Cyclic Boron Compounds. Part VIII.[1] Amino- and Hydrazino-boranes and Their Cyclic Dimers

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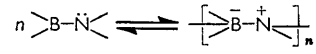
2-Amino-1,3,2-benzodioxaboroles, $(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n$ (R′ = H = R″; R′ = H and R″ = Me, Et, Pr^i, Bu^t, or Ph; and R′ = R″ = Me or Pr^i), have been prepared. Formation of dimers or oligomers, in the solid state or in solution but not in the gas phase, depends on R′ and R″. Monomers and oligomers in this and related systems are differentiated by (i) molecular weight, (ii) infrared spectral characteristics, and (iii) relative reactivities towards hydrolysis. Two related 2-amino-1,3,2-benzodiazaborolines, $[o\text{-}C_6H_4(NH)_2 > B{\cdot}NR'R'']_n$ have been obtained. Both for these and for 2-hydrazino-1,3,2-benzodioxaboroles, an unambiguous decision as to molecular aggregation is not possible. Criteria (ii) and (iii) were first established for the $2Me_2NBCl_2 \longrightarrow (Me_2NBCl_2)_2$ system, and further use was made of (iii) to establish that the kinetics of dimerisation in dilute solution in n-hexane at 25° is governed by a second-order rate expression.

THIS Paper relates, in the main, to the dimerisation of certain aminoboranes. Our studies have had the following objectives: (i) to examine the series $(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n$ and to establish the range of compounds for which $n = 1$ or 2; (ii) to provide methods for readily distinguishing monomers from dimers; (iii) to study the kinetics of the reaction $2Me_2NBCl_2 \longrightarrow (Me_2NBCl_2)_2$; and (iv) to examine compounds of types $(o\text{-}C_6H_4O_2 > B{\cdot}NHNR'R'')_n$ and $[o\text{-}C_6H_4(NH)_2 > B{\cdot}NR'R'']_n$. Results on the $(o\text{-}C_6H_4O_2B{\cdot}NR'R'')_n$ system and on the infrared spectroscopic distinction between monomeric and dimeric $(Me_2NBCl_2)_n$ have been briefly referred to elsewhere.[2]

Monomeric aminoboranes possess acceptor as well as donor sites (the boron and nitrogen atoms, respectively), and consequently oligomers or polymers are sometimes found.



In one or more members of each of eight structural types previously investigated [R_2NBX_2,[3-7] $R_2NB(R')X$,[6,8] $R_2NB(H)X$,[9] $RHNBCl_2$,[10] R_2NBH_2,[7,11] R_2NBHR',[12] H_2NBR_2,[13-15] and $RHNBR_2$[16]] there exist monomeric and/or dimeric (I) forms. Where monomer and dimer are both known, the latter is usually obtained by gently heating the former;[2] whilst in the gas phase, the dimer dissociates (for Me_2NBF_2, monomer and dimer co-exist in the vapour).[4]

As well as by their molecular weights, compounds (I) are characterised by their low chemical reactivity compared with that of their monomeric co-ordinatively

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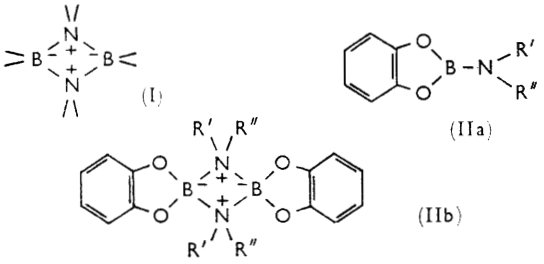
unsaturated analogues,[3] and by their low dipole moments.[3,14] Vibrational spectroscopic studies[15] of $(H_2NBMe_2)_2$ are consistent with a planar $(B{-}N)_2$ ring (I), and this has finally been confirmed by *X*-ray diffraction of crystalline $(Me_2NBX_2)_2$ (X = F or Cl).[17]



(I)

(IIa)

(IIb)

Trimeric [*e.g.*, $(Me_2NBH_2)_3$, which has a six-membered $(BN)_3$ ring in a chair conformation;[18] $(MeHNBH_2)_3$, known as two conformers;[19] and $(H_2NBH_2)_3$[20]] and polymeric [$(H_2NBH_2)_n$[2] and $(Me_2NBH_2)_n$[21]] aminoboranes are also known.

