The Tetrameric and Trimeric N-Isobutyl-B-phenylborazynes and the Thermal Change, Tetramer \rightarrow Trimer

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CYCLIC dimeric,¹ trimeric,² and tetrameric³ polyborazynes as well as linear^{4,5} polyborazynes have previously been described. A linear form $(n \sim 20)$ of the polyborazyne system $(PhBNBu^{i})_{n}$ was obtained by Gerrard and co-workers.⁵ We now report the cyclic forms (n = 3 and n = 4) of the same polyborazyne system and the conversion of the tetramer into the trimer on heating at 250°.

The trimer (I), m.p. 134° and the tetramer (II), m.p. 232° were both obtained in the base dehydrochlorination of isobutylammonium trichlorophenylborate, and isobutylamine-dichlorophenylborane,

This change is demonstrated by differential thermal analysis (D.T.A.) examination (see Figure), the trace of (II) clearly shows the change as an exothermic peak immediately after the compound begins to melt. The D.T.A. trace of the product (m.p. 129°) obtained on heating (II) to 250° is identical with that of (I). The product of this change has been fully characterized as (I) by full elemental analysis, molecular-weight determination cryoscopically in benzene, and by infrared spectroscopy.

 $Bu^{i}NH_{3}+PhBCl_{3}-+3Et_{3}N \rightarrow (PhBNBu^{i})_{3}+(PhBNBu^{i})_{4}+3Et_{3}NHCl_{3}$ $Bu^{i}NH_{2}, PhBCl_{2} + 2Et_{3}N \rightarrow (PhBNBu^{i})_{3} + (PhBNBu^{i})_{4} + 2Et_{3}NHCl_{3}$

Compounds (I) and (II) have been characterised by full elemental analysis, molecular weights by the vapour-pressure osmometer, and by mass spectrometry. The X-ray structural analysis of (II) has yet to be carried out. The B-N ringstretching frequency of the trimer is found at 1417 cm.⁻¹ and the tetramer at 1401 cm.⁻¹; however, only the trimer shows the δ (B–N) ring deformation mode at 725 cm.⁻¹ (738, shoulder).

In contrast to the above results base dehydrochlorination in the analogous n-propyl system gives only the borazine, (PhBNPrn), whereas the s-butyl and t-butyl systems appear to be resistant to further dehydrochlorination beyond the alkylaminochlorophenylborane stage.

> $Pr^{n}NH_{3}+PhBCl_{3}- + 3Et_{3}N \rightarrow$ $(PhBNPr^{n})_{s} + 3Et_{s}NHCl$

$$RNH_3^+PhBCl_3^- + 3Et_3N \rightarrow$$

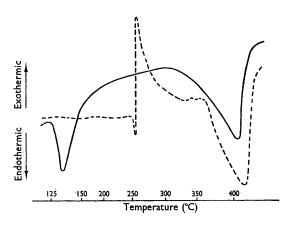
$$RNHB(Ph)Cl + 2Et_3NHCl + Et_3N$$

$$R = Bu^{g} \text{ and } Bu^{t}$$

On heating to above its melting point the tetramer (II) is changed, apparently quantitatively

and irreversibly, to the trimer (I).

$$(PhBNBu^{i})_{4} \longrightarrow (PhBNBu^{i})_{4}$$



FIGURE

D.T.A. traces of (I) (full line) and (II) (dotted line); heating rate, 10°/min.

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¹ M. F. Lappert and M. K. Majumdar, Proc. Chem. Soc., 1962, 88; J. Casanova, Jr., H. R. Kiefer, D. Kuwada, and A. H. Boulton, Tetrahedron Letters, 1965, 703; P. I. Paetzold, Z. anorg. Chem., 1963, 326, 47. ² Cf. K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, 1965. ³ H. S. Turner and R. J. Warne, Proc. Chem. Soc., 1962, 69. ⁴ A. D. Darra and R. J. Warne, Chem. Soc., 1962, 69.

A. B. Burg and J. Banus, J. Amer. Chem. Soc., 1954, 76, 3903; T. C. Bissot, D. H. Campbell, and R. W. Parry ibid., 1958, 80, 1868.

⁵ J. E. Burch, W. Gerrard, and E. F. Mooney, J. Chem. Soc., 1959, 2927.