STUDIES ON THE CYCLOTETRAZENOBORANE RING

AND RELATED SYSTEMS

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ABSTRACT

Work done previously on cyclotetrazenoboranes and other boron-nitrogen ring systems, excluding borazines, has been comprehensively reviewed.

The frequencies of the B-H stretching frequencies in Me_2N_4BH and Ph_2N_4BH have been studied in a range of solvents, and are shown to increase with increasing polarity of the solvent. No correlation is observed with the dielectric relationship $(\varepsilon-1)/(2\varepsilon+1)$ and non-linear relative shift (B.H.W.) plots are obtained against N-H, C=O, P-H, and transition metal hydride M-H vibrations. The results suggest that solvent interactions occur with parts of the molecules remote from the B-H bond, and are unlikely to be due mainly to dielectric effects.

Two routes for the preparation of B-substituted cyclotetrazenoboranes have been developed. The action of Grignard reagents on derivatives of the type R_2N_4BH produces compounds R_2N_4BR' in high yield, through the intermediate formation of magnesium containing complexes. Thermal degradation of a diorganoboron azide in the presence of an organic azide also produces boron-substituted cyclotetrazenoboranes.

The preparation of B-halogeno substituted cyclotetrazenoboranes has been achieved by two routes. Direct reaction of a derivative

of the type R_2N_4BH with N-bromosuccinimide has led to isolation of the very readily hydrolysable compound R_2N_4BBr. Dehydrohalogenation of a primary amine $-BCl_3$ adduct in the presence of triethylamine has also led to the isolation of a B-chloro cyclotetrazenoborane derivative.

Attempts to prepare unsymmetrically N-substituted cyclotetrazenoboranes by the reaction of a primary amine-borane (RNH_2BH_3) with an organic azide ($R'N_3$) have led to the isolation of mixtures of cyclotetrazenoborane derivatives RRN_4BH, $RR'N_4BH$ and $R'R'N_4BH$.

Throughout the work the U.V., I.R. and N.M.R. spectra of the compounds have been studied.

A detailed mass-spectrometric study of both B- and N-substituted cyclotetrazenoboranes has been made and a generalised fragmentation pattern has been derived. The use of computer techniques was also established to aid the handling and interpretation of the mass spectral data.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTORY SURVEY

BORON NITROGEN RING SYSTEMS

The systematic study of boron-nitrogen compounds had its origins in the discovery of borazine by Stock in 1926,[1] but since that time the field of boron-nitrogen chemistry has become extensive and is rapidly expanding.[2,3,4,5]

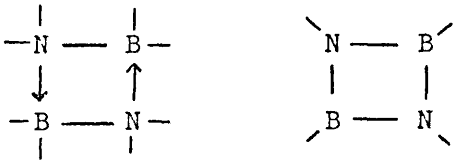
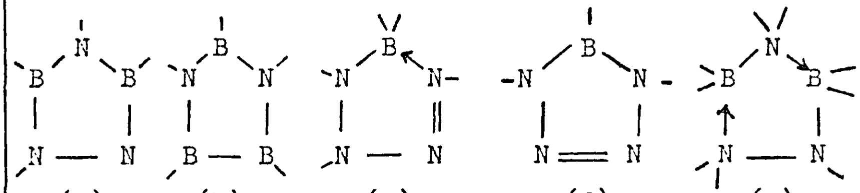
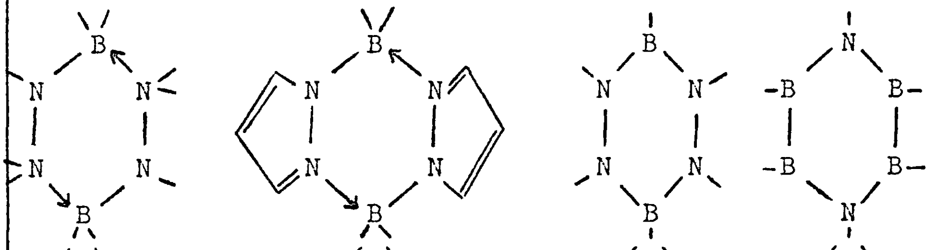
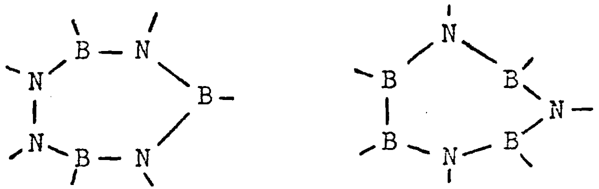
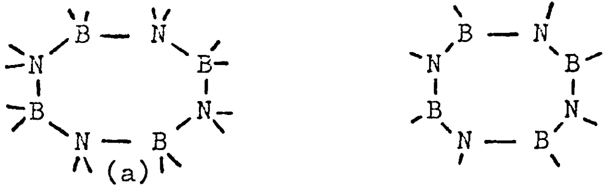
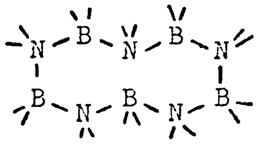
Boron-nitrogen heterocycles other than borazines have only recently been described and it is this area of chemistry which will be reviewed in some detail. Only cursory mention will be made of rings in which both the boron and nitrogen atoms are in four-coordinate environments dependent on dative π-bonding for their existence. In view of the number of adequate reviews[2,3,4,5,6,7,8,9] on the chemistry of the borazine ring system and its saturated derivatives, these will be excluded from the present survey, but relevant sections of this and other pertinent areas of chemistry will be presented when appropriate. The boron-nitrogen heterocyclic ring systems known at the present which will be reviewed here are summarised in Table 1-A.

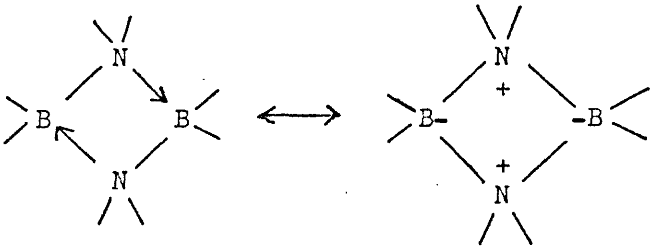
Four-membered boron-nitrogen ring systems

a) Boron-nitrogen cyclic dimers

Many aminoboranes are known to exist as dimers.[2,3,4,5,6,7,8,9,10] The molecules contain a four-membered B-N ring system, involving dative bonding through the lone pair of electrons on the nitrogen atom to the available p_z orbital of the boron atom as shown in equation 1-1.

TABLE 1-A

No. of Atoms in Hetero-cyclic Ring	Ring Systems Known
4	 (a) (b)
5	 (a) (b) (c) (d) (e)
6	 (a) (b) (c) (d)
7	 (a) (b)
8	 (a) (b)
10	

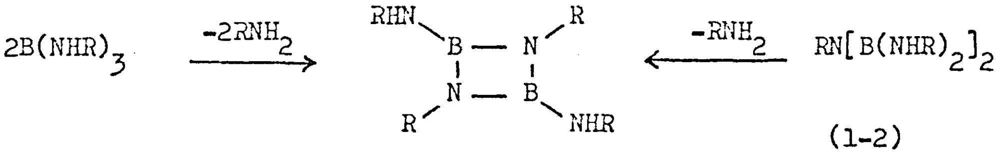


(1-1)

The crystalline and molecular structure of dimeric dimethylaminoboron dichloride, $[BCl_2N(CH_3)_2]_2$ was proved to contain a four-membered ring of boron and nitrogen atoms by X-ray analysis.[11] The parent ring compound $(BH_2NH_2)_2$ has recently been prepared[12] by the pyrolysis of cyclopentaborazane, but was thermodynamically unstable, being converted to the cyclotriborazane on standing in solution at room temperature. Pyrolysis of the cyclodiborazane led to the formation of the monomer BH_2NH_2 but no 1,3,2,4-diazadiborine was isolated.

b) s-diazadiborines

The first well-characterised example of an s-diazadiborine $(-BR-NR'-)_2$ was synthesised by Lappert and Majumdar[13,14,15] by the pyrolysis of either tris (t-butylamino) borane or bis (di-t-butylaminoboryl)-t-butylamine as shown in equation 1-2.



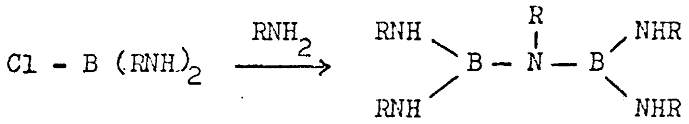
(1-2)

(1 - I)

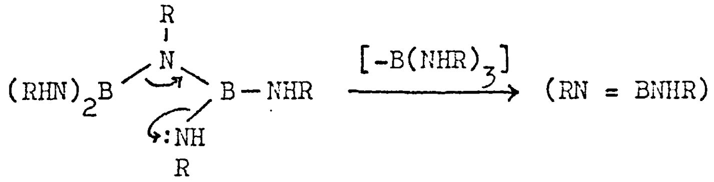
where $R = t\text{-}C_4H_9$

This was unusual in that borazines would normally be expected to be produced from such reactions, and a three-stage reaction scheme was postulated to account for the various polyborazyne compounds that could be formed, e.g.

1. Intermolecular condensation with the formation of a compound having a B-N-B skeleton.



2. Intramolecular 1,3-nucleophilic rearrangement

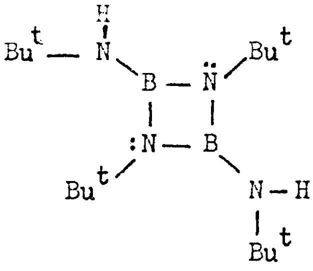


3. Polymerisation of the borazyne

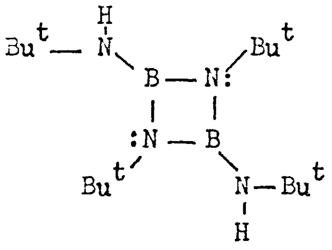
$$(RN = BNHR) \longrightarrow \frac{1}{n}\ (R-\overset{|}{N}-\overset{|}{B}-NHR)_n$$

Evidence for the mechanism rested mainly on the isolation of diborylamines as reaction intermediates, although these were only isolable under sterically favourable conditions.

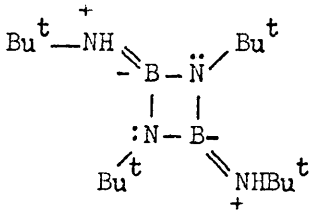
Structure 1-I was proved by elemental analysis, molecular weight determinations, infrared, nuclear magnetic resonance and mass spectrometry. 1-I was found to be diamagnetic implying that electron delocalisation within the ring was not significant and its stability was attributed to π-bonding, largely of an exocyclic nature. Infrared and nuclear magnetic resonance evidence indicated that 1 - I was a mixture of geometrical isomers 1-Ia and 1-Ib. The isomers were considered to exist because of restricted rotation about the exocyclic multiple bonds as shown in structure 1-Ic.



1-Ia



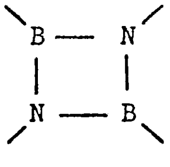
1-Ib



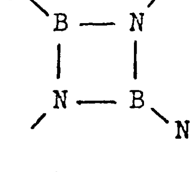
1-Ic

Molecular orbital calculations on the parent ring compound $(BHNH)_2$[16,17] indicated a square planar arrangement of atoms and suggested that the two π-orbitals which would be degenerate in isoelectronic cyclobutadiene were split considerably. A charge transfer transition between these levels was forbidden, but two allowed π - π* transitions close in energy should be found in the molecular U.V. spectrum.

Recent calculations by Baird et al.[18] on this system allowed also for the presence of exocyclic N atoms bonded to the boron atoms in the ring, as shown in structures 1-II and 1-III.



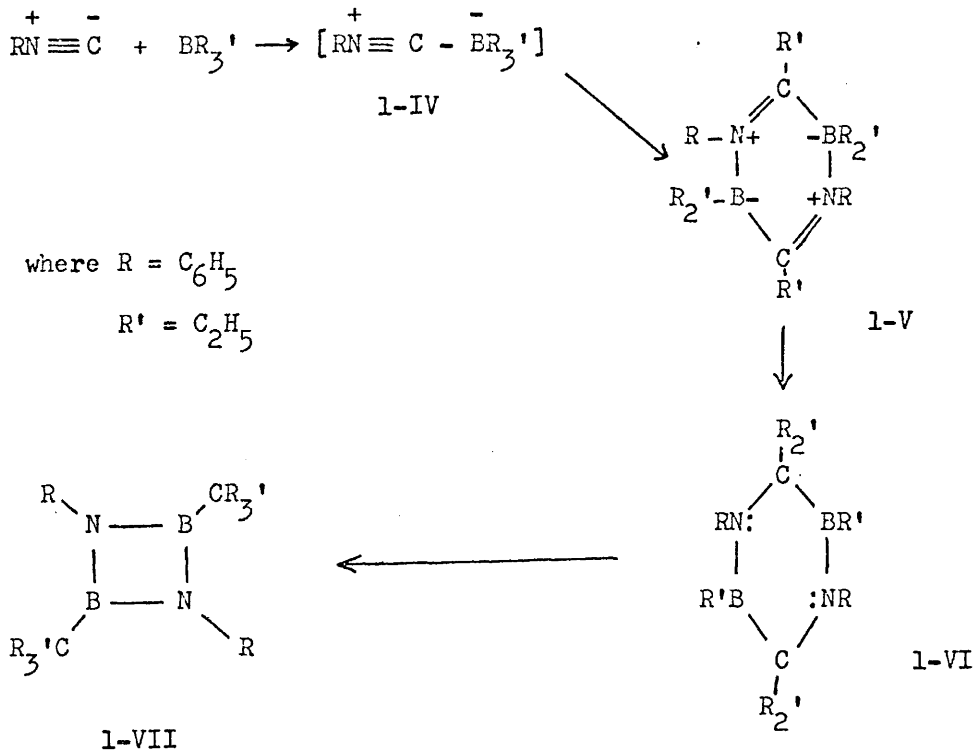
1-II



1-III

In the model B-N system each boron contributes one p_π orbital and zero electrons to the conjugation network and each nitrogen contributes one p_π orbital and two electrons. The calculations predicted an absence of a $(4n + 2)$ π-electron rule for aromaticity and a predominance of exocyclic over endocyclic π-bonding in the substituted rings in agreement with the qualitative conclusions made by Lappert. For ring system 1-III with exocyclic N atoms attached to the B atoms the exocyclic π-bond order was greater than the ring π-bond order and the latter was lower than for the unsubstituted ring 1-II, and hence it was concluded that the π-bonding in the ring was appreciably decreased by the presence of lone pair atoms at each boron atom. This was in direct contrast to the results obtained for aromatic hydrocarbon analogous systems.

1,3-Diaza-2,4-diborine ring systems have now also been prepared without the presence of lone pair atoms attached to the boron atom.[19] Isocyanides behave as Lewis bases towards diborane, forming adducts of type 1-IV, which can undergo a series of isomerisations at successively increasing temperatures to produce compounds 1-V, 1-VI and 1-VII as illustrated in the reaction scheme:-



where $R = C_6H_5$

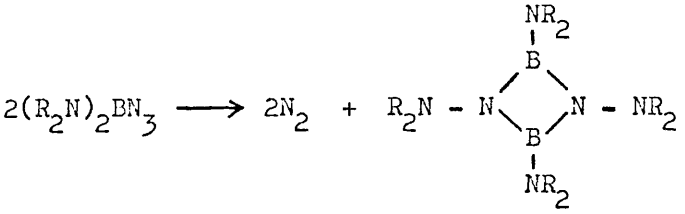
$R' = C_2H_5$

Compound 1-IV could only be identified fleetingly by its low temperature 'H N.M.R. and was rapidly converted at room temperature to 1-V, which was itself converted to 1-VI at 180°. The 1,3-diphenyl-2,4-bis (triethylcarbinyl)-1,3-diaza-2,4-diborine 1-VII was obtained by heating 1-VI in an evacuated sealed tube in an oven at 300° for five minutes, and was confirmed by analysis, m. wt., and its infrared spectrum. The U.V. absorption spectrum fell in intensity and its wavelength maximum was close to that of the anilinium ion suggesting little extension of the aromatic system into the adjacent nitrogen. The ^{1}H N.M.R. and ^{11}B N.M.R. spectra were readily rationalised in terms of the molecule, and its mass spectrum although not showing parent ions, possessed fragment ions containing two boron atoms. Compound 1-VII was found to be chemically very stable and unreactive when treated with a wide variety of common reagents, such as anhydrous hydrogen chloride, 37% hydrochloric acid, 50% methanolic potassium hydroxide, bromine in carbon tetrachloride solution and chromic acid, but on standing with chromic oxide in pyridine a small amount of 3-pentanone was isolated.

Preliminary evidence from ^{11}B N.M.R. and U.V. spectra did not suggest that π back-bonding of nitrogen electrons to the boron atoms occurred extensively. Molecular models indicated that stereochemical constraints imposed on attainment of planarity of the three rings might be the deciding factor.

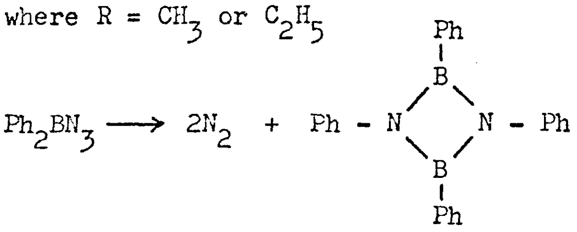
Paetzold[20] has over the recent years published a series of papers on boron azides, their preparations, photolytic and thermal decompositions, and the mechanisms of their thermal decompositions. The thermal and photolytic decomposition of a number of boron azides gave rise to further new diazadiborines.

Photolytic decompositions of $[(CH_3)_2N]_2BN_3$, $[(C_2H_5)_2N]_2BN_3$ and $(C_6H_5)_2BN_3$ gave high yields of the 1,3,2,4-diazadiborine ring system as shown in equations 1-3 and 1-4.



(1-3)

where R = CH_3 or C_2H_5



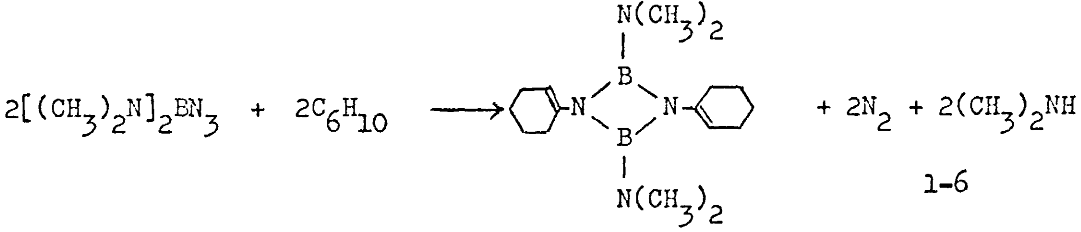
(1-4)

The constitution of the diazadiborine from bis (diethylamido)-borazide was established by saponification, which yielded quantitatively 1,1-diethylhydrazine and diethylamine as shown in equation 1-5. The products of the photolytic reaction proved

$$[(C_2H_5)_2NN - B - N(C_2H_5)_2]_2 + 6H_2O \rightarrow 2B(OH)_3 + 2(C_2H_5)_2NH + 2(C_2H_5)_2NNH_2 \quad (1\text{-}5)$$

that a transfer of the amido group from the B atom to the α N atom of the azide occurred almost exclusively, since in the formation of tetra-amidodiazadiborines other dissociation products were found in less than 3% yield. This indicated that nitrenes were not important intermediates and transfer of the amide group to form an N-N bond showed a new type of reaction involving a Curtius-type rearrangement.

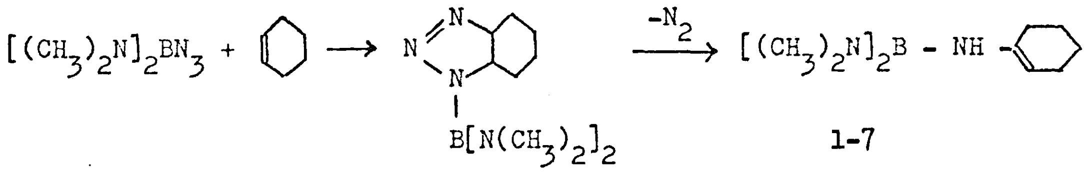
Thermal decomposition of boron azides of empirical formula X_2BN_3, where X = Cl, CH_3O, $(C_2H_5)_2N$ again furnished proof of transfer of group X from the B atom to the α-N atom of the N_3 group, but diazadiborines were not isolated. However if bis (dimethylamido) borazide was decomposed in cyclohexene then a diazadiborine of unexpected composition 1-VIII was formed as depicted in equation 1-6.



1-6

1-VIII

It was considered that the first step of the reaction was analogous to that of olefins with aromatic azides, namely the formation of a triazolin followed by evolution of nitrogen to yield an eneamine as represented in equation 1-7.



1-7

These eneamines then reacted in a manner typical for boron compounds with evolution of $(CH_3)_2NH$ and the formation of a boronimide, which dimerised to the diazadiborine ring.

Paetzold performed a systematic investigation of the thermal decomposition of diarylboron azides. Evidence for the migration of aryl groups from the B atom to the α N atom of the N_3 group was provided by a saponification study on the compounds. By heating diarylboron azides to 200°C for 2 → 3 hours in a sealed tube a mixture of rearrangement products was obtained. For example, Ph_2BN_3 gave a mixture of the diazadiborine and borazine ring systems, the former being preponderant. However, if the decomposition was performed by refluxing for a day at 120°C the formation of the borazine was completely suppressed in favour of the four-membered ring compound, the reaction being identical to that for photolytic decomposition (equation 1-4). Further, the pyrolysis of pure diazadiborine at 200°C did not yield a borazine. 5 → 8% of the products formed, which could not have arisen from the rearrangement process, were attributed to some "nitrene" formation as shown in the following reaction sequence 1-8.

$$Ar_2BN_3 \rightarrow [Ar_2B - \bar{\underline{N}}] \rightarrow Ar_2BNH_2 \xrightarrow{\text{saponification}} NH_3 \qquad 1\text{-}8$$

In general, thermal decomposition of alkyl aryl boron azides resulted in disproportionation to dialkyl- and diarylboron azides followed by their characteristic decomposition.

Methyl phenyl boron azide decomposed to yield a mixture of dimethyl diphenyl diazadiborine and trimethyl triphenyl borazine. Thermal rearrangement products such as borazines were obtained from dialkyl- or diaryl-boron azide pyridine adducts but no diazadiborine products were isolated.

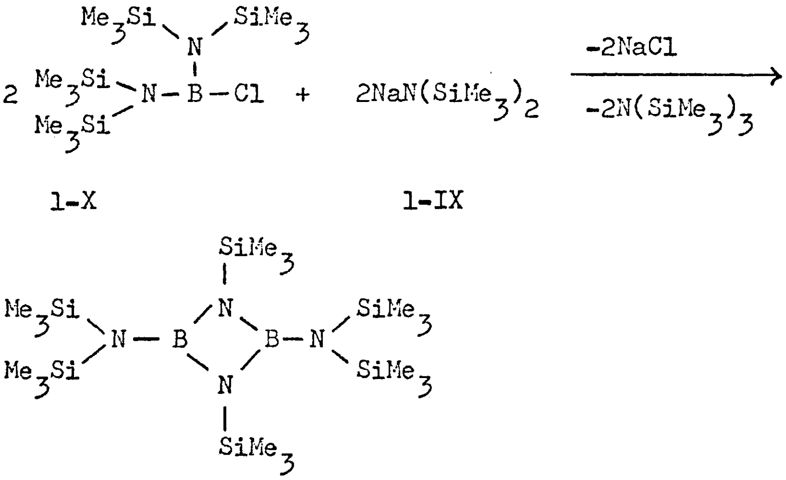
The formation of boron imides as intermediates has now been well established by their capture by 1,3-dipolar systems[21,22,23] to be described later, and by their isolation as stable entities capable of independent existence, for example $[C_6F_5B = NAr]$[24]. The mechanism of the thermal rearrangement of the azides to boronimides and four-membered ring systems was considered in some detail and will be discussed further in Chapter 3.

Little of the chemistry of the diazadiborines prepared by Paetzold has been studied, other than their hydrolysis already mentioned. The tetraryl diazadiborines, except the sterically hindered o-tolyl derivative, were found to be extremely sensitive to oxygen. For example $(PhB - NPh)_2$ yielded N_2, biphenyl (Ph - Ph) and triphenyl boroxine $(PhBO)_3$.

The compound hexakis trimethylsilyl-1,3-diaminocyclo-2,4-diboradiazetane 1-XI has been prepared[25,26,27] by the general route of treating an alkali metal bis (trimethyl silyl) amide 1-IX with a boron halide to form initially the bis [bis(trimethylsilyl) amino] haloborane, which could be converted to 1-XI by either[25] more vigorous reaction with further 1-IX or[26,27] by thermal condensation and elimination of trimethyl silyl halide. Examples of these reactions are shown in equations 1-9, 1-10 and 1-11.

$$BCl_3.Et_2O + 2NaN(SiMe_3)_2 \longrightarrow ClB[N(SiMe_3)_2]_2 + 2NaX + Et_2O \qquad (1\text{-}9)$$

1-IX 1-X



1-X 1-IX

(1-10)

1-XI

$$BF_3 + 2[(CH_3)_3Si]_2NLi \longrightarrow 2[(CH_3)_3Si]_2N - \underset{\overset{\downarrow}{1\text{-}XI}}{B(F)} - N[Si(CH_3)_3]_2 \qquad (1\text{-}11)$$

Compound 1-XI was a white solid (M.pt. = 212°C) sublimable at 110°C/0.1 mm. The ' H N.M.R. indicated that N atoms of the ring system were less effective in withdrawing electrons from the protons than the exocyclic nitrogen atoms, thus suggesting that electron delocalisation in the ring was not extensive, in agreement with previously mentioned conclusions. Dialkylamino substitution tended to cause a decrease in the acceptor properties of the boron, as shown by both chemical properties and N.M.R. spectroscopy, and therefore compounds of the type $R_2NB(Cl)N(SiMe_3)_2$ did not condense and the $SiCH_3$ signal was found at higher field. The relative ease of thermal condensation of B - N - Si compounds and their N.M.R. spectra indicated that the π-electron density at X in the scheme

$$X = N - Si \longleftrightarrow X - \overset{-}{N} - Si \longleftrightarrow X - N = Si$$

increased in the sequence $X = H < Me_3Si < Si(Me_3)_2N(F)B- < Si(Me_3)_2N(Cl)B- < Cl_2B-$, and that the weaker the N - Si (p → d) π bonding so the easier was the splitting of the silyl group by thermal condensation.

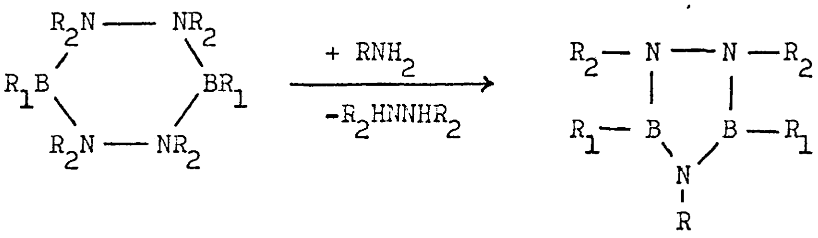
A recent X-ray analysis by Hess[28] showed 1-XI to be a monoclinic system with four molecules in the unit cell. The previously proposed structure was confirmed in that the four-membered ring and the substituents at nitrogen were co-planar. The average bond lengths found were N-N (endocyclic) 1.47, B-N (exocyclic) 1.43, N-Si 1.75, Si-C 1.88 Å. The short exocyclic bond tended to confirm the conclusion of exocyclic multiple bonding, although surprisingly the substituents on the

B and N atoms were shown to be mutually perpendicular.

Five-membered boron-nitrogen ring systems

a) 1,3,4-triaza-2,5-diborines

Only two examples of the preparation of this system have been reported 1-XII and 1-XIII. The amminolysis of a 1,2,4,5-tetraza-3,6-diborine[29] as shown in equation 1-12, and also the controlled

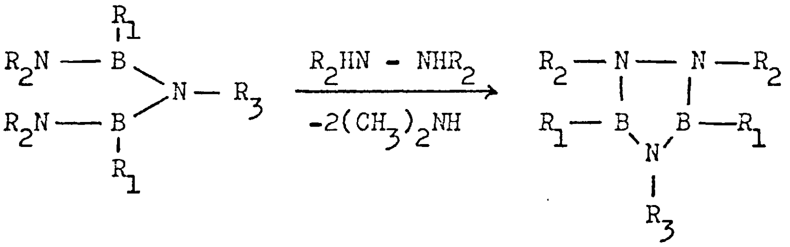


(1-12)

1-XII

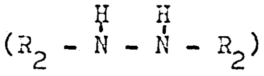
(where R = cyclohexyl, $R_1 = C_6H_5$, $R_2 = CH_3$)

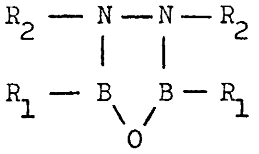
hydrazinolysis[30] of bis-(dimethylamino-phenyl-boryl) amine, as shown in equation 1-13. Compounds 1-XII and 1-XIII proved to be



(1-13)

1-XIII

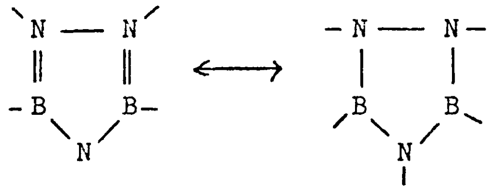
(where $R_1 = C_6H_5$, $R_2 = CH_3$ and R_3 = H) extremely sensitive to hydrolysis, probably yielding initially the ring compound 1-XIV; the remaining B-N bonds were then further hydrolysed to the symmetrical hydrazine ($R_2 - \overset{H}{N} - \overset{H}{N} - R_2$) and



(where $R_1 = C_6H_5$ and $R_2 = CH_3$)

1-XIV

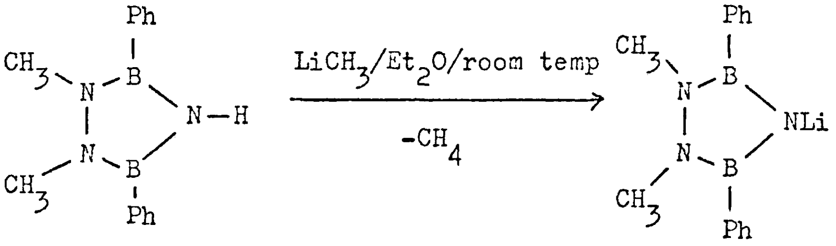
phenyl boronic acid $[PhB(OH)_2]$. The triazadiborines were relatively stable towards pyrolysis, and it was postulated that the stability of this ring was attributable to a substantial degree of resonance stabilisation as indicated in equation 1-14. The infrared bands in the 1400 cm^{-1} region tended to confirm this,



(1-14)

as this was considered to show the presence of a B = N stretching frequency.[31] More recently Nöth and Regnet[32] have considered the chemistry of 2,5-diphenyl-3,4-dimethyl-cyclo-1,3,4-triaza-2,5-diborine (TADBH) 1-XIII in some detail. Cyclo-1,3,4-triaza-2,5-diborines are isoelectric with the cyclopentadienyl anion and could be considered as a 6π electron system. Molecular orbital calculations[33] on this system indicated considerable energy difference between the lower occupied and higher unoccupied antibonding orbitals.

The reaction of (TADBH) 1-XIII with methyllithium in diethyl ether solution at room temperature gave the derivative (TADB. Li) 1-XV, metallated in the 1 position as shown in equation 1-15.

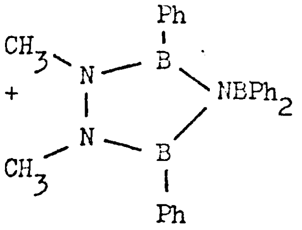


(1-15)

1-XV

It was discovered further that the general reaction of TADB.Li with non metal and metal halides was to produce the corresponding 1-substituted derivatives. For example, the (TADB.Li) 1-XV reacted readily with diphenyl boron chloride as illustrated in equation 1-16 to give a very stable triborylamine 1-XVI. Its stability was attributed to each boron

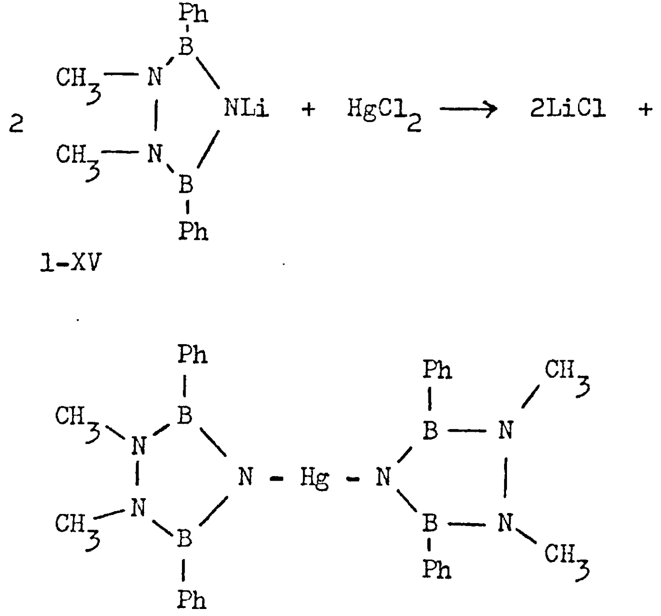
(1-XV) + $Cl_2BPh_2 \rightarrow$ LiCl +



(1-16)

1-XVI

atom being coordinated to a nitrogen atom. (TADB.Li) 1-XV also reacted with $HgCl_2$ as shown in equation 1-17, to yield the crystalline compound 1-XVII which was monomeric in benzene.


1-XV

1-XVII

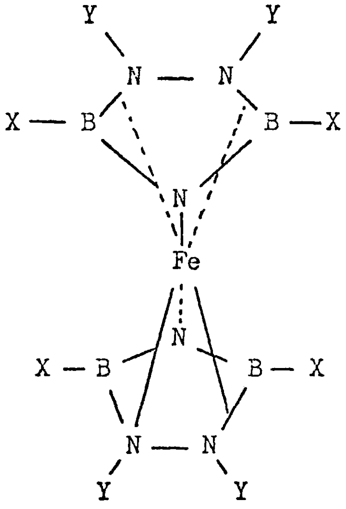
(1-17)

The reaction of (TADB.Li) (XV) with $FeCl_2$ was of particular interest since π bonded systems could possibly be formed, and it was found that from this reaction bis (2,5-diphenyl-3,4-dimethyl-cyclo-1,3,4-triaza-2,5-diborinyl) iron [II], 1-XVIII could be isolated as a dark brown solid as shown in equation 1-18. The 'H and "B N.M.R. spectra for 1-XVIII were similar to those of 1-XIII

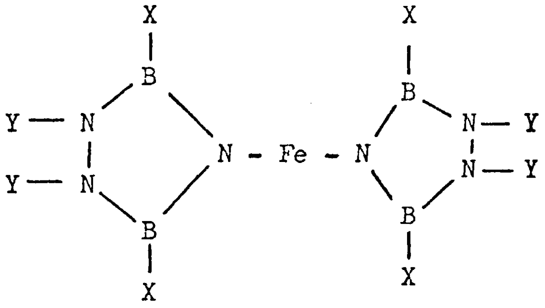
$$2[(TADB)Li] + FeCl_2 \longrightarrow 2LiCl + \underset{\text{1-XVIII}}{(TADB)_2Fe} \qquad (1\text{-}18)$$

and it was shown to be diamagnetic by the N.M.R. technique of

Fritz[34] in freshly prepared solutions. Compound 1-XVIII was soluble in solvents such as benzene, toluene, chloroform, T.H.F., or ether, but insoluble in pentane or hexane. It could not be sublimed, was attacked only slowly by hot water and not at all by alcohols and amines, but disintegrated rapidly in acid. Heating 1-XVIII with cyclopentadiene did not yield any ferrocene. Several possible structures for 1-XVIII were considered. In view of the predicted isosteric nature of the $(TADB)^-$ anion and the cyclopentadienyl anion the possibility of a metallocene type structure, one isomer of which is shown in 1-XIX, was considered. Structure 1-XX was thought unlikely as it would have been expected



1-XIX



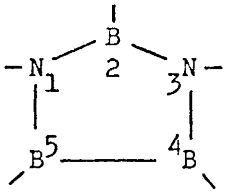
1-XX

to be paramagnetic, easily hydrolysed and with cyclopentadiene would react to give ferrocene. Other structures were eliminated by infrared and N.M.R. considerations. The fact that the compound was found to be monomeric and diamagnetic, as would be expected for a low-spin complex, favoured the metallocene structure 1-XIX, and this was further supported by its hydrolytic stability and lack of reactivity with cyclopentadiene.

The anomalous paramagnetic behaviour observed for the solid product on storing for several months was interpreted on the basis of a slow decomposition. The planarity of the TADB rings in 1-XIII and 1-XVIII was not certain.

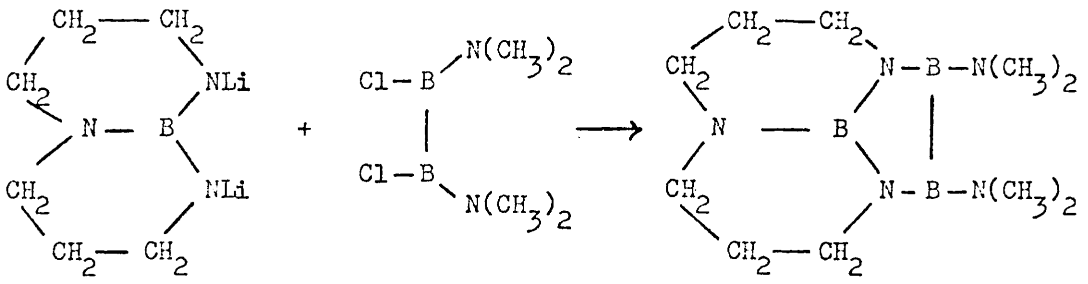
b) 2,5-diaza-1,3,4-triborines

The first reported preparation of the 2,5-diaza-1,3,4 triborine ring system 1-XXI utilised the N-metallated derivative of triazaboradecalin 1-XXII prepared by Niedenzu et al.[35]



1-XXI

Nöth and Abeler[36] reacted 1-XXII with sym. bis (dimethylamino) diboronchloride as shown in equation 1-19, to yield 1,2-bis (dimethylamino)-perhydro-2a,5a,8a-triaza-1,2,8b-triboracenaphthylene 1-XXIII.

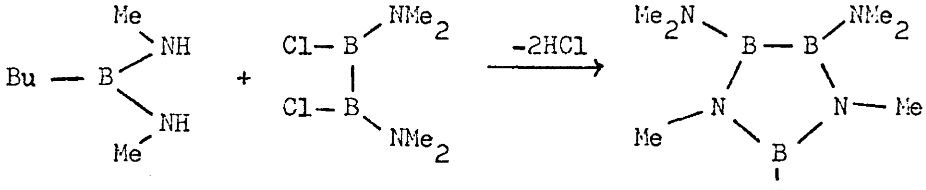


(1-19)

1-XXII 1-XXIII

The structure of 1-XXIII was confirmed by analysis, M. Wt., I.R. and N.M.R.

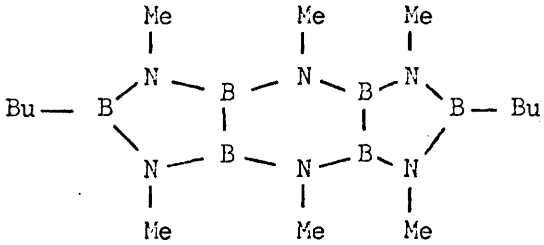
Recently, it has been reported[37] that the reaction of Bu-B $(NHMe)_2$ with $Cl(NMe_2)B$-$B(NMe_2)Cl$, which it had been anticipated might lead to the ring system 1-XXI by dehydrohalogenation in the presence of triethylamine as in 1-20, led instead to the formation



(1-20)

1-XXIV

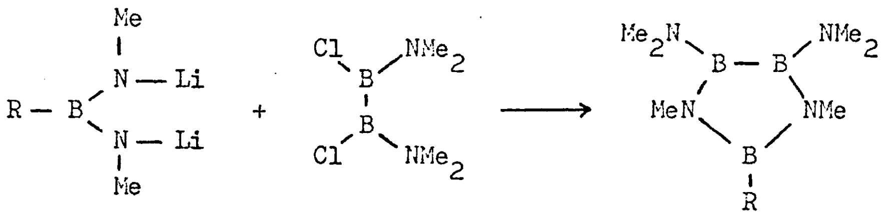
of the new compound 1-XXV. This contained two 2,5-diaza-1,3,4-



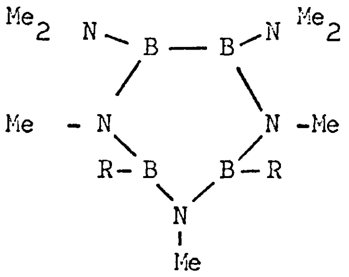
1-XXV

triborine rings condensed with a six membered 1,4-diaza-2,3,5,6-tetraborine ring system. The infrared, 'H and "B N.M.R. spectra were consistent with structure 1-XXV, and tended to eliminate a possible cage structure containing five, six and eight-membered boron-nitrogen ring systems.

The reaction of methyl lithium converted $MeB(NHMe)_2$ and $BuB(NHMe)_2$ to the N-lithium derivatives which in turn reacted with 1-XXIV as in 1-21 to yield the required 2,5-diaza-1,3,4-triborines 1-XXVIa and 1-XXVIb. These structures were consistent with the observed infrared and N.M.R. spectra. Side products of these reactions gave rise to compounds 1-XXVIIa and 1-XXVIIb which were derivatives of the new 1,3,5-triaza-2,4,6,7-tetraborine ring system.


(1-21)

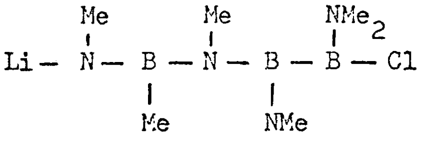
1-XXVIa R = Me
1-XXVIb R = Bu



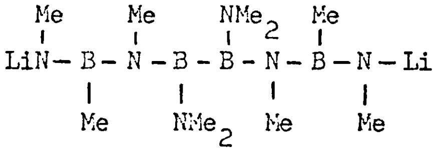
1-XXVIIa R = Me

1-XXVIIb R = Bu

The products 1-XXVIa and 1-XXVIb were probably formed by lithium chloride abstraction of the secondary product 1-XXVIII, whilst 1-XXVIIa and 1-XXVIIb were accounted for by Li_2NR abstraction from secondary product 1-XXIX or by insertion of a monomeric $RB-NCH_3$ group in the five-membered systems 1-XXVIa and 1-XXVIb.


$Li-\overset{Me}{N}-\underset{Me}{B}-\overset{Me}{N}-\underset{NMe}{B}-\overset{NMe_2}{B}-Cl$

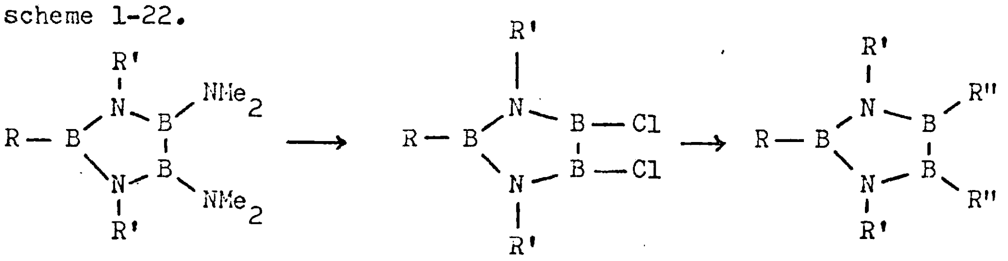
1-XXVIII


$LiN-\underset{Me}{B}-\overset{Me}{N}-\underset{NMe_2}{B}-\overset{NMe_2}{B}-\underset{Me}{N}-\overset{Me}{B}-\underset{Me}{N}-Li$

1-XXIX

Other attempted reactions for the preparation of the ring system 1-XXVI were unsuccessful.

A study of the substitution chemistry of the 1,3-diaza-2,4,5-triborine ring system indicated that replacement of the 4,5-dimethylamino substituents in compounds 1-XXIII, 1-XXVIa and 1-XXVIb using a variety of halogenating reagents led in general to only partial replacement, or the formation of adducts, although in some cases disubstitution could be carried out. Further, replacement of the halogen substituents by alkyl groups was effected only by the use of aluminium trialkyls. In this way the fully alkylated derivative could be produced by the reaction scheme 1-22.

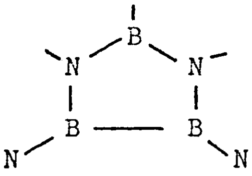


(1-22)

where R = Me or Bu, R' = Me

The order of stability of the compounds produced was dependent on the 4 and 5 substituents and decreased in the order $NMe_2 > Cl > alkyl$.

It would be of interest to know whether system 1-XXI was more stable than that depicted in equation 1-14. Molecular orbital calculations have been reported by two research groups with conflicting conclusions. Bochvar et al.[38] calculated that compounds of type 1-XXI should have considerable stability and be preparable. Balaban[39] however has indicated that contrary to these calculations the monocyclic compounds containing 3B and 2N heteroatoms were expected to be unstable whereas compounds containing 3N and 2B heteroatoms shown in equation 1-14 could be considered to have a 6π aromatic electron system. In a later paper published after both of the five-membered rings had been synthesised[40], Balaban rationalised the stability of the ring compound containing 3B and 2N atoms to the presence of the amino groups attached to the boron atoms. The reduction in stability recently observed for 1,2,3-trialkyl-1,3,2,4,5-diazatriborine ring systems with the substitution order $NR_2 > Cl > R$ in the 4,5 position indicated that this was a series of decreasing resonance stability. New molecular orbital calculations were considered for systems 1-XXI and 1-XXVIc.

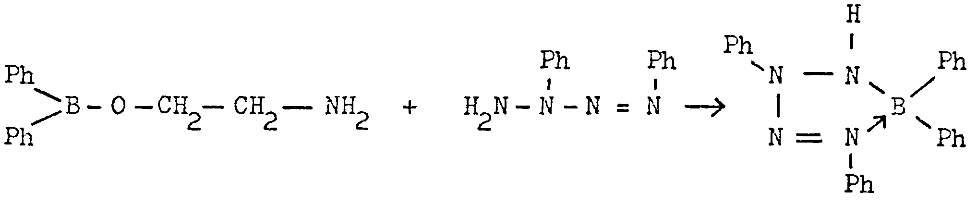


1-XXVIc

The calculations predicted a lack of aromaticity for the systems, being unstable relative to borazines, and showed the compounds to be typical of diboron-4-compounds, $R_2B_2Y_2$ (where Y = NR_2, OR, Cl, R). In agreement with the conclusions by Balaban and Simon,[40] the calculations clearly indicated that the bis-(dimethylamino-) derivatives 1-XXVIc should be more stable than those for 1-XXI. Good agreement was obtained between the calculated and predicted first electronic (π - π*) transitions for the derivative 1-XXVIa.

c) 1-bora-2,3,4,5-tetraza-4-cyclopentene

This system has been isolated[41] from the reaction of β-aminoethyl-diphenyl borinate with 2,4-diphenyl-tetrazene as indicated in equation 1-23. The 1,1,3,5-tetraphenyl-1-bora-2,3,4,5-tetraza-4-cyclopentene 1-XXX was isolated as a yellow solid,

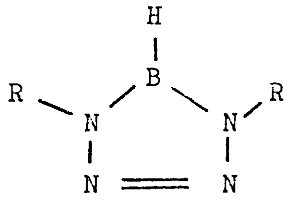

(1-23)

1-XXX

m.pt. 130° with decomposition. The diphenyl boryl group could be replaced by a heavy metal atom using aqueous solutions of heavy metal salts. Only those metal ions participated in this reaction that could form stable complexes with the chelate forming compound involved in 1-XXX.

d) The Cyclotetrazenoborane (C.T.B.) -Ring System

The discovery of this five-membered ring system 1-XXXI



1-XXXI

containing one boron and four nitrogen atoms[21,22] was the result of a systematic study of the reactions of decaborane with a variety of ligands. The reaction of phenyl or methyl azides caused the cleavage of decaborane with the production of the novel heterocycle R_2N_4BH as shown in equation 1-24. The experiment could be performed either in refluxing toluene or in

$$B_{10}H_{14} + 3RN_3 \longrightarrow R_2N_4BH + H_2 + 2N_2 + [R,N,B_9,H_{11}] \qquad (1\text{-}24)$$

where R = Ph or Me

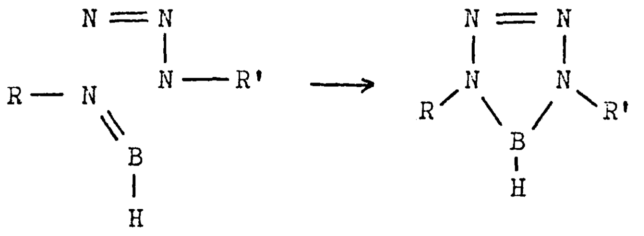
a sealed ampoule in the absence of solvent at 50°C. Nitrogen and hydrogen were evolved in approximately the molar ratio 2:1, but the nature of the polyborane residue was not established. The reaction was considered to proceed through the formation of a monomeric precursor of triorgano borazine [$RN = BH$] which then added on a molecule of organic azide. The reaction of organic azides with primary amineboranes which again could eliminate hydrogen to yield monomeric borazine precursors, gave the cyclotetrazenoborane ring system in excellent yield, as shown in equation 1-25. The reaction of aniline borane and methyl azide

$$RNH_2BH_3 + RN_3 \longrightarrow R_2N_4BH + 2H_2 \quad . \quad (1\text{-}25)$$

where R = Me or Ph

gave rise to 2-methyl,5-phenyl cyclotetrazenoborane. This product was also obtained by refluxing aniline hydrochloride, lithium borohydride and methyl azide in diethyl ether solution. The reaction mechanism postulated for the reaction of an amine with an organic azide was as shown in reaction scheme 1-26.

$$RNH_2BH_3 \longrightarrow [RN = BH] + 2H_2$$



(1-26)

In the light of evidence now available this however is probably an oversimplification (see Chapter 6).

Similarly a mechanism for the cleavage of decaborane by organic azide was thought to proceed by the initial elimination of hydrogen from decaborane and two moles of organic azide to give a typical di-ligand adduct which eliminated two moles of nitrogen to form an unstable intermediate. This cleaved to give the monomeric organoborazyne and an unstable polyborane fragment which reacted further as shown in the following scheme, 1-27.

$$B_{10}H_{14} + 2RN_3 \longrightarrow (RN_3)_2B_{10}H_{12} + H_2$$

$$(RN_3)_2B_{10}H_{12} \longrightarrow (RN)_2B_{10}H_{12} + 2N_2$$

$$(RN)_2B_{10}H_{12} \longrightarrow [RN = BH] + [R,N,B_9,H_{11}] \qquad (1\text{-}27)$$

where R = Me or Ph

The organoborazyne intermediate would then react with a third molecule of azide as in the previous mechanism 1-26.

The physical properties of the three cyclotetrazenoborane derivatives prepared are summarised in table 1-B. The diphenyl derivative was fairly stable to hydrolysis in air for prolonged periods, but over a period of months in a moist atmosphere the crystals slowly became coated with boric acid.

The careful hydrolysis of 2,5-diphenyl cyclotetrazenoborane with a concentrated aqueous ethanolic solution of hydrochloric acid at 60° gave boric acid and aniline hydrochloride with evolution of H_2 and N_2 as summarised in reaction scheme 1-28.

$$\begin{array}{rl} Ph_2N_4BH + 3H_2O \longrightarrow B(OH)_3 + H_2 + PhNH.N{:}N.NHPh & \\ \downarrow \text{HCl} \qquad & \\ 2PhNH_3Cl + N_2 & \qquad (1\text{-}28) \end{array}$$

The structure of the cyclotetrazenoboranes was established to be as in 1-XXXI by several experimental considerations. The elemental analysis led to the general molecular formula $RR'N_4BH$. The infrared spectra indicated the presence of characteristic phenyl

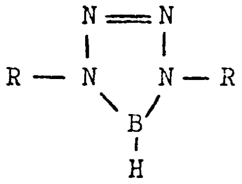
TABLE 1-B PHYSICAL PROPERTIES OF CYCLOTETRAZENOBORANE DERIVATIVES

PHYSICAL PROPERTY	Ph_2N_4BH	Me_2N_4BH	$MePhN_4BH$
Appearance, M.pt. and other physical properties	white crystalline solid M.pt. = 117°C Sublimes under reduced pressure at temperatures near 100° C Highly soluble in benzene and toluene but less soluble in light petroleum, cyclohexane, CS_2, Et_2O, $CHCl_3$ and CCl_4.	colourless liquid M.pt. = 11°C Vapour pressure ≏ 8 mms at 20°C. Miscible with all common organic solvents	colourless low melting solid M.pt. = 32°C B.Pt. = $80^\circ C/10^{-2}$mms Soluble in benzene, toluene and other organic solvents.
N.M.R. ''B δ (p.p.m.)(BCl_3)	+29.9	+26.1	≏ +29
J_{B-H} (c/sec)	164 ± 5	165 ± 5	Broad
N.M.R. 'H δ Ph	-7.5	-	-7.2
p.p.m. rel. to T.M.S. δ Me	-	-3.59	-
δ B-H	-	-4.10	-
J_{B-H} (c/sec)		166 ± 1	
U.V. absorption λ_{max} (mμ)	242, end absn.	198	242, end absn.
ε_{max} (l.cm^{-1} mole^{-1})	2.56×10^4	(6.3×10^3)*	1.25×10^4
I.R. absorption ^{11}B-H str (cm-1)	2651	2636	2656
^{10}B-H str (cm-1)	2661 sh	2655	2670

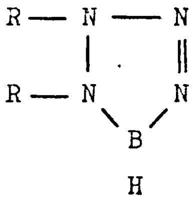
* This approximate value was obtained by calibrating a vapour spectrum from the visible side of a solution of known concentration.

or methyl vibrations. The sharp absorption around 2640 cm^{-1} with its associated shoulder at higher frequency was attributed to the ^{11}B-H and ^{10}B-H vibrations of a single boron-hydrogen bond (see Table 1-B). The absence of characteristic absorptions for BH_2, NH and NH_2 was also noted. The 'H N.M.R. shown in Table 2 gave further support for structure 1-XXXI, the equivalence of the methyl resonances in Me_2N_4BH tending to eliminate structure 1-XXXII below. The ''B N.M.R. showed doublets typical of a single B-H bond. The mass spectrum of Me_2N_4BH showed parent ion peaks at m/e 97 and 98, the ratio of which remained constant over a range of ionising potentials and was in agreement with calculated intensities assuming literature values of isotopic masses. A very brief attempt was made to rationalise the fragmentation pattern,[22] a topic which has now been considered in much greater detail, (see Chapter 5).

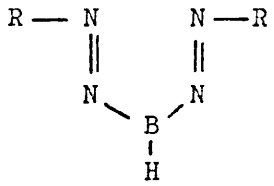
Three possible isomeric structures for a molecule of type R_2N_4BH could be written, namely 1-XXXI, 1-XXXII and 1-XXXIII.



1-XXXI



1-XXXII

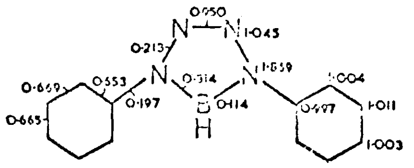


1-XXXIII

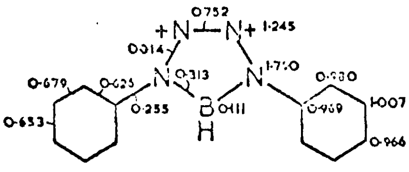
In fact it was found that the U.V. spectrum for Ph_2N_4BH was very similar to that observed for phenyl-substituted triazoles and tetrazoles and it was considered significant that the heterocyclic structures 1-XXXI and 1-XXXII were both formally analogous to triazoles in which the two carbon atoms were replaced by the isoelectronic B-N grouping. Structure 1-XXXIII was least likely, not only from preparative considerations which would involve considerable rearrangement, but also azo groups would be expected to absorb near 33,000 cm^{-1} andfurther delocalisation involving the boron atom might be expected to shift the absorption to even lower energy. The lowest energy band in the observed absorption spectrum of Ph_2N_4BH was at 41,200 cm^{-1} $\varepsilon_{max} = 2.56 \times 10^4$ l. cm^{-1} $mole^{-1}$). End absorption was also observed.

Molecular orbital calculations,[42] were carried out shortly after the preparation of the first C.T.B. derivative (Ph_2N_4BH) using a modified Hückel L.C.A.O. -M.O. method. Although care must be taken in attaching quantitative significance to such calculations, comparative studies were considered worthwhile since they should give a guide to the stability of the π energy levels and the charge distribution, and also the effect of isomerism on substitution at key points. The relative ordering of these quantities should be quite reliable since the basic σ framework of all these molecules was similar.

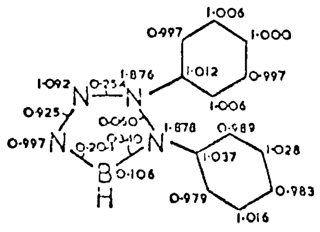
The charge distribution and π-bond orders in the two isomers of diphenyl cyclotetrazenoborane are shown in 1-XXXIV and 1-XXXV respectively, (page 32). It was interesting that the total



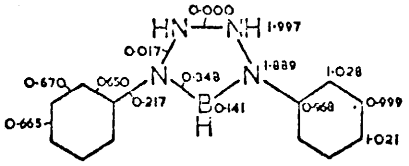
I-XXXIV



I-XLII



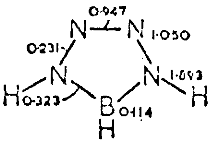
I-XXXV



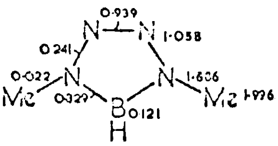
I-XLIII*

* Hückel charges

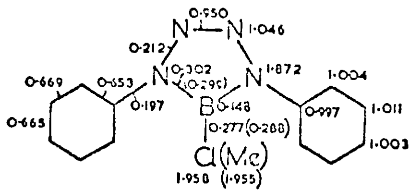
FIGURE [I-I]



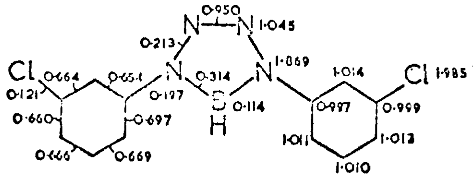
I-XXXVI



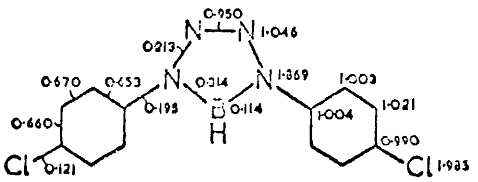
I-XXXVII



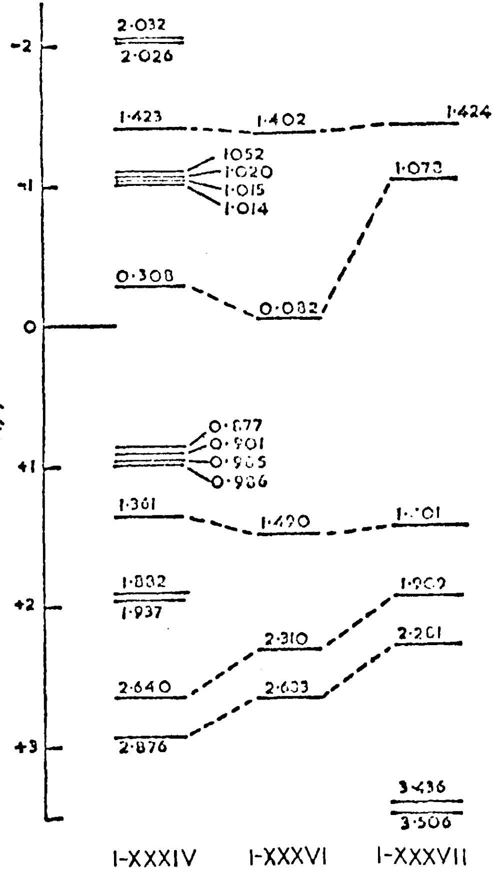
I-XXXVIII (I-XXXIX)



I-XL



I-XLI



delocalisation energy of the N_4B ring in 1-XXXIV was greater than that in 1-XXXV assuming coplanarity of all three rings in both cases. In 1-XXXV it was more likely that both phenyl rings would be inclined by at least 25° to the boron-nitrogen ring plane with a corresponding diminution of π energy. The greater stability of 1-XXXIV over isomer 1-XXXV was satisfyingly consistent with the previous experimental conclusions. As twisting of the phenyl ring would decrease the delocalisation energy it would not be expected to occur in isomer 1-XXXIV. The crystallographic unit cell dimensions together with molecular model considerations indicated that structure 1-XXXIV was preferable to structure 1-XXXV.

The π electron density on the boron in 1-XXXIV was unusually low for a compound in which this atom was attributed to competition with the nitrogens remote from the boron atom for available π-electrons. Calculations on a further eight derivatives 1-XXXVI ⟶ 1-XLIII of the same ring skeleton shown on page 32, were carried out to establish the trends in π stability assuming that the σ energy of the ring remained unaltered. Their bond orders and charge distributions are given in the respective structures. The total and ring delocalisation energies for all the derivatives 1-XXXIV ⟶ 1-XLIII are shown in Table 1-C.

TABLE 1-C DELOCALISATION ENERGIES FOR DERIVATIVES OF CYCLOTETRAZENOBORANE

Compound	1-XXXIV	1-XXXV	1-XXXVI	1-XXXVII	1-XXXVIII
Eπ (total) (βc-c)	28.892	27.225	12.967	25.063	33.043
Eπ (ring)	2.892	1.225 (1.130)*	2.967	3.063	3.128
Compound	1-XXXIX	1-XL	1-XLI	1-XLII	1-XLIII
Eπ (total) (βc-c)	35.101	36.992	36.993	31.097	32.759
Eπ (ring)	3.136	2.992	2.993	3.097	0.759

* Phenyl rings twisted by 25°.

It was immediately seen that the N_4B ring in both H_2N_4BH 1-XXXVI and Me_2N_4BH 1-XXXVII had π stability comparable to the diphenyl derivative 1-XXXIV and that both compounds should be preparable. The Me_2N_4BH 1-XXXVIIcompound was later isolated. The electron distribution was only slightly altered by the change of substituent.

If the hydrogen attached to boron in compound 1-XXXIV was replaced by chlorine or methyl substituents 1-XXXVIII and 1-XXXIX respectively, the stability of the heterocyclic ring was increased and the boron atom acquired a greater π charge. Such effects were not surprising in the case of 1-XXXVIII in view of the known character of boron-chlorine bonds. The overall implication was that substitution on the boron affected only that atom and its immediate neighbourhood. The calculations on 1-XL and 1-XLI demonstrated a complementary effect in that an inductive mesomeric substituent in either the para- or meta-position in the phenyl ring influenced only the charge distribution in that ring. The carbon atom to which the chlorine was attached carried the least π-charge in both systems. The positive character of this ring atom would in fact be greater than the calculations implied because of the withdrawal of σ-electron density by the electronegative chlorine atom. As would be expected, this substituent also slightly increased the delocalisation energy of the compound by π-participation, but in this case the inductive effect was negligible because of the near self-consistency of the field around the phenyl rings.

For all the cases examined the ring could hypothetically function both as an acceptor moiety via the boron atom or as a bidentate ligand via the azo nitrogen atoms. The latter should be quite strong since the two "unsaturated" nitrogen atoms would gain electron density through delocalisation at the expense of the pair bonded to substituents. The acceptor power of the boron was not expected to be marked despite its low electron density, since reorganisation from planar to pyramidal geometry of that part of the ring, which was necessary for formation of an addition compound of boron, would result in the loss of much of the stabilising ring energy. This conclusion was born out to some extent by the apparent absence of polymerisation in 1-XXXIV. An important derivative of the ring not yet prepared was 1-XLII. Quaternisation of the two "azo" nitrogen atoms resulted in electronic charge migrating from all other regions to the two "azo" nitrogens and appeared to be withdrawn mainly from the second pair of nitrogen atoms and the phenyl rings, whereas the boron electron density and B-N bond orders were but little changed. This implied that the boron atom would not become a stronger acceptor when the nitrogen atoms were involved in coordination. One further facet was the increased differential charge distribution in the phenyl rings where directing influences on substitution could become more marked. For compound 1-XLIII each nitrogen was "saturated" and contributed two electrons to the π system. Even if such a molecule was planar, which would introduce considerable strain and was therefore unlikely, the delocalisation energy would be small.

An investigation of the electronic spectra of the cyclotetrazenoboranes was performed. An energy level diagram for compounds 1-XXXIV, 1-XXXVI and 1-XXXVII is shown in figure [1-1] page 32 . Apart from $\pi \rightarrow \pi^*$ transitions, compounds containing the azo-grouping frequently showed peaks stemming from $n \rightarrow \pi^*$ transitions. Such transitions generally have low ε_{max} values [e.g. cis azobenzene, $\varepsilon\ (n \rightarrow \pi^*) = 1500$], but no corresponding peak was detected in the spectrum of diphenyl cyclotetrazenoborane. The first $\pi \rightarrow \pi^*$ transition in the diphenyl C.T.B. derivative 1-XXXIV could give rise to an intense absorption as there were four $\pi \rightarrow \pi^*$ transitions all strongly allowed and close in energy. The observed band system centred at 243 mμ (ε_{max} 2.6 x 10^4) was correlated with these transitions and using this somewhat arbitrarily, the directions of the spectral shifts in other derivatives was predicted to be as shown in table 1-D.

TABLE 1-D CALCULATED ELECTRONIC SPECTRA OF CYCLOTETRAZENOBORANE DERIVATIVES

Compound	1-XXXIV	1-XXXV	1-XXXVI	1-XXXVII	1-XXXVIII	1-XXXIX
λ_{max} (mμ)	243	639	183	191	244	244

Compound	1-XL	1-XLI	1-XLII	1-XLIII
λ_{max} (mμ)	245	251	929	160

It was interesting that isomer 1-XXXV was predicted to absorb at very long wavelengths, perhaps even in the visible region and this could be taken as further justification for considering Ph_2N_4BH to exist as isomer 1-XXXIV. The predicted value of 191 mμ for Me_2N_4BH agreed very well with the observed U.V. absorption maximum at 198 mμ. It was further shown that substitution at the boron atom by π donating entities had little effect on the position of the first electronic transition but that the stability of the N_4B ring was predicted to increase. A comparison of the apparent ε_{max} of the 242 mμ transitions in 2,5-diphenyl- and 2-methyl,5-phenyl C.T.B. derivatives (see Table 1-B, page 29), showed them to be in the approximate ratio 2:1 suggesting that interaction between the phenyl ring and the heterocyclic part of the molecule was weak and that this transition virtually stemmed from the phenyl rings alone.

The ease with which the vibrational spectra of Ph_2N_4BH,[21] and Me_2N_4BH,[43] could be accounted for in terms of the vibrations expected for the symmetric structure 1-XXXI was encouraging. In the latter case the interpretation was greatly assisted by the availability of the Raman spectrum and polarisation data, and also by the fact that many of the bands in the vapour phase infrared spectrum displayed distinctive band contours. For some reason in the 2,5-dimethyl derivative the ^{10}B satellites were less well resolved in the infrared bands due to the B-H and ring vibrations than in the corresponding absorptions of 2,5-diphenyl C.T.B., but the appearance of these satellites also afforded considerable help in identifying vibrations involving the boron atom. The assignment for Me_2N_4BH is presented in Table 1-E, page 39, and that for Ph_2N_4BH in Table 1-F page 40, and these will be further discussed in Chapters 3, 4 and 6. Two different nomenclatures were used for describing the vibrational modes. For the diphenyl derivative the nomenclature used to assign the ring modes was that used by Greenwood and Wright[44] for phenylboracyclopentane whereas in the dimethyl C.T.B. derivative that by K.W.F. Kohlrausch[45] for cyclopentene was utilised. Nine skeletal fundamental vibration modes were predicted for a planar five-membered ring with C_{2v}

TABLE I-E

Observed vibrational spectra of Me_2N_4BH

IR (liquid)		I.R. (gas)		Raman (liquid)			
cm^{-1}	Rel. I^a	cm^{-1}	Band type	cm^{-1}	Rel. I^a	Pol.	Assignment
3076	4 sh						Ternary combination
3006	18 sh			3003	34 sh	dp	C—H asym. stretch, ν_{19} (b_1)
2984	30	2995	*C*	2979	47 sh	dp?	C—H asym. stretch, ν_{30} (b_2)
2949	53	2954					C—H sym. stretch, ν_{20} (b_1)
2931	44 sh			2947	100	p	C—H sym. and asym. stretch ν_1 and ν_2 (a_1)
2896	21			2891	2		1454 + 1442
2856	11			2857	2	p?	1454 + 1408
2826	12	2834	*B*?	2824	7	p	2 × ∼1408 (A_1)
2805	7						1442 + 1363
2715	2						1363 + 1342 (A_1)
2698	5 sh						1480 + 1213
2644	61 sh	2643	*B*				^{10}B—H stretch ν_3 (a_1)
2636	65	2630	*B*	2637	29	p	^{11}B—H stretch
2495	2						1454 + 1046
2283	2						2 × 1140 (A_1) or 1213 + 1068 (A_1)
2149	2						1408 + 736 (A_1)
1935	2						1363 + 570 (A_1)
1630	2 br, sh						2 × 817 (A_1)
1540	9 br, sh						991 + 554 (B_2)
1480	38						
1474	37			1468	18	dp	CH_3 asym. deform., $\nu_4, \nu_{14}, \nu_{21}, \nu_{31}$ (a_1, a_2, b_1, b_2)
1454	39 sh	1444					
1442	49	1437		1439	13 sh	dp	CH_3 sym. deform., ν_5, ν_{22}, (a_1, b_1)
1434	63						
1408	95	1411	*A*	1408	10	p?	Ring stretch, ω_4^b, $\nu_{23}(b_1)$
1363	79	1375	*B*	1361	79	p	Ring stretch, ω_5^b, $\nu_6(a_1)$
1342	33			1340	15	p	Ring stretch, ω_3^b, $\nu_7(a_1)$
1310	4						736 + 570 (B_1)
1231	47 sh						953 + 283 $(A_1$ or $B_1)$
1213	74	1214		1216	3		C—N asym. stretch, ν_{24} (b_1)
1195	30 sh						CH_3 rock, ν_{32} (b_2)
1140	16 br, sh	1139	*B*	1139	0		CH_3 rock, ν_8 (a_1)
1095	18 br, sh						817 + 283 (B_2) or 570 + 522 (B_2)
1081	25						^{10}B—H in-plane deform., ν_{25} (b_1)
1068	42	1068	*A*				^{11}B—H
1046	26	1040	*B*	1045	4	p	C—N sym. stretch, ν_9 (a_1)
1034	25						2 × ∼520 (A_1)
991	100	991	*A*	988	14	dp	Ring stretch, ω_2^b, ν_{26} (b_1)
				964	10 sh	p	^{10}B ring stretch, ω_1^b, ν_{10} (a_1)
953	9			950	33	p	^{11}B
926	4			923	2	dp	CH_3 rock, ν_{27} (b_1)
829	19	830	*C*				^{10}B—H out-of-plane deform., ν_{33} (b_2)
817	51	817	*C*	818	3		^{11}B—H
783	2						∼520 + ∼270 (B_2)
736	72	734	*A*				Ring deform., ω_6^b, ν_{28} (b_1)
570	0			574	22	p	Ring deform., ω_7^b, ν_{11} (a_1)
				554	7 sh	p?	Ring deform., Γ_2^b, ν_{16} (a_2)
522	19	514	*C*				Ring deform., Γ_1^b, ν_{34} (b_2)
411	9			409	6	dp	Me—N deform., ν_{35} (b_2)
283	35 br	279 268		278	7	dp?	Me—N deform., ν_{12} and ν_{29} (a_1, b_1)

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[a] Intensities are measured relative to the strongest feature for which I = 100

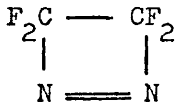
[b] The nomenclature of the ring modes is based on that used by KOHLRAUSCH 45 br = broad; sh = shoulder; p = polarized; dp = depolarized.

