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A NMR STUDY OF HINDERED INTERNAL ROTATION ABOUT THE P-N BOND IN AMINOFLUOROPHOSPHINES

by

Reynaldo Garcia Montemayor

A dissertation submitted in partial fulfillment
of the requirements for the degree of
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Abstract

A NMR STUDY OF HINDERED INTERNAL ROTATION ABOUT THE P-N BOND IN AMINOFLUOROPHOSPHINES

by

Reynaldo Garcia Montemayor

Co-chairman: Robert W. Parry

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The existence and nature of rotational isomers in (2-methylpiperidyl)difluorophosphine and its borane adduct were established by nuclear magnetic resonance techniques as part of a systematic investigation of the P-N bond in aminofluorophosphines.

Values of the free energy of activation, ΔG^{*}, for the chair-to-chair-interconversion process for piperidine and piperidyldifluorophosphine were determined to be 11.2 kcal/mole and 10.1 kcal/mole respectively, from the temperature dependence of their ^{1}H nmr spectra. The ^{19}F nmr spectrum of piperidyldifluorophosphine showed relatively free rotation about the P-N bond in the temperature range -65° to +100°C. The ^{1}H nmr spectra of 2-methylpiperidine, 3-methylpiperidine, and 4-methylpiperidine, as well as their corresponding difluorophosphine derivatives, indicated no chair-to-chair interconversion over a large temperature range. The data are best interpreted by assuming that these com-

pounds exist in one preferred conformation with the methyl group in an equatorial orientation. The ^{19}F nmr spectra of (2-methylpiperidyl)difluorophosphine showed conclusively the existence of two isomers: one has the fluorines directed towards the methyl group; and the other has the fluorines directed away from the methyl group. The fluorines in each isomer were shown to be non-equivalent.

Data for (2-methylpiperidyl)difluorophosphine indicated a large energy barrier to rotation about the P-N bond (the free energy of activation, ΔG^{*}, associated with hindered rotation was estimated to be greater than 22 kcal/mole). Although (2-methylpiperidyl)-difluorophosphine did not exhibit free rotation about the P-N bond (disappearance of distinct nmr signals for each isomer) at temperatures as high as +170°C, the corresponding (2-methylpiperidyl)-chlorofluorophosphine displayed free rotation at about =90°C. Values of the energy of activation, E_a=6.4 kcal/mole, and ΔG^{*}=17.4 kcal/mole associated with hindered internal rotation about the P-N bond in (2-methylpiperidyl)chlorofluorophosphine were obtained from the temperature variation of its ^{19}F nmr spectrum. The difference in the size of the energy barrier to rotation in these two molecules was explained in terms of a specific interaction between the fluorines of the PF_2-unit and the methyl protons in the ring. No evidence of isomers was indicated by the ^{19}F nmr spectra of (3-methylpiperidyl-difluorophosphine and (4-methylpiperidyl)difluorophosphine, consistent with a low energy barrier to rotation in these compounds.

This observation is in accord with the argument that specific PF_2-H_3C interaction is the major factor in the existence of isomers in (2-methylpiperidyl)difluorophosphine.

The ^{19}F nmr spectrum of (2-methylpiperidyl)difluorophosphine-borane indicated the presence of three rotational isomers. Structures of these isomers consistent with the ^{19}F nmr spectrum are: (1) the fluorines are directed towards the methyl group; (2) the fluorines are below the P-N-(C_2) plane; and (3) the fluorines are above the P-N-(C_2) plane. A fourth but unlikely configuration has the fluorines directed away from the methyl group, but severe steric interaction between the borane group and the methyl protons preclude the existence of such structure. The same specific PF_2-H_3C interaction as seen in (2-methylpiperidyl)difluorophosphine is still operative in the borane adduct. The ^{19}F nmr spectrum of (2-methylpiperidyl)-chlorofluorophosphine is consistent also with three isomeric forms in the same spatial orientation as the isomers of (2-methylpiperidyl)difluorophosphineborane.

To

Ying-Wai

and

Our Parents

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INTRODUCTION

Dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, was first synthesized by Kodama and Parry (1), (2) in their investigation of the system $(CH_3)_2NH$-F_3PBH_3, in which the free base was liberated by displacement of its borane adduct with trimethylamine:

$$F_3P.BH_3 + 2\ (CH_3)_2NH \longrightarrow (CH_3)_2NPF_2.BH_3 + (CH_3)_2NH.HF$$

$$(CH_3)_2NPF_2.BH_3 + N(CH_3)_3 \longrightarrow (CH_3)_2NPF_2 + (CH_3)_3N.BH_3\ .$$

Independently, Noth and Vetter (3) prepared $(CH_3)_2NPF_2$ by the reaction of tris-dimethylaminophosphine and boron trifluoride

$$((CH_3)_2N)_3P + 2\ BF_3 \longrightarrow (CH_3)_2NPF_2 + 2\ (CH_3)_2NBF_2\ .$$

Fleming (4) synthesized $(CH_3)_2NPF_2$ by the reaction of phosphorus trifluoride and dimethylamine,

$$PF_3 + 2\ (CH_3)_2NH \rightarrow (CH_3)_2NPF_2 + (CH_3)_2NH.HF$$

in her investigations of the coordinating properties of the aminophosphine and bisdimethylaminofluorophosphine. Subsequently, Cavell (5) reported the same synthetic route to $(CH_3)_2NPF_2$. Schmutzler (6) utilized the fluorinating property of antimony trifluoride and sodium fluoride in preparing $(CH_3)_2NPF_2$ from dimethylaminodichlorophosphine, which could be easily prepared from the reaction of phosphorus trichloride and dimethylamine (7), (8).

There are two basic sites in $(CH_3)_2NPF_2$ --- the nitrogen and

the phosphorus. Much investigation of this ligand has been concerned with the identity of the basic bonding site favored by a particular Lewis acid. The results of Fleming, Ter Haar, and Parry (4), (9) indicated that BF_3 coordinates through the nitrogen bonding site, while BH_3, B_3H_7, and B_4H_8 coordinate through the phosphorus bonding site.

An X-ray crystal structure determination on $(CH_3)_2NPF_2$ and its B_4H_8 adduct was subsequently undertaken by Morris, La Prade, and Nordman (10), (11). These crystal structure determinations revealed that the P-N bond in the free ligand is short, 1.625 A°, compared to the usually quoted value of 1.77 A° (12) for a single P-N bond *. In its B_4H_8 adduct, the P-N bond is even shorter, 1.593 A°, presumably due to the inductive effect of the boron-hydride group. Their study confirmed that the coordination site in the B_4H_8 adduct is on the phosphorus and not on the nitrogen. A somewhat unexpected configuration was shown for the ligand in which the phosphorus, nitrogen, and the two carbon atoms are essentially co-planar.

The unusually short P-N bond in the free ligand and its B_4H_8 adduct led to postulates of partial double bond character, possibly involving a $p\pi$-$d\pi$ interaction between the phosphorus and nitrogen. There have been reports of particularly short P-N bonds involving fluoro-substituted phosphorus compounds (13). This fact, coupled with the finding that the nitrogen atom is in a planar environment led

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* This is a point of great uncertainty; data for a number of P-N bond lengths appear in Appendix

to a suspicion that restricted rotation about this bond might be present in the free ligand.

The presence of such restricted rotation would create a non-equivalence in the environment of the two methyl groups in $(CH_3)_2NPF_2$, and therefore, two methyl proton signals might be expected in the ^1H nmr spectrum.

Nuclear magnetic resonance has been particularly useful in the studies of hindered internal rotation in various compounds like alkyl nitrites (14-16), nitrosoamines (17), amides (18-20), aminoboranes (21-24), and several others (25). Fleming (4) and Schmutzler (6), in their investigations of the free ligand, failed to observe any indication of the non-equivalence of the two methyl groups or of the existence of rotational isomers. In an effort to determine more about the nature of the P-N bond and about the structure of the molecule in the liquid phase, Van Doorne (26) undertook an nmr study of $(CH_3)_2NPF_2$, and of related dialkylaminodifluorophosphines. He found no evidence for the non-equivalence of the two methyl groups of $(CH_3)_2NPF_2$ in the ^1H and ^{19}F nmr spectra in the temperature range of -60°C to +60°C. He prepared methylphenylaminodifluorophosphine, $CH_3C_6H_5NPF_2$, which would be expected to show two sets of signals in the ^{19}F nmr spectrum corresponding to two possible isomers related by a 180° rotation of the alkyl and aryl groups about the P-N bond. The observed ^{19}F nmr spectrum showed only one doublet due to spin-spin coupling of the fluorine nuclei with the phosphorus nucleus. Each member of this doublet is further

split into a 1:3:3:1 quartet as a result of coupling with the methyl group. This observation suggested that if $CH_3C_6H_5NPF_2$ is essentially in the same spatial configuration as $(CH_3)_2NPF_2$, then it exists as one isomer exclusively, presumably one in which the bulky phenyl group is trans to the fluorine atoms.

The compound (2-methylpiperidyl)difluorophosphine, 2-(CH_3)-$C_5H_9NPF_2$, was then prepared by Van Doorne (26) by the reaction of 2-methylpiperidine and phosphorus trifluoride. Its physical properties seemed to indicate the existence of isomers in the light of the inferences made by Niedenzu and Dawson (27) for some aminoboranes. The continuously varying vapor pressure characteristics of asymmetrically substituted aminoboranes were attributed by them to the existence of geometric isomers caused by restricted rotation about the B-N bond; this was later confirmed by Brey and co-workers (23) and by Totani's group (24). The alkyl groupings in 2-$(CH_3)C_5H_9NPF_2$ are locked in a definite configuration because of the ring system, hence isomerism is not unexpected. Van Doorne obtained two sets of fluorine signals in the ^{19}F nmr spectrum of (2-methylpiperidyl)difluorophosphine. He attributed this observation to the existence of two isomers, and it was suggested that restricted rotation about the P-N bond provided evidence for partial double bond character resulting from $p\pi$ -$d\pi$ interaction. If the existence of isomers in 2-$(CH_3)C_5H_9NPF_2$ were due to a partial double bond between phosphorus and nitrogen, then the ^{19}F nmr spectrum might be expected to show temperature dependence. Such temperature

dependence is clearly seen in the case of asymmetrically substituted aminoboranes (21-24) which are assumed to have double bond character in the B-N linkage. Because of instrumentation problems, Van Doorne did not study the temperature dependence of the $2\text{-}(CH_3)C_5H_9NPF_2$ ^{19}F nmr spectrum, hence an element of doubt remained after his study was completed. In addition, interpretations of the observed ^{19}F nmr spectra of $2\text{-}(CH_3)C_5H_9NPF_2$ and its borane adduct have not been complete. In the light of these statements, the question surrounding the existence of isomers in assymetrically alkylated aminodifluorophosphines seemed to warrant further study.

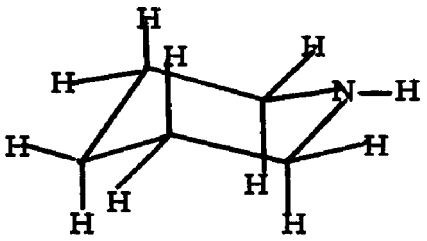
STATEMENT OF THE PROBLEM

This sutdy was undertaken to obtain more evidence on the question of isomers for alkylated-piperidyldifluorophosphines. The existence of isomers would be of significance in any treatment of the P-N bond. Isomerism in these compounds could be due to a restricted internal rotation brought about by a partial double bond character of the P-N bond, or by steric factors involving the alkyl substituent of the heterocyclic ring, or by both. It was hoped that a study of a series of methylpiperidyldifluorophosphines, in which the position of the alkyl substituent was systematically varied would provide insight into the role of steric factors and double bond character in any interpretation of the P-N bond.

RESULTS AND DISCUSSION

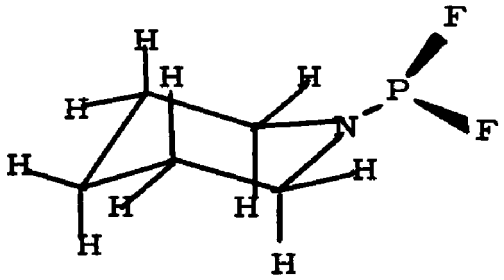
I - GENERAL OUTLINE OF RESEARCH

As part of a systematic investigation of the P-N bond in amino-fluorophosphines, the nuclear magnetic resonance spectra of a number of compounds have been carefully studied. The compounds used include:



^{1}H nmr spectrum

1. Piperidine

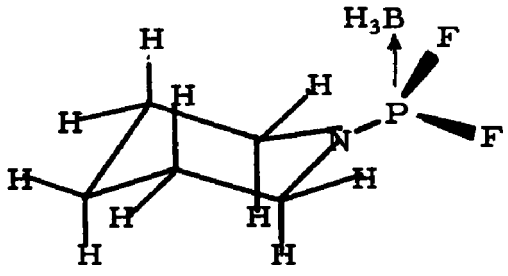


^{1}H nmr spectrum

^{19}F

^{31}P

2. Piperidyldifluorophosphine



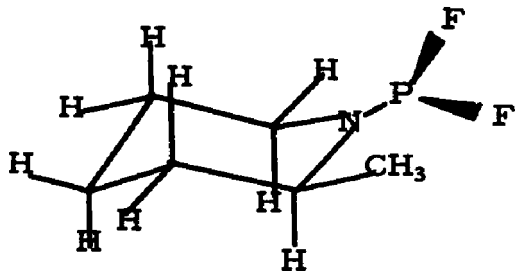
^{1}H nmr spectrum

^{19}F

^{31}P

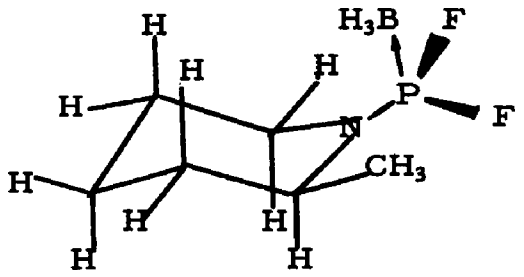
^{11}B

3. Piperidyldifluorophosphineborane



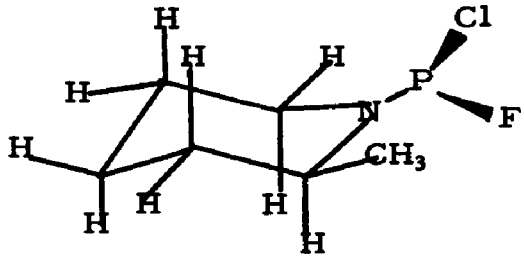
^{1}H nmr spectrum
^{19}F
^{31}P

4. (2-Methylpiperidyl)difluorophosphine



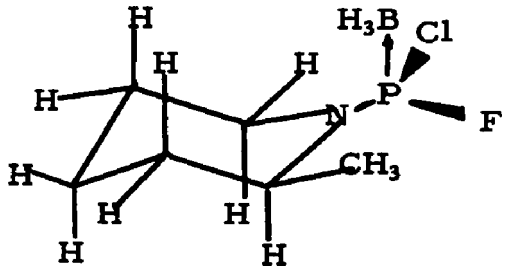
^{1}H nmr spectrum
^{19}F
^{31}P
^{11}B

5. (2-Methylpiperidyl)difluorophosphineborane



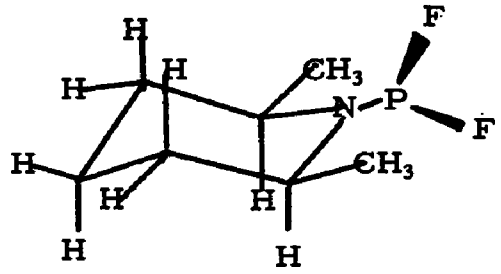
^{1}H nmr spectrum
^{19}F
^{31}P

6. (2-Methylpiperidyl)chlorofluorophosphine



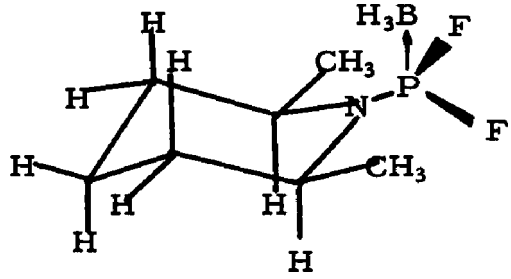
^{1}H nmr spectrum
^{19}F
^{31}P
^{11}B

7. (2-Methylpiperidyl)chlorofluorophosphineborane



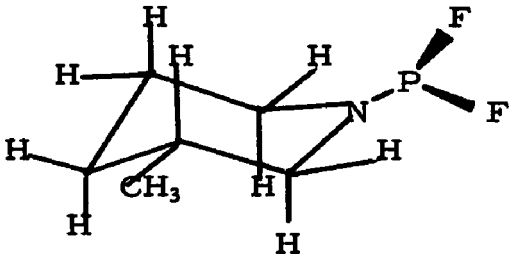
^{1}H nmr spectrum
^{19}F
^{31}P

8. (Cis-2,6-dimethylpiperidyl)difluorophosphine



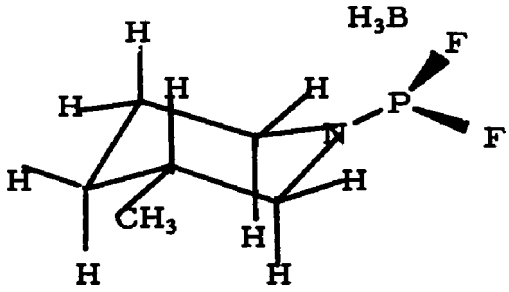
^{1}H nmr spectrum
^{19}F
^{31}P
^{11}B

9. (Cis-2,6-dimethylpiperidyl)difluorophosphineborane



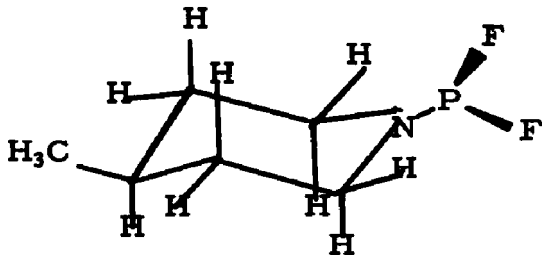
^{1}H nmr spectrum
^{19}F
^{31}P

10. (3-Methylpiperidyl)difluorophosphine



^{1}H nmr spectrum
^{19}F
^{31}P
^{11}B

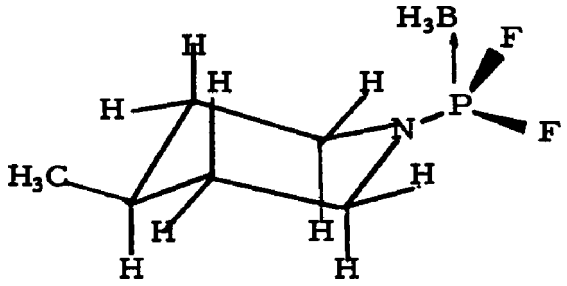
11. (3-Methylpiperidyl)difluorophosphineborane



^{1}H nmr spectrum

^{19}F

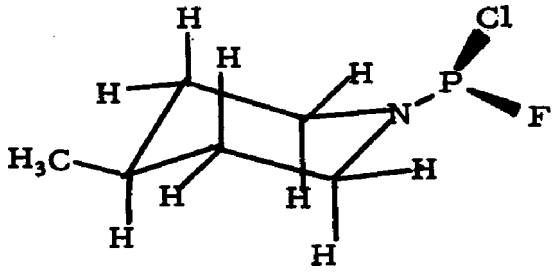
12. (4-Methylpiperidyl)difluorophosphine



^{1}H nmr spectrum

^{19}F

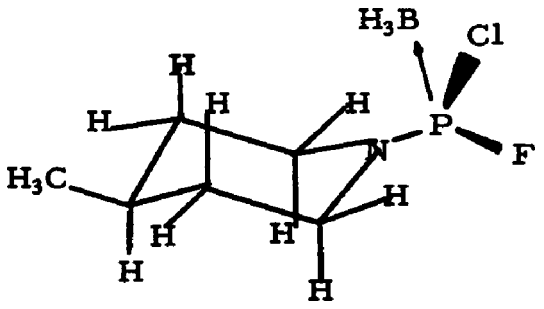
13. (4-Methylpiperidyl)difluorophosphineborane



^{1}H nmr spectrum

^{19}F

14. (4-Methylpiperidyl)chlorofluorophosphine



^{1}H nmr spectrum

^{19}F

15. (4-Methylpiperidyl)chlorofluorophosphineborane

If the isomerism observed in (2-methylpiperidyl)difluorophosphine

were due mainly to a restricted internal rotation about the P-N bond, then (3-methylpiperidyl)difluorophosphine should similarly show evidence of isomers. However, if steric factors and perhaps electronic factors involving the alkyl substituent of the ring play a predominant role in the existence of such isomers, then (3-methylpiperidyl)difluorophosphine would not be expected to exhibit isomerism inasmuch as steric factors are non-existent when compared to the 2-methyl analogue. The aminochlorofluorophosphines as well as(2,6-dimethylpiperidy)-difluorophosphine will serve to confirm the existence or absence of isomerism in these compounds.

II PIPERIDYLDIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

The ^{1}H, ^{19}F, ^{31}P, and ^{11}B nmr spectra of piperidyldifluorophosphine and its borane adduct were obtained on a Varian HA-100 Spectrometer. For a meaningful comparison, the ^{1}H nmr spectrum of piperidine was also carefully studied.

A. THE ^{1}H NMR SPECTRUM OF PIPERIDINE

Piperidine is a cyclohexane ring in which a nitrogen atom replaces a CH_2 unit of the ring.

The inversion of cyclohexane between its two conformations has been widely studied (28-31) by nuclear magnetic resonance techniques. From the low temperature variation of the ^{1}H nmr spectrum of cyclohexane, values of free energy, entropy, and enthalphy of activation for the inversion process have been obtained. The study of the inversion rates in the related heterocyclic piperidine has been less extensive (32-33). An intensive study of piperidine is described here.

At room temperature, the 100 MHz ^{1}H nmr spectrum of piperidine (Fig. 1) shows two broad, structureless peaks at

(a) $\delta = -1.44 \pm 0.02$ ppm. from TMS

(b) $\delta = -3.00 \pm 0.03$ ppm. from TMS.

The high-field peak at $\delta = -1.44$ ppm. corresponds to the

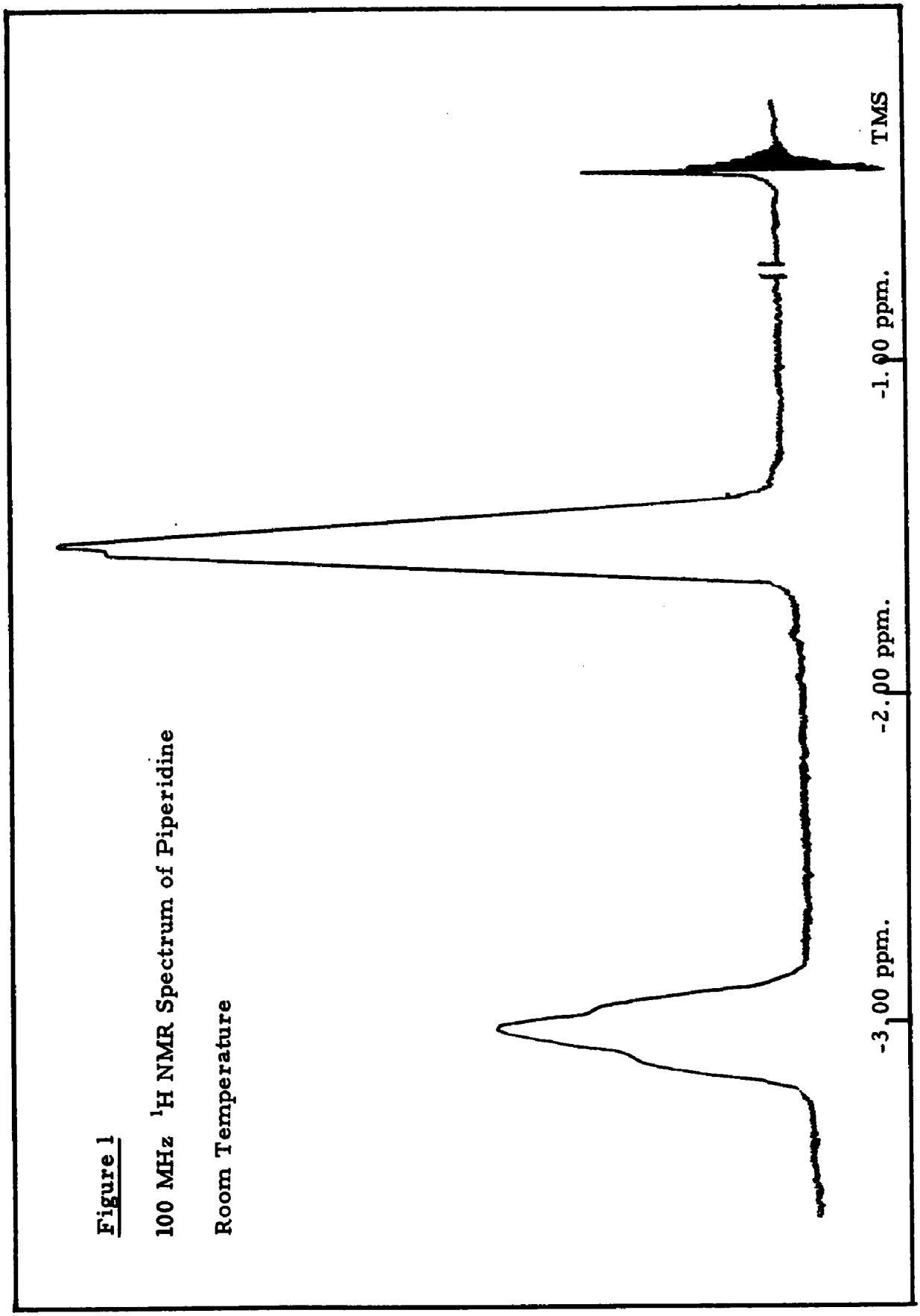


Figure 1

100 MHz ^{1}H NMR Spectrum of Piperidine

Room Temperature

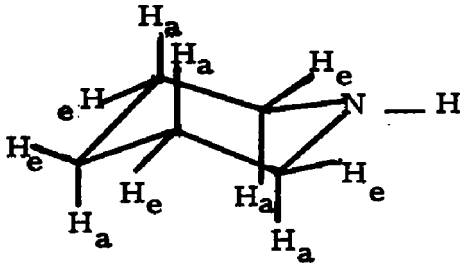
four β, two γ, and the single N-H protons; the low-field peak corresponds to the four protons α to the nitrogen atom. In agreement with this interpretation, the integrated area ratio of the two broad peaks is 7:4. These assignments are in accord with the room temperature studies of Bottini and Roberts (32) on piperidine. The data provide strong evidence for rapid interconversion between two equivalent chair forms, since this process effectively averages the chemical shifts of axial and equatorial protons in each of the methylene groups.

At -65°C, the ^{1}H nmr spectrum of piperidine (Fig. 2) consists of :

(a) a very broad peak centered at δ = -1.56 ± 0.02 ppm. (TMS)

(b) a broad peak centered at δ =-2.70 ± 0.03 ppm. (TMS)

(c) another broad peak centered at δ = -3.55 ± 0.03 ppm. (TMS).



Their respective integrated area ratios are 7:2:2. The two peaks at lower field now correspond to the two distinct signals of the equatorial and axial protons situated α to the nitrogen, indicating that the ring inversion process has been sufficiently retarded at -65°C. It is well known,especially from works of Jackman (34) and Musher (35), that axial protons are more shielded than equatorial protons. Therefore, the peak at δ =-3.55 ppm. can be assigned to the equato-

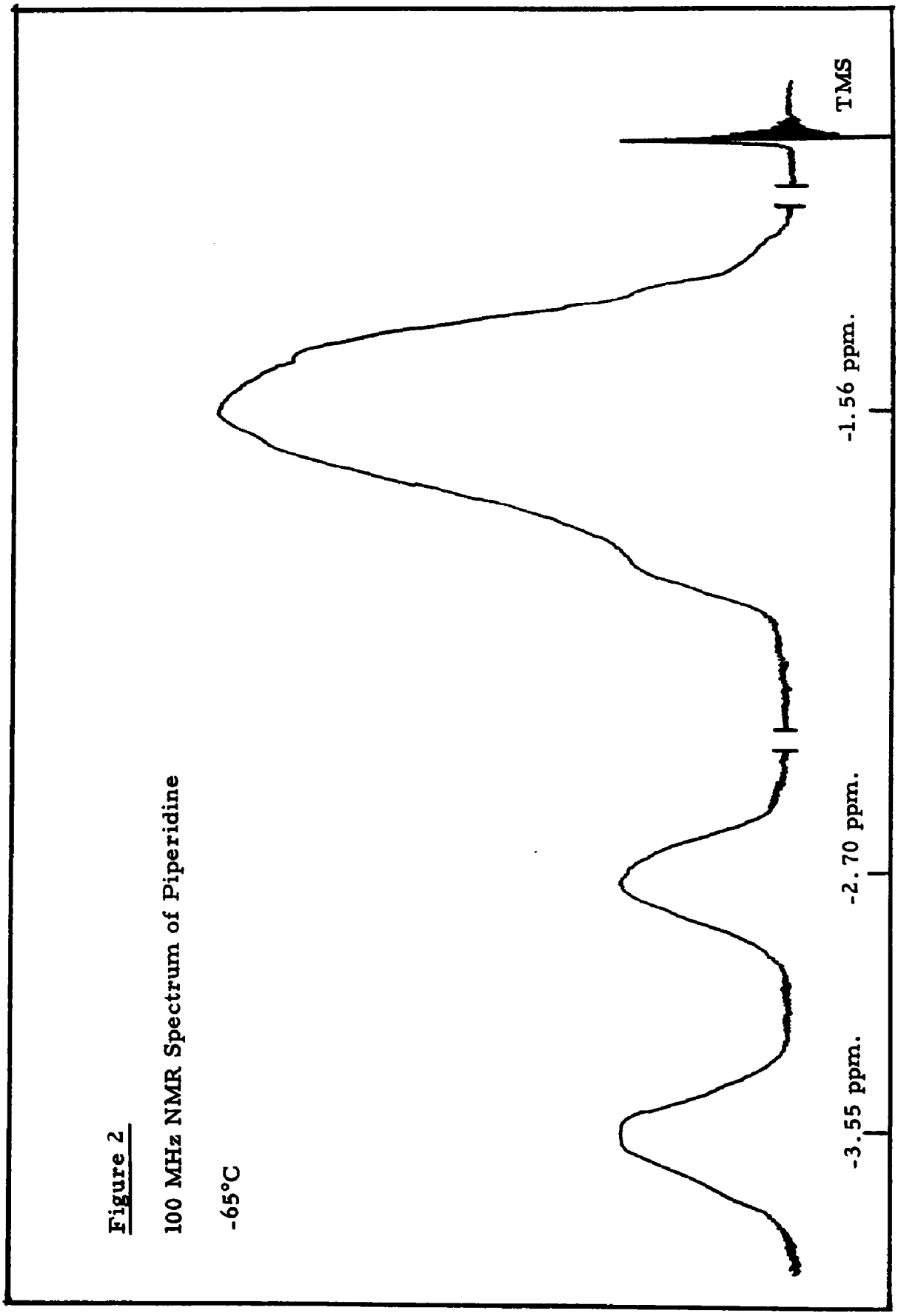


Figure 2

100 MHz NMR Spectrum of Piperidine

-65°C

rial protons, and the peak at δ=-2.70 ppm. can be assigned to the axially-oriented α protons. Upon raising the temperature (Fig. 3), the two low-field peaks gradually broaden until they eventually coalesce into a single, very broad peak at -40°C. Further increase in the temperature sharpens this peak until at room temperature it corresponds to the low-field peak of the ^{1}H nmr spectrum of piperidine taken at room temperature. The separation of the low-field peaks of the proton nmr spectrum at -65°C represents the geminal internal chemical shift between the axial and equatorial protons.

The temperature dependence of the ^{1}H nmr spectrum of piperidine can be interpreted in terms of a temperature dependent rate of chair-to-chair interconversion. A usual treatment (36), (37) of collapse of signals by exchanging nuclei gives

$$\tau = \frac{\sqrt{2}}{2\pi\delta_\nu}$$

where τ is the average time an exchanging nucleus spends in a given environment, and δ_ν is the internal chemical shift between the exchanging nuclei. τ is related to k_c, the first order rate constant for the interconversion process at coalescence by

$$k_c = 1/2\tau$$

such that

$$k_c = \frac{\pi\delta_\nu}{\sqrt{2}} \quad .$$

This relationship has been used by Jensen(28) in his work

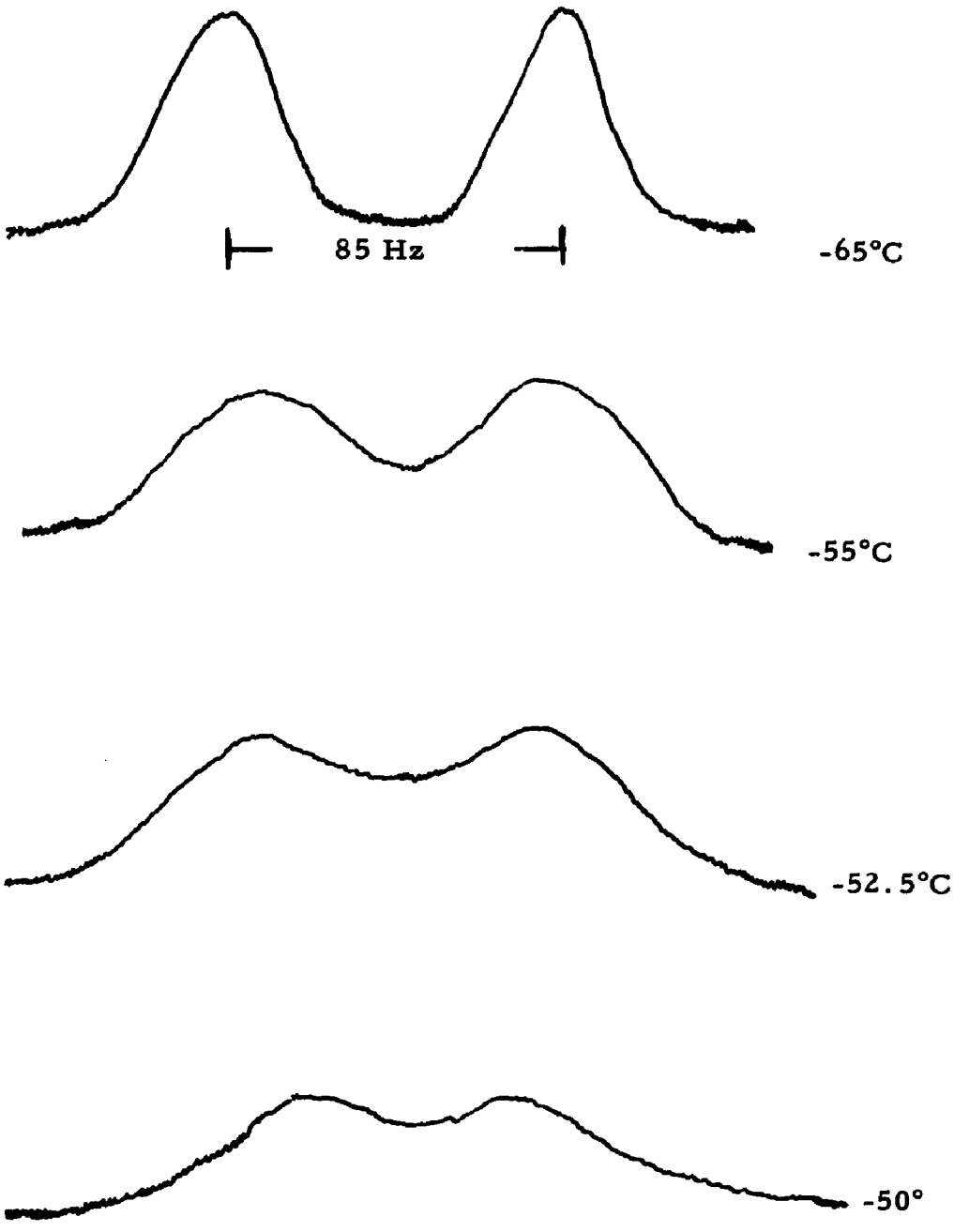


Figure 3

**100 MHz ^{1}H NMR Spectrum of the Low-Field Peak of Piperidine
Different Temperatures**

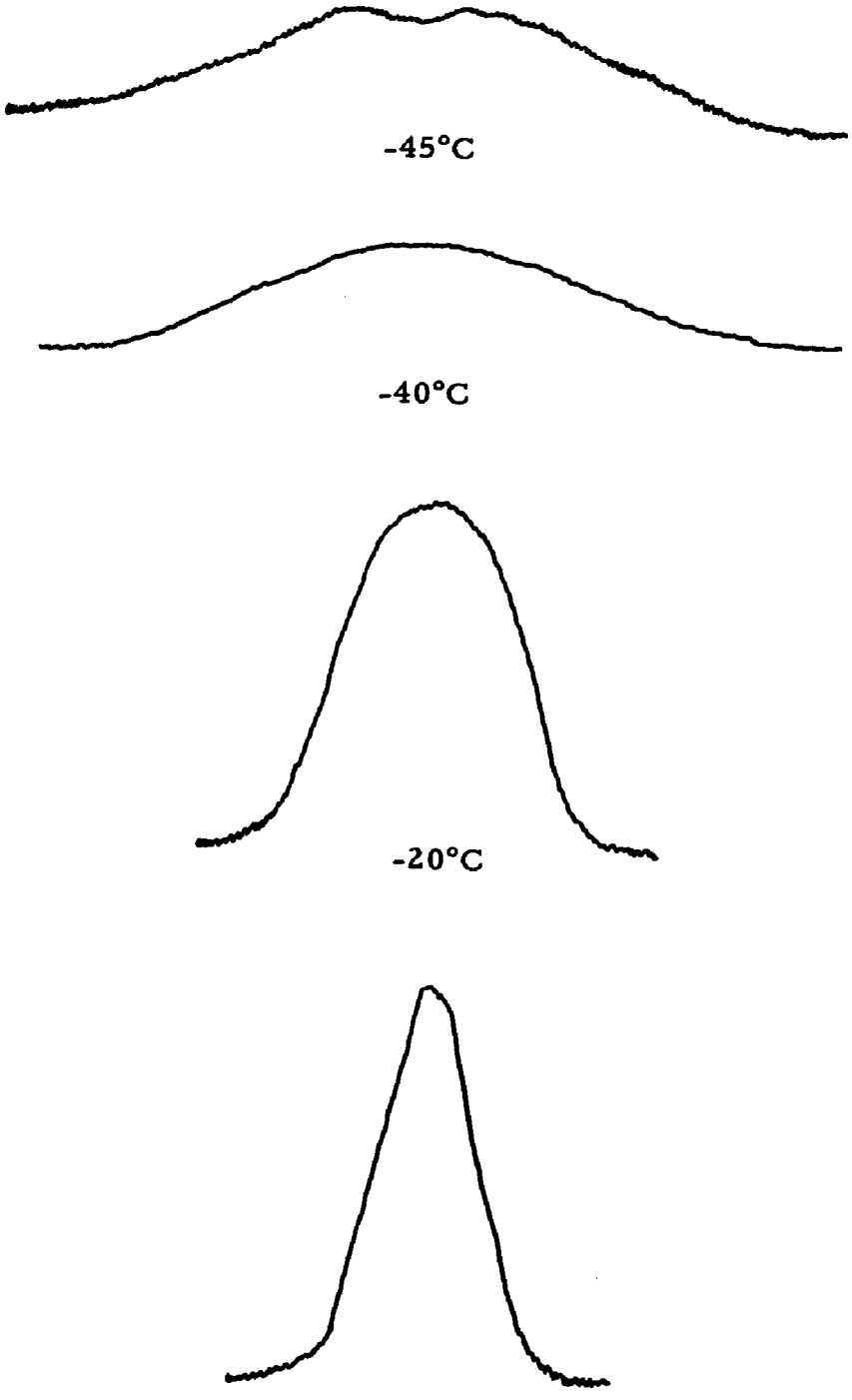


Figure 3 Continuation

with cyclohexane, but Harris and Sheppard (29) pointed out that this relationship holds true only when the line widths in the absence of exchange are effectively zero, i.e. very sharp peaks. The cyclohexane case does not satisfy the condition exactly, and a better relationship was shown to be

$$\tau = \frac{1}{\pi \delta_{\nu}}$$

which led to the expression

$$k_c = \frac{\pi \delta_{\nu}}{2} \quad .$$

The value of ΔG^{*}, the free energy of activation for the interconversion process is given (30) by the equation:

$$\Delta G^{*} = 2.303\ RT_c \left(\log \frac{k T_c}{h} - \log k_c \right)$$

where T_c is the coalescence temperature, k is the Boltzman constant, h is Plank's constant, and k_c is the first order reaction rate constant. The Harris and Sheppard treatment gave an estimated correction of +0.5 kcal/mole to Jensen's original value. Thus Jensen's value of 10.1 kcal/mole for the energy of activation for the interconversion process of cyclohexane became 10.6 kcal/mole.

The case of piperidine approaches that of cyclohexane's. The geminal internal chemical shift for piperidine at -65°C is 85 Hz(100 MHz oscillator), and the temperature of coalescence is -40°C ± 3°C (see Fig. 3). From these data, a ΔG^{*} value of 11.2 ± 0.2 kcal/mole is obtained as the free energy of activation for the chair-to-chair intercon-

version process at a temperature of -40°C. This value can be compared to the ΔG^* value of 10 kcal/mole for perfluoropiperidine (38). It is interesting to note that the ΔG^* of the interconversion process for cyclohexane is 10.6 kcal/mole (28-30), also not very different from the ΔG^* of 9.9 kcal/mole for perfluorocyclohexane (39).

Values of τ for different temperatures could be approximated by using the relationship (36), (37)

$$\tau = \frac{1}{\sqrt{2}} \left(\frac{1}{\delta_\nu^2 - \delta_\tau^2} \right)^{\frac{1}{2}}$$

where δ_τ is the separation of the two peaks at intermediate τ before coalescence.

Table I shows the various τ calculated for piperidine at different temperatures below the coalescence temperature. Using a modified form of Eyring's equation (28)

$$\text{Log } \tau T = (\Delta H^*/4.59)(1/T) - 10.620 - \Delta S^*/4.59$$

one can calculate the enthalphy and entropy of activation for the chair-to-chair interconversion process from a plot of log τT against $1/T$ (Fig. 4). The slope gives a value of the enthalphy of activation, $\Delta H^* = 6.3 \pm 0.5$ kcal/mole. Combining this result with the value of ΔG^* gives a value of $\Delta S^* = -21 \pm 2$ cal/mole-degree. Harris and Sheppard (29) obtained a ΔH^* value of 9.0 kcal/mole and ΔS^* value of -7.9 cal/mole-degree for cyclohexane. Tier's investigation on perfluorocyclohexane (39) yielded values of $\Delta H^* = 7.5$ kcal/mole and $\Delta S^* = -10.7$ cal/mole-degree. Hazebroek and Oosterhoof (40) contend that a negative value for the

Table I - Values of τ at Different Temperatures for Piperidine

T	1/T	δ_τ	τ	τT	Log τT
218.15 °K	4.58×10^{-3}	73 Hz	5.25×10^{-3}	1.14	0.0569
220.65	4.53×10^{-3}	67	4.35×10^{-3}	0.96	-0.0177
223.65	4.48×10^{-3}	57	3.58×10^{-3}	0.80	-0.0969
228.15	4.38×10^{-3}	10	2.67×10^{-3}	0.61	-0.2147

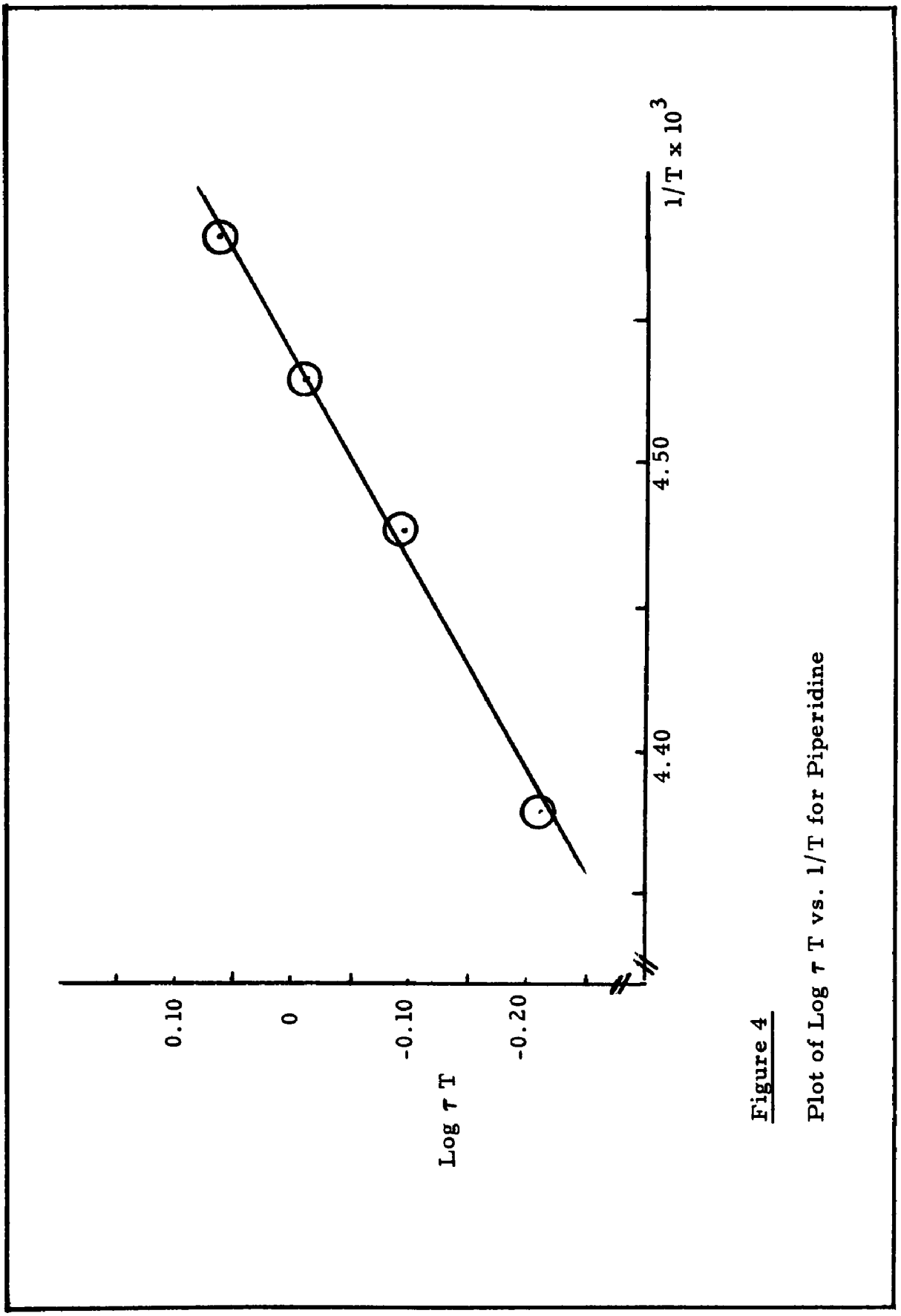


Figure 4

Plot of Log τ T vs. 1/T for Piperidine

entropy of activation (as found in cyclohexane and perfluorocyclohexane) would be consistent with a rigidly defined intermediate such as the planar form, while a positive value could arise from a more flexible and unsymmetrical transition state like the boat form. This study provides no basis for accepting or rejecting the contention of Hazebroek and Oosterhoof, but to the extent to which their conclusion is valid, a planar transition state is implied. The analogy to cyclohexane is close.

B. SYNTHESIS OF PIPERIDYLDIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

Piperidyldifluorophosphine, $C_5H_{10}NPF_2$, was first prepared (6) by fluorinating piperidyldichlorophosphine with SbF_3 or NaF in tetramethylsulfone. In this study, $C_5H_{10}NPF_2$ was synthesized by the reaction of piperidine and phosphorus trifluoride

$$2\ C_5H_{11}N + PF_3 \longrightarrow C_5H_{10}NPF_2 + C_5H_{11}N.HF\ .$$

Fig. 5 shows the infrared spectrum of $C_5H_{10}NPF_2$, which when compared to the infrared spectrum of piperidine (Fig. 6) shows the noticeable absence of N-H stretching frequency at about 3280 cm^{-1} and the presence of two strong peaks at 790 and 730 cm^{-1} (marked with *), characteristic of a F_2PNR_2 structure. Anal. Calculated for $C_5H_{10}NPF_2$: C, 39.21; H, 6.54; F, 24.84; N, 9.15. Found: C, 40.19; H, 7.17; F, 24.02; N, 9.53.

The borane adduct of $C_5H_{10}NPF_2$ was prepared by its reaction with diborane in ether at -78°C. The equation is:

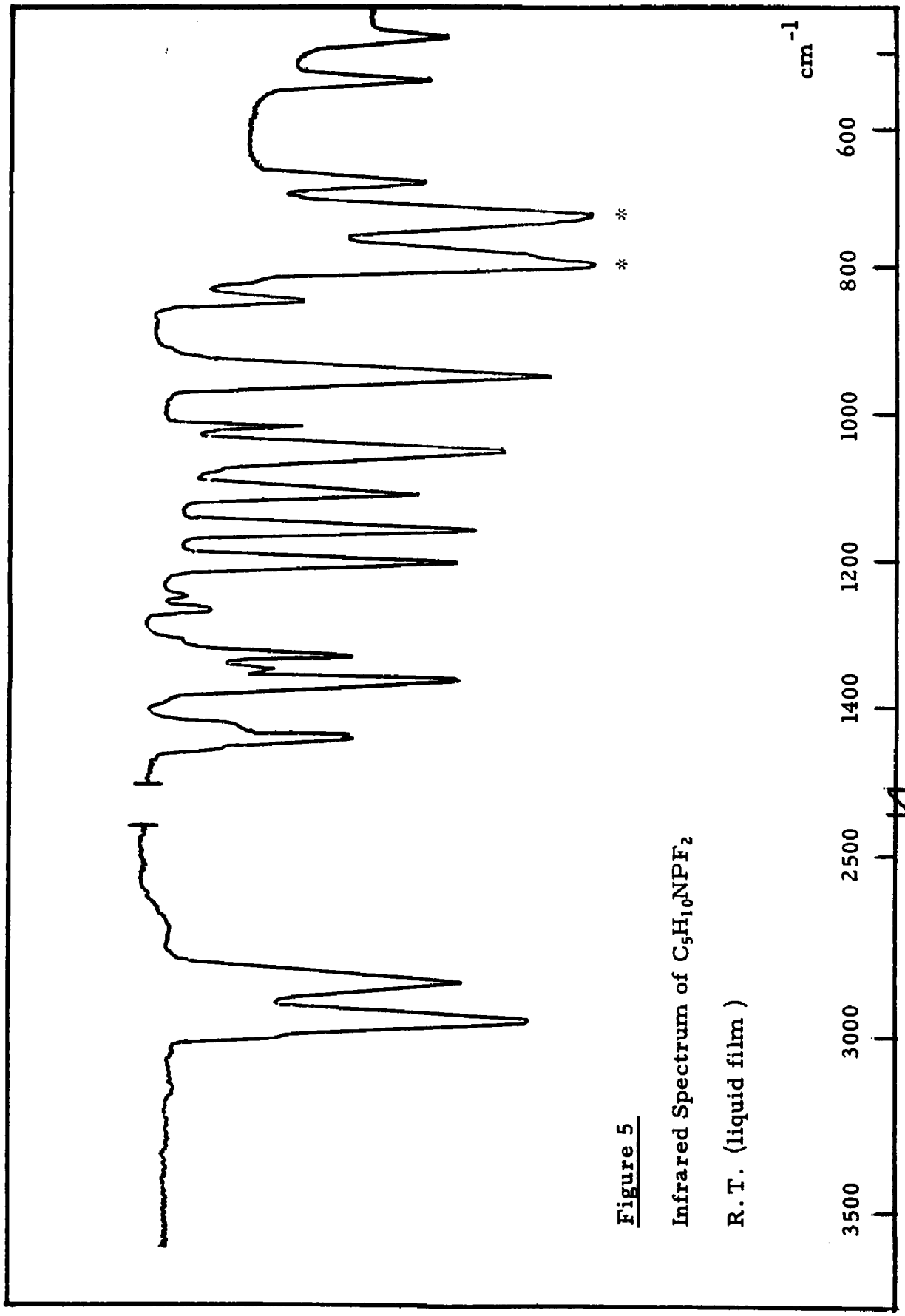


Figure 5

Infrared Spectrum of $C_5H_{10}NPF_2$

R.T. (liquid film)

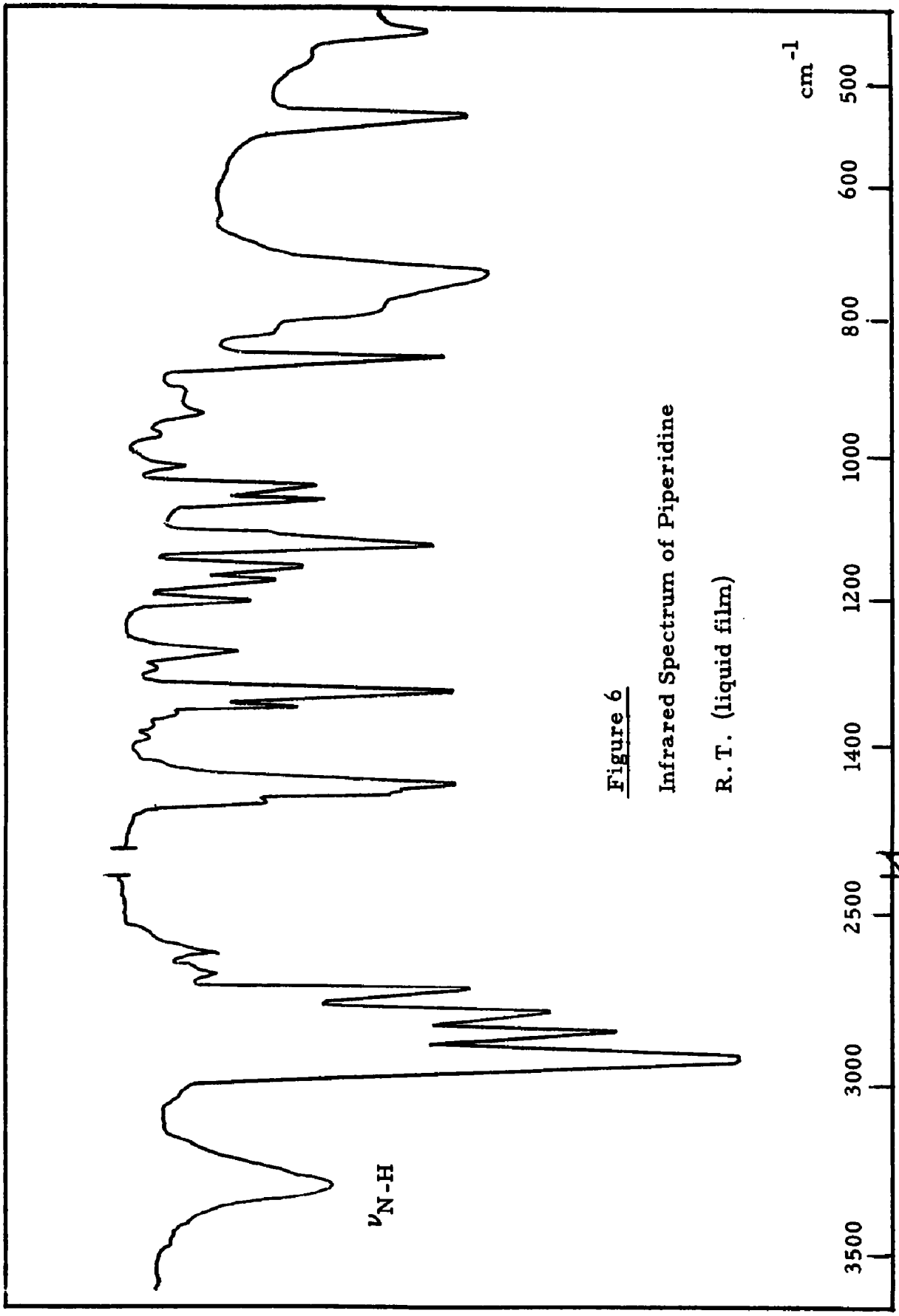


Figure 6

Infrared Spectrum of Piperidine

R.T. (liquid film)

$$C_5H_{10}NPF_2 + \tfrac{1}{2} B_2H_6 \rightarrow C_5H_{10}NPF_2.BH_3 .$$

Anal. Calculated for $C_5H_{10}NPF_2.BH_3$: C, 35.93; H, 7.78; F, 22.75; N, 8.38. Found: C, 36.15; H, 6.78; F, 23.05; N, 7.76.

The infrared spectrum of $C_5H_{10}NPF_2.BH_3$ (Fig. 7) shows the B-H stretching frequencies at 2420 and 2360 cm^{-1}, typical of borane adducts of dialkyldifluorophosphines.

Table II gives the infrared absorption frequencies of piperidine, $C_5H_{10}NPF_2$, and $C_5H_{10}NPF_2.BH_3$ in the range 4000 to 300 cm^{-1}.

C. THE ^1H NMR SPECTRUM OF $C_5H_{10}NPF_2$

Like the ^1H nmr spectrum of piperidine, the 60 MHz ^1H nmr spectrum (Fig. 8) of $C_5H_{10}NPF_2$ at room temperature consists of two broad and rather structureless peaks at

a) δ = -1.52 ± 0.02 ppm. (TMS)

b) δ = -3.12 ± 0.03 ppm. (TMS)

which agrees with the values reported by Reddy and Schmutzler (41). The integrated area ratio of the two peaks is 6:4, corresponding to six protons situated β and γ to the nitrogen, and four α-protons. The axial and equatorial protons are not distinguished due to a rapid interconversion between two chair forms.

