

**1191.** *The Reaction of Primary Amines with Boron Halides.*  
*Part I. Alkylamines: The Preparation of Borazoles and Borazocines*

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Primary alkylamines ( $R \cdot NH_2$ ) react with boron trichloride and boron tribromide to form mixtures of the 1 : 1 adduct (I), the borazene (II) and the alkylammonium tetrahalogenoborate (III), all of which may undergo thermal or base-promoted dehydrohalogenation. *sym-B*-Halogeno-*N*-alkylborazoles are the normal end-products of the reaction, but with hindered amines borazole formation may be inhibited, in some cases with formation of tetrameric borazynes ( $RNBX$ )<sub>4</sub>. These are shown to contain a new eight-membered boron-nitrogen ring system. The preparation and the physical and chemical properties of these compounds have been studied.

MANY attempts have been made in recent years to prepare polymers in which the main chain is composed of elements other than carbon, in the hope that the thermal stability would be greater than that of the known organic polymers. It is, paradoxically, in the organic field that the most useful thermally stable polymers have in fact been developed (*e.g.*, the polybenzimidazoles<sup>1</sup> and the polypyromellitimides<sup>2</sup>) but the impetus given to the development of some areas of organometallic chemistry has been significant. Our own work, which will be described in this and succeeding Papers, was directed towards the preparation of boron-nitrogen polymers.

The possibility of obtaining boron-nitrogen polymers analogous to organic polymers is based upon the possible analogy between the  $[sp^2]p_\pi^0$  boron- $[sp^2]p_\pi^2$  nitrogen and the  $[sp^2]p_\pi^1$  carbon- $[sp^2]p_\pi^1$  carbon pairs. In practice these analogies have a rather limited application: thus, the borazenes  $RR'BNR''R'''$ , containing three-co-ordinate boron and nitrogen undergo substitution rather than the addition characteristic of olefins. Most boron-nitrogen compounds are easily hydrolysed, though this tendency may be modified in some four-co-ordinate boron compounds [*e.g.*,  $Me_3N \cdot BCl_3$ ;  $(Me_2NBCl_2)_2$ ], in some cyclic compounds (*e.g.*, in the many heteroaromatic compounds described by Dewar<sup>3</sup>), and in sterically hindered compounds [*e.g.*,  $B(NMePh)_3$ ]. The high bond energy of the B-N bond (104.3 kcal./mole), and the high thermal stability of such known compounds as boron nitride and the alkylborazoles, led to the expectation that B-N polymers, if obtainable, would be more stable than organic polymers.

The trimeric borazynes (the borazoles) are well known, and have some aromatic character.<sup>4</sup> They are commonly found as the end product of reactions from which the monomeric borazyne,  $RBNR'$  (isoelectronic and isosteric with the acetylene  $RCCR'$ ), would be expected. In our efforts to prepare polymers two approaches were selected. The first was to discover whether by a suitable choice of substituents or experimental conditions the formation of the borazole might be suppressed in favour of higher cyclic or linear polyborazynes, or, alternatively, whether the same products might be obtained by rearrangement of borazoles. At the time this work was begun there was no clear-cut evidence that higher polyborazynes had ever been obtained. The second approach was to devise the means whereby chains of borazole rings might be made, linked together directly or through suitable bridging groups. In this Paper we describe part of our work on the first of these approaches, namely the study of the dehydrohalogenation of the 1 : 1 adducts of primary aliphatic amines and boron trichloride or boron tribromide. This system was selected as a suitable model for the study of the possible inhibition of borazole formation because it starts with readily accessible materials and had it been successful might have been suitable for commercial application.

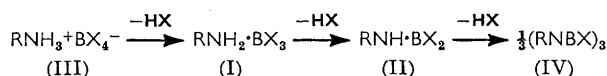
<sup>1</sup> H. Vogel and C. S. Marvel, *J. Polymer Sci.*, 1961, **50**, 511.

<sup>2</sup> J. I. Jones, F. W. Ochynski, and F. A. Rackley, *Chem. and Ind.*, 1962, 1686.

<sup>3</sup> M. J. S. Dewar, Boron-Nitrogen Chemistry, Advances in Chemistry Series No. 42, American Chemical Society, 1964, p. 227.

<sup>4</sup> E. G. H. Watanabe, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 1960, **82**, 3294.

The 1 : 1 adducts (I; X = Cl or Br) of primary aliphatic amines and boron halides may sometimes be made by direct addition of the components in solution. Often, however, the product of the reaction is a mixture of the 1 : 1 adduct, the borazene (II), and the tetrahalogenoborate (III). For example, with boron trichloride and *t*-butylamine the product contained about 25 moles % of the adduct, and the remainder was equally distributed between (II) and (III). In other cases, for example cyclohexylamine and benzylamine,<sup>5</sup> the product is a mixture of (II) and (III) alone. The adducts are also formed by the reaction of the boron halide with the alkylammonium halide in suspension in boiling toluene; at lower temperatures<sup>6</sup> the tetrahalogenoborates are formed. The dehydrohalogenation of the adducts, or of the mixtures formed when the adduct is expected, may be brought about thermally by heating under reflux in a suitable solvent, or by treatment with a suitable tertiary base, for example, triethylamine. The thermal dehydrohalogenation, first reported by Rideal<sup>7</sup> but first recognised as leading to borazole formation by Jones and Kinney,<sup>8</sup> takes place quite rapidly with most aromatic amines<sup>8-11</sup> at the temperature of boiling benzene, but more slowly with aliphatic amines,<sup>12</sup> with which it is convenient to use boiling chlorobenzene. Sometimes it is necessary (for example, with ammonia<sup>13</sup> or 2-chloroethylamine) or convenient to start with a hydrohalide, but the result is the same. The reaction proceeds with the elimination of two (or three) molecules of the hydrogen halide, with the formation of substantially pure *sym-B*-halogeno-*N*-alkylborazole which can be recovered (normally in yields exceeding 80%) by distillation of the solvent. The adducts of some hindered amines (*e.g.*, *t*-butylamine) lose less than two moles of hydrogen halide, and borazole is not formed. It is often assumed<sup>13a</sup> that the reaction takes place through a series of consecutive unimolecular reactions



It is, in practice, possible to start at any point in the series (III)  $\longrightarrow$  (II) and obtain the borazole (IV) as the product; nevertheless, the picture is clearly oversimplified. In particular, it is not normally possible to isolate the borazene (II) at any stage in the reaction. *o*-Toluidine-boron trichloride loses hydrogen chloride by two consecutive first-order reactions with a clear discontinuity after the evolution of one molecule of hydrogen chloride (Figure 1), and at this point the borazene (II) may be isolated from the solution; but in almost all other cases this simple pattern is not observed. In particular, with primary alkylamine-boron trichloride adducts the evolution of hydrogen chloride follows a fractional-order law: the results with methylamine-boron trichloride are shown in Figures 2 and 3. The rate of evolution of hydrogen chloride increases as the concentration of adduct decreases (Figure 2). This is not an autocatalytic effect, for the rate depends only on the residual concentration of the adduct (or, more strictly, on the hydrogen chloride yet to be eliminated) and not on the concentration of the products of the reaction. At all three concentrations one-third- or one-half-order plots give excellent straight lines over the range 5–85% reaction (Figure 3), and calculations using the Noyes equation on the three runs give orders in the range 0.25–0.35. These results may indicate that the role of the solvent is not merely that of an inert diluent; thus, when

<sup>5</sup> W. Gerrard and E. F. Mooney, *Chem. and Ind.*, 1958, 1259.

<sup>6</sup> W. Kynaston, B. E. Lacombe, and H. S. Turner, *J.*, 1960, 1772.

<sup>7</sup> S. Rideal, *Ber.*, 1889, **22**, 992.

<sup>8</sup> R. G. Jones and C. R. Kinney, *J. Amer. Chem. Soc.*, 1939, **61**, 1378.

<sup>9</sup> C. R. Kinney and M. J. Kolbezen, *J. Amer. Chem. Soc.*, 1942, **64**, 1584.

<sup>10</sup> C. R. Kinney and C. L. Mahoney, *J. Org. Chem.*, 1943, **8**, 526.

<sup>11</sup> W. Gerrard and E. F. Mooney, *J.*, 1960, 4028.

<sup>12</sup> L. F. Hohnstedt and D. T. Haworth, *J. Amer. Chem. Soc.*, 1960, **82**, 89.

<sup>13</sup> R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, L. B. Eddy, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 3308.

<sup>13a</sup> *E.g.*, E. K. Mellon, jun. and J. J. Lagowski, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 259; J. C. Sheldon and B. C. Smith, *Quart. Rev.*, 1960, **14**, 200.

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*p*-chlorofluorobenzene (b. p. 129.9°,  $\epsilon$  2.35) replaces chlorobenzene (b. p. 131.6°,  $\epsilon$  5.7) (Figure 3, curve 4) the rate of the reaction is significantly increased. These results are interesting, but do not provide sufficient evidence on which to base a mechanism. However, the fractional-order evolution of hydrogen chloride could be explained on the basis of an initial equilibrium state, or of a chain reaction.

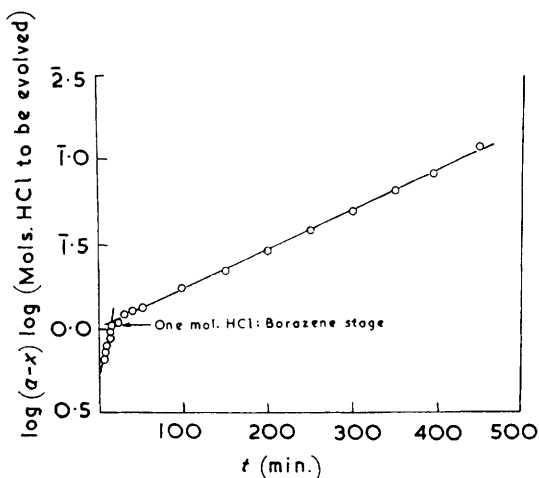


FIGURE 1

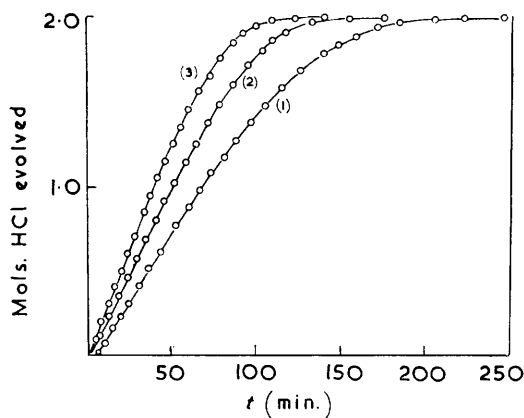


FIGURE 2

FIGURES 1—3. Thermal dehydrochlorination of primary amine-boron trichloride adducts

FIGURE 1. *ortho*- $C_7H_7 \cdot NH_2 \cdot BCl_3 \rightarrow 2HCl + \frac{1}{3}(C_7H_7NCl)_3$ ; in refluxing toluene

FIGURE 2.  $CH_3 \cdot NH_2 \cdot BCl_3 \rightarrow 2HCl + \frac{1}{3}(CH_3NCl)_3$ ; in refluxing chlorobenzene. Initial concentrations: (1) 0.675M, (2) 0.470M, (3) 0.345M

FIGURE 3.  $CH_3 \cdot NH_2 \cdot BCl_3 \rightarrow 2HCl + \frac{1}{3}(CH_3NCl)_3$ . Initial concentrations: (1) 0.675M, (2) 0.470M, (3) 0.345M

—○—○— In refluxing chlorobenzene.  
—□—□— In refluxing *p*-chlorofluorobenzene.

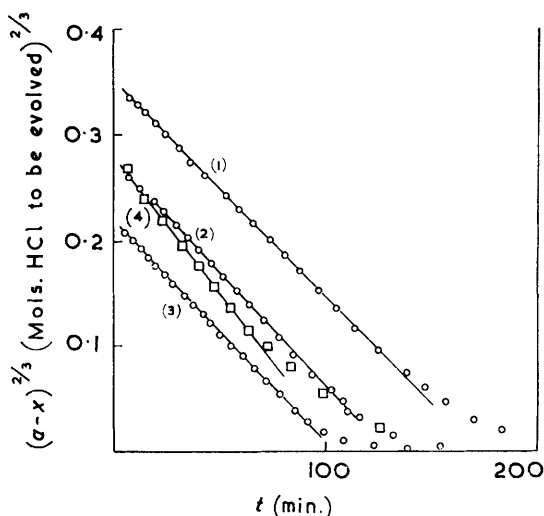


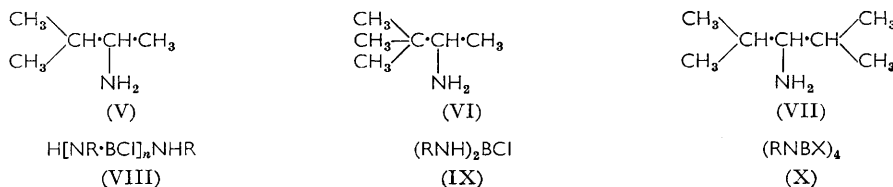
FIGURE 3

Schaeffer *et al.*<sup>13</sup> have attributed the increase in the yield of *B*-trichloroborazole from ammonium chloride in chlorobenzene<sup>14</sup> when the recovered solvent is used in the next preparation (from 40 to 90% in four repetitions) to a gradual build-up of intermediates in a series of stepwise reversible reactions. The effect noticed by Schaeffer *et al.* is in fact caused by the co-distillation of *B*-trichloroborazole with chlorobenzene. The yield increases in a series of runs until the chlorobenzene at the start of the reaction contains as much *B*-chloroborazole as will co-distil with it at the end; when toluene replaces chlorobenzene the initial yield is 80%, rising above 90% on repetition.

<sup>14</sup> C. A. Brown and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 3699.

Chemical dehydrohalogenation of the 1:1 adduct (I), or of the mixture of adduct, borazene (II), and tetrahalogenoborate (III), or of (II) or (III) separately, normally gives rise to the borazole (IV) in much the same yield as obtained by thermal dehydrohalogenation. The advantage of this procedure lies in the shorter reaction time, and in the milder conditions when primary amines with sensitive substituents are used. The results are occasionally variable with the lower amines (*e.g.*, methylamine). The most satisfactory base is triethylamine; if, for example, trimethylamine is used, base exchange takes place with formation of the more stable trimethylamine–boron trihalide adduct and no dehydrohalogenation is observed. On the other hand, the use of the strongly basic but highly hindered base di-isopropylethylamine<sup>15</sup> offers no advantage: with the adducts of primary alkylamines, borazole is formed with no improvement of yield, whilst with secondary and tertiary alkylamines (and in particular, with *t*-butylamine) there is little or no dehydrohalogenation. Clearly the first stage of base-induced dehydrohalogenation involves nucleophilic attack by the tertiary base, which may be sterically frustrated. If the donor qualities of the base are too great (as with trimethylamine), the primary amine rather than a halide ion is displaced. When triethylamine is used, the order of mixing of the reactants is immaterial: thus, the primary amine may be added to the base–boron trihalide adduct. In this case the reaction (as indicated by the precipitation of base hydrohalide) begins at a rather higher temperature, as might be expected in a situation in which the tertiary base must be displaced by the primary amine before reaction can begin.

Using the method of chemical dehydrochlorination, we have studied the preparation of *sym*-*B*-chloroborazoles from a series of aliphatic primary amines of increasing size and degree of branching; a representative collection of results is set out in Table 6. The result is determined by the degree of substitution of the  $\alpha$ - and  $\beta$ -carbon atoms of the primary amine. Thus, 2-amino-3-methylbutane (V) and other less hindered primary alkylamines gave good yields of the borazole, but with 3-amino-2,2-dimethylbutane (VI), 3-amino-2,4-dimethylpentane (VII), and other more highly hindered *s*-alkyl primary amines, no borazole was isolated. Compound (VI) gave a mixture of products, of which the major constituents were the borazene (II; R = C<sub>6</sub>H<sub>13</sub>, X = Cl) and the boronamine



(VIII; R = C<sub>6</sub>H<sub>13</sub>; *n* = 2). Compound (VII) gave a mixture of which the main constituents were the borazene (II; R = C<sub>7</sub>H<sub>15</sub>; X = Cl), the boronamine (VIII; R = C<sub>7</sub>H<sub>15</sub>; *n* = 2) and the bis(alkylamino)boron chloride (IX; R = C<sub>7</sub>H<sub>15</sub>). When the  $\alpha$ -carbon atom is fully substituted, *i.e.*, when the amine is a *t*-alkyl primary amine, the borazole is never a product but, depending on the nature of the substituents, tetrameric borazynes (X) may be formed. Table 1 lists those that have been prepared. The number of *t*-alkylamines examined was necessarily small, but they were chosen in an effort to make clear the structural factors required for tetramer formation. From this it appears that normally at least two of the  $\alpha$ -substituents must be methyl groups, and that branching at the  $\beta$ -carbon atom inhibits tetramer formation. The contrast between 1-amino-1-methylcyclohexane (which gives a borazyne tetramer) and 3-amino-3-methylpentane (which does not) affords a striking illustration of the greatly diminished hindrance when two ethyl groups on the  $\alpha$ -carbon atom become part of a cyclohexane ring. The yields tend to diminish as crowding of the  $\alpha$ -carbon atom increases, and for a given amine are lower

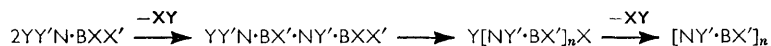
<sup>15</sup> S. Hünig and M. Kiessel, *Chem. Ber.*, 1958, **91**, 380.

TABLE I  
 Tetrameric borazynes (RNBX)<sub>4</sub>

Parent amine	X	Tetramer, m. p.	Parent amine	X	Tetramer, m. p.
1. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{NH}_2 \\   \\ \text{CH}_3 \end{array}$	Cl	249°	5. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}-\text{NH}_2 \\   \\ \text{CH}_3 \end{array}$	Cl	93°
2. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\cdot\text{CH}_2\cdot\text{C}-\text{NH}_2 \\   \\ \text{CH}_3 \end{array}$	Cl	162	6. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}-\text{CH}_2\cdot\text{C}-\text{NH}_2 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Cl	114
3. $\begin{array}{c} \text{CH}_2 \quad \text{CH}_2-\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \quad \text{CH}_3 \\   \\ \text{NH}_2 \end{array}$	Cl	271	7. $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3\cdot\text{C}-\text{CH}_2\cdot\text{C}-\text{NH}_2 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Cl Br	200 200
4. $\begin{array}{c} \text{CH}_3\cdot\text{CH}_2 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3\cdot\text{CH}_2 \quad \text{NH}_2 \end{array}$	Cl	Not formed	8. $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}-\text{C}-\text{NH}_2 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Cl	Not formed

for the bromo- than for the chloro-compound. Fluoro- and iodo-compounds (X; X = F or I) have not been obtained either directly or by indirect methods from the chloro- or bromo-compounds. 2-Amino-2,3-dimethylbutane (which does not give a tetrameric borazyne) appears to give a mixture consisting mainly of the borazene (II; R = C<sub>6</sub>H<sub>13</sub>, X = Cl) and the boronamine (VIII; R = C<sub>6</sub>H<sub>13</sub>, n = 3). 3-Amino-3-methylpentane gives a complex mixture from which no tetrameric borazyne was isolated.