It seems that polymerisation of aminoboranes requires (i) a highly electrophilic boron atom in the monomeric species, and (ii) favourable steric requirements which are clearly progressively more stringent in the series dimer < trimer < polymer. Condition (i) is indicated, for example, by the fact that amino dichloroboranes R_2NBCl_2, unlike $(R_2N)_2BCl$, are sufficiently electrophilic both to form adducts with pyridine[22] and to autocomplex (if R = Me). Condition (ii) was first demonstrated by Musgrave's experiments on $(R_2NBCl_2)_n$, dimers being found for $R_2 = Me_2$, $[CH_2]_4$ or $[CH_2]_5$, $CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$, but not when $R_2 = Et_2$, $Pr^n{}_2$, $Bu^n{}_2$, or $CHMe{\cdot}[CH_2]_4$, and is further illustrated below by our experiments on the $(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n$ system. The high activation energy (~16 kcal. mole^{-1}) estimated by Gunderloy and Erickson for the process $2Me_2NBCl_2 \longrightarrow (Me_2NBCl_2)_2$ may also be associated with (ii).[6]

2-Amino-, 2-Alkylamino-, and 2-Dialkylamino-1,3,2-benzodioxaboroles.—Representative members (see Table 1) of a series of amino-dioxaboranes of empirical formula (II*a*) have been prepared by methods (1)—(3). Reaction (1) is of the widest utility. Reaction (2) is also effective, but as $B(NH_2)_3$ does not exist it is not suitable for preparing 2-amino-1,3,2-benzodioxaborole (R′ = H = R″ in II). Reaction (3) suffers from the disadvantage that separation is difficult when (II) is oligomeric, as then both products are usually only sparingly soluble in nonpolar organic solvents. Two monomeric compounds (R′ = Et or Bu^n = R″) of this type had previously been obtained.[23]

TABLE 1

The 2-amino-1,3,2-benzodioxaboroles

Compound	B. p./mm.	M. p.	Normal state of aggregation	Susceptibility to hydrolysis	i.r. Stretching frequencies νBN (cm.$^{-1}$)	νNH (cm.$^{-1}$)
$C_6H_4O_2{>}B{\cdot}NH_2$ (III)		Subl. 220°/mm.	Oligomer	Stable and very slowly attacked by cold water	912 ± 5	3175, 3040 (3367—weak)
$C_6H_4O_2{>}B{\cdot}NHMe$ (IV)		300	Oligomer	Stable and very slowly attacked by cold water	910 ± 10	3185 ± 2
$C_6H_4O_2{>}B{\cdot}NHEt$ (V)		270	Dimer	Stable but slowly attacked by cold water	915 ± 10	3174 ± 2
$C_6H_4O_2{>}B{\cdot}NHPr^i$ (VI)	54/0·2		Monomer Dimer	Slowly attacked by moist air	1543 ± 2 * 922 ± 10	3425 ± 2 * 3195 ± 2
$C_6H_4O_2{>}B{\cdot}NHBu^t$ (VII)	68/0·3		Monomer	Readily attacked by moist air	1535 ± 2	3472 ± 2
$C_6H_4O_2{>}B{\cdot}NHPh$ (VIII)		266	Dimer	Stable but very slowly attacked by cold water	918 ± 10	3125 ± 2
$C_6H_4O_2{>}B{\cdot}NMe_2$ (IX)	54/0·3	64	Dimer	Stable and very slowly attacked by cold water	946 ± 10	—
$C_6H_4O_2{>}B{\cdot}NPr^i{}_2$ (X)		52	Monomer	Stable and very slowly attacked by cold water	1341 ± 2	—

* Monomer.

$$o\text{-}C_6H_4O_2B{\cdot}NR_2 + 2R'R''NH \longrightarrow 1/n(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n + R_2NH \quad (1)$$

$$o\text{-}C_6H_4(OH)_2 + B(NR'R'')_3 \longrightarrow 1/n(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n + 2R'R''NH \quad (2)$$

$$o\text{-}C_6H_4O_2BCl + 2R'R''NH \longrightarrow 1/n(o\text{-}C_6H_4O_2 > B{\cdot}NR'R'')_n + [R'R''NH_2]^+Cl^- \quad (3)$$

As the boron atom in (II*a*) is relatively little sterically-shielded, and in view of earlier indications that the boron atom in a 1,3,2-benzodioxaborole ring is extremely

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electrophilic (unlike in other "non-aromatic" dioxaboranes),[23,24] system (II) appeared to offer a useful model for investigating the influence of the substituents at nitrogen on propensity for oligomerisation and/or polymerisation.

