Bulletin 657

THE PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF PYRIDINES

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By F. R. McDonald, A. W. Decora, and G. L. Cook

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THE PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF PYRIDINES

by

F. R. McDonald,[1] A. W. Decora,[2] and G. L. Cook[3]

ABSTRACT

The proton NMR spectra of 32 pyridines in two solvents, carbon tetrachloride and benzene-d_6, are presented. The chemical-shift and differential-shift values are correlated with the substitutent position and with the solvent media. The ring protons and the protons on alkyl substituents are tabulated. The paramagnetic shift of the protons adjacent to the nitrogen is discussed, and a proposed structure for the pyridine-benzene complex that is consistent with the observed anomalous paramagnetic shift is presented. The utility of the data in the identification of pyridine compounds found in shale-oil naphtha is demonstrated.

INTRODUCTION

Bureau of Mines research into the composition of shale oils required characterizing the nitrogen compounds in the various fractions of the oils. In earlier investigations (*12–15*, *34*)[4] individual pyridines in a naphtha fraction of an oil were identified using a variety of analytical techniques available at the time of the investigations. The advent of nuclear magnetic resonance (NMR) spectroscopy offered advantages for characterizing the shale-oil pyridines with respect to the character and location of the alkyl substituent groups on the pyridine ring.

The NMR spectra that are reported in the literature (*2–3*, *5–7*, *10–11*, *22*, *25*, *27*, *31–32*), while helpful in shale-oil characterization research, do not provide a compilation of spectra of alkyl-substituted pyridines such as those found in shale oils. This is especially true with respect to the pyridines found in shale-oil naphtha that result from the mild hydrogenation of crude shale oil (*5*). Also, much of the early work was done on low-resolution instruments at 30 and 40 MHz (*2–3*) and on limited numbers of monosubstituted pyridines.

An interesting observation in NMR spectroscopy is that the chemical shifts of some protons are solvent dependent. This phenomenon is well known (*18*), and in most cases it has been reported that an aromatic solvent causes a diamagnetic (high-field or upfield) shift compared to the position of the shift in a nonaromatic solvent. This general observation has been reported for pyridines (*16*, *18*, *22*). For example, Murrell and Gil (*22*) observed that several pyridine proton resonance signals obtained either neat or in benzene were found at higher field than signals from the same pyridine in carbon tetrachloride. This dependency of the location of chemical shift upon the solvent has important analytical applications. For example, it can

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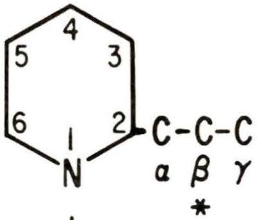
[4] Italicized numbers in parentheses refer to items in the list of "References Cited in Text" preceding the appendixes.

be used to add a second dimension to the NMR characterization of shale-oil pyridines, not only by providing a second group of chemical shifts (in benzene-d_6), but also by providing a differential shift whose magnitude and direction can be correlated with specific protons on the pyridine molecule.

Thirty-two pyridines that might be present in shale oil were chosen for this study, and the NMR spectra at 60 MHz in two solvents, benzene-d_6 and carbon tetrachloride, were recorded. The proton chemical shifts measured in this work were found to be solvent dependent; however, the observed chemical shifts in the two solvents were not in the expected direction. This observation led us to postulate a model to explain the theoretical concepts responsible for this anomalous shift.

NOMENCLATURE

The system used to locate the ring and alkyl protons is illustrated by the two formulas shown below. In formula I the carbon atom marked with the asterisk (*) is the 2β carbon atom. In formula II the carbon atom marked with the dagger (†) is the 4α carbon atom. Thus the number locates the position of the alkyl group on the ring, and the Greek letter locates the carbon atom in the alkyl substituent. The ring protons are designated by number only. The system is sufficient to locate the protons of the compounds used in this study.



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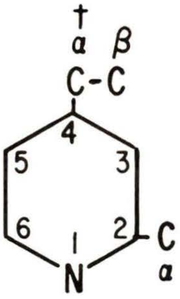

II

EXPERIMENTAL PROCEDURE

The compounds used in this study were obtained from the following sources:[5] (1) American Petroleum Institute Research Project No. 52, Samples Office, Carnegie-Mellon University, Pittsburgh, Pa.; (2) Aldrich Chemical Company, Milwaukee, Wis.; (3) Reilly Tar and Chemical Corp., New York, N.Y.; and (4) Dr. Nobuo Ikekawa, University of Tokyo, Tokyo-Ku, Japan. These compounds were 95-percent pure as established by gas-liquid chromatography, infrared spectroscopy, and nuclear magnetic resonance spectroscopy.

Spectra were obtained on 10-percent (by volume) solutions of the pyridine in carbon tetrachloride (CCl_4) or in benzene-d_6 (C_6D_6) with a Varian A–60 spectrometer.[6] Approximately 1.0 percent by volume of tetramethylsilane (TMS) was added as an internal reference. All chemical shifts were measured downfield from the TMS (0.00 ppm) position. Many of the spectra were obtained at two temperatures, 30° and 37° C. Preliminary chemical-shift assignments for proton resonances in the simple pyridines were made from available data (*2–3*, *7*, *10–11*, *22*, *24*). Proton decoupling techniques were employed to identify specific proton resonances for some of the pyridines. Although this technique had limited application because of the small chemical-shift differences, it was helpful when combined with structural and literature data.

An external audio-oscillator (Hewlett-Packard No. 200CD) coupled to a frequency counter (Hewlett-Packard No. 521C) was used to assist in the measurement of the chemical shifts. Average values were determined from repetitive runs on the same compound. In many cases, the audio-sideband

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[5] Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

[6] A sample concentration of 10 percent by volume was chosen after it was determined that the chemical shifts were insensitive to concentrations in the range of 6 to 20 volume-percent [a plot concentration (1 to 50 percent volume/volume) versus chemical shift was flat between 6 to 20 percent by volume].

technique was employed to accurately measure the chemical shifts to 0.5 Hz.

A listing of the chemical-shift data for the 32 pyridines measured from the spectra is presented in appendix B. The chemical shifts are given in parts per million from the TMS internal standard. In the case of multiplets, the chemical shift in the tables is the center of gravity of the multiplet. The differential shift $\delta\delta$ listed in the tables is the algebraic difference between the chemical shift in carbon tetrachloride and the chemical shift in benzene-d_6. The tables also list the chemical shifts of the protons at two different probe temperatures, 30° and 37° C.

An investigation to determine the stability of CCl_4 solutions was carried out by distilling the solvent (CCl_4) and using it immediately to obtain the spectrum of a test compound. The same compound was run again to observe any changes in the spectrum after the CCl_4 had been stored for 24 hours at room temperature in a humid atmosphere. A diamagnetic shift was observed on the samples that had been exposed for 24 hours. Based on these data, only freshly distilled reagent-grade solvents were used in this study.

The differential chemical shift $\delta\delta$ of a specific proton was determined by subtracting the chemical shift of the pyridine in benzene-d_6 from the chemical shift of the pyridine in carbon tetrachloride:

$$\text{Differential chemical shift } \delta\delta = \delta_{CCl_4} - \delta_{C_6D_6}. \quad (1)$$

A positive $\delta\delta$ indicates a diamagnetic, or upfield, shift of the resonance. A negative $\delta\delta$ indicates a paramagnetic, or downfield, shift of the resonance.

SPECTRAL ANALYSIS

The data collected in this investigation are presented in this section in categorical order to simplify the application of each facet to the overall picture. The NMR spectra of all of the pyridines studied are reproduced in appendix A. The figures represent the NMR of the pyridines in each of the two solvents, carbon tetrachloride and benzene-d_6. The first 30 spectra in appendix A, figures A–1 through A–30, were run at 30° C, while the remainder, figures A–31 through A–57 were run at 37° C.

EFFECT OF TEMPERATURE ON CHEMICAL SHIFT

The effect of temperature on the chemical shifts was demonstrated by observing the average chemical shifts and differential shifts of the ring protons of 15 monosubstituted pyridines at 30° and 37° C. These averaged shifts were derived from tables B–1 and B–2 and are presented in table 1. Comparison of both the average chemical shifts and average differential shifts in table 1 shows that temperature affects these shifts slightly. Similar results were obtained with all the other pyridines. The small effect of temperature does not invalidate any of the conclusions made in this study.

CHEMICAL SHIFTS OF RING PROTONS

The average chemical shifts of the ring protons of the 32 pyridines, derived from the data in table B–1, are presented in table 2 and are illustrated in figure 1. The illustration shows the chemical-shift ranges for the pyridine-ring protons in two solvents. Several interesting observations can be made from the averaged data. First, the chemical shifts of position 3, 4, and 5 protons for all of the pyridines studied undergo a diamagnetic (upfield) shift when the NMR spectrum of the pyridine is obtained in benzene-d_6 compared to the NMR spectrum of the same pyridine in carbon tetrachloride. These diamagnetic shifts are in the expected direction. Second, the chemical shifts of position 2 and 6 protons undergo a paramagnetic (downfield) shift when the NMR spectrum of the pyridine is obtained in benzene-d_6 compared to the NMR spectrum of the same pyridine in carbon tetrachloride. These paramagnetic shifts are not in the expected direction.

Table 1.—Effect of temperature on the average chemical shifts and differential shifts of 15 monosubstituted pyridines

Position of substitution	Average chemical shift, ppm	
	30° C	37° C
2 and 6 protons:		
In CCl_4	8.42	8.44
In C_6D_6	8.54	8.55
$\delta\delta$	−.12	−.11
3 and 5 protons:		
In CCl_4	7.03	7.03
In C_6D_6	6.74	6.82
$\delta\delta$	.29	.21
4 proton:		
In CCl_4	7.47	7.45
In C_6D_6	7.12	7.07
$\delta\delta$	.35	.38

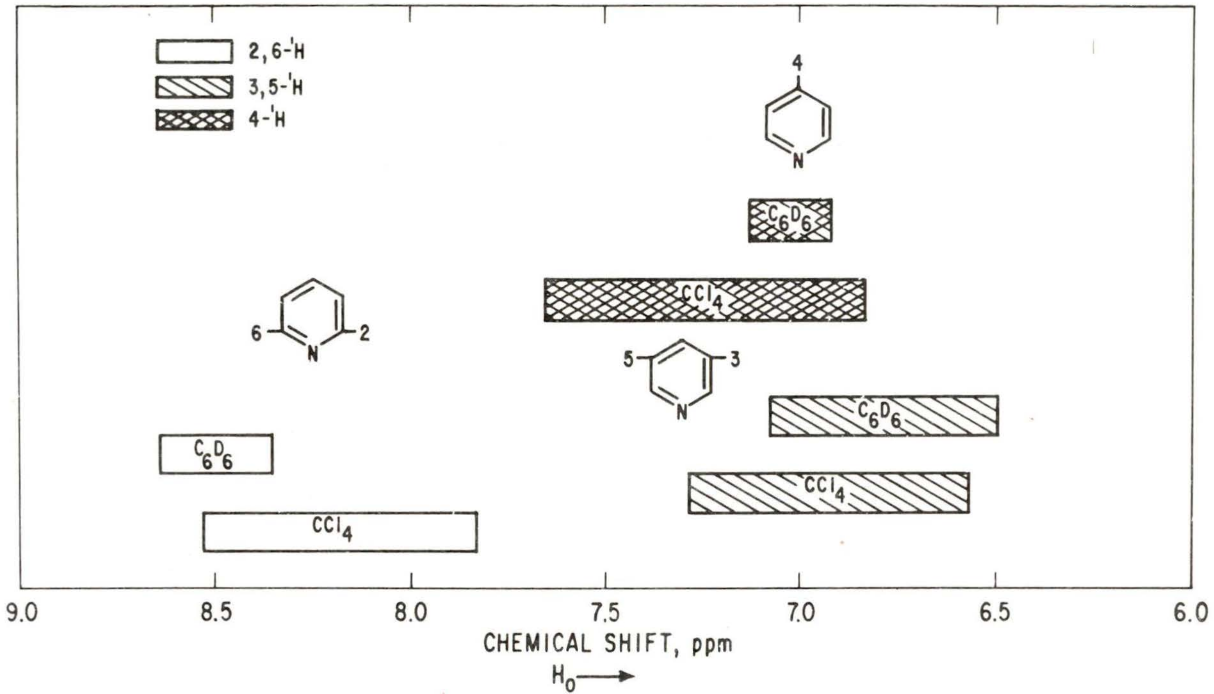

Figure 1.—Chemical-shift ranges for pyridine-ring protons in CCl_4 and C_6D_6.

Table 2 and figure 1 show that position 3 and 5 protons are the more shielded protons and are found the farthest upfield in the NMR spectrum. Posotion 4 protons are shielded to a lesser degree than position 3 and 5 protons and are found farther downfield. Position 2 and 6 protons are the least shielded and are found the farthest downfield. Position 3, 4, and 5 protons all become more shielded in the solvent benzene-d_6 than in the solvent carbon tetrachloride, and the proton resonances shift about 0.2 to 0.3 ppm to higher field. However, position 2 and 6 protons are less shielded in the solvent benzene-d_6 than in the carbon tetrachloride solvent. The average differential shift shows a downfield shift of about 0.1 ppm.

CHEMICAL SHIFTS OF ALKYL PROTONS OF MONOSUBSTITUTED PYRIDINES

The chemical shifts for the various alkyl protons on monosubstituted pyridines were averaged in a manner similar to those for the chemical shifts of the ring protons (table 2). The data for the alkyl protons of 15 monosubstituted pyridines in the two solvents and at the two temperatures, derived from the data in tables B–3 to B–6, are presented in table 3 and in figure 2. Trends in the chemical shifts can be observed from these averages. These trends are shown in the illustration where the average locations of the alkyl-proton chemical shifts are shown together with the average locations of the ring-proton chemical shifts.

Several observations can be made from figure 2. First, the same relative order of chemical shifts is observed for the alkyl protons as for the ring protons. The order of proton deshielding, for either ring or alkyl protons, is 2 and 6 > 4 > 3 and 5. Second, the effect of the location of the alkyl proton also can be observed—that is, the average chemical shifts indicate that the greater the distance the proton on the alkyl chain is removed

Table 2.—Average chemical shifts and differential shifts of the ring protons for 32 pyridines at 37° C

Position of substitution	Number of compounds	Average chemical shift, ppm
2 and 6 protons:	24	
In CCl_4	....	8.37
In C_6D_6	....	8.51
$\delta\delta$	....	−.14
3 and 5 protons:	26	
In CCl_4	....	6.98
In C_6D_6	....	6.78
$\delta\delta$	....	.20
4 proton:	15	
In CCl_4	....	7.38
In C_6D_6	....	7.06
$\delta\delta$	....	.32

from the ring, the greater the shielding and the farther upfield the proton resonance is found. The figure shows that the chemical shift of a pyridine proton is dependent upon (1) the position of substitution and (2) the distance of the proton from the ring. Although not shown, the same observations were made from the NMR spectra of the pyridines in benzene-d_6.

An additional effect is observed. The chemical shifts of most of the protons obtained in an aromatic solvent, such as benzene-d_6, show an effect due to the diamagnetic anisotropy of the aromatic solvent, namely a shielded or upfield resonance shift from their position in the inert carbon tetrachloride solvent. This is the well-known and predicted effect due to an aromatic solvent. This expected differential shift is shown by positive values of $\delta\delta$ and is observed for either position 3, 4, or 5 ring protons or 3α or 3β, 4α or 4β, and 5α or 5β alkyl protons. (See tables 2 and 3.) In contrast, the predicted shielding effect is not observed for position 2 or 6 ring protons or for 2α or 2β and 6α or 6β alkyl protons, but a deshielding effect is observed instead. If, however, the alkyl proton is further removed from the ring than two carbon atoms (specifically, a 2γ or a 6γ proton), this abnormal solvent shift is no longer observed.

Table 3.—Differential chemical shifts of the alkyl protons on monosubstituted pyridines at 37° C, ppm

Alkyl group	Alkyl proton position	Position of substitution: 2 and 6	3 and 5	4
Methyl.....	α	0.04	0.46	0.26
Ethyl......	α	−.02	.32	.21
	β	.00	.27	.18
n-Propyl....	α	−.02	....	.19
	β	−.03	....	.16
	γ	−.02	....	.11
i-Propyl....	α	....	....	.21
	β	....	....	.16
t-Butyl.....	α	....	....	....
	β	....	....	.14
n-Pentyl....	α	−.08	....	.14
	β	−.09	....	....
	γ, δ	.05	....	.11
	ϵ	.02	....	.03
n-Hexyl....	α	−.07	....	....
	β	−.03	....	....
	γ, δ, ϵ	−.03	....	....
	ζ	.04	....	....
5-Nonyl....	α	−.17	....	.21
	β	−.16	....	.28
	γ, δ	−.03	....	.08
	ϵ	.00	....	.09

CHEMICAL SHIFTS OF ALKYL PROTONS OF POLYALKYL-SUBSTITUTED PYRIDINES

The chemical shifts and the differential shifts of the alkyl protons of the polyalkyl pyridines were averaged to discern the trends in these values. These data were derived from tables B–7 to B–9. The average values for the polysubstituted pyridines are listed for comparison with the average values for the monosubstituted pyridines in table 4. The same trends for the alkyl protons of polyalkyl pyridines were noted as for the ring protons and the alkyl protons of the monosubstituted pyridines. That is, the order of deshielding for position of substitution is 2 and 6 > 4 > 3 and 5. Also, the β protons are more shielded than the α protons. The same trend of solvent effect is also observed: The 2α and 6α protons and the 2β and 6β protons of the polyalkyl pyridines undergo a diamagnetic (upfield) shift in the benzene-d_6 solvent compared to the carbon tetrachloride solvent. Even though the differential shift is not negative, the small diamagnetic shift of these protons compared to large dismagnetic shifts of the 3α, 4α, and 5α protons indicates that the benzene solvent is affecting these protons in the same way it affects position 2 and 6

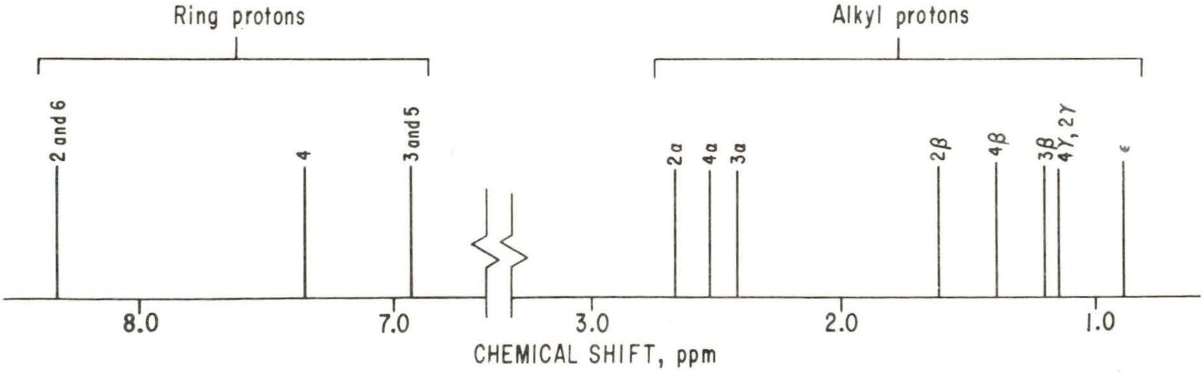

Figure 2.—Locations of average chemical shifts of ring protons and alkyl protons (from the NMR spectra in carbon tetrachloride at 37° C).

ring protons and the 2α or 2β and 6α or 6β alkyl protons in the monosubstituted pyridines.

The data in table 4 also show that the chemical shifts of the alkyl protons of polyalkyl pyridines are less than those of the monosubstituted pyridines. This trend of increased shielding with increase in amount of alkyl substitution is also observed for the ring protons of all of the 32 pyridines studied.

Among the pyridines, the compound 2,3,6-trimethylpyridine was found to give a unique spectrum. In a CCl_4 solution the methyl groups in positions 2 and 6 are equivalent. Each has a chemical shift of 2.39 ppm while the methyl protons in the 3 position occur at 2.19 ppm. In a C_6D_6 solution the 2- and 6-methyl protons are nonequivalent and appear at the following resonance positions: 2-methyl, 2.38 ppm; and 6-methyl, 2.45 ppm. The differential shift δδ, as shown in table 4, is 0.01 ppm for the 2-methyl and is −0.06 ppm for the 6-methyl protons. The 2-methyl protons have essentially no shift but the 6-methyl protons show a paramagnetic shift. The 3-methyl protons have a chemical shift of 1.87 ppm in C_6D_6 and a differential shift δδ of 0.32 ppm. This compound is the only pyridine studied that showed equivalency in chemical shift in CCl_4 for particular protons and nonequivalency for the same protons in C_6D_6.

Table 4.—Average chemical shifts and average differential shifts of protons on monosubstituted and polyalkyl-substituted pyridines in in CCl_4 at 37° C

Proton position	Average chemical shift	Average δδ
MONOSUBSTITUTED PYRIDINE		
2α and 6α	2.66	−0.05
4α	2.53	.20
3α and 5α	2.43	.38
2β and 6β	1.62	−.07
4β	1.38	.21
3β and 5β	1.19	.27
POLYALKYL-SUBSTITUTED PYRIDINE		
2α and 6α	2.37	.02
4α	2.21	.29
3α and 5α	2.18	.27
2β and 6β	....	....
4β	1.16	.20
3β and 5β	1.17	.16

THEORETICAL ASPECTS

CHEMICAL SHIFTS AND NUCLEAR SHIELDING OF PYRIDINES

The results of the present study of the proton NMR spectra of pyridines led to several observations:

1. The order of deshielding of the ring protons and alkyl protons is 2 and 6 > 4 > 3 and 5.
2. Alkyl protons at least three carbon atoms distant from the pyridine ring are outside the deshielding influence of the pyridine ring.
3. The chemical shifts of the ring protons and alkyl protons are found farther upfield with an increase in number of alkyl substituents. That is, there is increased shielding with an increase in alkyl substitution.

These results are consistent with the observations made by others on the NMR spectra of pyridines and also of benzenes.

The NMR spectra of pyridine may be regarded as an analog of the NMR spectra of benzenes. There is no effect of spin couplings of the nitrogen nucleus of pyridines since these couplings are eliminated by quadrupole relaxation. There is an effect on the chemical shifts of the ring and alkyl protons due to the electronegative character of the nitrogen atom, and the effect found by others is confirmed in the present study. The electronegative nitrogen atom affects the π-electron density about the carbon atoms both by a resonance and an inductive effect. The chemical shifts of position 3 and 5 protons are assumed to mostly reflect the inductive effect, and position 2, 6, and 4 chemical shifts of pyridines reflect mostly the resonance effect. This combination of resonance and inductive effects is responsible for the differences in the amount of shielding found at each carbon atom of the pyridine ring.

As the distance of the alkyl proton from the ring is increased it becomes more shielded. This fact is also well known, and Pople (*23*) has estimated that the screening effect varies with the inverse of the cube of the distance from the center of the benzene ring.

Increased shielding with increase in alkyl substitution cannot be explained by the larger ring current brought about by the inductive effect of the alkyl substituents since the shifts predicted from this effect should be in the direction opposite to that observed. Instead, the observed effect can be explained by the intermolecular separation of the pyridine and benzene molecules in the liquid phase. The work of Bothner-By and Glick (*4*) can be used to illustrate this effect. These authors performed a quantitative calculation based on a cylindrical-disk molecule. The results of their calculations showed that the secondary magnetic field due to a neighboring molecule was found to decrease inversely with the cube of the distance of separation. Polyalkylated benzenes, for example, undergo an increase in effective molecular volume with an increase in number of substituent groups. The increase in molecular volume also increases the mean separation of aromatic rings with increasing substitution, and therefore the substituted compounds may be expected to give rise to correspondingly smaller overall dilution shifts. This explanation is consistent with the chemical shifts observed for the pyridines in benzene-d_6 and in carbon tetrachloride.

EFFECTS OF SOLVENT ON THE NMR SPECTRA OF PYRIDINES

The effect of solvents on the resonance position of protons has been studied extensively. (See, for example, reference *18* and other references cited therein.) One of the factors contributing to the chemical shift, or resonance position, of a proton in NMR is the anisotropy of the solvent medium. In general the diamagnetic anisotropy of an aromatic solvent brings about an upfield (diamagnetic) shift of a proton when the spectrum of the compound is obtained in an aromatic solvent as compared to its chemical shift in a nonaromatic solvent.

To explain this solvent effect, Buckingham (*8–9*) and Hatton and Schneider (*17*) have proposed a simple expression that relates the effect of several factors on the observed chemical shift. This relationship can be stated as

$$\delta = \delta_G + \delta_B + \delta_A + \delta_W + \delta_E + \delta_C. \qquad (2)$$

The factors δ_G (shift of an isolated gaseous molecule) and δ_C (complexing factor) were added to the earlier expression of Buckingham by Hatton. Both authors attribute the effects on the chemical shifts to the orientation of rod-shaped molecules such as carbon disulfide and acetylene and disk-shaped molecules such as benzene with the solute molecule. They conclude that there are four significant contributions: δ_A—the shift due to the solvent magnetic anisotropy; δ_W—the shift due to van der Waals interaction between solvent and solute molecules; δ_E—the reaction-field effect or the shift due to polar effects; and δ_C—the shift due to specific molecular interactions, specifically, hydrogen bonding or complex formation in solution. They further state that, with the exception of the δ_A for disk-shaped molecules, such as C_6D_6, and possibly δ_E in some molecules, all of these contributions to the screening constant (chemical shift) are negative and cause a solvent shift of the solute proton signal to lower field. The diamagnetic anisotropy effect δ_A and in specific instances δ_E give a positive or upfield shift. The results of Abraham (*1*) and Hatton and Richards (*16*) generally support the effects discussed. Murrell and Gil (*22*) conducted research on the NMR spectra of pyridines in various solvents, and they too state that the ring protons on the pyridine molecule would be expected to shift in an upfield direction in an aromatic solvent as compared to their position in a nonaromatic solvent.

The results of the present work show that the ring protons positions 3, 4, and 5 do undergo an upfield shift in benzene-d_6 as compared to the chemical shift in CCl_4. Position 2 and 6 protons, contrary to the predicted effect, often showed a paramagnetic or downfield shift, which is indicated by the negative differential shift. The average differential shift observed for position 2 and 6 protons in the 32 pyridines is −0.14 ppm; for position 3 and 5 protons, 0.20 ppm; and for the position 4 proton, 0.32 ppm.

The chemical shifts of the protons on alkyl substituents are also solvent dependent. These data again show that, in general, the differential shift of a proton on a carbon in the 2 position on the ring is in a paramagnetic direction in an aromatic solvent relative to its position in a nonaromatic solvent. Clearly, in the case of both the ring protons and alkyl group protons in positions 2 and 6, the aromatic solvent benzene-d_6 brings about a paramagnetic differential shift.

Theoretical Interpretation

Other workers have postulated that the solvent effect on chemical shifts has to do with the orientation of the solvent and solute molecules (*1*, *9*, *16–17*, *22*, *26–27*, *29*, *35*). As pointed out earlier, six factors are postulated as contributing to the shielding effect on a particular sample proton. Generally, various individual factors can be eliminated if appropriate conditions are chosen to observe the resonance. For instance, using an internal reference rather than an external one eliminates the effect of the bulk diamagnetic susceptibility δ_B of the solvent. The effect of an isolated gaseous molecule δ_G is eliminated by obtaining the spectra of the samples as liquid solutions, and therefore these factors become constants.

The remaining effects (δ_A, δ_W, δ_E, and δ_C) vary in their contribution to the observed shift. The contribution of the van der Waals forces δ_W is considered insignificant in the system studied (*9, 30*). The diamagnetic anisotropy δ_A of the solvent molecule is a predominant effect when aromatic solvents are used. This effect is brought about by induced magnetic moments and is dependent on the orientation of the solute and solvent molecules (magnetic anisotropy). The secondary magnetic field caused by this induced magnetic moment is proportional to the inverse third power of the separation of the molecules. Therefore, if the molecules are arranged in a planar configuration, there will be a diminution of the external field at the solute proton which would cause a high-field shift. However, if the molecules were arranged in a perpendicular configuration, a low-field shift of the solute protons would be observed (*8–9*). The circulating field would, in the former case, shield the protons and in the latter case deshield the protons.

The polar effect δ_E and the complex effect δ_C, a special case of the polar effect, contribute significantly to the observed shift and the direction of the shift. With the contributing factors defined, the accumulated data can now be evaluated.

In an inert solvent such as CCl_4 the pyridine-ring protons appear at low field. In a donor solvent such as benzene, a shift of the protons to higher field is due to the increased shielding brought about by the diamagnetic anisotropy of the benzene, when the benzene is coplanar with the pyridine molecule. This shift is observed for the protons in positions 3, 4, and 5 on the pyridine ring, but position 2 and 6 protons show a shift to low field. This low-field, or paramagnetic, shift is opposite to the effect predicted on the basis of the diamagnetic anisotropy of the aromatic solvent. From this fact one can conclude that the δ_A effect, although contributing to the observed shift, is not the only contributing effect.

