_3N_3H_3$ according to their proton and boron-11 nmr spectral data. Reproductions of the proton nmr spectra of $H_2FB_3N_3H_3$, $H_2(CH_3)_2NB_3N_3H_3$, and H_2CH_3-

---

(10) K. Niedenzu, D. H. Harrelson, and J. W. Dawson, *Chem. Ber.*, 94, 671 (1961); W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 113 (1962).

(11) M. Chakravorty and R. F. Porter, *Inorg. Chem.*, **8**, 1997 (1969).

(12) D. T. Haworth and L. F. Hohnstedt, *J. Amer. Chem. Soc.*, **81**, 842 (1959).

Table II. Relative Chemical Shifts from Parent for Monosubstituted Borazine and Benzene Derivatives

	$H_2CH_3B_3N_3H_3$	$H_2(CH_3)_2N$-$B_3N_3H_3$	H_2CH_3O-$B_3N_3H_3$	$H_2FB_3N_3H_3$	$H_2ClB_3N_3H_3$	$H_2BrB_3N_3H_3$
			Proton Data			
ortho NH, ppm	+0.35	+1.17	+0.83	+0.80	+0.12	−0.07
CH, ppm[a]	+0.20	+0.60	+0.43	+0.31	−0.02	−0.22
para NH, ppm	+0.35	+0.65	+0.35	+0.24	+0.12	−0.07
CH, ppm[a]	+0.20	+0.62	+0.37	+0.22	+0.12	+0.03
meta BH, ppm	+0.10	+0.06	+0.06	+0.04	+0.09	+0.17
CH, ppm[a]	+0.20	+0.10	+0.04	+0.02	+0.03	+0.08
			Boron-11 Data			
BX, ppm	−6.0	+4.7	+3.5	+2.5	+1.8	+0.8
BH, ppm	−1.3	+0.2	−1.3	−2.7	−2.4	−3.2

[a] Chemical shift of proton for analogous monosubstituted benzene derivatives (see ref 15).

$OB_3N_3H_3$, and the assignments of lines are given in Figure 1. It is apparent that the chemical shifts of the *ortho* and *para* NH protons of these compounds are different. The spectrum of $H_2BrB_3N_3H_3$ was similar in appearance to that of $H_2ClB_3N_3H_3$,[6] an NH triplet and a BH quartet. The spectrum of $H_2CH_3B_3N_3H_3$, which also exhibits a simple NH triplet, has been previously reported.[13] The NH protons which are *ortho* and *para* to these substituents, Br, Cl, CH_3, are magnetically equivalent. The chemical shifts[14] of the *ortho*, *meta*, and *para* protons in these monosubstituted compounds relative to $H_3B_3N_3H_3$ are given in Table II. The relative chemical shifts of the *ortho* and *para* NH protons depend on the substituent, whereas the chemical shifts of the *meta* BH protons are essentially insensitive. It is of interest to note that the chemical shift of the *ortho* NH protons in $H_2FB_3N_3H_3$ is essentially the same as that for the NH protons in HF_2-$B_3N_3H_3$. All the NH protons in $HF_2B_3N_3H_3$ are *ortho* to a fluorine.

The relative chemical shifts of the *ortho* and *para* NH protons are probably the most important experimental data which can be used to understand the nature of the bonding in the borazine ring. The data are similar to those observed for the analogous series of monosubstituted benzene compounds.[15] Therefore, the interpretation of the nmr data is similar. The four major factors[15,16] which probably contribute to the relative chemical shift of the *ortho* and *para* protons are the changes in σ- and π-electron density, magnetic effects, and field effects. The relative shift of the *ortho* protons is probably due to changes in all four factors. However, the relative shift of the *para* proton is probably related to only a change in π-electron density. The changes in σ-electron density, magnetic effects, and field effects can be considered to be negligible because of the large distance between the *para* proton and the substituent. The borazine ring[17] is even larger than the benzene ring. The origin of the relative chemical shift of the *meta* BH proton is not understood, just as in the case of benzene derivatives.[15]