TABLE I-F

Infrared spectrum of 2,5-diphenylcyclotetrazenoborane (for description of phenyl modes *a*–*y* and hetero-ring modes I—VIII see refs. 90 and 44 respectively).

ν (cm.$^{-1}$)	Rel. ε	Assignment
72	<1	Lattice or torsional modes (?)
108	<1	
140	<1	
175	3	PhX ring out-of-plane deform. (*x* mode)
227	1	
247	<1	
254	<1	
300	1	PhX in-plane deform. (*u* mode)
420	3	Hetero-ring out-of-plane deform. (mode VIII)
473	3	PhX ring out-of-plane deform. (*y* mode)
548	17	PhX ring in-plane deform. (*t* mode)
620	4	Ph ring in-plane deform. (*s* mode)
668	8	Hetero-ring in-plane deform. (mode IV)
689	131	Ph ring out-of-plane deform. (*v* mode)
708	44	PhX ring in-plane deform. (*r* mode)
753	160	CH out-of-plane deform. (*f* mode)
811	41	^{11}B–H out-of-plane deform.
822	17	^{10}BH out-of-plane deform.
905	28	^{11}B hetero-ring sym. stretch (mode III)
915	16	^{10}B hetero-ring sym. stretch (mode III)
968	47	Hetero-ring in-plane deform. (mode VII)
1002	6	Ph ring in-plane deform. (*p* mode)
1031	19	CH in-plane deform. (*b* mode)
1045	8	BH in-plane deform.
1062	200	Hetero-ring A_1 stretch (mode I)
1077	17	CH in-plane deform. (*d* mode)
1091	65	^{11}B hetero-ring breathing (mode II)
1109	18	^{10}B hetero-ring breathing (mode II)
1159	13	CH in-plane deform. (*c* mode)
1177	20	CH in-plane deform. (*a* mode)
1190	60	^{11}B hetero-ring B_1 stretch (mode VI)
1200	20	^{10}B hetero-ring B_1 stretch (mode VI)
1291	7	PhN antisym. stretch (*q* mode)
1311	16	PhN sym. stretch (*q* mode)
1331	14	CC(Ph) B_1 stretch (*o* mode)
1379	20	(2 × 689)
1405	125	^{11}B hetero-ring antisym. stretch (mode V)
1418	41	^{10}B hetero-ring antisym. stretch (mode V)
1471	20	CC(Ph)B_1 stretch (*n* mode)
1505	170	CC(Ph) A_1 stretch (*m* mode)
1511sh	31	CC(Ph) A_1 stretch (*m* mode)
1600	70	CC(Ph) B_1 stretch (*l* mode)
1609	124	CC(Ph) A_1 stretch (*k* mode)
1664	4	(753 + 905) and (753 + 915)
1735	5	The four combination bands of HC out-of-plane deformations (1 + 3 pairs)
1793	6	
1811	5	
1868	6	
1887	6	
1944	4	
1963	5	
2651	18	^{11}B–H stretch
2661sh	7	^{10}B–H stretch
3046sh	16	C–H stretches
3053	21	
3073	13	
3083sh	8	
3102	5	
3115	4	

symmetry, distributed amongst the symmetry classes $4A_1$, $1A_2$, $3B_1$ and $1B_2$. The frequencies assigned to these related ring modes in the dimethyl and diphenyl C.T.B. derivatives however differed considerably, a fact as yet not fully rationalised. Of the ring vibrations the N=N stretching mode which was represented most nearly by a frequency near 1360 cm^{-1} in the Me_2N_4BH spectrum, occurred at a markedly lower frequency than the comparable mode in molecules like FN=NF (1524 cm^{-1}) and the cyclic perfluoro-azo compound 1-XLIV (1484 cm^{-1}) where there was little opportunity

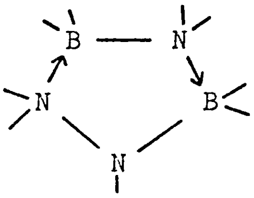


1-XLIV

for delocalisation of the π-electron density. The apparent decrease in the N=N stretching force constant could be related to appreciable transfer of the π-charge from the azo grouping to the C.T.B. ring, leading to a reduction in the effective bond order, in agreement with the molecular orbital calculations. It was also noteworthy that, although the sequence of frequencies of the ring modes for N_4B and $(CH_2)_4B$ rings were similar, nearly all the individual modes of the C.T.B. ring occurred at higher frequencies than those of the corresponding boracyclopentane ring. This presumably reflected the increased rigidity of the B-N heterocycle as a result of the 6-electron π-bonding system in the planar ring. In both Me_2N_4BH and Ph_2N_4BH the B-H infrared stretching vibrations were observed at relatively high frequency reflecting a comparatively low electron density on the boron atom as predicted by Perkins.[42] The internal methyl and phenyl vibrations were assigned principally by analogy with the spectra of simple compounds like dimethyl ether,[46] dimethyl amine,[47] and standard phenyl containing compounds.

e) Other five-membered ring systems

The ring system 1-XLV has only recently been reported.[48]



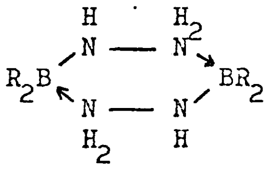
1-XLV

Four of these rings were shown to exist in a polyhedral cage compound which was effectively a dimer of two six-membered boron-nitrogen rings. This compound will be discussed in detail under six-membered boron-nitrogen rings, section (c) - the 1,2,4,5-tetraza-3,6-diborines.

Six-membered boron-nitrogen ring systems

a) Hydrazinoboranes

Hydrazinoboranes of the type $R_2B - NH - NH_2$ have been shown to dimerise forming cyclic structures as shown in 1-XLVI,[48a]

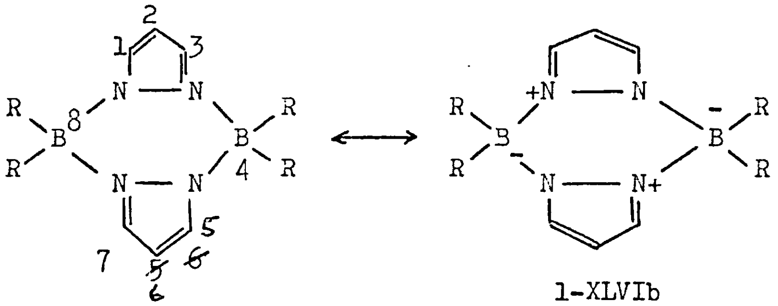


1-XLVI

depending on a coordinate bond formation from the N atom to the B atom.

b) "Pyrazaboles"

These could really be classed with compounds of (a) but because of their unusual features, great stability, the dimers being undissociable, and a wealth of derivatives they have been given the common name "pyrazaboles" with atom positions numbered as in 1-XLVIa. The pyrazaboles were prepared by refluxing pyrazole

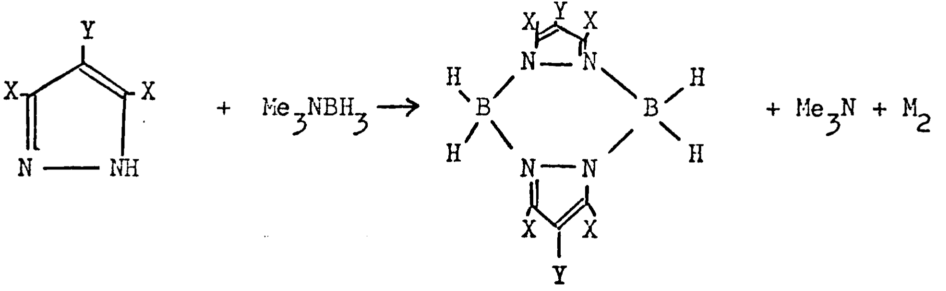


1-XLVIb

1-XLVIa

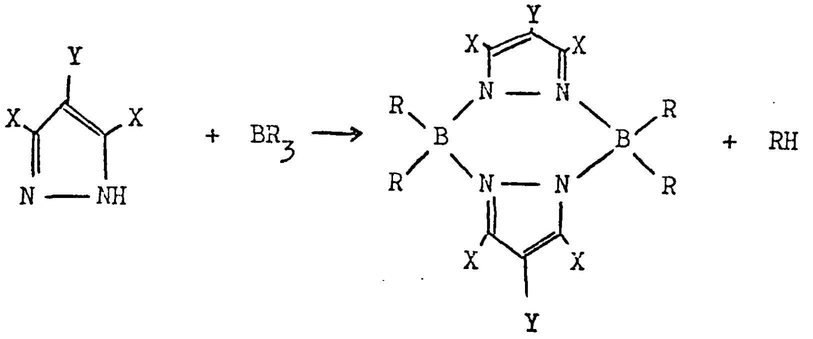
where R = H, alkyl or aryl

with trimethyl-amineborane in toluene or heating pyrazole with boron trialkyls or triaryls to 120 - 150°, as indicated by equations 1 - 29 and 1-30.[49,50] Substituted derivatives could be obtained by the use of substituted pyrazoles.



(1-29)

1-XLVII

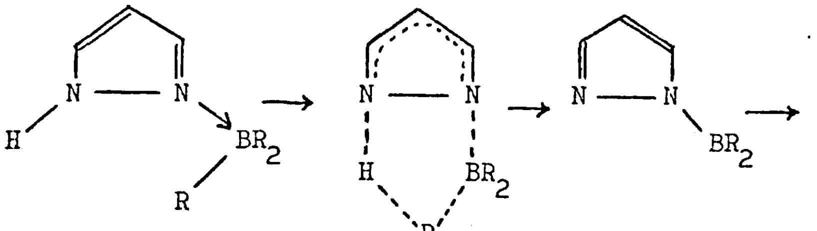


(1-30)

The nature of these compounds was shown by elemental analysis, m. wt. and infrared spectrometry which for 1-XLVII showed the presence of a strong BH_2 mode and the degradation products from boiling with hydrochloric acid which for 1-XLVII gave pyrazole and boric acid. Electronic and steric reasons suggested the structure shown for 1-XLVII. Equivalence of positions 1, 3, 5 and 7 and the 2, 6 positions was shown by 'H N.M.R. spectroscopy. The structure contained tetrahedral boron in a symmetrical environment, and was considered to be a resonance hybrid of 16 structures, two of which are shown in 1-XLVIa and 1-XLVIb, which would contain positive charges delocalised in the ligand and negative charges on the boron atoms. This was consistent with the inert nature of pyrazaboles to sodium hydroxide and other nucleophiles. Pyrazoles with strongly electron withdrawing substituents reacted to form pyrazaboles at a slower rate due to the reduced nucleophilicity at the 2-nitrogen. Pyrazaboles with very few exceptions were found to be extremely stable, unaffected by air and water and could be stored for long periods of time.

This stability could be further rationalised by the use of molecular models which showed that the N and B atoms, i.e. the prospective targets of electrophilic and nucleophilic attack respectively were much better shielded than the BR_2 group and the corresponding heteroatoms in, for example, analogous acetyl-acetone derivatives. It was of interest to note that an unstrained model of pyrazabole was puckered in the boat form, whereas one would have expected the molecule to be planar if coplanarity of the B-N bonds and tetrahedral angles around boron were preserved. Such a model however entailed considerable strain. A feature of the B unsubstituted pyrazaboles was the complex strong B-H stretching frequency observed which was interpreted as evidence for this puckered structure. The chemical shift of the 1,3,5,7-hydrogens in 2,6 disubstituted pyrazaboles seemed to parallel the inductive effects of the substituents and a similar trend was observed but to a lesser extent in 2,6-disubstituted-4,4,8,8-tetraethyl pyrazaboles.

The mechanism of pyrazabole formation may involve a five-centre transition state and if it is assumed that coordination at the 2 position would precede any bond breaking, the 1-H should be sufficiently close to an R group to permit intramolecular departure of RH, as shown in reaction scheme 1-31. It may be possible for the 1-dialkyl boryl fragment 1-XLVIII, apart from dimerising to



1-XLVIII

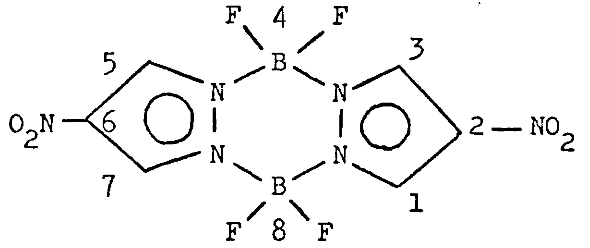
→ 1-XLVI (1-31)

react with pyrazole to give hydrogen poly (1-pyrazolyl) borates. It has been shown however that these disproportionate irreversibly at elevated temperatures to pyrazaboles and pyrazole[50]. Moreover, the electrophilicity of a BR_2 ought to surpass that of the pyrazole hydrogen, and hence the formation of hydrogen poly (1-pyrazolyl) borates should be insignificant. Whilst the transition state in the borane-pyrazole reaction involves a five-membered ring, the electrons are relayed along the pyrazoles π system and in that sense an eight-membered ring is formed in the transition state. The reaction with trimethylamine borane where a strong donor molecule was involved probably resulted in an equilibrium involving trimethylamine 1-pyrazolylborane being established, the reaction being driven to completion by removal of $(CH_3)_3N$ from the system and irreversible formation of pyrazabole.

The reaction of 1,2,4-triazole with Et_3B yielded the analogous 4,4,8,8-tetraethyl-sym-triazabole. This was obtained in lower yield than the corresponding pyrazabole, which was not surprising in view of the additional N atom that could interact in the coordinating stage of the reaction.

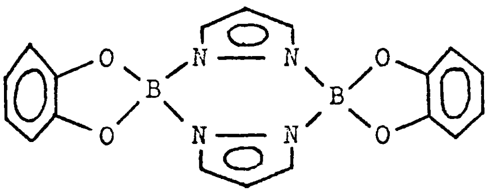
Chlorination, bromination and iodination of pyrazabole resulted in a rapid replacement of all four boron-bonded hydrogens, and formation of 4,4,8,8-tetrahalo-pyrazaboles; however, the 4,4,8,8-tetralkyl pyrazaboles were completely unaffected by chlorine or bromine. The 4,4,8,8-tetrafluoro derivative was obtained by Heitsch[51] by the action of an excess of a variety of fluorinating agents such as AgF_2, IF_5, BF_3, p-tolyliodine difluoride and SF_4 and Cl_2 followed by NaF on pyrazabole. By appropriately limiting the quantities of SF_4 in its reaction, mixtures could be obtained in which the predominant product was 4-fluoropyrazabole, 4,8-difluoro-pyrazabole or 4,4,8-trifluoropyrazabole. The order of stability for the 4,4,8,8-tetrahalopyrazaboles was $F > Cl > Br > I$. The 2,6-positions in pyrazaboles were remarkably inert towards halogenation, and this was considered to be compatible with the BR_2 acting as a powerful electron withdrawing group. The tetrafluoro derivative could be nitrated in 90% nitric acid without destroying the centre ring to yield 2,6-dinitro-4,4,8,8-tetrafluoropyrazabole 1-XLIX which could be reduced to the diamine. This, in turn, could be converted to diamides and other derivatives. Other compounds substituted in the 2,6-positions have been prepared, for example the

2,6-dicyano-, 2,6-dicarboxylic acid and its sodium salt, 2,6-dibromo-, 2,6-dilithio, 2,6-dicarboxaldehyde derivatives.



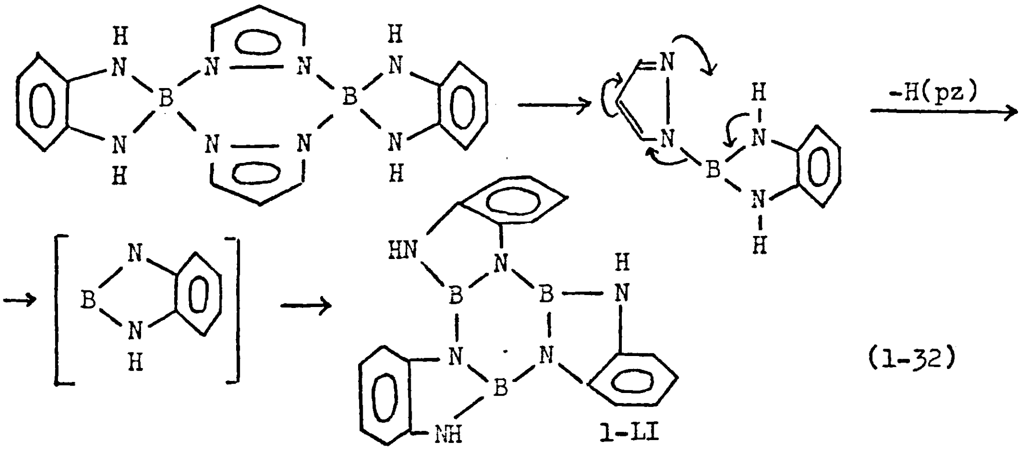
1-XLIX

The reaction of pyrazabole with an active hydrogen compound such as pyrocatechol, produced the 4,4,8,8-bis (o-phenyldioxy) derivative 1-L characterised by I.R., N.M.R. and direct synthesis.



1-L

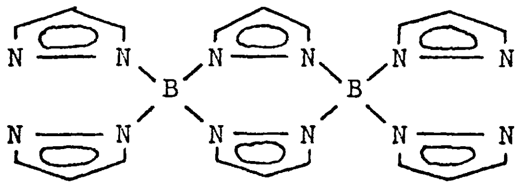
Similarly with phenol the 4,4,8,8-tetraphenoxy derivative was produced, but this was more readily hydrolysed than 1-L. Reaction with o-phenylenediamine did not yield the expected bis (N,N'-o-phenylenediamino) derivative but rather the known borazole derivative 1-LI possibly by the reaction scheme shown below, 1-32:-



(1-32)

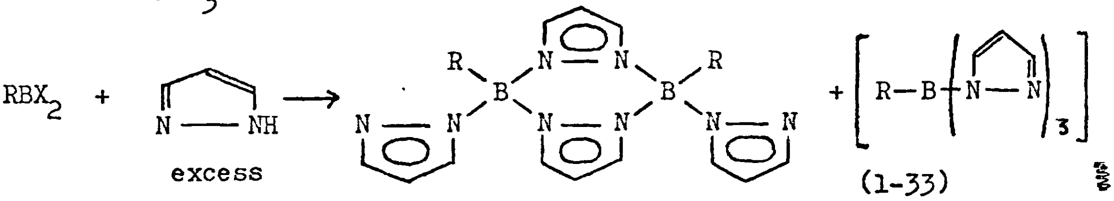
where pz = 1-pyrazolyl

When pyrazabole was heated with excess pyrazole, 4,4,8,8-tetrakis (1-pyrazolyl) pyrazabole 1-LII was formed. Compound 1-LII could



1-LII

also be obtained in lower yield from the pyrolysis of the free acid derived from tetrakis (1-pyrazolyl) borate ion or from the reaction of BCl_3 with excess pyrazole. The reaction of just 2 equiv. of pyrazole in the reaction with pyrazabole produced the 4,8-bis (1-pyrazolyl) pyrazabole. Similarly the 4,8-diphenyl derivative was prepared by direct synthesis from the trimethylamine complex of phenylborane. Both 4,8-derivatives probably existed as cis-trans isomers. The reaction of BX_3 and RBX_2 (where X = Cl, Br) with excess pyrazole resulted in rapid replacement of all halogens by 1-pyrazaboles and RB - $(pz)_3^-$ as the pyrazolinium salt as shown in reaction 1-33.

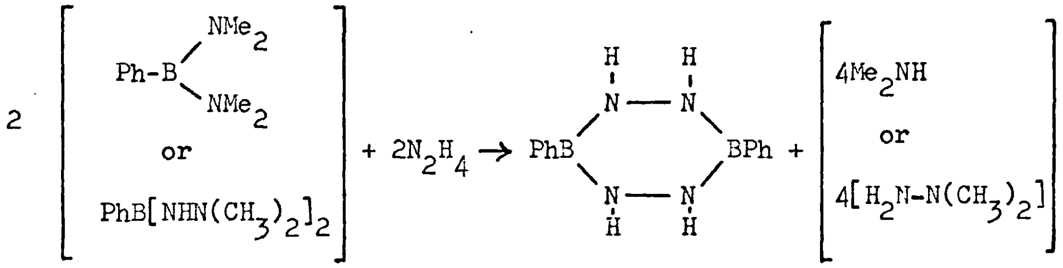


(1-33)

The order of reactivity for the group R dependency was halogen > hydrogen > alkyl > aryl.

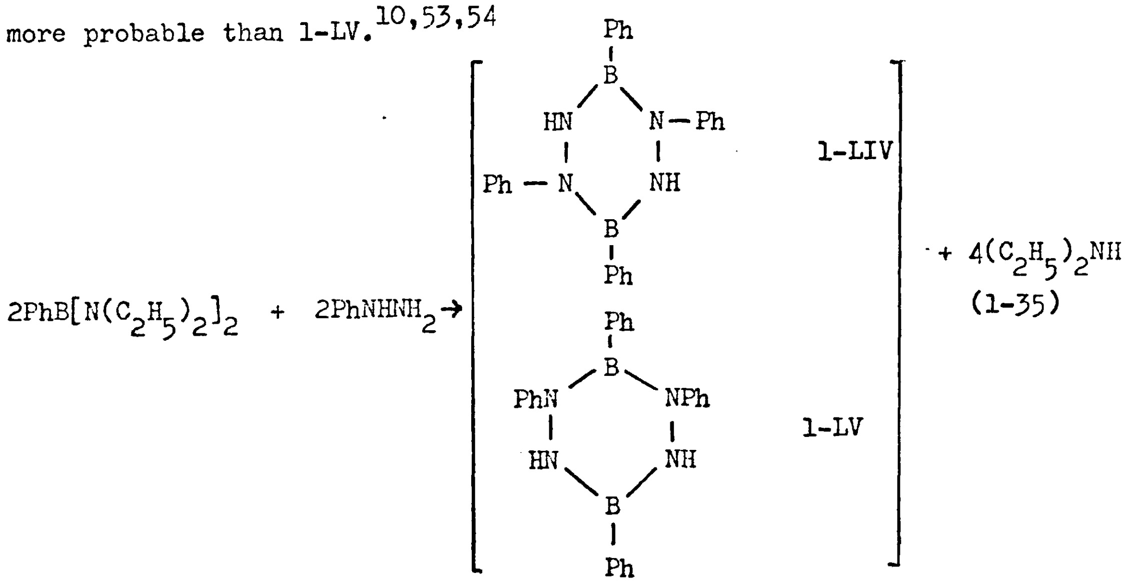
c) 1,2,4,5-tetraza-3,6-diborines

A number of cyclic borohydrazine heterocycles containing both B-N and N-N bonds have been reported. The first tetrazadiborine prepared 1-LIII utilised the now general preparative route of a transamination reaction. The hydrazinolysis of bis-(dimethylamino) phenylborane or alternatively bis-(N,N-dimethyl hydrazino) phenyl borane with hydrazine[48a,52,53] is represented in equation 1-34.



1-LIII (1-34)

The use of a monosubstituted hydrazine see equation 1-35 gave the possibility of two isomers. Which of these was formed was not determined, but it was thought that for steric reasons 1-LIV was more probable than 1-LV.[10,53,54]

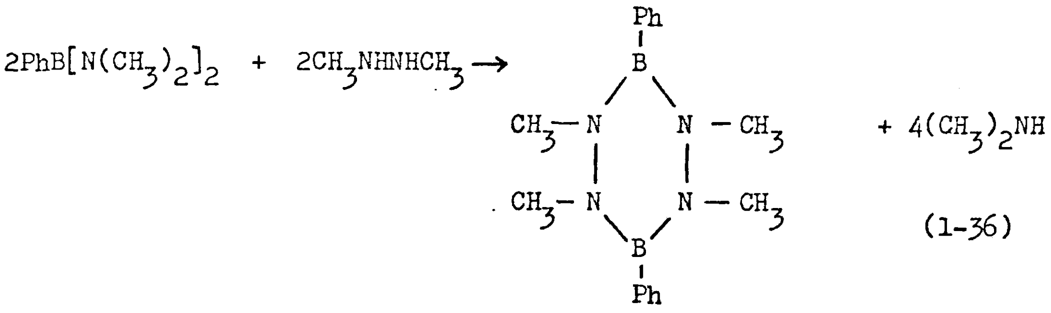


1-LIV

1-LV

(1-35)

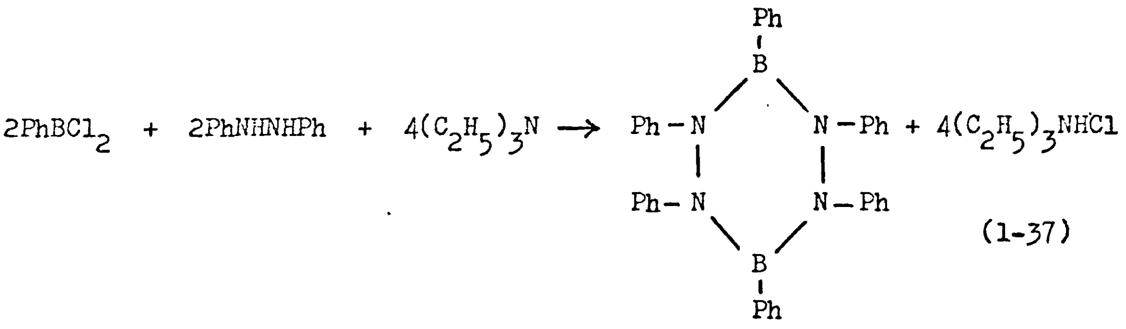
The transamination using disubstituted hydrazines, see equation 1-36 yielded hexasubstituted cyclic borohydrazines.[29]



(1-36)

1-LVI

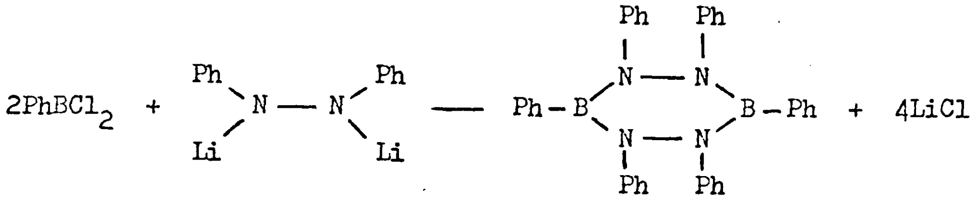
Several other synthetic procedures have now been developed including the use of haloboranes as starting materials by the elimination of hydrogen chloride from hydrazobenzene and phenyl dichloroborane using the standard tertiary amine technique as illustrated in equation 1-37.[54]



(1-37)

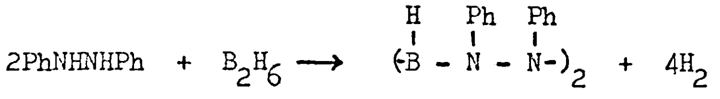
1-LVII

The hexaphenyl derivative 1-LVII was also prepared by Nöth et al.[48a] from the N,N-dilithiophenylhydrazine by the route shown in equation 1-38. A novel preparative route was also provided



(1-38)

by the reduction of azobenzene with diborane to yield 1-LVIII as shown in reaction 1-39.

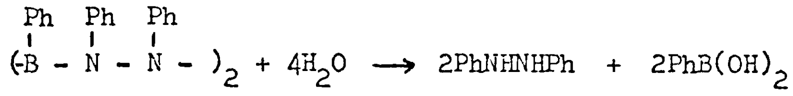


$$2PhNHNHPh + B_2H_6 \longrightarrow (\overset{H}{B} - \overset{Ph}{N} - \overset{Ph}{N}-)_2 + 4H_2 \qquad (1\text{-}39)$$

1-LVIII

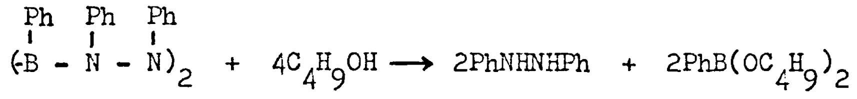
Cyclic borohydrazines have not yet been studied in great detail with a view to elucidating their structure, but the lack of reaction with an excess of hydrazine on 1-LIII to yield bis(hydrazino)-phenyl borane, $C_6H_5B(NHNH_2)_2$ was considered to support the concept of resonance stabilisation of the cyclic tetrazadiborine system. The infrared spectra showed bands at 1400 and 1372 cm^{-1} assigned to B-N modes which were at higher frequency than might be expected for B-N single bonds and some π bonding was considered to occur between the available electrons on the nitrogen atoms and the vacant boron orbitals.[29] Planarity of the ring was therefore inferred, which was in agreement with the 'H N.M.R. of 1-LVI, where only one type of methyl proton was observed.[29]

Chemically, reactions of the cycloborohydrazines with water and alcohols proceeded as might have been expected as shown in equations 1-40, 1-41 and 1-42.



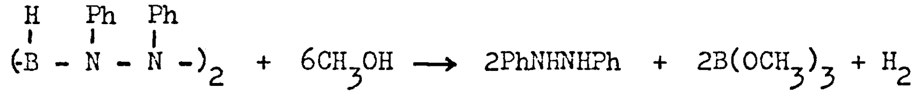
$$(\overset{Ph}{B}-\overset{Ph}{N}-\overset{Ph}{N}-)_2 + 4H_2O \longrightarrow 2PhNHNHPh + 2PhB(OH)_2 \qquad (1\text{-}40)$$

1-LVII



$$(\overset{Ph}{B}-\overset{Ph}{N}-\overset{Ph}{N})_2 + 4C_4H_9OH \longrightarrow 2PhNHNHPh + 2PhB(OC_4H_9)_2 \qquad (1\text{-}41)$$

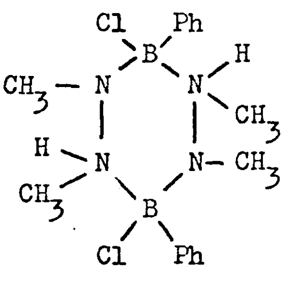
1-LVII



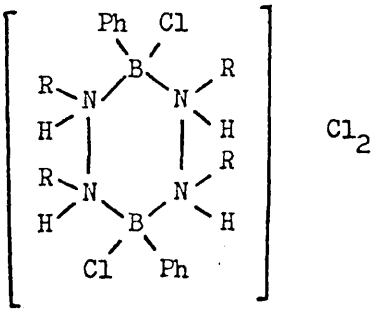
$$(\overset{H}{B}-\overset{Ph}{N}-\overset{Ph}{N}-)_2 + 6CH_3OH \longrightarrow 2PhNHNHPh + 2B(OCH_3)_3 + H_2 \qquad (1\text{-}42)$$

1-LVIII

The action of cyclohexylamine on 1-LVI gave the 1,3,5-triaza-2,5-diborine system previously described (page 15). Controlled addition of hydrogen chloride to tetrazadiborines allowed the isolation of a 2:1 adduct 1-LIX and a 4:1 adduct 1-LX,[29] and these could be considered to be representatives of class a) of these six-membered boron-nitrogen rings. At higher temperatures however an excess of



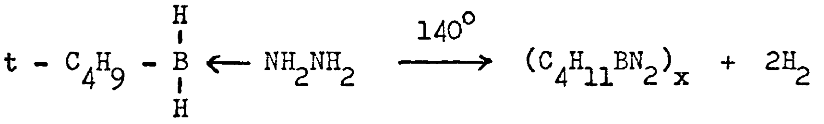
1-LIX



1-LX

hydrogen chloride cleaved the B-N bonds. An addition product $[PhB - NH-NH]_2.2BF_3$ was apparently formed on reaction of BF_3 with 1-LIII, which was stable to at least 130°. It was thought however since BF_3 readily cleaves a B-N linkage that the cyclic system was no longer present, but that the compound was better formulated as $Ph(F)B - NH - NHBF_2$ which had the required stoichiometry.[48a]

A novel addition to the chemistry of this ring system has recently been reported.[48] The first polyhedral cage structure of a compound containing only boron and nitrogen was produced by the thermal decomposition of hydrazine t-butylborane at 140°C with evolution of hydrogen in amounts consistent with reaction 1-43 and provided a white solid product 1-LXI m.pt. 161 - 163°C.

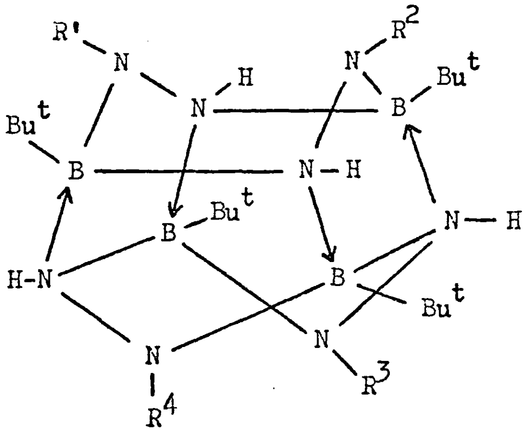


$$t - C_4H_9 - \overset{H}{\underset{H}{B}} \leftarrow NH_2NH_2 \xrightarrow{140^{\circ}} (C_4H_{11}BN_2)_x + 2H_2 \qquad (1-43)$$

1-LXI

Elemental analysis was compatible with the empirical formula depicted, and infrared evidence indicated the presence of N-H and absence of B-H bonds. Mass spectral data indicated that the compound was tetrameric, and 'H N.M.R. showed the presence of equal numbers of two types of hydrogens on nitrogen, and that all the t-butyl groups were identical. The "B N.M.R. showed the equivalence of all the boron atoms. Hydrolysis of 1-LXI with aqueous acid yielded t-butylboronic acid and hydrazine indicating that no rearrangement had occurred.

Chemically 1-LXI reacted with excess methyl isocyanate under mild conditions to provide a new compound 1-LXII which was composed of 2 equivalents of the isocyanate and 1 equivalent of compound 1-LXI. The 'H N.M.R. of 1-LXII showed four separate peaks for the t-butyl groups shown to be due to chemical shift and not coupling and four types of hydrogen on the nitrogen. The N.M.R. and chemical evidence was interpreted in terms of the structures shown in 1-LXI, 1-LXII, 1-LXIII and 1-LXIV. These could be described as dimers of two six-membered 1,2,4,5-tetraza-3,6-diborine rings in the boat form bonded to each other through four coordinate covalent nitrogen-boron bonds thus forming four five-membered rings:-



1-LXI R' = $R^2 = R^3 = R^4$ = H.

1-LXII R' = R^3 = H; $R^2 = R^4 = CONHCH_3$.

1-LXIII $\begin{cases} R^2 = R^3 = R^4 = CONHCH_3; \\ R' = H. \end{cases}$

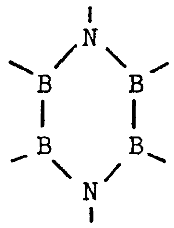
1-LXIV R' = $R^2 = R^3 = R^4 = CONHCH_3$.

Only conventional kinds of bond angles were required in these structures and a maximum coordination of boron and nitrogen was achieved.

It was considered that nucleophilic reactions of 1-LXI should occur at the more basic and less hindered trigonal nitrogens. Compound 1-LXII was the product of reaction of 1-LXI with 2 equivalents of isocyanate; reaction occuring at one trigonal nitrogen in each six-membered ring.

d) 1,4-diaza-2,3,5,6-tetraborines

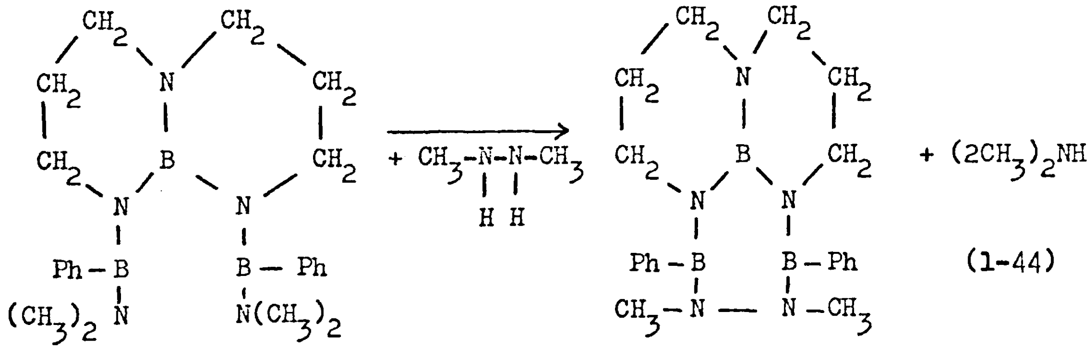
The one known derivative of this system has only recently been briefly reported,[37] and has already been discussed, (page 21).



Seven-membered boron-nitrogen ring systems

a) 1,2,4,6-tetraza-3,5,7-nitrogen ring systems

Only one derivative of this system has been reported.[55] This was formed by the reaction of 1,8-bis (dimethyl-aminophenyl boryl)-1,8,10,9-triazaboradecalin 1-LXV with sym. dimethyl hydrazine when a transamination reaction occurred yielding 1-LXVI which contained the novel heterocycle consisting of four nitrogen and three boron atoms as annular members, as shown in equation 1-44.

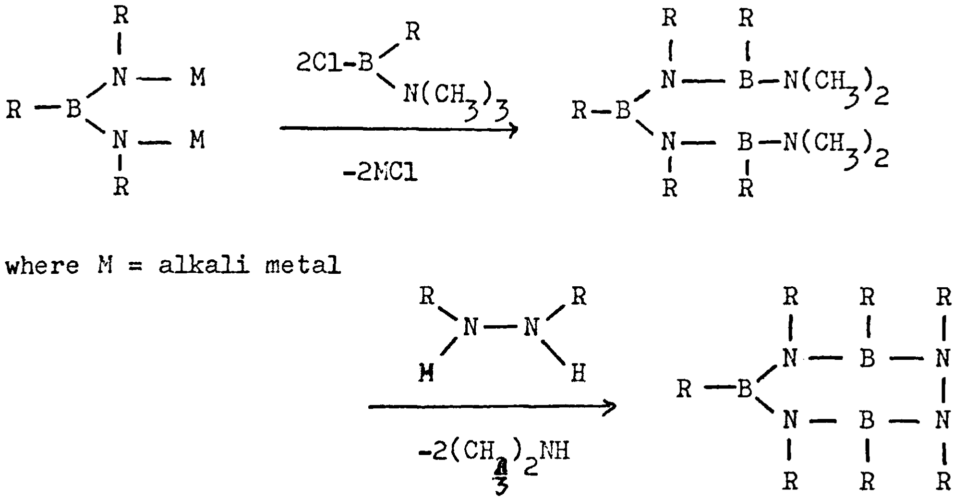


1-LXV

1-LXVI

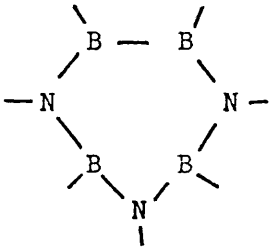
(1-44)

The boron and nitrogen atoms of the ring system were not all planar. Dawson et al. postulated that further simpler derivatives should be preparable by the following reaction scheme, 1-45.


where M = alkali metal

(1-45)

b) 1,3,5-triaza-2,4,6,7-tetraborine



The known derivatives of this system have only recently been briefly reported in the literature[37] and have already been mentioned, (page 22).

Eight-membered boron-nitrogen rings

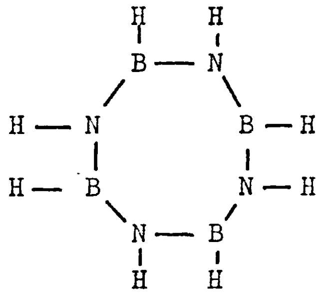
a) Cyclo-tetraborazane $(BH_2NH_2)_4$

This is the least well characterised of the cyclic borazanes reported,[12] and was prepared by treating the "diammoniate of diborane" with sodium amide in liquid ammonia, but was not readily purified.

A characteristic X-ray powder diffraction pattern of the compound was obtained.

b) s-tetrazatetraborines (or borazocines)

The high bond energy of the normal covalent B-N bond linkage (104.3 kcals/mole) is shown by the relatively large thermal stability of certain boron-nitrogen compounds, but commercially they were of little use as high temperature resistant materials owing to their hydrolytic stability. Turner et al.[56,57,58] searching for higher cyclic or linear polyborazynes of greater hydrolytic stability discovered the s-tetrazatetraborine (borazocine) ring system 1-LXVII. The normal reaction expected for dehydrohalogenation of primary amine trichloroboranes was the formation of borazines via the intermediate aminochloroboranes, but the use of highly hindered primary amines, preferably with the α-carbon atom fully saturated resulted in selective conversion into the B-haloborazocines. The first example of this system 1-LXVIII was prepared by the elimination of hydrogen chloride from the t-butylamine-BCl_3 adduct in the presence of a tertiary amine such as triethylamine as shown in equation 1-46.



1-LXVII

$$4t - C_4H_9NH_2BCl_3 + 8N(C_2H_5)_3 \longrightarrow (ClBN - tC_4H_9)_4 + 8(C_2H_5)_3N.HCl \quad (1\text{-}46)$$

1-LXVIII

The B-chloro borazocine was also prepared using potassium tetrachloroborate as shown by the following equation 1-47.

$$4KBCl_4 + 8(C_2H_5)_3N + 4(t - C_4H_9NH_2) \longrightarrow (Cl\text{-}B\text{-}N\text{-}tC_4H_9)_4 + 4KCl + 8(C_2H_5)_3N.HCl \quad (1\text{-}47)$$

Gerrard has more recently shown that dehydrohalogenation of each of the compounds $[Bu^tNH_3]^+BCl_4^-$, $Bu^tNH_2BCl_3$ and Bu^tNHBCl_2 by heating with triethylamine gave the borazocine in all cases[59].

Isobutylamine complexes of phenyl boron dichloride on triethylamine dehydrohalogenation yielded the trimer $(PhBNBu^i)_3$ (21% yield) and the tetramer $(PhBNBu^i)_4$ (4% yield) according to equations 1-48 and 1-49[60].

$$Bu^iNH_3^+PhBCl_3^- + 3Et_3N \longrightarrow (PhBNBu^i)_3 + (PhBNBu^i)_4 + 3Et_3NHCl \quad (1\text{-}48)$$

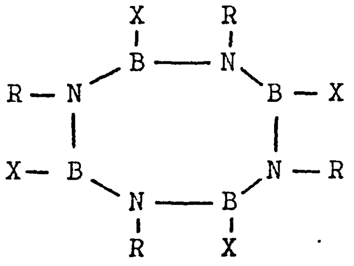
$$Bu^iNH_2PhBCl_2 + 2Et_3N \longrightarrow (PhBNBu^i)_3 + (PhBNBu^i)_4 + 2Et_3NHCl \quad (1\text{-}49)$$

With similar propylamine, sec. butylamine and tertiary butylamine complexes no evidence of tetramer formation was detected. The trimer $(PhB\text{-}NBu^i)_3$ and the tetramer $(PhBN\text{-}Bu^i)_4$ were both fully characterised by elemental analysis and m.wt. determinations both by osmometry and mass spectrometry. The B-N stretching frequency of the tetramer occurred at 1401 cm^{-1} but no deformation mode was observed around 725 cm^{-1}. On heating to above its melting point the tetramer was changed apparently quantitatively and irreversibly to the trimer. This change was

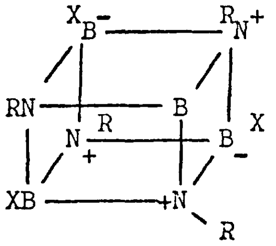
$$(PhBNBu^i)_4 \xrightarrow{250^o} (PhBNBu^i)_3$$

demonstrated by differential thermal analysis (D.T.A.).[61]

Borazocines have the empirical formula $B_4X_4N_4R_4$ for which several possible structures could be written. ^{11}B N.M.R. indicated a singlet at -30.3 ppm relative to BCl_3 corresponding to that expected for three coordinate boron atoms, the single resonance indicating an equivalence of the boron atoms. This together with the zero dipole moment of the system, the vibrational spectra,[62] a consideration of molecular models, and conclusively by an X-ray diffraction study,[57,58,63,64] distinguished between the two most likely structures 1-LXIX and 1-LXX, in favour of the former.

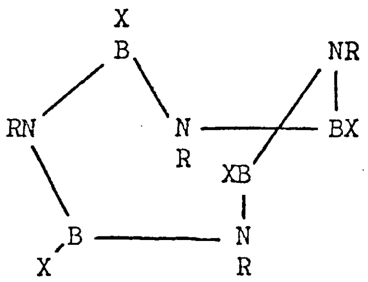


Eight-membered ring
1-LXIX

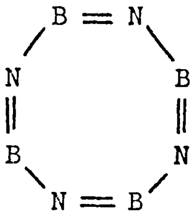


Cubane structure
1-LXX

The infrared and Raman vibrational study by Green et al.[57] showed that the eight-membered ring was most likely to exist in the boat conformation 1-LXXI and that the crown and chair conformation were unlikely. Such a structure would be expected to have localised



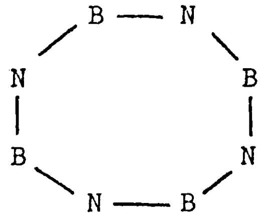
1-LXXI



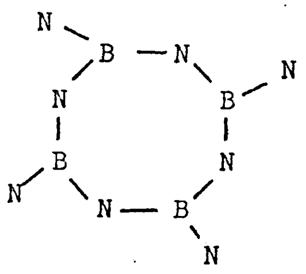
1-LXXII

alternating π-bonds 1-LXXII. Hoffman[16,17] in some extended Huckel calculations considered the five possible conformations, tub, chair, crown, planar and cubical for $(BHNH)_4$ and the isoelectronic cycloctadiene C_8H_8. In each case the tub conformer was favoured in agreement with structural conclusions, but relative to this the most stable arrangement the cubane structure, was more favourable for $(BHNH)_4$ than for C_8H_8. Calculations for the $(BHNH)_4$ negative ions led to the interesting prediction that in the anion the tub geometry was still the more favourable, whilst for the dianion the tub and planar forms were of very nearly equal energy, the latter being slightly more stable. It was interesting to note that for C_8H_8 both the anion and dianion favoured a planar form.

More recent calculations however[18] for system 1-LXXIII indicated that the π bond energy increased by 74% relative to a



1-LXXIII



1-LXXIV

non conjugated ring. This was evidently insufficient to overcome the steric and strain effects associated with a planar eight-membered ring since the $(BN)_4$ derivatives synthesised were shown to be non planar. The net bond orders and p_π orbital charges in various BN rings could be summarised as shown in the following sequences:-

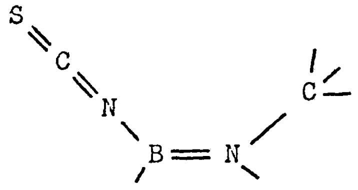
B-N bond orders $BN > (BN)_3 > (BN)_4 > (BN)_2$

Net charges on B and N $(BN)_3 > (BN)_4 > (BN)_2 > BN$

Calculations on system 1-LXXIV showed that the exocyclic B-N bond orders were greater than the ring bond orders and that the ring π bond orders were reduced relative to the ring unsubstituted with lone pair atoms at the boron. On the basis of structural evidence[64] the $(NBN)_4$ molecules were considered to comprise four isolated (NBN) units with only very weak conjugation between separate units. Even though the Huckel π-bond energy of $(NBN)_4$ was appreciably greater than that of four independent (NBN) units, the π energy must have been insufficient to overcome the steric and strain effects associated with a planar eight-membered ring.

Borazocines showed remarkably high molecular depression constants (53 → 95) which were greater than that for camphor (40). The borazocines were indefinitely stable in the laboratory atmosphere at room temperature, and immeasureably attacked by boiling water, but at 160° in a sealed tube for 20 hours, hydrolysis was 97% complete. Similarly metallic borohydrides, Grignard reagents, diazomethane, lithium alkyl reagents, iodinating and fluorinating agents failed to give any significant reaction, and the low reactivity to these reagents was attributed to steric effects. The halogen on the boron atom could be replaced in reactions leading to the formation of an exocyclic B-N bond and several pseudohalogen compounds have been well characterised. The tetra-B-isocyanate, isothiocyanate, isoselenocyanate and azide were formed under relatively mild reaction conditions by treating $(Bu^tNBCl)_4$ with the alkali metal pseudohalides in a suitable solvent but the cyanide and isocyanide derivatives were not obtained. Under forcing conditions partial replacement of chlorine by methylamino and ethylamino groups in $(Bu^tNBCl)_4$ could be achieved, but pure species were not isolated. Attempts at partial substitution of $(Bu^tNBCl)_4$ with potassium thiocyanate and separately sodium azide led somewhat surprisingly to mixtures of the tetra-substituted compounds only.

Initial X-ray work on chloro-substituted borazocines proved to be difficult,[57,63] but the borazocine $(Bu^tN\text{-}BNCS)_4$ was found more suitable.[64] The results for both of these compounds indicated an eight-membered ring with alternating boron and nitrogen atoms and B-N bond lengths. In $(Bu^tNBNCS)_4$ the ring could be regarded as consisting of four identical cis-borazene units 1-LXXV, each unit having coplanar atoms. The observed bond lengths and angles



1-LXXV

indicated considerable π-interaction between the NCS groups and the B-N units of the ring. Further support for π interaction came from the observation of parent ions in the mass spectrum of $[Bu^tNBNCS]_4$ whereas $[Bu^tNBCl]_4$ did not yield parent ions.

In a series of pseudohalogen substituted borazocines red shifts were observed in the U.V. absorptions due to both the heterocyclic ring and the pseudohalogen group further indicating π-interaction.

Ten-membered boron-nitrogen ring systems

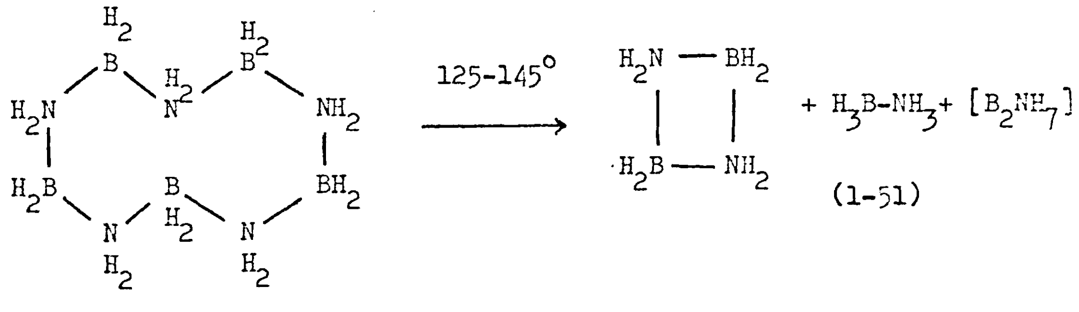
Cyclopentaborazanes

The preparation of the parent compound has been reported by Shore et al.[12,65] by the separate reactions of sodium acetylide and sodium amide with the diammoniate of diborane $BH_2(NH_3)_2BH_4$ in liquid ammonia as represented in equation 1-50. Other cycloborazanes were also produced in the reaction in differing amounts depending on the conditions employed. In all reactions cyclopentaborazane was the major product, but 5% of cyclotriborazane and still smaller

$$NaX + BH_2(NH_3)_2^+\ BH_4^- \xrightarrow[NH_3]{liquid} NaBH_4 + HX + NH_3 + \frac{1}{5}(BH_2NH_2)_5 \qquad (1\text{-}50)$$

and varying yields of cyclodiborazane were also formed. Cyclopentaborazane was also isolated from the reaction of metallic sodium with the diammoniate of diborane.

Cyclopentaborazane was a white microcrystalline solid, non sublimable in vacuum, which was extremely resistant to hydrolysis. Complete reaction could be effected only by acid hydrolysis at 160° for an extended period of time. It was characterised by analysis, infrared spectroscopy and its X-ray powder diffraction pattern. The thermal decomposition of $(BH_2NH_2)_5$ yielded cyclodiborazane $(BH_3NH_2)_2$ and other unidentified products. Ammoniaborane and a small amount of highly volatile material were isolated as shown in equation 1-51.



(1-51)

Two mechanisms have been postulated for the formation of the cyclic borazanes, and are indicated in schemes 1-52 and 1-53.

a) $\overset{+}{H_3NBH_2NH_3} + \overset{-}{NH_2} \longrightarrow H_3NBH_2NH_2 + NH_3$

b) $2H_3NBH_2NH_2 \longrightarrow H_3NBH_2NH_2BH_2NH_2 + NH_3$ (1-52)

c) $H_3N(BH_2NH_2)_n \longrightarrow (BH_2NH_2)_n + NH_3$

a) $H_3NBH_2\overset{+}{N}H_3 + NH_2^- \longrightarrow H_3NBH_2NH_2 + NH_3$ (1-53)

b) $\overset{+}{H_3NBH_2NH_3} + H_2NBH_2NH_3 \rightarrow H_3NBH_2NH_2BH_2\overset{+}{N}H_3 + NH_3$

c) $\overset{+}{H_3NBH_2NH_2BH_2NH_3} + NH_2^- \longrightarrow H_3NBH_2NH_2BH_2NH_2 + NH_3$

d) $H_3NBH_2NH_2BH_2NH_2 \begin{cases} +H_3NBH_2NH_3^+ \rightarrow & \text{extension of chain as in(1-53)(b)} \\ -NH_3 \longrightarrow & \text{cyclisation} \end{cases}$

CHAPTER II

SOLVENT EFFECTS ON THE B-H INFRARED STRETCHING FREQUENCY OF SUBSTITUTED CYCLOTETRAZENOBORANES

Only in the last few years have solvent effects on infrared group frequencies been systematically studied[66] and there still remains much uncertainty with regard to the nature of solvent effects on infrared vibrations in many compounds. In addition, the theoretical treatments which have been applied to solvent interactions are still far from adequate in accounting for observed shifts.

This investigation into the solvent effects on the B-H stretching frequencies of substituted cyclotetrazenoboranes was initiated in order to obtain evidence for the polarity of the B-H bond which was not apparent from molecular orbital studies[42] or from either the preliminary investigation of the chemistry of these compounds,[21,22] or an attempt to hydroborate ethylene or 1-butene using 2,5-dimethyl cyclotetrazenoborane.

EXPERIMENTAL

The Me_2N_4BH and Ph_2N_4BH were prepared by treating the appropriate amineborane with the particular organic azide and were purified by vacuum distillation or recrystallisation from light petroleum (B.Pt. 80 - 100°) in an inert atmosphere,[21,22] as will be described in detail in Chapter 3. The solvents were dried by standard procedures,[67] distilled and stored over 4A molecular sieves. The solutions were prepared in a dry, nitrogen filled glove container, and spectra were obtained using a Grubb-Parsons 'Spectromaster' grating spectrometer and 0.5 mm path length cell with NaCl windows. The spectromaster was accurately calibrated over the region of the spectrum 2700 cm^{-1} - 2400 cm^{-1} using the vapour spectrum of HBr,[68] run in duplicate. The accepted and observed frequencies, their relative errors and the reproducibility of the absorption bands are presented in Table 2-A. The frequencies quoted are those

TABLE 2-A

Accepted Literature Frequency cm^{-1}	Observed Frequency Spectrum 1 cm^{-1}	Observed Frequency Spectrum 2 cm^{-1}	Corrective Errors for Spectrum 1 cm^{-1}	Corrective Errors for Spectrum 2 cm^{-1}	Reproducibility cm^{-1}
2687.2	2686.0	2686.1	1.2	1.1	0.1
2674.9	2674.0	2673.8	0.9	1.1	0.2
2662.2	2661.1	2661.3	1.1	0.9	0.2
2648.9	2648.1	2647.9	0.8	1.0	0.2
2635.1	2634.1	2633.7	1.0	1.4	0.4
2620.8	2619.7	2619.5	1.1	1.3	0.2
2606.0	2605.0	2604.9	1.0	1.1	0.1
2590.8	2589.8	2589.5	1.0	1.3	0.3
2575.0	2573.9	2573.5	1.1	1.5	0.4
2542.1	2541.0	2540.7	1.1	1.4	0.3
2524.9	2523.9	2523.4	1.0	1.5	0.5
2507.3	2506.2	2505.8	1.1	1.5	0.4
2489.3	2488.0	2487.9	1.3	1.4	0.1
2470.8	2469.6	2469.2	1.2	1.6	0.4
2451.9	2450.7	2450.3	1.2	1.6	0.4
2432.6	2431.4	2431.3	1.2	1.3	0.1

for the average of the poorly resolved doublet of each band. The precision of the measurements was within ± 0.8 cm^{-1} of the absolute frequency, but the relative shifts were probably accurate to ± 0.5 cm^{-1} for non polar solvents and ± 0.8 cm^{-1} for polar solvents. The figures in Table 2-B were quoted to 0.1 cm^{-1} to avoid rounding off errors. The shifts in frequencies were quoted relative to the vapour spectrum of Me_2N_4BH, and an estimated vapour spectrum for Ph_2N_4BH.

RESULTS AND DISCUSSION

The corrected observed frequencies ν, frequency shifts $\Delta\nu$ and relative shifts $\Delta\nu/\nu$ were observed in a large range of solvents and are presented in Table 2-B. The ^{11}B-H and ^{10}B-H stretching vibrations were not completely resolved and the frequencies quoted were those for the weighted mean.

The theoretical explanations of solvent shifts were summarised by Hallam,[66] who pointed out that the Kirkwood-Bauer-Magat (K.B.M.) relationship or its extensions by Buckingham or

$$\Delta \nu/\nu \quad = \quad C\ (\varepsilon - 1)/(2\varepsilon + 1)$$

Pullin[66] fell short of a complete interpretation. Each of these treatments predicted a decrease in frequency with increasing polarity of solvent, since they were based on the model of a diatomic oscillator in a spherical solvent cavity and took no account of specific interaction between solvent and solute. In

TABLE 2-B SOLVENT SHIFT DATA FOR Ph_2N_4BH and Me_2N_4BH

SOLVENT	NUMBER^e	diphenylcyclotetrazenoborane			dimethylcyclotetrazenoborane				
		ν	$\Delta\nu$	$\Delta\nu/\nu x10^3$	ν	$\Delta\nu$	$\Delta\nu/\nu x10^3$	ε^b	$(\varepsilon-1)/(2\varepsilon+1)$
None^a	0	2648.5	0	0	2627.0	0	0	-	-
n-hexane	1	2648.7	0.2	0.07	2627.1	0.1	0.04	1.89	0.186
carbon disulphide	2	2649.7	1.2	0.45	2627.6	0.6	0.23	2.64	0.261
tetrachloroethylene	3	2649.8	1.3	0.49	2629.7	2.7	1.03	2.37^d	0.239
carbon tetrachloride	4	2650.7	2.2	0.83	2629.8	2.8	1.06	2.24	0.226
methylene iodide	5	2651.1	2.6	0.98	2630.8	3.8	1.44	5.32	0.371
p-xylene	6	2651.4	2.9	1.09	2628.2	1.2	0.46	2.27	0.229
cyclohexanone	7	2652.2	3.7	1.40	2632.4	5.4	2.05	18.3	0.460
m-xylene	8	2652.4	3.9	1.47	2629.3	2.3	0.87	2.37	0.239
benzene	9	2652.4	3.9	1.47	2631.2	4.2	1.60	2.28	0.230
o-xylene	10	2653.1	4.6	1.73	2629.9	2.9	1.10	2.57	0.256
mesitylene	11	2653.3	4.8	1.81	2629.3	2.3	0.87	2.28	0.230
toluene	12	2653.4	4.9	1.85	2630.6	3.6	1.37	2.39	0.240
methyl iodide	13	2653.6	5.1	1.92	2630.0	3.0	1.14	7.00	0.400
acetophenone	14	2654.2	5.7	2.15	2631.1	4.1	1.56	17.93	0.459
methylene bromide	15	2654.2	5.7	2.15	2632.6	5.6	2.13	7.70	0.409
bromoform	16	2654.3	5.8	2.19	2633.4	6.4	2.43	4.39	0.347
chlorobenzene	17	2654.6	6.1	2.30	2633.4	6.4	2.43	5.71	0.379
bromobenzene	18	2654.9	6.4	2.41	2630.7	3.7	1.41	5.40	0.373
aniline	19	2655.3	6.8	2.56	2634.2	7.2	2.73	6.89	0.399

chloroform	20	2656.1	7.6	2.86	2636.4	9.4	3.57	4.81	0.359
sym.tetrachloroethane	21	2656.2	7.7	2.90	2638.0	11.0	4.17	8.15[d]	0.413
ethyl acetate	22	2656.4	7.9	2.97	2632.9	5.9	2.24	6.02	0.385
1,2 dichloroethane	23	2657.3	8.8	3.31	2634.9	7.9	3.00	10.65	0.433
nitrobenzene	24	2658.0	9.5	3.57	2634.3	7.3	2.77	35.74	0.479
methylene chloride	25	2658.2	9.7	3.65	2636.3	9.3	3.53	9.08	0.422
nitromethane	26	2662.3	13.8	5.18	2640.6	13.6	5.15	39.4[c]	0.481
1,4 dioxan	27	-	-	-	2631.5	4.5	1.71	2.21	0.223
acetone	28	-	-	-	2634.5	7.5	2.85	20.70	0.465
pyridine	29	-	-	-	2635.0	8.0	3.04	12.30	0.441
nitrobenzene: carbon tetrachloride mixture:-									
1:3		2653.9	5.4	2.03	-	-	-		
1:1		2655.1	6.6	2.49	-	-	-		
3:1		2656.4	7.9	2.97	-	-	-		

[a] Vapour spectrum for Me_2N_4BH and estimated vapour spectrum for Ph_2N_4BH.

[b] Data at 20° from "Handbook of Chemistry and Physics", 47th Edition, Chemical Rubber Co., 1966 p. E. 58, except where otherwise stated.

[c] "Encyclopedia of Chemical Technology", Vol. 9, Ed. R.D. Kirk and D.F. Othmer, Interscience Encyclopedia Inc., New York, 1952.

[d] "Thorpes Dictionary of Applied Chemistry", J.F. Thorpe and M.A. Whiteley, 4th Edition, Vol. 1, Longmans Green and Co., London, 1937, p. 97.

[e] Represents the number of the solvent concerned as plotted in the figures.

order to ascertain whether the K.B.M. correlation with the dielectric relationship existed, $\Delta \nu/\nu$ for 2,5-dimethyl cyclotetrazenoborane and 2,5-diphenyl cyclotetrazenoborane were plotted against $(\varepsilon - 1)/(2\varepsilon + 1)$ for the solvents used, and the results are presented in figures [2-1A] and [2-1B]. It was apparent from these graphs that a wide spread of points existed and it was therefore concluded that a dielectric relationship between the frequency shift and the dielectric constant function of the solvent did not exist. This conclusion however must be made with a slight amount of reservation as Hallam,[69] obtained a spread of points only marginally better for the frequency shifts of C - X (where X = halogen) vibrations in a large series of solvents, and quoted this evidence in support of the K.B.M. relationship. For this reason an attempt has been made to draw a best straight line through the points. Contrary to predictions made solely on the grounds of dielectric effects it was found in general that the frequencies of the vibrations <u>increased</u> with increasing polarity of the solvent.

Bellamy, Hallam and Williams[70] studied the nature of the solvent effects by direct comparison of the relative X-H frequency shifts of two different solutes in a variety of different solvents. This had the advantage of eliminating all those properties of the solvents that operated to similar extents in the two cases. Linear

FIGURE [2-1A]

K.B.M. DIELECTRIC PLOT FOR Me_2N_4BH.

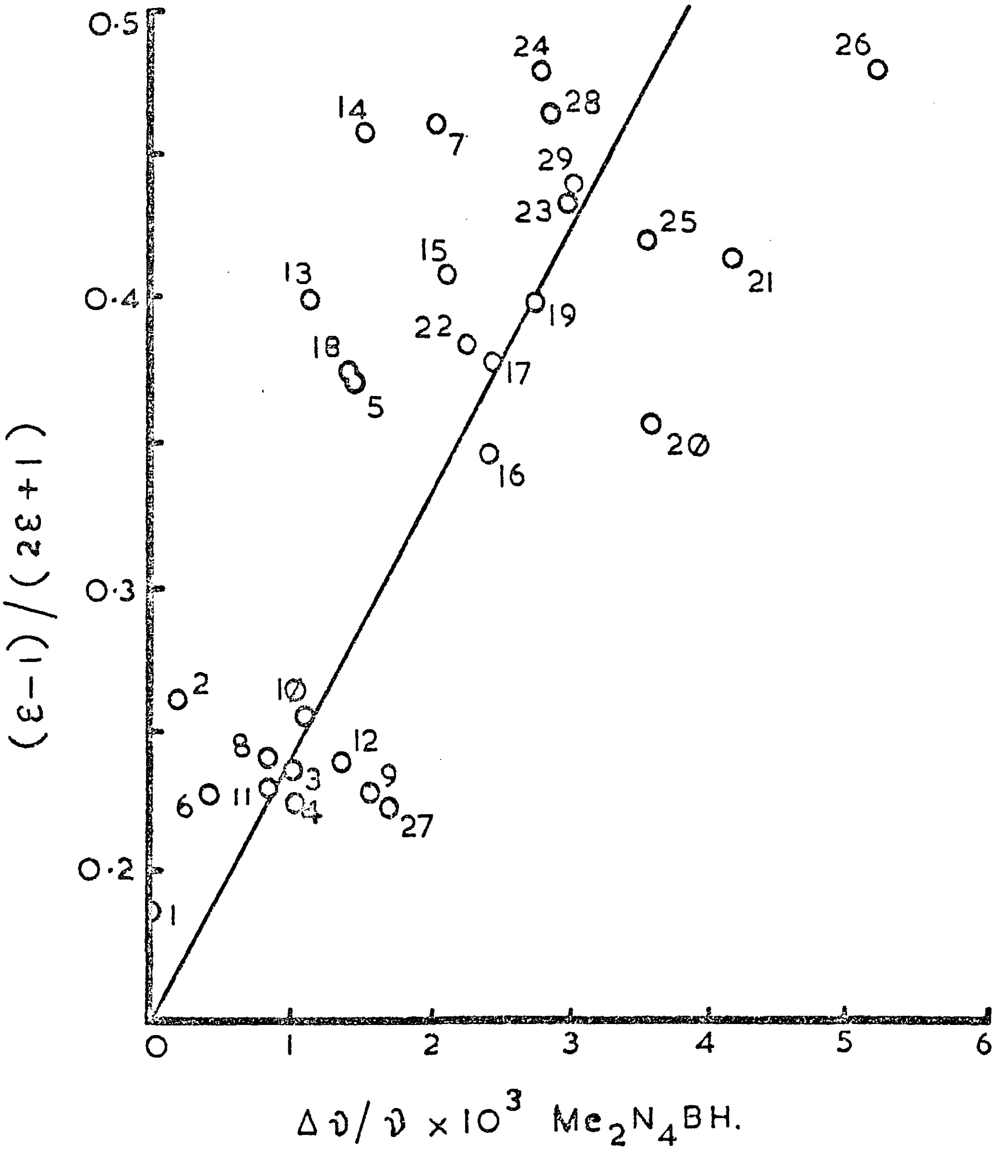
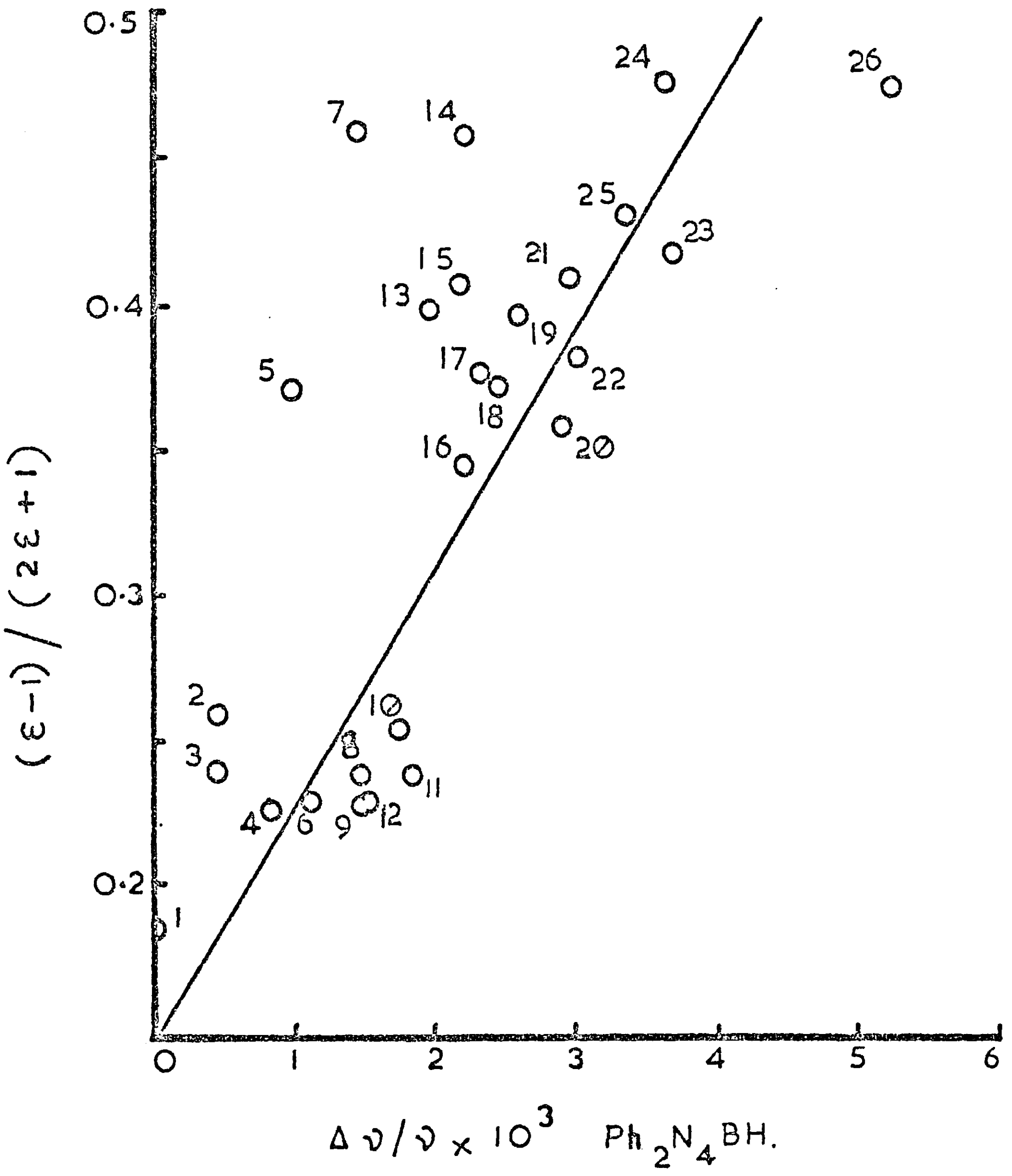


FIGURE [2-1B]

K.B.M. DIELECTRIC PLOT FOR Ph_2N_4BH.



plots were obtained, showing that the interaction between the solvent and the two solutes was of a similar nature, and few deviations from linearity were observed. It was concluded that solvent effects in these cases were purely local in character and, as the graphs did not have coincident slopes of 45° but varied widely, that overall properties such as the dielectric constant of the medium played little or no part in determining the size of the frequency shifts.

