THE BORAZOLES

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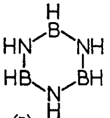
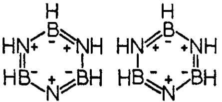
THE compound $B_3H_3N_3H_3$ (I) is a colourless mobile liquid which was first prepared by Stock and Pohland[1] from the addition compound of ammonia and diborane. Electron-diffraction measurements[2] showed the molecule to be planar and symmetrical, and Kekulé structures (II)[3] have become accepted. An interesting comparison with benzene was given by Wiberg and Bolz[4] who called the compound inorganic benzene or borazol, from which the familiar name borazole* is derived. Alfred Stock described the early investigations in his 1932 Baker Lectures,[6] a review by Wiberg[7] appeared in 1948, and a number of works contain sections on borazole.[8] The hydrogen atoms of borazole may be replaced by other groups and the properties of the ring are modified by *B*- and *N*-substituents.


(I)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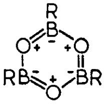
(III; R=Alk, Ar)

Borazole and its derivatives have attracted much interest because of the resemblance to aromatic organic compounds, but six-membered ring systems are quite common in inorganic chemistry. The properties of planar molecules such as the borazoles and boroxoles (III) can be related to dative π bonding between the atoms in the ring and the properties of "saturated" compounds such as $B_3H_6N_3H_3Me_3$[9] and $B_3H_6N_3Me_6$[10,11]

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* The name Borazine, recommended by an A.C.S. sub-committee,[5] is not yet accepted and the name borazole will be used throughout this Review.

[1] Stock and Pohland, *Ber.*, 1926, **59**, 2215.

[2] Stock and Wierl, *Z. anorg. Chem.*, 1931, **203**, 228.

[3] Stock, Wiberg, and Martini, *Ber.*, 1930, **63**, 2927.

[4] Wiberg and Bolz, *Ber.*, 1940, **73**, 209.

[5] Patterson, *Chem. Eng. News*, 1956, **34**, 560.

[6] Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N.Y., 1933, Chapter XIV.

[7] Wiberg, *Naturwiss.*, 1948, **35**, 182, 212.

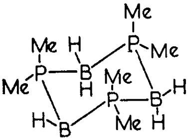
[8] Schlesinger and Burg, *Chem. Rev.*, 1942, **31**, 1; Bauer, *ibid.*, p. 43; Lappert, *ibid.*, 1956, **56**, 959; Bell and Emeléus, *Quart. Rev.*, 1948, **2**, 132; Stone, *ibid.*, 1955, **9**, 174; Gerrard, *J. Oil Colour Chemists' Assoc.*, 1959, **42**, 625; Smolin and Rapoport, "*s*-Triazine and Derivatives," Interscience Publishers, New York and London, 1959, Chapter XI.

[9] Bissot and Parry, *J. Amer. Chem. Soc.*, 1955, **77**, 3481.

[10] Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 2129; Campbell and Johnson, *ibid.*, 1959, **81**, 3800.

[11] Trefonas and Lipscomb, *J. Amer. Chem. Soc.*, 1959, **81**, 4435.

also depend on dative bonding from nitrogen to boron. Nitrogen is a strong electron-donor but is unable to accept electrons whereas tervalent phosphorus forms co-ordinate bonds with borine* and trimethylborine which are strengthened by the back release of electrons from B–H and B–Me bonds to vacant phosphorus *d* orbitals.[12] The remarkable stability of $B_3H_6P_3Me_6$[13] no doubt depends on such back-donation. Since the molecule has a chair configuration (IV) the angle PBH is approximately 109° and each phosphorus atom can receive electrons from four B–H bonds. Similar compounds, $B_3Me_6P_3Me_6$, $B_3H_6P_3(CF_3)_6$, and $B_3H_6As_3Me_6$ have also been prepared by Burg and his co-workers[13,14] but it is of interest that analogues of borazole, where each phosphorus atom could receive electrons from only two B–H bonds and the angle PBH would be 120°, have not yet been prepared.



(IV)

Synthesis of the Borazoles

Synthesis of the Borazole Ring.—Methods developed for the synthesis of the borazole ring may be viewed as condensations between amines and boron hydrides or halides at about 200°, with the elimination of hydrogen or hydrogen halide:

$$3BX_3 + 3NR_3 \rightarrow B_3X_3N_3R_3 + 6RX$$
$$(e.g., X = H, Cl, Br, Alk; R = H, Alk)$$

Trialkylborines also condense with amines, yielding *B*-trialkylborazoles and alkanes at temperatures higher than 300°. Frequently, derivatives of the amines, boron hydrides, or boron halides are used, either because they are more readily available and handled than the simple reagents, or because they yield directly borazoles with desired substituent groups.

Condensation between boron hydrides and amines. This was the first reaction developed to give products recognised as borazoles. Excess of ammonia reacts with diborane at 190° to give diboron tri-imide, $B_2H_6 + 3NH_3 \rightarrow B_2(NH)_3 + 6H_2$, but equivalent quantities of diborane and ammonia (*i.e.*, B:N ratio 1:1) react at a similar temperature and at atmospheric pressure, yielding hydrogen, a polymer of composition intermediate between $(BNH_2)_x$ and $(BNH)_x$, and borazole. Diborane and

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* I.U.P.A.C. makes no recommendation as to a name for BH_3. Pending a decision The Chemical Society uses "borine". The series B_nH_m are the polyboranes.

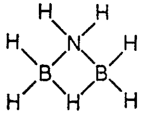
[12] Stone, *Chem. Rev.*, 1958, **58**, 101; Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[13] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872; Hamilton, *Acta Cryst.*, 1955, **8**, 199.

[14] Stone and Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 386; Burg and Brendel, *ibid.*, 1958, **80**, 3198.

tetraborane readily form addition compounds with ammonia at room temperature. $B_2H_6,2NH_3$ and $B_4H_{10},2NH_3$[15] contain the $(NH_3{\cdot}BH_2{\cdot}NH_3)^+$ cation,[16] which may well be related to the primary condensation products leading to the formation of borazoles. These ammonia addition compounds undergo the same condensation reaction as equivalent quantities of diborane and ammonia and after a short heating at 200°, the reaction tube is cooled in liquid air and opened *in vacuo*. Hydrogen is pumped away and borazole (b.p. 53°) remains the only volatile product and is distilled out in high purity. The yield of borazole is 33% from $B_2H_6,2NH_3$[1] and 40% from $B_4H_{10},2NH_3$.[3]

Excess of diborane and ammonia (or more specifically, diborane and the diborane–ammonia addition compound) yield B_2H_7N (V)[17] which is rather unstable and decomposes slowly even at room temperature, giving several products among which are diborane and borazole. B_2H_7N forms a 1:1 ammonia addition compound which decomposes at 200° producing a 45% yield of borazole.



(V)

Use of the boron hydride–amine condensation for the preparation of borazoles is severely limited by the difficult and involved preparation of the hydrides themselves. The early investigations relied on the preparation of the hydrides by the action of acids on suitably prepared metal borides: a yield of 11% of boron hydrides is the best recorded for the action of 8N-phosphoric acid on magnesium boride.[18] More convenient sources of boron hydrides have since proved to be the hydrogenation of boron trihalides in an electric discharge, and the decomposition of metal borohydrides. Even so, the use of boron hydrides is unsatisfactory since they require handling in the absence of oxygen, moisture, and grease in a carefully designed vacuum line, and the small amounts of borazoles prepared undoubtedly restricted the early investigations.

