THE BORAZINES

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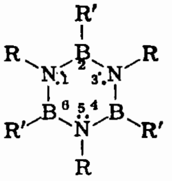
I. Introduction

The borazines are one of several compound types that are isoelectronic with benzene, and consequently they have attracted considerable attention since the parent compound borazine (I, R = R′ = H) was first isolated and characterized by Stock and Pohland (*164*). These investigators suggested a cyclic structure for borazine on the basis of chemical evidence, and this



(I)

was later substantiated by direct structural investigations (see Section V,A). It appears possible that Gustavson (*57*) prepared a borazine derivative in 1870 by allowing BCl_3 to condense with ethylamine (cf. ref. *174*), and Rideal (*138*) almost certainly did so in 1889 when he studied the reaction of BCl_3 with aniline. In 1939 Jones and Kinney (*82*) demonstrated that the latter reaction does indeed yield a borazine. The hydrogen atoms in the parent compound can be replaced by a variety of groups, and recently described methods for the preparation of several unsymmetrically-substituted derivatives suggest interesting possibilities for the study of isomeric borazines.

Borazole, the name given to I, $R = R' = H$, by Wiberg and Bolz (*186*) on the basis of its similarity to benzene (benzol), is no longer acceptable according to the Ring Index (*128*); the systematic name *s*-triazatriborine is preferred. However, I($R = R' = H$) and its derivatives undergo reaction predominantly at the boron sites, and it would appear advantageous to choose a name for this compound which emphasizes the boron atoms rather than the nitrogen atoms. The name borazine has been favored by investigators active in the field and is the name used in this review. Generally, line formulas or names derived from the atom on which substitution occurs are used. For example, $Me_3B_3N_3H_3$ or *B*-trimethylborazine is used in place of the systematic name 2,4,6-trimethyl-*s*-triazatriborine (*75*, *128*).

An attempt has been made in this review to cover the pertinent papers in the literature through May, 1962. Previous reviews have appeared in which the physical properties of borazines are compared with those of the analogous benzene derivatives (*185*) and which are chiefly concerned with the reactions and syntheses of borazines (*46*, *72*, *105*, *159*).

II. Synthesis of the Borazine Ring

The most satisfactory method available for the synthesis of borazines involves the condensation of amines with boranes. The majority of these reactions lead to symmetrically-substituted borazine rings, although some unsymmetrically-substituted borazines have been prepared using these methods. In general, it is possible to prepare borazines that are symmetrically substituted with respect to both the boron and the nitrogen atoms [cf. (I)] or to prepare borazines carrying the same substituents on all atoms (I, $R' = R$) by a judicious choice of reactants. A second method for the preparation of borazines carrying different substituents on the nitrogen and boron atoms proceeds in two steps: (a) the formation of a borazine ring carrying a portion of the required substituents by a condensation reaction, followed by (b) a substitution reaction. This second route to the borazines is limited to replacement of substituents (usually halogen) on the boron positions in the ring; substitution reactions on the nitrogen atoms in the borazine ring have not been observed often.

A. CONDENSATION REACTIONS

Condensation reactions between boranes and amines may be visualized as occurring via the formation of a borane-amine addition compound (IV),

$$\begin{array}{ccccccc} X_3B & + & NR_3 & \rightarrow & X_3BNR_3 & \rightarrow & X_2BNR_2 + RX \\ \text{(II)} & & \text{(III)} & & \text{(IV)} & & \text{(V)} \\ & & & & & & \downarrow \\ & & & & & & (XBNR)_3 + RX \\ & & & & & & \text{(VI)} \end{array} \qquad (1)$$

which then loses substituents (one from boron and one from nitrogen) in two successive steps to form the borazine ring *(9)*. The aminoborane intermediate (V) *(84, 168, 188)* and compound (IV) *(9, 13, 29, 71, 82, 85, 121, 124, 170, 174, 188)* have been isolated prior to their conversion into the corresponding borazine in several instances. The addition compound (IV) may be formed by direct combination of an amine with a borane *(2, 49, 85, 121, 143, 194)*, by the displacement of hydrogen halide from ammonium salts [Eq. (2)], or by the elimination of hydrogen in the reaction of a borohydride with an ammonium salt. The maximum yield for the preparation of borazine using the latter reaction occurs at a 2:1 mole ratio of $LiBH_4$ to NH_4Cl *(111)*. The reaction of a borohydride with an ammonium salt at elevated temperatures (200–250°) usually proceeds directly to the corresponding borazine with the elimination of two moles of hydrogen.

$$R_3NH^+X^- + BR'_3 \rightarrow R_3NBR'_3 + HX \qquad (2)$$

$R' = X = Cl$, $R = H, H, Bu^n$ *(174)*
$R' = X = Cl$, $R = H$ *(15)*
$R' = X = Cl$, $R = H$ *(17)*
$R' = X = Br$, $R = H, H, Me$ *(36)*
$R' = X = Br$, $R = H$ *(36, 148)*
$R' = X = Cl$, $R = H$ *(15, 36)*
$R' = X = Cl$, $R = H, H, Me$ *(36, 174)*
$R' = X = Cl$, $R = H, H, Et$ *(174)*

$$MBH_4 + HNR_3{}^+X^- \rightarrow [H_4B^-HNR_3{}^+] \rightarrow \underset{\displaystyle MX}{\underset{+}{H_3B_3N_3R_3}} + H_2 \qquad (3)$$

$M = Li$, $X = Cl$, $R = H$ *(111, 146, 177)*
$M = Na$, $X = Cl$, $R = Me, H, H$ *(64, 99)*
$M = Na$, $X = Cl$, $R = H$ *(64)*
$M = Na$, $X = Cl$, $R = H, H, Et$ *(64)*
$M = Li$, $X = Cl$, $R = H, H, Me$ *(145)*
$M = Li$, $X = Cl$, $R = H, H,$ phenyl *(9, 74)*

Borazines have been prepared at lower temperatures by substituting hydrazine salts for ammonium salts in reaction (3); no *N*-aminoborazines were formed in this process (*36*).

Conversion of the borane-amine adduct (IV) into the borazine (VI) occurs most readily when RX is a hydrogen halide. Adducts formed from boron halides and mono-alkyl- or -aryl-substituted amines lose hydrogen halides upon pyrolysis (*9, 15, 146, 170*), refluxing in a solvent such as C_6H_6, C_6H_5Br, C_6H_5Cl, or diglyme (*17, 49, 55, 64, 68, 71, 82, 148*), or upon treatment with a strong base like triethylamine (*106, 121, 145*). Triethylamine aids in the removal of hydrogen halides by the formation of insoluble triethylammonium halides. Pyrolytic reactions carried out in the presence of a specially prepared cobalt catalyst gave an increased yield of the borazine (*36*).

Vigorous pyrolytic conditions (e.g., temperatures up to 450°) have been employed to remove the elements of more complex compounds from the adduct.

$$3(n\text{-BuO})_2BNHEt \rightarrow (n\text{-BuO})_3B_3N_3Et_3 + 3n\text{-BuOH} \ (90,\ 109) \tag{4}$$

$$3BMe_3 + 3NH_2Me \rightarrow Me_3B_3N_3Me_3 + 6CH_4 \ (187) \tag{5}$$

$$3BEt_3 + 3NH_3 \rightarrow Et_3B_3N_3H_3 + 6C_2H_6 \ (194) \tag{6}$$

$$3BMe_3 + 3NH_3 \rightarrow Me_3B_3N_3H_3 + 6CH_4 \ (188) \tag{7}$$

$$3BMe_3 + 3C_6H_5NH_2 \rightarrow Me_3B_3N_3(C_6H_5)_3 + 6CH_4 \ (9) \tag{8}$$

Pyrolysis of di- or tri-aminoboranes also leads to the formation of a borazine ring.

$$3R'B(NHR)_2 \rightarrow R'_3B_3N_3R_3 + 3NH_2R \tag{9}$$

$$R' = C_6H_5\ (1);\ R' = \text{isoamyl}\ (110)$$

$$3B(NHR)_3 \rightarrow (RNH)_3B_3N_3R_3 + 3NH_2R \ (2,\ 90) \tag{10}$$

It is interesting to note in this connection that silyl fluoride is eliminated from silylaminoborondifluorides under milder conditions (*168*).

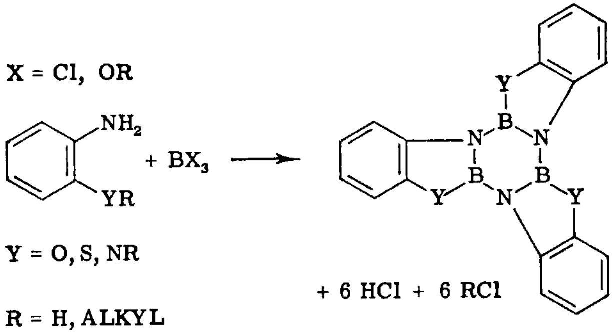
$$3(SiH_3)(Me)NBF_2 \rightarrow (CH_3)_3N_3B_3F_3 + 3SiH_3F \tag{11}$$

$$3(SiH_3)_2NBF_2 \rightarrow (SiH_3)_3N_3B_3F_3 + 3SiH_3F \tag{12}$$

If the adduct (IV) contains the elements of only one mole of hydrogen halide, the reaction stops at the intermediate aminoborane (V) unless drastic pyrolytic conditions are applied (*190, 191*). Refluxing amine-borane adducts (IV, X = H, R = H, H, alkyl) or amine adducts of higher boron hydrides (*151, 164, 165*) in a solvent (*67, 68*) or pyrolysis of the adducts (*9, 149, 151, 165, 171, 186, 188*) yields borazines and hydrogen. Borazine itself has been prepared from the diammoniate of diborane by pyrolysis of this compound (*186*) or by treatment with sodium acetylide (*155*). In the case of some borane adducts the intermediate aminoboranes (IV, X = H, R = H and alkyl) are trimeric (*13*, *171*) and can be considered as analogs of cyclohexane.

Unsymmetrically-substituted borazines have been prepared by the copyrolysis of mixtures of adducts. *B*-Methyl-, *B*-dimethyl-, and *B*-trimethyl-borazine are obtained in low yield upon heating a mixture of methyldiboranes and ammonia (*149*). *N*-Methyl- and *N*-dimethyl-borazine have been prepared in a similar manner (*150*), but also in poor yield. The copyrolysis of a mixture of ammonia-trimethylborane and methylamine-trimethylborane at 380° in an autoclave yielded *B*-trimethylborazine (5%), *N*-methyl-*B*-trimethylborazine (17%), *N*-dimethyl-*B*-trimethylborazine (13.5%), and hexamethylborazine (2.8%) (*178*). Unsymmetrically-substituted *B*-chloroborazines were obtained from the pyrolysis of borazine with *B*-trichloroborazine (*148*).

The borazine ring has been incorporated in polycyclic systems by allowing alkyl borates or boron trichloride to react in refluxing xylene with ortho-substituted anilines (*16*, *142*); this reaction occurred at lower temperatures in the presence of 2,6-lutidine.



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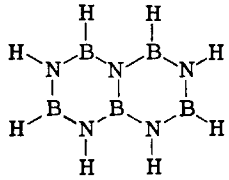
B. Polyborazines and Fused Borazine Rings

The controlled pyrolysis of gaseous borazine at 380° in a dynamic system yields hydrogen and a mixture of compounds from which can be separated the B—N analogs of naphthalene (VII) and biphenyl (VIII, $R_1 = R_2 = H$), a compound formulated as *B*-diaminoborazine (IX), and



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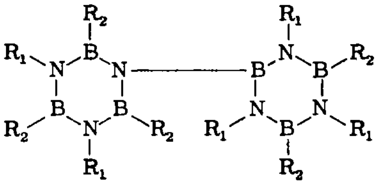

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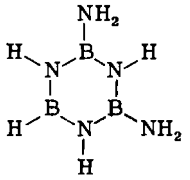
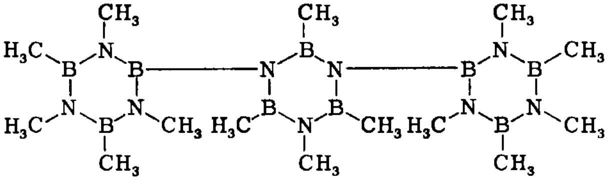


(IX)

derivatives of VII, VIII ($R_1 = R_2 = H$), and IX (*93, 113*). These structural assignments were made on the basis of chemical analyses, mass spectral data, infrared spectra, and nuclear magnetic resonance spectra. Similar results were obtained when gaseous borazine was allowed to decompose for 3½ months at ambient temperatures (*101, 192a*), although borazine has previously been reported to be stable in the gas phase (*148*). Pyrolysis of borazine in a static system (*93, 113, 164, 185*) yields a nonvolatile solid with the empirical composition BNH_x. The nature of the products depends upon the temperature of pyrolysis. This polymeric material constantly loses hydrogen upon heating, and it was suggested that the end-product is boron nitride (*185*). The presence of IX as an intermediate in the pyrolysis of boron nitride (*92*) is consistent with the observation (*91*) that *B*-triaminoborazines evolve amines at 300° to form first polyborazines bridged by alkylimine groups and finally cross-linked polymers (*2, 90, 91*).

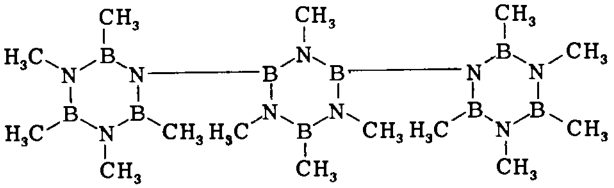
In contrast to the pyrolysis of borazine, pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace of (VII) ($R_1 = R_2 = CH_3$) (*179*). Upon independent pyrolysis of the isomeric pentamethylborazines most of the starting material is recovered unchanged together with small amounts of tri-, tetra-, and hexa-methylborazines. The latter disproportionation products could arise either by a depolymerization reaction followed by random polymerization (cf. Section III,B,*2*,*a*) or through a bridged transition state (cf. Section III,B,*1*,*b*).

