the exclusive products of the reaction, the latter appears to be at least the predominant product. Infrared: IVa: 1613, 1442, ν_{BN} 1402 cm^{-1}; IVb: 1611, 1445, ν_{BN} 1403 cm^{-1}.

Bromination of B-Tri-2,6-xylyl-N-trimethylborazine.—The same molar ratios and the same technique as described above were employed in the bromination of compound I; the tribromo derivative $C_{27}H_{33}B_3N_3Br_3$ (V) was isolated from the reaction mixture but not the dibromo derivative. Infrared: 1595, 1448, ν_{BN} 1402 cm^{-1}.

Stability to Hydrolysis.—A weighed sample of I was dissolved in the dioxane (95%)-water (5%) mixed solvent. After 1 month the solvent was gradually replaced by water. The crystal formed was collected by filtration on a sintered-glass funnel, washed with a small amount of methanol, dried under vacuum, and weighed (recovery: 100%; mp 282.5-283.5°; *Anal.* C, 74.68; H, 8.59; N, 9.74; mol wt, 439). The same technique was also applied to the hydrolysis experiments in the dioxane (95%)-1 *N* NaOH (5%) and the dioxane (95%)-1 *N* HCl (5%) solution after 150 hr (each recovery: 100%). All recovered crystals were identical with starting borazine as shown by melting point measurement, infrared, proton nuclear magnetic resonance spectra, and elemental analyses.

Physicochemical Determination.—Infrared spectra were recorded in carbon tetrachloride and carbon disulfide solution on a DS-201B spectrophotometer from Japan Spectroscopic Co., Ltd., Tokyo. Proton magnetic resonance spectra were taken with a Varian A-60 high-resolution nmr spectrometer operating at 60 Mc. In these experiments, carbon tetrachloride solutions were used with tetramethylsilane as an internal reference. Ultraviolet spectra were recorded in *n*-heptane solution using a Beckman DK-2A ratio recording spectrophotometer from Beckman Instruments Inc. Molecular weights were determined by a vapor pressure osmometer, Model 301A, from Mechrolab Inc.

Acknowledgment.—The author wishes to express his sincere thanks to Dr. H. Watanabe, Dr. T. Nakagawa, and Dr. K. Takeda for many helpful discussions and suggestions during this work.

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A Nuclear Magnetic Resonance Study of Hydrogen Bonding in Tris(2-N-methylaminoethyl) Borate and Similar Compounds[1]

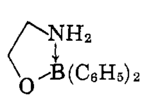
BY DEVON W. MEEK AND CHARLES S. SPRINGER, JR.

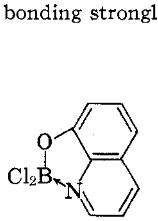
Received October 26, 1965

Tris(2-aminoethyl) borate, $B(OCH_2CH_2NH_2)_3$, and the analogous N-methylamino and N,N-dimethylamino compounds have been prepared by the transesterification of methyl borate with the appropriate 2-aminoethanol. The nuclear magnetic resonance spectra show that extensive association of the terminal amino groups occurs in pure tris(N-methylaminoethyl) borate and that this association can be broken apart by heating to 160° or by dissolution in polar organic solvents such as triethylamine or acetonitrile. In order to determine whether the association results from hydrogen bonding or internal B-N coordination, several model systems have been investigated. The spectra of $NH_2C_2H_5\cdot BF_3$, piperidine$\cdot BF_3$, and $(C_6H_5)_2BOCH_2CH_2NH_2$ in acetonitrile contain very complicated NCH_2 peaks and broad NH peaks which appear at low applied magnetic field (τ 5.26-5.56). The broadening of the NH peak in the boron-nitrogen adducts is attributed to the effect of the N^{14} quadrupole, whereas the complex splitting of the NCH_2 multiplet is attributed to coupling with B^{11} in the dative bond with nitrogen and possibly with the nitrogen protons. The spectra of $B(OCH_2CH_2NH_2)_3$ and $B(OCH_2CH_2NHCH_3)_3$, on the other hand, show sharp NH peaks at somewhat higher applied magnetic fields (τ 7.84, 6.78) and contain two sharp triplets attributed to the two sets of methylene protons in the $-O-CH_2-CH_2-N<$ units (τ_{OCH_2} 6.26-6.55; τ_{NCH_2} 7.23-7.57). The N-H peak of $B(OCH_2CH_2NHCH_3)_3$ appears as a sharp singlet in acetonitrile solutions owing to rapid exchange of the amine proton. Evidence is presented that the exchange is catalyzed by a trace (<8.7 ppm) of water in the hygroscopic solvent, acetonitrile, even after rigorous drying. All of the data indicate that intermolecular hydrogen bonding strongly predominates over $N\rightarrow B$ dative bonding in the association of $B(OCH_2CH_2NHCH_3)_3$.