Nevertheless, Schlesinger and his co-workers succeeded in preparing *B*-methyl-, *B*-dimethyl-, and *B*-trimethyl-borazoles by the condensation of methyldiboranes and ammonia[19] and similarly, *N*-methyl-, *N*-dimethyl-, and *N*-trimethyl-borazoles* by the condensation of diborane with mixtures of ammonia and methylamine.[20] The usual

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[15] Kadoma and Parry, *J. Amer. Chem. Soc.*, 1957, **79**, 1007.

[16] Schultz and Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 4; Shore and Parry, *ibid.*, pp. 8, 12; Parry and Shore, *ibid.*, p. 15; Shore, Girardot, and Parry, *ibid.*, p. 20; Parry, Kadoma, and Schultz, *ibid.*, p. 24; Taylor, Schultz, and Emery, *ibid.*, p. 27; Nordman and Peters, *ibid.*, 1959, **81**, 3551.

[17] Schlesinger, Ritter, and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 2297; Hedberg and Stosick, *ibid.*, 1952, **74**, 954.

[18] Wiberg and Schuster, *Ber.*, 1934, **67**, 1805.

[19] Schlesinger, Horvitz, and Burg, *J. Amer. Chem. Soc.*, 1936, **58**, 409.

[20] Schlesinger, Ritter, and Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 1296.

* In this and subsequent names, use of *N* implies *NN′N″*, and similarly for *B*.

yield of a particular borazole was a few millilitres of vapour requiring careful fractionation from other products.

Condensation of a borohydride with an ammonium salt. A major advance in borazole synthesis was the replacement of boron hydrides by lithium borohydride which is readily handled and is now commercially available. The borohydride readily undergoes a partial condensation with ammonium or alkylammonium chlorides, usually in some ethereal solvent, yielding hydrogen and lithium chloride at room temperature. After removal of the ether the reaction can be completed by pyrolysis of the residual product at 200 to 250°:

$$3LiBH_4 + 3R{\cdot}NH_3Cl \xrightarrow{25^\circ} 3BH_2{\cdot}NHR + 6H_2 + 3LiCl \xrightarrow{250^\circ} B_3H_3N_3R_3 + 9H_2 + 3LiCl$$

Despite the limited supply of borohydride in the initial work, Schaeffer and Anderson[21] were able to obtain *N*-trimethylborazole in gram quantities and in better than 70% yield from methylammonium chloride. The formation of the borazole may be accomplished in one step if a high-boiling ether, *e.g.*, dihexyl ether, is used as solvent. *N*-Triethyl-, *N*-tri-n-propyl-, and *N*-tri-isopropyl-borazoles have all been prepared by these methods.[22] Borazole itself has been obtained by the pyrolysis at 300° of lithium borohydride and ammonium chloride diluted with powdered "Pyrex" glass.[23] The borohydride method has not been widely adopted and is not suitable for the synthesis of *B*-substituted borazoles.

Condensation between boron halides and amines.—This reaction is now accepted as the most convenient preparation of borazoles. The action of boron trichloride and ammonia received early investigation though the only products reported were a boron trichloride–ammonia addition compound, triaminoborine, and diboron tri-imide.[24] As early as 1889 Rideal[25] found that aniline and boron trichloride reacted to give hydrogen chloride and a white solid considered to be BClNPh. This work was repeated by Jones and Kinney[26] who showed that Rideal's product was a trimer and they suggested its relation to borazole. Jones and Kinney's method, which was the first borazole synthesis well adapted to an ordinary laboratory, gave an 87·5% yield of *B*-trichloro-*N*-triphenylborazole. Aniline was added to boron trichloride in cold benzene, and after 24 hours at room temperature the mixture was filtered hot and the borazole crystallised on cooling:

$$3BCl_3 + 9NH_2Ph \rightarrow B_3Cl_3N_3Ph_3 + 6NH_3PhCl$$

[21] G. W. Schaeffer and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.
[22] Hough, G. W. Schaeffer, Dzurus, and Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 864.
[23] G. W. Schaeffer, R. Schaeffer, and Schlesinger, *J. Amer. Chem. Soc.*, 1951, **73**, 1612.
[24] Martius, *Annalen*, 1859, **109**, 79; Joannis, *Compt. rend.*, 1902, **135**, 1106.
[25] Rideal, *Ber.*, 1889, **22**, 992.
[26] Jones and Kinney, *J. Amer. Chem. Soc.*, 1939, **61**, 1378.

Although *B*-trichloro-*N*-tri-*p*-tolyl- and *B*-trichloro-*N*-trianisylborazoles have been prepared in a similar fashion,[27] difficulty has been reported in making analogous *N*-trialkylborazoles. This general synthetic route has received more attention following the report by Brown and Laubengayer[28] that ammonia gave only traces of borazole with boron trichloride yet ammonium chloride gave a 50% yield of *B*-trichloroborazole. Two variations of the method are described: a dry method involving the passage of boron trichloride vapour over ammonium chloride at 170°, and a liquid-phase method employing boiling chlorobenzene:

$$3BCl_3 + 3NH_4Cl \rightarrow B_3Cl_3N_3H_3 + 9HCl$$

It is likely that the use of the hydrochloride, rather than the free amine, moderates the vigour of the reaction and allows the formation of simple products. The use of methylammonium chloride in the above synthesis yields *B*-trichloro-*N*-trimethylborazole,[29,30] but higher monoalkylammonium chlorides require the presence of a calculated quantity of tertiary amine to facilitate the elimination of hydrogen chloride:[31]

$$R{\cdot}NH_3Cl + BCl_3 \rightarrow R{\cdot}NH_2,BCl_3 + HCl$$

$$3R{\cdot}NH_2,BCl_3 + 6Me_3N \rightarrow B_3Cl_3N_3R_3 + 6Me_3N,HCl$$

If a substituted boron chloride is employed (*e.g.*, phenyl- and dialkylamino-boron dichlorides give *B*-triphenylborazole[32,33] and *B*-trisdialkylaminoborazoles[34] respectively), it appears preferable to use the free amine rather than the hydrochloride owing to the decreased activity of the boron chloride species:

$$3BCl_2{\cdot}NR_2 + 9NH_3 \rightarrow B_3(NR_2)_3N_3H_3 + 6NH_4Cl$$

The condensation of an alkylamine with a substituted boron chloride requires the presence of a tertiary amine for completion:

$$3R{\cdot}NH_2,BCl_2{\cdot}NR'_2 + 6Et_3N \rightarrow B_3(NR'_2)_3N_3R_3 + 6Et_3N,HCl$$

The condensation of methylamine with fluorodimethylborine also requires vigorous conditions, *i.e.*, heating to 400°, but gives a *B*-trifluoroborazole

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[27] Kinney and Kolbezen, *J. Amer. Chem. Soc.*, 1942, **64**, 1584; Kinney and Mahoney, *J. Org. Chem.*, 1943, **8**, 526.

[28] Brown and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 3699.

[29] Hohnstedt and Haworth, Abstracts of Papers, 132nd Meeting, Amer. Chem. Soc., New York, N.Y., September 1957, p. 8 s.

[30] Ryschkewitsch, Harris, and Sisler, *J. Amer. Chem. Soc.*, 1958, **80**, 4515.

[31] Turner and Warne, *Chem. and Ind.*, 1958, 526.

[32] Ruigh, 16th International Congress of Pure and Applied Chemistry, Paris, 1957. "Papers Presented to the Section on Mineral Chemistry," Butterworths Scientific Publications, London, 1958, p. 545.

