CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

Nuclear Magnetic Resonance Studies of the Phosphorus-31 and Hydrogen-1 Nuclei in Aminophosphonium Compounds

BY S. R. JAIN, WALLACE S. BREY, JR., AND HARRY H. SISLER

Received August 29, 1966

The phosphorus and proton magnetic resonance spectra of a series of aminophosphonium chlorides have been obtained. The chemical shifts of phosphorus nuclei have been interpreted in terms of electronegativity and π bonding. The chemical shifts of NH_2 protons seem to be related to the basicity of phosphines. In a series of methyl-substituted compounds, J_{PCH_3} remains constant and independent of the nature of other substituent groups on phosphorus. Analytical and infrared data of some new aminophosphonium compounds have been listed.

Synthesis of aminophosphonium chlorides by the chloramination of phosphines has been well established.[1,2] A number of such compounds have been prepared in our laboratory in this way. Interesting results from the nuclear magnetic resonance spectra of some of these compounds[2] led us to extend the study in a more systematic way to determine the effect of substitution of different groups on the chemical shifts of ^{31}P and ^{1}H nuclei in these compounds. Though nuclear magnetic resonance data for a number of phosphorus compounds have been published[3–8] in recent years, most of the available data are for compounds containing oxygen. The reported references are either on ^{31}P chemical shifts or on proton magnetic resonance of phosphorus compounds. This paper reports a nuclear magnetic resonance study of both ^{31}P and ^{1}H nuclei and also the preparation and properties of some of the new aminophosphonium chlorides. Incidently, these are some of the few quaternary phosphorus compounds which contain N–P bonds and no oxygen.

Experimental Section

All operations were conducted in a moisture-free nitrogen atmosphere.

Materials.—Solvents used were dried over calcium hydride. Phenyldichlorophosphine and diphenylchlorophosphine were obtained from the Victor Chemical Works, and dimethylamine was obtained from the Matheson Co. Phosphorus trichloride, obtained from J. T. Baker Chemical Co., was redistilled before use.

Analysis.—Elemental analyses were carried out by the Galbraith Microanalytical Laboratories. Melting points were obtained with a Thomas–Hoover capillary melting point apparatus. Analytical and melting point data are listed in Table I.

Infrared Spectra.—The infrared spectra were recorded with a Beckman Model IR 10 grating infrared spectrophotometer. The spectra of solids were taken either in the form of pressed KBr pellets or as Kel-F mulls for the range 2.5–7.5 μ and as Nujol mulls in the range 7.5–20 μ. A summary of spectral bands is presented in Table II.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra for both ^{31}P and ^{1}H nuclei were determined with a Varian Model V-4300-2 high-resolution spectrometer equipped with a field homogeneity control, magnet insulation, and a superstabilizer, at 19.3 and 60.0 Mcps, respectively. The spectra of liquids were run as pure samples and those of solids were determined either in $CDCl_3$ or DMSO-d_6. The proton spectra were referenced by a substitution method, using a 6% solution of tetramethylsilane in chloroform. The field was swept continuously, first through the $CHCl_3$ peak of the reference tube, then through the peaks of the sample, and finally through the TMS peak. Because of the sensitivity of many of the materials to moisture, an internal standard was not used, and the proton shifts are not to be regarded as reported on the τ scale. ^{31}P chemical shifts were determined with respect to H_3PO_4 (85%) as external standard.

Synthesis of Phosphines.—Some of the phosphines used in the present investigation were synthesized as reported in the literature.[9–12] Trimethylphosphine was synthesized by the action of CH_3MgI on phosphorus trichloride, distilled along with ether, and the ethereal solution was used as such for chloramination. Dimethylaminodiphenylphosphine was prepared by the action of dimethylamine on diphenylchlorophosphine. Diphenylmethylphosphine was synthesized by the action of CH_3MgI on diphenylchlorophosphine.

Procedure for Chloramination Reactions.—The chloramine generator used in this study is similar to those described previously.[13,14] In all of the chloraminations the rates of flow of ammonia, nitrogen, and chlorine into the generator were 1.2:0.3:0.1 mole/hr, respectively. The experimental details of a typical reaction are described below.