It had been anticipated that if the polarity of the B-H bond in cyclotetrazenoborane derivatives was similar to that in pyrrole, as had been found for decaborane,[70] namely either $B^- - H^+$, or essentially non polar, a linear relationship between $\Delta\nu/\nu$ B-H and $\Delta\nu/\nu$ N-H would be found. In fact no correlation was found as shown in Figures [2-2A] and [2-2B], nor with the observed frequency shifts of any of the other X-H vibrations reported, although in some cases the range of solvents considered was limited[70]. The interaction effects of the B-H of cyclotetrazenoboranes and other X-H frequencies in solvents were therefore clearly different, suggesting that the major factor in the shift of the X-H frequency for cyclotetrazenoboranes was not attributable to hydrogen bonding with solvent molecules, in contrast to other X-H containing compounds.[70]

PLOTS OF FREQUENCY SHIFTS FOR CYCLOTETRAZENOBORANE DERIVATIVES AGAINST THOSE FOR PYRROLE

FIGURE [2-2A]

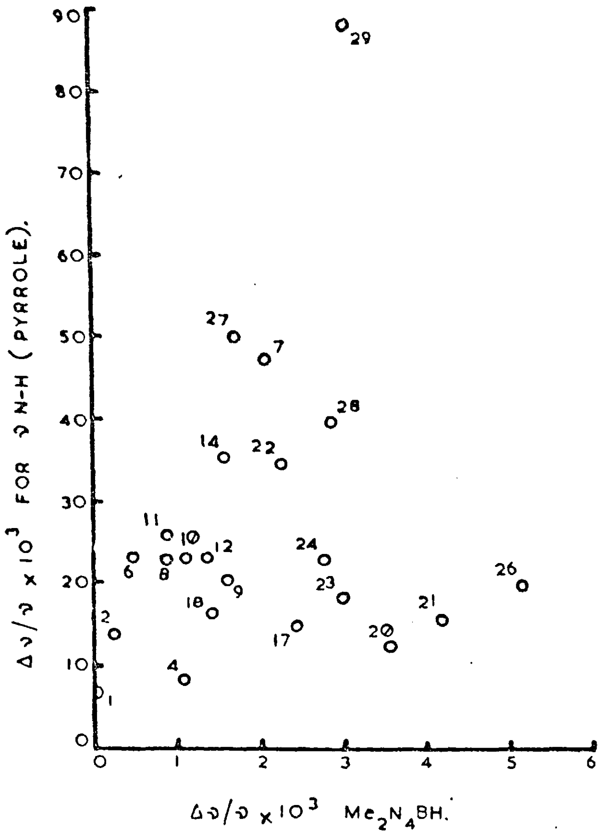
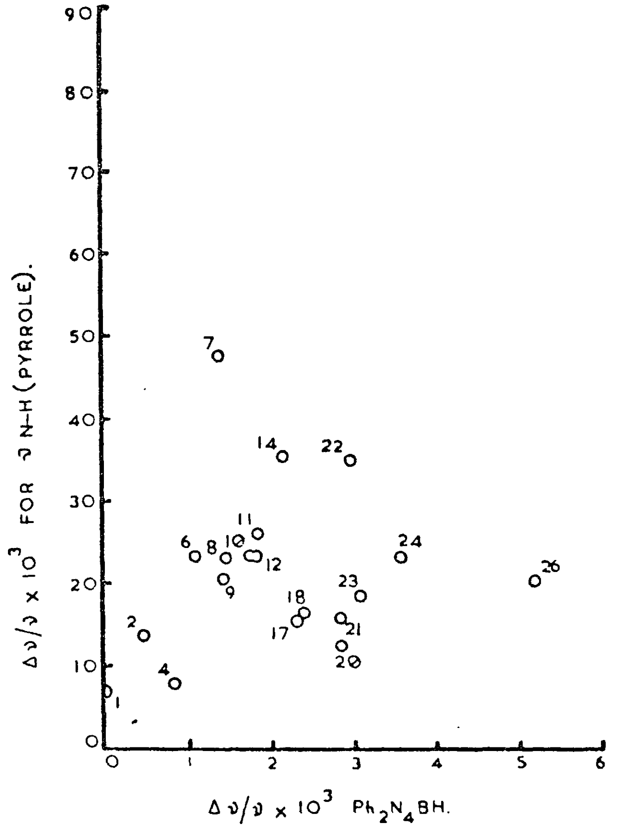


FIGURE [2-2B]



Bellamy and Williams[71] further showed that there existed a linear relationship between the shifts of carbonyl stretching frequencies in various solvents for a wide range of compounds containing the carbonyl grouping. In this case the free end of the dipole available for solvent interaction was exactly opposite to that for $\overset{-\leftarrow+}{X - H}$ i.e. $\overset{+\longrightarrow-}{>C = O}$. The observed solvent interaction effects were different in nature and overall patterns for the X-H and C=O dipoles. Dielectric constant factors would not have been expected to be influenced by the change in direction of the solute dipole and would have led to similar patterns of behaviour for the two cases.

It was therefore anticipated that if the polarity of the B-H bond in cyclotetrazenoboranes was similar to that in carbonyl compounds[71] i.e. $\overset{+\rightarrow-}{B - H}$, a linear relationship would exist between $\Delta\nu/\nu$ B-H and $\Delta\nu/\nu$ C=O of acetophenone. Some justification for this was presented in that plots of $\Delta\nu/\nu$ X-Cl against $\Delta\nu/\nu$ C=O of standard compounds had earlier been proved to give tolerable straight lines,[69] although some spread of points was observed. It is of interest to note, however, that a much better linear relationship was obtained between $\Delta\nu/\nu$ X-Cl and $\Delta\nu/\nu$ X-Cl of a standard compound.

Once again non linear plots were in practice obtained for $\Delta\nu/\nu$ B-H against $\Delta\nu/\nu$ C=O for acetophenone as represented in figures [2-3A] and [2-3B], and also for the frequency shifts of

PLOTS OF FREQUENCY SHIFTS FOR CYCLOTETRAZENOBORANE DERIVATIVES AGAINST THOSE FOR ACETOPHENONE

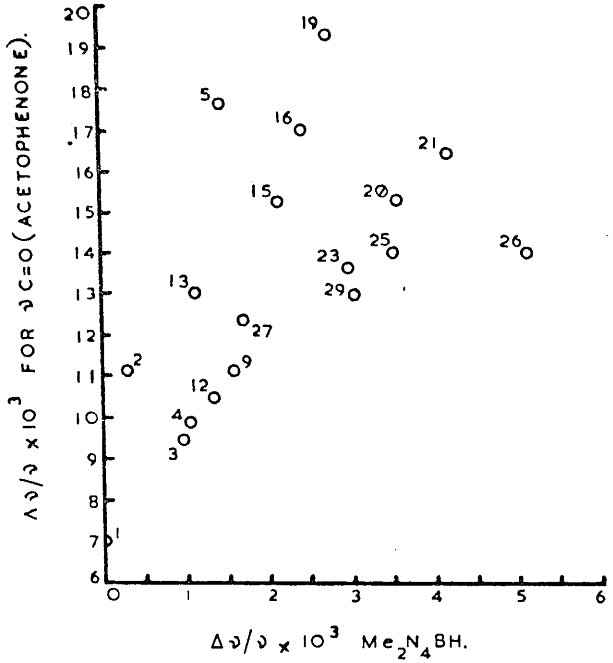


FIGURE [2-3A]

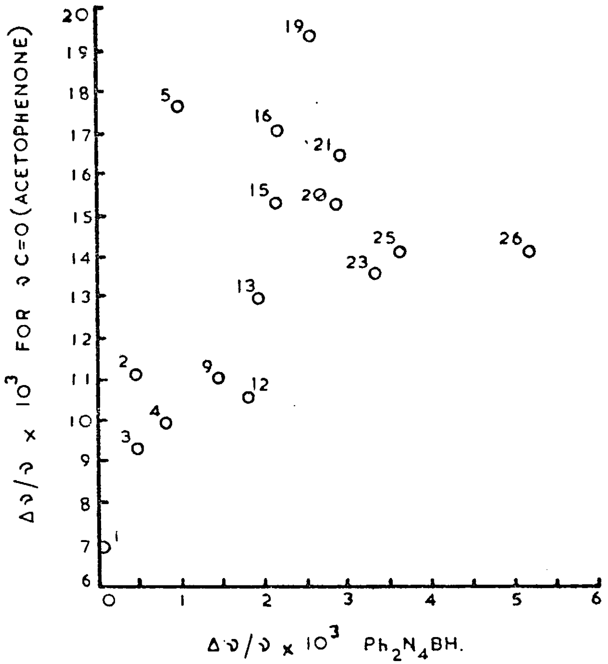
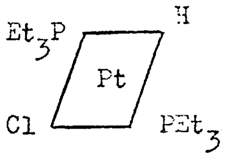


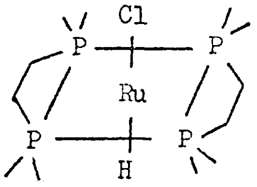
FIGURE [2-3B]

several other carbonyl containing compounds reported.[71]

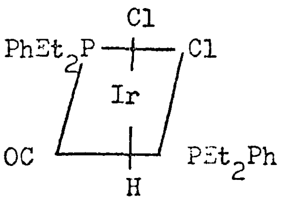
Similarly a non-linear relationship was observed of $\Delta\nu/\nu$ B-H with $\Delta\nu/\nu$ X-Cl using the frequency shifts reported by Hallam.[69] Typical plots are shown in figures [2-4A] and [2-4B].

It was anticipated that the nature of the interactions might more closely resemble those of certain transition metal hydrides in which similar <u>increases</u> of frequency with increasing polarity of the solvent had been observed.[72,73,74] However the range of solvents used was somewhat limited, and non-representative but mostly non-linear relative shift plots with the cyclotetrazenoborane derivatives were obtained, a few examples of which are shown in figures [2-5A] → [2-5F] for the Pt-H, Ru-H and Ir-H frequency shifts in





and



Similar non-linear relationships existed between the relative P-H frequency shifts of a series of phosphonates $(RO)_2P(O)H$ which were also shown to yield an <u>increasing</u> frequency shift with increasing polarity of the solvent,[75] and the frequency shift of cyclotetrazenoboranes.

PLOTS OF FREQUENCY SHIFTS FOR CYCLOTETRAZENOBORANE DERIVATIVES AGAINST THOSE FOR CIS-DICHLOROETHYLENE.

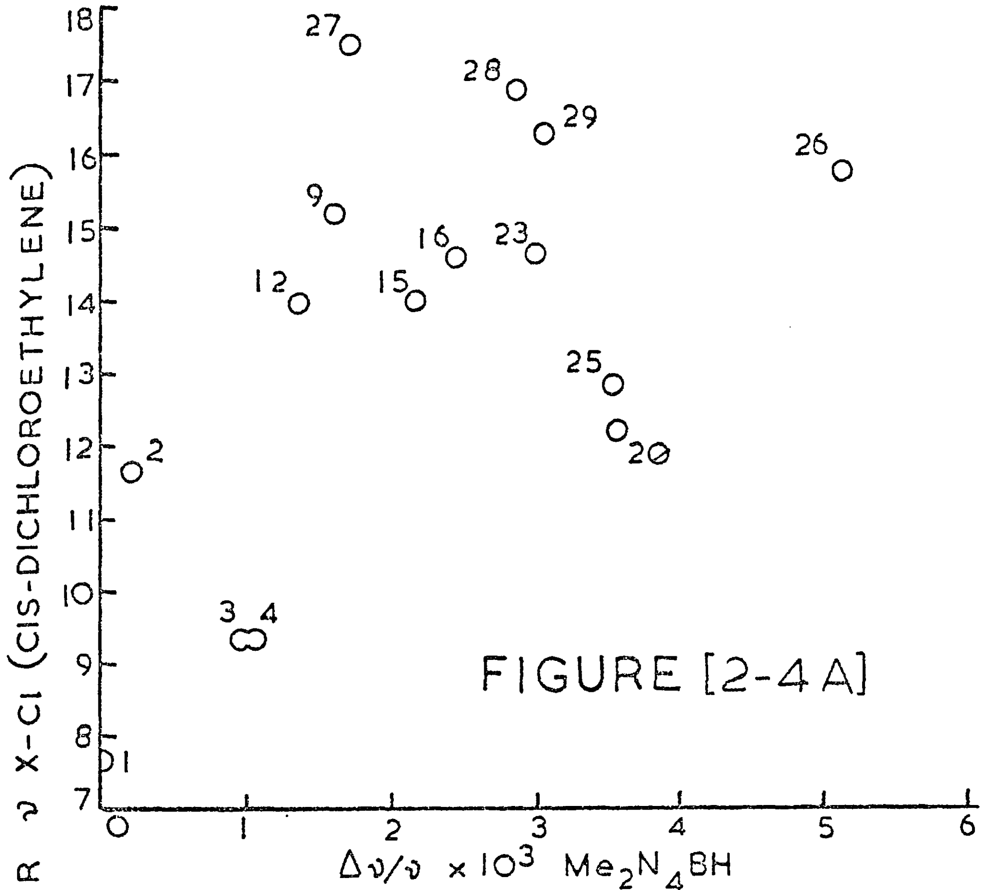


FIGURE [2-4A]

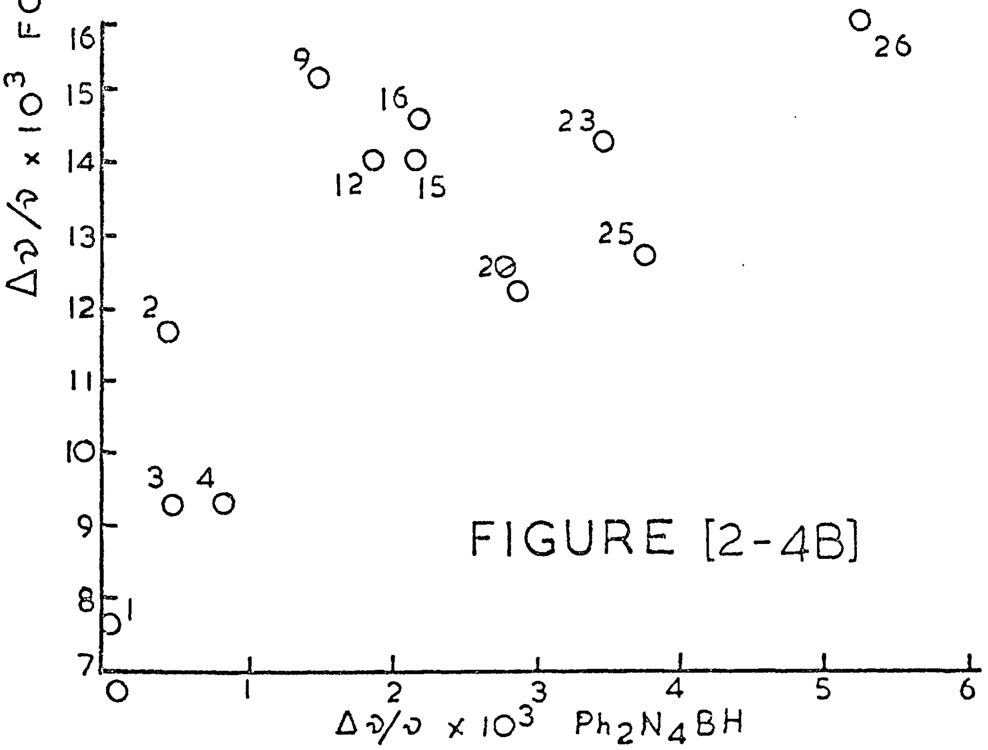


FIGURE [2-4B]

PLOTS OF FREQUENCY SHIFTS FOR METAL HYDRIDE DERIVATIVES AGAINST THOSE FOR Me_2N_4BH & Ph_2N_4BH.

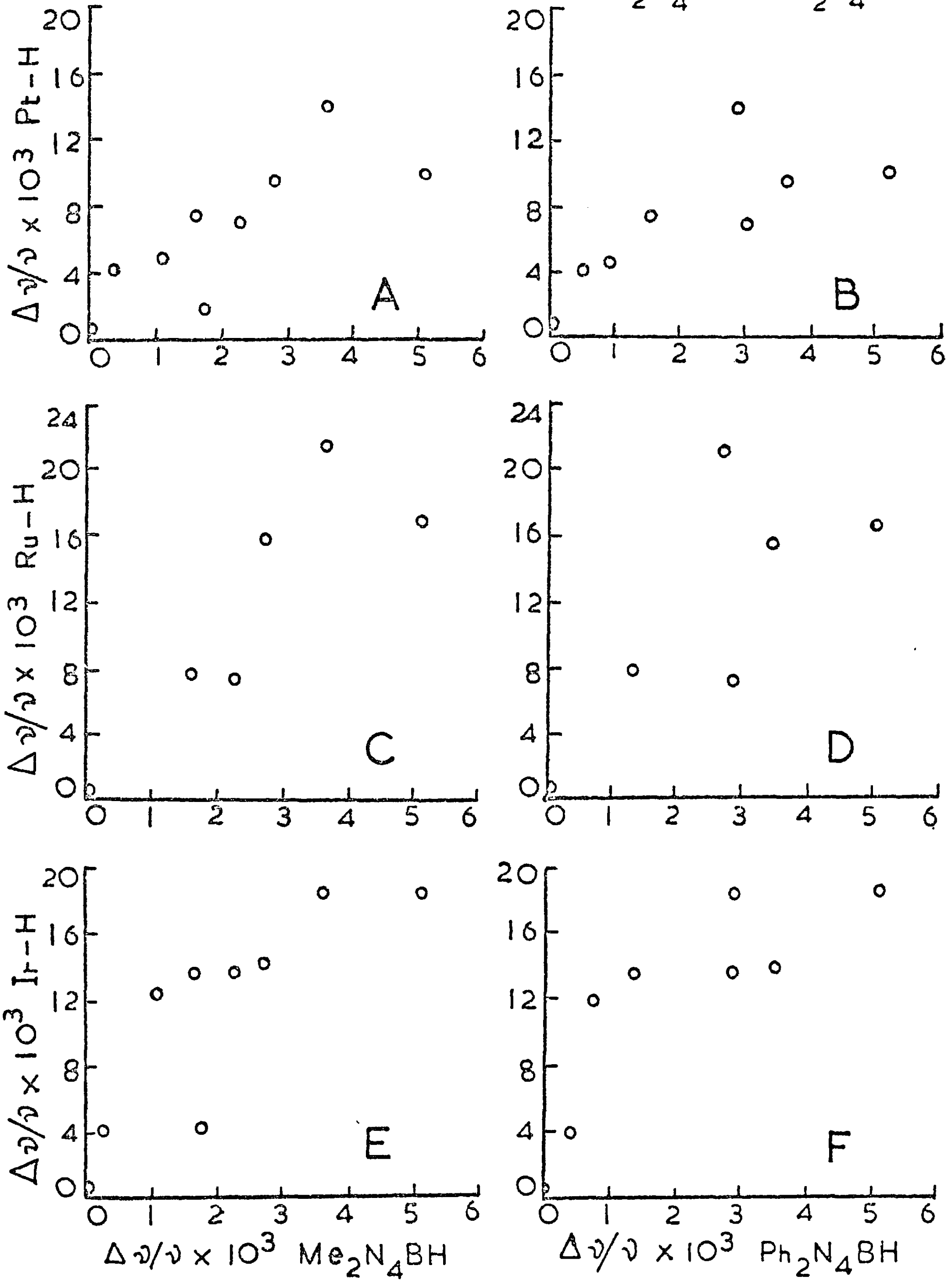
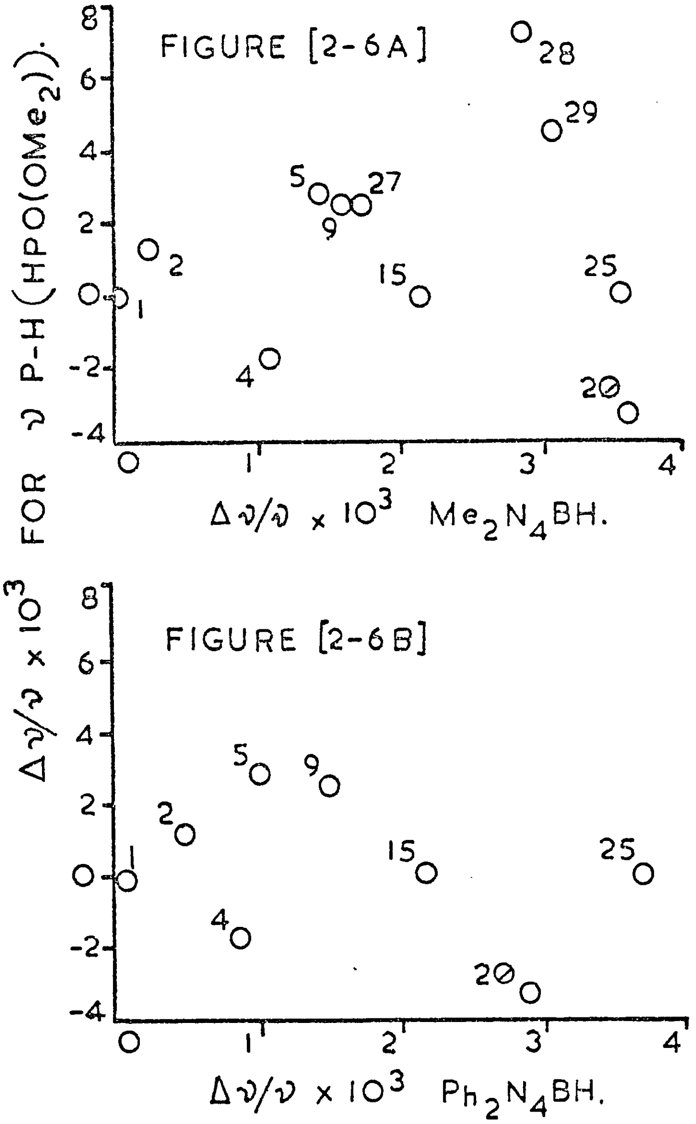


FIGURE [2-5]

PLOTS OF FREQUENCY SHIFTS FOR CYCLO-TETRAZENOBORANE DERIVATIVES AGAINST THOSE FOR DIMETHYL PHOSPHONATE.



Representative plots are shown in figures [2-6A] and [2-6B]. The relatively broad P-H stretching frequencies and the small shifts observed for these however did not follow the normal pattern of other ν (X-H) frequencies as in pyrrole and similar compounds, nor did they correlate with solvent dielectric constant or the K.B.M. (ε -1/2ε +1) function.[75]

In an attempt to determine whether specific interaction of the solutes with the solvent was occurring to a major extent, the effect of mixed solvents on the B-H stretching frequency of diphenyl-cyclotetrazenoborane was also investigated. The particular solvents chosen were nitrobenzene and carbon tetrachloride since these represented solvents in which large and small shifts were observed respectively. It was found that no splitting or broadening of the peak occurred, and that the frequency shift of the B-H plotted against the volume ratio of the solvents was close to linearity as shown in figure [2-7]. This therefore suggested that specific solvent-solute interactions did not play a major role, as splitting or broadening of the peak and a non-linear plot would have been expected, and this evidence favoured the shift being related to a dielectric effect. However, all other evidence - in particular the <u>increase</u> of frequency with increasing polarity of solvent - strongly favoured the occurrence of specific solvent interactions. Conclusive evidence may be

PLOT OF $\Delta\nu/\nu$ Ph_2N_4BH IN $PhNO_2/CCl_4$ MIXTURES.

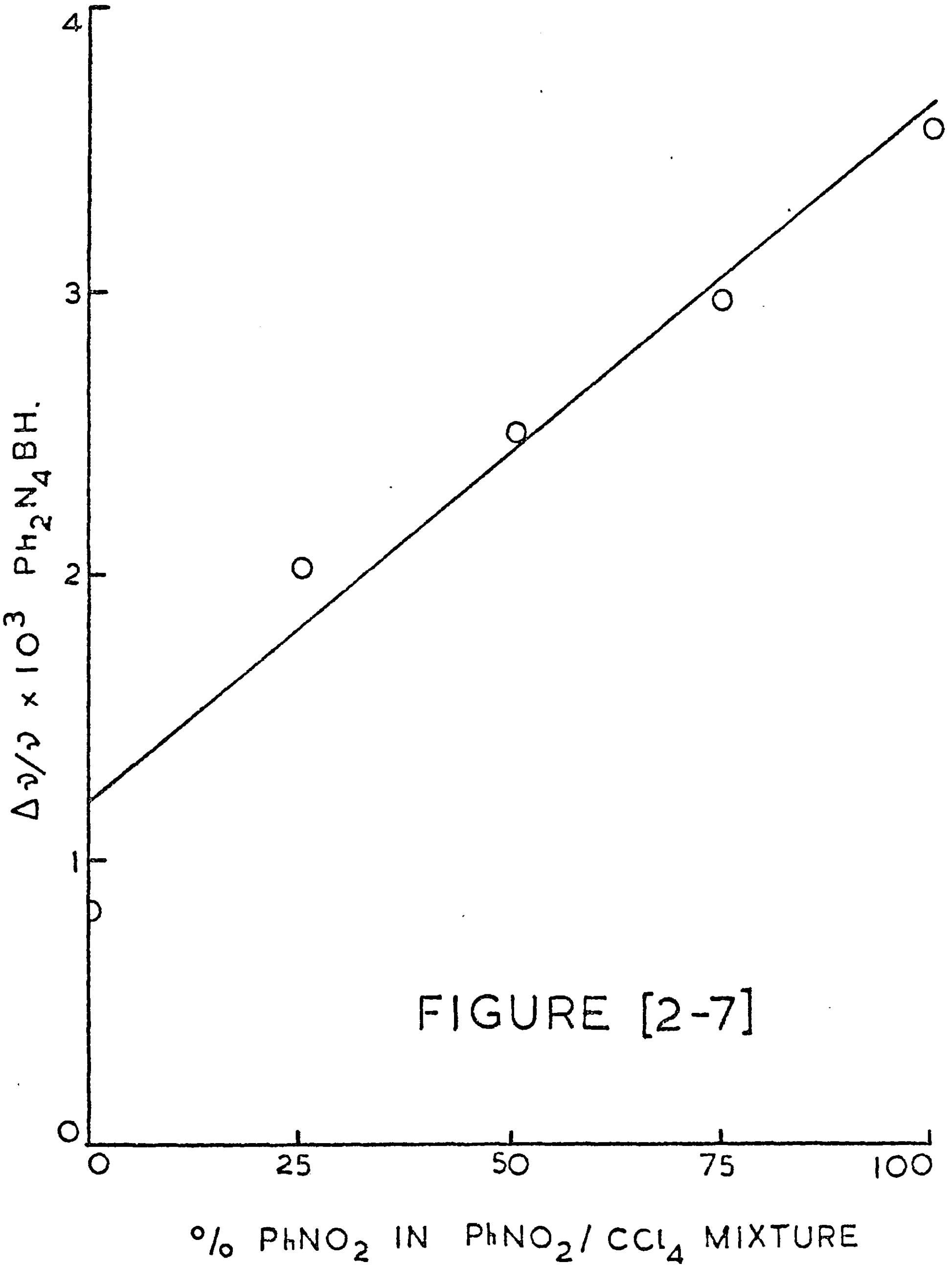


FIGURE [2-7]

difficult to obtain by this method since similar anomalous results for mixed solvent studies have been reported for carbonyl compounds.[76]

Instances of the phenomenon of *increasing* frequency of a vibrating group with increasing polarity of solvent are rare.[75,77,78,79] The small shifts observed for the P-H stretching frequencies in alkyl phosphonates,[75] except in the case of the strong electron donors, acetone and pyridine, were attributed to the similarities of the electronegativities of P and H, resulting in an unfavourable situation for the formation of hydrogen bonds. It was however observed that the shifts obtained in the P=O stretching frequency in these compounds occurred in the accepted pattern for $\overset{+}{X} = \overset{-}{O}$ dipoles,[71] and it was therefore considered that the abnormal P-H shifts might be the result of a material alteration in the charge distribution of the P-H bond, arising from electronic effects from other groups attached to the phosphorus atom.

Tentative explanations were similarly made for the occurrence of *increasing* frequency shifts with increasing polarity of solvent in the case of iron carbonylhalides[77] and nitrosyl chloride.[78,79] The explanations were based on valence bond descriptions of the molecules. The effects have been attributed to interaction of the solvent molecules with regions of the molecules remote from the vibrating group under investigation, and have been interpreted in terms of increased contributions of ionic canonical forms to the total wave function, e.g.

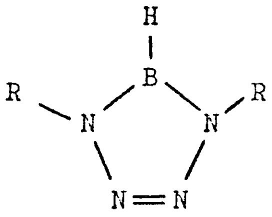
$$Cl - M \overset{\cdots}{-} C \overset{\cdots}{=} O \quad \text{and} \quad Cl^- \; M^+ - C \equiv O$$

$$Cl - N = O \quad \text{and} \quad Cl^- \; N^+ \equiv O$$

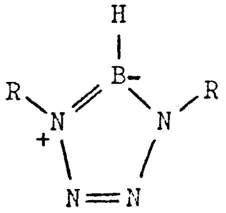
causing an increase in the bond order of the C-O or N-O bond. The analogous effects in transition metal hydrides occurred in compounds in which the vibrating group was trans to a halogen[73,74] and the explanation for these was that a halogen atom trans to a hydrogen carried more charge than the hydrogen, and would consequently be preferentially solvated in polar media. The tendency would be to increase the ionic contribution of the total wave function which would cause a corresponding increase in the strength of the M-H bond.

$$X - M - H \quad \text{and} \quad X^- \; M^+ - H$$

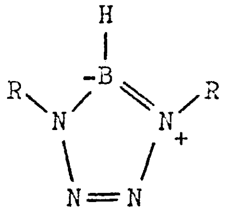
Although cyclotetrazenoborane derivatives have already been treated by an M.O. method,[42] it was useful to consider the alternative valence bond approach at least qualitatively. Canonical forms which can be written are:-



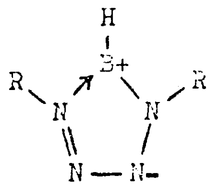
2-I



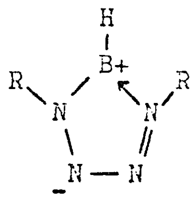
2-II



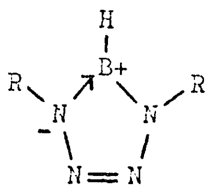
2-III



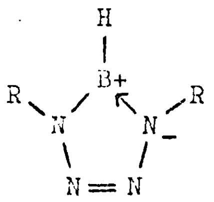
2-IV



2-V



2-VI



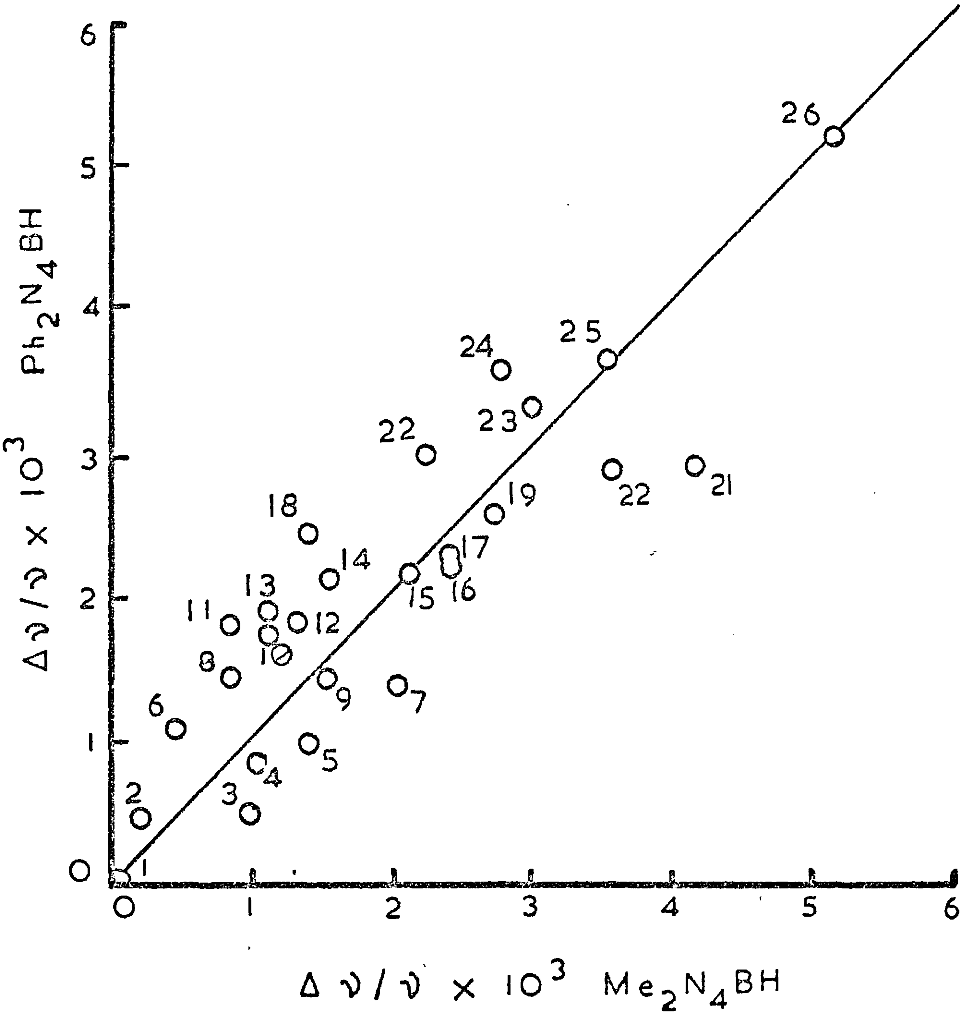
2-VII

It could therefore be suggested that solvent interaction occurs at the more electronegative nitrogen atoms, and hence causes increased contributions of forms 2-I → 2-VII to the total wave function.

A plot of $\Delta\nu/\nu$ for Me_2N_4BH v. $\Delta\nu/\nu$ for Ph_2N_4BH gave approximately a straight line, as shown in figure [2-8]. Similar linear relationships were observed for the P-H frequency shifts in a series of dialkyl phosphonates.[75] This indicated that the interaction of any one solvent with the two solutes was essentially of the same nature and supported the assumption that solvent interaction occurred predominantly with the heterocyclic ring. Opposed to this, however, was the observed slope of the line in figure [2-8] which approximated to 45° and would tend to indicate that some bulk factor such as the dielectric constant was responsible for the frequency shifts and that specific interactions did not play an important role. Alternatively the slope could be rationalised if it was considered that the specific interactions were highly associated with the heterocyclic ring and produced very similar solvent shifts in the B-H frequency for the two cyclotetrazenoboranes examined.

FIGURE [2-8]

FREQUENCY SHIFT RELATIONSHIP BETWEEN DIMETHYL- AND DIPHENYL- CYCLOTETRAZENOBORANE.



CHAPTER III

THE PREPARATION AND PROPERTIES OF B-H (D), B-ALKYL, B-ARYL AND B-VINYL SUBSTITUTED CYCLOTETRAZENOBORANES

RESULTS AND DISCUSSION

The polarity of the B-H bond is cyclotetrazenoboranes was not obvious from the solvent shift study on the B-H infrared stretching frequency described in Chapter II. Attempts to hydroborate butene-1 and ethylene by reaction with Me_2N_4BH, which might have produced evidence for the polarity, were unsuccessful yielding only unchanged starting materials.

The intermediate cyclotetrazenoboranes Me_2N_4BH and Ph_2N_4BH required for the reactions to be discussed in this chapter were in general prepared by the methods reported by Morris,[21,22] although several new methods were attempted for the synthesis of Me_2N_4BH. The cyclotetrazenoborane ring system was derived in preference to the formation of a borazine by the capture of a borazyne intermediate in the presence of an organic azide. It was thought possible that the reaction of an organic azide with a borazine might also lead to the preparation of the cyclotetrazenoborane ring system. However the reactions of tri-N-methyl borazine with methyl azide using variations of reaction time and temperature did not yield Me_2N_4BH.

The reaction of $(MeNHBH_2)_3$, an intermediate in the preparation of $(MeN - BH)_3$, with methyl azide gave rise to several products, from which Me_2N_4BH together with N-trimethylborazine was isolated by vacuum distillation. The two compounds were confirmed by comparison with their known standard infrared spectra.

One of the major complications during the course of this work on cyclotetrazenoboranes was the small quantity of compound preparable in any single experiment. This was because it was necessary to use sealed ampoules for the reactions in order to contain the volatile reactants and solvents. The evolution of H_2 during the reaction together with solvent vapour pressures therefore restricted the scale of the reaction performed.

An attempt was made to achieve a large scale preparation of Me_2N_4BH without the use of sealed tubes by the reaction of methylamine hydrochloride, sodium borohydride and dimethyl sulphate in monoglyme (B.pt. 83°C). This complex reaction gave rise to numerous uncharacterised products but Me_2N_4BH was not detected. A possible reason for this was that the temperature of reflux was not high enough for the methyl azide and amine borane produced in the reaction, to react together, but practical difficulties excluded raising the temperature by use of another solvent.

It has been found that in common with borazines,[80,81] the hydrogen attached to the boron atom in cyclotetrazenoboranes can be replaced by organic groups by means of Grignard reagents, and that the reaction proceeds through the formation of a magnesium-containing intermediate, as shown in reaction scheme 3-1.

$$R_2N_4BH \ + \ R'MgX \ \xrightarrow[\text{or T.H.F.}]{Et_2O} \ [R_2N_4BH.R'MgX] \quad ?$$

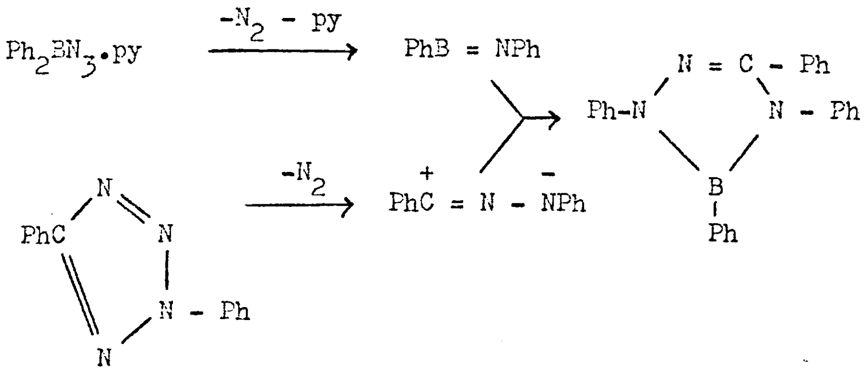
$$[R_2N_4BH.R'MgX] \ \xrightarrow[NH_4Cl \text{ soln.}]{\text{sat. aqueous}} \ R_2N_4BR' \qquad (3\text{-}1)$$

By this method the new compounds Ph_2N_4BPh, Ph_2N_4BMe, Et_2N_4BEt, Me_2N_4BMe were prepared. The compound Me_2N_4BVi was also prepared by this route although some reduction of the vinyl group took place to give a product contaminated with Me_2N_4BEt, and the latter compound was obtained by catalytic hydrogenation of the vinyl substituted compound. During the preparations, the magnesium containing intermediates separated as yellow crystalline solids from fluorescent solutions in the phenyl substituted compounds, or as colourless oily liquids or white crystalline solids in the fully alkylated compounds, and were readily decomposed with saturated aqueous ammonium chloride to give B-organo-substituted cyclotetrazenoboranes with hydrogen evolution.

The reaction of the hydrogen attached to boron with Grignard reagents therefore suggested that the B-H bond was essentially polarised $\overset{\delta+}{B} - \overset{\delta-}{H}$.

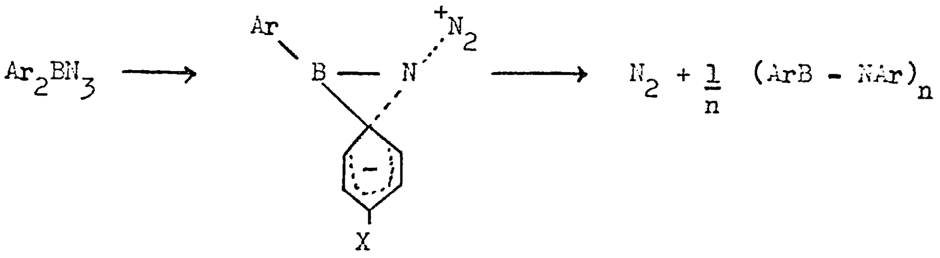
Paetzold[82] has (see Chapter I) shown that the thermal decomposition of diphenylboron azide proceeded through the loss of nitrogen, followed by a Curtius-type rearrangement to the boron imide intermediate [Ph - B = N - Ph], and that although this could be isolated as the dimer $(PhBNPh)_2$, cycloaddition with 1,3-dipolar compounds did occur. For example, on heating the pyridinate of diphenyl boron azide[83] in the presence of 2,5-diphenyl tetrazole, then 1,2,4,5-tetraphenyl-1-bora-2,3,5-triazacyclopentene- 3 was formed in

5% yield as shown in equation 3-2.



(3-2)

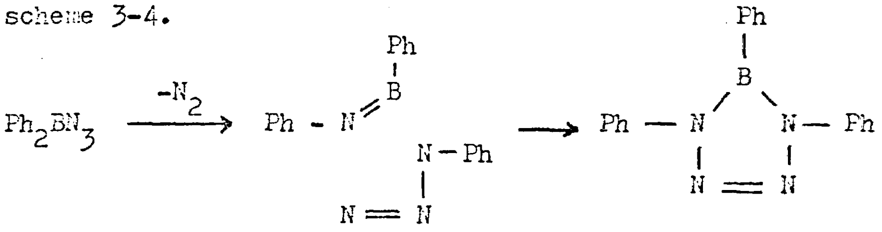
The mechanism of the formation of aryl boron imides was considered in some detail and in view of the fact that nitrene products were identified only in low yields, a "SYNCHRONOUS" mechanism was postulated involving the formation of a phenyl anion intermediate as shown in the reaction scheme 3-3.



(3-3)

In general it was concluded from experimental data that diorganoboron azides decomposed in a synchronous process with assistance from neighbouring organic groups. This assistance increased with electron-attracting properties and the bulky character of the neighbouring group.

The formation of triphenyl cyclotetrazenoborane was achieved by the thermal decomposition of diphenylboron azide in the presence of phenyl azide. This was considered to occur through 1,3 dipolar capture of the boron imide intermediate, as shown in reaction scheme 3-4.



(3-4)

Physical Properties

The physical properties of the compounds prepared are presented in Table 3-A except the principal bands in the vibrational spectra which are discussed separately, and the detailed mass spectra which will be reported in Chapter 5.

Electronic Spectra

The effect of substitution at the boron on the first electronic transition was slight for methyl, ethyl or phenyl groups, and the value of λ_{max} of 239 mμ for Ph_2N_4BMe compared reasonably well with the earlier prediction of 244 mμ for that compound.[42] However a bathochromic shift was observed when the substituent group was vinyl. This suggested that some π-interaction took place between the vinyl group and the boron atom since an isolated olefinic group would have been expected to absorb near 180 - 190 mμ. It is probable therefore that the absorption near

TABLE 3-A

PHYSICAL DATA FOR B-SUBSTITUTED CYCLOTETRAZENOBORANE R_2N_4BR'

Compound	mp°C	U.V. λ_{max}[a]	U.V. ε_{max}[b]	^{11}B N.M.R. δ (ppm)[c]	^{1}H N.M.R.[d] Group R	^{1}H N.M.R.[d] Group R'
Me_2N_4BD	10.5	198	-	-20.3 $\left[\begin{matrix}J_{BD}\\31\end{matrix}\right]$	δ $CH_3$6.65	-
Me_2N_4BMe	12.2	200	9.2×10^3	-26.8	δ $CH_3$6.55	δ $CH_3$9.51
Me_2N_4BEt	-	199	7.4×10^3	-26.7	δ $CH_3$6.55	δ C_2H_5 8.92[e]
Me_2N_4BVi	-	215	7.8×10^3	-22.5	δ $CH_3$6.46	δ Vi 3.59[e]
Et_2N_4BH	-50	199	7.3×10^3	-19.8 $\left[\begin{matrix}J_{BH}\\159\end{matrix}\right]$	δ CH_3,8.65; δ CH_2,6.02; J_{HH}, 7.2	δ BH, 5.42; J_{BH}, 163
Et_2N_4BEt	-34	204	5.5×10^3	-25.2	δ CH_3,8.70; δ CH_2,6.13; J_{HH},7.2	δ C_2H_5, 8.88[e]
Ph_2N_4BMe	116	239	2.4×10^4	-26.9	δ Ph, 2.66[e]	δ CH_3, 9.20
Ph_2N_4BPh	186	239	2.6×10^4	-26	δ Ph, 2.60[e]	δ Ph, 2.60[e]

[a] mμ; [b] $l.cm^{-1}mole^{-1}$; [c] ref. BF_3Et_2O; [d] tau values, ref. Me_4Si; [e] broad absorption or complex multiple

215 mμ corresponded to a $\pi \rightarrow \pi^*$ transition of the system, and the extrapolated intensity was comparable with that for fully alkylated cyclotetrazenoboranes. It is interesting to note that it was not found possible to detect $n \rightarrow \pi^*$ transitions in these compounds, whereas such transitions usually of weak intensity were often observed in compounds containing the azo-grouping.[84]

Nuclear Magnetic Resonance Spectra

The substitution of the hydrogen at boron by methyl, ethyl or phenyl groups resulted in a downward displacement in the ^{11}B N.M.R. chemical shift of the expected single resonance of about 6 ppm. This effect was of the same order of magnitude as that observed in borazines although there are some ambiguities in the literature.[85] B-vinyl substitution resulted in a downfield displacement of only about 2 ppm, and the difference was again probably attributable to π-interaction of the vinyl group with the boron atom. A similar effect was observed for borazines.[85] The ^{11}B N.M.R. spectrum for Et_2N_4BH showed the characteristic doublet shown in figure [3-1] from which a value for the coupling constant J_{B-H} was obtained. The ^{11}B N.M.R. of Me_2N_4BD is one of the few examples in which B-D coupling is observed as shown in figure [3-1]. The poorly resolved essentially symmetric triplet was analysed graphically to yield J_{BD} of 31 c/s, which compares well with the calculated value

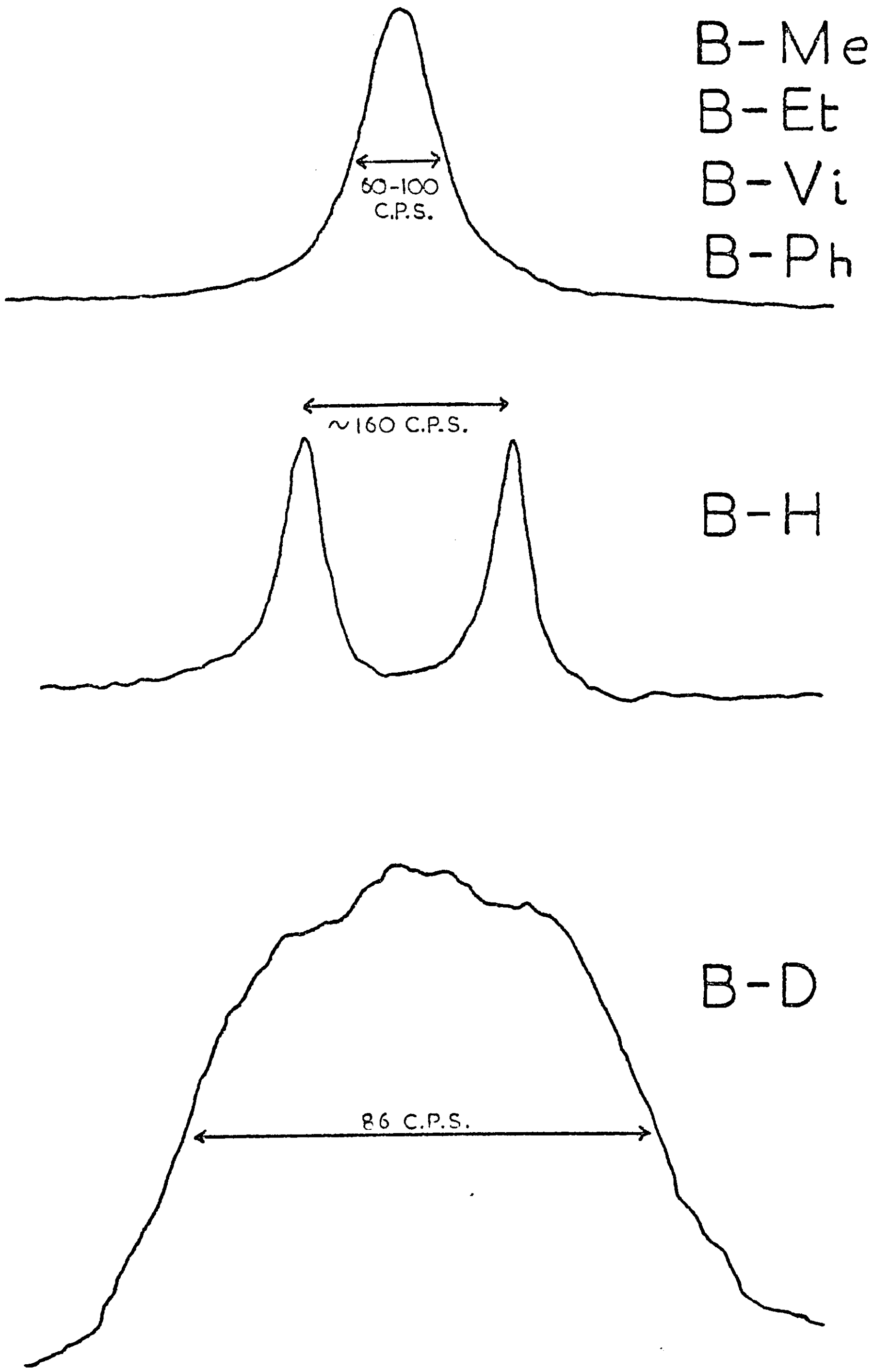


FIGURE [3-1]. ^{11}B N.M.R. SPECTRA.

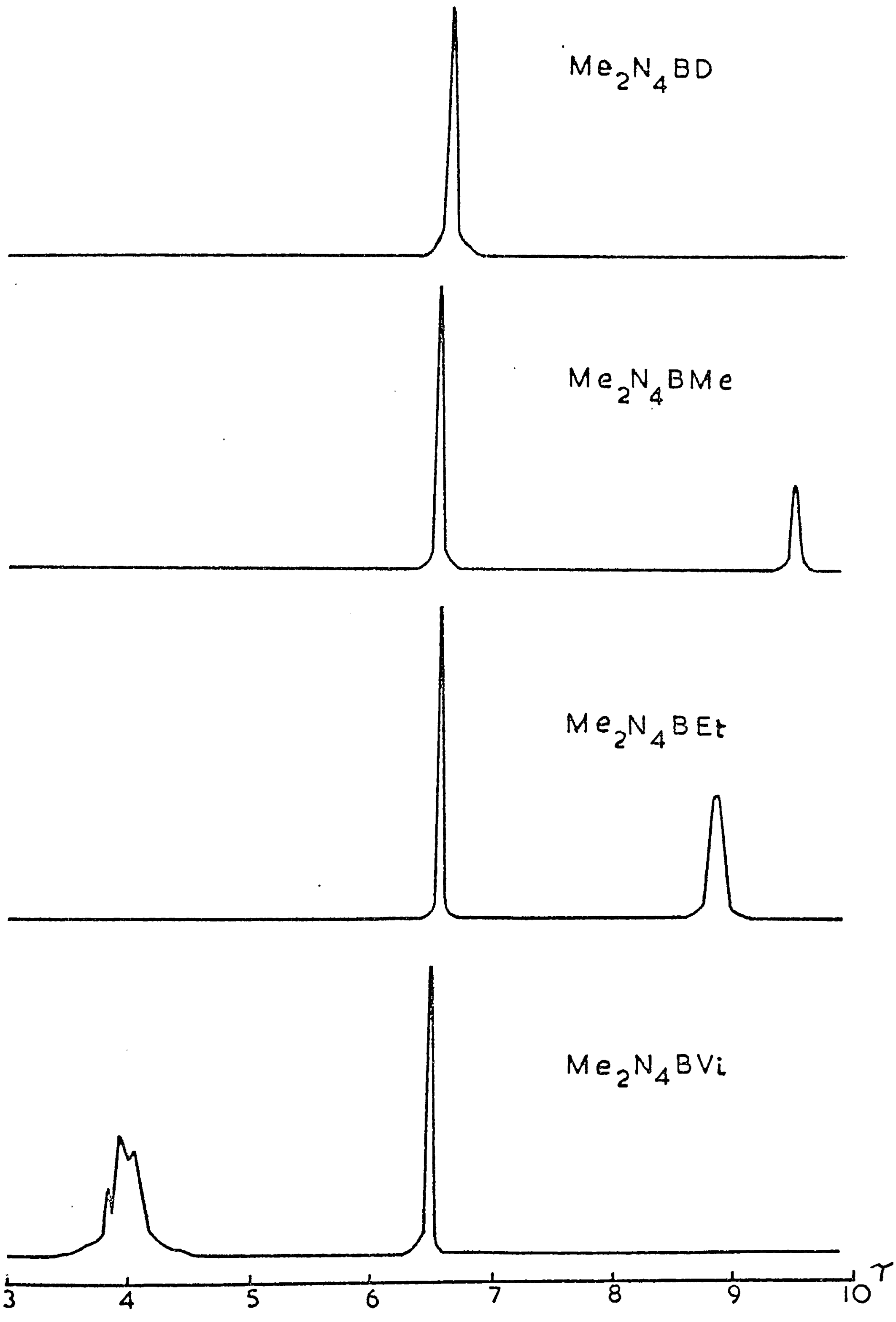
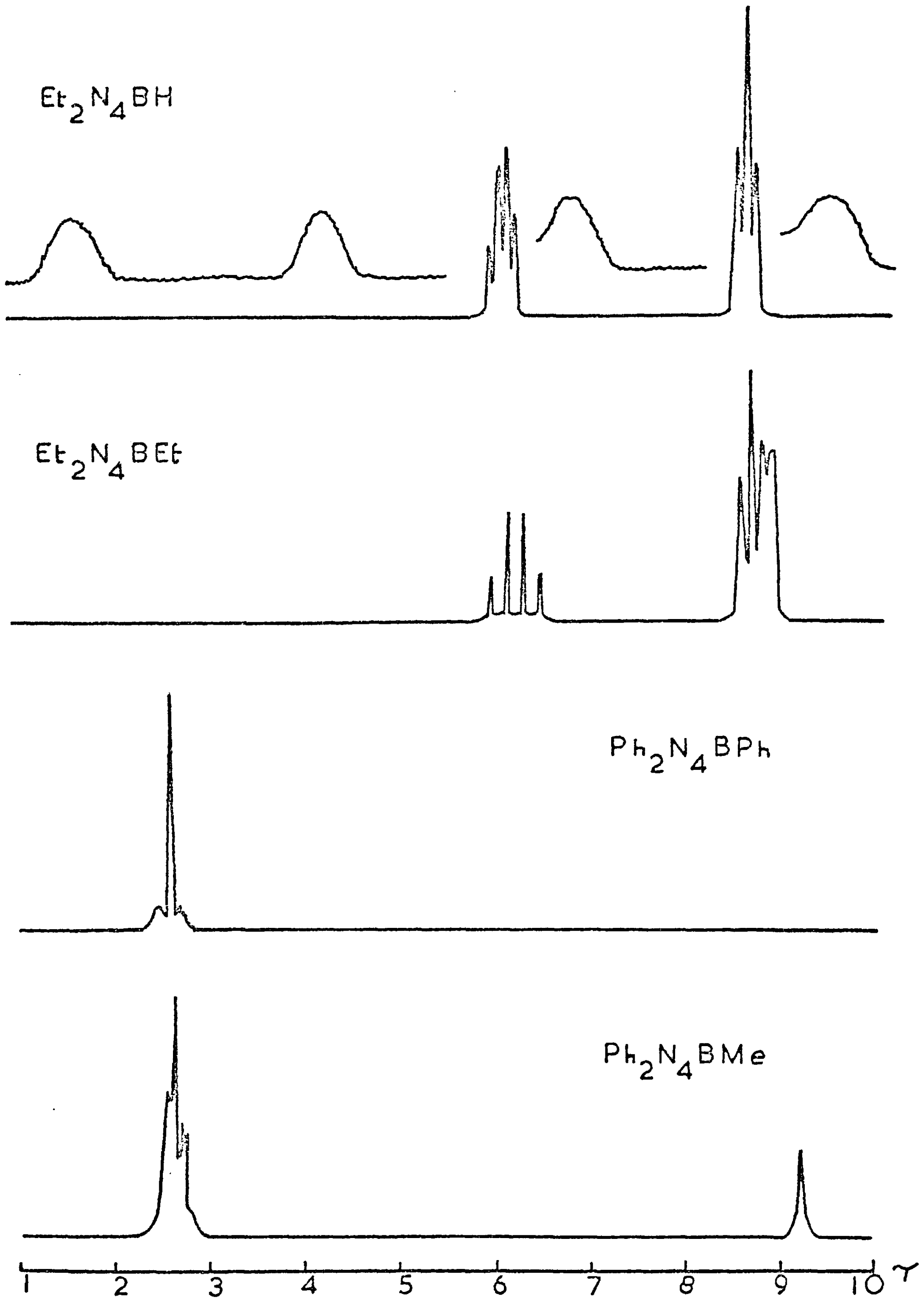


FIGURE [3-2]. ^1H N.M.R. SPECTRA.



FIGURE[3-3]. ^{1}H N.M.R. SPECTRA.

of 26 c/s on the basis of

$$\frac{J_{^{11}B-^{1}H}}{J_{^{11}B-^{2}D}} = \frac{k_1 \gamma_{^{1}H}}{k_2 \gamma_{^{2}D}}$$

assuming $k_1 = k_2$ and the observed $J_{''B-H}$ of 166 c/s

The proton N.M.R. of the compounds prepared are summarised in Table 3-A and Figures [3-2] and [3-3]. In all cases the observed integral ratios were in agreement with those expected for the protons in the compounds. It was observed that protons on a carbon atom adjacent to the boron were shifted to high field[85] in a similar manner to that observed in borazines. However in B-trimethyl-N-triphenyl borazine the methyl resonances were shifted so far to high field that they occurred upfield of Me_4Si[86] and this was interpreted as strong evidence for the phenyl rings lying perpendicular to the plane of the B_3N_3 ring. In B-methyl-N-diphenylcyclotetrazenoborane the methyl resonance occurred significantly downfield from that in B-methyl-N-dimethylcyclotetrazenoborane, suggesting therefore that the phenyl rings were coplaner with the BN_4 ring, since the ring current effect in the phenyl rings would then favour a downfield displacement. Similarly substitution of a phenyl group on the boron to yield Ph_2N_4BPh gave a very small downfield shift in the observed resonance for the phenyl group attached to the nitrogen when compared with that in Ph_2N_4BMe, possibly indicating that the phenyl group on the boron atom was also in the same plane as the N_4B ring.

When the substituent on the boron atom was an ethyl group the CH_2 protons accidently coincided with those of the CH_3 group, and a broad absorption showing some structure was observed near 8.9 τ for both Me_2N_4BEt and Et_2N_4BEt. This coincidence of the methylene and methyl resonances in an ethyl group attached to a boron atom was readily understood by consideration of the electronegativity of the boron atom.[87]

The effect of substitution at the boron atom on the electronegativities of the nitrogen atoms adjacent to the boron was estimated using the revised Dailey-Schoolery formula,[88,89]

$$E = 0.684\,(\tau_{CH_3} - \tau_{CH_2}) + 1.78$$

for Et_2N_4BH, $E = 3.58$ and Et_2N_4BEt, $E = 3.54$, with the implication[86] that the B-N π bonding is greater with the B-ethyl-substituted compound. This was in qualitative agreement with earlier[42] calculations on Ph_2N_4BH and Ph_2N_4BMe, in which the π-densities at boron were respectively calculated as 0.114 e and 0.148 e, but did not conform to the calculated slight decrease of the B-N π bond orders on B-methyl substitution (0.314 and 0.299 respectively).

In Me_2N_4BVi, the vinyl group occurred as a broad poorly resolved multiplet near 3.59 τ, and the methyl groups were unresolved at 40°. It would be interesting to examine the proton n.m.r. spectrum over a range of temperatures when information on the barrier

INFRARED SPECTRA

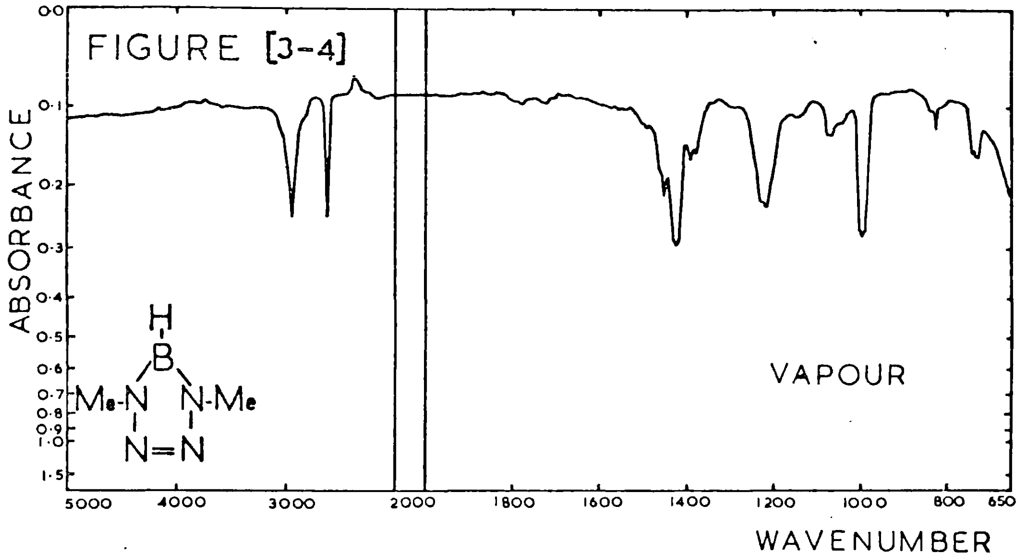


FIGURE [3-4]

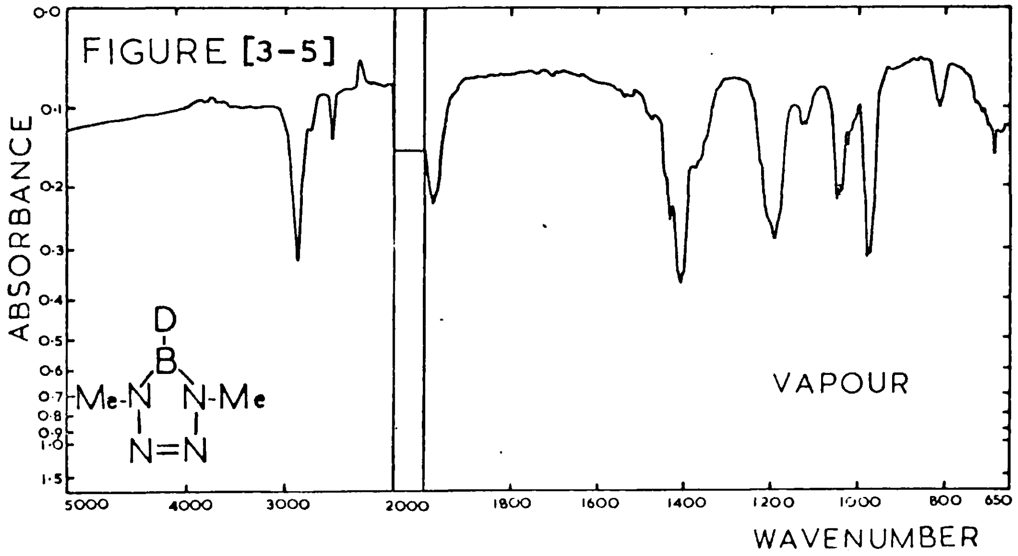


FIGURE [3-5]

INFRARED SPECTRA

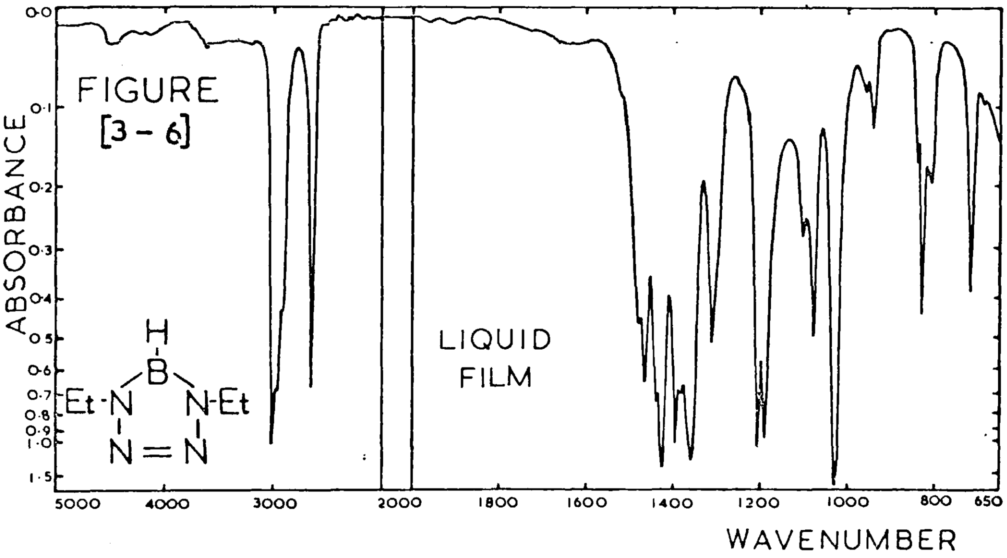


FIGURE [3-6]

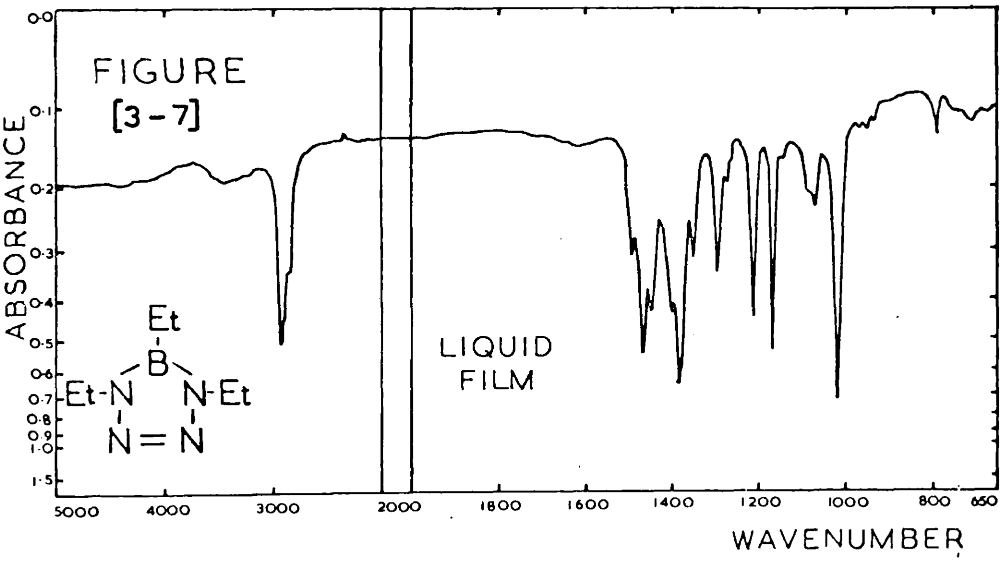


FIGURE [3-7]

INFRARED SPECTRA

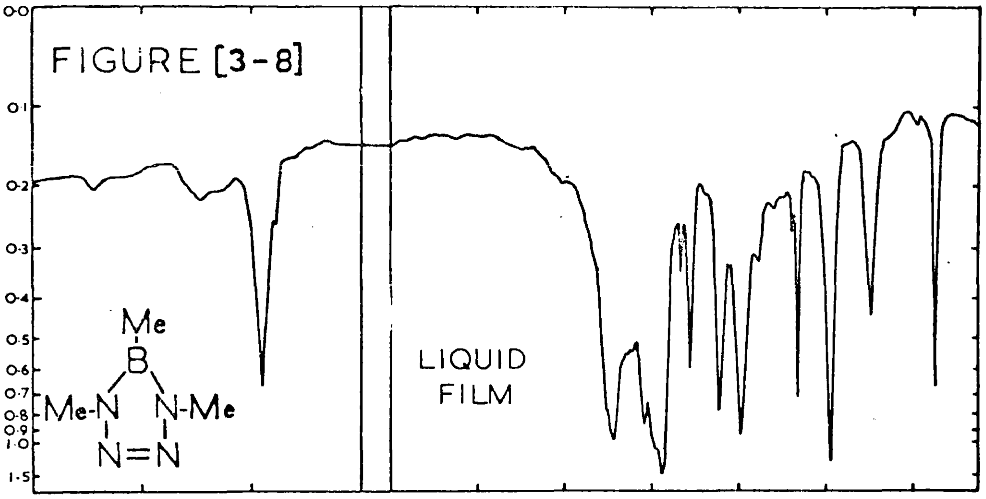


FIGURE [3-8]

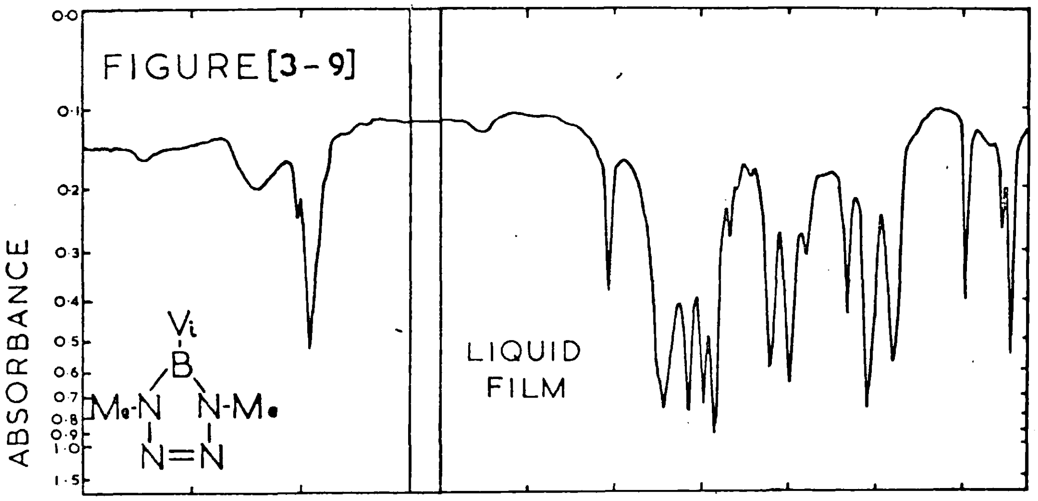


FIGURE [3-9]

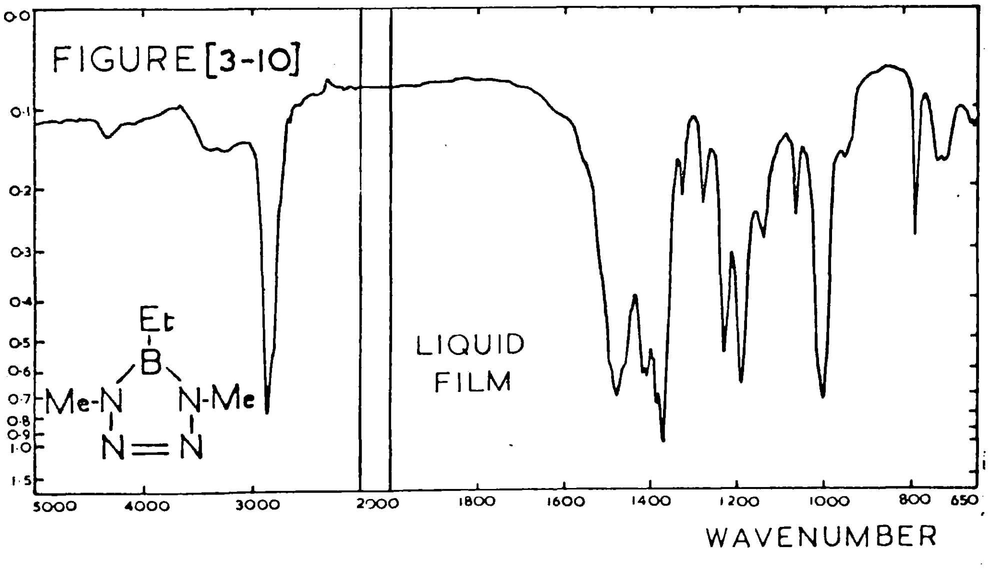


FIGURE [3-10]

INFRARED SPECTRA

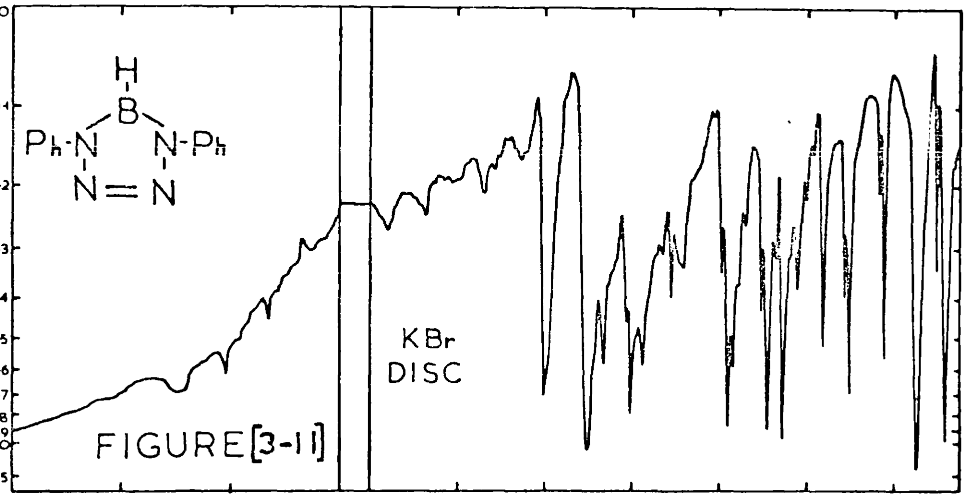


FIGURE [3-11]

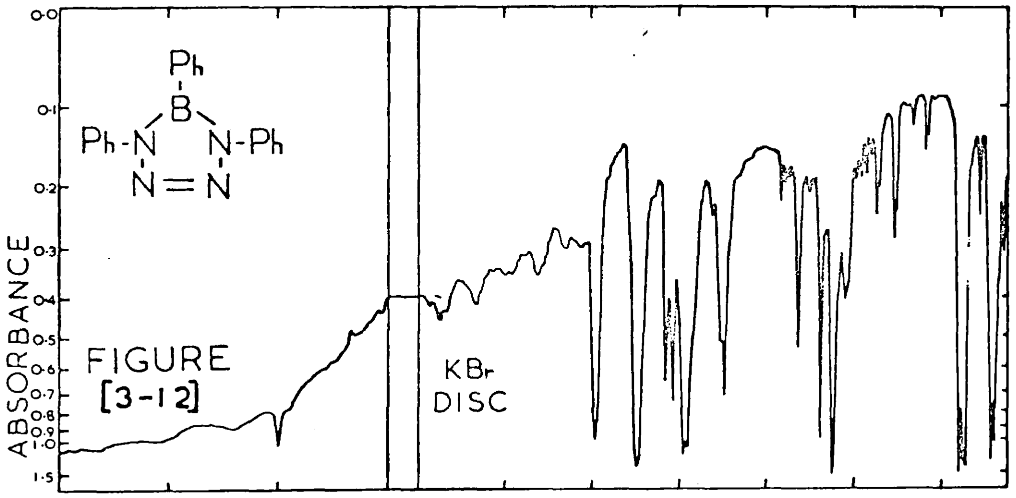


FIGURE [3-12]

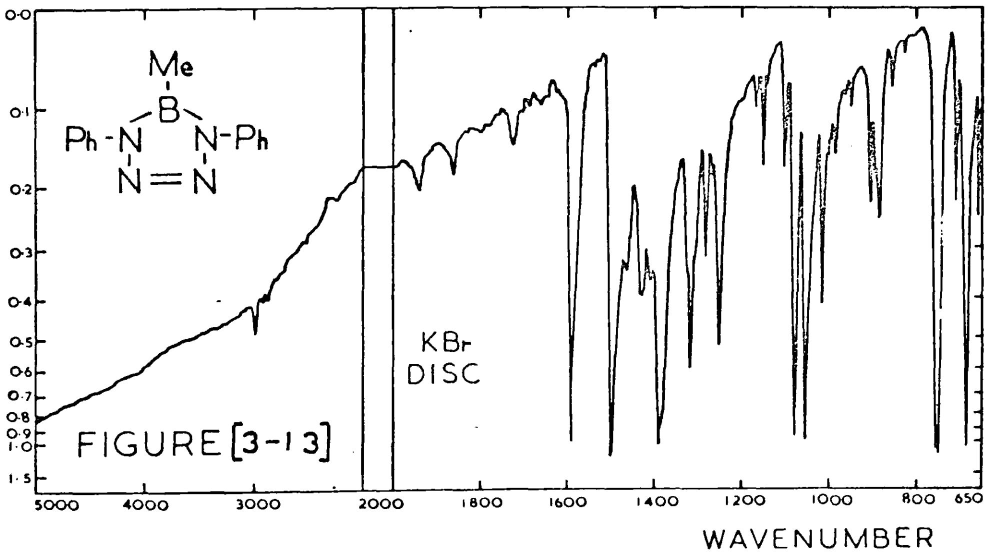


FIGURE [3-13]

to rotation of the vinyl group and hence the extent of π-interaction might be obtainable.