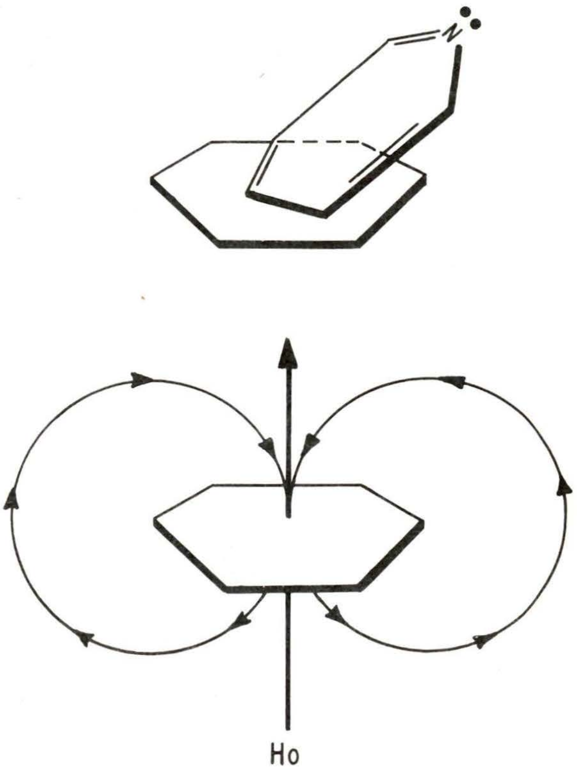

Figure 3.—Proposed structure for the pyridine-benzene complex and the induced secondary field on the benzene ring.

The presence of the electronegative atom, nitrogen, in the pyridine ring can be responsible for reaction field effects δ_E in the solvent-solute system. This reaction field can affect the field experienced by the individual protons of the pyridine solute.

A structure for the pyridine-benzene complex can be postulated based on the cumulative effect of the anisotropy of the components, solute and solvent, the polar nature of the solute, and the specific intermolecular interactions (complex formation) (*30*). The proposed geometry in figure 3 pictures the pyridine as being oriented at an angle to the plane of the benzene ring with position 3 and 5 protons toward the center of the benzene ring, the position 4 proton slightly off center, and position 2 and 6 protons oriented away from the plane of the benzene. This configuration would place position 3 and 5 protons in the most highly shielded position in relation to the induced secondary field in the benzene, the position 4 proton in a slightly less shielded orientation, and position 2 and 6 protons in a deshielded position with respect to the secondary induced field.

Table 5.—Chemical shifts of solutions of 3-methylpyridine in benzene-d_6 diluted with cyclohexane at 37° C, ppm

Benzene concentration, molal	Position of substitution			
	CH_3	2 and 6 protons	4 proton	5 proton
137.4[1]	1.858	8.480	6.988	6.738
125.4	1.908	8.442	7.015	6.754
115.3	1.938	8.404	7.038	6.763
106.7	1.971	8.417	7.071	6.787
99.3	1.996	8.392	7.083	6.796
92.8	2.013	8.392	7.104	6.812
87.2	2.025	8.392	7.112	6.821
78.3	2.050	8.404	7.140	6.840
77.7	2.062	8.392	7.140	6.835

[1] The original solution concentration was 1 molal in 3-methylpyridine.

This proposed geometry pictures the probable result of the most important of the shielding parameters. This orientation was originally proposed by the authors (*20–21*) and corresponds directly with an orientation later proposed by Ronayne and Williams (*27*). The proposed orientation fulfills all of the required conditions for a π-complex, which utilizes the pyridine π-electrons. The resultant ring current is modified by the nitrogen lone-pair electrons (*36*) and the benzene π-electrons. This π-complex results in the observed chemical shift of the pyridine protons in an aromatic solvent.

Evidence for Complex Formation

Further evidence for complex formation between benzene and pyridine solute molecules is revealed by experiments showing the effects of varying the concentration of these components in an inert solvent. In a set of experiments the effect of benzene-d_6 concentration on the chemical shifts of several protons of 3-methylpyridine was studied. The results are shown in table 5. The observed chemical shifts, upon successive dilution by cyclohexane, show a regular change. The chemical shifts for the methyl protons and position 5 and 4 protons increase regularly with dilution. The chemical shifts of position 2 and 6 protons decrease with dilution. These effects are consistent with the observation of the solvent effect on protons in these positions. These observations are consistent with the formation of a complex between benzene-d_6 and 3-methylpyridine involving a small equilibrium constant. Work by others (*28*, *33*) has shown that these kinds of data may be used to determine the magnitude of the equilibrium constant. This application has not been made in detail in the present work, but preliminary calculations show that the magnitude of the equilibrium quotient is approximately 1×10^{-4}.

IDENTIFICATION OF PYRIDINES IN SHALE-OIL NAPHTHA

A fraction obtained from separation of a gross mixture by gas-liquid chromatography was utilized to illustrate how the previously mentioned data were used in a qualitative identification of pyridines isolated from shale oil. The spectrum of this fraction at 37° C in CCl_4 is shown in figure 4. The fraction had a major and a minor constituent. Both compounds were pyridines as shown by NMR spectra and mass and infrared spectra. The data on the chemical shift of the ring protons in CCl_4 solution indicated that protons were present in positions 2 and 6, 3 and 5, and 4. Chemical-shift data and integration of the areas under the peaks indicated one proton in position 2 or 6, three protons in position 3 or 5, and one proton in position 4.

The band at 8.28 ppm is assigned to the position 2 or 6 proton; the band at 7.18 ppm is assigned to the position 4 proton; and the band at 6.92 ppm is assigned to one of the position 3 and 5 protons. The remaining position 3 and 5 protons are under the band at 6.65 ppm. In each case the assigned values fall within the ranges shown in figure 1. The position 2 or 6 proton at 8.28 ppm is within the range of chemical shifts observed for a disubstituted pyridine. The position 4 proton at 7.18 ppm is within the range of chemical shifts observed for disubstituted pyridines and in the case of the position 3 or 5 proton at 6.92 ppm, it falls in the range for a disubstituted pyridine. The two position 3 and 5 protons at 6.65 ppm are at a higher field than the lone position 3 or 5 proton described previously and fall within the range for trisubstituted pyridines.

A value of 2.37 ppm is given as the resonance position for methyl groups in positions 2 and 6 for 2,4,6-trimethylpyridine and a value of 2.17 ppm for the methyl protons in the 4 position. In the spectrum shown in figure 4, the band at *d* (2.38 ppm) had an integrated area equal to six protons and was assigned to methyl groups at positions 2 and 6, while the band at *b* (at 2.20 ppm) which had an integrated area equal to three protons was assigned to a methyl group in the 4 position. This compound was identified as 2,4,6-trimethylpyridine.

The second compound was identified as either 2-ethyl-3-methylpyridine or 2-ethyl-5-methylpyridine. The bands in the spectrum were assigned as follows: Band *a* at 1.26 ppm and band *e* at 2.70 ppm were assigned to the methyl and methylene protons of an ethyl group in the 2 position; band *c* at 2.26 ppm was assigned to a methyl group in either position 3 or 5 on the pyridine ring; the bands at 8.28 ppm, 6.92 ppm, and 7.18 ppm in figure 4 were assigned to the respective ring protons shown in structural formula II.

Data from the present study were used in the preceding manner to identify other pyridines in a shale-oil naphtha (*5*). Twenty-four alkyl pyridines identified by NMR spectroscopy comprised about 64 percent of the basic nitrogen fraction separated by gas-liquid chromatography from this shale-oil naphtha.

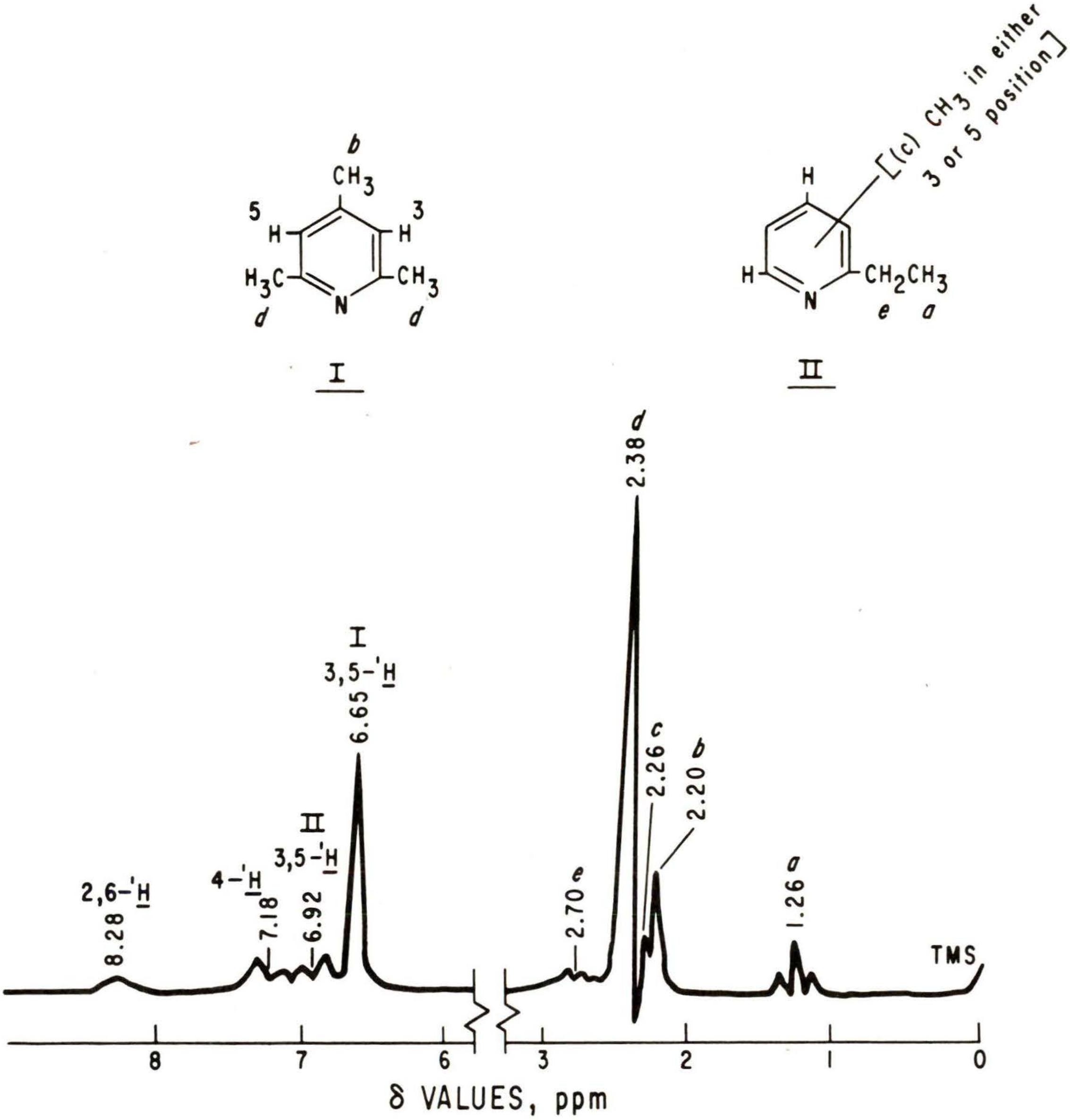

Figure 4.—NMR spectrum of a fraction of shale oil containing alkyl pyridines.

SUMMARY

The chemical shifts of the ring protons and the alkyl protons of 32 pyridines in carbon tetrachloride and benzene-d_6 solutions are given. The chemical shifts depend on the position of substitution and on the solvent. The differential shifts caused by a change in solvent are correlated with the substituent position. An unexpected paramagnetic shift of protons in positions 2 and 6 on the pyridine ring in an aromatic solvent as compared to their positions in a nonaromatic solvent was observed. A proposed π-complex structure is presented to account for the observed shifts that occur in the pyridine-ring protons and alkyl substituent group protons in an aromatic medium. A range of differential shifts based on these correlations is given. The utility of the data is demonstrated in an identification of two pyridines isolated from a fraction of shale oil.

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APPENDIX A.—CATALOG OF SPECTRA

This appendix contains reproductions of the 60-MHz proton NMR spectra of the 32 pyridines studied. The figures are arranged to show, first, the spectrum of a pyridine in carbon tetrachloride solvent and second, in benzene-d_6 solvent. All of the spectra shown in the illustrations were obtained at a probe temperature of 37° C.

Assignment of chemical shifts (δ) are shown on the spectra in parts per million from the internal reference, tetramethylsilane (TMS). The spectra were obtained at two different sweep widths, 500 and 1,000 Hz. The choice of width depended on the complexity of the multiplets in each individual spectrum and the authors' desire to convey as much information as possible from each spectrum. The chemical shifts in parts per million and the assignments are written above the resonance peaks. A structural formula of the pyridine is also shown in each illustration.

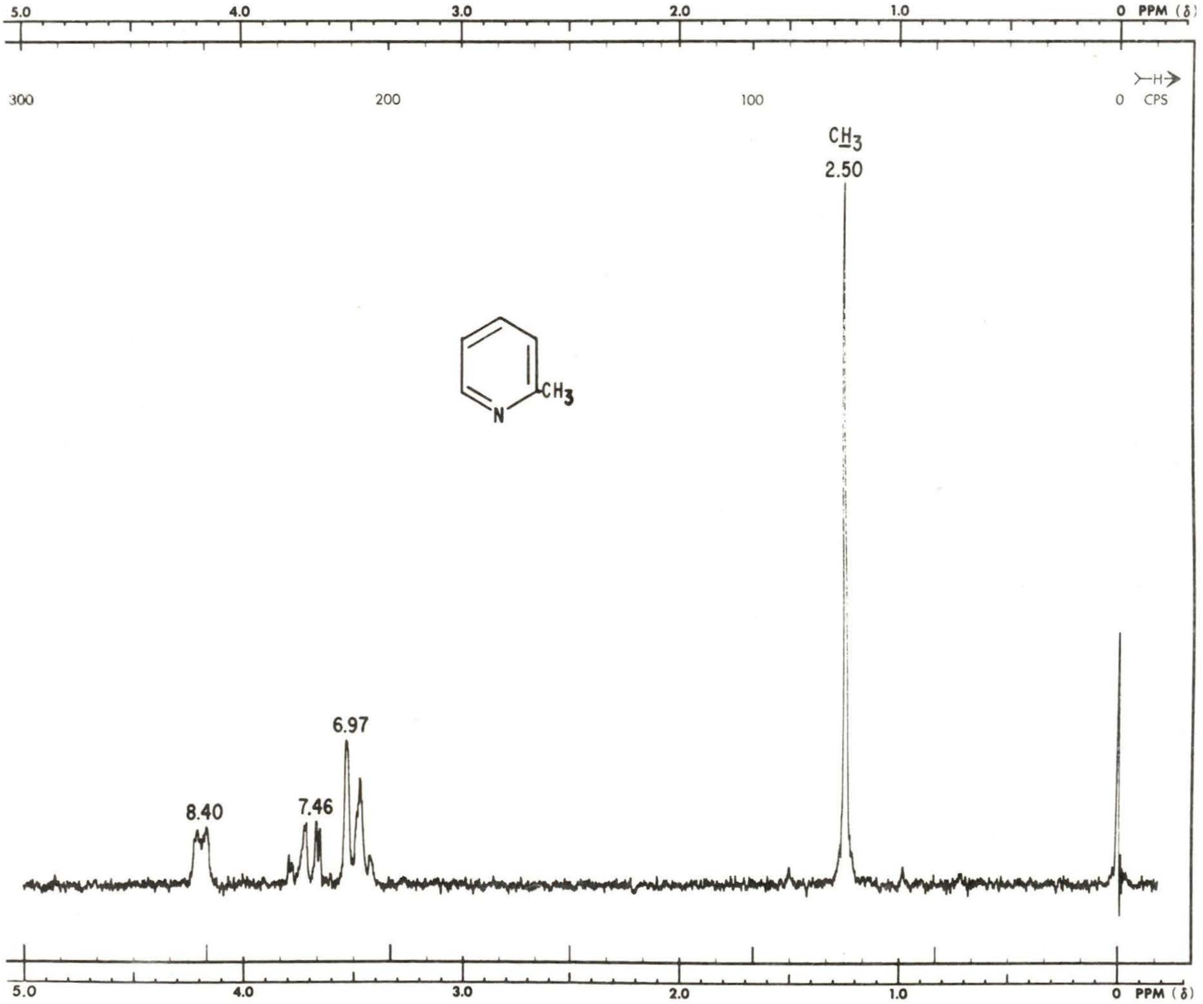

Figure A–1.—2-methylpryidine in CCl$_4$.

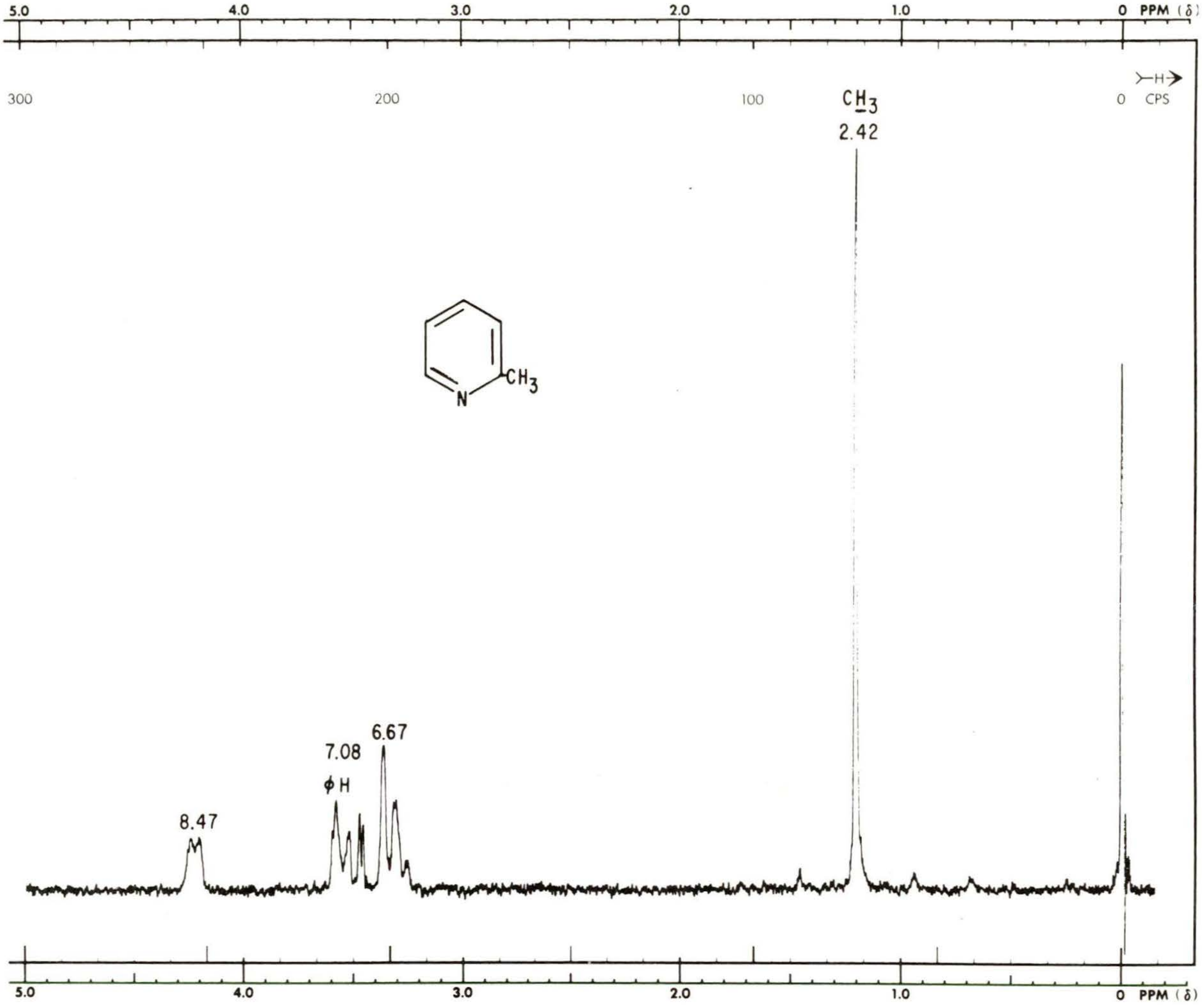

Figure A–2.—2-methylpyridine in C_6D_6.

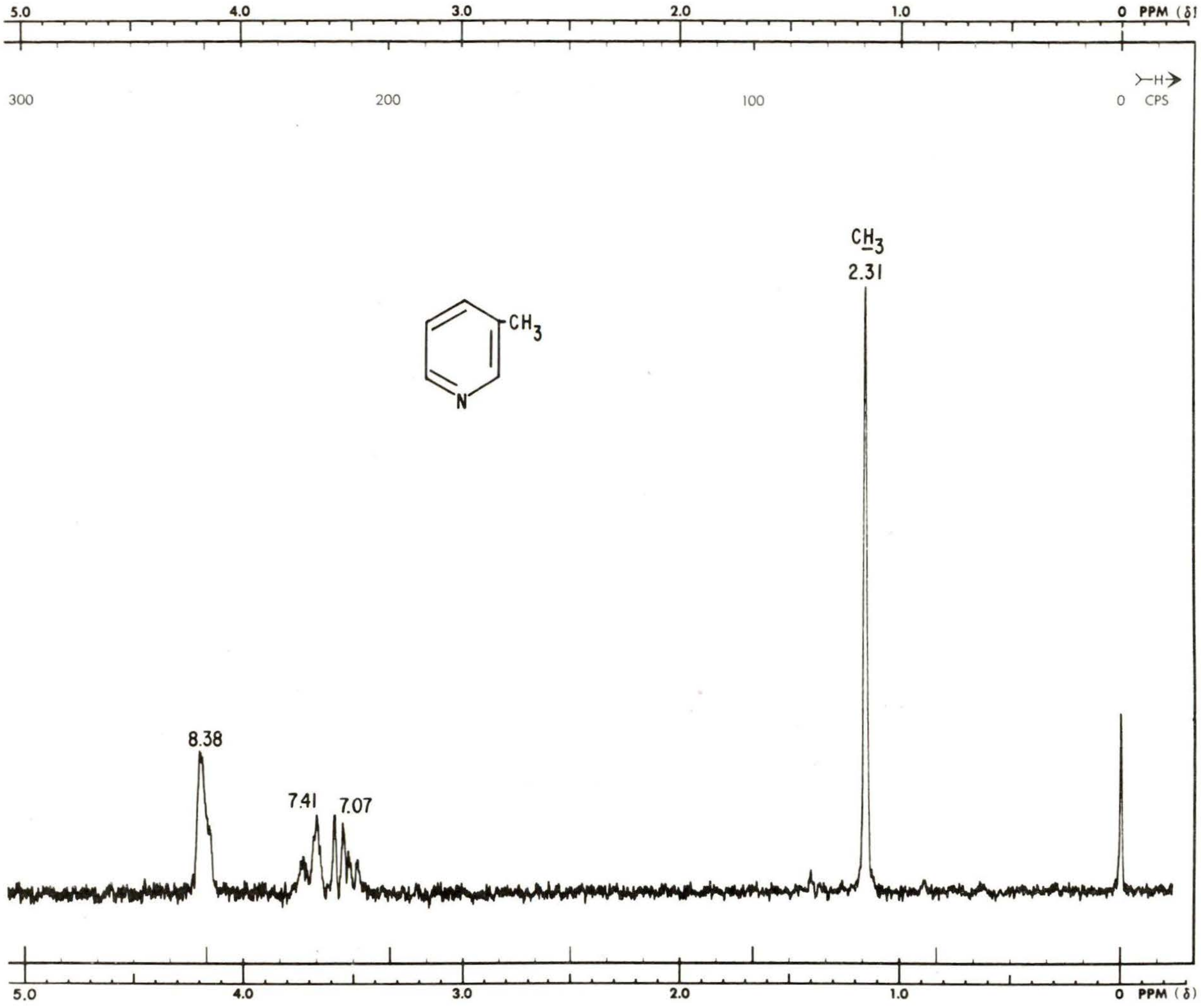

Figure A–3.—3-methylpyridine in CCl_4.

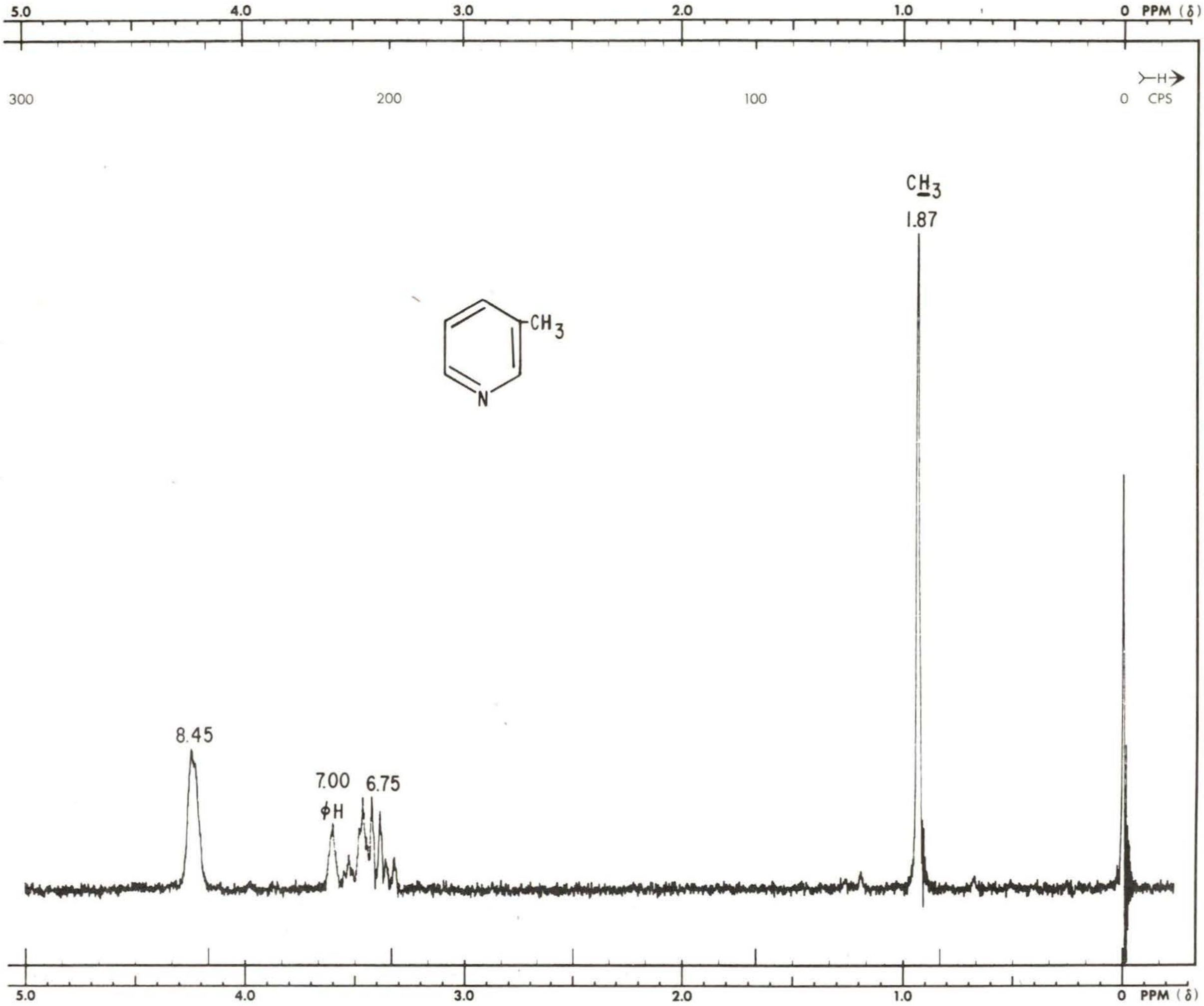

Figure A-4.—3-methylpyridine in C_6D_6.

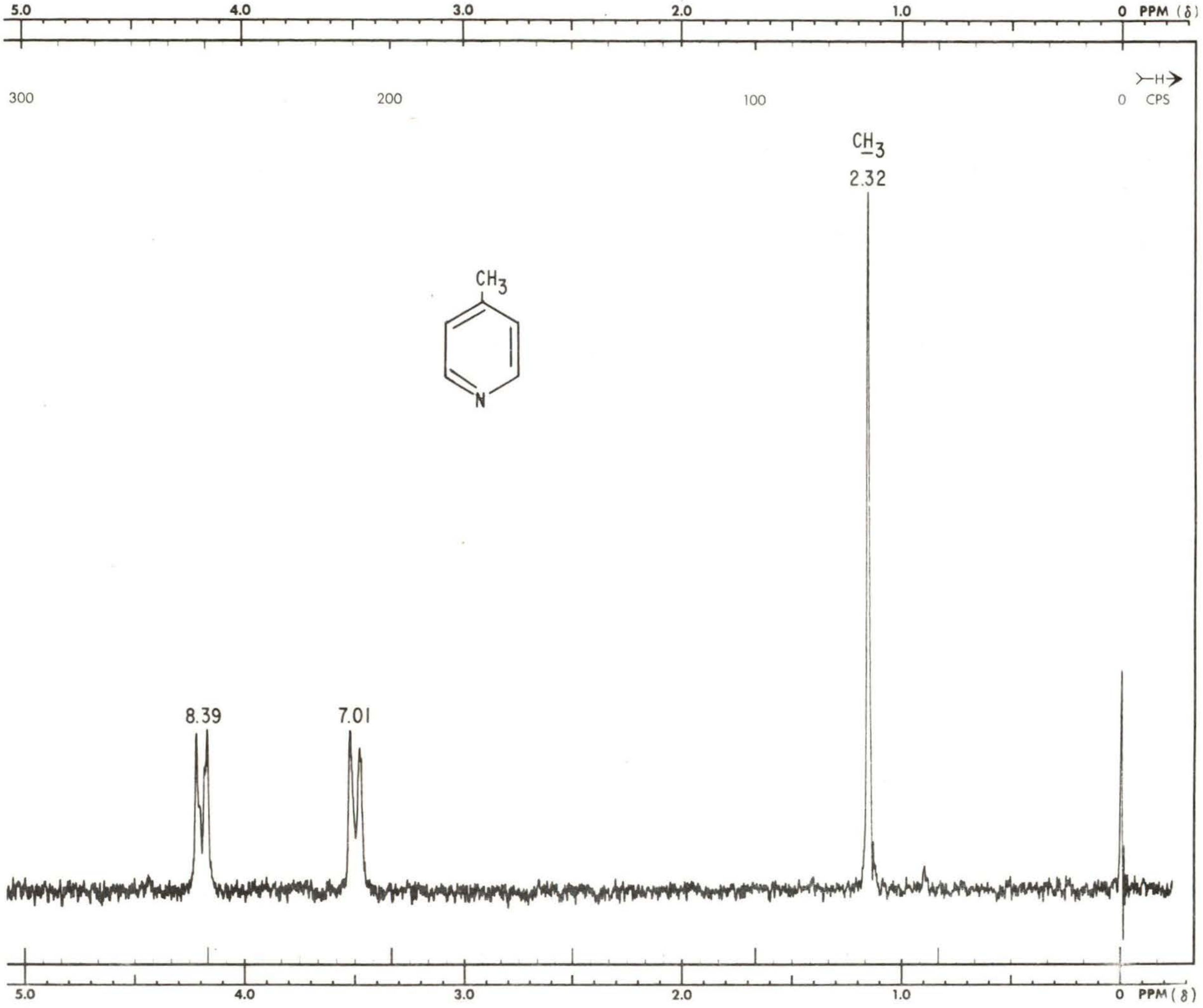

Figure A–5.—4-methylpyridine in CCl_4.