Focusing on the low-field peak, it is found that as the temperature falls, two broad peaks appear (Fig. 9). At -86.5°C values of the chemical shift are δ = -2.67 ± 0.03 ppm. (TMS) and δ = -3.54 ± 0.04 ppm. (TMS). Their integrated area ratio is 1:1. By analogy to the

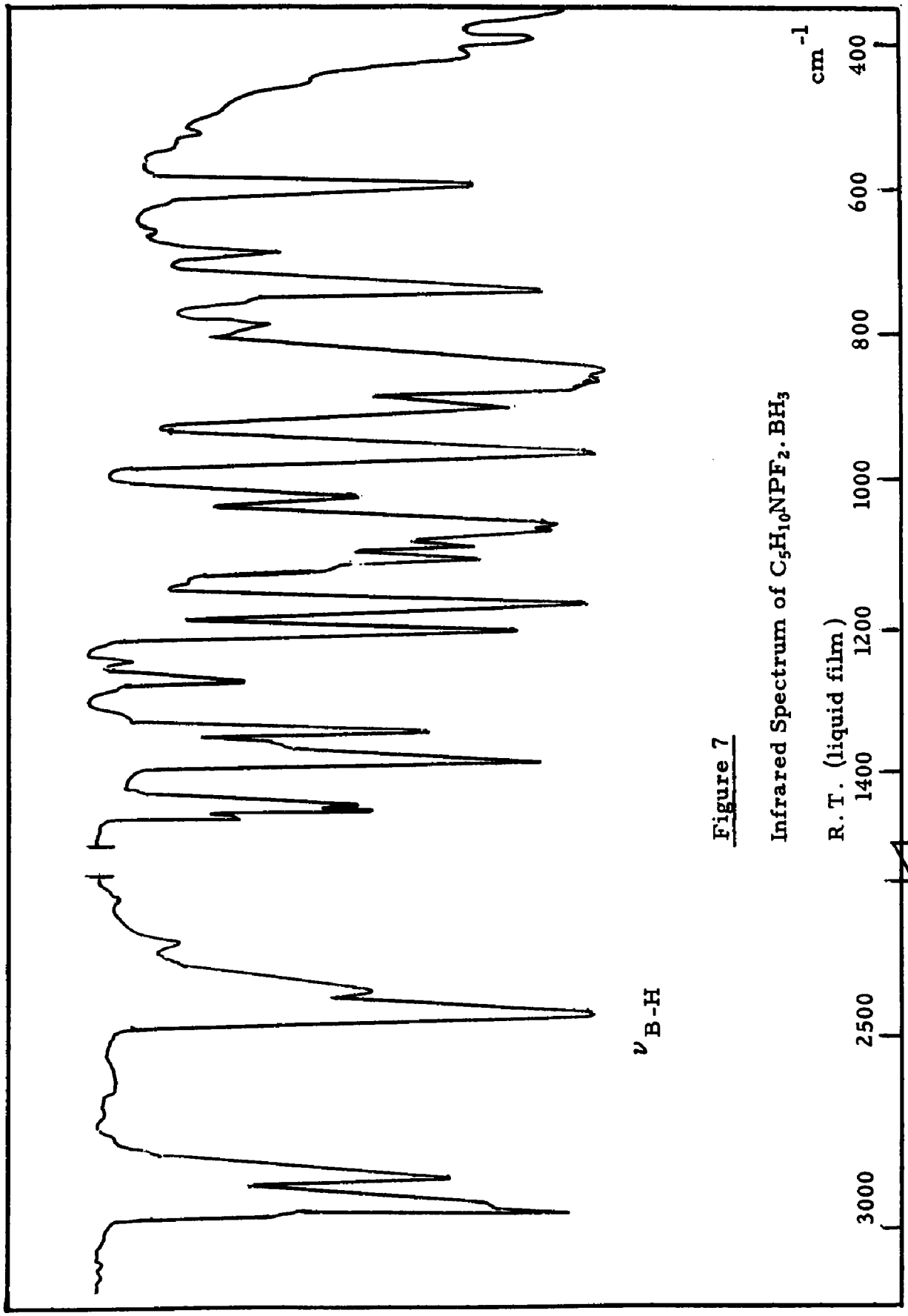


Figure 7

Infrared Spectrum of $C_5H_{10}NPF_2.BH_3$

R.T. (liquid film)

Table II - Infrared Absorption Frequencies of Piperidine, Piperidyldifluorophosphine, and Piperidyldifluorophosphineborane

Piperidine	$C_5H_{10}NPF_2$	$C_5H_{10}NPF_2 \cdot BH_3$
3280 w, b	2970 w, sh	2950 s
2920 vs	2930 s	2860 m
2840 s	2850 m	2420 s
2800 m	1460 w, sh	2360 m
2720 m	1445 m	2260 vw
2660 vw	1440 m	2440 vw
2620 vw	1430 w, sh	1470 w, sh
1460 w, sh	1370 m	1452 m
1445 m, sh	1355 w	1445 m
1440 m	1335 m	1385 s
1380 vw	1320 vw, sh	1370 w, sh
1360 vw	1270 w	1345 m
1325 w	1255 vw	1280 w
1310 m	1205 m	1260 vw
1280 vw	1160 m	1205 m
1250 w	1110 m	1170 s
1180 w	1055 s	1125 m, sh
1155 w	1015 w	1105 m
1140 w	955 s	1085 m, sh
1110 m	840 w	1070 s
1045 w	790 vs	1060 s
1030 w	740 vs	1020 m
1000 vw	680 m	970 s
930 vw	540 w	900 m
859 m	480 w	870 s
810 w, sh		850 s
790 w, sh		790 w
735 m, b		745 s
535 m		600 m
420 w		520 vw
		440 vw
		410 vw

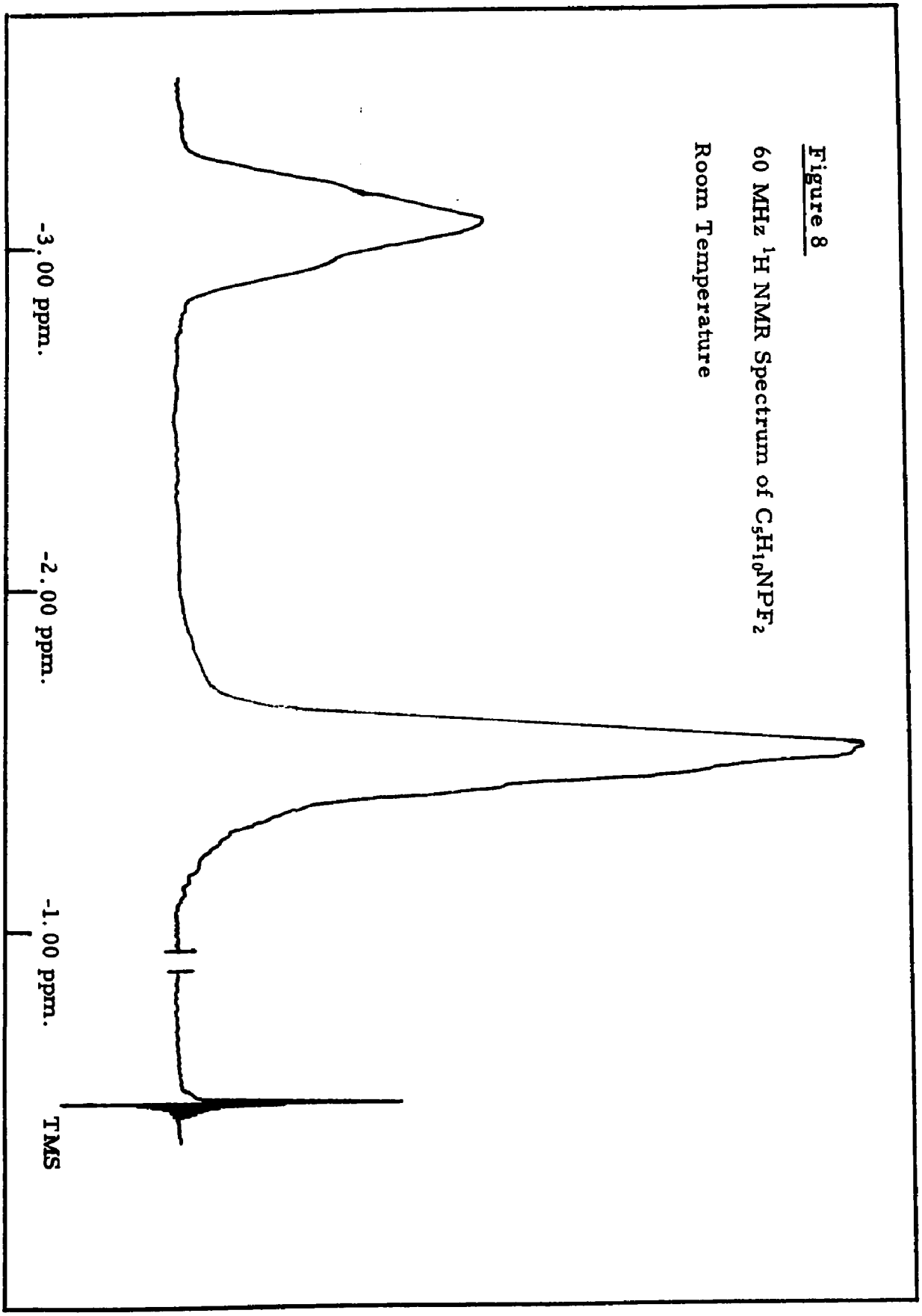


Figure 8

60 MHz ^1H NMR Spectrum of $C_5H_{10}NPF_2$

Room Temperature

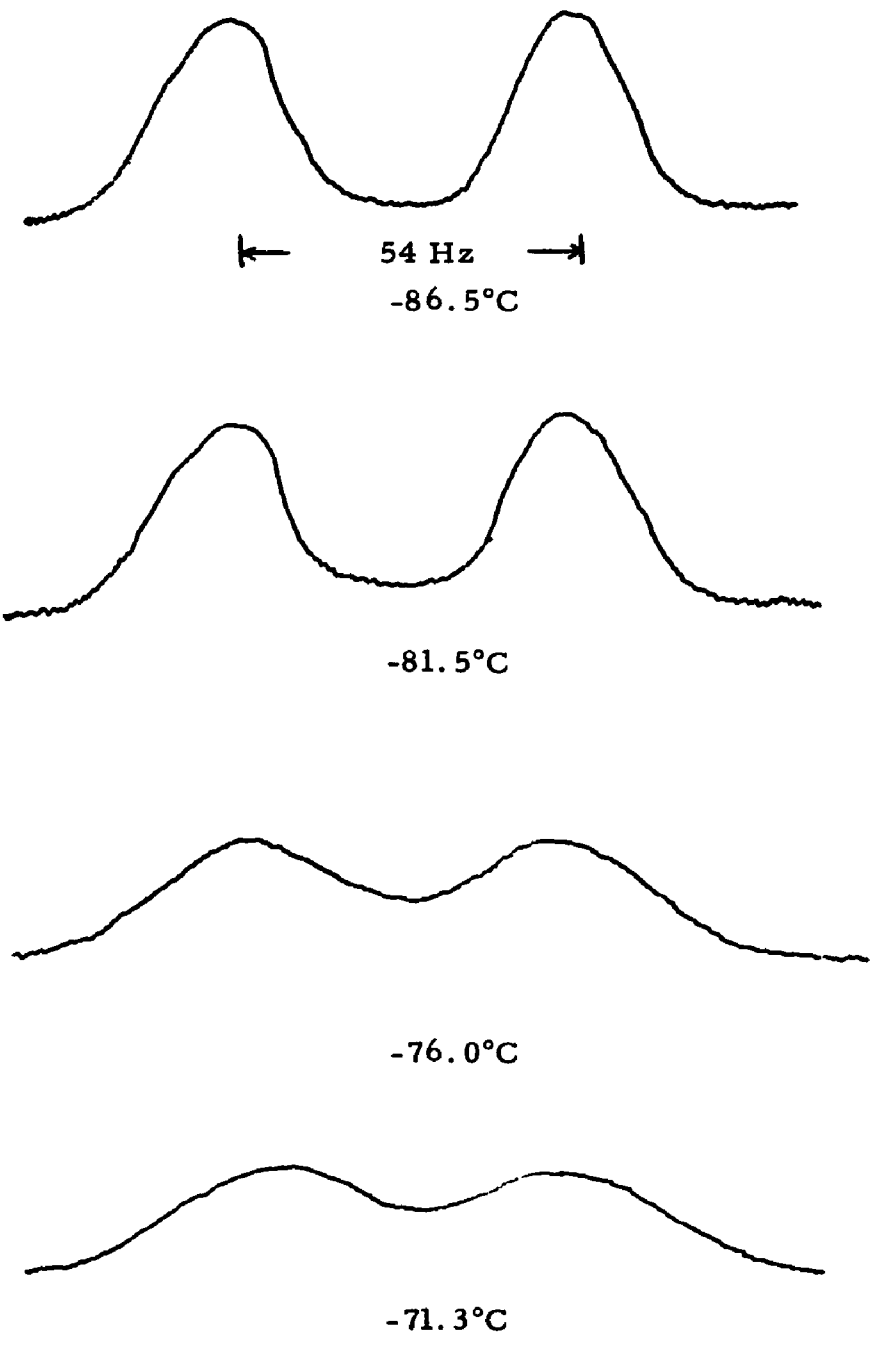


Figure 9

60 MHz ^{1}H NMR Spectrum of the Low-Field Peak of $C_5H_{10}NPF_2$

Different Temperatures (Solvent = TMS)

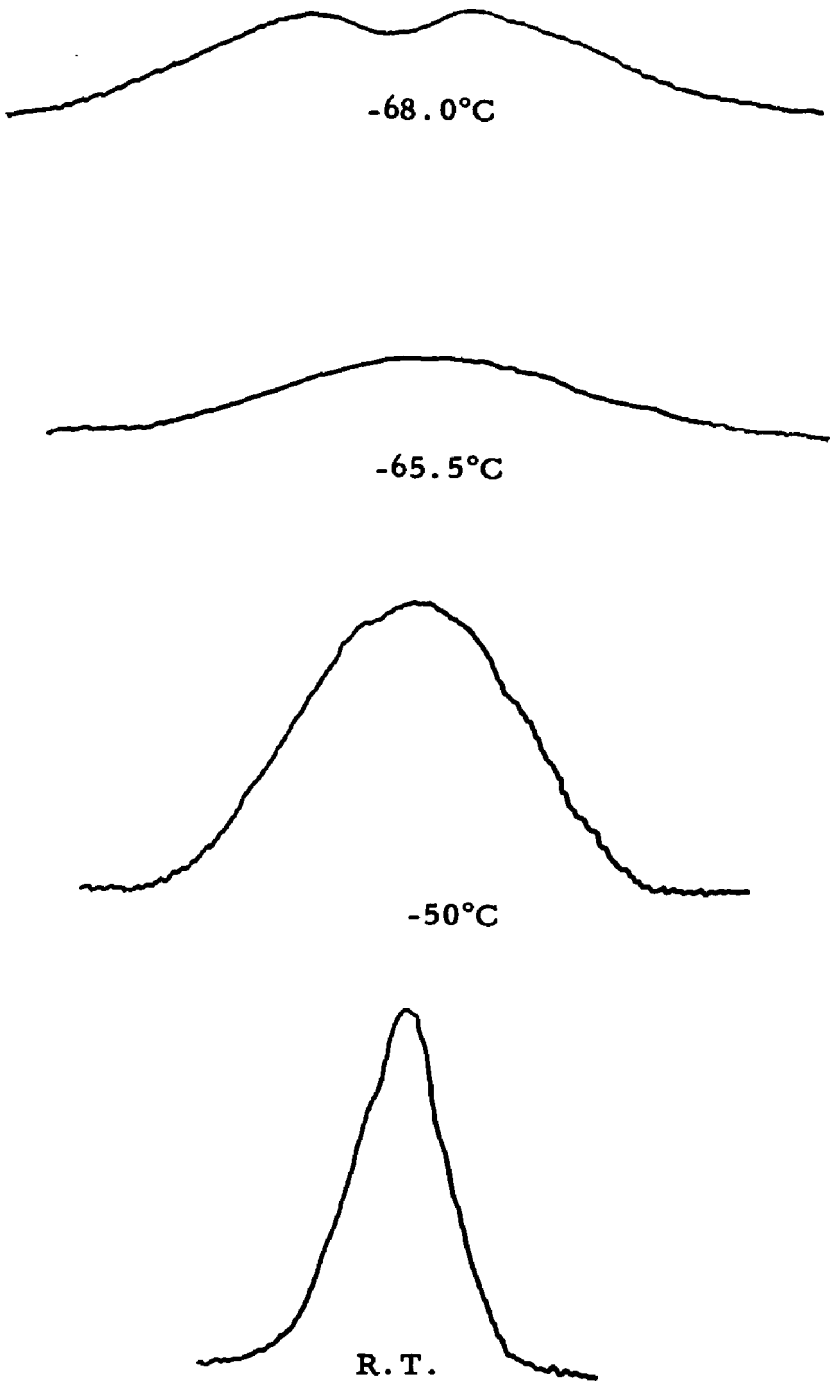


Figure 9

Continuation

piperidine case, the two low-field peaks at -86.5 °C can be assigned to the proton nmr signals for the two axial protons and the two equatorial protons α to the nitrogen. Upon raising the temperature, these two low-field peaks gradually broaden until coalescence occurs at -65.5 ± 0.5 °C. The coalesced peak sharpens a little bit until at room temperature, it corresponds to the low-field peak of the ^1H nmr spectrum of $C_5H_{10}NPF_2$.

The temperature dependence of the ^1H nmr spectrum of $C_5H_{10}NPF_2$ indicates that chair-to-chair interconversion of the piperidine ring still exists at room temperature even though the proton on nitrogen has been replaced by a PF_2-unit. The free energy, enthalphy, and entropy of activation for the interconversion process in $C_5H_{10}NPF_2$ can also be obtained from the temperature dependence of its ^1H nmr spectrum. The geminal internal chemical shift, δ_ν, in this case is 54 Hz (60 MHz oscillator), and the coalescence temperature is -65.5°C. From these, a value of 10.1 ± 0.2 kcal/mole is calculated for the free energy of activation, ΔG^* (see Appendix B). Table III shows the calculated τ values at different temperatures for $C_5H_{10}NPF_2$. From the plot of log τ T vs. 1/T (Fig. 10), ΔH^* for the interconversion process is found to be 7.8 ± 0.5 kcal/mole. ΔS^* is estimated to be -11.0 ± 1.0 cal/mole-degree.

D. THE ^1H NMR SPECTRUM OF $C_5H_{10}NPF_2.BH_3$

At room temperature, the 60 MHz ^1H nmr spectrum of $C_5H_{10}NPF_2.BH_3$ (Fig. 11) shows two broad peaks at

Table III - Values of τ at Different Temperatures for $C_5H_{10}NPF_2$

T	1/T	δ_τ	τ	τ T	Log τ T
191.65 °K	5.22×10^{-3}	52 Hz	15.25×10^{-3}	2.89	0.4609
197.15	5.08×10^{-3}	48	9.05×10^{-3}	1.78	0.2504
201.85	4.98×10^{-3}	38	5.88×10^{-3}	1.18	0.0718
205.15	4.88×10^{-3}	15	4.36×10^{-3}	0.89	-0.0487

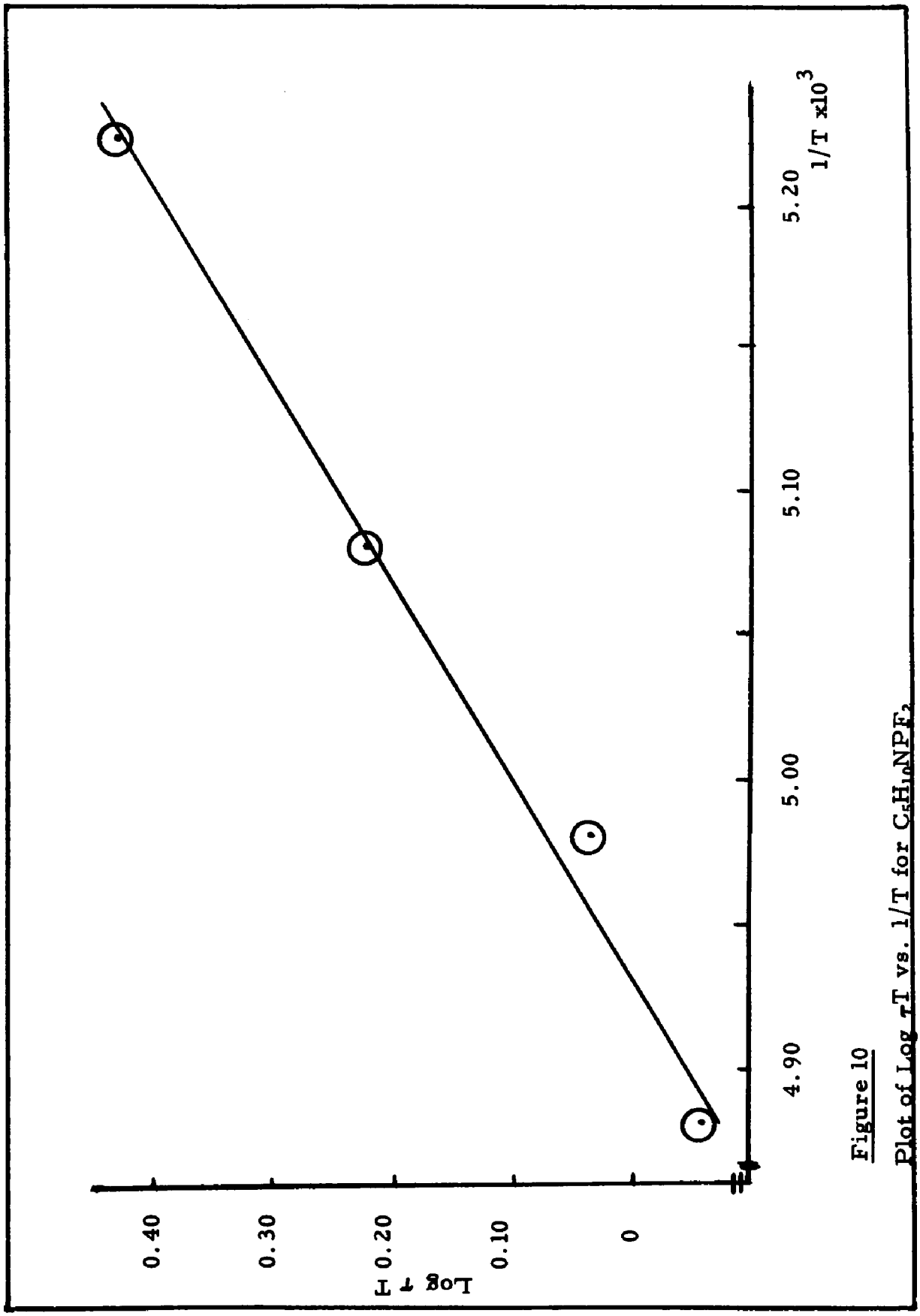


Figure 10

Plot of Log τT vs. 1/T for $C_5H_{10}NPF_2$

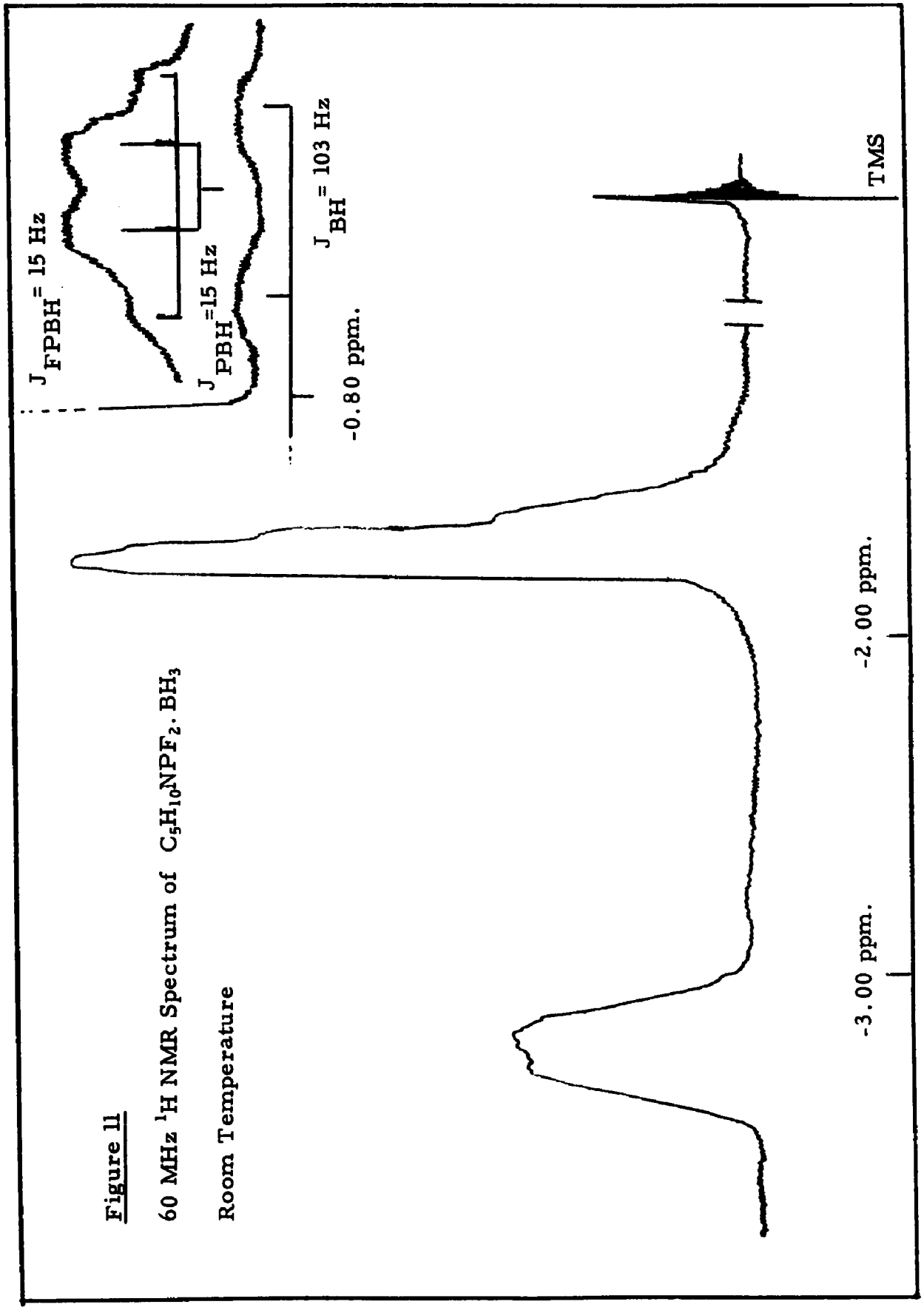


Figure 11

60 MHz ^{1}H NMR Spectrum of $C_5H_{10}NPF_2 \cdot BH_3$

Room Temperature

a) δ = -1.81 ± 0.02 ppm. (TMS)

b) δ = -3.31 ± 0.03 ppm. (TMS),

very similar in appearance to the structureless peaks observed in piperidine and $C_5H_{10}NPF_2$. This suggests that the borane adduct of $C_5H_{10}NPF_2$ also undergoes rapid interconversion between its two chair conformations. The integrated area ratio for the two peaks is 6:4. Just like the two previous cases, they could be assigned to the six protons β and γ to the nitrogen, and to the four α -protons. It is interesting to note that both peaks occur at much lower magnetic field when compared to the proton nmr spectra of piperidine and $C_5H_{10}NPF_2$. This fact reflects the effect of the coordination of the BH_3-group. The coordination of the BH_3- unit on the phosphorus introduces a deshielding effect on the electronic environment of the different proton nuclei such that the proton nmr signals occur at lower magnetic field. This shift is in agreement with simple inductive arguments. Negative charge moves toward the BH_3-group and reduces shielding of the protons.

At higher gain, the proton nmr signal due to the borane protons is observed as a severly broadened 1:1:1:1 quartet at δ = -0.80 ppm. (TMS). Two members of this quartet are overlapped by the other proton signals. The quartet splitting is attributed to spin-spin interaction of the borane protons with the boron nucleus giving a coupling constant of J_{BH} = 103 Hz. Each member of this quartet is further split into an apparent 1:3:3:1 quartet which could be interpreted as equal coupling of the borane protons with the phosphorus and fluorine nuclei. Coupling

with the phosphorus would give a 1:1 doublet with a coupling constant pf approximately 15 Hz. Further coupling with the two fluorine to the same extent would then split each member of this doublet into a 1:2:1 triplet, J_{FPBH} =15 Hz. Overlapping of these triplets would give the apparent 1:3:3:1 splitting pattern observed. These chemical shift and coupling constant values are in agreement with earlier reports (4), (42), (43) on substituted phosphineboranes.

E. THE ^{19}F NMR SPECTRA OF $C_5H_{10}NPF_2$ AND $C_5H_{10}NPF_2 \cdot BH_3$

The 94.1 MHz ^{19}F nmr spectrum of $C_5H_{10}NPF_2$ at room temperature (Fig.12-a) consists of a 1:1 doublet at δ = +64.5 ± 0.2 ppm. $(CFCl_3)$*. This splitting is due to coupling of the fluorines with the phosphorus nucleus giving a coupling constant of J_{PF}= 1200 ± 2 Hz. Each member of this doublet is split further into a 1:4:6:4:1 quintet which is attributed to additional coupling of the fluorines with the four equivalent protons situated in the α -position of the piperidine ring. The value of J_{HCNPF} is 3.3 ± 0.1 Hz. The two axial and equatorial α -protons are rendered equivalent because of the chair-to-chair interconversion process occuring at room temperature.

At temperatures below -65°C the high resolution splitting pattern of each member of the original doublet changes in form, and appears to be a six-line multiplet (Fig. 12-b). This suggests that the

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* Reddy and Schmutzler (41) reported a δ value $(CFCl_3)$ of +65.2 ppm. for the same compound.

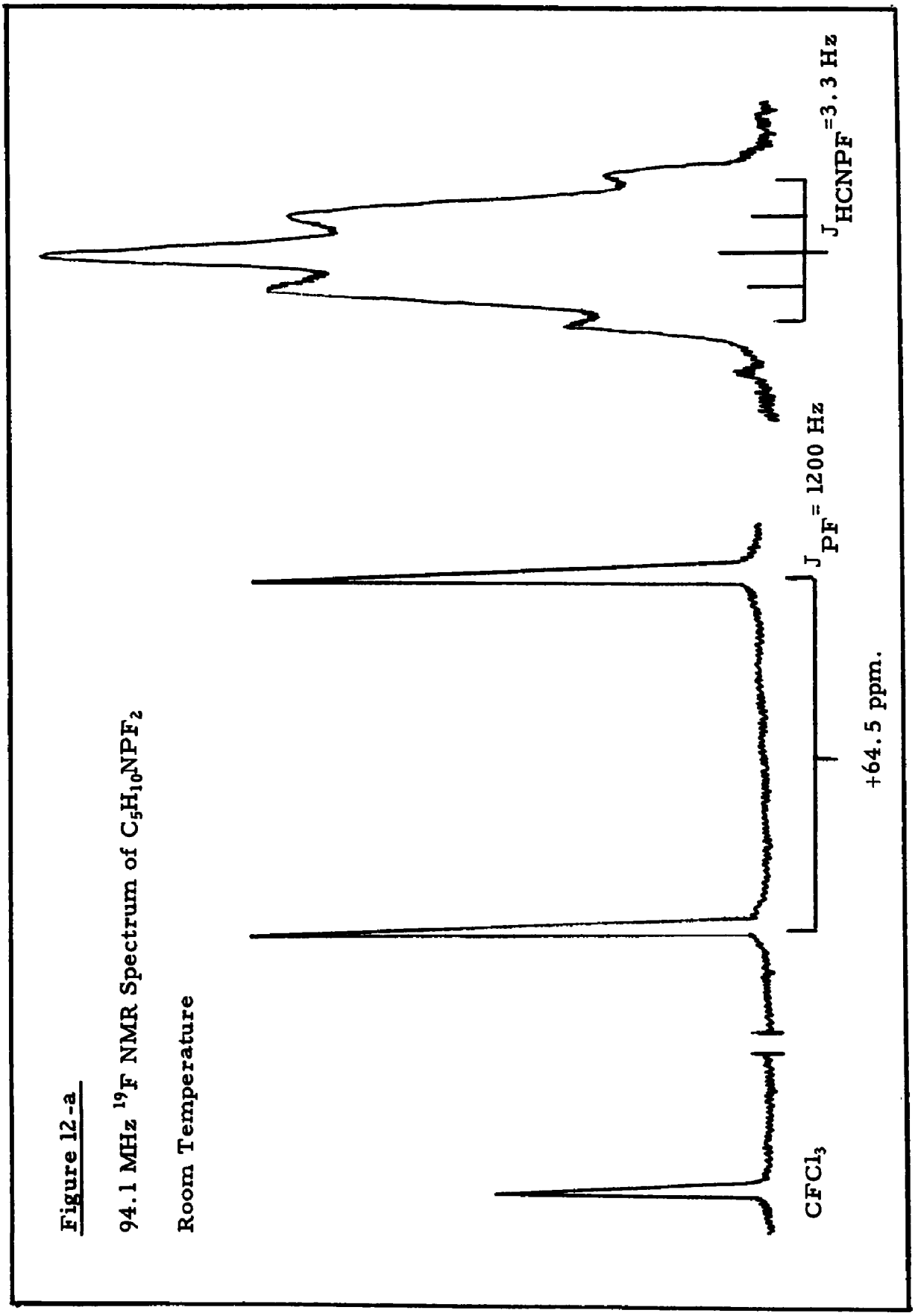


Figure 12-a
94.1 MHz ^{19}F NMR Spectrum of $C_5H_{10}NPF_2$
Room Temperature
$CFCl_3$
+64.5 ppm.
J_{PF} = 1200 Hz
J_{HCNPF}=3.3 Hz

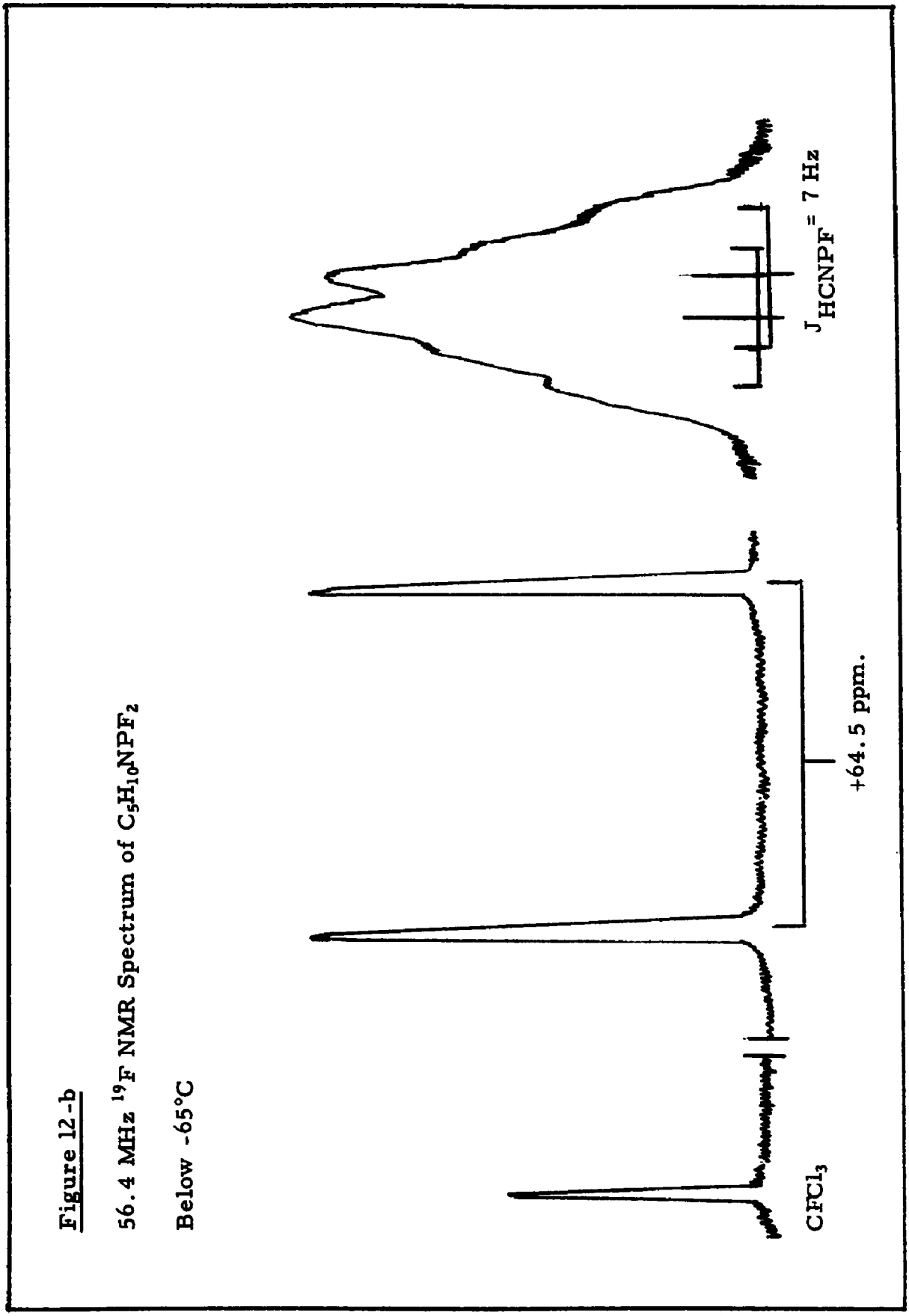


Figure 12-b

56.4 MHz ^{19}F NMR Spectrum of $C_5H_{10}NPF_2$

Below -65°C

two fluorines are now slightly non-equivalent because ring interconversion is no longer possible, and the observed splittings can be analyzed in terms of the two inner peaks of an AB quartet each of which is split into 1:2:1 triplet (J_{HCNPF} = 7 Hz) as a result of coupling with two ring protons. It is conceivable that the fluorines are experiencing spin-spin interaction with either pair of axial or equatorial protons α to the nitrogen. This point will be dealt with more extensively in the discussion of the results obtained for (3-methylpiperidyl)difluorophosphine.

For the borane adduct of $C_5H_{10}NPF_2$, the ^{19}F nmr spectrum (Fig.13) shows a similar 1:1 doublet at δ = +73.5 ± 0.2 ppm. ($CFCl_3$). The P-F coupling constant is J_{PF} = 1168 ± 2 Hz. Each member of this doublet, at room temperature, is split further into a 1:3:3:1 quartet (J_{HBPF} = 14.2 ± 0.1 Hz) because of coupling with the three borane protons. The magnitude of this coupling constant confirms the interpretation of the splittings observed in the BH_3 signal in the proton nmr spectrum of $C_5H_{10}NPF_2 . BH_3$. The fact that coupling with the ring protons is not observed in the borane adduct but was observed in the free ligand could be attributed to the appreciable electric quadrople moment of the ^{11}B nucleus, which tends to broaden nmr signals.

F. THE ^{31}P NMR SPECTRA OF $C_5H_{10}NPF_2$ AND $C_5H_{10}NPF_2 . BH_3$

The 40.4 MHz ^{31}P nmr spectra of $C_5H_{10}NPF_2$ and its borane adduct at room temperature (Figs.14 and 15) both show a 1:2:1 triplet, indicative of a phosphorus nucleus interacting with two fluorine nuclei.

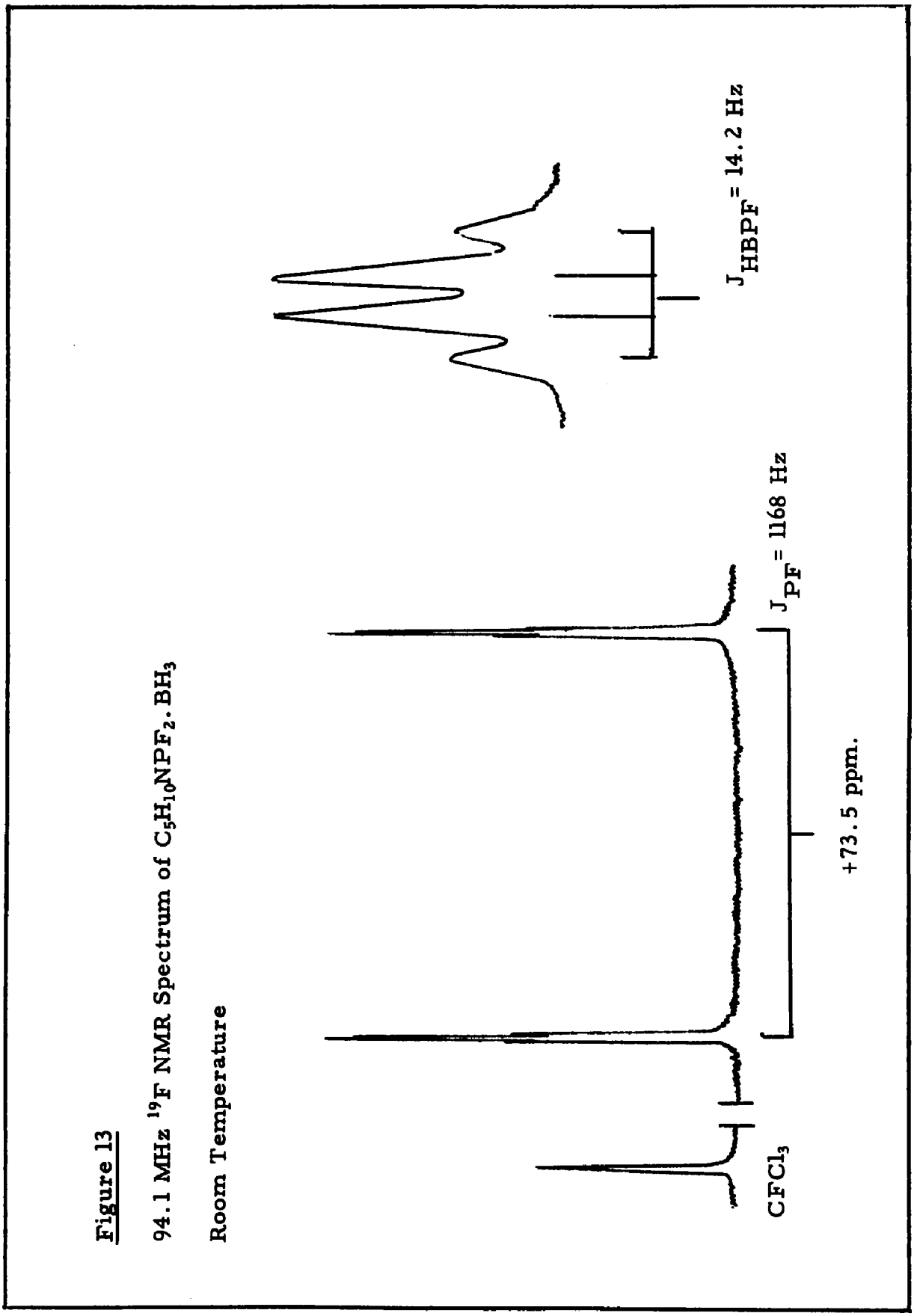


Figure 13

94.1 MHz ^{19}F NMR Spectrum of $C_5H_{10}NPF_2.BH_3$

Room Temperature

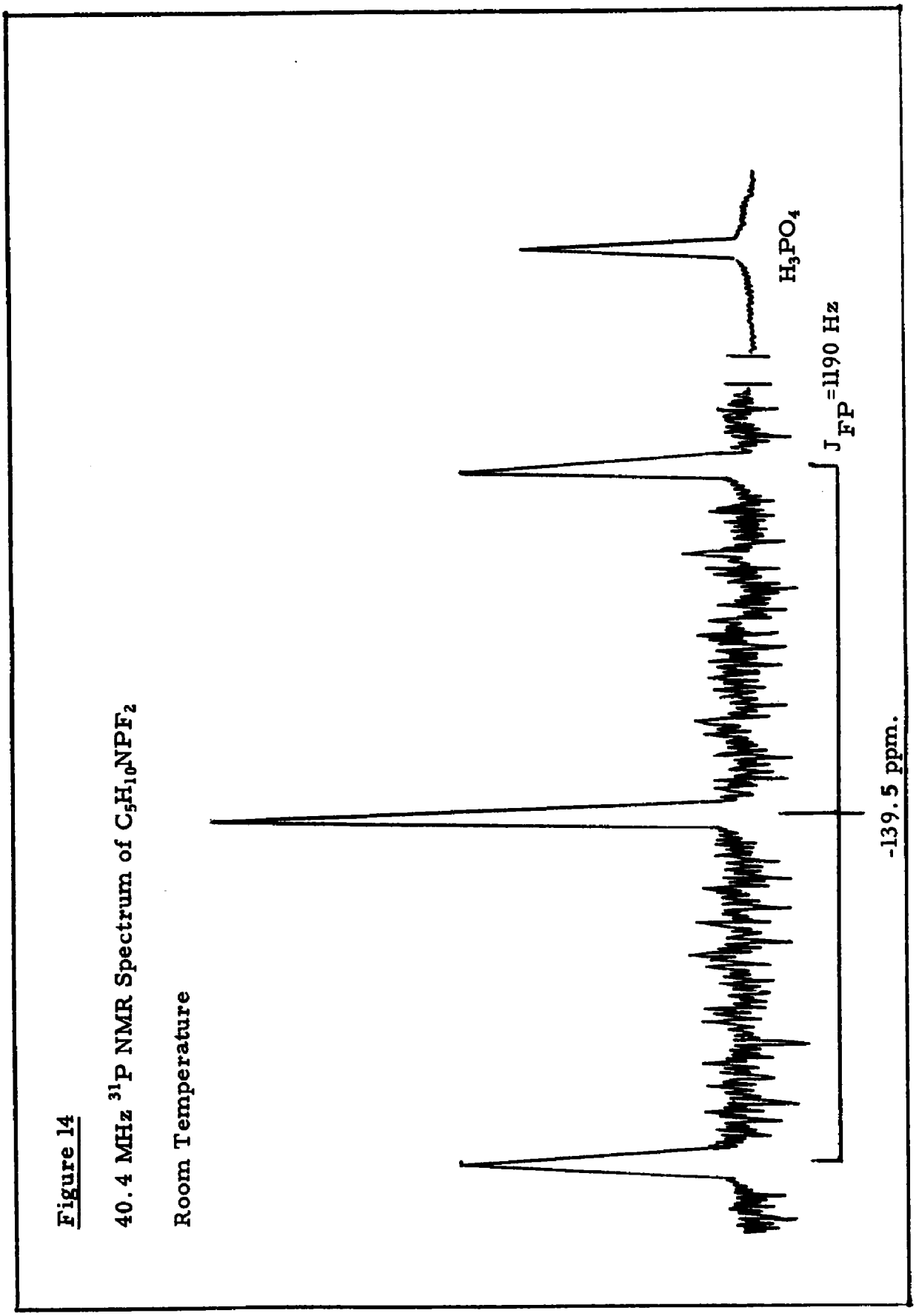


Figure 14

40.4 MHz ^{31}P NMR Spectrum of $C_5H_{10}NPF_2$

Room Temperature

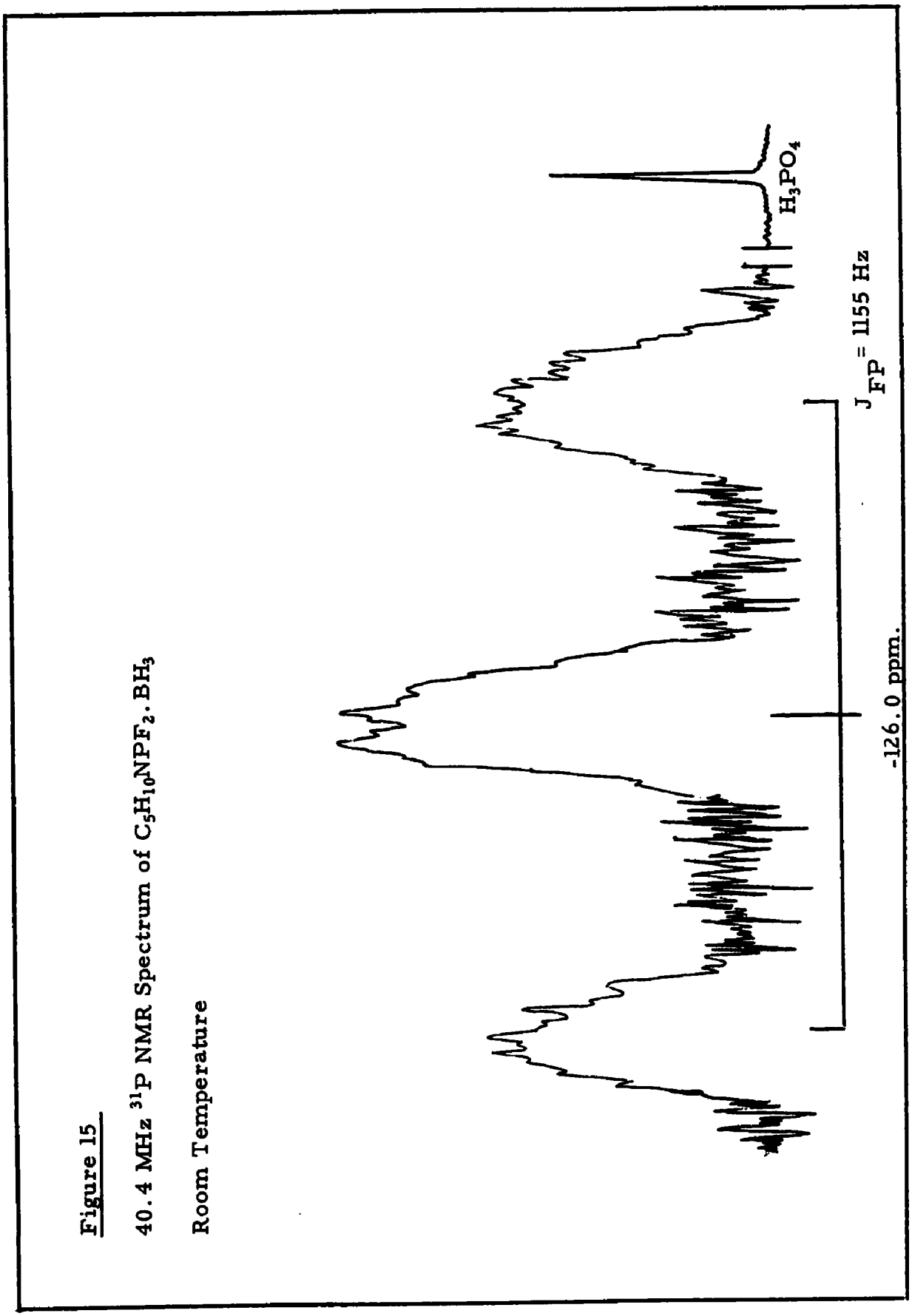


Figure 15

40.4 MHz ^{31}P NMR Spectrum of $C_5H_{10}NPF_2.BH_3$

Room Temperature

The ^{31}P chemical shift for $C_5H_{10}NPF_2$ is δ = -139.5 ± 0.5 ppm. (H_3PO_4), and its coupling constant, J_{FP} is 1190 ± 2 Hz. No further splitting is observed. The borane adduct gives a chemical shift of δ = -126.0 ± 0.5 ppm. (H_3PO_4), and a coupling constant J_{FP} = 1155 ± 2 Hz. Each member of the triplet observed for the borane adduct shows further splittings but unequivocal interpretation is not possible due to the high noise level.

G. THE ^{11}B NMR SPECTRUM OF $C_5H_{10}NPF_2.BH_3$

At room temperature, the 32.1 MHz ^{11}B nmr spectrum of $C_5H_{10}NPF_2.BH_3$ is a 1:3:3:1 quartet, 130.4 ± 0.5 ppm. upfield from $B(CH_3)_3$. The splitting pattern is due to coupling of the boron nucleus with the three equivalent borane protns, J_{HB} = 105 ± 1 Hz. Each member of this quartet is split further into 1:1 doublet, J_{PB} = 78 ± 1 Hz, indicative of a BH_3-group coordinating through the phosphorus atom. This is essentially what has been found in the earlier investigations of dialkyldifluorophosphineboranes.

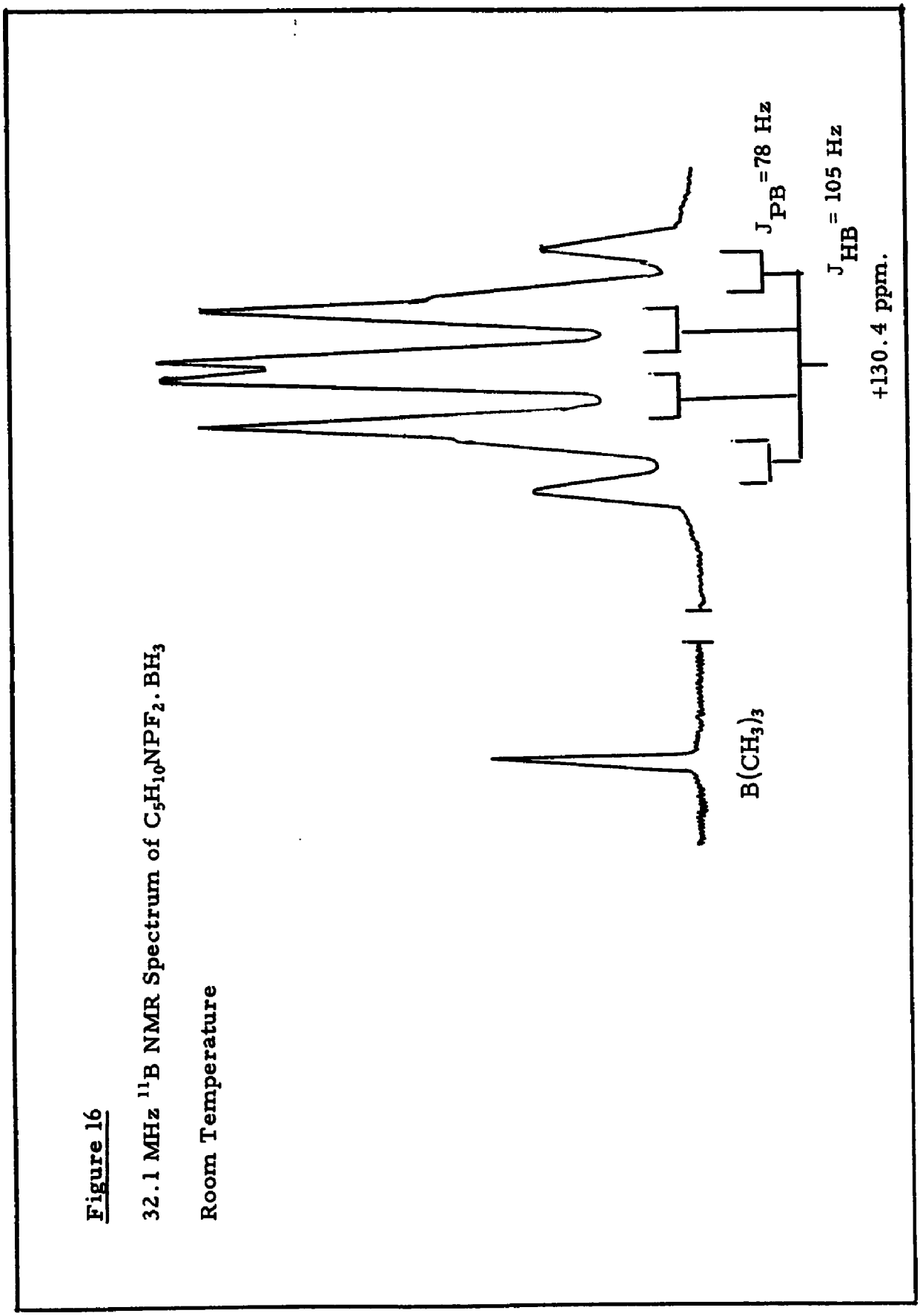


Figure 16

32.1 MHz ^{11}B NMR Spectrum of $C_5H_{10}NPF_2 \cdot BH_3$

Room Temperature

III - (2-METHYLPIPERIDYL)DIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

A. SYNTHESIS OF (2-METHYLPIPERIDYL)DIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

Samples of (2-methylpiperidyl)difluorophosphine, $2\text{-}(CH_3)C_5H_9NPF_2$, were prepared by two methods. One is a slight modification of Van Doorne's procedure using the reaction of 2-methylpiperidine with phosphorus trifluoride (26)

$$2\ \ 2\text{-}(CH_3)C_5H_{10}N + PF_3 \rightarrow 2\text{-}(CH_3)C_5H_9NPF_2 + 2\text{-}(CH_3)C_5H_{10}N.HF.$$

The other method is the fluorination of (2-methylpiperidyl)dichlorophosphine, prepared by the reaction of 2-methylpiperidine and phosphorus trichloride, with SbF_3

$$2\ \ 2\text{-}(CH_3)C_5H_{10}N + PCl_3 \rightarrow 2\text{-}(CH_3)C_5H_9NPCl_2 + 2\text{-}(CH_3)C_5H_{10}N.HCl$$

$$3\ \ 2\text{-}(CH_3)C_5H_9NPCl_2 + 2\ SbF_3 \rightarrow 3\ \ 2\text{-}(CH_3)C_5H_9NPF_2 + 2\ SbCl_3.$$

The infrared spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ shown in Fig. 17, checks with that reported by Van Doorne (26) who first prepared the compound. When compared with the infrared spectrum of 2-methylpiperidine (Fig. 18), it can be noticed that the N-H stretching frequency at about 3280 cm^{-1} is absent, and two strong peaks appear at 780 and 720 cm-1 indicative of a $-PF_2$ substituent on the nitrogen.

The borane adduct was prepared by the reaction of the free ligand with diborane in ether at -78°C

$$2\text{-}(CH_3)C_5H_9NPF_2 + \tfrac{1}{2}\ B_2H_6 \rightarrow 2\text{-}(CH_3)C_5H_9NPF_2.BH_3\ .$$

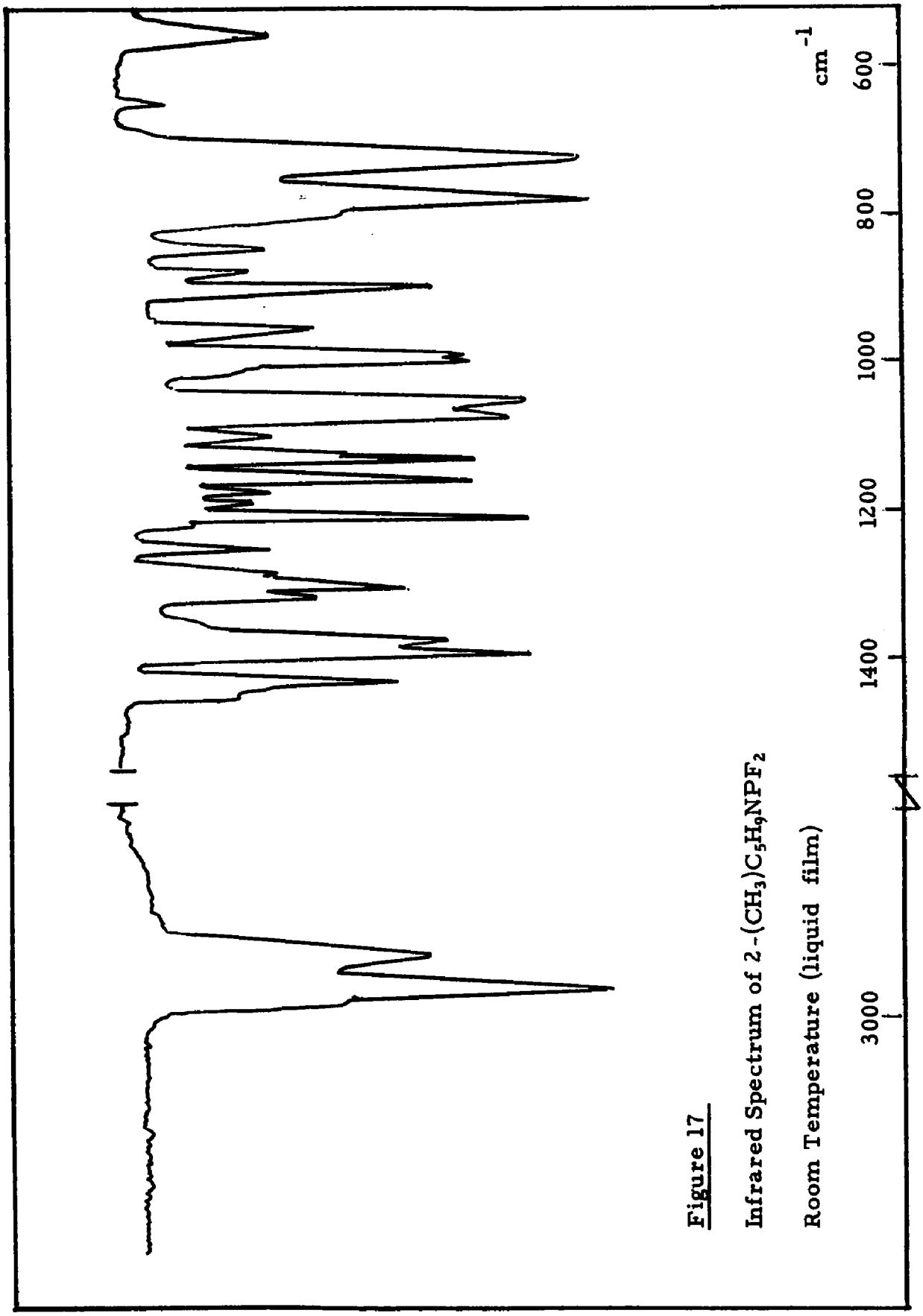


Figure 17

Infrared Spectrum of 2-$(CH_3)C_5H_9NPF_2$

Room Temperature (liquid film)

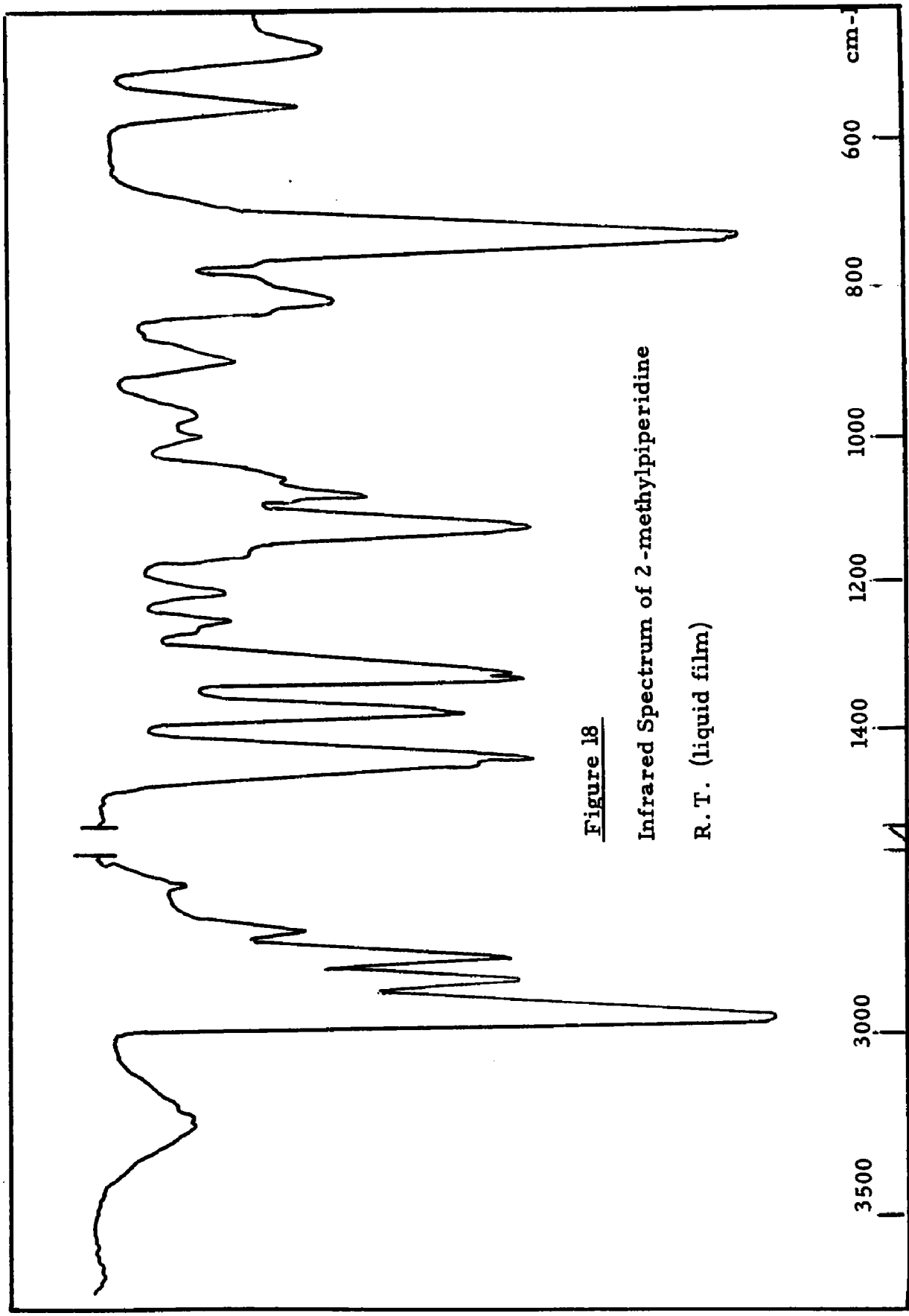


Figure 18

Infrared Spectrum of 2-methylpiperidine

R.T. (liquid film)

Its infrared spectrum is shown in Fig. 19, and it is identical to the spectrum obtained by Van Doorne (26).

B. THE ^{31}P NMR SPECTRA OF 2-$(CH_3)C_5H_9NPF_2$ AND 2-$(CH_3)C_5H_9$-$NPF_2.BH_3$

The 40.1 MHz ^{31}P nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ (Fig. 20), is a 1:2:1 triplet, with δ = -140.5 ± 0.5 ppm. (H_3PO_4), giving a P-F coupling constant of J_{FP} = 1192 ± 2 Hz. The spectrum reflects the coupling of the phosphorus nucleus with the fluorine atoms.

For the borane adduct, a similar splitting pattern is observed (Fig. 21), a 1:2:1 triplet with a chemical shift of δ = -126.5 ± 0.5 ppm. (H_3PO_4) and a coupling constant of J_{FP} = 1182 ± 2 Hz. In addition to the basic splitting brought about by the spin-spin interaction between the phosphorus and the two fluorine nuclei, each member of this triplet is broadened presumably due to the electric quadrople moment of the boron nucleus.