The discovery of *N*-lithioborazines presents a new and perhaps more specific synthetic route to the polyborazines (*179*). Decamethyl-*N*-*B*′-biborazyl (VIII, $R_1 = R_2 = Me$) was prepared by the elimination of lithium chloride from an equimolar mixture of *N*-lithiopentamethylborazine and *B*-chloropentamethylborazine. This type of reaction has been extended to combinations of *N*-mono-, -di-, and -tri-lithioborazine with *B*-mono-, -di-, and -tri-chloroborazine which yielded X, XI, XII, and the polymeric substance XIII.



(X)

Attempts to dehydrohalogenate mixtures of *N*-dimethyl-*B*-trimethylborazine and *B*-chloropentamethylborazine using tertiary amines did not yield the desired product.



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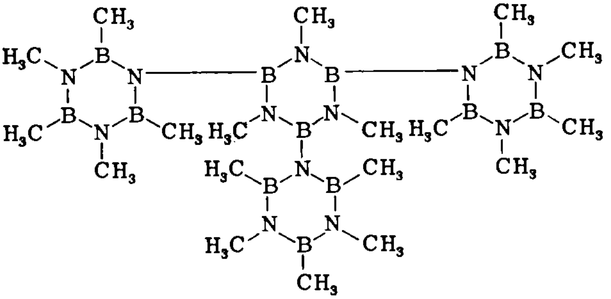

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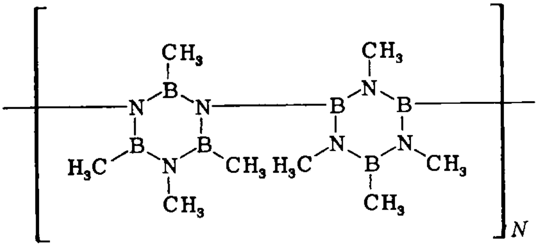
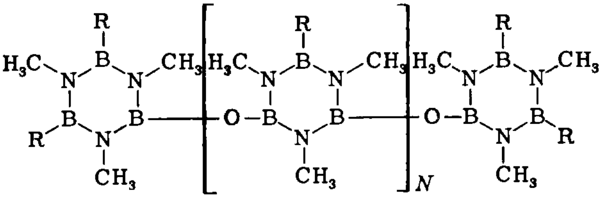


(XIII)

C. Polyborazines with Bridging Groups

Polycondensation of borazine rings joined together through an oxygen atom was effected by the controlled hydrolysis of mixtures of *B*-mono- and *B*-di-halogenoborazines (XIV, $n = 0 - 3$); hydrolysis of dihalogeno-



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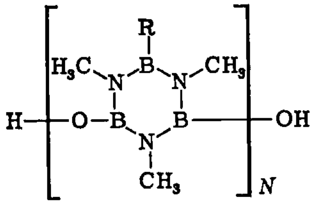
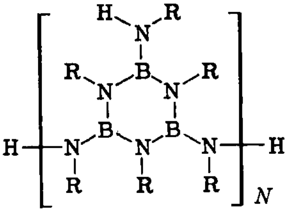


(XV)

borazines alone produced a glassy polymer (XV, $n = \sim 23$) (*179*). A compound similar to XIV [$n = 0$, R = $CH_2Si(CH_3)_3$] was obtained as a by-product of the reaction between *B*-trichloroborazine and $(CH_3)_3SiCH_2MgCl$ (*153*).

Polyborazines (XVI, R = Et) crosslinked with alkylimino groups have been prepared by the pyrolysis (600°) of *N*-trialkylaminoborazines;



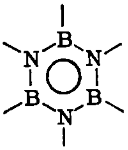
(XVI)

pyrolysis at lower temperatures yielded the condensation dimer XVI (R = Et, $n = 2$) (*2, 90, 91*). A short report has appeared describing the condensation of *B*-trialkylborazines with hexamethylene diisocyanate (*87*). No details are given, but it appears unlikely that the formation of these polymeric substances occurred by attack on the nitrogen sites in view of the noticeable lack of reactivity of these positions in the borazine ring.

Incorporation of the borazine ring into polycyclic systems is described in Section II,A.

III. Reactions of the Borazine Ring

Borazine rings can be formulated either as aromatic systems (XVII) in which three electron pairs are distributed in a π-type orbital extending over the whole molecule or as cyclic triamines (XVIII).



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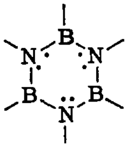


(XVIII)

Physical data indicate (see Section V) that some borazine rings are best described as aromatic systems, but very few reactions typical of aromatic systems have been observed for the borazine ring. The reactions of the borazine ring may be conveniently classified as addition reactions or as substitution reactions.

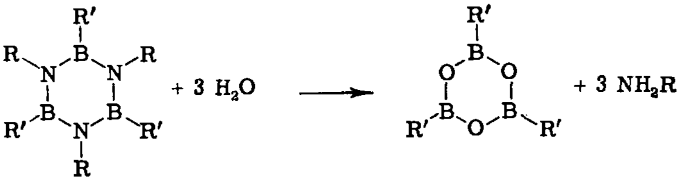
A. ADDITION REACTIONS

Although the borazine ring is isoelectronic with the benzene ring, the former undergoes some addition reactions with atoms joined by a polar bond much more readily than the latter. Dimethyl ether (*185, 186*), ammonia (*164, 185, 186*), and dimethylamine (*185, 186*) react slowly with borazine to yield glassy residues of indefinite composition. These reagents probably react as Lewis bases by adding initially to the boron sites in the borazine ring (see further on in this section). From the information available it appears, in some instances at least, that the attack of a reagent R″X on a borazine [Eq. (14)] to form a substituted borazine (XX) occurs through the formation of a more or less stable addition compound (XIX) [cf. (XXI)] (*187, 188*). Ring cleavage can also occur during the reaction with water (*149, 150, 164, 186, 187, 188*) or MeOH (*185*). In the absence of a B—H bond, the hydrolysis of a borazine with a limited amount of water yields a boroxyl [Eq. (15)], but if B—H bonds are present a *B*-trihydroxyborazine is formed [Eq. (16)] (*185*).

$$R'_3B_3N_3R_3 + 3R''X \rightarrow \underset{(XIX)}{(R'_3X_3)B_3N_3(R_3R''_3)} \rightarrow \underset{(XX)}{X_3B_3N_3R''_3} + 3R'R \qquad (14)$$

R″X = MeI (*164, 185*), MeOH (*186, 188*), HOH (*82, 85, 164, 186, 187, 188*), HCl (*164, 165, 178, 185, 186, 187, 188*), HBr (*164, 178, 185, 186*), Cl_2 (*164*), CH_3CO_2H (*15*).
R = R′ = H (*65, 186*), Me (*178, 187*).
R = phenyl, R′ = Cl (*82*).
R = *p*-anisyl, R′ = Cl (*85*).

It is interesting to note that the addition compound between bromine and borazine contains only two moles of bromine (*185, 186*), that alcohols other than methanol do not yield either adducts of type XIX or form the borazine XX (*14, 65*), and that silyl-substituted borazines undergo ring cleavage upon reaction with halogens (*25, 153*). Several compounds of the type XIX have been prepared from borazine itself, but no direct evidence is available concerning the structures of these particular compounds In several instances the substituted borazine (XX) has been obtained from the addition compound XIX [R′ = R = H, R″X = MeOH (*65*); R′ = R = Me, R″X = HCl (*187*); R′ = R = H, R″X = HCl, HBr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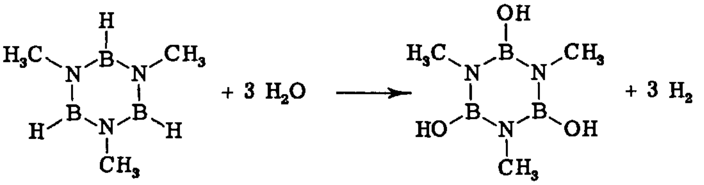
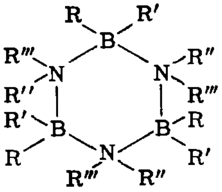
$R = H, CH_3 ; R' = CH_3$


(16)

(*186*)] while in others (XIX) has been postulated as an intermediate (*82*, *84*, *85*, *187*). The adduct formed between bromine and borazine decomposes to give a disubstituted compound (*186*).

$$H_3B_3N_3H_3 + 2Br_2 \rightarrow H_3B_3N_3H_3\cdot 2Br_2 \rightarrow B_3N_3H_4Br_2 + 2HBr \qquad (17)$$

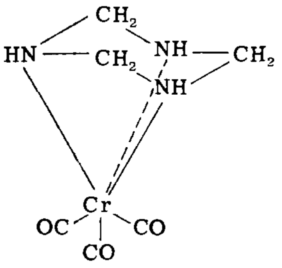
X-Ray diffraction studies of the compound $B_3N_3Me_6H_6$ indicate that it has a cyclic structure (XXI; $R = R'' = H$, $R' = R''' = Me$) and exists in the chair configuration (*171*); the hydrogen hyperfine splitting in the B^{11} nuclear magnetic resonance spectrum of this compound and of hexahydroborazine (XXI; $R = R' = R'' = R''' = H$) (*27*) also supports this formulation (*19*). Compounds of this type can be considered as the boron-nitrogen analogs of cyclohexane or as "saturated" borazines. Presumably the compound $B_3N_3H_9Me_3$ (XXI; $R = R' = R'' = H$, $R''' = Me$), which loses hydrogen at 200° to form a borazine and which has been resolved into two isomers (*44*), and $(R\cdot C{=}H\cdot NBRH)_3$ (*69*) also have a cyclic structure. Borazine has not been hydrogenated using conventional techniques; treatment of borazine with hydrogen in the presence of a catalyst causes an evolution of hydrogen and the formation of a polymeric material of indefi-


(XXI)

nite composition (*186*). An indirect hydrogenation of borazine (*27*) and of *N*-trimethylborazine (*44*) was accomplished by the reaction of the borazine-HCl adducts [(XXI), $R = R'' = R''' = H$, $R' = Cl$; (XXI), $R = R'' = H$, $R''' = Me$, $R'' = Cl$] with sodium borohydride [Eq. (18)]. Hexahydroborazine [(XXI), $R = R' = R'' = R''' = H$] is converted into borazine by pyrolysis at 200°.

$$H_3B_3N_3R_3 + 3HCl \rightarrow H_3B_3N_3R_3\cdot 3HCl \xrightarrow{NaBH_4} B_3N_3H_9R_3 + B_2H_6 + NaCl \qquad R = H, Me \tag{18}$$

Theoretically, borazines could form addition compounds with electron-pair acceptors (Lewis acids) if (*a*) the "π" electrons are localized on the nitrogen atoms or (*b*) the "π" electrons are delocalized as in benzene. In the former case the borazine could be considered as a cyclic amine and might act as a Lewis base. On the other hand, a delocalized π system in the borazine ring could be capable of forming "sandwich"-type compounds similar to dibenzenechromium. Although sandwich compounds containing borazine rings have not yet been formed, charge-transfer complexes between hexamethylborazine and tetracyanoethylene (*21*), chloranil (*21*), and iodine (*103*) have been observed in solution. Charge-transfer complexes are well known for benzenoid systems, but the charge-transfer spectrum observed with the borazine ring does not necessarily mean that a delocalized π system of electrons is present in this ring because amines have been reported to give charge-transfer complexes with I_2 also (*86*, *193*). Indeed, the isolation of a sandwich compound or a molecular-addition compound containing the borazine ring could not be taken as evidence that an aromatic system is involved, for if the "π" electrons are localized initially or become so under the influence of the acceptor (cf. dibenzene-chromium, ref. *80*) the borazine could be considered as a tridentate cyclic amine. Cyclic triamines can act as tridentate ligands as exemplified by the reaction of hexahydro-*s*-triazine with chromium hexacarbonyl to form $Cr(CO)_3(C_3N_3H_{12})$. The latter compound has been formulated as XXII (*98*). In view of these considerations,



(XXII)

it may be difficult to establish the bond nature of any complex compound of this type containing borazine which may be prepared even if a complete structure determination is made. The structures of the halogen-borazine adducts ($H_3B_3N_3H_3{\cdot}3Cl_2$, $H_3B_3N_3H_3{\cdot}2Br_2$) are of interest in this respect since trimethylamine-iodine adducts (*60, 167*) are known to contain iodine associated with the nitrogen atom (presumably through the lone pair electrons) in a linear N—I—I arrangement; this situation occurs even with γ-picoline in which the I—I axis is in the plane of the ring (*61*). Apparently the electronic charge is more available for bond formation from the nitrogen lone pair electrons than from the aromatic π cloud. On the other hand, the halogen-benzene adducts $C_6H_6{\cdot}I_2$ (*41*), $C_6H_6{\cdot}Br_2$ (*62*), and $C_6H_6{\cdot}Cl_2$ (*63*) contain the halogen atom associated with the entire benzene ring. When they are determined, the structures of the borazine-halogen complexes may clarify the disposition of the lone pair electrons in the borazine ring.

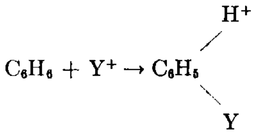
Partial localization of the π electrons on the nitrogen atom could lead to the borazine ring acting as an acceptor of electrons at the boron atom sites. Presumably the addition of polar molecules, HX (X = halogen) (*186, 187*), occurs because the electrophilic fragment (H^+) adds to the nitrogen atom while the nucleophilic moiety adds to the boron atom, since pyrolysis of the adduct yields *B*-halogeno-substituted borazines (*186, 187*). In view of this apparent electron-pair donating and accepting ability of the borazine ring an interesting possibility arises for the formation of addition compounds with the transition metals. If the "π" electrons are partially localized on the nitrogen atoms of the borazine ring, it can behave as a tridentate ligand, donating its electrons to available vacant *d* orbitals of a suitable transition metal atom, and it can also accept electron pairs at the boron sites from filled *d* orbitals of the transition metal. A compound formed in this manner might be difficult to distinguish from a "sandwich compound" resulting from interaction of delocalized "π" electrons on the borazine ring.

No addition compounds containing the borazine ring as an electron acceptor have been characterized; borazine was found to react slowly with amines and dimethyl ether to yield products that are apparently polymers (*186*) and not to be affected by di-*n*-butyl ether (*148*).