By analogy with benzene, the proton nmr data are consistent with the hypothesis that the π electrons of borazine are delocalized, at least partially, and substituents interact with this π system by means of a resonance effect to alter the π-electron density at the *ortho* and *para* positions. Extensive comparisons between borazine and benzene data further support this hypothesis. The relative chemical shifts of the *para* NH proton for borazine derivatives and the *para* CH proton[15,16] for the analagous benzene compounds (Table II) are very similar. Furthermore, there is also an excellent correlation between the relative chemical shift of the *para* NH proton and the *para* ^{13}C nmr chemical shift[18] data, as shown in Figure

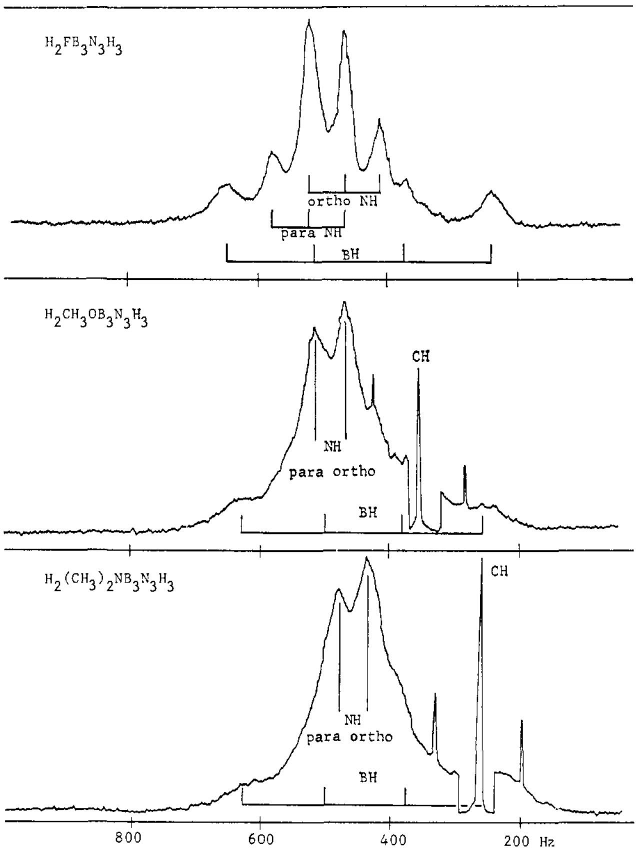

Figure 1. Proton nmr spectra (100 MHz).

---

(13) O. T. Beachley, Jr., *Inorg. Chem.*, 8, 981 (1969).

(14) There is an error or varying magnitude in the chemical shift measurements owing to the broadness and overlapping of the lines.

(15) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 35, 731 (1961).

(16) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966.

(17) W. Harshbarger, G. H. Lee, R F. Porter, and S. H. Bauer, *J. Amer. Chem. Soc.*, 91, 551 (1969).

(18) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, 42, 2427 (1965).

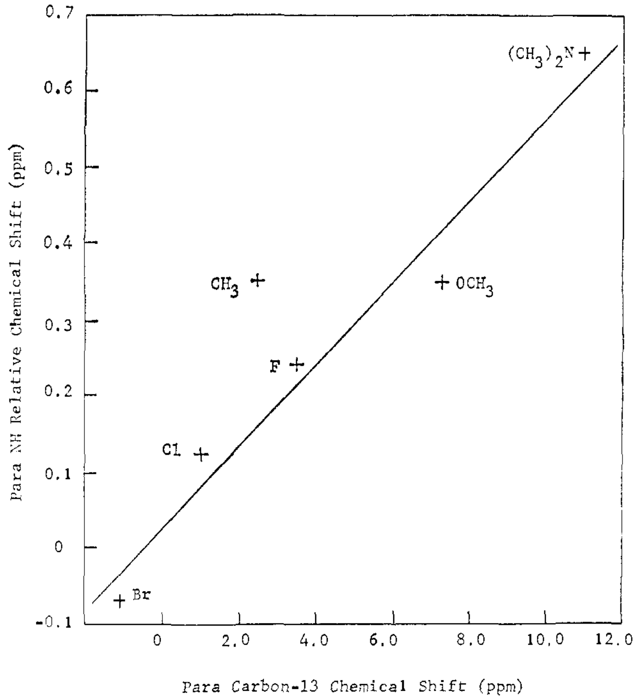

Figure 2. Relationship between the chemical shifts of the *para* proton of monosubstituted borazine and the *para* carbon of monosubstituted benzenes (see ref 18).