C. THE ^{11}B NMR SPECTRUM OF 2-$(CH_3)C_5H_9NPF_2.BH_3$

At room temperature, the 32.1 MHz ^{11}B nmr spectrum of the borane adduct of 2-$(CH_3)C_5H_9NPF_2$ shows (Fig. 22) a 1:3:3:1 quartet at δ = +130.4 ± 0.5 ppm. from $B(CH_3)_3$. The quartet results from B-H coupling (J_{HB} = 103 ± 1 Hz). Each member of this quartet is split into 1:1 doublets, with some overlapping of the peaks to give the appearance of a quintet. The doublet splitting is due to P-B coupling giving a J_{PB}

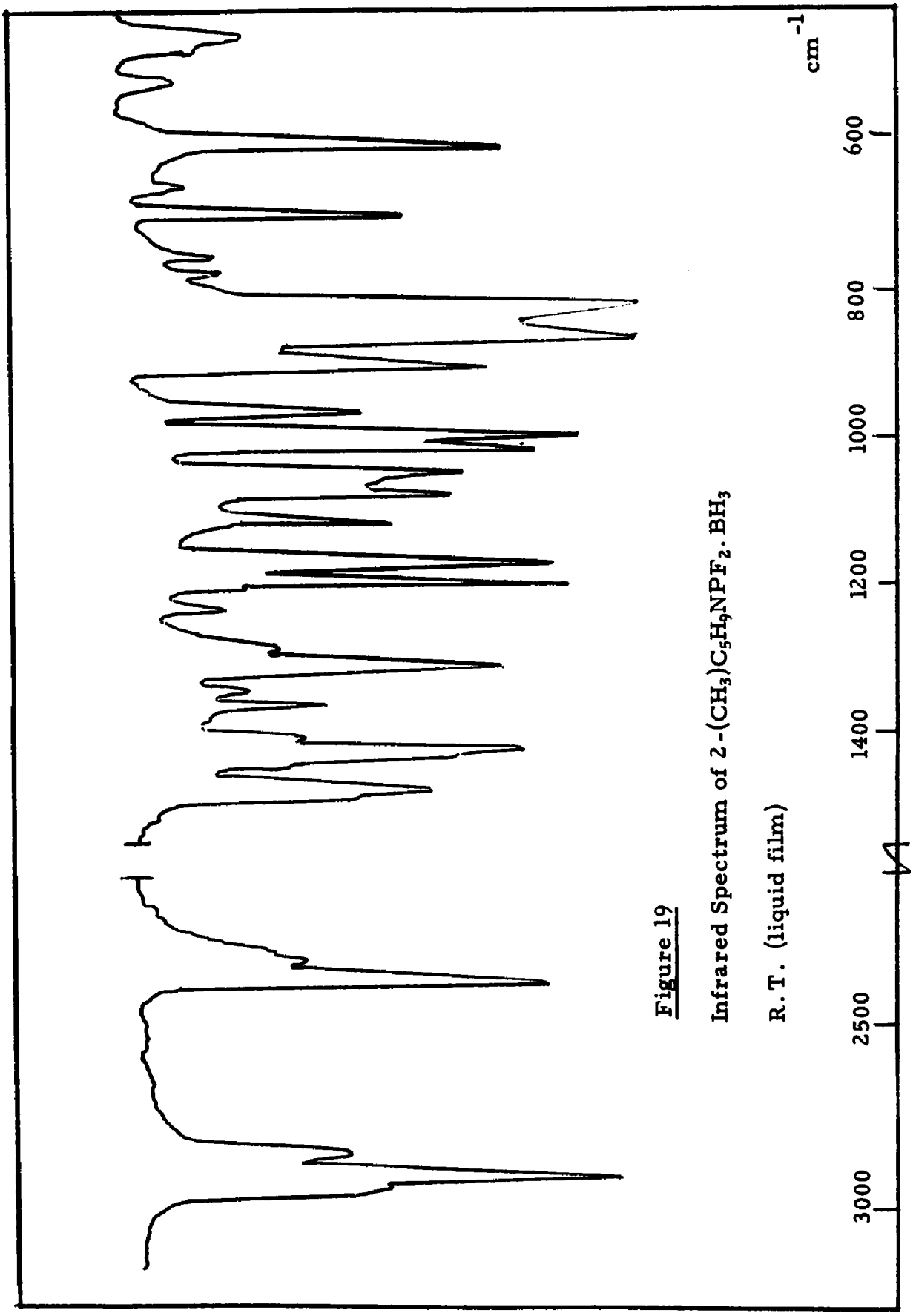


Figure 19

Infrared Spectrum of 2-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

R. T. (liquid film)

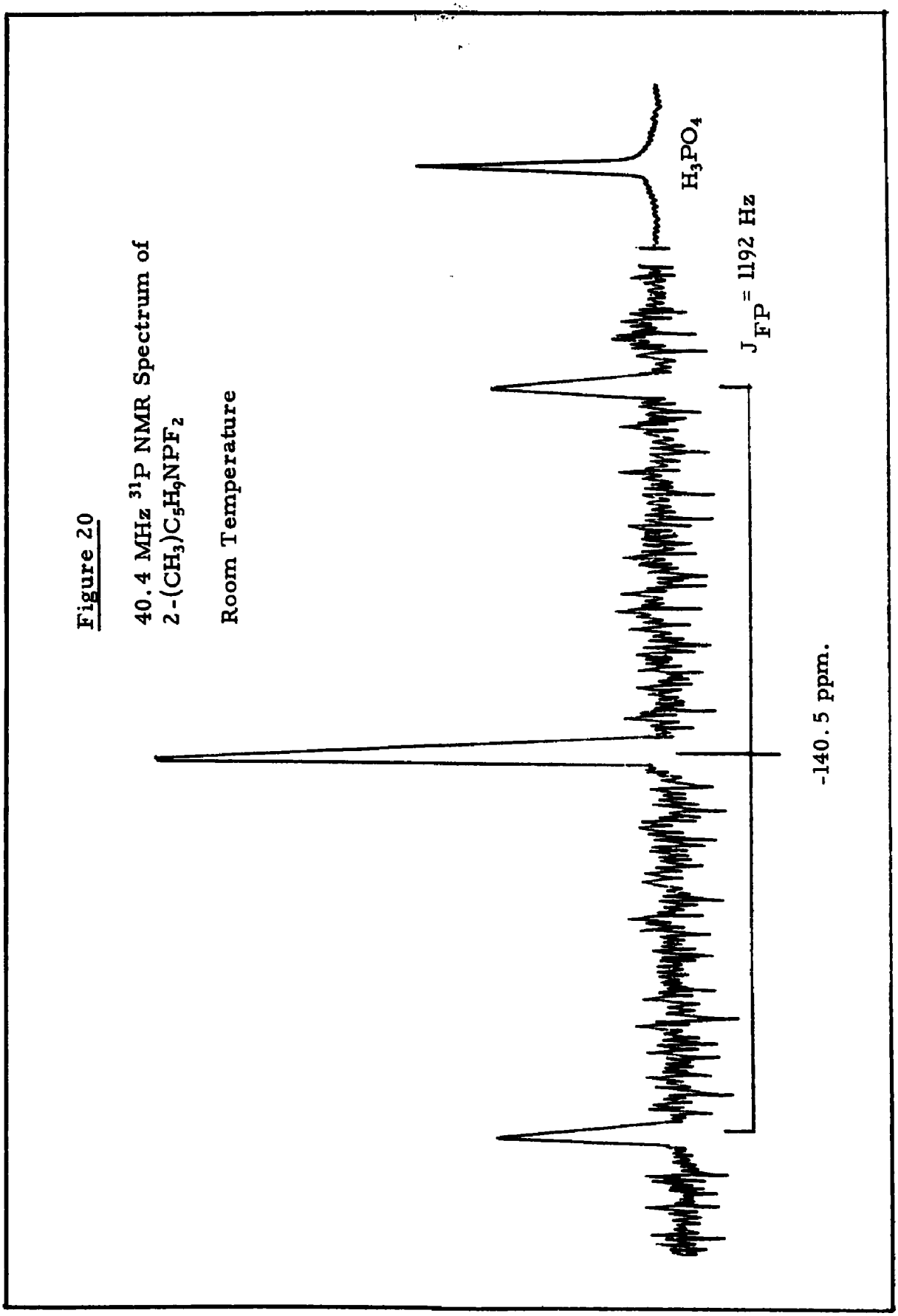


Figure 20

40.4 MHz ^{31}P NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2$

Room Temperature

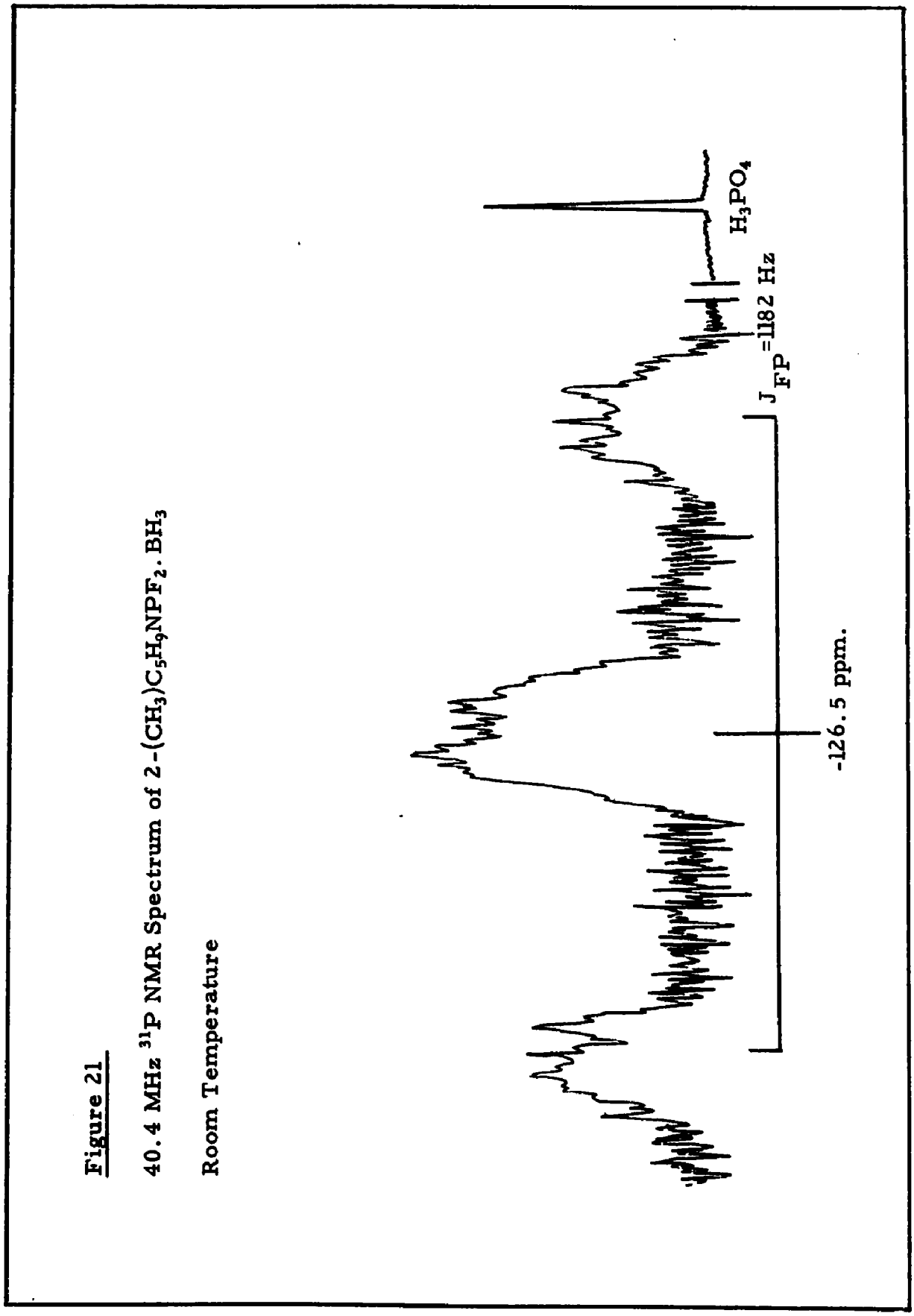


Figure 21

40.4 MHz ^{31}P NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2.BH_3$

Room Temperature

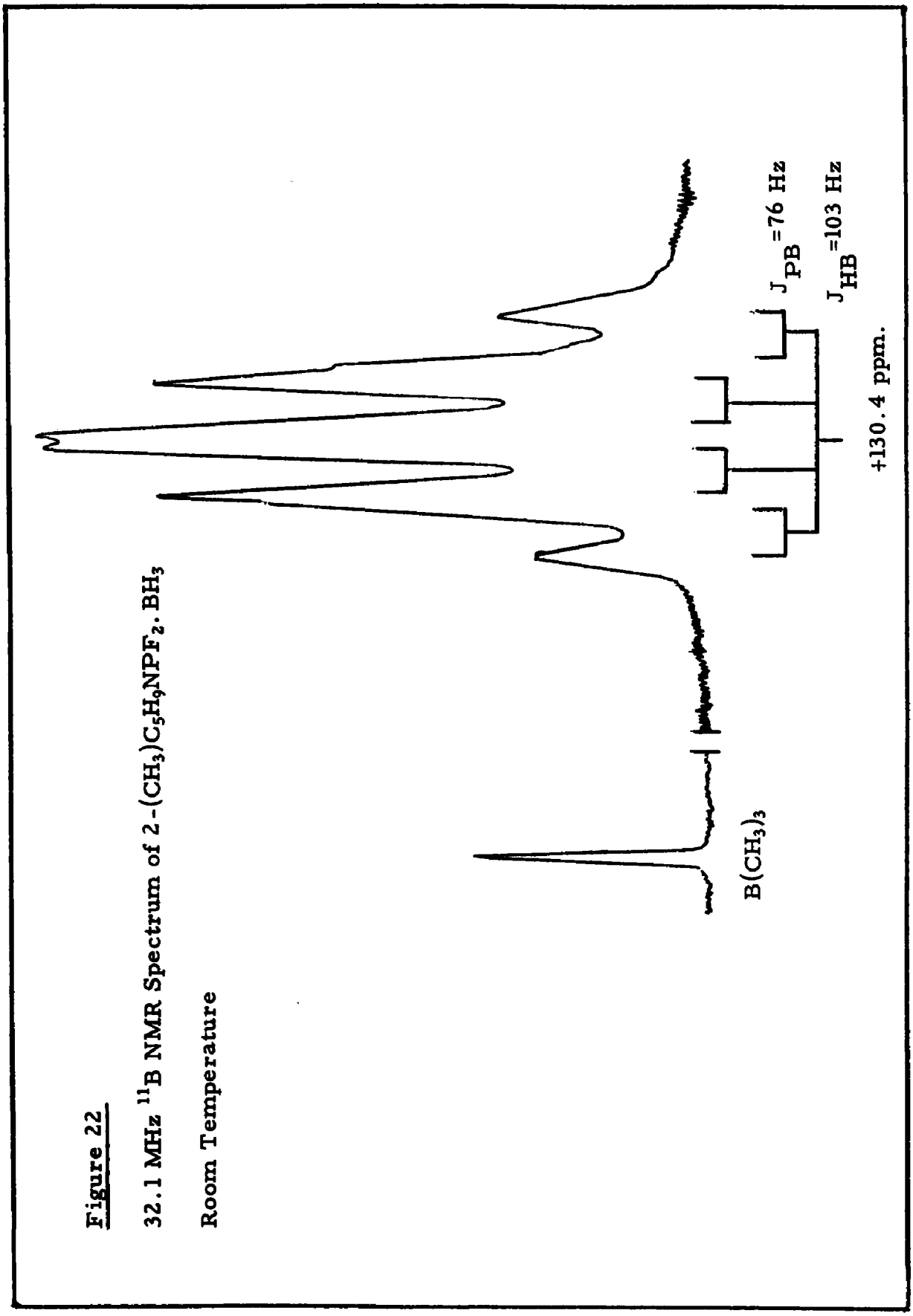


Figure 22

32.1 MHz ^{11}B NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

Room Temperature

value of 76 ± 1 Hz.

D. THE ^{1}H NMR SPECTRA OF 2-METHYLPIPERIDINE, 2-(CH_3)-$C_5H_9NPF_2$, AND 2-$(CH_3)C_5H_9NPF_2.BH_3$

1) 2-Methylpiperidine

It is essential to establish whether 2-methylpiperidine undergoes the process of interconversion between two equivalent chair forms, as was found to be the case for piperidine. For this reason, its ^{1}H nmr spectrum was studied as a function of temperature. It was found that the proton nmr spectrum of 2-methylpiperidine is not temperature dependent within the range of -65°C to +100°C, and remained essentially the same as the spectrum taken at room temperature (Fig. 23).

The room temperature ^{1}H nmr spectrum of 2-methylpiperidine has been published earlier (44). The observed spectrum consists of:

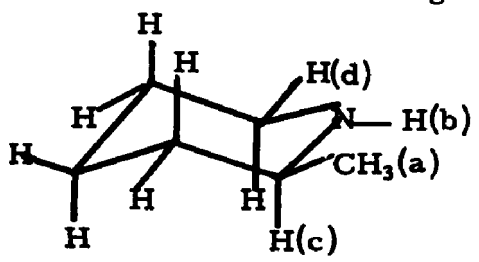
a) a doublet at δ = -1.02 ± 0.02 ppm. (TMS) with a coupling constant J_{HCCH} = 6.5 ± 0.1 Hz

b) a sharp peak at δ = -1.44 ± 0.02 ppm. (TMS) among a broad multiplet

c) a broad peak centered at δ = -2.55 ± 0.03 ppm. (TMS)

d) another multiplet which gives the appearance of a doublet, centered at δ = -2.97 ± 0.03 ppm. (TMS).

The integrated area ratios of these nmr signals are 3:7:2:1, respectively.



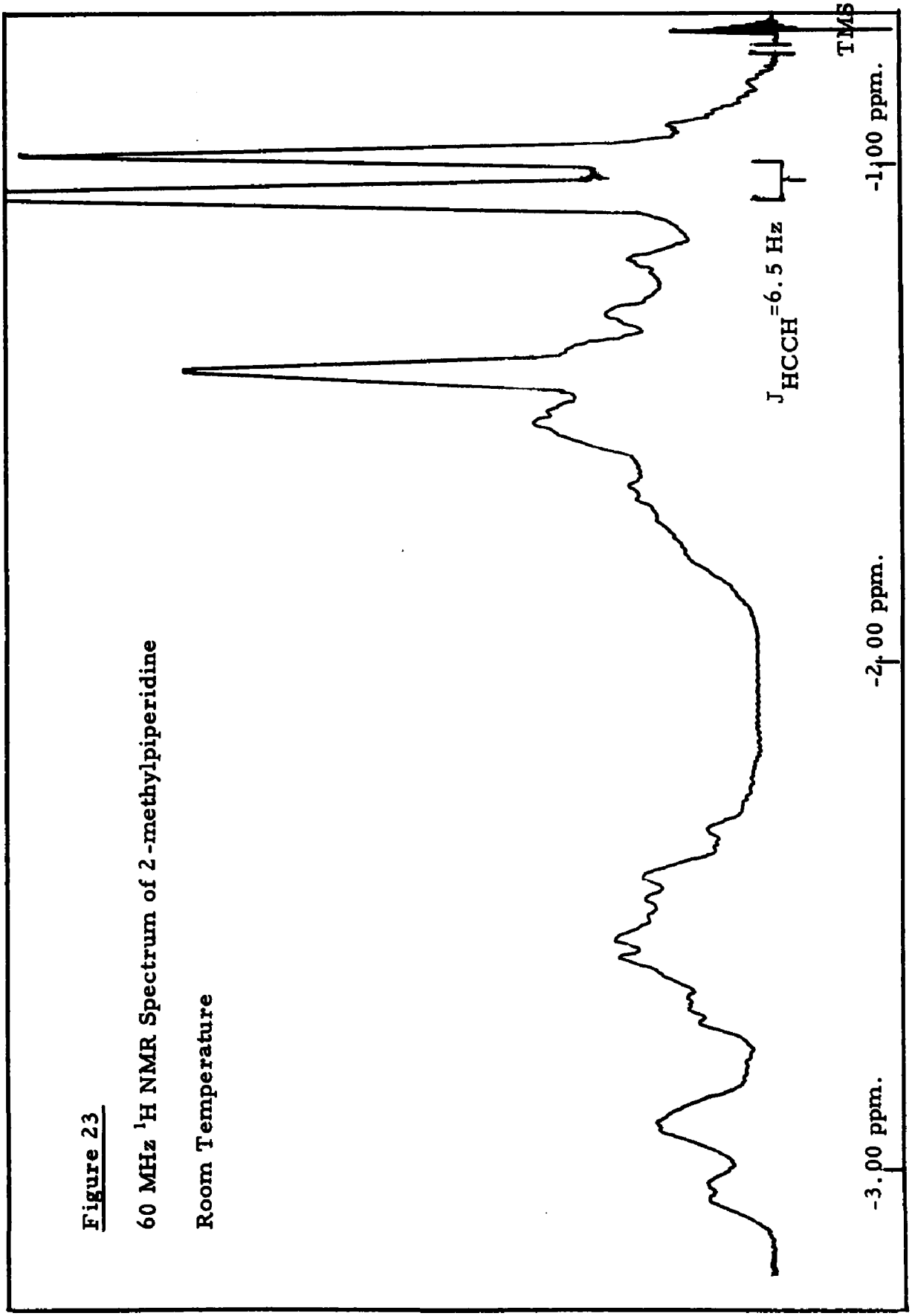


Figure 23

60 MHz ^{1}H NMR Spectrum of 2-methylpiperidine

Room Temperature

The doublet which appear at a chemical shift value of δ = -1.02 ppm. corresponds to the methyl protons coupled to the lone methine proton. The sharp peak at δ = -1.44 ppm. is the N-H peak which shows up in a rather broad multiplet. On the basis of the relative areas of the two signals at lower field, the doublet at δ = -2.97 ppm. is assigned to the lone equatorial proton α to the nitrogen, and the multiplet centered at δ = -2.55 ppm. is assigned to the two axial protons also situated α to the nitrogen. The doublet splitting of the nmr signal at lowest field represents coupling of the equatorial proton with the axial proton on the same carbon atom, giving a $J_{H_{eq}-H_{ax}}$ = 12.1 * 0.2 Hz. This value of coupling constant between geminal axial and equatorial protons agrees well with values obtained by Musher (45) in his works on cyclohexane derivatives.

These assignments assume that 2-methylpiperidine exists in one preferred conformation, such that axial and equatorial protons exhibit distinct nmr signals. It should be noted that a similar observation was made in the low-temperature proton nmr spectrum of piperidine which showed distinct signals for the axial and equatorial protons. It was mentioned earlier that axial protons have been found to be more shielded than equatorial protons (34), (35). The area ratio of the two lower field signals at δ= -2.97 and -2.55 ppm. assigned respectively to one equatorial and two axial protons, all α to the nitrogen atom, was found to be 1:2. It can be inferred from this that the methyl group, also α to the nitrogen, is in an equatorial orientation because if it were

otherwise, the area ratio of these two lower field signals would have been 2:1 rather than the observed 1:2.

The foregoing interpretation is substantiated by the fact that the proton nmr spectrum of 2-methylpiperidine did not show temperature dependence over a wide temperature range. In similar studies on perfluoro-(N-fluoro-2-methylpiperidine) (38), the completely fluorinated analogue of 2-methylpiperidine, as well as on perfluorocyclohexane (46-48), it was suggested that these compounds exist in one predominantly "locked" conformation. Double resonance data (44) revealed that the methine proton resonance is at δ = -2.57 ± 0.1 ppm. (TMS). This is consistent with the methyl group being in an equatorial position in the heterocyclic ring.

2) 2-$(CH_3)C_5H_9NPF_2$

The ^1H nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ at room temperature (Fig. 24) shows the absence of the N-H peak observed in the free amine. It consists of:

a) a doublet at δ = -1.08 ± 0.02 ppm. (TMS) with a coupling constant of J_{HCCH} = 6.7 ± 0.1 Hz; each member of this doublet is split further into another doublet giving a coupling constant of J_{PNCCH} = 1.05 ± 0.1 Hz

b) a broad, high-intensity peak at δ = -1.37 ± 0.02 ppm. (TMS)

c) a broad peak centered at δ = -2.98 ± 0.03 ppm. (TMS)

d) another broad peak centered at δ = -3.51 ± 0.04 ppm. (TMS).

The integrated area ratios of these peaks are 3:6:2:1 respectively.

Substitution of a PF_2-group for the N-H proton would not alter

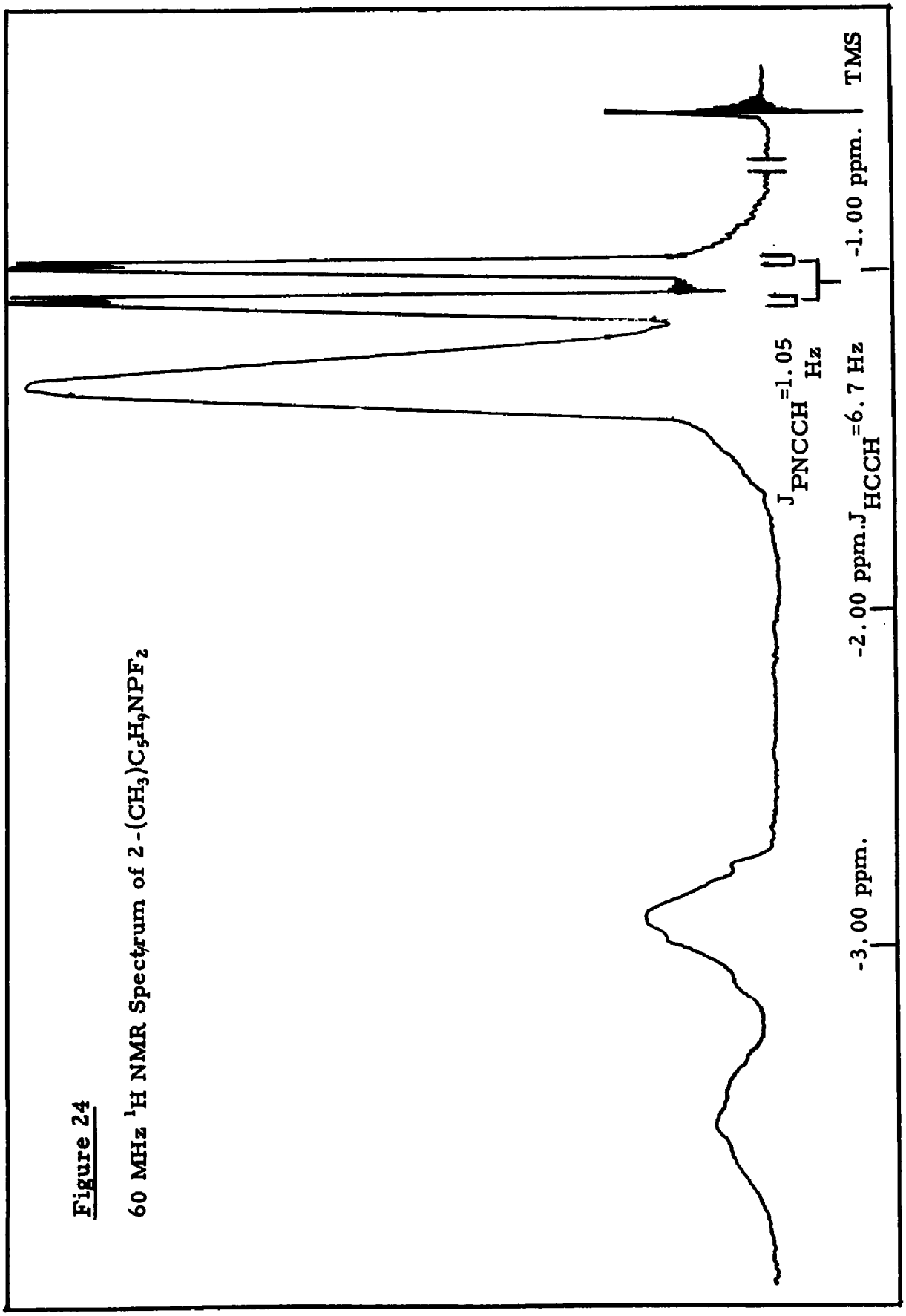


Figure 24

60 MHz ^1H NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2$

the structure of the molecule appreciably. Thus the assignment of these nmr signals will be similar to that made for the proton nmr spectrum of 2-methylpiperidine. The doublet of doublets at δ = -1.08 ppm. represents the methyl group resonance exhibiting coupling with the lone methine proton (J_{HCCH}=6.7 Hz), and also with the phosphorus nucleus (J_{PNCCH}= 1.05 Hz). The signal at lowest field is assigned to one of the α-methylene protons in an equatorial orientation. The peak at δ = -2.98 ppm. corresponds to the two axial protons, one of which is the methine proton, α to the nitrogen. The broad, high-intensity peak at δ = -1.37 ppm. belongs to the other ring protons.

It is interesting to note that the resonance signals of the different protonic nuclei in 2-$(CH_3)C_5H_9NPF_2$ occur at much lower magnetic field than the proton resonance signals in 2-methylpiperidine. This could be explained by the inductive effect brought about by the PF_2-group which presumably attracts electrons more effectively than H, thus creating a deshielding effect on the electronic environment of the various proton nuclei.

Like the ^1H nmr spectrum of 2-methylpiperidine, the proton nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ showed no temperature dependence in the range -65°C to +100°C. This means that 2-$(CH_3)C_5H_9NPF_2$ exists in one rigid conformation with the methyl group also occupying an equatorial position in the ring system.

3) 2-$(CH_3)C_5H_9NPF_2 . BH_3$

The ^1H nmr spectrum of 2-$(CH_3)C_5H_9NPF_2 . BH_3$ taken at room

temperature (Fig. 25), is quite similar to that of the free ligand. The only difference is that the nmr signals occur at even lower magnetic fields as expected from inductive arguments. The essential features are:

a) a doublet at δ = -1.09 ppm. ± 0.02 ppm. (TMS) with a coupling constant J_{HCCH} = 7.0 ± 0.1 Hz

b) a broad, high-intensity peak at δ = -1.48 ± 0.02 ppm. (TMS)

c) a rather broad peak centered at δ = -3.50 ± 0.04 ppm. (TMS)

d) another broad peak centered at δ = -3.82 ± 0.04 ppm. (TMS).

Integrated area ratios of these peaks are 3:6:2:1 .

At higher gain, the borane protons are seen as a severely broadened 1:1:1:1 quartet at δ = -0.83 ± 0.02 ppm. (TMS). Two members of the quartet are overlapped by the methyl resonance. The quartet splitting is due to coupling of the borane protons with the boron nucleus, giving a J_{BH} value of 100 ± 1 Hz. No further splittings like the ones in $C_5H_{10}NPF_2$ are observed.

As was the case with 2-$(CH_3)C_5H_9NPF_2$, the proton nmr of 2-$(CH_3)C_5H_9NPF_2.BH_3$ can be unambiguously interpreted. The methyl protons are coupled to the methine proton and show up as a doublet at δ = -1.09 ppm. Broadening of resonance signals by the boron nucleus could explain why no evidence of further coupling with the phosphorus nucleus is observed. Again, by using the integrated area ratios of the other peaks, the equatorial methylene proton is assigned to the signal at lowest field, δ = -3.82 ppm; the two axial protons α to the nitrogen

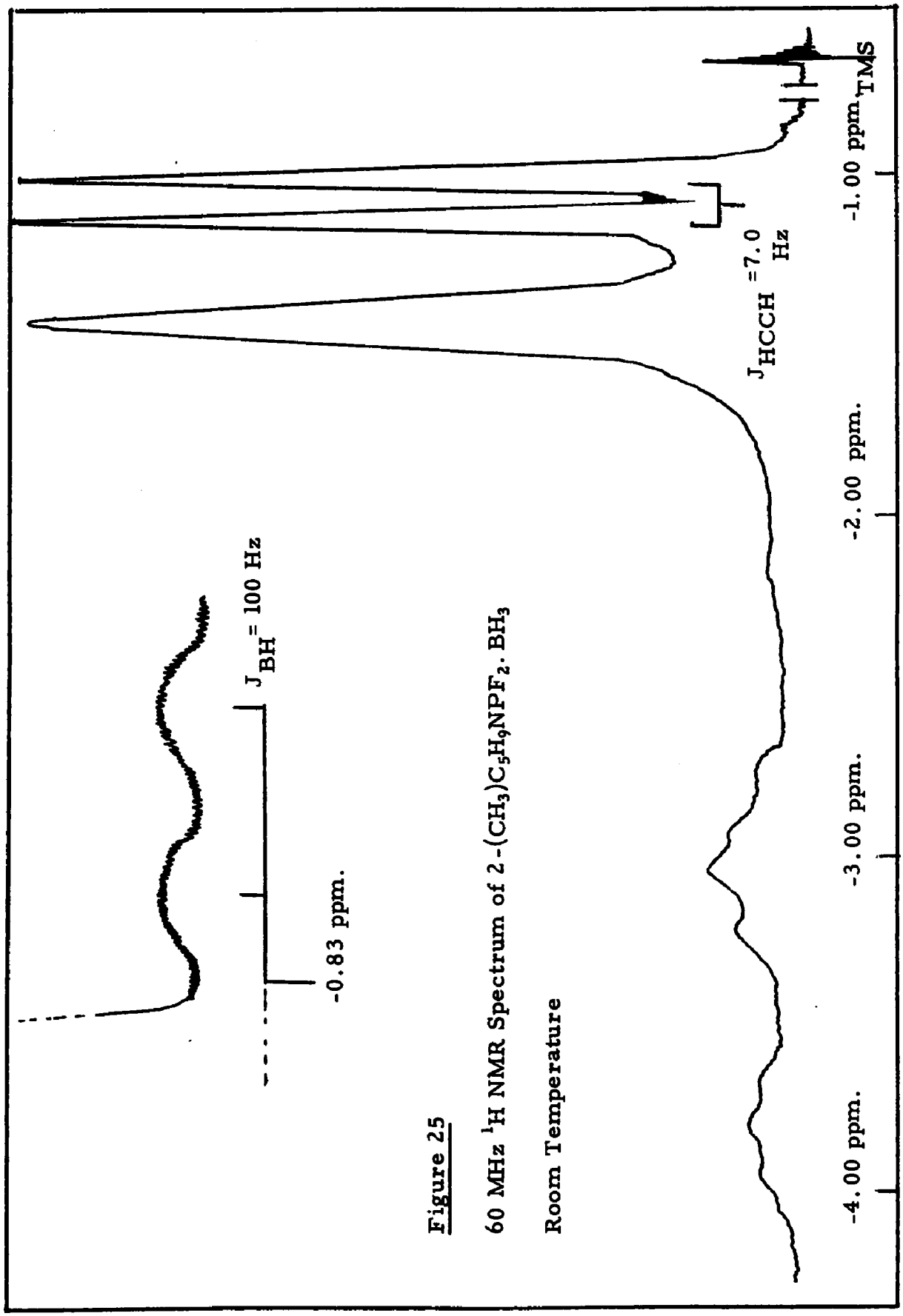


Figure 25

60 MHz ^{1}H NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2 . BH_3$

Room Temperature

to the signal at δ = -3.10 ppm; and the rest of the ring protons to the high-intensity peak at δ = -1.48 ppm.

E. THE ^{19}F NMR SPECTRUM OF 2-$(CH_3)C_5H_9NPF_2$

In Van Doorne's original investigation (26) of 2-$(CH_3)C_5H_9NPF_2$, he observed two sets of doublets for the ^{19}F nmr spectrum at room temperature. He attributed this to the existence of isomers resulting from restricted rotation about the P-N bond. Such an interpretation suggests appreciable double bond character in the P-N linkage, but more intensive study seemed justified since the conclusions are not above question.

The 94.1 MHz ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ at room temperature (Fig. 26) is identical to that reported by Van Doorne (26). It consists of two sets of 1:1 doublets:

a) a high-field doublet at δ = +66.7 ±0.2 ppm. ($CFCl_3$) with a coupling constant of J_{PF} = 1190 ± 2 Hz ; at higher resolution each member of this doublet appears to be a 1:1 doublet with 9.8 Hz separation between peaks,

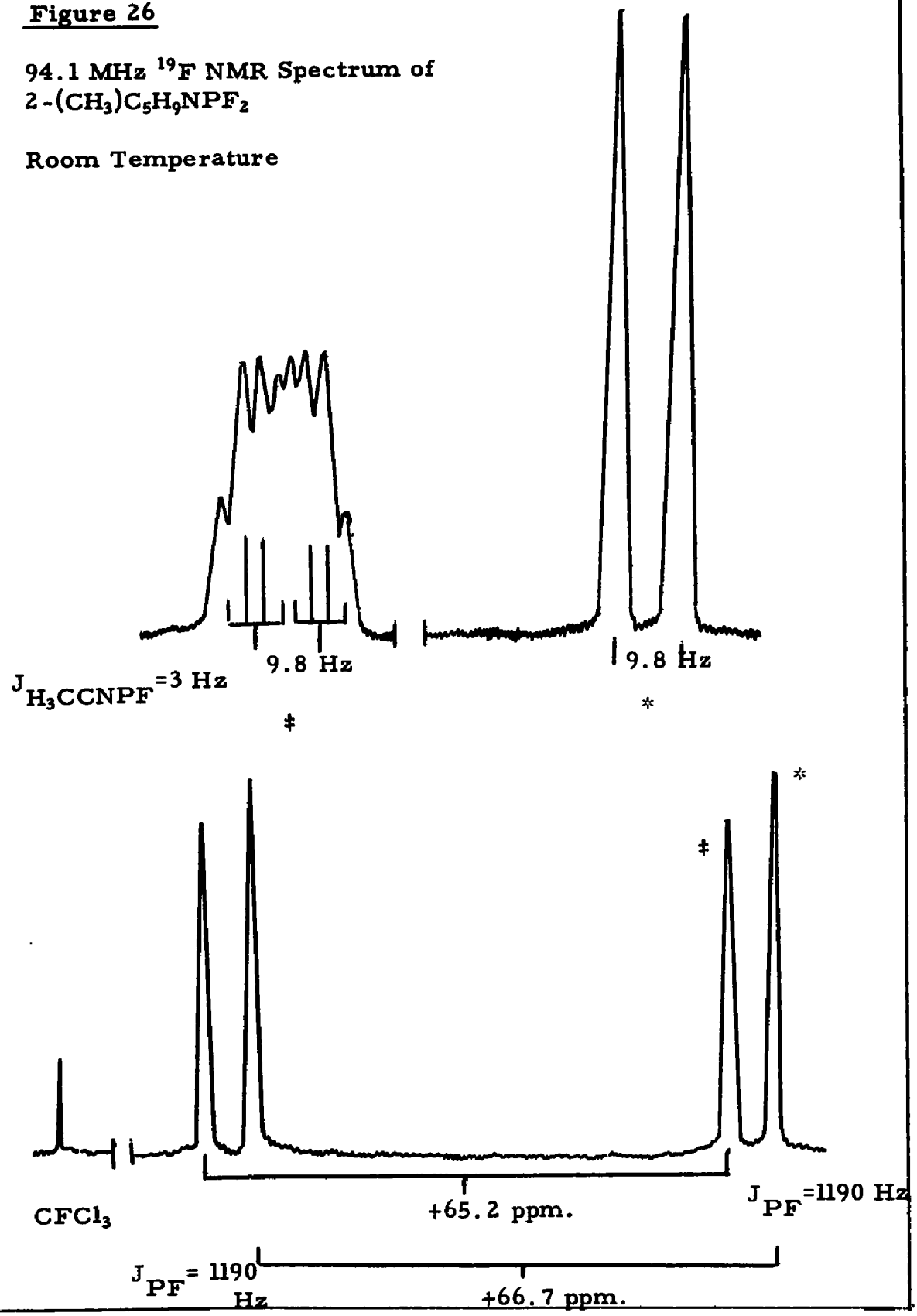
b) a low-field doublet at δ = +65.2 ± 0.2 ppm. ($CFCl_3$) with a coupling constant of J_{PF} = 1190 ± 2 Hz; at higher resolution each member of this doublet appears to be an eight-line multiplet with approximately 3 Hz separation between peaks.

These observations on the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ at room temperature could be adequately explained by either of two models: 1) the compound exists exclusively as one isomer with the two

Figure 26

94.1 MHz ^{19}F NMR Spectrum of
$2\text{-}(CH_3)C_5H_9NPF_2$

Room Temperature



fluorine atoms being non-equivalent such that the low-field doublet corresponds to one of the fluorine atom, and the high-field doublet corresponds to the other fluorine atom; or 2) the compound exists as two isomers with the low-field doublet belonging to one isomer and the high-field doublet belonging to the other isomer. If the first model is correct, then the area of the high-field doublet should be equal to that of the low-field doublet at all temperatures. The conclusion is demanded by the fact that each molecule would have one fluorine in one position and one in another.

Table IV gives the integrated area ratios of the hig-field doublet to the low-field doublet for the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ at different temperature. From this, one can see that the area ratio changes, with a trend favoring the high-field doublet as the temperature increases. Model 1 is clearly eliminated. These results, as well as the observations made on(2-methylpiperidyl)chlorofluorophosphine, 2-$(CH_3)C_5H_9NPFCl$, (to be discussed later) show that the observed ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ can be interpreted by means of a model which considers the existence of two isomers for the compound. It is now left to be shown why such isomers exist, whether the fluorine atoms in each isomer are magnetically equivalent or non-equivalent, and to fully interpret the splitting patterns in the ^{19}F nmr spectrum seen at higher resolution.

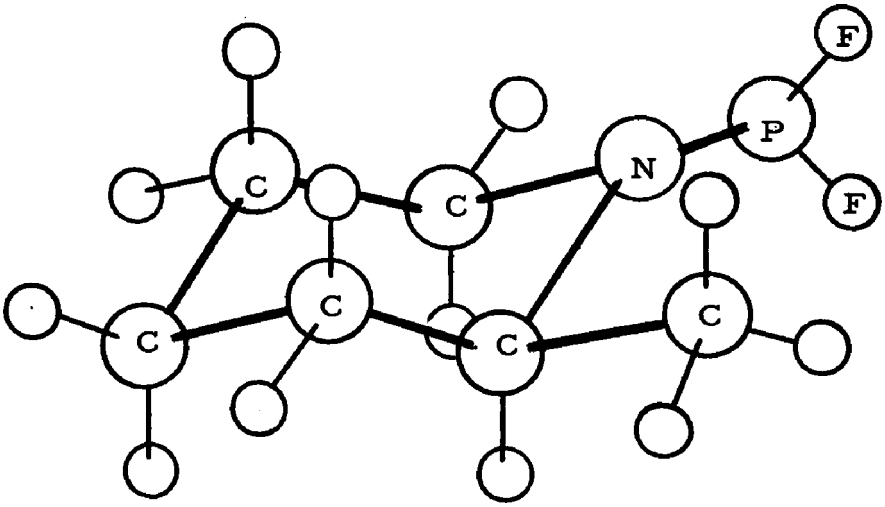
Taking into account the findings of Nordman and co-workers (10), (11) on the crystal structures of $(CH_3)_2NPF_2$ and its B_4H_8 adduct,

Table IV - Integrated Area Ratios of the High-Field Doublet to Low-Field Doublet in the ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2$ at Different Temperatures

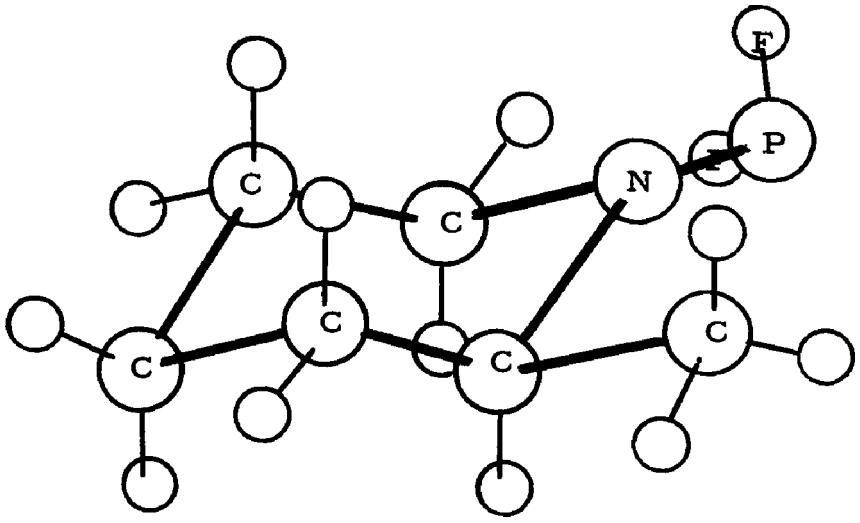
Temperature	Area Ratio
-20°C	0.790 ± 0.002
-10	0.936
0	0.943
+20	0.970
+40	0.988
+60	1.021
+80	1.048
+100	1.265

it would not be unreasonable to suggest that the two isomers of 2-(CH_3)-$C_5H_9NPF_2$ exist in the spatial arrangements shown in Fig. 27. One isomer has the two fluorine atoms directed towards the methyl group, and the other isomer has the two fluorine atoms directed away from the methyl group; the two fluorine atoms in both isomers bisected by the plane made by the phosphorus, nitrogen, and two carbon atoms in the heterocyclic ring. As mentioned earlier, the existence of such isomers would demand restricted rotation about the P-N bond which could result from a P-N double bond, from steric factors, or both.

Focusing now on the aspect of magnetic equivalence or non-equivalence of the fluorine atoms in a given compound, perhaps it would be beneficial to concentrate on the high-field doublet (δ = +66.7 ppm.) which corresponds to one of the isomers in question. Each member of this doublet appears to be a doublet itself at higher resolution. The separation is 9.8 Hz between peaks. Two magnetically equivalent fluorine atoms in one isomer would be expected to show a single peak at higer resolution. The fact that at higher resolution two peaks are observed, indicates that the two fluorine atoms in this particular isomer are not magnetically equivalent. The separation of 9.8 Hz between the peaks might be taken to represent either coupling between the two non-equivalent fluorine atoms or different chemical shift values. If the value of 9.8 Hz represents a coupling constant, it would be quite small when compared to other geminal fluorine coupling constants which vary from 152 to 343 Hz (49) in fluorosubstituted alkanes, and could be



Cis-form
(a)



Trans-form
(b)

Figure 27

Two Isomers of 2-$(CH_3)C_5H_9NPF_2$

as large as 400 Hz in ClF_3 (36). An experimental decision could be reached as to whether the 9.8 Hz separation between the two peaks represents a gem-difluoro coupling constant, $J_{FF'}$, or a chemical shift difference, by observing the ^{19}F nmr spectrum of the same compound at a lower radiofrequency (chemical shifts are field dependent while coupling constants are not). The 56.4 MHz ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ at room temperature is essentially the same as that obtained using 94.1 MHz as fixed radiofrequency oscillator, but in the former case the separation of the two peaks of each member of the high-field doublet is about 6 Hz rather than 9.8 Hz. The theoretical value of the peak separation would be 5.8 Hz at 56,4 MHz if the apparent splitting pattern were associated with a chemical shift phenomenon rather than a coupling constant between the two non-equivalent fluorines. Clearly, the separation of peaks represents a chemical shift difference.

The chair conformation of the heterocyclic ring brings about a slight non-equivalence of the two fluorines in each isomer. The degree of non-equivalence is not great, and therefore only a small difference in their chemical shift values is expected. When compared to the usual large geminal fluorine coupling constant, the ratio of the coupling constant to chemical shift is large. Consequently, a second order effect in the ^{19}F nmr spectrum is observed.

The two peaks of each member of the high-field doublet could then be treated as the two inner peaks of an AB quartet with the two outer peaks not distinguished from the noise level. A similar interpretation

has been advanced by Feeney and Sutcliffe (46) in their investigations of some fluorinated cyclohexanes. They observed that due to the rather small chemical shift difference between gem-fluorine atoms compared to the magnitude of their coupling constants, the two central intense bands of the pair of doublets (in an AB quartet) are close to each other resulting in ;the outer bands becoming so weak as to be indistinguishible from noise. As Van Doorne (26) has pointed out, the signal to noise ratio in the ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ has been determined to be about 50:1. Using this value one can estimate lower limits for the chemical shift and coupling constants of the gem- fluorine atoms (see Appendix C). Using the value of 9.8 Hz as the separation of the central bands of the AB quartet, one obtains the lower limit for the gem-fluoro coupling constant as 245 Hz. The chemical shift difference would be no less than 70 Hz. Table V gives the calculated values for the band energy and relative intensity of a theoretical AB spectrum, utilizing the limiting values for J as calculated above. It can be seen from Fig. 28-a that this theoretical spectrum fits the observed spectrum for one member of the high-field doublet.

One could treat the case of two non-equivalent fluorines bonded to phosphorus as an ABX system. Abraham and Bernstein (50) have drawn up a series of theoretical spectra for an ABX system by way of illustrating the simplifications that can occur in some limiting cases. One of the limiting cases they considered was that in which $\frac{1}{2}(J_{AX}-J_{BX})$ = 0, whereby the X region of the spectrum becomes a triplet, and the

Table V- Calculated Values for the Theoretical Spectrum for One Member of the High-Field Doublet in the ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2$

Band	Band Energy	Band Intensity
1	249.9	0.0387
2	4.9	1.9615
3	-4.9	1.9615
4	-249.9	0.0387

Table VI- Calculated Values for the Theoretical Spectrum for One Member of the Low-Field Doublet in the ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2$

Band	Band Energy	Band Intensity
1	0	0.0385
2	3.0	0.1155
3	6.0	0.1155
4	9.0	0.0385
5	245.0	1.9615
6	248.0	5.8845
7	251.0	5.8845
8	253.0	1.9615
9	253.8	1.9615
10	256.8	5.8845
11	259.8	5.8845
12	262.8	1.9615
13	507.8	0.0385
14	510.8	0.1155
15	513.8	0.1155
16	516.8	0.0385

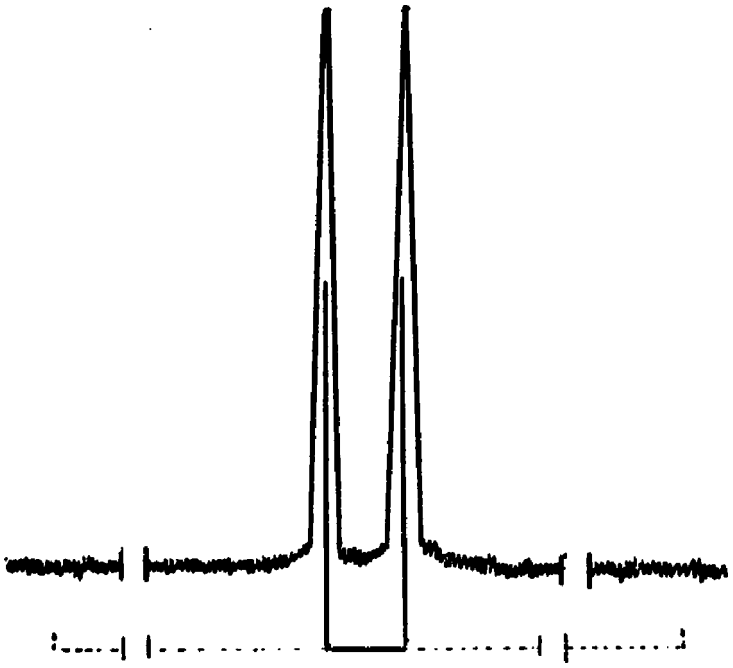


Figure 28-a

Theoretical ^{19}F NMR Spectrum of One Member of the High-Field Doublet of 2-$(CH_3)C_5H_9NPF_2$

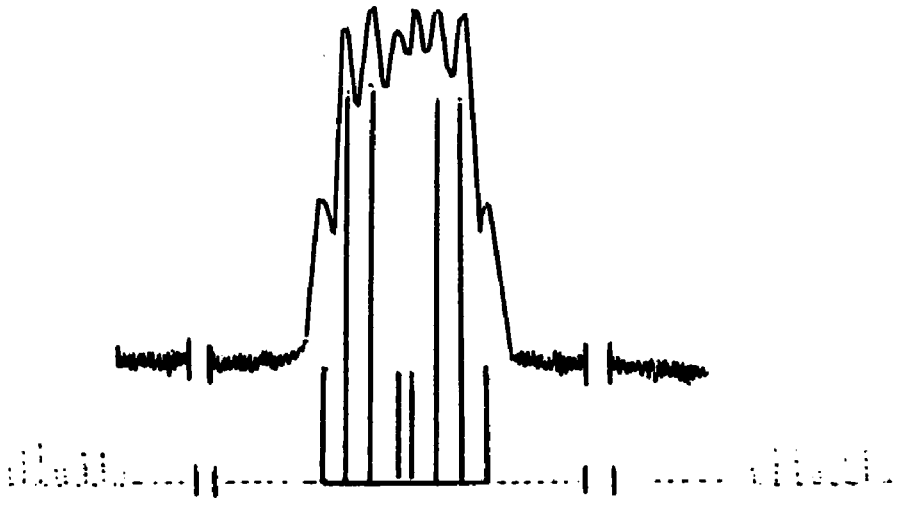


Figure 28-b

Theoretical ^{19}F NMR Spectrum of One Member of the Low-Field Doublet of 2-$(CH_3)C_5H_9NPF_2$

AB portion consists of a strong pair of doublets together with very weak outer bands. The spectrum duplicates that observed here. The ^{31}P nmr spectrum is a triplet (see Fig. 20) resulting from overlapping of the two pairs of doublets. In the AB region, i.e. ^{19}F, the two fluorines are only slightly non-equivalent such that $J_{AX}=J_{BX}=$ 1190 Hz and $\frac{1}{2}(J_{AX}-J_{BX}) = 0$, two pairs of doublets are seen.

Thus the observed splitting pattern of each member of the high-field doublet in the ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ is analyzed in terms of second order effects as the central peaks of an AB quartet with the two outer peaks not visible. The AB spectrum arises because of the two geminal fluorines which are rendered non-equivalent by virtue of the rigid conformation of the piperidine ring in this particular isomer of the compound.

Each member of the low-field doublet in the ^{19}F nmr spectrum of the same compound shows an eight-line multiplet at higher resolution. This splitting pattern for the low-field doublet can also be analyzed as two central bands of an AB quartet separated by 9.8 Hz. Again, the outer bands are not distinguishable from noise. Each of the two central bands is split further into a 1:3:3:1 quartet. This additional splitting represents a spin-spin interaction with the methyl group in the heterocyclic ring, giving a coupling constant of $J_{H_3CCNPF} = 3$ Hz.

Table VI shows the calculated values for the theoretical spectrum of one member of the low-field doublet, obtained from the AB part of an ABX_3 theoretical spectrum analyzed according to the method of Kowales-

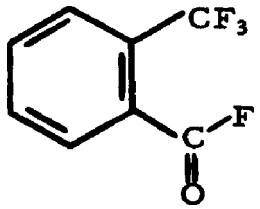
ki and de Kowaleski (51), and others (52-55). It is seen from Fig. 28-b that the AB part of the theoretical ABX_3 spectrum fits the observed splitting pattern in one member of the low-field doublet, with the two non-equivalent fluorine atoms representing the A and B nuclei and the methyl group in the heterocyclic ring as the three X nuclei.

If the high-field doublet was designated as being due to one isomer of the compound, the low-field doublet should be due to the other isomer. The fact that one isomer shows spin-spin interaction with the methyl protons while the other does not, although the two fluorines in both isomers are separated from the methyl group by the same number of bonds, forces one to conclude that the coupling mechanism involved in the isomer showing spin-spin interaction with the methyl group does not occur via the electronic bonds, but through some other mechanism. In other words, the spatial arrangement of the two fluorine atoms in both isomers, relative to the methyl group, influences the extent of spin-spin interaction, i.e. the spin-spin interaction occuring in the isomer responsible for the low-field doublet which shows coupling with the methyl group arises because of a "through-space" coupling mechanism. A similar spin-spin interaction is not observed in the isomer responsible for the high-field doublet because the geminal fluorine atoms are spatially oriented in such a way that "through-space" coupling with the methyl group is not possible.

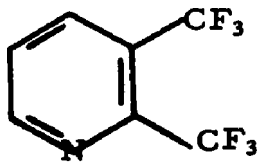
The idea of a "through-space" coupling mechanism is not a new one. It was first suggested by Petrakis and Sederholm (56) in their

interpretation of nmr fluorine-fluorine coupling constants in fluoro-substituted organic compounds. This suggestion was later substantiated by the closer examination of F-F coupling constants in a variety of organic compounds by Ng and Sederholm (57). According to this "through-space" coupling mechanism, fluorine atoms couple almost completely due to the direct overlap of orbitals on the two interacting fluorine nuclei of the compound exhibiting this particular coupling mechanism. In other words the spin-spin interaction comes about as a result of overlap of the electronic clouds of the fluorine atoms whenever the geometry of the molecule offers such oppurtunity, the interaction proceeding by way of an electronic structure where there is no bond per se.

The investigations of Ng and Sederholm (57) presented results of a crucial test for this "through-space" mechanism, in their study of the ^{19}F nmr spectra of molecules whose fluorine nuclei are in close spatial proximity and yet separated by at least five bonds so as to substantially eliminate any coupling through bonds. Their results for o-trifluoromethylbenzoylfluoride (I) and 2,3-bis-(trifluoromethyl)-pyridine (II) will be discussed briefly for the purpose of clarifying this concept of a "through-space" coupling mechanism.



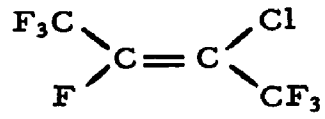
I



II

The ^{19}F nmr spectrum of I gave a doublet and a quartet, the

latter being at low-field. The coupling constant between the fluorine nuclei was found to be 10.9 Hz. The ^{19}F nmr spectrum of II showed two quartets, although not genuine 1:3:3:1 quartets, with a coupling constant of 12.8 Hz. These coupling constants for I and II can be compared with those obtained in trans-2-chloro-heptafluorobutene-2 (58),



The coupling constant between the two CF_3-groups (trans accross the double bond) is 1.3 Hz, which is considered normal for fluorine atoms separated by four saturated and one olefinic bonds. As the CF_3-groups in trans-2-chloro-heptafluorobutene-2 are trans accross the double bond, direct overlap between the electronic clouds of the fluorine atoms is virtually zero. In I, where the interacting fluorine nuclei are separated by one aromatic and four saturated bonds, the comparable through-bond coupling could be assumed to be of the order of 1 Hz as in the fluorinated-butene case. The 10.9 Hz coupling constant observed must be due almost entirely to "through-space" coupling, as the geometry of the molecule provides excellent opportunity for the direct overlap of the electronic clouds of the interacting fluorine nuclei. The same situation must exist in the spectrum of II, where the fluorine nuclei are separated by one aromatic and four saturated bonds such that any through-bond coupling should be no more than 1 or 2 Hz. The close spatial proximity of the fluorine nuclei affords enough overlap of their electronic clouds so that the observed coupling constant must be due almost entirely to

"through-space" coupling.

In the above discussion, long-range F-F coupling constants have been attributed to a "through-space" coupling mechanism. There have been reports by Roberts and co-workers (59), (60), and by Peake and Thomas (47) on long-range H-F spin-spin couplings exerted through five bonds. Such H-F spin-spin interactions have also been attributed to a "through-space" mechanism similar to that mentioned above. Therefore, the fact that the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$ shows two isomers with one isomer showing coupling between fluorine nuclei and methyl protons, while the other does not, although the two fluorines in both isomers are separated from the methyl group by the same number of bonds, is an indication that the "through-space" coupling mechanism is in operation in one isomer and not in the other. This apparent discrepancy is of course due to the difference in the spatial orientation of the geminal fluorines with respect to the methyl group in the two isomers. In view of these, it is therefore safe to assign the low-field doublet to the isomer with the two fluorine atoms directed towards the methyl group as shown in Fig. 27-a, whereby the fluorines are in a favorable orientation for their electronic clouds to overlap with the electronic clouds of the methyl protons such that coupling "through-space" is observed. The high-field doublet obviously belongs to the other isomer with the fluorine atoms directed away from the methyl group. In this isomer no overlap between the fluorine and proton electronic clouds is possible, and hence no evidence of spin-spin coupling is observed. It

is interesting to note that in the isomer exhibiting coupling with the methyl group, the nearest H-F distance as measured from a model is about 2.2 A°, well within the internuclear distance considered by Ng and Sederholm (57) as essential for the application of the "through-space" coupling mechanism.

An interesting feature of the ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9\text{-}NPF_2$ is that it showed no major changes in form as the temperature increased from -45°C to +170°C. The only variation noted was a change in the chemical shift difference between the low-field and high-field doublets. The difference was 102 Hz at -45°C and 82 Hz at +170°C, but the convergence of the peaks was not observed over this temperature range. The data indicate two isomers separated by a relatively large energy barrier. The source of the barrier, whether electronic, steric, or both is not given by the data. Additional information on the nature of the barrier is provided by a study of the compounds which follow.

F. THE ^{19}F NMR SPECTRUM OF $2\text{-}(CH_3)C_5H_9NPF_2.BH_3$

The 94.1 MHz ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2.BH_3$ at room temperature (Fig. 29) consists of two sets of doublets:

a) a low-field doublet (J_{PF} = 1185 ± 2 Hz) at δ = +73.1 ± 0.2 ppm. ($CFCl_3$)

b) a high-field doublet (J_{PF} = 1185 ± 2 Hz) at δ = +73.9 ± 0.2 ppm. ($CFCl_3$).

Under higher resolution (Fig. 30), each member of the low-field doublet consists of a 1:1:3:3:4:4:4:4:3:3:1:1 twelve-line multiplet, and each member of the high-field doublet consists of a 1:3:4:4:3:2 sextet.

Figure 29

94.1 MHz ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_9NPF_2 . BH_3$

Room Temperature

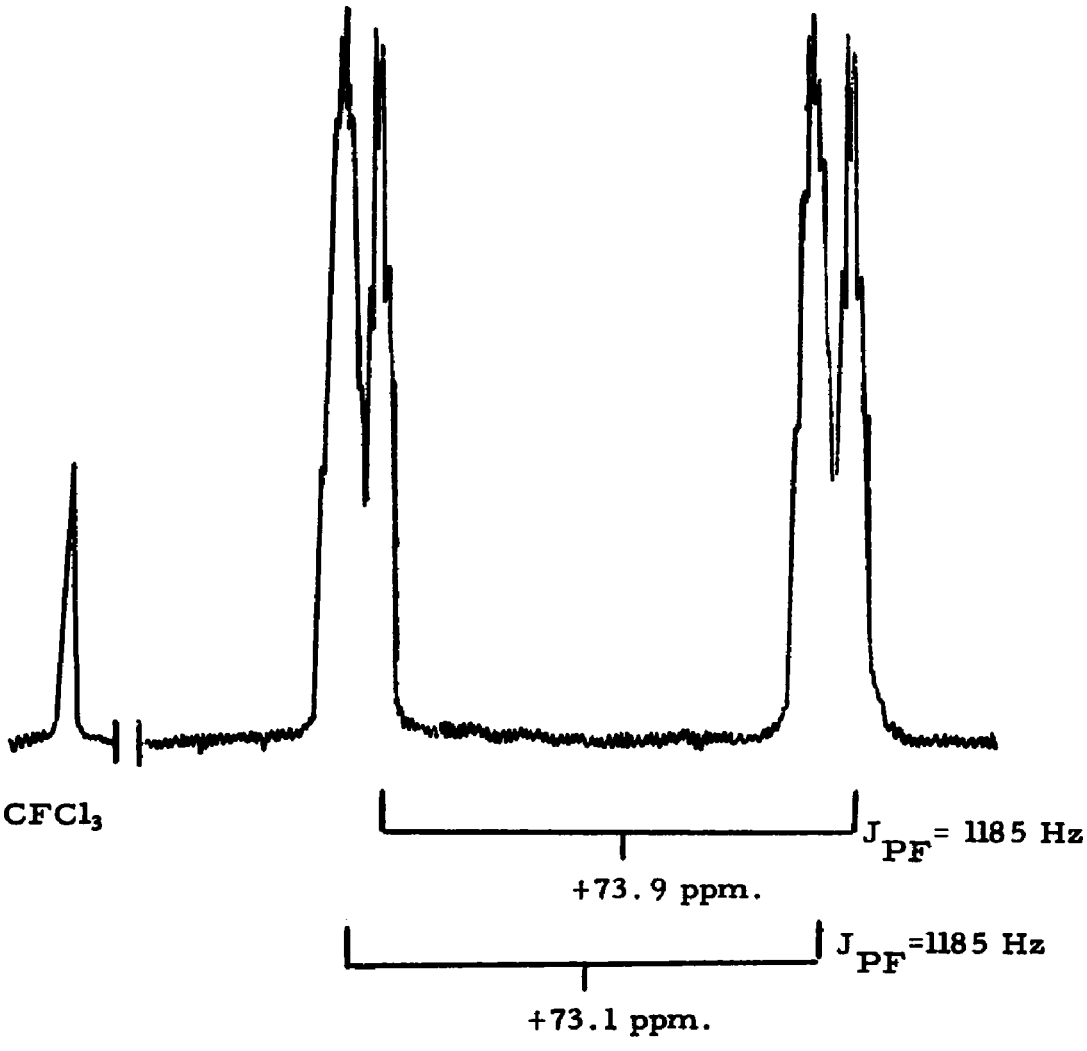
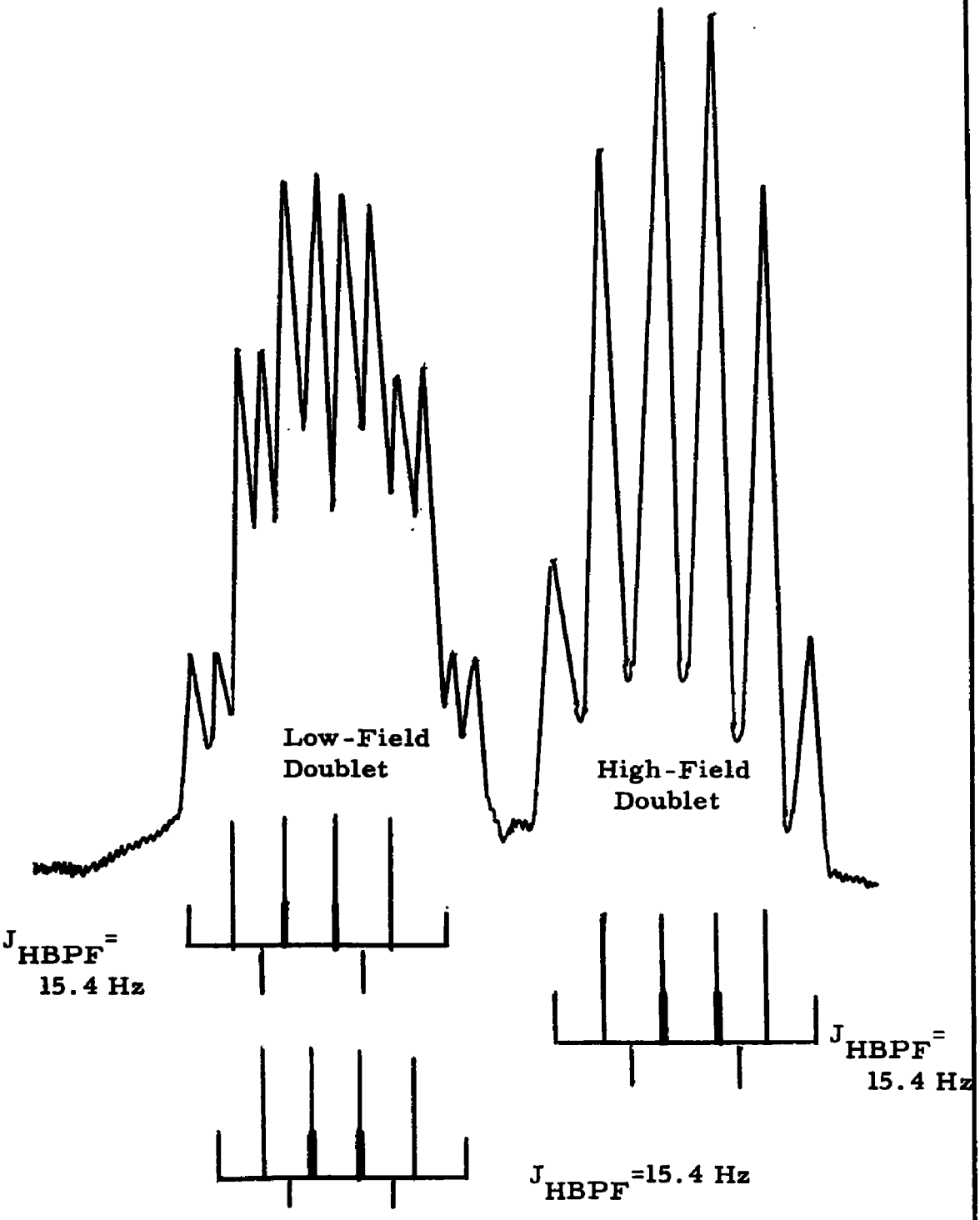


Figure 30

A Member of the High-Field Doublet and Low-Field Doublet in the ^{19}F NMR Spectrum of $2-(CH_3)C_5H_9NPF_2 \cdot BH_3$



The splitting pattern observed in each member of the high-field doublet could arise from two central peaks of an AB quartet separated by 31.3 Hz, with the outer bands of the quartet not distinguished from the noise level, just as it was interpreted in the case of 2-(CH_3)-$C_5H_9NPF_2$. On account of the two non-equivalent fluorine atoms, each of these central peaks could then be split into an overlapping 1:3:3:1 quartet due to coupling with the borane protons (J_{HBPF} = 15.4 ± 0.1 Hz). The 31.3 Hz separation between the central peaks is ruled out as a coupling constant by the fact that it is magnetic field dependent, showing up as 18 Hz in the ^{19}F nmr of the same compound taken with a 56.4 MHz oscillating radiofrequency.

