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Gentlemen:

Attached is the Second Annual Report covering the period from May 3, 1965 through May 2, 1966.

Bernard Grushkin
Bernard Grushkin
Principal Investigator

BG:lvd

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SYNTHESIS OF LINEAR, DOUBLE CHAIN LADDER POLYMERS FROM SUBSTITUTED TETRAPHOSPHONITRILES

Annual Report

Covering the Period

May 3, 1965 through May 2, 1966

By:

Bernard Grushkin, Principal Investigator

and

Robert M. Murch

Contract No. NASw-924: Modification No. 1

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ABSTRACT

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The objective of this contract is to prepare a new class of double-bridged ladder type polymers from tetrafunctional phosphonitrilic tetramers. During the first year three isomers of 2, 4, 6, 8 - tetrachloro - 2, 4, 6, 8 - tetraphenyltetraphosphonitrile, $[\phi PNCl]_4$, were isolated and structurally identified. The β-trans isomer was converted to the tetraamide which, by thermal deammoniation, would be converted to a polymer.

During the second year of this contract the following accomplishments have been made:

1. By thermally polymerizing β-trans-$[\phi PNNH_2]_4$ a soluble polymer of 20,000 MW has been obtained.
2. The above polymer was found to eliminate benzene above 400°C.
3. Synthesis of non-geminal tetrachloro tetramethyl tetraphosphonitrile, $[CH_3PNCl]_4$, has been accomplished; however, the compound is hydrolytically unstable.

author

OBJECTIVE OF THE PROGRAM

The ultimate objective of this investigation is to prepare a new class of double-bridged, ladder type polymers from cyclic tetrameric phosphonitriles. Successful ladder polymers are expected to be thermally stable beyond present day capabilities. This objective can be attained only if the substituents are arranged about the phosphonitrilic ring in such a manner that they can be linked together in double bridges.

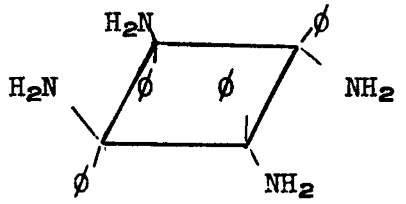
Having found an isomer of $[\phi PNCl]_4$ with a suitable structure for polymerizations, the following objectives were set for the second year of this contract:

1. Prepare and characterize ladder polymers from β-trans-$[\phi PNCl]_4$.
2. Synthesize new monomers, namely $[CH_3PNCl]_4$.
3. Prepare and characterize ladder polymers from the tetramethyl phosphonitriles.

SUMMARY

Phenyl Phosphonitrilic Polymers

Polymers were prepared from β-trans-$[\phi PNNH_2]_4$,



by thermal deammoniation at 260°C. Soluble polymers could be obtained with a molecular weight of 20,000 (DP 40). Structural characterization of the polymer has been difficult. Attempts to determine the NH/NH_2 ratio in this polymer have not been successful. However, infrared analysis of the polymer indicates that there are very few NH_2 groups present.

Heating the polymer results in elimination of benzene at about 400°C, the resulting material is a black charred mass.

Methylphosphonitriles

Attempts to prepare tetrachloro tetramethyltetraphosphonitrile by the following sequence of reactions were not successful.

$$\begin{tikzcd}
{[PNCl_2]_4} \arrow[r, "(CH_3)_2NH"] & {[(CH_3)_2NPNCl]_4} \arrow[r, "CH_3MgBr"] & {[(CH_3)_2NPNCH_3]_4} \arrow[d, "HCl"] \\
 & (CH_3)_2NH\cdot HCl+ \quad {[CH_3PNCl]_4} & {} \arrow[l]
\end{tikzcd}$$

Non-geminal tetraamino tetrachloro phosphonitriles could be obtained; however, the products resulting from their reaction with CH_3MgBr could not be readily isolated. This approach was abandoned in favor of the more direct synthesis from CH_3PCl_4 and ammonium chloride.

$$xCH_3PCl_4 + xNH_4Cl \longrightarrow [CH_3PNCl]_x + 4xHCl$$

The reaction does give poor yields of trimer and tetramer. However, because of hydrolytic instability separation of tetramer from the trimer is exceedingly difficult.

Ammonolysis of $[CH_3PNCl]_{3,4}$ results in a completely ammoniated product that is extremely hygroscopic. On the other hand the tetrakis-dimethylamide is less susceptible to hydrolysis. The oxidative stability of the tetrachloro tetramethyl tetramer was examined.

CONCLUSIONS

Thermal treatment of β-trans-$[\phi PNNH_2]_4$ produces a soluble polymer having a degree of polymerization of about 40. So far it has not been possible to accurately determine the extent of double-bridging in the polymer. The fact that this polymer is extremely soluble in chloroform precludes the possibility that it is highly crosslinked, however it does not eliminate the possibility of some side branching.

Polymers derived from phenyl phosphonitriles eliminate benzene at about 400°C. The mechanism for this elimination is not now well understood. It is believed, however, that initial benzene elimination results in the formation of phenylene bridges and that further benzene elimination is accompanied by complete degradation of the polymer.

Tetrachlorotetramethyltetraphosphonitrile, $(CH_3PNCl)_4$, can be synthesized from CH_3PCl_4 and ammonium chloride, however final yields of cyclic tetramer have been very poor. We believe that this is due, in part, to hydrolytic instability of $[CH_3PNCl]_X$. Separation of tetrameric isomers could not be achieved by the simple crystallization techniques used to separate isomers of $[\phi PNCl]_4$.

Tetrakis amides prepared from $[CH_3PNCl]_{3,4}$ were found to be hydrolytically unstable. Because of the hydrolytic instability of both the chloro and amide compounds we believe that working with large amounts of these materials would be exceedingly difficult.

RECOMMENDATIONS

1. Since the β-trans isomer of $[\phi PNCl]_4$ can be prepared in good yield, various methods will be used to prepare higher molecular weight ladder polymers from it. Emphasis will then be placed on characterizing the resultant polymers.

2. Sufficient methyl phosphonitrilic amide will be prepared for polymerization and thermal stability evaluation. If thermal stability of resulting polymers is exceptional, methods will then be sought to improve the yield of $[CH_3PNCl]_4$.

3. Prepare tetrameric phosphonitriles of the type $[RPNCl]_4$ with R groups other than phenyl or methyl.

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I. Introduction

Synthesis of polymers with cyclic phosphonitrilic backbones has recieved considerable attention. Phosphonitriles used to prepare these polymers were $[PNCl_2]_3$ and $[PNCl_2]_4$, having six and eight functional groups respectively (1) (2) (3). These polymers are usually highly crosslinked insoluble materials.

