Evidence from Mass Spectra and X-ray Photoelectron Spectra Concerning the Structure of Poly(aminoborane)

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Abstract

Thermal decomposition mass spectra of a new form of poly(aminoborane) exhibit ions containing $-NH_2BH_2-$ chains up to nine atoms in length along with species arising from hydrogen elimination during decomposition of the compound. The XPS spectrum of poly(aminoborane) suggests the presence of equal numbers of B and N atoms each in a single chemical environment. A large cyclic structure for the compound is indicated.

Introduction

We recently reported a new synthesis for a poly(aminoborane) [1] believed to be the same substance prepared earlier by different methods [2, 3] but incompletely characterized. The method of synthesis, and elemental composition of the compound are consistent with its formulation as $(NH_2BH_2)_n$, **1**, a polymer, however, no direct structural evidence was obtained and attempts to determine its molecular weight by both laser light scattering [3] and cryoscopy [1] failed [4]. The structure of the present compound is of particular interest because several compounds of the same empirical composition prepared by different routes are thought to exhibit both cyclic (cycloborazane) and linear structures. We wish to report here mass spectral and X-ray photoelectron results which afford new insight into the structure of the product.

Results and Discussion

Mass spectra under CI and EI conditions were obtained of the volatiles from thermal decomposition of freshly prepared samples of **1** in the heated inlet of the mass spectrometer. Spectra were obtained over a range of temperatures; the results presented here correspond to a temperature of about 175 °C chosen because of the indicated decomposition temperature of the solid in a thermogravimetry experiment [3] and a maximum in the ion current corresponding to the NH_2BH_2 monomer in the spectra. Perusal of the results (Tables I and II) indicates that a complex mixture of amino- and iminoborane fragments along with borazine, borazine derivatives and polynucleated borazines emanates from the decomposition. An attempt was made to identify the species responsible for the more abundant ions in the spectra but the analysis was not exhaustive inasmuch as numerous fragments and isotopomers may contribute to any given ion.

Assuming that an aminoborane polymer chain would cleave thermally in a symmetrical fashion (eqn. 1), fragments with $-BH_2$ and $-NH_2$ termini should result.

$$-NH_2BH_2NH_2BH_2- \xrightarrow{\Delta} -NH_2BH_2 + NH_2BH_2- \tag{1}$$

Depending on where the chain cleaved, fragments with equal numbers of boron and nitrogen atoms (*i.e.* NH_2BH_2 monomer and its oligomers) as well as fragments with unequal numbers of boron and nitrogen atoms could result. The CI spectrum contains the monomer (m/e = 29) and the dimer but no higher members while the EI spectrum also contains the trimer. Representative of fragments with unequal numbers of borons and nitrogens seen in the spectra are **2** and **3**. The largest such fragment identified among the decomposition products contained nine chain atoms. In several instances (*e.g.* **4**, m/e = 60) ions appeared corresponding to chain fragments terminated by BH_3 groups but it is not clear whether these reflect the presence of such terminal groups in the parent

$NH_2BH_2NH_2$

2

$BH_2NH_2BH_2NH_2BH_2$

3

$H_3B \cdot NH_2BH_2NH_2$

4

TABLE I. Mass Spectrum of Poly(aminoborane) Thermal Decomposition Products under C.I. Conditions.[a]