In the chemical dehydrohalogenation of the 1 : 1 adducts (I), (as in the case of thermal dehydrohalogenation), borazenes (II) are only isolated in those cases where borazole formation does not occur, but they are accompanied by the boronamines (VIII; n = 1, 2, or 3). This suggests that, whilst the aliphatic borazenes RNHBCl<sub>2</sub> are almost certainly the first products of the reaction, they readily undergo condensation to form the boronamines. Lappert and Majumdar<sup>15a</sup> have suggested that such a condensation, which in this case would give rise to RNH·BCl·NR·BCl<sub>2</sub>, is followed by an intermolecular 1,3-nucleophilic rearrangement leading to the formation of the monomeric borazyne, which then undergoes polymerisation, usually trimerisation, with borazole formation. There is, in fact, no evidence that monomeric borazynes are formed as intermediates, and it seems at least as probable that, in reactions of this type, compounds Y(NY'·BX')<sub>n</sub>X are built up by a series of condensation reactions and that cyclisation takes place, where this is sterically permitted, to form the ring of lowest energy. Normally this leads to borazole formation, but borazyne dimers<sup>15a</sup> and tetramers may be formed.



The boronamines Y[NY'·BX']<sub>n</sub>X, in this case H[NR·BCl]<sub>n</sub>Cl, have not been isolated from the products of the base-induced dehydrochlorination of hindered primary alkylamines, but the boronamines H[NR·BCl]<sub>n</sub>NHR (VIII) are always found when borazole or tetrameric borazyne formation is not possible. It seems reasonable to suppose that in these circumstances, and in the presence of a large excess of base, the condensation of two molecules of borazene, or of borazene with boronamine, H[NR·BCl]<sub>n</sub>Cl, takes place with elimination of boron trichloride (which is found as the 1 : 1 adduct with triethylamine) and formation

<sup>15a</sup> M. F. Lappert and M. K. Majumdar, Boron-Nitrogen Chemistry, Advances in Chemistry Series, No. 42, American Chemical Society, 1964, p. 227.



of  $\text{H}[\text{NR}\cdot\text{BCl}]_n\text{NHR}$  (VIII). Boronamines of type (VIII) are easily converted into the corresponding compounds  $\text{H}[\text{NR}\cdot\text{BCl}]_n\text{Cl}$  by treatment with excess of boron trichloride (see Experimental section).

Of the tetrameric borazynes, that from *t*-butylamine and boron trichloride,  $(\text{Bu}^t\text{NBCl})_4$  (XI) was first prepared and has been most thoroughly examined. It is a white solid, m. p.  $249^\circ$  with slight decomposition, insoluble in water but soluble in a wide range of organic solvents; in general, the solubility decreases with increasing polarity of the solvent. It separates from carbon tetrachloride in crystals containing two molecules of the solvent per molecule of tetramer. It has a high vapour pressure and sublimes very readily: it is not possible to determine the melting point in an evacuated melting-point tube unless the entire evacuated space is immersed in the heating bath. The melting point is strongly depressed by impurities, and is a very sensitive indication of purity. The molecular depression constant lies in the range 53—95. The value for camphor is 40, and it follows that, even if allowance is made for the lower melting point of camphor ( $177^\circ$ ), the latent heat of fusion of (XI) must be lower than that of camphor. It is interesting and significant that the molecular depression constant decreases with decreasing symmetry of the alkyl group; thus, it is 31 for the 1,1-dimethyl-*n*-propyl (*t*-pentyl) compound (X; R =  $\text{C}_5\text{H}_{11}$ , X = Cl) and 15 for the 1,1-dimethyl-*n*-pentyl compound (X; R =  $\text{C}_7\text{H}_{15}$ , X = Cl).

The composition has been established by direct elemental analysis and also by hydrolysis, which gives equimolar amounts of *t*-butylamine, boric acid, and hydrogen chloride. The molecular weight has been determined cryoscopically and ebullioscopically, and is confirmed by the presence of parent peaks in the mass spectrum of (XI) and of the corresponding isothiocyanate  $(\text{Bu}^t\text{NBNCS})_4$  (XII) and azide  $(\text{Bu}^t\text{NBN}_3)_4$ . The reactivity of the tetrameric borazynes is remarkably different from that of the corresponding trimeric borazynes, the *B*-halogenoborazoles (IV). They are indefinitely stable in the laboratory atmosphere at room temperature. They are insoluble in boiling water and are not measurably attacked by it, but at  $160^\circ$  in a sealed tube, hydrolysis of (XI) was 97% complete in 20 hr. A homogeneous solution of (XI) in boiling 50% aqueous dioxan was approximately 50% hydrolysed in 18 hr. Some rough measurements have shown that the rate is independent of pH over a wide range; this strongly suggests an  $\text{S}_{\text{N}}1$  reaction. With lithium and Grignard reagents there is no significant reaction, and our attempts to replace the chlorine atoms in (XI) by hydrogen (using lithium and sodium borohydrides) and by fluorine or iodine have failed. The remarkably low reactivity at the boron atoms is illustrated by the complete absence of any reaction when pure (XI) and diazomethane are brought together in ether solution.

On the other hand, reactions leading to the formation of an exocyclic B-N bond have been more successful. Thus, we have brought about partial replacement of chlorine in (XI) by methylamino- and ethylamino-groups, by treatment with the amines under forcing conditions, but we have been unable to isolate the pure species. However, the replacement of halogen by most of the pseudohalogens takes place under mild conditions, and we have obtained the tetra-*B*-isocyanate, isothiocyanate, isoselenocyanate, and azide by the reaction of (XI) with the alkali-metal pseudohalide in a suitable organic solvent. We have been unable to prepare the cyanide or isocyanide either directly or, in the latter case, by Raney nickel desulphurisation of the isothiocyanate. The reactions with potassium thiocyanate and with sodium azide take place particularly easily, and appreciable rates of reaction are observed at  $30^\circ$ . The structures of these compounds have been established on the basis of their spectra.<sup>16</sup> Organic thiocyanates and isothiocyanates are easily distinguished by the characteristic bands in the 2000—2200  $\text{cm}^{-1}$  region.<sup>17-20</sup> The

<sup>16</sup> G. L. Caldow and H. W. Thompson, *Spectrochim. Acta*, 1958, **13**, 212.

<sup>17</sup> E. Lieber, C. N. R. Rao, and J. Ramachandran, *Spectrochim. Acta*, 1959, **13**, 296.

<sup>18</sup> N. S. Ham and J. B. Willis, *Spectrochim. Acta*, 1960, **16**, 279, 393.

<sup>19</sup> C. V. Stevenson, W. C. Coburn, and W. S. Wilcox, *Spectrochim. Acta*, 1961, **17**, 933.

<sup>20</sup> M. F. Lappert and H. Pyszora, *Proc. Chem. Soc.*, 1960, 350.

thiocyanates show a sharp band of medium intensity ( $\epsilon_{\text{max.}}$  40—60; (integrated intensity \*  $0.2\text{--}0.5 \times 10^4$ ) in the range 2164—2174  $\text{cm.}^{-1}$ , the asymmetric stretching band, while in isothiocyanates there is a very strong band ( $\epsilon_{\text{max.}}$  400—750; integrated intensity  $10\text{--}20 \times 10^4$ ) in the range 2000—2100  $\text{cm.}^{-1}$ . The tetraisothiocyanate (XII) had  $\nu_{\text{as}}$  2078  $\text{cm.}^{-1}$  ( $\epsilon_{\text{max.}}$  1560;  $\Delta\nu_{\frac{1}{2}}$  42  $\text{cm.}^{-1}$ ; integrated intensity  $17.6 \times 10^4$ ), and on grounds of band frequency and intensity seems clearly to be an isothiocyanate. Lappert<sup>20</sup> has similarly identified several boron isothiocyanates; one of these compounds, tri-*B*-isothiocyanato-borazole, with which our compound may be compared, had  $\epsilon_{\text{max.}}$  1787,  $\Delta\nu_{\frac{1}{2}}$  54  $\text{cm.}^{-1}$ , integrated intensity<sup>21</sup>  $23.2 \times 10^4$ . That compound (XII) has the structure suggested is finally proved by X-ray-diffraction, which confirms the validity of the comparison with organic isothiocyanates. The structure of several boron isocyanates has been assigned<sup>20</sup> by comparison with those of organic isocyanates. In aryl isocyanates,  $\nu_{\text{as}}$  for the NCO group is found in the range 2240—2290  $\text{cm.}^{-1}$  (integrated intensity  $14\text{--}17 \times 10^4$ ) whereas in phenyl cyanate<sup>22</sup> there is a much weaker doublet (2235 and 2280  $\text{cm.}^{-1}$ ) and also a band (at 1190  $\text{cm.}^{-1}$ ), not present in isocyanates, attributable to the  $\text{C}_6\text{H}_5\text{--O--C}$  linkage; our tetraisocyanate (X;  $\text{R} = \text{Bu}^t$ ,  $\text{X} = \text{NCO}$ ) had  $\nu_{\text{as}}$  2278  $\text{cm.}^{-1}$  ( $\Delta\nu_{\frac{1}{2}}$  40  $\text{cm.}^{-1}$ ; integrated intensity  $14.9 \times 10^4$ ) and  $\nu_s$  1487  $\text{cm.}^{-1}$ . The values of  $\nu_{\text{as}}$  in Lappert's compounds<sup>20</sup> were in the range 2257—2289  $\text{cm.}^{-1}$  and  $\nu_s$  1483—1553  $\text{cm.}^{-1}$ . The tetraisoselenocyanate (X;  $\text{R} = \text{Bu}^t$ ,  $\text{X} = \text{NCSe}$ ) is presumed to be such by analogy with the isocyanate and isothiocyanate, and because  $\nu_{\text{as}}$  of the NCSe group is found at 2047  $\text{cm.}^{-1}$ , below but close to that of the isothiocyanate (2078  $\text{cm.}^{-1}$ ). A rather higher value would be expected for a selenocyanate on the basis of work with inorganic selenocyanate and isoselenocyanate complexes.<sup>23</sup>

A number of possible structures can be written for the tetrameric borazynes, but, in the light of the chemical and physical properties already described, the linear tetramer and structures involving four- or six-membered rings with side-chains, *e.g.*, (XIII) and (XIV), or linked four-membered rings (XV) seem improbable. The three structures (XVI), (XVII), and (XVIII) do appear to merit serious consideration. The eight-membered ring (XVI) cannot exist in planar form, but molecular models can be made of the boat, chair, and crown forms. The boat form appears, on inspection, to be the least strained. It can be regarded as made up of four *cis*-borazene units (XIX), *i.e.*, there is sterically favoured  $\pi$ -bonding between the boron and nitrogen atoms of the separate B-N pairs, but any extended delocalisation would be unlikely. The chair form is more highly strained; it can be regarded as made up of two *cis*-borazene units joined by other borazene units that are not orientated for effective *p*-orbital overlap. The crown form is the most highly strained, and *p*-orbital overlap is minimal. The bicyclo[2,2,2]octane analogue (XVII) can be reproduced as a molecular model; it is made up of three *cis*-borazene units attached to the bridgehead quaternary boron and nitrogen atoms. It is not possible to make a molecular model of the cubane analogue (XVIII), but cubane is known<sup>24</sup> and the structure of  $(\text{PhNAlPh})_4$  has been shown<sup>25</sup> to be based on the cubic arrangement of aluminium and nitrogen atoms. Compound (XVIII), unlike (XVI) and (XVII), contains only quaternary boron and nitrogen atoms. Compounds (XVII), (XVIII), and the three forms of (XVI) are all almost spherical with highly inaccessible boron and nitrogen atoms, and all are generally compatible with the low chemical reactivity, high volatility, and high solubility of the tetramers. The choice between these possibilities was made on the basis of the <sup>11</sup>B nuclear magnetic resonance (n.m.r.) spectra, on measurements of the electric polarisation,

\* All values of integrated intensity ( $\text{mole}^{-1} \text{l. cm.}^{-2}$ ) are given in terms of the "monomer"; *i.e.*, on the basis of a sub-unit containing one pseudohalogen group.

<sup>21</sup> Taken from a spectrum kindly communicated to us by Dr. M. F. Lappert.

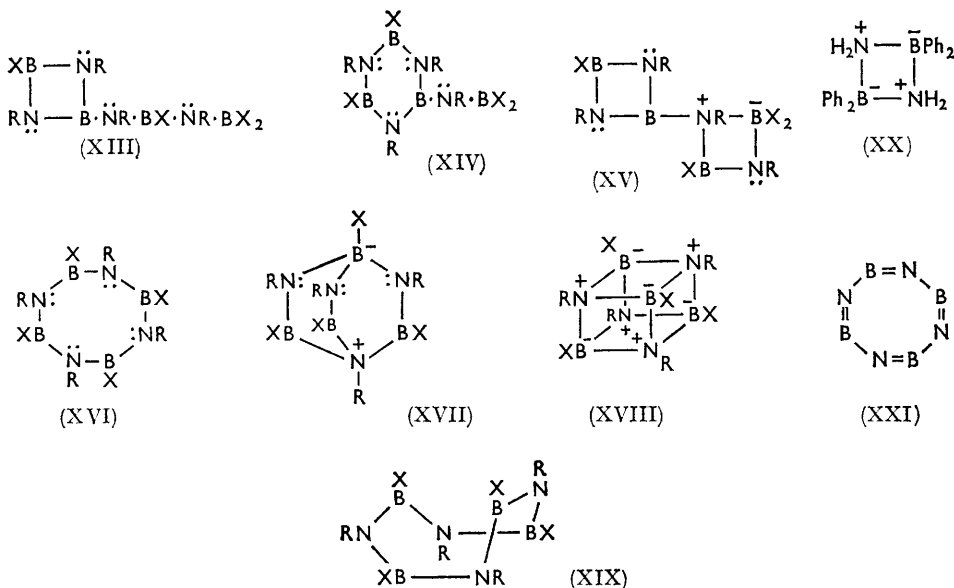
<sup>22</sup> D. Martin, *Angew. Chem. Internat. Ed.*, 1964, **3**, 311.

<sup>23</sup> A. Turco, C. Pecile, and M. Nicolini, *J.*, 1962, 3008; F. A. Cotton, D. M. I. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, 1962, **1**, 565.

<sup>24</sup> P. E. Eaton and T. W. Cole, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 3157.

<sup>25</sup> J. I. Jones and W. S. McDonald, *Proc. Chem. Soc.*, 1962, 366.

and of a study of the vibrational spectra; final proof was provided by an X-ray-diffraction study.



The  $^{11}\text{B}$  n.m.r. spectra of  $(\text{Bu}^t\text{NBCl})_4$  and  $(\text{Bu}^t\text{NBBR})_4$  were recorded by Dr. B. N. Figgis. In both cases there was only a single peak, and the chemical shifts of  $+17.4$  and  $+17.2$  p.p.m. ( $\text{BCl}_3 = 0$ ), respectively, were those to be expected of 3-co-ordinate boron atoms. The results, including those for a number of reference compounds, are set out in Table 2. It proved impossible to make a reference compound truly relevant to the structure (XVIII), *i.e.*, with three nitrogen and one chlorine atom attached to boron. However, the shifts for the borazene dimers (two nitrogen and two chlorine) and potassium tetrapyrrolylborate (four nitrogen) were very close, and it can probably be assumed that they provide a satisfactory comparison. Only the eight-membered ring structure (XVI) is compatible with these results.

TABLE 2

$^{11}\text{B}$  Chemical shifts in some boron-nitrogen compounds

Substance	Solvent	Chemical shift ( $\text{BCl}_3 = 0$ ) (p.p.m.)	Line width (p.p.m.)	Substance	Solvent	Chemical shift ( $\text{BCl}_3 = 0$ ) (p.p.m.)	Line width (p.p.m.)
<i>Tetramers</i>				<i>Four-co-ordinate boron compounds</i>			
$(\text{Bu}^t\text{NBCl})_4$	$\text{CCl}_4$	$+17.4$	$\sim 14$	$\text{NaB}(\text{OMe})_4$	$\text{CH}_3\text{OH}$	$+44.3$ <sup>26</sup>	
$(\text{Bu}^t\text{NBBR})_4$	$\text{CCl}_4$	$+17.2$	$\sim 20$	$\text{KB}(\text{NC}_4\text{H}_4)_4$ *	$\text{Me}_2\text{CO}$	$+46$	$\sim 6$
<i>Three-co-ordinate boron compounds</i>				$(\text{Bu}^t\text{NHBBCl}_2)_2$	$\text{CH}_2\text{Cl}_2$	$+43.3$	$\sim 4$
$(\text{HNBCl})_3$	$\text{MeCN}$	$+11$	$\sim 9$	$(\text{Me}_2\text{NBCl}_2)_2$	$\text{CH}_3\text{I}$	$+37.2$	$\sim 8$
$(\text{MeNBCl})_3$	$\text{CCl}_4$	$+14$	$\sim 16$				
$(\text{MeNBCH}_3)_3$	$\text{CCl}_4$	$+11$	$\sim 21$				
$\text{B}(\text{NEt}_2)_3$	—	$+16.3$ <sup>26</sup>					

\*  $\text{NC}_4\text{H}_4 = 1$ -pyrrolyl.

The total electric polarisation of  $(\text{Bu}^t\text{NBCl})_4$  has been measured in n-octane solution at  $20^\circ$  by Mr. E. Rushton of the National Physical Laboratory. On the basis of measurements on five solutions in the range up to  $0.15\text{M}$  a value of  $133.3$  c.c. was obtained. The electron polarisation, measured at six wavelengths and extrapolated to zero frequency,

<sup>26</sup> W. D. Phillips, H. C. Miller, and E. L. Muettterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.



was 119.8 c.c. The difference (13.5 c.c.) is attributable to the sum of the atom and orientation polarisations; if the atom polarisation were zero, the dipole moment would have the (maximum possible) value of 0.78 D. It is not normally possible to measure the atom polarisation directly, and in calculating dipole moments it is a common practice to introduce an arbitrary correction for it, for example by assuming it to be proportional to the molecular volume or the electron polarisation.<sup>27</sup> Thus, Watanabe and Kubo<sup>28</sup> have quoted dipole moments in the range 0.18—0.83 D for several symmetrical borazoles in which the sum of the electron and atom polarisations is taken to be 1.05 times the molar refraction for the *D* line. There does not seem to be any discernible basis for any of these approximations,<sup>29</sup> and it is likely that the value of the atom polarisation would be greatly different for the three possible structures for (XI). All structures believed to have high atom polarisations contain large opposed dipoles,<sup>30</sup> and thus (XVIII) in particular, with its extensive system of balanced dipoles, would be expected to have a large atom polarisation. The value found<sup>31</sup> for the symmetrical borazene dimer (XX) is 17.5 c.c., and (XVIII), and to a lesser extent (XVII), might well have larger values; (XIX) could have a value of the same order as (XX). It follows from the same considerations that (XVIII) and the boat (XIX) and chair forms of (XVI) could be expected to have very low or zero orientation polarisations. An attempt was therefore made to obtain an independent value of the dipole moment from measurements of the dielectric adsorption of solutions of  $(\text{Bu}^t\text{NBCl})_4$ . The measurements were made by Mr. E. Rushton (Standards Division, N.P.L.) and Dr. G. Williams (Basic Physics Division, N.P.L.) to whom this discussion is due. Over the range  $10^3$  to  $3.6 \times 10^{10}$  c./sec. there was no significant difference between the dielectric absorption of the solution and that of the pure solvent. The measurements were made at a series of fixed frequencies (see Experimental section), but it is unlikely that any appreciable maximum was missed since the value of the loss tangent,  $\tan \delta$ , would be 20% of the maximum value at one-tenth or ten times the frequency of the maximum. For the same reason, it is unlikely that there was a maximum beyond  $3.6 \times 10^{10}$  c./sec., for with the maximum possible dipole moment of 0.78 D the absorption at  $3.6 \times 10^{10}$  c./sec. arising from a maximum at  $1.8 \times 10^{12}$  would have been easily measurable. Further, it is known that, for example, solutions of acetone (relaxation time  $3 \times 10^{-12}$  sec.) show a maximum of  $\tan \delta$  at  $2 \times 10^{11}$  c./sec. and larger molecules at lower frequencies (nitrobenzene at  $10^{10}$  c./sec.). It is most unlikely that the relaxation time of a molecule the size of (XI) would be less than that of acetone, and thus the maximum would be expected at a lower frequency. It may thus be concluded that the dipole moment is sensibly zero, and that the difference of 13.5 c.c. represents the atom polarisation. The electrical measurements thus support the structure (XVI), probably in the boat conformation.