Functionality about the trimer or tetramer ring can be reduced by using compounds of the type $R_yP_3N_3X_{6-y}$ or $R_yP_4N_4X_{8-y}$, where R is an alkyl, aryl, alkoxy or aryloxy group.

Monomers of this type can be prepared by the following types of reactions:

(1) $xRPCl_4 + xNH_4Cl \rightarrow [RPNCl]_x + 4xHCl$

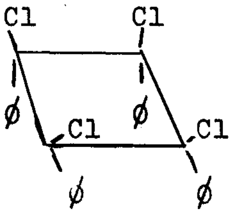
(2) $xRPCl_4 + xNH_3 \rightarrow [RPNNH_2]_x + 4xNH_4Cl$

Reaction of ϕPCl_4 with NH_4Cl produces trifunctional and tetrafunctional phenyl phosphonitriles.

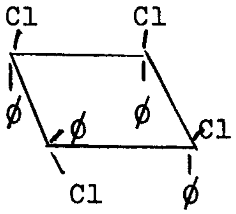
(3) $x\phi PCl_4 + xNH_4Cl \rightarrow [\phi PNCl]_x + 4xHCl$

$x = 3, 4$

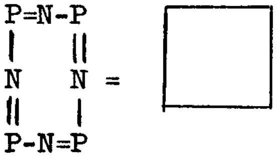
Four tetrameric products are possible. From their configurations, as illustrated below, it is readily seen that three of the isomers can be used to prepare double bridged polymers.

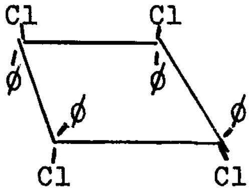


cis

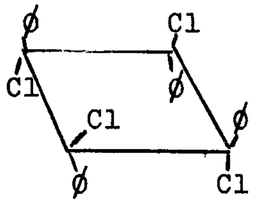


α-trans





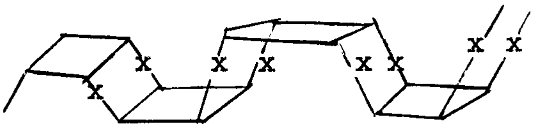
β-trans



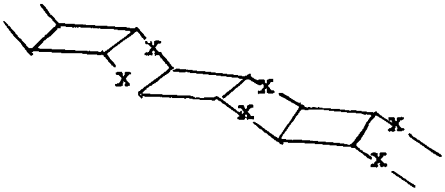
γ-trans

Monomers having the cis, β-trans or γ-trans configuration would be capable of forming ladder polymers of the following type:

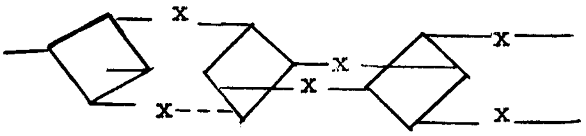
cis



β-trans



γ-trans



Polymers having the above linear structures should exhibit excellent thermal properties and also have good solubility characteristics in organic solvents. Thus, the ultimate objective is to prepare derivatives from these tetramers which, in turn, would be polymerized to form the desired double-bridged ladder polymers.

During the first year of this investigation reaction (3) was optimized to give good yields of tetramer. Of the tetrameric products, the β-trans isomer was the most abundant.

This report summarizes in detail our efforts to prepare ladder polymers from β-trans-[øPNCl]$_4$ and also the progress made in synthesizing other tetrafunctional monomers.

II. Results and Discussion

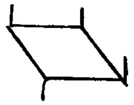
A. Phenyl Phosphonitriles.

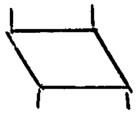
1. Preparation of γ-trans-$[\text{Ø}PNCl]_4$.

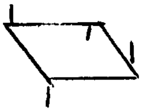
Of the four possible tetrameric isomers of $[\text{Ø}PNCl]_4$, three had been isolated as products from the reaction of $\text{Ø}PCl_4$ with NH_4Cl (4) (5) (6). Cis, α-trans and β-trans tetramers were isolated and identified structurally.

$$x\,\text{Ø}PCl_4 + xNH_4Cl \rightarrow (\text{Ø}PNCl)_{3,4,x} + 4xHCl$$


cis


α-trans


β-trans


γ-trans

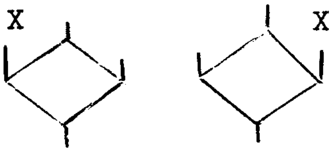
The fourth isomer, γ-trans-$[\text{Ø}PNCl]_4$, has never been isolated.

The reaction of hydrogen chloride with tetrakisdimethylamino tetramers, in glacial acetic acid, was used to regenerate the tetrachloro compound.

$$(1)\ 8HCl + [\text{Ø}PNN(CH_3)_2]_4 \rightarrow [\text{Ø}PNCl]_4 + 4(CH_3)_2NH\cdot HCl$$

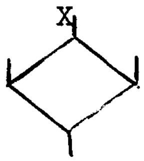
Starting with a single isomer of the tetrakisamide we were able to recover a mixture of the three known tetrachloro isomers, however the fourth isomer of $[\text{Ø}PNCl]_4$ could not be obtained by this reaction.

We attempted to prepare a monosubstituted dimethylamide from α-trans-$[\text{Ø}PNCl]_4$, which, in turn, would be treated with anhydrous HCl. Three monosubstituted products are possible.

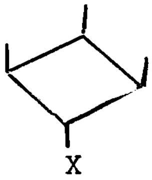


(a)

optical isomers



(b)



(c)

where $x = N(CH_3)_2$

It is readily seen that removal of the dimethylamido group from (b), accompanied by isomerization, would result in the formation of the γ-trans isomer.

According to our previous work with $[\text{Ø}PNCl]_4$, m.p. 260-3°, we had assumed it to be a mixutre of α-trans and β-trans isomers. On this basis it was used to prepare a monosubstituted derivative. The only product readily isolated from the reaction of $[\text{Ø}PNCl]_4$, m.p. 260-3°, with one molar equivalent of dimethylamine was $\emptyset_4P_4N_4N(CH_3)_2Cl_3$, m.p. 103-7°. This compound proved to be a derivative of the β-trans isomer. This was established by reacting the derivative with an excess of dimethylamine. Three molar equivalents of amine hydrochloride, recovered from this reaction, indicated that the starting material was monosubstituted. The completely dimethylaminated material was crystallized to melt at 175-8°, which is the melting point of β-trans-$[\emptyset PNN(CH_3)_2]_4$.

