Boron-Nitrogen Chemistry

An international symposium
Sponsored by U. S. Army Research
Office - Durham at Duke University,
Durham, N. C., April 23–25, 1963

Kurt Niedenzu, *Symposium Chairman*

ADVANCES IN CHEMISTRY SERIES **42**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D.C. 1964

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.fw001

Library of Congress Catalog Card 63-23167

PRINTED IN THE UNITED STATES OF AMERICA

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.fw001

Advances in Chemistry Series

Robert F. Gould, ***Editor***

AMERICAN CHEMICAL SOCIETY

APPLIED PUBLICATIONS

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

PREFACE

Research on boron-nitrogen compounds dates back to the early nineteenth century. Primarily, the inspired work of Alfred Stock provided the necessary impetus to activate this area of chemistry. His pupil, Egon Wiberg, developed the basic concepts of the more modern approaches, classifying boron-nitrogen derivatives into the three major groups of amine boranes, aminoboranes, and borazines according to the nature of the bond. Subsequently, however, investigation of the unique bonding situation in boron hydrides took precedence over other aspects of boron chemistry. Recently, interest in the chemistry of boron-nitrogen compounds has been rejuvenated, as is illustrated by the considerable increase in the number of publications in this area during the last few years. This resurgence of effort was based primarily on a reappraisal of Wiberg's concept of the isosterism between the C-C and B-N groupings. True, these two groups are not only isosteric, but also isoelectronic, and certain similarities of boron-nitrogen derivatives and corresponding hydrocarbons cannot be denied. But almost certainly analogies have been overemphasized and it seems at least somewhat premature to consider boron as an "organic" element. This also raises the more philosophical question as to whether or not dividing chemistry into various subdisciplines is still justified. In our time of rapid scientific advances we are faced with the paradox that even the specialist has to specialize further, while the burgeoning interest in interdisciplinary research requires the attention of scientists who appreciate the broad range point of view.

It is therefore encouraging to find among the papers of this symposium contributions from many subdisciplines of chemistry. Indeed, only a close collaboration of classical chemistry (with suitable modifications) and modern and advanced techniques will provide a desirable increase of our knowledge and understanding of science.

Since several years had passed since the rebirth of boron-nitrogen chemistry, the time appeared ripe for a general discussion of this area — hence this Symposium on Boron-Nitrogen Chemistry. The more important purposes of this symposium were to assemble the active workers in this area of science, to provide a forum for the presentation of most recent results, where new approaches would be predicted and future trends recognized, to promote personal contact among research workers in this area, and to discuss the general state of art in boron-nitrogen chemistry.

A brief look at the papers presented at the symposium illustrates two major advances in boron-nitrogen chemistry which have contributed much toward influencing the growth of research in this field. Since A. W. Laubengayer's synthesis of *B*-trichloroborazine (1955), the practice of using high vacuum techniques has been partially supplanted by more classical approaches, and the utilization of spectroscopy as a

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tool for explaining both structures and mechanisms has been stimulated by the investigations of J. Goubeau and his school. New instrumental methods — for instance, the applications of NMR spectroscopy — have been found extremely helpful in exploring former postulations. Advances in preparation are illustrated by the fact that ten years ago some two dozen substituted borazines were known, whereas today more than two hundred such compounds have been described in the literature. Incorporation of the B-N grouping in aromatic nuclei gave access to a whole new area of boron-nitrogen derivatives and the interest of the theoretician has been attracted by the evolution of new and exciting structures and reactions. It is obvious from reading the symposium papers that a fruitful collaboration is developing in the area of boron-nitrogen chemistry.

The symposium was supported by the U.S. Army Research Office-Durham, not only financially but also by active participation of various staff members in making the necessary arrangements. Many others have contributed to the realization of this symposium. Actually, the idea for it was born during a discussion between Professor Riley Schaeffer, Dr. John W. Dawson, Dr. George M. Wyman, and the writer. Later conversations with Dr. Lester P. Kuhn, Professor George E. Ryschkewitsch, and Professor Hermann J. Becher disclosed a growing interest in the organization of a meeting responsive to the purposes cited above. Also, the encouragement and willing cooperation of Professor Robert W. Parry are deeply appreciated. Finally, I would like to thank the Editor for agreeing to publish the symposium papers in Advances in Chemistry Series.

Kurt Niedenzu

U.S. Army Research Office-Durham
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Durham, N.C.

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In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Chemistry of Areneboronic Acids with Neighboring Amine Groups

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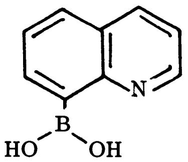
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch001

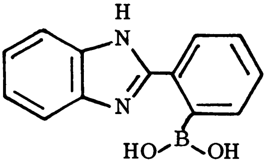
8-Quinolineboronic acid, 2-(2-boronophenyl)-benzimidazole, and 2-(2-boronobenzyl)benzimidazole were found to catalyze a reaction of chloroethanol with hydroxylic compounds (water or alcohols) in the presence of collidine. 2-(2-Pyridylethynyl)benzeneboronic acid, in which the borono and amine functional groups are farther separated than in these compounds, did not exhibit comparable activity; however, it underwent isomerization in chloroethanol to a substance which was an active catalyst. The unusual reactivity of these boron-nitrogen compounds is attributed to cooperation of the boronic acid and amine groups in acting on the hydroxylic substrates. Spectral data relevant to the structures of the compounds are presented and mechanistic pathways for the catalytic reactions are discussed.

A chemical phenomenon of considerable current interest is the enhancement in catalytic activity of certain functional groups which results when the groups are suitably oriented with respect to one another within a given molecule. In considering this chemistry it occurred to us that compounds possessing neighboring boronic acid and amine groups should provide a novel and interesting system for observation of a cooperative functional group effect. Such substances would possess basic and acidic sites capable of functioning in a concerted fashion. In addition, the boronic acid group, as a consequence of its facile esterification and exchange reactions, could serve as a binding site for alcoholic substrates. With this rational we undertook a study of 8-quinolineboronic acid (I), 2-(2-boronophenyl)benzimidazole (II), 2-(2-boronobenzyl)benzimidazole (III), and 2-(2-pyridylethynyl)-benzeneboronic acid (IV). The present paper summarizes information on the preparative methods employed, the spectral properties pertaining to the nature of the boron-nitrogen interactions, and the chemical reactions found to depend upon the proximity of the boronic acid and amine groups.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.



I



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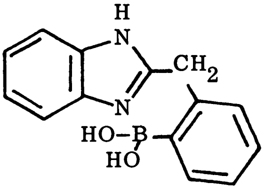

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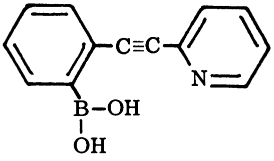
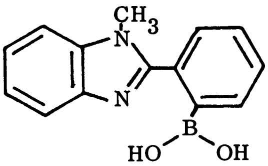


IV

Preparative Methods

8-Quinolineboronic acid (I) *(5)* and 2-(2-pyridylethynyl)benzeneboronic acid (IV) *(13)* were prepared from 8-bromoquinoline and 2-(2-pyridylethynyl)bromobenzene, respectively, by successive treatment with butyllithium (-70° C.), butyl borate, and water. Both compounds are amphoteric solids, soluble in dilute alkali and dilute acid but only very slightly soluble in water. They were characterized by oxidation by hydrogen peroxide and by preparation of solid derivatives with hydrogen chloride, *o*-phenylenediamine, and alcohols.

2-(2-Boronophenyl)benzimidazole (II) and 2-(2-boronobenzyl)-benzimidazole (III) were obtained conveniently by passing a stream of boron chloride into liquid 2-phenylbenzimidazole and 2-benzylbenzimidazole at about 300° and subsequently hydrolyzing the product *(8)*. This procedure failed when extended to 2-β-phenylethylbenzimidazole; however, it was employed successfully to introduce boron into 2-α-naphthylbenzimidazole. The benzimidazole-boron compounds are white solids which do not melt below 300° C. They were best characterized by conversion to catechol ester derivatives, which precipitated as sharp melting crystalline solids in essentially quantitative yield when alcoholic solutions of the boronic acids were added to a solution of catechol in alcohol. The position of boronation was demonstrated by conversion of the boronic acids to the corresponding phenols by oxidation with hydrogen peroxide in strongly acidic solution. Both II and III yielded a relatively insoluble complex when treated with a dilute solution of hydrogen peroxide in alcohol. As further confirmation of structure, II was converted by methylation to V, a substance which was synthesized independently from *N*-methyl-2-(2-lithiophenyl)-benzimidazole.



V

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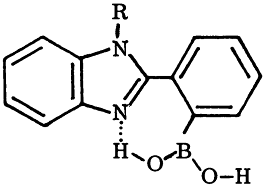
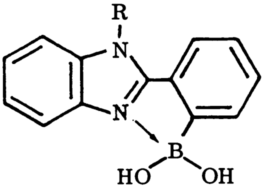
Spectral Properties and Interpretation

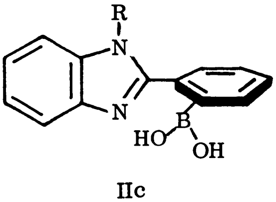
The minimum distances between boron and nitrogen in compounds I to IV, estimated from the normal bond angles and bond lengths found in heterocyclic compounds and boric acid and assuming no distortion resulting from interaction between boron and nitrogen, are 2.9, 2.7, 1.2, and 4.8 A., respectively. On this basis, the molecular geometry of III appears very favorable for the formation of a dative bond between boron and nitrogen, and the distance between boron and nitrogen in IV is clearly too great for direct coordination. Intramolecular boron-nitrogen bonding in I would not be expected, since the angle strain necessary to bring the atoms within bonding distance would be large. In this case, however, the hydroxyl group is well situated for nitrogen-hydrogen interaction. A prediction of the bonding at nitrogen in II (or V) is less clear. The geometry appears suitable for either nitrogen-hydrogen bonding (IIa) or for boron-nitrogen bonding (IIb, the angle strain in forming the five-membered ring should not be large). Furthermore, an open form (IIc) in which there is no intramolecular attraction between the boronic acid and amine functional groups is a possibility.



IIa



IIb

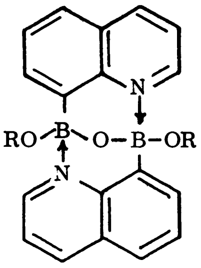


IIc

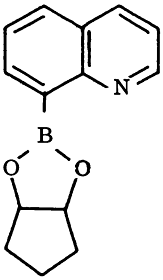
Evidence bearing on the actual structures of compounds I to IV was obtained from the infrared and ultraviolet spectra of these compounds and their derivatives. As one criterion for occurrence of a boron-nitrogen dative bond we used the appearance of a band between 8.35 and 8.56 microns, in conjunction with the absence of strong absorption between 7.2 and 7.6 microns. The justification is that a variety of amine complexes of boronic and borinic acid derivatives show a band between 8.35 and 8.65 microns which is considerably more intense than any found in the same region of the spectrum of the components of the complex. Furthermore, for a broader range of compounds known to possess boron-nitrogen dative bonds, Greenwood and Wade (4) have reported a band between 8.0 and 9.1 microns which seems to be associated with a stretching vibration of the boron-nitrogen bond.

With respect to the bands between 7.2 and 7.6 microns, it has been found that boronic acids and their tricovalent derivatives generally exhibit very strong absorption in this region. The absence of such bands in the spectrum of a B-O compound is indicative that the boron is tetracoordinated *(1, 7)*.

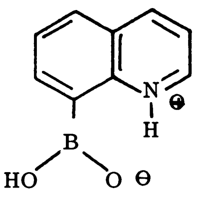
8-Quinolineboronic Acid. In spite of the fact that the geometry of 8-quinolineboronic acid is unfavorable for intramolecular boron-nitrogen bonding, the infrared spectrum of I, taken with the sample in a potassium bromide pellet, is characteristic of a tetracoordinated boron compound with a boron-nitrogen bond (relatively weak absorption in the 7.2-to 7.6-micron region; a band at 8.6 microns). We therefore conclude that 8-quinolineboronic acid in the solid state is probably associated and has tetracoordinated boron. Crystalline esters (VI, R = $n\text{-}C_4H_9$; $ClCH_2CH_2$) are known *(11)* in which boron from one molecule of the acid appears to be coordinated with nitrogen from another. On the other hand, 8-quinolineboronic acid forms a simple, cyclic ester (VII) *(11)* with *cis*-1,2-cyclopentanediol. This ester (sample in either chloroform or potassium bromide) absorbs strongly between 7.2 and 7.6 microns and very weakly between 8.35 and 8.65 microns; therefore the boron in VII is probably tricovalent, as expected for a monomolecular species in which intramolecular boron-nitrogen bonding is not feasible.



VI



VII



Ia

Since a basic nitrogen in 8-quinolineboronic acid is well situated for interaction with the O-H group joined to boron, a significant fraction of the molecules in solution might exist in the zwitterionic form (Ia). As a means of assessing the importance of this structure, the ultraviolet spectrum of 8-quinolineboronic acid was examined in 95% alcohol and also in an alcohol solution which was $0.1M$ in hydrochloric acid *(11)*. The spectrum of the neutral solution contained peaks at 318 mμ (log E 3.64), 304 mμ (log E 3.69), and 278 mμ (log E 3.74); on addition of acid a major peak developed at 318 mμ (log E 3.94), a shoulder appeared at 310 mμ (log E 3.90), and the broad maximum centered at 278 mμ for the neutral solution disappeared entirely. The spectra were essentially the same in dimethylformamide solutions (λ_{max} the same, log E somewhat greater). These changes parallel closely the spectral changes observed for quinoline. It may therefore be concluded that in solutions of 8-quinolineboronic acid in ethanol and in dimethylformamide the covalent bonding state of nitrogen is much

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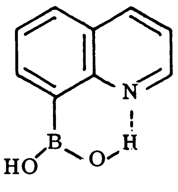
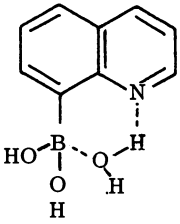
like that in quinoline — i.e., the population of ionic species such as Ia is low.

The ultraviolet spectral data do not, of course, exclude hydrogen bonded structures of type Ib or Ic. Indeed, from work described later it appears likely that esters of 8-quinolineboronic acid posses unique

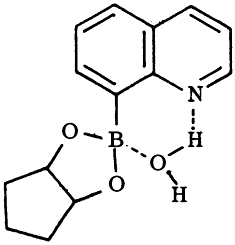


Ib



Ic

reactivity with respect to water. Direct physical evidence for interaction of water with an ester of 8-quinolineboronic acid was obtained by observing the infrared absorption of water in carbon tetrachloride solution *(11)*. The stretching vibrations of water are manifested by a strong band at 2690 mμ and a weak shoulder at 2750 mμ *(12)*. This spectrum was not altered detectably when a mixture of pyridine and the *cis*-1,2-cyclopentanediol ester of benzeneboronic acid (each at 3×10^{-3} *M*) was added to the solution. On the other hand, a pronounced change in the spectrum occurred when a solution of water in carbon tetrachloride was made 3×10^{-3} *M* in the *cis*-1,2-cyclopentanediol ester of 8-quinolineboronic acid; the intensity of the band at 2690 mμ decreased and that of the shoulder at 2750 mμ increased to the point where both bands were of equal intensity. An attractive explanation is that the spectral changes resulted from binding of water to the ester, as in VIIa. The high activity of the ester of 8-quinolineboronic acid relative to the benzeneboronate-pyridine combination may be attributed to the favorable geometrical relationship of boron and nitrogen in the quinolineboronate.



VIIa

Benzimidazole Derivatives *(8)*. Since compound III and the ester derivatives of II, III, and V absorb weakly in the 7.2- to 7.8-micron region, it may be concluded that boron is tetracoordinated in these compounds. The data from this region are less decisive for the boronic acids, II and V, which exhibit several bands of moderate intensity between 7.2 and 7.8 microns; however, in agreement with the structures involving boron-nitrogen coordination (such as IIb), these compounds and their ester derivatives do have a strong absorption band near 8.5 microns. The very broad, intense band in the range 3.4 to 4 microns, which is characteristic of benzimidazoles and seems to be related to the extent of intermolecular hydrogen bonding, is markedly altered in the spectra of the benzimidazoles which have boron in the neighborhood of nitrogen. The absorption is much reduced, as would be expected if the extent of intermolecular hydrogen bonding were reduced by competition from boron for the electron pair on nitrogen.

Ultraviolet spectral data relevant to the structural problem of the boronoarylbenzimidazoles are shown in Figures 1, 2, and 3. In interpreting these spectra it is helpful to consider the spectra of some related benzimidazoles. Thus, whereas benzimidazole (λ_{max} 272 mμ, log E 3.74; 279 mμ, log E 3.80) is transparent above 290 mμ, 2-phenylbenzimidazole absorbs strongly at 303 mμ (log E 4.37) and 315 mμ (shoulder, log E 4.15). The enhanced absorption of 2-phenylbenzimidazole at the longer wavelengths may be attributed to resonance involving the benzimidazole and phenyl rings. *o*-Substituents which increase the dihedral angle formed by the planes of the aromatic rings diminish the intensity of absorption and cause a marked shift in the maximum to lower wavelengths — for example, the spectra of 2-(2-tolyl)benzimidazole and 2-(2-bromophenyl)benzimidazole (λ_{max} 277 mμ, log E 4.00; 283 mμ, log E 4.00) are very similar to that of benzimidazole. Since $-B(OH)_2$ is a relatively large substituent, one would expect the spectra of II and V to resemble those of 2-tolyl- and 2-bromophenylbenzimidazole if steric effects alone were operative — that is, if the boronic acids had structure IIc. In fact, however, II and

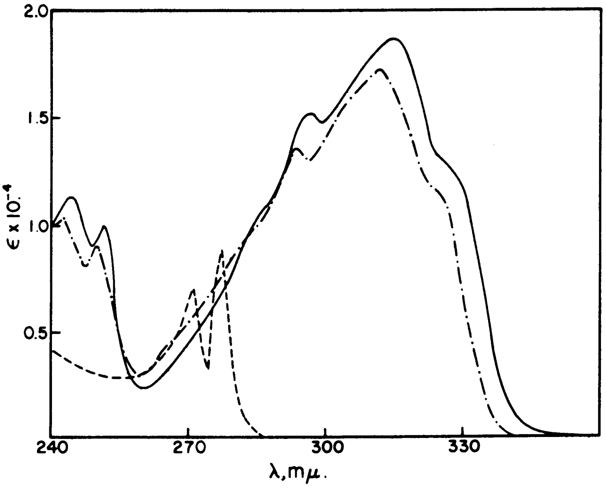


Figure 1. Ultraviolet absorption spectra in 95% ethanol

-·-·-·- *2-(2-Boronophenyl)benzimidazole*
——— *1-Methyl-2(2-boronophenyl)-benzimidazole*
------ *2-(2-boronobenzyl)benzimidazole*

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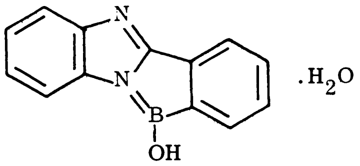
V absorb strongly in the region near 310 mμ (Figure 1). This feature is explicable on the basis that, as a consequence of boron-nitrogen coordination (as in IIb) or BOH-N bonding (as in IIa), the phenyl and benzimidazole rings in I and V are held in a sufficiently coplanar position to permit appreciable conjugation. An alternative explanation considered for compound II is that the bathochromic shift, relative to *o*-methylphenylbenzimidazole, resulted from an unsaturated, heterocyclic chromophore such as that in IId. Absorption at relatively long wavelength for a variety of unsaturated boron-nitrogen compounds has been ascribed by Dewar to the aromatic character of the boron-nitrogen heterocyclic system. This explanation is untenable here, however, since the spectra of II and VII are very similar, indicative of similar structures, yet the *N*-methyl derivative cannot form an aromatic compound analogous to IId. The spectrum of boronobenzylbenzimidazole (III) is typical of a simple benzimidazole (Figure 1). In this case, of course, the methylene group prevents conjugative interaction of the phenyl and benzimidazole rings.



IId

The spectral shifts observed when acid and base are added to solutions of II and V permit a decision between structures with boron-nitrogen coordination and BOH-N bonding. With the *N*-methyl derivative (V) the absorption maximum shifts to lower wavelengths when

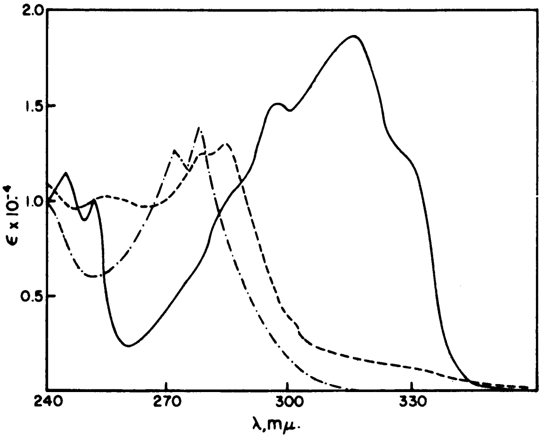


Figure 2. Ultraviolet absorption spectra of 1-methyl-2-(2-boronophenyl)-benzimidazole in 95% ethanol

——— *No added acid or base*
-·-·-·- *3 × 10^{-3}M in HCl*
------- *3 × 10^{-3}M in NaOH*

either acid or base is added (Figure 2); with the *N*-hydrogen analog (II) a similar shift occurs in acidic solution but the maximum is not appreciably altered when the neutral solution is made basic (Figure 3).

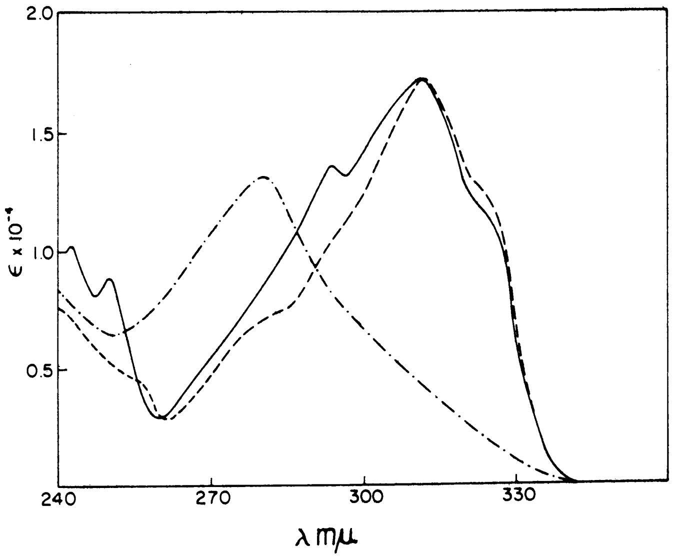
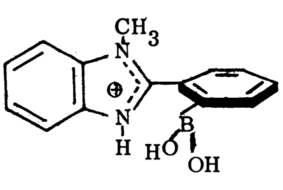


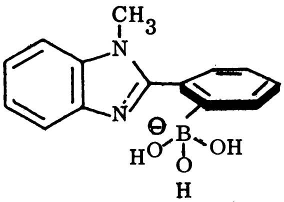
Figure 3. Ultraviolet absorption spectra of 2-(2-boronophenyl)benzimidazole in 95% ethanol

———	*No added acid or base*
-·-·-	*3 × 10^{-3} M in HCl*
-----	*3 × 10^{-3} M in NaOH*

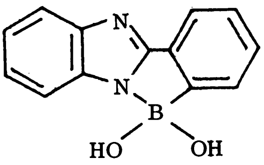
These facts are readily understood if boron-nitrogen bonding is responsible for maintaining the aromatic rings in the same plane. Both acid and base could cleave the bond between boron and nitrogen in V, giving Va and Vb, respectively, thereby permitting the rings to twist out of a plane. Compound II should behave analogously in acidic solution; but in alkaline solution an alternate mode of ionization, involving removal of hydrogen from nitrogen rather than addition of hydroxide to boron, is available (IIe). Ionization by this path would not disrupt the resonance interaction of the aromatic rings. On the other hand, the data are not well accommodated by structures in which coplanarity is achieved as a result of BOH-N bonding. In this case there is no satisfactory explanation for the difference in the response of II and V to the addition of alkali.



Va



Vb



IIe

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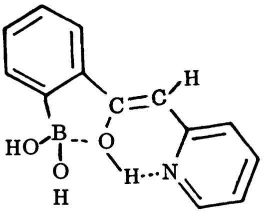
2-(2-Pyridylethynyl)benzeneboronic Acid *(3)*. The infrared spectrum of 2-(2-pyridylethynyl)benzeneboronic acid (IV) has a dominant absorption band at 7.25 microns, typical of a simple areneboronic acid. This evidence confirms the expectation that nitrogen is too far removed from boron to coordinate with it or to facilitate coordination by oxygen compounds.

When compound IV was heated in chloroethanol or in wet dimethylformamide which contained salicylic acid, it underwent a transformation involving addition of O-H to the carbon-carbon triple bond *(10)*. On mild hydrolysis, compound VIII was obtained. The structure assigned to VIII rests on analytical data, cleavage to 2-phenacylpyridine, preparation of crystalline derivatives with catechol and semicarbazide, and spectral data. Pertinent spectral features include the absence of a band near 4.5 microns (found in IV and its derivatives), the absence of absorption between 5 and 6 microns (the carbonyl region), a strong band at 6.2 microns (6.1 microns in the catechol ester derivative) attributable to a carbon-carbon double bond or an unusual carbonyl group, the absence of strong absorption between 7 and 8 microns, and the absence of strong bands in the 8.2- to 8.7-micron region. The last two observations are indicative that the boron is tetracoordinated and that boron-nitrogen coordination bonds are absent. In addition, compound VII is yellow (λ_{max}^{DMF} 383 mμ, log E 4.03). The yellow color of samples of 2-phenacylpyridine has been attributed to the presence of an enol tautomer *(2)*.



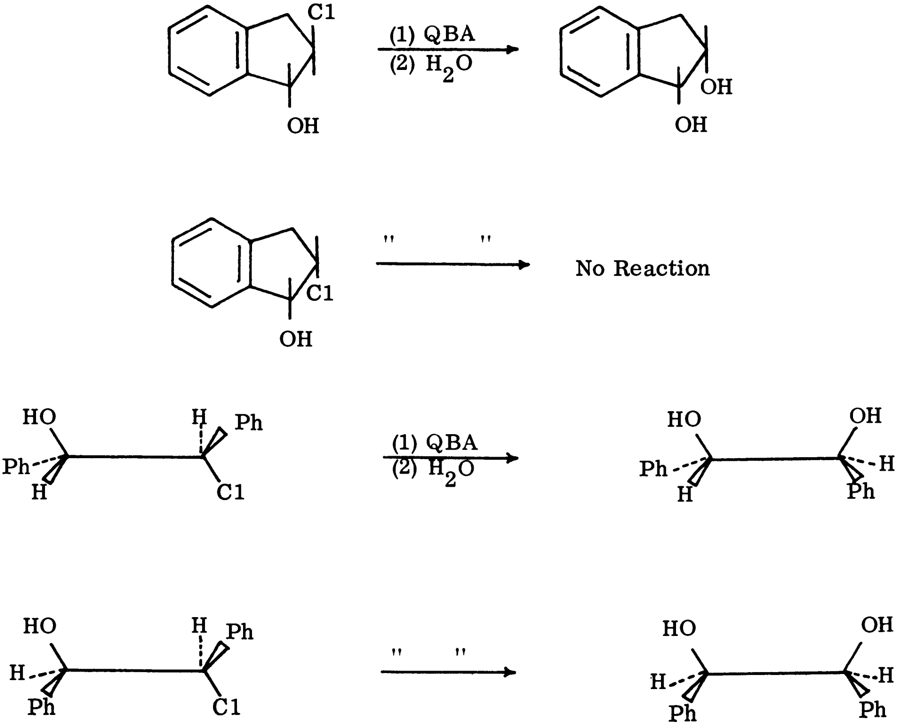
VIII

Chemical Reactivity

8-Quinolineboronic Acid. The rate of reaction of the boron-nitrogen compounds with chloroalcohols, judged by the rate of appearance of chloride ion, was employed as a probe for cooperative action of the neighboring boronic acid and amine groups. Chloroalcohols appeared attractive for this purpose, since they contain two functional groups (hydroxyl and alkyl halide), each of which is capable of reacting with one of the functional groups of the boron-nitrogen compound.

In the initial series of experiments *(5)*, equimolar amounts of chloroethanol and either 8-quinolineboronic acid or a mixture of benzeneboronic acid and quinoline were heated together in dimethylformamide solution at 90.0°. The rate of liberation of chloride ion was obtained by periodic sampling and titration for chloride by the Volhard method. The significant feature of these experiments is that 8-quinolineboronic acid reacted with chloroethanol much more rapidly (initial rate factor approximately 80) than did benzeneboronic acid and quinoline, a combination possessing the same functional groups as 8-quinolineboronic acid but located in separate molecules. 8-Quinolineboronic acid did not, however, exhibit enhanced activity toward a mixture of chloropentane and 1-butanol. It therefore appears that proper geometrical disposition of the pairs of function groups involved, boronic acid and amine on the one hand and hydroxyl and alkyl halide on the other, is essential for rapid formation of chloride ion under these conditions.

This conclusion was supported by studies with other haloalcohols. 8-Quinolineboronic acid accelerated the rate of reaction of 3-chloro-1-propanol and 4-chloro-1-butanol but did not influence the rate of reaction of 6-chloro-1-hexanol. Presumably the halide and alcoholic groups in the hexanol were too far separated. Of most interest were the displacement reactions which occurred with the pairs of stereisomeric alcohols, *cis*- and *trans*-2-chloro-1-indanol and *erythro*- and *threo*-2-chloro-1,2-diphenylethanol *(9)*. *trans*-2-Chloro-1-indanol and *erythro*-2-chloro-1,2-diphenylethanol were converted to boronate ester hydrochlorides, which on mild hydrolysis and addition of base afforded in high yield *cis*-1,2-indandiol and *dl*-hydrobenzoin, respectively. Under the same conditions benzeneboronic acid had no effect on these alcohols. 8-Quinolineboronic acid did not cause chloride ion to be liberated from *cis*-2-chloro-1-indanol, and its reaction with *threo*-2-chloro-1-indanol was very slow, affording a low yield of meso-hydrobenzoin. The reaction of 8-quinolineboronic acid with these chloroalcohols was therefore stereospecific and involved direct displacement of chloride from carbon by an oxygen function.



Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch001

Borate esters are known to undergo alcohol exchange reactions readily. It therefore appeared possible that the boron-nitrogen compounds might serve as catalysts for hydrolysis of chloroalcohols if a base were incorporated in the mixture to take up protons and thereby keep the boron-nitrogen compound in the active, basic state. Collidine (2,4,6-trimethylpyridine) was selected as a transfer base, since it is a stronger base than 8-quinolineboronic acid yet it does not directly influence the rate of chloride ion formation from chloroethanol. Experiments with wet dimethylformamide solutions which were 0.80*M* in chloroethanol, 0.86*M* in collidine, and 0.08*M* in 8-quinolineboronic acid indeed reveal catalytic activity of 8-quinolineboronic acid *(6)*. The rate of chloride ion formation was found to be several times greater in the mixture containing 8-quinolineboronic acid than in the control which did not contain 8-quinolineboronic acid, and the higher rate was maintained even after the number of moles of chloride ion produced exceed the moles of boronic acid by a factor of 4. Therefore, the quinolineboronic acid must have "turned over" in the system. On following the reaction by titration for glycol (with periodic acid) it was found that ethylene glycol was a major product of the catalytic reaction but that ethylene glycol was not formed in measurable amount in the noncatalytic control reaction. These data indicate that two independent reactions take place: (1) a solvolysis which is not influenced by 8-quinolineboronic acid and yields chloride ion but no ethylene glycol and (2) a specific hydrolysis, the rate of which is increased enormously by 8-quinolineboronic acid. An interesting feature of the catalysis is that OH of water rather than OH of the chloroalcohol served as the nucleophile, even though the concentration of the alcohol was relatively high.

$$HOCH_2CH_2Cl \xrightarrow{DMF} Cl^- + \text{nonglycol products} \qquad (1)$$

$$HOCH_2CH_2Cl + H_2O + C_8H_{11}N \xrightarrow[DMF]{QBA\ (cat.)} \qquad (2)$$

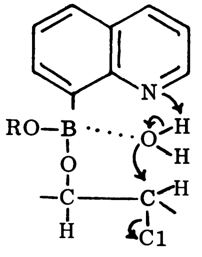
$$HO(CH_2)_2OH + C_8H_{11}N\cdot HCl$$

Although water was one of the components of the reaction, a large excess of water actually inhibited the reaction. In contrast, a large excess of water increased the rate of the noncatalyzed solvolysis reaction. Ethylene glycol also proved to be an inhibitor of the catalytic reaction. When present in the same concentration as chloroethanol, it reduced the rate of reaction by a factor of 2.7. Even more effective was *cis*-1,2-cyclopentanediol, which forms a relatively stable ester with 8-quinolineboronic acid. At a concentration equal to that of the boronic acid (0.08*M*) this diol stopped the catalytic reaction completely.

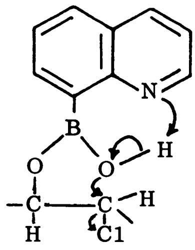
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch001

The catalytic hydrolysis of chloroethanol effected by 8-quinolineboronic acid must involve esterification of the bononic acid, displacement of chloride ion from the chloroalkyl group of the ester, transfer of a proton to the base collidine, and ester interchange, which affords more of the active chloroalkyl ester of 8-quinolineboronic acid. In support of this view, 8-quinolineboronic acid is known to form esters with chloroethanol and 3-chloro-1-propanol *(7)*. Direct involvement of a chloroalkyl ester in the catalytic reaction is indicated by the fact that both water and 1,2-diols inhibit the hydrolysis of chloroethanol. These substances would reduce the concentration of the chloroethyl ester, water by hydrolysis of the ester to the boronic acid and the diols by ester interchange to produce the more stable cyclic esters. The necessity for a suitably oriented basic atom near the boronic acid groups is demonstrated by the fact that neither benzeneboronic acid nor mixtures of benzeneboronic acid and quinoline duplicate the activity of 8-quinolineboronic acid. Furthermore, the requirement of a transfer base for catalytic activity shows that the nitrogen in quinolineboronic acid must be in the basic rather than the protonated form for activity in the hydrolytic reaction.

The key step in the sequence is that in which the carbon-halogen bond is broken. The experiments with the stereoisomeric chloroalcohols show that oxygen displaces chloride from carbon with inversion of configuration. This result can be accommodated by intermediate A or B.



A



B

In these formulations boron assists in activation of water (or OH) and also serves as a binding site in bringing the chloroalcohol and water into a favorable position for reaction. Nitrogen functions as a base in activating water (or OH).

Arylbenzimidazoleboronic Acids. In contrast to 8-quinolineboronic acid, the arylbenzimidazoleboronic acids (II and III) possess boron and nitrogen atoms favorably positioned for direct coordination. Indeed, the spectral data previously presented provide strong evidence for such coordination. It was therefore of interest to see whether these compounds would exhibit chemical and catalytic properties of the type found for 8-quinolineboronic acid.

Since compounds II and III were not appreciably soluble in dimethylformamide, the reactions were carried out in a mixture of chloroethanol and 1-butanol. For this, the boron compound and a five- to tenfold excess of collidine were dissolved in 5 ml. of 1-butanol at 89°, and at zero time sufficient prewarmed chloroethanol was added to bring the volume to 10 ml. The rate of formation of chloride ion in the solution was determined by titration of 1-ml. aliquots. Data for a series of reactions involving II, III, and, for comparison, 8-quinolineboronic acid, are recorded in Figure 4.

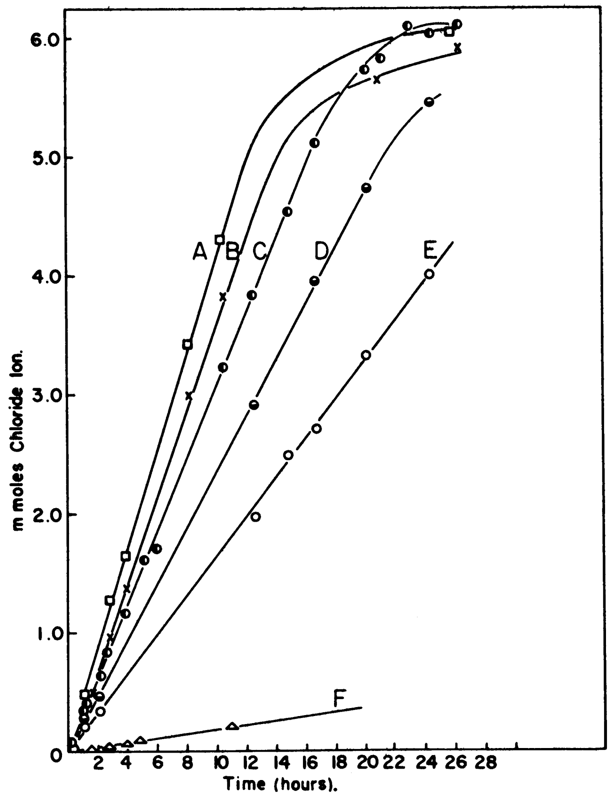


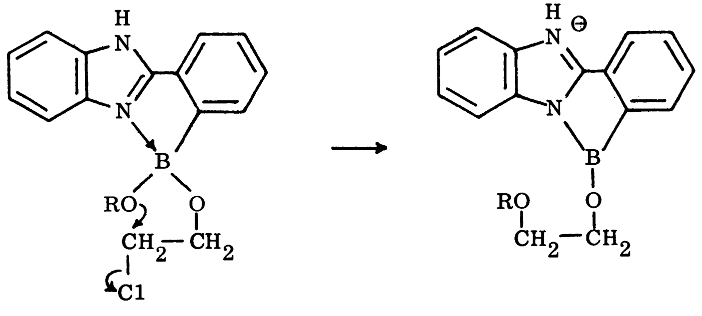
Figure 4. Chloride ion formation at 89° from chloroethanol in butanol. Solutions contained 5.00 mmoles of collidine

A. 1.03 mmoles of 8-quinolineboronic acid
B. 0.82 mmole of 2-(2-boronobenzyl)benzimidazole
C, D, E. 1.00, 0.75, 0.50 mmole, respectively, of 2-(2-boronophenyl)benzimidazole
F. No added boron compound

As shown by comparison of Reactions A to E with the control reaction, F, which contained only collidine as a base, the boron-nitrogen compounds did exert a profound effect upon the rate of chloride ion formation in this system. In each case (A to E) the extent of conversion to chloride ion was a linear function of time until essentially all collidine had been converted to hydrochloride. Over the range investigated (0.05*M* to 0.10*M* in boronophenylbenzimidazole) the rate was proportional to the concentration of the boron compound. Clearly the boronoarylbenzimidazoles were functioning catalytically in these reactions. Moreover, it was found in other control reactions that benzeneboronic acid did not accelerate the reaction of chloroethanol with 2-phenylbenzimidazole. Therefore, with the boronoarylbenzimidazoles as with 8-quinolineboronic acid, special activity of the boronic acid and amine groups must have derived from the proximity of these groups in a given molecule.

On titrating the products of the reactions for glycol it was found that the boronarylbenzimidazoles and 8-quinolineboronic acid differed in their mode of reaction. 8-Quinolineboronic acid showed a marked preference for water as compared to an alcohol as a nucleophilic substrate, even though the molar concentration of alcohol exceeded that of water by a factor of 10. In contrast, boronophenylbenzimidazole exhibited little if any selectivity with respect to water; yields of ethylene glycol were very low even when considerable water was present in the system. The chief product of the reaction of chloroethanol with boronophenylbenzimidazole appeared to be 2-butoxyethanol (61% yield by vapor phase chromatographic analysis, 21% isolated by extraction and distillation).

We suggest that ether formation may proceed by way of intermediate C. The boron group would bring the alcoholic substrates into position for reaction while nitrogen would impart nucleophilic character to oxygen in the ester linkages by virtue of coordination with boron. In the catalytic system, reaction of the product, D, with collidine and solvent would regenerate C.



C D

2-(2-Pyridylethynyl)benzeneboronic Acid *(13)*. The reaction of 2-(2-pyridylethynyl)benzeneboronic acid (IV) with chloroethanol, carried out under the conditions employed with boronophenylbenzimidazole(II), followed a different course. In this case no chloride ion was liberated during the first 10 minutes of reaction. A slow reaction set in after about half an hour and the rate gradually increased over a 4-hour period; thereafter the reaction proceeded at a uniform rate, comparable to that for compound III. This behavior suggested that the original boron-nitrogen compound was inactive or of low reactivity and that it had been transformed to a catalytically active one. In agreement with this conclusion, a new boron-nitrogen compound, assigned structure VIII (see section on spectra), was isolated from the reaction products. When this substance was added to a chloroethanol-butanol-collidine system, chloride ion was liberated at a uniform rate without an induction period and the rate constant was very close to that for the maximum rate of the reaction involving compound IV. Ethylene glycol was not formed in more than trace amounts.

These results are consistent with the view that the boron and nitrogen groups in IV are too distant for cooperative or synergetic activity. Boron and nitrogen are also relatively far removed from each other in VIII; however, in this case the basic activity of the nitrogen can be transferred to boron via an intervening O-H group.

Summary

Compounds I, II, III, and VIII were found to catalyze the release of chloride ion from chloroethanol in solvents containing collidine. Of these, 8-quinolineboronic acid was unique in that it induced hydrolysis of chloroethanol to ethylene glycol when water was present in the system in low concentration, even though the mole ratio of HOH to ROH was low. Studies with stereoisomeric chloroalcohols revealed that the reaction was stereospecific and that the substitution of chlorine by oxygen occurred with inversion of configuration. Compounds II, III, and VIII did not show selectivity toward water in these reactions; chloroethanol was converted largely to ether derivatives rather than to ethylene glycol.

It is suggested that the activity of compounds I, II, III and VII, as compared to a mixture of benzeneboronic acid and quinoline or to compound IV, in displacing chloride from chloroethanol depends upon a synergetic action of the boronic acid and amine functional groups. The data are consistent with the concept that reaction proceeds in each case through a state in which negative charge accumulated on an oxygen joined to boron. This charge may be induced by coordination of nitrogen with boron (compounds II and III) or by attack or nitrogen on hydrogen bound to the oxygen (compounds I and VIII). Boron is considered to act as a binding site, which orients the substrates favorably, as well as an acid site. The selective character of 8-quinolineboronic acid for water may be rationalized on the basis that the geometry of this molecule is particularly well suited for binding and activating water.

In agreement with these views, spectral data point to boron-nitrogen coordination in II and III and to coordination of boron to four oxygen atoms in compound VIII. Spectral evidence for unusual activity of water toward an ester of 8-quinolineboronic acid was also found.

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch001

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Received May 10, 1963. Work supported by the National Science Foundation.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch001

2

Reactions of Triphenylphosphinimines with Boron Compounds, Certain Organometals, and Lewis Acids

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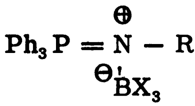
When triphenylphosphinalkylimines reacted with BF_3, BPh_3, Me_2SnCl_2, and Ph_2SnCl_2, a new class of complexes containing a B-N or Sn-N bond was obtained. The boron complexes have the general structure



$$\mathrm{Ph_3P} = \underset{\overset{|}{{}^{\ominus}\mathrm{BX_3}}}{\overset{\oplus}{\mathrm{N}}} - \mathrm{R},$$

where $X = F$ and Ph; $R = Me$, Et, iso-Pr, and *tert*-Bu. Their stability depended upon R. The composition of the corresponding Sn compounds corresponded to a 1 to 1 addition complex. The exact structure of these compounds is still under investigation.

Recently Zimmer and Singh reported on the R'X addition to triphenylphosphinalkylimines *(2)*. This reaction proceeded according to the following scheme:

$$[\mathrm{Ph_3P{=}N{-}R} \longleftrightarrow \mathrm{Ph_3\overset{\oplus}{P}{-}\overset{\ominus}{N}{-}R}] + \mathrm{R'X} \longrightarrow [\mathrm{Ph_3P{-}NRR'}]^{\oplus}\mathrm{X}^{\ominus}$$

where R'=Me and Et; R=Me, Et, *n* -Pr, iso-Pr, iso-Bu, and *tert*-Bu

In all other cases investigated (R' =*n*-Pr, iso-Pr, and *tert*-Bu) an elimination reaction occurred and alkylaminotriphenylphosphonium salts were obtained:

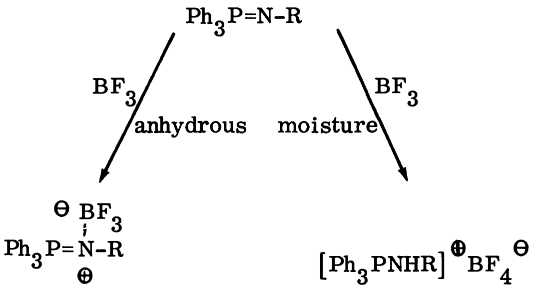
$$[\mathrm{Ph_3P{-}NRH}]^{\oplus}\mathrm{X}^{\ominus}$$

This reaction pointed to the fact that these triphenylphosphinalkylimines are strongly basic in nature. As a consequence a program was initiated to investigate their reactivity toward different Lewis acids.

The results obtained so far are reported here. While this work was in progress, a paper *(1)* appeared in which the preparation and some reactions with BF_3 and BPh_3 of the parent compound, $Ph_3P{=}NH$, were reported. These results are in agreement with our findings.

Reactions with BF_3 and BPh_3

These reactions involving BF_3 and BPh_3 are extremely sensitive toward moisture. In the case of BF_3 the reaction proceeded as follows:

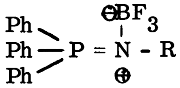


A

B

The compounds prepared are compiled in Tables I and II.

TABLE I. **Triphenylphos-**

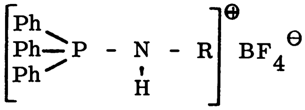
R	*M. P.,*[a] *°C.*	*Yield, %*	 $Ph_3P^{\oplus}=N(\overset{\ominus}{B}F_3)-R$ *Formula*
CH_3	224-26[b]	100	$C_{19}H_{18}BF_3NP$
C_2H_5	242-43[b]	100	$C_{20}H_{20}BF_3NP$
$CH(CH_3)_2$	240[b]	93.8	$C_{21}H_{22}BF_3NP$
$C(CH_3)_3$	181-82	64.0	$C_{22}H_{24}BF_3NP$[c]

[a] Uncorrected.

[b] Recrystallized from acetone.

[c] If suction was applied, this compound dissociated into Ph_3-P=N-*tert*-Bu and BF_3. It decomposed slowly under atmospheric pressure. consequently no analysis was made.

TABLE II. **Alkylaminotriphenylphos-**

R	*M. P., °C.*	*Yield %*	 $[Ph_3P-NH-R]^{\oplus}BF_4^{\ominus}$ *Formula*
CH_3	125-26[a]	88.0	$C_{19}H_{19}BF_4NP$
C_2H_5	129-31[a]	92.3	$C_{20}H_{21}BF_4NP$
$CH(CH_3)_2$	151-52[a]	85.5	$C_{21}H_{23}BF_4NP$
$C(CH_3)_3$	169[a]	74.7	$C_{22}H_{25}BF_4NP$

[a] **Recrystallized from chloroform-ethyl acetate mixture.**

The methyl and ethyl homologs of type A compounds proved to be very stable toward air. The isopropyl homolog decomposes slowly, but is stable enough to be analyzed. However, the *tert*-butyl homolog is extremely unstable toward moisture. On exposure to air it decomposes within a few minutes to yield the corresponding type B compound (see Table II). Obviously because of steric hindrance the N-B bond is very weak in this case, because upon application of suction to triphenylphosphine-*tert*-butyliminitrifluoroboron BF_3 disappeared and the parent triphenylphosphinalkylimine remained. Type A and B compounds were identified by checking C, H, and N analyses. Infrared spectroscopy could also be used advantageously for this purpose. All type B compounds exhibited a sharp absorption peak between 3240 and 3260 $cm.^{-1}$, corresponding to a N-H stretching frequency. This absorption was distinctly absent from the type A compounds.

phinalkyliminetrifluoroboron

Carbon, %		*Hydrogen, %*		*Nitrogen, %*	
Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
62.75	62.75	5.02	5.01	3.90	3.91
64.40	64.34	5.38	5.38	3.75	3.59
65.17	64.47	5.13	5.13	-	-
-	-	-	-	-	-

phonium Tetrafluoroborate

Carbon, %		*Hydrogen, %*		*Nitrogen, %*	
Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
60.19	60.10	5.02	5.38	3.70	3.90
61.12	60.54	5.34	5.36	3.56	3.91
61.96	61.43	5.65	5.61	3.44	3.74
62.74	62.85	5.94	6.23	3.33	3.39

TABLE III. Triphenylphos

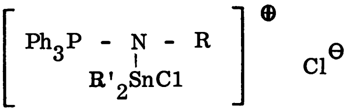
R	*M.P.,* °*C.*	*Yield* %	*Formula*
CH_3	155-56(dec.)	92.9	$C_{37}H_{33}BNP$
C_2H_5	147-48(dec.)	88.0	$C_{38}H_{35}BNP$
$CH(CH_3)_2$	170-72(dec.)	82.8	$C_{39}H_{37}BNP$
$C(CH_3)_3$	149-51(dec.)	81.0	$C_{40}H_{39}BNP$

[a] These compounds gave low (about 1 to 2%) C and H analyses, indicating oxygen uptake. The nature of these oxidation products is being investigated.

The reaction between triphenylboron and triphenylphosphinalkylimines also is sensitive toward moisture. If the reaction was not carried out under strictly anhydrous conditions, oils and sticky materials which defied work-up were isolated. Under anhydrous conditions the desired 1 to 1 complexes were obtained (Table III). These compounds could not be recrystallized. They were purified by trituration with anhydrous ether.

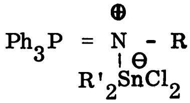
Reactions with R_2SnCl_2

Triphenylphosphinemethylimine reacted with dimethyltin dichloride and triphenylphosphinethylimine reacted with diphenyltin dichloride. After refluxing for a few hours in ether the resulting precipitate was collected. In either case analyses showed the compound to be a 1 to 1 addition compound. Two structures satisfy the analytical data of these compounds:



$$\left[Ph_3P-\underset{\underset{R'_2SnCl}{|}}{N}-R\right]^{\oplus}Cl^{\ominus}$$

and



$$Ph_3P=\overset{\oplus}{\underset{\underset{R'_2SnCl_2}{|\ominus}}{N}}-R$$

R = R' = Me

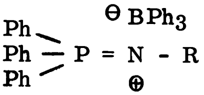
C R = Et; R' = Ph D

At present no experimental evidence to support either structure is available. However, since tin compounds with a coordination number of 5, as required by structure D, are very rare, structure C is the most likely one. The same argument can be applied for the structure of the second compound of this series. Further work on these and similar compounds is in progress.

Experimental

Melting points are uncorrected. Microanalyses were done by A. Bernhardt, Mikroanalytisches Laboratorium, Max Planck-Institut, Mulheim/Ruhr, Germany, and Galbraith Laboratories, Knoxville 21, Tenn.

phinalkylimintriphenylboron



$\mathrm{Ph_3P = \overset{\ominus\,BPh_3}{\underset{\oplus}{N}} - R}$

Carbon, %		*Hydrogen, %*		*Nitrogen, %*	
Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
83.33	83.37	6.20	6.62	2.63	2.68
-[a]	-	-	-	2.56	2.15
-[a]	-	-	-	2.50	1.99
-[a]	-	-	-	2.44	2,29

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch002

Triphenylphosphinalkylimine-Trifluoroboron Complexes. The appropriate triphenylphosphinalkylimine (0.01 mole) was dissolved in Na-dried ether (300 ml.) and BF_3 gas (after drying over P_2O_5) was passed through at a rate of two to three bubbles per second at -72°C. A N_2 atmosphere was maintained throughout and the reaction mixture was slowly stirred. When the precipitation stopped, passage of BF_3 was terminated and the mixture was stirred vigorously for half an hour. The precipitate was collected through suction filtration under a nitrogen atmosphere, then dried in vacuum over P_2O_5. Analytical samples were prepared by dissolving the compound in acetone. A small amount of insoluble residue was filtered off; the compound was recovered by precipitating it by adding dry ether.

Triphenylphosphinalkylimine-Triphenylboron Complexes. In a three-necked flask, thoroughly flushed with dry nitrogen and fitted with a stirrer and a dropping funnel, a solution of triphenylboron (1.21 grams, 0.005 mole) in Na-dried ether (200 ml.) was cooled to ice bath temperature and a solution of the corresponding phosphinimine (slightly more than the equivalent amount) was added dropwise, while being stirred. After the addition was complete ($\frac{1}{2}$ hour), the reaction mixture was refluxed and stirred for 5 more hours. A grayish precipitate which separated out was collected by suction filtration. It was triturated thoroughly with dry ether (containing a few drops of dry ethanol) to obtain the analytical samples.

Triphenylphosphinemethylimine-Dimethyltin Dichloride Adduct. Dimethyltin dichloride (2.197 grams, 0.01 mole) was suspended in 20 ml. of Na-dried ether. A small excess of triphenylphosphinemethylimine in 50 ml. of ether was added and it was refluxed for 2 hours. The resulting white precipitate was filtered, dried, and recrystallized from a mixture of chloroform and ether (m.p. 156-57°; yield 98%).

Analysis. Calculated for $C_{21}H_{24}Cl_2NPSn$: C, 49.34; H, 4.70; Cl, 13.90. Found: C, 48.82; H, 4.96; Cl, 13.41.

Triphenylphosphinethylimine-Diphenyltin Dichloride Adduct. This compound was analogously obtained from diphenyltin dichloride (1.72

grams; 0.0005 mole) and triphenylphosphinethylimine [yield 88%; m.p. 127-29 (from chloroform-ether)].

Analysis. Calculated for $C_{32}H_{30}Cl_2NPSn$: Cl, 10.95. Found: Cl, 11.26

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Received May 16, 1963. Work supported by financial aid of the U.S. Army through grant DAARO-D-31124-C122.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch002

Relations between Structure and Coordination Stability in Boroxazolidines

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch003

The presence of the N-B dative bond is shown in the tricyclic boric acid esters of triethanolamines, the bicyclic boronic acid esters of diethanolamines, and the monocyclic borinic acid esters of ethanolamines. The boroxazolidines have dipole moments in the range 8.5 to 11 debyes, showing a polar structure. The sizes of the nitrogen substituents in the bicyclic and monocyclic series influence the rates with which they neutralize aqueous strong acid; this is reflected in strong steric influences on the entropy of activation, although the free energies of activation show little systematic variation with changes in substituent. Boroester carbon atom substituents in the tricyclic series moderately affect entropy of activation. A mechanism is suggested for the hydrolysis of triptych boroxazolidine.

The first reported preparation of a boroxazolidine appeared in a German patent *(22)* in 1933, where a preparation of triethanolamine borate was reported. This interesting new substance remained unnoticed until it was rediscovered in 1951 *(3)* and its preparation was reduced to a convenient azeotropic process *(7)* in 1952. The class of related compounds was expanded by the preparation in 1955 of a few aryl boronic esters of diethanolamine *(17)* and in 1956 of about a dozen alkyl boronic esters of diethanolamine *(10)*. Extension to the aryl borinic esters of ethanolamine *(12, 13)* occurred at about the same time with the perfection by Letsinger and his students of a reliable procedure for preparing a variety of diaryl borinic acids. Subsequently, the number of known aryl boronic esters and diaryl borinic esters has been greatly extended *(5, 14, 20, 21, 33, 36)*, and over four dozen boric acid esters of variously substituted triethanolamines have been reported by Schleppnik and Gutsche *(24, 25)*.

Against the well-known background of knowledge of the extreme sensitivity of boron esters of the ordinary alcohols toward both atmospheric oxidation and hydrolytic cleavage *(26)*, it was immediately observed that the foregoing amino alcohol esters possess an unusual degree of stability with respect to these influences.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

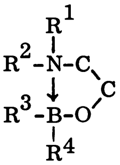
Brown and Fletcher *(3)* were the first to advance the idea that this stability is a result of N-B dative bonding within the molecule (Figure 1,a) of triethanolamine borate to produce a triptych structure, in contrast to the expected noncoordinated (or "cage") structure (Figure 1,b). Support was given to this conception by evidence presented by Musgrave and Park *(17)* to show that, in the parasubstituted aryl boronic esters of diethanolamine, the N-H infrared frequency undergoes a regular shift in wavelength which parallels the known polarity of the *p*-substituent on the *B*-aryl group. Thus, the boronic esters were represented as diptych structures (Figure 1,c), in contrast to the open structure (Figure 1,d). However, in a parallel infrared study of the diethanolamine esters of an extensive group of alkyl boronic acids *(10)*, Lawesson was unable to find any evidence of the kind of effect reported by Musgrave and Park, and he concluded that the only interaction present was probably a hydrogen bonding involving the amine hydrogen atoms. Nevertheless, the above-mentioned stability features in these compounds have persuaded most workers in this area that the best way to represent them is in terms of the N-B coordinated structure, so that such a formulation has persisted, not only among the

a. Triptych Boroxazolidine

b. 2,2',2''-Nitrilotriethyl Borate

c. Diptych Boroxazolidine

d. 2,2'-Iminodiethyl Boronate



$R^1R^2N\text{-}C\text{-}C\text{-}O\text{-}BR^3R^4$

e. Boroxazolidine

f. 2-Aminoethyl Borinate

g. 1,2-Bis (*B*-phenyl diptych-*N*-boroxazolidino) ethane

h. 1,2-Bis (diptych *B*-boroxazolidino) ethane

Figure 1. Structures of typical esters of amino alcohols and the boron acids

diethanolamine esters, but also among the monoethanolamine esters of the diaryl borinic acids (Figure 1,e and f) without any actual evidence for its presence.

A brief infrared study published by the author *(34)* early in the investigations discussed here offered frequency assignments which were thought to reflect N-B coordinate bond vibrations. However, subsequent studies of the same kind on additional compounds have failed to corroborate the suggested assignments, at least in any simple way, and certain papers *(2, 31)* in this symposium provide clear evidence that such attempts are premature and are unreliable within the context of molecules as complex as those considered here. Therefore, no confidence can be placed in infrared data as direct proofs of N-B dative bonding in this class of substances at the present time.

Thus, prior to the physicochemical investigations discussed below, the only experimental evidence supporting the N-B coordinated structure consisted of the contradictory reports concerning the infrared spectra of the diethanolamine esters, together with a few fragmentary rate studies into the acidic hydrolysis of triethanolamine and (a little later) nitrilotris(2-propanol) borates *(3, 26, 27)*, and even these were the subject of conflicting interpretations, since Steinberg and Hunter *(26, 27)* had offered the alternative suggestion that the comparatively slow interactions between these borates and strong acid are merely results of steric hindrance around the boroester constellation of atoms.

As a first step, it seemed desirable to attempt to resolve the question whether the resistance of triethanolamine borate to acidic degradation is to be attributed to the steric hindrance effect or to the presence of N-B dative bonding. In a fairly detailed kinetic study *(38)*, it was shown first that the interactions of this compound in both acid (HCl) and alkali (NaOH) in aqueous solution obey identical rate laws; in both environments the reaction is first-order and conforms to identical activation parameters. This was taken as evidence that the role of either acid or alkali is that of a "scavenger" or participant in a fast reaction which follows the rate-determining decomposition step. When rate studies were made of the reaction by which triethanolamine borate is formed in aqueous solution from the component compounds *(15)*, it was found that this process conforms kinetically, not to an initial N-B coordination between triethanolamine and boric acid, followed by boroester formation, but rather to a fast esterification giving the cage structure (Figure 1,b), followed by a rate-determining step to give Figure 1,a. Thus, the kinetic indications point toward the existence, in system-neutral aqueous solution, of an equilibrium between the structures of Figure 1,a and 1,b. A probable mechanism, consistent with the known facts, has been formulated as shown in Figure 2. The several rate and equilibrium constants indicated in that mechanism have been determined at 5° intervals from 10° to 30°, permitting the deduction of the appropriate activation and reaction enthalpies, entropies, and free energies which are summarized in Table I.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch003

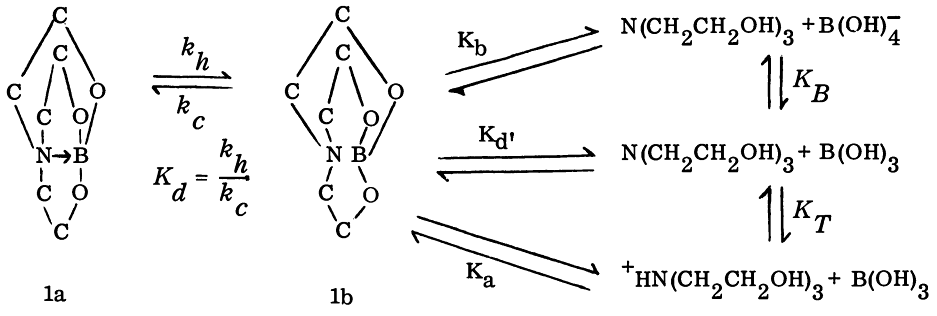


Figure 2. Proposed mechanism for hydrolysis of triptych boroxazolidine

The next step led to examination of N-B coordination in a series of *N*-substituted diethanolamine esters of phenyl dihydroxyborane *(20)*. These compounds also show a delayed basicity toward aqueous acid, but one of a higher order of rapidity than in the case of the triptych compounds. Thus it was necessary to study them in an aqueous acetone system in order to be able to reduce temperatures to a point where the reactions could be slowed to manageable limits. With the exception of the diisopropanolamine ester of the same boronic acid, all of these ester decompositions appeared to obey zeroth-order kinetics. While none of them has yet been studied completely in the sense of the case just discussed, this fact may indicate a mechanism which is not simple. As before, determination of rates over a range of temperatures permitted calculation of the activation parameters given in Table II.

Table I. Thermodynamic and Activation Functions for Acid Hydrolysis of Triptych Boroxazolidine

Constant[a]	ΔH, *Kcal. /Mole*	ΔS, *Cal. /Deg.*	ΔF_{298}, *Kcal. /Mole*
k_h	11.5	-31.2	20.8
k_c	20.0	0.2	20.0
K_d	-8.5	-31.4	0.8
K_a	7.2	58.4	-10.2
K_b	-6.1	0.0	-6.1
$K_{d'}$	10.4	33.4	0.5
$K_B^{(6,16)}$	3.4	-31.0	12.6
$K_T^{(35)}$	6.3	-21.6	12.7

[a] Thermodynamic parameters are for activation processes in first two lines, and for equilibria in others.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch003

Table II. Activation Parameters for Hydrolytic Cleavage of N-B Bonds in Phenyl Dihydroxyborane Esters

No.	*Amino Alcohol Used in Ester Formation*	ΔS^*, *Kcal./Mole*	ΔS^*, *Cal./Deg.*	ΔF^*_{298}, *Kcal./Mole*
2	Diethanolamine	15.9	-15.1	20.4
3	*N*-Methyldiethanolamine	16.2	-13.1	20.0
4	*N*-Ethyldiethanolamine	17.3	- 8.6	19.9
5	*N*-*n*-Butyldiethanolamine	17.3	- 6.9	19.4
6	*N*-Isopropyldiethanolamine	17,2	- 2.5	17.9
7	*N*-Benzyldiethanolamine	14.7	- 1.8	15.2
8	*N*-*tert*-Butyldiethanolamine	Too rapid to measure		
9	Iminobis(2-propanol)	15.5	8.8	12.9

These data reveal a very strong influence, by the size of the nitrogen substituent, on the rate of reaction with acid. This demonstrates the existence of the N-B coordinate bond in such compounds, since, without such coordination, it is impossible to conceive of any effect produced by a substituent to a beta-nitrogen atom which could influence sterically the comparatively remote boroester hydrolysis in the sense proposed by Steinberg and Hunter. In addition, the magnitude of the substituent effect on the enthalpies and entropies of activation gives a quantitative measure of the steric interaction between such substituents and the *B*-phenyl group.

The next series of rate studies dealt with the reaction in strong acid of a number of variously substituted ethanolamine esters of diaryl hydroxyboranes *(37)*. While the delayed basicity effect is still present in these compounds, the reaction rate is even greater than in the diptych or triptych systems. In many cases, the effects of nitrogen substituents in assisting the degradation appear to be so large that, even in predominantly organic solvents at dry ice temperatures, the rate is outside the limits of applicability of the indicator method *(3, 38)* as used in all this work. Nevertheless, a sufficient number of tractable cases was found to support the hypothesis that N-B coordination is general in these compounds also. The activation parameters for the cases observed are given in Table III. All the reactions in this group appear to obey a first-order rate law — i.e., independent of acid concentration but directly dependent on the concentration of boroxazolidine.

The final rate studies in this group of experiments dealt with a series of triptych boroxazolidines from the first group prepared by Schleppnik and Gutsche *(28)*. All members of this collection bore a substituted methyl group on just one of the three boroester carbon atoms (the 3-position). Triptych boroxazolidines thus substituted undergo the reaction with mineral acid at an even slower rate than does

Table III. Activation Parameters for Hydrolytic Cleavage of N-B Bonds in Monocyclic Boroxazolidines

No.	*Boroxazolidine*	ΔH^*, *Kcal./Mole*	ΔS^*, *Cal./Deg.*	ΔF^*_{298}, *Kcal./Mole*
10	*B*,*B*-Diphenyl-	22.1	23.0	15.2
11	*B*,*B*-Bis-(*p*-tolyl)-	9.6	-23.7	16.7
12	*B*,*B*-Bis-(*m*-tolyl)-	20.1	19.8	14.2
13	*B*,*B*-Bis-(*p*-anisyl)-	8.0	-28.9	16.6
14	*B*,*B*-Diphenyl-3-methyl-	19.8	14.2	14.5
15	*B*,*B*,3-Triphenyl-4-methyl-	16.3	2.9	15.4
16	*B*,*B*-Diphenyl-4,4,-dimethyl-	14.9	-2.8	15.7
17	*B*,*B*-Diphenyl-*N*-methyl-	18.2	12.9	14.4
18	*B*,*B*-Diphenyl-*N*-ethyl-	12.5	-10.8	15.7
19	*B*,*B*-Diphenyltetrahydroboroxazine	25.6	27.3	17.5

the parent compound, as had been shown earlier *(27)*. Thus, for the first time, the studies had to be performed under conditions somewhat above room temperature. The reactions, which were all first-order, were again observed as a function of temperature, leading to the activation parameters given in Table IV.

Table IV. Activation Parameters for Hydrolytic Cleavage of N-B Bonds in 3-Substituted Triptych Boroxazolidines

No.	*3-Substituent*	ΔH^*, *Kcal./Mole*	ΔS^*, *Cal./Deg.*	ΔF^*_{270}, *Kcal./Mole*
20	Methyl	10.1	-38.2	20.4
21	Ethyl	11.6	-34.5	20.9
22	*n*-Propyl	12.0	-32.9	20.9
23	Isopropyl	12.5	-33.3	21.5
24	Methoxymethyl	10.7	-33.1	19.6
25	Ethoxymethyl	9.2	-43.7	21.0
26	Isopropoxymethyl	9.2	-43.8	21.0
27	Allyloxymethyl	10.0	-36.5	19.9
28	Benzoxymethyl	11.8	-31.4	20.3
29	Phenoxymethyl	12.0	-29.5	20.0

Examination of these data shows that there is a slight effect on the free energy of activation associated with the substituent to the methyl group which itself is substituted on the borester carbon atom. This effect, shown in Figure 3, is surprising, since the substituent being varied is relatively remote from either possible site of reaction in the

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch003

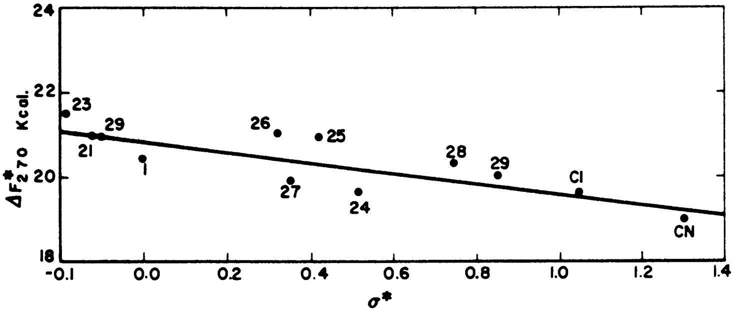


Figure 3. Relation between free energy of activation and polarity of substituents, R and R', in 3-RR'CH-triptch boroxazolidines subjected to acidic hydrolysis

molecule. However, the recently proposed Swain-Thornton rule *(29)* suggests a possible explanation. According to this rule, an electron-releasing substituent (in the customary parlance of organic chemists), even in a saturated bond system, alternately weakens and strengthens bonds as one moves away from the substituent, while electron-withdrawing substituents have the opposite effect. The relationship of a postulated N-B bond to the substituents in question here is exactly the one which would be necessary if this rule were to produce the observed effect, whereas the same result would produce on the B-O bonds an influence precisely opposite to that which is observed.

The self-consistency of the foregoing polar effect is even more remarkable in view of the fact that isokinetic plots *(11)*, shown in Figure 4, of the enthalpy data against the entropy data indicate the occurrence

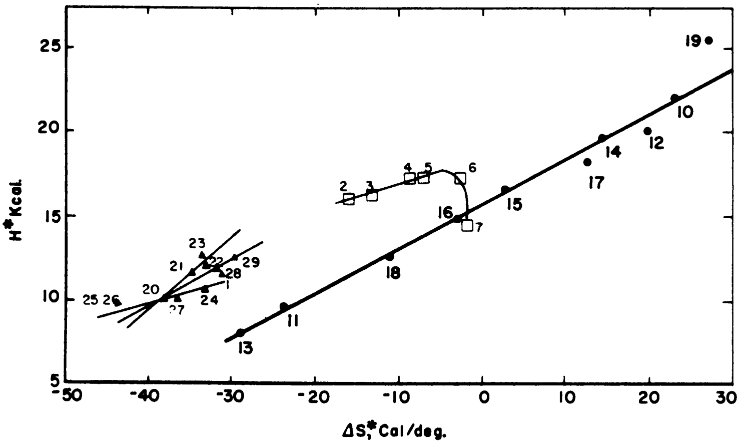


Figure 4. Isokinetic plots showing relations between enthalpies and entropies of activation in acidic hydrolysis of boroxazolidines. Compounds indicated by numbers corresponding to those in Tables II, III, and IV. No. 1 denotes unsubstituted triptych boroxazolidine

△ *Triptych*, □ *Diptych*, ○ *Monocyclic*

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of at least two (and perhaps three) mechanistic relationships within the observed reactions of the triptych series. Indeed, whereas both the diptych and monocyclic series appear individually to be homogeneous in this respect, the substituent effects within the triptych series seem to be much more complicated.

According to Leffler *(11)*, the positions of related reactions on the same isokinetic line indicate that they all proceed by the same mechanism. While we are inclined to doubt that this constitutes an absolute criterion of mechanistic similarity or dissimilarity, it seems certain that the observed differences in isokinetic curves reflect fundamental differences in the energetic requirements of the reactions which have been observed in the several series of compounds discussed here. In particular, the consistent relationship between enthalpy and entropy of activation, which the curves of Figure 4 reveal, constitutes, in our opinion, strong evidence of the pre-eminence of the entropic factor in determining the course of these reactions involving the N-B dative bond. Particularly in the diptych series, there seems to be little doubt that a progressively increasing steric requirement by the *N*-substituent is responsible for the abrupt curvature downward which develops in that isokinetic curve. In the monocyclic series this effect is not observed because (as one can see from molecular models) the molecular architecture provides very little space for the introduction of *N*-substituents much larger than the ethyl group. In the triptych series, the study of models shows that the substituents in question cannot possibly interfere sterically at either probable reaction site. However, they can interact somewhat with adjacent rings of the triptych structure, so that the variations in entropy of activation associated with these reactions are probably evidence of changes in degrees of freedom during the activation process, rather than of any direct steric hindrance.

In this connection, the reported preparation *(23)* of three diptych boroxazolidines from 1-phenyl-2-*N*-pyrrolidino-, piperidino-, and morpholinoethanols, respectively, should be mentioned. In these substances the nitrogen atom constitutes the center of a spiro system, as well as a member of the monocyclic boroxazolidine. This preparation, which occurs easily when the amino alcohol and borinic acid are warmed in alcoholic solution, is of interest in view of the fact that repeated efforts to prepare related spiro compounds in our laboratory have uniformly failed. These failures contributed to the conclusions already expressed regarding the extremely limited space available for *N*-substituents in the *B*, *B*-diphenyl boroxazolidines. The only difference between our amino alcohols and those used by Roth is the presence, in his cases, of an alpha-phenyl group on the alcohol moiety. The reason why such a change should contribute to success in the preparation of these spiro compounds is worthy of further study.

A further unexplained difference in the behaviors of boroxazolidines is to be found in the hydrolysis rates of a group of 1, 2-bis (*B*-phenyl diptych *N*-boroxazolidino)-ethanes (Figure 1,g) prepared in our laboratory and found to react in mineral acid in a manner similar to the diptych compounds already discussed, as compared to the properties of a series of diethanolamine esters of arylene and alkylene bisboronic acids (Figure 1,h) which have been reported in the patent literature *(32)*. Although no rate data are given, it is claimed that the latter substances are remarkably stable against hydrolysis, persisting unchanged

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in aqueous media for many weeks in certain cases. It is interesting to inquire why a mere exchange of the point of attachment of the boroxazolidino ring system to the hydrocarbon moiety (from N to B) should have such a dramatic stabilizing effect. Perhaps the answer may be found in the fact *(8)* that, despite the N-B dative bond, the boron atom may remain more positively charged (on an absolute basis) than the nitrogen atom as a result of charge redistributions throughout the remainder of the molecule. In any event, this problem, also, ought to be studied further.

During the course of efforts to obtain indirect information regarding N-B dative bonding by means of rate measurements, efforts were also made to obtain direct evidence through dipole moment measurements in dioxane solutions *(5)*. These data are given in Table V.

Table V. Dipole Moments of Boroxazolidines and Their Six- and Seven-Membered Ring Analogs in Dioxane

Compound	*Dipole Moment, Debyes*
Triptych boroxazolidine	8.8±0.12
B-Phenyl diptych boroxazolidine	8.5±0.19
B-Phenyl-*N*-methyl diptych boroxazolidine	9.1±0.21
B-Phenyl-*N*-ethyl diptych boroxazolidine	9.1±0.07
B-Phenyl-*N*-isopropyl diptych boroxazolidine	9.6±0.08
B-Phenyl-*N*-*n*-butyl diptych boroxazolidine	11.2±0.16
B, *B*-Diphenylboroxazolidine	8.7±0.01
B, *B*-Diphenyl-*N*-methylboroxazolidine	8.8±0.34
B, *B*-Diphenyl-*N*-ethylboroxazolidine	10.1±0.07
B, *B*-Diphenyl-*N*-isopropylboroxazolidine	10.3±0.02
B, *B*-Diphenyl tetrahydroboroxazine	9.0±0.22
B, *B*-Diphenyl tetrahydroboroxazepine	10.6±0.12

While not highly accurate, they reflect the presence of a strong element of polarity in all the compounds subjected to such study. The effect of the nitrogen substituents reveals approximately linear relationships in the diptych and monocyclic series, respectively, between substituent size [as expressed through the Taft *(30)* steric parameters] and the apparent dipole moment. Moreover, the dipole moment increases in a regular, though nonlinear, manner as the number of members in the coordinate ring is increased from five to seven *(1)*. All of these observations can be regarded as direct evidence of the N-B dative bond in all three boroxazolidine series.

Finally, a number of 2-pyridylalkanol esters of diphenyl hydroxyborane, which have been prepared both in our laboratory and by Neu *(18)*, also appear to be remarkably stable. When the reagent pyridyl alcohol and borinic acid are mixed in ethereal solution, the product precipitates very rapidly. However, there is, at least in certain cases, a noticeable delay between the mixing of the reagents and the precipitation of products. This delay is a rough function of the expected steric difficulty of closing a ring via the N-B dative bond. Recent solubility studies on a group of these materials *(36)*, the results of which are presented in Table VI, suggest that the delayed precipitation may be at least in part a result of a delayed or retarded rate of reaction.

Table VI. Solubilities in Absolute Ether of Diphenyl Hydroxyborane Esters of Pyridyl Alkanols

Pyridyl Alkanol	A^a	B^a	$\Delta H_{soln.}$, *Kcal./Mole*
2-Pyridyl diphenyl carbinol	- 790	0.50	-3.6
2-Pyridyl phenyl methyl carbinol	-2100	4.21	-9.6
6-Methyl-2-pyridyl carbinol	-1730	4.02	-7.9
2-Pyridyl carbinol	-1640	3.55	-7.5
2-(2-Pyridyl) ethanol	-1255	2.49	-5.7_5
3-(2-Pyridyl) propanol	- 529	0.20	-2.4

[a] Parameters in equation: Log $S = A/T + B$.

Conclusions

The evidence discussed here provides strong support, both direct and indirect, for the N-B coordinated — i. e., boroxazolidine — structure first postulated for the alkanolamine esters of boron acids by Brown and Fletcher. In addition, it provides the beginnings of a quantitative delineation of the effects of substituents, at various positions in such molecules, on the reactivity of this bond. However, the present evidence should not be regarded as conclusive, since there is virtually no information now at hand concerning the stability or reactivity of the *B*-alkyl analogs of the materials which have been discussed. Moreover, except for the single case of a mechanistic investigation which has been cited, one must concede complete ignorance regarding the details of boroxazolidine reactions in the presence of strong acid. Although certain tentative conclusions have been offered regarding the steric influences of boroxazolidine substituents, much more detailed study of these questions remains to be done.

Finally, relatively large areas of boroxazolidine chemistry appear to be almost completely unexplored, including the preparation and characterization of boroxazo polymers *(4, 36)*, the development of stable boroxazolidine structures (or related structures) for possible use in chemotherapy *(24, 25)*, the investigation of reactions, such as substitutions, on the intact boroxazolidine ring *(9)*, and the development of analytical methods for determining intact boroxazolidines *(19)*. It is to be hoped that the information developed up to the present time will facilitate and stimulate extensive further investigation of these interesting and important questions.

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Received May 10, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch003

4

Kinetics of the Gas Phase Association of Donors and Acceptors

Mechanism of the Reaction between B_2H_6 and NMe_3

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

The relative rates of association of several amines with boron trifluoride, and of the pair BF_3/B_2H_6 with trimethylamine, have been measured in a static and in a flow system. The ambient temperature and pressures of the reacting and diluent gases were controlled and could be varied over a considerable range. The ratio $k_{NH_3}/k_{NMe_3} \approx 0.1$ is independent of the temperature. The ratio $k_{NMe_3}/k_{NHMe_2} \approx 0.9$ is essentially independent of the nature of the diluent, the flow rates through the mixing chamber, etc. The ratio $k_{BF_3}/k_{B_2H_6}$ (competing for trimethylamine) was found to rise with increasing temperature and to fall with rising partial pressure of amine. A mechanism consistent with these observations involves the 1 to 1 complex of diborane with trimethylamine, as a low-concentration intermediate.

Among the simplest of imaginable chemical reactions is the gas-phase association of two molecular species, each of which by itself is stable under the conditions of the experiment. If this reaction is very fast, if it occurs at moderate or low temperatures—i.e., if $E_{act}/RT < 5$—and, in particular, if it can be demonstrated that the rate is over-all second-order but first-order with respect to each species, it is presumed that the reaction proceeds via bimolecular encounters between the reactant molecules. This research program is concerned with exploring the specific chemical factors that determine the observed rates.

The association reaction is evidently the inverse of the unimolecular decomposition of the adduct. However, the relationship between the measured rate constants is not a direct one, as is demonstrated below. For

$$AB + M \underset{k_x}{\overset{k_{-x}}{\rightleftharpoons}} AB^* + M \qquad (1a)$$

$$AB^* \xrightarrow[k_{ac}]{} AB^+ \xrightarrow[k_d]{} A + B \qquad (1b)$$

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

the steady-state condition on the transient species, at sufficiently high pressures of M, gives

$$\frac{dA}{dt} = k_{ac}\left(\frac{k_x}{k_{-x}}\right)\overline{\mathrm{AB}} \tag{2}$$

Thus, the rate is limited by the delay in the accumulation in the critical A - B bond of the energy necessary for dissociation; the ratio k_x/k_{-x} is merely a statistical factor, and there is no measure of k_d. On the other hand, for

$$\mathrm{A} + \mathrm{B} \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} \mathrm{AB}^+ \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftarrows}} \mathrm{AB}^* \tag{3a}$$

$$\mathrm{AB}^* + \mathrm{M} \xrightarrow[k_{-x}]{} \mathrm{AB} + \mathrm{M} \tag{3b}$$

the steady-state conditions on both AB^+ and AB^* lead to a somewhat involved expression for the rate expression, which reduces to

$$\begin{aligned} \frac{1}{k_{\mathrm{obsd}}} &= \frac{\alpha}{k_{-d}} + \left(\frac{k_{ac}}{k_{-ac}}\right)\left(\frac{k_d}{k_{-d}}\right)\frac{1}{k_{-x}\mathrm{M}} \\ \frac{d\,\overline{\mathrm{AB}}}{dt} &\equiv k_{\mathrm{obsd}}\,\mathrm{A}\cdot\mathrm{B} \\ \text{and}\quad \alpha &\equiv 1 + k_d/k_{-ac} \end{aligned} \tag{4}$$

where α is a measure of internal conversion inefficiency. At high pressures of M, the limiting value of k_{obsd} is determined by the association rate constant for the production of the transition state, and the relative probability for dissociation *vs.* that for diffusion of vibrational energy from the newly formed bond to other vibrational modes in the adduct. The magnitude of the pressure-dependent term depends on the stationary state population of AB* and on the ease of its de-excitation by M.

The measured rates of gas-phase association reactions of alkyl radicals suggest that $\alpha \approx 2$ to 3, assuming k_{-d} is merely the collision number. Also, it appears that k_{obsd} has a slight negative temperature coefficient for $2CH_3$ (161° to 814° range) but a small positive one for $2C_2H_5$ *(8)*. A fully satisfactory account of these data has yet to be given *(14)*. Extensive investigations of such free radical recombinations are limited by the difficulty of their preparation, lack of knowledge of their concentrations, their very short lifetimes, and in particular, the large number of side reactions which must be considered concurrently. It therefore proved attractive to study the association of analogous pairs such as $BF_3 + NR_3$. Kistiakowsky and coworkers *(7)* have developed a modified "flame diffusion" technique for measuring the absolute reaction rates of these donor-acceptor gas-phase reactions. Even though the solution of the coupled diffusion and thermal conductivity equations proved to be more complex than was first thought, considerable confidence may now be placed in these results, which are summarized in Table I.

Table I.

$$BF_{3(g)} + NR_{3(g)} \xrightarrow{k_{obsd}} R_3N{:}\ BF_{3(s)}$$

Amine	k_{obsd}	k_{obsd}/z, *(Coll. Yield)*	ΔH°, *Kcal. /Mole*	*I. P.*$_{NR_3}$
NH_3	2.7×10^{11}	0.001	-22.0	10.52
ND_3	1.4×10^{11}	0.0005	-----	11.52
NH_2Me	6.7×10^{11}	0.003	-26.0	8.97
$NHMe_2$	5.9×10^{12}	0.02	-28.2	8.24
NMe_3	2.8×10^{12}	0.01	-26.6	7.82
C_3H_5N	9.3×10^{12}	0.03	-(27-30)	-----
n-C_4H_9-NH_2	8.9×10^{12}	0.03	-----	8.71
tert-$C_4H_9NH_2$	6.3×10^{12}	0.02	-----	8.64
PMe_3	1.4×10^{13}	0.06	-18.9	(7.3)

Inspections of the values in Table I show that in a number of respects these reactions differ significantly from the association of alkyl radicals; values of α are large (17 for PMe_3 to 2000 for ND_3). Thus, the transition state for the donor-acceptor adduct has a much greater probability for dissociation than for stabilization by intramolecular energy transfer ($k_d \gg k_{-ac}$). While geometric considerations suggested that k_{NH_3}/k_{NMe_3} should be greater than unity, the reported ratio is 1/10. The reasons for $k_{NH_3}/k_{ND_3} = 2$; $k_{NHMe_2}/k_{NMe_3} = 2$;

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

and $k_{NH_2bu^n}/k_{NH_2Me}$ = 13 are far from obvious. The relatively low value of αp_{Me_3} is surprising. Since the absolute magnitudes of these rates are difficult to determine with precision over a range of pressures and temperatures, and since the primary interest lies in measurement of the effect of selected molecular parameters on the rates, this research program centered around the measurement of relative rates of addition, taking that of $[BF_3 + N(CH_3)_3 \longrightarrow (CH_3)_3N{:}BF_3]$ as the reference value. This was done by measuring the ratios of products generated in competitive systems:

$$BF_3 + \begin{Bmatrix} N(CH_3)_3 \\ NR_3 \end{Bmatrix}_{excess} \longrightarrow \begin{Bmatrix} (CH_3)_3N{:}BF_3 \\ R_3N{:}BF_3 \end{Bmatrix}$$

$$NMe_3 + \begin{Bmatrix} BF_3 \\ BX_3 \end{Bmatrix}_{excess} \longrightarrow \begin{Bmatrix} Me_3N{:}\ BF_3 \\ Me_3N{:}BX_3 \end{Bmatrix}$$

For the above systems, the phenomenological rate equations are:

$$A_{(g)} + B_{1\,(g)} \xrightarrow{k_1} AB_{1(s)} \qquad (5a)$$

$$A_{(g)} + B_{2(g)} \xrightarrow{k_2} AB_{2(s)} \qquad (5b)$$

$$\frac{dB_1}{dt} = -k_1\, A \cdot B_1 = -\frac{d(AB_1)}{dt} \qquad (6a)$$

$$\frac{dB_2}{dt} = -k_2\, A \cdot B_2 = -\frac{d(AB_2)}{dt} \qquad (6b)$$

so that if one analyzes the residual gases,

$$\frac{k_1}{k_2} = \frac{\ln B_1/B_1^0}{\ln B_2/B_2^0} \qquad (7)$$

These relations hold, provided that:

There are no side reactions—i. e., all the material which does not react by association remains in the gas phase as unperturbed B_1 and B_2; in particular, there should be no adsorption of the residual gases onto the solids generated.

The rates of production of solids are not limited by the nucleation and precipitation steps.

There are no displacement reactions, either between the freshly formed adduct and the residual gases, or subsequently after precipitation.

If one analyzes the solids produced,

$$\frac{k_1}{k_2} = \frac{\ln\left[1 - \frac{AB}{B_1^o}\right]}{\ln\left[1 - \frac{AB_2}{B_2^o}\right]} \approx \frac{AB_1}{AB_2} \cdot \frac{B_2^o}{B_1^o} \qquad (8)$$

In this case only ratios of quantities under initial and final conditions enter the rate expression.

The first set of experiments were performed in a static system, and the initial and final gas concentrations were analyzed by infrared absorption. The rates were measured at three different temperatures. To ensure thorough mixing of the reactants, small amounts of boron trifluoride diluted with nitrogen were slowly bled into the thermostated reaction vessel containing the mixed amines. A turbine rotating at 1000 to 1500 r.p.m. was placed so that its blades swept past, very close to the exits capillary of the bleed-in stopcock.

Titration Experiments

To establish the compatibility of a competing pair, a series of gas titrations was run; each amine was individually titrated with boron trifluoride, and the residual pressures were plotted as in Figure 1. Only ammonia and trimethylamine gave curves which indicated the absence of significant adsorption of the unreacted amines with the solids. The others ($NHMe_2$, NH_mEt_{3-m}, NH_2Pr^n, NH_2Bu^n, NH_2Am^n, Pyr) showed appreciable departures from linear dependence, as does $NHMe_2$ (Figure 1), or from 1:1 stoichiometry. Hence (k_{NH_3}/k_{NMe_3}) was selected for a study of its temperature dependence. If its value of 0.1 were due to a larger activation energy for $NH_3 + BF_3$ than for $NMe_3 + BF_3$, this ratio should rise with rising temperature.

Temperature Dependence of Relative Rates

Whenever a small amount of reaction took place, such that the concentration of ammonia did not change appreciably and the values of $\log_{10} p_i/p_f$ were small, the results tended to be widely divergent. For this reason, all runs in which $\log_{10} (p_i/p_f)_a < 0.0300$ were discarded. At room temperature the average of 12 values is:

$$(k_{NH_3}/k_{NMe_3})_{25°} = 0.087 \pm 0.15$$

At 0°, the average of 12 values is:

$$(k_{NH_3}/k_{NMe_3})_{0°} = 0.117 \pm 0.027$$

At 60°, the average of 14 values is:

$$(k_{NH_3}/k_{NMe_3})_{60°} = 0.111 \pm 0.054$$

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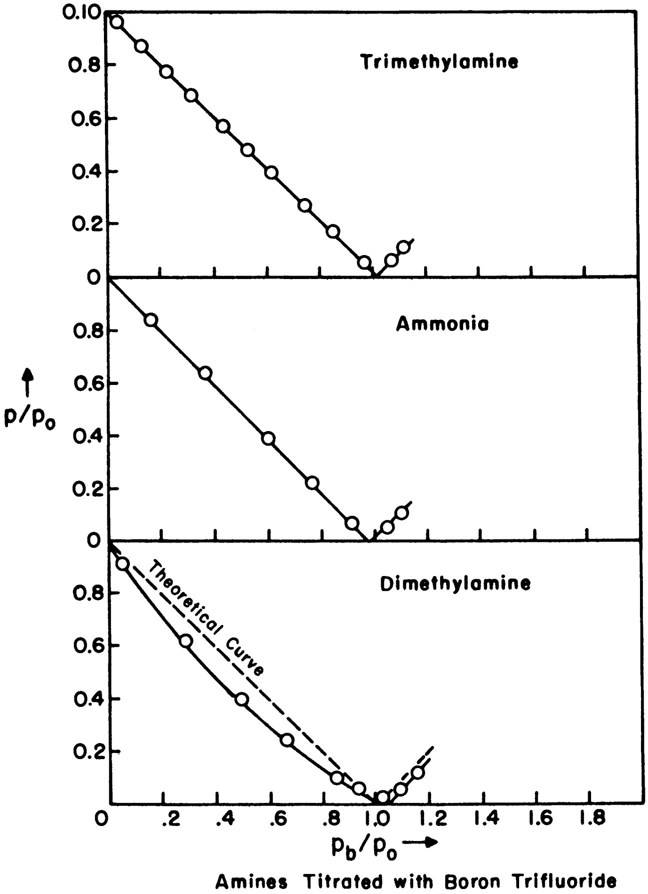

Figure 1. Gas-phase titration curves at room temperature for amines titrated with boron trifluoride

p_0. Initial pressure of base
p_b. Equivalent pressure of BF_3 added
p. Total pressure in cell

The random variation of the relative rate constants with temperature and the overlap of their root-mean-square deviations allow one to say only that the relative energy of activation for the two reactions is essentially zero. However, by plotting the data, limits on the magnitude of $(E_{NH_3} - E_{NMe_3})$ can be established. The slopes of the extremal lines, based on the root-mean-square deviations, are: $m_1 = -38$; $m_2 = 122$. For extreme differences in the activation energies these slopes give +76 and -242 cal. per mole. These results show that whereas at a relatively high ambient gas pressure, ammonia associates one tenth as rapidly with boron trifluoride as does trimethylamine, the difference is not due to an activation energy. The conclusion that $\alpha_{NH_3} \approx 10\,\alpha_{NMe_3}$ must be tempered by the possibility that in these experiments the high pressure limit had not been reached for the NH_3/

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BF_3 association (see Equation 11). The difference between the NH_3 and ND_3 rates is presumed to be due to a kinetic isotope effect calculable from estimated partition functions for the transition states *(7)*, wherein it is assumed that the transition states are rigid, being very similar to the stable adducts.

Test on Equilibration Rate

On two occasions, mixtures of the two bases were allowed to stand overnight in contact with quantities of the salts at 60° C., in order to determine if appreciable exchange took place according to the reaction

$$NH_{3(g)} + (CH_3)_3N{:}BF_{3(s)} \rightleftharpoons H_3N{:}BF_{3(s)} + (CH_3)_3N_{(g)} \qquad (9)$$

The results show that over a period of 15 hours appreciable exchange does take place. To determine if this also occurs over a shorter interval range of time, the same experiment was conducted

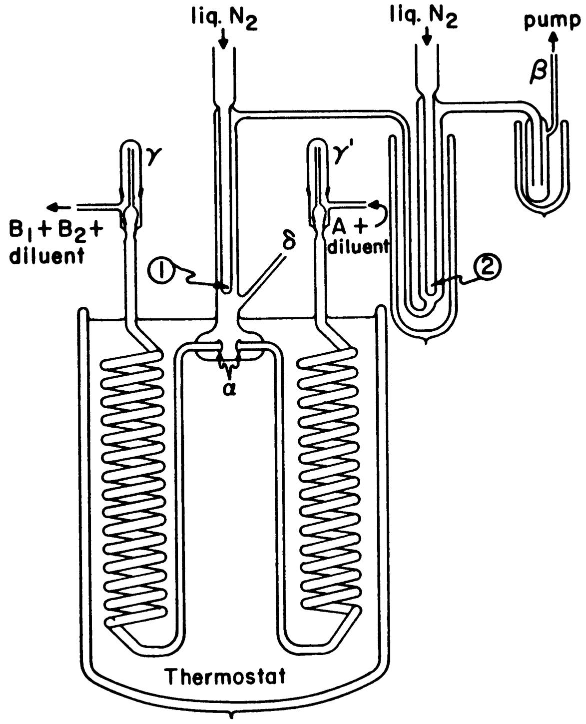

Figure 2. Diagram of flow reactor

Reagents, B_1 + B and A, enter flow control capillaries, γ , γ^1, from multiple-port stopcock. Sintered-glass plates, separated by 0.5 cm. δ is connection to manometer. Solids are collected on cold fingers 1 and 2. Negligible quantities are caught in trap β over varying time spans. It is concluded, from the randomness of observed variations and the small changes involved, that no appreciable exchange takes place in 30 minutes, which is much longer than the time required for a kinetics experiment. This suggests, however, that the method of measuring residual gas concentrations may introduce large errors in the results if measurements are not made rapidly.

Relative Rates in a Flow System

Since the measurement of relative rates of association based on the amounts of the competing gases which remain after reaction (static system) is limited to few pairs of reagents, the experimental procedure was modified to permit estimation of the relative rates from the amounts of solids produced. The apparatus is shown in Figure 2. Daen and Marcus *(4)* using a flow reactor obtained values for the relative rate constants of the methylamines with boron trifluoride, based on the analyses of the residual gases. Over a pressure range of 0.009 to 0.04 mm. of Hg they found that the ratio of rate constants for $k\text{NH}_2\text{Me}/k\text{NMe}_3$ was constant, independent of the ambient pressure. We have shown that reproducible analyses of the ratio of the product salts can be made directly from infrared transmission curves of the solution of the mixed products in acetonitrile or chloroform.

The following are compatibility conditions which the reagents must meet if reliable rate data are to be obtained:

The competing gases, B_1 and B_2, should not significantly react with each other, at least over a period of one-half hour.

The product salts must be stable toward displacement by the remaining gases:

$$AB_{1(g\text{ or }s)} + B_{2(g)} \longrightarrow AB_{2(g\text{ or }s)} + B_{1(g)} \qquad (10)$$

even though such a reaction may be thermodynamically favored.

There should be no appreciable solvent - solute displacement reactions.

Any gases adsorbed on the solids, and thus brought into the solution, should not react with the dissolved adducts.

We have demonstrated that these conditions are satisfied by the pair $NHMe_2$ and NMe_3, in competition for BF_3.

All the reagents used were carefully purified; special care was taken to eliminate water. Their infrared spectra were checked. The pure salts needed for calibration were prepared in the presence of excess boron trifluoride, and then we proved that residual amines adsorbed in these salts do not interfere with the determination of the correct salt ratio. Multiway stopcocks were used so that the desired flow conditions could be set up using the ambient gas only. Then the amine mixture and the BF_3 (+ carrier) were simultaneously connected to the flow tubes, at the specified flow pressures, so that clogging of the sintered glass disks in the reaction vessel by the solid products was minimized. The walls of the reaction vessels were pretreated with the reagents, to eliminate losses by adsorption. The majority of runs were performed in a cell approximately 2 cm. in diameter and 5

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cm. long; the fritted disks were 0.5 cm. apart (grade B). Some runs were carried out with the disks placed near the center of a spherical bulb 9.5 cm. in diameter.

The temperature of the reaction vessel was controlled by immersion in a water bath. The incoming reactants passed through the coils immersed in the same water bath, as shown in Figure 2.

Preliminary experiments showed that the measured $\frac{(CH_3)_3N{:}BF_3}{(CH_3)_2HN{:}BF_3}$ ratio increased the greater the distance of the collecting point from the mixing nozzle. Therefore, it was imperative that <u>all</u> the solid products formed be collected for analysis. Several systems were devised in attempts to trap all the product. The most successful one is shown in Figure 2. With this arrangement, no solids appeared in the small trap (β).