A recent study of the electric polarisation of hexamethylborazole<sup>32</sup> suggests that in this case, as in the tetrameric borazynes, the molecule is non-polar, and that the apparent dipole moment<sup>28</sup> arises from a large value of atom polarisation.

The tetrameric borazynes have characteristic infrared<sup>33</sup> (i.r.) and Raman spectra. Green, Kynaston, and Paisley<sup>34</sup> of this Laboratory have examined these spectra and, in order to assist in assigning the absorption bands, the spectra of fully deuterated  $(\text{Bu}^t\text{NBCl})_4$  and the corresponding *B*-bromo-, -isothiocyanato-, and -azido-compounds. They have

<sup>27</sup> E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

<sup>28</sup> H. Watanabe and M. Kubo, *J. Amer. Chem. Soc.*, 1960, **82**, 2428.

<sup>29</sup> J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 261.

<sup>30</sup> Cf. J. W. Smith, ref. 29, p. 270.

<sup>31</sup> G. F. Coates and J. G. Livingstone, *J.*, 1961, 1000.

<sup>32</sup> E. K. Mellon, jun., and J. J. Lagowski, *Inorg. Chem.*, 1964, **3**, 1694.

<sup>33</sup> The infrared spectra of all the borazocines described in this Paper have been issued in the DMS Index (Butterworths) on cards 9510—9526.

<sup>34</sup> J. H. S. Green, W. Kynaston, and H. M. Paisley, Boron-Nitrogen Compounds, Advances in Chemistry Series No. 42, American Chemical Society, 1964, p. 301. A full account of this work is in preparation.

shown that the boat conformation of the eight-membered ring (XIX) is the most likely structure, that the chair conformation is unlikely, and that the structures (XVII) and (XVIII) may be excluded.

The three structures (XVI), (XVII), and (XVIII) could be distinguished unequivocally by the determination of the number of isomers formed on partial substitution of the halogen atoms (see Table 3). The only reactions that lend themselves to this purpose

TABLE 3  
Number of isomers on partial substitution of tetrameric borazynes

Derivative	Eight-membered ring (XVI)	Bicyclic structure (XVII)	Cubane structure (XVIII)
Monosubstituted .....	1	2	1
Disubstituted .....	2	2	1
Trisubstituted .....	1	2	1

are the replacements by pseudohalogens, and we have tried to prepare and separate partially substituted isothiocyanato- and azido-compounds. When (XI) and two moles of potassium thiocyanate react together under conditions likely to favour partial substitution, the product obtained has an overall composition corresponding to partial substitution. However, by fractional crystallisation it can be separated very largely into fractions that are either the original chloro-compound containing a little sulphur or the tetraisothiocyanate containing a little residual chlorine, and from these the almost pure tetrasubstituted compounds can be obtained by crystallisation. The i.r. spectra of these fractions are consistent with the view that they are mixtures of  $(\text{Bu}^t\text{NBCl})_4$  and  $(\text{Bu}^t\text{NBNCs})_4$ . In one case, the i.r. spectrum of a fraction which on this basis would have contained ~70 moles % of the tetraisothiocyanate was compared with that of a similar artificial mixture of the pure components. The spectra are reproduced in Figure 4 (for the band frequencies see the Experimental section), and are almost superimposable. It seems altogether inconceivable that, if the product contained appreciable amounts of partially substituted products, the changes of symmetry consequent upon partial substitution would not produce marked changes in the vibrational spectra. However, another product from the same preparation gave a mass spectrum in which there was clear evidence of fragments derived from all the possible partial substitution products. That this is not an artefact is demonstrated by the fact that artificial mixtures are clearly revealed as such in the mass spectrometer. We are inclined to believe that, on the basis of the i.r. spectra, the products of our attempts to achieve partial substitution are mainly a mixture of the starting material and the fully substituted product, but that the presence of a small proportion of the partially substituted products may be selectively revealed in the mass spectrum. It is difficult to understand this pattern of substitution. It seems unlikely that substitution of one chlorine atom in (XI) by NCS would so increase the rate of reaction of the others that partial substitution products would be virtually absent. Other possible explanations, for example that partially substituted products disproportionate, are unconvincing.

The partial substitution of chlorine by the azido-group was next examined, and completely different behaviour was found. The i.r. spectra of the products were significantly different from those of artificial mixtures (see Figure 5), and appeared to consist of mixtures of the intermediate products; there was no conflict between the infra-red and the mass spectra. However, with the methods available to us we were unable to isolate or even to detect convincingly the pure components of these mixtures. There was, certainly, no indication of a preferential formation of mono- or tri-substituted derivatives such as might perhaps be expected if the structure were (XVII), and this provides limited evidence against this structure.

There is, therefore, a considerable body of evidence that the tetrameric borazynes are best represented by the eight-membered ring structure (XVI) and that they probably normally exist in the boat conformation (XIX). Such a structure would be expected to

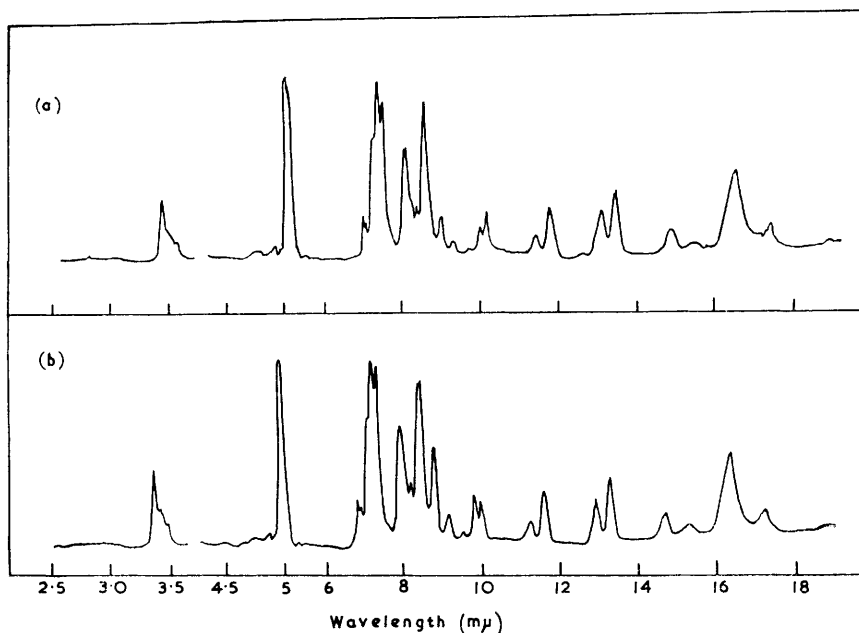


FIGURE 4. Infrared spectra of (a) product of attempted partial substitution of Cl by NCS in tetra-*B*-chlorotetra-*N*-*t*-butylborazocine; (b) a mixture of tetrachloro- and tetraisothiocyanato-borazocines of the same elemental composition

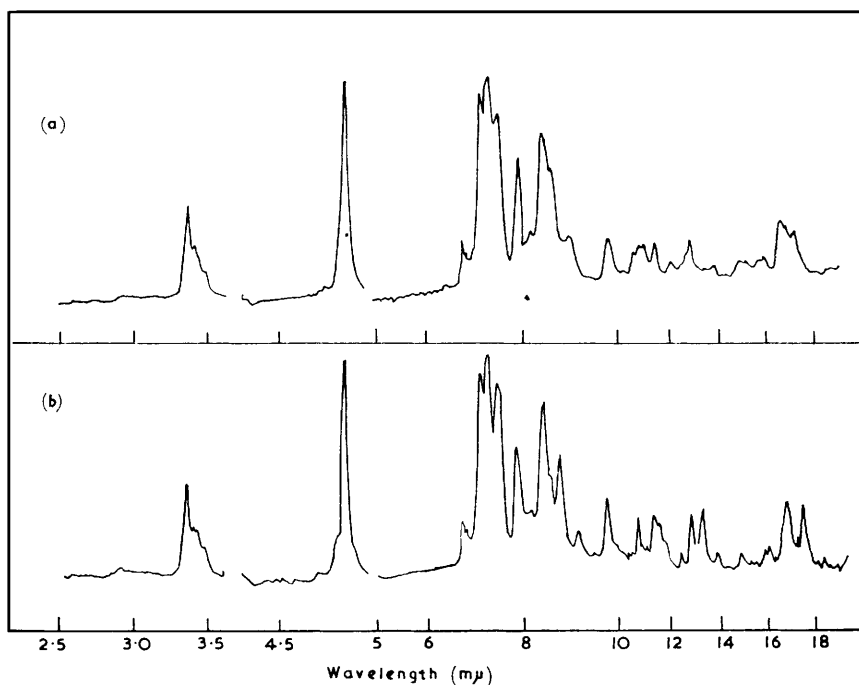


FIGURE 5. Infrared spectra of (a) product of attempted partial substitution of Cl by  $N_3$  in tetra-*B*-chlorotetra-*N*-*t*-butylborazocine; (b) a mixture of tetrachloro- and tetra-azido-borazocines of the same elemental composition

have localised alternating  $\pi$ -bonds, and the low reactivity would clearly be of steric origin. The parent from which these compounds are derived is (XXI) for which the systematic name is 1,3,5,7-tetraza-2,4,6,8-tetraborocine. The tetrameric borazines are substitution products of the octahydro-compound, for which Dr. R. S. Cahn has suggested the trivial name borazocine. The compound (XI) on this basis is tetra-*B*-chlorotetra-*N*-*t*-butylborazocine.

A complete confirmation of the structure of the borazocine ring has been obtained from an *X*-ray-diffraction study on two compounds carried out by Dr. P. T. Clarke in Mr. H. M. Powell's Laboratory at Oxford.<sup>35</sup> Work was begun on the borazocine (X) in which R = Me<sub>3</sub>C·CH<sub>2</sub>·CMe<sub>2</sub> and X = Cl, but the compound in which R = Me<sub>3</sub>C and X = NCS was found to be more suitable for accurate measurements. The results for both compounds show that there is an eight-membered ring of alternating boron and nitrogen atoms essentially

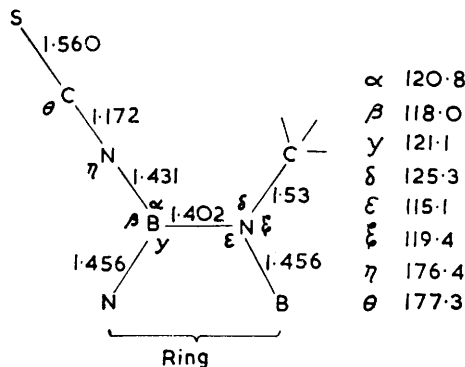


FIGURE 6

as in (XIX), and that there is an alternation of bond length in the ring which can be attributed to the formation of alternating  $\pi$ -bonds. The ring can be regarded as made up of four identical *cis*-borazene units; the bond angles and lengths of one unit for the compound when R = Me<sub>3</sub>C and X = NCS are set out in Figure 6. The angles around the boron and nitrogen atoms add almost exactly to 360°; the bonds are therefore in the same plane. With the exception of the cyclic B-N-B bond and the exocyclic B-N-C bond which are decreased and increased respectively by about 5° as a consequence of interference between the *t*-butyl and the isothiocyanate groups, all angles around these atoms are ~120°. The longer cyclic B-N bonds (1.456 Å) are slightly longer than the B-N bonds in boron nitride (1.446 Å)<sup>36</sup> and close to the estimated value for a pure single B-N bond made by the Schomaker-Stevenson rule,<sup>37</sup> which gives 1.45 Å. The shorter cyclic B-N bonds (1.402 Å) are slightly shorter than any reported for a borazole (the shortest, 1.415 Å, are for tri-*B*-chloroborazole),<sup>38</sup> and on the basis of Gordy's formula<sup>39</sup> would have a bond order of about 1.55. The exocyclic B-N bond (1.431 Å) also is shorter than would be expected; on the same basis it would have a bond order of about 1.4. Clearly there is a considerable interaction between the NCS group and the BN pair of the ring. That this is so is borne out by the abnormally large BNC angle of 176° (the corresponding angle in CH<sub>3</sub>NCS is 142°<sup>40</sup>) and by the abnormally short NC distance in the NCS group (1.172 Å as against 1.22 Å in CH<sub>3</sub>NCS<sup>39</sup>). This extended  $\pi$ -electron system is presumably the cause of the greater stability of the isothiocyanato- as compared with the chloro-compound in the mass spectrometer.

<sup>35</sup> P. T. Clarke, Ph.D. Thesis, Oxford 1964.

<sup>36</sup> R. S. Pease, *Nature*, 1950, **165**, 722; *Acta Cryst.*, 1952, **5**, 356; *J. Amer. Chem. Soc.*, 1952, **74**, 4219.

<sup>37</sup> J. C. Sheldon and B. C. Smith, *Quart. Rev.*, 1960, **14**, 215.

<sup>38</sup> K. Lonsdale, *Nature*, 1959, **184**, 1060.

<sup>39</sup> W. Gordy, *J. Chem. Phys.*, 1947, **15**, 305.

<sup>40</sup> C. I. Beard and B. P. Dailey, *J. Amer. Chem. Soc.*, 1949, **71**, 929.

Additional evidence for interaction of the pseudohalogen groups and the cyclic BN pairs lies in the stability of the tetra-azido-compound and in the ultraviolet (u.v.) spectra (Table 4).  $(\text{Bu}^t\text{NCl})_4$  in solution shows a single absorption band in the ultraviolet ( $\lambda_{\text{max.}}$  204.6;  $\log \epsilon_{\text{max.}}$  3.4). The effect of conjugation is seen in the shift of this band and the absorption of the pseudohalogen group to longer wavelengths with a considerable increase in intensity, an effect that is progressive from  $-\text{NCO}$  to  $-\text{NCSe}$ .

TABLE 4

X	$(\text{Bu}^t\text{NBX})_4$		EtX	
	$\lambda_{\text{max.}}$ (m $\mu$ )	$\log \epsilon^a$	$\lambda_{\text{max.}}$ (m $\mu$ )	$\log \epsilon$
Cl .....	204.6	3.40	—	—
$\text{N}_3$ .....	204.0, 229.2	3.78, 3.72	220, 287	2.18, <sup>b</sup> 1.3 <sup>b</sup>
NCO .....	206.1	3.67	207	1.81
NCS .....	208.8, 264.0	4.44, 3.92	250	2.94 <sup>c</sup>
NCSe .....	229.2, 286.6	4.60, 3.90	—	—

<sup>a</sup> Expressed in terms of the monomeric unit. <sup>b</sup> In ethanol (Yu. N. Sheinker, *Doklady Akad. Nauk. S.S.S.R.*, 1951, **77**, 1043). <sup>c</sup> In 95% pentane-5% dioxan (E. Svatek, R. Zahradnik, and A. Kjaer, *Acta Chem. Scand.*, 1959, **13**, 442).

The methods used for the preparation of the aliphatic primary amines are set out in the Experimental section. Both 2-amino-2,3-dimethylbutane and 2-amino-2,4-dimethylpentane was prepared from the corresponding nitriles. These nitriles could only be hydrolysed (to the amide) by hot strong sulphuric acid (70–80%), and rearrangement of the alkyl groups at this stage was feared. That these amines and also 3-amino-3-methylpentane and 2-amino-2-methylhexane (both of which were prepared<sup>41</sup> from the corresponding alcohol by reaction with urea and concentrated sulphuric acid) were substantially pure, and hence that no rearrangement had occurred in preparation, was shown by gas chromatography and the preparation of phenyl alkyl ureas of sharp melting point. A very important confirmation of purity came from a comparison of the original amine with the amine obtained by hydrolysis of the borazocine derived from it, and also in some cases with that obtained by hydrolysis of the non-borazocine part of the reaction product. In all cases the i.r. spectra were identical. Had there been isomerisation during preparation to a mixture of amines it is most unlikely that there would have been no discrimination between the isomers during the preparation of the borazocine. The Hofmann reaction on the amides from 2,2,3-trimethylbutyronitrile and 2,2,4-trimethylvaleronitrile unexpectedly gave the *NN'*-bis-ureas, the hydrolysis of which was successful under extreme conditions. 2-Amino-2,4,4-trimethylpentane (commercial *t*-octylamine) appeared to contain no more than 2% of impurity; the structure of the alkyl group in the borazocine derived from it is confirmed by the production of 2,4,4-trimethylpent-1-ene on hydrolysis.

*t*-Butylamine fully deuterated in the alkyl group was required for the preparation of the perdeuteroborazocines. *t*- $[\text{}^2\text{H}_9]$ Butyl compounds have usually been made from  $[\text{}^2\text{H}_6]$ -acetone by reaction with  $[\text{}^2\text{H}_3]$ methyl magnesium halides.<sup>42</sup> We found that the exchange between *t*-butyl chloride and  $\text{DCl-D}_2\text{O}$ , which has been studied by Setkina and Kursanov,<sup>43</sup> is a more convenient starting point. Details of the preparation of *t*- $[\text{}^2\text{H}_9]$ butyl chloride of 97% isotopic purity and its conversion into *t*- $[\text{}^2\text{H}_9]$ butyl $[\text{}^1\text{H}_2]$ amine are given in the Experimental section. The borazocines were made by small-scale adaptations of the usual methods.

#### EXPERIMENTAL

Solvents were commercial products dried by standard methods. Except where otherwise stated, melting points were taken *in vacuo*<sup>44</sup> and are uncorrected. Melting points of borazocines were determined with the evacuated space totally immersed.

The i.r. spectra were recorded by Mr. H. M. Paisley on a Grubb-Parsons GS-3 spectrometer.

<sup>41</sup> M. T. Harvey and S. Caplan, U.S.P. 2,247,495/1941.

<sup>42</sup> E.g., W. Zeil, H. Buchert, H. Heel, and H. Pförtner, *Z. Elektrochem.*, 1960, **64**, 769.

<sup>43</sup> V. N. Setkina and D. N. Kursanov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **120**, 427.

