Preparation, Physical and Spectroscopic Properties of *B*-Halogen and *B*-Pseudohalogen Δ^2-Tetrazaborolines, and Preparation of the Diboron Compound $Me_2N_4BBN_4Me_2$

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B-Halogen substituted Δ^2-tetrazaborolines have been prepared by treating methylamine–boron trichloride with methyl azide in the presence of a tertiary amine and by bromination of 1,4-dimethyl-Δ^2-tetrazaboroline with *N*-bromosuccinimide. Treatment of 5-chloro-1,4-dimethyl-Δ^2-tetrazaboroline with silver pseudohalides yielded cyano-, thiocyano- and selenocyano-derivatives, and with sodium amalgam gave the diboron compound $Me_2N_4BBN_4Me_2$. A detailed study of the i.r. and Raman spectra of the halogen and pseudohalogen derivatives was undertaken to determine the mode of bonding of the pseudohalogen substituents.

DURING the course of a wider investigation of the chemistry of the Δ^2-tetrazaboroline ring system, we had observed analogies between the Δ^2-tetrazaboroline and borazine ring systems.[1] We therefore concluded that *B*-halogen and *B*-pseudohalogen derivatives of the Δ^2-tetrazaboroline ring system should be preparable, and a number of different routes were examined.

The reactions of 5-chloro-1,4-dimethyl-Δ^2-tetrazaboroline with the silver pseudohalides AgCN, AgSCN, and AgSeCN were expected to yield *N*-bonded *B*-pseudohalogen derivatives. A study of the vibrational spectra strongly suggested that the CN and SeCN products were carbon and selenium bonded rather than nitrogen bonded, although the mode of attachment in the SCN derivative was less certain.

The reactivity of the B–Cl derivative prompted us to examine the formation of boron–boron bonds under mild conditions, in contrast to the standard method of preparing $(Me_2N)_2B{\cdot}B(NMe_2)_2$ from $(Me_2N)BCl$ which involves the inconvenient handling of dispersed molten sodium or a sodium–potassium alloy.[2]

RESULTS AND DISCUSSION

Preparation of B-*Halogen Substituted Tetrazaborolines.*—The preparation of *B*-halogen derivatives of Δ^2-tetrazaboroline was investigated by four separate routes, although the successful preparation proved to be unexpectedly difficult. The first possible route involved RNH_2BH_2Cl and RN_3 since derivatives of the type R_2N_4BH can be prepared by elimination of hydrogen from an amine–borane of the type RNH_2,BH_3 in the presence of an azide RN_3. Attempted hydrogen elimination from $MeNH_2BH_2Cl$ in the presence of MeN_3 failed to yield the corresponding Me_2N_4BCl.

A second possible route to *B*-halogen derivatives is by dehydrohalogenation of a primary amine–trihalogenoborane in the presence of an azide (Equation 1).

$$RNH_2,BX_3 + RN_3 \longrightarrow R_2N_4BX + 2HX \qquad (1)$$

Attempts to prepare Me_2N_4BCl, Ph_2N_4BCl, and Ph_2N_4BF from the reactions of the appropriate primary amines, boron trihalides and organic azides in stoicheiometric proportions gave a number of, as yet, uncharacterised products, but did not yield the Δ^2-tetrazaboroline ring system. The reactions were also carried out using an excess of primary amine, but again *B*-halogeno-Δ^2-tetrazaborolines were not isolated. A reaction carried out in the presence of a tertiary amine gave the expected 5-chloro-1,4-dimethyl-Δ^2-tetrazaboroline in 26% yield from reaction (2):

$$MeNH_2 + BCl_3 + MeN_3 + 2Et_3N \longrightarrow Me_2N_4BCl + 2Et_3NHCl \qquad (2)$$

Somewhat better yields were obtained from reactions using $EtPr^i_2N$ as the tertiary amine. However, a reaction involving BF_3 in the presence of $EtPr^i_2N$ yielded 1,3,5-trimethyl-2,4,6-trifluoroborazine as the only volatile product, and reaction with BBr_3 in the presence of Et_3N also failed to yield the expected Me_2N_4BBr.

