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.

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An Investigation of the Boron–Nitrogen Bonds in Some Aminoboranes

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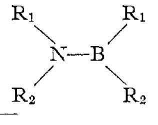
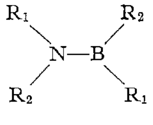
Simple Hückel calculations have been carried out in order to assess relative π-bond orders of the B–N bonds in a series of aminoboranes with various substituents. The results are shown to correlate well with relative bond orders as deduced from infrared stretching frequencies. The B^{11} nmr chemical 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]

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

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[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.

Wyman, Niedenzu, and Dawson[11] carried out infrared studies of a number of aminoboranes and applied Gordy's equation[12] to the B–N stretching frequencies to obtain approximate values of the B–N bond orders. The authors showed the presence of about 30–60% double-bond character of the B–N bonds in a group of 14 substituted aminoboranes. It was also observed that a phenyl substituent attached to either of the two atoms lowered the B–N stretching frequency, the effect being more pronounced where the phenyl group is attached to the nitrogen atom. This observation is consistent with the nmr data.[5–10]

In an attempt to elucidate the nature of B–N bonds, several authors[13–18] carried out LCAO–MO calculations on various boron–nitrogen compounds. Although the simple Hückel method for a π system is not as precise as other more sophisticated methods, the success of this method in explaining the properties of some boron–nitrogen compounds has been demonstrated by Dewar and Rogers.[14] It is, therefore, expected that such calculations should be able to yield information regarding the bond orders and electron densities adequate for correlation with the infrared spectra and the boron chemical shifts of aminoboranes.

Relatively few B^{11} chemical shifts for aminoboranes have been previously reported.[7,19] It was therefore decided to determine the shifts for several additional compounds in order to permit comparisons with the calculated electron densities.

Experimental Section

Nmr Studies.—The compounds were supplied by Dr. K. Niedenzu, who prepared and purified them according to published methods.[3] Chemical shifts of the boron atoms were determined in a Varian DP-60 spectrometer, operating at 19.3 Mc. Trimethyl borate was used as an external reference in a substitution method and shifts are expressed in parts per million from this reference.

MO Calculations.—The molecular orbital calculations were carried out using a FORTRAN II program written by Dr. A. R. Lepley. A modified version of a SHARE library subroutine EIGEN was used for the calculation of eigenvalues and eigenvectors. The program was capable of yielding energy level values, total π-molecular energies, π-electron densities, and π-bond orders.

The secular determinant $|H_{ij} - ES_{ij}| = 0$, where $H_{ij} = \int \psi_i H \psi_j \mathrm{d}\psi$ and $S_{ij} = \int \psi_i \psi_j$ was simplified by making the assumptions: (a) $S_{ij} = 0$ for $i \neq j$ and $S_{ij} = 1$ for $i = j$; (b) $H_{ij} = 0$ where the ith and the jth atoms are not formally bonded to each other.

The Coulomb and resonance integrals for the heteroatoms have been expressed in terms of the corresponding familiar carbon integrals α_c and β_{cc} in benzene. Thus

$$H[X_{p\pi},X_{p\pi}] = \alpha_c + h_X\beta_{cc}$$

$$H[X_{p\pi},Y_{p\pi}] = k_{XY}\beta_{cc}$$

The parameters h_N and h_B were obtained from the established values reported in the literature.[20]

The methyl group was treated by using inductive, conjugation, and heteroatom models. These parameters were also obtained from the same source, which also reported the values of the parameters k_{B-C} and k_{N-C}. However, on construction of Fisher–Hirschfelder molecular models, it was observed that the phenyl groups attached to either nitrogen or boron could not be in plane with the rest of the molecule. It was concluded that the phenyl groups had to be twisted through an angle of 45° out of plane in order to minimize steric effects. The parameters k_{B-C} and k_{N-C} were then lowered by a factor of cos 45° from the usual values of 0.7 and 0.8,[20] respectively, to be used as $k_{B-C_6H_5}$ and $k_{N-C_6H_5}$. For less common linkages such as $B-CH_3$ and $N-CH_3$, the parameters were varied from the corresponding $C-CH_3$ parameters until one single set of parameters gave results consistent with the experimental data, such as infrared and nmr studies. An auxiliary inductive parameter (AIP) of 0.05 for the heteroatom attached to the methyl group was found to give best results. The construction of a model containing phenyl groups indicated that not only are the phenyl groups in such molecules out of plane, but the B–N bond also seemed to be twisted to a small degree. This observation is consistent with the conclusion drawn by Becher and Baechle[21] from their infrared studies. A correction factor equal to cos 30° was included for k_{B-N} in the molecules containing a phenyl group. The various parameters used in this work are given in Table I.

TABLE I

COULOMB AND EXCHANGE PARAMETERS[a]

X	h_X	X—Y	k_{X-Y}
N	1.50	$B—CH_3$	0.35
B	−1.00	$B—C_6H_5$	0.49
CH_3	2.00	B—N	0.80
C	0.00		0.70[b]
		$N—CH_3$	0.50
		$N—C_6H_5$	0.57
		C=C	1.10[c]

[a] AIP = 0.05. [b] For phenyl-substituted aminoborane. [c] For vinyl double bond.

Results and Discussion

The results of the calculations are presented in Table II, with P_{B-N} representing the π-bond order of the B–N bond, and ϵ_B and ϵ_N the π-electron densities on the boron and nitrogen atoms, respectively. Also given in this table are positions of the infrared absorption bands assigned to the B–N stretching vibration, most of them taken from the literature, and the B^{11} nuclear resonance chemical shifts, as measured for several of the compounds.