Introduction

The B-N dative bond is one of the most common in nonmetallic coordination compounds. Several types of boron compounds which contain an aminoethyl or similar donor linkage have been reported to form internal[2] B-N dative bonds. Typical examples are 2-aminoethyl diphenylboronite (I)[3,4] and 8-oxyquinoline dichloroboronite (II).[5]


I


II

As a result of transannular interaction from the confined nitrogen atom, the boron derivatives of diethanolamine[4,6,7] and triethanolamine[7,8-10] have been reported to form B-N bonds in structures III and IV. However,

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[1] The authors gratefully acknowledge the support by Grant DA-ARO-D-31-124-G500 from the U. S. Army Research Office (Durham).

[2] Internal coordination, as used in this paper, refers to formation of a chelate within the molecule itself.

[3] R. L. Letsinger and I. Skoog, *J. Am. Chem. Soc.*, **77**, 2491 (1955).

[4] M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956).

[5] H. K. Soha, *J. Inorg. Nucl. Chem.*, **26**, 1617 (1964).

[6] O. C. Musgrave and T. O. Park, *Chem. Ind.* (London), 1552 (1955).

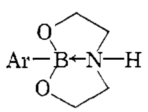
[7] P. M. Maithis, *Chem. Rev.*, **62**, 223 (1962).

[8] H. C. Brown and E. A. Fletcher, *J. Am. Chem. Soc.*, **73**, 2808 (1951).

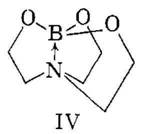
[9] H. Steinberg and D. L. Hunter, *ibid.*, **82**, 853 (1960).

[10] P. Castle, R. Stoesser, and E. F. Westrum, Jr., *J. Phys. Chem.*, **68**, 47 (1964).

the chelation of nitrogen to boron has not been established conclusively in any of these compounds.

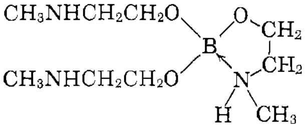


III



IV

A structure (V) with an internal B–N dative bond can be drawn for some tris(aminoalkyl) borates, B[O-(CH$_2$)$_x$NR$_2$]$_3$, and attempts have been made to use them as curing agents for epoxy resins on the assumption that such a bond exists.[11] However, because of the reduced acidity of boron in the BO$_3$ unit due to pπ–pπ back-bonding, of the simple alkyl compounds only methyl borate has been reported to form adducts, and then only with the most basic amines.[4,12–14]



V

Both B(OCH$_2$CH$_2$NH$_2$)$_3$ and B(OCH$_2$CH$_2$NHCH$_3$)$_3$, which were prepared in this study, are strongly associated at room temperature. A nuclear magnetic resonance study was initiated to determine the types and extent of intermolecular and/or intramolecular association in a selected series of tris(2-aminoethyl) borates. The nmr spectra of the compounds, when compared with the spectra of compounds with known nitrogen to boron dative bonds, indicate that no such bonds exist in this series of aminoborates.

Experimental Section

Reagents.—The 2-aminoethanols were obtained commercially and purified by vacuum distillation. Methyl borate was distilled at atmospheric pressure directly into the reaction vessels in order to minimize hydrolysis. Commercial acetonitrile was purified by the procedure of Muney and Coetzee.[15] The acetonitrile used as solvent was analyzed for water content with Karl Fischer reagent which previously had been standardized with a water-in-methanol solution. The water content was found to be less than the minimum measurable amount, which was 3.8×10^{-4} *M* (8.7 ppm; 2×10^{-5} mole fraction).

The C$_2$H$_5$NH$_2$·BF$_3$ and C$_5$H$_{10}$NH·BF$_3$ adducts were obtained from Alfa Inorganics and used without further treatment. 2-Aminoethyl diphenylboronite was prepared and recrystallized from hot ethanol. The melting point (187–188°) agreed with the literature value.[3]

Preparation of Tris(2-aminoethyl) Borates.—The three compounds B(OCH$_2$CH$_2$NH$_2$)$_3$, B(OCH$_2$CH$_2$NHCH$_3$)$_3$, and B[OCH$_2$CH$_2$N(CH$_3$)$_2$]$_3$ were prepared by transesterification of methyl borate with the appropriate 2-aminoethanol.[16] The compounds were purified by vacuum distillation and protected from atmospheric moisture.

