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The Nuclear Magnetic Resonance and Infrared Spectra of Some Aziridine Boranes

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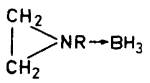
1. The ^{1}H and ^{11}B NMR and infrared spectra of three compounds derived from aziridine and *N*-(2-aminoethyl)aziridine have been measured.

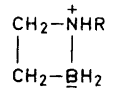
2. The spectra show that the compounds are aziridine-borane, *N*-(2-aminoethyl)aziridine-bis-borane and *N*-(ethylene)cyclotriborazane.

3. Vibrational assignments of the infrared spectra are made.

Åkerfeldt, Wahlberg and Hellström have described[1] the preparation of a number of borane complexes by the reaction of aziridine and 1-substituted aziridines with sodium borohydride. Two types of structure were considered for these products, *viz.* an aziridine-borane,



or a 1-substituted-1,2-azaboretidine



Initially the azaboretidine formulation was preferred.[2] The infrared and ^{1}H and ^{11}B nuclear magnetic resonance spectra of some of these compounds are described in the paper and show that in each case the aziridine-borane structure is the correct one.

EXPERIMENTAL

Three substances were kindly supplied by Dr. Åkerfeldt for spectroscopic examination. These were the borane derived from aziridine (I), that derived from *N*-(2-aminoethyl)-aziridine (II), and a self condensation product (III) obtained from the aziridine-borane (I).

Infrared spectra were measured as Nujol or Fluorube mulls over the range 4000–400 cm^{-1} with a Perkin-Elmer 337 grating spectrometer.

^{1}H nuclear magnetic resonance spectra were recorded with a Perkin-Elmer R10 spectrometer at 60 MHz and a Varian HA 100 spectrometer at 100 MHz relative to tetramethyl silane as internal standard. ^{11}B resonance spectra were determined at 19.252 MHz with the Perkin-Elmer spectrometer with boron trifluoride etherate as external standard. After measurement the materials were recovered from solution and their infrared spectra obtained. These showed that no decomposition had occurred.

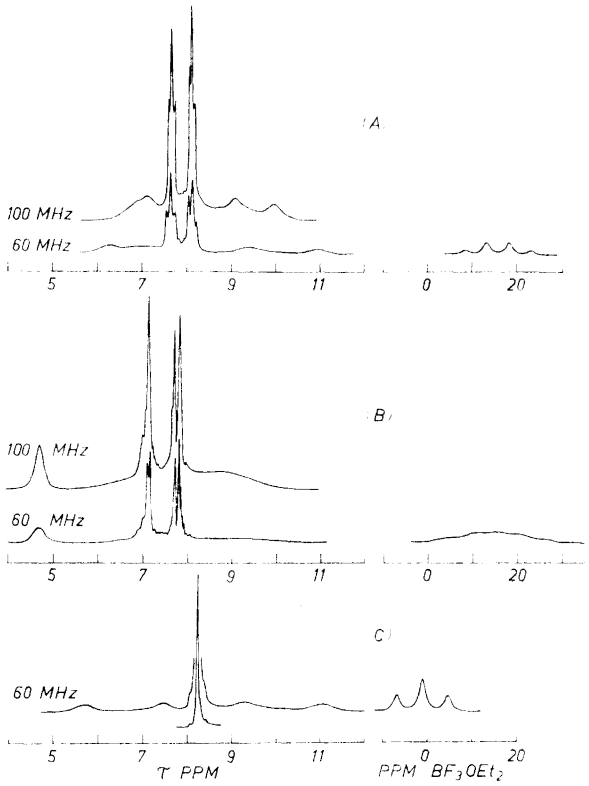
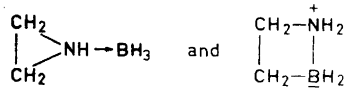


Fig. 1. ^{11}B and ^{1}H NMR spectra of (A) aziridine-borane; (B) *N*-(2-aminoethyl)aziridine-bisborane; (C) *N*-(triethylene)-cyclotriborazane. (A) and (C) in $CDCl_3$ solution; (B) solution in mixture of d_6-Me_2SO and benzene.