Assuming a harmonic oscillator model, one could write the familiar equation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \qquad (1)$$

where the symbols have their usual significance. According to Gordy,[12] the bond force constant K depends on the bond order P_{ij} in the following manner

$$K = 1.67P_{ij}[X_iX_j/d^2]^{3/4} + 0.30 \qquad (2)$$

where X_i and X_j are the electronegativities of atoms i and j, respectively, and d is the bond length. Combining eq 1 and 2, we have

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[11] G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).

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[21] H. J. Becher and H. T. Baechle, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 71.

$$K \propto \nu^2 \propto P_{ij} \tag{3}$$

Hence a plot of P_{ij} against ν^2 should result in a straight line within a reasonable degree. The simplifying assumptions made here are (a) the σ-bond character in a group of closely related aminoboranes does not change appreciably and (b) the B–N bond length remains virtually unchanged. Figure 1 shows a plot of the calculated bond orders against ν^2. The agreement with the theory is quite satisfactory. Best fit was obtained when the methyl groups were treated as heteroatoms, a result which is consistent with Streitwieser's view.[20]

As expected, the B^{11} resonance peaks were found to move upfield as the electron density on the boron atom increased. However, since electron density is not the only factor which determines the chemical shift of a nucleus, one should not expect a simple relationship between the two functions. The B^{11} chemical shift was also measured for the compound (benzylmethylamino)benzylphenylborane. Except for the possibility of greater steric interaction and slightly differing electronegativities of the benzyl groups as compared to the methyl groups, this molecule should be quite similar to (dimethylamino)methylphenylborane, for which the MO calculation was carried out. The observed B^{11} shift is roughly in line with what one would predict for the compound containing three methyl groups.

TABLE II

CALCULATED BOND ORDERS AND ELECTRON DENSITIES AND MEASURED INFRARED FREQUENCIES AND NUCLEAR MAGNETIC RESONANCE SHIFTS OF AMINOBORANES

Substituents		Infrared str freq, cm^{-1}	B nmr chem shift, ppm	Calculated		
On N	On B			$P_{B\text{-}N}$	ϵ_B	ϵ_N
2H	2H	...	...	0.539	0.158	1.842
$2CH_3$	2H	1194[a]	...	0.545	0.170	1.837
$2CH_3$	$2CH_3$	1530[b]	−26.5[e]	0.538	0.212	1.838
CH_3, H	$2CH_3$	1525[b]	...	0.534	0.206	1.841
2H	$2CH_3$	1515[c]	...	0.531	0.199	1.843
C_6H_5, CH_3	$2CH_3$	1388[d]	−27.8	0.476	0.178	1.837
C_6H_5, CH_3	C_6H_5, CH_3	1381[d]	−26.3	0.469	0.191	1.838
C_6H_5, H	$2CH_3$	1332	...	0.467	0.174	1.818
$2CH_3$	C_6H_5, $CH_2{=}CH$	1419	−21.9	0.461	0.244	1.873
$2CH_3$	CH_3, $CH_2{=}CH$	...	−21.4	0.516	0.259	1.841
$2CH_3$	C_6H_5, CH_3	1417[d]	...	0.481	0.194	1.870
CH_3, $C_6H_5CH_2$	C_6H_5, $C_6H_5CH_2$	...	−31.1	...	...	...

[a] W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950); this compound exists as a dimer. [b] H. J. Becher and J. Goubeau, *Z. Anorg. Chem.*, **268**, 133 (1952). [c] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 5553 (1959). [d] From ref 11. [e] From ref 19.

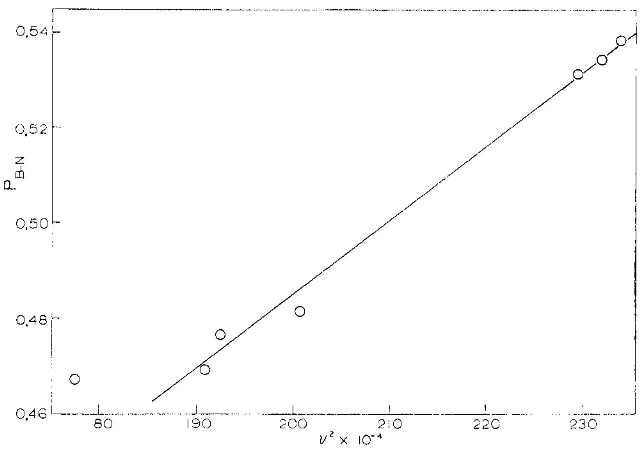

Figure 1.—Calculated π-bond order for representative aminoboranes plotted against the square of the observed B–N stretching vibration frequency.

The presence of an N-phenyl group lowers the B–N bond order. This is probably due to the partial withdrawal of electrons from the nitrogen atom by the phenyl group. Thus, when a hydrogen in aminodimethylborane is replaced by a phenyl group, the electron density on both boron and nitrogen is reduced.

It is interesting to observe the effect of N-methyl and B-methyl substituents on the B–N bond orders and the electron densities on the two heteroatoms. The present work shows that the bond order varies in the following manner: dimethylaminoborane > aminoborane > aminodimethylborane. Thus N-methyl substituents increase the bond order whereas B-methyl substituents decrease it. The B–N bond stretching frequencies of those compounds also should vary in the same manner. Unfortunately, however, this prediction cannot be tested experimentally since aminoborane exists in polymeric form[2] and dimethylaminoborane probably exists in a dimeric form.[11]

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