mole/sec. for methylsilane to 4.5×10^{-7} for tetramethylsilane. Such a trend would be expected if some of the nitrogen atoms abstract hydrogen atoms from silicon to form imine radicals which then disproportionate to nitrogen and hydrogen, since this reaction should become less important as the number of Si-H bonds in the molecule decreases.

The formation of ammonia from the methylsilanes does not prove, of course, that hydrogen abstraction occurs. The results of the present study indicate that ammonia is not produced by way of imine radicals resulting from hydrogen atom abstraction. This conclusion is based on the fact that ammonia was not formed in the reaction of active nitrogen with silane. The fact that ammonia was not formed from silane itself but was formed from the methylsilanes in increasing amount with increasing methyl substitution shows that it is the hydrogens attached to carbon rather than to silicon which are involved in ammonia formation. Since it seems likely that the imine radical is not an important intermediate in ammonia formation, it is suggested that the nitrogen atom must remove either two or three hydrogen atoms from the methyl group in one step. This implies that ammonia is formed directly by some sort of molecular process or that the amine radical, NH_2, is the intermediate. Some support for this view is provided by the observation that the ammonia obtained from CH_3SiD_3 was principally NH_2D.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Boron–Nitrogen Compounds. III.[1,2] Aminoboranes, Part 2: The B–N Bond Character in Substituted Aminoboranes

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The preparation of (amino)-monochlorophenylboranes, $R_2N\text{–}B(Cl)(C_6H_5)$, and of unsymmetrical tetrasubstituted aminoboranes is reported. The special feature of the B–N bond of aminoboranes has been investigated. Data have been collected and analyzed in order to ascertain the double bond character of this linkage. A theoretical study of electron delocalization in the aminoborane system is presented.

Aminoboranes are conventionally illustrated by the basic structure =N—B=. To understand the chemical and physical behavior of these compounds, the fundamental character of the B—N bond must be considered. To date little work has been done to elucidate the character of this linkage.

Primarily, there exists only one normal covalent bond (I), providing an electron deficiency on the boron. Naturally, this presents a very reactive state, which can explain most of the chemical reactions of aminoboranes. Participation of the free electron-pair of the nitrogen in the B–N linkage, however, promotes double bond character (II) as the electrons then residue in π-orbitals.

$$\underset{\text{I}}{=\ddot{\text{N}}\cdot\cdot\text{B}=} \longleftrightarrow \underset{\text{II}}{=\overset{(+)}{\text{N}}::\overset{(-)}{\text{B}}=}$$

A special kind of double bond, where one partner is responsible for the contribution of three electrons to the bond, is highly important in such situations. A convincing experimental proof of the double bond in most cases depends upon recognition of the parts played by bond distances, bond forces and the mechanism of chemical reactions, in consonance with certain empirical rules.

Planar arrangement of its three bonds, according a sp^2-hybridization, enables the free electron-pair of the nitrogen to participate as π-electrons in the double bond of aminoboranes. Such a planar arrangement of the nitrogen bonds in boron compounds has been established for aminoboranes[3] as well as for borazine[4] and boron nitride.[5] Furthermore, spectroscopic investigations of aminoboranes[6] provide convincing evidence for the double bond character of the B–N linkage.

In reference to the bond moment,[7] however, three electronic structures are necessary to describe the B–N bond of aminoboranes according to Pauling's theory.

$$\underset{\text{I}}{=\ddot{\text{N}}\cdot\cdot\text{B}=} \longleftrightarrow \underset{\text{II}}{=\overset{(+)}{\text{N}}::\overset{(-)}{\text{B}}=} \longleftrightarrow \underset{\text{III}}{=\overset{(-)}{\text{N}}:\ \overset{(+)}{\text{B}}=}$$

Which of these structures predominates should depend on the nature of the substituents bonded to the basic structure.

Since a boron–nitrogen grouping is isosteric and isoelectronic with a carbon–carbon grouping,[8] aminoboranes have been compared with analogous ethylene compounds. More than a quarter of a century ago Langmuir[9] suggested the correspondence of melting and boiling points as a sensitive criterion for the similarity of molecules. Indeed,

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(1) Boron–Nitrogen Compounds, II, THIS JOURNAL, **81**, 5553 (1959).