RESULTS AND DISCUSSION

The ^{11}B and ^{1}H NMR spectra of compounds (I), (II), and (III) are given in Fig. 1, and the corresponding infrared spectra in Fig. 2 and Table 1.

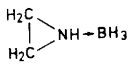
The analysis and molecular weight of substance (I) show that it has a molecular formula C_2H_8NB. Only two structures have therefore to be considered, *viz.*

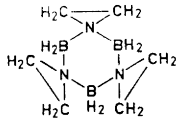


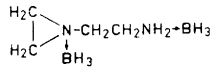
IV V

It is under these circumstances that spectroscopic methods have their most direct application to structure determination, since it is possible to compare

Table 1. Infrared spectra and partial vibrational assignments for compounds (I), (II), and (III).







3275	vs	ν-NH (A')				3249 s	antisymm. ν-NH_2
						3210 ms	symm. ν-NH_2
						3130 mw	
3105	vw	antisymm. ν-CH_2 (A' and A'')	3092	w	antisymm. ν-CH_2	3100 w	antisymm. ν-CH_2 Ring
						3090	
3015	vw	symm. ν-CH_2 (A')	3010	mw	symm. ν-CH_2	3009 w	symm. ν-CH_2
						2965 mw	antisymm. ν-CH_2 chain
						2955 mw	
						2880 w	symm. ν-CH_2
2620	w	(1374+1236)					
2370	sh		2430				
2350	sh		2380	vs	antisymm. ν-BH_2	2380 sh	antisymm. ν-BH_3
			2360			2370 vs	
2330	vs	antisymm. ν-BH_3 (A' and A'')	2320	s		2330 s	symm. ν-BH_3
2270	s	symm. ν-BH_3 (A')	2255	s	symm. ν-BH_2		
			2200	mw		2270 ms	
			1740	w			
			1680	w			
			1630	vw			
1620	w	NH-deformation (A')					
						1580 ms	NH_2-scissor
1450	s	CH_2-scissor (A')	1440	s	CH_2-scissor	1455 m	CH_2-scissor chain
						1446 w	
						1435 m	CH_2-scissor ring
						1400 w	
						1360 sh	
1374	s	CH_2-scissor (A'')				1355 m	
			1250	vs	CH_2-twist	1278 ms	CH_2-scissor
1236	m	CH_2-twist (A')	1230	s		1266 m	CH_2-twist
						1241 w	
1200	sh	Ring breathing (A')	1204	ms	Ring breathing	1196 m	Ring breathing
						1180 sh	
1190	vs	symm. BH_3 deform. (A' and A'')	1172	vvs	BH_2-scissor	1172 sh	
1154	sh		1160	s		1168 vs	symm. BH_3 deformation
		antisymm. BH_3 deform. (A')				1159 s	antisymm. BH_3 deformation
1139	mw						
						1125 vw	
						1120 w	
1126	m	CH_2-wag (A' and A'')	1119	m	CH_2-wag	1095 mw	CH_2-wag
1110	m		1092	m		1080 m	
						1058 mw	
			1044	m	B_3N_3ring?		
			1040			1035 w	
995	ms	CH_2-rock (A'')	1011	s	CH_2-rock	1008 s	CH_2-rock
954	s	CH_2-rock (A')	940	s		969 m	
						960 mw	
911	s	BH_3-rock	912	m	BH_2-wag	914 mw	BH_3-rock
						886 ms	

Table 1. Continued.

		841 m 816 m	B_3N_3ring?		
795 w 702 w 692 w	Ring modes?	730 vw		782 m	
682 w	BN-stretch (*A'*)			695 mw	BN-stretch
		449 w		468 vw	
		415 w		420 vw	

v=very; s=strong; m=medium; w=weak; sh=shoulder

the observed infrared and NMR spectra with those to be expected for structures (IV) and (V).

The ^{11}B NMR spectrum of substance (I) consists of a 1:3:3:1 quartet of chemical shift +15.8 ppm. and a J_{BH} coupling constant of 94 Hz. Structure (IV) would be expected to give rise to such a spectrum whereas a 1:2:1 triplet would be anticipated for structure (V). The chemical shift is similar in magnitude to that of related boranes,[3] *e.g.* +20.5 ppm for methylamine-borane, +15.1 for dimethylamine-borane and +9.1 for trimethylamine-borane and the coupling constant lies in the range of 90—100 Hz quoted by Schaeffer [4] for a boron atom attached to three protons. The corresponding value for a BH_2 group would lie in the 120—130 Hz range.

