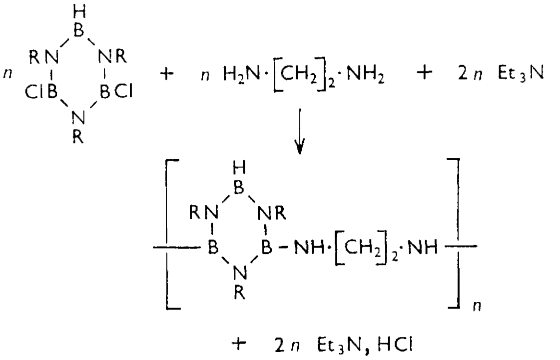
Synthesis and Properties of Linear Polyborazoles. Part I. Condensation of *B*-Dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and Aliphatic Diamines

By J. M. Turner

The linear polymerisation of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole through the aliphatic diamines, ethylene-, trimethylene-, tetramethylene-, and hexamethylene-diamine has been investigated, and certain properties (range and degree of plasticity, stability in air, hydrolytic and thermal stability) of the linear polyborazoles formed have been compared and related to their structure and degree of polymerisation.

Six syntheses of linear polyborazoles have been reported.[1-6] In this work, a difunctional borazole containing a ring of high hydrolytic stability was used so that resulting linear polymers might also be hydrolytically stable. It was also hoped that any linear polyborazoles formed would exhibit higher thermal and oxidative stabilities than carbon polymers and would, therefore, be useful materials at higher temperatures.

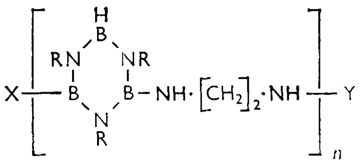
Ethylenediamine was first used as a linking agent. The initial, attempted syntheses were based on equation (1).



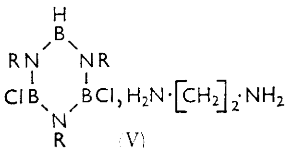
(1)

(R throughout designates a 2,6-dimethylphenyl group)

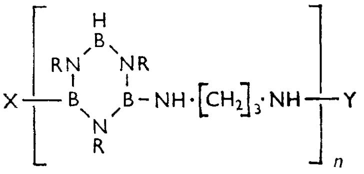
Three experiments were successively carried out in solvents of increasing boiling point (benzene, toluene, and xylene). In benzene, the major borazole product (76·7%) was soluble and solely from its molecular weight of 483 was concluded to be a monomer of structure (I) (M, 485). Some insoluble borazole material, m. p. 285—310°, was also formed. With toluene, the major borazole product (88·8%) was insoluble; it was different from the compound formed in benzene because it did not melt below 360°; its chlorine content was of the same order of magnitude as that of the dichloroborazole. A little soluble borazole material was also formed but was not plastic. Little triethylamine hydrochloride was formed. In xylene, there was a 68·4% yield of insoluble borazole material, m. p. 305—309° (Cl, 0·8%); its melting point signified that it was similar to the small amount of insoluble borazole material formed in benzene, and its low chlorine content that it was different from the insoluble borazole material formed in toluene. The remaining borazole material was soluble and plastic; this was the first plastic material formed in these experiments and was the type of product expected if linear polymerisation had occurred according to equation (1).



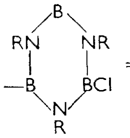
(I) $n = 1$, X = Cl, Y = H
(II) $n = 1$, X = Cl, Y = H,HCl
(III) $n = 3$, X = Cl, Y = H
(IV) $n = 3$—4, X = Cl, Y = H



(V)

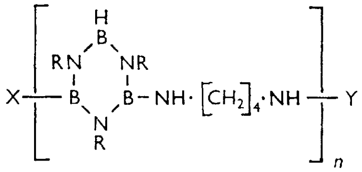


(VI) $n = 1$, X = Cl, Y = H

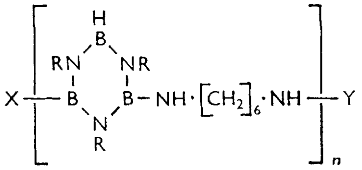


= D here and hereafter

(VII) $n = 3$, X = Cl, Y = H
(VIII) $n = 2$, X = Cl, Y = D
(IX) $n = 1$, X = Cl, Y = H,HCl



(X) $n = 1$, X = Cl, Y = D
(XI) $n = 1$, X = Cl, Y = H,HCl
(XII) $n = 2$, X = Cl, Y = D
(XIII) $n = 1$, X = Cl, Y = D



(XIV) $n = 5·5$, X = Cl, Y = H
(XV) $n = 1$, X = Cl, Y = H,HCl
(XVI) $n = 1$, X = NH·$[CH_2]_6$·NH_2, Y = H,HCl

The insolubility of the borazole products of low chlorine content and high melting point formed in

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[1] C. F. Blakely, Ministry of Aviation Symposium, " Fundamental Research on New Macromolecules," Sept. 1961.

[2] R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, 1962, **1**, 99.

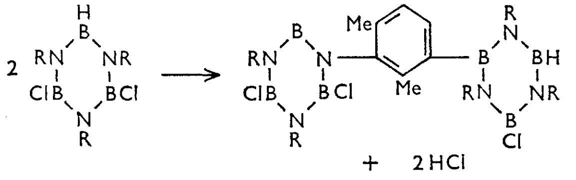
[3] B. M. Mikhailov and A. F. Galkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, No. 4, 641.

[4] V. Gutmann, A. Meller, and R. Schleger, *Monatsh.*, 1963, **94**, 1071.

[5] R. H. Toeniskoetter and K. A. Killip, *J. Amer. Chem. Soc.*, 1964, **86**, 690.

[6] V. V. Korshak, R. M. Oganesyan, and V. A. Zamyatina, *Isvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1964, 362.

benzene and xylene suggested that they were cross-linked or highly branched because strictly linear polyborazoles would be expected to be soluble to a high degree of polymerisation. Consequently, the stability of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole, triethylamine hydrochloride, and *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole in the presence of triethylamine in tetrahydronaphthalene (b. p. 202—205°), and of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole in the presence of triethylamine in xylene was examined. Refluxing was continued for $5\frac{1}{2}$ hours because this was the usual time used in the polymerisation experiments. Triethylamine hydrochloride was stable in boiling tetrahydronaphthalene but *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole suffered a 9·12% reduction in chlorine content through elimination of hydrogen chloride. This loss was greater when triethylamine was present (22%) and greater still when the solvent was xylene (34·7%). The infrared spectrum of the soluble borazole residue from the last control experiment (in xylene) was similar in many respects to that of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole. The main difference was the appearance of new absorption at 800 cm.$^{-1}$ which was assigned to two adjacent free ring-hydrogen atoms. Boron–hydrogen groups were still present. From the infrared evidence, it was thought that hydrogen chloride was lost from *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole as in equation (2).