A third possible route to *B*-halogen derivatives is by halogenation of B–H derivatives. Direct chlorination of Ph_2N_4BH did not yield the expected Ph_2N_4BCl. Only unchanged starting materials were recovered from an attempt to substitute Et_2N_4BH by reaction with iodine in the presence of picoline, and when Ph_2N_4BH was treated with iodine in the presence of pyridine, a red substance of probable formulation $py_2I^+I^-_3,Ph_2N_4BH$ was obtained.

Me_2N_4BBr was successfully prepared in good yield by treating Me_2N_4BH with *N*-bromosuccinimide in carbon tetrachloride solution, although when *N*-chlorosuccinimide was used, no Me_2N_4BCl was isolated.

A fourth possible route to *B*-halogenated derivatives involves the use of metal halides as halogenating agents. Thus, the reaction of Me_2N_4BH with $SnCl_4$ at −3° in carbon tetrachloride was investigated. A sublimable complex of uncertain composition was obtained and its mass spectrum showed the characteristic isotope distribution for the ions $SnCl_4^+$, $SnCl_3^+$, $SnCl_2^+$, $SnCl^+$, and Sn^+ and in addition $Me_2N_4BH^+$ and $Me_2N_4BCl^+$. In common with recently obtained results for the adduct $(Me_2N_4BMe)_2SnCl_4$,[3] no parent ion for a simple complex was observed.

The Me_2N_4BCl and Me_2N_4BBr obtained in these reactions were colourless, readily hydrolysable liquids, and were characterised by elemental analysis and mass

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[1] A. Finch, J. B. Leach, and J. H. Morris, *Organometallic Chem. Rev.* (*A*), 1969, **4**, 1.

[2] R. J. Brotherton, *Progr. Boron Chem.*, 1964, **1**, 1.

[3] B. Hessett, J. H. Morris, and P. G. Perkins, *J. Chem. Soc.* (*A*), 1971, 2466.

spectroscopy. During the examination of mass spectra of these compounds in some mass spectrometers, peaks were observed at *m/e* 208, 209, 210, 211 in the expected isotope ratios for two boron atoms, and this was interpreted as hydrolysis of the product within the mass spectrometer to yield $Me_2N_4BOBN_4Me_2$.

Preparation of B-*Pseudohalogen Substituted* Δ^2-*Tetrazaborolines*.—During an examination of the mass spectrum of the crude product from the preparation of Me_2N_4BCl, peaks were observed at *m/e* 138, 139 which were attributable to $Me_2N_4BN_3$ and the i.r. spectrum showed azide absorptions near 2150 cm^{-1}. This led to a search for other pseudohalide derivatives, and reaction of Me_2N_4BCl with AgCN, AgSCN, or AgSeCN led to replacement of the halogen by a pseudohalogen.

TABLE 1

Physical properties of tetrazaborolines

Compound	M.p. (°C)	$\lambda_{max.}$ (nm)	^{11}B n.m.r. δ(p.p.m.) [a]	^{1}H n.m.r. (δ p.p.m.) [b]	M^+ *m/e*
Me_2N_4BCl	12·3	214	−23·2	−3·50	131, *132* 133, *134*
Me_2N_4BBr	11·5	212	−21·1	−3·57	175, *176* 177, *178*
Me_2N_4BCN		*ca.* 200	−15·3	−3·72	122, *123*
Me_2N_4BSCN		(190), 203, 256	−17·0	−3·52	154, *155*
Me_2N_4BSeCN	40	204, (260wsh)		−3·20 [c]	

[a] BF_3,Et_2O reference. [b] Me_4Si reference. [c] Capillary sample externally referenced.