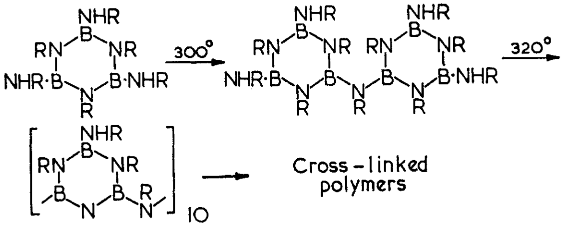
[33] Mikhailov and Kostroma, *Zhur. obshchei Khim.*, 1959, **29**, 1477; Mikhailov, Blokhina, and Kostroma, *ibid.*, p. 1483.

[34] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561.

and methane rather than a *B*-trimethylborazole and hydrogen fluoride.[35] Aubrey and Lappert[36] have reported an interesting variation of borazole synthesis involving the cyclisation of trisalkylaminoborines and the elimination of alkylamines at 200°:

$$3B(NHR)_3 \rightarrow B_3(NHR)_3N_3R_3 + 3NH_2R$$

The *B*-triaminoborazole evolves alkylamine at temperatures of 300° and higher by linking several borazole molecules with *B*-alkylimine groups. Condensation proceeds until a highly cross-linked polymer is obtained. This is stable up to 600° and is a possible forerunner of some technologically useful materials. It appears that the blocking of the nitrogen atoms in these polymers by alkyl groups is sufficient to avoid total condensation to boron nitride at high temperatures:



An extension of this method is the cyclisation of amino(butoxy)-borines, *e.g.*, $(BuO)_2BNHEt$ and $BuOB(NHEt)_2$, to give *B*-tributoxy-*N*-triethylborazole with elimination of ethylamine or butanol. Hydrazine hydrobromide does not give an *N*-triaminoborazole with boron tribromide at 200° but gives *B*-tribromoborazole with evolution of nitrogen.[37]

Substitution of the Borazole Ring.—It is possible to prepare a variety of new borazoles by the substitution of existing borazoles at *B*-H and *B*-Cl ring sites. The moderate tendency of amines to undergo substitution $NR_3 + AB \rightarrow NR_2A + RB$ is in contrast with the reactivity of boron trihalides, borines, and alkylborines, and borazoles usually experience substitution at the boron atom only. The availability of *B*-trichloroborazole and the non-existence of *N*-trichloroborazole have given a further emphasis to reactions at borazole *B*-positions.

Substitution of the B–H **group.** (i) B-*Alkylation and* B-*arylation.* Trimethylborine was among the first reagents found capable of this reaction and gave with borazole or *N*-methylborazole a mixture of the corresponding *B*-methyl, *B*-dimethyl, and *B*-trimethyl derivatives:[20]

$$2B_3H_3N_3H_3 + 2BMe_3 \rightarrow 2B_3H_2MeN_3H_3 + B_2H_2Me_4$$

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[35] Wiberg and Horeld, *Z. Naturforsch.*, 1951, **6 B,** 338.
[36] Lappert, *Proc. Chem. Soc.*, 1959, 59; Aubrey and Lappert, *J.*, 1959, 2927.
[37] Emeléus and Videla, *Proc. Chem. Soc.*, 1957, 288; *J.*, 1959, 1306.

Alkylation and arylation of borazoles now appears to be a practical procedure since the demonstration that Grignard and organo-lithium reagents react with *N*-trimethyl- and *N*-triphenyl-borazole, giving satisfactory yields of substituted products:[38]

$$B_3H_3N_3Ph_3 + PhMgBr \rightarrow B_3H_2PhN_3Ph_3 + HMgBr$$

B-Mono- and *B*-di-substituted borazoles can be obtained from appropriate quantities of *N*-triphenylborazole and alkylating reagent. *N*-Trimethylborazole, however, gives mixtures of *B*-mono-, *B*-di-, and *B*-tri-substituted products.

(ii) B-*Halogenation.* Only one substitution product, *B*-dibromoborazole, appears to have been characterised from the products of direct halogenation of borazole.[4] The action of chlorine on borazole gives a white crystalline sublimable product (of unknown composition) and hydrogen chloride at high temperature. Bromine forms an adduct $B_3H_3N_3H_3,2Br_2$ with borazole at 0°, and this complex decomposes at 60—100° into colourless sublimable crystals of *B*-dibromoborazole, and hydrogen bromide. Borazole reacts at room temperature with boron trichloride and boron tribromide, giving mixtures of *B*-mono- and *B*-di-halogenoborazoles.[23] *B*-Trihalogenoborazoles can be prepared by the action of hydrogen halides on borazoles at elevated temperatures. At room temperature hydrogen halides form the complexes $B_3R_3N_3R_3$, 3HX which eliminate hydrogen[4] ($R = H$, $X = Br$) at 100° or methane[39] ($R = Me$, $X = Cl$) at 450°, yielding *B*-trihalogenoborazoles.

(iii) B-*Hydroxylation and* B-*alkoxylation.* Water[40] and methanol[41] give 3:1 adducts with certain borazoles, which decompose on gentle heating into *B*-trihydroxy- and *B*-trimethoxy-borazoles. Ethanol[41] appears to behave similarly.

These substitution reactions have not generally proved convenient preparations of *B*-substituted borazoles. *B*-Trichloroborazole, however, has found favour as a preparative intermediate and the reactions described below find promising applications.

Substitution of the B–Cl Group. (i) *Replacement by hydrogen.* Ethereal lithium aluminium hydride readily reduces *B*-trichloroborazole to borazole, but difficulty was found in isolating the products, and the use of lithium borohydride proved more satisfactory.[42] The reduction of *B*-trichloro-*N*-triphenylborazole by lithium aluminium hydride proceeded without complications to give an 85% yield of *N*-triphenylborazole.[38]

(ii) B-*Alkylation and* B-*arylation.* Several laboratories concurrently reported the reaction of Grignard and organolithium reagents with

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[38] Smalley and Stafiej, *J. Amer. Chem. Soc.*, 1959, **81**, 582.

[39] Wiberg and Hertwig, *Z. anorg. Chem.*, 1947, **255**, 141.

[40] Wiberg, Hertwig, and Bolz, *Z. anorg. Chem.*, 1948, **256**, 177.

[41] Haworth and Hohnstedt, *J. Amer. Chem. Soc.*, 1959, **81**, 842.

[42] R. Schaeffer, Steindler, Hohnstedt, Smith, Eddy, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 3303.

B-trichloroborazoles to give *B*-trialkyl(aryl)borazoles.[29,30,43] Sisler and his co-workers were able to prepare the intermediate *BB*′-dibutyl-*B*″-chloro- and *B*-butyl-*B*′*B*″-dichloro-*N*-trimethyl-borazoles by adjusting the reagent proportions, but found the exchange of ethyl groups between *B*-chloro-*B*′*B*″-diethyl- and *BB*′-dichloro-*B*″-ethyl-*N*-trimethylborazoles too rapid to allow their separation, and fractionation of the mixture gave only *B*-trichloro-*N*-trimethylborazole in the low-boiling fraction.

