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A Multinuclear Nuclear Magnetic Resonance Study of $B_4H_8PF_2N(CH_3)_2$. Geometrical and Rotational Isomers and Their Dynamic Behavior[1,2]

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The ^1H, ^{11}B, ^{19}F, and ^{31}P NMR spectra of $B_4H_8PF_2N(CH_3)_2$ indicate that the compound exists as two isomers in solution. Low-temperature ^{19}F NMR spectra demonstrate that these isomers are geometrical in nature. At low temperatures (−125 °C) rotation about the P–B bond in one isomer becomes slow on the experimental time scale, while this rotation remains rapid in the second isomer. Spectral simulations yield a $\Delta G^{\ddagger}$ value of 7.8 kcal/mol for the barrier to rotation about the P–B bond in one of the geometrical isomers. At high temperature (80 °C) the two geometrical isomers interconvert rapidly on the ^{19}F NMR time scale. Simulations of the high-temperature spectra yield a $\Delta G^{\ddagger}$ value of 19 kcal/mol for the barrier to interconversion of these isomers. This value and other data including isotopic labeling studies are discussed in terms of the mechanism by which the geometrical isomers interconvert at high temperature.

Introduction

The existence of isomers in the $B_4H_8PF_2N(CH_3)_2$ molecule was established on the basis of the presence of two doublets in the ^{19}F NMR spectrum.[3] The doublets were found to reversibly coalesce to a single doublet at high temperature and the isomers were described as geometrical in nature, orginating from endo and exo orientation of the ligand with respect to the folded B_4 ring. In the same report[3] no evidence was observed for the presence of isomers in $B_4H_8PF_2H$. Interestingly, the crystal structure of $B_4H_8PF_2N(CH_3)_2$ indicated the presence of only the endo isomer.[4] In a later report[5] the presence of two doublets in the ^{19}F NMR spectrum of each of the $B_4H_8PF_2X$ compounds (X = F, Cl, Br, and I) was interpreted in terms of two isomers. However, the origin of these isomers as well as those in $B_4H_8PF_2N(CH_3)_2$ was attributed to restricted rotation about the phosphorus–boron bond.

A recent report from this laboratory of a ^{11}B NMR study of B_4H_8CO[6] demonstrated that this compound exists as two isomers in solution, and these isomers clearly cannot arise from restricted rotation about the B–C bond. Thus we have initiated a study of B_4H_8L complexes (L = Lewis base) in order to clarify the ambiguities concerning the nature of the isomers in these compounds. We are interested in the origin of the isomers, the factors which stabilize one isomer relative to the other, and the mechanism by which the isomers interconvert at high temperature. We have begun this project with a thorough study of $B_4H_8PF_2N(CH_3)_2$. A preliminary report[7] presented the low-temperature ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$ which demonstrated that the isomers previously reported for this compound are geometrical in nature (Figure 1), and at low temperature rotation about the P–B bond in one isomer becomes slow on the NMR time scale. This report presents the results of a multinuclear NMR study (^{11}B, ^{31}P, ^{19}F, and ^1H) of $B_4H_8PF_2N(CH_3)_2$, which includes variable-temperature NMR studies and isotope-exchange experiments. In addition the dynamic behavior of the $B_4H_8PF_2N(CH_3)_2$ molecule has been analyzed quantitatively via simulations of the temperature-dependent ^{19}F NMR spectra.

Experimental Section

Syntheses. All preparative procedures were carried out by using standard high-vacuum techniques.[8] The $B_4H_8PF_2N(CH_3)_2$[9] was prepared by reaction of $PF_2N(CH_3)_2$[10] with B_4H_8CO[11] and was carefully purified on a low-temperature vacuum fractionation column. The $B_4H_8PF_2N(CD_3)_2$ was prepared by an analogous procedure with $PF_2N(CD_3)_2$ which was prepared from $(CD_3)_2NH$ (Merck, 99% D) by published procedures.[10]

Spectroscopic Techniques. The ^1H (100.1 MHz), ^{19}F (94.1 MHz), ^{31}P (40.5 MHz), ^{11}B (32.1 MHz), and ^2H (15.4 MHz) NMR spectra were obtained on a highly modified Varian Associates XL-100-15 NMR spectrometer. Samples were run as ~20% (v/v) solutions in toluene-d_8 or n-pentane. Chemical shifts are reported relative to external Me_4Si (^1H), CF_3COOH (^{19}F), 85% o-H_3PO_4 (^{31}P), and BF_3OEt_2 (^{11}B). A negative sign denotes increased shielding. The 270-MHz ^1H NMR spectra were acquired on a Bruker HX-270 spectrometer at Florida State University. The proton-decoupled ^{19}F NMR spectra were acquired by using a double-tune matching network designed by Matson[12] which allows irradiation at both 100.1 and 94.1 MHz from a single coil. Low-temperature ^{19}F NMR spectra were obtained on ~20% (v/v) solutions in a 1:1 (v/v) mixture of toluene-d_8 and isopentane. High-temperature ^{19}F NMR spectra were acquired on ~20% (v/v) solutions in toluene-d_8. Standard variable-temperature accessories were employed. Temperatures were measured with a copper/constantan thermocouple before and after each run and were found to be consistent to ±1 °C.

Spectral Simulations. The simulated spectra were calculated by using the DNMR3[13] computer program which was converted to double precision and modified to execute on the University of South Carolina's IBM 370/168 computer. The matrix diagonalization routine ALLMAT was replaced with the IMSL[14] routine EIGCC. Calculated spectra were plotted on a Calcomp plotter.