Mass	%RA	Fragment Protonated[b]
17		(CI reagent)
18	7.9	NH_3
19	12.8	H_2O
27	12.5	$[H^{14}N^{10}BH]$
28	13.0	$[H^{14}N^{11}BH]$
29		(CI reagent)
30	48.7	$^{14}NH_2{}^{11}BH_2$
41	7.3	(CI reagent)
42	6.4	$\mu\text{-}{}^{14}NH_2{}^{10}B_2H_5$
43	8.6	$\mu\text{-}{}^{14}NH_2{}^{10}B^{11}BH_5$
44	16.5	$\mu\text{-}{}^{14}NH_2{}^{11}B_2H_5$
45	11.1	$^{14}NH_2{}^{11}BH^{14}NH_2$
55	3.5	$^{14}NH_2{}^{10}BH^{14}NH^{10}BH_2$
56	4.0	$^{14}NH_2{}^{10}BH^{14}NH^{11}BH_2$
57	8.0	$^{14}NH_2{}^{11}BH^{14}NH^{11}BH_2$, $^{14}NH_2{}^{10}BH_2{}^{14}NH_2{}^{10}BH_2$
58	12.2	$^{14}NH_2{}^{10}BH_2{}^{14}NH_2{}^{11}BH_2$, $H_3{}^{10}B\cdot{}^{14}NH_2{}^{10}BH_2{}^{14}NH_2$
59	15.8	$^{14}NH_2{}^{11}BH_2{}^{14}NH_2{}^{11}BH_2$, $H_3{}^{10}B\cdot{}^{14}NH_2{}^{11}BH_2{}^{14}NH_2$
60	17.7	$H_3{}^{11}B\cdot{}^{14}NH_2{}^{11}BH_2{}^{14}NH_2$
61	19.1	$H_3{}^{11}B\cdot{}^{14}NH_2{}^{11}BH_2\cdot{}^{14}NH_3$[c]
67	1.2	$^{10}BH_2{}^{14}NH_2{}^{10}BH_2{}^{14}NH^{10}BH$
68	1.8	$^{10}BH_2{}^{14}NH_2{}^{10}BH_2{}^{14}NH^{11}BH$
69	3.3	$^{10}BH_2{}^{14}NH_2{}^{11}BH_2{}^{14}NH^{11}BH$, $^{10}BH_2{}^{14}NH_2{}^{10}BH_2{}^{14}NH_2{}^{10}BH_2$
70	6.6	$^{11}BH_2{}^{14}NH_2{}^{11}BH_2{}^{14}NH^{11}BH$, $^{10}BH_2{}^{14}NH_2{}^{10}BH_2{}^{14}NH_2{}^{11}BH_2$
71	10.1	$^{10}BH_2{}^{14}NH_2{}^{11}BH_2{}^{14}NH_2{}^{11}BH_2$
72	12.1	$^{11}BH_2{}^{14}NH_2{}^{11}BH_2{}^{14}NH_2{}^{11}BH_2$
79	3.2	$H_3{}^{14}N_3{}^{10}B_3H_3$
80	7.1	$H_3{}^{14}N_3{}^{10}B_2{}^{11}BH_3$
81	9.8	$H_3{}^{14}N_3{}^{10}B^{11}B_2H_3$
82	10.5	$H_3{}^{14}N_3{}^{11}B_3H_3$

[a] Methane chemical ionization. Spectrum of volatiles of solid poly(aminoborane) at ~175 °C corresponding to maximum m/e = 30 ($NH_2BH_2 + H^+$). [b] Assumes monoprotonated ions. [c] Formally saturated species – mode of protonation not discerned.

TABLE II. Mass Spectrum of Poly(aminoborane) Thermal Decomposition Products under EI Conditions.[a]

Mass	%RA	Ion Composition[b]	Proposed Species
26	4.6	$^{14}N^{10}BH_2$	
27	14.6	$^{14}N^{10}BH_3$, $^{14}N^{11}BH_2$	
28	30.6	$^{14}N^{11}BH_3$	
29	9.2	$^{14}N^{11}BH_4$	$(NH_2BH_2)^+$
30	8.7	$^{14}N^{11}BH_5$	$(NH_2BH_2 + H)^+$