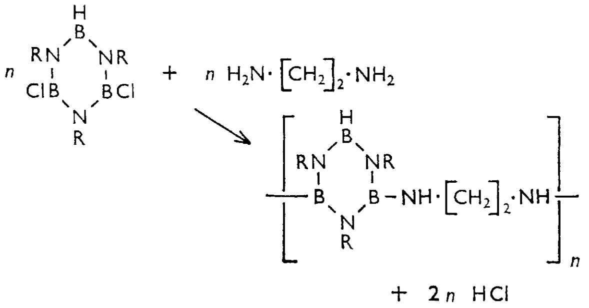


(2)

Another new bond in the above dimeric structure is the boron–aromatic carbon bond. According to Gerrard and his co-workers,[7] boron–phenyl absorptions occur at about 1446 cm.$^{-1}$. In borazole materials this absorption merges into that of the borazole ring and is indistinguishable. This is regrettable, since it would have provided additional proof for this mode of elimination of hydrogen chloride from *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole.

Such a side-reaction could give rise to cross-linked or highly branched insoluble polyborazoles. The infrared spectrum of the insoluble borazole material formed in xylene revealed an absorption at 3200—3050 cm.$^{-1}$ (an extension of the aromatic carbon–hydrogen absorption) and one at 800 cm.$^{-1}$ in addition to the expected ones (boron–hydrogen groups in particular were still present). Both these are characteristic of a cationic amino-group (NH_3^+); the 800 cm.$^{-1}$ absorption was, almost certainly, also caused by groups containing two adjacent free ring-hydrogen atoms. Alternatively, the absorption at 3200—3050 cm.$^{-1}$ could be caused by intermolecularly hydrogen-bonded amino-groups which absorb in the range 3400—3100 cm.$^{-1}$ [8,9] This could occur between terminal amino-groups. Were this the case, the absorption at 800 cm.$^{-1}$ would be entirely caused by groups of two adjacent free ring-hydrogen atoms. The insolubility of this material is thought, therefore, to be caused chiefly by cross-linking or chain-branching and may also be caused by the presence of some ionic amine hydrochloride groups ($-NH_3Cl$) or an increase in the molecular weight through hydrogen bonding between terminal amino-groups.

Since the loss of hydrogen chloride from *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole was far greater in the presence of triethylamine, soluble linear polyborazoles were more likely to be formed if this amine was excluded from the reaction. Two experiments based on equation (3) were carried out. Xylene and tetrahydronaphthalene were used as solvents. In both cases most of the borazole material was insoluble and had m. p. >360° and a chlorine content of the order of 14% showing them to be similar to the insoluble material previously formed in toluene in the presence of two mols. of triethylamine.



(3)

The complete analysis of the material formed in xylene suggested that it had structure (II) or (V). In the infrared spectrum, the aromatic carbon–hydrogen absorption at 3000 extended to 3180 cm.$^{-1}$ and there was also an absorption at 800 cm.$^{-1}$. The analogous material formed in tetrahydronaphthalene showed similar absorptions as did aniline hydrochloride. The latter had no separate peak in the 3180—3050 range. The borazole materials also had only one absorption attributed to amino-groups at 3320 cm.$^{-1}$ signifying that only secondary amino-groups were present. This fact, combined with the absorptions at 3180—3050 and at 800 cm.$^{-1}$ which were assigned to cationic amine hydrochloride groups, proved that structure (II) was relevant; structure (V) would have two amino-absorption bands instead because it contains primary amino-groups.

The possibility of the absorption at 3180—3050 cm.$^{-1}$ being attributed to intermolecularly hydrogen-bonded amino-groups, which would be possible with structure (V), and that at 800 cm.$^{-1}$ consequently being caused solely by two adjacent ring-hydrogen atoms, is elimin-

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[7] J. E. Burch, W. Gerrard, M. Goldstein, E. F. Mooney, and H. A. Willis, *Spectrochim. Acta*, 1962, 1403.

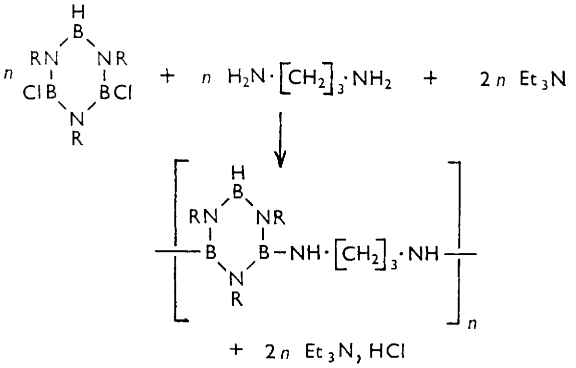
[8] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 1958, London, Methuen and Co. Ltd.

[9] G. B. B. M. Sutherland, *Discuss. Faraday Soc.*, 1950, **9**, 274.

ated because the borazole materials had chlorine contents of 13·8% compared with the theoretical value of 13·6% for structures (II) and (V). If groups containing two adjacent ring-hydrogen atoms had been formed, hydrogen chloride would have been lost and the chlorine contents would have been appreciably less than theoretical. The insolubility of these materials must have prevented the loss of hydrogen chloride.

Although the amount of hydrochloride (II) decreased as a higher-boiling solvent was used (88·8, 70·1, and 65·3% in toluene, xylene, and tetrahydronaphthalene, respectively) the soluble borazole materials were not plastic. It was thought that, if triethylamine were used as solvent, the elimination of hydrogen chloride would be forced, but that at the boiling point of triethylamine (89·5°) cross-linking or chain-branching would not occur. Soluble plastic linear polyborazoles (III and IV) were, in fact, successfully prepared by refluxing the insoluble hydrochloride (II) in triethylamine and by refluxing the *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and ethylenediamine, in a molar ratio of 1 : 1, in triethylamine. The structure and properties of these linear polyborazoles will be discussed later.

The polymerisation of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole through trimethylenediamine was also attempted initially in the presence of triethylamine. It was hoped that the reaction would proceed according to equation (4). In xylene all the borazole product was soluble. From its molecular weight and chlorine content, it was concluded to be mainly (VI), together with a little more highly polymeric material. In tetrahydronaphthalene, the major borazole product was insoluble, had m. p. 295—297°, and contained 1·45% chlorine. As for the similar insoluble compound formed from ethylenediamine, the infrared spectrum showed absorptions at 3140 and 800 cm.$^{-1}$. Again, these absorptions had two interpretations. They could be attributed to amine hydrochloride groups and possibly to groups containing two adjacent free ring-hydrogen atoms, or to intermolecularly hydrogen-bonded amino-groups and definitely, also, to groups with two adjacent free ring-hydrogen atoms. Boron–hydrogen groups were still present, as before. Since the chlorine content was low, even if amine hydrochloride groups were present, the chief cause of insolubility was most likely cross-linking or chain-branching. An increase in the molecular weight through hydrogen bonding might also contribute. A small amount of brown soluble plastic borazole material was also formed in this experiment.