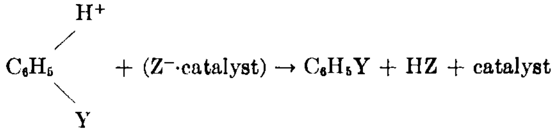
B. SUBSTITUTION REACTIONS

Borazine rings undergo substitution reactions primarily on the boron positions and very rarely on the nitrogen positions, the majority of the former reactions having been reported for *B*-halogenoborazines. Benzenoid systems are most readily substituted by electrophilic reagents, and generally a catalyst is required to aid in the formation of the attacking group.

$$YZ + \text{catalyst} \rightarrow Y^+(Z^- \cdot \text{catalyst}) \qquad (19)$$



$$C_6H_6 + Y^+ \rightarrow C_6H_5\begin{matrix} \diagup H^+ \\ \diagdown Y \end{matrix} \qquad (20)$$



$$C_6H_5\begin{matrix} \diagup H^+ \\ \diagdown Y \end{matrix} + (Z^- \cdot \text{catalyst}) \rightarrow C_6H_5Y + HZ + \text{catalyst} \qquad (21)$$

The intermediate carbonium ion [Eq. (20)] decomposes to give a substituted aromatic system because the latter has a much lower energy content than the former. By contrast, substitution reactions occur on the borazine ring without a catalyst. In view of the mode of addition of polar reagents to borazines and the fact that *B*-substitution occurs more readily than *N*-substitution, it would appear that most of the substitution reactions occur via attack of a nucleophilic species at the electron-deficient boron atoms, followed by either addition of the electrophilic portion of the reagent to the ring nitrogen atoms or elimination of a group from the boron position.

1. Substitution of Chlorine Attached to Boron

Perhaps the most convenient method for the preparation of borazines involves the condensation of boron trichloride with an appropriately-substituted ammonium salt to form symmetrically-*N*-substituted *B*-trichloroborazines. These compounds can react with a variety of reagents to yield tri-*N*-substituted tri-*B*-substituted borazines.

a. Substitution by Alkyl or Aryl Groups. Alkyl and aryl Grignard reagents (M = MgX) (*9, 37, 55, 66, 144, 153*), alkyl- and aryl-lithium reagents (M = Li) (*5, 55, 114*), and triphenylsilyl-potassium (*25*) or -lithium (*153*) react with B-trichloroborazines to form the corresponding *B*-tri-alkyl-, -aryl-, or -silyl-borazines [Eq. (22)]. An attempt to prepare

$$R_3N_3B_3Cl_3 + 3R'M \rightarrow R_3N_3B_3R'_3 + 3MCl \qquad (22)$$

B-perfluoroalkylborazines by the reaction of heptafluoro-*n*-propyl-lithium on *B*-trichloro-*N*-triphenylborazine was unsuccessful (*89*).

Usually sufficient Grignard or lithium reagent is added to substitute all the chlorine atoms on the borazine, but if a deficiency of reagent is employed [Eq. (23)] a mixture of products is obtained (*144*). Reaction (23)

$$Me_3N_3B_3Cl_3 + <3n\text{-}BuMgX \rightarrow \underset{45\%}{Me_3N_3B_3(n\text{-}Bu)_3} + \underset{35\%}{Me_3N_3B_3Cl(n\text{-}Bu)_2} + \underset{20\%}{Me_3N_3B_3Cl_2(n\text{-}Bu)} \quad (23)$$

apparently proceeds by the consecutive substitution of alkyl groups in a statistical manner, since the presence of one alkyl group does not markedly affect the rate of substitution of subsequent alkyl groups (*144*). This conclusion is not supported, however, by the distribution of products observed in the reaction of Grignard or lithium reagents with B—H bonds (*158*). Some investigators have indicated that it is difficult to separate *B*-alkyl- or -aryl-borazines from ether in high yield, however addition of tertiary amines to the reaction mixture increases the yield markedly (*37*).

b. Substitution by Hydrogen. Lithium aluminum hydride (*148, 158*), sodium borohydride (*29, 71, 186*), and lithium borohydride (*148*) have been used to substitute hydrogen for chlorine on the boron sites in borazines [Eqs. (24) and (25)]. The reaction of $LiAlH_4$ with *B*-trichloroborazine (*148*)

$$4R_3N_3B_3Cl_3 + 3LiAlH_4 \rightarrow 4R_3N_3B_3H_3 + LiCl + AlCl_3 \quad (24)$$

$$2R_3N_3B_3Cl_3 + 6MBH_4 \rightarrow 2R_3N_3B_3H_3 + 3B_2H_6 + 3MCl \quad (25)$$

apparently gives a poorer yield of the corresponding dehalogenated borazine than does the reaction with *B*-trichloro-*N*-triphenylborazine (*158*), which may be the result of a different mode of reaction. Aluminum hydride is reported to be one of the products in the reaction of $LiAlH_4$ with *B*-trichloroborazine [Eq. (26)], whereas all of the hydrogen atoms on the reducing agent are replaced on reaction with *B*-trichloro-*N*-triphenylborazine.

$$3LiAlH_4 + Cl_3B_3N_3H_3 \rightarrow B_3N_3H_6 + 3LiCl + 3AlH_3 \quad (26)$$

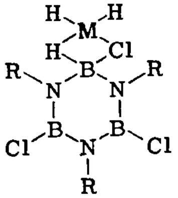
An interaction appears to occur between AlH_3 and borazine since the addition of AlH_3 to an etheral solution of borazine prevents the recovery of borazine from the mixture (*148*). Lithium hydride (*177*) and sodium trisisopropoxyborohydride (*94*) have also been employed to effect hydrogen substitution for chlorine atoms. The reaction between a borazine and sodium borohydride probably does not affect the substituent on nitrogen because *B*-trichloro-*N*-trideuteroborazine reacts with $NaBH_4$ to yield *N*-trideuteroborazine (*184*). These results lend indirect support to the

$$D_3N_3B_3Cl_3 \xrightarrow{NaBH_4} D_3N_3B_3H_3 \quad (27)$$

suggestion (*154*) that the borazine forms a bridged complex (XXIII) upon reaction with reducing agents. A complex of this type has also been suggested as the intermediate in the exchange of alkyl groups between $Cl_2EtB_3N_3Me_3$, $ClEt_2B_3N_3Me_3$, and $Et_3B_3N_3Me_3$ (*144*) and in the exchange of alkyl groups during the pyrolysis of certain isomeric alkylborazines (*179*).

c. Substitution by Amino, Hydroxyl, or Alkoxyl Groups. *B*-Trichloroborazines react with secondary amines (*47, 121, 158*) or their salts (*121*) to form *B*-triaminoborazines (XXIV); the reaction of ammonia with *B*-trichloroborazine is reported to yield *B*-triaminoborazine (XXIV, R = R′ = H) (*54*) as well as a polymeric material (*47*).

$$R_3N_3B_3Cl_3 + 3NHR'_2 \rightarrow \underset{\text{(XXIV)}}{R_3N_3B_3(NR'_2)_3} + 3HCl \qquad (28)$$

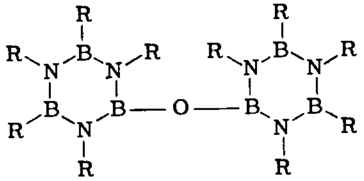


(XXIII)

Hydroxyl groups have been substituted for chlorine atoms on the boron sites in the borazine ring by reaction with water (*82, 85*), and the reverse of this conversion can be accomplished by treating the *B*-trihydroxyborazine with $SOCl_2$ (*5*). Alkoxyborazines have been prepared from *B*-trichloroborazines using sodium alkoxides (*14, 65*), and *B*-trisiloxylborazines (XXV, R = $OSiMe_3$) can be prepared in a similar manner (*153*). An interesting series of polyborazines are obtained from the reaction of *B*-monochloroborazines or *B*-dichloroborazines with water in the presence of triethylamine. The former compounds yield (XXVI), while the latter yield a polymeric substance (*179*).

$$R_3N_3B_3Cl_3 + 3H_2O \rightarrow R_3N_3B_3(OH)_3 + 3HCl \qquad (29)$$

$$R'_3N_3B_3Cl_3 + 3NaOR \rightarrow \underset{\text{(XXV)}}{R'_3N_3B_3(OR)_3} + 3NaCl \qquad (30)$$

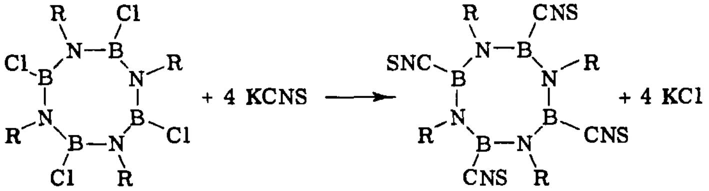


(XXVI)

d. Substitution by Miscellaneous Reagents. Several other reagents can replace chlorine atoms on the boron sites in borazines. The reaction [Eq. (31)] of potassium thiocyanate or silver cyanide with *B*-trichloroborazine

$$R_3B_3N_3Cl_3 + 3MX \rightarrow \underset{\text{(XXVII)}}{R_3B_3N_3X_3} + 3MCl \qquad (31)$$

in acetonitrile yields compounds which correspond to *B*-trithiocyanatoborazine[(XXVII); R = H, X = SCN] and *B*-tricyanoborazine [(XXVII); R = H, X = CN], respectively (*15*). Difficulty was encountered in freeing the latter compound of silver, and this may have been due to complex formation (see above). Reaction with silver nitrite and silver nitrate yielded precipitates of silver chloride under the same conditions, although the corresponding borazine [(XXVII); R = H, X = NO_2 or NO_3] could not be isolated (*15*). The reaction of silver perchlorate with *B*-trichloro-*N*-trimethylborazine yielded a solid, the stoichiometry of which corresponded to that expected for *B*-triperchlorato-*N*-trimethylborazine [(XXVII); R = Me, X = ClO_4] (*100*). This compound explodes violently when treated with water or when placed in a flame and should be treated with extreme caution. Similar observations have been reported concerning the stability of the reaction products of *B*-trichloroborazine with silver nitrite (*15*). The tetrameric borazyne (XXVIII), R = *t*-butyl, the boron-nitrogen analog of cyclooctatetraene, has been reported, and substitution of the chlorine atom attached to boron can be effected by treatment with potassium isothiocyanate (*175*).



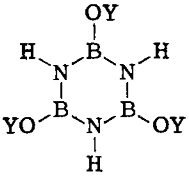
(32)

(XXVIII)

Anhydrous acetic acid reacts with borazine to form a 1:3 adduct (cf. Section III,A), but it attacks *B*-trichloroborazine by cleaving the ring with the concomitant liberation of hydrogen chloride and the formation of the dimeric aminoborane (XXIX) (*15*). Esters of phosphoric acid react with

$$2Cl_3B_3N_3H_3 + 12CH_3CO_2H \rightarrow \underset{\text{(XXIX)}}{3[(CH_3CO_2)_2BNH_2]_2} + 6HCl \qquad (33)$$

B-trichloroborazine to form compounds of type (XXX) [Y = P(O)(OR)$_2$] (*119*), while esters of phosphorus acid in the presence of aldehydes form



(XXX)

phosphinyl-substituted alkoxyborazines [(XXX); Y = —CHRP(OR)$_2$] (*12*). *B*-Trichloroborazine is reported to undergo reaction with benzene in boiling chlorobenzene containing AlCl$_3$ to give *B*-triphenylborazine in about 24% yield (*118*). If the mechanism of this reaction is similar to that proposed for a Friedel-Crafts type reaction, it would appear that the borazine ring can act as an electrophile under the influence of AlCl$_3$ since the complex AlCl$_3$ forms with benzene is not considered to be essential in the mechanism of the normal Friedel-Crafts process (*141*).

Diazomethane (*173*) and ethylene oxide (*123*) react with *B*-trichloroborazine. The product (XXXII) of the latter reaction is identical with

$$H_3N_3B_3Cl_3 + 3CH_2N_2 \rightarrow \underset{\text{(XXXI)}}{H_3N_3B_3(CH_2Cl)_3} \quad (34)$$

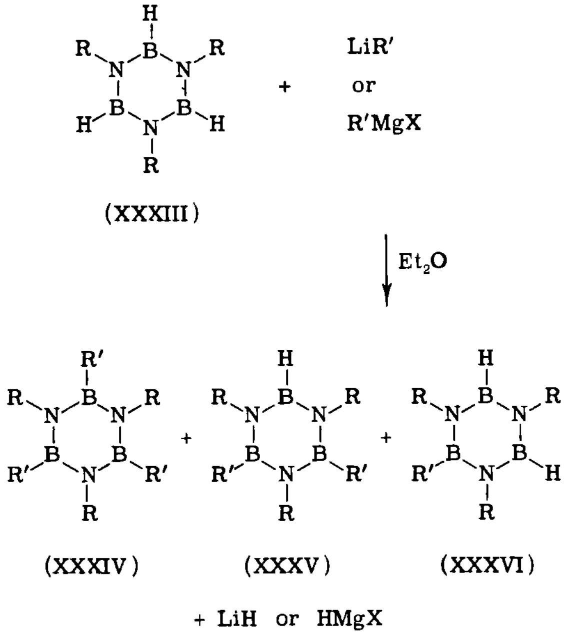
$$H_3N_3B_3Cl_3 + 3(CH_2)_2O \rightarrow \underset{\text{(XXXII)}}{H_3N_3B_3(OCH_2CH_2Cl)_3} \quad (35)$$

that obtained from the reaction of the appropriate chlorinated alcohol with *B*-triaminoborazine. The former reaction yields the only known halogenomethylborazine (XXXI); this type of reaction is also observed with *N*-triarylborazines (*163*).