Infrared Spectra

The principal bands in the infrared spectra of the substituted cyclotetrazenoboranes are listed below and are illustrated in Figures [3-4]→[3-13]. A number of the bands of the spectra were assigned by analogy with the previously examined compounds Me_2N_4BH and Ph_2N_4BH[21,43] shown in Tables 1-D and 1-E.

Me_2N_4BD liquid:- 3081 wsh; 3004 msh; 2977 ms; 2947 s; 2931 sh; 2898 m; 2854 w; 2825 w; 2801 w; 2635 m; 2028 wsh; 2004 sh; 1988 ms; 1957 wsh; 1672 w; 1621 w; 1539 wbsh; 1482 ms; 1475 ms; 1456 sh; 1451 ms; 1441 ms; 1431 s; 1409 vs; 1387 ms; 1361 ms; 1355 ms; 1342 ms; 1227 ms; 1214 ms; 1202 ms; 1135 w; 1078 w; 1067 mw; 1055 ms; 1031 m; 987 ms; 979 ms; 951 w; 934 w; 915 vw; 826 w; 815 m; 733 w; 709 w; 691 m; 642 m; 416 vw.

Vapour spectra gave type A bands frequency (PR separation) in cm^{-1}
642 (12.8), 733 (13.8), 815 (11.3), 979 (9.7), 1055 (12.0).

Type B bands: 1135 (8).

Type C bands: 691, 709.

Me_2N_4BMe:- 3002 sh; 2967 sh; 2941 s; 2915 sh; 2893 m; 2822 w; 1616 vw; 1520 sh; 1511 sh; 1506 s; 1495 sh; 1486 s; 1464 m; 1456 m; 1445 m; 1429 sh; 1422 sh; 1416 s; 1403 sh; 1397 sh; 1393 s; 1376 s; 1337 wm; 1318 m; 1285 vw; 1253 s; 1202 s; 1161 w; 1126 vw; 1101 vw;

1083 w; 1070 ms; 1031 vw; 1007 sh; 992 s; 908 sh; 898 m; 856 vw; 754 ms; 643 w; 575 w; 566 wm; 460 vw; 456 w; 452 vw.

Me$_2$N$_4$BEt:- 3309b vw; 2960 s; 2941 s; 2918 sh; 2882 s; 2825 w; 2806 w; 2731 vw; 2710 vw; 1567 w; 1546 w; 1522 sh; 1511 sh; 1502 sh; 1493 s; 1486 s; 1471 s; 1458 sh; 1429 s; 1416 s; 1403 sh; 1395 s; 1377 s; 1339 w; 1292 w; 1242 s; 1202 s; 1153 m; 1086 vw; 1075 w; 1026 sh; 1015 sh; 1005 s; 959 w; 797 m; 746 w; 728 w; 665 vw; 640 vw; 612 vw.

Me$_2$N$_4$BVi:- 3429b w; 3068 w; 2989 sh; 2967 m; 2945 s; 2933 sh; 2891 m; 2860 w; 2821 w; 1916 vw; 1620 m; 1520 sh; 1506 sh; 1493 s; 1486 s; 1429 s; 1395 s; 1366 s; 1337 w; 1322 vw; 1295 vw; 1247 s; 1203 s; 1166 w; 1082 sh; 1070 m; 1021 s; 1014 sh; 973 sh; 960 s; 794 m; 748 vw; 713 w; 693 s; 632 w; 559 vw.

Et$_2$N$_4$BH:- 2980 s; 2937 ms; 2911 sh; 2899 m; 2893 m; 2821 vw; 2641 ms; 1616 vw; 1477 sh; 1464 m; 1451 ms; 1429 ms; 1410 s; 1381 s; 1370 ms; 1344 s; 1300 m; 1292 sh; 1199 ms; 1182 ms; 1093 w; 1070 m; 1018 s; 943 vw; 928 w; 827 w; 815 m; 794 w; 708 w.

Et$_2$N$_4$BH Raman shifts:- 2986 s; 2940 s; 2913 s; (F?)2824 mw; 2493 ms; 2460 mw; 2234 w; 1458 mw; 1414 vw; 1376 ms; 1352 mw; 1094 vw; 1026 mw; 989 w (P); 934 s; 594 vw; 181 w; 151 mw.

Et$_2$N$_4$BEt:- 2976 s; 2960 s; 2935 s; 2915 sh; 2878 ms; 1626 vw b; 1504 sh; 1495 m; 1471 s; 1453 sh; 1447 ms; 1416 sh; 1403 ms; 1383 s; 1355 m; 1300 m; 1279 w; 1220 ms; 1176 s; 1147 vw; 1088 w; 1074 w; 1023 s; 969 vw; 951 vw; 936 vw; 801 vw; 792 w; 717bvw.

Ph_2N_4BMe:- 3104 vw; 3059 w; 3049 w; 2969 w; 2923 vw; 2852 vw; 1949 w; 1873 w; 1818 vw; 1795 vw; 1742 w; 1718 vw; 1701 vw; 1675 vw; 1597 s; 1590 sh; 1570 sh; 1558 sh; 1537 vw; 1530 vw; 1510 sh; 1502 s; 1471 m; 1464 m; 1458 sh; 1437 m; 1432 m; 1415 sh; 1412 m; 1389 s; 1383 s; 1331 sh; 1323 s; 1312 sh; 1290 m; 1274 w; 1261 ms; 1176 w; 1159 w; 1149 vw; 1109 w; 1085 s; 1060 s; 1021 m; 1004 w; 988 w; 963 vw; 952 w; 908 wm; 894 wm; 886 wm; 855 w; 829 vw; 761 s; 756 s; 717 m; 694 s; 680 wm; 665 m; 623 w; 614 w; 606 w; 585 sh; 580 w; 519 vw; 516 w; 508 m; 507 m; 498 sh; 423 sh; 422 w; 417 w.

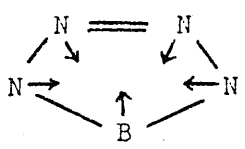
Ph_2N_4BPh:- 3104 vw; 3069 sh; 3047 w; 3020 sh; 2916 vw; 2852 vw; 2679 vw; 2523 vw; 1969 vw; 1953 vw; 1942 vw; 1880 vw; 1833 vw; 1812 vw; 1799 vw; 1770 vw; 1733 vw; 1715 sh; 1701 sh; 1672 vw; 1645 vw; 1634 vw; 1597 ms; 1572 sh; 1558 sh; 1543 sh; 1511 sh; 1497 s; 1456 w; 1433 m; 1416 m; 1393 ms; 1382 ms; 1370 sh; 1326 w; 1311 mw; 1302 m; 1292 sh; 1264 sh; 1190 vw; 1174 w; 1164 w; 1155 vw; 1135 wm; 1109 vw; 1086 ms; 1074 w; 1057 s; 1031 sh; 1026 w; 1020 sh; 1000 w; 996 vw; 988 w; 976 w; 968 vw; 963 vw; 953 w; 949 w; 912 w; 907 w; 879 vw; 867 w; 840 w; 834 w; 819 vw; 768 s; 759 s; 754 s; 721 w; 697 s; 689 s; 667 wm; 649 w; 617 w; 612 w; 588 wm; 523 wm; 504 wm; 467 w; 423 sh; 421 w.

Ring Modes

It was shown[21,43] that cyclotetrazenoboranes with C_{2v} symmetry had nine skeletal fundamental modes of vibration distributed amongst the symmetry classes as follows $4A_1$, $1A_2$, $3B_1$, and $1B_2$ of

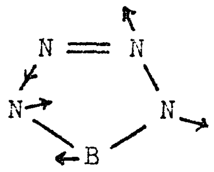
TABLE 3-B

FUNDAMENTAL N_4B RING VIBRATIONS



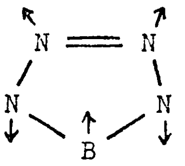
ω_1 II

A_1str



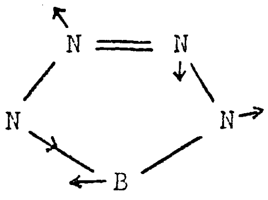
ω_2 V

B_1str



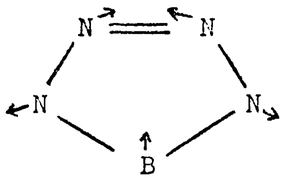
ω_3 III

A_1str



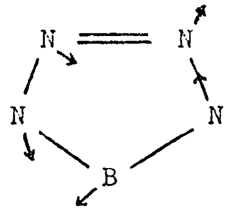
ω_4 VI

B_1str



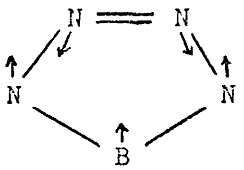
ω_5 I

A_1str



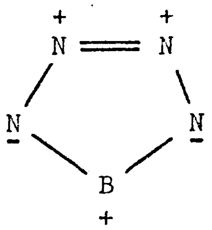
ω_6 VII

B_1def



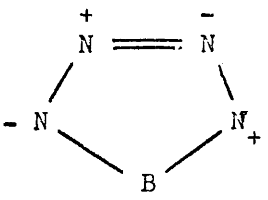
ω_7 IV

A_1def



Γ_1

B_2def



Γ_2

A_2def

which $3A_1$ and $2B_1$ modes were essentially stretching modes. These modes are summarised in table 3-B together with the two different nomenclatures utilised for Me_2N_4BH and Ph_2N_4BH in the previous assignments[21,43]. The frequencies at which these modes occurred was sensitive to the nature of the substituents on the ring, and in particular to the substituents at nitrogen. It should also be mentioned that when the boron or nitrogen substituent is ethyl or vinyl, the molecule would no longer belong to the C_{2v} point group, and it might be anticipated that inactive modes (A_2 for C_{2v} molecules) become allowed, although their intensities might be too low to be observed.

A number of bands in Me_2N_4BH were previously assigned to the ring stretching modes. In the present series of N-Me and N-Et substituted compounds corresponding frequencies were observed which varied only slightly on changing the substituents at the boron and these were therefore assigned to the analogous modes, and are listed in Table 3-C.

TABLE 3-C

RING STRETCHING MODES OF N-Me AND N-Et CYCLOTETRAZENOBORANES

Mode of Vibration	Group X in Me_2N_4BX					Et_2N_4BX	
	H	D	Me	Et	Vi	H	Et
ω_4	1408	1409	1397	1395	1395	1410	1413
ω_5	1363	1355	1376	1377	1366	1344	1355
ω_3	1342	1342	1337	1339	1337	1300	1300
ω_2 ^{10}B	-	987	1007	1026	1021	-	-
^{11}B	991	979	992	1005	1014	1018	1023
ω_1 ^{10}B	-	-	908	-	974sh	943	951
^{11}B	953	951	898	959	960	927	936

It was less easy to identify corresponding ring deformation modes, but the band at 736 cm^{-1} in Me_2N_4BH, which was assigned to the b_1 ring deformation ω_6, had counterparts in the other compounds as indicated:- Me_2N_4BD, 732 cm^{-1}: Me_2N_4BMe, 754 cm^{-1}: Me_2N_4BEt, 797 cm^{-1}: Me_2N_4BVi, 794 cm^{-1}: Et_2N_4BH, 794 cm^{-1}: Et_2N_4BEt, 792 cm^{-1}.

The assignment of ring modes in Ph_2N_4BH was necessarily more tentative in the absence of infrared band contours and Raman data,[21] and a number of bands differed considerably from those in Me_2N_4BH. However, the bands assigned to ring vibrations in the spectrum of Ph_2N_4BH had counterparts in the spectra of Ph_2N_4BMe and Ph_2N_4BPh, and these are listed in Table 3-D.

TABLE 3-D

RING MODES OF PHENYL-SUBSTITUTED CYCLOTETRAZENOBORANES

Ring Mode	V	VI	II	I	VII
Ph_2N_4BH	1418,1405:	1200,1190:	1109,1091:	1062:	968:
Ph_2N_4BMe	1412,1389:	1274,1261:	1109,1086:	1060:	988:
Ph_2N_4BPh	1416,1393:	- ,1264:	1109,1086:	1057:	953:
	III	IV	VIII		
Ph_2N_4BH	915,905:	668:	420		
Ph_2N_4BMe	894,886:	665:	422		
Ph_2N_4BPh	912,907:	667:	422		

C-N modes The C-N stretching modes of dimethylcyclotetrazenoborane were previously assigned to bands at 1046 (a_1) and 1213 (b_1) cm^{-1}, and the band at 1231 cm^{-1} was assigned to a combination band. In the series of N-methyl substituted compounds examined, a consistently strong band was observed near 1240 cm^{-1}, and could now preferably be considered as the antisymmetric C-N stretching mode. The band at 1213 cm^{-1} would then be the symmetric C-N stretching frequency. The C-N antisymmetric and symmetric stretching modes for the series of N-phenyl substituted compounds were attributed to consistent bands around 1311 and 1290 cm^{-1} respectively. Bands attributed to C-N vibrational modes in the cyclotetrazenoboranes are summarised in Table 3-E.

TABLE 3-E

Compound	Me_2N_4BX					Et_2N_4BX		Ph_2N_4BX		
X substituent	H	D	Me	Et	Vi	H	Et	H	Me	Ph
Antisym C-N stretch	1231	1227	1285	1242	1247	1199	1220	1311	1311	1311
Sym C-N stretch	1213	1202	1202	1202	1203	1182	1176	1291	1290	1302
C-N def	-	641	643	640	632	-	-	-	-	-

The C-N deformations of Me_2N_4BH were originally assigned to bands near 411 and 203 cm^{-1}. Weak bands were observed near 640 cm^{-1} in many of the substituted compounds, see Table 3-E and it is possible that this may be one of the C-N deformation modes. The C-N deformations for N-Et and N-Ph substituted cyclotetrazenoborane derivatives were not readily assigned.

Substituent vibrations:- (a) N-substituents. The internal vibrations associated with N-Me groups in the substituted compounds occurred at similar frequencies to those in Me_2N_4BH, and C-H stretching frequencies (3100 - 2850 cm^{-1}), CH_3 deformation (1500 - 1400 cm^{-1}) and CH_3 rocking (1200 - 900 cm^{-1}) regions could be identified.

Bands associated with N-ethyl groups were necessarily more complicated and complete assignments were not attempted due to severe overlapping of bands.

Phenyl modes for N-phenyl substituted compounds were observed at frequencies close to those previously reported for Ph_2N_4BH i.e. the C-H stretching frequencies (3110 - 2910 cm^{-1}), the four combination bands of C-H out of plane deformations (1970 - 1640 cm^{-1}), C-C (Ph) stretches (1620 - 1430 cm^{-1}), C-H in plane deformations (1200 - 1000 cm^{-1}), C-H out of plane deformations (770 - 750 cm^{-1}) and Ph and Ph-X deformations (720 - 400 cm^{-1}) were found. Some of the deformation modes are listed in Table 3-F.[90]

TABLE 3-F

PHENYL AND PHENYL-X DEFORMATION FREQUENCIES

CH o.o.p. def.	Ph_2N_4BH	753
	Ph_2N_4BMe	756,761
	Ph_2N_4BPh	754,759,768
PhX i.p. def.	Ph_2N_4BH	708
	Ph_2N_4BMe	717
	Ph_2N_4BPh	721
Ph ring o.o.p. def.	Ph_2N_4BH	689
	Ph_2N_4BMe	694
	Ph_2N_4BPh	697,689
PhX i.p. def.	Ph_2N_4BH	548
	Ph_2N_4BMe	508
	Ph_2N_4BPh	523

(b) B-substituents. The C-H stretching modes of B-Me groups were little affected by the proximity of the boron, and were not distinguished from other C-H vibrations in the vicinity in Me_2N_4BMe, but were readily recognised at 2973, 2919, 2852 cm^{-1} in Ph_2N_4BMe. In the deformation region, the antisymmetric modes were obscured by other vibrations, but the symmetric modes were probably best assigned to the band at 1318 cm^{-1} in Me_2N_4BMe and the band at 1323 cm^{-1} in Ph_2N_4BMe.

In Me_2N_4BVi, the vinyl C-H stretching frequency occurs at 3065 cm^{-1} and the C=C stretching mode was observed at 1620 cm^{-1}. The in-plane and out-of-plane hydrogen deformations which are normally observed near 990 and 910 cm^{-1} probably occurred in this compound as components of the complex bands observed near 1021 and 960 cm^{-1}. Again no attempt was made to characterise the ethyl vibrations in B-ethyl compounds due to the complexity of the spectra.

B-X vibrations: The poorly revolved B-H stretching frequencies of Et_2N_4BH at 2641 cm^{-1} together with in-plane deformations 1093, 1070 cm^{-1} and out-of-plane deformations 827, 815 cm^{-1} were readily assigned in similar manner to those for Me_2N_4BH. Consideration of the spectrum of the deuterated Me_2N_4BD further confirmed this assignment when the ^{10}B-D and ^{11}B-D stretching modes were observed at 2004 and 1988 cm^{-1}. The ^{10}B-D and ^{11}B-D in-plane and out-of-plane deformations occurred at 825, 816 cm^{-1} and 708, 690 cm^{-1}.

The B-C stretching frequency was found near 1070 and 1080 cm^{-1} for methyl, ethyl and vinyl substituents, but probably occurred at higher frequencies for phenyl substitution. The B-C deformation modes are less certain but the in-plane modes probably occurred near 565 cm^{-1} for Me_2N_4BMe, 506 cm^{-1} for Ph_2N_4BMe. The out-of-plane B-C deformation modes were probably below 400 cm^{-1}.

EXPERIMENTAL

Preparation of solvents and intermediates

Solvents were dried and purified by standard procedures[67]. Commonly obtainable intermediates were used as supplied by commercial organisations except where otherwise stated. LiD and $LiBD_4$ were used as supplied by Fluka (A.G. Chemische Fabrik Bucks S.G.). Methylamine and ethylamine were obtained by distillation from their aqueous solutions under vacuum, dried over KOH pellets and stored at -10°C.

Preparation of methyl and ethyl azides

An aqueous solution of sodium azide was placed in a flask fitted with a water condenser and tap funnel containing an excess of dialkyl sulphate. The top of the water condenser was connected to a trap cooled to -78°C. The dialkyl sulphate was added carefully to the refluxing azide solution and the alkyl azide was collected in the -78°C trap, assisted by reduction of the pressure within the system. This was further purified by fractionation on the vacuum line, dried over KOH pellets or 4A molecular seive and stored at -10°C.

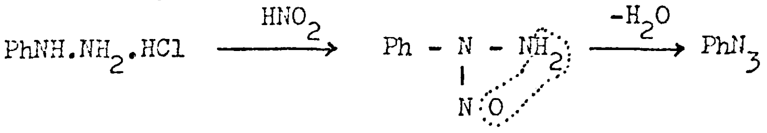
Reaction:- $2NaN_3 + (R)_2SO_4 \longrightarrow Na_2SO_4 + 2RN_3$

Preparation of phenyl azide

Phenyl azide was prepared by the method of Lindsay and Allen.[91] Water (300 ml) and conc. HCl (55.5 ml) were placed in a one litre three necked flask fitted with a mechanical stirrer, thermometer and a dropping funnel. The flask was then surrounded by an ice-salt freezing bath and phenylhydrazine (33.5 g.) was added dropwise with stirring. When the temperature of the flask contents had fallen to 0°C, 100 mls of ether was added, followed by dropwise addition of a freshly prepared solution of $NaNO_2$ (25 g.) in 30 mls of water, ensuring that the temperature did not rise above 5°C.

The reaction products were then steam distilled until 400 mls of distillate was obtained, and the ether layer was separated. The aqueous layer was extracted once with 25 mls of ether and the combined ether solutions were dried over 10 g. of anhydrous $CaCl_2$. The dried ether solution was placed in the flask of a distillation apparatus taking care to surround the flask by wire gauze and surround it with blast screens. The flask was immersed in a water bath at 25° - 30° and the ether was removed under reduced pressure. The temperature of the bath was then raised to 60 - 65° when the phenyl azide distilled under reduced pressure (B. pt. 49 - 50° at 5 mms) as a pungent pale yellow oil. Yield ~65%.

Reactions:-



$$PhNH.NH_2.HCl \xrightarrow{HNO_2} Ph-\underset{\displaystyle N{:}O}{\underset{|}{N}}-NH_2 \xrightarrow{-H_2O} PhN_3$$

Preparation of Lithium azide

This was prepared by the method of R. Huisgen and I. Ugi[92] lithium chloride (50 g. , 1.2 g. mol) and sodium azide (76.5 g , 1.2 g.mol) were placed in a flask containing dry methanol (400 mls), and refluxed under a stream of dry nitrogen. The methanol solution was filtered free of the sodium salt, and concentrated by removal of the methanol by distillation [care was taken not to let the distillation boil dry as LiN_3 decomposes explosively at $\sim$ 200°C]. The last of the solvent was removed under high vacuum at 100° for 12 hours. Lithium azide is extremely deliquescent, rapidly forming the monohydrate $LiN_3.H_2O$ and was therefore stored in a dessicator.

Reaction: $LiCl + NaN_3 \longrightarrow LiN_3 + NaCl$

Diborane

The diborane used in the experiments to be described was obtained mainly from a cylinder first cooled to -78°C obtained from the Callery Chemical Company, U.S.A., but prior to the availability of this supply was prepared by the method of Freeguard and Long.[93]

A three necked 250 mls flask was fitted with a tap funnel, an inlet, and an outlet tube which was in turn connected to a vacuum frame and hence through a series of traps, the first cooled to -78°C and subsequent ones to -196°C. $NaBH_4$ (4g , 0.1 g.mol) was placed in the flask and stirred magnetically with 20 mls of dried diglyme. Iodine (6.7 g. ,0.053 g.mol) was dissolved in diglyme and placed in the tap funnel. The flask was well swept out with nitrogen and the pressure within it reduced to near that of the solvent vapour. The I_2 solution was then added in small portions from the tap funnel, when the reaction was immediate and exothermic. Pumping was continued for 15 minutes after the final addition of iodine to ensure complete transfer of the diborane to the liquid nitrogen traps, the -78°C trap removing volatile solvent. The yield of diborane was approximately quantitative.

Reaction: $2NaBH_4 + I_2 \longrightarrow 2NaI + B_2H_6 + H_2$

Preparation of triphenyl boron

A one litre flask was fitted with a mechanical stirrer and oil seal, a 250 mls tap funnel and a reflux condenser, all the apparatus having been thoroughly dried overnight in an oven before use. Clean dry magnesium turnings (28 g., 0.11 g.mol) and a trace of iodine catalyst were placed in the flask and covered with dry ether and the whole apparatus was flushed carefully with dry nitrogen. A dry inert atmosphere was maintained throughout the experiment by means of a flow of nitrogen above the top of the condenser and tap funnel. A small amount of dry bromobenzene was added from the tap funnel and the mixture stirred vigorously until the Grignard reaction started. The rest of the bromobenzene (180 g., 0.11 g.mol) was added slowly, and when the reaction was complete the whole Grignard product was cooled to 0°C, and redistilled boron trifluoride etherate (54.3 g., 0.038 g.mol BF_3) was added dropwise with stirring when a vigorous reaction was obtained. On completion of the addition of $BF_3.Et_2O$, water (300 ml) was added and the flask and contents stirred thoroughly. The products were filtered under an atmosphere of nitrogen and the remaining solid extracted once more with a further portion of ether. The ether extracts were concentrated by distillation of the ether from the solution, the final traces being removed under vacuum leaving solid boron triphenyl. Yield = 62.2 g (~ 67% Theoretical).

Reactions:- $PhBr + Mg \xrightarrow{Et_2O} [PhMgBr]$

$$3[PhMgBr] + BF_3.Et_2O \longrightarrow BPh_3 + 3MgBrF$$

Preparation of diphenyl boron chloride

Boron triphenyl (29.3 g., 0.12 g.mol) was weighed into an ampoule in a dry nitrogen containing glove box and BCl_3 (7.1 g., 0 .06 g.mol) was condensed into it using a vacuum frame. The ampoule was sealed under vacuum and heated to 80° for two hours. The ampoule was opened in the oxygen free glove box, the contents transferred to a distillation apparatus, and the reaction products distilled under vacuum with heating when Ph_2BCl was obtained as a colourless low melting solid. (Yield ~ 30%).

Reaction: $2Ph_3B + BCl_3 \rightleftharpoons 3Ph_2BCl$

Also produced was $PhBCl_2$ which was collected in a trap at -196°C on the vacuum frame, probably due to a side reaction or disproportionation while some residue possibly of BPh_3 was left in the distillation flask.

Preparation of diphenyl boron azide

This was prepared by the method reported by Paetzold.[82]

Diphenyl boron chloride (11.73 g., 0.059 g.mol) was refluxed in benzene with a suspension of excess LiN_3 (7.62 g., 0.16 g.mol) for 60 hours under an atmosphere of dry nitrogen. The benzene solution was then filtered free of the lithium salts in a dry nitrogen containing glove box, and the benzene solution was concentrated by vacuum distillation. The remaining solution was transferred to a small (60 ml) distillation apparatus and the last of the benzene removed by further distillation under vacuum. The remaining azide was rapidly distilled with some decomposition between 100 - 120° under high vacuum using a mercury diffusion pump. The Ph_2BN_3 was confirmed by its infrared spectrum which showed a strong azide band at 2120 cm^{-1}. A glass-like solid, probably $(Ph\text{-}\overset{|}{N}\text{-}\overset{|}{B}\text{-}Ph)_2$, remained in the distillation flask.

Yield of Ph_2BN_3 = 4.0 g. (~ 33% Theoretical).

Reaction: $Ph_2BCl + LiN_3 \longrightarrow Ph_2BN_3 + LiCl$

The preparation of N,N',N''-trimethyl-cyclotriborazane

This was prepared by the reaction of methylamine and diborane in a molar ratio of 2:1 in a sealed ampoule at 130° for 16 hours. On cooling to room temperature a crystalline product of $(MeNHBH_2)_3$ was obtained together with uncharacterised volatile products which were removed by vacuum distillation. The $(MeNHBH_2)_3$ was used without further purification.

$$3MeNH_2BH_3 \xrightarrow{\text{above } 100^{\circ}} (MeNHBH_2)_3 + 3H_2$$

The preparation of N-trimethyl borazine

Methylamine and diborane were sealed in an ampoule under vacuum in the molar ratio of 2:1 as in the previous experiment, and pyrolysed at 220°C for 16 hours. The ampoule was opened under vacuum and the N-trimethylborazine collected by distillation of the reaction products through a trap at -78°C. The product was further purified by fractional vacuum distillation.

Reaction: $3MeNH_2BH_3 \longrightarrow (MeNHBH_2)_3 \longrightarrow (MeNBH)_3$

The preparation of Grignard reagents

The following general method was used for the preparation of Grignard reagents MeMgI, EtMgI and PhMgBr. The quantities of Grignard reagents prepared were determined by the quantity of the appropriate cyclotetrazenoborane derivative with which it was to be treated (shown in Table 3-G). A three-necked flask (250 mls) was fitted with a 100 mls tap funnel, a mercury sealed mechanical stirrer and a reflux condenser. The theoretical quantity of magnesium was placed in the flask and covered with dry diethyl ether and a small trace of iodine was added to activate the magnesium. The required alkyl or aryl halide in slight excess was dissolved in diethyl ether and placed in the tap funnel. The whole apparatus was carefully flushed with dry nitrogen and this atmosphere was maintained throughout the experiment by a flow of nitrogen at the top of the condenser and tap funnel. A small amount of the halide was run into flask with vigorous stirring. If the reaction did not start immediately it was initiated by warming the reactants with a hot water bath. The rest of the halide was slowly added until reaction was complete.

Reaction: $Mg + RX \xrightarrow{ether} RMgX$ (R = Me, Et or Ph,
X = I or Br)

Preparation of vinyl magnesium bromide

This was prepared in a similar manner to those previously described except that the water condenser was replaced by an acetone - solid CO_2 condenser and the solvent used for the preparation was in this case tetrahydrofuran.[94] The reaction was initiated using one drop of methyl iodide.

Reaction: $Mg + CH_2 = CHBr \xrightarrow{T.H.F.} CH_2 = CHMgBr$

Preparation of diphenyl cyclotetrazenoborane

In a typical preparation of Ph_2N_4BH as reported by Morris[21] a B.24 (250 ml) quickfit conical flask was charged with aniline (5.0 g., 0.034 g.mol), which had been dried by refluxing with KOH pellets and redistilled. Ether (50 ml) was condensed into the ampoule, by cold distillation under vacuum from $LiAlH_4$, together with diborane (580 mls., 0.027 g.mol), and the mixture was allowed to warm slowly to about 10°. Phenyl azide (6.4 g., 0.054 g.mol) was added and the mixture allowed to stand at room temperature for 60 hours. The product separated as large crystals which were filtered off and the mother liquor continued to deposit crystals until a total of 8.39 g (70%) was obtained.

Reaction: $PhNH_2BH_3 + PhN_3 \longrightarrow Ph_2N_4BH + 2H_2$

Preparation of dimethyl cyclotetrazenoborane

The preparation of Me_2N_4BH was carried out as reported by Morris.[22] Diborane (.0052 g.mol) and methylamine (.0104 g.mol) were condensed together with diethyl ether (10 ml) distilled from

$LiAlH_4$ under vacuum into a heavy walled glass ampoule at -196°C and were allowed to react by warming up slowly. Methyl azide (0.69 g, .012 g.mol) was then condensed into the ampoule using the vacuum line, and the ampoule was sealed and heated to 140° for 16 hours. The tube was cooled and opened on the vacuum line the reaction products being distilled through traps at -30°C, and -196°C, giving an almost quantitative yield of H_2, and the Me_2N_4BH was isolated in the -30°C trap. The product was further purified by fractional vacuum distillation. An unidentified involatile crystalline product remained in the ampoule. The presence of the solvent was not necessary for the reaction since equally good yields were obtained by direct heating of the amine borane with methyl azide in a sealed ampoule. Caution however must be used in this preparation as occasionally, when all three reactants were condensed into the ampoule at -196° without first allowing the amine and diborane to react, extremely violent explosions were obtained.

It is of interest that Morris[95] has recently found that Me_2N_4BH can also be prepared by heating equimolar quantities of Me_2SO_4, methylammonium azide and lithium borohydride in ether solvent in a sealed ampoule at 120° for 48 hours. The product Me_2N_4BH was isolated in good yield by high vacuum distillation through a trap at -30°C.

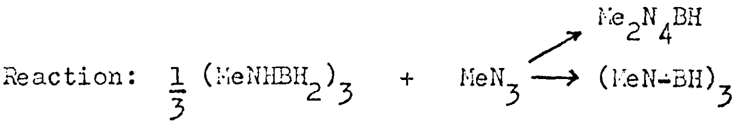
The attempted preparation of Me_2N_4BH by the reaction of N-trimethyl borazine with methyl azide

N-trimethyl borazine (1.31 g, 0.011 g.mol) and excess methyl azide were cold distilled into an ampoule and sealed under vacuum. Several ampoules were set up in this manner and heated either at 130° for 16 hours or 180° for 20 hours. In both cases some free nitrogen was produced and vacuum distillation produced colourless liquids in traps at -30°C. Methyl azide and its volatile decomposition products were collected at -196°C. An examination of the infrared spectra of the colourless liquids showed the absence of any Me_2N_4BH, but the presence of an intense N-H stretching frequency and the reduction in intensity of the B-H vibration suggested that amino substitution of the B-H occurred. Elemental analysis was inconclusive.

Attempted reaction: $\frac{1}{3}(MeN - BH)_3 + MeN_3 \longrightarrow Me_2N_4BH$

The reaction of N,N',N''-trimethyl cyclotriborazane with methyl azide

Crystalline $(MeNHBH_2)_3$ was heated with excess MeN_3 in a sealed ampoule at 130° for 48 hours, when a free flowing liquid was produced. Vacuum distillation of the products through traps at -30°C and -196°C yielded unused MeN_3 in the -196°C and a mixture of Me_2N_4BH and N-trimethyl borazine, which were not readily separated by further fractional vacuum-distillation, in the -30°C trap.

Reaction: 

$$\frac{1}{3}\,(\mathrm{MeNHBH_2})_3 \;+\; \mathrm{MeN_3} \xrightarrow{\nearrow\ \mathrm{Me_2N_4BH}} (\mathrm{MeN{-}BH})_3$$

The attempted large scale preparation of $\mathrm{Me_2N_4BH}$

$\mathrm{NaBH_4}$ (3.88 g. , 0.10 g.mol) and dry $\mathrm{MeNH_2.HCl}$ (6.9 g. , 0.10 g.mol) were stirred in a flask at room temperature with 100 mls of methylene glycol dimethyl ether (monoglyme B.Pt. 83°) under an atmosphere of dry nitrogen. Sodium azide (6.64 g., 0.10 g.mol) was quickly added to the flask and $\mathrm{(CH_3)_2SO_4}$ (6.42 g., 0.05 g.mol) was added dropwise, and the contents of the flask refluxed. Great difficulty was experienced in keeping the $\mathrm{MeN_3}$ produced in the reaction vessel, even with the use of an acetone-solid $\mathrm{CO_2}$ condenser. A white solid product sublimed in the condenser and its infrared spectrum showed the presence of a strong band around 2100 $\mathrm{cm^{-1}}$ possibly characteristic of an azide stretching frequency, together with complex B-H, C-H and N-H stretching regions. The reaction products were filtered free of solid sodium salts at room temperature, and vacuum distilled through traps at -35° and -196°C. Solvent and an azide product were collected at -196°C, while the -35°C trap yielded a small amount of liquid whose infrared spectrum was complex and probably due to a mixture of products, but showed the absence of any $\mathrm{Me_2N_4BH}$. The bulk of the reaction product was involatile and was not fully characterised.

The attempted exchange reaction between LiD and $(CH_3)_2N_4BH$

Lithium deuteride (0.59 g., 0.066 g.mol) was transferred to an ampoule in a dry nitrogen containing glove box, and Me_2N_4BH (0.83 g., 0.0084 g.mol) was vacuum distilled into the ampoule which was then sealed. The reactants were allowed to stand at room temperature for 12 hours, followed by heating at 90° for two hours. On opening the ampoule under vacuum a gas 0.0018 g.mol) was collected, the mass spectrum of which indicated an approximate composition as follows [m/e 2 (H_2) = 57.0%; m/e 3 (HD) = 8.2%; m/e 4 = 0.6%; m/e (N_2) = 34.2 %]. The infrared and mass spectra of the fraction, collected by vacuum distillation at -30°C, showed only the presence of unchanged Me_2N_4BH.

Attempted reaction: $Me_2N_4BH + LiD \rightleftharpoons Me_2N_4BD + LiH$

The attempted exchange reaction between Me_2N_4BH and $LiBD_4$

Me_2N_4BH (0.53 g., 0.0054 g.mol) was condensed into an ampoule into which $LiBD_4$ (0.133 g., 0.0052 g.mol) had been introduced in a dry nitrogen filled glove box. Diethyl ether was cold distilled from $LiAlH_4$ into the ampoule, which was then sealed under vacuum and heated to 140°C for 16 hours. The fraction collected by vacuum distillation of the reaction products through a trap at -40 proved to be essentially unchanged Me_2N_4BH

(0.20 g.,0.00204 g.mol), but the presence of some Me_2N_4BD was indicated by the B-D stretching frequency of weak intensity at 1988 cm^{-1} in the infrared spectrum. Infrared evidence also indicated that the solid product left in the ampoule was found to contain some Me_2N_4BH even after prolonged vacuum distillation.

Attempted reaction: $LiBD_4 + Me_2N_4BH \rightleftharpoons Me_2N_4BD + LiBD_3H$

The preparation of 2,5-dimethyl,1-deuterocyclotetrazenoborane (Me_2N_4BD)

Methyl ammonium chloride (1.10 g,0.016 g.mol), lithium boro-deuteride (0.4 g,0.016 g.mol) and methyl azide (1.38 g,0.024 g.mol) were heated in an ampoule at 130° for 60 hours in diethyl ether solvent distilled from $LiAlH_4$. Me_2N_4BD (0.35 g, 23% Theoretical yield) was collected as a colourless oily liquid by vacuum distillation through a trap at -40°C and further purified by distillation from a trap at 0°C. The compound was confirmed by infrared, N.M.R. and mass spectra. The intensities of the parent ion peaks at m/e 98, 99 due to ^{10}B and ^{11}B isotopes were in the expected ratios.

The preparation of diethylcyclotetrazenoborane

This was prepared by the general route already described for Me_2N_4BH, by heating ethylamine-borane (prepared from ethylamine and diborane in a 2:1 molar ratio) with ethyl azide and dry diethyl ether solvent in a sealed ampoule at 130° for 24 hours. The gas evolved during the reaction was collected using a Töpler pump when an almost quantitative yield of H_2 was observed (1170 ml., 0.05 g.mol., 98% Theoretical). The colourless oily

product of Et_2N_4BH was isolated by vacuum distillation through a trap at -10°C and further purified by redistillation. A small amount of a non-volatile liquid remained in the ampoule.
Found: C, 38.32; H, 8.91; N, 44.50; B, 8.36%. $C_4H_{11}N_4B$ requires C, 38.14; H, 8.80; N, 44.48; B, 8.58%. Molecular ion peaks were observed at m/e 125, 126 in the expected ratio for the isotopes ^{10}B and ^{11}B.

<u>The reaction of Grignard reagents with cyclotetrazenoboranes</u>

A solution or slurry of the cyclotetrazenoborane R_2N_4BH in ether solvent was added slowly from a tap funnel to the Grignard reagent, prepared as described previously, and the mixture stirred at room temperature for about 24 hours, under an atmosphere of dry nitrogen. It was also found that the utilisation of a tipping tube in place of the tap funnel made the experimental procedure for the addition of Ph_2N_4BH somewhat easier. When Ph_2N_4BH was added to PhMgBr the first small addition produced a deep green fluorescent solution. On further addition, the green fluorescent colour was replaced by a bright yellow precipitate and a bright yellow fluorescent solution. Similar colour changes were observed on addition of Ph_2N_4BH to MeMgI, but the complex was much more soluble. When Et_2N_4BH was added to EtMgI, no fluorescence was observed but a colourless viscous oil separated on standing.

Me_2N_4BH and MeMgI produced a similar oil, but the addition of an ether solution of Me_2N_4BH to ViMgBr produced a white crystalline complex. In general, the products were treated with an excess of saturated aqueous ammonium chloride solution and effervescence occurred, with evolution of hydrogen. The ethereal solutions were separated and the aqueous layer extracted with several portions of diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate or molecular seive, filtered and concentrated. In the case of Ph_2N_4BPh however this latter method had the disadvantage that Ph_2N_4BPh had a very low solubility in ether, and it was found that a better yield was obtainable by soxhlet extraction of the complex with moist ether in the normal laboratory atmosphere.

Ph_2N_4BPh and Ph_2N_4BMe were obtained as white crystals from the concentrated ether solutions, and were recrystallised from ether-light petroleum (B. Pt. 60 - 80°), Me_2N_4BMe, Me_2N_4BVi and Et_2N_4BEt were isolated as colourless liquids by distillation on the vacuum line and were collected in traps at -40°C. They were further purified by distillation from traps at 0°C. Gas-liquid chromatography of the vinyl substituted compound showed it to be a mixture of two products in the approximate ratio of 5:1 but an attempt to separate these by both vacuum fractionation and preparative scale G.L.C. proved unsuccessful. An examination of the mass spectrum showed parent ions at m/e 123, 124, 125 and 126 in the ratios for a 5.25:1 mixture of Me_2N_4BVi and Me_2N_4BEt. The subsequent fragmentation pattern further confirmed both compounds in the light of the generalised fragmentation which has been observed for these compounds, (see Chapter 5). The details of experimental quantities, yields and analysis data for all the Grignard reactions are summarised in Table 3-G.

During the preparation of Ph_2N_4BPh and Ph_2N_4BMe, the magnesium containing complexes were isolated by concentrating the ethereal solution after the parent compound had been added to the Grignard reagent, and the product filtered in a dry nitrogen filled glove box. Analysis on the complex formed from Ph_2N_4BH and PhMgBr found C, 56.75; H, 4.77; N, 13.28; B, 2.62; Mg, 3.06. This gave an empirical ratio of Mg:B:N:C:H of approximately 1:2:8:39:40 indicating possibly a 2:1 complex $2Ph_2N_4BH.PhMgBr$ coordinated with diethyl ether solvent. The analysis figures however were not readily rationalised with any simple theoretical stoichiometric complex. The complexes were extremely sensitive to air and moisture, rapidly changing colour from yellow to white, and were not characterised further.

Reaction: $R'MgBr + R_2N_4BH \longrightarrow [R'MgBr.R_2N_4BH](?)$

$$\downarrow \text{Hydrolysis, Sat } NH_4Cl \text{ soln.}$$

$$R_2N_4BR' + MgBrOH + H_2$$

TABLE 3-G

EXPERIMENTAL DATA

Compound	mmoles starting material	Yield %	Analysis found %				Analysis required %				Parent ions m/e
			C	H	B	N	C	H	B	N	
Me_2N_4BMe	15.1	79	32.4	8.2	9.7	50.2	32.2	8.1	9.7	50.0	111, 112
Et_2N_4BEt	11.5	80	46.6	9.6	7.3	36.5	46.8	9.8	7.0	36.4	153, 154
Ph_2N_4BMe	9.0	88	66.2	5.6	4.4	23.8	66.1	5.6	4.6	23.7	235, 236
Ph_2N_4BPh	13.5	72	72.2	5.2	3.6	18.5	72.5	5.1	3.6	18.8	297, 298
Me_2N_4BVi	14.4	64 (in 5:1 mixture)	-				-				123, 124
Me_2N_4BEt	-	-	-				-				125, 126

Preparation of Ph_2N_4BPh using diphenylboron azide

Diphenylboron azide (4.00 g.,0.019 g.mol) and phenyl azide (2.30 g.,0.019 g.mol) were dissolved in dry ether in a 200 ml. ampoule which was previously flushed with dry nitrogen in a glove box. The ampoule was sealed under vacuum and heated at 90 - 100° for 60 hours in a protective metal tube. A dark brown liquid was produced which on cooling deposited colourless crystals, and the nitrogen evolved during the reaction measured 364 ml at N.T.P. (84% of the theoretical quantity) using a Töpler pump. The gas was identified by mass spectrometry. The crystalline compound was filtered in the glove box and recrystallised from ether or light petroleum. The product was shown to be identical with that obtained from the Grignard reaction by its infrared and mass spectra. The molecular ion peak at m/e 298 was measured as m/e 298.1386 (theoretical m/e 298.1411). Yield 23%.

Catalytic hydrogenation of the Me_2N_4BVi mixture

The mixture of Me_2N_4BVi and Me_2N_4BEt (0.4996 g.) was dissolved in light petroleum (b.p. 60 - 80°), and placed with PtO catalyst in a standard hydrogenation apparatus. A typical zero-order reaction was observed, as shown in Figure 3-14, and a total of 85.0 ml. of hydrogen was absorbed (theoretical for a 5.25:1 mixture, 84.9 ml). The product was isolated by vacuum distillation, and showed parent ion peaks at m/e 125, 126.

THE CATALYTIC HYDROGENATION OF A MIXTURE OF Me_2N_4BVi & Me_2N_4BEt.

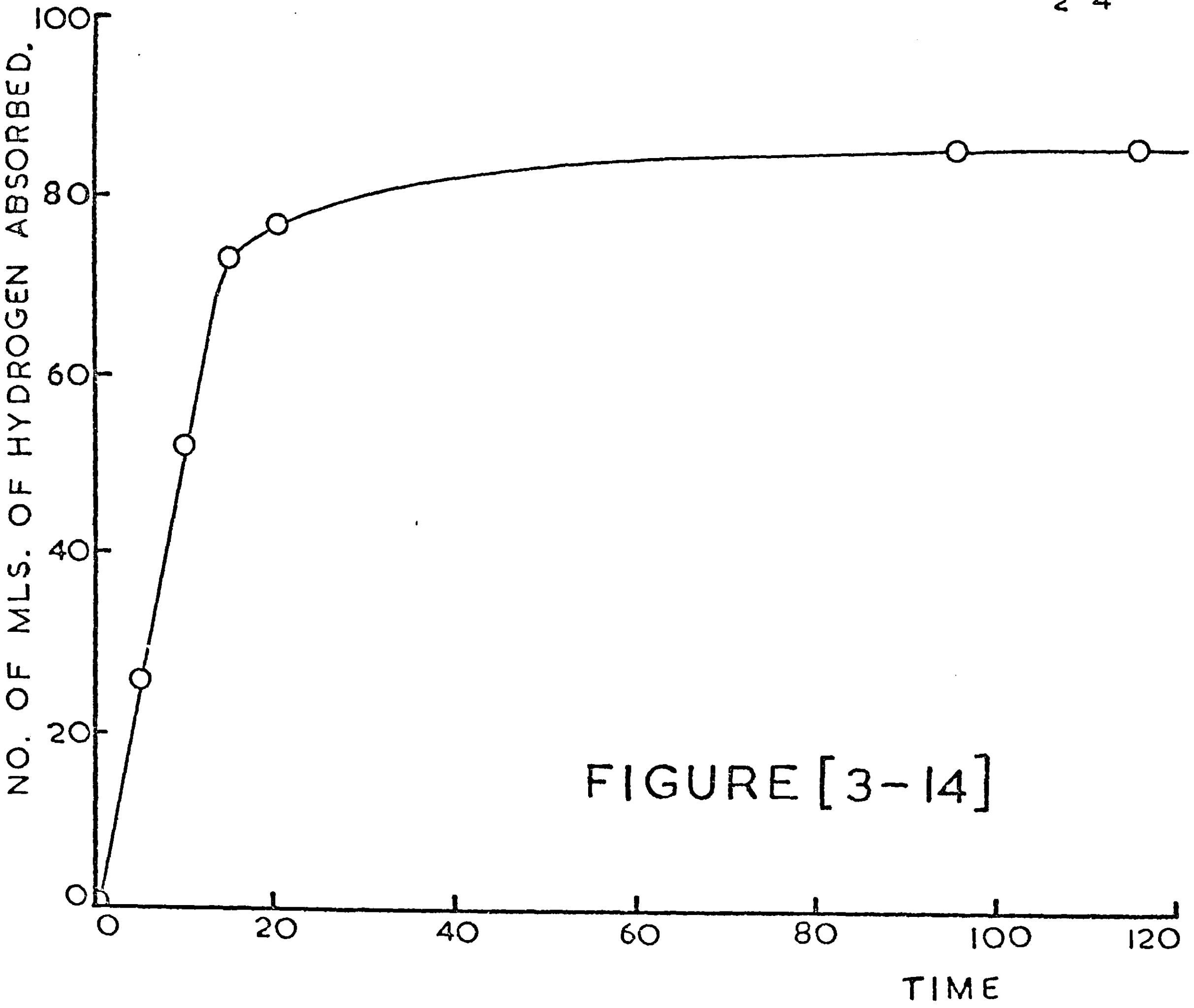


FIGURE [3-14]

Attempted hydroboration of ethylene with Me_2N_4BH

Equimolar quantities of Me_2N_4BH and ethylene, obtained from a cylinder supplied by the Callery Chemical Co. Ltd., together with ether solvent were sealed under vacuum in an ampoule and heated at 130° - 140°C for 48 hours. The reaction products were vacuum distilled through traps at -15°C, -40°C and -196°C. The -15°C trap did not contain any Me_2N_4BEt compound that might have been expected, while the -40°C trap was shown to contain unreacted Me_2N_4BH and the -196°C trap unreacted ethylene plus solvent ether.

Attempted reaction: $Me_2N_4BH + C_2H_4 \longrightarrow Me_2N_4BEt$

Attempted hydroboration of butene-1

Me_2N_4BH and butene-1, from a cylinder kindly donated by B.P. Chemicals U.K. Ltd., in equimolar ratios into two ampoules under vacuum. The ampoules were then sealed and one was heated at 60°C for 24 hours and the other one at 110° for 50 hours. In both cases vacuum distillation of the products through traps at -30°C and -196°C yielded the unchanged reactants.

Attempted reaction: $Me_2N_4BH + C_4H_8 \longrightarrow Me_2N_4BC_4H_9$

CHAPTER IV

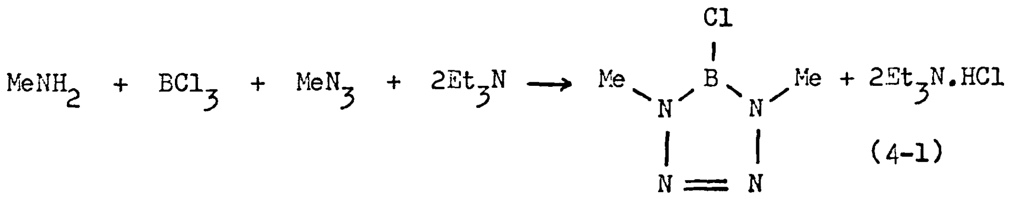
B-HALOGENO SUBSTITUTED CYCLOTETRAZENOBORANES

RESULTS AND DISCUSSION

The preparation of B-halogeno cyclotetrazenoboranes proved to be unexpectedly difficult, but the two derivatives Me_2N_4BCl and Me_2N_4BBr have been isolated and examined by a variety of physical techniques.

One possible route for the preparation of B-halogeno derivatives was the dehydrohalogenation of a primary amine-haloborane adduct and the capture of the borazyne intermediate by an organic azide. Attempts to prepare Me_2N_4BCl, Ph_2N_4BCl and Ph_2N_4BF from the reactions of boron halides and organic azides with both equimolar and excess quantities of primary amines gave numerous products, mostly uncharacterised, but in no case was the required B-halogeno cyclotetrazenoborane derivative isolated. A large number of competitive reactions could be postulated, and further work is required to determine the nature of the often readily hydrolysable products obtained.

The dehydrohalogenation reaction was proved to occur in the presence of the stoichiometric quantity of triethylamine, and in this manner B-chloro,2,5-dimethylcyclotetrazenoborane was isolated as a colourless, readily hydrolysable liquid in 26% yield as shown by equation 4-1. The compound was confirmed



(4-1)

4-I

by elemental analysis, 'H N.M.R., "B N.M.R., infrared and mass spectrometry.

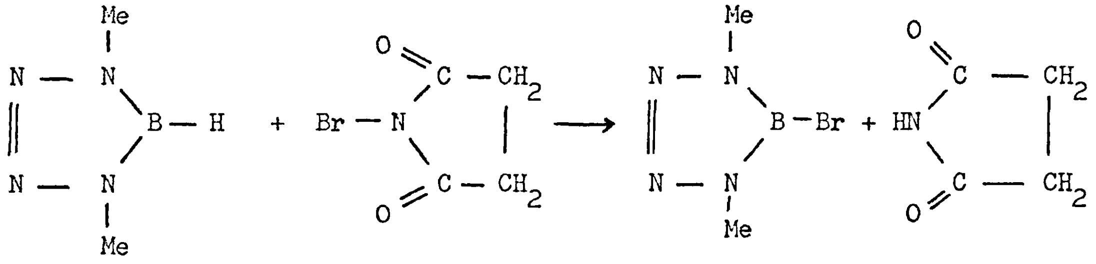
It was of interest that the infrared spectrum of the crude reaction product indicated the presence of an azide group and this was further explained by the mass spectrum which showed ions of low intensity at m/e 139, 138 in the isotopic ratio expected for a compound containing one boron atom. This indicated the presence of the compound $Me_2N_4BN_3$, possibly formed by the secondary reaction of Me_2N_4BCl with MeN_3. This impurity was removed from the B-chloro derivative by vacuum fractionation.

An anomaly exists in that the analogous reaction of BBr_3 with $MeNH_2$ and MeN_3 in the presence of $2Et_3N$ did not yield the expected Me_2N_4BBr, but a colourless, readily hydrolysable liquid was isolated in very low yield. The infrared spectrum of this product showed a very intense band at 2140 cm^{-1}, probably due to the presence of an azide band. The mass spectrum of the product, however, did not show parent ion peaks for any readily rationalisable cyclotetrazenoborane derivative, and further work is required to determine the nature of the reaction observed.

The reaction of $MeNH_2.BH_2Cl$ with MeN_3 which it might have been anticipated to produce Me_2N_4BCl with evolution of hydrogen did not yield any of the required compound. Furthermore direct halogenation of N-substituted cyclotetrazenoboranes proved unsuccessful. The attempted chlorination of Ph_2N_4BH gave products not fully characterised, whereas the attempted iodination of Et_2N_4BH in the presence of a small quantity of picoline, to eliminate any HI formed, led to the recovery of unchanged Et_2N_4BH.

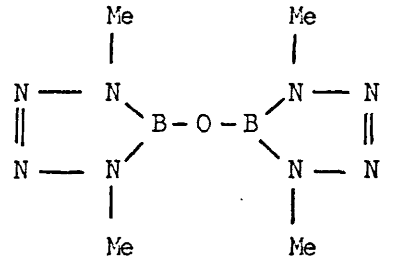
The reaction of Ph_2N_4BH with iodine in the presence of pyridine led to the formation of a deep red compound which analysed to give the approximate empirical formula ($C_{21}H_{22}N_5BI_4$), but a large proportion of the Ph_2N_4BH was recovered unchanged.

A successful method of preparation of Me_2N_4BBr in high yield was achieved by the reaction of N-bromo succinimide on Me_2N_4BH in refluxing CCl_4 solution, as shown in equation 4-2.



(4-2)

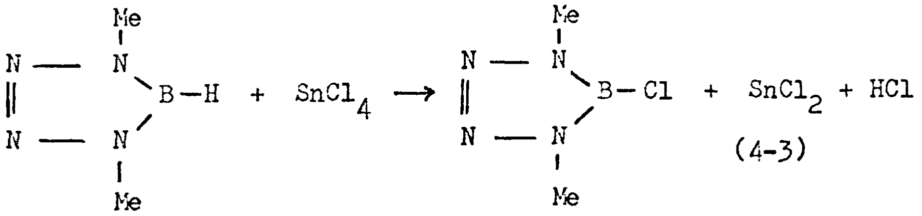
The Me_2N_4BBr was isolated as a colourless readily hydrolysable liquid and was identified by elemental analysis, ^1H N.M.R., ^{11}B N.M.R., infrared and mass spectrometry. The latter showed the parent ion peaks in the expected isotopic ratios at m/e <u>178</u>, 177, <u>176</u>, 175. A further interesting piece of information was derived from the mass spectrum taken on an instrument that was apparently contaminated with moisture. The base peak of the spectrum in this instance was not that for the parent ion Me_2N_4BBr but was consistently that of a group of peaks at m/e 211, 210, 209, 208 in the expected isotopic ratios for the presence of two boron atoms but zero bromine atoms in the ions. This can be interpreted by hydrolysis of the Me_2N_4BBr to give compound 4-II.



4-II

The reaction of Me_2N_4BH with N-chloro succinimide did not lead to the isolation of any Me_2N_4BCl even though initially a pale yellow solution was obtained due to the formation of free chlorine in solution. The attempted reaction between Et_2N_4BH and N-chloro succinimide, even on addition of a trace of free radical initiator and irradiation with a low intensity U.V. lamp, led to the recovery of unchanged Et_2N_4BH and N-chloro succinimide.

It was further anticipated that, in an analogous manner to that observed for borazines,[96] the reaction of Me_2N_4BH with $SnCl_4$ in carbon tetrachloride solution might lead to the formation of B-chloro 2,5-dimethyl cyclotetrazenoborane by the reaction scheme shown in 4-3. In practice it was found that when the reaction



(4-3)

4-I

was performed at -3°C in carbon tetrachloride solution a white adduct readily sublimable in vacuo was obtained.

$SnCl_4 + Me_2N_4BH \longrightarrow [SnCl_4 \cdot x\, Me_2N_4BH]$ (?)

The mass spectrum of the product showed the highly characteristic isotopic patterns expected for $SnCl_4$, $SnCl_3$, $SnCl_2$, SnCl, Sn and Me_2N_4BH ions, but no parent ion for a simple stoichiometric adduct could be observed even on reducing the electron voltage of the mass spectrometer.

The presence of Me_2N_4BCl 4-I in the product was also confirmed by the characteristic isotopic pattern at m/e 131, <u>132</u>, 133, <u>134</u>, and in addition ions were observed at m/e 211, <u>210</u>, 209, 208 attributable to its hydrolysis product identical with that previously mentioned, namely 4-II. Other ions detected were those for HCl. Elemental analysis on the sublimed white product again failed to establish a simple stoichiometry for the $SnCl_4 \cdot Me_2N_4BH$ adduct. An infrared spectrum of the solid showed the presence of the Me_2N_4BH in the adduct.

Prior to the performance of this latter experiment of $SnCl_4$ with Me_2N_4BH it had been anticipated that derivatives of the cyclotetrazenoborane ring system might be able to act as donor molecules in the formation of σ complexes with metal halide acceptors. It was found that solid products could be isolated in each case from the reactions of Me_2N_4BH or Ph_2N_4BH with metal halides such as $SnCl_4$, $HgCl_2$ and $TiCl_4$, but that these were not soluble in common organic solvents and could not be recrystallised. Infrared spectroscopy again showed the presence of the cyclotetrazenoborane system in the products but elemental analysis tended to indicate that the products were not pure compounds.

An important extension of this work, would be to study the reaction of one of the hydrolytically stable B-alkyl or B-aryl substituted cyclotetrazenoboranes (e.g. Me_2N_4BMe or Ph_2N_4BPh) with an acceptor metal halide such as $SnCl_4$ or $HgCl_2$. This would have the advantage of reducing the number of possible side reactions such as the halogenation of the cyclotetrazenoborane derivative.

Summary

The preparation of the B-halogeno cyclotetrazenoborane derivatives now opens a vast field of chemistry, and it is conceivable that many reactions analogous to those already substantiated for borazine chemistry will be found to occur.

Physical properties of B-halogeno cyclotetrazenoboranes

The physical properties of the B-halogeno cyclotetrazenoborane derivatives are summarised in Table 4-A, except the principal bands in the vibrational spectra which are recorded on page 143, and the detailed mass spectra which will be reported in Chapter V.

TABLE 4-A

PHYSICAL PROPERTIES OF B-HALOGENO CYCLOTETRAZENOBORANES

Compound	M.Pt. °C	U.V. λ_{max} mμ	^{11}B NMR δ(ppm)^{a}	^{1}H NMR τ^{b}	Mass spectra parent ions (m/e)
Me_2N_4BCl	12.3	214	-23.2	6.50	134, 133, 132, 131
Me_2N_4BBr	11.5	212	-21.1	6.43	178, 177, 176, 175

[a] Ref $BF_3.Et_2O$ [b] tau values, ref Me_4Si

Electronic Spectra

The effect of halogen substitution on the boron atom on the first electronic transition was to produce a bathochromic shift of similar magnitude to that observed for B-vinyl substituted cyclotetrazenoboranes. This suggests that some π interaction takes place between the halogen and boron atoms. Again $n \rightarrow \pi^*$ transitions were not observed for these compounds.

Nuclear Magnetic Resonance Spectra

The substitution of the hydrogen at the boron by chlorine or bromine produced the expected single ^{11}B N.M.R. resonance similar to those for Me_2N_4BMe etc. shown in Figure [3-1] Chapter 3. A downfield ^{11}B N.M.R. chemical shift of about 2 - 3 p.p.m. was observed which was less than that given for B-alkyl or aryl substitution, but was of the same order as the B-vinyl substitution. These observations were in qualitative agreement with the observed relative shifts of B-halogen, B-alkyl, B-aryl and B-vinyl substituted borazines.[85] The ^{11}B resonance of the B-chloro compound occurred at slightly lower field than that for the B-bromo compound and could be attributed to the greater electronegativity of the chlorine atom.

Single methyl resonances were observed in the ^1H N.M.R. spectra of the B-halogeno, 2,5-dimethyl cyclotetrazenoboranes similar to those obtained for other dimethyl derivatives shown in Figure [3-3] Chapter 3. The chemical shifts of these methyl protons were displaced to slightly lower field, than in the B-H(D), B-alkyl or B-aryl substituted derivatives.

Infrared spectra

The infrared spectra of the B-chloro and B-bromo cyclotetrazenoborane derivatives are shown in Figures [4-1] and [4-2], and the

INFRARED SPECTRA

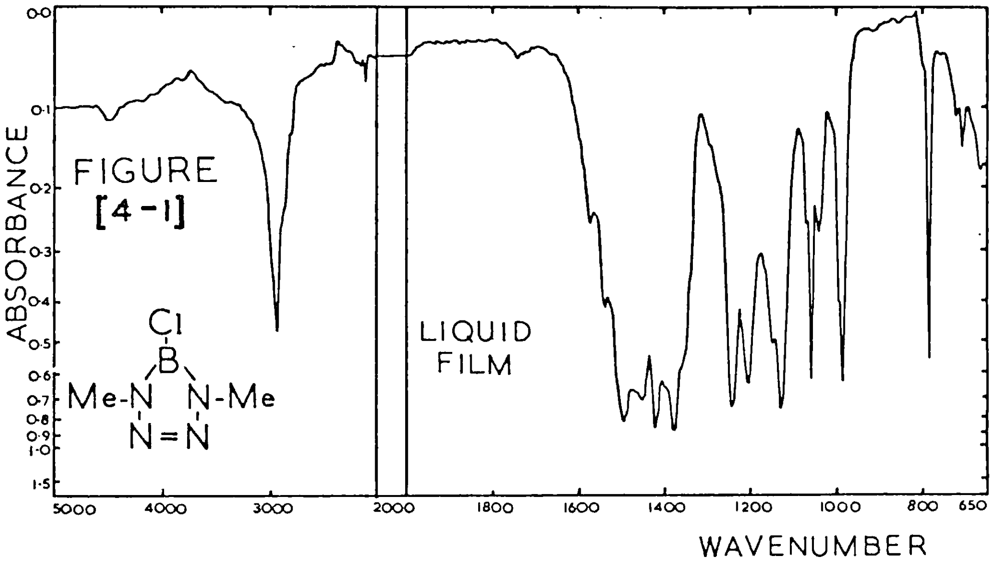


FIGURE [4-1]

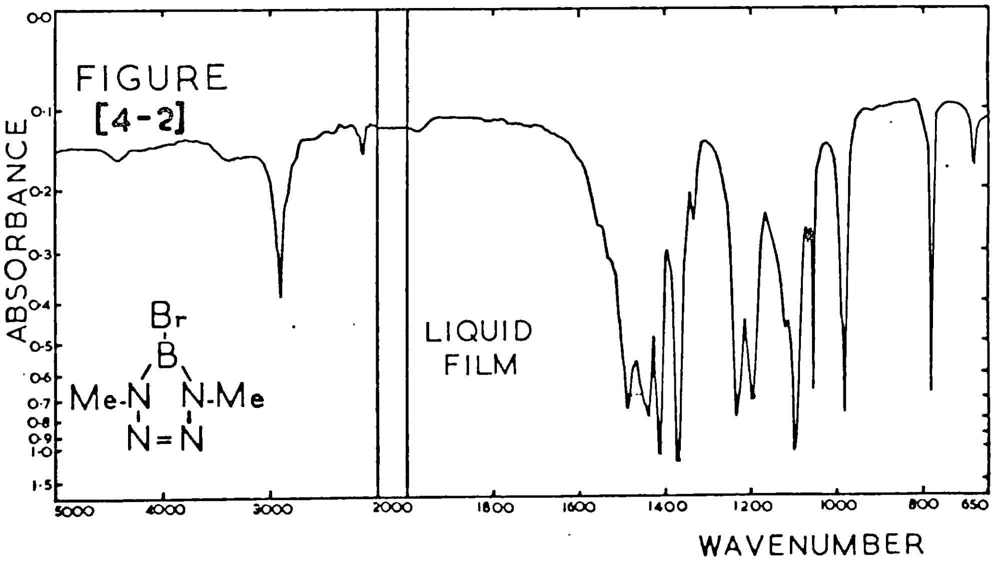


FIGURE [4-2]

principal bands in the spectra are listed below.

Me_2N_4BCl: 2972 ms; 2937 s; 2874 m; 2797 wm; 2155 w; 2105 w; 1742 w; 1590 sh; 1577 m; 1563 sh; 1553 sh; 1546 sh; 1539 sh; 1534 s; 1508 sh; 1493 sh; 1486 vs; 1464 vs; 1454 vs; 1439 vs; 1421 sh; 1410 vs; 1362 vs; 1351 s; 1344 sh; 1333 ssh; 1282 w; 1261 m; 1241 vs; 1202 vs; 1147 s; 1124 vs; 1068 m; 1056 vs; 1035 ms; 1004 w; 988 ssh; 980 vs; 906 w; 810 w; 794 w; 781 s; 753 w; 728 sh; 719 m; 706 m; 683 w; 667 w; 664 w; 639 w; 625 m; 606 s; 593 wm; 585 w; 472 w; 464 m; 458 w.

Me_2N_4BBr: 3082 wsh; 3058 wsh; 3026 wsh; 2972 m; 2937 s; 2882 m; 2829 vwsh; 2797 w; 2151 w; 2096 w; 1961 w; 1580 sh; 1572 sh; 1563 sh; 1553 m; 1536 sh; 1529 sh; 1520 sh; 1513 sh; 1502 ssh; 1493 ssh; 1482 vs; 1460 s; 1449 sh; 1441 vs; 1433 vs; 1409 vs; 1385 sh; 1366 vs; 1332 m; 1289 w; 1233 vs; 1203 vs; 1136 ssh; 1119 s; 1094 vs; 1066 s; 1053 vs; 985 s; 976 vs; 912 w; 791 w; 776 vs; 682 m; 673 wsh; 635 w; 614 m; 596 s; 582 m; 576 w; 459 w; 456 m; 453 wsh.

A number of the bands have again been assigned by analogy with the previously examined compounds as in Chapter 3.

Ring modes: Analogous ring stretching modes to those observed in the spectra of other cyclotetrazenoborane derivatives are listed in Table 4-B.

TABLE 4-B

Ring stretching modes of B-chloro and B-bromo, 2,5-dimethyl cyclotetrazenoboranes

Mode of vibration	Me_2N_4BCl cm^{-1}	Me_2N_4BBr cm^{-1}
ω_4	1410	1409
ω_5	1362	1366
ω_3	1333	1332
ω_2 ^{10}B	988	985
^{11}B	980	976
ω_1 ^{10}B	-	
^{11}B	906	912

Again it was less easy to identify the corresponding ring deformations, but strong bands at 781 cm^{-1} in Me_2N_4BCl and 776 cm^{-1} in Me_2N_4BBr agreed very well with bands attributed to the b_1 ring deformation ω_6 in previously examined compounds.

C-N modes: The C-N antisymmetric stretching modes were readily assigned to bands at 1241 cm^{-1} in Me_2N_4BCl and 1233 cm^{-1} in Me_2N_4BBr and the corresponding symmetric modes were attributed to the bands at 1202 cm^{-1} and 1203 cm^{-1} respectively. Again, very weak bands were observed at 639 cm^{-1} and 635 cm^{-1} respectively for Me_2N_4BCl and Me_2N_4BBr and these were consistent with previous assignments for one of the C-N deformation modes.

N-substituent vibrations: Internal vibrations associated with the N-Me groups occurred at similar frequencies to those observed for Me_2N_4BH[43] and the other B-substituted 2,5-dimethylcyclotetrazenoborane derivatives discussed in Chapter 3. The C-H stretching, CH_3 deformation and CH_3 rocking regions could be identified with the bands observed in the regions 3100 - 2850 cm^{-1}, 1500 - 1400 cm^{-1} and 1200 - 900 cm^{-1} respectively.

B-halogen vibrations The consistency with which the B-substituent stretching vibrations occur at relatively high frequency and in all cases at higher frequency than in similar borazine derivatives is encouraging, and this comparison is summarised in Table 4-C. The ^{10}B-X and ^{11}B-X stretching vibrations in Me_2N_4BCl and Me_2N_4BBr were observed as extremely sharp well-resolved bands at 1068, 1056 cm^{-1} and 1066, 1052 cm^{-1} respectively.

TABLE 4-C

Comparison of B-substituent stretching vibrations in borazine and cyclotetrazenoborane derivatives

Borazine derivative	B-X stretching frequency.cm^{-1} [97]	Cyclotetrazenoborane derivative	B-X stretching frequency cm^{-1}
$(MeN\text{-}BH)_3$	B-H 2565,2515,2455	Me_2N_4BH	B-H 2643, 2630
$(EtN\text{-}BH)_3$	B-H 2480	Et_2N_4BH	B-H 2641
$(PhN\text{-}BH)_3$	B-H 2556, 2504	Ph_2N_4BH	B-H 2661,2651
$(MeN\text{-}BMe)_3$	B-C 880	Me_2N_4BH	B-C 1083,1070
$(MeN\text{-}BCl)_3$	B-Cl 975	Me_2N_4BCl	B-Cl 1068,1056
$(MeN\text{-}BBr)_3$	B-Br 962	Me_2N_4BBr	B-Br 1066, 1052

The B-halogen deformation modes in the cyclotetrazenoborane derivatives were not readily assigned.