For the solids or their solutions, a dimeric structure (II*b*) is assigned (Table 1) for the primary and secondary alkylamino-derivatives (V and VI) and the phenyl compound (VIII), but a monomeric structure for the t-alkyl compound (VII). The evidence rests primarily on molecular weights, determined cryoscopically for solutions in nitrobenzene. It will be observed also that the infrared spectra, the m. p.s, and the susceptibility to hydrolysis offer distinctions between the monomers (II*a*) and the dimers (II*b*). At the time this work was carried out, boron-11 nuclear magnetic resonance facilities were not available to us, but this should also prove a powerful tool for distinguishing monomeric aminoboranes from their oligomers, in that in the latter the boron atoms are clearly more shielded.

The isopropyl derivative (VI), when freshly prepared and before distillation, was a liquid with ν(B–N) at ~1540 cm.$^{-1}$ and ν(N–H) at ~3425 cm.$^{-1}$. After distillation, it slowly solidified and the spectral characteristics were those of the dimer (see Table 1).

The 2-amino- (III) (prepared by Dr. G. Srivastava) and 2-methylamino-compounds (IV) are designated as oligomers, in Table 1. They were almost totally insoluble in organic solvents, which precluded the accurate determination of molecular weight cryscopically. Measurements of freezing point of a very dilute solution of (IV) in nitrobenzene suggests a trimeric structure, but the margin of error is considerable. In the vapour phase, (III) (probably like all the other compounds) is monomeric, as shown mass-spectrometrically. For the present, we prefer to designate solid (III) and (IV) non-commitally as "oligomeric," on the basis of the other data shown in Table 1.

Of the 2-dialkylamino-derivatives, only the lowest homologue (IX) is dimeric in solution. This is of interest also as providing the first example of a dimeric tetra-organosubstituted aminoborane. The relative water-stability of monomeric (X) is undoubtedly steric in origin, and is a property shared with other di-isopropylaminoboron compounds.[25]

Infrared spectra of the dimeric and oligomeric compounds show broad bands attributed to BN stretching frequencies at 930 ± 20 cm.$^{-1}$, which is in accord with previous observations for the BN stretching frequencies of a similar dimer, $(Me_2NBCl_2)_2$.[2] The monomeric 2-t-butylamino-1,3,2-benzodioxaborole (VII) has the BN stretching mode at 1535 ± 2 cm.$^{-1}$, which is in good agreement with BN stretching frequencies in other alkylaminoboranes,[26] whilst the position of the same mode in monomeric (X) is consistent with studies on sterically-hindered dialkylaminoboranes.[26]

The spectra of all the dimeric and oligomeric compounds show rather low NH stretching frequencies at 3225—3125 cm.$^{-1}$; this may be compared with the NH stretching frequency of the monomeric 2-t-butylamino-1,3,2-benzodioxaborole located at 3472 ± 2 cm.$^{-1}$.

2-Alkylamino- and Dialkylamino-1,3,2-benzodiazaborolines.—The dimeric nature and stability of some 2-amino-1,3,2-benzodioxaboroles prompted investigation of the possibility of dimerisation also occurring in the 2-alkylamino-1,3,2-benzodiazaborolines. The experiments carried out in order to effect a convenient preparation of such compounds or their precursors, are outlined in (4)—(8)

$$BCl_3 + o\text{-}C_6H_4(NH_2)_2,2HCl \longrightarrow 1/3(C_6H_4N_2HB)_3 + 5HCl \quad (4)$$

$$B(NEt_2)_3 + o\text{-}C_6H_4(NH_2)_2 \longrightarrow 1/3(C_6H_4N_2HB)_3 + 3Et_2NH \quad (5)$$

$$(Pr^i{}_2N)_2B{\cdot}NHBu^t + oC_6H_4(NH_2)_2 \longrightarrow 1/3(C_6H_4N_2HB)_3 + 2Pr^i{}_2NH + Bu^tNH_2 \quad (6)$$

$$(Pr^i{}_2N)_2B{\cdot}NHPr^n + oC_6H_4(NH_2)_2 \longrightarrow o\text{-}C_6H_4(NH)_2 > B{\cdot}NHPr^n + 2Pr^i{}_2NH \quad (7)$$

$$Et_2NBCl_2 + 2Et_3N + oC_6H_4(NH_2)_2 \longrightarrow o\text{-}C_6H_4(NH)_2 > B{\cdot}NEt_2 + 2Et_3NHCl \quad (8)$$