Diphenylmethylphosphine (0.01 mole) was dissolved in dry ether (60 ml) and exposed to the effluent gases of the chloramine generator. A white precipitate formed immediately in the reactor. The chloramination was continued for 15 min (0.025 mole of chloramine). After the completion of the reaction, the solution was filtered. The solids remaining on the filter were extracted with chloroform. A white material separated from the chloroform solution when an excess of ether was added. This was recrystallized from chloroform (yield 2.0 g) (79.5% of theory).

Other aminophosphonium compounds were synthesized in a similar manner.

---

(1) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

(2) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

(3) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem. Intern. Ed. Engl.*, **1**, 32 (1962).

(4) M. L. Nielsen and J. V. Pustinger, *J. Phys. Chem.*, **68**, 152 (1964).

(5) L. C. D. Groenweghe, L. Maier, and K. Moedritzer, *ibid.*, **66**, 901 (1962); *J. Chem. Eng. Data*, **7**, 307 (1962).

(6) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

(7) C. E. Griffin and M. Gordon, *J. Organometal. Chem.* (Amsterdam), **3**, 414 (1965).

(8) A. H. Cowley and R. P. Pinnell, *J. Am. Chem. Soc.*, **87**, 4454 (1965).

(9) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(10) A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(11) G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 3984 (1962).

(12) E. M. Evleth, L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

(13) R. Mattair and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 1619 (1951).

(14) H. H. Sisler, F. T. Neth, R. S. Drago, and D. Young, *ibid.*, **76**, 3906 (1954).

TABLE I

ANALYTICAL AND MELTING POINT DATA

		Analytical data, %									
		C		H		N		Cl		P	
Compound	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(CH_3)_3PNH_2]Cl$	214–215	28.25	28.25	8.69	8.80	10.98	10.77	27.80	27.58	24.29	23.98
$[(CH_3)_2P(C_6H_5)NH_2]Cl$	105–107	50.67	50.45	6.91	6.95	7.39	7.38	18.70	18.87	16.34	16.07
$[(CH_3)P(C_6H_5)_2NH_2]Cl$	165–166	62.01	62.15	6.01	6.14	5.56	5.47	14.09	14.24	12.31	12.15
$[(CH_3)_2NP(C_6H_5)_2NH_2]Cl$	181–183	59.89	60.11	6.46	6.38	9.98	10.02	12.63	12.82	11.03	11.28
$[[(CH_3)_2N]_2P(C_6H_5)NH_2]Cl$	145–146	48.49	48.23	7.73	7.90	16.96	17.01	14.31	14.52	12.50	12.48
$[[(CH_3)_2N]_2P(CH_3)NH_2]Cl$	106–108	32.35	32.11	9.23	9.45	22.63	22.80	19.10	18.95	16.69	16.49

TABLE II

INFRARED DATA (cm^{-1})[a]

$[(CH_3)_3PNH_2]Cl$

3130 s, 3090 s, 3010 s, 2960 s, 2890 s, 2620 w, 2340 w, 1430 sh, m, 1415 m, 1305 sh, w, 1295 s, 1145 w, 1080 w, 1005 s, 965 s, 870 w, 855 w, 775 sh, w, 760 m, 720 m

$[(CH_3)_2P(C_6H_5)NH_2]Cl$

3300–2900 b, vs, 2580 vw, 2330 sh, vw, 1620 sh, w, 1580 s, 1490 m, 1430 s, 1405 sh, w, 1310 sh, w, 1300 s, 1195 vw, 1155 sh, w, 1130 s, 995 s, 948 s, 905 w, 872 m, 775 sh, m, 740 s, 685 m, 580 b, m, 470 m, 415 m

$[(CH_3)P(C_6H_5)_2NH_2]Cl$

3200–2720 b, vs, 2560 vw, 2320 vw, 1580 w, 1550 m, 1480 w, 1430 s, 1405 sh, w, 1300 m, 1182 w, 1155 vw, 1115 s, 1040 w, 975 s, 905 s, 890 sh, m, 775 sh, m, 740 s, 715 m, 685 s, 498 s, 475 m, 460 m

$[(CH_3)_2NP(C_6H_5)_2NH_2]Cl$

3120 b, vs, 2940 b, vs, 2530 vw, 2320 vw, 1582 m, 1560 sh, m, 1548 s, 1535 sh, m, 1475 w, 1432 s, 1335 vw, 1295 s, 1168 s, 1115 vs, 1065 m, 992 vs, 952 s, 870 sh, w, 850 sh, w, 760 m, 725 s, 690 s, 538 s, 500 s, 445 w, 415 m