The ^1H spectrum of substance (I) fully confirms the conclusions from the ^{11}B spectrum. The data in Table 2 show that the resonance of a methyl or methylene group attached to nitrogen atom lies at a τ value of less than 8

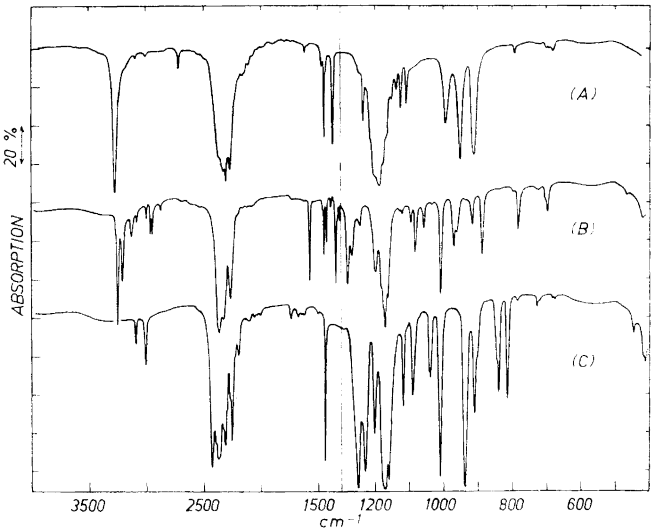
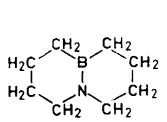


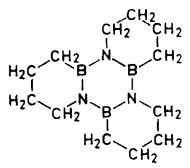
Fig. 2. Infrared spectra of (A) aziridine-borane; (B) *N*-(2-aminoethyl)-aziridine-bisborane; (C) *N*-(triethylene)cyclotriborazane. Spectra change abscissa scale at 1300 cm^{-1}.

Table 2.

		τB—CH_2 or B—CH_3	τN—CH_2 or N—CH_3
$Et_3N \cdot BMe$	(*a*)	9.36	
$EtMe_2N \cdot BMe_3$	(*a*)	10.32	7.73
$Me_3N \cdot BMe_3$	(*a*)	10.34	7.62
$Me_3N \cdot BH_3$	(*a*)		7.44
$Et_3N \cdot BH_3$	(*b*)		7.25
$Et_3N \cdot BMe_3$	(*b*)	9.48	7.51
$Me_2NH \cdot BMe_3$	(*b*)	9.62	7.60
$MeNH_2 \cdot BMe_3$	(*b*)	9.63	7.63
$NH_3 \cdot BMe_3$	(*b*)	9.68	
A, see below	(*c*)	9.1	7.1
B, » »	(*d*)	9.03	6.89
C, » »	(*e*)	9.65	7.37
D, » »	(*f*)	8.88	6.13
E, » »	(*g*)	R_1 R_2	
		Me Me 9.53	7.13
		Me Et 9.55	—
		Me Ph 10.22	—
		Me *p*-Tol 10.24	—
		Me *m*-Tol 10.23	—
		Me *o*-Tol 10.34	—
		Et Me 9.01	7.06
$B_{10}H_{13}Me$	(*h*)	9.24	—
$Me_2N \leftarrow CH_2-CH_2-NMe_2 \rightarrow BH_3$	(*i*)	7.39 (CH_3—$\overset{\uparrow BH_3}{N}$)	7.29 (CH_2—$\overset{\uparrow BH_3}{N}$)
$BH_3 \leftarrow Me_2N \cdot CH_2CH_2 \cdot NMe_2 \rightarrow BH_3$	(*i*)	7.41	6.88



A



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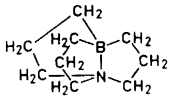

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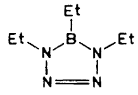

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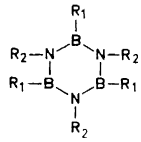