Ligand-Exchange Studies. In this experiment ^{11}B and ^2H NMR spectra were obtained on a sample of 13.8 mole % $B_4H_8PF_2N(CD_3)_2$ in C_6H_6. The spectra were carefully integrated by the use of a planimeter on large expansions. The sample tube was opened under vacuum, and the contents were condensed into a small volume (8 mL) glass tube fitted with a greaseless stopcock. Isotopically normal $PF_2N(CH_3)_2$ (0.257 mmol) was then condensed into the tube and the mixture was warmed to 72 °C for 10 min. The contents of the vessel yellowed significantly during this time; however, no noncondensable materials were produced. The volatile products were then fractionated on a low-temperature fractionation column. A small amount of viscous yellow oil remained in the glass tube. Mass spectral analysis of the recovered $PF_2N(CH_3)_2$–$PF_2N(CD_3)_2$ mixture was obtained on a Perkin-Elmer RMU-6 mass spectrometer to determine if $PF_2N(CD_3)_2$ was generated during the course of the experiment.

The recovered $B_4H_8PF_2NMe_2$ (0.0110 g, 0.069 mmol) was condensed into a 5-mm NMR tube along with C_6H_6. The resulting solution was 6.9 mole % $B_4H_8PF_2NMe_2$ or half the concentration of the original sample. The ^{11}B and ^2H NMR experiments were repeated under the conditions previously used except that 4 times as many transients were acquired to compensate for the twofold decrease in concentration. The spectra were again carefully integrated by the same method.

Results

^{11}B NMR Spectra. The proton-coupled ^{11}B NMR spectrum of $B_4H_8PF_2N(CH_3)_2$ is shown in Figure 2A. This spectrum is essentially the same as that reported by Centofanti et al.[3] The more shielded triplet of area 1 has been assigned to the substituted boron (B_1)[15] with the triplet structure arising from the near equivalence of J_{B-P} and J_{B-H} ($J_{B-P} \simeq J_{B-H}$ 175 Hz). The deshielded multiplet has been interpreted as an overlapping triplet of area 2 ($B_{2,4}$) and doublet of area 1 (B_3).[3]

Under conditions of complete proton decoupling (Figure 2B) the shielded triplet becomes a doublet (B_1, $\delta = -54.9$, $J_{PB} =$

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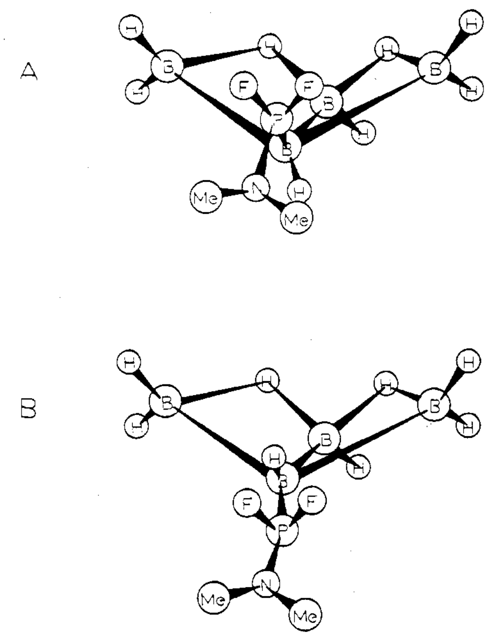


Figure 1. Structure of $B_4H_8PF_2N(CH_3)_2$: (A) endo placement of the ligand, (B) exo placement of the ligand.

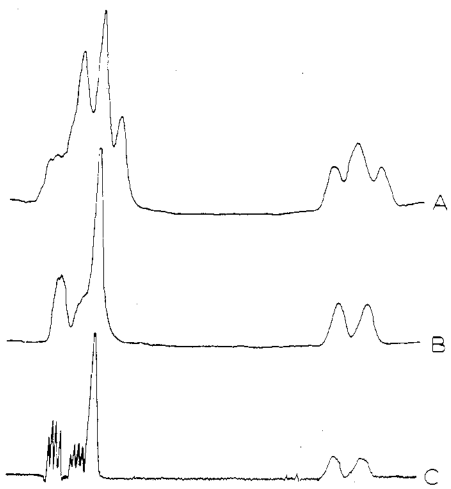


Figure 2. ^{11}B NMR spectra of $B_4H_8PF_2N(CH_3)_2$: (A) proton-coupled spectrum, (B) proton-decoupled spectrum, (C) line-narrowed, proton-decoupled spectrum. Spectral width is 3000 Hz.

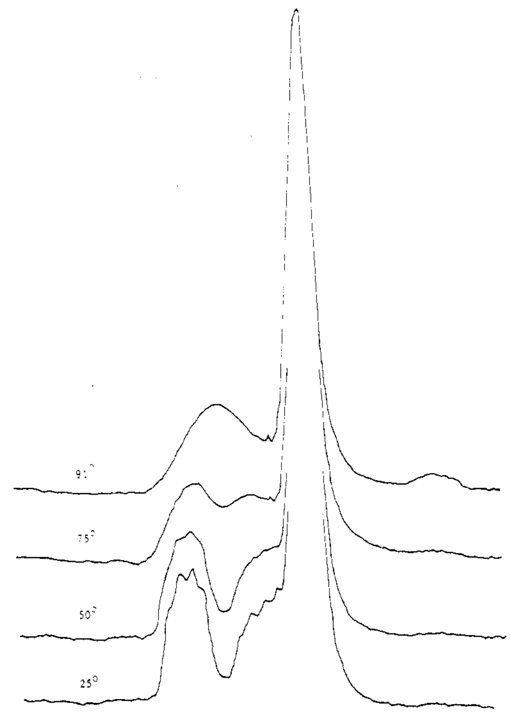


Figure 3. High-temperature dependence of the deshielded resonances in the proton-decoupled ^{11}B NMR spectrum of $B_4H_8PH_2N(CH_3)_2$.