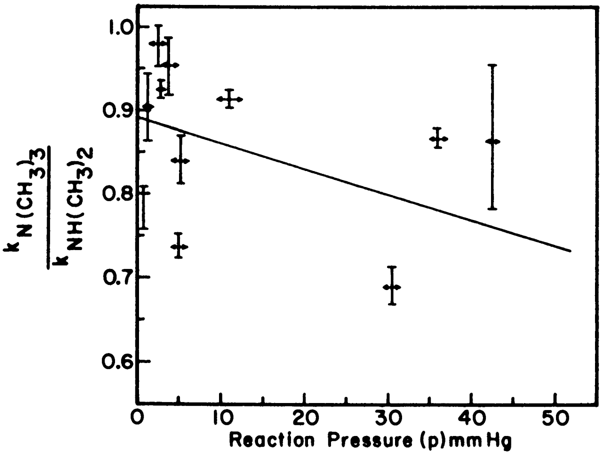

Figure 3. Ratios of rate constants as function of total pressure in reactor

Vertical lines show range of variation in ratios measured at mean pressures plotted; horizontal arrows indicate change in pressure during experiments due to gas depletion in storage vessels

N_2. Ambient gas

$$\frac{B_3 + B_2}{A} \approx \frac{10}{1}$$

$$\frac{N_2}{A + B_3 + B_2} \approx \frac{10}{1}$$

Straight line (least squares) gives

$$\frac{k_3}{k_2} = (0.89 - 0.003\,p) \pm 0.17$$

Data summarized in Table I

Results and Discussion

The ratio of the "observed" rate constants, as defined in Equation 8, may be expressed in terms of mechanistic parameters.

$$\left(\frac{k_1}{k_2}\right)_{\text{obsd}} \equiv \frac{\overline{AB}_1}{\overline{AB}_2}\ \frac{B_2^{\,o}}{B_1^{\,o}} = \frac{\alpha_1/k_{-d}^{(1)}}{\alpha_2/k_{-d}^{(2)}}\ \frac{(M + \theta_2)}{(M + \theta_1)} \qquad (11)$$

where $$\theta = \frac{k_d/\alpha}{k_{-x}}\left(\frac{k_{ac}}{k_{-ac}}\right)$$

Only when $M \gg \theta$ does the ambient gas exert no effect. Our results for the $NHMe_2$ - NMe_3 pair show a slight pressure dependence, but the slope cannot be ascertained with reliability, because of the scatter in the data (Figure 3). If this pressure effect is neglected,

$$k_{NMe_3}/k_{NHMe_2} = 0.89 \pm 0.17$$

over the pressure range 0.65 to 42.5 mm. of Hg. Further, it was demonstrated that the ratio was unaffected by:

(a) The ratio of di/tri used in these experiments (0.115 to 5.27)
(b) The size and shape of the reaction vessel
(c) The flow rate through the mixing chamber
(d) The ratio of the pressure of acid to the total pressure of base (varied over a factor of 4)
(e) The nature of the ambient gas (N_2, Ar, *n*-pentane)

The bimolecular character of such association reactions is strongly supported, as is the notion that di- and trimethylamines react with boron trifluoride with almost equal probability.

Since our value for the ratio of the rate constant is so close to unity, one might argue that "local depletion" controls the amounts of solid generated in our system. However, when the (total amine-BF_3) ratio was increased fourfold, the rate constant ratio measured still fell in the same range as that for lower (amine-BF_3) ratios. This demonstrates that local depletion is not a controlling factor. Another parameter open to question is the possibility of incomplete mixing at the nozzles. In the competitive system used here, provided the same ratio of di- and trimethylamine molecules surround each BF_3 molecule, Equation 11 holds, so that the efficiency of mixing the acid with the base mixture is not critical.

The accuracy of the value of (k_3/k_2), as calculated from Equation 11, depends on the accuracy of measurement of $\dfrac{(CH_3)_3N{:}BF_3}{(CH_3)_2HN{:}BF_3}$. In these experiments, all the product formed was collected and dissolved; losses in the collecting technique are presumed to be negligible. The analytical method was shown experimentally to be independent of adsorbed amine. The spectra of each solution of the products were recorded several times, over a period of hours. This gave a random scatter of the experimentally determined ratio. Therefore, reaction between the complexes and the acetonitrile was presumed to be negligible.

At very low pressures trimethylamine reacts with boron trifluoride more rapidly than at the higher pressures. Daen and Marcus *(4)*, working in the pressure range 0.009 to 0.04 mm. of Hg, obtained a (k_3/k_2) ratio of 12/5. Their average deviation was of the order of 20%. No apparent pressure effect was observed in their experiments. Measurements of the absolute rate constants by Kistiakowsky and coworkers gave 8/5 for this ratio at 0.1 mm. of Hg. However, they found a pressure dependence which within the experimental scatter of their data could be represented by the equation

$$\frac{10^{13}}{k} = a + \frac{b}{P} \tag{12}$$

The value of b for trimethylamine is so small that when P rises above 0.5 mm. of Hg the pressure-dependent term is negligible. On the other hand, the relatively large value of b for dimethylamine indicates that the rate constant, k_2, would continue to increase with pressure up to 2 to 3 mm. of Hg, before assuming its limiting value. The decrease of k_2 relative to k_3 when P is reduced below 1 to 2 mm. thus accounts for the slight slope of the curve of (k_3/k_2) *vs.* pressure, as shown in Figure 3.

The parameter, a, of Equation 12 is the inverse of the over-all rate constant at high pressures. The data of Kistiakowsky and Williams indicate that at high pressures dimethylamine associates about twice as rapidly with boron trifluoride than does trimethylamine. However, our value of $(k_3/k_2) = 0.89 \pm 0.17$ lies within the upper limit of their experimental scatter. Within the cited precision of these experiments there is agreement between the two methods over our experimental pressure range. It is evident, however, that a factor of one half for the ratio of the high pressure limiting rate constants is difficult to rationalize. Indeed, these authors predicted that the ratio would be roughly unity on the basis of an Eyring-Garvin model. To account for a value of (k_3/k_2) which is even slightly less than unity one may argue that $\Delta H°$ association of BF_3 with $NH(CH_3)_2$ is -28.2 kcal. per mole, whereas it is -26.6 kcal. per mole for $N(CH_3)_3$. This is suggestive of a somewhat stronger interaction potential for the dimethylamine-boron trifluoride pair. Also, dimethylamine might have a slight edge on the efficiency of internal energy conversion (α smaller), in that the barriers for rotation about its $N-CH_3$ bonds are probably lower.

Acid Pairs in Competition for a Base

In contrast to the considerable amount of data available on the relative rates of addition of bases to boron trifluoride, there is a paucity of information on the relative rates of addition of various acids to a reference base such as trimethylamine. The kinetics of addition of diborane to phosphine has been studied *(3)*. As yet, the relative acidity of boron trichloride and boron trifluoride as Lewis acids has not been determined. Early data suggest that the boron trifluoride is the weaker electron acceptor *(5, 10)*.

In this work we have shown first that the pairs BF_3-BCl_3, BF_3-BMe_3, and BCl_3-B_2H_6 are not compatible (Table II). We have no

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information regarding the compatibility of BCl_3-BMe_3. However, we have demonstrated that one can measure the relative rates for BF_3 and B_2H_6 competing for trimethylamine. In mixtures of boron trifluoride-boron trichloride an equilibrium is rapidly established between the mixed halides *(6)*, so that one must deal with four reactants, rather than two, in a rather complex kinetic system. It also appears that in mixtures of diborane with boron trichloride similar scrambling reactions occur. This may not be the case for gaseous mixtures of boron trifluoride and boron trimethyl, but we have demonstrated that BF_3 displaces BMe_3 from the solid salt, $Me_3N{:}BMe_3$.

Table II. Available Data on Compatibility of Acid Pairs

	BCl_3	BMe_3	B_2H_6
BF_3	Rapid scrambling of gas phase *(6)*	BF_3 displaces BMe_3 from its solid salts with $t_{1/2} \approx$ several minutes (Price and Bauer)	Compatible (Martinez and Bauer)
BCl_3	———	?	Gases react slowly. Chloroform solutions of pure salts are compatible. Acids attack freshly generated salts (Martinez and Bauer)
BMe_3	↗	———	Gases react but rates may be slow enough for competitive study *(13)*
BBr_3	Scrambling of gas phase. Equilibrium established in few hours *(9)*	?	Gases react slowly; similar to BCl_3 *(12)*

Procedure and Results

The gaseous reagents used in this work were obtained in cylinders from commercial sources. Diborane, boron trifluoride, and trimethylamine were purified in a distillation train, but the nitrogen used as a carrier was taken directly from the cylinder. The specified purity of nitrogen (used as a diluent) was 99.996%. Except for details, the experimental procedure was similar to that used previously.

As the entire reaction vessel system was constructed with a minimum of lubricated joints, the portion of the system containing all visible solid was broken from the rest of the system. The solid was extracted with analytical reagent grade chloroform. In the analysis of the resulting solution, aliquot portions were scanned with the Model 21 infrared spectrometer in the region of 9.5 to 11.5 microns in order

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to determine the relative amounts of the salts produced. The ratio was estimated from a Beer's law calibration plot.

In extracting the solid produced in the rate experiments carried out at room temperature and above, it was observed that not all the solid dissolved in the chloroform; no residue was found for runs made at the lower temperatures. The quantity of the insoluble material increased as the temperature of the experiment was increased, so that the upper temperature limit for this experiment proved to be 60° C. Attempts to identify the insoluble material were unsuccessful. The side product, which was found to be soluble in water and in acetone, formed principally on the cold finger. Useful data were obtained at -80°, -35°, 25°, and 50° C. The results were summarized in Figure 4.

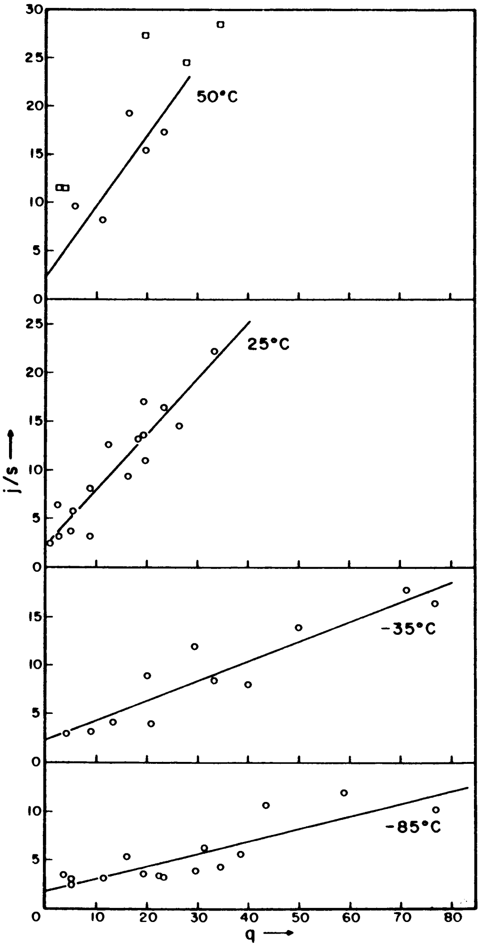

Figure 4. Plot of over-all reaction rate vs. reciprocal of trimethylamine steady-state concentration for different temperatures

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

$$j/s = \frac{(P_{B_2H_6})}{(P_{BF_3})}\ \frac{[Me_3N:BF_3]}{[Me_3N:BH_3]}$$

$$q = [Me_3N]^{-1}_{,}\ \text{cc./mole}$$

Inspection of the processed data shows a linear dependence between the ratio $j/s \equiv \frac{P_{B_2H_6}}{P_{BF_3}}\ \frac{[Me_3N:BF_3]}{[Me_3N:BH_3]}$ and the reciprocal of the average steady-state trimethylamine concentration, q. The lines as drawn in Figure 4 were obtained by least squares. j/s did not correlate with the total steady-state pressure, nor with its inverse, nor with the ratio of the total pressure to that of the amine. Analytically,

$$j/s = \alpha + \beta q \tag{13}$$

Within experimental error, α is independent of temperature. However, a plot of the log β *vs.* the reciprocal of the absolute temperature gave, by least squares,

$$\log \beta = -6.620 - 271.7/T \tag{14}$$

β in moles per cc.

$$\langle\alpha\rangle = 2.2$$

Discussion of Mechanism

The association of boron trifluoride with trimethylamine has been described above. The observed rate constant is: $k_f = 2.8 \times 10^{12}$ cc. mole^{-1} sec.$^{-1}$ The reaction between trimethylamine and diborane may follow one of several mechanisms. The following are incompatible with our data.

$$B_2H_6 \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} 2\ BH_3 \tag{15}$$

$$BH_3 + NMe_3 \xrightarrow[k_{15}]{} H_3B{:}NMe_3$$

The imposition of a steady-state condition leads to:

$$\frac{d[Me_3N:BH_3]}{dt} = \frac{k_{15}}{2}[Me_3N]\left\{\left(8K_d[B_2H_6] + \frac{k_{15}}{k_{-d}}[Me_3N]^2\right)^{1/2} - \frac{k_{15}}{k_{-d}}[Me_3N]\right\} \tag{16}$$

The magnitude of K_d has been given *(10)*; on re-estimating the entropy for BH_3, we recommend

$$\log_{10} K_{d(\text{atm.})} = 7.775 - 6205/T \tag{17}$$

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

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The value for k_{15} should be temperature independent, and possibly a bit larger than k_f. For k_{-d} a value in the neighborhood of 10^{13} to 10^{14} cc. mole^{-1} sec.$^{-1}$ is reasonable *(1)*. One may therefore introduce several approximations in the above expression, to reduce the ratio of salts produced to:

$$\frac{[B_2H_6]}{[BF_3]}\;\frac{d[Me_3N{:}BF_3]}{d[Me_3N{:}BH_3]} = \frac{k_f}{2k_d}\,[Me_3N] \tag{18}$$

This requires that the measured ratio decrease with rising temperature and increase with rising P_{NMe_3}, contrary to observation. Similarly,

$$B_2H_6 + NMe_3 \xrightarrow{k_{19}} H_3B{:}NMe_3 + BH_3 \tag{19}$$

$$BH_3 + NMe_3 \xrightarrow[k_{15}]{} H_3B{:}NMe_3$$

The imposition of a steady-state condition on Mechanism 19 leads to:

$$\frac{d[Me_3N{:}BH_3]}{dt} = 2k_{19}\,[Me_3N]\,[B_2H_6] \tag{20}$$

$$\frac{[B_2H_6]}{[BF_3]}\;\frac{d[Me_3N{:}BF_3]}{d[Me_3N{:}BH_3]} = \frac{k_f}{2k_{19}}$$

For the reaction,

$$B_2H_6 + PH_3 \xrightarrow{k'_{19}} H_3B{:}PH_3 + BH_3 \tag{21}$$

Brumberger and Marcus *(3)* found $k'_{19} = 2.3$ cc. mole^{-1} sec.$^{-1}$ at 0° C. Also, they found that the activation energy was 11.4 kcal. per mole, and the steric factor was 3×10^{-5}, of the same order of magnitude as generally observed in hydrocarbon abstraction reactions. Even if one allows a factor of 10^8 for the ratio k_{19}/k'_{19} because of the greater base strength of NMe_3 compared with PH_3, our data are not consistent with what one would expect for such a mechanism, since the indicated ratio would decrease with rising temperature, and would show no dependence on the amine pressure. One must therefore find a mechanism which favors the formation of the borane salt at the lower temperatures.

We propose that the reaction between the diborane and the trimethylamine occurs as follows:

$$B_2H_6 + NMe_3 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} NMe_3{:}BH_3{\cdot}BH_3 \tag{22a}$$

$$Me_3N + Me_3N{:}BH_3{\cdot}BH_3 \xrightarrow{k_b} 2\ Me_3NBH_3 \tag{22b}$$

Under the steady-state condition, steps a and b yield

$$\frac{d[\mathrm{Me_3N{:}BH_3}]}{dt} = \frac{2k_a k_b [\mathrm{B_2H_6}]\ [\mathrm{NMe_3}]^2}{k_{-a} + k_b\ [\mathrm{NMe_3}]} \qquad (23)$$

With the BF_3 reaction as a reference, the above leads to

$$\frac{[\mathrm{B_2H_6}]}{[\mathrm{BF_3}]}\ \frac{d[\mathrm{Me_3N{:}BF_3}]}{d[\mathrm{Me_3N{:}BH_3}]} = \frac{k_f}{2k_a} + \frac{k_f}{2K_a k_b [\mathrm{NMe_3}]} \qquad (24)$$

where K_a is the equilibrium constant for Reaction 22a in moles per cc.

Expression 24 is of the proper functional form not only with respect to the effect of temperature but also with respect to the trimethylamine pressure dependence. The integrated form of Equation 24 may be obtained under the assumption that the amounts of salts produced are small enough that the amounts of acid used in their production remain essentially unchanged (steady-state concentration due to gas inflow). Application of the differential form interprets the real case more closely than does imposing the necessary restrictions to obtain the integrated form. Even so, in applying the differential form, an average value for the concentration of trimethylamine must be used. On comparing the consequent equation with the experimental expression for j/s, one may identify α with $k_f/2k_a$ and β with $k_f/2K_a k_b$. Within the precision of the experiments α has no temperature dependence; an average value $\langle\alpha\rangle = 2.2$ is proposed. Using the above quoted magnitude for k_f one finds

$$k_a = 6.4 \times 10^{11}\ \text{cc. mole}^{-1}\ \text{sec.}^{-1}$$

This is the limiting rate for very high amine pressures for the formation of the 1 to 1 complex. At 298° K., the smoothed experimental value for $\beta = 2.94 \times 10^{-8}$ mole cc.$^{-1}$, so that $K_a k_b = 4.8 \times 10^{19}$ cc.^{2} mole^{-2} sec.$^{-1}$ at that temperature.

The temperature dependence of β is due to the nonvanishing of the sum of the enthalpy increment in Equation 22a and the activation energy for 22b. One may plot log $\frac{[K_a k_b]}{T}$ *vs.* $1/T$ as in Figure 5. The slope gives

$$\Delta H_a^{\circ} + E_b = -1.65\ \text{kcal. per mole}$$

Thus, the net process in going from the reactants in Equation 22a to the transition state of 22b is slightly exothermic.

The assumption of the 1 to 1 complex between trimethylamine and diborane has been proposed previously. Arguments for the existence of the triethylamine-borane complex at -64° have been given by Brown and coworkers *(2)*; a similar 1 to 1 complex has been proposed by Parry and Shore *(11)*. Our kinetic data require merely that this complex be present in very small amounts during the course of the reaction.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

General Conclusions

It is now evident that these association reactions are far from simple. Subtle and as yet incompletely investigated factors are operative during the sequence of stages through which the parent species pass on toward becoming parts of the adducts. In oversimplified form these may be enumerated:

Description of those encounters between A and B molecules in which their electron configurations are sufficiently perturbed so that a configuration suitable for adduct formation can result; consider dependence on relative kinetic energy, impact parameter, relative orientation, and specific features in their intermolecular interaction potential.

For such encounters, description of the distortions which occur in their structures, particularly in the acid molecule.

Estimation of the probability for the redistribution of energy from vibrational and internal rotational modes in which large amplitudes are localized around the newly formed bond to modes in which large amplitudes appear in other parts of the molecules. Consider dependence of this stabilization on the detailed composition and geometry of the reactants.

Estimation of the probability for the exchange reactions: $AB_1 + B_2 \longrightarrow AB_2 + B_1$ and $A_1B + A_2 \longrightarrow A_2B + A_1$. Compare these rates with that of precipitation of AB_1 and A_1B.

Description of the formation of crystal embryos and nuclei, and of the rate of growth of the Lewis salt crystals. Consider possible re-evaporation of reactant species from these hot crystals because of insufficiently rapid transfer of the heat of condensation to the ambient gas.

Consider possible exchange reactions such as $(AB_1)_{solid} + B_2 \longrightarrow (AB_2)_{solid} + B_1$, on the surfaces of the hot crystals.

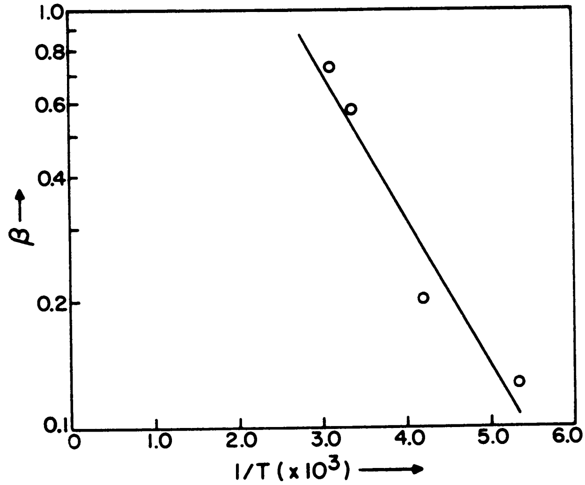

Figure 5. Plot of log $[K_a k_b/T]$ vs. reciprocal of absolute temperature

Acknowledgment

We express our sincere appreciation to the Office of Naval Research for the extended support given to this project. We are particularly thankful for the personal interest shown in our research efforts. We also thank the U. S. Army Research Office for providing travel funds to the Symposium on Boron-Nitrogen Chemistry (April 1963).

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Received May 31, 1963

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch004

The Solvolysis of Amineboranes

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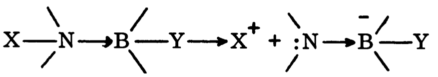
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch005

Amineboranes may react with proton-containing materials via several paths, depending on the structure of the amineborane and the properties of the attacking reagent. Protonolysis of the methylamineboranes in water solution probably proceeds by displacement of a BH_3 group when a proton attacks the amine nitrogen. In the reaction of pyridineboranes with 1-propanol a pyridine molecule is displaced by an incoming alcohol molecule. A third type of reaction involves the production of an amineboronium cation when a proton attacks a B-H bond directly. This occurs with pyridinediphenylboranes and water. Experimental evidence, resulting from a study of solvolysis rates of a number of amineboranes, is presented in support of the above mechanisms and correlated with structural features in the amineboranes.

Addition compounds of amines with borane, BH_3, or substituted boranes are of much interest because of the variety of ways in which these compounds conceivably may react. The heterolytic dissociation of the boron-nitrogen bond is one possibility; a number of other reactions seem possible and can be analyzed by a simple consideration of the electronic structure of the addition compounds. The formation of the dative nitrogen-boron bond amounts to a shift of electron density away from the nitrogen atom and toward the boron atom, and this effect should be transmitted to the bonds adjacent to the coordinate bond. Thus, reactions which remove positive ions from the nitrogen atom should be favored relative to the uncombined amine, and, similarly, removal of negative ions from boron should be made easier in the addition compound than in the free borane. Stated as a more general proposition, quaternization of the amine nitrogen facilitates the loss of any of the nitrogen substituents as Lewis acids, whereas quaternization of the boron atoms favors loss of any of the boron substituents as Lewis bases.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.



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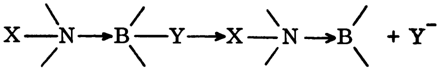
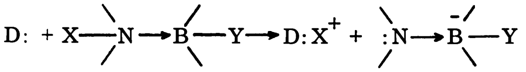


(2)

The degree of enhancement of reactivity in this sense would depend on the strength of the dative bond and on other factors which influence the electron density on the nitrogen and boron atoms.

However, simple acid-base dissociations leading to ionic products, as in Equations 1 and 2, may be rare in solution. Instead, another reactant or the solvent may participate in the dissociation step. Therefore, bimolecular reactions should be considered. In such reactions donor molecules (or nucleophiles) would be expected to attack at points where low electron density exists or can be generated by concurrent displacement of another base. Thus a nitrogen substituent or a boron atom could be attacked.



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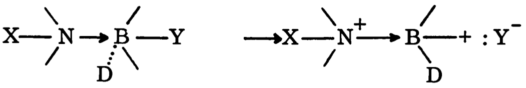
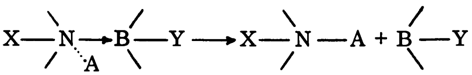


(4)

The result is, in Equation 3, the displacement of an aminobrate ion from substituent X. A particular example of the general reaction may be the conversion of the addition compounds of boron trichloride with secondary or primary amines to aminoboranes *(11)* or borazenes *(16)*, respectively. Here a tertiary amine aids the reaction by absorbing protons. In Equation 4, a base (Y^- or the amine) is displaced and a new substituent or boron appears. Examples of this reaction may be found — e.g., in simple amine displacements *(14)* or in the formation of the complex $(C_4H_9)_2BCl \cdot 2py$ *(8)*. It has been suggested *(7)* that this compound is the chloride salt of the ion $(C_4H_9)_2B(py)_2^+$, so that chloride ion has been displaced by pyridine.

By similar reasoning, the attack of acceptor molecules (electrophiles) could occur either at the nitrogen atom or at the electron-rich boron substituents. The first reaction would lead to the displacement of borane



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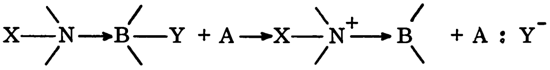


(6)

or another nitrogen substituent where the second reaction would produce loss of a boron substituent.

The various reaction schemes proposed above, taken singly or in combinations, appear adequate for a speculative explanation of many of the known reactions of amineboranes. But since hardly any reactions have been studied with the intent to gain detailed information about reaction paths, it has so far been difficult to establish the existence of the proposed reaction steps, to assess their relative speeds, and to determine the relation between structure and preferred modes of reaction. This paper presents new experimental results on the solvolysis of methylamineboranes and various pyridineboranes and discusses the mechanisms involved.

Experimental

Reaction of 1-Propanol with Pyridineboranes. A number of substituted pyridineboranes were prepared from the purified amines and diborane *(2, 6)*. Thermostated solutions of these in 1-propanol, from 0.01 to 0.10M in strength, were analyzed at measured intervals by the iodate method *(12)*. In some duplicate experiments the rate of hydrogen evolution was measured and gave substantially similar results. The measurements fit very well for a reaction which is first order in amineborane. The first-order rate constants were determined at five temperatures ranging from 0.01° to 65°C. The results are listed in Table I.

Table I. Reaction of Pyridineboranes with 1-Propanol

Arrhenius parameters for first-order rate constants and activation energies. $\log k = A - B/T$; k in sec.^{-1}

Pyridineborane	*A*	$B \times 10^{-3}$	$\Delta H^{\ddagger}$, *Kcal/Mole*
Pyridine	11.05	5.100	23.34
3-Methyl-	11.51	5.316	24.33
2-Ethyl-	12.32	5.240	23.98
2-Methyl-	11.59	5.143	23.54
4-Methyl-	12.13	5.576	25.52
2, 6-Dimethyl-	11.42	4.704	21.52
2, 4-Dimethyl-	11.43	5.213	23.86

Protonolysis of Dimethylamineborane. The reaction of the methylamineboranes in dilute aqueous acidic solutions proceeds quantitatively to produce the corresponding ammonium ion, boric acid, and hydrogen, according to the over-all equation

$$R_3NBH_3 + H_3O^+ + H_2O \rightarrow 2R_3NH^+ + B(OH)_3 + 3H_2$$

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch005

The progress of this reaction was followed as a function of time by recording the change in pH of the solution with a glass electrode and a Sargent recorder equipped with a resistance - matching adapter. The ionic strength was held constant at 0.10*M* with KCl and data were obtained for initial concentrations in the following ranges: HCl, 0.01 to 0.001*M*; R_3NBH_3, 0.005 to 0.001*M*. The temperature was controlled within 0.005° C. The data closely fit a rate law where the reaction is first order with respect to amineborane as well as to acid concentration, and this fit extends over at least two half lives. Rate data for at least five temperatures between room temperature and 50° C. led to the activation energies and parameters for the Arrhenius equation given in Table II.

Table II. Reaction of Methylamineboranes with Aqueous Acid

Arrhenius parameters for second order rate constants and activation energies. $\log k = A - B/T$; k in l. mole^{-1} . sec.$^{-1}$

Methylamineborane	*A*	$B \times 10^{-3}$	$\Delta H^{\ddagger}$, *Kcal./Mole*
Methyl	14.90	3.520	16.1
Dimethyl	14.38	4.637	21.2
Trimethyl	14.74	5.623	25.7

Discussion

The reaction of pyridineborane with 1-propanol in pure alcohol and in alcohol-water mixtures has been reported in some detail *(13)*. The variation of rate with dielectric constant, giving a linear log *k vs*. $(D-1)/2(D+1)$ plot with negative slope, indicated a decrease in polarity of the transition state relative to the ground state. This is consistent with the assumption that the nitrogen-boron bond is broken in the rate-determining step. The results reported here prove this assumption to be correct. From the data in Table I it is seen that the activation energy of the reaction in the series pyridineborane, 3-methylpyridineborane, 4-methylpyridineborane increases in the same way as the enthalpy of dissociation of the nitrogen-boron bond *(4)*. An increase in donor-acceptor bond strength should increase the electron density in the boron-hydrogen bond and make loss of hydride easier. Thus hydride loss in the rate-determining step would produce a trend opposite to the observed one and can be ruled out.

This result becomes more obvious yet from a consideration of steric effects of pyridine substituents. It has been demonstrated, for the pyridines at least, that the dissociation enthalpies of addition compounds with one Lewis acid are linearly related to the dissociation enthalpies of addition compounds with another Lewis acid *(4)*. This relation holds, provided that there are no steric interactions between donor and acceptor, or that the steric interactions acid 1 - donor and acid 2 - donor are the same.

In Figure 1 the activation energy for the propanolysis reaction is plotted *vs*. the enthalpy for the reaction $pyH^+ \cdot CH_3SO_3^- \longrightarrow py + CH_3SO_3H$ *(5)*. The points for pyridine, 3-methylpyridine, and 4-methylpyridine correspond to absence of steric effects and define the expected linear relation if the rate-determining step involves dissociation of the nitrogen-boron bond. Where there is 2-substitution on pyridine, the

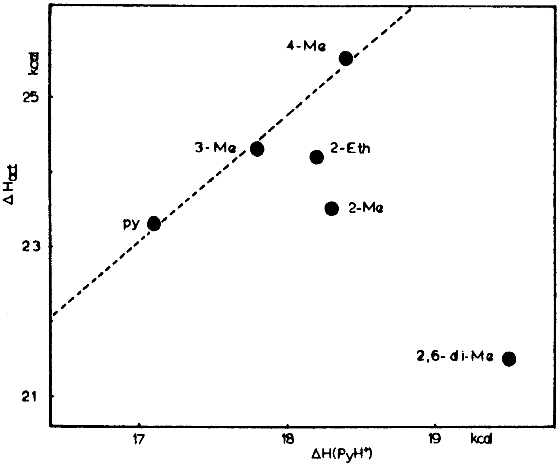


Figure 1. Activation energy for reaction of pyridineboranes with 1-propanol vs. dissociation enthalpy of pyridinium ions

activation energy is lower than expected because in the dissociation steric repulsions are relieved. The vertical distance from the straight line can be interpreted as a measure of the loss of strain energy in the transition state.

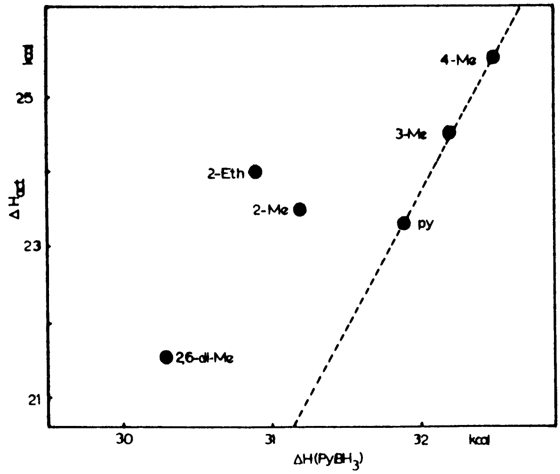
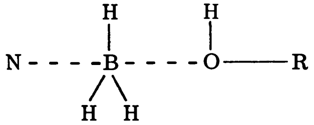


Figure 2. Activation energy for the reaction of pyridineboranes with 1-propanol vs. enthalpy of the reaction $PyH^+ + CH_3SO_3^-$ $Py + CH_3SO_3H$

In Figure 2 the activation energy is plotted *vs.* the enthalpy for the reaction py $BH_3 \longrightarrow$ py + BH_3. The latter enthalpies were calculated from the dissociation enthalpies into pyridine and B_2H_6 *(3)* and the estimated enthalpy of dissociation of diborane *(15)*. In this plot, the vertical deviation from the linear relation is in a direction opposite to the displacement in Figure 1. Thus the relief of strain on formation of the transition state from the pyridineboranes is smaller than the relief of strain when the pyridine borane is completely dissociated. It is therefore concluded that the transition state has a stretched nitrogen-boron bond. Since the activation energies are much lower than the enthalpies of dissociation into pyridine and borane, it is concluded that the transition state is stabilized by interaction with 1-propanol. A likely stabilized configuration is



$$\mathrm{N}{-}{-}{-}{-}\overset{\mathrm{H}}{\underset{\mathrm{H\ \ H}}{\mathrm{B}}}{-}{-}{-}{-}\overset{\mathrm{H}}{\mathrm{O}}\text{———}\mathrm{R}$$

The methylamineboranes also appear to react by stretching of the boron-nitrogen bond in the slow step, even though the reaction here is a protonolysis. We arrive at this conclusion through the observation that the activation energies for protonolysis follow the same order as the dissociation enthalpies *(1, 10, 12)*. This would seem to rule out attack at the boron-hydrogen bond (hydride loss) and would imply attack at the nitrogen atom instead with concurrent displacement of a BH_3 group.

The two modes of solvolysis mentioned above are to be contrasted with the observation that pyridinediphenylboranes are hydrolyzed in an essentially different fashion *(9)*. Here deuterium - isotope effects indicated that water attacks the boron-hydrogen bond; increases in electron density on boron, produced by suitable substitution on the benzene rings, promoted the reaction rate. In this reaction system the transition state for the hydride-loss reaction is electronically analogous to triphenylmethylcarbonium ion, distorted by the close proximity of a hydride group.

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Received May 17, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch005

Vibrational Frequencies, Assignments, and Force Constants for Some Compounds Containing Boron-Nitrogen Dative Bonds

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

The experimental results from spectroscopic investigations of a number of Lewis complexes having the general formula R_3NBX_3, where R may be H, D, or CH_3, X may be H, D, F, Cl, or Br, and B may be B^{10} or B^{11}, are used to establish the normal range for the stretching frequency of the B-N dative bond between 700 and 800 cm.$^{-1}$ Normal coordinate calculations for the A_1 class frequencies substantiate the experimental conclusions. However, they also show coupling of the B-N motion with other skeletal motions usually present which, in some molecules, may be extensive enough to alter the character of the vibration completely and prevent any simple correlation between frequency and bond strength.

Lewis complexes containing a boron-nitrogen dative bond frequently result from the attack of nitrogen bases on boron hydrides. Many other examples may be prepared by direct combination of the acid and base or by displacement methods, the total number of such compounds now known being appreciable. Spectroscopic studies may be expected to yield information of considerable interest regarding the boron-nitrogen bond in these complexes, which in turn should be related to other chemical and physical properties.

Investigations in this laboratory in recent years have been directed toward the complete study of a number of simpler Lewis complexes, many of them containing B-N dative bonds. Principal attention has been given to establishing correct assignments of fundamentals through the extensive use of isotopic substitution. At the present time, normal coordinate calculations are being carried out to confirm assignments and provide force constant data.

Experimental investigations of the following compounds are reasonably complete and are discussed in the present paper: H_3NBH_3, $(CH_3)H_2NBH_3$, $(CH_3)_2HNBH_3$, $(CH_3)_3NBH_3$, H_3NBF_3, $(CH_3)_3NBCl_3$, and $(CH_3)_3NBBr_3$. In all cases except the mono- and dimethylamine complexes, isotopic species containing 92% or more B^{10} have been studied. In addition, deuterium substitution has been employed wherever possible with both boron isotopes. Methods of preparation and purification

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

have followed established procedures described in the literature with identification of the material by powder x-ray diffraction or other physical properties. Purity has been judged by analysis, comparison of physical properties with those reported, and comparison of spectra obtained after successive repurification.

Spectra have been obtained by both Raman and infrared methods, with the former being more useful for the less stable compounds. Methods for obtaining Raman spectra of samples dissolved in liquid ammonia or liquefied dimethyl ether below the boiling point have been described *(4, 12)*. A technique employing multilayer interference filters similar to that used by Brandmuller *(3)* and Tobin *(13)* has also been used successfully for obtaining spectra of as little as 50 mg. of crystalline powders at any temperature between -170° and 25°C.

Infrared spectra have been obtained using Perkin-Elmer Model 21 spectrophotometers equipped with calcium fluoride, sodium chloride, or potassium bromide prisms. Samples usually have been in the form of mulls or dispersed in KBr disks, although in some cases, thin films have been formed by evaporation onto windows maintained at low temperatures. Some variations of peak positions with temperature or physical state have been noted, but in most cases these have not been large and well within the normal range.

Several spectra from at least two different samples have been obtained for practically all compounds. The data tabulated represent averages from all spectra obtained for the state specified.

Discussion

An important feature of the vibrational spectrum of a Lewis complex is the frequency associated with the dative bond, since this quantity may be expected to give some sort of measure of the strength of the bond and thus be of chemical significance. However, the stretching motion of this bond may be expected to couple to a greater or lesser extent with other skeletal motions to give frequencies which may or may not be typical group frequencies. It therefore is important not only to establish the range within which the uncoupled frequency occurs but also to study environmental factors which result in coupling, thus causing the dative bond frequency to appear outside its normal range.

In the case of boron-nitrogen dative bonds, spectroscopic studies appearing in the literature have assigned a value falling in the range between about 980 and 1250 $cm.^{-1}$ to the dative bond frequency. These investigations have dealt with H_3NBF_3 *(6)*, $C_5H_5NBF_3$ *(7)*, $H_3NB(CH_3)_3$ *(5)*, and $(CH_3)_3NBH_3$ *(9)*, but none have included B^{10} isotopic varieties. The spectral range cited is comparable to that established for other single bond frequencies — e.g., the C-N frequencies found in aliphatic amines — but the frequency typical of a single bond should represent a rough upper limit for the dative bond frequency, since the bond strength in a less stable complex may be expected to fall significantly below that for a normal single bond. In addition, considerable variation in the C-N frequencies occurs in the lower amines where coupling effects are important. Similar effects may be expected in complexes. The work discussed in the present paper was undertaken to provide additional data, so that reliable assignments could be made.

Ammonia-Borane. The complex, H_3NBH_3, contains only hydrogen atoms in addition to the boron and nitrogen, and consequently relatively little coupling with the dative bond frequency is to be expected. This molecule thus presents the most favorable case for the unequivocal identification of a frequency associated with the B-N dative bond. Since hydrogen attached to nitrogen does not exchange readily with hydrogen bonded to boron, it is possible to prepare deuterated derivatives by substitution on either or both ends of the molecule. Five isotopic species preserving the full symmetry of the molecule have been prepared and studied by taking advantage of this fact, four containing natural boron and the fifth containing 96% B^{10}. At the time this compound was studied, the techniques for obtaining Raman spectra of powders has not been developed and the samples were examined in liquid ammonia or liquid dimethyl ether solution. Solvent interference in certain regions of the spectrum prevented identification of some of the fundamentals. However, a moderately intense characteristic polarized line was observed in the spectra of all species in the general region between 700 and 800 cm.$^{-1}$ This frequency is too low for any of the hydrogen motions and the polarization property eliminates the possibility that it is one of the E rocking motions of the end groups.

Confirmation of the assignment to the B-N motion may be obtained from the isotope effects *(11)*. If the complex is considered as a pseudo-diatomic molecule with rigid end groups, the ratio of the B-N frequencies of two isotopic molecules should be equal to the square root of the ratio of the reduced masses, the end groups being considered as point masses. The agreement between the frequency ratio and the reduced mass ratio shown in Table I is well within the degree of approximation. Normal coordinate calculations for the A_1 species discussed later also support this assignment and confirm the absence of coupling effects (see Table VI). The fundamentals of H_3NBH_3 are given in Table II.

Table I. Comparison of B-N Stretching Frequency in Isotopic Varieties of Ammonia-Borane (in Liquid NH_3 or ND_3 Solution)

Compound	*νB-N, Cm.$^{-1}$*	ν^*/ν	$\sqrt{\mu/\mu^*}$
H_3NBH_3	787	--	--
H_3NBD_3	737	0.94	0.95
D_3NBH_3	754	0.96	0.97
D_3NBD_3	708	0.90	0.91
$D_3NB^{10}D_3$	713	0.91	0.93

One other observation in the spectrum of H_3NBH_3 is worthy of note. Both liquid NH_3 and liquid $(CH_3)_2O$ were employed as solvents in the investigations. The positions of solute bands were found not to differ significantly between the two solvents, except in the case of the band assigned to the B-N stretching frequency. This band, which had its maximum at 755 cm.$^{-1}$ in the ether solution, shifted about 30 cm.$^{-1}$ to 787 cm.$^{-1}$ in liquid ammonia. This indicates a significant solute-solvent interaction with one of the solvents, probably with ammonia, since it is known that the related complex, H_3NBF_3, does form solvates with NH_3. This interaction does not appear to act through the hydrogens of the solute, since the N-D frequencies of the solute in liquid ND_3 agreed within a few cm.$^{-1}$ with the positions of the same bands in dimethyl ether. This comparison in the case of NH_3 complex was not possible because of solvent interference.

Methylamine-Boranes. These complexes are similar in many respects to the H_3NBH_3 complex, and their Raman spectra were obtained in the same solvents, liquid NH_3 and $(CH_3)_2O$. Only the normal species of mono- and dimethylamine-borane were studied, but spectra of the trimethylamine complex were obtained from both normal and B^{10}-enriched varieties. Data for the $(CH_3)_3NBD_3$ complex prepared with natural boron are available in the literature *(9)*. The spectra of the methylamine complexes exhibited more frequencies in the skeletal region than in the case of H_3NBH_3 because of the contributions of the methyl groups. However, in each case, a band was clearly observed near the position of the band assigned to the B-N frequency in H_3NBH_3. These bands were similar in intensity and polarization to the ammonia-borane band and also showed the same marked solvent sensitivity. No other band in the amine complexes showed this sensitivity. In the trimethylamine complex, substitution of B^{10} shifted this band from 667 cm.$^{-1}$ in the normal complex to 676 cm.$^{-1}$ in the isotopic, further supporting the assignment to the B-N frequency. The band at 1250 cm.$^{-1}$ previously assigned to this mode *(9)* was not significantly affected by B^{10} substitution. The assignment of fundamentals exclusive of the methyl group frequencies for the trimethylamine complex is given in Table II.

Table II. Assignments of Fundamental Frequencies for Ammonia- and Trimethylamine-Boranes, R_3NBH_3, in Liquid Ammonia Solution

Class	$H_3NB^{11}H_3$, *Cm.*$^{-1}$	$(CH_3)_3NB^{11}H_3$, *Cm.*$^{-1}$	*Assignment*
A_1	3183	850	N-R stretch
	1060	341	N-R deformation
	2285	2270	B-H stretch
	1175	1169	B-H deformation
	787	667	B-N stretch
E	3309	1003	N-R stretch
	1600	431	N-R deformation
	2316	2330	B-H stretch
	1026	1117	B-H deformation
	-	915	BH_3 rock
	-	-	NR_3 rock

Preliminary normal coordinate calculations for $(CH_3)_3NBH_3$ based on the use of a point mass for the methyl groups confirm the proposed assignments and also indicate a significant coupling between the symmetric NC_3 and B-N stretching modes (Table VI). This coupling in part accounts for the low value of the B-N frequency, although the value calculated for the B-N force constant is also less than in ammonia-borane (Table VII). No calculations have been carried out for the mono- and dimethylamine complexes, but the frequency assigned to the B-N stretch shows a continuous and regular decrease with the number of methyl groups attached to the nitrogen. This relationship, shown in Figure 1, suggests a progressive decrease in the B-N force constant, probably accompanied by a simultaneous increase in the coupling between the B-N and N-C stretching modes.

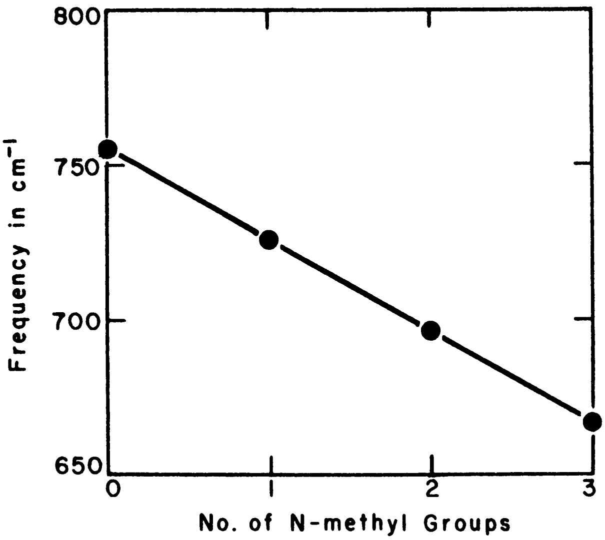

Figure 1. B-N stretching frequency in methylamine-boranes as a function of number of methyl groups on nitrogen (dimethyl ether solution)

Ammonia-Boron Trifluoride. This compound is the simplest of the boron halide complexes and vibrational data have been reported for both the hydrogen and deuterium species *(2, 6)*. In the present work, four isotopic varieties involving hydrogen, deuterium, B^{10}, and B^{11} were prepared and studied. Forty-two of the 44 fundamentals have been observed and assigned, the results for the normal hydrogen compound being listed in Table III. In general, the data agree well with the results reported by Goubeau and Mitschelen *(6)* but less well with the results of Russian workers *(2)*.

Extensive normal coordinate calculations have been carried out for this complex using all data *(10)*. The results show that the symmetric B-N and BF_3 stretching modes are strongly coupled to give two skeletal

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

motions which are best described as out-of-phase and in-phase $N-B-F_3$ stretching motions (Table II). The higher, out-of-phase mode assigned at 1002 cm.$^{-1}$ involves a significant motion of the boron atom and shows a corresponding B^{10} isotopic shift. The in-phase or breathing mode is assigned at 741 cm.$^{-1}$ and is insensitive to the boron mass. As a result of the mixing, neither frequency can be considered to give a true indication of the strength of the B-N dative bond. The calculated force constant, however, is significantly greater than in the case of the BH_3 complexes (Table VII).

Trimethylamine-Boron-Halides. Complexes of trimethylamine with boron trifluoride, boron trichloride, and boron tribromide, both natural and enriched B^{10} varieties, have been prepared and their Raman spectra obtained in the solid state and their infrared spectra from samples dispersed in KBr disks. Assignments have been made which are consistent with the results from the preceding complexes and with data available in the literature. These are given in Table III for the normal compounds. At the present time, normal coordinate calculations are incomplete for the halide complexes, and confirmation of assignments from this source is not available.

The spectrum of the BF_3 complex showed a marked similarity to that of H_3NBF_3 with appropriate allowance for the additional frequencies contributed by the methyl groups. Preliminary calculations for the A_1 frequencies, treating the methyl groups as point masses, have been carried out for this molecule and indicate that a situation similar to that of H_3NBF_3 with respect to mixing of the BF_3 and B-N stretching

Table III. Assignments of Fundamental Frequencies for Some Lewis Complexes of the Type R_3NBX_3^{a} (Cm.$^{-1}$)

	H_3NBF_3	Me_3NBF_3	Me_3NBCl_3	Me_3NBBr_3	*Assignment*
A_1	3275	847	828	828	N-R stretch
	1437	(340)	(332)	(318)	N-R deform.
	741^b	927^b	536	516	B-X stretch
	513	547	(383)	275	B-X deform.
	1002^b	697^b	748	689	B-N stretch
E	3335	991	968	960	N-R stretch
	1596	428	445	434	N-R deform.
	875	-	183	184	NR_3 rock
	1133	1142	755	677	B-X stretch
	471	458	(270)	194	B-X deform.
	316	(323)	-	-	BX_3 rock

( ) Assignments uncertain.

a/ Frequencies for compounds prepared from natural isotopic mixture of boron.

b/ Mixed modes; description not accurate.

modes is present — namely, that these couple to give two group frequencies involving the N-B-F_3 framework. The higher, out-of-phase mode again shows a significant sensitivity to the boron mass, shifting from 927 to 952 cm.$^{-1}$ on B^{10} substitution while the in-phase mode assigned at 697 cm.$^{-1}$ is much less affected. Both frequencies are appreciably lower than the corresponding one in the ammonia complex and the B-N force constant also appears to be lower, in analogy to the corresponding borane complexes.

In the case of the trichloride and tribromide complexes, the frequencies associated with the BX_3 group are sufficiently low that less coupling with the B-N frequency is to be expected and the latter should appear in a typical position. It has been assigned to bands at 748 and 689 cm.$^{-1}$ in the spectra of the respective complexes, the former comparable to the B-N frequency of H_3NBH_3 in dimethyl ether solution at 755 cm.$^{-1}$ Both frequencies shifted about 20 cm.$^{-1}$ on B^{10} substitution, as would be expected.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

Normal Coordinate Calculations

If the methyl groups are considered rigid and approximated by point masses, the preceding complexes, with the exception of the mono- and dimethylamine-boranes, all have the common formula, Y_3 X-ZW_3 , with either a known or probable C_{3v} symmetry. Normal coordinate calculations based on these assumptions have been exceedingly valuable in establishing the nature of the vibrational mode accompanying specific frequencies, in addition to providing data valuable for comparative purposes.

Numerical computations have been carried out on an IBM 7090 computer using an iterative least squares procedures and the standard GF method of Wilson. The program is essentially similar to several machine programs for the calculation of force constants which have been described recently; the papers by Overend and Scherer *(8)* and Aldous and Mills *(1)* may be cited particularly. Symmetry force constants were selected as the basis for the calculations, rather than the constants of a more specialized potential function such as the Urey-Bradley, since it was felt they were of more fundamental significance and could be directly related to the assigned frequencies. Although the total number of such constants is relatively large for an Y_3 X-ZW_3 molecule— viz., 15 for the A_1 class and 21 for the E class— sufficient isotopic data were available so that the full problem was determinate in the case of H_3NBH_3 and H_3NBF_3 . For the other molecules, it was reasoned that the off-diagonal elements of the F matrix connecting symmetry coordinates relating to opposite ends of the molecule could reasonably be expected to be small and insensitive to most frequencies. Such constants were constrained to zero in initial calculations and then later their influence on the frequency fit was examined while the principal constants were constrained to their final values. In general, the frequency fit was only slightly improved in this second step and the values of these off-diagonal constants remained small.

Full details of the computational program will be published elsewhere. In brief, for each symmetry class, individual secular equations for each molecular species of a particular complex in the form

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

$(GF)L = L\lambda$ are solved for the eigenvalues, λ, and the eigenvector matrix, L. The L matrices for all species are then used to construct a composite Jacobian matrix, J, with elements of the form $(\delta\lambda_i/\delta F_{jk})$ which is used in the least squares equation, $J'WJF = J'W\Delta\lambda$, to calculate a vector of corrections, ΔF, to the initial values of the force constants. In this equation W is a weight matrix and $\Delta\lambda$ is a vector of differences between experimental and calculated eigenvalues. The corrected values of the force constants obtained in this way are used as the starting point of a new cycle and the iteration is continued until no further improvement in eigenvalues results. A similar process is carried out for the other symmetry class.

Table IV. Symmetry Coordinates for R_3NBX_3 Type Complexes

Bond	*Angles*
r = N-R	α = R-N-R
T = B-N	β = R-N-B
d = B-X	γ = X-B-N
	δ = X-B-X

A_1 Species

$$S_1 = a(\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 = a(\Delta d_1 + \Delta d_2 + \Delta d_3)$$

$$S_3 = T$$

$$S_4 = c[f(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$$

$$S_5 = c[f(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3) - (\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3)]$$

E Species

$$S_7 = b(\Delta r_2 - \Delta r_3)$$

$$S_8 = b(\Delta d_2 - \Delta d_3)$$

$$S_9 = b(\Delta\alpha_3 - \Delta\alpha_1)$$

$$S_{10} = b(\Delta\delta_3 - \Delta\delta_1)$$

$$S_{11} = b(\Delta\beta_2 - \Delta\beta_3)$$

$$S_{12} = b(\Delta\gamma_2 - \Delta\gamma_3)$$

a, b, c, f = normalization constants.

In the three cases for which results are given in Table V, the final average deviations between the observed and calculated A_1 frequencies were in the range of 1 to 3 cm.$^{-1}$, or a few tenths of 1%. No calcula-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

tions have been carried out as yet in which the observed frequencies have been corrected for anharmonicity, and the extent to which such corrections will affect the force constants, particularly the off-diagonal force constants, is yet to be evaluated.

In addition to frequencies and force constants, the program also calculates the normalized eigenvectors, L, the dispersions of the force constants, and the distribution of the potential energy of a given frequency among the various symmetry coordinates. The dispersions of the force constants are calculated from the following equations, as given by error theory, where N is the number of experimental frequencies and N_c the number of force constants.

$$\sigma^2 = \Sigma w_i \cdot \Delta\lambda_i^2/N - N_c$$

$$\sigma(F_{ij}) = [\, J'WJ)_{ii}^{-1}]^{1/2} \cdot \sigma$$

Table V. Symmetry Force Constants and Dispersions for H_3NBH_3, $(CH_3)_3NBH_3$, and H_3NBF_3

A_1 Class (Md./A.)

	H_3NBH_3		$(CH_3)_3NBH_3$		H_3NBF_3	
Ident.	*Constant*	σ	*Constant*	σ	*Constant*	σ
F_{11}	5.38	0.10	4.85	0.01	5.77	0.06
F_{22}	3.02	0.03	2.87	0.02	7.02	0.00
F_{33}	2.90	0.00	2.36	0.00	4.14	0.19
F_{44}	0.52	0.00	0.65	0.00	0.72	0.02
F_{55}	0.57	0.01	0.56	0.07	1.34	0.00
F_{12}	0.04	0.04	0.09	-	0.00	0.00
F_{13}	0.00	0.00	0.01	-	0.00	0.03
F_{14}	-0.89	0.01	0.82	0.04	-0.81	0.13
F_{15}	0.00	0.02	-0.05	-	0.00	0.00
F_{23}	0.01	0.00	0.00	-	-0.23	0.45
F_{24}	0.03	0.01	-0.01	-	0.29	0.16
F_{25}	0.11	0.00	-0.20	0.01	1.24	0.00
F_{34}	-0.24	0.00	-0.24	0.00	0.01	0.00
F_{35}	-0.37	0.01	-0.35	0.07	-1.02	0.02
F_{45}	0.02	0.02	0.00	-	-0.01	0.29

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

At the present time, the elements of the weight matrix, W, have been taken proportional to $1/\nu^2$ with no attempt to adjust the weights to reflect experimental uncertainty in band positions. The dispersions, therefore, reflect primarily the latitude within which the force constants may be adjusted without significantly affecting the frequency fit — i. e., the intrinsic uncertainty within which the constants may be determined. The potential energy distributions in symmetry coordinate space provide information about the form of the normal coordinates, as do the eigenvectors. However, the potential energy distributions appear to provide a somewhat better indication of the extent to which various symmetry coordinates are mixed in a mode characterized by a given frequency.

Although most of the off-diagonal force constants assumed only small values in the calculations, some reached an appreciable magnitude. Since the associated dispersions of these constants were much

Table VI. Potential Energy Distribution in Symmetry Coordinate Space for A_1 Class Frequencies

Frequency, Cm.$^{-1}$					*Coordinate Description*
		H_3NBF_3			
3275	*1437*	*1002*	*741*	*513*	
0.92	0.08	0.00	0.00	0.00	N-H stretch
0.08	0.86	0.00	0.04	0.02	N-H deform.
0.00	0.05	0.59	0.31	0.05	B-N stretch
0.00	0.01	0.50	0.50	-0.01	B-F stretch
0.00	0.00	-0.09	0.15	0.94	B-F deform.
		H_3NBH_3			
3183	*2285*	*1175*	*1060*	*787*	
0.92	0.00	0.00	0.08	0.00	N-H stretch
0.00	1.00	0.00	0.00	0.00	B-H stretch
0.00	0.00	1.01	0.01	-0.02	B-H deform.
0.08	0.00	0.01	0.92	-0.01	N-H deform.
0.00	0.00	-0.02	-0.02	1.03	B-N stretch
		$(CH_3)_3NBH_3$			
2270	*1169*	*850*	*667*	*341*	
0.97	0.03	0.00	0.00	0.00	B-H stretch
0.03	0.99	-0.01	-0.02	0.00	B-H deform.
0.00	0.00	0.76	0.26	-0.02	C-N stretch
0.00	-0.02	0.32	0.64	0.05	B-N stretch
0.00	0.00	-0.08	0.12	0.96	N-C deform.

less than their magnitude, one must assume that these constants are significant in the fitting process and, consequently, should be included. It is likely that the magnitude of these off-diagonal constants may be relatively sensitive to uncertainties in the problem contributed by neglect of anharmonicity and lack of knowledge of the exact geometry. However, the arbitrary constraint of all off-diagonal constants to zero introduces a degree of artificiality into the problem which significantly reduces confidence in the values of the diagonal constants.

Although symmetry force constants are closely associated with the frequencies, they are somewhat less directly related to the chemical features of the molecule, the simpler valence force constants relating to bond stretching and bond deformation being more easily understood. Unfortunately, as is well known, the symmetry force constants cannot be resolved into the full set of valence force constants without making specific assumptions with regard to some of the valence force constants. However, certain of the valence force constants can be solved for uniquely and the values thus obtained are of interest, particularly since they are of the bond stretching type and thus provide information concerning the strength of a given bond. Valence force constants for those complexes for which calculations have been carried out are listed in Table VII. Since the data do not include all of the molecules which have been studied experimentally, detailed comparisons do not appear justified. However, the values of the constants listed are reasonable and in accord with what might be expected from a knowledge of the chemical behavior of the compounds.

TABLE VII. Valence Force Constants of R_3NBX_3 Complexes (Md./A.)

	H_3NBF_3	H_3NBH_3	Me_3NBH_3
f_{BN},	4.14	2.90	2.36
f_{BX}	6.73	2.88	2.7
f_{NR}	5.80	5.66	(4.8)
f_{rr}	-0.018	1.140	--
f_{xx}	0.144	0.073	--
f_{rx}	0.000	(0.1)	--
f'_{rx}	-0.010	(0.1)	--
$f_{r,BN}$	0.000	0.000	0.006
$f_{x,BN}$	-0.135	0.003	0.001

Acknowledgment

The support of the National Science Foundation in the various investigations from which this article has been derived is gratefully acknowledged. The experimental data have been obtained principally by C. L. Cluff and R. L. Amster and are discussed in detail in their doctoral dissertations.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

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Received May 17, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch006

7

Vibration Spectra and Structural Problems of Some Aminoboranes

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch007

The range of the BN-stretching frequencies and their coupling with the vibrations of adjacent bonds are discussed for monoaminoboranes with varying substitution. The decrease of the BN frequency by the introduction of phenyl groups on the nitrogen atom must be explained by a decrease in the BN force constant. The different resonance structures causing this change in the bond order as well as their dependence on steric strain are discussed, combining Raman, infrared, and ultraviolet spectroscopic data. The available observations suggest that a cis-configuration of two phenyl groups on the BN bond is unfavorable.

The molecular symmetry of a compound can be determined with the aid of its vibration spectrum, which also may permit a calculation or estimate of some bond force constants. Since the complete assignment of vibrational spectra with many frequencies is very difficult, the interpretation of spectra is often restricted to vibrations of selected bonds or bond angles. However, the coupling between different vibrations can change the value of a special group frequency. This depends on the modes and values of frequencies which belong to the same symmetry species. Therefore coupling influences on more or less characteristic vibrations must be studied, either by comparison of different spectra with varying substituents on the characteristic group, or by frequency calculation of the isolated group frequencies on the one side and of a complete set of coupled frequencies on the other.

The present paper deals with the assignment of vibrations of the BN linkage and of adjacent bonds or bond angles in aminoboranes, and also draws some conclusions concerning the bond order of the BN linkage and its dependence on steric influences.

For some aminoboranes of the type X_2BNR_2 ($X = CH_3$, Cl, or Br and $R = H$ or CH_3) a coplanar configuration of trigonal sp^2 bonds for both B and N atoms was evidenced by the interpretation of vibration spectra *(5, 9)*. When substituents X and R of these aminoboranes are single atoms or can be regarded as nearly rigid groups with respect to the other vibrations of the molecule, the grouping X_2BNR_2 exhibits

Table I. Symmetric Vibrations

	$\delta_s BX_2$	$\delta_s NC_2$	$\nu_s BX_2$	$\nu_s NC_2$
$(CH_3)_2BNH_2$	318		710	
$(CH_3)_2BND_2$	?		687	
$(CH_3)_2BN(CH_3)_2$	255?	433	645	990
$Cl_2BN(CH_3)_2$	257	391	530	923
$Br_2BN(CH_3)_2$	167	316	480	867

All frequencies in $cm.^{-1}$

Table II. Raman and Infrared

Raman	*Infrared*	
220 m-s		$\delta_S BCl_2$
305 m		
410 w		
448 m-s		$\delta C_6, A_1$
540 m		$\nu_S BCl_2$
620 m		$\delta C_6, B_1$
	695 s	$\gamma C_6, B_2$
770 m-w	765 s	$\gamma CH, B_2$
800 m	790 m	$\nu_2 N\text{-}C_6, A_1$
840 w	835 vw	$\gamma CH, A_2$
	905 m-w	$\gamma CH, B_2$
920 vs	925 vs	$\nu_{as}\,{}_{10}BCl_2$
950 ?	955 m	$\nu_{as}\ BCl_2$
	980 vw	$\gamma CH, B_2$
1005 vs	1000 m-w	$\nu C_6, A_1$
1030 W	1020 m	$\delta CH, A_1$

All frequencies in $cm.^{-1}$
s = strong, m = medium, w = weak, v = very.

the BN-stretching frequency and four other symmetrical vibrations. These five frequencies are presented for several aminoboranes in Table I.

It is apparent that the BN-stretching vibration varies only slightly within this series of compounds, and thus can be regarded as nearly characteristic. On the other hand the vibrations of substituents X and R against B and N shift over a wide spectral range, depending on the masses of the substituents and on the force constants. They also show a mutual coupling effect, since the $\nu_S NC_2$ shifts for more than 10% within the series Me_2BNM_2 - Cl_2BNMe_2 - Br_2BNMe_2, and likewise the $\nu_S BC_2$ decreases within the row Me_2BNH_2 - Me_2BND_2 - Me_2BNM_2

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch007

of Some Aminoboranes

$\delta_s ND_2$	νBN	$\delta_s NH_2$	$\nu_s ND_2$	$\nu_s NH_2$
	1447	1620		3460
1145	1470		2500	
	1525			
	1528			
	1516			

Spectrum of Liquid $Cl_2BN(Ph,Me)$

Raman	*Infrared*	
	1037 s	δNCH_3 ?
1077 w	1075 m-w	$\delta CH, B_1$
1125 m	1120 s	νNC ?
1160 m	1152 vw	$\delta CH, B_1$
1175 w	1172 w	$\delta CH, A_1$
1235 m	1235 s	$\nu_1 N\text{-}C_6, A_1$
	1280 w	$\delta CH, B_1$
	1310 vw	?
1402 m-s	1400 vs	νBN
1450 m	1450 m	$\delta NCH_3, \nu C_6, B_1$
1485 w	1480 w	δNCH_3 ?
1500 m-w	1500 vs	$\nu C_6, A_1$
1600 s	1595 s	$\nu C_6, A_1$ and B_1
3012 s	3005 s	νCH

($Me = CH_3$). A frequency calculation of the vibrations presented in Table I was performed, utilizing a valence-force potential function, a force constant $k_{BN} = 7.0$ mdyn. per A. for the BN bond, and appropriate force constants for the other bonds and bond angles, deduced from a similar calculation of $B(CH_3)_3$, BCl_3, BBr_3, and $HN(CH_3)_2$ *(2, 9)*. All calculated frequencies appeared in the same spectral range as those observed. This calculation illustrates that the increase in the BN stretching frequency from Me_2BNH_2 to Me_2BNMe_2 is mainly due to coupling effects. The force constant of the BN bonds in Table I does not change within the accuracy (about 5%) of the calculation.

In additional spectroscopic examinations the influence of phenyl substitution on the BN bond of aminoboranes was studied. From the vibration spectra of the aminoboranes $Me_2BN(H, Ph)$ and Cl_2BNPh_2 (Ph = phenyl) it was concluded that the BN stretching is much lower in these compounds than in the compounds referred to in Table I, and that it is observed at 1330 and 1378 $cm.^{-1}$ respectively *(3)*.

Similar assignments were later given for the BN stretch in other *N*-phenylated aminoboranes *(7, 12)*. In order to detect a possible influence of frequency coupling in this vibration, it was necessary to assign as many fundamentals of the investigated compounds as possible, utilizing both Raman and infrared data. The complete Raman and infrared spectrum of $Cl_2BN(Ph, Me)$ is presented in Table II as an example *(1)*. Several weak frequencies of the region from 1650 to 3000 $cm.^{-1}$, which certainly belong to harmonics of the fundamentals, are omitted.

The notation of the internal vibrations of the grouping $>N-C_6H_5$ within Table II is as follows: γ indicates an out-of-plane bending, δ an in-plane bending vibration; ν is a mode involving mostly a stretching of the bonds within the ring (νC_6) or adjacent to the ring ($\nu N-C_6$). Because of the strong coupling between the stretching vibration of the nitrogen atom against the C_6 group and a C_6 vibration (which should be expected near 1000 $cm.^{-1}$ without such coupling), these two vibrations are described as $\nu_1 N-C_6$ and $\nu_2 N-C_6$. The notation of symmetry species gives the symmetry properties of the $N-C_6H_5$ vibrations with respect to the group symmetry, C_{2v}, of monosubstituted benzene derivatives.

In order to get some information on the BN bond and the arrangement of the adjacent bonds, only consideration of the skeletal vibrations of these bonds and bond angles, respectively, is necessary. However, since the arguments for a reliable assignment are not sufficient in the region of skeletal bending modes below 600 $cm.^{-1}$, only the stretching vibrations of the BN and the adjacent bonds in some *N*-phenylated aminoboranes will be discussed (Table III). The vibration of the nitrogen atom against the C_6H_5 group is described by the two frequencies $\nu_1 N-C_6$ and $\nu_2 N-C_6$ mentioned above, accounting for its coupling with an C_6 vibration. The case is the same for the $B-C_6$ stretching vibration. The assignment of a νNC stretching vibration in Table III is not certain, since an exchange with a NCH_3-rocking vibration near 1030 $cm.^{-1}$ cannot be excluded.

This series of compounds shows only a small shift of the BN-stretching vibration, though the νBX_2 frequencies vary considerably

Table III. Some Stretching Vibrations of $Cl_2BN(Ph, Me)$, $Me_2BN(Ph, Me)$, and (Ph, Me)BN(Ph, Me) (1)

	$\nu_s BX_2$	$\nu_{as} BX_2$	$\nu_2 N-C_6$	νNC	$\nu_1 N-C_6$	νBN
$Cl_2BN(Ph, Me)$	540	925	800	1120	1235	1400
$Me_2BN(Ph, Me)$	665	1120	800	1120	1255	1385
(Ph, Me)BN(Ph, Me)	680	875, 1215	770 ?	1120	1250	1385

Frequencies in $cm.^{-1}$

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch007

with X. Therefore, the νBN in these compounds is as characteristic of the BN bond in *N*-phenylated aminoboranes as is the frequency near 1500 cm.$^{-1}$ in *N*-alkylated compounds. Contrary to this observation, the substitution of methyl groups by phenyl on the boron atom results in no significant change of the BN vibration, which can be seen from a comparison of the symmetrical stretching frequencies of the C_2BNC_2 grouping in Me_2BNMe_2 and Ph_2BNMe_2 *(1)* as illustrated in Table IV.

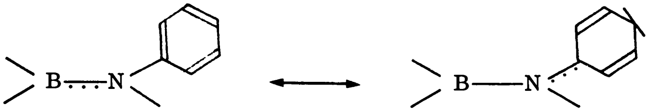
Table IV. Some Stretching Frequencies in Me_2BNMe_2 and Ph_2BNMe_2

	$\nu_S BC_2$	$\nu_S NC_2$	νBN
Me_2BNMe_2	645	990	1525 cm^{-1}
Ph_2BNMe_2	680, 1195	925	1519 cm^{-1}

The nearly constant value of νBN in the *B*-methyl- and *B*-phenyl-aminoboranes gives additional evidence that there is no remarkable change in the coupling effect of the substituent vibrations on the BN stretching, if a methyl substituent is exchanged against phenyl group. Therefore, one can estimate the ratio of the force constants k_{BN} in *N*-alkyaminoboranes and *N*-phenylaminoboranes with the relation

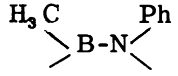
$$\frac{k_{BN\,(I)}}{k_{BN\,(II)}} = \frac{\nu^2_{BN\,(I)}}{\nu^2_{BN\,(II)}}$$

where (I) refers to values of alkylated and (II) to those of *N*-phenylated aminoboranes. Compared with $k_{BN} = 7.0$ mdyn. per A. in alkylated aminoboranes, the BN force constant in the *N*-phenylated derivatives amounts to only ~5.8 mdyn. per A. This decrease has already been explained by a competition of the boron atom and the phenyl group with respect to the lone electron pair of nitrogen, corresponding to a resonance with the structures



(3, 12)

Such a resonance favors coplanarity of the boron and nitrogen bonding planes with the C_6 ring. However, it could be reasoned from the ultraviolet spectrum of the borazine derivative $(MeBNPh)_3$ (which did not indicate any interaction between the π-electrons of the phenyl groups and the π-electrons of the BN bonds) that coplanarity of the bond planes is avoided *(4)*. This must be because of steric strains in the arrangement



$$\begin{matrix} H_3C & & Ph \\ & \rangle B\text{-}N\langle & \end{matrix}$$

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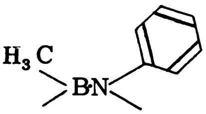
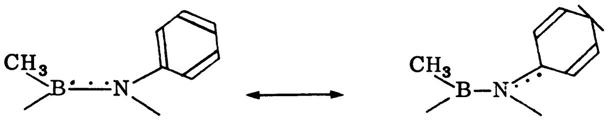
If in the aminoborane, $Me_2BN(Ph, Me)$, only the phenyl group is twisted out of the plane of the trigonal bonds on B and N, one should not expect a remarkable transfer of π-electrons from the BN bond to the phenyl group. However, examination of the ultraviolet spectrum of the aminoborane, $(Me)_2BN(Ph, Me)$, illustrated that interaction of the lone electron pair of nitrogen with the phenyl group is not canceled as in the borazine derivative, $(MeBNPh)_3$. A solution in heptane exhibited two absorption peaks in the region from 360 to 220 $m\mu$, which by their wavelength (λ = 292 and 242 $m\mu$) and their intensities (ϵ = 2000 and 10,500 liters per mole cm.) were very similar to those of methylaniline *(1)*. This difference in the behavior of an *N*-phenylated borazine can be explained as follows: In the borazine, $(MeBNPh)_3$, the lone pair of nitrogen participates to a larger degree in the BN bonds, so that the steric hindrance within the arrangement must be reduced by a twisting of the phenyl group about the N-C bond only. However, in the aminoborane the inductive and resonance effects between the phenyl group and the lone electron pair of the nitrogen are not overcome by its sharing of the BN-bond. As a consequence the steric strain should not only be avoided by a twisting of the phenyl group, but also by a small twisting about the BN bond. Therefore, the resonance energies of both structures are somewhat decreased.

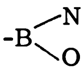




Some further observations confirmed this concept of steric influences on the bond order in *N*-phenylated aminoboranes very well. Within the series Cl_2BNMe_2 – $Cl_2BN(Ph, Me)_2$ – Cl_2BNPh_2 the BN stretching shifts from 1528 to 1400 and 1378 cm^{-1} Most of the decrease occurs at the first stage, though it is to be expected that two phenyl groups on the nitrogen should withdraw the lone electron pair much more strongly than would only one group. However, it can easily be seen from molecular models of the Cl_2BNPh_2 that the steric hindrance between the two phenyl groups requires much twisting about the NC bonds and the steric strain between the phenyl groups and the Cl atoms is diminished. Thus a smaller twist about the BN bond is necessary to account for the rest, which therefore may diminish the withdrawing effect of the second phenyl group. If there are bulkier groups on the boron atom, the steric strain should again be very large. This is to be expected for Ph_2BNPh_2 and $Ph_2BN(Ph, Me)$, because the phenyl rings on boron tend to be coplanar with the boron bonds. [(For $PhBCl_2$ such coplanarity has already been established *(8)*.] The infrared absorptions of $Ph_2BN(Ph, Me)$, studied in connection with other aminoboranes of the type $X_2BN(Ph, Me)$, could be assigned in some spectral regions by a comparison with the spectra of

Ph_2BNMe_2 and $Me_2BN(Ph, Me)$ *(1)*. In the frequency region of 1300 to 1400 cm^{-1}, where the BN stretching was expected, the most intensive band occurred at 1315 and not at 1385 cm^{-1} as in other aminoboranes of this type. This indicates a further weakening of the BN bond, to be expected because of steric considerations.

In the aminoboranes, (Ph, Me)BN(Ph, Me), the two phenyl groups on the BN bond could be in either cis- or trans- position *(10)*. The referenced steric strain and its relation to the resonance energy led to an expectation of higher stability for the trans isomer. As anticipated, the assignment of the vibration spectrum of (Ph, Me)BN(Ph, Me) revealed that in view of the configuration on the BN bond only one structure was present in any appreciable degree *(1)*. The stretching vibrations of the BN and the adjacent bonds have been given in Table III. In the case of an equilibrium between cis and trans modification, more frequencies have to be expected than are recorded.

In search for an aminoborane where the steric strain of the possible rotational isomers would not differ as much as in (Ph, Me)BN(Ph, Me), the compound (phenylmethylamino)methylethoxyborane, $(MeC_2H_5O)BN(Ph, Me)$, was prepared *(1)*. Because of many frequencies observed in the region of the  stretching vibrations, the vibration spectrum of the compound was not very helpful in detecting cis-trans isomers. However, the NMR spectrum of the substance clearly showed an equilibrium of two configurations (in a ratio of about 10 to 1), since the signals attributed to the NCH_3 and BCH_3 groups were both accompanied by a satellite of lower intensity. An analogous observation was described by Kubo for the compound (Cl, Me)BN(Ph, Me) and by Brey for (Ph, benzyl)BN(benzyl, Me) *(6, 11)*. At room temperature the rates of the rotational isomers within these three compounds are very different, which again shows the great influence of steric strain on the stability of the structures.

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Received June 6, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch008

8

Theoretical Investigations on Boron-Nitrogen Molecules

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A method previously applied to the study of hydrocarbon conformations is here used to investigate a variety of conformational problems in boron-nitrogen chemistry. Barriers and isomerization energies as well as charge distributions are presented for many simple boron-nitrogen molecules of the borazane, aminoborane, and borazarobenzene types. The usual resonance picture of the B-N bond is highly misleading, and the nitrogen always carries a larger negative net charge.

Recently we have developed an extended Hückel LCAO-MO (linear combination of atomic orbitals - molecular orbital) method which allows one to make a surprisingly good guess at the wave functions of medium sized molecules *(11)*. The procedure makes no initial distinction between aromatics and aliphatics, or between organic and inorganic molecules. In the first application of the theory we performed calculations on nearly all simple hydrocarbons and were able to describe semiquantitatively a wide variety of phenomena such as barriers to internal rotation, cis-trans isomerism, and the relative roles of σ and π frameworks in aromatics. In this contribution we have extended our calculations to a wide variety of compounds involving boron and nitrogen, a field where theoretical work has been nearly absent and which because of its rapidly developing nature offers an unsurpassed opportunity for a theorist to stick out his neck and make some predictions. In what follows we present some of the results of these calculations, the details of which will be published elsewhere.

One important point should be made initially: The line between molecules that do in fact exist and those that do not is rather thin for the theorist today. Stability of molecules is a thermodynamic property and one could never on the basis of a theoretical calculation make the positive statement that a particular molecule should be stable, without having performed a calculation on all molecules which could be possible decomposition or reaction products. With the present state of the art any calculation would have to be approximate; one is then faced with the possibility of erroneous conclusions due to a different degree of goodness of calculations for the molecule and its components.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Let us illustrate this with an example. We can calculate that HBNH is stable with respect to B + N + 2H. This does not imply that it exists for any reasonable length of time, for it may be unstable with respect to $BN+H_2$ or $B_3N_3H_6$. Moreover, it is conceivable that a calculation on $BN + H_2$ or $B_3N_3H_6$ could be "worse" than one on HBNH, and we would be led to predict stability where none exists. I dwell on this point so that when a statement is made below, attributing stability to such and such a molecule, it will be understood that the claim should be augmented with a disclaimer expressing the above ideas. I would also like to apologize for my unfamiliarity with what molecules have or have not been synthesized.

Method of Calculation

Details of the automated program are given in previous papers *(11)*. A molecular orbital is computed as a linear combination of atomic orbitals, with a basis set consisting of 2*s* and 2*p* Slater orbitals on B, N, and C and 1*s* on H. (The program is equipped to handle all first-row elements, but calculations have been carried out only with B, N, C, and H so far.) The set of Hückel equations

$$\sum_i (H_{ij} - ES_{ij})C_{ij} = 0 \qquad j = 1,2,3, \ldots$$

is solved with all interactions and overlaps retained. The H_{ii} are chosen as valence state ionization potentials, the values used being essentially those of Skinner and Pritchard *(18, 20)*.

	$H_{ii}(2s)$, E.V.	$H_{ii}(2p)$, E.V.	$H_{ii}(H\ 1s)$, E.V.
B	−15.2	−8.5	−13.6
C	−21.4	−11.4	
N	−26.0	−13.4	

The parameters for nitrogen are an average of the two common N valence states (sp^4, s^2p^3). The H_{ij} are approximated by the relation

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

with $K = 1.75$. Energies and wave functions are calculated and the latter subjected to a Mulliken population analysis *(16)*, yielding gross atomic populations or net charges, and overlap populations. The latter are analogs of bond orders in the simple Hückel theory. From some previous work on hydrocarbons the coordinates of a large number of saturated and unsaturated molecules were available, constructed with C—C 1.54 A., C=C 1.34 A., C—C aromatic 1.40 A., and C–H 1.10 A., tetrahedral angles at unstrained aliphatic carbons, and 120° HCH angles in olefins. Convenience dictated the use of these geometries in our calculations on boron-nitrogen compounds, though we are well aware that a B—N single bond distance is about 0.05 A. longer than the value used. Borazane and aminoborane were processed with more realistic B—N, B—H, N—H distances as well as with some different

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assumptions regarding the N valence state. It was found that energetic relationships and qualitative charge distributions were fairly insensitive to these changes.

Polarity of the B—N Bond

In Figure 1 we show the results of the population analysis for borazane, aminoborane, and borazine, and for comparison give similar diagrams for the analogous carbon compounds. It is apparent that in each case the nitrogen is much more negative than the boron. For borazane there is a net transfer of 0.43 electron from the ammonia moiety to the borane, but the nitrogen still remains negative at the expense of its hydrogens. In aminoborane, in the π system 0.23 electron is transferred from N to B, but the effect in the σ system is reversed and the total charge transfer is 0.28 electron from B to N. In borazine the calculations show 0.27 π electron transferred from N to B, but again the greater electronegativity of the nitrogen overrides this, so that in the total charge distribution the nitrogen is negative. The top-filled orbitals in aminoborane and borazine are σ type.

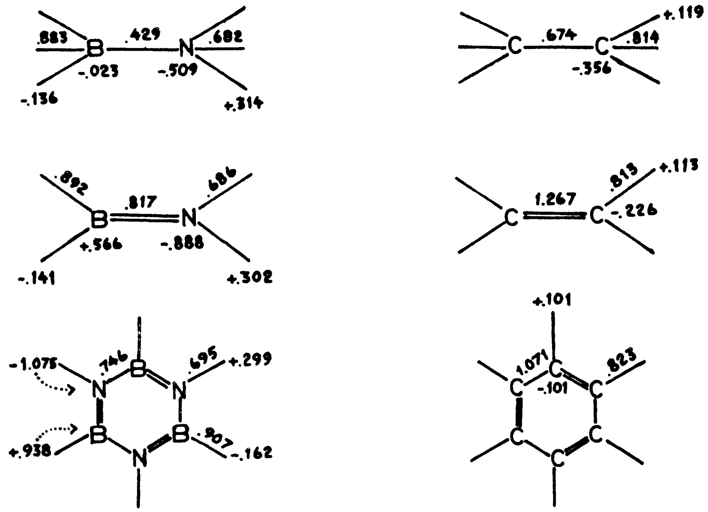

Figure 1. Population analysis of wave functions for borazane, aminoborane, and borazine compared to ethane, ethylene, benzene
Signed quantities are net charges, unsigned numbers Mulliken overlap populations

Now for some 30 years people have been writing resonance structures for B—N compounds which imply charge transfer from N to B. While this is certainly true in the π system, the total charge distribution in fact certainly shows the opposite effect in aminoboranes and borazine, but not in borazane. To my knowledge the only workers who fully recognize the possibility of this have been Becher *(2)*, Goubeau *(10)*, and Coates and Livingstone *(8)*. Becher measured the dipole moments of some methyl-substituted borazanes and aminoboranes and concluded that the aminoborane B—N bond moment was close to zero. While our calculation actually indicates that this moment has the direc-

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tion B→N, Becher's conclusions and ours agree that in all B—N compounds the nitrogen bears a larger negative net charge than the boron. I would like therefore to enter an earnest plea for the abandonment of the misleading formulation of $B^- - N^+$ and a re-examination of the reactions of B—N compounds in view of the fact that a better picture of the charge distribution is $B^+ - N^-$.

Borazanes and Aminoboranes

In Figure 2 we show the calculated charge distributions in some simple borazanes and aminoboranes. As usual with simple LCAO-MO calculations, these no doubt exaggerate somewhat the distribution of electrons. The qualitative conclusions of an examination of various stereochemical problems for these molecules are given below.

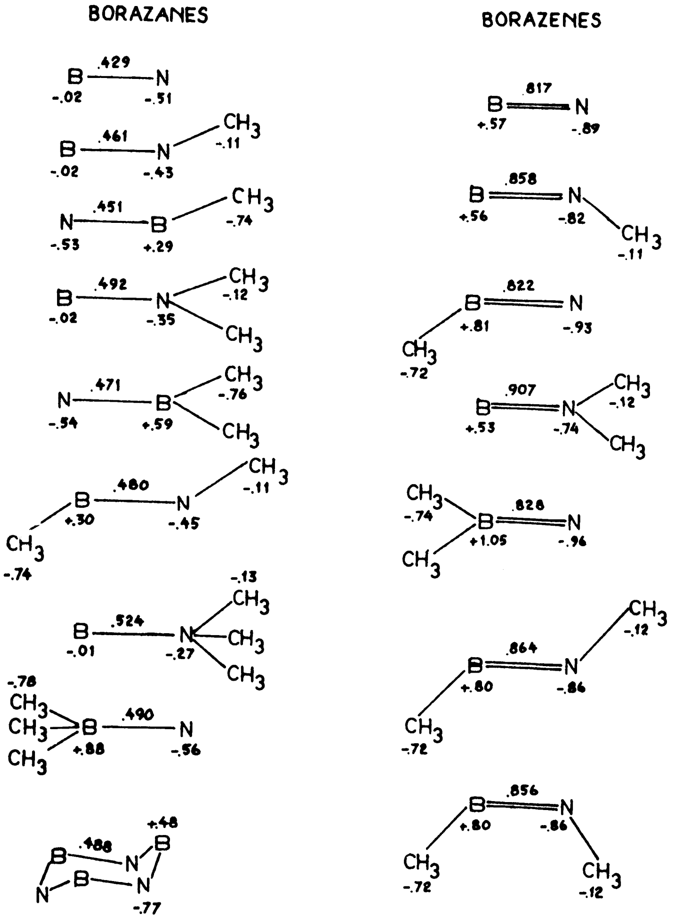

Figure 2. Charge distributions in some borazanes and borazenes
Only B-N overlap populations are shown. Charge next to CH_3 refers to C charge only; charges on H are not shown

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1. The barrier to internal rotation in borazane is predicted to be in the region of 1.5 kcal. per mole in favor of the staggered form.

2. It would be interesting to look in the vacuum ultraviolet spectra of the borazanes for the internal charge transfer transition corresponding to an electron being excited from the B—N bonding orbital (charge mainly on N) to the B—N antibonding orbital (charge mainly on B). Our calculations show that this transition should most conveniently be observed in *N*-trimethylborazanes, though there may be some difficulty in obtaining a spectrum, since a nearby transition involves excitation of B—H bonding electrons with probable ensuing bond fracture. Several charge transfer transitions might be observable in the aminoboranes.

3. The barrier to rotation in aminoborane is estimated to be near 10 kcal. per mole, very much less than the corresponding ethylene barrier. For (dimethylamino)borane this torsional barrier is somewhat greater, for (amino)dimethylborane about the same as in aminoborane. Tentatively we find that in the excited charge transfer state corresponding to a $\pi \rightarrow \pi^*$ excitation, the molecule still prefers a planar disposition in contrast to ethylene, which favors a D_{2d} geometry for the related state *(17)*. The first $\sigma \rightarrow \pi^*$ excited state prefers a twisted molecule. The order of magniture of the calculated aminoborane barrier appears to be correct *(4)*.

4. In *N*-methyl-*B*-methylborazane, the energy difference between the *gauche* and *trans* arrangements is calculated to be very similar to that in the hydrocarbon analog, *n*-butane, but the potential maximum corresponding to a methyl group on B eclipsing a hydrogen on N is expected to be of much higher energy in the B—N compound.

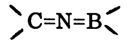
5. The isomerization energy of *cis*- to *trans*-(methylamino)methylborane is expected to be similar to that of *cis*- to *trans*-2-butene. A less certain result is that the heat of formation of (amino)dimethylborane should be very close to that of *cis*-(methylamino)methylborane, while the (dimethylamino) borane - *trans*-(methylamino)methylborane isomerization energy should be greater than that of the isobutylene-*trans*-2-butene pair.

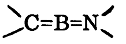
6. Buttlar, Gaines, and Schaeffer's *(7)* hypothesis that the boat-chair equilibrium in cyclotriborazane might not be as unfavorable to the boat form as it is in cyclohexane has been confirmed. The boat-chair difference in the former compound has been calculated at about one half of the corresponding cyclohexane energy difference. Moreover, ΔE between axial and equatorial methyl cyclotriborazane is predicted to be less than the corresponding energy in cyclohexane for *N*-methyl, more for *B*-methyl. This is in agreement with the evidence quoted by the above authors. Incidentally, the N hydrogen in piperidine is predicted to favor the axial location, the B hydrogen even more so in the as yet unsynthesized cyclic $(CH_2)_5BH$ (planar configurations at B and N have not yet been examined). Cyclodiborazane is expected to be much more resistant to distortions from planarity than cyclobutane.

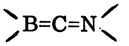
7. Calculations were performed for cis and trans conformations of isomeric analogs of butadiene, with the atom arrangements

1	2	3	4
B=N-B=N	B=N-N=B	N=B-B=N	B=B-N=N

These are arranged in order of calculated decreasing stability, left to right. In each case the trans conformation is favored, and as expected from a simple charge model, the cis-trans energy difference is less than that in butadiene for 1 and 4, and more for 2. Surprisingly, the calculation shows a very small difference between the cis and trans forms of 3. Derivatives of 1, 2, and 3 are known. The following allene analogs are arranged in order of decreasing stability.







Isocyanate boranes can be considered derivatives of the first of these.

8. Lappert and Majumdar report the synthesis of the first $(BHNH)_2$ derivative *(14)*. Since the carbon analog, cyclobutadiene, is of considerable interest, we have looked at the conformations of the BN compound in some detail. However, because of the presence of amino substituents on the borons of the actual molecule prepared by Lappert, no conclusions can be reached as to its conformation from our calculations on $(BHNH)_2$. We find that $(BHNH)_2$ prefers a planar arrangement of atoms, and with little deviation, if any at all, from a square arrangement. The study is not yet complete, since we have examined so far only distortions of the B—N ring. If we consider the π-electron system of this molecule, we find that the two states which would be degenerate in cyclobutadiene are split considerably. Here the charge transfer transition (corresponding to an excitation from one of the above-mentioned levels to the other) is forbidden, but two allowed $\pi \rightarrow \pi^*$ transitions, close in energy, should be found in the molecular ultraviolet spectrum.

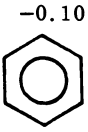
9. In connection with the question of the conformation of the recently synthesized derivatives of the B—N analog of cyclo-octatetraene *(22, 23)* we have examined a number of geometrical arrangements for C_8H_8 and $(BHNH)_4$. We find the tub configuration favored for both, and relative to this conformation the cubane arrangement is more favorable for $(BHNH)_4$ than for C_8H_8. The anion and dianion of cyclooctatetraene are found to prefer the planar geometry, in agreement with NMR and ESR evidence *(12, 13, 21)*; it is an interesting conclusion of the calculation that it predicts retention of tub geometry for the hypothetical $(BHNH)_4^-$ and approximately equal energies for tub and planar $(BHNH)_4^{-2}$.

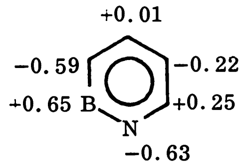
10. In the equilibrium conformation of propylene one of the methyl hydrogens eclipses the double bond. A calculation shows that this is also likely to be the equilibrium geometry in (amino)methylborane, but that in (methylamino)borane the methyl hydrogens will be staggered with respect to the B—N bond.

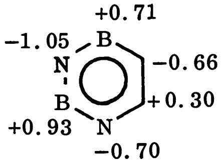
11. A general observation independent of our calculations can be made on steric problems where a BH_2 or BH_3 group is involved. These groups will generally cause greater steric problems than a corresponding methylene or methyl group, since not only are the B-H bonds longer, but, because of the ordering of electronegativities, hydrogens bonded to B acquire considerable negative charge. The converse statement is applicable to NH_2 and NH_3 groups.

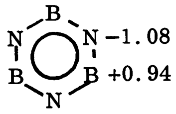
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch008

We have performed LCAO-MO calculations for both the σ and π electron systems of benzene, the three borazarobenzenes, 11 diboradiazarobenzenes, and the three triboratriazarobenzenes. In general the energy of the σ electrons emerged as a function only of the number of various bonds involved, while the π energy varied considerably. Dewar's conjecture regarding the relative stabilities of the borazarobenzenes *(9)* is confirmed — i.e., in order of decreasing thermochemical stability we have 2,1- , 4,1- , 3,1-borazarobenzene. The most stable of the diboradiazarobenzenes is the isomer 2,4-dibora-1,3-diazarobenzene, followed by 4,6-dibora-1,3-diazarobenzene. In general, isomers with B—B or N—N bonds are unfavored. Of the triboratriazarobenzenes, borazine is easily the most stable. Total charge distributions are shown for the most stable isomer of each class:









The calculation shows also that borazarene and 2,4-dibora-1,3-diazarobenzene are much less stable than either borazine or benzene. One general principle emerges: B and N "like" to come adjacent into a molecule, and if a molecule already has positions of alternating negative and positive charge density, a very stable B—N compound would be one with a nitrogen in what was originally the most negative site in the molecule, and a boron in an adjacent most positive location.

We have also calculated wave functions for 2,1-borazaronaphthalene, 10,9-borazarophenanthrene, and some of the other compounds synthesized by Dewar and coworkers. The qualitative features of the charge distributions are in agreement with those calculated by Dewar *(9)*. We show only for comparison in Figure 3 the results of our population analysis for the π and σ + π systems of 2,1-borazaronaphthalene.

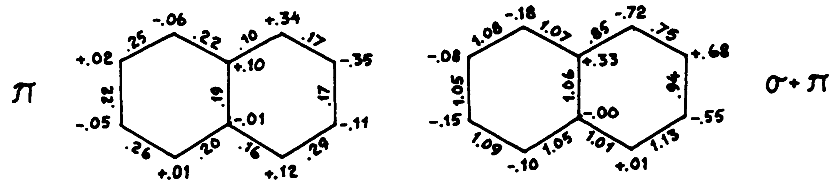
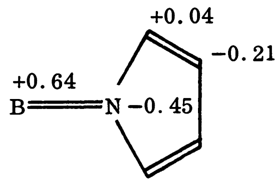
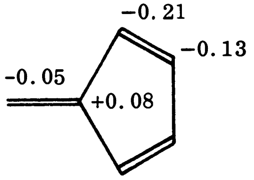


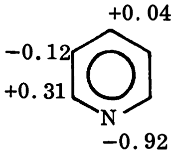
Figure 3. Population analysis for π and σ + π frameworks in 2,1-borazaronaphthalene

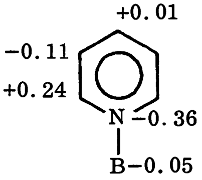
Becher has synthesized a substituted B—N analog of fulvene *(3)*. The calculated σ + π charge distribution in $C_4H_4NBH_2$ (6,1-borazarofulvene ?) is shown below, along with the corresponding fulvene diagram. While fulvene is experimentally and in theory about 30 kcal. per mole less stable than benzene, the borazarofulvene is calculated to be about 25 kcal. per mole more stable than the isomeric borazarene.

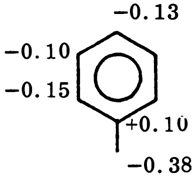




We have also performed a series of calculations on some substituted pyridine boranes. Charge distributions for pyridine, pyridine-borane, and toluene are shown below.



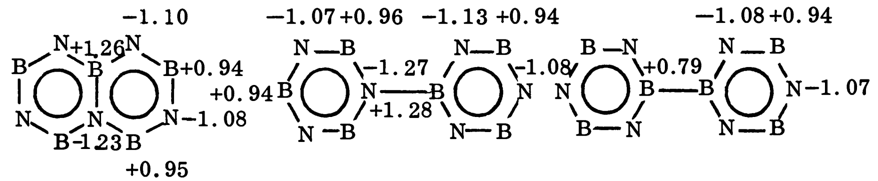




The calculations show that, of the picolines, 2-methylpyridine is most stable, followed by 4-, 3-, while in the adduct the 4-methylpyridine borane is favored, followed by 3-, 2-. On examination of the reaction forming the pyridine boranes, the net result is that the heat of formation of the 2-methylpyridine adduct is substantially greater than that of the 3- or 4-methyl isomer — in agreement with the measured heats of Brown and Domash *(6)*.

In the charge distribution for pyridine borane, the charge on carbons 3, 4, and 5 is changed little from pyridine, while the charge on positions 2 and 6 is increased. In this calculation coordination with BH_3 not only produces charge transfer from N to B but also from N to its neighboring carbons (the N—C overlap population is also greater in $PyBH_3$). Probably this is an artifact of the calculation which uses the same parameters for N in pyridine and pyridine borane. Though the $PyBH_3$ NMR anomaly as reported by Brey *et al.* *(4)* can be explained on the basis of our computation, invoking increased ring currents, the calculation is probably not reliable here and the explanation for the deshielding at select positions in the pyridine borane lies in the removal of N paramagnetic anisotropy. A similar effect is noted in pyridinium cation *(1, 19)*.

We have also examined the per-*B*, *N*-naphthalene *(15)* and per-*B*,*N*-biphenyl linked via a B—N bond *(15)* and a B—B bond *(5)*. In the naphthalene analog the gap between filled and unfilled orbitals is large and only slightly smaller than in borazine. This situation, very different from the benzene-naphthalene progression, indicates the trend which culminates in a colorless hexagonal boron nitride. The B—N linked biphenyl analog prefers to be slightly twisted, while the B—B linked compound should be planar. (The *N*-hydrogens which are the source of steric difficulties in the planar form are positively charged and thus appear "smaller.") The total charge distributions shown below may be of some interest when NMR spectra of these compounds are examined.



Acknowledgment

I thank W. N. Lipscomb and M. E. Lesk for discussions and computational assistance, and the Harvard Computation Center supported by the National Science Foundation for computation time. M. F. Lappert kindly brought to my attention the work of Coates and Livingstone.

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Received May 14, 1963.

The Force Constants of Various Boron-Nitrogen Compounds

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch009

Force constants of various types of boron-nitrogen compounds have been calculated from the vibrational spectra on the basis of a valence force model. The force constant, k_{BN}, of amine boranes was found to be about 3.5 mdyn. per A., whereas for aminoboranes a value of 7.0 mdyn. per A. was obtained. For borazines calculated values for k_{BN} range from 5.7 to 6.3 mdyn. per A. Some general features of the force constants — for instance, their utilization to evaluate bond orders — are discussed.