The splitting pattern in each member of the low-field doublet appears to be an overlapping of two six-line multiplets of the same splitting pattern as that seen in the high-field doublet. An examination of the model of the compound reveals a possibility of three isomers, as shown in Fig. 31. One isomer has the geminal fluorines inclined towards the methyl group, and two very closely related isomers differ only in the sense that one has the fluorines above the P-N-(C_2) plane and the other below the same plane. A fourth isomer with the fluorines inclined away from the methyl group is not possible due to a severe steric interaction which would exist between the incoming BH_3-group and the methyl group. Therefore, it is now possible to assign the high-field doublet to the first isomer considered (Fig. 31-a), and the low-field doublet (actually two sets of closely-spaced doublets) to the last

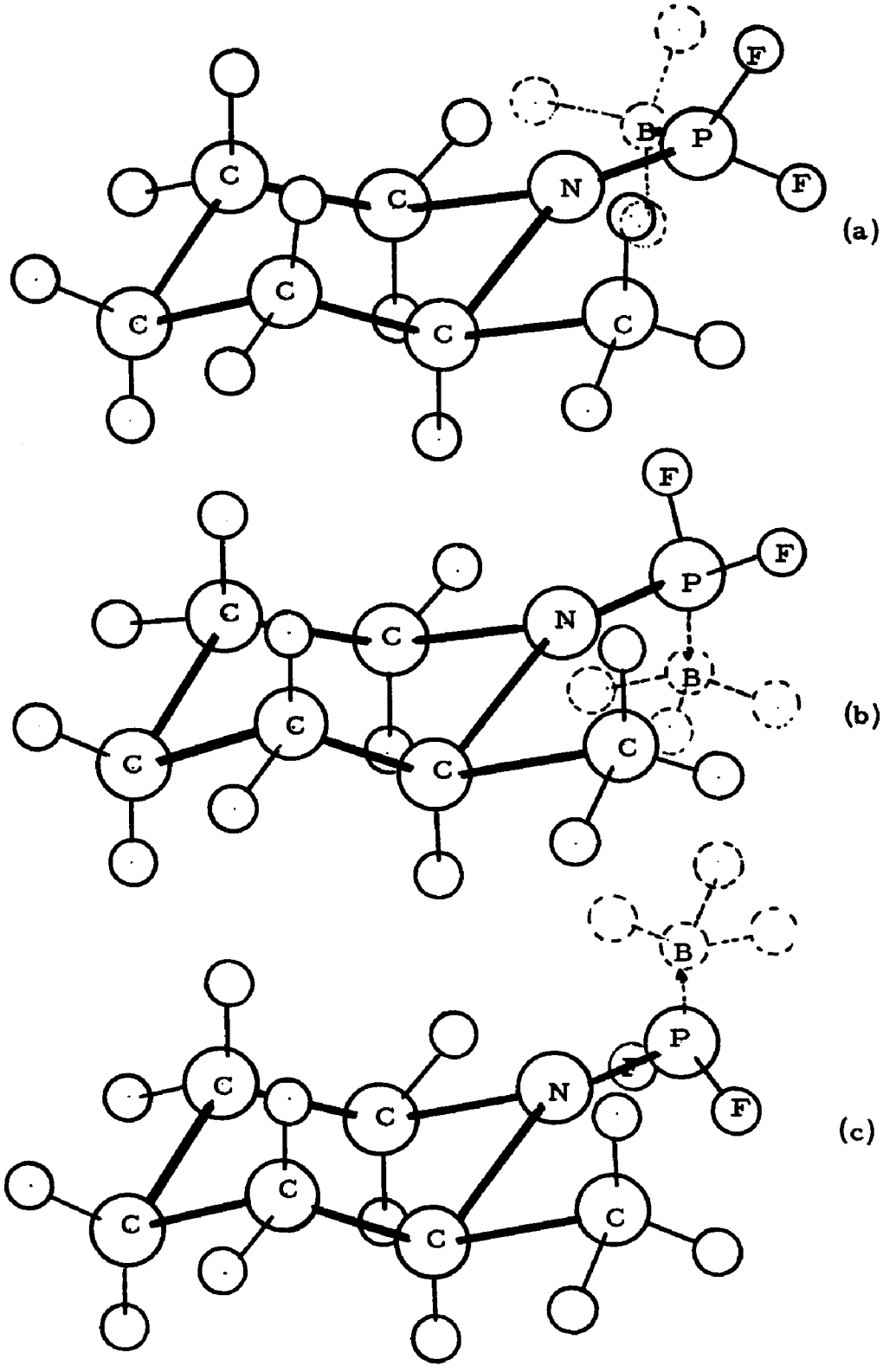


Figure 31

Three Isomers of 2-$(CH_3)C_5H_9NPF_2 . BH_3$

two isomers mentioned (Figs. 31-b and 31-c). The same basic splitting patterns are still present in each of these two closely-spaced doublets (with a chemical shift difference of 6.7 Hz), namely two central peaks of an AB quartet separated by 31.3 Hz, each member of which is split into overlapping 1:3:3:1 quartet with $J_{HBPF} = 15.4 \pm 0.1$ Hz.

IV - (2-METHYLPIPERIDYL)CHLOROFLUOROPHOSPHINE AND ITS BORANE ADDUCT

A. SYNTHESIS OF (2-METHYLPIPERIDYL)CHLOROFLUOROPHOSPHINE AND ITS BORANE ADDUCT

(2-methylpiperidyl)chlorofluorophosphine, $2\text{-}(CH_3)C_5H_9NPFCl$, was prepared by the reaction of 2-methylpiperidine and fluorodichlorophosphine in ether:

$$2 \quad 2\text{-}(CH_3)C_5H_{10}N + PFCl_2 \longrightarrow 2\text{-}(CH_3)C_5H_9NPFCl + 2\text{-}(CH_3)C_5H_{10}N.HCl \ .$$

The identity of the solid reaction product, the hydrochloride of 2-methylpiperidine, was established by comparing its Debye-Scherer X-ray diffraction pattern with that of $2\text{-}(CH_3)C_5H_{10}N.HCl$ formed from the reaction of 2-methylpiperidine and PCl_3.

The infrared spectrum of $2\text{-}(CH_3)C_5H_9NPFCl$ is shown in Fig. 32, and it can be compared with the infrared spectrum of 2-methylpiperidine (Fig. 18). It is evident that the N-H stretching frequency (3280 cm^{-1}) is not present, and that there is a strong peak at 775 cm^{-1} indicative of the P-F group as observed by Fleming (4) in $((CH_3)_2N)_2PF$. Chloride analysis confirms the composition of the compound : % Cl calculated = 19.13; % Cl found = 19.30.

The borane adduct was prepared in the usual way by the reaction of the free ligand and diborane in ether at -78°C

$$2\text{-}(CH_3)C_5H_9NPFCl + \tfrac{1}{2} B_2H_6 \rightarrow 2\text{-}(CH_3)C_5H_9NPFCl.BH_3$$

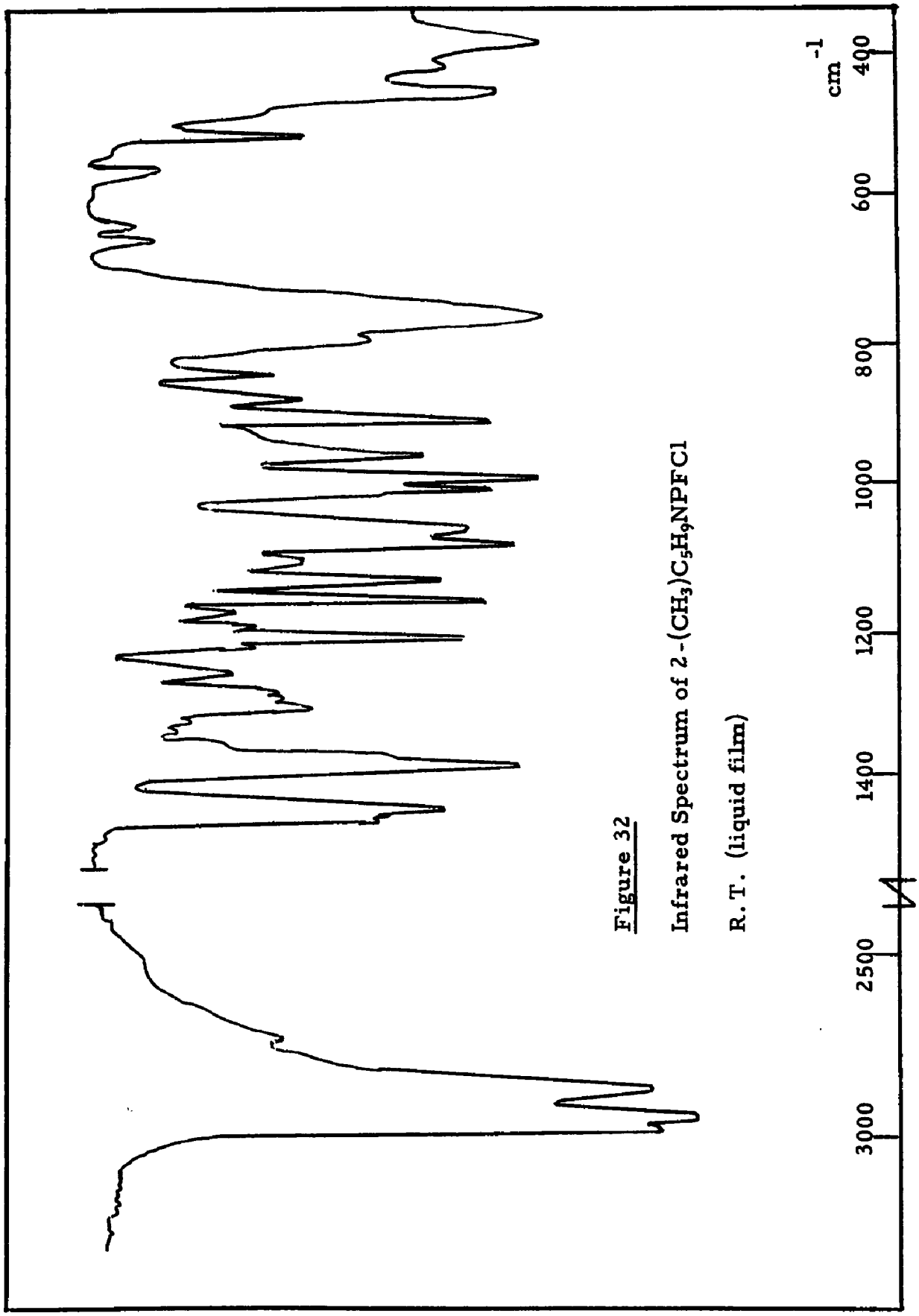


Figure 32

Infrared Spectrum of 2-$(CH_3)C_5H_9NPFCl$

R.T. (liquid film)

Its infrared spectrum (Fig. 33) shows the characteristic B-H stretching frequencies at 2410 and 2340 cm^{-1}. Chloride analysis shows %Cl = 17.89 compared to %Cl calculated = 17.75.

Table VII gives the infrared absorption frequencies of 2-methylpiperidine, 2-$(CH_3)C_5H_9NPFCl$, and 2-$(CH_3)C_5H_9NPFCl.BH_3$ at room temperature for the sake of comparison.

B. THE ^{31}P NMR SPECTRA OF 2-$(CH_3)C_5H_9NPFCl$ AND 2-$(CH_3)C_5H_9NPFCl.BH_3$

The 40.4 MHz ^{31}P nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ at room temperature (Fig. 34) shows as a 1:1 doublet due to coupling of the phosphorus nucleus with the lone fluorine nucleus, in contrast to the 1:2:1 triplet splitting seen in the difluoro-analogue. The chemical shift is measured to be $\delta = -166.2 \pm 0.5$ ppm. (H_3PO_4), and a coupling constant of $J_{FP} = 1180 \pm 2$ Hz can be calculated.

The borane adduct gives a similar ^{31}P nmr spectrum at 0°C (Fig. 35). It consists of a 1:1 doublet, $\delta = -143.1 \pm 0.5$ ppm. (H_3PO_4) and $J_{FP} = 1180 \pm 2$ Hz. Each member of this doublet is a multiplet which is poorly resolved, presumably due to additional coupling with the boron nucleus. However, due to the rather high noise level, no certainty in the multiplicity of each member of the big doublet could be discerned.

The ^{31}P nmr spectra of 2-$(CH_3)C_5H_9NPFCl$ and its borane adduct are consistent with the presence of only one fluorine atom bonded to the phosphorus, in each of these compounds.

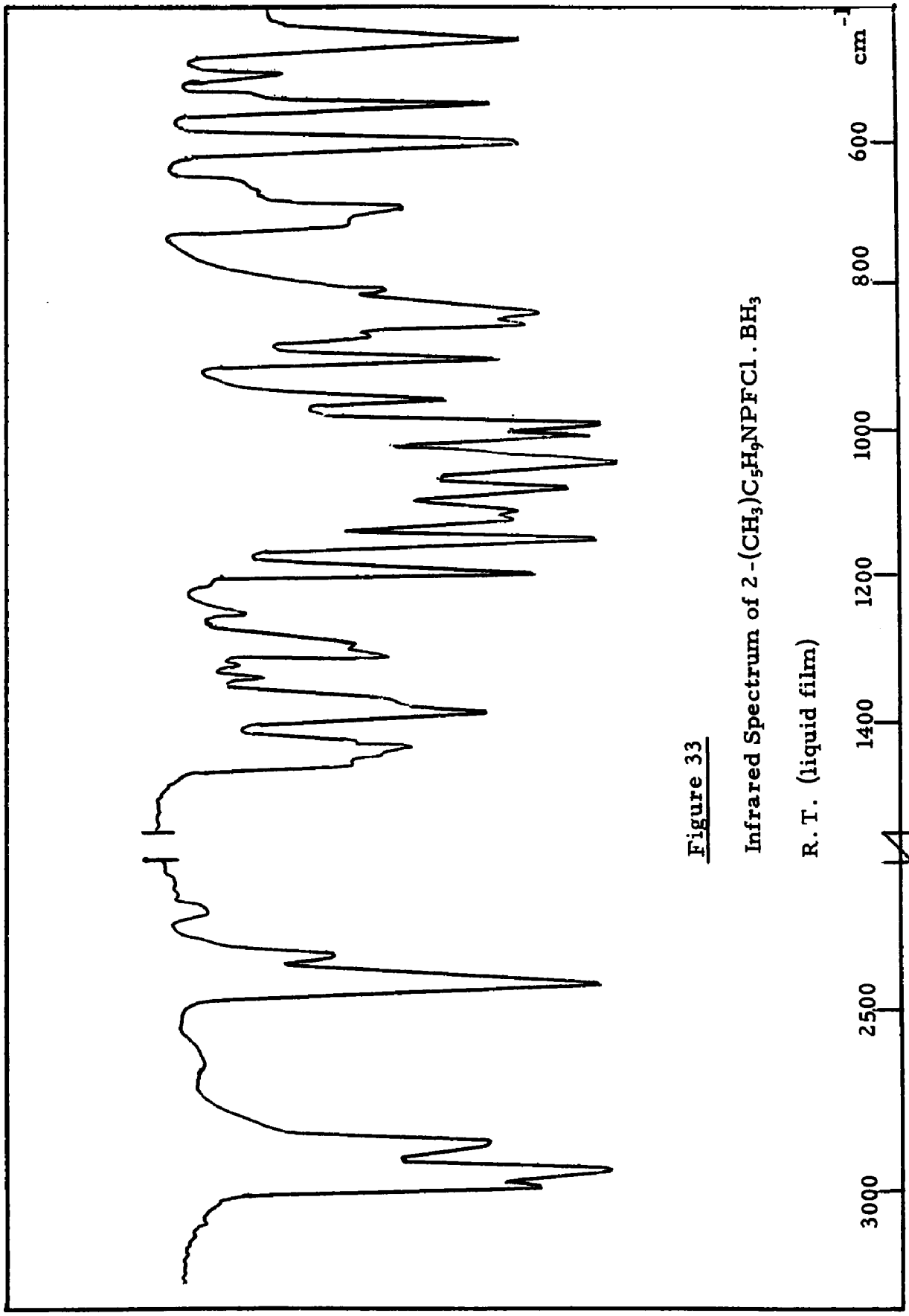


Figure 33

Infrared Spectrum of 2-$(CH_3)C_5H_9NPFCl.BH_3$

R.T. (liquid film)

Table VII - Infrared Absorption Frequencies of 2-Methylpiperidine, 2-$(CH_3)C_5H_9NPFCl$, and 2-Methylpiperidylfluorochlorophosphineborane

2-Methylpiperidine	2-$(CH_3)C_5H_9NPFCl$	2-$(CH_3)C_5H_9NPFCl.BH_3$
3280 w, b	2980 s	2970 m
2950 s	2950 s	2960 s
2860 m	2880 s	2860 m
2800 m	2750 w, sh	2410 s
2730 w	;470 m, sh	2340 w
2600 vw	1445 m	2220 vw
1460 m, sh	1390 s	1460 w, sh
1440 m	1350 w	1440 m
1380 m	1335 w, sh	1380 m
1335 m	1310 m	1340 vw
1330 m	1290 m	1330 vw
1320 m	1265 w	1310 w
1300 w, sh	1230 w, sh	1296 w, sh
1260 w	1215 m	1260 vw
1225 w	1200 w	1200 m
1155 w, sh	1185 w	1160 m
1120 m	1160 m	1135 w
1080 w	1140 m	1110 w
1055 vw, sh	1120 m	1085 m
1050 vw, sh	1085 m	1045 m
1000 vw	1065 m	1010 m
970 w	1015 m	995 m
895 w	1000 m	965 w
810 w	970 w	910 m
725 s	915 m	880 w, sh
550 w	890 w	860 m
475 w	860 w	849 m
	810 w, sh	810 w, sh
	775 s, b	800 vw, sh
	690 w	720 vw, sh
	660 vw	700 w
	570 w	680 vw, sh
	520 w	615 m
	465 m	560 m
	430 w, sh	515 w
	400 w	470 m

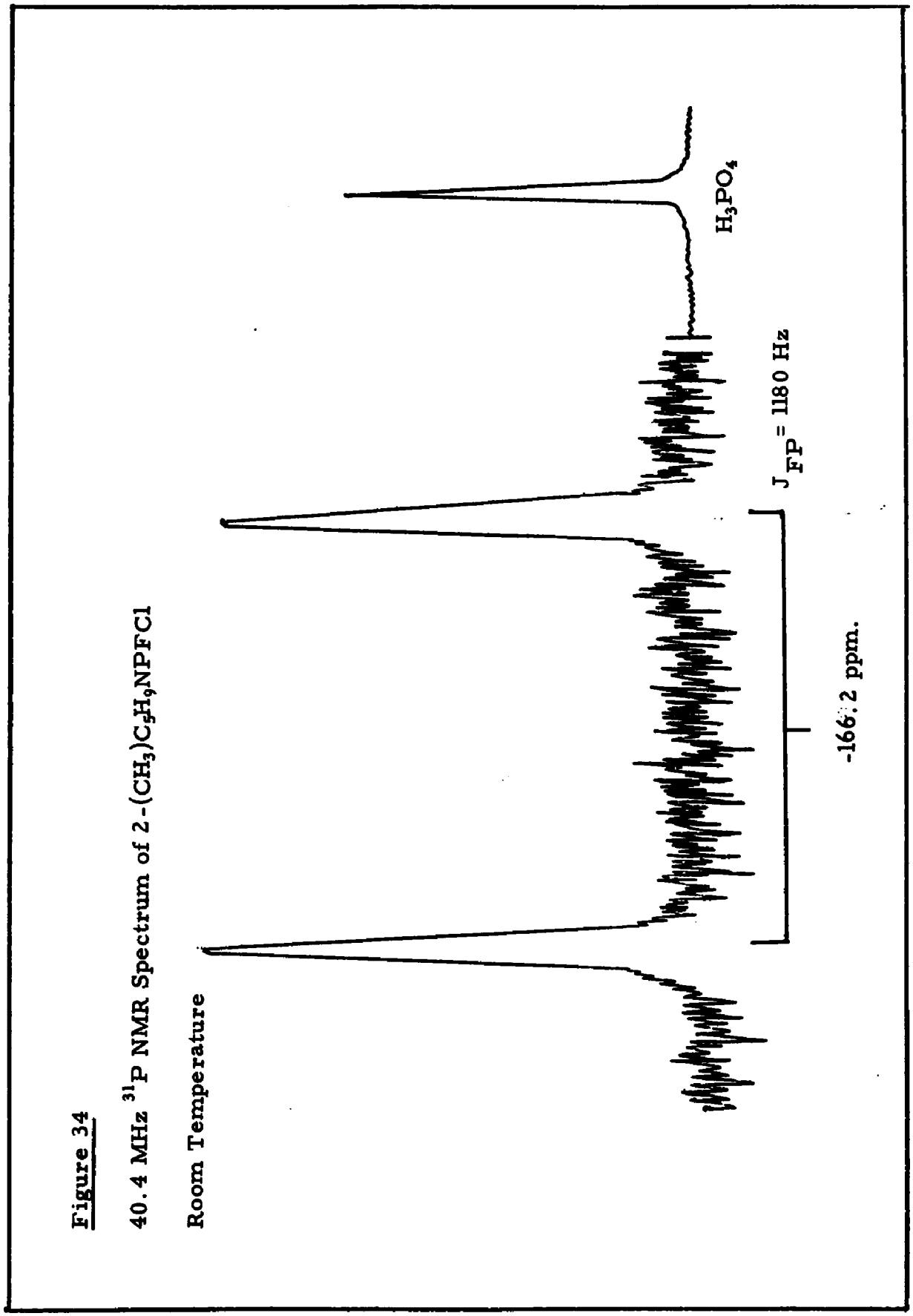


Figure 34

40.4 MHz ^{31}P NMR Spectrum of 2-$(CH_3)C_5H_9NPFCl$

Room Temperature

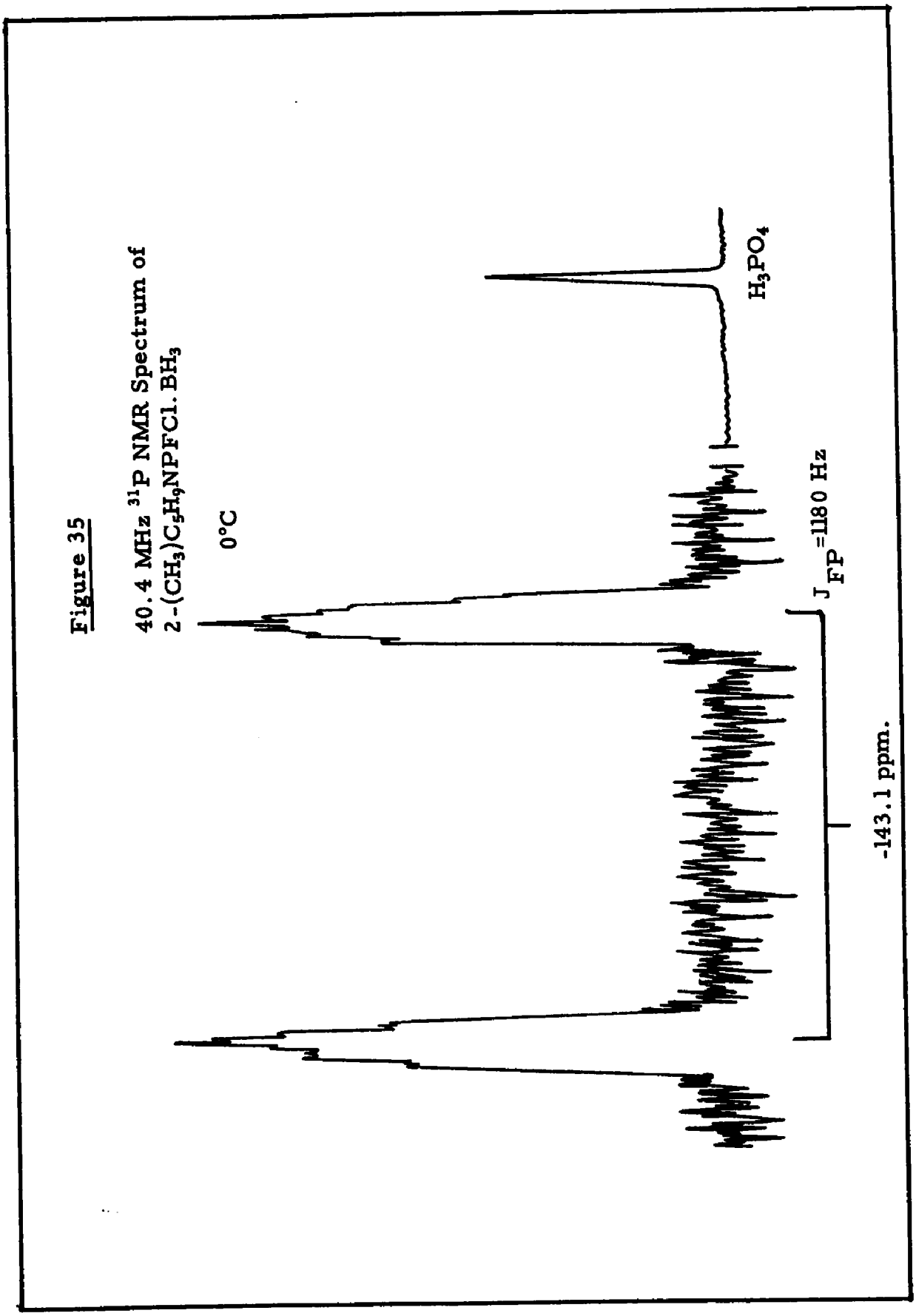


Figure 35
40.4 MHz ^{31}P NMR Spectrum of
2-$(CH_3)C_5H_9NPFCl.BH_3$
0°C
H_3PO_4
J_{FP}=1180 Hz
-143.1 ppm.

C. THE ^{11}B NMR SPECTRUM OF 2-$(CH_3)C_5H_9NPFCl.BH_3$

This compound starts to decompose at the ambient temperature of the nmr probe, hence its various nmr spectra were taken at 0°C. Its 32.1 MHz ^{11}B nmr spectrum (Fig. 36) shows a 1:3:3:1 quartet at δ = + 124.2 ± 0.5 ppm. from $B(CH_3)_3$. Each member of this quartet is split into a doublet. The 1:3:3:1 quartet is due to coupling of the boron nucleus with the three equivalent borane protons (J_{HB} = 102 ± 1 Hz). Each 1:1 doublets is a result of P-B coupling (J_{PB} = 70 ± 1 Hz).

D. THE ^1H NMR SPECTRA OF 2-$(CH_3)C_5H_9NPFCl$ AND 2-(CH_3)-$C_5H_9NPFCl.BH_3$

The room temperature 60 MHz ^1H nmr spectrum of 2-(CH_3)-C_5H_9NPFCl (Fig. 37) consists of

a) a doublet of doublets at δ = -1.22 ± 0.02 ppm. (TMS)

b) a broad but intense peak at δ = -1.52 ± 0.02 ppm. (TMS)

c) a broad peak showing some splittings centered at δ = -3.12 ± 0.03 ppm. (TMS)

d) a broad hump centered at δ = -3.78 ± 0.04 ppm. (TMS).

The integrated area ratios of these peaks are respectively 3:6:2:1.

On the basis of their integrated areas, assignments of these nmr signals is straightforward. The initial doublet at δ = -1.22 ppm. corresponds to the methyl protons split by the methine proton giving a J_{HCCH} value of 6.9 ± 0.1 Hz which is a normal geminal H-C-CH_3 coupling constant (61-63). Further splitting of this basic doublet by

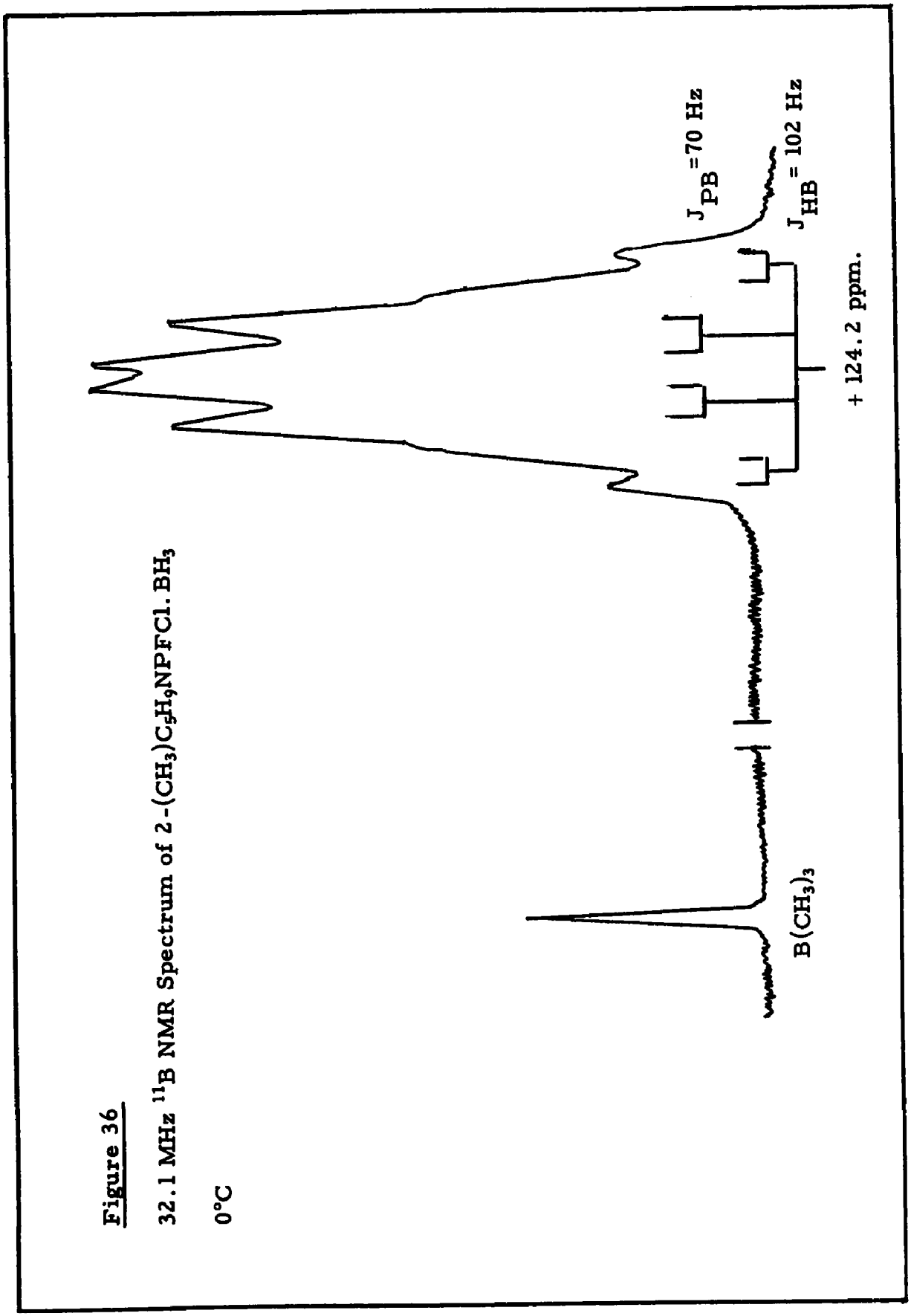


Figure 36

32.1 MHz ^{11}B NMR Spectrum of 2-$(CH_3)C_5H_9NPFCl.BH_3$

0°C

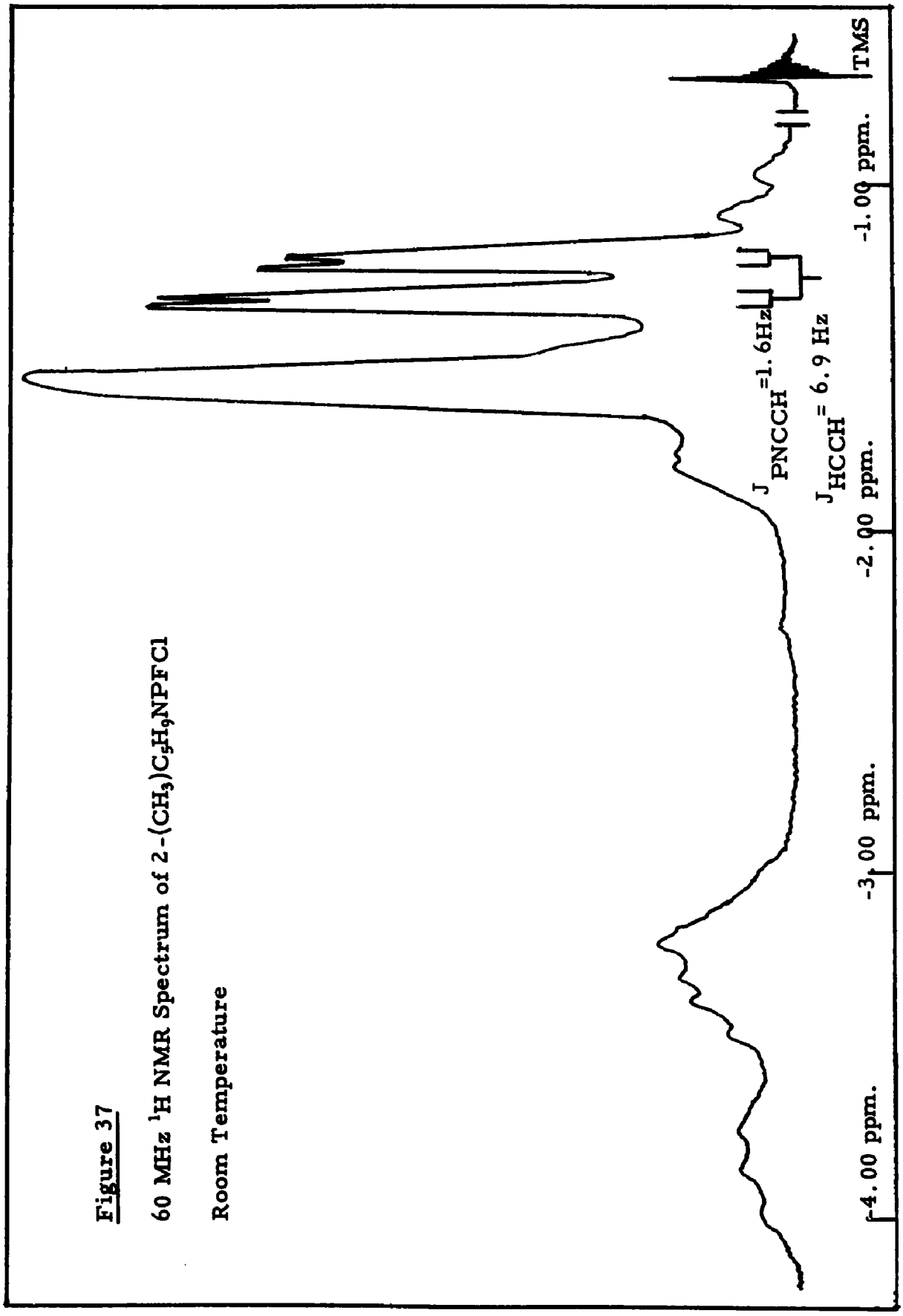


Figure 37

60 MHz ^{1}H NMR Spectrum of 2-$(CH_3)C_5H_9NPFCl$

Room Temperature

the phosphorus nucleus into another doublet gives a coupling constant, $J_{PNCCH} = 1.6 \pm 0.1$ Hz, which is in accord with the value of J_{PNCCH} found in $2\text{-}(CH_3)C_5H_9NPF_2$. The lowest field peak at $\delta = -3.78$ ppm. corresponds to the α-proton in an equatorial orientation. The peak at $\delta = -3.12$ corresponds to the two axial protons α to the nitrogen. The broad but intense peak at $\delta = -1.52$ ppm. takes care of the rest of the protons in the piperidine ring.

The proton nmr spectrum of $2\text{-}(CH_3)C_5H_9NPFCl$ did not show any temperature dependence in the range -65°C to +100°C, much like the proton nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$.

The 60 MHz ^1H nmr spectrum of the borane adduct shows (Fig. 38)

a) a doublet of doublets at $\delta = -1.23 \pm 0.02$ ppm. (TMS)

b) an intense, broad peak at $\delta = -1.55 \pm 0.03$ ppm. (TMS)

c) a broad peak centered at $\delta = -3.22 \pm 0.03$ ppm. (TMS)

d) a very broad peak centered at $\delta = -3.92 \pm 0.04$ ppm. (TMS).

Their respective integrated area ratios are 3:6:2:1.

At much higher gain, the borane protons are observed at $\delta = -0.78 \pm 0.02$ ppm. (TMS) as a severely broadened 1:1:1:1 quartet due to coupling with the boron nucleus. Two members of this quartet, $J_{BH} = 100 \pm 1$ Hz, are overlapped by the methyl protons' signal.

Interpretation of the spectrum can be made in a fashion similar to that made for $2\text{-}(CH_3)C_5H_9NPFCl$. The methyl protons show up as a doublet at $\delta = -1.23$ ppm. due to coupling with the lone methine

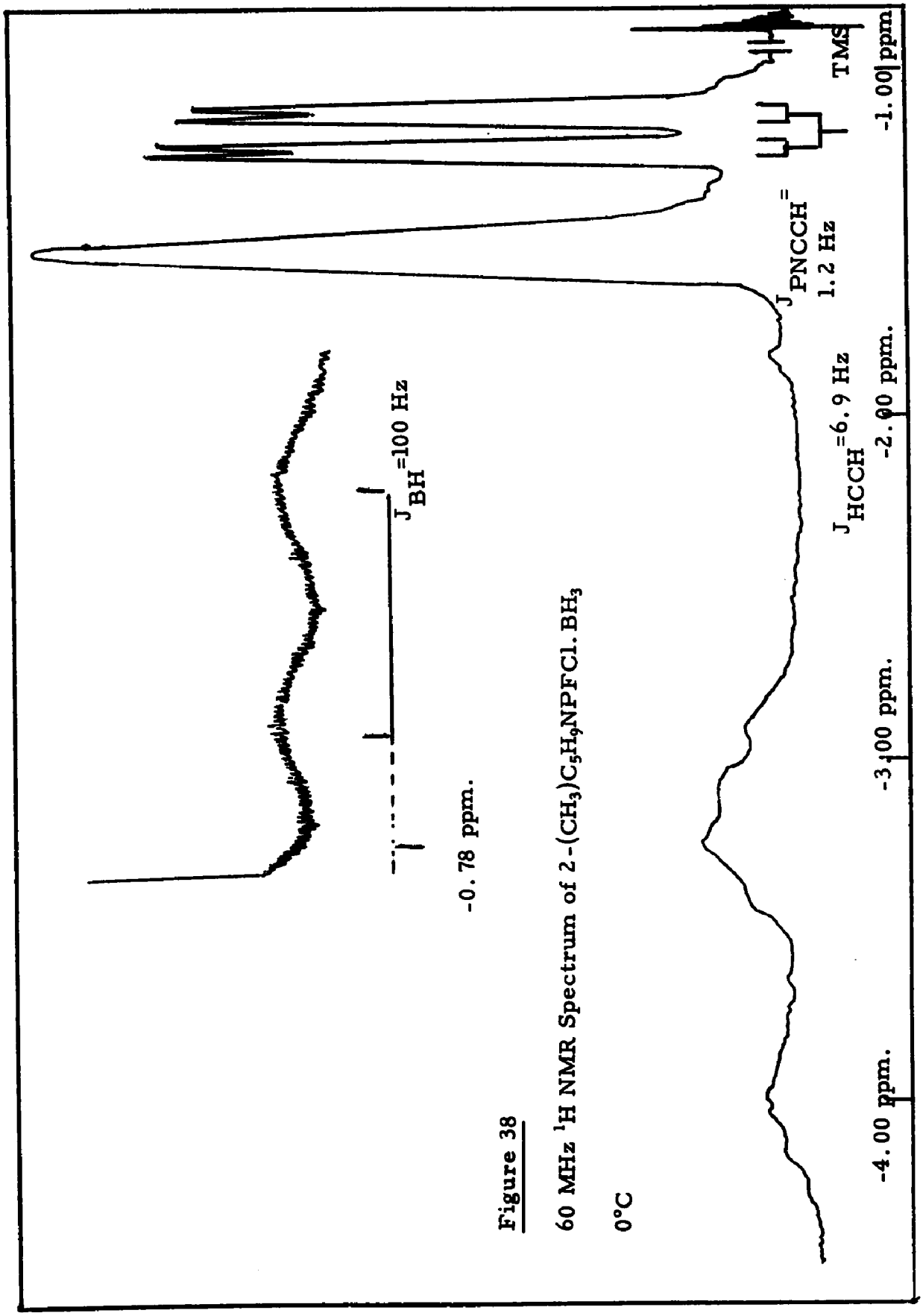


Figure 38

60 MHz ^{1}H NMR Spectrum of 2-$(CH_3)C_5H_9NPFCl.BH_3$

0°C

proton to give a $J_{HCCH} = 6.9 \pm 0.1$ Hz, and further split by coupling with the phosphorus nucleus, $J_{PNCCH} = 1.2 \pm 0.1$ Hz. Again, the lowest field peak at $\delta = -3.92$ ppm. is assigned to the lone equatorial α-proton, and the peak at $\delta = -3.12$ ppm. is assigned to the two remaining α- protons in axial positions. At $\delta = -1.55$ ppm. is a broad peak that represents the other ring protons. The deshielding effect of the BH_3-group coordinated through the phosphorus, on the electronic environment of the α -protons is manifested in the much lower field nmr signals of these protons when compared to their corresponding nmr signals in 2-$(CH_3)C_5H_9NPFCl$.

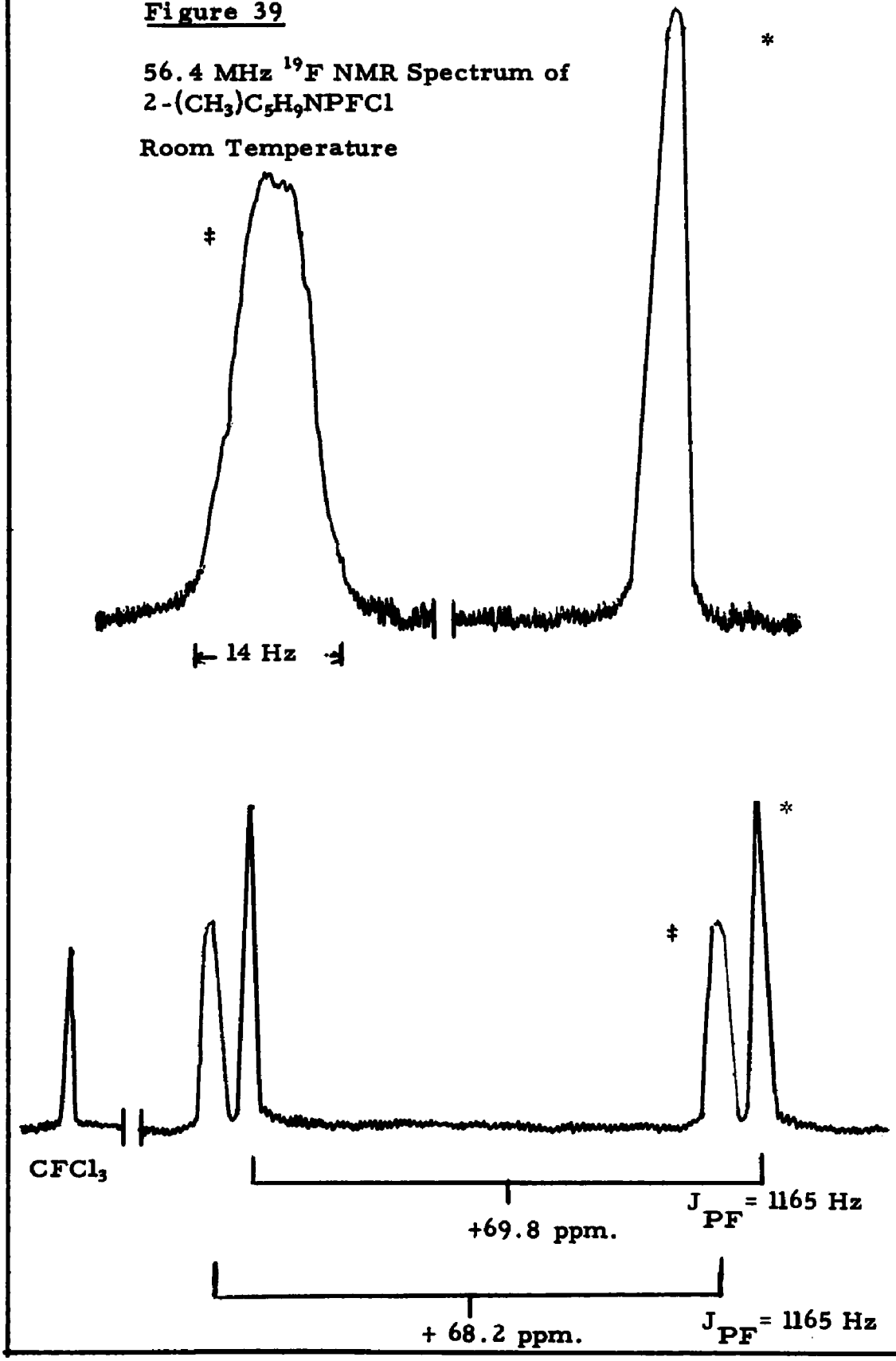
E. THE ^{19}F NMR SPECTRUM OF 2-$(CH_3)C_5H_9NPFCl$

As discussed earlier, the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9N$-PF_2 consists of two sets of doublets, a high-field doublet at $\delta = +66.7$ ppm. ($CFCl_3$), and a low-field doublet at $\delta = +65.2$ ppm. ($CFCl_3$). That these nmr signals are not due to the compound existing only as one isomer with two non-equivalent fluorines giving distinct signals, was ruled out by the observation that the area ratio of the high-field doublet to the low-field doublet changes with temperature. The ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ provides further evidence that 2-$(CH_3)C_5H_9$-NPF_2 does exists as more than one isomer. If this were not the case and one maintains that 2-$(CH_3)C_5H_9NPF_2$ exists as one isomer exclusively at room temperature, then the ^{19}F nmr spectrum of the closely related 2-$(CH_3)C_5H_9NPFCl$ would be expected to give only one set of doublets

Figure 39

56.4 MHz ^{19}F NMR Spectrum of
2-$(CH_3)C_5H_9NPFCl$

Room Temperature



corresponding to a spin coupling between the lone fluorine nucleus and the phosphorus nucleus. However, the 56.4 MHz ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ at room temperature (Fig. 39) shows two sets of 1:1 doublets:

a) a high-field doublet at δ = + 69.8 ± 0.2 ppm. ($CFCl_3$) with a J_{PF} value of 1165 ± 2 Hz

b) a low-field doublet at δ = +68.2 ± 0.2 ppm. ($CFCl_3$), J_{PF} = 1165 ± 2 Hz.

At higer resolution each member of the high-field doublet remains as a singlet. Members of the low-field doublet on the other hand, show up as a broad, unresolve multiplet with a line width of about 14 Hz, suggesting a splitting pattern similar to that of the low-field doublet of the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$. The poor resolution which each of the member of the low-field doublet shows could be attributed to the presence of the chlorine nucleus which has a rather appreciable quadrople moment.

The non-equivalence of the fluorine atoms in each of the two isomers of 2-$(CH_3)C_5H_9NPF_2$ is further established by the fact that the members of the high-field doublet is a singlet even at higher resolution in 2-$(CH_3)C_5H_9NPFCl$ which has only one fluorine atom in each isomer. In the former compound, having two magnetically non-equivalent fluorines in each isomer, the high-field doublet is shown to consist of an apparent doublet separated by 9.8 Hz. This doublet really represents the central lines of the expected AB quartet. In the case of only one

fluorine, a singlet is expected and observed.

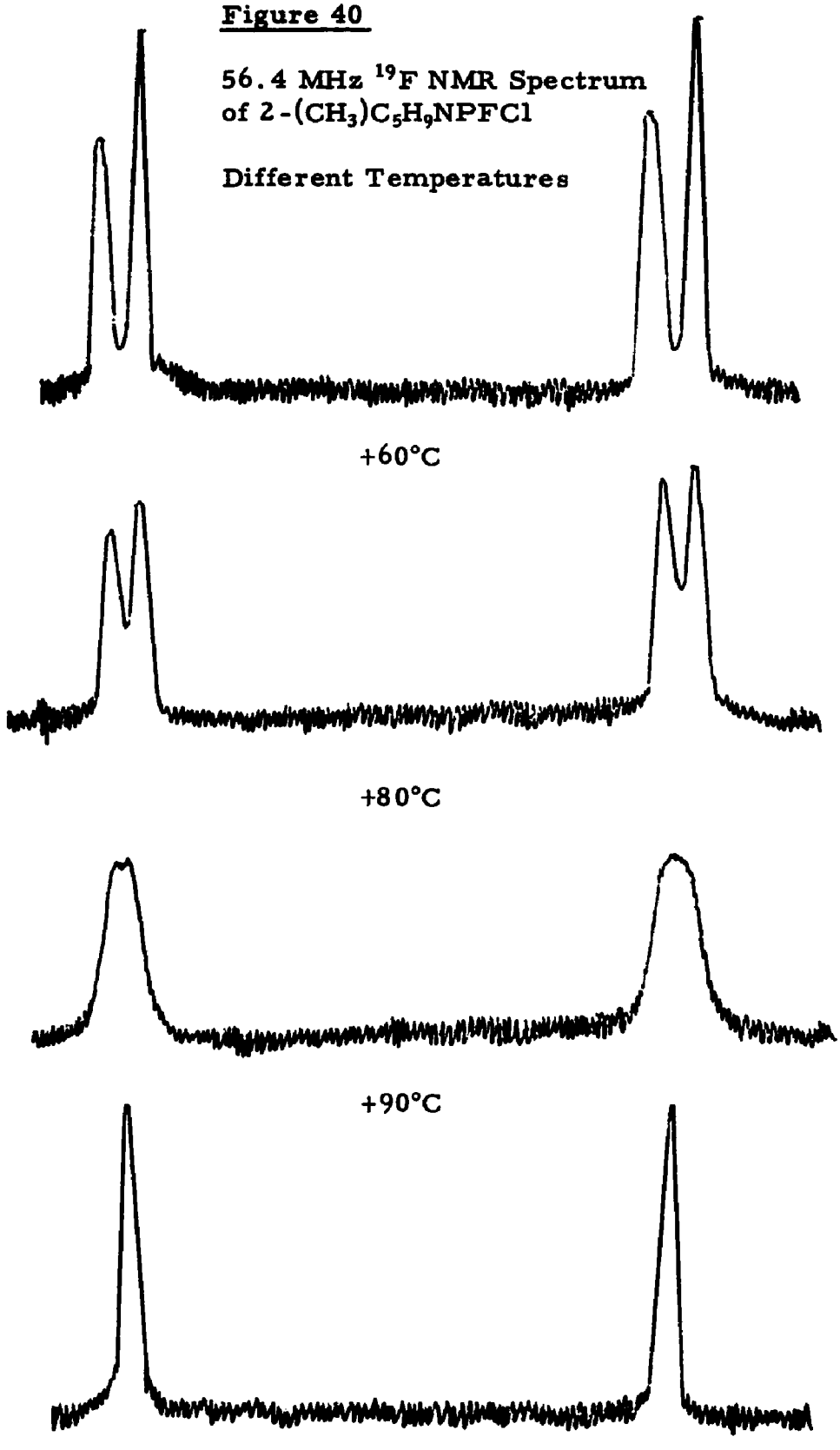
From the observations made on its ^{19}F nmr spectrum, it is clear that 2-$(CH_3)C_5H_9NPFCl$ exists also as two isomers at room temperature. And like 2-$(CH_3)C_5H_9NPF_2$, one could attribute the two sets of doublets to these two isomers. The high-field doublet corresponds to the isomer with the fluorine and the chlorine atoms on the phosphorus directed away from the methyl group in the piperidine ring; and the low-field doublet corresponds to the isomer with the fluorine and chlorine atoms directed towards the methyl group allowing some "through-space" coupling to exist as evidenced by the unresolved multiplicity that appears at higher resolution.

A temperature dependence study on the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ was undertaken, and the results are shown in Fig. 40. From -20°C to about +40°C, the chemical shift difference between the high-field and low-field doublets remains essentially constant. At temperatures greater than +40°C, the two peaks start to broaden, until coalescence is observed at +90°C. Above +90°C, the solitary doublet, with a chemical shift intermediate between the two original sets of doublets, sharpens. This temperature dependence of the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ offers unequivocal evidence that at temperatures greater than +90°C, the fluorine atoms in the two isomers of the compound are rendered equivalent by a rotation about the P-N bond, such that the observed spectrum at these temperatures represent an average of the two originally distinct nmr signals. Such rotation contrasts

Figure 40

56.4 MHz ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_9NPFCl$

Different Temperatures



sharply with the lack of rotation noted for 2-$(CH_3)C_5H_9NPF_2$ over the temperature range -45°C to +170°C.

The experimental activation energy, E_a, identified with the barrier height restricting internal rotation about the P-N bond, can be obtained from measurements of the rate of internal rotation at a series of temperatures *. Rogers and Woodbrey (20) have found that the most precise measure of τ, the mean lifetime of an exchanging nucleus in a given environment, is the line-shape parameter r, given by the intensity ratio of the maximum to central minimum in a pair of overlapping lines. r is related to τ by the relation

$$\tau \delta_\nu = \frac{1}{\pi \sqrt{2}} \left(r + \left(r^2 - r \right)^{\frac{1}{2}} \right)^{\frac{1}{2}}$$

where δ_ν is the internal chemical shift difference between the two nmr signals. Figs. 41-a and 41-b give the ^{19}F nmr spectrum of one member of each of the high-field and low-field doublets at different temperatures, from which values of r, and hence τ can be calculated (Table VIII).

Fig. 42 shows the plot of log $1/2\tau$ vs. $1/T$. From this plot, an energy of activation, E_a, of 6.4 ± 0.4 kcal/mole, and log A = 6.2 ± 0.2 could be obtained. The free energy of activation, ΔG^*, associated with a

* Data are fitted to the Arrhenius equation

$$\text{Log } 1/2\tau = \log A - E_a / 2.303\ RT$$

where τ has its usual meaning of the mean lifetime of an exchanging nucleus in a given environment, and A is a frequency factor representing the number of times per second the molecule tries to penetrate the barrier to rotation.

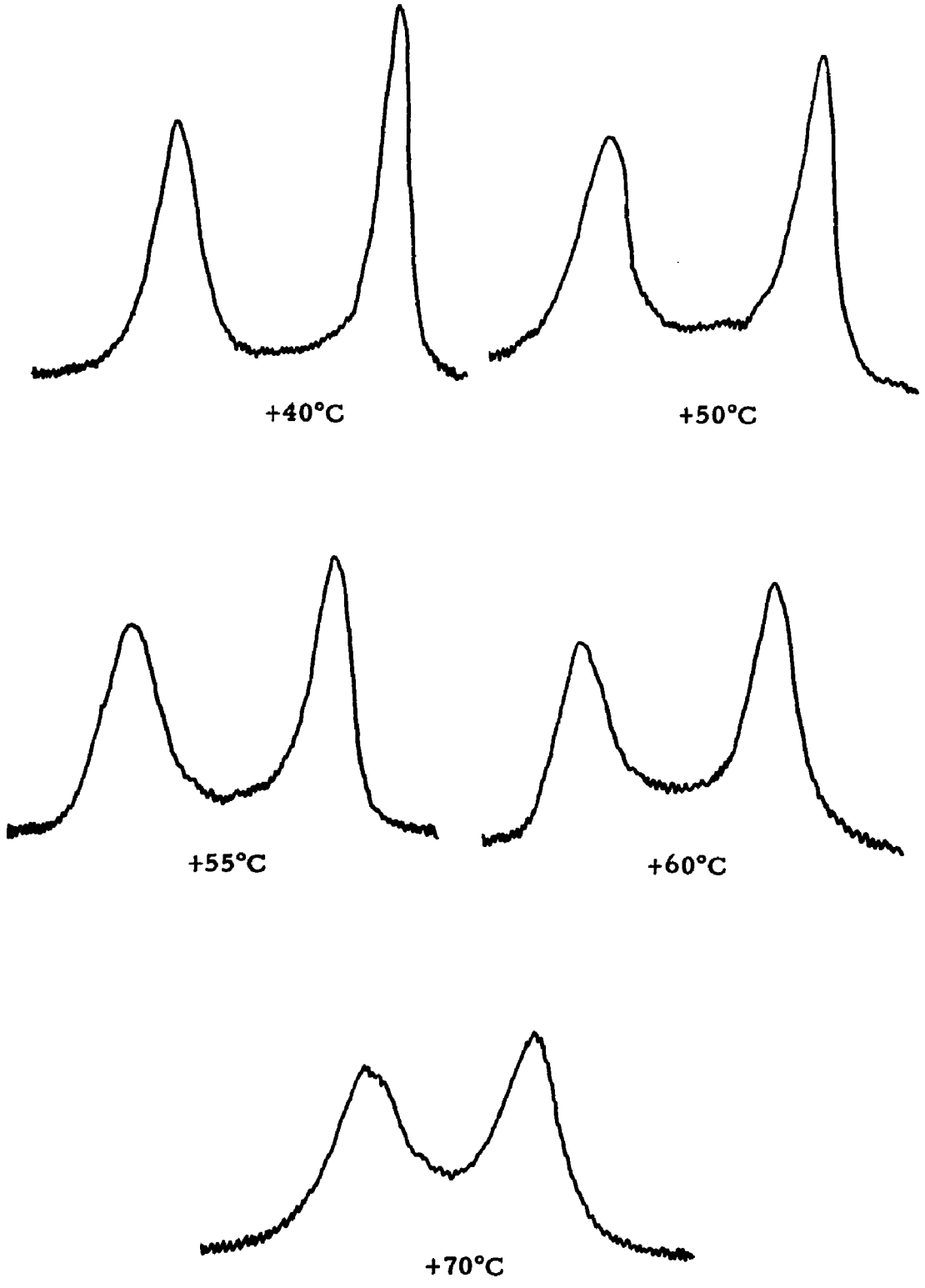


Figure 41

A Member of Each of the High- and Low-Field Doublets in the ^{19}F NMR Spectrum of 2-$(CH_3)C_5H_6NPFCl$

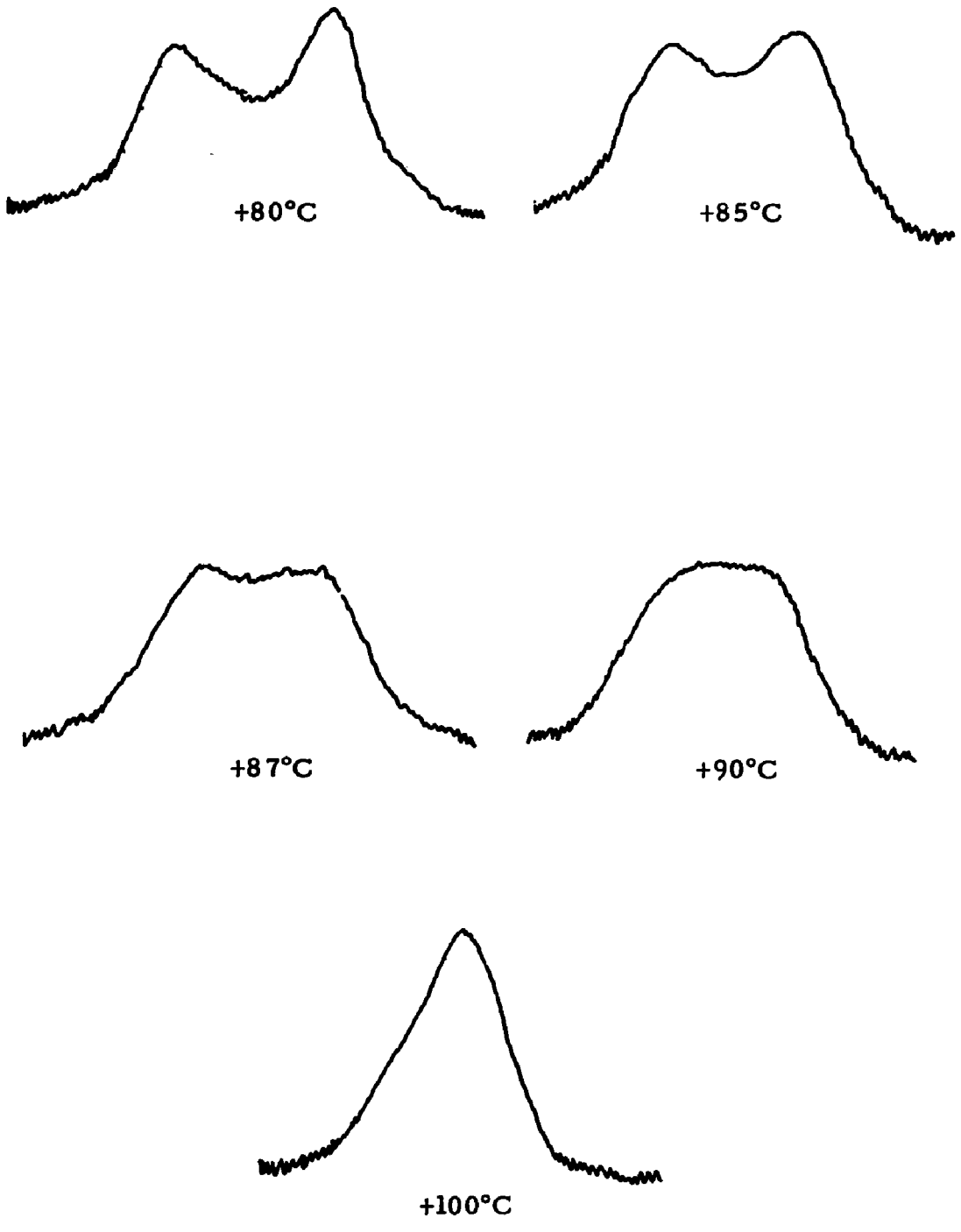


Figure 41

Continuation

Table VIII- Temperature Dependence of the Rate of Internal Rotation About the P-N Bond in $2\text{-}(CH_3)C_5H_9NPFCl$

T	1/T	r	$1/2\tau$	Log $1/2\ \tau$
313.15 °K	3.19×10^{-3}	7.08 ± 0.08	60.75	1.784 ± 0.010
323.15	3.09	5.52 ± 0.05	69.19	1.840 ± 0.010
328.15	3.05	4.87 ± 0.02	73.93	1.869 ± 0.010
333.15	3.00	3.57 ± 0.02	87.34	1.941 ± 0.009
343.15	2.91	1.95 ± 0.01	124.22	2.096 ±0.006
353.15	2.83	1.52 ± 0.01	145.10	2.161 ± 0.004
358.15	2.79	1.25 ± 0.01	166.06	2.221 ± 0.003
360.15	2.78	1.19 ± 0.01	174.46	2.242 ± 0.002

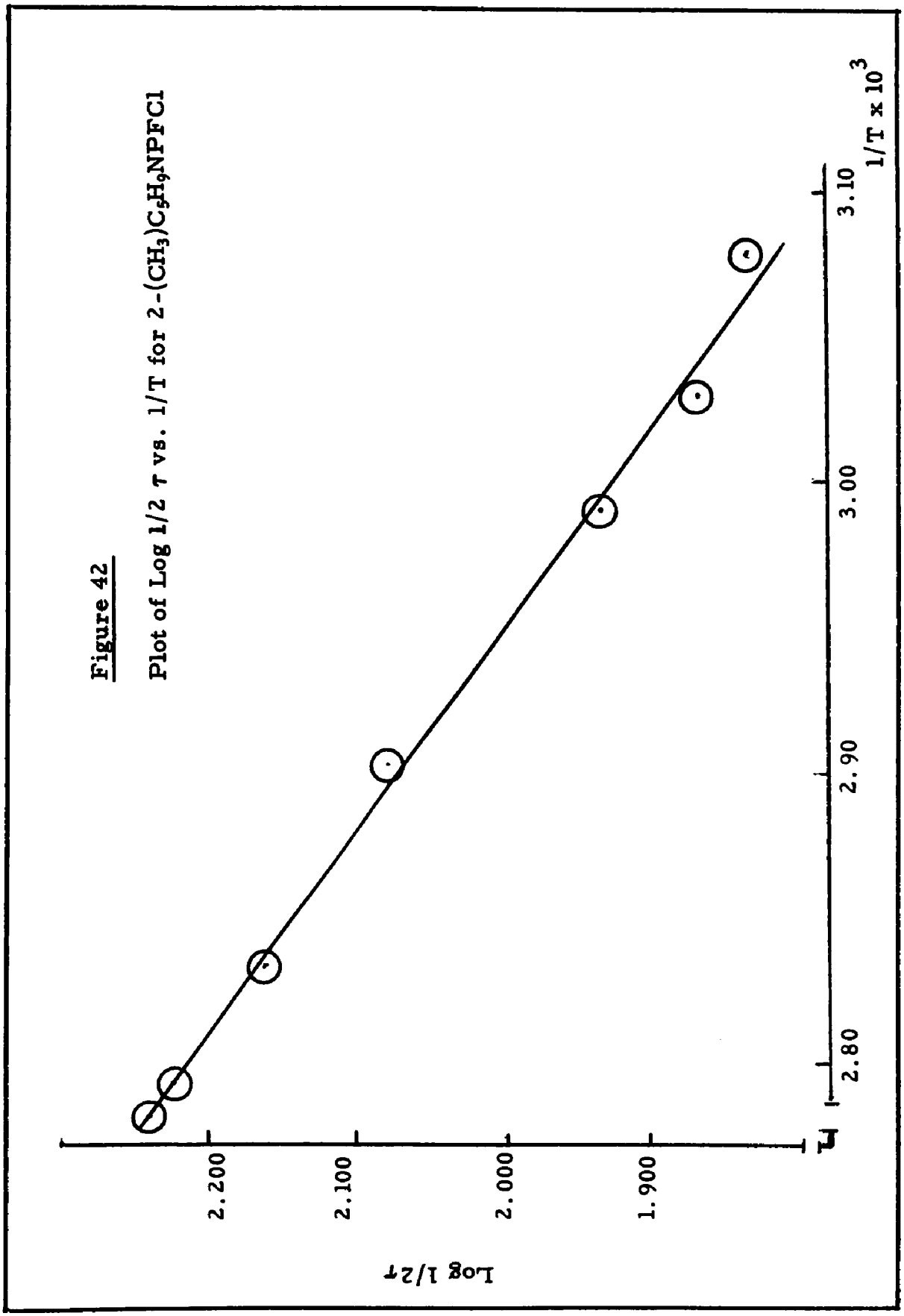


Figure 42

Plot of Log 1/2 τ vs. 1/T for 2-$(CH_3)C_5H_9NPFCl$

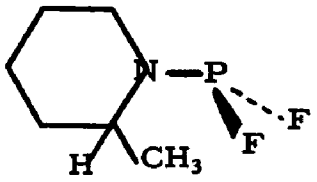
hindered internal rotation about the P-N bond in 2-$(CH_3)C_5H_9NPFCl$ is calculated to be 17.4 ± 0.3 kcal/mole.

