

Synthesis of Charged and Neutral
Boron-Containing Heterocyclic Systems

By

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DEDICATION

To my parents, Donald and Irene Abate.

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Abstract of Dissertation Presented to the
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SYNTHESIS OF CHARGED AND NEUTRAL
BORON-CONTAINING HETEROCYCLIC SYSTEMS

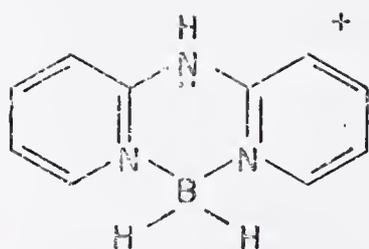
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Kenneth Abate

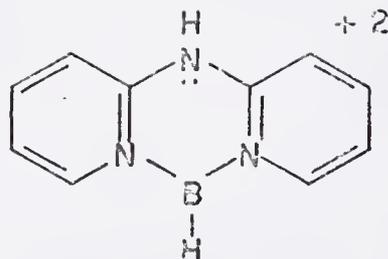
December, 1971

Chairman: Professor G. E. Ryschkewitsch
Major Department: Chemistry

Trimethylamine moniodoborane was reacted with 2,2'-dipyridyl-
amine in an attempt not only to get halide displacement but also trans-
amination to produce a cyclic boron cation (I).



I

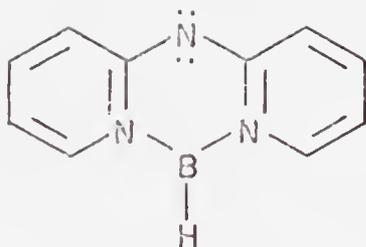


II

This cation, dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+), was pre-
pared and was the basic structure for all subsequent attempts to pre-
pare a charged heterocyclic aromatic system (II).

Dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) appeared to
be the ideal system. It already had fourteen electrons available for

delocalization if the bridging nitrogen and the boron could be made sp^2 hybridized. It was hoped that the cation (I) would eliminate hydrogen spontaneously to produce (III) but this did not occur so other reactions were attempted. The most obvious reaction to attempt on (I) would be hydride abstraction.

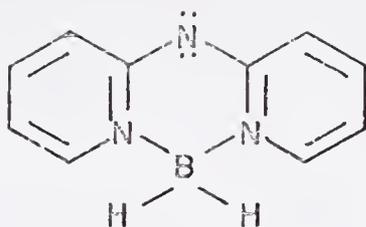


III

A variety of hydride abstracting agents were used and although evidence was obtained which showed that hydride abstraction occurred, no heteroaromatic cation could be isolated.

An attempt was made to modify the cation (I) in order to add to its stability after hydride abstraction by mono-halogenating the boron portion. A halo-substituent on a trigonal boron could possibly share a pair of non-bonded electrons with boron and thus help stabilize it. Some surprising results were obtained which eventually led to a set of fluoro-substituted boron cations but still no heteroaromatic system.

It was observed that the hydrogen on the bridging nitrogen in (i) was acidic and could easily be removed to produce a stable, highly colored zwitterion (IV). This zwitterion seemed to be a better system yet for the formation of a heteroaromatic compound by making the boron



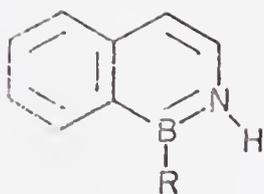
IV

trigonal. If the instability of the heteroaromatic system (II) was due to the plus two charge on it, the heteroaromatic system formed (III) by hydride abstraction from (IV) would only develop a plus one charge and possibly be more stable. Again, evidence for hydride abstraction was obtained but no heteroaromatic system was isolated.

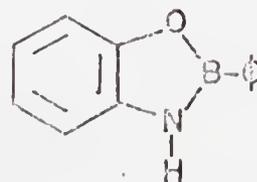
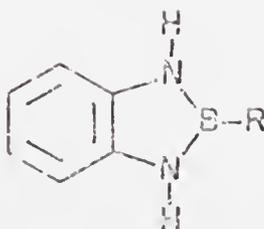
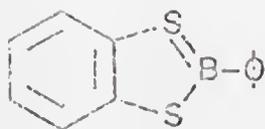
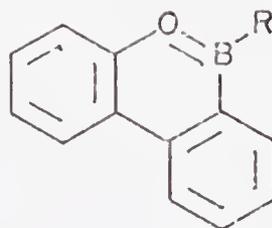
The reactivity of the bridge nitrogen in the neutral zwitterion was investigated. Both neutral and charged species were isolated with groups attached to the nitrogen. As a consequence of this work, a synthesis for the preparation of 2,2'-dipyridylmethylaniline was developed.

CHAPTER I
INTRODUCTION

During the late fifties and early sixties, there was a flourish of work in the area of heteroaromatic compounds containing a boron atom and either nitrogen, oxygen or sulfur atom being substituted for two carbon atoms in an aromatic system. Ulmschneider and Goubeau reported the first heteroaromatic compounds other than borazine or boron nitride in 1957 (1). Most of the work on boron-containing heteroaromatic compounds was done by M. J. S. Dewar and co-workers (2,3) who prepared a large number of compounds with B-N or B-O bonds and studied their properties. A few examples of known heteroaromatic compounds are listed below.

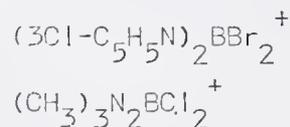
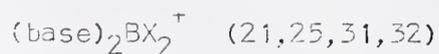
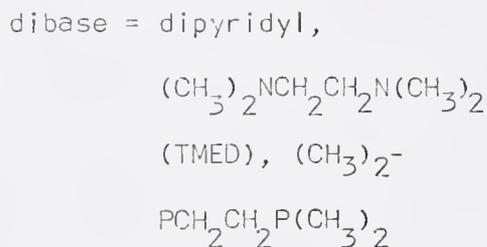
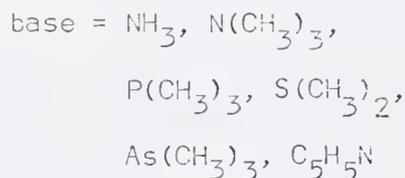


R = OH, C₆H₅

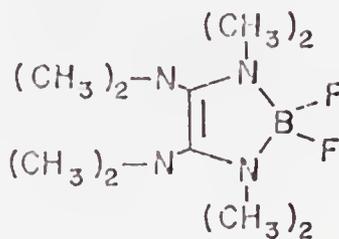
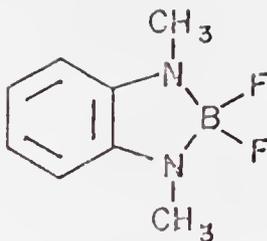
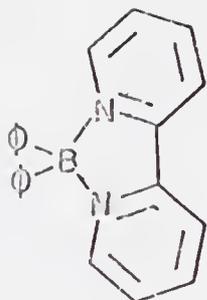


These compounds, when compared to corresponding open-chain analogs, showed an increase in stability toward hydrolysis. A limited number were stable in acids or bases but few approached the stability of their carbon analogs. In general, the ones containing B-N bonds were more stable than those containing B-O or B-S bonds.

Concomitant with the development of boron-containing hetero-aromatic systems, four coordinate boron cation chemistry came into existence. Beginning with the classical work of Parry and co-workers (4-9) on the structure of the "diammonate of diborane" and due to the work of researchers such as Mikhailov, Nöth, Douglass, Muetterties and Ryschkewitsch, boron cation chemistry has rapidly developed and several good reviews have been written (10-12). A few examples of boron cations are listed according to the number and kinds of ligands attached to boron and ascending charge type.



(dibase)BX₂⁺ (16,24,28,29)



(base)₂BHX⁺ (33)

X = C₆H₁₃; base = C₅H₅N

X = Cl; base = 4-picoline

(dibase)BHX⁺ (15)

X = Br; dibase = TMED

(base)(base')BH₂⁺ (19,20,23,26,30)

base = N(CH₃)₃

base' = P(CH₃)₃, 4-picoline,

ONC₅H₅, OS(CH₃)₂, OP(CH₃)₃

(base)(base')BHX⁺ (18,19,26,33)

X = Cl, Br

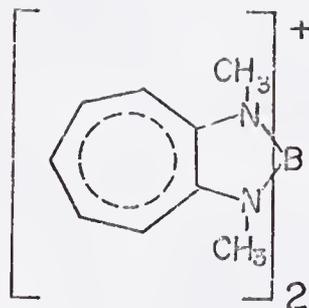
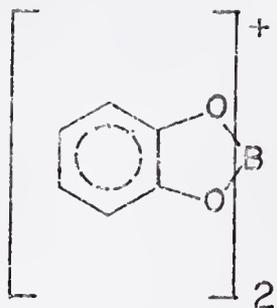
base = N(CH₃)₃; base' = 4-picoline



X = Cl

base = C₅H₅N

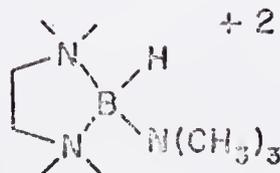
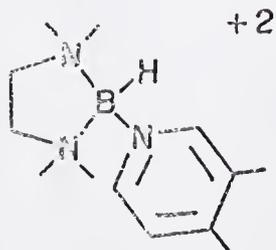
base' = NH(CH₃)₂



base = C₅H₅N, 4-picoline

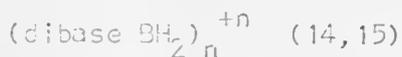


X = Br; base = C₅H₅N





dibase = dipyridyl



n is uncertain

dibase = tetramethylbutylene-diamine,
tetramethylpropylene-diamine

Although cations have been made using a wide variety of ligands and usually range in charge from one to three (excluding polymeric cations), only a few papers have been published which mention ions derived from BR' ($\text{R} = \text{H}, \text{F}$; $\text{R}' = \text{H}, \text{F}$) and a diamine or some other difunctional donor moiety forming chelated ions (13-15, 25).

It was the purpose of this work to investigate the possibility of using chelated four coordinate boron cations to synthesize trigonal boron heteroaromatic systems.

Aromatic compounds are compounds with cyclic conjugated molecules in which the π -electrons occupy delocalized ring-shaped orbitals concentrated above and below all the ring atoms. These compounds usually exhibit an enhanced stability evidenced by greater heats of formation than expected and undergo substitution reactions more readily than addition reactions. The delocalized bonding or resonance interactions give rise to bond lengths which are intermediate in length between a normal single and a normal double bond. In order for electron delocalization to occur, each atom in the ring system must have an available p-orbital so that it may share π -electrons with its neighbors. For monocyclic systems Hückel's rule predicts that the total number of π -electrons must be $4n+2$ where n is an integer. There are many examples of compounds in which one or more hetero atoms replace

carbon in the ring system.

Because nitrogen has one more electron than does carbon, the N^+ ion is isoelectronic with a neutral carbon atom. Any aromatic system in which a carbon atom has been replaced by a N^+ ion will remain aromatic; for example, pyridinium ion is isoelectronic with benzene. Since boron has one less electron than carbon, the B^- ion and the neutral carbon atom are isoelectronic. Replacement of a carbon atom in an aromatic system by the B^- ion should produce an isoelectronic aromatic system. No ions of this type have yet been isolated but one has been reported and is very unstable (41).

If two carbon atoms are replaced, one by a N^+ and the other by a B^- , in an aromatic system, the resulting isoelectronic system should be aromatic. A large number of compounds have been prepared which are derived from normal aromatic systems having a pair of carbon atoms replaced with a B^- and a N^+ .

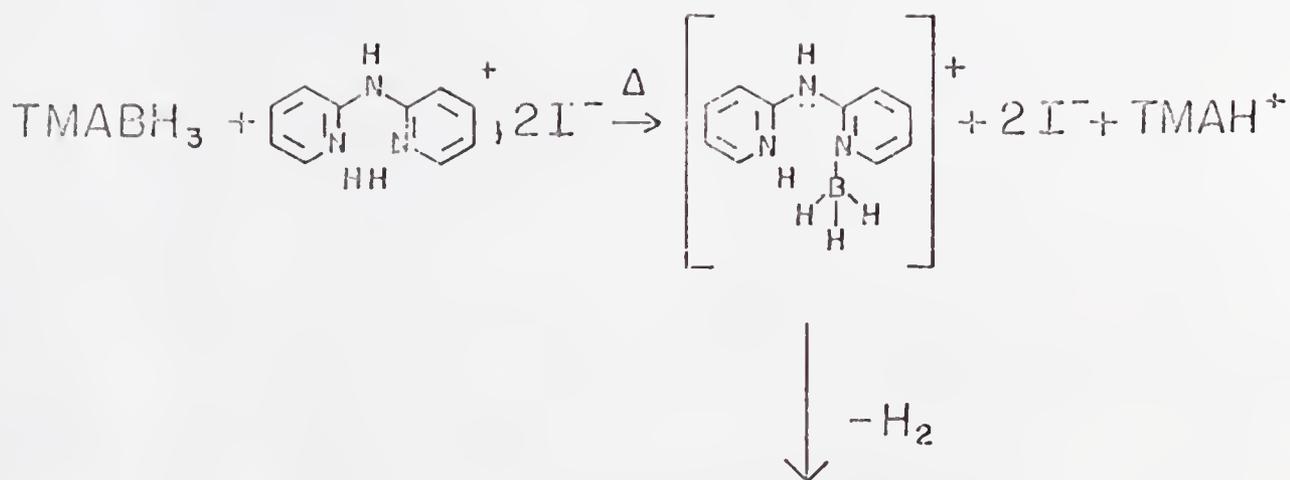
With 2,2'-dipyridylamine as the ligand, attempts to prepare a model system which could eventually be converted into a heteroaromatic system were made. A number of proposed reaction schemes are outlined in the following.

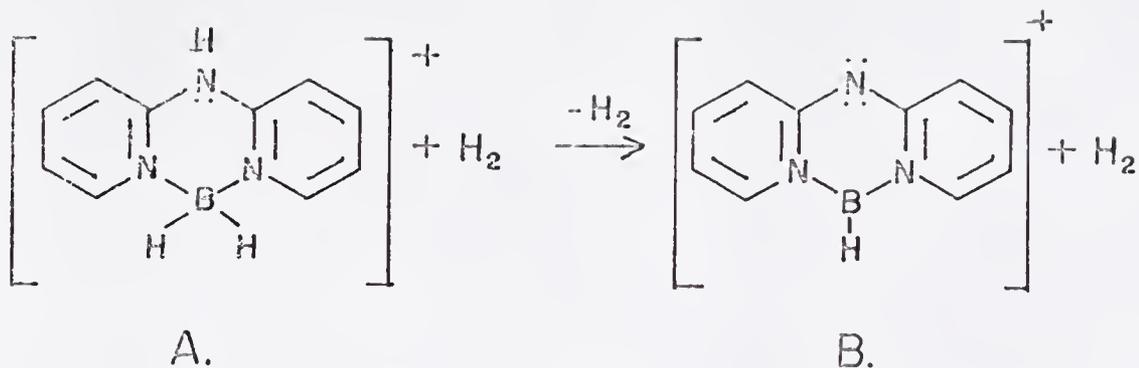
If ring closure on 2,2'-dipyridylamine with a BH_2 unit could be accomplished, a three-membered fused ring system would be obtained. Although the boron portion would be tetrahedral, the system would have fourteen π -electrons and would appear to be a good chemical precursor for forming an aromatic heterocyclic system isoelectronic to anthracene. To accomplish this, the boron portion would have to become trigonal.

Miller and Muetterliches (13) prepared borane cations of the

general formula $H_2B(\text{base})_2$ (base = NR_3 , PR_3 , AsR_3 , SR_2) by taking a donor-substituted borane and heating in a sealed tube with onium salts of the type DH^+X^- . The restrictions on X^- were that they must be stable toward reduction and large so as not to compete with the donor. For this reason, iodide ion and polyhedral borane ions such as $B_{12}H_{12}^{-2}$ were used. The biggest restriction in this synthesis on the donor was steric. With sterically hindered donors such as triethylamine, cations could not be prepared. Very weak donors such as arsines and sulfides were prepared by having equal amounts of HX and the donor sealed with the base-borane adduct, for their onium salts were difficult to isolate.

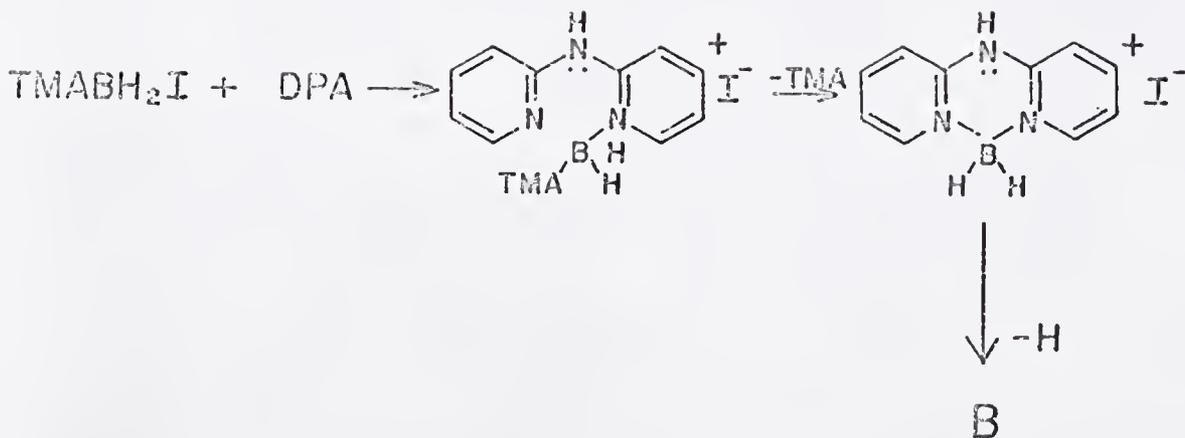
Using a similar reaction scheme, if iminodi(2,2'pyridinium) (2+) iodide and trimethylamine borane ($TMABH_3$) in a 1:1 molar ratio were heated in a sealed tube, one may expect the following reaction to occur.

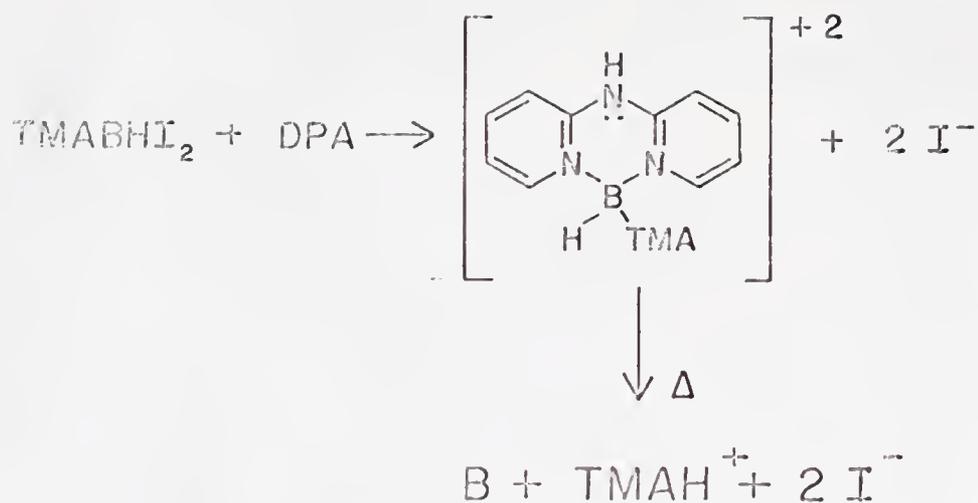




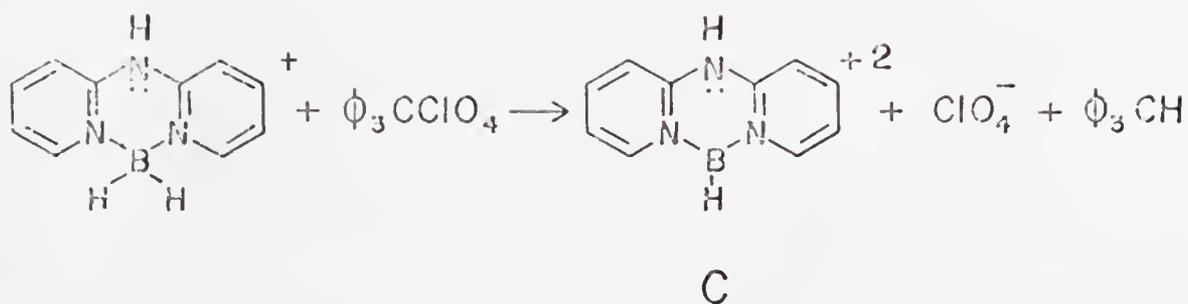
Muetterties also prepared cations by the following reaction scheme: $(H_2BD_2)^+ + 2D' \rightarrow (H_2BD'_2)^+ + 2D$. He observed experimentally that reaction occurred most readily when the new donor (D') was a stronger donor or one with chelating ability. One would therefore expect to get the desired product by heating $(TMA)_2BH_2^+I^-$ with 2,2'-dipyridylamine (DPA) and get loss of two moles of TMA and formation of A and, perhaps, B.

Two other alternate methods which involve trimethylamine-monoiodoborane ($TMABH_2I$) and trimethylamine-diiodoborane ($TMABH_2I_2$) appeared feasible.



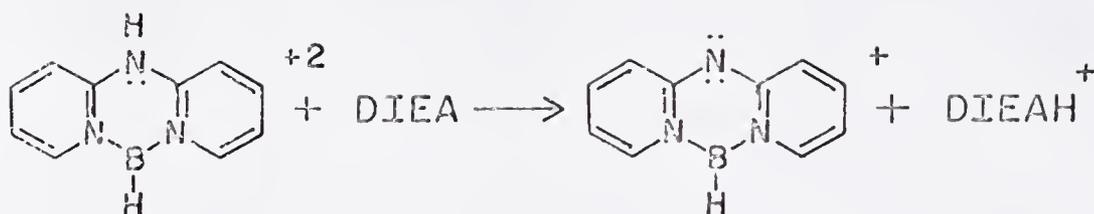


If ring closure were accomplished to form a cation (A) but aromaticity were not obtained spontaneously by hydrogen elimination, there would be a number of synthetic techniques which could be used to form the desired aromatic heterocycle. Hydride abstraction, with triphenylmethyl perchlorate, could possibly be used to obtain a trigonal boron but the disadvantage of this method would be the development of a plus two charge.



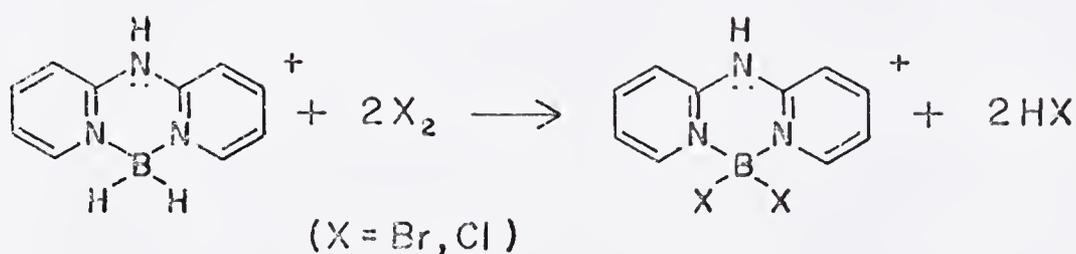
The development of a plus two charge would probably facilitate proton loss from C to produce B. Any number of bases could be used to accomplish this. The only major restriction would be that the base should be sterically hindered so that it could not easily coordi-

nate to the boron portion. Diisopropylethylamine (DIEA) would be a good base to use.

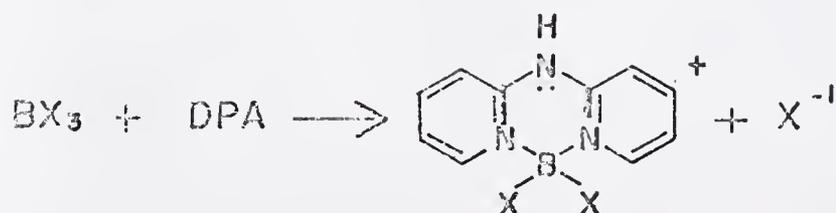


If the systems containing a B-H bond cannot be formed, perhaps a halogenated analog could be prepared. A halogen attached to the boron portion could share a pair of its non-bonded electrons with the boron and help stabilize the system.

Synthesis of a halogenated boron cation could be effected by either direct halogenation of the cation (A) or ring closure starting with a boron trihalide and 2,2'-dipyridylamine.