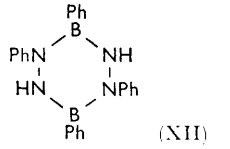
Schemes (4)—(6) afforded a borazine, which has previously been described.[27] The insolubility of the products of schemes (7) and (8) and the complication of endocyclic B–NH links prevents at this time an assignment as to degree of molecular aggregation.

Hydrazinoboranes.—A number of these compounds have recently been obtained.[28,29] Reactions (9)—(11a) were here employed; the last of these was demonstrated by Dr. B. Prokai, who also used an analogous procedure (11b) for obtaining the related phosphorus(III) compound.

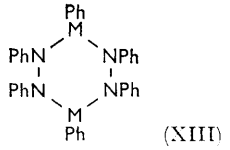
$$o\text{-}C_6H_4O_2 > B{\cdot}NEt_2 + R'R''N{\cdot}NH_2 \longrightarrow 1/n(o\text{-}C_6H_4O_2 > BNH{\cdot}NR'R'')_n + Et_2NH \quad (9)$$

$$PhB(NH{\cdot}NHPh)_2 \xrightarrow{heat} \tfrac{1}{3}(XII) + PhNH{\cdot}NH_2 \quad (10)$$

$$PhNH{\cdot}NHPh + PhMCl_2 + 2Et_3N \longrightarrow \tfrac{1}{2}(XIII) + 2[Et_3NH]^+Cl^- \quad (11a,\ M = B)\ (11b,\ M = P)$$



(XII)



(XIII)

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The two compounds (XI; R'R'' = H,Ph or Me_2) are crystalline solids, sparingly soluble in non-polar organic solvents. The molecular weight (measured ebullioscopically) of the dimethylhydrazino-derivative showed it to be monomeric in the vapour. However, infrared spectroscopic characteristics of solid mulls, especially the ν(B–N) at ~910 cm.$^{-1}$ suggests an oligomeric, and possibly dimeric structure of type (II), for the solids. The only dimeric hydrazinoborane previously reported is $(Ph_2B{\cdot}NH{\cdot}NH_2)_2$.[28]

The Dichlorodimethylaminoborane System.—As briefly reported before,[2] monomeric and dimeric dichlorodimethylaminoboranes $(Me_2NBCl_2)_n$ are distinguished *inter al.* by (i) a strong absorption at 1515 cm.$^{-1}$ in the spectrum of the liquid monomer (νBN), absent from the dimer which, however, has a new absorption at 932 cm.$^{-1}$; and (ii) that the monomer, unlike the dimer, is completely and quantitatively hydrolysed by cold water. The shift of B–N stretching frequency on passing from monomer to dimer is consistent with there being considerable BN double-bond character in the 3-co-ordinate monomer. On the other hand, for $(Ph_2B{\cdot}NH_2)_2$ it has been suggested [30] that the BN stretching mode lies at much higher frequency (1552 cm.$^{-1}$) than that now found in $(Me_2NBCl_2)_2$. A detailed analysis of the spectra of gaseous $Me_2N{\cdot}BX_2$ (X = F, Cl, Br, or I) has recently been published.[4]

The rate of dimerisation of $Me_2N{\cdot}BCl_2$ in n-hexane (~0·6% solution) at 25° has been followed volumetrically, using (ii), by estimating the amount of chloride ion in samples treated with cold water. The data fit the second-order rate equation (12), as is consistent with a molecular process.

$$1/c = (7{\cdot}91 \times 10^{-5})t + 19{\cdot}9 \qquad (12)$$

Other kinetic data are available from the work of Gunderloy and Erickson, who used a different method for following rates.[6] It is clear that dimerisation in this and related systems is a slow process.