Force constants can be derived from the vibrational spectra. In particular, the valence force constants, like the bond distances, permit an evaluation of the bond relations between atom pairs. The present results agree with the results of experimental determination of bond distances. Table I recalls the results for the classical element combinations C-C, C-N, and C-O. With increasing order of the bond, the bond distance decreases and the force constants increase. However, whereas changes in the bond distance have a range of about 30%, the change in the force constants amounts to about 200%. This is a definite advantage of the force constants.

Force constants can be calculated from the vibrational spectra on the basis of certain models. The models utilized are extremely important for the results and also for a possible comparison of different force constants: Results are comparable only if they are obtained with similar models. A further very important basis for obtaining force constants is the assignment of the found frequencies to the vibrations of the molecule. The following discussion is based on the so-called "valence force model." In using this model it is assumed that forces exist along the valence bonds of the atoms as well as other forces which preserve the bond angles, and that there are reciprocal forces effective between the valence forces and those forces preserving the angles.

The values of those force constants which preserve the angles are normally in the neighborhood of 10 to 20% of the valence force constants; the reciprocal force constants range from negative values to 30%. Therefore the latter are at present mostly responsible for any uncertainty. Basically one has to assume an error of about 5 to 10% in the valence force constants, even if similar models are utilized. The

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

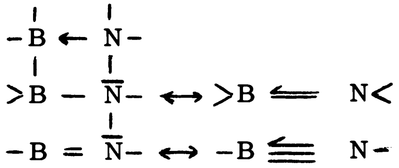
Table I. Distances and Valence Force Constants of Various Atom Groupings of C-C, C-N, and C-O

	r A-B, A.	ω *Cm*$^{-1}$	f_{ab}, *Mdyn/A.*
$H_3C - CH_3$	1.543	992	4.5
$H_2C = CH_2$	1.339	1621	9.7
$HC \equiv CH$	1.205	1974	15.7
$H_3C - NH_2$	1.475	1044	5.0
$H_2C = NH$	1.24	1660	10.0
$HC \equiv N$	1.156	2100	17.5
$H_3C - OH$	1.428	1050	5.2
$H_2C = O$	1.230	1750	10.3
$C = O$	1.128	2155	18.8

deviations obtained through assumption of harmonic vibrations are of only very limited importance, especially if atoms with an atomic weight over 10 are considered.

Calculations were made mainly according to the Wilson F-G matrix method. Mathematical work increases for more complicated molecules, but any mathematical operation is easily accomplished with modern computers. A particular difficulty of all calculations is caused by the large number of possible mathematical solutions. These can be limited, however, through the use of isotopes. In Stuttgart Fadini *(5)* has developed a calculating method which enables the calculations of force constants from frequencies without testing. In the following only valence force constants were used.

A. Stock and E. Wiberg identified three basic groups of boron-nitrogen compounds in analogy to the isoteric carbon compounds:



1. Amine borane $-\overset{|}{\underset{|}{B}} \leftarrow \overset{|}{\underset{|}{N}}-$
2. Aminoborane $>B - \overline{\underset{|}{N}}- \leftrightarrow >B \Leftarrow N<$
3. Borazine $-B = \overline{N}- \leftrightarrow -B \overset{\leftarrow}{\equiv} N-$

Of the last group, no monomeric compound has yet been isolated; they are known only in polymeric form. In the early fifties we began a spectroscopic investigation of the various classes of compounds in order to clarify the bonding situation for boron-nitrogen compounds, first, with the aid of the Raman effect, and later also with infrared spectra.

Amine Boranes

For the first group of compounds, amine boranes, which are addition compounds of nitrogen derivatives and boranes, the first (very simplified) calculations revealed values for f_{BN} in the neighborhood of about 3.5 mdyn. per A. Later calculations considered the effect of coupling and gave values which range from 2.5 to 3.1 mdyn. per A. [Table II and *(13)*].

Table II. Force Constants of Some Addition Compounds of Boron and Nitrogen Compounds

	$F_3B - NH_3$	$H_3B - NH_3$	$(H_3C)_3B\delta - NH_3$	$H_3B - NH_2NH_2$
k_{BN}, mdyn/A	3.08	2.91	2.48	2.46
r_{BN}	1.60		1.63	

These values differ about 20%. Since they are calculated with comparable models, these differences are beyond the normal limit of error. However, at present these differences will not be discussed. Nevertheless, it is interesting to compare the experimentally obtained values with those which are expected. For a calculation of these expected values, an empirical formula as given by Siebert *(12)* has been found very helpful:

$$k_{AB} = 7.20 \frac{Z_A \times Z_B}{n_A^3 \times \omega_B^3}$$

where Z = number of nuclear charges and n = main quant number of the bonding electrons.

This equation is valid to the first approximation for the sp^3 hybridization *(6)*. For demonstration purposes, the relationships between the various force constants of some nitrogen single bonds of a few elements of the first group of the periodic system are combined in Table III.

Table III. Force Constants of Various Nitrogen Single Bonds

	BeN	*BN*	*CN*	*NN*
According to Siebert	3.1	3.9	4.7	5.5
Exptl.	1.5	2.9	4.8	5.4
Difference, %	-52	-26	+2	-2

The experimental values of Table III are derived from $Cl_2Be \cdot 2HN(CH_3)_2$, $H_3B \cdot NH_3$, H_3CNH_2, and $[H_3NNH_3]^{+2}$. The values for CN and NN are in good agreement with the values calculated according to Siebert's method. The values for BN and especially for BeN are considerably below the values obtained by Siebert's method. These deviations are definitely beyond the normal limit of errors. The increasing deviation in the direction of beryllium can be considered confirmation that a systematic deviation of force constants towards increasing polarity of the bond occurs for these elements. In general, high polarity results in a pronounced weakening of the force constant. The polarity of the boron-nitrogen bond in these addition compounds is evidenced also by their high dipole moments.

Aminoboranes

The spectroscopic investigation of the second class of boron-nitrogen compounds — namely, the aminoboranes — by Becher *(2)* showed that an almost characteristic frequency in the neighborhood of 1400 to 1500

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch009

cm.$^{-1}$ can be assigned to the BN vibration. From these values a force constant, k_{BN}, of about 7.0 mdyn. per A. has been calculated. This value is far above those for addition compounds of the first type. Therefore the existence of a coordinative π-bonding was assumed. One obtains a certain similarity with ethylene derivatives, indicated unequivocally in these compounds by a tendency to polymerize. Because of the polarity of the bond, polymerization occurs easily, frequently leading to dimers, and less frequently to trimeric compounds. As indicated by the crystal structure investigation of $[Cl_2BN(CH_3)_2]_2$ *(9)*, a four-membered ring system, B_2N_2, exists in these dimers. The BN bond is influenced by the substituents which have an effect on the force constant and on the tendency to polymerize.

Trimeric Borazines

The next group of boron-nitrogen compounds to be considered is the trimeric borazines. Edsall and Crawford *(4)* calculated for this benzenelike substance a force constant $k_{BN} = 6.3$ mdyn. per A. This value is probably the upper limit, whereas the lower limit will be about 5.7. A wide variety of material was obtained from several investigators for this type of compound *(3, 10)*. The most important result is that ring vibrations, in contrast to the isosteric benzene derivatives, do not show the constance observed in the aromatic system. This indicates (in analogy to both other classes of boron-nitrogen compounds) that the influence of the mass of substituents, the coupling of vibrations of substituents with the ring vibrations, and the occurrence of mesomerism are of utmost importance. If one considers the strong infrared ring vibration near 1350 to 1500 cm.$^{-1}$ (compare Table IV), it is clear that for the interpretation of the relationships a change in the force constants in the B_3N_3 ring has to be assumed.

Table IV. ω_{Ring}

$(HNBF)_3$	1497		1517
$(HNBH)_3$		1465	
$(HNBCl)_3$	1442		1452
$(H_3CNBH)_3$	1412		1411
$(H_3C_2NBCH_3)_3$	1402		

On the basis of the highest value observed for the fluoro compounds, one has to assume that the highest force constant of a BN borazine ring system is obtained in these compounds. Very often a split of this infrared absorption is observed which has to be related to the presence of both boron isotopes ($^{11}B_3N_3$ 51%, $^{11}B_2{}^{10}BN_3$ 38%, $^{11}B^{10}B_2N_3$ 10%, $^{10}B_3N_3$ 1%). Deviation of k_{BN} in the borazines is probably in the neighborhood of 10%, as observed for the addition compounds.

If one assumes in these three types of compounds (as in the isoteric carbon derivatives) in first approximation the bond orders of 1, 1.5, and 2.0, one obtains an increase in the force constants with the bond order, just as in the corresponding carbon compounds (Figure 1). Thus

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch009

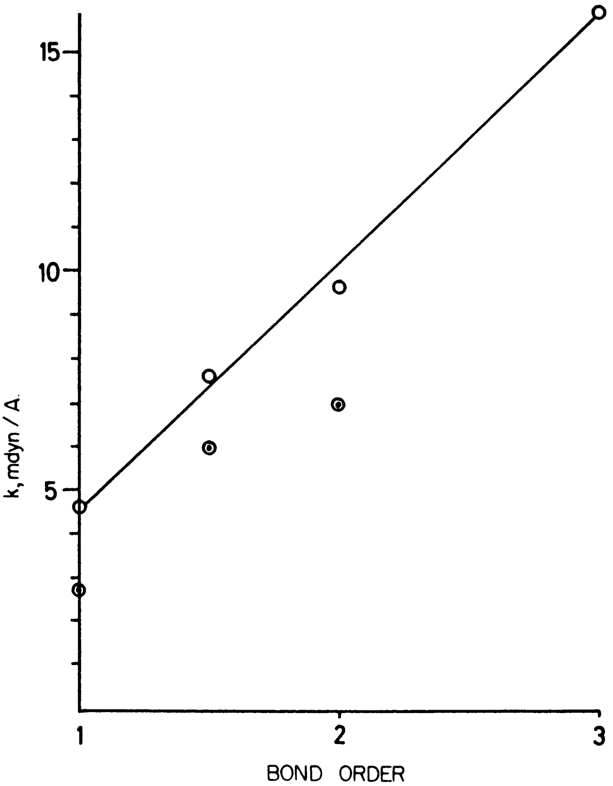


Figure 1. Comparison of the force constants CC-(O) and boron-nitrogen compounds (⊙)

force constants can be utilized for obtaining the bond order. Some examples are summarized in Table V. It is difficult to fix force constants for the normal single and the normal double bond. As a standard one can use either the experimental force constants of the addition compound, and then the value BO I is obtained, or a second value (Siebert's value) can be used, equal to a steady increase with the bond order, and then the for the addition compounds (as indicated earlier) are below the value of the normal single bonds. Independent of any standard is the fact that the values for f_{BN} range between a single and a double bond.

A comparison of these results with the corresponding ones of other element-boron bonds shows an interesting picture, illustrated in Table VI.

It is obvious that the experimental value for a boron-nitrogen single bond is too low, especially if compared with the experimental values for other element combinations. However, these combinations were taken from the high symmetrical compounds BX_4^-, a type of compound not known in the boron-nitrogen combination. The most important result, however, is that the boron-nitrogen combination at room temperature is capable of forming the highest bond orders. Of all element combinations of the boron, this is the only one which at room temperature obtains a value of nearly 2 for bond orders. The combination boron-oxygen and boron-fluorine have a value of approximately 1.4. During

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch009

Table V. Force Constants and Bond Orders

Substance	f_{BN}	*BO I*
$X_3B - NY_3$	2.8	1.0
$0_3B_3 - (NR_2)_3$	4.0	1.3
$R_2B - NCO$	5.8	1.7
$B - (NR_2)_3$	6.0	1.7
$H_3B_3 - (NH)_3$	6.3	1.8
$X_2B - N\,Y_2$	7.0	2.0
$B - N_2^{3-}$	7.0	2.0
B - N (band spectra)	8.3	2.3

the last few years we often tried to obtain boron-oxygen compounds of a higher bond order. Thus we tried to obtain salts of the dimethylboric acids *(7)*. In the course of these investigations, we observed that the ion disproportionates into trimethylborane and methylborates, which polymerize via addition of dimethylborates. However, other investigators have demonstrated within the last few years that in monomeric B_2O_3, B_2O_2, and HBO_2 very high force constants occur at high temperatures. Thus at high temperatures the maximum of the bond order is shifted from the boron-nitrogen bond to the boron-oxygen linkage. The boron-fluorine combination is never capable of forming a high bond order, because of the high polarity of the bonds.

If one compares the relationships between the boron-nitrogen bond with the combinations of nitrogen with other elements of the first row of the periodic system, as well as with elements of the second period (as indicated in Table VII), one obtains completely normal behavior. If one excludes the combination NF, which is not capable of forming higher bond orders (since too many electrons are present in this particular combination), the result is that combinations with strongly electronega-

Table VI. Force Constants of Various Element Combinations with Boron

	BC	*BN*	*BO*	*BF*
Single bond experimental	3.5	2.8	4.6	5.1
According to Siebert	3.5	3.9	4.5	5.1
Highest value at room temperature	3.6	7.0	6.3	7.2
Bond order at room temperature	1.1	1.8	1.4	1.4
Band spectra		8.3	13.5	7.7
Bond order		2.1	3.0	1.5

of Various Boron-Nitrogen Compounds

BO II		
0.72		
1.0	$^{-0}_{-0}B-\bar{N}R_2$	$^{-0}_{-0}B\quad NR_2$
1.5	$R_2B-\bar{N}=C=O$	$R_2B\quad N=C=O$
1.5	$(R_2N)_2B-NR_2$	$(R_2N)_2B-\bar{N}R_2$
1.6	$^{-BH}_{-BH}N-H$	$^{-BH}_{-BH}N-H$
1.8	$X_2B-\bar{N}Y_2$	$X_2B\quad NY_2$
1.8	$N=B=N^{3-}$	
2.1		

tive elements like oxygen, nitrogen, and carbon permit the formation of a triple bond. The CN compounds already show a strong tendency to polymerize, indicating the decrease in the stability of the multiple bonding. This effect is more pronounced in the boron-nitrogen compounds, which are capable only of forming double bonds. In addition they show a strong tendency for polymerization — i.e., instability. This tendency to polymerize is so strong that in compounds where one could expect a triple bond, only polymers are obtained. Finally, for beryllium only force constants which are far below the expected value of a single bond have been observed. All reactions which in boron chemistry lead to the formation of a double bond — for instance, the elimination of HCl of amine addition compounds according to the equation

$$Cl_2Be\cdot 2HN(CH_3)_2 \xrightarrow{-HCl} ClBeN(CH_3)_2\cdot NH(CH_3)_2$$

do not show the expected course of the reaction even at very high temperatures (400° to 500°) *(11)*. With decreasing electronegativity of a bond partner of the nitrogen, the capability to form multiple bondings

Table VII. Force Constants and Bond Orders of Various Nitrogen Bonds With Various Elements

	BeN	*BN*	*CN*	*NN*	*ON*
Siebert	3.1	3.9	4.7	5.5	6.3
I max	1.5	7.0	17.9	22.6	23.9
Bond order I	0.5	1.8	3.0	3.0	3

	MgN	*AlN*	*SiN*	*PN*	*SN*
Siebert	2.8	3.1	3.3	3.6	3.7
I max		1.9	4.1	6.1	12.4
Bond order I		0.6	1.2	1.7	3

towards nitrogen decreases. The boron-nitrogen combination is exactly on the border, with an electronegativity value of 2.0.

The second period of the periodic system presents a similar picture. Again chlorine is not considered, and sulfur with approximately the same electronegativity as carbon is able to form a triple bond. In the case of phosphorus, if one neglects the PN molecule, which is stable only at very high temperatures (although it has a high force constant and a high bond order), the highest force constant for the PN combination is obtained for the $(CH_3)_3P\text{-}NH_2{}^+$ with the value 6.1 *(1)*. This force constant corresponds to a bond order of 1.7. In analogy to the boron (which has approximately the same electronegativity as phosphorus), phosphorus compounds polymerize very easily, as illustrated by the examples F_3PNCH_3 and Cl_3PNCH_3 *(8)*. In the case of silicon the tendency towards the formation of higher bond orders decreases rapidly, and aluminum corresponds in its behavior completely with that of beryllium. This short review indicates clearly that the boron-nitrogen bond readily falls in line with all the other nitrogen-bonded elements.

In analogy to the C-C bond, the boron-nitrogen bond is the border of those element combinations which are capable of multiple bonding, but in addition show a strong tendency to polymerize. This fact is responsible to a large degree for the particular properties of boron-nitrogen compounds.

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Received July 24, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch009

LCAO-MO Calculations on Boron Compounds

I. Aminoboranes

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch010

The primary purpose of this study was to reproduce reported experimental observations for a series of heteroatomic boron compounds by simple LCAO-MO Hückel calculations, employing as input data only basic atomic or group parameters derived without reference to the particular molecular environments considered here. Hückel calculations for aminoboranes (using the four possible input parameter sets derivable from other molecules) were compared, point by point, with experimental observations of seven aspects of the behavior of aminoboranes upon substitution. Each experimental observation was correctly predicted. More important, the trend of the calculational results is insensitive to the choice among the input parameter sets.

Rigorous Pariser-Parr and Pople self-consistent field (SCF) calculations for borazines and heteroaromatic boron compounds have been reported *(2, 10)*. Calculations of this kind are tedious, expensive, and difficult, requiring elaborate computer programs and much computer time, as well as a fairly precise knowledge of the molecular geometries and bond distances of the compounds.

In view of the considerable success which the much simpler Hückel calculations have had in the field of organic π-systems, it was felt desirable to attempt to reproduce reported experimental observations for a series of heteroatomic boron compounds by theoretical calculations into which no preconceived notions of the molecular bonding to be expected were incorporated. Many new classes of boron heteroatomic compounds, some even previously unimagined, are being prepared today. To hope for success in developing Hückel procedures general enough to treat the planar portions of these boron-containing molecules (already discovered and as yet undiscovered), it is imperative to be able to use as input data only basic group parameters derived without reference to the molecular environment in which they later find themselves.

As preliminary preparation, linear combination of atomic orbitals-molecular orbital (LCAO-MO) calculations for a wide variety of heteroatomic boron compounds were performed by the Hückel technique.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

The main emphasis was placed on derivation and evaluation of input parameters, especially for substituent groups in such compounds as substituted borazines and boroxines, substituted heteroaromatic boron compounds, and substituted aminoboranes. An indication for the choice of input parameters and the theoretical justification for such choices was derived from earlier work on δ_K values *(6-9, 11)* [the effect of substituent groups on properties of free radicals and molecules of B, C, N, O, and S compounds].

The series of molecules chosen for comparison of calculated and observed molecular properties was the aminoboranes, RR'B-NR''R''', for which the molecular geometries are so imprecisely known that Pariser-Parr and Pople calculations are infeasible.

Details of Calculations

The Hückel calculational procedure for π-systems is described in standard texts on quantum chemistry *(4, 14)*.

The basic input elements are the diagonal Coulomb integrals, α, and the off-diagonal resonance integrals, β. α may be regarded as proportional to the effective valence state ionization potential of the π-electron and for heteroatoms $\alpha_X = \alpha_C + \delta_X \beta_{CC}$. β is arbitrarily assigned a value of 1.00 for the C-C bond in benzene (β_{CC}), and values of β for linkages of all other atom pairs are expressed as $\beta_{XY} = \eta_{XY} \beta_{CC}$, where η may be considered approximately proportional to the overlap integral, S_{XY}. The choice of values for δ and η has been the subject of numerous articles. For common atomic linkages and substituent groups a collection of "standard" values has been assembled *(12)*. For less common linkages, evaluation is often performed by fitting the results of a calculation for one such molecule to observed experimental results and then carrying the set of parameters so derived over to related compounds (hoping that the parameters remain fairly invariant). This was the procedure followed in the present study.

α_B and α_N had originally been evaluated by Mulliken *(13)* from consideration of borazine:

$$\alpha_B = \alpha_C - \beta_{CC}$$

$$\alpha_N = \alpha_C + \beta_{CC}$$

β_{BN} was evaluated by Kubo *(15)* as 0.87 β_{CC} from consideration of the BN overlap integral in borazine. β_{BN} had also been estimated as 0.57 β_{CC} by Dewar *(5)* by fitting the experimentally observed highest occupied molecular orbital of X, IX-borazarophenanthrene to the results of a calculation, using the above values for α_B and α_N. These two values for β_{BN} span approximately the range from almost neutral B-N to $B^- - N^+$. They should presumably bracket the value for β_{BN} in any intermediate situation. Consequently, calculations were carried out utilizing each of the above values of β_{BN} to ascertain the sensitivity of the results to a choice of β_{BN}.

All of the aminoboranes calculated in this study contained substituent groups on both the boron and nitrogen atoms. For that reason, it was necessary to consider how the integrals for substituent groups would be affected by substitution of these groups for an H on a B or N atom of a π-system, rather than for the H on a C atom of a π-system. Earlier

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch010

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research on δ_K values had shown that a substituent group produced an almost identical effect on the π-electron of boron, carbon, or nitrogen *(6-9,11)*. Therefore, it should be possible to utilize the standard Hückel parameters for the substituted methyl or phenyl groups on the B or N atoms of aminoborane.

There are two sets of parameters in current usage for substituent methyl groups. One includes an inductive effect of the methyl group on the atom to which it is attached *(1)*; the other does not *(3)*.

The trend of the calculational results is insensitive to the choice among the four input parameters sets. The experimental data are therefore compared to only one set of calculational results — that using $\beta_{BN} = 0.87\ \beta_{CC}$ with inclusion of an inductive effect due to the methyl group.

Results and Discussion

The experimental observations chosen to be reproduced by the theoretical calculations were those reported by Wyman, Niedenzu, and Dawson *(16)* in an article on the infrared spectra, bond character, and hydrolytic stabilities of organo-substituted aminoboranes.

The first observations to be compared with theoretical calculations concern the introduction of *N*-phenyl groups. There are three inferences from experimental data which can be checked against the calculational results presented in Table I, where data are so arranged that the substituent groups on the boron are kept constant while a phenyl group is substituted for a hydrogen atom or a methyl group on the nitrogen. Each point to be compared is listed separately, followed directly by the discussion pertaining to it.

Table I. *N*-Phenylaminoboranes

Substituents		*Bond Orders*		*Charges*	
N	*B*	*B-N*	*N-Ph*	*B*	*N*
Me, H	Me_2	0.5975	—	0.2930	1.7394
Ph, H	Me_2	0.5454	0.3811	0.2744	1.6755
Me, H	Me_2	0.5975	—	0.2930	1.7394
Me_2	Me_2	0.6017	—	0.3072	1.6904
Ph, Me	Me_2	0.5604	0.2806	0.2897	1.6538
Me_2	Ph, Me	0.5926	—	0.3885	1.6690
Ph, Me	Ph, Me	0.5397	0.3916	0.3711	1.6119
Me_2	2-(*p*-MePh)	0.5764	—	0.4662	1.6543
Ph_2	2-(*p*-MePh)	0.4853	0.3742	0.4428	1.5602

"Introduction of an *N*-phenyl group brings about considerable lowering of the double bond character of the B-N linkage" *(16)*. Results of the calculations clearly indicate a lowering in the B-N bond order upon substitution of a phenyl group for a hydrogen atom or a methyl group on nitrogen.

"This lowering of B-N bond order is caused by resonance interaction of the unshared electron pair of the nitrogen atom with the adjacent phenyl group" *(16)*. Two aspects of the calculations verify this conclusion: There is a sizable calculated N-Ph bond order, and the calculated electron density on nitrogen is lowered by introduction of a phenyl group onto the nitrogen.

"Such interaction results in increased electron deficiency at the boron atom" *(16)*. In each case the calculated electron density on the boron atom is lower for the *N*-phenyl-substituted compound.

The second set of observations concerns the introduction of *B*-aryl groups. The necessary calculations are presented in Table II.

Table II. *B*-Arylaminoboranes

Substituents		*Bond Orders*		*Charges*	
N	*B*	*B-N*	*B-Ph*	*B*	*N*
Me_2	H_2	0.6674	—	0.2836	1.6579
Me_2	Me_2	0.6017	—	0.3072	1.6904
Me_2	Ph, Me	0.5926	0.3641	0.3885	1.6690
Me_2	2-(*p*-MePh)	0.5764	0.3642	0.4662	1.6543
Ph, Me	Me_2	0.5604	—	0.2897	1.6538
Ph, Me	Ph, Me	0.5397	0.3709	0.3711	1.6119

"Resonance interaction with the aryl group is again possible, leading to an increased double-bond character for the *B*-phenyl bond" *(16)*. The calculations indicate a sizable B-Ph bond order.

"This resonance interaction leads to a corresponding decrease in double-bond character for the B-N link" *(16)*. In each case, upon substitution of an aryl group on to boron the calculated B-N order is lessened.

"The effect of *B*-aryl groups seems less pronounced than that of *N*-phenyl groups" *(16)*. The lowering of the calculated B-N bond order for *B*-phenyl substitution is considerably less than that for *N*-phenyl substitution.

"The electron density around the boron atom is not diminished" *(16)*. On the contrary, the calculated charge on boron shows that the electron density on the boron atom is raised by aryl substitution. This is due to the "amphoteric" character of the phenyl group, which allows it to donate electrons to an electron-deficient center or attract them from an electron-rich center.

Conclusions

Comparison of results of these calculations with reported experimental observations proves that the Hückel technique can be applied with considerable success to at least certain types of heteroatomic boron compounds. The trend of the calculational results is (happily!) insensitive to the particular choice among the four proposed sets of input parameters. The results based on the various parameter sets show merely a regular modest over-all difference in the calculated charges and bond orders.

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Received May 27, 1963. Research supported by the Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. AF 49(638)-1220.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch010

11

Proton Magnetic Resonance Study of Bonding in Aminoboranes and Substituted Pyridine-Boranes

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

The existence of restricted rotation about the nitrogen-boron bond because of partial double bond character has been established by NMR spectroscopy for several unsymmetrical aminoboranes containing phenyl groups. In (methylphenylamino)dimethylborane, the activation energy for rotation is 10.8 ± 0.7 kcal. per mole, and the *B*-methyl peaks merge at about 100° C. Cis-trans isomers are indicated by the spectra of three other aminoboranes. For (methylphenylamino)methylphenylborane, the trans isomer is energetically favored by 1.7 ± 0.5 kcal. per mole, and the *B*-methyl peaks merge at about room temperature. Appreciable magnetic nonequivalence is produced only by the anisotropy of a phenyl group directly attached to the nitrogen or boron atom. The chemical shifts of alkyl-substituted pyridine boranes are moderately concentration-dependent. The change in chemical shift on forming the borane addition compounds is not simply related to the extent of electron donation by the nitrogen to the boron.

In the application of proton magnetic resonance techniques to the study of conformation, structure, and electronic effects in several types of compounds containing the nitrogen-boron bond, the areas of principal interest are:

Study of partial double bond character and restricted rotation in aminoboranes. Such character would impart an essentially planar configuration to the molecule; if magnetic environments are different for the two possible placements of a hydrogen-containing group, duplicate peaks will be seen in the spectrum *(3)*.

Consideration of effects of molecular geometry and electronic effects on the nuclear magnetic resonance (NMR) spectra of the aminoboranes.

Interpretation of the shifts observed in proton resonance spectra of pyridine-boron addition compounds, as compared with those of the

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In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

base. The compounds formed by amines and the BH_3 group have been studied previously with respect to the relationships between basic strength of the amine, steric interactions of the two members of the acid-base pair, and heats of formation *(5)*. It appears interesting to determine what information can be gained about the relationship between compound stability and electronic effects by examination of the NMR spectra.

Experimental

All spectra were determined on a Varian spectrometer operating at either 56.4 or 60.0 megacycles. The magnet was equipped with field stabilizer, insulating jacket, and field homogeneity control coils. Side bands were applied from an audio-oscillator, continuously monitored by a Hewlett-Packard frequency counter. Temperature-dependence studies were carried out with a Varian variable-temperature probe, which utilizes a stream of heated or cooled gas blown around the sample tube. Temperatures were determined by means of a thermocouple placed near the sample and calibrated in blank runs against a thermocouple placed at the normal location of the sample. Materials were dissolved in carbon tetrachloride unless otherwise specified. Chemical shifts are referred to tetramethysilane as an internal standard, assigning to this reference the arbitrary value of 10.00 p.p.m.

The following aminoboranes were prepared according to procedures described in the literature *(6, 7)*: (methylphenylamino)dimethylborane, b.p. 67° C. at 14.0 mm.; (methylphenylamino)dichloroborane, b.p. 97° C. at 13.0 mm.; (methylphenylamino)phenylchloroborane, b.p. 150-3° C. at 8.5 mm.; (cyclohexylmethylamino)dimethylborane, b.p. 76° C. at 16.0 mm.; (diethylamino)dichloroborane, b.p. 72.8° C. at 61.9 mm. All distillations were carried out in a Nester and Faust spinning band column. Vapor pressures were determined for several of the materials over a range of at least 40° C. For (cyclohexylmethylamino)dimethylborane, the vapor pressure is given by the equation

$$\log_{10} p_{\mathrm{mm\ Hg}} = -(2.481 \times 10^3)/T + 8.313$$

with a standard deviation of 0.0026. Samples of (methylphenylamino)-methylphenylborane, (benzylmethylamino)benzylphenylborane, (benzylmethylamino) dimethylborane, and (α-pipecolino)dimethylborane were supplied by K. Niedenzu. These either were in sealed tubes or were redistilled before use.

The pyridine boranes were prepared by passing diborane into the nitrogen base, removing excess base under vacuum, and purifying the addition product remaining by crystallization from octane or sublimation *(4)*. NMR samples were taken from materials used in kinetic studies *(4, 10)*.

Restricted Rotation in (Methylphenylamino)dimethylborane

The proton resonance spectrum of this material as the neat liquid, shown in Figure 1, contains four peaks at room temperature. The low-field peak is due to the phenyl group, the middle peak is due to the *N*-methyl group, and the two peaks at high field are those of the two *B*-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

methylgroups. As the temperature of the sample is raised, the latter two peaks first broaden out, then partially overlap one another, then merge, and finally narrow to a single sharp peak. No dimeric structure can account for both the room temperature spectrum and the temperature variation of the spectrum *(11)*. Accordingly, it is concluded that there is restricted rotation about the N-B bond deriving from partial double bond character. At temperatures above about 125° C., the rate of rotation about this bond is sufficiently great so that the NMR experiment sees only the average magnetic environment of the two nonequivalent positions for the *B*-methyl groups.

In a previous communication *(11)*, preliminary estimates of the rates of interconversion of the two forms of this molecule were given. These measurements have now been extended and refined. The average lifetime of the individual forms has been calculated from line-broadening at lower temperatures, from the distance between the two maxima in the temperature range where the peaks are moving together, and from the contours of the peaks, using the complete line shape function applicable to the case of equal populations for the two environments, for temperatures above the point of merging *(8)*. The line width at low temperatures was measured and found to be negligible in the three methods of calculation employed. Calculations of the ratio of minimum to maximum intensity in the partially merged region, which are more strongly affected by the value of $1/T_2$ *(3)*, were not employed.

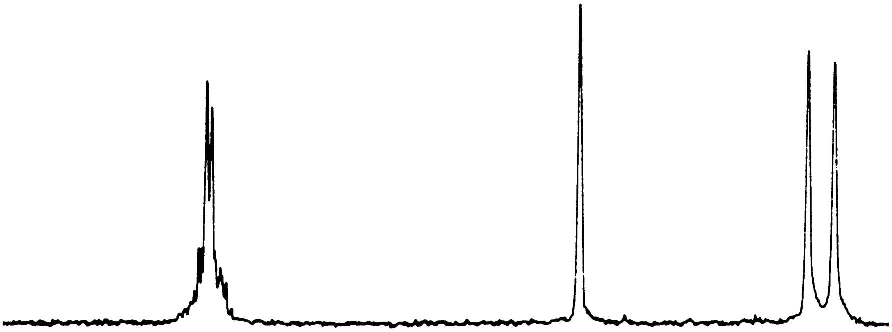

Figure 1. Proton resonance spectrum of (methylphenylamino)dimethylborane at 30°. Field increases to the right

The results are given in Figure 2, where the logarithm of the reciprocal lifetime is plotted against the reciprocal of the absolute temperature, and are described by the equation

$$1/\tau = 2.9 \times 10^{8}\ e^{-10.8\ \text{kcal.}/RT}\ \text{sec.}^{-1}$$

with an estimated error for the activation energy of ± 0.7 kcal. Both the activation energy and the frequency factor lie very close to those reported for the compound *N*, *N*-dimethylacetamide, in which there is partial double bond character in a carbon-nitrogen bond *(9)*.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

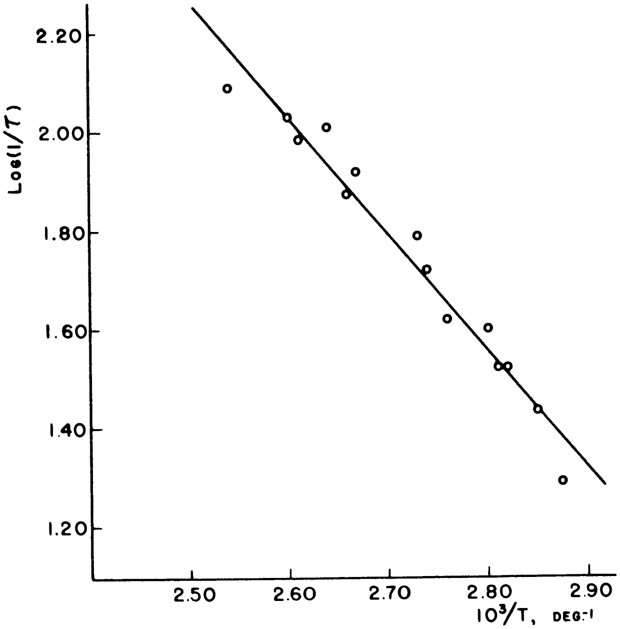

Figure 2. Plot for determination of activation energy for rotation in (methylphenylamino) dimethylborane

cis-trans Isomerism in Aminoboranes

Three other compounds examined show indications of the existence of cis-trans isomers. Extensive studies have been carried out on (methylphenylamino)methylphenylborane. Here each of the two types of methyl groups shows two distinct resonance peaks at temperatures below room temperature. In addition to the information about this molecule reported elsewhere *(1)*, the ratio of the two forms has now been carefully determined as a function of temperature by measurement of relative areas of peaks in the NMR spectrum. The results are shown in Figure 3, with the slope at room temperature corresponding to an enthalpy difference of 1.7 ± 0.5 kcal. per mole.

The favored isomer is that in which the methyl group resonances are both to higher field, corresponding to greater shielding, than the corresponding resonances in the less favored isomer. Examination of molecular models shows that the trans molecule cannot have the phenyl groups in the molecular plane, but that each group must be skewed out of plane in such a way that the methyl group which is cis to it can lie near enough to the extended sixfold axis of the ring to be shielded by the ring. This is consistent with the results reported for dimethylstilbene, where the trans isomer is slightly favored in the equilibrium mixture and shows a larger NMR shift to high field for the methyl group than the cis isomer *(12, 13)*.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

A feature of great interest in the spectrum of this compound is that the *N*-methyl resonances of the two isomers appear at 6.80 and 6.90 p.p.m. at -25° C., while the merged peak at +75° is at 6.90. This is in contrast to the behavior of the *B*-methyls, for which, as expected, the merged peak has a chemical shift which is the concentration-weighted average of the separate isomer peaks. The change of the *N*-methyl from the expected position must be due to an effect upon the shift of the methyl group in one or both of its environments. This is reasonable if the weakening of the pi N-B bond leads to a change of hybridization of the nitrogen atom, with possible loss of planarity of the bonds surrounding the nitrogen.

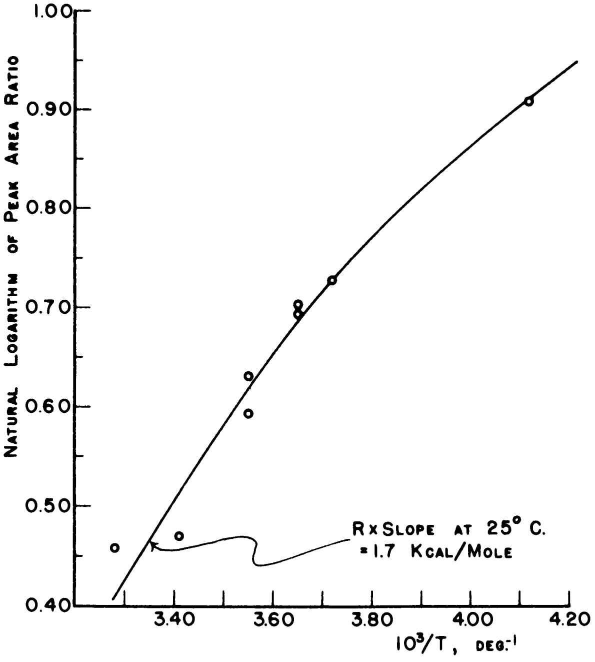

Figure 3. Temperature dependence of the equilibrium ratio of trans to cis isomers for (methylphenylamino) - methylphenylborane

(Benzylmethylamino) benzylphenylborane shows a spectral pattern somewhat more difficult to interpret, because the resonances of the *N*-methyl group and the *B*-methylene group very nearly coincide. The phenyl peaks fall on the downfield side of 3 p.p.m. The *N*-methylenes are assigned two peaks, one at 5.56 of relative intensity 1.19 and the other at 5.81 of intensity 0.77. The *B*-methylene is assigned a peak at 7.20, with intensity 1.96. The *N*-methyls are assigned two peaks, one at 7.32 of relative intensity 1.70 and the other at 7.40 of intensity 1.38. These intensities are normalized to correspond to seven hydrogens. There are thus clearly two isomers present, although the spectrum shows no change with temperature from -25° to +75°. The resonance of the methylene group attached to the same atom as the phenyl shows only a single peak.

A third compound, (methylphenylamino)phenylchloroborane, shows the spectrum of only a single isomer when examined as the neat liquid at room temperature. However, the peak corresponding to the methyl group is very much broader than in other (methylphenylamino)boranes, indicating that rotation about the N-B bond is somewhat restricted, and that two isomers could be distinguished at sufficiently low temperature.

Spectra of Other Aminoboranes

A number of other compounds have been examined, in which substitution is symmetrical, or in which the magnetic environment of the hydrogens is so similar in the two conformations that no distinction can be seen in the NMR spectrum. One can, accordingly, draw no conclusions about the extent of pi bonding between nitrogen and boron in these molecules.

(Alpha-pipecolino)dimethylborane showed a complex pattern corresponding to the ring hydrogens and only a single peak, at 9.77 p.p.m., for the two methyl groups. The position of this peak did not change from -15° to +50°. (Benzylmethylamino)dimethylborane shows a complex absorption at 2.90, a single methylene peak at 4.82, an *N*-methyl peak at 7.39, and again a single peak for the two *B*-methyl groups at 9.62 p.p.m. The spectrum shows no evidence of change with temperature over the range -25° to +32°. (Diethylamino)dichloroborane shows only the quartet and triplet peaks characteristic of an ethyl group. (Cyclohexylmethylamino)dimethylborane shows a single *B*-methyl peak upfield, a single *N*-methyl peak downfield, a broad hump for most of the cyclohexyl protons about midway between the methyl peaks, and a broad band below the *N*-methyl peak, corresponding to the hydrogen alpha to the nitrogen. Again there is no indication of nonequivalence. (Phenylmethylamino)dichloroborane shows a phenyl resonance with much fine structure resolved and a single, very sharp, methyl peak.

Chemical Shifts of Derivatives of Pyridineborane

The NMR spectra of the hydrogens of pyridineborane and a number of alkyl-substituted pyridineboranes have been compared with those of the free bases. The materials were dissolved in carbon tetrachloride at several concentrations and the chemical shifts were extrapolated to infinite dilution. The results are shown in Table I. The hydrogens in the 2- and 6- positions would be expected to show the greatest degree of unshielding as electrons are transferred from the base to the borane. Clearly this does not occur in most of the materials. Those in position 4, as well as 3 and 5, show a greater effect than the 2 and 6 hydrogens. The only reasonable explanation is that electron density is transferred from all positions in the ring, but that, somehow, this is partially offset in the 2- and 6- positions by another effect which shields the hydrogens in these locations.

In the addition compound of pyridine itself, the downfield shift in position 4 is 0.47 p.p.m., that in positions 3 and 5 is 0.45, while that in positions 2 and 6 is only 0.05. For the addition compound of 4-methylpyridine, the downfield shift is 0.28 p.p.m. in the 3- and 5-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

positions and again only 0.05 in the 2- and 6- positions. For the compounds substituted in either or both of the positions adjacent to the pyridine nitrogen, the unshieldings differ less among the various ring positions, or reverse the trend, as for 2-methylpyridine, where the chemical shift difference is largest in position 6.

At least two explanations may be advanced for the somewhat unexpected results for hydrogens in positions 2 and 6. The first involves a solvent effect which has been postulated to explain some of the observed shifts in substituted benzenes dissolved in various media. Dipoles in the solvent may be induced by the N^+-B^- dipole, and then in turn induce dipoles in other parts of the solute molecules. The resultant dipoles between the carbon atoms in positions 2 and 6 and the hydrogens attached to these carbons would have components with negative ends on the hydrogens, leading to increased electron density and greater shielding. If the solvent effect were transmitted far enough to reach the hydrogens in the 3-, 4-, and 5- positions, it would have the opposite result on the chemical shift, for it would tend to move electrons from the hydrogen atoms toward the ring carbons. The fact that the chemical shift changes on formation of the borane vary with the nature of the substituents and the geometry of the molecule may be taken as evidence that the solvent does play a part in determining the chemical shift.

Table I. Chemical Shifts of Pyridines and Pyridineboranes

(Tau values, in carbon tetrachloride, extrapolated to infinite dilution)

			Ring Hydrogens		
	CH_3	CH_2	*3, 5*	*4*	*2, 6*
Pyridine			2.87	2.48	1.50
Pyridineborane			2.42	2.01	1.45
2-Methylpyridine	7.45		2.97	2.50	1.53
2-Methylpyridineborane	7.28		2.87	2.37	1.30
2-Ethylpyridine	8.75	7.25	3.02	2.55	1.52
2-Ethylpyridineborane	8.67	6.83	2.72	2.22	1.30
4-Methylpyridine	7.72		3.00		1.63
4-Methylpyridineborane	7.52		2.72		1.58
2,4-Dimethylpyridine	7.58, 7.72		3.18, 3.20		1.79
2,4-Dimethylpyridineborane	7.34, 7.53		3.09, 3.15		1.79
2,6-Dimethylpyridine	7.57		3.17	2.65	
2,6-Dimethylpyridineborane	7.20		2.82	2.42	

An alternative possibility is that the hydrogens in the 2- and 6- positions are shielded by the magnetic anisotropy of the N-B bond. Without knowledge of the nature of this anisotropy, it is not possible to predict the direction of the chemical shift which would be produced. A third explanation may be based on an analogy to the effects which are found when pyridine is converted to pyridinium ion *(2)*. The nitrogen atom in the free base contributes a paramagnetic shift to the hydrogens

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

in position 2. When the ion is formed, this paramagnetic effect is removed but the decrease in electron density on the α-carbon produces an almost equal downfield shift.

A further point of interest is the substantial unshielding observed in every case for the alkyl groups attached to the pyridine ring. The magnitude of the unshielding is too great to be explained by "electronic effects" of the usual type, transmitted through bonding electrons. A hyperconjugative interaction of the methyl groups with the ring is possible, but there is no evident reason why this should be greater in the borane than in the free base. That the unshielding does not vary greatly with position in the ring indicates that it cannot be explained solely by either solvent-transmitted polarization or N-B bond anisotropy. The maximum unshielding effect is observed in the methylene group of 2-ethylpyridine. Examination of molecular models indicates that the conformation of the ethyl group in which the methyl group is directed away from the N-B bond is favored in the borane. This would force each methylene hydrogen to be close to the N-B bond for a larger fraction of the time if that hydrogen were one of three in a methyl group. Thus it appears that we have a clue as to the nature of one of the unshielding factors operative for alkyl groups in the 2-position.

It is necessary to conclude, therefore, that the chemical shifts change on formation of a pyridineborane from the free base in a manner which can not be related directly to the strength of the nitrogen-boron bond, but includes contributions from a number of other factors, which remain to be resolved in detail.

Acknowledgment

The senior author acknowledges with appreciation helpful comments of K. Niedenzu and M. F. Lappert.

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Received May 15, 1963. Work supported in part by the Nuclear Program of the State of Florida.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch011

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Proton Magnetic Resonance of Aminoborane Derivatives

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

The proton magnetic resonance spectra of some aminoborane derivatives were recorded at room temperature. The assignments of observed signals were made and the chemical shifts and spin coupling constants were evaluated. The electron transfer from boron to nitrogen in aminoboranes is smaller than in the corresponding ammonia-boranes. However, the double bond character of $\mathrm{N}\overset{\rightharpoonup}{=}\mathrm{B}$ bonds gives rise to the presence of interconvertible cis-trans isomers for an RR'NBR'R''' type compound. For an RR'NBR''$_2$ type compound, the NMR spectrum suggests that the two R'' groups are magnetically nonequivalent, because of the $\mathrm{N}\overset{\rightharpoonup}{=}\mathrm{B}$ bond-hindering rotation about its axis.

The present work has been undertaken as part of a program of physicochemical investigations on a variety of compounds containing an N-B bond or bonds, which may be considered to have begun with studies on the nuclear magnetic resonance of borazoles *(12, 13, 23, 24)* and ammonia-boranes *(17)*. Whereas borazole ($B_3N_3H_6$) and ammonia-borane (H_3NBH_3) are isoelectronic with benzene and ethane, respectively, aminoborane (H_2NBH_2) is isoelectronic with ethylene. The N-B bonds in the derivatives of this hypothetical compound represent typical examples of double bonds involving a donor-acceptor bond. [Unsubstituted aminoborane is unstable and exists in polymeric forms *(22)*.] The present investigation has been undertaken in an attempt to discuss the nature of N-B bonds in these compounds from the date of proton magnetic resonance and to examine the possible existence of isomers resulting from an N=B double bond.

Brey, Fuller, and Ryschkewitsch *(4)* have also reported the existence of geometric cis-trans isomers resulting from an $\mathrm{N}\overset{\rightharpoonup}{=}$bond, as revealed by the nuclear magnetic resonance spectra of some aminoboranes other than that studied in the present investigation.

Experimental

Tris(diethylamino)borane *(9)*, $B(Et_2N)_3$. Boron trichloride (1 mole) was allowed to react with diethylamine (6 moles) in toluene at about - 70° C. The product was purified by fractional distillation under reduced pressure [b.p., 84° C./6 mm. Hg; lit. *(9)*, 50-53° C./0.4 mm. Hg].

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

(Diethylamino)dichloroborane *(11)*, Et_2NBCl_2. The product of reaction between tris(diethylamino)borane (1 mole) and boron trichloride (2 moles) was purified by fractional distillation under reduced pressure [b.p., 75-75.5°C./63-64 mm.Hg; lit. *(19)*, 148°C.].

Diethyl(diethylamino)borane *(17)*, Et_2NBEt_2. The solution of ethylmagnesium bromide in absolute ether was added drop by drop to the benzene solution of an equivalent amount of (diethylamino)dichloroborane. The mixture was refluxed for several hours. After filtration followed by removal of solvents, the product was purified by distillation (b.p., 154° C.). A nitrogen atmosphere was used throughout.

(Diethylamino)borane *(25)*, Et_2NBH_2. The solution of (diethylamino)dichloroborane in triethylene glycol dimethyl ether was added drop by drop to the solution of sodium borohydride in the same solvent. The mixture was stirred at room temperature for 2 to 3 hours. The product was distilled under reduced pressure and collected in a trap cooled with dry ice in acetone (ca. -70° C.). This process was repeated twice [b.p. (6 mm.Hg) < 0° C.].

(Ethylphenylamino)dichloroborane *(15)*, $EtPhNBCl_2$. The solution of *N*-ethylaniline in benzene was added drop by drop to the solution of boron trichloride in the same solvent and mixed thoroughly at 6° C. The resulting 1 to 1 adduct ($BCl_3 \cdot NHEtPh$) was allowed to react with the calculated amount of triethylamine. Dehydrochlorination took place on heating with reflux for 3 hours. After filtration, the solvent was removed by evaporation. The product was distilled under reduced pressure (b.p., 67° C./3 mm.Hg).

Diethyl(ethylphenylamino)borane *(15)*, $EtPhNBEt_2$. The preparation of this compound from (ethylphenylamino)dichloroborane and ethylmagnesium bromide in mole ratio 1 to 2 was similar to that of diethyl(diethylamino)borane described above (b.p., 68° C./6 mm.Hg).

(Methylphenylamino)dichloroborane *(15)*, $MePhNBCl_2$. The 1 to 1 addition compound of boron trichloride and *N*-methylaniline was subjected to dehydrochlorination with triethylamine, the same method being used as for (ethylphenylamino)dichloroborane (b.p., 94-98° C./7 mm.Hg).

Methyl(methylphenylamino)chloroborane, $MePhNBMeCl$. Methyldichloroborane was dissolved in dry ether cooled to about -70° C. The equivalent amount of *N*-methylaniline in ether was added to it drop by drop. After the calculated amount of triethylamine was added to the mixture in small quantities at room temperature, heating was continued with reflux for 3 hours. The resulting triethylamine hydrochloride was removed by filtration. Ether was driven off. The residue was distilled in the stream of nitrogen under reduced pressure (b.p., ca. 79.5° C./9 mm.Hg). No data are available in the literature for comparison.

The proton magnetic resonance spectra were recorded at room temperature by means of a JNM-3 NMR spectrometer from the Japan Electron Optics Laboratory Co. operating at 40 Mc. and an A-60 NMR spectrometer from Varian Associates operating at 60 Mc. In experiments with the former spectrometer, 10 to 20% carbon tetrachloride solutions were used with cyclohexane as an internal standard, while about 10% solutions in the same solvent were employed for 60 Mc. with tetramethylsilane as an internal standard. When chemical shifts were expressed in τ values by means of conversion with the observed shift

(1.45 p.p.m. of tetramethylsilane relative to cyclohexane), complete agreement was obtained between the two sets of results, as far as the chemical shifts are concerned. When relative chemical shifts were comparable with splittings, the absorption curves of composite peaks naturally depended on the frequency used. The following assignments and discussion are made on the basis of data of higher resolution.

Assignments

The NMR spectrum of tris(diethylamino)borane showed a 3,4 pattern characteristic of ethyl groups. The signals of methyl and methylene groups appeared at τ values of 9.07 and 7.19, respectively. (Throughout the present article, chemical shifts are expressed in τ values.) The spin coupling constant, J, was 7.2 c.p.s.

(Diethylamino)dichloroborane gave rise to a simple 3,4 pattern of equivalent ethyl groups. The pattern was similar to that of the foregoing compound, except that the quartet lines of the methylene signal were slightly broader.

The spectrum of diethyl(diethylamino)borane could be interpreted as being comprised of a 3,4 pattern arising from ethyl groups bonded to nitrogen and a composite group of lines attributable to ethyl groups bonded to boron. The non-first-order pattern of B-C_2H_3 signals reveals the existence of intermediate coupling due to a low ratio of the chemical shift to the spin coupling constant *(17)*.

Seven prominent peaks in the spectrum of (diethylamino)borane could be attributed to the 3,4 pattern of ethyl groups bonded to nitrogen. However, closer examination through analysis by means of NMR integrated intensities revealed the presence of very flat absorptions at 5.48, 7.62, 9.75, and 11.88. These quartet lines of almost equal intensities and spacings were assigned to protons directly bonded to ^{11}B with its nuclear spin, $I = 3/2$. The spin coupling constant, $J(^{11}BH) = 128$ c.p.s., is of the right order of magnitude compared with $J(^{11}BH) = 138$ c.p.s. for borazole *(12)*. [The peak heights of multiplet components of proton signals remain equal to one another, when and only when the nuclear spin giving rise to quadrupole collapse of the multiplet structure is 3/2 *(20)*.]

The spectrum of (ethylphenylamino)dichloroborane was comprised of a typical 3,4 pattern due to ethyl groups and a complicated group of lines attributable to nonequivalent protons in phenyl groups.

Diethyl(ethylphenylamino)borane gave a spectrum bearing striking resemblance to that of the foregoing compound, except that an additional group of lines attributable to B-C_2H_5 protons overlapped the 1 : 2 : 1 triplet of methyl protons in ethyl groups attached to nitrogen.

(Methylphenylamino)dichloroborane showed a sharp intense peak due to methyl protons and a composite group of lines attributable to nonequivalent protons in phenyl groups.

Methyl(methylphenylamino)chloroborane gave rise to two sharp signals at 6.73 and 9.58 attributable to N-CH_3 and B-CH_3 protons, respectively, and a group of lines due to protons in phenyl groups. In addition, two weak peaks of equal integrated intensity appeared at 6.80 and 9.20, as shown in Figure 1. These satellite lines are discussed below.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

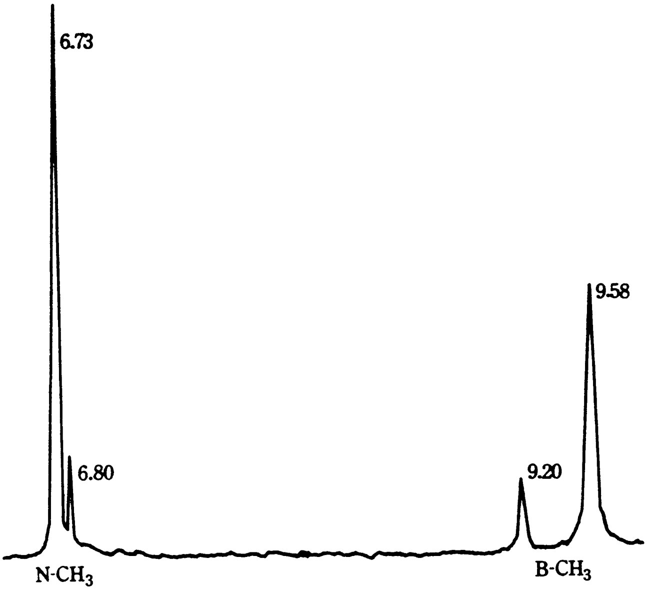


Figure 1. Portion of proton magnetic resonance spectrum of methyl(methylphenylamino)chloroborane revealing the existence of isomers. Weak peaks attributable to a less abundant isomer

Table I. Proton Chemical Shifts (in τ Values) and Spin Coupling Constants J of Some Aminoboranes

		NCH_3			BCH_3	
Compound	NC_6H_5	NCH_2	CCH_3	BH	BC_2H_5	$J(HH)$, *C. P. S.*
$B(Et_2N)_3$		7.19	9.07			7.2
Et_2NBCl_2		6.68	8.85			7.1
Et_2NBEt_2		6.94	8.95		9.12-9.22	7.5(NEt), 7.3(BEt)
Et_2NBH_2		7.19	8.85	8.68		7.1, $J(^{11}BH)$=128
$EtPhNBCl_2$	2.62-3.02	6.29	8.88			7.1
$EtPhNBEt_2$	2.72-3.13	6.54	9.00		8.63-9.42	7.0(NEt)
$MePhNBCl_2$	2.73-2.85	6.72				
MePhNBMeCl	2.70-3.05	6.73, 6.80			9.58, 9.20	

Discussion

The numerical values of chemical shifts and spin coupling constants are summarized in Table I. They are of the correct order of magnitude compared with those of borazoles *(12, 13)* and ammonia-boranes *(17)* already studied, indicating the adequacy of the present assignments.

According to Dailey and Shoolery *(7)*, a linear relation holds between the internal chemical shift, $\delta = \Delta CH_3 - \Delta CH_2$, of ethyl signals and the electronegativity of an atom bonded to the ethyl group.

$$E.N. = 0.695(\Delta CH_3 - \Delta CH_2) + 1.71$$

On the basis of this relation, the internal chemical shifts of ethyl groups and the electronegativity of nitrogen were evaluated for various aminoboranes as shown in Table II, in which the corresponding data for related compounds are listed for comparison.

Table II. Internal Chemical Shifts of Ethyl Groups and Electronegativity of Nitrogen in Some Aminoboranes

Compound	$\Delta CH_3 - \Delta CH_2$, *P.P.M.*	*Electronegativity of Nitrogen*
$B(Et_2N)_3$	1.87	3.01
Et_2NBCl_2	2.17	3.22
Et_2NBEt_2	2.01	3.11
Et_2NBH_2	1.66	2.86
$EtPhNBCl_2$	2.59	3.51
$EtPhNBEt_2$	2.46	3.42
NEt_3	1.83	2.98
Et_3NBEt_3	2.29	3.30
$(EtNBEt)_3$	2.57	3.50

Let aminoboranes be represented by diethyl(diethylamino)borane, which has the most symmetric structure among compounds studied in the present investigation. The corresponding representatives of amines, ammonia-boranes, and borazoles are triethylamine, triethylamine-triethylborane, and hexaethylborazole, respectively. Table II shows that the electronegativity of the nitrogen of triethylamine, diethyl(diethylamino)borane, and triethylamine-triethylborane increases in this order. This indicates that the electron transfer from nitrogen to boron is smaller in diethyl(diethylamino)borane than in triethylamine-triethylborane. This is in qualitative agreement with the results of dipole moment measurements on some aminoboranes and ammonia-boranes carried out by Becher *(2)*, who has shown that the N-B bond moment in the former group of compounds is smaller than that in the latter.

Direct comparison between the electronegativity of nitrogen in diethyl(diethylamino)borane with the apparently great value for hexaethylborazole is of little significance, because Dailey-Shoolery's empirical equation does not take into account the diamagnetic ring current induced by the external magnetic field in a borazole ring. As has been discussed *(17)*, the ring current makes a negative contribution *(3)* to the chemical shifts of protons in the same molecule, the effect being smaller for methyl protons than for methylene protons in ethyl groups. As a result, the internal chemical shift of ethyl groups increases and

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

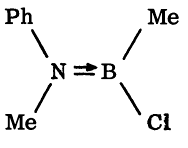
leads to the overestimation of the electronegativity of nitrogen in borazoles.

The increase of the electronegativity of nitrogen in (diethylamino)-dichloroborane over that of diethyl(diethylamino)borane, 0.11, is indicative of the induction effect of chlorine, as is also the corresponding difference of almost the same magnitude, 0.09, between (ethylphenylamino)dichloroborane and diethyl(ethylphenylamino)borane. The apparent increase in electronegativity of nitrogen in diethyl(ethylphenylamino)borane over that of diethyl(diethylamino)borane is due to the effect of diamagnetic ring currents, in addition to the effect of electron withdrawal by the phenyl group.

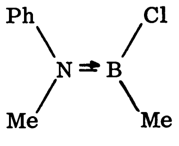
The electronegativity of nitrogen of tris(diethylamino)borane is smaller than that of diethyl(diethylamino)borane, presumably for the following reason. The migration of lone pair electrons cannot take place from three nitrogen atoms at a time. Accordingly, the averaged extent of transfer from nitrogen to boron becomes small, leading to the decrease in the electronegativity of nitrogen.

(Diethylamino)borane also gave an abnormally small electronegativity of nitrogen. Possibly, it represents a different type of compounds and simple comparison with diethyl(diethylamino)borane is not feasible. In fact, it was found from cryoscopic as well as dielectric investigation that (dimethylamino)borane *(8)* and some aminodiarylboranes containing an NH_2 or NHMe group *(5)* form dimer molecules, whereas all known tetrasubstituted aminoboranes appear to be monomeric *(17)*.

Methyl(methylphenylamino)chloroborane showed strong absorptions of equal integrated intensity at 6.73 and 9.58 attributable to $N\text{-}CH_3$ and $B\text{-}CH_3$ protons, respectively. Two weaker lines at 6.80 and 9.20 having equal intensity can be interpreted as the $N\text{-}CH_3$ and $B\text{-}CH_3$ signals, respectively, of a less abundant isomer. This provides conclusive evidence of the possibility of cis-trans geometric isomerism resulting from a double bond involving a dative bond. Niedenzu and Dawson *(16)* have inferred the presence of interconvertible cis-trans isomers for unsymmetrical tetraorgano-substituted aminoboranes from the existence of a boiling point range in place of a sharp boiling point and the continuing variance of vapor pressure characteristics.



trans form



cis form

It is presumed that the effect of diamagnetic ring current induced in the aromatic rings is mainly responsible for the chemical shift difference between the cis and trans isomers. In fact, the observed spacing (0.38) between the two $B\text{-}CH_3$ signals is much greater than that (-0.07) between $N\text{-}CH_3$ signals. This is because the distance between the phenyl group and the methyl group bonded to boron changes from one isomer to the other, whereas the position of the methyl group bonded to nitrogen relative to the phenyl group is practically the same for the two isomers.

For the sake of simplicity, let two extreme cases be considered. If the phenyl ring is at right angles to the molecular plane, geometric consideration leads to the conclusion that the B-CH_3 proton signal of the trans form is on the higher field side and therefore the trans form is more stable than the cis form. On the other hand, if the molecule is coplanar, the ring current makes a negative contribution to the chemical shift of the B-CH_3 protons. As a result, the strong peaks must be assigned to the cis form of planar molecules. It is difficult to choose between these alternatives from the nuclear magnetic resonance data alone. The former presumption seems to be likely from steric reasons, whereas conventional resonance theory would favor the latter.

The B-C_2H_5 signals of diethyl(ethylphenylamino)borane cover a wider range than the corresponding signals of diethyl(diethylamino)-borane. Whereas the latter can be fitted to a theoretical pattern calculated by Corio *(6)* for an A_3B_2 spin system with the internal chemical shift, $\delta = \Delta\ CH_3 - \Delta\ CH_2$, equal to -0.12_3 p.p.m. and the spin coupling constant, $J = 7.3_5$ c.p.s., the former could not be approximated with any of theoretical calculations having J/δ as a parameter. A question may be raised as to the adequacy of treating B-C_2H_5 as an A_3B_2 system by disregarding further splitting of ethyl proton signals due to a magnetic boron nucleus. Although a boron atom directly attached to a hydrogen atom gives rise to the multiplet structure of proton signals (a quartet for ^{11}B and a septet for ^{10}B) *(12)*, it is not unreasonable to suppose that boron nuclei undergoing quadrupole relaxation do not affect the characteristic pattern of ethyl signals for the following reason. The multiplet structure starts to disappear when the characteristic time of spin flipping is equal to $1/\Delta\omega$, where $\Delta\omega$ denotes the multiplet splitting in frequency units *(11)*. Whereas the spin coupling constant, J_{BH} in borazole is large (138 c.p.s.), those between a boron nucleus and ethyl protons across two or more chemical bonds are too small to be measurable *(14)*. In fact, Onak *et al.* *(19)* have observed the ^{11}B nuclear magnetic resonance spectra of a number of boron compounds and evaluated spin coupling constants between directly bonded boron and hydrogen but not those between a boron nucleus and a proton separated by two or more chemical bonds. Therefore, one is led to suppose that the B-C_2H_5 signal of diethyl(ethylphenylamino)borane consists of two A_3B_2 type patterns of intermediate coupling superposed on each other. Because of different substituents attached to nitrogen along with the $N \rightleftarrows B$ bond hindering rotation about its axis, two ethyl groups attached to boron are no longer magnetically equivalent and give different ethyl signals in the NMR spectrum. This provides additional evidence that the function of an $N \underline{\rightarrow} B$ bond simulates a C=C double bond. An analogous conclusion for the double bond character of an N-B bond has been derived more clearly by Ryschkewitsch *et al.* *(21)* from the proton magnetic resonance spectrum of (methylphenylamino)dimethylborane, $(CH_3NC_6H_5)B(CH_3)_2$, and by Barfield, Lappert, and Lee *(1)* from a similar study on (dimethylamino)phenylchloroborane, $(CH_3)_2NBClC_6H_5$, although in these compounds cis-trans isomers do not exist

The ^{11}BH quartet of (diethylamino)borane is much broader than the corresponding quartet observed for borazole *(12)*. This indicates that the lifetime of the states of ^{11}B nuclei of this compound with a given

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

z-component, I_z, of the nuclear spin is shorter than that of borazole, because the average fluctuating field gradients at the nuclei due to the neighboring electrons and nuclei are great, the correlation time for molecular reorientation is long, or both *(20)*. The corresponding septet due to protons bonded to the less abundant boron isotope, ^{10}B, with $I = 3$ was too weak to be observable.

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Received May 24, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch012

Preparation and Structure of Tris(dialkylboryl-2-pyridylamino)borane

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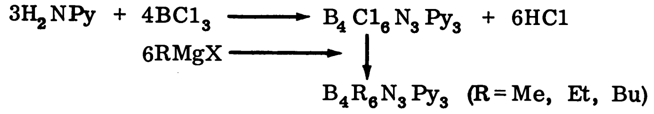
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

The reaction between boron trichloride and 2-aminopyridine was examined. Treating the reaction mixture with appropriate Grignard reagents afforded a new type of compounds whose composition is represented by $B_4R_6N_3Py_3$. The mass spectrum of the ethyl derivative showed the most prominent peak at 465 due to $B_4R_5N_3Py_3$ ions and a successive elimination of ethyl groups. The proton NMR spectrum when R equals Me gave rise to a single sharp methyl signal, demonstrating a planar C_{3h} structure for this series of molecules. The ultraviolet spectra of these compounds showed very intense absorptions at 266 mμ (log ϵ = 4.36) and 352 mμ (log ϵ = 4.22), indicating the presence of large conjugate systems. Infrared spectra and dipole moment data were also consistent with this model.

The addition of boron trichloride to primary amines in an inert solvent, in general, affords borazine or triaminoborane derivatives, depending upon the mole ratio of the parents, the latter products on pyrolysis giving borazine derivatives almost quantitatively: Interaction of boron trichloride with aniline gives *B*-trichloro-*N*-triphenylborazine *(16)* or trisphenylaminoborane *(1)* and the latter is converted into *B*-tris(phenylamino)-*N*-triphenylborazine by pyrolysis. However, the steric hindrance of the substituent in primary amine prevents the formation of a borazine ring, and ortho-substituted anilines for which larger steric interferences are expected *(22)* react with boron trichloride to give a variety of new boron compounds *(8, 9, 15)*. The reaction of 2-aminobiphenyl with boron trichloride gives 10-chloro-9-aza-10-boraphenanthrene. In this connection, it is of interest to examine the reaction of boron trichloride with 2-aminopyridine, which has less steric hindrance at the ortho position to the amino group than aniline or 2-aminobiphenyl.

The action of 3 moles of 2-aminopyridine on excess boron trichloride in toluene gave, presumably, an addition compound, which on heating lost 6 moles of hydrogen chloride. The reaction product was not isolated but treated directly with Grignard reagent to give a stable alkyl derivative. Molecular weight data and elemental analyses showed this derivative to have the composition of about $B_4R_6N_3Py_3$.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.



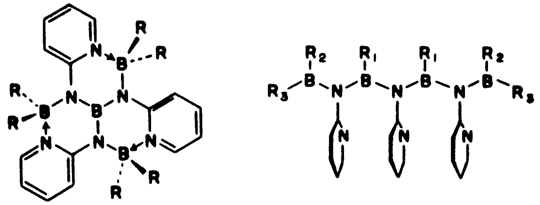
$$\begin{array}{l} 3H_2NPy + 4BCl_3 \longrightarrow B_4Cl_6N_3Py_3 + 6HCl \\ \qquad 6RMgX \longrightarrow \big\downarrow \\ \qquad\qquad\qquad B_4R_6N_3Py_3 \ (R = Me,\ Et,\ Bu) \end{array}$$

These compounds were soluble in many nonpolar organic solvents, such as benzene and carbon tetrachloride, and were easily hydrolyzed by hydrochloric acid.

The composition of product was supported by other physicochemical investigation. Molecular weight increment due to the increase in the number of methylenes in the alkyl group introduced by Grignard reagent showed that each molecule involves six or seven alkyl groups. The mass spectrum of ethyl derivative showed parent peaks at around mass 494, and a series of patterns due to successive eliminations of six ethyl groups from the parent. The feature of each pattern was also explained in terms of the natural abundances of isotopes to indicate the boron content in a molecule to be 4.

The proton NMR spectra, in conjunction with the molecular weight values and elemental analysis, provided definite evidence for this structure. The methyl groups in the methyl derivative showed a sharp single line, indicating that they are all equivalent. Furthermore, the ratio between signal intensity due to alkyl protons and that due to pyridyl protons showed that twice as many alkyl groups as pyridyl groups are present in these molecules.

The only possible structure which is consistent with all of the foregoing observations is represented in Figure 1, Structure I, three alkyl groups being below and the other three above the molecular plane. Further evidences for this planar structure are found in the ultraviolet spectra, the longest-wavelength absorption at 348 mμ (log ε = 4.22) suggesting a large conjugate system, and in the ^{11}B NMR spectrum of ethyl derivative, which consists of two signals having a relative intensity ratio of about 3.5 to 1. The dipole moments and infrared and Raman spectra are also consistent with this model.



I II

Structure I Structure II

Figure 1. Two possible structures

Experimental

Reaction. Ethyl Derivative. In a 500-ml. three-necked flask, equipped with a stirrer, dry ice condenser, and Claisen head provided with a nitrogen inlet and a drying tube, was placed 100 ml. of dry toluene and the flask was cooled in an ice bath. Boron trichloride (47 grams, 0.40 mole) was distilled into the flask through the dry ice condenser. After the drying tube had been replaced with a dropping funnel and the exit end of the condenser fitted with the drying tube, a solution of 18.8 grams (0.20 mole) of 2-aminopyridine in 200 ml. of dry toluene was added dropwise with stirring over a period of 1 hour. After the addition was completed, the reaction mixture was refluxed for 17 hours to eliminate hydrogen chloride. Then, ethylmagnesium bromide, prepared in the usual manner from 44 grams (0.40 mole) of ethyl bromide and 10 grams (0.41 mole) of magnesium turnings, was added in small portions with vigorous stirring over a period of 1 hour to the reaction mixture at room temperature. The reaction mixture was then refluxed for another 2 hours and 10 ml. of methanol was added to decompose the excess of Grignard reagent. Then it was filtered through a sintered-glass funnel, and the filtrate was concentrated to 100 ml. Addition of 300 ml. of methanol precipitated crystalline material. Recrystallizations from chloroform-methanol mixture gave 10.8 grams (32.8%) of colorless crystals (m.p. 193.5-94°). Found: C, 65.62; H, 8.88; N, 17.00; B, 8.84. $C_{27}H_{42}N_6B_4$ requires: C, 65.65; H, 8.57; N, 17.02; B, 8.76%.

Butyl Derivative. The molar ratios and technique cited above were employed to prepare the butyl derivative. The resulting product was obtained in 39.4% yield as colorless needles (m.p. 143-43.5°). Found: C, 70.97; H, 10.02; N, 12.61; B, 6.45. $C_{39}H_{66}N_6B_4$ requires: C, 70.73; H, 10.05; N, 12.69; B, 6.53%.

Methyl Derivative. Processing of the reaction mixture after the Grignard reaction in the manner described above did not furnish the corresponding methyl derivative. A modification was necessary to prevent its decomposition in the process of decomposing the excess of Grignard reagent.

After the addition of Grignard reagent, the solvent was removed from the reaction mixture under reduced pressure and 7 ml. of methanol was added drop by drop to the solid residue. A vigorous reaction took place to decompose the unaltered Grignard reagent. To this reaction mixture was added 300 ml. of methanol and then the precipitate was collected by filtration. Addition of methanol to a benzene solution of this precipitate afforded the methyl derivative in 35.6% yield. Two further recrystallizations from the same solvent pair furnished the analytical sample (m.p. 241.5-42°). Found: C, 61.70; H, 7.70; N, 20.48; B, 10.76. $C_{21}H_{30}N_6B_4$ requires: C, 61.55; H, 7.38; N, 20.51; B, 10.56%.

Analytical. The usual micro-Dumas method was applied to the determination of nitrogen without any particular precautions, whereas carbon and hydrogen were determined by a modification *(21)* of the usual microdetermination method which was improved to prevent low carbon analyses observed for some borazine derivatives *(12, 30)*. Boron was determined by a flame spectrophotometric method *(32)* which had been developed for determining boron in boron-nitrogen compounds.

Molecular Weight. The molecular weights of these compounds were measured by the freezing point depression in benzene as well as by the boiling point elevation in acetone with an ebulliometer *(25)* from

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

the Shibayama Kagaku Co., Ltd., Tokyo. The results are shown in Table I, together with calculated values for $B_4R_6N_3Py_3$.

Table I. Molecular Weights of Tris-(dialkylboryl-2-pyridylamino) boranes

Compound	*Cryoscopy*	*Ebulliometry*	*Av.*	*Calcd.*
Me derivative	407, 399	419	408	409.8
Et derivative	494, 476	503	491	494.0
Bu derivative	659	697	678	662.3

Mass Spectra. Mass spectra were recorded by the Hitachi Co., Ltd., with a Hitachi mass spectrometer Model RMU-6, and also by Atlas Mess- und Analysen Technik G. m. b. H., Bremen, with an Atlas mass spectrometer CH4. The mass spectrum of the ethyl derivative containing isotopically normal boron is given in Table II.

Table II. Mass Spectrum of Isotopically Normal Tris-(diethylboryl-2-pyridylamino) borane

m/e	*Intensity*[a]	*Fragment*	*m/e*	*Intensity*[a]	*Fragment*
495	0.10		369	0.35	
494	0.17		368	2.42	
493	0.35	Parent	367	10.51	$B_3N_3Py_3Et_2$
492	0.28		366	7.18	
491	0.14		365	2.45	
			364	0.78	
483	0.10		363	0.63	
482	0.50		362	0.53	
481	1.83	$CH_2B_4N_3Py_3Et_5$	361	0.53	
480	1.87		360	0.32	
479	1.85				
478	1.24		353	0.17	
477	0.49		352	0.28	
476	0.14		351	0.79	
			350	0.88	
467	4.98		349	1.36	
466	26.99		348	1.15	$B_4N_3Py_3Et$
465	100.00	$B_4N_3Py_3Et_5$	347	0.88	
464	84.66		346	0.53	
463	30.38		345	0.32	
462	5.18		344	0.11	
439	0.19		340	0.21	
438	1.06		339	1.30	$B_3N_3Py_3Et$
437	4.41		338	0.97	
436	11.81	$B_4N_3Py_3Et_4$	337	0.67	
435	11.14		336	0.51	
434	5.38		335	0.79	
433	1.62		334	1.76	
432	0.37		333	6.52	$B_3N_2Py_2Et_4$
			332	4.60	
409	0.35		331	1.83	
408	1.00		330	0.53	

Table II. (Continued)

m/e	*Intensity*[a]	*Fragment*	*m/e*	*Intensity*[a]	*Fragment*
407	3.16	$B_4N_3Py_3Et_3$			
406	2.91		323	0.44	$B_4N_3Py_3$
405	1.50		322	0.53	
404	0.62		321	1.06	
403	0.25		320	0.76	
			319	0.23	
380	0.74	$B_4N_3Py_3Et_2$			
379	1.29		277	0.28	$B_3N_2Py_2Et_2$
378	2.54		276	2.10	
377	2.68		275	12.34	
376	1.67		274	9.06	
375	0.74		273	3.47	
374	0.30		272	1.55	
			271	0.85	
			270	0.60	
			269	0.30	

[a] Relative peak intensities expressed relative to 100 for *m/e* 465.

Shapiro *et al.* *(26)* stated that the spectra for the compounds containing both methyl groups and boron atoms have either an overlap or a complex species because boron differs in mass units only slightly from the methyl group, and that in the ethyl derivatives the separation is more distinct. Furthermore, the spectrum of triethylborane showed that ethyl groups are more easily cleaved from triethylborane, than hydrogens or methyl groups are cleaved from ethyl groups. These facts suggested that the ethyl derivative is the most suitable object for the mass spectroscopic investigation, and these expectations are realized in the spectrum shown in Table II: Two series of weak peaks were observed in the *m/e* region of 494 and 479, probably due to parent superposed by parent minus one hydrogen and the cleavage of C-C bonds in ethyl groups, respectively. The most prominent peak at mass 465 can be reasonably explained as due to $B_4Et_5N_3Py_3$ ions corresponding to loss of one ethyl group. The feature that is important for analysis of molecular formula can be calculated straightforwardly on the basis of the natural isotopic abundance, as discussed below.

The mass spectrum of the methyl derivative was also recorded to confirm the assignment of the ethyl derivative fragments, the peaks at higher mass region being tabulated in Table III.

NMR Spectra. The proton magnetic resonance spectra were obtained at room temperature with a Varian A-60 high resolution NMR spectrometer operating at 60 Mc. The integrater was also employed for comparison of the signal intensity due to alkyl with that of pyridyl group. In these experiments, 10% carbon tetrachloride solutions were used with tetramethylsilane as an internal reference. The results are summarized in Table IV.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

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Table III. Mass Spectrum of $B_4Me_6N_3Py_3$

m/e	*Intensity*[a]	*Fragment*	*m/e*	*Intensity*[a]	*Fragment*
397	2.99		341	0.40	
396	22.05		340	1.48	
395	100.00		339	7.41	$B_3N_3Py_3Me_2$
394	88.53	$B_4N_3Py_3Me_5$	338	5.26	
393	32.67		337	2.00	
392	6.26		336	0.74	
391	0.98		335	0.80	$B_4N_3Py_3Me$
			334	0.63	
381	0.83		333	0.46	
380	3.62				
379	4.59	$B_4N_3Py_3Me_4$	326	0.9	
378	2.75		325	2.7	
377	0.96		324	3.5	
			323	4.6	$B_3N_3Py_3Me$
366	0.52		322	3.9	
365	1.74		321	2.9	
364	1.68	$B_4N_3Py_3Me_3$	320	2.2	
363	1.05		319	1.8	
362	0.57		318	1.2	$B_4N_3Py_3$
			317	0.7	
354	0.31				
353	0.48	$B_3N_3Py_3Me_3$	279	5.6	
352	0.38		278	25.9	
351	0.46		277	38.1	$B_3N_2Py_2Me_4$
350	1.19		276	24.2	
349	1.65	$B_4N_3Py_3Me_2$	275	35.6	
348	1.24		274	11.5	
347	0.78		273	4.8	
346	0.48				

[a] Relative peak intensities expressed relative to 100 for *m/e* 465.

Table IV. Proton Chemical Shifts (in τ Values) and Spin Coupling Constants J of Tris(dialkylboryl-2-pyridylamino) boranes, $(R_2B\cdot Py\cdot N)_3B$

Compound, R	*Chemical Shifts, τ,*		*Coupling Constants in Pyridine Proton, C. P. S.*
	B-R	*Py*	
Me	$(B\text{-}CH_3)$ 9.76	1.95 2.33-2.83 3.33	6.0 6.2
Et	$(B\text{-}CH_2C)$ 9.00 $(B\text{-}C\text{-}CH_3)$ 9.40	2.05 2.33-2.83 3.33	6.7 $J(CH_2, CH_3) = 8$
n-Bu	$(B\text{-}C_4H_9)$ 8.33-9.83	2.10 2.33-2.83 3.38	5.4 5.9

A very sharp intense line of the methyl derivative appearing at 9.76 in τ value was ascribed to protons in methyl groups bonded to boron. (Throughout the present paper, chemical shifts are expressed in τ values.) Ethyl groups in the ethyl derivatives yielded a composite group of lines, suggesting existence of intermediate coupling. These ethyl signals were compared with theoretical calculations by Wiberg and Nist *(31)* for an A_3B_2 spin system to evaluate the spin coupling constant and the relative internal shift, δ, between methyl and methylene proton signals. The theoretical spectrum calculated with this pair of values, $\delta = 0.4$ p.p.m., $J = 8$, yields a fairly good fit with experiments. Butyl signals which appeared at 8.33 to 9.83 were too complex for analysis. Pyridyl groups in each compound yield an *ABMX* type of signals in the region of 1.95 to 3.38. These were not analyzed because it was difficult to make assignment based on these NMR data alone and nothing was to be gained from the discussion of these signals in relation to the present molecular structure determination.

The ^{11}B NMR spectrum of the ethyl derivative was recorded by Varian Associates, Palo Alto, Calif., using HR-100 with the substitution of a 32.1-Mc. r.f. unit for the 100-Mc. unit. The spectrum gives two signals at -7.2 ± 0.2 and +16.8 ± 0.2 p.p.m., methyl borate being used as an external standard. Planimeter measurement of the areas of the two signals gives an area ratio of about 3.5 to 1 of the higher field to the lower field signal.

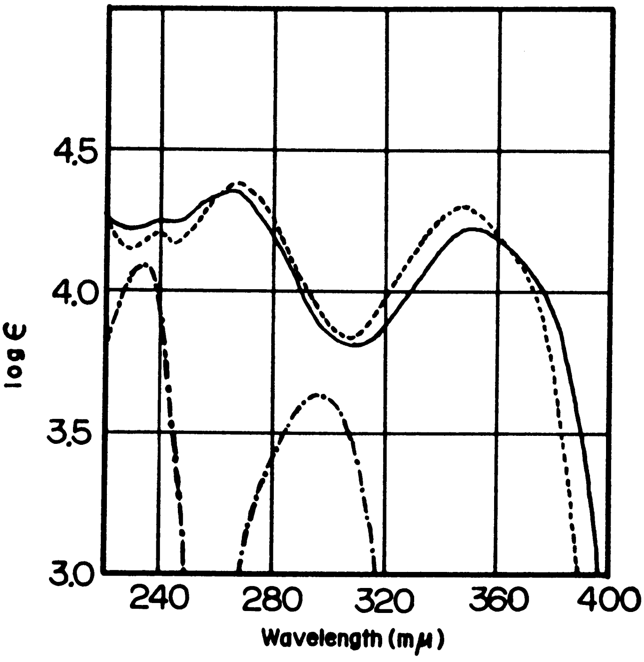


Figure 2. Ultraviolet spectra

------ *Methyl derivative*

——— *Ethyl and n-butyl derivatives*

-· -· -· - *2-Aminopyridine*

Ultraviolet Spectra. The ultraviolet spectra were recorded in ethanol solution over a region of 220 to 500 mμ, using a Hitachi recording spectrophotometer Model EPS-2, Hitachi Co., Ltd. The spectra of these compounds in 95% ethanol solution are shown in Figure 2.

Infrared and Raman Spectra. Infrared spectra were recorded over a rock-salt region on a DS-201B type spectrophotometer from the Optical Research Institute, Tokyo Kyoiku University. Polystyrene was the calibration standard. The spectra were taken in solutions, both carbon bisulfide and carbon tetrachloride being used as solvent.

The spectra are represented in Figure 3, along with tentative assignments of major bands to various modes of vibration. In Figure 3 are listed the absorptions of solutions in carbon bisulfide, except in regions where the solvent showed its own absorptions. In these regions, the curves of carbon tetrachloride solutions are given.

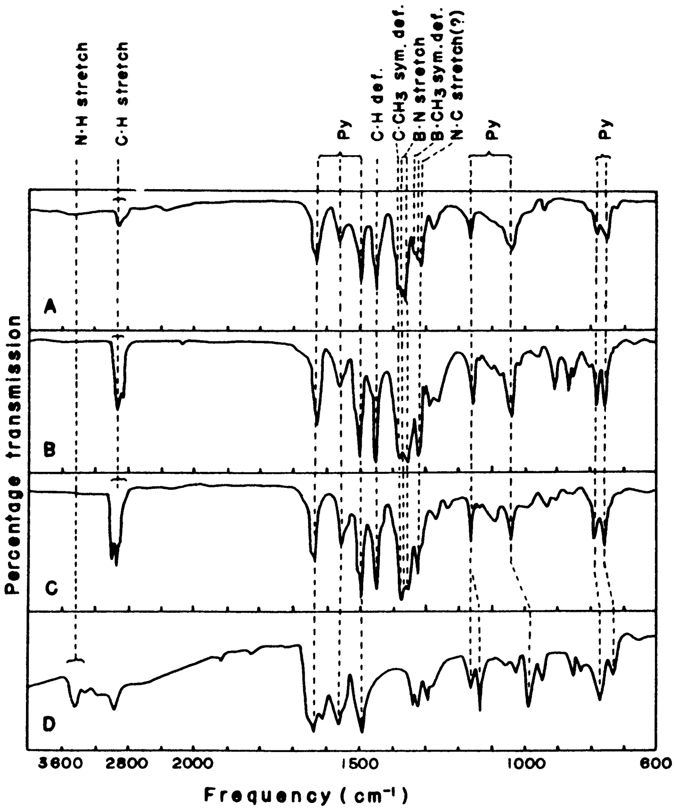


Figure 3. Infrared spectra of tris(dialkylboryl-2-pyridylamino)boranes

A. Methyl derivative B. Ethyl derivative
C. Butyl derivative D. 2-Aminopyridine

The Raman spectrum of the methyl derivative was determined by means of a Raman spectrometer, Model RL-II, from Yukigosei Kogyo

Co., Ltd., Tokyo. A saturated carbon tetrachloride solution was employed and only one band was observed at 1264.95 cm.$^{-1}$

Dipole Moment. The dielectric constants of benzene solutions were measured by means of a heterodyne beat apparatus provided with a platinum cell *(10, 17)*. The measurements were carried out at 25° C. on four different concentrations appropriately chosen below about 2.5% by weight for each sample. The changes of the dielectric constant (α) and density of the solution (β) with the weight fraction of the solute were evaluated by the least squares method.

The molar polarization of the solute was calculated by a method similar to that introduced by Halverstadt and Kumler *(14)*, differing in that densities were used rather than the specific volumes. The sum of electronic and atomic polarization was approximated with 1.05 times the molar refraction for *D* line. The results are summarized in Table V.

Table V. Dipole Moments of Tris(dialkylboryl-2-pyridylamino)-borane, $(R_2B\cdot Py\cdot N)_3B$, at 25°C. in Benzene

R	α	β, *G./Ml.*	P_2	MR_D	*(D)*
Me	1.84	0.15	257.7	133	2.40
Et	1.74	0.22	293.6	161	2.48
n-Bu	0.79	0.12	293.5	216	1.80

Discussion

The observed molecular weights shown in Table I, in conjunction with the elemental analyses and the starting materials, lead to the assumption of chemical formula of $B_4R_6N_3Py_3$ for the reaction product which was obtained by the reaction of boron trichloride with 2-aminopyridine followed by an appropriate Grignard reaction. This is discussed below.

The molecular weight determinations afford still another support for this formula. The difference between the molecular weight of the methyl derivative and that of the ethyl derivative may reasonably be attributed to the variation in number of methylene groups. The molecular weight difference 490—408 corresponds to 5.9 methylene, indicating the presence of six alkyl groups in the molecule. Similar calculations on the other two combinations—i.e., methyl-butyl and ethyl-butyl—give 6.4 and 6.7 for the number of alkyl groups.

In the mass spectrum of ethyl derivative, the most prominent peak of the parent peak region, is located at mass 493 instead of at 494 where one can expect the highest peak due to the parent. But this can be easily explained by the fact that the peak height of the parent minus one hydrogen is usually higher than that of the parent, and the contribution from the parent can be recognized by comparing the peak height of 494 with that of 491. If this pattern is composed of a single species of fragment, the calculation requires that the peak at 491 be higher than that at 494, as observed on the other fragments.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

A strong series of peaks was observed in the *m/e* region of 461 to 467. Surveying the mass spectrum of the ethyl derivative, one can easily recognize four series of peaks of a similar feature to each other at intervals of mass 29, the mass of the highest peaks in each mass group being 465, 436, 407, and 378. Furthermore, they are followed by two weaker series of peaks around 349 and 320. This interval of 29 corresponds to the mass of the ethyl group and indicates a successive elimination of the six ethyl groups from the parent—i.e., the peaks at mass 465, 436, 407, 378, 349, and 320 regions are associated with $B_4Et_5N_3Py_3$, $B_4Et_4N_3Py_3$, $B_4Et_3N_3Py_3$, $B_4Et_2N_3Py_3$, $B_4EtN_3Py_3$, and $B_4N_3Py_3$, respectively.

The molecular structures represented in Figure 1 allow ready interpretations for the mass groups of 367, 333, and 275 as due to the loss of BEt_2 and 2Et groups, the loss of diethylboryl-2-pyridylamino group (Et_2 BPyN), and the loss of Et_2 BPyN and 2Et groups, respectively.

Table VI. Comparison of Calculated and Observed Intensities of Various Fragments in Mass Spectra of the Ethyl Derivative

m/e	*Fragment*	*Calculated Value*				*Observed Value(H)*	
		B_5	B_4	B_3		B_4	B_3
467		2.9	3.4	0		5	
466		89.0	26.5	3.3		27	
465	$B_4R_5N_3Py_3$	100.0	100.0	100.0		100	
464		45.7	78.8	68.0		85	
463		10.5	25.7	15.6		30	
462		1.2	3.8	1.2		5	
461		0.1	0.2				
438			3.0			9	
437			24.8			37	
436	$B_4R_4N_3Py_3$		100.0			100	
435			79.4			94	
434			26.2			45	
433			3.9			14	
369				2.3			3
368				21.7			23
367	$B_3R_2N_3Py_3$			100.0			100
366				62.4			68
365				13.9			23
364				1.0			7
				(x^a=1/5)	(x^a=1/10)		
277				1.2	1.2		2
276				15.8	16.0		17
275	$B_3R_2N_2Py_2$ $(B_3R_2N_2Py_2\text{-}H)$			100.0	100.0		100
274				85.6	73.8		73
273				29.2	21.1		28
272				4.5	2.6		13

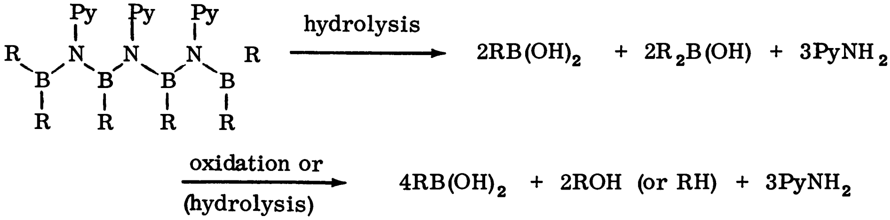
[a] Defined by $(1-x)(B_3R_2N_2Py_2) + x(B_3R_2N_2Py_2\text{-}H)$.

The feature of each mass group is also important for the interpretation. Attempts were made to fit the intensity data for the 465, 436, 367, and 275 mass groups by assuming that C-H and C-C bond cleavages are negligible as described. In the synthesis of the polyisotopic spectra, the following isotopic distributions for carbon, hydrogen, nitrogen, and boron were used: ^{12}C : ^{13}C = 98.892 : 1.108, ^{1}H : D = 99.985 : 0.015, ^{14}N : ^{15}N = 99.635 : 0.365, ^{10}B : ^{11}B = 18.7 : 81.3.

The calculated polyisotopic spectra for the relative intensities in each mass group are given in Table VI, in which the observed relative intensities to the highest peak in each group are also listed for comparison. To show how the relative intensities vary in the region of 465 with the boron content in a fragment, in Table VI are shown calculations for 3, 4, and 5 boron-containing fragments, although the 3 and 5 boron-containing species are not reasonably conceivable. Comparison of these three calculated spectra with the observed one shows that this fragment contains four boron atoms. In the 275 region, 1/5 and 1/10 contribution from the fragment, $B_3R_2N_2Py_2$ minus one hydrogen, was taken into account to obtain better fit to the observed spectrum. The agreement between the observed and calculated relative intensities lends further support to their assignments and to the molecular structure of the parent.

If we accept the probable assumptions that *(a)* in the reaction of boron trichloride and 2-aminopyridine, boron can form three new bonds only with the amino nitrogen and the nitrogen can establish two bonds only with boron—i. e., N-Py bond is stable—and *(b)* the composition of the reaction product is $B_4N_3Py_3R_6$, it is easily derived that only two boron-nitrogen skeletons are possible: One is a C_{3h} symmetrical model illustrated by Structure I and the other is a normal chain model, Structure II in Figure 1.

Although the data discussed hitherto do not permit a choice between these alternatives, the experimental result of hydrolysis supports and the NMR spectra afford definite evidences for Structure I. Treating a suspension of this compound in water with hydrochloric acid led to complete decomposition, and from 1 mole of the butyl derivative were recovered 2.7 moles of alkyldihydroxyborane, 2.8 moles of 2-aminopyridine, some alcohol, and some boric acid. This fact indicates that all nitrogen atoms are involved as pyridyl-amino groups and at least three alkyl groups are attached to three boron atoms. In the case of the normal chain model, Structure II, the hydrolysis can be expected to go on along the following scheme to give 4 moles of alkyldihydroxyborane.



whereas the C_{3h} model, Structure I, can reasonably be expected to yield 3 moles of alkyldihydroxyborane,

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

$$(R_2B\cdot Py\cdot N)_3B \xrightarrow{\text{hydrolysis}} B(OH)_3 + 3R_2B(OH + 3PyNH_2$$

$$\xrightarrow[\text{(hydrolysis)}]{\text{oxidation or}} 3RB(OH)_2 + B(OH)_3 + 3ROH \text{ (or RH)} + 3PyNH_2$$

The experimental result of 2.7 moles is favorable to Structure I.

The proton magnetic resonance spectrum of the methyl derivative in carbon tetrachloride consists of pyridyl proton resonances spread over a range of 1.95 to 3.33, and a sharp single line at 9.76 in τ value. The R_1 set of Structure II (Figure 1) is not environmentally equivalent to the terminal groups, which also fall into two species, whereas all methyl groups in Structure I comprise the one set of spectroscopically equivalent methyl protons which can explain the methyl signal to be a singlet.

Dailey and Shoolery *(7)* have shown that a linear relation holds between the electronegativity and the internal chemical shift, $\tau(CH_3) - \tau(CH_2)$, in an ethyl group.

$$\text{E.N.} = 0.695 \left\{\tau(CH_3) - \tau(CH_2)\right\} + 1.71$$

On the basis of this relation, the electronegativity (E.N.) of boron was calculated to be 1.99. Comparison of this value with the electronegativity (1.8) of boron in triethylborane *(23)* evaluated in the same way leads to the conclusion that the extent of electron transfer from nitrogen to boron through the donor-acceptor π-bond is less than that from boron to nitrogen through the σ-bond because of the electronegativity difference. This implies that $-BR_2$ groups are bonded to nitrogen with their CBC planes perpendicular to the B(center)NPy plane—i.e., the molecular plane—as illustrated in Figure 1, Structure I.

The ratios of the integrated intensity of alkyl proton signals to that of pyridyl proton signals are listed in Table VII together with the calculated values for $B_4R_6N_3Py_3$. This agreement between the observed and the calculated ratios confirms again that twice as many alkyl groups as pyridyl groups are present in this series of molecules.

Table VII. Intensity Ratios in NMR Spectra of Tris(di-R-boryl-2-pyridylamino)boranes

R	*R/Py*	
	Obsd.	*Calcd. for* $B_4R_6N_3Py_3$
Me	1.45	1.50
Et	2.64	2.50
-Bu	4.44	4.50

In Structure I there are two types of boron atoms, one center boron and three surrounding borons, and in Structure II there are also two types of boron atoms, but they form two pairs. For Structure I, ^{11}B

NMR spectrum can be expected to show two signals having relative intensities of 1 to 3, while for Structure II, the spectrum is expected to show two peaks of equivalent intensity. The experimental intensity ratio of 3.5 to 1 supports Structure I.

The value of dipole moment 2.48 *D* is considerably large for Structure I, whose symmetry C_{3h} demands a zero moment. Though distortion from symmetrical configuration could occur through steric repulsion, the explanation is presumably atomic polarization—i.e., the excitation of molecular vibrations having a low frequency and large effective charge which lead to the existence of a temporary moment.

The ultraviolet spectra are shown in Figure 2 along with the curves of 2-aminopyridine for comparison. Those of the methyl and ethyl derivatives closely resemble each other and differ markedly from that of the starting material. The intense absorption at 350 mμ (log $\epsilon = 4.22$) provides further evidence for the large conjugate π-system, suggesting that three pyridyl groups lie in the molecular plane as Structure I.

Figure 3 represents the infrared spectra of these compounds and 2-aminoborane, along with tentative assignments of major bands to various modes of vibration. These compounds are too complex to permit unequivocal assignments, but extensive investigation of infrared spectra of alkyldiboranes *(18, 20)* facilitates the assignment of the bands due to alkylboryl groups. Comparison of the spectra of alkyl derivatives with 2-aminopyridine allows ready assignment of absorptions due to pyridyl groups. The degenerate deformation vibrations of methyl groups are known to appear at about 1450 cm.$^{-1}$, and accordingly the band at 1442 cm.$^{-1}$ in each derivative was assigned to this mode. The symmetric deformation vibration also is expected to appear in the vicinity, depending upon the electronegativity of atoms bonded to the methyl groups *(4, 5, 19)*. From the NMR spectrum of the ethyl derivative, the electronegativity of boron is calculated as 1.99, which leads to an expected wave number of 1320 cm.$^{-1}$ for the symmetric deformation of methyl groups in the methyl derivative. The assignment of 1314- and 1324-cm.$^{-1}$ bands to the pair of B-$(CH_3)_2$ symmetric deformation was also supported by their disappearance in the spectra of higher alkyl derivatives.