(2) Supported by the Office of Ordnance Research, U. S. Army.

(3) J. Goubeau and H. J. Becher, *Z. anorg. allgem. Chem.*, **268**, 133 (1952).

(4) S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

(5) A. Brager and H. Shdanow, *C. R.* (*Doklady*) *Acad. Sci. SSSR*, **29**, NS 8, 629 (1940).

(6) Compare for instance: H. J. Becher, *Z. anorg. allgem. Chem.*, **289**, 262 (1957).

(7) H. J. Becher, *ibid.*, **270**, 273 (1952).

(8) J. Goubeau, *Naturw.*, **35**, 246 (1948).

(9) I. Langmuir, THIS JOURNAL, **41**, 1543 (1919); **42**, 274 (1920).

physicochemical properties of alkylated aminoboranes are in close agreement with those of the corresponding ethylene derivatives. This relationship suggests a consistent tendency of the π-electrons of the nitrogen to participate in boron–nitrogen bonding.

As described above, this behavior will depend on the character of the substituents attached to the basic structure. If linked to the boron atom, electron-attracting groups should increase the double bond character of the B–N linkage, if attached to the nitrogen they should have the opposite effect. Moreover, an aminoborane should exhibit a greater resonance energy when more double bond character exists. For instance, a structure such as that of (methylphenylamino)-methylphenylborane, $(CH_3)(C_6H_5)N\text{-}B(CH_3)(C_6H_5)$, should have double bond character, as this would permit resonance of all the π-electrons of the system. Preferably, the phenyl groups should be in the *trans* position and in plane, as a distortion of the plane of the $(CH_3)\text{–}B\text{–}(C_6H_5)$ and $(CH_3)\text{–}N\text{–}(C_6H_5)$ groups as compared to the B–N plane would hinder conjugation for steric reasons.

Assuming it is reasonable to compare the structures of aminoboranes and ethylenes and assuming a B–N double bond is existent, *cis–trans* isomerism should be possible in this particular system, since, under these circumstances, rotation around the B–N axis would be hindered. The minimum condition for such an occurrence resides in the presence of two different substituents attached to the basic structure in the proper spatial arrangement, *i.e.*, two groups bonded to the boron which are different between themselves but which are identical to the two substituents on the nitrogen, *e.g.*, $R^1R^2{=}N\text{–}B{=}R^1R^2$.

To extend the rather limited knowledge of aminoboranes along lines discussed above, several experimental investigations have been undertaken.

Unsymmetrical tetraorgano substituted aminoboranes have not hitherto been described in the literature. Recently, however, the preparation of organic substituted aminoboranes through the reaction of Grignard compounds with (amino)-dichloroboranes has been reported.[1] The disadvantage of this method resides in the consistently simultaneous replacement of both chlorine atoms by identical organic groups. A stepwise replacement, affording aminoboranes with either an organic group and a chlorine atom or two different organic groups attached to the boron, was not realized. As will be described below such multiply substituted aminoboranes can be prepared through an alternative procedure: dichloroörganoboranes react with secondary amines to yield (amino)-monochloroboranes, which then, through treatment with Grignard reagents, form tetraorgano substituted aminoboranes.

The present investigation is based primarily on the utilization of dichlorophenylborane as a starting material. This compound can be prepared very effectively through the reaction of boron trichloride with tetraphenyl metals (Sn, Pb) in benzene solution. The utilization of a solvent corresponding to the substituent in the aryl metal reagent promotes extraordinarily high yields. The preparation of alkyldichloroboranes *via* tetraalkyl tin compounds has been reported recently.[10]

Dichlorophenylborane reacts with equimolar amounts of secondary amines to form addition compounds of the general formula $R_2NH\cdot Cl_2B(C_6H_5)$. On treatment with a tertiary amine, the addition compounds lose hydrogen chloride, thus providing (amino)-monochloroboranes according to the equation

$$R_2NH\cdot Cl_2B(C_6H_5) + (C_2H_5)_3N \longrightarrow R_2N\text{-}B(Cl)(C_6H_5) + (C_2H_5)_3NHCl$$

The remaining halogen atom of the resultant (amino)-monochloroborane can be replaced by an organic group through a Grignard reaction

$$R_2N\text{–}B(Cl)(C_6H_5) + R'MgX \longrightarrow R_2N\text{–}B(R')(C_6H_5) + 0.5MgCl_2 + 5MgX_2$$

This reaction illustrates a method for the preparation of aminoboranes with two different organic groups attached to the boron atom. Such aminoboranes have not been described previously in the literature. If an unsymmetrical secondary amine having no phenyl substituent reacts with dichlorophenylborane and the product then is treated with a proper Grignard compound, a completely unsymmetrical tetraorgano substituted aminoborane can be obtained.