TABLE 2

Ring modes of 1,4-dimethyl-Δ^2-tetrazaborolines

Mode	Species	H *	D *	Cl	Br	CN	SCN	SeCn	Me *	Et *	Vinyl *
ω_4	b_1	1408	1409	1410	1409	1411	1416	1420	1397	1395	1395
ω_5	a_1	1363	1357	1362	1366	1380	1372	1360	1376	1377	1366
ω_3	a_1	1342	1342	1337	1336	1333	1330	1340	1337	1339	1337
ω_2	b_1	991	979	980	976	986	982	986	992	1005	1014
ω_1	a_1	953	951	906	955	885	928	915	898	959	960
ω_6	b_1	736	733	781	776	788	788	788	754	797	794
ω_7	a_1	570	580	593	582	614	597	609			
Γ_2	a_2	554	561		533						
Γ_1	b_2	522	416					512			

* See J. B. Leach and J. H. Morris, *J. Organometallic Chem.*, 1968, **13**, 313.

Physical Properties of B-*Halogeno- and* B-*Pseudohalogeno*-Δ^2-*tetrazaborolines*.—The physical properties of the *B*-substituted derivatives are summarised in Table 1, except the principal bands in the vibrational spectra, and the detailed mass spectra, some of which are reported elsewhere.[4]

Vibrational Spectra.—The i.r. and Raman spectra of the five compounds were examined (*a*) in order to ascertain whether or not characteristic ring modes would be affected by change of substituent at the boron atom, (*b*) to identify characteristic boron-substituent frequencies in a related series of compounds, and (*c*) to establish the mode of attachment of pseudohalogen groups to a boron atom in a related series of compounds.

Conclusions based on a comparison of i.r. band shapes and intensities with compounds reported earlier,[5] and also on the Raman data led to the probable assignment of ring modes in Table 2. The assignments are based on the assumption of essentially C_{2v} symmetry for all the molecules and although the true symmetry will in some cases probably be lower than this, we feel that the ring modes will be relatively unaffected by small deviations from this symmetry.

The five ring-stretching modes are remarkably consistent over the series of compounds with the possible exception of the lowest frequency a_1 mode ω_1. Presumably this mode is the one most likely to be coupled with other a_1 modes in the vicinity, particularly with the B–X stretching frequency.

It was not possible to identify with complete certainty the B–X stretching frequencies of the *B*-halogen and *B*-pseudohalogen derivatives. The B–Cl and B–Br a_1 stretching frequencies might have been expected to show as strong, polarised Raman lines in the 600—900 cm^{-1} region,[6] and because of mass effects, the B–Br frequency would be expected to be at lower frequency shifts than the B–Cl mode. The only strong Raman line observed in this region is the strong polarised line near 600 cm^{-1} which occurs in most of the compounds and has been assigned to the ring deformation ω_7 (see Table 2). Outside this region the polarised lines at 455 and 374 cm^{-1} respectively in Me_2N_4BCl and Me_2N_4BBr must, therefore, be considered as the B–Cl and B–Br stretching modes, and it must be noted that the symmetry breathing modes of BCl_3 and BBr_3 occur at 471 and 279 cm^{-1} respectively.[7] Undoubtedly, the simple description is at best an approximation, and strong coupling must occur with other modes of the same species!

Vibrational spectroscopy has been widely used as a

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[4] E. F. H. Brittain, J. B. Leach, and J. H. Morris, *Org. Mass Spectrometry*, 1968, **1**, 459.

[5] J. B. Leach and J. H. Morris, *J. Organometallic Chem.*, 1968, **13**, 313.

[6] A. Meller, *Organometallic Chem. Rev.*, 1967, **2**, 1.

[7] L. H. Long and D. Dollimore, *J. Chem. Soc.*, 1954, 4457.

method of determining the mode of bonding of a pseudohalogen group in organometallic compounds.[8,9] There has been less published information on B–[CN] derivatives, although BH_3CN^- and BH_3NC^- have been reported[10] to have the CN stretching frequencies 2180 and 2070 cm^{-1}. The CN stretching frequency in the Me_3N,BH_2CN addition compound was in the region 2185—2280 cm^{-1}.[11] The i.r. spectrum of $Me_2N_4B[CN]$ showed a number of bands in the region 2000—2300 cm^{-1}. The two most intense bands were at 2115 and 2152 cm^{-1} although a sharp but weak band was observed at 2239 cm^{-1}. The Raman spectrum however showed only a single sharp strong polarised line at 2241 cm^{-1}. We therefore believe that to be the –CN stretching frequency, and the compound to be the normal cyanide derivative Me_2N_4BCN.