EXPERIMENTAL

Preparation of 2-Amino-1,3,2-benzodioxaborole (by Dr. G. Srivastava).—Liquid ammonia (~50 ml.) was condensed into a vessel containing 2-diethylamino-1,3,2-benzodioxaborole (5·46 g.) and the mixture was set aside for 12 hr. Removal of volatile matter and washing with light petroleum (b. p. 40—60°) afforded the white, crystalline (III) (3·86 g., 100%). *2-Amino-1,3,2-benzodioxaborole* was purified by sublimation at 220°/1 mm. (Found: C, 53·8; H, 4·6; B, 7·9; N, 10·2. $C_6H_6BNO_2$ requires C, 53·7; H, 4·6; B, 8·0; N, 10·4%) (see also Table 1). The compound was insoluble in a large number of organic solvents. The mass spectrum showed that the highest significant peak was that due to the monomeric molecular parent ion.

Preparation of 2-Alkyl- and 2-Phenyl-amino-1,3,2-benzodioxaboroles.—All the 2-alkyl- and 2-phenyl-amino-1,3,2-benzodioxaboroles were synthesised by one of three methods [equation (1)—(3)]; we therefore give only one example of each method. Other data are shown in Tables 1 and 2.

TABLE 2

2-Alkyl and 2-phenyl-amino-1,3,2-benzodioxaboroles

Compound	Method (Eq. 1 or 3)	Yield (%)	Found (%) ‡ C	H	B	N	M *	Formula	Required (%) C	H	B	N	M
IV	1	91	56·2	6·2	7·1	9·0	500 †	$(C_7H_8BNO_2)_3$	56·4	5·4	7·3	9·4	447
V	1	83	59·3	6·2	6·5	8·6	334	$(C_8H_{10}BNO_2)_2$	59·0	6·1	6·6	8·6	326
VI	1	94	61·1	6·8	6·1	7·8	377	$(C_9H_{12}BNO_2)_2$	61·5	6·5	6·1	7·9	354
VII	3	72	63·1	7·2	5·7	7·3	181	$C_{10}H_{14}BNO_2$	62·9	7·4	5·7	7·3	191
VIII	1	85	68·0	4·4	5·2	6·6	423	$(C_{12}H_{10}BNO_2)_2$	68·3	4·7	5·1	6·6	422

* Determined cryoscopically in nitrobenzene. † Approximate; see discussion. ‡ These and other carbon and hydrogen analyses were determined by Mr. V. Manohin and his staff, to whom we offer our best thanks; nitrogen was determined by the Kjeldahl, and boron by the Thomas procedure.

(*a*) Aniline (1·3 g., 1 mol.) in light petroleum (b. p. 40—60°; 10 ml.) was added to 2-diethylamino-1,3,2-benzodioxaborole (2·67 g., 1 mol.) in the same solvent (20 ml.) at −78°. A precipitate formed immediately, and, after solvent was removed at 20°/12 mm., 2-phenylamino-1,3,2-benzodioxaborole (2·94 g., 99·7%) (Found: B, 4·9%) was obtained. Recrystallisation from nitrobenzene gave *2-anilino-1,3,2-benzodioxaborole* (VIII) (2·5 g., 84·8%), m. p. 266—268° (see Tables 1 and 2).

(*b*) t-Butylamine (4·13 g., 2 mol.) in light petroleum (b. p. 40—60°; 10 ml.) was added to 2-chloro-1,3,2-benzodioxaborole (4·36 g., 1 mol.) in the same solvent (50 ml.) at −78°. The mixture was allowed to attain room temperature and was set aside for 4 hr. The white precipitate of t-butylammonium chloride (3·22 g.) (Found: Cl, 31·6. Calc. for $C_4H_{12}ClN$: Cl, 32·4%) was removed by filtration and was washed with light petroleum (b. p. 40—60°; 2 × 10 ml.). Distillation of the filtrate gave *2-t-butylamino-1,3,2-benzodioxaborole* (VII) (3·9 g., 72%), b. p. 68°/0·3 mm., n_D^{20} 1·5060 (Found: C, 63·1; H, 7·2; B, 5·7; N, 7·3%; *M*, 181. $C_{10}H_{14}BNO_2$ requires C, 62·9; H, 7·4; B, 5·7; N, 7·3%; *M*, 191), and a white residue of t-butylammonium chloride (1·2 g.).