No compounds containing *B*-perfluoroalkyl groups have been characterised[44] and attempts to prepare a *B*-perfluoroalkyl-borazole by the action of heptafluoro-n-propyl-lithium on *B*-trichloro-*N*-triphenylborazole were unsuccessful. There is a brief report that *B*-trichloroborazole undergoes a Friedel–Crafts reaction with benzene and aluminium chloride in boiling chlorobenzene to give a 24% yield of *B*-triphenylborazole.[45]

(iii) *Metathesis with metal salts.* Very pure sodium alkoxides react with *B*-trichloroborazoles giving *B*-trialkoxyborazoles·[46]

$$B_3Cl_3N_3R_3 + 3NaOR' \rightarrow B_3(OR')_3N_3R_3 + 3NaCl$$

Similarly, it now appears that CN, CNS, Br, NO_2, and NO_3 groups may be introduced into the borazole ring by the reaction of sodium or silver salts of the appropriate anion with *B*-trichloroborazoles.[47]

(iv) *Amination.* Primary and secondary amines give *B*-trisalkylaminoborazoles with *B*-trichloroborazole, but it is doubtful whether ammonia gives an isolatable *B*-triaminoborazole:[34,48]

$$B_3Cl_3N_3R_3 + 3NHR'_2 \rightarrow B_3(NR'_2)_3N_3R_3 + 3HCl$$

Amination of the *B*-chloro-group proceeds so readily that stoicheiometric quantities of the reagents may be employed, and even amine hydrochlorides may be used, though yields are lower.

Chemistry of the Borazoles

The chemistry of borazoles described in the above sections is now considered in detail and with particular regard to postulated mechanisms.

Ring Formation.—It is known that hydrogen linked to boron is easily replaced by electronegative groups. Water, halogens, and hydrogen halides, for example, react with diborane giving B–O, B–Cl, and B–Br bonds. Similarly, ammonia and diborane at 400° give boron nitride, $(BN)_n$,[1]

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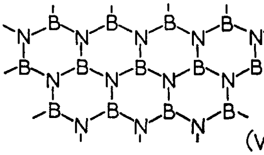
[43] Groszos and Stafiej, *J. Amer. Chem. Soc.*, 1958, **80**, 1357.
[44] Lagowski and Thompson, *Proc. Chem. Soc.*, 1959, 301.
[45] Niedenzu and Dawson, *Angew. Chem.*, 1959, 651.
[46] Bradley, Ryschkewitsch, and Sisler, *J. Amer. Chem. Soc.*, 1959, **81**, 2635.
[47] R. Schaeffer, Brennon, and Dahl, Abstracts of Papers, 133rd Meeting, Amer. Chem. Soc., San Francisco, Calif., April 1958, p. 37L.
[48] Gould, U.S.P. 2,754,177/1956.

whose structure consists of layers of coplanar condensed six-membered rings which may be regarded as an infinitely large "polyborazole" (VI).[49]



(VI)

The reaction of ammonia and diborane at only 200° gives borazole and a poorly characterised polymer of approximate composition $(BNH)_n$, which can be viewed as a partially cross-linked polyborazole. It therefore seems likely that the condensation of amines with boranes proceeds in a stepwise fashion. Wiberg elaborated this concept in detail and postulated the following condensation chain[7] on the grounds of the existence of compounds related to (*a*), (*b*), and (*c*):

$$\tfrac{1}{2}B_2H_6 + NH_3 \rightarrow \underset{(a)}{BH_3,NH_3} \xrightarrow{-H_2} \underset{(b)}{BH_2\cdot NH_2} \xrightarrow{-H_2} \underset{(c)}{BH{:}NH} \rightarrow B_3H_3N_3H_3$$

BH_3,NH_3 and other compounds of type (*a*) are well characterised. Compounds of type (*b*) are well known although the simplest tend to polymerise. For example, $BH_2\cdot NH_2$ is reported only as a high polymer,[7] $BH_2\cdot NHMe$ is a trimer,[9] and $BH_2\cdot NMe_2$ is monomeric only at high temperatures and is a dimer[7] or trimer[11] at room temperature. The only examples of type (*c*) compounds, BMe:NPh[50] and B(OMe):NH,[4] have been shown subsequently to be $B_3Me_3N_3Ph_3$[51] and $B(OMe)_3,NH_3$[41] respectively.

It is therefore possible to propose an alternative condensation sequence where cyclisation is not the final step but occurs as an equilibrium between (*b*) and the trimer (*d*):

$$\underset{(a)}{BH_3,NH_3} \xrightarrow{-H_2} \underset{(b)}{BH_2\cdot NH_2} \rightleftharpoons \underset{(d)}{B_3H_6N_3H_6} \xrightarrow{-H_2} B_3H_3N_3H_3$$

Compounds related to (*d*) are known to be converted into borazoles on heating, and there is evidence that this is possible without the intermediate formation of type (*b*) and (*c*) compounds. For example, borazoles react with three molecules of water to give, in the first place, adducts closely similar to compound (*d*) which yield on pyrolysis either boroxoles,

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[49] Pease, *Nature*, 1950, **165**, 722; *Acta Cryst.*, 1952, **5**, 356; *J. Amer. Chem. Soc.*, 1952, **74**, 4219.

[50] Wiberg and Hertwig, *Z. anorg. Chem.*, 1948, **257**, 138.

[51] Becher *Z. anorg. Chem.*, 1957, **289**, 262.

$B_3R_3O_3$, on the one hand or *B*-trihydroxyborazoles and boron nitride on the other:

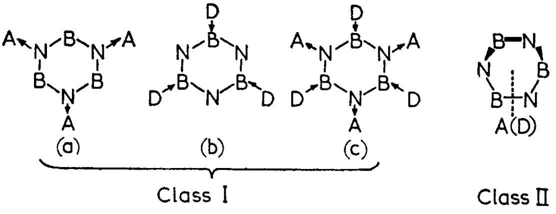
$$B_3Me_3N_3Me_3 \xrightarrow{H_2O} B_3Me_3O_3{}^{39} \quad B_3Me_3N_3H_3 \xrightarrow{H_2O} B_3Me_3O_3{}^{40}$$

$$B_3H_3N_3Me_3 \xrightarrow{H_2O} B_3(OH)_3N_3Me_3{}^{40} \quad B_3H_3N_3H_3 \xrightarrow{H_2O} (BN)_n{}^{4}$$

It is difficult to rationalise the formation of two kinds of ring systems, borazoles and boroxoles, if their formation is consistently due to depolymerisation of compounds of type (*d*) and subsequent recyclisation *via* species of types (*b*) and (*c*). The reaction of boron trichloride and amines yields aminodichloroborines, $BCl_2{\cdot}NR_2$, but trimers of these have not been reported and it remains to be seen if they are unstable intermediates in the formation of *B*-trichloroborazoles.

Borazoles are unstable at high temperatures, giving involatile polymers. The extent of this further condensation can be controlled either by blocking the ring positions with alkyl groups or by choice of temperature, and is well illustrated by the work of Lappert[36] (see p. 205). Controlled pyrolysis of borazoles is certain to yield some interesting polyborazoles, and this technique has already been shown to give $B_6N_6H_{10}$ and $B_5N_5H_8$ which are analogues of biphenyl and naphthalene.[52] Borazole is relatively stable in the gas phase and virtually no decomposition is observed after half an hour at 200°. At 500° only 27% decomposes in the same time, giving hydrogen and a material best represented by $(BNH)_n$. It is notable that liquid borazole is much less stable, even at room temperature, and this is consistent with the decomposition's being a condensation between several molecules.

Addition Compounds.—The borazole ring possesses both electron acceptor (boron) and donor (nitrogen) sites and is capable, in principle, of giving several types of addition compounds. Class I are considered to be formed by dative σ bonds, whereas Class II are viewed as being formed by dative π bonds.