EXPERIMENTAL

Solvents and intermediates Solvents and intermediates were again purified and dried by standard procedures[89]. The preparations of Me_2N_4BH, Et_2N_4BH and Ph_2N_4BH were performed as described in Chapter 3.

Preparation of methylamine borane: This was prepared as reported by Nöth et al[98]. Finely powdered methylamine hydrochloride (8 g., 0.12g.mol) was dried under vacuum and placed in a two-necked flask fitted with a reflux condenser and a tap funnel, and covered with dry ether. A sludge of $LiBH_4$ (2.6 g., 0.12 g.mol) in ether was added dropwise under an atmosphere of dry nitrogen from the tap funnel, to the cooled methylamine hydrochloride solution until the hydrogen evolution ceased. The reaction products were filtered and the ether solution evaporated under vacuum and recrystallised from benzene and light petroleum.

Reaction: $MeNH_2.HCl + LiBH_4 \longrightarrow MeNH_2BH_3 + LiCl + H_2$

Preparation of $MeNH_2BH_2Cl$: The preparation of $MeNH_2BH_2Cl$ was prepared as reported by Nöth et al.[99] An ethereal solution of HCl was prepared by passing dry HCl through ether and was standardised by titration against standard NaOH solution. Methylamine borane (2.31 g. 0.051 g.mol) in solution in 40 mls ether was titrated dropwise with the required quantity of ethereal

HCl solution (39.5 mls, 1.61 M HCl, 0.05 g.mol) for the reaction shown below. The products were filtered after 0.5 hours and the

$$MeNH_2BH_3 \quad + \quad HCl \longrightarrow MeNH_2BH_2Cl \quad + \quad H_2$$

ether evaporated under vacuum to yield $MeNH_2BH_2Cl$. The product was recrystallised from benzene and light petroleum (30 - 40°) M.pt. = 47°. (Lit = 47°). Yield = 3.42 g. (86% Theor.).

Attempted preparation of Ph_2N_4BCl from the dehydrohalogenation of aniline and boron trichloride in the presence of phenyl azide

Boron trichloride (2 g., 0.017 g.mol) was condensed into a solution of aniline (4.76 g. 0.051 g.mol) in toluene (10 ml) and on warming a white precipitate of the $PhNH_2BCl_3$ adduct was obtained, to which was added a solution of phenyl azide (2 g., 0.017 g.mol) in toluene (15 ml). The reactants were shaken at room temperature when a yellow coloured solution was obtained together with an insoluble white compound, which was filtered in a dry nitrogen containing glove box, and shown to be aniline hydrochloride (4 g., 0.031 g.mol). Yellow-white crystals (1.55 g) were isolated by removal of the toluene from the filtered solution by vacuum distillation. The product could be recrystallised from diethyl ether although a darkening of the product sometimes occurred yielding greenish coloured crystals. The infrared spectra of both the crude yellowish product and these green crystals were however almost identical. Further attempts to isolate a pure compound by recrystallisation from toluene light petroleum (60 - 80°) and chloroform led to further decomposition of the product. An analysis obtained on the yellow crystalline compound (C = 51.77, H = 5.37, N = 10.61, B = 5.91, Cl = 20.31 %) was incomplete and not readily rationalised. It was interesting that exposure of the yellow crystals to the atmosphere resulted in fairly rapid decolorisation of the product with the evolution of HCl as an acid gas. Hydrolysis of the crystals in water yielded a white insoluble compound which could be recrystallised from acetone and water, but was subject to decomposition possibly by oxidation or photolysis. The infrared spectrum of the hydrolysis product showed the presence of an intense -OH stretching frequency, but analysis obtained for the compound was unreliable.

Attempted reaction: $3PhNH_2 + BCl_3 + PhN_3 \rightarrow Ph_2N_4BCl + 2PhNH_2.HCl$

The attempted preparation of Ph_2N_4BF from the dehydrohalogenation of aniline and boron trifluoride etherate in the presence of phenyl azide

Boron trifluoride etherate (2.24 g., 0.028 g.mol BF_3), aniline (7.92 g., 0.085 g.mol) and phenyl azide (3.36 g., 0.028 g.mol) were left to react at room temperature in diethyl ether solvent in a stoppered 250 ml flask. After several days a viscous red oil insoluble in ether was produced. The reaction products were vacuum distilled, when isolation of unreacted phenyl azide and aniline in a trap at -35°C and the ether solvent in a trap at -196°C was obtained. The residue was a red-black coloured tar-like compound, the infrared spectrum of which showed many complex, broad poorly resolved bands, B-F, N-H and phenyl vibrations being indicated. The compound was not characterised further.

Attempted reaction:

$$BF_3.Et_2O + PhN_3 + 3PhNH_2 \longrightarrow Ph_2N_4BF + Et_2O + 2PhNH_2.HF$$

The attempted preparation of Me_2N_4BCl by the dehydrohalogenation of methylamine and boron trichloride in the presence of methyl azide

Methylamine and boron trichloride in the molecular ratios of (a) 1:1 and (b) 3:1 respectively were condensed into two separate ampoules together with dry light petroleum (40 - 60°) solvent. The ampoule contents were allowed to warm up and react and then methyl azide (1 molar ratio relative to the BCl_3) was condensed into each ampoule. The ampoules were sealed under vacuum and heated to 120°C for 16 hours and the reaction products were fractionated under vacuum, when in both experiments only solvent was found to be volatile.

A white crystalline residue remained in the ampoule in case (a) and a similar product was obtained by a small scale distillation of the products in case (b) the residue from which proved to be methylamine hydrochloride (2 molar equivalent relative to BCl_3). The infrared spectra of the crystalline products obtained showed the presence of many complex broad vibrations and elemental analysis although showing the presence of C, H, N, B and Cl did not indicate the formation of any single compound.

Attempted reactions:

(a) $MeNH_2 + BCl_3 + MeN_3 \longrightarrow Me_2N_4BCl + 2HCl$

(b) $3MeNH_2 + BCl_3 + MeN_3 \longrightarrow Me_2N_4BCl + 2MeNH_2.HCl$

The preparation of Me_2N_4BCl from the dehydrohalogenation of methylamine and boron trichloride in the presence of triethylamine and methyl azide

Triethylamine (4.64 g., 0.046 g.mol) was transferred to an ampoule and BCl_3 (2.7 g. 0.023 g.mol), $MeNH_2$ (0.71 g., 0.023 g.mol) and MeN_3 (1.31 g., 0.023 g.mol) were condensed into it under vacuum in the order indicated, and the ampoule sealed. In three separate experiments the contents of the ampoule were allowed to react at room temperature for three days, 70°C for 19 hours and 130°C for 19 hours. The ampoules from each experiment were opened in turn under vacuum and the reaction products were distilled through a trap at -40°C. Both of the ampoules that had been heated yielded a very small quantity of Me_2N_4BCl as a colourless readily hydrolysable liquid from the seemingly solid mass of reaction products, but the experiment performed at room temperature did not give rise to any of the required product.

A much better yield of Me_2N_4BCl was produced by the introduction of an ether solvent distilled from $LiAlH_4$ in the ampoule together with the reactants as in the previous experiment. and heating to 130° for 15 hours. The product could be isolated by either fractionation of the products directly or by initial filtration of the ether solution in a dry nitrogen containing glove box, followed by vacuum distillation of the ether solution through a trap at -40°C. The crude product was purified by further vacuum fractionation through a trap at 0°C, the required product again being collected at -40°C. Found C 18.38; H 4.48; N 42.29; B 10.82, Cl 24.62%; $C_2H_6N_4BCl$ requires C 18.14, H 4.57, N 42.33, B 8.17, Cl 26.77. Mass spectrometry showed parent ion peaks in the expected isotopic ratios at m/e <u>134</u>, 133, <u>132</u>, 131. Yield = 26%.

Reaction:

$$MeNH_2 + BCl_3 + MeN_3 + 2Et_3N \longrightarrow Me_2N_4BCl + 2Et_3N.HCl$$

<u>The attempted preparation of Me_2N_4BBr from the dehydrohalogenation of methylamine and boron tribromide in the presence of triethylamine and methyl azide</u>

Triethylamine (6.67 g., 0.067 g.mol), boron tribromide (8.30 g., 0.033 g.mol) from which traces of free bromine were removed by shaking with mercury, methylamine (1.03 g., 0.033 g.mol), methyl azide (1.89 g., 0.033 g.mol) and ether distilled from $LiAlH_4$ were sealed in an ampoule under vacuum as in the previous experiment and heated at 130° for 16 hours. Vacuum distillation of the products through a trap at -40°C gave rise to a small amount (0.19 g.) of a colourless readily hydrolysable liquid with physical characteristics similar to those expected for Me_2N_4BBr. The infrared spectrum was however, different and more complex than that of Me_2N_4BBr prepared from Me_2N_4BH and N-bromo-succinimide, (see page 142). The mass spectrum of the product showed groups of peaks possibly containing a single boron atom around 131, 117, 103, 101, 89, 87 and 73.

Attempted reaction:

$$BBr_3 + MeN_3 + MeNH_2 + 2Et_3N \longrightarrow Me_2N_4BBr + 2Et_3N.HBr$$

The attempted preparation of Me_2N_4BCl from $MeNH_2BH_2Cl$ and MeN_3

Methyl azide and $MeNH_2BH_2Cl$ in equimolar quantities were sealed together with dry benzene solvent in ampoules under vacuum. The reactions of these compounds both at room temperature and on heating to 100°C for 16 hours gave rise to numerous products which could be partially separated by vacuum fractionation and sublimation. The gas liberated during the reaction was shown by mass spectrometry to be mainly nitrogen and not the expected hydrogen. Attempts to characterise the products by infrared spectroscopy and elemental analysis proved unsuccessful.

Attempted reaction: $MeNH_2BH_2Cl + MeN_3 \longrightarrow Me_2N_4BCl + 2H_2$

The attempted chlorination of Ph_2N_4BH

Chlorine (0.34 g., 0.0048 g.mol) was condensed under vacuum into a solution of Ph_2N_4BH (0.21 g., 0.0095 g.mol) in carbon tetrachloride to which a single small crystal of iodine catalyst had been added. The reactants were warmed to room temperature and stirred magnetically for two hours. Infrared and mass spectra of a sample of the gas obtained from the experiment showed a small quantity of HCl to be present, together with unused chlorine. Concentration of the carbon tetrachloride solution and addition of light petroleum (60 - 80°) precipitated a white compound, the infrared spectrum of which was complex, but showed the presence of some unchanged Ph_2N_4BH. The attempted recrystallisation of the small quantity of inhomogeneous material obtained, using chloroform and light petroleum did not yield a pure compound.

Attempted reaction: $Ph_2N_4BH + Cl_2 \longrightarrow Ph_2N_4BCl + HCl$

The attempted iodination of Et_2N_4BH

Iodine (2 g., 0.0079 g.mol) and a small amount of picoline (0.5 g., 0.0054 g.mol) dissolved in carbon tetrachloride were added slowly from a tap funnel to a solution of Et_2N_4BH (1 g., 0.0079 g.mol) and picoline (1.5 g., 0.016 g.mol) in carbon tetrachloride under an atmosphere of dry nitrogen. A brown deposit collected on the side of the reaction flask which did not dissolve or react on refluxing. The reaction products were fractionated under vacuum when Et_2N_4BH and picoline were both isolated in large amounts. The nature of the brown solid was not determined.

Attempted reaction: $Et_2N_4BH + I_2 + \text{pic} \longrightarrow Et_2N_4BI + (\text{pic H})I$

pic = picoline

The attempted iodination of Ph_2N_4BH

A solution of iodine (2.93 g., 0.012 g.mol) and pyridine (0.912 g., 0.012 g.mol) in benzene was slowly added from a tap funnel to a benzene solution of Ph_2N_4BH (2.56 g., 0.012 g.mol) with vigorous magnetic stirring under an atmosphere of dry nitrogen. Decolourisation of the iodine did not occur as had been observed on a small test-tube scale, but a deep red coloured compound was precipitated. After several hours stirring followed by refluxing for 30 minutes the red product was filtered in a dry nitrogen containing glove box. The benzene was removed by vacuum distillation from the filtrate leaving a pale yellow crystalline compound (1.5 g.) which was shown to be unchanged Ph_2N_4BH by infrared spectroscopy, the yellow colour probably being accountable to traces of iodine. Exposure of the compound to the atmosphere resulted in its rapid decolourisation. The red product showed the presence of free I_2 in its mass spectrum, and analysis (Found C 29.08; H 2.59, N 8.37, B 1.26, I 56.0) gave an empirical ratio of C:H:N:B:I; 20.9:22.4:5.16: 1:3.8.

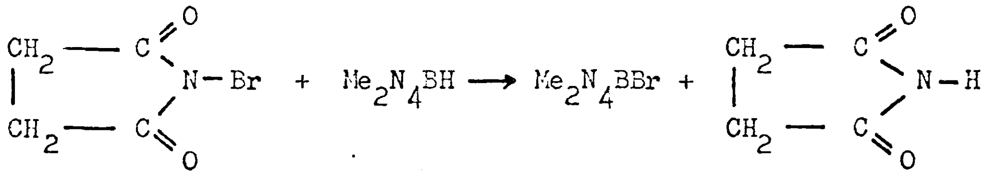
Attempted reaction: $Ph_2N_4BH + I_2 + py \longrightarrow Ph_2N_4BI + (py\ H)I$

py = pyridine

The preparation of Me_2N_4BBr from the reaction of Me_2N_4BH with N-bromo succinimide

Freshly distilled Me_2N_4BH (0.95 g., 0.0097 g.mol) was dissolved in dry carbon tetrachloride (60 ml) and placed in a 250 ml. flask fitted with a reflux condenser. The apparatus was purged with nitrogen and this inert dry atmosphere was maintained throughout the experiment by means of a nitrogen by-pass connected to the top of the condenser. N-bromosuccinimide (1.78 g., 0.01 g.mol), dried under vacuum, was added to the flask. No apparent reaction occurred at room temperature, but on refluxing a brown solution due to the formation of free bromine was obtained. After half an hour refluxing the reaction solution was decolourised, and the flask was quickly stoppered. The reaction products were filtered free of the solid succinimide in a dry nitrogen containing glove box. The filtrate was vacuum distilled through a trap at -15°C when the Me_2N_4BBr was isolated as a clear colourless readily hydrolysable liquid. The product was purified by several fractionations on the vacuum line. Yield = 0.77 g. (43% Theoretical). Found: C, 13.75; H, 3.58; N 31.77, B 7.74, Br 43.16, $C_2H_6N_4BBr$ requires: C = 13.58, H 3.42, N 31.69, B 6.12, Br 45.18. Mass spectrometry showed the presence of the expected parent ion peaks at m/e 178, 177, 176, 175.

Reaction:

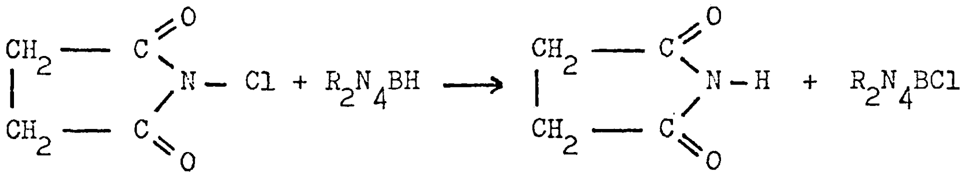


The attempted preparation of Me_2N_4BCl and Et_2N_4BCl by the reaction of N-chloro succinimide with Me_2N_4BH and Et_2N_4BH

In the same manner as in the previous experiment equimolar quantities of Me_2N_4BH and Et_2N_4BH were refluxed with N-chloro succinimide in carbon tetrachloride solution. In the experiment with Me_2N_4BH a pale yellow coloured solution was obtained after refluxing for 20 minutes. Further vigorous refluxing for 50 minutes led to an unexpected darkening of the solution together with a black solid probably of charred succinimide. Fractionation of the reaction products under vacuum did not give evidence for the formation of any Me_2N_4BCl, but a small quantity of chloroform was isolated and identified by mass spectrometry.

Gently refluxing with magnetic stirring of the reactants in the experiment with Et_2N_4BH did not produce any colouration in the solution even on irradiation with a low intensity ultraviolet lamp and the addition of a small quantity of benzoyl peroxide as a potential free radical initiator. Fractionation of the reaction products under vacuum led to the recovery of unreacted Et_2N_4BH and unchanged N-chloro succinimide.

Attempted reaction:



R = Me or Et

The attempted preparation of Me_2N_4BCl by the reaction of $SnCl_4$ with Me_2N_4BH

A solution of $SnCl_4$ (3.33 g., 0.013 g.mol) in carbon tetrachloride was slowly added with mechanical stirring from a tap funnel to a solution of Me_2N_4BH (1.18 g., 0.012 g.mol) in carbon tetrachloride at -3°C under an atmosphere of dry nitrogen.

A white precipitate was immediately formed and stirring was continued for an hour. The reaction products were then fractionated under vacuum when a white solid sublimed and was collected in a trap at $-15^{o}C$. Further less volatile white solid was also sublimed under vacuum onto a cold finger at $-78^{o}C$ placed in the reaction flask. Infrared and mass spectrometry showed the existence of both $SnCl_4$ and Me_2N_4BH in the sublimed products. A rather interesting feature was that of the effect of passing infrared radiation through the sample dispersed in a KBr pressed disc, which caused its decomposition, and the disc initially white became deep red in colour. Elemental analysis on the less volatile $SnCl_4.Me_2N_4BH$ product was not readily understood on the basis of simple stoichiometric adducts of $SnCl_4$ and Me_2N_4BH or other simple compounds.

Found C 6.93, H 1.97, N 9.30, B 4.01, Cl 35.28, Sn (by difference) = 42.51%, which gives an empirical ratio of B:Sn:N:Cl:C:H; 1:0.95:1.75:2.62:1.52:5.2.

The attempted preparation of an adduct of $SnCl_4$ and Me_2N_4BH

$SnCl_4$ (0.91 g., 0.0035 g.mol) and $(CH_3)_2N_4BH$(0.33 g., 0.0034 g.mol) were condensed under vacuum together with dry benzene into an ampoule. The reactants were allowed to warm up to room temperature when a clear solution was obtained. The solvent benzene was removed by vacuum distillation leaving a white solid (1.20 g.), which would not redissolve in benzene, nor could it be recrystallised or soxhlet extracted unchanged from any of the common organic solvents tried. Elemental analysis on both the adduct and its aqueous hydrolysis product proved to be irreproducible indicating that the compounds were inhomogeneous.

Attempted reaction: $SnCl_4 + Me_2N_4BH \longrightarrow [SnCl_4.Me_2N_4BH]$

<u>The attempted preparation of an adduct of $HgCl_2$ and Me_2N_4BH</u>

Ethereal solutions of Me_2N_4BH(0.22 g., 0.0022 g.mol) and $HgCl_2$(0.49 g., 0.0018 g.mol) were mixed in a dry nitrogen containing glove box. Precipitation did not occur, but removal of the ether by distillation left a white solid (0.62 g.) which it was not found possible to recrystallise unchanged from ether, benzene, toluene, carbon tetrachloride or chloroform. An infrared spectrum of the white product showed the presence of the Me_2N_4BH system, but elemental analysis was not informative.

Attempted reaction: $HgCl_2 + Me_2N_4BH \longrightarrow Me_2N_4BH.HgCl_2$

<u>The attempted preparation of an adduct of $TiCl_4$ with Ph_2N_4BH</u>

A deep red solution was immediately produced by the mixing of dry benzene solutions of $TiCl_4$ (1.15 g., 0.0072 g.mol) and Ph_2N_4BH (1.37 g., 0.0062 g.mol) in a dry nitrogen containing glove box. Concentration of the solution by vacuum distillation of the benzene produced yellowish crystals. These were quickly filtered and stoppered, but the crystals had a distinct tendency to decolourise even in the glove box, probably due to decomposition. Infrared spectroscopy showed the presence of the diphenyl cyclotetrazenoborane derivative in the crystals.

CHAPTER V

THE MASS SPECTRA OF B- AND N- SUBSTITUTED CYCLOTETRAZENOBORANES

A detailed investigation of the mass spectra of three series of cyclotetrazenoborane derivatives was undertaken (a) to analyse the fragmentation and rearrangement patterns of the molecules in an attempt to obtain a generalised pattern for the breakdown of the cyclotetrazenoborane ring system and (b) to confirm the proposed structures of the molecules. The only reported mass spectrum of the cyclotetrazenoboranes was a preliminary communication of the spectrum of Me_2N_4BH[22].

The three series of compounds studied were:-

<u>Series 1</u> B-H(D) substituted cyclotetrazenoboranes, Me_2N_4BH, Me_2N_4BD, Et_2N_4BH, $MePhN_4BH$, and Ph_2N_4BH.

<u>Series 2</u> B-alkyl, aryl or vinyl substituted cyclotetrazenoboranes, Me_2N_4BMe, Me_2N_4BEt, Me_2N_4BVi, Et_2N_4BEt, Ph_2N_4BMe, Ph_2N_4BPh.

<u>Series 3</u> B-halogeno substituted cyclotetrazenoboranes, Me_2N_4BCl, Me_2N_4BBr.

Series 1 has been considered in the greatest detail, an attempt being made to assign the complete fragmentation of the molecules. Inevitably some of the postulated electron transfer mechanisms and fragment ion structures must be somewhat speculative but are presented here as a rationalisation of the observed fragmentation. Series 2 and 3 were examined and shown to follow the same generalised major fragmentation as for Series 1.

The molecules were particularly suited to mass spectral analysis because of the natural abundance of the ^{10}B and ^{11}B isotopes which occur in the ratio 19.6:80.4%.[100] These gave a readily recognised triplet in the parent and fragment ion peaks due to contributions from ^{10}B, ^{11}B, ^{13}C and ^{15}N isotopes, and peaks due to metastable ions containing boron were also easily distinguished due to the ^{10}B, ^{11}B isotopic ratio. In all of the abundance ratio calculations[101] the parent peak was taken to be monoisotopic with respect to ^{10}B, and M + 1, M + 2 to the appropriate contributions from ^{11}B, ^{13}C etc. The major peak was always M + 1 and has been underlined in the text. In the compounds Me_2N_4BCl and Me_2N_4BBr the presence of the characteristic chlorine and bromine isotopes also assisted the mass spectral interpretation of the fragmentation.

Table 5-A records all peaks of relative abundance greater than 1% of the base peak for the compounds studied.

TABLE 5-A

MASS SPECTRA OF CYCLOTETRAZENOBORANES

Series 1

2,5-Dimethyl-cyclotetrazenoborane

m/e	10	11	12	13	14	15	25	26	27	28	29
o/o	1	5	5	9	1	7	2	6	13	23	2
m/e	30	33	34	37	38	39	40	41	42	43	52
o/o	2	6	1	2	6	12	38	28	82	5	2
m/e	53	54	55	56	66	67	68	69	70	93	97
o/o	4	4	9	1	2	4	7	20	2	2	25
m/e	98	99									
o/o	100	4									

2,5 Dimethyl, 1-deutero-cyclotetrazenoborane

m/e	14	15	28	29	31	32	39	40	41	42
o/o	1	3	1	3	2	1	1	8	9	10
m/e	43	44	54	55	56	68	69	70	71	98
o/o	44	1	1	1	5	1	2	11	1	26
m/e	99	100								
o/o	100	3								

2,5-Diethyl-cyclotetrazenoborane

m/e	13	14	15	24	25	26	27	28	29	30
o/o	7	1	7	1	2	10	48	80	32	13
m/e	33	36	37	38	39	40	41	42	43	44
o/o	2	1	2	5	13	11	17	26	6	3
m/e	50	51	52	53	54	55	56	57	65	66
o/o	1	3	6	15	47	30	90	3	2	3
m/e	67	68	69	70	71	80	81	82	83	84
o/o	5	7	7	1	1	2	7	6	20	1
m/e	96	97	98	110	111	125	126	127		
o/o	1	4	10	3	10	25	100	7		

2-Methyl,5-Phenyl-cyclotetrazenoborane

m/e	14	15	16	17	18	25	26	27	28	29
o/o	1	6	1	2	8	1	4	10	25	3
m/e	30	31	36	37	38	39	40	41	42	43
o/o	17	7	3	12	16	34	27	15	36	7
m/e	44	45	47	48	49	50	51			
o/o	3	1	1	1	6	18	24			

m/e	52	53	54	55	56	57	58	59	60
o/o	13	5	5	4	2	4	3	1	2
m/e	61	62	63	64	65	66	67	68	69
o/o	5	7	14	13	30	26	20	2	1
m/e	70	71	72	73	74	75	76	77	78
o/o	2	5	1	2	5	9	17	24	11
m/e	79	80	81	82	83	84	85	86	87
o/o	7	5	6	2	4	2	3	1	1
m/e	88	89	90	91	92	93	94	95	97
o/o	1	3	6	17	6	22	4	1	1
m/e	98	99	100	101	102	103	104	105	106
o/o	2	1	1	4	31	100	38	10	2
m/e	113	114	115	116	117	118	119	120	121
o/o	3	6	1	3	9	1	1	4	12
m/e	122	123	127	128	129	130	131	132	133
o/o	18	5	2	3	1	7	33	48	4
m/e	154	159	160	161					
o/o	1	19	80	7					

2,5-Diphenyl-cyclotetrazenoborane

m/e	16	17	18	26	27	28	37	38	39
o/o	2	24	97	2	4	12	5	8	28
m/e	40	41	43	48	49	50	51	52	53
o/o	3	3	2	1	5	18	26	10	2

m/e	54	55	56	57	61	62	63	64	66
o/o	1	1	1	1	4	8	16	17	19
m/e	67	69	73	74	75	76	77	78	79
o/o	2	1	2	7	16	24	50	6	1
m/e	81	83	84	85	86	87	88	89	90
o/o	1	1	2	6	1	2	3	4	5
m/e	91	92	93	94	96	97	99	100	101
o/o	22	3	18	1	2	8	1	3	11
m/e	102	103	104	105	111	112	113	114	115
o/o	24	41	18	1	1	1	3	4	5
m/e	116	117	118	119	125	126	127	128	129
o/o	4	4	3	1	6	2	7	23	8
m/e	137	138	139	140	141	142	150	151	152
o/o	1	2	3	5	6	3	1	1	3
m/e	153	154	155	163	164	165	166	167	168
o/o	3	3	1	2	4	18	27	16	12
m/e	169	176	177	178	179	190	191	192	193
o/o	1	1	5	3	3	2	10	24	44
m/e	194	195	196	221	222	223			
o/o	100	29	2	15	60	8			

Series 2

1,2,5-trimethyl-cyclotetrazenoborane

m/e	11	13	15	17	18	24	25	26	27
o/o	1	1	2	2	10	1	3	6	11

m/e	28	29	30	37	38	39	40	41	42	43
o/o	4	2	4	1	2	4	16	15	13	2
m/e	44	51	52	53	54	55	56	57	66	67
o/o	1	1	1	4	18	11	36	1	1	2
m/e	68	69	70	82	83	84	111	112	113	
o/o	3	14	1	4	21	2	22	100	3	

2,5-dimethyl,1-ethyl-cyclotetrazenoborane

m/e	28	29	30	31	32	39	40	41	43	44
o/o	63	2	1	7	8	2	3	5	3	53
m/e	45	46	53	54	55	56	57	66	67	68
o/o	4	3	1	3	4	9	5	1	3	5
m/e	69	70	71	81	82	83	84	86	95	96
o/o	5	4	2	1	4	17	2	1	1	1
m/e	97	98	99	111	112	125	126	127		
o/o	4	2	1	1	3	25	100	7		

2,5-dimethyl,1-vinyl-cyclotetrazenoborane

m/e	26	27	28	29	30	32	35	36	37	38
o/o	14	14	24	1	3	2	1	3	9	4
m/e	39	40	41	42	43	47	50	51	52	53
o/o	9	19	7	35	4	1	1	2	4	8
m/e	54	55	56	57	58	59	62	64	65	66
o/o	10	13	1	7	1	2	2	2	5	11
m/e	67	68	69	70	71	79	80	81	82	83
o/o	6	10	3	1	1	1	2	4	1	1
m/e	94	95	96	123	124	125				
o/o	2	4	1	24	100	5				

1,2,5-triethylcyclotetrazenoborane

m/e	13	15	18	26	27	28	29	30	32	36
o/o	1	1	3	2	9	10	11	3	1	1
m/e	37	38	39	40	41	42	43	44	51	52
o/o	3	2	11	21	6	7	2	3	1	3
m/e	53	54	55	56	57	58	65	66	67	68
o/o	12	42	10	27	1	2	1	3	7	21
m/e	69	70	71	78	79	80	81	82	83	84
o/o	9	9	1	1	1	2	9	30	16	34
m/e	85	91	92	93	94	95	96	97	98	108
o/o	2	1	1	1	1	2	3	7	1	1
m/e	109	110	111	112	125	126	137	138	139	140
o/o	2	7	27	2	3	6	7	3	14	5
m/e	153	154	155							
o/o	23	100	7							

2,5-Diphenyl,1-methyl-cyclotetrazenoborane

m/e	17	18	26	27	28	37	38	39	40	41
o/o	2	8	2	3	7	22	3	12	2	2
m/e	43	44	49	50	51	52	53	55	57	61
o/o	1	1	1	3	9	8	1	1	1	2
m/e	62	63	64	65	66	69	74	75	76	77
o/o	2	4	6	6	1	1	2	4	5	6
m/e	78	79	87	88	89	91	92	93		
o/o	11	1	2	3	5	3	1	1		

m/e	100	101	102	103	104	105	106	113	114	115
o/o	1	5	11	4	17	24	1	2	2	3
m/e	116	117	118	127	128	129	130	131	139	140
o/o	18	48	3	2	4	1	2	2	1	1
m/e	141	164	165	166	167	178	179	180	181	182
o/o	1	1	3	5	3	2	2	3	2	1
m/e	190	191	192	193	194	205	206	207	208	209
o/o	1	2	6	19	3	2	9	47	100	15
m/e	210	235	236	237	238					
o/o	1	19	85	12	1					

1,2,5-triphenyl-cyclotetrazenoborane

m/e	24	26	27	28	29	31	32	36	37	38
o/o	1	3	5	52	2	1	4	1	2	3
m/e	39	40	41	42	43	44	49	50	51	52
o/o	11	1	7	2	9	8	1	4	10	4
m/e	53	54	55	56	57	58	60	61	62	63
o/o	1	1	7	3	11	1	1	5	4	5
m/e	64	65	66	67	68	69	70	71	73	74
o/o	5	9	2	3	1	5	4	6	1	4
m/e	75	76	77	78	79	80	81	82	83	84
o/o	5	5	18	19	2	1	4	2	4	1
m/e	85	86	87	88	89	90	91	92	93	94
o/o	4	2	6	4	6	1	4	1	3	1
m/e	95	96	97	98	99	100	101	102		
o/o	4	2	3	1	2	3	6	8		

m/e	103	104	105	107	108	109	110	111	112	113
o/o	2	3	1	1	1	3	1	3	2	7
m/e	114	115	116	117	119	120	121	122	123	124
o/o	11	4	1	1	1	1	2	1	2	1
m/e	125	126	127	128	129	133	134	135	136	137
o/o	3	5	4	5	1	1	6	7	1	2
m/e	138	139	140	141	142	149	150	151	152	153
o/o	1	3	3	2	8	2	3	4	3	1
m/e	154	162	163	164	165	166	167	168	169	175
o/o	1	1	2	3	7	11	8	1	1	1
m/e	176	177	178	179	180	181	185	186	190	191
o/o	2	2	12	50	5	1	2	1	1	3
m/e	192	193	194	203	204	205	216	217	240	241
o/o	2	3	1	1	2	1	1	1	1	1
m/e	242	252	255	266	267	268	269	270	271	272
o/o	2	1	1	2	6	28	67	100	20	2
m/e	297	298	299	300						
o/o	8	50	8	1						

Series 3

2,5-dimethyl,1-chloro-cyclotetrazenoborane

m/e	13	14	15	26	27	28	29	30	31	33
o/o	4	2	11	1	4	13	4	8	2	1
m/e	35	36	37	38	39	40	41	42	43	44
o/o	5	38	4	16	10	25	2	7	34	1
m/e	45	46	47	48	49	50	51	52	53	57
o/o	3	12	16	4	5	7	4	1	1	3
m/e	58	59	60							
o/o	2	5	7							

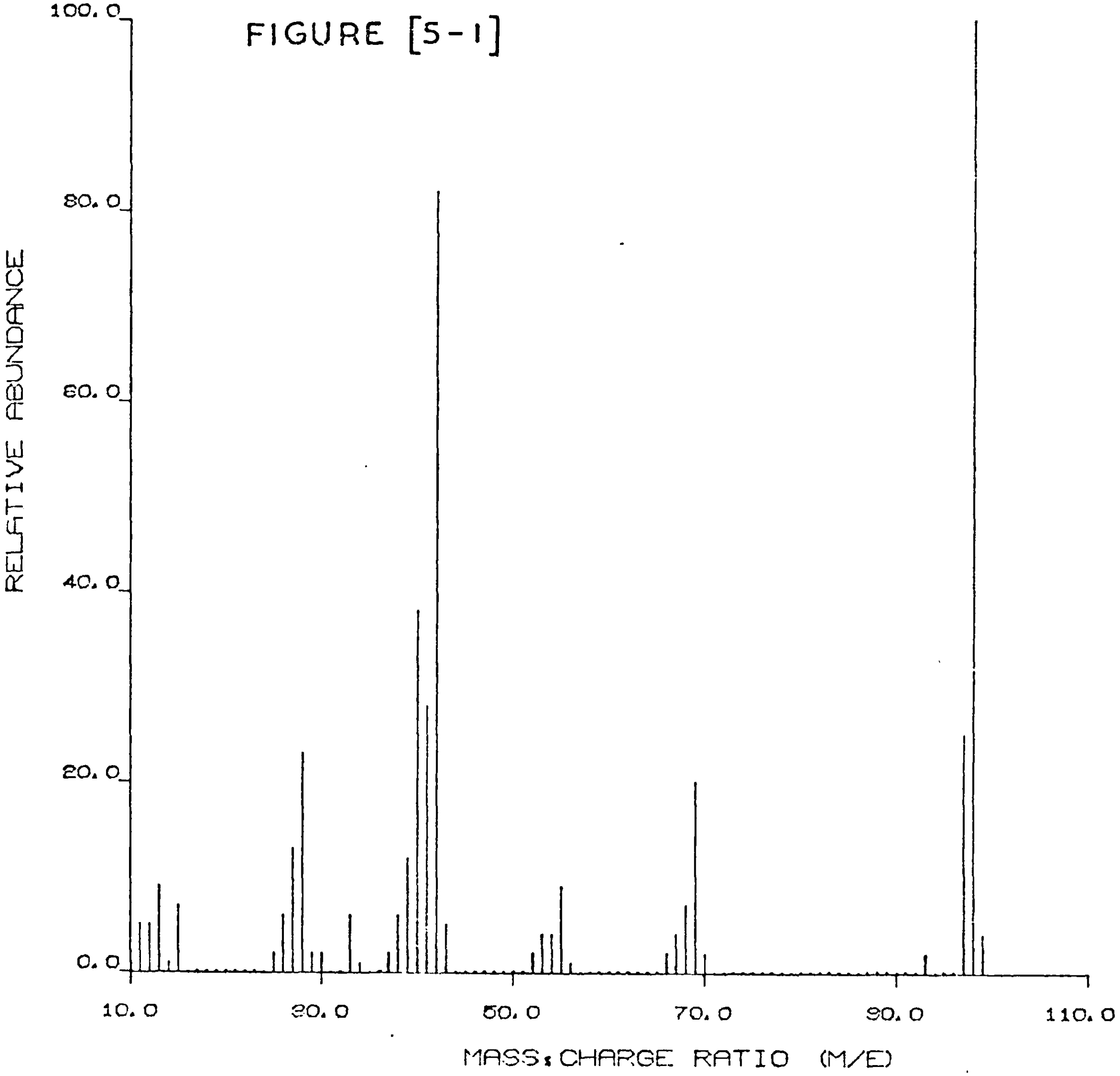
m/e	61	62	63	64	66	67	68	71	72	73
o/o	18	10	7	3	2	5	1	1	5	18
m/e	74	75	76	77	78	87	88	89	90	91
o/o	42	22	42	7	9	1	5	20	2	6
m/e	101	102	103	104	105	106	131	132	133	134
o/o	3	4	9	5	2	1	25	100	12	31
m/e	135									
o/o	1									

2,5-dimethyl,1-bromo-cyclotetrazenoborane

m/e	13	14	15	16	17	18	24	25	26	27
o/o	2	9	23	1	1	5	2	3	5	13
m/e	28	29	30	32	33	35	36	37	38	39
o/o	83	5	10	8	3	4	31	8	23	30
m/e	40	41	42	43	46	47	51	52	53	54
o/o	88	9	48	65	1	1	1	3	5	7
m/e	56	57	58	59	60	61	62	63	64	65
o/o	1	33	2	2	1	2	1	2	2	1
m/e	66	67	68	69	70	72	73	74	75	76
o/o	8	23	20	64	4	8	8	3	1	3
m/e	77	78	79	80	81	82	83	88	89	90
o/o	1	1	7	14	7	13	3	1	5	15
m/e	91	92	93	94	95	96	103	104	105	106
o/o	18	15	16	4	1	4	2	8	22	15
m/e	107	108	114	115	116	117	118	119	120	121
o/o	19	7	1	1	3	8	28	23	54	5
m/e	122	131	132	133	134	135	145	146	147	148
o/o	21	2	10	16	6	14	1	2	5	3
m/e	150	175	176	177	178	179				
o/o	1	28	100	31	100	4				

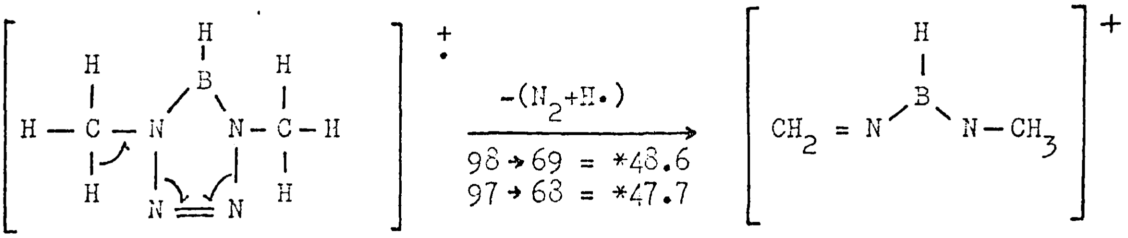
2, 5-DIMETHYLCYCLOTETRAZENOBORANE

FIGURE [5-1]



SERIES 1

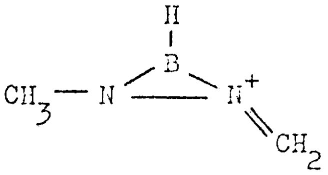
The fragmentation of 2,5-dimethylcyclotetrazenoborane has been summarised in the spectrum shown in Figure [5-1]. Peaks due to the relative isotopic abundances of the parent ion $[Me_2N_4BH]^{+\cdot}$ 5-I were observed at m/e 97, 98, 99 in the ratios $(M + 1)/M = 4.140$, $(M + 2)/M = 0.156$ (calculated 4.000, 0.160) and the peak at 98 was the base peak of the spectrum. Earlier work[42] suggested that the initial ionisation was by loss of an electron from the lone pair of one of the azo-nitrogen atoms. The first major fragmentation occurred by loss of $(N_2 + H\cdot)$ to give peaks at m/e 68, 69, 70, which could possibly be interpreted as the ion $[CH_2 = N\text{-}BH\text{-}NCH_3]^+$ 5-IIA by the fragmentation and rearrangement scheme:-



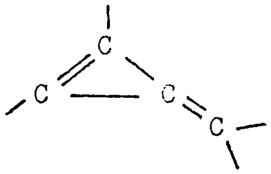
5-I m/e 97, 98

5-IIA m/e 68, 69

In view of the recent interest in possible small ring aromatic boron systems[102] an attractive alternative would be the cyclic structure 5-IIB which is formally isoelectronic with the triafulvene system 5-III.

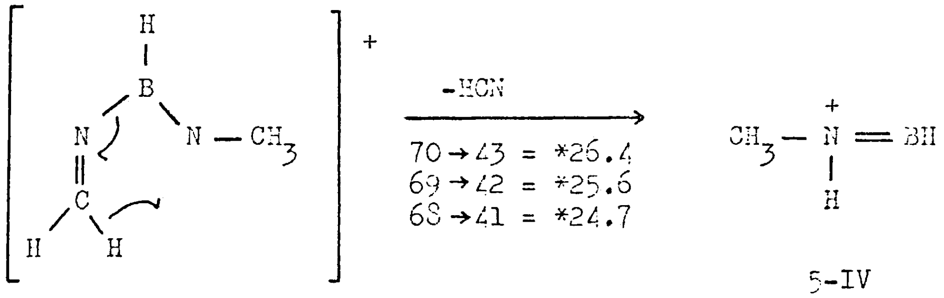


5-IIB



5-III

There was a small peak at m/e 83 presumably corresponding to loss of CH_3. from 5-I and the peak at m/e 55 probably occurred either by loss of (N_2 + CH_3.) from 5-I or by loss of CH_2 from 5-II. The next major fragmentation occurred through loss of HCN from 5-II accompanied by hydrogen transfer giving rise to the prominent peak at m/e 42, of probable structure 5-IV.



5-II

5-IV
m/e 41, <u>42</u>, 43

An alternative but minor fragmentation of 5-II occurred through loss of successive hydrogen atoms to give peaks at m/e 66, 67, 68, 69 and the observed metastable transitions were 70→69 = *68.0; 69→68 = *67.0; 68→67 = *66.0; 67→66 = *65.0. Ion 5-IV also readily lost hydrogen atoms:-

$$5\text{-IV} \xrightarrow{-H\cdot} CH_3\text{-}\overset{\bullet}{N}^{+}{=}\,BH \xrightarrow{-H\cdot} CH_2 = \overset{+}{N} = BH$$

43→42 = *41.0

42→41 = *40.1

41→40 = *39.1

5-V m/e 40, 41, 42

42→41 = *40.1

41→40 = *39.1

40→39 = *38.1

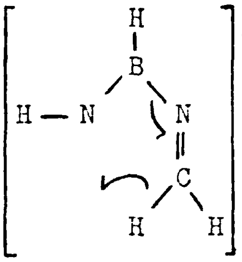
5-VI m/e 39, 40, 41

$$5\text{-IV} \xrightarrow{-2H\cdot} 5\text{-VI}$$

42→40 = *38.1

41→39 = *37.1

The source of the peak at m/e 55 was not established by an observed metastable transition, although it probably arose by loss of (N_2 + CH_3.) from 5-I and had a possible structure $[HN\text{-}BH\text{-}N{=}CH_2]^+$ 5-VII. This then broke down further with loss of HCN viz:



$$\xrightarrow{-HCN} \quad H_2\overset{+}{N} = BH$$

55→28 = *14.3

54→27 = *13.5

5-VII m/e 54, 55

5-VIII m/e 27, 28

The fragmentation pattern outlined above satisfactorily accounted for all the major peaks in the spectrum of dimethylcyclotetrazenoborane.

The mass spectrum of 2,5-dimethyl,1-deuterocyclotetrazenoborane corrected for a small amount of Me_2N_4BH impurity is shown in Figure [5-2]. The molecular ion peaks occurred at m/e 98, 99, and 100

2, 5-DIMETHYL, 1-DEUTEROCYCLOTETRAZENOBORANE

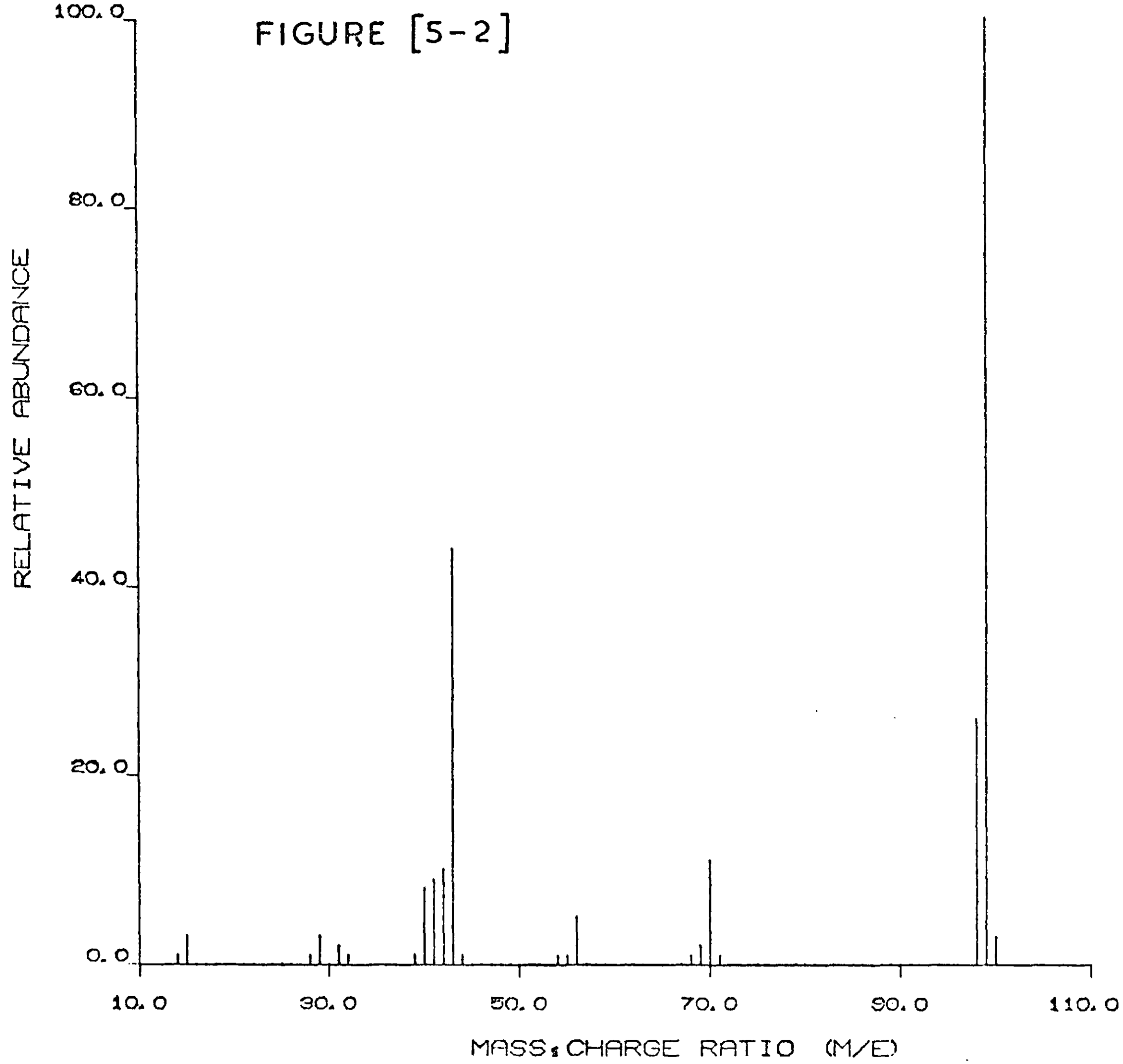
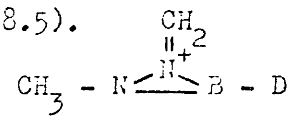


FIGURE [5-2]

in the expected isotopic ratios and the peak at m/e 99 was the base peak in the spectrum.

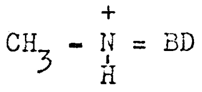
The first major fragmentation was by loss of (N_2 + H•) to produce peaks at m/e 69, <u>70</u> and 71 (species 5-IXA or 5-IXB), (99→70 = *49.5; 98→69 = *48.5).

$[CH_2 = N - BD - NCH_3]^+$ or  $CH_3 - N\overset{\overset{CH_2}{\|}\;\overset{+}{N}}{<\!=\!=\!>}B - D$

5-IXA　　　　　　　　5-IXB

In agreement with the fragmentation pattern of Me_2N_4BH loss of N_2 only did not occur. Since the species m/e <u>70</u> was produced and not <u>69</u> this was confirmatory evidence of the earlier statement that the H• loss was from the side chain and not loss of deuterium from the boron. All major breakdowns in Me_2N_4BD produced peaks at one mass unit higher than in Me_2N_4BH showing that the D was retained throughout the subsequent fragmentation.

Loss of HCN with H transfer occurred from species 5-IX to produce the prominent peak at m/e 43 5-X of possible structure:-

 $CH_3 - \underset{H}{\overset{+}{N}} = BD$

70→43, * = 26.4

69→42, * = 25.6

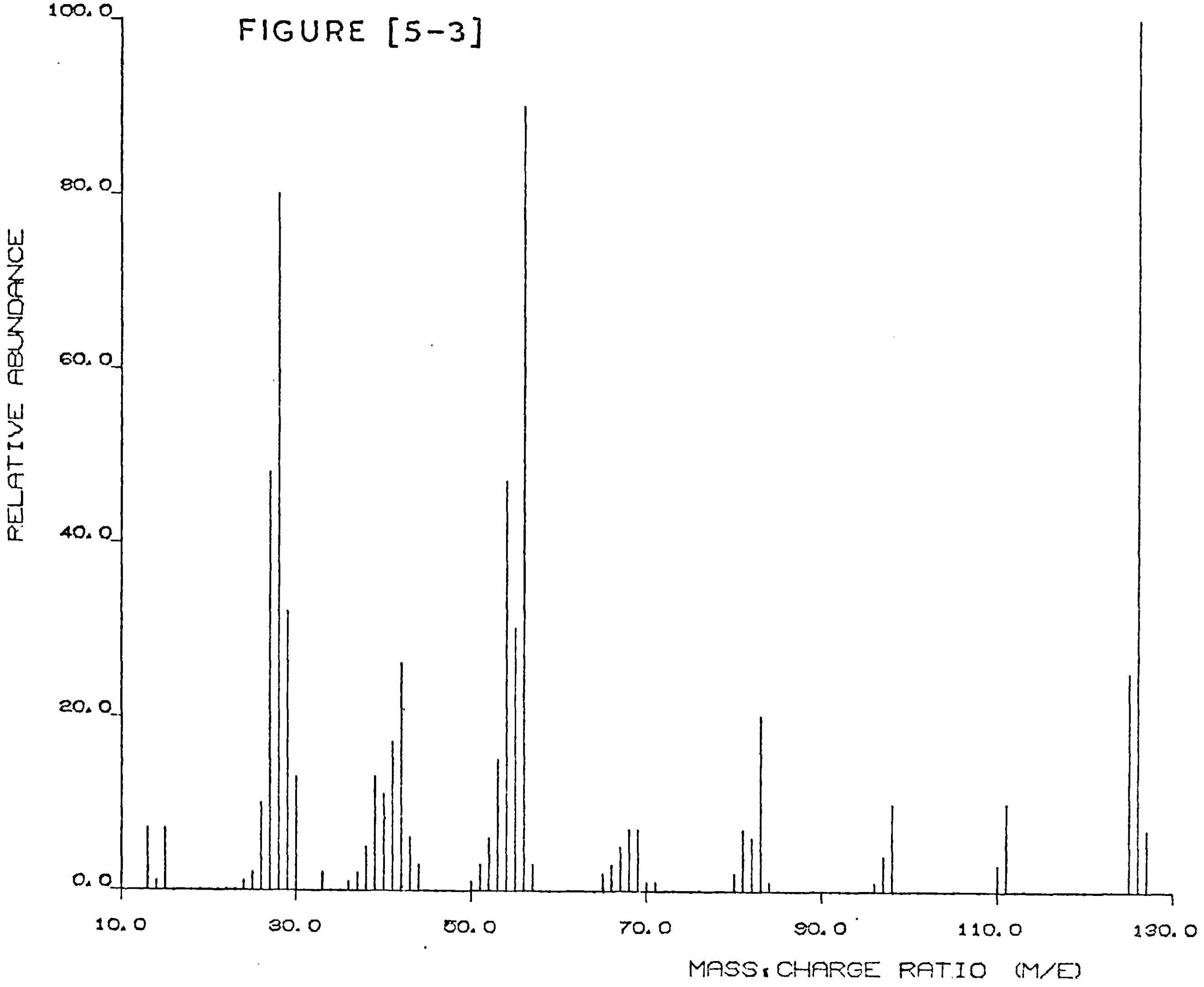
5-X

m/e 42, <u>43</u>, 44

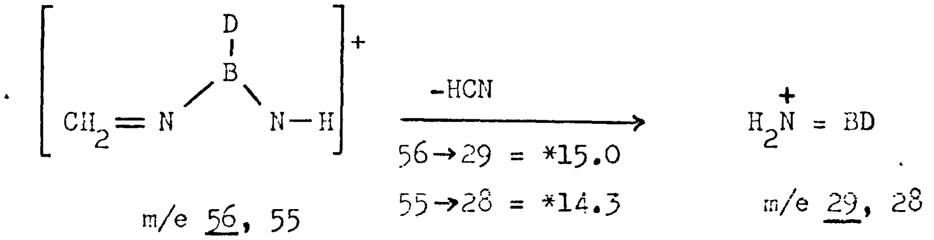
As in Me_2N_4BH there was a loss of (N_2 + CH_3•) to produce peaks at m/e 55, <u>56</u> and again no metastable peaks were observed for this transition. Loss of HCN from the peak at 56 was proved by metastable

2, 5-DIETHYLCYCLOTETRAZENOBORANE

FIGURE [5-3]



transitions viz:

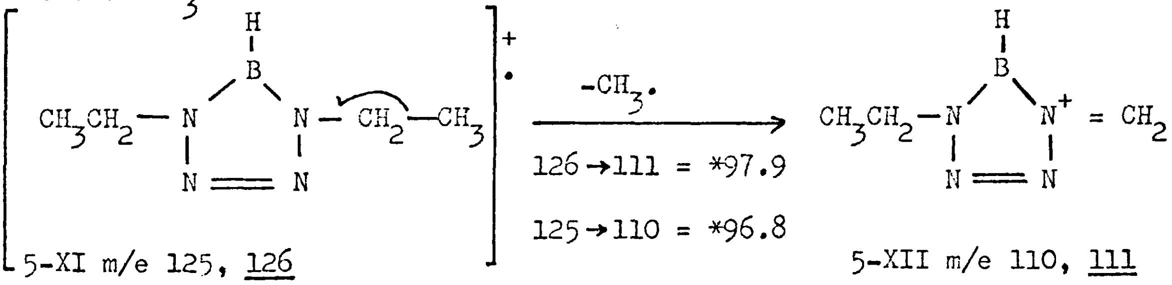


The spectrum and principal fragmentations of 2,5-diethylcyclotetrazenoborane are shown in Figure [5-3]. Strong peaks due to the parent ion $[Et_2N_4BH]^{+\cdot}$ (5-XI) were observed at m/e 125, 126 and 127 and the isotopic ratios of these were (M + 1)/M = 4.162, (M + 2)/M = 0.249 (calculated 4.061 and 0.286). The peak at m/e 126 was also the base peak of the spectrum. The fragmentation of Et_2N_4BH was more complex than that of Me_2N_4BH, and a study of the metastable transitions enabled most of the peaks in the spectrum to be assigned.

Fragmentation of the parent ion $[Et_2N_4BH]^{+\cdot}$

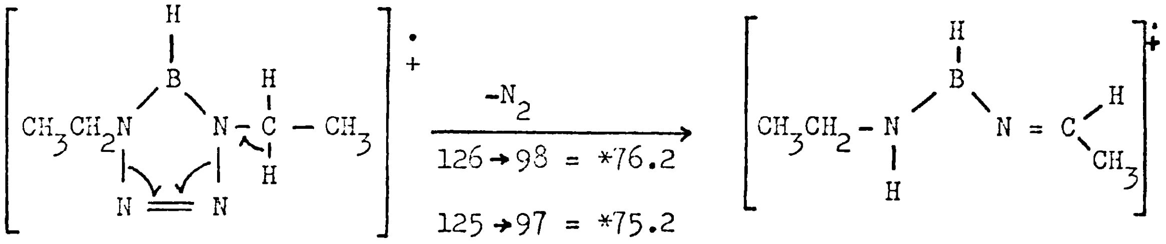
The fragmentation of the parent ion was significantly different from that of Me_2N_4BH, since several routes now occurred.

(i) Loss of CH_3.



The isotopic ratios for 5-XII were (M + 1)/M = 4.05 and (M + 2)/M = 0.215 (calculated 4.43 and 0.214).

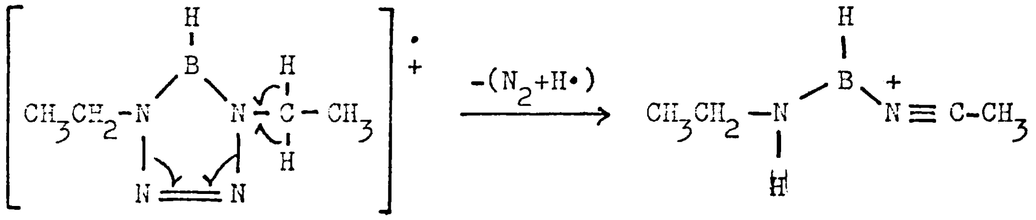
(ii) Loss of N_2, and hydrogen atom transfer.



5-XI

5-XIII m/e 97, 98

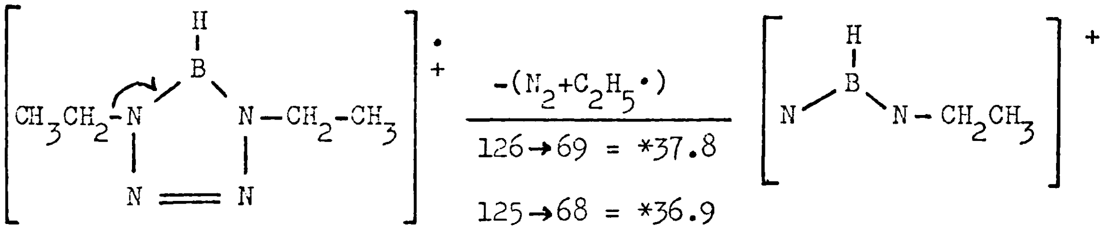
(iii) Loss of (N_2 + H•) and hydrogen atom transfer



5-XI

5-XIV m/e 96, 97

(iv) Loss of (N_2 + C_2H_5•)



5-XI

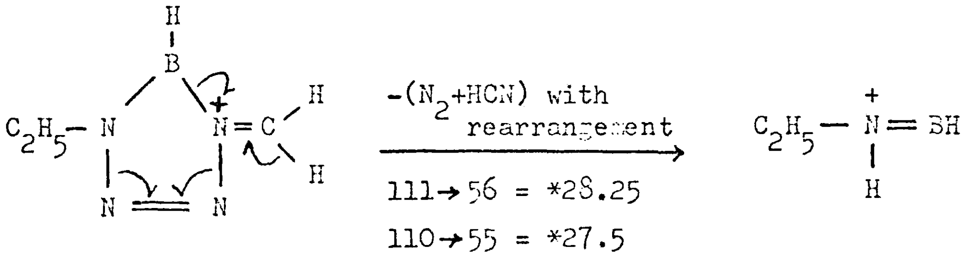
5-XV m/e 68, 69

It was apparent from the intensities of the peaks in the range m/e 96 - 99 that route (ii) was the major fragmentation process. However it was difficult to interpret the intensity ratios solely on the basis of route (ii) and route (iii) was proposed in order to account for the observed peak intensities without the supporting evidence of metastable transitions.

The further breakdown of the species formed by routes (i) to (iv) became involved, but the large number of metastable transitions observed greatly assisted the interpretation of the fragmentation, and most of the peaks at lower masses could be assigned.

Fragmentation of primary daughter ions

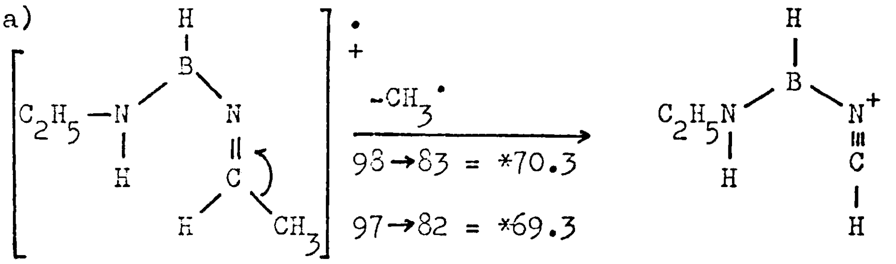
(v) Species 5-XII lost 55 mass units and was probably best interpreted as loss of (N_2 + HCN) with H rearranged to give the species $C_2H_5\overset{+}{N}H = BH$ 5-XVI which was analogous to the species 5-IV and 5-X formed in the fragmentation of Me_2N_4BH and Me_2N_4BD.



5-XII m/e 110, 111 5-XVI m/e 55, 56

(vi) A minor fragmentation of species 5-XIII, produced by route (i), probably involved the loss of ($C_2H_5\cdot$) to contribute to the peaks at 68, 69 and 70, although this was not confirmed by the appearance of metastable ions. However, the major fragmentation occurred through loss of $CH_3^{\bullet}$, and was confirmed by appropriate metastable transitions but was further complicated by the possibility of two routes:-

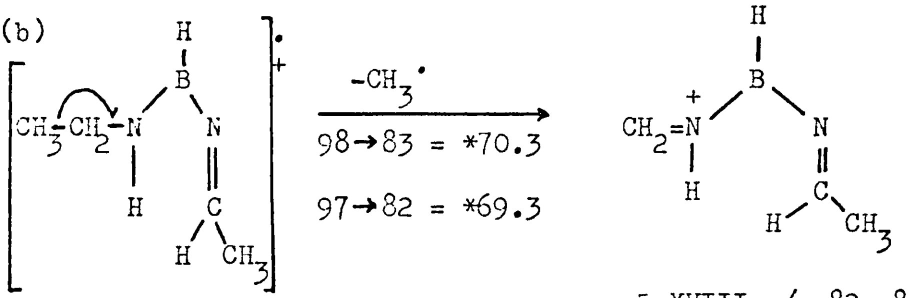
(a)



5-XIII m/e 97, 98

5-XVII m/e 82, 83

(b)



5-XIII

5-XVIII m/e 82, 83

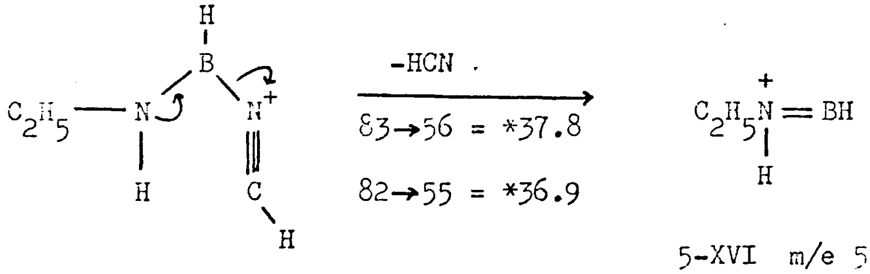
It was necessary to postulate both routes for the fragmentation of 5-XIII since metastable ions indicated that ions of mass 82 and 83 yielded daughter ions at both 55, 56 and 41, 42.

(vii) Since species 5-XIV was, at the most, only a minor constituent of the peak at m/e 97, its subsequent fragmentation was not observed.

(viii) The further fragmentation of species 5-XV probably occurred through loss of ($C_2H_5\cdot$) since metastable peaks were observed corresponding to the transitions 69→40 = *23.2 and 68→39 = *22.4.

Fragmentation of secondary daughter ions

(ix) Species 5-XVII lost HCN to give species 5-XVI identical to that produced from route (v).



5-XVI m/e 55, 56

5-XVII m/e 82, 83

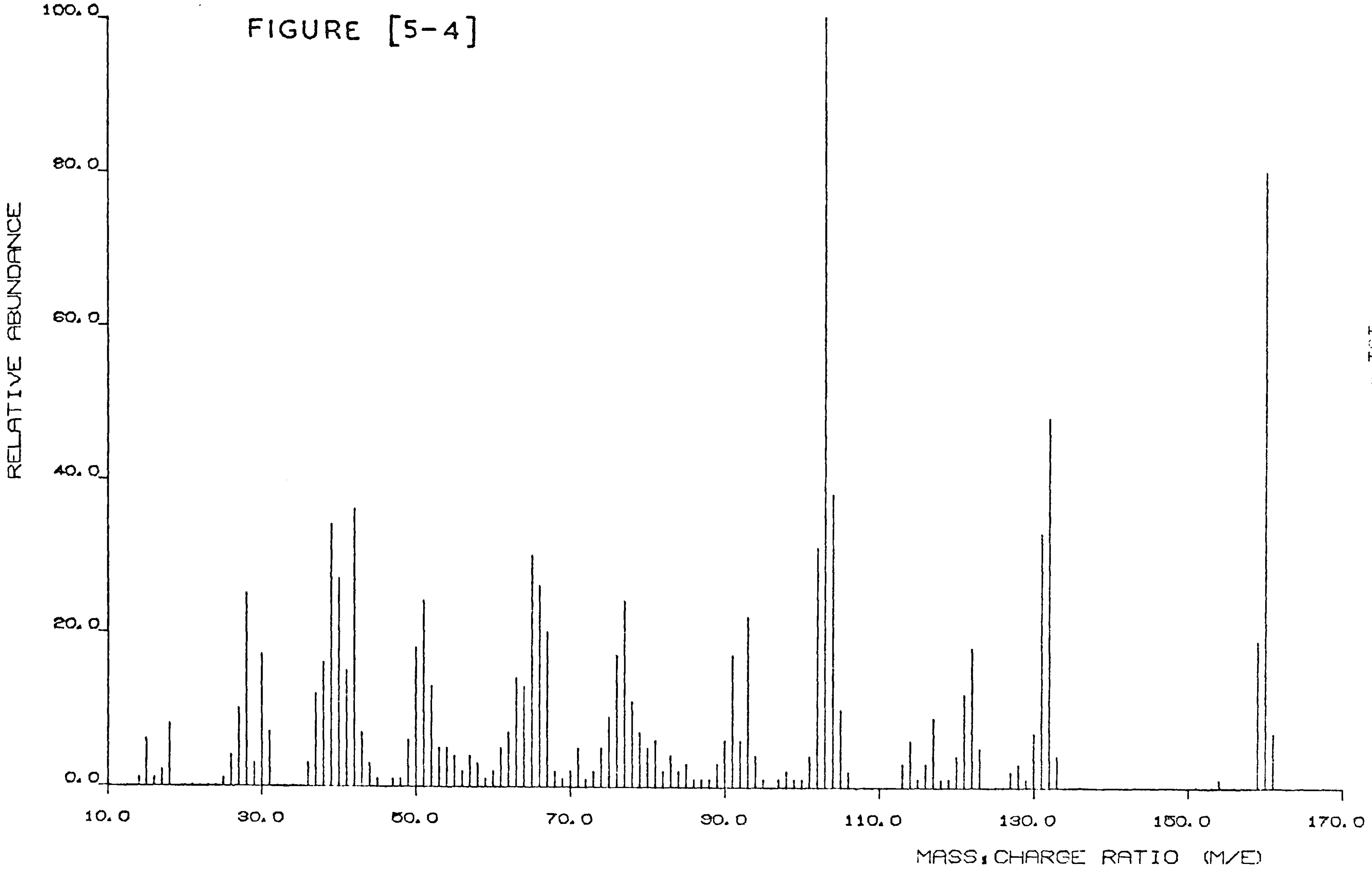
(x) The peaks at m/e 41, 42 of possible structure $CH_2 = \overset{+}{N}H - BH_2$ 5-XIX could occur from both species 5-XVI by loss of CH_2 (56→42 = *31.5, 55→41 = *30.6) and from species 5-XVIII by loss of CH_3CN (83→42 = *21.3, 82→41 = *20.5).

Further fragmentation Further fragmentation occurred from species 5-XVI and 5-XIX through hydrogen loss. Several other transitions were observed leading to peaks in the range m/e 24→29, e.g. 52→25 = *12.0 and 51→24 = *11.3.

The breakdown pattern of 2-methyl-5-phenylcyclotetrazenoborane has been summarised in figure [5-4].

2-METHYL, 5-PHENYLCYCLOTETRAZENOBORANE

FIGURE [5-4]



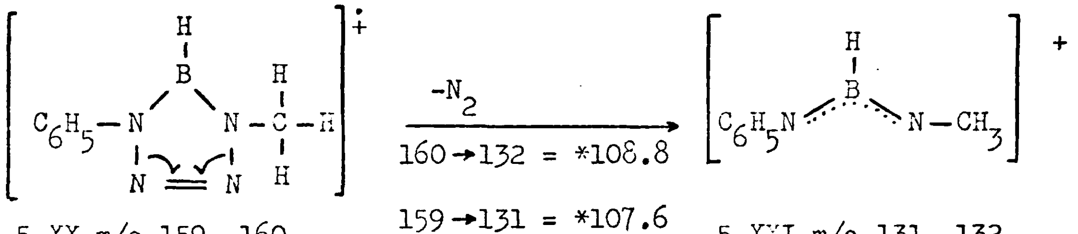
The introduction of a phenyl substituent on the ring necessarily made a complete assignment more difficult since much of the fragmentation was associated with breakdown of the phenyl group. However, the essential details of the fragmentation were obtained, and the major peaks were assigned.

The isotopic contributions to the parent ion $[Me(Ph)N_4BH]^{+\cdot}$, 5-XX, gave rise to peaks at m/e 159, <u>160</u>, 161 in the ratios $(M+1)/M = 4.194$, $(M+2)/M = 0.382$ (calculated 4.211 and 0.368), and although these were still very intense, the base peak of the spectrum occurred at m/e 103. Other major peaks occurred at m/e 132, 122, 93 and 77.

<u>Fragmentation of the parent ion $[Me(Ph)N_4BH]^{+\cdot}$</u>

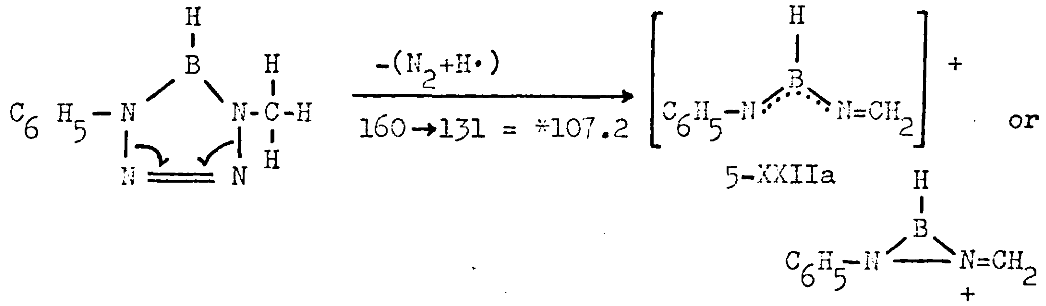
As in Et_2N_4BH, both loss of N_2 and $(N_2 + H\cdot)$ could occur since the peaks at m/e 131 and 132 were of comparable abundance.

(i) Loss of N_2



5-XX m/e 159, <u>160</u>   5-XXI m/e <u>131</u>, 132

(ii) Loss of $(N_2 + H\cdot)$



5-XXIIb

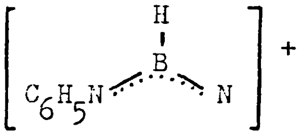
Species 5-XXII subsequently lost HCN with accompanying H transfer to produce $[C_6H_5NHBH]^+$ 5-XXIV (131→104 = *82.6, 130→103 = *81.6). Structure 5-XXIV was analogous to structures 5-IV, 5-X and 5-XVI in the previously considered cyclotetrazenoboranes.

Fragmentation of primary daughter ions

The fragmentation of daughter species was not simple although mass losses could be identified from the appearance of metastable ions. For instance, the loss of 15 mass units from 5-XXI was probably best interpreted in terms of the fragmentation route (iii).

(iii)

$$\text{5-XXI} \xrightarrow[\substack{132\rightarrow117\ =\ *103.7 \\ 131\rightarrow116\ =\ *102.7}]{-CH_3\cdot}$$



5-XXIII m/e 116, 117

Alternative fragmentation occurred with loss of 29 mass units and could be interpreted in terms of loss of $CH_3N\cdot$ from 5-XXI to produce $[C_6H_5N = BH]^{+\cdot}$, (132→103 = *80.4, 131→102 = *79.4).

