Derivatives of Δ^2-Tetrazaboroline. Part VII.[1] Unsymmetrically *N*-Substituted Δ^2-Tetrazaborolines.

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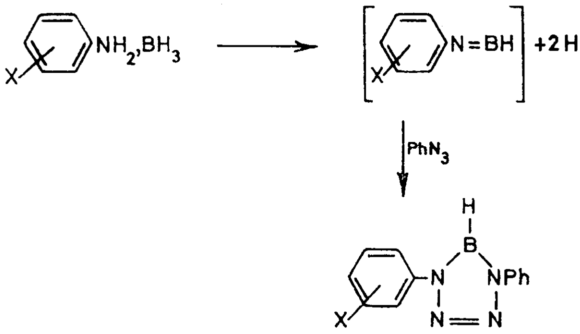
The products of the reactions between *o*-, *m*-, and *p*-mono-substituted aniline–boranes, $XC_6H_4NH_2,BH_3$ and phenyl azide have been shown to be mixtures of the 1,4-substituted-Δ^2-tetrazaborolines Ph_2N_4BH, $Ph(XC_6H_4)$-N_4BH, and $(XC_6H_4)_2N_4BH$; this randomization of substituents appears to be a general feature in preparations of unsymmetrically substituted tetraza-Δ^2-borolines. The preparation and properties of 1,4-*di*-*p*-chlorophenyl-Δ^2-tetrazaboroline is reported. Simple calculations on the unsymmetrically substituted phenyl tetrazaborolines have yielded values for the π-bond orders, π-charge distributions, π-stabilization energies, and energies of bands expected for their first electronic transitions.

THE results of work [1-9] on the Δ^2-tetrazaboroline ring system have prompted a search for new derivatives with functional substituents. Points of interest are (*a*) the effects of steric hindrance on the formation of tetrazaborolines and (*b*) experimental tests of earlier [4] and current MO predictions.

We have previously [4] calculated π-bond orders, π-charge distributions, and energies of first electronic transitions for a number of symmetrically substituted 1,4-diphenyl-Δ^2-tetrazaborolines in which both phenyl rings contain one substituent. We have now synthesized one of these, di-(*p*-chlorophenyl)-Δ^2-tetrazaboroline and report its physical properties. Because of the difficulty of obtaining suitable starting materials to prepare other compounds in the series we then chose to study systems for which starting materials are readily available, namely substituted 1,4-diphenyltetrazaborolines in which only one phenyl ring carried a substituent. Thus, in the present work we have carried out MO calculations on, and attempted the synthesis of, the series of compounds $Ph(XC_6H_4)N_4BH$ ($X = o$-, m-, or p-Me or Cl).

It was anticipated that the reactions between *o*-, *m*- or *p*-methyl- or chloroaniline–boranes and phenyl azide would yield unsymmetrically *N*-substituted tetrazaborolines according to the following reaction scheme:



(1)

However, we found that the reaction was more complex and yielded a mixture of tetrazaborolines. As a result of these observations, further studies were made on the preparation of other unsymmetrically substituted tetrazaborolines.

RESULTS AND DISCUSSION

1,4-*Di*-*p*-*chlorophenyl*-Δ^2-*tetrazaboroline*.—This compound was prepared by treating *p*-chloroaniline–borane with *p*-chlorophenyl azide; it had m.p. 158°.

Spectroscopic Properties.—The first band in the electronic spectrum at 250·2 nm. ($\varepsilon_{max.}$ 3·47 × 10^4 l. cm.$^{-1}$ mole^{-1}) is in excellent agreement with the predicted [4] value of 251 nm. and suggests that the current improved calculations should be reliable.

The chemical shift of —19·2 p.p.m. (J_{BH}, 166 Hz) downfield from boron trifluoride–diethyl ether of the ^{11}B n.m.r. indicated similar shielding of the boron atom to that in diphenyltetrazaboroline, in agreement with the calculated [4] π-charges of the two molecules. A typical AA'BB' proton spectrum centred at τ 2·48 was observed for the substituted phenyl groups.