<sup>44</sup> H. S. Turner, *Chem. and Ind.*, 1962, 817.



The n.m.r. spectra were measured by Dr. B. N. Figgis at University College on a Varian V4300B NMR spectrometer. The u.v. spectra were recorded by Mr. M. A. Francis on an Optica CF4 DRNI spectrophotometer. The mass spectra were measured by Mr. H. M. Paisley on an A.E.I. MS9 mass spectrometer, and at the Research Laboratories of the British Petroleum Company Ltd. on an A.E.I. MS2.

*Preparation of Hindered Alkylamines* (With B. LARCOMBE, W. S. McDONALD, and M. A. YOUNG).—(a) *s-Alkyl primary amines*. 3-Amino-2,2-dimethylbutane (b. p. 102—103°;  $n_D^{20}$  1.4096) was prepared by catalytic reduction<sup>45</sup> of pinacolone oxime<sup>46</sup> in 75% yield from the ketone. 2-Amino-3-methylbutane (b. p. 83°) and 3-amino-2,4-dimethylpentane (b. p. 130—132°;  $n_D^{25}$  1.4185) were prepared by reductive amination of the corresponding ketones.<sup>47</sup> The yields (76% and 60%, respectively) were raised above those claimed by Adkins<sup>47</sup> by increasing the proportion of ammonia to 4 mols. per mol. ketone.

(b) *t-Alkyl primary amines*. *t*-Butylamine was the commercial product. *t*-Pentylamine was prepared by hydrolysis<sup>48</sup> of commercial *t*-pentylurea (Eastman Kodak, practical). 1-Amino-1-methylcyclohexane (b. p. 73°/75 mm.;  $n_D^{22}$  1.4540) was obtained by hydrolysis<sup>48</sup> of 1-methylcyclohexylurea, prepared from 1-methylcyclohexanol after Harvey and Caplan.<sup>41, 48</sup> The urea, m. p. (sealed tube) 135—137° (Found: C, 62.3; H, 6.9; N, 17.5.  $C_8H_{16}NO_2$  requires C, 61.5; H, 10.3; N, 17.95%) was obtained in 27—30% yield; overall yield of amine, 20—25%. 3-Amino-3-methylpentane (b. p. 108—110°;  $n_D^{21}$  1.4139) was similarly obtained in an overall yield of 18%. 2-Amino-2-methylhexane<sup>49</sup> (b. p. 128—130°;  $n_D^{22}$  1.4132) was obtained in the same manner. The urea<sup>50</sup> (m. p. 108—109°; lit., 102°) was obtained in ~23% yield from the alcohol; the amine (20% yield from the alcohol) was obtained by hydrolysis of the urea with 50% sodium hydroxide solution at 180° for 4 hr. in an autoclave.

2-Amino-2,3-dimethylbutane and 2-amino-2,4-dimethylpentane were prepared from the corresponding nitriles, which were obtained by a modification<sup>51</sup> of the method of Ziegler and Ohlinger.<sup>52</sup> Liquid ammonia (2 l.) was treated with ferric nitrate (1.0 g.), and then sodium (2.0 g.). Air was bubbled into the solution until the blue colour was discharged ( $\frac{1}{2}$  min.) after which the rest of the sodium (44 g., 2 moles in all) was added; when all had dissolved, isobutyronitrile (138 g., 2.0 moles) was run in. Isopropyl bromide (369 g., 3.00 moles) was then added as fast as possible without excessive boiling of the liquid ammonia ( $\sim\frac{1}{2}$  hr.). The liquid ammonia was allowed to boil under reflux for 30 hr. and then taken off. The residue was treated with water and worked up for 2,2,3-trimethylbutyronitrile, b. p. 150—152° (lit.,<sup>53</sup> 152°), m. p. 22—25°; yield 125 g. (56%) (Found: C, 75.8; H, 11.9; N, 12.3. Calc. for  $C_7H_{13}N$ : C, 75.6; H, 11.8; N, 12.6%). The nitrile was also obtained (59% overall) by a two-stage methylation of isovaleronitrile by the same method. The nitrile (125 g.), sulphuric acid (500 ml.;  $d$  1.84), and water (370 ml.) were heated with stirring at 95—100° for 12 hr. The mixture was cooled, diluted to 2 l., and the amide filtered off; more was extracted by chloroform from the filtrate, giving a total of 126 g. (87%), m. p. 128—131° (lit.,<sup>54</sup> 133—134°). Bromine (32.0 ml.) was dissolved in a solution of sodium hydroxide (90 g.) in water (750 ml.) at 0°. The powdered amide (64.5 g.) was added, and the mixture stirred at 0° until the amide had dissolved and an oil began to separate. The mixture was heated during  $\frac{1}{2}$  hr. to 80° and maintained at, 80—90° for  $\frac{1}{2}$  hr. After cooling during 3 hr. *NN'*-bis-(1,1,2-trimethylpropyl)urea was filtered off (50 g., 88%), m. p. 226°, not raised by recrystallisation (Found: C, 68.8; H, 12.3; N, 12.2.  $C_{13}H_{28}N_2O$  requires C, 68.4; H, 12.4; N, 12.3%). The amine, b. p. 101—103° (lit.,<sup>55</sup> 104°), was obtained by hydrolysis with 50% aqueous potassium hydroxide at 200° for 8 hr. in an autoclave; yield, 86%. Alternatively, the amide was converted<sup>56</sup> into the urethane (b. p. 90—93°/13 mm.;  $n_D^{20}$  1.4395) by the Hoffman reaction in methanol solution; yield 96% (Found:

<sup>45</sup> E. Rohrmann and H. A. Shonle, *J. Amer. Chem. Soc.*, 1944, **66**, 1519.

<sup>46</sup> Cf. *Org. Synth.*, 1931, **11**, 54.

<sup>47</sup> E. J. Schwoegler and H. Adkins, *J. Amer. Chem. Soc.*, 1939, **61**, 3499.

<sup>48</sup> *Org. Synth.*, 1949, **18**, 29.

<sup>49</sup> D. F. March, *J. Pharmacol.*, 1948, **94**, 225.

<sup>50</sup> J. J. Ritter and P. R. Minieri, *J. Amer. Chem. Soc.*, 1948, **70**, 4047.

<sup>51</sup> J. B. Cloke, E. Stehr, T. R. Steadman, and L. C. Westcott, *J. Amer. Chem. Soc.*, 1945, **67**, 1589.

<sup>52</sup> K. Ziegler and H. Ohlinger, *Annalen*, 1932, **495**, 84.

<sup>53</sup> C. R. Harris and V. W. de Atley, U.S.P. 2,455,995/1947.

<sup>54</sup> A. Haller and E. Bauer, *Compt. rend.*, 1909, **149**, 6.

<sup>55</sup> M. H. Danzig and H. B. Hass, *J. Amer. Chem. Soc.*, 1944, **66**, 2018.

<sup>56</sup> Cf. E. Jeffreys, *Amer. Chem. J.*, 1899, **22**, 14.

C, 60.6; H, 10.8; N, 8.6.  $C_8H_{17}NO_2$  requires C, 60.3; H, 10.8; N, 8.8%). The urethane was hydrolysed to the amine using the same conditions as for the urea.

*2,2,4-Trimethylvaleronitrile* was prepared by alkylation of isobutyronitrile with isobutyl bromide and sodamide, according to the procedure of Sperber *et al.*,<sup>57</sup> in 53% yield, b. p. 88—89°/60 mm. (Found: C, 76.5; H, 11.8; N, 10.5.  $C_8H_{15}N$  requires C, 76.8; H, 12.1; N, 11.2%). The nitrile was converted into the amide by treatment with 80% sulphuric acid;<sup>57</sup> the yield of material of b. p. 75°/0.04 mm. and m. p. 71—72° (lit.,<sup>58</sup> 71°) was 79%. A Hoffmann reaction on the amide<sup>59</sup> gave NN'-bis-(1,1,3-trimethylbutyl)urea in 88% yield. It crystallised from light petroleum as colourless needles, m. p. 151—153° (Found: C, 70.3; H, 12.3; N, 10.5.  $C_{15}H_{32}N_2O$  requires C, 70.3; H, 12.5; N, 10.9%). The amine, b. p. 118—119°,  $n_D^{22}$  1.4101 (lit.,<sup>60</sup> b. p. 121—122°/747 mm.;  $n_D^{30}$  1.4009) was obtained in 90% yield by hydrolysis with 50% aqueous potassium hydroxide at 200° for 5 hr. Alternatively, the amide was converted<sup>56</sup> into the urethane; the yield of colourless oil, b. p. 102—104°/20 mm.,  $n_D^{25}$  1.4360, was 74% (Found: C, 63.3; H, 11.05; N, 8.0.  $C_9H_{19}NO_2$  requires C, 62.4; H, 11.0; N, 8.1%). The amine was obtained by hydrolysis as for the urea, in 95% yield.

The amine samples were converted by reaction with phenyl isocyanate in light petroleum (b. p. 100—120°) into the alkyl phenyl ureas; the m. p.s, and analyses are given in Table 5.

TABLE 5  
Alkylphenylureas

No.	Amine	B. p.	M. p. of alkylphenylurea
1	3-Amino-3-methylpentane .....	108—110°	136—139° <sup>a</sup>
2	2-Amino-2,3-dimethylbutane .....	101—103	147—149° <sup>a</sup>
3	2-Amino-2-methylhexane .....	128—130	121.5—122.5° <sup>b</sup>
4	2-Amino-2,4-dimethylpentane .....	118—119	102—104° <sup>b</sup>
5	2-Amino-2,4,4-trimethylpentane .....	139—140	138—140

No.	Found (%)			Formula	Calc. (%)		
	C	H	N		C	H	N
1	71.2	9.2	12.9	$C_{13}H_{20}N_2O$	70.9	9.15	12.7
2	71.0	9.15	12.8	$C_{13}H_{20}N_2O$	70.9	9.15	12.7
3	71.4	9.25	12.15	$C_{14}H_{22}N_2O$	71.8	9.45	12.0
4	71.6	9.25	12.4	$C_{14}H_{22}N_2O$	71.8	9.45	12.0
5	72.35	9.6	11.35	$C_{15}H_{24}N_2O$	72.5	9.75	11.3

<sup>a</sup> Mixed m. p. of these two ureas 125—140°. <sup>b</sup> Mixed m. p. of these two ureas 84—96°.

*Examination of the Purity of t-Alkyl Primary Amines by Gas-Liquid Chromatography* (With M. A. FRANCIS).—The measurements were carried out on a Perkin-Elmer Fractometer, Model 451, using a "PA" column ("Tween 80" as the stationary phase) with a flame ionisation detector. The t-pentylamine was found to contain ~0.5% of n-pentylamine, but no other detectable impurity. 3-Amino-3-methylpentane and 2-amino-2,3-dimethylbutane were well separated one from the other (*t* 10.2 and 8.7 min.); on separate examination at high sensitivity, neither showed separable impurities in excess of 0.5%. 1-Amino-1-methylcyclohexane, 2-amino-2-methylhexane, and 2-amino-2,4-dimethylpentane were cleanly separated (*t* 8.5, 4.1, and 3.1 min.); when examined separately at high sensitivity, all showed a small peak (*t* 0.6 min.), below 1% of the total. The first showed four small peaks in addition to the main peak; the total impurity was only ~1.5%. The second showed no additional impurities. The third showed only one additional impurity peak (*t* 6.9 min.) which appeared to be identical with one of the small impurity peaks found in 1-amino-1-methylcyclohexane (*t* 6.9 min.); the total impurity revealed was ~1%. In the case of 2-amino-2,4,4-trimethylpentane (commercial *t*-octylamine, redistilled, b. p. 139—140°) no  $C_8$  amines were available for comparison, but, under the conditions used above, two impurity peaks (*t* 10.0 and 8.3 min.; main peak 5.5 min.), corresponding to 0.5% and 1.2% of impurity, were observed.

sym-B-Chloro-N-alkylborazoles (A).—All preparations were conducted under a blanket of dry nitrogen. A 2-l. 3-neck flask, fitted with a sealed<sup>6</sup> Vibromixer agitator impeller and a double-surface condenser surmounted by a solid-CO<sub>2</sub> cold-finger condenser, containing toluene

<sup>57</sup> N. Sperber, D. Papa, and E. Schwenk, *J. Amer. Chem. Soc.*, 1948, **70**, 3091.

<sup>58</sup> R. Locquin and L. Leers, *Compt. rend.*, 1924, **179**, 56.

<sup>59</sup> C. Mentzer, N. P. Buu-Hoi, and P. Cagniant, *Bull. Soc. chim. (France)*, 1943, **10**, 141.

<sup>60</sup> D. P. Konowalow, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1124 (*Chem. Zentr.*, 1906, I, 738).

(500 ml.) was cooled in an ice-bath, and boron trichloride (120.3 g., 1.025 moles) was distilled in. A solution of triethylamine (315 ml., 227.5 g., 2.25 moles) in toluene (300 ml.) was then added, followed by the primary alkylamine (1.00 mole) in toluene (200 ml.). The mixture was heated; when the temperature reached  $\sim 50^\circ$  a rapid precipitation of triethylammonium chloride took place, and the temperature rose rapidly to the boiling point. After 1 hr. under reflux, the mixture was cooled and filtered. The yield of triethylammonium chloride was usually quantitative. The filtrate was evaporated and the borazole isolated, normally by distillation but in some cases (*e.g.*, the *N*-methyl and *N*-cyclohexyl compounds) by sublimation, crystallisation, or both. Small amounts of triethylammonium chloride were sometimes still present in the crude borazole, but could be removed by dissolving in isopentane or light petroleum, in which the salt is insoluble. Yields were normally in the range 75–95%.

*sym*-B-Chloro-*N*-alkylborazoles (B).—The apparatus and procedure was as in (A) except that the addition of boron trichloride was followed by the primary amine and then by the triethylamine. In this case the precipitation of triethylammonium chloride began at room temperature but was completed by refluxing for 1 hr. The product was worked up as in (A); yields were similar.

*sym*-B-Chloro-*N*-alkylborazoles (C). The apparatus was as in (A) except that the third neck bore a small solid- $\text{CO}_2$  cold-finger condenser through which boron trichloride was introduced drop by drop. The finely divided primary alkylamine hydrochloride (1.00 mole) was suspended in toluene (850 ml.) and heated under reflux while boron trichloride was passed in at the rate of 1–3 drops/sec. Hydrogen chloride was vigorously evolved, while excess boron trichloride was retained by the exit cold-finger. It was found that a rate of addition could be chosen so that little or no accumulation of boron trichloride occurred until slightly over one mole had been added. When this point was reached (as indicated by an increase in the rate at which boron trichloride dripped from the exit cold-finger), evolution of hydrogen chloride diminished, and it was possible by evaporation to recover the 1 : 1 adduct  $\text{R}\cdot\text{NH}_2\cdot\text{BCl}_3$ , usually contaminated with a little borazole. Methylamine–boron trichloride was obtained in this way, *m. p.* 125–127° (decomp.) after crystallisation from benzene–light petroleum [Found: B, 7.4; Cl, 71.25%; *M* (cryoscopic in benzene), 182. Calc. for  $\text{CH}_5\text{BCl}_3\text{N}$ : B, 7.3; Cl, 72.0%; *M*, 148.3]. If refluxing was continued, the slower evolution continued at a rate depending on the nature of the amine, with the ultimate formation of the borazole (see below).

The mixture was cooled in an ice-bath and triethylamine (315 ml., 227.5 g., 2.25 moles) in toluene (300 ml.) added dropwise. Some precipitation began at once; the reaction was carried to completion by heating under reflux for 1 hr. The mixture was worked up as before. The yield of triethylammonium chloride was normally less than 2.0 moles, since some hydrogen chloride was eliminated thermally from the adduct during its preparation from the hydrochloride.

Some borazoles prepared by these methods are listed in Table 6. *sym*-B-Chloro-*N*-2-chloroethylborazole was prepared from 2-chloroethylamine hydrochloride which was prepared *in situ* from oxazolidone and hydrogen chloride. Alternatively, oxazolidone and boron trichloride were heated together in toluene solution to give the borazole.

*By-product in the Preparation of tri-B-Chlorotri-N-ethylborazole.*—The borazole was prepared by method (A) from ethylamine (2.55 g. mol.). After distilling off the borazole, a fraction, *b. p.* 140–166°/0.02 mm. (21.8 g.) was collected. Further fractionation gave *bis*(*di*-B-chlorotri-*N*-ethylborazolyl)ethylamine, a yellow oil, *b. p.* 158–160°/0.01 mm. (10.39 g.), slowly crystallising at room temperature [Found: C, 32.9; H, 7.1; B, 13.1; Cl, 28.5; N, 17.65%; *M* (cryoscopic) 510.  $\text{C}_{14}\text{H}_{36}\text{B}_6\text{Cl}_4\text{N}_7$  requires C, 33.1; H, 6.95; B, 12.8; Cl, 27.9; N, 19.35%; *M*, 508]. The hydrochloride and platinichloride of the amine obtained by hydrolysis of this compound had identical i.r. spectra with those of authentic ethylamine.