Subsequently it was found that the starting material, melting at 260-3°, is not a mixutre of α-trans and β-trans isomers, but rather, it is pure β-trans isomer (7).

Since not enough α-trans-$[\emptyset PNCl]_4$ was available to carry out the proposed reactions, this approach was abandoned. No further effort has been made to obtain γ-trans-$[\emptyset PNCl]_4$.

2. The Structure of $[\emptyset PNCl]_4$, m.p. 260-263°.

Our belief that $[\emptyset PNCl]_4$, m.p. 260-3°, was a mixture of two isomers was based on the fact that this material, when reacted with dimethylamine, monomethylamine or ammonia, resulted in the formation of two different isomeric derivatives. These results were always obtained when the reaction was carried out in benzene or chloroform.

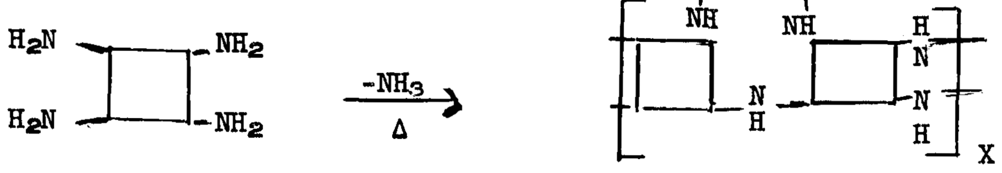
Smalley et al. (7) reported the formation of only a single derivative when this reaction is carried out in tetrahydrofuran. We have carried out the aminolysis in THF and have corroborated the results of Smalley et al.

Keat and Shaw (8) reported that phosphonitrilic amides isomerize when refluxed with the amine hydrochloride in chloroform. We have tried to effect an isomerization by refluxing β-trans-$[\emptyset PNN(CH_3)_2]_4$ with dimethylamine hydrochloride in refluxing benzene and THF. In neither case was any isomerization noted.

At present we cannot explain the anomalous behavior of β-trans-$[\emptyset PNCl]_4$, i.e., aminolysis in benzene results in the formation of two products whereas aminolysis in THF results in only one product. This situation is further complicated by the fact that aminolysis of α-trans and cis-$[\emptyset PNCl]_4$ give single products.

3. Deammoniation of β-trans-$[\emptyset PNNH_2]_4$.

When β-trans-$[\emptyset PNNH_2]_4$ is heated above 240°C ammonia is eliminated and a polymer is formed.



The deammoniation reaction has been carried out several times in a melt and in solution. Data are summarized in Table I. Number average molecular weights were obtained by vapor pressure osmometry in chloroform. The determined molecular weight was found to be a function of concentration. For example, four VPO determinations for a single polymer sample gave the following result.

g./l.	MW.
10.0	14,300
15.0	23,100
19.95	22,190
29.95	33,300

By plotting $^1/\mathrm{MW}$ vs. g./l. and extrapolating to infinite dilution, a value of 11,700 was obtained for the molecular weight.

It is noteworthy that in one instance a polymer fraction quite soluble in chloroform was recovered with a number average molecular weight of 20,000. This represents an average degree of polymerization of 40 units. It might be inferred that, because of the polymers great solubility in chloroform, there is a minimum of crosslinking and that the polymer is, to a great extent, linear.

The polymerization, when carried out in solution, did not give higher molecular weight polymers. Polymers prepared in di(n-octyl) ether, B.P. 291°, had a molecular weight of approximately 4,400. The polymer began to precipitate from solution during the course of the ammonia elimination. This is probably why the degree of polymerization is rather low.

A similar problem arises when polymerization is carried out in the melt. Initially the melt is quite fluid, however as ammonia evolution progresses the melt becomes more viscous until finally it sets up as a foamed solid. Ideally, a solvent should be used in which the polymer is soluble throughout the course of the reaction.

Thermal deamination of β-trans-[ØPNNHCH$_3$]$_4$ was carried out at 280-290°C. Methylamine was eliminated during the heating. The glassy solid resulting from this polymerization was completely soluble in chloroform. The molecular weight determined by VPO in $CHCl_3$ was 1,800.

4. Polymer Characterization.

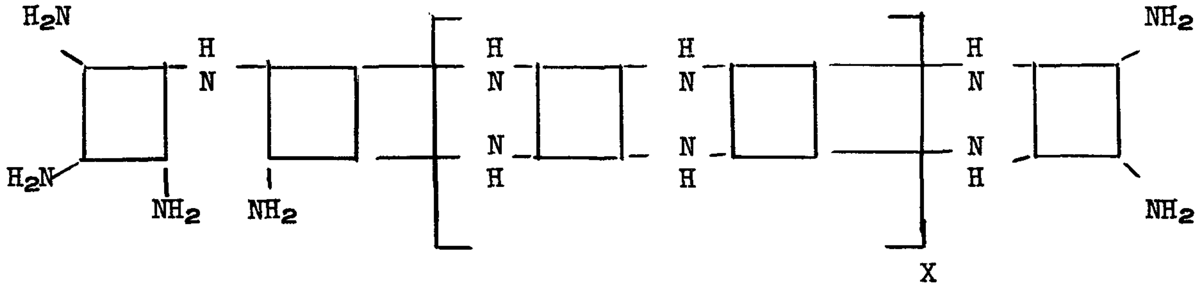
We have attempted to characterize the polymer by determining the ratio of -NH to -NH_2 groups. A completely double bridged polymer would have very few NH_2 groups, whereas single bridged or a highly crosslinked polymer would have a large number of NH_2 groups. The infrared spectra from 1600 to 1000 cm.$^{-1}$ for polymers with molecular weights ranging from 11,700 to 2,400 are reproduced in Figure 1 . The shoulder appearing at 1560 cm.$^{-1}$ for lower molecular weight polymers and in the spectrum of β-trans-[ØPN(NH_2)]$_4$ is due to NH_2 absorption. This absorption is very small for the polymer of 11,700 molecular weight, thus implying that the polymer has a small number of NH_2 groups. This

TABLE I

Deamination of β-trans [ØPNNH$_2$]$_4$ at 260°C

Run No.	[ØPN(NH$_2$)]$_4$ Used	mmoles NH$_3$ Evolved	% of Residue Sol. in CHCl$_3$	Wt. of Fractions Precipitated	Mol. Wt.	ANALYSIS			
						C	H	N	P
1	5.0 g. (9.06 mmoles)	12.67 (70%)	Comp. Sol.	0.55 0.27 0.75 0.25	8,340 7,400 4,082 2,040	54.03	4.65	14.25	19.44
2	5.0 g. (9.06 mmoles)	10.85 (60%)	Comp. Sol	2.0 0.4 1.80	990 3,000 4,400	53.88	4.62	13.07	19.34
3	10.0 g. (18.12 mmoles)	31.28 (86%)	55% (5.5 g.)	1.03 1.74 0.30 0.25 1.20	11,700 6,250 3,230 2,470 1,655	55.84	5.11	14.86	20.61
4	25 g. (45.5 mmoles)	65.2 (71.8%)	Comp. Sol.	3.3 2.0 3.0 1.0 3.6	9,500 8,000 7,400 4,900 2,470				
5	40 g.	75%		5 g. 3 g. 8 g.	20,000 11,000 9,000				

would be expected for a polymer which is double bridged to a large degree.