(*c*) Bis(di-isopropylamino)-t-butylaminoborane (3·19 g., 1 mol.) was added to catechol (1·24 g., 1 mol.) at 20°, and the mixture was heated (3 hr.) under reflux. The di-isopropylamine (1·39 g., 61%) (authentic infrared spectrum) evolved was collected at −78°. The residue gave 2-t-butylamino-1,3,2-benzodioxaborole (VII) (1·67 g., 77·6%), b. p. 60°/0·1 mm. (Found: B, 5·6; N, 7·4. Calc. for $C_{10}H_{14}BNO_2$: B, 5·7; N, 7·3%), and a solid residue (1·03 g.), m. p. 214°.

Preparation of 2-Dialkylamino-1,3,2-benzodioxaboroles.—(*a*) Dimethylamine (3·0 g., 1 mol.) in light petroleum (b. p. 40—60°; 10 ml.) was added to 2-diethylamino-1,3,2-benzodioxaborole (3·19 g., 1 mol.) in light petroleum (b. p. 40—60°; 50 ml.) at −78°. Warming to room temperature,

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and removal of solvent gave a crude product (2·57 g.), from which on distillation was obtained 2-*dimethylamino*-1,3,2-*benzodioxaborole* (2·28 g., 88%), b. p. 54°/0·3 mm., m. p. 64° (it became a dimeric, white solid very soon after distillation) (Found: C, 59·3; H, 6·0; B, 6·6; N, 8·6%; *M*, 315. $C_8H_{10}BNO_2$ requires C, 59·0; H, 6·1; B, 6·6; N, 8·6%; *M*, 326).

(*b*) Di-isopropylamine (13·6 g., 2·2 mol.) in light petroleum (b. p. 40—60°; 20 ml.) was slowly added to 2-chloro-1,3,2-benzodioxaborole (9·43 g., 1 mol.) in the same solvent (50 ml.) at −78°. After filtration and washing with warm benzene (3 × 20 ml.), the residue afforded di-isopropylammonium chloride (10·5 g., 100%) (Found: Cl, 24·3. Calc. for $C_6H_{16}ClN$: Cl, 25·8%). The filtrate, on being freed from solvent, gave 2-*di-isopropylamino*-1,3,2-*benzodioxaborole* (11·3 g., 84·6%), m. p. 52° (Found: C, 65·5; H, 8·1; B, 4·9; N, 6·3%; *M*, 211. $C_{12}H_{18}BNO_2$ requires C, 65·8; H, 8·2; B, 4·9; N, 6·4%; *M*, 219). The m. p. was unchanged after exposure to the atmosphere for 24 hr.

Preparation of 2-*Hydrazino*-1,3,2-*benzodioxaboroles*.—(*a*) Phenylhydrazine (3·2 g., 1 mol.) was added to 2-diethylamino-1,3,2-benzodioxaborole (4·5 g., 1 mol.) in benzene (20 ml.) at 20° and the mixture was set aside for 12 hr. After filtration and washing with benzene (2 × 10 ml.), the residue was the white, crystalline 2-*phenylhydrazino*-1,3,2-*benzodioxaborole* (4·16 g., 78%), m. p. 237° (decomp.) (Found: C, 63·9; H, 5·7; B, 4·8; N, 12·0. $C_{12}H_{11}BN_2O_2$ requires C, 63·8; H, 5·0; B, 4·8; N, 12·4%).

(*b*) *NN*-Dimethylhydrazine (1·5 g., 1 mol.) was added to 2-diethylamino-1,3,2-benzodioxaborole (4·7 g., 1 mol.) in light petroleum (20 ml.) at 20°. After the exothermic reaction had ceased, filtration afforded crystalline 2-(NN-*dimethylhydrazino*)-1,3,2-*benzodioxaborole* (4·15 g., 95%), m. p. 266° [Found: C, 53·0; H, 6·5; B, 6·0; N, 15·2%; *M*, 164. $(C_8H_{11}BN_2O_2)_2$ requires C, 53·6; H, 6·1; B, 6·0; N, 15·6%; *M*, 258]. The molecular weight was determined ebullioscopically in chloroform.