(4)

When triethylamine was excluded and the solvent was tetrahydronaphthalene, good yields of soluble plastic linear polyborazoles (VII and VIII) were obtained. Besides hydrogen chloride, insoluble by-products were formed. These contained mainly (IX) but also some trimethylenediamine dihydrochloride. In the first of these experiments, the linear polyborazole formed after 5½ hours' refluxing was further refluxed in tetrahydronaphthalene in the presence of triethylamine in an effort to increase the molecular weight; a product (VIII) of lower chlorine content than that of the linear polyborazole from the next experiment (IX), in which no triethylamine was used at this stage, was obtained but both had the same degree of polymerisation (trimeric).

With tetra- and hexa-methylenediamine, the reactions proceeded similarly and soluble plastic linear polyborazoles (X, XII, XIII, XIV) were formed in high yield. The by-products were hydrogen chloride, tetra- and hexa-methylenediamine dihydrochloride, and (XI) and (XV). In the last experiment, two mols. of hexamethylenediamine were used to see whether the second mol. would increase the elimination of hydrogen chloride and therefore afford polymers of higher molecular weight. Some improvement was effected; there was an increase from a trimeric linear polyborazole to a mixture of penta- and hexa-mers. The yield (33·9%) was diminished, however, because most of the borazole material was insoluble and from this and its chlorine content of 5·4% it was deduced to have structure (XVI), of which the theoretical chlorine content is 5·4%.

The possibility of increasing the molecular weight without causing cross-linking or chain-branching of the linear polyborazoles was also attempted by including two moles. of ethyldi-isopropylamine in a reaction in tetrahydronaphthalene between one mol. of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and one mol. of trimethylenediamine. *B*-Dichloro-*N*-tri-(2,6-dimethylphenyl)borazole lost only 0·32% more of its chlorine on refluxing in tetrahydronaphthalene in the presence of ethyldi-isopropylamine than when refluxed alone in this solvent for the same time, so this base would not be expected to cause cross-linking to the extent of giving rise to insoluble polyborazoles. This was found to be so, but unfortunately there was no improvement in the degree of polymerisation; as in the experiments in which no tertiary amine was present, a trimeric linear polyborazole resulted. Ethyldi-isopropylamine is sterically hindered and therefore not likely to form a hydrochloride readily, and so it is unlikely to aid polymerisation.

The difficulty in forming linear polyborazoles when using ethylenediamine as a linking agent was thought to be caused by steric hindrance; this bridging group is just sufficiently long to join two of these borazole units, which contain large 2,6-dimethylphenyl groups. When the length of the linking group was increased by the presence of a third methylene group on using trimethylene diamine, the percentage yield of linear polyborazole increased markedly. When a trimethylene diamine link is used, the borazole units are separated. The yields increased further as the chain length of the diamines increased (Table 1).

The structures of the linear polyborazoles were not strictly those designated by the formulæ; the molecular weights indicated that other polymers were present and the infrared spectra that hydrogen chloride had been lost by condensation between chlorine atoms on the boron atoms and hydrogen atoms on the 2,6-dimethylphenyl groups according to equation (2). Yet the consequent cross-linking or chain-branching must be insufficient to cause insolubility. The infrared spectra also indicated in most cases the presence of terminal groups other than those represented in the formulæ given for the linear polyborazoles. For example, (VIII), (X), and (XIII) were formulated with two terminal chlorine atoms but their infrared spectra revealed the presence of primary and secondary amino-groups also. The *X*-ray patterns were crystalline in some cases and dark and diffuse in others; the latter type is typical of glasses. Unchanged *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole was probably present in (X) according to *X*-ray evidence.

A comparison of the range of plasticity in nitrogen of the linear polyborazoles is interesting (Table 2).

The drop in temperature at the lower end of the range on passing from linear polyborazoles (III) and (IV) to the others was marked. The reason for this must be steric hindrance. Also, (III) and (IV) at no time became mobile but remained fairly stiff. When a third methylene group was introduced into the links, free rotation of the borazole units was possible and the material softened at a lower temperature and eventually became very mobile. As the length of the bridging group increased further, the temperature of initial softening decreased. Similar observations were made by Russian workers.[10] For linear polyborazoles containing the same bridging group, the initial softening temperature increased with degree of polymerisation. Materials (XII), (XIII), and (XIV) illustrated this admirably. On moving from a trimer to a pentamer–hexamer mixture, the softening temperature rose from 95 to 210°. The extent of softening decreased too. This suggests that the insoluble borazole materials of low chlorine content and high melting point might be linear polyborazoles of higher molecular weight. The pentamer–hexamer mixture never even became tacky and certainly not mobile, whereas the trimer (and dimer) did become mobile eventually. The explanation in this case could be that as the chain length increases, the individual chains become tangled. On heating, some energy is used partially to disentangle them before they can soften. The softening range of 265—286° of (IV) is higher than any recorded so far for linear polyborazoles. Wagner and Bradford's material containing 23 units[2] had a lower softening range, 180—200°. The highest previously recorded range of softening was 195—220° for a material linked through 2,2-di-*p*-hydroxyphenyl)-propane.[3]

Linear polyborazoles (IV), (VII), (VIII), and (XIV) were stable to atmospheric moisture, but those containing long bridging groups from tetra- and hexamethylenediamine and of low degrees of polymerisation (X, XII, and XIII) were unstable.

All the linear polyborazoles were decomposed on refluxing in water. The molecular weights and melting points of the hydrolysed products indicated that mixtures of borazoles resulted; most of the bridging groups were removed. Many hydrolysates contained *B*-trihydroxy-*N*-tri-(2,6-dimethylphenyl)borazole.[11] Infrared evidence indicated that in many cases hydrolysis was incomplete. All hydrolysates retained the absorption at 800 cm.$^{-1}$ and this is in agreement with the postulated mechanism for the elimination of hydrogen chloride from *B*-dichloro-*N*-tri-(2,6-dimethyl)phenylborazole (equation 2) in which boron–carbon bonds were formed; such bonds are hydrolytically stable.[1] As expected from steric considerations and degrees of polymerisation, (IV) was more stable than (III) and both had better hydrolytic stability than (VII) and (VIII) which were superior to (XIV). Polymers (X), (XII), and (XIII) were quickly hydrolysed.

Most previously recorded examples of linear polyborazoles have been synthesised from borazole rings of poor hydrolytic stability because of the choice of alkyl substituents on the ring-nitrogen atoms. Those synthesised by Mikhailov and Galkin[3] which contained hexamethylenediamine bridging groups and methyl or ethyl substituents on the ring-nitrogen were hydrolysed by atmospheric moisture.

Even in the presence of alkyl substituents on the ring-nitrogen atoms, hydrolytic stability has been conferred by the use of bulky boron substituents. Seyferth *et al.*[12] synthesised *B*-tri(trimethylsilylmethyl)-*N*-trimethylborazole and it was stable to basic hydrolysis. Its dimer bridged by four methylene groups was unstable. The loss of one trimethylsilylmethyl substituent provided accessibility for hydrolytic attack which would commence at the ring nitrogen atoms.