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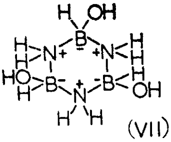
[52] Moews and Laubengayer, Abstracts of Papers, 136th Meeting, Amer. Chem. Soc., Atlantic City, N.J., September 1959, p. 53 N.

σ-Bonded compounds. Three possible types of σ-complexes are given above (A = electron acceptor, D = electron donor). It is to be expected that the aromatic character of the borazole ring would greatly reduce the donor or acceptor potential of the nitrogen or boron atoms, and it is not surprising that possible examples of compounds of type (*a*) are unknown and type (*b*) are rare. Wiberg[4] found that addition of ammonia, trimethylamine, and dimethyl ether to borazole occurred slowly over a period of days to yield amorphous products of no significant composition. Moreover, borazole is reported to form no addition compound with, or to be appreciably affected at 100° by, di-n-butyl ether.[42] Hence it is doubtful whether definite addition compounds are given by electron donors with borazole, or even whether the addition products are derivatives of borazole rather than linear polymers due to ring cleavage.

There are several well-defined addition compounds of the form $B_3H_3N_3H_3,3AD$ (AD = H_2O, MeOH, HCl, HBr, MeI), and although there is no direct evidence about their structures, they have been regarded consistently as compounds of type (*c*). The molecules AD above are known to form adducts in other systems by ionic dissociation and the electronegative fragment of AD is therefore assumed to be the electron donor which adds to boron. Hence $B_3H_3N_3H_3,3H_2O$ is formulated as a trimeric aminohydroxyborine (VII).


(VII)

It is notable that the same ring structure has been established by *X*-ray diffraction for $B_3H_6N_3Me_6$.[11] There are more examples of type (*c*) compounds, where six dative σ bonds replace the borazole π bonds, than compounds of types (*a*) and (*b*) which contain only three dative σ bonds.

The compounds $B_3H_3N_3H_3,3AD$ eliminate hydrogen on pyrolysis and show no tendency to dissociate into the original components. Hence these addition compounds are probably the intermediates in the substitution reactions of borazole with reagents AD which yield $B_3D_3N_3H_3$, *e.g.*:

$$B_3H_3N_3H_3 + 3HCl \rightarrow B_3H_3Cl_3N_3H_6 \rightarrow B_3Cl_3N_3H_3 + 3H_2$$

It is significant that addition compounds are formed with three molecules of AD, even in the presence of excess of borazole. The one exception appears to be $B_3H_3N_3H_3,2Br_2$.[4] It may be supposed that addition of the first AD molecule reduces the borazole resonance energy and this can be offset by the formation of an adduct containing the maximum number of donor–acceptor bonds. Consequently, 1:1 and 1:2 addition compounds are unstable, and hence rare.

π-Bonded complexes. The presence of π molecular orbitals in the borazole ring suggests the possibility that compounds of class II are

formed with molecules possessing similar π orbitals, but this has not been investigated seriously. Benzene is isosteric with borazole and favourable π orbital overlap may be possible between them. The substituent groups of the borazole and benzene rings will affect the stability of such complexes and one might expect the 1,3,5-trinitrobenzene–hexamethylborazole system to yield a significantly stable addition compound. In this connection it is interesting that *B*-trichloro-*N*-tri-*p*-tolylborazole and *B*-trichloro-*N*-tri-*p*-anisylborazole crystallise from benzene with one molecule of solvent per borazole molecule.[27]

Exchange Reactions.—It is difficult to view the substitution of borazoles by organometallic reagents, alkylborines, and boron halides, described in earlier sections, as proceeding through addition compounds of class I (*c*), and moreover these reagents appear to react in a stepwise manner giving mono-, di-, and tri-substituted borazoles rather than the complete substitution shown by water and hydrogen chloride:

$$\text{(i)}\quad B_3H_3N_3Ph_3 + RM \rightarrow B_3H_2RN_3Ph_3 + MH\ (R = Me, Ph;\ M = Li, MgCl)$$

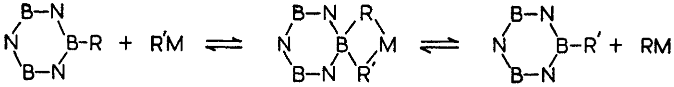
$$B_3H_3N_3Ph_3 + 2RM \rightarrow B_3HR_2N_3Ph_3 + 2MH$$

$$\text{(ii)}\quad B_3Cl_3N_3Me_3 \xrightarrow{Bu^nMgBr} B_3Bu^nCl_2N_3Me_3,\ B_3Bu^n{}_2ClN_3Me_3,\ B_3Bu^n{}_3N_3Me_3$$

$$\text{(iii)}\quad B_3H_3N_3H_3 \xrightarrow{BX_3} B_3H_2XN_3H_3,\ B_3HX_2N_3H_3\ (X = Cl, Br)$$

$$\text{(iv)}\quad B_3H_3N_3H_2Me \xrightarrow{BMe_3} B_3H_2MeN_3H_2Me,\ B_3HMe_2N_3H_2Me,\ B_3Me_3N_3H_2Me$$

One possible mechanism involves a bridged complex (VIII).



(VIII)

[R, R′ = H, Alk, Hal; M = MgCl(Br), BAlk$_2$, BHal$_2$]

Sisler and his co-workers[30] postulated such a mechanism for the *B*-ethyl exchange observed between *BB*′-dichloro-*B*″-ethyl-, *B*-chloro-*B*′*B*″-diethyl-, and *B*-triethyl-*N*-trimethyl-borazoles, and pointed out that the absence of exchange in the corresponding *B*-n-butylchloroborazoles may be related to the varying stability of complex (VIII) with methyl or n-butyl groups in the bridging positions. Although there is no direct evidence for this exchange mechanism, it is nevertheless useful in correlating a number of observations. For example, *B*-trichloroborazole may be reduced by lithium aluminium hydride or borohydride in ethereal solvents, but the resulting borazole cannot be distilled from the products of lithium aluminium hydride reduction unless excess of lithium hydride is added.[42] It seems likely that the borazole may form a complex of type (VIII) with the AlH_3 or BH_3 species produced in the reaction. However, if the borane complex dissociates to any extent, diborane will be evolved and the dissociation will become complete, allowing isolation of the borazole by distillation. This will not occur with the aluminium hydride complex as this hydride is involatile.

Simple Substitution Reactions.—Although many borazole substitution reactions appear to involve one or more types of molecular complex, a number of reactions may well be of the familiar kind of nucleophilic substitution of organic chemistry:

$$\begin{aligned} &\text{B–Cl} + \text{EtO}^- \rightarrow \text{B–OEt} + \text{Cl}^- \\ &\text{B–Cl} + \text{BH}_4^- \rightarrow \text{B–H} + \text{Cl}^- + \tfrac{1}{2}(\text{B}_2\text{H}_6) \\ &\text{B–Cl} + \text{Br}^- \rightarrow \text{B–Br} + \text{Cl}^- \end{aligned}$$

An investigation of the chloride-ion exchange of *N*-trisubstituted *B*-trichloroborazoles might confirm the existence of S_N1 or S_N2 borazole reactions and provide the first detailed evidence of ring activation with variation of nitrogen substituent. Although there are no known examples, electrophilic substitution is expected to occur at the borazole nitrogen atom. By analogy with other fields of chemistry it is probable that NO^+, NO_2^+, and PhN_2^+ species would react with borazoles, giving products that can be correlated with initial *N*-substitution.