An accurate method was sought for determining the ratio of NH to NH_2 in the polymer. Non-aqueous titrations, NMR spectra and reactions of the polymer with aldehydes were tried.

Samples of the polymer, as well as several phosphonitrilic compounds, were titrated with perchloric acid for basic nitrogen. Titrations were carried out in glacial acetic acid with crystal violet as the indicator. Acetic acid is a leveling solvent in which compounds containing basic nitrogen functional groups are readily titrated. For example, pyridine, which is too weak a base to titrate in water is easily titrated in glacial acetic acid. Results of these titrations are given in Table II.

No titration of $[PNCl_2]_4$ with perchloric acid was observed; however, Bode et al.(9) have reported the precipitation of $P_4N_4Cl_8 \cdot 2HClO_4$ from a glacial acetic acid solution of $P_4N_4Cl_8$ and approximately 60 percent perchloric acid. Based on our results with $[PNCl_2]_4$ it was assumed that the ring nitrogens were not the basic sites. However, in light of results of Bode et al. and, more recently, those of Moeller and Kokalis(10) and Shaw et al.(11) there is substantial evidence that at least one ring nitrogen is titrated by the acid. Thus, the result obtained for the titration of $(\phi_5P_3N_3)_2NH$ wherein two equivalents of acid per equivalent of dimer were used, can now be attributed to the ability of each PN ring to take up one equivalent of perchloric acid. Furthermore, it is now concluded that, although these polymers can be titrated with perchloric acid, one cannot determine the NH to NH_2 ratio from the results, consequently this analytical approach was abandoned.

The proton nuclear magnetic resonance specturm was obtained for a deaminated polymer fraction of 9,500 molecular weight. The spectrum showed a broad absorption at $\tau \sim 5.5$ and a strong aromatic proton absorption at $\tau \sim 2.2$. The area ratio was approximately 1:20. The absorption at $\tau \sim 5.5$ disappeared when D_2O was added to the sample tube. Thus the absorption is due to either NH or NH_2.

Treatment of compounds or polymers, which have active hydrogen, with trichloroacetyl isocyanate, $Cl_3CC(O)NCO$, produces a better n.m.r. spectrum for quantitative determination of the active hydrogen. Reaction of $Cl_3CC(O)NCO$ with amino groups would give the following:

$$R\text{-}NH_2 + 2Cl_3CC(O)NCO \rightarrow R\text{-}N[C(O)NHC(O)CCl_3]_2$$

TABLE II

Titration of PN Compounds in Glacial Acetic Acid

Compound or Sample	Molecular Weight	Experimental Basicity in Acetic Acid meq./g.	Theor. Basicity for N Exo to the PN Ring
$(PNCl_2)_4$	463.55	None	None
β-trans-$(\phi NPNMe_2)_4$	664.66	3.04 2.02	6.02
β-trans-$(\phi NPNH_2)_4$	552.42	3.56 3.55	7.25
β-trans-$(\phi NPNHMe)_4$	608.51	3.25 3.28	6.57
α-trans-$(\phi PNNH_2)_4$	552.41	5.06 5.19	7.24
$(\phi PN)_4$	799.63	Insoluble in HAc	
trans-$\phi_3P_3N_3(NH_2)_3$	414.31	4.36 4.45	7.24
cis-$\phi_4P_3N_3(NH_2)_2$	475.38		
$\phi_5P_3N_3NH_2$	536.46	1.83 1.85	1.86
$(\phi_5P_3N_3)_2NH$	1055.9	1.86	0.95
Polymer Sample 3716-14-1	9500*	1.75 1.78	Unknown
Polymer Sample 3716-28 P11C	7400	2.16 2.28	Unknown
Polymer Sample 3716-28 P11E	2470	2.05 2.08	Unknown

*Molecular weight determined by VPO in chloroform.

Prior to reaction with the polymer, $\phi_5P_3N_3NH_2$ and $(\phi_5P_3N_3)_2NH$ were treated with $Cl_3CC(O)NCO$. Reaction of $\phi_5P_3N_3NH_2$ with $Cl_3CC(O)NCO$ results in the formation of the disubstituted compound $\phi_5P_3N_3N[C(O)NHC(O)CCl_3]_2$. The proton n.m.r. peak due to -NH- between carbonyl groups τ = -0.71 (Figure 2), whereas the amide protons of $\phi_5P_3N_3NH_2$ have an n.m.r. absorption at τ = 7.1 (Figure 3). Addition of $Cl_3CC(O)NCO$ to $(\phi_5P_3N_3)_2NH$ results in the disappearance of the n.m.r. peak at τ = 8.2 due to NH, however no peak is observed downfield.

The deammoniated polymer (MW 9500) was treated with trichloroacetyl isocyanate. The amide proton between two carbonyl groups had an n.m.r. absorption peak at τ = -1.5. The ratio of amide protons to phenyl protons, calculated from the ratio of the area of the peak at τ = -1.5 and that of aromatic protons at τ = 2, was 1:14. Based on the n.m.r. results obtained for the treatment of $\phi_5P_3N_3NH_2$ with $Cl_3CC(O)NCO$ one can calculate that this polymer (DP of 19) has 13 or 14 NH_2 groups. Any structure drawing for this polymer would have a substantial number of double bridges.

The n.m.r. spectrum of a polymer of 20,000 molecular weight had a broad peak at about τ = 5, however it was not large enough to permit an area determination with any accuracy. Treatment of the polymer with $Cl_3CC(O)NCO$ did not produce any noticeable change in the n.m.r. specturm.

Based on the above results, it is concluded that the use of n.m.r. spectroscopy is of limited value for determining the ratio of NH or NH_2 to ϕ groups in the polymer, and is of no value for higher molecular weight polymers, wherin the ratio of NH_2 to ϕ would be very low.