The principal bands in the i.r. spectrum are reported in the Experimental section. Characteristic B–H stretching and deformation modes can be assigned by analogy with earlier compounds [2,8] and although the N_4B ring modes are less readily discerned, the frequencies (cm.$^{-1}$) associated with each ring mode (in parentheses) are tentatively assigned to 1073 (I); 1107, 1099 (II); 1399, 1393 (V); 1201, 1189 (VI); 970 (VII); 418 (VIII). Characteristic 1,4-disubstituted phenyl vibrations can be assigned by analogy with those quoted by Whiffen.[10]

The mass spectrum is reported in the Experimental

Part VI, E. F. H. Brittain, J. B. Leach, and J. H. Morris, *Org. Mass. Spec.*, 1968, **1**, 459.

[2] N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 1965, 6205.

[3] A. J. Downs and J. H. Morris, *Spectrochim. Acta*, 1966, **22**, 957.

[4] J. H. Morris and P. G. Perkins, *J. Chem. Soc.* (*A*), 1966, 576.

[5] J. H. Morris and P. G. Perkins, *J. Chem. Soc.* (*A*), 1966, 580.

[6] J. B. Leach and J. H. Morris, *J. Chem. Soc.* (*A*), 1967, 1590.

[7] E. F. H. Brittain, J. B. Leach, and J. H. Morris, *J. Chem. Soc.* (*A*), 1968, 340.

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

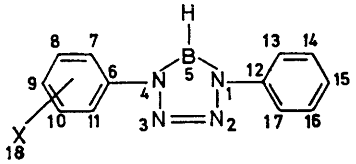
[9] E. F. H. Brittain, J. B. Leach, and J. H. Morris, Enfield Symposium on Mass Spectrometry, July 1967; 'Mass Spectrometry,' ed. R. Brymner and J. R. Penney, Butterworths, London, 1968, 195.

[10] D. H. Whiffen, 'Molecular Spectroscopy,' Institute of Petroleum, 1955, 111.

section. Molecular-ion peaks in the expected isotopic ratios were observed at m/e 289, *290*, 291, *292*, 293, *294*. (The predominant ions due to ^{11}B are italicized.) The first fragmentation observed was loss of N_2 to give base peaks of the spectrum at m/e 261, *262*, 263, *264*, 265, *266* attributed to $[ClC_6H_4NB(H)NC_6H_4Cl]^{+\cdot}$ and this was confirmed by metastable ion peaks. An alternative minor fragmentation of the molecular ion is loss of Cl• to give the characteristic peak pattern due to $[(ClC_6H_4)(C_6H_4)N_4BH]^+$ at m/e 244, *245*, 246, *247*. Loss of Cl• also occurs from the (molecular ion $-N_2)^+$ species to yield ions at m/e 226, *227*, 228, *229*: these, in turn, can lose a further Cl• to give peaks at m/e 191, *192*, both of these fragmentations being confirmed by metastable ions. Further fragmentation involves cleavage of the aryl rings. An intense ion is observed at m/e *137* corresponding to $[ClC_6H_4N{=}BH]^{+\cdot}$ analogous to the observed fragmentations for phenyl tetrazaboroline derivatives.[7,11]

TABLE 1

Calculated π-bond orders and charge distributions



(Bonds and atoms are not stated where they are symmetrical)