One could compare this ΔG^* value with those obtained for compounds shown to have considerable double bond character. In aminoboranes (21-24), (64) E_a has been found to range from 10 to 15 kcal/mole; in certain amides (18-20) E_a ranged from 10-18 kcal/mole, and ΔG^* = 15 to 24 kcal/mole; some nitrites (14-16) gave values of E_a = 10 kcal/mole; and nitrosoamines (17) have E_a = 23 kcal/mole and ΔG^* = 25 kcal/mole. All or most of these compounds have been established to exhibit isomerism on account of restricted internal rotation.

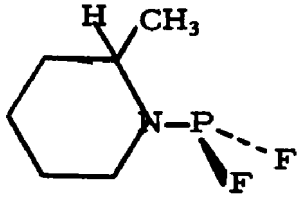
One other comparison is instructive. In the closely related compound 2-$(CH_3)C_5H_9NPF_2$, an approximate estimate of the free energy of activation associated with restricted rotation about the P-N bond gives a value of $\Delta G^* > 22$ kcal/mole. Steric factors associated with the rotation of a PFCl-group should be at least as large as those associated with the rotation of a PF_2-unit. In fact, one would anticipate more steric hindrance when the larger chlorine atom replaces the smaller fluorine atom. The difference in the barrier height must then be sought in band energy terms; steric arguments alone are inadequate.

One might argue that when the fluorine is replaced by a chlorine on phosphorus, the d-levels of phosphorus go up in energy and become less available to participate in $p\pi$-$d\pi$ bonding. The lower degree of double bond character would then give a lower barrier to rotation. This prediction is, in fact, borne out by experiment in that the barrier to

rotation in 2-$(CH_3)C_5H_9NPFCl$ is lower than that for 2-$(CH_3)C_5H_9NPF_2$. The problem is that the change in barrier height is too large when chlorine replaces fluorine, and the argument does not explain all observations. Note that in 2-$(CH_3)C_5H_9NPF_2$, the equilibrium ratio of the trans to cis-isomer goes up as the temperature is raised (Table IV), and the cis-



Cis-form*



Trans-form*

isomer is more stable by 738 cal/mole than the trans-isomer (see Appendix E). Double P-N bond arguments do not provide a suitable rationalization for this fact.

The most logical source of the energy difference is an interaction between the PF_2-unit and the CH_3-group on the piperidyl ring. Such an intramolecular "hydrogen bond" is also suggested by the through-space coupling of the fluorines and hydrogens of the methyl group in the cis-form. Replacement of one fluorine by chlorine would reduce the PF_2-H_3C interaction and give rise to a barrier which is lower than that required in 2-$(CH_3)C_5H_9NPF_2$.

It is also significant to note that the nearest H _ F distance was estimated from models to be 2.2 A°. This distance could be compared to the F-H-F hydrogen bonding distance found in $(HF)_n$ which is 2.55 A°

* The ring system is in a chair form. This schematic representation is for the sake of clarity and ease of presentation.

with 6.7 kcal/mole hydrogen bond energy, and to the value of 2.66 A° found in KHF_2 which has about 27 kcal/mole hydrogen bond energy (65). In both of these comparisons the hydrogen atoms are far more protonic than those in the CH_3-group, hence larger hydrogen bond energy would be expected.

To the extent that the foregoing arguments are valid, one can predict that the corresponding difluorophosphine derivative of 3-methyl-piperidine will not show evidence of isomers because specific PF_2-H_3C interaction would not be possible on account of the position of the methyl group in the ring.

F. THE ^{19}F NMR SPECTRUM OF 2-$(CH_3)C_5H_9NPFCl.BH_3$

An interpretation similar to that made for the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2.BH_3$ could be applied to the spectrum of 2-$(CH_3)C_5H_9$-NPFCl.BH_3. It consists (Fig. 43) of an apparent two sets of doublets:

a) a high-field doublet, J_{PF}= 1269 ± 2 Hz at δ= +60.3 ± 0.2 ppm. ($CFCl_3$), each member of which at higher resolution shows up as 1:3:3:1 quartet, J_{HBPF}= 15.8 ± 0.1 Hz

b) a low-field doublet, J_{PF}= 1269 ± 2 Hz at δ = +56.6 ± 0.2 ppm. ($CFCl_3$), each member of which show up as an eight-line multiplet (1:1:3:3:3:3:1:1) on higher resolution.

The high-field doublet can thus be assigned to one isomer with the fluorine and the chlorine atoms directed towards the methyl group. In this particular isomer, the lone fluorine nucleus spin couples with

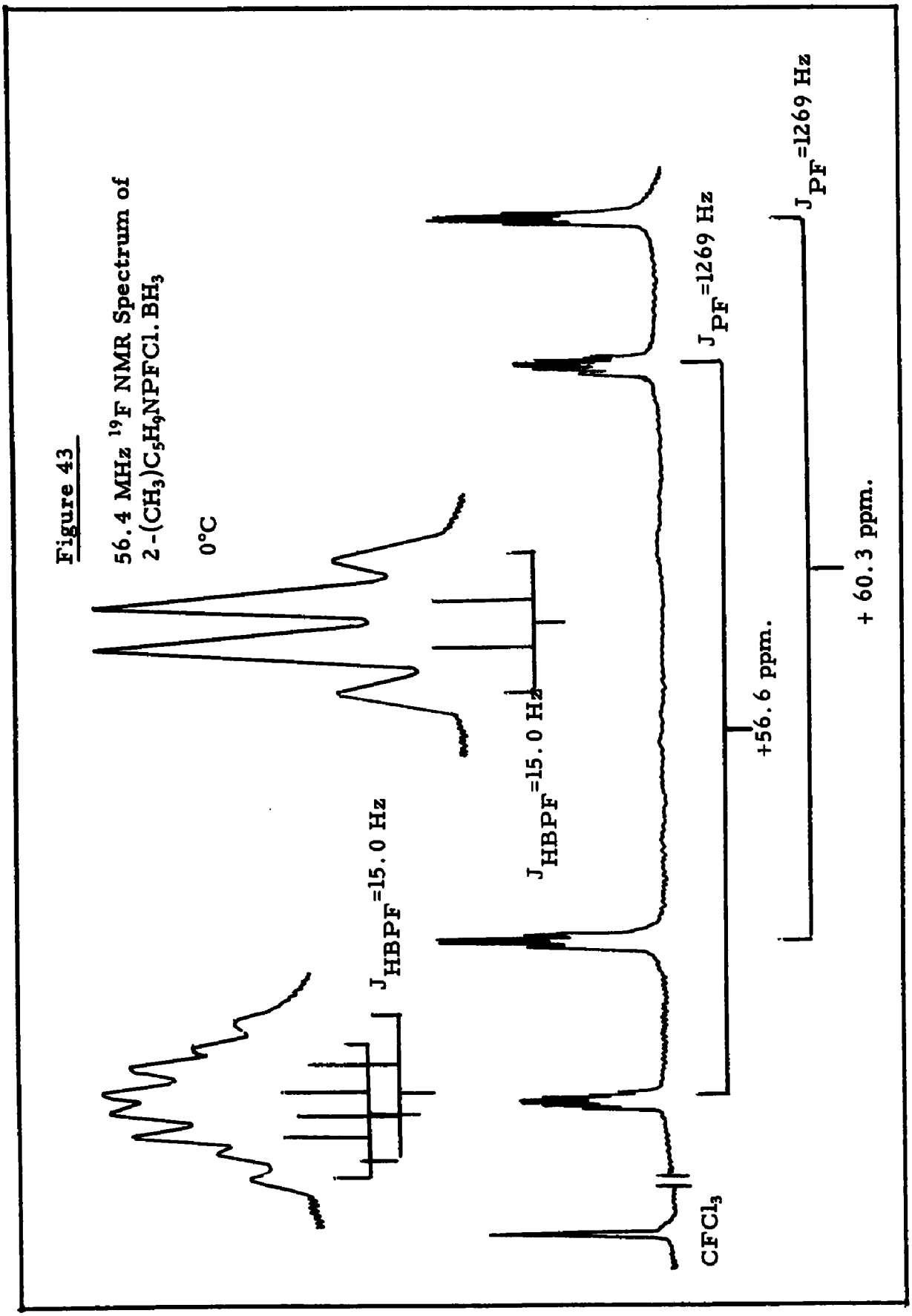


Figure 43
56.4 MHz ^{19}F NMR Spectrum of
2-$(CH_3)C_5H_9NPFCl.BH_3$
0°C
J_{HBPF}=15.0 Hz
J_{HBPF}=15.0 Hz
J_{PF}=1269 Hz
J_{PF}=1269 Hz
+56.6 ppm.
+ 60.3 ppm.
$CFCl_3$

the three equivalent borane protons to give a coupling constant of J_{HBPF} = 15.8 Hz. Just as it was in the case of the low-field doublet of 2-(CH_3)-$C_5H_9NPF_2.BH_3$, the high resolution structure of each member of the low-field doublet in the ^{19}spectrum of 2-$(CH_3)C_5H_9NPFCl.BH_3$ can be interpreted as two very closely separated 1:3:3:1 quartets with J_{HBPF} = 15.0 ± 0.1 Hz. These correspond to the two other isomers in which one has the fluorine and chlorine atoms below the P-N-(C_2) plane, and the other has the fluorine and chlorine atoms above this plane. The quartet splitting pattern is similarly attributed to coupling of the lone fluorine nucleus with the borane protons.

An attempt was made to study the ^{19}F nmr spectrum of 2-(CH_3)-$C_5H_9NPFCl.BH_3$ as a function of temperature, but it was not possible to do so since it was found to decompose rather easily at higher temperatures.

V - (CIS-2,6-DIMETHYLPIPERIDYL)DIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

If the structures proposed for the two isomers of 2-(CH_3)-$C_5H_9NPF_2$ were correct, then an analogous compound having two methyl groups in the 2- and 6-positions of the piperidine ring should exhibit no isomerism. In order to verify this hypothesis, and to present further proof of the existence of isomers in 2-$(CH_3)C_5H_9NPF_2$, studies were made of the various nmr spectra of (cis-2,6-dimethylpiperidyl)-difluorophosphine, cis-2,6.$(CH_3)_2C_5H_8NPF_2$, and its borane adduct, cis-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$.

A. SYNTHESIS OF CIS-2,6-$(CH_3)_2C_5H_8NPF_2$ AND CIS-2,6-$(CH_3)_2$-$C_5H_8NPF_2.BH_3$

Cis-2,6-$(CH_3)_2C_5H_8NPF_2$ was prepared by fluorinating the corresponding dichloro-compound using SbF_3, after all attempts to bring about the reaction of cis-2,6-dimethylpiperidine and PF_3 failed:

$$2\ \text{cis-2,6-}(CH_3)_2C_5H_9N + PCl_3 \rightarrow \text{cis-2,6-}(CH_3)_2C_5H_8NPCl_2 + \text{cis-2,6-}(CH_3)_2C_5H_9N.HCl$$

$$3\ \text{cis-2,6-}(CH_3)_2C_5H_8NPCl_2 + 2\ SbF_3 \rightarrow 3\ \text{cis-2,6-}(CH_3)_2\text{-}C_5H_8NPF_2 + 2\ SbCl_3\ .$$

The infrared spectrum of cis-2,6-$(CH_3)_2C_5H_8NPCl_2$ (Fig. 44) when compared to that of cis-2,6-dimethylpiperidine (Fig. 45) shows the notable absence of N-H stretching frequency at about 3375 cm^{-1}. The

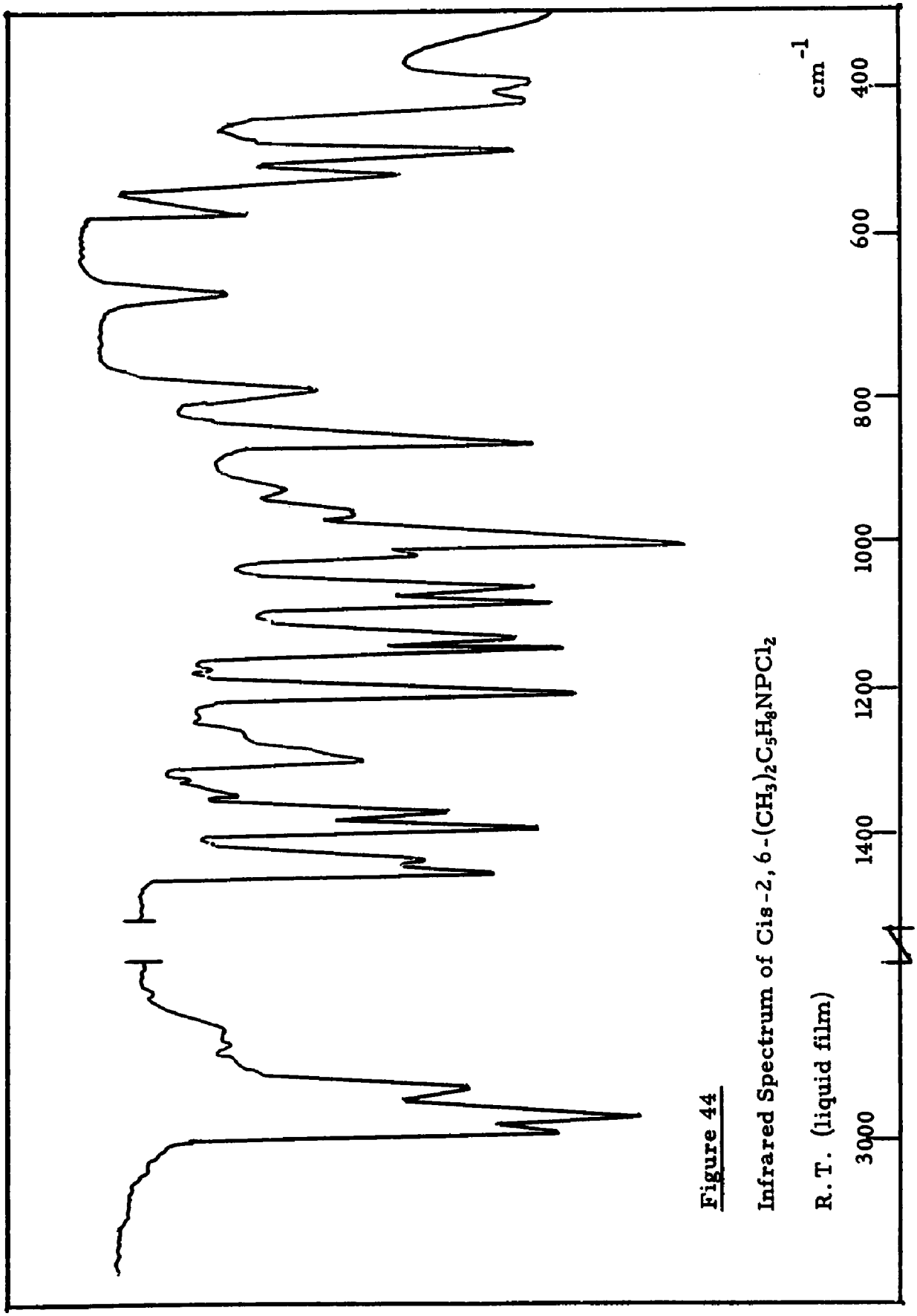


Figure 44

Infrared Spectrum of Cis-2,6-$(CH_3)_2C_5H_8NPCl_2$

R.T. (liquid film)

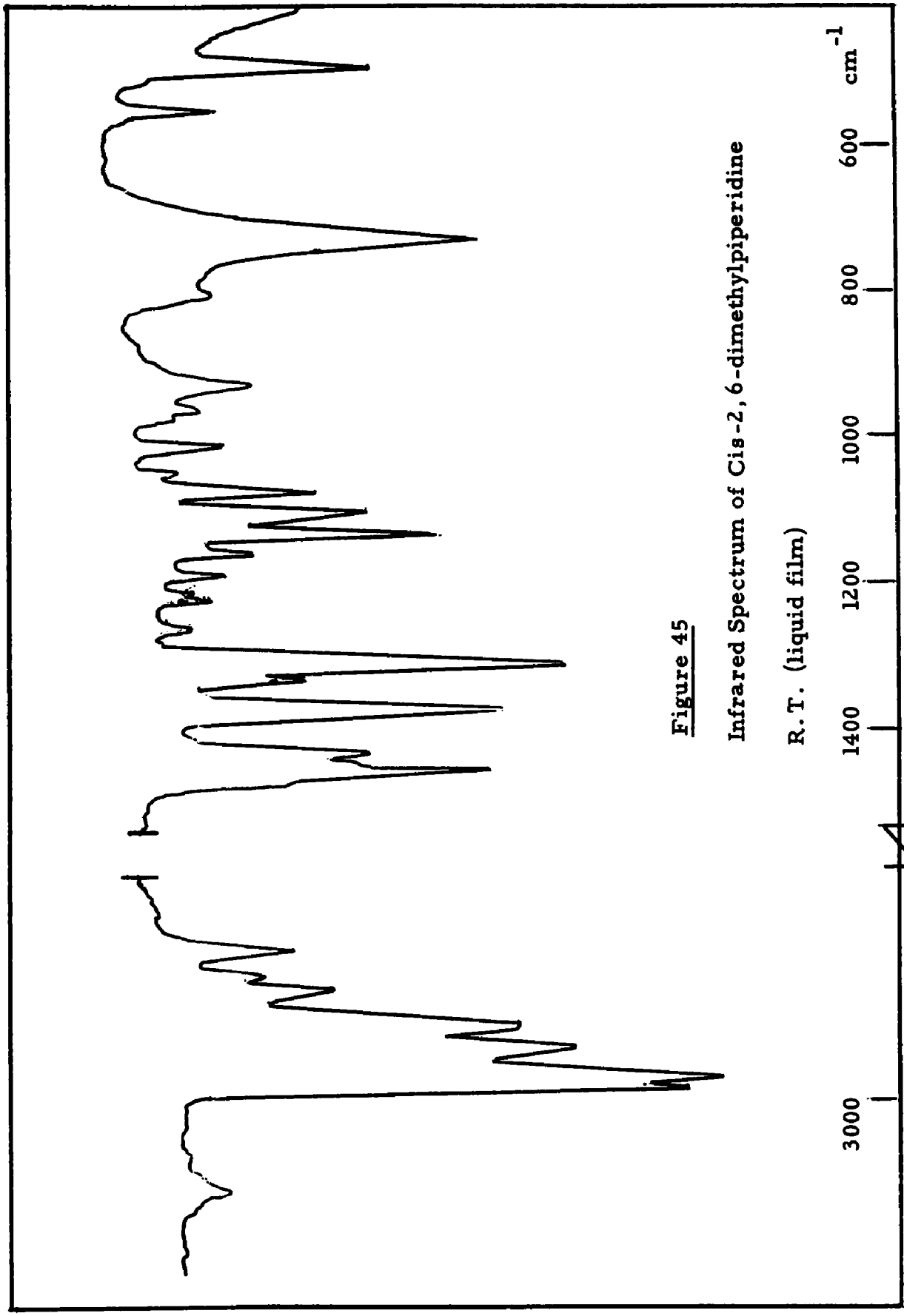


Figure 45

Infrared Spectrum of Cis-2,6-dimethylpiperidine

R.T. (liquid film)

infrared spectrum of cis-2,6-$(CH_3)_2C_5H_8NPF_2$ (Fig. 46) also shows no N-H stretch, and in addition two strong $-PF_2$ peaks at 785 and 730 cm^{-1}. Anal. Calculated for cis-2,6-$(CH_3)_2C_5H_8NPCl_2$: C, 39.40; H, 6.55; Cl, 32.80; N, 6.55. Found: C, 39.23; H, 6.51; Cl, 33.24; N, 6.50. Calculated for cis-2,6-$(CH_3)_2C_5H_8NPF_2$: C, 46.40; H, 7.73; F, 21.10; N, 7.73. Found: C, 46.28; H, 7.68; F, 20.94; N, 7.72.

The borane adduct was prepared by reaction of the free ligand with diborane in ether at -78°C

$$\text{cis-2,6-}(CH_3)_2C_5H_8NPF_2 + \tfrac{1}{2} B_2H_6 \rightarrow \text{cis-2,6-}(CH_3)_2C_5H_8NPF_2.BH_3$$

Its infrared spectrum (Fig. 47) shows the typical B-H stretching frequencies at 2410 and 2360 cm^{-1}.

Table IX gives the infrared absorption frequencies of cis-2,6-dimethylpiperidine, cis-2,6-$(CH_3)_2C_5H_8NPCl_2$, cis-2,6-$(CH_3)_2C_5H_8NPF_2$, and cis-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$ for the sake of comparison.

B. THE ^{31}P NMR SPECTRA OF CIS-2,6-$(CH_3)_2C_5H_8NPCl_2$, CIS-2,6-$(CH_3)_2C_5H_8NPF_2$, AND CIS-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$

At room temperature, the 40.4 MHz ^{31}P nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPCl_2$ (Fig. 48) shows the expected singlet at δ = -156.9 ± 0.5 ppm. (H_3PO_4). Similarly, the ^{31}P nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPF_2$ (Fig. 49) shows the expected 1:2:1 triplet, J_{FP} = 1185 ± 2 Hz due to coupling with the two fluorine nuclei, with a chemical shift of δ = -143.3 ± 0.5 ppm. (H_3PO_4). The borane adduct of cis-2,6-$(CH_3)_2C_5H_8NPF_2$ exhibits a similar triplet at δ = -127.5 ± 0.5 ppm.

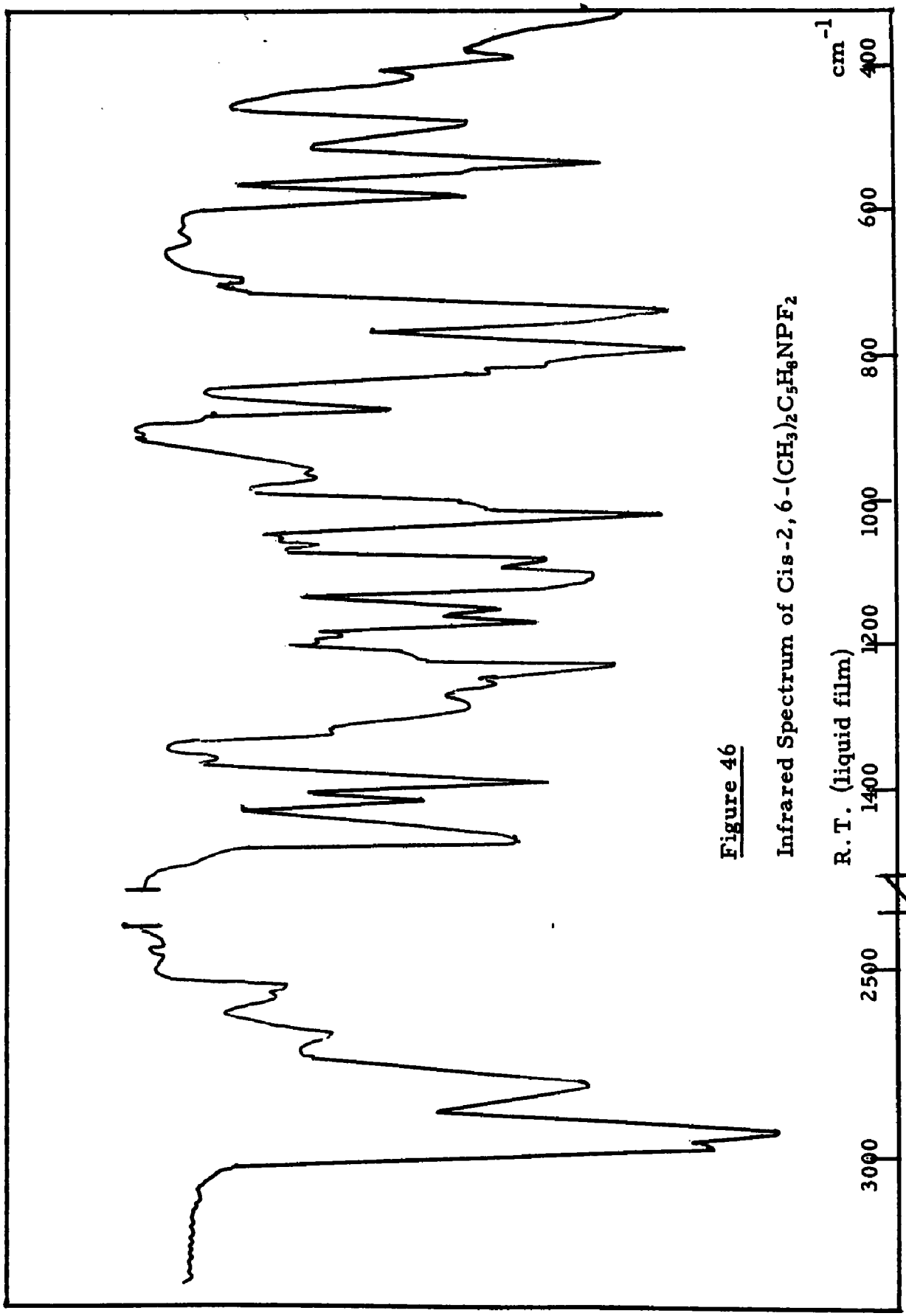


Figure 46

Infrared Spectrum of Cis-2,6-$(CH_3)_2C_5H_6NPF_2$

R.T. (liquid film)

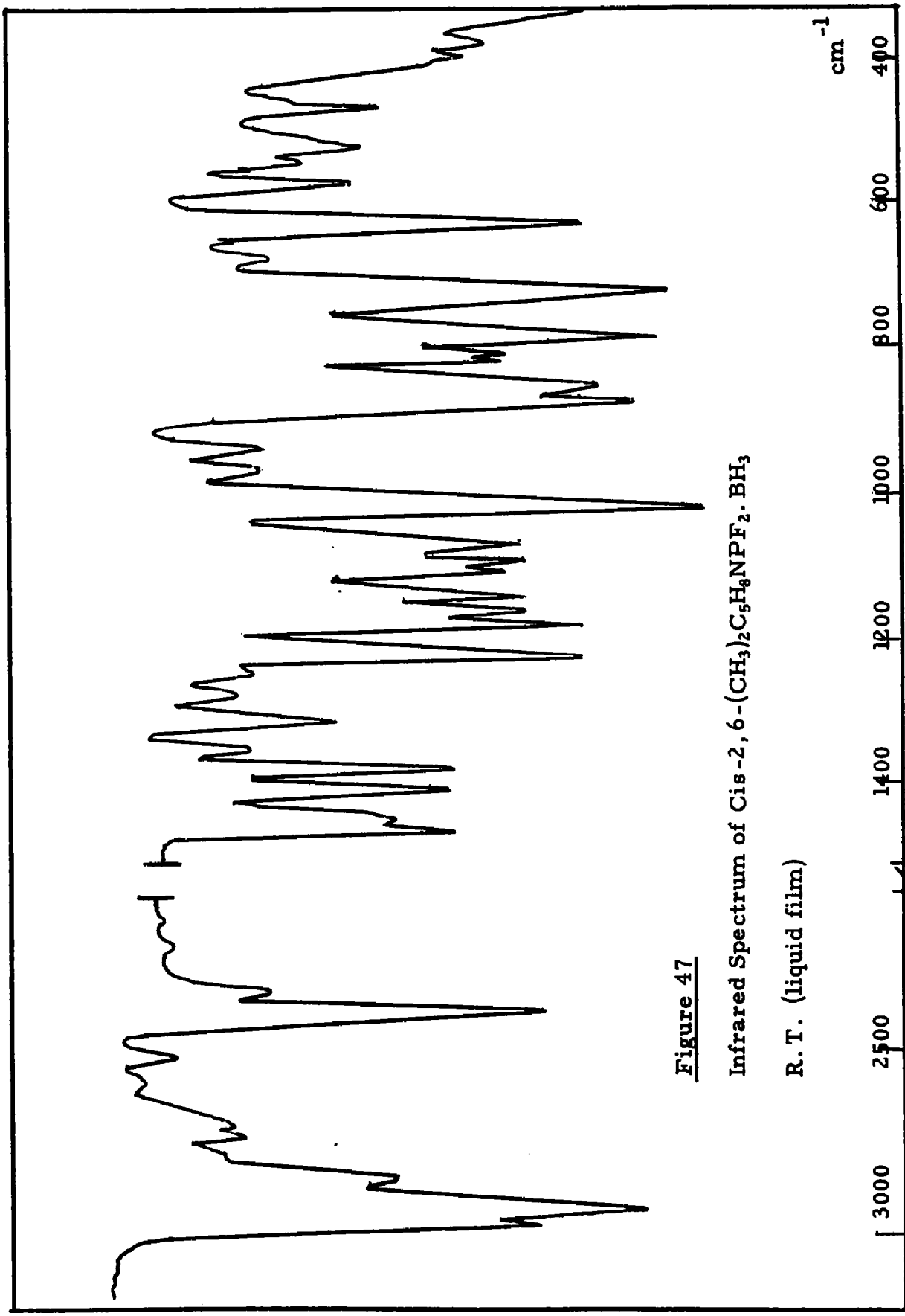


Figure 47

Infrared Spectrum of Cis-2,6-$(CH_3)_2C_5H_6NPF_2 \cdot BH_3$

R.T. (liquid film)

Table IX - Infrared Absorption Frequencies of 2,6$(CH_3)_2$-C_5H_9N, 2,6-$(CH_3)_2C_5H_8NPCl_2$, 2,6-$(CH_3)_2C_5H_8NPF_2$, and 2,6-$(CH_3)_2C_5H_8NPF_2 . BH_3$

2,6-$(CH_3)_2C_5H_9N$	2,6-$(CH_3)_2C_5H_8N$-PCl_2	2,6-$(CH_3)_2$-$C_5H_8NPF_2$	2,6-$(CH_3)_2$-$C_5H_8NPF_2 . BH_3$
3375 vw	2970 s	2980 s	2980 s
2960 s	2940 s	2940 s	2940 s
2940 s	2870 m	2860 m	2860 m
2869 m	2860 sh	2740 m	2740 w
2800 m	2740 vw	2540 w	2710 w
2700 w	2700 vw	2460 vw	2540 vw
2670 vw	1460 m	1460 m	2410 s
2600 w	1445 m	m405 w	2360 w
1460 w, sh	1400 m	1380 m	1465 m
1450 m	1380 m	1350 vw	1460 vw
1440 sh	1355 w	1315 s	1450 w
1430 w	1330 vw	1280 m	1410 m
1370 m	1310 w	1250 m	1380 m
1330 w	1280 vw	1220 s	1350 vw
1315 m	1220 s	1190 vw	1315 w
1265 vw	1190 vw	1180 vw	1280 w
1230 vw	1155 m	1160 m	1250 w
1220 vw	1140 m	1145 m	1220 s
1190 w	1085 m	1100 m	1180 s
1155 w	1075 m	1075 m	1160 m
1130 m	1030 w, sh	1065 w	1140 m
1100 w	1010 s	1020 s	1105 m
1070 w	1000 sh	970 w	1090 m
1045 vw	970 w	950 w	1075 m
101- w	945 vw	870 w	1060 sh
975 vw	870 m	825 sh	1020 s
970 vw	805 w	810 sh	980 w
925 w	680 w	785 s	940 w
810 vw	570 w	730 s	880 sh
735 m	550 vw	685 vw	870 s
555 w	520 m	640 vw	850 s
	490 s	580 w	810 s
	420 m	530 m	785 s
	390 w	475 w	730 s
		410 w	640 s
		385 w	580 w
			530 w
			475 w
			410 w

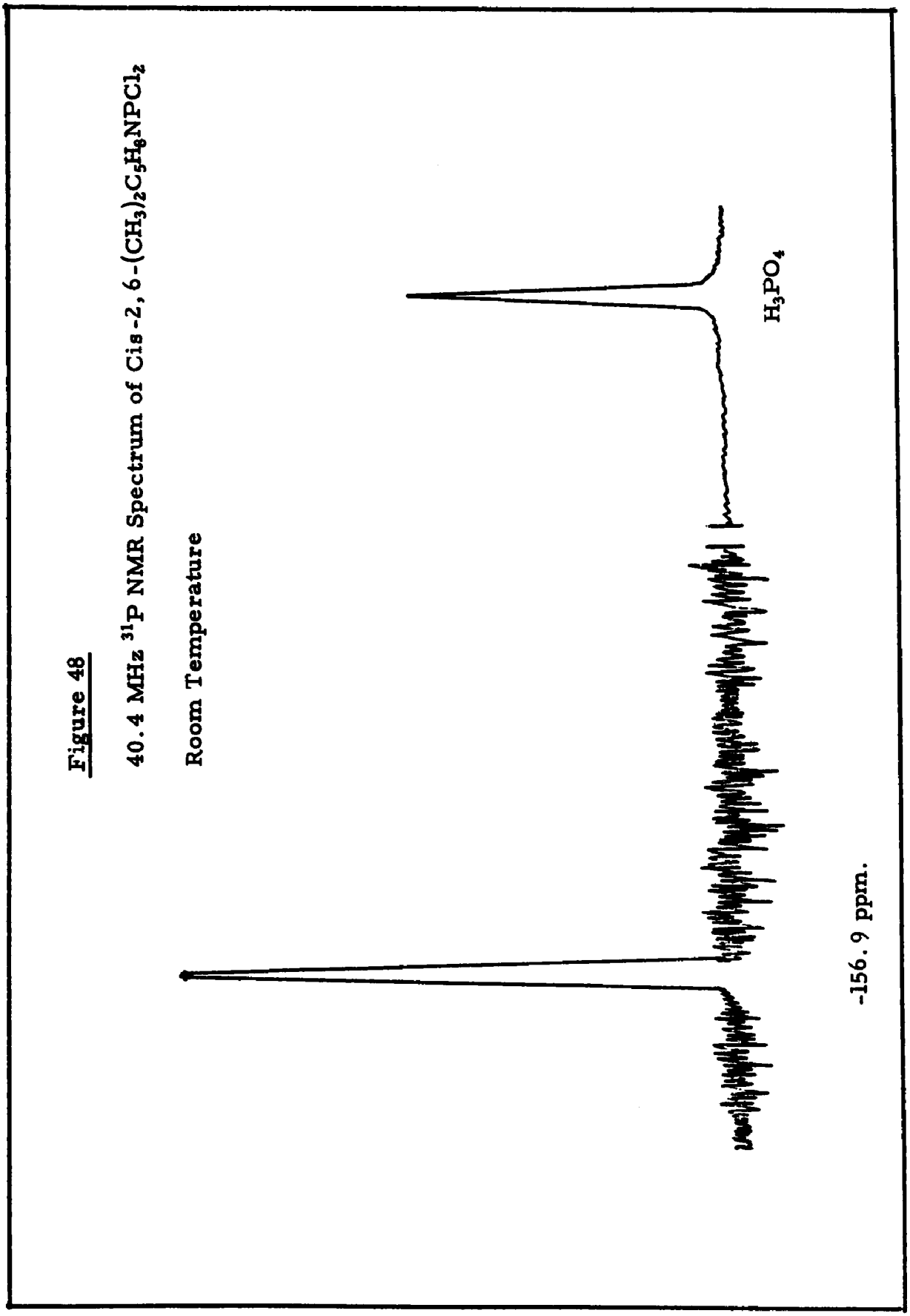


Figure 48

40.4 MHz ^{31}P NMR Spectrum of Cis-2,6-$(CH_3)_2C_5H_6NPCl_2$

Room Temperature

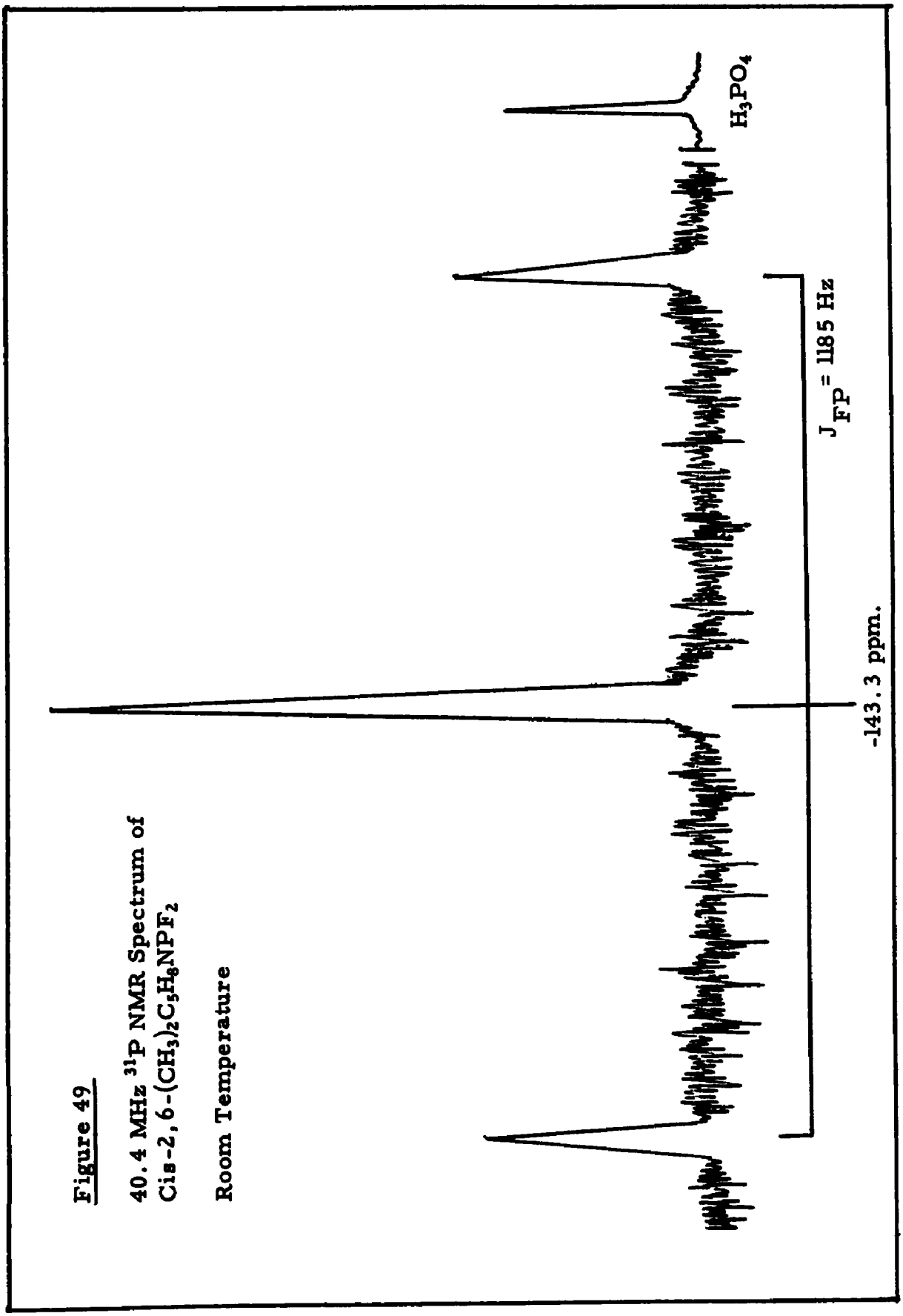


Figure 49

40.4 MHz ^{31}P NMR Spectrum of
Cis-2,6-$(CH_3)_2C_5H_6NPF_2$

Room Temperature

(H_3PO_4), J_{FP}= 1185 ± 2 Hz (Fig. 50) also due to coupling with the two fluorine nuclei. Each member of the triplet is broadened and shows some splitting. However, the high noise level prevents an unequivocal analysis of the splitting pattern.

C. THE ^{11}B NMR SPECTRUM OF CIS-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$

At room temperature, the 32.1 MHz ^{11}B nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$ (Fig. 51) consists of a 1:3;3:1 quartet at δ = +129.8 ± 0.5 ppm. from $B(CH_3)_3$, each member of which is split into a 1:1 doublet, with some overlapping of peaks. The quartet structure is due to coupling with the borane protons giving J_{HB}= 103 ±1 Hz. Additional coupling with the phosphorus nucleus would split each of the member of this quartet into doublets to give J_{PB}= 78 ± 1 Hz. This splitting pattern in the ^{11}B nmr spectrum has been typical of the borane adducts of the compounds thus far studied.

D. THE ^{1}H NMR SPECTRA OF CIS-2,6-DIMETHYLPIPERIDINE, CIS-2,6-$(CH_3)_2C_5H_8NPCl_2$, CIS-2,6-$(CH_3)_2C_5H_8NPF_2$, AND CIS-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$

The proton nmr spectrum of cis-2,6-dimethylpiperidine has been reported (66), together with the spectrum of the corresponding trans isomer in which one methyl group is in an axial position while the other methyl group is in an equatorial position. Both spectra are quite similar; the only difference is a sharp singlet at δ= -1.4 ppm.

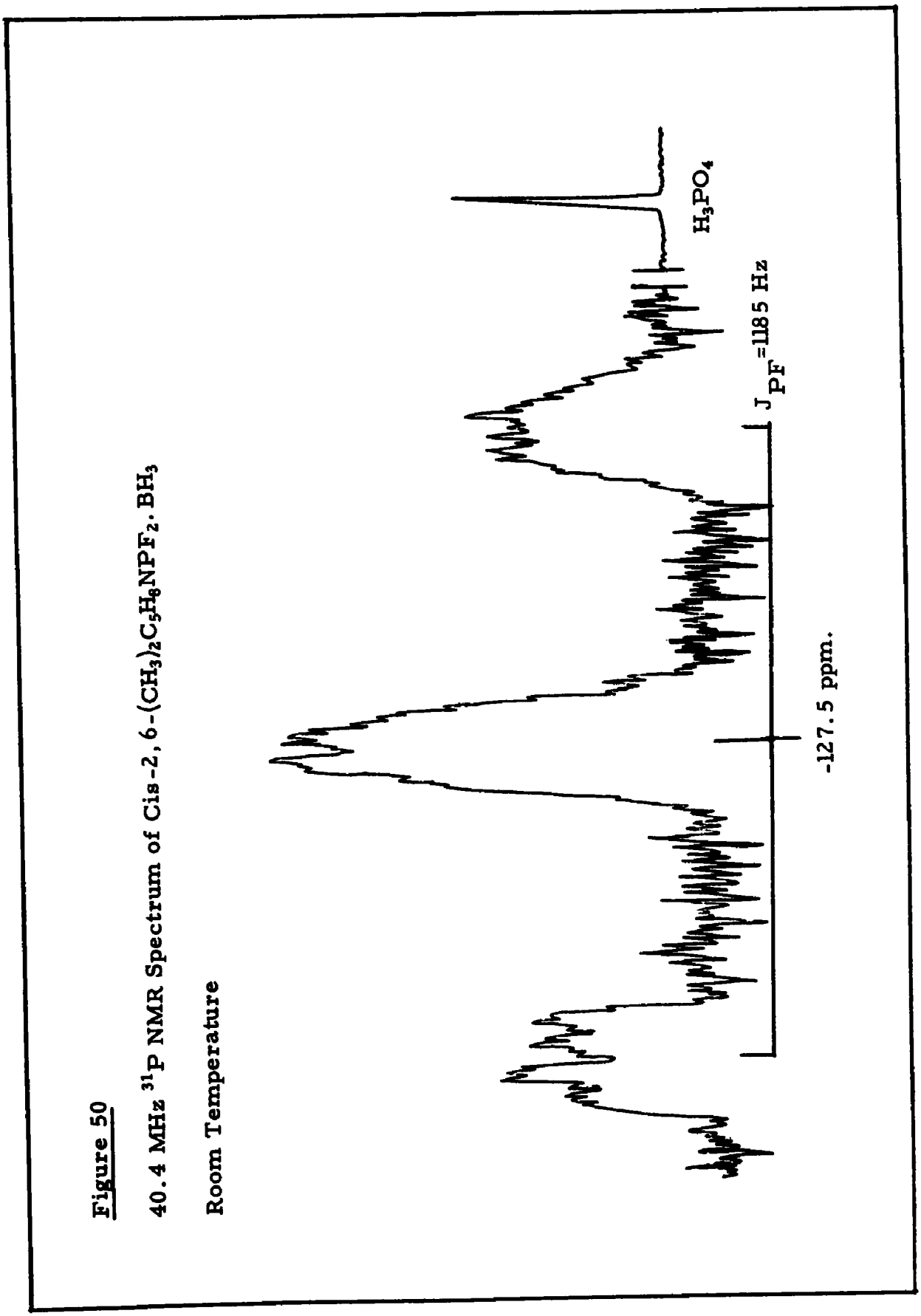


Figure 50

40.4 MHz ^{31}P NMR Spectrum of Cis-2, 6-$(CH_3)_2C_5H_8NPF_2 . BH_3$

Room Temperature

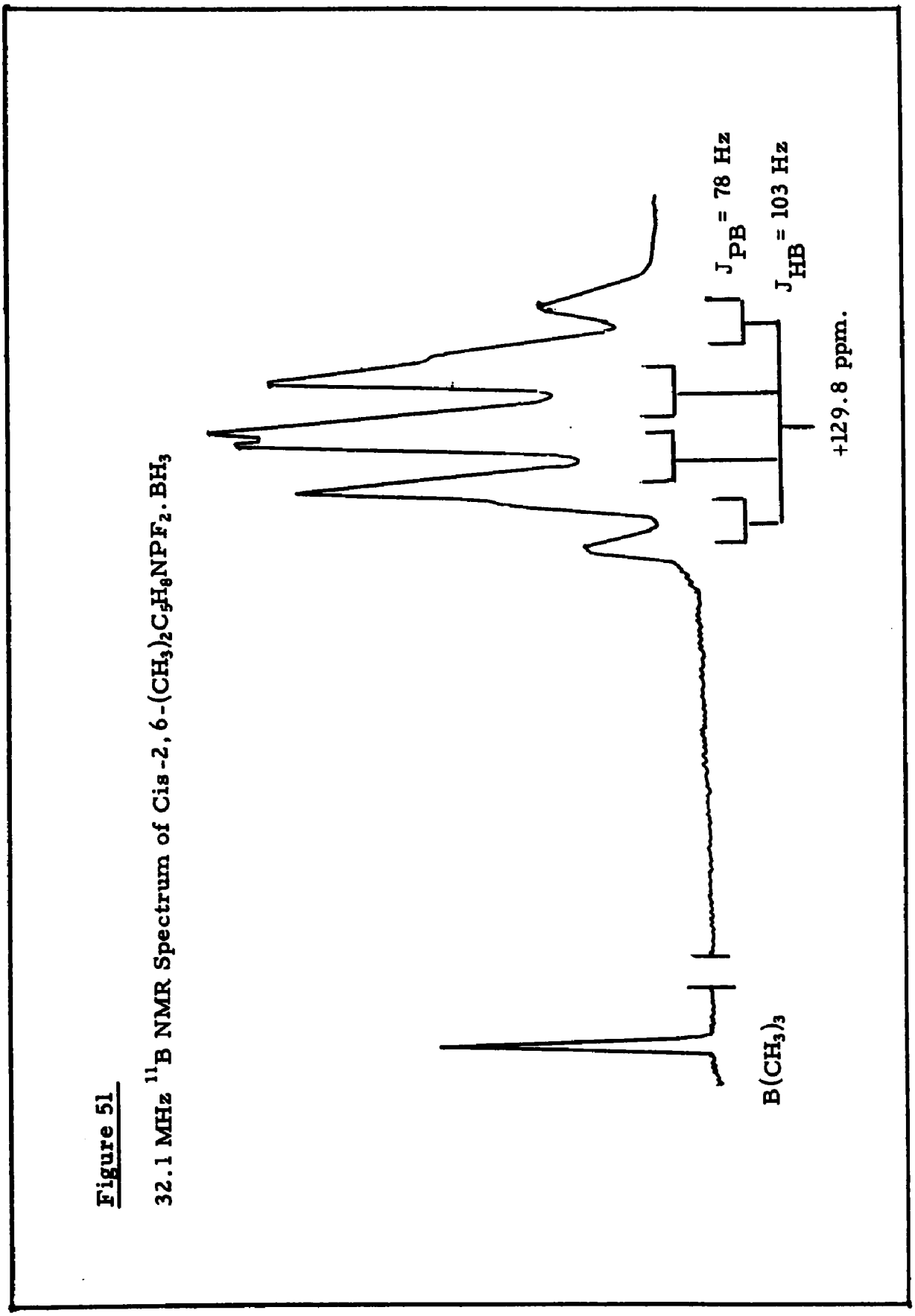


Figure 51

32.1 MHz ^{11}B NMR Spectrum of Cis-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$

(TMS) presumably due to the N-H proton, present in the trans isomer and conspicuously unseen in the cis isomer.

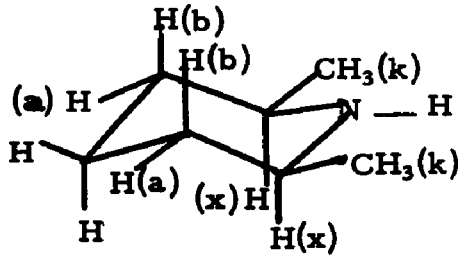
The proton nmr spectrum of the 2,6- dimethylpiperidine which was used as a starting material for this study is shown in Fig. 52. It is evident that no sharp singlet is present at δ = -1.4 ppm. (TMS) indicating that the starting material was mostly, if not all, in the cis-conformation. However, to be realistic, it would be safe to say that the amount of the trans-isomer in the starting material was insignificant in terms of its nmr signals. The proton nmr spectrum of cis-2,6-dimethylpiperidine as obtained experimentally is in accord with the literature data (66). It consists of

a) a doublet, J_{HCCH} = 6.2 ± 0.1 Hz, at δ = -1.00 ± 0.02 ppm. (TMS)

b) a broad, complex multiplet that starts from approximately δ = -2.0 ppm., continuing to higher magnetic field,

c) an eleven-line multiplet centered at δ = -2.60 ± 0.03 ppm. (TMS).

Integrated area ratios are 6:7:2 respectively.



The literature values are (66):

methyl protons (doublet, J =6.3 Hz)	δ = -0.96 ppm. (TMS)
H_a (equatorial) from spin decoupling	=-1.65
H_b (axial) from spin decoupling	=-1.00

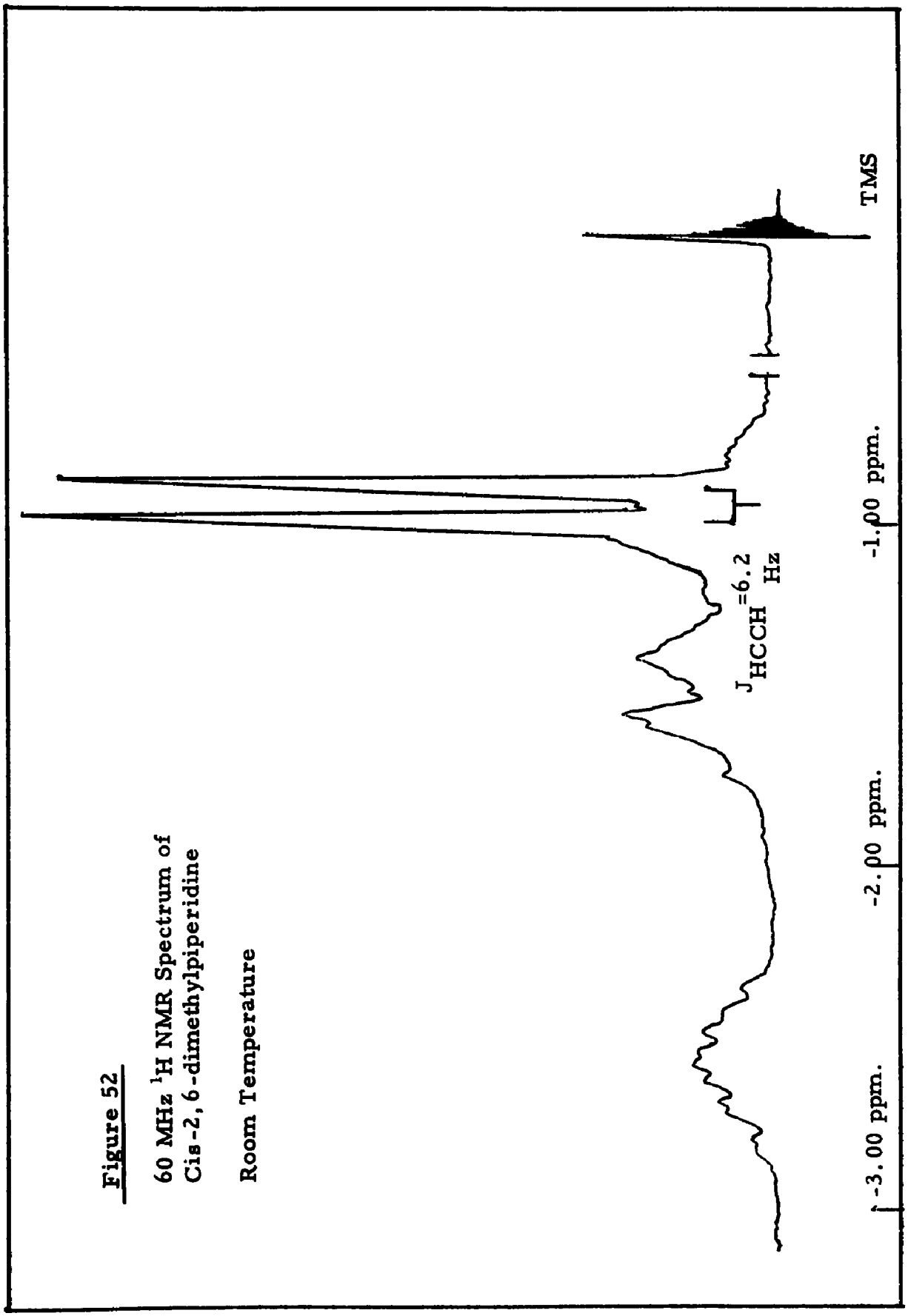


Figure 52

60 MHz ^{1}H NMR Spectrum of
Cis-2,6-dimethylpiperidine

Room Temperature

H_x (axial)	-2.55 ppm. (TMS)
J_{ax}	1.9 ± 0.2 Hz
J_{bx}	10.6 ± 0.2 Hz.

The eleven-line multiplet at δ = -2.60 ppm. (TMS) shown in Fig. 53 at higher resolution, is due to the equivalent methine protons in an axial orientation. It can be viewed (66) as the X spectrum of an $ABXK_3$ system with J_{AX} less than J_{BX}. The splitting pattern can be analyzed as an original 1:1 doublet due to coupling with the H_b proton to give a J_{BX}= 10.5 ± 0.1 Hz coupling constant, each of which is split into another 1:1 doublet due to coupling with the H_a proton, J_{AX} =2.1 ± 0.1 Hz. Each member of the latter doublet is further split into a 1:3:3:1 quartet on account of coupling with the methyl group giving J_{KX}= 6.3 ± 0.1 Hz.

In view of the above discussion, it is reasonable to assume that the compound formed from the reaction of cis-2,6dimethylpiperidine with the appropriate halogenating agen would exists in the same conformation, i.e. the methyl group cis- to one another and occupying equatorial sites in the piperidine ring.

The ^1H nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPCl_2$ shown in Fig. 54 consists of

a) a 1:1 doublet at δ = -1.37 ± 0.02 ppm. (TMS), J_{HCCH} = 7.1 ± 0.1 Hz

b) a broad peak centered at δ = -1.67 ± 0.02 ppm. (TMS)

c) a multiplet centered at δ = -4.13 ± 0.04 ppm. (TMS), similar to the low-field, eleven-line multiplet observed in cis-2,6-dimethylpiperidine.

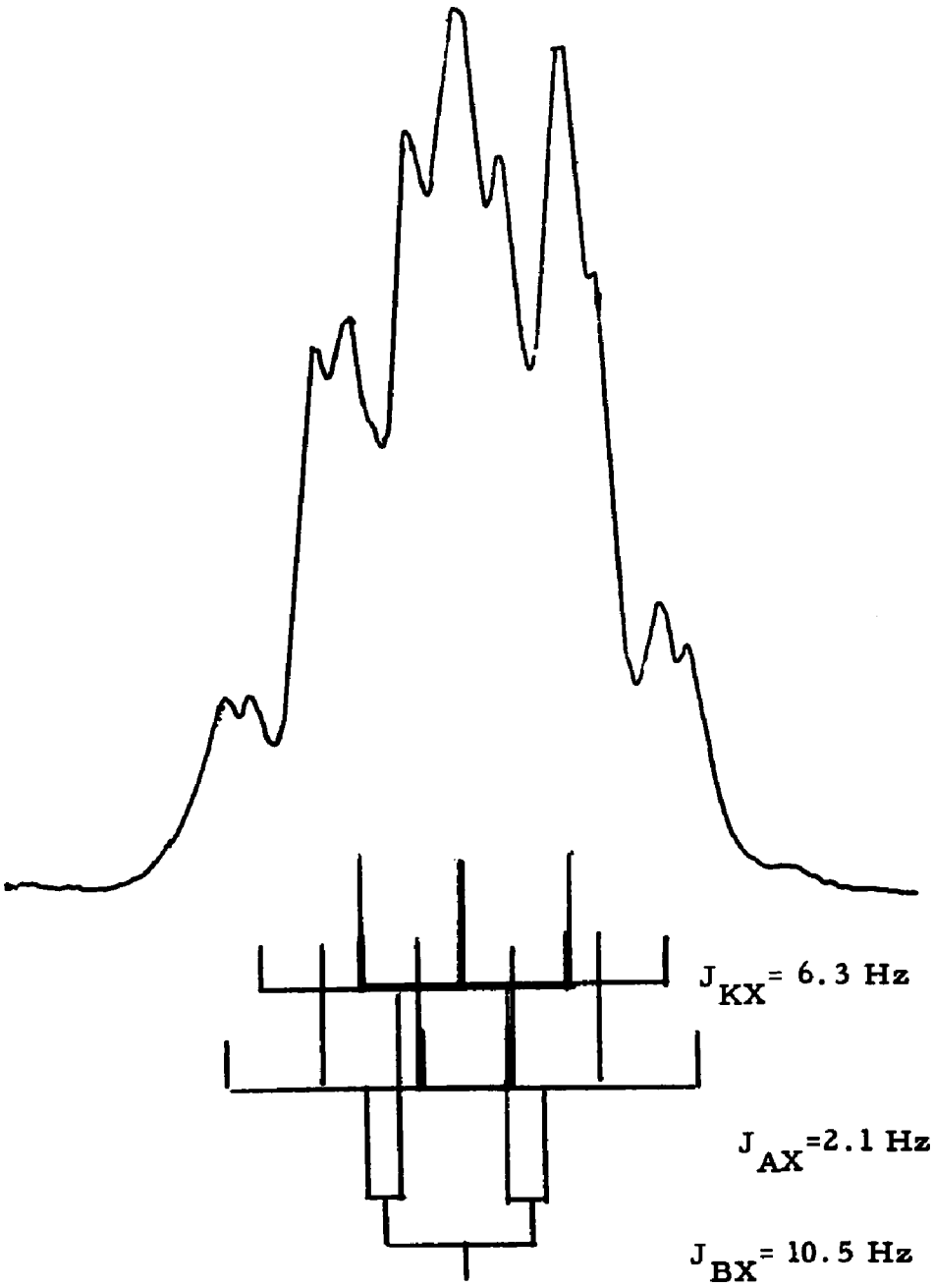


Figure 53

Lowest Field Multiplet in the 60 MHz ^{1}H NMR Spectrum of Cis-2,6-dimethylpiperidine

Room Temperature

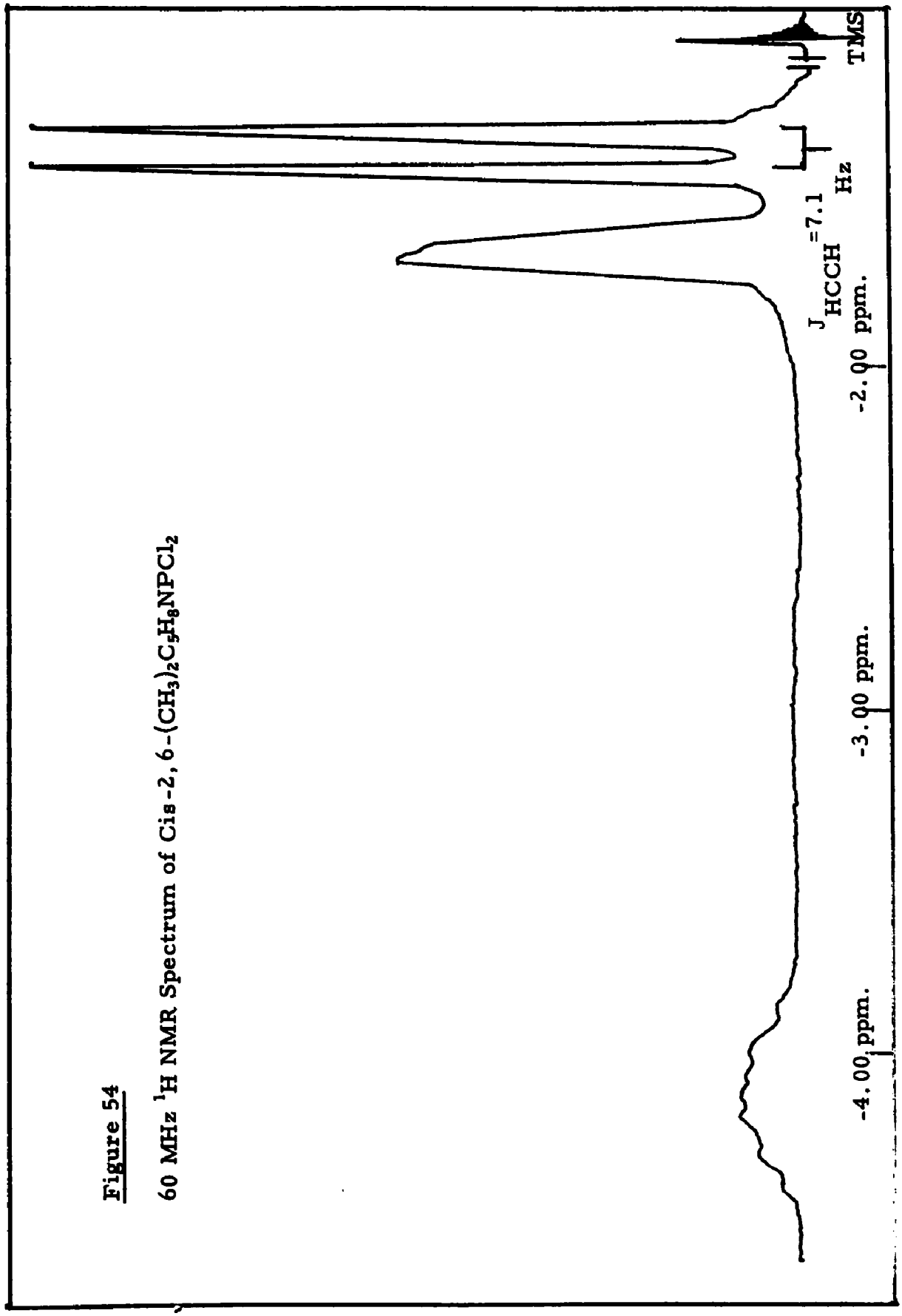


Figure 54

60 MHz ^1H NMR Spectrum of Cis-2,6-$(CH_3)_2C_5H_8NPCl_2$

Their integrated area ratios are 6:6:2 respectively.