Tris(2-N,N-dimethylaminoethyl) borate is a colorless liquid which distilled at 125–126° (2.5 mm).

Anal. Calcd for C$_{12}$H$_{30}$BN$_3$O$_3$: C, 52.27; H, 10.99; N, 15.27. Found: C, 52.11; H, 11.08; H, 15.22.

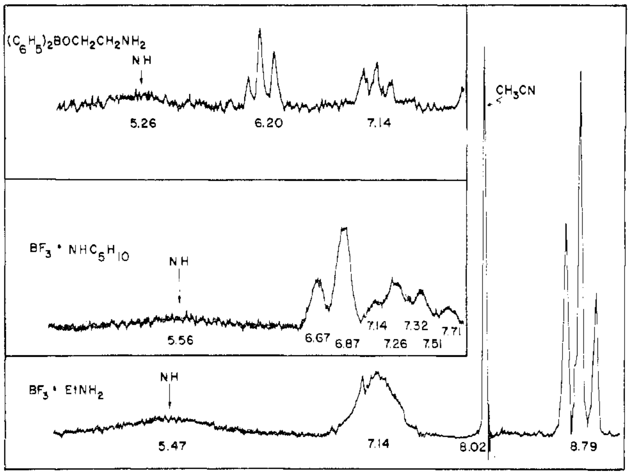


Figure 1.—Portions of the proton nmr spectra of BF$_3$·NH(C$_2$H$_5$)$_2$, BF$_3$·NHC$_5$H$_{10}$, and (C$_6$H$_5$)$_2$BOCH$_2$CH$_2$NH$_2$ in acetonitrile. The numbers under the resonance peaks are the chemical shifts (τ, ppm) relative to tetramethylsilane = 10.0. The acetonitrile peak is omitted from the two upper spectra.

Tris(2-N-methylaminoethyl) borate is a colorless, viscous oil which distilled at 85–87° (2 mm).

Anal. Calcd for C$_9$H$_{24}$BN$_3$O$_3$: C, 46.37; H, 10.38; N, 18.02. Found: C, 46.55; H, 10.49; N, 17.88.

Tris(aminoethyl) borate was a white crystalline solid which melted at 95°. This compound hydrolyzed too rapidly for accurate analyses to be obtained. However, its melting point, in a sealed tube, agreed with the literature value.[17]

The three compounds were further characterized by their infrared and nmr spectra.

Nmr Spectra.—All nmr spectra were run on a Varian A-60 nmr spectrometer with a 60-Mc probe. All spectra were run at 40° unless otherwise stated. For those run at different temperatures, the Varian A-60 variable temperature controller was employed.

The samples were prepared in a drybox which was flushed continuously with dry nitrogen. For the studies in which the exact concentrations were critical, the various components of each solution were weighed individually and all transfers were done in the drybox.

Semiprecision glass nmr tubes, 17.8 cm × 5 mm (Varian Associates), were filled in a drybox with micropipets.

All nmr peak positions are given in τ units (parts per million relative to tetramethylsilane = 10) and are measured with an accuracy of ±0.01. The peak positions of triplets are given as the position of the central component. Those of quartets are given as the center of symmetry of the positions of the four components. The multiplets in the spectra exhibit large enough chemical shift differences and are resolved cleanly so that the center-of-gravity rule need not be applied.

All spectra were calibrated with tetramethylsilane or some other sharp peak, the position of which had been previously calibrated relative to TMS (notably, CH$_3$CN or B(OCH$_3$)$_3$).

Results

The principal regions of the proton nmr spectra of three compounds which serve as model compounds and are known to contain B–N dative bonds are reproduced in Figure 1. Two especially distinguishing features in the spectra are: (a) the broadness and low τ values of the N–H peak and (b) the complex nature of the resonance peak in the N–CH$_2$ region.

The broad N–H peak can be attributed to the effect of the N^{14} quadrupole which is very common for pro-

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[11] British Patent 928,835 (1963).

[12] S. V. Urs and E. S. Gould, *J. Am. Chem. Soc.*, **74**, 2948 (1952).

[13] H. Landesman and R. E. Williams, *ibid.*, **83**, 2663 (1961).

[14] D. M. Young and C. D. Anderson, U. S. Patent 3,065,236 (1962).

[15] W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).

[16] H. C. Brown, E. J. Mead, and C. J. Shoaf, *J. Am. Chem. Soc.*, **78**, 3613 (1956).