Com-pound	Formula	Bond	π-Bond order	Atom	π-Charge density
(I)	Ph_2N_4BH	1—5	0·282	1	1·900
		1—2	0·188	2	1·037
		2—3	0·962	5	0·087
		4—6	0·162	6	0·990
		6—7	0·657	7	1·009
		7—8	0·669	8	1·003
		8—9	0·665	9	1·007
(II)	(o-ClC_6H_4)PhN_4BH	1—5	0·282	1	1·900
	(Cl at 7)	1—2	0·188	2	1·037
		2—3	0·961	5	0·087
		4—6	0·161	6	0·994
		6—7	0·654	7	1·005
		7—8	0·666	8	1·007
		8—9	0·666	9	1·008
		9—10	0·665	10	1·005
		10—11	0·668	11	1·010
		11—6	0·658	18	1·991
		7—18	0·096	Others	As (I)
		Others	As (I)		
(III)	(m-ClC_6H_4)PhN_4BH	1—5	0·282	1	1·900
	(Cl at 8)	1—2	0·188	2	1·037
		2—3	0·962	5	0·087
		4—6	0·162	6	0·991
		6—7	0·658	7	1·013
		7—8	0·666	8	0·999
		8—9	0·662	9	1·011
		9—10	0·666	10	1·004
		10—11	0·669	11	1·012
		11—6	0·657	18	1·991
		8—18	0·097	Others	As (I)
		Others	As (I)		
(IV)	(p-ClC_6H_4)PhN_4BH	1—5	0·282	1	1·900
		1—2	0·188	2	1·037
		2—3	0·961	5	0·087
		4—6	0·161	6	0·993
		6—7	0·657	7(11)	1·010
		(6—11)			
		7—8	0·670	8(10)	1·006
		(10—11)			
		8—9	0·662	9	1·003
		(9—10)			
		9—18	0·096	18	1·991
		Others	As (I)	Others	As (I)
(V)	(o-MeC_6H_4)PhN_4BH	1—5	0·282	1	1·900
	(Me at 7)	1—2	0·188	2	1·037
		(3—4)	(0·189)		
		2—3	0·961	5	0·088
		4—6	0·159	6	1·006
		6—7	0·645	7	0·988
		7—8	0·658	8	1·019
		8—9	0·667	9	1·011
		9—10	0·665	10	1·014
		10—11	0·666	11	1·014
		11—6	0·661	18	1·967
		7—18	0·182	Others	As (I)
		Others	As (I)		
(VI)	(m-MeC_6H_4)PhN_4BH	1—5	0·282	1	1·900
	(Me at 8)	1—2	0·188	2	1·037
		2—3	0·961	5	0·087
		4—6	0·161	6	0·994
		6—7	0·660	7	1·025
		7—8	0·657	8	0·982
		8—9	0·653	9	1·023
		9—10	0·668	10	1·007
		10—11	0·667	11	1·021
		11—6	0·656	18	1·967
		8—18	0·183	Others	As (I)
		Others	As (I)		
(VII)	(p-MeC_6H_4)PhN_4BH	1—5	0·282	1	1·900
		1—2	0·188	2	1·037
		2—3	0·961	5	0·088
		4—6	0·159	6	1·002
		6—7	0·656	7(11)	1·013
		(6—11)			
		7—8	0·671	8(10)	1·019
		(10—11)			
		8—9	0·654	9	0·986
		(9—10)			
		9—18	0·182	18	1·967
		Others	As (I)	Others	As (I)

TABLE 2

Calculated ring energies and positions of the first electronic transitions

	E_π (β units)		Electronic spectra 1st band	
Compound	Ring only	Total E_π	$\Delta(\beta)$	Δ(nm.) *
$(C_6H_5)_2N_4BH$	3·016	29·016	1·04942	243 *
(o-ClC_6H_4)$(C_6H_5)N_4BH$	3·056	29·056	1·03746	246
(m-ClC_6H_4)$(C_6H_5)N_4BH$	3·056	29·056	1·04051	245
(p-ClC_6H_4)$(C_6H_5)N_4BH$	3·056	29·056	1·02270	249
(o-MeC_6H_4)$(C_6H_5)N_4BH$	3·191	35·191	0·98220	260
(m-MeC_6H_4)$(C_6H_5)N_4BH$	3·192	35·192	0·99773	256
(p-MeC_6H_4)$(C_6H_5)N_4BH$	3·191	35·191	0·96226	265

* Calibrated arbitrarily by setting first energy gap of 1,4-diphenyl-Δ^2-tetrazaboroline equal to 243 nm. This gives a value of β equal to 3·16 ev (*cf.* the S.C.F. value of 2·39 ev).