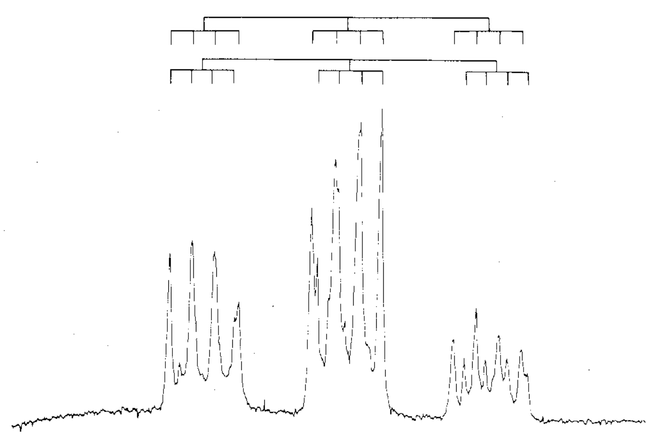


Figure 4. ^{31}P NMR spectrum of $B_4H_8PF_2N(CH_3)_2$ at ambient temperature. Spectral width is 5000 Hz.

175 Hz). The deshielded multiplet collapses to a poorly resolved quartet of area 1 (B_3, $\delta = 3.6$) and a singlet of area 2 ($B_{2,4}$, $\delta = -3.9$) plus an additional resonance ($\delta = -0.5$) which appears as a shoulder on the deshielded side of the area 2 singlet. With the application of computer line narrowing[16] this shoulder as well as the resonance at lower shielding becomes a well-resolved quartet (Figure 2C). These quartets were found to coalesce at high temperature as is shown in Figure 3. These spectral changes are reversible except for a small amount of decomposition of the sample. The two quartets can be assigned to the B_3 atoms of the two geometrical isomers of $B_4H_8PF_2N(CH_3)_2$. The quartet structure of these resonances arises from ^{11}B–^{11}B coupling between B_1 and B_3 ($J_{B_1B_3} = 24$ Hz) as Stampf et al.[17] reported previously. The presence of only one resonance for $B_{2,4}$ and a single doublet for B_1 is best explained by coincidental overlap of nonequivalent resonances.

^{31}P NMR Spectra. The 40.5-MHz ^{31}P NMR spectrum of $B_4H_8PF_2N(CH_3)_2$ (Figure 4) has not been previously reported. This spectrum clearly indicates the presence of two isomers. The pattern observed is complex but can be interpreted in a first-order manner as two overlapping triplets of quartets. The triplet structure arises from spin–spin coupling with two equivalent fluorines. The multiplicity observed in each member of the triplet arises from coupling with the directly bonded boron. The chemical shifts for the two isomers are essentially identical ($\delta = +127$); however, in the predominant isomer the P–F coupling is slightly smaller than that in the second isomer (1110 Hz vs. 1150 Hz). For P–B couplings the reverse is true (175 Hz vs. 170 Hz). The result of these conditions is that the extent of overlap of the resonances due to the two isomers decreases from the least shielded to the more shielded members of the triplets. In the least shielded multiplet only five lines are resolved while in the most shielded multiplet eight lines are well resolved.

^{1}H NMR Spectra. The proton NMR spectrum of $B_4H_8PF_2N(CH_3)_2$ was reported by Centofanti et al.[3] but only the methyl proton resonance was observed. This region of the spectrum was said to consist of a doublet from coupling to phosphorus ($^3J_{HP} = 10.8$ Hz), each member of which was further split into a triplet from coupling to the two fluorine atoms ($^4J_{HF} = 3.0$ Hz). The methyl region of the spectrum obtained in this laboratory is shown in Figure 5. This spectrum is more complex than a doublet of triplets, but it can

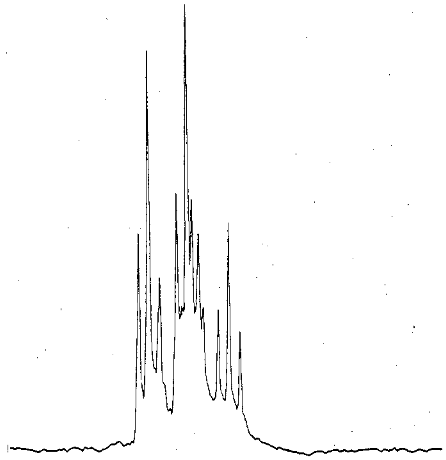


Figure 5. Methyl region of the ^1H NMR spectrum of $B_4H_8PF_2$-$N(CH_3)_2$. Spectral width is 125 Hz.

be interpreted on a first-order basis as two overlapping doublets of triplets. The doublets are centered at $\delta = 1.87$ and $\delta = 1.75$ from Me_4Si with $^3J_{HP} = 11.2$ Hz in the less shielded resonance and $^3J_{HP} = 10.5$ Hz in the more shielded resonance. The triplet structure arises from coupling to the two fluorine nuclei ($^4J_{HF} = 3.2$ Hz in both multiplets). These two resonances were found to coalesce reversibly to a single doublet of triplets at high temperature.

The 100-MHz ^1H NMR spectrum of uncomplexed $PF_2N(CH_3)_2$ was obtained and found to consist of the expected doublet of triplets. The only temperature dependence observed for this spectrum was a broadening below −80 °C as might be expected from increased viscosity of the sample.

The terminal protons on B_2 and B_4 and the bridging protons were observed in the ^{11}B-decoupled spectrum at 2.95 and −2.12 ppm, respectively.

^{19}F NMR Spectra. The reversible spectral changes in the ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$ as a function of temperature can be divided into three sections. Between −125 and −40 °C rotation about the P–B bond in one geometrical isomer changes from slow to fast on the experimental time scale.[7] Between −40 and +60 °C the relative populations of the two geometrical isomers change as a function of temperature. At 60 °C the isomers are present in approximately equal concentrations; however, the interconversion of the isomers is slow on the ^{19}F NMR time scale. Above 60 °C this interconversion becomes increasingly rapid and the two doublets coalesce to a single doublet. The variable-temperature ^{19}F NMR results will be presented in three segments corresponding to the three situations described above starting at low temperature and going to high temperature.

The experimental ^{19}F NMR spectra obtained between −125 and −94 °C and the "best fit" calculated spectra are shown in Figure 6. The experimental spectra were acquired under conditions of proton decoupling in order to remove the unresolved H–F coupling as a source of line width. The peaks marked with asterisks arise from a small amount of impurity in the sample. The resonances due to this impurity overlap with one of the doublets of interest, and at temperatures below −105 °C this decreases the resolution in these resonances. The calculated to experimental "best fits" for spectra acquired below this temperature were obtained by fitting the resonances which were not affected by the impurity. At temperatures above −105 °C the impurity has no significant effect on the overall line shape of any resonance and the fit of calculated to experimental data is good for all resonances in the spectra.