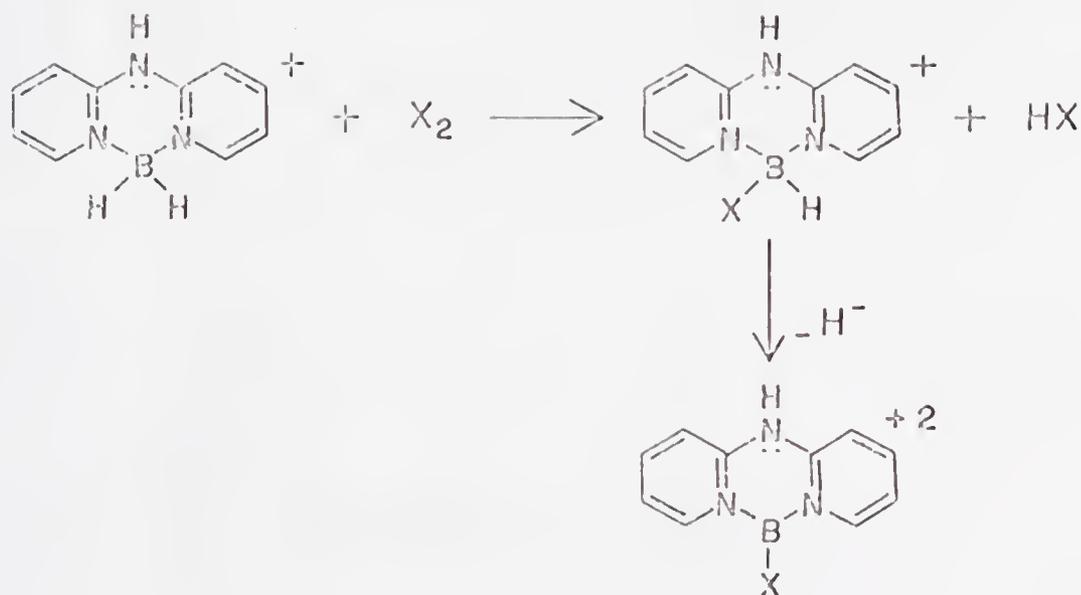
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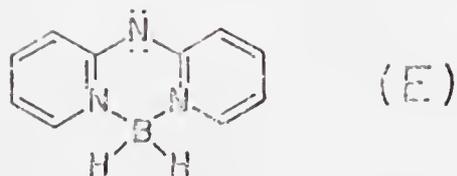
D

A heterocyclic aromatic system could now be achieved by halide loss.

If one were able to monohalogenate so that the boron was bonded to the ring system, a halide and a hydrogen, the technique of hydride abstraction could again be attempted to produce a heteroaromatic system.



Attempts to prepare this heteroaromatic analog to anthracene using the techniques discussed above were made and, although no heteroaromatic system was isolated, a zwitterion (E) was isolated.



This stable, highly colored compound exhibited unique reactivity which was studied in detail.

CHAPTER II
MATERIALS AND INSTRUMENTATION

Materials

Cylinder gases were obtained from Matheson Company and were used for the most part without further purification.

Ammonium hexafluorophosphate was obtained from Ozark-Mahoning Company.

Amine-boranes were obtained from Callery Chemical Company and were used without further purification.

2,2'-Dipyridylamine was supplied by either Aldrich Chemical Company, Inc. or Reilly Tar and Chemical Corporation and was used without further purification.

Sodium borohydride was obtained from Metal Hydrides, Inc. in good purity.

All solvents except 1,2-dimethoxyethane (monoglyme) and diethylene glycol dimethyl ether (diglyme), supplied by various commercial sources, were used without purification except for drying over calcium hydride or Molecular Sieves 3A. Monoglyme and diglyme were stored over calcium hydride for a few days and were then fractionally distilled from lithium aluminium hydride saving the middle 80%.

Instrumentation

Infrared spectra were obtained on a Beckman IR-10 spectrophotometer. Samples were prepared as KBr pellets. Liquid amines were

run neat if possible, using either sodium chloride or potassium bromide plates.

Proton nmr spectra were taken on a Varian A-60 instrument with tetramethylsilane as internal reference. ^{19}F nmr spectra were run at 94.1 MHz with perfluorobenzene as internal reference. ^{11}B nmr spectra were run at either 32.1 MHz with external boron trifluoride etherate or at 25.2 MHz with trimethylborate external standard.

Ultraviolet and visible spectra were obtained on either a Beckman DB-G spectrophotometer or a Cary 15 recording spectrophotometer using 1 cm square fused silica cells.

Melting points were taken on a Thomas-Hoover apparatus and were not corrected.

Elemental analyses were obtained from Peninsular Chem-Research, Inc., Galbraith Laboratories, Inc., or Atlantic Microlab, Inc.

All pH measurements were taken with a Corning 12 Research pH meter with a Beckman Ag-AgCl glass electrode vs. a saturated calomel electrode.

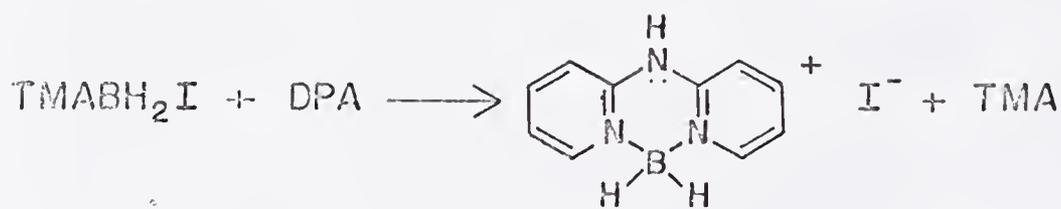
Mass spectra were obtained on a Perkin-Elmer RMU-6E model mass spectrometer over the range from 10-300 amu at an ionizing voltage of 70 V.

CHAPTER III
EXPERIMENTAL

Synthesis

Synthesis of dihydro (2,2'-iminodipyridine-N¹,N^{1'}) boron

(1+) iodide (1-) and hexafluorophosphate (1-).--



Into a 250 ml Erlenmeyer flask containing a magnetic stirring bar were placed trimethylamine-borane (1.46g, 0.020 mole) and 100 ml of reagent-grade benzene which had been dried over Molecular Sieves 3A. With vigorous stirring, solid I₂ (2.59g, 0.020 mole) was added in small portions over a thirty-minute period. After each addition the flask was loosely stoppered in order to minimize exposure to moisture yet to allow hydrogen to escape. After all the I₂ had reacted, there was quickly added to the resulting reddish solution a warmed solution of 2,2'-dipyridylamine (3.42g, 0.020 mole in 75 ml of dry benzene). Depending on the temperature of the 2,2'-dipyridylamine solution, one could have obtained either an immediate lightening of the solution if

the solution were hot or an immediate darkening of the reaction mixture occurred, and a solid was formed if the 2,2'-dipyridylamine solution was only warmed. A reflux condenser with a t-tube attached for the flushing of nitrogen and a CaCl_2 drying tube were quickly put into place and the solution was heated to just below reflux. As warming occurred, the solution lightened and the solid dissolved until a light yellow solution resulted. As the solution warmed, trimethylamine evolved and the solution again became turbid. After approximately 48 hours, no more trimethylamine evolved and a yellow solution with a yellow solid was left.

The product (5.85g, 94.1%) was collected after suction filtration and washing with 30 ml of cold dry benzene and three 20 ml portions of dry diethylether. The melting point of the crude light yellow solid was 173-175° with decomposition. After recrystallization from methylene chloride - diethyl ether, the product became white and melted sharply at 178.5°.

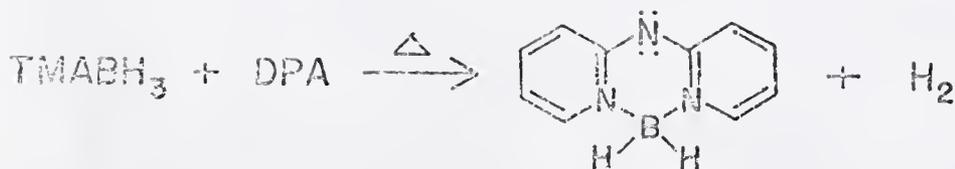
The infrared spectrum of the product showed absorptions at 3060, 3000 (w), 2960, 2890, 2830, 2770 (w), 2470, 2410, 2360 (w), 1645 (s), 1600, 1590, 1520 (s), 1485 (s), 1460, 1375, 1255 (s), 1190, 1170, 1150, 1120, 1045 (w), 910, 785 (s), 735 (w), 600 (w), and 545 (w) cm^{-1} . The proton nmr was run in CH_3NO_2 with internal tetramethylsilane as reference and showed two multiplets centered at -8.12 ppm and -7.47 ppm with an intensity ratio of 3 to 1 respectively. The ^{11}B nmr was run in CH_3CN and showed a triplet at $+6.0 \pm 0.6$ ppm from borontrifluoride etherate. The solution was saturated but the signal was so weak that coupling constants could not be calculated readily from the spectrum.

Conversion to hexafluorophosphate salt.---The iodide salt was converted to the hexafluorophosphate salt in 97.6% yield by quick precipitation with excess 5M NH_4PF_6 solution from a warmed solution of the iodide in 0.05M HCl and cooling in an ice-bath. The product was then filtered and dried under vacuum over CaSO_4 . The white solid melted at 178-180°. The infrared spectrum in a KBr pellet showed absorptions at 3370, 2495, 2440, 1690 (s), 1600, 1580 (s), 1300 (s), 890 (s-broad), 780 (s), and 560 (s) cm^{-1} . The proton nmr was run in CH_3NO_2 with internal tetramethylsilane as reference and showed two multiplets of equal intensity which were centered at -8.27 ppm and -7.53 ppm. The ^{11}B spectrum was run in CH_3CN and showed a triplet at +6.7 ppm from borontrifluoride etherate. The signal was so weak that 3-H coupling constant could not be calculated.

The analysis calculated for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{BPF}_6$ was C, 36.51; H, 3.37; N, 12.77. Found: C, 36.37; H, 3.41; N, 12.70.

Synthesis of dihydro[(2,2'-iminodipyridinato)(1-)- $\text{N}^1, \text{N}^{1'}$]
boron.---There are two methods for the preparation of dihydro [(2,2'-iminodipyridinato)(1-)- $\text{N}^1, \text{N}^{1'}$] boron. The first method prepares dihydro [(2,2'-iminodipyridinato)(1-)- $\text{N}^1, \text{N}^{1'}$] boron by a more direct route from trimethylamine-borane and 2,2'-dipyridylamine. The second method is less direct but the product is purer.

(a) From 2,2'-dipyridylamine and trimethylamine-borane.---



Into a Erlenmeyer flask containing a magnetic stirring bar were placed trimethylamine-borane (3.65g, 0.050 mole), 2,2'-dipyridylamine (8.56g, 0.050 mole) and 175 ml of reagent grade toluene which had been dried over Molecular Sieves 3A. A water-cooled reflux condenser with a t-tube for nitrogen gas flow at the top was set in place, and the solution stirred and heated to a gentle reflux. (Some solid may persist until the toluene becomes warm.) As the solution was heated, trimethylamine was evolved as indicated by odor and by moist pHydron paper turning blue when placed in the nitrogen stream.

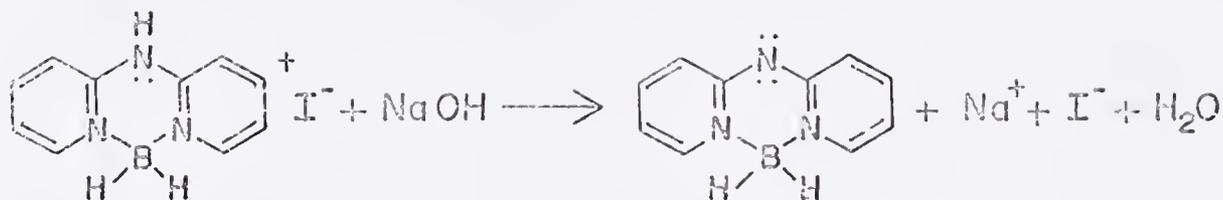
After forty hours trimethylamine evolution stopped and an orange solution with some orange solid remained. The toluene was stripped off under vacuum and the product (9.41g) was collected as an orange solid.

The orange impurity was removed by dissolving the solid in 500 ml of warmed aqueous 1M HCl and adding 25 ml NH_4PF_6 . An off-white solid immediately precipitated. The mixture was cooled in an ice-bath, suction filtered and washed with three 30 ml portions of ether. The off-white solid (12.5g) was then dried under vacuum over CaCl_2 .

With the majority of the impurities removed, the dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorobphosphate (1-) (1.93g) was dissolved in 160 ml of hot water and with vigorous stirring 30 ml of 2M NaOH was slowly added. (Care was needed here, for the warmer the solution, the greater was the tendency for the product to form large lumps. If the solution was cooled until a very slight turbidity was noticed and then the 2M NaOH solution added, a more granular product resulted.) There was an immediate bright yellow precipitate. The mixture was cooled in an ice-bath, suction filtered, washed with

two 30 ml portions of ice cold water, and dried under vacuum over CaCl_2 . The yellow solid (0.94g, 87.4%) melted at 106-107.5°.

(b) Neutralization of the cation.--



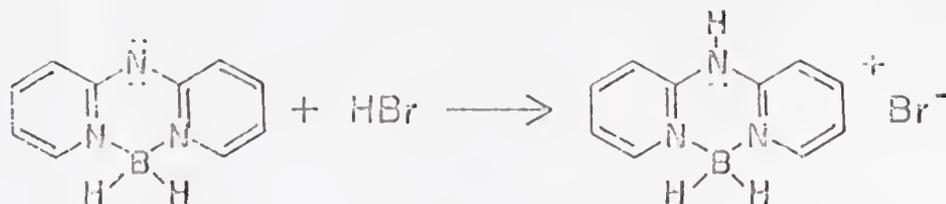
Dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) iodide (1-) (15.55g, 0.050 mole) was dissolved in 250 ml of warm 0.05M HCl solution to give a colorless solution. The solution was cooled in an ice-bath to room temperature and with vigorous stirring 45 ml of 2M NaOH was slowly added. The mixture was cooled in an ice-bath, suction filtered, washed with three 30 ml portions of ice cold water and dried under vacuum over CaCl_2 . The bright yellow solid (7.94g, 86.8%) melted at 106-107.5°.

The infrared spectrum in a KBr pellet showed absorption at 2340 (broad, structured), 1640 (s), 1560, 1470 (s,broad), 1270 (w), 1210 (w), 1130, 1120, 1080 (w), 1065, 1030 (w), 920 (w), 875 (v.w), 775 (s), 730 (w), and 560 (v.w) cm^{-1} . The proton nmr was run in CH_3CN and showed two multiplets of equal intensity at -7.55 ppm and -6.58 ppm from internal tetramethylsilane. The ^{11}B nmr spectrum was run in CH_3CN and showed a triplet at $+5.9 \pm 0.6$ ppm from borontrifluoride etherate. The B-H coupling constant was approximately 110 Hz.

The analysis calculated for $\text{C}_{10}\text{H}_{10}\text{N}_3\text{B}$ was C, 65.62; H, 5.51; N, 22.96. Found: (i) C, 65.73; H, 5.68; N, 22.28 and (ii) C, 65.65;

H, 5.66; N, 22.84.

Synthesis of dihydro (2,2'-iminodipyridinato)(1-)-N¹,N^{1'} boron (1+) bromide (1-).--



A 50 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (3.69g, 0.0202 mole) and 40 ml of methylene chloride which had been dried over Molecular Sieves 3A. Slowly HBr (Matheson cylinder gas) was passed through a trap, cooled in a methylocyclohexane slush and then bubbled through the yellow solution. After 20 minutes the color had disappeared and a white solid had precipitated. The mixture was then stirred for an additional five minutes.

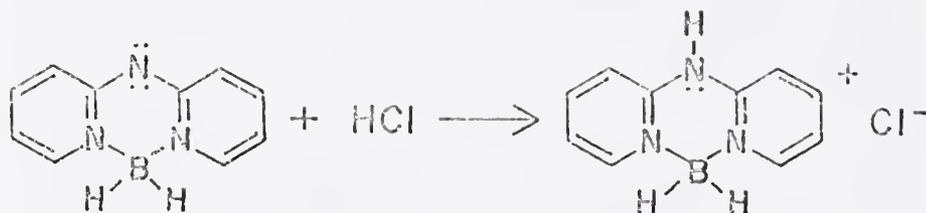
The methylene chloride was removed by blowing dry nitrogen across the solution and the remaining solid was dried under vacuum over CaCl₂ for nine hours. The white product (5.40g, 151% yield) melted at 162-164°.

The product was recrystallized by dissolving the white solid (5.00g, 0.019 mole) in 160 ml of warm CH₃CN and letting the solution cool slowly. When precipitation started, the mixture was cooled in an ice-bath, 250 ml dry diethyl ether was added, and the mixture was again cooled. The product (4.11g, 80% yield) was filtered by suction and dried under vacuum over CaCl₂. The white solid started to yellow at 176° and melted at 185° with decomposition. The infrared spectrum of

the product showed absorptions at 3060 (w), 2910 (s), 2760 (s), 2460 (s), 2400, 2360 (w), 1650 (s), 1590, 1520 (s), 1480 (s), 1455 (s), 1370, 1250 (s), 1190 (w), 1170 (w), 1145 (w), 1040 (w), 905, 890 (w), 800, 775 (s), 730 (w), 600 (v.w), and 540 (v.w) cm^{-1} . The proton nmr was run in CH_3NO_2 with tetramethylsilane as internal reference and showed two multiplets of intensity ratio 3:1 at -8.12 ppm and -7.44 ppm respectively.

The analysis calculated for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{BBr}$ was C, 45.50; H, 4.20; N, 15.92; Br, 30.27. Found: C, 45.71; H, 4.26; N, 16.03; Br, 30.10 and C, 45.69; H, 4.31; N, 15.88; Br, 30.29.

Synthesis of dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) chloride (1-).--



A 50 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron (0.915g, 0.005 mole) and 40 ml of methylene chloride which had been dried over Molecular Sieves 3A. Slowly HCl (obtained from Matheson) was bubbled through the yellow solution until the color disappeared. The colorless solution was then stirred for five minutes.

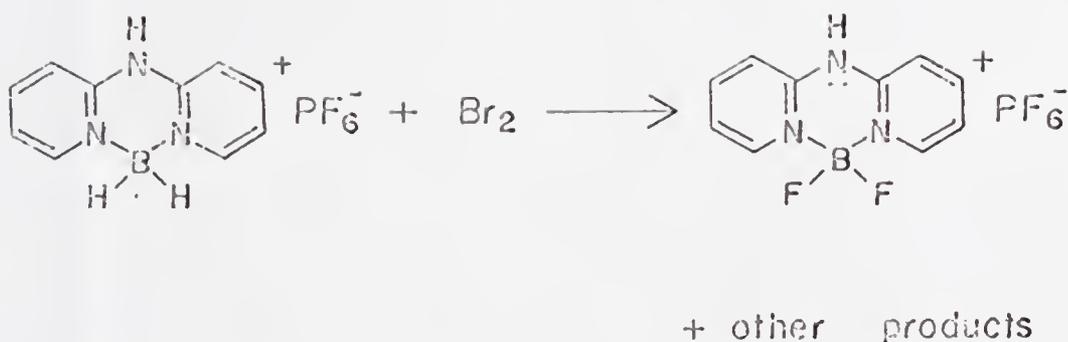
The solution was transferred to a 250 ml beaker and 150 ml of diethyl ether was added. The beaker was cooled in an ice-bath and

the product (1.02g, 98.5%) was suction-filtered, washed with 30 ml diethyl ether, and vacuum-dried over CaCl_2 . The white solid melted at $192.5\text{--}193^\circ$ with decomposition.

The infrared spectrum of the product showed absorptions at 3060 (w), 2820 , 2770 , 2475 , 2400 (w), 2360 (v.w), 1650 (s), 1590 , 1525 (s), 1495 (s), 1460 , 1375 (w), 1225 , 910 , 805 (w), and 780 (s) cm^{-1} . The proton nmr was run in CH_3CO_2 with internal tetramethylsilane as reference and showed two multiplets of intensity ratio 3:1 at -7.89 ppm and -7.38 ppm respectively.

The analysis calculated for $\text{C}_{10}\text{H}_{11}\text{BCl}$ was C, 54.72; H, 5.05; N, 19.14; Cl, 16.15. Found: C, 54.96; H, 5.05; N, 19.04; Cl, 16.42.

Synthesis of difluoro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate (1-).--



Into a 125 ml Erlenmeyer flask containing a magnetic stirring bar were placed dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate (1-) (0.905g, 2.75 mole) and 25 ml of nitroethane which had been dried over Molecular Sieves 3A. With stirring, bromine (0.500g, 3.13 mole) was added drop-wise and the resulting solution was stirred

for four hours. At this time a ^1H -nmr was run and there was no starting material left, as evidenced by a complete downfield shift in the spectrum from the reactants. The excess bromine was destroyed by adding drop-wise cyclohexane until the solution was decolorized.

The mixture was then transferred to a 300 ml beaker and 200 ml of dry diethyl ether was added. An off-white solid precipitated and the mixture was cooled in an ice-bath. The mixture was suction-filtered and partially dried by allowing air to pass through the collected precipitate for a period of about five minutes.

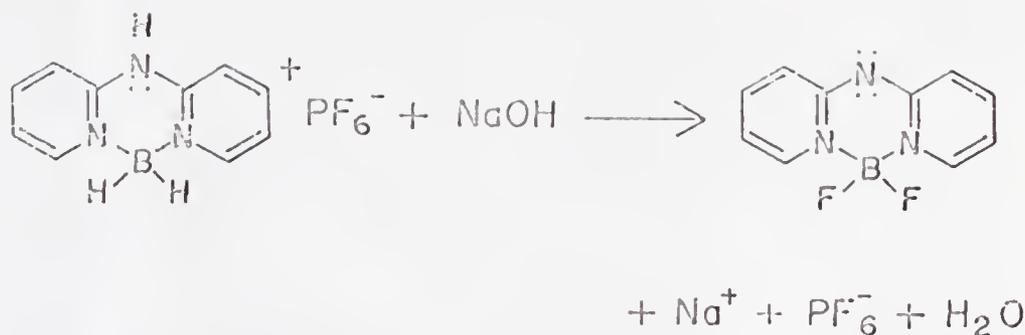
The off-white solid was then dissolved in 100 ml of hot water, 5 ml of 5M NH_4PF_6 was added, and the mixture was cooled in an ice-bath. The white product (0.713g, 71.3%) was collected after suction filtration, washing with 30 ml of ice cold water and three 30 ml portions of dry ether. The white product melted at $187\text{--}188^\circ$. On subsequent runs the yield varied from 45% to 75% with no apparent reason.

The infrared spectrum taken in a KBr pellet showed absorptions at 3100 (w, broad), 1655 (s), 1610 (s), 1530 (s), 1495 (s), 1460, 1275, 1265, 1180 (s), 1140 (s, structured), 1040, 1025 (s), 850 (s, broad), 780 (s), and 560 cm^{-1} . The proton nmr was run in CH_3NO_2 with internal tetramethylsilane as reference and showed two multiplets of equal intensity at -8.48 ppm and -7.67 ppm . The ^{11}B nmr was run in CH_3CN and showed a triplet with extremely small splitting at 0.0 ppm from borontrifluoride etherate. The ^{19}F nmr was run in CH_3CN with trifluoroacetic acid as external reference and showed a doublet with an intensity ratio of 2.8 at -6.2 ppm with a P-F coupling constant of 740 Hz and a quartet with an intensity ratio of 1 at 63.2 ppm with a B-F coupling constant of about 25 Hz.

The analysis calculated for $C_{10}H_9N_3BF_6P$ was C, 32.91; H, 2.49; N, 11.51; F, 41.64. Found: C, 33.17; H, 2.73; N, 11.50; F, 41.98.

Synthesis of difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}]

boron.--

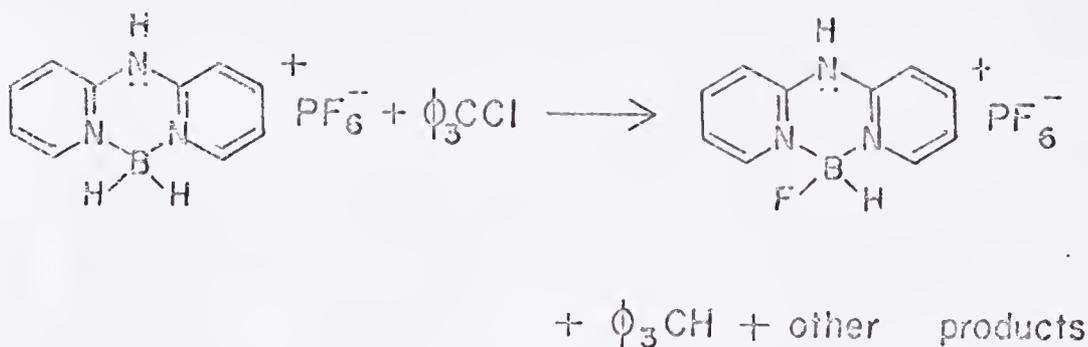


Difluoro (2,2'-iminodipyridine-N¹,N^{1'}) boron (1+) hexafluorophosphate (1-) (0.713g, 1.96 mole) was dissolved in 100 ml of warmed water in a 250 ml beaker. The solution was then cooled until a very slight turbidity was noticed. With vigorous stirring 15 ml of 2M NaOH was slowly added and a light yellow solid formed. The mixture was cooled in an ice-bath, suction-filtered, washed with 30 ml of ice cold water and dried under vacuum over CaCl₂. The light yellow product (0.587g, 82.4%) melted at 149.5-150°. The infrared spectrum of the product showed absorptions at 3090 (w), 3050 (w), 2400 (v.w), 1630 (s), 1563 (s), 1545 (s), 1485 (v.s, broad), 1290, 1255 (v.w), 1175, 1155 (med. s), 1140 (med. s), 1120 (med. s), 1090 (s, structured), 1035, 1020, 1005 (s), 865, 780 (s), 755, 680 (w), 580 (w), and 560 (w) cm⁻¹. The proton nmr was run in CH₃CN with internal tetramethylsilane as reference and showed two multiplets of equal intensity at -7.92 ppm and -7.01 ppm. The ¹⁹F spectrum was run in CH₃CN with internal hexafluorobenzene as reference and showed a quartet at -28.6 ppm. The B-F coupling con-

stant was calculated to be 29.5 Hz.

