evacuated Kel-F T piece onto the SbF_5 that had been cooled to −196°. The SbF_5-XeF_2-HF mixture was then warmed to and kept at room temperature for 5 min to ensure complete reaction. The mixture was then cooled to −64° and HF solvent removed under vacuum at this temperature.

Preparation of $2XeF_2 \cdot AsF_5$ and $XeF_2 \cdot AsF_5$. A weighed amount of AsF_5 was distilled onto an XeF_2-HF mixture kept at −196° (*ca.* 10 mmol of XeF_2 in 10 ml of HF). The procedure was then exactly the same as for the preparation of the XeF_2-SbF_5 compounds.

Preparation of $Xe(SO_3F)_2$ and $FXeSO_3F$. Both compounds were prepared from HSO_3F and XeF_2 by the same procedure as was used for the XeF_2-SbF_5 compounds. Approximately 10 mmol of HSO_3F was used in each case. The products were stored under dry nitrogen at −78°.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work and for the award of a scholarship to G. J. S.

Registry No. $Xe(SO_3F)_2$, 25523-77-7; $FXeSO_3F$, 25519-01-1; XeF_2, 13709-36-9; ^{129}Xe, 13965-99-6; $XeF^+SbF_6^-$, 30864-32-5; $XeF^+AsF_6^-$, 26024-71-5; $Xe_2F_3^+AsF_6^-$, 21308-45-2.

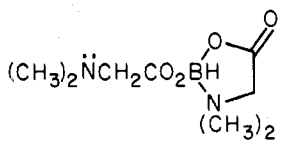
Contribution from the Chemistry Department,
University of South Dakota, Vermillion, South Dakota 57069

Cyclic Borane Derivatives of Amino Acids[1]

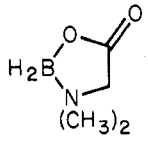
NORMAN E. MILLER

Received October 9, 1973 AIC30743S

New five- and six-member heterocycles which are formally cyclized amino acid boranes have been characterized as air-stable volatile solids. The markedly different hydrolysis rates for the two five-membered heterocycles is interpreted as arising from different mechanisms. The chemistry of the ring systems has been explored and new types of boranes have been synthesized, including cations and the novel strong base



A study of the chemistry of the cyclic borane I was begun

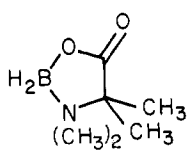


I

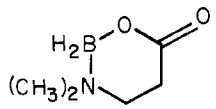
after it was isolated and characterized as an intermediate in the hydrolysis of (ethyl dimethylglycine)trimethylamineboron(1+) cation.[2] New types of boranes and several new transformations have emerged from the study and these are described in two sections, one dealing with the parent heterocycles and the other with derivatives.

Heterocyclic Amino Acid Boranes

The heterocycle I may be considered to be the cyclized product by hydrogen loss of the borane adduct of *N,N*-dimethylglycine and as such would be the first in a potentially large new class of heterocycles derivable from amino acids. Three parent homologous cyclic systems with dimethylated nitrogens have now been made, related to glycine, 2-aminoisobutyric acid, and 3-aminopropionic acid, compounds I-III.



II



III

These three are white crystalline materials, sublimable without decomposition near 100° under high vacuum. Characterizations by analysis, molecular weight, ir, nmr, and mass spectral patterns are given in the experimental details and Tables I-III. The cyclic structures are supported by the mass spectral molecular weight (P − 1 peaks), volatility, and solution molecular weight (for I). While some puckering of the ring in III might be expected, there is no nmr evidence for it. *N*-CH_3 resonance is a singlet down to −30°, explicable by planar or rapidly inverting configurations.

The methylenic protons of I are sufficiently acidic to undergo rapid exchange in D_2O solution when midly basic as shown by the collapse of the methylene proton nmr singlet in aqueous trimethylamine. This exchange was substantiated as reversible by isolation of the deuterated material and reconverting it to the normal hydrogen compound. The time scale for the nmr signal collapse was about 4 min at 37° in 10% aqueous trimethylamine, corresponding approximately to a half-life of 0.5 min. It is remarkable that the cyclization by borane can enhance the methylenic protons of dimethylglycine from no exchange in 1 *M* hydroxide[3] to that observed for I. Inductive effect of the borane normally releases electrons and decreases acidity; consequently, an explanation must be found elsewhere, perhaps in solvation and π-bonding stabilizations of the anion of I produced by proton abstraction.

The acid nature of the methylenic protons in I was employed in the first synthesis of II wherein excess sodium hydride was slurried with a solution of methyl iodide and I in dimethylformamide (eq 1). Because the product was free

(1) Presented in part at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 8-10, 1972.
(2) N. E. Miller, *J. Amer. Chem. Soc.*, 92, 4564 (1970).
(3) W. E. Thompson, R. J. Warren, I. B. Eisdorfer, and J. E. Zaremba, *J. Pharm. Sci.*, 55, 857 (1966).

Table I. Mass Spectra[a]

$(CH_3)_2NCH_2CO_2BH_2$ (I)		$(CH_3)_2NC(CH_3)_2CO_2BH_2$ (II)		$(CH_3)_2N(CH_2)_2CO_2BH_2$ (III)	
m/e	Rel intens[b]	*m/e*	Rel intens[c]	*m/e*	Rel intens[d]
				130	0.4
115	2	143	4	129	2
114 (P − 1)	57[e]	142 (P − 1)	45[e]	128 (P − 1)	32[e]
113	16	141	7	127	9
		99	12		
		98	6		
59	4	87	7	59	4
58 $(CH_3)_2NCH_2$	100	86 $(CH_3)_2NC(CH_3)_2$	100	58 $(CH_3)_2NCH_2$	100
57	4	85	7	57	8
56	15	84	43	56	14
55	4	83	14	55	7
54	6	82	17	54	4
		81	5		
		44	21	44	4
43	7	43	73	43	4
42	2.5	42	44	42	14
41	6	41	41	41	3
40	4	40	11	40	3
		39	24		
30	4.6				

[a] Commercial analysis: Morgan-Schaeffer, Montreal, Canada, using a Hitachi Perkin-Elmer RMU-6D. [b] 40° direct inlet, 50-eV bombardment. [c] 40° direct inlet, 70-eV bombardment. [d] 60° direct inlet, 70-eV bombardment. [e] The parent peak does not appear.

Table II. Infrared Absorptions, cm^{-1} [a]

$(CH_3)_2NC(CH_3)_2CO_2BH_2$ (II): 2440 m, 2360 m, 1725 s, 1405 w, 1380 m, 1375–1365 m, doublet, 1315 s, 1250 m, 1210 s, 1165 s, 1140 w, 1120 w, 1105 w, 1080 s, 1025 m, 1005 w, 970 s, 930 m, 885 m, 810 m, 770 w, 740 m

$(CH_3)_2N(CH_2)_2CO_2BH_2$ (III): 2400 m, 2350 w, 2280 w, sh, 1680 s, 1405 vw, 1380 m, 1355 s, 1320 s, 1300 w, sh, 1255 w, 1240 w, 1210 s, doublet, 1160 s, 1140 s, 1120 m, 1055 m, 1030 m, 1020 s, 1000 m, 965 m, 935 w, 900 w, 850 w, 825 m, 775 w, 735 w

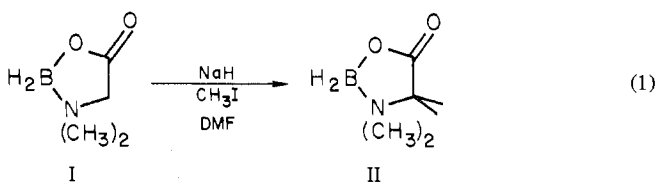
$(CH_3)_2N(BH_3)CH_2CO_2BHO_2CCH_2N(CH_3)_2$ (IV): 2500 m, 2380 m, 2320 m, doublet, 2270 m, 2060 w, 1770 s, 1715 s, 1405 m, 1325 w, 1305 w, 1285 m, 1270 m, 1240 s, 1200 m, 1160 m, 1140 m, 1125 s, 1105 m, 1070 m, 1045 m, 1025 w, 1000 s, 975 m, 965 m, 930 m, 875 s, 850 w, 830 m, 790 w, 750 m