By using aryl substituents on the ring-nitrogen atoms, hydrolytic stability often improves.[13] Blakely[1] formed a linear polyborazole of some hydrolytic stability (it was extracted with N-hydrochloric acid during its preparation) from *B*-phenyl-*N*-triphenylborazole and

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[10] V. V. Korshak, B. A. Zamyatina, and R. M. Oganesyan, *Isvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, No. 10, 1850.

[11] R. K. Bartlett, H. S. Turner, R. J. Warne, and M. A. Young, *Chem. and Ind.*, 1964, 1026—1027.

[12] D. Seyferth, W. R. Freyer, and M. Takamizawa, *Inorg. Chem.*, 1962, **1**, 710.

[13] S. J. Groszos and S. F. Stafiej, *J. Amer. Chem. Soc.*, 1958, **80**, 1357.

the di-Grignard reagent of *p*-dibromobenzene. An added factor contributing to the hydrolytic stability in this case was the presence of boron–carbon bonds formed through the phenylene bridging group, although this link would have an opposing effect also because of the small electron-withdrawal from the bonded boron atoms. The final effect in practice seems to be that of greater hydrolytic stability.

The most thermally stable linear polyborazole was (VIII) which was based on trimethylenediamine. It was superior to (IV) which had ethylenediamine links. No polyborazole lost weight below 210° either in air or nitrogen. The thermograms of (X) in air and of (XIII) in air and in nitrogen showed a levelling off at 12—18, 12—16, and 10—16%, respectively. The weight of methyl groups in (X) and (XIII) is 19·2 and 18·6%, respectively. Degradation may, therefore, commence at the methyl groups on the phenyl groups.

Much higher thermal stabilities have been reported for borazoles and polyborazoles. Many were determined by heating the substance in sealed evacuated tubes, however, and frequently the method of assessing these properties was not described. Comparisons can therefore only be made with reservations.

From the investigations of Newsom *et al.*,[14] it appears that borazoles containing phenyl substituents are generally more easily decomposed than those with alkyl substituents because phenyl groups, when perpendicular to the plane of the borazole ring, withdraw electrons from their bonded atoms and so weaken that bond. This is in harmony with a claim made by Mikhailov and Galkin;[3] the linear polyborazole formed by the reaction of *B*-n-butyl-*B*-di-n-butylmercapto-*N*-trimethyl(or ethyl)borazole and hexamethylenediamine was said to decompose only above 400°. The linear polyborazoles synthesised in this work contained aromatic substituents on the borazole rings and decomposed from 210° onwards.

The insoluble borazole material of m. p. 305—309° and containing 0·8% of chlorine, which was formed in xylene from *B*-dichloro-*N*-tri(2,6-dimethylphenyl)borazole, ethylenediamine, and triethylamine, was slightly less stable in nitrogen than its linear counterpart (IV). The stability in nitrogen of the corresponding insoluble borazole material formed when using trimethylenediamine was intermediate between those of its two linear counterparts (VII and VIII). This suggests that these insoluble borazole materials were linear polyborazoles of high molecular weight because a cross-linked polyborazole would be expected to have a thermal stability superior to that of a corresponding linear polyborazole. Both these insoluble borazole materials were stable to atmospheric moisture and had *X*-ray patterns which contained broad, diffuse bands. The complete analysis of the material formed using ethylenediamine was grossly deficient. Such difficulties have frequently been encountered in the analysis of cross-linked polyborazoles.[1]

TABLE 1

Linear polyborazole ...	(III)	(IV)	(VII)	(VIII)	(X)	(XII)	(XIV)
Yield (%)	23·4	25·4	88·5	80·2	98·8	93·1	93·9

TABLE 2

Linear polyborazole	(III)	(IV)	(VII)	(VIII)	(X)	(XII)	(XIII)	(XIV)
Range of plasticity	235—303°	265—286°	130—226°	130—205°	100—155°	95—145°	85—130°	210—? No true m. p.
Degree of polymerisation ...	3	4	3	3	2	3	2	5—6

EXPERIMENTAL

General.—Drying. Benzene and toluene were dried by passage over molecular sieve type 5A. The remaining water content, determined by Karl Fischer titration, was reduced to <30 p.p.m. before the solvents were used. Xylene, tetrahydronaphthalene, ethylene- and trimethylenediamine were refluxed with and distilled from sodium. Chloroform and methyl alcohol were shaken overnight with anhydrous calcium chloride. Tetramethylenediamine was liberated from its monohydrochloride and dried (KOH). Hexamethylenediamine was distilled. Nitrogen was passed through anhydrous magnesium perchlorate.

Handling of materials susceptible to moisture. Such materials (chloroborazoles, polyborazoles) were handled in a dry-box when necessary.

Analyses and molecular weights. Unless otherwise stated, these were by E. and F. Pascher, Bonn, Germany.

X-*Ray results.* Co-K_α radiation and an 11·48 cm. camera were used to obtain powder diffraction patterns.

Infrared spectra. Vibrational spectra in the region 4000—650 cm.$^{-1}$ were obtained on a Hilger and Watts H800 spectrophotometer. Most were taken on Nujol mulls, a few on Florube mulls, and some on carbon tetrachloride solutions. The spectra of the linear polyborazoles are recorded in Table 4 and those of their hydrolysates in Table 5.

Thermogravimetric analysis. A Stanton thermobalance was used and two analyses (one in air and one in nitrogen) were carried out on each sample. The rate of heating was 400° hr.$^{-1}$ unless stated otherwise, the sample size was 0·2—0·25 g. and pure alumina crucibles were used. The samples were weighed before and after on a separate balance.

Plasticities in nitrogen. The range of plasticity in nitrogen of the linear polyborazoles was determined by placing 0·1 g. of material in a 10 ml. flask which was continuously flushed with nitrogen and had a glass rod in it. A large nickel crucible containing cerrebend was warmed with a micro-burner until the alloy had melted. The flask

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[14] H. C. Newsom, W. D. English, A. L. McCloskey, and W. G. Woods, *J. Amer. Chem. Soc.*, 1961, **83**, 4134.