Experimental

Dichlorophenylborane, $Cl_2B(C_6H_5)$.—One hundred grams (0.24 mole) of commercially available tetraphenyltin was covered with 1200 cc. of dry benzene. The mixture was cooled in ice and 80 ml. (0.98 mole) of boron trichloride was added. On slow warming, the tetraphenyltin went into solution; the reaction mixture was refluxed for 3 hours. The solvent then was removed off and the residue distilled under nitrogen at normal pressure, yielding a fraction boiling at 145–205°. Redistillation *in vacuo* afforded 119 g. (0.75 mole) of pure dichlorophenylborane. This reaction affords a considerably higher yield than the one calculated according to the equation

$$Sn(C_6H_5)_4 + 2BCl_3 \longrightarrow 2Cl_2B(C_6H_5) + Cl_2Sn(C_6H_5)_2$$

However, diphenyltin dichloride was the only by-product of the preparation which was identified. The formation of tin tetrachloride was not observed.

An analogous reaction in which the tetraphenyltin was replaced by the corresponding lead compound provided an equally facile synthesis but with consistently lower yields.

(*n*-Butylmethylamino)-chlorophenylborane, $(C_4H_9)(CH_3)\text{-}N\text{–}B(Cl)(C_6H_5)$.—A solution of 65 ml. (0.5 mole) of dichlorophenylborane in 600 cc. of dry benzene was cooled in ice and 59 ml. (0.5 mole) of dry, freshly distilled *n*-butylmethylamine was added. The cooling bath was removed and the stirred mixture was allowed to reach room temperature. A solution of 70 ml. (0.5 mole) of dry, freshly distilled triethylamine in 200 cc. of dry benzene was added and the mixture was refluxed for 3 hours. After filtration of the reaction mixture, the benzene was evaporated and the residue distilled *in vacuo*, yielding 66 g. (69%) of a colorless liquid, b.p. 72° (1 mm.).

Table I describes the (amino)-chlorophenylboranes which were prepared using the same molar ratios and the techniques cited above.

The molecular weights of these compounds were determined on the freshly distilled products. It is of interest to note that these determinations must be made immediately since most of the compounds tend to dimerize on standing for a relatively short period of time. The dimerization products are usually solid materials of relatively great stability toward chemical attack.

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[10] F. E. Brinckman and F. G. A. Stone, Abstr. of Papers, 135th A.C.S. Meeting, April 5–10, 1959, Boston, Mass., p. 26-M.

TABLE I

(AMINO)-CHLOROPHENYLBORANES, $(R^1)(R^2)N-B(Cl)(C_6H_5)$

Chlorophenylborane	B.p. °C.	Mm.	Yield, %		Mol. wt.	Analyses, % B	N	C	H	Cl
(Dimethylamino)-	81	3	73	Calcd.	167.5	6.5	8.4	57.3	6.6	21.2
				Found	171	6.6	8.4	57.3	6.8	21.0
(Diethylamino)-	67	2	72	Calcd.	195.5	5.5	7.2	61.4	7.7	18.15
				Found	192	5.6	7.2	61.4	7.6	17.9
(Methylphenylamino)-	103–110	3	74	Calcd.	229.5	4.7	6.1	68.1	5.7	15.5
				Found	220	4.8	6.3	68.0	5.9	15.5
(Ethylphenylamino)-	105–128	2	70	Calcd.	243.5	4.4	5.7	68.8	6.2	14.55
				Found	...	4.8	5.6	68.1	6.1	14.9
(Piperidino)-	82	2	76	Calcd.	207.4	5.2	6.8	63.7	7.3	17.1
				Found	203	5.6	7.0	63.2	7.0	16.9
(*n*-Butylmethylamino)-	70–72	1	69	Calcd.	209.5	5.2	6.7	63.0	8.2	16.8
				Found	204	5.4	7.0	63.1	8.0	16.6