[17] L. H. Thomas, *J. Chem. Soc.*, 820 (1946).

tons bonded directly to a nitrogen atom. The broad peak signifies that the nitrogen proton is not undergoing rapid exchange with another proton. The τ values are much lower than those of uncomplexed aliphatic amines, which normally range from 8.25 to 9.50, and are consistent with a strong B–N dative bond. Coordination by the amine reduces the electron density around the nitrogen nucleus and, consequently, the hydrogen nuclear moment is deshielded, relative to the uncomplexed amine, causing it to undergo resonance at a lower applied magnetic field.

The other distinguishing feature in the spectra of the BF_3 adducts is the complex nature of the NCH_2 peaks. For example, in the $C_2H_5NH_2{\cdot}BF_3$ spectrum, instead of a sharp quartet with a coupling constant equal to that of the CH_3 triplet ($J_{HH} = 7.32$ cps), one observes a very complex peak in the region for a methylene group attached to nitrogen. Similar complex NCH_2 peaks are observed in the spectra of $C_5H_{10}NH{\cdot}BF_3$ and 2-aminoethyl diphenylboronite (Figure 1).

Recently, a similar phenomenon has been noted by Miller and Onyszchuk[18] for the triethylamine–boron trichloride adduct in chloroform. In this case, Miller attributed the spin–spin splitting to either N^{14} ($I = 1$) or B^{11} ($I = {}^3/_2$). The methylene resonance in $(C_2H_5)_3N$ would normally be split into a quartet by the methyl protons. If the nitrogen were causing the second-order splitting, 12 lines would be expected; if the boron were responsible, 16 lines would be expected. The resolution in the spectra was insufficient for the authors to decide which effect predominated even though $J_{N^{14}H}$ and $J_{B^{11}H}$ are known.

It is not possible to tell conclusively from our spectra whether the complex NCH_2 resonance results from coupling with the N^{14} or the boron nuclei. However, if N^{14} were responsible, one should observe the same type of coupling in alkylammonium salts, but no analogous coupling is observed at the α-methylene group. The only long-range H–N^{14} coupling in tetraalkylammonium salts is at the β hydrogens.[19] Very recently, three reports of B^{11}–H^1 long-range coupling have been published.[18,20,21] It seems very probable, then, that the complex NCH_2 peaks in the BF_3 adducts result from coupling with the B^{11}, B^{10}, and N–H^1 nuclei and that the spectrometer did not resolve the NCH_2 resonance into the 12 or more individual components.

Figure 2 shows the appropriate regions of the proton nuclear magnetic resonance spectra of the three tris(2-aminoethyl) borates. The only other peaks observed in each spectrum were those of the tetramethylsilane (τ 10.00) and the acetonitrile solvent (τ 8.03 ± 0.01). The signal to noise ratio in the spectrum of $B(OCH_2CH_2NH_2)_3$ is lower owing to its limited solubility in acetonitrile, but the two methylene triplets and the N–H resonance are clearly visible.

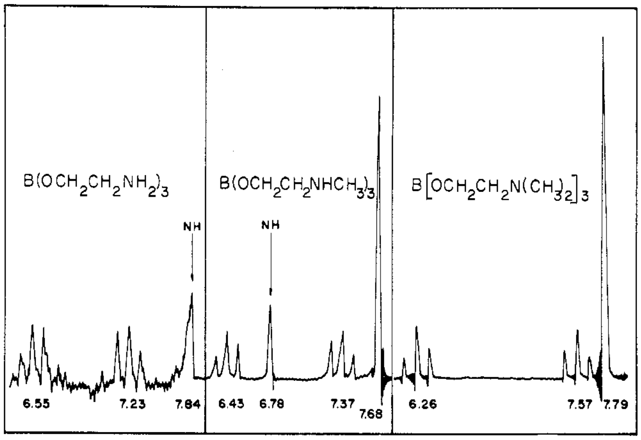

Figure 2.—Proton nmr spectra of the tris(2-aminoethyl) borates in acetonitrile. The resonance peaks of acetonitrile (solvent) and tetramethylsilane (internal standard) are omitted. The numbers under the peaks designate the chemical shifts (τ, ppm).

