Polymerization of Difunctional Ions Containing the –N–B–N– Linkage: a Polymeric Boron($n+$) Ion

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Summary A novel polymeric boron($n+$) ion has been prepared by vinyl polymerization of salts of the trimethylamine-(4-vinylpyridine)dihydroboron(1+) ion.

MULTIPLE intermolecular displacement of halide from boron in halogenoborane–amine adducts by polyamines, a modification of synthetic methods described by Nöth, Beyer, and Vetter,[1] and Douglass[2] for the preparation of mononuclear boron(1+) ions, seems to be a useful means of building multiple –N–B–N– units into a polyion structure. Thus, treatment of an excess of trimethylamine–iodoborane with tetramethylethylenediamine (tmed)[3,4] and pentamethyldiethylenetriamine (pmdt)[3] leads to the formation of the corresponding di- and tri-nuclear boronium iodides (I[†][5] and II).

$$Me_3NBH_2{\cdot}NMe_2{\cdot}CH_2{\cdot}CH_2NMe_2{\cdot}BH_2{\cdot}NMe_3{}^{2+}\quad 2I^-$$

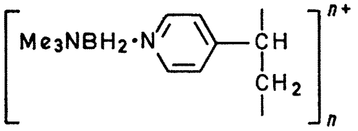
(I)

$$[Me_3NBH_2{\cdot}NMe_2{\cdot}CH_2{\cdot}CH_2]_2NMe{\cdot}BH_2{\cdot}NMe_3{}^{3+}\quad 3I^-$$

(II)

For the purpose of obtaining higher polymeric species, however, we have recently prepared mononuclear boron(1+) ions containing a reactive $-CH{=}CH_2$ function and, through vinyl polymerization, joined the monomeric species in such a manner that fragments containing the –N–B–N– unit are attached to every other carbon atom of a polyethylene backbone. The trimethylamine-(4-vinylpyridine)dihydroboron(1+) ion (III) is a potentially interesting precursor for new derivatives of polyfunctional boron($n+$) ions and offers a precedent for the synthesis of polyboronium ions *via* polymerization at a functional group which is removed from the –N–B–N– linkage.[3c] We further believe that the polymerization product (IV) represents the first reported case of the preparation, isolation, and characterization of an authentic polyboronium ion containing more than three boron atoms.

(III)



(IV)

TABLE

^{1}H *n.m.r. spectra*

Salt and solvent	Signal	Relative intensity	Chemical shift (p.p.m.)[a]
$C_7H_7NMe_3NBH_2{}^+PF_6{}^-$ in$(CD_3)_2SO$	singlet, $(CH_3)_3N-$	9·0	−3·0
	multiplet, $-\mathit{CH}{=}\mathit{CH}_2$	3·0	−6·2 to −7·4
	unsym. doublet, $(C_5\mathit{H}_4N-)$	2·0	−8·4
	unsym. doublet, $(C_5\mathit{H}_4N-)$	2·0	−9·1
$C_7H_7NMe_3NBH_2{}^+BPh_4{}^-$ in CD_3CN	singlet $(C\mathit{H}_3)_3N-$	1·2	−2·6
	multiplet $(C_5\mathit{H}_4N-)$ $(C_6\mathit{H}_5-)(-\mathit{CH}{=}\mathit{CH}_2)$	3·0	−6·8 to −8·6
$[C_7H_7NMe_3NBH_2{}^+BPh_4{}^-]_n$ in CD_3CN	unsym. multiplet $(\mathit{CH}_3)_3N-, {>}\mathit{CH}-\mathit{CH}_2-$	11·8	−2·5
	multiplet $(C_6\mathit{H}_5-)$	20·0	−6·7 to −7·6
	unsym. doublet $(C_5\mathit{H}_4N-)$	2·0	−7·8
	unsym. doublet $(C_5\mathit{H}_4N-)$	2·0	−8·5

[a] Relative to internal Me_4Si.

[†] Ion (I) has been prepared by the reaction of Me_3N with $(CH_2NMe_2BH_2I)_2$ (ref. 5).

The monomeric ion was prepared from the reaction of 4-vinylpyridine (1·32 g, 12·6 mmole) with Me_3NBH_2I (2·50 g, 12·6 mmole) in benzene (50 ml.) under N_2. The solid iodide salt (60% yield) was converted into the insoluble hexafluorophosphate, m.p. 69—70°, by precipitation from water with NH_4PF_6. The i.r. spectrum shows a doublet (2450 and 2495 cm^{-1}) characteristic of the $-BH_2$ group. A 10^{-3} M-solution in acetonitrile exhibited a molar conductance of 194 mho which is consistent for a 1 : 1 electrolyte. The tetraphenylborate salt of (III) was obtained by precipitation with $NaPh_4B$.

Polymerization of the PF_6^- and Ph_4B^- salts of (III) was carried out by dissolving 0·6—0·7 mmole of monomer in 5—6 ml of a solution of acetonitrile containing 1 mg per ml of dibenzoyl peroxide and heating the solution at 60° for 2 hr. The polymers were recovered by evaporation of solvent *in vacuo*; the dry hexafluorophosphate species (m.p. 113°) being recovered as a clear film and the tetraphenylborate as a light brown solid. The polyion salts exhibit much lower solubilities than the corresponding monomers in polar organic solvents and show characteristically different i.r. and n.m.r. spectra. A distinguishing feature in the n.m.r. (Table) is that resonance signals due to the vinyl protons of the monomer are replaced by signals at higher field attributed to $-CH$ and $-CH_2$ in the polymer.

The monomeric ion obtained from Me_3NBH_2I and 2-vinylpyridine did not polymerize under similar conditions, possibly due to steric hindrance which is not important in the 4-vinyl derivative. Boiling the acetonitrile solution under reflux for 2 days resulted in degradation of the boronium salt and formation of polymeric 2-vinylpyridine.

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