Only one (amino)-monohalogenoborane, prepared by a different procedure, has recently been reported.[11] Surprisingly such compounds are thermally quite stable and can be distilled *in vacuo* without apparent decomposition; the monomers are, however, sensitive toward hydrolysis. On exposure to air, they fume very strongly and some react explosively with water. Hydrolysis and other solvolysis reactions (for instance the exothermic reaction with alcohols) apparently first rupture the boron–halogen bond; (amino)-phenylboronic acids $R_2N-B(OH)(C_6H_5)$, might be the intermediate reaction products, as esters of such compounds are known.[12] However, the free acids have not been isolated as they appear to be unstable. The boron–nitrogen bond is attacked rapidly by water and phenylboronic acid is the only product of hydrolysis which has been isolated and identified.

(*n*-Butylmethylamino)-ethylphenylborane, $(C_4H_9)(CH_3)$-$N-B(C_2H_5)(C_6H_5)$.—A Grignard solution was prepared from 39 g. (0.25 mole) of ethyl iodide in 250 cc. of dry ether. A mixture of 41.9 g. (0.2 mole) of (*n*-butylmethylamino)-chlorophenylborane in 400 cc. of dry benzene was added to the filtered Grignard solution. The reaction was completed by refluxing for several hours. After filtration of the mixture, two-thirds of the solvent was evaporated. The concentrate was filtered free of precipitated materials and the remaining solvent evaporated. The residue was distilled under reduced pressure and the resultant aminoborane purified by redistillation *in vacuo*, affording 20.7 g. (51%) of a colorless liquid, b.p. 77°(3 mm.) (not sharp). The b.p. of the aminoborane showed a range of approximately 15–20°, even though a 100-mm. Widmer column was used for the distillation. Several fractions were cut off (73°, 77°, 81°, 73–89°) all of which gave identical analyses. On treatment with hydrogen chloride only the starting *n*-butylmethylamine could be isolated and identified.

The presence of benzene (or other higher boiling solvents) during the preparation of aminoboranes *via* the Grignard method is not necessary, as the reaction can be performed in ethereal solution alone with equal facility. In several cases this procedure proved to be advantageous, though the reaction must be run at lower refluxing temperatures. The preparation of (diethylamino)-diethylborane is given as an example of this alternate method of preparing organic substituted aminoboranes.

(Diethylamino)-diethylborane, $(C_2H_5)_2N-B(C_2H_5)_2$.—To a solution of 30.8 g. (0.2 mole) of dichloro-(diethylamino)-borane in 400 cc. of dry ether, 12 g. (0.5 mole) of magnesium was added. The mixture was stirred vigorously and a solution of 45.8 g. (0.42 mole) of ethyl bromide in 200 cc. of dry ether was dropped in at such a rate that the reaction mixture refluxed steadily. When the addition was completed, the contents of the flask were refluxed for another 3–4 hours. After filtration, the ether was removed and the residue distilled at normal pressure, yielding 22 g. (78%) of pure (diethylamino)-diethylborane, b.p. 154° (lit.[13] b.p. 161°).

Table II describes various tetrasubstituted aminoboranes which were prepared using the molar ratios and the techniques as cited above.

The reaction of (amino)-monochloroboranes with Grignard compounds proceeds very smoothly. It seems remarkable that explosions, which previously were observed while treating (amino)-dichloroboranes with Grignard reagents,[1] did not occur during the Grignard reaction with an (amino)-monochloroborane. Nevertheless, the yields of the tetraorgano substituted aminoboranes are relatively low (averaging 50–60%), possibly due to rearrangement reactions during the Grignard procedure. Both low and high boiling by-products containing boron and nitrogen could be isolated. But, though sharp boiling points were observed, the structure of these fractions, which contain about 20% of the boron content of the pertinent (amino)-monochloroborane, has not been successfully explained. There is evidence that, in addition to the reflux temperatures, the presence of "dimeric" (amino)-halogenoboranes and the concentration of the Grignard reagent influences the yields as well as the formation and character of the by-products. This comment also applies to the (amino)-dihalogenoboranes; such behavior should be investigated more completely and we are endeavoring to clarify the situation.