*Thermal Dehydrochlorination of Methylamine–Boron Trichloride.*—The apparatus consisted of a 1-l. 3-neck flask fitted with a sealed Vibromixer agitator impeller and a double-surface condenser. This flask was swept with nitrogen, the outflow being taken from the top of the condenser and led through a short air-condenser into a second 1-l. 3-neck flask also fitted with a sealed Vibromixer agitator impeller and a magnetic stirrer capsule. In the first flask was put methylamine–boron trichloride and the solvent (145 ml.), and in the second water (150 ml.) and Bromocresol Green. The mixture in the first flask was raised rapidly to the boiling point (4–7 min.) while the hydrogen chloride that was evolved was absorbed in a spray of water in the second flask. Absorption of hydrogen chloride was complete, and no back pressure was

TABLE 6  
 sym-N-Alkyl-B-chloroborazoles (RNBCl)<sub>3</sub>

No.	R	Yield (%)	B. p.	M. p.	Method used
1	Methyl <sup>12, 61, 62</sup>	85 <sup>c</sup>		160°	A, B, C
2	Ethyl <sup>61</sup>	80	66°/0.1 mm.	55—57	A, B, C
3	n-Propyl	82		80	A, B <sup>d</sup>
4	Isopropyl	80	78—79/0.2	48.5	A, B
5	n-Butyl <sup>61</sup>	79	118/0.2	~30	B, C
6	s-Butyl <sup>e</sup>	88	94—96/0.04		B, C
7	Isobutyl <sup>f</sup>	80	94—96/0.05	~37	B, C
8	n-Hexyl <sup>63</sup>	80	160/0.15		A, B
9	n-Octyl	82	205/0.1		A, C
10	1,2-Dimethyl-n-propyl <sup>64</sup>	67	119/0.1		B
11	Allyl	71	89/0.1		A
12	Benzyl <sup>65</sup>	79 <sup>c</sup>		126	A, B
13	2-Phenylethyl <sup>63</sup>	95 <sup>c</sup>		140	A, B
14	2-Chloroethyl <sup>63, 66</sup>	70	133/0.07		C <sup>g</sup>
15	2-Bromoethyl <sup>65</sup>	77	~175/0.1	84	C <sup>g</sup>
16	3-Bromopropyl <sup>65</sup>	72	190/0.2	63	C <sup>g</sup>
17	4-Bromobutyl	55	210/0.1		C <sup>g</sup>

No.	Found (%)					Formula	Calc. (%)				
	C	H	B	Cl	N		C	H	B	Cl	N
1 <sup>a</sup>	16.05	3.8	14.4	47.3	18.75	C <sub>2</sub> H <sub>5</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	16.0	4.0	14.4	47.5	18.7
2	26.8		11.8	39.3	15.6	C <sub>6</sub> H <sub>15</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	26.9	5.5	12.1	39.7	15.7
3	33.7	6.0	10.5	33.6	13.2	C <sub>9</sub> H <sub>21</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	34.9	6.8	10.5	34.0	13.6
4	34.5	6.4	10.6	33.8	13.1	C <sub>9</sub> H <sub>21</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	34.9	6.8	10.5	34.0	13.6
5	40.6		9.15	29.7	11.8	C <sub>12</sub> H <sub>27</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	40.9	7.7	9.2	30.2	11.9
6	40.9		9.2	29.6	11.9	C <sub>12</sub> H <sub>27</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	40.9	7.7	9.2	30.2	11.9
7	40.8		8.75	29.4	11.9	C <sub>12</sub> H <sub>27</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	40.9	7.7	9.2	30.2	11.9
8	50.7	9.0	7.5	24.2	9.7	C <sub>18</sub> H <sub>39</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	49.5	8.95	7.45	24.4	9.65
9	55.5	9.8	5.9	20.3	8.0	C <sub>24</sub> H <sub>51</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	55.4	9.9	6.25	20.5	8.1
10 <sup>b</sup>	45.9	8.6	8.9	26.0	10.4	C <sub>15</sub> H <sub>35</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	45.7	8.4	8.25	27.1	10.65
11	35.0	4.8	10.2	35.4	13.3	C <sub>9</sub> H <sub>15</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	35.6	5.0	10.7	34.2	13.7
12	55.1	5.3	7.2	23.1	9.2	C <sub>21</sub> H <sub>47</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	55.6	4.7	7.15	23.5	9.25
13	58.0	4.9	6.6	21.3	8.7	C <sub>24</sub> H <sub>51</sub> B <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	58.1	5.5	6.5	21.4	8.5
14	20.2	3.1	9.1	55.6	11.0	C <sub>6</sub> H <sub>12</sub> B <sub>3</sub> Cl <sub>6</sub> N <sub>3</sub>	19.4	3.25	8.7	57.3	11.3
15	16.5 <sup>h</sup>	2.8	6.6	50.6 <sup>i</sup>		C <sub>6</sub> H <sub>12</sub> B <sub>3</sub> Br <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	14.25	2.4	6.4	48.6 <sup>i</sup>	
16	23.9 <sup>h</sup>	4.6	6.9	45.7 <sup>i</sup>	8.9	C <sub>9</sub> H <sub>18</sub> B <sub>3</sub> Br <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	19.8	3.3	5.95	44.9 <sup>i</sup>	7.7
17	29.1 <sup>h</sup>	4.6		40.4 <sup>i</sup>	8.8	C <sub>12</sub> H <sub>24</sub> B <sub>3</sub> Br <sub>3</sub> Cl <sub>3</sub> N <sub>3</sub>	24.5	4.1		41.7 <sup>i</sup>	7.1

<sup>a</sup> Found, *M*, 216; Calc., *M*, 226. <sup>b</sup> Found, *M*, 396; Calc., *M*, 394. <sup>c</sup> Purified by sublimation and crystallisation. <sup>d</sup> When triethylamine was replaced by di-isopropylethylamine the yield was 75%. <sup>e</sup> DMS Card no. 9514. <sup>f</sup> DMS Card no. 9515. <sup>g</sup> The free amines are unstable. <sup>h</sup> Some exchange of chlorine for bromine had occurred during the preparation. <sup>i</sup> Calculated as chlorine.

caused by the absorber. The solution in the absorber was titrated continuously with standard alkali. In the runs (1, 2, 3, and 4) recorded in Figures 2 and 3, the quantities of adduct were, respectively, 0.098, 0.050, 0.070, and 0.072 mole. In the first three runs the solvent was chlorobenzene, and in the fourth *p*-chlorofluorobenzene. The rate of nitrogen flow was normally 5.8 l./hr.; it was shown in a repeat of run 3 that doubling the rate had a negligible effect on the results. The boron content of the absorber at the conclusion of all runs was negligible.

The results for *o*-toluidine-boron trichloride were obtained in a similar apparatus.

sym-B-Trichloroborazole.—Finely ground ammonium chloride (82.4 g., 1.54 moles) in toluene (700 ml.) was treated with boron trichloride as in (C) above. When boron trichloride began to accumulate in the exit condenser addition was terminated (4½ hr.), and heating under reflux was continued until no more hydrogen chloride was evolved. The solvent was distilled off, and the borazole (75 g., 79%; m. p. 82°) recovered by sublimation at 60—70°/15 mm. When the toluene recovered from this preparation was used as solvent for a second preparation the yield rose to 90%.

Attempted Preparation of Borazole.—(a) From 3-amino-2,2-dimethylbutane. The method was

<sup>61</sup> H. S. Turner and R. J. Warne, *Chem. and Ind.*, 1958, 526.

<sup>62</sup> K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561.

<sup>63</sup> Report of the National Chemical Laboratory, 1958, 53 (H.M. Stationery Office).

<sup>64</sup> R. K. Bartlett, H. S. Turner, R. J. Warne, and M. A. Young, *Chem. and Ind.*, 1964, 1026.

<sup>65</sup> Report of the National Chemical Laboratory, 1959, 37 (H.M. Stationery Office).

<sup>66</sup> K. John, G. P. 1,162,363/1964.



as in (A) using boron trichloride (0.40 mole) triethylamine (0.85 mole), and the amine (38.5 g., 0.381 mole) in toluene (total 500 ml.). Triethylammonium chloride (73 g., 0.53 mole; 1.4 mol.) was precipitated. The oil obtained by evaporation of the filtrate was separated by distillation (17 mm.) into the impure borazene (10.1 g.), a colourless oil, b. p.  $\sim 60^\circ$  (Found: B, 5.5; Cl, 34.0.  $C_6H_{14}BCl_2N$  requires B, 5.7; Cl, 39.0%), and a yellow oil (35 g.), b. p.  $70-120^\circ$  (Found: Cl, 17.7%), consisting largely of the boronamine  $RNH \cdot BCl \cdot NR \cdot BCl \cdot NHR$  ( $R = C_6H_{13}$ ). The pure compound was isolated by fractional distillation as a colourless oil, b. p.  $121^\circ/0.06$  mm. [Found: C, 54.4; H, 10.5; B, 6.4; Cl, 18.0; N, 10.5%;  $M$  (cryoscopic), 380.  $C_{18}H_{41}B_2Cl_2N_3$  requires C, 55.2; H, 10.5; B, 5.5; Cl, 18.1; N, 10.7%;  $M$ , 392]. There was no evidence of borazole formation.

The boronamine (3.58 g., 0.000915 mole), triethylamine (3.0 ml., 0.0215 mole), and boron trichloride (0.0125 mole) in toluene (20 ml.) were heated under reflux for  $1\frac{1}{2}$  hr. The liquid was filtered, evaporated, and distilled *in vacuo* to give  $RNH \cdot BCl \cdot NR \cdot BCl \cdot NR \cdot BCl_2$  ( $R = C_6H_{13}$ ), b. p.  $120-122^\circ/0.06$  mm., a colourless oil (Found: C, 46.7; H, 9.1; B, 7.15; Cl, 30.9; N, 9.0.  $C_{15}H_{34}B_3Cl_4N_3$  requires C, 46.7; H, 8.5; B, 6.85; Cl, 30.0; N, 8.9%).

(b) From 3-amino-2,4-dimethylpentane. The method was as in (B) using boron trichloride (57.0 g., 0.485 mole), the amine (55.0 g., 0.478 mole), and triethylamine (107 g., 1.06 mole) in toluene (total 400 ml.) Triethylammonium chloride (101 g.; 0.732 mole, 1.52 mol.) was collected. The oil obtained by evaporation was taken up in isopentane (500 ml.) and a small quantity of insoluble oil removed; the soluble matter was recovered by evaporation. The solvent distillates appeared to contain borazene  $RNH \cdot BCl_2$  ( $R = C_7H_{15}$ ) (Cl: 0.063 g.-atom; B, 0.031 g.-atom). The oil was fractionally distilled at 0.025 mm. giving fractions: (a) contents of the cold-trap, containing nitrogen (0.062 g.-atom), chlorine (0.063 g.-atom), and boron (0.034 g.-atom), probably a mixture of triethylamine ( $\sim 0.03$  mole) and borazene ( $\sim 0.03$  mole); (b) 12.35 g., b. p.  $< 81^\circ$ ; (c) 32.7 g. b. p.  $81-100^\circ$ ; (d) 4.20 g., b. p.  $100-124^\circ$ ; (e) 15.10 g., b. p.  $124-128^\circ$ ; and a residue, 8.22 g. (Found: B, 5.35; Cl, 13.4; N, 6.1%). Recombination and redistillation of (b), (c), and (d) gave the borazene  $RNH \cdot BCl_2$  ( $R = C_7H_{15}$ ) a colourless mobile liquid, b. p.  $116-118^\circ/76$  mm. (Found: C, 40.2; B, 5.65; Cl, 35.6; N, 6.7.  $C_7H_{16}BCl_2N$  requires C, 42.9; B, 5.5; Cl, 36.2; N, 7.2%) and bis-(2,4-dimethyl-3-pentyl)boron chloride (17.7 g.), a colourless oil b. p.  $72-74^\circ/0.03$  mm. solidifying at room temperature to a white solid (Found: C, 60.0; B, 4.15; Cl, 13.4; N, 10.0.  $C_{14}H_{32}BCl_2N_2$  requires C, 61.2; B, 3.95; Cl, 12.9; N, 10.2%). Redistillation of fraction (e) gave the boronamine  $RNH \cdot BCl \cdot NR \cdot BCl \cdot NHR$  ( $R = C_7H_{15}$ ) (6.5 g.), a colourless viscous oil, b. p.  $112-117^\circ/0.03$  mm. (Found: C, 54.6; B, 4.95; Cl, 16.35; N, 9.1.  $C_{21}H_{47}B_2Cl_2N_3$  requires C, 58.1; B, 5.0; Cl, 16.35; N, 10.9%). There was no evidence of borazole formation.

*Interaction of t-Butylamine and Boron Trichloride.*—t-Butylamine (120.0 ml., 1.146 moles) in isopentane (240 ml.) was added during 1 hr. to a stirred solution of boron trichloride (135.8 g., 1.158 moles) in isopentane (400 ml.) at below  $-40^\circ$ . The suspension was filtered, the solid washed thoroughly with more solvent, and then pumped dry. The product (144 g.; Found: Cl, 60.5%) contained t-butylammonium tetrachloroborate (99 g., 0.43 mole) and t-butylamine-boron trichloride (45 g., 0.24 mole), from which the latter was extracted by cold chloroform. The 1:1 adduct crystallised from benzene as white needles, decomposing above  $110^\circ$  (Found: C, 25.6; H, 4.3; B, 5.9; Cl, 54.6; N, 7.2.  $C_4H_{11}BCl_3N$  requires C, 25.2; H, 5.8; B, 5.7; Cl, 56.0; N, 7.3%); DMS Card No. 9511. The filtrate was fractionally distilled, and t-butylamino-boron dichloride (29.3 g., 0.19 mole), b. p.  $65-66^\circ/64$  mm. was collected as a colourless mobile liquid which reacts vigorously with water (Found: C, 29.8; H, 6.6; B, 6.8; Cl, 44.9; N, 8.7.  $C_4H_{10}BCl_2N$  requires C, 31.2; H, 6.5; B, 7.05; Cl, 46.2; N, 9.1%); DMS Card No. 9512. A residue ( $\sim 10$  g.) of a mixture of t-butylaminoboron dichloride dimer and t-butylamine-boron trichloride (Found: Cl, 48.5%) remained in the distillation flask. Samples of t-butylamino-boron dichloride were kept in sealed tubes *in vacuo* at room temperature and at  $\sim -20^\circ$ . Crystals of the dimer appeared in the former after 4 weeks; after 5 weeks the unchanged monomer (52%) was distilled *in vacuo* from the dimer and sealed again *in vacuo*. Within 1 day dimer had crystallised; after 6 days 63% had dimerised. After 1 year the samples stored at  $-20^\circ$  contained 66% monomer. The crude dimer thus obtained (m. p.  $125-126^\circ$ ) was crystallised from cyclohexane, giving colourless needles, m. p.  $135-136^\circ$  [Found: C, 30.3; H, 7.0; B, 6.9; Cl, 45.1; N, 8.4%;  $M$  (cryoscopic), 278.  $C_8H_{20}B_2Cl_4N_2$  requires C, 31.2; H, 6.5; B, 7.05; Cl, 46.2; N, 9.1%;  $M$ , 308]; DMS Card No. 9513. It was not wetted by, and only slowly dissolved in, boiling water.



*Thermal Dehydrochlorination of t-Butylamine-Boron Trichloride.*—This was carried out as for methylamine-boron trichloride, using the 1:1 adduct (18.83 g., 0.099 g. mole) in chlorobenzene (100 ml.). A total of 0.111 g.-atom of Cl<sup>-</sup> and 0.006 g.-atom of boron appeared in the absorber. The boron was almost certainly carried over as t-butylaminoboron dichloride, so that Cl<sup>-</sup> carried over as hydrogen chloride was ~0.099 g.-equiv. The chlorobenzene was distilled from the reaction solution, leaving a brown solid residue (7.60 g.). The recovered chlorobenzene gave (after reaction with water and titration), amine (0.033 g. mole), Cl<sup>-</sup> (0.073 g.-atom), and boron (0.034 g.-atom), and was believed to contain originally ~0.034 mole of t-butylaminoboron dichloride. This was not isolated by distillation, but, on keeping, the dimer slowly deposited. The residue (Found: C, 34.6; H, 7.7; B, 5.4; Cl, 39.5; N, 11.4%); was clearly a mixture, and was not identified. It was immediately and completely soluble in cold water, and thus contained neither the borazocine nor the t-butylaminoboron dichloride dimer.

*Tetra-B-chlorotetra-N-t-butylborazocine.*—(a) The apparatus consisted of a 5-l. 3-neck flask fitted with a sealed Vibromixer agitator impeller and a double-surface condenser surmounted by a solid-CO<sub>2</sub> cold-finger condenser. Triethylamine (463 g., 640 ml., 4.57 moles) and toluene (2 l.) were put in the flask, and gaseous boron trichloride (242.5 g., 2.07 moles) was passed in through a rotameter while the apparatus was cooled in an ice-bath. A solution of t-butylamine (146 g., 210 ml., 2.00 moles) in toluene (210 ml.) was then added: there was no significant evolution of heat. After replacing the cold-finger condenser by a second double-surface condenser, the mixture was gently heated. When the temperature reached about 60° a vigorous reaction set in; triethylammonium chloride was precipitated, and the solvent boiled. Refluxing was continued for 1 hr., after which the mixture was cooled, poured on to crushed ice (2000 g.) and eventually stirred at 50–60° for ½ hr. After filtering to remove a little insoluble material, the toluene layer was stirred again with water (2000 g.) at 50–60° for 15 min., separated, and dried (K<sub>2</sub>CO<sub>3</sub>). Evaporation to dryness under reduced pressure gave the crude borazocine (175 g., 0.373 mole, 74.5% from t-butylamine), m. p. 175–185°, as a light-brown crystalline solid.

(b) The apparatus was generally as before, but with a 2-l. flask containing toluene (650 ml.). Air was excluded by a small excess pressure of nitrogen. With the contents of the flask at 0° boron trichloride (124.3 g., 1.06 moles) was passed in; a solution of t-butylamine (76.4 g., 110.0 ml., 1.05 moles) in toluene (250 ml.) was then added during 30 min., followed by triethylamine (217 g., 300.0 ml., 2.14 moles) in toluene (250 ml.). A reaction occurred during the last addition, and triethylammonium chloride was precipitated. The cold-finger condenser was removed and the mixture was heated under reflux for 1 hr., cooled to room temperature, and filtered. The triethylammonium chloride on the filter was washed with toluene and dried (283 g., 2.06 moles). The combined filtrate and washings were evaporated to dryness under reduced pressure; water (500 ml.) was added, and the mixture heated under reflux until the solid had broken down to a pale brown powder. This was filtered off, washed with water, and dried *in vacuo* or in air below 100°. The yield of the crude borazocine was 89.1 g. (0.190 mole, 72.5% from t-butylamine), m. p. 185–200°.

(c) Triethylamine (9.5 g., 0.094 mole) was added to potassium tetrachloroborate<sup>6</sup> (58% as KBCl<sub>4</sub>; 0.041 mole) suspended in toluene (150 ml.) at room temperature, followed by t-butylamine (2.92 g., 0.040 mole) in toluene (10 ml.). The mixture was heated under reflux for 2 hr., cooled, and filtered. The filtrate was worked up as in (b) to give the crude borazocine (2.98 g., 63% from t-butylamine), m. p. 195–199°; identity was confirmed by i.r. spectrum.

(d) t-Butylaminoboron dichloride (5.62 g., 0.0365 mole) in toluene (50 ml.) was added to triethylamine (3.7 g., 0.0365 mole) in toluene (100 ml.), with stirring, at 0°. The mixture was heated slowly to the boil, refluxed for 1 hr., cooled, and filtered. Working up as in (b) gave crude borazocine (2.95 g., 69% from the borazene), m. p. 196–200°; identity was confirmed by i.r. spectrum.

(e) t-Butylammonium tetrachloroborate<sup>6</sup> (11.3 g.; 0.05 mole) was suspended in toluene (70 ml.) and treated with triethylamine (16.2 g., 0.160 mole) in toluene (50 ml.) at room temperature. The mixture was heated to boiling with stirring, and refluxed for 1 hr. The product was filtered and worked up as in (b), giving crude borazocine (3.23 g., 55% from the tetrachloroborate), m. p. 190–195°; identity was confirmed by i.r. spectrum.

(f) A preparation was carried out exactly as in (a) on a 0.35-molar scale, but in the presence of benzonitrile (0.35 mole). The course of the reaction was quite normal, but the yield of

borazocine was slightly lower than usual (64%). There was no evidence that the benzonitrile had participated in the reaction.

(g) A preparation was carried out as in (b) using boron trichloride (32.25 g., 0.275 mole), t-butylamine (20.3 g., 0.278 mole), and trimethylamine (34.1 g., 0.578 mole). After heating under reflux, the mixture was cooled and filtered. The solid on the filter (55 g.) was extracted with water, leaving a white, insoluble residue (26.5 g., 0.150 mole) of trimethylamine-boron trichloride, m. p. 240° (lit., 242—243°) (Found: C, 19.9; H, 4.9; B, 5.8; Cl, 59.8; N, 7.8. Calc. for  $C_3H_9NCl_3B$ : C, 20.4; H, 5.1; B, 6.15; Cl, 60.3; N, 8.0%). The filtrate was evaporated to dryness *in vacuo*, and treated with water. An insoluble residue (5.8 g., 0.033 mole) of trimethylamine-boron trichloride was collected by filtration. No borazocine was found in the products.