It is well recognized that boron-nitrogen bonds having some double-bond character usually exhibit very strong absorptions due to their stretching vibration in the region of 1350 to 1500 cm.$^{-1}$ *(2, 3, 6, 11, 13, 24, 27, 28, 29)*, and in these molecules three very strong absorptions were observed in this wave number range. Of these three bands, two observed in the methyl derivative at 1354 and 1364 cm.$^{-1}$ were assigned to the degenerate B-N stretching vibration, because the B-N stretching vibrations were assigned to bands at 1353 and 1367 cm.$^{-1}$ in tris(phenylmethylamino)borane *(2)*, whose molecular structure resembles Structure I of our compounds.

Although there are still many bands to be assigned in the low-wave number region, further assignments have not been performed because there are many possible ways of assignment at present and resulting ambiguous assignments can yield no fruitful result for structure determination.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

Conclusions

This series of physicochemical investigations shows clearly that the reaction between 2-aminopyridine and boron trichloride followed by the Grignard reaction gives a new type of boron-nitrogen compound as sketched in Figure 1, Structure I. Attempts to prepare the ethyl derivative by altering the stoichiometry of the equation gave unsatisfactory yields. However, no definite conclusions with regard to the reaction mechanism can be drawn at present.

To test the steric-hindrance hypothesis, the reactions of 3- and 4-aminopyridine with boron trichloride were examined under the same conditions as 2-aminopyridine. However, in these cases it was not possible to obtain the corresponding isomer, the products being not yet identified.

Acknowledgment

The authors express their gratitude to D. K. Takeda, director of this laboratory, for his encouragement throughout the course of this work.

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Received June 5, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch013

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Hydrolyses of Some Boron-Nitrogen Derivatives

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch014

The hydrolyses of a variety of boron-nitrogen compounds have been investigated in homogeneous solvent-water solutions which contain a large excess of water. Under these conditions, hydrolysis rates followed pseudo-first-order kinetics in all cases. Hydrolyses of series of tri(amino)-boranes and tetra(amino)diborons suggest that steric effects have significant influence on the observed hydrolysis rates of these materials.

A variety of organoboron compounds containing covalent boron-nitrogen bonds have been described in the literature. Although qualitative references have been made to the hydrolytic stability of these materials, no comparative hydrolysis rate studies have been reported. The present paper includes the results of semiquantitative hydrolysis rate studies carried out at intervals for several years. Some of the initial results have been discussed *(14)*. Although the experimental techniques used in these studies might not meet the strict criteria normally required for a quantitative kinetic investigation, the results allow comparisons to be made between the boron-nitrogen derivatives investigated. It is also possible to compare the general hydrolytic stability of some of the boron-nitrogen systems with related boron-oxygen compounds which were the subject of a previous investigation in this laboratory *(13)*.

Most previous reports of the hydrolytic stability of boron-nitrogen compounds refer to hydrolytic stability in heterogeneous aqueous systems or in the presence of atmospheric moisture. In the present work a variety of boron-nitrogen compounds were hydrolyzed in dilute (0.02 to 0.07 mole per liter) homogeneous solvent-water solutions. Hydrolysis rates were followed by titrating the amount of free amine formed and assuming that appearance of free amine is directly related to B-N hydrolysis. The first-order plots obtained from B-N compounds derived from a variety of amines and the known chemistry of these materials tends to confirm this assumption. The reversibility of the hydrolysis reaction ($>\text{B-OH} \rightarrow >\text{B-N}<$) has been demonstrated in a few cases involving formation of stable B-N rings, but this reaction is extremely slow and can be ignored in the present discussion. Solvents used were acetone, tetrahydrofuran, and dioxane. No measurable differences in rates were observed when these different solvents were used in identical hydrolysis experiments. An example of this is the hydrolysis of tet-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch014

rakis(dimethylamino)diboron, which hydrolyzed at essentially the same rate in acetone and tetrahydrofuran (see Table II). A large excess of water was present in all cases, and the hydrolysis reactions followed pseudo-first-order kinetics. Plots of the logarithms of the moles of unhydrolyzed starting materials *vs.* time approached linearity up to at least 50% hydrolysis for all reactions which were slow enough to follow accurately. The analytical procedure used involved rapid titration of the free amine formed during hydrolysis, except for derivatives of aromatic amines, which required alternative techniques. The over-all objective of this study was the determination of relative hydrolysis rates, and probable hydrolysis mechanisms are not discussed in detail.

The hydrolyses of a number of tri(amino)boranes derived from both primary and secondary amines were investigated. Observed hydrolytic first-order rate constants and half lives of these materials are shown in Table I. Half lives refer to hydrolyses of 50% of all B-N bonds in the molecule. Tri(amino)boranes derived from aliphatic primary amines hydrolyzed rapidly, except for the sterically hindered *tert*-butyl derivative. Steric effects also appear to be significant factors in the hydrolysis of secondary amine derivatives. Tris(di-*n*-butylamino)- and tris (diphenylamino)boranes, in which approach to the boron atoms and possible formation of a tetrahedral transition state are severely restricted, were comparatively stable in homogeneous solutions.

Table I. Hydrolyses of Tri(amino)Boranes

B(NRR')₃					
R	*R'*	*Solvent*	*Temp., °C.*	*Half Life*	*Rate Constant, Sec.$^{-1}$*
H	CH_3	90% acetone	25	<30 sec.	
H	$\underline{n}$-C_3H_7	90% acetone	25	<30 sec.	
H	$\underline{i}$-C_3H_7	90% acetone	25	<30 sec.	
H	$\underline{n}$-C_4H_9	90% acetone	25	<30 sec.	
H	$\underline{i}$-C_4H_9	90% acetone	25	<30 sec.	
CH_3	CH_3	90% acetone	25	53 sec.	1.31×10^{-2}
CH_3	CH_3	90% acetone	0	2.0 min.	5.78×10^{-3}
H	$\underline{tert}$-C_4H_9	90% acetone	25	23 min.	5.02×10^{-4}
H	$\underline{tert}$-C_4H_9	90% acetone	0	20 min.	5.78×10^{-4}
C_2H_5	C_2H_5	90% acetone	25	5.5 hr.	3.50×10^{-5}
C_2H_5	C_2H_5	90% acetone	0	58 hr.	3.32×10^{-6}
$\underline{n}$-C_4H_9	$\underline{n}$-C_4H_9	90% tetrahydrofuran	25	30 hr.	6.42×10^{-6}
C_6H_5	C_6H_5	90% dioxane	25	40 days	2.01×10^{-7}

Hydrolyses of certain tri(amino)boranes have been discussed *(1)* to illustrate the importance of electronic effects in reactions of these materials. Although the evidence is not conclusive, it appears to us that steric effects predominate in most of the present hydrolysis reactions.

Without considering specific details of the respective hydrolysis mechanisms, the simplified assumption can probably be made that the rate-determining step involves either nucleophilic attack on boron by water molecules or protonation of the B-N nitrogen. Neither one of these alternative simple mechanisms can be used to give a consistent explanation for the order of observed hydrolysis rates of tri(amino)boranes and tetra(amino)diborons. The observed order does appear to be consistent, however, with steric effects as judged from experience in related systems and consideration of appropriate molecular models.

Table II. Hydrolyses of Tetra(amino)diborons

$B_2(NRR')_4$					
R	*R'*	*Solvent*	*Temp., °C.*	*Half Life*	*Rate Constant, Sec.$^{-1}$*
H	CH_3	90% acetone	0	<30 sec.	
CH_3	CH_3	90% acetone	25	1.5 hr.	1.28×10^{-4}
CH_3	CH_3	90% acetone	0	5.8 hr.	3.32×10^{-5}
CH_3	CH_3	90% tetrahydrofuran	25	1.25 hr.	1.54×10^{-4}
CH_3	CH_3	90% tetrahydrofuran	0	6.5 hr.	2.96×10^{-5}
n-C_4H_9	n-C_4H_9	90% tetrahydrofuran	25	~200 hr.	9.23×10^{-7}

Hydrolysis experiments with three tetra(amino)diborons are illustrated in Table II. The dimethylamino and di-*n*-butylamino derivatives are significantly more stable than the comparable aminoboranes, but tetra(methylamino)diboron hydrolyzes rapidly. Examination of molecular models indicates that the boron atoms in the diboron compounds are significantly more sterically hindered than those in the analogous tri(amino)boranes and that approach of water molecules as well as formation of a tetrahedral transition state would be severely restricted in the diborons. Tetrakis(di-*n*-butylamino)diboron (half life ~ 200 hours) is one of the most hydrolytically stable of the B-N compounds which have been studied.

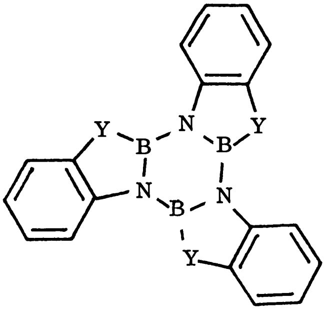
Table III. Hydrolyses of Borazines

$(RBNR')_3$					
R	*R'*	*Solvent*	*Temp., °C.*	*Half Life*	*Rate Constant, Sec.$^{-1}$*
n-C_3H_7NH	n-C_3H_7	90% acetone	0	<30 sec.	
i-C_3H_7NH	i-C_3H_7	90% acetone	25	<30 sec.	
C_6H_5	CH_3	90% dioxane	25	<30 sec.	
i-C_3H_7	CH_3	90% acetone	0	35 sec.	1.98×10^{-2}
C_2H_5	CH_3	90% acetone	0	1 min.	1.16×10^{-2}
CH_3	CH_3	90% acetone	0	7.5 min.	1.54×10^{-3}
C_6H_5	H	90% acetone	25	8.5 min.	1.36×10^{-3}
C_6H_5	C_6H_5	90% tetrahydrofuran	25	1-2 hr.	$1\text{-}2 \times 10^{-4}$

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch014

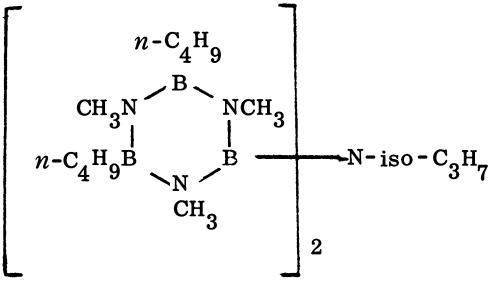
Hydrolysis rates were determined for a number of borazines, as shown in Table III. Because of the complexities involved in considering possible hydrolysis mechanisms of these compounds, it is even more difficult to discuss results in terms of specific reaction routes than in simple derivatives such as the tri(amino)boranes and diborons. However, it is possible to draw some general conclusions from the data. It is apparent that *B*-trimethyl-*N*-triphenylborazine is the most stable borazine which was investigated. Comparison with *B*-triphenyl-*N*-trimethyl-, hexamethyl-, and hexaphenylborazines suggests that hydrolytic stability is enhanced by aromatic groups on nitrogen and decreased by aromatic groups on boron. The hydrolysis rates of hexamethyl-, *B*-triethyl-*N*-trimethyl-, and *B*-triisopropyl-*N*-trimethylborazines are not considered to be significantly different, although hexamethylborazine appears to hydrolyze at the slowest rate. The rapid hydrolysis rates observed with the *B*-triaminoborazines are probably due to the initial hydrolysis at the *exo*-boron-nitrogen bonds. Initial cleavage of these bonds in *B*-triaminoborazines has been reported *(11)*.

Three additional borazine derivatives, the polycyclic compounds (I and II) and the diborazinylamine (III), have been hydrolyzed as



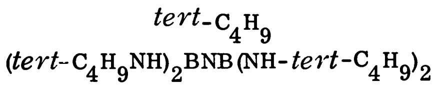
I, Y = NH

II, Y = O



III

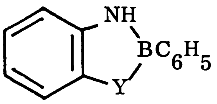
shown in Table IV. The borazine (I) is stable in neutral 82% acetone at ambient temperature, but its hydrolysis rate is greatly increased by the addition of base; it hydrolyzes still more rapidly in the presence of acid. The oxygen-containing borazine (II) is significantly less stable in neutral 82% acetone at ambient temperatures. The diborazinylamine (III) hydrolyzed rapidly at 0° in 90% tetrahydrofuran. The aminoborane derivative (IV) is moderately stable (half life 5 hours) because of the



$$(tert\text{-}C_4H_9NH)_2B\overset{tert\text{-}C_4H_9}{N}B(NH\text{-}tert\text{-}C_4H_9)_2$$

IV

bulky *tert*-butyl groups surrounding the boron atoms. 2-Phenylbenzo-1,3-diaza-2-boroline (V) has a half life of 47 hours at 23° C. in 82% acetone. This was reduced to 3.7 minutes by the addition of sodium hydroxide. The mono-oxygen analog (VI) hydrolyzed rapidly in heterogeneous water solution at 23° and would undoubtedly hydrolyze at a rate too fast to measure by the method used under homogeneous conditions.



V. Y = NH

VI. Y = O

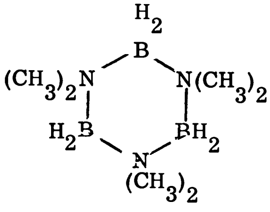
Table IV. Hydrolyses of Some Miscellaneous Boron-Nitrogen Derivatives

Compound	*Solvent*	*Temp., °C.*	*Half Life*	*Rate Constant, Sec.$^{-1}$*
I	82% acetone	23	4.3-6 days	$1.34\text{-}1.87 \times 10^{-6}$
II	82% acetone + NaOH[a]	23	3.4 min.	3.34×10^{-3}
II	82% acetone + HCl[a]	23	<30 sec.	
II	82% acetone	23	9 hr.	2.14×10^{-5}
III	90% tetrahydrofuran	0	2.2 min.	5.25×10^{-3}
IV	90% acetone	25	5 hr.	3.85×10^{-5}
V	82% acetone	23	47 hr.	4.10×10^{-5}
V	82% acetone + NaOH[b]	23	3.7 min	3.12×10^{-3}
VI	Water	23	5 min.	2.31×10^{-3}
VII	90% tetrahydrofuran	25	(No hydrolysis observed after 35 days)	

[a] 3 equivalents added per mole of II.

[b] 1.25 equivalents added per mole of V.

The most stable boron-nitrogen derivative investigated was the trimer *(6, 15)* of dimethylaminoborane (VII). This compound appeared to be completely stable in homogeneous acetone-water for 35 days at 25° C. These data confirm earlier qualitative observations relating to the hydrolytic stability of cyclic tetrahedral boron derivatives of this type *(3, 6, 7)*.



VII

In several cases it is possible to compare directly the hydrolytic stability of boron-nitrogen derivatives with related boron-oxygen systems. The hydrolytic half life of tri(*tert*-butylamino)borane is 23 minutes, whereas that of *tert*-butyl borate is 14 minutes under comparable conditions *(14)*. The oxygen-substituted derivatives (II and VI) are also less hydrolytically stable than the comparable nitrogen-substituted compounds (I and V). These results suggest that boron-nitrogen compounds are more stable than analogous B-O derivatives, but this must be considered a tentative conclusion, since direct comparison is difficult and has been noted only in these few cases and the differences are small. In a general qualitative sense, B-N derivatives appear to be more hydrolytically stable than related B-O compounds, but this increased stability could arise from the additional steric effect introduced by the extra substituent on nitrogen.

Experimental

Solvents. Acetone (reagent grade) was either redistilled from calcium sulfate or purified by the formation and subsequent decomposition of the acetone-sodium iodide addition product. Hydrolysis rates determined in acetone purified by these two methods were indistinguishable. Tetrahydrofuran was redistilled from sodium hydride before use.

Boron-Nitrogen Compounds. Tri(methylamino)-, tri(*n*-propylamino)-, tri(isopropylamino)-, tri(isobutylamino)-, tri(*tert*-butylamino)-, tris (diethylamino)-, and tris(dimethylamino)boranes were prepared by the reactions of the appropriate amines with boron trichloride *(2, 9, 10)*. Tris(di-*n*-butylamino)borane, a new compound, was also prepared (in 73% yield) from boron trichloride; b.p. 155°/0.55 mm., n_D^{24} = 1.4570). Tris(diphenylamino)- and tri(*n*-butylamino)boranes were prepared by transamination reactions described previously *(8)*.

The preparation of tetrakis(dimethylamino)-, tetrakis(di-*n*-butylamino)-, and tetra(methylamino)diborons have also been described previously *(4)*.

The simple borazines which were investigated were prepared by known methods. The polycyclic borazines (I and II), 2-phenylbenzo-1,3-dioxa-2-boroline (V), and 2-phenylbenzo-1,3-dioxa-2-borole (VI) were also prepared by previously reported procedures *(5)*.

Preparation of III. Bis-(*B*-dibutyl-*N*-trimethylborazinyl-*B*)-isopropylamine (III) was prepared by the addition of 1.1 grams (0.019 mole) of isopropylamine to a mixture of 10.0 grams (0.038 mole) of *B*-chloro-*B*-dibutyl-*N*-trimethylborazine *(12)* and 3.8 grams (0.038 mole) of triethylamine in 20 ml. of toluene. This mixture was refluxed for 12 hours, and the resulting amine hydrochloride removed by filtration. Fractional distillation of the filtrate resulted in 3.4 grams (34% yield) of the bis(borazinyl)amine; (b.p. 205-24/1 mm., m.p. 80.4-82.8°).

Analyses Calculated for $C_{25}H_{61}N_7B_6$: B, 12.4; N, 18.7; molecular weight 525. Found: B, 12.6; N, 17.9; molecular weight (cryoscopic in benzene), 565.

Preparation of IV. Liquid boron trichloride (114.7 grams, 0.98 mole) was added to a stirred solution of 642 grams (8.8 moles) of *tert*-butylamine in 1 liter of toluene at -78° C. over a 25-minute period in a dry nitrogen atmosphere. The mixture was slowly warmed to room

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch014

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temperature overnight. The resulting solid, *tert*-butylamine hydrochloride (300.6 grams, 93%), was removed by filtration. Distillation of the filtrate yielded excess amine and 114.6 grams (51.5% yield) of tri(*tert*-butylamino)borane. Continued distillation yielded 39.6 grams of a yellow solid. Redistillation and recrystallization of this higher boiling fraction yielded IV; (b.p. 112-113°/0.25 mm., m.p. 59-60°).

Analyses Calculated for $C_{20}H_{49}N_5B_2$: C, 63.05; H, 12.96; N, 18.39; B, 5.67; molecular weight, 381. Found: C, 62.00; H, 12.61; N, 18.3; B, 5.63; molecular weight (cryoscopic in benzene), 3.95.

Hydrolysis Procedure. Hydrolysis rates of aliphatic amine derivatives were determined by the following standard Procedure A. Procedure B was used for derivatives of aromatic amines.

Procedure A. A sample of the boron-nitrogen compound which would give approximately 5 to 15 meq. of amine on complete hydrolysis was weighed into a 50-ml. volumetric flask in an atmosphere of dry nitrogen. Slightly less than 45 ml. of solvent was added, and the flask was shaken until the sample dissolved completely. The resulting solution was placed in a constant temperature bath along with a separate distilled water solution. When these solutions had equilibrated to the desired temperature, 5 ml. of water was added to the solution containing the sample to be hydrolyzed. This solution was immediately brought to 50 ml. by the addition of solvent (also at the bath temperature) and the final solution was placed quickly in the constant temperature bath. The stopwatch was started at this point. The above operations were performed as rapidly as possible. At desired time intervals, 2-ml. aliquots were withdrawn and added immediately to a 500-ml. Erlenmeyer flask which had been half filled with ice (prepared from distilled water) and to which 100 ml. of distilled water and 3 drops of methyl purple had been added. This ice-water solution was titrated immediately with 0.02*N* hydrochloric acid to the methyl red end point.

Blank runs in the absence of water showed that less than 2% of the amino substituents on boron atoms were titrated under these conditions. The results given in the tables were not corrected for this blank hydrolysis. Acetone was used as a solvent wherever possible. In some cases, the acetone insolubility of the B-N derivatives required the use of tetrahydrofuran or dioxane. The hydrolysis of materials with first-order half lives of 30 seconds or less could not be followed accurately.

Procedure B. The hydrolysis rates of aromatic amine derivatives [I, II, V, hexaphenylborazine, and tris(diphenylamino)borane] were determined by an alternative method, which involved a gravimetric method based on the water insolubility of these compounds. The B-N compound was first dissolved in the solvent-water solution at a given temperature. After a desired time interval, the solution was added to a large excess of ice water and the unhydrolyzed material was filtered and weighed. Blank hydrolyses in heterogeneous water showed that these materials could be recovered quantitatively.

Acknowledgment

The authors thank H. Goldsmith and L. L. Petterson for the preparation of many of the compounds used in these hydrolysis studies.

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Received May 20, 1963.

Reaction of Trimethylamine with $H_2AlBH_4 \cdot N(CH_3)_3$

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch015

The $H_2AlBH_4 \cdot N(CH_3)_3$ complex absorbs one mole of $N(CH_3)_3$ to form $H_2AlBH_4 \cdot 2N(CH_3)_3$. This material is not stable and disproportionates to $AlH_3 \cdot N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3$. An equilibrium exists among these three species. Preliminary results on the interaction of $N(CH_3)_3$ and $HAl(BH_4)_2 \cdot N(CH_3)_3$ are also reported.

The reaction of amines with the boron hydrides has been studied by many investigators and several reaction modes have been observed. Boron when bonded to bridging hydrogens was found to be susceptible to nucleophilic attack and symmetrical cleavage of diborane upon treatment with tertiary amines occurred readily *(1, 6)*. On the other hand, the reaction of nucleophiles with aluminum borohydride has been little studied. The borohydride groups in aluminum borohydride are believed to be bonded to aluminum by two hydride bridges *(2)* and in this respect aluminum borohydride resembles diborane. The results of an early study *(5)* on the reaction of trimethylamine with $Al(BH_4)_3$ suggested that some symmetrical cleavage of the bridge bonds occurred. The system was found to be complicated and the presence of several species was indicated. However, more recently it was shown that treatment of $HAlBH_4N(CH_3)_2$ and $Al(BH_4)_2N(CH_3)_2$ with trimethylamine resulted in a rapid quantitative cleavage of the hydride bridges according to the equations *(3)*:

$$(CH_3)_2NAl(BH_4)_2 + 2N(CH_3)_3 \longrightarrow H_2AlN(CH_3)_2 + 2BH_3N(CH_3)_3$$

$$(CH_3)_2NAl(BH_4)H + N(CH_3)_3 \longrightarrow H_2AlN(CH_3)_2 + BH_3N(CH_3)_3$$

The reaction of trimethylamine with similar derivatives was extended to include $H_2AlBH_4 \cdot N(CH_3)_3$ and the preliminary results of a study of the $HAl(BH_4)_2 \cdot N(CH_3)_3$-$N(CH_3)$ system were obtained.

Experimental

Materials. The hydrido aluminum borohydride complexes were prepared as described *(3)*. Trimethylamine was obtained from the Mathieson Co. and used after drying over lithium aluminum hydride and fractionating through a -64° bath.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Reaction of $H_2AlBH_4 \cdot N(CH_3)_3$ with $N(CH_3)_3$. Sealed Bulb Experiments. A 0.356-gram sample of H_2AlBH_4 and 5 ml. of paraffin oil were placed in a 25-ml. pressure flask equipped with a Fischer-Porter Teflon needle valve. Trimethylamine (0.987 gram) was condensed into the flask, and the mixture was allowed to stand at 25° for 24 hours. Upon fractionation 0.564 gram of trimethylamine was recovered. Sublimation of the residue at 0° produced 0.172 gram of trimethylamine-borone (m.p. 92-93°). After 6 hours the temperature of the residue was raised to 35° and the sublimation was continued. The next batch of sublimate collected over a 15-minute period contained both B-H and Al-H materials (as evidenced by infrared). Finally a 0.101-gram sample of $AlH_3 \cdot 2N(CH_3)_3$ was isolated (m.p. 95-98°). Thus 2.07 moles of TMA were consumed per mole of borohydride derivative. The procedure was repeated using 0.321 gram of $H_2AlBH_4 \cdot N(CH_3)_3$, 0.879 gram of trimethylamine, and 5 ml. of toluene instead of paraffin oil. After the excess TMA had been removed (0.501 gram was recovered), while the reaction flask was held at -45°, a sample of the remaining solution was taken to obtain a B^{11} NMR spectrum. This consisted only of a quadruplet centered at 26.3 p.p.m. relative to methyl borate, J_{BH} = 100 c./s.

Tensiometric Titrations. The procedure used has been described *(4)*. A solution of 0.216 gram of $H_2AlBH_4 \cdot N(CH_3)_3$ in 5 ml of *n*-decane was treated with known amounts of trimethylamine. If only 15 minutes at 25° were allowed to establish equilibrium, curve a in Figure 1 was obtained. The titration was repeated using 0.196 gram of $H_2BH_4 \cdot N(CH_3)_3$ in 4 ml. of *n*-decane and 6 hours at 25° was allowed to establish equilibrium after each addition of amine. The second titration is shown in curve b of Figure 1.

Reaction of $HAl(BH_4)_2 \cdot N(CH_3)$ with $N(CH_3)_3$. Sealed Bulb Experiments. The procedure followed is identical to that described above. A solution of 0.428 gram of $HAl(BH_4)_2 \cdot N(CH_3)$ in 5 ml. of paraffin oil comsumed 0.632 gram of trimethylamine, and a 0.194-gram sample of $BH_3 \cdot N(CH_3)_3$ (m.p. 91 - 92°) was obtained by fractionation. Similarly, a solution of 0.401 gram of $HAl(BH_4)_2 \cdot N(CH_3)_3$ in 5 ml. of toluene consumed 0.592 gram of $N(CH_3)_3$. A B^{11} NMR spectrum of this solution consisted of a quadruplet, δ = 25.9 p.p.m., J_{BH} = 101 c./s. relative to methylborate. Small amounts of a noncondensable gas (shown to be hydrogen by mass spectral analysis) were present in these two runs.

Tensiometric Titrations. When the titration was performed at 25°, equilibrium was not attained and the pressure did not remain constant over a 15-minute period after addition of amine. However, when the titration was performed at 0° the pressure was constant over a 15-minute period after reaching thermal equilibrium and its value was recorded. A solution of 0.176 gram of $HAl(BH_4)_2 \cdot N(CH_3)_3$ in 4 ml. of *n*-decane gave an end point ratio of amine to hydride of 1.07. Because of the lower observed pressures, the break was not as sharp as those shown in Figure 1.

Attempted Isolation of $H_2AlBH_4 \cdot 2N(CH_3)_3$. A 0.401-gram (3.89 mmole) sample of $H_2AlBH_4 \cdot N(CH_3)_3$ was placed in a weighed flask was 10 ml. of dried diethyl ether; then 3.82 mmoles of trimethylamine were condensed into the flask. The flask was stirred 10 minutes at -78° and warmed to -35°. The ether was removed at this temperature under vacuum and the solid residue was dried under vacuum for 1 hour at -35°.

The flask was warmed to 0°; the residue remained as a white solid without change for several hours. The flask was then quickly weighed and the weight of the residue was found to be 0.641 gram [Calculated for $H_2AlBH_4 \cdot 2N(CH_3)_3$, 0.632 gram]. The solid liquefied on standing at 25° for several minutes. Approximately 2 ml. of toluene were added to the flask and the solution was aged one day before obtaining its B^{11} NMR spectrum.

A 0.625-gram (6.08 mmole) sample of $H_2AlBH_4 \cdot N(CH_3)_3$ was treated with 6.04 mmoles of trimethylamine in the above manner. After removal of the ether, the residue was allowed to age at ambient temperature for 24 hours. Sublimation at 0° yielded 0.096 gram of $BH_3 \cdot N(CH_3)_3$, (m.p. 94°). Sublimation of the remaining material at higher temperatures (20° to 45°) produced liquids and wet solids which were obviously impure.

NMR Studies. All the B^{11} NMR spectra were obtained on a Varian Model 4300B spectrometer operating at 12.8 megacycles. Trimethylborate in capillary tubes was used as a standard in every case and toluene as a solvent.

Decomposition of $H_2AlBH_4 \cdot 2N(CH_3)_3$. The B^{11} NMR spectrum of the sample described above consisted of a quadruplet (δ_4 = 26.0 J_{BH} = 100) and a quintuplet (δ_5 = 56.6 J_{BH} = 86). The relative areas of the two were found to be BH_3/BH_4 = 0.739. In another experiment 0.379 gram (3.68 mmoles) of $H_2AlBH_4 \cdot N(CH_3)_3$ in 1 ml. of toluene was placed in a bulb equipped with a NMR tube extension on one side. Trimethylamine (3.60 mmoles) was condensed into the reactor and allowed to mix at -78°. The bulb was warmed at 25° and a sample of the solution was poured into the NMR tube and the NMR spectrum was run. Only a quintuplet was present (δ = 56.4 J_{BH} = 85). After 2 hours the spectrum was rerun and the presence of a quadruplet was observed (δ_4 = 26.2 J_{BH} = 99); after approximately 8 hours no further change in the relative areas of the quadruplet and quintuplet could be detected; BH_3/BH_4 = 0.724. When an attempt was made to repeat the above experiment with 0.315 gram (2.68 mmoles) of $HAl(BH_4)_2 \cdot N(CH_3)_3$ and 2.65 mmoles of $N(CH_3)_3$ it was not possible to obtain a B^{11} NMR spectrum that did not show the presence of a quadruplet. The best spectrum obtained had a ratio of areas of BH_3/BH_4 = 0.12. The quadruplet increased much more rapidly than when $H_2AlBH_4 \cdot N(CH_3)_3$ was employed.

Equilibrium Experiments. A series of solutions was prepared containing trimethylamine-alane and trimethylamine-borane in toluene, in varying ratios. Initially only a quadruplet (δ = 26.1 J_{BH} = 100) was present in the B^{11} NMR spectrum of solution A (see Table I). However, after 24 hours a quintuplet (δ_5 = 56.6 J_{BH} = 85) was also observed. All the solutions were allowed to age 3 days and their spectra taken. The pertinent data are presented in Table I. The relative areas of the quintuplet and quadruplet were determined with the aid of a planimeter, and the value reported represents the average of three measurements each on eight traces. The equilibrium constant was calculated based on the expression

$$k_1 = \frac{[AlH_3.NMe_3]\,[BH_3.NMe_3]}{[H_2AlBH_4.2NMe_3]}$$

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch015

assuming that the quadruplet was due to $BH_3 \cdot N(CH_3)_3$ and the quintuplet to $H_2AlBH_4 \cdot 2N(CH_3)_3$, respectively.

Results and Discussion

$H_2AlBH_4 \cdot N(CH_3)_3$-$N(CH_3)_3$ System. The reaction of $H_2AlBH_4 \cdot N(CH_3)_3$ with an excess of trimethylamine at ambient temperature proceeded according to the stoichiometry shown below.

$$H_2AlBH_4 . N(CH_3)_3 + 2N(CH_3)_3 \longrightarrow H_3Al . 2N(CH_3)_3 + BH_3N(CH_3)_3$$

The complete degradation of the borohydride group was confirmed by the B^{11} NMR spectrum of the reaction mixture. It consisted solely of a quadruplet and no evidence of the quintuplet, due to the borohydride group in the starting material, was found. Thus BH_4 was completely converted to a BH_3 group. Isolation of trimethylamine-borane and bis(trimethylamine) alane, although in moderate yield, further supported the above equation. Formally the reaction is analogous to those reported for $HAlBH_4N(CH_3)_3$ and $Al(Bh_4)_2N(CH_8)_2$ with trimethylamine, except that the alane moiety is capable of consuming an equivalent of the amine to form $AlH_3 . 2N(CH_3)_3$ *(4)*.

However, evidence was found of the stepwise addition of trimethylamine to $H_2AlBH_4 \cdot N(CH_3)_3$ when the reaction was followed by a tensiometric titration procedure. A sharp increase in pressure was noted after only one equivalent of trimethylamine was added, when a short time was allowed to establish apparent equilibrium (Figure 1, *a*). When the titration was repeated and 6 hours was allowed for the apparent equilibrium to be established, a break occurred in the pressure *vs.* composition curve at a mole ratio of reactants of 1.9 (see Figure 1, *b*), in fair agreement with the sealed bulb experiments.

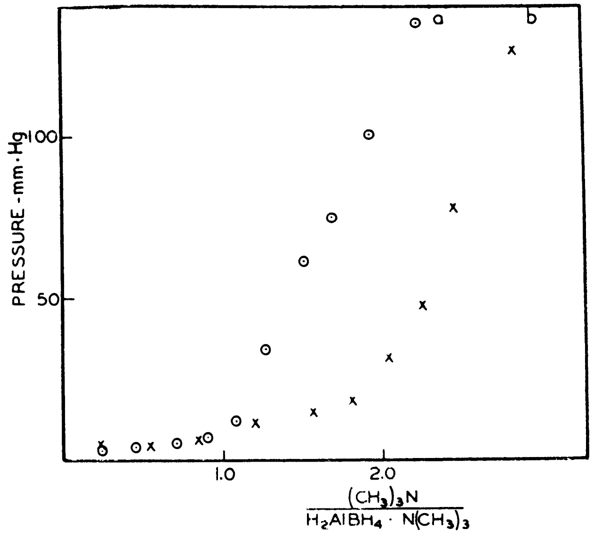


Figure 1. Tensiometric titration of $H_2AlBH_4 . N(CH_3)_3$ with trimethylamine

The initial rapid consumption of one mole of the amine cannot be due to cleavage of the hydride bridge bonds, since the liberated trimethylamine-alane would have reacted rapidly with the excess amine *(4)*.

$$H_2AlBH_4.N(CH_3)_3 + N(CH_3)_3 \longrightarrow AlH_3.N(CH_3)_3 + BH_3.N(CH_3)_3$$

Furthermore, the B^{11} NMR spectrum of a 1 to 1 mixture of trimethylamine and $H_2AlBH_4 \cdot N(CH_3)_3$ confirmed the absence of symmetrical bridge cleavage, since the observed quintuplet demonstrated that boron was still bonded to four equivalent hydrogens. Therefore the boron is still present as a borohydride group and the second amine must also be coordinated to the aluminum. Thus the initial step in the reaction is the formation of the complex, $H_2AlBH_4 \cdot 2N(CH_3)_3$. Chemical evidence of the nature of the bonding of the aluminum in these borohydride derivatives suggests that aluminum contributes only one bonding orbital to each borohydride group *(3, 5)*. Therefore, the bonding in this bisaminate may be similar to that in $AlH_3 \cdot 2N(CH_3)_3$.

The $H_2AlBH_4 \cdot 2N(CH_3)_3$ complex was not stable in solution and decomposed slowly to trimethylamine-borane and alane derivatives, either $AlH_3 \cdot N(CH_3)_3$ or $AlH_3 \cdot 2N(CH_3)_3$, or a mixture of both. The decomposition could be followed by B^{11} NMR and was found to be incomplete even after long standing, which suggested that an equilibrium had been established. The existence of an equilibrium was confirmed by examining the B^{11} NMR spectra of solutions containing various mole ratios of trimethylamine-alane and trimethylamine-borane. The spectra demonstrated that both borohydride and borane (BH_3) groups were present in all the mixtures. The chemical shift and the coupling constants of the quadruplet and quintuplet were identical to those observed in solutions initially containing only $H_2AlBH_4 \cdot 2N(CH_3)_3$. The equilibrium was found to be established slowly when approached from both sides, requiring approximately 8 to 12 hours at ambient temperature. An attempt was made to isolate the bisamine complex. Addition of an equivalent of trimethylamine to $H_2AlBH_4 \cdot N(CH_3)_3$ in ether resulted in the quantitative formation of a white solid which was apparently stable at temperatures below 0°. It liquefied on warming and the NMR of this liquid after it has stood for one day at ambient temperature was identical to the NMR of a equimolar mixture of trimethylamine-alane and trimethylamine-borane which had been allowed to age. The B^{11} NMR of an equilibrium mixture of aged $H_2AlBH_4 \cdot 2N(CH_3)_3$ is shown in Figure 2.

The exact nature of all the species present in solution is not known, since the B^{11} NMR spectrum does not distinguish between the bis- and monoaminates – $H_2AlBH_4 \cdot N(CH_3)$ and $H_2AlBH_4 \cdot 2N(CH_3)_3$ – nor does it give any information concerning the aluminum-containing products.

The attempted rectification of the equilibrium mixture by fractional sublimation was only partially successful. Low yields of trimethylamine-borane were obtained in a pure state, but the remaining components could not be separated. Infrared and H^1 NMR spectra of the mixture did not help in identifying the other products.

Although several possible equilibria could be operating in the system, the basic reaction involved is probably the dissociation of the bisaminate.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch015

$$H_2AlBH_4.2N(CH_3)_3 \xrightarrow{k_1} AlH_3.N(CH_3)_3 + BH_3.N(CH_3)_3$$

However, after an appreciable concentration of trimethylamine-alane is produced, a second reaction is also likely because of the lower steric requirements of bistrimethylamine-alane over the bisaminate of the monoborohydride derivative.

$$H_2AlBH_4.2N(CH_3)_3 + AlH_3.N(CH_3)_3 \xrightarrow{k_2} AlH_3.2N(CH_3)_3 + H_2AlBH_4.N(CH_3)_3$$

Both of the above equilibria produce species which will react rapidly with excess trimethylamine. A direct nucleophilic displacement of hydride by trimethylamine from a borohydride group in $H_2AlBH_4 \cdot 2N(CH_3)_3$ is felt to be less likely, since it is difficult to explain why the displacement should be slow in this case, whereas the reaction of trimethylamine with $HAlBH_4 N(CH_3)_2$ and $Al(BH_4)_2N(CH_3)_2$ was extremely rapid. Disproportionation of $H_2AlBH_4 \cdot 2N(CH_3)_3$ into species containing more than one borohydride group per aluminum is also felt to be unlikely.

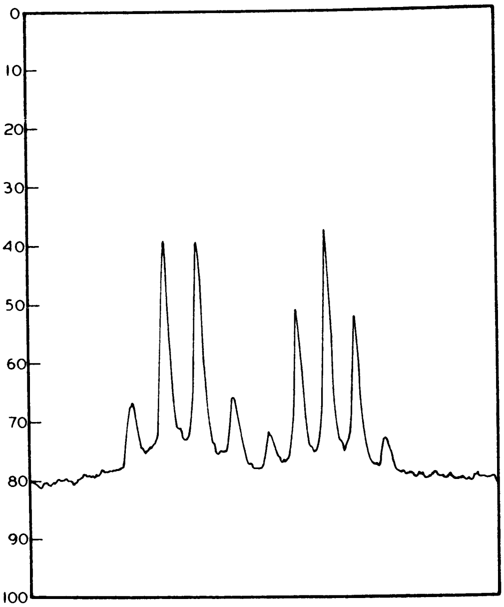


Figure 2. B^{11} NMR spectrum of equilibrium decomposition mixture of $H_2AlBH_4 . 2N(CH_3)_3$

To test the assumption that one or both of the above equilibria are important in this system, a series of solutions initially containing only trimethylamine-borane and trimethylamine-alane, in varying ratios, was prepared. After suitable aging the relative distribution of boron between borohydride and borane groups was determined using B^{11} NMR. The concentrations of the various species were calculated, assuming that only the first equilibrium above applied. The value found for k_1 was 1.25 ± 0.18. When a solution initially containing the exact composition $\bar{H}_2AlBH_4 \cdot 2N(CH_3)_3$ was allowed to attain equilibrium, the value calculated for k_1 was 1.06 (see Table I for details). An attempt was made to calculate a value for the combined k_2/k_1 corresponding to the equilibrium

$$2AlH_3.N(CH_3)_3 + BH_3.N(CH_3)_3 \longrightarrow H_2AlBH_4.N(CH_3)_3 + AlH_3.2N(CH_3)_3$$

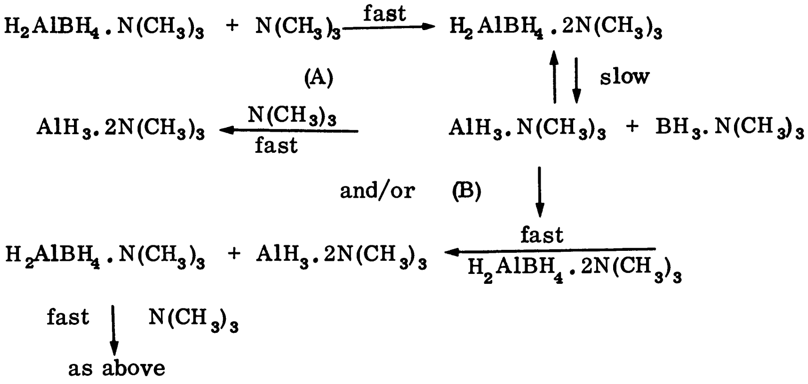
but large negative values were obtained. The relatively constant value obtained for k_1 suggests that the most important equilibrium in the system involves the initial dissociation of the bisaminate, although one cannot eliminate the possibility that errors in the data do not allow calculation of k_2/k_1 when the constant is large.

Table I. Equilibrium Studies on System $AlH_3N(CH_3)_3$ -$BH_3 \cdot N(CH_3)_3$

Soln.	*Initial Concn., Moles/Liter* *AlH_3NMe_3*	 *BH_3NMe_3*	*Relative Areas* *$BH_3/(BH_4 + BH_3)^a$*	*k_1*
A	2.10	2.37	0.494 ± 0.006	1.08
B	2.17	1.36	0.187 ± 0.014	1.29
C	1.39	3.20	0.728 ± 0.005	1.66
D	2.66	2.04	0.402 ± 0.008	0.97
E	1.52	2.46	0.650 ± 0.004	1.23
F	$H_2AlBH_4 \cdot 2N(CH_3)_3$ concn. = 3.68		0.420 ± 0.003	1.06

[a] Fraction of boron present as BH_3 group.

When two equivalents of trimethylamine were added to $H_2AlBH_4 \cdot N(CH_3)_3$, conversion of the borohydride group to a borane group could be followed by B^{11} NMR and was complete after 8 hours. No evidence of the previously observed equilibrium was found. Several reaction schemes are compatible with the experimental observations. Two similar schemes are:



Probably both Reactions A and B occur in competition with each other, although it is impossible to determine to what extent this occurs. The formation of the bisaminate of aluminum hydride ensures that the equilibrium is continually shifted so that complete conversion occurs.

When triethylamine was used instead of trimethylamine, evidence of an equilibrium in the conversion of borohydride groups to borane groups was again obtained. However, the presence of two different amines complicates the system further, so that even less is known about the nature of the species and the equilibria involved. Furthermore no indications of the formation of the bisaminate, $H_2AlBH_4 \cdot N(CH_3)_3 \cdot N(C_2H_5)_3$, were observed, although it may be present in the reaction mixture. The degree of dissociation of such a species into triethylamine and $H_2AlBH_4 \cdot N(CH_3)_3$ would undoubtedly be greater than the corresponding trimethylamine derivative, so that an appreciable amount of free triethylamine is probably present even when a 1 to 1 ratio of reactants is employed. Thus it is not meaningful to calculate an equilibrium constant, since only the total conversion of borohydride groups to BH_3 groups may be observed. When two or more equivalents of triethylamine were used, complete conversion did not occur and some borohydride groups were still present. This is probably due to the low stability of the $AlH_3 \cdot N(CH_3)_3 \cdot N(C_2H_5)_3$ and $AlH_3 \cdot 2N(C_2H_5)_3$ *(4)* complexes which would allow a considerable concentration of $AlH_3 \cdot N(CH_3)_3$ or the monotriethylamine adduct to exist in solution, not shifting the equilibrium.

$HAl(BH_4)_2 . N(CH_3)_3$-$N(CH_3)_3$ System. The reaction of $HAl(BH_4)_2 \cdot N(CH_3)_3$ with excess trimethylamine was found to approach the following stoichiometry:

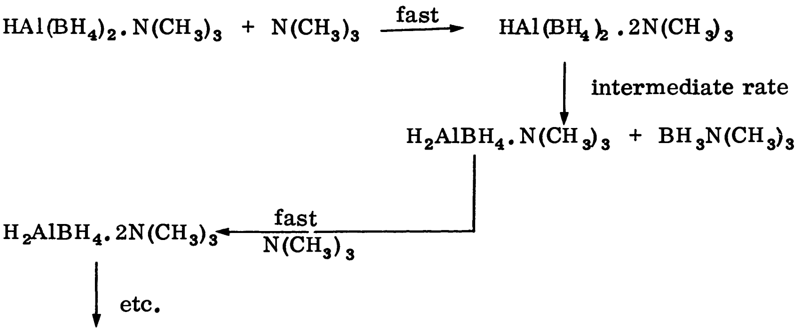
$$HAl(BH_4)_2.N(CH_3)_3 + 3N(CH_3)_3 \longrightarrow AlH_3.2N(CH_3)_3 + 2BH_3.N(CH_3)_3$$

although small amounts of hydrogen gas were also obtained even after careful drying of the amine. Complete conversion of the borohydride to a borane group was confirmed by B^{11} NMR as before. Trimethylamine-borane was again isolated from the reaction mixture in moderate yield.

When tensiometric titrations were performed at ambient temperature, a break in the curve of pressure *vs.* composition occurred at molar ratios of trimethylamine to $HAl(BH_4)_2 \cdot N(CH_3)_3$ between 1.3 and

1.6. It was apparent that equilibrium had not been obtained in the system. When the temperature at which the titration was performed was lowered to 0°, a break occurred at a molar ratio of reactants of 1.1. The results suggest the existence of a bisaminate of the type $HAl(BH_4)_2 \cdot 2N(CH_3)_3$ which is less stable toward either reaction with excess amine or dissociation into $BH_3 \cdot N(CH_3)_3$ and the previously discussed $H_2AlBH_4 \cdot N(CH_3)_3$. This is not surprising in view of increased steric hindrance that would be expected in going from a H_2AlBH_4 moiety to a $HAl(BH_4)_2$ species. The B^{11} NMR spectra of 1 to 1 mixtures of $HAl(BH_4)_2N(CH_3)_3$ and trimethylamine were examined, in order to determine if any cleavage of the borohydride group had occurred. The spectrum of a freshly prepared solution consisted predominantly of a quintuplet, but conversion to a quadruplet occurred rapidly and it was not possible to prepare a solution in which some cleavage was not apparent.

This system is considerably more complicated than the previous one, because of the difunctionality of the borohydride derivative. There are numerous possible reaction paths by which the conversion of a BH_4 group to a BH_3 can occur. A plausible example is shown below:



The species $H_2AlBH_4 \cdot 2N(CH_3)_3$ would then decompose as shown in the discussion of the previous system, so that the final products would be $AlH_3 \cdot 2N(CH_3)_3$ and $BH_3 \cdot N(CH_3)_3$. Obviously a much more detailed study of this system is needed to confirm this type of reaction scheme and to locate the equilibria involved.

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Received May 10, 1963. Work performed under Contract Number DA-01-021 ORD-11878.

16

Boron Compounds

VI. New Compounds with Boron-Nitrogen Bonds

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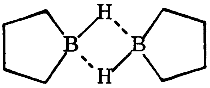
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch016

Compounds with B-N-B bonds have been prepared through interaction of bisborolanes with primary amines or ammonia. The elimination of hydrogen from BH- and NH- groups is catalyzed by amines. The reaction of bisborolanes with amines is compared with the behavior of alkyldiboranes — for instance, $B_2H_2R_4$ — toward amines. The preparation of novel boron- and nitrogen-containing ring compounds from alkyldiboranes and amines is described, and transboronation reactions of compounds with B-N and B-N-B bonds are discussed. In addition, novel B-N heterocycles of the naphthalene and indene types were prepared.

Recently it was reported that bisborolanes (Table I), in contrast to the tetraalkyldiboranes, $B_2H_2R_4$, are stable at room temperature toward hydrolysis, alcoholysis, and oxidation *(3)*.



Bisborolane

Table I. Properties of Bisborolanes

	B.P., °C.(Mm.)	*M.P., °C.*	n_D^t	d_4^t
Bisborolane	76-77(10)	-	1.4894^{20}	0.8541^{20}
Bis(3-methyl borolane)[a]	95(12)	-	1.4762^{20}	0.8307^{20}
Bis(3,4-dimethyl borolane)[a]	120-124(12)	~30	1.4683^{25}	-

[a] Mixture of isomers

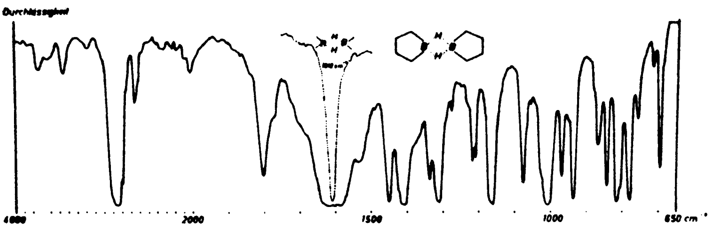


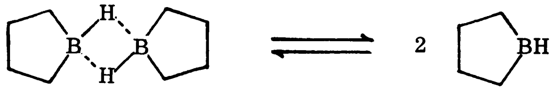
Figure 1. Infrared spectrum of bisborolane

d = 0.05 mm., NaCl prism

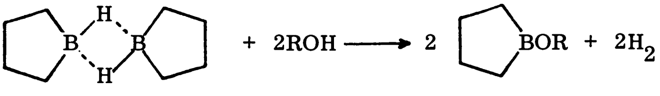
——— Undiluted

- - - 4% solution in cyclohexane

The B-H bonds of the five-membered boron heterocycle (compare Figure 1) react only at elevated temperatures (above 100° C.) with olefins and alkines to the corresponding alkyl and alkenylborolanes. Diazomethane is not decomposed by bisborolanes at room temperature. This leads to the conclusion that borolanes are dimeric compounds, since even traces of alkylboranes catalyze the decomposition of diazomethane into nitrogen, polymethylene, and organoboron compounds of higher molecular weight *(2, 8, 9)*. Hence the B-H bonds of bisborolanes at room temperature have no catalytic effect on the alkyl group exchange of trialkylboranes *(4, 7)*. Only at about 100°C. does an equilibrium exist containing the monomeric form, and only then can the

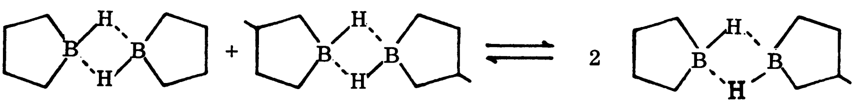


B-H bonds of these compounds react with alcohols, with elimination of hydrogen and formation of alkoxyborolanes. All other reactions usually



typical of organoboron compounds — for instance, hydroboration and oxidation — are possible with bisborolanes only at elevated temperatures. The following exchange reactions belong in this group.

A mixture of different bisborolanes can be separated at room temperature. Only above 100°C. can the organic radicals exchange until equilibration is achieved.



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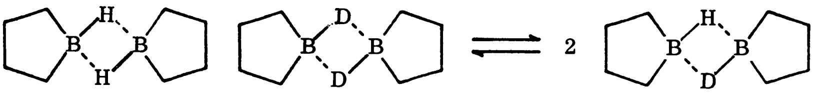
The equilibration can be followed by gas chromatography *(11)*. Analogously, when bisborolanes and bis(1-deuteroborolane) are heated, equilibrated mixtures are formed in which the starting materials are partially preserved and a compound with $B\overset{H}{\underset{D}{}}B$ is formed.



$\nu_{max.}$ $(BH_2B)\cdot 1612\ cm.^{-1}$ $\nu_{max.}$ $(BD_2B)\cdot 1180\ cm.^{-1}$ $\nu_{max.}$ $(BHB)\cdot 1655\ cm.^{-1}$

$\nu_{max.}$ $(BDB)\cdot 1205\ cm.^{-1}$

These exchange reactions could be observed by infrared spectroscopy or mass spectroscopy.

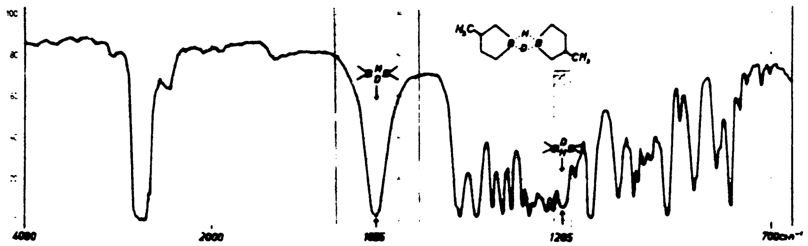
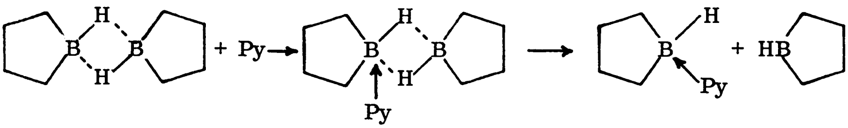


Figure 2. Infrared spectrum of bis-(3-methylborolane) formed from 3-methylborolane and B-deutero-3-methylborolane

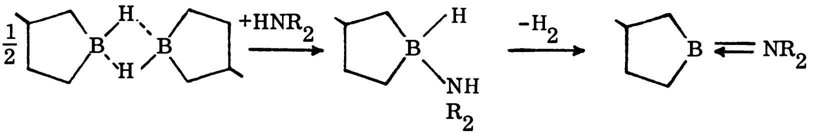
We could now determine that the exchange reactions mentioned above are also possible at room temperature; if a small amount of pyridine is added to a mixture of different bisborolanes, mixed bisborolanes are formed immediately, in a concentration corresponding approximately to the amount of pyridine added. One must conclude that the amine reacts with the stable dimeric borolane. Free borolane, as well as pyridine-borolane, is obtained by a nucleophilic attack of the pyridine nitrogen on the intact bridge bonding between the two boron atoms.



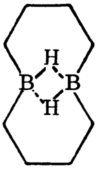
The free borolane can now react with 3-methylborolane to yield the mixed bisborolanes. The effect of pyridine is apparently stoichiometric — that is, once pyridine-borolane is formed, no additional borolane is liberated at room temperature.

The reactivity of bisborolanes toward pyridine at room temperature led us to study in more detail the behavior of bisborolanes and similar compounds toward various amines. It was anticipated that the stable bisborolanes would behave differently from noncyclic alkyl diboranes — for instance, compounds of the formula $B_2H_2R_4$. Indeed, we could observe that different reactions between the two types of compounds are possible. In both cases, new classes of compounds were synthesized.

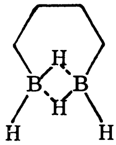
As with pyridine, bisborolanes react with other nitrogen derivatives — for instance, diethylamine, benzylamine, ethylamine, aniline, and ammonia— in the temperature range of 0° to 30°C. Depending upon the strength of the added donor molecules, the BH_2B bridge bond of bisborolanes is more or less easily attacked and split. If a primary or secondary amine, or ammonia, is utilized in this reaction, the first step is the formation of an amine-borolane (borazane), which transforms readily into an aminoborolane (borazene) with elimination of hydrogen.



(Benzylamino)borolane (a crystalline material) is formed from benzylamine-borolane just above 0°C. No splitting of the boron-carbon bonds occurs. Similarly, other amine-borolanes — for instance, aniline-borolane — eliminate hydrogen only from the BH bonds. An isomerization (exchange of alkyl groups) of the organoboron compound can be excluded for this reaction, on the basis of previous results concerning the conditions of such reactions. The quantitative formation of aminoborolanes therefore is good evidence of the proposed structure of bisborolanes *(3)*. Another structural formula which is based on more theoretical considerations has recently been proposed for borolanes *(1, 13)*, and is illustrated, as an example, for the bis(tetramethylene)-1, 2-diborane.



The formula appears unlikely, at least for the stable products described herein. This does not contradict the fact that for the dimer formed from borolane and borane, the "symmetrical" formula



has to be discussed, based on infrared and B^{11}-NMR measurements, if this compound was prepared at low temperatures from butadiene and diborane *(12)*. We obtained this dimer from borolane and borane at higher temperatures (about 120° to 130°C.) by the following comproportionation reaction:

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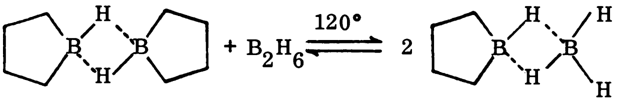


(wide) $\nu_{max.}$ $(BH_2B)\cdot 1567$ cm.$^{-1}$

$\nu_{max.}$ $(BH_2)\cdot 2500$ cm.$^{-1}$

On the basis of our experimental results, the compound obtained by this method probably has the "asymmetrical" formula.

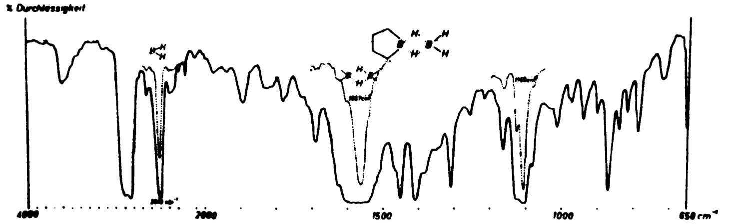


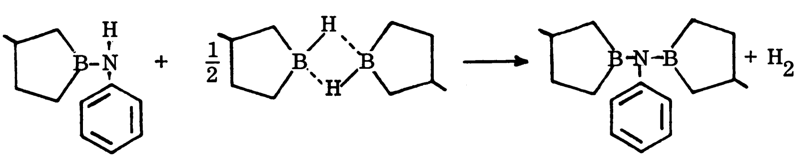
Figure 3. Infrared spectrum of borolane-borane

d = 0.05 mm., NaCl prism

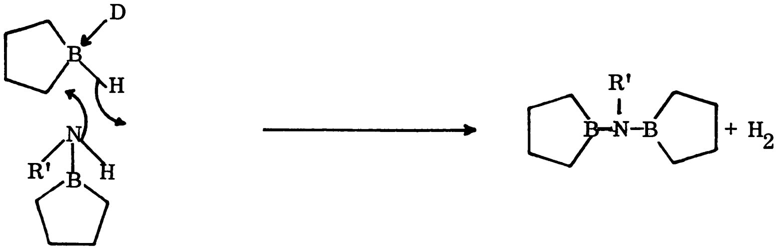
____ *Undiluted*

\- - - *5% solution in cyclohexane*

Under the influence of bisborolanes, NH-containing *B*-aminoborolanes split off hydrogen slowly at elevated temperatures (about 150°C.). Predominantly high molecular weight compounds of unknown structure are obtained. However, distillable compounds can be isolated from the reaction mixture. For example, upon the reaction of 1-(phenylamino)-3-methylborolane with bis(3-methylborolane), in addition to higher molecular weight compounds, the bis(3-methylborolanyl)phenylamine is obtained.



No polymer products formed when small amounts of a tertiary amine — for instance, triethylamine — were added. At 150°C., for example, the bis(3-methylborolanyl)phenylamine is formed readily and in high yield under such circumstances. Under the influence of the amine, the formation of compounds with B-N-B bonds is probably accelerated. One can assume that through a nucleophilic attack of the nitrogen of the tertiary amine on the boron atom of the borolane the hydride hydrogen becomes more "movable." In a four-center type reaction the hydrogen atom can then react with the acid hydrogen of the nitrogen atom of the aminoborolane and is split off.



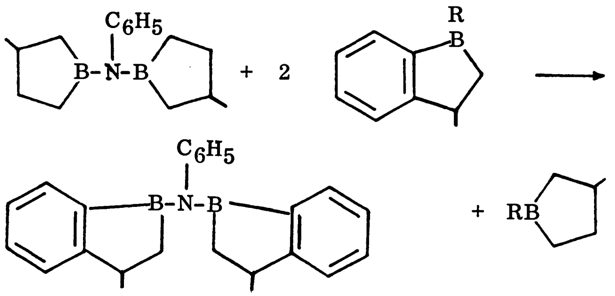
By this method we obtained the following bis(3-methylborolanyl)-amines:

Table II. Bis(3-methylborolanylamine)

R	*B.P., °C./Mm.*	d_4^{20}	n_D^{20}	*Yield, %*
C_2H_5	121-23/11.5	0.8618	1.4762	90
$CH_2-C_6H_5$	137-38/0.4	0.9309	1.5229	75
C_6H_5	98.5-100/0.3	0.9337	1.5195	87

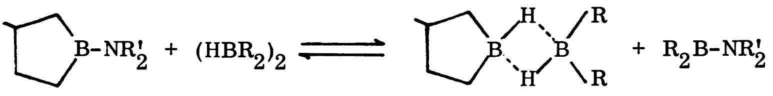
In addition to compounds of higher molecular weight, 1-aminoborolane is formed by the reaction of ammonia with bisborolane. The 1-aminoborolane reacts with additional bisborolane to form the corresponding compound with a B-N-B bond. The yields in this reaction, however, are less favorable than in the preparation of the B-N-B compounds from primary amines. Tris(borolanyl)amine has not yet been prepared.

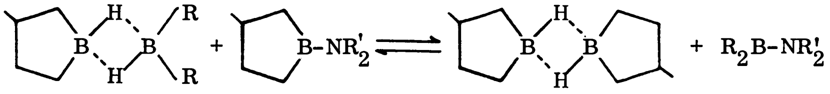
Compounds with B-N-B bonds can be transboronated with alkylboranes or alkyldiboranes. This method of preparation is always advantageous if the alkyl- or arylborane contains boron-carbon bonds which are easily split by aminolysis with NH-containing agents. This is, for instance, the case in the presence of B-C_{aryl} bonds. These compounds are obtained in good yields in an NH-free medium. For example, a crystalline compound with B-N-B bonds is obtained from bis(3-methylborolanyl)phenylamine and 1-propyl-3-methyl-1-boraindan *(5)*



M.p. 107 - 08°C.

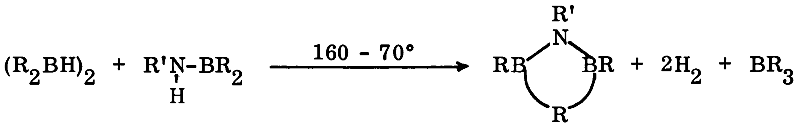
Corresponding transboronation reactions are also possible between alkyldiboranes and aminoboranes or compounds with B-N-B linkages. In the equilibration mixtures





the formation of compounds with B-N or B-N-B bonds with boron in the five-membered ring systems — for instance, borolane, or boraindan — is usually favored over and above the formation of corresponding compounds with simple alkyl substituents on the boron.

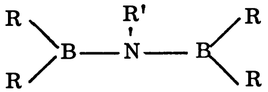
The corresponding B-N-B compounds originating from tetraalkyldiboranes, $B_2H_2R_4$, and (alkylamino)dialkylboranes of the formula $R_2B = NHR'$ cannot be prepared. Hydrogen is generated upon heating a mixture of these two starting materials to about 160° to 170°C.; however, this forms not only from the BH- and NH- groups, but also from BH- and CH_2- or CH_3- groups of alkyl radicals *(6)*. Cyclization products of the following type are obtained.



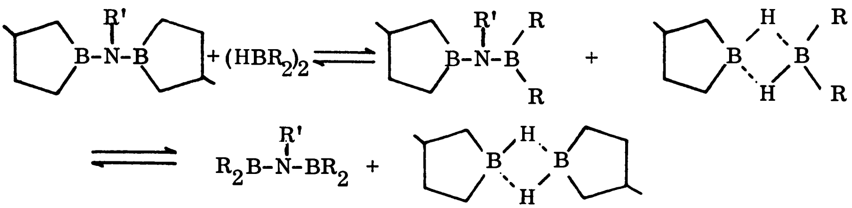
$R = C_2H_5$

$R' = C_6H_5$

B-N-B compounds of the following type *(10)*

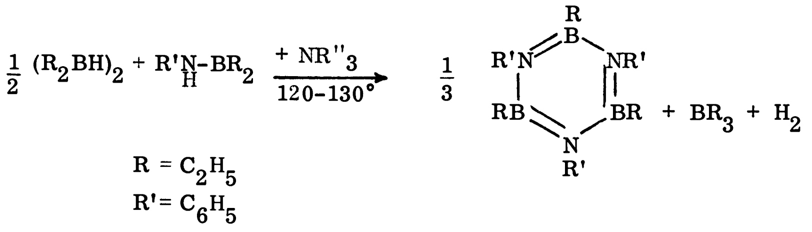


could not be prepared by transboronation under mild conditions. In exchange reactions, indicated in the following equations,

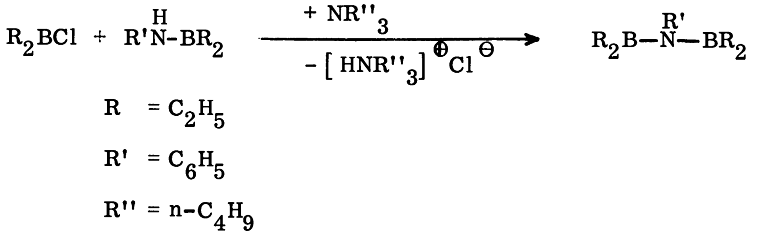


In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

and in aminolysis reactions, compounds with B-N-B bonds are apparently not very stable *(10)*. If a tertiary amine is utilized as a catalyst in the aminolysis of BH- bonds, the corresponding borazines, in addition to trialkylborane and hydrogen, are obtained in excellent yields. The reaction has to be classified as a simultaneous transboronation and disproportionation of alkylboranes.



In an attempt to prepare the simple bis(dialkylboryl)arylamines from dialkylchloroboranes and (arylamino)dialkylboranes according to the following equation



$$R_2BCl + R'\overset{H}{N}\text{-}BR_2 \xrightarrow[-[HNR''_3]^{\oplus}Cl^{\ominus}]{+NR''_3} R_2B\text{—}\overset{R'}{N}\text{—}BR_2$$

R = C_2H_5
R' = C_6H_5
R'' = n-C_4H_9

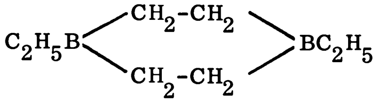
borazines were formed in nearly quantitative yields (96.4%).

$$3R_2BCl + 3R'\underset{H}{N}\text{-}BR_2 + 3NR''_3 \longrightarrow (RBNR')_3 + 3BR_3 + 3\ HNR''_3$$

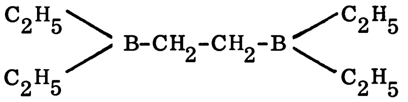
We assume that in the presence of free amine, $R_2B\text{-}NR'\text{-}BR_2$ compounds cannot be prepared because of a preference for disproportionation reactions.

If free amine is not present, the heterocycles mentioned above are formed from alkyldiboranes and aminodialkylboranes. For example, the reaction of ethyldiborane with (phenylamino)diethylborane results in a compound $C_{12}H_{19}B_2N$ (b.p. 75°/0.3 mm.), to which we assign the structure of a 1,3-diethyl-2-phenyl-1,3-dibora-2-azacyclopentane. Mass spectra indicate species of molecular weights 199/198/197 for two boron atoms. With triethylaluminum, this compound exchanges ligands between boron and aluminum, and in addition to triethylborane higher boiling alkylboranes were obtained, which could be separated from the triethylborane by gas chromatography. Mass spectra analysis indicated that they are compounds with the molecular weights of 136 and 166, each containing two boron atoms. On the basis of the mass spectrum and the method of formation of the compounds with mass 136, it was assigned a structure of a 1,4-diboracyclohexane.

The compound with mass 166 is to be assigned a structure of 1,2-bis(diethylboryl)ethane, based on the results of this investigation.

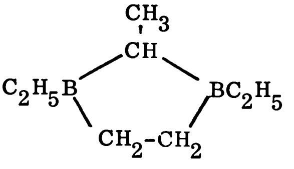


1,4-Diethyl-1,4-diboracyclohexane (136)

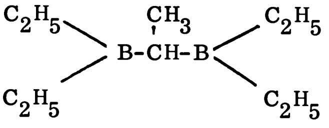


1,2-Bis(diethylboryl)ethane (166)

The isomeric compounds

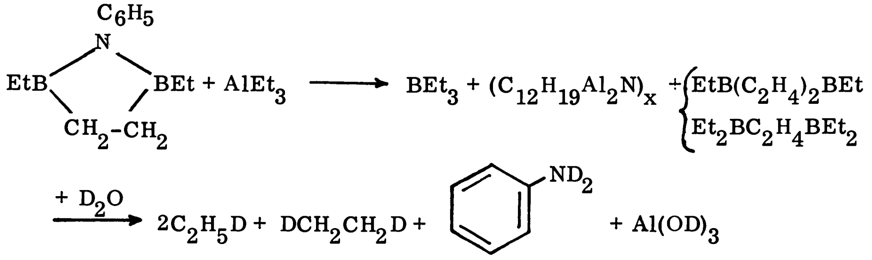


1,3-Diethyl-2-methyl-1,3-diboracyclopentane (136)



1,1-Bis(diethylboryl)ethane (166)

are present to only a very minor degree, which is demonstrated by the following: On separation of the boron-containing compounds, a residue is obtained containing organoaluminum materials. Deuterolysis provided, except for monodeuteroethane (from the ethyl groups), only 1,2-dideuteroethane (from the ethylene groups). There was no evidence of 1,1-dideuteroethane in the mass spectrum. Ligand exchange and consequent deuterolysis appeared to occur as follows:



Aniline was isolated quantitatively. Very small amount of o-deutero-N-D_2-aniline could be recognized, indicating the formation of a heterocycle due to substitution of the phenyl group of born. Similar ortho-substitution patterns have been known only for the arylalkylboranes *(5)*.

Propyldiborane and (phenylamino)dipropylborane react in the same manner as the ethylboron compounds. Instead of a compound with the molecular weight 199 (from the ethylboron compounds), one obtains heterocycles with a molecular weight of 241, for which the two following structures are possible:

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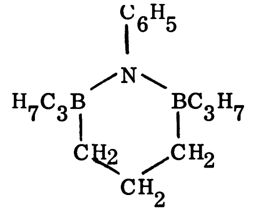
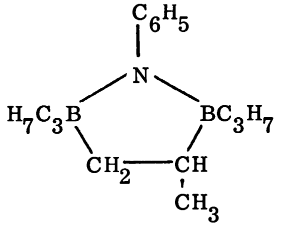


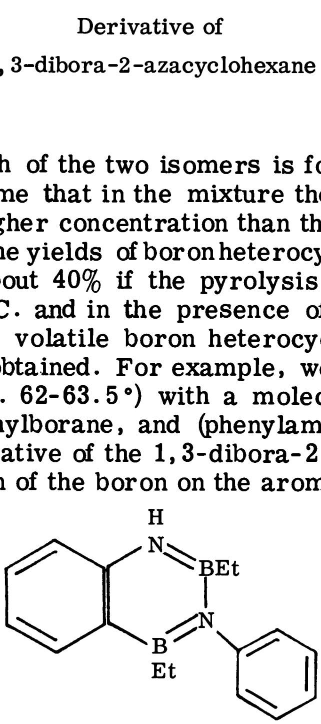
Derivative of
1, 3-dibora-2-azacyclohexane



Derivative of
1, 3-dibora-2-azacyclopentane

Which of the two isomers is formed preferentially is not certain. We assume that in the mixture the six-membered ring system is present in higher concentration than the five-membered system.

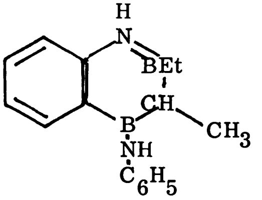
The yields of boron heterocycles with B-N-B bonds can be increased to about 40% if the pyrolysis is performed under pressure at about 200 °C. and in the presence of trialkylborane. On distillation of the more volatile boron heterocycles, higher distilling reaction products are obtained. For example, we obtained a well-crystallized compound (m.p. 62-63.5°) with a molecular weight of 262 from ethyldiborane, triethylborane, and (phenylamino)diethylborane. This compound is a derivative of the 1,3-dibora-2,4-diazanaphthalene, formed via substitution of the boron on the aromatic nucleus.



B.p. 143°/0.2 mm.

M.p. 62-63.5°

The infrared absorption for the valence vibration of the NH-bond was recorded for this compound at 3430 cm^{-1} If this is compared with compounds with NH bonds whose nitrogen atoms are not within a ring (NH-valence vibration near 3400 cm^{-1}), it becomes evident that this absorption has shifted. An isomeric liquid compound of the following structure



$\nu_{max.}$ (NH) • 3400, 3430 $cm.^{-1}$

could also be isolated.

The diboradiazanaphthalene mentioned above is easily split by hydrolysis. It is, however, remarkably resistant towards air.

Apparently the new ring formation reactions are also possible with other alkylboranes and aminoalkylboranes. Instead of the alkylboranes, certain borohydrides can be utilized in the reaction. For

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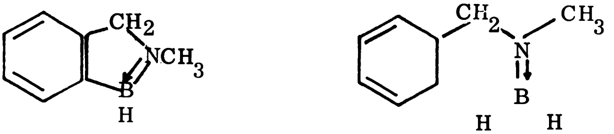
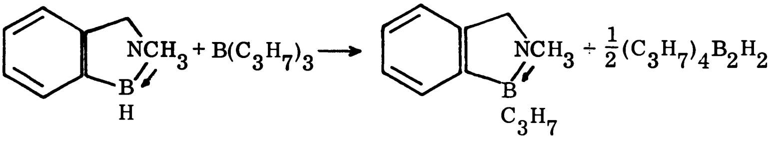
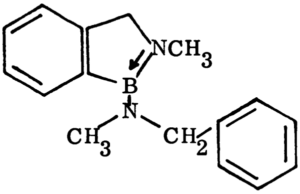
example, another B-N ring compound could be formed from *N*-methylbenzylamine and triethylamine-borane. The mixture generates hydrogen and amine on heating to about 200°C. About 65% of the pyrolysis product can be distilled off under reduced pressure. The remainder consists of polymeric compounds. The first fraction (b.p. 102-06°/16 mm.) consists primarily of the following two compounds, which crystallize as a mixed dimer:



With tripropylborane the 1-propyl-2-methyl-1-bora-2-azaindene (b.p. 115-16°/11 mm.) can be isolated from that mixture, according to the equation



In the higher boiling fraction of the pyrolysis product (b.p. 127-132°C./0.2 mm.) only small amounts of ortho-disubstituted C_6H_4 radicals could be determined by infrared spectroscopy ($\nu \sim 750$ cm.$^{-1}$), in addition to primarily monosubstituted phenyl derivatives. The BN ratio of the higher boiling mixture is 1 to 2. Furthermore, a B-H grouping [ν_{max} (NBH): 2450 cm.$^{-1}$] could be identified. On decomposition with alcohol, primarily molecular hydrogen is formed from the hydride group. This indicates that the primary reaction product consists of bis(*N*-methylbenzylamino)borane, whereas 1-(*N*-methylbenzylamino)-2-methyl-1-bora-2-azaindene



B.p. 120 - 22°/0.2 mm.

is formed only as a minor product.

The yields of boron- and nitrogen-containing heterocycles are not outstanding in this last case. However, utilization of the ring formation reactions in many cases provides good possibilities for the synthesis of BN heterocycles from very simple starting materials. It is necessary, however, to eliminate concurring reactions to the widest possible degree. Further studies of the behavior of various mixtures of compounds (in extension of the afore-mentioned results) should be very interesting.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch016

Experimental

Preparation of Aminoborolanes and Aminoalkylboranes. 1-(Benzylamino)-3-methylborolane. A 50-ml. three-necked flask was equipped with dropping funnel, stirrer, and descending condenser with receiver. The flask was charged with 8.4 grams (51 mmoles) of bis(3-methylborolane) and at room temperature 11 grams (102.3 mmoles) of freshly distilled benzylamine were added with stirring. A solid amine-borolane was precipitated and because of some warming of the reaction mixture some hydrogen was evolved with immediate formation of small amounts of aminoborolane. The mixture was warmed to a maximum of about 120° to 130°C. Elimination of hydrogen began at about 50° and was very rapid at about 80°. The reaction was completed after about 2 to 3 hours. Finally, the liquid material was distilled under reduced pressure. A small fraction (b.p. 50-80°/0.2 mm.) was obtained, and finally, 17.2 grams (90%) of pure 1-(benzylamino)-3-methylborolane (b.p. 84.5-85°).

Analysis. Calculated for $BNC_{12}H_{18}$: B, 5.80; N, 7.50; C, 77.06; H, 9.64; molecular weight, 186.9. Found: B, 5.69; N, 7.73; C, 76.82; H, 9.51; molecular weights (by mass spectroscopy) 187/186.

1-(Phenylamino)-3-methylborolane. In a similar procedure 1-(phenylamino)-3-methylborolane was obtained from 25.1 grams (0.270 mole) of aniline and 22 grams (0.134 mole) of bis(3-methylborolane) in 88.8% yield (b.p. 123-24°/10 mm.).

Analysis. Calculated for $BNC_{11}H_{16}$: B, 6.26; N, 8.09; C, 76.40; H, 9.32; molecular weight, 173.1. Found: B, 6.30; N, 8.64; C, 75.86; H, 9.16; molecular weights (by mass spectroscopy), 173/172.

1-(Ethylamino)-3-methylborolane. At 80° C. 10 grams (22.2 mmoles) of dry ethylamine were added to 13.5 grams (82.3 mmoles) of bis(3-methylborolane). On distillation of the reaction product under reduced pressure 7.4 grams (36%) of pure 1-(ethylamino)-3-methylborolane (b.p. 35-37°/8 mm.) were obtained, in addition to 4.9 grams (34.4%) of pure bis(3-methylborolanyl)ethylamine (b.p. 118-19°/8 mm.)

Analysis. Calculated for BNC_7H_{16}: B, 7.67; N, 11.19; C, 67.20; H, 12.91; molecular weight, 125.0. Found: B, 8.51; N, 10.96; C, 67.42; H, 12.71; molecular weight (by mass spectroscopy), 125/124.

Calculated for $B_2NC_{12}H_{25}$: B, 10.59; N, 6.83; C, 70.25; H, 12.29; molecular weight, 204.9. Found: B, 10.90: N, 6.82; C, 68.58: H, 11.61; molecular weights (by mass spectroscopy), 205/204/203.

Amino-3-methylborolane. Dry ammonia was introduced into 22 grams (0.134 mole) of bis(3-methylborolane) at 60° with stirring until no more ammonia was absorbed. During the addition hydrogen evolved continuously. The colorless liquid (about 28 grams) was distilled; 13.8 grams (53%) of 1-amino-3-methylborolane (b.p. 86-88°/0.1 mm.) were obtained besides 7.8 grams of a viscous residue.

Analyses. Calculated for BNC_5H_{12}: B, 11.17; molecular weight 96.9. Found: B, 10.07; molecular weights (cryoscopic method), 136, 134; (by mass spectroscopy), 97/96.

1-(Diethylamino)borolane. A mixture of 10.2 grams (75 mmoles) of bisborolane and 13.1 grams (177 mmoles) of diethylamine was heated to about 100°. The reaction was completed within 3 hours. Under reduced pressure the material was distilled and the (diethylamino)borolane (b.p. 54°/12 mm.) was obtained in 84% yield.

Analysis. Calculated for BNC_8H_{18} : B, 7.78; N, 10.07; C, 69.10; H, 13.02; molecular weight, 139.0. Found: B, 7.58; N, 9.81; C, 68.59; H, 12.74; molecular weights (by mass spectroscopy) 139/138.

(Phenylamino)borolane and (phenylamino)dialkylborane. A mixture of 28.6 grams (0.26 mole) of 1-propylborolane (isomeric mixture of normal and isopropyl compounds) and 26 grams (0.28 mole) of freshly distilled aniline was heated in a 100-ml. flask equipped with reflux condenser and magnetic stirrer to 140-50°C. The reaction was completed after about 4 hours. The colorless liquid was distilled under reduced pressure. Besides 4 grams of a prerun containing some (phenylamino)borolane and 2.4 grams of residue, 45.5 grams of a colorless liquid (b.p. 121-25°/8.5 mm.) were obtained. The latter consisted of a compound with a molecular weight of 203/202 [with 1 boron atom = (phenylamino)propylbutylborane] and a compound with a molecular weight of 217/216 [with 1 boron atom = (phenylamino)dibutylborane] (mass spectroscopy analysis). The infrared spectra of the mixture indicated only a NH valence vibration at 3400 cm^{-1} and no absorption of an NH_2 group.

Analysis. Calculated for $BNC_{13}H_{22}$: B, 5.33. Found: B, 5.27.

1-(Diethylamino)-3-methyl-1-boraindan (via Transboronation). When a mixture of 5.4 grams (31.4 mmoles) of 1-propyl-3-methylboraindan and 9.4 grams (67.6 mmoles) of 1-(diethylamino)borolane was distilled under reduced pressure over a 20-cm. column, 7.5 grams of a mixture of 1-propylborolane and 1-(diethylamino)borolane over a boiling range of 75 to 90° (55 to 65 mm.), 1.5 grams of intermediate run and 4.9 grams of 1-(diethylamino)-3-methyl-1-boraindan (b.p. 67°/0.2 mm.) were obtained, besides 0.2 gram of residue.

Analysis. Calculated for $BNC_{13}H_{20}$: B, 5.38; N, 6.69; C, 77.70; H, 10.01; molecular weight 201/200. Found: B, 5.30; N, 6.91; C, 78.23; H, 10.12; molecular weights (by mass spectroscopy), 201/200.

(Phenylamino)dialkylborane (from Aniline and Tetraalkyldiborane). When 21.1 grams of 94% tetraethyldiborane (remainder triethylborane, approximately 0.283 mole of $B_2H_2Et_4$) were added slowly with stirring to 26.3 grams (0.263 mole) of aniline at room temperature, elimination of hydrogen started immediately. At low temperature the mixture became solid. During the addition period of about 90 minutes the temperature was slowly increased to about 70° to 80°. On distillation of the reaction product, besides some triethylborane, 36 grams (88.5%) of (phenylamino)diethylborane (b.p. 80-90°/8 mm.) were obtained.

Analysis. Calculated for $BNC_{10}H_{16}$: B, 6.73; N, 8.69; C, 74.60; H, 10.01; molecular weight, 161.0. Found: B, 6.86; N, 8.95; C, H, 10.08; molecular weights (by mass spectroscopy, 161/160.

(Phenylamino)dipropylborane (b.p. 108-12°/8 mm.) was prepared in a corresponding manner.

(Phenylamino)diethylborane (from Aniline and Diethylchloroborane. In a 500-ml. flask 156 grams (1.675 moles) of freshly distilled aniline were dissolved in 200 ml. of hexane and with stirring 62.5 grams of ethylchloroborane (b.p. 74-78°; 38.8% Cl = 0.502 mole of Et_2BCl + 0.09 mole of $EtBCl_2$) were added slowly at room temperature. The mixture began to boil. After the addition, which took about 80 minutes, the mixture was heated to 80° for about an hour and a voluminous precipitate was formed. After addition of another 200 ml. of hexane, the

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch016

mixture was filtered and the residue was washed with hexane. After evaporation of the solvent and of about 24 grams of aniline, 67 grams (82.7%) of impure (phenylamino)diethylborane (b.p. 80-105°/15 mm.) and 19.5 grams of residue (mainly a borazine) were obtained. Rectification of the aminoborane over a column yielded 52.4 grams (64.7%) of pure (phenylamino)diethylborane (b.p. 95°/15 mm.) The infrared spectrum was identical with the spectrum of the compound obtained from aniline and tetraethyldiborane. On distillation of the (phenylamino)diethylborane, occasionally a small amount of aniline hydrochloride sublimed into the condenser.

Preparation of Bis-(borolanyl)amines. *N,N*-Bis(3-methylborolanyl) aniline. To a mixture of 20.7 grams (0.12 mole) of 1-(phenylamino)-3-methylborolane and 11 grams (0.0671 mole) of bis(3-methylborolane) 0.1 ml. of triethylamine was added and the mixture was heated to 150°. After 4 1/2 hours, the reaction was completed and the colorless liquid was distilled under reduced pressure, resulting in a yield of 87% bis-(3-methylborolanyl)phenylamine (b.p. 98-100°/3 mm.) The colorless compound had no NH band at 3400 $cm.^{-1}$, but strong absorptions near 1598, and at 1495 and 1455 $cm.^{-1}$ On alcoholysis at room temperature with 1-butanol primary amine was formed, as indicated by the NH_2 band at 3350 and 3450 $cm.^{-1}$

Analysis. Calculated for $B_2NC_{16}H_{25}$: B, 8.57; N, 5.53; C, 76.00; H, 9.96; molecular weight, 253. Found: B, 8.52; N, 5.60; C, 76.19; H, 9.96; molecular weights (by mass spectroscopy), 253/252/251.

N, N-Bis(3-methylborolanyl)benzylamine. This compound was obtained as described above from 1(benzylamino)-3-methylborolane and bis-(3-methylborolane) after addition of a small amount of tertiary amine in 75% yield (b.p. 137-38°; n_D^{20} 1.5229; d_4^{20} 0.0309). Upon addition of butyl alcohol, benzylamine and 1-butoxy-3-methylborolane were formed.

Analysis. Calculated for $B_2NC_{17}H_{27}$: B, 8.12; N, 5.25; C, 76.45; H, 10.12; molecular weight, 267.0. Found: B, 8.30; N, 5.20; C, 76.09; H, 10.06; molecular weight. (cryoscopic), 272, 266.

N, N-Bis(3,4-dimethylborolanyl)aniline. A mixture of 4.6 grams (23.95 mmoles) of bis(3,4-dimethylborolane) and 2.14 grams (23 mmoles) of freshly distilled aniline was warmed to 80° to 100°. After addition of about 0.5 ml. of tri-*n*-propylamine, it was heated to 150°. The reaction was complete after 3 hours. Distillation under reduced pressure resulted in 4.1 grams (81%) of bis(3,4-dimethylborolanyl)-aniline (b.p. 115°/0.3 mm.) as a colorless, viscous liquid.

Analysis. Calculated for $B_2NC_{18}H_{29}$: B, 7.70; N, 4.98; C, 76.90; H, 10.42; molecular weight, 281.1. Found: B, 7.89; N, 5.34; C, 76.07; H, 10.37.

N, N-Bis-(3-methylborolanyl)ethylamine. A mixture of 4.31 grams (34.5 mmoles) of 1-(diethylamino)-3-methylborolane, 3 grams (18.3 mmoles) of bis(3-methylborolane), and 0.5 ml. of triethylamine was heated to 135-45° for 4 hours. Upon distillation of the reaction mixture in vacuum, 6.35 grams (90%) of bis(3-methylborolanyl)ethylamine (b.p. 121-23°/11.5 mm., n_D^{20} 1.4762, d_4^{20} 0.8618) were obtained.

Analysis. Calculated for $B_2NC_{12}H_{25}$: B, 10.59; N, 6.83; C, 70.25; H, 12.29; molecular weight, 204.9. Found: B, 10.62; N, 6.84; N, 6.84; C, 70.10; H, 12.15; molecular weights (by mass spectroscopy), 205/204/203.

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N,N-Bis(3-methyl-1-boraindanyl)aniline (via Transboronation). A mixture of 8.5 grams (33.5 mmoles) of bis(3-methylborolanyl)phenylamine and 23.8 grams (138.2 mmoles) of 1-propyl-3-methyl-1-boraindan was heated to 150° to 170°C for several hours. Upon distillation under reduced pressure, 7.2 grams of propyl-3-methylborolane (b.p. 78-82°/70 to 80 mm.), 10.4 grams of a fraction boiling at 105-08°/10-11 mm. (and consisting of propyl-3-methylborolane, and 1-propyl-3-methyl-1-boraindane), 1.8 grams of an intermediate run, and finally 5.5 grams (46.8% yield) of the desired compound (b.p. 164-65°/10^{-3} mm.) were obtained. The colorless, highly viscous liquid obtained by the high vacuum distillation slowly crystallized upon warming to 60° to 80°. The compound could be recrystallized from hexane (m.p. 170°-80°). In the infrared spectrum, no NH and no BH absorption bands were observed.

Analysis. Calculated for $B_2NC_{24}H_{25}$: B, 6.21; N, 4.01; C, 82.50; H, 7.22; molecular weight, 349.1. Found: B, 6.15; N, 4.18; C, 81.86; H, 7.28; molecular weight (cryoscopic method), 338.

Preparation and Identification of Various B-N Heterocycles. 1,3-Diethyl-2-phenyl-1,3-dibora-2-azacyclopentane and 1,3-Diethyl-2-phenyl-1,3-dibora-2,4-diazanaphthalene and Isomeric Compounds. A mixture of 33.4 grams (0.201 mole) of (phenylamino)diethylborane, 29.1 grams (0.297 mole) of triethylborane, and 6.4 grams (0.086 mole) of tetraethyldiborane was heated in a 200-cc. autoclave for 16 hours at 180° and for 9 hours at 200° under shaking. The pressure increased to about 50 atm. at 190°. Upon cooling to room temperature, the gas was blown off and then the mixture heated for 2 more hours to 210° to 225°, whereby the pressure increased to 30 atm. at 220°. Then the yellow-green liquid (52 grams) was distilled, to give 20.9 grams of triethylborane and 12.3 grams of residue and the following two fractions:

1. 7.4 grams (b.p. 65-73°/0.2 mm.). The gas chromatographic analysis indicated 97.6% of $C_{12}H_{19}B_2N$, besides 2.4% impurities. The infrared spectrum indicated monosubstitution of the aromatic ring with very little ortho-disubstitution. A very weak NH- band was observed at 3435 $cm.^{-1}$ This compound is 1,3-diethyl-2-phenyl-1,3-dibora-2-azatetralin as an impurity.

Analysis. Calculated for $B_2NC_{12}H_{19}$: B, 10.88; N, 7.04; C, 72.44; H, 9.63; molecular weight, 198.9. Found: B, 10.87; N, 7.34; C, 71.38; H, 9.72; molecular weights (by mass spectroscopy), 199/198/197.

2. 10.1 grams (b.p. 140-45°/0.2 mm., m.p. 62-63.5° after recrystallization from cyclohexane. The infrared spectrum indicated a sharp NH- band at 3430 $cm.^{-1}$, BN- bands between 1450 and 1500 $cm.^{-1}$, ortho-disubstitution (755 $cm.^{-1}$), and monosubstitution (700 $cm.^{-1}$) of an aromatic nucleus. This compound is 1,3-diethyl-2-phenyl-1,3-dibora-2,4-diazanaphthalene. Small amounts of the liquid isomer 1-phenylamino-2-methyl-3-ethyl-1,3-dibora-4-azadihydronaphthalene could be isolated from the mother liquor.

Analysis. Calculated for $B_2N_2C_{16}H_{20}$: B, 8.27; N, 10.69; C, 73.35; H, 7.68; molecular weight, 261.9. Found: B, 8.36; N, 9.90; C, 72.75; H, 7.97; molecular weights (by mass spectroscopy), 262/261/260.

Decomposition of 1,3-Diethyl-2-phenyl-1,3-dibora-2-azacyclopentane. The compound (7.6 grams, 38.2 mmoles) was mixed with 8.9 grams (78 mmoles) of triethylaluminum. Triethylborane and, under reduced pressure, higher alkylboranes were removed by distillation. The distillate (analyzed by gas chromatography) consisted of 95.4% triethylborane, 4.3% diethylbutylborane (from Et_2AlBu), and some higher boiling compounds. The latter were enriched by distillation over a small column. The mixture consisted of two higher boiling organoboron compounds, A and B, which were separated by gas chromatography and could be identified by mass spectroscopy.

A. 1,4-Diethyl-1,4-diboracyclohexane, molecular weights 136/135/134, with two boron atoms; major fractions of 107 and 79, each containing two boron atoms.

B. 1,2-Bis(diethylboryl)ethane, molecular weights 166/165/164, with two boron atoms; major fraction of 137, containing two boron atoms.

The organoboron compounds remaining after distillation of the aluminum compounds were dissolved in 50 ml. of ether and decomposed with 5 ml. of D_2O. A gas mixture was obtained containing 12% HD (and very small amounts of H_2 and D_2) and 86% ethane (C_2H_5D : $C_2H_4D_2$ $\approx 4:1$). Three grams of aniline were isolated, mainly N-D_2-aniline, besides traces of N-O_1-aniline. Practically no *o*-deuteroaniline is formed (CD-absorption near 2260 cm.$^{-1}$).

Decomposition of 1,3-Diethyl-2-phenyl-1,3-dibora-2,4-diazanaphthalene. Seven grams of the compound were mixed with 9.1 grams of triethylaluminum and the triethylborane was removed by distillation (87.3%, 4.6 grams). After dilution with ether, the residue was decomposed and 5.5 ml. of D_2O and monodeuteroethane were evolved. The aniline, simultaneously formed, contains N-D_2-aniline, *o*-deutero-N-D_1-aniline, and *o*-deutero-N-D_2-aniline (= H/D exchange at the nitrogen).

1,3-Dipropyl-2-phenyl-1,3-dibora-2-azacyclohexane and Isomeric Methylcyclopentane (Formation and Proof). A mixture of 66.1 grams of tetrapropyldiborane and tripropylborane was heated with 51.3 grams of (phenylamino)dipropylborane to 165-70°. The reaction was completed within 4 to 5 hours. Under reduced pressure, 35.3 grams of tripropylborane, 21.9 grams of propyldiborane, 5.3 grams of intermediate run, and 7.7 grams of residue were obtained, besides 33.3 grams of a material boiling between 60° and 80°/0.2 mm., and analyzing as $C_{15}H_{25}B_2N$. On rectification of this material, 10 grams of a compound with a constant boiling point of 80°/0.2 mm. were obtained. Infrared spectroscopy did not indicate NH- bonds. Then 1.33 grams of this compound were mixed with 1.4 grams of triethylaluminum, triethylborane was removed under reduced pressure, and the residue was decomposed with D_2O. Beside HD and monodeuterated ethane, monodeuteropropane and dideuteropropane could be identified.

2-Methyl-1-bora-2-azaindene. With stirring, 24.4 grams (0.209 mole) of triethylamine-borane were added over a period of 30 minutes at 130° to 26.4 grams (0.207 mole) of N-methylbenzylamine. Hydrogen and some triethylamine were obtained. The temperature was slowly increased to 200-10° and additional hydrogen and triethylamine were formed. Over all, 17 grams of amine and 8.9 liters of H_2

were obtained. The nearly colorless reaction mixture was distilled under reduced pressure. Besides a fraction boiling at 102-03°/16 mm. (8.6 grams), 7.6 grams of a material distilling at 120-30°/0.2 mm. and 8.5 grams of nondistillable residue were obtained.

The first fraction solidified on cooling and was washed with a little cyclohexane. It had a melting range of 66° to 96°. The crystals were a mixture of 2-methyl-1-bora-2-azaindene and (*N*-methylbenzylamino)-borane in the molar ratio of 1 to 1. The infrared spectrum indicates BH- bands between 2350 and 2500 cm.$^{-1}$ with maxima near 2430 cm.$^{-1}$ Besides monosubstitution of the aromatic ring, some ortho-disubstitution could be observed.

The second fraction was rectificated and 4 grams of bis(*N*-methylbenzylamino)borane (b.p. 127-32°/0.2 mm.) were obtained.

Analysis. Calculated for $BN_2C_{16}H_{21}$: B, 4.13; N, 11.11; H, 3.97; molecular weight, 252.1. Found: B, 4.33; N, 10.80; H, 3.3; molecular weight (cryoscopic method), 243.

The infrared spectrum showed a BH- band near 2450 cm.$^{-1}$ However, the presence of the isomeric 1-(*N*-methylbenzylamino)-2-methyl-1-bora-2-azaindene cannot be excluded completely.

1-Propyl-2-methyl-1-bora-2-azaindene. The solid mixed dimer of the previous experiment (7.5 grams) was mixed with 18 grams of tripropylborane at 110°C. for 1 hour. Under reduced pressure, a mixture of tripropylborane and tetrapropyldiborane could be distilled off; furthermore, about 3.5 grams of (*N*-methylbenzylamino)borane (b.p. 110-15°/11 mm.) were obtained. On heating for another hour to 200°, a gas consisting of hydrogen, C_3H_6, and C_3H_8 was evolved. On distillation of the residue of pyrolysis 1.4 grams of a prerun, 5 grams of residue, and 5 grams of the desired compound with a boiling range of 86° to 140°/0.3 mm. were obtained. The rectification resulted in 2 grams of the pure compound (b.p. 115-16°/11 mm.). On rectification of the main fraction 1-(*N*-methylbenzylamino)-2-methyl-1-bora-2-azaindene (3 grams, b.p. 120-22°/0.2 mm.) was also obtained. The infrared spectra gave evidence of mono- and ortho-disubstitution of the aromatic nucleus.

Preparation of Borazines. *B*-Triethyl-*N*-triphenylborazine. A mixture of 15.3 grams (0.095 mole) of (phenylamino)diethylborane and 11.7 grams (0.102 mole) of triethylamine-borane was heated for 3 1/2 hours to 110° to 130°. The triethylborane formed was distilled off with the triethylamine. Finally, under reduced pressure, the excess of triethylamine-borane was removed. On cooling, the residue crystallizes completely. It was recrystallized from hexane and the infrared spectrum showed a very strong BH- absorption at 2530 cm.$^{-1}$ This residue consisted of 71% *B*-triethyl-*N*-triphenylborazine and 29% *B*-diethyl-*N*-triphenylborazine (m.p. 124-26°).

Analysis. Calculated for $B_3N_3C_{22}H_{26}$: B, 8.91; N, 11.52; C, 72.3; H, 7.15; H (active), 2.74. Found: B, 8.22; N, 10.93; N, 10.93; C, 71.86; H, 7.59; H (active), 0.786.