(*c*) Bis(diethylamino)phenylborane (7·48 g., 1 mol.) was added to phenylhydrazine (9·59 g., 2·75 mol.) in light petroleum (b. p. <40°; 25 ml.). The mixture was refluxed (1 hr.) until a pale yellow solid appeared, which was filtered off. *Bis*(*phenylhydrazino*)*phenylborane* (6·46 g., 67%), m. p. 118—120° (Found: C, 72·0; H, 6·0; N, 18·4. $C_{18}H_{19}BN_4$ requires C, 71·5; H, 6·3; N, 18·5%), was crystallised from benzene and light petroleum (b. p. <40°). The infrared absorption maxima were: 3333w (νH–N), 1600s, 1493s, 1462vs (νB–N), 1300b, 1250m, 1062vs, 1020vw, 990vw, 948vw, 877vw, 749s (δC–H out-of-plane), 689s.

Bis(phenylhydrazino)phenylborane (2·71 g.) was heated at 150—170°/0·01 mm., for 1 hr. Phenylhydrazine (0·94 g., 97%), (authentic infrared spectrum) was trapped at −78°/0·01 mm. The residual yellow solid (1·60 g., 93%), m. p. 180—190° was crystallised by dissolving it in benzene and then adding an excess of light petroleum (b. p. <40°). The microcrystal were filtered off, repeatedly washed with light petroleum, and finally dried at 50—60°, to afford *perhydro*-1,3,4,6-*tetraphenyl*-1,2,4,5-*tetra*-*aza*-1,3-*diborine* (XII) (1·12 g., 65%), m. p. 130° (Found: C, 73·2; H, 6·0; N, 13·8%; *M*, 322. $C_{24}H_{22}B_2N_4$ requires C, 74·0; H, 5·8; N, 14·2%; *M*, 387). The infrared absorption maxima were: 3344m, 3322w (νN–H), 2959w, 1587s, 1558m, 1481s, 1449m, 1429s, 1364sh, 1333vs, 1297m, 1235m, 1157w, 1105vw, 1070vw, 1043vw, 1020w, 758s, 746m (δC–H out-of-plane), 714sh, 695s, 685sh.

(*d*) (by Dr. B. Prokai). Addition of hydrazobenzene (8·89 g., 1 mol.) in benzene (150 ml.) to phenyldichloroborane (7·65 g., 1 mol.) was exothermal and afforded a pale yellow solid. Triethylamine (3·6 g., 2 mol.) was added and the mixture was heated (1 hr. at 40—60°). Triethylammonium chloride (98%) was filtered off and from the filtrate there was obtained *perhydrohexaphenyl*-1,2,4,5-*tetra*-*aza*-1,3-*diborine* (XIIIa) (12·0 g., 92%), m. p. 154° (Found: C, 79·8; H, 5·7; B, 4·0; N, 10·1. $C_{36}H_{30}B_2N_4$ requires C, 80·0; H, 5·6; B, 4·0; N, 10·0%). Attempted syntheses of the same compound from hydrazobenzene and either $C_6H_5B(OH)_2$ or $(C_6H_5BO)_3$ failed.

Compound (XIIIa) was readily solvolysed by n-butanol. Thus from (XIIIa) (7·4 g., 1 mol.) and the alcohol (4·05 g., 4 mol.) in light petroleum (b. p. 60—80°; 15 ml.), there was obtained, after reflux (5 hr.), a precipitate of hydrazobenzene (4·7 g., 93%), m. p. 129° (Found: N, 15·3. Calc. for $C_{12}H_{12}N_2$: N, 15·4%); and, in the filtrate, di-n-butoxyphenylborane (5·9 g., 92%), b. p. 141°/13 mm., n_D^{20} 1·4751 (Found: B, 4·6. Calc. for $C_{14}H_{23}BO_2$: B, 4·63%).

Preparation of Perhydrohexaphenyl-1,2,4,5-*tetra*-*aza*-1,3-*diphosphorine* (XIIIb) (by Dr. B. Prokai).—Hydrazobenzene (14·8 g., 1 mol.) in benzene (200 ml.) was added to phenyldichlorophosphine (14·4 g., 1 mol.) in the same solvent (50 ml.) at 20°. Triethylamine (16·7 g., 2 mol.) was added and the mixture was refluxed (2 hr.). Triethylammonium chloride (22·0 g., 99·6%) was filtered off, and removal of solvent from the filtrate afforded the cyclic *compound* (XIIIb) (15·1 g., 67%), m. p. 144—146° (Found: C, 73·1; H, 5·4; N, 9·3; P, 9·7. $C_{36}H_{30}N_4P_2$ requires C, 74·9; H, 5·2; N, 9·7; P, 10·7%).