A least-squares analysis of the Erying plot of the rate constant/temperature data pairs obtained from these data (−125 to −94 °C) yield values of $\Delta H^{\ddagger} = 8.2 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 1.3 \pm 0.1$ eu, and $\Delta G^{\ddagger}_{298} = 7.9 \pm 0.8$ kcal/mol for rotation about the P–B bond in one geometrical isomer.

The experimental ^{19}F NMR spectra obtained between 0 and +58 °C are shown in Figure 7. The spectra obtained at different temperatures differ in the relative intensities of the two doublets observed. The chemical shifts of the two doublets do not change over this temperature region, and at 58 °C the interconversion of the two geometrical isomers remains slow on the experimental time scale. The observed changes in the relative intensities of the two doublets result from changes in the difference in free energy between the two isomers as a function of temperature.

Values of $\Delta G°$ at each temperature can be calculated from the integrated intensities of the two doublets. On the assumption that $\Delta H°$ and $\Delta S°$ of the two isomers are constant over the temperature range from 0 to 58 °C, the slope and Y intercept of a plot of $\Delta G°$ vs. T are the values of $\Delta S°$ and $\Delta H°$, respectively. A linear least-squares analysis of the data in Table I gives a value of 4.5 ± 0.4 eu for $\Delta S°$ and 1.5 ± 0.1 kcal/mol for $\Delta H°$. Calculation of $\Delta G°_{298}$ with these values gives a value of 0.16 ± 0.01 kcal/mol which is within 10% of the value of 0.15 kcal/mol obtained from the integration of the 25 °C ^{19}F spectrum. From these values of $\Delta S°$ and $\Delta H°$ one can calculate the temperature at which the populations of the two isomers become equal. At this temperature $\Delta G°$

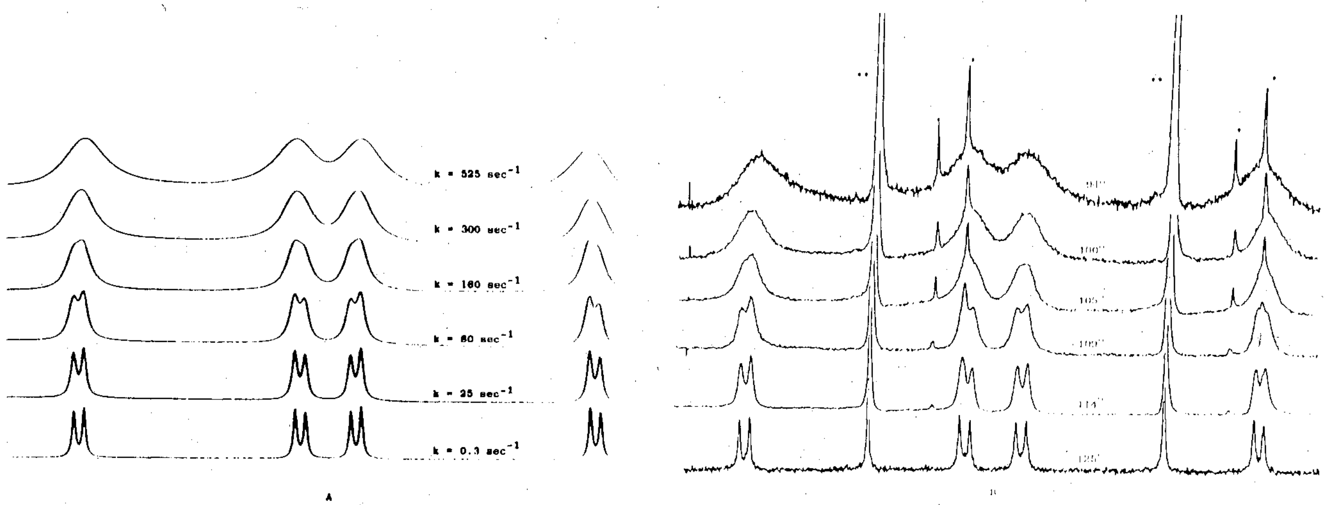


Figure 6. Low-temperature ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$: (A) computer-simulated spectra, (B) experimental spectra. Spectral width is 2500 Hz. Peaks marked with asterisks (*) result from a small amount of impurity in the sample. Peaks marked with double asterisks (**) arise from the second geometrical isomer which shows no low-temperature dependence.

Table I. Ratios of Isomer Populations and ΔG° Values for $B_4H_8PF_2N(CH_3)_2$

T, °C (K)	P_A/P_B	ΔG°, cal/mol
0 (273)	1.72	294
25 (298)	1.28	146
38.5 (312.5)	1.18	102
49 (322)	1.12	72
58 (331)	1.04	25

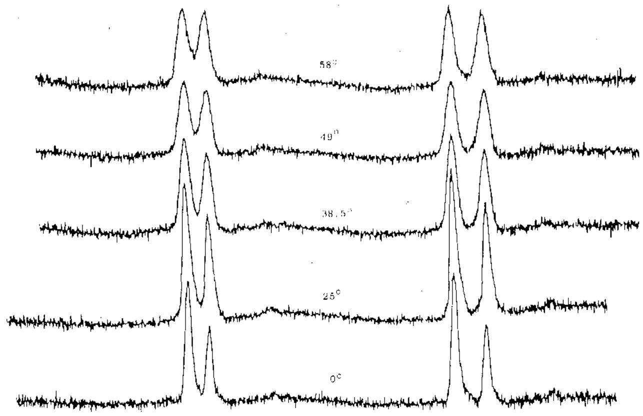


Figure 7. ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$ between 0 and +58 °C showing the temperature dependence of the relative intensities of the two overlapping doublets. Spectral width is 2500 Hz.