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TABLE II. *(continued)*

Mass	%RA	Ion Composition[b]	Proposed Species
36	1.8	$^{14}N^{10}B_2H_2$	
37	8.3	$^{14}N^{10}B^{11}BH_2$, $^{14}N^{10}B_2H_3$	
38	14.4	$^{14}N^{10}B_2H_4$	
39	14.8	$^{14}N^{10}B^{11}BH_4$	
40	13.0	$^{14}N^{10}B_2H_6$, $^{14}N^{11}B_2H_4$	$(BH_2NHBH)^+$
41	17.8	$^{14}N^{10}B^{11}BH_6$	
42	25.9	$^{14}N^{11}B_2H_6$	$(BH_2NH_2BH_2)^+$
43	18.1	$^{14}N_2{}^{10}BH_5$	
44	18.8	$^{14}N_2{}^{11}BH_5$	$(NH_2BHNH_2)^+$
51	6.2	$^{14}N_2{}^{10}B_2H_3$	
52	20.6	$^{14}N_2{}^{10}B^{11}BH_3$, $^{14}N_2{}^{10}B_2H_4$	
53	28.2	$^{14}N_2{}^{11}B_2H_3$, $^{14}N_2{}^{10}B^{11}BH_4$	$((HNBH)_2-H)^+$
54	3.0	$^{14}N_2{}^{10}B_2H_6$, $^{14}N_2{}^{11}B_2H_4$	$(HNBH)_2{}^+$
55	7.7	$^{14}N_2{}^{10}B_2H_7$, $^{14}N_2{}^{10}B^{11}BH_6$	
56	3.1	$^{14}N_2{}^{10}B^{11}BH_7$, $^{14}N_2{}^{11}B_2H_6$	$(NH_2BH_2NHBH)^+$
57	8.1	$^{14}N_2{}^{11}B_2H_7$	$((NH_2BH_2)_2-H)^+$
61	2.8	Not identified	
62	7.4	Not identified	
63	8.9	Not identified	
66	1.3	$^{14}N_2{}^{10}B_3H_8$	
67	4.2	$^{14}N_2{}^{10}B_2{}^{11}BH_8$	
68	3.8	$^{14}N_2{}^{10}B^{11}B_2H_8$, $^{14}N_2{}^{10}B_3H_{10}$	
69	4.6	$^{14}N_2{}^{11}B_3H_8$, $^{14}N_2{}^{10}B_2{}^{11}BH_{10}$	$(BH_2NH_2BH_2NHBH)^+$
70	3.8	$^{14}N_2{}^{10}B^{11}B_2H_{10}$	
71	6.3	$^{14}N_2{}^{11}B_3H_{10}$	$(BH_2NH_2BH_2NH_2BH_2)^+$
72	1.8	$^{14}N_2{}^{11}B_3H_{11}$	$(BH_2NH_2BH_2NH_2\cdot BH_3)^+$
73	1.4	$^{14}N_2{}^{11}B_3H_{12}$	$(BH_3\cdot NH_2BH_2NH_2\cdot BH_3)^+$
75	4.1	$^{14}N_3{}^{10}B_3H_3$	
76	10.5	$^{14}N_3{}^{10}B_2{}^{11}BH_3$, $^{14}N_3{}^{10}B_3H_4$	
77	14.9	$^{14}N_3{}^{10}B^{11}B_2H_3$, $^{14}N_3{}^{10}B_2{}^{11}BH_4$, $^{14}N_3{}^{10}B_3H_5$	
78	25.9	$^{14}N_3{}^{11}B_3H_3$, $^{14}N_3{}^{10}B^{11}B_2H_4$, $^{14}N_3{}^{10}B_2{}^{11}BH_5$, $^{14}N_3{}^{10}B_3H_6$	
79	60.4	$^{14}N_3{}^{11}B_3H_4$, $^{14}N_3{}^{10}B^{11}B_2H_5$, $^{14}N_3{}^{10}B_2{}^{11}BH_6$	
80	100	$^{14}N_3{}^{11}B_3H_5$, $^{14}N_3{}^{10}B^{11}B_2H_6$	
81	38.6	$^{14}N_3{}^{11}B_3H_6$	$(H_3N_3B_3H_3)^+$
82	4.7	$^{14}N_3{}^{10}B_3H_{10}$	
83	5.4	$^{14}N_3{}^{10}B_2{}^{11}BH_{10}$, $^{14}N_3{}^{10}B_3H_{11}$	
84	4.0	$^{14}N_3{}^{10}B^{11}B_2H_{10}$, $^{14}N_3{}^{10}B_2{}^{11}BH_{11}$	
85	5.8	$^{14}N_3{}^{11}B_3H_{10}$, $^{14}N_3{}^{10}B^{11}B_2H_{11}$	
86	2.0	$^{14}N_3{}^{11}B_3H_{11}$	$((NH_2BH_2)_3-H)^+$
91	1.8	$^{14}N_4{}^{10}B_3H_5$	
92	1.8	$^{14}N_4{}^{10}B_2{}^{11}BH_5$, $^{14}N_4{}^{10}B_3H_6$	
93	2.7	$^{14}N_4{}^{10}B^{11}B_2H_5$, $^{14}N_4{}^{10}B_2{}^{11}BH_6$, $^{14}N_4{}^{10}B_3H_7$	
94	4.0	$^{14}N_4{}^{11}B_3H_5$, $^{14}N_4{}^{10}B^{11}B_2H_6$, $^{14}N_4{}^{10}B_2{}^{11}BH_7$	