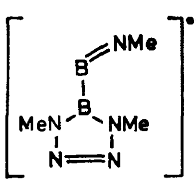
Similarly, the selenocyanate derivative showed bands in the i.r. at 2101, 2158, and 2238 cm^{-1}, but only one strong Raman line at 2240 cm^{-1}. Work on transition-metal derivatives of –SeCN and –NCSe has suggested that the normal derivatives have higher ν_3 stretching frequencies than iso-derivatives,[12] and we therefore believe that the compound prepared is the normal derivative Me_2N_4BSeCN.

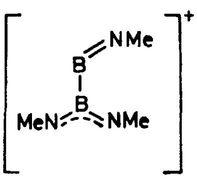
The situation with the thiocyanate derivative is less certain. The compound showed i.r. bands at 2053 and 2110 cm^{-1}, and a polarised Raman line at 2090 cm^{-1}. Earlier workers have assumed the isothiocyanate configuration in a number of boron derivatives,[13] and have found i.r. bands at similar frequencies. The assumptions were based in part on u.v. spectra and molar refractivities, although no Raman data were recorded. We believe our data to be somewhat more consistent with the isothiocyanate geometry, but not sufficiently definitive to rule out the normal thiocyanate geometry.

Electronic Spectra.—All the compounds showed moderate intensity bands near 200 nm. In addition it was expected that the spectra would help in determining the mode of bonding in the pseudohalogen derivatives. Thus $Me_2N_4B[SCN]$ showed in addition a weaker band near 256 nm. The spectrum of $Me_2N_4B[SeCN]$ was similar except that the low-energy band near 260 nm was only observed as a weak shoulder. Preliminary CNDO/SCF/MO calculations on a series of tetrazaborolines are in general agreement with the assignment of normal rather than iso-derivatives.[14]

Preparation of the Diboron Compound, $Me_2N_4BBN_4Me_2$.—We have found that Me_2N_4BCl reacts under mild conditions with sodium amalgam to give $Me_2N_4BBN_4Me_2$.

The mass spectrum of the compound showed parent ions at *m/e* 192, 193, 194, and the latter ion was mass measured to 194·13675 a.m.u. ($C_4H_{12}N_8{}^{11}B_2$ requires 194·13711 a.m.u.). Fragments at *m/e* 137 and 108 are probably assigned to ions (1) and (2) respectively.


(1)


(2)

In addition, the mass spectrum showed peaks due to ions derived from $Me_2N_4B–O–BN_4Me_2$ and Me_2N_4BOH. These are $[Me_2N_4BOBN_4Me_2]^{\cdot+}$, $[MeNBOBN_3Me_2]^{\cdot+}$, $[MeNBOB(NMe)NCH_2]^+$, $[Me_2N_4BOH]^{\cdot+}$, and $[C_2H_7ON_2B_2]^+$.

The i.r. spectrum showed a band at 3420 cm^{-1} which probably arises from the presence of a small quantity of Me_2N_4BOH.

The ^1H n.m.r. showed a single methyl resonance at −3·4 p.p.m. from tetramethylsilane.

EXPERIMENTAL

Solvents and intermediates were dried and purified by standard procedures. Me_2N_4BH And Ph_2N_4BH were prepared as described previously.[1] $MeNH_2BH_2Cl$ Was prepared by the method of Nöth and Beyer,[15] m.p. 47°. MeN_3 Was prepared by treating aqueous sodium azide with dimethyl sulphate. (CAUTION: A recent serious **explosion** in these laboratories with pure azide has resulted in this work being discontinued.)