Physical Properties

The melting points and boiling points of a number of borazoles are given in Table 1. All are colourless, volatile liquids or crystalline solids and use of the letters *p*, *d*, and *n*, indicates where vapour pressure, density, and refractive index data are available. Despite the chemical differences between borazoles and their benzene analogues, properties which depend on structural similarities are frequently compared. For example, the ratios of the absolute boiling points of a number of methyl analogues[39] are approximately 0·93. Several groups of workers have studied liquid borazole, and values of the viscosity obtained by Eddy, Smith, and Miller[53] fall close to the straight line

$$\log \eta = 4{\cdot}45 \times 10^4 \times T^{-2} - 3{\cdot}037 \ (\eta \text{ poise, } T^\circ\text{K}).$$

This indicates association at low temperatures and provides an interesting difference between borazole and benzene.

[53] Eddy, Smith, and Miller, *J. Amer. Chem. Soc.*, 1955, 77, 2105.

TABLE 1

Compound	M.p.	B.p./mm.	Data	Ref.
$B_3F_3N_3Me_3$	85°	224°	*p*	35
$B_3Cl_3N_3H_3$	84	192*	*p, d*	28, 37
$B_3Cl_3N_3Me_3$	162–164			31, 34, 54
$B_3Cl_3N_3Et_3$	57–59			31, 54
$B_3Cl_3N_3Bu^n_3$	30	115–120/0·5		31
$B_3Cl_3N_3(C_6H_{11})_3$	217–219			54
$B_3Cl_3N_3Ph_3$	273–275			26, 33, 43, 54, 55
$B_3Cl_3N_3(C_6H_4{\cdot}Me)_3$	308–309			27, 54
$B_3Cl_3N_3(C_6H_4{\cdot}OMe)_3$	233–238			27, 54
$B_3Cl_2HN_3H_3$	33·0–33·5	152*	*p*	23
$B_3Cl_2Bu^nN_3Me_3$	−4 to −6	101/1·1	*n*	30
$B_3ClH_2N_3H_3$	−34·6	109·5*	*p*	23
$B_3ClBu^n_2N_3Me_3$		122/1·1	*n*	30
$B_3Br_3N_3H_3$	128–129			37, 42
$B_3Br_3N_3Et_3$	78–82			54
$B_3Br_3N_3Ph_3$	292–293			33
$B_3Br_2HN_3H_3$	49·5–50	167*	*p*	23
$B_3BrH_2N_3H_3$	−34·8	122*	*p*	23
$B_3H_3N_3H_3$	−56·3	53	*p, d, n*	4, 22, 53, 54
$B_3H_3N_3H_2Me$		84*	*p*	20
$B_3H_3N_3HMe_2$		108*	*p*	20
$B_3H_3N_3Me_3$	−1 to 0	132	*p, d, n*	9, 20, 21, 22, 40, 54
$B_3H_3N_3Et_3$	−49·1	184*	*p, d, n*	22, 54
$B_3H_3N_3Pr^n_3$		225*	*p, d, n*	22
$B_3H_3N_3Pr^i_3$	−6·5	203*	*p, d, n*	22
$B_3H_3N_3(C_6H_{11})_3$	98·9			54
$B_3H_3N_3Ph_3$	160–161			38, 54, 55
$B_3H_3N_3(C_6H_4{\cdot}CH_3)_3$	149–150			54
$B_3H_3N_3(C_6H_4{\cdot}OMe)_3$	137–138			54
$B_3H_2MeN_3H_3$	−59	87*	*p*	19
$B_3H_2MeN_3H_2Me$		124*	*p*	20
$B_3H_2MeN_3Me_3$		162		38
$B_3H_2MeN_3Ph_3$	142			38
$B_3H_2PhN_3Ph_3$	215			38
$B_3HMe_2N_3H_3$	−48	107*	*p*	19
$B_3HMe_2N_3H_2Me$		139*	*p*	20
$B_3HMe_2N_3Me_3$		187		38
$B_3HMe_2N_3Ph_3$	206			38
$B_3HMeEtN_3Ph_3$	128			38
$B_3HPh_2N_3Ph_3$	207			38
$B_3Me_3N_3H_3$	31·8	125*	*p*	19, 40
$B_3Me_3N_3H_2Me$		158*	*p*	20
$B_3Me_3N_3Me_3$	99	221*	*p*	38, 39
$B_3Me_3N_3Ph_3$	267–269			43, 55
$B_3MeEtPr^nN_3Ph_3$	131			38
$B_3Me_2Bu^nN_3Ph_3$	113			38
$B_3Et_3N_3H_3$	−54	66–67	*d*	56
$B_3Et_3N_3Me_3$	1–2	98/1·8	*n*	30
$B_3Et_3N_3Ph_3$	169–171			43
$B_3Pr^n_3N_3H_3$		108/9		57
$B_3Pr^n_3N_3Ph_3$	169–171			43
$B_3Pr^i_3N_3H_3$		70/0·5		57

* Estimated from vapour pressure data

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[54] Hohnstedt and Haworth, *J. Amer. Chem. Soc.*, 1960, **82,** 89.

[55] Becher and Frick, *Z. anorg. Chem.*, 1958, **295,** 83.

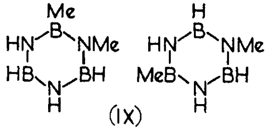
[56] Zhigach and Krongauz, *Proc. Acad. Sci.* (*U.S.S.R.*), 1956, **111,** 725.

[57] Hawthorne, *J. Amer. Chem. Soc.*, 1959, **81,** 5836.

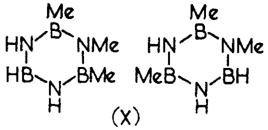
TABLE 1—*continued*

Compound	M.p.	B.p./mm.	Data	Ref.
$B_3Pr^i_3N_3Ph_3$	197–198			43
$B_3Bu^n_3N_3H_3$		110/0·6	*n*	32, 57
$B_3Bu^n_3N_3Me_3$	−18 to −17	140/1·1	*n*	30
$B_3Bu^n_3N_3Ph_3$	129–132			43
$B_3Bu^i_3N_3Ph_3$	185–187			43
$B_3Bu^s_3N_3H_3$		94/0·7		57
$B_3(CH{:}CHCl)_3N_3H_3$	127–128·5			32
$B_3(CH_2{\cdot}CH{:}CH_2)_3N_3Me_3$	−37 to −39	110–112/1·3	*n*	30
$B_3(CH_2{\cdot}CH{:}CH_2)_3N_3Ph_3$	98–99			43
$B_3Ph_3N_3H_3$	184–185			32, 45, 55
$B_3Ph_3N_3Me_3$	270			38, 55
$B_3Ph_3N_3Ph_3$	413–415			33, 43
$B_3(OH)_3N_3Ph_3$	95–130			26
$B_3(OH)_3N_3(C_6H_4{\cdot}OMe)_3$	112–120			27
$B_3(OMe)_3N_3H_3$	110–111			41
$B_3(OMe)_3N_3Me_3$		62–65/0·07	*n*	46
$B_3(OEt)_3N_3H_3$	53–54			41
$B_3(OEt)_3N_3Me_3$		80/0·10	*n*	46
$B_3(OPr^n)_3N_3Me_3$		101–103/0·15	*n*	46
$B_3(OPr^i)_3N_3Me_3$		85–87/0·10	*n*	46
$B_3(OBu^n)_3N_3Me_3$		130–134/0·30	*n*	46
$B_3(OBu^n)_3N_3Et_3$		153–156/0·4	*d, n*	36
$B_3(OBu^t)_3N_3Me_3$	84–87	120–125/0·52		46
$B_3(OPh)_3N_3Me_3$	81–84	185–187/0·07		46
$B_3(NHMe)_3N_3H_3$	85–105			48
$B_3(NHMe)_3N_3Me_3$		110/0·1	*d, n*	36
$B_3(NMe_2)_3N_3H_3$	112–113			34, 48
$B_3(NHEt)_3N_3Et_3$		145–150/0·1	*d, n*	36
$B_3(NEt_2)_3N_3H_3$		164/10		34, 48
$B_3(NEt_2)_3N_3Et_3$		84		34
$B_3(NHPr^i)_3N_3Pr^i_3$		106/0·03	*d, n*	36
$B_3(NHBu^n)_3N_3Bu^n_3$		158/0·005	*d, n*	36
$B_3(NHBu^s)_3N_3Bu^s_3$		135/0·01	*d, n*	36
$B_3(NHBu^t)_3N_3Bu^t_3$		103/0·04	*d, n*	36
$B_3(NH{\cdot}C_6H_{11})_3N_3(C_6H_{11})_3$	52–55			36
$B_3(NHPh)_3N_3Ph_3$	152–155			36
$B_3(NPh_2)_3N_3H_3$	> 300			34
$B_3(NH{\cdot}CH_2Ph)_3N_3(CH_2Ph)_3$		> 250/0·005	*d, n*	36
$B_3(C_5H_{10}N)_3N_3Et_3$		94–96/3		34

