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Trimeric 2-Aziridinyl-4,4,6-trimethyl-1,3,2-dioxaborinane, a Stable Aminoborane

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The title compound, 2-aziridinyl-4,4,6-trimethyl-1,3,2-dioxaborinane, was prepared by treating 4,4,6-trimethyl-1,3,2-dioxaborinane with aziridine and from the reaction of 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane with 1-aziridinyllithium. Unlike 2-dimethylamino-4,4,6-trimethyl-1,3,2-dioxaborinane[1] which readily undergoes hydrolysis, the title compound is not affected even in boiling alcoholic sodium hydroxide. The ^{11}B nmr, ^{1}H nmr, molecular weight data, mass spectroscopy, infrared spectroscopy, and chemical reactions indicate that the title compound is a trimeric aminoborane, unique in that it contains no hydrogen or halogen substituents on either boron or nitrogen.

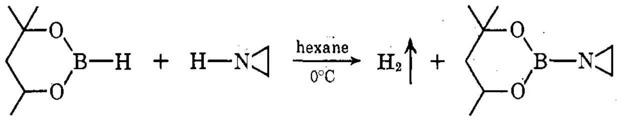
Introduction

The nature of the B–N bond in aminoboranes has been thoroughly investigated and evidence of multiple-bond character has been documented by numerous workers.[2] The stability of aminoboranes with respect to chemical degradation is attributed partially to multiple-bond character of the B–N bond but primarily to association and steric effects. Bulky substituents on either boron or nitrogen generally add to the stability of the aminoborane species although reducing the degree of association.

All of the reported trimeric aminoboranes appear to have either hydrogen or halogen (or both) bonded to the basic B–N grouping, a presumed steric requirement. In this paper we report the synthesis and characterization of a stable, trimeric aminoborane having no hydrogens or halogens bonded to boron or nitrogen.

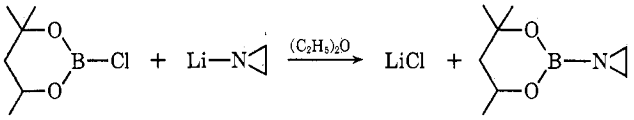
Discussion

General Data.—The reaction of 4,4,6-trimethyl-1,3,2-dioxaborinane[1] (I) with aziridine in various aprotic solvents proceeds readily at temperatures near 0° to give a good yield of 2-aziridinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (II). The aminoborane was initially isolated as a water-clear, viscous, distillable oil (bp 82° (1.5 mm)). Initial attempts to crystallize the product failed. However, after several weeks at room temperature the aminoborane solidified and could be recrystallized from any number of solvents, including acetone, benzene, acetonitrile, etc. It was subsequently found that a solid product was readily obtained when the reaction solvent was replaced with acetone and the acetone solution cooled in a Dry Ice–acetone bath.



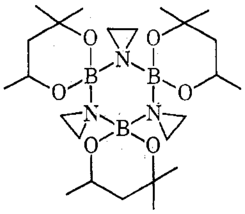
I II (1)

Another synthetic route to II was the reaction of the *B*-chloro analog of I with 1-aziridinyllithium.



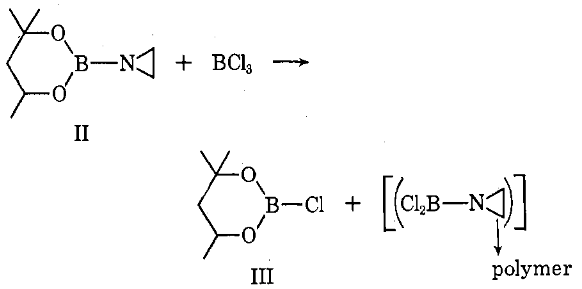
III II (2)

Aminoboranes in general are rather easily hydrolyzed to a B–OH species and the corresponding amine. Attempts to hydrolyze II resulted in only slight reaction even under such drastic conditions as heating (80°) a tetraglyme solution of II with alcoholic caustic for 24 hr. The unexpected hydrolytic stability of II suggested that the aminoborane was an associated species, probably a dimer or a trimer. Molecular weight data obtained in benzene and acetone were in accord with the trimeric formulation IV. Chemical evidence for IV was provided by the reaction of II with BCl_3, $NaOCH_3$, C_4H_9Li, and C_6H_5NCO.



IV

At −20° liquid BCl_3 reacted with solid II forming a yellow complex which decomposed at room temperature to give the *B*-chloro derivative of the parent dioxaborinane and a brown polymeric residue, presumably from the polymerization of the aziridine moiety.