TABLE I

CHEMICAL SHIFTS, COUPLING CONSTANTS, AND RELATIVE AREAS OF THE RESONANCE PEAKS IN TRIS(2-AMINOETHYL) BORATES[a]

Assignment	$B(OCH_2CH_2NH_2)_3$	$B(OCH_2CH_2NHCH_3)_3$	$B[OCH_2CH_2N(CH_3)_2]_3$
CH_3 singlet			
τ, ppm		7.68	7.79
Area		2.9	6.0
NCH_2 triplet			
τ, ppm	7.23	7.37	7.57
J_{HH}, cps	5.4	5.3	6.1
Area	. . .[b]	2.0[c]	2.3
OCH_2 triplet			
τ, ppm	6.55	6.43	6.26
J_{HH}, cps	5.4	5.3	6.1
Area	. . .[b]	1.9	2.0[c]
NH singlet			
τ, ppm	7.84	6.78	
Area	. . .[b]	1.0[c]	

[a] Concentrations of $B(OCH_2CH_2NHCH_3)_3$ and $B[OCH_2CH_2N(CH_3)_2]_3$ were ~20% (by volume), whereas the solution of $B(OCH_2CH_2NH_2)_3$ is saturated at 40° (<20% by volume). [b] Spectrum of $B(OCH_2CH_2NH_2)_3$ was not integrated owing to the low signal to noise ratio. [c] Peak on which the relative areas are based.

The resonance peak assignments, coupling constants, and relative areas are presented in Table I. The spectrum of the –O–CH_2–CH_2–N< group is a simple A_2X_2 case where the protons of the –O–CH_2– group could be denoted A and the protons of the –CH_2–N group X. The coupling constant $J_{AX}(cis) = J_{AX}(trans) = 5.4$ cps for the NH_2 case, 5.3 cps for the $NHCH_3$ case, and 6.1 cps for the $N(CH_3)_2$ borate case.

The three alcohols from which the tris(2-aminoethyl) borates were prepared also exhibit simple A_2X_2 spectra. The integrated areas of the peaks correlate very well with the existence of rapid exchange between the NH and OH protons in the alcohols.

The resonance positions of the CH_3 singlets and NCH_2 triplets move systematically to higher applied magnetic fields as the number of methyl groups on nitrogen increases, whereas the positions of the OCH_2 triplets decrease. The same trends were observed in the corresponding borate esters although the positions of the OCH_2 peaks decreased to a greater extent in the esters than in the alcohols (compare Tables I and II). The

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(18) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).
(19) P. G. Gassman and D. H. Heckert, *J. Org. Chem.*, **30**, 2859 (1965).
(20) A. J. Bannister and N. N. Greenwood, *J. Chem. Soc.*, 1534 (1965).
(21) C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

TABLE II

NMR SPECTRAL DATA OF THE 2-AMINOETHANOLS IN ACETONITRILE[a]

Assignment	$HOCH_2CH_2$-NH_2	$HOCH_2CH_2$-$NHCH_3$	$HOCH_2CH_2N$-$(CH_3)_2$
CH_3 singlet			
τ, ppm		7.66	7.80
Area		2.9	5.7
NCH_2 triplet			
τ, ppm	7.37	7.44	7.64
J_{HH}, cps	5.3	5.4	6.0
Area	5.0[b]	2.1	2.3
OCH_2 triplet			
τ, ppm	6.57	6.48	6.47
J_{HH}, cps	5.3	5.4	6.0
Area	2.0[d]	2.1	3.0[c,d]
NH–OH singlet			
τ, ppm	7.42	6.88	6.43
Area	*b*	2.0[d]	*c*

[a] Concentrations of the solutions were ~20% (by volume). [b] The N–H and O–H peaks of $HOCH_2CH_2NH_2$ undergo rapid exchange, and the time-averaged peak appears in the NCH_2 triplet; the total area of the NH_2, CH_2, and OH protons equals 5 relative to that of the OCH_2 group which equals 2. [c] The O–H peak of $HOCH_2CH_2N(CH_3)_2$ appears in the OCH_2 peak; the total area of the protons equals 3. [d] Peak on which the relative areas are based.

shift of the CH_3 and NCH_2 peaks to higher τ values may be attributed directly to the increased shielding around the nitrogen from the inductive effect of each methyl group added. However, this argument does not explain the shift of the OCH_2 peaks to lower τ values. Several other workers have noted the same reversed effects on the α and β protons in some *n*-haloalkanes.[22,23] However, in isopropyl halides both the α and β protons shift to lower τ values with increasing electronegativity of the halogen.[23] These unusual substituent effects have yet to be explained satisfactorily.

Discussion

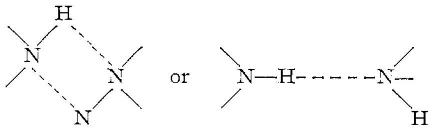
In contrast to the B–N dative-bonded compounds, the NH peaks in the borate esters are very sharp. For the N–H peaks to be as sharp as shown in Figure 2, the quadrupole broadening effect of N^{14} must have been eliminated.[24] A second important aspect of the N–H peaks is their much lower τ values than are normal for "free" N–H.[24] However, the most significant feature in the spectra of all the tris(2-aminoethyl) borates is the sharp triplet for the NCH_2 resonance. Also, the sharp CH_3 singlet in both $B(OCH_2CH_2NHCH_3)_3$ and $B[OCH_2CH_2N(CH_3)_2]_3$ shows no evidence of coupling with N^{14}, B^{11}, or B^{10}.