There are, however, other observations that deserve more detailed attention at the present time. During the purification of the (methylphenylamino)-methylphenylborane through distillation, white crystals appeared in the pure liquid. After filtration, some of the clear filtrate crystallized within seconds, and the crystals on the filter partially liquified. Molecular weight determinations were not influenced by such behavior; analyses of the products were identical. This characteristic appears likely to exclude "dimeric" structures. Likewise, distillation of (ethylphenylamino)-ethylphenylborane gave a product which partially crystallized even in the condenser. In this case, however, it was possible to retain a portion of the filtrate free of newly precipitated crystals for a short time, during which period an infrared spectrum was taken. A second run of the same sample showed slight but apparently characteristic differences in comparison with the first spectrum, indicating the appearance of a second species. The second spectrum, furthermore, was identical to those taken of the freshly distilled, unfiltered compound and of another specimen which had been allowed to stand for 6 hours, and of two additional samples which were stored for 24 and 48 hours, respectively. Analytical data including molecular weight determinations of all the samples were identical and within the indicated period of time there was no evidence of dimerization. None of these samples crystallized completely when allowed to stand at room temperature, though the crystalline part amounted to an estimated 90%. Attempts to wash out the liquid portion of the material and attempts to obtain pure crystals by recrystallization failed to produce the desired result. Autoxidation occurs very readily. B–N cleavage of the samples resulted only in ethylaniline as the nitrogen-containing component. Finally, on distillation of (*n*-butylmethylamino)-ethylphenylborane, the same gradual elevation of the b.p. was observed as during its preparation. After about half the substance had been distilled, it was possible to collect

[11] C. E. Erickson and F. C. Gunderloy, Jr., Abstr. of Papers, 136th A.C.S. Meeting, Sept. 13–18, 1959, Atlantic City, N. J., p. 54-N.

[12] B. M. Mikhailov and T. V. Kostroma, *C. A.*, **51**, 15441 (1957).

[13] E. Wiberg and P. Buchheit, according to J. Goubeau, FIAT Rev. German Sci., Vol. XXIII, 228.

TABLE II

TETRAORGANO SUBSTITUTED AMINOBORANES, $(R^1)(R^2)N\text{-}B(R^3)(R^4)$[a, b]

					Analyses, %			
Borane	M.p. or b.p. (mm.), °C.	Yield, %		Mol. wt.	B	N	C	H
(Diethylamino)-diethyl-	154	83	Calcd.	141.1	7.7	9.9	68.2	14.4
			Found	143	7.5	9.9	68.2	14.2
(Dimethylamino)-methylphenyl-	43 (2)	68	Calcd.	135.0	8.0	10.4	71.2	10.45
			Found	139	8.2	10.5	71.2	9.6
(Methylphenylamino)-methylphenyl-	98 (3)	64	Calcd.	209.1	5.2	6.7	80.4	7.7
			Found	203	5.3	6.9	80.2	7.8
(Diethylamino)-ethylphenyl-	98 (4)	59	Calcd.	189.1	5.7	7.4	76.2	10.65
			Found	183	5.9	7.4	76.1	10.6
(Ethylphenylamino)-ethylphenyl-	106–114 (3)	64	Calcd.	237.1	4.6	5.9	81.0	8.5
			Found	229	5.0	5.7	79.5	8.6
(Diethylamino)-diphenyl-[14]	B. 161 (11)	78	Calcd.	237.1	4.6	5.9	81.0	8.5
	M. 36–38		Found	229	4.6	5.8	80.8	8.6
(Diphenylamino)-diethyl-	B. 124 (6)	81	Calcd.	237.1	4.6	5.9	81.0	8.5
	M. 23–24		Found	228	4.4	5.8	80.6	8.2
(Piperidino)-diphenyl-[14]	B. 200–203 (14)	69	Calcd.	249.2	4.35	5.6	81.9	8.1
	M. 65–66		Found	248	4.5	5.7	81.3	8.0
(Piperidino)-methylphenyl-	75 (3)	49	Calcd.	187.1	5.8	7.5	77.0	9.7
			Found	187	5.8	7.5	77.1	9.7
(*n*-Butylmethylamino)-ethylphenyl-	73–89 (3)	51	Calcd.	203.1	5.3	6.9	76.8	10.9
	Stabilizing at 77 (3)		Found	199	5.3	6.8	76.8	11.0