II III V (3)

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* To whom correspondence should be addressed.

[1] W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966).

[2] K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Academic Press, New York, N. Y., 1965, p 48, and references therein.

Sodium methoxide in hot tetraglyme was effective in cleaving the B–N bond with the near-quantitative liberation of aziridine. Prolonged heating of II with alcoholic sodium hydroxide in THF also gave some aziridine but the bulk of the aminoborane was recovered unchanged, as was the case with concentrated hydrochloric acid in tetraglyme.

Butyllithium reacted with II in diethyl ether to form an oil which was slightly soluble in diethyl ether. Attempts to characterize this oil were unsuccessful. However, a fraction believed to be 2-butyl-4,4,6-trimethyl-1,3,2-dioxaborinane (by infrared and nmr) was obtained on distillation of the oil under high vacuum.

With phenyl isocyanate in various solvents no reaction was observed at temperatures up to 120° (refluxing xylene). When the isocyanate and II were heated neat, a polymerization of the isocyanate occurred. Normally simple aminoboranes add to isocyanates yielding *N*-boronated urea derivatives[3,4] or metathesis products.[5]

Infrared Spectra.—The infrared spectrum of the parent dioxaborinane (I) exhibits a strong absorption at 1415 cm^{-1} which we assign to the B–O stretching frequency. This band is shifted to the 1250-cm^{-1} region in the spectrum of II (Figure 1) in agreement with the expected reduction of the B–O bond order when the hydrogen is replaced with nitrogen. The absence of a new absorption band in the 1500–1400-cm^{-1} region indicates the absence of a simple monomeric aminoborane since the B–N stretching frequency in aminoboranes falls in this region. A new band of moderate intensity at 1045 cm^{-1} is assigned to the B–N absorption of the cyclotriborazine ring. The appearance of a number of new bands of moderate to strong intensities between 950 and 1200 cm^{-1} lends a degree of uncertainty to the exactness of the above assignments; however, an infrared study of ethylene derivatives of boric acid by Blau, *et al.*,[6] appears to support these assignments. Also, an examination of the infrared spectrum of the comparably structured, though monomeric, 2-dimethylamino-4,4,6-trimethyl-1,3,2-dioxaborinane (VI) reveals a strong band of 1540 cm^{-1}, which can be assigned to the B–N stretching mode, and an intense 1410-cm^{-1} absorption, assigned to the B–O group.

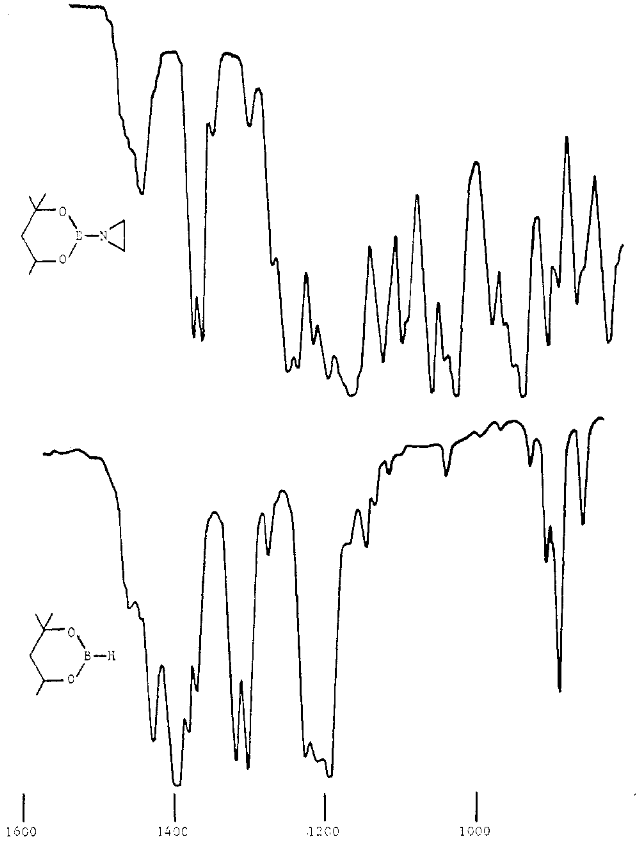
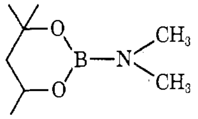


Figure 1.—Infrared spectra of $(C_6H_{12}O_2B)N(CH_2)_2$ and $(C_6H_{12}O_2B)H$ in 1500–800-cm^{-1} region.