Calculations. Molecular orbital calculations on the compounds $Ph(XC_6H_4)N_4BH$ (X = o-, m-, or p-Cl or Me) were carried out by the modified Hückel approach discussed earlier,[4] with the additional refinement of iteration of both the α- and β- parameters to self-con-

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

sistency. Values of the π-bond orders, π-electron charge densities, the ring and total π-energies, and positions of the bands of the first electronic transition for the compounds, are presented in Tables 1 and 2.

Attempted Preparation of Unsymmetrically Substituted Tetrazaborolines.—Reactions between substituted aniline–boranes and phenyl azide in all cases yielded white crystalline products, which were subsequently shown to be mixtures of tetrazaborolines of the types $(XC_6H_4)_2N_4BH$, $Ph(XC_6H_4)N_4BH$, and Ph_2N_4BH by the following methods.

Elemental analyses for each product totalled 100%, but were generally in poor agreement for the expected simple compounds $Ph(XC_6H_4)N_4BH$. I.r. and n.m.r. spectra showed features characteristic of tetrazaborolines although these also were not consistent with the simple compounds $(XC_6H_4)(C_6H_5)N_4BH$. However, these data were compatible with mixtures of tetrazaborolines.

Previous work on the mass spectra of tetrazaborolines has established general fragmentation patterns for a wide varety of tetrazaborolines.[1,7,9,11] The principal features of the mass spectra of the products of the reactions between substituted aniline–boranes and phenyl azide are reported in the Experimental section, and these spectra confirm beyond reasonable doubt that the products were mixtures of the tetrazaborolines $(XC_6H_4)_2N_4BH$, $Ph(XC_6H_4)N_4BH$, and Ph_2N_4BH. Thus, we observed that for products derived from *m*- or *p*-chloro- or methyl-aniline–boranes, not only were parent ions observed for the compounds $Ph(XC_6H_4)N_4BH$ but parent ions for species Ph_2N_4BH and $(XC_6H_4)_2N_4BH$ were also present. Previously established fragmentation patterns strongly indicate that these species were unlikely to arise from fragmentation and, consequently, must have been present in the original products. Furthermore, their subsequent characteristic fragmentation lends additional support to their identity. The mass spectra of products from *o*-substituted aniline–boranes did not show the presence of any $(XC_6H_4)_2N_4BH$, although small amounts of $Ph(XC_6H_4)N_4BH$ and large amounts of Ph_2N_4BH were observed.

Attempts to separate the components of the products by fractional crystallization, fractional sublimation, or t.l.c. were only partially successful.

In the light of these experiments the preparation[5] of methylphenyltetrazaboroline was reinvestigated. The reaction between methylamine–borane and phenyl azide in ether at elevated temperatures gave dimethyltetrazaboroline and methylphenyltetrazaboroline which were readily isolated and purified by vacuum distillation; the residue from the distillation contained impure diphenyltetrazaboroline. Previously, the compound was isolated from the reaction products of aniline–borane and methyl azide.

Similarly, the reaction between equimolar quantities of ethylamine–borane and methyl azide produced dimethyltetrazaboroline, ethylmethyltetrazaboroline, and diethyltetrazaboroline; treatment of this mixture with phenylmagnesium bromide gave a mixture of dimethyl-, ethylmethyl-, and diethyl-5-phenyltetrazaboroline in the statistically expected concentration ratio of 1 : 2 : 1.

Furthermore, it was found that when dimethyltetrazaboroline and diethyltetrazaboroline or dimethyltetrazaboroline and ethylazide were heated at 130°, the reactions gave mixtures of dimethyl-, ethylmethyl-, and diethyl-tetrazaboroline, the compounds being characterized by g.l.c. and mass spectrometry.