$(CH_3)_2NHCH_2CO_2BHO_2CCH_2N(CH_3)_2^+PF_6^-$ (VI): 2520 w, 1745 s, 1700 s, 1415 m, 1325 m, 1290 s, 1265 s, 1250 w, sh, 1205 w, 1155 m, sh, 1140 s, 1125 s, 1110 m, 1075 s, 1050 w, 1025 w, 1000 s, 970 m, 925 m, 880 s, 865 s, 835 s, 785 m, 720 w

$(CH_3)_3NCH_2CO_2BHO_2CCH_2N(CH_3)_2^+PF_6^-$ (VII): 2540 w, 1765 s, 1725 s, 1400 m, multiplet, 1325 w, 1275 s, 1255 m, 1230 m, 1210 m, 1070 m, 980 m, 970 w, 930 m, 920 m, 885 s, 850 s, 780 w, 750 w, 725 w

$(CH_3)_2NHC(CH_3)_2CO_2BHO_2CC(CH_3)_2N(CH_3)_2^+PF_6^-$ (VIII): 2540 w, 1735 s, 1700 s, doublet, 1365 w, 1300 s, 1280 s, 1210 m, 1175 w, 1135 s, 1120 m, 1035 s, 1020 w, 975 m, 945–930 m, 840 s

[a] Run on a Perkin-Elmer 237B as mineral oil mulls. Absorption intensities are indicated as s (strong), m (medium), w (weak), vw (very weak), and sh (shoulder). Those absorptions in common with or masked by mineral oil are not listed.



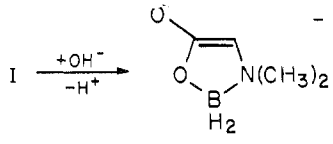
(1)

I II

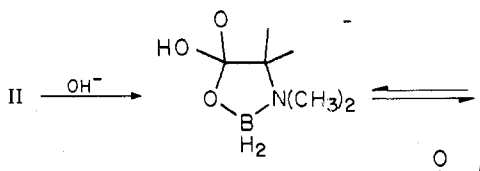
of traces of unreacted I, which the work-up would not have removed, the low yield (25–50%) may be ascribed to side reactions rather than unreactivity of I.

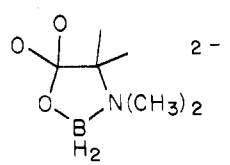
A significantly greater shelf life was observed for II and III as compared to I. (While I was nearly completely degraded in a matter of months when in screw-cap vials, II was not noticeably affected after 1 year so stored.) This is traceable to hydrolytic stabilities. Quantitative data[4] for the hydrolysis of II summarized in Tables IV and V show an approximate second-order dependence on hydroxide along with a rate three magnitudes smaller than that of I. (The very small rates and the inherent experimental problems make a closer scrutiny of the differential rate dependence difficult at this time.) Such differences in rates and hydroxide dependence require that there be different mechanisms for the hydrolyses. The rate differences can scarcely be attributed to α-methyl substitution, for example, as this feature results in a mere decrease of saponification rate for ethyl isobutyrate by one-third as compared to ethyl acetate.[5]

A tentative explanation for the rate data is that I has an anionic active intermediate resulting from methylene proton loss, while II has an active intermediate related to the ortho-acetate structure resulting from hydroxide attack and then equilibrium proton loss (see eq 2 and 3). Other borane cations have shown a second-order dependence[6] on hydroxide



(2)





(3)

(4) Obtained by Mr. Dan Herting of this department.

(5) "International Critical Tables," McGraw-Hill, New York, N. Y., 1930, p 133.

(6) (a) N. E. Miller, *Inorg. Chem.*, 8, 1693 (1969); (b) N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, *ibid.*, 8, 862 (1969).

Table III. Proton Nmr Resonances[a]

	Chem shift[b]	Solvent	Rel intens	Assignment
$(CH_3)_2\overline{NCH_2CO_2BH_2}$ (I)	3.42	CH_2Cl_2	1	$-CH_2-$
	2.76		3	$-N(CH_3)_2-$
$(CH_3)_2\overline{NC(CH_3)_2CO_2BH_2}$ (II)	2.67	CH_2Cl_2	1	$-N(CH_3)_2-$
	1.45		1	$-C(CH_3)_2-$
$H_3BN(CH_3)_2CH_2CO_2\overline{BHN(CH_3)_2CH_2CO_2}$ (IV)	3.63	CH_2Cl_2		Side chain $-CH_2-$
	3.55, 3.52 doublet			Ring $-CH_2-$
	2.81			Ring and side chain $-N(CH_3)_2$
	2.70			Ring $-N(CH_3)_2-$
$(CH_3)_2NHCH_2CO_2\overline{BHN(CH_3)_2CH_2CO_2}^+PF_6^-$ (VII)	3.97	CD_3CN	1	Side chain $-CH_2-$
	3.63		1	Ring $-CH_2-$
	2.93		3	Side chain $-N(CH_2)_2-$
	2.78, 2.72 doublet		3	Ring $-N(CH_3)_2-$
$(CH_3)_3NCH_2CO_2\overline{BHN(CH_3)_2CH_2CO_2}^+PF_6^-$ (VI)	4.13	CD_3CN	2	Side chain $-CH_2-$
	3.63		2	Ring $-CH_2$
	3.28		9	$-N(CH_3)_3$
	2.78, 2.72 doublet		6 total	$-N(CH_3)_2-$
$(CH_3)_2NHC(CH_3)_2CO_2\overline{BHN(CH_3)_2C(CH_3)_2CO_2}^+PF_6^-$ (VIII)	2.65	CD_3CN	1	(?) Ring $-N(CH_3)_2-$
	2.52, 2.40 doublet		1 total	(?) Side chain $-N(CH_3)_2-$
	1.58		1	Side chain $-C(CH_3)_2-$
	1.48		1	Ring $-C(CH_3)_2-$
$(CH_3)_2\overline{N(CH_2)_2CO_2BH_2}$ (III)	2.72	$CDCl_3$	1.17	$-N(CH_3)_2-$
	2.45, 2.82, 2.97, 3.07, 3.18[c]		1	$-(CH_2)_2-$

[a] Run on Varian A-60A nmr spectrophometer. [b] Chemical shifts in ppm *downfield* from internal tetramethylsilane. [c] Multiplet bands, the most distinct of which are listed.

Table IV. Hydrolysis of $(CH_3)_2\overline{NC(CH_3)_2CO_2BH_2}$ (II)[a] [29.8°, (OH^-) = 0.90 *M*, 3.9 mg of Substrate]

t, sec	V_t[b]	$V_\infty - V_t$	*t*, sec	V_t[b]	$V_\infty - V_t$
0		1.555	20,000	0.598	0.957
580	0.060	1.495	30,200	0.792	0.763
1,140	0.100	1.455	52,400	1.099	0.456
2,200	0.133	1.422	65,500	1.220	0.335
3,600	0.177	1.378	75,600	1.310	0.245
6,000	0.250	1.305	93,400	1.400	0.155
12,900	0.440	1.115			

[a] Pseudo-first-order rate constant, 2.37×10^{-5} sec^{-1}. [b] Gas buret reading; approximately in ml. Conversion factor is 0.895 ml/unit.

and may proceed by schemes similar to eq 3. The postulated dianion intermediates are like those proposed for second-order hydroxide dependence in alkaline hydrolyses of anilides[7a] or actylacetone[7b] as well as in the Cannizzaro reaction under certain conditions.[7c]

Synthesis of the heterocycles proceeds by three routes but none is especially clean, convenient, or well understood. The difficulties appear to stem from the bifunctionality of the ligating amino acids which permits polymer formation during synthesis. The synthetic routes may be classified as (a) cyclization displacements in borane cations with iodide and/or trimethylamine leaving groups, (b) cleavage of amino acid ester ligand, and (c) methylation of I previously described.