VI

The aziridine ring protons show a stretching frequency at 3030 cm^{-1} (Figure 2) which we assign to the ν_{asym} mode. The ν_{sym} mode is overlapped by the CH_3 ν_{asym} mode at 2970 cm^{-1}. The complexity of the spectrum in the 1200-cm^{-1} region makes the assignment of the aziridine ring-breathing vibration uncertain. The spectral absorptions of I, II, and VI are shown in Table I.

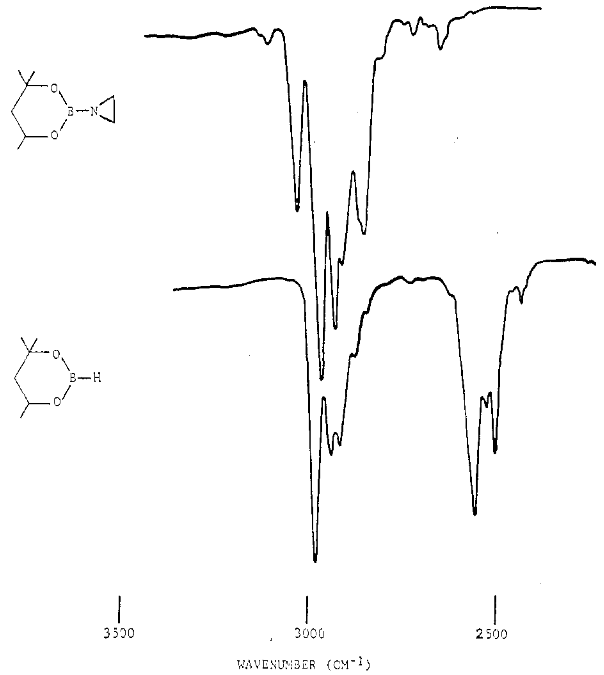


Figure 2.—C–H and B–H stretching region of $(C_6H_{12}O_2B)N(CH_2)_2$ and $(C_6H_{12}O_2B)H$.

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[3] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 2108 (1964).

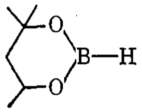
[4] H. Beyer, J. W. Dawson, H. Jenne, and K. Niedenzu, *ibid.*, 2115 (1964).

[5] T. L. Heying and H. D. Smith, Jr., *Advan. Chem. Ser.*, **No. 42**, 201 (1964).

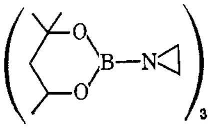
[6] J. A. Blau, W. Gerrard, M. F. Lappert, B. A. Mountfield, and H. Pyszora, *J. Chem. Soc.*, 380 (1960).

TABLE I

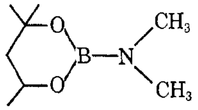
INFRARED SPECTRA OF I, II, AND VI



3005 s, 2960 m, 2940 m, 2885 sh, 2845 sh, 2580 s, 2450 m, sh, 2520 m, 1475 sh, 1470 m, 1443 s, 1415 s, 1397 s, 1385 s, 1339 s, 1322 s, 1280 w, 1241 s, 1226 s, 1212 s, 1150 w, 1140 sh, 1120 w, 1042 w, 930 w, 913 m, 904 s, 865 m, 802 m, 753 m



3020 m, 2965 s, 2922 s, 3850 m, 2790 w, 1447 m, 1380 b, s, 1350 sh, w, 1300 w, 1275 sh, m, 1255 b, s, 1227 s, 1209 s, 1180 s, 1170 s, 1135 s, 1105 s, 1073 s, 1055 sh, s, 1044 s, 987 m, 975 sh, m, 965 sh, s, 955 s, 920 m, 900 m, 870 m, 820 m, 778 m, 740 m



2970 s, 2930 s, 2910 s, 2870 s, 2790 s, 1520 s, 1470 s, 1420 s, 1370 s, 1300 s, 1270 m, 1225 s, 1200 s, 1160 s, 1100 m, 1070 m, 1020 m, 963 w, 925 w, 890 m, 853 m, 820 w, 770 m