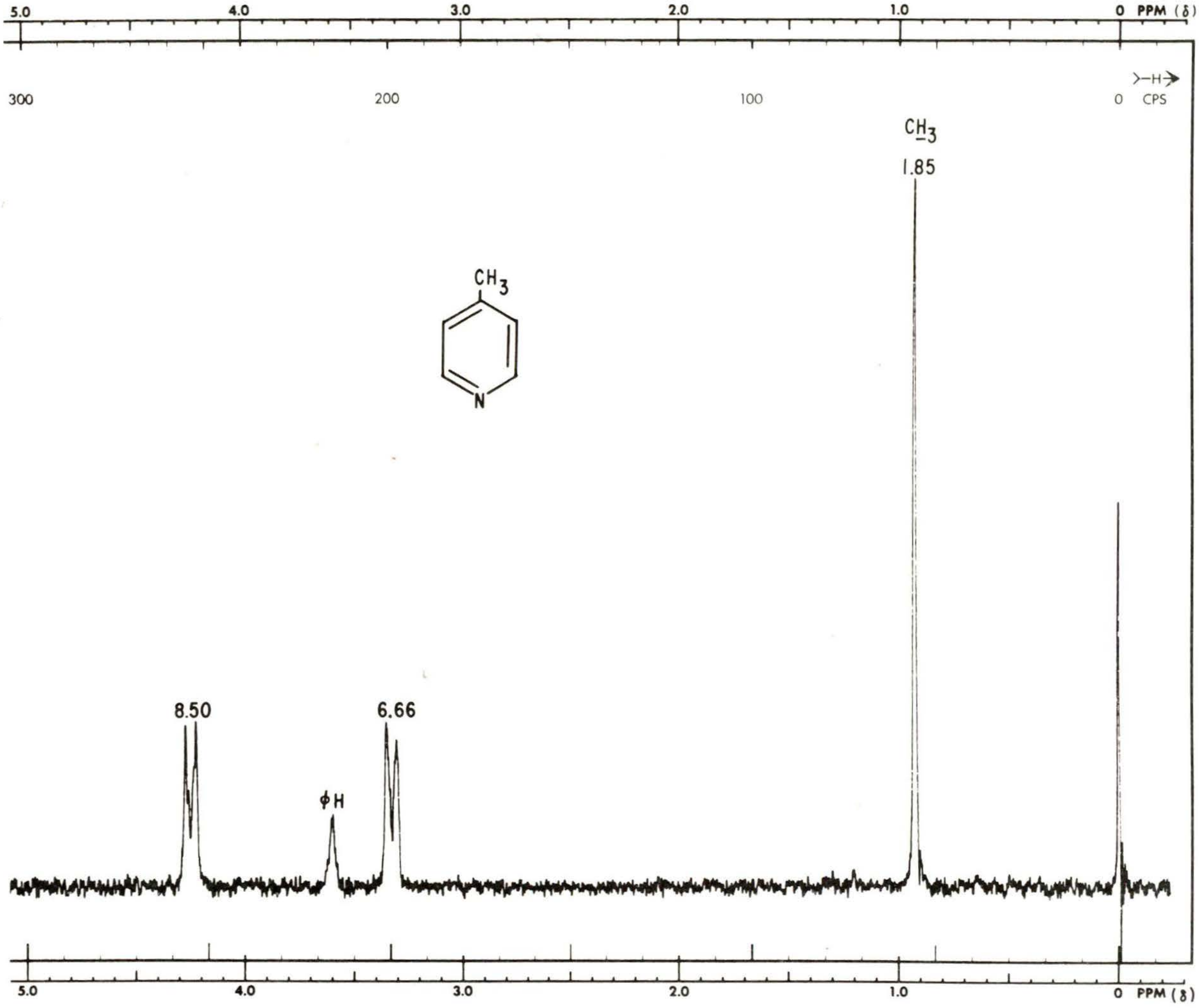

Figure A–6.—4-methylpyridine in C_6D_6.

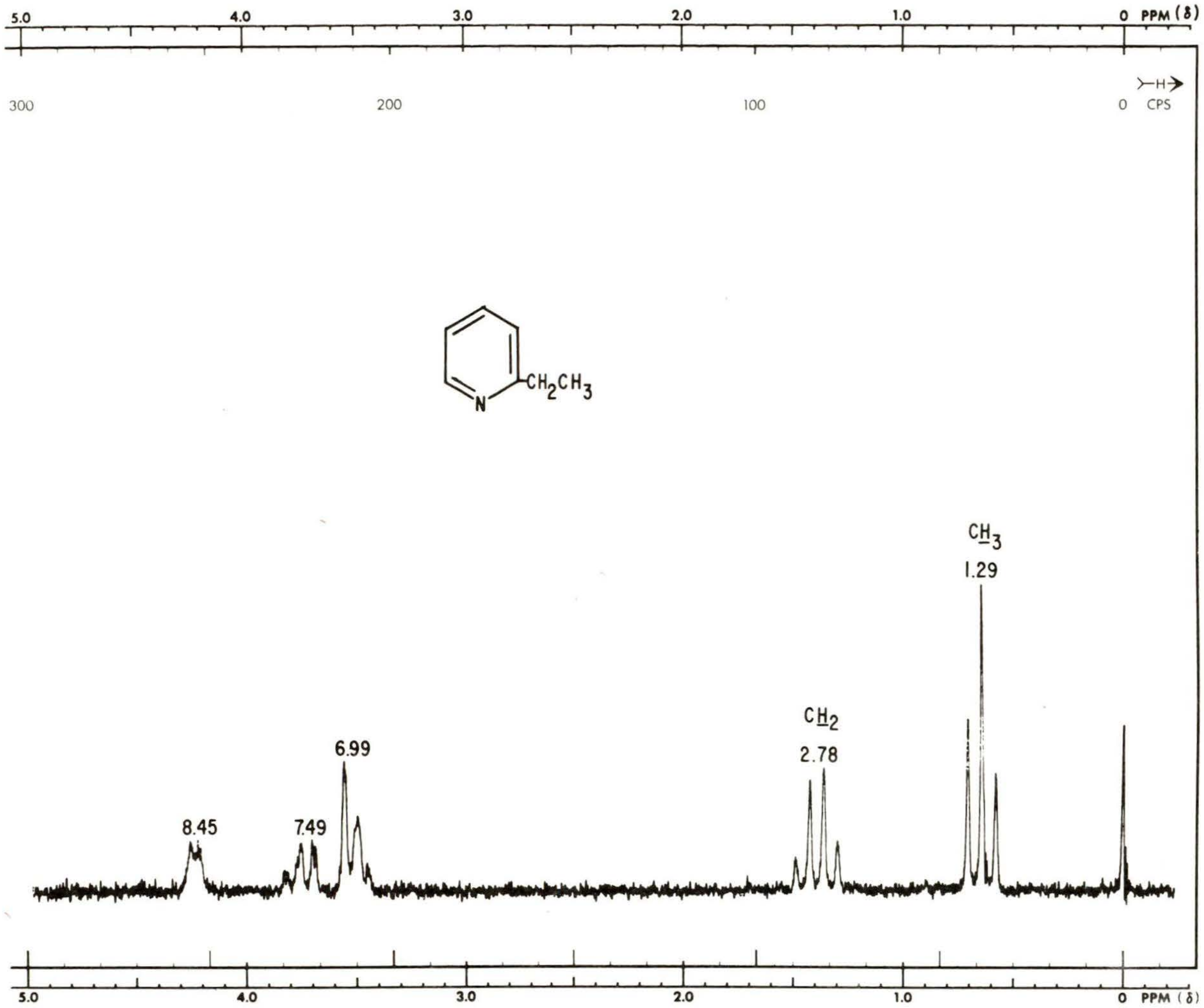

Figure A-7.—2-ethylpyridine in CCl_4.

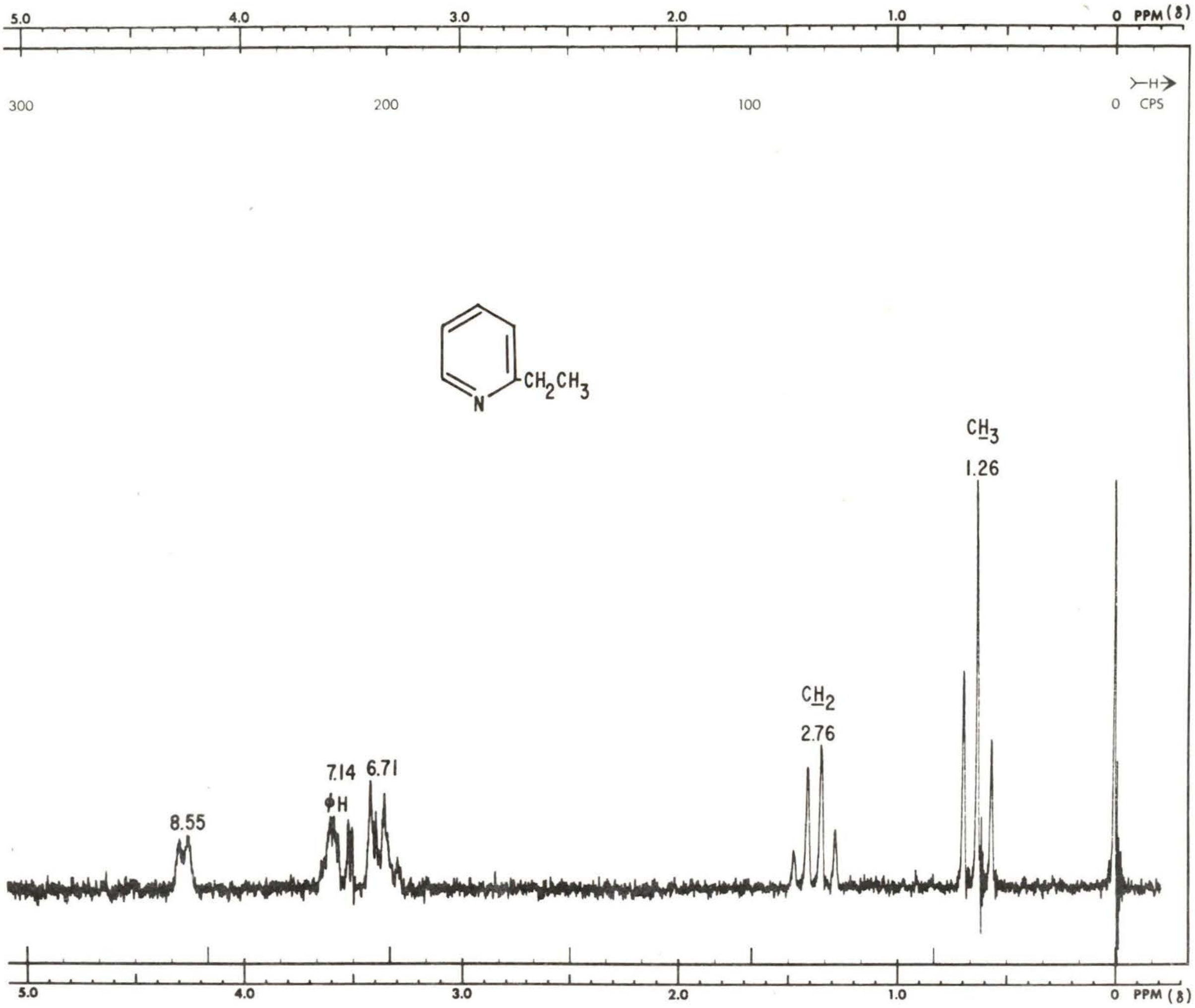

Figure A–8.—2-ethylpyridine in C_6D_6.

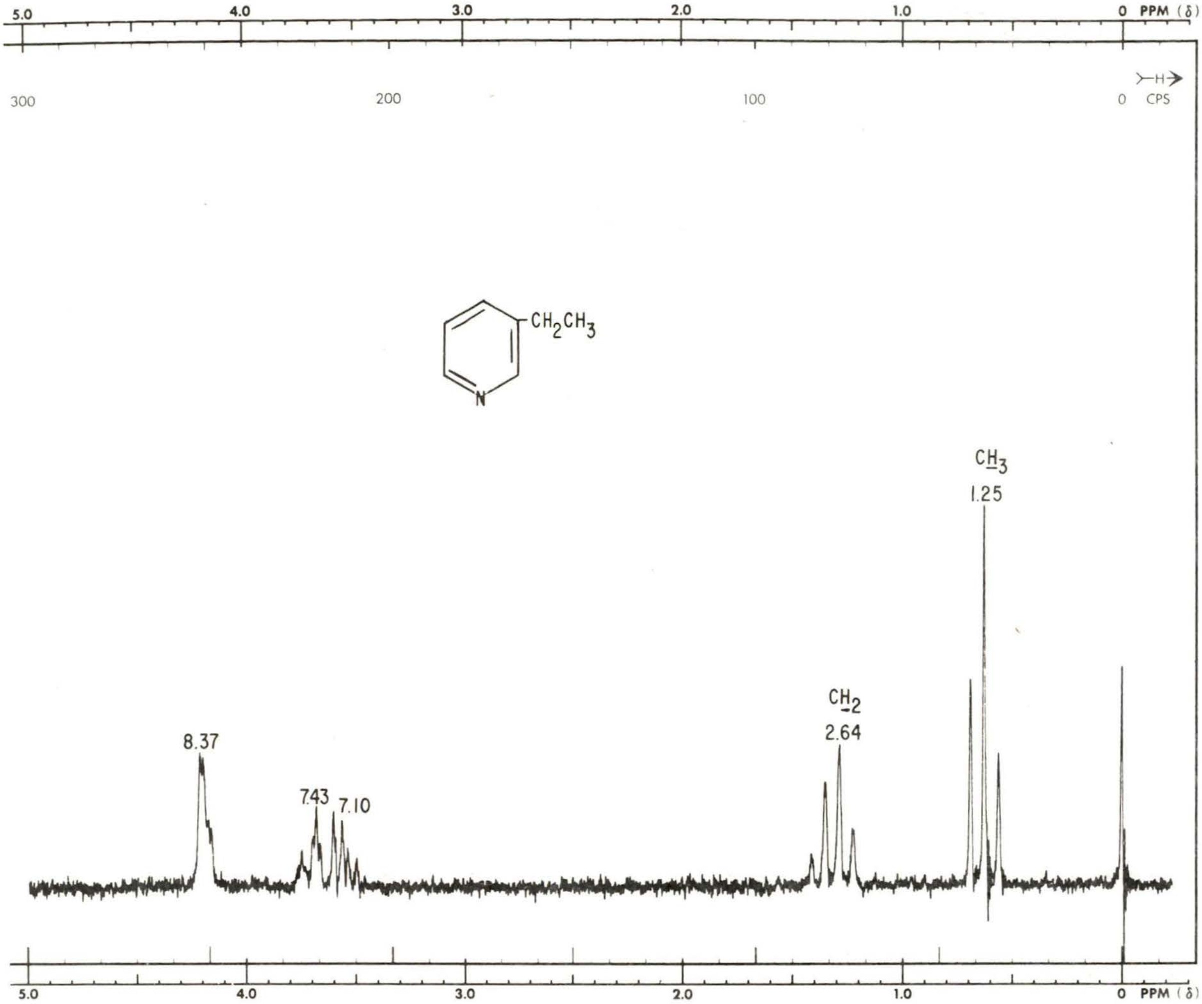

Figure A-9.—3-ethylpyridine in CCl$_4$.

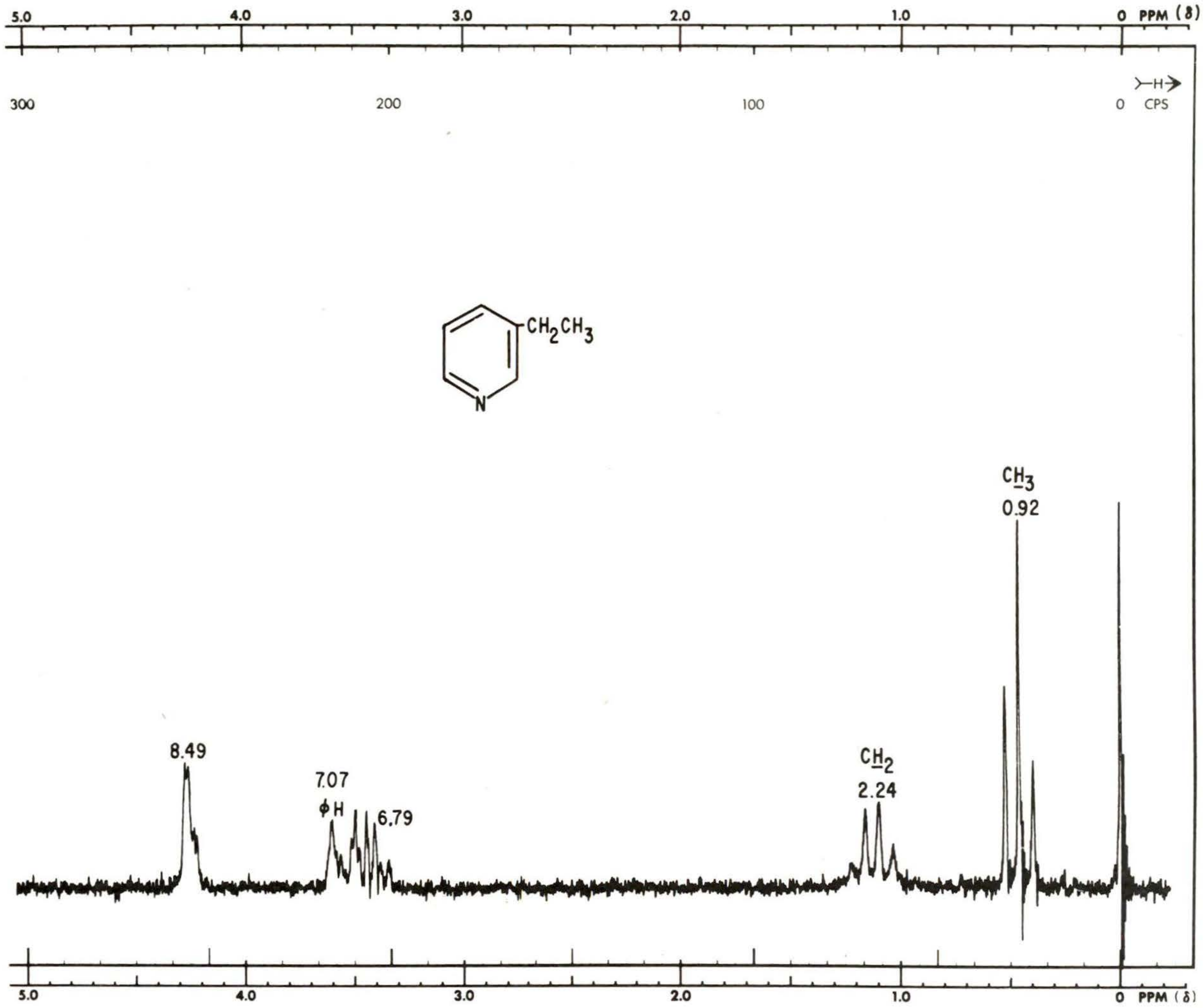

Figure A–10.—3-ethylpyridine in C_6D_6.

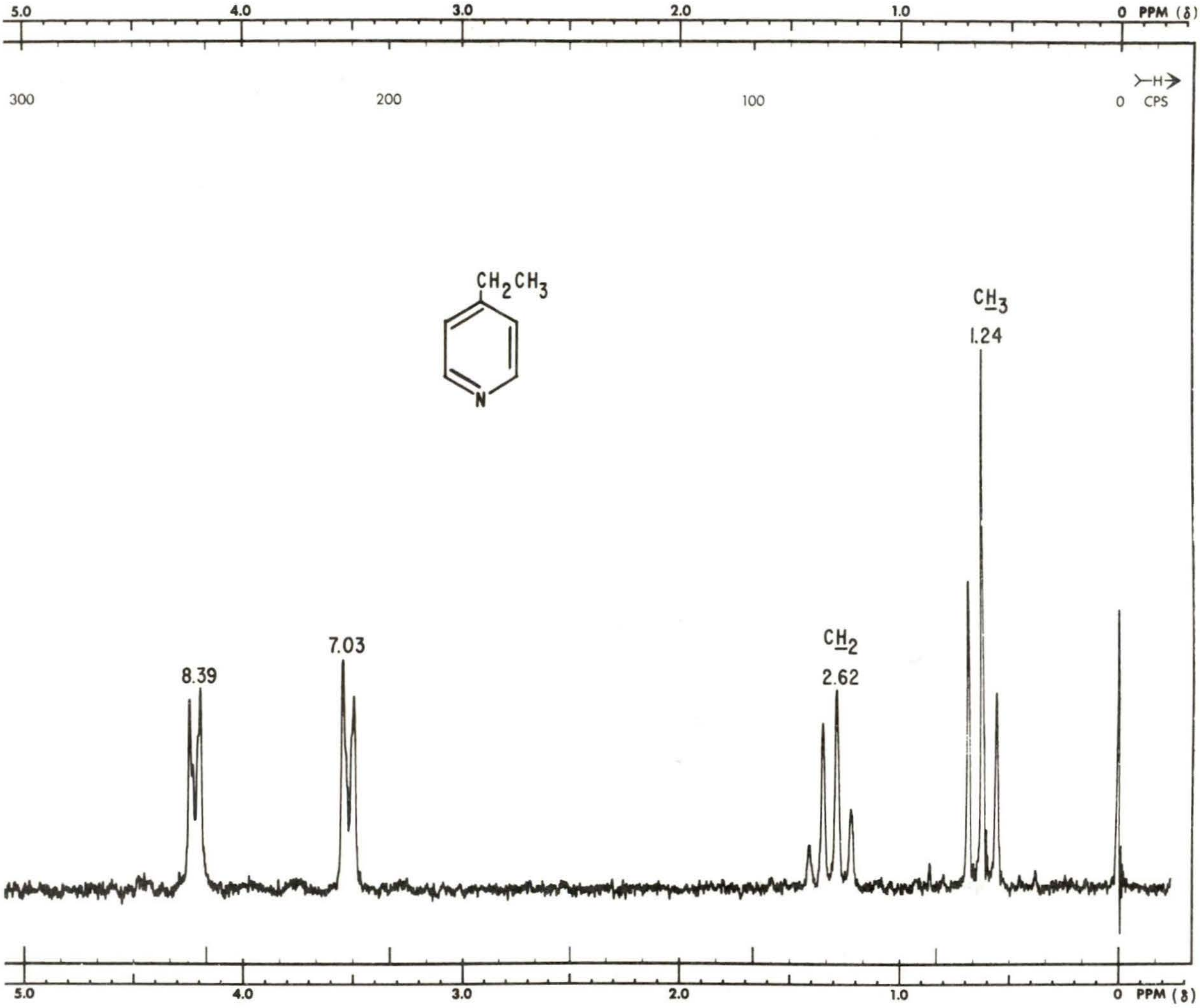

Figure A-11.—4-ethylpyridine in CCl_4.

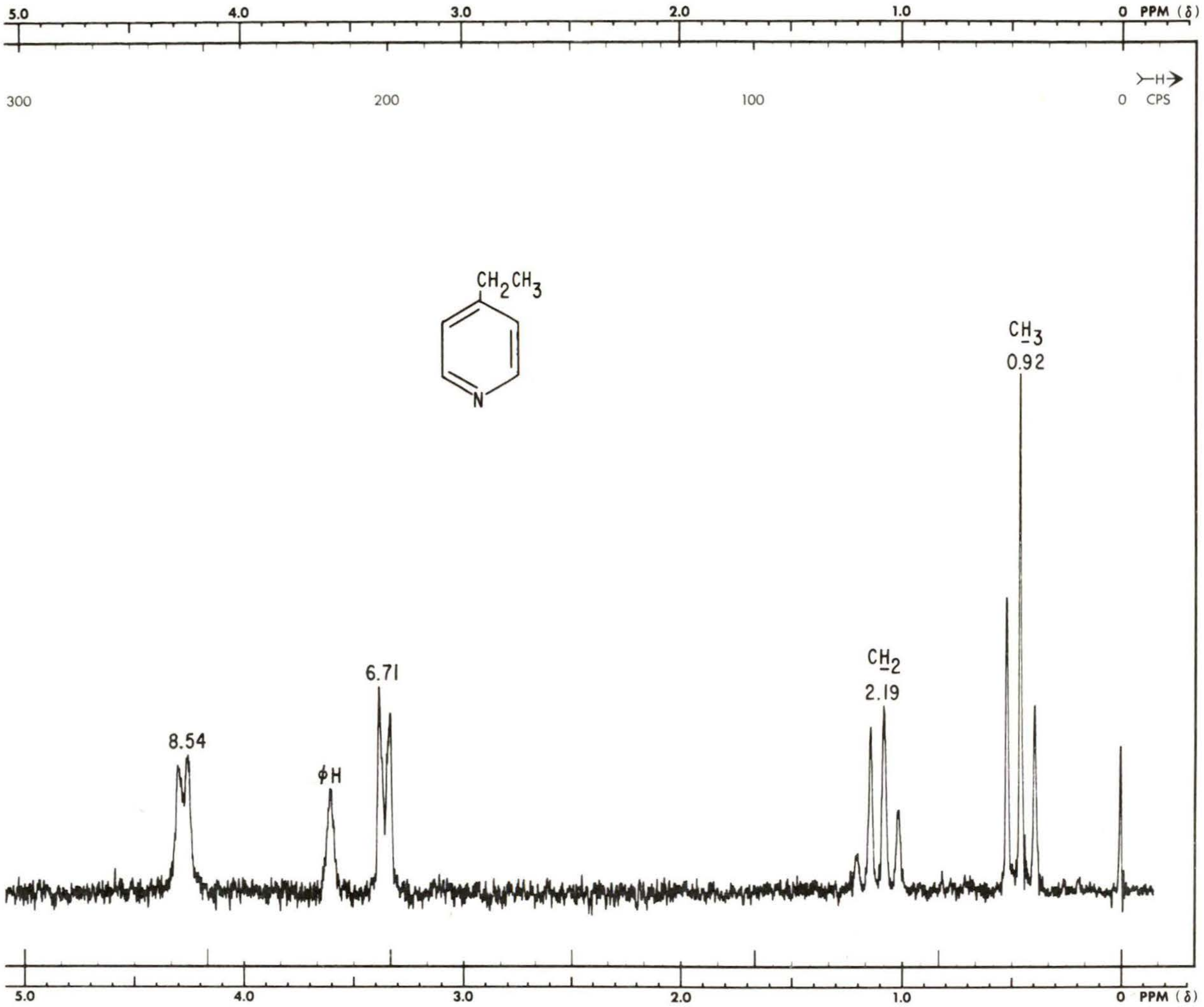

Figure A-12.—4-ethylpyridine in C_6D_6.