The analysis calculated for $C_{10}H_8N_3BF_2$ was C, 54.84; H, 3.68; N, 19.19. Found: C, 54.51; H, 3.88; N, 19.19.

Synthesis of fluorohydro (2,2'-iminodipyridine-N¹,N^{1'}) boron (1+) hexafluorophosphate (1-).--



A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro (2,2'-iminodipyridine-N¹,N^{1'}) boron (1+) hexafluorophosphate (1-) (3.37g, 0.010 mole), chlorotriphenylmethane (2.79g, 0.010 mole), and 25 ml of dry nitromethane which had been stored over Molecular Sieves 3A. The flask was then corked and within three minutes of stirring, all the solid dissolved and an orange solution resulted.

After twenty hours of stirring, some solid ammonium hexafluorophosphate (about 1-2g) was added and allowed to mix for ten minutes. The mixture was then transferred to a 600 ml beaker, 400 ml of diethyl ether was added and the mixture was cooled in an ice-bath. The solid was collected by suction filtration and dried.

The impure solid was then dissolved in 100 ml of hot water, 3 ml of 5M NH_4PF_6 solution was added and the solution was again cooled. The white product (1.69g, 48.7% yield) was collected by suction fil-

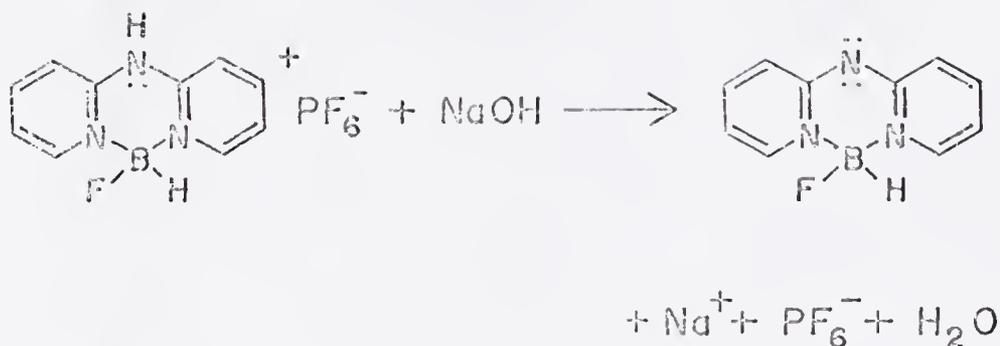
tration, washed with three 30 ml portions of diethyl ether and dried under vacuum over CaCl_2 . The white solid melted at 151-152°, with decomposition.

The product was recrystallized by dissolving the solid (1.52g) in 75 ml of hot water, adding 3 ml 5% NH_4PF_6 , cooling in an ice-bath and suction filtering. The white solid (1.33g, 87%) was dried under vacuum over P_2O_5 at 60°. The product melted at 170° with decomposition. The infrared spectrum of the product showed absorptions at 2900 (s), 2480, 1660 (s), 1610, 1540 (s), 1495 (s), 1460, 1275, 1200, 1180, 1160, 1140, 1045 (w), 1010 (w), 850 (s, broad), 775 (s), and 560 (s) cm^{-1} . The proton nmr spectrum was run in CH_3CO_2 with internal tetramethylsilane as reference and showed two multiplets of equal intensity at -3.75 ppm and -7.75 ppm. The ^{19}F spectrum was run in CH_3CO_2 with internal hexafluorobenzene as reference and showed a doublet at -101.1 ppm and a very broad hump at -5.5 ppm. The F-F coupling constant was calculated to be 707 Hz.

The analysis calculated for $\text{C}_{10}\text{H}_{10}\text{N}_3\text{BF}_7\text{P}$ was C, 34.61; H, 2.91; N, 12.11; F, 38.33. Found: C, 34.32; H, 2.76; N, 11.90; F, 37.74. Although the agreement between the calculated and the found values of the analysis was good, it was found later that there was an impurity present. This impurity was mostly difluoro (2,2'-iridinodipyridine- $\underline{\text{N}}^{\text{I}}$, $\underline{\text{N}}^{\text{I}}$) boron (1+) hexafluorophosphate. If one assumed that the same ratio between product and impurity was obtained upon conversion to the "neutral" adducts, the ratio would be approximately 8:2 as evidenced by mass spectrum parent peak intensities of the "neutral" adducts later generated.

Synthesis of fluorohydro [(2,2'-iminodipyridinato)(1-)-

N¹,N^{1'}] boron.---



Fluorohydro (2,2'-iminodipyridine-N¹,N^{1'}) boron (1+) hexafluorophosphate (1-) (1.29g, 0.00371 mole) was dissolved in 150 ml of warmed water in a 300 ml beaker. The solution was then placed in an ice-bath and cooled until a very slight turbidity was noticed. With vigorous stirring 15 ml of 2M NaOH was slowly added and a light yellow solid was formed. The mixture was cooled to ice temperature, suction filtered, washed with 30 ml of ice cold water and dried under vacuum over CaCl_2 . The light yellow product (0.546g, 73.0% yield) melted at 136° . At this point a mass spectrum was run and showed that there was about a 20% impurity of difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron. Attempts were made to sublime the desired product from the impurity but were for the most part unsuccessful. Elution chromatography proved more successful.

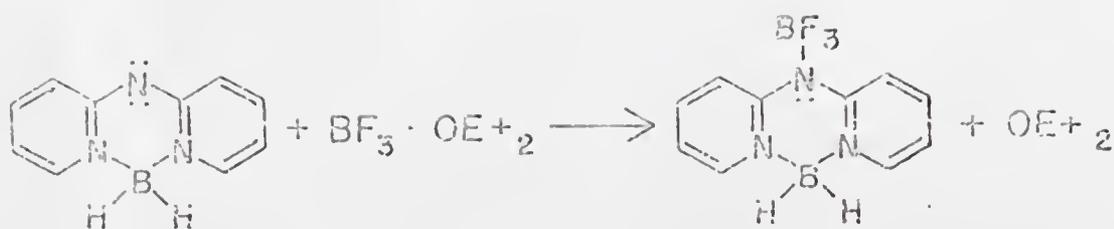
A column 2.2 cm wide was packed with neutral activated alumina (60g) and 1g of the impure product was placed on the column with 5 ml of methylene chloride. The column was then developed with approximately one gallon of benzene and finally cleared with 500 ml of methyl-

ene chloride. There were forty-one fractions in all. The first four fractions were about 250 ml and the other fractions were about 80 ml. Again a mass spectrum was run and now only a 10% impurity remained. The purified sample was again passed through a chromatography column similar to the one described above and 0.2g of pure fluoro hydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron was obtained with less than 0.5% impurity as evidenced by mass spectrum parent peak intensity ratios. The light yellow compound melted at 135.5°. The infrared spectrum of the product showed absorptions at 3090 (w), 3050 (w), 2420, 1650 (s), 1575 (s), 1545 (s), 1485 (v.s, broad), 1245, 1170, 1135 (s), 1135 (s), 1125 (s), 1095 (s), 1065 (s), 1030, 1000 (s), 960 (s), 865 (w), 785 (s), 775 (s), 740 (w), 640 (w), and 560 (w) cm⁻¹. The proton nmr was run in CH₃CN with internal tetramethylsilane as reference and showed two multiplets of equal intensity ratio at -7.23 ppm and -6.97 ppm. The ¹⁹F nmr was run in CH₃CN with hexafluorobenzene as an internal reference and showed a quintet at +15.0 ppm. By using an expanded spectrum, the B-F and H-F coupling constants were calculated and were found to be 77.1 Hz and 64.2 Hz respectively.

The analysis calculated for C₁₀H₉N₃BF was C, 59.75; H, 4.51; N, 20.90; F, 9.45; B, 5.38. Found: C, 59.50; H, 4.59; N, 20.69; F, 9.30; B, 5.59.

Synthesis of dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}]

boron - boron trifluoride (1:1).--



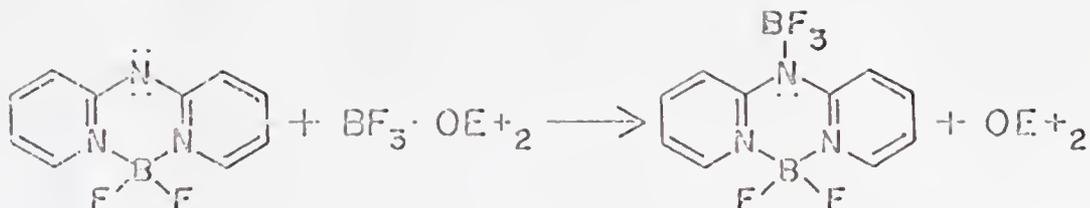
A 125 ml Erlenmeyer flask was charged with dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (4.58g, 0.025 mole) and taken into an inert atmosphere chamber. The solid was dissolved in 40 ml of dry methylene chloride to give a yellow solution. Slowly, with stirring, boron trifluoride etherate (3.30 ml, 0.0260 mole) was added and the solution was decolorized and became warm. After about five minutes a few white crystals could be noticed and within ten minutes there was a large quantity of small white crystals in the reaction mixture. The crystals were suction-filtered, but because they were very fine, a portion passed through the filter paper and the filtrate had to be filtered again. The white crystals were then washed with three 30 ml portions of diethyl ether and dried under vacuum.

The fine white crystals (2.65g, 42.4% yield) softened at 100°; at 191° they started to yellow and by 198° were a red-brown slush but did not completely melt. The infrared spectrum showed absorptions at 3120 (w), 2480, 2395, 2350 (w), 1620 (s), 1585 (s), 1475 (s), 1450 (s), 1360 (s), 1290, 1260 (s), 1175 (s), 1155, 1110 (s, broad, structured), 1080 (s), 1050, 1000 (s), 895 (s), 880 (s), 785 (s), 745 (w), 635, 610 (w), 500 (w), 430 (w), and 400 (w) cm⁻¹. The proton nmr was run in CH₃CN with internal tetramethylsilane as internal reference and showed a complex multiplet centered at -7.70 ppm. The multiplet was 66 Hz wide. The ¹⁹F nmr was run in CH₃CN with hexafluorobenzene as internal reference and showed a clean quartet at -20.60 ppm; the B-F coupling constant was 16.5 Hz.

The analysis calculated for C₁₀H₁₀N₃B₂F₅ was C, 47.88; H, 4.02; N, 16.76; B, 8.62; F, 22.72. Found: C, 47.75; H, 3.87; N, 16.50; B, 8.95; F, 22.44.

Synthesis of difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}]

boron - boron trifluoride (1:1).--



A 25 ml Erlenmeyer flask was charged with difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (0.898g, 0.0041 mole) and was taken into an inert atmosphere chamber. The solid was dissolved in 5 ml of dry methylene chloride to give a yellow solution. Slowly, with stirring, boron trifluoride etherate (0.52 ml, 0.0042 mole) was added drop-wise and the yellow color faded. After swirling for twenty minutes no precipitate could be noticed, so 35 ml of diethyl ether was added and a light yellow solid precipitated out of solution. The yellow solid (0.580g, 42%) was suction-filtered, washed with 30 ml of diethyl ether and dried under vacuum.

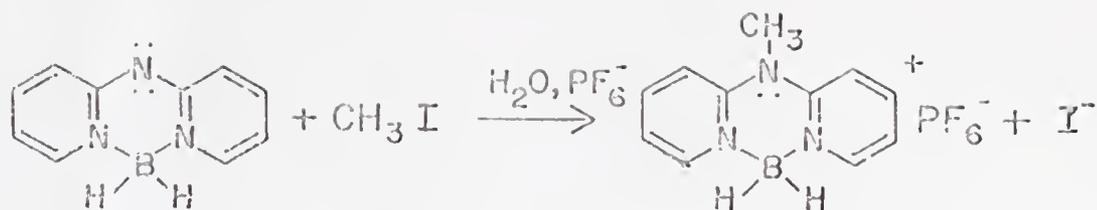
An alternate method for the preparation of difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron - boron trifluoride (1:1) was by reacting boron trifluoride with difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron on the vacuum line. A 50 ml round-bottom flask was charged with difluoro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (2.19g, 0.010 mole), a magnetic stirring bar and the flask were placed on a high vacuum line.

After evacuation, 40 ml of dry methylene chloride was transferred to the reaction vessel and the solid dissolved with stirring to give a yellow solution. The solution was cooled to liquid nitrogen temperature and boron trifluoride (obtained from Matheson, 0.0104 mole) was condensed on the frozen solution. The solid was allowed to warm and the solution was stirred. As the reaction proceeded a light yellow solid precipitated. After twenty minutes of reaction, while slowly warming, all the methylene chloride and the slight excess of boron trifluoride was removed. The solid was dried under vacuum for eight hours. The light yellow solid softened and started to darken around 170° and melted with decomposition around 191°. The infrared spectrum of the product showed absorptions at 3100 (w), 3070 (w), 2720 (w), 2680 (w), 1660 (s), 1630, 1610, 1550 (s), 1485 (s, broad, structured), 1460, 1385 (broad, structured), 1275, 1265, 1190 (broad, structured), 1130 (s, broad, structured), 1090 (s), 1020 (s), 910 (w), 885, 870, 780, 640 (w), and 535 (w, broad) cm^{-1} . The proton nmr spectrum was run in CH_3NO_2 with internal tetramethylsilane as reference and showed a complex multiplet at -7.90 ppm, 70 Hz wide. The ^{19}F nmr spectrum was run in CH_3CN with hexafluorobenzene as internal reference and showed two quartets of area ratio of 3:2.1 at -21.6 ppm and -10.3 ppm respectively. The B-F coupling for the quartet at -21.6 ppm was 15.1 Hz and the B-F coupling constant for the quartet at -10.3 ppm was 23.7 Hz.

The analysis calculated for $\text{C}_{10}\text{H}_8\text{N}_3\text{B}_2\text{F}_5$ was C, 41.87; H, 2.81; N, 14.65; B, 7.54; F, 33.12. Found: C, 41.64; H, 2.78; N, 14.43; B, 7.80; F, 33.34.

Synthesis of dihydro [(2,2'-(methylimino)dipyridine-N¹,N^{1'})]

boron (1+) hexafluorophosphate (1-).--



A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (1.83g, 0.010 mole) and 50 ml of methyl iodide. All the dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron dissolved with stirring to give a yellow solution. Within fifteen minutes a turbidity was noticed and the mixture was allowed to stir for 72 hours to ensure complete reaction. At that time the excess methyl iodide was removed by blowing with nitrogen gas and finally by drying under vacuum over CaCl₂. The whitish-yellow solid (3.28g, 101%) softened at 175° and decomposed without melting. (The excess weight could have been due to an impurity in the methyl iodide or due to some trapped methyl iodide which was not fully removed upon drying. In any case, it was removed when the hexafluorophosphate salt was made.)

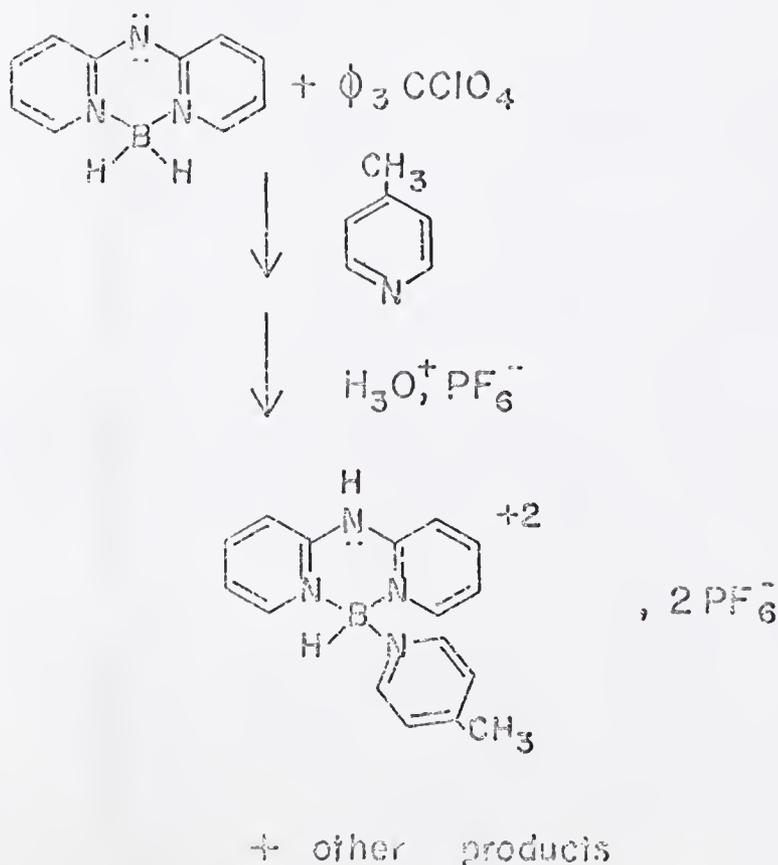
The solid (3.28g) was then converted to the hexafluorophosphate salt by dissolving in 10 ml of warmed water and adding 6 ml of 5M NH₄PF₆. There was an immediate white precipitate. The mixture was then cooled in an ice-bath, suction-filtered, washed with 50 ml of diethyl ether, and dried under vacuum over CaCl₂. The white solid (3.13g,

90.6%) melted at 213.5-215.5° with decomposition. The infrared spectrum of the product showed absorptions at 3120 (w), 2990, 2430, 2390, 1625 (s), 1600 (s), 1570 (w), 1485 (s, broad, structured), 1370 (s), 1275, 1210, 1185 (s), 1130, 1080 (w), 1060 (w), 840 (s, broad, structured), 560 (s), and 425 (w) cm^{-1} . The proton nmr was run in D_3CCN with internal tetramethylsilane as reference and showed a singlet at -3.75 ppm and two complex multiplets at -7.52 ppm and -8.34 ppm. The multiplet at -8.34 was 22 Hz wide. The intensity ratios agreed well with the expected 3:4:4 (singlet:multiplet:multiplet).

The analysis calculated for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{BF}_6\text{P}$ was C, 38.51; H, 5.83; N, 12.25. Found: C, 38.21; H, 5.75; N, 12.13.

Synthesis of hydro (4-picoline)(2,2'-iminodipyridine- $\text{N}^1, \text{N}^{1'}$)

boron (2+) hexafluorophosphate.--



A 125 ml Erlenmeyer flask was charged in the dry box with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $\text{B}^{\text{I}},\text{N}^{\text{I}}$] boron (0.902g, 0.00500 mole), triphenylmethylperchlorate (1.39g, 0.00500 mole), and 30 ml of dry acetonitrile. Upon addition of the solvent, heat was evolved and a yellow solution with a white solid resulted. The flask was then capped with a rubber serum bottle cap, taken out of the dry box, and the reaction mixture was stirred for five minutes. At this time, 4-picoline (4.6 ml, 0.00500 mole) was syringed into the reaction mixture. All the white solid dissolved and a yellow solution was obtained which was then stirred for 24 hours.

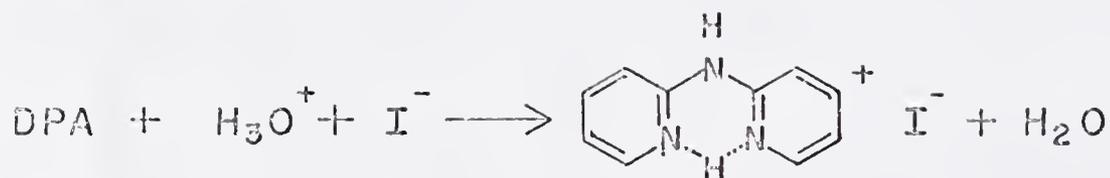
The solution was placed into a 600 ml beaker and 400 ml of diethyl ether was added to precipitate a yellow solid. The beaker was cooled in an ice-bath and the solid collected by suction filtration. The product was partially dried by letting air pass over it for about five minutes. The solid was dissolved in 100 ml of hot water, to which 4 ml of 4M HCl had been added, and the mixture was filtered. To the filtrate was added 5 ml of 5M $\text{Mg}_4\text{P}_2\text{O}_7$ and the mixture was cooled in an ice-bath. An off-white solid was filtered off and dried under vacuum over CaCl_2 ; it melted at 152° with decomposition.

The product was recrystallized from hot water with an 83% recovery and became white. The white solid melted at $162-165^\circ$ with decomposition. The infrared spectrum of the product showed absorptions at 3120 (w), 2970 (w), 2990 (w), 2510, 1660 (s), 1600, 1560 (w), 1535 (s), 1495 (s), 1460, 1275, 1250, 1180 (w), 1150, 1110 (s), 850 (s, broad, structured), 760, 750 (w), 720 (w), 630 (w), and 565 (s) cm^{-1} . The proton nmr was run in CH_3CO_2 with tetramethylsilane as internal reference and showed a very complex multiplet at -7.42 ppm

which was 87 Hz wide and a singlet at -2.63 ppm. The intensity ratio agreed well with the theoretical.

The analysis calculated for $C_{16}H_{17}N_4BF_6P$ was C, 33.95; H, 3.03; N, 9.90. Found: C, 33.87; H, 3.23; N, 10.02.

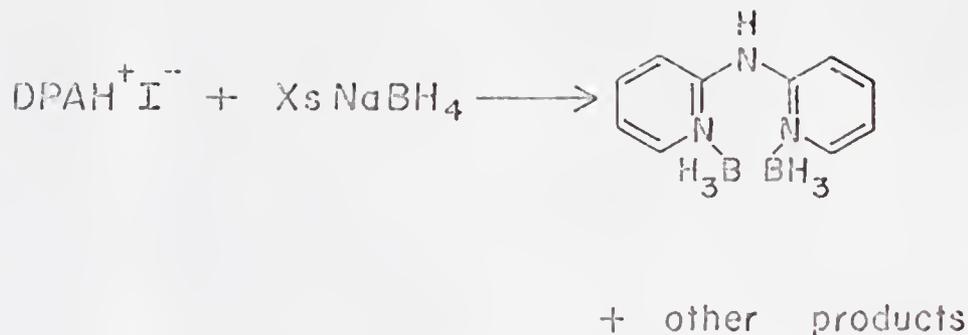
Synthesis of 2,2'-dipyridylammonium (1+) iodide.--



Although non-stoichiometric quantities were used, the desired product was obtained. To a warmed solution of 2,2'-dipyridylamine in 2M HNO_3 was added a concentrated NH_4I solution. A gray precipitate immediately formed. The mixture was cooled in an ice-bath and the precipitate was collected by suction filtration. The gray solid was dissolved in warm water, filtered and the filtrate cooled in an ice-bath. A white precipitate formed. The product was collected by suction filtration and dried under vacuum over CaSO_4 . The white solid darkened when exposed to air. The product melted at 217° with decomposition.

The analysis calculated for $C_{10}H_{11}N_3I$ was C, 40.02; H, 3.69; N, 14.00. Found: C, 39.49; H, 3.39; N, 13.65 and C, 39.40; H, 3.37; N, 13.33.

Synthesis of 2,2'-dipyridylamine-bisborane.--



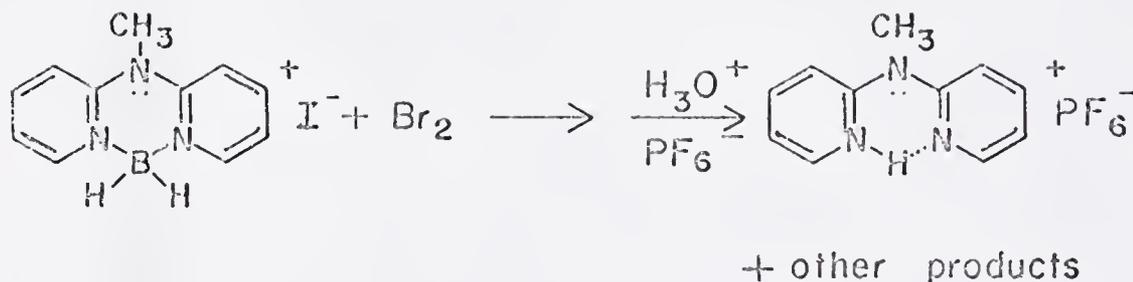
In an inert atmosphere chamber, a 500 ml round-bottom flask was charged with 2,2'-dipyridylammonium (1+) iodide (4.27g, 0.0142 mole), a magnetic stirring bar, and 100 ml of CH_2Cl_2 which had been dried over Molecular Sieves 3A. With stirring, small portions of sodium borohydride were added and after each addition the reaction mixture was allowed to stir until vigorous gas evolution abated. After all the sodium borohydride (1.51g, 0.0400 mole) was added, the flask was stoppered, removed from the dry box and the reaction mixture was stirred for an additional 20 hours.

The off-white product (1.61g, 58%) was collected after mixing the reaction mixture with 400 ml of H_2O , cooling in an ice-bath, and filtering. The white solid was then dried under vacuum over CaCl_2 and melted sharply at $138.5\text{--}139^\circ$ with decomposition. The infrared spectrum of the product showed absorptions at 3240, a very broad structured band from 2310-2420, 1630, 1620 (shoulder), 1575 (s), 1530 (s), 1455 (s), 1330, 1270 (w), 1240 (w), 1220 (w), 1190 (w), 1160, 1120 (w), 1090 (w), 1075 (w), 1055 (w), 960 (w), 930 (w), 770, 585 (w), and 515 (w) cm^{-1} . The proton nmr spectrum was taken in CH_3CN with in-

ternal tetramethylsilane as reference and showed a highly complex set of peaks which could not be interpreted. There was a structured triplet at -7.16 ppm, a broad structured singlet at -7.62 ppm, a three-peaked, highly structured multiplet at -8.01 ppm, a broad structured doublet at -8.50 ppm and a very broad singlet which was approximately 30 Hz wide at -9.47 ppm.