In an effort to find reagents which react preferentially with NH_2 groups rather than with NH groups β-trans-$[\phi PNNH_2]_4$ was treated with benzaldehyde and salicaldehyde. In neither case was there any evidence for a reaction leading to a unique product.

5. Benzene Elimination

A chloroform insoluble polymer which was prepared by heating β-trans-$[\phi PNNH_2]_4$ to eliminate 86% of the available NH_3, was heated to 395°C in helium and kept at that temperature for 12 hours. During this time a gas was eliminated. The gas was collected on a vacuum system shown in Figure 4 . By infrared spectroscopy the gas was determined to be a mixture of benzene and ammonia. Quantitative estimation of each constitutent was made by determining the total pressure in a known volume (total number of moles), then weighing the gas, By using the following equations the amounts of NH_3 and benzene were determined.

$$\text{Total wt. of gas} = MW_{NH_3}\cdot X + MW_{\phi}(\text{total moles} - X)$$

X = moles NH_3

X+Y = total moles

Y = moles benzene

Results are graphically illustrated in Figure 5 for thermally treating the polymer at 395° and also at 475°C. The residue, after heating at 475° for 12 hours, contained 14.09 percent carbon and 3.01 percent hydrogen.

A TGA was obtained for this polymer and is shown in Figure 6. The 10 percent loss in weight between 0° and 350°C is due to the evolution of ammonia and chloroform that was occluded in the polymer. This was observed for gas samples recovered during the isothermal study described in the previous paragraph. Also, as noted in the previous paragraph, benzene and NH_3 are eliminated above 400°C. The striking feature of this thermogram is the "gradual" weight loss from 400 to 800°C. This might be compared to the TGA obtained for a similar polymer derived from trans-$[\phi PNNH_2]_3$ as illustrated in Figure 7. The heating rate was 3°/min. for both samples.

It would appear that because of the benzene eliminated from polymers derived from phenyl phosphonitriles, the upper limit of thermal stability is in the range of 350 to 400°C.

II. Results and Discussion

B. Methyl Phosphonitriles

1. Preparation of Methyl Phosphonitrilic Compounds From $(PNCl_2)_4$

(a) Reaction of $(PNCl_2)_4$ with MeMgBr

Before attempting to prepare $[CH_3PNCl]_4$ by the method that Tesi and Slota used to prepare $[CH_3PNCl]_3$,(12) we attempted to react $[PNCl_2]_4$ directly with methyl magnesium bromide. The reaction was carried out in anhydrous diethyl ether under a helium atmosphere. After refluxing the mixture of tetramer and Grignard Reagent for six hours the mixture was poured over ice and extracted with benzene. From the benzene solution only unreacted tetramer was recovered.

The reaction was carried out again. However, chlorobenzene was added to the mixture after six hours. Evaporation of the solvent and extraction of the residue with benzene gave only unreacted $[PNCl_2]_4$.

When the reaction with tetramer was conducted in tetrahydrofuran we observed an exothermic reaction at room temperature and the product appeared to contain PN cyclics and $P\text{-}CH_3$ bonds (see Figure 8). Infrared absorptions at 1300 cm.$^{-1}$ and 750 cm.$^{-1}$ are characteristic of $P\text{-}CH_3$ bonds. We have encountered difficulites in isolating compounds from this reaction mixture and have recently discovered that this mixture contains an appreciable amount of magnesium. The instability of these compounds may be due to complex formation with magnesium salts. In the work of Tesi and Slota, they treated the products of the Grignard Reaction with a large excess of dimethylamine before any separation was attempted. The excess amine may have broken the complex, thus permitting isolation of products.

(b) Preparation of $[MePNCl]_4$ via $[NMe_2PNCl]_4$ and MeMgBr

The three-step route to the preparation of tetrachlorotetramethylphosphonitrilic cyclic tetramer,

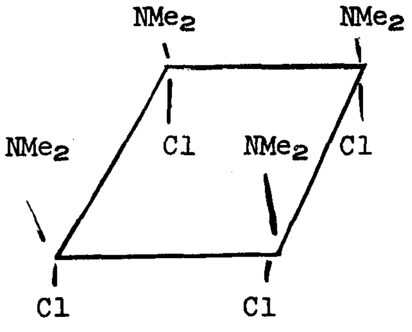
(1) $[PNCl_2]_4 + 8Me_2NH \rightarrow [PN(NMe_2)Cl]_4 + 4HCl\cdot HNMe_2$

(2) $[PN(NMe_2)Cl]_4 + 4\ MeMgBr \rightarrow [MePN\ NMe_2]_4 + 4\ MgBrCl$

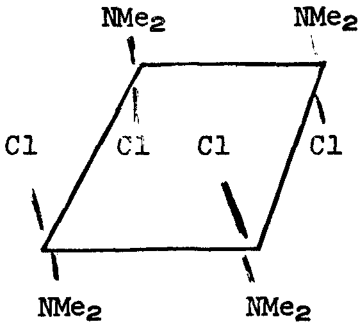
(3) $[MePNNMe_2]_4 + 4HCl \rightarrow [MePNCl]_4 + 4HNMe_2$

is analogous to the reaction sequence used for cyclic trimers by Tesi and Solta.(12) This three-step synthesis was devised because the alkylation of phosphonitrilic chlorides with Grignard Reagents is either impossible, or at best, very difficult. By replacing half the chlorines with dimethylamino groups, the reactivity of the remaining halogens is enhanced enough to permit facile reaction with methylmagnesium bromide. Subsequently the dimethylamino groups could be replaced by halogens in a simple nucleophilic displacement reaction.

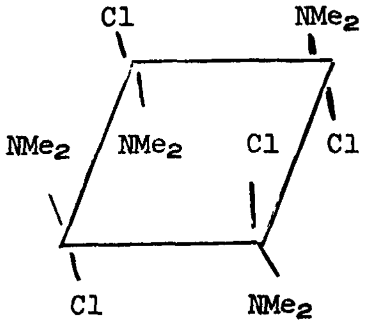
The first step of the procedure, the replacement of four nongeminal chlorines in $[PNCl_2]_4$ is not a simple reaction. The degree of substitution can vary from one to eight and many of these products have been observed while attempting tetrasubstitution.(13) In addition, there are ten tetrakisdimethylamino isomers and only three non-geminal isomers are potential precursors for ladder-polymers. The three desired products are:



cis



β-trans



γ-trans

The dimethylamination has been carried out in various solvents, benzene, tetrahydrofuran, diethylether, chloroform and even in a two phase benzene-water system. Shaw(13) reports 59 percent yields of one non-geminal tetrakisdimethylamino-tetramer, but we have not been able to isolate this isomer in yields greater than 15 percent. We have, however, obtained a mixture of non-geminally, tetrasubstituted cyclic tetramers in yields approaching 50 percent. This result was obtained by conducting the reaction in tetrahydrofuran at 0° as suggested by Moffett.(14) The characterization of the products as tetrakisdimethylaminotetrachlorophosphonitrilic cyclic tetramer was accomplished by elemental analysis infrared spectra and n.m.r. spectra.