= 0 and $T = \Delta H^\circ/\Delta S^\circ$. Substitution of the values obtained for ΔH° and ΔS° into this equation gives a value of 59.4 °C for this temperature. The ^{19}F NMR spectra show this temperature to be between 58 and 63.5 °C in excellent agreement with the calculated value. It should be emphasized that this temperature is not the temperature at which the resonances due to the two isomers coalesce; it is the temperature at which the intensities of the two doublets become equal.

The spectra which reflect the rate of interconversion of the two isomers are those acquired above 60 °C. Above this temperature the two doublets coalesce to a single doublet, demonstrating that the interconversion of the two isomers becomes fast on the experimental time scale. The experimental spectra obtained between 63.5 and 80 °C and the "best-fit" calculated spectra are shown in Figure 8. The agreement between calculated and experimental spectra is very good. The decreased resolution in the deshielded resonances of the experimental spectra at 70.5 and 73 °C relative to the calculated spectra is due to the presence of a small amount of $H_3BPF_2N(CH_3)_2$ which results from decomposition of the sample. A least-squares analysis of the Erying plot of the rate constant/temperature data pairs (63.5–80 °C) gives values of $\Delta H^\ddagger = 28 \pm 3$ kcal/mol, $\Delta S^\ddagger = 30 \pm 3$ eu, and $\Delta G^\ddagger_{298} = 19 \pm 2$ kcal/mol for the interconversion of the endo and exo isomers.

Ligand-Exchange Studies. The isotope-exchange experiment was conducted in an attempt to determine whether or not dissociation of the ligand occurs as part of the mechanism of the interconversion of the endo and exo isomers of $B_4H_8PF_2N(CH_3)_2$. The ^{11}B NMR spectra were recorded and integrated to provide a standard by which errors in the concentrations of the samples could be negated. The integrated intensities of the ^{11}B and ^2H NMR spectra obtained from the original sample of $B_4H_8PF_2N(CD_3)_2$ (13.8 mole %) in C_6H_6 were 2219 and 789, respectively. The intensities of the spectra acquired after combining the original sample with $PF_2N(CH_3)_2$, heating the mixture to 72 °C for 10 min, and recovering the complex were 1259 (^{11}B) and 300 (^2H). The theoretical intensity of the ^2H spectrum of the sample prepared after the "exchange" can be calculated from the equation

$$({}^{11}B_A/{}^{11}B_B)^2H_B = {}^2H_A \qquad (1)$$

where $^{11}B_A$ and $^{11}B_B$ are the integrated intensities of the ^{11}B spectra acquired after and before the "exchange" and ^2H_A and ^2H_B are the analogous values for the ^2H spectra. Substitution of the appropriate values into this equation gives 447 as the theoretical intensity of the ^2H spectrum. The observed value of 300 is one-third less than this calculated value, indicating that approximately one-third of the $PF_2N(CD_3)_2$ was displaced by $PF_2N(CH_3)_2$.

Mass spectral analysis of the free base recovered from the "exchange" experiment showed a 2:1 ratio of $PF_2N(CH_3)_2$ to $PF_2N(CD_3)_2$. Quantification of this result in terms of the NMR results is not possible because the absolute amount of each isotopic species which was incorporated into the decomposition products is not known.

Discussion

When this study was initiated, ^{19}F NMR spectra had indicated the presence of two isomers in $B_4H_8PF_2X$ compounds (X = $(CH_3)_2N$, F, Cl, Br, and I).[3,5] These isomers had been discussed as geometrical isomers arising from endo and exo placement of the ligand with respect to the boron ring (for X = $(CH_3)_2N$)[3] and as rotational isomers arising from restricted rotation about the P–B bond (for X = $(CH_3)_2N$, F, Cl, Br, and I) in a single geometrical isomer, the endo isomer.[5] Stampf et al.[6] had demonstrated by ^{11}B NMR that B_4H_8CO exists as two isomers. These isomers could not arise from restricted rotation about the B–C bond.

The low-temperature ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$ demonstrate that the isomers observed at room tem-

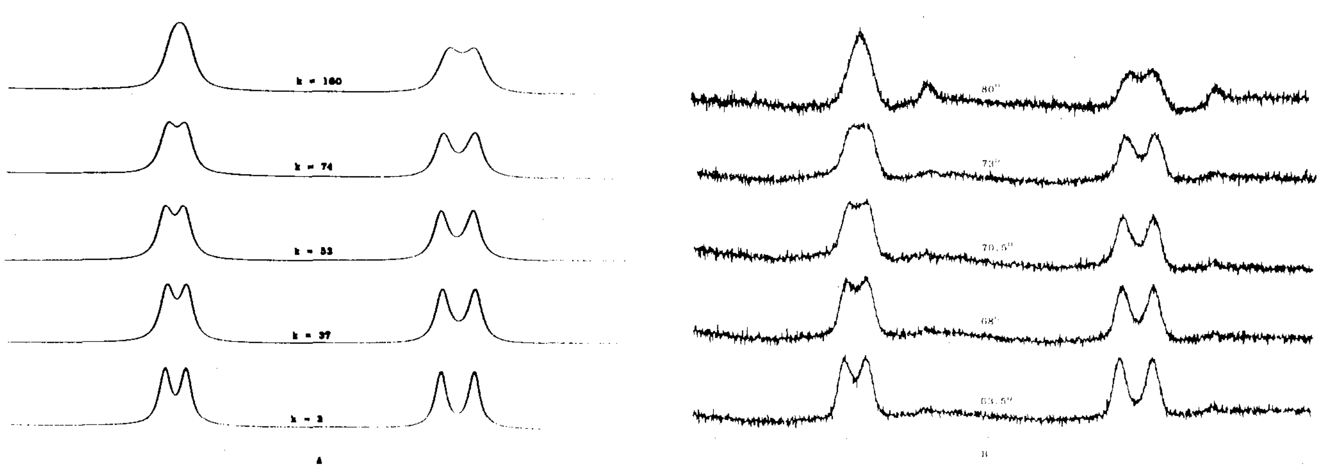


Figure 8. High-temperature ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$: (A) computer-simulated spectra, (B) experimental spectra. Spectral width is 2500 Hz.