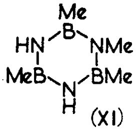
Isomerism.—*B*- and *N*-Methylborazole are examples of isomers whose structures are known unambiguously. From *N*-methylborazole, Schlesinger, Ritter, and Burg[20] prepared *BN*-dimethylborazole (IX), *BB'N*-trimethylborazole (X), and *BB'B''N*-tetramethylborazole (XI). Each appeared to be a single compound although there are two possible structures of both (IX) and (X). It is not known which of the possible isomers were prepared and the problem of position isomerism has not been investigated since 1938.



(IX)



(X)



(XI)

Molecular Structure.—Borazole was shown to have a benzene-like configuration by Stock and Wierl,[2] and the small dipole moment observed by Ramaswamy[58] was presumably caused by the presence of impurities. The structure was confirmed by Bauer[59] and structural data for hexagonal boron nitride, borazole, *N*-trimethylborazole, and *B*-trichloroborazole appear in Table 2.

The positive inductive effect of *N*-methyl and the negative inductive effect of *B*-chloro-groups both lead to greater double-bonding between boron and nitrogen in the borazole ring. This increase in aromatic character is reflected by shorter boron–nitrogen interatomic distances in *N*-trimethylborazole and *B*-trichloroborazole.

TABLE 2

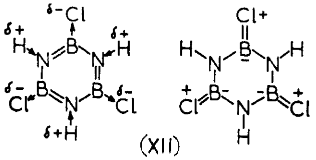
Compound	B–N (Å)	Substituents	Method	Ref.
$(BN)_n$	1·446		*X*-Ray diffrn.	49
$B_3H_3N_3H_3$	1·44 ± 0·02		Electron diffrn.	59
$B_3H_3N_3Me_3$	1·42 ± 0·02	N–C = 1·48 ± 0·03 Å	,, ,,	60
$B_3Cl_3N_3H_3$	1·41 ± 0.02	B–Cl = 1·78 ± 0·03 Å	,, ,,	60
	1·413 ± 0·010	B–Cl = 1·760 ± 0·015 Å	*X*-Ray diffrn.	61
	1·415	B–Cl = 1·735 Å	,, ,,	62

It is difficult to obtain reliable values for the lengths of pure single and double boron–nitrogen bonds. If the trigonal covalent radii of boron and nitrogen[63] are taken to be 0·8 Å and 0·74 Å (trigonal being assumed to be similar to tetrahedral nitrogen) and the appropriate allowance, 0·09 Å, is made for the electronegativity difference,[64] the estimated boron–nitrogen single bond length is 1·45 Å. This value suggests that the bonds in hexagonal boron nitride are approximately single bonds, which seems plausible in view of the differences in structure, electrical properties, and colour between boron nitride and graphite. Hexagonal layers occur in graphite but the electrical conductivity and characteristic black lustre have been attributed to the aromatic character of the carbon–carbon bonds. The most acceptable boron–nitrogen double-bond value is probably 1·218 Å, found in the short-lived BN species.[65] Application of Gordy's formula,[66] $n = aR^{-2} + b$, where n is bond order, R is bond length, and a and b are constants characteristic of any pair of atoms, suggests that the boron–nitrogen bonds in *B*-trichloroborazole have about 20% of double-bond character; but numerical values of bond order should be accepted

[58] Ramaswamy, *Proc. Indian Acad. Sci.*, 1935, **2**, *A*, 364, 630.
[59] Bauer, *J. Amer. Chem. Soc.*, 1938, **60**, 524.
[60] Coffin and Bauer, *J. Phys. Chem.*, 1955, **59**, 193.
[61] Coursen and Hoard, *J. Amer. Chem. Soc.*, 1952, **74**, 1742.
[62] Lonsdale, *Nature*, 1959, **184**, 1060.
[63] Wells, "Structural Inorganic Chemistry," Oxford University Press, 2nd Edition, 1950, p. 58, 347.
[64] Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.
[65] Douglas and Hertzberg, *Canad. J. Res.*, 1940, *A*, **18**, 179.
[66] Gordy, *J. Chem. Phys.*, 1947, **15**, 305.

with caution. Molecular diamagnetic anisotropy may be taken as a criterion of aromatic character, and a comparison of the anisotropies of variously substituted borazoles would be of great interest. Although only one compound, *B*-trichloroborazole, has been studied,[67] the approximate value, $\Delta K = 18 \times 10^{-6}$ c.g.s. units, at least confirms that *B*-trichloroborazole has some aromatic character.

Coursen and Hoard[61] showed that molecules of crystalline *B*-trichloroborazole are arranged in layers, and the short N–H · · · Cl distances between adjacent molecules suggested some type of electrostatic attraction. Lonsdale[62] provided further evidence that the hydrogen and chlorine atoms in *B*-trichloroborazole are oppositely charged, by a comparison with the similar crystal structure of 1,3,5-trichlorobenzene. Although intermolecular H · · · · Cl distances are less in *B*-trichloroborazole than in 1,3,5-trichlorobenzene, the intermolecular H · · · · H and Cl · · · · Cl distances are greater in *B*-trichloroborazole. The short B–N and long B–Cl bond lengths lend support to structure (XII*a*) rather than structure (XII*b*) for *B*-trichloroborazole. In $PhBCl_2$, where double bonding between boron and chlorine is generally assumed to occur, the B–Cl bond lengths[60] are 1·72 Å. It is significant that *B*-trichloroborazole is thermally unstable and evolves hydrogen chloride even at room temperature,[68] since this would be characteristic of structure (XII*a*) rather than (XII*b*).



(*a*) (*b*)

(Arrows indicate direction of the inductive effect.)