Assignment of these nmr signals is rather easy on the basis of their area ratios, in conjunction with the previous assignment of peaks done on cis-2,6-dimethylpiperidine. The methyl group shows up as a high-field doublet with the same magnitude of coupling constant brought about by spin-interaction with the methine protons. No evidence of coupling with the phosphorus nucleus is observed. The methine protons on the 2- and 6-positions correspond to the low-field multiplet which exhibit the same splitting pattern as that seen in cis-2,6-dimethylpiperidine. The broad peak at δ = -1.67 ppm. is attributed to the rest of the ring protons.

Similarly, the proton nmr spectrum of the difluoro-analogue, cis-2,6-$(CH_3)_2C_5H_8NPF_2$ (Fig. 55) consisting of

a) a 1:1 doublet, J_{HCCH} = 7.2 ± 0.1 Hz at δ = -1.11 ± 0.02 ppm. (TMS) showing no further splitting at higher resolution

b) a broad peak centered at δ = -1.43 ± 0.02 ppm. (TMS)

c) a multiplet centered at δ = -3.62 ± 0.04 ppm. (TMS)

with area ratios 6:6:2, could be interpreted in the same manner.

This is also the case for the borane aduct of cis-2,6-$(CH_3)_2$-$C_5H_8NPF_2$ whose proton nmr spectrum (Fig. 56) shows

a) a doublet at δ = -1.44 ± 0.02 ppm. (TMS), J_{HCCH} = 6.8 ± 0.1 Hz

b) a broad peak at δ = -1.75 ± 0.02 ppm. (TMS)

c) a multiplet centered at δ = -4.10 ± 0.04 ppm. (TMS).

Their respective area ratios are 6:6:2.

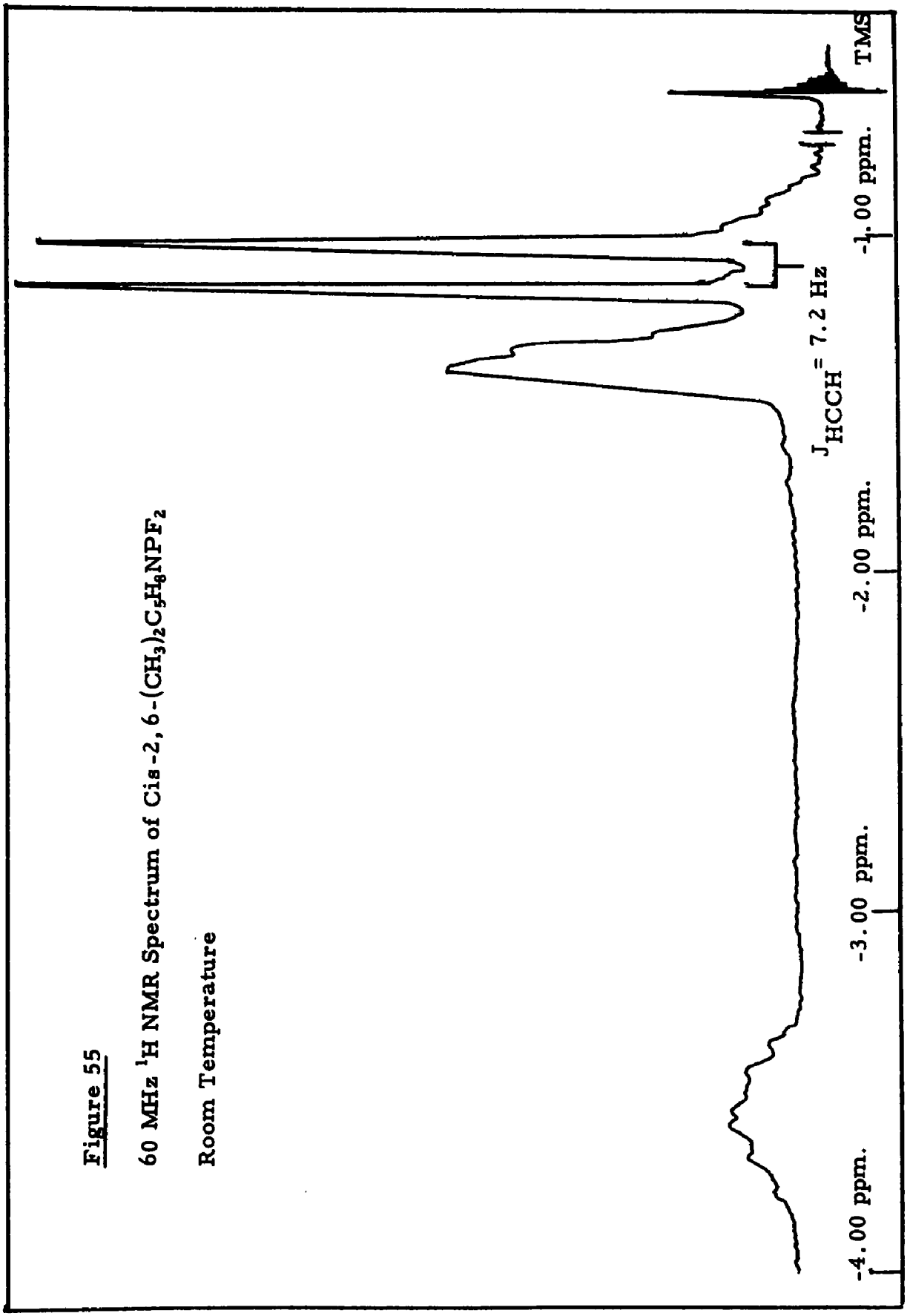


Figure 55

60 MHz ^{1}H NMR Spectrum of Cis-2,6-$(CH_3)_2C_5H_8NPF_2$

Room Temperature

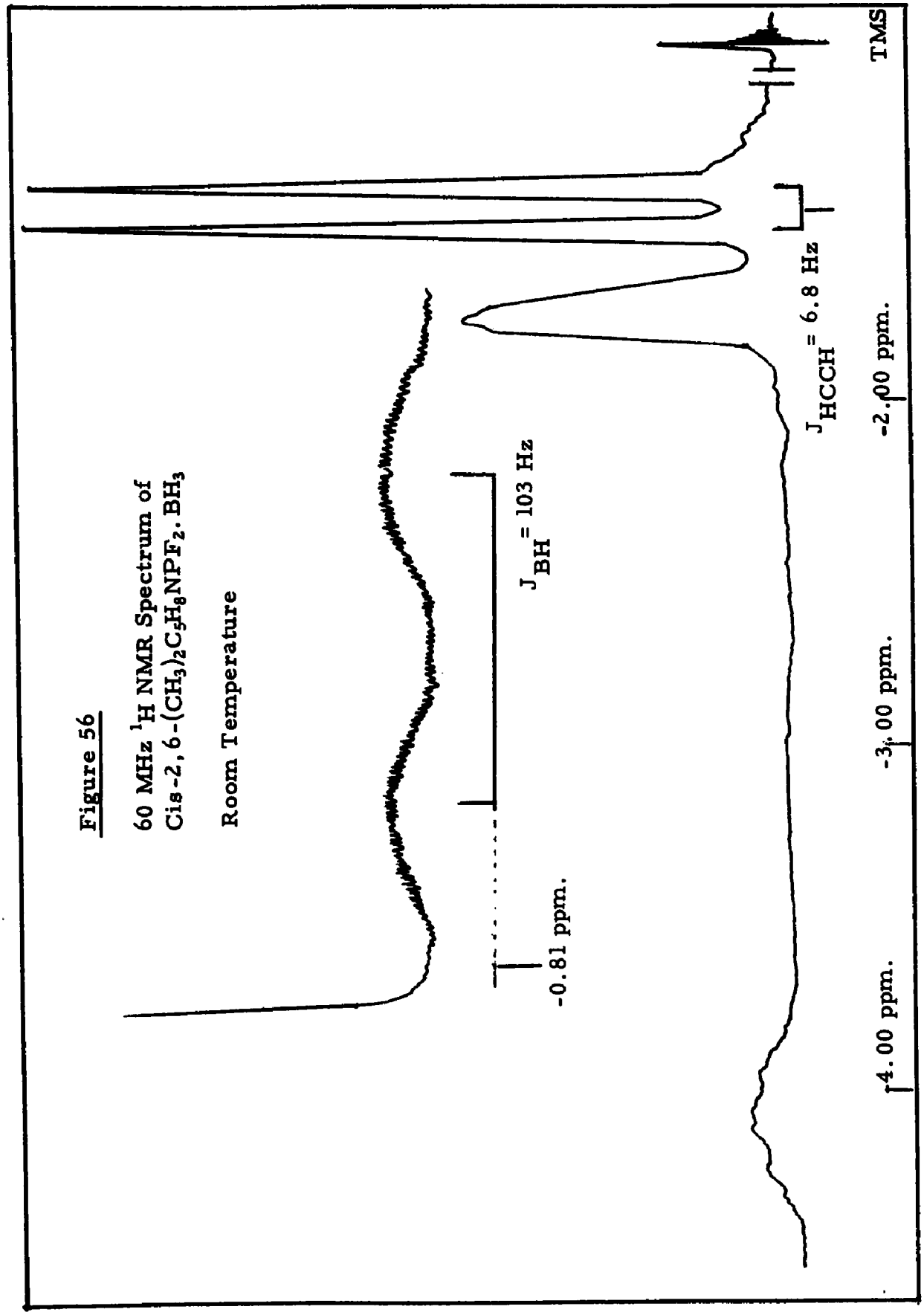


Figure 56
60 MHz ^{1}H NMR Spectrum of
Cis-2,6-$(CH_3)_2C_5H_8NPF_2 \cdot BH_3$
Room Temperature
J_{BH} = 103 Hz
-0.81 ppm.
J_{HCCH} = 6.8 Hz
TMS
4.00 ppm.
3.00 ppm.
2.00 ppm.

In addition to these peaks, the BH_3 nmr signal is visible at higher gain, consisting of a 1:1:1:1 quartet at δ = -0.81 ± 0.02 ppm. (TMS). Two members of this quartet are overlapped by the methyl proton signal. A value of J_{BH} = 103 ± 1 Hz is calculated for the spin-spin interaction between the borane protons and the boron nucleus.

E. THE ^{19}F NMR SPECTRA OF CIS-2,6-$(CH_3)_2C_5H_8NPF_2$ AND CIS-2,6-$(CH_3)_2C_5H_8NPF_2 . BH_3$

It was postulated that the ^{19}F nmr spectrum of cis-2,6-$(CH_3)_2$-$C_5H_8NPF_2$ would not show any evidence of isomerism if the suggested structures for the isomers observed in 2-$(CH_3)C_5H_9NPF_2$ and 2-(CH_3)-C_5H_9NPFCl are corredct, since the structures of the isomers would be equivalent and would be indistinguishible from each other.

Indeed, no evidence of isomerism is seen in the ^{19}F nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPF_2$. This fact is manifested by the lone doublet observed in its spectrum (Fig. 57). The doublet is due to spin coupling with the phosphorus nucleus by the fluorine nuclei, giving a coupling constant of J_{PF} = 1190 ± 2 Hz and a chemical shift of δ = +65.6 ± 0.5 ppm. ($CFCl_3$). If isomers were present, more than one set of doublets would be obtained (see for example the ^{19}F nmr spectra of 2-$(CH_3)C_5H_9NPF_2$ and 2-$(CH_3)C_5H_9NPFCl$).

Each member of the basic doublet remains as an unresolved, broad singlet at higher resolution. This could indicate that the fluorines are still in much the same spatial orientations as they were in

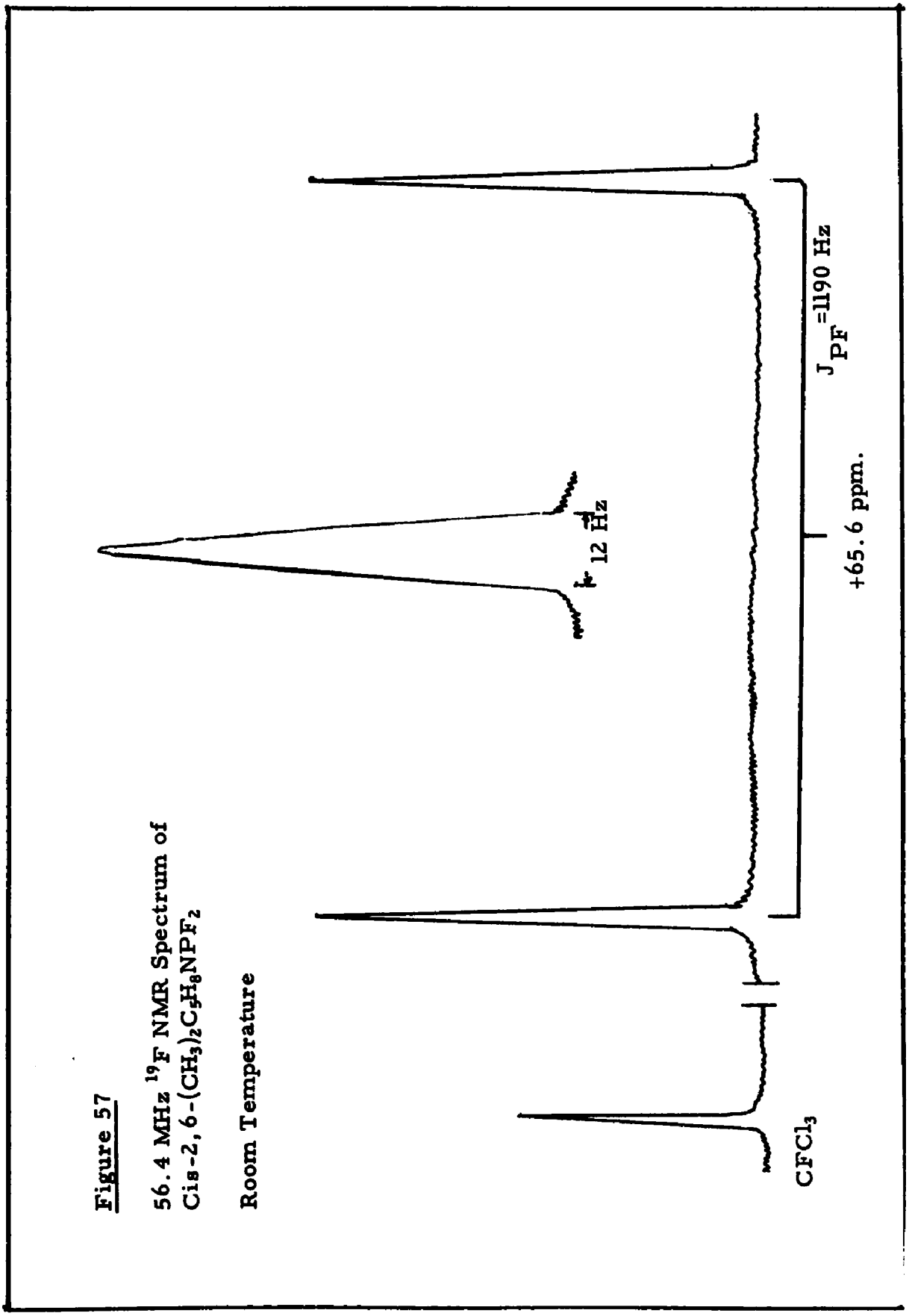


Figure 57

56.4 MHz ^{19}F NMR Spectrum of
Cis-2,6-$(CH_3)_2C_5H_8NPF_2$

Room Temperature

2-$(CH_3)C_5H_9NPF_2$, i.e. directed towards the methyl groups and bisected by the plane made by P-N-(C_2). Only one isomer is possible (Fig. 58). However, it could be that the fluorines are above the P-N-(C_2) plane, as the ^{19}F nmr spectrum of the borane adduct seems to suggest.

The ^{19}F nmr spectrum of the borane adduct at room temperature (Fig. 59) shows similarly only a doublet (J_{PF}= 1172 ± 2 Hz at δ = +73.4 ppm. ($CFCl_3$)), suggesting the absence of isomerism. Each member of this doublet is split into a 1:3:3:1 quartet, J_{HBPF}= 14.5 ± 0.5 Hz, typical of coupling with the three equivalent borane protons. From steric grounds, it seem reasonable that the structure of the borane adduct of cis-2,6-$(CH_3)_2C_5H_8NPF_2$ would be one in which the two fluorines are above the P-N-(C_2) plane and the BH_3 group below this same plane as Fig. 60 shows. A structure in which the P-N-(C_2) plane bisects the -PF_2 angle would be sterically hindered.

From the above discussions, it can be seen that the ^{19}F nmr spectra of cis-2,6-$(CH_3)_2C_5H_8NPF_2$ and its borane adduct are consistent with the structural arguments cited on page 66.

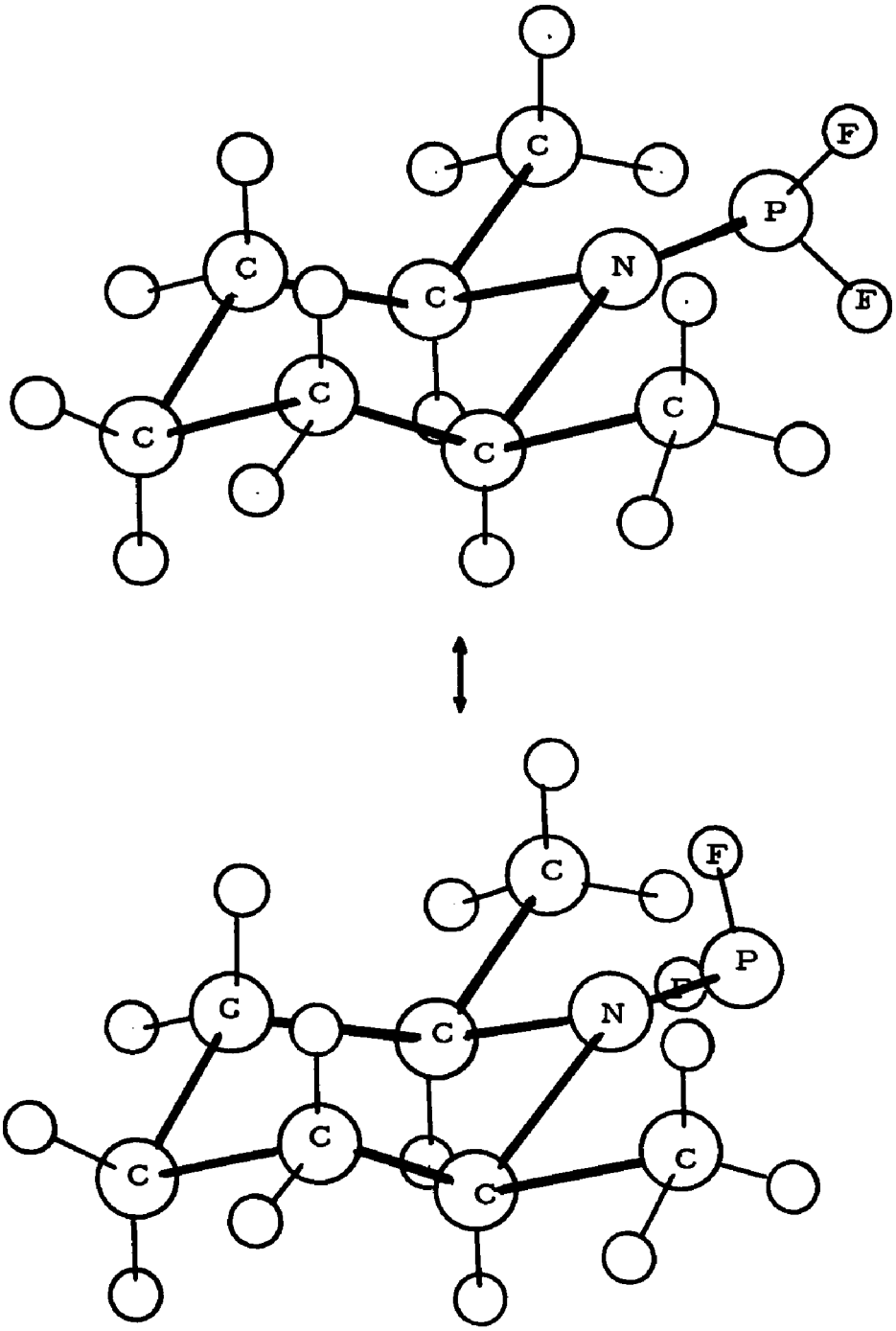


Figure 58

Possible Structure of Cis-2,6-$(CH_3)_2C_5H_8NPF_2$

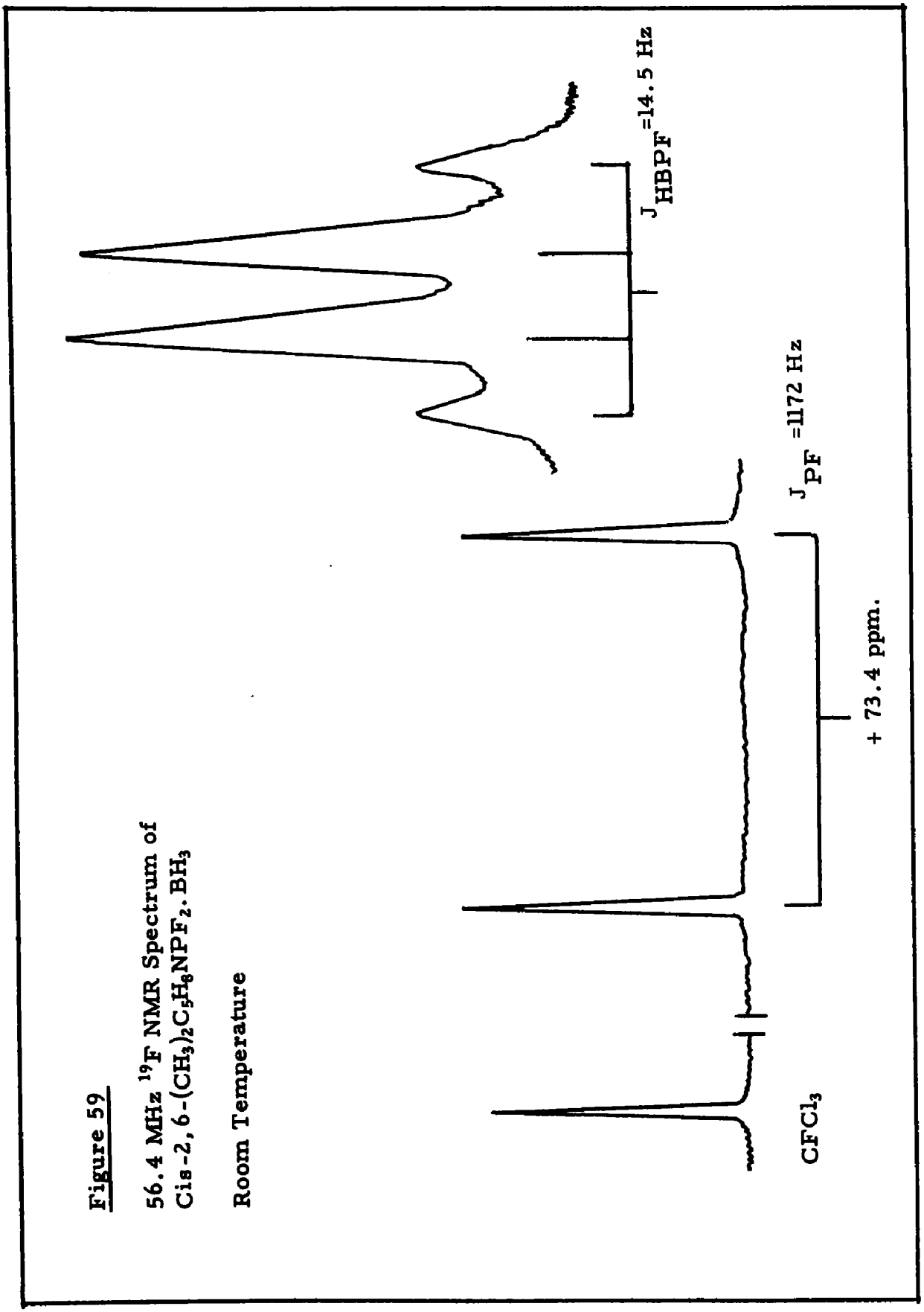


Figure 59

56.4 MHz ^{19}F NMR Spectrum of Cis-2,6-$(CH_3)_2C_5H_6NPF_2.BH_3$

Room Temperature

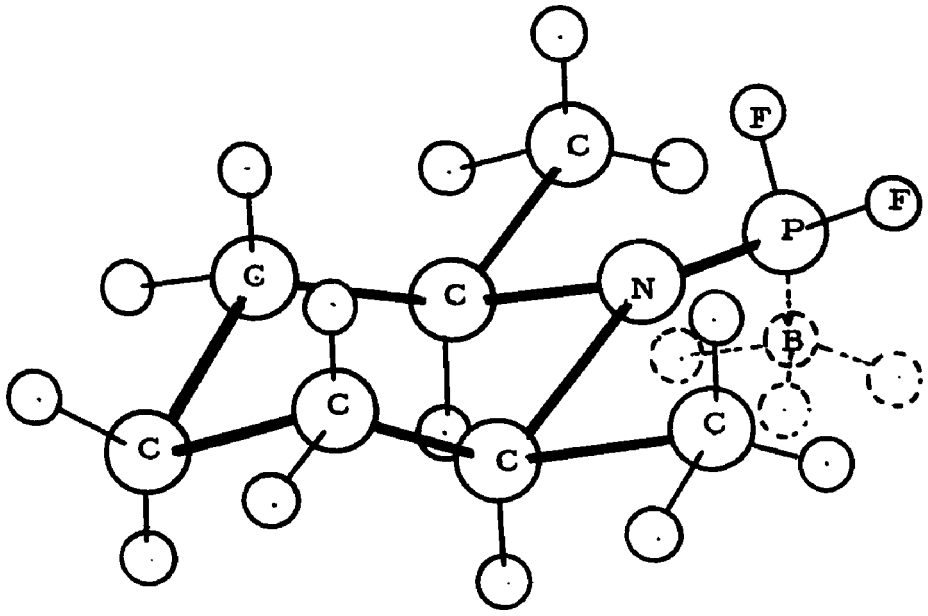


Figure 60

Possible Structure of Cis-2,6-$(CH_3)_2C_5H_8NPF_2 . BH_3$

VI - (3-METHYLPIPERIDYL)DIFLUOROPHOSPHINE AND ITS BORANE ADDUCT

In order to obtain more information on the question of PF_2-H_3C interaction (page 106), a study on (3-methylpiperidyl)difluorophosphine, 3-$(CH_3)C_5H_9NPF_2$, was undertaken. This compound is very closely related to 2-$(CH_3)C_5H_9NPF_2$ with the position of the methyl group, the only difference between them. Interaction of the two fluorines in the PF_2-unit with the methyl protons would be negligible in 3-$(CH_3)C_5H_9NPF_2$, hence the argument clearly predicts the existence of only one isomer if free rotation would be allowed.

A. SYNTHESIS OF 3-$(CH_3)C_5H_9NPF_2$ AND 3-$(CH_3)C_5H_9NPF_2 . BH_3$

3-$(CH_3)C_5H_9NPF_2$ can be prepared conveniently by the direct reaction of 3-methylpiperidine and phosphorus trifluoride

$$2\ \ 3\text{-}(CH_3)C_5H_{10}N\ +\ PF_3 \longrightarrow 3\text{-}(CH_3)C_5H_9NPF_2\ +\ 3\text{-}(CH_3)C_5H_{10}N . HF$$

or by fluorination of its dichloro-analogue with SbF_3

$$2\ \ 3\text{-}(CH_3)C_5H_9NPCl_2\ +\ 2\ SbF_3 \rightarrow 3\ \ 3\text{-}(CH_3)C_5H_9NPF_2\ +\ 2\ SbCl_3 .$$

Fig. 61 shows its infrared spectrum, which, upon comparison with the infrared spectrum of 3-methylpiperidine (Fig. 62), reveals the absence of N-H stretching frequency at 3260 cm^{-1}, and the presence

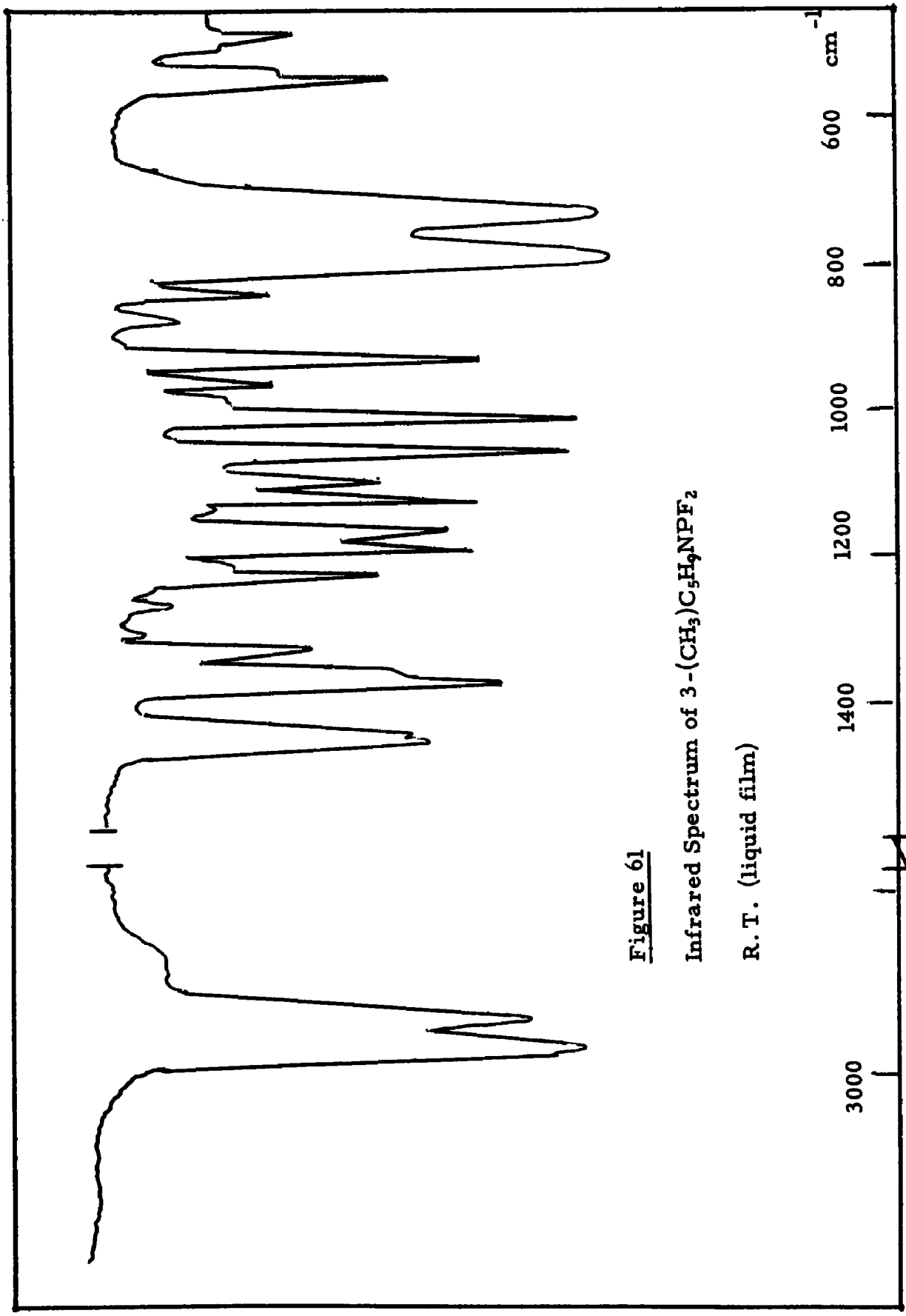


Figure 61

Infrared Spectrum of 3-$(CH_3)C_5H_9NPF_2$

R. T. (liquid film)

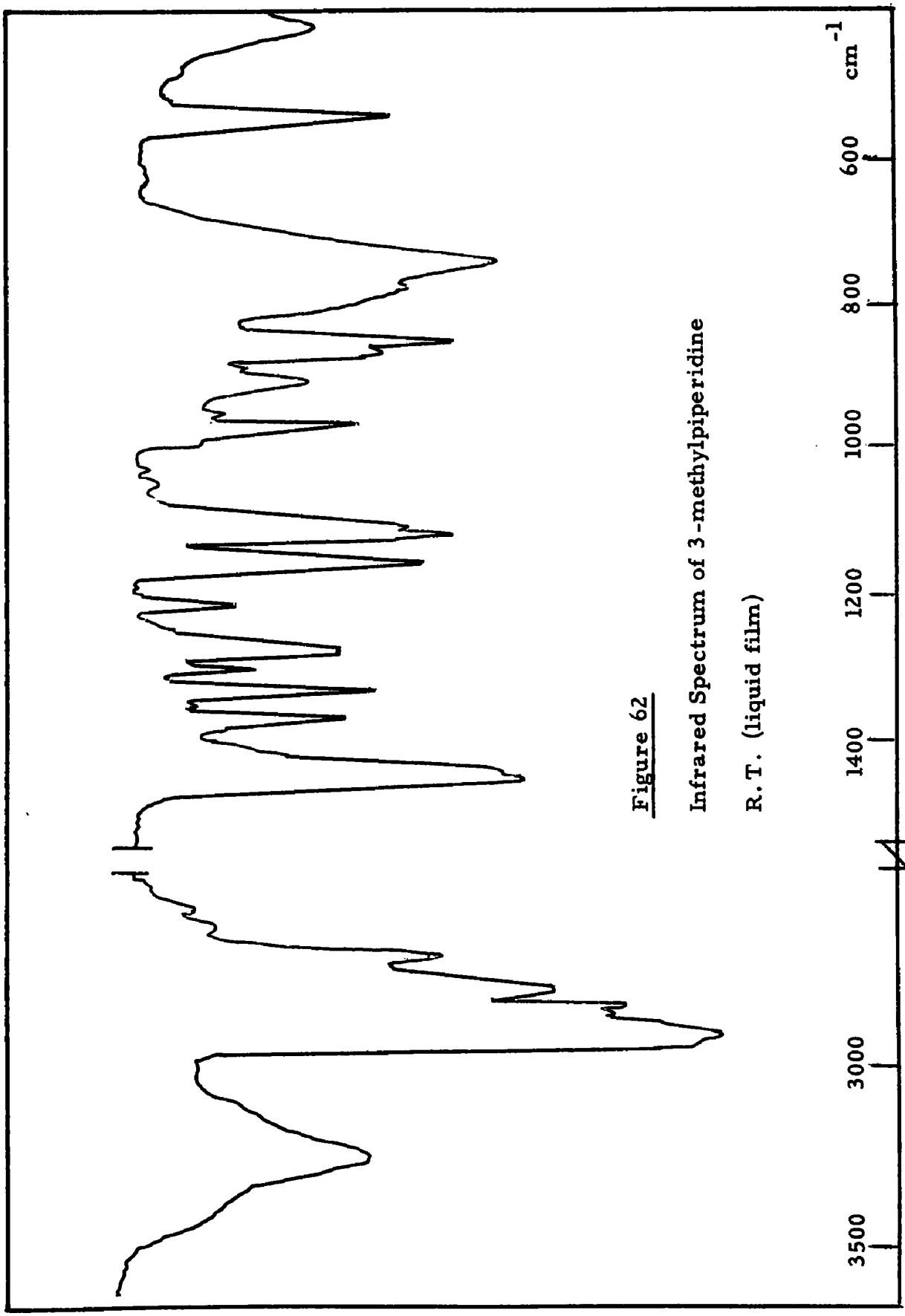


Figure 62

Infrared Spectrum of 3-methylpiperidine

R.T. (liquid film)

of two strong absorptions at 795 and 735 cm^{-1}. Anal. Calculated for 3-$(CH_3)C_5H_9NPF_2$: C, 43.11; H, 7.24; N, 8.28. Found: C, 42.63; H, 6.78; N, 8.37.

Its borane adduct was prepared by reaction with diborane in ether at -78°C

$$3\text{-}(CH_3)C_5H_9NPF_2 + \tfrac{1}{2} B_2H_6 \longrightarrow 3\text{-}(CH_3)C_5H_9NPF_2.BH_3 .$$

The infrared spectrum of 3-$(CH_3)C_5H_9NPF_2.BH_3$ shown in Fig. 63 shows the characteristic B-H stretching frequencies at 2405 and 2360 cm^{-1}. Anal. Calculated for 3-$(CH_3)C_5H_9NPF_2.BH_3$: C, 39.83; H, 8.35; N, 7.74. Found: C, 38.88; H, 7.87; N, 7.78.

Table X gives the infrared absorption frequencies of 3-methylpiperidine, 3-$(CH_3)C_5H_9NPF_2$, and 3-$(CH_3)C_5H_9NPF_2.BH_3$.

B. THE ^{31}P NMR SPECTRA OF 3-$(CH_3)C_5H_9NPF_2$ AND 3-$(CH_3)C_5H_9NPF_2.BH_3$

At room temperature, the 40.4 MHz ^{31}P nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ (Fig. 64) is a 1:2:1 triplet at δ = -137.2 ± 0.5 ppm. (H_3PO_4). The splitting pattern is typical of difluorophosphines, giving a coupling constant of J_{FP} = 1195 ± 2 Hz representing the spin-spin interaction of the phosphorus nucleus with the two fluorine nuclei.

The borane adduct also shows a 1:2:1 triplet (Fig. 65), as expected, at δ = -126.2 ± 0.5 ppm. (H_3PO_4). Again, coupling of the phosphorus with the fluorine nuclei gives the triplet splitting pattern, with J_{FP}= 1158 ± 2 Hz. In addition, the phosphorus exhibits further spin-spin

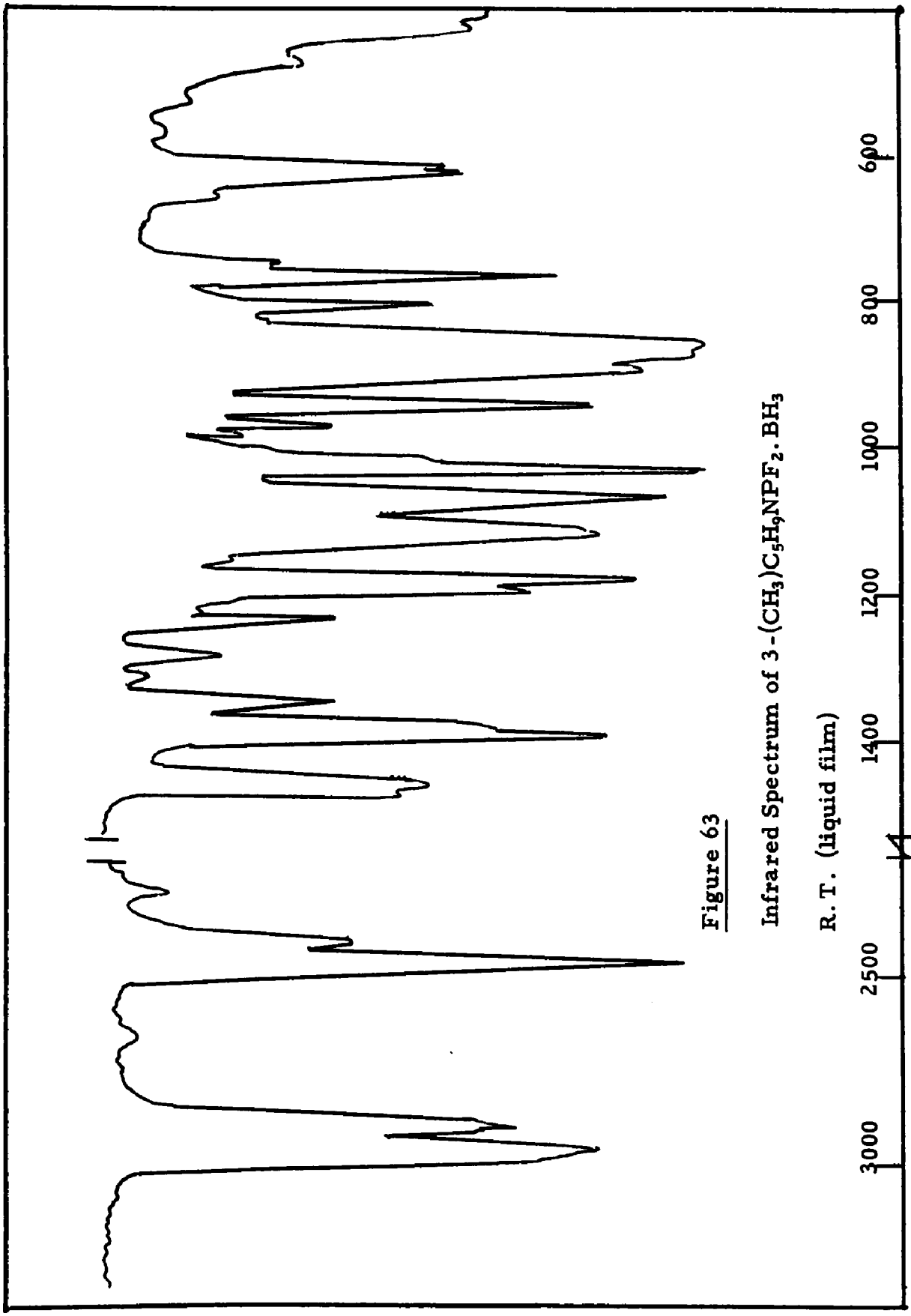


Figure 63

Infrared Spectrum of 3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

R. T. (liquid film)

Table X - Infrared Absorption Frequencies of 3-(CH_3)-$C_5H_{10}N$, 3-$(CH_3)C_5H_9NPF_2$, and 3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

3-$(CH_3)C_5H_{10}N$	3-$(CH_3)C_5H_9NPF_2$	3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$
3260 m, b	2930 s	2940 s
2920 s	2860 s	2860 s
2865 sh	2700 vw, sh	2855 sh
2840 m, sh	1460 m	2620 vw
2800 m	1450 m, sh	2405 s
2720 m	1380 s	2360 w
2640 vw, sh	1365 sh	2230 vw
1450 m	1335 w	1455 m
1430 m, sh	1305 vw	1440 sh
1370 w	1275 w	1385 s
1350 vw	1225 ,	1375 m, sh
1330 w	1215 sh	1340 w
1300 w	1190 m	1305 vw
1275 w	1170 m	1280 w
1215 w	1145 w, sh	1225 w
1155 m	1125 m	1210 vw
1125 m	1100 w	1185 m, sh
1100 sh	1085 sh	1175 s
1040 vw	1060 s	1145 vw
1025 vw	1015 s	1112 s
990 sh	985 w, sh	1100 sh
965 w	965 w	1060 s
950 w, sh	930 m	1020 s
900 w, b	880 w	1010 sh
880 sh	845 w	980 w
860 w	795 s	960 w
845 m	735 s	940 s
775 w, sh	625 vw	890 s, sh
735 m, b	550 w	850 s, b
550 w	540 w, sh	800 m
440 vw	505 vw, sh	755 s
	490 vw	735 sh
	410 vw	620 m
		610 m, sh
		570 vw
		520 vw
		465 vw

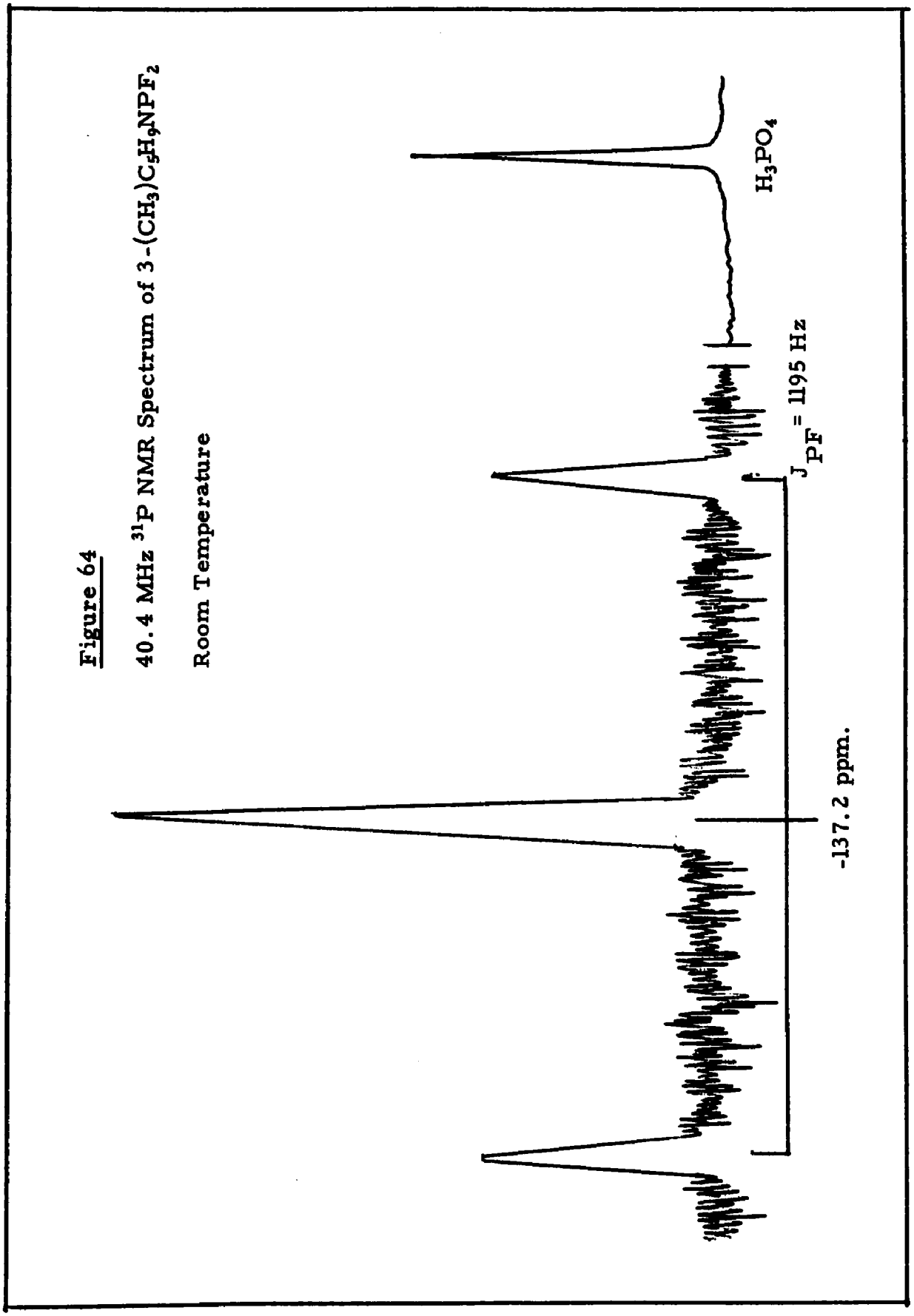


Figure 64

40.4 MHz ^{31}P NMR Spectrum of 3-$(CH_3)C_5H_9NPF_2$

Room Temperature

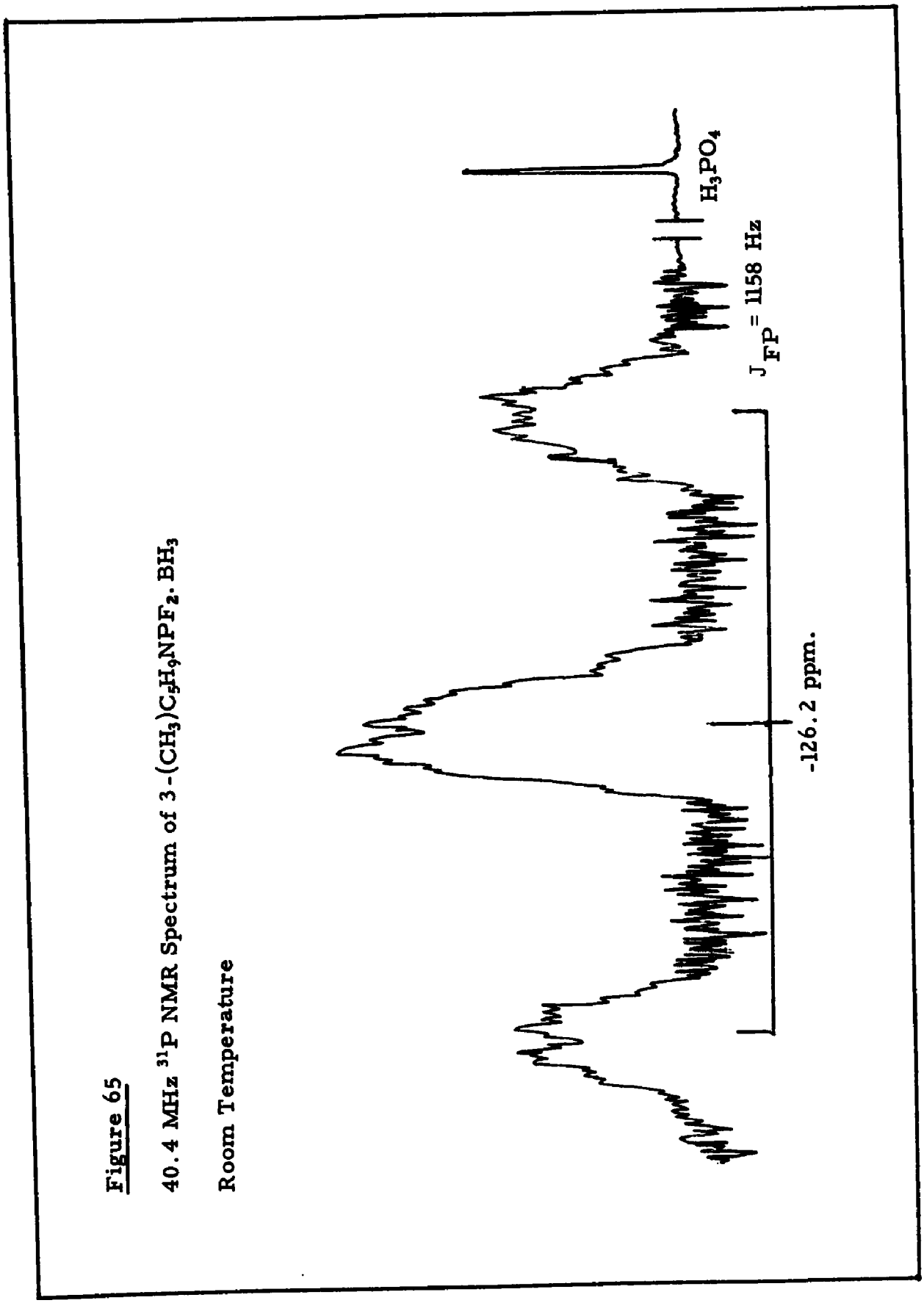


Figure 65

40.4 MHz ^{31}P NMR Spectrum of 3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

Room Temperature

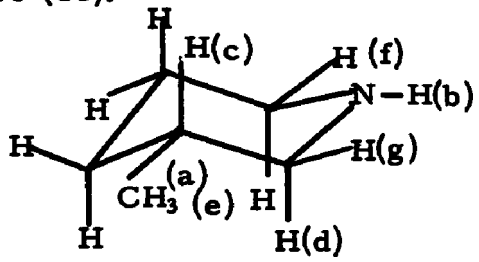
interaction with the boron nucleus and as a result each member of the basic triplet appears to be split into a 1:1:1:1 quartet. However, the high noise level makes unequivocal and objective interpretation difficult.

C. THE ^{11}B NMR SPECTRUM OF 3-$(CH_3)C_5H_9NPF_2.BH_3$

The 32.1 MHz ^{11}B nmr spectrum of 3-$(CH_3)C_5H_9NPF_2.BH_3$ (Fig. 66) shows a 1:3:3:1 quartet at δ =+130.1 ± 0.1 ppm. from $B(CH_3)_3$, each of which at higher resolution, is split into 1:1 doublets. Coupling of the boron nucleus with the borane protons would give the quartet splitting, J_{HB} = 101 ± 1 Hz, and further coupling with the phosphorus nucleus would give the additional splitting of the original quartet, J_{PB} = 81 ± 1 Hz.

D. THE ^1H NMR SPECTRA OF 3-METHYLPIPERIDINE, 3-$(CH_3)C_5H_9N$-PF_2, AND 3-$(CH_3)C_5H_9NPF_2.BH_3$

The proton nmr spectrum of 3-methylpiperidine has been reported earlier in the literature (44):



a) -0.82 ppm. (TMS)

b) -1.47 ppm. (TMS)

c) -1.55 ppm. (TMS)

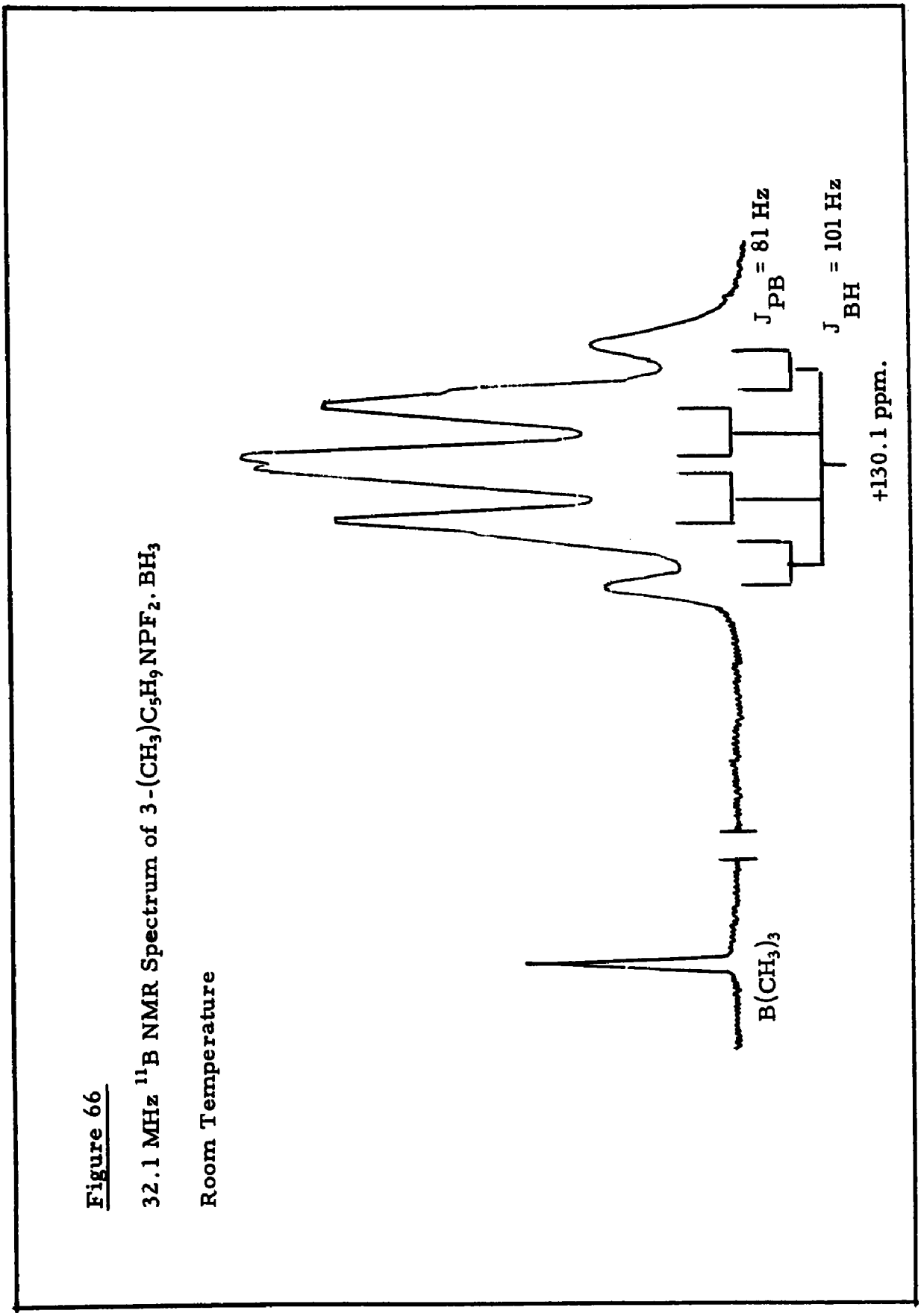


Figure 66

32.1 MHz ^{11}B NMR Spectrum of 3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

Room Temperature

d) -2.21 ppm. (TMS)

e) -2.52 ppm. (TMS)

f) and g) -3.00 ppm. (TMS).

The experimentally obtained 60 MHz ^1H nmr spectrum of 3-methylpiperidine (Fig. 67) is in good agreement with the reported spectrum. The high-field doublet at δ = -0.83 corresponds obviously to the methyl protons, J_{HCCH} = 6.2 ± 0.1 Hz. A singlet due to the N-H proton is observed amidst a multiplet centered at δ = -1.53 ppm. Peaks corresponding to the other protons at δ = -2.20. 2.52, and 2.98 ppm. (TMS) are also evident.

It is interesting to note that distinct signals for equatorial and axial protons on the 2- and 6-positions of the piperidine ring are recognized, in addition to the equatorial orientation of the methyl group. No temperature dependence in the proton nmr spectrum is observed in the range -65°C to +100°C. This is an indication that no ring interconversion process is occuring, and that the molecule exists as one conformer.

The 60 MHz ^1H nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ at room temperature (Fig. 68) gives a very similar spectrum, with the exception that no N-H peak is evident:

a) a doublet at δ = -1.03 ± 0.02 ppm. (TMS), J_{HCCH} = 6.3 ± 0.1 Hz

b) a complex multiplet centered at δ = -1.78 ± 0.02 ppm. (TMS)

c) a broad and complex multiplet centered at δ = -2.72 ± 0.03 ppm. (TMS)

d) and a broad triplet at δ = -3.63 ± 0.04 ppm. (TMS).

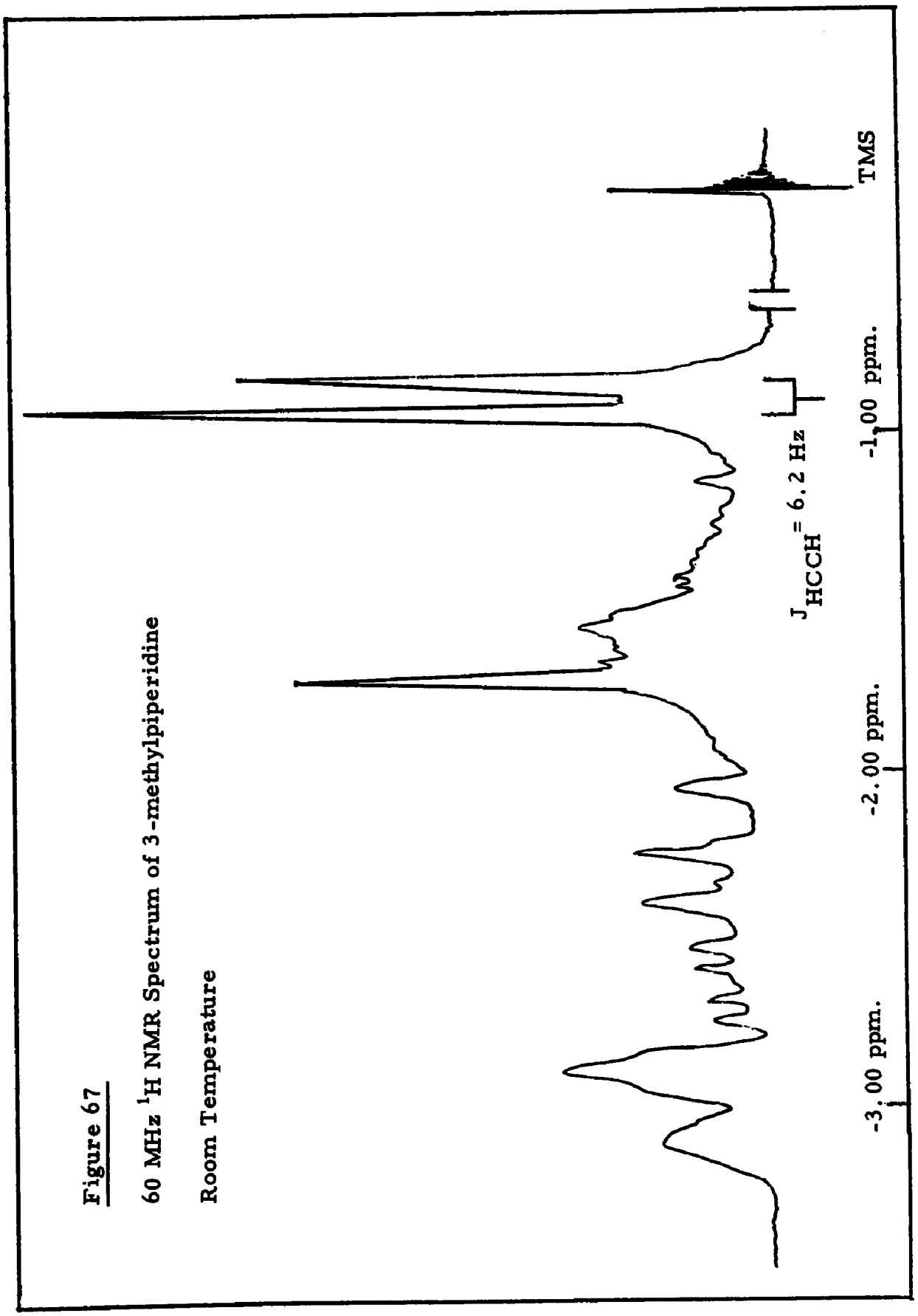


Figure 67

60 MHz ^{1}H NMR Spectrum of 3-methylpiperidine

Room Temperature

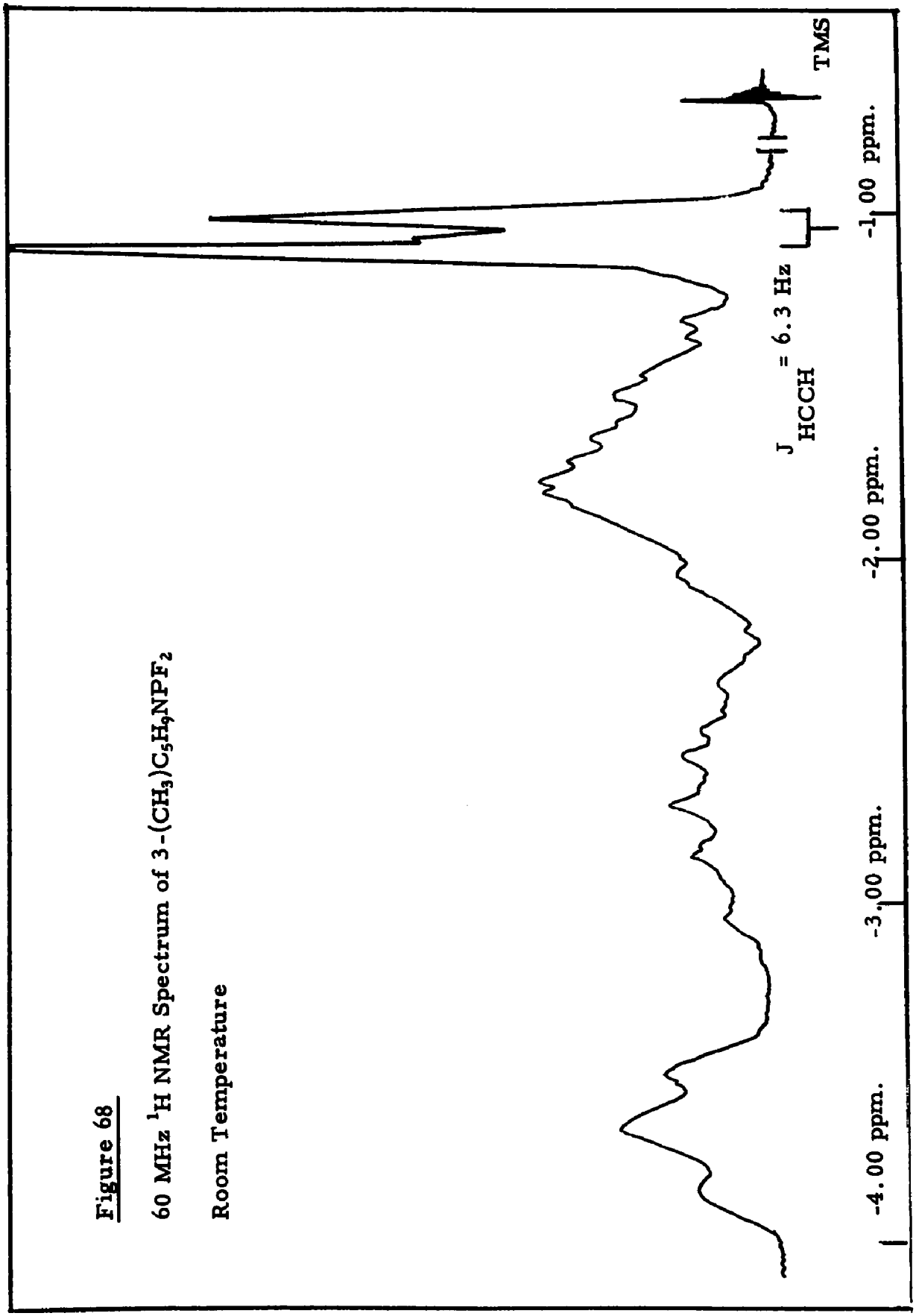


Figure 68

60 MHz ^1H NMR Spectrum of 3-$(CH_3)C_5H_4NPF_2$

Room Temperature

The area ratios are 3:5:2:2 respectively. Using these area ratios as a basis, assignment of the various nmr signals can be made with little difficulty. The high-field doublet at δ =-1.03 ppm. belongs to the methyl proton. The low-field signal at δ =-2.72 ppm. is due to the axial protons, and the signal at δ = -3.63 is due to the equatorial protons on the 2- and 6-positions. The inductive effect of the PF_2-group is manifested in the nmr signals occuring at lower magnetic fields than in 3-methylpiperidine. The broad multiplet centered at δ =-1.78 ppm. corresponds to the other ring protons.