[a] Molecular weights were determined cryoscopically in benzene on the freshly distilled compounds. [b] It will be noted that only in those cases where *cis–trans* isomerism is possible, do we have a boiling point range rather than a sharp b.p. Due to the apparently rapid interchange between molecular modifications, it is not possible to present numerical physical constants of both isomers. However, the existence of a boiling range and the continuing variance of vapor pressure characteristics of one modification *vis-a-vis* the apparent mixture due to interchange provides additional evidence supporting the presence of interconvertible *cis–trans* isomers.

some material boiling at 77°(3 mm.). On redistillation of this constant boiling material, the same gradual increase in the b.p. within identical limits was observed. Fractions were removed at various temperature levels, but they all gave identical analyses and spectra. Again, rupture of the B–N bond resulted in the recovery of one, and only one, secondary amine, identical to the starting material. An explanation of these phenomena is presented in the Discussion.

Discussion

The present investigation involves an attempt to analyze the experimental data as regards the nature of the B–N bond of aminoboranes and to investigate the influence of substituents on the basic structure $=N—B=$.

On the basis of the physical behavior of some aminoboranes, as described in the Experimental part, the observed phenomena may tentatively be attributed to a *cis–trans* isomerism in this particular boron–nitrogen system.

These various data are at hand: (a) among unsymmetrical tetraorgano substituted aminoboranes there exist two, and only two, different "modifications" of one single compound, showing differences in their physical behavior. (b) Molecular weight determinations and analyses confirm that the two different "modifications" have identical empirical formulas. (c) Rupture of the B–N bond in any case always produces the secondary amine, used as the starting material. (d) "Modification"–transformation, *i.e.*, equilibration, occurs very rapidly without addition of further energy at room temperature.

On the basis of the above cited data, certain conclusions can be drawn illustrating the existence of two isomers having identical empirical formulas. There are, however, three possible methods for obtaining two isomers of unsymmetrical tetraorgano substituted aminoboranes: (i) intermolecular disproportionation, (ii) intramolecular disproportionation, (iii) rotation about the B–N bond (*i.e.*, *cis–trans* isomerization).

Since the molecular weights of each fraction are identical, there cannot be intermolecular disproportionation except in those rare cases where the disproportionating groups have the same weight. This does not apply to the examples at hand.

Intramolecular disproportionation cannot occur except in two cases: (1) Exchange of one or more groups of the boron substituents with those on the nitrogen. This is not possible since only the original secondary amine was recovered. (2) Exchange in position of the B-attached group. This, however, would have the same effect as rotation about the B–N bond. Therefore, the spatial arrangement of the groups within the isomers would not be different from that obtained by rotation; the mechanism of isomer formation would be the only variation.

Since isomer equilibration occurs at room temperature without the application of additional energy and, since rotation about the B–N bond (excluding the existence of steric hindrance) requires little energy, the latter is the more probable mechanism. Furthermore, if extensive bond breaking did occur, it is almost certain that a degree of intermolecular disproportionation would occur with the formation of many isomers.

Therefore, since both types of disproportionation have been eliminated, only rotation about the B–N

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(14) B. M. Mikhailov and N. S. Fedotov, *C.A.*, **51**, 8675 (1957).

bond is left as an explanation of the existence of these isomers. Further, infrared investigations when analyzed in terms of the relative degree of electronegativity of the substituents tend to confirm the hypothesis of electron delocalization being the primary factor in explaining the appearance of double bond character in the B–N system and the resultant *cis–trans* isomerization.

In tetrasubstituted aminoboranes such as (ethylphenylamino)-ethylphenylborane, one isomer will have *trans* configuration, the other being the *cis* form. The very rapid rearrangement of either form into a mixture of both could be attributed to the presence of the electron structure III, as described in the Introduction. Since, in that structure, no double bond but rather a quasi ionic character is involved, its participation in the electronic equilibrium would be likely to be responsible for the nearly spontaneous isomerization. In the same way the diffuse boiling points of several of the aminoboranes might be explained as being due to the fact that the lower boiling *cis* and higher boiling *trans* form (or *vice versa*) are in equilibrium. The mixture shows a range of boiling points, but the first fractions may be overly enriched with one form. However, a very fast isomerization might occur, due to equilibration of the three electron structures, thus demonstrating the bond character of an aminoborane.