$[[(CH_3)_2N]_2P(C_6H_5)NH_2]Cl$

3120 b, s, 2950 b, s, 2530 vw, 2310 vw, 1582 w, 1540 m, 1480 w, 1445 sh, w, 1435 s, 1415 sh, w, 1290 s, 1195 sh, w, 1180 w, 1162 s, 1125 s, 1065 m, 995 d, vs, 960 s, 880 vw, 780 m, 745 s, 730 m, 700 m, 650 w, 505 s

$[[(CH_3)_2N]_2P(CH_3)NH_2]Cl$

3300–2700 b, s, 2560 vw, 2320 vw, 1560 m, 1545 w, 1465 sh, 1445 b, m, 1320 w, 1295 s, 1175 s, 1160 s, 1110 vw, 1070 s, 985 b, s, 910 m, 870 sh, w, 790 s, 760 s, 745 m, 725 s, 625 w, 460 b, w

[a] s, strong; m, medium; w, weak; sh, shoulder; d, doublet; b, broad.

TABLE III

NMR PARAMETERS FOR PHOSPHINES

	Phosphine	τC_6H_5	$\tau CH_3(N)$	$\tau CH_3(P)$	J_{PNCH}, cps	J_{PCH}, cps	$\delta_{^{31}P}$,[b] ppm
I[a]	$(CH_3)_3P$			9.11		2.7	+62[c,d]
II[a]	$(C_6H_5)_3P$	2.90					+7[c,d]
III	$(C_6H_5)_2P(CH_3)$	3.42		9.10		4.4	+28[c]
IV	$(C_6H_5)P(CH_3)_2$	3.18		9.26		3.6	+46[d]
V[a]	$[(CH_3)_2N]_3P$		7.57		8.82		−123[c]
VI[a]	$[(CH_3)_2N]_2P(CH_3)$		7.37	8.86	8.73	7.49	−86.4[c]
VII[a]	$[(CH_3)_2N]P(CH_3)_2$		7.53	9.01	9.77	5.55	−39[c]
VIII	$[(CH_3)_2N]_2P(C_6H_5)$	3.11	7.70		8.8		−100[f]
IX	$[(CH_3)_2N]P(C_6H_5)_2$	3.31	7.97		9.9		−64[f]

[a] Nmr data reported previously. See ref 6 for compounds I and II and ref 8 for compounds V–VII. [b] Nmr data reported previously. [c] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78,** 5715 (1956). [d] W. A. Henderson and S. A. Buckler, *ibid.*, **82,** 7591, 5794 (1960). [e] See ref 5. [f] L. Maier, *Helv. Chim. Acta*, **46,** 2667 (1963).

Results and Discussion

The nuclear magnetic resonance data are presented in Tables III and IV. In general, for proton magnetic resonance spectra of these compounds, $CDCl_3$ was used as solvent. However, in cases where the compounds are not sufficiently soluble in $CDCl_3$, DMSO-d_6 was used. As far as possible, only one solvent was used to compare the spectral data in a particular series. In each case for which the chemical shifts and coupling constants are listed, the spectra were well resolved and the absorptions possessed the expected multiplicity. In only a few cases, the absorption signals for NH_2 protons appeared as doublets, but otherwise they appeared as singlets. In the multiplet pattern for each of the phenyl groups, the chemical shift reported corresponds to the strongest peak. The ^{31}P chemical shifts are found to be slightly dependent upon the solvents used; *e.g.*, the chemical shift of ^{31}P in $[(C_6H_5)_3PNH_2]Cl$ in DMSO is found to be −30.0 ppm while in $CHCl_3$ it is −32.0 ppm. The effect of change in concentration on the ^{31}P chemical shift is found to be negligible within the limit of accuracy, which is about ±1.0 ppm.