Coordination of the BH_3 group provides an additional deshielding effect in the various protonic nuclei in the molecule, and as a result nmr signals in the borane adduct occur at even lower magnetic fields. The ^1H nmr spectrum of $3\text{-}(CH_3)C_5H_9NPF_2.BH_3$ (Fig. 69) consists of:

a) a doublet at δ = -1.08 ± 0.02 ppm. (TMS), J_{HCCH} = 6.2 ± 0.1 Hz

b) a broad multiplet whose center is at δ = -1.79 ppm. (TMS) ± 0.02 ppm.

c) a rather broad peak centered at δ = -2.89 ± 0.03 ppm. (TMS)

d) and a broad triplet with a chemical shift of δ = -3.80 ± 0.04 ppm. (TMS).

Their integrated area ratios are 3:5:2:2 respectively. At higher gain, a 1:1:1:1 quartet, attributed to the borane protons coupling with the boron nucleus is observed with a chemical shift of δ = 0.77 ± 0.02 ppm. (TMS) and a coupling constant J_{BH} = 100 ± 1 Hz. Two members of this quartet are badly overlapped by the methyl proton's nmr signal.

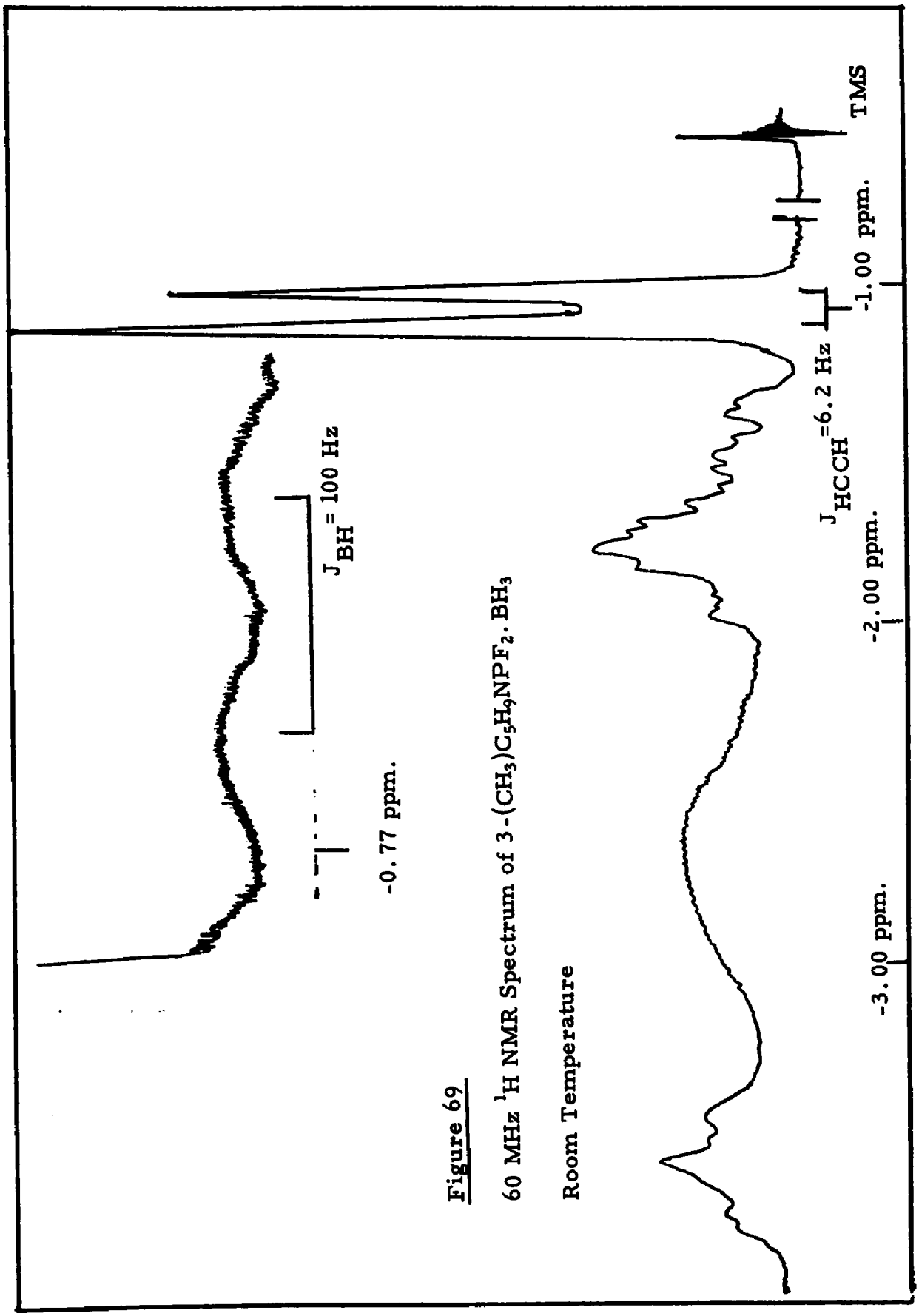


Figure 69

60 MHz ^{1}H NMR Spectrum of 3-$(CH_3)C_5H_9NPF_2.BH_3$

Room Temperature

E. THE ^{19}F NMR SPECTRUM OF 3-$(CH_3)C_5H_9NPF_2$

The ^{19}F nmr spectra of 2-$(CH_3)C_5H_9NPF_2$ and 2-$(CH_3)C_5H_9NPFCl$ indicated the presence of isomers in these compounds. In contrast, the spectrum of 3-$(CH_3)C_5H_9NPF_2$ does not show any evidence of isomerism. As shown in Fig. 70, it consists of only one doublet at δ = +64.3 ± 0.2 ppm. ($CFCl_3$). The doublet is due to coupling with the phosphorus nucleus giving a J_{PF} value of 1180 ± 2 Hz. At higher resolution, each member of this doublet is split into a six-line multiplet which appears to be an apparent doublet whose members are split further into 1:2:1 triplets. The splitting of each member of the original doublet could be ascribed to the non-equivalence of the two fluorine atoms in the molecule. The area ratio of these high resolution doublets remain constant at approximately 1:1 through a series of temperatures ranging from -45°C to 100°C. This fact supports the non-equivalence of the fluorine atoms. If the high resolution doublet structure were due to the existence of isomers, then their area ratio might be expected to change with temperature. It is interesting to note that the separation between these high resolution doublet (94.1 MHz oscillator) is temperature dependent. At -45°C, it is 29.5 ± 0.3 Hz. It decreases to 26.2 Hz at ambient temperature, and becomes 23.2 Hz at +100°C. In addition to being temperature dependent, this separation is also magnetic field dependent, i.e. 16.5 Hz at ambient temperature using a 56.4 MHz radio-frequency oscillator (theoretical value is 15.7 Hz). This suggests that such separation between the high resolution doublet is not associated

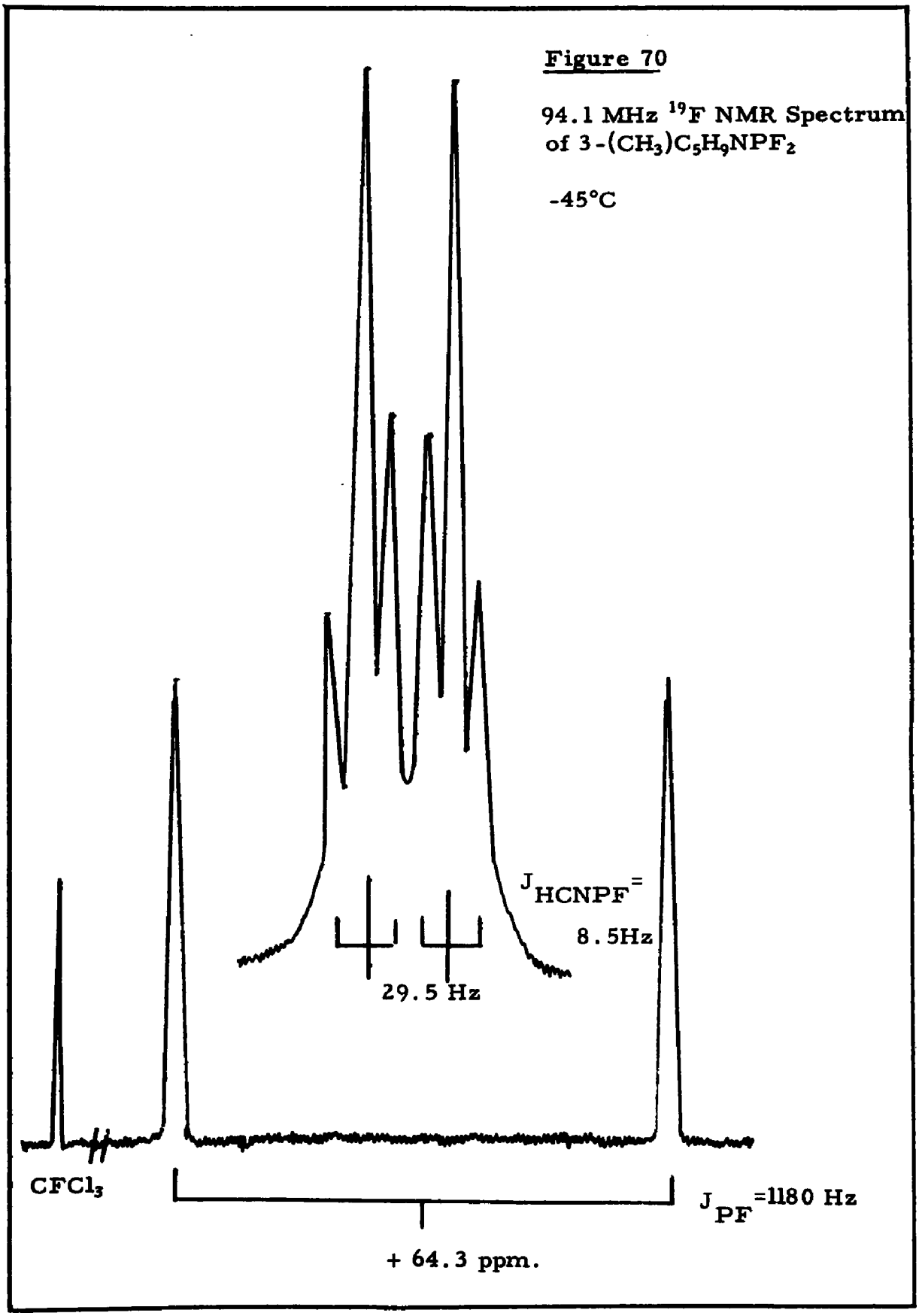
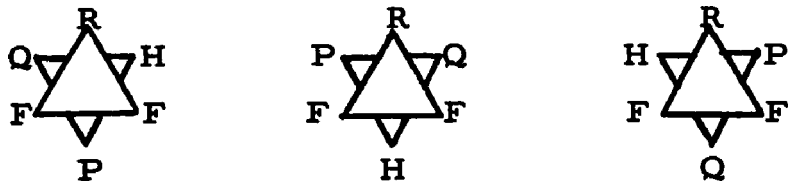


Figure 70
94.1 MHz ^{19}F NMR Spectrum of $3-(CH_3)C_5H_9NPF_2$
-45°C
J_{HCNPF}= 8.5Hz
29.5 Hz
$CFCl_3$
J_{PF}=1180 Hz
+ 64.3 ppm.

with spin-spin interaction but rather with a chemical shift phenomenon.

The observed ^{19}F nmr spectrum can be interpreted as the AB spectrum of an ABX system. The two fluorines are the A and B nuclei, and phosphorus is the X nucleus. In this particular system, J_{AB} is the geminal fluoro coupling constant; $J_{AX} = J_{BX}$, is the phosphorus-fluorine coupling constant which in this case is measured to be 1180 Hz. Like the ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPF_2$, the apparent doublet structure of each member of the basic doublet in the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ can be analyzed as the two central peaks of an AB quartet whose outer peaks are not distinguished from the noise level. That this splitting is not a coupling constant is shown by its field dependence.

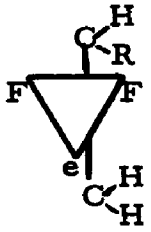
It seems fitting at this point to clarify the aspect of non-equivalence of the two fluorine atoms in 3-$(CH_3)C_5H_9NPF_2$. In their investigations on asymmetrically substituted ethanes, Drysdale and Phillips (67) found the fluorines in compounds of the type CF_2R-CHPQ to be non-equivalent even at temperatures at which the internal rotation about the C-C bond is assumed to be rapid. It was pointed out by Nair and Roberts (68) that the fluorines in the three rotational isomers



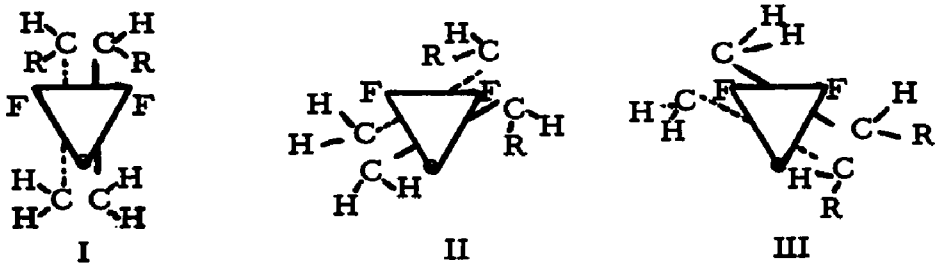
are not equivalent, and their chemical shifts are not necessarily averaged by rapid rotation unless the residence times of the molecule in

each of the various rotational conformations are equal.

The case of 3-$(CH_3)C_5H_9NPF_2$ can be looked at in a similar fashion. If one looks down the P-N molecular axis, the molecule can be schematically represented as



where R corresponds to the rest of the ring system containing a methyl group in the 3-position. The various stages of internal rotation about the P-N bond can be conveniently represented as

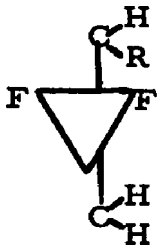


I II III

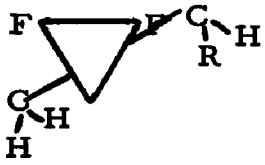
where the dotted lines represent equivalent conformations if interconversion of the ring is possible.

In the case of piperidyldifluorophosphine where R = H (i.e. no methyl substituent on the ring), the ring system has been shown (page 32) to be interconverting between two chair forms. The fluorine atoms are equivalent in conformation I because of ring interconversion. Due to interconversion of the piperidine ring, conformations II and III, containing non-equivalent fluorine atoms, are mirror images. Residence time of the molecule in each of these two conformation must be the same (mirror-image isomers), hence the fluorines will be magnetically equi-

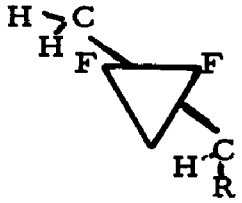
valent. No evidence for non-equivalence of the two fluorines in piperidyldifluorophosphine was found at room temperature. However, if the interconversion of the ring system is prevented by sufficiently lowering the temperature,



IV



V



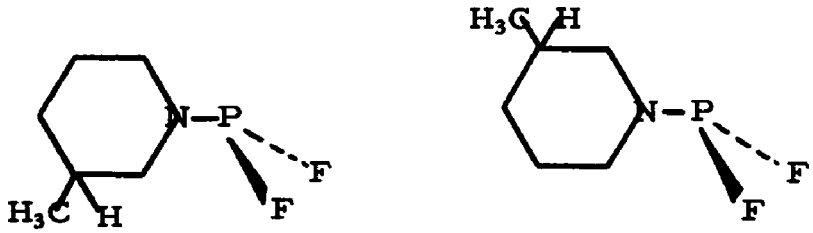
VI

the fluorines are not equivalent in any of these three conformations, and there is no symmetry relationship (i.e. mirror-image isomers) demanding equal residence time in each of these conformations. The ^{19}F nmr spectrum of piperidylfifluorophosphine at temperatures below -65°C showed the non-equivalence of the two fluorine atoms.

Ring interconversion at room temperature does not occur in $3\text{-}(CH_3)C_5H_9NPF_2$. This case is similar to that of piperidyldifluorophosphine below -65°C. It is clear that the two fluorines are not equivalent and that the residence time of the molecule in the various rotational conformations may not be equal such that their respective chemical shifts are not averaged by rapid rotation about the P-N bond. A difference in the relative residence times of the molecule would imply that the apparent degree of non-equivalence of the fluorines will vary with temperature. This is borne out by the fact that the separation of the high resolution doublet of each member of the original doublet in the

^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ changes with temperature.

The ^{19}F nmr spectrum is consistent with free rotation about the P-N bond and with a single configuration for 3-$(CH_3)C_5H_9NPF_2$, but the data do not unequivocally prove the existence of a single isomer. It appears from ^{1}H nmr and other data on related molecules that differences in the ^{19}F nmr signal between the configurations *



would not be detectable in the ^{19}F nmr spectrum with the equiptment used in this study.

The observation that the high resolution doublet of each member of the original doublet in the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ is further split into 1:2:1 triplet suggests that the fluorines are experiencing spin-spin interaction with two equivalent ring protons to give a coupling constant, $J_{HCNPF} = 8.5 \pm 0.5$ Hz. "Through-space" coupling is ruled out due to the position of the methyl group in this particular compound. In addition, coupling with the methyl group in some way would give the wrong splitting multiplicity. There are two sets of equivalent pairs of ring protons which could spin couple with the fluorines; the two equatorial and two axial protons, all of which are α to the nitrogen. The triplet splitting pattern could arise if the fluorine nuclei couples appre-

---

* The ring system is in a chair form. This schematic representation is for the sake of clarity and ease of presentation.

ciably with the two axial protons and not with the two equatorial protons, or vice-versa.

Earlier studies on substituted cyclohexanes (69), (70) have shown that axial hydrogen nuclei couple much more strongly than hydrogen nuclei in equatorial orientations. Studies by Peake and Thomas (47) on hydrosubstituted-perfluorocyclohexanes gave values of H-F coupling constants which show that axial protons couples more than equatorial protons. Takahashi, Davis, and Roberts (60) showed that pseudoaxial protons couples with fluorine nuclei to a greater extent than pseudo-equatorial protons in substituted cyclobutanes. Basing on these literature reports, it would not be far-fetched to assign the triplet splitting pattern to coupling of the fluorines with the two axial protons α to the nitrogen, and not to the equatorial protons.

The ^{19}F nmr spectrum of $3\text{-}(CH_3)C_5H_9NPF_2$ can now be fully interpreted as a basic doublet, $J_{PF} = 1180$ Hz, each of which is shown to consist of two central peaks of an AB quartet due to the non-equivalence of the fluorine atoms in the molecule. Each member of this two central peaks is further split into a 1:2:1 triplet as a result of the coupling with the two axial protons in the 2- and 6-positions of the heterocyclic ring.

F. THE ^{19}F NMR SPECTRUM OF $3\text{-}(CH_3)C_5H_9NPF_2.BH_3$

The ^{19}F nmr spectrum of $3\text{-}(CH_3)C_5H_9NPF_2.BH_3$ showed no indication of isomers. At room temperature the spectrum (Fig. 71) consists of a 1:1 doublet at $\delta = +73.5 \pm 0.2$ ppm. ($CFCl_3$) due to coupling with the

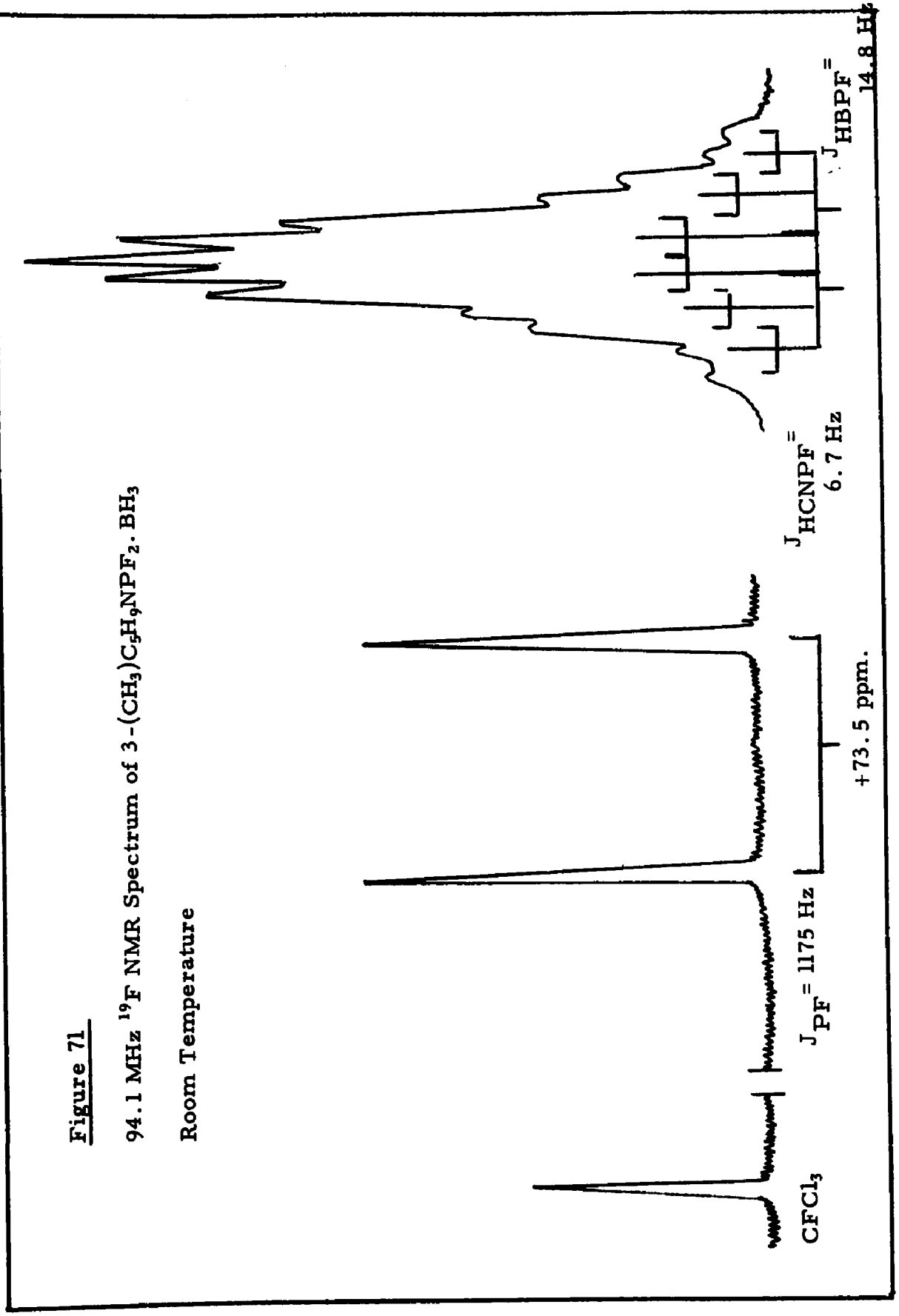


Figure 71

94.1 MHz ^{19}F NMR Spectrum of 3-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

Room Temperature

phosphorus nucleus nucleus, J_{PF}= 1175 * 2 Hz. Each member of this doublet is split into a 13-line multiplet at higher resolution. In the same way that the fluorine atoms in 3-$(CH_3)C_5H_9NPF_2$ are non-equivalent, the fluorines in its borane adduct would also be non-equivalent. The high resolution splitting pattern in the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$. BH_3 can thus be interpreted in terms of two central peaks of an AB quartet, separated by 26.2 Hz, each of which is split into 1:3:3:1 quartet (J_{HBPF}= 14.8 * 0.5 Hz) due to spin-spin interaction of the fluorines with the borane protons. Each member of this 1:3:3:1 quartet is further split into a 1:2:1 triplet (J_{HCNPF} = 6.7 * 0.5 Hz) on account of coupling with the two axial protons in the α -position. Overlapping of these peaks would bring about the multiplet observed.

The fact that the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$. BH_3 did not give any indication of isomerism would be consistent with the hypothesis that no appreciable hindrance to rotation about the P-N bond is presence in 3-$(CH_3)C_5H_9NPF_2$. However, the data do not provide proof of free rotation since the ^{19}F nmr signal may not show such small differences as those expected between the two possible isomeric structures.

VII - (4-METHYLPIPERIDYL)DIFLUOROPHOSPHINE, (4-METHYLPIPERIDYL)CHLOROFLUOROPHOSPHINE, AND THEIR BORANE ADDUCTS

Because of the position of the methyl group, (4-methylpiperidyl)difluorophosphine, 4-$(CH_3)C_5H_9NPF_2$, is not expected to show isomerism in its ^{19}F nmr spectrum. Nevertheless, it could give deeper insight on the non-equivalence of the fluorine atoms, and verify the interpretation of the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ and its borane adduct. (4- methylpiperidyl)chlorofluorophosphine, 4-$(CH_3)C_5H_9NPFCl$, would be expected to compliment the observations made on 4-(CH_3)-$C_5H_9NPF_2$ just as 2-$(CH_3)C_5H_9NPFCl$ did on the findings on 2-(CH_3)-$C_5H_9NPF_2$.

A. SYNTHESIS OF 4-$(CH_3)C_5H_9NPF_2$, 4-$(CH_3)C_5H_9NPFCl$, AND THEIR BORANE ADDUCTS

4-$(CH_3)C_5H_9NPF_2$ was prepared by the direct reaction of 4-methylpiperidine and phosphorus trifluoride

$$2\ \ 4\text{-}(CH_3)C_5H_{10}N\ +\ PF_3 \longrightarrow\ 4\text{-}(CH_3)C_5H_9NPF_2\ +\ 4\text{-}(CH_3)C_5H_{10}N.HF\ .$$

Its infrared spectrum (Fig. 72), when compared to the infrared spectrum of 4-methylpiperidine (Fig. 73) shows the absence of N-H stretching frequency at about 3270 cm^{-1}, and the presence of two strong peaks at 795 and 735 cm^{-1} indicative of the PF_2-group.

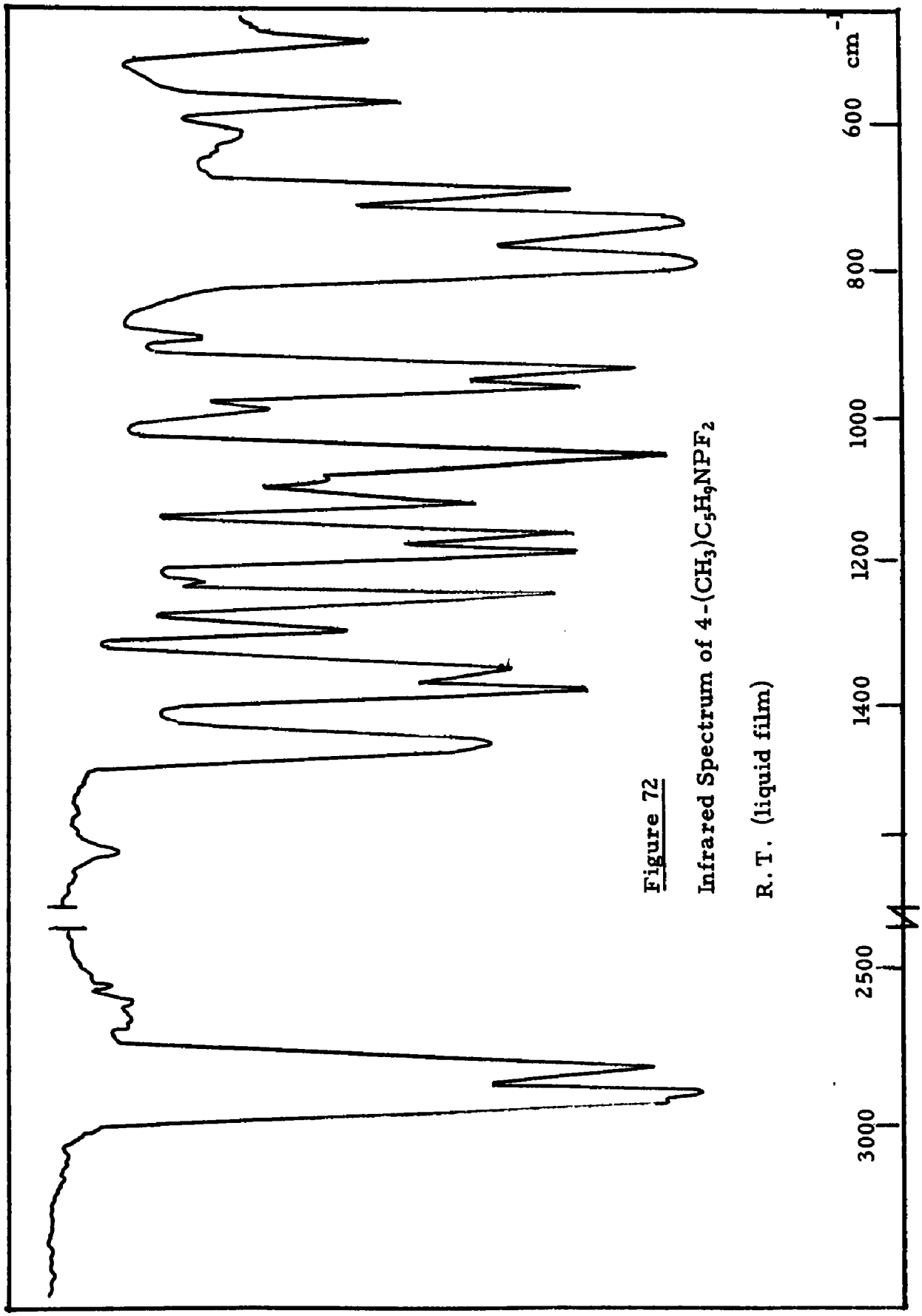


Figure 72

Infrared Spectrum of 4-$(CH_3)C_5H_9NPF_2$

R.T. (liquid film)

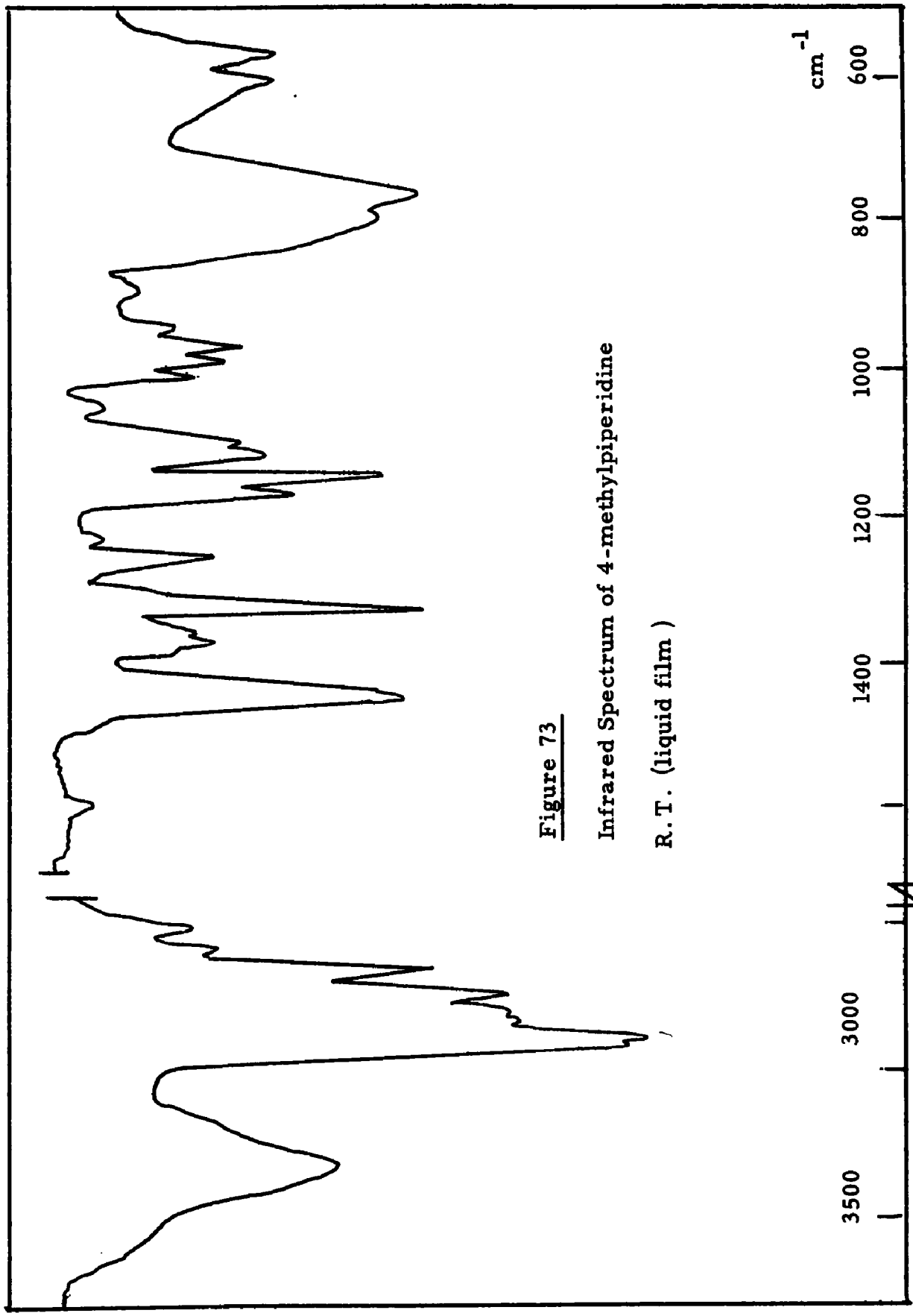


Figure 73

Infrared Spectrum of 4-methylpiperidine

R. T. (liquid film)

$4\text{-}(CH_3)C_5H_9NPFCl$ was prepared by the reaction between the free amine and $PFCl_2$ in ether

$$2\ 4\text{-}(CH_3)C_5H_{10}N + PFCl_2 \longrightarrow 4\text{-}(CH_3)C_5H_9NPFCl + 4\text{-}(CH_3)C_5H_9NH.HCl\ .$$

Its infrared spectrum shown in Fig. 74, does not show any N-H stretching frequency, but a broad, strong absorption at 780 cm^{-1} similar to that seen in the infrared spectrum of $2\text{-}(CH_3)C_5H_9NPFCl$, is evident.

Their borane adducts were prepared in the usual manner by reaction with diborane in ether at -78°C:

$$4\text{-}(CH_3)C_5H_9NPF_2 + \tfrac{1}{2}\,B_2H_6 \rightarrow 4\text{-}(CH_3)C_5H_9NPF_2.BH_3$$

$$4\text{-}(CH_3)C_5H_9NPFCl + \tfrac{1}{2}\,B_2H_6 \rightarrow 4\text{-}(CH_3)C_5H_9NPFCl.BH_3\ .$$

Their infrared spectra are shown in Figs. 75 and 76. Characteristic B-H stretching frequencies at 2410 and 2360 cm^{-1}, and 2420 and 2360 cm^{-1} respectively, are quite prominent.

Tables XI and XII give the infrared absorption frequencies of 4-methylpiperidine, $4\text{-}(CH_3)C_5H_9NPF_2$, $4\text{-}(CH_3)C_5H_9NPF_2.BH_3$, $4\text{-}(CH_3)C_5H_9NPFCl$, and $4\text{-}(CH_3)C_5H_9NPFCl.BH_3$ for purposes of comparison.

B. THE ^1H NMR SPECTRA OF 4-METHYLPIPERIDINE, $4\text{-}(CH_3)C_5H_9NPF_2$, $4\text{-}(CH_3)C_5H_9NPFCl$, AND THEIR BORANE ADDUCTS

1) 4-Methylpiperidine

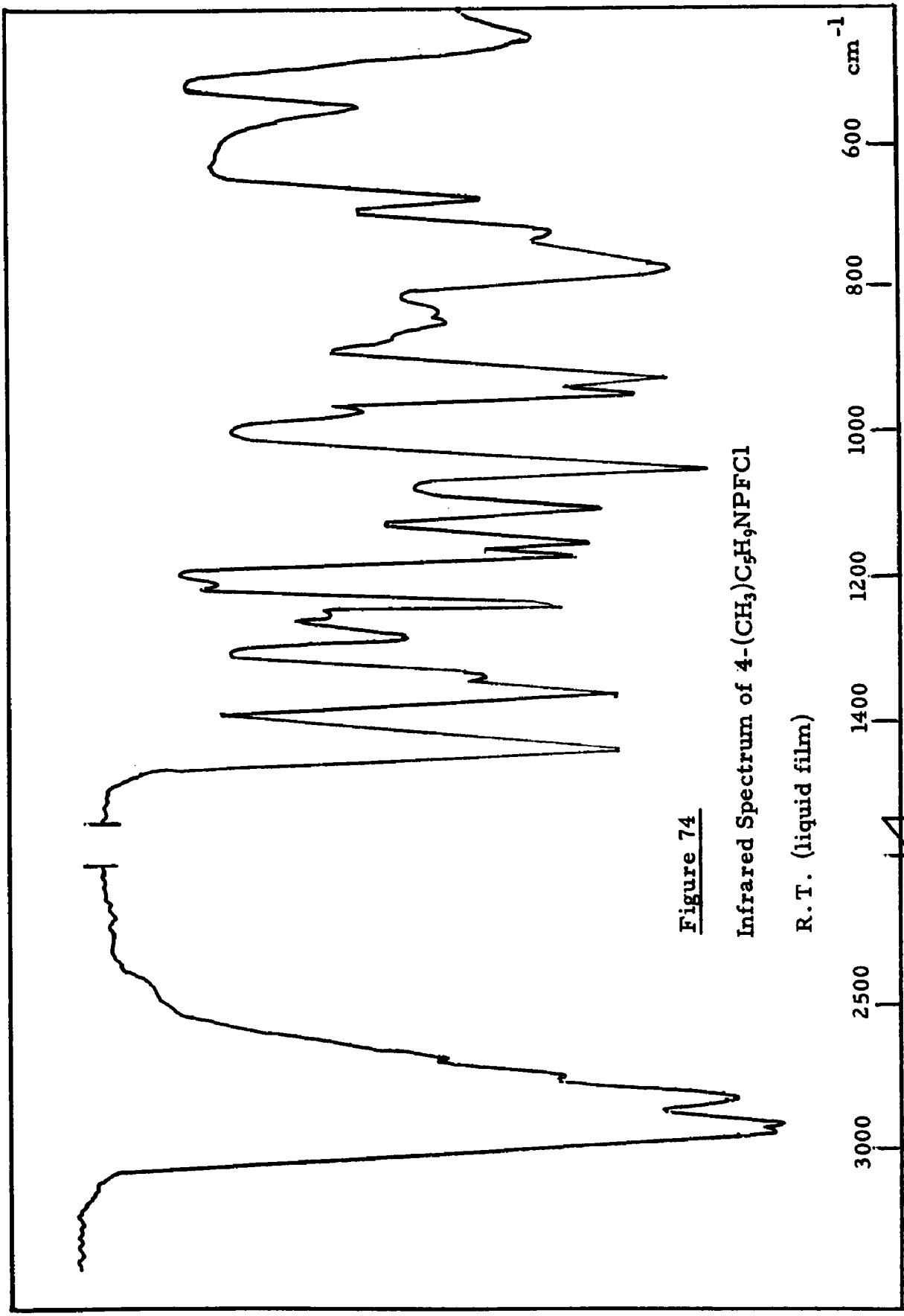


Figure 74

Infrared Spectrum of 4-$(CH_3)C_5H_9NPFCl$

R.T. (liquid film)

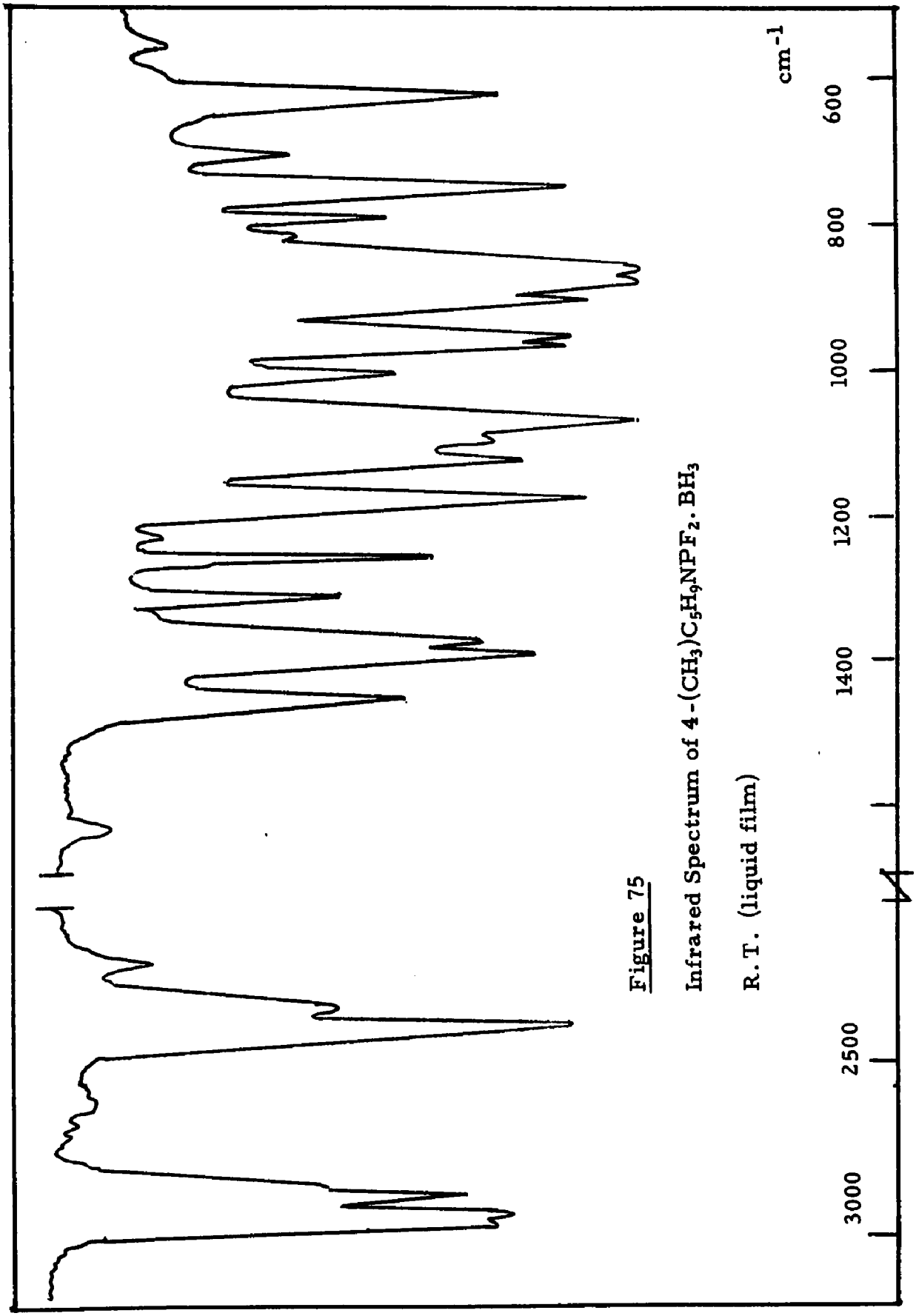


Figure 75

Infrared Spectrum of 4-$(CH_3)C_5H_9NPF_2 \cdot BH_3$

R.T. (liquid film)

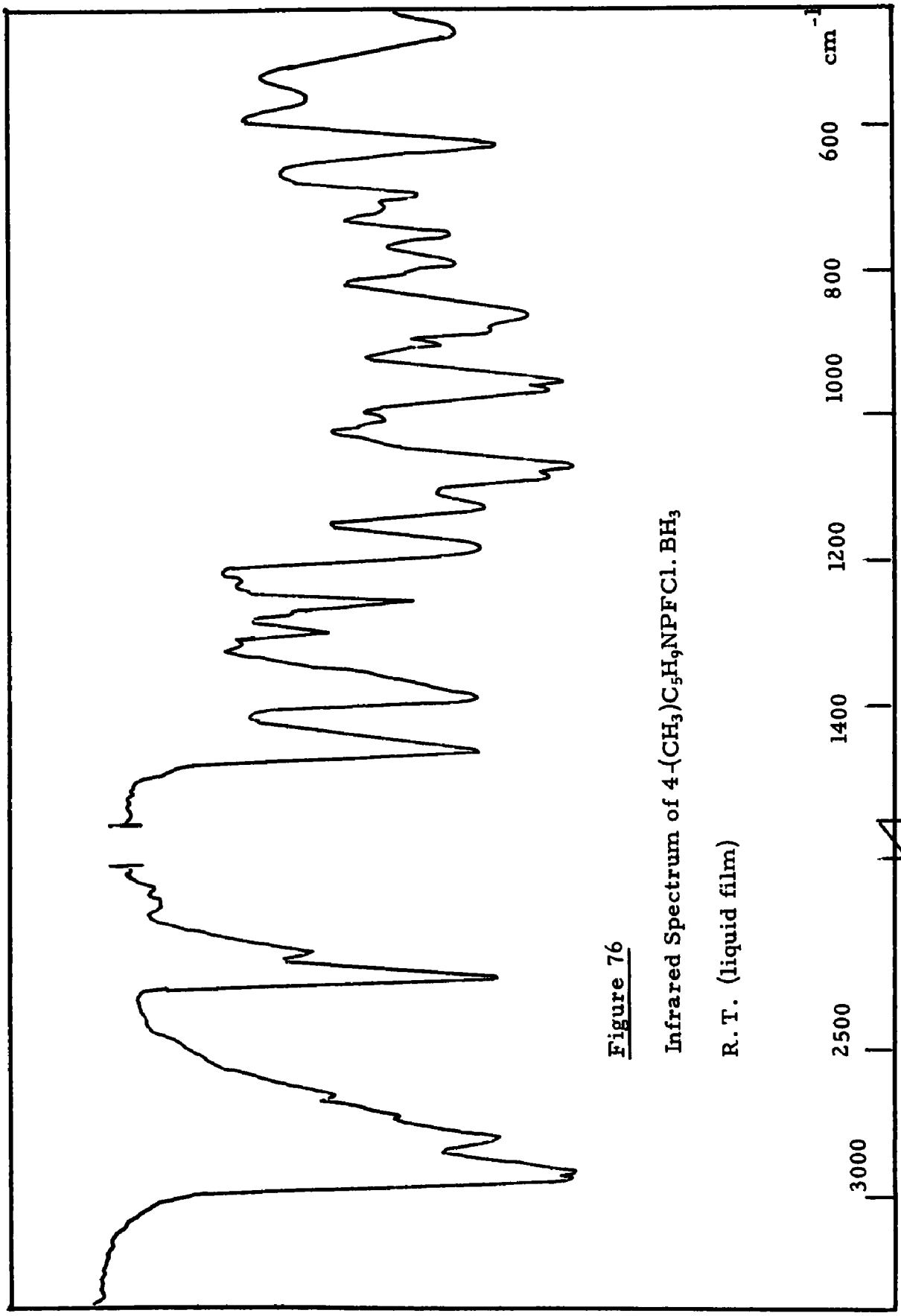


Figure 76

Infrared Spectrum of 4-$(CH_3)C_5H_9NPFCl.BH_3$

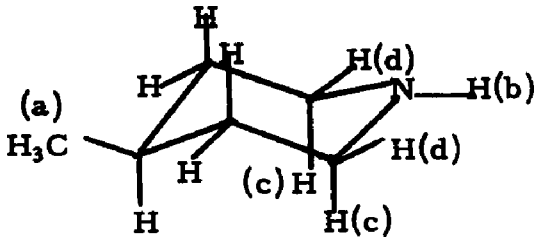
R.T. (liquid film)

Table XI - Infrared Absorption Frequencies of 4-$(CH_3)C_5H_{10}N$, 4-$(CH_3)C_5H_9NPF_2$, and 4-$(CH_3)C_5H_9NPF_2 . BH_3$

4-$(CH_3)C_5H_{10}N$	4-$(CH_3)C_5H_9NPF_2$	4-$(CH_3)C_5H_9NPF_2 . BH_3$
3270 m, b	2950 s, sh	2960 s
2940 s	2920 s	2925 s
2910 s	2850 s	2880 s
2860 m, sh	2720 vw	2610 vw
2840 m, sh	2670 vw	2410 s
2800 m	2620 vw	2360 m, sh
2720 m	1610 vw, b	2220 vw, b
2680 w	1450 m	1635 vw, b
2620 w	1380 s	1450 m
1600 vw, b	1355 m	1390 s
1440 m	1295 m	1365 m
1370 w	1250 s	1300 m
1360 w	1225 vw	1255 m
1320 m	1190 w	1230 vw
1255 w	1170 s	1175 s
1230 vw	1120 m	1130 w, sh
1170 w, sh	1085 w, sh	1120 m
1145 m	1060 s	1085 w, sh
1115 w	990 w, sh	1065 s
1090 w	960 s	1000 m
1045 vw	940 s	965 s
1005 w	890 w	950 s
985 w	795 s	900 s
970 w	735 s	875 s
940 vw	700 m	855 s
900 vw	600 w	805 vw
790 m, b	580 w	790 w
760 m, b	490 w	750 s
600 w		695 w
560 w		620 m
		545 vw

Table XII - Infrared Absorption Frequencies of 4-$(CH_3)C_5H_9NPFCl$ and 4-$(CH_3)C_5H_9NPFCl.BH_3$

4-$(CH_3)C_5H_9NPFCl$	4-$(CH_3)C_5H_9NPFCl.BH_3$
2950 s	2960 s
2930 s	2930 s
2850 s	2860 s
2800 sh	2800 sh
2740 w	2420 s
1440 m	2360 w
1365 m	1465 m
1338 m	1395 m
1280 w	1305 w
1235 m	1260 w
1210 vw	1180 m
1173 m	1128 m
1165 m	1085 sh
1105 m	1070 s
1050 s	1010 w
980 w	970 s
948 s	953 s
928 s	910 w
850 w,b	870 sh
789 s,b	855 m,b
725 m	790 w
690 m	750 w
560 w	715 vw
460 m	690 vw
	620 m
	570 w
	480 w



The proton nmr spectrum of 4-methylpiperidine has also been reported in the literature (44), and is in good agreement with the spectrum obtained in this study (Fig. 77). The essential features are:

a) a doublet at δ = -1.03 ± 0.02 ppm. (TMS), J_{HCCH} = 5.5 ± 0.1 Hz

b) a multiplet which contains the N-H peak at δ = -1.52 ± 0.2 ppm. (TMS)

c) a broad triplet centered at δ = -2.66 ± 0.03 ppm. (TMS) showing further splitting,

d) a broad doublet, also showing some splitting, at δ = -3.12 ± 0.04 ppm. (TMS).

Their respective area rations are 3:6:2:2 .

The high-field doublet is assigned (44) to the methyl protons coupled to the methine proton; the coupling constant J_{HCCH} is 5.5 ± 0.1 Hz. From their integrated areas, the two lower field signals at δ = -2.66 and -3.12 ppm. can be assigned to the two axial and two equatorial protons respectively, all of which are α to the nitrogen. This assignment is based on studies (34), (35) on the shielding differences between axial and equatorial hydrogen nuclei in cyclohexane derivatives which showed that axial protons are more shielded than equatorial protons. The multiplet at δ = -1.52 ppm. belong to the other ring protons plus the N-H proton.

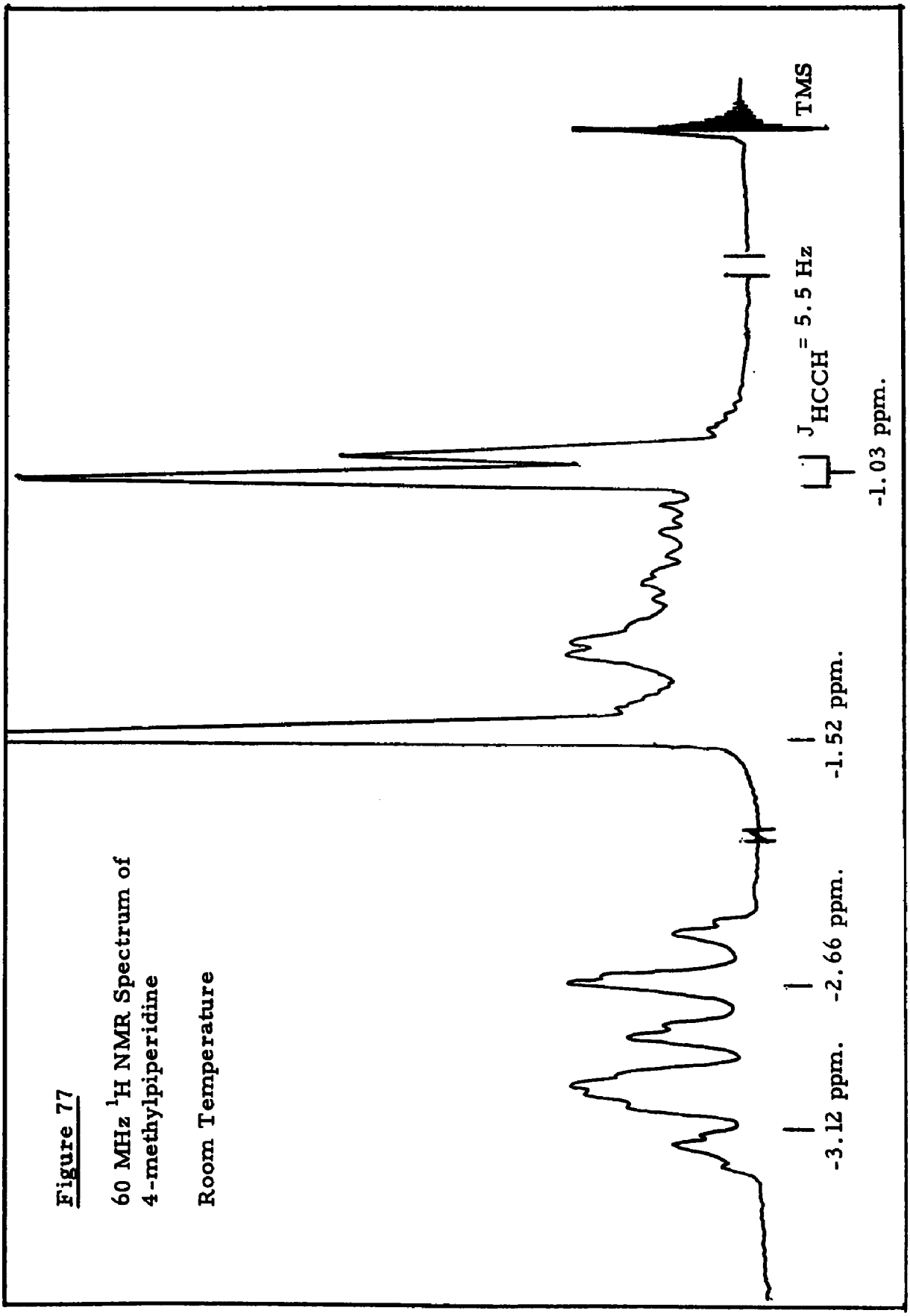


Figure 77

60 MHz ^{1}H NMR Spectrum of 4-methylpiperidine

Room Temperature

2) 4-$(CH_3)C_5H_9NPF_2$

At room temperature, the ^1H nmr spectrum of 4-$(CH_3)C_5H_9NPF_2$ (Fig. 78) shows

a) a doublet at δ = -1.07 ± 0.02 ppm. (TMS), J_{HCCH} = 5.8 ± 0.1 Hz

b) a broad multiplet centered at δ = -1.44 ± 0.02 ppm. (TMS)

c) a broad peak with a chemical shift of δ = -2.85 ± 0.03 ppm. (TMS)

d) a broad peak showing some sort of a triplet structure, centered at δ = -3.74 ± 0.04 ppm. (TMS).

Respective area ratios of these nmr signals are 3:5:2:2.

The assignments of these peaks are the same as those made for 4-methylpiperidine. The only notable difference is the shift to lower field of the various nmr signals, attributed to the inductive effect of the fluorines attatched to the phosphorus.

3) 4-$(CH_3)C_5H_9NPFCl$

A marked similarity is evident in the proton nmr spectra of 4-$(CH_3)C_5H_9NPF_2$ and 4-$(CH_3)C_5H_9NPFCl$ (Fig. 79). This observation is not surprising in view of the very close relationship between the two compounds. It consists of:

a) a doublet at δ = -1.17 ± 0.02 ppm. (TMS), J_{HCCH} = 5.6 ± 0.1 Hz

b) a broad multiplet centered at δ = -1,85 ± 0.02 ppm. (TMS)

c) a peak which has a chemical shift of δ = -2.96 ± 0.03 ppm. (TMS)

d) another peak centered at δ = -3.80 ± 0.04 ppm. (TMS).

Area ratios are 3:5:2:2.

Again, assignments would be identical to that made for the

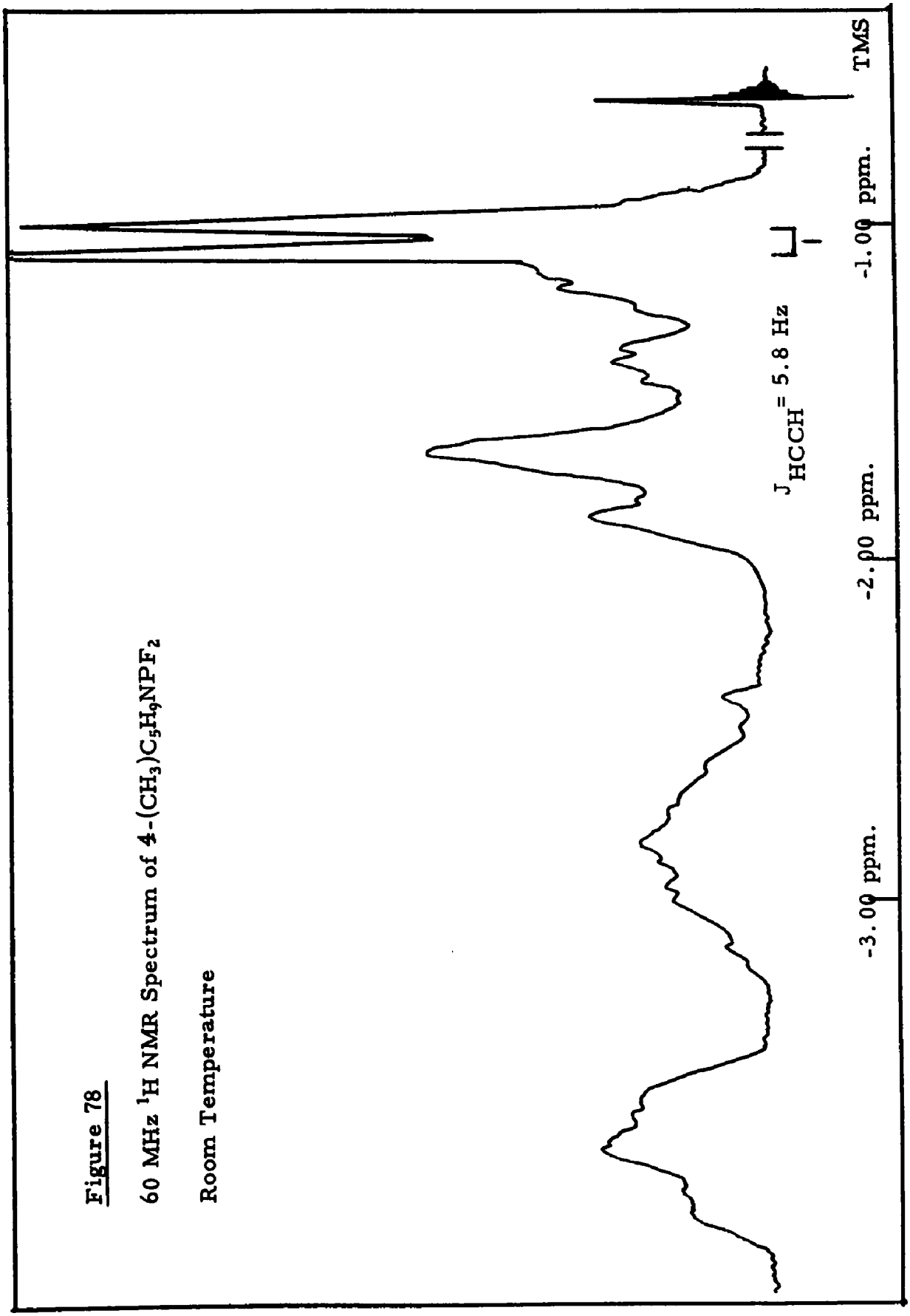


Figure 78

60 MHz ^{1}H NMR Spectrum of 4-$(CH_3)C_5H_9NPF_2$

Room Temperature

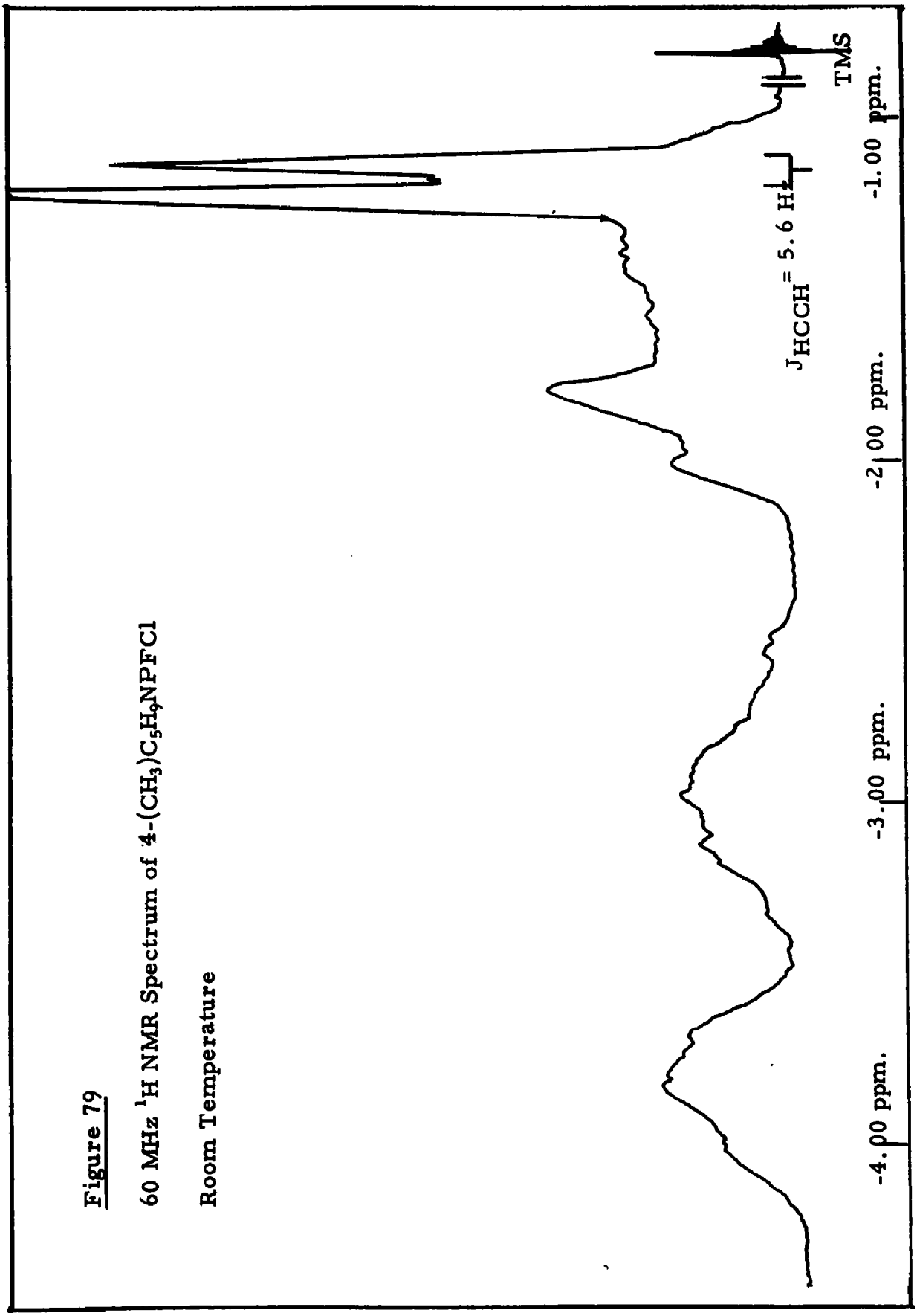


Figure 79

60 MHz ^{1}H NMR Spectrum of 4-$(CH_3)C_5H_4NPFCl$

Room Temperature

proton nmr of 4-methylpiperidine.