(h) A preparation was begun as in (b) on the 0.1-molar scale, in which ethyl di-isopropylamine replaced triethylamine; the mixture was heated under reflux for 2 hr. On cooling to 0°, the lower oily layer partly solidified. The solid (11.3 g.) was slightly impure di-isopropylethylammonium chloride, and was completely soluble in water. Evaporation of the filtrate gave a solid (19.8 g.), and a toluene distillate containing boron (0.02 g.-atom) and chlorine (0.028 g.-atom) probably mainly present as the borazene. The solid was triturated with cyclohexane: the residual white crystalline powder (14.0 g.) was completely soluble in water (Found: C, 46.4; H, 10.0; B, 2.2; Cl, 34.5; N, 6.8%), and appeared from the analysis and the i.r. spectrum to consist of a mixture of di-isopropylethylammonium chloride and the corresponding tetrachloroborate. The cyclohexane on evaporation gave a brown syrup (3.5 g.), which on treatment with water gave the borazocine (0.6 g., 5% overall yield).

*Purification of the Borazocine.*—The purity of the crude borazocine varies with the preparation, but it can normally be obtained sufficiently pure for all normal purposes, m. p. (*in vacuo*) >235°, by (a) dissolving in isopentane or light petroleum (b. p. 40—60°) (~3 ml./g.), filtering, and recovering by evaporation; (b) subliming the product at 140—150°/0.05 mm.; and (c) crystallising from acetone (~2.1 ml./g.), ethyl acetate (~1.7 ml./g.), cyclohexane (~3 ml./g.), or acetonitrile (~35 ml./g.). The sublimation stage can often be omitted. The m. p. is raised to 249° by further crystallisation.

The borazocine is thus obtained as a white crystalline solid. When hydrolysed by heating with an excess of water in a sealed tube at 160°, it gives equimolar amounts of t-butylamine, hydrogen chloride, and boric acid (Found: C, 40.7; H, 7.5; B, 9.0; Cl, 30.0; N, 12.0.  $C_4H_9BClN$  requires C, 40.9; H, 7.75; B, 9.2; Cl, 30.2; N, 12.0%). The molecular weight in benzene was 466 (cryoscopic) and 463 (ebullioscopic) corresponding to the tetramer ( $C_4H_9BClN$ )<sub>4</sub> (Calc. 469). Some approximate values of solubility at room temperature are (g./ml.): carbon disulphide, 3; n-heptane, 0.9; benzene, 0.8; n-decane, 0.7; ethyl acetate, 0.15; acetone, 0.1; nitrobenzene, 0.07; dimethoxyethane, 0.05; cyclohexane, 0.03; sulphur dioxide, 0.01; acetonitrile, 0.006.

The borazocine separates from carbon tetrachloride with solvent of crystallisation, which is readily lost from the surface of the crystals but is only completely removed on sublimation *in vacuo*. The *solvate* appears to contain 2 molecules of solvent per molecule of borazocine (1.20 g. crystals gave 0.73 g. borazocine and 0.47 g. carbon tetrachloride; *i.e.*, borazocine: carbon tetrachloride, 1:1.96). It was difficult to get good analyses (Found: C, 29.5; H, 4.8; Cl, 49.0.  $C_{16}H_{36}B_4Cl_4N_4 \cdot 2CCl_4$  requires C, 27.8; H, 4.7; Cl, 54.8%).

Attempts to determine the molecular depression constant were complicated by the slow decomposition of the borazocine at the melting point. Thus, when anthracene was used as the solute with pre-melting of the constituents, values in the range 100—120 were obtained. When pure hexacosane (m. p., 56.3—56.35°) was used as solute, and intimately mixed with the borazocine without pre-melting, the values obtained ranged from 53 ( $2.39 \times 10^{-2}$  mole/100 g. solvent) to 95 ( $0.51 \times 10^{-2}$  mole/100 g. solvent). The lower value is regarded as more reliable, since in this case the fluxing by the low-melting solute is more effective, and, as the actual melting point is lower (depression 12.7°), decomposition during melting is less.

*Stability of Tetra-B-chlorotetra-N-t-butylborazocine.*—Samples of the borazocine have been kept for over 5 years under normal conditions in air without any sign of decomposition (appearance, m. p., i.r. spectrum). At higher temperatures, decomposition takes place: the m. p. in air is 200—225°. Even in an evacuated tube there is some decomposition above about 130°. Thus, an attempt to measure the vapour pressure at 160° by the dynamic method using

TABLE 7  
 Tetra-*B*-halogenotetra-*N*-alkylborazocines (RNBX)<sub>4</sub>

No.	R	X	Preparation method	Yield (%)	M. p.	<i>M</i>		DMS card no.
						Found	Calc.	
1	<i>t</i> -Butyl	Cl	A, B	70—85	249°	463 <sup>b</sup> 466 <sup>a</sup>	469	9516
2	<i>t</i> -Butyl	Br	A	52	243.5—245	650 <sup>b</sup>	647	9517
3	1,1-Dimethyl- <i>n</i> -propyl	Cl	A	67	159.5—162	550 <sup>a</sup>	525	9522
4	1-Methylcyclohexyl	Cl	A	49	272—274	620 <sup>b</sup>	629	9526
5	1,1-Dimethyl- <i>n</i> -pentyl	Cl	B	53	93	629 <sup>b</sup>	637	9524
6	1,1,3-Trimethyl- <i>n</i> -butyl	Cl	B	22	112—114	598 <sup>a</sup>	637	9525
7	1,1,3,3-Tetramethyl- <i>n</i> -butyl	Cl	A	18	201.5—203.5	660 <sup>b</sup>	695	9523
8	1,1,3,3-Tetramethyl- <i>n</i> -butyl	Br	A	4.5	198.5—200	—	874	—

No.	Found (%)					Formula	Calc. (%)				
	C	H	B	Hal.	N		C	H	B	Hal.	N
1	40.7	7.5	9.0	30.0	12.0	C <sub>16</sub> H <sub>36</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	40.9	7.75	9.2	30.2	12.0
2	30.4	5.7	6.6	49.5	8.5	C <sub>16</sub> H <sub>36</sub> B <sub>4</sub> Br <sub>4</sub> N <sub>4</sub>	29.7	5.6	6.7	49.4	8.7
3	46.5	8.3	8.5	26.8	10.6	C <sub>20</sub> H <sub>44</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	45.7	8.4	8.25	27.1	10.65
4	54.3	8.6	6.8	22.4	9.1	C <sub>28</sub> H <sub>52</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	53.4	8.35	6.9	22.5	8.9
5	53.0	9.8	7.2	22.1	8.6	C <sub>28</sub> H <sub>50</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	52.6	9.5	6.8	22.2	8.8
6	52.8	9.5	6.1	22.05	9.3	C <sub>28</sub> H <sub>50</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	52.6	9.5	6.8	22.2	8.8
7	56.1	10.6	5.5	20.3	8.9	C <sub>32</sub> H <sub>68</sub> B <sub>4</sub> Cl <sub>4</sub> N <sub>4</sub>	55.2	10.1	6.2	20.4	8.1
8	44.6	8.4	4.8	35.4	6.4	C <sub>22</sub> H <sub>68</sub> B <sub>4</sub> Br <sub>4</sub> N <sub>4</sub>	44.1	7.8	5.0	36.7	6.45

<sup>a</sup> Cryoscopic. <sup>b</sup> Ebullioscopic.

nitrogen gas with the apparatus of Hirt, Steger, and Simard,<sup>67</sup> was frustrated by a slow decomposition of the borazocine.

*Hydrolysis.*—(i) Finely powdered borazocine (0.1035 g., 0.220 mmole) and water (1.00 ml.) were sealed in a glass tube and heated in boiling xylene (139°) for 20½ hr. The product contained 0.544 milliequivalent of ionisable chlorine, corresponding to 62% hydrolysis.

(ii) In a similar experiment at ~160° (in refluxing cyclohexanol) hydrolysis was 97% complete.

(iii) A solution of the borazocine (0.02M) in 50% aqueous dioxan was heated under reflux for 18½ hr. The solution was then 0.0098M in chloride ion, corresponding to 49% hydrolysis.

(iv) Similar experiments were carried out with aqueous dioxan that was initially 0.02N in sodium hydroxide and in sulphuric acid. The degree of hydrolysis was 55% and 48.5%, respectively.

*Tetra-B-chlorotetra-N-t-butylborazocine: By-products in Preparation.*—A preparation was carried out as in (a) using *t*-butylamine (0.876 mole). Triethylammonium chloride (1.80 moles by weight and by Cl<sup>-</sup> titration) was precipitated. The filtrate was evaporated *in vacuo*, the residue dissolved in isopentane, and the solution filtered and again evaporated *in vacuo*. The solid product (108 g.) was crystallised from carbon tetrachloride (180 ml.) giving borazocine-carbon tetrachloride complex containing 55 g. (0.47 g. mol.) of borazocine. The filtrate was evaporated and the residue distilled at 0.1 mm. The lower fractions (up to 125°) were mixtures of borazocine and an oil (borazocine content probably ~3 g.). The oil was not identified; it had N : Cl : B = 1.3 : 1 : 1.2. At higher temperatures the borazocine sublimed (total ~30 g.). The total of borazocine from the distillation was ~0.28 mole, and the total from the preparation 0.75 mole (85%). Hydrogen chloride (0.12 g.-equiv.) was extracted by washing from the various solvent distillates.

*Tetra-B-bromotetra-N-t-butylborazocine.*—This was prepared by method (a) from *t*-butylamine (1.03 moles); boron tribromide (1.07 moles) was used as a solution in toluene (145 ml.). The reaction mixture was worked up for the borazocine as in (b); 1.95 moles of triethylammonium bromide was obtained. The crude product (86 g., 52%) had m. p. 190—195°. It was taken up in light petroleum (b. p. 40—60°), filtered to remove a small residue of triethylammonium bromide, evaporated, and crystallised from ethyl acetate (1.7 ml./g.) followed by acetonitrile (60 ml./g.).

*Tetra-B-chlorotetra-N-1',1'-dimethylpropylborazocine.*—Prepared as in (a) from *t*-pentylamine (0.50 mole). After filtration of the triethylammonium chloride (1.0 mole), the crude

<sup>67</sup> R. C. Hirt, J. E. Steger, and G. L. Simard, *J. Polymer Sci.*, 1960, **43**, 319.

borazocine (65 g.) was recovered by evaporation and crystallised from light petroleum (b. p. 60—80°), giving two crops of the borazocine (total 44 g.; m. p. 154—156°). This was purified by crystallisation from n-butyl acetate (10 ml./g.) followed by isobutyronitrile (15 ml./g.) to give a colourless crystalline solid.

The borazocine decomposes slightly at the melting point. The molecular-depression constant was determined as for the t-butyl compound (above). When pre-melted with the solute values were in the range 40—70, but when the components were intimately mixed but not pre-melted a value of  $31 \pm 3$  was obtained in the concentration range  $6 \times 10^{-3}$  to  $22 \times 10^{-3}$  mole/100 g. solvent. This value is the more reliable.

*Tetra-B-chlorotetra-N-1'-methylcyclohexylborazocine.*—Prepared by method (a) from 1-amino-1-methylcyclohexane (0.38 mole). The triethylammonium chloride precipitate (118 g.) was filtered off and extracted with water, leaving the insoluble borazocine (17.4 g., m. p. 234°). The organic filtrate was evaporated to dryness, and the solid residue crystallised from benzene, when two crops (total 12.0 g.; m. p. 210—220°) were obtained. The pure borazocine separated as colourless crystals from toluene or xylene (12 ml./g.).

*Tetra-B-chlorotetrakis-N-1',1'-dimethylpentylborazocine.*—Prepared by method (b) from 2-amino-2-methylhexane (0.252 mole). Triethylammonium chloride (0.458 mole; 1.82 mol.) was formed. Evaporation of the filtrate gave a brown crystalline paste (38.6 g.). A portion (10 g.) when treated with water gave the borazocine (5.5 g., 53%; m. p. 83—91°). The remainder was taken through isopentane solution (treatment with Celite removed a little insoluble oil) and crystallised from ethyl acetate, giving two crops of crude borazocine (13.5 g., 45%; m. p. 85—90°). The mother liquors from the crystallisation gave a brown oil (11 g.) on evaporation (Found: C, 51.8; H, 10.0; B, 7.1; Cl, 19.0; N, 11.0%). This was distilled *in vacuo* (0.3 mm.). No clear-cut separation was obtained, but the higher-boiling material (180—200°) had a composition close to that of the brown oil; the i.r. spectrum suggested that it may have been the boronamine  $\text{RNH}\cdot\text{BCl}\cdot\text{NR}\cdot\text{BCl}\cdot\text{NHR}$  ( $\text{R} = \text{C}_7\text{H}_{15}$ ) contaminated with borazocine. The borazocine crystallised from acetone (7 ml./g.) followed by isobutyronitrile (14 ml./g.) as colourless plates.

When the pure borazocine (1.00 g.) was refluxed with water for 1 hr., 0.98 g. was recovered unchanged. The water contained no detectable amount of chloride ion. The m. p. was unchanged after 50 hr. at 105° *in vacuo*.

The borazocine (0.75 g.) and 2.5N-sodium hydroxide (2.0 ml.) were heated in a sealed tube for 16 hr. at 140°. The upper layer of the amine was distilled off as the azeotrope with water and dried initially over sodium hydroxide, and then over calcium hydride. The i.r. spectrum was identical in all respects with that of the starting material.

The borazocine does not decompose on melting, and so the molecular depression constant was determined as for the t-butyl compound, but with pre-melting. The value was  $15.5 \pm 0.5$  in the concentration range  $6\text{—}18 \times 10^{-3}$  mole/100 g. solvent.

*Tetra-B-chlorotetrakis-N-1',1',3',3'-trimethylbutylborazocine.*—Prepared by method (b) from 2-amino-2,4-dimethylpentane (0.253 mole). Triethylammonium chloride (56 g., 0.405 mole, 1.60 mol.) was precipitated; evaporation of the filtrate gave a semi-solid mass (38 g.). This was treated with warm water to give the crude borazocine (8.5 g., 22%), m. p. 101°. It separated from acetone (8 ml./g.) as colourless crystals, and was recrystallised from isobutyronitrile (20 ml./g.).

The liquors from the hydrolysis of the crude product were made alkaline, and the amine distilled out as the azeotrope with water; after drying, it had b. p. 119—120°. This product, the original amine, and amine obtained by hydrolysis of the borazocine had identical i.r. spectra.

*Tetra-B-chlorotetrakis-N-1',1',3',3'-tetramethylbutylborazocine.*—Prepared by method (a) from commercial t-octylamine (2-amino-2,4,4-trimethylpentane) (0.233 mole). Triethylammonium chloride was precipitated. The filtrate was evaporated to dryness and the residue treated with water, giving the crude borazocine (11.8 g., 18%), which was purified by crystallisation from light petroleum (b. p. 100—120°; 8 ml./g.) followed by isobutyronitrile (102 ml./g.). It formed colourless needles.

The borazocine (0.75 g.) was hydrolysed by heating with 2.5N-sodium hydroxide in a sealed tube at 200° for 16 hr. The organic layer was separated and dried. It was shown to be very pure 2,4,4-trimethylpent-1-ene by comparison of the i.r. spectrum with that of an authentic sample.

*Tetra-B-bromotetrakis-N-1',1',3',3'-tetramethylbutylborazocine.*—Prepared by method (a) from



commercial t-octylamine (2-amino-2,4,4-trimethylpentane) (26.0 g., 0.20 mole) using boron tribromide (51 g., 0.201 mole) in toluene (70 ml.). The crude borazocine (4.3 g.) was isolated by treating the reaction product with water. Continuous extraction of this product for 48 hr. with light petroleum gave an insoluble residue (2.05 g.; largely boric acid) and a soluble fraction (1.95 g., 4.5%). It was obtained as colourless needles by crystallising from n-butyl acetate (6 ml./g.) or isobutyronitrile (75 ml./g.).

*Attempted Preparation of Tetra-B-iodotetra-N-t-butylborazocine.*—Boron tri-iodide (Light's "ultra-pure"; 11.03 g., 0.028 mole) in toluene (30 ml.) was treated with t-butylamine (3.0 ml., 2.05 g., 0.028 mole) in toluene (20 ml.) under nitrogen at 0°. A heavy white precipitate was deposited (presumed to be the 1 : 1 adduct). Triethylamine (8.00 ml., 5.78 g., 0.0572 mole) in toluene (15 ml.) was added, when two liquid layers separated; on heating, the lower layer was replaced by a precipitate. The mixture was heated under reflux for 1 hr. The precipitate (15.2 g.) was collected; on dissolving in water, an insoluble residue (0.45 g.) remained: it was not identified, but the i.r. spectrum was quite unlike those of the borazocines. The filtrate was evaporated *in vacuo* below 50°: there was only a small residue (0.85 g.), wholly soluble in water.

*Attempt to Prepare Borazocine from 2-Amino-2,3-dimethylbutane.*—The method was as in (b), using boron trichloride (31.12 g., 0.265 mole), 2-amino-2,3-dimethylbutane (26.8 g., 0.265 mole), and triethylamine (54.2 g., 0.536 mole) in toluene (total 400 ml.). Triethylammonium chloride (58.5 g., 0.425 mole; 1.625 mol.) was collected. Evaporation *in vacuo* gave a brown liquid residue (34.6 g.) (Found: C, 48.25; H, 10.0; B, 6.4; Cl, 25.8; N, 10.5%) which dissolved completely in cold water to give a nearly neutral solution. This residue (23 g.) was separated *in vacuo* at 120° into a volatile fraction (14.4 g.), probably consisting of impure borazene  $C_6H_{13}NH \cdot BCl_2$  (Found: C, 40.3; H, 9.5; B, 5.7; Cl, 35.6; N, 7.8. Calc. for  $C_6H_{14}BCl_2N$ : C, 39.6; H, 7.8; B, 6.0; Cl, 39.0; N, 7.7%), and a residue (7.6 g.) [Found: C, 50.0; H, 9.5; B, 7.4; Cl, 19.4; N, 11.7%; *M* (cryoscopic), 522. Calc. for  $C_{24}H_{54}B_3Cl_3N_4$ : C, 53.6; H, 10.5; B, 6.05; Cl, 19.8; N, 10.4%; *M*, 537] probably consisting mainly of the boronamine  $RNH \cdot BCl \cdot NR \cdot BCl \cdot NR \cdot BCl \cdot NHR$ , where  $R = C_6H_{13}$ . There was no evidence for the formation of borazole or borazocine.

*Attempt to Prepare Borazocine from 3-Amino-3-methylpentane.*—This was done as in the previous preparation on a 0.198-molar scale; triethylammonium chloride (1.58 mol.) was obtained. The crude reaction product after evaporation of solvent was completely soluble in water. In further working up neither borazole nor borazocine was isolated.