It is worthwhile to examine the chemical shifts of ^{31}P nuclei in various aminophosphonium compounds, shown in Table IV, with respect to the chemical shift of triphenylaminophosphonium chloride. If each of the phenyl groups is replaced by an NH_2 group, there is apparently no change in the chemical shifts. This is also true for methylaminophosphonium chlorides as indicated when the chemical shifts of $[(CH_3)_2P(NH_2)_2]Cl$ (−42.3 ppm) and $[(CH_3)_2P(C_6H_5)NH_2]Cl$ (−42.8 ppm) are compared. Successive replacement of phenyl groups by methyl groups results in a downfield shift of phosphorus. Each methyl group seems to contribute an amount of about −6.6 ppm to the downfield shift. This is in agreement with an earlier observation[5] on quaternary phosphorus compounds, where the replacement of one phenyl group by one methyl group causes a shift of −8.0 ppm.

Substitution of a dimethylamino group for a phenyl group (series III) causes a downfield shift of ^{31}P nuclei from −30.0 ppm in $[(C_6H_5)_3PNH_2]Cl$ to −40 ppm in $[(C_6H_5)_2P[N(CH_3)_2]NH_2]Cl$. However, further replacement of phenyl groups by dimethylamino groups does not have any effect on the chemical shift. An irregular trend is also observed when a methyl group is replaced by a dimethylamino group (series IV). There seems to be no quantitative correlation between chemical shift and nature of the group attached in this series of compounds, since the observed shifts of

TABLE IV

NMR PARAMETERS FOR AMINOPHOSPHONIUM SALTS

Compound	Solvent for pmr	$\tau_{C_6H_5}$	τ_{NH_2}	τ_{CH_3}	τ_{NCH_3}	J_{PCH}, cps	J_{PNCH}, cps	$\delta_{^{31}P}$, ppm	Solvent for ^{31}P nmr
			Series I						
$[(C_6H_5)_3PNH_2]Cl$[a]	$CDCl_3$	2.36	2.68					−32.0	$CHCl_3$
	DMSO	2.42	2.87					−30.0	DMSO
$[(C_6H_5)_2P(CH_3)NH_2]Cl$	$CDCl_3$	2.55	3.0	7.43		14.1		−38.0	DMSO
$[(C_6H_5)P(CH_3)_2NH_2]Cl$	$CDCl_3$	2.45	3.7	7.78		14.5		−42.8	DMSO
$[(CH_3)_3PNH_2]Cl$	DMSO-d_6		4.74	8.19		14.5		−49.6	DMSO
			Series II						
$[(C_6H_5)_3PNH_2]Cl$	DMSO	2.42	2.87					−30.0	DMSO
$[(C_6H_5)_2P(NH_2)_2]Cl$[b]	DMSO-d_6	2.44	3.78					−31.9 ± 2	DMSO
$[(C_6H_5)P(NH_2)_3]Cl$[b]	DMSO-d_6	2.47	4.58					−29.4	DMSO
			Series III						
$[(C_6H_5)_3PNH_2]Cl$	$CDCl_3$	2.36	2.68					−32.0	$CHCl_3$
								−30.0	DMSO
$[(C_6H_5)_2P[N(CH_3)_2]NH_2]Cl$	$CDCl_3$	2.35	2.95		7.05		11.7	−42.2	$CHCl_3$
								−39.9	DMSO
$[(C_6H_5)P[N(CH_3)_2]_2NH_2]Cl$	$CDCl_3$	2.35	2.88		7.15		10.4	−43.0	$CHCl_3$
								−41.0	DMSO
$[[(CH_3)_2N]_3PNH_2]Cl$[c]	$CDCl_3$		3.66		7.11		9.5	−42.6	$CHCl_3$
								−39.0	DMSO
			Series IV						
$[(CH_3)_3PNH_2]Cl$	DMSO-d_6		4.74	8.19		14.5		−49.6	DMSO
$[(CH_3)_2P[N(CH_3)_2]NH_2]Cl$[d]	$CDCl_3$		3.70	7.8	7.08	14.5	11.1	−54.0	$CHCl_3$
$[(CH_3)P[N(CH_3)_2]_2NH_2]Cl$	$CDCl_3$		3.57	8.0	7.16	14.8	9.9	−53.0	$CHCl_3$
$[[(CH_3)_2N]_3PNH_2]Cl$	$CDCl_3$		3.66		7.11		9.5	−42.6	$CHCl_3$
			Series V						
$[(CH_3)_2P(NH_2)_2]Cl$[e]	DMSO-d_6		4.8	8.37		14.2		−42.3	DMSO
NH_2Cl	$(C_2H_5)_2O$		6.26						

[a] Synthesis reported in ref 1. [b] Synthesized by S. E. Frazier and H. H. Sisler, *Inorg. Chem.*, **5**, 925 (1966). [c] Analytical data to be published. [d] Data from the Ph.D. thesis of D. F. Clemens, University of Florida, 1965. [e] Synthesized by H. H. Sisler and S. E. Frazier, *Inorg. Chem.*, **4**, 1204 (1965).