Displacement and Cyclization

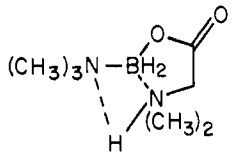
The original synthesis of I was an intramolecular displacement of trimethylamine in dilute solution[2] (eq 4). Currently, I has been obtained in fair (40-50%) yield by displacement of iodide and then trimethylamine from trimethylamine-iodoborane (eq 5 and 6). Even though yields were

$$(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5^+ \xrightarrow[-C_2H_5OH]{OH^-} (CH_3)_3NBH_2N(CH_3)_2CH_2CO_2 \rightarrow I \quad (4)$$

$$(CH_3)_4N^+(CH_3)_2NCH_2CO_2^- + (CH_3)_3NBH_2I \rightarrow (CH_3)_4N^+I^- + (CH_3)_3N + I \quad (5)$$

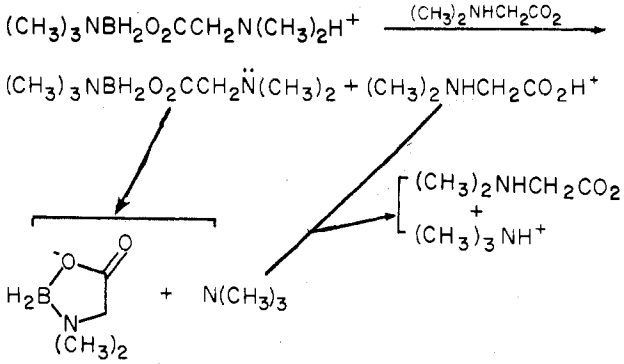
$$(CH_3)_2NHCH_2CO + (CH_3)_3NBH_2I \rightarrow (CH_3)_3NH^+I^- + I \quad (6)$$

moderate, nearly quantitative amounts of $(CH_3)_4N^+I^-$ and $(CH_3)_3NH^+I^-$ were obtained. The mechanism for transformation 6 is of interest as a four-centered intramolecular cyclization is feasible.



But other mechanisms can reasonably be suggested, such as eq 7 and 8. Evidence favoring this mechanism is the

$$(CH_3)_3NBH_2I + (CH_3)_2NHCH_2CO_2 \rightarrow (CH_3)_3NBH_2O_2CCH_2N(CH_3)_2H^+ \quad (7)$$



rather similar dynamic displacement occurring in $(CH_3)_2\overline{NCH_2CO_2BHO_2CCH_2N(CH_3)_2}$, discussed subsequently under Derivatives.

Similarly III was prepared in very low yield by reaction of 3-dimethylaminopropionic acid and trimethylamine-iodo-

(7) (a) S. S. Biechler and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 79, 4927 (1957); (b) R. G. Pearson and E. A. Mayerle, *ibid.*, 73, 926 (1951); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1950, p 350.

Table V. Hydrolysis of II–Hydroxide Dependence [29.8°; Ionic Strength 0.9]

(OH^-), M	10^5k_1, sec^{-1}	$10^5k_1/(OH^-)$, $sec^{-1}\ M^{-1}$	$10^5k_1/(OH^-)^2$, $sec^{-1}\ M^{-2}$
0.90	2.35[a]	2.61	2.90
0.60	0.860	1.43	2.4

[a] Average of two runs.

borane (eq 9). Here, less than 10% product is formed even

$$(CH_3)_2NHCH_2CH_2CO_2 + (CH_3)_3NBH_2I \rightarrow (CH_3)_3NH^+I^- + III \quad (9)$$

in very dilute solutions; most of the reaction appears to be polymerization rather than cyclization.

Cleavage of Amino Acid Ester Ligand

In attempts to prepare II by the intramolecular cyclization of a borane cation, a cleavage of the ester ligand was instead observed and II was isolated directly (eq 10). The borane

$$(CH_3)_2NC(CH_3)_2CO_2C_2H_5 + {}^1/_2B_2H_6 \rightarrow (CH_3)_2\overset{BH_3}{N}C(CH_3)_2CO_2C_2H_5 \xrightarrow[N(CH_3)_3]{I_2} II,\ C_2H_5N(CH_3)_3^+,\ (CH_3)_3NH^+ \quad (10)$$

adduct in eq 10 was prepared as a low-melting crystalline substance. Iodine was absorbed up to $^1/_2$ molar equiv by this adduct, and subsequent addition of trimethylamine led to isolation of ethyltrimethylammonium and trimethylammonium cations along with about 25% of II. Despite considerable study of experimental conditions, the yield was not improved. The reaction course remains obscure, but a cleavage of ethyl group from the ester may be inferred from the isolation of equivalent amounts of $(CH_3)_3NC_2H_5^+$ and II. It is likely that the amino acid ester–iodoborane produced by iodination undergoes the cleavage as it is known that trimethylamine–iodoborane cleaves ether at 40°.[8]

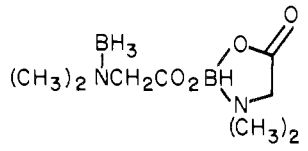
Incidentally, the rather indirect route to the cation $(CH_3)_3NBH_2N(CH_3)_2CO_2C_2H_5^+$ was attempted because the more direct method of combining the amino acid ester and trimethylamine–iodoborane did not work in benzene or chloroform.

Derivatives

The most interesting derivatives of the heterocyclic amino acid boranes resulted from attempts to synthesize the parent ring I according to a method recently reported[9] using sodium borohydride and dimethylglycine hydrochloride in refluxing glyme.

Experiments here following the reported method and also using other solvents did not give any significant amounts of I. Instead we isolated a water-insoluble white solid that analyzes for I yet has very different properties. It initially[10] was characterized as a polymer.

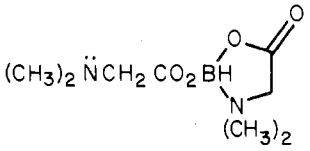
Molecular weight measurement, spectra, and chemical evidence show that the polymer is a dimer of I and has the novel structure IV. In methylene chloride a molecular weight of 230, determined by vapor pressure depression technique, agrees with the theoretical value 228.



IV

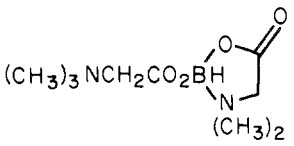
The infrared spectrum shows two carbonyl absorptions at 1705 and 1770 cm^{-1}, as well as a rather unique high BH stretch at 2500 cm^{-1}. The ^{11}B nmr spectrum consists of two approximately equal-intensity resonances, a quartet and a doublet at 6.7 ppm upfield and 5.4 ppm downfield from boron trifluoride etherate, respectively, implicating a BH_3 and a BH site in the molecule. The essential features then of the dimer were apparent from physical measurements, but the linkage of the side chain (whether as shown or *vice versa* with nitrogen bonding the ring boron) was determined from chemical arguments.

The borane group could be removed in good yield by addition of trimethylamine and subsequent volatilization of trimethylamine–borane. This transboranation was quite slow in chloroform, requiring more than 3 hr. The clear oil of low volatility which resulted on work-up was characterized by chemical arguments as the free base V. Diborane adds to

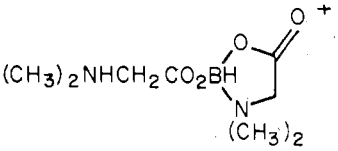


V

it rapidly to re-form IV, and methyl iodide and hydrogen bromide react to give the novel borane cations VI and VII.[11]

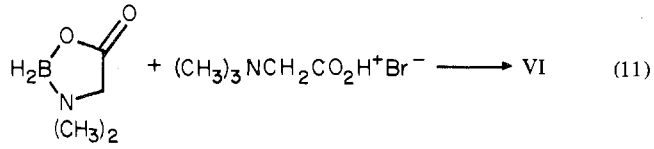


VI



VII

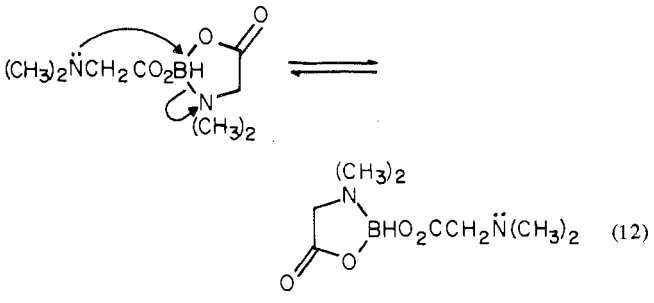
Conclusive evidence for side-chain linkage is the alternative synthesis of VI from I and betaine hydrobromide (eq 11).



(11)

Because the nitrogen is quaternized in the betaine salt, the only conceivable linkage accessible for side-chain attachment is the carboxylate, thus fixing the linkage in IV.

Proton nmr for the free base V (Figure 1) reveals rapid exchange (eq 12) between side chain and ring *N*-methyl pro-



(12)

(8) G. E. Ryschkewitsch and W. W. Lochmaier, *J. Amer. Chem. Soc.*, 90, 6260 (1968).