Preparation of 5-*Chloro*-1,4-*dimethyl*-Δ^2-*tetrazaboroline*.—In a typical experiment a heavy-walled glass ampoule of *ca.* 150-ml capacity was charged with triethylamine (4·6 g, 0·046 mol). Diethyl ether (20 ml), boron trichloride (2·7 g, 0·023 mol), methylamine (0·71 g, 0·023 mol), and methyl azide (1·31 g, 0·023 mol) were condensed in under vacuum, and the ampoule was sealed. It was then heated at 130 °C for 15 h; the product was worked up either by direct vacuum distillation of the products through a trap at −40° or alternatively by first filtering the ether solution in a dry nitrogen-filled glove-box. The crude product was further purified by vacuum fractionation through a trap at 0 °C, and collected in a trap at −40 °C. The yield of 26% was slightly improved by using $EtPr^i{}_2N$ instead of triethylamine (Found: C, 18·4; H, 4·5; B, 10·8; Cl, 24·6; N, 42·3. $C_2H_6BClN_4$ requires C, 18·1; H, 4·6; B, 8·1; Cl, 26·8; N, 42·3%). Molecular ions for $C_2H_6N_4BCl^+$ were observed in the expected isotopic ratios at *m/e* 131, 132, 133, 134.

Preparation of 5-*Bromo*-1,4-*dimethyl*-Δ^2-*tetrazaboroline*.—Freshly distilled 1,4-dimethyl-Δ^2-tetrazaboroline (0·95 g, 0·0097 mol) was dissolved in dry carbon tetrachloride (60 ml)

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[8] (*a*) M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 133; (*b*) J. S. Thayer and R. West, *Adv. Organometallic Chem.*, 1967, **5**, 169.

[9] (*a*) M. R. Booth and S. G. Frankiss in 'Spectroscopic Methods in Organometallic Chemistry,' ed. W. O. George, Butterworths, London, 1970, p. 200; (*b*) M. R. Booth and S. G. Frankiss, *Spectrochem. Acta*, 1970, **26***A*, 859.

[10] (*a*) J. R. Berscheid, jun., and K. F. Purcell, *Inorg. Chem.*, 1970, **9**, 624; (*b*) R. C. Wade, E. A. Sullivan, J. R. Berscheid, jun., and K. F. Purcell, *Inorg. Chem.*, 1970, **9**, 2146.

[11] S. S. Uppal and H. C. Kelly, *Chem. Comm.*, 1970, 1619.

[12] (*a*) J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205; (*b*) J. L. Burmeister, *Co-ordination Chem. Rev.*, 1968, **2**, 225.

[13] (*a*) M. F. Lappert and H. Pyszora, *J. Chem. Soc.* (*A*), 1968, 1024; (*b*) M. F. Lappert and H. Pyszora, *J. Chem. Soc.* (*A*), 1967, 854, and references cited therein.

[14] D. R. Armstrong, P. G. Perkins, J. M. Scott, and J. Stewart, unpublished results.

[15] H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 928.

in a 25-ml flask fitted with reflux condenser and nitrogen by-pass to maintain a nitrogen atmosphere. *N*-Bromosuccinimide (1·78 g, 0·01 mol) dried *in vacuo*, was added and the mixture was refluxed for 0·5 h. The solution was filtered in a glove-box under dry nitrogen, and the filtrate was distilled under reduced pressure, through a trap at −15 °C in which the *product* collected. It was further purified by several fractionations on the vacuum line and gave 0·77 g, 43% yield (Found: C, 13·8; H, 3·6; B, 7·7; Br, 43·2; N, 31·8. $C_2H_6BBrN_4$ requires C, 13·6; H, 3·4; B, 6·1; Br, 45·2; N, 31·7%). Molecular ions for $C_2H_6N_4BBr^+$ were observed in the expected isotopic ratios at *m/e* 175, 176, 177, 178.

Preparation of B-*Pseudohalogen Derivatives of* 1,4-*Dimethyl*-Δ^2-*tetrazaboroline*.—The general method involved the condensation of 5-chloro-1,4-dimethyl-Δ^2-tetrazaboroline into a flask containing a slight excess of the appropriate silver pseudohalide and benzene which had been dried and distilled from lithium aluminium hydride. The mixture was then refluxed under nitrogen for 3 h and then filtered; the filtrate was distilled under vacuum.