perature arise from endo and exo placement of the ligand and not from restricted rotation about the P–B bond in a single geometrical isomer as had been previously postulated.[5]

As the temperature is lowered from room temperature, the doublet due to one isomer, the predominant one, broadens and eventually disappears from the spectrum. At −125 °C two new doublets of doublets have grown into the spectrum in place of the original doublet which collapsed. These spectral changes are best interpreted in terms of two geometrical isomers at high temperatures. As the temperature is lowered, rotation about the P–B bond in one geometrical isomer becomes slow with respect to the ^{19}F NMR time scale while this rotation in the other isomer remains rapid. The resultant spectrum consists of three doublets, two of which are further split into doublets. The two doublets of doublets arise from the nonequivalent fluorine atoms in a single rotational isomer in one of the geometrical isomers. Another rate process capable of giving the same kind of ^{19}F spectral changes at low temperature is restricted internal rotation about the phosphorus–nitrogen bond. It is possible that complexation of B_4H_8 to phosphorus could significantly hinder P–N rotation. However, we have prepared and studied[18] a series of $B_4H_8PF_2X$ complexes where X = F, Cl, Br, and I and their low-temperature ^{19}F behavior is analogous to that of $B_4H_8PF_2N(CH_3)_2$ ruling out slow P–N rotation as the source of the observed spectral changes. The other doublet, which remains virtually unchanged as the temperature is lowered, arises from the other geometrical isomer in which rotation about the P–B bond is still rapid with respect to the experimental time scale at −125 °C.[7]

An alternative explanation for the invariant behavior of one doublet in the low-temperature ^{19}F spectra can also be advanced. Instead of rapid conformational exchange of the fluorine atoms in one geometrical isomer the persistence of the doublet could indicate a strong conformational preference for a geometry in which the two fluorine atoms are equivalent. However, the lack of any change in this doublet at elevated temperatures (i.e., >60 °C) would require an inordinately large barrier to internal rotation about the boron–phosphorus bond. In fact, as we have pointed out earlier,[6] if rotation about the B–P bond is slow on the NMR time scale at +40 °C, a barrier to internal rotation of greater than 16 kcal/mol is required. Such a barrier in a phosphine–borane seems excessively large.

The variable-temperature, multinuclear NMR data presented here support this interpretation of the low-temperature ^{19}F NMR data. The observation in the proton-decoupled ^{11}B NMR spectrum of two quartets for the B_3 atoms (Figure 2) of the two isomers is additional evidence that these isomers are geometrical in nature. The reversible, high-temperature coalescence of these quartets (Figure 3) confirms that these resonances arise from the B_3 atoms in two geometrical isomers. The resonances of the two isomers overlap extensively in the ^{31}P NMR spectrum (Figure 4); however, interpretation of this spectrum in terms of two geometrical isomers is unambiguous. The two doublets of triplets observed for the methyl protons in the ^1H NMR spectrum (Figure 5) could arise from restricted rotation about the P–N bond. The ^1H NMR spectrum of uncomplexed $(CH_3)_2NPF_2$ was obtained and it consists of a single doublet of triplets. This fact plus the reversible high-temperature coalescence of the two doublets of triplets to a single doublet of triplets in $B_4H_8PF_2N(CH_3)_2$ demonstrates that the room-temperature ^1H spectrum results from the presence of two geometrical isomers.

An interesting question at this point is how are the isomers formed. Most probably the isomers arise from nonstereospecific attack of the ligand in the formation of the adduct. It has been suggested that B_5H_{11} exists in equilibrium with B_4H_8 and BH_3.[19] It has also been established that B_4H_8CO exists in equilibrium with B_4H_8 and CO.[20] Therefore, regardless of whether the B_4H_8L compounds are prepared from B_5H_{11} or B_4H_8CO, there is free B_4H_8 present with which the base can react (eq 2). This reaction removes B_4H_8 as B_4H_8L and

$$\left.\begin{array}{l} B_5H_{11} \rightleftarrows B_4H_8 + BH_3 \\ \\ B_4H_8CO \rightleftarrows B_4H_8 + CO \end{array}\right] \xrightarrow{+L} B_4H_8L \qquad (2)$$

causes the generation of additional B_4H_8. Thus the isomers are most likely formed nonstereospecifically and relative populations at equilibrium are determined by $\Delta G°$ for the two isomers.

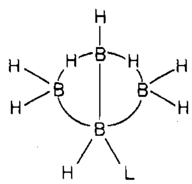
The reversible spectral changes observed in the variable-temperature ^{19}F NMR spectra of $B_4H_8PF_2N(CH_3)_2$ are amenable to analysis by DNMR techniques. These spectral changes also enable one to develop experiments which provide information concerning the mechanism by which the endo and exo isomers interconvert.

DNMR analysis of the low-temperature spectral changes gives a value of 7.8 ± 0.8 kcal/mol for the barrier to rotation about the P–B bond in one of the geometrical isomers. Because this is the first example of a rotational barrier in a phosphine–borane adduct obtained by NMR, barrier values for analogous compounds are not available. Barriers for rotation about the P–B bond in some phosphine–borane (BH_3) adducts have been determined by microwave spectroscopy.[21–25] These barriers fall between 4.15 kcal/mol (H_3BPF_3)[21] and 1.57 kcal/mol ($H_3BP(CH_3)H_2$).[22] Thus, the much higher barrier of 7.8 kcal/mol presumably contains contributions from steric and/or electronic interactions not present in these smaller molecules and not directly associated with the P–B bond itself.