The analysis calculated for $C_{10}H_{15}N_3B_2$ was C, 60.59; H, 7.60; N, 21.13. Found: C, 60.35; H, 7.62; N, 21.24.

Synthesis of 2,2'-dipyridylmethylammonium (1+) hexafluoro-
phosphate salt.



A 50 ml Erlenmeyer flask was charged with dihydro [(2,2'-(methylimino) dipyridine-N¹,N^{1'})] boron (1+) iodide (1-) (1.62g, 0.00500 mole), a stirring bar and 25 ml of dry CH₃NO₂. With vigorous stirring, bromine was almost immediately decolorized until the last drop or so of bromine was added and then a brown solid formed and the solution remained amber colored.

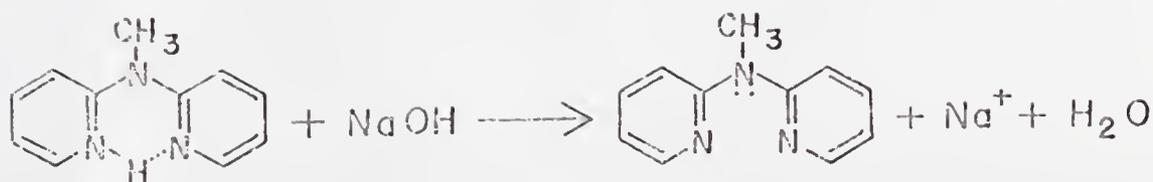
After stirring the reaction mixture for ten hours, the mixture was placed in a 500 ml beaker and 200 ml of diethyl ether was added to precipitate an amber solid. The mixture was then filtered and partially dried by letting air pass over the solid. To the solid were

added 50 ml of 4M HCl, 80 ml of hot water and 10 ml of 0.1M Na_2SO_3 . (The 0.1M Na_2SO_3 was used to destroy any triiodide ion or any mixed trihalide ion which had formed.) With addition of the Na_2SO_3 solution, the amber solution was decolorized to a very light yellow. To the hot solution was now added 5 ml of 5M NH_4PF_6 and the solution cooled in an ice-bath. Upon cooling, a very fine white precipitate formed. The solid (0.737g, 44.5%) was filtered, washed with three 30 ml portions of diethyl ether and dried under vacuum over CaCl_2 . The white solid melted at 174-176°.

The solid (0.735g) was recrystallized from 150 ml of hot water in an 85% yield (0.627g) and had a melting point of 180-181°. The infrared spectrum of the product showed absorptions at 3130 (w, broad), 1635, 1595 (s), 1570, 1535, 1460, 1440, 1400 (w), 1380 (w), 1310 (w), 1260 (w), 1185 (w), 1145 (w), 1070 (v.w), 955 (w), 890, 840 (s, broad, structured), 785, 760, 735 (w), 720 (w), and 560 (s) cm^{-1} . The proton nmr was taken in CH_3NO_2 with internal tetramethylsilane as reference and showed a singlet at -3.81 ppm of intensity ratio three and two complex multiplets at -7.56 ppm and -8.35 ppm, both with an intensity ratio of four.

The analysis calculated for $\text{C}_{11}\text{H}_{12}\text{N}_3\text{F}_6\text{P}$ was C, 39.89; H, 3.65; N, 12.68. Found: C, 39.57; H, 3.65; N, 12.52 and C, 39.95; H, 3.77; N, 12.91.

Synthesis of 2,2'-dipyridylmethylamine.--



2,2'-dipyridylmethylammonium (1+) hexafluorophosphate (0.500g, 0.00151 mole) was placed into a 60 ml separatory funnel along with 25 ml of water and 5 ml of 2M NaOH. The free amine was then extracted with five 25 ml portions of diethyl ether and the ethereal solution was dried over 3g of anhydrous Na_2CO_3 . The ether was removed under vacuum and the slightly yellow-colored liquid amine (0.173g, 62%) was pumped on for 24 hours over CaCl_2 .

A mass spectrum was run at this point and no peaks occurred above 186 mass units and the majority of the fragments could be accounted for. The product boiled at approximately 240° .

The infrared spectrum of the product taken neat between KBr plates showed absorptions at 3060, 3010, 2160 (broad), 1585 (s, broad), 1470 (s, broad), 1425 (s, broad), 1355 (s), 1330 (s), 1280 (s), 1140 (s, broad), 1080, 1055, 985 (s), 895, 775 (s), 740 (s), 640 (w), 620 (w, broad), 570, 530, and 410 cm^{-1} . The proton nmr was run in DCCl_3 with internal tetramethylsilane as reference and showed two very complex multiplets and a singlet; one multiplet at -6.30 ppm of intensity ratio six, the other multiplet at -8.26 ppm of intensity ratio two, and the singlet at -3.82 ppm of intensity ratio three.

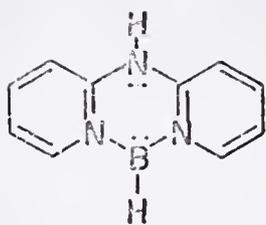
The analysis calculated for $\text{C}_{11}\text{H}_{11}\text{N}_3$ was C, 71.33; H, 5.99; N, 22.68. Found: C, 71.24; H, 6.09; N, 22.80.

Structure Proof

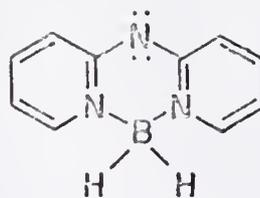
Structure proof of dihydro [(2,2'-iminodipyridinato)(1-)- $\text{N}^1, \text{N}^{1'}$] boron.--It was noticed that the proton nmr spectrum of dihydro (2,2'-iminodipyridine- $\text{N}^1, \text{N}^{1'}$) boron (1+) iodide (1-) and that of the corresponding hexafluorophosphate salt had two multiplets in the aro-

matic region which were of different intensity ratios. The iodide salt had a multiplet intensity ratio of 3:1 and the hexafluorophosphate salt had a multiplet intensity ratio of 1:1. The nmr of the other halide salts (i.e., chloride and bromide) were very similar to that of the iodide salts and also had two multiplets in the ratio of 3:1. This suggested some sort of association between the halide ion and the boronium ion. If it were HX that was associated, a base should remove it and this was attempted on a small scale in an nmr tube.

A sample of the iodide salt was dissolved in CH_3OH , placed in an nmr tube, and its spectrum was run. To the nmr tube was now added three drops of diisopropylethylamine and the solution changed from slightly yellow to an intense yellow and a small amount of precipitate formed. The solid was filtered off and the nmr of the intense yellow solution was run. There were still two complex multiplets in the aromatic region but they were now shifted about 30 Hz upfield and were of equal intensity and, also, the spectrum of the amine was shifted downfield to that of the protonated ammonium ion. This suggested that a proton had been removed. (In general, protonation of an amine or cation formation from an amine borane produces a downfield shift in the proton nmr spectrum.) Other alkylamines were tried and they also removed a proton as evidenced by a downfield shift in their proton nmr spectra. Eventually it was found that the iodide salt in an aqueous solution could be converted to the "neutral" adduct by adding sodium hydroxide and filtering off a bright yellow solid. The yellow compound analyzed well for $\text{C}_{10}\text{H}_{10}\text{N}_3\text{B}$. The question now arose--from where was the proton removed? There are two tautomers, A and B, both of which seemed possible.



A



B

Tautomer A would be a trigonal boron in a heterocyclic system that was stable in air and aqueous sodium hydroxide and tautomer B would be a stable amide zwitterion. The infrared spectrum of this "neutral" compound was taken and the 2300-2500 cm^{-1} region showed a highly structured band at 2350 cm^{-1} . This was in the region where amine borane B-H stretching occurred but the observed band was of no structural help. In the infrared spectrum of the cation the N-H stretch was not easily discernible and therefore could not be used in the structure proof. Tautomer A was eliminated on the basis of the following evidence.

If the "neutral" compound was reacted with DCl, the infrared spectrum in the 2300-2500 cm^{-1} region looked exactly like that of the HCl adduct. There were three peaks corresponding to a BH_2 cation. The H-N and D-N stretches could not be identified.

The neutral compound was allowed to react with methyl iodide and a cation was isolated which contained a methyl group. In the B-H stretching region of its infrared spectrum, there could be found three peaks characteristic to a cationic BH_2 group.

Finally, the ^{11}B nmr was run and a clean triplet was ob-

erved. This proved beyond a doubt that tautomer B was the intense yellow solid.

One can convert dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate (1-) to its conjugate base in the same manner as was done with the iodide salt and then to any of the halide salts simply by bubbling HX into a methylene chloride solution of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron (neutral compound) and stripping off the solvent.

Neutral-cation equilibrium.--Because it took a very long time for all the trimethylamine to evolve and because very soon after mixing the reactants (trimethylamine + tetrachloroborane and 2,2'-dipyridylamine) the characteristic intense yellow color of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron was observed, it was thought that there must be some sort of equilibrium occurring in the preparation of dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) iodide between the ammonium salt, trimethylamine, trimethylammonium iodide, and dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron. To test and see if this was actually the case, the following qualitative experiment was carried out.

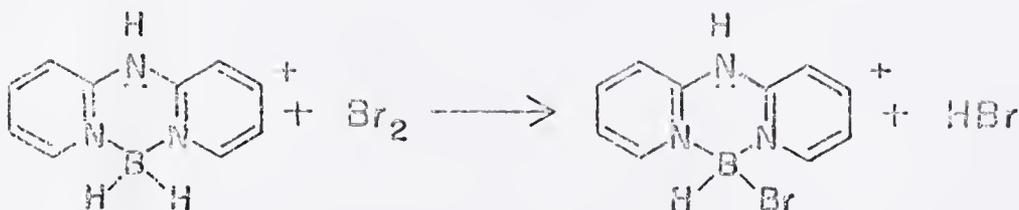
A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, trimethylammonium iodide, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron, and 70 ml of dry benzene. The stirring reaction mixture was brought to just below reflux. While warming the mixture, trimethylamine began to evolve as evidenced by its odor and by the action of the effluent on damp phnydrion paper. After forty-eight hours, trimethylamine evolution ceased and the reaction mixture was cooled. Upon work-up, dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) iodide

was recovered in a substantial amount as evidenced by the proton nmr of the product.

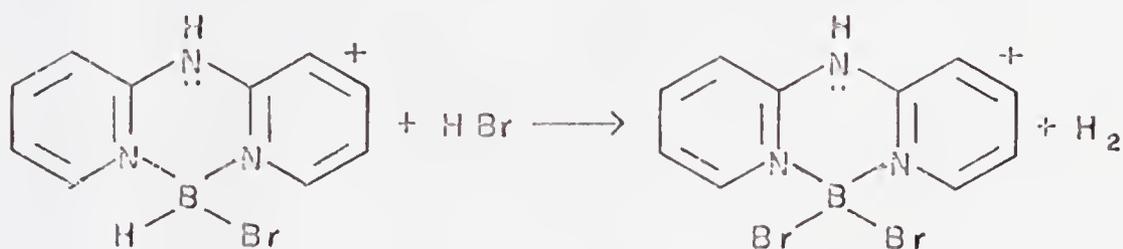
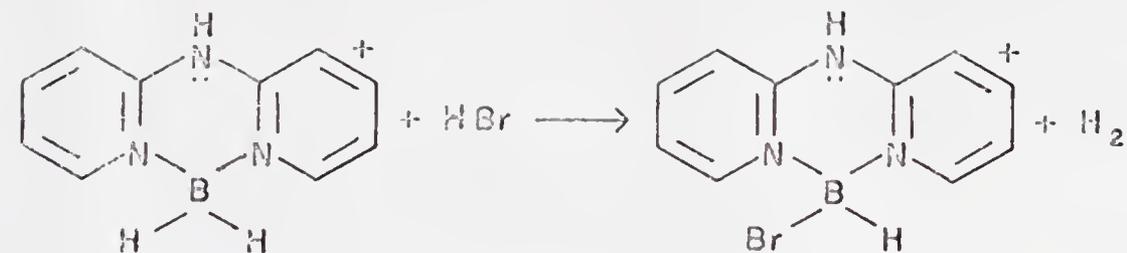
Corroborative Experiments

Difluorination of dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate.-- In the preparation of difluoro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate (1-) there are a number of possibilities which could describe the reaction pathway. Does bromination occur first and then halide exchange to produce a fluorinated product, or does fluorination occur first and the bromine only produce the fluorinating agent? Several reactions were carried out to answer this question.

It was noticed that during the reaction of bromine with dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate (1-), the bromine was immediately decolorized, an acidic gas appeared above the solution, and the glass reaction vessel was etched. When the bromine reacted, the first step would produce a B-Br species and an HBr molecule would be formed.



The HBr could then either react with a B-H and/or the hexafluorophosphate.



It has been demonstrated by Gebald and Jones (40) that in strongly acidic aqueous solutions alkali hexafluorophosphates hydrolyze via a H_3O^+ , PF_6^- intermediate which then decomposes into PF_5 and HF species. If traces of water in the solvent were not removed, a species such as H_3O^+ , PF_6^- could possibly initiate the fluorination reaction (41). Although not much is known about the reaction mechanism, there is also a class of reactions known as Swarts reactions which use HF and antimony pentafluoride to halogenate a variety of substances (42). A well-known fluorinating agent is SbF_5 and HF . Therefore, it would not be unreasonable for the system HBr and PF_6^- to act as the fluorinating agent by forming "H PF_5 " which then decomposes to HF and PF_5 . Either separately or together, HF and PF_5 could be the actual fluorini-

nating agent.

To find out if bromination of a B-H bond was necessary, the following two experiments were carried out.

Experiment A.--A 50 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) bromide (1-) and 30 ml of dry CH_3NO_2 . Because not all the bromide salt dissolved, bromine (0.27 ml, 5 mmole) was added to the slurry dropwise with stirring. Almost immediately, the bromine was decolorized until the last drop was added and a yellow solution resulted. The solution was stirred for ten minutes and became colorless with a white solid suspended in it. Solid ammonium hexafluorophosphate (about 2g) was added and the mixture was stirred for five hours. At this time, the reaction mixture was placed into a large beaker and 300 ml of dry diethyl ether was added to precipitate an orange solid. The beaker was cooled in an ice-bath, the solid was suction-filtered, and partially dried by allowing air to pass over the solid. The product was dissolved in 100 ml of warm water, filtered and 5 ml of 5M NH_4PF_6 was added to the solution. The solution was cooled in an ice-bath and an off-white solid (0.737g, 41%) was collected by suction filtration and dried under vacuum over CaSO_4 . The off-white product melted at 152° and was identified by its infrared spectrum and proton nmr spectrum as difluoro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate.

Experiment B.--A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate (1-) (2.83g, 11 mmole) and 70 ml of dry CH_3NO_2 . Hydrogen bromide, which was purified by passing it through a trap

cooled in a methylocyclohexane slush, was bubbled into the stirring slurry. Within a minute, all the solid dissolved and a clear colorless solution resulted. The HBr was bubbled through the solution for an additional five minutes to make sure the solution was saturated. The flask was stoppered and the solution was allowed to stir. After ten minutes, a slight turbidity was noticed and the solution started to yellow. After four hours the solution was very yellow but still only slightly turbid. At this time, the reaction mixture was poured into a large beaker and 400 ml of diethyl ether was added to precipitate out a yellow solid. The beaker was cooled in an ice-bath and the product was suction-filtered and partially dried by passing air through it. The product was dissolved in 150 ml of warm water, filtered, and 5 ml of 5% NH_4PF_6 was added. Immediately, an off-white precipitate formed. The mixture was cooled in an ice-bath, suction-filtered, washed with 50 ml of diethyl ether, and dried under vacuum over CaSO_4 . The product (1.40g) was identified as a mixture of a small amount of difluoro (2,2'-iminodipyridine- $\text{N}^1, \text{N}^{1'}$) boron (1+) hexafluorophosphate (1-) and 2,2'-dipyridylammonium (1+) hexafluorophosphate by its infrared and proton nmr spectra.

This would seem to indicate that although complete fluorination on boron will occur, it does so slowly, and that bromination first followed by fluoride exchange is the probable reaction pathway.

Bromine-hexafluorophosphate as a general fluorinating agent.--

Because of the ease of fluorination of dihydro (2,2'-dipyridine- $\text{N}^1, \text{N}^{1'}$) boron (1+) hexafluorophosphate with bromine, the possibility of using bromine and a dihydro-boronium hexafluorophosphate as a synthetic route to a difluoro boronium salt was investigated. The reaction of

dihydro bis-4-picoline boronium (1+) hexafluorophosphate with bromine was studied.

A 50 ml Erlenmeyer flask was charged with a magnetic stirring bar, bis-(4-picoline) boronium hexafluorophosphate (2.06g, 6 mmole) and 25 ml of dry CH_3NO_2 . A bromine solution (1.23g, 6 mmole in 10 ml CH_3NO_2) was prepared.

Into an nmr tube were placed 50 drops of the bis-(4-picoline) boronium hexafluorophosphate solution and 20 drops of the bromine solution. The proton nmr of the resulting solution was run at 1, 5, 10, 15, 30, 240 and 600 min. The remaining portions of the reaction solutions were mixed, stoppered and allowed to react.

The reaction mixture in the flask went from amber to light orange within five minutes and was allowed to react for four hours. At the end of four hours, cyclohexene was added dropwise to destroy any bromine which remained in the solution and the solution became colorless. The reaction mixture was transferred to a 600 ml beaker and 400 ml of diethyl ether was added. Only a small amount of precipitate was obtained. After filtration, an aqueous work-up with ammonium hexafluorophosphate was attempted but nothing was recovered.

The nmr tube portion of the reaction showed that bromination occurred within one minute as evidenced by a downfield shift of the ring protons. No further changes occurred in the spectrum after 10 hours, although some material started to fall out of solution.

At the same time, the reaction of bromine with dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate was run on a large scale and in an nmr tube with the reactants in the same concentration as the previous experiment. As evidenced by a downfield

shift in the nmr spectrum, bromination occurred within a minute and within 10 minutes, peaks corresponding to the fluoro-substituted product began to appear and grow. After 15 minutes, material started to precipitate and eventually a spectrum could not be taken. Upon aqueous work-up, the major portion yielded the expected product, di-fluoro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate. It was concluded on the basis of the previous two experiments that the system $\text{Br}_2, \text{PF}_6^-$ was not a general fluorinating agent for boron cations and that the reactivity exhibited by dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate was indeed unique to this system.

Attempted isolation of a bromine substituted product.--

Several attempts were made to isolate a brominated product of dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+).

Experiment A.-- A 500 ml three-necked, round-bottomed flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron (0.915g, 5 mmole) and 100 ml of dry benzene. Into the neck was placed a ground glass stopcock as a dry nitrogen gas inlet, in the center neck was placed a 50 ml burette with a ground glass joint, and in the third neck was placed a CaCl_2 drying tube. A bromine solution (1.87g in 100 ml of dry benzene) was prepared and placed in the burette. The burette was lightly stoppered to keep bromine loss and exposure to moisture to a minimum.

To the stirring solution of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron, the bromine solution was slowly added. Care was taken to let all the bromine react before the next drop was added. This should have kept HBr loss to a minimum. The bromine reacted immediately and a light yellow solid in a colorless solution was left.

After 44.0 ml (5.09 mmoles) was added, the solvent was removed under vacuum and the light yellow solid was taken into the dry box. The solid melted in a sealed capillary at 286° with decomposition. The product was not soluble enough in methylene chloride, acetonitrile or nitromethane to give a usable proton nmr. The infrared spectrum did not show any B-H stretching vibrations. A small portion was exposed to the atmosphere and appeared to rapidly hydrolyze. The light yellow solid decomposed in the dry-box to a light green material.

The analysis on the light yellow material calculated for $C_{10}H_{10}N_3BBr_2$ was C, 35.03; H, 2.94; N, 12.26; and Br, 46.62. Found: C, 34.71; H, 2.87; N, 11.93; and Br, 46.78.

Experiment B.--A 50 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro (2,2'-iminodipyridine- $N^{1},N^{1'}$) boron (1+) bromide (1-) (1.32g, 5 mmole) and 25 ml of dry CH_3NO_2 . To the stirring slurry was added bromine (0.80 ml, 14.5 mmole), drop by drop. Up until about 0.30 ml was added, the solution turned amber and a white precipitate formed. With the addition of all the bromine, the reaction mixture became a clear amber solution. After stirring for 18 hours while stoppered, cyclohexene was added to destroy any excess bromine and an orange oil and a white precipitate dropped out of solution. The reaction mixture was placed in a 400 ml beaker and 300 ml of diethyl ether was added to precipitate out an off-white solid. The mixture was suction-filtered and partially dried by briefly allowing air to pass over the solid. The oil and white solid were then dissolved in 40 ml of water and a green, acidic solution resulted. To the solution was added 4 ml of 5M NH_4PF_6 and an off-white solid precipitated. The mixture was cooled in an ice-bath, filtered, and dried

under vacuum over CaSO_4 . The white solid (0.523g) melted at 191-194° and was identified by comparing its infrared and nmr spectra to the spectra of an authentic sample as 2,2'-dipyridylanmonium (1+) hexafluorophosphate.

Halide displacement by an amine.--Hydro (4-picoline) (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (2+) hexafluorophosphate was prepared by hydride abstraction from dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron with triphenylmethyl perchlorate, subsequent addition of 4-picoline, and finally an aqueous work-up. Since bromination appeared to occur so readily, attempts were made to displace bromine from the product of bromine reacting with dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron.

Experiment A.--A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron (1.83g, 10 mmole) and 60 ml of dry CH_3CO_2 . To the resulting solution, bromine (0.54 ml, 10 mmole) was added dropwise and with stirring. The bromine was immediately decolorized while a white solid precipitated from solution. Upon addition of the last drop, the bromine color persisted. After stirring for five minutes, 4-picoline (19.2 ml, 20 mmole) was slowly added. All the solid dissolved and an orange solution resulted. In about five minutes, a tan solid began to form. The reaction mixture was stirred overnight and the solvent was stripped off with a water aspirator to leave some brown crystals behind. The crystals were dissolved in 100 ml of hot water to which three ml of 4M HNO_3 had been added, 5 ml of 5M NH_4PF_6 was added and the solution was allowed to cool in an ice-bath. A brown precipitate (2.21g) was collected by suction filtration and dried under vacuum.

over CaSO_4 . The brown solid was identified as the ammonium salt 2,2'-dipyridylamine with a mixture of tribromide and hexafluorophosphate as the counter ions.

Experiment B.--A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron (1.83g, 10 mmole) and 70 ml of dry 4-picoline. The solution was stirred and bromine (0.55 ml, 10 mmole) was slowly added. The first 0.44 ml of bromine was immediately decolorized but further addition of bromine resulted in an orange-colored solution which darkened rapidly to amber. The reaction mixture was allowed to stir for 36 hours and a light brown solution with a light brown solid in it resulted. The reaction mixture was poured into a 600 ml beaker and about 150 ml of water was added. Vigorous gas evolution resulted. The solution was neutralized with 4M HCl, 10 ml of 5M NH_4PF_6 was added, and the solution was cooled in an ice-bath. No precipitate formed, and an additional 2g of solid NH_4PF_6 was added. If hydro (4-picoline)(2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (2+) hexafluorophosphate had been present, a precipitate should have been formed at this point.

Experiment C.--A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate (3.29g, 10mmole) and 70 ml of dry 4-picoline. To the resulting slightly turbid solution was added bromine (0.55 ml, 10 mmole). The first 0.44 ml of bromine was immediately decolorized but the last portion gave the solution a very dark amber color. The solution was stirred for 60 hours and a small amount of dark solid formed. The reaction mixture was placed into a 600 ml beaker and 20 ml

of H_2O was added. Vigorous gas evolution resulted and no product could be isolated.

Experiment D.--A 125 ml Erlenmeyer flask was charged with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)- $N^1, N^{1'}$] boron (0.915g, 5 mmole), 4-picoline (11 ml, 11.5 mmole) and 50 ml of dry CH_2Cl_2 . With stirring, bromine (0.27 ml, 5 mmole) was slowly added. A Vigreux column was put into place and the solution was brought to reflux. After refluxing for 36 hours, the cooled reaction mixture was diluted with 400 ml of diethyl ether. The resulting brown solid, after filtering and partial drying, was dissolved in 100 ml of hot water, and the solution was heated with 5 ml of 0.1M Na_2SO_3 and then with 5 ml of 5% NH_4PF_6 . The solution was slowly cooled and brown, long, needle-like crystals formed. The crystals (0.611g) were filtered and dried under vacuum over $CaSO_4$. The infrared and proton nmr spectra indicated that the solid was the salt of 2,2'-dipyridylamine with probably a mixture of tribromide and hexafluorophosphate as counter ions.

It was concluded from these experiments that although bromination occurred, bromide displacement could not be affected by 4-picoline from the proton-cation even when the 4-picoline was in very large excess.

Essentially the same experiments were attempted using dihydro [(2,2'-iminodipyridinato)(1-)- $N^1, N^{1'}$] boron, iodine and 4-picoline. The iodine appeared to react but no product could be isolated with 4-picoline substituted on the boron.