*Tetra-N-perdeutero-t-butylborazocines.*—*t*-[ $^2H_9$ ]Butyl chloride. Deuterium oxide (99.83 atoms %; 20.0 g., 1.00 mole) was stirred vigorously at room temperature while purified thionyl chloride (9.50 ml., 0.132 mole) was introduced below the surface through a fine capillary. The introduction required about  $\frac{1}{2}$  hr. and reaction was complete in another  $\frac{1}{2}$  hr. The product (27.3 g.), containing approximately 0.25 g.-equiv. of  $^2HCl$  and contaminated with sulphur dioxide (1.75 g.), which it was unnecessary to remove, was shaken in a sealed flask at 30° for 159 hr. with redistilled t-butyl chloride (19.5 g., 0.211 mole). The t-butyl chloride was separated, washed once with brine and twice with saturated sodium hydrogen carbonate solution, and dried ( $K_2CO_3$ ): yield, 18.89 g. The product was equilibrated in the same way with deuteriochloric acid from 20 g.  $D_2O$  for 21 days, then with acid from 40 g.  $D_2O$  for 25 days and finally with acid from 40 g.  $D_2O$  for 52 days. The product (11.46 g., 0.113 mole, 53.5%) had, on the basis of the area below the C-H stretching bands, a residual  $^1H$  content of ~3%. The mass spectrum (measured at the Research Laboratories of the British Petroleum Company) showed  $C_4^2H_9Cl$ , 80%;  $C_4^1H^2H_8 \cdot Cl$ , 15%;  $C_4^1H_2^2H_7 \cdot Cl$ , 5%;  $C_4^1H_3^2H_6 \cdot Cl$ , <2%; corresponding to about 3 atoms %  $^1H$  in the sample. A gas-chromatographic examination of the sample with silicone grease, Apiezon L grease, and "Tween 80" stationary phases, in conditions under which the isomeric butyl chlorides were separated, showed no detectable impurity (upper limit 0.5%).

*Tri*[ $^2H_3$ ]methylacetamide.—A Grignard reagent was prepared under nitrogen from the perdeutero-t-butyl chloride (10.66 g., 0.105 mole) and iodine-activated magnesium turnings (3.20 g., 0.132 g.-atom) in tetrahydrofuran (140 ml.) that had been distilled from lithium aluminium hydride. With the solution initially at 4°, dry carbon dioxide was passed in with vigorous stirring; the temperature rose to 30°. The reaction mixture was decomposed with 2*N*-sulphuric acid; the organic layer was separated, and the aqueous layer extracted with ether. The acid was extracted from the combined organic solutions into 2*N*-sodium hydroxide. This alkaline solution was repeatedly extracted with ether and isopentane, then acidified, and the



acid extracted with isopentane. The acid (9.035 g., 0.081 mole; 77.5%) was obtained by distillation, b. p. 95—97°/63—64 mm., and solidified on keeping. (Neutralisation Equiv. 109.0. Calc. 111.1.) The acid (8.88 g., 0.080 mole) and redistilled phthaloyl chloride (25.0 ml.) were distilled with stirring at atmospheric pressure. The crude chloride was collected at 101—103°; redistillation gave 8.53 g. (82% from the acid), b. p. 103—104°/763 mm. The chloride (8.12 g.; 0.063 mole) was converted into the amide by passing ammonia over a stirred ethereal solution. The amide (6.75 g., 0.062 mole), m. p. 157—158.5°, was extracted from the mixture with acetone. The overall yield of amide from the butyl chloride was 61%.

$[^2\text{H}_9]$ -*t*-butyl $[^1\text{H}_2]$ amine.—Chlorine was passed into ice-cold 10% sodium hydroxide solution to give a 0.57N-hypochlorite solution. This solution (228 ml., 0.130 g.-equiv.) was stirred at 0°, and the amide (6.70 g., 0.061 mole) added. After 2 hr. at 0°, the solution was warmed during 2 hr. to room temperature; the amine was then distilled through a short Vigreux column as the azeotrope into 25.0 ml. 2.5N-sulphuric acid (yield, by back titration, 80%). This solution was treated with sodium chloride (10 g.) and saturated potassium hydroxide solution (25 ml.) and the amine distilled as before, with the minimum of water, on to saturated potassium hydroxide solution (15 ml.) The amine was pumped *in vacuo* from this mixture through columns of potassium hydroxide pellets and calcium hydride (16 mesh) into a trap at -80°. After further drying over calcium hydride (vacuum techniques) the anhydrous amine (4.015 g., 0.0488 mole) was obtained (80% from the amide). The overall yield from the deuterio-*t*-butyl chloride was 48%.

The purity of the amine was examined by gas chromatography on a Perkin-Elmer Fractometer, Model 451, using a "W" column [poly(ethylene glycol) on polytetrafluoroethylene]. Under conditions allowing a clear-cut separation of all the isomeric butylamines the deuterio-compound showed only a single peak: the estimated upper limit of separable impurities was 0.5%.

Tetra-B-halogenotetra-N- $[^2\text{H}_9]$ -*t*-butylborazocines.—Method B was adopted for the ~0.025-molar scale using vacuum techniques<sup>68</sup> for the measurement and transference of the reactants. Two runs for the preparation of the chloro- and bromo-compounds, on the scale of 0.0182 and 0.0175 mole, respectively, gave yields of 51% and 34%. The reaction mixtures were worked up by method (a), and unreacted amine was recovered from the aqueous liquors. In another run, the pure amine (0.012 mole) was combined with this recovered amine to give 61% of the B-chloroborazocine, and in a final run amine recovered from this run (containing much triethylamine) was also converted into chloroborazocine. Overall, the amine (0.0479 mole) gave borazocine (0.0087 mole) a conversion of 73%. The crude borazocine was in both cases purified by solution in isopentane, filtration, and evaporation. Tetra-B-chlorotetra-N- $[^2\text{H}_9]$ -*t*-butylborazocine was sublimed *in vacuo* and formed colourless crystals, m. p. 248—252° from acetone. The second batch had the same m. p. but was pale yellow, and solutions were sufficiently fluorescent to interfere with the measurement of the Raman spectrum. The fluorescent substance was removed by percolation of a solution in carbon disulphide through a column of activated charcoal. Tetra-B-bromotetra-N- $[^2\text{H}_9]$ -*t*-butylborazocine was recrystallised from acetonitrile giving white needles, m. p. 237—238.5°. An examination of the i.r. spectra of these compounds suggested that there had been no loss of deuterium during the preparation.

Treatment of Tetra-B-chlorotetra-N-*t*-butylborazocine.—(a) *With methylmagnesium bromide.* Methylmagnesium bromide solution was prepared from magnesium turnings (2.4 g.; 0.099 g.-atom) and methyl bromide (50 ml. of a 2.5M-solution in ethyl ether) in ether (50 ml.). The borazocine (4.69 g., 0.010 mole) was added, and the solution was heated under reflux for 24 hr., after which it was chilled and treated with ammonium chloride (13 g.) in water (100 ml.). The ether layer was separated, and the aqueous layer further extracted; the combined ether extracts were washed, dried, and evaporated. The residue, a white solid (4.57 g.) was unchanged borazocine.

(b) *With methyl-lithium.* A 1.5M-solution of methyl-lithium in ethyl ether was prepared according to Gilman *et al.*<sup>69</sup> from a lithium dispersion (Foote Mineral Company). The borazocine (4.69 g., 0.010 mole) and the methyl-lithium solution (40 ml., 0.060 mole) were heated under nitrogen in a sealed tube at 75° for 40 hr. and at 100° for 190 hr. The tube was cooled to -80° and opened. There was considerable pressure (methane?), and part of the contents was lost in a minor explosion. The remaining product was transferred with ether and

<sup>68</sup> Cf., e.g., H. S. Turner and R. J. Warne, *J.*, 1953, 789.

<sup>69</sup> H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Amer. Chem. Soc.*, 1933, 55, 1252.

evaporated to give a white solid (8.66 g.), which separated from its solution in dimethoxyethane in heavy, sticky, white crystals (Found: C, 30.7; H, 6.8; B, 2.0; Cl, 0.5; I, 39.8; Li, 2.2; N, 2.5%). No unchanged borazocine nor any recognisable borazocine derivative was isolated.

(c) *With n-butyl-lithium.* The borazocine (4.69 g., 0.010 mole) and butyl-lithium (2.15M in n-heptane; Foote Mineral Company; 25 ml., 0.054 mole) were heated in a sealed tube in the absence of air at 105° for 18 hr. On opening, the product was filtered, giving a white solid and a light brown filtrate. The solid reacted vigorously with water, giving a strongly alkaline solution containing 0.048 g.-equiv. OH<sup>-</sup> and 0.006 g.-equiv. Cl<sup>-</sup>. The filtrate on evaporation gave unchanged borazocine, slightly impure (4.35 g.). There was no evidence for the formation of *B*-butylborazocine.

(d) *With sodium borohydride.* The borazocine (4.69 g., 0.01 mole) and sodium borohydride (2.27 g., 0.060 mole) in diethylene glycol dimethyl ether (25 ml.) were stirred under nitrogen; the temperature was raised to 100° during 3 hr. and kept at 100° for 22 hr. The solvent was distilled off *in vacuo*, and the residual white solid was extracted with light petroleum (b. p. 60–80°). The insoluble material was substantially sodium borohydride, containing 0.0028 g.-equiv. Cl<sup>-</sup> (7% of that in the original borazocine). The soluble fraction was recovered by evaporation as a white solid (4.43 g.): this was unchanged borazocine; the i.r. spectrum showed no trace of B–H absorption in the 2500-cm.<sup>-1</sup> region.

(e) *With lithium borohydride.* The borazocine (1.10 g., 0.00234 mole) and lithium borohydride (0.256 g., 0.01175 mole) in dimethoxyethane (12 ml.) were heated under reflux under nitrogen for 5½ hr., cooled, and filtered. The small solid residue contained 0.00045 g.-equiv. Cl<sup>-</sup> (~5% of that in the original borazocine). The filtrate was evaporated *in vacuo*, and the residue sublimed at 135°/0.03 mm. for 8 hr. to give 1.06 g. slightly impure borazocine, m. p. 236–243°. The i.r. spectrum showed no B–H absorption in the 2500-cm.<sup>-1</sup> region.

*Action of Diazomethane on Tetra-B-chlorotetra-N-t-butylborazocine.*—To a dry ethereal solution of diazomethane (180 ml. containing 0.155 mole CH<sub>2</sub>N<sub>2</sub>)<sup>70</sup> at –10° was added a filtered solution of the borazocine (9.38 g., 0.020 mole) in ether (150 ml.) during ½ hr. There was no visible reaction; the mixture was kept at *ca.* –5° for 2 hr., and then allowed to warm to room temperature. The yellow colour of the diazomethane slowly faded until, after 4 days, the solution was colourless, with little or no suspended solid, although some polymethylene had formed on ground surfaces above the liquid. Evaporation of the solution gave the borazocine (9.40 g.) identical (m. p., i.r. spectrum) with the starting material.

*Reaction of Tetra-B-chlorotetra-N-t-butylborazocine with Amines.*—(a) *Methylamine.* The borazocine (4.69 g., 0.010 mole) and dry methylamine (4.0 ml. at –80°; 0.1 mole) in isopentane (15 ml.) were heated in a sealed tube in the absence of air at 100° for 16 hr. The tube was cooled and opened; after warming to room temperature, during which excess of methylamine boiled off, the product was filtered to remove methylammonium chloride, identified by its i.r. spectrum (0.0184 mole by titration, corresponding to 46% replacement). Evaporation of the filtrate gave a product (3.83 g.) which crystallised from light petroleum (b. p. 40–60°; 7 ml.) as a white solid (0.34 g.), m. p. 187–189°. The liquors on evaporation gave a white solid (0.63 g.), m. p. 193–194° [Found: C, 45.9; H, 7.8; B, 9.1; Cl, 19.0; N, 18.4%; *M* (cryoscopic), 465. Calc. for C<sub>18</sub>H<sub>44</sub>B<sub>4</sub>Cl<sub>2</sub>N<sub>6</sub>: C, 47.1; H, 9.6; B, 9.35; Cl, 15.5; N, 18.4%; *M*, 458]. The two products had virtually identical i.r. spectra: these were consistent with partial substitution of chlorine by methylamino-groups. A sharp N–H stretching band was present at 3480 cm.<sup>-1</sup>.

In another run, the borazocine (7.50 g., 0.016 mole), methylamine (3.25 ml. at –80°; 0.0805 mole), ethyldi-isopropylamine (13.8 ml., 0.080 mole) and benzene (20 ml.) were heated in a sealed tube at 108° for 144 hr. The product was filtered to remove a crystalline mixture (3.20 g.) of methylammonium chloride and ethyldi-isopropylammonium chloride (containing 0.0493 g.-equiv. of Cl<sup>-</sup>, corresponding to 77% replacement), and the filtrate was evaporated to give a pale yellow semi-solid mass (5.54 g.), readily and completely soluble in isopentane (Found: C, 46.4; H, 9.6; B, 10.7; Cl, 7.8; N, 26.7%). The i.r. spectrum was much more diffuse; the N–H stretching band had not shifted, but was broader and weaker.

(b) *Ethylamine.* The borazocine (5.15 g., 0.011 mole), ethylamine (25 ml. of a 1.92M-solution in benzene, 0.048 mole) and ethyldi-isopropylamine (8.25 ml., 0.048 mole) were heated in a sealed tube at 108° for 144 hr. The mixed amine hydrochlorides (Cl<sup>-</sup> content 0.02675 g.-equiv., corresponding to 61% replacement) were filtered off, and the filtrate evaporated to give

<sup>70</sup> *Org. Synth.*, 1935, 15, 3.

a yellow oil (4.58 g.) (Found: C, 46.4; H, 10.0; B, 9.65; Cl, 12.6; N, 21.3. Calc. for  $C_{20}H_{48}B_4Cl_2N_6$ : C, 49.3; H, 9.9; B, 8.9; Cl, 14.6; N, 17.25%).

*Tetra-B-isocyanatotetra-N-t-butylborazocine*.—Tetra-*B*-chlorotetra-*N*-*t*-butylborazocine (4.705 g., 0.010 mole) and finely powdered potassium cyanate<sup>71</sup> (4.075 g., 0.051 mole) in dimethyl sulphoxide (125 ml.) were heated at 70–75° with stirring for 24 hr.; the solvent was removed under reduced pressure below 70°. The residual yellowish solid (8.85 g.) was continuously extracted with benzene. The insoluble residue contained 0.038 g.-equiv. of Cl<sup>-</sup>; the extract, on evaporation, gave a white solid (4.8 g.). Crystallisation from acetonitrile gave 2.35 g. of the *borazocine*, a white solid, m. p. 236.5–237° [Found: C, 48.1; H, 7.4; B, 9.4; N, 22.6%; *M* (cryoscopic), 485.  $C_{20}H_{36}B_4N_8O_4$  requires C, 48.4; H, 7.3; B, 8.75; N, 22.6; *M*, 495]. Some samples of the tetraisocyanate do not melt if heated slowly from room temperature. The i.r. spectrum of the tetraisocyanate was measured on a Grubb-Parsons GS-3 spectrometer at a concentration of 0.0378N in carbon tetrachloride. The cell path was 0.0105 cm. (determined by the fringe technique) and the slit width 3 cm.<sup>-1</sup>; the extinction coefficient *vs* wave-number curve was integrated with a planimeter between 2170 and 2380 cm.<sup>-1</sup>. The NCO band at 2278 cm.<sup>-1</sup> had an apparent molar extinction coefficient of 1375, a half-band width of 40 cm.<sup>-1</sup> and an integrated intensity of  $14.9 \times 10^4$ . A complete i.r. spectrum is reproduced on DMS Card No. 9519.

*Tetra-B-isothiocyantetra-N-t-butylborazocine*.—Tetra-*B*-chlorotetra-*N*-*t*-butylborazocine (20.0 g., 0.0426 mole) and potassium thiocyanate (technical; 21.90 g., ~0.21 mole) were heated under reflux in 240 ml. dry acetone for 16 hr. A white solid separated from the originally clear solution. The solvent was distilled off, and the solid product extracted with cyclohexane to give 21.6 g. (91%) of crude isothiocyanate, m. p. 226–236°. Recrystallisation from dimethoxyethane then *n*-butyl acetate gave the *borazocine* as colourless crystals, m. p. 291° [Found: C, 43.2; H, 6.6; B, 7.5; N, 19.7; S, 23.0%; *M* (ebullioscopic), 536.  $C_{20}H_{36}B_4N_8S_4$  requires C, 42.9; H, 6.5; B, 7.7; N, 20.0; S, 22.9%; *M*, 559.2].

*Tetra-B-isothiocyantetra-N-[<sup>2</sup>H<sub>9</sub>]-t-butylborazocine* was prepared in the same manner on the 0.001-molar scale. The crude product (0.585 g., 98%) gave, on crystallisation from dimethoxyethane then *n*-butyl acetate, 0.38 g. (64%) of the pure *borazocine*, m. p. 288°.

Tetra-*B*-chlorotetra-*N*-*t*-butylborazocine (2.35 g., 0.005 mole) and potassium thiocyanate (technical; 3.07 g., ~0.031 mole) in dry dimethoxyethane (75 ml.) were shaken at room temperature for 8½ days. The precipitate was collected; it contained the tetraisothiocyanate (1.28 g., 0.0023 mole) and potassium chloride (0.015 g.-equiv.). During another 5 days more tetraisothiocyanate (0.29 g., 0.005 mole) and potassium chloride (0.0026 g.-equiv.) deposited. Evaporation of the filtrate gave a solid, which on leaching with water gave a mixture (1.16 g.) of the tetraisothiocyanate and unchanged chloroborazocine (~3 : 1).

The i.r. spectrum of the tetraisothiocyanate was recorded at a concentration of 0.0534N in carbon tetrachloride. The cell path of 0.00863 cm. was determined by the fringe technique, and a slit width of 3 cm.<sup>-1</sup> was used; the extinction coefficient *vs* wave-number curve was integrated with a planimeter between 1990 and 2160 cm.<sup>-1</sup>. The NCS band at 2078 cm.<sup>-1</sup> had an apparent molar extinction coefficient of 1560, a half-width of 42 cm.<sup>-1</sup> and an integrated intensity of  $17.6 \times 10^4$ . A complete i.r. spectrum is recorded on DMS Card No. 9518. The corresponding figures taken from the i.r. spectrum of tri-*B*-isothiocyantoborazocine (Dr. M. F. Lappert, personal communication) were 2088 cm.<sup>-1</sup>; 1787; 54 cm.<sup>-1</sup>;  $23.2 \times 10^4$ .

*Attempted Partial Replacement of Chlorine in Tetra-B-chlorotetra-N-t-butylborazocine by Isothiocyanate*.—(a) The *borazocine* (12.00 g., 0.0255 mole) in acetone (500 ml.) was stirred vigorously under gentle reflux while potassium thiocyanate (5.00 g., 0.0513 mole) in acetone (250 ml.) was added as uniformly as possible during 4 hr.; refluxing was thereafter continued for another 36 hr. The mixture was then evaporated and extracted as before, giving 12.1 g. of *product* (Found: Cl, 12.9; S, 12.6.  $C_{18}H_{36}B_4Cl_2N_6S_2$  requires Cl, 13.75; S, 12.4%); the cyclohexane-insoluble fraction from the extraction contained 0.049 g.-equiv. of Cl<sup>-</sup> and 0.002 g.-equiv. of NCS<sup>-</sup>. The organic material (11.3 g.) was crystallised from light petroleum (b. p. 60–80°; 150 ml.), and further fractions obtained by evaporation. Thus were obtained fractions (A) (3.8 g.) (Found: Cl, 0.95; S, 22.54%); (B) (0.6 g.) (Found: Cl, 1.0; S, 23.27%); (C) (0.47 g.) (Found: Cl, 3.3; S, 22.8%); (D) (0.15 g.) (Found: S, 16.3%) and (E), obtained by evaporating the final concentrate to dryness (5.76 g.) (Found: Cl, 24.0; S, 4.04%). With the possible exception of (D), these fractions behaved either as the tetraisothiocyanate (Calc.