(9) L. F. Hohnstedt, P. J. Dolan, E. F. Rothgery, and T. G. Johans, paper presented at the 7th Midwest Regional Meeting of the American Chemical Society, St. Louis, Mo., 1971.

(10) N. E. Miller, paper presented at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., 1972.

(11) The counterions for borane cations VI–IX are to be understood to be hexafluorophosphate.

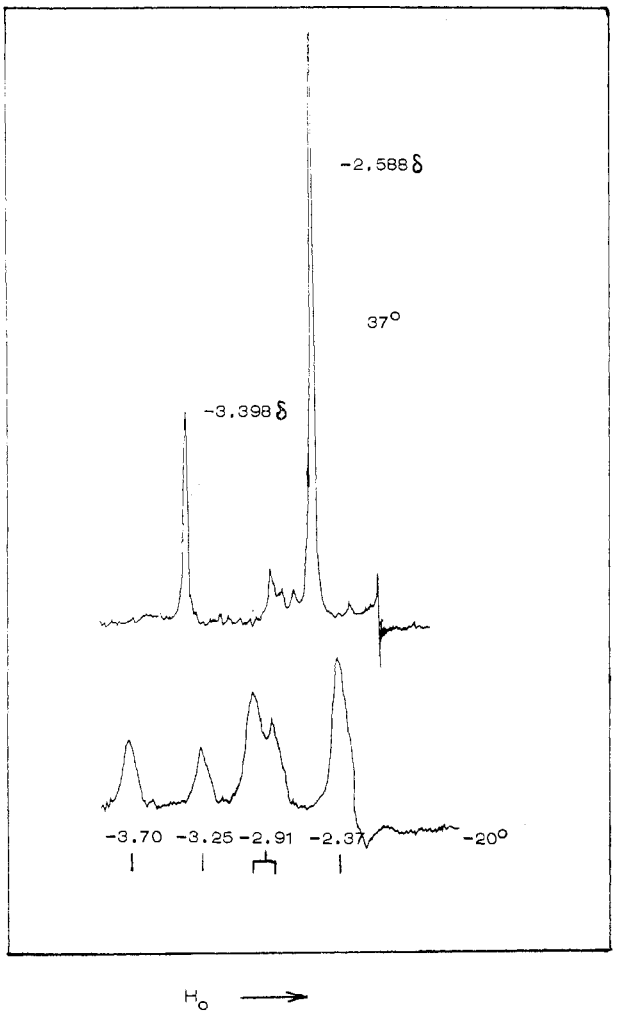
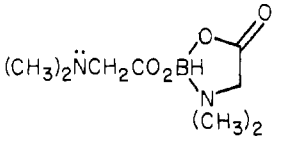


Figure 1. ^1H nmr data in $CDCl_3$ for

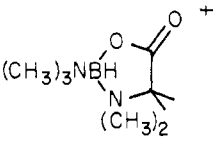


tons above 0°. This dynamic process is also supportive of earlier speculation that the ring I is formed by an intramolecular cyclization-displacement in aqueous solution.[2]

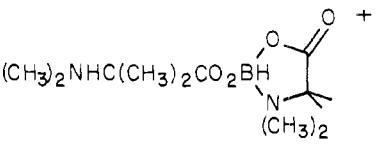
The cations VI and VII are new types to be added to the ever-growing roster of water-stable borane cations.[12] That a single BH bond should assist in the holding of two amino acid moieties together so well in water is an important structural feature with some implication for future research. As the oxygen environment about the ring boron is akin to boronic anhydrides which are noted for facile hydrolysis,[13] the observed stability must relate to the chelate ring and the electrical effect of hydrogen on boron.

The borane group in IV is not like that of typical amine-boranes in that it does not react rapidly nor cleanly with iodine (and subsequent treatment with a base does not produce a cation). Some of the difficulty apparently arises because the ring may be cleaved during iodination (*vide infra*), but the sluggish rate is not understood. Possibly the BH_3 group interacts strongly with the ring carboxyl group and is not free in solution. Infrared data lend support in that the carbonyl stretches are less separated in methylene chloride ($\Delta\bar{\nu} \approx 40$ cm^{-1}) than in mineral oil mulls ($\Delta\bar{\nu} \approx 60$ cm^{-1}). An interaction in solution would be expected to change the structural features of the side-chain carbonyl to resemble more closely that in the ring and lead to similar stretching frequencies.

Attempts to prepare borane cations from the more stable ring II were hampered by low reaction rate and ring cleavage. Iodination followed by treatment with trimethylamine did give a small yield of two cations VIII and IX. The product



VIII



IX

cation IX can only arise from ring cleavage, no doubt from HI produced during iodination. Infrared and analytical evidence, along with isolation of analytically pure IX, support the structure assignments. It is interesting to note that the NH infrared absorption in IX is a sharp singlet as compared to the broad, weak multiplet of the homologous cation VII. Less hydrogen-bonding interaction of the side-chain amine proton with the carbonyls is clearly indicated.

It is apparent from their structures that species IV–IX have dissymmetric ring boron sites.

Proton Nmr

Tentative proton nmr resonance assignments (Table III) are summarized in Figure 2. These were based on arguments comparing structurally analogous species. In general it appears that species of ring system I with polar side chains have asymmetric ring environments (split methylene and/or ring *N*-methyl resonances).

The argument for the resonance assignments begins with the observation that cation VI, a betaine cation derivative of I, has a closely spaced doublet in the *N*-methyl region suggestive of differing environments on the ring faces. The larger singlet of correct intensity for nine protons appearing downfield at −3.28 ppm must be from the $(CH_3)_3N$ moiety on the side chain. The inferred ring asymmetry can most reasonably be explained by configurations with close approach of the side chain to the ring. Absence of a split in the ring CH_2 resonance could be accounted for by the smaller size and greater distance from the side chain. The closely analogous cation species VII, differing by replacement of methyl by hydrogen on side-chain nitrogen, would be expected to have nearly identical chemical shifts for ring protons and similar splitting, and indeed, these are observed. (The upfield shift of 0.4 ppm of the side-chain *N*-methyl resonance would be normal for replacement of methyl by hydrogen.) Alternatively, the doublet might be from side-chain *N*-methyl protons split by spin–spin coupling (HNCH) but this would place the singlet ring *N*-methyl proton peak at a field lower than that of *any* other compound of ring system I or II; consequently, the former assignment is favored. The absence of NH splitting in that case may result from rapid exchange mediated by hydrogen-bonding interactions.

A similar assignment for cation IX of ring system II is advanced, even though this requires the protons of the ring *C*-methyls to be magnetically equivalent but not the ring *N*-methyls. The alternative assignment of the doublet to side-chain *N*-methyl with HNCH spin–spin splitting is less accept-

(12) A summary of the development of this field is found in D. P. Shitov, S. L. Ioffe, V. A. Tartakouskii, and S. S. Novikov, *Russ. Chem. Rev.*, 39, 905 (1970).

(13) K. Torssell, *Progr. Boron Chem.*, 1, 389 (1964).