Attempted synthesis of the borane adduct of dihydro [(2,2'-iminodipyridinato)(1-)- $N^1, N^{1'}$] boron.--

Experiment A.--A 300 ml three-necked round-bottomed flask was charged in the dry box with a magnetic stirring bar, dihydro [(2, 2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron (1.83g, 10 mmole), sodium borohydride (1.21g, 32 mmole), and 100 ml of dry monoglyme. The flask was removed from the dry-box and under a nitrogen atmosphere a 125 ml equal-pressure dropping funnel was set into place. An iodine solution (1.27g, 11 mmole in 50 ml of dry monoglyme) was added to the dropping funnel. Slowly with vigorous stirring the iodine solution was added over a period of 60 minutes. The iodine reacted immediately and hydrogen was evolved. After all the iodine was added, the monoglyme was blown off with nitrogen and the yellow solid was pumped on for twenty-four hours with a water aspirator. The yellow solid was extracted with 100 ml of methylene chloride. After the methylene chloride was removed, a yellow solid (1.79g) remained. The product melted at 91.5-93°. The analysis calculated for $C_{10}H_{13}N_5B_2$ was C, 61.02; H, 6.65; N, 21.35; B, 10.98. Found: C, 55.24, 55.47; H, 6.79, 6.93; N, 18.51, 18.89; B, 9.92, 10.03.

Attempts to purify the product by recrystallization and sublimation were to no avail.

Experiment B.--On a high vacuum line freshly prepared and purified diborane (4 mmole) was condensed on an ethereal solution of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron (0.354g, 1.82 mmole in 30 ml of dry diethyl ether). The frozen reaction mixture was allowed to warm up with stirring for twenty minutes and then was frozen with liquid nitrogen. The solution was allowed to warm to -77. The temperature was kept constant by submerging the reaction vessel in a CO_2 -acetone bath. The reaction mixture was stirred for 40 minutes

at this temperature. The solvent was removed and the product, a very light yellow solid, was dried under vacuum for 16 hours at room temperature. The product was weighed and pumped on for an additional 24 hours with no additional weight loss. The added weight (0.0373g, 2.70 mmole) due to "BH₃" was too large to be the desired product.

The experiment was repeated using methylene chloride as the solvent and the same results were obtained. That more weight was added cannot be explained.

Reactivity of dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}]
boron - boron trifluoride (1:1).--A 50 ml round-bottom flask was changed in the dry box with a magnetic stirring bar, dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron - boron trifluoride (1:1) (0.624g, 2.49 mmole), and 50 ml of methylene chloride. The reaction mixture was then placed on a high vacuum line, desecrated and frozen to liquid nitrogen temperature. Anhydrous HCl (116.5 mm in a 515 ml bulb, 4.19 mmole) was measured out and the HCl was condensed on the frozen methylene chloride solution. The reaction mixture was allowed to warm and stir for 40 minutes and the pressure never went above 282 mm. The solution was then condensed and again allowed to warm up, and was stirred for 30 minutes. All the reaction mixture was condensed with liquid nitrogen; no non-condensable had been formed during the total 70-minute reaction time. The HCl and methylene chloride were then removed and condensed on 20 ml of 1.0M NaOH solution. After all the solvent had been removed and the HCl had reacted with the aqueous NaOH, the reaction vessel was pumped on for an additional 16 hours. The NaOH solution was titrated with 1.0M HCl using bromophenol blue and only 2.3 mmole of HCl was recovered. The infrared and proton nmr

Spectra showed that some changes had taken place. Instead of a large very complex multiplet centered at -7.70 ppm, the proton nmr showed two multiplets of intensity ratio 1:1; one at -7.3 ppm and the other at -8.2 ppm from internal tetramethylsilane. The infrared spectrum showed additional peaks which could have been BF_3Cl^- ion (44).

Because of the addition of HCl to dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron - boron trifluoride, an attempt was made to determine if boron trifluoride could add to dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) chloride (1-). Although qualitative, the following experiment was of great value. A 50 ml flask was charged with dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) chloride (1-), placed on a high vacuum line, and evacuated. Excess boron trifluoride was then condensed on the solid with liquid nitrogen and then allowed to warm up. This was repeated ten times and then all the boron trifluoride was removed. The infrared and proton nmr spectra were run and were almost identical to that of the product of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron - boron trifluoride (1:1) and HCl.

CHAPTER IV

PHYSICAL MEASUREMENTS

Electronic Spectra

The electronic spectra of the conjugate pairs dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) chloride (1-) and its conjugate base, difluoro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) chloride (1-) and its conjugate base, and fluorohydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) chloride (1-) and its conjugate base are shown in Figures 1, 2, and 3. The spectra of the chloride salts were obtained by dissolving the "neutral" adduct of the conjugate pair in 0.10M HCl.

Acid-Base Dissociation Constant Determinations Using Electronic Spectra

It was noticed that the neutral adducts dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron, fluorohydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron, and difluoro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron were yellow in color and their protonated salts were colorless. The spectra were taken in water with a Cary 15 recording spectrophotometer or with a Beckman DB recording spectrophotometer using 1 cm square fused silica cells. The extreme pH solutions were made by using 0.10M HCl or 0.10M NaOH. In these solutions the absorbances corresponded to its cation or its neutral conjugate base, respectively. It was found that the protonated form of adducts and the unprotonated form of the adducts differed greatly in absorbance and it

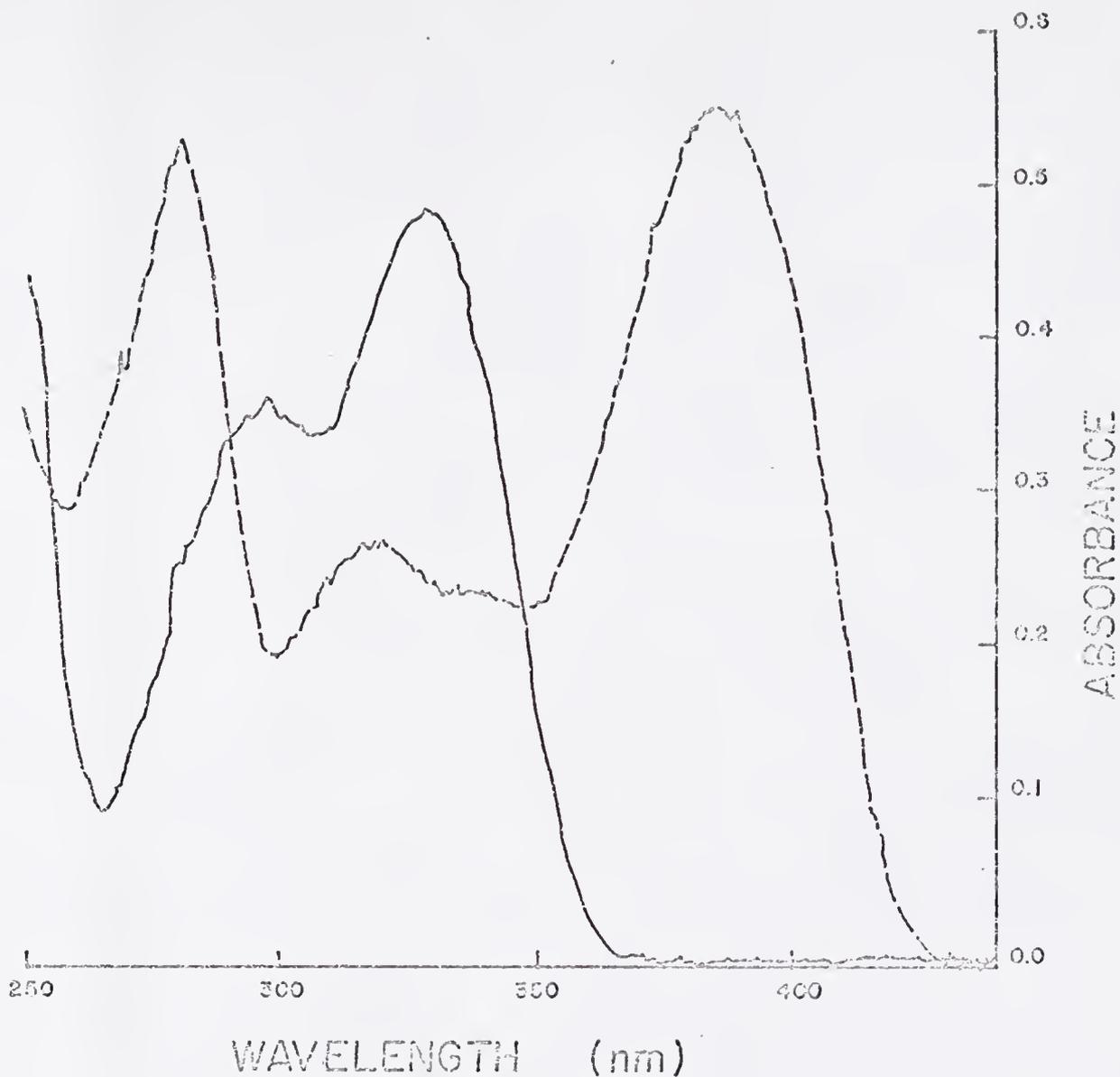
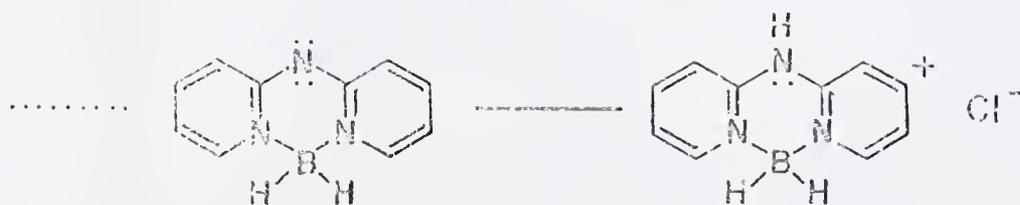


Figure 1. Electronic spectra of dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^1'$) boron (1+) chloride and its conjugate base.



$$[\text{Absorbing species}] = 4.62 \times 10^{-5}$$

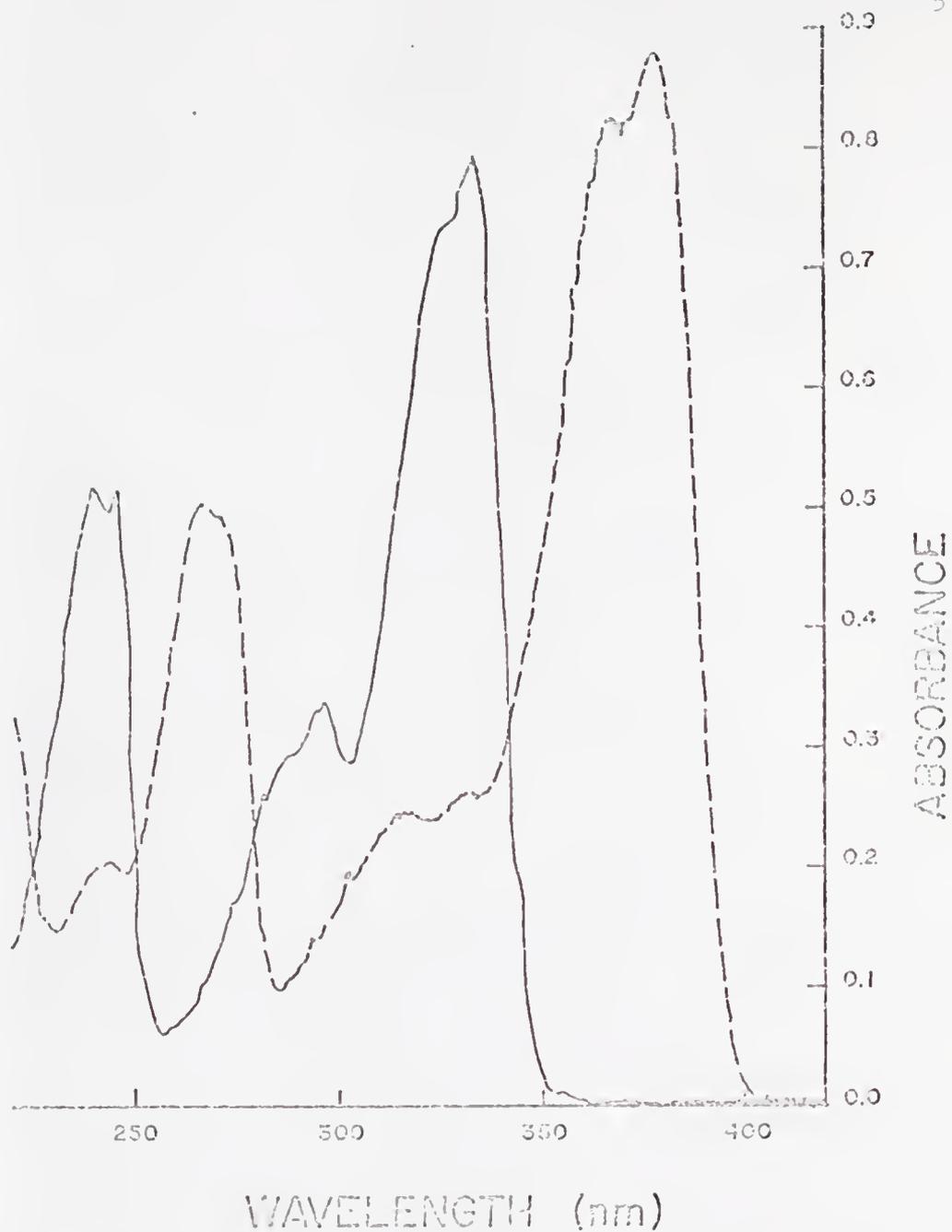
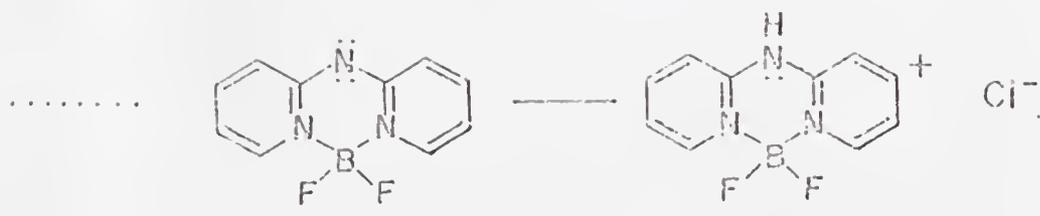


Figure 2. Electronic spectra of difluoro(2,2'-imidodipyridine- κ^1, κ^1')boron (1+) chloride and its conjugate base.



$$[\text{Absorbing species}] = 3.36 \times 10^{-2}$$

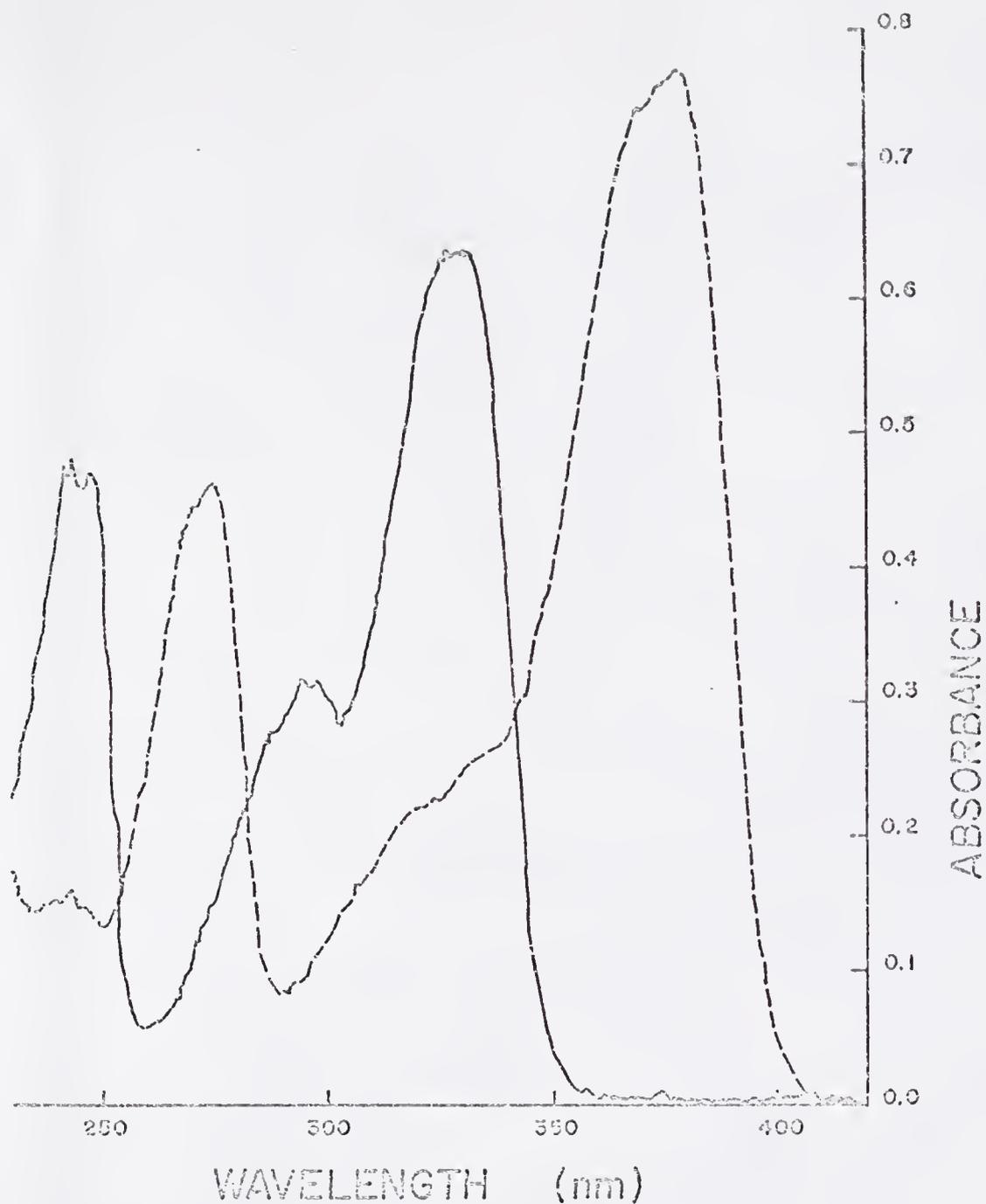
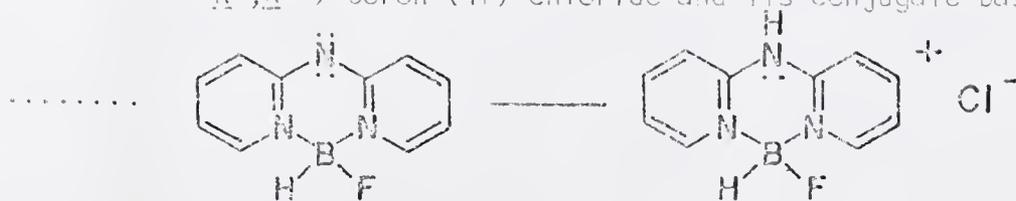


Figure 3. Electronic spectra of fluorohydro (2,2'-iminodipyridine- N^1, N^1') boron (1+) chloride and its conjugate base.



$$[\text{Absorbing species}] = 4.37 \times 10^{-5}$$

was possible, by carefully monitoring the pH of the solution, to determine the K_a of the acid-base conjugate pairs spectrophotometrically.

Using the method described by Deutsch and Taube (35), and by assuming that as the pH is lowered the unprotonated form is converted to the protonated form, the following relationship applies

$$K_a = \frac{[H^+] (\epsilon_{\lambda}^{obs} - \epsilon_{\lambda}^H)}{(\epsilon_{\lambda}^{neut} - \epsilon_{\lambda}^{obs})}$$

where $[H^+]$ is the hydronium ion concentration, ϵ_{λ}^{obs} is the extinction coefficient observed at wavelength λ of the intermediate pH solutions, ϵ_{λ}^H is the extinction coefficient observed at wavelength λ of the completely protonated form and $\epsilon_{\lambda}^{neut}$ is the extinction coefficient observed at wavelength λ of the completely unprotonated form. The pH of the intermediate solutions was kept invariant by using suitable buffers and care was taken to choose a wavelength to monitor that was not affected by the absorptions of the buffers (36). Only those pH's where the transmittance fell in the middle 60% range of the total difference between the completely protonated and completely unprotonated forms were used in the calculations of the K_a , and the pH of the buffered solutions was checked with a Corning 12 Research pH meter using the expanded scale.

By taking the spectra of every pH unit from 6 to 9, the pH range where the acid and base forms were in equilibrium was found. The uv spectra of those solutions whose pH varied approximately 0.15 of a pH unit within this range were taken against a buffer solution reference and extinction coefficients were calculated. From the extinction

TABLE I

Dihydro[(2,2'-iminodipyridinato)(1-)-N¹,N¹']boron-glyhydro(2,2'-iminodipyridine-N¹,N¹')boron(1+)chloride(1-)

[Absorbing species] = 4.62×10^{-5} ,

$\lambda = 385 \text{ m}\mu$

Solution number	pH	$T_{385 \text{ m}\mu}$	$(\text{cm}^{-1}\text{M}^{-1}) \times 10^{-3}$	$K_a \times 10^6$
1	2.630	1.000	0.00	-----
2	7.805	0.709	3.22	6.67
3	7.981	0.645	4.11	6.39
4	8.042	0.625	4.42	6.29
5	8.137	0.594	4.87	5.99
6	11.900	0.317	10.8	-----

Average $K_a = 6.34 \pm 0.27 \times 11^{-2}$, $\text{p}K_a = 8.2$

TABLE 2

Difluoro(2,2'-iminodipyridinato)(1-)- Δ^1, Δ^1 boron - difluoro(2,2'-iminodipyridine- Δ^1, Δ^1) boron(IV) chloride(1-)

[Absorbing species] = 5.56×10^{-5} . $\lambda = 380 \text{ m}\mu$

Solution number	pH	$T_{380 \text{ m}\mu}$	$(\text{cm}^{-1} \text{M}^{-1}) \times 10^{-3}$	$K_a \times 10^6$
1	2.640	1.000	6.00	-----
2	5.580	0.555	7.59	1.19
3	5.614	0.595	6.70	1.15
4	5.495	0.638	5.83	1.24
5	5.425	0.577	5.06	1.20
6	5.539	0.721	4.25	1.17
7	11.310	0.196	20.9	-----

Average $K_a = 1.19 \pm 0.03 \times 10^{-6}$. $\text{p}K_a = 5.0$

TABLE 3

Fluorohydro[(2,2'-imino)pyridinato(1-)-N¹,N^{1'}][boron-fluorohydro(2,2'-imino)pyridine-N¹,N^{1'}]boron(1±)chloride(1-)

[Absorbing species] = 4.37×10^{-5} , $\lambda = 375 \text{ m}\mu$

Solution number	pH	$T_{375 \text{ m}\mu}$	$(\text{cm}^{-1}\text{M}^{-1}) \times 10^{-3}$	$K_a \times 10^7$
1	1.570	1.000	0.00	-----
2	6.765	0.357	10.2	2.18
3	6.635	0.403	9.02	2.28
4	6.550	0.443	8.10	2.26
5	6.415	0.502	6.84	2.32
6	6.340	0.554	5.84	2.16
7	6.205	0.603	5.03	2.38
8	6.115	0.651	4.30	2.37
9	5.960	0.713	3.34	2.47
10	1? 265	0.160	18.2	-----

Average $K_a = 2.30 \pm 0.10 \times 10^{-7}$, $\text{p}K_a = 6.6$

coefficients and the pH of the solutions, the K_a was obtained. The concentration of the absorbing species, the wavelength monitored, the data obtained and the calculated K_a 's are listed in Tables 1, 2, and 3.

Infrared Spectra

The infrared spectra were all taken in KBr pellets on a Beckman IR-10 except that of 2,2'-dipyridylmethyamine which was taken neat between KBr plates. Since the infrared data have already been presented along with the synthesis of the compounds in Chapter III, only the trends will presently be discussed.

In general, the only portion of the spectra which could be used for structure assignments was the B-H stretching region (2200 - 2500 cm^{-1}), for the cyclic systems studied had many absorptions in the 600 - 2000 cm^{-1} region which could not be assigned with any degree of accuracy.

All the boronium salts had similar infrared spectra except for the differences resulting from the anions used. The B-N stretching vibrations and the B-H deformation vibrations were not assignable, for the amines had strong absorptions in this region of the spectrum; also, the more complicated the system became, the more difficult it became to make positive assignments without doing a detailed study. Taylor (37) has shown, contrary to previously reported assignments (39), that B-N stretching in alkylamine boranes occurs in the region 650 - 750 cm^{-1} and not at 1100 - 1250 cm^{-1} and also suggested that the strong bands which are observed at 1100 - 1250 cm^{-1} in amine boranes are a result of coupling of the B-N motions with other skeletal motions.

It is interesting to note that simple theory predicts two

peaks in the B-H stretching region for a BH_2^- type molecule resulting from symmetric and asymmetric stretching motions. Contrary to this, the majority of the boron cations studied in this work had three peaks in the B-H stretching region (a band at 2470 cm^{-1} , a slightly weaker band at 2400 cm^{-1} and a weak band at 2360 cm^{-1}). That additional peaks are observed has been explained on the basis of an interaction between vibrational levels associated with two different vibrations or combinations of vibrations (39,44,45). This phenomenon, called Fermi resonance, arises when two closely spaced vibrational energy levels of the same symmetry species interact. Often it is seen when a fundamental and an overtone or combination band interact, eigenfunctions of the latter type absorptions exhibit fundamental character and intensity. When this interaction occurs, the energy levels repel and one vibrational level is raised and the other lowered relative to the unperturbed state. Similar reasoning has been applied to a number of aldehydes possessing additional C-H stretching vibrations (46).