(continued overleaf)

TABLE 11. *(continued)*

Mass	%RA	Ion Composition[b]	Proposed Species
95	9.0	$^{14}N_4{}^{11}B_3H_6$, $^{14}N_4{}^{10}B^{11}B_2H_7$, $^{14}N_3{}^{10}B_4H_{13}$	
96	6.7	$^{14}N_4{}^{11}B_3H_7$, $^{14}N_3{}^{10}B_3{}^{11}BH_3$	$(H_3N_3B_3(NH_2)H_2)^+$
97	7.9	$^{14}N_3{}^{10}B_2{}^{11}B_2H_{13}$	
98	3.9	$^{14}N_3{}^{10}B^{11}B_3H_{13}$	
99	2.9	$^{14}N_3{}^{11}B_4H_{13}$	$(BH_2NH_2BH_2NH_2BH_2NH_2BH_2-H)^+$
103	3.4	$^{14}N_4{}^{10}B_4H_7$	
104	3.5	$^{14}N_4{}^{10}B_3{}^{11}BH_7$	
105	7.9	$^{14}N_4{}^{10}B_2{}^{11}B_2H_7$	
106	12.8	$^{14}N_4{}^{10}B^{11}B_3H_7$	
107	13.4	$^{14}N_4{}^{11}B_4H_7$	$(H_2(BH_2)N_3B_3(NH_2)H_2)^+$
108	3.3	$^{14}N_5{}^{10}B_3H_8$	
109	3.4	$^{14}N_5{}^{10}B_2{}^{11}BH_8$, $^{14}N_4{}^{10}B_4H_{13}$	
110	3.9	$^{14}N_5{}^{10}B^{11}B_2H_8$, $^{14}N_4{}^{10}B_3{}^{11}BH_{13}$	
111	5.7	$^{14}N_5{}^{11}B_3H_8$, $^{14}N_4{}^{10}B_2{}^{11}B_2H_{13}$	$(H_3N_3B_3(NH_2)_2H)^+$
112	2.6	$^{14}N_4{}^{10}B^{11}B_3H_{13}$	
113	2.1	$^{14}N_4{}^{11}B_4H_{13}$	$((NH_2BH_2)_3NHBH-H)^+$
121	1.8	$^{14}N_5{}^{10}B_2{}^{11}B_2H_9$	
122	2.4	$^{14}N_5{}^{10}B^{11}B_3H_9$	
123	3.4	$^{14}N_5{}^{11}B_4H_9$, $^{14}N_6{}^{10}B_3H_9$	$(H_2(BH_2)N_3B_3(NH_2)_2H)^+$
124	1.5	$^{14}N_6{}^{10}B_2{}^{11}BH_9$	
125	2.1	$^{14}N_6{}^{10}B^{11}B_2H_9$	
126	1.4	$^{14}N_6{}^{11}B_3H_9$	$(H_3N_3B_3(NH_2)_3)^+$
127	1.8	Not Identified	
128	4.4	$^{14}N_5{}^{10}B_4H_{18}$, $^{14}N_4{}^{10}B^{11}B_4H_{18}$, $^{14}N_5{}^{10}B_5H_8$	
129	3.5	$^{14}N_5{}^{10}B_3{}^{11}BH_{18}$, $^{14}N_4{}^{11}B_5H_{18}$, $^{14}N_5{}^{10}B_4{}^{11}BH_8$	$(BH_2(NH_2BH_2)_4)^+$
130	3.8	$^{14}N_5{}^{10}B_2H_{18}$, $^{14}N_5{}^{10}B_3{}^{11}B_2H_8$	
131	6.6	$^{14}N_5{}^{10}B^{11}B_3H_{18}$, $^{14}N_5{}^{10}B_2{}^{11}B_3H_8$	
132	6.2	$^{14}N_5{}^{11}B_4H_{18}$, $^{14}N_5{}^{10}B^{11}B_4H_8$	$((NH_2BH_2)_4NH_2)^+$
133	2.6	$^{14}N_5{}^{11}B_5H_8$	$(H_4N_5B_5H_4)^+$
147	1.4	$^{14}N_6{}^{10}B_2{}^{11}B_3H_{10}$	
148	1.4	$^{14}N_6{}^{10}B^{11}B_4H_{10}$	
149	1.4	$^{14}N_6{}^{11}B_5H_{10}$ (?)	$(H_4N_5B_5(NH_2)H_3)^+$
155	1.3	$^{14}N_6{}^{10}B_4{}^{11}B_2H_9$	
156	1.3	$^{14}N_6{}^{10}B_3{}^{11}B_3H_9$	
157	1.4	$^{14}N_6{}^{10}B_2{}^{11}B_4H_9$	
158	1.4	$^{14}N_6{}^{10}B^{11}B_5H_9$	
159	1.1	$^{14}N_6{}^{11}B_6H_9$	$((H_3N_3B_3H_2)-(H_2N_3B_3H_3)-H)^+$
169	1.4	$^{14}N_7{}^{10}B_6H_{11}$	
170	2.7	$^{14}N_7{}^{10}B_5{}^{11}BH_{11}$	
171	4.3	$^{14}N_7{}^{10}B_4{}^{11}B_2H_{11}$	
172	4.9	$^{14}N_7{}^{10}B_3{}^{11}B_3H_{11}$	
173	3.1	$^{14}N_7{}^{10}B_2{}^{11}B_4H_{11}$	