2. Substitution of Hydrogen or Alkyl Groups Attached to Boron

Many of the substitution reactions observed with chlorine attached to boron also occur with hydrogen attached to boron, although these substitution reactions have not been as extensively investigated. Deuterium, diborane-d_6, and sodium borodeuteride undergo exchange reactions with borazine at the boron sites only (*28*), which in the case of the last two named compounds appears to be consistent with the suggestion (*154*) that a bridged intermediate is involved [cf. (XXIII)].

a. Substitution by Alkyl or Aryl Groups. The reaction of *N*-triphenylborazine or *N*-trimethylborazine with Grignard reagents or alkyl- or aryllithium reagents supports the suggestion that the hydrogen atoms in these compounds are hydridic or pseudo-halogen in nature (*158*). *B*-mono- (XXXVI) and -di-substituted borazines (XXXV) were obtained in good yield upon alkylation of *N*-triphenylborazine [(XXXIII), R = C$_6$H$_5$];

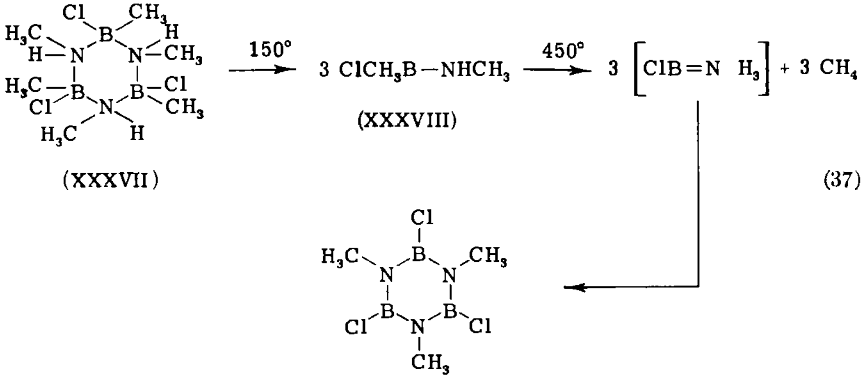


(36)

only one product was obtained in each case. In contrast to this behavior, *N*-trimethylborazine yielded appreciable amounts of all possible substitution products [(XXXIV), (XXV), and (XXXVI), R = Me] under the same conditions. A statistical distribution of products is not obtained upon alkylation or arylation of *N*-triphenylborazine indicating that the introduction of a substituent on the boron atom alters the reactivity of the remaining B—H sites (contrast with reaction of *B*-trichloroborazine, Section III,B,*1*,*a*). In the case of *N*-triphenylborazines, both methyl and phenyl groups substituted on boron sites decrease the rate at which further substitution occurs; the order of the reactivity of the compounds in this series appears to be unsubstituted > monosubstituted > disubstituted. Substitution of alkyl groups deactivates the borazine ring to a lesser degree in *N*-trimethylborazine than in *N*-triphenylborazine (*158*).

Trimethylborane reacts with borazine at 100° to yield a mixture of all the possible *B*-substituted derivatives, although *B*-trimethylborazine is the major product (*150*). No nitrogen sites were substituted, which is in keeping with the results observed with other alkylating reagents.

b. Substitution by Halogen Atoms. *B*-Halogenoborazines can be prepared by the action of a hydrogen halide (*164*, *165*, *178*, *185*, *186*, *187*, *188*) or a halogen (*185*, *186*) on the corresponding borazine (*164*, *185*, *186*) or trialkylborazine (*187*, *188*) at elevated temperatures. As is discussed in Section III,A this reaction proceeds through the formation of an intermediate addition compound. Alkyl groups or hydrogen atoms on the boron atom are eliminated as alkanes or molecular hydrogen, respectively; alkyl groups on the nitrogen sites are retained during the pyrolysis reaction. If these reactions are conducted in the presence of excess (over a 3:1 molar ratio) hydrogen halide, complete ring cleavage results (*187*). It has been suggested (*185*, *186*) that the elimination of alkanes is not a simple molecular displacement, but proceeds through formation of the 1:3 adduct (XXXVII), which in turn dissociates into the corresponding aminoborane (XXXVIII); (XXXVIII) eliminates methane and recombines to form a borazine [Eq. (37)].



(37)

The high temperature reaction of borazine with NH_4Cl to yield small amounts of *B*-trichloroborazine (*146*) can be considered as an extension of the reaction between borazine and HCl under the same conditions.

Boron trihalides react with borazine at room temperature to yield a mixture of mono- and di-substituted borazines as well as hydrogen and unidentified nonvolatile products (*146*).

c. Substitution by Miscellaneous Reagents. The hydridic character of the hydrogen atoms on boron sites is also exemplified by the stepwise reaction of diazomethane with *N*-triarylborazines to form *B*-mono-, *B*-di-, and *B*-tri-methyl-*N*-triarylborazines (*163*). The stepwise course of this reaction is consistent with the results obtained for the successive replacement of the hydrogen atoms in *N*-triarylborazines by alkyl groups using Grignard reagents (cf. Section III,B,*2*,*a*).

3. Substitution of Amino Groups Attached to Boron

Amino groups attached at the boron sites in borazines can be replaced by other amino groups [Eq. (38)] (*38*, *39*, *47*, *124*, *187*), but in some instances polycondensation competes with the transamination reaction (*47*).

$$(R_2N)_3B_3N_3R'_3 + 3R''_2NH \rightarrow (R''_2N)_3B_3N_3R'_3 + R_2NH \qquad (38)$$

Unsymmetrically-substituted *B*-triaminoborazines have been prepared by reacting symmetrically-substituted *B*-triaminoborazines with the appropriate amine in equimolar proportions (*91*). Hydrazine and unsymmetrical-dimethylhydrazine have also been employed in this type of reaction [Eq. (38)] to obtain *B*-trihydrazinoborazines (*124*, *187*).

B-Triaminoborazines react with an excess of an alcohol or perhalogenoalcohol to yield *B*-trialkoxyborazines [Eq. (39)] (*124*, *187*); *B*-mono- and -di-alkoxyborazines can be prepared by using stoichiometric amounts of the reagents (*91*). All amino or alkylamino groups attached to the boron

$$(R_2N)_3B_3N_3R'_3 + 3R''OH \rightarrow (R''O)_3B_3N_3R'_3 + 3R_2NH \qquad (39)$$

sites are easily replaced by alcohols, and the order of replacement is $NH_2 \gg N_2H_3 > NHR > NR_2$ (*187*).

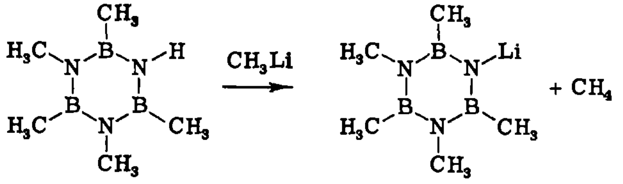
Boron trichloride (*47*, *124*), phosphonyl chloride (*124*), and HCl (*47*) displace —NR_2 groups from the boron sites of borazine rings to form *B*-trichloroborazines [cf. Eq. (40)].

$$(R_2N)_3B_3N_3H_3 + XCl \rightarrow Cl_3B_3N_3H_3 + R_2NX \qquad (40)$$
$$X = -BCl_2,\ -POCl_2,\ -H.$$

4. Substitution on the Nitrogen Atom

Although substitution on the nitrogen sites in the borazine ring is not commonly observed, ND_3, DCl, and DCN were found to exchange with hydrogen attached to nitrogen atoms at a rate which is comparable to that with which these substances add to the borazine (*28*). The results of the exchange experiments between DCl and borazine indicate that the adduct $B_3N_3H_6{\cdot}3DCl$ does not decompose into borazine nor does the adduct exchange with borazine.

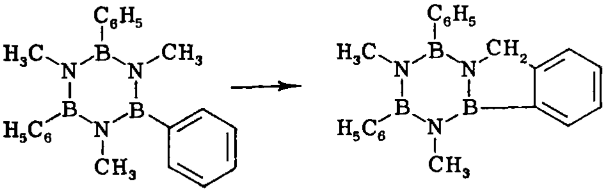
Hydrogen atoms attached to nitrogen positions in the borazine ring can be replaced by lithium [Eq. (41)] using methyl-lithium (*178*, *179*).



(XXXIX) (XL) (41)

A nearly quantitative yield of *N*-lithio-pentamethylborazine (XL) can be obtained from *B*-trimethyl-*N*-dimethylborazine (XXXIX), but the reaction of *B*-trimethylborazine with methyl-lithium in a 1:1 mole ratio gives predominantly *N*-monolithio-*B*-trimethylborazine with lesser amounts of the *N*-di- and -tri-lithio derivatives. This reaction has been used to prepare a variety of unsymmetrically-substituted borazines (*178*) as well as polymeric borazines. A similar replacement of hydrogen atoms on the nitrogen sites has been observed with Grignard reagents (*59*).

The pyrolysis of *B*-triphenyl-*N*-trimethylborazine proceeds by the elimination of hydrogen from the methyl group and the ortho position of the benzene ring [Eq. (42)] with the concomitant formation of a five-membered ring.


(42)

IV. Commercial Uses of Borazines

Borazines have been used in proportional counters for neutron detection (*58*, *114*), as gasoline additives (*122*, *152*), and as polymerization catalysts (*81*). Although attempts to make borazine polymers have been successful (see, for example, refs. *87*, *131*, and *179* and Sections II,C and II,B), no commercially important polymers have been reported.

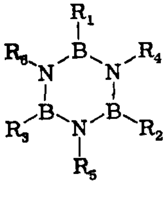
V. Physical Properties of Borazines

The similarity of the physical properties of borazine (Table I) and benzene has often been cited to support the statement that the former can be looked upon as "inorganic benzene," in spite of the apparent difference in the chemistry of these ring systems. When compared with a series of benzene derivatives, those properties of the analogous borazines that are dependent upon structural similarities vary in a predictable manner. For example, the ratio of the boiling points (expressed in °K) of methyl borazines to the boiling points of the analogous benzene derivatives is approximately 0.93 (*187*). The physical properties of borazine appear to be those expected for an unassociated liquid, although it has been suggested (*154*) that the temperature dependence of viscosity for borazine (*34*) indicates association at low temperatures in contrast with benzene. On the other hand, Trouton's constant, Eötvös' constant, and the value of the product of the viscosity (η) and molar volume (V_m) indicate that borazine is not associated to any appreciable extent. The product ηV_m for borazine is about half the corresponding value for benzene at normal temperatures, but associated liquids exhibit a ηV_m value of about 100 times that of unassociated liquids (*115*).

TABLE I
THE PHYSICAL PROPERTIES OF BORAZINE

Boiling point 55.0° (*186*)
Melting point −56.2° (*34*)
$\log P_{mm} = -1828.2/T + 8.6829$ (−55°C to −15°) (*186*)
$\log P_{mm} = -1565.5/T + 7.6616$ (−15°C to +20°) (*186*)
$\log P_{mm} = -1538.0/T + 7.5668$ (+20°C to +50°) (*186*, see also ref. *164*)
D (gm/cm³) $= 1.1551 - 0.001074T$ ($T = 238.2$ to 313.9) (*34*)
D (gm/cm³) $= 0.8613 - 0.00097t$ ($t = -40$ to +10) (*74*, *186*)
$n_D^{20} = 1.3821$ (*34*, *74*)
Molar refraction at 20° = 22.26 (*74*)
Molar volume at 0° = 93.5 (*74*)
Trouton's constant = 21.1 (*74*), 21.4 (*186*)
$\Delta H_v = 7034$ cal/mole (*74*, *186*)
Critical temperature = 252° (*186*)
η (poise) $= 47.3(10^{-5})D^{1/3}e^{665.5D/T}$ (*34*)
γ (dynes/cm) $= 58.3 - 0.1207(D^{2/3})$ (*34*, see also ref. *186*).
γ (at m.p.) = 31.09 dynes/cm (*186*)
Parachor = 207.7 (*186*)
Molecular surface tension $= 503 - 2.0t$ (*186*)
Diamagnetic anisotropy $= -49.6 \times 10^{-6}$ e.m.u. (*180*)
Dipole moment: gas phase, 0.67 Debye (*136*); benzene solution, 0.50 Debye (*96*)

The physical properties that have been reported for substituted borazines are summarized in Table II, and borazines that have not been characterized other than by their elemental analysis or their reactions appear in Table III. The compounds in these tables are listed according to the boron substituents and the nitrogen substituents which have been arbitrarily numbered according to (XLI).

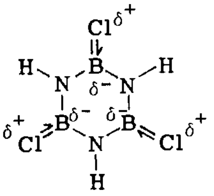


(XLI)

A. MOLECULAR STRUCTURE

X-ray data on borazine were reported by Stock, but the Debye-Scherrer pattern proved too complex for analysis at the time (*164*). The similarity between electron diffraction photographs of borazine and benzene led to an assignment of D_{3h} symmetry to the former (*166*), and this symmetry group has been assumed in the analysis of electron diffraction data on *N*-trimethylborazine and *B*-trichloroborazine (*22*). Structural parameters for several borazines and for one cyclohexane-type derivative [(XXXVIII); R = R′ = H, R″ = R‴ = Me] are given in Table IV. Electron diffraction data indicate that all atoms in the borazine ring are coplanar to within 0.1 Å (*6*). Preliminary X-ray studies conducted on microcrystals of borazine and benzene (*40, 139*) indicate a similar arrangement of molecules in the unit cell.

The structural parameters obtained from X-ray crystallographic data for $Cl_3B_3N_3H_3$ (*24*) indicate that the ring atoms are coplanar to less than 0.01 Å and that the molecule has D_{3h} symmetry within experimental error. The larger intermolecular H—H′ and Cl—Cl′ distances and the smaller Cl—H′ distances observed in *B*-trichloroborazine as compared with the corresponding distance in *s*-trichlorobenzene suggest that a greater charge exists on the chlorine and hydrogen atoms in the former compound (XLII). Because of significant contributions of (XLII) to the structure, there is less aromatic character in *B*-trichloroborazine than in the analogous benzene derivative (*95*). This observation is in agreement with trends established from diamagnetic anisotropy data (Section V,F).



(XLII)

The molecular structure of $B_3N_3H_6Me_6$ has been elucidated from X-ray data, although the crystallographic space group was not unequivocally assigned. This molecule is in the chair form with C_{3v} symmetry within experimental error, and it is interesting to note that no sterically satisfactory, fixed arrangement of the methyl hydrogens could be found (*172*). The B—N bond distance observed in this compound approaches that expected for a single bond (*45*).