TABLE 3

Infrared vibrational frequencies

Expt.:			Fourth control expt.	4	5	3	9
A *	*B*-Dihydroxy-*N*-tri-(2,6-dimethylphenyl)-borazole	*B*-Dichloro-*N*-tri-(2,6-dimethylphenyl)-borazole	Residual borazole compound	(II)	(II)	Insoluble borazole material	Insoluble borazole material
B	3530						
	3460						
C				3320	3320	3490	3490
						3340	3380
D				3180	3150	3200	
				↓	↓	↓	3140
				3050	3000	3050	
E	3005	3003	2990	2990	2990	2995	3000
		3030	3040	3020			
F	Masked by Nujol	Masked by Nujol	Masked by Nujol	Masked by Nujol	Masked by Florube	Masked by Nujol	Masked by Nujol
G	2512	2510	2507	2502	2495	2495	2498
H		1600		1600	1600	1600	1600
				1500	1500	1500	
I	1432	1430	1425	1430	1425	1430	1430
	↓	↓	↓	↓	↓	↓	↓
	1400	1370	1385	1370	1385	1370	1385
J	1260	1263	1258	1258		1258	1255
K	1165	1160	1160	1165	Masked by Florube	1165	1160
	1092	1088	1088	1085		1088	1090
	1035	1030	1025	1033		1032	1033
	987	980	988	985		980	985
L				800	Masked by Florube 800 (in Nujol)	800	800
M			800			800	800
N		754					
		748					
O	765	765	765	760	Masked by Florube	760	760
	735	725	720	725		730	735
P	712						
	700						

* *A*, Material. *B*, OH stretch. *C*, NH and NH_2 stretch. *D*, NH_3^+ stretch or intermolecularly hydrogen bonded amino-groups. *E*, Aromatic CH stretch of monosubstituted nucleus. *F*, Aliphatic CH stretch. *G*, BH stretch. *H*, C=C skeletal in-plane vibrations. *I*, BN stretch. *J*, CN stretch. *K*, 1,2,3-Substituted aromatic rings. *L*, NH_3^+ rock. *M*, 2 Adjacent free ring-H atoms. *N*, BCl stretch. *O*, 3 Adjacent free ring-H atoms. *P*, BN out-of-plane deformation characteristic doublet.

TABLE 4

Infrared vibrational frequencies

Expt.:	3	6	7	10	11	12	13	14
A *	Soluble borazole material	(III)	(IV)	(VII)	(VIII)	(X)	(XII)	(XIII)
B								
C	3490	3500	3490	3500	3500			3490
	3330	3420	3400	3400	3410	3490	3350	3350
		3360	3340		3360	3350		
D				3050				
				↓		3150	3170	
				3140				
E	2985	3000	2990	3000	3000	3000	2990	3000
F				Masked by Nujol				
G	2480	2500	2500	2500	2500	2500	2500	2500
H	1500	1500	1500	1500	1500	1500	1500	1500
J	1430	1430	1430	1430	1435	1435	1435	1435
	↓	↓	↓	↓	↓	↓	↓	↓
	1385	1395	1385	1395	1395	1395	1410	1395
J	1257	1260	1255	1258	1260	1260	1260	1255
K	1155	1160	1160	1160	1160	1163	1160	1160
	1090	1090	1090	1090	1090	1090	1085	1087
	1025	1030	1030	1030	1028	1028	1030	1028
	982	985	985	982	985	985	983	983
L				800		800	800	
M	800	800	800	800	800	800	800	800
O	763	763	763	760	763	760	760	760
	725		735	735	735	720	735	735
P	690	705	710	710	710	700	700	700
	675	695	675	700	700	690	690	690

* See footnotes, Table 3.

was lowered into the cerrebend until all the material was surrounded by the hot alloy. A thermometer was placed in the cerrebend and the temperature slowly raised while the material was prodded with the glass rod. The temperatures at which the material began to soften and become like a stiff dough, at which it became like putty in mouldability, at which it became tacky, and finally very mobile, were noted. In order to determine the upper limit more accurately a m. p. determination in a sealed tube was done. The results are shown in Table 6.

TABLE 5

Infrared vibrational frequencies

Expt.:	6	7	10	11	13	14	15
A *				Hydrolysate of linear polyborazole			
B	3530	3540	3510	3530	3530	3540	3480
	3490	3490		3500	3490	3490	
C	3340	3340	3400		3400	3380	3390
D		3180			3170		
E	2990	2980	2990	2990	2980	2980	2950
F				Masked by Nujol			
G							
H	1500	1500					1485
I	1430	1430	1435	1435	1430	1430	1435
	↓	↓	↓	↓	↓	↓	↓
	1395	1390	1400	1400	1390	1390	1375
J	1257	1258	1257	1255	1257	1255	1260
K	1160	1160	1160	1160	1160	1160	1160
	1088	1090	1088	1090	1090	1090	1090
	1028	1030	1028	1030	1030	1028	1030
	985	985	985	980	985	985	987
L		800			800		
M	800	800	800	800	800	800	805
O	765	765	763	765	763	760	765
	735	735	720	735	735		735
P	715	722	713	722	720	720	725
	700	713	700	713	715	712	712

* See footnotes, Table 3.

TABLE 6

Plasticities in nitrogen

	Temp. at which material is:						
Expt.	Stiff dough	Like putty	Tacky	Pulled into threads	Plastic	Very mobile	M. p.
6	235°	240—300°					298—303°
7			265°		275°		282—286
10	130		145		155	170°	226
11	130		145		155	170	205
12	100		105	115°		135	140—155
13	95		110			120	145
14	85		95	100	110	125	130
15 *	210	230	240		260		>360

* In this case the descriptive terms " stiff dough, like putty, tacky, and plastic " should be replaced by " slight softening, marked softening, adhered together, and darkened and softened further," respectively.

Stabilities in air. The stabilities of the linear polyborazoles (VII, XI—XVI) and the insoluble borazole materials (III) and (X) were assessed by measuring the change in weight of material left exposed on a watch glass to the air for 26 days. Weight changes of 2% or less were meaningless when considered in relation to the weights of material used, and materials which underwent such weight changes have been stated to be stable in air.

Hydrolytic stabilities. To determine the percentage weight losses on hydrolysis, known weights of the linear polyborazoles were refluxed in distilled water for 1—8 hr. The insoluble hydrolysed materials were then filtered off, dried at 110°, weighed, and their m. p. and infrared spectrum taken. In some cases, partial analyses were done and molecular weights determined. The infrared data are in Table 5.

Preparation of Monomeric Borazoles.—B-*Dihydroxy*-N-*tri*-(2,6-*dimethylphenyl*)*borazole.* Prepared by the method of Bartlett, Turner, Warne, Young, and McDonald,[15] this *borazole* had m. p. 250—254° (Found: C, 67·0; H, 6·9; B, 7·3; N, 9·8%; *M*, 424. $C_{24}H_{30}B_3N_3O_2$ requires C, 67·8; H, 7·1; B, 7·65; N, 9·9%; *M*, 424·5). The infrared spectrum is recorded in Table 3.

B-*Dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole.* Thionyl chloride was used as the chlorinating agent and pyridinium chloride as catalyst.[15] Yields of *ca.* 95% of *product* were obtained, m. p. (in sealed capillaries) 240—244° (Found: C, 61·4; H, 5·8; B, 6·55; Cl, 15·4; N, 9·0%; *M*, 478. $C_{24}H_{28}B_3Cl_2N_3$ requires C, 61·58; H, 5·85; B, 7·03; Cl, 15·4; N, 9·1%; *M*, 461·5). The *X*-ray pattern was good and the strongest line corresponded to 7·19 Å. The infrared spectrum is in Table 3.