A further mode of fragmentation of species 5-XXI involved the loss of 41 mass units, which could occur in several ways such as loss of $CH_3NBH\cdot$, CH_3CN or $C_3H_5\cdot$ from partial fragmentation of the phenyl ring. There was a metastable ion corresponding to 132→91 = *62.8 but no metastable ion for the transition 131→90 which should arise if ^{10}B was retained in the charged fragment. Loss of $CH_3NBH\cdot$ was therefore the most probable route to produce the species $C_6H_5N^{+\cdot}$ of m/e 91 (132→91 = *62.8).

The peaks in the ranges m/e 74 - 78 and 63 - 67 together with a number of metastable ions resulted from the further fragmentation of 5-XXI and 5-XXII and were probably due to breakdown of the phenyl ring.

Fragmentation of the secondary daughter ions

Species 5-XXIII underwent several fragmentations which were probably best interpreted in terms of rupture of the phenyl ring since losses of 26, 27, 52 and 53 mass units occurred, e.g. 117→91 = *70.8, 117→90 = *69.2, 117→65 = *36.1, 117→64 = *35.0.

The peak at m/e 93 was probably due to $C_6H_5NH_2^{+\cdot}$ produced by thermal decomposition in the heated inlet system. This was confirmed in the mass spectrum of diphenylcyclotetrazenoborane by mass measurement.

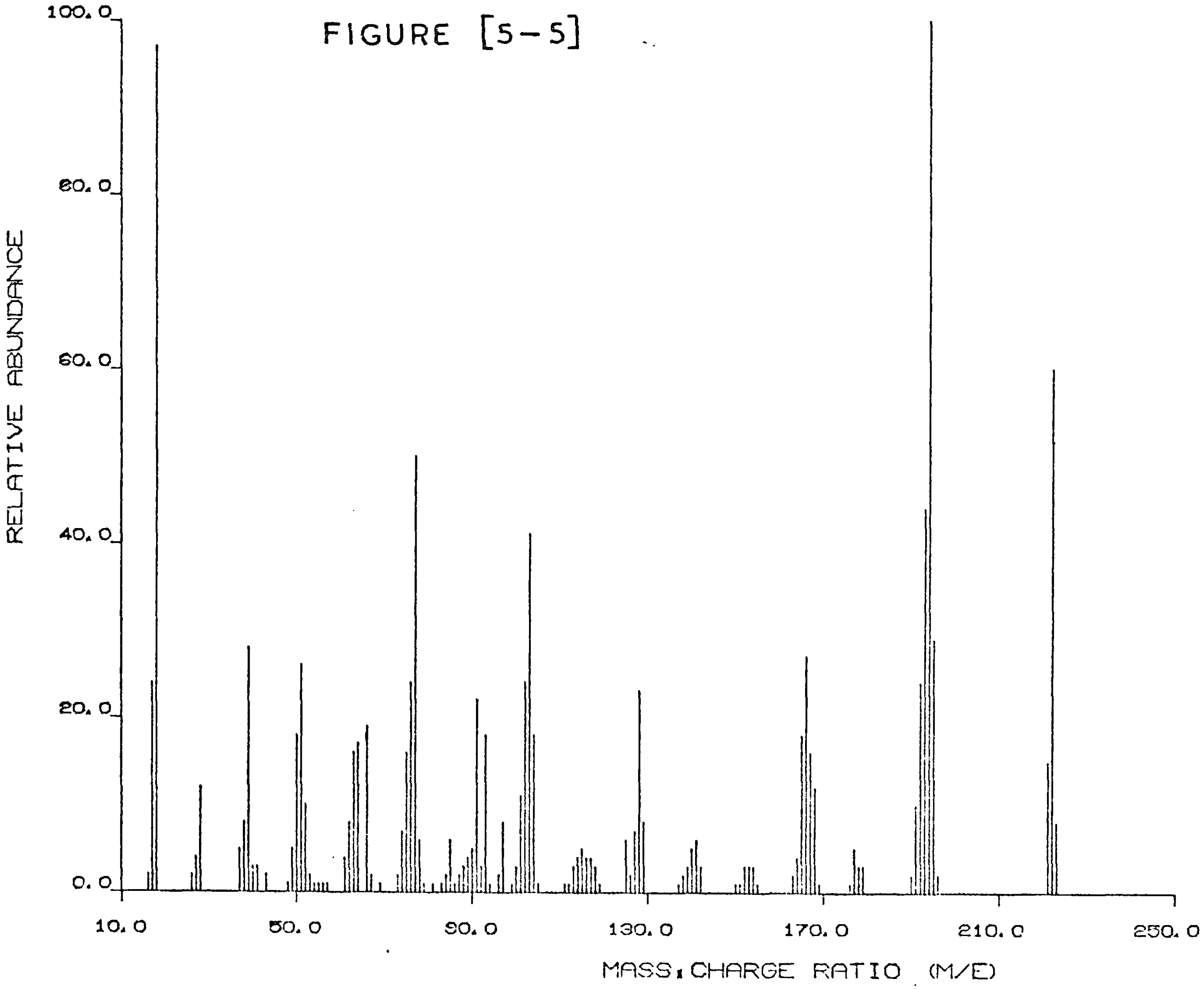
The spectrum below m/e 77 was presumably mainly due to fragmentation of this species and breakdown of the phenyl ring from the parent compound.

The fragmentation of 2,5-diphenylcyclotetrazenoborane is shown in Figure [5-5]. The spectrum was much more complex than the simpler derivatives and it was therefore difficult to assign much of the fragmentation unambiguously.

Parent ion peaks of moderate intensity were observed at m/e 221, 222 and 223 with the isotopic ratios (M+1)/M = 4.249 and (M+2)/M = 0.614, (calculated 4.010 and 0.533).

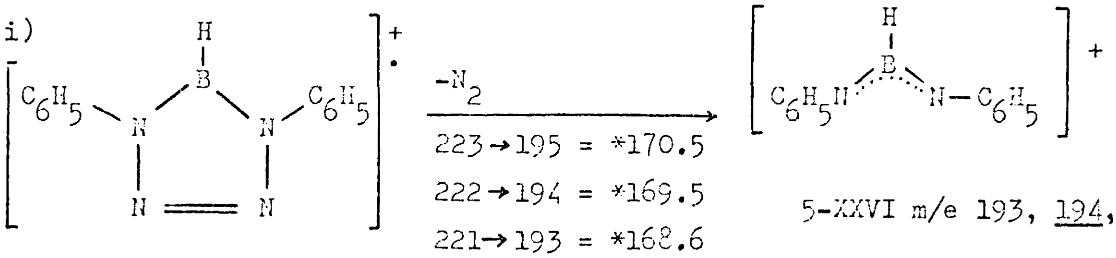
2, 5-DIPHENYLCYCLOTETRAZENOBORANE

FIGURE [5-5]



Fragmentation of the molecular ion occurred through loss of N_2 although the relative intensities of the peaks at m/e 193, 194 suggested that some loss of (N_2 + H•) still occurred.

(i)



$-N_2$

223→195 = *170.5

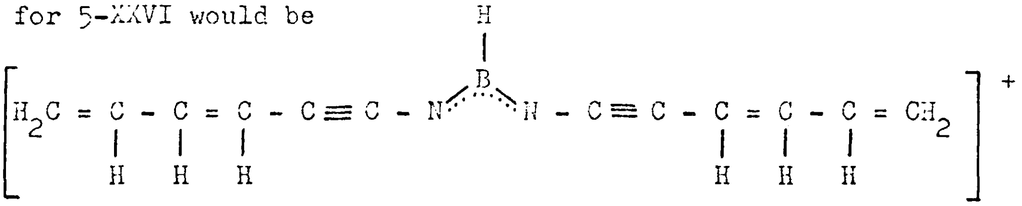
222→194 = *169.5

221→193 = *168.6

5-XXV m/e 221, 222, 223

5-XXVI m/e 193, 194, 195

Species 5-XXVI would appear to have considerable stability since the peak at m/e 194 was the base peak of the spectrum. It has been suggested[103] that the benzene ring opens upon electron impact. If this were to happen in this system, a possible structure for 5-XXVI would be



in which extensive delocalisation of the charge could occur.

Subsequent fragmentation of 5-XXVI occurred predominantly by cleavage of successive carbon atoms from the phenyl substituents and hydrogen loss, producing groups of peaks around m/e 177, 166, 154, 141, 128 and 117. Many of these cleavages were supported by metastable transitions, Table 5-B.

TABLE 5-B

METASTABLE ION PEAKS FROM SPECIES 5-XXVI

*

$194 \xrightarrow{-27} 167 = 143.76$

$193 \xrightarrow{-27} 166 = 142.78$

$194 \xrightarrow{-17} 177 = 161.49$

$193 \xrightarrow{-17} 176 = 160.50$

$194 \xrightarrow{-40} 154 = 122.25$

$194 \xrightarrow{-54} 140 = 101.0$

$194 \xrightarrow{-66} 128 = 84.5$

$194 \xrightarrow{-79} 115 = 68.2$

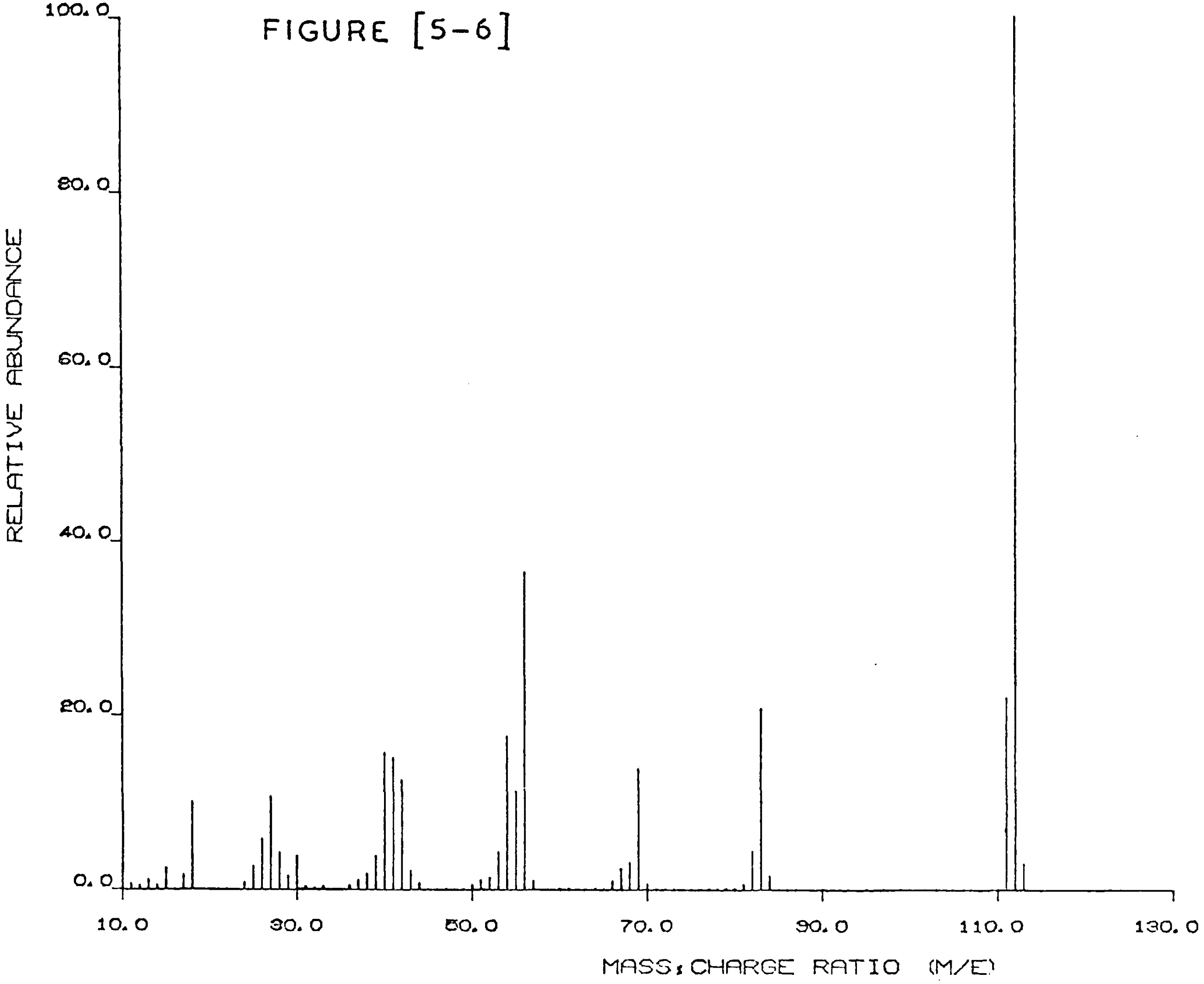
$193 \xrightarrow{-79} 114 = 67.3$

Other fragmentation of 5-XXVI possibly occurred through loss of C_6H_5. to give peaks at m/e 116, <u>117</u> due to $[C_6H_5NBHN]^{+\cdot}$ or loss of $[C_6H_5N^\bullet]$ to give peaks at m/e 102, <u>103</u>, due to $[C_6H_5NBH]^{+\cdot}$, although neither was confirmed with metastable transitions. Alternatively, decomposition of 5-XXVI could occur so as to eliminate $[C_6H_5NBH]$ and produce a daughter ion of m/e 91 of structure $[C_6H_5N]^{+\cdot}$ (194→91 = *42.7, 193→91 = *42.9). Only one metastable was observed as might be expected if the boron atom were eliminated in the neutral fragment.

The large peak at m/e 77 was presumably due to $[C_6H_5]^+$ which could be produced by many routes. Peaks at lower mass numbers were mainly due to breakdown of the phenyl ring with contributions

1, 2, 5-TRIMETHYLCYCLOTETRAZENOBORANE

FIGURE [5-6]

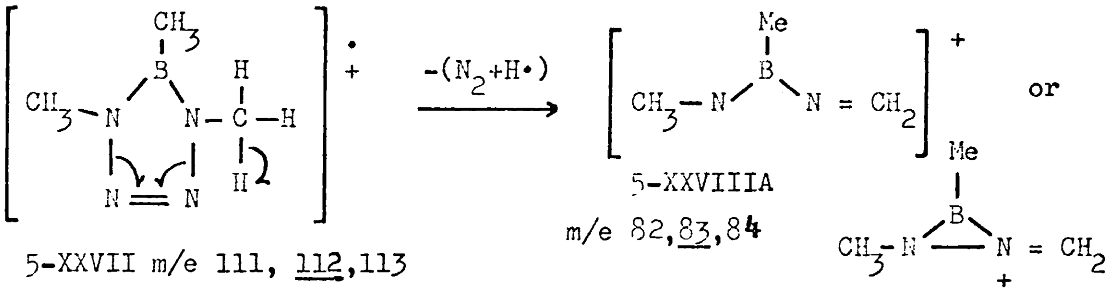


from small fragments containing B and N.

Series 2

The fragmentation of 1,2,5-trimethylcyclotetrazenoborane has been summarised in the spectrum shown in figure [5-6]. The base peak was the ^{11}B parent ion at m/e 112 5-XXVII and the peaks at m/e 111 and 113 were in the correct ratio.

One of the most significant features was that a large peak (20%) due to loss of (N_2 + H•) and zero loss of N_2 was observed probably yielding the ion 5-XXVIIIA or 5-XXVIIIB .



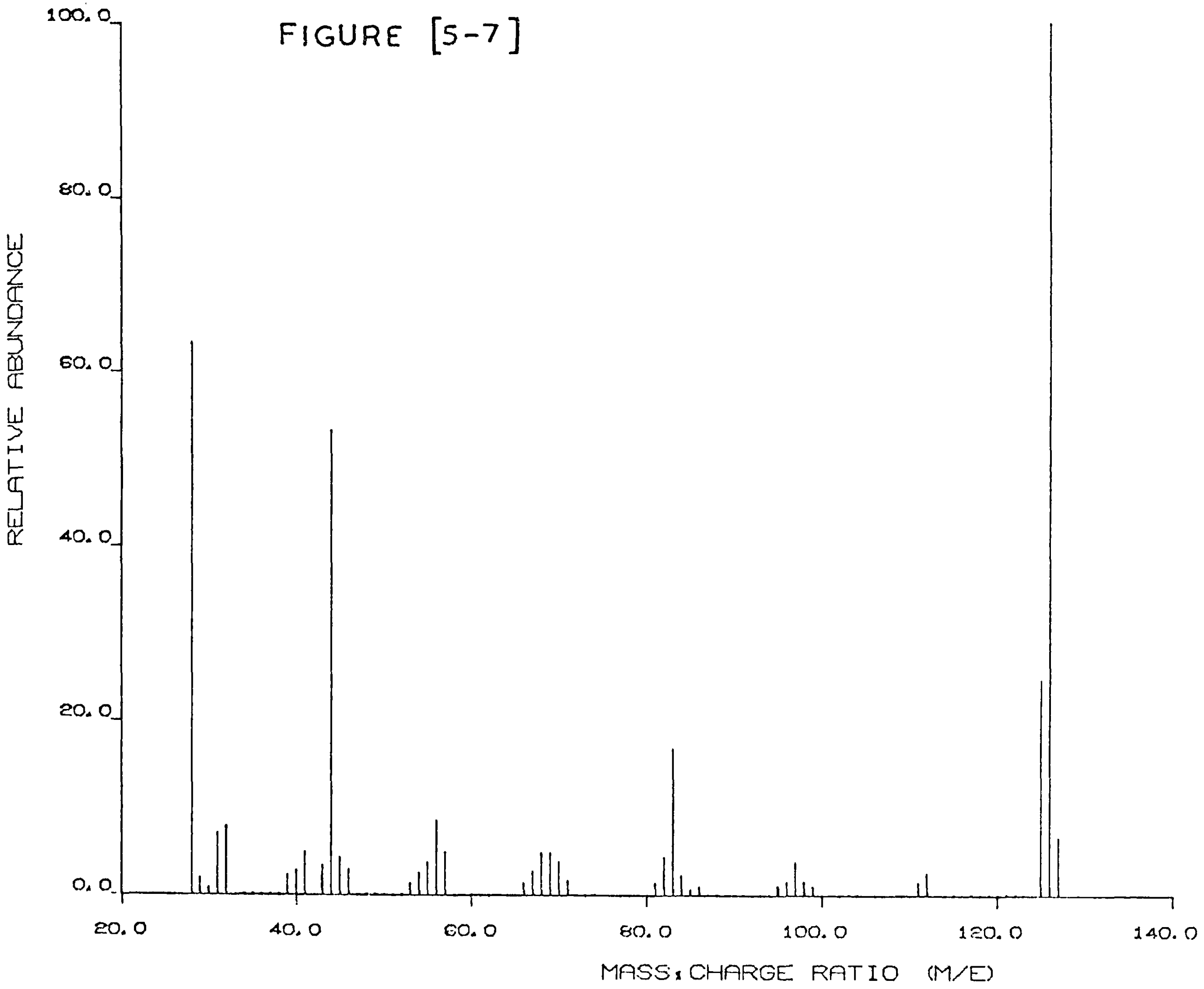
5-XXVII m/e 111, 112,113

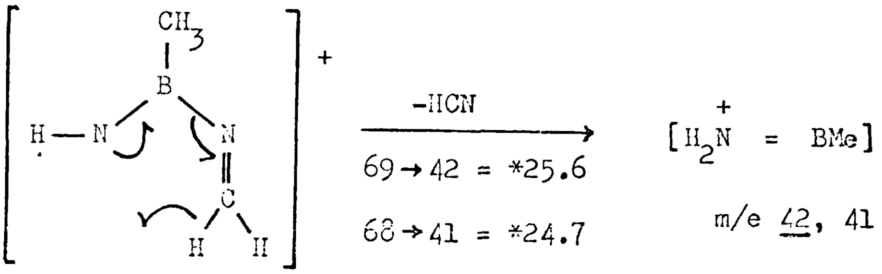
5-XXVIIIA m/e 82,83,84

The next major fragmentation occurred through loss of HCN from 5-XXVIII to yield $CH_3-\overset{+}{\underset{H}{N}}=BCH_3$ 5-XXIX m/e 57, 56, 55 and this was confirmed by metastable transitions, (83→56 = *37.8, 82→55 = *37.0). The source of the peak at m/e 69 was not established by an observed metastable transition, although it probably arose by loss of (N_2 + CH_3.) from 5-XXVII and had a possible structure $[HN-B(CH_3)-N=CH_2]^+$ 5-XXX. This then broke down further by loss of HCN viz:

2, 5-DIMETHYL, 1-ETHYLCYCLOTETRAZENOBORANE

FIGURE [5-7]





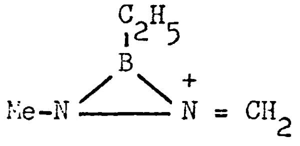
5-XXX m/e 69,68

The mass spectrum of 2,5-dimethyl,1-ethylcyclotetrazenoborane is shown in figure [5-7].

The molecular ion peak containing the ^{11}B isotope at m/e 126 was again the base peak in the spectrum. Loss of (N_2 + H•) produced the peaks at m/e 96, 97, 98 5-XXXIA or 5-XXXIB although in this case no metastable peaks were observed for the process.

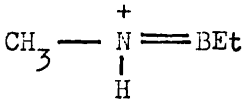
$[Me\text{-}N\text{-}BEt - N = CH_2]^+$

5-XXXIA



5-XXXIB

Species 5-XXXI then lost HCN to produce species 5-XXXII

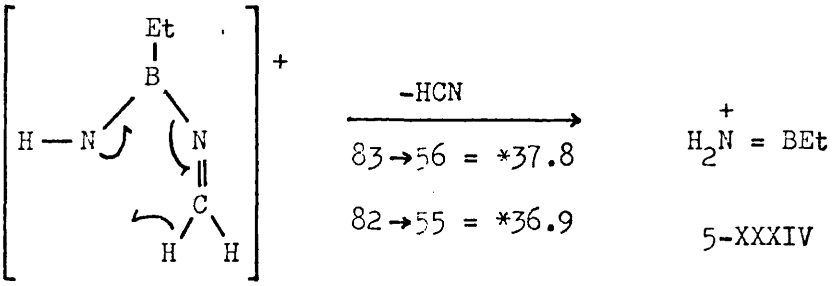


$CH_3 - \overset{+}{\underset{H}{N}} = BEt$

5-XXXII m/e 69, 70

assuming a hydrogen transfer also occurred.

The molecular ions could lose (N_2 + CH_3•) to produce the peaks at m/e 82, 83, 84 (126→83 = *54.7; 125→82 = *53.8), probably represented by the species $[HN{-}B(Et)N{=}CH_2]^+$ 5-XXXIII. This was the first occasion on which this fragmentation for the 2,5-dimethyl substituted cyclotetrazenoboranes had been confirmed by the presence of a metastable transition. An intense metastable ion proved the loss of HCN from 5-XXXIII to yield 5-XXXIV.



5-XXXIII

5-XXXIV

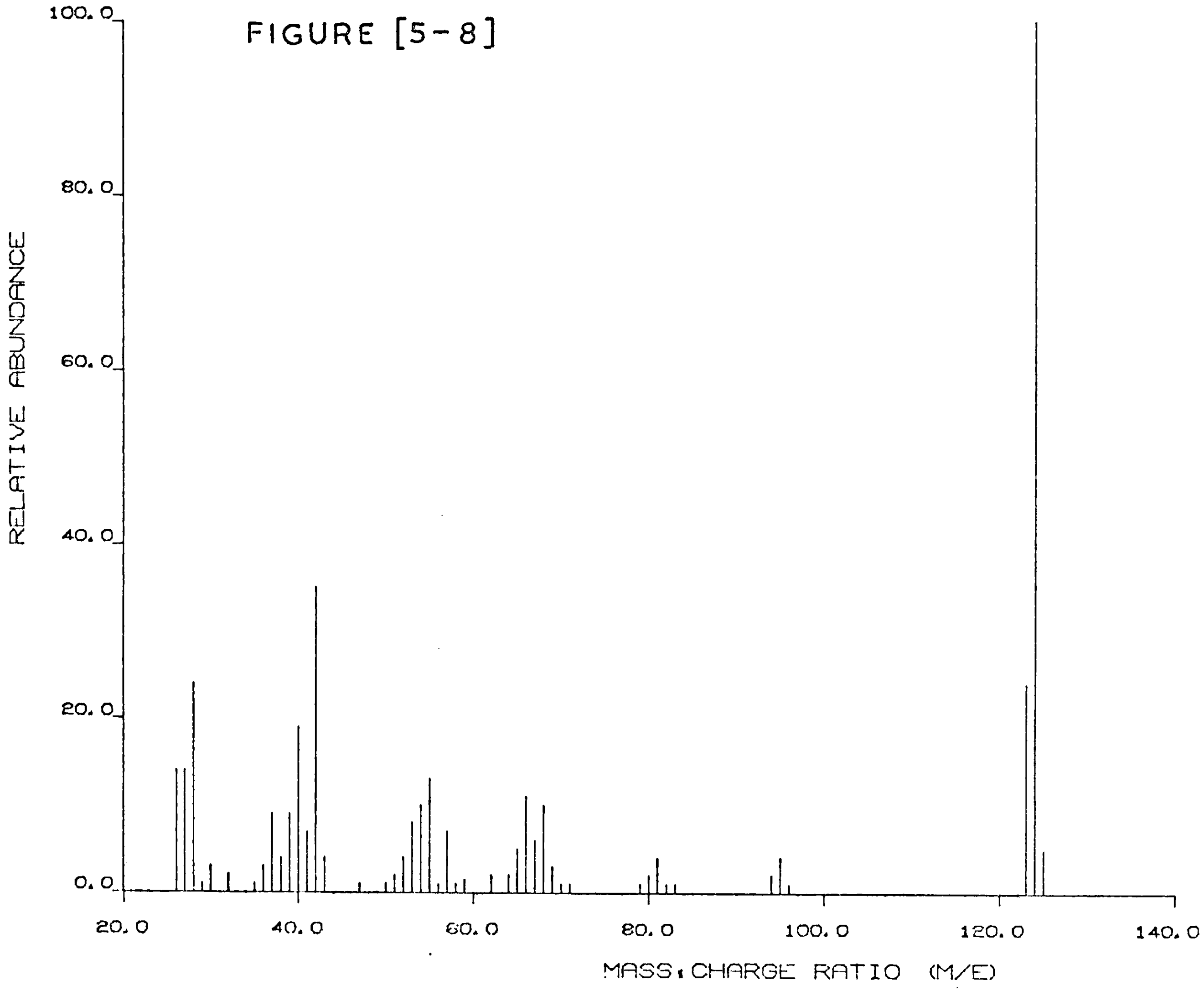
The peak at m/e 111 was presumably due to loss of $CH_3^{\bullet}$ from the molecular ion. It was curious that the peak at m/e 112 was slightly larger than the peak at m/e 111 since in Me_2N_4BH the peak at m/e 84 due to loss of CH_2 was very small. No metastable peak for this transition was observed.

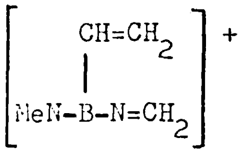
The mass spectrum of <u>2,5-dimethyl,1-vinylcyclotetrazenoborane</u> corrected for the presence of a small amount of 2,5-dimethyl,1-ethyl cyclotetrazenoborane impurity formed during its preparation is shown in figure [5-8].

Once more the molecular ion at m/e 124 was the base peak in the spectrum. The major molecular ion fragmentations were again loss of (N_2 + H•) to produce 5-XXXIVA or 5-XXXIVB, and the loss of

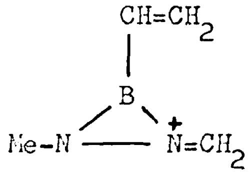
2, 5-DIMETHYL, 1-VINYLCYCLOTETRAZENOBORANE

FIGURE [5-8]





5-XXXVA

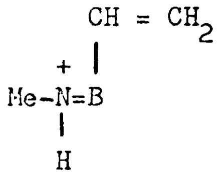


5-XXXVB

124→95, * = 72.78

123→94, * = 71.84

$(N_2 + CH_3\cdot)$ to produce peaks at m/e 80, 81. Loss of HCN was observed from 5-XXXV to yield 5-XXXVI.



95→68 = *48.67

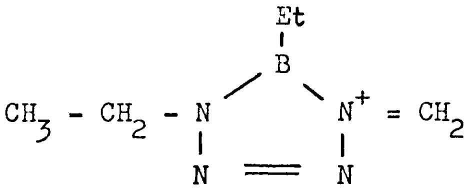
94→67 = *47.75

5-XXXVI

The fragmentation observed for 1,2,5-triethylcyclotetrazenoborane is shown in Figure [5-9]. The base peak was again the parent ion containing ^{11}B as for the 2,5-diethylcyclotetrazenoborane.

Fragmentation of the parent ion

Again methyl loss occurred to give peaks at m/e 138, 139, 140 which could be assigned to structure 5-XXXVII.



5-XXXVII m/e 139, 138

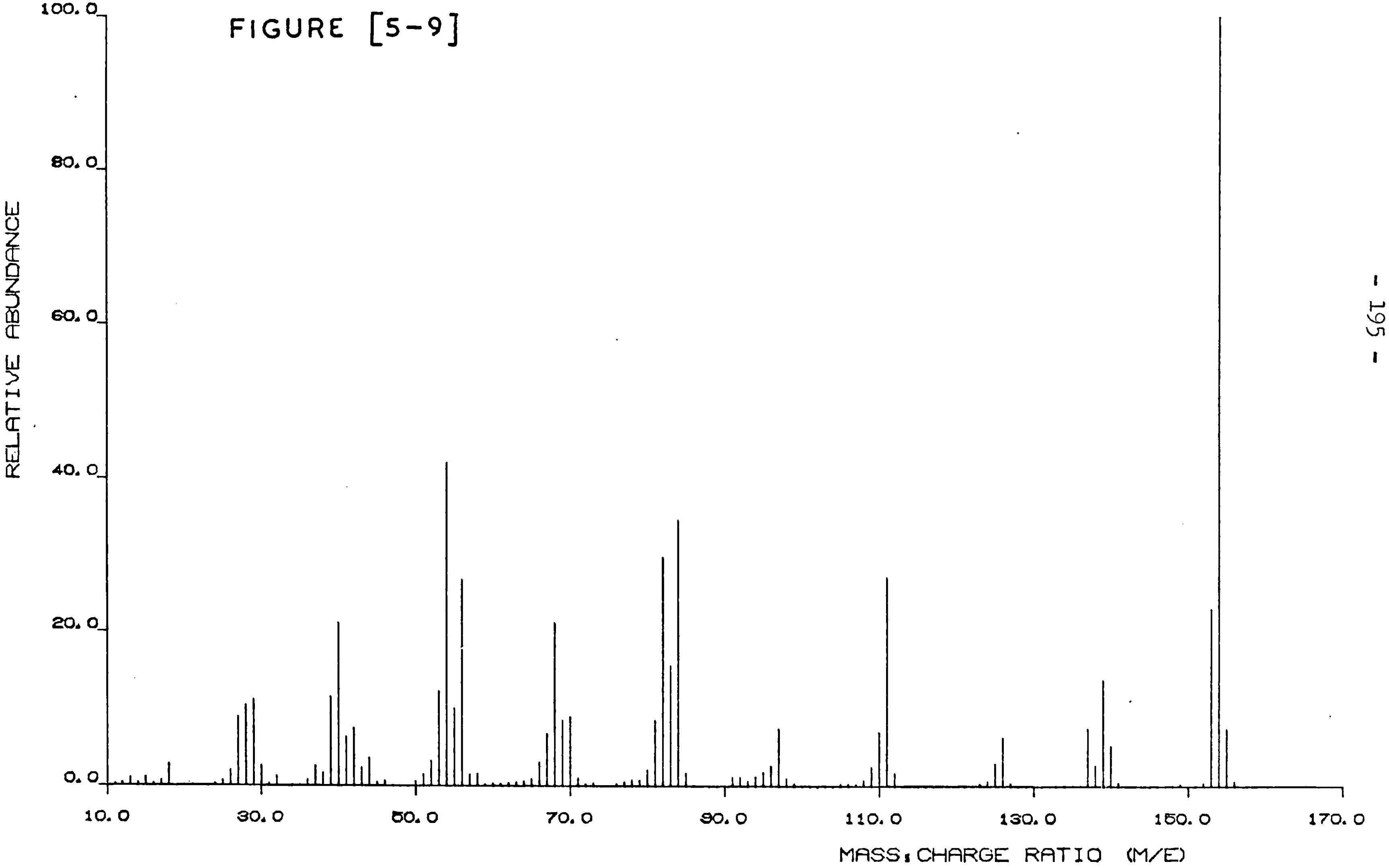
154→139 = *125.4

153→138 = *124.5

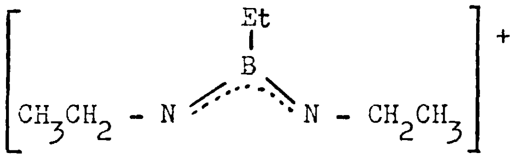
Loss of N_2 also occurred from the parent ions to give peaks at m/e 125, 126, 127 due to species 5-XXXVIII although the high intensity of the 125 peak indicated that loss of $(N_2+H\cdot)$

1, 2, 5-TRIETHYLCYCLOTETRAZENOBORANE

FIGURE [5-9]



also occurred.

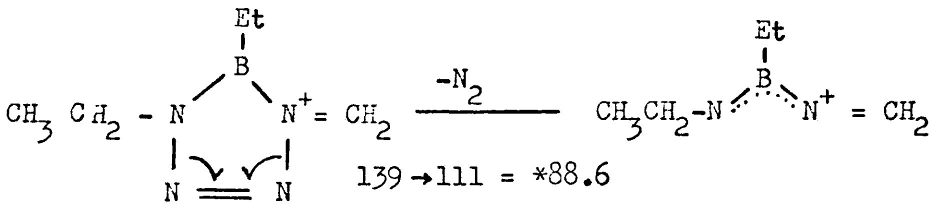


5-XXXVIII

Further fragmentation

5-XXXVIII further fragmented by loss of an ethyl group to produce peaks at m/e 96, 97, and 98, although this did not now occur simultaneously with N_2 loss as in the diethyl compound.

N_2 loss occurred from 5-XXXVII to give peaks at 110, 111, 112 which then gave peaks at m/e 83, 84, 85, by loss of HCN together with hydrogen transfer.

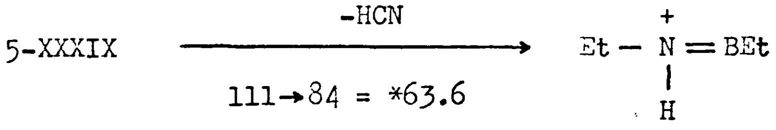


139→111 = *88.6

138→110 = *87.7

5-XXXVII m/e 138,139,140

5-XXXIX m/e 110, 111, 112



$$\text{5-XXXIX} \xrightarrow{-\text{HCN}} \text{Et}-\overset{+}{\underset{\text{H}}{\text{N}}}=\text{BEt}$$

111→84 = *63.6

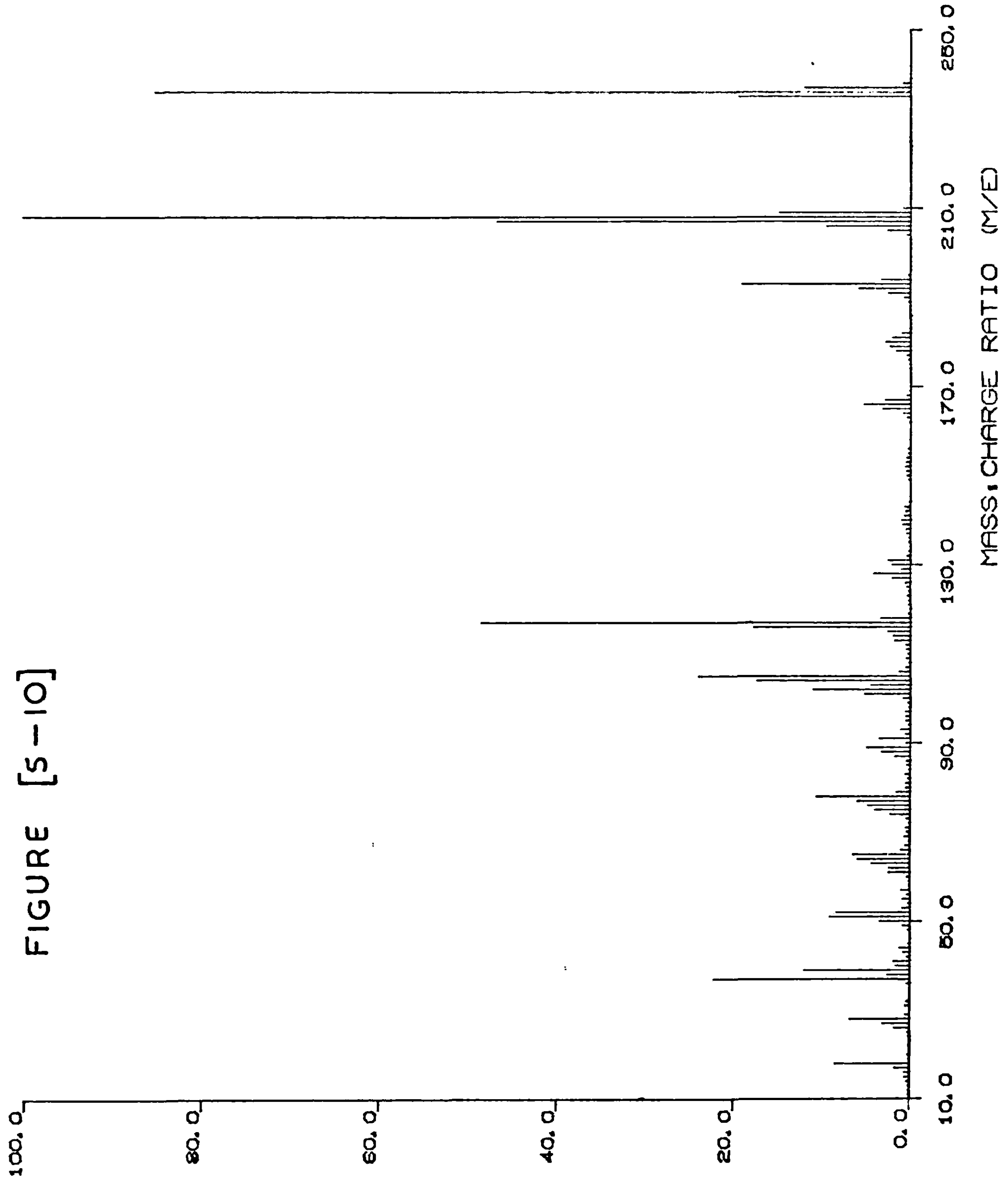
110→83 = *62.6

5-XL m/e 83, 84, 85

This fragmentation observed was similar to that observed in the diethyl derivative except that there was no metastable in the triethyl compound corresponding to the simultaneous loss of N_2 and HCN.

FIGURE [5-10]

2, 5-DIPHENYL, 1-METHYLCYCLOTETRAZENOBORANE



Ion 5-XL was analogous to ions 5-IV, 5-X, 5-XVI, 5-XXIV, 5-XXIX, 5-XXXII, 5-XXXVI in the previously considered cyclotetrazenoborane derivatives.

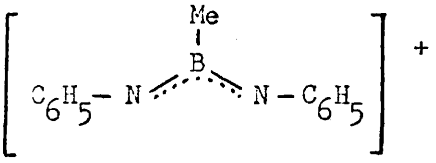
The mass spectrum of 2,5-diphenyl,1-methylcyclotetrazenoborane is shown in figure [5-10]. The intensities of the parent peaks at 235, 236 and 237 were in the correct ratios. It was interesting that a loss of $CH_3\cdot$ from the parent ion was not observed, again supporting the stability of the bond between the boron atom and the exocyclic substituent.

N_2 was again lost from the parent ion to give peaks at m/e 207, 208,209 and again as in the diphenyl compound (N_2 + H•) loss also occurred since the peak at m/e 207 was too intense to arise solely from N_2 loss.

$$[(C_6H_5)_2N_4BCH_3]^{+\bullet} \xrightarrow{-N_2}$$

$$236 \rightarrow 208 = {*}183.3$$

$$235 \rightarrow 207 = {*}182.4$$



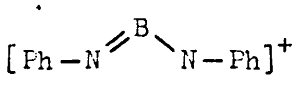
$$\left[C_6H_5-N\overset{\overset{Me}{|}}{\cdots B\cdots}N-C_6H_5\right]^+$$

5-XLI

An intense set of peaks was observed at m/e 116, 117, 118 and this probably corresponded to a loss of [PhN] from the 5-XLI to yield $[Ph - N = B - Me]^{+\bullet}$ 5-XLII although this was not confirmed by metastable ions.

Metastable peaks were observed however for the breakdown of the peaks at m/e 207, 208 to give the species at m/e 192, 193.

The only reasonable postulate in this case was the loss of a methyl group from the boron to give 5-XLII, although it does not



$[Ph-N{=}B-N-Ph]^+$

m/e 192, 193, 194

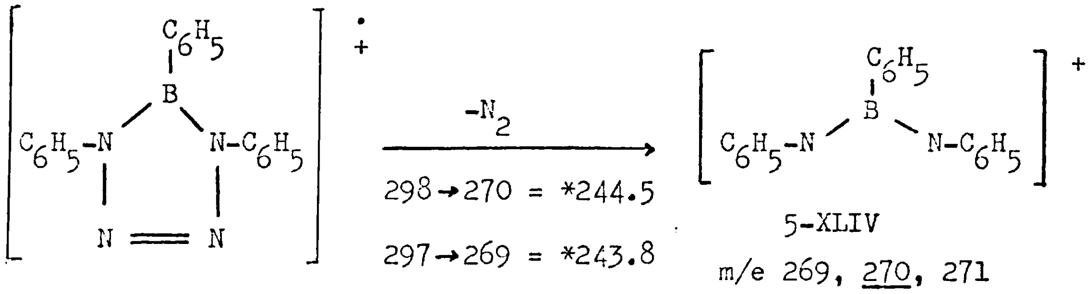
5-XLII

208→193 = *179.0

207→192 = *178.1

seem likely that a positive charge would reside on the boron atom.

The spectrum of 1,2,5-triphenylcyclotetrazenoborane is shown in Figure [5-11]. The parent ion peaks at m/e 297, 298, 299 were a little less intense than in the diphenyl compound. The peak at m/e 298 was mass measured and proved to be $Ph_2N_4{}^{11}BPh$ (m/e observed 298.1386, m/e calculated 298.13897)[99]. Loss of N_2 from the parent ion occurred to give the species 5-XLIV and again loss of (N_2 + H•) was responsible for the high intensity of the m/e 269 peak.

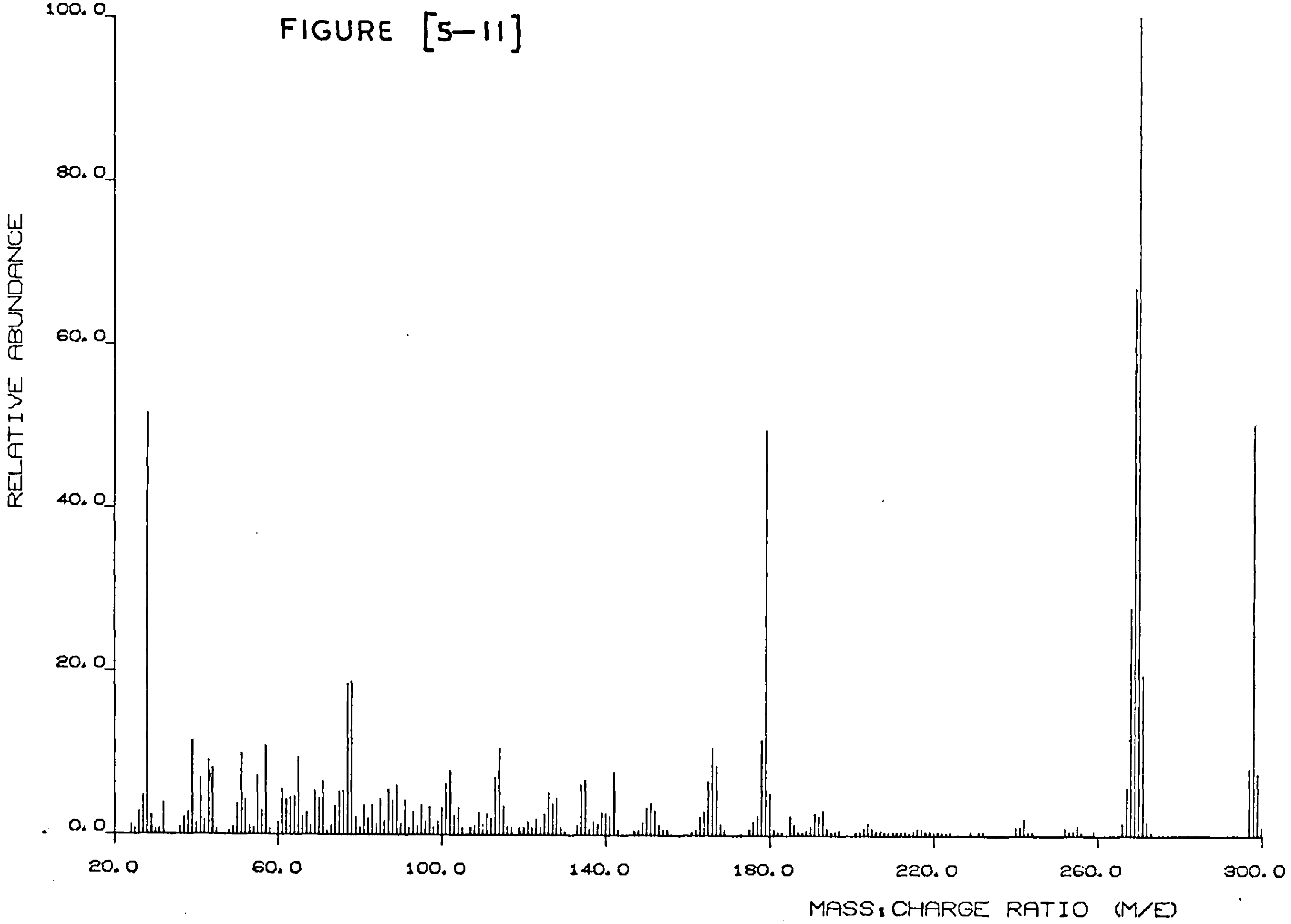


m/e 297, 298, 299

The other significant loss was of PhN from 5-XLIII to yield the species 5-XLV but this loss was not confirmed by metastable peaks. The peak at m/e 179 was mass measured and proved

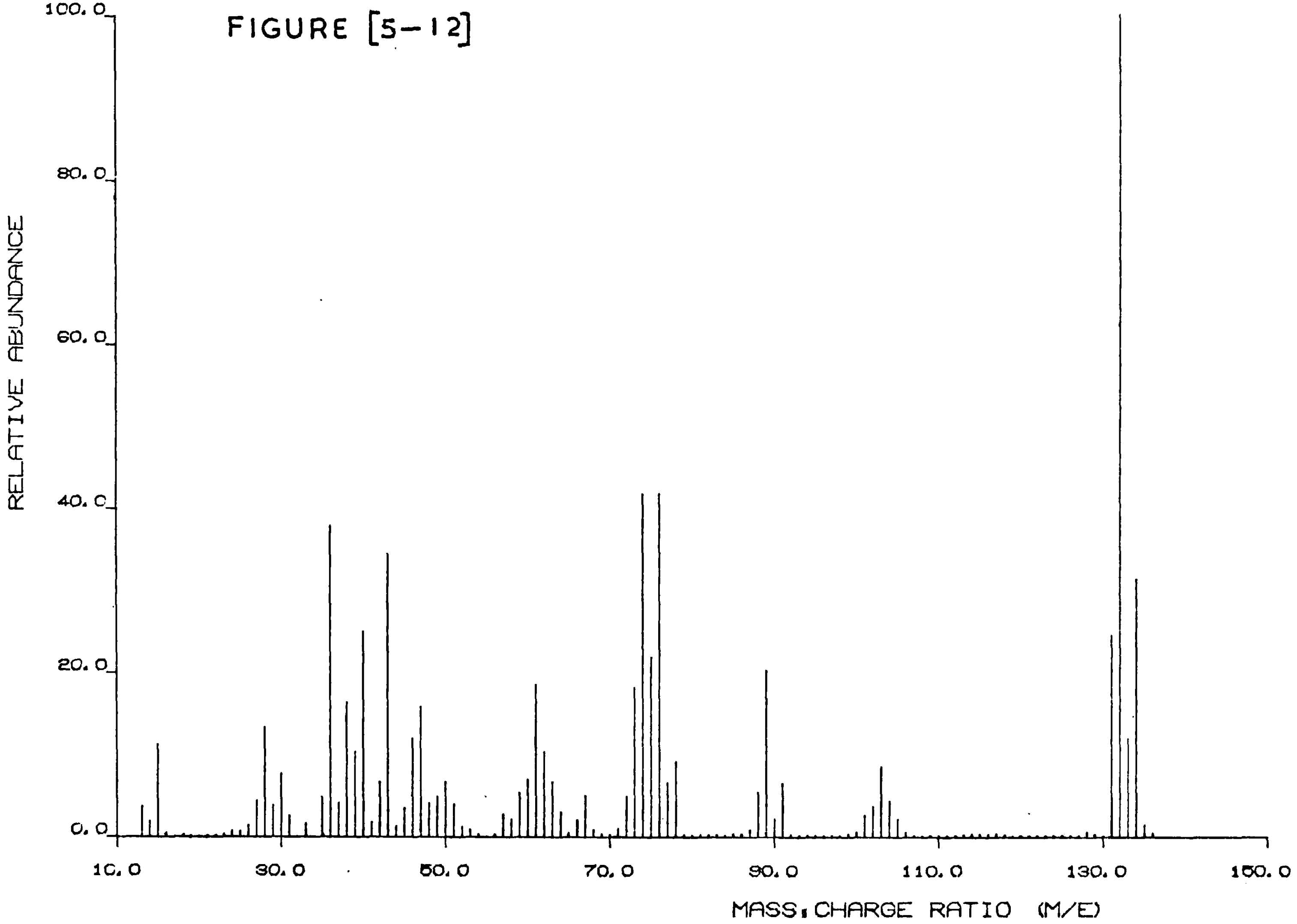
FIGURE [5-11]

1, 2, 5-TRIPHENYLCYCLOTETRAZENOBORANE



2, 5-DIMETHYL, 1-CHLOROCYCLOTETRAZENOBORANE

FIGURE [5-12]



$[C_6H_5 - N = B - C_6H_5]^{+\bullet}$ 5-XLV m/e 178, 179, 180

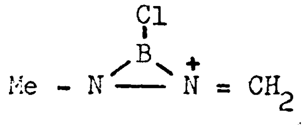
to be $C_{12}H_{10}N^{11}B$ as expected (Observed m/e 179.092, Calculated m/e 179.09063).[82]

Series 3

The mass spectrum of 2,5-dimethyl,1-chlorocyclotetrazenoborane is shown in Figure [5-12]. Molecular ion peaks were observed in the expected isotopic ratios due to the presence of species containing the isotopes $^{10}B^{35}Cl$ (m/e 131), $^{11}B^{35}Cl$ (m/e 132), $^{10}B^{37}Cl$ (m/e 133) and $^{11}B^{37}Cl$ (m/e 134). Fragmentation by loss of (N_2 + H•) occurred to produce the peaks at m/e 102, 103, 104 and 105; attributable to

$[Me - N - B(Cl) - N = CH_2]^+$ or

5-XLVIA



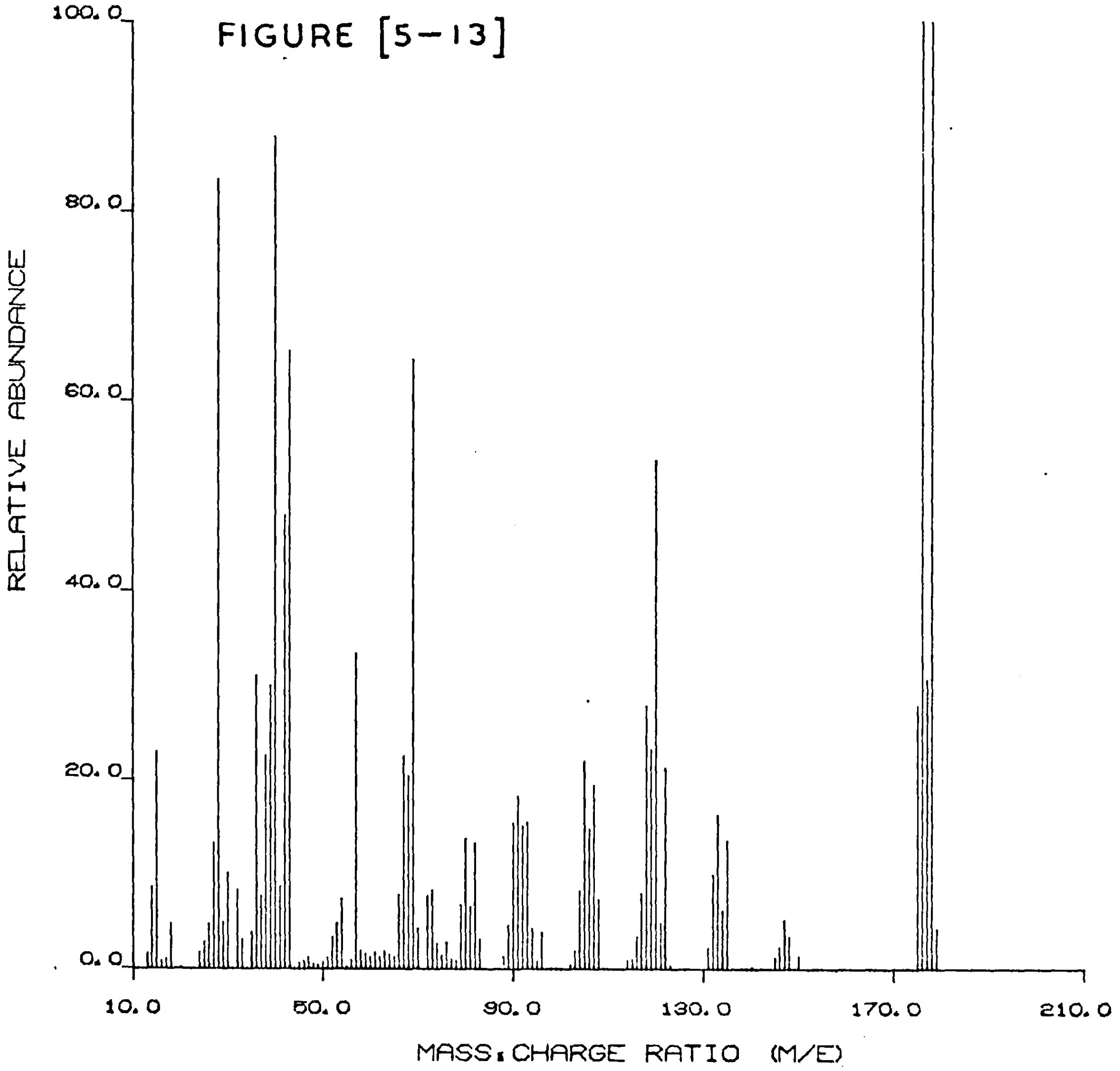
5-XLVIB

Loss of (N_2 + CH_3•) to produce the peaks at m/e 88, 89, 90 and 91 was also observed. HCN loss from 5-XLVI gave rise to species $CH_3\overset{+}{N}H = BCl$ 5-XLVII. None of the fragmentations at the higher m/e values involved breakdown of the B-Cl bond.

The mass spectrum of 2,5-dimethyl-1 bromocyclotetrazenoborane is shown in Figure [5-13]. Once again the molecular ion peaks containing "B isotope were the base peaks, there being two of almost equal intensity due to the almost equal isotopic abundances of ^{79}Br and ^{81}Br. The molecular ion peaks were observed in the expected ratios at

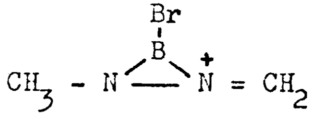
2, 5-DIMETHYL, 1-BROMOCYCLOTETRAZENOBORANE

FIGURE [5-13]

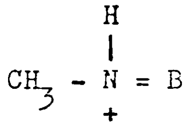


m/e 175, 176, 177 and 178. The major fragmentations were analogous to those observed in the previously examined 2,5-dimethyl substituted cyclotetrazenoborane derivatives.

(i) Loss of $(N_2 + H\cdot)$ to produce peaks at m/e 146, 147, 148, and 149, of probably structure 5-XLVIIIA or 5-XLVIIIB

$[CH_3 - N - BBr - N = CH_2]^+$ or 

5-XLVIIIA 5-XLVIIIB

(ii) Loss of HCN from 5-XLVIII to produce species 5-XLIX,  $CH_3 - \overset{H}{\underset{+}{N}} = BBr$ at m/e 119, 120, 121 and 122. The ion 5-XLIX was analogous to ions 5-IV, 5-X, 5-XVI, 5-XXIV, 5-XXIX, 5-XXXII, 5-XXXVI, 5-XL and 5-XLVII in the compounds previously considered.

(iii) Loss of $(N_2 + CH_3\cdot)$ from the parent ion accounted for the peaks at m/e 132, 133, 134 and 135.

It is interesting to note that the B-Br bond appears to have been retained in the fragment at m/e 104, 105, 106, 107 probably from the species $(HN = BBr)^{\overset{\bullet}{+}}$ and also at m/e 89, 90, 91 and 92 which correspond to $(B - Br)^+$.

In summary, derivatives of cyclotetrazenoboranes yielded strong parent ion peaks which were the base peaks for 2,5 aliphatic substitution in the ring. The loss of $(N_2 + H\cdot)$ from the parent ion was virtually complete for 2,5 dimethyl derivatives whilst for other derivatives fragmentation by loss of N_2 was predominant together with a slight contribution from (N_2 + H•). The loss of (N_2 + H•) involved loss of the H• from the side chain and not from the boron substituent, and it was apparent that the B-R" bond was remarkably stable under electron impact conditions, even for such dissimilar substituents as H(D), alkyl, aryl, vinyl and halogen.

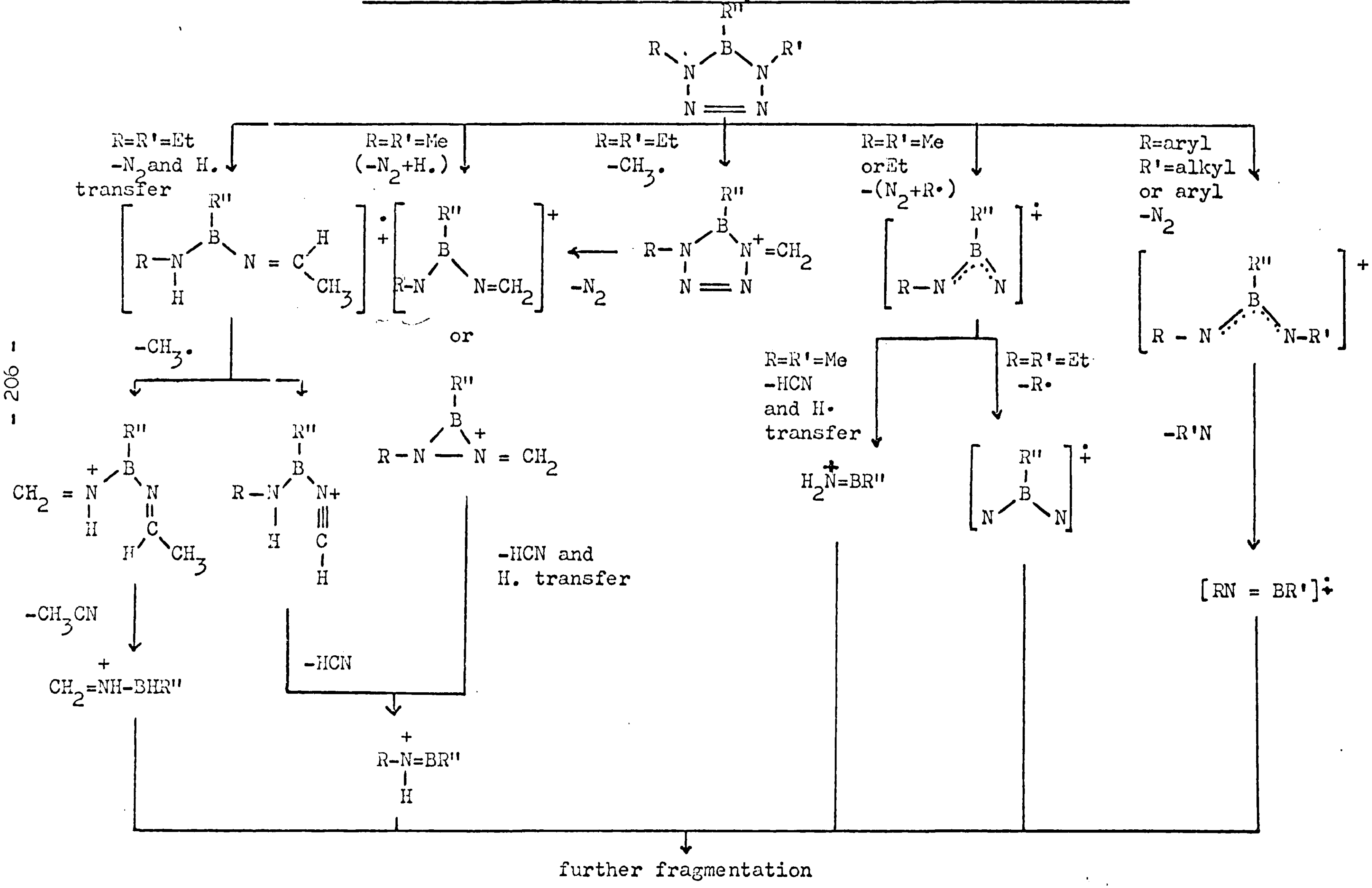
It also appeared that the subsequent fragmentation was determined largely by the nature of the 2,5 substituent groups. A predominant fragmentation involved loss of HCN in some stage of the breakdown of compounds containing only alkyl substituents at nitrogen to produce an ion of the type $R - \underset{H}{\overset{+}{N}} = BR''$. In 2,5-dimethyl derivatives a different initial fragmentation led to species $(H_2\overset{+}{N} = BR'')$ by loss of HCN. However when one or more of the 2 or 5 substituents was phenyl, loss of R-N could occur to give the ion $[PhN{=}BX]^{\dot{+}}$. It was interesting that this should be such a common stable ion and tended to confirm the stability of the borazyne entity discussed in Chapters 1 and 3.

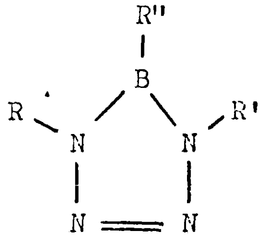
A generalised fragmentation for cyclotetrazenoborane derivatives is shown in table 5-C.

Earlier work (discussed in Chapter 1) strongly indicated that symmetrically substituted cyclotetrazenoborane derivatives were molecules with C_{2v} symmetry, but did not conclusively decide between possibly structures 5-L and 5-LI. A molecule with the

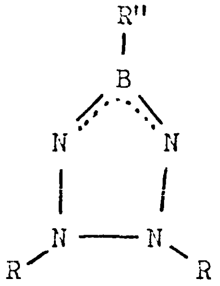
TABLE 5-C

Generalised fragmentation for cyclotetrazenoborane derivatives





5-L



5-LI

structure 5-LI would be less likely to eliminate N_2, and the mass spectral results strongly supported structure 5-L, since the primary fragmentation of all the molecules studied involved the loss of N_2.

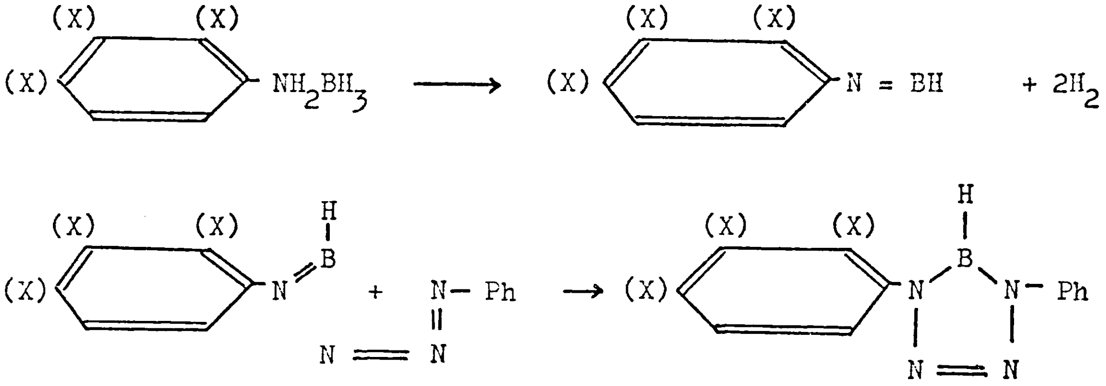
CHAPTER VI

THE PREPARATION OF UNSYMMETRICALLY N-SUBSTITUTED CYCLOTETRAZENOBORANES

RESULTS AND DISCUSSION

Perkins[104] has carried out molecular orbital calculations by an improved method on a number of diphenyl cyclotetrazenoboranes in which one phenyl ring had been substituted and has predicted the bond orders, π-electron charge densities, the ring and total π-energies, and the position of the first electronic transition in these compounds. The results of these calculations are summarised in tables 6-A and 6-B, although the results for the methyl-substituted phenyl derivatives were considered to be less reliable than those for the chlorine substituted phenyl derivatives.

It was anticipated that the unsymmetrically N-substituted cyclotetrazenoboranes (6-II) → (6-VII) would be preparable by the reactions of the appropriate o -, m-, p-methyl or chloro-substituted aniline-boranes with phenyl azide by the evolution of hydrogen as shown in reaction scheme 6-1.



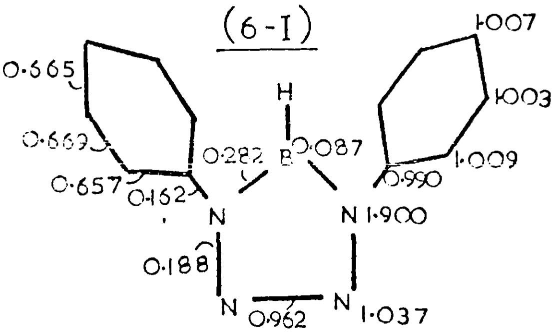
where X = Cl or Me

(6-1)

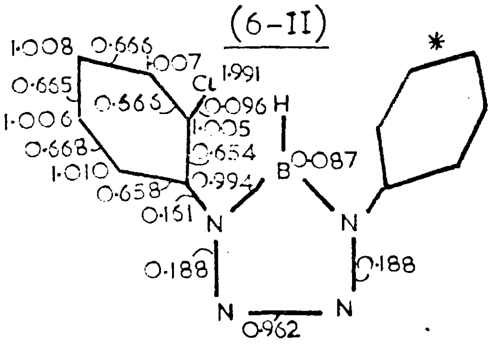
TABLE [6–A]

CALCULATED π – BOND ORDERS AND CHARGE DISTRIBUTIONS.

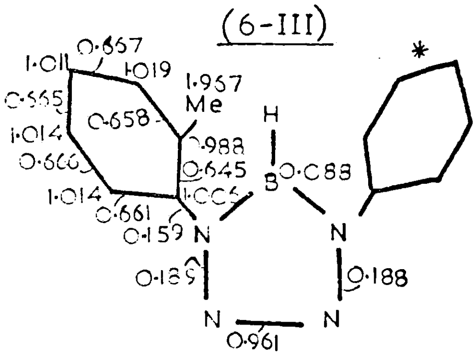
(6-I)



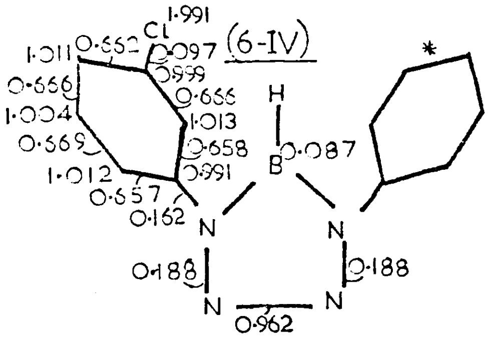
(6-II)



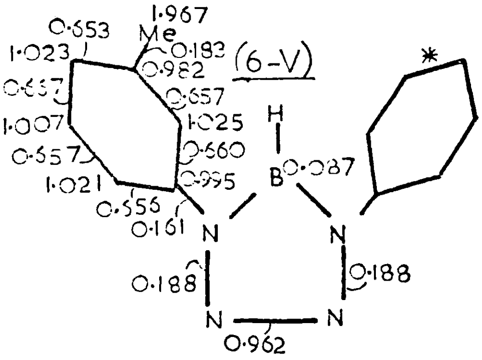
(6-III)



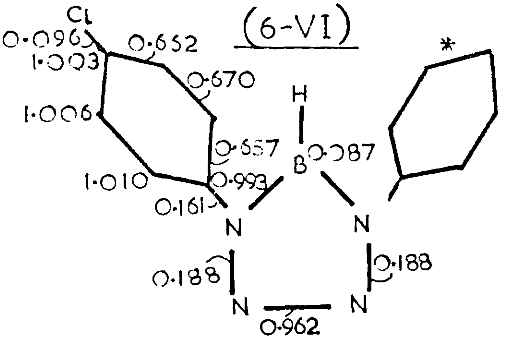
(6-IV)



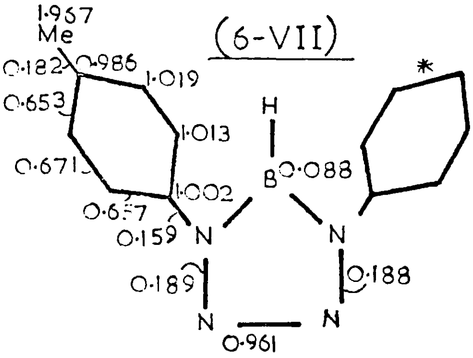
(6-V)



(6-VI)



(6-VII)



* π BOND ORDERS AND CHARGE DISTRIBUTIONS IN BN_4 AND UNSUBSTITUTED C_6H_5 RINGS WHEN NOT SHOWN ARE THE SAME AS IN STRUCTURE (6–I).

TABLE 6-B

CALCULATED RING ENERGIES AND POSITIONS OF THE FIRST ELECTRONIC TRANSITION

Compound	$E\pi$ (β units)		Electronic Spectra 1st band	
	Ring only	Total $E\pi$	$\Delta(\beta)$	Δ^*(mμ)
(6-I)	3.016	29.106	1.04942	243
(6-II)(o-Cl)	3.056	29.056	1.03746	246
(6-III)(m-Cl)	3.056	29.056	1.04051	245
(6-IV)(p-Cl)	3.056	29.056	1.02270	249
(6-V)(o-Me)	3.191	35.191	0.98220	260
(6-VI)(m-Me)	3.192	35.192	0.99773	256
(6-VII)(p-Me)	3.191	35.191	0.96226	265

* Calibrated arbitrarily by setting 1st energy gap of (6-I) = 243 mμ. This gave β = 3.16 (which was reasonably satisfactory as the S.C.F. value was 2.39 eV).

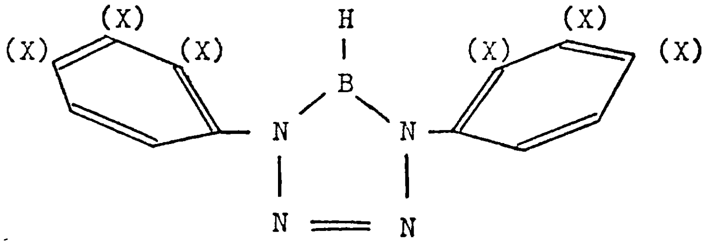
In all cases white crystalline solids were isolated from the reactions. The yield obtained was dependent on the nature of the phenyl substituent and decreased in the order p- $>$ m- $\gg$ o -, the very low yields of product from the reactions involving o -substituents possibly being attributable to steric factors.

The infrared spectra of all the products showed the characteristic high B-H stretching frequencies around 2650 cm^{-1} as well as many other vibrations attributable to N-aryl substituted cyclotetrazenoborane derivatives. C-H and C-Cl stretching frequencies were observed around 2900 - 3000 cm^{-1} and 800 - 850 cm^{-1} respectively, characteristic of the methyl and chloro vibrations in the substituted phenyl products.