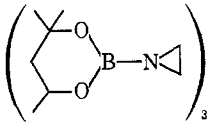
Nmr.—The ^1H nmr spectrum at 100 MHz shows a broad, poorly resolved multiplet centered at τ 6.4 with an area ratio of 1 which we assign to the single tertiary proton on the dioxaborinane ring.[7] The aziridine protons appear as a single, though somewhat broader than expected, absorption band centered at τ 8.2 when measured at 60 MHz. At 100 MHz the absorption band appears as a poorly resolved doublet centered at τ 8.2. The broadness of the band assigned to the aziridine ring protons is undoubtedly a result of the steric requirements of the dioxaborinane ring in a trimeric system. When chemical models are examined, a number of sterochemical possibilities are seen. In all cases it appears that the aziridine ring protons are not in equivalent environments due to the lack of symmetry of the adjacent dioxaborinane ring, the methyl groups of the dimethyl carbon atom being much closer to one $-CH_2$ group than to the other. The apparent splitting, although unresolved, also suggests the nonequivalence of the methylene groups as well as the protons themselves. One of the methylene protons of the dioxaborinane ring appears as two doublets centered at τ 8.60 and τ 8.74. The other proton is a part of a complex pattern near τ 9.05, the methyl region. The methyl protons appear at τ 8.90 (singlet) and τ 8.95 (doublet).

The ^{11}B nmr spectrum provided further evidence for trimerization. The spectrum consisted of a single sharp peak of chemical shift -5.18 ppm relative to boron trifluoride etherate [$+13.3$ ppm relative to $B(OCH_3)_3$]. Similar values have been reported for other cyclotriborazanes.[8,9]

Mass Spectrum.—The principal peaks in the mass spectrum of II are listed in Table II. The *m/e* 43 peak was chosen as the normalizing peak. There is some doubt as to the origin of the *m/e* 43 peak since it could logically arise from $^+BO_2$ or $HN^+(CH_2)_2$. Monomeric aminoboranes generally fragment in the mass spectrum to yield an $^+NR_2$ fragment as the most intense peak in the spectrum. This is accompanied by an M^+ fragment due to the ready extraction of a proton from a residual fragment. In the spectrum of II the *m/e* 43 peak is attributed to the $HN^+(CH_2)_2$ ion but some contribution from $^+BO_2$ is probable since a large portion of the spectrum can only be rationalized as due to the formation of hydrocarbon fragments from the dioxaborinane ring.

TABLE II[a,b]

MASS SPECTRUM OF



(P) (70 eV)

m/e	Rel intens	Positive species
507	<1.0	P_3
465	<1.0	$P_3 - N(CH_2)_2$
296	48.78	$P_2 - N(CH_2)_2$
295	24.39	$P_2 - NH(CH_2)_2$
169	58.54	P
168	17.07	P − H
154	24.39	$P - CH_3$
114	58.54	
113	24.39	
112	17.07	
111	12.20	
110	17.07	
88	39.02	
87	48.78	
86	14.63	
84	12.20	
83	73.17	
82	14.63	
70	62.20	
69	21.95	
68	12.20	
67	14.63	
59	10.98	
56	15.85	
55	93.90	
45	19.51	
44	39.02	
43	100.00	$HN(CH_2)_2$, (BO_2)
42	90.24	$N(CH_2)_2$
41	68.29	
39	20.73	
29	14.63	
28	24.39	
27	14.63	

[a] Spectrum obtained at 70 eV. [b] Major peaks only.

Evidence for the presence of a trimeric species is provided by the presence of very weak peaks at *m/e* 507 and 465 arising from the M^+ ion of the trimer and the trimer minus an aziridine fragment, respectively. The peak at *m/e* 296 is attributed to the dimer ($M^+ = 338$) minus an aziridine fragment. The monomer parent ion appears at *m/e* 169 and is relatively intense.

A complete interpretation of the mass spectrum cannot be made at this time because of the lack of in-

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[7] See W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966), for a nmr analysis of I.

[8] D. F. Gaines and R. Schaeffer, *ibid.*, **85**, 3592 (1963).

[9] R. L. Williams, *Acta Chem. Scand.*, **23**, 149 (1969).

formation on the behavior of the dioxaborinane ring system in the mass spectrograph.

Experimental Section

Apparatus and Materials.—The infrared spectra were measured on a Perkin-Elmer 257 grating spectrometer or the Model 137B Infracord. Mass spectra were obtained using a Hitachi RMU-6 spectrometer at 70 eV. Proton (^{1}H) and boron (^{11}B) nmr spectra were obtained with a Varian HA-100 spectrometer, ^{1}H at 100 MHz and ^{11}B at 32.1 MHz. Proton spectra were also obtained at 60 MHz using a Varian T-60 or A-60 instrument. Molecular weights were obtained with a Mechrolab osmometer, Model 301A, at 37°. Elemental analyses were obtained from Galbraith Microanalytical Laboratory, Knoxville, Tenn. The mass spectral analyses were performed by Dr. Dwight Fisher of West Coast Technical Service, San Gabriel, Calif.