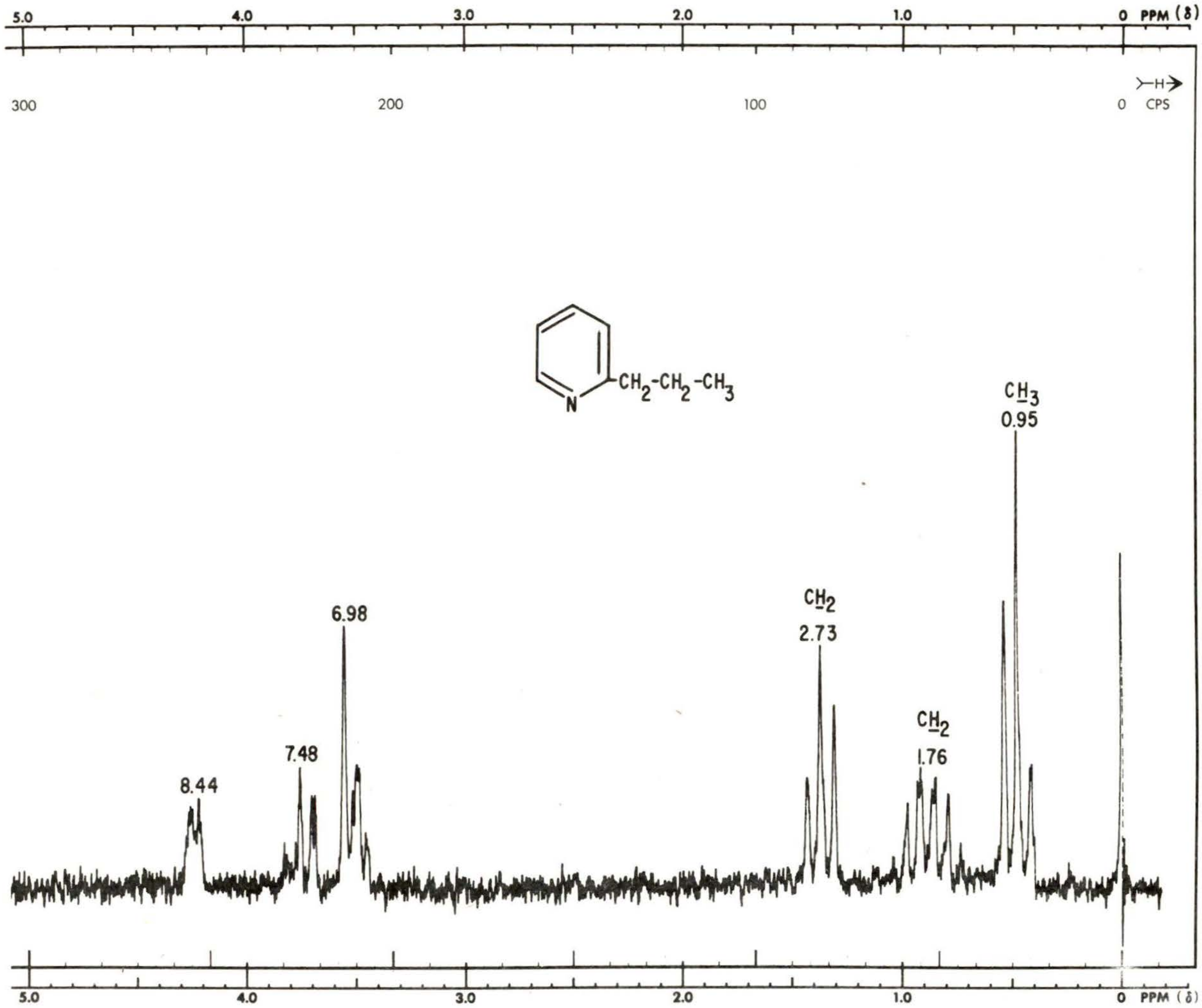

Figure A-13.—2-propylpyridine in CCl_4.

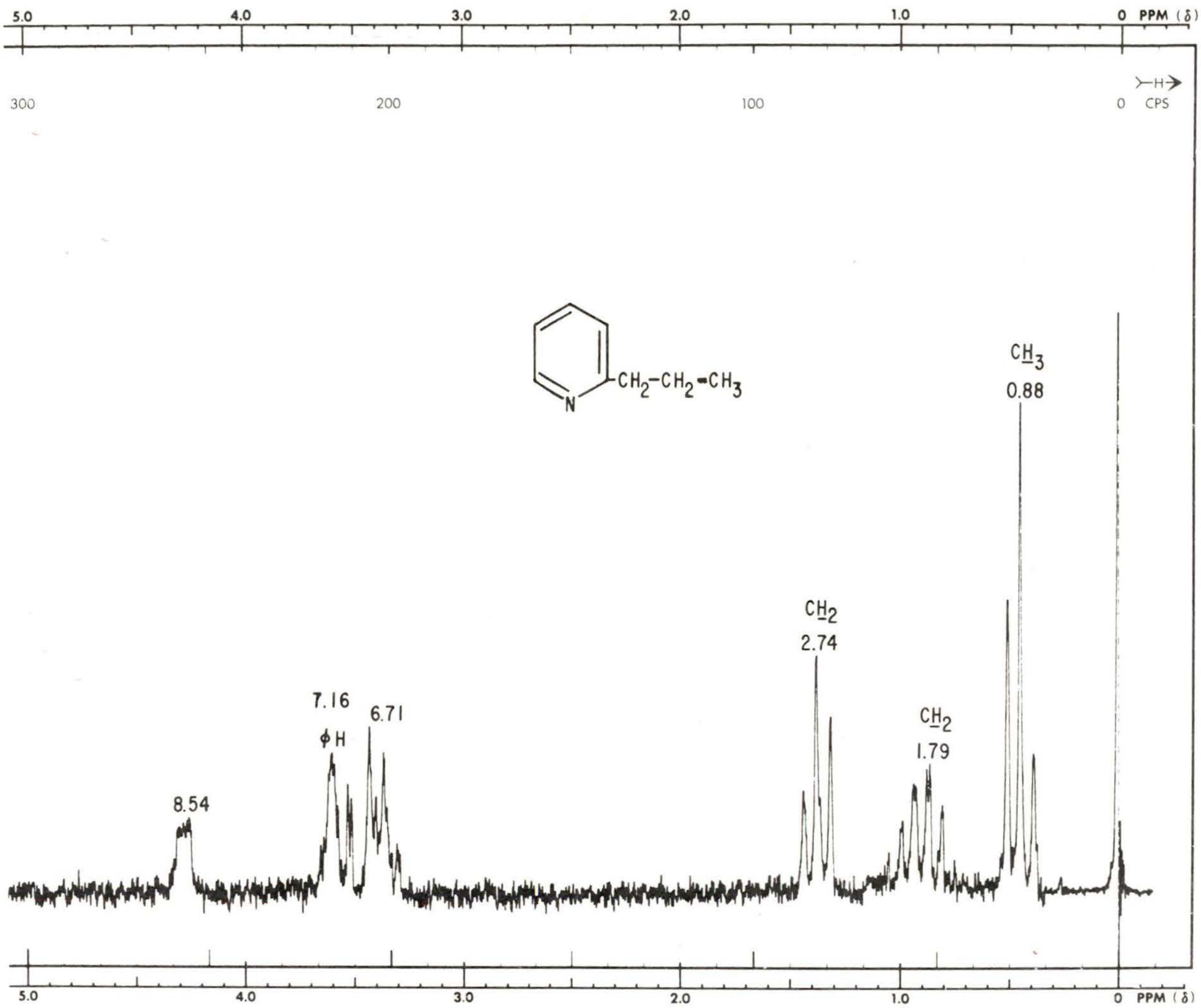

Figure A-14.—2-propylpyridine in C_6D_6.

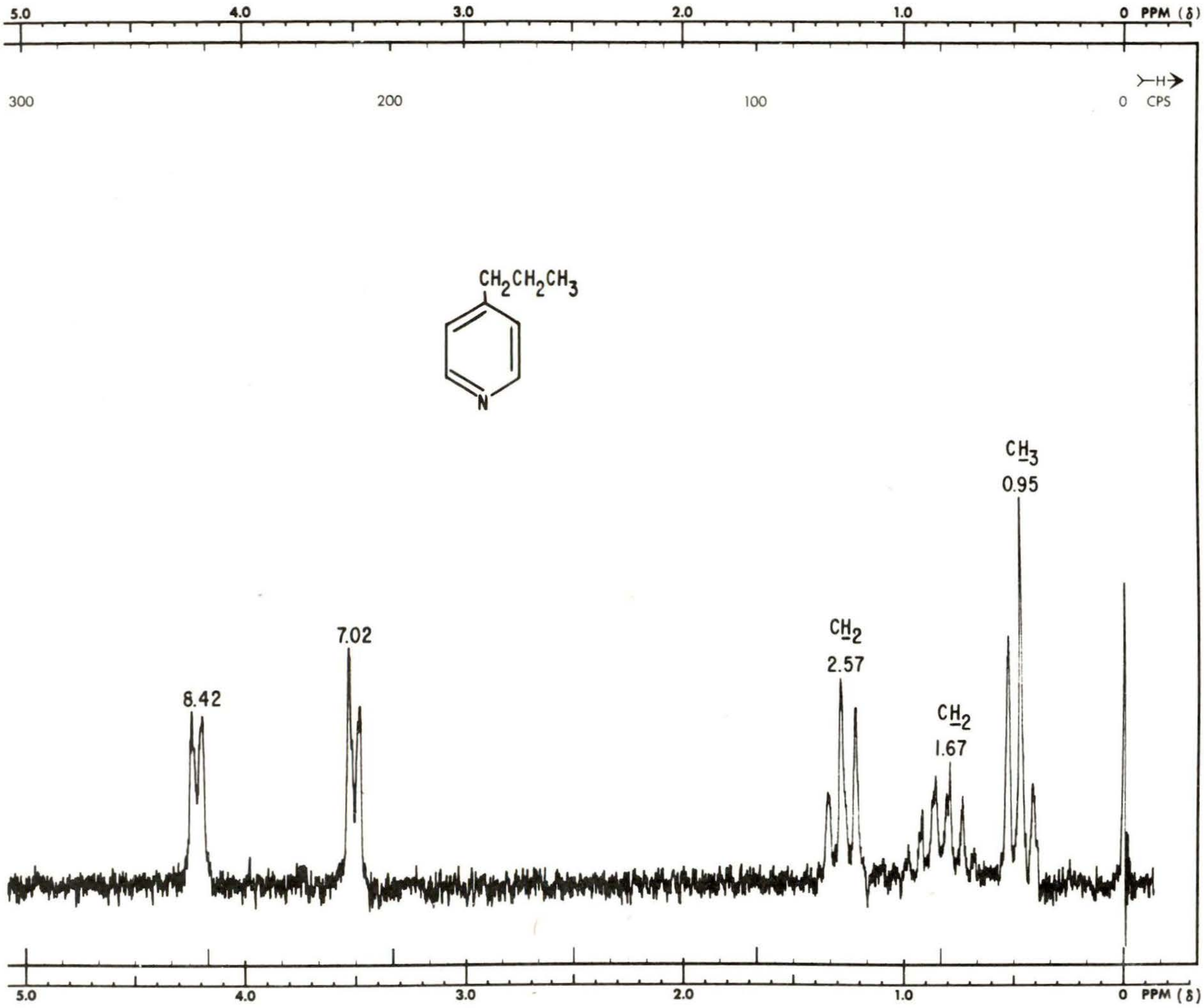

Figure A-15.—4-propylpyridine in CCl_4.

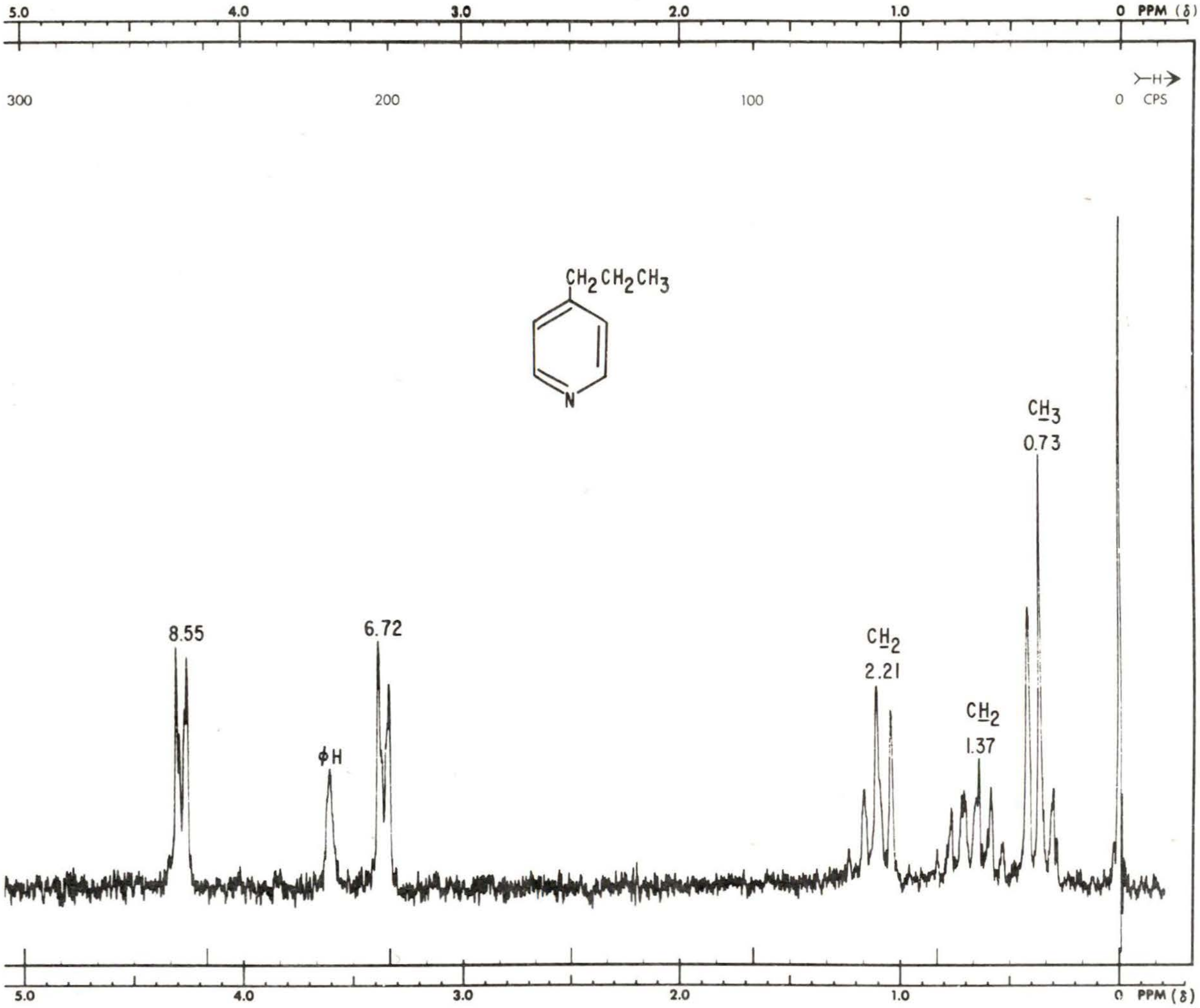

Figure A–16.—4-propylpyridine in C_6D_6.

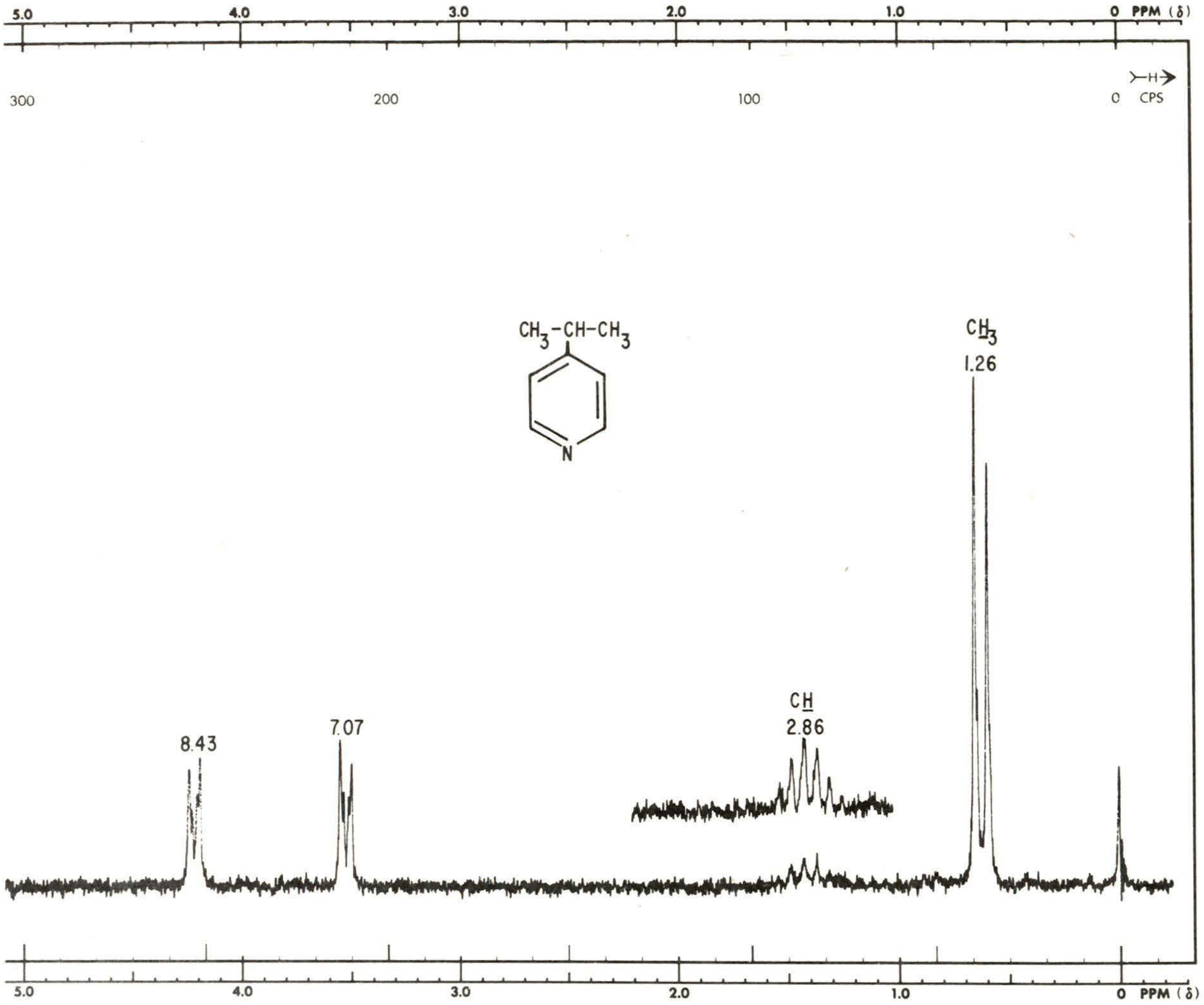

Figure A–17.—4-isopropylpyridine in CCl_4.

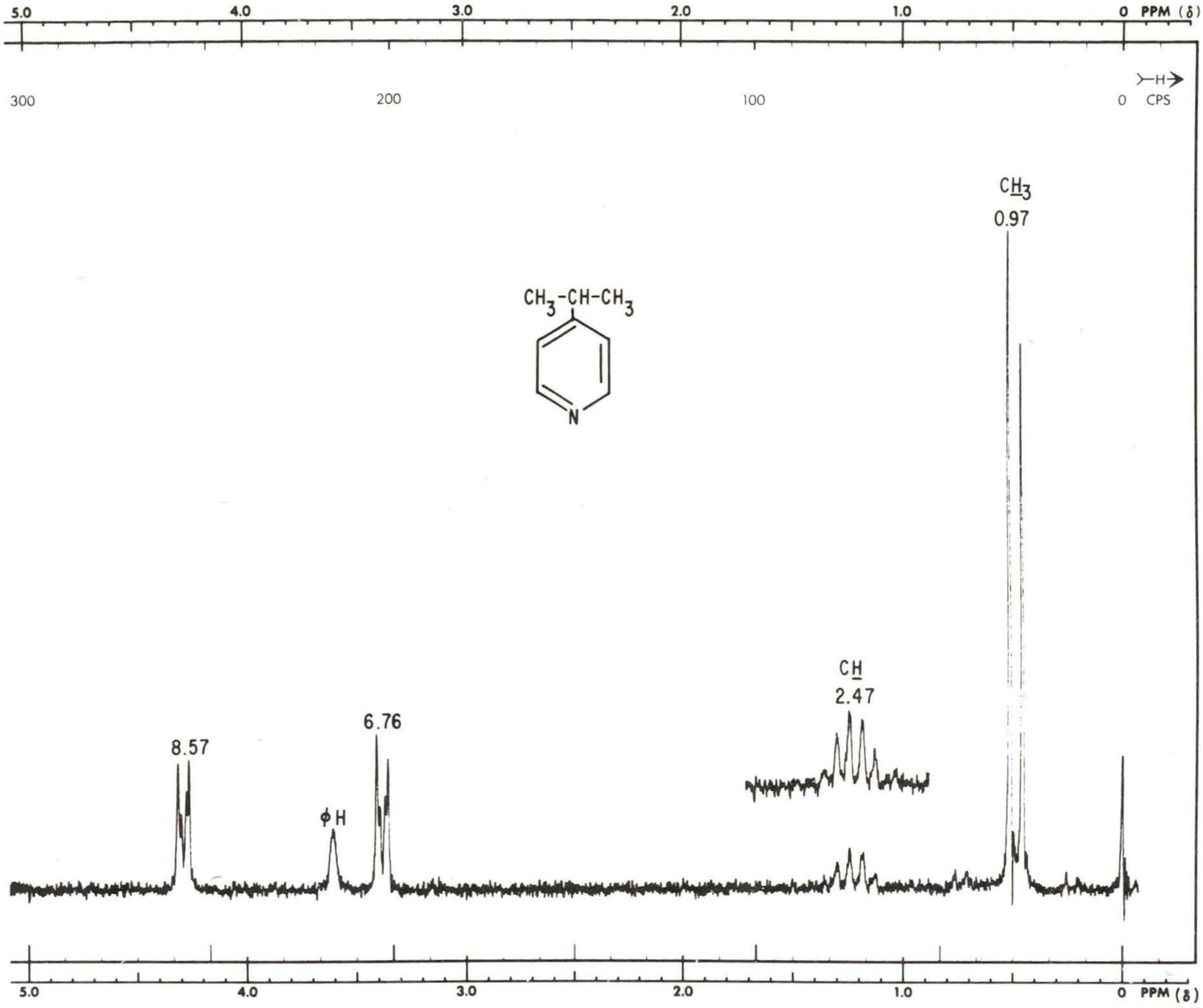

Figure A–18.—4-ispropylpyridine in C_6D_6.

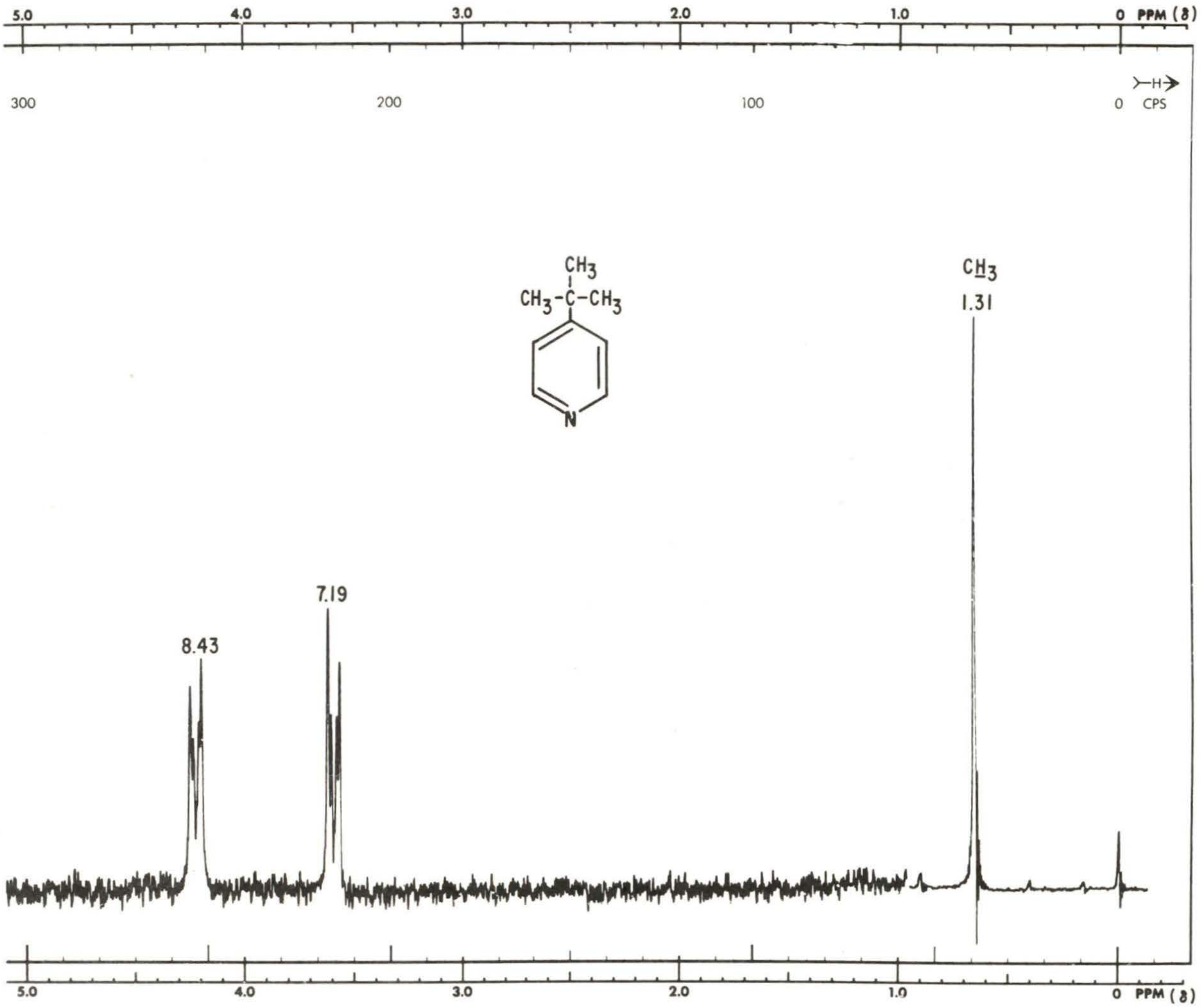

Figure A-19.—4-*t*-butylpyridine in CCl_4.

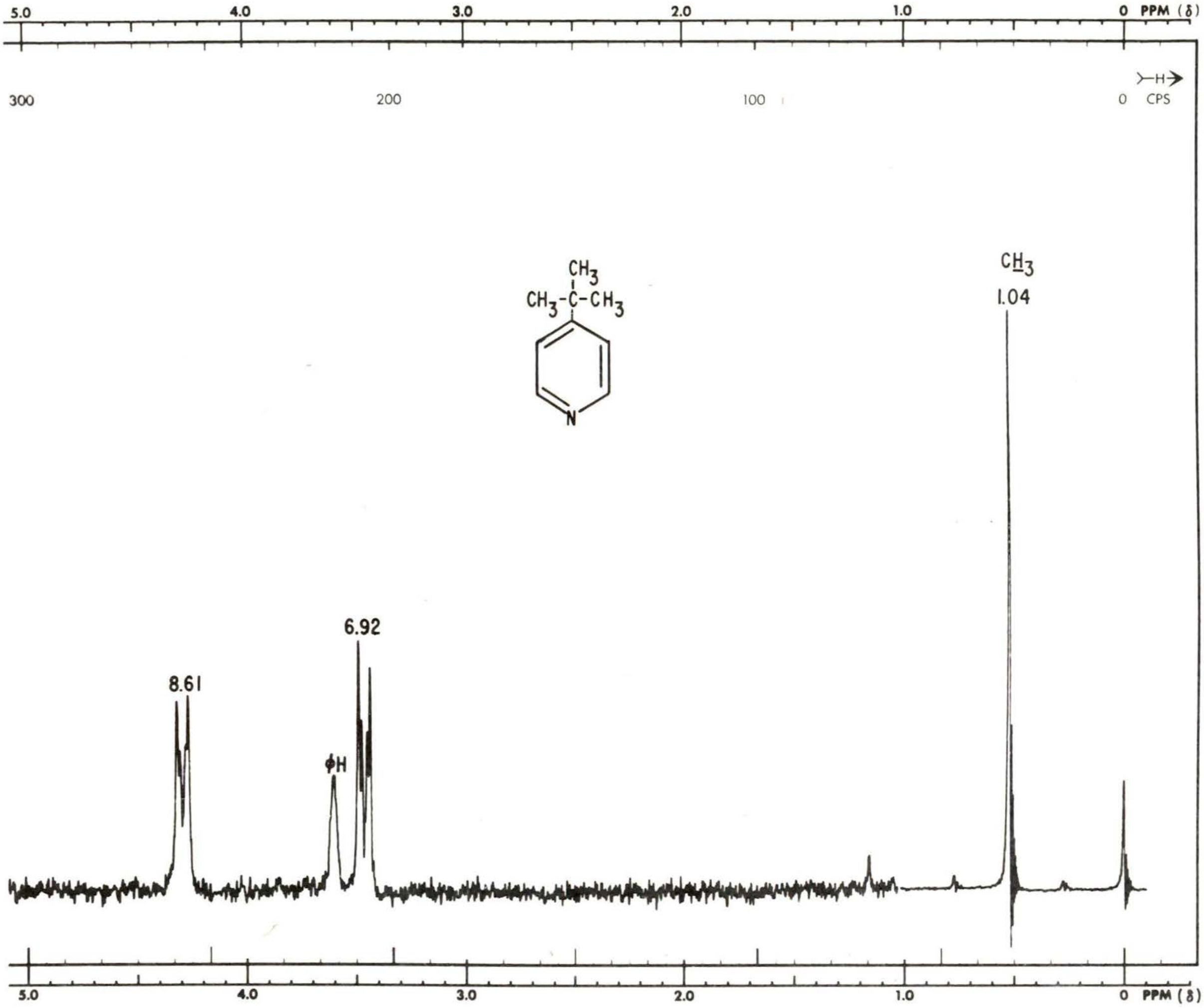

Figure A–20.—4-*t*-butylpyridine in C_6D_6.