E

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ppm, whilst that of a CH_2—B group lies above 9 ppm, these correlations holding whether or not the hetero atom carries a formal electrical charge. The observed chemical shifts of approximately 7.6 and 8.1 ppm for the CH_2 groups in substance (I) are not therefore in accord with structure (V), which contains a CH_2—BH_2 group. On the other hand they are consistent with an aziridine structure and show a close similarity to the ^1H spectra of aziridine, and 1-substituted aziridines such as 1-aziridine propionitrile and methyl 1-aziridine propionate.[5] The latter two have "deceptively simple" A_2X_2 spectra with resonances about 8.3 and 8.9 ppm, arising from the protons *syn* and *anti* to the 1-substituent. Coordination of the nitrogen as in the borane will be expected to shift the CH_2 resonances downfield in a similar fashion to the downfield shift of the α-methylene groups in aliphatic amines on salt formation.[6]

The BH absorption appears as a 1:1:1:1 quartet arising from coupling of the protons to the ^{11}B nucleus. The J_{BH} is approximately 90 Hz and the chemical shift is τ 8.58 ppm. The NH group is an ill-defined hump at approximately 7.0 ppm but its presence is clearly revealed by comparison of the 60 MHz spectrum with that at 100 MHz when its position does not alter whereas the overlapping components of the BH quartet move. The value agrees with the range 7.0—7.4 found recently by Brown *et al.* for the NH group in some trialkylcyclotriborazanes.[7]

It is possible to check the validity of structure (IV) from the integral curve of the 100 MHz spectrum. The highest and lowest field peaks of a BH quartet arise solely from the ^{11}B isotope (present in 80 % concentration) and are unaffected by contributions from the ^{10}BH septets.[8] These components therefore each make a contribution of 0.6 H atom to the total integral for structure (IV). Superimposed on the lowest field peak is a further 1 H atom from the NH group. Hence the highest field component should be 0.075 of the total integral and the lowest 0.200. The observed values are 0.07_4 and 0.19_5, whereas structure (V) would require 0.05 and 0.300.

Structure (IV) is also strongly supported by the infrared spectrum (Fig. 2). The presence of an NH group is revealed by the strong band at 3278 cm^{-1} (ν_{NH}) and only a weak band at 1620 cm^{-1} (δ_{NH}). For an NH_2 group, a strong pair of bands near 3300 cm^{-1} and a strong band in the 1600 cm^{-1} region would be expected.[9] Usually, when $\overset{+}{N}H$ or $\overset{+}{N}H_2$ groups are examined, these correlations are inapplicable, since the anion of the salt is most commonly that of a mineral acid which strongly hydrogen bonds to the $\overset{+}{N}H$ group and lowers the $\overset{+}{N}H$ or $\overset{+}{N}H_2$ frequencies to below 3000 cm^{-1}. When hydrogen bonding is absent or weak, *e.g.* in the tetraphenylborates of amines[10] or in boron compounds[11] such as $(Et_3\overset{+}{N}H)_2B_{10}H_{10}^{2-}$, the correlation is a valid one.

The CH_2 stretching frequencies are particularly weak. There is no absorption between 3000 and 2900 cm^{-1}, but there are two small peaks at 3105 and 3015 cm^{-1} which can be assigned to the antisymmetric and symmetric stretching modes of the methylene groups. No data are available for the

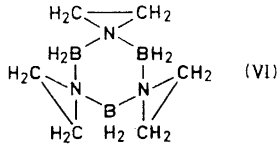
ν-CH_2 frequencies of either aziridinium or azaboretidine rings. However, it would be expected that they would not differ greatly from those of the corresponding hydrocarbons, since all the ring atoms have the same hybridization, although the presence of hetero atoms might affect the intensities.[12] For example the stretching frequencies of the CH_2 groups in amines are similar to those of hydrocarbons and change by less than 20 cm^{-1} on salt formation.[13] Bellamy quotes the range 3077—3058 and 3012—3003 for cyclopropane rings [14] and states that the strain in cyclobutane is insufficient to raise the CH stretching frequency above 3000 cm^{-1}.[15] Moreover, the CH stretching frequencies of aziridine and *N*-methylaziridine have been reported [16] in the range 3199—3000 cm^{-1} and Tempé has observed [17] at least one band in the range 3080—3050 for thirteen *N*-substituted aziridines. The observed CH frequencies therefore are consistent only with structure (IV).