The B-H stretching frequencies of the BH_2 group in the cations are shifted to higher frequency compared to the B-H stretching frequencies of the BH_3 group in 2,2'-dipyridylamine - bisborane and to the BH_2 group in dihydro[(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$]boron. Both of these were broad bands from $2280 - 2460\text{ cm}^{-1}$ with a great deal of structure which is typical for an amine borane. The B-H absorptions for dihydro[(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$]boron-boron trifluoride (1:1) were very much like those of the cations. There were three B-H stretching vibrations in the region $2350 - 2500\text{ cm}^{-1}$.

In the compound fluoro-hydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (I+) hexafluorophosphate there was a singlet observed at 2480

cm^{-1} which could be attributed to B-H stretching. In fluorohydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron a singlet at 2420 cm^{-1} was assigned to the B-H stretching vibration.

Assignments for B-F stretching in the BF_2 and BF cations were made by a direct comparison with the $\text{B}\frac{1}{2}$ cation. In the neutral compounds containing BF_2 or BF units, the B-F vibrations were assigned by comparison to the spectra of the BH_2 analog.

In the cation difluoro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate new bands appeared at 1275, 1140, 1042 and 1025 cm^{-1} which could be assigned to B-F stretching vibrations although the band at 1275 cm^{-1} could well be a combination or difference band. The band at 1140 cm^{-1} can be assigned to the asymmetric B-F stretching fundamental (43). One of the bands at 1042 and 1025 cm^{-1} can be due to the symmetrical B-F stretch coupling with the B-H stretching motions and the other band is unpredicted. No more definite assignments can be made for either band. In the case of fluorohydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) hexafluorophosphate, bands are observed which can be assigned to B-F stretching vibrations or B-F stretching vibrations coupled with some other mode at 1275, 1140, 1045 and 1025 cm^{-1} . Again, more positive assignments cannot really be made.

In difluoro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron new bands appeared at 1175, 1155, 1090 and 1000 cm^{-1} when compared to its $\text{B}\frac{1}{2}$ analog. In the case of fluorohydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron new bands appeared at 1158, 1155, 1095, 1000, and 960 cm^{-1} . No definite assignments can be made at this time.

The sample spectra of dihydro (2,2'-iminodipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (1+) chloride (1-) and of dihydro [(2,2'-iminodipyridinato)(1-)-

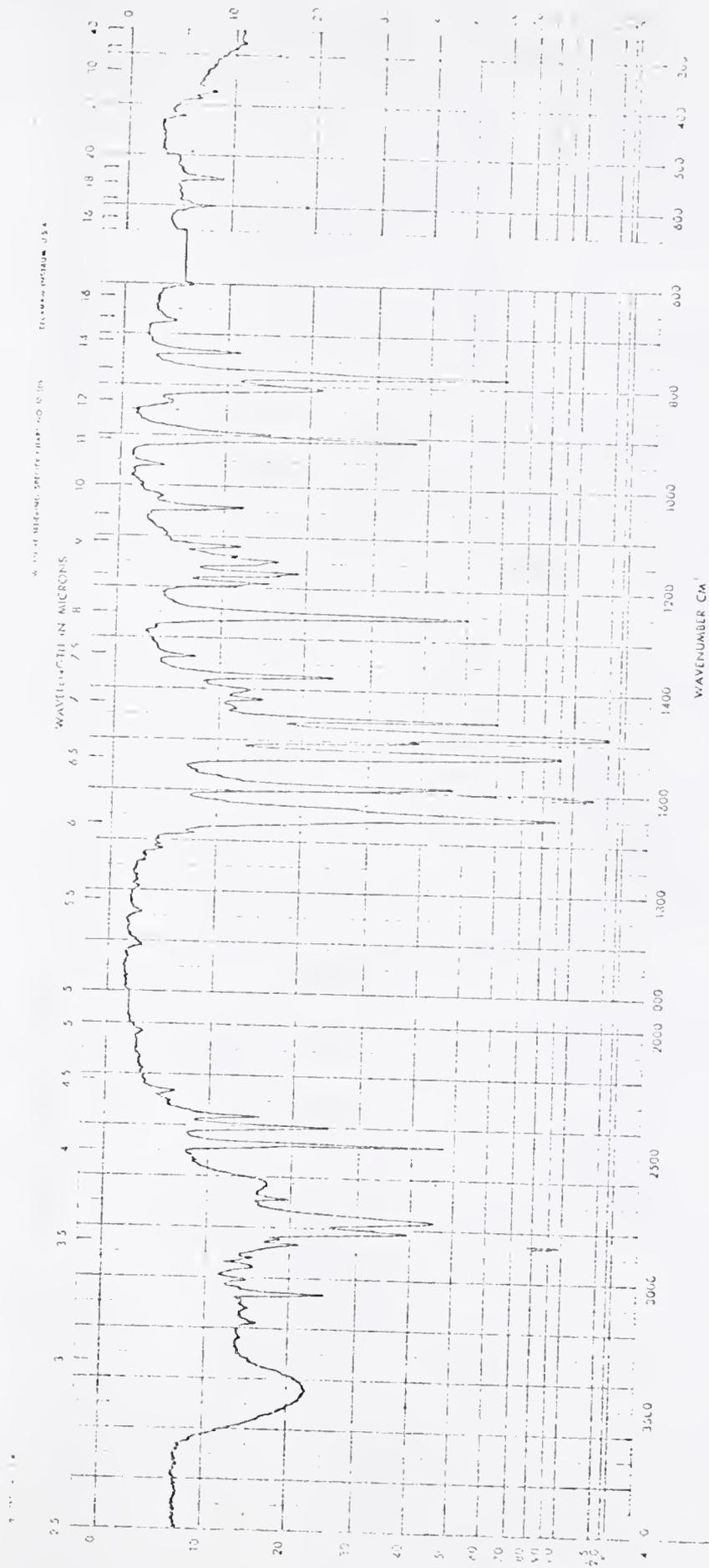


Figure 4. Infrared spectrum of dihydro (2,2'-iminodipyridine-N₁,N_{1'}) boron (1+) chloride.

$\underline{N^1, N^{1'}}$] boron are shown in Figures 4 and 5.

Mass Spectra

The purity of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N^1, N^{1'}}$] boron, fluorohydro [(2,2'-iminodipyridinato)(1-)- $\underline{N^1, N^{1'}}$] boron, difluoro [(2,2'-iminodipyridinato)(1-)- $\underline{N^1, N^{1'}}$] boron, and 2,2'-dipyridylmethylamine were checked by mass spectra. These spectra were obtained on a Hitachi Perkin-Elmer RMV-6E Model mass spectrometer over the range 10 - 300 amu at 70 V ionization voltage. All the samples were introduced at 100° except that of dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N^1, N^{1'}}$] boron which was run at 95°. The cracking patterns were complicated but the pattern in the region of the parent peak agreed with the expected molecular weight values based on natural element abundance. The important peaks are listed in Table 4.

Nuclear Magnetic Resonance Spectra

The proton nmr spectra of the neutral compounds and the charged salts were taken on a Varian A-60 instrument with tetramethylsilane as an internal reference. The ^{19}F nmr spectra were run at 94.1 MHz with perfluorobenzene as an internal standard. ^{11}B nmr spectra were run at 32.1 MHz with external borontrifluoride etherate as a reference, and either acetonitrile, nitromethane or methylene chloride were used as solvents. In many cases the N-H and B-H resonances were either very broad or could not be found, but, except for these protons, the integrated intensities of the proton spectra agreed well with the expected values. The chemical shifts, δ , in parts per million and coupling constants, J, in Hertz (Hz), of proton resonances, fluorine resonances and boron resonances are reported in Tables 5 to 9, and also have

TABLE 4
Mass Spectra Data

Dihydro[(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron

m/e	Intensity	Assignment
185	2	$^{13}\text{C}_2 \text{ } ^{12}\text{C}_5 \text{H}_{10} \text{N}_3 \text{ } ^{11}\text{B}$
184	14	$^{13}\text{C}_1 \text{ } ^{12}\text{C}_9 \text{H}_{10} \text{N}_3 \text{ } ^{11}\text{B}$
183	41	$^{12}\text{C}_{10} \text{H}_{10} \text{N}_3 \text{ } ^{11}\text{B}$
162	15	$^{12}\text{C}_{10} \text{H}_9 \text{N}_3 \text{ } ^{11}\text{B}$

Difluoro[(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron

m/e	Intensity	Assignment
221	4	$^{13}\text{C}_2 \text{ } ^{12}\text{C}_8 \text{H}_8 \text{N}_3 \text{ } ^{11}\text{BF}_2$
220	29	$^{13}\text{C}_1 \text{ } ^{12}\text{C}_9 \text{H}_8 \text{N}_3 \text{ } ^{11}\text{BF}_2$
219	31	$^{12}\text{C}_{10} \text{H}_8 \text{N}_3 \text{ } ^{11}\text{BF}_2$
218	7	$^{12}\text{C}_{10} \text{H}_7 \text{N}_3 \text{ } ^{11}\text{BF}_2$

Fluorohydro[(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron

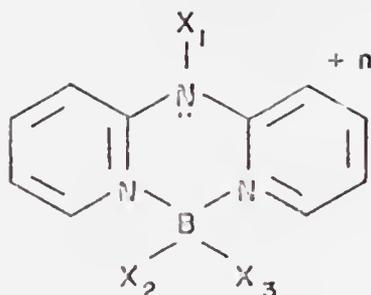
m/e	Intensity	Assignment
201	4	$^{13}\text{C}_{12} \text{ } ^{12}\text{C}_9 \text{H}_9 \text{N}_3 \text{ } ^{11}\text{B}$
200	18	$^{12}\text{C}_{10} \text{H}_9 \text{N}_3 \text{ } ^{11}\text{B}$
199	4	$^{12}\text{C}_{10} \text{H}_8 \text{N}_3 \text{ } ^{10}\text{B}$
		$^{12}\text{C}_{10} \text{H}_7 \text{N}_3 \text{ } ^{11}\text{B}$

TABLE 4 (Continued)

2,2'-dipyridylmethanamine

m/e	Intensity	Assignment
186	2	$^{13}\text{C}_1\ ^{12}\text{C}_{10}\text{H}_{11}\text{N}_3$
185	11	$^{12}\text{C}_{11}\text{H}_{11}\text{N}_3$
184	9	$^{12}\text{C}_{11}\text{H}_{10}\text{N}_3$

TABLE 5
Proton NMR Data of PF_6^- Salts



Compounds	Aromatic Protons		CH_3	
	δ , ppm	M^a	δ , ppm	M^a
$X_1 = \text{H}; X_2 = \text{H}; X_3 = \text{H}; n = 1$	-7.53 -8.27	m m		
$X_1 = \text{H}; X_2 = \text{H}; X_3 = \text{F}; n = 1$	-7.73 -8.26	m		
$X_1 = \text{H}; X_2 = \text{F}; X_3 = \text{F}; n = 1$	-7.67 -8.48	m m		
$X_1 = \text{H}; X_2 = \text{H}; X_3 = 4\text{-pic}^b;$ $n = 2$	-7.42	m	-2.63	s
$X_1 = \text{CH}_3; X_2 = \text{H}; X_3 = \text{H}; n = 1$	-7.52 -8.34	m m	-3.73	s

^aSymbols: M, multiplicity; s, singlet; m, complex multiplet

^b4-pic = 4-methylpyridine

been presented with the synthesis of the compounds in Chapter III.

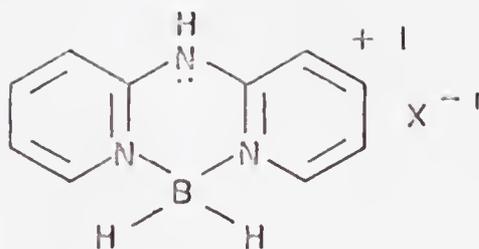
The proton spectrum of 2,2'-dipyridylamine showed three multiplets at -6.83 ppm, -7.60 ppm, and -8.23 ppm from internal tetramethylsilane with intensity ratios of 1:2:1 respectively. The cations (BH_2 , BFH , BF_2) all showed a definite downfield shift (Tables 5 and 6). If the anion was hexafluorophosphate, there were two multiplets with an intensity ratio of 1:1, but if the anion was a halide, the multiplets had an intensity ratio of 3:1 (the most downfield multiplet being of intensity ratio 3). The neutral adducts were in the same region as the free amine but exhibited only two multiplets of intensity ratio 1:1 (Table 7).

As a fluorine atom was substituted for a hydrogen atom on the boron portion, in the neutral adducts, a downfield shift occurred with only a very slight reduction in the separation between the two multiplets. This was expected, for previous work had shown that halide substitution on boron in cations containing substituted pyridine caused a downfield shift of the aromatic protons (47,48,49).

The cations derived from proton addition to the neutral adducts with hexafluorophosphate as the counter ion all showed a downfield shift with fluorine substitution, with the separation between multiplets again decreasing with increasing fluorine substitution. The largest relative downfield shift and the greatest relative decrease in multiplet separation occurred with monofluorine substitution. In the halide salts of the BH_2 cations, there was a slight downfield shift on going from chloride to bromide to iodide, although both multiplets did not shift similarly (Table 6).

The proton nmr of the hexafluorophosphate salt of the N-methyl-

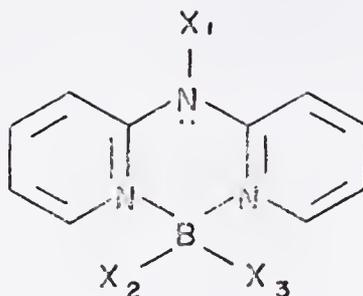
TABLE 6
Proton NMR Data of Halide Salts



Compound	Aromatic Protons	
	δ , ppm	M ^a
X = I ⁻	-7.47	m
	-8.12	m
X = Br ⁻	-7.44	m
	-8.12	m
X = Cl ⁻	-7.38	m
	-7.89	m

^aSymbols: M, multiplicity; m, complex multiplet

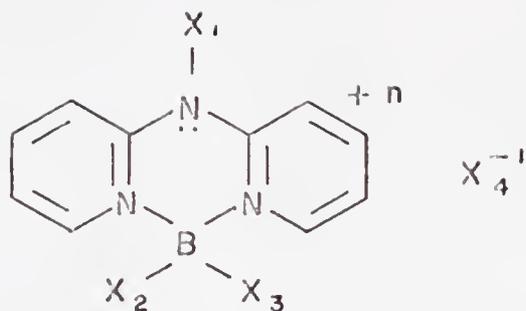
TABLE 7
Proton NMR Data of Neutral Adducts



Compounds	Aromatic Protons	
	δ , ppm	M ^a
$X_1 = -; X_2 = H; X_3 = H$	-6.58 -7.55	m m
$X_1 = -; X_2 = H; X_3 = F$	-6.97 -7.83	m m
$X_1 = -; X_2 = F; X_3 = F$	-7.01 -7.92	m m
$X_1 = BF_3; X_2 = H; X_3 = H$	-7.70	m
$X_1 = BF_3; X_2 = F; X_3 = F$	-7.90	m

^aSymbols: M, multiplicity; m, complex multiplet

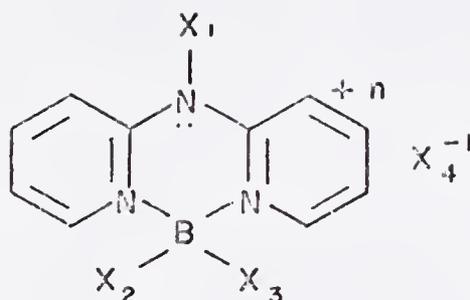
TABLE 8

 ^{11}B NMR Data of Salts and Neutral Adducts

Compounds	δ , ppm	$J_{\text{B-H}}$ Hz	M^a
$\text{X}_1 = \text{H}; \text{X}_2 = \text{H}; \text{X}_3 = \text{H};$ $\text{X}_4 = \text{I}; n = 1$	6.0 0.6		3
$\text{X}_1 = \text{H}; \text{X}_2 = \text{H}; \text{X}_3 = \text{H};$ $\text{X}_4 = \text{PF}_6; n = 1$	6.7		3
$\text{X}_1 = -; \text{X}_2 = \text{H}; \text{X}_3 = \text{H};$ $\text{X}_4 = -; n = 0$	5.9 -0.6	110	3
$\text{X}_1 = \text{H}; \text{X}_2 = \text{F}; \text{X}_3 = \text{F};$ $\text{X}_4 = \text{PF}_6; n = 1$	0.0		

^aSymbols: M, multiplicity

TABLE 9
 ^{19}F NMR Data of Fluorinated Compounds



Compounds	δ , ppm	J, Hz	M ^a
$X_1 = \text{H}; X_2 = \text{F}; X_3 = \text{F};$ $X_4 = \text{PF}_6; n = 1$	-94.5 -25.1	$J_{\text{P-F}} = 740$ $J_{\text{B-F}} = 25$	2 4
$X_1 = -; X_2 = \text{F}; X_3 = \text{F};$ $X_4 = -; n = 0$	-28.6	$J_{\text{B-F}} = 29.5$	4
$X_1 = \text{H}; X_2 = \text{F}; X_3 = \text{H};$ $X_4 = \text{PF}_6; n = 1$	-101.1 -6.5	$J_{\text{P-F}} = 707$	2 B
$X_1 = -; X_2 = \text{F}; X_3 = \text{H};$ $X_4 = -; n = 0$	15.0 15.0	$J_{\text{B-F}} = 77.1$ $J_{\text{H-F}} = 64.2$	5
$X_1 = \text{BF}_3; X_2 = \text{H}; X_3 = \text{H};$ $X_4 = -; n = 0$	-20.6	$J_{\text{B-F}} = 16.5$	4
$X_1 = \text{BF}_3; X_2 = \text{F}; X_3 = \text{F};$ $X_4 = -; n = 0$	-10.3 -21.6	$J_{\text{B-F}} = 23.7$ $J_{\text{B-F}} = 15.1$	4 4

^aSymbols: M, multiplicity; B, very broad band

substituted cation exhibited in the aromatic region two multiplets of intensity ratio 1:1, with almost the same chemical shift as the hexafluorophosphate salt of the cation with a proton on nitrogen.

The proton nmr of 2,2'-dipyridylmethylamine was shifted downfield upon protonation. There was very little shift of the methyl group resonance but the aromatic resonances behaved quite differently. In the free amine there were two multiplets, one at -6.30 ppm of intensity ratio six and the other multiplet at -8.26 ppm of intensity ratio two. Upon protonation, the multiplets shifted downfield to -7.56 ppm and -8.95 ppm and were now of equal intensity. Definite assignments cannot be made without further investigation.

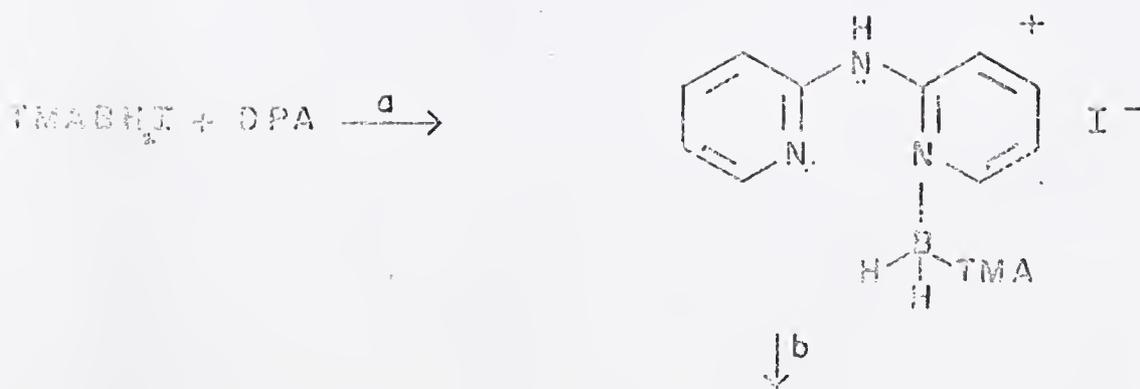
The ^{19}F nmr were run with hexafluorobenzene as internal reference at 94.1 MHz. In the neutral adducts and in the cations, increased fluorine substitution caused a downfield shift in the chemical shift of the B-F resonances. The doublet attributed to hexafluorophosphate remained at almost the same chemical shift in the cationic systems as expected. In all cases the B-F resonances appeared as quartets except in the case of fluorohydro $[(2,2'\text{-iminodipyridinato})(1\text{-})\text{-}\underline{\text{N}}^1, \underline{\text{N}}^{1'}]$ boron and its conjugate acid where a quintet and a very broad band respectively were obtained (Table 9). That a quintet of intensity ratio 1:2:2:2:1 was obtained was due to $J_{\text{B-F}}$ and $J_{\text{H-F}}$ being almost equal.

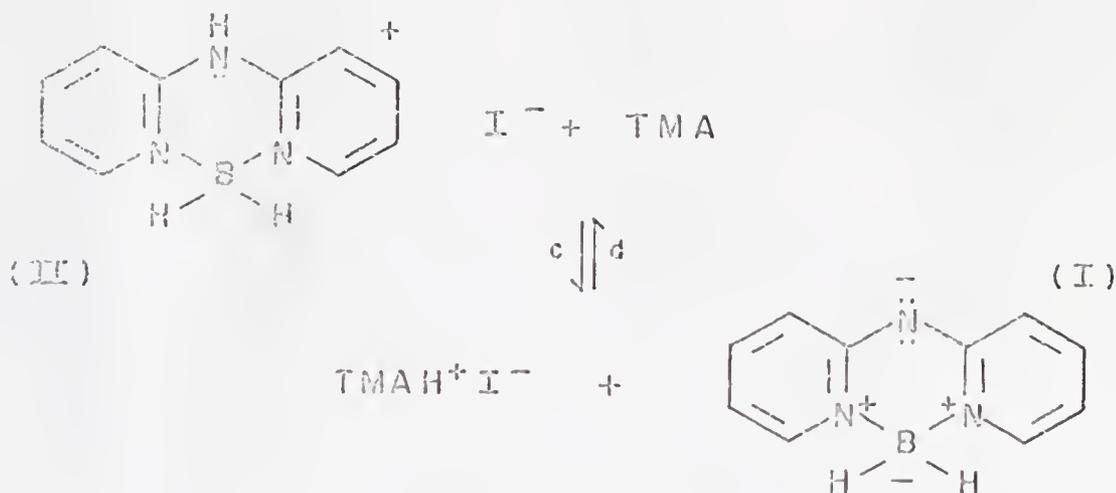
The ^{11}B nmr spectra were run on only a few compounds (Table 8). All the spectra showed a triplet although the only one whose coupling constant could be calculated was dihydro $[(2,2'\text{-iminodipyridinato})(1\text{-})\text{-}\underline{\text{N}}^1, \underline{\text{N}}^{1'}]$ boron. The $J_{\text{B-H}}$ was about 110 Hz. The other compounds were determined to be triplets but these data were obtained using an oscilloscope.

CHAPTER V
DISCUSSION

Because the systematic names of many compounds discussed here may at times be either very long or cumbersome, these compounds will be named and assigned a number. From then on, only the number will be used. A glossary, attached as an appendix to this dissertation, will list the number, name, and structure of the compounds in question for ready reference. Abbreviations are also listed there in alphabetical order.

Dihydro [(2,2'-iminodipyridinato)(1-)-N¹,N^{1'}] boron (I) was prepared in excellent yield by two methods. The first method involved both transamination and halide displacement. Trimethylamine-monoiodoborate (TMABH₂I) was allowed to react with 2,2'-dipyridylamine (DPA) in pure benzene. The results can be explained by the following reaction sequence:





The first step (a) is expected to be rapid iodide displacement from an amine-iodoborane to yield a bis(amino) boron cation with a pendant nitrogen donor site on one of the amine functions. This intermediate was never isolated but a solid could be observed immediately after mixing of the reactants. Shortly thereafter trimethylamine could be detected and the solution became yellow and as time progressed the yellow color increased in intensity. Step (a) is analogous to a well-known reaction between TMABH_2I and substituted pyridines where the product formed rapidly and was stable. The intermediate can then undergo transamination utilizing the pendant amine donor and liberating trimethylamine (b). This internal transamination to give a chelated cation was expected, for a pyridine donor bonded to a trimethylamine- BH_2^+ unit activates the cation with respect to transamination (20,34).

Upon work-up, the yellow solid, crude dihydro (2,2'-imino-dipyridine- B^+H_2) boron (1+) iodide (II), could be obtained in good yield. Because trimethylamine is quite volatile and the benzene solution was heated to just below reflux, evolution of all the trimethylamine should have occurred in a much shorter time than forty-eight

hours. This suggested that amine was retained in solution by some chemical means. The intense yellow color of the benzene solution during the reaction could also suggest the presence of a species unexpected at the time of the first experiments. It was later shown that there is an equilibrium (c and d) which can be shifted almost completely to yield the cyclic boron cation and free TMA. The iodide salt of the boron cation (II) can then be readily converted to the neutral zwitterion (I) by any number of bases. The existence of such an equilibrium was demonstrated by a number of related experiments.