$[[(CH_3)_2N]_2P(CH_3)NH_2]Cl$ and $[(CH_3)_2NP(CH_3)_2NH_2]Cl$ are more downfield than either tris(dimethylamino) or trimethyl derivatives.

Comparison of these data on the chemical shifts of ^{31}P nuclei broadly indicate that the shielding of phosphorus varies with the substituent group as: $C_6H_5 \simeq NH_2 > N(CH_3)_2 > CH_3$. Since both NH_2 and $N(CH_3)_2$ groups are more electronegative than the phenyl group, this order is consistent with the recent work of Letcher and Van Wazer[15] in which it was established that, for quaternary phosphorus compounds, there is a substantial contribution to the chemical shift from the amount of π bonding, as well as from the electronegativity. These two factors operate in such a way that an increase in electronegativity of the group increases the shielding and an increase in bond order resulting from π bonding reduces the shielding. These authors have also calculated the amount of π bonding in compounds of the type MPZ_3 where M = O, S, or Se and have reported considerable π bonding in the compounds having Z = NH_2 or $N(CH_3)_2$ groups. In the present case, more shielding of ^{31}P nuclei in $[(C_6H_5)_3PNH_2]Cl$ than in $[(CH_3)_3PNH_2]Cl$ might be explained to some extent as resulting from the more electronegative nature of the phenyl group than of the methyl group. However, in the case of compounds having an amino or dimethylamino group, the amount of π bonding plays a major role in accounting for the observed chemical shift.

The proton magnetic resonance data for neutral phosphines and their aminophosphonium salts are listed in Tables III and IV. A downfield shift in proton resonances, particularly in P–CH_3 protons, in all phosphonium compounds reflects an expected decrease in electron density on the phosphorus resulting from quaternization. Assuming that an upfield shift reflects an increase in electron density, an order of base strengths of phosphines may be derived from the NH_2 proton resonances of the aminophosphonium compounds. From the chemical shifts, two sequences of the tendency of phosphines to donate electrons to the amino group can be deduced: $(CH_3)_3P > (CH_3)_2P(C_6H_5) > CH_3P(C_6H_5)_2 > (C_6H_5)_3P$ and $(CH_3)_3P > [(CH_3)_2N]_3P > (C_6H_5)_3P$. These sequences are in accord with the order of basicity of phosphines as reported in the literature.[16,17]

The magnitudes of the coupling constants J_{PCH} and J_{PNCH} increase when the phosphorus atom is quaternized. This change in magnitude in J_{PCH} is associated with increased s character in P–C bonds[8] resulting from quaternization, in the course of which the bonding

---

(15) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

(16) W. A. Henderson and S. A. Buckler, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

(17) R. R. Holmes and R. P. Carter, Jr., *Inorg. Chem.*, **2**, 1146 (1963).

orbitals change from p^3 to sp^3. At the same time, substitution of the more electronegative NH_2 group on the phosphorus atom is expected to divert additional s character into P–C bonds.[6,8] The increment in J_{PCH} with increase in s character is also observed in the case of phenyl- and dimethylamino-substituted methylphosphines as given in Table III. These results seem to contradict those of Manatt, *et al.*,[18] who found that for methyl-substituted phosphines increase in s character decreases the magnitude of J_{PCH}. However, it is possible that the sign of this coupling constant may differ in the phosphines from that in the phosphonium salt.

It is interesting to note that the values of the J_{PCH} coupling constants remain constant (14.4 ± 0.3 cps) in a series of methyl-substituted aminophosphonium chlorides regardless of the other substituents on the phosphorus atom. Similar results have also been obtained by earlier workers[6,7] on some other methyl-substituted phosphonium salts. This constancy is also observed to a smaller degree in the case of J_{PNCH}, the magnitude of which is 10.6 ± 1.1 cps.