In a recent paper Koppman et al.(15) obtained the n.m.r. spectra of a number of dimethylamino derivatives of PN trimers. They showed that geminal substitution involves P^{31}-H coupling of about 13.6 c/s while vacinal substitution involves P^{31}-H coupling of 17.7 c/s. Applying this realationship to the tetramers one can differentiate between geminal and non-geminal substitution for products that have been characterized as cyclic tetramers from elemental analysis and infrared spectra. Separation and characterization of specific non-geminal isomers was not attempted. Figures 9 and 10 show the infrared and n.m.r. spectra of a product that had a m.p. of 192-4°. The IR spectrum shows it to be a tetramer and the n.m.r. spectrum indicates that it contains two different non-geminally substituted products. Similarly, Figures 11 & 12 show IR and n.m.r. spectra for a product with a m.p. of 156-60°. This is predominantly a single non-geminally substituted isomer. Figures 13 & 14 show these spectra for a product that is predominantly two non-geminally substituted isomers.

The second step of this reaction sequence, the Methyl Grignard coupling with $[PNCl\ NMe_2]_4$ was conducted twice with mixtures of the non-geminally substituted tetramers. In the first attempt the reactants were combined in tetrahydrofuran and because no sign of magnesium salts was apparent, it was presumed no reaction had occurred. Toluene was added to the reaction mixture, the ethers removed and then a heavy precipitate and a negative Gilman test indicated the reaction had occurred. The product that was isolated had an infrared spectrum (Figure 15) that indicated the presence of a phosphonitrilic tetramer substituted with methyl groups. Isolation of the product, however, was not accomplished. Apparently the product was destroyed in attempts to isolate specific compounds.

The reaction was repeated with the mixed isomers of $[Me_2NPNCl]_4$ described above. As before, the coupling proceeded smoothly and a product giving the appropriate infrared spectrum was obtained (see Figure 16). However, attempts to recrystallize the solid product resulted in degradation since no single isomer could be isolated and further work-up caused the melting point of this product mixture to decrease until it had turned to a viscous oil. Attempts to sublime products from this oil resulted in evolution of amine and the remaining material was a dry powder.

The third step was not investigated in view of the lack of success in obtaining any characterizable product from the Grignard Reaction.

(c) Preparation of $[MePNCl]_4$ via $[PNBr_2]_4$

The difficulty in replacing chlorines with alkyl groups in phosphonitriles is related to the relative reactivity of the P-Cl and P-N bonds. It has been postulated that alkyl Grignard Reactions with phosphonitriles are unsuccessful because the organometallic reagent attacks the ring as rapidly as the phosphorus-halogen link.(16) With this idea in mind, it seemed profitable to attempt Grignard Reactions with phosphonitrilic bromides. An attempt to prepare octabromophosphonitrilic cyclic tetramer was initiated. Three methods were looked at briefly but before these reactions could be fully evaluated, we solved the problem of controlling the Grignard addition to $(PNCl_2)_n$ and the need for $(PNBr_2)_n$ was essentially eliminated. A brief summary of these efforts can be made. The attempted exchange of Br for Cl with PBr_3 and PBr_5-PBr_3 did not occur. In a similar attempt, acetylbromide was refluxed with $(PNCl_2)_4$ for four hours but no exchange could be detected. Treating $(PNCl_2)_4$ with $AlBr_3$ and bromine did lead to the production of a gas, probably ClBr. The isolation of products was not accomplished before the need for such products disappeared.

A fourth scheme to obtain bormophosphonitriles was the attempted replacement of half the dimethylamines in octakisdimethylaminophosphonitrilic cyclic tetramer, $[PN(Me_2N)_2]_4$. However, rather than replacement of the dimethylamino groups with bromine, the preferred reaction was the insoluble HBr adduct which could be characterized by its infrared spectrum, i.e. a shift of the PN absorption peak and the appearance of an absorption at 2300 cm.$^{-1}$ (10).

(d) Preparation via $[\phi NMe\ PNCl]_4$

One other possible route to $[MePNCl]_4$ that was investigated was a method similar to the three-step process described in section (b) above. This involved the non-geminal tetrasubstitution of $[PNCl_2]_4$ with N-methylaniline. Work reported by John, Moeller and Audrieth(17) indicated that high yields of non-geminal tetrasubstituted arylaminophosphonitrilic cyclic tetramers can be obtained because aryl amines have enough steric hinderance to prevent more than one aryl amine per phosphorus. Thus it should be possible to get high yields of $[PNCl\ NMe\phi]_4$. Presumably this could then be coupled with Grignard Reagent and then the anilino group replaced with ammine to yield $[PNMe\ NH_2]_4$. The first step in this sequence was attempted twice. The product from the first attempt was not a tetra-anilino compound, and the product from the second attempt was a mixture that proved hard to separate or identify.

2. Preparation by Reaction of CH_3PCl_4 and NH_4Cl

The preparation of a variety of $(RPNCl)_n$ and $(R_2PN)_n$ compounds by the following reactions have been extensively reported.(18)

1. $xR_2PCl_3 + xNH_4Cl \rightarrow [R_2PN]_X + 4xHCl$

2. $xRPCl_4 + xNH_4Cl \rightarrow [RPNCl]_X + 4xHCl$

(Where R is chlorine, bromine, and phenyl)

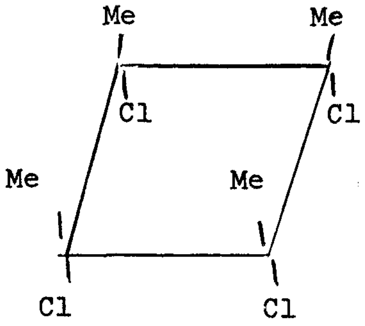
Previous work in these laboratories led to the development of a method that gives high yields of $[\phi PNCl]_3$ and $[\phi PNCl]_4$.(4) Using these techniques we have been able to synthesize $[MePNCl]_{3,4}$ from CH_3PCl_4 and NH_4Cl. One important condition for obtaining a high yield of cyclics from this reaction is avoiding too high a temperature. By using ammonium chloride that is freshly prepared and of very fine particle size we have been able to carry out the reaction in the temperature range of 90° to 125°. The reaction has been carried out in both hexachlorobutadiene and chlorobenzene.