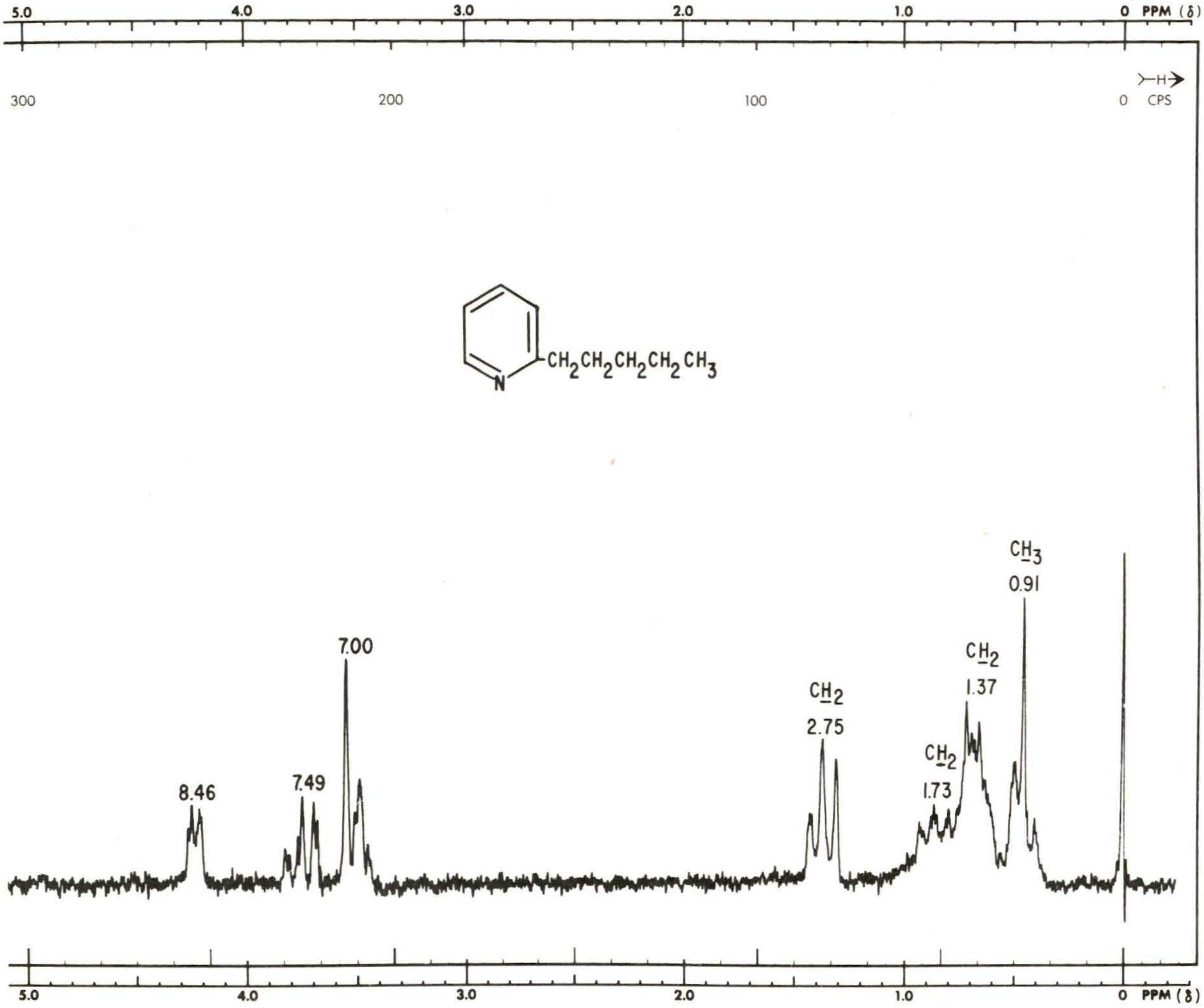

Figure A-21.—2-pentylpyridine in CCl_4.

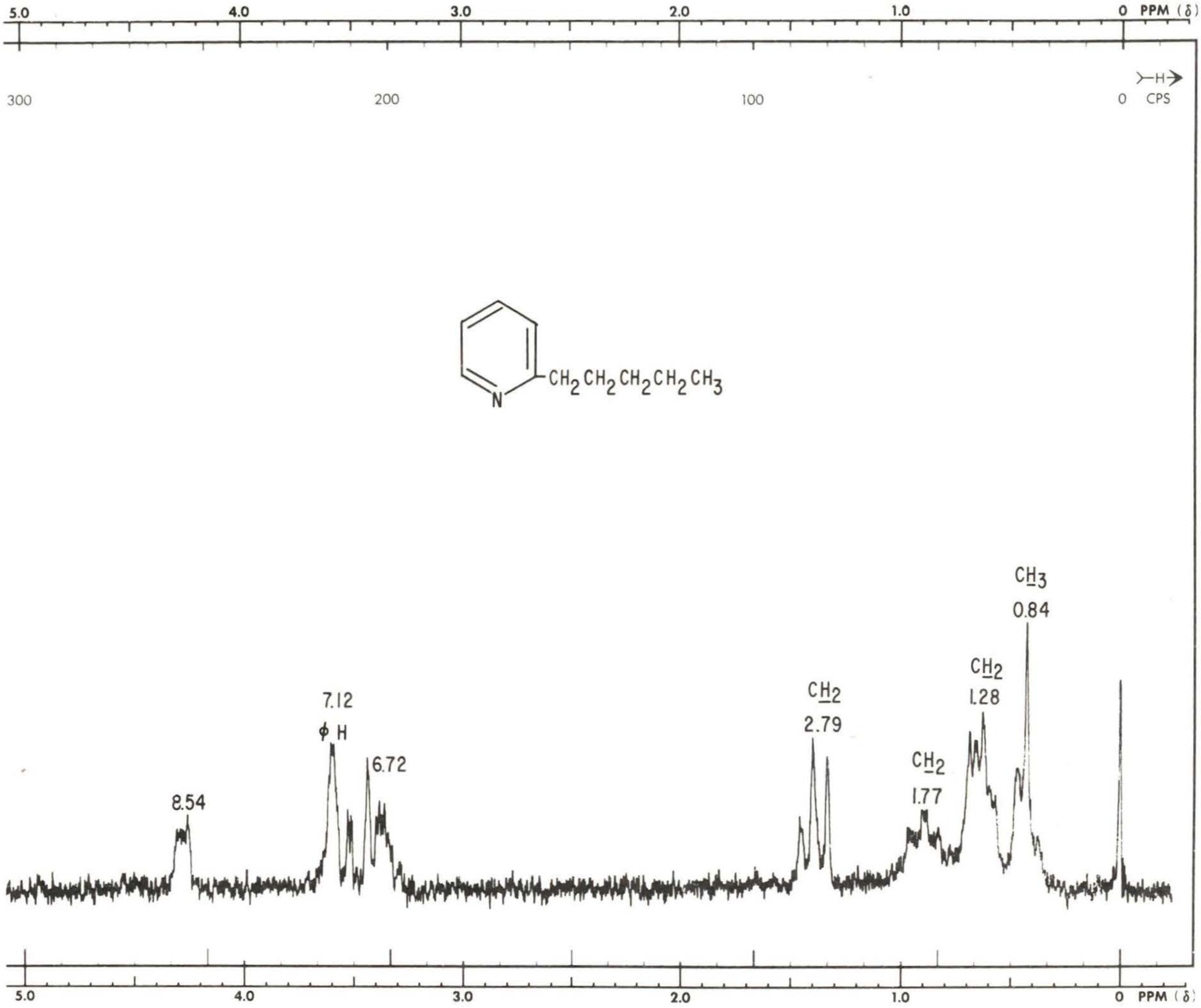

Figure A–22.—2-pentylpyridine in C_6D_6.

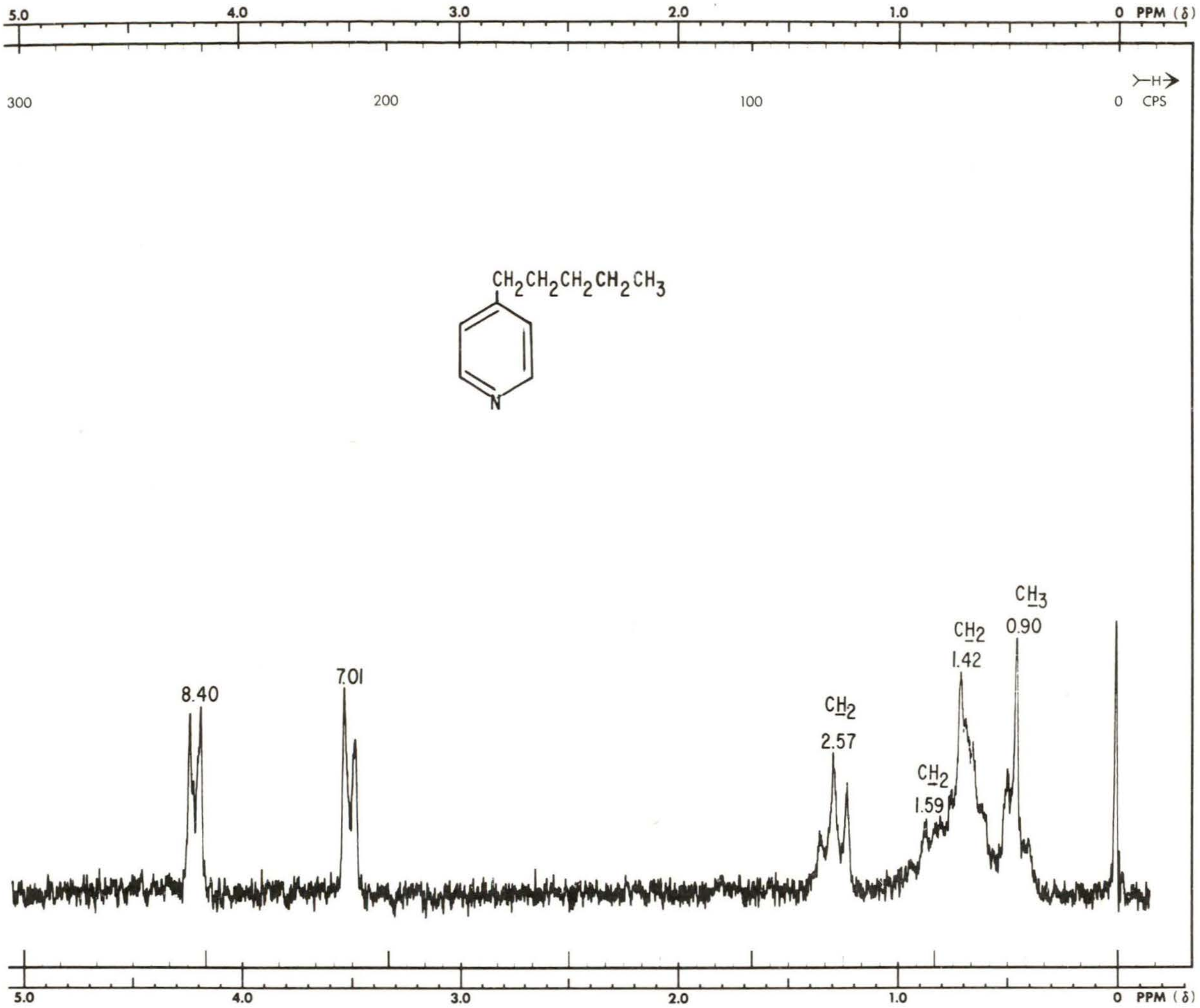

Figure A-23.—4-pentylpyridine in CCl_4.

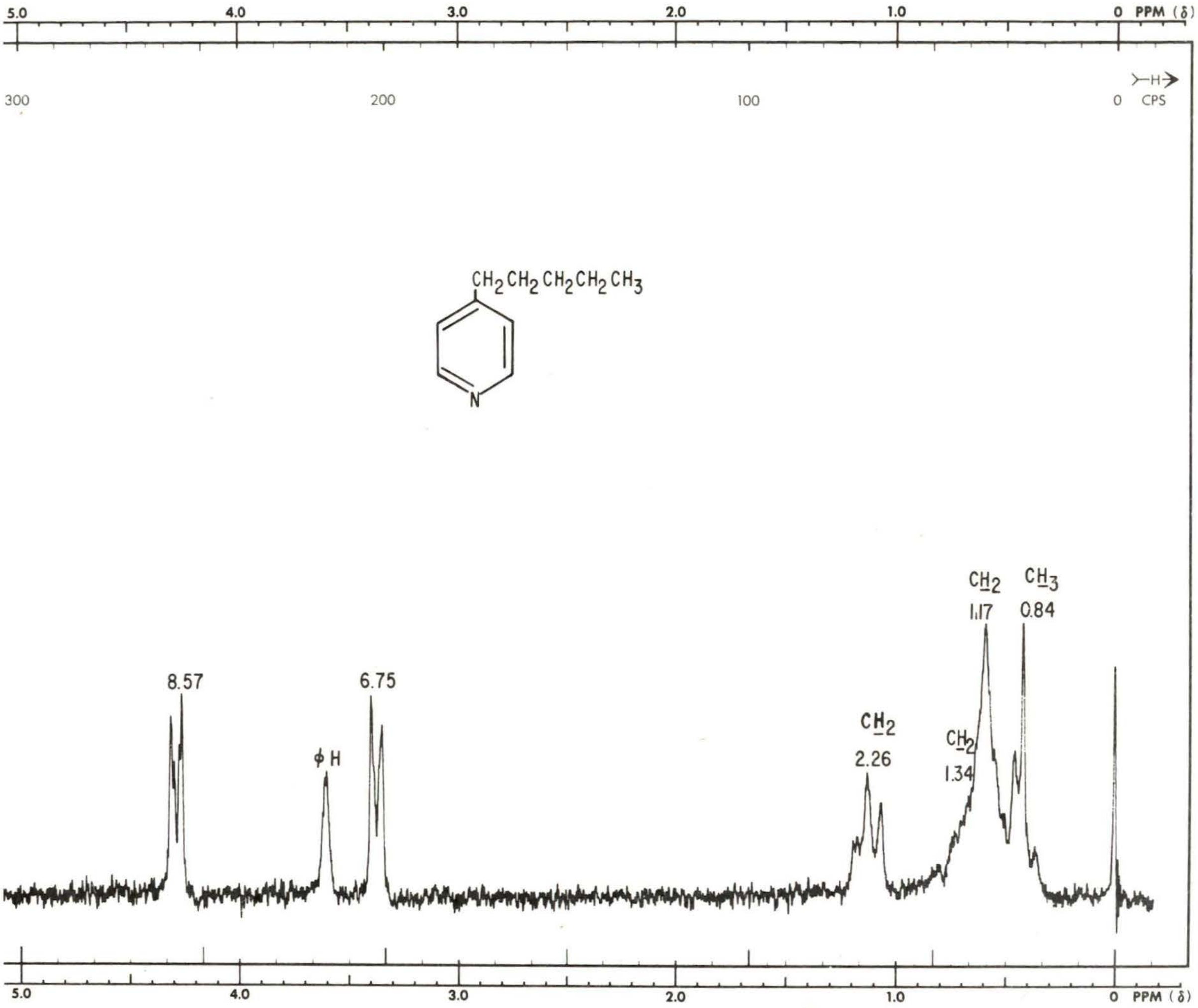

Figure A–24.—4-pentylpyridine in C_6D_6.

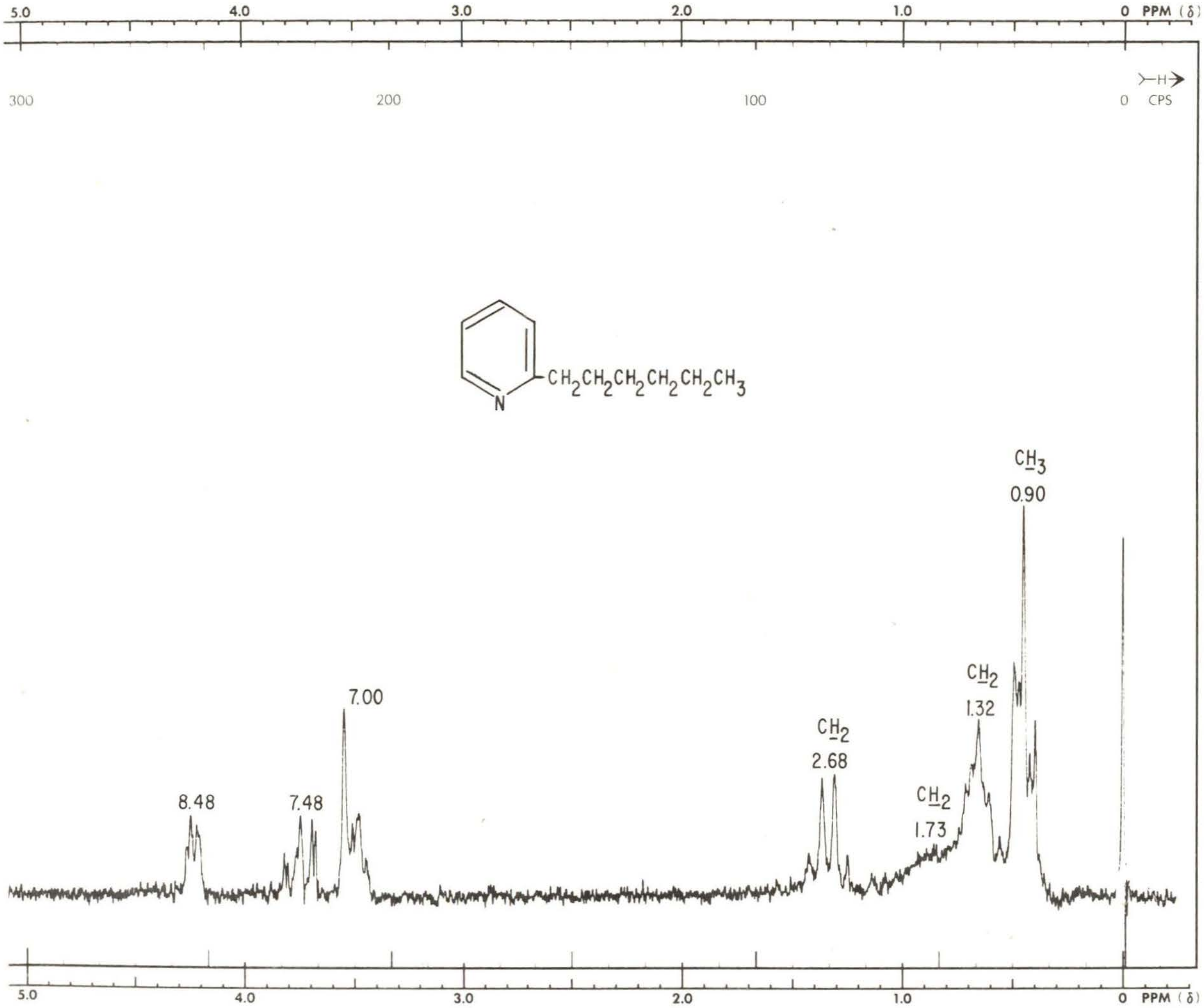

Figure A-25.—2-hexylpyridine in CCl_4.

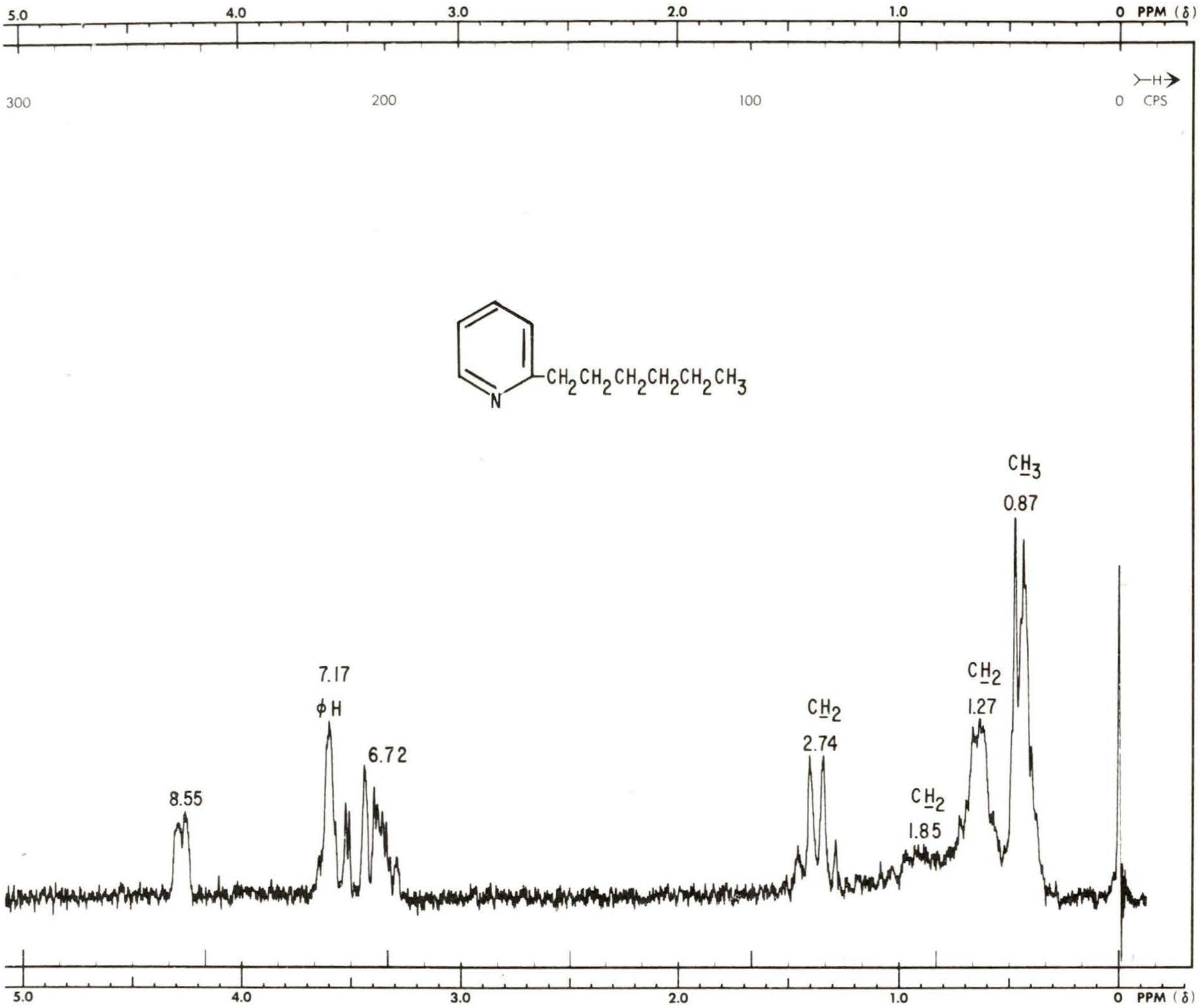

Figure A-26.—2-hexylpyridine in C_6D_6.

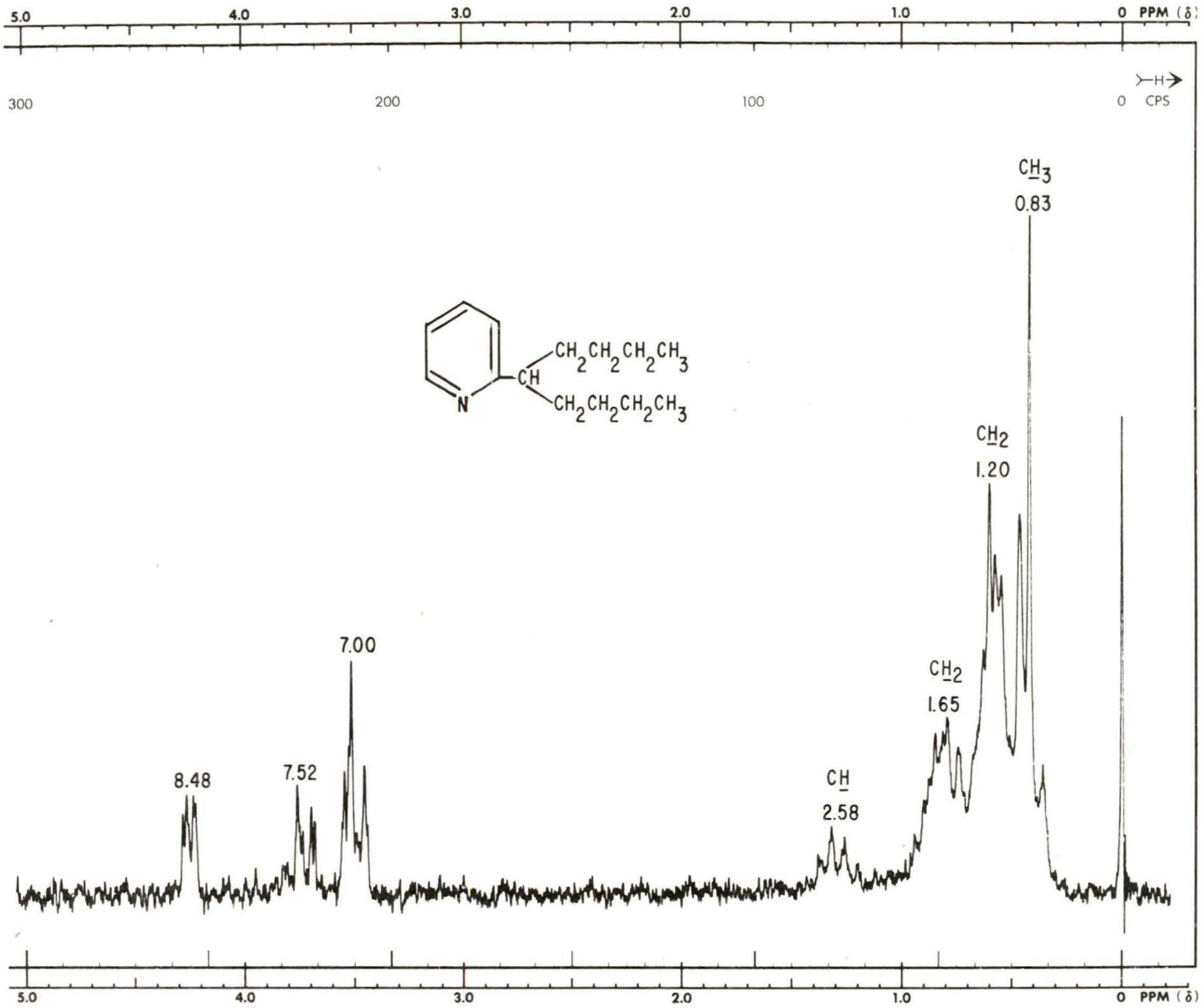

Figure A-27.—2-(5-nonyl)pyridine in CCl_4.

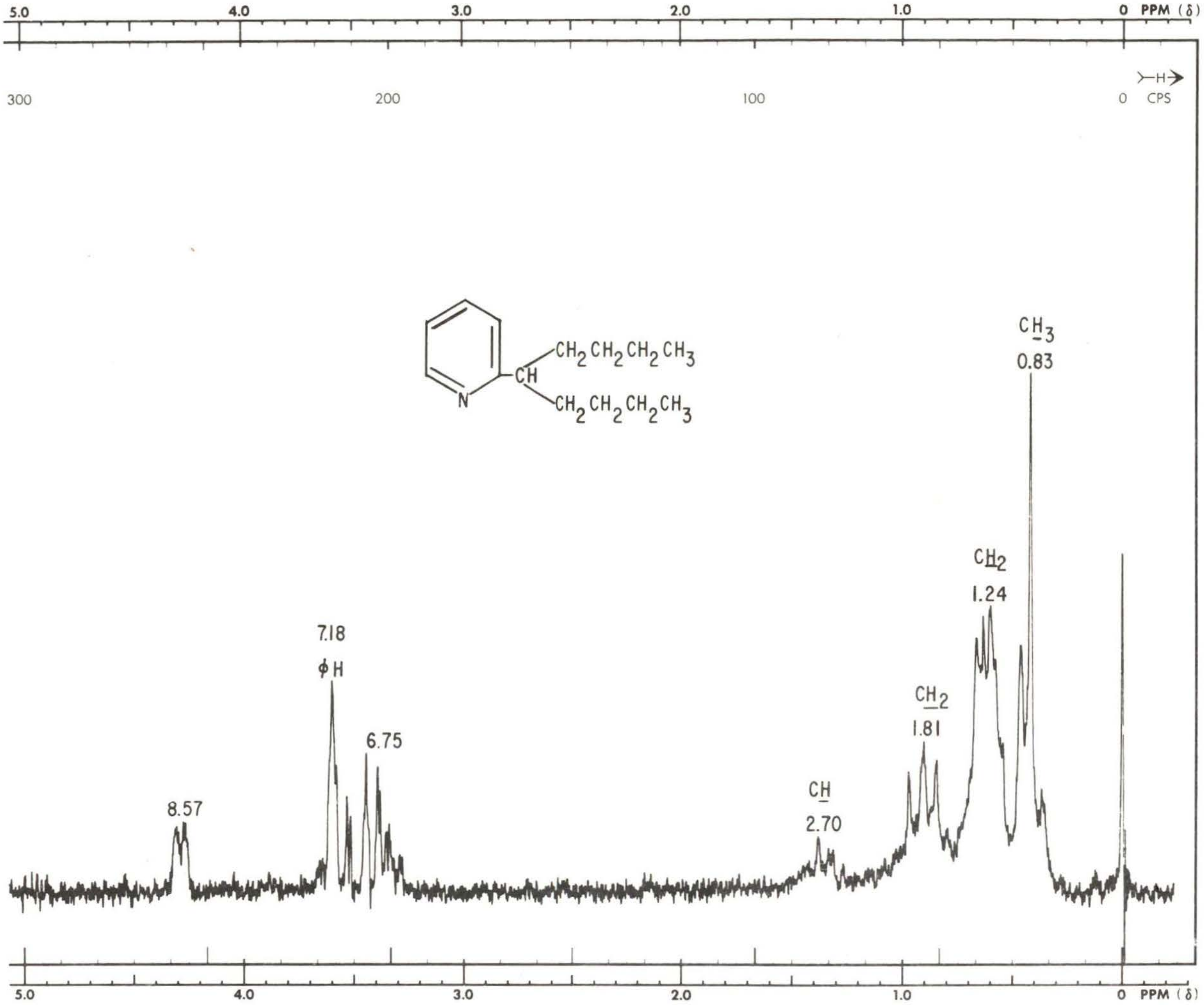

Figure A–28.—2-(5-nonyl)pyridine in C_6D_6.