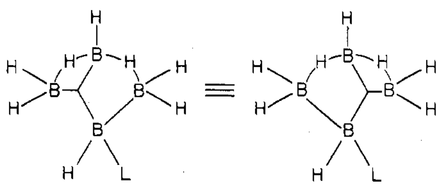
An examination of models of the endo and exo isomers and a consideration of the crystal structure of $B_4H_8PF_2N(CH_3)_2$ indicate that the endo isomer would experience greater steric interactions and possibly greater electronic H–F interactions which would hinder rotation about the P–B bond. One would expect these same steric and electronic interactions to destabilize the endo isomer relative to the exo isomer. However, the ^{19}F NMR spectra show that rotation about the P–B bond is more hindered in the more stable isomer. The thermodynamic analysis of the ^{19}F NMR spectra between 0 and 58 °C resolves this apparent contradiction. The difference in the ground-state free energy of the two geometric isomers is rather small ($\Delta G°_{298}$ = 0.16 kcal/mol), being the difference of two nearly equal but opposite terms (i.e., $\Delta G° = \Delta H° - T\Delta S°$). While the dominance of the enthalpy term at low temperature favors one isomer, raising the temperature increases the relative contribution of the entropy term, $-T\Delta S$, which favors the other isomer. If, by virtue of its greater freedom of rotation about the B–P bond, the exo isomer is favored by the entropy term, then the endo isomer must be favored by the enthalpy term. At temperatures above ~58 °C, the exo isomer appears to be slightly favored, presumably by the increased importance of the temperature-weighted entropy term. However, as the temperature is lowered, enthalpy effects become dominant and the endo isomer becomes the favored isomer. Indeed, at low temperatures, it is the favored endo isomer in which rotation about the B–P bond becomes slow and then stops relative to the NMR time scale. "Freezing out" this rotation in the *predominant* isomer at low temperature is consistent with the assumption that the entropy term favors the less restricted exo isomer at high temperatures. This interpretation is consistent with the crystal structure[4] which found only the endo isomer. La Prade and Nordman attributed the differences in the geometry of the B_4H_8 moiety between $B_4H_8PF_2N(CH_3)_2$ and B_4H_{10} to a nonbonded repulsion between a fluorine atom on the ligand and the $B_{2,4}$ terminal hydrogens.[4] The factors which stabilize the endo isomer by 1.5 kcal/mol in terms of $\Delta H°$ are not obvious, and this area deserves further study.

While the spectral changes observed in the low-temperature ^{19}F spectra clearly arise from restricted rotation about the P–B bond in one geometrical isomer, the mechanism by which the geometrical isomers interconvert at high temperature is far less obvious. Most of the intramolecular rearrangements which occur in boron hydrides and substituted boron hydrides which are amenable to study by NMR involve hydrogen interchange between bridging and nonbridging sites or shift of a bridging hydrogen to an unoccupied B–B edge.[26] Because interconversion of isomers such as analyzed here for $B_4H_8PF_2N(CH_3)_2$ is not known for other boron hydrides, there are no precedents which give insight into the mechanism by which these isomers interconvert.

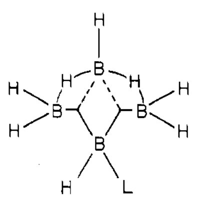
In order to consider possible mechanisms an understanding of the bonding within the B_4H_8 ring is necessary. The *styx* structure[27] which is consistent with the NMR and X-ray data for $B_4H_8PF_2N(CH_3)_2$ is the 2113 structure, and the possible representations of this structure are presented in structures A–C.



A



B



C

There appear to be three basic mechanisms by which the endo and exo isomers of $B_4H_8PF_2N(CH_3)_2$ could interconvert: (1) ligand dissociation and recombination in the opposite orientation; (2) ring inversion (flipping); and (3) rotation of B_1 about the B_1–B_3 axis. The ligand dissociation mechanism leaves the bonding within the boron framework intact; however, it requires breakage of the P–B bond. The "ring flip" mechanism requires no formal bond breaking. LaPrade and Nordman[4] reported a value of 137° for the dihedral angle between the $B_1B_2B_3$ and $B_1B_3B_4$ triangles in $B_4H_8PF_2N(CH_3)_2$. Thus, extensive rehybridization of B_1 and B_3 would be required in order to reach the planar transition state required by the "ring flip" mechanism. Rotation of B_1 about the B_1–B_3 axis requires a formal breaking of the $B_2B_1B_4$ open, three-center, two-electron bond in structure A. In structure B this rotation requires breaking either the B–B, two-center, two-electron bond or the closed, B–B–B three-center, two-electron bond. For structure C, which employs the partial three-center, two-electron bonds which Lipscomb[28] has recently proposed, such a rotation requires breaking either the B_1–B_2–B_3 or the B_1–B_2–B_4 partial, closed, three-center, two-electron bond.

Examination of these mechanisms in light of the experimental evidence is in order. Leach et al.[29] have observed two resonances (quartets) for the $B_{2,4}$ terminal protons in B_4H_{10} in the 220-MHz proton NMR spectrum. These resonances arise from the different environments of the protons as a result of the folded nature of the B_4 ring. Attempts to resolve two resonances for the analogous protons of $B_4H_8PF_2N(CH_3)_2$ in the 270-MHz ^1H NMR spectrum were unsuccessful. Had two resonances been observed, their high-temperature coalescence would have indicated that the "ring flip" mechanism is operative while lack of this coalescence would have pointed to another mechanism. In the isotopically normal compound the methyl ^1H resonances overlap with those of the $B_{2,4}$ terminal protons. Therefore, spectra of the methyl-deuterated compound were obtained, but it was again not possible to resolve two resonances for the $B_{2,4}$ terminal protons. Application of ^{11}B decoupling might have aided our attempts to observe two resonances; however, ^{11}B decoupling was not possible on the instrument used.