An "equivalent" C—C bond length (1.406 Å) has been calculated using an empirical relationship for the B—N bond in $H_3B_3N_3H_3$ and an estimated bond order of 1.58 derived (*160*). A bond order of 1.20 for the B—N bond in $Cl_3B_3N_3H_3$ has been estimated from Gordy's formula (*51*) assuming 1.45 Å for the B—N single bond length and 1.281 Å for the B—N double bond length (*154*). The value for the B—N double bond length is taken from the equilibrium bond distance for the lower $^3\Pi$ state of the diatomic molecule BN (*33*). A comparison of the C—C distance in the species C_2 (1.31 Å) and C_2H_4 (1.35 Å) (*169*) suggests that the value for the BN double bond distance in the $^3\Pi$ state is about 0.04 Å too small for the hypothetical species $H_2B{=}NH_2$. If the empirical correction is made, the calculated B—N

TABLE II[a]
THE PHYSICAL PROPERTIES OF BORAZINES

B-Substituents			*N*-Substituents						
R_1	R_2	R_3	R_4	R_5	R_6	Reference	m.p.	b.p./mm.	Other properties
H	Me	Me	H	H	Me	(*150*)		139	log $P = -1965/T + 7.652$; $\Delta H_v = 8916$; $T = 21.6$
H	Me	Me	H	H	H	(*149*)	−48	107	log $P = -2019/T + 8.200$; $\Delta H_v = 9230$; $T = 24.3$
H	Me	Me	Me	Me	Me		32.8 (*178*)	187 (*158*)	$D/t = 0.87/35$, IR (*178*)
H	Me	Me	Ph	Ph	Ph	(*163*)	205–7	101.2/38 (*178*)	
H	Me	Me	←4-BrC_6H_4→^{b,c}			(*163*)	211–3		
H	Me	Et	Ph	Ph	Ph	(*158*)	128		
H	Ph	Ph	Ph	Ph	Ph	(*158*)	207		
H	Br	Br	H	H	H	(*146*)	49.5–50.0	167.1	log $P = -2849/T + 9.352$; $\Delta H_v = 13037$; $T = 29.6$
H	Cl	Cl	H	H	H	(*146*)	33.0–33.5	151.9	log $P = -1994/T + 7.572$; $\Delta H_v = 9125$; $T = 21.5$
H	Cl	Cl	←2,6-$Me_2C_6H_3$→			(*173*)			IR; NMR
H	NH_2	NH_2	H	H	H	(*101, 103*)			*MS*
H	H	Me	H	H	Me	(*150*)		124	log $P = -1732/T + 7.245$; $\Delta H_v = 8013$; $T = 20.2$
H	H	Me	H	H	H	(*149*)	−59	87	log $P = -1800/T + 7.880$; $\Delta H_v = 8230$; $T = 22.8$
H	H	Me	Me	Me	Me	(*178*)	−14.5	162 (*158*) 76.2/38 (*158*)	$D/t = 0.85/25$, IR (*178*)
H	H	Me	Ph	Ph	Ph		140–2 (*158*) 138–41 (*163*)		
H	H	Me	←4-MeC_6H_4→			(*163*)	150–1		
H	H	Me	←3-MeC_6H_4→			(*163*)	137–8		
H	H	Ph	H	H	H	(*112*)	73.5–75		
H	H	Ph	Ph	Ph	Ph	(*158*)	215		
H	H	Br	H	H	H	(*146*)	34.8	122.3	log $P = -2172/T + 8.373$; $\Delta H_v = 9939$; $T = 25.1$
H	H	Cl	H	H	H	(*146*)	−34.6	109.5	log $P = -1846/T + 7.703$; $\Delta H_v = 8445$; $T = 22.1$
H	H	H	H	H	H		See Table I		X (*164*); NMR (*77, 132*); IR (*26, 183*); R (*26*), UV (*133*); See also Table I
H	H	H	H	H	Me	(*150*)		84	log $P = -1713/T + 7.669$; $\Delta H_v = 7975$; $T = 22.3$
H	H	H	H	Me	Me	(*150*)		108	log $P = -1832/T + 7.685$; $\Delta H_v = 8375$; $T = 21.9$
H	H	H	Me	Me	Me		−7.8 (*71*)	133 (*74*)	log $P = -2009/T + 7.812$ (*74, 150, 188*); $\Delta H_v = 9200$ (*74*); $T = 22.9$ (*74*) $D/t = 0.8699/0$ (*74*); $n/t = 1.4404/20$ (*74*); MR = 37.98 (*74*); $\chi_m = -78.6$ (*180*) IR (*64, 178*); UV (*137*); ED (*22*); R (*182*); NMR (*78, 132*)

H	H	H	Et	Et	Et	(*74*)	−49.1 (*71*)	184	$\log P = -2012.4/T + 7.238$; $\Delta H_v = 9210$; $T = 20.2$; MR = 50.90; $D/t = 0.8604/0$ $n = 1.4380/20$; IR (*11*)
H	H	H	Pr^n	Pr^n	Pr^n	(*74*)		225	$\log P = -2190.4/T + 7.2793$; $\Delta H_v = 1002$; $T = 20.2$; MR = 66.39; $D/t = 0.8485/0$; $n = 1.4484/20$
H	H	H	Pr^i	Pr^i	Pr^i	(*74*)	−6.7 (*5*)	203	$\log P = -2249.0/T - 7.6001$; $\Delta H_v = 1029$; $T = 21.6$; MR = 64.66; $D/t = 0.8648/0$; $n = 1.4434/20$
H	H	H	Bu^n	Bu^n	Bu^n	(*107*)		109–11/3.5	$n = 1.4524/20$
H	H	H	Bu^i	Bu^i	Bu^i	(*107*)		92/3	$D/t = 0.8245/20$; $n = 1.4466/20$
H	H	H	C_6H_{11}	C_6H_{11}	C_6H_{11}	(*71*)	98.9		
H	H	H	Ph	Ph	Ph		157–8 (*71*) 154–5 (*9*)		IR (*9*), UV (*10*)
H	H	H	←4-BrC_6H_4→			(*163*)	234–5		
H	H	H	←3-BrC_6H_4→			(*163*)	125–5.4		
H	H	H	←4-MeC_6H_4→				149–50 (*71*) 150–2 (*9*)		
H	H	H	←3-MeC_6H_4→			(*163*)	165.5–6.5		
H	H	H	←4-$MeOC_6H_4$→				137–8 (*71*) 139–40 (*163*)		
CN	CN	CN	H	H	H	(*15*)	$d > 200$		
Me	Et	Pr^n	Ph	Ph	Ph	(*158*)	131		
Me	Br	Br	Me	Me	Me	(*178*)	127–9		IR
Me	Cl	Cl	Me	Me	Me	(*178*)	145–6		IR
Me	Me	Bu^n	Ph	Ph	Ph	(*158*)	113		
Me	Me	Br	Me	Me	Me	(*178*)	127–9		IR
Me	Me	Me	H	Me	Me	(*178*)		187–6	IR; $D/t = 0.88/25$
Me	Me	Me	H	H	Me	(*150*)		158	$\log P = -2294/T + 8.207$; $\Delta H_v = 10440$; $T = 24.5$; $D/t = 0.86/25$; IR (*178*)
Me	Me	Me	H	H	H		31.5 (*149*)	129 (*149*)	$\log P = -2199/T + 8.3779$; $\Delta H_v = 10060$ (*149, 188*); $\log P = -3258/T + 11.8488$; $\Delta H_v = 14900$ (*188*); $T = 23.3$ (*149*); $D/t = 0.84/35$ (*178*); IR (*178*); X (*188*); R (*53*); UV (*137*)
Me	Me	Me	Me	Me	Me		99 (*158*) 97.1 (*187*)	221 (*187*)	$\log P = -2523.7/T + 7.9871$; $\Delta H_v = 11540$; $T = 23.4$ (*187*); MR = 50.0; $\chi_m = -119$ (*180*) DM = 0.76 (*181*); NMR (*78*); IR (*178, 183*)
Me	Me	Me	Et	Et	Et	(*78*)			NMR
Me	Me	Me	Pr^i	Pr^i	Pr^i	(*152*)	68–70	101	

TABLE II (*Continued*)

B-Substituents			*N*-Substituents						
R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	Reference	m.p.	b.p./mm	Other properties
Me	Me	Me	Ph	Ph	Ph		267–9 (*55*)		MR = 108.5 (*181*); χ_m = −234 (*180*); DM = 0.18 (*181*); IR (*9, 183*); NMR (*78*); UV (*10*)
CH$_2$Cl	CH$_2$Cl	CH$_2$Cl	H	H	H	(*173*)	117–8		IR
Et	Et	Et	H	H	H	(*66*)	−46.4	173	log $P = -2167/T + 7.746$; $\Delta H_v = 9880$; $T = 22.1$; $D/t = 0.886/20$; IR; $v/20 = 1.48$ (*194*)
Et	Et	Et	Me	Me	Me		1–2 (*144*)	98/1.8 (*144*)	MR = 63.9 (*181*); χ_m = −146 (*180*); DM = 0.83 (*181*); n = 1.4791/22.5 (*144*); IR (*144*); NMR (*78*)
Et	Et	Et	Et	Et	Et		88.5–9.5 (*66*)		MR = 77.7; DM = 0.37 (*181*); χ_m = −189 (*180*); NMR (*78*); IR (*181, 183*); UV (*181*)
Et	Et	Et	Ph	Ph	Ph		169–71 (*55*)		NMR (*78*); IR (*183*); MR = 122.3 (*181*); χ_m = −264 (*180*); DM = 0.47 (*181*)
C_2H_3	C_2H_3	C_2H_3	Ph	Ph	Ph	(*130, 131*)	187–9		
C_2H_2Cl	C_2H_2Cl	C_2H_2Cl	H	H	H	(*143*)	127–8.5		
Pr^n	Pr^n	Pr^n	H	H	H			108/9 (*67*)	UV (*68*); IR (*68*); NMR (*68*)
Pr^n	Pr^n	Pr^n	Ph	Ph	Ph	(*55*)	169–71		
Pr^i	Pr^i	Pr^i	H	H	H			70/0.5 (*67*)	IR (*68*); UV (*68*); NMR (*68*)
Pr^i	Pr^i	Pr^i	Ph	Ph	Ph	(*147*)	197–8		
C_3H_5	C_3H_5	C_3H_5	Me	Me	Me	(*144*)	−(37–9)	110–12/13	n = 1.5047/22.5; IR
C_3H_5	C_3H_5	C_3H_5	Ph	Ph	Ph	(*56, 131*)	98–9		
Bu^n	Bu^n	Bu^n	Me	Me	Me	(*144*)	−(4–6)	101/1.1	n = 1.4876/22.5; IR
Bu^n	Bu^n	Cl	Me	Me	Me	(*144*)		122/1.13	n = 1.4807/22.5; IR
Bu^n	Bu^n	Bu^n	H	H	H			110/0.6 (*67*)	n = 1.4494/25 (*67*); UV (*68*); NMR (*68*)
Bu^n	Bu^n	Bu^n	Me	Me	Me	(*144*)	−(18–7)	140/1.1	n = 1.4759/22.5; IR (*144, 153*)
Bu^n	Bu^n	Bu^n	Bu^n	Bu^n	Bu^n	(*143*)		90–8/0.1	
Bu^n	Bu^n	Bu^n	Ph	Ph	Ph	(*147*)	129–32		IR (*183*)
Bu^s	Bu^s	Bu^s	H	H	H	(*67*)		94/0.7	IR (*68*); NMR (*68*); UV (*68*)
Bu^i	Bu^i	Bu^i	H	H	H	(*68*)		72.1/0.03	IR; NMR; UV
Bu^i	Bu^i	Bu^i	Ph	Ph	Ph	(*55*)	185–7		
Bu^t	Bu^t	Bu^t	H	H	H	(*68*)		60/0.10	IR; NMR; UV
Pn^n	Pn^n	Pn^n	H	H	H	(*68*)		125/0.07	IR; NMR; UV
←——Me$_2$CHCH$_2$CH$_2$——→			H	H	H	(*110*)		114–15.5/0.1	D/t = 0.8485/20; n = 1.4538/20

← Me$_2$CHCH$_2$CH$_2$ →			Et	Et	Et	(*110*)	43–5	113–4/0.06	
← Me$_2$CHCH$_2$CH$_2$ →			Bu^i	Bu^i	Bu^i	(*110*)	53–5	126–8/0.06	
← Me$_2$CHCH$_2$CH$_2$ →			Ph	Ph	Ph	(*110*)	93.5–5.5	180–1/0.06	
Hx^n	Hx^n	Hx^n	H	H	H	(*68*)		140/0.05	UV (*68*); IR (*68*); NMR (*68*)
Ph	Ph	Ph	H	H	H		183–5 (*9, 32*) 181–182.5 (*108*) 175–6 (*118*) 179–82 (*37*)		IR (*9, 117*); UV (*10, 125*)
Ph	Ph	Ph	Me	Me	Me		261–7 (*117*) 249 (*9*) 270 (*158*)		IR (*9, 20, 117*); UV (*10*)
Ph	Ph	Ph	Et	Et	Et	(*106, 108*) (*109*)	205–6		
Ph	Ph	Ph	Ph	Ph	Ph		413–5 (*55*)		IR (183)
← 4-MeC$_6$H$_4$ →			H	H	H	(*108, 109*)	189–90		
← 4-MeC$_6$H$_4$ →			Et	Et	Et	(*109*)	222–5		
← 4-MeC$_6$H$_4$ →			Ph	Ph	Ph	(*109*)	282–4		
← 4-BrC$_6$H$_4$ →			H	H	H	(*109*)	292–3		
← 4-ClC$_6$H$_4$ →			H	H	H	(*109*)	269–70		UV (*125*)
Bz	Bz	Bz	H	H	H	(*68*)			UV; IR; NMR
← terphenyl →			Me	Me	Me	(*20*)			IR
← 1-C$_{10}$H$_7$ →			H	H	H	(*108*)	185–7		
← 1-C$_{10}$H$_7$ →			Et	Et	Et	(*108*)	269–71		
2Py	2Py	2Py	Me	Me	Me	(*20*)			IR
← Me$_3$SiCH$_2$ →			Me	Me	Me	(*153*)	64		IR
← EtMe$_2$SiCH$_2$ →			Me	Me	Me	(*153*)		183–4/1.0	$D/t = 0.8977/24$; $n = 1.4875/25$
← Bu^{n}Me$_2$SiCH$_2$ →			Me	Me	Me	(*153*)		213–4/0.9	$D/t = 0.8855/25$; $n = 1.4845/25$
← Me$_3$SiOSi(Me)$_2$CH$_2$ →			Me	Me	Me	(*153*)		175–6/0.55	$D/t = 0.9158/25$; $n = 1.4517/25$; IR
Br	Br	Br	H	H	H		128–9 (*36*) 126–8 (*148*)		
Br	Br	Br	Et	Et	Et	(*71*)	78–84		
Cl	Cl	Cl	H	H	H	(*15, 17, 181*)	83.9–84.5		$\log P = -2497/T + 8.25$; $\Delta H_v = 12300$ (*17*); $\log P = -3743/T + 11.73$, $\Delta H_s = 17000$ (*17*); $D/t = 1.5/25$; NMR (*78, 116, 156*); IR (*3, 183, 184*); UV (*73*); X (*24*); DM = 0.56 (*181*)
Cl	Cl	Cl	Me	Me	Me		162–4 (*71*)		MR = 50.8; DM = 0.47 (*181*); NMR (*78*); IR (*178, 183*)
Cl	Cl	Cl	Et	Et	Et		57–9 (*71*)		NMR (*78*); IR (*183*)
Cl	Cl	Cl	Bu^n	Bu^n	Bu^n	(*174*)	30	115–20/0.5	IR (*183*)