With an excess of triethylborane the mixture can be transformed into pure *B*-triethyl-*N*-triphenylborazine. It was heated for about 3 1/2 hours with triethylborane to about 100°, and the crystals were washed with cyclohexane (in which the borazine is very slightly soluble); pure crystals (m.p. 151-53°) were obtained. The infrared spectrum did not indicate any BH- band.

Analysis. Calculated for $B_3N_3C_{24}H_{30}$: B, 8.27; N, 10.69; C, 73.30; H, 7.71. Found: B, 8.25; N, 9.95; C, 73.25; H, 7.68.

B-Triethyl-*N*-triphenylborazine from (Phenylamino)diethylborane and Diethylchloroborane. A mixture of 25.2 grams (0.241 mole) of freshly distilled (diethyl)chloroborane, 38.7 grams (0.241 mole) of (phenylamino)-diethylborane, and 53.5 grams (0.288 mole) of tri-*n*-butylamine was refluxed for 3 to 4 hours (140°). On cooling, the liquid separated into two phases, the lower phase crystallizing partially. On distillation besides a fraction boiling at 88-92° [17.59 grams consisting primarily of triethylborane and (diethyl)chloroborane], a fraction (31.29 grams) consisting of triethylborane (4.3%), tributylamine (79.4%), and (phenylamino)diethylborane (14.6%) was obtained. Finally, 10.6 grams of pure (phenylamino)diethylborane can be recovered. The residue (consisting mainly of borazine and tributylamine hydrochloride) is added with heptane. Borazine (18.4 grams, m.p. 167-68°) and tributylamine hydrochloride (320 grams) were obtained.

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Received June 13, 1963. No. V in this series was published in *Liebigs Ann. Chem.* 644, 1(1961).

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch016

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Contributions to the Chemistry of Boron

XXIV. Preparation and Properties of Some Hydrazinoboranes I

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch017

Several types of hydrazinoboranes have been prepared by hydrazinolysis of various chloroboranes and aminoboranes. Chemically, the hydrazinoboranes resemble the aminoboranes, as has been shown by their behavior toward nucleophilic and electrophilic reagents.

Interest in boron-nitrogen chemistry has been focused principally on aminoborane and borazine derivatives. The hydrazinoboranes have attracted less attention, although they offer interesting aspects from both the preparative and theoretical points of view. Dative π-bonding between the nitrogen's lone electron pair into the empty p_z-orbital of the boron atom in hydrazinoboranes of the type $R_2B\text{-}NH\text{-}NH\text{-}BR_2$ may result in a conjugation effect, well established in the isoelectronic butadiene system. Because of electronegativity considerations, this effect will almost certainly not be as pronounced as in the carbon analog. A study of the B-N linkage in hydrazinoboranes will also show the influence of an electronegative group, X ($X = NR_2$, NHPh, $NHBR_2$), on the B-N bond in an aminoborane, $R_2B\text{-}NHX$. In addition to these considerations, the hydrazinoboranes also offer access to new heterocyclic and polymeric boron compounds with a B-N-N-B unit, and a great number of hydrazinoboranes of low molecular weight are to be expected.

Early attempts to produce hydrazinoborane, $H_2B\text{-}NH\text{-}NH\text{-}BH_2$, through pyrolysis of hydrazine-bis(borane), $H_3B\cdot NH_2\text{-}NH_2\cdot BH_3$, were unsuccessful *(10, 30)* until Goubeau and Ricker prepared it by pyrolysis of $N_2H_4\cdot BH_3$ *(13)*. Hydrazino-1,2-bis(dialkylboranes), $R_2B\text{-}NH\text{-}NH\text{-}BR_2$, were first reported in 1959 *(23)*. They were obtained by hydrazinolysis of trialkylboranes *(18)*, tetraalkyldiborane *(25)* (chloro)alkylboranes *(25)*, (mercapto)alkylboranes *(17)*, and aminoboranes *(21, 23, 25)*. In addition, some (hydrazino) phenylboranes *(21)*, a *B,B',B''*-tris(hydrazino)-borazine *(22)*, and the cyclic 1,4-diphenyl-2,3,5,6-tetraza-1,4-diborine *(21)* were synthesized.

Preparation

The methods for preparing hydrazinoboranes are not necessarily the same as those for aminoboranes, although these methods suggest themselves. The normal procedure for aminolysis of a boron halide can be disturbed in the hydrazinolysis process, because the free amino group in the expected hydrazinoborane, $R_2B\text{-}NH\text{-}NH_2$, may act as the hydrogen halide acceptor. Indeed, the yields of hydrazinoboranes obtained by the action of hydrazine on chlorodialkyl- and diphenylboranes are negligible, if the reaction is carried out in ether solution at room temperature. This is due to the formation of an ether-insoluble salt of the composition $R_2BCl \cdot 2\ N_2H_4$:

$$R_2BCl \ + \ 2\ N_2H_4 \ \rightarrow \ [R_2B(N_2H_4)_2]Cl \qquad (1)$$

$$R = Pr,\ Ph$$

The composition of these compounds suggests their formulation as cationic complex salts of boron, since similar compounds containing amines instead of hydrazine as a ligand are readily formed *(16, 20, 28, 29)*.

Replacement of hydrazine by $Me_2N\text{-}NH_2$ in the reaction according to Equation 1 leads to reasonable yields of (dimethylhydrazino)-dialkyl- or diphenylborane:

$$R_2BCl \ + \ 2\ Me_2N\text{-}NH_2 \ \rightarrow \ R_2B\text{-}NH\text{-}NMe_2 \ + \ Me_2N\text{-}NH_2 \cdot HCl \qquad (2)$$

The difficulties encountered in solvolyzing the B-Cl bond by hydrazine demanded a more convenient and versatile preparative method—the hydrazinolysis of aminoboranes. Since these compounds are easily accessible, hydrazinoboranes are also readily prepared. The hydrazinoboranes synthesized by this route as well as by the method of Equation 2 are summarized in Table I.

Interaction of $Me_2N\text{-}NH_2$ with tris(dimethylamino)borane leads to solid, sublimable tris(dimethylhydrazino)borane:

$$3\ Me_2N\text{-}NH_2 \ + \ B(NMe_2)_3 \ \rightarrow \ (Me_2N\text{-}NH)_3B \ + \ 3\ HNMe_2 \qquad (3)$$

The evolution of dimethylamine begins at room temperature, but heating to 60° to 80°C. is required to drive the reaction to completion. Similarly, $(Me_2N\text{-}NH)_2BH$ was prepared from $(Me_2N)_2BH$; the B-H bond does not react with primary or secondary amines at temperatures below 120° *(26)*. The B-B bond in tetrakis(dimethylamino)diboron is also not affected by treatment with $Me_2N\text{-}NH_2$:

$$B_2(NMe_2)_4 \ + \ 4\ H_2N\text{-}NMe_2 \ \rightarrow \ B_2(NH\text{-}NMe_2)_4 \ + \ 4HNMe_2 \qquad (4)$$

This is somewhat surprising, because the B-B bond is readily broken down by the action of primary amines on $R(Me_2N)B\text{-}B(NMe_2)R$ *(27)* and less easily on $B_2(NMe_2)_4$ *(7)*.

Transamination of $B(NMe_2)_3$ with phenylhydrazine in various molar quantities resulted in the formation of $B(NH\text{-}NHPh)_3$, but not of $Me_2NB(NH\text{-}NHPh)_2$ or $(Me_2N)_2B\text{-}NH\text{-}HNPh$ (reactions to be reported elsewhere), while with $PhB(NMe_2)_2$ the reactions

$$PhB(NMe_2)_2 \ + \ H_2N\text{-}NHPh \ \rightarrow \ PhB(NMe_2)NH\text{-}NHPh \ + \ HNMe_2 \qquad (5)$$

$$PhB(NMe_2)_2 \ + \ 2\ H_2N\text{-}NHPh \ \rightarrow \ PhB(NH\text{-}NHPh)_2 \ + \ 2\ HNMe_2 \qquad (6)$$

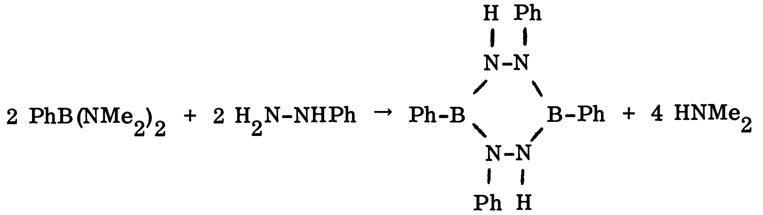
Table I. Synthesis

No.	*Compound*	*Method*^{a}	*Yield, %*	*B.P., ^{o}C.*
1.	$Et_2B\text{-}NH\text{-}NH\text{-}BEt_2$	B	85	65–8 (9 mm.)
2.	$Pr_2B\text{-}NH\text{-}NH\text{-}BPr_2$	B	92	122 (12 mm.)
3.	$Bu_2B\text{-}NH\text{-}NH\text{-}BBu_2$	B	90	118 (1 mm.)
4.	$Ph_2B\text{-}NH\text{-}NH_2$	B	95	147 ^{c}
5.	$Bu_2B\text{-}NH\text{-}NH_2$	B	99	38-39 ^{c}
6.	$Bu_2B\text{-}NH\text{-}NMe_2$	A, B	77, 85	48 (mm.)
7.	$Ph_2B\text{-}NH\text{-}NMe_2$	A, B	41, 82	135 (5 mm.) ^{e}
8.	$PhB(NH\text{-}NMe_2)_2$	A, B	52, 77	76-78 (1 mm.)
9.	$HB(NH\text{-}NMe_2)_2$	B	91	33-35 ^{c}
10.	$B(NH\text{-}NMe_2)_3$	B	95	103 ^{c}
11.	$B_2(NH\text{-}NMe_2)_4$	B	97	72-75 ^{c}
12.	$PhB(NMe_2)NH\text{-}NHPh$	B	36	57-58 ^{c}
13.	$PhB(NH\text{-}NHPh)_2$	B	21	122-125 ^{c}
14.	$Bu_2B\text{-}NH\text{-}NHPh$	B	85	144 (1 mm.)
15.	$Ph_2B\text{-}NH\text{-}NHPh$	B	92	94 ^{c}
16.	$[PhB\text{-}NH\text{-}NH]_2$	B	80–97	257-58 ^{c}

[a] Method B corresponds to transamination of an aminoborane with a hydrazine, method A to hydrazinolysis of the appropriate chloroborane.

[b] Determined cryoscopically in benzene solution.

occurred simultaneously at room temperature. In refluxing toluene solution, 2 moles of Me_2NH are evolved per mole of phenylhydrazine and the aminoborane and a tetraphenylcyclo-2,3,5,6-tetraza-1,4-diborine are formed.



(7)

However, it has not yet been determined whether this or the other possible N isomer has been obtained. This reaction shows that replacement of the hydrogen atom of the PhHN group proceeds only at elevated temperatures and therefore the reaction sequence

$$Bu_2B\text{-}NH_2 + H_2N\text{-}NHPh \xrightarrow{0^\circ} Bu_2B\text{-}NH\text{-}NHPh + NH_3 \qquad (8)$$

$$Bu_2B\text{-}NH\text{-}NHPh + Bu_2B\text{-}NH_2 \xrightarrow{160^\circ} Bu_2B\text{-}NH\text{-}N(Ph)BBu_2 + NH_3 \qquad (9)$$

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In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

of Hydrazinoboranes

N_D^{20}	Calcd.			Found		
	B	N	MW	B	N	MW[b]
1.4417	12.9	16.7	167.9	12.7	16.2	172
1.4459	9.7	12.5	224.0	9.5	12.4	224
1.4510	7.7	10.0	280.8	7.6	10.1	278
-	5.5	14.3	196.1	5.2	14.3	402[d]
-	-	17.9	155.9	-	18.1	-
1.4122	5.9	15.2	184.1	5.8	15.2	181
-	4.8	12.5	224.1	4.8	12.7	226
-	5.3	27.2	206.1	5.0	27.0	200
-	8.3	43.1	130.0	8.1	42.5	131
-	5.7	44.7	188.1	5.6	44.2	186
-	8.4	43.4	258.0	8.0	43.1	250
-	4.5	17.6	239.1	3.9	17.6	237
-	3.6	18.5	302.2	4.0	16.8	302
1.5130	4.7	12.1	232.3	4.7	11.8	225
-	-	10.3	272.1	-	10.1	269
-	9.2	23.8	235.9	9.2	22.7	238[f]

[c] Melting points not corrected, taken in sealed capillary tubes.

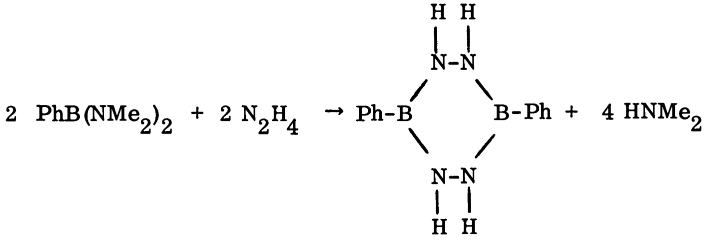
[d] Ebullioscopically in benzene.

[e] Lit. (21); b.p. (No. 7) 123 (3 mm.); (No. 8) b.p. 80 (2 mm.).

[f] Cryoscopically in $CHBr_3$.

is easily controlled by temperature conditions.

The 2,3,5,6-tetraza-1,4-diborine ring system was also synthesized by transamination of $PhB(NMe_2)_2$ or $PhB(NH\text{-}NMe_2)_2$ with anhydrous hydrazine, in accordance with the observations of Niedenzu, Beyer, and Dawson *(21)*:



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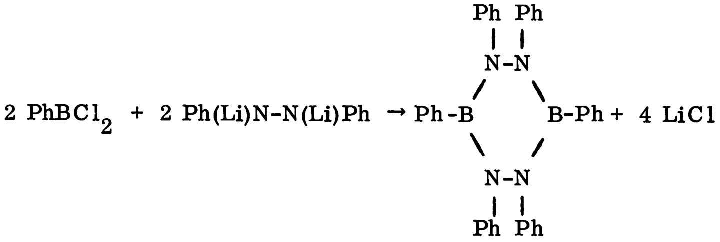
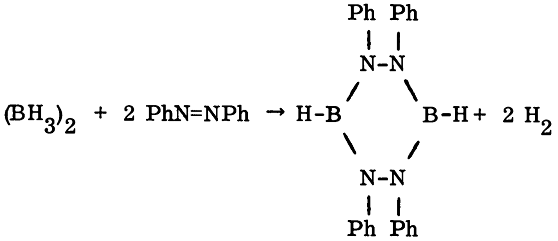
by reaction of (dichloro) phenylborane with (dilithio)diphenylhydrazine:



(11)

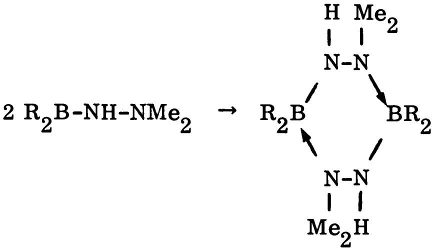
or by reduction of azobenzene with diborane:



(12)

Chemical Properties

Hydrazinoboranes might be expected to react with both nucleophilic and electrophilic reagents, since they possess potential donor and acceptor properties. The latter are in general strongly reduced because of π-bonding. But the donor properties of the nitrogen atoms in R_2B-NH-NMe_2 should be different, the nitrogen atom of the Me_2N group having greater basicity than the nitrogen atom of the N-H group, whose basicity is expected to be strongly decreased by back-coordination of its electron lone pair into the p_z-boron orbital. But so far no evidence has been found that (dimethylhydrazino)dialkyl- or diphenylborane polymerizes, for instance, according to



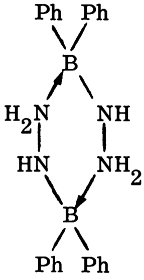
(13)

This corresponds to the behavior of (amino)dialkylboranes, which generally do not polymerize, unless steric factors and certain electronic factors permit this. Examples are Me_2B-NH_2 *(32)*, Me_2B-NHMe *(31)*, and Ph_2B-NH_2 *(9)*.

Hydrazinoboranes readily undergo transhydrazination reactions; this fact can be considered evidence of the acceptor properties of these compounds, since this process is probably a nucleophilic displacement *(3, 11, 24)*. Thus hydrazinolysis of Ph_2B-NH-NMe_2, or Ph_2B-NMe_2, leads to (hydrazino)diphenylborane:

$$Ph_2B\text{-}NH\text{-}NMe_2 + NH_2\text{-}NH_2 \rightarrow PH_2B\text{-}NH\text{-}NH_2 + H_2N\text{-}NMe_2 \qquad (14)$$

This compound is crystalline and shows in boiling benzene solution the molecular weight of a dimer. Therefore structure I is suggested for it. The infrared spectrum shows three bands in the N-H stretching region (3300, 3227, and 3118 $cm.^{-1}$), supporting this suggestion. The compound decomposes above 150° C.



I

(Dialkyl)hydrazinoboranes result from the interaction of hydrazine with hydrazino-1, 2-bis(dialkylboranes):

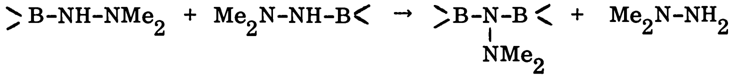
$$Bu_2B\text{-}NH\text{-}NH\text{-}BBu_2 \; + \; N_2H_4 \; \rightarrow \; 2\ Bu_2B\text{-}NH\text{-}NH_2 \qquad (15)$$

but these compounds are stable only at room temperature. On attempted distillation in vacuo they decompose into the starting materials—e.g., Reaction 15 is reversed. This is reminiscent of the formation of H_2B-NH-NH-BH_2 in the pyrolysis of N H •BH

$$2\ N_2H_4{\cdot}BH_3 \; \rightarrow \; H_2B\text{-}NH\text{-}NH\text{-}BH_2 \; + \; N_2H_4 \; + \; 2\ H_2 \qquad (16)$$

The first step in this idealized equation would be the evolution of hydrogen with formation of H_2B-NH-NH_2, followed by rearrangement to H_2B-NH-NH-BH_2, a reaction analogous to the transamination.

(Dimethylhydrazino)boranes are fairly stable, but at high temperature condensation takes place. Thus $B(NH\text{-}NMe_2)_3$ withstood 5 hours of heating to 150°; even at 210° there was little decomposition, but after 15 hours of heating to 290° dimethylhydrazine was the main volatile product of a decomposition process. This suggests a condensation according to



$$>B\text{-}NH\text{-}NMe_2 \; + \; Me_2N\text{-}NH\text{-}B< \; \rightarrow \; >B\text{-}\underset{\substack{|\\ NMe_2}}{N}\text{-}B< \; + \; Me_2N\text{-}NH_2 \qquad (17)$$

The residue of this decomposition was a yellow, brittle solid, having a B:N ratio of 1:17 showing that reaction according to Equation 17 cannot be the only one.

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Hydrazinoboranes of all types react very readily with electrophilic reagents, such as HCl, BF_3, BCl_3, or $(BH_3)_2$.

$B(NH\text{-}NMe_2)_3$ and excess hydrogen chloride in diethyl ether solution combine in a 1 : 15 molar ratio, the product, $B(NH\text{-}NMe_2)_3 \cdot 5\ HCl$, being insoluble in this solvent. Solids of the composition $B(NH\text{-}NMe_2)_3 \cdot 2\ HCl$ and $B(NH\text{-}NMe_2)_3 \cdot 3\ HCl$ can be isolated as reaction intermediates. Similarly, $Pr_2B\text{-}NH\text{-}NMe_2$ adds 1 mole of HCl from the gas phase. The structure of the adducts has not been determined, but the following reaction gives evidence of an intact B-N bond in these products.

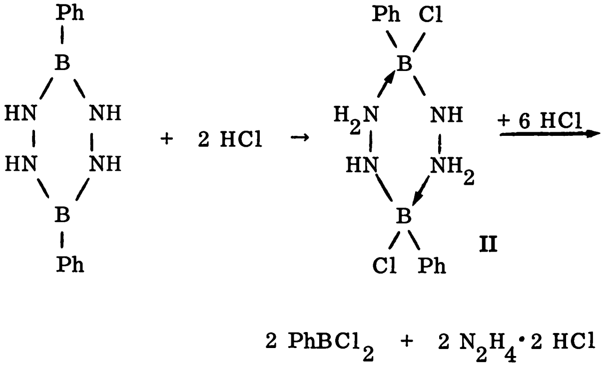
Both diphenyl- and dipropyl(phenylhydrazino)borane react rapidly with HCl in ether solution at -40° with cleavage of the B-N bond, even if an excess of the borane is present:

$$R_2B\text{-}NH\text{-}NHPh + 2\ HCl \rightarrow R_2BCl + PhHN\text{-}NH_2 \cdot HCl \qquad (18)$$

The same is true of hydrazino-1, 2-bis(dialkylborane), but in this case a 1:2 addition product is formed at low temperature:

$$R_2B\text{-}NH\text{-}NH\text{-}BR_2 \xrightarrow{+\ 2\ HCl} R_2B\text{-}NH\text{-}NH\text{-}BR_2 \cdot 2\ HCl \xrightarrow{+\ 2\ HCl} 2\ R_2BCl + N_2H_4 \cdot 2\ HCl \qquad (19)$$

This type of reaction also takes place with $[PhB\text{-}NH\text{-}NH]_2$. A solid adduct, $[PhB\text{-}NH\text{-}NH \cdot HCl]_2$, is the first isolable product, but in the presence of more HCl the B-N bonds are broken. We assume that the reactions take place according to the equations



(20)

The expected 1:4 adduct, addition of HCl onto the lone pairs of electrons of the nitrogen atoms of the NH groups in II, has not been observed.

(Halogeno)hydrazinoboranes have so far not been obtained through direct action of halogenoboranes on hydrazines, but they should form in the interaction process between a boron halide and a hydrazinoborane. Trifluoroborane reacts with $(Bu_2B\text{-}NH)_2$ according to

$$Bu_2B\text{-}NH\text{-}NH\text{-}BBu_2 + 2\ BF_3 \rightarrow 2\ Bu_2BF + F_2B\text{-}NH\text{-}NH\text{-}BF_2 \qquad (21)$$

The solubility behavior of the resulting hydrazino-1,2-bis(difluoroborane) suggests this compound to be of polymeric nature, like $F_2B\text{-}NH_2$ *(16)*. In contrast to this cleavage reaction $[PhB\text{-}NH\text{-}NH]_2$ seems to form the addition product, $[PhB\text{-}NH\text{-}NH]_2 \cdot 2\ BF_3$. No $PhBF_2$ is formed, and the product shows no sign of decomposition up to 130°. Since BF_3 readily cleaves the B-N linkage, it is more likely that the product obtained no longer contains the intact cyclic system, but is better formulated as $Ph(F)B\text{-}NH\text{-}NHBF_2$. We cannot yet prove this structure, but this interpretation would not violate the observed stoichiometry. Diphenylfluoroborane and difluoro(phenylhydrazino)borane are the products of interaction of BF_3 and $Ph_2B\text{-}NH\text{-}NHPh$:

$$Ph_2B\text{-}NH\text{-}NHPh + BF_3 \rightarrow Ph_2BF + PhHN\text{-}NH\text{-}BF_2 \qquad (22)$$

Trichloroborane reacts more vigorously with hydrazinoboranes than BF_3. No addition products have been isolated. At room temperature B-N bond cleavage of the original hydrazinoborane occurs. Dichloro(dimethylhydrazino)borane results from BCl_3 and either (dimethylhydrazino)dipropylborane or tris(dimethylhydrazino)borane:

$$Pr_2B\text{-}NH\text{-}NMe_2 + BCl_3 \rightarrow Pr_2BCl + Cl_2B\text{-}NH\text{-}NMe_2 \qquad (23)$$

$$B(NH\text{-}NMe_2)_3 + 2\ BCl_3 \rightarrow 3\ Cl_2B\text{-}NH\text{-}NMe_2 \qquad (24)$$

Diborane also interacts with hydrazinoboranes, and the B-H bond containing hydrazinoboranes may be prepared in this manner. Hydrazino-1,2-bis(diethylborane) was converted into a solid by the action of diborane in ether solution and in the gas phase, and its composition approached the (hydrazino)-1,2-bis(borane). The idealized equation is

$$Et_2B\text{-}NH\text{-}NH\text{-}BEt_2 + (BH_3)_2 \rightarrow H_2B\text{-}NH\text{-}NH\text{-}BH_2 + (Et_2BH)_2 \qquad (25)$$

No complete exchange of the alkyl groups has been achieved; this may be due either to the experimental conditions or to the ligand exchange catalyzed by B-H bonds *(15)*.

Oxidation of hydrazinoboranes of the type $R_2B\text{-}NH\text{-}NH\text{-}BR_2$ or $R_2B\text{-}NH\text{-}NHPh$ should give the corresponding azoboranes. Mercuric oxide, bromine, and iodine in the presence of a base have been used as oxidizing agents, but with $Bu_2B\text{-}NH\text{-}NH\text{-}BBu_2$ nitrogen rather than azoborane was formed according to

$$Bu_2B\text{-}NH\text{-}NH\text{-}BBu_2 + 2\ Br_2 \rightarrow 2\ Bu_2BBr + N_2 + 2\ HBr \qquad (26)$$

Several color changes during the reaction indicate the intermediate formation of the expected azoboranes.

Experimental

Anhydrous hydrazine was prepared according to the procedure of Bock and Rudolph *(6)*. 1,1-Dimethylhydrazine, 1,2-dimethylhydrazine, and phenylhydrazine were commercial products. They were dried over BaO and fractionally distilled. The preparation of aminoboranes is described in earlier papers *(24, 26, 27)* and also by many other authors

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(1, 4, 21). All reactions were carried out with exclusion of moisture under an atmosphere of pure nitrogen, if not stated otherwise.

Preparation of $Pr_2BCl \cdot 2\ N_2H_4$. When 2.8 grams of N_2H_4 were slowly dropped into a stirred solution of 7.45 grams of Pr_2BCl at 0°; a white crystalline precipitate formed. The solid was filtered off after several hours. Yield: 8.1 grams of $Pr_2BCl . 2\ N_2H_4$ (94%). Only a small amount of liquid remained after the removal of the solvent. The solid showed a melting range from 117° to 129° (decomp.). It dissolved in water, from which an oil separated slowly. Recrystallization from $CHCl_3$ did not improve the melting point. Calcd. for $C_6H_{22}BClN_4$: B 5.5, Cl 18.0, N 28.g. Found: B 5.4, Cl 17.8, N 28.0.

$Ph_2BCl \cdot 2\ N_2H_4$ was obtained similarly. Calcd. for $C_{12}H_{18}BClN_4$: B 4.1, Cl 13.4, N 21.2. Found: B 3.9, Cl 13.2, N 20.9.

(Dibutyl)dimethylhydrazinoborane (This preparation is given as an example). Twelve grams of $Me_2N\text{-}NH_2$ were dissolved in 100 cc. of anhydrous diethyl ether under nitrogen and 16.0 grams of Bu_2BCl were added with stirring. After the exothermic reaction had subsided, the mixture was heated to reflux for 1 hour. The solid ($Me_2N\text{-}NH_2 \cdot HCl$) was filtered off, the ether was removed, and the remaining liquid was distilled. Yield: 12 grams of $Bu_2B\text{-}NH\text{-}NMe_2$ (77%)[b.p. 47 - 18° (2 mm.)]. The compound is a clear colorless liquid, which dissolves in ethers and hydrocarbons but reacts rapidly with proton-active solvents.

Tris(dimethylhydrazino)borane (Example of the hydrazinolysis of an aminoborane). $B(NMe_2)_3$ (14.2 grams) was dropped into 25 grams of $Me_2N\text{-}NH_2$ with stirring. Bubbling of the mixture indicated the evolution of Me_2NH. After this evolution subsided, the mixture was heated to 80°. After 3 hours 12.3 grams of Me_2NH had accumulated in a cold trap. Heating for an additional hour yielded 1.1 grams of Me_2NH, affording a nearly quantitative yield of dimethylamine. Excess dimethylhydrazine was removed in vacuo and tris(dimethylhydrazino)-borane sublimed at 50° to 60° (1 mm.). Yield: 15.5 grams (82%) [m.p. 103°]. If excess dimethylhydrazine is not removed and the mixture is kept standing overnight, $(Me_2N\text{-}NH)_3B$ crystallizes in large plates. The compound dissolves easily in ether, tetrahydrofurane, benzene, toluene, $CHCl_3$, and CCl_4. It dissolves less readily in CS_2 or petroleum ether. In the presence of ethyl alcohol, methanol, or water a fairly rapid solvolysis occurs.

Other hydrazinoboranes were prepared in a similar fashion. For the preparation of (hydrazino)dialkylboranes, (amino)dialkylboranes ($R_2B\text{-}NH_2$) were used. Reaction with $R_2B\text{-}NMe_2$ required a higher reaction temperature. The aminoborane was generally used in excess.

1-Phenyl-1, 2-bis(dialkylboryl)hydrazine. $Bu_2B\text{-}NH\text{-}NHPh$ (10.7 grams) and 5.7 grams of $Bu_2B\text{-}NH_2$ were heated to 160° to 180°. Ammonia was evolved. After 3 hours the temperature was raised to 220° for a few minutes. Distillation of the yellow mixture in vacuo yielded 3.1 grams of $Bu_2B\text{-}NH_2$ [b.p. 56° (9 mm.)], 6.6 grams of $Bu_2B\text{-}NH\text{-}NHPh$ [b.p. 140-45° (1 mm.)], and 4.5 grams (32%) of $Bu_2B\text{-}NH\text{-}NPh\text{-}BBu_2$ [b.p. 170-80° (1 mm.)] n_D^{20} 1.4887. Calcd. for $C_{22}H_{42}B_2N_2$: B 6.1, N 7.8. Found: B 5.8, N 7.9. Mol. weight: calcd. 356, found: 350.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch017

(Phenyl)(dimethylamino)phenylhydrazinoborane and bis(phenylhydrazino)phenylborane. $PhB(NMe_2)_2$ (9.35 grams) dissolved in 25 cc. of xylene was treated with 5.7 grams of $PhHN-NH_2$ at room temperature in a vacuum of 50 mm. After several hours crystals separated and the solution turned blue. The crystals [4.5 grams of $PhB(NMe_2)-NH-NHPh$ (36%), m.p. 57-58°] were filtered off and the solution was concentrated. A second crop of material was not homogeneous, but the third consisted of 3 grams of $PhB(NH-NHPh)_2$ (21%) [m.p. 122-25° (decomp.)].

1,4-Diphenyl-2,3,5,6-tetraza-1,4-diborine. The compound formed by reaction of N_2H_4 with $PhB(NMe_2)_2$ or $PhB(NH-NMe_2)_2$ in benzene solution at room temperature. The amines evolved were removed in a vacuum. The product was recrystallized from CHCl (yield 80 to 97%,) (m.p. 257-58°), but part of the crystal always melted at 155-60°, solidifying on further heating [lit. m.p. 156° *(21)*]. It dissolves sparingly in benzene, nitrobenzene, dioxane, ether, and $CHCl_3$. $CHBr_3$ is one of the most satisfactory solvents.

Hexaphenyl-2,3,5,6-tetraza-1,4-diborine. Hydrazobenzene (9.2 grams in 150 cc. of ether) was treated with an ether solution containing 102 mmoles of LiBu. The resulting suspension of $Li_2N_2Ph_2$ was heated to complete the reaction and was treated with 7.9 grams of $PhBCl_2$ after cooling. The mixture turned yellow and a white precipitate appeared. After heating to reflux for 2 hours, the solid was removed and treated with hot benzene. Yield: 4.5 grams of "LiCl." Calcd. 4.3 grams. The solvent of the filtrate was stripped off and the residue recrystallized several times from benzene-petroleum ether [yield: 6.0 grams of $Ph_6B_2N_4$ (62%), m.p. 156-58°]. On hydrolysis of this compound, hydrazobenzene (m.p. 124-26°) and phenylboronic acid (m.p. 210-14°) were obtained. Calcd. for $C_{36}H_{30}B_2N_4$: B 4.0, N 10.4. Found: B 4.4, N 10.0. Mol. weight: calcd. 540; found 552, 558.

2,3,5,6-Tetraphenyl-2,3,5,6-tetraza-1,4-diborine. Ten grams of azobenzene were dissolved in the necessary amount of ether. Diborane was passed into the stirred solution. The reaction started immediately, as shown by color changes to deep brown and green and evolution of some hydrogen. Finally the solution became colorless after some hours. Ether was replaced by benzene and the mixture was then heated, while hydrogen was evolved. On concentration, white needles separated. These were recrystallized from benzene-petroleum ether [yield: 8.9 grams (84%), m.p. 110-12°]. The compound is readily hydrolyzed, especially in the presence of alcohols. Methanolysis yields hydrazobenzene [m.p. 126° (91%)], hydrogen (98%), and methyl borate (98%). Calcd. for $C_{24}H_{22}B_2N_4$: B 5.6, N 14.4, H^- 0.52. Found: B 5.4, N 14.2, H^- 0.50. Mol. weight: Calcd: 388; found 372, 378.

(Hydrazino)diphenylborane. $Ph_2B-NH-NMe_2$ (4.1 grams) was dissolved in 20 cc. of benzene and treated with 0.6 gram of N_2H_4 at room temperature. A solid precipitated. Benzene and dimethylhydrazine were removed by distillation and the residue was recrystallized from hot benzene. Yield: 3.5 grams of $Ph_2B-NH-NH_2$, m.p. 147°.

(Hydrazino)dibutylborane. $Bu_2B-NH-NH-BBu_2$ (2.8 grams) was dissolved in 10 cc. of ether and treated with 320 mg. of N_2H_4. The hydrazine dissolved. On removal of the solvent an oily liquid remained, which crystallized slowly (m.p. 38-39°). The substance showed three not very well resolved bands at 3425 to 3250 $cm.^{-1}$ and a strong NH_2 deformation band at 1608 $cm.^{-1}$ Distillation of 15.5 grams of Bu_2B-NH-NH_2 yielded 1.5 grams of N_2H_4 [b.p. 23-35° (25 mm.), m.p. -1°] and 12.9 grams of Bu_2B-NH-NH-BBu_2 [b.p. 95-7° (.0.01 to 0.05 mm.)], n_D^{20} 1,4490.

(Phenylhydrazino)dibutylborane. Bu_2B-NH-NH-BBu_2 (4.85 grams, 17.3 mmoles) was added to 3.9 grams of PhHN-NH (35.8 mmoles). The mixture was heated with stirring under nitrogen; 440 mg. of N_2H_4 were collected between 110° and 12°. Fractionation of the residue yielded 5.7 grams of Bu_2B-NH-NHPh (71%) [b.p. 141-44° (1 mm.)]. Calcd.: N 12.06; found: 12.15. It was also identified by its infrared spectrum.

Pyrolysis of B(NH-$NMe_2)_3$. A sample of B(NH-$NMe_2)_3$ was heated in an evacuated tube for 5 hours to 150°. No change had taken place. At 210° a slight decomposition was indicated by the formation of a small amount of Me_2N-NH_2, but the main part of the crystals was still unchanged (m.p. 103-04°). After 15 hours of heating to 290° a liquid and a yellow solid had formed. The liquid consisted mainly of Me_2N-NH_2, as shown by the refractive index and the infrared spectrum (b.p. 61-5°, n_D^{19} 1.4156). The solid was brittle and did not dissolve in the conventional organic solvents. It contained 14.4% B and 30.8% N.

Reaction of B(NH-$NMe_2)_3$ with HCl. A. One gram of B(NH-$NMe_2)_3$ (5.3 mmoles), dissolved in 20 cc. of ether, was treated with 26 cc. of a 0.2 HCl solution in ether (5.2 mmoles of HCl). The precipitate formed was filtered off, washed with ether, and dried. Yield: 660 mg. of B(NH-NMe_2)·2 HCl (97%). On evaporation of the filtrate 0.60 gram of impure B(NH-$NMe_2)_3$ (m.p. 100-03°), remained. Calcd. for $C_6H_{23}BCl_2N_6$: B 4.2, Cl 27.2. Found: B 4.0, Cl 27.4.

B. B(NH-$NMe_2)_3$ (2.0 grams, 10.6 mmoles), dissolved in 50 cc. of ether, was stirred and treated with 18.6 cc. of a 1.7M HCl solution in ether (31.6 mmoles of HCl). A precipitate formed immediately. It was filtered off after 4 hours. The filtrate, which contained no more HCl, left no residue on evaporation of the solvent. Yield: 3.0 grams of B(NH-$NMe_2)_3$·3 HCl. Calcd. for $C_6H_{24}BCl_3N_6$: B 3.6, Cl 35.8, N 28.2. Found: B 3.8, Cl 34.7, N 27.6.

C. B(NH-$NMe_2)_3$ (1.0 gram, 5.3 mmoles) was treated as above with 26.6 cc. of a 2N HCl solution in ether (53.2 mmoles). The precipitate was crystalline. The filtrate left no residue and consisted of an ether solution of HCl, containing 25.4 mmoles of HCl. Calcd. for $C_6H_{26}BCl_5N_6$: B 2.9, Cl 47.8, N 22.6. Found: B 2.8, Cl46.6, N 20.1.

Reaction of Pr_2B-NH-NHPh with HCl. Pr_2B-NH-NHPh (0.75 gram, 3.7 mmoles) was dissolved in 8.0 cc. of ether and 8 cc. of a solution of HCl in ether, containing 11.3 mmoles of HCl, were dropped into the hydrazinoborane at -40°. A precipitate formed. The solution then contained 0.455 mmoles per ml. of "HCl." Thus 11.1 - 7.3 = 3.8 mmoles of HCl had been consumed. The precipitate consisted of 561 mg. of impure PhHN-NH_2·HCl [m.p. 235°(lit. 240); calcd. Cl 24.5, found 23.4]. After removal of the ether and excess HCl 470 mg. of

Pr_2BCl remained. Thus it appeared that only 1 mole of HCl had been consumed, since the Cl content of the Pr_2BCl formed also gives HCl on hydrolysis.

Reaction of PH_2B-NH-NHPh with HCl. Ph_2B-NH-NHPh (0.924 gram, 3.4 mmoles) was treated as above with 6.8 mmoles of HCl in ether. Phenylhydrazine hydrochloride [0.448 gram (91.5%), m.p. 241°; calcd.: Cl 24.5; found: 24.4] precipitated. Ph_2BCl was isolated as its pyridine adduct [m.p. 78-80° (not recrystallized): calcd. for $C_{17}H_{15}BClN$: B 3.9, Cl 12.7. Found: B 3.5, Cl 12.3].

Reaction of Pr_2B-NH-NH-BPr_2 with HCl. Pr_2B-NH-NH-BPr_2 (0.324 gram, 1.45 mmoles) was treated in vacuum with 80.7 cc. of gaseous HCl. The reaction at -40° consumed 62.9 cc. (2.80 mmoles) within 45 minutes. The solid formed reacted with more HCl at room temperature. Of the added 94.7 cc., 54.0 cc. were consumed. A liquid had formed and was distilled off at room temperature. It consisted of 358.7 mg. of Pr_2BCl (2.71 mmoles, 93%. Calcd.: Cl 26.8. Found: Cl 26.2). Three and six-tenths mmoles of HCl were consumed per mole of the hydrazinoborane, indicating that a mixture of $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot 2$ HCl had formed.

Reaction of $[PhB\text{-NH-NH}]_2$ with HCl. A. $[PHB\text{-NH-NH}]_2$ (0.341 gram, 1.44 mmoles), dissolved in 40 cc. of $CHCl_3$, was treated at -40° with 18.7 cc. of a HCl solution in ether containing 2.88 mmoles of HCl. A precipitate formed, and was filtered off. Yield: 0.385 gram $[PhB\text{-NH-NH}\cdot HCl]_2$ (87%); decomposition above 300° without melting. Calcd. for $C_{12}H_{16}B_2Cl_2N_4$: B 7.0, N 18.2, Cl 22.9. Found: B 6.4, N 18.5, Cl 21.5. The same product was also obtained by passing gaseous HCl over finely divided $[PhB\text{-NH-NH}]_2$ at room temperature. Found: B 6.9, Cl 22.2.

B. $[PhB\text{-NH-NH}]_2$ (0.456 gram, 1.93 mmoles) was treated with 7.72 mmoles of HCl in ether (53.6 cc.) at 0°. The solid formed was filtered off. It contained no B. Yield: 0.363 gram (calcd. for $N_2H_4 \cdot 2$ HCl: 0.4 gram; found: N 24.7, Cl 64.4, N:Cl = 1.0: 1.8). This corresponds to a mixture of $N_2H_4 \cdot HCl$ (calcd. N 41.0, Cl 51.9) with $N_2H_4 \cdot 2$ HCl (calcd. N 26.6, Cl 67.5). The filtrate on hydrolysis gave $PhB(OH)_2$, [m.p. 211-13°, lit. 216° *(14)*] and HCl.

Reaction of Bu_2B-NH-NH-BBu_2 with BF_3. Gaseous BF_3 (93.7 cc.) was condensed onto 0.348 gram of the hydrazinoborane (1.37 mmoles). After no further pressure change was observed at room temperature, excess BF_3 was removed at -80° and 29.3 cc. were recovered. This corresponds to a $(Bu_2B\text{-NH})_2$:BF_3 ratio of 1 to 2.1. The liquid formed was removed at room temperature and condensed at -40°, yielding 415 mg. of impure Bu_2BF (calcd. for Bu_2BF: 394 mg. The higher yield may be due to formation of some $BuBF_2$ as indicated by the higher BF_3 consumption). The solid residue (176 mg.) contained 21.8 mg. of N (calcd. for $B_2F_4H_2N_2$: N 21.9). The product did not dissolve in petroleum ether or benzene, and only slightly in ether. Hydrolysis of the product is otherwise slow, but is quick in hot sodium hydroxide solution.

Reaction of $[PhB\text{-NH-NH}]_2$ with BF_3. $[PHB\text{-NH-NH}]_2$ (0.608 gram, 2.56 mmoles) was dissolved in 60 cc. of $CHCl_3$ and cooled to 0°. With stirring 1.3 cc. of $BF_3 \cdot OEt_2$ and 15 cc. of ether were slowly added. The precipitate that formed slowly was filtered off after several hours, washed with a little ether, and dried. Yield: 0.854

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch017

gram, m.p. 130-40° with decomposition. Calcd. for $C_{12}H_{14}B_4F_6N_4$: B 11.6, F 30.7, N 15.1. Found: B 10.8, F 27.3, N 14.1. From the filtrate no $PhBF_2$ could be isolated. The analytical data indicate that the compound still contained some impurity, probably ether.

Reaction of Ph_2B-NH-NH-Ph with BF_3. Ph_2B-NH-NHPh (0.992 gram, 3.65 mmoles), dissolved in 50 cc. of ether, was cooled to -50°. With vigorous stirring a solution of 6.95 mmoles of BF_3 in 60 cc. of ether was slowly added. Most of the solvent was filtered off and the filtrate was distilled. Besides ether and some undetermined amount of $BF_3 \cdot OEt_2$, 0.69 gram of Ph_2BF distilled at 47° (1 mm.). It formed a 1:1 addition compound with aniline: $Ph_2BF \cdot NH_2Ph$ [m.p. 159-62°. Calcd. for $C_{18}H_{17}BFN$: B 3.8, N 4.9, F 6.6. Found: B 3.5, N 4.8, F 6.0]. The distillation residue was combined with the precipitate and recrystallized from benzene ether. Yield: 0.47 gram of F_2B-NH-NHPh [m.p. 178° (with decomp.). Calcd. for $C_6H_7BF_2N_2$: B 6.9, N 18.0, F 24.4. Found: B 6.7, N 17.6, F 23.6].

(Dichloro)dimethylhydrazinoborane. A. Four cubic centimeters of Pr_2B-NH-NMe_2 were treated with excess liquid BCl_3 at -60°. The mixture was stirred and slowly warmed to -40°, then after 1 hour to -20°. Most of the BCl_3 was then distilled off, and the rest of the liquid material at room temperature in a high vacuum (Pr_2BCl and some BCl_3). Crystals [m.p. 148-51° (decomp.)] remained. Calcd. for $C_2H_7BCl_2N_2$: B 7.7, N 19.9, Cl 50.4. Found: B 7.8, N 19.4, Cl 51.2.

B. $B(NH\text{-}NMe_2)_3$ (0.574 gram) was treated with excess liquid BCl_3. After 3 hours the unreacted BCl_3 was distilled off in a vacuum. The residue weighed 1.218 grams, corresponding to a 95% conversion to Cl_2B-NH-NMe_2. It started decomposition with melting at 140° to 150°.

Reaction of Et_2B-NH-NH-Et_2 with Diborane. Excess diborane was passed into a stirred solution of 1.97 grams of Et_2B-NH-NH-BEt_2 in 50 cc. of ether. After an hour all volatile material was removed and the procedure was repeated. The solid which remained was then treated with diborane at 47°. It dissolved only slowly in concentrated HCl with H_2 evolution, but more readily in hot aqueous bases. It still contained CH groups, as shown by its infrared spectrum. Found: B 30.2, N 39.0, B:N = 1: 0.99. Calcd. for H_2B-NH-NH-BH_2: 38.7 B, 50.3 N.

Oxidation of Bu_2B-NH-NH-BBu_2. $(Bu_2B\text{-}NH)_2$ (0.775 gram, 2.7 mmoles) in 5 ml. of petroleum ether was cooled to -40°. A solution of bromine in Et_3N (0.8 mmole of Br per cc.) was dropped into the stirred hydrazinoborane solution. At the beginning the bromine color was immediately discharged, and a gas (N_2) evolved rather quickly. The color of the solution sometimes became brown to blue. After 14 cc. of the bromine solution were added, the color turned to brown-red. The nitrogen formed was measured: 58 cc. of N_2 (standard conditions, 97%). Most of the solvent was removed and the triethylammonium bromide precipitated with petroleum ether (0.86 gram). From the filtrate a small amount of Bu_2BBr was isolated [b.p. 62° (10 mm.). Calcd. for $C_8H_{18}BBr$: Br 39.2. Found: 38.6].

Discussion

The chemistry of hydrazinoboranes resembles in many respects the chemistry of aminoboranes. Hydrazinolysis of aminoboranes or hydrazinoboranes shows the same features as the transamination

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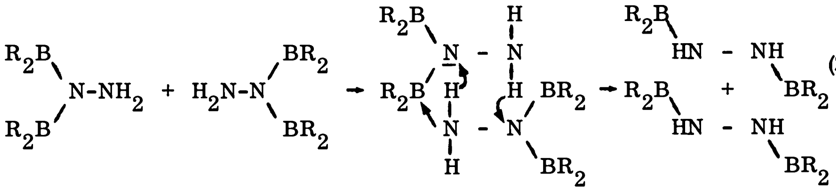
reaction, H_2N-NH_2 reacting more readily than MeHN-NHMe. That hydrazinoboranes $R_2B-NH-NH-BR_2$ and $R_2B-NH-NHR$ are formed, and not the isomers $(R_2B)_2N-NH_2$ and $H_2N-N(BR_2)R$, can readily be seen from the infrared spectra, that do not show the δ-NH_2 frequency in the neighborhood of 1600 cm^{-1}. Furthermore, there is only one ν-NH band of low intensity in the spectra between 3390 and 3420 $cm.^{-1}$ 1,2-Substitution on hydrazine is expected if the addition-elimination mechanism for the transamination is operative. Hydrazino-1, 1-bis-(dialkylboranes) would almost certainly rearrange to the 1,2-disubstituted hydrazine, if this reaction is not prevented by steric factors. This is because the free H_2N group will be able to attack nucleophilically at a boron atom, causing migration of a proton:


(27)

The hydrazinoboranes synthesized (see Table I) dissolve as monomers in benzene. No polymerization was noted except for $Ph_2B-NH-NH_2$. Somewhat surprising is the high melting point of $B(NH-NMe_2)_3$ and $B_2(NH-NMe_2)_4$, since aminoboranes of corresponding molecular weight are all liquids. In the solid state there may be association through coordinative B-N bonds or hydrogen bridging (this is subject to further studies), but the infrared spectra in Nujol mull of $B(NH-NMe_2)_3$ show only one NH-stretching frequency at 3310 $cm.^{-1}$, indicating no hydrogen bridges. The monomeric nature of this compound in solution is also confirmed by the H^1 NMR spectra, where only one sharp signal for the protons of the Me_2N group is found at -2.32 p.p.m. [compared with $Si(CH_3)_4$] and a broad, not well resolved band for the NH protons at -3.30 p.p.m. The spectra clearly show the absence of the $B-NMe_2$ grouping (signal at - 2.25 p.p.m.).

The same type of bonding may account for the unusual melting behavior of $[PhB-NH-NH]_2$. On heating, the crystals melt only partially at 155° to 160° and this part resolidifies on further heating. Finally a clear melt is obtained at 257-58°. This effect needs further study until more than a speculative explanation can be given. The low solubility in benzene or toluene is unexpected for a compound of this type, but it definitely shows the correct molecular weight in $CHBr_3$ solution. Lack of a strong absorption in the 1600-$cm.^{-1}$ region in the infrared spectra excludes the four-membered ring $[PhB-N-NH_2]_2$, which is also excluded on the grounds discussed above. Although this compound behaves peculiarly, there is no doubt as to its cyclic nature. Similar conclusions were drawn by Niedenzu, Beyer, and Dawson *(21)*, who described this compound recently.

The statement of Brown and Subba Rao *(8)* that 2 moles of hydridic hydrogen are consumed in the reduction of azobenzene to aniline corresponds to the observed ring formation. In the present study no reduction to aniline was observed; this was also found by Wiberg and

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

(see Equation 12), which on hydrolysis yields hydrazobenzene, hydrogen, and boric acid.

Isolation of $PhB(NMe_2)NH\text{-}NHPh$ shows that mixed dimethylaminophenylhydrazinoboranes can be prepared. Generally boranes containing ligands of the same type — e.g., nearly the same electronegativity — tend to disproportionate into the more symmetric boranes. Thus $(Me_2N)_2B\text{-}NHBu$ is unstable, in contrast to $(Me_2N)_2B\text{-}NHBu$ *(16)*. Recently reported examples of mixed tris(amino)boranes are $(iso\text{-}Pr_2N)_2B\text{-}NHR$ and $(PhHN)_2B\text{-}NH_2$ *(2, 4)*. Since $PhB(NMe_2)NH\text{-}NHPh$ is thermally unstable and transformed into $[PhB\text{-}NH\text{-}NPh]_2$, it shows that a condensation of the type

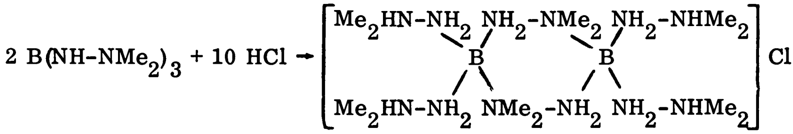
$$B\text{-}NH\text{-}NHPh + Me_2N\text{-}B \rightarrow B\text{-}NH\text{-}N(Ph)\text{-}B + Me_2NH \qquad (28)$$

proceeds more readily than the condensation according to Equation 17, for which a temperature as high as 290° is required. The mechanism for these types of condensations is probably the same as for the transamination *(3, 4, 11, 24)*.

Electrophilic reagents attack the nitrogen atoms in the hydrazinoboranes. The site of the attack cannot be predicted unequivocally, although it will probably occur at the more basic nitrogen atom. For instance, the infrared spectrum of $B(NH\text{-}NMe_2)_3 \cdot 2\,HCl$ shows only a very weak NH_2 deformation band and this is evidence that the HCl attacks the Me_2N group preferably. In $B(NH\text{-}NMe_2)_3 \cdot 5\,HCl$ absorption at 1605 cm^{-1} is strong, and NH_2 groups are therefore present. Nevertheless it is difficult to interpret the observed stoichiometry of the $B(NH\text{-}NMe_2)_3\text{-}HCl$ reaction. This hydrazinoborane compares with tri(isopropylamino)borane, $B(NH\text{-}CHMe_2)_3$, which reacts with HCl in ether according to

$$B(NH\text{-}CHMe_2)_3 + 4\,HCl \rightarrow [Cl_2B(NH_2\text{-}CHMe_2)_2]Cl + Me_2CHNH_2 \cdot HCl \qquad (29)$$

If $B(NH\text{-}NMe_2)_3$ behaved analogously, and HCl adds to the Me_2N groups also, a consumption of 7 moles of HCl should be observed, but only 5 were consumed. Among the various possible explanations of this stoichiometry, the following can be discussed:



$$2\,B(NH\text{-}NMe_2)_3 + 10\,HCl \rightarrow \left[\begin{array}{ccccc} Me_2HN\text{-}NH_2 & & NH_2\text{-}NMe_2 & & NH_2\text{-}NHMe_2 \\ & B & & B & \\ Me_2HN\text{-}NH_2 & & NMe_2\text{-}NH_2 & & NH_2\text{-}NHMe_2 \end{array}\right] Cl_{10} \qquad (30)$$

The presence of HCl_2^- ions can also be discussed, but so far no evidence has been found for this assumption. The cleavage of the B-N bond in $Ph_2B\text{-}NH\text{-}NHPh$ by HCl is not surprising, because here HCl will attack at the B-N bond. Any further addition will initiate the cleavage. Presence of a polar solvent favors the cleavage reactions.

Disproportionation of various boranes is of increasing importance to the preparation of mixed boranes *(4, 12, 27)*, and the usefulness of this method has now been demonstrated with hydrazinoboranes. But it is surprising that the reaction of BCl_3 with $Pr_2B\text{-}NH\text{-}NMe_2$ or $B(NH\text{-}NMe_2)_3$ yields (dichloro)dimethylhydrazinoborane rather than the BCl_3 adduct, $Cl_2B\text{-}NH\text{-}NMe_2 \cdot BCl_3$. Steric hindrance would not exclude an addition of this type, suggesting that the compound is not a monomer, but a dimer or polymer.

Acknowledgment

It is a pleasure to thank E. Wiberg for encouraging the present investigation by stimulating discussions and the Institut für Anorganische Chemie as well as the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for generous financial support.

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Received May 20, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch017

Reaction of Nitric Oxide with Tri-n-butylborane

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch018

Nitric oxide reacts with tri-*n*-butylborane at room temperature to yield three major product which are believed to be R_2NOBR_2 (II), $R_2BN(OR)NO$ (III), and $R_2BNROBR_2$ (IV). Mild hydrolysis of IV yields R_2BOH and $RNHOBR_2$ (I), which is a cyclic dimer. A mechanism proposed for the reaction involves the formation of a *C*-nitroso and a *B*-nitroso compound, which react with R_3B to yield II and IV, respectively.

As part of a continuing study of the chemistry of nitric oxide, an interesting reaction between nitric oxide and tri-*n*-butylborane has been discovered, which takes place at room temperature and gives rise to some novel compounds containing boron, oxygen, and nitrogen. In this paper we describe these products and suggest a mechanism for their formation.

The reaction may be carried out either by stirring tri-*n*-butylborane in an atmosphere of nitric oxide in a closed system, or by bubbling nitric oxide through the liquid tri-*n*-butylborane. In either case care must be taken to remove nitrogen dioxide from the nitric oxide and to exclude air from the system. The reaction is over when there is no further pressure change or gas absorption. The reaction was allowed to run for several hours longer to ensure its completion. Analysis of the gas after reaction in a closed system revealed that there were no major gaseous products and that 0.8 mole of nitric oxide reacted with 1 mole of tri-*n*-butylborane. Two minor gaseous products were 1-butene and *n*-butane, which were formed in yields of 0.08 and 0.02 mole per mole of borane, respectively.

The crude reaction mixture was a pale yellow liquid, from which no pure product could be obtained by careful fractional distillation. Gas chromatography was also ineffective, because decomposition occurred under the conditions required to pass the material through the column. Evidence for the structure of the reaction products had to be obtained from subsequent chemical reactions of the original reaction product. The infrared spectrum (cell = 0.1 mm.) of the crude reaction mixture contained no bands at frequencies above 1500 cm.$^{-1}$ except for the saturated C-H bands, indicating the absence of significant amounts of hydroxyl- or carbonyl-containing substances.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch018

Dilution of the crude reaction mixture with an equal volume of cold methanol resulted in the rapid precipitation of a white solid. Acid hydrolysis of this solid yielded di-*n*-butylborinic acid and *N*-butylhydroxylamine. Reaction of di-*n*-butylborinic acid with *N*-butylhydroxylamine resulted in the rapid formation of crystalline solid which, on the basis of elementary analysis, mode of formation, and hydrolysis, is probably (*N*-*n*-butylamino-oxy)di-*n*-butylborane, R_2BONHR (I), where R = *n*-butyl. The similarity in the infrared spectra of the crystals obtained from the reaction mixture and of the synthetic crystals indicates that the former is also I. Analysis, by infrared, of the crude liquid reaction mixture before the addition of methanol indicates that 0.08 mole of I was obtained from 1 mole of R_3B. Much more I must have been formed by a chemical reaction between its precursor and methanol which occurs rapidly in the cold. This is discussed further below.

Acid hydrolysis of the crude reaction mixture yielded di-*n*-butylborinic acid and *N*,*N*-di-*n*-butylhydroxylamine. Esterification of di-*n*-butylborinic acid with *N*,*N*-di-*n*-butylhydroxylamine yielded a liquid product which on the basis of its elementary analysis, its mode of formation, and hydrolysis, is probably (*N*,*N*-di-*n*-butylamino-oxy)di-*n*-butylborane, R_2BONR_2 (II). From the relevant infrared spectra it is clear that the crude reaction mixture contains a substantial amount of II. After hydrolysis of 24 grams of the crude reaction product in aqueous acid the mixture contained two layers—the upper organic layer and the lower aqueous layer in which the basic hydrolysis products (6 grams) were soluble. Analysis of the basic hydrolysis products by vapor-phase chromatography showed that mono- and dibutylhydroxylamine were formed in the molar ratio of approximately 2 to 1 and that no other amines were present in significant amount. Steam distillation of the organic layer under nitrogen yielded two fractions. The more volatile fraction was di-*n*-butylborinic acid (14 grams), identified by its infrared spectrum and by conversion to a solid derivative with 8-quinolinol *(3)*. No significant amount of boronic acid was found, indicating that the borane is oxidized only to the borinate level of oxidation by nitric oxide. The less volatile fraction (4 grams) of the steam distillate was redistilled at reduced pressure through a spinning band column to yield a substance whose analysis and molecular weight indicate the empirical formula $R_3B(NO)_2$ (III). The structure of this compound is discussed further below. Comparison of the infrared spectrum of III with that of the crude reaction product indicates that III is a major reaction product.

Enough information to deduce the structure of the substance which yields R_2BONHR upon treatment with cold methanol is now at hand. The analytical data obtained in the hydrolysis experiments show a fairly good material balance for the sum of the two reactions: the reaction of tri-*n*-butylborane with nitric oxide followed by acid hydrolysis.

$$R_3B + 0.8\ NO \longrightarrow 0.13\ R_3B(NO)_2 + 0.15\ R_2NOBR_2 + IV \xrightarrow{H_2O} 0.3\ RNHOH$$

$$+ 0.15\ R_2NOH + 0.8\ R_2BOH + 0.13\ R_3B(NO)_2$$

Since, in the initial reaction mixture before hydrolysis, R_2NOH is present as R_2NOBR_2 and no free R_2BOH is present, the substance (IV) which gives rise to $RNHOBR_2$ on treatment with methanol must contain approximately (0.8-0.15)/0.3 or 2 boron atoms per nitrogen atom and must give rise to 2 moles of dibutylborinic acid upon acid hydrolysis. We formulate this substance as $R_2BNROBR_2$ (IV). Further evidence for the presence of easily hydrolyzable IV was obtained by shaking a dilute solution of the crude reaction mixture in CCl_4 under nitrogen for a few moments with water and then drying. This treatment resulted in the appearance of a very strong infrared band at 3627 cm.$^{-1}$, which is the O-H band of dialkylborinic acids in CCl_4 solution, and a somewhat weaker band at 3200 cm.$^{-1}$, which is the N-H band of $RNHOBR_2$. A similar experiment with a dilute solution of R_2BONR_2 also produced the band at 3627 cm.$^{-1}$ but of much lower intensity, showing that IV is much more readily hydrolyzable than II. The rapid solvolysis of IV is represented by the equation

$$R_2BNROBR_2 + R'OH \longrightarrow R_2BOR' + RNHOBR_2$$

where R' is H or methyl.

The reaction between tri-*n*-butylborane and nitric oxide can thus be represented by the equation

$$R_3B + 0.8\,NO \longrightarrow 0.13\,R_3B(NO)_2 + 0.15\,R_2BONR_2 + 0.3\,R_2BNROBR_2$$

which accounts for all of the major products.

Experimental

Addition of Nitric Oxide to Tri-*n*-butylborane. Nitric oxide, after passing through a column of Ascarite (sodium hydroxide on asbestos, Arthur H. Thomas Co., Philadelphia, Pa.), and a bubbler, was led into 120 grams of tri-*n*-butylborane (Callery Chemical Co., Callery, Pa.) contained in a three-necked flask equipped with a magnetic stirrer. The exit gases were passed through a bubbler and then through sodium hydroxide traps. The flask was cooled in a pan of water. The reaction is completed in two or three days, depending on the rate of stirring. The weight of the liquid after the reaction was approximately 127 grams.

The same reaction was carried out on a smaller scale in a 52-ml. vacuum line. Tri-*n*-butylborane (1.35 grams, 7.4 mmoles) was placed in a 333-ml. flask, which was attached to the line. The small amount of gas dissolved in the liquid was pumped off and NO was admitted. The organoborane absorbed 5.9 mmoles of NO and evolved 0.15 mmole of 1-butene. *n*-Butane and 1-butene were determined by gas chromatography, using a dimethylsulfolone column.

(*n*-Butylamino-oxy)di-*n*-butylborane (I). An equal volume of methanol was added to 127 grams of the cooled reaction mixture. White crystals, which formed, were filtered. The filtrate was repeatedly cooled and filtered in order to obtain additional product. The yield after crystallization from petroleum ether (b. p. 40-60° C.) ranged from 20 to 30 grams (m. p. 92-94° C.). Elemental analysis suggested that the crystals are impure R_2BONHR. Calculated for $C_{12}H_{28}BNO$: C, 66.36; N, 6.57; H, 13.15; B, 5.09. Found: C, 69.24; H, 13.10; N, 6.27; B, 5.40. Preparation of pure I is described below.

The crystals (2 grams) were hydrolyzed with 50 ml. of 10% hydrochloric acid by refluxing the solution for 1 hour under nitrogen, yielding 1 gram of a top layer. The top layer was treated with 1 gram of 8-quinolinol dissolved in 24 ml. of 95% ethanol, a method used by Douglass *(3)* for the preparation of solid derivatives of aralkylborinic acid. When the derivative did not precipitate out of solution, the solution was concentrated and cooled with dry ice. On cooling, crystals of the derivative came out of solution. The product was filtered (1.6 grams) and crystallized from cold 95% ethanol, yielding yellow crystals (m. p. 37-39°C.). (All melting points and boiling points are uncorrected.) The extinction coefficient of the derivative in CCl_4 at 415 mμ was 3100.

Analysis. Calculated for $C_{17}H_{24}BNO$: C, 75.85; H, 8.98; B, 4.02; N, 5.2. Found: C, 75.62; H, 9.24; B, 4.37; N, 5.21.

The hydrochloric acid solution was washed with ether to remove a small amount of *n*-butylboronic acid and made alkaline with concentrated sodium hydroxide solution under nitrogen, and a small amount of sodium diethyldithiocarbamate was added to prevent the decomposition of *N*-*n*-butylhydroxylamine formed *(4)*. The alkaline solution was extracted with ether. The ethereal solution was dried and concentrated, yielding 0.86 gram of slightly wet *N*-*n*-butylhydroxylamine crystals. The crystals were dissolved in ether and treated with oxalic acid dissolved in ether to yield the crystalline oxalate. The oxalate was recrystallized from ethanol (m. p. 138-39°).

Analysis. Calculated for $C_6H_{13}NO_5$: C, 40.21; H, 7.3; N, 7.7. Found: C, 40.19; H, 7.06; N, 7.54.

Di-*n*-butylborinic acid (0.74 gram) was added to 0.75 gram of *N*-*n*-butylhydroxylamine under N_2 and without the use of a solvent. White crystals formed around the flask and droplets of water were observed in the flask the following day. The crystals were washed with methanol, yielding 1.04 grams of dried crystals. The crystals were recrystallized from petroleum ether (m. p. 92-94°).

Analysis. Calculated for $C_{12}H_{28}BNO$ (213): C, 67.61; H, 13.28; B, 5.07; N, 6.57. Found: C, 67.64; H, 12.86; B, 5.57; N, 6.62. Molecular weight 404 (freezing point depression, benzene); 426, 403 (vapor pressure osomometer, manufactured by Mechrolab, Inc., 1062 Linda Vista Ave., Mountain View, Calif.).

***N*, *N*-Di-*n*-butylhydroxylamine.** The crude reaction mixture (4.08 grams) was hydrolyzed with 50 ml. of 20% hydrochloric acid solution under N_2. The top layer (2.58 grams) was treated with 8-quinolinol, yielding 2.85 grams of crude crystalline 8-quinolyl dibutylborinate.

The hydrochloric acid solution was washed with ether and made alkaline under N_2, and sodium diethyldithiocarbamate was added. Crystals came out of the alkaline solution. They were filtered, washed with cold water, dissolved in ether, and dried over sodium sulfate. The ethereal solution was concentrated to obtain the *N*, *N*-di-*n*-butylhydroxylamine crystals. Yield: 0.17 gram; [m. p. 51°; lit. *(2)* 52-53°]. An ether solution of the crystals was treated with oxalic acid to form the oxalate. The oxalate was recrystallized from ethanol [m. p. 142-43°; lit. *(2)* m. p. 144-45.5°].

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch018

Analysis. Calculated for $C_{10}H_{21}NO_5$: C, 51.04; H, 8.95; N, 5.95. Found: C, 50.68; H, 8.42; N, 6.10.) (Elemental analyses were performed on this compound, because confusion arose from the isolation of the two hydroxylamines.)

Ratio of *N*-*n*-Butylhydroxylamine and *N*, *N*-Di-*n*-butylhydroxylamine Obtained from Reaction Mixture. The hydrochloric acid solution from the hydrolysis of 2 grams of the reaction mixture was extracted with ether to remove small amounts of *n*-butylboronic acid. The HCl solution was made alkaline, treated with sodium diethyldithiocarbamate, and extracted with ether. The ethereal solution was concentrated to yield a mixture of the two hydroxylamines. The hydroxylamines were analyzed by gas chromatography using a Theed column (Fisher Scientific Co., Fair Lawn, N. J.). The mole ratio between *N*-*n*-butylhydroxylamine and *N*, *N*-di-*n*-butylhydroxylamine was 2 to 1.

(*N*-Nitroso-*N*-butoxyamino)dibutylborane, $R_2BN(OR)N{=}O$ (III). The crude reaction mixture (2 grams) was placed in a three-necked, round-bottomed flask, equipped with a simple distillation head and condenser, and 50 ml. of 10% HCl solution was added. With a slow flow of N_2 through the apparatus, the flask was heated to hydrolyze the top layer. The contents were then distilled into a 50-ml. separatory funnel. At first, di-*n*-butylborinic acid and water distilled off. Then, the appearance of the distillate changed and the second fraction was collected in another separatory funnel. The combined second fractions from 12 such experiments were exposed to air for several hours to convert any borinic acid to boronic acid and washed with aqueous mannitol solution. The washed fraction (3.7 grams) was distilled on a spinning band column (Nester and Faust, 2401 Ogletown Road, Newark, Del.). The fraction (0.3 gram) boiling at 84° at 2.5 mm. analyzed for (*N*-nitroso-*N*-butoxyamine)-di-*n*-butylborane.

Analysis. Calculated for $C_{12}H_{27}BN_2O_2$: C, 59.50; H, 11.16; N, 11 57; B, 4.46; molecular weight, 242. Found: C, 59 49; H, 10.92; N, 11.47; B, 6.01; molecular weight, 277 ± 10.

The extinction coefficient of the compound was 1020 at 293 mμ in CCl_4 and 5000 at 228 mμ in methanol.

Hydrolysis of III. One-half gram (2 mmoles) of III was refluxed in 10 ml. of concentrated sulfuric acid and 20 ml. of water in a nitrogen atmosphere for 3 hours. The material which collected in a liquid nitrogen trap was found to contain 1.9 mmoles of nitrous oxide and a mixture of *cis*- and *trans*-butene and 1-butene (1.3 mmoles).

Reaction between Tri-*n*-butylborane and Nitrosobenzene. Nitrosobenzene (1 gram) dissolved in benzene was added dropwise to 1.7 grams of tri-*n*-butylborane in benzene. The reaction mixture warms slightly during the addition of the nitrosobenzene. The mixture, amber in color, was allowed to stand overnight. Then the benzene was removed under vacuum, yielding a solid residue; the infrared spectra of the residue did not show any NH band of aniline. Methanol was added to the residue but was pumped off when the residue dissolved in methanol.

The residue was hydrolyzed with 50 ml. of water containing 1 ml. of concentrated H_2SO_4 and the volatile matter was distilled off with water. Two fractions were collected. The first fraction (0.2 gram) was mainly di-*n*-butylborinic acid. The second fraction (0.1 gram) contained azoxybenzene. The aqueous material in the flask was filtered and extracted with ether. The ether solution was concentrated to yield 0.09 gram of *n*-butylboronic acid.

The aqueous portion was neutralized with KOH. The alkaline solution was filtered and extracted with ether. The ethereal solution was concentrated to yield 0.22 gram of residue, which was mainly aniline. After the removal of aniline from the alkaline solution, the solution was acidified. A dark-colored precipitate came out of solution. It was not identified.

Reaction of Tri-*n*-butylborane with *n*-Butyl Nitrite. To 7.3 grams (0.04 mole) of tri-*n*-butylborane, cooled in an ice bath, were added dropwise with stirring 2.0 grams (0.02 mole) of *n*-butyl nitrite in a slow stream of nitrogen. About 10 minutes after the addition there was a sudden rapid evolution of heat and gas which blew the apparatus apart momentarily at the joint between the reaction flask and the liquid nitrogen trap and also blew some of the liquid reaction mixture into the tubing connecting the two. The reaction mixture was allowed to come to room temperature, and stirred 2 hours. 1-Butene was found in the liquid nitrogen trap. After hydrolysis by refluxing with 10% hydrochloric acid, the upper layer of dibutylborinic acid was removed, and the aqueous acid layer was worked up in the manner described under hydrolysis of tributylborane-nitric oxide reaction product. Analysis by vapor phase chromatography showed the presence of *N*-*n*-butylhydroxylamine and *N*,*N*-di-*n*-butylhydroxylamine.

Discussion of Reaction Products

Since each of the three major reaction products represents a new type of boron-nitrogen compound, a brief discussion of their properties seems in order. Little can be said about $R_2BNROBR_2$, since we were not able to isolate it from the reaction mixture, nor to synthesize it independently. However, its existence seems to be required to account for the products formed upon methanolysis and hydrolysis.

The NMR spectrum of III has a triplet at $\delta = 4.2$, referred to $(CH_3)_4Si$, indicating the presence of a butyl group on oxygen. There are no bands in the region $\delta = 2.5$, which is characteristic of butyl on nitrogen; hence there are no *N*-butyl groups. Integration of the peaks shows that the ratio of protons on carbon adjacent to oxygen to the remaining protons is 2 to 28. This is compatible with a structure having two butyl groups on boron and one on oxygen, whose ratio would be 2 to 25. The proposed structure for III is

$$R_2B\text{-}N(OR)\text{-}N{=}O$$

Although III is not hydrolyzed by boiling in dilute hydrochloric acid, it was successfully hydrolyzed by prolonged refluxing (3 hours) in a solution of 1 part of sulfuric acid to 2 parts of water (vol./vol.) to give an approximately quantitative yield of nitrous oxide and a substantial amount of butenes

$$R_2B\text{-}(OR)\text{-}N{=}O + H_2O \xrightarrow{\text{acid}} N_2O + R_2BOH + ROH$$

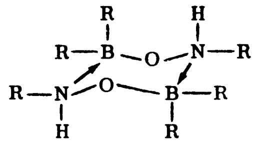
$$ROH \xrightarrow{\text{acid}} H_2O + \text{butenes}$$

The butenes were formed by the isomerization and dehydration of the butanol during the heating in strong acid. The liquid hydrolyzate was inadvertently exposed to air overnight before analysis and therefore showed the presence of *n*-butylboronic acid rather than the borinic acid required by the above equation.

The (*N*-*n*-butylamino-oxy)di-*n*-butylboranes, described in detail elsewhere, are a new and interesting class of compounds. In view of their facile formation from and hydrolysis to di-*n*-butylborinic acid and *N*-butylhydroxylamines, we can be confident of their structures. Synthetic II prepared by the esterification of *N*,*N*-di-*n*-butylhydroxylamine with di-*n*-butylborinic acid was not absolutely pure, being contaminated with a small amount of di-*n*-butylborinic acid, as evidenced by a weak OH band at 3627 cm.$^{-1}$ Molecular weight in benzene of a 0.05 *M* solution at 35° shows that it is monomeric (calculated for R_2NOBR_2: 269; found: 230 + 20). Crystalline I on the other hand was found to be dimeric, at 35° [calculated for $(RNHOBR_2)_2$: 426; found: 415 ± 20]. The dimer must be either acyclic or cyclic, as illustrated below. The acyclic structure should have two N-H stretching bands in dilute solution, one due to the tricoordinated N at 3400 to 3500 cm.$^{-1}$ and one due to the tetracoordinated N at about 3200 cm.$^{-1}$ In the cyclic structure both nitrogens are tetracoordinated. Our compound in fact has only one N-H band in dilute CCl_4 solution and it is found at 3200 cm.$^{-1}$; hence we believe that it has the cyclic structure.

$RNHOBR_2 - NHROBR_2$

Acyclic I



Cyclic I

The inability of R_2NOBR_2 to form a cyclic structure and hence to dimerize can now be explained on the basis of steric hindrance. In the case of $(RNHOBR_2)_2$ there are two axial butyl groups; one is above and the other is below the ring, so there are no axial-axial interactions between two butyl groups. If R_2NOBR_2 had a cyclic structure, there would be four axial butyl groups: two above and two below the ring. Hence there would be two axial-axial interactions between butyl groups. It is felt that these steric interactions prevent the formation of the cyclic dimer in the case of R_2NOBR_2.

Reaction Mechanism. A reasonable mechanism by which the observed products are formed is given in the following series of steps:

$$R_3B + NO \longrightarrow R_3BNO \qquad (1)$$

$$R_3BNO \longrightarrow R_2BNOR \qquad (2a)$$

$$R_2BNOR + NO \longrightarrow R_2BN(OR)N{=}O \qquad (3a)$$

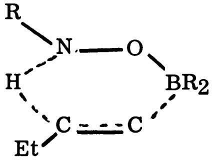
$$R_3BNO + NO \longrightarrow RNO + R_2BNO \qquad (2)$$

$$R_2BNO + R_3B \longrightarrow R_2BNROBR_2 \qquad (3)$$

$$RNO + R_3B \longrightarrow [RNOBR_3] \longrightarrow R_2NOBR_2 \qquad (4)$$

$$\longrightarrow RNHOBR_2 + C_4H_8$$

The initial adduct formed in step 1 is a free radical which either rearranges (2a) and then reacts with NO to form III, or reacts with nitric oxide before rearranging to yield a *C*-nitroso and a *B*-nitroso compound (step 2). Each of these reacts with an R_3B to yield the hydroxylamine derivatives II and IV (steps 3 and 4). To account for the 1-butene and $RNHOBR_2$ which are formed in small but equivalent yield, it is suggested that the intermediate formed in step 4 reacts in two ways: migration of a butyl group from boron to nitrogen to yield the major product (II), and intramolecular hydrogen transfer from carbon to nitrogen to yield the minor product, 1-butene and I.



To demonstrate the validity of the proposed mechanism it is necessary to show that tri-*n*-butylborane reacts with nitroso compounds to give the type of compound described. We shall report the results of such studies elsewhere. Nitrosobenzene reacts vigorously with tri-*n*-butylborane and after hydrolysis of the reaction mixture yields di-*n*-butylborinic acid, in agreement with the proposed mechanism. The amine fraction contained a mixture including aniline and azoxybenzene. Although the reaction with nitrosobenzene differs in detail from the reaction predicted for nitrosobutane, this difference is not surprising in view of the tendency of aromatic nitroso compounds to produce a variety of products in oxidation-reduction reactions.

n-Butyl nitrite was also found to react at room temperature with tri-*n*-butylborane to yield, after hydrolysis, R_2BOH, ROH, RNHOH, 1-butene, and R_2NOH. The first step in this reaction appears to be

$$RONO + R_3B \longrightarrow R_2BOR + RNO$$

The nitroso compound then reacts with additional tri-*n*-butylborane to yield I, II, and 1-butene. Thus the proposed mechanism is consistent with a number of observations. [After this paper was submitted for publication an abstract of a paper on the reaction between triethylborane and nitric oxide by Brois *(1)* came to our attention. We are in complete agreement with Brois on the structure of products II, III, and IV, although Brois does not mention I. We are in disagreement with his mechanism.]

Acknowledgment

We are indebted to Norman S. Bhacca, Varian Associates, for obtaining and interpreting the NMR spectrum of III. We are also indebted to Roger Bowman of this laboratory for some of the molecular weight determinations and infrared spectra, and to Arthur Garrison of Clemson College, who did some of the early experiments. Elemental

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch018

microanalyses were performed by C. Tiedcke, Laboratory of Microchemistry, Teaneck, N. J.

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Received May 22, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch018

19

Amination of Borate Esters with Diamines

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch019

Alkoxyboranes can be aminated with amines and diamines at moderate temperatures. To facilitate this aminolysis with aromatic diamines of high molecular weight, a solvent was found necessary for certain alkoxyboranes that otherwise formed two-phase systems with the diamines and did not react. Linear polymers were produced from dialkoxyborane and diamines, while highly cross-linked polymers were produced when trialkoxyboranes and diamines reacted.

Aminoboranes and other boron-nitrogen bonded compounds are readily solvolyzed in alcohols of low molecular weight, at least up to C_4. In such reactions, the boron-nitrogen bond is replaced by a boron-oxygen bond and the corresponding amine is liberated in the forward reaction:

$$>BNHR + R'OH \rightleftarrows >BOR' + RNH_2 \qquad (1)$$

Under special conditions, the converse reaction, amination of borate esters, proceeds easily. While earlier reports *(4, 5, 7, 9)* suggested that the amination is difficult, Letsinger and Hamilton *(10)* and Brotherton and Steinberg *(3)* have shown that the reaction is driven toward amination when the boron-containing species can enter into five-membered ring formation with *o*-phenylenediamine, but is more difficult with aniline and *p*-phenylenediamine. Another factor, removal of the alcohol from the reaction mixture, was recognized by Mikhailov and Aronovich *(12)*, who reported the rates of alcohol removal and, by inference, their dependence upon the base strengths of the amines. In some cases the aminations were 90% complete.

A tentative series of reactivities for the ability toward displacement of various groups has been proposed *(1, 13, 14)*, subject to polar, steric, and volatility factors:

$$-OR > -NH_2 \geq -N_2H_3 \geq -NHNR_2 > -NHR > -NR_2$$

in the conversion of *B*-triaminoborazines to *B*-trialkoxyborazines by treatment with alcohols and in their transaminations with amines.

The reversal of at least part of this order was further confirmed during the present investigation, and the influence of the volatility fac-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch019

tor was observed. Although Brotherton and Steinberg did not report the nature of the product from the reaction of triisopropoxyborane and *p*-phenylenediamine, it could be inferred that a polymer formed. In this investigation we have examined the reaction of diamines with both trialkoxyboranes and dialkoxyboranes and made a brief investigation of the polymers formed. During the work it was found that the solvent, xylene, was effective in reversing the direction of Reaction 1, since it eliminated immiscibility of the reactants. Other similar solvents could undoubtedly be used.

Experimental

Materials. Trimethoxyborane (Callery Chemical Corp.) was distilled (b.p. 67° C.) before use. Triisobutoxyborane was prepared from BCl_3 and isobutyl alcohol. Distillation yielded a fraction boiling at 207° C. with an index of refraction, n_D^{20}, 1.4037 (lit. 1.4029). Phenyldiisobutoxyborane was prepared from phenylboronic acid, $PhB(OH)_2$ (American Potash and Chemical Corp.), and isobutyl alcohol by the azeotropic removal of water. Anal. Calcd.: B, 4.62. Found: B, 4.53, 4.52; n_D^{20} 1.4705 [lit. *(2)* 1.4711].

The amines were commercially available and were recrystallized and dried whenever a technical grade material was used.

Apparatus. The driving force for the amination reactions was the rapid removal of the alcohol. This was conveniently done by continuous distillation with a fractional distillation column of about 30 theoretical plates equipped for total reflux and controlled take-off. An alkoxyborane was first fractionated in such a column, then the same column was used to separate the reaction products from an amine and the same alkoxyborane. The still pot served as a reaction vessel. The boranes were handled with hypodermic syringes to assure minimum contact with moisture. High vacuum techniques were used for some of the separations and sampling operations. All the equipment was purged with either dry air or nitrogen.

Procedure 1. Trimethoxyborane and *p,p'*-Methylenedianiline. Trimethoxyborane (53.9 mmoles) was added to 21.8 mmoles of *p,p'*-methylenedianiline (Dow Chemical Co.). The temperature was raised to 67° and $(CH_3O)_3B$ was observed to reflux. The reflux temperature gradually dropped to that of the boiling point of the methanol-trimethoxyborane azeotrope [b.p. 53.2°; 76.2% $(MeO)_3B$; lit. b.p. 54.6°; 68% $(MeO)_3B$]. The azeotrope was removed over a period of 22 hours. Occasionally, a period at total reflux was necessary to build up the azeotrope concentration in the head of the column after the removal of some of the azeotrope. After no additional azeotrope was observed, 17.9 mmoles of trimethoxyborane was removed through the distillation column. The pot residue was a hard opaque material which did not soften at 230°, but only when it was heated in a Meker burner flame. On exposure to air, *p,p'*-methylenedianiline formed on its surface and was identified by a mixed melting point with the starting material (m.p. 89-93°; lit. m. p. 89.5°). Anal. Calcd. for 1 to 1 polymeric product: B, 4.54; diamine, 82.9. Found: B, 2.47; diamine, 83.2. The diamine was weighed as free amine after alkaline hydrolysis of a sample of the polymer and isolation and drying of the diamine.

Procedure 2. Trimethoxyborane and Aniline. A mixture of 98.8 mmoles of aniline and 98.8 mmoles of trimethoxyborane was refluxed for 21 hours at 68° ; the reactants were completely miscible. No change in the reflux temperature was observed.

Procedure 3. Triisobutoxyborane, $(C_4H_9O)_3B$, and *p, p'*-Methylenedianiline. When 48.2 mmoles of *p, p'*-methylenedianiline was added to 46.0 mmoles of $(C_4H_9O)_3B$ and heated for 8 hours at the reflux temperature of the borane, 207°, no drop in the reflux temperature was observed. Two phases were noted in the still pot, the lower layer being the diamine. Vigorous stirring did not promote reaction.

Procedure 4. Triisobutoxyborane and *p, p'*-Methylenedianiline in Xylene. Commercial (mixed) xylene (20 ml., b. p. 137-40° ; n_D^{20} 1.495-1.505) which had been dried over sodium was added to the reactants in Procedure 3. At 140°, the reflux temperature, the borane and diamine were miscible with stirring. The reflux temperature slowly dropped from 136° to 105-06° (b.p. isobutyl alcohol, 106-08°) in 1 hour. Over a period of 32 hours, 63.4 mmoles of isobutyl alcohol was removed (n_D^{20} 1.4102; lit. 1.3958). At the end of the time period, butanol evolution ceased. Some of the isobutyl alcohol was recovered from the redistillation of the xylene. Unreacted triisobutoxyborane [Anal. Calcd. B, 4.70. Found: B, 4.12; n_D^{20} 1.4065 (lit. 1.4029)] was recovered from the reaction pot by distillation. The difference in weight between the starting diamine and the polymeric residue was equivalent to a weight gain of 55.8 grams per mole of borate ester consumed. It would be expected for a 1 to 1 linear polymer that a $C_4H_9OB<$ group would be attached to each diamine and that the weight gain would be theoretically 83.9 grams per mole of borate ester consumed. The weight gain for total amination and thereby cross linking would be 10.8 grams per mole of borate ester consumed.

The polymeric residue was opaque, hard, and brittle. An odor of isobutyl alcohol persisted over the solid. It did not soften at 230° but on heating in a Meker burner flame it became fluid. The product lacked hydrolytic stability, releasing the diamine at the exposed surface.

Procedure 5. Triisobutoxyborane and *p*-Toluidine in Xylene. To 20 ml. of xylene were added 48.7 mmoles of *p*-toluidine and 40.6 mmoles of triisobutoxyborane. After 21.2 mmoles of isobutyl alcohol was collected over a 24-hour period, the reaction slowed down to the point that an additional 16 hours of heating gave but a few drops more of the alcohol. An additional 101.1 mmoles of *p*-toluidine was added and the mixture heated for 83 hours at 140°. A total of 88.2 mmoles of isobutyl alcohol was collected with some loss during collection over the total of 123 hours. Three cuts of the xylene-isobutyl alcohol mixture were taken over the total time period. Each cut was weighed and the per cent xylene in each cut was determined by gas-liquid chromatography. Tris-*p*-toluidinoborane crystallized from the xylene in the still pot in a crude yield of 88.7%. Recrystallization from benzene gave well defined crystals [m.p. 165° ; lit *(8)*, 165-66°]. Anal.: Calcd. $(CH_3C_6H_4NH)_3B$, 3.29. Found: B, 3.84, 3.35. Unreacted *p*-toluidine (25.3 mmoles) was recovered [m.p. 45 (lit. 45°)].

The data from Procedures 1 to 5 are summarized in Table I.

Procedure 6. Phenyldiisobutoxyborane and Diamines in Xylene (Table II). *p, p'*-Methylenedianiline. The 48.9 mmoles of the diamine

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch019

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and 57.3 mmoles of $PhB(C_4H_9O)_2$ were mixed with 17.4 grams of xylene and heated to 140°. The isobutyl alcohol-xylene mixture was collected in three fractions during the 27-hour reaction time. The per cent xylene was determined in each. A total of 97.5 mmoles of isobutyl alcohol was collected. Theoretical for the 48.9 mmoles of diamine used was 97.8 mmoles. Unreacted borane, $PhB(OC_4H_9)_2$, was recovered (6.8 mmoles) from the reaction product. Filaments could be drawn from the residue at 70°.

The polymeric residue became fluid at about 110° and on further heating up to 320° under reduced pressure it lost a clear liquid containing boron value and during heating became more viscous. The cooled residue after vacuum treatment now became fluid at 190° at atmospheric pressure under nitrogen. Filaments could be pulled from the soft mass. At room temperature they were flexible, but hydrolyzed in air after 1 hour.

N,N-Diphenyl-*p*-phenylenediamine. To 20 ml. of xylene were added 50.7 mmoles of the diamine (Naugatuck Chemical Division, U. S. Rubber Co.) and 51.0 mmoles of $PhB(OC_4H_9)_2$. A single xylene-isobutyl alcohol cut, collected over the 165-hour reaction time, contained 87.1 mmoles of isobutyl alcohol. After reduced pressure heating, the product resembled pitch and filaments could be pulled from the softened material. The product lacked hydrolytic stability. Unreacted phenyldiisobutoxyborane was recovered from the reaction (0.9 mmole). When 16.5 mmoles of the diamine and 28.1 mmoles of $PhB(OC_4H_9)_2$ were sealed in a borosilicate glass tube and heated to 300° for 30 hours, no change was observed in the physical appearance of the diamine.

Piperazine. Recrystallized piperazine (Union Carbide Chemical Corp., 55.8 mmoles) reacted with 53.0 mmoles of $PhB(OC_4H_9)_2$ in 20 ml. of xylene at 140°. Isobutyl alcohol was observed during the 30-hour run by a drop in reflux temperature to 108°. Some piperazine was carried over (b.p. 145°) by the xylene. The product had a crystalline appearance and had no polymeric properties.

N,N'-Diphenylethylenediamine. The 50 mmoles of $PhB(OC_4H_9)_2$ in 25 ml. of xylene was added dropwise to 51.8 mmoles of the diamine (Distillation Products Industries) in 28 ml. of xylene which was heated to 140°. The reflux temperature did not drop during the addition and only after all of the borane had been added did the temperature drop to 108° C., indicating isobutyl alcohol was being evolved. The amount released could not be determined because of solvent loss. The solid, after vacuum treatment and heating, cooled to a definite crystalline habit and had no polymeric properties.

p-Toluidine. To 20 ml. of xylene were added 25.8 mmoles of $PhB(OC_4H_9)_2$ and 56.0 mmoles of toluidine (Distillation Products Industries). The reaction was heated to 140° and an isobutyl alcohol-xylene mixture was found to contain 47.6 mmoles of isobutyl alcohol, or 92% of the theoretical.

Discussion

This work has in general confirmed the findings of Mikhailov and Aronovich *(12)* and Brotherton and Steinberg *(3)*. They, with others

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Table I. Reactions

Amine	*Amine, Mmoles*	*$(RO)_3B$, Mmoles*	*Reaction Temp., °C.*
p, p′-Methylenedianiline	21.8	$R=CH_3$- 53.9	67.2
Aniline	98.8	$R=CH_3$- 98.8	67.2
p, p′-Methylenedianiline	48.2	$R=C_4H_9$- 46.0	207
p, p′-Methylenedianiline	48.2	$R=C_4H_9$- 46.0	140
p -Toluidine	149.8[b]	$R=C_4H_9$- 40.6	140

[a] Part of $(MeO)_3B$ recovered as azeotrope with MeOH produced.

[b] With 48.7 mmoles toluidine, reaction ceased after 40 hours and 101.1 mmoles added.

Part of butanol lost during collection.

Table II. Reactions of
(Xylene

Amine	*Amine, Mmoles*	*$PhB(OC_4H_9)_2$, MMoles*	*Reaction Temp. °C.*
p, p′-Methylenedianiline	48.9	57.3	140
N, N′-Diphenyl-*p* -phenylenediamine	50.7	51.0	140
Piperazine	55.8	53.0	140
N, N′-Diphenylethylenediamine	51.8	50.0	140

(6, 10, 11, 15), have successfully aminated borate esters, reversing the reported trend of displacement *(1, 13, 14)*. They did not, however, report on polymeric products that may have been formed from the reactions of diamines with trialkoxyboranes and with phenyldialkoxyboranes. The reactions reported here are extended to other diamines and to the polymeric products formed from difunctional and trifunctional boranes.

Mikhailov and Aronovich aminated the isobutoxy esters of boric acid and its aryl derivatives with aromatic monoamines of moderate molecular weight in the presence of excess amine and at the boiling point of the amine. The reaction temperatures they reported ranged of $(RO)_3B$ with Amines

Solvent	*Time, Hours*	*ROH, Mmoles*	*Recovered $(RO)_3B$, Mmoles*	*Remarks*
None	22	23.8	41.7[a]	Polymer, highly cross-linked, >230° softening point
None	21	None	—	No azeotrope formed
None	8	None	—	No butyl alcohol, 2 phases present
Xylene	32	63.4	17.1	Polymer, highly cross-linked, >230° softening point
Xylene	123	88.2[c]	—	36.0 mmoles $B(NHC_6H_9CH_3)_3$ and 25.3 mmoles toluidine recovered

$PhB(O\text{-}i\text{-}C_4H_9)_2$ with Diamines solution)

Time, Hours	*Iso-C_4H_9OH, Mmoles*	*Recovered $PB(OC_4H_9)_2$, Mmoles*	*Remarks*
27	97.5	6.8	Polymer, m.p. ~190°
165	87.1	0.9	Pitchlike polymer
30	Obsd.	—	Piperazine carried over; residue crystalline
22	Obsd.	—	Liquid residue, crystallized at 25°

from 210° to 250°. At these temperatures, it must be assumed that the borate esters and the amines were miscible. In a specific case, triisobutoxyborane reacted with *p*-toluidine (b.p. 200°) to yield isobutyl alcohol within an 8-hour reaction time, and in our laboratories, these were found to be miscible. In our work, however, *p, p'*-methylenedianiline and triisobutoxyborane were immiscible at or above 207° (the boiling point of the ester) and after 8 hours no butanol was isolated even with stirring. The base strength and steric requirements of *p*-toluidine would not be expected to be much different than those of *p, p'*-methylenedianiline. The only difference in their reactivity appears to be the lack

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of miscibility of the high molecular weight diamine with the borate ester. At 25° and 300° C., *N,N'*-diphenyl-*p*-phenylenediamine was found to be immiscible with phenyldiisobutoxyborane in a sealed borosilicate glass tube.

In each of the above cases, when the solvent, xylene, was added to the reaction mixture, the reactants were miscible, and isobutyl alcohol was released at 140°. The amination reaction took place slowly and the steric and base strength effects of the diamines were evident from the rate of isobutyl alcohol removal (Tables I and II), and in accord with the literature *(12)*. When *p,p'*-methylenedianiline reacted with trimethoxyborane, no solvent was needed, since the two were miscible and they reacted at the reflux temperature of the borane (67°).

Xylene as a reaction medium was used by Brotherton and Steinberg *(3)* in their amination of triisopropoxyborane with aniline. The effect of the type of solvent used was illustrated when only a slow reaction occurred between *p*-phenylenediamine and triisopropoxyborane in xylene, but when bis(2-ethoxyethyl) ether (b.p. 187-89°) was used as a solvent, the same reactants yielded isopropyl alcohol more readily, perhaps because of the higher temperature of the reaction. They did not mention whether the reaction failed without a solvent. Although not described, the product of the diamine-triisopropoxyborane reaction may have been a cross-linked polymer, on the basis of our results (Table I).

The polymeric materials from *p,p'*-methylenedianiline and triisobutoxyborane or trimethoxyborane were probably cross-linked because of the trifunctionality of the borate esters. Evidence for the formation of a three-dimensional network was in part based on the physical properties of the products. They were hard, hornlike substances that softened only at temperatures greater than 230°. Filaments could not be pulled from the softened material, indicating a lack of linearity in the product. Further evidence was obtained from the stoichiometry of the borate ester consumed in the diamine reaction. The 28.9 mmoles of triisobutoxyborane that reacted was equivalent to 86.7 mmoles of butoxy groups attached to the boron and the 48.2 mmoles of diamine, in turn, was equivalent to 96.4 mmoles of amine groups.. The 63.4 mmoles of isobutyl alcohol recovered from the reaction was 73% of the amount expected for complete amination. Although the reactants were present in a 1 to 1 mole ratio at the beginning of the reaction, the diamine reacted to eliminate a majority of all of the butoxy groups on a given boron and triisobutoxyborane was recovered from the reaction. That all of the butoxy groups could be eliminated was in part confirmed when the totally aminated borane, tri-*p*-toluidinoborane, was prepared from *p*-toluidine and triisobutoxyborane in xylene at 140°. An excess of amine was necessary for the 88.7% yield obtained.

In the case of trimethoxyborane, the borate ester was in excess at the beginning of the reaction (53.9 to 21.8 mmoles). Trimethoxyborane was recovered from the reaction partly as the azeotrope with methanol during the reaction and, after the reaction appeared to cease, as the pure material. The 12.2 mmoles of trimethoxyborane consumed was equivalent to 36.6 mmoles of methoxy groups, while the diamine was equivalent to 43.6 mmoles of amine groups. The diamine, being functionally in excess, may thus have totally aminated all of the borate ester that was consumed and thereby led to the formation of the cross-linked polymer. The methanol recovered was 65% of the theoretical expected from total amination.

When the difunctional phenyldiisobutoxyborane reacted with *p,p'*-methylenedianiline, the reaction proceeded faster than with triisobutoxyborane and the amination was complete on the basis of the isobutyl alcohol recovered. This faster rate of amination is in agreement with the findings of Mikhailov *(12)*. The polymer that formed was not cross-linked and the filaments could be drawn from the heat-softened material. From this, it appears that at this temperature only one hydrogen of each amine group has reacted with borate ester. With *N,N'*-diphenyl-*p*-phenylenediamine, the isobutyl alcohol evolution was much slower, possibly because of the base strength and steric effects of the secondary amine. This trend was also observed by Mikhailov *(12)*. The polymeric product was likewise linear, since filaments could be drawn from the heat-softened material. The solid products from the reaction of phenyldiisobutoxyborane with piperazine or *N,N'*-diphenylethylenediamine did not have polymeric properties. Five-membered borole ring formation cannot be ruled out in either case and may account for the crystalline appearance of the products.

As pointed out by Mikhailov and Aronovich, heating an aminoborane, such as phenyldi-*p*-tolylaminoborane, to 260° to 270° will cause borazine formation by deamination. At the temperatures at which the aminated products were formed in their work, this side reaction cannot be ruled out, although it was minimized in our work by the lower amination temperatures possible in a solvent, as illustrated by the high yield of tritoluidinoborane obtained in this work.