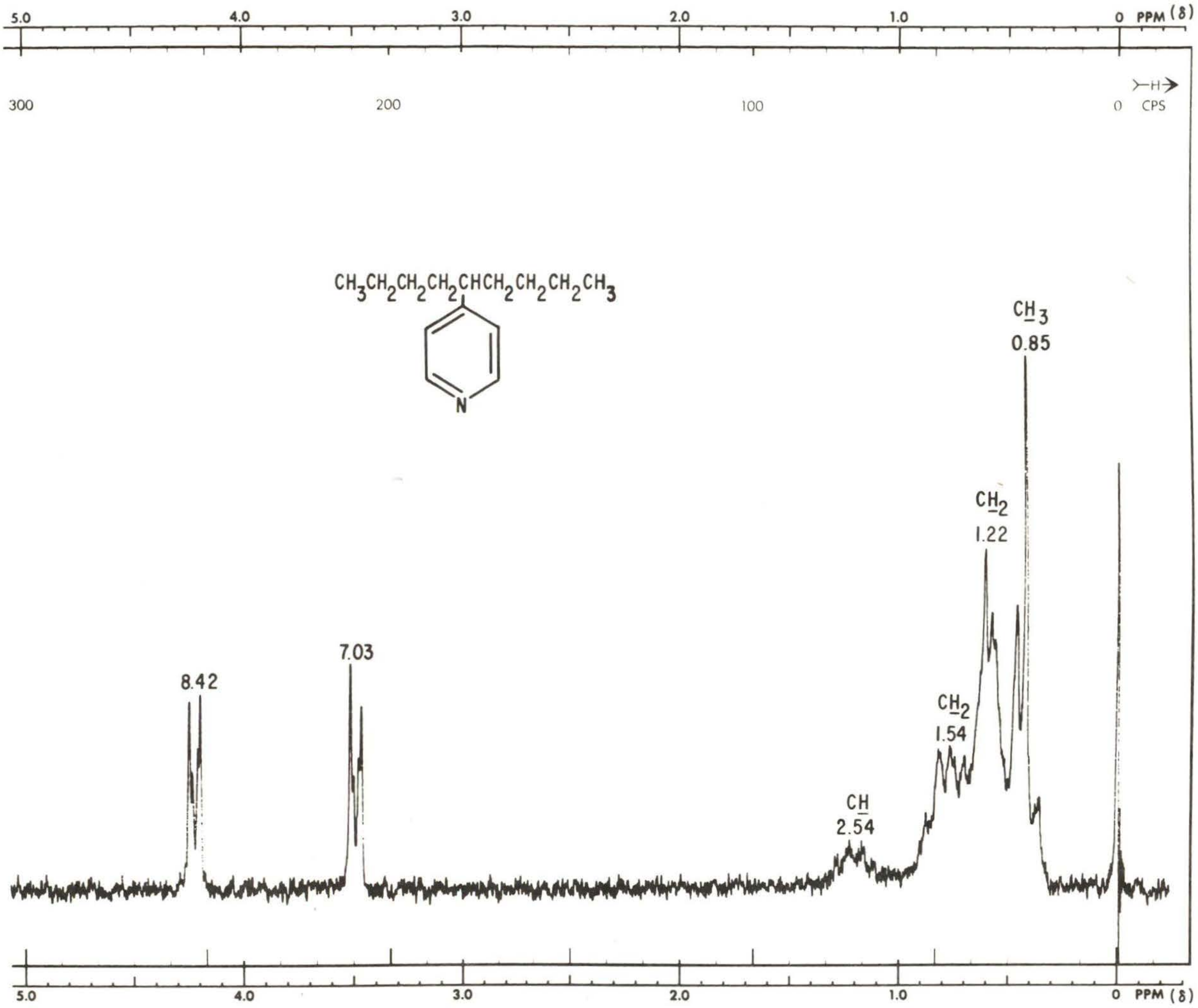

Figure A–29.—4-(5-nonyl)pyridine in CCl_4.

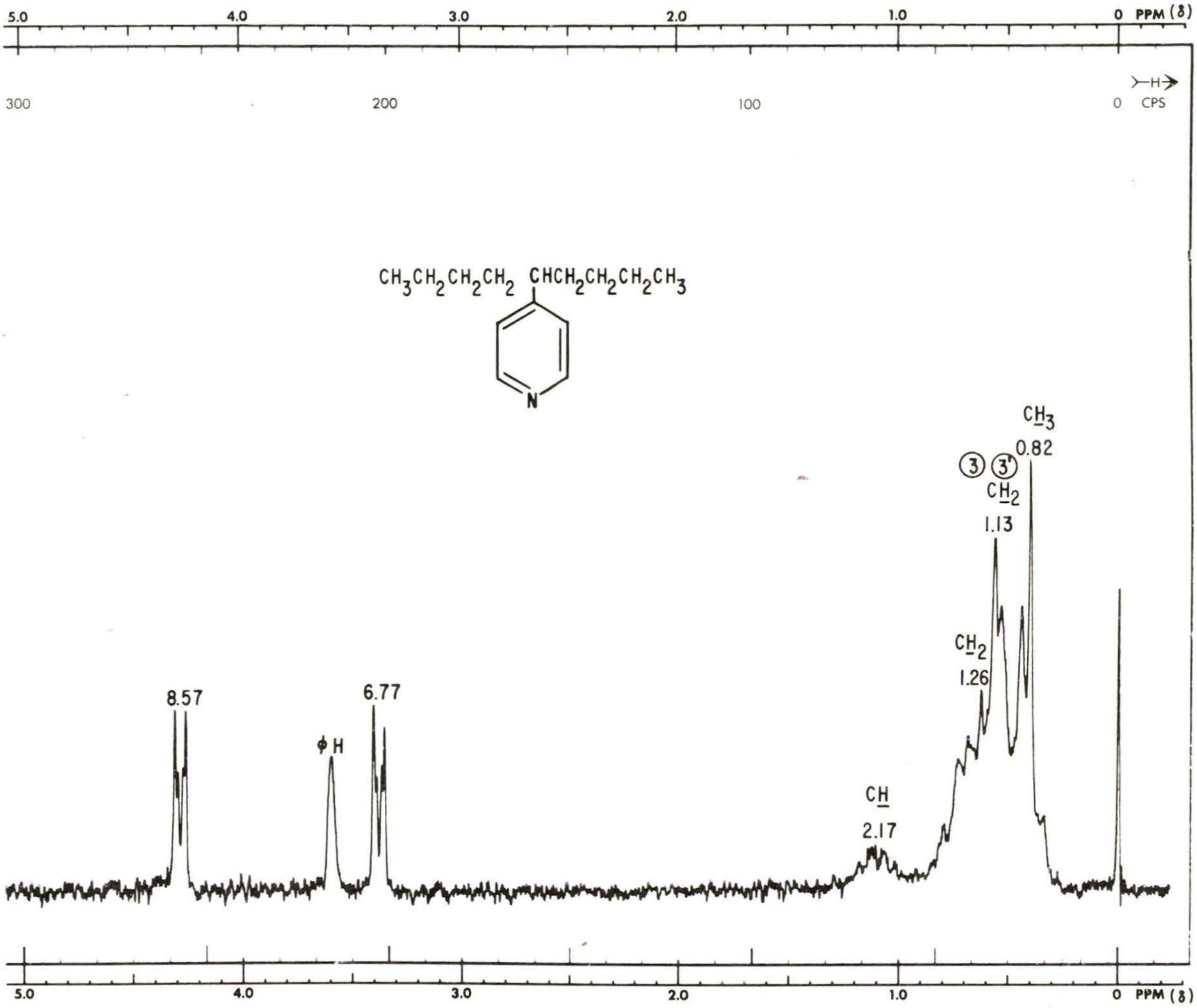

Figure A-30.—4-(5-nonyl)pyridine in C_6D_6.

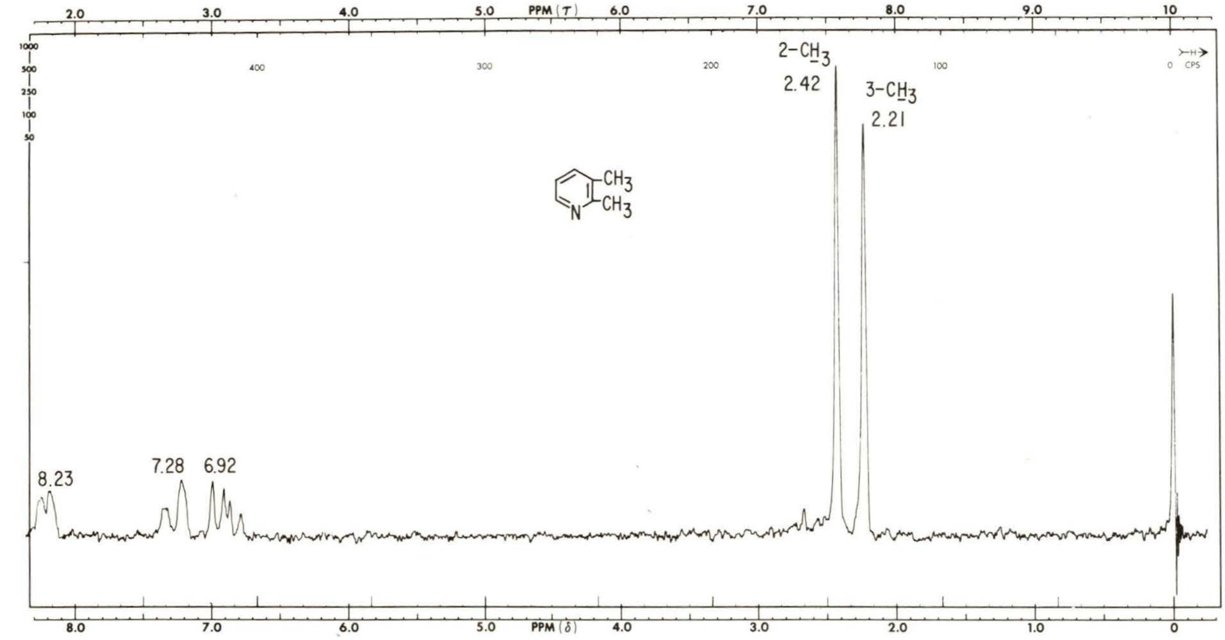

Figure A–31.—2, 3-dimethylpyridine in CCl_4.

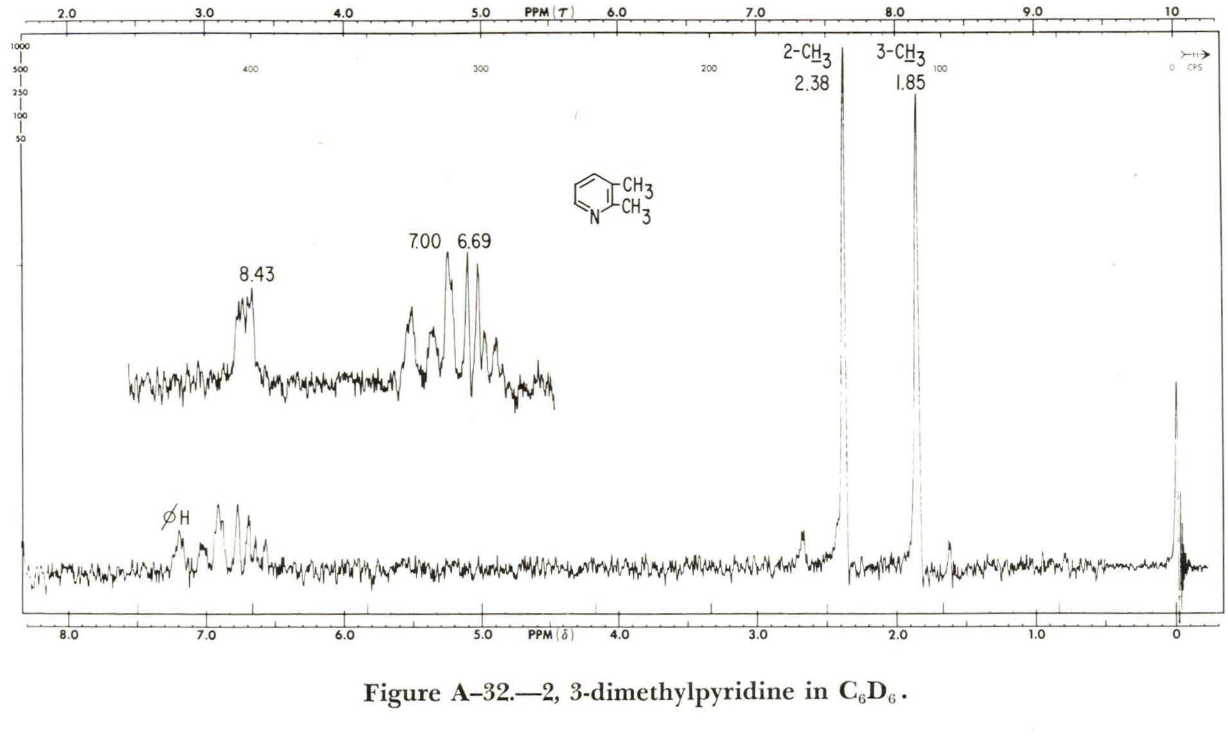

Figure A–32.—2, 3-dimethylpyridine in C_6D_6.

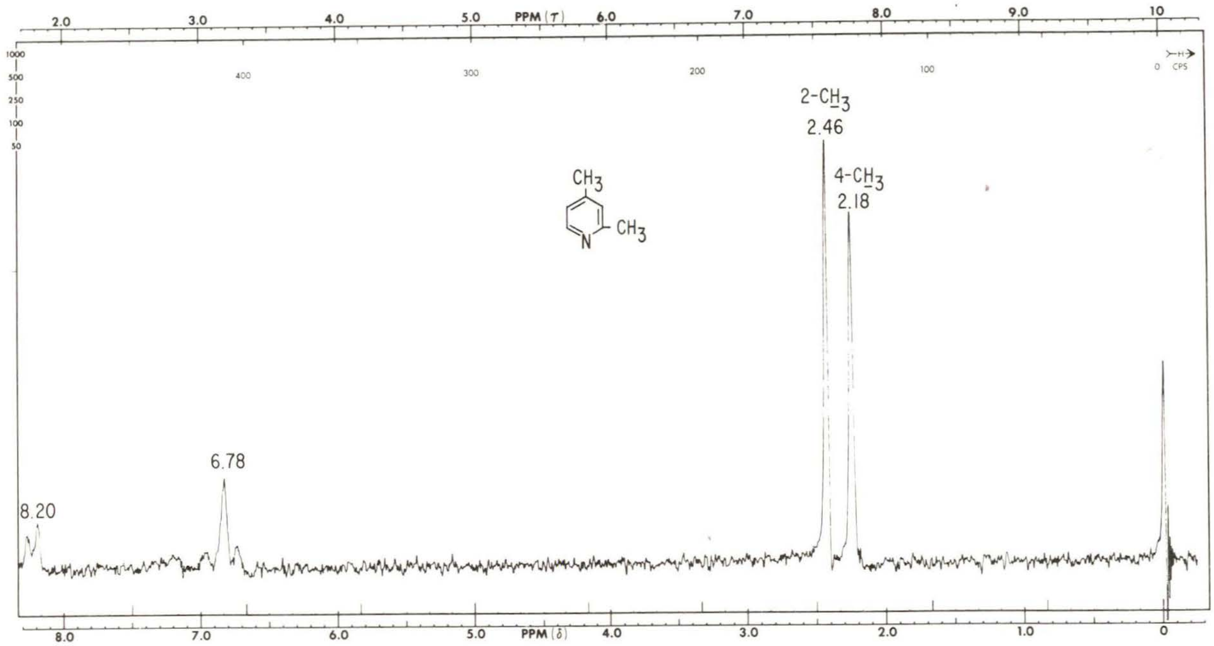

Figure A–33.—2, 4-dimethylpyridine in CCl_4.

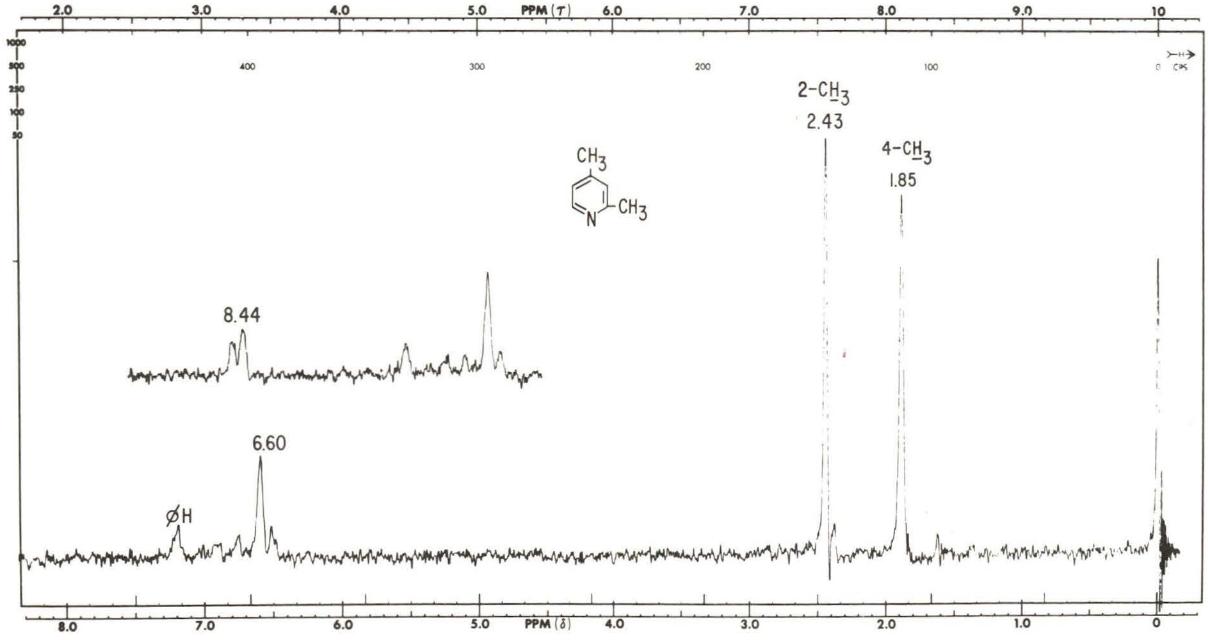

Figure A–34.—2, 4-dimethylpyridine in C_6D_6.

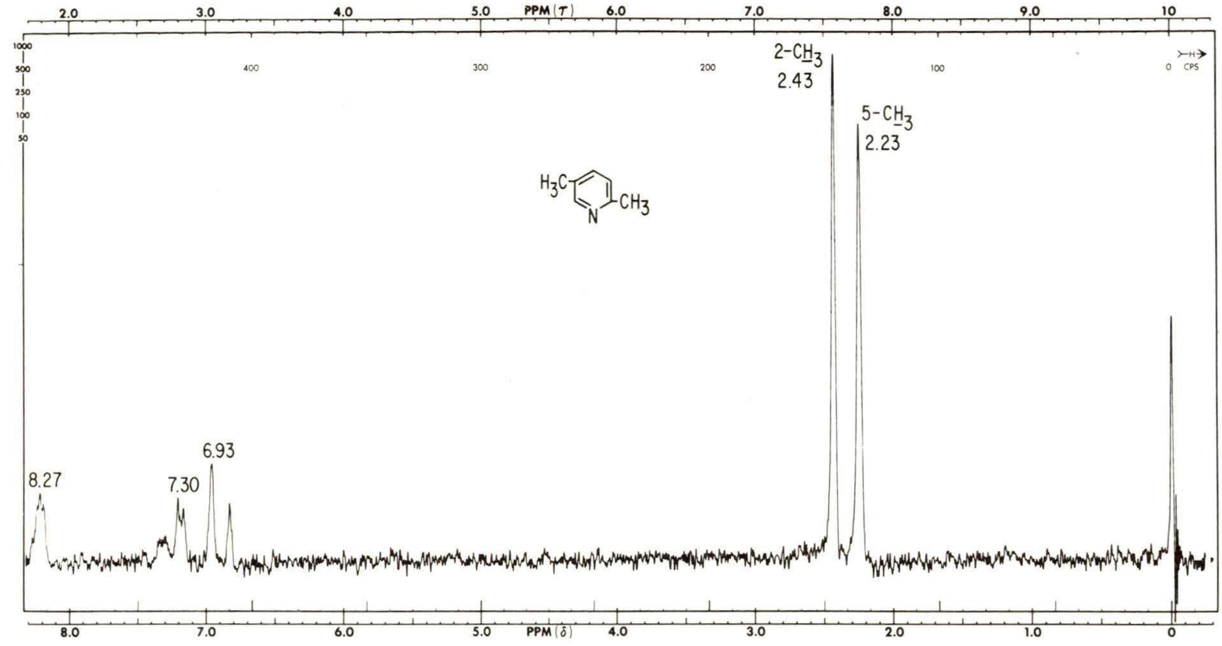

Figure A-35.—2, 5-dimethylpyridine in CCl_4.

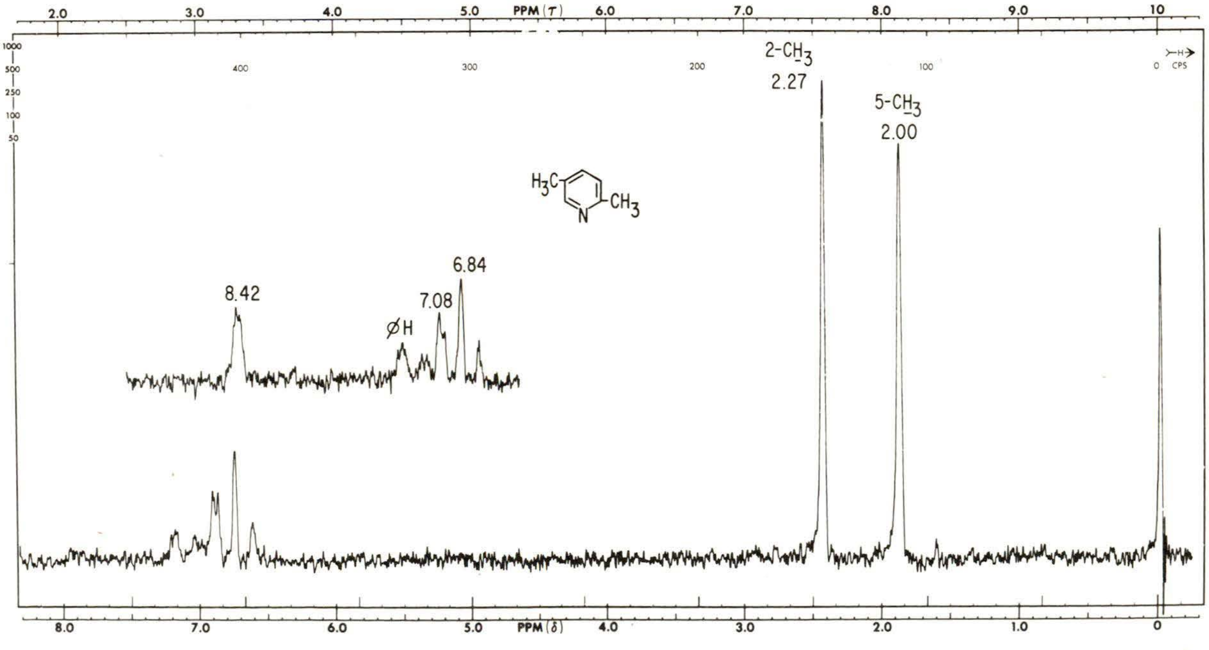

Figure A-36.—2, 5-dimethylpyridine in C_6D_6.

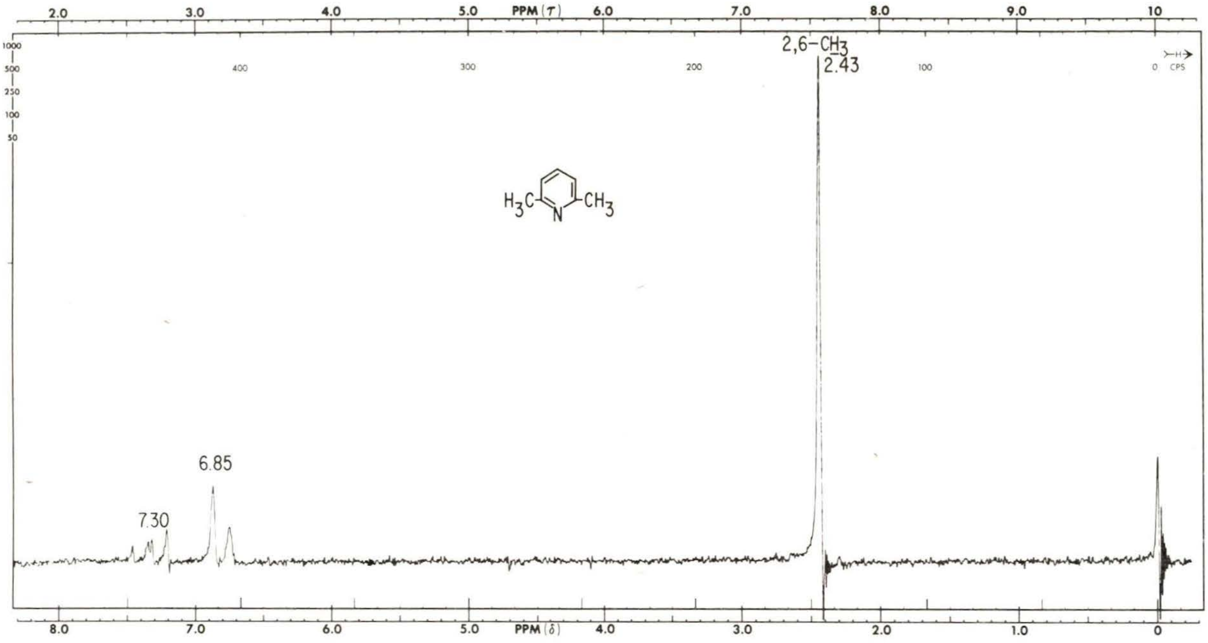

Figure A–37.—2, 6-dimethylpyridine in CCl_4.

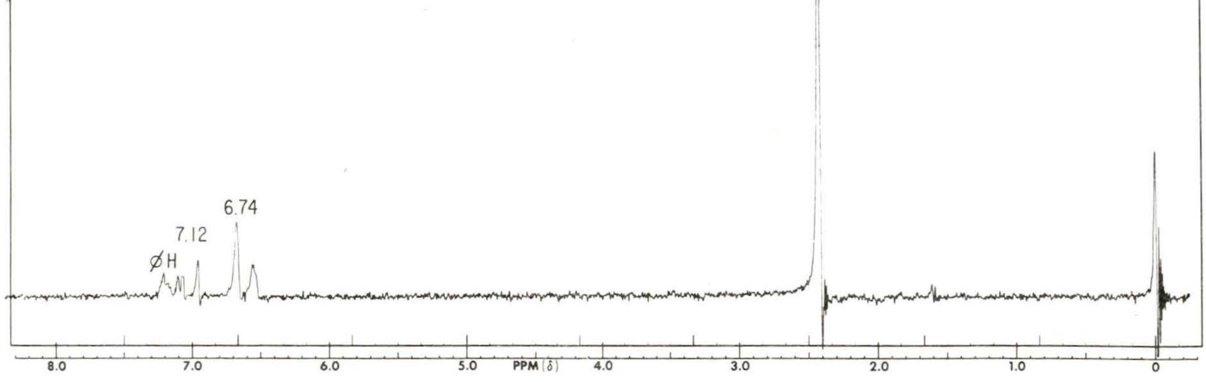

Figure A–38.—2, 6-dimethylpyridine in C_6D_6.

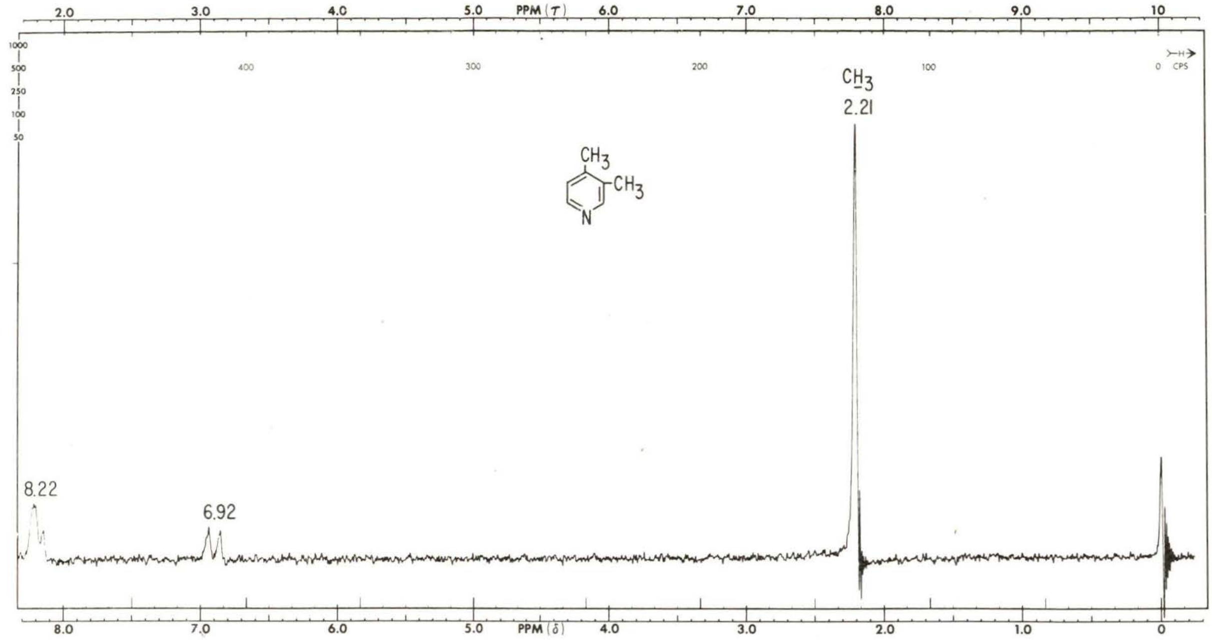

Figure A-39.—3, 4-dimethylpyridine in CCl_4.