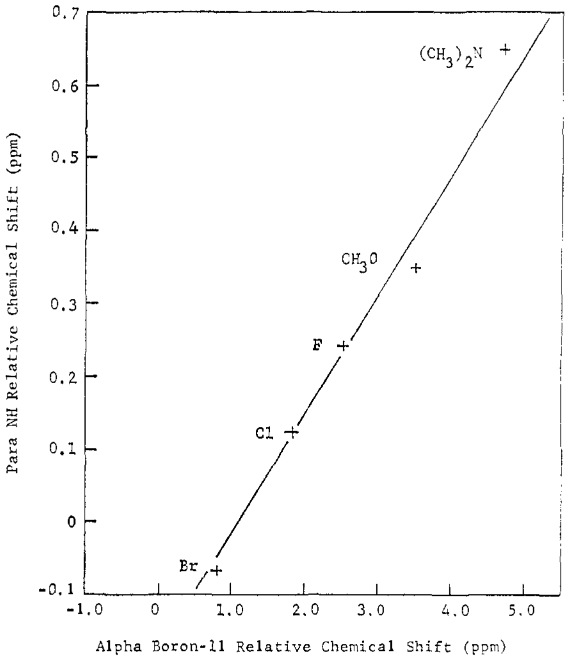

Figure 3. Relationship between *para* proton and boron-11 chemical shifts.

2, as well as the reactivity parameter,[19] $\sigma_R{}^0$. All of these parameters in benzene chemistry are recognized to be related to changes in π-electron density. Only the data for the methyl group are inconsistent with other data. It must be emphasized that even though these correlations support the hypothesis of electron delocalization in borazine chemistry, they probably should not be used to infer the extent of delocalization. However, it is intriguing to note that the relative chemical shifts of the *para* protons in analogous borazine and benzene[15] derivatives are generally within several hertz of each other, whereas the relative chemical shifts of the *ortho* NH protons are generally twice those of the CH protons in benzene compounds. These data could mean that the extent of delocalization in borazine is approximately half that in benzene, the result obtained in molecular orbital calculations.[2]

The boron-11 nmr data (Table I) also support the hypothesis that the relative chemical shift of the *para* NH proton is related to the change in π-electron density, which originates at the boron to which the substituent is bound. The boron-11 spectra of all compounds consisted of unsymmetrical doublets. The more intense line has been interpreted[13] as due to the superposition of the BX singlet and one line of the BH doublet. The less intense line is due to the other line of the BH doublet. The boron-11 nmr chemical shift[20] is believed to be due to changes in π-electron density. Therefore, the chemical shift of the boron atom bound to the substituent should be a measure of the extent of the π interaction between the substituent and the ring, and be related to the change in π-electron density at the *para* position and, consequently, the relative chemical shift of the *para* proton. The excellent correlation between the relative boron-11 chemical shift for the boron bound to the substituent (the more intense line) and the relative shift of the *para* NH proton (Figure 3) supports this hypothesis. The chemical shift of the *meta* boron atoms is not understood.

In conclusion, the substituent bound to a boron atom of the borazine ring influences the nmr chemical shift of the *para* proton. The origin of the relative chemical shift of the *para* proton has been interpreted in terms of the changes in π-electron density generated by the π interaction between the substituent and the ring and transmitted by the delocalized π electrons. There are also other possible interpretations of the data such as field effects and transmission through two three-atom π-electron systems, but they seem less likely considering the excellent correlations between the borazine and benzene data.

Acknowledgments. We wish to thank the National Science Foundation, Grant No. GP-8330, and the Research Foundation of the State University of New York for financial support of this research. We also wish to thank Dr. D. H. Marr, Hooker Chemical Co., Grand Island Research Center, for running the 100-MHz spectra and Dr. G. Templeman for running the boron-11 spectra.

[19] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).

[20] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).