Infrared and Raman Spectra.—The Raman spectrum of liquid borazole and the infrared absorption of borazole vapour from 400 to 7000 cm.$^{-1}$ have been described in detail.[69] Fundamental frequencies assigned on the basis of D_{3h} symmetry gave a satisfactory correlation with the fundamental frequencies of benzene, and force constants were calculated for borazole. The allocation of certain spectral bands in borazole and *N*-trimethylborazole is shown in Table 3. The natural abundance ratio $^{11}B \cdot {}^{10}B$ is approximately 4:1 but identification of the splitting caused by the isotope effect was complicated by the large number of allowed combinations.[69]

The intensity of the 1465 cm.$^{-1}$ band in borazole is attributed to charges on the boron and nitrogen atoms, and the effect of ring substituents is

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[67] Lonsdale and Toor, *Acta Cryst.*, 1959, **12**, 1048.

[68] Hohnstedt and Haworth, *Chem. Eng. News*, Sept. 16th, 1957, 67.

[69] Crawford and Edsall, *J. Chem. Phys.*, 1939, **7**, 223; Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131; Spurr and Chang, *J. Chem. Phys.*, 1951, **19**, 518.

illustrated by Table 4. This characteristic band occurs at 1492 cm.$^{-1}$ in the spectra of *B*-aminoborazoles,[34,36] and Lappert[36] also considered absorption near 720 cm.$^{-1}$ to be characteristic of *B*-aminoborazoles and *B*-alkoxyborazoles

TABLE 3

$B_3H_3N_3H_3$ ν (cm.$^{-1}$)	$B_3H_3N_3Me_3$ ν (cm.$^{-1}$)	
718	1056	BH, NH In-plane bending
918	1107	,, ,,
1465	1425	In-plane ring deformation (*E′*)
	1342	,, ,, ,,
	1294	,, ,, ,,
2530	2485	BH Stretching
3490		NH Stretching
6880		NH Stretching overtone

TABLE 4

Compound	ν (cm.$^{-1}$)	Ref.	Compound	ν (cm.$^{-1}$)	Ref.	Compound	ν (cm.$^{-1}$)	Ref.
$B_3H_3N_3H_3$	1465	69	$B_3H_3N_3Me_3$	1425	69	$B_3H_3N_3Ph_3$	1401	55
$B_3Me_3N_3H_3$	1451*	70	$B_3Et_3N_3Me_3$	1404	30	$B_3Me_3N_3Ph_3$	1380	55
$B_3Ph_3N_3H_3$	1472	55	$B_3Ph_3N_3Me_3$	1405	55			
$B_3Cl_3N_3H_3$	1445	55	$B_3Cl_3N_3Me_3$	1392	55	$B_3Cl_3N_3Ph_3$	1373	55

* Raman frequency. Different assignment from that originally proposed.

Ultraviolet Spectra.—The ultraviolet spectrum of borazole has been related to that of benzene by Platt, Schaeffer, and their co-workers,[71] and the observed spectra were compared with computed energies in a semi-empirical molecular-orbital treatment of the ground states and first excited states by Roothaan and Mulliken.[72] The 1700 Å band in the borazole spectrum is analogous to the 1800 Å band in the benzene spectrum and the intensity is characteristic of $V \leftarrow N$ transitions. Diffuse bands which occur near 1950 Å in the spectrum of borazole are weaker than the 2000 Å bands in benzene but stronger than the 2600 Å bands in benzene.

Rector, Schaeffer, and Platt[73] also examined three substituted borazoles. *B*-Trimethyl- and *B*-trichloro-borazole absorb at similar wavelengths to borazole but *N*-trimethylborazole absorbs at longer wavelengths and the strongest band occurs at 1900 Å. The relative positions of these spectra were believed to indicate the degree of aromatic character, and structure (XII*b*) was accordingly proposed for *B*-trichloroborazole. However, the evidence of bond lengths shows that

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[70] Goubeau and Keller, *Z. anorg. Chem.*, 1953, **272**, 303.

[71] Platt, Klevens, and G. W. Schaeffer, *J. Chem. Phys.*, 1947, **15**, 598; Jacobs, Platt, and G. W. Schaeffer, *ibid.*, 1948, **16**, 116.

[72] Roothaan and Mulliken, *J. Chem. Phys.*, 1948, **16**, 118.

[73] Rector, G. W. Schaeffer, and Platt, *J. Chem. Phys.*, 1949, **17**, 460.

B-trichloroborazole has more aromatic character than borazole and an alternative explanation of the spectral data is offered.

The replacement of *N*-hydrogen by methyl, as in *N*-trimethylborazole, produces two separate effects. (*a*) The electron density of the borazole ring is increased and this causes a red shift in the spectrum. (*b*) The donor properties of nitrogen are increased: this leads to a greater degree of aromatic character and causes a further red shift. When methyl replaces *B*-hydrogen as in *B*-trimethylborazole, the two effects are opposed. (*a*) The increased electron density of the ring would cause a red shift. (*b*) The acceptor properties of boron are reduced. This leads to reduced aromatic character and would cause a blue shift. Chlorine has a negative inductive effect and in *B*-trichloroborazole: (*a*) the electron density of the ring is reduced (blue shift), and (*b*) the acceptor properties of boron are increased and hence the aromatic character of the ring is increased (red shift). These opposing influences may again be roughly equivalent, which would account for the similar spectra of *B*-trichloroborazole and borazole.

Steric hindrance. The ultraviolet spectra of four symmetrical triphenylborazoles were investigated by Becher and Frick.[74] Borazole[71] does not absorb between 2000 and 4600 Å and bands observed near 2600 Å in the spectra of *B*-trimethyl-*N*-triphenylborazole and *N*-trimethyl-*B*-triphenylborazole are due to unconjugated phenyl groups. Methyl attached to the borazole ring prevents the phenyl groups from achieving co-planarity. Red shifts of increased intensity occurring in the spectra of *B*- and *N*-triphenylborazole confirm that there is reduced steric hindrance and greater conjugation in the absence of methyl groups.

Thermodynamic Properties.—Crawford and Edsall[69] calculated the entropy, free energy, and enthalpy of gaseous borazole from spectral measurements, and used vapour-pressure data to obtain thermodynamic values for the liquid. A heat-capacity equation for gaseous borazole[75] was derived from these values.

The heat of hydrolysis of *B*-trichloroborazole measured by Van Artsdalen and Dworkin[76] was 113·8 ± 0·07 kcal./mole at 25° c. The heat of formation of crystalline *B*-trichloroborazole and the boron–nitrogen bond energy were calculated from the observed heat of hydrolysis and from the heats of formation of water, boric acid, and ammonium chloride. A recalculation by Cottrell,[77] who used more recent thermochemical values, gave 106·5 kcal. for the boron–nitrogen bond energy in *B*-trichloroborazole. This was compared with 104 kcal. for the boron–nitrogen bond energy in trisdimethylaminoborine, recalculated by

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[74] Becher and Frick, *Z. phys. Chem. (Frankfurt)*, 1957, **12**, 241.

[75] Spencer, *J. Amer. Chem. Soc.*, 1945, **67**, 1859.

[76] Van Artsdalen and Dworkin, *J. Amer. Chem. Soc.*, 1952, **74**, 3401.

[77] Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 2nd Edition, 1958, p. 240.

Cottrell from the heat of hydrolysis measured by Skinner and Smith.[78] Trisdimethylaminoborine is a planar molecule[79] in which some double bonding between boron and nitrogen is also believed to occur.

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[78] Skinner and Smith, *J.*, 1953, 4025.
[79] Becher, *Z. anorg. Chem.*, 1956, **287**, 285.