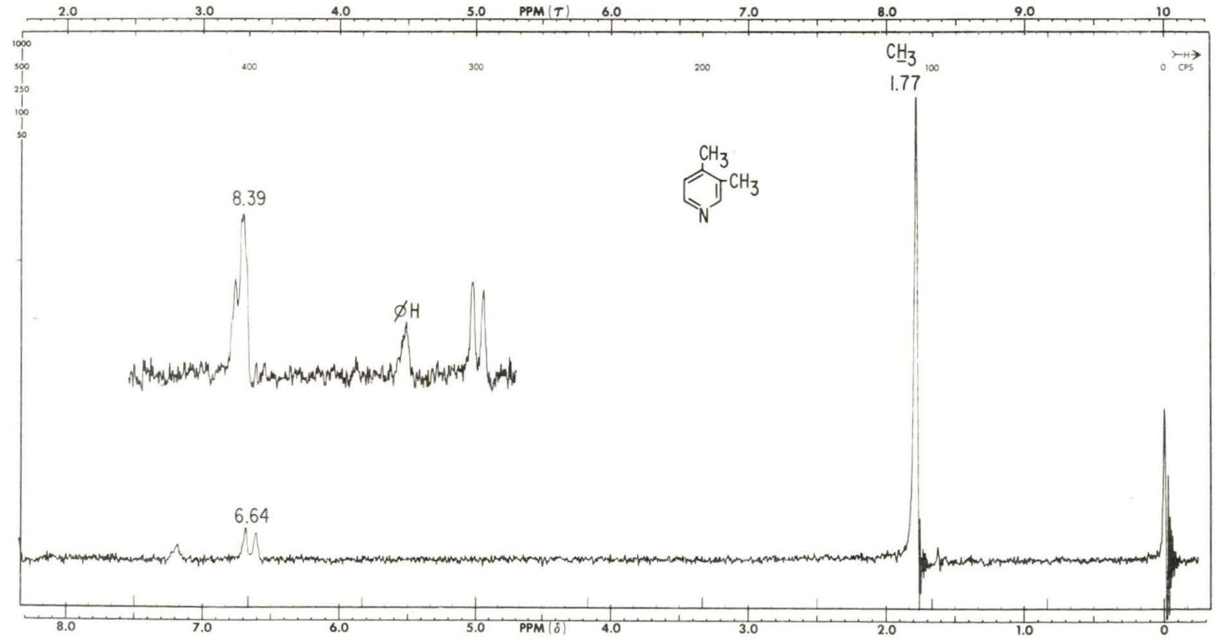

Figure A-40.—3, 4-dimethylpyridine in C_6D_6.

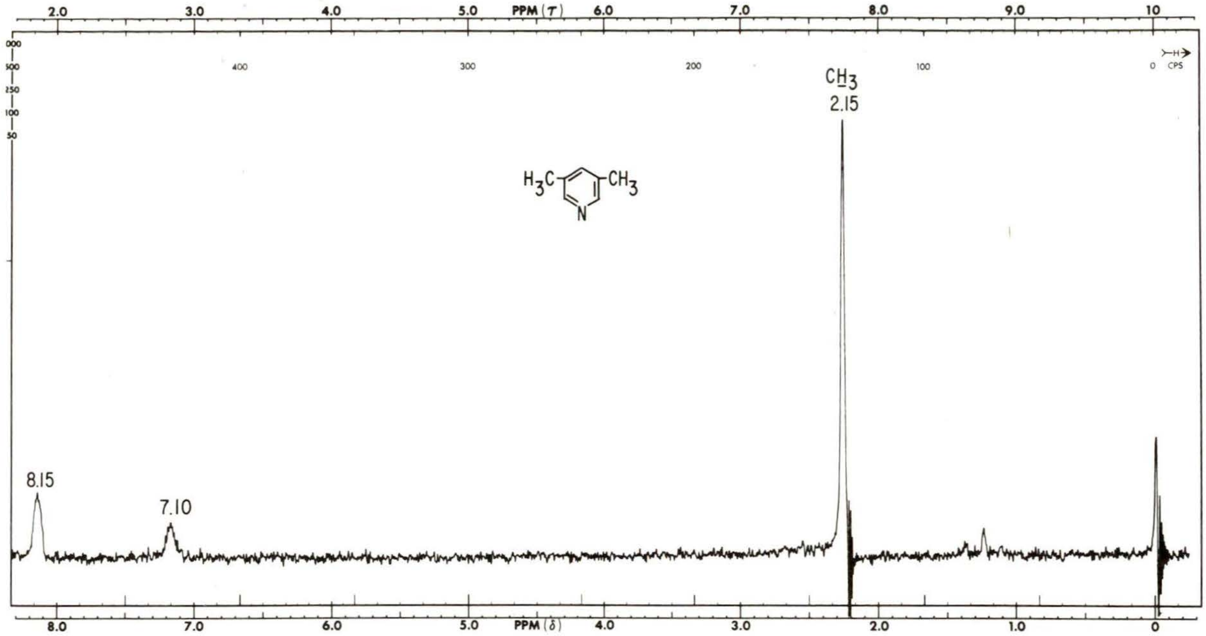

Figure A–41.—3, 5-dimethylpyridine in CCl_4.

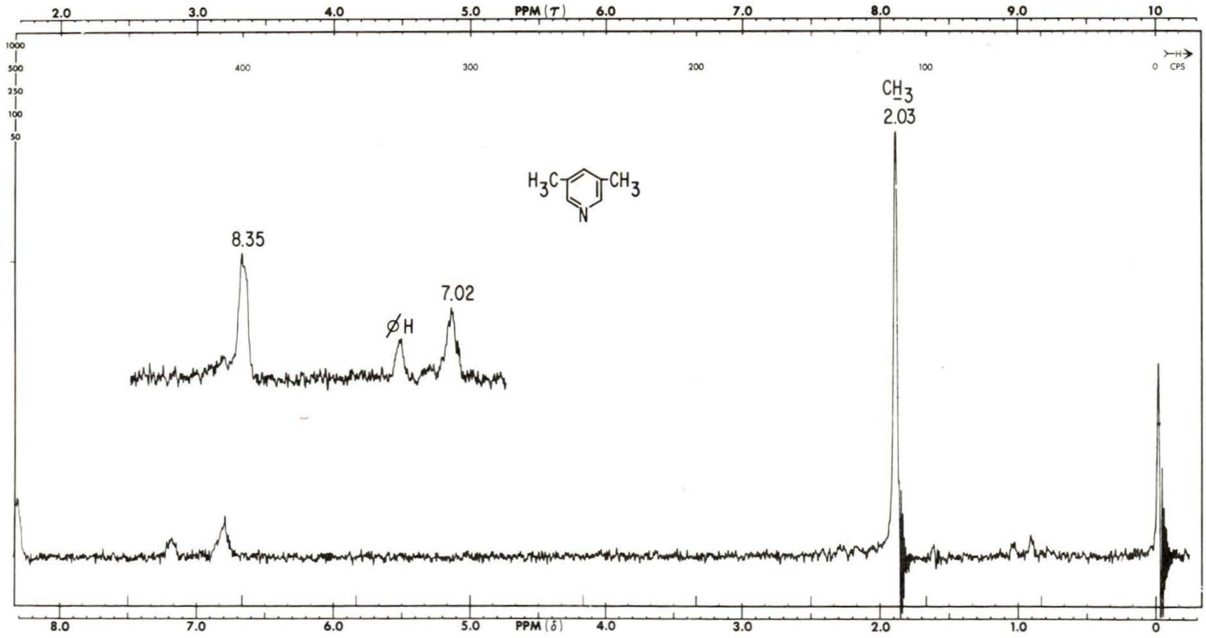

Figure A–42.—3, 5-dimethylpyridine in C_6D_6.

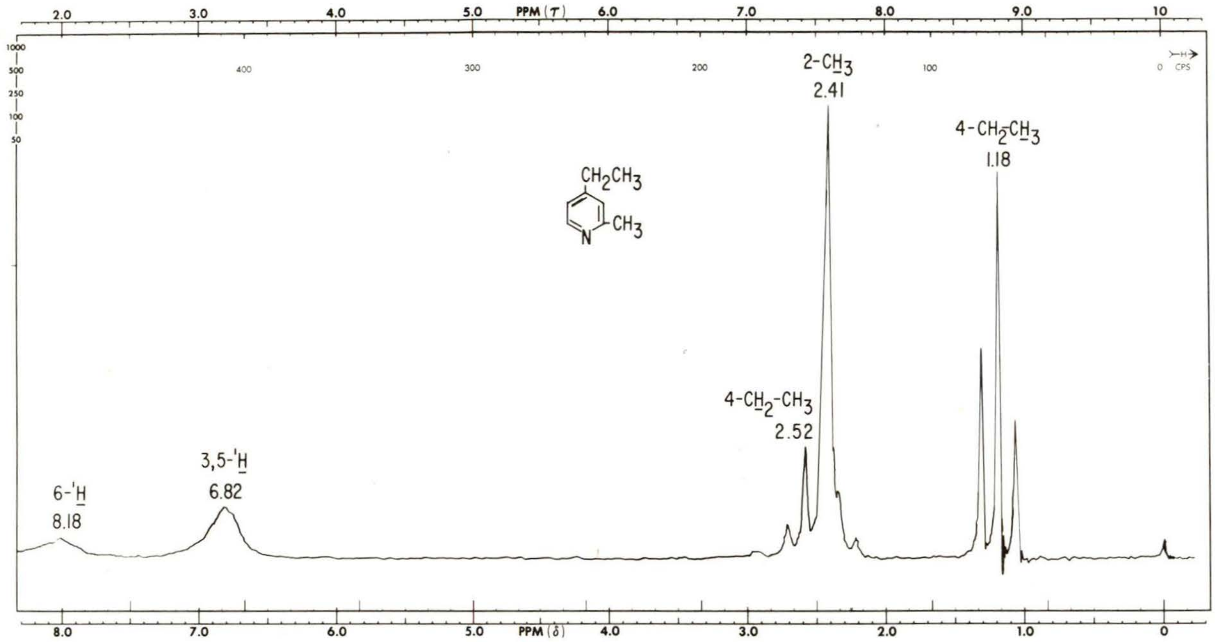

Figure A–43.—2-methyl-4-ethylpyridine in CCl_4.

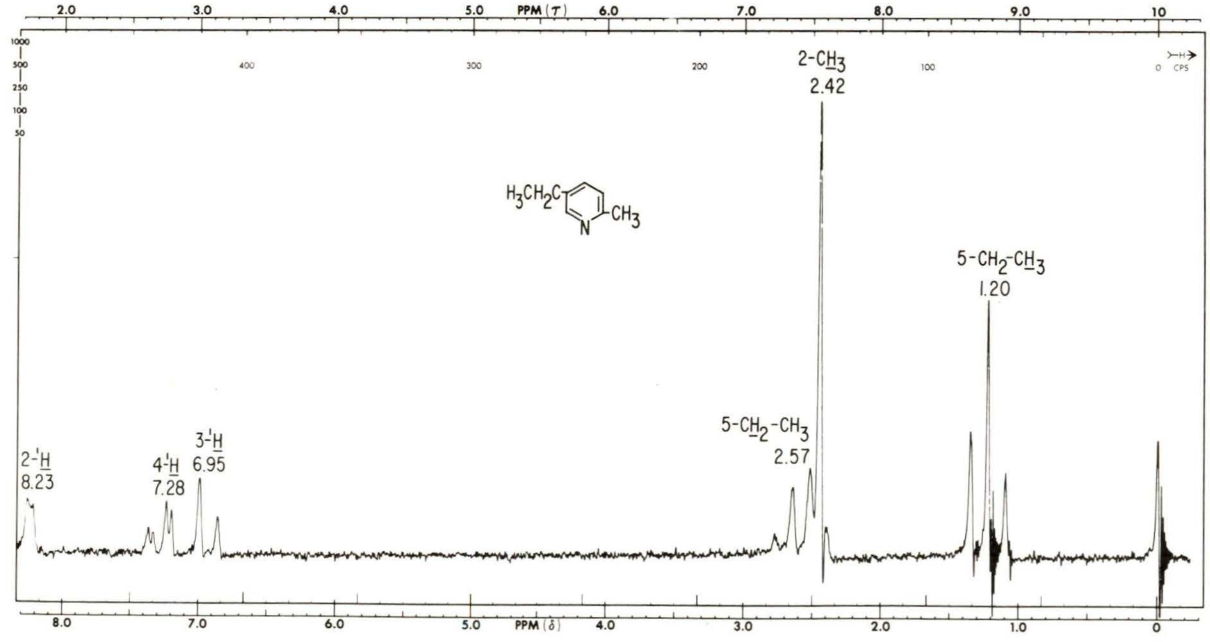

Figure A–44.—2-methyl-5-ethylpyridine in CCl_4.

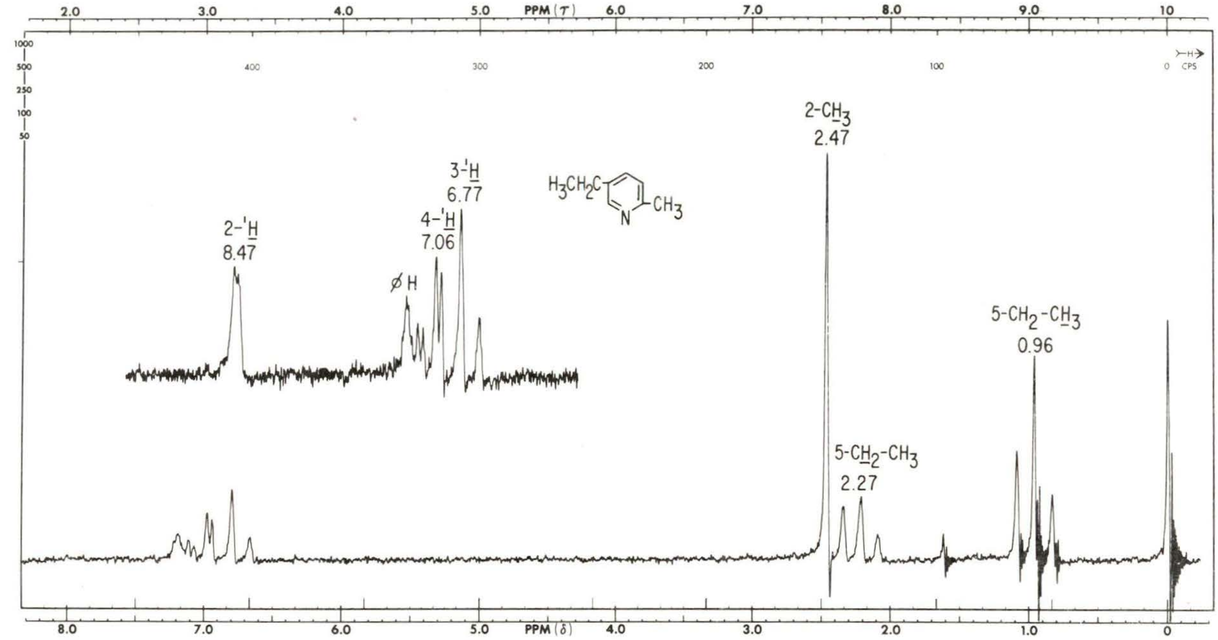

Figure A–45.—2-methyl-5-ethylpyridine in C_6D_6.

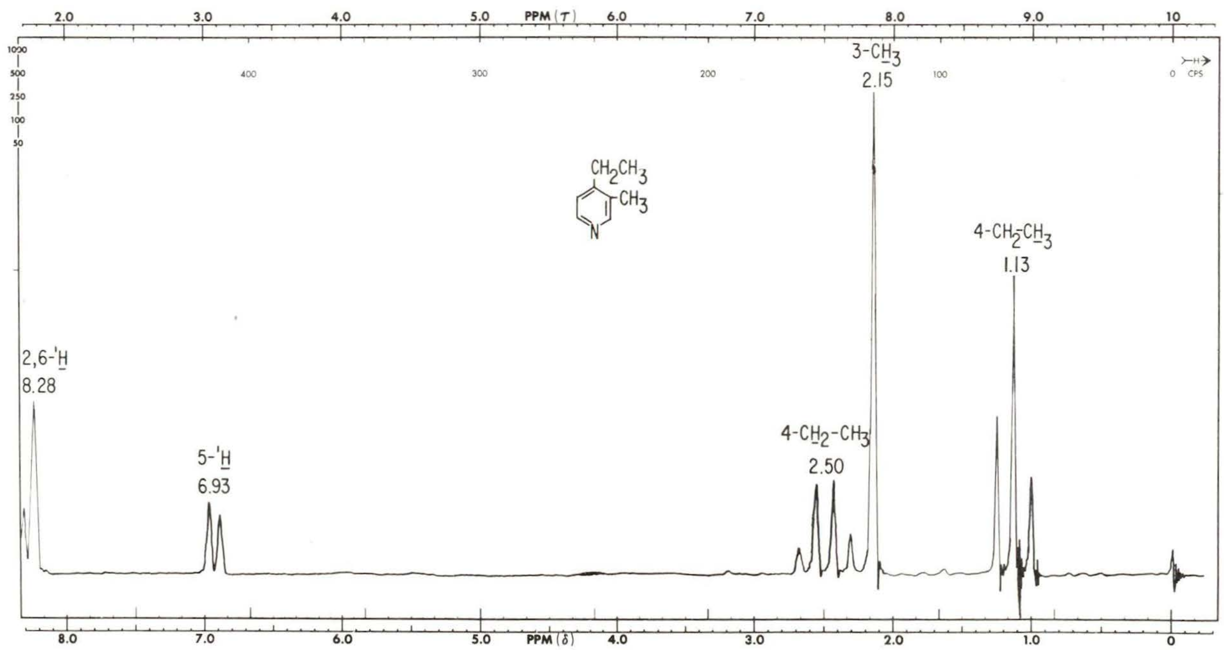

Figure A–46.—3-methyl-4-ethylpyridine in CCl_4.

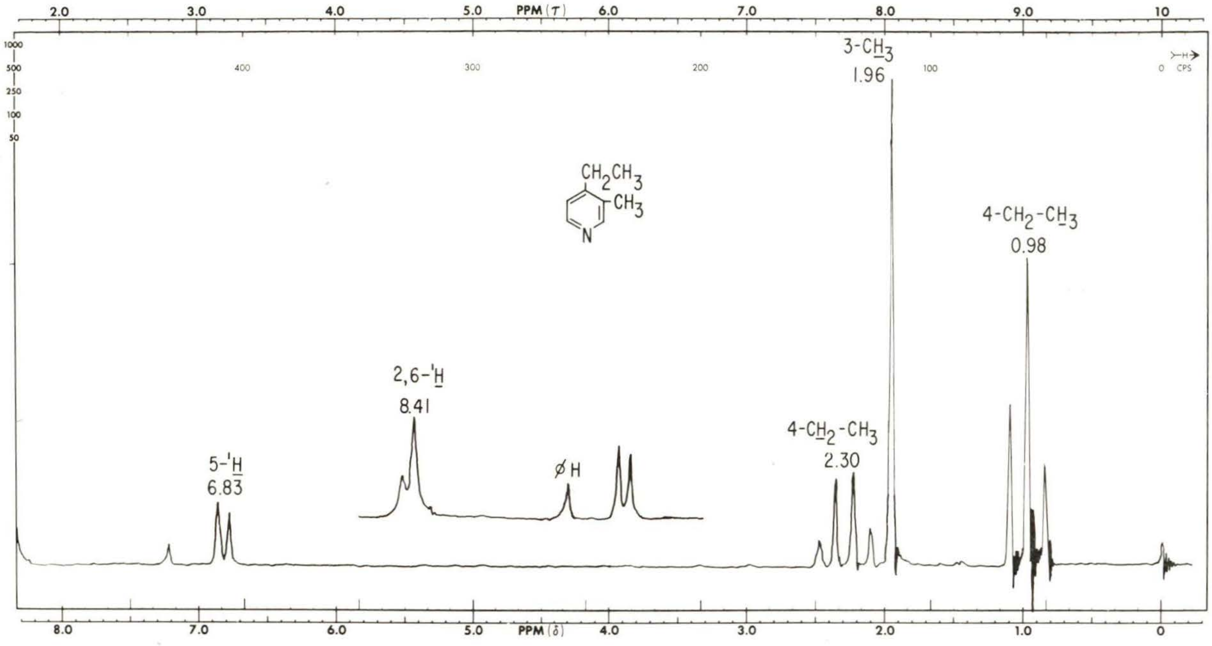

Figure A–47.—3-methyl-4-ethylpyridine in C_6D_6.

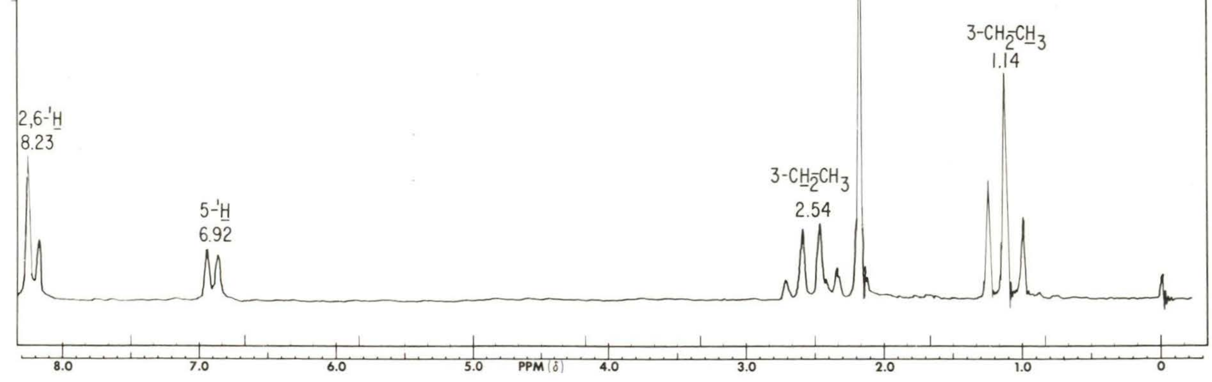

Figure A–48.—3-ethyl-4-methylpyridine in CCl_4.

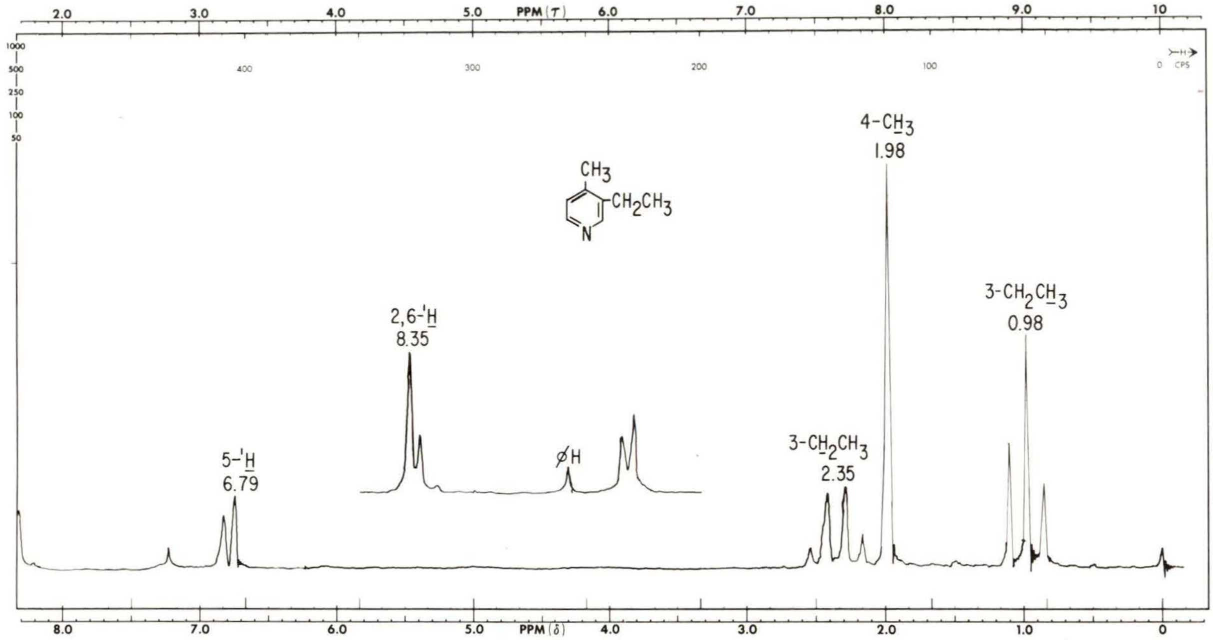

Figure A–49.—3-ethyl-4-methylpyridine in C_6D_6.

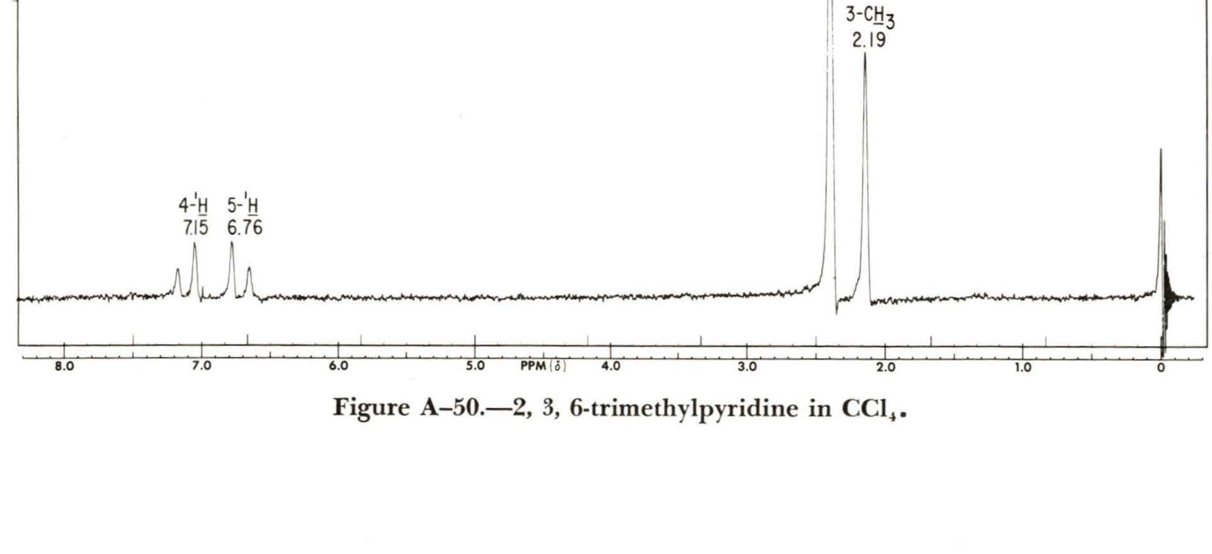

Figure A–50.—2, 3, 6-trimethylpyridine in CCl_4.

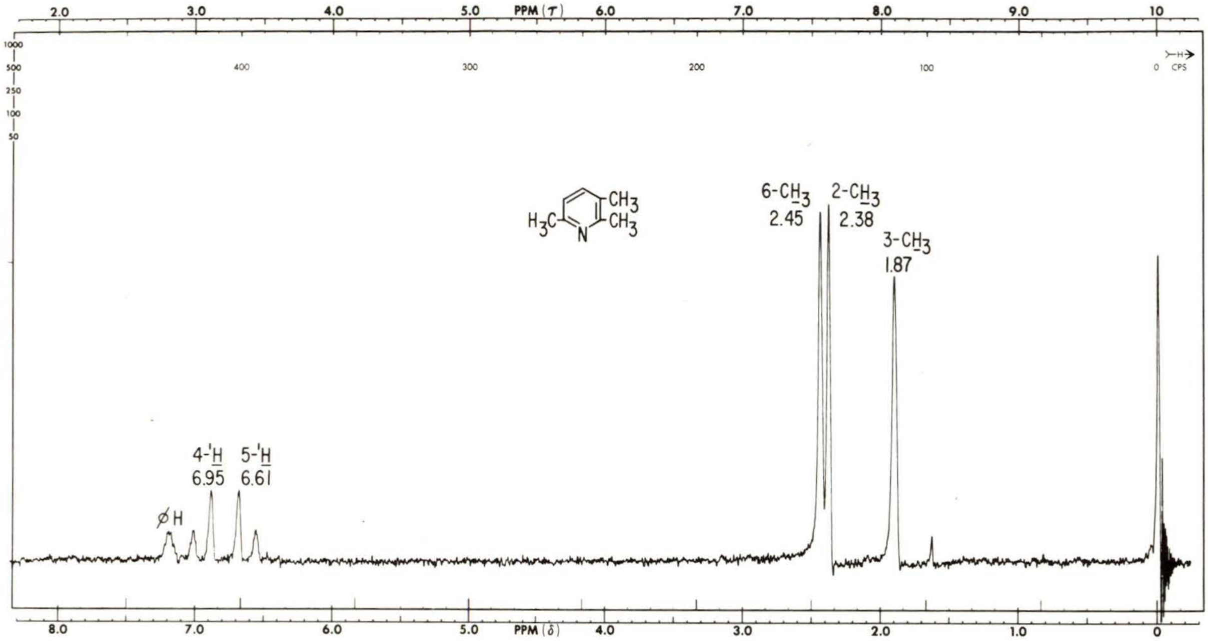

Figure A–51.—2, 3, 6-trimethylpyridine in C_6D_6.