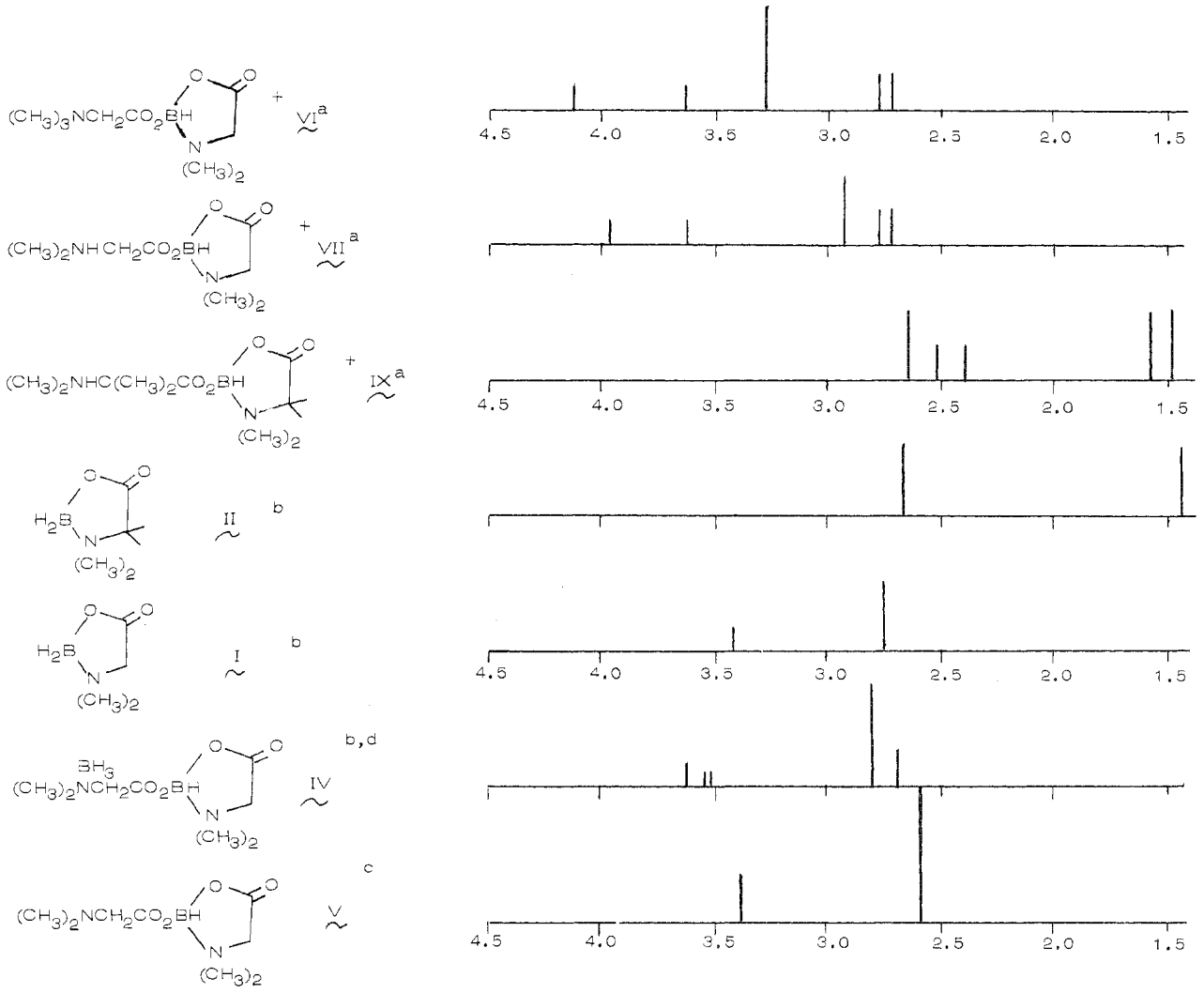


Figure 2. ^{1}H nmr summary: (a) CD_3CN solvent; (b) CH_2Cl_2 solvent; (c) $CDCl_3$ solvent, 80°; (d) relative intensities not known as accurately as depicted.

able because it reckons magnetic equivalence for both ring faces.

Resonances for the neutral species IV (related to cation VI, having CH_3^+ in the latter replaced by BH_3) are rationalized by assuming accidental overlap of half of a doublet ring *N*-methyl peak with a side-chain *N*-methyl singlet. Two types of methylene environments are observed, one split by 2 Hz and having a shift similar to that of methylene in ring I.

Conclusion

What has been established is that cyclic dimethylated amino acid boranes have excellent stability and that a diversity of heterocycles may be anticipated as better synthesis methods emerge. Preliminary hydrolysis studies suggest that cyclic systems of the α-amino acid will be the least stable, especially in alkali.

Continuing efforts to investigate the structure-chemistry relationship in the amino acid boranes are likely, especially since there is an added incentive of practical application. *B*-Arylated analogs to I, for example, are reported to have broad insecticidal, fungicidal, and herbicidal activity,[14] and a new antibiotic, boromycin, has a five-membered boron heterocycle involving a valine ester which is structurally similar to I and II.[15]

(14) G. Baum, *J. Organometal. Chem.*, 22, 269 (1970), and references cited therein.

Experimental Details

Manipulation of air-sensitive materials was carried out in chemical high-vacuum apparatus equipped with Delmar-Urry greaseless valves and O-ring joints. Diborane was commercial grade (Callery), stored in stainless steel cylinders at −78° between use. Chloroform, glyme (1,2-dimethoxyethane), and tetrahydrofuran were purified and dried by standard techniques with phosphoric anhydride (for $CHCl_3$) or lithium aluminum hydride (for ethers). Other solvents and reagents were commercial grade.

***N,N*-Dimethylglycinatoborane, I. a. $(CH_3)_3NBH_2I$ and Dimethylglycine.** Dimethylglycine was prepared by passing aqueous dimethylglycine hydrochloride through a Rexyn 201 ion-exchange resin (OH^- form), evaporating the solvent, and subliming the residual amino acid at 100° under vacuum. A suspension of 371 mg (3.60 mmol) of dimethylglycine in 4 ml of dry chloroform was treated with 5.1 ml of chloroform solution containing 3.60 mmol of trimethylamine-iodoborane (prepared from iodine and trimethylamine-borane). The nature of the suspension changed in about 0.5 hr, at which time a heavy crystalline solid was separated by filtration and identified by ir as $(CH_3)_3NH^+I^-$. Evaporation of the filtrate under vacuum left a residue which was subsequently taken up in water and transferred to a sublimer. Water was removed under vacuum and the resulting residue was sublimed at 120° under high vacuum to give 176 mg, 43%, of I.

b. **$(CH_3)_3NBH_2I$ and $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$.** The title tetramethylammonium salt was prepared by treating 25.0 mmol of $(CH_3)_4N^+OH^-$ in about 400 ml of solution (prepared from tetramethylammonium bromide passed through Rexyn 201 (OH^-) resin, and shown to be halide free) with 1.747 g (12.52 mmol) of dimethyl-

(15) I. O. Dunitz, D. M. Hawley, D. Miklous, D. N. J. White, Yu. Berlin, R. Marusic, and V. Prelog, *Helv. Chim. Acta*, 54, 1709 (1971).

glycine hydrochloride. The very basic solution was evaporated on a film evaporator to a wet crystalline mass. Repeated treatment with chloroform followed by evaporation removed traces of water. A final treatment with 30 ml of chloroform and filtration gave a solution of the tetramethylammonium dimethylglycinate and apparently solvated, insoluble $(CH_3)_4N^+Cl^-$, 1.63 g (1.4 g theory), identified by infrared data. The chloroform solution when combined with 12.4 mmol of $(CH_3)_3NBH_2I$ in 15 ml of chloroform immediately precipitated a white solid. After stirring 1 hr, filtration separated 2.15 g (2.5 g theory) of tetramethylammonium iodide and a filtrate which produced a sticky residue on solvent evaporation. Sublimation of the residue gave I, but in a waxy condition; yield 39%. Resublimation after taking up in water gave a hard crystalline product.

c. **Attempted Synthesis from Diborane and Dimethylglycine.** Combination of diborane (0.69 mmol) and 1.50 mmol of sublimed dimethylglycine in methylene chloride led to considerable gas evolution at low temperature. After 2 hr, the cloudy mixture was filtered and the filtrate evaporated. Neither the precipitate nor residue gave infrared evidence for I, but the spectrum of the precipitate was clean and sharp.

d. **Further Characterization of I.** A three-times sublimed sample of I melted at 119–121°. Its solution molecular weight by freezing point depression in water was 117 compared to the theoretical value 114 (−0.412° depression for 47.5 mg in 1.8357 g of water). Gas-phase molecular weight measurements were high (158 for 2.101 mg, 1.17 mm, 309.9 ml, 161.6°) no doubt because low pressure and high molecular polarity exaggerated adsorption errors.

There was no uv absorption for I in water or aqueous trimethylamine at concentrations near 0.1%.

e. **Deuteration of Methylenic Carbon.** The proton resonance of a 39.5-mg portion of I in 0.5 ml of Silanor D_2O (Merck & Co. brand of 99.7 atom % D water with sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DDS, reference) containing about 1.1 mmol of trimethylamine (corresponding to a 2 *M* solution) was monitored. When the methylenic resonance had vanished, the solution was evaporated and the residue sublimed to give 33.3 mg of C-deuterated I, as inferred from a new infrared pattern. This was taken up in 0.4 ml of H_2O and 0.18 ml of 25% aqueous trimethylamine (final solution was about 1.9 *M* in trimethylamine). After 10 min at room temperature, the cyclic compound was recovered as before and found not to be entirely converted to I. The treatment was repeated on the 23.9 mg recovered, this time with added DSS reference. Recovery yielded 17.2 mg of I with an infrared spectrum identical with that of the starting material.