The preparation of methylphosphorus tetrachloride from methylphosphorus dichloride was accomplished by using a stoichiometric amount of chlorine. An excess of chlorine can result in chlorination of the methyl group.(19)

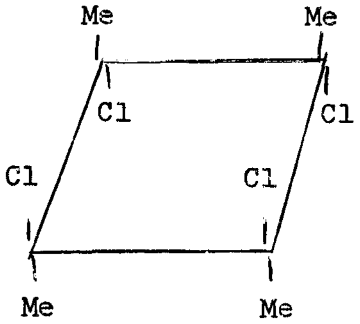
The reaction was initially conducted between $MePCl_2$, Br_2 and NH_4Br due to our belief that $MePCl_4$ would decompose below the reaction temperature. This reaction was unsuccessful, no product was isolated.

With $MePCl_4$ and a six-fold excess of NH_4Cl in hexachlorobutadiene only 30% of the expected HCl was obtained. A very small amount of solid product was isolated from this reaction after distilling off the hexachlorobutadiene. It was later discovered that $[MePNCl]_3$ and $[MePNCl]_4$ are volatile enough to distill with hexachlorobutadiene, but this was not realized until the used solvent had been discarded.

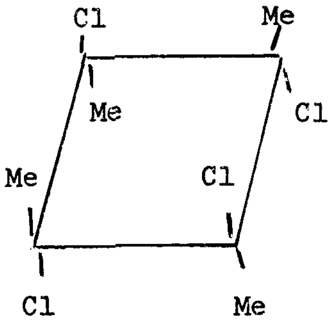
The reaction was repeated and approximately a theoretical yield of HCl was obtained. Upon distillation of the reaction solution methyl-containing phosphonitrilic trimer and tetramer were recovered from the distillate, the distillation column and head, and the residue which remained in the flask. Recrystallization of these products from heptane resulted in the isolation of three distinct phosphonitrilic compounds. A tetramer melting at 175-181° was isolated (see Figure 17 for infrared spectra). Molecular weight by vapor pressure osmometry in chloroform was 362 (theory for tetramer is 382). The proton n.m.r. spectrum, with the phosphorus decoupled, showed a single peak which indicated that the compound melting at 175-181° has four methyl groups in an identical environment. This would imply the isomer is either <u>cis</u>, <u>β-trans</u> or <u>γ-trans</u>.



cis



β-trans



γ-trans

A second compound obtained, m.p. 80-92°, had an infrared spectrum (see Figure 18) that also was consistent with that of a tetramer, but no molecular weight data nor n.m.r. spectra were obtained for the sample because it appeared to degrade during attempts to purify it.

A third compound, m.p. 163-163.5°, had an infrared spectrum (Figure 19 , characteristic of a cyclic trimer. The molecular weight was 307 (calcl'd for trimer 286). The phosphorus decoupled proton n.m.r. spectrum for this trimer showed a single peak which indicated that it has the cis configuration. The elemental analysis showed the following:

Found	C, 13.7; H, 3.6; N, 13.5; Cl, 31.4; P, 26.7
(Calc'd) for $[CH_3PNCl]$	C, 12.6; H, 3.1; N, 14.7; Cl, 37.2; P, 32.5

The evidence strongly suggests that some oxygen has replaced the chlorine. This conclusion could also be reached from changes in the infrared spectra where the appearance of bands at 2600 $cm.^{-1}$ and 970 $cm.^{-1}$ indicate the formation of POH and POP bonds respectively. The n.m.r. spectra also show this degredation by the development of very complex peaks for the methyl protons. This implies a larger number of environments for these methyl groups.

Although work with methyl phosphonitriles had established that they are unstable and can change on contact with air or solvents of reagent grade purity, we could not be certain that this was the primary reason for the relatively low yields, (less than 20%) that we observed for this preparation. One possible source of trouble is the starting material $MePCl_2$. Analysis of the material, that had been presumed to be pure, showed:

Found	C, 10.5; H, 2.7; P, 24.4; Cl, 53.4
Calc'd for CH_3PCl_2	C, 10.3; H, 2.6; P, 26.5; Cl, 60.6

Apparently the starting material contains a relatively large amount of hydrolyzed material, which could have been a contributing cause to low yield by this procedure.

3. Reactions of Methylphosphonitrilic Cyclics

(a) Oxidation of $[CH_3PNCl]_n$

The observed degradation of methylphosphonitrilic chloride cyclics was accompanied by the replacement of chlorine by oxygen. Although this could be readily explained as hydrolysis, there was no proof that the introduction of oxygen did not occur by some other mechanism. For this reason studies of both the hydrolytic and oxidative stability were conducted. The material for both of these studies was purified after sealing in a vacuum system by carrying out six consecutive sublimations. The material obtained from this purification had the following analysis:

Found	C, 12.8; H, 3.2; N, 14.6; Cl, 37.2; P, 32.5
Calc'd for $(MePNCl)_n$	C, 12.6; H, 3.1; N, 14.7; Cl, 37.2; P, 32.5

The infrared spectrum (Figure 20) indicates the material is primarily cyclic trimer and a proton n.m.r. spectrum (with phosphorus decoupling) indicated that both trimer isomers are present in approximately equal amounts.

The material was exposed to a stream of dry oxygen for twenty-four hours. After this period the elemental analysis, infrared and n.m.r. spectra were essentially unchanged. Apparently the degradation does not involve oxygen.

(b) Hydrolysis of $[CH_3PNCl]_3$

The previously described sublimations also led to a material that had the following analysis:

Found	C, 12.7; H, 3.1; N, 14.5; Cl, 37.1; P, 32.2
Calc'd for $(MePNCl)_n$	C, 12.6; H, 3.1; N, 14.7; Cl, 37.2; P, 32.5

The infrared spectra(Figure 21) and the proton n.m.r. spectra with phosphorus decoupling indicated that this material was a mixture of both isomers of cyclic trimer and about 75% cis-trichlorotrimethylcyclotriphosphonitrile. Wet nitrogen passed over this material caused a change in composition as indicated by the following figures:

Before hydrolysis:	%C, 12.7; %H, 3.1; %N, 14.5; %Cl, 37.1
After hydrolysis:	%C, 10.5; %H, 3.9; %N, 12.1; %Cl, 31.0

The radical change may be seen by comparing the infrared spectra of the material before (Figure 21) and after (Figure 22) this exposure.