The above series of experiments suggests, therefore, that the previously postulated[2] mechanism (2) for the formation of tetrazaborolines is oversimplified.

$$\begin{tikzcd} R^1NH_2,BH_3 \arrow[r] & {[R^1N{=}BH]} + 2H_2 \arrow[d, "R^2N_3"] \\ & R^1R^2N_4BH \end{tikzcd} \qquad (2)$$

In order to account for the observed 'scrambling' of the *N*-substituent groups, several possible mechanisms were considered. The first assumed that the *N*-substituents exchanged by essentially a free-radical method. However, Sales[12] failed to observe any e.s.r. signal on solutions of tetrazaborolines, although Pearson[13] found that 1,4-dimethyltetrazaboroline was able to initiate the polymerisation of methylmethacrylate at 0° in the absence of oxygen.

Another plausible mechanism envisages the dynamic cleavage of the tetrazaboroline by two routes to produce boronimide and azide intermediates, followed by the recombination of all possible fragments:

$$\begin{aligned} R^1R^2N_4BR^3 &\rightleftharpoons [R^1N{=}BR^3] + R^2N_3 \\ R^1R^2N_4BR^3 &\rightleftharpoons [R^2N{=}BR^3] + R^1N_3 \\ [R^1N{=}BR^3] + R^1N_3 &\rightleftharpoons R^1{}_2N_4BR^3 \\ [R^2N{=}BR^3] + R^2N_3 &\rightleftharpoons R^2{}_2N_4BR^3 \qquad (3) \end{aligned}$$

However, as yet no borazines have been detected in the reaction products.

EXPERIMENTAL

Solvents and Intermediates.—Solvents and amines were dried and purified by standard procedures. Diborane (Callery Chemical Co.) was used from a cylinder first cooled to −78°. Organic azides * were prepared as reported previously.[2,8] Dimethyl- and diethyl-tetrazaboroline were prepared as before.[5,8]

p-Chlorophenyl azide was prepared by treating *p*-chlorophenylhydrazine hydrochloride (25 g., 0·14 mole) (Aldrich Chemicals) in hydrochloric acid (7 ml.) and diethyl ether (150 ml.) with a freshly prepared solution of sodium nitrite (15 g., 0·218 mole) with the temperature below 5°. The *p*-chlorophenyl azide was extracted by steam distillation followed by careful drying and vacuum distillation of the product. The product (8·72 g., 41%) was identified by i.r. and ^1H n.m.r. spectroscopy, and mass spectrometry.

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* Attention is drawn to the necessary precautions.[8]

[12] K. Sales, personal communication.

[13] R. G. Pearson, personal communication.

Preparation of 1,4-*Di*-p-*chlorophenyl*-Δ^2-*tetrazaboroline.*—Diborane (0·019 mole) was condensed into an ethereal solution of *p*-chloroaniline (5 g., 0·039 mole) *in vacuo.* To this solution was added *p*-chlorophenyl azide (5·98 g., 0·039 mole); the reactants were stirred magnetically until all the white precipitate initially formed dissolved to give a yellow solution after which the mixture was set aside for a few days at room temperature. The crystalline product was filtered off and recrystallized from benzene or light petroleum (80—100°). An attempt to purify the product by sublimation at 140—160° led to its decomposition, and *p*-chlorophenyl azide, identified by i.r. spectroscopy, was liberated as a pale yellow liquid. The yield of bis-*p*-chlorophenyltetrazaboroline was 5·63 g., (50%) (Found: C, 49·4; H, 3·2; B, 3·7; Cl, 24·2; N, 19·3. $C_{12}H_9BCl_2N_4$ requires C, 49·6; H, 3·1; B, 3·7; Cl, 24·4; N, 19·3%).