Thus, comparison of the spectra of the borate esters (Figure 2) with the spectra of compounds with known B–N bonds (Figure 1) can be summarized as follows. (1) The NH peaks in the spectra of the 2-aminoethyl borates are sharp, indicative of rapid exchange, whereas the NH peaks in the spectra of the BF_3 adducts are very broad. (2) The NCH_2 resonance is a sharp triplet in the spectra of the esters, in contrast to the complex nature of the NCH_2 region whenever a B–N dative bond is formed. Heitsch[21] noticed splitting of both NCH_2 and NCH_3 protons owing to coupling with B^{11} and B^{10} even in the weak $B(CH_3)_3$ complexes.

The above comparisons demonstrate that no appreciable boron–nitrogen dative bonding exists in these tris(2-aminoethyl) borates. Since the viscosity of the esters varies inversely with their molecular weights, both $B(OCH_2CH_2NH_2)_3$ and $B(OCH_2CH_2NHCH_3)_3$ must be associated more extensively than $B[OCH_2CH_2N(CH_3)_2]_3$.

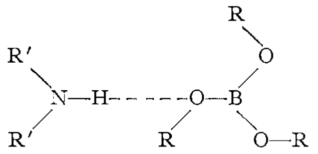
Both the physical properties and the nmr spectra of the borate esters can be rationalized if one invokes hydrogen bonding as the principal association process. Hydrogen bonding also would explain the ability of a trace amount of water in the hygroscopic solvent acetonitrile to catalyze the rapid exchange of the amine protons, the fact that the NH peaks of the borates undergo smaller chemical shifts than those affected by the stronger dative bond interaction, and finally the trend in viscosity of the borates.

There are two possible types of inter- or intramolecular hydrogen bonds possible in the borate esters. The amine proton could be hydrogen-bonded to another nitrogen atom



The nitrogen possibility is rejected because this is the type of hydrogen bonding in pure liquid diethylamine, and the NH resonance position in diethylamine (τ 9.29) occurs at a much higher τ value than the NH peaks in $B(OCH_2CH_2NH_2)_3$ and $B(OCH_2CH_2NHCH_3)_3$ (τ 7.84, 6.78, Figure 2).[25]

The other type of intermolecular (*vide infra*) hydrogen bonding possible in the borates is that to an oxygen atom.



The low τ values for the NH peak are consistent with a strong hydrogen bond to oxygen. The hydrogen-bonded species can be formed and broken rapidly to produce a small concentration of the nonhydrogen-bonded species which would be susceptible to water-catalyzed N–H exchange. (A possible scheme by which a trace of water may catalyze exchange of the amine proton is given by Springer and Meek.[25])

Nmr Spectrum of $B(OCH_2CH_2NHCH_3)_3$ as a Function of Temperature.—Figure 3 shows pertinent portions of the spectra of pure $B(OCH_2CH_2NHCH_3)_3$ at different temperatures. Both the OCH_2 and NCH_2 peaks were unresolved at 40 and 60° owing to the high viscosity of the sample at these temperatures. How-

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[22] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

[23] B. P. Bothner-By and C. Naar-Colin, *ibid.*, **80**, 1728 (1958).

[24] S. L. M. Jackman, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959.

[25] C. S. Springer, Jr., and D. W. Meek, *J. Phys. Chem.*, **70**, 481 (1965).

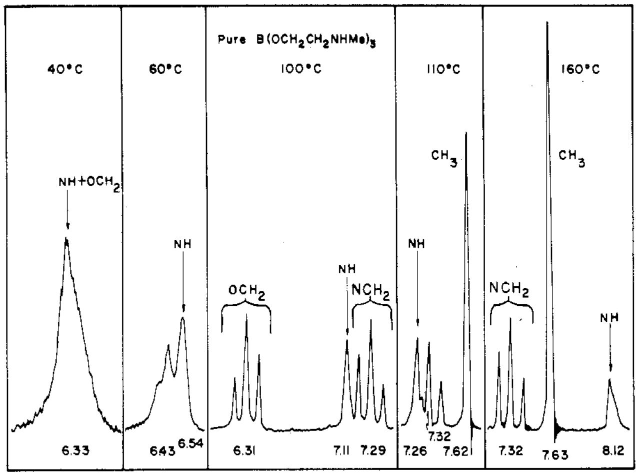

Figure 3.—Temperature dependence of selected regions, containing the N–H resonance, of the proton nmr spectrum of pure tris(2-N-methylaminoethyl) borate. Temperatures and chemical shifts of the peaks are given by the numbers in each portion of the figure.