Although trimethoxyborane reacted with *p,p'*-methylenedianiline in 22 hours without a solvent, aniline did not react under the same conditions in 21 hours. Jones and Kinney *(7)* also found that triethoxyborane did not react with aniline. However, Brotherton and Steinberg *(3)* reported that in the presence of xylene, triisoproxyborane reacted slowly with aniline to form trianilinoborane, while Mikhailov and Aronovich *(12)* found that a solvent was not necessary to aminate triisobutoxyborane with aniline at 184° to form triianilinoborane. The differences in the reactivities of the different types of borate esters with aniline are outside the scope of this investigation and a subject of another investigation.

All of the polymeric materials produced in this work could be heated in nitrogen to 320° without charring; however, they all lacked hydrolytic stability in air.

In the amination of trimethoxyborane, triisobutoxyborane, and phenyldiisobutoxyborane, we have relied on the higher volatility of methanol and isobutyl alcohol. Their removal from the reaction mixture which contained the less volatile borate esters, amine or diamine, and the boron-nitrogen compound made it possible for the aminolysis reaction to proceed. If the amine was volatile, the reaction was only partially effective, as shown by piperazine (b.p. 145). The amination did not occur unless there was an intimate contact between the borane and the amine, which was accomplished by xylene. Other solvents may be even

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch019

more effective. For the total amination of a borate ester, an excess of the amine appears to be necessary.

Acknowledgment

The authors are indebted to Z. Nagy and R. Pfost for assistance in the gas chromatographic analyses.

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Received May 16, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch019

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch020

20

Some Reactions of Dialkylaminoborons

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Consideration of the established hydroboration, chloroboration, and phenylboration reactions prompted attempts to extend this concept to aminoboration. Although addition to ethylenic bonds did not occur, addition to organic isocyanates and isothiocyanates gave the expected boroureas. When applied to boron isocyanates and isothiocyanates, however, disproportionations involving the boron substituents prevailed in good yield. Ultimately by such disproportions examples of the novel PhB(NR_2)NCX series of compounds were prepared.

Three types of reactions involving the addition of borine and its derivatives to carbon-carbon unsaturation had been described when this research was undertaken: the well-known hydroboration reaction and the recently reported instances of chloroboration and phenylboration *(3)*. With the hope that the scope of these reactions could be broadened to include aminoboration, the reactions of tris(dimethylamino)boron and bis(dimethylamino)phenylboron with several olefins were attempted. Like boron trichloride and phenylboron dichloride, these aminoborons induced the polymerization of cyclohexene but, unlike the chlorides, did not add to norbornadiene.

Concurrently, the reaction of these aminoborons with phenylisocyanate was attempted, since here a 1, 2 addition could also be expected. In these instances exothermic reactions occurred to give the expected boroureas in good yield according to the following reaction:

$$3\ C_6H_5NCX + B\left[N(CH_3)_2\right]_3 \longrightarrow B\left[C_6H_5NCXN(CH_3)_2\right]_3 \qquad (1)$$

I

a. X = O

b. X = S

These reactions were extended to include the use of phenylisothiocyanate to give the corresponding borothioureas. The similar tetrakis(dimethylamino)diboron readily added 4 moles of phenylisocyanate or phenylisothiocyanate.

To prove that the addition proceeded as shown in Reaction 1 and not in the reverse manner, the trisborourea (Ia) was subjected to ethanolysis, which readily occurred, giving triethylborate and phenyldimethylurea in quantitative yield. The corresponding thiourea was more resistant to alcoholysis and required refluxing in aqueous dioxane to give phenyldimethylthiourea and benzeneboronic acid.

At this time, Beyer, Niedenzu, and Dawson *(1)* reported identical observations in the cases of bis(dimethylamino)phenylboron and tetrakis(dimethylamino)diboron and also established the stepwise reaction of the aminoboron groups. Lappert advised the authors of his successful application of the chloroboration and phenylboration reactions in the isocyanate system *(4)*. Consequently, effort in this area was stopped, although the reaction of bis(dimethylamino)phenylboron with toluene diisocyanate or hexamethylene diisocyanate apparently gave the expected polyboroureas. The reaction was extended to include diethylaminoborons and substituted arylisocyanates by Reaction 2.

$$\mathrm{PhB}\left[\mathrm{N(C_2H_5)_2}\right]_2 + 2\,\mathrm{ArNCO} \longrightarrow \mathrm{PhB}\left[\mathrm{NArCON(C_2H_5)_2}\right]_2 \qquad (2)$$

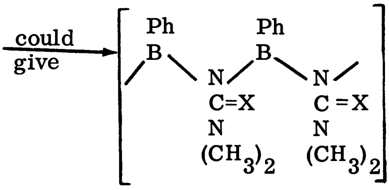
II

a. Ar = *o*-tolyl

b. Ar = phenyl

If this type of aminoboration could be properly applied to boron isocyanates or boron isothiocyanates, a linear polymer having a B-N backbone could result. This would be an opportunity to arrive at such a linear B-N polymer by a route that does not involve an elimination reaction.

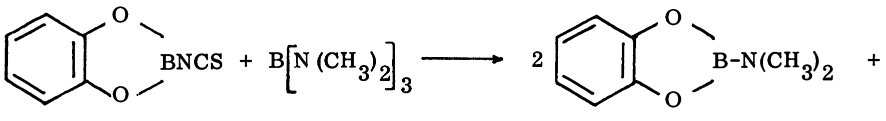
$$\mathrm{PhB}\left[\mathrm{N(CH_3)_2}\right]_2 + \mathrm{PhB(NCX)_2}$$



(3)

Although the pseudohalogen character of the -NCX group attached to boron usually favors its displacement rather than addition—e. g., $>$B-NCO + ROH $\longrightarrow$ $>$B-OR + (HNCO)—it was believed that the case at hand could be an exception, since cleavage of the $\overset{|}{\underset{|}{\mathrm{B}}}$-NCX B-N bond in such a displacement would lead only to the formation of another B-N bond—i. e., $>$B-NR$_2$.

To establish a prototype, tris(dimethylamino)boron was allowed to react with *o*-phenylene isothiocyanatoboronate [prepared in good yield by slightly modifying the method of Lappert and Pyszora *(5)*] in a 1 to 3 ratio. The desired borourea analog was not obtained and it was subsequently determined that the following disproportionation occurred to give III in 75% and IV in 98.5% yield:



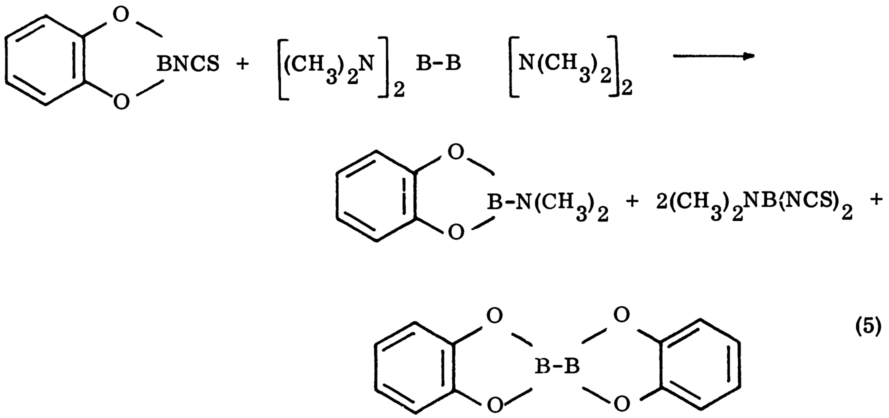
III

$(CH_3)_2NB(NCS)_2$ (4)

IV

To identify III it was alternately prepared from *o*-phenylene chloroboronate and dimethylamine in the presence of triethylamine. Subsequently it was shown that the type of disproportionation in Reaction 4 is general, whether isothiocyanate or isocyanate groups were involved.

When tetrakis(dimethylamino)diboron was treated with *o*-phenylene isothiocyanatoboronate, an interesting reaction occurred which involved not only disproportionation but also cleavage of the boron-boron bond.



(5)

The products were isolated in good agreement with this stoichiometry: 2-(1, 3, 2-benzodioxaborolo)-1, 3, 2-benzodioxaborole, by comparison of its properties with those previously reported elsewhere *(6)*, was indicated as the third product.

When phenylboron diisothiocyanate was heated with an equimolar quantity of bis(dimethylamino)phenylboron and the mixture subsequently distilled, a liquid of constant boiling point was recovered which accounted for more than 90% of the weight of starting materials. Its infrared spectrum differed from that of the starting mixture, but showed features characteristic of the phenyl, isocyanato, and dimethylamino groups. Its mass spectrum, in every detail, was in accord with that of compound V, which was the first example of this type of trisubstituted boron derivative. The use of bis(diethylamino)boron resulted in the formation of VI.

$$+\ \mathrm{Ph\,B[N(CH_3)_2]_2} \longrightarrow 2\ \mathrm{Ph\,B[N(CH_3)_2]\,NCS} \qquad (6)$$

V

$\mathrm{Ph\,B(NCS)_2}$

$$+\ \mathrm{Ph\,B[N(C_2H_5)_2]_2} \longrightarrow 2\ \mathrm{Ph\,B[N(C_2H_5)_2]\,NCS} \qquad (7)$$

VI

The analogous reaction occurred when the corresponding phenylboron diisothiocyanate was replaced by the diisocyanate. In the hope that coordination of the diisothiocyanate with a Lewis base would offset this tendency to disproportionate and permit addition to occur, the pyridine and lutidine adducts were prepared and treated with the bis-(dialkylamino)phenylborons, but to no avail.

Since the dialkylamino and isothiocyanate groups were now in the same molecule, attempts were made to induce IV and V to self-polymerize. Heating in a sealed system led to the evolution of a considerable quantity of benzene as well as a myriad of other decomposition products. Catalysts such as triethylamine and dibutyltin dioctoate, often useful to promote the formation of polyurethanes from diols and diisocyanates, were ineffective.

Final proof that the -NCX groups retained pseudohalogen character in these compounds was gained when diethylaminophenylboronisothiocyanate was treated with ethanol and the boron was completely recovered as diethyl benzeneboronate.

Experimental

Boron-tris(dimethylphenylurea) (Ia). Under nitrogen, 3.58 grams (0.025 mole) of tris(dimethylamino)boron was added dropwise to a stirred solution of 8.92 grams (0.075 mole) of phenylisocyanate in pentane during 1 hour, during which time a precipitate formed. After an additional 2.5 hours of stirring, the flask was removed to a dry box where the solution was filtered, and the residue was washed with pentane and dried under vacuum (yield, 80%). The material could be recrystallized from chloroform, but this was found to be unnecessary (m.p. 197°C.). (Most of these compounds were observed to shrink and undergo other visual changes well below the quoted melting points. These were reproducible and affected by introduction of impurities. Therefore we believe this behavior to be natural for the compounds and not indicative of impurities. This has been verified by other analyses.)

Analysis. Calculated for $C_{27}H_{33}BN_6O_3$: C, 64.80; H, 6.67; B, 2.02; N, 16.80. Found: C, 64.27; H, 7.80; B, 2.00; N, 16.79.

I (2.0 grams) was placed in a 100-ml. flask and 25 ml. of absolute ethanol was added. The flask was heated to 85°C. and the volatile materials were distilled away, leaving 2.0 grams (100%) of solid identified by infrared, melting point, molecular weight, and mixed melting point as phenyldimethylurea. Triethylborate was determined mass spectrometrically in the distillate.

Boron-tris(dimethylphenylthiourea) (Ib). A solution of 4.29 grams (0.03 mole) of tris(dimethylamino)boron and 12.15 grams (0.09 mole) of phenylisothiocyanate in ~75 ml. of benzene was refluxed for 41 hours. Some precipitate appeared in the hot solution and on cooling became considerable. This solid (11.0 grams or 67%) was removed, washed with heptane, and dried at 110°C. An additional 1.1 grams was recovered from the mother liquor. Recrystallization was not necessary to obtain a pure product (m.p. 183-85°C.), although this compound is soluble in a number of solvents, from which it can be recrystallized.

Analysis. Calculated for $C_{27}H_{33}BN_6S_3$: C, 59.10; H, 6.06; B, 1.97; N, 15.30. Found: C, 58.67; H, 7.19; B, 1.70; N, 16.58.

Ia (5.0 grams) was refluxed for 1 hour in 50 ml. of absolute ethanol and recovered unchanged. Ia (3.7 grams) was dissolved in hot dioxane, water was added, and the solution was refluxed for 1.5 hours and concentrated to dryness. The residue was recrystallized from benzene, separating the boric acid and giving phenyldimethylthiourea (m.p. 134-36°C. and otherwise identified).

Phenylboron-bis(diethyl-*o*-tolylurea) (IIa). A solution of 4.35 grams (0.0187 mole) of bis(diethylamino)phenylboron and 5.0 grams (0.0376 mole) of *o*-tolylisocyanate in 100 ml. of pentane was stirred for 56 hours, during which time a yellow precipitate formed. This solid was collected, washed with pentane, and dried (4.0 grams). Recrystallization from benzene gave a yellow powder melting at 115-16°C.

Analysis. Calculated for $C_{30}H_{39}BN_4O_2$: C, 72.10; H, 7.89; B, 2.21. Found: C, 72.43; H, 7.71; B, 2.14.

Phenylboron-bis(diethylphenylurea) (IIb). This compound was prepared in essentially the same manner as IIa. It melted at 205-09°C. and on hydrolysis gave phenyldiethylurea (m.p. 80-82°C.).

Reaction of *o*-Phenylene Isothiocyanatoboronate and Tris(dimethylamino)boron (Reaction 4). *o*-Phenylene isothiocyanatoboronate [25.0 grams (0.141 mole)] and pentane (50 ml.) were stirred at 0° C. under nitrogen and to this was added dropwise a solution of 10.1 grams of tris(dimethylamino)boron. A precipitate separated during a 3-hour period and the mixture was allowed to come to room temperature overnight. On cooling in ice the mixture solidified, but on warming to 10°C. it was filtered. The residue was refluxed in pentane and filtered to give 11.8 grams (98%) of dimethylaminoborondiisothiocyanate (IV) (m.p. 150° C.).

Analysis. Calculated for $C_4H_6BN_2S_2$: C, 28.10; H, 3.53; B, 6.33; N, 24.6; S, 37.4. Found: C, 27.79; H, 391; B, 6.64; N, 24.3; S, 36.7.

Infrared and mass spectral analyses were in complete agreement with the structure of IV.

When the filtrate was cooled to 0°C., a precipitate formed, which was removed, redissolved in pentane, filtered, and cooled to give 10.0 grams of *o*-phenylene dimethylaminoboronate (III). An additional 7.2 grams was recovered from the recrystallization liquor of IV (m.p. 59-61°C.).

Analysis. Calculated for $C_8H_{10}BNO_2$: C, 59.00; H, 6.19; B, 6.63; N, 8.60. Found: C, 58.77; H, 6.21; B, 6.92; N, 8.81.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch020

A compound identical in every respect was prepared from the reaction of equimolar quantities of dimethylamine and *o*-phenylene chloroboronate in pentane in the presence of triethylamine.

Reaction 4 was repeated using *o*-phenylene isocyanatoboronate. Because of solubility similarities, the products could not be readily separated; mass spectral analysis, however, indicated that the same reaction had occurred.

Reaction of *o*-Phenylene Isothiocyanatoboronate and Tetrakis(dimethylamino)diboron (Reaction 5). *o*-Phenylene isothiocyanatoboronate (10.0 grams, 0.568 mole) and 50 ml. of pentane were placed in a 100-ml. flask wrapped with aluminum foil and cooled to < 15° C. and to this was added, dropwise with stirring, a solution of 2.81 grams of tris(dimethylamino)boron (~5 minutes). A yellow semisolid had formed, but on warming to room temperature it began to turn white. The mixture was allowed to stand overnight. The now hard mass was crushed, agitated in pentane, and filtered, giving 8.0 grams of residue. Concentration and cooling of the filtrate gave *o*-phenylene dimethylaminoboronate.

The residue was refluxed in benzene and filtered while hot. Pentane was added to the filtrate, which was cooled to 0° C., whereupon dimethylaminoboron diisothiocyanate precipitated. The benzene-insoluble portion melted at 320-25° C. and resembled 2-(1, 3, 2-benzodioxaborolo)-1, 3, 2-benzodioxaborole, tentatively reported elsewhere *(6)*.

Dimethylaminophenylboronisothiocyanate (V). To phenylboron diisothiocyanate (11.6 grams, 0.0568 mole) and 20 ml. of refluxing pentane was added bis(dimethylamino)phenylboron (10.0 grams, 0.0568 mole) in 20 ml. of pentane. The mixture became homogeneous and stirring at room temperature was continued overnight. The pentane was removed and the residue distilled at 110° C./0.5 mm. (18.0 grams, 83%; n_D^{34} = 1.5913).

Analysis. Calculated for $C_9H_{11}BN_2S$: C, 56.80; H, 5.79; B, 5.79; N, 14.75. Found: C, 57.70; H, 6.71; B, 5.63; N, 14.83.

The infrared and mass spectra were in complete agreement with this structure.

Diethylaminophenylboronisothiocyanate (VI). A solution of 13.2 grams (0.0569 mole) of bis(diethylamino)phenylboron in 100 ml. of benzene was added (10 minutes) to a solution of 11.6 grams of phenylboron diisothiocyanate in 75 ml. of benzene and refluxed for 1.5 hours. The benzene was removed and the residue distilled at 155° C./8 mm. to give 24.0 grams (97.1%) of essentially pure diethylaminophenylboronisothiocyanate.

Acknowledgment

The authors acknowledge the technical assistance of H. A. Schroeder and the support of this work by the Office of Naval Research.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch020

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Received May 10, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch020

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Cyclic Boron Compounds

VI. A BN Substituted Cyclobutadiene Analog. Synthesis Structure, Stereochemistry, and Mechanism of Formation

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch021

The first example of a cyclic 3-coordinate boron-nitrogen ring compound (the dimeric borazyne, isoelectronic with a cyclobutadiene derivative), 1, 3-di-*tert*-butyl-2, 4-di-*tert*-butylamino-1,3-diaza-2,4-boretane, has been obtained and characterized. Physical measurements (^1H nuclear magnetic resonance and infrared spectral and mass spectrometric data) confirm the structure and provide information on the bonding. Cis/trans isomerism, due to restricted rotation about two bonds, is demonstrated. A proposal for the mechanism of elimination-cyclization reactions, leading to diazaboretanes, borazines, or borazocines is made, which involves diborylamines as intermediates, isolable only under sterically favorable conditions.

Of the borazynes (XB=NY) and their oligomers, only the cyclic trimers (the borazines) *(12, 15)* and recently the tetramers (the borazocines) *(18)* have been well characterized; polymeric, presumably linear, derivatives have also been described *(5, 7, 8)*. We now report the preparation of a cyclic dimer, systematically named 1,3-di-*tert*-butyl-2,4-di-*tert*-butylamino-1, 3-diaza-2, 4-boretane (V). [A preliminary account of this work has been published *(10)*].

Reactions leading to its formation are indicated in the reaction scheme shown below; the yields in each step were high. Compounds II to VI, which have been characterized (see Tables I and II), represent novel classes of boron compounds; an example of a bisborylamine is known *(13)* and tris-*tert*-butylaminoborane (I) has been obtained previously *(1)*. *Tert*-Butylaminochlorophenylborane (VI) is not related to the main reactions: It was prepared

$$\mathrm{Ph.BCl_2 + PH.B(NHBu^t)_2 \longrightarrow 2\ Ph.B(Cl).NHBu^t}$$

in an effort, which proved unsuccessful, to obtain successively $\mathrm{Cl.(Ph)B.NBu^t.B(Ph).NHBu^t}$, $\mathrm{Bu^tNH.(Ph)B.NBu^t.B(Ph).NHBu^t}$, and $\mathrm{(PhB.NBu^t)_2}$.

Table I. Characterization of New BN Compounds

Compound	*B.P./Mm.(M.P.), C.*	n_D^{20}	d_4^{20}	$[R_L]_D$ *Found*	$[R_L]_D$ *Calcd.*[a]
II[b]	74-78/10.0	1.4330			
III	82-86/0.02	1.4548	0.9014	114.0	114.8
IV	98-100/0.01 (52-54)	1.4630			
V	72-74/0.005	1.4582	0.8666	97.0	98.0
VI	58-60/0.01	1.5143	1.005	58.4	57.7

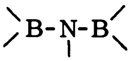
[a] Calculated values obtained by using Vogel's values (*19*) and the value 3.0 (or 3.94 for monophenyl substituted boron) (*17*) for boron.

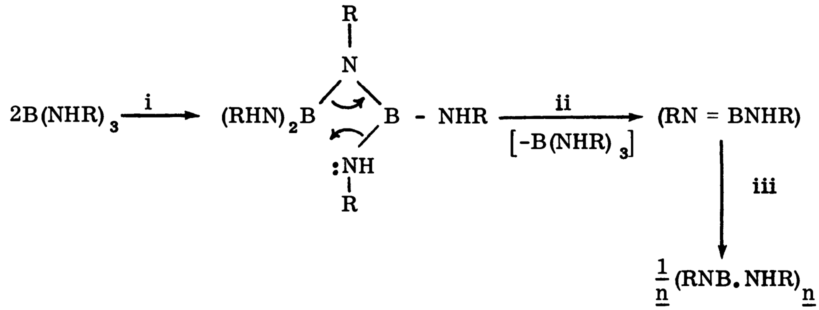
[b] As yet obtained only in ~90% purity.

Table II. Analysis of New Boron Compounds

Compound	*Found*						*Required*					
	C%	*H%*	*N%*	*Cl%*	*B%*	*M.W.*	*C%*	*H%*	*N%*	*Cl%*	*B%*	*M.W.*
II	-	-	15.5	14.8	5.5	-	-	-	14.7	18.6	5.6	-
III	55.9	10.7	16.3	10.3	6.3	356, 364	55.8	10.5	16.3	10.3	6.3	344
IV	62.3	12.4	18.5	-	5.9	383	64.0	12.8	18.4	-	5.8	380
V	61.4	12.4	18.0	-	7.0	307, 308,[a] 316	62.3	12.4	18.2	-	7.0	308
VI	61.6	7.4	7.3	18.6	-	-	61.5	7.7	7.2	18.2	-	-

[a] From mass spectrum.

Polyborazynes are invariably formed by elimination reactions from borazenes, XX'B.NYY', and we regard the mechanism as a three-step process: (i) an intermolecular condensation with formation of a compound having a  skeleton; (ii) an intramolecular 1,3-nucleophilic rearrangement; and (iii) polymerization of the borazyne. This is illustrated for the case of a trisaminoborane. Evidence rests primarily upon our isolation of compounds III and IV. Bisborylamines [$(XX'B)_2NR$] have not previously been obtained; their reactivity with respect to ii may depend significantly upon steric factors. The degree of polymerization (iii) of the borazyne, whether cyclic or linear, appears also to be controlled by steric factors. In a diazaboretane the proximity of groups attached to B and N is lower than in a borazine. Molecular models show that *B-tert*-butylamino and *N-tert*-butyl groups can be accommodated in a planar 4-membered ring, but not so readily in a planar 6-membered one.



Evidence for structure V rests on full elemental analysis, molecular weight determinations (cryoscopic and ebullioscopic, in benzene), and the mass spectrum, determined on an A.E.I. MS2 instrument. This shows the molecular ion (308^+) to be the largest of any significance; other abundant species are 293^+, 237^+, 181^+, and 125^+. The 293^+ ion is evidently formed from the parent by loss of a methyl group. The subsequent fragmentation pattern is interesting and shows that the ions at atomic masses 237, 181, and 125 are formed by loss of successive *tert*-butyl groups, followed by rearrangement of a single hydrogen atom.

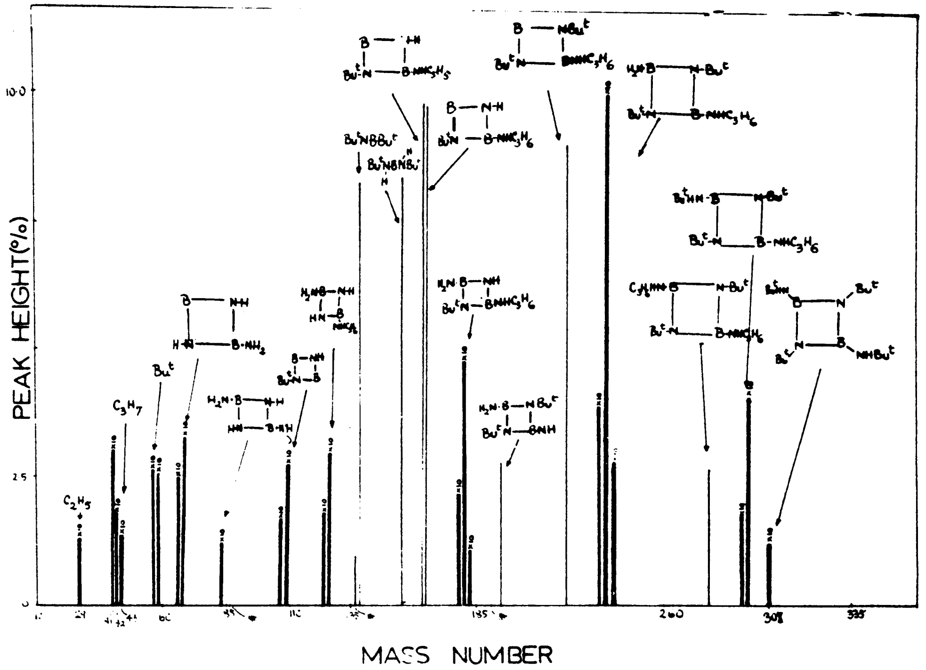


Figure 1. Schematic mass spectrum of 1,3-di-tert-butyl-2,4-di-tert-butylamino-1,3-diaza-2,4-boretane

Isotopic effects not indicated

Further evidence for this pattern is the appearance in the mass spectrum of metastable ions (denoted by asterisks in Figure 1) at masses 191.7 (= $237^2/293$), 138.2 (= $181^2/237$), and 86.3 (= $125^2/181$), which, being decomposed in the mass spectrometer before magnetic deflection, are readily recognized by their diffuse appearance. The identification of metastable ions confirms that successive *tert*-butyl groups are lost, rather than smaller fragments totaling 56 mass units, since they relate the pairs of ions by the relationship $M_1{}^2/M_2$.

Another feature of the mass spectrum is significant: the persistence of the four-membered ring structure in daughter ions, which suggests that the ring is inherently stable.

Evidence for diazaboretane intermediates from electron bombardment of borazines has previously been obtained *(16)*, and a diphosphaboretane has been described *(9)*.

The diazaboretanes are of interest also because formally they may be regarded as isoconjugate with the cyclobutadienes. The instability of the latter has been explained in terms of molecular orbital theory *(11)*. Thus, cyclobutadiene would have a doubly degenerate e_g orbital containing only two electrons with both e_g electrons unpaired. The same picture is not valid for the diazaboretanes, since the substitution of BN for CC destroys the degeneracy of the e_g orbitals. It is not surprising, therefore, that compound V proved to be diamagnetic, and it would not be appropriate to conclude that the nonbonding electrons of the cyclic nitrogen atoms are localized. Nevertheless, we believe that π-bonding is largely exocyclic and that this is responsible, at least in part, for the stability of V. The evidence is spectroscopic and indicates that V is a mixture of geometrical isomers Va and Vb.

^1H nuclear magnetic spectra were obtained at 60 Mc. per second and ambient temperature in a Varian A60 spectrometer. Investigations were made both for the neat liquid and for a 10% (v./v.) solution in carbon tetrachloride. The portions of the spectra associated with CH_3 groups are shown in Figures 2 (neat liquid) and 3 (CCl_4 solution). The difference in the two spectra is largely attributed to the decreased viscosity of the solution. Because of the additional resolution in the solution spectrum, this was chosen as the most satisfactory for diagnostic purposes. The band positions (on the τ scale) are summarized in Table III.

Table III. Band Positions

	Band No. (Figs. 2 and 3)							
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
τ	8.68	8.76	8.80	7.25	7.39	7.50	7.55	7.60

The large differences in τ values, between the pure liquid and the carbon tetrachloride solution, may be due to preferential "layering" of the planes in solution. This explanation is based on analogy with the benzene ^1H nuclear magnetic resonance spectrum and solvent effects *(6)*.

The solution spectrum is more complex than expected from the presence of a single isomer. Two possible structures are Va and Vb.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch021

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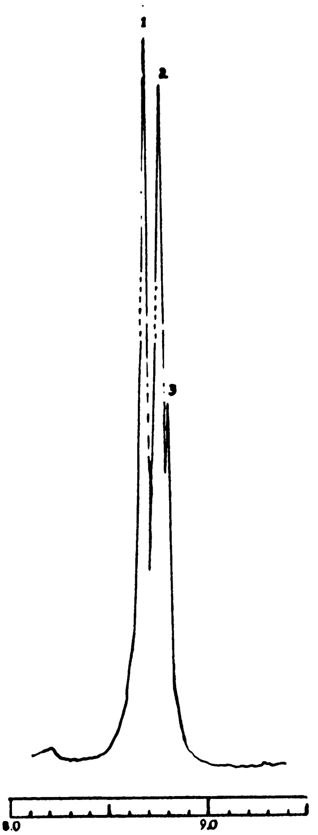


Figure 2. Portion of 'H magnetic resonance spectrum of 1, 3-di-tert-butyl-2, 4-di-tert-butylamino-1, 3-diaza-2, 4-boretane
At 60 Mc. per second, pure liquid

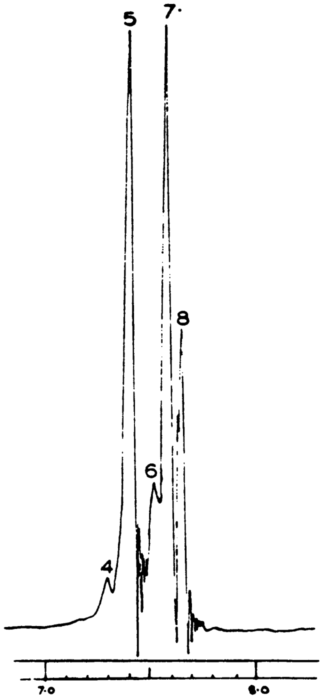
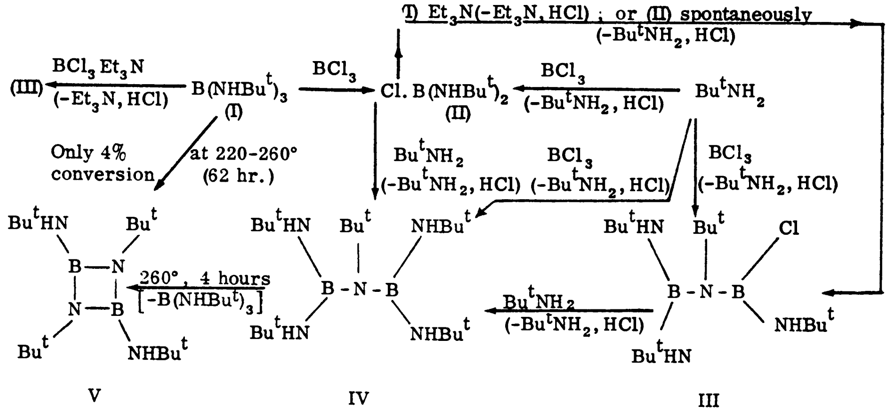


Figure 3. Portion of 'H nuclear magnetic resonance spectrum of 1, 3-di-tert-butyl-2, 4-di-tert-butylamino-1,3-diaza-2,4-boretane
At 60 Mc. per second, 10% (v./v.) solution in CCl_4

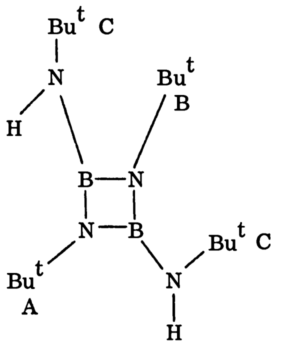
Isomerism arises from restricted rotation about both the exocyclic BN bonds. This appears to be a reasonable assumption, particularly on the basis (Vc) that multiple bonding is largely exocyclic rather than cyclic; the possibility of cis/trans isomerism in BN systems has been demonstrated *(4, 14)*.

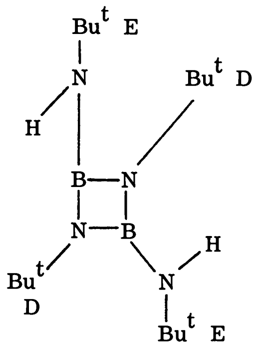
Assuming ring planarity in each case, structure Va has three (or even four; the two marked C may also differ significantly) distinct butyl groups in abundance ratio 2:1:1, while structure Vb has only two butyl environments, in equal abundance. On this basis then, and assuming absence of spin multiplets, we should expect the *'H* spectrum of Va to consist of three bands in the intensity ratio 2:1:1, while that of Vb should comprise two equally intense bands. The expectation would be in substantial agreement with the observed solution spectrum if an assignment shown in Table IV is accepted, coupled with an isomeric abundance ratio trans / cis — i.e., Vb/Va — , of ~2.

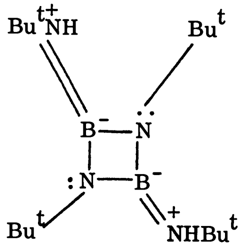


The field order of bands assigned to A, D, and B groups would accord with expectations.

The N - H group (for both isomers) is associated with the broad absorption centered around $\tau = 5.42$.


Va


Vb


Vc

The infrared spectrum (2 = 15 microns), recorded on a Perkin Elmer PE21 instrument, using rock salt optics, of the diazaboretane is reproduced in Figure 4. Assignments of some of the absorption bands are indicated in Table V, together with similar data on compounds II, III, IV, and VI (see also Figure 5); assignments for tris-*tert*-butylaminoborane have been given *(2)*.

The infrared spectrum of the diazaboretane in the region 3300 to 3500 cm.$^{-1}$, both in carbon tetrachloride solution and on a capillary film, was measured using a Unicam SP700 grating spectrophotometer. The capillary film spectrum is reproduced in Figure 5. Absorption maxima in the NH stretching region are at 3462 (a), 3428 (b), and 3394 (c) cm.$^{-1}$ In carbon tetrachloride solution these bands shift only very slightly. The frequencies and extinction coefficients for bands in the NH stretching region, using carbon tetrachloride solutions, are indicated in Table VI, together with similar data on I and IV. Possible

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch021

Table IV. Assignment

	Band No. (see Fig. 3)				
	4	*5*	*6*	*7*	*8*
Assignment (see Va and Vb)	A or B	D	B or A	E	D

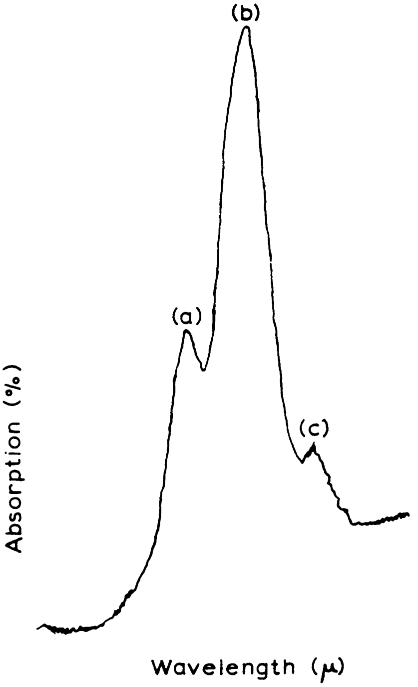


Figure 4. Infrared spectrum of 1, 3-di-tert-butyl-2, 4-di-tert-butylamino-1, 3-diaza-2, 4-boretane

Capillary film 3300- to 3500-cm.$^{-1}$ region

impurities in V might have been IV, the starting material for preparation of V; I, the by-product obtained in the preparation of V; and *tert*-butylamine (ν max. 3375 and 3308 cm.$^{-1}$ in dilute carbon tetrachloride solution), a potential hydrolysis product. The spectral results (accurate to ±1cm.$^{-1}$) indicate that bands a, b, and c all arise from compound V, or at any rate from none of the obvious potential impurities. Band b, in carbon tetrachloride, shows indications of being a doublet. Our present interpretation of these data is that bands a and b arise from the NH stretching modes of the cis (Va) and trans (Vb) forms, respectively, while band c may be due to Fermi resonance or may be a "hot" band. An alternative explanation, but a rather tenuous one, is that there is long-range coupling with asymmetric a and symmetric c stretching modes for the cis, but only a single infrared-active

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch021

Table V. Assignments of Selected Absorption Bands (Cm. $^{-1}$ of Compounds II to VI)

Compound	*ν(NH)*	*ν(BN)*	*δ[CH(Bu^t)]*	*ν(CN)*	*ν(BCl)*
II	3448	1493	1389 1362	1217	952
III	3448 3410	1493	1389 1362	1215	955
IV	[a] 3465 3439 3386	1488	1387 1361	1229	-
V	[a] 3463 3426 3394	1481	1391 1362	1220	-
VI	3378	1475	1389 1361	1221	935

[a] Only with these compounds was high resolution used in this range.

(asym.) mode for the trans. Either explanation would be consistent with the intensity results. Changes in dipole moment will be different for the cis and trans forms, and therefore it is not reasonable to expect an exact correspondence between extinction coefficient ratios on the one hand, and ratios cis / trans isomers derived from the *H* nuclear magnetic spectra, on the other.

Table VI. NH Frequencies (Cm. $^{-1}$) and Intensities in CCl_4 Solutions of Compounds I, IV, and V

Compound	*I*	*IV*	*V*
νNH(ε)	3375, 3308	3465 (27.2), 3439 (36.5), 3386 (11.3)	3462 (13.2), 3428 (33.6), 3394 (5.9)

Experimental

Interaction of Trichloroborane (1 Mole) and *tert*-Butylamine (6 Moles). Trichloroborane (14.10 grams, 1 mole), in light petroleum (b.p. 30 - 40°) (25 ml.) at -78° C., was slowly added with continuous stirring to *tert*-butylamine (53.0 grams, 75 ml., 6 moles) in the same solvent (250 ml.) at -78°C. The reaction, which was exothermic, resulted in formation of white precipitate. The mixture was allowed to stand at 20°. The white *tert*-butylammonium chloride (40.9 grams Calculated for $C_4H_{12}NCl$: 39.5 grams. Found: N, 12.5; Cl, 29.4. Calculated for $C_4H_{12}NCl$: N, 12.8; Cl, 32.4%) was filtered off and washed with more solvent. The washings and the filtrate were freed from the solvent. The residue (22.40 grams, 85%) afforded: tris-*tert*-butylaminoborane (I)(15.40 grams, 57%)(b.p. 38-40°/0.05 mm., n_D^{20}

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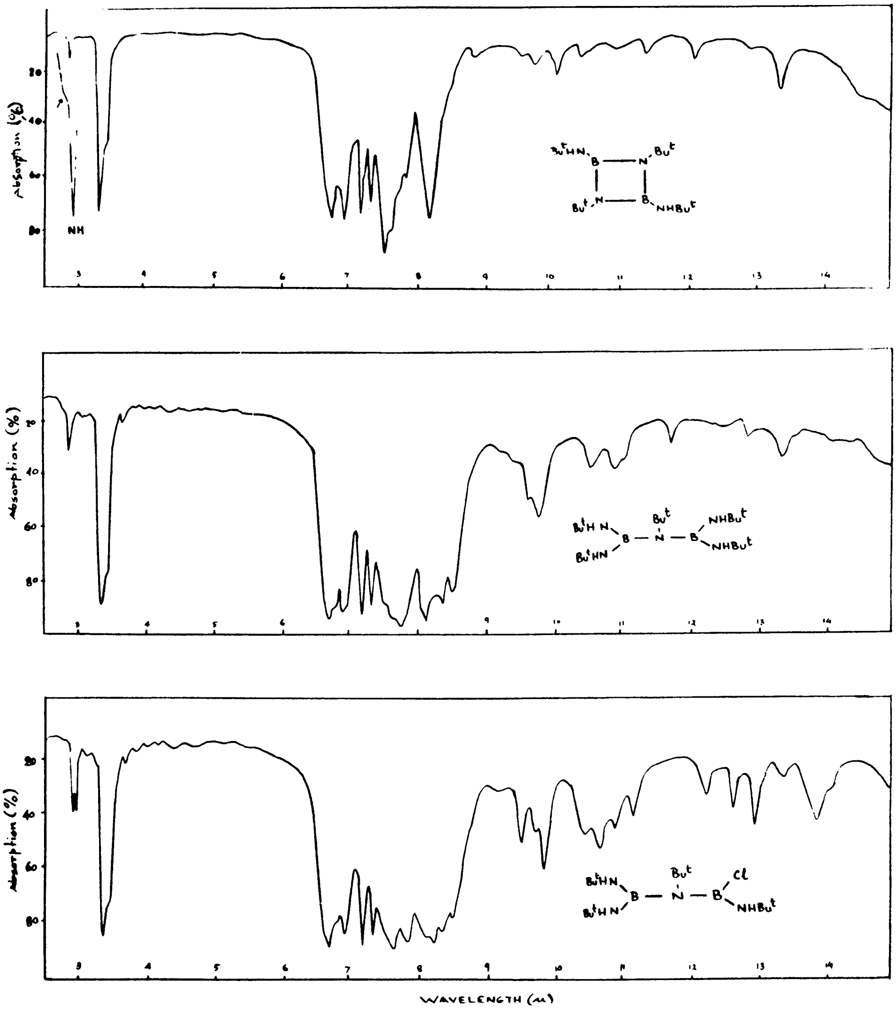

Figure 5. Infrared spectra of some tert-butylaminoboranes
2- to 15- micron region

1.4270) (Found: C, 63.5; H, 11.8; N, 18.9; B, 4.8%; M.W. 216. Calculated for $C_{12}H_{30}N_3B$: C, 63.4; H, 13.2; N, 18.5; B, 4.8%; M.W. 227); *B-tert*-butylamino-*B*-chloro-*B′*,*B′*-di(*tert*-butylamino)-diboryl-*tert*-butylamine (III) (5.40 grams, 26.3%) (see Tables I and II for physical constants and analytical figures). [In this discussion mole is defined as molar proportion.]

Interaction of Trichloroborane (1 Mole) and *tert*-Butylamine (5 Moles). Trichloroborane (50.0 grams, 1 mole) in light petroleum (b.p. 0 – 30°) (25 ml.) at -78° reacted with *tert*-butylamine (115 grams, 220 ml., 5 moles) in the same solvent (300 ml.) at -78°. The procedure was as described in the foregoing experiment. The following fractions were obtained:

Bis(*tert*-butylamino)chloroborane (II) (impure) (32.37 grams, 41.5%)

(b.p. 35-42°/1.0 mm., n_D^{20} 1.4320) (Found: Cl, 14.0%). On redistillation further separation was possible, the fractions being: bis(*tert*-butylamino)chloroborane, (II) (impure) (19.1 grams) (b.p. 38-40°/1.0 mm., n_D^{20} 1.4320) (Found: Cl, 14.2; B, 5.7; $C_8H_{20}N_2ClB$ requires Cl, 18.6; B, 5.6%); and a liquid (10.94 grams (b.p. 40 - 42°/1.0 mm., n_D^{20} 1.4311) (Found: Cl, 11.0%).

Compound III (26.10) grams, 36%) (b.p. 86-98°/0.01 mm., n_D^{20} 1.4565 (Found: N, 16.2; Cl, 10.3; B, 6.4. $C_{16}H_{39}N_4ClB_2$ requires N, 16.3; Cl, 10.3; B, 6.3%). In a further experiment using 5 moles of *tert*-butylamine, the yield of compound III was 39.5%.

Spontaneous Dehydrochlorination of Bis (*tert*-butylamino)chloroborane. Impure bis (*tert*-butylamino)chloroborane (18.70 grams) eliminated *tert*-butylammonium chloride spontaneously. Thus, after 72 hours at 20° the hydrochloride was filtered off and the filtrate was fractioned: bis(*tert*-butylamino)chloroborane (II) (12.57 grams, 67%; see Tables I and II); a middle fraction (1.62 grams) (b.p. 80–84°/10 mm., n_D^{20} 1.4317): and compound III (2.07 grams)(b.p. 92°/0.1 mm., 1.4530) (Found: Cl, 10.3; B, 6.2%).

Interaction of Bis(*tert*-butylamino)chloroborane and *tert*-Butylamine. Bis-(*tert*-butylamino)chloroborane (30.2 grams, 1 mole) reacted with excess *tert*-butylamine (35.0 grams) in light petroleum (b.p. 0 – 30°) (150 ml.). The reaction was vigorous and was accompanied by the formation of white *tert*-butylammonium chloride. The precipitate was filtered off and washed with more solvent. The washings and the filtrate were freed from the solvent and the residue afforded: compound I (24.64 grams, 69%) (b.p. 52-54°/0.01 mm., n_D^{20} 1.4275) (Found: B, 4.8; N, 18.7. Calculated for $C_{12}H_{30}N_3B$: B, 4.8; N, 18.5%); and a liquid (2.54 grams) (b.p. 90 - 92°/0.01 mm., n_D^{20} 1.4572) (Found: B, 6.2; Cl, 6.5%).

Interaction of Bis (*tert*-butylamino)chloroborane and Triethylamine. Bis(*tert*-butylamino)chloroborane (12.10 grams, 2 moles) was refluxed with triethylamine (3.25 grams, 4.65 ml., 1 mole) in benzene (15 ml.) for three hours. The white precipitate, consisting mainly of triethylammonium chloride (1.7 grams, 39%) (Found: Cl, 27.1. Calculated for $C_6H_{16}NCl$: Cl, 26.0%), was filtered off. The filtrate, freed of solvent, afforded: a liquid (4.55 grams) (b.p. 70–74°/10 mm., n_D^{20} 1.4355) (Found: Cl, 12.8; B, 5.9%); a middle fraction (1.84 grams), b.p. 74–80°/10 mm.; and compound III (1.27 grams) (b.p. 78-80°/0.05 mm., n_D^{20} 1.4448) (Found: Cl, 9.6%).

Interaction of Tris *tert*-butylaminoborane (I) and Trichloroborane in presence of Triethylamine. Trichloroborane (8.50 grams, 1 mole), in light petroleum (b.p. 40 – 60°) (25 ml.) at -78°, was slowly added with continuous stirring to a mixture of tris *tert*-butylaminoborane (33.08 grams, 2 moles) and triethylamine (14.6 grams, 20 ml., 2 moles), in the same solvent (100 ml.) at -78°. The reaction was exothermic, with the formation of white precipitate. The reaction mixture was refluxed for 3 hours. The white precipitate (14.0 grams) was filtered off and washed with further quantities of light petroleum. Triethylaminetrichloroborane (8.10 grams, 51%) (m.p. 92°) (Found: N, 6.5; B, 5.5. Calculated for $C_6H_{15}NCl_3B$: N, 6.4; B, 5.0%) was separated as the water-insoluble portion of the original white precipitate, while the water-soluble portion consisted mainly of triethylammonium chloride. The amount of triethylammonium chloride (5.50

grams, 55%) was estimated by determining the chloride ion content of the aqueous solution. The filtrate, freed from solvent, was distilled to give: compound II (impure) (21.32 grams, 51.5%) (b.p. 40 – 60°/ 0.01 mm., n_D^{20} 1.4307) (Found: Cl, 15.7; B, 5.5%); a middle fraction (1.41 grams); and compound III (7.76 grams, 20.4%) (b.p. 80 – 84°/ 0.01 mm., n_D^{20} 1.4556) (Found: N, 16.1; Cl, 10.0; B, 6.7%). A brown resin (0.96 grams) was obtained as the residue.

Preparation of Bis(di-*tert*-butylaminoboryl)-*tert*-butylamine (IV). Compound III (7.70 grams, 1 mole) in benzene (25 ml.) was refluxed with excess *tert*-butylamine (25.0 ml., 17.6 grams) for 3 hours and was then set aside for 12 hours. The *tert*-butylammonium chloride (1.80 grams, 83%) (Found: Cl, 31.0. Calculated for $C_4H_{12}NCl$: Cl, 32.4%) was filtered off. The filtrate, freed of solvent, on distillation gave *bis(di-tert-butylaminoboryl)-tert-butylamine (IV)* (6.20 grams, 73%) (see Tables I and II).

Preparation of 1,3-Di-*tert*-butyl-2,4-di-*tert*-butylamino-1,3-diaza-2,4-boretane (V). Compound IV (10.16 grams, 1 mole) was heated at 260° for 4 hours. Volatile matter (0.20 grams, 1.3891) was trapped at -78°. Distillation of the residue afforded: compound I (5.19 grams, 87%) (b.p. 32-35°/0.03 mm., n_D^{20} 1.4267) (Found: N, 18.3; B, 4.9%); a middle fraction (0.66 gram) (b.p. 60-82° /0.04 mm., n_D^{20} 1.4465); and *1, 3*-di-*tert*-butyl-*2, 4*-di-*tert*-butylamino-*1, 3*-diaza-*2, 4*-boretane (V) (2.45 grams, 60%) (see Tables I and II).

Pyrolysis of Tris-*tert*-butylamino borane(I). Tris-*tert*-butylamino - borane (15.44 grams) was pyrolyzed at 220° to 250° for 62 hours. The volatile matter (0.34 grams, 6.7%, n_D^{20} 1.3818) was trapped at -78°. Distillation of the residue afforded: compound I (12.92 grams, 85%) (b.p. 38-40°/0.05 mm., n_D^{20} 1.4272) (Found: B, 4.9%); and compound V (0.39 grams, 37%) (b.p. 118°/0.02 mm., n_D^{20} 1.4564) (Found: B, 6.9%; M.W., 316).

Lack of Reaction between Compound III and Triethylamine. Compound III (7.10 grams, 1 mole) was refluxed with triethylamine (2.10 grams, 3 ml., 1 mole) for 3 hours. A trace of white precipitate was formed and was filtered off. Distillation of the filtrate afforded the original material (III) (5.70 grams, 80%) (b.p. 88-90°/0.01 mm., n_D^{20} 1.4556) (Found: Cl, 9.9%) and a residue (0.50 gram) of brownish resin.

Pyrolysis of Compound III. Compound III (28.49 grams) was heated at 242-254° for 10 hours. The residual brownish liquid (27.72 grams, 98%) was distilled into: a liquid (15.69 grams) (b.p. 72-80°/10 mm., n_D^{20} 1.4314) (Found: Cl, 11.6; B, 5.4%), probably a mixture of compounds I and II; a middle fraction (0.28 gram); a liquid (1.86 grams) (b.p. 72-74°/0.005 mm., n_D^{20} 1.4548) (Found: Cl, 8.0; B, 6.4%); a further fraction (3.43 grams) (b.p. 80-82°/0.005 mm., n_D^{20} 1.4623) (Found: Cl, 11.1; B, 7.1%); and finally a residue (6.0 grams) of dark brown resin.

Interaction of Bis(*tert*-butylamino)phenylborane and Dichlorophenylborane. Dichlorophenylborane (17.50 grams, 1 mole), in light petroleum (b.p. 0 - 40°) (25 ml.), was slowly added to bis(*tert*-butylamino) phenylborane (25.08 grams, 1 mole), in the same solvent (100 ml.) at -78°. The reaction was highly exothermic with the formation of a white precipitate. The reaction mixture was set aside for 12 hours. The white precipitate, consisting mainly of *tert*-butylammonium chloride (4.52 grams) (Found: Cl, 29.8. Calculated for $C_4H_{12}NCl$: Cl, 32.4%), was filtered off and was washed with benzene, ether, and light petroleum (b.p. 0 - 40°). The washings and the filtrate were combined and the solvents were removed under reduced pressure. Distillation of the residue afforded *tert*-butylaminochlorophenylborane (VI) (30.18 grams, 72%) (see Tables I and II).

The dark brownish residue from the distillation was extracted with hot benzene. Partial evaporation of the extract, followed by addition of light petroleum (b.p. 0 - 40°), yielded *B*-triphenylborazine (impure) (4.07 grams) (m.p. 178 - 180°) (Found: C, 69.4; H, 6.3; N, 17.0%; M.W. 309. Calculated for $C_{18}H_{18}N_3B_3$: C, 70.0; H, 5.8; N, 13.6%; M.W. 308).

Acknowledgement

We are grateful to R. A. Saunders, A. E. Williams, and I. C. I., Ltd. (Dyestuffs Division), for the mass spectral data, P. A. Barfield and J. Lee for the nuclear magnetic spectral data, and N. Paddock and H. Pyszora for the magnetic and infrared spectral measurements, respectively.

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Received June 6, 1963. Part V of this series *(3)* previously published under the title "Cyclic Organic Compounds."

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch021

22

Cyclic Boron Compounds

VII. Cyclic Boroureas and Borocarbamates

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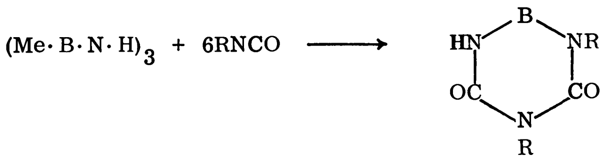
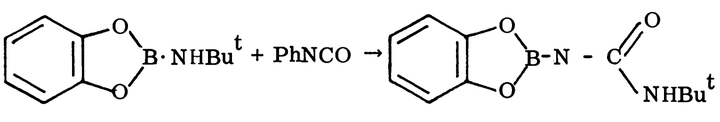
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch022

Cyclic boroureas have been prepared by reaction of phenyl isocyanate with either *B, B',B''*-tris (diethylamino)borazine, $(Et_2N \cdot B \cdot NEt)_3$, or *tert*-butylaminobis(diisopropylamino)borane, $(Pr^i_2N)_2B \cdot NHBu^t$. Similarly, from tris(*tert*-butylamino) borane, $B(NHBu^t)_3$, and carbon dioxide, a cyclic borocarbamate has been obtained. Analogous examples of aminoboration of phenyl isocyanate and phenyl isothiocyanate using tris(*tert*-butylamino) borane, affording acyclic derivatives, $B[N(Ph) \cdot C(:X) \cdot NHBu^t]_3$, (X = O or S), have been demonstrated. Structures have been confirmed by alcoholic degradations and infrared spectra. It is suggested that the mechanism of the reactions from aminoboranes involves successive addition and elimination steps.

While this work was in progress *(6)*, we became aware of the experiments of others, which also involve aminoboration of organic isocyanates and/or isothiocyanates. Thus, *B,B',B''*-trimethylborazine, (MeB·NH) , with isocyanates gave (Equation 1) cyclic boroureas *(4)*. This has been confirmed, although the possibility of various alternative and structurally isomeric species was recognized *(3)*. Other examples—e.g., Equation 2 *(6)*—of aminoboration of isocyanates and isothiocyanates have been described *(3, 6, 7, 8)*.



(1)

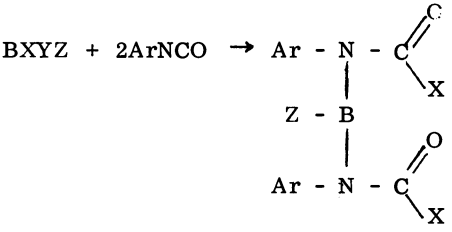


(2)

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch022

The present work also forms part of a program on the boration reactions of unsaturated compounds. Thus, initially it was shown that chloroboration and phenylboration of certain olefins could be effected *(10)*; and later, that this could be extended (Equation 3) to phenyl iso- and isothiocyanates *(12)*. Relevant to aminoborations are observations that aminostannanes, such as $Me_3Sn \cdot NMe_2$, and other metal- or metalloid-amino derivatives react—e.g., Equation 4—with many unsaturated compounds, including phenyl iso- and isothiocyanates, in an analogous fashion *(5, 9)*.



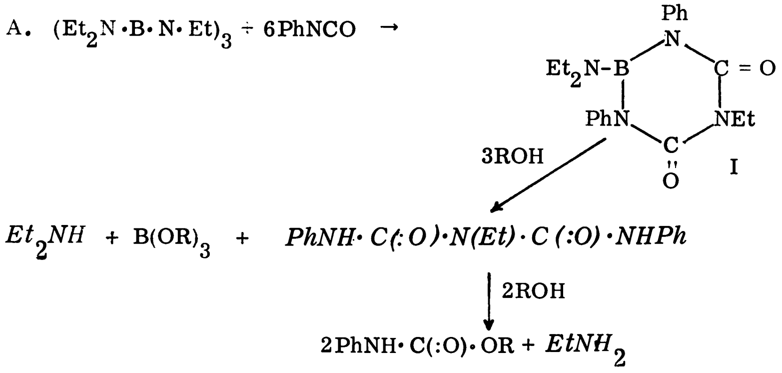
(3)

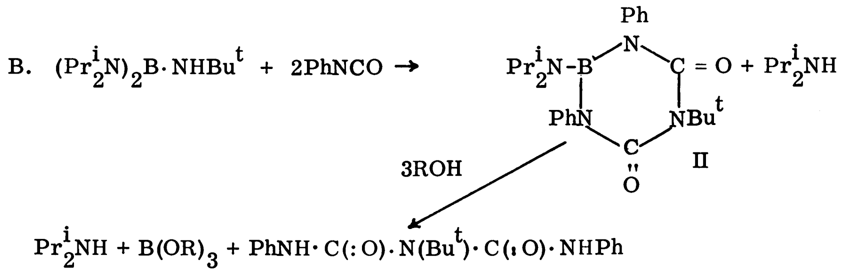
$$Me_3Sn \cdot NMe_2 + U = Q \rightarrow Me_3Sn - U - Q - NMe_2 \quad (4)$$

Acyclic boroureas *(13)* and borourethanes *(14)* have been made independently by other methods, the former from isocyanatoboranes and amines, and the latter from aminoboranes and organic urethanes.

Discussion

Reactions leading to cyclic boroureas and borocarbamates, and the alcoholic degradation of these species, are outlined in reaction schemes A to C; no attempt was made to isolate those compounds indicated in italics in scheme A.





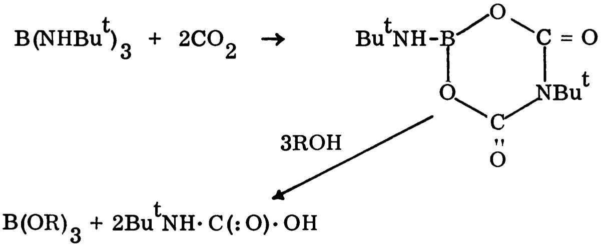
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch022

Table I.[a] Characterization of Boroureas,

Compound	*M.P., °C.*	*N-H Str., Cm.$^{-1}$*	*C-H Aromatic Str., Cm.$^{-1}$*	*C-H Aliphatic Str., Cm.$^{-1}$*	*C=O Str., Cm.$^{-1}$*
I	65-68		3040 sh	2976 vs 2933 sh	1704 sh 1626 vs
II	142-45		2941 s	2899 sh	1706 s 1667 vs
III	118-20	3413 sh 3367 s		2950 vs	1686 sh 1675 vs
IV, X=O	125-30	3387 s	3030 sh	2967 vs	1695 sh 1653 s
V, X=S	130-33	3289 s 3257 s	2967 s	2899 sh	

[a] bend. =bending mode, str. = stretching mode, sh = shoulder, s = strong, vs = very strong, w = weak.

C.



III

By contrast to scheme C, the aminoboration of phenyl iso- and isothiocyanate (scheme D), using tris(*tert*-butylamino)-borane, did not give cyclic boroureas or thioureas, but gave acyclic derivatives, which failed to cyclize (by elimination of *tert*-butylamine) upon pyrolysis. Even with a deficiency of phenyl isocyanate, all three *tert*-butylamino groups were replaced. Structure IV (X = O) was confirmed by alcoholysis of IV to afford *tert*-butylcarbanilide and orthoborate.

D. $B(NHBu^t)_3 + 3PhNCX \rightarrow B[N(Ph)\cdot C(:X)\cdot NHBu^t]_3$ IV

X = O or S

The contrasting results in (B) and (D) are attributed to the greater steric hindrance of replacement of Pr^i_2N- compared with Bu^tNH-, when either is attached to boron. Further examples of steric effects are our failure to observe any reaction between phenyl isocyanate and *B*-chloroborazines, e.g., with $(Cl\cdot B\cdot N\cdot R)_3$, R = Bu^n, Pr^i, or Ph; reflux after 48 hours. Similarly, it was noted *(15)* that $(Me_2N\cdot B\cdot NH)_3$ and phenyl isocyanate not only formed a ring compound analogous to I, but also gave V; while with phenyl isothiocyanate, the sulfur analog of V was the only product isolated. These results indicate that insertion re-

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Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

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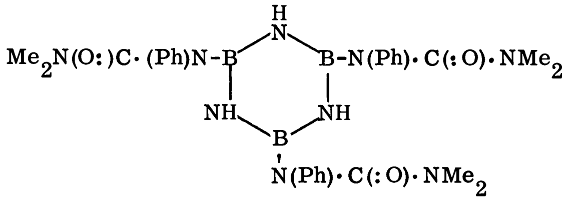
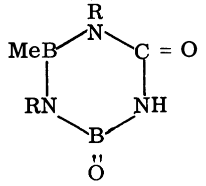
Borocarbamates, and a Dithioborocarbamate

C-C Ring Str., Cm.$^{-1}$	*B-N Str., Cm.$^{-1}$*	*Bu^t Bend, Cm.$^{-1}$*	*N-C Str., Cm.$^{-1}$*	*C-H Out-of Plane Bending, Cm.$^{-1}$*	
1595 vs	1439 vs		1250 w	752.7 vs 691.4 vs	
1590 vs 1575 s	1437 s	1370 s	1224 s	749.7 vs 689.7 vs	
		1389 vs	1205 s		B=O str. cm.$^{-1}$ 1359 s
1597 s	1449 s 1437 s	1389 s	1214 s	749.2 vs 691.1 vs	
1618 s 1600 s	1431 s	1389 s		716.7 vs 689.7 vs	C=S str? cm.$^{-1}$ 1198 s

actions into the $>B \cdot NMe_2$ bond are more facile than into the diethyl homolog.



V

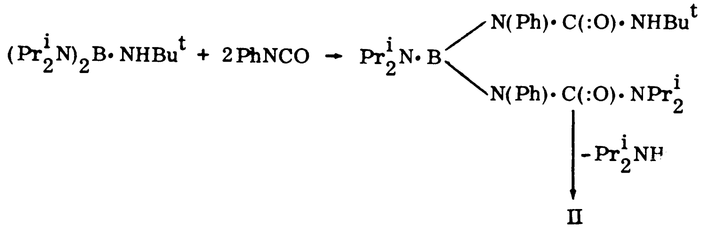


VI

Some characteristics of the new boron compounds are indicated in Table I.

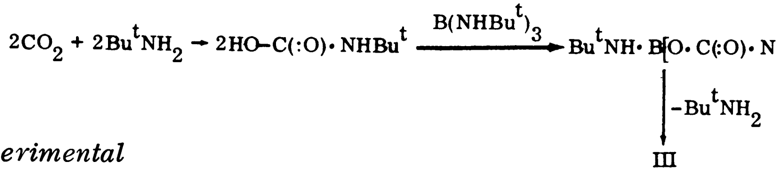
We regard the mechanism of these aminoboration reactions as involving successive addition and elimination steps. This is illustrated in two instances in schemes (E) and (F); in (F), traces of free amine were required for reaction to proceed. For this reason, we prefer, in absence of further experimental data, to formulate the product of Reaction 1 as VI, and not as indicated in Equation 1.

E.



$$(\mathrm{Pr^i_2N})_2\mathrm{B\cdot NHBu^t} + 2\mathrm{PhNCO} \rightarrow \mathrm{Pr^i_2N\cdot B}\begin{cases}\mathrm{N(Ph)\cdot C(:O)\cdot NHBu^t}\\ \mathrm{N(Ph)\cdot C(:O)\cdot NPr^i_2}\end{cases} \xrightarrow{-\mathrm{Pr^i_2NH}} \mathrm{II}$$

F.



$$2\mathrm{CO_2} + 2\mathrm{Bu^tNH_2} \rightarrow 2\mathrm{HO\text{-}C(:O)\cdot NHBu^t} \xrightarrow{\mathrm{B(NHBu^t)_3}} \mathrm{Bu^tNH\cdot B[O\cdot C(:O)\cdot NHBu^t]_2} \xrightarrow{-\mathrm{Bu^tNH_2}} \mathrm{III}$$

Experimental

Scheme A. Phenyl isocyanate (5·58 grams) was heated under reflux with the borazine (2·95 grams) *(2)* in light petroleum (30 ml.) (b.p. 60 - 80°) for 3 hours. On removal of solvent, the crude borourea (I) (8 20 grams), (m.p. 60 - 65°), was obtained. After recrystallization from benzene it had a melting point of 65 - 68° (Found: C, 68·3; H, 6·9; N, 15·1; B, 3·3%; MW. 352. $C_{20}H_{25}N_4O_2B$ requires C, 68·7; H, 7·0; N, 15·2; B, 3·2%; MW. 363).

1-Octanol (in excess) was added to I (1.95 grams). The mixture was refluxed for 1 hour. Distillation afforded tri-*n*-octoxyborane (2.05 grams, 95%), (b.p. 176°/0.4 mm., n_D^{20} 1.4384 (Found: B, 2.69. Calculated for $C_{24}H_{51}O_3B$:B, 2.72%) [Lappert *(11)* gives b.p. 174°/0.4 mm., n_D^{20} 1.4377]. From the solid residue, there was obtained *n*-octyl *N*-phenylcarbamate (2.40 grams, 90%) (m.p. 72 - 74°) (Found: N, 6.1. $C_4H_{23}NO_2$ requires N, 5.9%); this appears to be a new compound.

Scheme B. Two experiments were carried out, using an equimolar or a 1 to 2 molar ratio of borane to isocyanate. In both instances, the latter stoichiometry was established; only the former experiment is described.

tert-Butylamino-bis(diisopropylamino)borane (4·40 grams) *(2)* was heated under reflux with phenyl isocyanate (1·80 grams) in light petroleum (ca. 30 ml.) (b.p. 40 - 60°) for 4 hours. Only a small amount of product appeared to have been formed and solvent was therefore removed. Benzene (ca. 30 ml.) was then added, in order to enable a higher reflux temperature to be employed. After 3 hours further refluxing, the mixture was cooled, and addition of light petroleum (ca. 15 ml.) (b.p. 40 - 60°) precipitated the cyclic borourea (II) (2·8 grams, 90%) (m.p. 142 - 45°) (Found: C, 68·5; H, 7·5; N, 13·4; B, 2·72%; MW. 403. $C_{24}H_{33}N_4O_2B$ requires C, 69·0; H, 7·9; N, 13·3; B, 2·75%; MW. 420). Removal of volatiles from the filtrate led to recovery of the starting borane (2·30 grams).

A mixture of II (2·00 grams) and *n*-butanol (1·06 grams) was heated under reflux for 0.5 hour. Diisopropylamine (0·45 gram, 93%) (authentic infrared spectrum) was condensed at -78°/760 mm. A white solid crystallized, when the residue was cooled, and complete precipitation was effected by addition of light petroleum (ca. 5 ml.) (b.p. 40 - 60°). The solid was identified as *N*, *N'*-di-*tert*-butyl-biuret (1·40 grams, 88%)

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch022

(m.p. 137 - 40°) (Found: N, 13·7; $C_{18}H_{21}N_3O_2$ requires N, 13·5%); this appears to be a new compound. The filtrate afforded tri-*n*-butoxyborane (1·0 gram, 95%) (b.p. 95°/5 mm., n_D^{20} 1·4094) (Found: B, 4·68. Calculated for $C_{12}H_{27}O_3B$: B, 4·72%) [Lappert *(11)* gives b.p. 115°/15 mm., n_D^{20} 1·4085].

Scheme C. Solid carbon dioxide (in excess) was washed with light petroleum and added to tris-(*tert*-butylamino) borane (4·00 grams) at 20°. Initially there appeared to be no reaction, but addition of a trace of *tert*-butylamine resulted in the exothermal formation of a white solid. The mixture was shaken for 0.5 hours with light petroleum and the cyclic borocarbamate (III) (4·15 grams, 96%) (m.p. 118 - 20°) (Found: C, 49·8; H, 7·4; N, 11·6; B, 4·45. $C_{10}H_{19}N_2O_4B$ requires C, 49·6; H, 7·9; N, 11·6; B, 4·50%) was thus obtained.

To compound III (5·40 grams), 1-butanol (4·80 grams) was added and the mixture was refluxed for 1 hour, while volatile material was collected in a trap at -78°. There was thus obtained tri-*n*-butoxyborane 4·90 grams, 95%) (b.p. 110°/10 mm., n_D^{20} 1·4081) (Found: B, 4·72%), while in the trap was isolated the white solid *N*-*tert*-butylcarbamic acid, identical to a specimen produced from *tert*-butylamine and carbon dioxide.

Scheme D (X = O). Two experiments were carried out, using 1 to 2 and 1 to 3 molar ratios of borane to isocyanate. In both instances, the latter stoichiometry was established; only the former experiment is described.

The borane (3·00 grams) was dissolved in light petroleum (ca. 40 ml.) (b.p. 40 - 60°). Addition of phenyl isocyanate was exothermal; the mixture was heated under reflux for 3 hours. The acyclic borourea (IV; X = O) (4·4 grams, 85%) (m.p. 125 - 30°) (Found: C, 67·9; H, 8·4; N, 14·3; B, 1·95%; MW. 541. $C_{33}H_{45}N_6O_3B$ requires C, 68·0; H, 7·7; N, 14·4; B, 1·88%; MW. 584) was obtained by filtration and recrystallization from benzene. From the filtrate, tris-(*tert*-butylamino) borane (1·00 gram) (authentic infrared spectrum) was obtained.

Compound IV (X = O) (3·20 grams) was heated under reflux with 1-butanol (1·20 grams) for 1 hour. Precipitation was completed, after cooling the mixture, by addition of light petroleum. *N*-*tert*-butyl-*N'*-phenylurea (2·7 grams, 86%) (m.p. 148 - 50°) (Found: N, 14.4. $C_{11}H_{14}N_2O$ requires N, 14·7%) was thus obtained; it appears to be a new compound. From the filtrate, tri-*n*-butoxyborane (1·00 gram, 80%) (n_D^{20} 1·4096) (Found: B, 4·70%) was recovered.

Compound IV (X = O) was recovered substantially unchanged after being heated at 120°/0·02 mm., for 2 hours.

Scheme D (X = S). A mixture of the borane (2·60 grams) and phenyl isothiocyanate (3·10 grams) in light petroleum (ca. 40 ml.) (b.p. 40 - 60°) was heated under reflux for 3 hours. No reaction appeared to have taken place, so the solvent was removed and the residue was heated under reflux for a further 2 hours. After the resulting solid had been cooled and recrystallized from benzene, there was obtained the acyclic borothiourea (IV; X = S) (4·40 grams, 77%) (m.p. 130 - 33°) (Found: C, 62·5; H, 8·4; N, 12·9; S, 14·9. $C_{33}H_{45}N_6S_3B$ requires C, 62·5; H, 7·2; N, 13·1; S, 15·1%).

Physical Measurements

Molecular weights were determined using a Mechrolab molecular weight bridge, Model 310A (based on the lowering of the vapor pressure). Infrared spectra were taken on a Perkin-Elmer PE 21 instrument, using sodium chloride optics.

Acknowledgment

Most of the work described in this paper was carried out with generous support which we gratefully acknowledge, from the Office of Aerospace Research, U.S. Air Force, through its European Office.

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Received June 6, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch022

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

23

Heteroaromatic Boron Compounds

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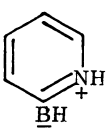
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

This paper reviews the chemistry of a new class of heteroaromatic compounds containing boron atoms as components of six-membered aromatic rings; over twenty ring systems of this kind have been reported during the last five years. These compounds are of a different order of stability to any previously known organic compounds of boron and their discovery has opened up a whole new field of heteroaromatic chemistry. Boron can now be regarded as a respectable "organic" element.

Organoboron chemistry has been a somewhat neglected field, mainly because the majority of such compounds are unpleasant to handle. The situation has been transformed in recent years by the discovery of a new class of heteroaromatic compounds containing boron atoms as components of six-membered aromatic rings, and resembling normal organic compounds in their chemical stability. Nearly all the work so far reported in this field has been carried out by the author and his colleagues, first at Queen Mary College in the University of London, and later at the University of Chicago. The purpose of this paper is to give a brief summary of the field *(1)* and an account of recent unpublished work.

Basic Principles

Since the B^- and N^+ ions are isoelectronic with neutral carbon atoms, one can derive from any "normal" aromatic compound a series of isoelectronic heterocycles by replacing two carbon atoms, one by B^- and the other by N^+. For example, benzene can give rise to three isoelectronic compounds (I, II, and III), which like benzene itself should be aromatic and highly resonance-stabilized.



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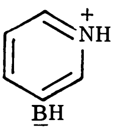

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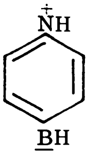

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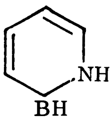

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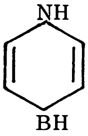

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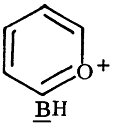


(VI)

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Of these three isomers, I and III should be most stable, since uncharged resonance structures (IV and V) can be written for them; the isomer (III) is mesoionic. Further, one would expect I to be more stable than III, since the resonance responsible for its aromaticity involves a smaller separation of charge. These predictions are supported by the available evidence; no derivatives of II have yet been reported, and the few known compounds containing the ring system III are less stable than those containing I.

It should also be possible to replace the nitrogen atoms in compounds of this kind by other analogous heteroatoms—e.g., oxygen or sulfur; however, one would expect such compounds—e.g., VI—to be less stable than the nitrogen-containing analogs. The aromaticity involves a separation of charge, represented by the contribution of dipolar resonance structures — e.g., I, VI; such contributions should be less important in the case of structures containing $>O^+$ or $>S^+$ than $>NH$.

These ideas are not new. Borazine and the common form of boron nitride have long been regarded as heteroaromatic analogs of benzene and graphite, in which all the carbon atoms have been replaced by B^--N^+ pairs. However, no other ring systems of this kind were reported until five years ago.

Nomenclature

The compounds described in this article present a problem of nomenclature which was not envisaged when the present rules were devised.

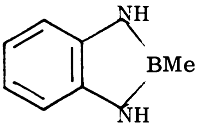
It is natural to name a heteroaromatic compound after the isoconjugate hydrocarbon from which it is derived, by using prefixes to describe the extra heteroatoms. In the usual system the prefixes *bora*, *aza*, *thia*, *oxa*, etc., imply replacement of a methine group (CH) by the corresponding heteroatom. This is quite satisfactory in the case of the usual heteroatoms (O, N, S) since these contain more valence electrons than carbon; neutral heterocycles containing these atoms are derived from hydrocarbons by replacing neutral carbon atoms by ions N^+, O^+, etc., and this is equivalent to replacing the neutral group CH by a neutral atom, N, O, etc.

This does not work in the case of boron, because boron contains fewer valence electrons than carbon. Heteroaromatic boron compounds are derived from hydrocarbons by replacing carbon atoms by B^-. The prefix *bora* cannot be used to describe this. Thus current nomenclature would describe I as 1,2-azaboradihydrobenzene; such a name would obscure its aromatic character and relationship to benzene.

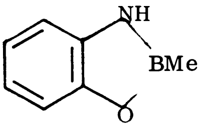
The compounds in question are derived from normal aromatic compounds by replacing two carbon atoms, one by B^-, the other by N^+, O^+, etc. R. S. Cahn has suggested that such a compound be named after the parent aromatic system, using the two normal prefixes followed by an extra prefix, *aro*; to emphasize the departure from normal nomenclature, and in the interests of euphony, the order of the two prefixes is inverted. Thus I would be named 2,1-*borazarobenzene*. We have adopted this system of nomenclature. We have also adopted Cahn's suggestion that the parent monocyclic ring system (I) be named *borazarene*. The corresponding oxygen compound (VI) would then be named *boroxarene*.

Compounds Containing Boron Linked to Two Heteroatoms

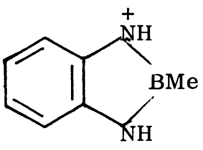
The first known heteroaromatic boron compounds (other than borazine or boron nitride) were reported in 1957 by Ulmschneider and Goubeau *(38)*. They obtained VII and VIII by heating trimethylboron with *o*-phenylenediamine and *o*-aminophenol, respectively. Ulmschneider and Goubeau did not study the properties of VII and VIII and apparently failed to realize their theoretical interest. The compounds should be aromatic, being iso-π-electronic with indole and benzofuran (cf. the zwitterionic resonance structures, IX and X).



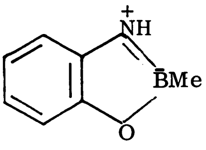
VII



VIII

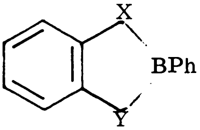


IX

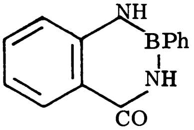


X

Shortly after this a series of analogous 2-phenyl derivatives (XI) was reported by Dewar, Kubba, and Pettit *(20)*, who obtained them from the appropriate *o*-disubstituted benzene and phenylboron dichloride. They noted that the compounds were far more resistant to hydrolysis than analogous open-chain derivatives of phenylboronic acid—e.g., PhB(NHPh)$_2$. They attributed the difference to aromatic stabilization of the ring compounds, this also being indicated by the resemblance of the ultraviolet spectra of XI to those of analogous "normal" aromatics e.g., indole, benzthiazole.



XI: X, Y = O, S, NH



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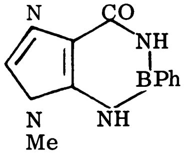

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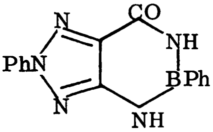
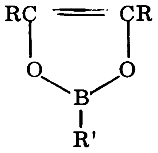
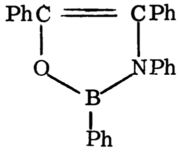


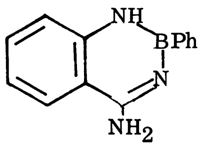
XIV



XV: R = Ph, Me
R' = Ph, Me$_2$CH



XVI



XVII

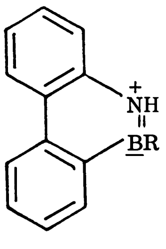
Since then a large number of analogous compounds have been prepared by condensing boronic acids, or derivatives of boronic acids, with suitable compounds containing two functional groups—e.g., the quinazolone analogs (XII) *(1)*, the purine analogs (XIII) *(1)*, the aza-purine analogs (XIV) *(1)*, and the furan analogs (XV) *(29, 39)* and (XVI) *(35)*. All these compounds are isoconjugate with normal aromatics, and all contain boron atoms flanked by heteroatoms in the boron-containing ring. All these compounds are more resistant to hydrolysis than are analogous open-chain analogs; nevertheless they are by no means stable to hydrolysis. The only compound of this type that is not attacked by water alone, let alone by acid or base, is 1-amino-3-phenyl-4,3-borazaroisoquinoline (XVII), which is reported *(39)* to crystallize unchanged from boiling water. Therefore although these compounds are interesting, they differ very much in chemical stability from "normal" aromatic systems.

The rest of this article will be concerned with compounds where one of the ring atoms adjacent to boron is carbon; these show chemical stability of an altogether different order.

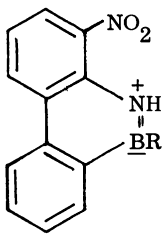
Compounds Related to 10,9-Borazarophenanthrene

The first compounds of this kind to be prepared were a series of derivatives (XVIII) of 10,9-borazarophenanthrene *(19)*. Condensation of 2-aminobiphenyl with boron trichloride and aluminum chloride gave 10-chloro-10,9-borazarophenanthrene (XVIIIa). The reaction presumably involves a Friedel-Crafts cyclization of an intermediate arylaminoboron dichloride, $ArNHBCl_2$, being the first case reported of a Friedel-Crafts reaction involving a boron chloride. Hydrolysis of XVIIIa gave the corresponding hydroxy derivative (XVIIIb), while reaction with Grignard reagents or lithium aluminum hydride gave alkyl—e.g., XVIIIc or aryl—e.g., XVIIId—derivatives, or the parent 10,9-borazarophenanthrene (XVIIIe).

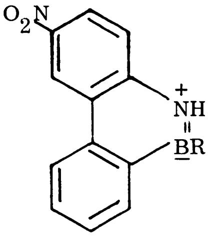
In this synthesis the boron trichloride could be replaced by phenylboron dichloride, giving XVIIId directly. Later we *(11)* found that the hydroxyl group in XVIIIb could be replaced directly by treating XVIIIb with Grignard reagents or lithium aluminum hydride; this unusual reaction provides the best route to the 9-alkyl or 9-aryl derivatives, or



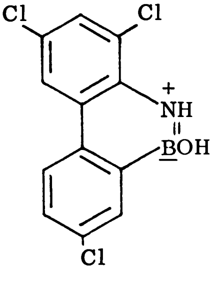
XVIII: a, R=Cl
b, R=OH
c, R=CH$_3$
d, R=Ph
e, R=H



XIX: R=OH, CH$_3$



XX: R = OH, CH$_3$



XXI

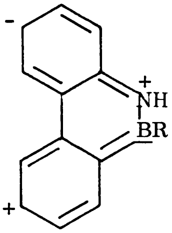
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

to the parent compound (XVIIe), since XVIIIb is easier to handle and purify than XVIIIa (in which the chlorine is very reactive and very easily hydrolyzed).

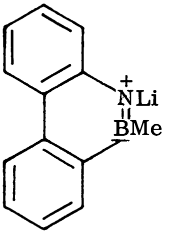
These compounds showed stability of a different order to any previously known organic compounds of boron. Thus XVIIIa-d resisted attack by boiling 40% potash or boiling concentrated hydrochloric acid. The parent compound (XVIIIe) is hydrolyzed easily to XVIIIb; however, it is unusually inert for a boron hydride, failing to react with carbonyl compounds or acid chlorides.

Nitration of XVIIIb or XVIIIc gave *(18)* a mixture of the isomeric mononitro derivatives; these proved to be the 6- (XIX) and 8- (XX) isomers, in agreement with predictions of reactivity made using a molecular orbital treatment. This treatment predicted that the 2-position should be the third most reactive; chlorination *(16)* of XVIIIb gave first the 6,8-dichloro derivative, and then the 2,6,8-trichloro derivative (XXI), confirming this prediction also. Similar orientation was observed *(15)* in Friedel-Crafts acetylation of XVIIb or XVIIIc.

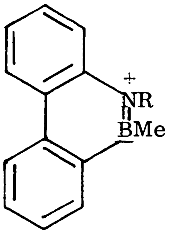
The dipole moment of XVIIIc is very small [0.16 *D* *(28)*]. This seems at first sight to imply that the dipolar structures indicated in XVIII are unimportant and that resonance effects in the central ring of XVIII must be small. This, however, is not so. Molecular orbital calculations indicate that XVIII should have only a very small dipole moment, but at the same time a large resonance energy. The polarity due to the N→B dative π-bond is balanced by polarization of the π-electrons in the terminal benzene rings. This can be represented in resonance notation by contribution by structures such as XXII.



XXII

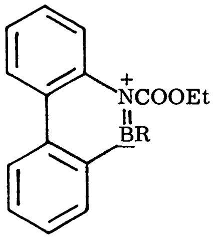


XXIII

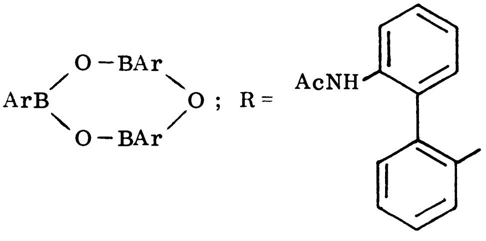


XXIV

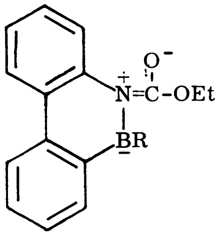
Reaction of 10-methyl-10,9-borazarophenanthrene (XVIIIc) with methyllithium gave the *N*-lithio derivative (XXIII) *(23)*; this with alkyl halides or sulfates has provided a series of N-substituted borazarophenanthrenes (XXIV) *(17, 23, 24)*. These, like XVIII, are stable to aerial oxidation or hydrolysis. On the other hand the urethanes (XXV), prepared *(24)* likewise, oxidize rapidly in air to a product formulated as XXVI. This result indicates that the stability of XVIII cannot be due merely to the fact that the boron atom forms part of a ring; the stability must be due to a resonance stabilization which is weakened when a +*E* group–e.g., -COOEt–is attached to nitrogen, owing to the cross conjugation indicated by the resonance structure (XXVII). A similar explanation probably accounts for the rapid conversion *(22)* of XVIIIb to the diazonium ion (XXVIII) on treatment with sodium nitrite in acetic acid; presumably the *N*-nitroso derivative (XXIX) is first formed and breaks down to XXVIII, the B-N bond in XXIX being weakened by cross conjugation.



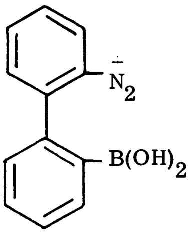
XXV: R=Me, Ph



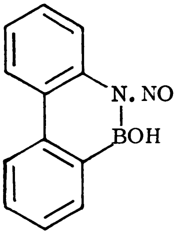
XXVI



XXVII

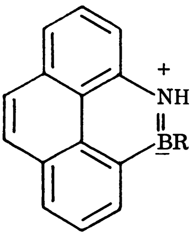


XXVIII



XXIX

The method of synthesis used to prepare XVIII can be extended to analogous benzo derivatives. In this way the following compounds have been obtained *(4)*, by heating appropriate derivatives of 2-aminobiphenyl with boron trichloride or phenylboron dichloride in presence of aluminum chloride. Full details will be given elsewhere in due course. In each case a number of derivatives, with various groups attached to boron, were prepared by the methods indicated above.



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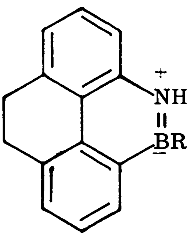
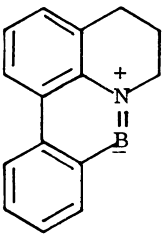
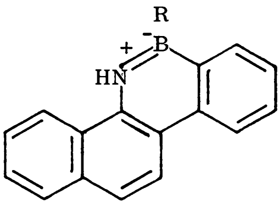


XXXI

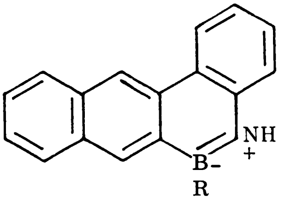


XXXII

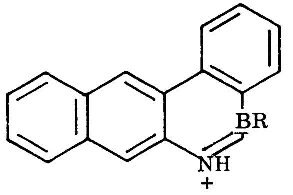


XXXIII

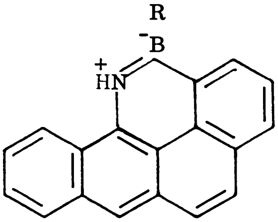
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023



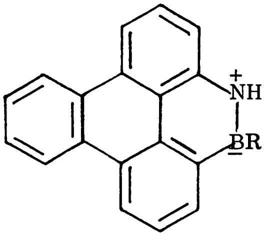
XXXIV



XXXV

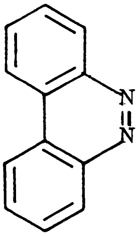


XXXVI

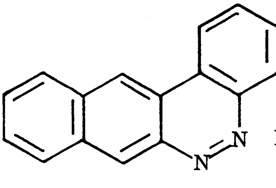


XXXVII

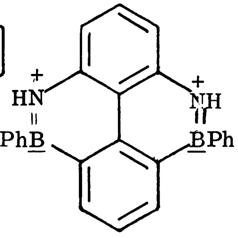
The borazarobenz[*a*]anthracene (XXXIV) was prepared from 2(*o*-aminophenyl)naphthalene; here the cyclization could have taken place in the 1- position, giving a borazarochrysene isomeric with XXXIII. The structure of XXXIV was established by an amusing degradation *(26)*, which incidentally provides a novel and very convenient route to polycyclic benzocinnolines. Treatment of XVIIIc with nitrous acid leads, as we have seen, to a diazonium salt (XXVIII) in which the B-N bond is broken; if this is allowed to stand in acetic acid solution, boric acid is expelled and benzo[*c*]cinnoline (XXXVIII) is formed almost quantitatively by an internal diazo-coupling reaction. The same reaction applied to XXXIV or XXXV gave the same dibenzo[*c, g*] cinnoline (XXXIX), proving the structure of XXXIV. This synthesis of benzocinnolines is superior to those previously described, since the starting materials are more accessible.



XXXVIII

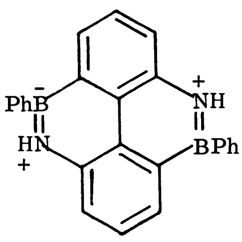


XXXIX

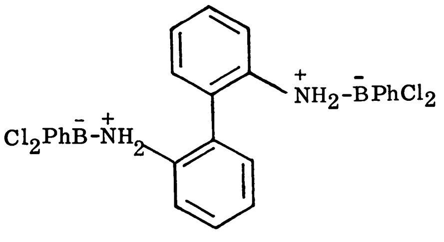


XL

This general synthetic route has also been used to prepare *(2)* a compound containing two boron atoms, 5,9-diphenyl-5,9-dibora-4,10-diazaropyrene (XL), by heating 2,6-diaminobiphenyl with 2 moles of phenylboron dichloride in the presence of aluminum chloride. Attempts to prepare the isomeric compound (XLI) from 2,2'-diaminobiphenyl failed; presumably coordination of the nitrogen atoms with the phenylboron dichloride in the intermediate (XLII) leads to deactivation of both rings of the biphenyl nucleus.



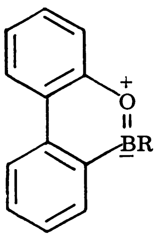
XLI



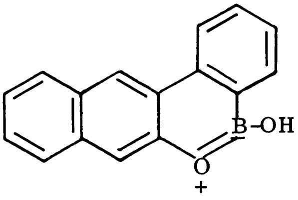
XLII

Compounds Related to 10, 9-Boroxarophenanthrene

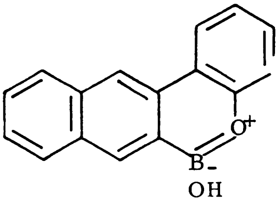
The first compound of this type, 10-hydroxy-10, 9-boroxarophenanthrene (XLIIIa), was first prepared *(9)* by heating 2-hydroxybiphenyl with boron trichloride and aluminum chloride, followed by hydrolysis. The same compound was later obtained *(22)* from XVIIIc by diazotization in acetic acid and by pouring the resulting solution of XXVIII into boiling water. This second method of synthesis has also been used to prepare the benzo derivatives (XLIV and XLV) from the corresponding hydroxyborazarobenz[*a*]anthracenes (XXXIV and XXXV).



XLIII; a, R = OH
b, R = Ph



XLIV

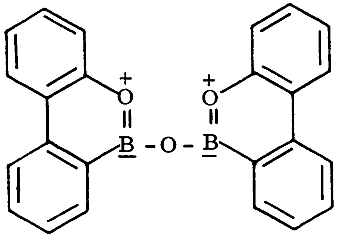


XLV

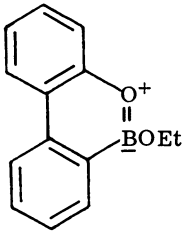
The spectra of these compounds resemble those of the isoconjugate borazarene derivatives, but the oxygen-containing ring systems are certainly less aromatic. Thus 10-phenyl-10, 9-boroxarophenanthrene (XLIIIb) can be prepared *(9)* by treating the corresponding chloride with phenyllithium in a nitrogen atmosphere, but it is rapidly oxidized to XLIIIa by air. The corresponding borazarophenanthrene (XVIIId) is not attacked by air even on prolonged exposure. As was pointed out above, derivatives of boroxarene would be expected to be less aromatic than corresponding derivatives of borazarene.

Ether Formation in B-Hydroxy Compounds

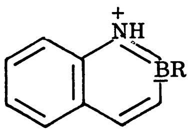
In the previous sections a number of compounds have for convenience been formulated as *B*-hydroxy derivatives, although they exist as such only in solution. The majority on isolation form ethers or anhydrides by loss of water. Thus XLIIIa on isolation forms the ether or anhydride (XLVI) *(9)*. This reaction has of course numerous counterparts in boron chemistry. One also finds, as might be expected, that nucleophilic displacements on boron occur very easily. Thus the B-hydroxy compounds (or their anhydrides) can be converted to ethers simply by recrystallization from the corresponding alcohol — e.g., XLIIIa is converted by crystallization from ethanol into 10-ethoxy-10,9-boroxarophenanthrene (XLVII) *(9)*. The ethers are likewise hydrolyzed to their components with extreme ease and can be preserved only in the absence of water.



XLVI



XLVII



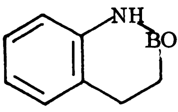
XLVIII a, R=Cl
b, R=Ph
c, R=OH
d, R=OR'
e, R=Me
f, R=H

Compounds Derived from 2,1-Borazaronaphthalene

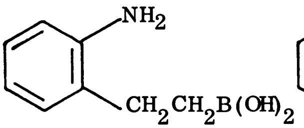
The method of synthesis described above is applicable only to derivatives of 10,9-borazarophenanthrene. However, a similar synthesis can be used to make compounds containing only one ring fused with borazarene. When *o*-aminostyrene was heated with boron trichloride or phenylboron dichloride in the absence of a catalyst, 2-chloro-(XLVIIIa) or 2-phenyl- (XVIIIb) 2,1-borazaronaphthalene was formed in good yield *(8)*. Hydrolysis of XLVIIIa gave the 2-hydroxy derivative (XLVIIIc), isolated as its anhydride, which could be converted to ethers (XLVIIId) by recrystallization from alcohols. Treatment of the anhydride or the ethers with alkyl or aryllithium gave the corresponding 2-alkyl or 2-aryl derivatives — e.g., XLVIIIb, e — while reaction with lithium aluminum hydride gave the parent compound, 2,1-borazaronaphthalene (XLVIIIf).

These compounds again showed extraordinary stability to hydrolysis by hot concentrated alkali or acid, except for XLVIIIf, where hydrolysis of the borohydride grouping took place. This chemical stability was shown *(10)* to be due to resonance stabilization rather than to the mere presence of a cyclic structure by reduction of XLVIIIc to the dihydro derivative (XLIX); XLIX, unlike XLVIIIc, was hydrolyzed immediately by cold dilute acid or alkali, giving the aminophenylethylboronic acid (L). Reduction leaves the boron-containing ring of XLVIII intact, but of course destroys any aromatic character it may have.

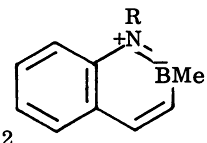
The reactions of XLVIII have not been studied in as much detail as have been those of the 10,9-boroazarophenanthrenes. A number of N-alkyl derivatives (LI) have been prepared *(17)* via the N-lithio



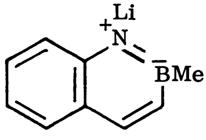
XLIX



L

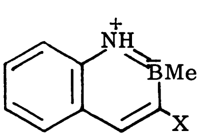


LI

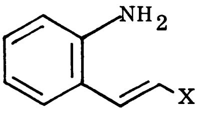


LII

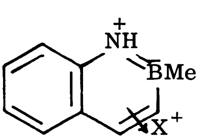
derivative (LII), itself prepared from XLVIIIe with methyllithium, while bromination or chlorination of XLVIIIe in acetic acid has been shown *(10)* to give a mixture of the 3-bromo- or 3-chloro derivative (LIII) together with the trans-ω-halo-*o*-aminostyrene (LIV). It is difficult to explain this orientation in terms of the conventional mechanism for electrophilic substitution; for molecular orbital calculations do not indicate a uniquely high reactivity at the 3- position in XLVIII. We believe that a π-complex (LV) is first formed by attack on the 3,4- bond, the bond order of which is much greater than that of any bond in the benzenoid ring; rearrangement of LV gives the isomeric arenonium ion (LVI) which can either lose a proton to form LIII, or react as indicated with acetic acid to give LIV.