It was thought that the DDS may be acting as a catalyst, but a fresh sample of I in D_2O without reference DDS lost the methylene peak in 4 min and excluded the possibility.

2-Dimethylaminoisobutyratoborane, II. a. Synthesis by Methylation of I. A 69.6-mg portion of 53% mineral oil dispersion of sodium hydride (15.4 mmol) was freed of mineral oil by washing three times with 5 ml of hexane under nitrogen. Then, 4 ml of dry DMF and a solution of 2.1 ml (34 mmol) of methyl iodide and 176 mg (1.54 mmol) of I was added. Gas evolution commenced and the mixture warmed itself vigorously. The mixture was cooled and stirred 1 hr and then filtered. Solvent evaporation left a large amount of solvated sodium iodide along with the product. Subsequent extraction with methylene chloride also extracted some sodium iodide solvate along with the product. Evaporation and sublimation under high vacuum to 120° gave 52 mg, 24%, of II as a crystalline solid, mp 179–190° (with decomposition under vacuum). A different sample of an identical infrared spectrum was analyzed.

Anal. Calcd for $(CH_3)_2\overline{NC(CH_3)_2CO_2BH_2}$: C, 50.4; H, 9.9; N, 9.8. Found: C, 49.4; H, 9.6; N, 9.5.

Alternate use of potassium *tert*-butoxide as the base in the methylation in DMF or butanol gave only a trace of II along with unreacted I. Aqueous sodium hydroxide also yielded only starting material.

b. **Synthesis from Ethyl 2-Dimethylaminoisobutyrate.** (Ethyl 2-dimethylaminoisobutyrate)-borane was prepared by adding 4.1 mmol (measured as a gas) of diborane with 8.2 mmol of amino ester in a flask attached to a high-vacuum line. A small amount of gas (hydrogen, probably) was evolved on warming to room temperature. After 1 hr of stirring, the noncondensable gas was removed to leave the adduct as an oil that could be made to crystallize at −78° only with great effort. The adduct melts between 0° and room temperature. It was taken up in 40 ml of dry chloroform, and a solution of 1.045 g (4.12 mmol) iodine in about 30 ml of chloroform was added in 15 min. After an additional 30 min the solution became colorless, and trimethylamine, 3.90 mmol measured as a gas, was added at −78°. In less than 5 min at this temperature, a small amount of white solid had formed. Another 4.14 mmol of trimethylamine was added and the mixture kept cold an additional 0.5 hr. After standing for 2 days, the mixture was filtered to give 341 mg, 22%, of insoluble solid identified as trimethylammonium iodide by its ir spectrum. Concentration of the filtrate produced a crop of ethyltrimethylammonium iodide that was separated by filtration. Further concentration left a semisolid residue that evolved gas on dissolution in ethanol. Evaporation and extraction of the residue with ether gave an ether-soluble portion that was sublimed under high vacuum at 100–120° to give 344 mg of II, 30%. Heating of the residue to 160° under high vacuum resulted in no more product. Of the several preparations completed, the highest yield was 38% and the lowest was 16%.

Variation of experimental parameters did not improve the yield. Addition of 25% excess iodine until a faint yellow color appeared after the molar amount of trimethylamine was added, followed by an additional 25% of trimethylamine, did give a residue that bubbled less on work-up with ethanol, but from it only 19% of II was isolated.

When chloroform was partially removed after iodination (before addition of trimethylamine), it was found to contain no hydrogen iodide.

In one experiment, the amino acid ester–borane was iodinated in chloroform with $^1/_2$ molar equiv of iodine (I:B = 1). No trimethylamine was added but the volatiles were removed and treated with trimethylamine, whereupon 38% of the expected trimethylethylammonium iodide was isolated. The residue after solvent removal would not give *any* II when worked up as usual.

In another experiment, 8.0 mmol of borane adduct, 8.0 mmol of iodine, and 15.8 mmol of triethylamine were combined but no product resulted; the mixture now failed to decolorize when one-sixth of the iodine had been added.

c. **Hydrolysis.**[4] The hydrolysis rate of II was studied in a manner similar to that reported for I.[2] A check on the hydrolysis of $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2H_5^+PF_6^-$ at 0.3 *M* OH^-, ionic strength 0.9, and 29.8° gave a first-order rate of 6.3×10^{-4} sec^{-1}, in good agreement with the 6.5×10^{-4} sec^{-1} reported.[2] Apparatus and reagents were thus assured for valid comparison of hydrolysis rates of I.

Two runs in 0.9 *M* OH^- and one run at 0.6 *M* OH^- were made at 29.8° and ionic strength 0.9. Analysis of the data in conventional ways revealed pseudo-first-order kinetics for the runs and an apparent third-order rate constant (see Table V). The long half-life prevented extensive study of the kinetics.

3-Dimethylaminopropionatoborane, III. A solution of 4.4 mmol of trimethylamine–iodoborane in 20 ml of dry chloroform was added slowly *via* a syringe to a mixture of 543 mg (4.64 mmol) of 3-dimethylaminopropionic acid in 200 ml of dry chloroform. A nearly clear solution with a small oil droplet resulted with vigorous stirring. In about 0.5 hr the solution became cloudy and precipitation of a solid continued several hours. The mixture was filtered after stirring for 1 day, and 591 mg of crystalline solid was isolated and found to contain trimethylammonium iodide and other material by infrared analysis. The filtrate was concentrated to a white solid which was distilled at 100° under high vacuum; it began melting at 90°. The condensate collected was resublimed to give 53 mg of III; mp 96–100° dec.

Anal. Calcd for $(CH_3)_2\overline{N(CH_2)_2CO_2BH_2}$: C, 46.6; H, 9.4; N, 10.9. Found: C, 46.3; H, 9.7; N, 10.6.

When left for days in warm, moist air (90% relative humidity and 30°) III remained unchanged by appearance and infrared examination. It dissolves in water and evolves hydrogen with strong (1–6 *M*) hydroxide, but does not bubble in 6 *M* hydrochloric acid.

In deuteriochloroform, the sharp singlet *N*-CH_3 resonance did not split even when cooled to −40°. The broadening that was observed at −40° probably arises from the solution being supersaturated.

Amino Acid Preparations. Ethyl 2-Dimethylaminoisobutyrate. A mixture of 24.4 g (125 mmol) of ethyl 2-bromoisobutyrate and 20 ml (300 mmol) of dimethylamine was sealed in a 200-ml glass ampoule for 2 days at which time no more crystals seemed to be forming. It was heated at 40° for 1 more day, cooled, and opened. The mixture was dissolved in hydrochloric acid, maintaining acidity carefully, and then extracted twice with ether to remove unreacted materials. The aqueous solution was mixed with 100 ml of ether and then made basic with sodium carbonate. The ether was separated and combined with two consecutive extractions of 150 ml each. Concentrations and distillation through a short-path still gave the product, bp 61–62° (12 mm) (lit.[16] bp 62.6–64°), 15.5 g, 78%.

2-Dimethylaminoisobutyric Acid. An aqueous solution (about 5%) of ethyl 2-methylaminoisobutyrate was heated at 60–80° for 2 days until neutral. Evaporation on a film evaporator and sublimation under high vacuum at 100° gave the amino acid as a hard white solid.

Betaine and Betaine Hydrobromide. Ethoxycarbonylmethyltrimethylammonium bromide, $(CH_3)_3NCH_2CO_2C_2H_5^+Br^-$, was pre-

pared in 91% yield as a white solid by combining equimolar amounts of trimethylamine and ethyl bromoacetate in ether. After 10 hr the salt was filtered, washed with ether, and vacuum-dried. A solution of 4.5 g in 100 ml of water was passed through a Rexyn 201 (OH^-) column and the effluent was concentrated on a rotating-film evaporator to a solid. Drying under high vacuum gave the off-white solid betaine which did not melt to 250°.