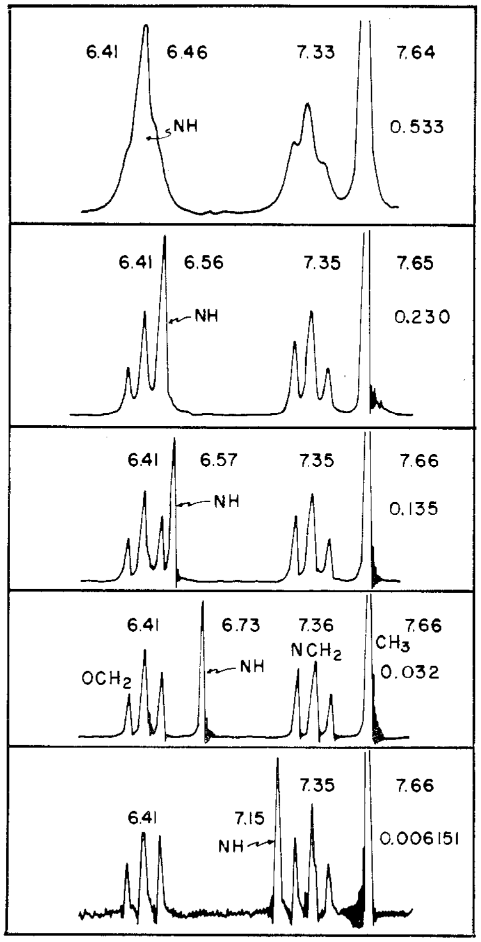

Figure 4.—Concentration dependence of selected parts of the proton nmr spectrum of tris(2-N-methylaminoethyl) borate in CH_3CN at 40°. Concentrations are given in mole fractions of $B(OCH_2CH_2NHCH_3)_3$.

ever, the spectrum is resolved clearly into the components of the triplets and the N–H peak at 100° and above. The position of the NH resonance moves systematically to higher τ values with increasing temperature.

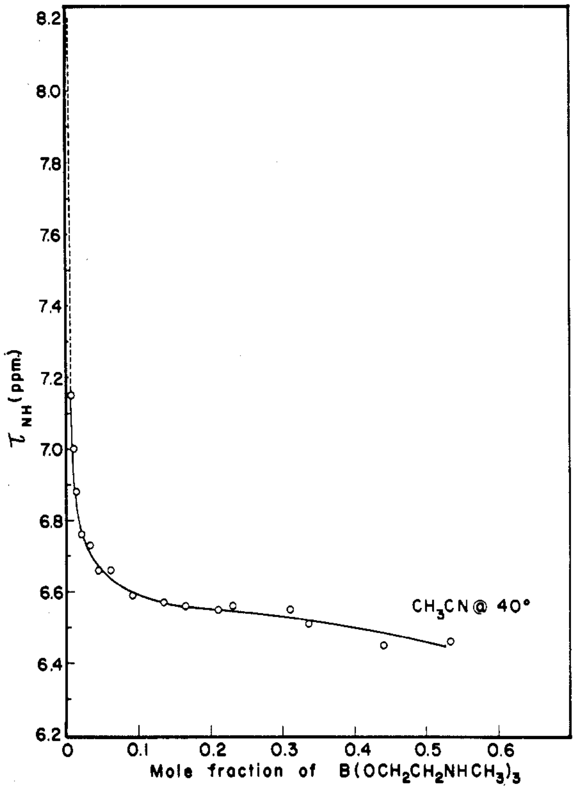

Figure 5.—Concentration dependence of the NH resonance position (τ_{NH}, ppm) in the proton nmr spectrum of tris(2-N-methylaminoethyl) borate in acetonitrile.

In the temperature dependence study, since only one NH peak is seen at all temperatures, the hydrogen-bonded protons must be in rapid equilibrium with the free amine protons. As the compound is heated, the equilibrium shifts toward the free NH species, and the resonance position moves systematically toward higher applied magnetic fields. This is consistent with a smaller degree of hydrogen bonding at the higher temperatures.