TABLE II (*Continued*)

B-Substituents			*N*-Substituents						
R_1	R_2	R_3	R_4	R_5	R_6	Reference	m.p.	b.p./mm	Other properties
Cl	Cl	Cl	C_6H_{11}	C_6H_{11}	C_6H_{11}	(*71*)	217–9		
Cl	Cl	Cl	Ph	Ph	Ph		273–5 (*71*)		IR (*9, 183*)
Cl	Cl	Cl	← 4-MeC_6H_4 →			(*71*)	307–9		
Cl	Cl	Cl	← 4-$MeOC_6H_4$ →			(*71*)	233–8		
F	F	F	Me	Me	Me		85 (*189*)	224 (*189*)	$\log P = 3165.2/T + 10.8256$; $\Delta H_v = 14500$ (*168*)
NHMe	NHMe	NHMe	H	H	H	(*54*)	85–105		
NHMe	NHMe	NHMe	Me	Me	Me	(*2*)		110/0.1	IR (*3*); $D/t = 1.016/20$; $n = 1.5082/20$; MR = 61.7
NHEt	NHEt	NHEt	Et	Et	Et	(*2*)		145–50/0.1	IR (*3*); $D/t = 0.933/20$; $n = 1.4826/20$; MR = 89.8
$NHPr^i$	$NHPr^i$	$NHPr^i$	Pr^i	Pr^i	Pr^i	(*2*)		106/0.03	IR (*3*); $D/t = 0.8220/20$; $n = 1.4628/20$; MR = 118.0
$NHBu^n$	$NHBu^n$	$NHBu^n$	Bu^n	Bu^n	Bu^n	(*2*)		158/0.005	IR (*3*); $D/t = 0.900/20$; $n = 1.4730/20$; MR = 144.3
$NHBu^s$	$NHBu^s$	$NHBu^s$	Bu^s	Bu^s	Bu^s	(*2*)		135/0.01	IR (*3*); $D/t = 0.892/20$; $n = 1.4695/20$; MR = 144.2
$NHBu^t$	$NHBu^t$	$NHBu^t$	Bu^t	Bu^t	Bu^t	(*2*)		103/0.04	IR (*3*); $D/t = 0.883/20$; $n = 1.4631/20$; MR = 144.0
← NHC_6H_{11} →			C_6H_{11}	C_6H_{11}	C_6H_{11}	(*2*)		52–5	
NHPh	NHPh	NHPh	Ph	Ph	Ph	(*2*)		152–5	IR (*3*)
← $NH(CH_2C_6H_5)$ →			Bz	Bz	Bz	(*2*)		>250/0.05	IR (*3*); $D/t = 1.156/20$; $n = 1.642/20$; MR = 208.1
N_2HMe_2	N_2HMe_2	N_2HMe_2	Me	Me	Me	(*124*)	55–9	134/3	IR
N_2HMe_2	N_2HMe_2	N_2HMe_2	Et	Et	Et	(*124*)		140/3	IR
NH_2	NH_2	NH_2	H	H	H	(*47*)			IR
NH_2	NH_2	NH_2	Et	Et	Et	(*124*)	54	138–40/5	IR
NMe_2	NMe_2	NMe_2	H	H	H	(*34*)	112–3		IR (*48, 50*)
NMe_2	NMe_2	NMe_2	Me	Me	Me	(*124*)	66	122–4/3	
NMe_2	NMe_2	NMe_2	Et	Et	Et	(*124*)	61	102–4/3	
NMe_2	NMe_2	NMe_2	Pr^i	Pr^i	Pr^i	(*152*)		128–32/1.6	
NMePh	NMePh	NMePh	H	H	H	(*42*)	128–32		IR (*48, 50*)
NEt_2	NEt_2	NEt_2	H	H	H			120/2 (*54*)	IR (*47, 48, 50*); $D/t = 0.9160/20$ (*47*); $n = 1.4728/20$ (*47*)
NEt_2	NEt_2	NEt_2	Me	Me	Me	(*124*)		138/5	
NEt_2	NEt_2	NEt_2	Et	Et	Et	(*124*)		133–5/5	
NEtPh	NEtPh	NEtPh	H	H	H		85–7 (*48*)		IR (*50*)
NPr_2^n	NPr_2^n	NPr_2^n	H	H	H		32–5 (*47*)	170–2 (*47*)	IR (*48, 50*)
NPr_2^i	NPr_2^i	NPr_2^i	H	H	H		138–43 (*47*)		IR (*48, 50*)
NBu_2^n	NBu_2^n	NBu_2^n	H	H	H	(*47*)		200/0.05	IR (*48, 50*); $D/t = 0.8986/20$; $n = 1.4720/20$
NBu^nPh	NBu^nPh	NBu^nPh	H	H	H		79–81 (*48*)		IR (*48, 50*)
NBu_2^i	NBu_2^i	NBu_2^i	H	H	H	(*47*)	47–52	167/0.3	IR (*48, 50*); $n = 1.4690/20$
← $N(C_6H_{11})_2$ →			H	H	H	(*48*)	>300		IR (*50*)
NPh_2	NPh_2	NPh_2	H	H	H	(*47*)	>325		IR (*49, 50*)
NBz_2	NBz_2	NBz_2	H	H	H	(*50*)	148–50		IR

← $NH\cdot C_6H_{11}$ →			Et	Et	Et	(*121*)		94–6/3	
OH	OH	OH	Ph	Ph	Ph	(*82*)	130		
OH	OH	OH	← 4-$MeOC_6H_4$ →			(*84*)	112–120		
OMe	OMe	OMe	H	H	H	(*65*)	110–111		
OMe	OMe	OMe	Me	Me	Me	(*14*)		62–5/0.07	IR (*3*); $n = 1.4610/23$
OMe	OMe	OMe	Et	Et	Et	(*124*)		93–6/3	IR
OEt	OEt	OEt	H	H	H	(*65*)	53–4		
OEt	OEt	OEt	Me	Me	Me	(*14*)		79.5/80.5/0.10	IR (*3*); $n = 1\ 4540/22.5$
OEt	OEt	OEt	Et	Et	Et	(*124*)		133–6/3	IR
OPr^n	POr^n	OPr^n	Me	Me	Me	(*14*)		101–3/0.015	IR (*3*); $n = 1.4561/22$
OPr^i	OPr^i	OPr^i	Me	Me	Me	(*14*)		85–7/0.10	IR (*3*); $n = 1.4460/23$
OBu^n	OBu^n	OBu^n	H	H	H	(*47*)			IR
OBu^n	OBu^n	OBu^n	Me	Me	Me	(*14*)		130–4/0.30	IR (*3*); $n = 1.4572/23$
OBu^n	OBu^n	OBu^n	Et	Et	Et	(*90*)		153–6/0.4	IR (*3*); $D/t = 0.9311/20$; $n = 1.4544/20$
OBu^t	OBu^t	OBu^t	Me	Me	Me	(*14*)	84–7	120–5/0.52	IR (*3*)
OPh	OPh	OPh	Me	Me	Me	(*14*)	81–4	185–7/0.07	IR (*3*)
← Me_3SiO →			Me	Me	Me	(*153*)	22–3	130/0.85	IR
SCN	SCN	SCN	H	H	H	(*15*)	147–50		
$SiPh_3$	$SiPh_3$	$SiPh_3$	Me	Me	Me		248–51 (*153*)		IR (*25, 153*)
$SiPh_3$	$SiPh_3$	$SiPh_3$	Ph	Ph	Ph	(*25*)	55–8		IR

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[a] The following abbreviations have been used throughout this table.

m.p. = melting point
b.p. = boiling point
D/t = density in gm/cm^3 at temperature t.
p = pressure in mm of mercury.
T = Trouton's constant
ΔH_v = heat of vaporization, calories/mole
ΔH_s = heat of sublimation, calories/mole
MR = molar refraction, ml.
v/t = viscosity, centistokes, at temperature t
χ_m = diamagnetic anisotropy $\times 10^6$, emu
DM = dipole moment (measured in benzene at 25°), debyes
MS = mass spectra
IR = infrared spectra
UV = ultraviolet spectra
NMR = nuclear magnetic resonance
R = Raman spectra
X = X-ray
ED = electron diffraction

Functional derivatives: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Ph, phenyl; Hx, hexyl; Bz, benzyl; Py, pyridyl; *n*, normal; *i*, iso; *s*, secondary; *t*, tertiary.

[b] This type of designation indicates that the same substituent occurs on all the positions.

[c] Substituted benzene rings are numbered with respect to their point of attachment to either boron or nitrogen. Thus, 4-BrC_6H_4 indicates that the benzene ring attached to a boron or nitrogen is substituted with bromine in the 4-position.

TABLE III

BORAZINES NOT CHARACTERIZED BY THEIR PHYSICAL PROPERTIES

B-Substituents			*N*-Substituents			
R_1	R_2	R_3	R_4	R_5	R_6	References
H	Me	Me	← 4-ClC_6H_4 →[a,b]			*(163)*
H	Me	Me	← 3,4-$(MeO)_2C_6H_3$ →			*(163)*
H	Me	Me	← 2-$C_{10}H_7$ →			*(163)*
H	OH	OH	← 2,6-$(CH_3)_2C_6H_3$ →			*(5)*
H	H	Me	← 4-ClC_6H_4 →			*(163)*
H	H	Me	← 4-$MeOC_6H_4$ →			*(163)*
Me	Me	Me	H	Li	Li	*(178)*
Me	Me	Me	H	H	Li	*(178)*
Me	Me	Me	Me	Li	Li	*(178)*
Me	Me	Me	Me	Me	Li	*(178)*
C_2H_3	C_2H_3	C_2H_3	Et	Et	Et	*(130)*
C_2H_3	C_2H_3	C_2H_3	C_6H_{11}	C_6H_{11}	C_6H_{11}	*(130)*
C_2H_3	C_2H_3	C_2H_3	Bz	Bz	Bz	*(130)*
C_2H_3	C_2H_3	C_2H_3	← 4-MeC_6H_4 →			*(130)*
C_3H_5	C_3H_5	C_3H_5	Et	Et	Et	*(56)*
C_3H_5	C_3H_5	C_3H_5	C_6H_{11}	C_6H_{11}	C_6H_{11}	*(56)*
C_3H_5	C_3H_5	C_3H_5	Bz	Bz	Bz	*(56)*
C_3H_5	C_3H_5	C_3H_5	← 4-MeC_6H_4 →			*(56)*
← 4-PhC_6H_4 →			Me	Me	Me	*(114)*
← 4-PhC_6H_4 →			Ph	Ph	Ph	*(20)*
← 1-$C_{10}H_7$ →			Me	Me	Me	*(114)*
Br	Br	Br	Me	Me	Me	*(36)*
Cl	Cl	Cl	Pr^i	Pr^i	Pr^i	*(152)*
Cl	Cl	Cl	← 4-BrC_6H_4 →			*(49)*
F	F	F	SiH_3	SiH_3	SiH_3	*(168)*
NHEt	NHEt	NHEt	H	H	H	*(91)*
NHEt	NEt_2	NEt_2	Et	Et	Et	*(91)*
N_2H_3	N_2H_3	N_2H_3	H	H	H	*(120, 123)*
NEt_2	OBu^t	OBu^t	H	H	H	*(91)*
NCS	NCS	NCS	Bu^t	Bu^t	Bu^t	*(175)*
NO_2	NO_2	NO_2	H	H	H	*(15)*
← O-CH_2CH_2Cl →			H	H	H	*(123)*
OBu^n	NHEt	NHEt	Et	Et	Et	*(91)*
OBu^t	OBu^t	OBu^t	H	H	H	*(91)*
ONO	ONO	ONO	H	H	H	*(15)*

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[a] This type of designation indicates that the same substituent occurs on all the positions.

[b] Substituted benzene rings are numbered with respect to their point of attachment to either boron or nitrogen. Thus, 4-BrC_6H_4 indicates that the benzene ring attached to a boron or nitrogen is substituted with bromine in the 4-position.

TABLE IV
BOND DISTANCES AND BOND ANGLES IN BORAZINE AND ITS DERIVATIVES

Parameter	Compound	Value	Method[a]	Reference
B—N	$H_6B_3N_3Me_6$	1.59 ± 0.027 Å	X	*(172)*
	$H_3B_3N_3H_3$	1.44 ± 0.02 Å	E	*(6)*
	$H_3B_3N_3Me_3$	1.42 ± 0.02 Å	E	*(22)*
	$Cl_3B_3N_3H_3$	1.413 ± 0.010 Å	X	*(24)*
N—C	$H_6B_3N_3Me_6$	1.49 ± 0.040 Å	X	*(172)*
	$H_3B_3N_3Me_3$	1.48 ± 0.03 Å	E	*(22)*
B—Cl	$Cl_3B_3N_3H_3$	1.760 ± 0.015 Å	X	*(24)*
∠BNB	$Cl_3B_3N_3H_3$	121 ± 1°	X	*(24)*
	$H_6B_3N_3Me_6$	113 ± 1°	X	*(172)*
∠NBN	$Cl_3B_3N_3H_3$	119 ± 1°	X	*(24)*
	$H_6B_3N_3Me_6$	114 ± 2°	X	*(172)*
∠CNC	$H_6B_3N_3Me_6$	104 ± 2.5°	X	*(172)*
∠BNC	$H_6B_3N_3Me_6$	109.5 ± 3.5°	X	*(172)*

[a] E, electron diffraction; X, X-ray diffraction.

bond orders for $H_3B_3N_3H_3$, $H_3B_3N_3Me_3$, and $Cl_3B_3N_3H_3$ are 1.48, 1.56, and 1.58, respectively.