Anal. Calcd for $(CH_3)_3NCH_2CO_2$: C, 51.3; H, 9.5; N, 12.0. Calcd for $(CH_3)_3NCH_2CO_2 \cdot 0.5H_2O$: C, 47.7; H, 9.6; N, 11.1. Found: C, 47.6; H, 9.3; N, 10.0.

The suspected hydration of the sample must have occurred during analysis as the infrared spectrum of the product showed little OH absorption.

The hydrobromide was made by dissolving 400 mg (3.41 mmol) in 2 ml of methanol and condensing on 3.65 mmol of gaseous hydrogen bromide. On warming to room temperature a white solid was produced. Volatiles were pumped off to give 585 mg of solid, 87%. The infrared spectrum showed two carbonyl stretching frequencies suggestive of a mixture. This product was judged sufficiently pure for use, however.

(Dimethylglycinatoboranyloxycarbonylmethyl)dimethylamine-Borane, IV. A mixture of 1.347 g (35.6 mmol) of sodium borohydride and 4.609 g (33.0 mmol) of *N,N*-dimethylglycine hydrochloride was placed in a 100-ml flask with a magnetic stirbar under nitrogen, about 20 ml of dry glyme was added, and stirring was commenced. Gas evolution began immediately and slacked off within 2 hr at room temperature, but reflux under nitrogen was continued an additional 2 hr. After the mixture had cooled, solvent was removed under vacuum. The residue was added to about 100 ml of 0° water with vigorous stirring. Much gassing occurred and the product formed a stable foam. The mixture (and foam) was filtered and the solid adduct, IV, was washed with water and air-dried; yield 1.2036 g, 32% based on amino acid. Recrystallization was effected by taking up in methylene chloride and adding hexane till the solution became cloudy. White, crystalline IV was obtained; yield 1.204 g, mp 162–163° dec.

Anal. Calcd for IV: C, 41.8; H, 8.8; N, 12.2; B, 9.4. Found: C, 42.0, 42.7; H, 8.8, 9.0; N, 12.0, 12.5; B, 9.8.

The ^{11}B nmr run in methylene chloride at 32.08 MHz showed a doublet ($J_{BH} = 145$ Hz) at −5.4 ppm and a quartet ($J_{BH} = 91.5$ Hz) at +6.7 ppm from external boron trifluoride–etherate reference, assignable to BH and BH_3 moieties, respectively.

Molecular weight measurement was carried out by vapor pressure suppression in methylene chloride. The sample was contained in solution in one leg and solvent in another leg of the apparatus[17] separated by a glycerine manometer. Dried solvent used in both legs had been preequilibrated together under vacuum overnight to ensure both samples of the same vapor pressure. The legs were isolated and the sample was added. Molecular weights of 272 and 230 were observed (the latter datum is more reliable because the stirring bars in the apparatus had been changed to give more uniform mixing) corresponding closely with the theoretical value 230. Sample size was 45.9 mg and the pressure lowering was 1.79 Torr for a working mass of 2.8994 g of solvent. At 19.9° a vapor pressure of 337 Torr was assumed for methylene chloride. Hydrolytic hydrogen analysis was made using platinum black and basic or acidic conditions. Samples were contained in sealed glass vessels. Hydrogen was Toepler pumped. The following amounts were found: 0.0164 mmol/mg in 0.4 *M* H_2SO_4, 0.0157 mmol/mg in about 0.5 *M* sodium hydroxide, and 0.0156 mmol/mg in *ca.* 1 *M* H_2SO_4 with no catalyst. Calculated for IV: 0.0174 mmol/mg. The reason for the low values (by 6%) is not known. In the basic hydrolysis a volatile yellow material with an amine odor was detected in the cold trap preceding the Toepler pump. Some decomposition, possibly consuming hydrogen, of the amino acid may be occurring during hydrolysis.

Structure Proof. IV. A mixture of 176 mg (1.53 mmol) of I and 374 mg (1.88 mmol) of betaine hydrobromide was heated under nitrogen until it melted and evolved gas. After cooling, opening, dissolution in water, and metathesis with ammonium hexafluorophosphate, 115 mg of white solid was obtained with an ir spectrum nearly identical with that of VI. On recrystallization from hot water pure VI could be recovered in the later crops.

(Dimethylglycinatoboranyloxycarbonylmethyl)dimethylamine, V. A suspension of 314 mg (1.36 mmol) of IV in chloroform was treated with 1.25 mmol (measured as a gas) of trimethylamine and allowed to stir at room temperature. After 3 hr a colorless solution resulted, and this was kept at room temperature overnight before solvent was removed under vacuum *via* a U trap. After solvent removal the trap was cooled to −78° and pumping continued for 1 day. The trimethylamine–borane collected in the trap amounted to 52 mg, 50% of theory (but some was lost in solvent evaporation; other experiments showed nearly 70% recovery). The oily residue in the reactor was considered to be essentially the title compound. Its nmr was run in chloroform and the solution was returned to reactor. Diborane, 0.704 mmol measured as a gas, was added and a gelatinous solid slowly formed with stirring and became more granular on stirring 2 hr. Removal of solvent under vacuum left 316 mg of white residue which yielded 252 mg of IV (identified by ir) after recrystallization (and removal of insolubles) from methylene chloride–hexane. An 80% recovery was achieved.

$(CH_3)_2NHCH_2CO_2\overline{BHO_2CCH_2N(CH_3)_2}^+PF_5^-$, VII. The free base V was prepared in a reactor on the vacuum line as described from 2.87 mmol of IV and a slight excess of trimethylamine in chloroform. Gaseous hydrogen bromide (2.74 mmol) was added and a semisolid mass was formed. After 2 hr of stirring at room temperature the solvent was removed under vacuum to give a hygroscopic solid. It was taken up in water and ammonium hexafluorophosphate solution was added, whereupon an oil separated. It crystallized reluctantly and formed an extraordinarily bulky solid entrapping much solution. After filtration and drying, the solid was recrystallized in 50% recovery out of 1:1 methanol–methylene chloride by addition of hexane; mp 160–162° dec. Recrystallization from hot water gave a dark-hued solid which had the same ir as that from organic solvents, with broad NH, doublet carbonyl, and singlet BH absorption.

Anal. Calcd for $(CH_3)_2NHCH_2CO_2\overline{BHO_2CCH_2N(CH_3)_2}^+PF_6^-$: C, 26.5; H, 5.0; N, 7.7. Found: C, 26.6; H, 5.0; N, 7.7.

$(CH_3)_3NCH_2CO_2\overline{BHO_2CCH_2N(CH_3)_2}^+PF_6^-$, VI. The free base V was prepared from 1.45 mmol IV and treated in chloroform with 1.54 mmol methyl iodide, measured as a gas. A solid slowly formed, and after stirring overnight solvent was removed under vacuum to leave a white solid. The solid was dissolved in water, metathesized to the hexafluorophosphate and worked up with warm water to give 300 mg, VI, 49%, mp 176–178°. A doublet carbonyl and singlet BH absorptions were observed in the ir spectrum.

Anal. Calcd for $(CH_3)_3NCH_2CO_2\overline{BHO_2CCH_2N(CH_3)_2}^+PF_6^-$: C, 28.8; H, 5.4; N, 7.4. Found: C, 28.8; H, 5.2; N, 7.4.

Recrystallization could be effected from water but not from methanol which apparently decomposed the cation.

$(CH_3)_2NHC(CH_3)_2CO_2\overline{BHO_2CC(CH_3)_2N(CH_3)_2}^+PF_6^-$, VIII, and $(CH_3)_3N\overline{BHO_2CC(CH_3)_2N(CH_3)_2}^+PF_6^-$, IX. Under nitrogen, a solution of 126 mg (0.88 mmol) of II and 1.63 mmol of trimethylamine in 1 ml of chloroform was treated dropwise over 10 min with 217 mg (0.86 mmol) of iodine in 8 ml of chloroform *via* a syringe. The final solution, of a burgundy color, was allowed to stand 1 hr. Solvent was removed leaving a brown tar which was dissolved in water containing a trace of sodium bicarbonate to keep neutral. Metathesis with ammonium hexafluorophosphate gave 80.4 mg of white solid, mp 160–170°, dependent on heating rate. Recrystallization from hot ethanol gave 25 mg of VIII.

Anal. Calcd for $(CH_3)_2NHC(CH_3)_2CO_2\overline{BHO_2CC(CH_3)_2N(CH_3)_2}^+PF_6^-$: C, 34.5; H, 6.3; N, 6.7. Found: C, 33.7; H, 6.2; N, 6.2.