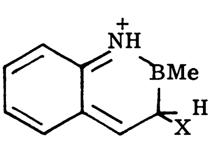
LIII. X = Cl, Br



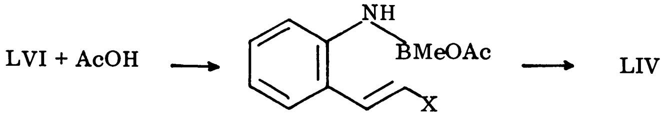
LIV. X = Cl, Br



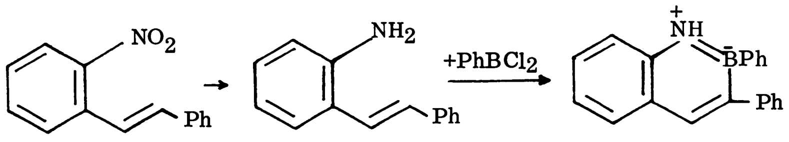
LV. X = Cl, Br



LVI. X = Cl, Br

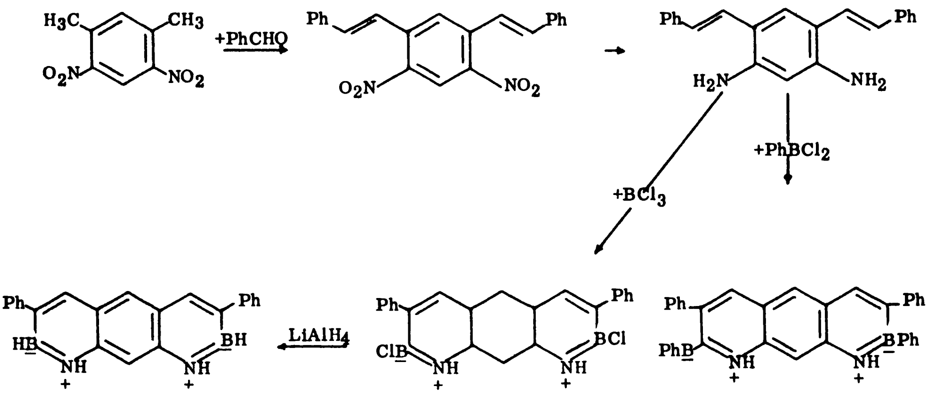


The method of synthesis used to make XLVIII has been extended to a few other compounds. Thus 2,3-diphenyl-2,1-borazaronaphthalene (LVII) has been prepared *(14)*, by the route:



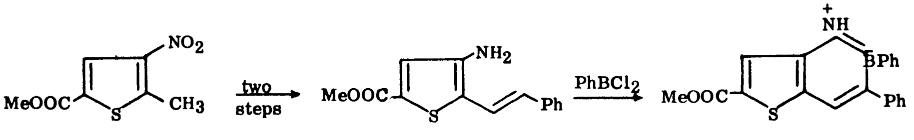
LVII

A similar synthesis was used *(2)* to prepare derivatives (LVIII, LIX) of 2,7-dibora-1,8-diazaroanthracene from 2,4-dinitro-*m*-xylene:



LVIII LIX

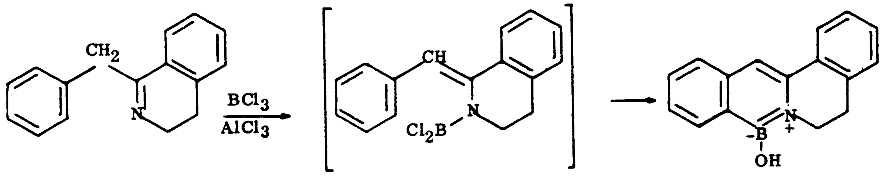
The following reactions led *(25)* to a derivative (LX) of 5,4-borazarobenzothiophene, the first known compound containing a second heteroaromatic ring fused to borazarene.



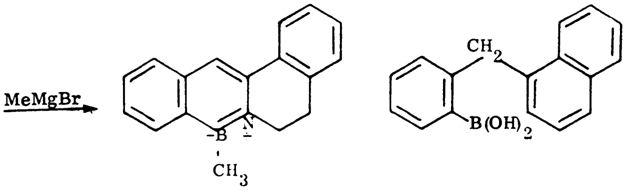
LX

Compounds with Heteroatoms at Bridgeheads

An interesting modification of the Friedel-Crafts cyclization procedure was provided by the following synthesis *(14)* of 7-hydroxy- (LXIII) and 7-methyl-7,16-borazaro-5,6-dihydrobenz [*a*]anthracene (LXIV):



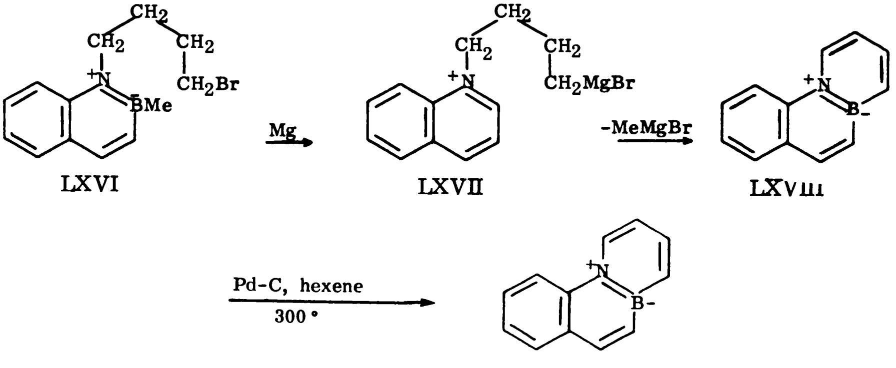
LXI LXII LXIII



LXIV LXV

Attempts to dehydrogenate LXIV failed; this ring system seems relatively unstable, probably undergoing facile hydrolysis and isomerization to LXV. Attempts to cyclize 1-benzylisoquinoline or 2-benzylpyridine in a similar manner failed to give any new compounds.

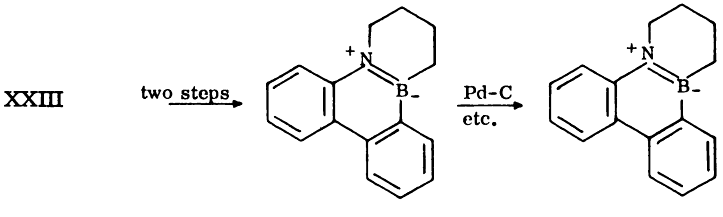
The first heteroaromatic compound of this kind to be prepared, with boron and/or nitrogen at the bridgehead between two aromatic rings, was 12,11-borazarophenanthrene (LXIX) *(14)*. Condensation of the *N*-lithio derivative (LII) with 1,4-dibromobutane gave 1(4-bromo-1-butyl) 2-methyl-2,1-borazaronaphthalene (LXVI). The corresponding Grignard reagent (LXVII) underwent cyclization with elimination of methylmagnesium bromide to 1,2,3,4-tetrahydro-12, 11-borazarophenanthrene (LXVIII), which could be dehydrogenated over palladized charcoal to LXIX. This seems to be a stable aromatic system; we are studying its properties in detail. The cyclization of LXVII to LXVIII is an interesting disproportionation reaction, presumably facilitated by the ease with which boron undergoes nucleophilic attack. The reaction must be reversible and almost thermoneutral; the driving force is presumably the gain in translational entropy when one molecule of LXVII is replaced by two molecules, one of LXVIII and one of methylmagnesium bromide. The dehydrogenation of LXVIII to LXIX took place surprisingly easily and in good yield.



LXVI LXVII LXVIII

LXIX

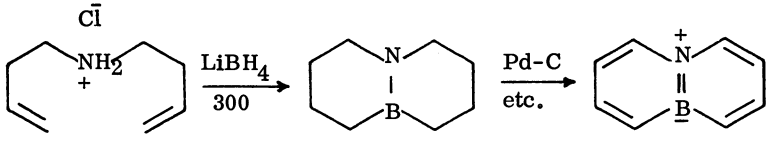
A similar series of reactions, starting with 10-methyl-9-lithio-10, 9-borazarophenanthrene (XXIII), has given *(6)* 15,14-borazarotriphenylene (LXXI) vis the 1,2,3,4-tetrahydro derivative (LXX). This again seems to be a stable aromatic molecule.



LXX LXXI

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

The parent system, 10,9-borazaronaphthalene (LXXIV), has probably also been synthesized *(3)* by the following route:

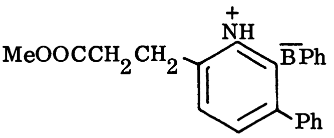


LXXII LXXIII LXXIV

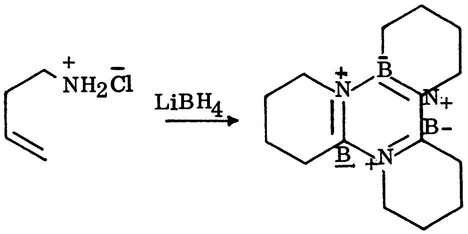
Bis(1-Δ_3-butenyl)amine hydrochloride (LXXII) when heated under pressure with lithium borohydride gave 1,2,3,4,5,6,7,8-octahydro-10,9-borazaronaphthalene (LXXIII). Dehydrogenation of LXXIII on a small scale over palladized charcoal in hexene at 300° gave a crystalline solid with an odor very similar to that of naphthalene. The synthesis is being repeated on a larger scale in order to characterize the product.

Borazarene

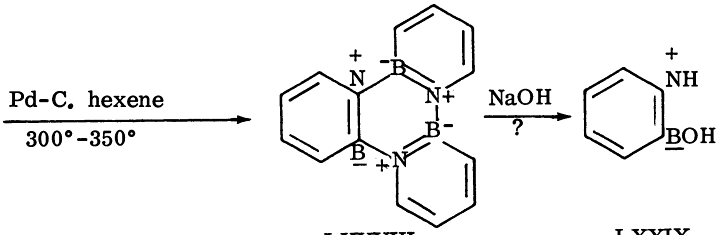
One derivative of the parent monocyclic ring system, borazarene (I), has been definitely characterized *(25)*. Desulfurization of LX over Raney nickel under carefully controlled conditions gave the diphenylborazarylpropionic ester (LXXV). Preliminary experiments indicated that this compound is stable to acid or alkali, implying that it is aromatic — as theory would suggest.



LXXV



LXXVI LXXVII

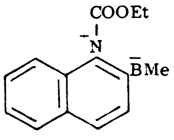


LXXVIII LXXIX

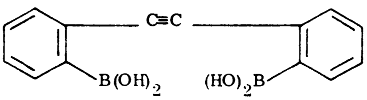
A second synthesis, which should be of much more general applicability, is indicated above *(3)*. When 4-amino-1-butene hydrochloride was heated under pressure with lithium aluminum hydride, 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-14, 16,18-tribora-13,15,16-triazarotriphenylene (LXXVII) was formed. Dehydrogenation of LXXVII over palladized charcoal in hexene at 300° to 350° C. gave 14,16,18-tribora-13,15,17-triazarotriphenylene (LXXVII), the ultraviolet spectrum of which was very similar to that of triphenylene. This characteristic spectrum disappeared when LXXVII was treated with cold dilute alkali. Since LXXVIII is a borazine derivative, and should therefore undergo hydrolytic fission, and since the borazarene ring system seems to be stable to mild alkaline hydrolysis, judging by the behavior of LXXV, it seems almost certain that LXXVIII must have undergone fission to 3 molecules of 2-hydroxyborazarene (LXXIX). The synthesis is being repeated on a large scale in order that the product may be isolated and characterized.

Boron-Containing Analogs of Naphthalene, Quinoline, and Isoquinoline

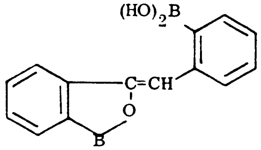
The preparation of 2,1-borazaronaphthalene was described above; attempts to make the corresponding boroxaronaphthalene have failed. The 2,1-borazaronaphthalene system is, as might be expected, considerably more stable and less reactive than 10,9-borazarophenanthrene. The corresponding urethane *(17)* (LXX) was stable in air, unlike XXV, and the parent compound (XLVIIIa) was much less easily oxidized than was XVIIIe. Likewise the borazaronaphthalenes failed to react with nitrous acid. Attempts to prepare 2,1-boroxaronaphthalene from boron trichloride or phenylboron dichloride with *o*-hydroxystyrene gave only tars.



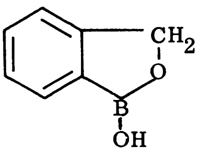
LXXX



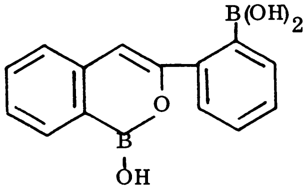
LXXXI



LXXXII



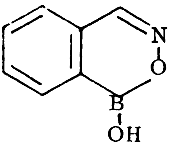
LXXXIII

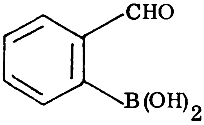


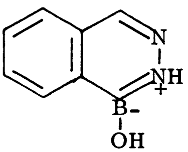
LXXXIV

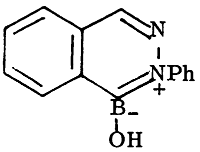
A derivative of the isomeric 1,2-boroxaronaphthalene has, however, probably been prepared. Letsinger and Nazy *(30)* found that tolan-2,2'-diboronic acid (LXXXI) isomerized in presence of alkali to a compound which they formulated as LXXXII, by analogy with boronophthalide (LXXXIII) *(37)*. However, it seems *(9)* more likely that the compound was in fact the isomeric *o*-3(1-hydroxy-1,2-boroxaronaphthyl)benzeneboronic acid (LXXXIV).

An analogous boroxaroisoquinoline (LXXXV) has been reported by Snyder, Reedy, and Lennarz *(37)*, who obtained it by the action of hydroxylamine on *o*-formylboronic acid (LXXXVI). They did not describe its properties or comment on the possibility that it might be aromatic. We have re-examined the compound and find that it is resistant to hydrolysis, although its acid properties indicate that it is only weakly aromatic (see below). Since borazaro compounds should be more stable than analogous boroxaro ones, we studied the reaction between LXXXVI and hydrazine *(12)*. As we had anticipated, the product, 4-hydroxy-4,3-borazaroisoquinoline (LXXXVII), was a highly aromatic compound, completely resistant to hydrolysis and behaving as a protic acid rather than a Lewis acid (see below). The hydroxyl group in LXXXVII could be replaced by methyl or hydrogen in the usual way, and nitration of LXXXVII gave in good yield a mixture of mononitro derivatives. Phenylhydrazine likewise reacted with LXXXVI to give an almost quantitative yield of 3-phenyl-4-hydroxy-4,3-borazaroisoquinoline (LXXXVII).

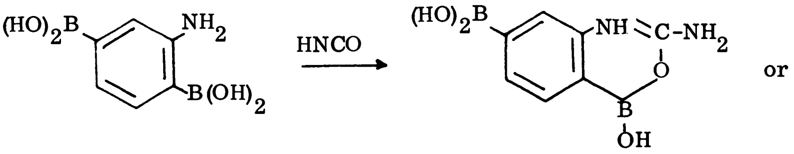

LXXXV


LXXXVI

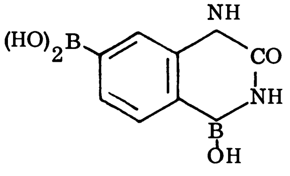

LXXXVIII

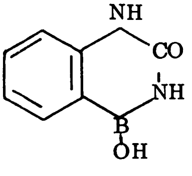

LXXXVIII

A few derivatives of 4,3-borazaroquinoline have also been prepared. Soloway obtained a compound by the route indicated below, which he formulated as either LXXXIX or XC; he preferred the latter structure—which certainly seems the more likely on theoretical grounds *(36)*. We have made the analogous 4-hydroxy-4,3-borazaro-2-quinoline (XCI) both by Soloway's method from *o*-nitrobenzeneboronic acid, and by Friedel-Crafts cyclization of the adduct from phenylurea and boron tribromide in the presence of aluminum bromide. These compounds seem to show only feeble aromaticity, as might be expected from analogy with quinazolone; the amide resonance in compounds of this type decreases the aromaticity of the ring.



LXXXIX

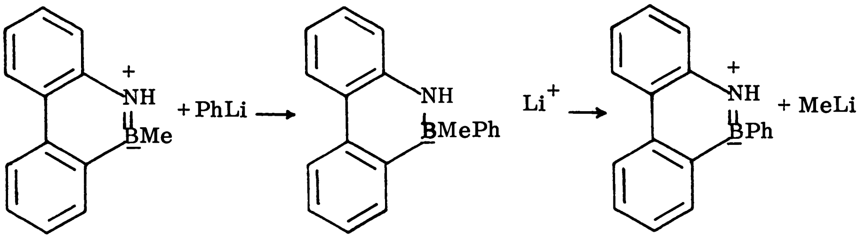

XC


XCI

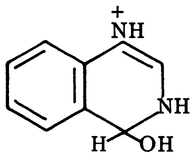
Acidic Properties

All derivatives of boric acid previously described have behaved as Lewis acids. One of the most interesting features of the new compounds we have been making is that their *B*-hydroxy derivatives in most cases behave as protic acids. Thus the spectra of 10-hydroxy-10,9-borazarophenanthrene (XVIIIb), or of 2-hydroxy-2,1-borazaronaphthalene (XLVIIIc), in alcohol or in alkali are almost identical, implying that salt formation takes place by loss of a proton from the hydroxyl group rather than by coordination of base onto boron. Likewise the analogous compounds with alkyl or aryl attached to boron — e.g., XVIIIc, XLVIIIb — show no acid properties in alcoholic solution; while with very strong bases they form salts by loss of a proton from nitrogen (cf. XXIII) rather than by coordination of the base with boron.

Undoubtedly coordination of bases with boron is possible, since nucleophilic displacements of groups attached to boron are often observed; thus the replacement *(23)* of methyl by phenyl when XVIIIc is treated with phenyllithium presumably takes place in the following way:



XCII



XCIII

However, the intermediate coordination compounds — e.g., XCII — are unstable, just as are the corresponding intermediates formed during nucleophilic substitutions in "normal" aromatic compounds — e.g., in the alkaline hydrolysis of *p*-nitrochlorobenzene.

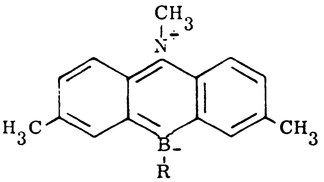
Spectroscopic evidence indicates that 10-hydroxy-10,9-boroxarophenanthrene (XLIIIa) also behaves as a protic acid; the ultraviolet spectrum of XLIIIa in ethanol shows a characteristic double peak at about 300 mμ, which is shifted to lower frequences by addition of alkali; the absorption is almost unaffected by addition of mannitol. This is a striking result; for XLIII seems to be much less aromatic than the corresponding borazarophenanthrene (XVIIIb), and yet the mesomerism in the central ring is sufficient to hinder coordination of bases onto the boron atom. Borazaro analogs of hydrocarbons must be highly aromatic. The same situation seems to hold in the case of 4,3-borazaroisoquinoline, the 4-hydroxy derivative (LXXXVII) of which is also a protic acid.

The borazaroquinolone system (XCI) would be expected to be less aromatic than borazaroisoquinoline for two reasons. First, the 1,3-orientation of the nitrogen atoms must be unfavorable from analogy with quinazoline, which with dilute acid forms salts containing the ion (XCIII); if nucleophilic addition can occur so readily here, it must also occur readily in 4,3-borazaroquinolones — e.g., XCI. Secondly, a hydroxy group in the 2- position should still further reduce the aromaticity, judging by comparison of quinazolone with quinazoline. Addition of mannitol led *(13)* to a marked increase in acidity in the case of 4-hydroxy-4,3-borazaro-2-quinolone (XCI), suggesting that the compound was behaving as a Lewis acid. The same was true of the hydroxyboroxaroisoquinoline (LXXXV), which should be less aromatic than the nitrogen analog (LXXXVII). Both compounds also show a marked hypsochromic shift of their ultraviolet spectra when dissolved in alkali.

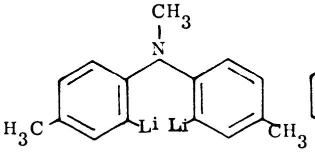
An increase in acidity on addition of mannitol does not necessarily in itself indicate that boron is behaving as a Lewis acid. Thus the hydroxyboroxarophenanthrene (XLIIIa) also shows a small increase in acidity in the presence of mannitol, although here the spectroscopic evidence indicates unequivocally that it is still behaving predominantly as a protic acid.

Derivatives of 4, 1-Borazarene and Boroxarene

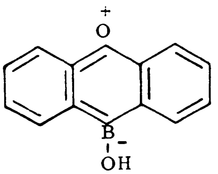
As was pointed out above, 4,1-borazarene (III) and the corresponding boroxarene should be less stable than their 2,1-isomers (I and VI). So far only two ring systems have been described containing such structures. Maitlis *(32)* prepared 10-phenyl- (XCIVa) and 10-hydroxy- (XCIVb) 3,6,9-trimethyl-10,9-borazaroanthracene from bis(2'-lithio-*p*-tolyl)*N*-methylamine (XCV) with phenylboron dichloride, or with boron trichloride followed by hydrolysis; while Davidson and French *(5)* obtained 10-hydroxy-10,9-boroxaroanthracene (XCVI) in a similar way from 2,2'-dilithiodiphenyl ether. These compounds were very much less aromatic than any of the derivatives of borazarene. They showed characteristic absorption bands in the long wave region which disappeared on addition of alkali, implying that they act as Lewis acids. Even the *B*-phenyl derivative (XCIVa) behaved likewise.



XCIV: a, R=Ph
b, R=OH



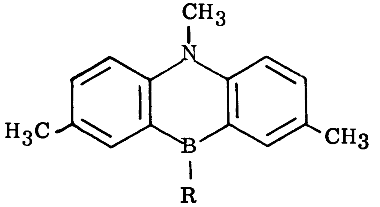
XCV



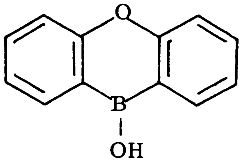
XCVI

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

It is of course true that the central ring of anthracene is only weakly aromatic, judging by the ease with which anthracene is converted to 9,10-dihydro derivatives; the low aromaticity of XCIV and XCVI may be due largely to this, combined with the unfavorable charge separation involved in the zwitterionic structures (XCIV and XCVI). These compounds probably approximate closely to the uncharged classical structures (XCVII and XCVIII).



XCVII



XCVIII

Ultraviolet Spectra

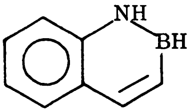
Alternant hydrocarbons normally show four electronic transitions in the long wave region, due to π-π^* transitions of electrons between the two highest occupied and two lowest unoccupied molecular orbitals. The two intermediate transitions are, however, degenerate in a simple m.o. model; first-order *(33)* configuration interaction between them leads to a splitting, two distinct bands appearing in the ultraviolet-visible spectrum. Of these the one at longer wavelengths has a low extinction coefficient (L_b band), due to a cancellation of transition moments, the band at shorter wavelengths being correspondingly strengthened. This interpretation, which was given some time ago by Dewar and Longuet-Higgins *(21)*, seems to have been generally accepted.

Consider now a heteroaromatic compound, isoconjugate with such a hydrocarbon. The heteroatoms can influence the energies of π-m.o.'s and π-π^* transitions in three ways.

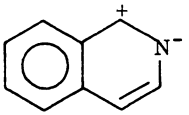
First, there is the effect of the difference in electronegativity between heteroatoms and carbon; a simple perturbation treatment *(31)* shows that this should have little effect on the transition energies. The first and fourth transitions (L_a, B_a) should be unaffected, to a first approximation at least, while although the degeneracy of the second and third transitions will be removed, the mean of their transition energies should remain approximately unchanged.

Secondly, the removal of the degeneracy between the second and third transitions should reduce the configuration interaction between them. This will reduce the splitting of the two levels concerned, but this will be balanced by the fact that the unmixed states are no longer degenerate. The net result should be that the L_b and B_b bands remain almost unchanged in wavelength, but that the extinction coefficient of the weak L_b band should be greatly increased.

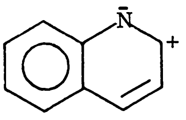
Thirdly, the introduction of heteroatoms will alter the resonance integrals of the bonds containing them. This effect is probably not important in itself; for the resonance integrals of π-bonds involving various combinations of B, C, and N probably do not differ greatly from one another. A much more important factor is likely to be the change in bond orders and bond lengths due to the uneven sharing of π-electrons. This can be represented in resonance notation as an increase in the importance of ionic excited structures with a corresponding decrease in the bond orders of associated bonds. The effect should be particularly large in derivatives of borazarene, where the "ionic" structures are in fact neutral and the unexcited structures zwitterionic. Thus in 2, 1-borazaronaphthalene there must be a large contribution to the ground state by the neutral structure (XCIX); as a result the bond orders of the C-B, B-N, and N-C bonds must be low. (This intuition is confirmed by m. o. calculations; see below.) The resulting decrease in the bond resonance integrals will lead to changes in the π-π* transition energies.



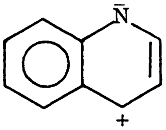
XCIX



C



CI



CII

One might further predict that the spectrum of 2, 1-borazaronaphthalene should resemble more closely that of isoquinoline than that of quinoline; for in isoquinoline the ionic structures (C) are much the most important—and these are iso-π-electronic with XCIX. In the case of quinoline structures CI and CII should be of comparable importance according to simple resonance theory, and in CII the 2, 3-bond is double.

These somewhat intuitive arguments seem to be supported by the available evidence. Thus Figure 1 compares the spectra of naphthalene, isoquinoline, and 2, 1-borazaronaphthalene; the resemblance between the last two spectra is very striking. There is an equally striking correspondence between the spectra of phenanthridine and 10, 9-borazarophenanthrene, and of 4,3-borazaroisoquinoline and quinazoline.

Similar relationships seem to hold between the spectra of the other boron heteroaromatics and those of analogous hydrocarbons and nitrogen heterocycles. An interesting comparison is provided by the spectra of 10, 9-borazarophenanthrene (XVIIIe) and 12, 11-borazarophenanthrene (LXIX) (Figure 2); the spectra of these isomeric compounds are similar but show significant shifts in the wavelengths of the absorption bands. This would be expected, since the bond orders of corresponding bonds in the two isomers must differ.

Other Physical Properties

The new heteroaromatic compounds described above are very interesting from a theoretical point of view. The π-electron distribu-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

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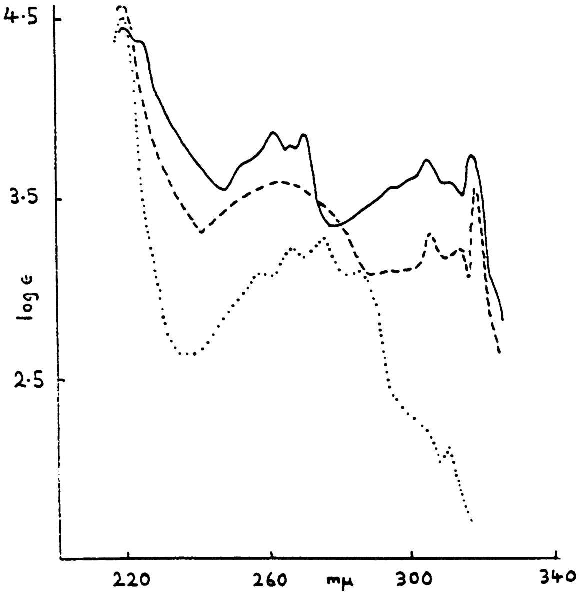


Figure 1. Ultraviolet absorption spectra in cyclohexane of 2, 1-borazaronaphthalene (_____), isoquinoline (_ _ _ _), and naphthalene (. . . .)

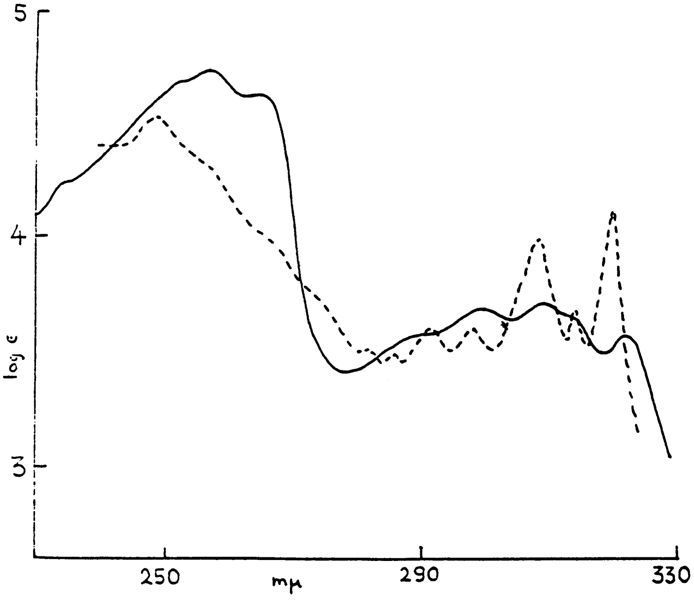


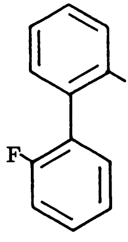
Figure 2. Ultraviolet absorption spectra of 12, 11-borazarophenanthrene (_____) and 10, 9-borazarophenanthrene (_ _ _ _)

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

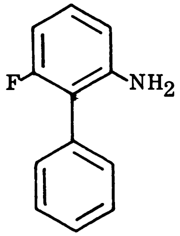
tions in them are strongly perturbed in comparison with "normal" aromatic systems, and they therefore provide an excellent testing ground for chemical theory. Various properties are therefore being studied for comparison with theoretical prediction; reference has already been made to work of this kind on chemical reactivity, dipole moments, and light absorption.

Another line of investigation that could be of interest in this connection is provided by nuclear magnetic resonance spectroscopy. An ideal approach would be to study the chemical shifts of C^{13} in various positions in the rings; for these could be directly related to the π-electron distributions. Unfortunately the synthetic difficulties involved would be excessive. However, information of a very similar kind can be obtained by studies of NMR spectra of atoms attached at various positions in the ring. For this purpose fluorine seems ideal, the chemical shifts being large enough to make spin coupling and ring current effects relatively unimportant. We have therefore been studying chemical shifts in the fluorine NMR spectra of a large variety of monofluoro derivatives of various aromatic compounds, including hydrocarbons and nitrogen heterocycles.

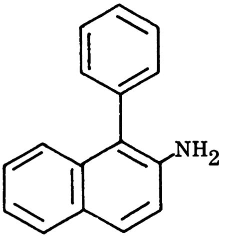
As part of this program, we have made and examined a number of monofluoro derivatives of 10-methyl-10,9-borazarophenanthrene (XVIIIe). These were prepared in the usual way from the corresponding fluoro-2-aminobiphenyls. No difficulty was encountered in preparing the 2-, 6-, or 7-fluoro derivatives of XVIIIc. Cyclization of 2-amino-3'-fluorobiphenyl gave only a single product; this must surely have been the 3-fluoro derivative rather than the 1-fluoro, since the Friedel-Crafts cyclization with boron trichloride is an electrophilic substitution and since fluorine is strongly para-directing in such reactions. Attempts to cyclize 2'-fluoro- (CIII) or 6-fluoro- (CIV) 2-aminobiphenyl failed, presumably because of steric hindrance between the ortho-fluorine and the ortho-hydrogen in the other ring; similar difficulties were encountered in attempts to prepare borazaro derivatives of benzo[*c*]phenanthrene from 2-amino- (CV) 2'-amino- (CVI) 1-phenylnaphthalene.



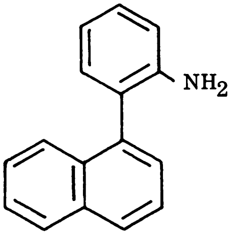
CIII



CIV



CV



CVI

Preliminary evaluation of these data suggests that the fluorine NMR results should be very useful in assessing and developing m.o. theories of π-electron systems.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
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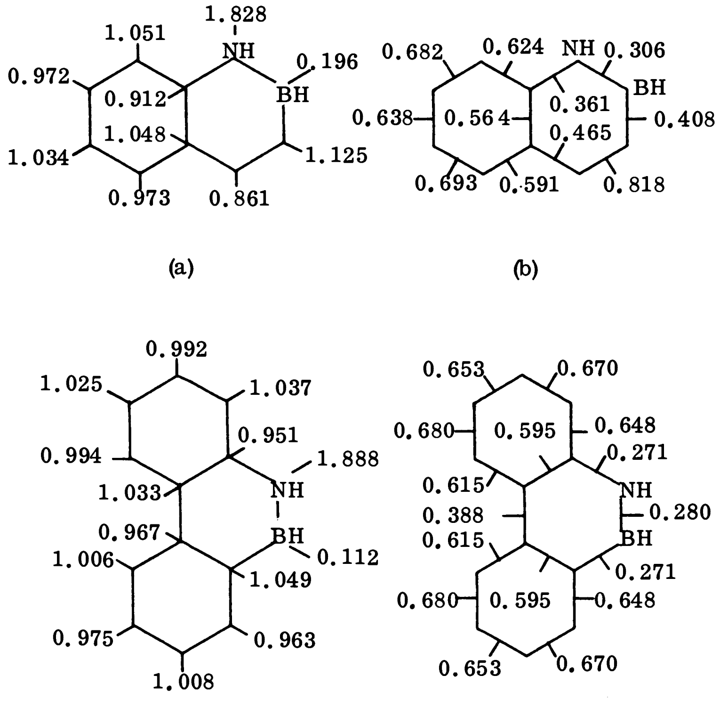
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

Molecular Orbital Treatment

The simple Hückel m.o. method is of doubtful value for molecules containing heteroatoms, for reasons which are well known. We have nevertheless carried out calculations of this kind for several of our boron-containing aromatics in the hope that the results might be of some interest. The necessary parameters were fixed *(27)* by fitting the ionization potentials of several of the compounds, the ionization potentials being deduced from the charge transfer spectra of molecular complexes formed by them with *s*-trinitrobenzene or tetracyanoethylene. The exact values of the parameters should not affect the results qualitatively — and one certainly cannot attach any quantitative significance to calculations of this kind. Figure 3 shows the charge densities and bond orders calculated in this way for 2,1-borazaronaphthalene and for 10,9-borazarophenanthrene.



(a) (b)

(c) (d)

Figure 3. Charge densities (a, c) and bond orders (b, d) in 2, 1-borazaronaphthalene (a, b) and 10, 9-borazarophenanthrene (c, d)

The calculated formal charges on nitrogen and boron are small (< 0.2 *e*); in resonance terminology, the uncharged resonance structures are the most important. Nevertheless the resonance energies calculated for the boron-containing rings are appreciable; that for the borazaronaphthalene is the greater, in agreement with the chemical evidence that this is the more stable system of the two.

The charge distributions in 10,9-borazarophenanthrene are interesting; if they are used as an index of reactivity to electrophilic reagents, we arrive at a correct prediction that reactivity should be greatest in the 6- and 8-positions, the latter predominating, and that the 2- position should be next most reactive, but some way behind the first two. Calculations of localization energies lead to the same predicted order of reactivity, as we have seen.

Electrophilic substitution in 2,1-borazaronaphthalene takes place almost exclusively in the 3- position. The localization energies in this ring system are greatest for the 3- and 8- positions, the values for both being almost identical; on the other hand the charge density at the 3- position is much greater than at any other point in the molecule. Other examples are known where charge density is a better guide to reactivity than localization energy, in the case of very reactive molecules containing heteroatoms. In this case, however, the exclusive attack in the 3- position could be due to the initial formation of a π-complex between the reagent and the borazaronaphthalene, as was suggested above; π-complex formation should take place preferentially at the 3,4- bond, the order of which is much higher than that of any other bond in the molecule.

The Hückel method is not satisfactory for molecules containing heteroatoms; it would be much better to use some kind of s.c.f. treatment for molecules of this kind. The best approach would seem to be some modification of the Pople *(34)* approximation, and we hope to develop a satisfactory general treatment of conjugated systems along these lines. The physical and chemical properties of our new boron-containing aromatics are proving very helpful in this connection, since they provide a very stringent test, the π-electron distributions in them being very nonuniform (cf. Figure 3).

Acknowledgment

Most of the work described in this paper was carried out with support from the Army Office of Ordnance Research, the National Institutes of Health, U. S. Public Health Service, the National Science Foundation, and the U. S. Atomic Energy Commission.

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Received May 13, 1963. Report prepared with support from the Army Office of Ordnance Research. For a more detailed review of work up to the end of 1961, see *(7)*.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch023

LCAO-MO Calculations on Boron Compounds

II. Borazines

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch024

Molecular orbital calculations for borazines using an LCAO technique have been performed in the framework of the following approximations: Hückel, Pariser-Parr (without iteration), and Pople (iterated to self-consistency utilizing the Pariser-Parr approximations for the integrals). Several theoretical models for choice of input parameters have been utilized. Modified values for boron electron-repulsion integrals, which take into account electron correlation effects, have been calculated for each choice of theoretical model. Comparison of the calculated LCAO-MO-SCF results for molecular energy levels against known experimental data and examination of the magnitude of the terms of the final SCF Hamiltonian matrix to be diagonalized indicated a reasonable choice for a calculational model.

For conjugated molecules with a planar nuclear framework, it is possible to separate the atomic orbitals into noncombining classes, π and σ, according to whether or not they have a node in the nuclear plane.

One of the methods extensively used in the quantum mechanical study of the π-electrons of conjugated molecules is the semiempirical molecular orbital theory developed by Hückel. According to this theory the mobile electrons can be treated as occupying a set of delocalized molecular orbitals, eigenfunctions of a one-electron Hamiltonian representing the kinetic energy, the field of the nuclei, and the smoothed out distribution of the other electrons. By approximating the orbitals as linear combinations of atomic orbitals centered on the various atoms and estimating certain integrals empirically, the theory has been developed in a simple form enabling it to be applied to a wide range of molecules *(3,19)*.

However, although it has the merit of great simplicity, the Hückel procedure has serious defects, connected with the difficulty of precisely defining the one-electron Hamiltonian. Strictly speaking, the problem should be formulated in terms of the complete many-electron Hamiltonian in which the interelectronic repulsions are included explicitly *(6,15)*

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch024

The Pariser-Parr and Pople theories start from this π-electron approximation, in which the π-electrons are treated separately from the rest, and it is supposed that the effect of the σ-electrons on the π-structure can be represented by a "core" in whose potential the π-electrons move *(13,15)*. The potential of an atom contributing to the core represents that due to the nuclear charge and to all the σ-electrons associated with the atom.

The molecular orbital equations rigorously derived from the correct many-electron Hamiltonian are simplified by a series of systematic approximations and reduce to equations comparable with those used in the semiempirical method based on an incompletely defined one-electron Hamiltonian, but the Pariser-Parr and Pople equations differ in that they include certain important terms representing electronic interaction. In the Pople method these systematic integral approximations are applied to the self-consistent equations of Roothaan *(16)*.

Recent studies of heterocyclic systems by the Roothaan self-consistent field (SCF) technique have provided a justification for the Hückel method and at the same time indicated suitable values for and demonstrated origins of the various parameters arising in the Hückel method *(1)*. One example is that the SCF analog of the familiar Hückel Coulomb integral, α, is identified with the diagonal element of the final SCF Hamiltonian to be diagonalized. This analogy is of considerable use in the present studies.

Borazine

Borazine (formerly called borazole) has been called "inorganic benzene" because of its similarity in both structure and physical properties to benzene, with which it is isoelectronic. Many of its properties are believed to arise from the "π" system of this molecule.

Mulliken had postulated that on theoretical grounds a one-to-one correspondence and close resemblance between the electron configuration and over-all states of borazine and benzene are to be expected *(7,14)*. Mulliken and Roothaan performed a semiempirical Hückel-type calculation of borazine and compared the results with the observed ultraviolet spectrum *(17)*. By taking a reasonable value for the difference in electronegativity of boron and nitrogen, they obtained a value of β in fair agreement with theoretical expectations.

In the intervening years since Mulliken's Hückel calculation on borazine, the Pariser-Parr and Pople methods for calculations of the electronic structures of π-systems based on the correct many-electron Hamiltonian have been used successfully for calculations on many organic π-systems.

At the Centre de Méchanique Ondulatoire Appliquée, there is a general research program on the applicability and validity of the Pariser-Parr and Pople calculations for various types of molecules, including alternant and nonalternant hydrocarbons and heterocyclics. It was of interest to treat borazine by these methods, in order to develop a theoretical calculational model for B-N bonds in π-systems.

Details of Calculations

Molecular orbital calculations for borazines using a linear combination of atomic orbitals (LCAO) technique have been performed in the framework of the following three approximations:

Hückel
Pariser-Parr
Pople

These calculations were carried out on the IBM 7090 in Paris and the IBM 7094 at the Martin Co. Computing Center in Baltimore with the aid of an entirely automatic program written by G. Besis, Centre de Méchanique Ondulatoire Appliquée.

The most difficult part of the borazine calculation was the choice of a theoretical model from which to evaluate the necessary input parameters for the Pariser-Parr and Pople calculations.

Model I. It seemed preferable to try to treat borazine as the other heteroatomic compounds had been treated (without imposing a preconceived notion of what one imagined the bonding in borazine should be). After inspecting the results of the preliminary calculations, it would then be possible to modify the σ-core, if necessary, for agreement with experimental observations.

In view of the fair success of Mulliken's Hückel calculation and the relationship of Hückel to SCF calculations, a model for the Pariser-Parr and Pople calculations was chosen which was an analog of the original Mulliken model. The physical implications of this model with respect to bonding in the σ- and π-frameworks of borazine are discussed below, after the results of the calculation are presented.

The Mulliken model required uniquely that the π-electron would see a potential on the boron or the nitrogen atom approximately equivalent to that which a π-electron in a free neutral boron or nitrogen atom would see. (That this Model I is contradictory to the popular notion that borazine is composed of B^- and N^+ atoms is obvious. B^-atom denotes the original valence state of the boron atom from which the borazine is considered to be formed — namely, B^- has three electrons in its σ-frame and a fourth extra electron which it donates to the π-system. N^+ denotes the original valence state in which N has only three electrons in its σ-framework and a fourth which it donates to the π-system. However, this Model I is surprisingly close to what appears to be a fairly accurate representation of the true molecular binding, both σ and π, of borazine.)

The basic parameters necessary for the calculations are the valence state ionization potentials of the boron and nitrogen, modified values for the one-center two-electron repulsion integrals which include a correction for electron correlation, and correspondingly scaled values for the two-center two-electron repulsion integrals. For these modified one-center two-electron repulsion integrals $(pp|pp)$, simple expressions had been derived by Pariser and Parr for carbon and nitrogen:

$$(pp|pp) = I - A$$

where I = valence state ionization potential and A = valence state electron affinity.

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These expressions were later shown to be the leading term of a more exact expression which could be derived from spectroscopic term values *(9)*. However, because boron originally has less than a half-filled shell, the above expression was shown not to be valid for the *(pp|pp)* of boron and the modified value for the one-center two-electron repulsion integral of boron (7.094 e.v.) was derived exactly from the complete expansion in spectroscopic term values *(10)*. The two-center two-electron repulsion integrals were then scaled as usual.

In calculations of this type β is usually treated as an empirical parameter. To pick a reasonable value of β for the preliminary calculations, the suggestion of Kubo that $\frac{\beta_{BN}}{\beta_{CC}} = \frac{S_{BN}}{S_{CC}}$ was followed (where S is the magnitude of the overlap integral) *(20)*. It also would have been possible to evaluate β from the observed ultraviolet spectrum of borazine and the energy formulas Pariser and Parr give for *s*-triazine, which has the same symmetry, but these formulas are critically dependent on the values of the one- and two-center electron repulsion integrals. For this reason β was not evaluated by this second procedure for the preliminary calculation.

Calculational Results. There are several points at which SCF calculations of benzene and borazine must bear a definite predetermined relationship to each other, in order to reproduce the observed experimental similarities of the two molecules.

Ionization Potentials. The ionization potential of borazine was measured by electron impact as 10.3 ± 0.2 e.v., and the ionization potential of benzene was measured as 9.6 ± 0.2 e.v. *(12)*. The ionization potential of benzene is known to be due to removal of a π-electron. It seems probable that the ionization potential of borazine is also due to removal of an electron from its π-system, since to remove an electron from a B-H or N-H bond is known to require more energy *(11)* (at least 12.4 e.v. are necessary to remove an electron from a B-H bond and an estimated 17 e.v. are necessary to remove an electron from an N-H bond), and to remove an electron from the B-N σ-framework can reasonably be postulated to require more energy, because to remove an electron from a σ-bond is known to require 1.14 e.v. more than to remove an electron from a π-bond between the same two types of atoms.

The ionization potential of an electron from a π-system is proportional to the energy of the highest occupied molecular orbital (HOMO) plus a correction factor. For hydrocarbons the SCF calculated energy of the highest occupied molecular orbital plus 2 e.v. is equivalent to the measured electron impact ionization potential. Therefore, the SCF calculated energy of the HOMO of benzene should be about -11.6 ± 0.2 e.v., and that of borazine, -12.3 ± 0.2 e.v. The SCF calculational result for the HOMO of benzene was -11.58 e.v. and for borazine, -11.84 e.v. These results are in reasonably good agreement with expectation.

To verify the absolute magnitudes of the calculated energy levels, ionization potentials are of more value than ultraviolet spectra, which can only give differences between energy levels.

Comparison of Diagonal Terms in Final SCF Hamiltonian. The analog of the Hückel Coulomb integral, α, is the diagonal term in the final SCF matrix. The entire final SCF Hamiltonians for both benzene and borazine were calculated. The diagonal term for benzene (-5.96 e.v.) is equivalent to α_C in a Hückel calculation. The corresponding terms in borazine for boron and nitrogen (-2.32 and -9.23 e.v.) are equivalent to α_B and α_N in the Hückel calculations. To fulfill the condition that this SCF calculation for borazine is really a good approximation to Mulliken's calculation, α_B should be about the same amount greater than α_C that α_N is less than α_C. This condition is moderately satisfied. More important is that these differences also be close to the $\beta_{\text{Hückel}}$ to satisfy the following conditions:

$$\alpha_B = \alpha_C - \beta$$

$$\alpha_N = \alpha_C + \beta$$

The value of $\beta_{\text{Hückel}}$ to be used in comparisons of this type is -4.8 e.v. Therefore, these SCF calculations seem to indicate that Model I is a reasonably good approximation for a theoretical calculational model of borazine.

Physical Implications. This model for the π-system of borazine implies certain definite conclusions about the σ-framework of borazine, since the effective potential of an atom in the core is due to both its nuclear charge and its σ-electrons.

At first thought, to have a π-electron in borazine see a potential as if it were in a neutral boron or nitrogen atom might be construed to suggest that there is no σ-framework connecting the boron and nitrogen. However, this is not the case. Rather, it has been reported very recently that in cases where a covalent-type bond exists between boron and nitrogen, such as in $X_3B{:}NY_3$ compounds, experimental dipole moments show that even in these compounds there is virtually no charge transfer from nitrogen to boron *(8)*. Similarly, in a true covalent B-N bond, the greater electronegativity of the nitrogen would be expected to lead to the result that the most of the electron density in a B-N σ-bond will be on the nitrogen atom.

The final calculated π-electron density shows π-electron charges of 0.478 on boron and 1.522 on nitrogen. This is coupled with σ-electron densities in which σ-electron charge has been transferred from the boron to the nitrogen.

It is gratifying that this model, which was originally chosen solely on the basis of the properties required to satisfy the conditions for calculations on the π-system of borazine, reproduces very well the behavior to be anticipated for both the σ- and π-systems of this molecule.

Model II. As a check on the sensitivity of the calculations to the choice of a theoretical model, it was desirable to have an SCF calculation for borazine based on the "fashionable" B^- - N^+ model.

One previous SCF calculation of this type had been attempted by Davies *(4)*. However, he carried out this calculation in terms of $\Delta\omega$, differences in diagonal elements of the final SCF Hamiltonian, and ΔG, differences in repulsion integrals, without committing himself to their absolute values.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch024

In order to have a valid comparison of an SCF calculation of this Model II with that of Model I, a complete SCF calculation was performed for a B^- - N^+ model of borazine. The effective Slater nuclear charges used correspond to B^- and N^+ and the electron repulsion integrals were those calculated rigorously for the B^- and N^+ atoms.

The evaluation of the necessary input parameters for this model was more difficult than that for Model I, for the following reason. To evaluate the modified value of the one-center two-electron repulsion integral of B^- $(pp|pp)_B$ - [which physically resembles $(pp|pp)_C$ in a π-system, since both the B^- and the C have three electrons in a σ-framework and donate one electron to the π-system], it is necessary to have the valence state electron affinities of B^- to form B^{-2} in at least two different valence states. The electron affinity of B^- to form B^{-2} even in the ground state had never been measured experimentally. This ground state electron affinity of B^- can be estimated from the rigorous extrapolation procedure of Edlen *(5)*. However, it is not possible to evaluate subsequently the necessary valence state promotional energies of B^{-2}. This difficulty was circumvented by extrapolating directly the different valence state electron affinities of B^- *(2)*. The values for the one-center two-electron repulsion integral of B^- calculated by two independent methods, spectroscopic expansion and estimation by the Pariser-Parr expression (4.74 and 4.02 e.v.), agreed well *(2)*. This was gratifying in view of the fact that each calculation depends on extrapolated values for the electron affinities of B^- in different valence states.

Calculational Results. Applying the same criteria for the relationships which must be satisfied between the SCF calculations of benzene and borazine, it can be seen that this Model II for borazine, B^- and N^+, leads to completely unreasonable calculational results.

Ionization Potentials. From measured ionization potentials of benzene and borazine and comparison with the SCF calculated HOMO of benzene, the SCF calculated energy of the HOMO of borazine should be of the order of -12.3 ± 0.2 e.v. The SCF calculated energy for the HOMO of Model II is -20.17 e.v., about 8 e.v. too high.

Comparison of the Diagonal Terms in the Final SCF Hamiltonian. The diagonal terms in the final SCF Hamiltonian for boron (+7.64 e.v.) and nitrogen (-19.78 e.v.) show much too large a difference from that of carbon in benzene (-596 e.v.).

Physical Implications. The calculated π-electron charge distribution from this Model II is 0.045 on boron and 1.955 on nitrogen. This would imply that there is virtually no π-electron donation from nitrogen to boron. This is contrary to the experimental results on quadrupole coupling constants in graphitic boron nitride, which suggest that 0.45 electron is donated to the boron if the boron electrons form three planar trigonal bonds to the neighboring nitrogen atoms *(18)*.

On all bases, this model of B^- - N^+ does not appear to be a reasonable physical model for borazine.

Naphthalene and Diphenyl Analogs of Borazine

The complete SCF calculations for the naphthalene and diphenyl analogs of borazine were carried out for both Models I and II. Again, the calculations for Model I gave results which were consistently close to those of corresponding calculations for the hydrocarbons, while Model II gave results which were unreasonable.

Conclusions

LCAO-MO-SCF calculations for borazine have been performed for two theoretical models for borazine. The results of the calculations for Model I when compared with experimental and theoretical criteria indicate that this model is a promising one for future calculations on B-N pairs in π-systems of the borazine type. The results of the calculations for Model II, B^{-} - N^{+} are always less reasonable for borazines when judged by the same criteria.

Complete calculational results for charges, bond orders, energy levels, total energies, coefficients of atomic orbitals in all molecular orbitals, and Hamiltonian matrix elements for borazine and its naphthalene and diphenyl analogs by the Hückel, Pariser-Parr, and Pople methods will be published in full elsewhere.

Acknowledgment

One of us (J. J. K.) thanks the Soroptimist Federation of the Americas for a study grant.

We also thank Sol James, Chief of Automatic Computations, Martin Co. Computing Center, for arranging to have some of the calculations run at the Martin Co. Computing Center.

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Received May 27, 1963. Research supported in part by the Chemistry Branch, Office of Naval Research, the Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. AF49(638)-1220, and the Ordnance Materials Research Office.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch024

25

Synthesis of B-Organofunctional Borazine Derivatives

A Review of Recent Work at the Massachusetts Institute of Technology

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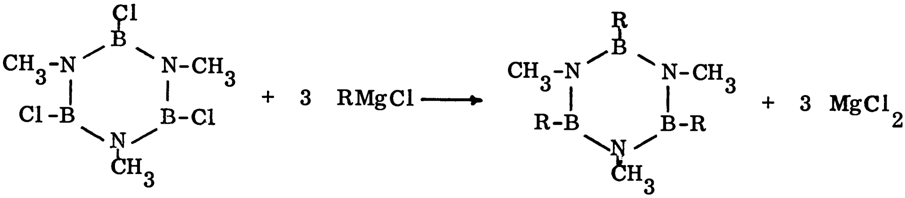
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025

B-Tris-(trimethylsilylmethyl)-*N*-trimethylborazine was easily synthesized by the Grignard procedure, and was hydrolytically stable (through steric hindrance). Liquid borazines of the structure $[(CH_3)_2RSiCH_2BNCH_3]_3$ were also prepared. Silicon-substituted borazines also were accessible through the chloroplatinic acid-catalyzed addition of Si-H containing chlorosilanes and siloxanes to *B*-trivinyl-*N*-triphenylborazine. Other addition reactions of this vinylborazine were examined, and pure, crystalline products were obtained, with $CBrCl_3$, CBr_4, C_6H_5SH, $(C_6H_5)_2PH$, HBr, $(C_6H_5)_3SnH$, and $(C_2H_5)_3SnH$. The condensation of silicon-containing dichloroboranes with aniline produced borazines. Borazines containing Si-O-B and Si-B linkages are described.

Hexamethylborazine is very stable thermally [it was recovered unchanged after it had been heated for 3 hours at 500° C. *(3)*], but it is relatively unstable toward hydrolysis. It was one object of this research to prepare liquid borazines which would be stable hydrolytically as well as thermally. Another purpose was to prepare polymeric borazines in which the polymerization process would occur through functionality attached to boron atoms of the borazine ring. The combination of organosilicon chemistry with borazine chemistry through the synthesis of silicon-substituted borazines was used during the major part of this research as the approach which might yield results of value in terms of both objectives.

The supposition that the major portion of hydrolytic attack on the borazine ring system would occur at the boron atom (as long as neutral or basic conditions were maintained) led to the logical suggestion that if one could prevent attack at the boron atom, one would have a hydrolytically stable borazine. The prevention of hydrolysis in readily hydrolyzable systems by sterically hindering approach of the attacking reagent is well known through many examples, and this approach was taken in this research. The highly branched trimethylsilylmethyl group therefore was of interest to us, since replacement of methyl groups attached to boron in hexamethylborazine by this group should introduce the desired steric factor. It had been shown by several groups of workers that *B*-trihalo-*N*-triorganoborazines reacted with Grignard reagents to give the corresponding *B*-triorganoborazines *(2, 15)*. We used this procedure for the synthesis of *B*-tris-(trimethylsilylmethyl)-*N*-trimethylborazine, a crystalline solid *(9)*.



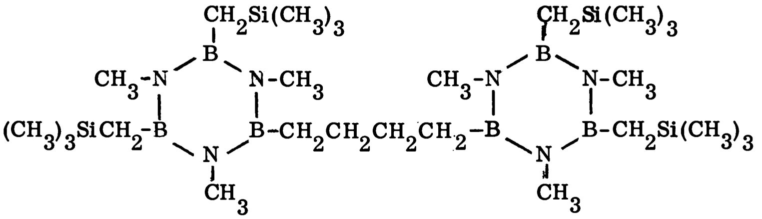
$R = (CH_3)_3SiCH_2$

This compound had the desired hydrolytic stability. It was stable toward air oxidation and toward hydrolysis under neutral or mildly alkaline conditions. It was not decomposed by alkaline hydrogen peroxide at room temperature, but was destroyed by hot, aqueous hydrochloric acid. This gain in hydrolytic stability was, unfortunately, accompanied by a loss in thermal stability. The trimethylsilylmethyl-substituted borazine showed appreciable stability only up to 400° C. and was completely decomposed when heated for 3 hours at 500° C. *(8)*. Liquid borazines were obtained when the trimethylsilyl group's symmetry was disturbed. Thus the compounds $[(CH_3)_2(C_2H_5)SiCH_2BNCH_3]_3$ and $[(CH_3)_2(n\text{-}C_4H_9)SiCH_2BNCH_3]_3$ were high-boiling, viscous liquids. Of particular interest was the borazine derived from the reaction of the Grignard derivative of chloromethylpentamethyldisiloxane with *B*-trichloro-*N*-trimethylborazine, $[(CH_3)_3SiOSi(CH_3)_2CH_2BNCH_3]_3$. Although this point was not investigated, this borazine should be capable of being incorporated into polysiloxane systems through conventional siloxane redistribution-polymerization techniques. $(CH_3)_3SiCH_2MgCl$ did not appear to react with *B*-trichloro-*N*-triphenylborazine, even under forcing conditions *(7)*. Under comparable and even under much milder conditions CH_3MgBr reacts with this borazine to give *B*-trimethyl-*N*-triphenylborazine in good yield. Evidently steric interference by adjacent phenyl groups attached to nitrogen can become important when it is attempted to introduce highly branched substituents on boron.

An attempt was made to link such silicon-substituted borazines into larger units through difunctional organic linking units. Thus, the partially substituted borazine, *B*-chloro-*B*-bis-(trimethylsilylmethyl)-*N*-trimethylborazine was prepared by the reaction of *B*-trichloro-*N*-trimethylborazine with a deficiency of $(CH_3)_3SiCH_2MgCl$ The reaction of this borazine with the di-Grignard reagent from 1,4-dichlorobutane gave the carbon-bridged borazine, I *(8)*.

Compound I was not stable toward hydrolysis. Apparently a decrease in the steric shielding of just one of the three boron atoms of the three boron atoms of the borazine ring provides a site for hydrolytic attack, and the borazine system is destroyed. The bridged bis-borazine also was thermally much less stable than *B*-tris-(trimethylsilylmethyl)-*N*-trimethylborazine.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025



I

An alternate approach to the preparation of silicon-substituted borazines involved the hydrosilylation of *B*-trivinyl-*N*-triphenylborazine. This unsaturated borazine was prepared by Pellon *et al.* *(4, 5)*, and its polymerization and copolymerization behavior was studied by these authors. Our work showed that trichlorosilane did not add to $[CH_2=CHBNC_6H_5]_3$ in the presence of radical initiators such as benzoyl peroxide. However, Si-H-containing chlorosilanes and siloxanes added to the olefinic double bonds of this borazine in good yield in the presence of chloroplatinic acid *(11)*.

$$3\quad \text{Si-H} \quad + \quad [CH_2{=}CHBNC_6H_5]_3 \xrightarrow{H_2PtCl_6} [\quad \text{Si}CH_2CH_2BNC_6H_5]_3$$

The direction of addition as shown was established in the case of dimethylchlorosilane by conversion of the $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$ produced to the completely methylated compound, $[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$, by the Grignard procedure and oxidation of the latter with alkaline hydrogen peroxide. Only β-trimethylsilylethanol, $(CH_3)_3SiCH_2CH_2OH$, was formed, and this established the absence of any $(CH_3)_3SiCH(CH_3)$ groups, since these would have resulted in formation of the other isomeric alcohol, $(CH_3)_3SiCH(CH_3)OH$. Of particular interest was that pentamethyldisiloxane and *sym*-heptamethyltrisiloxane also added readily to *B*-trivinyl-*N*-triphenylborazine in the presence of chloroplatinic acid to give $[(CH_3)_3SiOSi(CH_3)_2CH_2CH_2BNC_6H_5]_3$ and $[\{(CH_3)_3SiO\}_2Si(CH_3)CH_2CH_2BNC_6H_5]_3$, respectively. Here again we have siloxanes capable of being introduced into polysiloxane systems through standard equilibration techniques. Furthermore, these reactions indicate that higher polysiloxanylethylborazines should be accessible via similar addition of Si-H-terminated polysiloxanes of the type $(CH_3)_3SiO[(CH_3)_2SiO]_nSiO(CH_3)_2H$, although this point has not yet been investigated.

The availability of $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$ and $[CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3$ in principle also made possible the preparation of β-siloxanylethylborazines. However, neither of the two procedures tried, cohydrolysis with chlorosilanes and condensation with lithium trimethylsilanolate, was wholly satisfactory. In the cohydrolysis with trimethylchlorosilane the $[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$ and $[CH_3(OH)_2SiCH_2CH_2BNC_6H_5]_3$ produced condensed at a much slower rate than trimethylsilanol, so only hexamethyldisiloxane was formed from the latter. It is believed that steric hindrance, probably due to other ring substituents, explains this rather difficultly effected condensation of borazinylsilanols. The cohydrolysis experiments led to the isolation of $[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$ in the case of the monochloro compound, and of a resinous solid in the case of the dichloro compound. The reaction of the chlorosilyl-substituted borazines with lithium trimethylsilanolate gave the expected trimethylsiloxy derivatives, but in poor yield:

$$6\ (CH_3)_3SiOLi + [CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3 \longrightarrow 6\ LiCl + [\{(CH_3)_3SiO\}_2Si(CH_3)CH_2CH_2BNC_6H_5]_3$$

A third route to silicon-substituted borazines involved the synthesis of a suitable silicon-substituted borane and the reaction of the latter with an amine to form the borazine ring. This several-step procedure proved to be unsatisfactory because of the low over-all yield. The procedure examined may be summarized by the following equations.

$$(CH_3)_3SiCH{=}CH_2 \xrightarrow[\text{excess}]{B_2H_6} (CH_3)_3Si(C_2H_4)BH_2 \xrightarrow{CH_3OH} (CH_3)_3Si(C_2H_4)B(OMe)_2$$

$$\xrightarrow{PCl_5} (CH_3)_3Si(C_2H_4)BCl_2 \xrightarrow{C_6H_5NH_2} (CH_3)_3Si(C_2H_4)B(NHC_6H_5)_2$$

$$\xrightarrow{340^\circ} [(CH_3)_3Si(C_2H_4)BNC_6H_5]_3$$

A portion of the dimethyl trimethylsilylethylboronate was oxidized with alcoholic hydrogen peroxide. Gas chromatographic analysis of the alcohols produced showed that a mixture of 55% α-trimethylsilylethanol and 45% β-trimethylsilylethanol was present. Hence the hydroboration product contained a 55 to 45 mixture of $(CH_3)_3SiCH(CH_3)B(OCH_3)_2$ and $(CH_3)_3SiCH_2CH_2B(OCH_3)_2$. This is in agreement with previous results, which showed that when an excess of diborane source was used in the hydroboration of trimethylvinylsilane, the α-trimethylsilylethyl group was present in higher percentage in the product than the β-trimethylsilylethyl group *(6)*. The directive effects in the hydroboration of trimethylvinylsilane have been discussed *(14)*.

Silicon-substituted borazines in which the Si-O-B or Si-B linkages were present were also examined. The reaction of sodium trimethylsilanolate with *B*-trichloro-*N*-trimethylborazine in ether solution gave $[(CH_3)_3SiOBNCH_3]_3$ in 60% yield This compound, however, was hydrolytically unstable. The action of triphenylsilyllithium on *B*-trichloro-*N*-trimethylborazine in ether-tetrahydrofuran medium resulted in formation of *B*-tris-(triphenylsilyl)-*N*-trimethylborazine, $[(C_6H_5)_3SiBNCH_3]_3$, in 55% yield. This is the first compound containing a silicon-boron bond to be reported *(1, 9)*. This compound also was hydrolytically unstable, the action of water causing complete disruption of the borazine ring:

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025

$$[(C_6H_5)_3SiBNCH_3]_3 + 9\ H_2O \longrightarrow 3\ (C_6H_5)_3SiH + 3\ B(OH)_3 + 3\ CH_3NH_2$$

B-Tris-(triphenylsilyl)-*N*-trimethylborazine is stable in dry air. Its bromination gave as an initial reaction cleavage of the Si - B bond, triphenylbromosilane being isolated.

The addition of other reagents to *B*-trivinyl-*N*-triphenylborazine was also examined. Triphenyltin hydride added readily in refluxing toluene solution to give $[(C_6H_5)_3SnCH_2CH_2BNC_6H_5]_3$ in 74% yield. The direction of addition was confirmed by oxidation of the product to $(C_6H_5)_3SnCH_2CH_2OH$, whose structure was shown to be as written by means of its nuclear magnetic resonance spectrum. Triethyltin hydride did not react with the vinylborazine under these conditions, but it added in the presence of a radical initiator, 2, 2'-azobisisobutyronitrile, to give $[(C_2H_5)_3SnCH_2CH_2BNC_6H_5]_3$ in 84% yield *(11)*.

Diphenylphosphine reacted with $[CH_2=CHBNC_6H_5]_3$ in the presence of *tert*-butyl peroxide, forming crystalline $[(C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$. This phosphorus-substituted borazine was converted to the phosphine sulfide, $[(C_6H_5)_2P(S)CH_2CH_2BNC_6H_5]_3$, and to the mercuric chloride adduct, $[(C_6H_5)_2P(HgCl_2)CH_2CH_2BNC_6H_5]_3$ *(10)*. Radical-initiated addition of benzenethiol to the vinylborazine gave $[C_6H_5SCH_2CH_2BNC_6H_5]_3$. In a similar manner smooth radical-initiated addition of bromotrichloromethane and carbon tetrabromide was effected.

$$3\ CBrX_3 + [CH_2{=}CHBNC_6H_5]_3 \longrightarrow [CX_3CH_2CHBrBNC_6H_5]_3$$

X=Cl and Br

Noteworthy is the formation of stable 1 to 1 solvates of the compound where X = Br, with benzene and carbon tetrachloride *(12)*.

Benzoyl peroxide-initiated addition of hydrogen bromide to *B*-trivinyl-*N*-triphenylborazine in benzene solution gave $[BrCH_2CH_2BNC_6H_5]_3$, whose structure was confirmed by its NMR spectrum. In diethyl ether, on the other hand, complete destruction of the borazine was observed on treatment of $[CH_2{=}CHBNC_6H_5]_3$ with gaseous hydrogen bromide, the only crystalline product isolated being aniline hydrobromide. This difference in behavior is very likely a reflection of the different states of HBr in these solvents, HBr being present essentially in the molecular form in benzene and as the strongly acidic oxonium salt in ether. Attempted condensation of $[BrCH_2CH_2BNC_6H_5]_3$ with Grignard reagents resulted in β-elimination. Thus the action of phenylmagnesium bromide on this borazine gave hexaphenylborazine rather than the hoped-for $[C_6H_5CH_2CH_2BNC_6H_5]_3$ *(12)*.

$$3\ C_6H_5MgBr + [BrCH_2CH_2BNC_6H_5]_3 \longrightarrow [C_6H_5BNC_6H_5]_3 + C_2H_4 + 3\ MgBr_2$$

During this research *B*-triethynyl-*N*-triphenylborazine was prepared for the first time, but its chemical reactions and general stabil-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025

ity have not yet been investigated. The reaction of HC≡CMgBr with *B*-trichloro-*N*-triphenylborazine in tetrahydrofuran gave this compound in about 50% yield *(13)*.

The *B*-organofunctional borazines prepared during the course of this work are listed in Table I.

Table I. *B*-Organofunctional Borazines

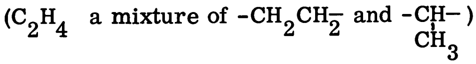
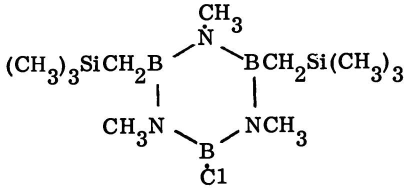
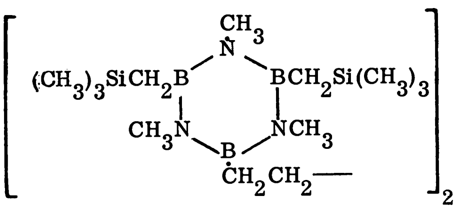
Compound	*M.P., °C.*	*B.P., °C. (Mm.)*	*Ref.*
$[(CH_3)_3SiCH_2BNCH_3]_3$	59-60		*(9)*
$[(CH_3)_2(C_2H_5)SiCH_2BNCH_3]_3$		183-4 (1.0)	*(9)*
$[(CH_3)_2(\underline{n}\text{-}C_4H_9)SiCH_2BNCH_3]_3$		213-4 (0.9)	*(9)*
$[(CH_3)_3SiOSi(CH_3)_2CH_2BNCH_3]_3$		175-6 (0.55)	*(9)*
$[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$	157-9		*(11)*
$[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$	164-6		*(11)*
$[CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3$	170-2		*(11)*
$[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$	137		*(11)*
$[(CH_3)_3SiOSi(CH_3)_2CH_2CH_2BNC_6H_5]_3$	86-7		*(11)*
$[\{(CH_3)_3SiO\}_2Si(CH_3)CH_2CH_2BNC_6H_5]_3$		Oil	*(11)*
$[(CH_3)_3Si(C_2H_4)BNC_6H_5]_3$  (C_2H_4 a mixture of $-CH_2CH_2-$ and $-\underset{CH_3}{CH}-$)	132-146		*(13)*
		105-8 (0.03)	*(8)*
	93-4		*(8)*
$[(CH_3)_3SiOBNCH_3]_3$	22-3	130 (0.85)	*(9)*
$[(C_6H_5)_3SiBNC_6H_5]_3$	248-51		*(1, 9)*
$[(C_6H_5)_3SnCH_2CH_2BNC_6H_5]_3$	219-21		*(11)*

Table I. *B*-Organofunctional Borazines (continued)

Compound	*M.P., °C.*	*B.P., °C. (Mm.)*	*Ref.*
$[(C_2H_5)_3SnCH_2CH_2BNC_6H_5]_3$	87-8		*(11)*
$[(C_6H_5)_2PCH_2CH_2BNC_6H_5]_3$	160-2.5		*(10)*
$[(C_6H_5)_2P(S)CH_2CH_2BNC_6H_5]_3$	217-9		*(10)*
$[(C_6H_5)_2P(HgCl_2)CH_2CH_2BNC_6H_5]_3$	267-9		*(10)*
$[C_6H_5SCH_2CH_2BNC_6H_5]_3$	134-5		*(12)*
$[BrCH_2CH_2BNC_6H_5]_3$	165-6		*(12)*
$[CCl_3CH_2CHBrBNC_6H_5]_3$	212-3		*(12)*
$[CBr_3CH_2CHBrBNC_6H_5]_3$	241-1.5		*(12)*
$[CH_2BrCHBrBNC_6H_5]_3$	257-8		*(12)*
$[HC{\equiv}CBNC_6H_5]_3$	264-5		*(14)*

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Received May 1, 1963. A review of work carried out in the senior author's laboratories at the Massachusetts Institute of Technology since September 1958 in the general area of borazine chemistry. Research supported by the U. S. Air Force under Contracts AF 33(616)-5582, AF 33(616)-7124, and AF 33(657)-8532, monitored by Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. This support is gratefully acknowledged.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch025

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Chemistry of B-Fluorinated Borazines

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch026

The preparation and properties of some *B*-fluorinated borazines are reported. Features of their infrared spectra, some general considerations with respect to the diagnosis of a borazine structure by infrared spectroscopy, and possible correlations of borazines to other pseudoaromatic systems are discussed.

The aromatic character of borazine and its derivatives is still a controversial subject. It is reasonable to assume, however, that substitution at the boron atom with electron-attracting groups will increase the participation of the free electron pair of the nitrogen in the B-N linkage and hence should increase the aromaticity of the borazine molecule.

Although a large number of borazines of the general formula $(\text{-BR-NR'-})_3$ are known *(15)*, the variety of substituted borazines is limited. For instance, borazines with *N*-substituents other than H, alkyl, or aryl are not known; of *B*-halogenated compounds, the *B*-fluorinated borazines were virtually unknown until recently *(10)* and only one *B*-iodinated derivative has been mentioned in the literature *(13)*. Thus, further synthetic studies are necessary if an expanded knowledge of the borazine system is to be realized. One approach to this problem is presented by the present investigation of *B*-fluorinated borazines.

Preparation and General Properties of B-Fluorinated Borazines

Several *B*-fluorinated borazines have now been prepared by transhalogenation of *B*-trichloroborazines with various fluorinating agents, such as metal fluorides, antimony trifluoride, and mixtures of antimony halides.

So far, the most convenient method of preparing *B*-trifluoroborazines has been to transhalogenate the chloro compounds with titanium tetrafluoride.

One mole of *B*-trichloroborazine and 0.3 mole of titanium tetrafluoride are powdered separately, mixed, covered with a small amount of TiF_4 powder, and slowly heated until the reaction is self-sustaining. Upon completion of the reaction (normally about 10 minutes), volatile materials are distilled off under reduced pressure (ca. 70 mm.). This material is redistilled at room temperature at approximately

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

1.0-mm. pressure to remove titanium tetrachloride and the residual fluorinated borazine is purified by vacuum distillation, recrystallization, or sublimation.

Using this method, the following compounds were obtained:

$[-BF-NH-]_3$, m.p. (subl.) 122° C.
$[-BF-NCH_3-]_3$, m.p. 90.5° C.
$[-BF-NC_2H_5-]_3$, b.p. 26°C. (3 mm.)
$[-BF-N(nC_3H_7)-]_3$, b.p. 59° C. (3 mm.)
$[-BF-N(nC_4H_9)-]_3$, b.p. 88-90° C. (3 mm.)

The structures were established by elemental analysis, molecular weight determination, infrared data, and a NMR investigation *(11)*. Although *B*-fluorinated borazines hydrolyze easily, their reaction with water or dilute aqueous acid is not as rapid nor as vigorous as the comparable reaction of their chlorinated counterparts. On the other hand, contact of *B*-trifluoroborazines with alcohols produces a nearly explosive reaction which results in complete decomposition of the borazine ring.

Two mixed *B*-fluoro-chloroborazines — $B_3F_2ClN_3H_3$ (v.p. 7 mm., 31°) and $B_3FCl_2N_3H_3$ (m.p. 49-51°) — have been prepared.

Both of these borazines can be obtained by reaction of *B*-trichloroborazine with slightly more than the stoichiometric requirement of antimony trifluoride in the manner described above. The yield of the difluoro derivative is increased considerably if, after the trichloroborazine is mixed with the SbF_3, some $SbCl_5$ is added to the mixture to start the reaction. To obtain reasonable yields of the desired products, careful temperature control is an absolute necessity. As a rule, the reaction vessel is cooled in a dry ice-methanol bath immediately after ignition of the reaction mixture and cooling is maintained until the vigorous reaction has almost subsided.

The mixed halogenated borazines are extremely sensitive to hydrolysis and, on heating, they readily disproportionate to *B*-trichloro- and *B*-trifluoroborazine. Therefore it is not surprising that, on refluxing a mixture of *B*-trichloroborazine with *B*-trifluoroborazine, no reaction occurs but the starting materials are almost quantitatively recovered.

Preliminary experiments indicate that the chlorine of the mixed fluoro-chloroborazines is more reactive than the fluorine. Work with the two compounds, however, is severely hampered by their consistent tendency to disproportionate. In addition, only $B_3FCl_2N_3H_3$ has been isolated as a pure material, whereas the $B_3F_2ClN_3H_3$ still appears to be contaminated with small amounts of impurities. However, once these difficulties are overcome, the mixed halogenated borazines offer a new route to a variety of substituted borazines, such as inorganic analogs of aniline, styrene, and phenol.

Infrared Spectra of B-Fluorinated Borazines

The infrared spectra of *B*-fluorinated borazines were recorded in the vapor phase, as liquid films and as mulls in Nujol and Kel-F on

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch026

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Perkin-Elmer Model 21 and Beckman IR 8 spectrophotometers, using sodium chloride optics.

Trifluoroborazine. — The strongest absorption of the *B*-trifluoroborazine was recorded at 1510 cm.$^{-1}$ with a shoulder at 1528 cm.$^{-1}$ and this absorption has consequently been assigned as due to B-N stretch, the shoulder indicating a B^{10} isotope effect. Two doublets in the 730-cm.$^{-1}$ region can be assigned to out-of-plane vibrations of the B-N ring.

Generally, the B-N stretching frequency in the 1350- to 1500-cm.$^{-1}$ region has been used to identify the borazine structure. However, many other compounds containing normal covalent B-N bonds also absorb in this same region. A recent survey of more than 100 variously substituted borazines made in this laboratory demonstrated that the presence of a borazine ring structure in a given B-N compound can be unambiguously determined by the simultaneous existence of the B-N stretch and an out-of-plane vibration in the 700-cm.$^{-1}$ region.

An absorption at 1401 cm.$^{-1}$ is probably also related to a B-N stretching mode, since an analogous band is also found in *B*-trichloroborazine. The NH stretching frequency was recorded near 3500 cm.$^{-1}$ A band of medium intensity at 922 cm.$^{-1}$ is probably indicative of a N-H in-plane bend, coupled perhaps with B-N ring bending if the parent borazine, $B_3N_3H_6$, is used for comparison *(17)*. The only remaining absorption of medium-to-strong intensity, recorded at 1136 cm.$^{-1}$, was consequently assigned as due mainly to a B-F vibration.

***B*-Monochlorodifluoroborazine.**-The NH frequency of this compound was recorded at 3460 cm.$^{-1}$ The B-N mode was evidenced by a relatively broad strong peak at 1513 to 1507 cm.$^{-1}$ with a shoulder at 1530 cm.$^{-1}$, and a band corresponding to the 1401-cm.$^{-1}$ absorption of *B*-trifluoroborazine was evidenced at 1406 cm.$^{-1}$ An additional band of about equal intensity was recorded at 1482 cm.$^{-1}$ The B-F frequency was recorded at 1339 cm.$^{-1}$ A doublet (1042 and 1038 cm.$^{-1}$) which was not observed in the trifluoro derivative can reasonably be assigned as B-Cl stretch, unless another doublet (of weaker intensity) at 827 to 823 cm.$^{-1}$ is related to the latter mode. Other features of the spectra of the trifluoro- and the difluoromonochloroborazine are almost identical, except that, in the 730-cm.$^{-1}$ region of the latter, two additional absorption peaks could be observed. Only a relatively weak vapor phase spectrum was obtained of *B*-monofluorodichloroborazine, the general features of which are in agreement with those discussed above.

General Features of Spectra of *B*-Fluorinated Borazines.-The B-N stretching frequencies of *B*-fluorinated borazines are observed near 1500 cm.$^{-1}$, wheareas the corresponding modes of the chlorinated products are observed near 1430 cm.$^{-1}$ One might assume that such occurrence illustrates an increase in the B-N bond order. However, coupling of B-F and B-N modes may be present in *B*-fluoroborazines, resulting in higher than normal B-N ring frequencies (and lower than normal B-F frequencies) without necessarily having stronger B-N bonds.

The major controversy on the assignment of absorptions seems to reside, however, in the assignment of the B-F frequency. This is illustrated by values for the B-F vibration reported for $(CH_3)_2BF$ at 1260 cm.$^{-1}$ *(3)* and for the etherate of CF_3BF_2 at 1115 cm.$^{-1}$ *(14)*.

However, comparison of modes related mainly to *B*-halogen stretching of *B*-trifluoroborazines with those of their chlorinated counterparts seems to substantiate the assignment of the B-F frequency, as illustrated in Table I.

Table I. *B*-Halogen Stretch of Borazines

	ν B-F, Cm. $^{-1}$	*ν B-Cl, Cm.* $^{-1}$	
$(\text{-BX-NH-})_3$	1136	1032	*(16)*
$(\text{-BX-NCH}_3\text{-})_3$	1170	975	*(16)*
$(\text{-BX-NC}_2\text{H}_5\text{-})_3$	1150	1025	*(4)*
$(\text{-BX-NC}_3\text{H}_7\text{-})_3$	1153	960	*(4)*
$(\text{-BX-NC}_4\text{H}_9\text{-})_3$	1148	934	
$B_3F_2ClN_3H_3$	1139	1038	
$B_3FCl_2N_3H_3$	1138	1032	

Diagnosis of Borazine Ring Structure by Infrared Spectroscopy

A recent survey of the infrared spectra of borazines was made, to provide a diagnostic aid for the recognition of a borazine ring structure.

Attention was first drawn by Lappert *(1, 9)* to a medium-intensity doublet in the 720-cm.$^{-1}$ region in the spectra of *B*-aminoborazines and *B*-alkoxyborazines. In a later work, this absorption was definitely related to out-of-plane vibrations of the B-N ring *(2)*. Gerrard and coworkers *(6)* arrived at the same conclusion, but made no attempt to consider these vibrations for general diagnostic purposes in borazine chemistry.

On the basis of the study cited above, the combination of the B-N out-of-plane vibration of a borazine ring with the B-N stretching frequency can be considered an indication of the existence of a borazine structure. However, the purpose of this study is merely to provide a rapid and preliminary diagnosis of the six-membered B-N ring system.

The out-of-plane vibration of borazines can be identified as a medium-to-strong intensity band in the 700-cm.$^{-1}$ region. Certain regional trends seem to be apparent (Table II). Limitations to the diagnostic use of these merely empirical trends can arise from several factors.

It has been suggested *(17)* that NH and BH in-plane bending modes of borazines are observed near 700 cm.$^{-1}$

Aromatic ring vibrations are known to occur in the indicated region of the spectra.

Boron-carbon linkages ($B\text{-}C_2$) can be found in the 600 to 700-cm.$^{-1}$ region.

Coupling effects have so far not been studied to any appreciable degree in the borazine system.

However, unlike the modes just mentioned, the out-of-plane ring vibration of the borazine ring is evidenced in most cases by a relatively strong absorption. It is most often observed either as a broad band

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch026

Table II. Out-of-Plane Vibrations of the Symmetrically Substituted Borazine Ring

B-Substituents	*Range Cm.*$^{-1}$
N-substituents, H-.	General range, 686-717 Cm^{-1}
RR'N-	686-717
X-CH_2-	685-702[a]
Aryl	~706
Alkoxy	710-715[b]
Alkyl	709-717
Halogen	640-740[c]
N-Substituents, C_6H_5.	General range, 698-701 Cm^{-1}
RR'N	699[b]
H-, alkyl	698-701
Halogen	640-740[c]
N-Substituents, CH_3.	General range, 704-733 Cm^{-1}
RR'N	704-713
Halogen	650-720[c]
Alkoxy	715-728
Alkyl	~733

[a] X = for instance, halogen or -Si≤.

[b] Compounds of this group were available in very limited number only; revision of frequency range may be necessary.

[c] This unusual wide range is easily explained through large differences in size and electronegativity of the various halogens.

or showing a shoulder through splitting. This is due to a B^{10} isotope effect analogous to the one established for the B-N stretching frequency.

In a few cases the out-of-plane vibration of a borazine is of very limited intensity. The effect of electronic interaction of some phenylated borazines with the solvent has been discussed *(7)*. Recognizing such an effect, it is possible to identify the out-of-plane vibration by recording the spectra in different solvents or as pellets.

In several cases the out-of-plane vibration could not be identified. So far these exceptions have been limited to borazines with bulky substituents, such as *tert*-butyl groups. A certain relation to polycondensed borazines seems to exist.

In polynucleated borazine chains the out-of-plane vibration of the borazine ring was observed in the 685 to 710 cm.$^{-1}$ region of the infrared spectrum. This range seems to be relatively independent of the structural combinations of the borazine rings: The vibration was observed in the spectra of borazines of the biphenyl and naphthalene types, and also when two or more borazine rings were connected by bridges of other atoms or groups of atoms. However, if the side branches attached to the borazine rings consist of amino groups, the

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch026

position of the out-of-plane vibration shifts to about 720 cm.$^{-1}$; in the case of alkoxy side chains a further shift to about 740 cm.$^{-1}$ was noted.

In cross-linked borazine polymers, the out-of-plane vibration could no longer be detected. Since for boron nitride, cyclic six-membered species of alternating boron and nitrogen atoms have been established as structural units, it is reasonable to assume a similar preservation of the borazine nuclei in cross-linked polymeric borazines. Indeed, the B-N stretch of the borazine ring is easily recognized in all spectra of the polymers. It seems reasonable to conclude that cross linking limits out-of-plane vibrations through the influence of steric factors. This, then, might also be the case in borazines with bulky substituents and thus would explain why it is not possible to observe out-of-plane vibrations in these compounds.

Correlation of Pseudo-Aromatic Ring Systems

A comparison of the infrared spectra of *B*-trifluoroborazine, *B*-difluoromonochloroborazine, and *B*-dichloromonofluoroborazine and the spectra of the corresponding triazines *(8)* indicates some interesting features of these two pseudoaromatic systems. The B-F vibration of borazine is observed near 1140 cm.$^{-1}$ and is relatively independent of substitution. In the triazines, however, a range has been found for the C-F absorption varying from 1089 to 1001 cm.$^{-1}$ Both heterocyclic systems exhibit ring vibrations in a consistent pattern, those of the borazines occurring at somewhat lower energy than the corresponding vibrations of the triazines.

Other symmetrically fluorinated ring systems can be included in a general comparison (Table III).

Table III. Degenerate Ring Stretching Vibrations of Symmetrically Fluorinated Aromatic and Pseudoaromatic Systems

Compound	ν*Cm.*$^{-1}$ *(Vapor Phase)*	
1,3,5-Trifluorobenzene *(12)*	1618	1473
Cyanuric fluoride, $(FCN)_3$	1585	1427
B-Trifluoroborazine	1510	1401
Hexafluorocyclotriphosphazene, $(NPF_2)_3$ *(5)*	1343	1297

If ring vibrations can be directly related to the aromaticity of a molecule, the data of Table III correspond to the present experimental results, indicating a decrease in the aromaticity in the order benzene> triazine>borazine>phosphazene. However, it is evident that this correlation neglects the considerable mass effect of the phosphorous atom. Further studies will be devoted to this problem and might well include other heterocyclic systems such as the trimeric thiazines and boroxines.

Acknowledgment

The authors are grateful to M. Kubo, Nagoya University, Japan, D. Seyferth, Massachusetts Institute of Technology and H. Watanabe, Shionogi Research Laboratory, Japan, for supplying infrared spectra of a variety of substituted borazines.

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Received May 6, 1963. Work supported by the U. S. Army Research Office – Durham.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch026

LCAO-MO Calculations on Boron Compounds

III. Heteroaromatic Boron Compounds

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch027

Molecular orbitals for the π-systems of aromatic hydrocarbons, where a B-N pair replaces a C-C pair, have been calculated, using an LCAO technique with the Hückel, Pariser-Parr, and Pople approximations. Several theoretical models were used to choose input parameters, and modified values for boron electron-repulsion integrals were calculated, taking into account electron correlation effects. Complete LCAO-MO-SCF calculations were performed for each choice of input parameters. One choice gave good agreement between localization energies calculated by the Pople method and experimental results, as well as correct prediction of the order of stabilization of the borazarenes. The most effective model is discussed with reference to the σ-bonding of heteroaromatic boron compounds and borazines.

In the past five years a new class of heteroaromatic boron compounds, in which the boron atoms are incorporated into six-membered aromatic rings, has been synthesized by Dewar and his colleagues *(5)*. These compounds are very stable and bear a close resemblance to the parent aromatic hydrocarbons. In most of the compounds reported a C-C pair has been replaced by an isoelectronic B-N pair.

It was of interest to perform various types of LCAO-MO calculations, especially LCAO-MO-SCF (linear combination of atomic orbitals - molecular orbital - self-consistent field) calculations, on the π-systems of these heteroaromatic boron compounds and to compare their calculated properties with those of the corresponding aromatic hydrocarbons.

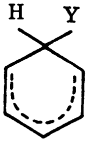
Since it had been shown that even for hydrocarbons a discrepancy exists between predicted chemical reactivities as calculated from charge distributions or localization energies (and also between reactivities predicted from localization energies calculated in the three approximations) *(2)*, a series of localization energy calculations by all three techniques was performed for the compounds of Dewar. The reactivities calculated by localization energies, as well as those predicted from charge distributions, may then be compared with the experimental data.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Details of Calculations

The theoretical background of the calculational methods for the quantum mechanical study of the π-electrons of conjugated molecules has been described *(1)*, as well as the theoretical models utilized for the calculations of B-N pairs and the choices of input parameters, and the modified values for boron electron-repulsion integrals which take into account correlation effects.

Using the activated complex model of Wheland, the contribution of the π-electrons to the potential barrier has been calculated by the calculational methods for three types of chemical reactions: electrophilic, nucleophilic, and radical. In the activated complex, the carbon which is attacked in the reaction is surrounded by four single bonds, each containing a pair of electrons, and thus the carbon cannot be part of the delocalized bond. Two electrons are necessary to form the CY bond. For benzene the intermediate complex would have the form



A delocalized bond exists that extends over all the carbon skeleton except the carbon which is attacked *(3)*.

Localization energy is defined as the energy of the activated complex minus the energy of the original molecule.

The numerical calculations reported here were carried out on the IBM 7094 at the Martin Co. Computing Center with the aid of an automatic program written by G. Bessis of the Centre de Mécanique Ondulatoire Appliquée and with supplementary programs written by Jane Flinn of the Martin Co. Computing Center, using an LCAO technique in the framework of the Hückel, Pariser-Parr (without iteration), and Pople approximations.

The calculations were carried out for both Model I *(1)*, in which the π-electron in the aromatic system sees an effective "core" similar to the one which a π-electron would see in an almost neutral boron or nitrogen atom (this calculational model was effective for describing the properties of borazine itself); and Model II, corresponding to the B^--N^+ model for B-N pairs in conjugated systems (this model was unreasonable for borazine, but turns out to be more reasonable for the heteroaromatic compounds). The values of β were estimated by the approximate ratios of the overlap integrals *(1)*.

For the heteroaromatic B-N compounds Model II may be a promising choice for a calculational model, at least for prediction of chemical reactivities by localization energy criteria.

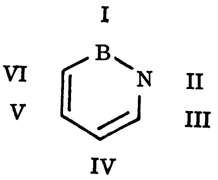
Results and Discussion

Coefficients of atomic orbitals in the molecular orbitals, SCF Hamiltonian matrix elements, energy levels, π-charge densities, bond orders, and chemical reactivities were calculated by all three techniques for the molecules mentioned below. These calculations will be

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch027

published in full elsewhere. In the present article only results of pertinent chemical interest are reported.

Localization Energies and Reactivities. I, II-Borazarene. From general considerations of the effect on chemical reactivities of substitution of heteroatoms into an aromatic ring, Dewar has pointed out that for electrophilic attack, nitrogen, being more electronegative than carbon, should deactivate the positions of opposite parity to itself, and boron, being less electronegative than carbon, should activate the positions of opposite parity to itself. For I, II-borazarene,



the simplest of the B-N compounds, this would imply that positions III and V would be deactivated and positions IV and VI would be activated. Therefore, it is to be expected that positions IV and VI will be most susceptible to electrophilic attack. Table I presents the electrophilic localization energies calculated by the three methods for borazarene, utilizing Models I and II. Hückel calculations and both Pariser-Parr (P+P_O) and Pople (P+P_F) calculations for Model I indicate that position IV is the most reactive, while P+P_O and P+P_F calculations for

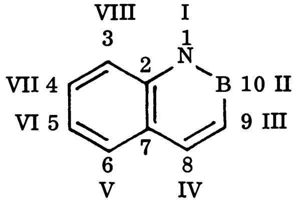
Table I. ΔE_π^+ Electrophilic Localization Energies

		ΔE_π^+			π-Charge Densities	
		β	e.v.	e.v.		
Compound	*Position*	*Hückel*	P+P_O	P+P_F	*Hückel*	P+P_F
	D					
I, II-Borazarene (Model I)	N II	-3.1471	27.4812	27.5945	1.5397	1.4035
	III	-2.5951	26.5097	26.1234	0.8269	0.7924
	IV	-2.4338	25.1769	25.2838	1.0653	1.0900
	V	-2.8985	26.5246	26.5765	0.8527	0.8888
	VI	-2.6285	25.8664	25.8985	1.1469	1.1204
	B I	-2.4601	25.6817	25.5325	0.5684	0.7049
	D					
I, II-Borazarene (Model II)	N II	-3.1471	45.3543	48.7801	1.5397	1.9462
	III	-2.5951	25.3604	25.2846	0.8269	0.5773
	IV	-2.4338	24.5158	24.2061	1.0653	1.2358
	V	-2.8985	31.3629	27.5535	0.8527	0.8357
	VI	-2.6285	22.7762	23.6791	1.1469	1.2784
	B I	-2.4601	23.3849	24.2751	0.5684	0.1266

Model II indicate that position VI is the most reactive. Hückel, Pariser-Parr, and Pople π-charge densities for both Models I and II indicate that position VI is the most susceptible to electrophilic attack. Because of the lack of experimental data it is not possible to choose between the two calculational models on this basis.

The values for localization energies for nucleophilic and radical attack on I, II-borazarene were also calculated.

II, I-Borazaronaphthalene. In naphthalene itself the α-positions (I, IV, V, and VIII) are most susceptible to electrophilic attack. For these molecules, the Roman numerals correspond to Dewar's numbering system and the arabic numerals to the one used here, since it is necessary for reporting π-charge densities and bond orders to have a number for each position in the molecule, not merely for the positions bearing H atoms. In II, I-borazaronaphthalene nitrogen should deactivate positions IV, V, and VII, while boron should activate positions III, VI, and VIII. General considerations thus indicate that positions III and VIII should be the most reactive. Hückel and $P+P_O$ and $P+P_F$ electrophilic localization energy calculations for Model I indicate that position VIII would be most susceptible to electrophilic attack. $P+P_O$ and $P+P_F$ calculations for Model II indicate that position III would be the most reactive site for electrophilic attack. Hückel, Pariser-Parr, and Pople π-charge densities for Models I and II indicate that position III would be the most reactive.



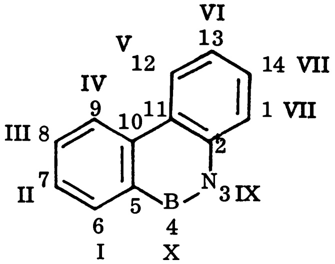
Fortunately in this case the experimental data are available *(4)*. Electrophilic substitution in II, I-borazaronaphthalene takes place almost exclusively in the III position.

In this case Model II seems to predict the electrophilic reactivity more accurately than Model I. However, prudence should be exercised in judging the merits of Models I and II solely on this basis. Dewar has pointed out that this exclusive electrophilic attack in the III position could be due to initial formation of a π-complex preferentially at the III-IV bond, which has the highest bond order in the molecule no matter which calculational method or model is utilized.

The nucleophilic and radical localization energies for II, I-borazaronaphthalene were also calculated.

X, IX-Borazarophenanthrene. In phenanthrene, positions I, III, VI, VIII, IX, and X are inherently the most reactive to electrophilic attack; positions IV and V are sterically hindered. In X, IX-borazarophenanthrene nitrogen will deactivate positions I, III, V, and VI, while boron will activate positions II, IV, VI, and VIII. Therefore, one would expect positions VI and VIII to be the most susceptible to electrophilic attack. Hückel and $P+P_O$ and $P+P_F$ electrophilic localization energy calculations for both models indicate that position VIII is the most reactive, followed by position VI. This checks with the experimentally determined order of reactivity *(4)*.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch027



For electrophilic attack, localization energy calculations for X, IX-borazarophenanthrene seem to be independent of choice of model. Nucleophilic localization energy calculations for this molecule also appear to be model-independent.

Charges and Bond Orders. The calculated bond orders for I, II-borazarene are presented in Table II.

Table II. I, II-Borazarene

	Bond		*Bond Orders*	
		Hückel	*$P+P_F$*	
	D		*Model I*	*Model II*
	II, III	0.5725	0.6362	0.2140
	III, IV	0.7083	0.6646	0.7889
	IV, V	0.6455	0.6782	0.5137
	V, VI	0.6421	0.6206	0.7986
	VI, I	0.6724	0.7084	0.3636
B-N	I, II	0.5114	0.5574	0.2119

The calculated π-charge densities for both the interior and exterior positions of II, I-borazaronaphthalene (Table III, A) and X, IX-borazarophenanthrene (Table IV, A) and the calculated bond orders for these molecules (Table III, B, and Table IV, B) are compared with the calculated values reported by Dewar *(4)*.

The general trend of charges and bond orders calculated in this study parallels that reported by Dewar *(4)*. The largest dissimilarities among the results are, as would be expected, in the calculated charges on boron and nitrogen and the calculated B-N bond orders.

The calculated charges on the carbon atoms in the positions adjacent to the boron or nitrogen show only relatively small variations due to choice of calculational model, and the calculated charges on the remainder of the positions in the molecule remain fairly invariant to the choice of model. The calculated bond orders are a bit more sensitive to the choice of model. There are moderate differences among the various calculational results not only in the bond orders between the heteroatom and its adjacent carbons but also between adjacent carbon atoms elsewhere in the rings.

In view of the lack of experimental data, such as NMR chemical shifts, which could shed some light on the charge distributions of these mole-

Table III. II, I-Borazaronaphthalene

A. π-Charge Densities

	J	*D*	D	*Hückel*	$P+P_F$ *Model I*	$P+P_F$ *Model II*
	Atom		*Charges*			
N	1	I	1.828	1.6068	1.4323	1.9530
	2		0.912	0.9158	0.8596	0.7088
	3	VIII	1.051	1.0355	1.0034	1.0169
	4	VII	0.972	0.9612	0.9791	0.9798
	5	VI	1.034	1.0207	1.0248	1.0634
	6	V	0.973	0.9635	0.9917	0.9931
	7		1.048	1.0302	1.0587	1.1246
	8	IV	0.861	0.8048	0.8708	0.8360
	9	III	1.125	1.1289	1.1094	1.2132
B	10	II	0.196	0.5325	0.6702	0.1112

B. Bond Orders

Bond			*Bond Orders*			
	1, 2	I, IX	0.361	0.4453	0.4987	0.1762
	2, 3	IX, VIII	0.624	0.5979	0.5427	0.6029
	2, 7	IX, X	0.564	0.5418	0.5515	0.5934
	3, 4	VIII, VII	0.682	0.7034	0.7462	0.7090
	4, 5	VII, VI	0.638	0.6170	0.5779	0.6169
	5, 6	VI, V	0.693	0.7159	0.7510	0.7117
	6, 7	V, X	0.591	0.5601	0.5248	0.5800
	7, 8	X, IV	0.465	0.5367	0.5485	0.4196
	8, 9	IV, III	0.818	0.6940	0.6959	0.8500
	9, 10	III, II	0.408	0.6302	0.6411	0.3264
B-N	10, 1	II, I	0.306	0.5253	0.6211	0.2124

cules, one cannot determine, at this time, which model may be preferable for calculation of charges and bond orders.