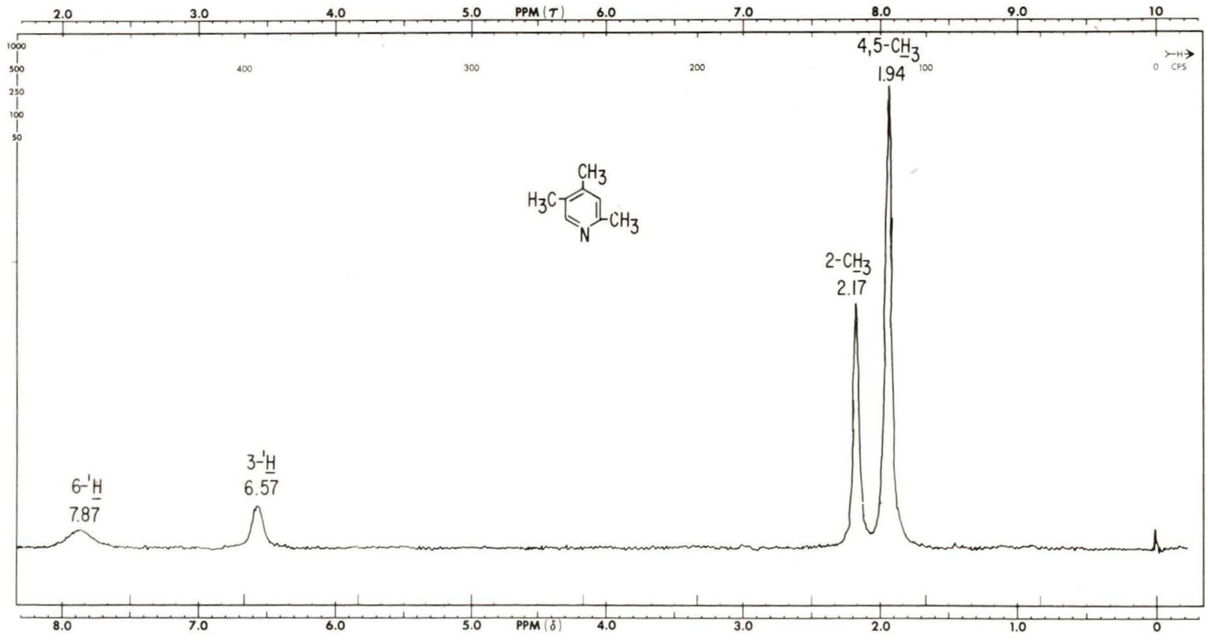

Figure A–52.—2, 4, 5-trimethylpyridine in CCl_4.

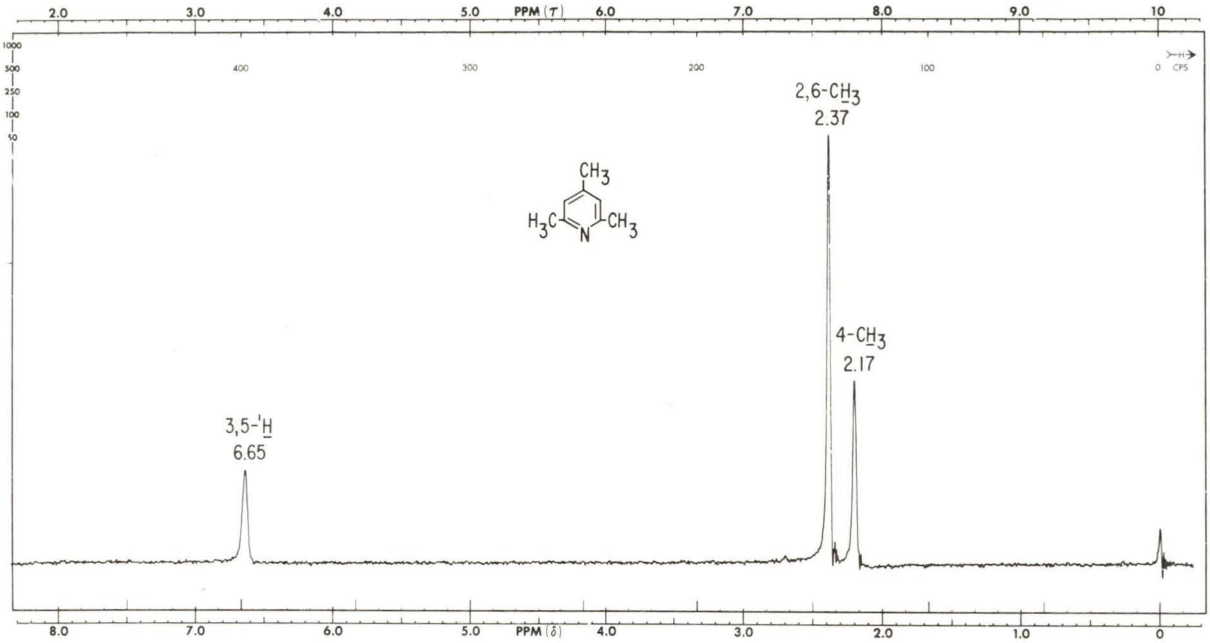

Figure A–53.—2, 4, 6-trimethylpyridine in CCl_4.

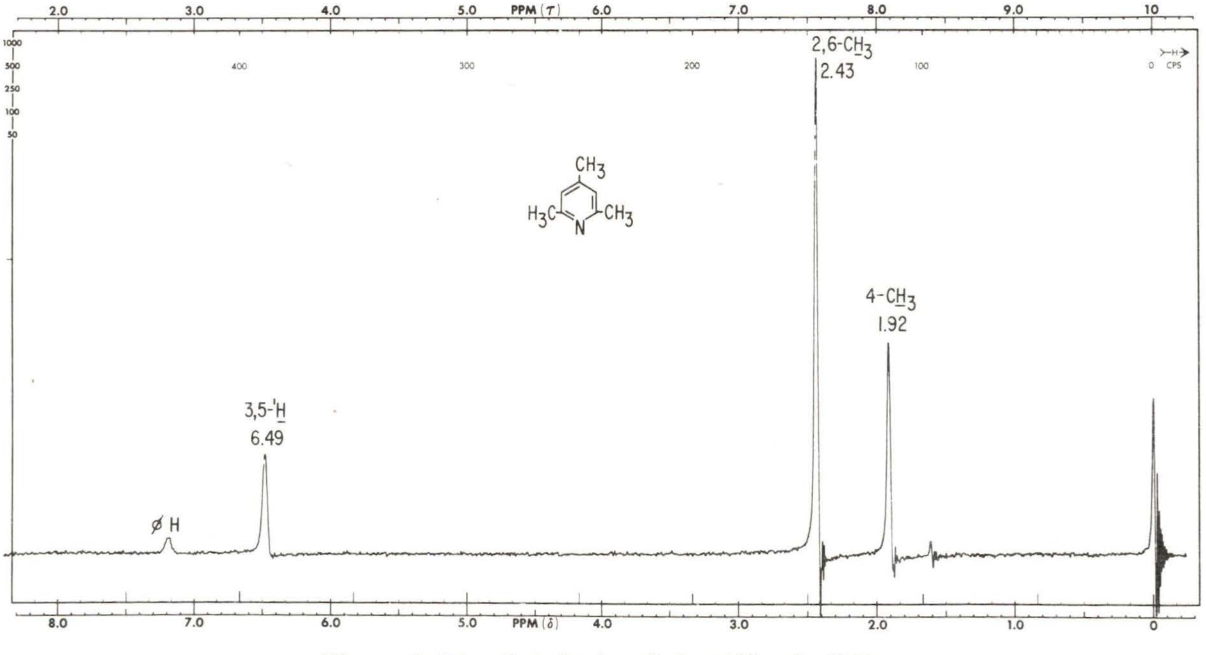

Figure A–54.—2, 4, 6-trimethylpyridine in C_6D_6.

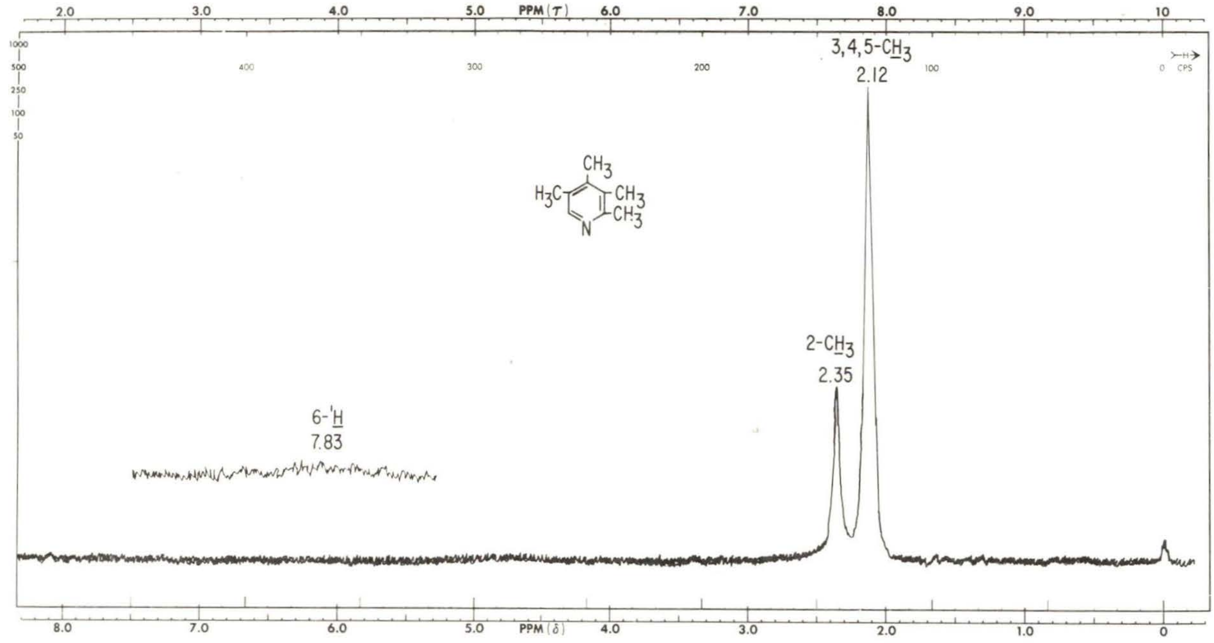

Figure A–55.—2, 3, 4, 5-tetramethylpyridine in CCl_4.

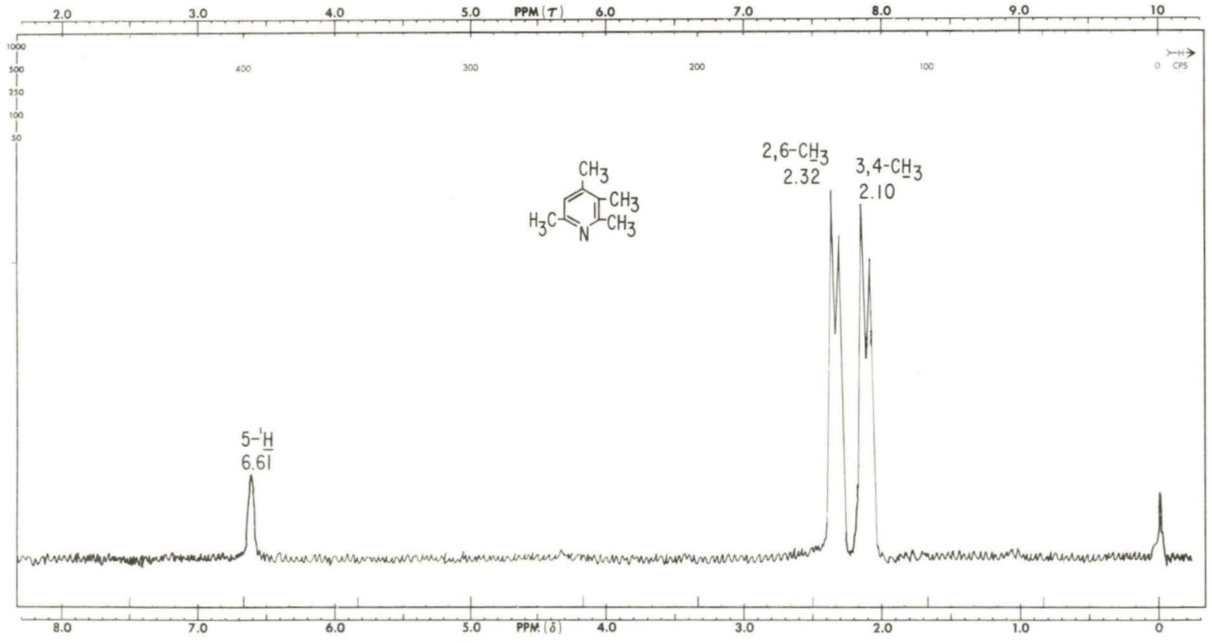

Figure A–56.—2, 3, 4, 6-tetramethylpyridine in CCl_4.

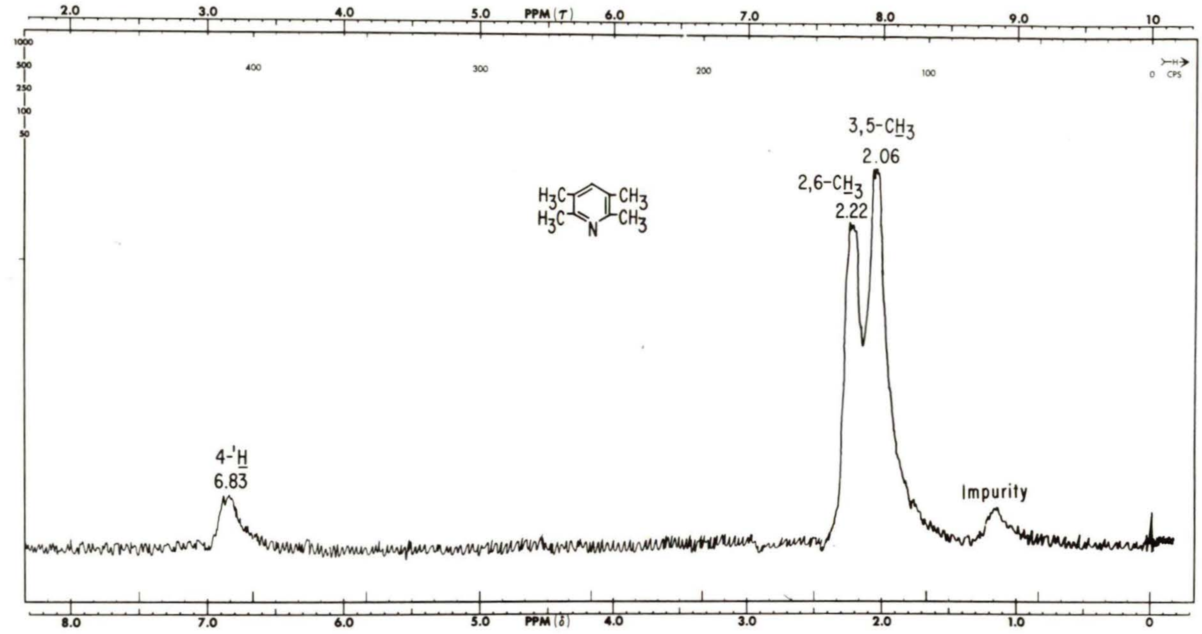

Figure A–57.—2, 3, 5, 6-tetramethylpyridine in CCl_4.

APPENDIX B.—DATA DERIVED FROM SPECTRA

The tables included in this appendix list the chemical shifts and differential chemical shifts of the 32 pyridines studied. Selected data from these tables were used in the text of this bulletin to describe pertinent research results.

Table B–1.—Chemical shifts and differential shifts of the ring protons on 32 pyridines in two solvents at 37° C, ppm

Compound	Ring position								
	2 and 6			3 and 5			4		
	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$
Pyridine	8.42	8.60	−0.18	7.28	6.87	0.41	7.65	7.06	0.59
2-Methylpyridine	8.42	8.53	−.11	7.00	6.61	.39	7.43	7.05	.38
3-Methylpyridine	8.39	8.45	−.06	7.08	6.80	.28	7.39	6.92	.47
4-Methylpyridine	8.42	8.64	−.22	6.99	6.93	.06	....	....	....
2-Ethylpyridine	8.45	8.49	−.04	7.00	6.76	.24	7.43	7.10	.33
3-Ethylpyridine	8.37	8.52	−.15	7.14	6.82	.32	7.40	7.08	.32
4-Ethylpyridine	8.43	8.62	−.19	7.03	6.95	.08	....	....	....
2-Propylpyridine	8.50	8.57	−.07	6.97	6.74	.23	7.47	7.11	.36
4-Propylpyridine	8.45	8.55	−.10	7.00	6.87	.13	....	....	....
4-Isopropylpyridine	8.43	8.59	−.16	7.07	6.97	.10	....	....	....
4-*t*-Butylpyridine	8.47	8.57	−.10	7.20	7.07	.13	....	....	....
2-Pentylpyridine	8.47	8.57	−.10	6.97	6.78	.19	7.48	7.12	.36
4-Pentylpyridine	8.42	8.44	−.02	7.03	6.79	.24	....	....	....
2-Hexylpyridine	8.45	8.57	−.12	7.00	6.75	.25	7.47	7.10	.37
2-(5-Nonyl)pyridine	8.53	8.59	−.06	6.97	6.76	.21	7.50	7.12	.38
4-(5-Nonyl)pyridine	8.46	8.57	−.11	7.01	6.76	.25	....	....	....
2,3-Dimethylpyridine	8.23	8.43	−.20	6.92	6.69	.23	7.28	7.00	.28
2,4-Dimethylpyridine	8.20	8.44	−.24	6.78	6.60	.18	....	....	....
2,5-Dimethylpyridine	8.27	8.42	−.15	6.93	6.84	.09	7.30	7.08	.22
2,6-Dimethylpyridine	....	....	......	6.85	6.74	.11	7.30	7.12	.18
3,4-Dimethylpyridine	8.22	8.39	−.17	6.92	6.64	.28	....	....	....
3,5-Dimethylpyridine	8.15	8.35	−.20	....	....	....	7.10	7.02	.08
2-Methyl-4-ethylpyridine	8.18	(1)	......	6.82	(1)	....	....	....	....
2-Methyl-5-ethylpyridine	8.23	8.47	−.24	6.95	6.77	.18	7.28	7.06	.22
3-Methyl-4-ethylpyridine	8.28	8.41	−.13	6.93	6.83	.10	....	....	....
3-Ethyl-4-methylpyridine	8.23	8.35	−.12	6.92	6.79	.13	....	....	....
2,3,6-Trimethylpyridine	....	....	......	6.76	6.61	.15	7.15	6.95	.20
2,4,5-Trimethylpyridine	7.87	(1)	......	6.57	(1)	....	....	....	....
2,4,6-Trimethylpyridine	....	....	......	6.65	6.49	.16	....	....	....
2,3,4,5-Tetramethylpyridine	7.83	(1)	......	....	....	....	....	....	....
2,3,4,6-Tetramethylpyridine	....	....	......	6.61	(1)	....	....	....	....
2,3,5,6-Tetramethylpyridine	....	....	......	....	....	....	6.83	(2)	....

[1] Insufficient sample.

[2] 4-proton resonance obscured by benzene resonance.

Table B–2.—Chemical shifts and differential shifts of the ring protons on 15 monosubstituted pyridines in two solvents at 30° C, ppm

Compound	Ring position								
	2 and 6			3 and 5			4		
	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$	δ_{CCl_4}	$\delta_{C_6D_6}$	$\delta\delta$
2-Methylpyridine	8.40	8.47	−0.07	6.97	6.67	0.30	7.46	7.08	0.38
3-Methylpyridine	8.38	8.45	−.07	7.07	6.75	.32	7.41	7.00	.41
4-Methylpyridine	8.39	8.50	−.11	7.01	6.66	.35	....	....	....
2-Ethylpyridine	8.45	8.55	−.10	6.99	6.71	.28	7.49	7.14	.35
3-Ethylpyridine	8.37	8.49	−.12	7.10	6.79	.31	7.43	7.07	.36
4-Ethylpyridine	8.39	8.54	−.15	7.03	6.71	.32	....	....	....
2-Propylpyridine	8.44	8.54	−.10	6.98	6.71	.27	7.48	7.16	.32
4-Propylpyridine	8.42	8.55	−.13	7.02	6.72	.30	....	....	....
4-Isopropylpyridine	8.43	8.57	−.14	7.07	6.76	.31	....	....	....
4-*t*-Butylpyridine	8.43	8.61	−.18	7.19	6.92	.27	....	....	....
2-Pentylpyridine	8.46	8.54	−.08	7.00	6.72	.28	7.49	7.12	.37
4-Pentylpyridine	8.40	8.57	−.17	7.01	6.75	.26	....	....	....
2-Hexylpyridine	8.48	8.55	−.07	7.00	6.72	.28	7.48	7.17	.31
2-(5-Nonyl)pyridine	8.48	8.57	−.09	7.00	6.75	.25	7.52	7.18	.34
4-(5-Nonyl)pyridine	8.42	8.57	−.15	7.03	6.77	.26	....	....	....

Table B–3.—Chemical shifts of the alkyl protons on monosubstituted pyridines in CCl_4 at 30° C, ppm

Alkyl group	Alkyl proton position	Position of substitution		
		2 and 6	3 and 5	4
Methyl	α	2.50	2.31	2.32
Ethyl	α	2.78	2.64	2.62
	β	1.29	1.25	1.24
n-Propyl	α	2.73	....	2.57
	β	1.76	....	1.67
	γ	.95	....	.95
i-Propyl	α	....	....	2.86
	β	....	....	1.26
t-Butyl	α	....	....	....
	β	....	....	1.31
n-Pentyl	α	2.75	....	2.57
	β	1.73	....	1.59
	γ, δ	1.37	....	1.42
	ε	.91	....	.90
n-Hexyl	α	2.68	....	....
	β	1.73	....	....
	γ, δ, ε	1.32	....	....
	ζ	.90	....	....
5-Nonyl	α	2.58	....	2.54
	β	1.65	....	1.54
	γ, δ	1.20	....	1.22
	ε	.83	....	.85

Table B–4.—Chemical shifts of the alkyl protons on monosubstituted pyridines in C_6D_6 at 30° C, ppm

Alkyl group	Alkyl proton position	Position of substitution		
		2 and 6	3 and 5	4
Methyl	α	2.42	1.87	1.85
Ethyl	α	2.76	2.24	2.19
	β	1.26	92	.92
n-Propyl	α	2.74	....	2.21
	β	1.79	....	1.37
	γ	.88	....	.73
i-Propyl	α	....	....	2.47
	β	....	....	.97
t-Butyl	α	....	....	....
	β	....	....	1.04
n-Pentyl	α	2.79	....	2.26
	β	1.77	....	1.34
	γ, δ	1.28	....	1.17
	ε	.84	....	.84
n-Hexyl	α	2.74	....	....
	β	1.85	....	....
	γ, δ, ε	1.27	....	....
	ζ	.87	....	....
5-Nonyl	α	2.70	....	2.17
	β	1.81	....	1.26
	γ, δ	1.24	....	1.13
	ε	.83	....	.82

Table B–5.—Chemical shifts of the alkyl protons on monosubstituted pyridines in CCl_4 at 37° C, ppm

Alkyl group	Alkyl proton position	Position of substitution		
		2 and 6	3 and 5	4
Methyl.	α	2.47	2.31	2.27
Ethyl.	α	2.75	2.57	2.58
	β	1.27	1.19	1.20
n-Propyl. . . .	α	2.73	. . . .	2.51
	β	1.77	. . . .	1.60
	γ	.87	. . . .	.89
i-Propyl. . . .	α	. . . .	. . . .	2.83
	β	. . . .	. . . .	1.19
t-Butyl.	α	. . . .	. . . .	. . . .
	β	. . . .	. . . .	1.26
n-Pentyl. . . .	α	2.72	. . . .	2.58
	β	1.69	. . . .	1.52
	γ, δ	1.32	. . . .	1.42
	ε	.87	. . . .	.90
n-Hexyl. . . .	α	2.68	. . . .	. . . .
	β	1.75	. . . .	. . . .
	γ, δ, ε	1.32	. . . .	. . . .
	ζ	.90	. . . .	. . . .
5-Nonyl. . . .	α	2.60	. . . .	2.39
	β	1.64	. . . .	1.52
	γ, δ	1.15	. . . .	1.20
	ε	.82	. . . .	.82

Table B–6.—Chemical shifts of the alkyl protons on monosubstituted pyridines in C_6D_6 at 37° C, ppm

Alkyl group	Alkyl proton position	Position of substitution		
		2 and 6	3 and 5	4
Methyl.	α	2.43	1.85	2.01
Ethyl.	α	2.77	2.25	2.37
	β	1.27	.92	1.02
n-Propyl. . . .	α	2.75	. . . .	2.32
	β	1.80	. . . .	1.44
	γ	.89	. . . .	.78
i-Propyl. . . .	α	. . . .	. . . .	2.62
	β	. . . .	. . . .	1.03
t-Butyl.	α	. . . .	. . . .	. . . .
	β	. . . .	. . . .	1.12
n-Pentyl. . . .	α	2.80	. . . .	2.44
	β	1.78	. . . .	. . . .
	γ, δ	1.27	. . . .	1.31
	ε	.85	. . . .	.87
n-Hexyl. . . .	α	2.75	. . . .	. . . .
	β	1.78	. . . .	. . . .
	γ, δ, ε	1.29	. . . .	. . . .
	ζ	.86	. . . .	. . . .
5-Nonyl. . . .	α	2.77	. . . .	2.18
	β	1.80	. . . .	1.24
	γ, δ	1.18	. . . .	1.12
	ε	.82	. . . .	.73

Table B–7.—Chemical shifts of the alkyl protons on polyalkyl-substituted pyridines in CCl_4 at 37° C, ppm

Compound	Alkyl proton position	Position of substitution				
		2	3	4	5	6
2,3-Dimethylpyridine.	α	2.42	2.21	. . . .	. . . .	. . . .
2,4-Dimethylpyridine.	α	2.46	. . . .	2.18	. . . .	. . . .
2,5-Dimethylpyridine.	α	2.43	. . . .	. . . .	2.23	. . . .
2,6-Dimethylpyridine.	α	2.43	. . . .	. . . .	. . . .	2.43
3,4-Dimethylpyridine.	α	. . . .	2.21	2.21	. . . .	. . . .
3,5-Dimethylpyridine.	α	. . . .	2.15	. . . .	2.15	. . . .
2-Methyl-4-ethylpyridine.	α	2.41	. . . .	2.52	. . . .	. . . .
	β	. . . .	. . . .	1.18	. . . .	. . . .
2-Methyl-5-ethylpyridine.	α	2.42	. . . .	. . . .	2.57	. . . .
	β	. . . .	. . . .	. . . .	1.20	. . . .
3-Methyl-4-ethylpyridine.	α	. . . .	2.15	2.50	. . . .	. . . .
	β	. . . .	. . . .	1.13	. . . .	. . . .
3-Ethyl-4-methylpyridine.	α	. . . .	2.54	2.19	. . . .	. . . .
	β	. . . .	1.14	. . . .	. . . .	. . . .
2,3,6-Trimethylpyridine.	α	2.39	2.19	. . . .	. . . .	2.39
2,4,5-Trimethylpyridine.	α	2.17	. . . .	1.94	1.94	. . . .
2,4,6-Trimethylpyridine.	α	2.37	. . . .	2.17	. . . .	2.37
2,3,4,5-Tetramethylpyridine.	α	2.35	2.12	2.12	2.12	. . . .
2,3,4,6-Tetramethylpyridine.	α	2.32	2.10	2.10	. . . .	2.32
2,3,5,6-Tetramethylpyridine.	α	2.22	2.06	. . . .	2.06	2.22

Table B–8.—Chemical shifts of the alkyl protons on polyalkyl-substituted pyridines in C_6D_6 at 37° C, ppm

Compound [1]	Alkyl proton position	Position of substitution				
		2	3	4	5	6
2,3-Dimethylpyridine	α	2.38	1.85	....	....	....
2,4-Dimethylpyridine	α	2.43	....	1.85	....	....
2,5-Dimethylpyridine	α	2.27	....	....	2.00	....
2,6-Dimethylpyridine	α	2.42	....	....	....	2.42
3,4-Dimethylpyridine	α	....	1.77	1.77	....	....
3,5-Dimethylpyridine	α	....	2.03	....	2.03	....
2-Methyl-5-ethylpyridine	α	2.47	....	....	2.27	....
	β	....	....	....	.96	....
3-Methyl-4-ethylpyridine	α	....	1.96	2.30	....	....
	β	....	....	.98	....	....
3-Ethyl-4-methylpyridine	α	....	2.35	1.98	....	....
	β	....	.98	....	....	....
2,3,6-Trimethylpyridine	α	2.38	1.87	....	....	2.45
2,4,6-Trimethylpyridine	α	2.43	....	1.92	....	2.43

[1] The chemical shifts of the three tetramethylpyridines, 2,4,5-trimethylpyridine, and 2-methyl-4-ethylpyridine were not measured in C_6D_6 because of a lack of sample.

Table B–9.—Differential chemical shifts of the alkyl protons on polyalkyl-substituted pyridines at 37° C, ppm

Compound	Alkyl group carbon	Ring carbon				
		2	3	4	5	6
2,3-Dimethylpyridine	α	0.04	0.36	....	....	....
2,4-Dimethylpyridine	α	.03	....	0.33	....	....
2,5-Dimethylpyridine	α	.16	....	....	0.23	....
2,6-Dimethylpyridine	α	.01	....	....	....	0.01
3,4-Dimethylpyridine	α	....	.44	.44	....	....
3,5-Dimethylpyridine	α	....	.12	....	.12	....
2-Methyl-5-ethylpyridine	α	−.05	....	.30	....	....
	β	....	....	.24	....	....
3-Methyl-4-ethylpyridine	α	....	.19	.20	....	....
	β	....	....	.15	....	....
3-Ethyl-4-methylpyridine	α	....	.19	.21	....	....
	β	....	.16	....	....	....
2,3,6-Trimethylpyridine	α	.01	.32	....	....	−.06
2,4,6-Trimethylpyridine	α	−.06	....	.25	....	−.06

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