Elemental analyses on the products were in poor agreement with those expected for the simple compounds (6-II → 6-VII) with the exception of the product from the reaction of p-toluidine borane and phenyl azide, which on one occasion agreed well with 2-p-tolyl,5-phenyl cyclotetrazenoborane although this was possibly fortuitous.

^{11}B nuclear magnetic resonance studies on the compounds showed broad, poor resolved doublets, characteristic of cyclotetrazenoborane derivatives, with coupling constants of the order of 160 - 170 c.p.s. and chemical shift of -18 → -21 p.p.m. from $BF_3.Et_2O$. ^1H nuclear magnetic resonance studies showed the presence in all cases of aryl resonances around 2.1 → 3.0 τ, and for methyl substituted phenyl derivatives, methyl resonances at 7.65 → 7.75 τ. Integral ratios for the number of protons in the phenyl groups relative to those in the methyl groups was often found to vary from the expected 3:1 ratio, and for the products derived from the reactions of o -, m-, and p-toluidine-boranes with phenyl azide the approximate ratios obtained were respectively, 39:1, 7:2 and 2:1.

Mass spectrometric studies on the products led to the explanation of these results. It was observed that for m- and p-chlorine and methyl derivatives, not only were parent ions observed for molecules (6-III), (6-IV), (6-VI) and (6-VII) respectively, but that in each case parent ions for species (6-I) and also those for a derivative in which both the phenyl groups contained the methyl or chlorine substitutent as in (6-VIII) were present.



6-VIII

where X = Me or Cl

For o-substituted derivatives the mass spectrum did not show the presence of any species 6-VIII, but the presence of small amounts of either species 6-II or 6-V together with a large quantity of species 6-I was indicated. In all cases the derivatives described were confirmed not only by their characteristic parent ions, but also by their subsequent fragmentation which followed the generalised pattern established in Chapter 5.

The mass spectral results readily accounted for the poor elemental analysis, in particular the high C and Cl analysis for m- and p-derivatives due to the presence of some 6-VIII in each case. The low C and H figures for the o-methyl derivative were also consistent with the presence of very little 6-V relative to the high proportion of 6-I. The one acceptable analysis for 6-VII obtained for the product from p-toluidine-borane and phenyl azide was possibly fortuitous and may have been accountable to a statistical production of the 6-I, 6-VII and 6-VIII derivatives. Similarly, the high ratio of methyl protons to phenyl protons shown by the 'H N.M.R. integrals indicated the formation of 6-VIII derivatives for m- and p-substituted phenyl compounds, and the high proportion of 6-I formed relative to 6-V accounted for the low ratio observed for the o-CH_3 substituted phenyl derivative.

Attempts to separate the cyclotetrazenoborane isomers by fractional crystallisation, did not lead to the isolation of any single species, although the composition of the mixture was altered. It was also anticipated that chromatography might lead to the separation of the isomers, but thin-layer chromatography on silica and alumina indicated that many compounds were often formed, some of which were probably caused by decomposition of the compounds on the stationary phase. A possible route for separation of the isomers would be to react the cyclotetrazenoborane mixture with an alkyl or aryl Grignard reagent, followed by isolation of the mixed hydrolytically stable, B-alkyl or B-aryl cyclotetrazenoboranes and separation of the isomers by column chromatography.

When p-Cl $C_6H_4NH_2BH_3$ was reacted with PhN_3 in the presence of excess p-chloroaniline a large increase in yield occurred, but three cyclotetrazenoborane derivatives were again produced. Fractional sublimation of the products under high vacuum using an oil bath over a range of temperature of 140° - 160° led to a partial separation of the products, but once again a pure isomer could not be isolated.

In the reaction of p-nitroaniline with diborane and phenyl azide a bright yellow precipitate was obtained but this was not characteristic of a cyclotetrazenoborane product.

The reaction obtained by heating ethylamineborane with methyl azide led to the formation of Me_2N_4BH, $MeEtN_4BH$ and Et_2N_4BH in a similar manner as for the previously mentioned substituted phenyl derivatives. Recent work by Morris[95] showed that the reaction of these products with phenyl magnesium bromide gave a mixture of the B-phenyl substituted derivatives $Me_2N_4BPh:MeEtN_4BPh:Et_2N_4BPh$ in the statistically expected ratio of 1:2:1.

It was also found that on heating Me_2N_4BH and Et_2N_4BH at 130°, and in a separate experiment on heating Me_2N_4BH with ethyl azide at 130°, the reaction products contained a mixture of Me_2N_4BH, $MeEtN_4BH$ and Et_2N_4BH. The three compounds in all of the above experiments were characterised by mass spectrometry and vapour phase chromatography.

$$EtNH_2BH_3 + MeN_3 \xrightarrow{130^{\circ}} Me_2N_4BH,\ MeEtN_4BH,\ Et_2N_4BH \qquad (6\text{-}2)$$

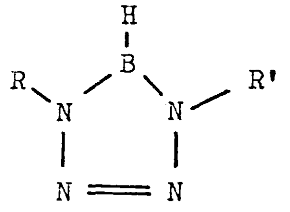
$$Me_2N_4BH + Et_2N_4BH \xrightarrow{130^{\circ}} Me_2N_4BH,\ MeEtN_4BH,\ Et_2N_4BH \qquad (6\text{-}3)$$

$$Me_2N_4BH + EtN_3 \xrightarrow{130^{\circ}} Me_2N_4BH,\ MeEtN_4BH,\ Et_2N_4BH \qquad (6\text{-}4)$$

This series of experiments represented by 6-2 → 6-4 indicated that the "scrambling" of the N-substituent groups could occur at any stage. The mechanism previously postulated for the formation of cyclotetrazenoboranes, shown in 6-5 must now be considered an oversimplification.

$$RNH_2BH_3 \quad = \quad [RN = BH] \ + \ 2H_2$$

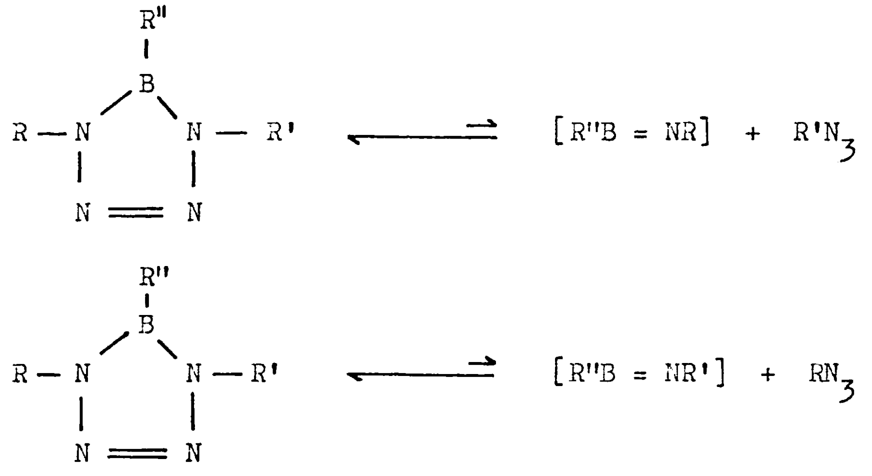
$$[RN = BH] + R'N_3 =$$



(6-5)

One possible mechanism to account for the observed reactions would be that of a free radical exchange of groups. Opposed to this, however, was that E.S.R. experiments by Sales[105] on solutions of cyclotetrazenoboranes did not give evidence for the presence of free radicals. However Pearson[106] has shown that dimethyl cyclotetrazenoborane was capable of acting as a polymerisation initiator for methyl methacrylate $CH_2 = CH(CH_3)CO(OCH_3)$ at 0°C in the absence of oxygen probably by a free radical process.

Another plausible mechanism which could be postulated to account for all the observed reactions would be the attainment of a dynamic equilibrium, in which the cyclotetrazenoborane molecule cleaved by a reaction of unknown molecularity, to produce transiently in two ways boron imide and azide intermediates. The recombination of these could lead to three possible products as shown in reaction scheme 6-6.



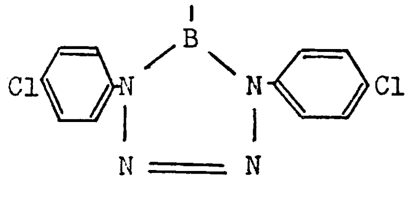
$$[R'' - B = N - R] + RN_3 \rightleftharpoons R_2N_4BR''$$

$$[R'' - B = N - R'] + R'N_3 \rightleftharpoons R'_2\,N_4BR'' \qquad (6\text{-}6)$$

An attempted to study the kinetics of the formation of $MeEtN_4BH$ from the reaction of Me_2N_4BH and Et_2N_4BH at 130° using mass spectrometry proved unsuccessful because the sensitivity readings were found to be insufficiently reproducible. A possible way for future study of this reaction would be to analyse the products using vapour phase chromatography.

The preparation of 2-methyl,5-phenyl-cyclotetrazenoborane was achieved by Morris[22] from the reaction of anilineborane with methyl azide. To establish the generality of the production of mixtures from the reactions of primary amineboranes RNH_2BH_3 with organic azides $R'N_3$, and also to further establish the equivalence of the 2 and 5 positions in the cyclotetrazenoborane ring, the preparation of 2-phenyl, 5-methyl-cyclotetrazenoborane was further investigated. The alternative reactants to those used by Morris, i.e. methylamineborane and phenyl azide on heating in an ether solvent led to the isolation of pure Me_2N_4BH and $MePhN_4BH$ by vacuum distillation. The products were confirmed by mass, infrared, ^1H and ^{11}B N.M.R. spectrometry. The infrared spectrum of the residue indicated the presence of some Ph_2N_4BH but this was not isolated in a pure form.

In order to test the calculations by Perkins[42] for one pure compound the di-p-chloro-phenyl-cyclotetrazenoborane derivative 6-IX was prepared by the reaction of p-chloroaniline borane with



6-IX

$$p\text{-}ClC_6H_4NH_2BH_3 + p\text{-}ClC_6H_4N_3 \longrightarrow (p\text{-}ClC_6H_4)_2N_4BH + 2H_2 \qquad (6\text{-}7)$$

6-IX

p-chlorophenyl azide as shown in equation 6-7. The compound was identified by its elemental analysis, mass, infrared, ^{1}H and ^{11}B N.M.R., and electronic spectra.

Physical Properties

As the products obtained in most cases from the reactions of aryl amine boranes $XC_6H_4NH_2BH_3$ with phenyl azide were mixtures of compounds, the actual physical properties observed have no absolute meaning and are only briefly summarised in Table 6-C.

TABLE 6-C

PHYSICAL PROPERTIES OF PRODUCTS FROM REACTIONS OF $XC_6H_4NH_2BH_3$ WITH PhN_3

Product of Reaction from $PhN_3+XC_6H_4NH_2BH_3$	U.V. λ max mμ	Calc.U.V. λ' max mμ	^{11}B N.M.R. rel. to BF_3Et_2O	^{1}H N.M.R. ppm
X = o-CH_3	242.0	260	δ =-18.8ppm J_{B-H}=171 cps	τPh 2.1→3.4 τMe 7.70
X = m-CH_3	-	256	-	τPh 2.2→3.6 τMe 7.71
X = p-CH_3	244.0	265	δ =-21.0ppm J_{B-H} =173 cps	τPh 2.2→3.4 τMe 7.66
X = o-Cl	-	246	δ = -19.3ppm J_{B-H} =154 cps	τPh 2.1→3.5
X = m-Cl	243.5	245	δ = -18.8ppm J_{B-H} =177 cps	τPh 2.1→3.1
X = p-Cl	250.3	249	δ = -19.1ppm J_{B-H} =166 cps	τPh 2.1→3.6

The physical properties of 2,5-di-p-chlorophenyl cyclotetrazenoborane are summarised in Table 6-D, except the infrared spectrum which is listed separately.

TABLE 6-D

PHYSICAL PROPERTIES OF 2,5-DI-p-CHLOROPHENYL CYCLOTETRAZENOBORANE

U.V. λ max(mμ)	Calc. U.V. λ max(mμ)	^{1}H N.M.R. ppm *	^{11}B N.M.R. rel to BF$_3$.Et$_2$O	Mass Spectra Parent ions	M.Pt. $^{\circ}$C
250.2	251	τPh=2.48	δ =-19.2ppm J=166cps	m/e 289, 290, 291, 292, 293, 294	158

*τ value quoted as the symmetric centre of the observed resonance.

Electronic spectra

The excellent agreement between the predicted[42] and observed red shift for the first electronic transitions for 2,5-di-p-chlorophenyl cyclotetrazenoborane was very satisfactory and gave extra vindication for the treatment of these molecules as cyclic structures with some π-electron delocalisation. It was not considered justified to compare the λ_{max} values observed for the mixed phenyl substituted products obtained with the calculated figures for unsymmetrically N-substituted aryl cyclotetrazenoboranes.

Infrared Spectra

The infrared spectra of the products from reactions of o-, m-, p- $XC_6H_4NH_2BH_3$ with phenyl azide (where X = Cl or Me) have already been briefly discussed and the principal bands have

THE INFRARED SPECTRUM OF DI-PARA-CHLOROPHENYL CYCLOTETRAZENOBORANE.

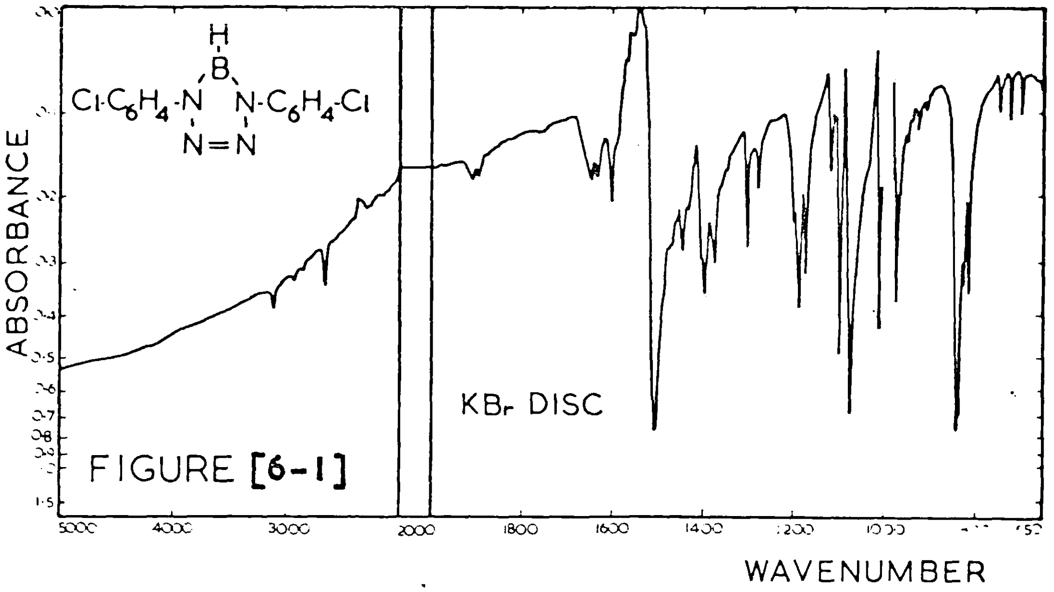
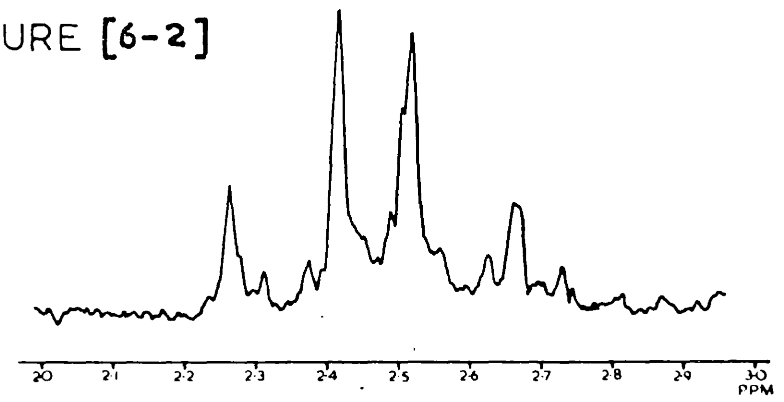


FIGURE [6-1]

THE ^{1}H N.M.R. SPECTRUM OF DI-PARA-CHLOROPHENYL CYCLOTETRAZENOBORANE.

FIGURE [6-2]



not been tabulated or the spectra reproduced here since pure compounds were not isolated.

The observed infrared spectrum of di-p-chlorophenyl is shown in Figure [6-1] and the principal bands are listed in Table 6-E.

TABLE 6-E

THE INFRARED SPECTRUM OF 2,5-DI-(p-CHLOROPHENYL) CYCLOTETRAZENOBORANE

3096 w; 3084 w; 2845 vw; 2660 w; 1908 w; 1894 w; 1653 sh; 1642 w; 1621 w; 1603 w; 1590 sh; 1563 sh; 1546 sh; 1497 vs; 1482 sh; 1464 msh; 1439 m; 1425 sh; 1399 sh; 1393 m; 1370 m; 1359 sh; 1300 m; 1277 w; 1267 sh; 1201 m; 1193 sh; 1189 s; 1174 ms; 1170 sh; 1117 w; 1107 w; 1099 s; 1073 vs; 1053 sh; 1031 sh; 1009 s; 976 m; 970 ms; 962 sh; 945 w; 936 w; 922 w; 917 sh; 903 w; 835 vs; 831 vs; 821 ms; 810 ms; 747 w; 726 w; 702 w; 638 wb; 629 wb; 571 ms; 545 ms; 503 sh; 499 sh; 490 s; 487 s; 418 w.

Substitution of the chlorine in the phenyl ring necessarily altered the vibrations associated with the phenyl ring. Characteristic 1,4-disubstituted phenyl vibrations were observed and could be assigned by analogy with those quoted by Whiffen[90]. Typical vibrations observed were:- C-H stretch, 3100 - 3080 cm^{-1}; C-H def. combination bands at 1908 and 1894 cm^{-1}; C-C stretching vibrations 1640 - 1400 cm^{-1}, C-H in plane deformations 1200 - 1000 cm^{-1};

C-H out of plane deformations 970 - 800 cm^{-1}; phenyl ring deformations 700 - 400 cm^{-1}.

N_4B ring modes:- The ring mode vibrations for the BN_4 ring were less readily discernible than in previous cases possibly owing to coupling of vibrations of the same symmetry species, but some of the ring modes have been assigned by analogy with the previously examined compounds, (see Chapter 3), and are shown in Table 6-F.

TABLE 6-F

N_4B RING MODES OF 2,5-DI(p-CHLOROPHENYL) CYCLOTETRAZENOBORANE

Ring Mode	I	II	V	VI	VII	VIII
Frequency	1073	1107, 1099	1399,1393	1201,1189	970	418(?)

B-H vibrations

The characteristic high frequency B-H stretching vibration was observed as a poorly resolved band at 2660 cm^{-1}. The B-H deformation modes were not obvious but probably the in-plane and out of plane deformations lay within the broad bands around 1053 cm^{-1} and 810 cm^{-1}, respectively.

Nuclear Magnetic Resonance spectra

The ^{11}B N.M.R. resonance of di-p-chlorophenyl cyclotetrazenoborane showed a fairly well resolved doublet at -19.2 ppm relative to $BF_3.Et_2O$. This represented only a very slight difference in shielding of the boron atom relative to that in Ph_2N_4BH and was in very good agreement with the predictions made by Perkins[42] for the π-charge distributions on the boron atoms in the two molecules, (see Chapter 1, page 32).

The 'H N.M.R. resonance of the substituted phenyl groups in di-p-chlorophenyl cyclotetrazenoborane was observed at $\tau = 2.48$ ppm as a symmetric set of bands as shown in Figure [6-2] typical of an AA'BB' system.

Mass spectra

The cyclotetrazenoborane parent ions observed from the products of the reactions of o-, m- or p- $XC_6H_4NH_2BH_3$ with phenyl azide (where X = CH_3 or Cl) are listed below together with an indication of the subsequent fragmentation, which in many instances was substantiated by the observation of metastable ion peaks.

(a) Product from the reaction of o-Cl $C_6H_4NH_2BH_3$ with PhN_3

The parent ion $[(o\text{-}ClC_6H_4)(C_6H_5)N_4BH]^{+\cdot}$ m/e 255, <u>256</u>, 257, <u>258</u> was shown to lose N_2 to give peaks at m/e 227, <u>228</u>, 229, <u>230</u> followed by loss of Cl· to give the peaks around m/e 193. Intense peaks at m/e 221, <u>222</u>, 223 were observed showing the presence of a large quantity of $[Ph_2N_4BH]^{+\cdot}$ and all the characteristic fragmentations of this compound discussed in Chapter 5 were observed. Again an intense peak at m/e 103 was obtained attributable to

$[PhN{=}BH]^{+\cdot}$ by either loss of $[PhN\cdot]$ or $[C_6H_4ClN\cdot]$ from the $(M-N_2)$ fragment of Ph_2N_4BH and $(o\text{-}ClC_6H_4)(C_6H_5)N_4BH$ respectively.

(b) Product from the reaction of $m\text{-}ClC_6H_4NH_2BH_3$ with PhN_3 .

Three sets of characteristic parent ions at m/e (221, 222, 223); (255, 256, 257, 258); and (289, 290, 291, 292, 293, 294) corresponding respectively to $[(C_6H_5)_2N_4BH]^{+\cdot}$; $[(m\text{-}ClC_6H_4)(C_6H_5)N_4BH]^{+\cdot}$; and $[(m\text{-}ClC_6H_4)_2N_4BH]^{+\cdot}$ were observed. All three of these could fragment by loss of N_2 to yield sets of peaks having the major ions 194, 228 and 262 respectively, followed by loss of $(PhN\cdot)$; $(PhN\cdot)$ or $(ClC_6H_4N\cdot)$; and $(ClC_6H_4N\cdot)$ respecively to yield sets of peaks around 103; 137 or 103; and 137 respectively. Alternatively loss of $Cl\cdot$ from the $[M-N_2-Cl\ ]^{+}$ peak occurred for the $(m\text{-}ClC_6H_4)_2N_4BH$ derivative to give peaks around m/e 192.

(c) Product from the reaction of $p\text{-}ClC_6H_4NH_2BH_3$ with PhN_3

Again three sets of characteristic parent ions were observed at m/e (221, 222, 223); (255, 256, 257, 258); and (289, 290, 291, 292, 293, 294) corresponding to $[(C_6H_5)_2N_4BH]^{+\cdot}$; $[(p\text{-}ClC_6H_4)(C_6H_5)N_4BH]^{+\cdot}$; and $[(p\text{-}ClC_6H_4)_2N_4BH]^{+}$ were observed. All three of these fragmented by loss of N_2 to yield sets of peaks having the major ions 194; 228 and 262 respectively and these in turn were able to lose $(PhN\cdot)$; $(C_6H_4ClN\cdot)$ or $(PhN\cdot)$; and $(C_6H_4ClN\cdot)$ to give peaks at m/e 103; 103 or 137; and 137 respectively. Alternatively the $(P-N_2)^{+}$ ions from $(C_6H_4Cl)(C_6H_5)N_4BH$ and $(C_6H_4Cl)_2N_4BH$ could lose $Cl\cdot$ and in the latter case this could be followed by further loss of $Cl\cdot$.

(d) Product from the reaction of o-$MeC_6H_4NH_2BH_3$ with PhN_3

Two sets of parent ions were observed at m/e 221, 222, 223 and 235, 236, 237 corresponding to $[(C_6H_5)_2N_4BH]^{+\cdot}$ and $[(MeC_6H_4)(C_6H_5)N_4BH]^{+\cdot}$ respectively. Again the fragmentation of the $[Ph_2N_4BH]^{+\cdot}$ as in all the previous and subsequent cases was identical with that described in Chapter 5. It was interesting however that the first fragmentation observed was that of loss of $(N_2+H\cdot)$ to give ions at m/e 206, 207, 208, although the intensity of the 208 peak indicated that loss of N_2 occurred also.

(e) Product from the reaction of p-$CH_3C_6H_4NH_2BH_3$ with PhN_3

Three sets of parent peaks were observed at m/e 221, 222, 223; 235, 236, 237 and 249, 250, 251 due to $[(C_6H_5)_2N_4BH]^{+\cdot}$; $[(p\text{-}MeC_6H_4)(C_6H_5)N_4BH]^{+\cdot}$ and $[(p\text{-}MeC_6H_4)_2N_4BH]^{+\cdot}$. The high value of the m/e 221 peak together with a fairly intense peak at m/e 220 was attributable to loss of $(N_2+H\cdot)$ from the parent peak at m/e 250. Similarly loss of N_2 or $(N_2+H\cdot)$ from m/e 236 gave peaks at m/e 208 and 207 respectively.

Further fragmentation as in all of the products examined, was complex due to the cleavage of the aryl ring systems.

The mass spectrum of 2,5-di-p-chlorophenyl cyclotetrazenoborane

The mass spectrum of 2,5-di-p-chlorophenyl cyclotetrazenoborane is summarised in Figure [6-3], and ions with a relative abundance of greater than 1% are listed in Table 6-G.

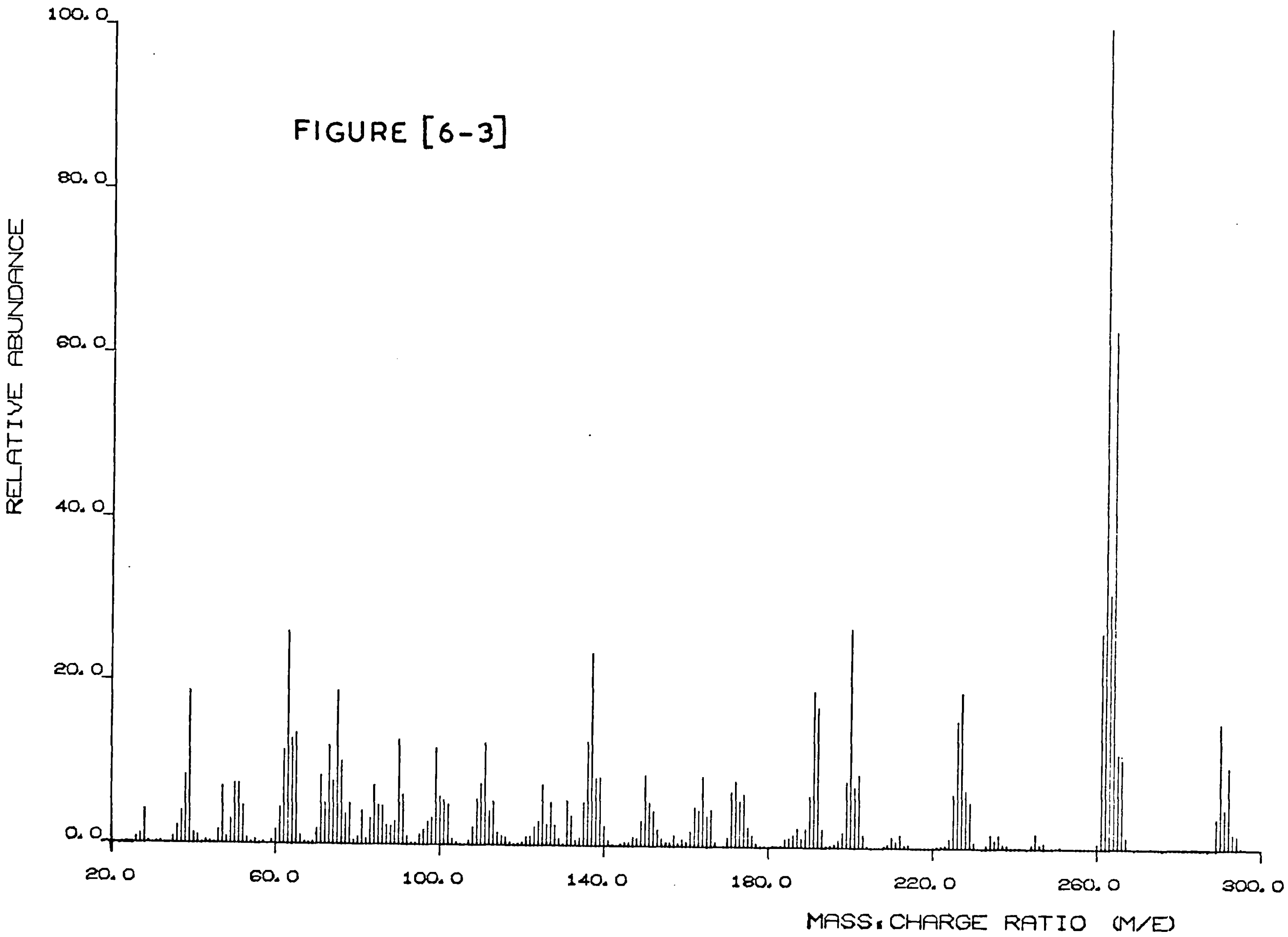
TABLE 6-G

MASS SPECTRUM OF 2,5-DI-p-CHLOROPHENYL CYCLOTETRAZENOBORANE

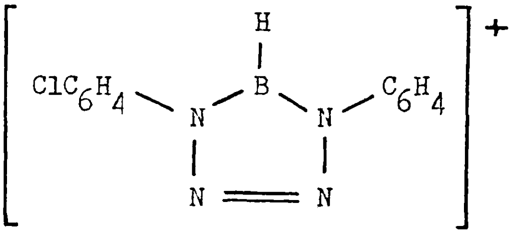
m/e	26	27	28	35	36	37	38	39	40	41	46	47	48	49	50	51
o/o	1	1	4	1	2	4	8	18	1	1	2	7	1	3	7	7
m/e	52	53	60	61	62	63	64	65	66	70	71	72	73	74	75	76
o/o	5	1	2	4	11	26	13	14	1	2	8	5	12	8	19	10
m/e	77	78	80	81	82	83	84	85	86	87	88	89	90	91	92	95
o/o	4	5	1	4	1	3	7	5	5	2	2	3	13	6	1	1
m/e	96	97	98	99	100	101	102	103	108	109	110	111	112	113	114	
o/o	2	3	3	12	6	5	5	1	2	6	7	12	4	5	2	
m/e	115	116	121	122	123	124	125	126	127	128	129	131	132	133	134	
o/o	1	1	1	1	2	3	7	3	5	2	1	5	4	1	1	
m/e	135	136	137	138	139	140	141	147	148	149	150	151	152	153	154	
o/o	5	13	23	8	8	2	1	1	1	3	9	5	4	2	1	
m/e	157	159	161	162	163	164	165	166	170	171	172	173	174	175	176	
o/o	1	1	2	5	4	8	4	5	1	7	8	5	6	2	1	
m/e.	184	185	186	187	188	189	190	191	192	193	197	198	199	200	201	
o/o	1	1	1	2	1	2	6	19	17	2	1	2	8	27	7	
m/e	202	203	210	211	212	224	225	226	227	228	229	230	234	235	236	
o/o	9	2	1	1	2	1	6	15	19	7	6	1	2	1	2	
m/e	245	247	260	261	262	263	264	265	266	267	289	290	291	292	293	
o/o	2	1	1	26	100	31	63	12	11	1	4	15	5	10	2	
m/e	294															
o/o	2															

FIGURE [6-3]

2, 5-DI-PARA-CHLOROHENYLCYCLOTETRAZENOBORANE



Parent ion peaks in the expected isotopic ratios were observed at m/e 289, 290, 291, 292, 293, 294. The first fragmentation observed was loss of N_2 to give the base peaks of the spectrum at m/e (261, 262, 263, 264, 265, 266) attributed to $[ClC_6H_4NB(H)NC_6H_4Cl]^+$, and this was confirmed by metastable ion peaks. An alternative minor fragmentation of the parent ion was the loss of Cl• to give the characteristic peak pattern due to



at m/e 244, 245, 246, 247. Loss of Cl• occurred from the $(M-N_2)^+$ peaks to yield ions at m/e 226, 227, 228 and 229 and these in turn could lose a further Cl• to give peaks at m/e 192, 191, both of these fragmentations being confirmed by metastable ions. Further fragmentation involved cleavage of the aryl rings. It was extremely satisfactory that a strong ion was observed at m/e 137 corresponding to $[ClC_6H_4N{=}BH]^+$ analogous to the observed fragmentations for phenyl cyclotetrazenoborane derivatives discussed in Chapter 5.

EXPERIMENTAL

The reaction of o-, m- and p-methyl or chloro substituted aniline-boranes with phenyl azide

The required freshly distilled primary aryl amine was dissolved in ether (40 ml) and diborane was condensed into it under vacuum

TABLE 6-H

EXPERIMENTAL DETAILS FOR THE REACTIONS OF SUBSTITUTED ANILINEBORANES

$XC_6H_4NH_2BH_3$ WITH PHENYL AZIDE

$XC_6H_4NH_2$ Xsubstituent	No.of g. mol. $XC_6H_4NH_2$ used	No. of g.mol. B_2H_6	No. of g.mol. PhN_3	Yield %*	Approx. M.Pt. °C observed	Analysis*
-o-CH_3	.042	.021	.042	very low	98	C,63.13; H,5.13; N,24.81; B,4.58. $C_{13}H_{13}N_4B$ requires C,66.14; H,5.55; N,23.73; B,4.58.
m-CH_3	.042	.021	.042	15	-	-
p-CH_3	.047	.023	.047	33	87	C,66.35; H,5.56; N,23.52; B,4.37. $C_{13}H_{13}N_4B$ requires C,66.14; H,5.55; N,23.73; B,4.58.
o-Cl	.045	.023	.045	very low	82	-
m-Cl	.042	.021	.042	36	-	C,53.61; H,4.03; N,19.65; B,4.12; Cl,14.82. $C_{12}H_{10}N_4BCl$ requires C,56.18; H,3.93; N,21.85; B,4.22; Cl,13.82.
p-Cl	.039	.019	.039	49	119→ 126	(A) C,47.25; H,3.01; N,18.9; B,3.69; Cl,22.58; (B) C,52.85; H,3.81; N,20.69; B,3.63; Cl,16.04. $C_{12}H_{10}N_4BCl$ requires C,56.18; H,3.93; N,21.85. B, 4.22; Cl,13.82.
Using excess p-$ClC_6H_4NH_2$	.094	.019	.039	73	121→ 129	C,52.04; H,3.72; Cl,17.61. $C_{12}H_{10}N_4BCl$ requires C,56.18 H,3.93; Cl,13.82.
p-NO_2	.033	.016	.033	-	-	C,43.05; H,4.19; N,14.05; B,5.43. $C_{12}H_{10}N_4BNO_2$ requires C,53.97; H,3.77; N,26.23; B=4.05

*Theoretical figures calculated assuming product to be the unsymmetrically N-substituted product.

and allowed to react. Freshly distilled phenyl azide was added to the amineborane formed and the mixture allowed to stir at room temperature. Details of the quantities of reactants used in the individual reactions are summarised in Table 6-H. The white adducts initially formed dissolved on stirring to form clear pale yellow solutions, the time required for stirring being dependent on the nature of the phenyl substituent and ranged from a few hours to a few days except for the o-Me derivative which required about six weeks. The reactants were then left to stand for several days and in some instances weeks.

Mixed cyclotetrazenoborane derivatives were obtained as white crystalline solids from all the reactions. In the reactions involving o- and m-phenyl substituents, the cyclotetrazenoborane products were isolated by concentration followed by low temperature crystallisation and filtration under an atmosphere of dry nitrogen whereas reactions involving p-substituents readily led to the formation of crystals at room temperature. The use of an excess of p-chloroaniline in the reaction of p-chloroanilineborane with phenyl azide gave rise to a substantial increase in the yield obtained. This product could be sublimed under vacuum over a range of temperature 140° - 160°. The fractions obtained had a higher melting point and contained progressively more of species 6-VIII, shown by mass spectrometry and infrared spectroscopy, with increase of temperature of sublimation.

However a single pure species could not be isolated, possibly because of rearrangement occurring at the temperature of sublimation.

Recrystallisation of the cyclotetrazenoborane products could be effected using benzene or light petroleum solvents under an atmosphere of dry nitrogen. The yields, melting points and elemental analyses obtained for the products are summarised in Table 6-H.

Attempted reaction: $XC_6H_4NH_2BH_3 + PhN_3 \longrightarrow (XC_6H_4)(Ph)N_4BH + 2H_2$

The reaction of p-nitroanilineborane with phenyl azide

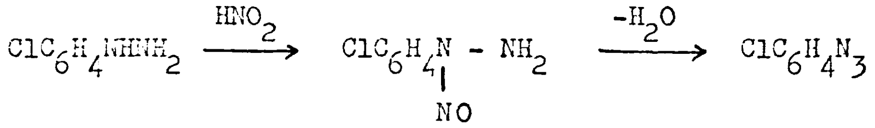
Diborane was condensed under vacuum into p-nitroaniline dissolved in 200ml of ether and allowed to react. Phenyl azide was then added and the reactants left to stir at room temperature. In about 30 minutes a bright yellow solid started to precipitate and this was obtained in large yield by leaving overnight and subsequent filtration in a dry nitrogen containing glove box. The product could not be purified by recrystallisation, sublimation or soxhlet extraction, and the infrared spectrum of the product was complex. An analysis obtained on a well washed sample of the crude product was not readily rationalised. The analysis figures and quantities of reactants used are shown in Table 6-H.

Attempted reaction: $pNO_2C_6H_4NH_2BH_3 + PhN_3 \longrightarrow (NO_2C_6H_4)(Ph)N_4BH + 2H_2$

Preparation of p-chlorophenyl azide

This was prepared in a similar manner to that for the preparation of phenyl azide (Chapter 3, p.115). In this way p-chlorophenyl hydrazine hydrochloride (25 g., 0.140 g.mol), used as supplied by Aldrych Chemicals, and was slowly reacted in hydrochloric acid solution in the presence of ether (100 ml.) solvent with a freshly prepared solution of sodium nitrite (15 g., 0.218 g.mol) keeping the temperature below 5°C. The p-chloro phenyl azide was extracted in ether solution by steam distillation followed by careful drying and vacuum distillation of the product. Care was taken to surround the distillation apparatus with blast screens in case of explosions. The product was identified by infrared, 'H N.M.R. and mass spectrometry. Yield = 8.72 g. (41 % Theoretical).

Reaction:



$$ClC_6H_4NHNH_2 \xrightarrow{HNO_2} ClC_6H_4\underset{\displaystyle NO}{\underset{|}{N}} - NH_2 \xrightarrow{-H_2O} ClC_6H_4N_3$$

Preparation of 2,5-di-p-chlorophenyl cyclotetrazenoborane

Diborane (0.019) g.mol was condensed into an ethereal solution of p-chloroaniline (5 g., 0.039 g.mol) under vacuum and allowed to react. To this was added p-chlorophenyl azide (5.98 g., 0.039 g.mol) and the reactants were stirred magnetically until all of the white precipitate initially formed dissolved to give a yellow solution. On standing for a few days at room temperature a crystalline product was obtained. This was filtered and recrystallised from benzene or light petroleum (80 - 100°). Surprisingly an attempt to purify the product by sublimation at 140 - 160° led to its decomposition, and p-Cl phenyl azide was liberated as a pale yellow liquid and identified by infrared spectroscopy. The di-p-chlorophenyl cyclotetrazenoborane was characterised by infrared, 'H N.M.R., "B N.M.R., and mass spectroscopy. Yield of product = 5.63 g. (50% Theoretical). [Found: C, 49.37; H, 3.21; N, 19.31; B, 3.66; Cl, 24.21%. $C_{12}H_9N_4BCl_2$ requires C, 49.55; H, 3.12; N, 19.26; B, 3.71; Cl, 24.36%.

<u>The reaction of Me_2N_4BH with Et_2N_4BH</u>

Me_2N_4BH and Et_2N_4BH were freshly distilled under vacuum and mixed together in equimolar quantities. A few drops of the mixture were placed into a number of small ampoules in a dry nitrogen containing glove box. The ampoules were sealed under vacuum and heated for a range of time from zero to 80 hours in a constant temperature fluidised sand bath. It was found that with increasing time of heating an increasing amount of $MeEtN_4BH$ was produced. The $MeEtN_4BH$ was detected (a) by mass spectrometry by the build up of the parent ion peak at m/e 112, and (b) by vapour phase chromatography which showed the build up of a third peak. This third peak had a similar shape, and a retention time intermediate to those for Me_2N_4BH and Et_2N_4BH which had been previously characterised. All three peaks showed a characteristic tailing at the end of the peak. It was of interest that at room temperature no formation of $MeEtN_4BH$ was observed.

Reaction:

$Me_2N_4BH + Et_2N_4BH \longrightarrow MeEtN_4BH, Me_2N_4BH, Et_2N_4BH$

The reaction of ethylamine-borane with methyl azide

Equimolar quantities of ethylamineborane, prepared directly from ethylamine and diborane, and methyl azide in dry diethyl ether solvent were heated in a sealed ampoule at 130° for 16 hours. Vacuum distillation of the reaction products led to the isolation of a colourless material in a trap at -35°C. The product was further purified by vacuum fractionation and was shown by mass spectrometry and vapour phase chromatography to be a mixture of Me_2N_4BH, $MeEtN_4BH$ and Et_2N_4BH.

Reaction: $EtNH_2BH_3 + MeN_3 \longrightarrow Me_2N_4BH, MeEtN_4BH, Et_2N_4BH$

The reaction of Me_2N_4BH with ethyl azide

Equimolar quantities of Me_2N_4BH and ethyl azide in diethyl ether solvent were heated in a sealed ampoule at 130° for 48 hours. Vacuum distillation of the reaction products gave a colourless volatile liquid in a trap at -40°C, which was shown by mass spectrometry and vapour phase chromatography to be a mixture of Me_2N_4BH, $MeEtN_4BH$

and Et_2N_4BH. A small amount of uncharacterised residue remained in the ampoule.

Reaction: $Me_2N_4BH + EtN_3 \longrightarrow Me_2N_4BH, MeEtN_4BH, Et_2N_4BH$

The new synthesis of $MePhN_4BH$ from methylamineborane and phenyl azide

Equimolar quantities of methylamineborane, prepared directly from methylamine and diborane, and phenyl azide in diethyl ether solvent were heated in a sealed ampoule at 130°C for 36 hours. The reaction products were then vacuum distilled when the first product collected in a trap at -30°C was Me_2N_4BH which distilled at room temperature, and was characterised by infrared and mass spectrometry. The second product isolated was $MePhN_4BH$ which distilled at 60°C under high vacuum, and this was confirmed by infrared, ^{11}B and ^{1}H N.M.R. spectrometry. The residue, although impure was shown to contain some Ph_2N_4BH by its infrared spectrum. Yield of $MePhN_4BH$ = 65%.

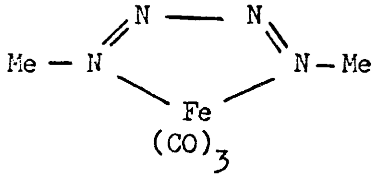
Reaction: $MeNH_2BH_3 + PhN_3 \longrightarrow Me_2N_4BH, MePhN_4BH, Ph_2N_4BH$

CHAPTER VII

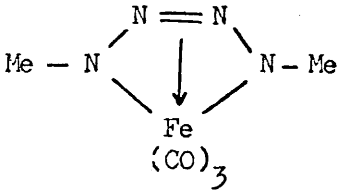
OTHER REACTIONS OF CYCLOTETRAZENOBORANES AND RELATED SYSTEMS

Many of the reactions attempted and described in this chapter have not been completely characterised, and further work will be required before the often complex reaction systems are fully understood.

It was anticipated that it should be possible to prepare systems related to the cyclotetrazenoboranes, in which the boron atom was replaced by another element. Only recently has one such system been briefly reported[107], but there is still some doubt about its structure and systems 7-Ia and 7-Ib have been suggested.

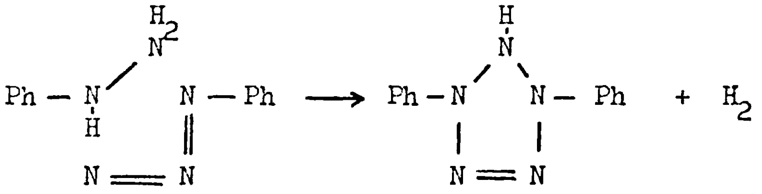


7-Ia



7-Ib

An attempt to prepare a cyclic pentazene by the reaction scheme 7-1 by heating phenyl hydrazine and phenyl azide in diethyl ether solvent led to the isolation of a deep red product together

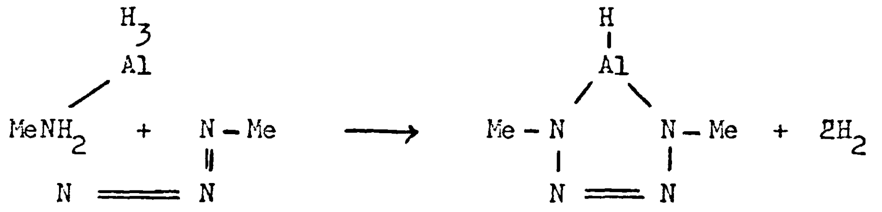


(7-1)

with the liberation of a small quantity of nitrogen. The infrared spectrum of the product showed the presence of phenyl stretching, deformation and overtone vibrations, and also an intense N-H stretching frequency. The absence of an azide stretching frequency in the compound was interesting. Elemental analysis did not establish a simple stoichiometric formula for the compound.

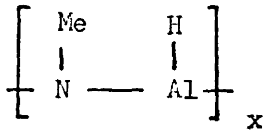
In analogy with the reaction of lithium borohydride with methylamine hydrochloride and methyl azide which led to the isolation of Me_2N_4BH, it was considered that the reaction of lithium aluminium hydride with methylamine hydrochloride and methyl azide might lead to the formation of an aluminium-nitrogen ring compound, by the reaction scheme shown in 7-2.

$$LiAlH_4 + MeNH_2.HCl \longrightarrow [MeNH_2.AlH_3] + LiCl + H_2$$



(7-2)

The white product isolated from the reaction however was shown by elemental analysis to have the empirical formula CH_3NAlH and was possibly an aluminium-nitrogen linked polymer, 7-II

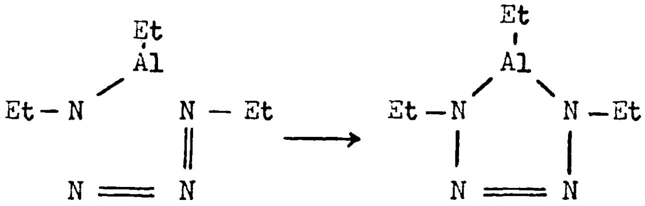


$$\left[\overset{\overset{Me}{|}}{N} - \overset{\overset{H}{|}}{Al} \right]_x$$

7-II

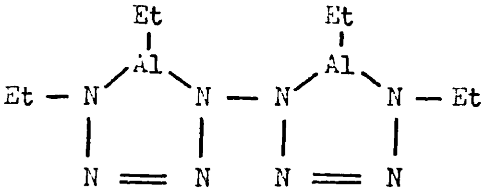
Another possible route to the five-membered aluminium-nitrogen ring system was by the reaction of Et_2AlN_3 and EtN_3, in an analogous fashion to that for the reaction of Ph_2BN_3 and PhN_3 (see Chapter 3), as shown in 7-3. The reactions led initially to

$$Et_2AlN_3 \longrightarrow [EtAl = NEt] + N_2$$



(7-3)

the formation of a white adduct, which was essentially unchanged on heating at 130° for six hours, but prolonged heating for either (a) 24 hours or (b) 9 days led to the formation of red-brown insoluble compounds with nitrogen evolution. Full elemental analysis obtained on the separate products from reactions with heating conditions (a) and (b) added quantitatively to 100%, and tended to indicate the formation of compounds with empirical formula $C_7H_{16}Al_2N_8$ and $C_4H_{10}AlN_4$ respectively. It was interesting that the empirical ratios of Al:N were 1:4 in both cases and the possibility of a five-membered AlN_4 ring cannot not be excluded. The $C_4H_{10}AlN_4$ could be rationalised in terms of coordinated polymeric structures or as the simple dimer 7-IV, although insufficient evidence is yet available to confirm this.



7-IV

The structure for a compound of molecular formula $C_7H_{16}Al_2N_8$ was not readily understood.

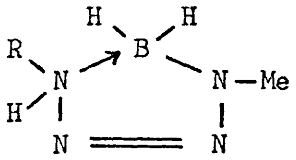
In view of the possible π-delocalisation of the electrons in the cyclotetrazenoborane ring, it was of interest to test the potential formation of π-complexes with metal carbonyl derivatives.

The attempted direct reaction of $Mo(CO)_6$ with Me_2N_4BH in tetrahydrofuran solvent led only to the recovery of unchanged $Mo(CO)_6$ and Me_2N_4BH, which was shown by infrared spectroscopy to be contaminated with a carbonyl grouping.

It has only recently been reported[108] that the reaction of hexamethylborazine with $(CH_3CN)_3Cr(CO)_3$ led to the isolation of the π-complex $Me_3N_3B_3Me_3.Cr(CO)_3$. The attempted reactions of $(CH_3CN)_3\ M(CO)_3$ where M = Mo, Cr or W, with Me_2N_4BH or with the more hydrolytically stable Me_2N_4BMe led in all cases to the isolation of compounds, in which infrared spectroscopy indicated the presence of the cyclotetrazenoborane and also complex metal carbonyl vibrations. The compounds obtained were very unstable and were not isolated in a pure form.

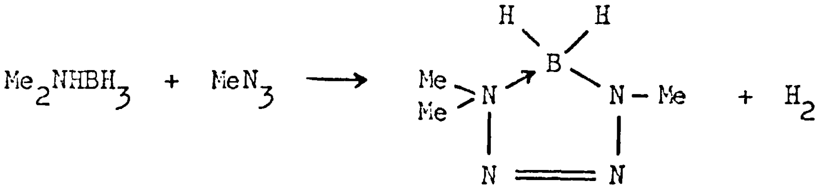
Further, it was anticipated that it might be possible to prepare charge transfer complexes in a similar manner to that observed for borazines,[109] by the reaction of cyclotetrazenoborane derivatives with tetracyanoethylene. In an investigation conducted in collaboration with Wells,[110] it was found that on mixing cyclohexane solutions of Me_2N_4BH and tetracyanoethylene the immediate formation of a yellowish colour was observed but an effervescence was also noted and the electronic spectrum observed varied rapidly with time. Similarly, the reaction of the hydrolytically stable Me_2N_4BMe also led to the immediate formation of a yellow-red coloration. An electronic spectrum run immediately on this solution indicated the formation of a broad band showing some complex resolution at approximately 400 mμ possibly suggesting the initial production of a charge transfer complex. (N.B. B-trimethyl-N-trimethyl borazine + tetracyanoethylene in chloroform give a broad charge transfer band at λ_{max} 461 mμ). The electronic spectrum however changed rapidly and this became obscured, probably due to a secondary reaction occurring and the system was not investigated further.

Secondary uncharacterised crystalline by-products were observed in many of the preparations of cyclotetrazenoborane derivatives from the reactions of primary amineboranes with organic azides. It was considered that some of these might correspond to intermediate products in the preparation of cyclotetrazenoboranes of type 7-IV.



7-IV

It was anticipated that the reaction of dimethylamineborane with methyl azide would also form a similar intermediate to 7-V as shown in the reaction scheme 7-4.



(7-4)

7-V

When this reaction was performed by heating at 140°C for 48 hours in the absence of solvent a colourless product was isolated. Infrared spectroscopy indicated that the product contained a BH_2 group, and also the characteristic high frequency B-H vibration attributable to a cyclotetrazenoborane derivative was observed. Preparative scale vapour phase chromatography led to the separation of a fraction shown to be pure Me_2N_4BH by infrared and mass spectrometry, and a trace of a second product whose infrared spectrum showed a more complex B-H vibration around 2450 cm^{-1}, but which was not identified further. The reaction was repeated in the presence of ether solvent* by heating either (a) at 70°C for 15 hours, or (b) at 130°C for 15 hours. Vacuum distillation of the products from these reactions led to the separation of colourless liquids in traps at -40°C.

* FOOTNOTE

This was done in view of the potentially explosive nature of these reactions in the absence of solvent, (see Chapter 3).

Reaction conditions (a) led only to the isolation of Me_2N_4BH, characterised by infrared and mass spectrometry, whereas using the conditions (b) in addition to Me_2N_4BH a further product was present. The infrared spectrum of this showed a B-H vibration at 2450 cm^{-1} and the mass spectrum showed a set of ions at m/e 123, <u>122</u>, 121, 120 in isotopic ratios characteristics of a species containing three boron atoms attributable to N-trimethylborazine for which the major ion in this set is known to be m/e 122 and not the predictable value of m/e 123.[111]

The Me_2N_4BH prepared in these reactions was presumably produced by the reaction 7-5.

$$Me_2NHBH_3 + MeN_3 \longrightarrow Me_2N_4BH + H_2 + CH_4 \qquad (7\text{-}5)$$

Attempts to prepare the parent cyclotetrazenoborane, H_2N_4BH by the reaction of hydrazoic acid and ammoniaborane were unsuccessful.[95] It was considered feasible that this compound might be preparable by the reaction of ammonium azide with diborane, as shown in 7-6.

$$NH_4N_3 + \tfrac{1}{2}B_2H_6 \longrightarrow H_2N_4BH + 2H_2 \qquad (7\text{-}6)$$

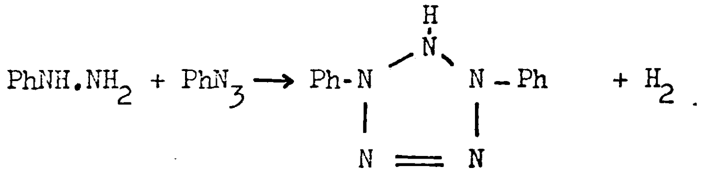
In practice the reaction led to the isolation of a white glue-like solid together with hydrogen evolution. An infrared spectrum of the solid product showed the presence of intense N-H, B-H and azide vibrations. The "B N.M.R. spectrum of the solid product in ether solution gave a well resolved doublet at 3.9 ppm relative to $BF_3.Et_2O$, J_{B-H} = 114 c.p.s., indicative of a four coordinate boron species. In the 'H N.M.R., three broad peaks were observed at approximately 5.48, 7.68, 9.70 τ which showed some complex resolution at high sensitivity. The rest of the spectrum was obscured by diethyl ether resonances. Elemental analysis showed the compound to contain an extremely large percentage of nitrogen but was not readily rationalised with a simple molecular structure.

EXPERIMENTAL

The attempted preparation of 2,5-diphenyl cyclopentazene

Phenyl hydrazine (0.540 g. 0.005 g.mol), phenyl azide (0.595 g, 0.005 g.mol) and diethyl ether solvent were sealed in an ampoule under vacuum and heated to 130° for 24 hours. A dark red liquid was produced and the gas liberated was collected using a Topler pump and shown by mass spectrometry to be nitrogen (0.0028 g.mol). The ether solution was concentrated and on addition of light petroleum (60 - 80°) a red precipitate was isolated which could be recrystallised from ether-light petroleum. Elemental analysis was incomplete and found C, 69.3; H, 6.38; N, 19.3; which gave an empirical ratio of C:H:N of 5.78:6.38:1.37.

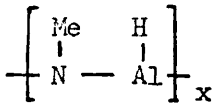
Attempted reaction:



The reaction of lithium aluminium hydride with methylamine hydrochloride and methyl azide

Equimolar quantities of $LiAlH_4$ and methylamine hydrochloride dissolved in diethylether solvent under vacuum were allowed to react at -78°C. On warming slightly one molar equivalent of gas was evolved, which was collected using a Töpler pump and shown to be hydrogen by mass spectrometry. Methyl azide (1 molar equivalent) was condensed into the reaction ampoule under vacuum and the reactants allowed to warm up slowly. The reaction products were then filtered at -78° and washed with recondensed ether using a low temperature vacuum filtration apparatus. Removal of the ether from the filtrate by vacuum distillation led to the isolation of a white solid. [Found C, 21.20; H, 7.04; N, 24.52; Al, 47.24 (by difference). CH_3NAlH requires C, 21.06; H, 7.07; N, 24.56; Al, 47.31].

Attempted reaction: $LiAlH_4 + MeNH_2.HCl + MeN_3 \rightarrow Me_2N_4AlH + LiCl + 3H_2$



Observed reaction: $LiAlH_4 + MeNH_2.HCl + MeN_3 \rightarrow \left[\overset{Me}{\underset{}{N}} - \overset{H}{\underset{}{Al}} \right]_x$

Preparation of diethylaluminium azide

For this reaction and for the reaction of diethyl aluminium azide with ethyl azide (to follow), a glove box was very carefully purged with dry nitrogen, the last traces of oxygen being removed using B.T.S. Katalysator supplied by

Badische Anilin and Soda-Fabrik A.G. (Germany), and also by leaving a small amount of free Et_2AlCl in the box.

The preparation of Et_2AlN_3 was achieved by the method reported by Prince and Weiss[112]. Finely powdered sodium azide, (4.5 g, 0.069 g.mol) which had been vacuum dried for several days at 115°, slurried in 50 ml of dry benzene, was treated at room temperature with vigorous stirring, with diethylaluminium chloride (8.30 g, 0.069 g.mol) as supplied by Cyclo Chemicals Ltd. There was a gradual change in the appearance of the solid which after 24 hours failed to settle without agitation. Filtration gave a clear solution, which tests showed to contain no chloride. Removal of the benzene from the solution by vacuum distillation and refiltration left diethylaluminium azide as a mobile colourless liquid.

Reaction: $Et_2AlCl + NaN_3 \longrightarrow Et_2AlN_3 + NaCl$

The reaction of diethylaluminium azide with ethyl azide

Three ampoules were prepared which were connected via taps to suitable B.10 vacuum line connections, and these were thoroughly purged with dry nitrogen and weighed. The freshly prepared diethyl aluminium azide was filtered under vacuum directly into the ampoules, the taps of which were then closed and the ampoules reweighed. In three separate experiments, vacuum condensation of an equimolar quantity of ethyl azide into the ampoules was followed by vacuum distillation of diethyl ether from $LiAlH_4$ into two of the ampoules (A and B), and light petroleum (40 - 60°) into the other ampoule (C). The ampoules were then sealed under vacuum and allowed to warm up slowly to room temperature. Initially, clear solutions were obtained and in the case (C) two separate clear liquid layers were observed probably corresponding to Et_2AlN_3 and the solution of ethyl azide in light petroleum. On further standing in all three cases, a turbidity was observed, followed by precipitation without effervescence of a white solid which was possibly an adduct.

Tube A on heating to 130° for 6 hours was shown to contain only a trace of liberated nitrogen, and the white solid produced was filtered in the glove box. The filtrate was fractionated under vacuum and shown to contain unreacted Et_2AlN_3, ether and a trace of ethyl azide. The white solid was not identified. Tube B on heating to 130° for 20 hours produced a red tar-like compound together with a red coloured solution, and about 0.6 molar equivalents of liberated N_2. On cooling to -196°C followed by warming to room temperature the red tar-like compound was converted to a dark red-brown solid, which was filtered in a dry nitrogen containing glove box. It was not found to be readily recrystallised from common organic solvents. (Found C, 31.82; H, 5.97; Al, 20.24; N, 41.72. $C_7H_{16}Al_2N_8$ requires C, 31.58;

H, 6.06; Al, 20.27; N, 42.09). The filtrate was fractionated under vacuum and shown to contain a small amount of an involatile viscous red oil as well as some unreacted EtN_3 and solvent ether. The viscous red oil showed an intense azide stretching frequency, but was not fully characterised.

Tube C was unchanged after heating to 130° for 4 hours, but after 20 hours the reaction appeared identical with that obtained from Tube B. The heating was continued for another 8 days to ensure completion of the reaction, and the ampoule was then found to contain almost 1 molar equivalent of liberated N_2 using a Töpler pump. Again the red tar produced in the reaction solidified on cooling to -196°C and warming to room temperature, and was isolated by filtration in a dry nitrogen containing glove box, but could not be recrystallised unchanged. [Found C, 34.56; H, 6.89; Al, 19.15; N, 39.00. $C_4H_{10}AlN_4$ requires C, 34.04; H, 7.12; Al, 19.12; N, 39.70].

Attempted reaction: $Et_2AlN_3 + EtN_3 \longrightarrow Et_2N_4AlEt + N_2$

<u>Reaction of Me_2N_4BH with molybdenum carbonyl</u>

$Mo(CO)_6$ (5.61 g., 0.021 g.mol) was sealed in an ampoule under vacuum with dry tetrahydrofuran solvent (20 ml) and Me_2N_4BH (1.53 g, 0.015 g.mol). No apparent reaction was observed at room temperature, but on heating at 90°C for 24 hours all of the $Mo(CO)_6$ dissolved and a brownish solution was obtained, which was allowed to stand at room temperature for 2 days. The ampoule was opened under vacuum and shown to contain only a trace of uncondensed gas (0.0016 g.mol), shown to be carbon monoxide by infrared spectroscopy, and vacuum fractionation of the products through a trap at -30°C led to the isolation of a colourless product. An infrared spectrum of this product showed the presence of a strong C = O stretching frequency at 1970 cm^{-1} probably due to the presence of some sublimed $Mo(CO)_6$, but was otherwise identical with that for Me_2N_4BH. Further vacuum fractionation did not lead to the recovery of pure Me_2N_4BH. Vacuum sublimation of the solid product led only to the isolation of unchanged $Mo(CO)_6$.

Preparation of $(MeCN)_3Mo(CO)_3$, $(MeCN)_3Cr(CO)_3$ and $(MeCN)_3W(CO)_3$

These tris-nitrile derivatives were prepared by the method of Tate et al.,[113] by the direct reaction of metal carbonyl in excess refluxing acetonitrile, when almost quantitative evolution of 3 moles of gas was obtained. The reaction time required was dependent on the metal derivative used. Thus $Mo(CO)_6$, $Cr(CO)_6$ and $W(CO)_6$ required 4, 24 and 48 hours refluxing time respectively. The excess acetonitrile was removed in each case by vacuum distillation and the products used without further purification.

Reaction: $M(CO)_6 + 3MeCN \longrightarrow (MeCN)_3M(CO)_3 + 3CO$

The attempted preparation of $Mo(CO)_3.Me_2N_4BH$

$Mo(CO)_3(MeCN)_3$ was stirred at room temperature with an equimolar quantity of Me_2N_4BH in dry dioxan solvent. No apparent reaction took place on standing overnight and the reactants were therefore refluxed for 1 hour under an atmosphere of dry nitrogen when the solid darkened in colour. The solution was filtered free of dark solid and the solvent distilled from the filtrate under vacuum, when a red product was isolated. An infrared spectrum taken immediately on the product indicated the presence of both Me_2N_4BH and a strong complex carbonyl vibration, but on standing for 14 days a change in the spectrum indicated that the product had decomposed. Extraction of a small quantity of almost unchanged product was achieved by recrystallisation under an atmosphere of dry nitrogen with ether or light petroleum (40 - 60°) but the attempted recrystallisation from benzene led to its decomposition. An attempt to purify the product by vacuum sublimation also led to decomposition of the product and a vapour was condensed on the probe which was shown by infrared spectroscopy to be Me_2N_4BH.

Attempted reaction: $Mo(CO)_3(MeCN)_3 + Me_2N_4BH \rightarrow Mo(CO)_3.Me_2N_4BH$

The attempted preparation of $Cr(CO)_3(Me_2N_4BH)$

Me_2N_4BH (1.29 g, 0.013 g.mol) and 1,4-dioxan dried over $LiAlH_4$ were cold condensed onto $Cr(CO)_3(MeCN)_3$ (0.011 g.mol) and allowed to stir magnetically at room temperature for 16 hours. [Care $Cr(CO)_3(MeCN)_3$ is pyrophoric]. The yellow product obtained was filtered in a dry nitrogen containing glove box, but showed some signs of decomposition, dark yellow tar-like materials being isolated. The solvent was removed from the yellow-brown coloured dioxan filtrate by vacuum distillation and again a solid product was isolated. The infrared spectra of the products showed the presence of both Me_2N_4BH and complex carbonyl vibrations but attempts to purify the products by sublimation and recrystallisation were unsuccessful.

Attempted reaction: $Cr(CO)_3(MeCN)_3 + Me_2N_4BH \longrightarrow Cr(CO)_3Me_2N_4BH + 3MeCN$

The attempted preparation of $W(CO)_3.(Me_2N_4BMe)$.

$W(MeCN)_3(CO)_3$ (0.0032 g.mol) were stirred magnetically for 3 days at room temperature with Me_2N_4BMe (0.86 g., 0.0077 g.mol) in dry 1,4-dioxan giving a brown liquid. Filtration in a dry nitrogen containing glove box yielded a small quantity of a brown-blue solid. The solvent was removed from the filtrate by vacuum distillation at room temperature leaving a brown product, an infrared spectrum of which showed the presence of Me_2N_4BMe and a complex carboxyl vibration. Sublimation of the product led only to its decomposition and mass spectra of the crude products did not yield evidence for the formation of the required complex.

Attempted reaction: $W(MeCN)_3(CO)_3 + Me_2N_4BMe \rightarrow W(CO)_3.Me_2N_4BMe + 3MeCN$

The reaction of dimethylamineborane with methyl azide

Equimolar quantities of dimethylamineborane, prepared directly from dimethylamine and diborane, and methyl azide were sealed in ampoules (a) in the absence of solvent [Care! see footnote, page 241], and (b) in a later reaction in the presence of diethyl ether solvent.

Ampoules prepared as in (a) were heated to 140° for 48 hours, and the reaction products vacuum distilled through a trap at -40°C. An infrared spectrum on the product collected from this trap showed the presence of two products containing boron-hydrogen bonds, but these could not be separated by vacuum fractionation. Preparative scale vapour phase chromatography led to the isolation of a very small quantity of each of the two principal components detected. Infrared spectroscopy and mass spectrometry showed the least volatile of these products to be pure Me_2N_4BH. The other product however tended to decompose on the column and block the exit tip, and the resulting small amount of product isolated gave an infrared spectrum which indicated the absence of a high frequency B-H mode of cyclotetrazenoboranes, but confirmed the presence of a more complex B-H vibration near 2450 cm^{-1}.

Ampoules prepared as in (b) were heated either (i) at 70°C for 15 hours or (ii) at 130° for 15 hours. Vacuum distillation of the products from these reactions led to the isolation of colourless products in traps at -40°C. Only a very small yield of this volatile product was obtained from reaction (i) and was shown to be pure Me_2N_4BH by infrared and mass spectroscopy. The infrared spectrum of the product from reaction (ii) was shown to contain not only the characteristic high frequency B-H vibration of Me_2N_4BH but also another B-H mode at 2450 cm^{-1}. A mass spectrum of the product showed the presence of parent ions for Me_2N_4BH and also a group of ions at m/e 123, <u>122</u>, 121, 120 whose relative abundances were typical of ions containing three boron atoms. This was attributable to N-trimethyl borazine for which the mass spectrum is known.[111]

In all the reactions secondary crystalline products were obtained, but were not fully characterised.

Attempted reaction: $Me_2NHBH_3 + MeN_3 \longrightarrow Me_3N_4BH_2 + H_2$

Observed reaction: $Me_2NHBH_3 + MeN_3 \longrightarrow Me_2N_4BH + H_2 + CH_4$

<u>The reaction of ammonium azide with diborane</u>

Ammonium azide (0.786 g. 0.0131 g.mol) was transferred to a 100 ml ampoule with diethyl ether 8 mls, and diborane (0.0066 g.mol) was condensed under vacuum into the ampoule which was then sealed. The NH_4N_3 which had previously been insoluble in the ether dissolved with the evolution of a colourless gas. The ampoule was heated to 140° for 24 hours and allowed to stand for several months when an almost clear solution was obtained. The gas evolved during the reaction was collected (0.0324 g.mol) and shown to be entirely hydrogen by mass spectrometry. The products of the reaction were vacuum distilled when the only volatile compound detected was solvent ether. A white polymeric glue-like compound remained in the ampoule. This was purified by redissolving in ether, filtering in a dry nitrogen-containing glove box and removing the solvent under vacuum. The product was sensitive to the laboratory atmosphere. The sample was insoluble in $CDCl_3$ and reacted with acetone. [Found C, 2.05; H, 4.79; B, 16.62; N, 65.1].

Attempted reaction: $NH_4N_3 + \frac{1}{2}B_2H_6 \longrightarrow H_2N_4BH + 2H_2$

CHAPTER VIII

EXPERIMENTAL AND INSTRUMENTAL TECHNIQUES

Vacuum Techniques

A general purpose preparative vacuum frame was designed and used throughout the work described. A separate section of the frame incorporated an analytical section with a Töpler pump for gas analysis. Standard attachments were used for vacuum filtration sublimation, and distillation. Thick walled ampoules (100 — 150 mls) were designed to enable them to be opened under vacuum. Distillation on the vacuum frame was effected by surrounding the traps on the frame by slush baths or liquid nitrogen.

Glove-box techniques

A preparative Lintott glove box, fitted with a 18" entry port, a shelf and metal grid for support of apparatus was thoroughly purged with dry nitrogen and dried with trays of molecular sieves and phosphorus pentoxide. For experiments requiring the complete absence of oxygen a B.T.S. Katalysator supplied by Badische Anilin and Soda-Fabrik A.G., Germany was introduced into the box. A fan was used to ensure circulation of the gas in the glove box. A gas tight electrical supply into the box allowed for the use of mechanical and magnetic stirrers, and a hot plate. Small outlet pipes allowed a vacuum pump to be connected to apparatus in the box for filtration and distillation purposes. When not in use the glove ports were kept closed to minimise gas diffusion through the neoprene gloves.

Vapour phase chromatography

Vapour phase chromatography was performed on an analytical scale using a Perkin Elmer F11 gas chromatograph. A column of length 4 metres and $\frac{1}{8}$" internal diameter, made of stainless steel and packed with dimethyl silicone ($2\frac{1}{4}\%$) on chromosorb G (80 - 100 mesh) was used on all occasions. Preparative scale V.P.C. was done on a Wilkins Aerograph Autoprep 705 using a column of length 20 ft and internal diameter $\frac{3}{8}$" made of aluminium and packed with SE 30 on chromosorb W (45 - 60).

Infrared Spectra

These were recorded on a Grubb-Parsons Spectromaster grating spectrometer between 4000 and 400 cm^{-1} and the observed frequency bands listed for the various five-membered ring derivatives were run on this instrument. In addition the spectra were run on a Unicam S.P.200 spectrometer between 5000 cm^{-1} and 650 cm^{-1} and these were reproduced in the Figures shown throughout this thesis. The spectra were run for thin films of pure liquids or as nujol mulls or KBr pressed discs for solids. Vapour spectra were obtained in a 10 cm cell with KBr windows.

Raman Spectrum

The Raman spectrum of pure liquid Et_2N_4BH was obtained on a Hilger and Watts E.612 Spectrograph fitted with flint glass prisms and PL12 mercury arc source with potassium nitrite filter.

The exciting line was the Hg 4358 Å line. The spectrum was recorded photographically and measured using a travelling microscope. The frequency shifts were calculated using the following Algol computer program which was written for an Elliott 4120 computer as in Table 8-A.

The data format for the program J.B.L.1.

X,Y,Z and E,F,G are two sets of constants dependent on the instruments in different regions of the spectrum.

I is the value of the frequency at which changeover to use of constants E,F,G rather than X,Y,Z occurs.

H is the wavelength of the exciting line.

N is the number of travelling microscope readings taken of the spectrum from the photographic plate.

S is the travelling microscope reading of the reference line (in this case the Hg 4343 Å) to which those for the observed lines should be compared.

T represents the series of travelling microscope readings of the observed lines in the spectrum.