Delocalization Energies. Certain other calculated properties might also give some indication as to the preferable choice of input model. An observed physical property which one would like reproduced by theoretical calculations is the stability order.

I, II-borazarene	>	I, IV-borazarene	>>	I, III-borazarene
Most stable				Unstable

This stability order is derived from Dewar's statement, "No derivatives of I, III-borazarene have yet been reported, and the few known compounds containing the ring system I, IV-borazarene are less stable than those containing I, II-borazarene" *(4)*.

Table IV. X, IX-Borazarophenanthrene

A. π-Charge Densities

	Atom J	Atom D	D	Hückel	$P+P_F$ Model I	$P+P_F$ Model II
			Charges			
	1	VIII	1.037	1.0374	1.0066	1.0198
	2		0.951	0.9443	0.8791	0.7347
N	3	IX	1.888	1.6339	1.4505	1.9558
B	4	X	0.112	0.4712	0.6248	0.0902
	5		1.049	1.0848	1.0757	1.1050
	6	I	0.963	0.9182	0.9729	1.0116
	7	II	1.008	1.0099	1.0195	1.0256
	8	III	0.975	0.9396	0.9603	0.9593
	9	IV	1.006	1.0073	1.0149	1.0127
	10		0.967	0.9252	0.9217	0.9089
	11		1.033	1.0325	1.0598	1.1218
	12	V	0.994	0.9864	0.9959	0.9989
	13	VI	1.025	1.0249	1.0309	1.0669
	14	VII	0.992	0.9844	0.9874	0.9887

B. Bond Orders

	Bond J	Bond D	D	Hückel	$P+P_F$ Model I	$P+P_F$ Model II
			Bond Orders			
	1, 2	VIII	0.648	0.6133	0.5795	0.6183
	2, 3	IX	0.271	0.3954	0.4206	0.1632
	2, 11		0.595	0.5692	0.5822	0.6058
B-N	3, 4	IX, X	0.280	0.5480	0.6840	0.2118
	4, 5	X	0.271	0.5426	0.5316	0.2710
	5, 6	I	0.648	0.5571	0.5393	0.6313
	5, 10		0.595	0.5241	0.5510	0.6039
	6, 7	I, II	0.670	0.7045	0.7315	0.6844
	7, 8	II, III	0.653	0.6268	0.6013	0.6410
	8, 9	III, IV	0.680	0.6905	0.7205	0.6908
	9, 10	IV	0.615	0.6043	0.5747	0.6079
	10, 11		0.388	0.4407	0.4337	0.3605
	11, 12	V	0.615	0.5950	0.5740	0.6034
	12, 13	V, VI	0.680	0.6953	0.7188	0.6962
	13, 14	VI, VII	0.653	0.6350	0.6101	0.6312
	14, 1	VII, VIII	0.670	0.6900	0.7190	0.6971

It is possible to calculate the delocalization energies of the various borazarenes by an extension of the methods customarily utilized for aromatic hydrocarbons. For normal aromatic compounds, from the total energy of the molecule the energies of the separated pairs are subtracted to obtain the delocalization energies, which are in turn directly related to stabilities. The results of these calculations for the borazarenes indicate that while Model I does not reproduce the order of stabilities, Model II correctly predicts the order I, II > I, IV >> I, III Using Model II, the signs of the delocalization energies (in electron volts) are negative for I, II- and I, IV- (as one would expect for stable molecules) but positive for I, III-. This implies that I, III- may actually be unstable with respect to the separated pairs.

Conclusions

From the results of localization energy calculations for II, I-borazaronaphthalene in which Model II predicts the correct position for electrophilic attack and Model I does not, one might be tempted to infer that Model II is preferable for calculations of B-N pairs in these heteroaromatic boron systems. While it would not be judicious to base a choice of input models solely on the agreement with one experimental observation, the additional corroboration furnished by the delocalization energy calculations (in which the stability order is correctly predicted by Model II but not by Model I) indicates that Model II must not be too unreasonable a choice for B-N in the heteroaromatic compounds. For these compounds Model II (or a model close to it) seems preferable to Model I.

The changes in the behavior of the σ-frameworks as a function of the neighboring atoms lends credence to the conclusion that, while for borazine Model I (B-N) was the more effective, for the heteroaromatic boron compounds Model II ($B^- - N^+$) would be the more effective, since here initially the boron will have a higher σ-electron density and the nitrogen a lower σ-electron density than B-N pairs in borazine.

This analysis in terms of the changes in σ-framework to be expected for B-N pairs in different molecular environments appears to be a fairly sound criterion on which to base an initial choice of input model for calculations of the π-electron systems of these molecules.

Obviously, research remains to be done, in order to obtain the optimum sets of input parameters for LCAO-MO calculations on B-N compounds. The studies reported here were undertaken as preliminary calculations from which to project the direction of subsequent research in this field. From these studies theoretical models have been found to enable one to calculate desired properties for both borazines and heteroaromatic boron compounds with at least a moderate degree of accuracy.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch027

Acknowledgment

We thank Raymond Daudel, Odilon Chalvet, and G. Bessis, Centre de Mécanique Ondulatoire Appliquée, Paris, France, for the Pariser-Parr-SCF program used for these calculations.

We also thank Sol James, Chief of Automatic Computations, Martin Co. Computing Center, for arranging to have the calculations run at the center and Jane Flinn for her help in writing the supplementary programs and performing the computations.

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Received May 27, 1963. Research supported by the Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. AF49(638)-1220.

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The Formation and Behavior of Polycyclic Borazines

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch028

Condensation of borazine to polycyclic boron-nitrogen polymers has been studied in a silent electrical discharge of the ozonizer type. The effects of design of discharge apparatus, concentration of borazine vapor, partial pressure of hydrogen, residence time of borazine and polycyclic borazines in the discharge, and distance of the quenching trap from the discharge region have been examined. Intermolecular condensation of borazine by dehydrogenation to form diborazinyl, $B_6N_6H_{10}$, can be repressed by adding hydrogen to the discharge tube. Formation of borazanaphthalene, $B_5N_5H_8$, has been maximized to give 16% yields using a cyclic system. When crystalline or undercooled borazanaphthalene is held in the dark at room temperature, it decomposes very slowly yielding hydrogen, borazine, diborane, and nonvolatile polymeric materials. This instability resembles the decomposition of liquid borazine under similar conditions.

The pyrolysis of borazine vapor at 380° C. has been reported to give small yields of borazanaphthalene ($B_5N_5H_8$), diborazinyl ($B_6N_6H_{10}$), 2,4-diaminoborazine ($B_3N_5H_8$), and hydrogen. The reaction was very slow and the kinetic data suggested that a free radical mechanism was occurring *(5)*. Using the scavenger, diphenylpicrylhydrazyl, Co^{60} γ-radiolytic decompositions of $B_3N_3H_6$ have supported the proposed radical mechanism *(9)*. Further evidence of this type of mechanism was the isolation of benzyl bromide in the preparation of *B*-tribromoborazine from BBr_3 and $CH_3NH_3^+Br^-$ in toluene *(1)*. Substitution on an aliphatic side chain occurs by a free radical mechanism, whereas substitution to the aromatic nucleus is ionic.

Other investigators have prepared polycyclic borazines and their derivatives by different methods. Manatov and Margrave *(6)* studied the products of the decomposition of liquid borazine, when stored at room temperature, using mass spectrometric analysis. Derivatives of diborazinyl and borazanaphthalene have been made as secondary products from Grignard reactions *(2,7)* and from condensation reactions using *N*-lithio derivatives of pentamethylborazines *(8)*. These methods have given either very small yields or substituted derivatives.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

In this investigation we attempted to show the presence of the proposed free radicals during the thermal condensation of borazine vapor by taking electron paramagnetic resonance spectra at various temperatures. An electrical discharge provides more rigorous initiation of free radicals but maintains the milder thermal conditions necessary to prevent the further decomposition of products. These conditions are necessary to obtain larger yields of polycyclic borazines. A mass spectrometric analysis of the products coming directly from the discharge showed that polycyclic borazines were formed. A detailed investigation of the factors influencing the formation of polycyclic borazines was then required in order to obtain maximum yields from a cyclic electrical discharge system.

Experimental and Discussion

Materials and Analytical Methods. Borazine was prepared by the reduction of *B*-trichloroborazine *(3)* and purified by vacuum distillation to give a product of very high purity *(5)*. The polycyclic borazines were characterized using the mass spectrometer described previously *(5)*.

Electron Paramagnetic Resonance Study of Borazine. The electron paramagnetic resonance spectra were taken with an X- band spectrometer, a homodyne crystal spectrometer with 100-kcps (kilocycles per second) field modulation, and using a Varian Associates' 6-inch magnet. The spectrometer operated at 9.1 kmcps (kilomegacycles per second). Microwave frequencies were obtained from a Hewlett-Packard Model X532B wave meter to within ±1 mcps (megacycle per second). The magnetic fields were measured using a proton probe mounted on the axis of the static field about 1/2 inch from the center line of the microwave cavity. Proton oscillator frequencies were measured with a Hewlett-Packard Model 524D scaler. The spectrometer had a sensitivity of radical concentration of 10^{-10} *M*. The sample of borazine at 40-mm. pressure was sealed in a thin-walled quartz tube heated with a stream of nitrogen. Spectra were taken at 20°, 100°, 200°, 250°, 300°, and 350° C.

No detectable evidence of the formation of free radicals was observed. There was a very small amount of white solid in the tube at the conclusion of the experiment. These results indicated that either no free radicals were formed or their steady-state concentration was less than the sensitivity of the instrument. Another reason for not observing radicals would be a wide line width due to a high relaxation time with a short lifetime between states. The absence of a spectrum might be consistent with the very slow observed rate for the pyrolytic decomposition of borazine. Therefore, the free radical mechanism may still be involved.

Decomposition of Borazine Using Electrical Glow Discharge in Mass Spectrometer. A preliminary experiment was done using the mass spectrometer to determine the decomposition products of borazine in an electrical discharge.

The glass discharge apparatus was placed in the forechamber of the mass spectrometer. The discharge was maintained between two nickel plates, 1/2 inch in diameter, placed 1 inch apart. The discharge region was separated from the ionization chamber of the mass spectrom-

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch028

eter by a small pinhole. A high frequency coil of the Tesla type manufactured by the Central Scientific Co., No. 80730, was used to generate the discharge. The borazine vapor was supplied from an auxiliary vacuum system with a variable leak device to regulate the borazine pressure.

Three condensed volatile products were formed: $B_5N_5H_8$, *m/e* 129-133; $B_6N_6H_{10}$, *m/e* 154-160; and a new material, *m/e* 180-185. The mass spectra of $B_5N_5H_8$ and $B_6N_6H_{10}$ agreed with previous results *(5, 6)* The material of *m/e* 180-185 would correspond to a boraza analog of anthracene or an isomer thereof. There was no diaminoborazine formed, as was found in the thermal decomposition of liquid *(6)* and gaseous *(5)* $B_3N_3H_6$. The mechanisms must be different for the thermal and electrical discharge decompositions of $B_3N_3H_6$, but both probably are of the free radical type. The Co^{60} γ-radiolytic and thermal decompositions do not have the same mechanisms *(9)*. Since the radiolytic and electrical discharge processes are similar, the mechanisms are also probably similar.

Changes in the pressure of borazine and intensity of the discharge had no effect on the distribution or yield of products. At extremely low pressures of borazine, 10^{-2} and 10^{-4} mm. of Hg, none of the polycyclic borazines were observed. However, decomposition of the borazine had occurred, as shown by the formation of hydrogen.

Experiments Using Ozonizer-Type Discharge. To find the optimum conditions for maximum conversion of $B_3N_3H_6$ to polycyclic borazines, it was necessary to determine the effect of the discharge variables. The use of a variety of induction coils and the length of the discharge tube had no effect on the per cent conversion of $B_3N_3H_6$ to polycyclic borazines. Induction coils manufactured by Max Kohl A. G., Central Scientific Co., and Welsh Scientific Co., No. 2391A, were used. The Welsh coil and the 24-inch discharge tube, using dilute solutions of sulfuric acid and copper sulfate as electrolytes, initiated the largest conversion of $B_3N_3H_6$ per unit time. The discharge tube was always at room temperature.

Partial Pressure of $B_3N_3H_6$. The partial pressure of borazine vapor was varied by maintaining the supply bulb at a preselected temperature and allowing the vapor to pass through the discharge. The condensable products, constantly removed by a quenching trap, were fractionated before repassing the unconverted $B_3N_3H_6$ through the discharge. A -5°C. trap was used to remove $B_6N_6H_{10}$, -46° for $B_5N_5H_8$ and -196 C. for unconverted $B_3N_3H_6$. The nonvolatile products remained in the quenching trap. The distance of this trap from the discharge had no effect on the per cent yield of products. The maximum per cent conversion to $B_5N_5H_8$ resulted from the 0°C. conditions.

Additional Hydrogen Pressure. Hydrogen, one of the volatile products of the decomposition, was added in predetermined amounts to observe its effect on the condensation reaction. The static system, open to the quenching trap at -78°C. and the borazine supply bulb at 0°C., was operated continuously for 24 hours. The mean value of the initial and final hydrogen pressure is used in Figure 1. The percentage of $B_5N_5H_8$ decreased with increasing hydrogen pressure until pressures of 120 mm. of hydrogen were reached. Beyond this pressure a constant percentage of $B_5N_5H_8$ of 0.6 was maintained.

The formation of $B_6N_6H_{10}$ by intermolecular condensation with dehydrogenation was repressed. In electrical discharges of the ozonizer

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch028

Table I. Effect of Varying

Passes of $B_3N_3H_6$	*Temp. of $B_3N_3H_6$ in Supply Bulb, °C*[a]	*Initial $B_3N_3H_6$, Grams*	*$B_3N_3H_6$ Decomposed, Gram*
6	-46	1.3600	0.3880
8	0	3.0876	0.0728
12	+40	2.9908	0.0504

[a] Error in % $B_5N_5H_8$ and $B_6N_6H_{10}$ is a weighing error of 0.5 mg. in 80-gram bulb used.

type, active hydrogen was obtained when low pressures were used *(4)*. If a hydrogen atom were knocked off a borazine molecule, a borazinyl radical would be formed. The probability would be very great that another hydrogen atom would react to reform $B_3N_3H_6$ and repress the intermolecular condensation to form $B_6N_6H_{10}$. However, this process would not hinder ring rupture, which must be the initial reaction for the formation of $B_5N_5H_8$.

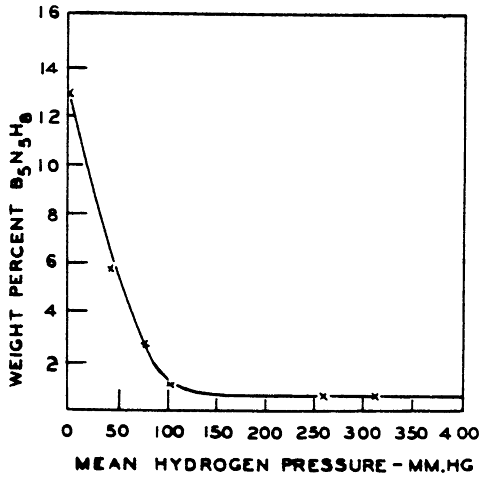

Figure 1. Effect of hydrogen pressure on yield of $B_5N_5H_8$. Static system

Semistatic Experiments with Additional Hydrogen Pressure. The static system with hydrogen decreased the yield of $B_5N_5H_8$. A semistatic system might increase the yield by decreasing the residence time, preventing further decomposition of volatile products.

A predetermined amount of dry hydrogen was introduced into the apparatus so that, at the end of the discharge interval, the mean hydrogen pressure would be 79 mm., reproducing a pressure used in the static system. With the borazine supply at 0 °C. and the quenching trap, -196 °C., at 40 cm. from the end of the reaction tube, the discharge was turned on for a preselected time, the discharge interval. After this time, the hydrogen was measured and removed. The procedure was then repeated—for example, 60 times for the 3-minute discharge interval to give a total discharge time of 3 hours.

Temperature of $B_3N_3H_3$ Supply Bulb

$B_5N_5H_8$ Formed, Gram	*%[a] $B_5N_5H_8$*	*$B_6N_6H_{10}$ Formed, Gram*	*%[a] $B_6N_6H_{10}$*
0.0089	2.3±0.3	0.0028	0.79±0.4
0.0093	13±1	0.0013	1.8 ±1.4
0.0045	9.0±2	0.0010	2.0 ±2.0

As shown in Figure 2, short discharge intervals of 3 to 10 minutes reproduced the results of the experiments with the $B_3N_3H_6$ supply at 0°C. without additional hydrogen. The per cent $B_5N_5H_8$ then decreased as the intervals became longer, giving finally at intervals of 60 minutes the results of the static system with 79 mm. of hydrogen. All these experiments were run for 3 hours.

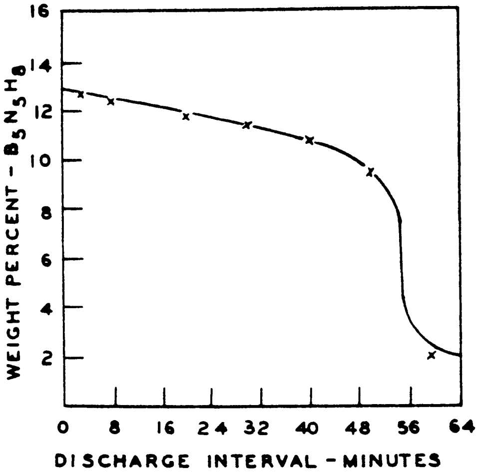

Figure 2. Effect of discharge interval on yield of $B_5N_5H_8$. Semistatic system. 79 mm. Hg hydrogen

To get larger quantities of $B_5N_5H_8$, the total time of discharge, the number of discharge intervals made, was increased. The 20- and 30-minute intervals were used because they gave the best yields of $B_5N_5H_8$ per unit experimental time. Less time was required for the addition and removal of hydrogen.

In Figure 3, the effect of the total discharge time on the yield of $B_5N_5H_8$ is shown. The per cent yield of $B_5N_5H_8$ decreased with total time, but the quantity of $B_3N_3H_6$ decomposed per hour of discharge remained constant. This decrease in yield is probably due to the decomposition of $B_5N_5H_8$ upon standing rather than failure to form initially. There was a greater decrease in the 20-minute interval experiments than in those at 30 minutes, which is consistent with the $B_5N_5H_8$ decomposing with time.

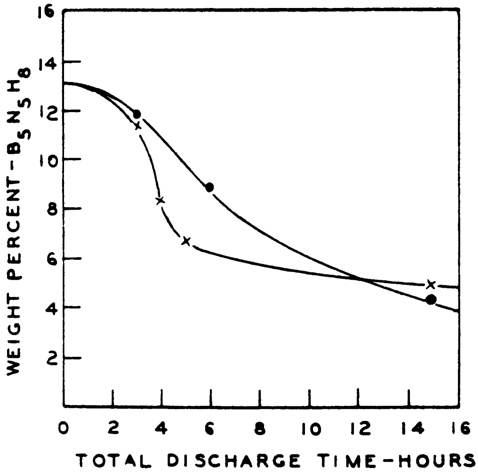

Figure 3. Effect of total discharge time on yield of $B_5N_5H_8$. Semistatic system. 79-mm. Hg hydrogen

● *20-minute discharge interval*

× *30-minute discharge interval*

Distance of Quenching Trap from Discharge Region. In all previous experiments, the quenching medium was 40 cm. from the end of the discharge region. The formation of $B_5N_5H_8$ must result from the cleavage of the borazine ring and the production of many small fragments. Thus, on increasing the distance of the quenching trap, there would be a longer reaction time and the possibility of increased yields.

The results of these experiments were inconclusive, the yield of $B_5N_5H_8$ being constant or slightly decreased. The minimum and maximum distances were 40 and 120 cm., the other experimental conditions of hydrogen and $B_3N_3H_6$ being constant. The temperature of the quenching trap at -46°, -78°, or -196°C. did not change yield. Thus, the reaction to form $B_5N_5H_8$ must be complete at some distance close to the discharge region.

Decomposition of Borazine Using Cyclic System. A cyclic system, diagrammed in Figure 4, was designed to prepare larger quantities of $B_5N_5H_8$.

A 50-ml. flask, *A*, serving as a $B_3N_3H_6$ supply bulb, was connected to the 24-inch discharge tube which joined stopcock 1 and the cold finger trap, *C*. The cycle was completed by attaching *C* to flask *A*, by means of the magnetic valve, 4. For the periodic removal of *H*, trap *D*, joined to *C* by magnetic valve 5, led to stopcock 3, the 2-liter bulb, *B*, and finally the vacuum system. Stopcock 2 isolated the $B_3N_3H_6$ cycle from the vacuum system. The electrical discharge supplied by the Welsh induction coil, No. 2391A, was conducted in the tube by dilute solutions of copper sulfate and sulfuric acid.

In a typical experiment, 6 grams of borazine was distilled into flask A, with stopcocks 1 and 3 closed and 2 open. After stopcock 2 had been closed, trap *C* was cooled to -46°C. and the borazine warmed to 0°C. With the ice-water mixture above the borazine-return side arm, stopcock 1 was opened and the discharge started. The unconverted borazine and polycyclic borazines condensed on *C* and the $B_3N_3H_6$ then dripped

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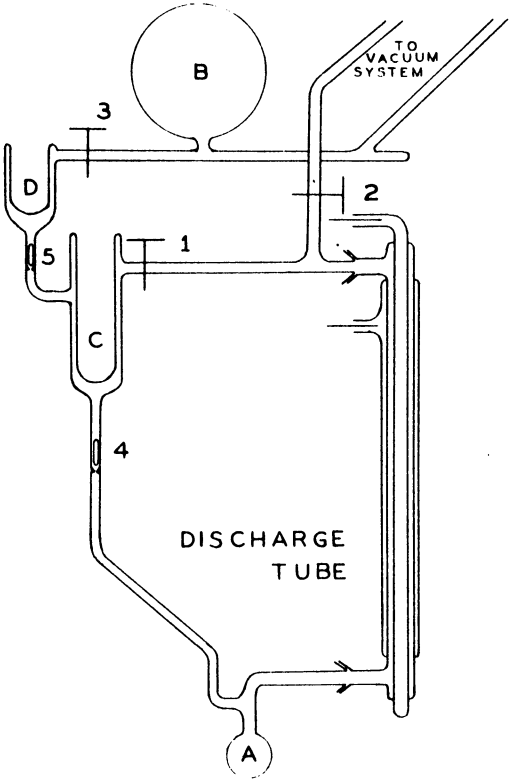

Figure 4. Cyclic electrical discharge system

down and filled the region above magnetic valve 4. This valve was opened and the $B_3N_3H_6$ returned to the supply bulb. After approximately 30 minutes of discharge, trap *D* was cooled to -196°C., and stopcock 3 and then magnetic valve 5 were opened. The hydrogen expanded into bulb *B* and any $B_3N_3H_6$ condensed in the trap. Stopcock 3 and magnetic valve 5 were closed and the 5 mm. of hydrogen was pumped away after passing through another -196°C. trap on the vacuum system to prevent loss of $B_3N_3H_6$. Trap *D* was then warmed to room temperature and the borazine returned to the discharge apparatus through valve 5. This procedure was repeated after every 30 minutes of discharge.

After 5 hours, the products of the reaction were fractionated as previously described; 1.1719 grams of $B_3N_3H_6$ had been decomposed to yield 0.1930 gram of $B_5N_5H_8$ (16.45%) as the only product volatile at room temperature. These results were found to be reproducible. The nonvolatile products were on the walls of cold finger *C* and the borazine return tube.

In an attempt to investigate the nonvolatile solids, 30 ml. of toluene, dried over sodium, was distilled into the apparatus. It was cycled through the apparatus by keeping trap *C*, containing the nonvolatile solids, at 0°C. After these solids had been extracted, approximately 25 times, the toluene solution was transferred to a sublimator. Most of the solids were insoluble and were not studied because of difficulty in obtaining a sample. The toluene, removed by vacuum distillation, was pure and no volatile material remained in the sublimator. About 0.2 gram of nonvolatile solids was obtained and heated with an oil bath. At 50°C. decomposition occurred, as shown by the presence of hydrogen and a volatile material which collected in a -196°C. trap. At 90°C. part of the material in the sublimator melted. There was no sublimation to the cold finger at temperatures up to 200°C. The volatile material collected at -196°C. was fractionated and approximately 30 mg. of $B_5N_5H_8$ was obtained. Part of the extracted solids must then have decomposed to yield $B_5N_5H_8$. No further information was obtained about this material, since it was impossible to get a pure sample.

The cyclic apparatus was designed using the results of the earlier discharge experiments. The residence time of $B_3N_3H_6$ and polycyclic borazines in the discharge, the partial pressure of $B_3N_3H_6$, and the inherent instability of $B_5N_5H_8$ had to be considered. The 24-inch discharge tube in conjunction with the Welch induction coil, No. 2391A, and the borazine at 0°C. gave the best conditions of partial pressure and flow rate to decompose the largest quantity of $B_3N_3H_6$ per unit time and yield the most $B_5N_5H_8$. The temperature of the quenching trap, -46°C., placed 35 cm. from the discharge tube, was determined using several considerations. The temperature had to be low enough to condense the polycyclic borazines but high enough to keep the $B_3N_3H_6$ a liquid, so that it could return to the 0° supply bulb. If some of the $B_5N_5H_8$ dissolved in the borazine and returned to the 0° bulb, the hydrogen and low vapor pressure of $B_5N_5H_8$ would prevent any appreciable quantity from getting back into the discharge region. The hydrogen was removed every 30 minutes, so that there would be enough hydrogen to repress the formation of $B_6N_6H_{10}$ and little enough to provide short residence times.

Decomposition of $B_5N_5H_8$ upon Standing. A sample of pure $B_5N_5H_8$ (0.690 mmole), which had been fractionated three times through a -5° trap and into -46°C. to remove any $B_6N_6H_{10}$ and $B_3N_3H_6$, was allowed to stand at room temperature in the dark. The mass spectrum showed this to be a pure sample. To check the decomposition periodically, the sample was cooled to -196°C. and the H_2 measured by means of a Toepler pump and gas buret assembly. The total H_2 evolved after 20 days was 0.117 mmole; after 34 days, 0.152 mmole; and after 56 days, 0.193 mmole. The condensable volatile products of the decomposition were $B_3N_3H_6$ and B_2H_6 in almost equal amounts, as shown by mass spectral analysis. The nonvolatile material was a glass.

After the removal of all volatile material, the nonvolatile glass was heated to 60°C., which initiated the evolution of H_2 and a volatile material collecting at -196°C. This material was fractionated and shown to be $B_5N_5H_8$ by its mass spectrum. These observations are similar to those for the pyrolysis of the nonvolatile residues of the original electrical discharge decomposition products.

$B_5N_5H_8$ is not stable at room temperature and decomposes in a manner similar to that of liquid $B_3N_3H_6$ *(6)*, to give H_2, B_2H_6, $B_3N_3H_6$, and a nonvolatile glass. This instability explains the small yields of $B_5N_5H_8$ in the pyrolytic decomposition of borazine.

Research is being continued on the physical and chemical properties of $B_5N_5H_8$. Decomposition, the addition reaction of $B_5N_5H_8$ with

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch028

anhydrous HCl and HBr, and the subsequent pyrolysis of the products are being studied.

Acknowledgment

We thank the National Science Foundation and the Advanced Research Project Agency for financial support for this research, and the U. S. Borax Corp. for supplying the *B*-trichloroborazine. We are grateful to Richard F. Porter for the mass spectral analyses and J. L. Ragle fo.. the electron paramagnetic resonance study.

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Received May 14, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch028

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch029

29

A New Boron-Nitrogen Ring System

The Tetrameric Borazynes

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The tetrameric borazynes, $(RNBX)_4$ (X = Cl or Br), are obtained by the dehydrohalogenation of the 1:1 adducts of tertiary-alkyl primary amines with boron trichloride or boron tribromide. They are stable crystalline solids showing, in remarkable contrast to the *B*-chloroborazoles, a very low chemical reactivity. On the basis of electrical measurements, nuclear magnetic resonance and vibrational spectroscopy, and x-ray diffraction studies they have been shown to be eight-membered ring compounds standing in the same relation to the borazines as cyclo-octatetraene to benzene. Their chemical reactions have been studied. In contrast to the very low chemical reactivity with most reagents, the halogen atoms are easily replaced by pseudohalogens. Some interesting examples of anomalous behavior on partial substitution have come to light.

The possibility of obtaining boron-nitrogen polymers analogous to organic polymers with carbon chains is based on the analogy between the $[sp^2]p_\pi^0$ boron-$[sp^2]p_\pi^2$ nitrogen and the $[sp^2]p_\pi^1$ carbon - $[sp^2]p_\pi^1$ carbon pairs, and the interest in such polymers as thermally stable materials rests upon the high bond energy of the B-N bond (104.3 kcal. per mole) and the high temperature stability of certain boron-nitrogen compounds already examined, such as boron nitride and the alkylborazines. Such analogies have a rather limited application — thus, for example, aminoboranes, RR'BNR''R''', containing three-coordinate boron and nitrogen, are usually easily hydrolyzed, though this tendency may be modified by a suitable choice of substituents.

The trimeric borazynes (the borazines) are well known and have some aromatic character *(7)*. They are the usual products of reactions from which the monomeric borazyne, RBNR' (isoelectronic and isosteric with the acetylene RCCR'), would be expected. It was therefore of interest to discover whether by the suitable choice of experimental conditions or substituents or both, the formation of the trimers might

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

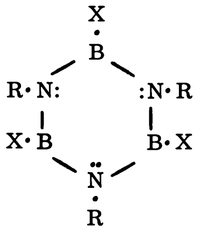
be avoided in favor of higher cyclic or linear polymers. In fact, a series of cyclic tetrameric borazynes has been discovered which constitutes a new boron-nitrogen ring system *(6)*. This paper outlines our work on the preparation, structure, and reactions of this series of compounds.

The dehydrohalogenation of the 1:1 adducts (I) of primary amines and boron trihalides was selected as a suitable model for the study of the possibility of inhibition of borazine formation. When these adducts, or alternatively the mixture of 1:1 adduct, tetrahalogenoborate (II), and dihalogenoaminoborane (III) which may be formed when equimolar quantities of amine and boron trihalide are mixed, are heated in solution or treated with a suitable tertiary base, hydrogen halide is eliminated.

RNH_2, BX_3 X=Cl, Br $\qquad R\overset{+}{N}H_3\ \overset{-}{B}Cl_4 \qquad R\ddot{N}H \cdot BX_2$

I II III

The course of the reaction depends on the nature of the amine; it is not necessarily the same for the two sets of conditions. In the aliphatic series the products are determined by the degree of substitution of the α-carbon atom of the amine. Thus while 1,2-dimethylpropylamine and other less hindered primary alkylamines give good yields of *sym-N*-alkyl-*B*-halogenoborazines (IV), 1-isopropyl-2-methylpropylamine and other more highly hindered secondary alkyl primary amines give mixtures which include the aminoborane (III), the halogeno-bis-(alkylamino)-borane (V), and compound (VI) and from which the borazine may be absent.



IV

$(R\ddot{N}H)_2BX \qquad R\ddot{N}H \cdot BX \cdot \ddot{N}R \cdot BX \cdot \ddot{N}HR$

V VI

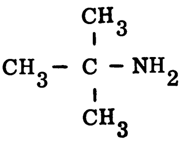
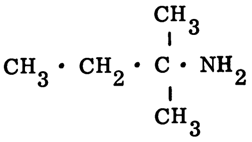
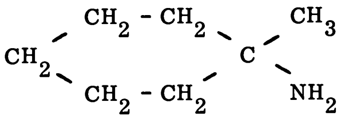
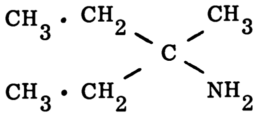
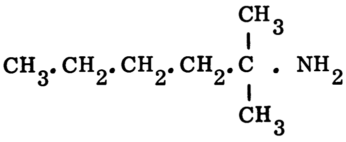
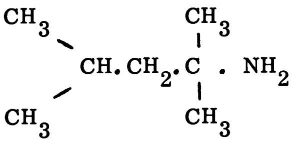
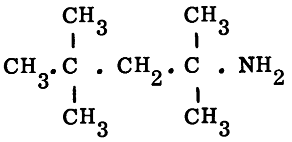
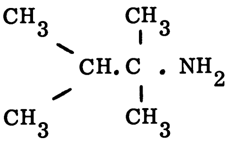
When the α-carbon atom is fully substituted — i.e., when the amine is a tertiary alkyl primary amine — the borazine is never found among the reaction products, but depending on the nature of the substituents tetrameric borazynes (VII) may be forund. Some of these compounds are listed in Table I.

$(RNBX)_4$

VII

From the comparatively limited series of examples it appears that branching at the β-carbon atom of the tertiary alkylamine inhibits tetramer formation and that normally two at least of the α-substituents must be methyl groups. The contrast between 1-methylcyclohexylamine

Table I. Tetrameric Borazynes $(RNBX)_4$

	Parent Amine	*X*	*Tetramer M.P., °C.*
1.	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-NH_2$	Cl Br	249 240
2.	 $CH_3\cdot CH_2\cdot\underset{CH_3}{\overset{CH_3}{C}}\cdot NH_2$	Cl	162
3.		Cl	271
4.		Cl	Not formed
5.	 $CH_3.CH_2.CH_2.CH_2.\underset{CH_3}{\overset{CH_3}{C}}.NH_2$	Cl	93
6.		Cl	114
7.	 $CH_3.\underset{CH_3}{\overset{CH_3}{C}}.CH_2.\underset{CH_3}{\overset{CH_3}{C}}.NH_2$	Cl Br	200 200
8.		Cl	Not formed

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

and 1-ethyl-1-methylpropylamine is strikingly illustrative of the greatly diminished hindrance when two ethyl groups on the α-carbon atom form part of a cyclohexane ring. In those cases where tetramer formation was inhibited, the products appeared to be mixtures of low molecular weight polyborazynes, $(RNBCl)_n$.

Of the tetrameric borazynes, that from *tert*-butylamine and boron trichloride, (*tert*-$BuNBCl)_4$ (VIII), has been the most thoroughly examined. It is a white solid [m.p. 249° (in vacuo)], easily soluble in

(*tert*-$BuNBCl)_4$

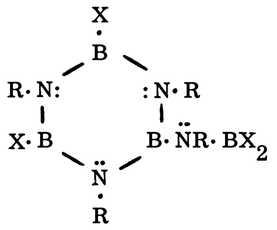
VIII

nonpolar but much less so in polar organic solvents. When crystallized from carbon tetrachloride it separates with two molecules of solvent per molecule of tetramer. Its composition has been established by direct elementary analysis and also by hydrolysis, which gives *tert*-butylamine, boric acid, and hydrogen chloride in equimolar amounts. The molecular weight has been determined cryoscopically and ebullioscopically and is confirmed by the presence of peaks in the 560 *m/e* region of the mass spectrum of the corresponding isothiocyanate, (*tert*-$BuNBNCS)_4$. The compound sublimes very readily and the molecular depression constant falls within the limits of 53 and 95 (camphor, 40). Even after allowance is made for the higher melting point, the latent heat of fusion of VIII must be below that of camphor.

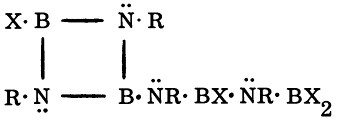
The reactivity of the tetrameric borazynes is in striking contrast to that of the *B*-chloroborazines. They are insoluble in and not measurably attacked by boiling water. In homogeneous solution in boiling 50% aqueous dioxane the rate of hydrolysis is very low and some rough measurements on VIII have indicated that it is independent of pH over a very wide range. This strongly suggests an S_N1 reaction. With lithium and Grignard reagents there is no significant reaction, and attempts to replace the halogen atoms by hydrogen using lithium and sodium borohydrides have failed. When pure (*tert*-$BuNBCl)_4$ is dissolved in an ethereal solution of diazomethane at room temperature there is no reaction, a truly remarkable indication of the low reactivity at the boron atoms. With the lower aliphatic amines partial replacement of chlorine may be brought about under forcing conditions but pure species have not been isolated. Attempts to replace the chlorine atoms by fluorine or iodine have so far failed. On the other hand, replacement of halogen by most of the pseudohalogens takes place under mild conditions. Thus the tetra-*B*-isocyanate, isothiocyanate, isoselenocyanate, and azide have been prepared by the reaction of VIII with an alkali-metal salt in a suitable organic solvent. The product of the reaction of the chloro compound with potassium thiocyanate was identified as the isothiocyanate on the basis of the infrared absorption spectrum. Chlorine has not been replaced by cyanide or isocyanide. The pseudohalogen derivatives are all at least as stable as the chloro compound. The tetraazide, for example, melts with little decomposition at 276° C. The tetraisothiocyanate, unlike VIII, shows parent peaks in the mass spectrum.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch029

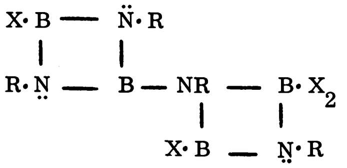
A number of possible structures may be written for the tetrameric borazynes. In the light of the physical and chemical properties described above, the linear tetramer and structures such as IX, X, and XI seem highly improbable and the three structures (XII, XIII, and XIV) have been given serious consideration.



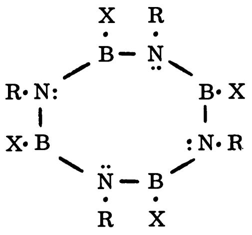
IX



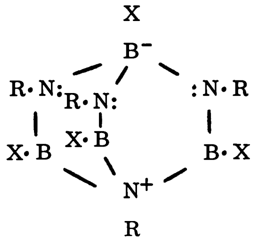
X



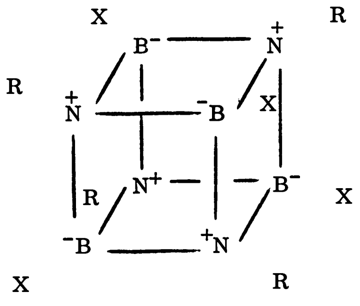
XI



XII



XIII



XIV

Planar forms of XII are sterically impossible, but molecular models of the boat, chair, and crown forms can be made. The boat form is apparently strain-free; within the ring sterically favored π-bonding is possible between boron and nitrogen atoms of the separate B-N pairs, but not between those of adjacent pairs. The chair and crown forms are more overcrowded and opportunities for *p*-orbital overlap show a concurrent decrease. A molecular model of XIII can be made, but not of XIV, although analogous cubane derivatives of carbon *(2)* and of aluminum and nitrogen *(3)* are known. In all these cases the molecule is almost spherical, with highly inaccessible boron atoms, and all the structures are generally compatible with the low reactivity, high volatility, and solubility of the tetramers.

The three likely structures could be distinguished unequivocally by the determination of the number of isomers formed on partial substitution (Table II) and attempts have been made to achieve partial replacement of chlorine in VIII by the isothiocyanato and azido groups. When VIII reacts with a deficiency of potassium thiocyanate, a product is obtained with a gross composition corresponding to partial substitution, but by fractional crystallization this can be separated very largely into VIII and the tetraisothiocyanate. The mass spectra of such products suggest a mixture of partially substituted products, but their infrared spectra can be duplicated exactly by artificial mixtures of VIII and tetraisothiocyanate of the same over-all composition, and it seems inconceivable that the changes of symmetry on partial substitution would not produce detectably different vibrational spectra. The azido compounds behave differently. Here the products appear on the basis of the same criteria to be mixtures of intermediate products — for example, a product with an over-all composition corresponding approximately to (*tert*-$BuNB)_4Cl_{1.5}(N_3)_{2.5}$ was estimated by mass spectrometry to contain roughly 45% (*tert*-$BuNBN_3)_4$, 20% (*tert*-$BuNB)_4Cl(N_3)_3$, 20% (*tert*-$BuNB)_4Cl_2(N_3)_2$, 5% (*tert*-$BuNB)_4Cl_3N_3$, and 10% (*tert*-$BuNBCl)_4$. However, it has not been possible to separate the pure compounds by fractional crystallization, and the structure of the tetramers has been assigned on the basis of physical studies.

Table II. Number of Isomers on Partial Substitution of Tetrameric Borazynes

Derivative	*Eight-Membered Ring (XII)*	*Bicyclic Structure (XIII)*	*Cubane Structure (XIV)*
Monosubstituted	1	2	1
Disubstituted	2	2	1
Trisubstituted	1	2	1

The ^{11}B nuclear magnetic resonance spectra of (*tert*-$BuNBCl)_4$ (VIII) and (*tert*-$BuNBBr)_4$ contain only a single boron resonance, and a comparison of the chemical shifts with those of reference compounds (see Table III) strongly suggests that the tetramers contain only 3-coordinate boron atoms. Only structure XII can be reconciled with these observations.

Measurements of the dielectric absorption of solutions of (*tert*-$BuNBCl)_4$ show that there are no detectable maxima in the range 10^3 to 3.6×10^{10} c./s.: The dipole moment is therefore zero or very small. This result is compatible with the boat and chair forms of the eight-membered ring structure (XII) and with the cubane analog (XIV) but probably not with the bicyclo-octane analog (XIII). If the orientation

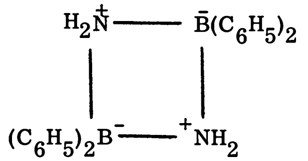
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch029

Table III. ^{11}B Chemical Shifts in Some Boron-Nitrogen Compounds

Substance	*Chemical Shift (BCl_3 = 0), P.P.M.*
Tetramers	
(*tert*-$BuNBCl)_4$	+17.4
(*tert*-$BuNBBr)_4$	+17.2
Three-coordinate boron compounds	
$(HNBCl)_3$	+11
$(CH_3NBCl)_3$	+14
$B(NEt_2)_3$	+16.3[5]
Four-coordinate boron compounds	
$B(OMe)_4^-$	+44.3[5]
$B(NC_4H_4)_4^-$ [a]	+46
(*tert*-$BuNHBCl_2)_2$	+43.3
$(Me_2N.BCl_2)_2$	+37.2

[a] NC_4H_4 = 1-pyrrolyl.

polarization is indeed zero, the difference (13.7 c./c.) between the total electric polarization (133.5 c./c.) obtained from dielectric constant measurements on dilute solutions and the electron polarization (119.8 c./c.) derived from measurements of the refractive index of solutions at a series of wavelengths in the visible region is attributable to the atom polarization. Coates and Livingstone *(1)* have given a value of 17.5 c./c. for the atom polarization of the dimer of aminodiphenylborane (XV). Structure XIV, with a more extensive system of balanced dipoles than the cyclic dimer, and, to a lesser extent, structure XIII would be expected to have larger or at least comparable values of atom polarization. Even if the orientation polarization were not zero, the maximum possible value of the dipole moment (on the highly improbable assumption of zero atom polarization, which would, of course, rule out structures XIV and XIII) would be only 0.74 Debye. In view of the bulky substituents and the possibility of molecular distortion through overcrowding, even this value would probably not be inconsistent with our conclusions.



XV

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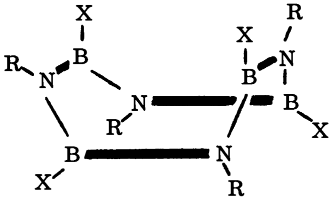
The experiments on partial substitution of chlorine by azido group in VIII, though incomplete, may be said to provide some evidence against the bicyclic structure (XIII) in that there was no evidence for the preferential formation of mono- or trisubstituted derivatives.

The mass spectra of (*tert*-BuNBCl)$_4$ and the tetraisothiocyanate have been recorded and the formulas of most of the main fragments have been assigned. These do not appear to allow any absolutely clear-cut distinction to be made between the three likely structures, but may be said to favor the eight-membered ring. In Table IV the probable structures of the larger fragments are set out in terms of the fragmentation of molecules containing an eight-membered ring. The tetraisothiocyanate is the more stable; the two heaviest fragments contain the intact ring, whereas this is not found in any fragment from (*tert*-BuNBCl)$_4$. A comparison of these results with those of Lappert *(4)* demonstrates that the four-membered borazyne dimer ring has greater stability than that of the tetramers.

The tetrameric borazynes have characteristic vibrational spectra and in order to assist in assigning the absorption bands fully deuterated (*tert*-BuNBCl)$_4$ and the corresponding *B*-bromo, isothiocyanato, and azido compounds have been prepared from $(CD_3)_3C \cdot NH_2$. A study of these spectra (see the Appendix) has demonstrated that the boat conformation of the eight-membered ring (XVI) is the most likely structure, that the corresponding chair conformation is unlikely, and that structures XIII and XIV may be excluded.

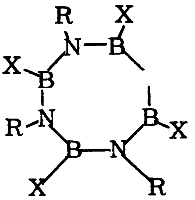
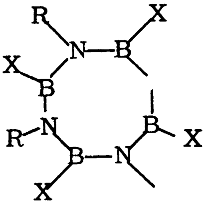
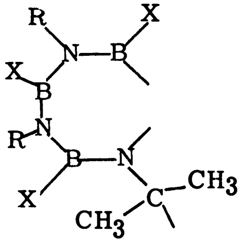
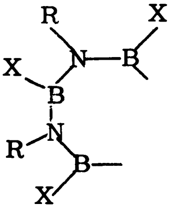
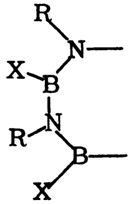
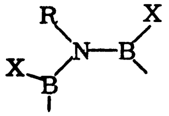


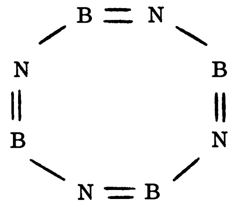
XVI

The consensus of the evidence is that the tetrameric borazynes are best represented by the eight-membered ring structure (XII) and probably normally exist in the boat conformation (XVI). The ring may have localized alternating π-bonds: The low reactivity is steric in origin. This view of the structure finds confirmation in the preliminary results of an x-ray diffraction study on single crystals of (*tert*-BuNBNCS)$_4$ carried out by P. T. Clarke in H. M. Powell's laboratory. The boat conformation of the ring and the alternation of B-N bond lengths within the ring are clearly shown. The BNCS group is essentially linear; the interaction between the isothiocyanate groups and the boron-nitrogen pairs of the ring implied by this presumably explains the greater stability of (*tert*-BuNBNCS)$_4$ in the mass spectrometer.

The parent compound of the series has structure XVII and is systematically named 1,3,5,7-tetraza-2,4,6,8-tetraborocine, and the tetrameric borazynes are to be regarded as substitution products of the octahydro compound, for which the trivial name borazocine has been suggested by R. S. Cahn; VIII is thus tetra-*B*-chlorotetra-*N*-*tert*-butylborazocine.

Table IV. **Larger Fragments Found in Mass Spectra of Some Tetrameric Borazynes**

		$(^{t}BuNBCl)_4$	$(^{t}BuNBNCS)_4$
Parent	Ring Intact	No	Yes
Parent - CH_3		No	Yes
		Yes	Yes
		Yes	No
		No	Yes
		No	Yes
 1/2 Molecule - CH_3		Yes	Yes
		Yes	Yes



XVII

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch029

The reactions leading to the formation of (*tert*-BuNBCl)$_4$ have been examined. *tert*-Butylamine reacts with boron trichloride to give a mixture of the 1:1 adduct, *tert*-butylammonium tetrachloroborate, and dichloro-*tert*-butylaminoborane, and each of these undergoes dehydrochlorination in the presence of triethylamine to give VIII. The course of the dehydrochlorination of the 1:1 adduct *tert*-BuNH$_2$ · BCl$_3$, depends critically on the nature of the tertiary base. Thus while triethylamine gives rise to VIII, the strongly basic but highly hindered base diisopropylethylamine does not. On the other hand trimethylamine displaces *tert*-butylamine from the adduct with formation of Me$_3$N· BCl$_3$. This strongly suggests that in this case, and probably in analogous cases, the first stage of the reaction involves nucleophilic attack by the base, and if the donor qualities of the base are too great (as with trimethylamine) the primary amine rather than a chloride ion is displaced. The thermal dehydrochlorination of many primary aliphatic amine-boron trichloride complexes gives rise to the same products as dehydrochlorination by a base. The decomposition of *n*-PrNH$_2$ · BCl$_3$ in boiling chlorobenzene to give *B*-chloro-*N*-*n*-propylborazine and 2 moles of hydrogen chloride shows essentially first-order kinetics. The elimination of hydrogen chloride from *tert*-butylamine-boron trichloride under the same conditions becomes extremely slow after one mole is evolved and the product contains dichloro-*tert*-butylaminoborane but no tetramer.

Many aspects of the chemistry of the borazocines remain to be elucidated. In particular there is a need for a thorough examination of the substitution reactions, including kinetic studies.

Acknowledgment

We are indebted to B.N. Figgis, University College, for the nuclear magnetic resonance spectra and for discussion of the results, to the British Petroleum Co., Ltd., for the measurement and interpretation of the mass spectra in their research laboratories, and to E. Rushton, Standards Division, National Physical Laboratory, for the electrical measurements.

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Received May 24, 1963.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch029

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

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The Vibrational Spectra and Structure of Some Tetrameric Borazynes

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch030

The infrared (5000 to 200 cm.$^{-1}$; solid, solutions in CS_2, CCl_4) and Raman (solutions in CS_2, *n*-heptane) spectra of $[(CH_3)_3CNBCl]_4$ and $[(CD_3)_3CNBCl]_4$ have been measured; depolarization ratios of the Raman lines were measured for the former compound. Infrared data were also obtained (5000 to 420 cm.$^{-1}$) for $[RNBX]_4$, R = $(CH_3)_3C$, $(CD_3)_3C$; X = Br, NCS.

Using complete assignments for $(CH)_3CNH_2$ and $(CD_3)_3CNH_2$, assignments have been made of the frequencies for R = $(CH_3)_3C$, $(CD_3)_3C$, X = Cl, associated principally with the *tert*-butyl group. The remaining frequencies have been considered in terms of four model structures for the ClBNC skeleton: *(a)* XIII (point group C_3), *(b)* XIV (T_d), *(c)* the chair conformation of XII (C_i), and *(d)* XVI (S_4). At least eight, and probably 11, polarized Raman lines have no infrared counterpart and the C_3 and T_d models are therefore excluded. Unless several additional polarized Raman lines have escaped detection, the C_i model is also unlikely and the boat (S_4) structure is that most consistent with the observed spectra.

A Raman-active pair (species *a* for S_4) of essentially B-N stretching modes can be assigned at 1313, 1305 cm.$^{-1}$, with a similar infrared active pair (*b* or *e*) at 1370, 1396 cm.$^{-1}$ for $[(CH_3)_3CNBCl]_4$. For $[(CH_3)_3CNBBr]_4$ the latter pair is at 1385, 1355, cm.$^{-1}$, and for $[(CH_3)_3CNBNCS]_4$ at 1420, 1382 cm.$^{-1}$. Other observed frequencies of the ClBNC skeleton cannot be ascribed with certainty to specific vibrations.

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Amine Addition Compounds of H_3BCO and B_4H_8CO

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University of Michigan, Ann Arbor, Mich.

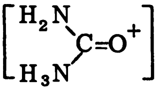
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch031

The methylamine adducts of H_3BCO and B_4H_8CO have been characterized. The structure of $H_3BCO \cdot 2NH_2CH_3$ has been established as $[NCH_3H_3{}^+]\ [H_3BC\overset{O}{\nearrow}\text{-}NCH_3{}^-]$ using reaction chemistry and x-ray diffraction techniques. The new anion $H_3BCONHCH_3{}^-$, is formally analogous to carbomate anion in which BH_3 replace the isoelectronic oxygen atom. On the basis of chemical reactions, strong evidence for the structures of $H_3BCO \cdot 2NH_3$, $H_3BCO \cdot 2NH(CH_3)_2$, $H_3BCO \cdot N(CH_3)_3$, and $B_4H_8CO \cdot 2NH_3$ is given. Oxygen in a carbamate anion appears to be replaceable by several borane Lewis acids.

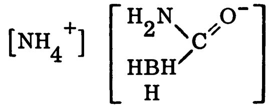
Carbon monoxide-borane, H_3BCO, was first prepared by Burg and Schlesinger *(4)* through an ingenious high pressure reaction between CO and B_2H_6. The molecule has C_{3v} symmetry, with the boron, carbon, and oxygen atoms being collinear *(2, 6, 7, 17)* and with a dipole moment of 1.80 *D (16)*.

In their original study, Burg and Schlesinger *(4)* noted that carbon monoxide-borane reacts with trimethylamine to give trimethylamine-borane and free CO, suggesting a simple base displacement reaction. On the other hand, ammonia reacts with H_3BCO to give a triammoniate of carbon monoxide-borane, $H_3BCO \cdot 3NH_3$, which liberates ammonia on warming to give a relatively stable white solid "diammoniate of carbon monoxide-borane," $H_3BCO \cdot 2NH_3$. The structure of the "diammoniate" was never established, although several structural postulates were based on the reaction of the compound with sodium in liquid ammonia solution *(4)*. At 78 °C., one equivalent of hydrogen is liberated rapidly and a second equivalent is liberated over a 12-hour period at -49 °C. Such observations have suggested representation of the solid as a diammonium salt, $(NH_4)_2X$. One such representation used in an advanced inorganic textbook *(1)* is: $[NH_4{}^+]_2[COBH^{-2}]$. The structural problem represented by the diammoniate of carbon monoxide—borane could not be resolved by conventional x-ray diffraction techniques, since the solid as originally prepared was amorphous and did not give even a powder pattern, let alone a single crystal. The spectral data of Taylor and Cluff *(13)* eliminated unequivocally a structure containing the dihydridodiaminoboron (III) cation, $[H_2B(NH_3)_2{}^+]$,

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

or the borohydride anion, $[BH_4^-]$, thus eliminating such structural possibilities as $[H_2B(NH_3)_2^+][HCO^-]$ and  $\left[\begin{matrix} H_2N \\ \quad C{=}O^+ \\ H_3N \end{matrix}\right]$ $[BH_4^-]$. The spectra did not, however, provide suitable evidence for an independent structural analysis.

This present paper reports the results of separate chemical and physical studies of several methylamine adducts of H_3BCO and establishes, by analogy, the structure of the diammoniate of borane carbonyl as:



In a formal sense the structure is analogous to that of ammonium carbamate, except that a BH_3 group replaces the isoelectronic oxygen atom in the carbamate anion. Such a replacement was first suggested in this laboratory as a result of an earlier analogy used by Mulliken *(10)* relating the BH_3 group and the isoelectronic exygen atom and the B_2H_6 and isoelectronic O_2 molecules. Although the original formal analogy of BH_3 and O proved to be of little value in an absolute sense, it has provided the basis for rather extensive structural interpretations *(8, 11)*. Its expansion to include such Lewis acids as B_4H_8 as well as BH_3 provides a sound structural interpretation for the newly synthesized diammoniate of carbon monoxide—tetraborane *(18)*.

Reactions of Carbon Monoxide–Borane with Ammonia and Methylamines

Reaction of H_3BCO and NH_3. Although the direct reaction of carbon monoxide—borane and ammonia produces an amorphous solid, the corresponding reaction in dimethyl ether, beginning at a temperature of -126° C. and continuing to -80°C. over a 4-hour period, gives a white crystalline product with a definite x-ray powder pattern. The compound is considerably more stable than that formed by direct reaction of H_3BCO and NH_3. It is not vigorously hydrolyzed by water, but can be hydrolyzed completely with HCl in a sealed tube at 175°C. The analytical ratio of nitrogen to boron in the hydrolysis product was 2.05 to 1.00. Complete analysis of the carbon monoxide—borane ammonia addition product was difficult because of the interaction of CO and H^- prior to and during analysis to give methanol. On the basis of the stoichiometry of compound formation, the satisfactory N-B ratio, and the apparent homogeneity of the original product, the formula $H_3BCO \cdot 2NH_3$, is established. A product with an identical x-ray diffraction pattern resulted when the reaction was carried out in diethyl ether rather than dimethyl ether. Because of differences in melting point of the ethers, the reaction in diethyl ether covered the temperature range -111° to -80°C.

Reaction of H_3BCO and CH_3NH_2. Monomethylamine reacts with H_3BCO in the same manner as NH_3. The crystalline white solid, prepared in either dimethyl or diethyl ether, has the composition $H_3BCO \cdot 2NH_2CH_3$ and is surprisingly stable. The solid was stable for at least 48 hours in normal laboratory air and dissolved in water without evolution of gas. It could be recovered unchanged from water solution, if

In Boron-Nitrogen Chemistry; Niedenzu, K.;
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the solution were less than 4 hours old. More prolonged standing gave rise to a cloudy solution and a definite precipitate.

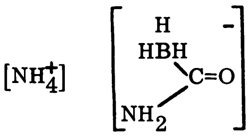
The Reaction of H_3BCO and $(CH_3)_2NH$. Dimethylamine and H_3BCO react in dimethyl or diethyl ether at low temperatures to give the white crystalline $H_3BCO \cdot 2NH(CH_3)_2$. The compound has a slight sublimation pressure and appeared to be somewhat less stable than the methylamine adduct, although the relative stabilities were not investigated in detail.

Reaction of H_3BCO and $(CH_3)_3N$. Burg and Schlesinger *(4)* noted that trimethylamine does not displace CO when H_3BCO and $N(CH_3)_3$ are in contact at -80°C., but found that the base displacement reaction proceeds very rapidly at room temperature. No evidence for a low temperature interaction of H_3BCO and $N(CH_3)_3$ was reported.

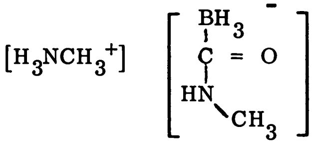
In the present study the reaction of H_3BCO and $N(CH_3)_3$ was conducted under conditions identical to those used with NH_3 and the other two amines. A precipitate was noted in ether solution at -100°C. It dissolved as the temperature was raised to -80°C. A solid product was isolated at -80°C. as the solvent and excess amine were distilled away. The stoichiometry of the reaction suggested the formula $H_3BCO \cdot N(CH_3)_3$. On further warming of the solid, CO was released, but even at room temperature the yield of recovered CO was very low. About 10% of the theoretical $(CH_3)_3NBH_3$ was sublimed from the reaction mixture and identified by its x-ray diffraction pattern. A nonvolatile oil remained as a residue. Products were not further characterized.

Structures for Amine Reaction Products

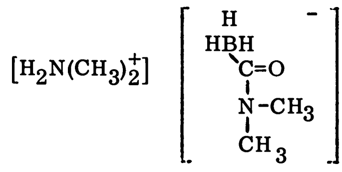
By using the structural analogies previously described the products from the foregoing reactions can be represented as:



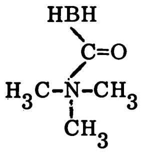
$H_3BCO \cdot 2NH_3$



$H_3BCO \cdot 2NH_2CH_3$



$H_3BCO \cdot 2NH(CH_3)_2$



$H_3BCO \cdot N(CH_3)_3$

Evidence for Structure of $H_3BCO \cdot 2NH_2CH_3$

Since $H_3BCO \cdot 2NHCH_3$ appeared to be the most stable of the carbon monoxide—borane adducts, the structural aspects of its chemistry were explored rather intensively in both water and liquid ammonia solution.

Liquid Ammonia Chemistry. Sodium Reaction. Sodium in liquid ammonia reacts with $H_3BCO \cdot 2NH_2CH_3$ as indicated by the following equation:

$$[H_3NCH_3^+]\,[H_3BCONHCH_3^-] + Na \rightarrow 1/2\,H_2 + H_2NCH_3 + Na^+[H_3BCONHCH_3^-]$$

Even in the presence of a large excess of sodium only one equivalent of hydrogen was ever liberated. The resulting product was a saltlike solid with the composition indicated by the above formula. Liberation of a second equivalent of hydrogen was never observed with this compound.

Aqueous Solution Chemistry. Reaction with Sodium Tetraphenylboron. Since $[H_3CNH_3^+]\,[BPh_4^-]$ is quantitatively insoluble in water, the following reaction of $H_3BCO \cdot 2NH_2CH_3$ in water solution would be expected.

$$[CH_3NH_3^+]\,[H_3BCONHCH_3^-] + Na[BPh_4] \rightarrow Na^+[H_3BCONHCH_3^-] + [CH_3NH_3^+]\,[BPh_4^-]\downarrow$$

The reaction was observed quantitatively as indicated and the resulting $Na^+[H_3BCONHCH_3^-]$ had an x-ray powder pattern identical to that of the salt obtained from the sodium reaction in liquid ammonia.

On standing, a second mole of $[H_3NCH_3^+]\,[BPh_4^-]$ slowly formed in water solution, as would be suggested by the following hydrolysis reactions:

$$Na^+\,[H_3BCONHCH_3^-] + HOH \rightarrow Na^+[H_3BCOOH^-] + H_2NCH_3$$

$$H_2NCH_3 + H_2O \rightarrow [H_3NCH_3^+]\;OH^-$$

$$[H_3NCH_3^+] + [BPh_4^-] \rightarrow [H_3NCH_3^+]\,[BPh_4^-]\downarrow$$

Molecular Weights in Water Solution. The molecular weight of $H_3BCO \cdot 2H_2NCH_3$ is 104 on the basis of the formula given. In water solution dissociation into 2 ions should give an apparent molecular weight of about 52. The observed apparent molecular weight in water solution at infinite dilution as determined by freezing point depression was 51.3. The corresponding sodium salt, $Na^+[H_3BCONHCH_3^-]$, has a formula weight of 95. Its apparent molecular weight in water should be 47.5. The value observed from freezing point depression was 46.2.

Electrical Conductivity of Aqueous Solutions of $H_3BCO \cdot 2NH_2CH_3$. Conductance measurements made on aqueous solutions of $[H_3NCH_3^+]\,[H_3BCONHCH_3^-]$ over the concentration range of 1.3×10^{-4} to 36×10^{-4} molar gave data represented graphically in Figure 1. The curve is decidedly different from that expected for a strong electrolyte. It is significant, however that the curve levels off at an equivalent conductance of about 120, suggesting initial strong dissociation into two ions followed by a possible second ionization of the anion $[H_3BCONHCH_3^-]_{aq} \rightleftharpoons H^+_{aq} + [H_3BCONCH_3^{-2}]$ or by a possible displacement of the amine by water The behavior of methylammonium *N*-methyl carbamate, $[CH_3NH_3^+]\,[CO_2NHCH_3^-]$, was very similar, as might be expected (Figure 1).

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch031

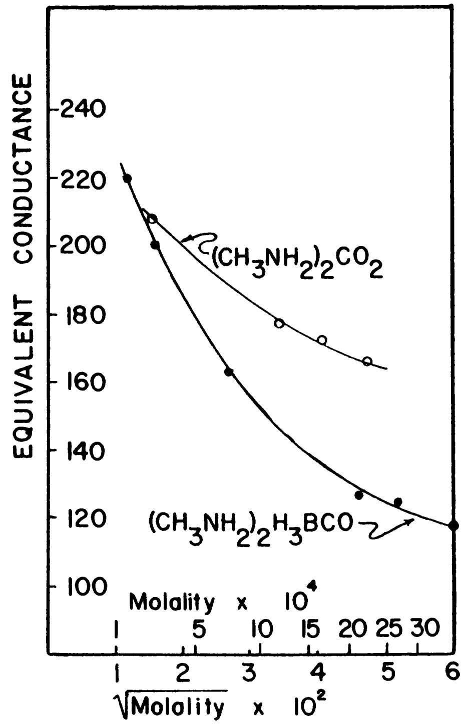


Figure 1. Equivalent conductance of $(CH_3NH_2)_2H_2BCO$ and $(CH_3NH_2)_2CO_2$ in water at 25.0°C.

X-Ray Diffraction Study of Solid, $H_3BCO \cdot 2NH_2CH_3$. Although single crystals of the diammoniate of carbon monoxide-borane could not be obtained, crystals of the bismethylamine adduct could be obtained. X-ray examination showed them to be orthorhombic with

$$a = 7.964 \text{ A.}$$
$$b = 11.58 \text{ A.}$$
$$c = 7.414 \text{ A.}$$

and containing four formula units per cell. The space group is $\underline{Pna2_1}$. A structure analysis based on 659 observed reflections yielded the structure shown in Figure 2.

All hydrogen atoms were resolved in the final electron density synthesis. The methylammonium ion has the staggered configuration and an N-C distance of 1.47 A. The O, N, C, B skeleton of the anion is very nearly planar. The central carbon atom and its surrounding O, N, and B atoms are, as expected, coplanar within experimental error. The methyl group deviates from this plane by only 0.04 A.

Interatomic distances in the anion are C-B=1.600 A., C-O=1.281 A, C (central) -N = 1.343 A., and N-C (methyl) = 1.453 A. The geometry of the anion is very similar to that found in other compounds containing the -CONHC- group.

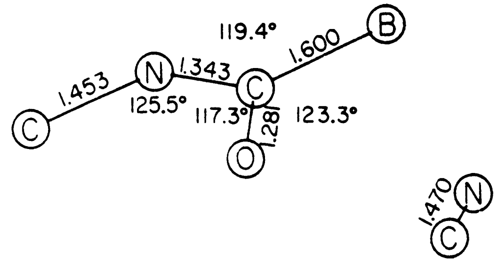
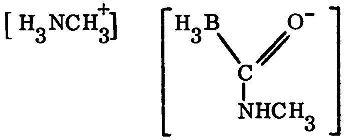


Figure 2. Structure of boranocarbamate anion [$H_3BCONH_2^-$], and nitrogen and carbon of methylamine cation

Structural Summary on $H_3BCO \cdot 2NH_2CH_3$ and Related Amine Adducts

The evidence supporting the structure


$$[H_3NCH_3^+] \left[\begin{matrix} H_3B & & O^- \\ & C & \\ & NHCH_3 & \end{matrix} \right]$$

is conclusive. The anion is stable in liquid ammonia solution, is slowly hydrolyzed in water solution, and is clearly identified in the crystal. By analogy one can write comparable structures for the ammonia and dimethylamine adducts. The basis for the difference in the behavior of trimethylamine is clearly revealed, since transfer of the methyl group in adduct formation would be difficult.

Ammonia and Alkyl Amine Adducts of Carbon Monoxide—Tetraborane, B_4H_8CO

A second boron hydride-carbon monoxide adduct was isolated by Burg and Spielman *(5)*, from the reaction of B_5H_{11} and CO in a sealed tube under pressure. Since earlier systematic arguments *(12)* had suggested that B_4H_8 is, under some circumstances, a somewhat stronger Lewis acid than BH_3, the replacement of H_3B by B_4H_8 could give a diammonium adduct of B_4H_8CO with the formula:

$$[NH_4^+]\ [B_4H_8CONH_2^-]$$

Such a postulate has been verified, as indicated by the following data.

Reaction of B_4H_8CO with Ammonia

B_4H_8CO and NH_3, present in excess, react as the temperature rises over an 8- to 10-hour period from -95° to -50°C. Excess ammonia was removed slowly as the temperature rose from -63° to 25°C. over

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch031

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

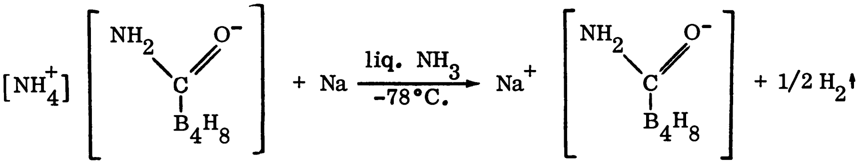
a 24-hour period. The resulting product was free of H_3NBH_3 and was a white solid which gave no x-ray powder pattern. The stoichiometry of formation indicated rather clearly the formula $B_4H_8CO \cdot 2NH_3$, but analytical results left something to be desired (as was also true in earlier reports of boron hydride carbonyls). Observed: C, 9.31%; H, 10.84%; N, 24.80%; B, 47.51. Calculated for $B_4H_8CO \cdot 2NH_3$: C, 10.57; H, 12.43; N, 24.69; B, 46.94. Molecular weight in liquid NH_3 = 120. Theory for $B_4H_8CO \cdot 2NH_3$ = 113.5 Strangely enough, the product obtained from the direct reaction seemed to be more stable and of higher purity than that obtained in either dimethyl or diethyl ether.

The solid from the direct reaction appears to be stable in liquid ammonia and to react slowly with water, giving H_2 gas.

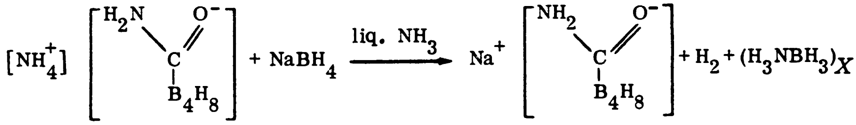
Structure of $B_4H_8CO \cdot 2NH_3$

Since no crystalline form of the diammoniate of carbon monoxide-tetraborane has yet been prepared, it has been necessary to infer its structure from chemical reactions of the type used successfully with $BH_3CO \cdot 2NH_2CH_3$.

Liquid Ammonia Chemistry. Reaction with Sodium. Sodium in liquid ammonia reacts with $B_4H_8CO \cdot 2NH_3$ in liquid ammonia to liberate in one hour one equivalent of H_2 per mole of $B_4H_8CO \cdot 2NH_3$. No significant amount of extra hydrogen was liberated during the next hour. The reaction is in agreement with the equation:



Reaction with Sodium Borohydride. Sodium borohydride, when present in excess, reacts with $B_4H_8CO \cdot 2NH_3$ as would be expected for a typical ammonium salt *(14)*



The resulting sodium salt, $Na^+[H_2NCOB_4H_8^-]$, is the same as that produced in the sodium reaction (infrared evidence).

Reactions in Tetrahydrofuran. In earlier work in this laboratory it was found that ammonium salts in ether suspension react with lithium borohydride to give H_3NBH_3 *(15)*. The corresponding reaction expected for $B_4H_8CO \cdot 2NH_3$ would be:

$$NH_4^+[B_4H_8CONH_2^-] + LiBH_4 \xrightarrow[\text{0-25°C.}]{\text{THF}} H_3NBH_3 + 1/2\,H_2 + Li^+[B_4H_8CONH_2^-]\downarrow$$

14 hours

The resulting H_3NBH_3 was soluble in the ether and could be separated from the ether-insoluble lithium salt. H_3NBH_3 was identified by its infrared spectrum. The anion in the lithium salt also gave an infrared spectrum characteristic of the anion identified in the two preceding reactions.

Aqueous Chemistry of $B_4H_8CO \cdot 2NH_3$ and $Na[B_4H_8CONH_2]$. Although $B_4H_8CO \cdot 2NH_3$ reacts slowly with water to liberate H_2, it was possible to carry out a rapid metathesis reaction in water under conditions such that the total time between addition of water and separation of precipitate was less than 15 seconds. The equation for the process is:

$$[NH_4^+][B_4H_8CONH_2^-] + NaBPh_4 \xrightarrow[0°C.]{H_2O} \downarrow [NH_4^+][BPh_4] + Na^+[B_4H_8CONH_2^-].$$

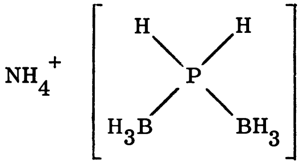
When the reaction was conducted properly, the salt, $Na[B_4H_8CONH_2]$, was identical to that obtained by the synthetic procedures described earlier.

On standing in water containing dissolved $NaBPh_4$, the compound $Na[B_4H_8CONH_2]$ gradually gives a precipitate of $[NH_4][BPh_4]$ as indicated by the hydrolysis reaction:

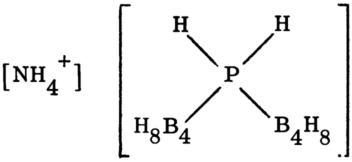
$$[B_4H_8CONH_2^-] + 2H_2O + Na^+ + BPh_4^- \rightarrow NH_4BPh_4 \downarrow + Na^+ + OH^- + [B_4H_8COOH^-]$$

Discussion

The replacement of the oxygen atom of the carbamate anion with a BH_3 or a B_4H_8 group suggests that oxygen atoms in many other oxyacid anions might be systematically replaced by BH_3 or B_4H_8 groups to give new families of boron hydride derivatives. One known compound whose structure can be easily interpreted in view of the above arguments is the compound $B_2H_6 \cdot PH_3 \cdot NH_3$ obtained by the reaction between $[H_3BPH_3]_n$ and NH_3. The structure suggested is analogous to that of a hypophosphorous acid salt:

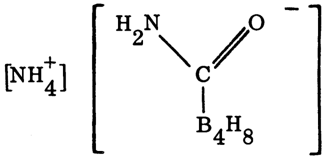


If the model is correct, it should be possible to synthesize the corresponding B_4H_8 salt:

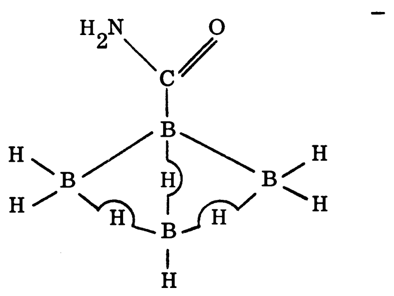


Conclusions

All of the chemical evidence cited strongly suggests for $B_4H_8CO \cdot 2NH_3$ the formula:

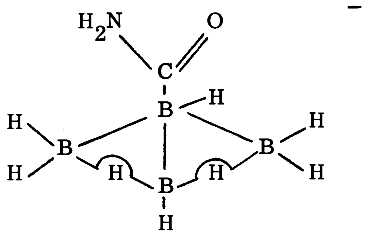


The details of the structure of the $[B_4H_8CONH_2^-]$ anion cannot be deducted from the foregoing evidence, but symmetrical cleavage arguments *(12)* applied to B_5H_{11} suggest the formula



with the position of the hydrogens remaining uncertain. A BH unit, bonded tothe rest of the boron framework by three bridge bonds, would be particularly fascinating, since it would be unique in boron hydride structures.

An alternative structure, based on the topological arguments of Lipscomb *(19)* would give the same arrangement of borons but a slightly different arrangement of hydrogens without the three bridge bonds to one boron:



An x-ray structural study of $R_2NF_2PB_4H_8$, being conducted in this laboratory, will provide more evidence on the question of the hydrogen positions.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch031

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Received June 10, 1963. Work supported by the National Science Foundation.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch031

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Boron-Nitrogen Bonds in the Higher Boranes

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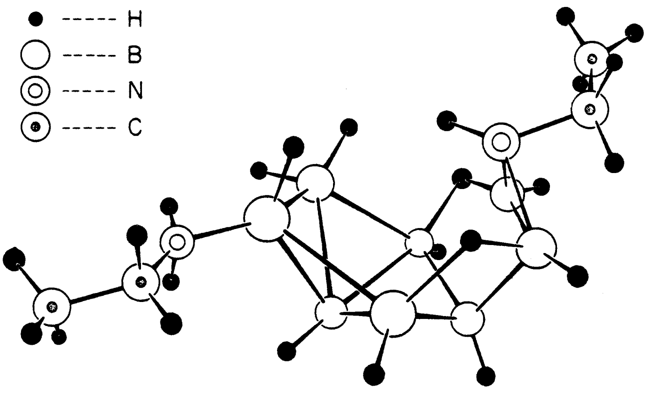
Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch032

The $EtNH_2B_8H_{11}NHEt$ molecular structure, in which both a ligand N and a bridge N occur, is a particularly stable system. The relation of this structure to the problem concerning the boron radius is presented briefly.

Although a number of observations of mass spectra of boronhydride mixtures suggest the presence of a B_8 hydride, no stable hydride of this type has yet been well characterized. It is therefore remarkable that the nitrogen-bridged (NHEt) and ligand-substituted (NH_2Et) derivative $EtNH_2B_8H_{11}NHEt$ *(41)* is so stable. Here, we examine the question of primary amines which in their reactions may more generally yield stable derivatives of the higher boranes. In addition, the high precision of the bond distances in this compound forms a basis for reexamination of the elusive "covalent radius" (if any) of boron, and the boron-boron distances in the B_8 framework lead to some understanding of the instabilities of the B_8 group of boron hydrides.

$EtNH_2B_8H_{11}NHEt$

The molecular structure has been established by x-ray diffraction methods *(41)*. A total of 1566 independent diffraction maxima from a



crystal having four molecules in a unit cell ($a = 24.35$, $b = 5.98$, $c = 9.00$ A., and $\beta = 94° 51'$) has been refined to a value of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.134$. Only the H atoms of one CH_3 group, probably undergoing hindered rotation, could not be located with certainty.

The greater stability of this compound, as compared with that of the B_8 hydride fraction, suggests that stable boron frameworks may be made from higher boranes and their derivatives by using primary amines, such as ethylamine, in the degradation reaction. It is possible that amines of the type H_2NR are unique in some of these degradative reactions, because the resulting bridge NHet group has only N-H in the polyhedral surface (which contains eight B's, the bridge N, two terminal H's on B, one H on the bridge N, and two bridge H atoms). For this reason, the bridge N looks sterically like a BH_2 group to the rest of the polyhedron, and the open face is neatly filled by H atoms at approximately van der Waals contacts. Thus it is unlikely that HNR_2 is a suitable reagent for these degradation reactions, and, of course, NR_3 cannot form a bridged N arrangement without loss of R. Loss of BH_3 in the preparation *(19)* of $EtNH_2B_8H_{11}NHEt$ from $B_9H_{13}L$ and H_2NEt from $B_9H_{13}L$ and H_2NEt is consistent with symmetrical cleavage, and hence NH_3 is probably not suitable. [Graybill, Pitochelli, and Hawthorne *(19)* thought that the reaction yielded $B_9H_{12}NH_2Et^-$ ion when NH_2Et was used as reagent, but made the remarkable statement that "other amines were strangely ineffective."] It is therefore suggested that primary amines may occupy a nearly unique place in the preparation of bridge N derivatives of the higher boranes.

Two functions are probably served by the ligand group (here $L = EtNH_2$) which is bonded to the boron framework by a single B-N bond. The first is a general stabilization produced by the partial transfer of negative charge to the boron framework, thus adding some flexibility in values of the over-all charges. Probably more important, however, is the second effect of charge transfer into the boron framework — in order to facilitate H atom rearrangement to the situation which best adjusts to the local charge requirements.

The Boron Radius

This new compound provides some of the most precisely determined B-N distances, which here have standard deviations of about 0.007 A. The bridged N has two B-N bonds which are 1.573 and 1.574 A. in length, while the ligand B-N distance is 1.581 A. in length. These rather unexpectedly long B-N distances are in agreement with B-N distances such as 1.58 A. in $H_3NB_3H_7$ *(51)*, 1.57 and 1.60 A. in $NH_3BH_2NHE_3{}^+Cl^-$ *(50)*, 1.57 A. in cubic BN *(63)* and 1.59 A. in $BH_2NME_2)_3$ *(43)*. If we take 1.58 A. as representative of the B-N single bond, and 1.47 A. as the N-N single bond distance, and make an electronegativity correction of $-0.08|x_B - x_N|$, the boron radius is 0.925 A., a surprisingly large value. A similarly large value of 0.895 A. occurs when one applies the H radius of 0.37 A. and a small (0.01 A.) electronegativity correction to the BH distance *(15)* of 1.255 A. in BH_4^- ion. The values are comparable to, but even larger than the single bond radius of 0.88 A. assigned by Pauling.

On the other hand, one can find systematic evidence of boron radii as low as 0.80 or 0.81 A. *(23)*, which is the single bond metallic radius assigned by Pauling. The icosahedral $B_{12}H_{12}^{-2}$ ion has an average B-B distance, d, of 1.77 A. which, when corrected to a single distance, d_1, by the equation $d = d_1 - 0.6 \log n$ *(52)*, where the bond order, n, is 13/20, leads to a single bond-boron radius of 0.83 A. Moreover, the shortest B-B distance (1.60 A.) in all of the hydrides occurs in B_6H_{10} *(29)*, which in all resonance structures has a single bond between these two atoms. In addition the tetrahedrally bonded B atom in tetragonal boron is 1.60 A. *(32)* from its neighboring B atoms. One might be suspicious that this tetrahedral B in tetragonal boron is abnormally compressed, or that some double bonding occurs in the short distance in B_6H_{10} (we are at present studying the structure of $B_4H_6C_2Me_2)_3$ *(59)*, but nevertheless, these short values support the short boron radius.

In the halides, multiple bonding probably does occur, and this effect together with differences in the numbers and amounts of Cl···Cl repulsions leads to the progression of distances of 1.75, 1.73, 1.70, and 1.70 A. in, respectively, BCl_3 *(58)*, B_2Cl_4 *(3)*, B_4Cl_4 *(1)*, and B_8Cl_8 *(35)*, (a compound which certainly exists!). The corresponding B radii are 0.84, 0.82, and 0.79, obtained after subtraction of 0.99 for the Cl radius and an electronegativity correction of 0.08 A. Remarkably enough, however, the B-Br distance *(7)* of 1.934 A. in terminally substituted B_2H_5Br leads after subtraction of 1.11 A. for the Br radius and an electronegativity correction of 0.064 A. to a large B radius of 0.89 A.

Probably less multiple bonding occurs in BBr bonds as compared with that in BCl bonds, but certainly there is no vacant orbital on the B in B_2H_5Br, as there is in the chlorides. A resonance or conjugation effect also appears to be present in the B-N bond of length 1.523 A. in $B_{10}H_{12}(NCCH_3)_2$ *(55)*, and in the B-N bond of length 1.507 A. in $B_9H_{13}NCCH_3$ *(62)*. After correction of 0.08 A. for electronegativity, these bonds lead to boron radii of 0.87 and 0.85 A., respectively, but the effect of conjugation with the triple bond has not been included. Unfortunately, when conjugation with multiple bonds becomes an obvious possibility, the supposed state of hybridization of one of the bonded atoms becomes different from the usual situation; there has been a recent tendency to turn attention away from conjugation to hybridization in these cases.

Finally, a resonance effect which stabilizes the bonding, and presumably shortens the B-B distances, has been proposed *(10)* mostly to account for the rather systematic requirement of a smaller B radius in the boron hydrides themselves. The major point here is that the equation $d = d_1 - 0.6 \log n$ is not equally valid for atoms in different coordination number *(12)*.

Even when all of these effects are taken into account, the boron radius obtained from different compounds still varies over several hundredths of an Angstrom, and we conclude that bond distance discussions in boron chemistry still have to be restricted to very closely related compounds.

In Boron-Nitrogen Chemistry; Niedenzu, K.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1964.

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch032

Table I. Boron Radius

Compound	*Bond Distance*	*Radius*	*Reference*	*Method*
B...B				
B_2	1.589	0.795	*(28, 53)*	S[a]
B_2H_6	1.77 ± 0.01[b]	0.885	*(26)*	E[a]
B_2F_4	1.67 ± 0.04	0.835	*(60)*	X[a]
B_2Cl_4	1.75 ± 0.05	0.875	*(3)*	X
B_4Cl_4	1.71 ± 0.04	0.855	*(1)*	X
B_8Cl_8	1.80 (av.) ± 0.04	0.90	*(36)*	X
$B_3H_7NH_3$	1.744 ± 0.005[b]	0.872	*(51)*	X
$B_{10}H_{16}$	1.74 ± 0.06	0.87	*(20)*	X
$Cu_2B_{10}H_{10}$	1.80 (av.)	0.835[c]	*(10)*	X
$K_2B_{12}H_{12}$	1.77 ± 0.01	0.83[d]	*(64)*	X
B...N				
$B^{11}{\equiv}N^{14}$	1.281		*(28)*	S
$B{\equiv}N$	1.45 ± 0.01	0.79	*(7, 22)*	X
B-N cubic	1.57	0.91[e]	*(63)*	X
$(CH_3)_3NBH_3$	1.62 ± 0.15	0.96	*(4)*	E
$B_2H_5NH_2$	1.50 ± 0.02	0.84	*(27)*	E
$B_2H_5N(CH_3)_2$	1.55 ± 0.02	0.89	*(27)*	E
$[(NH_3)_2BH_2]^+Cl^-$	1.58 ± 0.02	0.92	*(50)*	X
$H_3NB_3H_7$	1.581 ± 0.003	0.921	*(51)*	X
H_3NBF_3	1.60 ± 0.02	0.94	*(30)*	X
$(CH_3)_3NBF_3$	1.585 ± 0.03	0.925	*(18)*	X
$H_3CH_2NBF_3$	1.58 ± 0.03	0.92	*(17)*	X
$(CH_3)_3NB(CH_3)_3$	1.60	0.94	*(16)*	X
$C_5H_5NBF_3$	1.53	0.87	*(66)*	X
$[BH_2N(CH_3)_2]_3$	1.59 ± 0.03	0.93	*(61)*	X
$C_2H_5NH_2B_8H_{11}NHC_2H_5$	1.574 ± 0.009	0.914	*(41)*	X
	1.581 ± 0.007	0.921		
$B_9H_{13}NCCH_3$	1.507 ± 0.01	0.85	*(62)*	X
$B_{10}H_{12}(NCCH_3)_2$	1.523 ± .007	0.86	*(55)*	X
$B_3N_3(NCH_3)_3$	1.42 ± 0.02	0.76	*(6)*	E
$B_3N_3H_6$	1.44 ± 0.02	0.78	*(5)*	E
$B_3Cl_3(NH)_3$	1.41 ± 0.01	0.75	*(8)*	X
B...H				
$B^{11}H^1$	1.2325	0.87[e]	*(28)*	S
$B^{11}H^2$	1.2311	0.87	*(28)*	S

Table I. (Cont'd.)

$(B^{11}H^{1})^{+}$	1.215	0.855	*(28)*	S
BH_4^{-}	1.255 ± 0.02	0.895	*(15)*	NMR
B_2H_6	1.19 ± 0.03	0.83	*(26)*	E
B_4H_{10}	1.19	0.83	*(49)*	E
B_5H_9	1.23 ± 0.07	0.87	*(24)*	X
	1.22	0.86	*(34)*	M
$B_3H_3(NCH_3)_3$	1.20	0.84	*(6)*	E
B...X, X=halogen				
$B^{11}F^{19}$	1.262	0.70[e]	*(28)*	S
BF_3	1.30	0.74	*(46)*	S
	1.33	0.77	*(7)*	E
B_2F_4	1.32 ± 0.04	0.76	*(60)*	X
$H_3N.BF_3$	1.39 ± 0.03	0.83	*(30)*	X
H_3CH_2-BF_3	1.37	0.81	*(17)*	X
$(CH_3)_3N$-BF_3	1.39	0.83	*(18)*	X
H_3CCNBF_3	1.32	0.76	*(31)*	X
$B^{11}Cl^{35}$	1.7157	0.81[e]	*(28)*	S
BCl_3	1.75 ± 0.02	0.84	*(2)*	X
			(58)	X
			(39)	E
B_2Cl_4	1.73 ± 0.02	0.82	*(3)*	X
B_4Cl_4	1.70 ± 0.03	0.79	*(1)*	X
B_8Cl_8	1.70 ± 0.04	0.79	*(36)*	X
$Cl_2B(CH_2)_2BCl_2$	1.755 ± 0.04	0.845	*(45)*	X
$(Cl_3B)_3(NH)_3$	1.75 ± 0.01	0.84	*(8)*	X
$B^{11}Br^{79}$	1.887	0.837[e]	*(28)*	S
BBr_3	1.87 ± 0.02	0.82	*(39)*	E
B_2H_5Br	1.934	0.884	*(7)*	M

Miscellaneous

B...C				
$B(CH_3)_3$	1.56 ± 0.02	0.83[e]	*(39)*	E
$Cl_2B(CH_2)BCl_2$	1.58 ± 0.05	0.85	*(45)*	X
$(CH_3)_2B_2H_4$	1.61	0.88	*(25)*	E

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch032

Table I. (Cont'd.)

B...O				
BO	1.2049	0.58^e	*(28)*	S
B...S				
BS	1.6091	0.61^e	*(65)*	S
$B_{10}H_{12}[S(CH_3)_2]_2$	1.925	0.925	*(56)*	X
B...P				
$(H_2N)_3PBH_3$	1.88 ± 0.013	0.79^e	*(47)*	X
$[(H_3C)_2PBH_2]_3$	1.935 ± .009	0.835	*(21)*	X

a. E electron diffraction, X x-ray diffraction, M microwave techniques, S other spectroscopic studies of gas molecules, NMR nuclear magnetic resonance.

b. Three-center bridge H bond (B-H-B).

c. (*52*, p. 255). $0.835 = [1.80 + 0.6 \log(11/16)]/2$ where $11/16 =$ bond order

d. (*52*, p. 255). $0.83 = [1.77 + 0.6 \log(13/20)]/2$ where $13/20 =$ bond order

e. For all bonds between unlike atoms the formula (*52*, pp. 89, 224 ff)

$$D(A\text{-}B) = r_A + r_B - C\left|X_A - X_B\right| \quad \text{is used,}$$

where $C = 0.08$ and

	r_A	$\lvert X_A - X_B \rvert$
C	0.77	0.5
N	0.74	1
O	0.74	1.5
P	1.10	0.1
S	1.04	0.5
F	0.72	2
Cl	0.99	1
Br	1.11	0.8
H	0.37	0.1

Structural Principles

The replacement of bridge H by a bridge-N(HR)-group has previously been found in $B_2H_5NH_2$ and $B_2H_5NMe_2$ *(27)*, but the possibility that the principle is more general has been suggested *(41)*. There is a striking similarity of the bridged $-NH_2-$ group to the doubly hydrogen bridged $\overset{\mathrm{H}}{\text{——}}\mathrm{BH_2}\overset{\mathrm{H}}{\text{——}}$ group. In addition, Hoffmann has pointed out

Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ch032

to us the similarity of the internal bonding in $EtNH_2B_8H_{11}$ NHEt to that in B_9H_{15} *(33)*. Thus a second general principle of bonding is the substitution of $-NH_2-$ for $\overset{H}{\text{———}}BH_2\overset{H}{\text{———}}$.

But a third general principle may be of importance in understanding the instabilities of the B_7 and B_8 hydrides. In $EtNH_2B_8H_{11}$NHEt, as in all other known hydrides, ions, and nitrogen derivatives, the open face is neatly filled with H atoms about 2.0 to 2.6 A. apart. In addition, the terminal H atoms point away from the polyhedral or molecular center, and are about 3 A. apart. All intermolecular contacts in all of the known crystal structures are H···H contacts. Thus in the larger polyhedral hydrides and derivatives, relatively few H atoms are required to close the open regions with H···H contacts. On the other hand, the small hydrides, like B_2H_6 and B_4H_{10}, have already very close contacts which make attack by electron pair donors more difficult. It is the B_7 and B_8 hydrides in which the H···H contacts across the open face of the molecule are possibly not sufficiently close to prevent ligand attack. While BH_2 groups might allow more efficient filling of the open face, the proportion of BH_2 groups, as compared with bridge H atoms, is limited by the topological theory.

Still another, and perhaps also important, feature of the boron framework of the $EtNH_2B_8H_{11}$ NHEt molecule is the relatively long set of B···B distances all around the periphery of the B_8 group. Thus the average B···B distance is 1.90 A. around the periphery, but 1.76 A. if peripheral B···B bonds are omitted. One might ask if the open B_7 and B_8 would show this same suggestion of peripheral instability if they could be isolated.

In summary, the striking stability of this nitrogen derivative of a clearly less stable boron hydride analog offers promise of a new area of research in the chemistry of boron-nitrogen compounds.

Table II. B···B Distances (A)

Compound	*Edge*	*Internal*	*Reference*	*Method*
B_2H_6	1.77 ± 0.01(2B)[a]		*(26)*	E
$B_3H_8^-$	1.80		*(54)*	X
	1.77(B)			
B_4H_{10}	1.842 ± 0.005(B)		*(48)*	X
	1.712 ± 0.005		*(44)*	X
B_5H_9	1.77 ± 0.02(B)	1.66 ± 0.02[4][b]	*(13)*	X
B_5H_{11}	1.76 ± 0.04(av)(B)	1.72 ± 0.04[5]	*(38)*	X
		1.87 ± 0.04[5]	*(44)*	X
B_6H_{10}	1.794 ± 0.009(B)	1.74 ± 0.01[5]	*(29)*	X
	1.74 ± 0.010(B)	1.753 ± 0.009[5]		
	1.60 ± 0.01	1.80 ± 0.01[5]		
$EtNH_2B_8H_{11}NHEt$	1.922 ± 0.009	1.730 ± 0.009[5]	*(41)*	X
		1.719 ± 0.010		
	1.901 ± 0.009	1.723 ± 0.008		
	1.925 ± 0.009	1.749 ± 0.009		
	1.820 ± 0.008(B)	1.773 ± 0.009		
	1.835 ± 0.009(B)	1.791 ± 0.009		
		1.800 ± 0.009		
		1.787 ± 0.007		
		1.808 ± 0.01		

Table II. (Cont'd.)

B_9H_{15}	1.95 ± 0.02	1.80 ± 0.02[5]	(9)	X
	1.85 ± 0.02(B)	1.73		
	1.88 ± 0.02(B)	1.76		
	1.82 ± 0.02(B)	1.74		
	1.87 ± 0.02(B)	1.77		
	1.78 ± 0.02(B)	1.83		
		1.80		
		1.76		
		1.77		
$B_9H_{13}(CH_3CN)$	1.865 ± 0.006	1.731 ± 0.011[5]	(62)	X
	1.870 ± 0.008	1.766 ± 0.008		
	1.842 ± 0.008(B)	1.745 ± 0.007		
		1.760 ± 0.009		
		1.722 ± 0.009		
		1.785 ± 0.011		
		1.825 ± 0.006		
$(B_{10}H_{10})^{-2}$		1.73 ± 0.03(av)[4] [c]	(10)	X
		1.81 ± 0.03(av)[5] [c]		
		1.86 ± 0.04(av)[5] [c]		
$B_{10}H_{14}$	2.01 ± 0.02	1.77 ± 0.02[5]	(37)	X
	1.80 ± 0.02(B)	1.72	(44)	X
	1.77 ± 0.02(B)	1.76		
		1.78		
		1.78		
		1.71		
		1.80		
$B_{10}H_{12}(CH_3CN)_2$	1.860 ± 0.008	1.766 ± 0.008[5]	(55)	X
	1.849 ± 0.008	1.764		
	1.881 ± 0.008(B)	1.746		
		1.746		
		1.749		
		1.742		
		1.837		
$B_{10}H_{16}$	1.71 ± 0.06(B)	1.76 ± 0.06(av.)[4]	(20)	X
		1.74 ± 0.06[d]		
$(B_{12}H_{12})^{-2}$		1.755 ± 0.007[5]	(64)	X
		1.780 ± 0.007[5]		
$B_{18}H_{22}$	1.823 ± 0.004(B)	1.791 ± 0.004[5]	(57)	X
	1.790 ± 0.005(B)	1.784		
	1.782 ± 0.005(B)	1.776		
	1.838 ± 0.005	1.757		
	1.976 ± 0.004	1.798		
	1.968 ± 0.004	1.799		
		1.790		
		1.816		
		1.777 ± 0.005		
		1.737 ± 0.004		
		1.760		
		1.759		
		1.783		
		1.719 ± 0.005		
		1.788 ± 0.004		
Iso-$B_{18}H_{22}$	1.792 ± 0.003(B)	1.794 ± 0.003	(14)	X
	1.786 ± 0.004(B)	1.781		
	1.784 ± 0.004(B)	1.771		
	1.958 ± 0.003	1.759		
	1.990 ± 0.006	1.781		
		1.796		
		1.798		
		1.832		
		1.744		
		1.764		

Table II. (Cont'd.)

	1.753			
	1.755			
	1.794			
	1.781			
	1.717			
	1.725			
$B_{20}H_{16}$	1.765	± 0.006	*(11)*	X
	1.806	± 0.004		
	1.793			
	1.781			
	1.815	± 0.005		
	1.764	± 0.004		
	1.873			
	1.803			
	1.784	± 0.005		

a. (B) three-center (B-H-B) bridge bond; (2B) double bridge bond.
b. Number in [ ] indicates coordination number of central or internal boron, exclusive of terminal H.
c. Bond distances are averages of apex to equatorial, equatorial *n* to equatorial *m*, equatorial *n* to equatorial *n*, respectively.
d. Apex to apex distance between two B_5H_8.

Acknowledgment

The experimental study, carried out in collaboration with P. G. Simpson, will be published elsewhere. We acknowledge discussions with R. Hoffmann, and support of the experimental study by the Office of Naval Research and the U. S. Army Research Office (Durham).

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Received May 8, 1963.

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Publication Date: January 1, 1964 | doi: 10.1021/ba-1964-0042.ix001

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