The ir showed singlet BH, NH, and doublet CO stretching absorptions. Another preparation adding iodine to II in chloroform followed with 1 molar equiv of trimethylamine led to a hexafluorophosphate which was recrystallized from ethanol, mp 153–155°, analyzing for a 1:2 mixture of VIII and IX.

Anal. Calcd for $^2/_3(CH_3)_3N\overline{BHO_2CC(CH_3)_2N(CH_3)_2}^+PF_6^-$ and $^1/_3(CH_3)_2NHC(CH_3)_2CO_2\overline{BHO_2CC(CH_3)_2N(CH_3)_2}^+PF_6^-$: C, 32.5; H, 6.4; N, 7.6. Found: C, 32.5; H, 6.3; N, 7.5.

The infrared spectrum showed weak absorptions for VIII and other strong absorptions including three unequal carbonyl absorptions.

Acknowledgment. Support of this research by Grant 14902 of the National Science Foundation is sincerely appreciated. The author thanks Dr. Richard Middaugh of the Chemistry Department, University of Kansas, Lawrence, Kans., for obtaining the ^{11}B nmr spectrum.

Registry No. I, 28333-37-1; I-coordinated species, 28471-38-7; II, 51015-74-8; II-coordinated species, 51015-90-8; III, 51015-75-9; III-coordinated species, 51022-57-2; IV, 51015-76-0; IV-coordinated

(16) L. Kahovec and K. W. F. Kohlrausch, *Monatsh. Chem.*, 74, 112 (1942).

(17) Details of the technique are to be published.

species, 51015-91-9; V, 51015-77-1; V-coordinated species, 51015-92-0; VI, 51015-94-2; VI-coordinated species, 51015-96-4; VII, 51051-50-4; VII-coordinated species, 51051-51-5; VIII, 51051-53-7; VIII-coordinated species, 51051-54-8; IX, 51016-00-3; IX-coordinated species, 51016-02-5; $(CH_3)_3NBH_2I$, 25741-81-5; $(CH_3)_2NCH_2CO_2H$, 1118-68-9; $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$, 28333-38-2; ethyl 2-dimethylaminoisobutyrate, 51015-89-5; diborane, 19287-45-7; 3-dimethylaminopropionic acid, 6300-04-5.

Contribution from the Department of Chemistry, Brock University, St. Catharines, Ontario L2s 3A1, Canada

Boron-11 and Fluorine-19 Nuclear Magnetic Resonance Pairwise Interaction Parameters. Application to Donor-Acceptor Interactions in Boron Trihalide Adducts[1]

J. STEPHEN HARTMAN* and JACK M. MILLER*

Received November 9, 1973 AIC30820J

^{11}B and ^{19}F chemical shifts and ^{11}B-^{19}F coupling constants of boron trihalide adducts fit Malinowsky's criteria of "pairwise additivity." Hard and soft donor atoms give rise to very different donor-halogen pairwise interaction parameters. These are of use in determining the donor atom in an adduct when the Lewis base involved has more than one potential donor site. Various correlations of pairwise parameters, including those involving different central nuclei, appear promising.

Introduction

In several types of compounds, chemical shifts of nuclei other than protons have been shown to be pairwise additive with respect to the substituent groups,[2] and the same is true for several cases of coupling constants between directly bonded atoms.[2] Thus the chemical shift (or spin-spin coupling) can be expressed as $\delta = \Sigma\eta_{i,j}$ where $\eta_{i,j}$ is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all substituents about a central atom, excluding the nucleus observed in the nmr experiment. Thus in the case of a complex $D{\cdot}BF_2Cl$

$$\delta_{^{11}B} = \eta_{F,F} + 2\eta_{F,Cl} + \eta_{D,Cl} + 2\eta_{D,F}$$

$$\delta_{^{19}F} = \eta'_{F,Cl} + \eta'_{D,Cl} + \eta'_{D,F}$$

$$J_{^{11}B-^{19}F} = \eta''_{F,Cl} + \eta''_{D,Cl} + \eta''_{D,F}$$

where η is different in each of the above equations. Pairwise additivity has been demonstrated for ^{19}F, ^{11}B, ^{13}C, ^{27}Al, ^{93}Nb, and other chemical shifts and for directly bonded couplings J_{C-F}, J_{Si-H}, J_{Sn-H}, and other systems.[3,4]

We have shown that pairwise additivity rules apply to the ^{11}B and ^{19}F chemical shifts and ^{11}B-^{19}F coupling constants of the mixed tetrahaloborate anions.[3a] Our recent studies of mixed boron trihalide adducts[5-7] have provided nmr data which seemed to involve certain irregularities. It turns out that these data can be correlated by pairwise additivity parameters though not by direct additivity parameters and that a few seeming irregularities in chemical shift are a result of trends in the pairwise parameters. Thus we report here the extension of our calculations of pairwise interaction parameters in tetrahaloborate anions to our nmr data on mixed boron trihalide adducts.

Experimental Section

Calculations were based on chemical shifts and coupling constants given in Table I (see paragraph at end of paper regarding supplementary material). These data were collected from a number of studies carried out in this laboratory. The data were used to calculate the sets of pairwise parameters for (i) ^{19}F chemical shifts, (ii) ^{11}B chemical shifts, and (iii) ^{11}B-^{19}F coupling constants, shown in Tables II-IV, respectively. The calculations were carried out on a Burroughs B5500 computer using a least-squares fitting routine. When the resulting pairwise parameters were used to recalculate the original nmr parameters, deviations between calculated and observed parameters were small (Table I). Standard deviations between observed and calculated parameters were as follows: (i) ^{19}F chemical shift, ±0.44 ppm in a range of 85.5 ppm; (ii) ^{11}B chemical shift, ±0.67 ppm in a range of 139 ppm; (iii) ^{11}B-^{19}F coupling constant, ±0.72 Hz in a range of 113.6 Hz. These deviations are similar to those reported by Spielvogel and Purser.[3b]

Since the halogen-halogen pairwise parameters for the neutral adducts are almost identical with those determined previously for the tetrahaloborate anions,[3a] the values for these parameters given in Tables II-IV are those calculated from the complete data set including both the neutral adducts and the tetrahaloborate anions.

The availability of nmr data is limited by various unfavorable features of some of the adduct systems, including low solubility, rapid decomposition, rapid halogen redistribution, and unfavorable halogen-redistribution equilibria giving near-zero amounts of certain mixed adducts. Also it was not possible to resolve splittings due to ^{11}B-^{19}F coupling in several series of oxygen-donor adducts. Thus each of Tables II-IV gives pairwise interaction parameters for a different group of compounds. Due to a combination of several unfavorable factors little information is available on iodine-containing adducts.

Results

^{19}F Chemical Shift Parameters. The donor-halogen parameters for the adducts of oxygen donors and trimethylamine ("hard donors"[8]) show a pronounced decrease in the order $\eta_{D,F} > \eta_{D,Cl} > \eta_{D,Br}$ whereas the reverse order is found for the "soft" donors[8] Me_2S and Me_3P (Table II), as well as the soft donor Me_3PS. [We are aware of the

(1) Presented in part at the 56th Canadian Chemical Conference, Montreal, June 1973.

(2) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 46, 1830 (1967).

(3) (a) J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 11, 940 (1972); (b) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, 93, 4418 (1971).

(4) (a) E. R. Malinowski, *J. Amer. Chem. Soc.*, 91, 4701 (1969); (b) E. R. Malinowski and T. Vladimiroff, *ibid.*, 86, 3575 (1964); (c) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 42, 444 (1965); (d) R. G. Kidd and H. G. Spinney, *J. Amer. Chem. Soc.*, 95, 88 (1973); *Inorg. Chem.*, 12, 1967 (1973).

(5) M. J. Bula, D. E. Hamilton, and J. S. Hartman, *J. Chem. Soc., Dalton Trans.*, 1405 (1972).

(6) B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 2603 (1972).

(7) M. J. Bula and J. S. Hartman, *J. Chem. Soc., Dalton Trans.*, 1047 (1973).

(8) R. G. Pearson, *J. Chem. Educ.*, 45, 581, 643 (1968); *Chem. Brit.*, 3, 103 (1967); *J. Amer. Chem. Soc.*, 85, 3533 (1963).