4) The Borane Adducts of 4-$(CH_3)C_5H_9NPF_2$ and 4-$(CH_3)C_5H_9NPFCl$

The spectra of the borane adducts are not very different. That of 4-$(CH_3)C_5H_9NPF_2 . BH_3$ (Fig. 80) shows

a) a doublet at δ = -1.11 ± 0.02 ppm. (TMS), J_{HCCH} = 6.0 ± 0.1 Hz

b) a broad multiplet with a chemical shift of δ = -1.60 ± 0.02 ppm. (TMS)

c) a broad peak centered at δ = -3.00 ± 0.03 ppm. (TMS)

d) another broad peak showing some structure at δ = -3.80 ± 0.04 ppm. (TMS).

Area ratios are 3:5:2:2.

At higher gain, the borane protons show up as a severely broadened 1:1:1:1 quartet at δ = -0.95 ±0.02 ppm. (TMS). Two members of this quartet are badly overlapped by the methyl protons' signal. A coupling constant of J_{BH} = 104 ± 1 Hz is observed for the spin-spin interaction between the borane protons and the boron nucleus.

A similar situation is present in the proton nmr spectrum of 4-$(CH_3)C_5H_9NPFCl . BH_3$. This is evident in Fig. 81:

a) a doublet at δ = -1.18 ±0.02 ppm. (TMS), J_{HCCH} = 6.0 ± 1 Hz

b) a broad multiplet centered at δ = -1.87 ± 0.03 ppm. (TMS)

c) a broad peak with a chemical shift of δ = -3.09 ± 0.04 ppm. (TMS)

d) another broad peak at δ = -3.94 ± 0.04 ppm. (TMS).

Area ratios are 3:5:2:2.

At higher gain, the borane protons are observed with a chemical shift of δ = -1.05 ± 0.02 ppm. (TMS), J_{BH} = 99 ± 1 Hz.

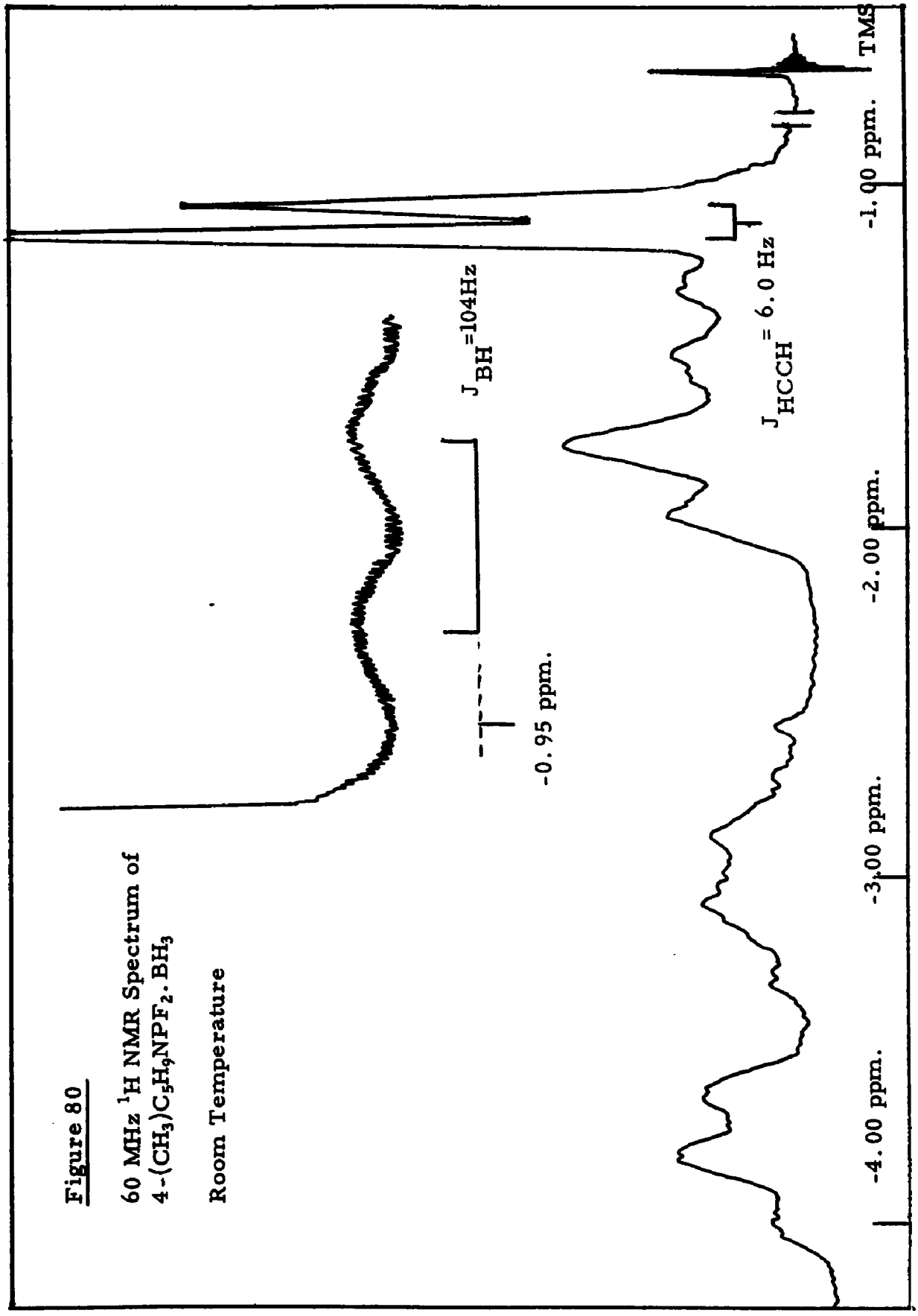


Figure 80

60 MHz ^{1}H NMR Spectrum of 4-$(CH_3)C_5H_4NPF_2.BH_3$

Room Temperature

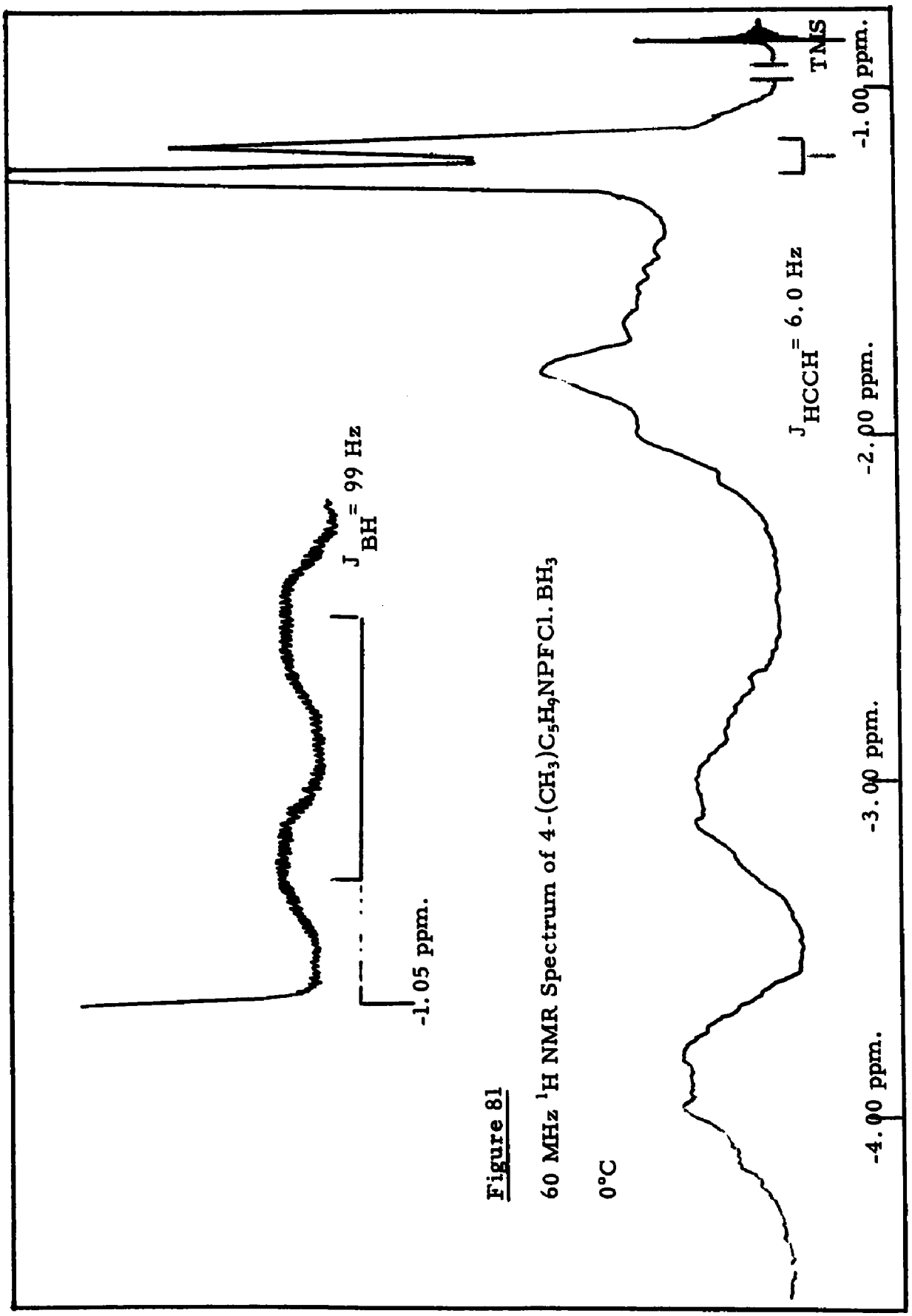


Figure 81

60 MHz ^{1}H NMR Spectrum of 4-$(CH_3)C_5H_9NPFCl.BH_3$

0°C

C. THE ^{19}F NMR SPECTRA OF 4-$(CH_3)C_5H_9NPF_2$ AND 4-$(CH_3)C_5H_9NPFCl$

As shown in Fig. 82, the ^{19}F nmr spectrum of 4-$(CH_3)C_5H_9NPF_2$ does not show any evidence for the presence of isomers. It consists of a doublet, J_{PF} = 1286 ± 2 Hz, with a chemical shift of δ = +63.7 ± 0.2 ppm. ($CFCl_3$) due to spin coupling with the phosphorus nucleus. At higher resolution, each member of this basic doublet is split into an apparent doublet, each of which is split further into 1:2:1 triplet. This splitting pattern is quite similar to that observe in the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$, and suggests that it could be analyzed along the same line of reasoning. The doublet-like structure separated by 11 Hz could then be interpreted as the two inner bands of an AB quartet. This second order effect is brought about by the slight non-equivalence of the two fluorine atoms as noted earlier for cases where inversion of the piperidine ring is blocked by substitution. As it was in the spectrum of 3-$(CH_3)C_5H_9NPF_2$, the additional splitting into 1:2:1 triplets of these central bands can be attributed to coupling with the two axial protons α to the nitrogen, giving a coupling constant J_{HCNPF} = 6.3 ± 0.5 Hz.

That the doublet-like character of each member of the original doublet is due to the non-equivalence of the fluorine atoms, is corroborated by the ^{19}F nmr spectrum of 4-$(CH_3)C_5H_9NPFCl$. It consists (Fig. 83) of a doublet, J_{PF} = 1275 ± 2 Hz, at δ = +67.6 ± 0.2 ppm. ($CFCl_3$). This doublet is due to spin-spin interaction between the fluorines and the phosphorus nucleus. At higher resolution, each member of this

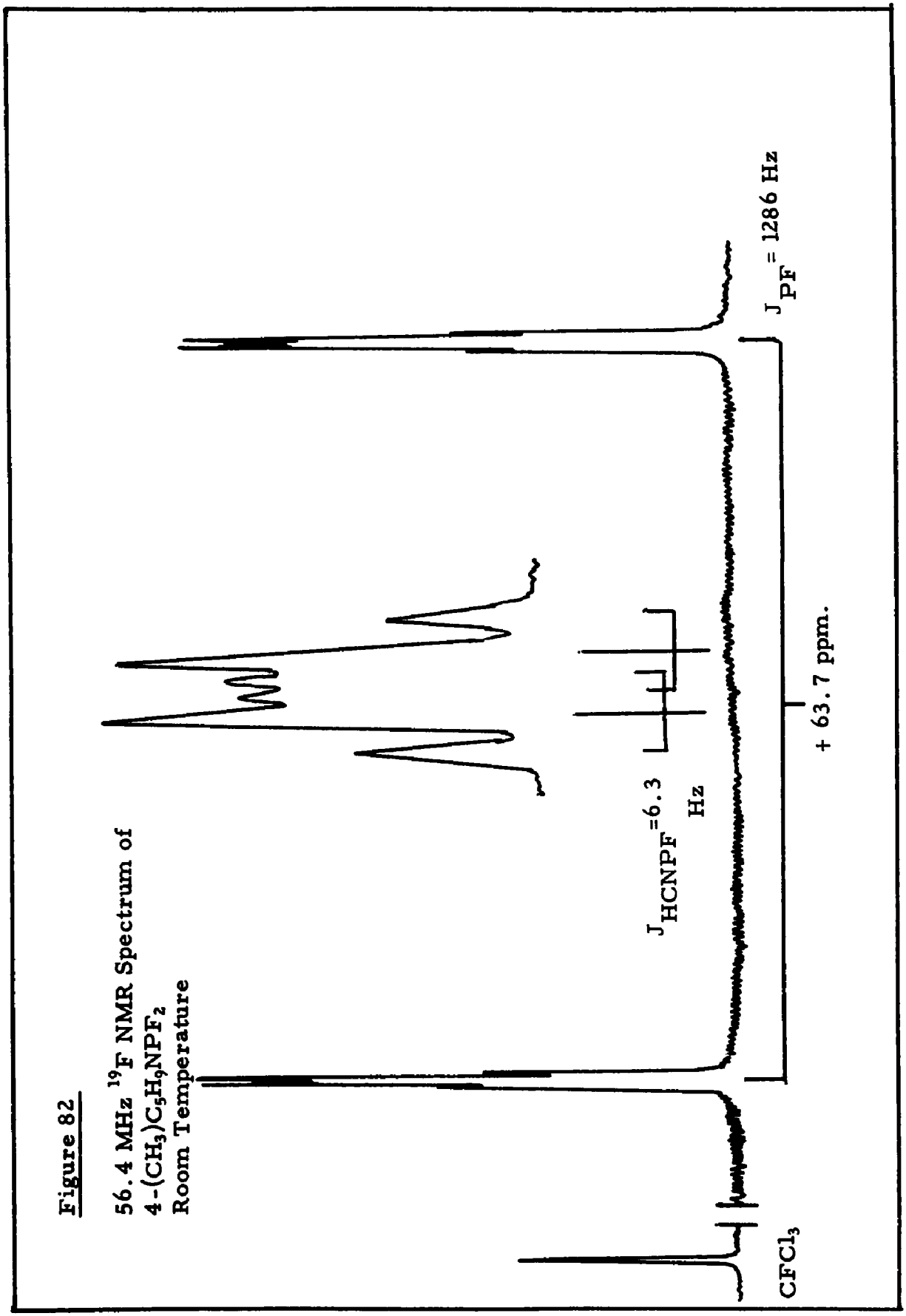


Figure 82

56.4 MHz ^{19}F NMR Spectrum of
4-$(CH_3)C_5H_9NPF_2$
Room Temperature

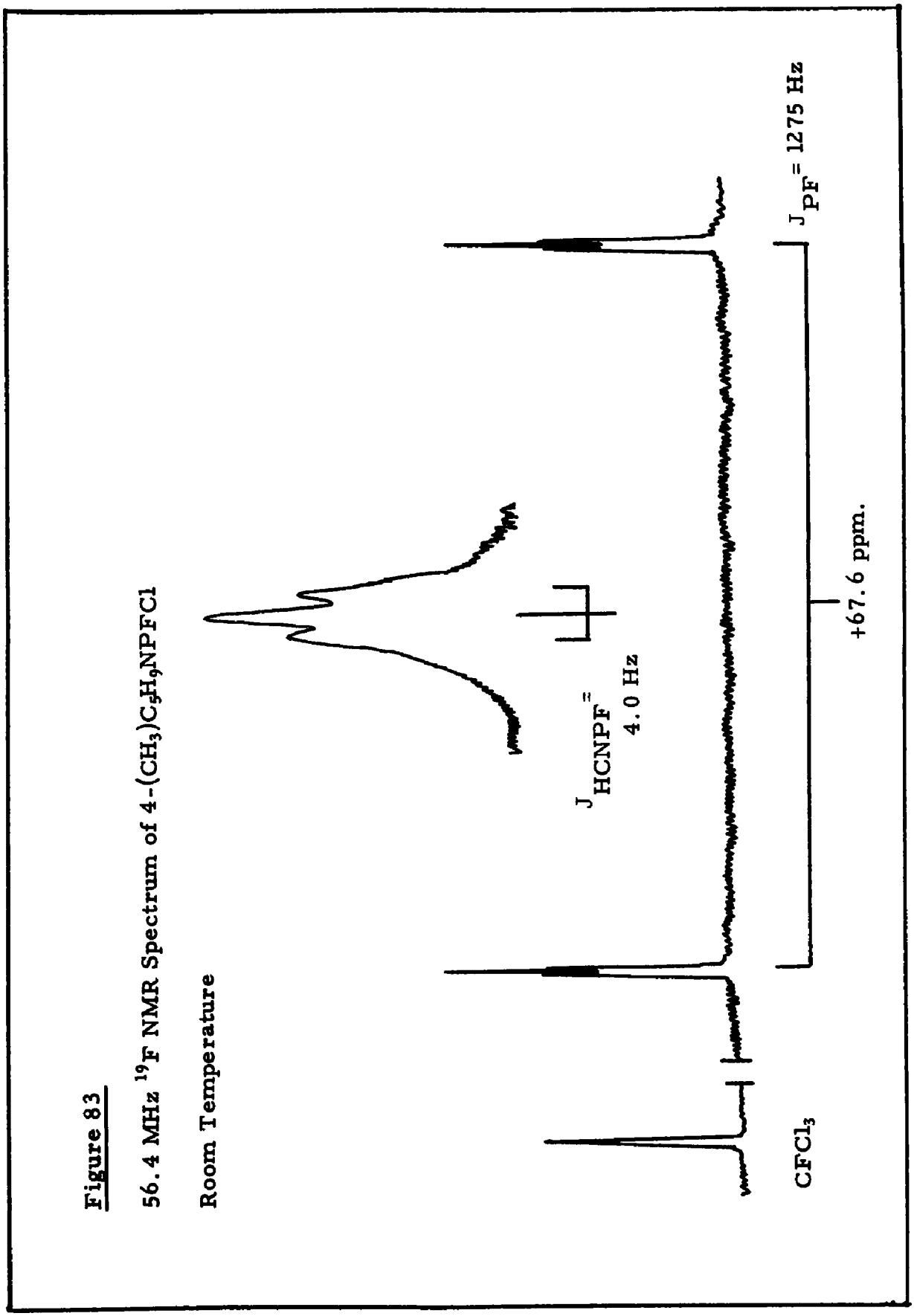


Figure 83

56.4 MHz ^{19}F NMR Spectrum of 4-$(CH_3)C_5H_9NPFCl$

Room Temperature

doublet is split into a simple 1:2:1 triplet, J_{HCNPF}= 4.0 * 0.5 Hz. There is only one fluorine in the molecule, and it shows up as a distinct signal soupling with the phosphorus and axial protons on the 2- and 6-positions of the ring. Comparing its ^{19}F nmr spectrum with that of the closely related 4-$(CH_3)C_5H_9NPF_2$ which has two fluorine atoms, it would not be difficult to see that the doublet-like splitting in each member of the original doublet of the latter compound is due to the non-equivalence of its two fluorine atoms. It is significant that neither 4-(CH_3)-$C_5H_9NPF_2$ nor 4-$(CH_3)C_5H_9NPFCl$ exhibit isomers. According to the model proposed earlier, rotation about the P-N bond should be relatively free for compounds with the methyl groups in the 4-position. The single set of basic doublets in the ^{19}F nmr spectrum of each molecule is consistent with such free rotation and a single isomer of each compound.

D. THE ^{19}F NMR SPECTRA OF 4-$(CH_3)C_5H_9NPF_2.BH_3$ AND 4-$(CH_3)C_5H_9NPFCl.BH_3$

The ^{19}F nmr spectrum of 4-$(CH_3)C_5H_9NPF_2.BH_3$ is shown in Fig. 84. It is a 1:1 doublet, J_{PF}= 1255 * 2 Hz, with a chemical shift of δ = +71=0 * 0.2 ppm. ($CFCl_3$). At higher resolution, each member of this doublet is split into a 1:3:3:1 quartet. In turn, each member of this quartet is split into a 1:2:1 triplet. The quartet structure is due to coupling of the fluorines with the borane protons, giving a coupling constant of J_{HBPF}= 15.2 * 0.5 Hz. The additional splitting of the members of this quartet could again be attributed to coupling with the

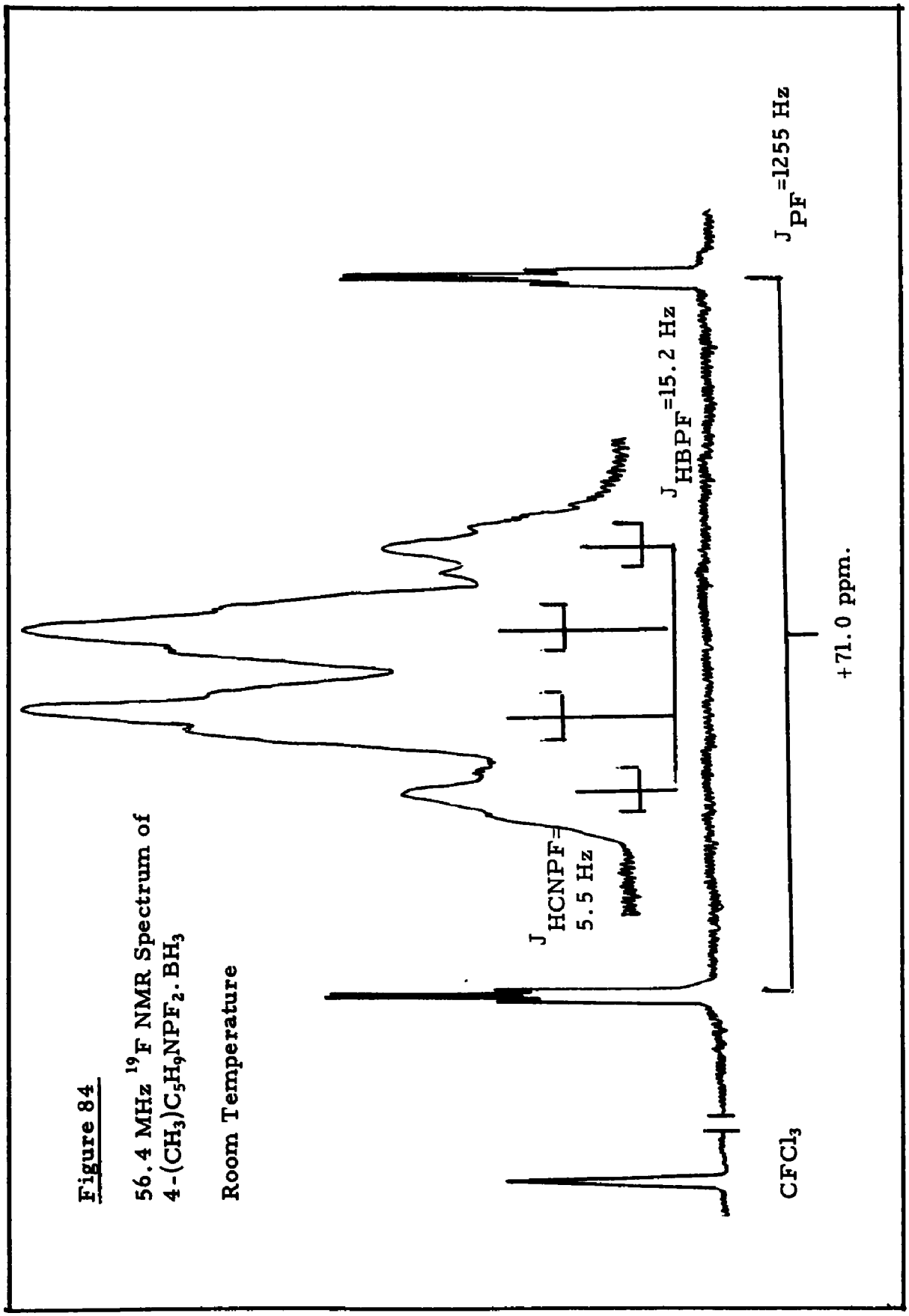


Figure 84

56.4 MHz ^{19}F NMR Spectrum of
4-$(CH_3)C_5H_9NPF_2.BH_3$

Room Temperature

two axial protons α to the nitrogen, giving J_{HCNPF} = 5.5 ± 0.5 Hz just like the case of 3-$(CH_3)C_5H_9NPF_2.BH_3$.

It should be pointed out that the ^{19}F nmr spectrum of 4-(CH_3)-$C_5H_9NPF_2.BH_3$ does not bear out the non-equivalence of the fluorine atoms. In the free ligand, 4-$(CH_3)C_5H_9NPF_2$, it was noted that the separation of the inner bands of the AB quartet brought about by the non-equivalence of the two fluorine atoms, is 11 Hz. This can be compared to the coupling constant value of J_{HBPF} = 15.2 Hz in the borane adduct representing the spin-spin interaction of the fluorines with the borane protons. Because of the larger value of J_{HBPF}, the slight non-equivalence of the fluorine atoms in 4-$(CH_3)C_5H_9NPF_2.BH_3$ is not apparent.

The ^{19}F nmr spectrum of 4-$(CH_3)C_5H_9NPFCl.BH_3$ (Fig. 85) consists of a basic doublet, J_{PF} = 1210 ± 2 Hz, with a chemical shift of δ = +59.0 ± 0.2 ppm. ($CFCl_3$), due to coupling of the fluorine nucleus with the phosphorus nucleus. At higher resolution, each member of this doublet is split into a 9-line multiplet. This splitting pattern can be attributed to a 1:3:3:1 quartet due to spin coupling with the borane protons, J_{HBPF} = 14.8 ± 0.5 Hz. Further splitting of each member of this quartet into 1:2:1 triplets with overlapping of some peaks, J_{HCNPF} = 7.0 ± 0.2 Hz would reproduce the observed spectrum. The triplet structure can again be ascribed to the spin-spin interaction of the fluorine nucleus with the two axial hydrogens in the 2- and 6-positions of the piperidine ring.

It is therefore apparent that the observations made on the ^{19}F

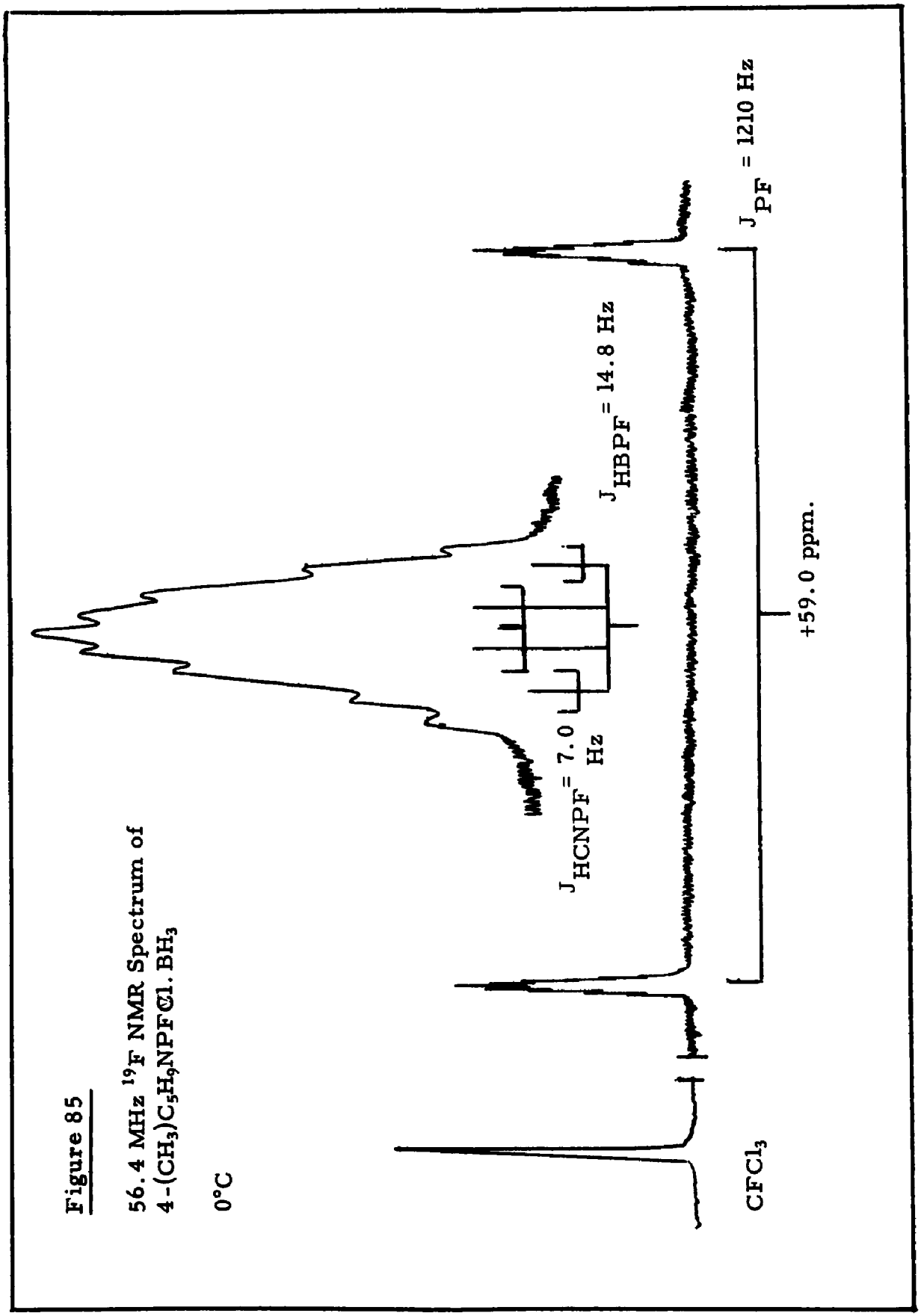


Figure 85
56.4 MHz ^{19}F NMR Spectrum of
4-$(CH_3)C_5H_9NPF\text{Cl}.BH_3$
0°C
J_{HCNPF} = 7.0 Hz
J_{HBPF} = 14.8 Hz
J_{PF} = 1210 Hz
+59.0 ppm.
$CFCl_3$

nmr spectra of 4-$(CH_3)C_5H_9NPF_2$, 4-$(CH_3)C_5H_9NPFCl$, and their borane adducts lend support to the postulated interpretation for the observed ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$. The evidence indicates no isomerism in 3-$(CH_3)C_5H_9NPF_2$. This is in agreement with a model suggested for the isomers of 2-$(CH_3)C_5H_9NPF_2$. Relatively free rotation about the P-N bond is indicated. The high resolution splitting pattern of the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ was interpreted as due to a slight non-equivalence of the fluorine atoms in the molecule even with relatively free rotation. The fact that the same splitting pattern in the high resolution ^{19}F nmr spectrum of 4-$(CH_3)C_5H_9NPF_2$, where the possibility of isomers is ruled out, is observed confirms such interpretation.

VIII - OVERALL DISCUSSION

At low temperatures (below -65°C) the proton nmr spectra of piperidine and piperidyldifluorophosphine show distinct axial and equatorial hydrogens on the piperidine ring. From the temperature dependence of the proton nmr spectra of piperidine and piperidyldifluorophosphine, it was found that the free energy of activation, ΔG^{*}, for the chair-to-chair interconversion process is 11.2 kcal/mole and 10.1 kcal/mole respectively. At room temperature these compounds are rapidly interconverting between two equivalent chair conformations. The room temperature ^{19}F nmr spectrum of piperidyldifluorophosphine showed spin-spin interaction of the fluorine nuclei with four equivalent ring protons α to the nitrogen atom. Because of rapid chair-to-chair interconversion between conformers, equatorial and axial hydrogens are equivalent, and so are the fluorines. However, at temperatures lower than -65°C where no ring interconversion process is taking place, the ^{19}F nmr spectrum of piperidyldifluorophosphine indicated a slight non-equivalence of the two fluorine atoms. No evidence for the presence of restricted rotation about the P-N bond was obtained in the ^{19}F nmr spectrum of piperidyldifluorophosphine because there was no possibility of isomerism in the sense that even if there was a considerable hindrance to internal rotation, both stable isomeric forms would be indistinguishible.

The proton nmr spectra of 2-methylpiperidine, 3-methylpiperidine, and 4-methylpiperidine show both axial and equatorial hydrogen atoms over a large temperature range. The methyl group is best assigned to an equatorial orientation. The corresponding difluorophoshine derivatives of these amines would be expected to exist also in the same preferred conformation.

The ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ indicated the presence of rotational isomerism, manifested in two distinct sets of doublets --- a high-field and a low-field doublets. The possibility that these two ^{19}F nmr signals are due to a single isomer of the compound with two non-equivalent fluorines was ruled out on the basis of the finding that the area ratio of the high-field doublet to the low-field doublet changes with temperature. This behavior would not be expected for two non-equivalent fluorines in the same molecule. The area ratio of the two sets of doublets should remain constant at all temperatures if two different fluorine atoms in the same molecule were being observed. The change in the area ratio of the two doublets with temperature was an indication that the nmr signals are due to two isomers. An estimate of the ΔH° of the interconversion between isomers gives 738 cal/mole. The high-resolution splitting pattern of these basic doublets suggested the non-equivalence of the two fluorine atoms in each isomer, a fact consistent with the observations of Nair and Roberts (68) on the spectrum of $R_1F_2CCR_2R_3R_4$ type of compounds.

The ^{19}F nmr spectrum of 2-$(CH_3)C_5H_9NPFCl$ lends support to the hypothesis that 2-$(CH_3)C_5H_9NPF_2$ exists as two isomers with the fluorines in each isomer slightly non-equivalent. If no isomerism exists in 2-$(CH_3)C_5H_9NPFCl$, its ^{19}F nmr spectrum is expected to give only one basic doublet because there is only one fluorine atom in the molecule. The fact that two sets of doublets were observed raises little doubt as to the existence of two isomers in this compound. A comparable interpretation of the data for 2-$(CH_3)C_5H_9NPF_2$ offers strong evidence for the existence of isomers.

The structures of the isomers observed in 2-$(CH_3)C_5H_9NPF_2$, consistent with its ^{19}F nmr spectrum, could be visualized as one with the fluorines directed away from the methyl group and the other with the fluorines directed towards the methyl group. No evidence of isomerism was evident in the ^{19}F nmr spectrum of cis-2,6-$(CH_3)_2C_5H_8NPF_2$, a finding that supports the validity of the postulated structures of the isomers of 2-$(CH_3)C_5H_9NPF_2$, inasmuch as the presence of methyl groups in the 2- and 6-positions of the piperidine ring makes the two possible isomeric forms indistinguishible.

In both isomers of 2-$(CH_3)C_5H_9NPF_2$, the F-P-F angle is bisected by the plane made by P, N, and two C atoms adjacent to the nitrogen. This is in accord with the molecular structure of $(CH_3)_2NPF_2$ (10). These isomers are related by a 180° rotation about the P-N bond, and their existence could be thought of as being brought about by a hin - dered internal rotation about this bond. However, a temperature dependence study on the ^{19}F nmr spectrum of the closely related compound

$2\text{-}(CH_3)C_5H_9NPFCl$ showed that the energy barrier associated with a hindered internal rotation about the P-N bond is only 6.4 Kcal/mole and a ΔG^* of 17.4 kcal/mole. In contrast, the ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ showed no major changes in form as the temperature was increased from -45°C to +170°C. The only variation was a change in the chemical shift difference between the low-field and the high-field doublets. The data indicate that a relatively large energy barrier to rotation about the P-N bond is present in this molecule compared to $2\text{-}(CH_3)C_5H_9NPFCl$ (ΔG^* estimated to be greater than 22 kcal/mole).

Steric factors associated with the rotation of a PFCl-group should be at least as large as those associated with the rotation of a PF_2-unit. In fact, one would anticipate more steric hindrance when the larger chlorine atom replaces the smaller fluorine atom. The difference in barrier height must then be sought in bond energy terms; steric arguments alone are inadequate.

One might argue that when fluorine is replaced by a chlorine on phosphorus, the d-levels of phosphorus go up in energy and thus become less available to participate in $p\pi$-$d\pi$ bonding. The lesser degree of double bond character would then give a lower barrier to rotation. However, the change in barrier height seems too large when one fluorine is replaced by chlorine. Thus double bond arguments involving the P-N bond do not provide a suitable rationalization for this observation.

The most logical source of the difference in the size of the energy barrier between $2\text{-}(CH_3)C_5H_9NPF_2$ and $2\text{-}(CH_3)C_5H_9NPFCl$, is the

specific interaction between the PF_2-unit and the CH_3-group on the piperidyl ring. Such an intramolecular "hydrogen bond" is suggested by the through-space coupling of the fluorines on the PF_2-unit and the protons of the methyl group. Replacement of one fluorine in 2-(CH_3)-$C_5H_9NPF_2$ by chlorine would reduce this specific CH_3-F_2P interaction, thus giving rise to a lower rotational energy barrier in 2-$(CH_3)C_5H_9$-NPFCl.

The importance of this specific CH_3-F_2P interaction in the determination of the nature of the isomerism observed in 2-(CH_3)-$C_5H_9NPF_2$ is further substantiated by the observation that the ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ did not show any evidence for the existence of isomers *. A model shows that the steric interaction of the fluorine atoms with the methyl group is essentially non-existent in this compound. In this case, interconversion between the two possible isomeric structures is very likely. The absence of isomers in 3-$(CH_3)C_5H_9NPF_2$ is backed up by the ^{19}F nmr spectra of 4-$(CH_3)C_5H_9NPF_2$ and 4-(CH_3)-C_5H_9NPFCl.

Steric interaction of the PF_2-unit and the borane group with the methyl protons is a major factor in the structures of the isomers observed in 2-$(CH_3)C_5H_9NPF_2.BH_3$. Its ^{19}F nmr spectrum indicated the existence of three possible isomers. Two of these have the fluorine atoms either above or below the P-N-(C_2) plane; the third has the fluo-

* The ^{19}F nmr spectrum is consistent with free rotation about the P-N bond and with a single configuration for 3-$(CH_3)C_5H_9NPF_2$, but the data do not prove the existence of a single isomer (see discussion on page 156).

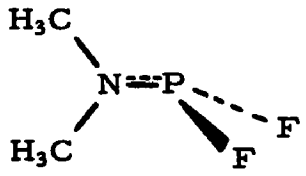
rines directed towards the methyl group. A fourth, but unlikely structure would have the fluorines directed away from the methyl group. However, severe steric interaction between the incoming borane group and the methyl moiety seem to preclude the existence of this structure.

The same situation is present in the case of $2\text{-}(CH_3)C_5H_9NPFCl.BH_3$ whose ^{19}F nmr spectrum also shows three isomers. The interpretation of the ^{19}F nmr spectrum of this compound is more straightforward and clear-cut than that of $2\text{-}(CH_3)C_5H_9NPF_2.BH_3$ because there is only one fluorine atom, and therefore the difficulty associated with having to consider non-equivalence of absorbing nuclei is eliminated.

The existence of isomers in $2\text{-}(CH_3)C_5H_9NPF_2$ is therefore not a necessary consequence of steric factors alone or of an appreciable double bond character of the P-N linkage. The results of this study indicate that specific interaction between the PF_2-unit and the methyl group in the 2-position of the piperidyl ring plays a major role in the isomerism observed in this compound.

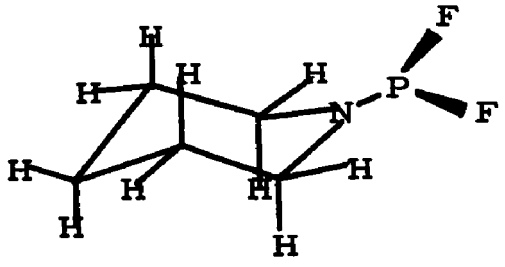
IX - SUMMARY

1. The molecule $(CH_3)_2NPF_2$ has unexpected geometry (10) in which the two methyl groups, the nitrogen, and the phosphorus atom lie in essentially a single plane. This fact, coupled with an unexpectedly short P-N bond distance suggest a double P-N bond. The structure is then:

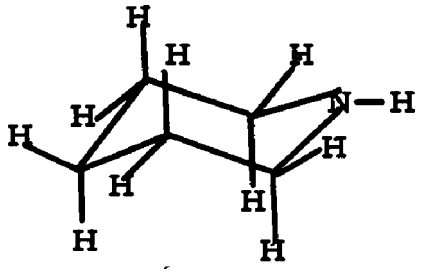


2. The partially double bonded structure shown above suggests non-equivalent methyl groups --- a situation which should be clearly apparent in the proton nmr spectrum. No evidence for non-equivalence of the methyl groups is apparent in a careful analysis of the proton nmr spectrum. This fact suggests free rotation about the P-N bond.

3. A structure closely related to that of $(CH_3)_2NPF_2$ has the methyl groups converted to methylene groups and included in a piperidine ring. The resulting structure is:



In order to understand the proton nmr of this compound, the ^1H nmr

of piperidine 

was investigated.

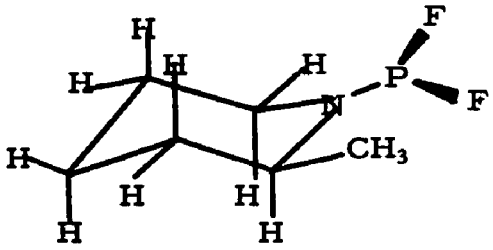
At room temperature, the piperidine ring flips back and forth between chair conformations at a frequency such that the axial and equatorial protons appear to be equivalent when nuclear magnetic resonance spectroscopy is used as a probe. At low temperatures (below -40°C) the chair-to-chair interconversion is slowed down to such a degree that the axial and equatorial hydrogens are clearly identifiable. The value of the free energy of activation for interconversion, ΔG^{*}, is 11.2 kcal/mole; that for the enthalphy of activation, ΔH^{*}, is 6.3 kcal/mole.

Piperidyldifluorophosphine also shows rapid interconversion of chair forms at room temperature, and equivalence of axial and equatorial hydrogens is observed. At low temperatures (below -65°C), piperidyldifluorophosphine similarly shows easily distinguished axial and equatorial hydrogens.

Neither the ^{19}F or ^{1}H nmr spectra of piperidydifluorophosphine provide any evidence for restricted rotation about the P-N bond over a wide temperature range. In the temperature region where rapid rotation and rapid chair-to-chair interconversion occur, both fluorines of the molecule are equivalent as would be expected. In the corresponding low temperature situation where chair-to-chair interconversion of the

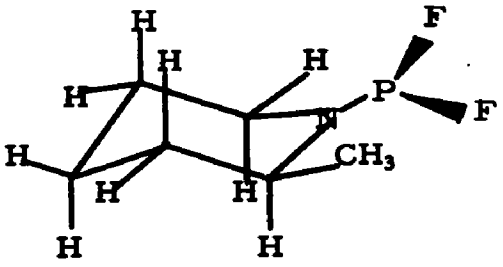
piperidyl ring is slowed down and the axial and equatorial hydrogens are differentiable, the two fluorine atoms should not be magnetically equivalent even with "so-called" free rotation about the P-N bond. A slight non-equivalence of the two fluorines is indeed apparent in the low temperature ^{19}F nmr spectrum of piperidyldifluorophosphine.

4. If a methyl group is placed in the 2-position of the piperidyldifluorophosphine, the resulting structure is

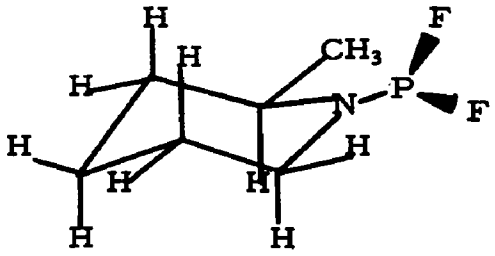


In order to understand this structure, the proton nmr spectrum of 2-methylpiperidine was investigated. The data show that at room temperature, chair-to-chair interconversion of the heterocyclic ring does not occur; axial and equatorial protons are distinct. Interconversion of the ring is found to be similarly blocked in (2-methylpiperidyl)-difluorophosphine.

The ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2$ shows conclusively the existence of two isomers. Models indicate that these two isomers have the configurations:



cis-form

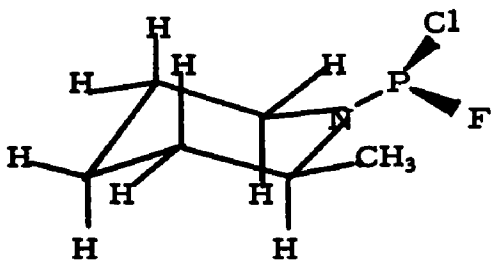


trans-form

The data indicate that the model in which the methyl group is cis- to the PF_2-unit has lower energy than the other model by about 738 cal/mole. This is attributed to an attraction between the PF_2- and CH_3-groups in the cis-form. A barrier to rotation about the P-N bond is clearly apparent in this molecule, but the barrier is ascribed to an interaction of the type found in fluoroform (75-77) involving fluorines from the PF_2-unit and the protons of the methyl group. The high resolution ^{19}F nmr spectrum also suggest the non-equivalence of the two fluorine atoms in each isomer.

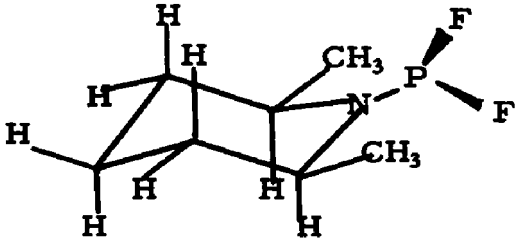
5. Models indicate that there are 3 possible isomeric structures for the borane adduct of $2\text{-}(CH_3)C_5H_9NPF_2$. The ^{19}F nmr spectrum of $2\text{-}(CH_3)C_5H_9NPF_2.BH_3$ indeed show evidence for the presence of three isomers. One configuration has the fluorines of the PF_2-unit directed towards the methyl group in the 2-position; the two other configuration has the fluorines either above or below the P-N-(C_2) plane. The same specific PF_2-H_3C interaction is still operative in this molecule.

6. When one fluorine in $2\text{-}(CH_3)C_5H_9NPF_2$ is replaced by chlorine, the structure obtained is:



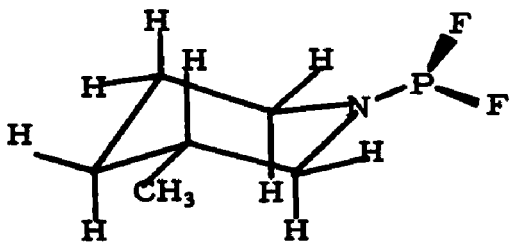
This molecule also exhibits isomers and a barrier to rotation, but the barrier is much lower than that for the difluoro case (ΔG^* associated with hindered internal rotation about the P-N bond in 2-(CH_3)-C_5H_9NPFCl is 17.4 kcal/mole; for 2-$(CH_3)C_5H_9NPF_2$, ΔG^* was estimated to be greater than 22 kcal/mole). Such an observation is consistent with a model in which specific interaction of the methyl protons and the lone fluorine atom would provide the barrier to rotation.

7. If the methyl groups are placed in the 2- and 6-position of piperidyldifluorophosphine, one obtains the following structure:



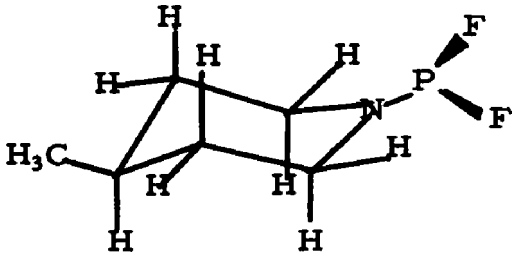
In this molecule, isomers of the type observed in 2-(CH_3)-$C_5H_9NPF_2$ would be indistinguishible sush that isomerism is not anticipated. No evidence of isomers was apparent in its ^{19}F nmr spectrum. This fact supports the postulated configurations of the isomers of 2-$(CH_3)C_5H_9NPF_2$.

8. If the methyl group is placed in the 3-position of piperidyldifluorophosphine, the resulting structure is:



Interaction between the fluorines of the PF_2-unit and the methyl group is no longer possible, hence isomerism in this molecule is not expected. The ^{19}F nmr spectrum of 3-$(CH_3)C_5H_9NPF_2$ did not show any evidence for the presence of isomers, although it is not certain whether the ^{19}F nmr data would be sensitive enough to show the existence of isomers with the methyl group in the 3-position of the ring. The data also indicated that the two fluorine atoms are non-equivalent, as anticipated, even though a low energy barrier to rotation about the P-N bond is implied.

9. Piperidyldifluorophosphine with a methyl group in the 4-position would be of the structure:



Because of the unique position of the methyl group in this molecule, isomers of the type seen in 2-$(CH_3)C_5H_9NPF_2$ are not possible. Such isomers would be indistinguishible, and no PF_2-H_3C interaction is possible such that rotation about the P-N bond is relatively free. However, its ^{19}F nmr spectrum served to verify the observation of the non-equivalence of the fluorine atoms in 3-$(CH_3C_5H_9NPF_2$, whose ^{19}F nmr spectrum is consistent with one isomeric structure and relatively free rotation about the P-N bond.

EXPERIMENTAL PROCEDURES

I SYNTHESIS OF PIPERIDYLDIFLUOROPHOSPHINE

Piperidyldifluorophosphine, $C_5H_{10}NPF_2$, was prepared by the direct reaction of piperidine and phosphorus trifluoride, following a modification of the procedure first used by Van Doorne (26).

About 10 grams of the amine was placed in a one-liter reaction flask equipped with stopcock and a magnetic stirring bar. The flask was connected to the vacuum line, the amine frozen with liquid nitrogen, then the flask was subsequently evacuated. A previously measured amount of PF_3 which would give a pressure of a little more than one atmosphere in a one-liter volume, was condensed into the reaction flask. The flask was then allowed to warm to room temperature, and stirring was begun as soon as the amine liquified. The reaction was allowed to proceed for 12 hours, after which time an orange coloration appeared and solid formations were evident. The stopcock was opened and all volatiles were distilled through traps held at -78°C and -196°C. The white, solid aminehydrofluoride remained in the reaction vessel and was discarded. Excess PF_3 was trapped at -196°C, while the -78°C trap contained a mixture of the aminophosphine and unreacted amine. This mixture was distilled into a clean, one-liter reaction flask and treated with PF_3 as before. This cycle was repeated two times, after

which no evidence of solid formation was observed. The aminophosphine trapped at -78°C as a clear liquid represented a yield of about 80%.

II SYNTHESIS OF PIPERIDYLDIFLUOROPHOSPHINEBORANE

The borane adduct of piperidyldifluorophosphine was prepared *in situ* in an nmr tube joined to a 100 ml. reaction flask equipped with a stopcock, by its reaction with diborane in ether at -78°C. Diborane, in excess of the amount needed to react with the aminophosphine, was condensed into the nmr tube. About 1 ml. of anhydrous ether then followed, the stopcock closed, and the tube immersed in a -78°C slush bath for an hour. After this reaction period, the -78°C slush bath was replaced with a -196°C liquid nitrogen bath. 0.5 gram of piperidyldifluorophosphine was then condensed into the nmr tube and the reaction was allowed to proceed at -78°C for one hour. The mixture was allowed to warm to room temperature, and the more volatile products distilled out of the reaction tube held at -23°C, through a trap at -196°C. Ether and excess diborane were recovered in the liquid nitrogen trap, while the desired product was retained in the nmr tube. Yields of close to 95% were obtained in several reaction runs.

III SYNTHESIS OF 2-$(CH_3)C_5H_9NPF_2$, 3-$(CH_3)C_5H_9NPF_2$, AND 4-$(CH_3)C_5H_9NPF_2$

The preparation of these compounds involved the same proce-

dure ustilized in the synthesis of piperidyldifluorophosphine, by directly reacting the free amine with phosphorus trifluoride.

IV SYNTHESIS OF 2-$(CH_3)C_5H_9NPF_2.BH_3$, 3-$(CH_3)C_5H_9NPF_2.BH_3$, 4-$(CH_3)C_5H_9NPF_2.BH_3$, CIS-2,6-$(CH_3)_2C_5H_8NPF_2.BH_3$, 2-$(CH_3)C_5H_9NPFCl.BH_3$, AND 4-$(CH_3)C_5H_9NPFCl.BH_3$

These compounds were prepared by exactly the same procedure used in preparing the borane adduct of $C_5H_{10}NPF_2$ by the reaction of the aminophosphine with diborane in ether at -78°C.

V SYNTHESIS OF CIS-2,6-$(CH_3)_2C_5H_8NPF_2$

Cis-2,6-$(CH_3)_2C_5H_8NPF_2$ was prepared by fluorinating Cis-2,6-$(CH_3)_2C_5H_8NPCl_2$ with SbF_3. This method was also successful in preparing 2-$(CH_3)C_5H_9NPF_2$ and 3-$(CH_3)C_5H_9NPF_2$.

About 10 ml. of PCl_3 in 100 ml. of ether was placed in a 3-necked, 250 ml. round-bottom flask immersed in an ice-bath and equipped with a magnetic stirring bar and reflux condenser. 12 grams of cis-2,6-dimethylpiperidine in 20 ml. ether was added dropwise into the reaction vessel with stirring, and immediate formation of white precipitate ensued. After the addition was complete, stirring was continued for 15 minutes, after which time the solution was filtered under vacuum through a sintered glass funnel beneath a nitrogen blanket. The filtrate was warmed gently until almost all of the ether has evaporated. The flask was attatche to the vacuum line, cooled to 0°C, and the excess

PCl_3 was distilled out. The clear liquid remaining in the reaction vessel at 0°C was shown to be cis-2,6-$(CH_3)_2C_5H_8NPCl_2$.

The compound cis-2,6-$(CH_3)_2C_5H_8NPCl_2$ was fluorinated in the vacuum line by the slow addition of SbF_3 via a bent side-arm tube. A cold water bath served to keep the reaction mixture cool. The mixture was stirred for about an hour. The products were then distilled through traps held at -78° C and -196°C. The desired product was retained at the -78°C trap as a clear liquid. The yield was about 60% based on the amine charged.

VI SYNTHESIS OF 2-$(CH_3)C_5H_9NPFCl$ AND 4-$(CH_3)C_5H_9NPFCl$

The syntheses of 2-$(CH_3)C_5H_9NPFCl$ and 4-$(CH_3)C_5H_9NPFCl$ were essentially the same as that for $C_5H_{10}NPF_2$, except that $PFCl_2$ was used and ether acted as a solvent for the reaction.

In a typical run, about 10 grams of the amine in 50 ml. ether was placed in a 1-liter reaction flask equipped with a stopcock and a magnetic stirring bar. The flask was attatched to the vacuum line, its liquid contents frozen by liquid nitrogen, and then evacuated. A measured amount of $PFCl_2$ known to give a pressure of about one atmosphere in a 1-liter volume, was condensed into the reaction flask. The flask was then allowed to warm temperature. The mixture was stirred for 12 hours, after which time the reaction flask was cooled to -112°C and

the volatiles distilled out through a trap held at -196°C. Some $PFCl_2$ were collected at the -196°C trap. The -112°C bath in which the reaction flask was immersed was replaced with a liquid nitrogen bath, and $PFCl_2$ was condensed in as before. It was found that two such treatments are sufficient to essentially complete the reaction. The volatile materials were then distilled through traps at 0°C and -196°C. Ether and excess $PFCl_2$ were recovered in the liquid nitrogen trap, while the desired product, showing a slight yellow coloration was retained at the ice trap. The yield was approximately 50% based on the amine used.

APPENDIX A

GENERAL TECHNIQUES

A. HIGH-VACUUM TECHNIQUES

Standard high-vacuum techniques of Sanderson (71) and Jolly (72) were used in the preparation and handling of the compounds investigated. All stopcocks and standard taper joints were greased with Silicone Grease. Materials of low volatility were handled in a glove bag in an atmosphere of dry nitrogen.

B. SPECTROSCOPIC TECHNIQUES

Infrared Spectra

The infrared spectra were obtained with a Beckman IR-10 or Beckman IR-20 operating in the 4000-300 cm^{-1} region. For volatile materials, a gas cell with 10 cm. path length and KBr windows was used. Low volatility materials were studied as liquid films between KBr plates.

Notation for Vibrational Spectra

For intensities and band shapes: br = broad; sh = shoulder;

v = very; s = strong; m = medium; and w = weak.

NMR Spectra

The various nmr spectra were obtained using Varian Associates Models HA-60, HA-56/60, or HA-100 Spectrometers. The ^{19}F nmr spectra were run on Model HA-56/60 with the fixed frequency oscillator operating at 56.4 MHz, or on Model HA-100 with the oscillator set at 94.1 MHz. ^{31}P and ^{11}B nmr spectra were also recorded on the latter model with the oscillator operating at 40,4 and 32.1 MHz, respectively.

Chemical shifts were obtained by tube interchange. Signal separations were measure by calibration of the sweep of known frequency, except when using the HA-60 or HA-56/60 models. Samples were prepared by condensing and sealing pure compounds in thin-walled nmr tubes, except for samples run at temperatures greater than 100°C in which case a thick-walled nmr tube was used. The following standards were used: tetramethylsilane (TMS) for the proton nmr spectra; fluorotrichloromethane ($CFCl_3$); for the ^{19}F nmr spectra; 85% phosphoric acid (H_3PO_4) for the ^{31}P nmr spectra; and trimethylboron$[B(CH_3)_3]$ for the ^{11}B nmr spectra.

NMR Notation

Coupling constants, J, are expressed in hertz, Hz. Their assignment is indicated by the appropriate subscript, i.e. J_{HBPF} refers to spin-spin interaction between the fluorine nucleus and the

proton nucleus bonded to boron, across the F-P-B-H bonds. Chemical shifts, δ, are calculated according to the equation (36)

$$\delta = \frac{H_{sample} - H_{reference}}{H_{reference}}$$

and expressed in parts per million, ppm. Thus relative to the appropriate standard, low-field shifts are negative and high-field shifts are positive.

C. STARTING MATERIALS

1. Phosphorus trifluoride was obtained from Ozark Mahoning Co., and used without further purification.
2. Phosphorus trichloride was obtained from Matheson, Coleman, and Bell, and used as received.
3. Fluorodichlorophosphine was prepared by the reaction of $((CH_3)_2N)_2PF$ and HCl (73).
4. Dimethylaminodifluorophosphine was prepared by the method reported by Parry and co-workers (74).
5. Bis-dimethylaminofluorophosphine was prepared by the method described by Fleming (4).
6. Piperidine and Alkylpiperidines were obtained from Aldrich Chemical Co., distilled over KOH, and stored over KOH. They were redistilled immediately before use.

7. Diborane was obtained from the Callery Chemical Co., and was purified by passing through a -126°C trap to remove higher hydrides.

8. Antimony trifluoride was obtained from K and K Laboratories, and was used without further purification.

9. Diethyl ether was obtained from Mallinckrodt Co., in an anhydrous condtion and used as received.

APPENDIX B

Calculation of ΔG^* for the Chair-to-chair Interconversion Process for Piperidine.

$\delta_\nu = 85$ Hz; $T_c = 233.15°K$; $k = 1.3805 \times 10^{-16}$; $h = 6.62 \times 10^{-27}$

$k_c = (\pi\delta_\nu)/2 = (3.1416 \times 85)/2 = 133.5$

$$\Delta G^* = 2.303\, RT_c \left(\log \frac{k\, T_c}{h} - \log k_c \right)$$

$$= 2.303 \times 1.987 \times 233.15 \left(\log \frac{13.805 \times 10^{-17} \times 233.15}{6.62 \times 10^{-27}} - \log 133.5 \right)$$

$\Delta G^* = 11.2 \pm 0.2$ kcal/mole

Calculation of ΔG^* for the Chair-to-chair Interconversion Process in $C_5H_{10}NPF_2$.

$\delta_\nu = 54$ Hz; Tc = 208.15°C

$k_c = (3.1416 \times 54)/2 = 85$

$$\Delta G^* = 2.303 \times 1.987 \times 208.15 \left(\log \frac{13.805 \times 10^{-17} \times 208.15}{6.62 \times 10^{-27}} - \log 85 \right)$$

$\Delta G^* = 10.1 \pm 0.2$ kcal/mole

APPENDIX C

From equations which can be found in (25) and (36), the separation between the central peaks of an AB quartet is equal to 2C-J, i.e.

$$2C - J = 9.8 \qquad \text{Equation 1}$$

$$C = \tfrac{1}{2}\left(\delta^2_{AB} + J^2 \right)^{\frac{1}{2}} \qquad \text{Equation 2}$$

where δ_{AB} is the chemical shift difference between the two pairs of doublets, and J is the coupling constant between A and B nuclei.

The equation for the intensity ratio of the central to the outer bands in an AB quartet is given to be

$$\frac{2C + J}{2C - J} \qquad \text{Equation 3}$$

which in this case is measured to be greater than 50:1, such that

$$\frac{2C + J}{2C - J} > 50 \qquad \text{Equation 4}$$

From Equation 2, Equation 4 becomes:

$$\frac{\left(\delta^2_{AB} + J^2 \right)^{\frac{1}{2}} + J}{\left(\delta^2_{AB} + J^2 \right)^{\frac{1}{2}} - J} > 50 \qquad \text{Equation 5}$$

from which

$$\left(\delta^2_{AB} + J^2 \right)^{\frac{1}{2}} > 1.04 \qquad \text{Equation 6}$$

Substituting this relation to Equations 1 and 2, one obtains

$$9.8 + J > 1.04\, J \qquad \text{Equation 7}$$

such that $J > 245$. If this limiting value for J is then substituted in

Equations 1 and 2,

$$9.8 + 245 < (\delta^2_{AB} + 245 \times 245)^{\frac{1}{2}} \qquad \text{Equation 8}$$

one gets the chemical shift limiting value, $\delta_{AB} > 70$ Hz.

APPENDIX D

Literature Values of P-N Bond Lengths

P-N Bond Lengths	Compound	Reference
1.769 A°	$H_3NPO_3^-$	12
1.653	$(H_2N)_3P.BH_3$	78
1.67 - 1.71	$Na_3(HNPO_2)_3.4H_2O$	79
1.671 & 1.686	$(NP(N(CH_3)_2)_2)_4$	80
1.66 - 1.72	$(CH_3NPO(OCH_3))_3$	81
1.66 &1.77	$(CH_3NPCl_3)_2$	82

APPENDIX E

Calculation for ΔH° for the Cis- and Trans- Isomers of $2\text{-}(CH_3)C_5H_9NPF_2$

$$\text{Log}\ \frac{K_2}{K_1} = \frac{+\Delta H^\circ (T_2 - T_1)}{2.303\ RT_2T_1}$$

$T_2 = 373.15°K$

$T_1 = 253.15°K$

$K_2 = 1.265$

$K_1 = 0.790$

$K_2/K_1 = 1.60$

$$\Delta H^\circ = \text{Log}(K_2/K_1) \times \frac{2.303 \times R \times T_2 \times T_1}{(T_2 - T_1)}$$

$$= \frac{0.20412 \times 4.59 \times 373.15 \times 253.15}{120}$$

$\Delta H^\circ = 738$ cal/mole

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