4,4,6-Trimethyl-1,3,2-dioxaborinane (I).[10]—To a 1-l. three-necked flask, equipped with a condenser, mechanical stirrer, and 250-ml dropping funnel, was added 250 ml of *dry* tetraglyme and 24.0 g (0.63 mol) of lithium aluminum hydride. (*Caution!* The addition of lithium aluminum hydride to tetraglyme should be done slowly, with stirring and cooling, to avoid overheating and ignition of the $LiAlH_4$.) The mixture was heated to 100–150° under a slow nitrogen purge and 150 g (0.56 mol) of 2,2′-oxybis(4,4,6-trimethyl-1,3,2-dioxaborinane) was added dropwise over a 40-min period. The product was rapidly removed from the reaction pot while still hot by vacuum distillation and redistilled at reduced pressure (bp 64° (82 mm), 57° (55 mm); lit.[1] bp 50–52.5° (46 mm)). Infrared and nmr spectra verified the purity of the product[10] (yield >60%).

2-Aziridinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (II). **Method A.**—A solution of 8.6 g (0.2 mol) of aziridine in 20 ml of hexane was added dropwise to a solution of 25.4 g (0.2 mol) of I in 100 ml of hexane at 0°. The addition required 1 hr, and the reaction was considered complete on cessation of H_2 evolution. The hexane was distilled off at atmospheric pressure and the residue, a clear viscous liquid, was vacuum distilled (bp 82° (1.5 mm)). The infrared spectrum of the product was free of N–H and B–H absorptions. The absence of a strong absorption band in the 1400–1500-cm^{-1} region, characteristic of the B–N bond in monomeric aminoboranes, suggested that the compound was associated. The ^{1}H nmr spectrum showed the expected absorptions at τ 6.4 (ring CH), 8.2 (aziridine CH_2), 8.90, and 8.95 (methyl groups); mp 82–83°. *Anal.* Calcd for $C_8H_{16}BNO_2$: C, 56.85; H, 9.54; B, 6.40; N, 8.30; O, 18.93. Found: C, 56.69; H, 9.89; B, 6.47; N, 8.19.

Method B.—The procedure was generally the same as above with the exception that when the reaction was complete, the solvent was replaced with acetone and the acetone solution cooled to −80°. An off-white solid separated and was collected on a fritted-glass filter and recrystallized from hot methanol.

Method C.—An ether solution of 16.2 g of 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane was added dropwise to an ether suspension of 1-aziridinyllithium, prepared by adding 7.5 g of C_4H_9Li in hexane to 4.1 g of aziridine in diethyl ether. The resulting product was obtained as a semisolid by filtering the reaction mixture to remove the LiCl and concentrating the filtrate. The product was crystallized from acetone at −80°. Infrared, nmr data, and the melting point were used to characterize the product; yield 3.0 g (18%).

2-Dimethylamino-4,4,6-trimethyl-1,3,2-dioxaborinane (IV).—Equimolar amounts of dimethylamine and 4,4,6-trimethyl-1,3,2-dioxaborinane were allowed to react as described above for the preparation of II. The boiling point and infrared spectrum of VI were in agreement with the literature values.[1]

Reaction of II with BCl_3.—A 100-ml round-bottomed flask containing 0.85 g (0.005 mol) of II was connected to a standard high-vacuum line and evacuated. The flask was then cooled to −196° and 0.005 mol of BCl_3 was condensed in. The contents of the flask reacted at −20° to form a yellow solid which on further warming yielded a clear liquid and a yellow solid. The liquid was removed under high vacuum and identified by its infrared spectrum as 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane.

Reaction of II with $NaOCH_3$.—An excess of sodium methoxide (approximately 20% excess) was mixed with 0.4 g of II in a 50-ml boiling flask and the mixture was covered with 15 ml of tetraglyme. The flask was heated to 150–160° at which time gas evolution was observed. The gas was collected at −196° and an infrared spectrum identified it as aziridine. The yield was approximately 60% theory based on the weight of II.

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[10] A slight modification of the procedure by R. H. Fish, *J. Amer. Chem. Soc.*, **90**, 4435 (1968).