The isotope-exchange experiment demonstrates that at temperatures where the isomer interconversion is rapid, dissociation of the ligand can occur. This dissociation could be promoted by the presence of excess $(CH_3)_2NPF_2$ in the experiment. The amount of decomposition observed during the course of this experiment was significantly greater than that observed during the course of the high-temperature NMR experiments when no excess base was present. The high-temperature ^{11}B NMR spectra show no change in the magnitude of the P–B coupling constant up to 91°. Although this evidence does not support a dissociative mechanism, neither does it exclude one. It is possible that the ligand dissociates and the free acid and base are protected from other species in solution by a solvent cage. They could then recombine to give a rearranged molecule. If this process happens fast with respect to ^{11}B and ^{31}P relaxation, all spin–spin coupling is maintained. Therefore, no mechanism can be totally excluded on the basis of whether or not it requires ligand dissociation.

The $\Delta G^{\ddagger}$ value of 19 kcal/mol for the interconversion of the two isomers shows that this is a relatively high energy process. The $\Delta S^{\ddagger}$ value of 30.4 eu/mol for the interconversion of the endo and exo isomers indicates that the transition state has significantly higher entropy than does the ground state. Intuitively one might think that this implies a mechanism involving ligand dissociation. However, if the ligand dissociates, but remains in the same solvent sphere, and recombines fast relative to ^{11}B and ^{31}P nuclear spin relaxation (as it must to retain J_{B-P}), a significant increase in entropy would not be expected. Likewise the planar transition state of the "ring flip" mechanism should not have significantly higher entropy than the ground state. Therefore, the available data lead us to postulate that the interconversion of endo and exo isomers involves breaking of bonds *within* the boron framework. Such bond breaking should increase the rotational degrees of freedom for the molecule and presumably could account for the $\Delta S^{\ddagger}$ value of 30 eu/mol. Once the framework bonding is disturbed, isomer interconversion could occur via rotation of B_1 about the B_1–B_3 axis or by another rearrangement within the boron framework.[30] Distinction between these pathways is not possible since both are consistent with the experimental data.

In conclusion the presence of isomers in $B_4H_8PF_2N(CH_3)_2$ is indicated in the ^{19}F, ^{11}B, ^{31}P, and ^1H NMR spectra of the compound. The low-temperature ^{19}F NMR spectra demonstrate that these isomers are geometrical in nature, and at low-temperature rotation about the P–B bond in the predominant isomer, the endo isomer, becomes slow on the ^{19}F NMR time scale. Spectral simulations yield a barrier of 7.8 kcal/mol for this rotation, and this is the highest value reported for a phosphine–borane. The activation parameters obtained from simulations of the high-temperature ^{19}F spectra yield insight into the mechanism by which the geometrical isomers interconvert. In light of these interesting results for B_4H_8-$PF_2N(CH_3)_2$ studies of other B_4H_8L complexes are currently in progress in our laboratory.

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(30) If part of the framework bonding involving B_1 is disturbed, rehybridization of B_3 and closure of the bonding to B_1 could cause interchange of the isomers. This mechanism is somewhat analogous to what we have referred to as the "ring flip" mechanism; however, rehybridization of only one boron atom is necessary. This rehybridization could be much more facile once the framework electronic structure is perturbed.

Contribution from the Chemical Dynamics Laboratory, University of Minnesota, Minneapolis, Minnesota 55455

Hydrolysis Mechanism of BH_4^- in Moist Acetonitrile. 3. Kinetic Isotope Effects

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The present work and a concurrent paper[1] show that, in the presence of acetic acid, BH_4^- in acetonitrile is rapidly converted to $BH_3OCOCH_3^-$ and that previous kinetic studies of the hydrolysis of BH_4^- in such solutions[2] actually referred to the hydrolysis of $BH_3OCOCH_3^-$. As previously shown, the substrate (now shown to be $BH_3OCOCH_3^-$) complexes with acetic acid, with a complexing constant of about 160. That complex hydrolyzes by spontaneous and water-catalyzed paths. The present paper shows that the latter reaction is *accelerated* 15–40% by the substitution of D for H on boron. The rate is reduced, by a factor of $\sim$1.75, by replacing all the hydroxylic hydrogen with deuterium. These results are consistent with $BH_3OC(CH_3)O{\cdot}HOCOCH_3$ (**2**) as the acetic acid–substrate complex. The displacement of the incipient biacetate ion by water is rate determining in this process. Isotopic substitution at either postion reduces the rate of the spontaneous process. Its mechanism is uncertain.

A kinetic study of the acidolysis of tetrahydroborate ion ("borohydride") in moist acetonitrile[2] gave evidence that the reaction proceeds via a mechanism involving the accumulation of an intermediate complex. The reversible formation of a complex, **1**, between borohydride ion and acetic acid was proposed to account for this kinetic requirement. Subsequent NMR studies of intermediates and of isotopic exchange in the reactants in the acidolysis reaction[1] confirm that the intermediate proposed by Modler and Kreevoy is formed reversibly in the course of the reaction but indicate that it does not accumulate. Instead, the rate-determining stage of the reaction involves a second intermediate, trihydroacetoxyborate ion, $CH_3COOBH_3^-$, which plays the role assigned to BH_4^- by Modler and Kreevoy. The place of **1** is taken by the H-bonded acetic acid complex of $CH_3COOBH_3^-$, **2**. With these substitutions the rate law of Modler and Kreevoy[2] is still applicable.

The present kinetic study, by examining the effect of deuterium substitution in the reactants, leads to additional insight into the reaction mechanism. Through the use of a borohydride salt more readily obtainable in pure form, the kinetic data of Modler and Kreevoy[2] are refined to give more precise rate constants. The water-promoted pathway is shown to involve nucleophilic attack by water on the complex **2**.

Experimental Section

Materials. Commercial acetonitrile, 99% pure or better, was stirred 24 h over molecular sieves, decanted, stirred an additional 24 h over calcium hydride, and distilled from calcium hydride through a short fractionating column. The samples used in the kinetic experiments contained water concentrations ranging from less than 0.01 to 0.025 M. Sodium tetrahydroborate, both 98% powder and stable aqueous solution (4.4 M $NaBH_4$ in 14 M NaOH), sodium tetradeuterioborate, cesium acetate (ultrapure), and bis(triphenylphosphin)iminium chloride ($(Ph_3P)_2N^+Cl^-$) were obtained from the Alfa Division of the Ventron