A molecule of structure (IV) has a C_s symmetry. There are thirty normal modes of vibration, seventeen of A' symmetry and thirteen of A'' symmetry. However, some further simplification is possible since there are fifteen vibrations associated with the aziridine ring. The designation and description of these have been given by Katritzky and Ambler [18] for aziridine and *N*-methylaziridine. A further three vibrations, one stretching (A') and two deformation (A' and A'') are associated with the NH group. Of the remaining twelve vibrations, there are three stretching and three deformation modes of the BH_3 group which can be further subdivided into two vibrations of A' symmetry with symmetric and antisymmetric bond motion within the group, and one of A'' symmetry with antisymmetric bond movement. It is probable, however, that the A' and A'' antisymmetric vibrations will differ only slightly in frequency. There are also two BH_3 rocking modes (A' and A''), a BN stretch (A') and three vibrations associated with movement of the BH_3 group against the aziridine ring (A' and A'') or twisting of the $HNBH_3$ unit against the ring (A''). Some of these can be assigned from correlation tables [19] and by comparison with those of the model compounds, trimethylamine-borane,[20] and aziridine and *N*-methylaziridine. The antisymmetric and symmetric BH_3 stretching modes occur as strong bands at 2330 (A' and A'') and 2270 cm^{-1} (A'), the shoulders on the high frequency side partly arising from the $^{10}BH_3$ components for which a frequency increase of about 10 cm^{-1} can be calculated. The first overtone of the 1190 cm^{-1} band will also lie in this region. The corresponding symmetric and antisymmetric BH_3 deformation modes appear as a broad band at 1190 (A' and A'') while the strong band at 911 cm^{-1} is a BH_3 rocking mode. The corresponding band in trimethylamine-borane is at 915 cm^{-1}. The B—N stretching vibration cannot be assigned with certainty but by analogy to the assignment of Taylor for trimethylamine-borane it may be the weak band at 682 cm^{-1}.

The assignment of the remaining bands to CH_2, CC and CN modes is much less definite. However, the CH_2-scissoring vibration is remarkably sharp and occurs at 1450 cm^{-1}, with a second CH_2-scissoring vibration lying at 1374 cm^{-1}. The band at 1236 cm^{-1} is by analogy to aziridine probably a CH_2-twisting vibration, while the ring breathing mode occurs as a shoulder at 1200 cm^{-1} on the side of the BH_3-deformation band. The bands at 1126 and 1110 cm^{-1} can be assigned as CH_2-wagging modes, and those at 995 and 954 cm^{-1} as

CH_2 rocking modes while the weak bands in the 800—700 cm^{-1} range are probably ring deformations.

Substance (III), obtained from aziridine-borane by reflux in benzene solution, had a molecular weight corresponding to a trimer of the starting borane less six hydrogens. It seemed likely therefore that it was a cyclotriborazane of structure (VI)



(VI)

This view is supported convincingly from both the NMR and infrared spectra.

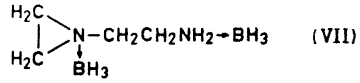
The ^{11}B NMR spectrum consists of a 1:2:1 triplet of chemical shift —1.3 ppm relative to boron trifluoride etherate and with a J_{BH} coupling constant of 110 Hz. This shows that there is a BH_2 group present and the chemical shift is adequately close to that of BH_2 groups in similar environments,[21] *e.g.* $B_3H_6(NHMe)_3$, +6.2 ppm, J_{BH} 101 Hz; $BH_2(NMe_2)_2BH_2$, —4.6 ppm, J_{BH} 113 Hz.

The ^1H NMR spectrum shows a single sharp peak of chemical shift τ 8.26 ppm, arising from CH_2 groups all in the same magnetic environment, as required by structure (VI). The BH absorption consists of the expected quartet with a chemical shift of 8.42 ppm and a coupling constant of about 110 Hz. Using a similar argument to that for aziridine-borane the integral of the highest field component of the BH quartet should be 0.067 of the total integral for structure (VI). The observed value is 0.06_2.