As in the case of the more symmetrical substituted aminoboranes,[1] the infrared spectra of the described compounds afford a means of determining the B–N bond absorption. Aminoboranes with one phenyl group attached to the boron reflect such absorption through the appearance of one of the strongest bands of the spectra in the 6.8 μ region. Apparently this indicates the attractive character of the B-attached phenyl ring for the free electron-pair of the nitrogen (and demonstrates the rather consistent double bond character of the B–N linkage), as earlier investigations[1] of the more symmetrical aminoboranes have shown a wider range for this particular absorption.

To demonstrate the sensitivity of the infrared spectra as a criterion of the bond character, some calculations of the boron–nitrogen stretching frequency and wave length were made using Gordy's rule.[15] The rule is stated in mathematical form by equation I

$$k = 1.67n[X_B X_N/d^2]^{0.75} + 0.30 \qquad \text{(I)}$$

These values of the variables were used to calculate the force constants: (a) bond orders, $n = 1, 2$ or 3; (b) electronegativity of boron, $X_B = 2.0$; electronegativity of nitrogen, $X_N = 3.0$; (c) bond distance of B–N, $d = 1.44$ Å. and $d = 1.36$ Å.

The values for the electronegativity were obtained by consulting Pauling's table of electronegativities.[16] The bond distance "*d*" has not been accurately measured for a boron–nitrogen double bond; therefore approximate experimental values or computed estimates were used for this parameter. A value of 1.44 Å. was assumed since this value was obtained experimentally for the boron–nitrogen distance in borazine.[4] If boron–nitrogen systems are analogous to carbon–carbon systems, this bond length is probably slightly exaggerated, just as the carbon–carbon distance in benzene is slightly longer than the ethylene carbon–carbon double bond. If Pauling's double bond atomic radii[17] are used to estimate the boron–nitrogen double bond, a value of 1.36 Å. is obtained. Both values were used in the computation.

The computed values of the force constants were substituted into the familiar equation II

$$\nu = \frac{1}{\lambda} = 1307\sqrt{\frac{k}{\mu}} \qquad \text{(II)}$$

in order to obtain the frequencies and wave lengths. In this equation ν is the frequency, λ the wave length and μ the reduced mass of boron and nitrogen atoms. Calculations were made for boron isotope 11 and nitrogen 14, since these isotopes are the most common. The wave length due to the stretching of the boron 10 and nitrogen 14 bond was calculated to be approximately 0.974 of the computed boron 11–nitrogen 14 wave length. The presence of nitrogen isotopes other than nitrogen 14 can be neglected. The results of these approximate calculations are found in Table III.

TABLE III

COMPUTED WAVE LENGTHS OF B–N STRETCH FREQUENCIES USING GORDY'S RULE

Bond order	Interatomic distance, Å.	λ, μ
1	1.44	9.6
2	1.44	6.8
2	1.36	6.56
2	1.20	6.0
3	1.27	
3	1.44	11.6

The wave lengths found for both bond distances $d = 1.44$ Å. and $d = 1.36$ Å. when $n = 2$ are close to a bond wave length which has been observed experimentally in the 6.8 μ region. This bond was assigned to the boron–nitrogen stretching frequency.

It is quite obvious that the weakness of this treatment lies in the lack of a fixed experimentally determined B–N bond distance for the compounds studied. A more subtle weakness could lie in the use of an empirical rule to draw theoretical conclusions about the nature of the B–N bond. Furthermore, Gordy[15] has defined the bond order used in his rule as "the effective number of covalent (electron pair) or electrovalent (ionic) bonds acting between two atoms." Hence, the agreement between experiment and theoretical results tells us only that two electron pairs have interacted in some way to form a bond. It does not tell us whether the bond is ionic or covalent.

In the absence of an accurate boron–nitrogen bond distance, it is necessary to examine the sensitivity of bond order to bond distance if any valid conclusions are to be drawn. To do this one must assume that the experimentally observed bands near 6.8 μ reflect the B–N stretching frequency. If one works backward from this band at 6.8 μ, which has been shown to be in close agreement with a calculated value, to compute the force constant, a

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(15) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(16) L. Pauling, "The Nature of the Chemical Bond," Table 11-3, Cornell Univ. Press, Ithaca, N. Y., 1946, p. 64.