(continued on facing page)

TABLE II. *(continued)*

Mass	%RA	Ion Composition[b]	Proposed species
174	2.4	$^{14}N_7{}^{10}B^{11}B_5H_{11}$	
175	1.9	$^{14}N_7{}^{11}B_6H_{11}$	$(H_3(BH_2)N_5B_5(NH_2)_2H_2)^+$

[a] 70 eV spectrum of volatiles above poly(aminoborane) solid at ~175 °C. Spectrum corresponded to maximum m/e = 29 ion current. [b] Not all possible isotopomer and deprotonated species shown in every case.

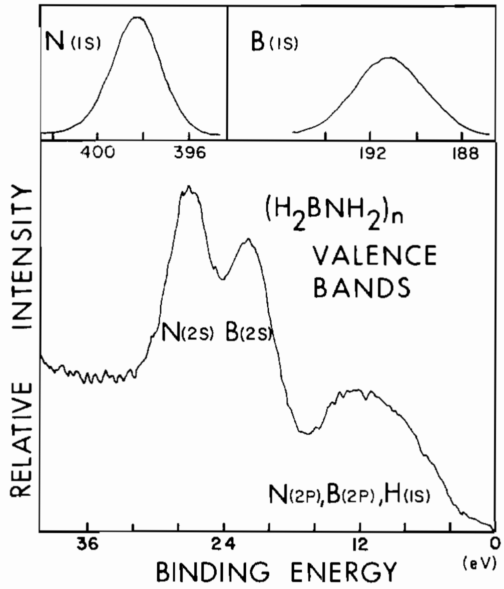


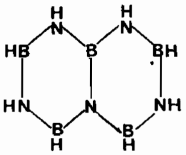
Fig. 1. XPS spectrum of poly(aminoborane) excited by MgK_α radiation showing the N(1s), B(1s) and valence band structures.

polymer since hydrogen migration can be expected under these conditions.