Two isomers have been predicted for borazine on the basis of a "general stereochemical law" *(134)*, but this suggestion is not supported by any of the present structural evidence. Apparently, delocalization of the nitrogen *p* electrons was not taken into account in the formulation of this law.

B. DIPOLE MOMENTS

A dipole moment of 0.67 Debye is reported for borazine in the gas phase, but the questionable purity of the sample makes the results tentative *(136)*. A more recent value of 0.50 Debye for the dipole moment of $H_3B_3N_3H_3$ in benzene solution has been reported together with values in the range 0.18–0.72 Debye for seven borazine derivatives. The existence of these moments was attributed either to deviations from planarity (cf. Section V,A) or to low frequency molecular vibrations which accounted for a large atomic polarization *(181)*. However, apparent dipole moments of several symmetrical benzene derivatives have been found illusionary by measuring the dielectric constant and dielectric loss of solutions of these compounds as a function of frequency in the anamolous dispersion region *(32)*. The existence of appreciable dipole moments for borazine and its derivatives is by no means completely established. It has been suggested on the basis of atomic and orientation polarization data that $Cl_4B_4N_4Bu_4{}^t$ has no dipole moment and is in a boat configuration *(175)*.

C. NUCLEAR RESONANCE SPECTRA

1. Nuclear Magnetic Resonance

a. ^{11}B Resonance. The nuclear magnetic resonance spectrum of borazine and its derivatives is consistent with a cyclic structure. An estimation of the fractional *s* character in the bonding of BH_3 adducts with amines and ethers has been made from the magnitude of the B—H spin coupling constants by assuming that the boron atoms in borazine and *N*-trimethylborazine are in an sp^2 hybridized state (*132*). ^{11}B chemical shifts and the B—H spin coupling constants for several borazines are given in Table V.

TABLE V

^{11}B CHEMICAL SHIFTS AND B—H SPIN COUPLING CONSTANTS FOR CYCLIC BORON-NITROGEN SYSTEMS

Compound	Chemical shift (ppm)[a]	J_{B-H} (cps)	References
$Cl_4B_4N_4Bu^t_4$	−30.1		(*175*)
$Br_4B_4N_4Bu^t_4$	−30.3		(*175*)
$H_3B_3N_3H_3$	−30.4	136	(*132*)
		140	(*76*)
$Cl_3B_3N_3Me_3$	−31.3		(*102*)
	−33.5		(*175*)
$H_3B_3N_3Me_3$[b]	−32.4	134	(*132*)
$R_3B_3N_3H_3$	−34.9 to −36.1		(*68*)
$Me_3B_3N_3Me_3$	−36.2		(*102*)
	−36.5		(*42*)
$Cl_3B_3N_3H_3$	−36.5		(*175*)
$Me_3B_3N_3Ph_3$	−36.5		(*42*)
$Ph_3B_3N_3Me_3$	−38.5		(*42*)

[a] Chemical shifts are presented relative to the BF_3—Et_2O adduct.

[b] R = alkyl. These data represent nine *B*-trialkylborazines.

^{11}B chemical shifts for $Cl_3B_3N_3Me_3$ and $Me_3B_3N_3Me_3$ are unaltered when tetracyanoethylene or I_2 is added to a solution of either of these borazines, although color changes, indicative of complex formation, occur (*102*).

b. ^1H Resonance. Proton chemical shifts and coupling constants which have been reported are collected in Table VI. The difference in chemical shifts between methyl protons and methylene protons in ethyl-substituted borazines was used to estimate the electronegativity of the boron atom (1.7) and of the nitrogen atom (3.4–3.5) in the borazine ring. The marked deviation from usually accepted values is explained on the basis of partial double bonding in the ring (*78*, *125a*). The B—H and N—H chemical shifts in *B*-trichloroborazine and *N*-trimethylborazine are essentially the same as

TABLE VI

PROTON CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS

Type of proton	Compound	Chemical shift, (ppm)[a]	Spin coupling constant (cps)	Reference
B—CH_3	$Me_3B_3N_3Ph_3$	0.00		*(78)*
	$Me_3B_3N_3Me_3$	−0.60		*(78)*
		−0.62		*(42)*
	$Me_3B_3N_3Et_3$	−0.67		*(78)*
B—CH_2CH_3	$Et_3B_3N_3Ph_3$	−0.55[b]		*(78)*
	$Et_3B_3N_3Et_3$	−1.08[b]		*(78)*
	$Et_3B_3N_3Me_3$	−1.15[b]		*(78)*
N—CH_2—CH_3 (methyl)	$Me_3B_3N_3Et_3$	−1.20	$J_{\mathrm{H-H}} = 7.2$	*(78)*
	$Et_3B_3N_3Et_3$	−1.20	$J_{\mathrm{H-H}} = 8.1$	*(78)*
	$Cl_3B_3N_3Et_3$	−1.22	$J_{\mathrm{H-H}} = 8.0$	*(78)*
N—CH_3	$Ph_3B_3N_3Me_3$	−2.71		*(42)*
	$Me_3B_3N_3Me_3$	−2.98		*(42)*
		−3.18		*(78)*
	$Et_3B_3N_3Me_3$	−3.10	$J_{\mathrm{N-H}} = 3.0$[c]	*(78)*
	$H_3B_3N_3Me_3$	−3.20		*(78)*
	$Cl_3B_3N_3Me_3$	−3.28		*(42)*
		−3.35		*(78)*
N—CH_2—CH_3 (methylene)	$Me_3B_3N_3Et_3$	−3.58	$J_{\mathrm{H-H}} = 7.2$	*(78)*
	$Et_3B_3N_3Et_3$	−3.77	$J_{\mathrm{H-H}} = 8.1$	*(78)*
	$Cl_3B_3N_3Et_3$	−3.80	$J_{\mathrm{H-H}} = 8.0$	*(78)*
B—H	$H_3B_3N_3Me_3$	−4.65	$J_{^{11}\mathrm{B-H}} = 125$	*(78)*
	$H_3B_3N_3H_3$	−4.67	$J_{^{11}\mathrm{B-H}} = 138$	*(77)*
			$J_{^{10}\mathrm{B-H}} = 48$[c]	*(77)*
N—H	$Cl_3B_3N_3H_3$	−5.53[b]		*(78)*
	$H_3B_3N_3H_3$	−5.65	$J_{\mathrm{N-H}} = 56$	*(77)*
phenyl	$Me_3B_3N_3Ph_3$	−7.35[b]		*(78)*
	$Et_3B_3N_3Ph_3$	−7.35[b]		*(78)*
	$Ph_3B_3N_3Me_3$	−7.42[b]		*(42)*

[a] All shifts reported relative to $Si(CH_3)_4$.

[b] Unresolved.

[c] Estimated.

for borazine. These shifts are apparently insensitive to the substituent effects, reflected in the electronic spectra (Section V,D), and, after correction for the effect of the ring current, correspond to the proton in —C═CH—C—. The latter correlation has been used to support the partial double-bond character of the B—N bonds in borazines *(78)*. Incidentally, the presence of a ring current is the basis for one definition of aromaticity *(35)*.

Alkyl proton shifts in nine *B*-trialkylborazines indicated that no alkyl isomerism had occurred during synthesis *(68)*.

The proton magnetic resonance spectrum of $B_3N_3H_{12}$ could not be recorded (*27*), but the spectrum of $B_3N_3H_6Me_6$ consists of a quartet (B—H) superimposed on a strong single resonance (N—CH_3) (*19*). It can be inferred from the reported spacing of the B—H quartet (2 ppm) that the spin coupling constant, $J_{^{11}B-H}$, for this compound is approximately 80 cps, indicating an sp^3 hybridized state for the boron atom (*132*), which is consistent with the suggestion that this compound is the boron-nitrogen analog of cyclohexane.

2. Nuclear Quadrupole Resonance

An estimate of 68% double-bond character in *N*-trimethylborazine was obtained from the ^{11}B quadrupole coupling constant for this compound (*88*), while approximately 80% double-bond character was obtained from line-width measurements on *B*-trichloroborazine (*88, 156*). In contrast, the double-bond contribution to the B—N bond in boron nitride is 45% (*156*).

The frequency of the ^{35}Cl resonance line for *B*-trichloroborazine is lower that that observed for boron trichloride, and this is taken as evidence for some degree of aromaticity for the borazine ring (*156*). The ^{35}Cl resonance line in *B*-trichloro-*N*-trimethylborazine or *B*-trichloro-*N*-triphenylborazine (*116*) was not observed.

D. ELECTRONIC SPECTRA

The ultraviolet absorption bands for borazine and for substituted borazines are summarized in Tables VII and VIII, respectively. Several *B*-trialkylborazines show only a weak end absorption (*68*), and this observa-

TABLE VII

ULTRAVIOLET ABSORPTION BANDS AND THEIR ASSIGNMENTS FOR BORAZINE

Bands observed				Corresponding benzene transition	Calculated band energy (ev)		
(Å)	(ev)	Reference	Assignment		(*140*)	(*126*)	(*30*)
			${}^1A'_1 \rightarrow {}^3A'_1$	${}^1A_{1g} \rightarrow {}^3B_{1u}$	5.9		
			${}^1A'_1 \rightarrow {}^3E'$	${}^1A_{1g} \rightarrow {}^3E_u^-$	6.4		
1995	6.2	(*79, 133*)	${}^1A'_1 \rightarrow {}^1A'_2$	${}^1A_{1g} \rightarrow {}^1B_{2u}$	6.5	6.50	5.7
1962	6.3						
1928	6.4						
1895	6.5						
			${}^1A'_1 \rightarrow {}^3A'_2$	${}^1A_{1g} \rightarrow {}^3B_{2u}$	6.9		
1852[a]	6.7	(*137*)	${}^1A'_1 \rightarrow {}^1A'_1$	${}^1A_{1g} \rightarrow {}^1B_{1u}$	7.2	6.80	6.1
1710[b]	7.2	(*137*)	${}^1A'_1 \rightarrow {}^1E'$	${}^1A_{1g} \rightarrow {}^1E_u^-$	7.7	7.98	8.8

[a] Estimated.

[b] Gas phase.

tion is in agreement with the data given in Table VIII. The borazine bands at 6.2–6.5 electron volts are assigned to the ${}^1A'_2$ transitions (*79*) instead of to the ${}^1A'_1$ transitions (*133*) on the basis of the assumption that the latter are hidden by the intense ${}^1E'$ band; no bands were found at wavelengths greater than 2000 Å.

TABLE VIII
THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BORAZINES (*137*)

Compound	Band (Å)	Band (ev)	Extinction coefficient	Assignment
$Cl_3B_3N_3H_3$	1901	6.5	~2000[b]	${}^1A'_1 \rightarrow {}^1A_2$
	1852[a]	6.7[a]	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1783	7.0	8000	${}^1A'_1 \rightarrow {}^1E'$
$Me_3B_3N_3H_3$	1908	6.5	~2000[b]	${}^1A'_1 \rightarrow {}^1A'_2$
	1852[a]	6.7[a]	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1761	7.1	6000	${}^1A'_1 \rightarrow {}^1E'$
$H_3B_3N_3Me_3$	2278	5.4	1200	${}^1A'_1 \rightarrow {}^1A'_2$
	2242	5.5		
	2198	5.6		
	2174[a]	5.7[a]	—	${}^1A'_1 \rightarrow {}^1A'_1$
	1942	6.4	28000	${}^1A'_1 \rightarrow {}^1E'$
	1901	6.5		
	1859	6.7		

[a] Estimated.
[b] Diffuse.

Of the three molecular orbital treatments concerned with the structure of borazine which have appeared, two are semi-empirical (*126*, *140*), and the other is a self-consistent calculation which includes the donation of *p* electrons from the nitrogen atom to the boron atom (*30*). Parameters included in the latter treatment are used to explain the bathochromic shift observed with *N*-trisubstituted borazines (*137*); a B—N bond order of 0.663 and a B—N bond distance of 1.42 Å have been calculated from this model (cf. Section V,A). The spectral energies calculated from all treatments are summarized in Table VII.

The salient feature of the spectra of the substituted borazines is the bathochromic shift observed for *N*-trimethylborazine. Oscillator strengths have been calculated for several of the transitions, and it has been suggested that the frequency spread between the ${}^1A'_2$ and ${}^1E'$ transitions reflects the amount of double-bond character in borazine derivatives. The relative chemical effects of substituents that exert an *ortho-para* directing influence in benzene have been related to the effects of these substituents on the electronic spectra of borazines (*137*).

A comparison of the absorption bands due to the benzene ring in the spectra of *N*-triphenylborazine and *B*-triphenylborazine with those in aniline, toluene, and several substituted biphenyls indicates that there is significant conjugative interaction between the borazine ring and the phenyl substituents together with some delocalization of the "nitrogen π" electrons (*10*). The absence of conjugation in $Me_3B_3N_3Ph_3$ and $Ph_3B_3N_3Me_3$ is attributed to the loss of planarity due to steric hindrance. The spectra of two phenyl-substituted borazines are similar to the spectrum of 1,3,5-triphenylbenzene (*125*).

A stable π complex was predicted between 1,3,5-trinitrobenzene and $Me_3B_3N_3Me_3$ (*154*), and, although no report concerning this particular complex has appeared, complexes between hexamethylborazine and tetracyanoethylene (TCNE) and between hexamethylborazine and chloranil have been characterized by charge transfer bands appearing in the ultraviolet region of the spectrum (*21*). As expected, the stability constant of the hexamethylborazine-TCNE complex (0.7 ± 0.3 liter·mole^{-1}) is lower than that of the corresponding hexamethylbenzene-TCNE complex measured under equivalent conditions; values of 263 (*104*) and 27.6 ± 0.5 have been reported for the stability constant of the latter complex. Ionization potentials for hexamethylborazine estimated from the wavelengths of the charge transfer bands are 8.5 ev from the $Me_3B_3N_3Me_3$-TCNE complex and 8.7 ev from the $Me_3B_3N_3Me_3$-chloranil complex; the calculated ionization potential for hexamethylbenzene is 8.15 ev (*42a, 43*).