Linear Polymerisation of B-*Dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole through Aliphatic Diamines.—Control experiments: stabilities in refluxing solvents.* Refluxing was

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[15] R. K. Bartlett, H. S. Turner, R. J. Warne, M. A. Young, and (in part) W. S. McDonald, *Proc. Chem. Soc.*, 1962, 153.

carried out under nitrogen for 5½ hr. Any hydrogen chloride liberated while refluxing in a solvent was collected in distilled water and titrated with standard sodium hydroxide. When triethylamine hydrochloride was used or formed, it was filtered off from the hot solution under nitrogen and dried; the solvent was evaporated from the filtrate under reduced pressure.

Triethylamine hydrochloride in tetrahydronaphthalene. Triethylamine hydrochloride (2·74 g.) and tetrahydro naphthalene (15 ml.) were used. 2·69 g. of material, m. p. 262—266°, was recovered and *X*-rays confirmed it to be triethylamine hydrochloride. No hydrogen chloride was liberated.

B-*Dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole in tetrahydronaphthalene.* The borazole (1·50 g.) and tetrahydronaphthalene (15 ml.) were used. 1·47 g. of soluble residue, m. p. 212—214° (Cl, 14·0%), was recovered. After recrystallisation, the m. p. was 242—244°.

B-*Dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole in tetrahydronaphthalene in the presence of excess of triethylamine.* The borazole (2·57 g.) and tetrahydronaphthalene (10 ml.) were used. A small amount of insoluble borazole material was separated from the triethylamine hydrochloride by vacuum sublimation. 0·335 g. of material, m. p. 262—266°, was formed and *X*-rays confirmed it to be triethylamine hydrochloride. 0·015 g. of borazole material was separated from the latter, m. p. >360°. 2·44 g. of soluble residue, m. p. 227—231° (Cl, 12·2%), was obtained.

B-*Dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole in xylene in the presence of excess of triethylamine.* The borazole (2·32 g.) and xylene (10 ml.) were used. 0·48 g. of material, m. p. 262—266°, was formed and *X*-rays confirmed it to be triethylamine hydrochloride. 0·11 g. of borazole material was separated from the latter, m. p. >360°. 2·08 g. of soluble residue, m. p. 244—246°, $M = 707$ (Cl, 11·5%). The infrared spectrum is in Table 1.

Linear Polymerisation Through Ethylenediamine.—Seven experiments were carried out. In experiments 1, 2, and 3, the reactants, *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole, ethylenediamine, and triethylamine were used in the molar ratio of 1 : 1 : 2; excess of triethylamine was present in experiments 6 and 7. The only reactants, *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and ethylenediamine, in experiments 4 and 5 were in a molar ratio of 1 : 1.

In all experiments the dichloroborazole was dissolved in the solvent under nitrogen by refluxing, and the amine(s) dissolved in some of the same solvent and slowly added; the mixture was refluxed for 5½ hr. except in experiments 1, 6, and 7 (36·5, 12, and 40 hr., respectively). In experiments 4 and 5, where hydrogen chloride elimination was expected, the outgoing gases were passed through distilled water and the hydrogen chloride was estimated by titration with standard sodium hydroxide. Insoluble materials were filtered off under nitrogen, dried, and weighed. All filtrates were evaporated to dryness under reduced pressure. All solids of m. p. 262—266° were confirmed by *X*-rays to be triethylamine hydrochloride.

In experiment 1, 1·21 g. of ethylenediamine, 9·25 g. of the borazole, 4·05 g. of triethylamine, and 150 ml. of benzene were used. 3·51 g. of solid, m. p. 262—266°, was filtered off after 5½ hours' refluxing and the filtrate was refluxed for a further 28 hr. No more insoluble material was formed so the benzene was distilled off under reduced pressure and replaced by triethylamine; the solution was then refluxed for 3 hr. The triethylamine was then replaced by benzene. 1·52 g. of insoluble material, m. p. 285—310° (B, 6·8%), was obtained after filtering off and washing with water; the aqueous filtrate, after evaporation to dryness, yielded 0·23 g. of solid, m. p. 262—266°. From the benzene filtrate, 7·45 g. of borazole (I) ($M = 483$) was obtained.

In experiment 2, 0·402 g. of ethylenediamine, 3·09 g. of the borazole, 1·353 g. of triethylamine, and 25 ml. of toluene were used. The insoluble solids were separated by vacuum sublimation giving 0·25 g. of sublimate, m. p. 262—266° and 3·10 g. of involatile residue (II), m. p. >360° (Cl, 13·5%). 0·46 g. of soluble material (Cl, 5·65%), which never became plastic on heating, was also isolated.

In experiment 3, 0·520 g. of ethylenediamine, 4·0 g. of the borazole, 1·75 g. of triethylamine, and 35 ml. of xylene were used. The insoluble solids were separated by refluxing under nitrogen in chloroform and filtering the hot solution, giving 2·18 g. of soluble solid, m. p. 262—266°, and 2·66 g. of insoluble solid, m. p. 305—309° (Found: C, 64·9; H, 7·2; B, 5·9; Cl, 0·7; N, 14·0%). The insoluble borazole material was stable in air, had a poor *X*-ray pattern which contained broad diffuse bands of which the strongest corresponded to 7·19 Å, and began to lose weight at 290° in air and at 246° in nitrogen; its infrared spectrum is in Table 1. 1·05 g. of xylene-soluble yellow solid (Cl, 3·26%) which became plastic on heating, was obtained; its infrared spectrum is in Table 3.

In experiment 4, 0·616 g. of ethylenediamine, 4·74 g. of the borazole, and 35 ml. of xylene were used. 0·0355 g. of hydrogen chloride, 1·39 g. of soluble material of uncertain m. p. (Cl, 10·85%) and no plasticity, and 3·80 g. of insoluble *solid* of m. p. >360° [Found: C, 59·64; H, 6·4; B, 6·2; Cl, 13·8; N, 13·0. $C_{26}H_{36}B_3Cl_2N_5$ (II) requires C, 59·85; H, 6·9; B, 6·2; Cl, 13·6; N, 13·4. The infrared spectrum of this insoluble solid is recorded in Table 3.

In experiment 5, 0·730 g. of ethylenediamine, 5·61 g. of the borazole, and 35 ml. of tetrahydronaphthalene were used. 0·1872 g. of hydrogen chloride, 4·14 g. of insoluble solid (II), m. p. >360° (Cl, 13·8%), and 1·92 g. of soluble solid of uncertain m. p. and no plasticity (Cl, 5·1%) were obtained. The infrared spectrum of (II) is in Table 3.