The infrared spectrum of compound (III) shows a number of similarities to that of aziridine-borane arising partly from the presence of aziridine rings and partly from the closeness of BH_2 and BH_3 frequencies. Thus, the ν-CH_2 stretching bands at 3092 and 3010 cm^{-1} are comparable to those observed with aziridine-borane but are of greater intensity, confirming the presence of aziridine rings. The antisymmetric and symmetric BH_2 stretching modes occur as a group of bands around 2380 cm^{-1}, the complexity arising presumably because of coupling between the three BH_2 vibrators. The BH_2-scissoring vibration occurs as a very intense band at 1172 cm^{-1} with the band at 1160 cm^{-1} probably also being a BH_2-scissoring mode. The only other BH_2 mode assignable with confidence is the wagging vibration, which is found as a medium strength band at 912 cm^{-1}.

The CH_2-scissoring vibration is at 1440 cm^{-1}, the CH_2-twisting modes at 1250 and 1230 cm^{-1} while the aziridine ring breathing vibration lies at 1204 cm^{-1}. Methylene wagging and rocking vibrations can be assigned to the bands at 1119, 1092 cm^{-1} and 1011, 940 cm^{-1} and have similar values to those observed for aziridine-borane. The only bands of reasonable intensity not accounted for are at 1040, 841, and 816 cm^{-1} and these may be tentatively associated with the borazane ring. Similar bands are reported by Burg and Sandhu [22] for the spectrum of *N*-(hexamethyl)-cyclotriborazane and that at 1068 cm^{-1} is assigned to a ring vibration.

Compound (II) is formed from *N*-(2-aminoethyl)-aziridine by a similar reaction to that of aziridine and may therefore be given the structure (VII). This structure



(VII)

is consistent with both the NMR and infrared spectra of the substance.

The ^{11}B NMR spectrum shows a broad absorption centred on a chemical shift of 17 ppm and with a number of poorly resolved maxima spaced by approximately 100 Hz. The spectrum is not incompatible with two overlapping 1:3:3:1 quartets of J_{BH} coupling constant about 100 Hz such as would be expected for structure (VII).

The ^1H NMR spectrum consists of a broad peak at τ 4.71 ppm of intensity equivalent to two protons, a sharp peak (at 100 MHz) at 7.15 ppm equivalent to four protons and two peaks with maxima at 7.74 and 7.84 ppm, both of two proton magnitude. Underlying these last three peaks is a broad shallow absorption whose maximum is at about 8.8 ppm. which arises from the BH protons.

Comparison of the observed chemical shifts with those given by Åkerfeldt *et al.*[1] for related compounds shows that the 7.15 ppm absorption comes from the two CH_2 groups of the open chain while the 7.74 and 7.84 peaks originate in the aziridine ring protons, which are *syn* and *anti* with respect to the BH_3 group attached to the aziridine nitrogen atom.

The infrared spectrum cannot be assigned in detail. However, the presence of an NH_2 group is shown clearly by the antisymmetric and symmetric NH_2-stretching bands at 3249 and 3210 cm^{-1} together with the NH_2 scissoring band at 1580 cm^{-1}. The aziridine ring CH_2 groups reveal themselves by the stretching bands at 3100, 3090, and 3009 cm^{-1} while the stretching vibrations of the chain methylenes appear as bands at the expected frequencies, *viz.* 2965, 2955, and 2880 cm^{-1}. The differentiation of methylenes is also shown in the deformation region where there are bands at 1455 and 1435 cm^{-1} which arise from the open chain and aziridine CH_2 groups, respectively.

The vibrations of the BH_3 groups lie in the same regions as those of aziridine-borane, *viz.* 2370, 2330, 2270 cm^{-1} for the stretching vibrations, 1168 and 1159 cm^{-1} for deformation modes, and 914 cm^{-1} for the rocking vibration. There is also a moderately weak band at 695 cm^{-1} which can be assigned to the BN stretching vibration.

Assignments of the remaining bands also follow the same general trend as for aziridine-borane but there are extra bands which must be attributed to the open chain part of the molecule. Tentative allocations are given in Table 1.

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