<sup>71</sup> *Inorg. Synth.*, 1946, 2, 86.

S, 22.9%) contaminated with tetrachloro-compound (Calc. Cl, 30.2%) or *vice versa* and the i.r. spectra were consistent with this view. The i.r. spectrum of (D) was compared with that of an artificial mixture of the same overall composition: the spectra were almost superimposable (see Figure 4; Table 8 contains a list of the absorption bands). On the other hand, a mass-spectrometric analysis of (E) (carried out at the Research Laboratories of the British Petroleum Company Ltd.) showed the presence of all the possible products of partial substitution, and the artificial mixture of the same elemental composition behaved as such under the same conditions.

TABLE 8

Infrared absorptions of (i), a fraction of the product of attempted partial substitution of Cl by NCS in tetra-*B*-chlorotetra-*N*-*t*-butylborazocine, and (ii), a mixture of tetrachloro- and tetraisothiocyanato-borazocines of the same elemental composition

Fraction (D)	Artificial mixture	Fraction (D)	Artificial mixture	Fraction (D)	Artificial mixture	Fraction (D)	Artificial mixture
2975m	2975m	1420s	1420s	1142w	1144m	775w	776w
2935w	2935w	1391vs	1390vs	1104vw	1098w	753m	754m
2915sh	2915sh	1368s	1368vs	1023w	1024w	681w	681w
2870w	2870w	1271m	1268m	1008w	1007w	653vw	653vw
2080vs	2080vs	1247sh		894vw	893vw	611m	611m
1479w	1479w	1226w	1227w	865w	864w	580w	580w
1467w	1467w	1194s	1193s				

(b) In another experiment  $(\text{Bu}^t\text{NCl})_4$  (12.21 g., 0.026 mole) and potassium thiocyanate (5.05 g., 0.052 mole) were dissolved in dimethoxyethane (300 ml.) at room temperature. The clear solution was shaken at 30° for 13 days, and then evaporated *in vacuo* to give an orange solid (17.45 g.). Extraction of this (17.2 g.) with light petroleum (b. p. 60–80°) gave on evaporation a yellow solid (A) (13.3 g.) (Found: C, 44.2; H, 7.8; Cl, 17.6; N, 15.5; S, 11.8%); the insoluble solid contained 0.045 g.-equiv. of  $\text{Cl}^-$ . (A) (10.0 g.) was refluxed with acetone (42 ml.) and filtered. The insoluble matter (3.5 g.), when crystallised from toluene (15 ml.), gave white crystals (2.57 g.) of slightly impure tetraisothiocyanate, m. p. 265–268° (Found: Cl, 0.4; S, 21.8%) and a more soluble fraction (0.60 g.) (Found: Cl, 4.5; S, 20.3%). The acetone solution crystallised on cooling to give a little, slightly contaminated, tetraisothiocyanate (0.46 g.) (Found: Cl, 1.8; S, 21.0%); the filtrate on evaporation gave impure  $(\text{Bu}^t\text{NCl})_4$  (5.58 g.), m. p. 180–192° (Found: Cl, 25.1; S, 3.36%). This fraction (5 g.) on crystallisation from acetone (9 ml.) gave  $(\text{Bu}^t\text{NCl})_4$  (1.75 g.), m. p. 243–246° (Found: Cl, 30.7; S, 0.0%); the mother-liquors on evaporation to dryness and recrystallisation from acetone (5.5 ml.) gave crystals (1.16 g.) (Found: Cl, 28.6; S, 3.2%) and solid recovered from the liquors (1.56 g.) (Found: Cl, 21.9; S, 6.7%).

*Tetra-B-isothiocyanatotetrakis-N-1',1'-dimethylpropylborazocine.*—The *B*-chloroborazocine (7.01 g., 0.0133 mole) and potassium thiocyanate (6.73 g., 0.067 mole) were heated under reflux in acetone (330 ml.) for 54 hr. The inorganic fraction contained 0.028 g.-equiv. of  $\text{Cl}^-$  and 0.039 g.-equiv. of  $\text{SCN}^-$ ; the organic product (6.99 g.), separated as for the *t*-butyl compound, had m. p. 115–160° decomp. (Found: Cl, 11.8; S, 11.6%). Further treatment with potassium thiocyanate in acetone gave a product (Cl, 1.15; S, 19.7%) which from ethyl acetate gave the colourless *tetraisothiocyanate*, m. p. 245.5: (Found: C, 46.7; H, 7.25; B, 6.5; Cl, <0.1; N, 19.0; S, 21.5.  $\text{C}_{24}\text{H}_{44}\text{B}_4\text{N}_8\text{S}_4$  requires C, 46.8; H, 7.14; B, 7.03; Cl, 0.0; N, 18.2; S, 20.9%).

*Action of Raney Nickel upon Tetra-B-isothiocyanatotetra-N-t-butylborazocine.*—The borazocine (0.10 g., 0.00018 mole) in methanol was heated under reflux for 5 hr. with freshly prepared Raney nickel<sup>72</sup> (1.0 g.). The suspension was filtered, and the filtrate evaporated. There was no residue, but the distillate contained amine (0.0009 g.-equiv. by titration).

*Tetra-B-isoselenocyanatotetra-N-t-butylborazocine.*—Tetra-*B*-chlorotetra-*N*-*t*-butylborazocine (4.20 g., 0.00895 mole) and potassium selenocyanate (7.82 g., 0.054 g.-equiv., 50% excess) were heated under reflux and stirred in dry acetone (50 ml.) for 5 hr. The initially clear solution soon became opalescent, and potassium chloride was deposited. After evaporating to dryness, the grey solid (11.8 g.) was continuously extracted with light petroleum (b. p. 40–60°); the extract gave on evaporation the crude product (3.48 g.), which, on crystallisation from benzene (15 ml./g.), gave colourless crystals of the *tetraisoselenocyanate*, decomposing with blackening at

<sup>72</sup> *Org. Synth.*, 1941, **21**, 15.



296° [Found: C, 32.4; H, 4.9; B, 6.3; N, 15.1; Se, 40.0; *M* (Mechrolab Osmometer), 720.  $C_{20}H_{36}B_4N_8Se_4$  requires C, 32.1; H, 4.8; B, 5.8; N, 15.0; Se, 42.3%; *M*, 747]. The i.r. spectrum is reproduced on DMS Card No. 9521.

*Tetra-B-azidotetra-N-t-butylborazocine*.—Tetra-*B*-chlorotetra-*N-t*-butylborazocine (4.696 g., 0.010 mole) and sodium azide (commercial: 3.25 g., 0.050 mole) in dry dimethyl sulphoxide (100 ml.) were stirred under nitrogen. The temperature was raised from the initial 50° to 75° during 4 hr. and kept at 75° for a further 19 hr. The solvent was removed *in vacuo* (bath below 60°), and the residue extracted with water; the water-insoluble matter (4.83 g.) was crystallised twice from light petroleum (b. p. 100–120°; 7 ml./g.) to give white crystals of the *tetra-azide*, m. p. 275–276° [Found: C, 39.2; H, 7.0; B, 8.5; Cl, <0.1; N, 45.9%; *M* (Mechrolab Osmometer), 500.  $C_{16}H_{36}B_4N_{16}$  requires C, 38.8; H, 7.3; B, 8.7; Cl, 0.0; N, 45.3%; *M*, 496]. The compound was insensitive to percussion or rubbing; it sublimed *in vacuo* at 160° without decomposition.

A solution of the tetra-azide (8.7 mg./l.;  $7.04 \times 10^{-5}N$ ) in *n*-hexane showed an intense absorption at 228.5  $m\mu$  ( $\log \epsilon$  3.68 referred to the monomeric unit  $Bu^tNBN_3$ ). A sample of ethyl azide (0.8 g./l.;  $1.1 \times 10^{-2}N$ ) had an absorption maximum at 289  $m\mu$  ( $\log \epsilon$  1.3). A complete i.r. spectrum of the tetra-azide is reproduced on DMS Card No. 9520.

Tetra-*B*-azidotetra-*N*-[ $^2H_9$ ]t-butylborazocine was prepared similarly from tetra-*B*-bromotetra-*N-t*-[ $^2H_9$ ]butylborazocine (0.00075 mole). It was crystallised from light petroleum (b. p. 60–80°) then acetonitrile-*n*-butyl acetate, m. p. 270–272°.

*Attempted Partial Replacement of Chlorine by Azide*.—Tetra-*B*-chlorotetra-*N-t*-butylborazocine (11.75 g., 0.025 mole) in dimethoxyethane (250 ml.) was treated with a solution of sodium azide (3.27 g., 0.050 mole) in dry redistilled dimethyl sulphoxide, and the mixture shaken under nitrogen for 12 days at 30°. Removal of the solvent *in vacuo* gave a residue (13.4 g.), from which by extraction with light petroleum (b. p. 60–80°) a white solid (11.0 g.) was obtained (Found: C, 41.6; H, 8.1; B, 8.1; Cl, 10.8; N, 29.0%). This product (8.5 g.) when crystallised from light petroleum (b. p. 60–80°; 11 ml.) gave white crystals (1.05 g.) (Found: C, 39.6; H, 7.8; B, 9.1; Cl, 5.8; N, 37.5%) and a white solid was recovered from the liquors (7.32 g.) (Found: C, 41.5; H, 8.3; B, 8.5; Cl, 11.8; N, 27.8%). The former (0.75 g.) by crystallisation from acetonitrile (30 ml.) gave fractions (in order of increasing solubility): (A), (0.3 g.), m. p. 273–275° (Found: C, 39.5; H, 7.5; B, 8.7; Cl, 3.2; N, 40.5%); (B) (0.28 g.), m. p. 273–276° (Found: C, 39.7; H, 7.7; B, 8.3; Cl, 6.8; N, 39.7%); and (C) (0.18 g.), m. p. 200° (Found: C, 40.9; H, 7.9; B, 9.1; Cl, 10.2; N, 30.7%).

The latter product (5.74 g.) was similarly separated into fractions: (D) (0.35 g.), m. p. 234–238° (Found: C, 38.5; H, 7.8; B, 7.5; Cl, 10.1; N, 28.2%); (E) (1.89 g.), m. p. 249–254° (Found: C, 41.1; H, 7.8; B, 9.5; Cl, 10.5; N, 33.1%); and (F) (2.5 g.) m. p. 168–171° (Found: C, 41.6; H, 8.1; B, 9.2; Cl, 12.4; N, 23.9%). None of these products corresponds to a definite product of intermediate substitution (see Table 9): moreover the tendency found with the isothiocyanate partial substitution products to separate on crystallisation into pure  $(Bu^tNBCl)_4$  and pure tetrasubstitution product is absent.

TABLE 9  
Required (%) analysis figures for azidochloroborazocines

	C	H	B	Cl	N
$(Bu^tNB)_4Cl_2N_3$ .....	40.4	7.6	9.05	22.4	20.6
$(Bu^tNB)_4Cl_2(N_3)_2$ .....	39.8	7.5	8.95	14.7	29.0
$(Bu^tNB)_4Cl(N_3)_3$ .....	39.3	7.4	8.8	7.3	37.2

A product from another preparation with a composition (Found: C, 39.8; H, 7.4; B, 8.8; Cl, 10.1; N, 33.6%) corresponding approximately to  $(Bu^tNB)_4Cl_{1.5}(N_3)_{2.5}$  was examined mass-spectrometrically at the Research Laboratories of the British Petroleum Company Ltd. The pure tetra-azido-compound, examined as a standard, did not exhibit a parent peak, but the cracking pattern was analogous to that of  $(Bu^tNBCl)_4$  and  $(Bu^tBNCS)_4$ . On the basis of the heights of the peak having *m/e* corresponding to the parent minus 15, the composition was estimated at:  $(Bu^tNBN_3)_4$ , 45%;  $(Bu^tNB)_4Cl(N_3)_3$ , 20%;  $(Bu^tNB)_4Cl_2(N_3)_2$ , 20%;  $(Bu^tNB)_4Cl_3N_3$ , 5%;  $(Bu^tNBCl)_4$ , 10%; corresponding to  $(Bu^tNB)_4Cl_{1.2}(N_3)_{2.8}$ . The i.r. spectrum of the same sample (Figure 5 and Table 10) was different from that of a mixture of  $(Bu^tNBCl)_4$  and  $(Bu^tNBN_3)_4$  of the same overall elemental composition.



TABLE 10

Infrared absorptions of (i), a product of attempted partial substitution of Cl by N<sub>3</sub> in tetra-*B*-chlorotetra-*N*-*t*-butylborazocine, and (ii), a mixture of tetrachloro- and tetra-azido-borazocines of the same elemental composition

Sample	Artificial mixture	Sample	Artificial mixture	Sample	Artificial mixture	Sample	Artificial mixture
2975m	2980m	1396vs	1397vs	1112w	1140m	825vw	820vw
2940w	2940w	1370sh	1370sh		1095w	781sh	785w
2915sh	2915w	1362vs	1365vs	1022w	1024w	774w	757w
2870sh	2880sh	1330s	1330s	944vw	948w	740vw	730vw
	2175sh	1260m	1266m		925sh	923vw	719vw
2135vs	2137vs	1220vw	1220vw	908w	894w	666vw	680vw
1475w	1478w	1186s	1185s		880sh	630vw	632vw
1460w	1460w	1160sh	1164sh	869w	865sh	598w	604w
						581w	581w

*Unsuccessful Metatheses on Tetra-B-chlorotetra-N-t-butylborazocine.*—(1) *Replacement of chlorine by iodine.* There was no reaction between the chloroborazocine and potassium iodide under reflux in acetone solution. The original chloro-compound was recovered quantitatively in pure condition (m. p. and i.r. spectrum).

(2) *Replacement of chlorine by cyano.* Replacement was attempted by reaction of the chloroborazocine (*a*), with anhydrous lithium cyanide<sup>73</sup> in dimethylformamide at 100°; (*b*), by reaction of potassium cyanide in tetramethylurea at 100°; (*c*), by milling with freshly prepared silver cyanide in acetonitrile at 30° for 28 days; (*d*), by milling with potassium cyanide at 30° for prolonged periods in acetonitrile, dimethylformamide, liquid sulphur dioxide, and dimethyl sulphoxide (in the last case the conditions were the same as those adopted in the successful preparation of the tetrakisocyanate). In no case was any evidence of reaction obtained. In most cases there was an almost quantitative recovery of unchanged chloroborazocine.

*Dipole Moment of Tetra-B-chlorotetra-N-t-butylborazocine.*—Table 11 gives the molarities, weight fractions, dielectric constants, and specific volumes at 20° of solutions of tetra-*B*-chlorotetra-*N*-*t*-butylborazocine in *n*-octane. The *n*-octane was Eastman Kodak practical grade, washed repeatedly with concentrated sulphuric acid, then with water and sodium hydroxide

TABLE 11

[X]	<i>w</i>	$\epsilon$	<i>v</i>	[X]	<i>w</i>	$\epsilon$	<i>v</i>
0.1510	0.097470	1.9763	1.3698	0.0604	0.039917	1.9597	1.4023
0.1208	0.078635	1.9700	1.3810	0.0302	0.020134	1.9537	1.4140
0.0906	0.059431	1.9652	1.3915	0.0000	0.00000	1.9478	1.4260

solution, and finally dried (Na<sub>2</sub>SO<sub>4</sub>) and distilled. It was kept over sodium. The borazocine had m. p. 248°. The dielectric constants of the solutions were determined by Mr. E. Rushton on the apparatus described by Hartshorn, Parry, and Essen.<sup>74</sup> The temperature was controlled to within 0.01°, and measurements were made at 63 c./sec., 1 Kc./sec., and 10 Kc./sec.; within the estimated accuracy of 0.02% the results were identical. The total polarisation was derived by Halverstadt and Kumler's method,<sup>75</sup> except that the actual measured value of the dielectric constant of the solvent was used in the calculations. At this range of concentrations the plots of dielectric constant  $\epsilon_{12}$  and specific volume  $v_{12}$  against the weight fraction  $w_2$  were linear, but in some earlier measurements in *n*-heptane in the range 0.13—0.83M the  $\epsilon_{12}/w_2$  plot was slightly concave towards the  $\epsilon$  axis. The slopes of these straight lines ( $\alpha$  and  $\beta$  in Halverstadt and Kumler's equation) were calculated by the least-squares method, and in this way a value of 133.3 c.c. was obtained for the total molar polarisation (the value derived from the measurements in *n*-heptane was 132.5).

Refractive-index measurements were made by Mrs. B. Aldous on a Guild Watts spectrometer using a 60° hollow prism. Results on the dilute solutions used for measurement of the dielectric constant were unsatisfactory, so a 0.84035M-solution of the borazocine in *n*-octane was measured at 20.0° at six wavelengths between 4047 and 7065 Å. The plot of  $v^2$  against  $R_2$  was a straight

<sup>73</sup> I. H. Johns and H. R. DiPietro, *J. Org. Chem.*, 1964, **29**, 1970.

<sup>74</sup> L. Hartshorn, J. V. L. Parry, and L. Essen, *Proc. Phys. Soc.*, 1955, **68**, B, 422.

<sup>75</sup> I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

line, and by application of the least-squares method a value for  $R_{\infty}$ , the electron polarisation, of 119.8 c.c. was obtained. If it is assumed that this value of the electron polarisation is valid (*i.e.*, that the value obtained from refractive-index measurements on more dilute solutions would be the same) the residual polarisation attributable to atom and orientation polarisation is 13.5 c.c.; if the atom polarisation were zero, this would be equivalent to a dipole moment of 0.78D.

A series of measurements of the loss tangent,  $\tan \delta$ , of solutions of tetra-*B*-chlorotetra-*N*-*t*-butylborazocine in *n*-decane and of the pure solvent were made by Mr. E. Rushton and Dr. G. Williams at 1 Kc./sec. (Shearing bridge); 1 and 100 Mc./sec. (Hartshorn-Ward apparatus); 500, 1000, 1500, 2000, and 3000 Mc./sec. (co-axial slotted-line apparatus<sup>76</sup>); 9000 and 36,000 Mc./sec. (cylindrical-cavity resonator). The *n*-decane was purified as for *n*-octane (above); two concentrations were used, 0.185M and 0.695M; these would be expected to give easily measurable differences of loss tangent,  $\tan \delta_P$  ( $\tan \delta_{12} - \tan \delta_1$ ), for a dipole moment in the range to be expected ( $\leq 0.8$  D). Apart from one spurious result at 1500 Mc./sec. ( $\tan \delta_P$  0.063: over six times that expected on the basis of the maximum possible dipole moment of 0.78 D) which was shown to be due to impurity in one particular solution,  $\tan \delta_P$  was zero within the experimental error over the entire frequency range.

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<sup>76</sup> G. Williams, *J. Phys. Chem.*, 1959, **63**, 534.

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