TABLE 8-A

```
PAGAN JPL1;
"BEGIN" "INTEGER" N, A;
   "REAL" X, Y, Z, E, F, G, S, I, T, H;
   "REAL" X, Y, Z, E, F, G, I, H, N, S;
   A := N;
   "BEGIN" "REAL" "ARRAY" D[1 : A], L[1 : A];
       A := 0;

INPUT: "READ" T;
       A := A + 1;
       D[A] := T;
       "IF" A < N "THEN" "GO TO" INPUT;
       "PRINT" PREFIX(','), ' POSITION,FREQUENCY
             CM-1   ';
       "IF" D[1] > S "THEN" "GO TO" NEXT "ELSE" "GO TO"
       ALTERNATIVE;

NEXT: "FOR" A := 1 "STEP" 1 "UNTIL" N "DO"
       "BEGIN" L[A] := 1000000000.0*((1/H) -
          (1/(X + Y/(Z + ABS(S - D[A])))));
          "IF" L[A] > I "THEN" L[A] := 1000000000.0*
          ((1/H) - (1/(E +F/(G + ABS(S - D[A])))));
          "PRINT" ALIGNED(4, 3), D[A], PREFIX(','),
          ALIGNED(5, 1), L[A];
       "END";
       "GO TO" ZEROS;

ALTERNATIVE: "FOR" A := 1 "STEP" 1 "UNTIL" N "DO"
       "BEGIN" L[A] := 1000000000.0*((1/H) -
          (1/(X + Y/(Z - ABS(S - D[A])))));
          "IF" L[A] > I "THEN" L[A] := 1000000000.0*
          ((1/H) - (1/(E + F/(G - ABS(S - D[A])))));
          "PRINT" ALIGNED(4, 3), D[A], PREFIX(','),
          ALIGNED(5, 1), L[A];
       "END";

ZEROS:
   "END";
"END";  .
```

Nuclear Magnetic Resonance Spectra

These were obtained on a Perkin Elmer R.10 Spectrometer, at 60 MHz for ^{1}H and 19.3 MHz for ^{11}B spectra. Proton chemical shifts were obtained with reference to internal tetramethylsilane as standard, and solutions in usually non-protonic solvents or pure liquids were used. ^{11}B chemical shifts were obtained with reference to external $BF_3.Et_2O$.

Ultraviolet Spectra

These were obtained on a Unicam SP.800 Spectrophotometer. The λ_{max} values for the volatile compounds were obtained from vapour spectra, and those for the non-volatile compounds were obtained as solutions in cyclohexane. The extinction coefficients of the latter compounds were measured directly, but those of the vapours were estimated from the sides of the bands observable in cyclohexane solution.

Mass Spectra

The mass spectra were obtained on A.E I. M.S.2, M.S.9 and M.S.12 mass spectrometers. Solid compounds were introduced by direct insertion probes, and volatile liquids by cold inlet and hot box systems.

Two computer programs have been written to assist in the handling of mass spectrometry data.

Program J.B.L. 4., shown in Table 8-B using crude intensity data, prints out in columns the mass peak (m/e), the crude intensity figure fed in, the relative intensity of the peak

TABLE 8-B

```
 JBL 4;
 "BEGIN"  "INTEGER"  I,  J,  N,  M,  S,  T,  X,  Y,  Z;
    "REAL"  B,  D,  E,  K,  L,  U,  V,  SUM;
   "INTEGER"  "ARRAY"  A[0 : 50];
    I := 0;INSTRING(A,  I);I := 0;OUTSTRING(A,  I);
    "READ"  U,  X,  B,  K,  Y;
    "PRINT"  PREFIX(',`),
    'L`        M/E   , INTENSITY ,   REL INT   ,   100I/SIGMA I  `;
    "BEGIN" "REAL" "ARRAY" P[1 : X], C[1 : X], R[1 : X];
       N := 0;T := 0;E := K - U;V := 0;SUM := 0;
 STEP A: E := E + U; N := N + 1; P[N] := E;
       "IF"  N < X  "THEN"  "GO TO"  STEP A;
 STEP B: "READ"  L;
        T := T + 1;C[T] := L; R[T] := L*100/B;SUM := SUM + L;
       "IF"  T < X  "THEN"  "GOTO"  STEP B;
        T := 0;
 STEP B2: T := T + 1;
        "IF"  R[T] > V  "THEN"  V := R[T];
        "IF"  R[T] > 0.1 "THEN" "PRINT" ALIGNED(5, 2),P[T],
        PREFIX(' ,`), ALIGNED(7, 1), C[T], ALIGNED(5, 2),
        R[T], ALIGNED(5,  2), C[T]*100/SUM;
       "IF"  T < X  "THEN"  "GO TO"  STEP B2;
       V := (ENTIER((V + 9)/10))*10;
        S := (ENTIER(P[1]/10))*10;
        D := (ENTIER((P[X] + 9)/10))*10;
        "IF"  (D - S)*Y/U > 1600  "THEN"  "GO TO"  STEP D
        "ELSE" "GO TO"  STEPC;
STEP C: SET ORIGIN(500,  0); WAY(0,  3);
        "FOR" J := 0  "STEP" 1 "UNTIL" 5 "DO" "BEGIN"
        DRAWLINE(0,  200*J); DRAWLINE( - 12,  200*J);
        MOVEPEN( - 130,  200*J);
           "PRINT" PUNCH(5), DIGITS(2), ALIGNED(5, 1),V*J/5;
           MOVEPEN(0,  200*J);
        "END";
        MOVEPEN( - 110,  400); WAY(1,  4);
        "PRINT"  PUNCH(5),  'RELATIVE ABUNDANCE`;
        MOVEPEN((D - S)*Y - 800,  1090);
        WAY(0,  4); PUNCH(5);
        I := 0; OUTSTRING(A,  I);
        PUNCH(1); MOVEPEN(0,  0);
        "FOR" M := 0 "STEP" 1 "UNTIL"
       ENTIER(Y*(D - S)/200 + 0.99) "DO"
         "BEGIN"  DRAWLINE(200*M,  0);
```

CONTINUED

```
          DRAWLINE(200*M, -12); MOVEPEN(200*M -90, - 50);
          WAIT(0,  3);
          "PRINT" PUNCH(5), DIGITS(2), ALIGNED(5, 1),
         S + (M*200/Y); MOVEPEN(200*M,  0);
     "END";
      MOVEPEN((D - S)*Y - 550,   - 100); WAIT(0,  4);
      "PRINT"  PUNCH(5),  'MASS:CHARGE RATIO (M/E)';
      "FOR"  Z := 1  "STEP"  1  "UNTIL"  X  "DO"
      "BEGIN"  MOVEPEN((P[1] - S - D)*Y + (Z*Y*D), 0);
         DRAWLINE((P[1] -S -D)*Y + (Z*Y*D),R[Z]*1000/V);
      "END";
      MOVEPEN((D - S)*Y,  0);
      STOP;
STEPB: SET ORIGIN(2400,  1); WAIT(0,  3);
     "FOR"  J := 0  "STEP"  1  "UNTIL"  10  "DO"
      "BEGIN" DRAWLINE(0, 200*J); DRAWLINE( -12, 200*J);
         MOVEPEN( - 130,  200*J);
         "PRINT" PUNCH(5),DIGITS(2),ALIGNED(5, 1),V*J/10;
         MOVEPEN(0,  200*J);
      "END";
      WAIT(1,  4);
      MOVEPEN( - 110,  1000);
      "PRINT"  PUNCH(5),  'RELATIVE ABUNDANCE';
     MOVEPEN((D - S)*Y - 1800,  2140);
      WAIT(0,  4); PUNCH(5);
      I := 0; OUTSTRING(A,  I);
      MOVEPEN(0,  0);
      "FOR" M := 0 "STEP" 1 "UNTIL"
      ENTIER((D - S)*Y/200 + 0.99) "DO"
      "BEGIN"  DRAWLINE(200*M, 0); DRAWLINE(200*M, - 12);
         MOVEPEN(200*M - 90,   - 50);
         WAIT(0,  3);
         "PRINT" PUNCH(5),  DIGITS(2),  ALIGNED(5,  1),
         S + (M*200/Y); MOVEPEN(200*M,  0);
      "END";
      MOVEPEN((D - S)*Y - 550,   - 100); WAIT(0,  4);
      "PRINT"  PUNCH(5),  'MASS:CHARGE RATIO (M/E)';
      "FOR"  Z := 1  "STEP"  1  "UNTIL"  X  "DO"
      "BEGIN"  MOVEPEN((P[1] - S - D)*Y + (Z*Y*D),  0);
         DRAWLINE((P[1] -S -D)*Y + (Z*Y*D),R[Z]*2000/V);
      "END";
      MOVEPEN((D - S)*Y,  0);
  "END";
"END";
```

expressed as a percentage, and the percentage of the total ion current carried by the ion. It is not necessary to feed in the m/e values of peaks as well as the intensities as this is done automatically knowing the first m/e value (K), and the total number of peaks.

In addition using an on-line Elliott 4296 digital graph-plotter the program produces line diagrams showing the relative abundance of the various ions. This is for convenience done in two possible ways, corresponding to STEP C: and STEP D: respectively. The diagram,if it is possible,will be plotted on a (5" x 8") axis suitable for academic reports, but otherwise will automatically be plotted on an axis of (10" x ?) as required, where (? > 8"). The relative abundance axis is not restricted to plotting values up to 100% but will automatically divide the percentage axis into five equal parts, having first determined the largest value and rounded it upwards to a value of 10, and label the divisions accordingly. This has the advantage that a small section of spectrum could be plotted out in which the base peak was not necessarily present. Similarly the lowest and highest values of the m/e units are rounded downwards and upwards respectively to a multiple of 10, and these represent the m/e values at which the plotter will start and stop plotting respectively. The program also allows for non-unit m/e steps to be plotted out by the value U in the data tape, which can be 0.5 for m/e step = $\frac{1}{2}$, 0.333 etc. for m/e step = $\frac{1}{3}$, etc. Labelling of the axes and title of the spectrum on the diagram are also automatically allowed for.

Data Format for J.B.L. 4

This is listed in order of appearance on the data tape.

'Title' This must be typed inside quotation marks and can have up to 50 letters. This title will then appear on the diagram and also on the data print out.

U = Mass unit increment to be plotted. N.B. Fractional values of U must be expressed as a decimal (e.g. 0.5 not $\frac{1}{2}$).

X = Total number of mass peaks to be plotted inclusive if required of half mass peaks etc.

B = Intensity of the base peak of the spectrum.

K = Value of the first m/e peak to be plotted. Note that if this is an exact multiple of 10 it is preferable to put this as 1 unit less, together with the appropriate zero for its intensity in L (to follow) and increase in the value of X, otherwise it will be drawn coincident with the relative abundance axis.

Y = The number of graph plotter steps per integral mass unit on the m/e axis. This factor arises to ensure sensible division of the m/e axis. The graph plotter is designed to move 200 plotter steps in an inch. Therefore for example if U = 1 and Y = 20 then 1 mass unit will be plotted every $\frac{1}{10}$ ". Similarly for U = $\frac{1}{2}$, Y = 20 then two half mass units will be plotted every $\frac{1}{10}$ "; U = $\frac{1}{3}$, Y = 20 then three $\frac{1}{3}$ mass units will be plotted every $\frac{1}{10}$ "; and for U = 1, Y = 10 the 2 mass units will be plotted every $\frac{1}{10}$ ". In general therefore to produce an easily determinable and readable m/e axis, (200/Y) must be a simple integer. To produce a line diagram on the (8" x 5") axis the difference between the upper and lower m/e values, rounded upwards and downwards respectively to a multiple of 10, when multiplied by the factor Y/U must be less than or equal to 1600 (plotter steps). In practice the only limitation to reducing the value of Y is the line width of the pen on the graph plotter, and it is found that four lines in $\frac{1}{10}$ " (i.e. Y = 5, U = 1) is the maximum for the lines to be clearly discernible.

L = The series of intensity readings corresponding to an ascending order of m/e values. It should be noted that if half masses etc. are included the appropriate zero values for non-existing half masses must be included.

Program J.H.M. 1[95] calculates which fragmentations of observed ions can account for the positions of observed metastable ion peaks and prints out in columns the observed metastable ion positions (M OBS), the m/e value of the initial ion (M1), the m/e value of the ion to which M1 fragments (M2), the m/e difference between M_1 and M_2 (M_1 - M_2), and the calculated value of the position for the metastable ion peak = $\frac{{M_2}^2}{M_1}$ (M CALC).

TABLE 8-C

```
  JHM1;
"BEGIN"  "INTEGER"  X,  Y,  I;
   "REAL"  Z;
   "INTEGER"  "ARRAY"  A[0 : 20];
   I  := 0;
   INSTRING(A,  I);
   I  := 0;
   OUTSTRING(A,  I);
   "READ"  X,  Y,  Z;
   "BEGIN"  "REAL"  M3,  M4;
      "INTEGER"  M1,  M2,  M5,  N,  I,  J,  K;
      "REAL"  "ARRAY"  R[1 : X],  C[1 : Y];
      N  := 0;
      I  := 0;

STEP A: "READ"  M1;
      N  := N + 1;
      R[N]  := M1;
      "IF"  N < X  "THEN"  "GO TO"  STEP A;

STEP B: "READ"  M3;
      I  := I + 1;
      C[I]  := M3;
      "IF"  I < Y  "THEN"  "GO TO"  STEP B;
      "PRINT"  PREFIX(','),
      'M OBS,        M1,        M2,        M1-M2,      M CALC,';
      "FOR"  J  := 1  "STEP"  1  "UNTIL"  Y  "DO"
      "BEGIN"  M3 := C[J];
         K  := 1;

   START: N  := 0;

   NEXT: N  := N + 1;
         M1  := R[N];
         M2  := R[K];
         M4  := M2*42/M1;
         M5  := M1 - M2;
         "IF"  M5 > 0  "THEN"
         "BEGIN" "IF" (M4-M3)*(M4-M3)  <  Z  "THEN" "PRINT"
            ALIGNED(3, 2), M3, PREFIX(','), M1, M2, M5, M4;
         "END";
         "IF"  N < X  "THEN"  "GO TO"  NEXT;
         K  := K + 1;
         "IF"  K < X  "THEN"  "GO TO"  START;
      "END";
   "END";
 END";
```

Data Format for J.H.M. 1 program

'Title': This must be typed inside quotation marks and can have up to 20 letters.

X = The total number of ions observed.

Y = The total number of metastables observed.

Z = The square of the error in m/e value to be allowed between observed and calculated metastable transitions.

M1 = The series of m/e values of the observed ions.

M3 = The series of m/e values of the observed metastable ions.

REFERENCES

1. A. Stock and E. Pohland; Chem. Ber., 1926, 59, 2215.

2. K. Niedenzu and J.W. Dawson; "Boron-Nitrogen Compounds"; Anorganische und allgemeine Chemie in einzeldarstellungen, Band VI., Springer-Verlag, Berlin, Heidelberg, New York, 1965.

3. "Boron-Nitrogen Chemistry"; Advances in Chemistry Series, No. 42; American Chemical Society, Washington D.C., 1964.

4. H. Steinberg and R.J. Brotherton; "Organoboron Chemistry"; Volume 2, Boron-Nitrogen and Boron-Phosphorus compounds; Interscience, 1966.

5. E.L. Muetterties; "The Chemistry of Boron and its compounds"; Wiley and Sons, 1967.

6. J.C. S~~c~~heldon and B.C. Smith; Quart. Rev. 1960, 14, 200.

7. W. Gerrard; "Organic Chemistry of Boron"; Academic Press, 1961, 174 - 181.

8. E.K. Mellon and J.J. Lagowski; Adv. Inorg. Chem. Radiochem., 1963, 5, 259 - 305.

9. B.M. Mikhailov; Russ. Chem. Rev. 1960, 459 - 468.

10. M.F. Lappert, M.K. Majumdar and B.P. Tilley; J. Chem. Soc. (A) 1966, 1590 and references cited therein.

11. H. Hess; Z. Krist. 1963, 118, (5/6), 361.

12. K.W. Boddeker, S.G. Shore and R.K. Bunting; J. Amer. Chem. Soc. 1966, 88, 4396.

13. M.F. Lappert and M.K. Majumdar; Proc. Chem. Soc. 1963, 88.

14. M.F. Lappert and M.K. Majumdar; As reference 3, p.208.

15. M.F. Lappert and M.K. Majumdar; Chem. Eng. News, 5th May, 1963, 4, 40.

16. R. Hoffmann; J. Chem. Phys. 1964, 40, 2474.

17. R. Hoffmann; as reference 3 page 83.

18. N.C. Baird and M.A. Whitehead; Canad. J. Chem.,1967, 45, 2059.

19. J. Casanova, H.R. Kiefer, D. Kuwada and A.H. Boulton; Tetrahedron Letters, 12, 703 (1965).

20. P. Paetzold; Fortschr. Chem. Forsch., 1967, 8, 437 and references cited therein.

21. N.N. Greenwood and J.H. Morris; J. Chem. Soc. 1965, 6205,

22. J.H. Morris and P.G. Perkins; J. Chem. Soc. 1966 (A), 580.

23. P. Paetzold - private communication.

24. P. Paetzold and W.M. Simson; Angew. Chem. 1966, 78, 825.

25. P. Geymayer, E.G. Rochow and U. Wannagat; Angew. Chem. I.E., 1964, 3, 633.

26. P. Geymayer, E.G. Rochow and U. Wannagat; Monatsh., 1966, 97, 429.

27. C.R. Russ and A.G. MacDiarmid; Angew. Chem. I.E. 1964, 3, 509.

28. H. Hess; Angew. Chem. I.E. 1967, 6, 975.

29. H. Nöth and W. Regnet; Z. Naturforsch; 1963, 18b, 1138.

30. K; Niederzu, H. Jenne and P. Fritz; Angew. Chem. 1964, 76, 535.

31. G.M. Wyman, K. Niedenzu and J.W. Dawson; J. Chem. Soc. 1962, 4068.

32. H. Nöth and W. Regnet; Z. Anorg. Chem., 1967, 352, 1.

33. H. Schick; calculations quoted in 32.

34. H.P. Fritz and K.E. Schwarzhans; J. Organometallic Chem., 1964, 1, 208.

35. K. Niedenzu, P. Fritz, and J.W. Dawson; Inorg. Chem., 1964, 3, 1077.

36. H. Nöth and G. Abeler; Angew. Chem. I.E. 1965, 4, 522.

37. H. Nöth and G. Abeler; Chem. Ber., 1968, 101, 969.

38. D.A. Bochvar and A.A. Bagaturyants; Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk. 1963, 785.

39. A.T. Balaban and Z. Simon; Rev. Roumaine de Chim., 1964, 9, 99.

40. A.T. Balaban and Z. Simon; Rev. Roumaine de Chim., 1965, 10, 1059.

41. F. Umland and C. Schleyerbach; Angew. Chem. I.E., 1965, 2, 151.

42. J.H. Morris and P.G. Perkins; J. Chem. Soc. (A), 1966, 576.

43. A.J. Downs and J.H. Morris; Spectrochim. Acta, 1966, 22, 957.

44. N.N. Greenwood and J.C. Wright; J. Chem. Soc. 1965, 448.

45. K.W.F. Kohlrausch; "Ramanspektren", p 331-352, Akad Verlagsgesellschaft Becker and Erler Kom.-Ges., Leipzig, (1943).

46. G. Herzberg; "Infrared and Raman spectra of polyatomic Molecules", p. 353, Van Nostrand, New York (1945).

47. M.J. Buttler and D.C. McKeen; Spectrochim. Acta., 1965, 21, 465.

48. J.J. Miller and F.A. Johnson; J. Amer. Chem. Soc., 1968, 90, 218.

48a. H. Nöth and W. Regnet; as reference 3, page 166.

49. S. Trofimenko; J. Amer. Chem. Soc. 1967, 89, 3165.

50. S. Trofimenko; J. Amer. Chem. Soc. 1967, 89, 4948.

51. C.W. Heitsch; Abstracts, 153rd National Meeting of the American Chemical Society, Miami, April, 1967, L109.

52. H. Nöth; Z. Naturforsch, 1961, 16b, 470.

53. K. Niedenzu, H. Beyer and J.W. Dawson; Inorg. Chem., 1962, 1, 738.

54. R.H. Cragg, M.F. Lappert, M.K. Majumdar and B. Prokai; Preprints of papers submitted at symposium on B-N chemistry, Duke University, Durham, North Carolina, April, 1963, p.152, quoted in reference 2.

55. P. Fritz, K. Niedenzu and J.W. Dawson; Inorg. Chem., 1964, 4, 886.

56. H.S. Turner and R.J. Warne; Proc. Chem. Soc. 1962, 69.

57. H.S. Turner and R.J. Warne; As reference 3, p.290.

58. H.S. Turner and R.J. Warne; J. Chem. Soc. 1965, 6421.

59. W. Gerrard and I.M. Butcher; J. Inorg. Nucl. Chem., 1965, 27, 823.

60. B.R. Currell, W. Gerrard and M. Khodabocus; J. Organometallic Chem., 1967, 8, 411.

61. B.R. Currell, W. Gerrard and M. Khodabocus; Chem. Comm., 1966, 77.

62. J.H.S. Green, W. Kynaston and H.M. Paisley; As reference 2, page 501.

63. P.T. Clarke and H.M. Powell; Abstracts of papers XIXth I.U.P.A.C., conference, London, 1963, 202.

64. P.T. Clarke and H.M. Powell; J. Chem. Soc. (B), 1966, 1172.

65. C.W. Hickam; Diss. Abs. 1965, 25, 6946

66. H.E. Hallam; "Infrared Spectroscopy and Molecular Structure", Ed. Mansel Davies, Elsevier, 1963, p.419.

67. Weissberger; Proskauer, Riddick and Toops, "Organic Solvents", Interscience 1955.

68. I.U.P.A.C. Commission on Molecular Structure and Spectroscopy; "Table of wavenumbers for the calibration of infrared spectrometers", Butterworths, London 1961, p.574.

69. H.E. Hallam and T.C. Ray; Trans. Farad. Soc., 1962, 58, 1299

70. L.J. Bellamy, H.E. Hallam and R.L. Williams; Trans Farad. Soc., 1958, 54, 1120.

71. L.J. Bellamy and R.L. Williams; Trans. Farad. Soc., 1959, 55, 14.

72. D.M. Adams; Proc. Chem. Soc., 1961, 431.

73. D.M. Adams; Institute of Petroleum, "Spectroscopy", Ed. M.J. Wells, 1962, p.1.

74. J. Chatt; Tilden Lecture of Chemical Society, Proc. Chem. Soc. 1962, 318.

75. J.G. David and H.E. Hallam; J. Chem. Soc. 1966 (A), 1103.

76. K.B. Whetsel and R.E. Kagarise; Spectrochim. Acta. 1962, 18, 315, 329, 341.

77. C.C. Barraclough, J. Lewis and R.S. Nyholm; J. Chem. Soc. 1961, 2582.

78. L.J. Bellamy; "The infrared spectra of complex molecules", 2nd Ed. Metheun and Co. Ltd., London, 1958, p.382.

79. R.L. Williams; private communication.

80. A. Grace and P. Powell; J. Chem. Soc. (A), 1966, 673.

81. J.H. Smalley and E.F. Stafiej; J. Amer. Chem. Soc. 1959, 81, 582.

82. P. Paetzold; Z. Anorg. Chem.1963, 326, 53.

83. P. Paetzold; Z. Anorg. Chem.,1963, 326, 58.

84. C.N.R. ~~Reeo~~ Rao; "U.V. and Visible Spectroscopy", Butterworths, 1961.

85. H. Steinberg and R.J. Brotherton; "Organoboron Chemistry Volume 2, Boron-nitrogen and Boron-phosphorus Compounds", Interscience, 1966, p.365ff.

86. E.F. Mooney; Spectrochim. Acta, 1962, 18, 1355.

87. J.W. Emsley, J. Feeney and L.H. Sutcliffe; "High Resolution Nuclear Magnetic Resonance Spectroscopy", Volume 2, 1966, p. 673ff.

88. B.P. Dailey and J. Schoolery; J. Amer. Chem. Soc. 1955, 77, 3977.

89. J.R. Cavanaugh and B.P. Dailey; J. Chem. Phys. 1961, 34, 1099

90. D.H. Whiffen; "Molecular Spectroscopy", Institute of Petroleum, 1955, p.111.

91. R.O. Lindsay and C.F. Allen; Org. Synth., 22, 96.

92. R. Huisgen and I. Ugi; Chem. Ber. 1957, 90, 2925

93. G.F. Freeguard and L.H. Long; Chem. and Ind. 1965, 471.

94. D. Seyf~~o~~erth; "Organic Synthesis Collective Volume 4", p.528.

95. J.H. Morris; unpublished work.

96. G.A. Anderson and J.J. Lagowski; Chem. Comm. 1966, 649.

97. A. Meller; Organometallic Chem. Rev. 1967, 2, 1.

98. H. Nöth and H. Beyer; Chem. Ber. 1960, 93, 2251.

99. H. Nöth and H. Beyer; Chem. Ber. 1960, 93, 928.

100."Handbook of Chemistry and Physics", 47th Ed. Chemical Rubber Publishing Co. Cleveland, 1966-7, p.B-6.

101.J.H. Beynon; "Mass spectrometry and its applications to Organic Chemistry", Elsevier, Amsterdam, 1960.

102.J.J. Eisch and L.J. Gonsior; J. Organometallic Chem. 1967, 8, 53.

103.R.I. Reed; Quart. Rev., 1966, XX(4), 527.

104.P.G. Perkins; University of Strathclyde, private communication.

105.K. Sales; Queen Mary College, London, private communication.

106.R.G. Pearson; Kingston College of Technology, private communication.

107.M. Dekker and G.R. Knox; Chem. Comm. 1967, 1243.

108.R. Prince and H. Werner; Angew Chem. 1967, 79, 63.

109.Niedenzu and Dawson as reference 2, p.113.

110.Dr. C.H.J. Wells; Kingston College of Technology, private communication.

111.Mass Spectrometry Data Centre; Atomic Weapons Research Establishment, Aldermaston.

112.R. Prince and H. Werner; Angew. Chem., 1967, 79, 63.

113.D.P. Tate, W.R. Knipple and J.M. Augl; Inorg. Chem., 1962, 1, 433.

Derivatives of Cyclotetrazenoborane. Part III.[1] Solvent Effects on the B–H Stretching Frequency of Substituted Cyclotetrazenoboranes

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Derivatives of Cyclotetrazenoborane. Part III.[1] Solvent Effects on the B–H Stretching Frequency of Substituted Cyclotetrazenoboranes

By **J. B. Leach** and **J. H. Morris**, Department of Chemistry, Kingston College of Technology, Kingston-upon-Thames, Surrey

The frequencies of the B–H stretching vibrations of Me_2N_4BH and Ph_2N_4BH have been studied in a range of solvents. They *increase* with increasing polarity of the solvent. No correlation is observed with the dielectric relationship $(\varepsilon - 1)/(2\varepsilon + 1)$ and non-linear relative shift (B.H.W.) plots are obtained against N–H, C=O, and transition-metal hydride M–H vibrations. The results suggest that solvent interactions occur with parts of the molecules remote from the B–H bond, and are unlikely to be due mainly to dielectric effects.

ONLY recently have solvent effects on infrared group frequencies been systematically studied,[2] and their nature in many compounds is uncertain. Theoretical treatments of solvent interactions are far from adequate in accounting for observed solvent shifts.

We started to investigate the effect of solvent on the B–H stretching frequencies of substituted cyclotetrazenoboranes to obtain evidence for the polarity of the B–H bond, since this was not apparent either from a molecular orbital study of the ring system,[3] or from a preliminary investigation of the chemistry of these compounds.[4] Although we could not thus determine this polarity, the solvent effects were of interest, being different from previously reported X–H stretching frequency shifts.[5]

EXPERIMENTAL

Me_2N_4BH and Ph_2N_4BH were prepared from the primary amine–borane and the organic azide,[1,4] and purified by vacuum distillation or recrystallisation from light petroleum (b. p. 80—100°) in an inert atmosphere. The solvents were dried by standard procedures, distilled, and stored over 4A molecular sieve. Solutions were prepared in a dry, nitrogen-filled glove box, and spectra were obtained on a Grubb–Parsons Spectromaster grating spectrometer and 0·5 mm. path-length cells with NaCl windows. The spectrometer was calibrated in the range 2700—2400 cm.$^{-1}$ with gaseous HBr,[6] and the precision of the measurements is within $\pm 0{\cdot}8$ cm.$^{-1}$ of the absolute frequency, but the relative shifts are probably accurate to $\pm 0{\cdot}5$ cm.$^{-1}$ for non-polar solvents, and $\pm 0{\cdot}8$ cm.$^{-1}$ for polar solvents. The figures in the Table are quoted to 0·1 cm.$^{-1}$ to avoid rounding-off errors. The shifts in frequencies are quoted relative to the vapour spectrum of Me_2N_4BH, and an estimated vapour spectrum for Ph_2N_4BH.

RESULTS AND DISCUSSION

The observed frequencies, ν, and relative frequency shifts, Δν/ν, are in the Table. The ^{11}B–H and ^{10}B–H stretching vibrations were not completely resolved owing to the broadness of the peaks in solution, and the frequencies quoted are those for the weighted mean.

The theoretical explanations of solvent shifts have been summarised by Hallam,[2] who pointed out that the Kirkwood–Bauer–Magat (K.B.M.) relationship

$$\Delta\nu/\nu = C(\varepsilon - 1)/(2\varepsilon + 1)$$

or its extensions by Buckingham or Pullin (see ref. 2) are inadequate. Each treatment predicts a decrease in frequency with increasing polarity of solvent, since they are based on the model of a diatomic oscillator in a spherical solvent cavity and take no account of specific

Solvent shifts for Ph_2N_4BH and Me_2N_4BH

	Ph_2N_4BH		Me_2N_4BH	
Solvent	ν	$10^3\Delta\nu/\nu$	ν	$10^3\Delta\nu/\nu$
None[a]	$2648{\cdot}_5$	0	$2627{\cdot}_0$	0
n-Hexane	$2648{\cdot}_7$	0·07	$2627{\cdot}_1$	0·04
Carbon disulphide	$2649{\cdot}_7$	0·45	$2627{\cdot}_6$	0·23
Tetrachloroethylene	$2649{\cdot}_8$	0·49	$2629{\cdot}_7$	1·03
Carbon tetrachloride	$2650{\cdot}_7$	0·83	$2629{\cdot}_8$	1·06
Methylene di-iodide	$2651{\cdot}_1$	0·98	$2630{\cdot}_8$	1·44
p-Xylene	$2651{\cdot}_4$	1·09	$2628{\cdot}_2$	0·46
Cyclohexanone	$2652{\cdot}_2$	1·40	$2632{\cdot}_4$	2·05
m-Xylene	$2652{\cdot}_4$	1·47	$2629{\cdot}_3$	0·87
Benzene	$2652{\cdot}_4$	1·47	$2631{\cdot}_2$	1·60
o-Xylene	$2653{\cdot}_1$	1·73	$2629{\cdot}_9$	1·10
Mesitylene	$2653{\cdot}_3$	1·81	$2629{\cdot}_3$	0·87
Toluene	$2653{\cdot}_4$	1·85	$2630{\cdot}_6$	1·37
Methyl iodide	$2653{\cdot}_6$	1·92	$2630{\cdot}_0$	1·14
Acetophenone	$2654{\cdot}_2$	2·15	$2631{\cdot}_1$	1·56
Methylene dibromide	$2654{\cdot}_2$	2·15	$2632{\cdot}_6$	2·13
Bromoform	$2654{\cdot}_3$	2·19	$2633{\cdot}_4$	2·43
Chlorobenzene	$2654{\cdot}_6$	2·30	$2633{\cdot}_4$	2·43
Bromobenzene	$2654{\cdot}_9$	2·41	$2630{\cdot}_7$	1·41
Aniline	$2655{\cdot}_3$	2·56	$2634{\cdot}_2$	2·73
Chloroform	$2656{\cdot}_1$	2·86	$2636{\cdot}_4$	3·57
1,1,2,2-Tetrachloroethane	$2656{\cdot}_2$	2·90	$2638{\cdot}_0$	4·17
Ethyl acetate	$2656{\cdot}_4$	2·97	$2632{\cdot}_9$	2·24
1,2-Dichloroethane	$2657{\cdot}_3$	3·31	$2634{\cdot}_9$	3·00
Nitrobenzene	$2658{\cdot}_0$	3·57	$2634{\cdot}_3$	2·77
Methylene dichloride	$2658{\cdot}_2$	3·65	$2636{\cdot}_3$	3·53
Nitromethane	$2662{\cdot}_3$	5·18	$2640{\cdot}_6$	5·15
1,4-Dioxan	—	—	$2631{\cdot}_5$	1·71
Acetone	—	—	$2634{\cdot}_5$	2·85
Pyridine	—	—	$2635{\cdot}_0$	3·04
Nitrobenzene–carbon tetrachloride mixture				
1 : 3	$2653{\cdot}_8$	2·03	—	—
1 : 1	$2655{\cdot}_1$	2·49	—	—
3 : 1	$2656{\cdot}_4$	2·97	—	—

[a] Vapour spectrum for Me_2N_4BH and estimated vapour spectrum for Ph_2N_4BH.

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[1] Part II, J. H. Morris and P. G. Perkins, *J. Chem. Soc.* (*A*), 1966, 580.

[2] H. E. Hallam, in " Infrared Spectroscopy and Molecular Structure," ed. Mansel Davies, Elsevier, 1963, p. 419.

[3] J. H. Morris and P. G. Perkins, *J. Chem. Soc.* (*A*), 1966, 576.

[4] N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 1965, 6205.

[5] L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

[6] I.U.P.A.C. Commission on Molecular Structure and Spectroscopy, " Tables of Wave Numbers for the Calibration of Infrared Spectrometers," Butterworths, London, 1961, p. 574.

interaction between solvent and solute. To ascertain whether the K.B.M. correlation with the dielectric relationship existed, $\Delta\nu/\nu$ for dimethylcyclotetrazenoborane and diphenylcyclotetrazenoborane were plotted against $(\varepsilon - 1)/(2\varepsilon + 1)$ for the solvents. A simple linear correlation was not observed, and contrary to predictions based solely on dielectric effects, the frequencies of the vibrations usually *increased* with increasing polarity of the solvent.

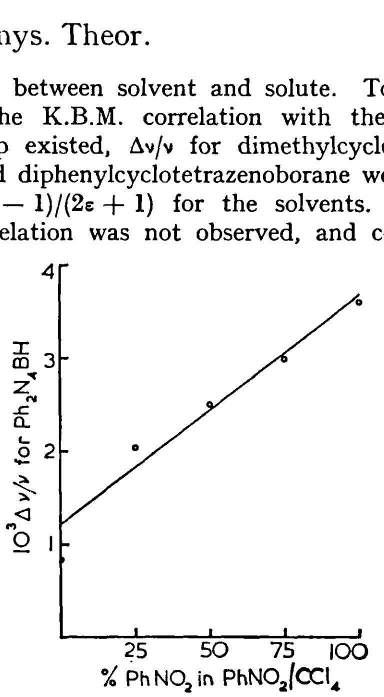
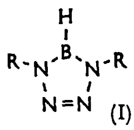


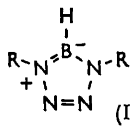
FIGURE 1

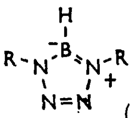
Further, we expected that if the polarity of the B–H bond were similar either to that[5] in decaborane and pyrrole, *i.e.*, $B^-–H^+$ or essentially non-polar, or to that of the carbonyl group C=O,[7] *i.e.*, $B^+–H^-$, a linear relationship should exist between the relative frequency shifts $\Delta\nu/\nu$ of the B–H frequency of cyclotetrazenoboranes and either the N–H frequency of pyrrole or the C=O frequency of acetophenone. No satisfactory plot was obtained. It might further have been expected that the nature of the interactions would more closely resemble those of certain transition-metal hydrides in which similar increases of frequency with increasing polarity of solvent had been observed.[8-10] However, since the range of solvents used[9] was somewhat limited, non-representative yet mostly non-linear relative shift plots with the cyclotetrazenoborane derivatives were obtained.

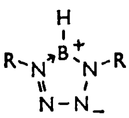
In an attempt to determine whether solutes and solvents interacted specifically to a major extent, we investigated the effect of mixed solvents on the B–H stretching frequency of diphenylcyclotetrazenoborane. Nitrobenzene and carbon tetrachloride were chosen since large and small shifts, respectively, were observed in them. The peak was not split or broadened, and its position was closely linear with the volume ratio of the solvents (Figure 1). This suggests that specific solvent–solute interactions are unimportant, but all the other evidence, and in particular the *increase* of frequency with increasing polarity of solvent, strongly favours their occurrence. Similar anomalous results for mixed solvent studies have been reported for carbonyl compounds.[11]

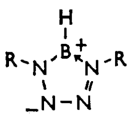
Instances of increasing frequency of a vibrating group with increasing polarity of solvent are rare. With iron carbonyl halides[12] and nitrosyl chloride,[13,14] tentative explanations have been based on valence-bond descriptions of the molecules. The effects have been attributed to interaction of the solvent molecules with regions of the molecules remote from the vibrating group under investigation, and have been interpreted in terms of increased contributions of ionic canonical forms to the total wave function, *e.g.*, Cl–M–C=O and $Cl^-M^+–C≡O$; Cl–N=O and $Cl^-N^+≡O$. This increases the bond order of the C–O or N–O bond. The analogous effects in transition-metal hydrides occur where the vibrating group is *trans* to a halogen,[9,10] and the explanation is that since a halogen atom *trans* to hydrogen carries more charge than the hydrogen, it will be preferentially solvated in polar media. The tendency will be to increase the ionic contribution to the total wave function, thus increasing the strength of the M–H bond (X–M–H and $X^-M^+–H$).

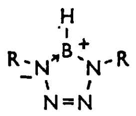

(I)

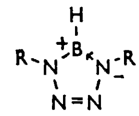

(II)


(III)


(IV)


(V)


(VI)


(VII)

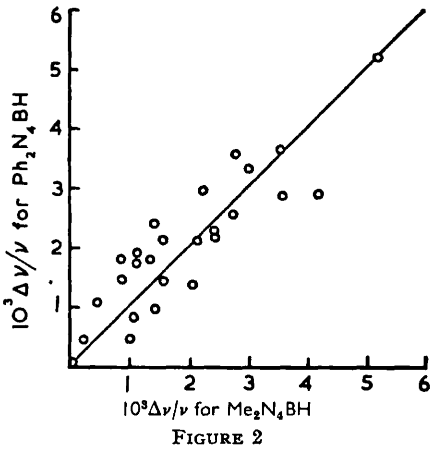


FIGURE 2

Although cyclotetrazenoboranes have been treated

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[7] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 14.

[8] D. M. Adams, *Proc. Chem. Soc.*, 1961, 431.

[9] D. M. Adams, Institute of Petroleum, " Spectroscopy," ed. M. J. Wells, 1962, p. 1.

[10] J. Chatt, Tilden Lecture of Chemical Society, *Proc. Chem. Soc.*, 1962, 318.

[11] K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, 1962, **18**, 315, 329, 341.

[12] C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1961, 2582.

[13] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co., Ltd., London, 1958, p. 382.

[14] R. L. Williams, personal communication.

by an M.O. method,[3] it is useful to consider the alternative valence-bond approach qualitatively. Canonical forms are (I)—(VII), so we suggest that the solvent interacts at the more electronegative nitrogen atoms, thus increasing the contributions of forms (IV)—(VII) to the wave function. The assumption that solvent interacts mainly with the heterocyclic ring is supported since a plot of $\Delta\nu/\nu$ for Me_2N_4BH against $\Delta\nu/\nu$ for Ph_2N_4BH is straight (Figure 2), indicating that the interaction of any one solvent with the two solutes is essentially of the same nature.

We thank Dr. R. L. Williams and Dr. A. Finch for discussions, and The Chemical Society for a grant from the Research Fund.

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Derivatives of Cyclotetrazenoborane. Part IV.[1] Mass spectra of substituted Cyclotetrazenoboranes

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Derivatives of Cyclotetrazenoborane. Part IV.[1] Mass spectra of substituted Cyclotetrazenoboranes

By **E. F. H. Brittain, J. B. Leach,** and **J. H. Morris,** Department of Chemistry, Kingston College of Technology, Kingston upon Thames, Surrey

The mass spectra of a series of 2,5-disubstituted cyclotetrazenoboranes have been studied. The compounds Me_2N_4BH, Et_2N_4BH, $Me(Ph)N_4BH$, and Ph_2N_4BH all give strong molecular ion peaks, and major fragmentations due to loss of N_2 or N_2 + H· confirm that the substituents are in the 2 and 5 positions. Other major fragmentations include cleavage of ethyl or phenyl substituents, and loss of HCN from a number of the daughter ions.

A DETAILED study of the mass spectra of a number of cyclotetrazenoborane derivatives was undertaken (*a*) to analyse the fragmentation and rearrangement patterns of the molecules in an attempt to obtain a generalised pattern for the breakdown of the cyclotetrazenoborane ring system, and (*b*) to confirm the proposed structures of the molecules. Details of the mass spectra of the cyclotetrazenoboranes have not been reported previously except for a preliminary communication of the mass spectrum of dimethylcyclotetrazenoborane.[2] This work has been a detailed investigation of the fragmentation of Me_2N_4BH, Et_2N_4BH, $Me(Ph)N_4BH$, and Ph_2N_4BH. The molecules are particularly suited to mass spectral analysis because of the natural abundance of the ^{10}B and ^{11}B isotopes which occur in the ratio 19·6 : 80·4%.[3] These give a readily recognised triplet in the parent and fragment ion peaks due to contributions from ^{10}B, ^{11}B,

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[1] Part III, J. B. Leach and J. H. Morris, *J. Chem. Soc.* (*A*), 1967, 1590.

[2] J. H. Morris and P. G. Perkins, *J. Chem. Soc.* (*A*), 1966, 580.

[3] 'Handbook of Chemistry and Physics,' Chemical Rubber Publishing Co., Cleveland, 47th edn., p. B-6.

^{13}C, and ^{15}N isotopes, and peaks due to metastable ions containing boron are easily distinguished due to the ^{10}B, ^{11}B isotopic ratio.

The details of the breakdown of the compounds studied have been confirmed by observation of appropriate metastable transitions. The molecular ion peak has been taken to be monoisotopic with respect to ^{10}B, and $M + 1$, $M + 2$ are the peaks due to contributions from ^{11}B and ^{13}C, etc., the major peak is always $M + 1$.

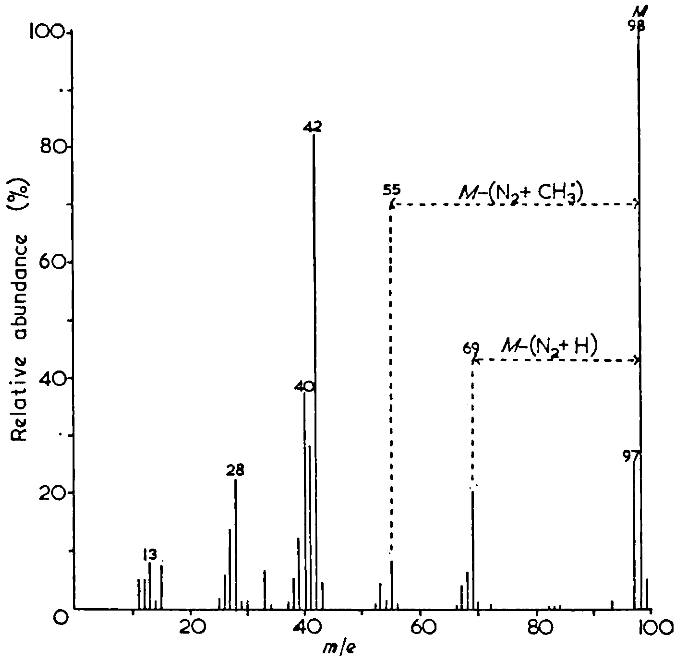
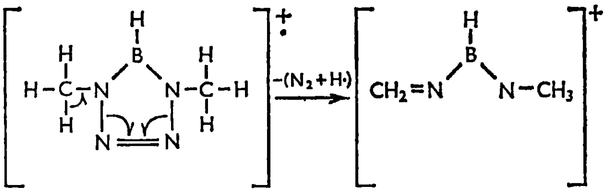


FIGURE 1 Mass spectrum of 2,5-dimethylcyclotetrazenoborane

The mass spectrum of 2,5-dimethylcyclotetrazenoborane is shown in Figure 1. Peaks due to the relative isotopic abundances of the parent ion $[Me_2N_4BH]^{+\cdot}$ (I) were observed at *m/e* 97, *98*, and 99, in the expected ratios and the peak at 98 is the base peak of the spectrum. Earlier work[2] has suggested that the initial ionisation is by loss of an electron from the lone pair of one of the azo-nitrogen atoms. The first major fragmentation occurs by loss of $N_2 + H\cdot$ to give peaks at *m/e* 68, *69*, and 70, which we interpret as the ion $[CH_2{=}N{-}BH{-}NCH_3]^+$ (II) by the fragmentation and rearrangement scheme:



$98 \rightarrow 69 = {}^{*}48{\cdot}6$

$97 \rightarrow 68 = {}^{*}47{\cdot}7$

(I) *m/e* 97, *98* (II) *m/e* 68, *69*

There is a small peak at *m/e* 83 presumably corresponding to loss of $CH_3\cdot$ from (I) and the peak at *m/e* 55 probably occurs either by loss of $(N_2 + CH_3)\cdot$ from (I) or by loss of CH_2 from (II). The next major fragmentation occurs through loss of HCN from (II) accompanied by hydrogen transfer giving rise to the prominent peak at *m/e* 42 of probable structure $CH_3{-}\overset{+}{N}H{=}BH$ (III) ($70 \rightarrow 43 = {}^{*}26{\cdot}4$, $69 \rightarrow 42 = {}^{*}25{\cdot}6$, $68 \rightarrow 41 = {}^{*}24{\cdot}7$).

An alternative but minor fragmentation of (II) occurs through loss of successive hydrogen atoms to give peaks at *m/e* 66, 67, 68, and 69 and the observed metastable transitions are $70 \rightarrow 69 = {}^{*}68{\cdot}0$; $69 \rightarrow 68 = {}^{*}67{\cdot}0$; $68 \rightarrow 67 = {}^{*}66{\cdot}0$; $67 \rightarrow 66 = {}^{*}65{\cdot}0$. Ion (III) also readily loses both 1 and 2 hydrogen atoms with appropriate metastable peaks.

The source of the peak at *m/e* 55 has not been established by a metastable transition, although it probably arises by loss of $(N_2 + CH_3\cdot)$ from (I) and has a possible structure $[HN{-}BH{-}N{=}CH_2]^+$. This then breaks down further with loss of HCN (metastables $55 \rightarrow 28 = {}^{*}14{\cdot}3$; $54 \rightarrow 27 = {}^{*}13{\cdot}5$). The fragmentation pattern outlined above satisfactorily accounts for all the major peaks in the spectrum of dimethylcyclotetrazenoborane.

The mass spectrum of 2,5-diethylcyclotetrazenoborane is shown in Figure 2. Strong peaks due to the parent ion $[Et_2N_4BH]^{+\cdot}$ (IV) are observed at *m/e* 125, *126*, and 127 and the peak at *m/e* 126 is also the base peak of the spectrum. The fragmentation of Et_2N_4BH is more complex than that of Me_2N_4BH, and a study of the metastable transitions has enabled most of the peaks in the spectrum to be assigned.

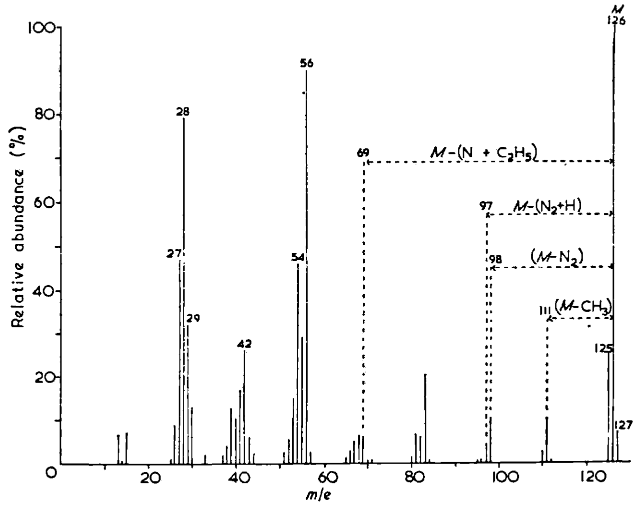
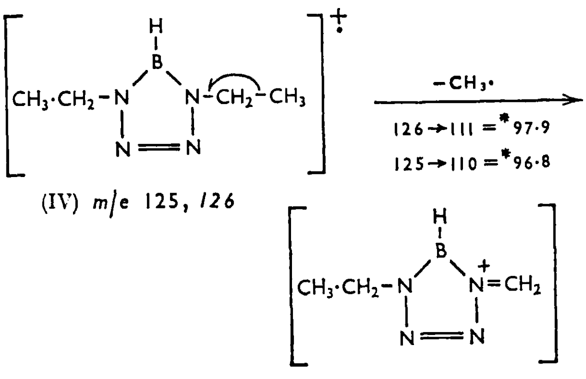


FIGURE 2 Mass spectrum of 2,5-diethylcyclotetrazenoborane

Fragmentation of the Parent Ion $[Et_2N_4BH]^{+\cdot}$.—The fragmentation of the parent ion is significantly different from that of Me_2N_4BH, since several routes now occur.

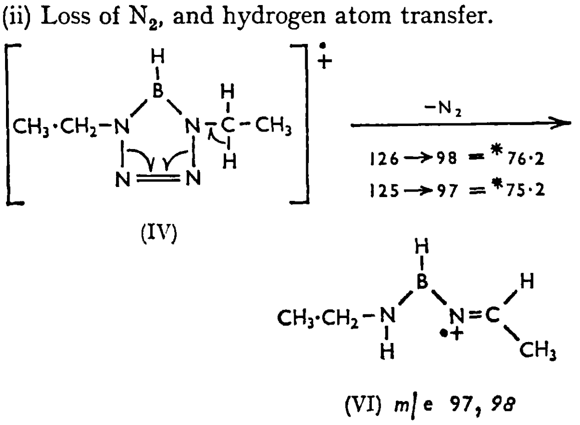
(i) Loss of $CH_3\cdot$



(IV) m/e 125, *126*

(V) m/e 110, *111*

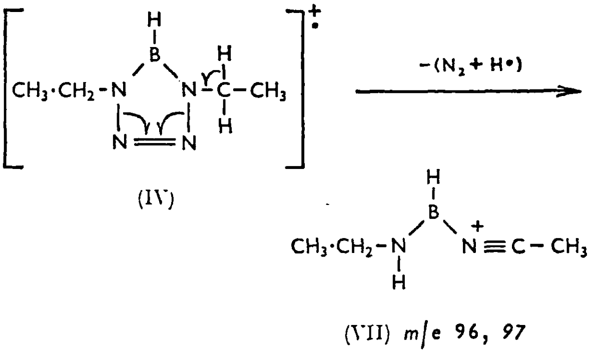
(ii) Loss of N_2, and hydrogen atom transfer.



(IV)

(VI) m/e 97, *98*

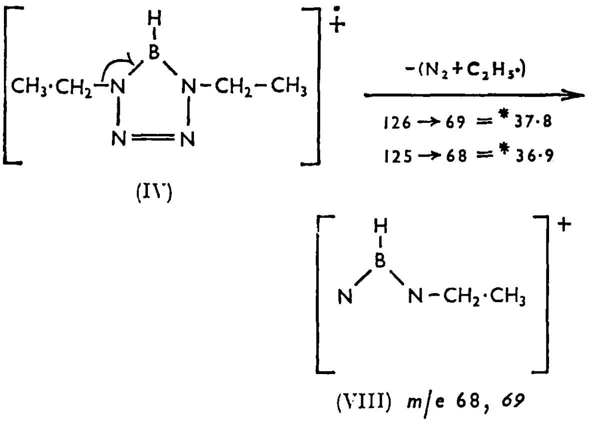
(iii) Loss of (N_2 + H·) and hydrogen atom transfer.



(IV)

(VII) m/e 96, *97*

(iv) Loss of (N_2 + $C_2H_5\cdot$)



(IV)

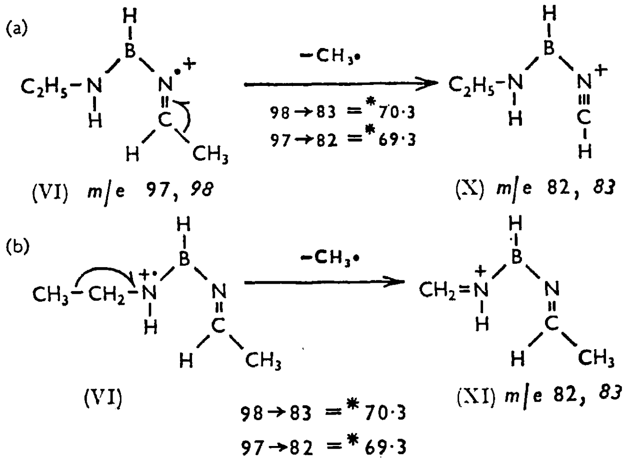
(VIII) m/e 68, *69*

It is apparent from the intensities of the peaks in the range *m/e* 96—99 that route (ii) is the major fragmentation process. However, it is difficult to interpret the relative intensities solely on the basis of route (ii) and route (iii) is proposed in order to account for the observed peak intensities without the supporting evidence of metastable transitions.

The further breakdown of the species formed by routes (i) to (iv) becomes involved, but the large number of metastable transitions observed greatly assist the interpretation of the fragmentation, and most of the peaks at lower masses can be assigned.

Fragmentation of Primary Daughter Ions.—(v) Species (V) loses 55 mass units (111 ⟶ 56 = *28·25, 110 ⟶ 55 = *27·5) which is probably best interpreted as loss of N_2 + HCN with H rearranged to give the species $C_2H_5\overset{+}{N}H{=}BH$ (IX) which is analogous to species (III) formed in the fragmentation of Me_2N_4BH.

(vi) A minor fragmentation of species (VI) produced by route (ii) probably involves the loss of $C_2H_5\cdot$ to contribute to the peaks at 68, *69*, and 70, although this has not been confirmed by the appearance of metastable ions. However, the major fragmentation occurs through loss of $CH_3\cdot$, and is confirmed by appropriate metastable transitions but is further complicated by the possibility of two routes:



(VI) m/e 97, *98*

(X) m/e 82, *83*

(VI)

(XI) m/e 82, *83*

It is necessary to postulate both routes for the fragmentation of (VI) since metastable ions indicate that ions of mass 82 and 83 yield daughter ions at both 55 and 56, and 41 and 42.

(vii) The further fragmentation of species (VIII) probably occurs through loss of $C_2H_5\cdot$ since metastable peaks were observed corresponding to the transitions 69 ⟶ 40 = *23·2 and 68 ⟶ 39 = *22·4.

Fragmentation of Secondary Daughter Ions.—(viii) Species (X) loses HCN (83 ⟶ 56 = *37·8, 82 ⟶ 55 = *36·9) to give species (IX) identical to that produced from route (V).

(ix) The peaks at *m/e* 41, *42* of possible structure $CH_2{=}\overset{+}{N}H{-}BH_2$ (XII) can occur from both species (IX) by loss of CH_2 (56 → 42 = *31·5, 55 → 41 = *30·6) and from species (XI) by loss of CH_3CN (83 → 42 = *21·3, 82 → 41 = *20·5).

Further fragmentation occurs from species (IX) and (XII) through hydrogen loss. Several other transitions are observed leading to peaks in the range *m/e* 24 → 29, *e.g.*, 52 → 25 = *12·0 and 51 → 24 = *11·3.

The mass spectrum of 2-methyl-5-phenylcyclotetrazenoborane is shown in Figure 3.

The introduction of a phenyl substituent on the ring necessarily makes a complete assignment more difficult since much of the fragmentation is associated with breakdown of the phenyl group. However, the essential details of the fragmentation have been obtained, and the major peaks have been assigned.

The parent ion $[\mathrm{Me(Ph)N_4BH}]^{+\cdot}$ (XIII), gives rise to peaks at *m/e* 159, *160*, and 161, and although these are still very intense, the base peak of the spectrum now occurs at *m/e* 103. Other major peaks occur at *m/e* 132, 122, 93, and 77.

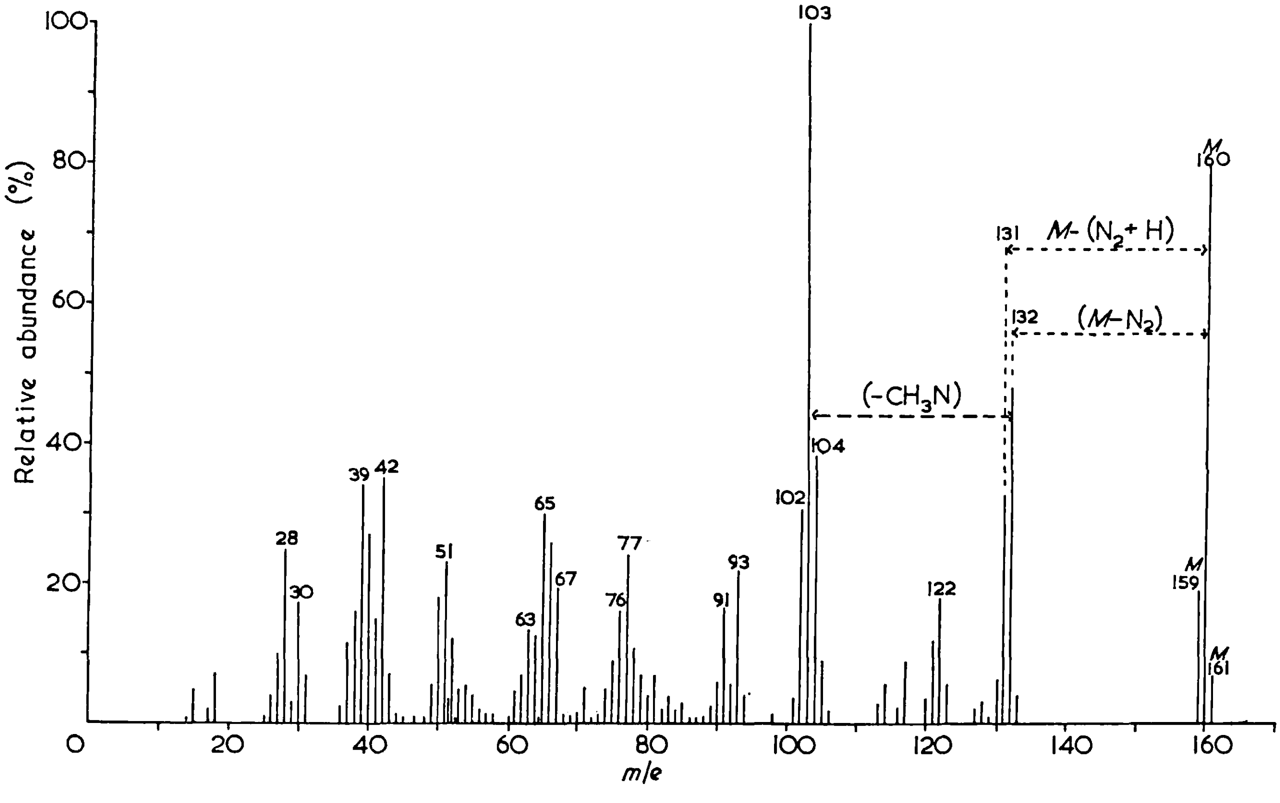
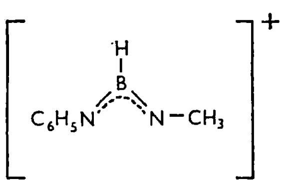


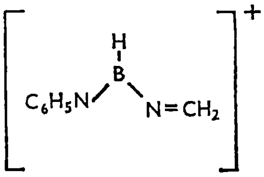
FIGURE 3 Mass spectrum of 2-methyl-5-phenylcyclotetrazenoborane

Fragmentation of the Parent ion $[\mathrm{Me(Ph)N_4BH}]^{+\cdot}$.—As in Et_2N_4BH, both loss of N_2 and N_2 + H· can occur since the peaks at *m/e* 131 and 132 are of comparable abundance. Metastable transitions for the loss of N_2 are 160 → 132 = *108·8; 159 → 131 = *107·6, which produce a species of possible structure



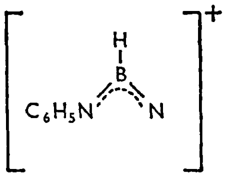
(XIV) *m/e* 131, *132*

The only observed metastable transition for the loss of N_2 + H· is 160 → 131 = *107·2 to produce a species



which may subsequently lose HCN with accompanying H transfer to produce $[C_6H_5NHBH]^+$ (131 → 104 = *82·6, 130 → 103 = *81·6).

Fragmentation of Primary Daughter Ions.—The fragmentation of daughter species is not simple although mass losses can be identified from the appearance of metastable ions. For instance, the loss of 15 mass units from (XIV) is probably best interpreted in terms of loss of $CH_3\cdot$ to yield (XV). Alternative fragmentation



(XV)

$132 \rightarrow 117 = {}^*103{\cdot}7$

$131 \rightarrow 116 = {}^*102{\cdot}7$

occurs with loss of 29 mass units and can be interpreted in terms of loss of $CH_3N\cdot$ from (XIV) to produce $[C_6H_5\text{-}N{=}BH]^{+\cdot}$ ($132 \rightarrow 103 = {}^*80{\cdot}4$, $131 \rightarrow 102 = {}^*79{\cdot}4$) of which *m/e* 103 is the base peak of the spectrum.

A further mode of fragmentation of species (XIV) involved the loss of 41 mass units, which could occur in several ways such as loss of $CH_3NBH\cdot$, CH_3CN, or $C_3H_5\cdot$ from partial fragmentation of the phenyl ring. There is a metastable ion corresponding to $132 \rightarrow 91 = {}^*62{\cdot}8$ but no metastable ion for the transition $131 \rightarrow 90$ which should arise if ^{10}B is retained in the charged fragment. Loss of $CH_3NBH\cdot$ is therefore the most probable route to produce the species $C_6H_5N^{+\cdot}$ of *m/e* 91 ($132 \rightarrow 91 = {}^*62{\cdot}8$).

The peaks in the ranges *m/e* 74—78 and 64—67 together with a number of metastable ions result from the further fragmentation of (XIV), and are probably due to breakdown of the phenyl ring.

Fragmentation of the Secondary Daughter Ions.—Species (XV) undergoes several fragmentations which are probably best interpreted in terms of rupture of the phenyl ring since losses of 26, 27, 52, and 53 mass units occur, *e.g.*, $117 \rightarrow 91 = {}^*70{\cdot}8$, $117 \rightarrow 90 = {}^*69{\cdot}2$, $117 \rightarrow 65 = {}^*36{\cdot}1$, $117 \rightarrow 64 = {}^*35{\cdot}0$.

The peak at *m/e* 93 is probably due to $C_6H_5NH_2^+$

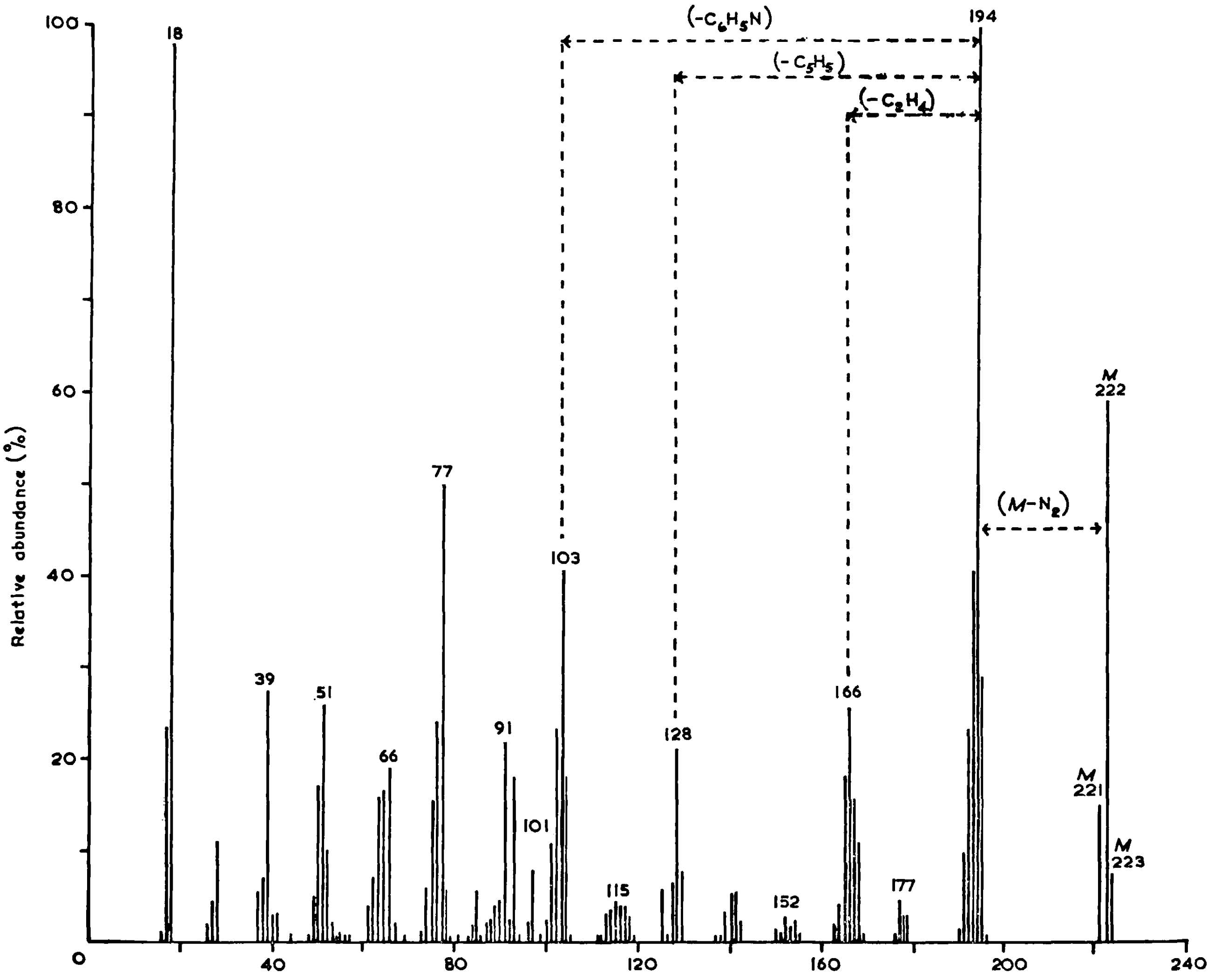
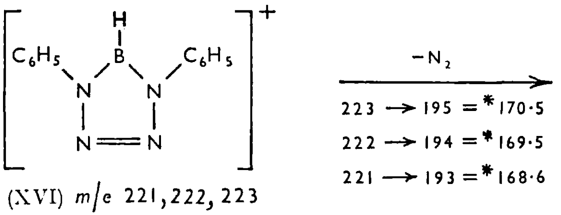


FIGURE 4 Mass spectrum of 2,5-diphenylcyclotetrazenoborane

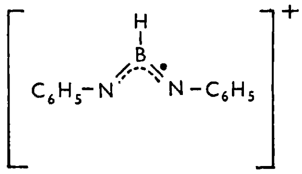
produced by thermal decomposition in the heated inlet system. This has been confirmed in the mass spectrum of diphenylcyclotetrazenoborane by mass measurement. The spectrum below *m/e* 77 is presumably mainly due to fragmentation of this species and breakdown of the phenyl ring from the parent compound.

The mass spectrum of 2,5-diphenylcyclotetrazenoborane is shown in Figure 4. The spectrum is much more complex than the simpler derivatives and it is therefore difficult to assign much of the fragmentation unambiguously.

Parent ion peaks of moderate intensity are observed at *m/e* 221, *222*, and 223. Fragmentation of the molecular ion occurs almost completely through loss of N_2 although the relative intensities of the peaks at *m/e* 193, 194 suggest that some loss of $N_2 + H\cdot$ still occurs.

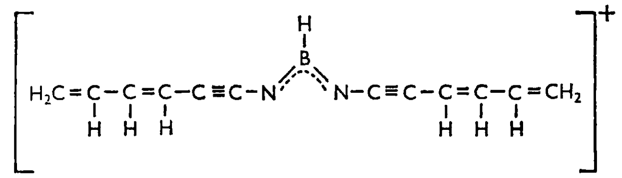


(XVI) *m/e* 221, *222*, 223



(XVII) *m/e* 193, *194*, 195

Species (XVII) would appear to have considerable stability since the peak at *m/e* 194 is the base peak of the spectrum. It has been suggested[4] that the benzene ring opens upon electron impact. If this were to happen in this system, a possible structure for (XVII) would be



in which extensive delocalisation of the charge could occur.

Subsequent fragmentation of (XVII) occurs predominantly by cleavage of successive carbon atoms from the phenyl substituents and hydrogen loss, which produces groups of peaks around *m/e* 177, 166, 154, 141, 128, and 117. Many of these cleavages are supported by metastable transitions (Table).

Other fragmentation of (XVII) possibly occurs through loss of $C_6H_5\cdot$ to give peaks at *m/e* 116 and *117* due to $[C_6H_5NBHN]^+$, or loss of $[C_6H_5N\cdot]$ to give peaks at *m/e* 102 and *103*, due to $[C_6H_5NBH]^{+\cdot}$ although neither is confirmed by metastable transitions. Alternatively, decomposition of (XVII) can occur so as to eliminate $[C_6H_5NBH]$ and produce a daughter ion of *m/e* 91 of structure $[C_6H_5N]^{+\cdot}$ ($194 \longrightarrow 91 = {}^*42{\cdot}7$, $193 \longrightarrow 91 = {}^*42{\cdot}9$).

Metastable ion peaks from species (XVII)

$194 \xrightarrow{-27} 167 = {}^*143{\cdot}76$

$193 \xrightarrow{-27} 166 = {}^*142{\cdot}78$

$194 \xrightarrow{-17} 177 = {}^*161{\cdot}49$

$193 \xrightarrow{-17} 176 = {}^*160{\cdot}50$

$194 \xrightarrow{-40} 154 = {}^*122{\cdot}25$

$194 \xrightarrow{-54} 140 = {}^*101{\cdot}0$

$194 \xrightarrow{-66} 128 = {}^*84{\cdot}5$

$194 \xrightarrow{-79} 115 = {}^*68{\cdot}2$

$193 \xrightarrow{-79} 114 = {}^*67{\cdot}3$

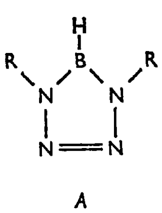
The large peak at *m/e* 77 is presumably due to $C_6H_5^+$ which could be produced by many routes. Peaks at lower mass numbers are mainly due to breakdown of the phenyl ring with contributions from small fragments containing B and N.

In summary, derivatives of cyclotetrazenoborane yield strong parent ion peaks which are the base peaks for aliphatic substitution in the ring. Major fragmentation occurs through loss of N_2, which can also be accompanied by loss of H•.

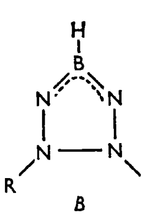
The loss of $(N_2 + H\cdot)$ is virtually complete for Me_2N_4BH whereas in $Me(Ph)N_4BH$ loss of N_2 or $(N_2 + H\cdot)$ occur approximately equally, while in Ph_2N_4BH the fragmentation is mainly the loss of N_2 with slight contribution from $(N_2 + H\cdot)$. We therefore conclude that the hydrogen is probably lost from the substituent group rather than from the boron atom.

It also appears that the subsequent fragmentation is determined largely by the nature of the substituent groups. In compounds containing only alkyl substituents loss of HCN predominates, whereas when one or more of the groups is phenyl, loss of R–N can occur to give the ion $[PhNBH]^{+\cdot}$. In the spectrum of $Me(Ph)N_4BH$, this corresponds to the base peak of the spectrum, whereas in that of Ph_2N_4BH the peak of *m/e* 103 has a relative abundance of 41%.

Earlier work,[5,6] strongly indicates that symmetrically substituted cyclotetrazenoborane derivatives are molecules with C_{2v} symmetry but does not conclusively decide between possible structures *A* and *B*. A molecule



A



B

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[4] R. I. Reed, *Quart. Rev.*, 1966, vol. XX, 4, 527.

[5] N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 1965, 6205.

[6] A. J. Downs and J. H. Morris, *Spectrochim. Acta*, 1966, **22**, 957.

[7] J. B. Leach and J. H. Morris, to be published.

with the structure *B* would be less likely to eliminate N_2, and the mass spectral results strongly support structure *A*, since the primary fragmentation of all the molecules studied involves the loss of N_2.

EXPERIMENTAL

Mass spectra of the pure liquids Me_2N_4BH, Et_2N_4BH, and $Me(Ph)N_4BH$ were obtained on an AEI MS2 mass spectrometer operating at 70 ev using a gallium inlet system at 120°. Source pressures were in the range $0{\cdot}4$—$1{\cdot}6 \times 10^{-6}$ mm. The mass spectrum of crystalline Ph_2N_4BH and improved metastable ion peaks for all compounds were obtained on an AEI MS 12 mass spectrometer. Ph_2N_4BH was introduced into the ion beam using a direct insertion probe. Metastable ion peaks were allocated using a program on an Elliott 4120 computer.

Preparations.—The compounds were prepared by treatment of a primary amine-borane with the appropriate organic azide.[6,7]

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[7/370 *Received, March 28th*, 1967]