Preparation of 2-*Amino*-1,3,2-*benzodiazaborolines*.—(*a*) *o*-Phenylenediamine (3·7 g., 1 mol.) in methylene dichloride (30 ml.) was added with stirring to diethylaminodichloroborane (5·3 g., 1 mol.) and triethylamine (3·5 g., 2 mol.) in methylene dichloride (30 ml.) at −78°. After the mixture had attained 20°, diethyl ether (30 ml.) was added and triethylammonium chloride (7·9 g., 100%) was filtered off. The filtrate gave 2-*diethylamino*-1,3,2-*benzodiazaboroline* (4·6 g., 71%), m. p. 94° (Found: C, 62·9; H, 8·1; B, 5·5; N, 22·2. $C_{10}H_{16}BN_3$ requires C, 63·6; H, 8·5; B, 5·7; N, 22·2%) on removal of the solvent.

(*b*) *o*-Phenylenediamine (1·6 g., 1 mol.) and bis(di-isopropylamino)-n-propylaminoborane (4·0 g., 1 mol.) in chlorobenzene (10 ml.) were refluxed (½ hr.) at 120°. After cooling, followed by filtration and washing, the residue gave 2-*n*-*propylamino*-1,3,2-*benzodiazaboroline* (1·4 g., 54%), m. p. 245° (Found: C, 61·0; H, 6·9; B, 6·1; N, 24·1. $C_9H_{14}BN_3$ requires C, 61·8; H, 8·0; B, 6·3; N, 24·0%). The filtrate gave di-isopropylamine (3·2 g., 2·2 mol.).

(*c*) *o*-Phenylenediamine (1·28 g., 1 mol.) and bis(di-isopropylamino)-t-butylaminoborane (3·35 g., 1 mol.) were refluxed (2 hr.) in chlorobenzene (10 ml.). After cooling and filtration, the diazaboroline (1·23 g., 89·4%), m. p. >300° (Found: B, 9·2; N, 24·0. Calc. for $C_{18}N_{15}B_3N_6$: B, 9·3; N, 24·2%) remained. The filtrate gave t-butylamine (0·8 g., 92·5%) and di-isopropylamine (2·4 g., 100%).

(*d*) *o*-Phenylenediamine dihydrochloride (5·46 g., 1 mol.) and boron trichloride (3·55 g., 1 mol.) were refluxed (6 hr.) in chlorobenzene (30 ml.). After the evolution of hydrogen chloride had ceased, the reaction mixture was allowed to cool. It was then filtered and washed with benzene; the residue gave the diazaboroline (3·28 g., 93·7%), m. p. >300° (Found: C, 62·3; H, 4·6; B, 9·0; N, 24·0%).

(*e*) *o*-Phenylenediamine (2·27 g., 1 mol.) and tris(diethylamino)borane (4·73 g., 1 mol.) were refluxed in chloro-

benzene (20 ml.) for 2 hr. After cooling, followed by filtration, the residue was the diazaboroline (1·18 g., 74·9%), m. p. >300° (Found: B, 9·1; N, 23·9%). The filtrate gave diethylamine (1·28 g., 2·8 mol.).

TABLE 3

Dimerisation of Me_2NBCl_2 in n-hexane at 25°

Time (hr.)	Time (sec. × 10^{-4})	Concn. of monomer (mole/l.)	1/concn.
0	0	0·0510	19·61
1	0·36	0·0510	19·61
3	1·08	0·0476	21·01
6	2·16	0·0440	22·73
22	7·92	0·0385	25·97
28	10·08	0·0374	26·74
45	16·20	0·0306	32·68

The Kinetics of Dimerisation.—Preliminary experiments with dimethylaminodichloroborane [3] indicated that the dimerisation in solution at 25° was slow. The method used was based on the fact that, while the monomer possesses two easily-hydrolysable chlorine atoms, the dimer has none and is completely inert to cold water. A small quantity of pure monomer (0·321 g.) was placed in a known volume (50 ml.) of hexane. The solution was kept at a constant temperature of 25°. Small volumes of the solution were removed at regular intervals and the amount of dimer formed was determined by hydrolysing unchanged monomer and estimating its chlorine content (see Table 3).

A plot of the data corresponded to the second-order equation (Eqn. 12).

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