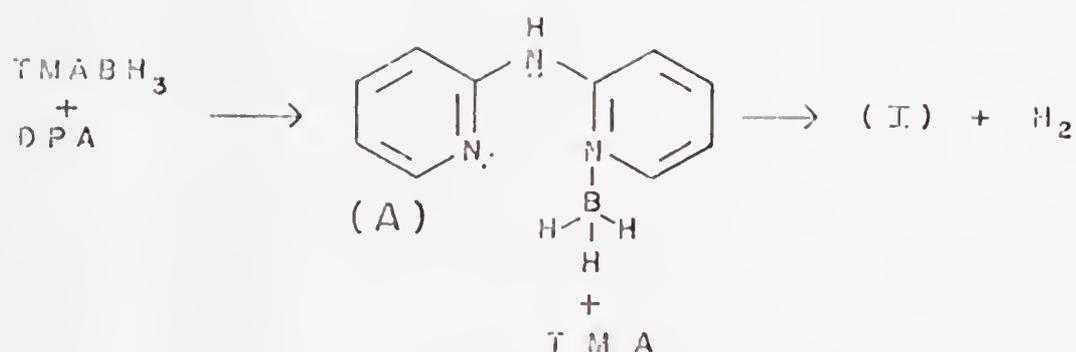
A flask was charged with a magnetic stirring bar, TMAHI, (I), and dry benzene. The mixture was brought to reflux and TMA evolution was noticed. When TMA evolution ceased, a light yellow solid remained in the flask and was identified by its infrared and proton nmr spectra to be the iodide salt of (II). Once (II) was formed, the imino proton could be removed by bases such as sodium hydroxide or alkyl amines.

The quantitative protonation of (I) to produce (II) could readily be accomplished by bubbling into a methylene chloride solution of (I) anhydrous hydrogen chloride or hydrogen bromide until the characteristic yellow color of (I) disappeared. This constituted a convenient method of preparation for the chloride and bromide salts of (II), which because of their solubilities could not be prepared by precipitation from aqueous solution.

The results of the experiments with TMAHI and (I), HX and (I), and proton removal from the imino nitrogen in the boron cation (II) with sodium hydroxide, diisopropylamine and diisopropylethylamine led to the conclusion that equilibrium (c) and (d) does in fact occur. Trimethylamine is a strong enough base to remove a proton from the

boron cation (II) to form an ammonium ion. This is essentially the reason that trimethylamine takes a very long time to cease evolving and that the intense yellow color characteristic of the neutral zwitterion (I) can be observed so shortly after mixing of the reactants.

The second method for the preparation of (I), TMABH_3 and DPA, has less direct precedent in its detailed mechanism. The most probable reaction path is one which involves transamination and then either intra- or intermolecular hydrogen loss to produce (I).



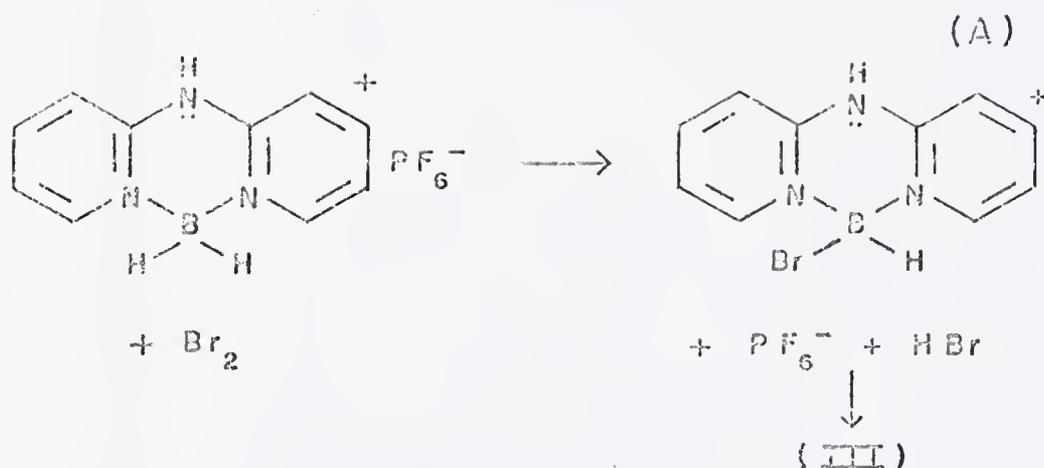
Activation of N-H acidity by coordination to a BH_3 has been shown (50, 51) and could be expected to occur once a DPA has become coordinated to a BH_3 . Analogous to the reaction of borohydride with an ammonium ion to produce hydrogen and the amineborane, the coordinated intermediate (A) can then eliminate hydrogen and form an adduct. The imino nitrogen would not form a bond to boron for the steric requirements would most likely prevent this, but the pendant pyridine nitrogen would be in close proximity and could readily serve as a donor site.

The pK_a 's of the pyridine nitrogen and the amino nitrogen should be similar. Both should be able to form a stable bond to boron, but the strain of a four-membered ring with respect to that of a six-

membered ring system leads to the preferred product.

Attempts to brominate the hexafluorophosphate salt of (II) with bromine produced a completely unexpected result. Instead of getting the expected brominated product, a fluorinated product, difluoro (2,2'-iminodipyridine-N₁,N_{1'}) boron (1+) hexafluorophosphate (III) was isolated.

The reaction of the hexafluorophosphate salt of (II) with bromine to produce (III) most likely occurs by initial bromination at boron and subsequent fluorination. The results of the experiments with the hexafluorophosphate salt of (II) with bromine and hydrogen bromide and the bromide salt of (II) with bromine and ammonium hexafluorophosphate seem to substantiate that bromination is followed by fluorination.



It has been demonstrated (47) that bromine will react with hydrogens attached to boron in boron cations to produce HBr and a cation which has bromine substituted on boron. These bromo-substituted cations are hydrolytically unstable and the bromine can be displaced by an amine. To determine if bromination was a needed first step or if bromine - hexafluorophosphate was the fluorinating agent,

the following experiment was run.

A flask was charged with a magnetic stirring bar, the bromide salt of (II), and dry CH_3NO_2 . Slowly with stirring bromine was added and was immediately decolorized up until the very last portion. With further stirring the solution became colorless. Solid ammonium hexafluorophosphate was then added and the slurry stirred for five hours. Upon aqueous work-up, (III) was isolated in 41% yield.

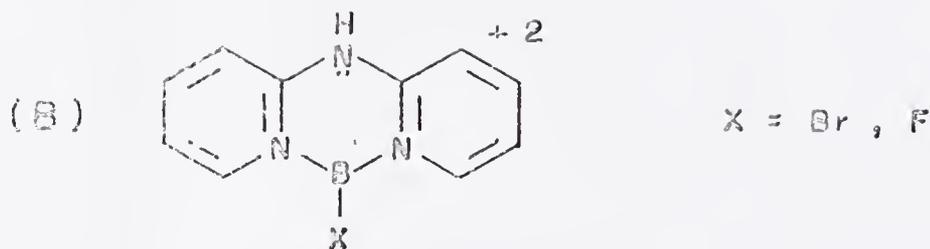
This showed that bromine - hexafluorophosphate was not the fluorinating agent. For all practical purposes, the bromine had completely reacted before PF_6^- was present in the system, yet fluorination occurred.

To finally show that bromination was a needed first step, the following reaction was run.

A flask was charged with a magnetic stirring bar, the hexafluorophosphate salt of (II) and dry CH_3NO_2 . With stirring, anhydrous HBr was bubbled into the reaction mixture until the solution was saturated (about 10 minutes). The flask was stoppered and the reaction mixture was stirred for four hours. Upon aqueous work-up, the isolated product contained very little (III) and was mostly 2,2'-dipyridylammonium (1+) hexafluorophosphate. In bromination with bromine, one of the expected products would be B-Br . This could react with PF_6^- to produce the fluorinating agent. In the above experiment, no B-Br adducts were formed for it has been previously shown that HBr and (I) only produce the bromide salt of (II) and no bromination on boron. If some product of $\text{H}^+ - \text{PF}_6^-$ was the actual fluorinating agent, (III) should have been isolated upon work-up but was not. The results of the two previous experiments show that bromination on boron is a needed

first step and that the system bromine -PF₆⁻ is not the fluorinating agent. Whether the fluorinating agent is PF₅, HF, HF and PF₆⁻, or F⁻ ion has not been determined. It has been demonstrated that PF₆⁻ will decompose to HF and PF₅ in strongly acidic media (40). In non-aqueous solvents fluoride ion is a strong nucleophile and could easily displace bromide.

That difluorination occurs can be explained by the following.



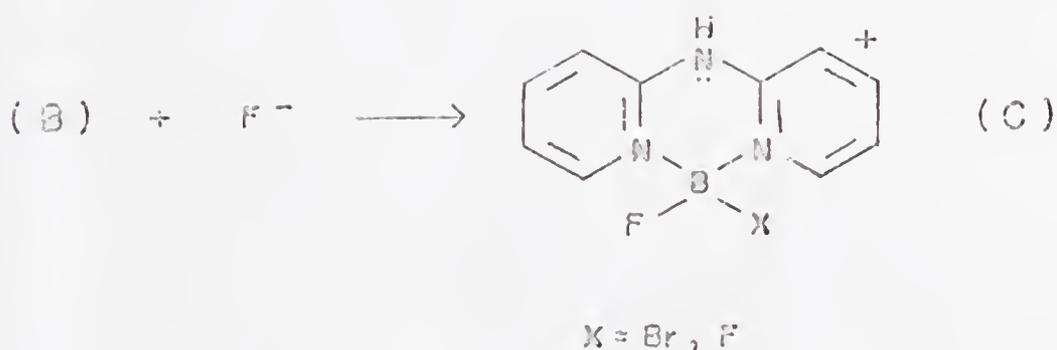
Hydride loss appears to be easier in the chelate cation (A) than in a non-chelated system. Once a halide is attached to boron, a trigonal intermediate (B) may be formed. Multiple bonding by the halide to boron might facilitate hydride loss.

To demonstrate that hydride loss is easier in the chelated system (A) and to test the feasibility of using bromine and hexafluorophosphate as a general fluorinating agent, the following reaction was run.

A flask was charged with a magnetic stirring bar, bis (4-picolyl) boronium hexafluorophosphate and dry CH₃NO₂. With stirring, bromine was added dropwise. The bromine was immediately decolorized up until the last portion was added and then the reaction mixture remained a light orange. The reaction vessel was stoppered and allowed

to react for four hours. The reaction was monitored by proton nmr and showed that bromination occurred within one minute and no further changes occurred (47).

That no further reaction occurred leads to two conclusions. The first is that bromine $-PF_6^-$ is not a general fluorinating agent. Although bromination occurred rapidly, fluorination did not follow. The system contained a cation with a bromine substituted on boron, HBr and PF_6^- . These same conditions produced (III) in the chelated system. The second conclusion that can be drawn is that chelation does facilitate hydride loss after halogenation has occurred on boron. Most likely chelation and co-planarity of the two rings play an important part in the reactivity of (A). Co-planarity would assist in the formation of (B) and contribute to its stability once formed. Once (B) is formed, it can then act as a Lewis acid and coordinate to a fluoride ion.



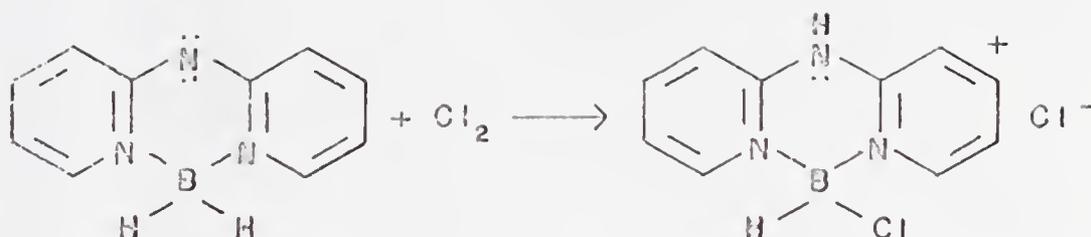
If cation (C) contains two fluorine atoms attached to boron, then (III) is produced. If a bromine boron bond is present, subsequent displacement of a bromide by fluoride would yield (III). The reaction could also involve PF_5 , PF_6^- , HF and PF_6^- , or HF which

fluorinate directly.

The reaction of triphenylmethylchloride and the hexafluorophosphate salt of (II) to produce fluorohydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^1'$) boron (1+) hexafluorophosphate (IV) most likely occurs by hydride abstraction followed by fluoride addition. It has been demonstrated that triphenylmethyl carbonium ion is able to abstract hydridic hydrogens from boron in amineboranes (52). When donors are present in the system such as amines or acetonitrile, they readily form adducts with the resulting boron species. In the case of hydride abstraction from the hexafluorophosphate salt of (II), the two most obvious donors would be a chloride ion or a fluoride ion from PF_6^- . Because no chloro-substituted products were isolated, three possibilities must be considered. The first is that the mono-chloro substituted product may be hydrolytically unstable and decompose upon aqueous work-up; the second is that the chlorinated product never forms and a fluorinated product forms immediately; the third is that if a chloro-substituted product does form, the chlorine is displaced by a fluorine. Since yields are low, all three possibilities exist. If all three possibilities did occur, the premise that the mono-chloro-substituted product was hydrolytically unstable would lower the yield of (IV) by 30 to 50 percent. This assumes that all the possibilities have an equal probability of occurring, (IV) is hydrolytically stable and there is an equal chance for a chloride or fluoride to initially become bonded to boron after hydride abstraction has occurred.

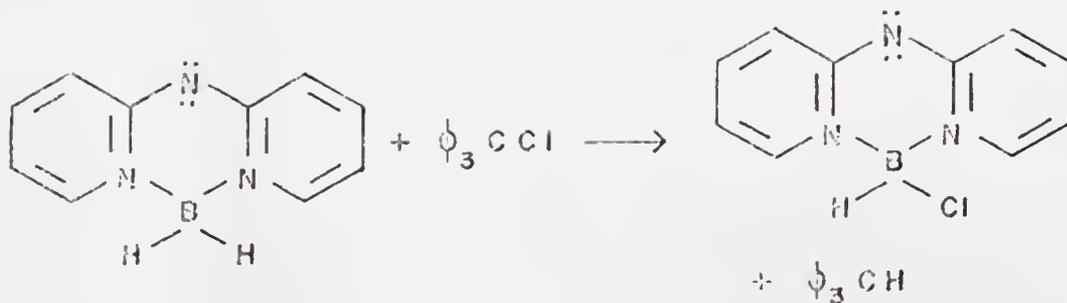
That the chloro-substituted product is unstable to hydrolysis is suggested by several observations. If one bubbles chlorine through (I) for a short period of time, no stable product can be isolated,

although a solid is formed which rapidly decomposes upon exposure to the atmosphere.



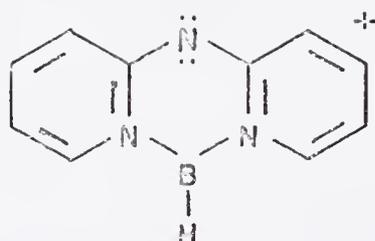
In the above reaction presumably a chlorine was substituted on boron and the resulting cation readily hydrolyzed. It was earlier demonstrated that when a bromine was substituted on boron is a boron cation, that the cation hydrolyzed readily.

To determine if a stable chloro-substituted neutral compound could be isolated the following reaction was attempted. If (1) is allowed to react with triphenylmethylchloride in dry CH_2NO_2 , triphenylmethane can be detected by its nmr spectrum but no product containing boron and chlorine can be isolated after aqueous work-up. That triphenylmethane can be detected indicates that hydride abstraction did occur and the only nucleophile in the system is chloride ion. It is not unreasonable to assume that the chloride ion replaced a hydride to yield a chlorine-substituted product.

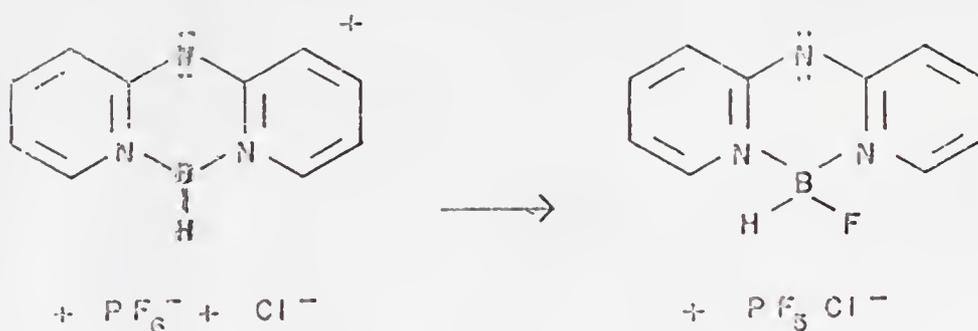


The resulting neutral species apparently decomposed upon attempted aqueous work-up.

That an acidic gas forms above the reaction mixture is probably due to traces of water in the solvent. This acidic gas may again aid in fluorination by assisting the formation of HF, P-F species and fluoride ion which may be responsible for the production of the difluoro derivative as an impurity. After hydride abstraction has occurred, an intermediate containing a trigonal boron will be formed.



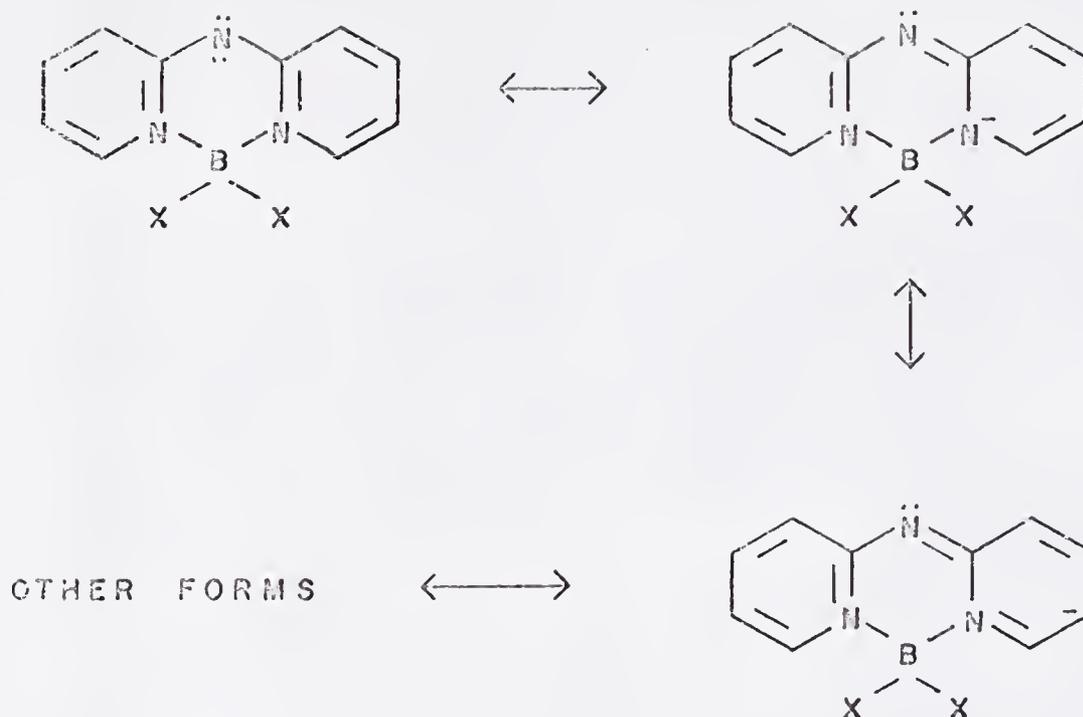
This is the same type of intermediate that led to difluorination in the presence of PF_6^- and an acidic gas. Because the difluoro derivative (III) was isolated in a very small yield when little acid was generated, implies that acid is needed along with PF_6^- to produce difluorination and that the absence of acid minimizes the decomposition of PF_6^- to F^- , HF, and P-F containing products which enhance difluorination. Without acid to decompose PF_6^- , the only source of fluoride ion is PF_6^- . One could envision a transfer of fluoride ion to a trigonal boron intermediate and a chloride ion becoming bonded to phosphorous to form a PF_5Cl^- ion.



Both (III) and (IV) can be converted to neutral zwitterions by removal of a proton to form difluoro [(2,2'-iminodipyridinato)(1)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron (V) and fluorhydro [(2,2'-iminodipyridinato)(1)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$] boron (VI) respectively.

That all three species, (I), (V), and (VI), form is quite interesting. The amide derived from aniline is extremely basic and only with great difficulty can a proton be removed from aniline to form the amide. Also, the hydrogen in 2,2'-dipyridylamine is very difficult to remove as a proton due to the basic nature of aryl-substituted amines in general. In (I), (V), and (VI) there are two aromatic systems attached to the imino-nitrogen and one would have predicted that proton removal to generate an amide would be very difficult.

In aniline and 2,2'-dipyridylamine when a proton is removed, one goes from a neutral to a negatively charged species, whereas, in the preparation of (I), (V), and (VI), one goes from a charged to a neutral species. The lack of charge in (I), (V), and (VI) (other than formal charges) may be one reason for their stability. Another reason may be because the pyridine rings are joined by a BX_2 unit to form a co-planar system, extra stability may be introduced into the system by enhanced conjugation.



It is interesting to note that the fluoro-substituted neutral compounds should have increased stability and decreased reactivity towards electrophilic reagents due to inductive effects. The fluoro substituents should pull electron density from the pyridine rings toward them and concomitantly remove electron density from the imino nitrogen. This withdrawal of electron density should make electrophilic reactions less favorable on the bridging nitrogen. One would then have predicted that this was the reason why attempted methylation by methyl iodide on the fluoro-substituted derivatives failed to produce the expected N-methyl-substituted product, whereas, in the unfluorinated case (I), the N-methyl-substituted product (VIII) was isolated in good yield. Although methylation of the fluoro-substituted derivatives (V, VI) seemed to have taken place, an unexpected side reaction occurred. When (V) and (VI) were allowed to react with methyl iodide, a solid was formed which

upon aqueous work-up exhibited two distinct methyl groups in the proton NMR. Attempts were made to purify the methylated product or separate reaction products but were unsuccessful. The predicted decrease in reactivity of (V) and (VI) toward a carbonium ion could not be verified but fluorination does seem to enhance an undetermined side reaction presumably after initial methylation of the imino nitrogen had occurred.

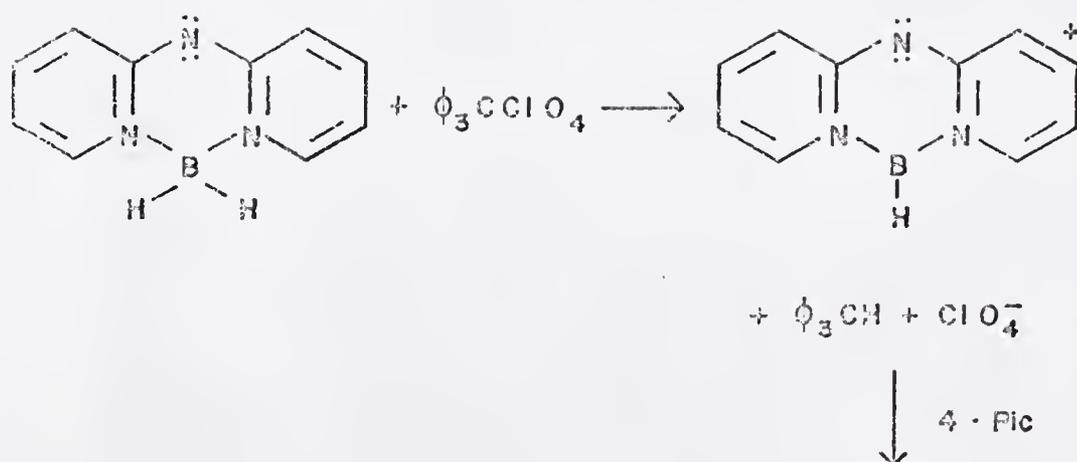
Another factor which must be considered when discussing the stability of the N-methyl perivatives is the steric factor. The imino nitrogen even in the fluoro-substituted derivatives should be a strong enough base to form a stable product with a methyl carbonium ion. Unfavorable steric interactions between hydrogens attached to the pyridine rings and the methyl hydrogens might be large enough to cause substantial weakening of the bond between the imino nitrogen and the methyl group.

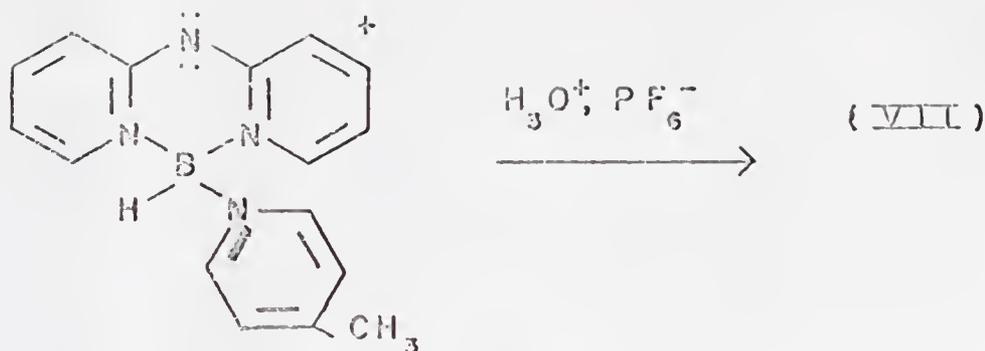
The pK_a 's of the three neutral carbonium (I), (V), and (VI) have been determined and the greater electron withdrawing ability of a fluorine atom over a hydrogen atom is clearly reflected. The order of acid strength exhibited by the neutral compounds is $\text{CH}_2 > \text{CHF} > \text{BF}_2$ (I > V > VI). This is not at all unexpected. Gilje and Pohan (50,51) determined the pK_a of the nitrogen-attached hydrogen for the BH_3 and BF_3 adducts of dimethylamine to be 10.4 and 7 respectively. The increased acidity of the BF_3 adduct over that of BH_3 was attributed to greater electron withdrawing ability of BF_3 over BH_3 . The difference between the pK_a 's of (I) and (V) is 0.2. That the pK_a differences should be so close is a little surprising but can be explained by the following.