The Preparation of Methylphenyltetrazaboroline from Methylamine–Borane and Phenyl Azide.—Equimolar quantities of methylamine–borane, prepared directly from methylamine and diborance, and phenyl azide in diethyl ether were heated in a sealed ampoule at 130° for 36 hr. The reaction products were then vacuum distilled. The first product, distilled at room temperature and collected at −30°, was dimethyltetrazaboroline which was characterized by its i.r. [3] and mass spectra.[7] The second product, distilled at 60° under high vacuum, was shown to be methylphenyltetrazaboroline by i.r. and ^{11}B and ^{1}H n.m.r. spectroscopy.[5] The residue was shown to contain diphenyltetrazaboroline from its i.r. spectrum.[2] The yield of methylphenyltetrazaboroline was 65%.

The Reactions of Substituted Aniline–Boranes with Phenyl Azide.—The required aniline, diborane, and phenyl azide were treated as in the preparation of bis-*p*-chlorophenyltetrazaboroline. The reaction involving *p*-chloroaniline was repeated with a threefold excess of *p*-chloroaniline, and this resulted in a substantial increase in the yield of product. The product was sublimed *in vacuo* at *ca.* 140—160°. The fractions obtained with increasing temperature had a higher m.p. and contained progressively more of the bis-*p*-chlorophenyltetrazaboroline as indicated by mass spectrometry and i.r. spectroscopy. However, a single, pure species was not isolated, possibly because of rearrangement at the temperature of sublimation.

The Reaction of Ethylamine–Borane with Methyl Azide.—Equimolar quantities of ethylamine–borane, prepared directly from ethylamine and diborane, and methyl azide were heated in dry diethyl ether in a sealed ampoule at 130° for 16 hr. Vacuum distillation of the reaction products led to the isolation of a colourless material in a trap at −35°. The product was further purified by vacuum fractionation and was shown by mass spectrometry and g.l.c. to be a mixture of dimethyl-, ethylmethyl-, and diethyl-tetrazaboroline. Subsequently, the mixed product was treated [8] with an excess of phenyl Grignard reagent in diethyl ether; the products were hydrolysed with saturated aqueous ammonium chloride, and were extracted with ether. The ethereal solution was dried over molecular sieve and then distilled under reduced pressure to give a colourless liquid in a trap at −20° which was examined by g.l.c. and mass spectroscopy. The chromatograph consisted of three peaks with no tailing in the ratio 1 : 2 : 1, and mass spectrometry confirmed the presence of dimethyltetrazaboroline, ethylmethyltetrazaboroline, and diethyltetrazaboroline.

The mixed products were submitted to Dr. R. L. Williams at E.R.D.E., Waltham Abbey, Essex, for sensitivity tests. With regard to impact sensitivity, the liquid can be regarded as a normal safe organic liquid, since no ignition took place with fall heights of up to 100 cm. Temperature of ignition could not be determined although the material began to smoke at 202° and continued to do so until 308°. A dark brown residue remained. On ignition with a small flame, the material burned quietly with a yellow flame.

The Reaction of Dimethyltetrazaboroline with Ethyl Azide.—Equimolar quantities of dimethyltetrazaboroline and ethyl azide in diethyl ether were heated in a sealed ampoule at 130° for 48 hr. Vacuum distillation of the reaction products gave a colourless, volatile liquid in a trap at −40°, which was shown by mass spectrometry and g.l.c. to be a mixture of dimethyl-, ethylmethyl-, and diethyl-tetrazaboroline. A small amount of uncharacterized residue remained in the ampoule.

The Reaction of Dimethyltetrazaboroline with Diethyltetrazaboroline.—Dimethyl- and diethyl-tetrazaboroline were freshly distilled under vacuum and mixed together in equimolar quantities. A few drops of the mixture were placed in a number of small ampoules in a nitrogen-containing glove box. The ampoules were sealed *in vacuo* and heated for varying periods of time in a constant-temperature fluidized sand-bath. It was found that with increasing time of heating, an increasing amount of ethylmethyltetrazaboroline was produced. The ethylmethyltetrazaboroline was detected (*a*) by mass spectrometry by the build-up of the parent ion peak at *m*/*e* 112 and (*b*) by g.l.c. which showed the increase of a third peak. This peak had a shape both similar to, and a retention time intermediate between those for dimethyl- and diethyl-tetrazaboroline which had been previously characterized. All three peaks showed characteristic tailing. It was of interest that no formation of ethylmethyltetrazaboroline was observed at room temperature.