At the temperatures of the decomposition, hydrogen elimination (eqn. 2) is also expected to take place. Sequential elimination steps can lead to borazine formation which was observed in nearly all

$$-NH_2BH_2NH_2BH_2- \xrightarrow[-H_2]{\Delta} -NH_2BHNHBH_2- \qquad (2)$$

spectra and grew in relative intensity as the temperature increased. In addition to borazine, evidence was found for the boron–nitrogen analogs of naphthalene [5] (m/e = 133) and biphenyl [5] (m/e = 160) as well as several amino and boryl-borazines. Several of these compounds including **5** and **6** have been identified as products of the pyrolysis of gaseous borazine [5], so they were probably formed by the same pathway in these experiments.



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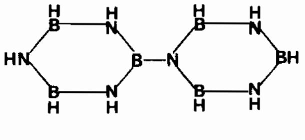

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Thus, the array of ions appearing in these spectra is consistent with thermally-induced fragmentation of either a linear chain or large cyclic, $(NH_2BH_2)_n$, polymer. There was no indication of chain branching in the fragments observed.

The X-ray photoelectron spectrum (XPS) of poly(aminoborane) was obtained using MgK_α (1253.6 eV) radiation. The N(1s) and B(1s) lines along with the valence bands are shown in Fig. 1. The results derived from these spectra are as follows. First, both the N(1s) and B(1s) lines are symmetrical, indicating that the nitrogen and boron in the sample exist each in a single unique chemical environment. Second, the relative intensities of the N(1s) and B(1s) lines, after correction for the photoionization cross sections [6], indicate that the atomic concentrations of nitrogen and boron are approximately equal. Third, the measured absolute binding energies of N(1s) = 398.2 eV and B(1s) = 191.1 eV are both higher than those of the counterpart boron nitride for which N(1s) = 397.9 eV and B(1s) = 190.2 eV [11]. These small shifts toward higher binding energies are consistent with and expected for hydrogenation of second row elements. Fourth, the valence band spectrum exhibits single N(2s) and B(2s) bands in the inner valence region (17–32 eV) and a broad rounded structure corresponding to the bonding MO's consisting of N(2p), B(2p), and H(1s) AO's in the inner valence region (0–17 eV). *Ab initio* band structure calculations by Armstrong *et al.* [7], have predicted that an alternating B–N bond model appears to be more stable than a symmetric B–N bond model. The calculated valence bands for either model failed to provide a good fit to the experimental valence band structure. In summary, the XPS results show that the sample consists of nitrogen and boron in equal abundances and in single chemical bonding environments which are characterized by bonding molecular orbitals between B, N and H atoms.

The indication of single boron and nitrogen environments suggests a cyclic structure for **1**. This is in concert with the fact that all other crystalline poly(aminoboranes) presently known are believed to have cyclic structure (*i.e.* cycloborazanes). If cyclic, the ring size of **1** would have to exceed five NH_2BH_2 units since its X-ray powder pattern is different from all the $(NH_2BH_2)_n$ (n = 2, 3, 4 and 5) [1, 8–10].

Experimental

The poly(aminoborane) was prepared according to the method published earlier [1].

Freshly prepared samples were placed in glass melting point capillaries about 2 cm in length and transfered to the heated inlet of a Hewlett Packard Model 5930A mass spectrometer. Spectra were scanned over a range of temperatures as the inlet was heated. A sharp increase in the ion current was observed starting at about 175 °C where decomposition of the poly(aminoborane) begins [3].

X-ray photoelectron spectra were obtained using a Perkin Elmer-Physical Electronics Industries Model 550 instrument employing MgK_α radiation. The poly(aminoborane) sample was prepared by synthesizing it directly onto a platinum substrate. The spectra were calibrated using the value $Pt(4f_{7/2})$ = 70.9 eV [11]. The initial spectra indicated severe charging effects due to the insulating nature of the sample. This charging was controlled by flooding the sample with low energy (~2 eV) electrons. Minor impurities of oxygen and carbon were observed. These were most likely adsorbates on the surfaces of the crystallites.

Acknowledgements

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