It is noteworthy that although the structures (I), (V) and

(I) are very different from the molecules studied by Gilje and Ronan, the effect of fluorine substitution on boron is clearly evident. Because structures (I) and (V) have only two B-H or B-F bonds compared to three in the dimethylamine adducts and because the number of bonds between the boron substituent and the acidic nitrogen hydrogen is greater in (I) and (V) than in the dimethylamine adducts, one would predict that the inductive effect of fluorine would be felt less in (I) and (V) than in the dimethylamine adducts. This would probably be the case if there were no mesomeric effects to be considered in (I) and (V). The π -clouds of the ring systems help transmit the electron-withdrawing effect of fluorine and greatly enhance the weak inductive effects in (I), (V), and (VI).

Attempts to prepare a trigonal heteroaromatic system from the reaction of (I) with a triphenylmethylperchlorate by hydride abstraction failed to yield any isolable product. To test if hydride abstraction actually occurred, the experiments with (I), triphenylmethylperchlorate, and 4-picoline were carried out.

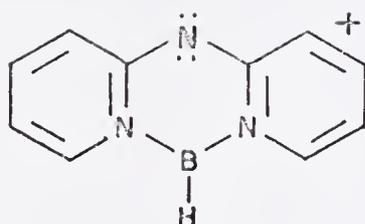




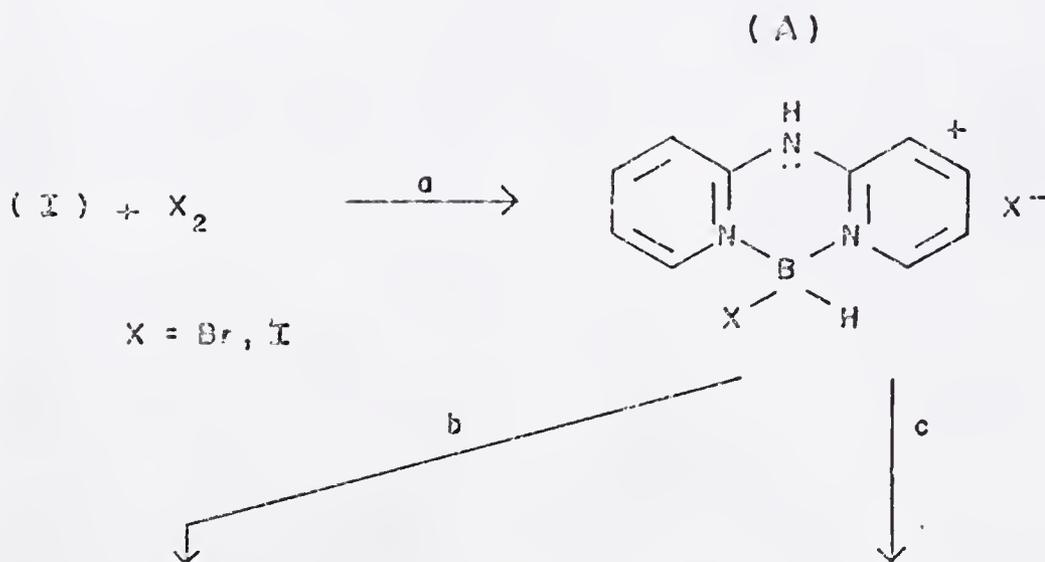
This reaction proceeded quickly and the products obtained showed that hydride abstraction did indeed occur (triphenylmethane and hydro (4-picoline)(2,2'-iminedipyridine- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$) boron (2+) hexafluorophosphate (VII) were isolated). Attempts to prove that bromine and iodine reacted with (I) to yield a product which contained a halogen substituted on the boron by displacing the halogen with a 4-picoline failed.

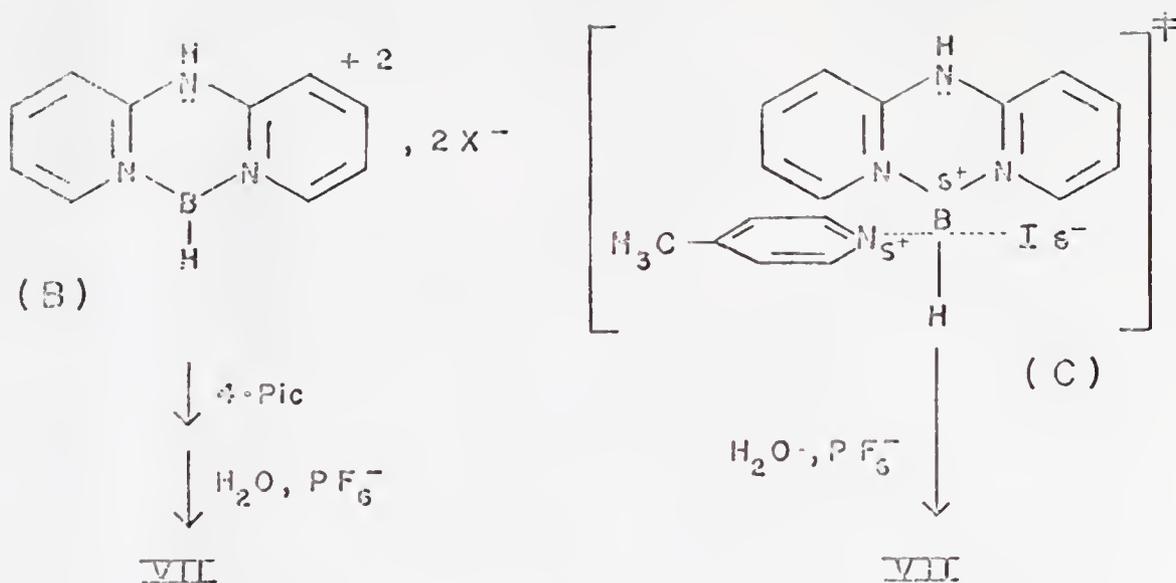
A flask was charged with (I), CH_3NO_2 and the resulting solution was allowed to react with bromine. After the reaction was complete, as evidenced by decolorization of bromine, 4-picoline was added. At this point, even though reaction conditions were varied from stirring at room temperature to reflux, no 4-picoline-substituted product (VII) could be isolated upon aqueous work-up. In several experiments, 4-picoline was used as the solvent but isolation of (VII) was not accomplished. What was isolated in several instances was the hydrolysis product of a bromo-substituted cation, 2,2'-dipyridylammonium (1+) hexafluorophosphate. The same experiments were run using iodine instead of bromine with similar results. If the only reaction that did occur between (I) and bromine or iodine was halogenation, the halogenated product, as expected, would be hydrolytically unstable and rapidly decompose. In general, an aromatic amine such as 4-picoline will replace a bromide or an iodide on boron (47). Although bromine

or iodine appeared to react rapidly with (I), no stable product could be isolated. The experiments involving (I), bromine or iodine, and 4-picoline lead to the following conclusions. In hydride abstraction, a three-coordinate boron would at some time be formed.



This intermediate would have a plus one charge distributed throughout the entire ring system. The intermediate could quickly react with a molecule of 4-picoline and would remain a plus one cation. This is not the case for a halide displacement at boron. At first glance, two reaction schemes can be envisioned for the reaction between (I) and either bromine or iodine. They are based on analogy to the chemistry of boranes and pyridine-substituted cations.





Once the halogen reacts to form a B-X bond and liberates HX, the imino nitrogen would be basic enough to react and form intermediate (A).

There are two pathways to get from intermediate (A) and 4-picoline to product VII. Pathway (b) is highly unlikely, for elimination of iodide ion would cause a plus two charge to develop. Intermediate (B) would become a very strong acid, lose a proton and if the 4-picoline were in excess, form 4-picolinium ion and the expected product (VII) as in hydride abstraction. Pathway (c) would involve a five-coordinate transition state (C) which would be very sterically rigid, develop a plus two charge (the greater the extent of reaction the closer to a +2 charge developed) and would have adjacent positive charges formed. Neither pathway seems to be plausible and the facts appear to be in agreement with this conclusion.

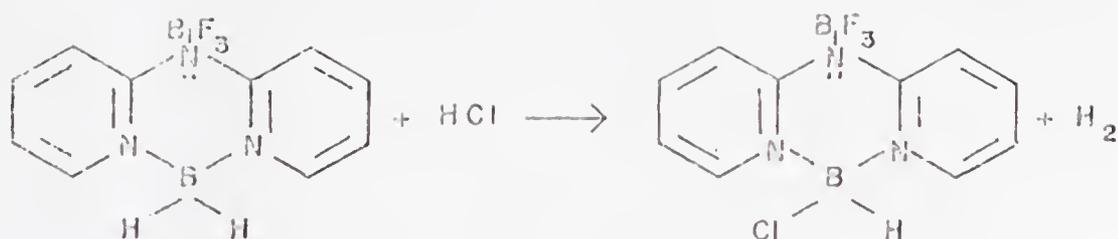
The preparation of 2,2'-dipyridylmethylamine took advantage of the fact that cations with a halogen substituted on boron, for example, intermediate (A), readily hydrolyze to liberate the coordinated amine as one of the products. The product of the reaction of bromine with the iodide salt of dihydro (2,2'-(methylimino) dipyridine-N¹,N^{1'})

boron (1+) (III) was hydrolyzed and produced 2,2'-dipyridylmethylammonium (1+) hexafluorophosphate in a moderate yield. 2,2'-dipyridylmethylamine was readily prepared by dissolving 2,2'-dipyridylmethylammonium (1+) hexafluorophosphate in water, adding sodium hydroxide solution, and extracting the desired amine with diethyl ether. The ether solution was dried over anhydrous sodium carbonate. The ether was then removed under vacuum and the amine isolated as a viscous liquid. This amine had never been prepared before, for conventional methods used for alkylation of an amine would alkylate the pyridine rings first, irreversibly and deactivating the aliphatic nitrogen. Both 2,2'-dipyridylamine and 2,2'-dipyridylmethylamine upon protonation with aqueous acid form the plus one salt, whereas, dipyridyl, 2,2'-dipyridylmethane form the plus two salt upon protonation. Because the corresponding hydrogens in each of the pyridine rings of 2,2'-dipyridylamine and 2,2'-dipyridylmethylamine are equivalent in the proton nmr, one can speculate a proton bifurcating the two pyridine rings to form a chelate.

In the preparation of the chloride and bromide salt of (II), only the desired product was isolated and the anhydrous HX did not react with the hydrogens on boron. The question arose whether this was due to an electronic effect (the positive charge on the cation). To answer this question, the imino nitrogen in (I) was blocked with BF_3 .

(I) was dissolved in methylene chloride and a stoichiometric amount of boron trifluoride etherate was added. The solution was stirred and after five minutes a white crystalline material precipitated. The product, dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{\text{N}}^1, \underline{\text{N}}^{1'}$]

boron - boron trifluoride (IX), was filtered and dried under vacuum. (IX) was then allowed to react with anhydrous HCl. If reaction had occurred between (IX) and HCl, hydrogen should have been produced as predicted by the following reaction scheme.



No hydrogen was evolved but a portion of the HCl was used up. Infrared and proton nmr spectra indicated that a new compound was partially formed. This new compound appeared to have a proton substituted for a BF_3 group in the dipyridyl and the infrared spectrum was strikingly characteristic to BF_2Cl^- .

To see if this actually could have been what had happened, the following experiment was carried out.

The chloride salt of (II) was placed on a vacuum line and BF_3 was allowed to condense upon it and then warm up. The BF_3 was condensed and allowed to warm up several times and the excess removed. Some BF_3 was absorbed and the infrared and proton nmr indicated that the same product as from the reaction of (IX) and HCl had been formed.

That the reaction of the chloride salt of (II) with boron trifluoride and the reaction of anhydrous hydrogen chloride with dihydro [(2,2'-iminodipyridinato)(1-)- $\text{N}^1, \text{N}^{1'}$] boron - boron trifluoride (1:1) (IX) gives the same product is not totally unexpected. Waddington and Klarberg (49) have prepared salts of chlorotrifluoroborate

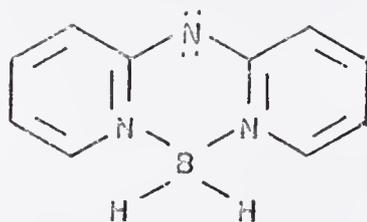
from the chloride salt of a number of cations and BF_3 . The infrared spectra of the products have been studied. By analogy, one would expect the chlorotrifluoroborate anion to form from the reaction of the chloride salt of (II) and boron trifluoride. That the same product forms in the reaction of (IX) with HCl can be rationalized in the following way. In the adduct (IX) there probably is some steric strain between the coordinated boron trifluoride and the rest of the ring system. This strain can be readily removed by exchanging a proton for a BF_3 and at the same time a B-Cl bond can be formed. Since hydrogen should attract electrons less than the boron trifluoride substituent, the electrons on the nitrogen should be less tightly held and allowed to participate more in conjugation. This process is not energetically favorable for two of the strongest bonds are being broken. The relief of steric strain and the release of electrons for conjugation appear to partly compensate for this. Also, there could be a stabilization due to the lattice energy of the new salt formed which allows the reaction to proceed.

A final point to be discussed is the rationalization of the electronic spectra of (I), (V), and (VI) and their conjugate acids. Except for minor structural differences, the electronic spectra of the three neutral species and of the three conjugate acids are the same. Fluorination gives a small blue shift and slightly more structure, but, other than that, no differences can be observed. In (I), (V), and (VI), upon protonation, their color completely disappears and, as one increases solvent polarity (hexane, to methyl chloride, to water), there is a blue shift (the 0-0 band goes from 431 nm to 425 nm to 385 nm respectively in the case of I) and loss of vibrational structure. It would seem quite

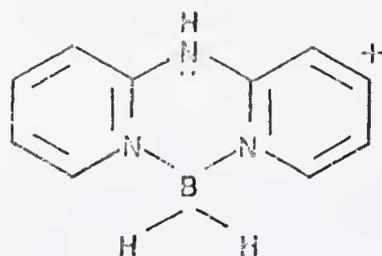
correct to assign the lowest energy band to a $n \rightarrow \pi^*$ transition. Because the molar absorptivity is around 10^4 , this is not likely the case, but is likely an intramolecular charge-transfer, a process which usually has high absorptivities. It is difficult to really distinguish between an $n \rightarrow \pi^*$ transition and a charge-transfer transition. The only real difference is case and magnitude of electronic rearrangement. Compounds (I), (V), and (VI) are zwitterions and the imino nitrogen most likely has one pair of electrons involved in conjugation with the neighboring pyridine rings. The other pair of electrons on the imino nitrogen can participate in either $n \rightarrow \pi^*$ or charge-transfer transitions. The pyridine rings can readily act as acceptors. Because of the magnitude of the extinction coefficient, the observed transitions for the lowest energy singlet - singlet transition in compounds (I), (V), and (VI) were assigned to a charge-transfer transition.

GLOSSARY

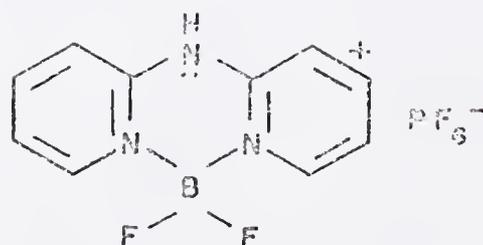
- i. Dihydro (2,2'-iminodipyridinato(1-)- $\underline{N}^1, \underline{N}^{1'}$) boron



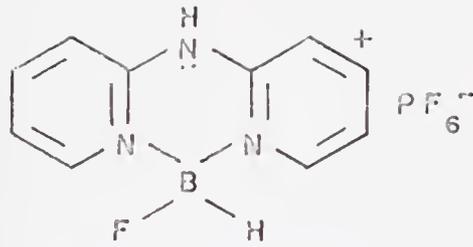
- ii. Dihydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+)



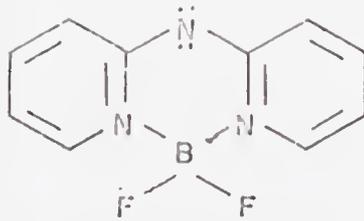
- iii. Difluoro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate



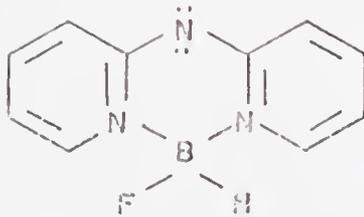
IV. Tetrahydro (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (1+) hexafluorophosphate



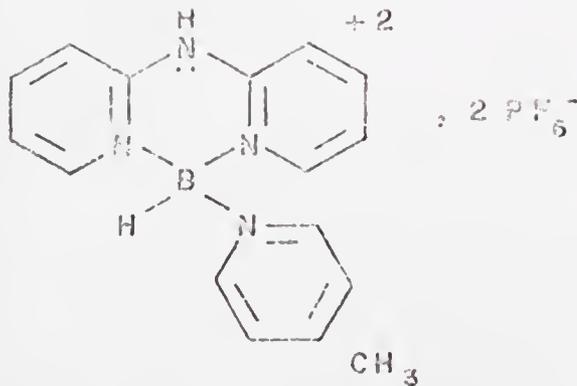
V. Difluoro (2,2'-iminodipyridinato(1-)- $\underline{N}^1, \underline{N}^{1'}$) boron



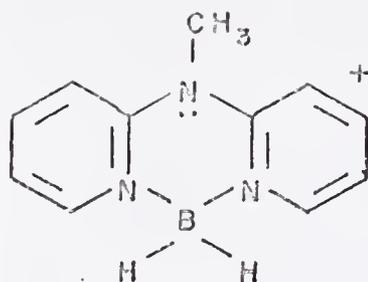
VI. Fluoro (2,2'-iminodipyridinato(1-)- $\underline{N}^1, \underline{N}^{1'}$) boron



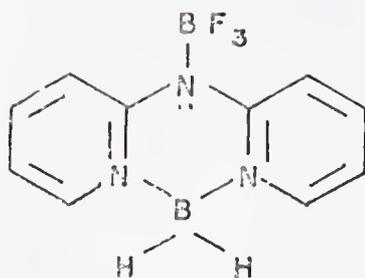
VII. Hydro (4-picoline) (2,2'-iminodipyridine- $\underline{N}^1, \underline{N}^{1'}$) boron (2+) hexafluorophosphate



VIII. Dihydro [2,2'-(methylimino)dipyridine- $\underline{N}^1, \underline{N}^{1'}$] boron (1+)



IX. Dihydro [(2,2'-iminodipyridinato)(1-)- $\underline{N}^1, \underline{N}^{1'}$] boron - boron trifluoride (1:1)



Abbreviations

DILA	Diisopropylethylamine
DPA	2,2'-dipyridylamine
TMA	Trimethylamine
TMAHI	Trimethylammonium iodide
TMABH ₃	Trimethylamine borane
TMAEH ₂ I	Trimethylamine monoiodoborane
A ₂ 2H ₂ ⁺ I ⁻	Bis-(trimethylamine)boronium iodide

BIBLIOGRAPHY

1. D. Ulmschneider and J. Goubeau, Ber., 90, 2733 (1957).
2. M. J. S. Dewar, Prog. in Boron Chem., Vol. 1, Pergamon Press, Belfast, Ireland, 1964, 235-63.
3. M. J. S. Dewar, Adv. Chem. Series, 42, 227-50 (1964).
4. D. R. Schulte and R. W. Parry, J. Amer. Chem. Soc., 80, 4 (1958).
5. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 80, 8 (1958).
6. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 80, 12 (1958).
7. R. W. Parry and S. G. Shore, J. Amer. Chem. Soc., 80, 15 (1958).
8. S. G. Shore, P. R. Girjodot and R. W. Parry, J. Amer. Chem. Soc., 80, 20 (1958).
9. R. W. Parry, G. Kodama and D. R. Schulte, J. Amer. Chem. Soc., 80, 24 (1958).
10. O. P. Shitov, S. L. Ioffe, V. A. Tartakovskii and S. S. Novikov, Russian Chemical Reviews, 39 (11), 905 (1970).
11. R. J. Brotherton and H. Steinberg, Prog. in Boron Chem., Vol. 3, Pergamon Press, Belfast, Ireland, 1970, 211.
12. E. L. Muetterties, The Chemistry of Boron and Its Compounds, John Wiley, New York, 1967.
13. N. E. Miller and E. L. Muetterties, J. Amer. Chem. Soc., 86, 1033 (1964).
14. G. Ryschkewitsch and T. E. Sullivan, Inorg. Chem., 9, 399 (1970).
15. G. L. Smith and H. C. Kelly, Inorg. Chem., 8, 2000 (1969).
16. N. Wiberg and J. W. Butler, J. Amer. Chem. Soc., 85, 244 (1963).
17. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 89, 3145 (1967).
18. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 89, 4240 (1967).
19. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 90, 7234 (1968).

20. K. C. Nainan and G. E. Ryschkewitsch, J. Amer. Chem. Soc., 91, 330 (1969).
21. C. W. Makosky, G. L. Galloway and G. E. Ryschkewitsch, Inorg. Chem., 6, 1972 (1967).
22. K. C. Nainan and G. E. Ryschkewitsch, Inorg. Chem., 7, 1316 (1968).
23. N. E. Miller, Inorg. Chem., 8, 1963 (1969).
24. J. M. Davidson and C. M. French, J. Chem. Soc. (London), 3364 (1962).
25. E. L. Muetterties, Pure Appl. Chem., 10, 53 (1965).
26. G. E. Ryschkewitsch, Progress in Coordination Chemistry, M. Cais, Ed., Elsevier Publishing Co., New York, 1968, 278.
27. J. E. Douglas, G. R. Roehig and On-Hou Ma, J. Organometal Chem., 8, 421 (1967).
28. J. M. Davidson and C. M. French, Chem. Ind. (London), 750 (1959).
29. D. H. Nöth and H. Beyer, Ber., 93, 2251 (1960).
30. D. H. Nöth and H. Vetter, Ber., 97, 110 (1964).
31. B. M. Mikhailov, T. A. Shchegoleva and V. D. Shelvdyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 2165 (1964); English trans. Acad. of Sci. USSR Bull., 2065 (1964).
32. R. Fetterolf, Master's Thesis, University of Florida, 1964.
33. W. J. Rademaker, Doctoral Dissertation, University of Florida, 1969.
34. T. E. Sullivan, Doctoral Dissertation, University of Florida, 1970.
35. E. Deutsch and H. Taube, Inorg. Chem., 7, 1532 (1968).
36. R. C. Weast, Ed., Handbook of Chemistry and Physics, 50th Edition, The Chemical Rubber Company, New York, 1970, D-102.
37. R. C. Taylor, in Boron-Nitrogen Chemistry, Advances in Chemistry Series, N. 42, American Chemical Society, Washington, D. C., 1964, 59.
38. A. R. Katritzky, J. Chem. Soc. (London), 2049 (1959).
39. R. S. Drago, Physical Methods in Inorganic Chemistry, Reinhold Publishing Corporation, New York, 1965, 194-95.

40. A. E. Gebald and M. M. Jones, Inorg. Nucl. Chem., 31, 771 (1969).
41. M. J. S. Dewar and R. Jones, Tetrahedron Letters, No. 22, 2707 (1968).
42. M. Hudlicky, Chemistry of Organic Fluorine Compounds, MacMillan Company, New York, 1962, 93.
43. R. L. Amster and R. C. Taylor, Spectrochimica Acta, 20, 1487-1502 (1964).
44. T. C. Waddington and F. Klarberg, J. Chem. Soc., 2339 (1960).
45. G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co., Inc., Princeton, N. J., 1945, 101-102; 215-19; 261-64.
46. D. F. Eggers, Jr., and W. E. Lingren, Anal. Chem., 28, 1528 (1956).
47. M. C. Mathur, Doctoral Dissertation, University of Florida, 1970.
48. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, 58-132.
49. L. M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Edition, Pergamon Press, Belfast, Ireland, 1969, 201-18.
50. J. W. Gilje and R. J. Ronan, Inorg. Chem., 7, 1248 (1968).
51. R. J. Ronan and J. W. Gilje, Inorg. Nucl. Chem. Letters, 7, 359-63 (1971).
52. L. E. Benjamin, D. A. Carvalho, S. F. Stafiej and E. A. Takacs, Inorg. Chem., 9, 1844 (1970).

BIOGRAPHICAL SKETCH

Kenneth Abate was born in Detroit, Michigan, on January 9, 1944. Because his father was in the Armed Services, he traveled extensively during his youth. In December, 1965, he received the degree of Bachelor of Science with a major in Chemistry from Wayne State University. Following graduation, Mr. Abate enrolled in the Graduate School of Michigan Technological University and received in June, 1967, the degree of Master of Science with a major in Chemistry. From September, 1967, until the present time, he has pursued his work toward the degree of Doctor of Philosophy with a major in Chemistry at the University of Florida. During this time, he worked as a graduate teaching assistant, received two DuPont Teaching Awards, and was awarded a one-half-time Interim Instructorship.

Kenneth Abate is a member of the American Chemical Society and two professional chemical fraternities, Alpha Chi Sigma and Phi Lambda Upsilon.

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George E. Ryschkewitsch, Chairman
Professor of Chemistry

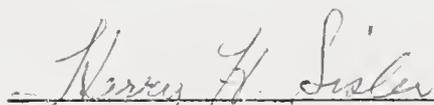
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George P. Butler
Professor of Chemistry

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Professor of Soils

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Harry H. Sisler
Professor of Chemistry

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Associate Professor of Chemistry

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1971

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