Whereas the chemical shifts of $(CH_3)_2N$ protons are almost unaffected by other substituents on the phosphorus atom (τ 7.11 ± 0.06), the chemical shifts of CH_3 protons show appreciable change with the other substituents on the phosphorus. This probably results from the $(CH_3)_2N$ protons being, three bonds (P–N–C–H) away from phosphorus and therefore not much affected by the change in electron density on the phosphorus atom caused by the other substituent. Also, spectra of methyldimethylaminophosphonium chlorides, on comparison with those of the corresponding phosphines, show a large downfield shift of $P-CH_3$ protons and large increment in J_{PCH} on quaternization, thus suggesting that, as concluded by earlier workers[2] from other evidence, chloramination occurs on the phosphorus atom rather than the nitrogen atom.

Infrared spectra of the new aminophosphonium chlorides prepared during the course of this investigation are summarized in Table III. These spectra are similar to spectra of other phosphonium salts as reported earlier[2] and the spectral bands can be assigned accordingly. The general occurrence of a strong band in the region 1290–1300 cm^{-1} in all of these compounds probably results from $P-CH_3$ or $P-N(CH_3)_2$ vibrations.[19] The strong absorptions in the region of 980–950 cm^{-1} in dimethylaminophosphines have been assigned to the $P-N(CH_3)_2$ group;[12] this band appears in the range 995–950 cm^{-1} in the spectra of aminophosphonium chlorides.

Acknowledgment.—We wish to thank the National Institutes of Health for partial support of this research through project No. CA-08263-01 and the National Science Foundation for partial support of this research through a Science Development Grant with the University of Florida.

[18] S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).

[19] L. J. Bellamy "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 323.

Contribution from the Department of Chemistry,
Marshall University, Huntington, West Virginia 25701

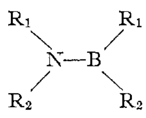
An Investigation of the Boron–Nitrogen Bonds in Some Aminoboranes

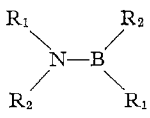
By M. R. CHAKRABARTY, C. C. THOMPSON, Jr., and WALLACE S. BREY, Jr.[1]

Received October 4, 1966

Simple Hückel calculations have been carried out in order to assess relative π-bond orders of the B–N bonds in a series of aminoboranes with various substituents. The results are shown to correlate well with relative bond orders as deduced from infrared stretching frequencies. The B^{11} nmr chemical shifts are also found to be related to the π-electron densities calculated for the boron atoms.

The nature of B–N bonds in aminoboranes has recently been of considerable interest.[2,3] In 1948[4] Wiberg postulated that the filled p orbital of the nitrogen atom and the empty p orbital of the boron atom might be involved in forming a partial double bond in aminoboranes. The double-bond character of the B–N linkage may thus result in *cis–trans* isomerism in a substituted aminoborane, *e.g.*





The results of proton magnetic resonance studies of some aminoboranes containing at least one substituent having protons substantiated this hypothesis.[5–10]

---

[1] Department of Chemistry, University of Florida, Gainesville, Fla.

[2] K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press Inc., New York, N. Y., 1965, pp 48–65.

[3] K. Niedenzu, *Angew. Chem.*, **3**, 86 (1964).

[4] E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

[5] G. E. Ryschkewitsch, W. S. Brey, Jr., and A. Saji, *J. Am. Chem. Soc.*, **83**, 1010 (1961).

[6] W. S. Brey, Jr., M. E. Fuller, G. E. Ryschkewitsch, and A. S. Marshall, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 100.

[7] H. Baechle, H. J. Becher, H. Beyer, W. S. Brey, Jr., J. W. Dawson, M. E. Fuller, II, and K. Niedenzu, *Inorg. Chem.*, **2**, 1065 (1963).

[8] P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc.*, 421 (1961).

[9] W. S. Brey, Jr., K. N. Scott, and M. R. Chakrabarty, "Restricted Rotation in Some Aminoboranes," Abstracts of Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

[10] T. Totani, H. Watanabe, and M. Kubo, "Proceedings of the XIIIth Colloque Ampere," North-Holland Publishing Co., Amsterdam, 1965, p 366.