Me_2N_4BCN And $Me_2N_4B[SCN]$ melted just below room temperature. Me_2N_4BSeCN melted at 40°. Me_2N_4BCN showed parent ions at *m/e* 122 and 123, and $Me_2N_4B[SCN]$ showed parent ions at *m/e* 154 and 155.

Preparation of Me_2N_4BBN,Me_2.—Me_2N_4BCl (*ca.* 0·8 g) Was dissolved in dry ether *in vacuo* and an excess of 2% sodium amalgam was added to it; the mixture was shaken at room temperature for several days and then filtered in a dry-box. Excess of solvent was removed under reduced pressure to leave colourless, sublimable *crystals* (Found: C, 24·3; H, 6·0; B, 10·2; Cl, 0; N, 54·2. $C_4H_{12}B_2N_8$ requires C, 24·8; H, 6·2; B, 11·1; Cl, 0; N, 57·8%).

N.m.r. Spectra.—These were obtained on Perkin-Elmer R10 and R14 spectrometers operating respectively at 60 (^1H) and 19·25 (^{11}B), and 100 MHz (^1H). Spectra were obtained on pure liquids or solutions in deuteriochloroform. Proton chemical shifts were obtained with reference to internal tetramethylsilane, and ^{11}B shifts with reference to external BF_3,OEt_2.

Mass Spectra.—These were obtained on A.E.I. MS 2 and MS 9 mass spectrometers using gallium inlet or direct insertion systems. Mass measurement was carried out on prominent ions of $Me_2N_4BBN_4Me_2$.

Infrared Spectra.—These were recorded on a Grubb-Parsons Spectromaster grating spectrometer and on a Perkin-Elmer 337 grating spectrometer between 4000—400 cm^{-1} using thin films of pure liquid or mulls in Nujol or hexachlorobutadiene.

Raman Spectra.—These were recorded on a Cary 81 spectrometer equipped with a Spectra Physics 125 He–Ne laser source. Spectra were obtained on pure liquids in capillary cells. The frequency shifts (cm^{-1}), relative intensities in parentheses and polarisation data for the compounds are as follows.

Me_2N_4BCl: 2950(35)P, 2935(23), 2875(6), 2810(8)P, 1481(7)dP?, 1465(9)dP?, 1455(9), 1417(14)P, 1371(43)P, 1337(4)P, 996(14)P, 984(7)dP, 783(3)dP, 596(100)P, 455(28)P, 268(9)dP?, 248(11)dP?, 176(40)dP?

Me_2N_4BBr: 2946(19)P, 2802(3)P, 1484(6)dP?, 1460(7), 1451(7)dP, 1414(13)P, 1372(68)P, 1336(4)P, 1236(1), 1201(3)dP, 1099(1), 1056(1), 1000(8)P, 981(8)dP, 955(1), 781(4)dP, 586(100)P, 553(6), 374(36)P, 277(8)dP, 242(38)P, 232(16)dP, 148(50)dP.

$Me_2N_4B[CN]$: 2965(25), 2910(10), 2241(100), 1535(13), 1483(20), 1465(20), 1428(23), 1372(60), 1342(13), 1290(2), 1230(7), 1160(10), 1005(11), 660(17), 640(22), 614(74), 500(22), 480(22), 445(21), 418(30), 375(11).

$Me_2N_4B[SCN]$: 2950(10), 2915(2), 2115(19), 2090(22), 1530(11), 1503(35), 1468(10), 1455(6), 1420(25), 1372(100)P, 1333(3), 1270(18), 985(3), 890(3), 625(11), 597(43), 416(17)P?, 290(38)dP, 255(3), 225(5).

$Me_2N_4B[SeCN]$: 2960(19), 2240(55), 1435(24), 1360(88), 1210(16), 660(13), 641(36), 609(100), 485(16), 417(40), 285(16).

Ultraviolet Spectra.—These were obtained on Unicam SP 800, Unicam SP 1800, and Perkin-Elmer 450 spectrophotometers in the gas phase. A 10-cm gas cell was used for some of the compounds.

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