(17) *Ibid.*, Table 21-2, p. 164.

value of 7. 7 dynes/cm. is found. Further substitution of this value into equation I provides an expression showing the variation of bond order "n" with bond distance "d." This expression is found to be

$$n = 1.16d^{1.5} \qquad \text{(III)}$$

From this equation, it is evident that the character of a B–N bond absorbing at 6.8 μ does not vary drastically with the bond distance. In order to obtain single or triple bond orders, *i.e.*, $n < 1.5$ or $n > 2.5$, it is necessary to have single bond lengths less than 1.18 Å. or triple bonds greater than 1.68 Å., respectively. Either case seems highly improbable, so one may assume that, if the bond at 6.8 μ indicates a stretching of boron–nitrogen, there must be a double bond involved.

In summation, the present investigation: (a) provides evidence corroborating a theory involving electronic shifts in the structures of aminoboranes, (b) contributes evidence for the assumption of double bond character and ethylene-like structures of this particular boron–nitrogen system, (c) describes an experimental procedure for the preparation of unsymmetrical tetraorgano substituted aminoboranes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY]

Radical-catalyzed Additions to α,β-Unsaturated Boronic Esters[1,2]

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Dibutyl ethyleneboronate, propene-2-boronate and 1-propene-1-boronate have been synthesized and their reactions with free radicals investigated. Bromotrichloromethane adds readily to the double bond of each of the three esters, carbon tetrachloride to the first two, and hexyl mercaptan to the only one tested, the first. The 1:1 adducts obtained represent the first general synthesis of aliphatic boronic esters (and their derivatives) containing other non-hydrocarbon functional groups. The first transfer constant in the reaction of dibutyl ethyleneboronate with carbon tetrachloride (calculated by means of a convenient new equation valid for dilute solutions) is $3.3\ (\pm 0.7) \times 10^{-3}$, which provides strong evidence that the intermediate radical is stabilized by carbon–boron π-bonding. Simple molecular orbital calculations with appropriately selected parameters for boron predict accurately the qualitative chemical and spectral behavior of the α,β-unsaturated boronic esters and acids.

Study of α,β-unsaturated organoboron compounds may furnish useful information on two types of problems: the synthesis of organoboron compounds which contain other functional groups, discussed immediately below, and the determination of the strength of carbon–boron π-bonding, discussed under Transfer Constants and Molecular Orbital Calculations.

The number of known organoboron compounds containing other functional groups is severely restricted because of the ease with which carbon–boron bonds are broken by bases, oxidizing agents or acids and because of the small number of methods for making carbon–boron bonds, which ordinarily require the use of a Grignard reagent or other conditions incompatible with most types of functional groups.[3] The introduction of other functional groups after a boronic acid group is already present is a well-known practice in the aromatic series,[3,4] and in the present work is extended to aliphatic compounds by starting with α,β-unsaturated boronic esters, readily synthesized from the recently available vinyl-type Grignard reagents.[5] The selection of ethyleneboronic acid and its dibutyl ester as the starting point was dictated by anticipated reactivity and experimental convenience. The double bond of previously known α,β-unsaturated boronic acids is made unreactive by the presence of a phenyl,[6] a chloro[7] or two methyl groups[8] at the β-position. Known α,β-unsaturated organoboron compounds in which the double bond should be highly reactive (and in which it shows some evidence of conjugation with the vacant *p*-orbital of the boron atom) include vinyldimethylboron, trivinylboron and several related compounds,[9] as well as vinylboron difluoride,[10] all of which require vacuum techniques for handling.

Ethyleneboronic acid,[11] $CH_2{=}CHB(OH)_2$, was

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(1) Preliminary Communication: D. S. Matteson, THIS JOURNAL, **81**, 5004 (1959).

(2) Supported in part by National Science Foundation Grant G 9916.

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(11) During the course of this investigation, similar preparation of all the α,β-unsaturated boronic acids and esters reported in the present article was announced without experimental details by H. Normant and J. Braun, *Compt. rend.*, **248**, 828 (1959); *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1397 (1959); *C. A.*, **54**, 1266 (1960).