In experiment 6, 3·32 g. of the insoluble borazole solid (II) formed in experiment 4 and 200 ml. of triethylamine were used. 3·60 g. of insoluble solids were obtained and 0·65 g. of yellow soluble *solid* (23·4% yield) which became plastic on heating [Found: C, 67·7; H, 7·2; B, 6·5; Cl, 2·6; N, 15·2%; *M*, 1525. $C_{78}H_{103}B_9ClN_{15}$ (III) requires C, 67·7; H, 7·4; B, 7·05; Cl, 2·6; N, 15·2%; *M*, 1382]. This material had a dark, diffuse *X*-ray pattern (typical of a glass) in which the strongest line corresponded to 7·44 Å. After 7 hours' refluxing in water, there was a 14·3% weight loss and part of the hydrolysate had m. p. 285—291° and part m. p. >360°.

In experiment 7, 0·923 g. of ethylenediamine, 7·09 g. of *B*-dichloro-*N*-tri-2,6-dimethylphenylborazole, and 100 ml. of triethylamine were used. 8·18 g. of insoluble solid were obtained and 1·79 g. of yellow *soluble* solid (25·4% yield) which became plastic on heating [Found: C, 67·6; H, 6·9; B, 7·7; Cl, 2·2; N, 14·2%; *M*, 1707. $C_{40}H_{70}B_{12}ClN_{20}$ (IV; $n = 4$) requires C, 68·2; H, 7·5; B, 7·1; Cl, 1·9; N, 15·3%; *M*, 1830]. This material had a more crystalline *X*-ray pattern than the corresponding material from experiment 6, but was still dark and diffuse with the strongest line corresponding to 7·44 Å. After 8 hours' refluxing in water, there was a 13·9% weight loss and the hydrolysate had m. p. 285—291°. In air, the material was stable. It began to lose weight at 270° in air and 252° in nitrogen.

Linear Polymerisation Through Trimethylenediamine.—Four experiments were carried out. In experiments 8 and 9, the reactants, *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole, trimethylenediamine, and triethylamine were used in the molar ratio of 1 : 1 : 2. There were only *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and the diamine in experiments 10 and 11 and their molar ratio was 1 : 1.

The experimental procedure was that for ethylenediamine.

In experiment 8, 0·678 g. of trimethylenediamine, 4·23 g. of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole, 1·85 g. of triethylamine, and 35 ml. of xylene were used. Of the insoluble solids, 1·50 g. was soluble in chloroform and had m. p. 262—266° and 0·32 g. of m. p. >360° (Found: Cl, 39·7. Calc. for $C_3N_2H_{12}Cl_2$: Cl, 49·0%) was insoluble. The presence of trimethylenediamine dihydrochloride was indicated by *X*-rays 4·51 g. of xylene-soluble yellow plastic *solid* was obtained [Found: C 1,6·4; N, 11·8%; *M*, 1052. $C_{51}H_{64}B_6Cl_2N_8$ (VI) requires Cl, 7·2; N, 12·1%; *M*, 927].

In experiment 9, 0·681 g. of the diamine, 4·25 g. of the borazole, 1·86 g. of triethylamine, and 30 ml. tetrahydronaphthalene were used. Owing to the violence of the rereaction, some reactants were lost. 3·00 g. of insoluble solid of m. p. 295—297° (Found: C, 62·2; H, 6·3; B, 8·4; Cl, 1·45; N, 9·9%) were obtained. This material was stable in the air and its *X*-ray pattern contained broad diffuse bands, the strongest of which corresponded to 7·34 Å; its infrared spectrum is recorded in Table 3, and it began to decompose in air at 318° and in nitrogen at 264°. 0·87 g. of soluble yellow plastic solid was obtained.

In experiment 10, 0·462 g. of propylenediamine, 2·88 g. of the borazole, and 25 ml. of tetrahydronaphthalene were used. After 5½ hours' refluxing, 0·64 g. of insoluble *solid* (Found: Cl, 22·4. $C_{24}H_{40}B_3Cl_2N_5$ (IX) requires Cl, 13·3%) was obtained; *X*-rays indicated the presence of trimethylenediamine dihydrochloride. Excess of triethylamine was added to the filtrate, which was then refluxed for 3 hr.; 0·32 g. of insoluble solid, m. p. 262—266°, was obtained. 2·48 g. of tetrahydronaphthalene-soluble brown plastic *solid* was obtained [Found: C, 67·5; H, 7·3; B, 7·3; Cl, 2·5; N, 14·3%; *M*, 1539. $C_{81}H_{109}B_9ClN_{15}$ (VII) requires: C, 68·3; H, 7·6; B, 6·8; Cl, 2·5; N, 14·7%; *M*, 1484]. This material was stable in the air but after 5 hours' refluxing in water lost 18·51% by weight; the hydrolysate (*M*, 650) melted partly at 250—254°, partly at 285—290°, and partly at >360°. It had a crystalline *X*-ray pattern in which the strongest line was equivalent to 7·23 Å. In air, it began to decompose at 220° and at 210° in nitrogen.

In experiment 11, 1·14 g. of trimethylenediamine, 7·12 g. of the borazole, and 25 ml. of tetrahydronaphthalene were used. 0·687 g. of hydrogen chloride and 0·97 g. of insoluble solid (Cl, 19·3%) in which trimethylenediamine dihydrochloride was indicated to be present by *X*-rays were obtained. 5·70 g. of tetrahydronaphthalene-soluble yellow plastic *solid* was obtained [Found: C, 67·3; H, 7·0; B, 7·0; Cl, 4·9; N, 12·2%; *M*, 1495. $C_{78}H_{100}B_9Cl_2N_{13}$ (VIII) requires: C, 67·5; H, 7·2; B, 7·0; Cl, 5·1; N, 13·1%; *M*, 1386]. This material was stable in air but after 5 hours' refluxing in water it had lost 15·28% by weight; the hydrolysate (Found: B, 8·92; N, 10·21; *M*, 564) melted partly at 276—280° and partly at 286—291°. Its *X*-ray pattern was dark and diffuse and the strongest line corresponded to 7·24 Å. In air, it began to decompose at 188° and at 300° in nitrogen.

Linear Polymerisation Through Tetramethylenediamine.—One experiment (12) only was carried out. The two reactants, *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and tetramethylenediamine were in a molar ratio of 1 : 1.

The procedure was that for ethylenediamine.

0·784 g. of tetramethylenediamine, 4·114 g. of the borazole, and 40 ml. of tetrahydronaphthalene were used. 0·0704 g. of hydrogen chloride and 0·701 g. of insoluble solid (Found: Cl, 35·3. $C_4N_2H_{14}Cl_2$ requires Cl, 44·1%) were obtained. *X*-Rays indicated the presence of tetramethylenediamine dihydrochloride in the latter. 4·13 g. of soluble yellow plastic *solid* was formed [Found: C, 65·8; H, 6·9; B, 7·4; Cl, 8·2; N, 11·6%; *M*, 949. $C_{56}H_{66}B_6Cl_2N_8$ (X) requires: C, 66·5; H, 7·0; B, 6·9; Cl, 7·6; N, 11·9%; *M*, 938]. This material was unstable in air; after 26 days' standing in air, there was a 6·1% weight gain and the initial shining, yellow resin became a dull, pale orange material. After refluxing in water for 1 hr., there was a 20·5% weight loss; the hydrolysate (*M*, 696) had m. p. 276—277°. Its *X*-ray pattern was good and the strongest line corresponded to 7·19 Å. In air, it began to decompose at 228°; there was a levelling at 12—18% weight loss. In nitrogen, it began to decompose at 246°.