I.r. Spectra.—Routine spectra were recorded on a Unicam SP 200 spectrometer between 5000 and 650 cm.$^{-1}$. Definitive spectra were obtained on a Grubb–Parsons Spectromaster grating spectrometer between 4000 and 400 cm.$^{-1}$. Spectra were obtained on thin films of pure liquids, or as Nujol mulls and pressed KBr discs for solids.

The i.r. spectrum of 1,4-*di*-*p*-chlorophenyltetraza-Δ^2-boroline showed the following bands: 3096w, 3084w, 2845vw, 2660w, 1908w, 1894w, 1653sh, 1642w, 1621w, 1603w, 1590sh, 1563sh, 1546sh, 1497vs, 1482sh, 1464msh, 1439m, 1425sh, 1399sh, 1393m, 1370m, 1359sh, 1300m, 1277w, 1267sh, 1201m, 1193sh, 1189s, 1174ms, 1170sh, 1117w, 1107w, 1099s, 1073vs, 1053sh, 1031sh, 1009s, 976m, 970ms, 962sh, 945w, 936w, 922w, 917sh, 903w, 835vs, 831vs, 821ms, 810ms, 747w, 726w, 702w, 638wb, 629wb, 571ms, 545ms, 503sh, 499sh, 490s, 487s, 418w.

N.m.r. Spectra.—These were obtained on a Perkin-Elmer R10 spectrometer operating at 60 MHz (^{1}H) and 19·3 MHz (^{11}B). Proton chemical shifts were obtained with reference to internal tetramethylsilane, and ^{11}B shifts with reference to external boron trifluoride–diethyl ether. Solutions in non-protonic solvents (CCl_4 or $CDCl_3$) or neat liquids were used.

U.v. Spectra.—These were obtained on a Unicam SP 800 spectrophotomer as solutions in cyclohexane.

Mass Spectra.—The mass spectra were obtained on AEI. MS2, MS9, and MS12 mass spectrometers. Solid compounds were introduced by direct-insertion probes, and volatile liquids by cold inlet and hot box systems.

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

The molecular ions from the products of reaction between substituted anilines–boranes and phenyl azide are listed below, together with an indication of the subsequent fragmentation which in many instances was substantiated by the observation of metastable transitions.

(a) *Product from the Reaction of* o-*Chloroaniline–Borane with Phenyl Azide.*—The parent ion $[\mathrm{Ph}(o\text{-}\mathrm{ClC_6H_4})\mathrm{N_4BH}]^{+\cdot}$ (*m*/*e* 255, *256*, 257, *258*) was shown to lose N_2 to give peaks at *m*/*e* 227, *228*, 229, *230* followed by loss of Cl• to give the peaks around *m*/*e* 193. Intense peaks at *m*/*e* 221, *222*, 223 were observed showing the presence of a large quantity of $[\mathrm{Ph_2N_4BH}]^{+\cdot}$ and all the characteristic fragmentations of this compound [7] were observed. Again an intense peak at *m*/*e* 103 was obtained attributable to $[\mathrm{PhN{=}BH}]^{+\cdot}$ by either loss of [PhN•] or $[\mathrm{C_6H_4ClN}\cdot]$ from the $(M - \mathrm{N_2})$ fragment of $\mathrm{Ph_2N_4BH}$ and $(o\text{-}\mathrm{ClC_6H_4})(\mathrm{C_6H_5})\mathrm{N_4BH}$ respectively.