A preliminary report has appeared concerning fluorescence studies on aryl-substituted borazines; gamma rays and neutrons were used as the exciting radiation (*114*).

E. INFRARED AND RAMAN SPECTRA

Electron diffraction studies (cf. Section V,A) have established that borazine belongs to symmetry point group D_{3h}. A nonlinear, 12-atom molecule has 30 normal modes of vibration, but, in this case, symmetry considerations show that 20 of these modes constitute 10 doubly degenerate pairs. The distribution of the 20 fundamental frequencies expected is shown in Table IX.

The infrared and Raman spectra of borazine have been recorded and the fundamental frequencies assigned (*26*), but the assignment was hampered by the absence of a number of the E' fundamentals in the Raman spectrum. In 1950 a more complete gas phase infrared spectrum of borazine in the 500–7000 cm^{-1} region was reported (*135*), and the fundamentals and overtones were assigned. A more recent study (*184*) of the gas phase infrared spectrum of *N*-trideuteroborazine indicates that the assignments of the out-of-plane B—H and N—H bending frequencies (A''_2) should be revised.

A normal coordinate treatment on borazine was carried out assuming a simple valence force potential (*26*); the application of a Urey-Bradley force field gave unsatisfactory results. This treatment is one of the first published examples of Wilson's method for the approximate separation of low and high frequency vibrations in factoring secular equations (*192*). Deviations of the calculated A''_2 frequencies from experimentally obtained frequencies were ascribed to interactions between bonds in the meta position, and, although recalculation of these frequencies on this basis (*162*, *183*) improved the agreement, the difficulty seems to have been an incorrect assignment (*184*). The distribution of potential energy among normal coordinates for borazine has also been calculated (*183*), but these calculations were made prior to the reassignment of the A''_2 frequencies. The stronger lines in the spectrum of *B*-trichloroborazine have been assigned on the basis of a calculation of the distribution of potential energy among normal coordinates (*183*) and by a comparison with the infrared spectrum of *B*-trichloro-*N*-trideuteroborazine (*184*). A normal coordinate treatment of *N*-trimethylborazine assuming D_{3h} symmetry and that methyl groups are point masses (*11*) was attempted using infrared spectra which appear in the literature (*135*). The Raman spectra in the literature for this compound are in agreement (*11*, *182*), but the infrared spectra are inconsistent (*135*, *182*). The force constants that have been estimated for various vibrations in borazine and in *N*-trimethylborazine are summarized in Table X. It should be noted that the force constant for the

TABLE IX
FUNDAMENTAL FREQUENCY DISTRIBUTION OF BORAZINE

Symmetry of species	Type[a]	Number of frequencies
A'_1[b]	IR inactive Raman active (P)	4
A''_1[b]		0
A'_2[b]	IR inactive Raman inactive	3
A''_2[b]	IR active Raman inactive	3
E'[c]	IR active Raman active (D)	7
E''[c]	IR inactive Raman active (D)	3

[a] Planar vibrations are denoted by a single prime, nonplanar vibrations by a double prime. (P) and (D) represent Raman polarized and Raman depolarized, respectively.

[b] Nondegenerate.

[c] Degenerate.

TABLE X

FORCE CONSTANTS FOR BORAZINE AND *N*-TRIMETHYLBORAZINE

Vibration	Borazine, 10^5 dyne/cm	Reference	*N*-Trimethylborazine, 10^5 dyne/cm	Reference
B—N stretch	6.300	*(26)*	6.4005	*(11)*
B—H stretch	3.423	*(26)*	3.3756	*(11)*
N—X stretch	6.524	*(26)*	3.1072	*(11)*
Planar ring distortion	0.525	*(26)*	0.640	*(11)*
Planar B—H bend	0.35	*(26)*		
Planar N—H bend	0.65	*(26)*		
Nonplanar B—H bend	0.28	*(184)*	0.383	*(11)*
Nonplanar N—H bend	0.245	*(184)*	0.472	*(11)*
B—N torsion	0.098	*(184)*	0.006	*(11)*

TABLE XI

B—N STRETCHING FREQUENCIES OF BORAZINE DERIVATIVES[a]

Derivative[b]	Frequency range, (cm^{-1})	Number of compounds studied	References
$(NR_2)_3B_3N_3X_3$ (R = H, alkyl, aryl)	1285–1517	22	*(3, 46, 47, 48, 50)*
$R_3B_3N_3X_3$ (R = aryl)	1368–1479	5	*(9, 20, 46, 117, 183)*
$Me_3B_3N_3X_3$	1376–1477	7	*(9, 46, 53, 178, 183)*
$R_3B_3N_3X_3$ (R = alkyl)	1382–1475	18	*(20, 46, 68, 144, 153, 183)*
$H_3B_3N_3X_3$	1401–1465	4	*(9, 26, 135, 178, 182, 183, 184)*
$(RO)_3B_3N_3X_3$ (R = alkyl, aryl, $SiMe_3$)	1407–1450	11	*(3, 14, 153, 183)*
$Cl_3B_3N_3X_3$	1378–1445	9	*(9, 14, 46, 178, 183, 184)*
$X_3B_3N_3H_3$	1441–1517	25	*(9, 26, 46, 48, 50, 53, 93, 124, 135, 173, 178, 184)*
$X_3B_3N_3Me_3$	1370–1513	21	*(3, 9, 14, 20, 46, 117, 124, 144, 153, 178)*
$X_3B_3N_3R_3$ (R = alkyl)	1414–1497	12	*(3, 46, 124, 183)*
$X_3B_3N_3D_3$	1410–1436	2	*(184)*
$X_3B_3N_3R_3$ (R = aryl)	1285–1404	12	*(9, 46, 183)*
Polyborazines	1410–1470	15	*(46, 59, 93, 96, 101, 179)*

[a] The strong band in the spectrum of $Cl_3B_3N_3Me_3$ at 1458 cm^{-1} has been assigned to the B—N stretching mode *(14)*, but it is more likely that this mode should be assigned to the band at 1395 cm^{-1}.

[b] X represents any substituent.

B—N stretching frequency in the borazine ring is less than that of a B—N single bond (*52*), and, using this type of data, the B—N bond in borazine has been estimated to have 25–28% double-bond character (*53*, *162*).

Partial and complete infrared spectra have been reported for approximately 85 borazine derivatives, and the characteristic frequencies are summarized in Tables XI and XII. The bands reported for *B*-tri-*n*-butoxyborazine (*179*) are not included in these tables since this compound was not isolated and characterized, but was identified by its spectrum.

TABLE XII

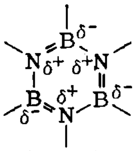
Ring Substituent Stretching Frequencies in Borazines

Vibration	Frequency range, (cm^{-1})	Number of compounds studied	References
N—H stretch $X_3B_3N_3H_3$	3390–3509	23	(*26, 47, 48, 59, 68, 93, 135, 173, 178, 183, 184*)
N—H stretch $(NHR)_3B_3N_3X_3$	3425–3448	8	(*3*)
N—D stretch	2570–2632	3	(*28, 184*)
B—H stretch	2475–2556	8	(*5, 9, 26, 93, 135, 178, 182, 184*)
B—D stretch	1887	2	(*28*)
B—O stretch	1280–1330	10	(*3, 14, 46, 124*)
B—Cl stretch[b]	833–987[a]	6	(*14, 46, 178, 183, 184*)
B—Me stretch	858–891	10	(*178, 183*)

[a] An associated band appears at 1032–1155 cm^{-1} (*14*).

[b] The assignment for this vibration has been recently disputed.

A strong band, usually with a shoulder on the high-frequency side, occurs near 1400 cm^{-1} in the infrared spectra of most borazines and is assigned to the B—N stretching mode (*183*); Gordy's rule (*122*) indicates that this frequency should occur at 1471 cm^{-1}. The fact that this band is generally the strongest in the spectrum indicates considerable polarity in the B—N bond (*135*), suggesting that (XLIII) is an important canonical structure. Assignment of the 1400 cm^{-1} band is complicated in the *N*-trimethylborazines because the *N*-methyl deformation frequencies occur in the same region (*3*). The absence of this band has been used to establish


(XLIII)

that *B*-tri(terphenyl)-*N*-trimethylborazine is not planar (*20*). However, other spectra reported in this reference (*20*) are not in agreement with those recorded by other workers (*117*, *144*); physical properties are not given for the polyphenyl borazines studied. The B—N stretching frequency is also absent from one of the —B—O—B—linked polymers reported (*179*), although it is present in similar compounds.

Attempts have been made to relate the B—N frequency to the identity of ring substituents (see, e.g., references *9*, *46*, *48*, *153*) but an examination of Table XI shows only that the B—N stretching frequency is more sensitive to nitrogen substitution than to boron substitution. This conclusion is in agreement with the data from electronic spectra (cf. Section V,D).

The intensity of the N—H band in borazine (*135*) and in *B*-trichloroborazine (*48*) indicates a polar bond in these compounds; however, the intensity of this band is much lower for *B*-tris(dialkylamino)borazines (*48*). Several reports of the preparation of *B*-triaminoborazine have appeared (*47*, *54*, *101*, *120*, *123*), but there is some disagreement concerning its properties. The positions of the N—H bands reported for this compound are not in agreement (*47*, *124*). The appearance of a band at 3045 cm^{-1} in *B*-trihydrazinoborazines has been used to support the structural assignment of these compounds (*124*). On the basis of the electron-donating ability of the amino group, the N—H frequencies of *B*-triaminoborazines decrease in the order *B*-tris(dialkylamino)- > *B*-tri(alkylarylamino)- > *B*-tris(diarylamino)-borazine (*48*).

The intensity of the B—H stretching band is much greater in borazine than in *N*-trimethylborazine, the intensity of this band for the former compound being about equal to that for $AlBH_4$ (*135*).

The band assigned to the B—O stretching mode occurs at a lower frequency than the corresponding band for compounds of the type $B(OR)_3$, and this has been attributed to a decrease in B—O double-bond character due to double bonding in the ring (*3*, *46*). A band in the 1100 cm^{-1} region has been assigned to the B—Cl stretching mode since it disappears on substitution of another group for the chlorine atom (*46*). This assignment is complicated in *B*-trichloro-*N*-trimethylborazine since a strong band due to an *N*-methyl rocking vibration is expected in the same region (*183*).

Arguments leading to a tentative assignment of strong bands at 920–1238 cm^{-1} in the spectra of *B*-triaminoborazines to the N—H in-plane deformation mode are based on the incorrect assignment of D_{6h} symmetry to borazine (*48*). Several investigators have observed bands (usually doublets) in the 700 cm^{-1} region (*3*, *48*), and these are considered to be characteristic of substituted borazines in which substituents on the ring can conjugate with the borazine ring.

Extensive assignments of frequencies due to the C—H stretching and deformation modes in *B*-triaminoborazines have been made (*50*) but are not included in this review.

F. DIAMAGNETIC ANISOTROPY

An attempt was made, using a self-consistent molecular-orbital approach, to calculate the diamagnetic anisotropy of borazine, but the validity of this approach could not be ascertained because of a lack of precise experimental data (*31*). The same method gave satisfactory results for benzene. An estimate of molecular parameters for borazine has been made from its diamagnetic anisotropy, with the conclusion that the B—N bonds in borazine have 24% double-bond character (*180*). Measured diamagnetic anisotropies for borazines and several benzenoid systems (for comparison) are listed in Table XIII.

TABLE XIII
DIAMAGNETIC ANISOTROPIES

Compound	Value × 10^6 emu/mole	Reference
$Cl_3B_3N_3H_3$	−18	(*96*)
$H_3B_3N_3H_3$	−36	(*180*)
$Me_3B_3N_3Me_3$	−37	(*180*)
$Et_3B_3N_3Et_3$	−40	(*180*)
sym-$C_6H_3Br_3$	−47	(*96*)
C_6H_6	−59.7	(*73*)

The mean diamagnetic susceptibilities of seven borazine derivatives were measured and diamagnetic anisotropies for three of them calculated using a value for χ_{11} estimated from that of benzene. The validity of this procedure is supported by a calculation of the value of χ_{11} for borazine using Pascal's rule (*180*), although the use of Pascal constants for this purpose has been criticized (*31*). The diamagnetic anisotropy for *B*-trichloroborazine was calculated using crystal susceptibilities and Pascal constants, and it is suggested that the diamagnetic anisotropy is a measure of aromatic character (*96*).

G. THERMOCHEMICAL DATA

References to values reported for the heats of vaporization and sublimation for various borazines obtained from vapor pressure measurements are given in Table II.

The entropy, free energy function, and heat capacity for borazine have been calculated from infrared spectroscopic data (*26*) which were later revised (Section V,E), and equations for the entropy (*26*) and heat capacity (*161*) have been derived. The heats of formation of gaseous and liquid borazine have been calculated from the heat of combustion (*83*). Earlier values for the B—N bond strength in *B*-trichloroborazine (*45*, *157*, *176*) have been revised (*23*), and a value of 106.5 kcal is now accepted.

H. MASS SPECTROSCOPY

The mass spectra of borazine, *B*-trichloroborazine, *B*-trimethylborazine (*97*), and of three deuterated borazines (*28*) have been reported. Data for borazine itself suggests that the B—H bond in this compound is more easily cleaved than the C—H bond in benzene.

Products from the pyrolysis of borazine have been investigated using mass spectrometric techniques (*93*, *101*), and these data indicate that ring cleavage occurs with borazine to a greater extent than with benzene (*4*).

VI. Conclusion

The results of various types of physical-chemical investigations indicate that there is partial delocalization of the three pairs of electrons originally associated with the nitrogen atoms in the borazine ring, although the delocalization is not as extensive as in benzene and its derivatives. This conclusion is in general agreement with the chemical properties of the borazine ring.

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