Linear Polymerisation Through Hexamethylenediamine.—Three experiments were conducted. In experiments 13 and 14, the reactants, *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole and hexamethylenediamine were used in the molar ratio of 1 : 1 but in experiment 15, 1 : 2. Procedure was that for ethylenediamine.

In experiment 13, 1·56 g. of tetramethylenediamine, 6·22 g. of the borazole, and 40 ml. of tetrahydronaphthalene were used. 0·3394 g. of hydrogen chloride and 0·92 g. of insoluble solid (Found: Cl, 33·4. $C_6N_2H_{18}Cl_2$ requires Cl, 37·6%) were obtained; *X*-rays indicated the presence of hexamethylenediamine dihydrochloride in it and the m. p. of a sublimed portion was 257—260°, identical to that of pure hexamethylenediamine dihydrochloride. 6·51 g. of soluble yellow plastic *solid* was isolated [Found: C, 66·6; H, 7·60; B, 6·9; Cl, 5·8; N, 11·5%; *M*, 1500. $C_{84}H_{112}B_9Cl_2N_{13}$ (XII) requires: C, 68·6; H, 7·6; B, 6·6; Cl, 4·8; N, 12·4%; *M*, 1470]. This material was unstable in air; after 26 days' standing in air, there was a 12·1% weight gain and the initial shining, yellow resin became a dull, pale orange material. After refluxing in water for 1 hr., there was a 15·59% weight loss; the hydrolysate (N, 9·81%; *M*, 631) melted partly at 276—280° and part had not melted at 360°. The *X*-ray pattern was good and the strongest line corresponded to 6·52 Å. In air, it began to decompose at 240° and at 222° in nitrogen.

In experiment 14, 1·755 g. of hexamethylenediamine, 6·98 g. of the borazole, and 55 ml. of tetrahydronaphthalene were used. After 5½ hours' refluxing, 0·303 g. of hydrogen chloride had been evolved and 1·46 g. of insoluble solid (Cl, 12·1%). To the filtrate, excess of triethylamine was then added and the mixture was refluxed for 5 hr. 0·326 g. of insoluble solid, m. p. 262—266°, was then obtained; *X*-rays confirmed it to be triethylamine hydrochloride. 6·87 g. of soluble yellow plastic *solid* was isolated [Found: C, 66·2; H, 7·2; B, 6·85; Cl, 7·15; N, 11·6%; *M*, 1076. $C_{54}H_{70}B_6Cl_2N_8$ (XIII) requires: C, 66·9; H, 7·2; B, 6·8; Cl, 7·3; N, 11·6%; *M*, 968]. The material was unstable in air; after 26 days' standing in air, there was a 9·3% weight gain and the initial shining, yellow resin became a dull, pale orange material. After refluxing in water for 1 hr., there was a 22·81% weight loss; part of the hydrolysate melted at 285—287° and part had not melted by 360°. It had a good *X*-ray pattern in which the strongest line corresponded to 6·52 Å. In air, it began to decompose at 252°; there was a levelling at 12—16% weight loss. In nitrogen, decomposition also commenced at 252° and there was a levelling off at 10—15% weight loss.

In experiment 15, 2·37 g. of hexamethylenediamine, 4·71 g. of the borazole, and 55 ml. of tetrahydronaphthalene were used. 0·188 g. of hydrogen chloride was evolved. The mixture of insoluble solids was separated by refluxing with dry chloroform for ½ hr. whereupon 1·284 g. was soluble (Found: Cl, 34·7. $C_6N_2H_{18}Cl_2$ requires Cl, 37·6%) (*X*-rays indicated the presence of hexamethylenediamine dihydrochloride) and 3·84 g. was insoluble (Found: Cl, 5·38. Calc. for $C_{36}H_{59}B_3ClN_7$ (XVI) requires: Cl, 5·40%). 1·72 g. of tetrahydronaphthalene-soluble, tough, yellow *solid* was isolated [Found: C, 70·3; H, 7·7; B, 6·5; Cl, 1·2; N, 12·8%; *M*, 2827. $C_{330}H_{464}B_{33}Cl_2N_{55}$ (XIV) requires: C, 70·4; H, 8·25; B, 6·35; Cl, 1·3; N, 13·7%; *M*, 2811]. This material was stable in air but after 4 hours' refluxing in water lost 32·3% by weight and part of the hydrolysate melted at 270—278° and part had not melted by 360°. It had a dark, diffuse *X*-ray pattern in which no separate lines could be distinguished; the two main halos corresponded to 8·55 and 4·13 Å. In air and in nitrogen decomposition commenced at 240°.

Use of Ethyldi-isopropylamine in Polymerisation.—Control experiment: stability of B-*dichloro*-N-*tri*-(2,6-*dimethylphenyl*)*borazole in tetrahydronaphthalene in the presence of two mols. of ethyldi-isopropylamine.* 3·5878 g. of the borazole was refluxed in 15 ml. of tetrahydronaphthalene for 5½ hr. in the presence of 2·060 g. of ethyl di-isopropylamine. The insoluble solid formed was filtered off from the hot mixture under nitrogen and the filtrate was evaporated to dryness under reduced pressure. 0·24 g. of insoluble solid (Found: Cl, 21·7. $C_8NH_{20}Cl$ requires Cl, 21·4%) was obtained. The soluble residue had a chlorine content of 13·95% and its *X*-ray photograph was similar to that of *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole.

Linear polymerisation through trimethylenediamine in the presence of ethyldi-isopropylamine. *B*-dichloro-*N*-tri-(2,6-dimethylphenyl)borazole, trimethylenediamine, and ethyldi-isopropylamine were used in the molar ratio of 1 : 1 : 2. Procedure was as for ethylenediamine.

3·588 g. of the borazole, 0·5753 g. of the diamine, 2·060 g. of ethyldi-isopropylamine, and 20 ml. of tetrahydronaphthalene were used. No hydrogen chloride was evolved. 0·7490 g. of insoluble solid (Cl, 36·2%) was obtained; *X*-rays indicated the presence of trimethylenediamine dihydrochloride and ethyl di-isopropylamine hydrochloride. 3·678 g. of soluble yellow plastic *solid* was obtained [Found: C, 66·5; H, 7·0; B, 7·4; Cl, 5·6; N, 12·8%; *M*, 1330. $C_{78}H_{100}B_9Cl_2N_{13}$ (VIII) requires: C, 67·5; H, 7·2; B, 7·0; Cl, 5·2; N, 13·1%; *M*, 1386·5].

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British Ceramic Research Association,
Stoke-on-Trent.
[Present address: 35 Buttermere Drive,
Allestree, Derby.]
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