(b) *Product from the Reaction of* m-*Chloroaniline–Borane with Phenyl Azide.*—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 $[(\mathrm{C_6H_5})_2\mathrm{N_4BH}]^{+\cdot}$, $[(m\text{-}\mathrm{ClC_6H_4})(\mathrm{C_6H_5})\mathrm{N_4BH}]^{+\cdot}$, and $[(m\text{-}\mathrm{ClC_6H_4})_2\mathrm{N_4BH}]^{+\cdot}$ 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•), (PhN•) or $(\mathrm{ClC_6H_4N}\cdot)$, and $(\mathrm{ClC_6H_4N}\cdot)$ respectively to yield sets of peaks around 103, 137 or 103, and 137 respectively. Alternatively loss of Cl• from the $[M - \mathrm{N_2}\text{–}\mathrm{Cl}]^+$ peak occurred for the $(m\text{-}\mathrm{ClC_6H_4})_2\mathrm{N_4BH}$ derivative to give peaks around *m*/*e* 192.

(c) *Product from the Reaction of* p-*Chloroaniline–Borane with Phenyl Azide.*—Again three sets of characteristic parent ions at *m*/*e* (221, *222*, 223), (225, *256*, 257, *258*), and (289, *290*, 291, *292*, 293, *294*) corresponding to $[(\mathrm{C_6H_5})_2\mathrm{N_4BH}]^{+\cdot}$, $[\mathrm{Ph}(p\text{-}\mathrm{ClC_6H_4})\mathrm{N_4BH}]^{+\cdot}$, and $[(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{N_4BH}]^{+\cdot}$ 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•), $(\mathrm{C_6H_4ClN}\cdot)$ or (PhN•), and $(\mathrm{C_6H_4ClN}\cdot)$ to give peaks at *m*/*e* 103, 103 or 137, and 137 respectively. Alternatively the $(M - \mathrm{N_2})^+$ ions from $(\mathrm{C_6H_4Cl})(\mathrm{C_6H_5})\mathrm{N_4BH}$ and $(\mathrm{C_6H_4Cl})_2\mathrm{N_4BH}$ could lose Cl• and in the latter case this could be followed by further loss of Cl•.

(d) *Product from the Reaction of* o-*Toluidine–Borane with Phenyl Azide.*—Two sets of parent ions were observed at *m*/*e* 221, *222*, 223 and 235, *236*, 237 corresponding to $[(\mathrm{C_6H_5})_2\mathrm{N_4BH}]^{+\cdot}$ and $[(\mathrm{MeC_6H_4})(\mathrm{C_6H_5})\mathrm{N_4BH}]^{+\cdot}$ respectively. Again the fragmentation of the $[\mathrm{Ph_2N_4BH}]^{+\cdot}$ was as previously reported.[7] The first fragmentation of $[\mathrm{Ph}(\mathrm{MeC_6H_4})\mathrm{N_4BH}]^{+\cdot}$ observed was loss of $(\mathrm{N_2} + \mathrm{H}\cdot)$ 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-*Toluidine–Borane with Phenyl Azide.*—Three sets of parent peaks were observed at *m*/*e* 221, *222*, 223; 235, *236*, 237 and 249, *250*, 251 due to $[\mathrm{Ph_2N_4BH}]^{+\cdot}$, $[\mathrm{Ph}(p\text{-}\mathrm{MeC_6H_4})\mathrm{N_4BH}]^{+\cdot}$ and $[(p\text{-}\mathrm{MeC_6H_4})_2\mathrm{N_4BH}]^{+\cdot}$. The high value of the *m*/*e* 221 peak together with a fairly intense peak at *m*/*e* 220 was attributable to loss of $(\mathrm{N_2} + \mathrm{H}\cdot)$ from the parent peak at *m*/*e* 250. Similarly loss of N_2 or $(\mathrm{N_2} + \mathrm{H}\cdot)$ from *m*/*e* 236 gave peaks at *m*/*e* 208 and 207 respectively.

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

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