The fact that the NH peak appears so low ($\tau \sim 6.33$) at 40° indicates that $B(OCH_2CH_2NHCH_3)_3$ must exhibit extensive intermolecular hydrogen bonding at room temperature. Thus, the trend in physical properties from a white solid for $B(OCH_2CH_2NH_2)_3$ to a viscous liquid for $B(OCH_2CH_2NHCH_3)_3$ to a mobile liquid for $B[OCH_2CH_2N(CH_3)_2]_3$ is explicable.

Nmr Spectrum of $B(OCH_2CH_2NHCH_3)_3$ as a Function of Concentration in Acetonitrile.—Portions of the spectra at different concentrations are shown in Figure 4. Resolution in the spectra decreases as the concentration increases owing to the increasing viscosity of the solutions. Thus, the spectrum at a mole fraction of 0.533 is similar to that of the pure borate at 40° (Figure 3).

The resonance positions of the CH_3, OCH_2, and NCH_2 peaks remained constant, within experimental error, throughout the concentration range from 0.00615 to 0.533 mole fraction. However, the sharp NH peak of $B(OCH_2CH_2NHCH_3)_3$ in acetonitrile solution changed resonance positions smoothly from τ 6.33 in the pure compound to τ 7.15 at a mole fraction of 0.00615 (Figure 5). The strong hydrogen bonds persist to a concentration well below a mole fraction of 0.1, where they begin to be broken in favor of hydrogen bonds with the solvent. In the low-concentration region the NH resonance position increases rapidly with decreasing concentration. Thus, the solvent–solute hydrogen bonds do not affect the NH resonance as strongly as the ones between borate molecules (*vide infra*). This is quite reasonable since acetonitrile is only a moderately strong hydrogen-bond acceptor.[26–28]

Attempts to determine the equilibrium constant for the association process in acetonitrile were unsuccessful since the curve representing the plot of τ_{NH} against concentration becomes almost asymptotic at infinite dilution (Figure 5) and, therefore, makes the determination of an intercept or a meaningful slope impossible.

One can conclude that tris(2-methylaminoethyl) borate is a highly associated substance in the pure state at room temperature and that the association can be broken by heating the pure compound to 160° or by dissolving it in large amounts of acetonitrile. Since plots of the NH peak positions against concentration from both nmr and infrared studies show a continuous variation with no inflection in the curves, the association of borate molecules must involve *intermolecular* $>$N–H - - - - O$<$ hydrogen bonds rather than intramolecular ones.

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Reactions of Hexachloro- and 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatrienes with Sodium Phenoxide[1]

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Treatment of hexachlorocyclotriphosphazatriene with sodium phenoxide followed by ammonolysis afforded two isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ in comparable yields, and they were different from the third isomer obtained from an isomer of $P_3N_3(NH_2)_2Cl_4$ by phenoxylation. The three isomers of $P_3N_3(NH_2)_3(OC_6H_5)_3$ were also obtained. A similar treatment of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene afforded three isomers of $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$, and the isomer obtained in the smallest yield was also prepared by phenoxylation of an isomer of $P_3N_3(C_6H_5)_2(NH_2)_2Cl_2$. The structures of these isomers were assigned on the basis of proton magnetic resonance spectra and chromatographic adsorption sequence. The results indicate that the substitution pattern of the phenoxylation is predominantly nongeminal with a slight *cis* preference over *trans*.

Introduction

Some patterns of successive replacements of chlorine atoms in hexachlorocyclotriphosphazatriene have been examined; hence, dimethylamine reacts by nongeminal substitution,[2–4] whereas ethylenimine,[5] potassium fluoride (or fluorosulfite),[6] and mercaptide[7] follow geminal patterns. Recently, *trans*-2,4,6-trisdimethylamino-2,4,6-triphenoxycyclotriphosphazatriene was isolated[8] in 30% yield by dimethylaminolysis of the mixture produced by phenoxylation of $P_3N_3Cl_6$. For such substitutions, evaluation of the reaction parameters is hindered since low material balances were obtained.

We have studied the reactions of hexachloro- and 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene with sodium phenoxide in acetone. Not only were the reactions found to follow a nongeminal substitution pattern, but also semiquantitative evaluations of reaction parameters were made.

Results and Discussion

Hexachlorocyclotriphosphazatriene was treated with various proportions of sodium phenoxide. The complex mixture of products after chromatographic separation gave pure only chloropentaphenoxycyclotriphosphazatriene (I), mp 69–71°, and one isomer of dichlorotetraphenoxycyclotriphosphazatriene (II), mp 75–77°. The former compound[9] and the melting point (75–76°) of the latter[10] have been reported previously.

Ammonolysis of I gave aminopentaphenoxycyclotriphosphazatriene (III), which was identified by elemental analysis.

A *cis*-2,4-dichloro structure was assigned to II since

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