(c) Preparation of Derivatives of $[CH_3PNCl]_n$

The extreme instability of (MePNCl) cyclics makes it desirable to obtain a polymerizable species with as few manipulations as possible. Therefore, we attempted to convert the reaction product of NH_4Cl and $MePCl_4$ into its amine derivatives without isolating the intermediate phosphonitrilic chlorides. This procedure was not successful, which implies that the amino compounds, $(MePN\ NH_2)_n$, are as unstable as the chlorides, $(MePNCl)_n$.

A similar preparation of the dimethylamino derivatives, however, gave an acceptable yield of mixed cyclics of the type (MePN NMe_2), these cyclics seem to be much more stable than either the amides or chlorides. Figures 23 and 24 show infrared spectra of a mixture of dimethylaminomethylphosphonitrilic cyclics before and after exposure to a stream of air saturated with water. Unlike the $(MePNCl)_n$ compounds, there seems to be relatively little hydrolysis.

(d) Derivatives of $(Me_2PN)_n$

It was believed that functionality in such compounds as $[(CH_3)_2PN]_3$ or $[(CH_3)_2PN]_4$ may be created by suitable reactions of the methyl groups. One such reaction, with bromine, has been carried out.

In carbon tetrachloride, at room temperature, $[(CH_3)_2PN]_3$ (m.p. 187-9°) was treated with four equivalents of bromine. After several hours a solid formed. This solid was filtered and recrystallized from chloroform, m.p. 235-6°. An infrared spectrum of this product is shown in Figure 25. The strong absorption band at 1180 $cm.^{-1}$ for $[(CH_3)_2PN]_3$ is absent, rather, there is an absorption band at 1240 $cm.^{-1}$. Elemental analysis of this product is as follows:

Found:	C, 23.13; H, 6.47; N, 13.48; P, 26.92; Br, 24.90
For $C_6H_{17}P_3N_3Br$:	C, 23.70; H, 5.64; N, 13.80; P, 30.50; Br, 26.25

Molecular weights by VPO in chloroform was 352, 359 and 339. For a monosubstituted trimer, $P_3N_3(CH_3)_5(CH_2Br)$ the molecular weight is 304. Although the analysis is not exceptionally good for phosphorus or bromine, it does suggest that a monosubstituted product has been prepared.

Since further bromination of the trimer may have been hindered by its lack of solubility in CCl_4, we have repeated the reaction in freshly distilled glacial acetic acid under a helium atmosphere. Using four moles of Br_2 per mole of $[(CH_3)_2PN]_3$ no reaction was observed at room temperature (disappearance of bromine color). Also, in the presence of UV from a low pressure lamp (2537Å, 15 watts) no reaction was observed. However, when the temperature was raised to about 80°C the bromine color rapidly disappeared. The solution then was evaporated to dryness at reduced pressure. A waxy residue remained which could not be worked up to yield a singular product.

III. Experimental

A. Phenyl Phosphonitriles

1. Reaction of β-trans-$[\phi PNCl]_4$ with one Equivalent of Dimethylamine

To 63 g. (0.1 mole) of $[\phi PNCl]_4$, m.p. 260-3°, in 1 l. of benzene was added 0.15 mole of dimethylamine in 500 ml. of benzene. The reaction was carried out at room temperature. After 24 hours the solution was filtered and 0.07 mole of dimethylamine hydrochloride was recovered. The volume of the filtrate was reduced to approximately 500 ml. Twenty grams of unreacted $[\phi PNCl]_4$, m.p. 240-258°, thus was recovered. Further volume reduction and addition of hexane to the chloroform solution gave, in several increments, 24 g. of a solid melting at 102-5°. Upon recrystallization from hexane this solid melted at 103-7°.

From the filtrate were also crystallized several fractions with melting ranges from 180 to 220° and several oils.

One gram of the fraction melting at 103-7° was treated with a large excess of dimethylamine in benzene. From this reaction 4.65 mmoles of dimethylamine hydrochloride was recovered. A crystalline solid, m.p. 170-6°, was recovered from the filtrate by evaporation. This solid recrystallized to melt at 175-8°. The melting point of β-trans-$[\phi PNN(CH_3)_2]_4$ is 176-8°. There was no depression of the melting point when the two samples were mixed.

2. Polymerization Reactions

a. Deamination of β-trans-$[\phi PN(NH_2)]_4$.

(1) In the Melt

Ten grams (18.10 mmoles) of β-trans-$[\phi PN(NH_2)]_4$ was heated to 260°C in a nitrogen atmosphere. The evolved gas was collected in water and titrated with 0.1 N HCl. After two hours 31.2 mmoles of NH_3 had evolved (86 percent of available NH_3). The product was then washed with chloroform. Only 5.5 grams or 55 percent of the polymer dissolved in the chloroform. Several polymer fractions were collected by adding pentane to the chloroform solution. Molecular weights were determined for each fraction by vapor pressure osmometry (see Table 1 , Run No. 3). Run No. 4 was carried out in the same manner as No. 3 .

In another experiment, three grams of tetrakisamide was heated to 260°C until 50 percent of the available ammonia evolved. The reaction then was stopped and an additional gram of tetrakisamide was added to the already partially polymerized tetramer. The mixture was again heated to 260°C and again the reaction was stopped when 50 percent of the available NH_3 had evolved. Once more an additional gram of tetrakisamide was added; however, the mixture was now heated at 260° until no more ammonia evolved. A total of 12.67 mmoles of NH_3 was titrated or 70 percent of the available ammonia. The polymer was completely soluble in chloroform. Pentane was used to precipitate polymer fractions. Molecular weights of these fractions are recorded in Table 1 , Run No. 1 .

In a resin kettle 40 g. of β-trans-$[\phi PNNH_2]_4$ (0.0726 mole) was heated to 260°C. Ammonia, evolved from the melt, was passed into water and titrated with acid. After two hours, 0.109 mole of NH_3 had evolved. The flask was quenched in ice water to stop the reaction.

The solid was taken up in chloroform and fractionally precipitated with n-hexane. The first fraction, 17 g., had a molecular weight of 15,400. This fraction was reprecipitated from $CHCl_3$-hexane. The first fraction, 5.0 g., had a number average molecular weight of 20.000. A second fraction of approximately 3 grams had a molecular weight of 11,000.

(2) In Solution

Five grams (9.05 mmoles) of β-trans-$[\phi PN(NH_2)]_4$ in 50 ml. of di(n-octyl) ether (B.P. 291°) was heated to 260°C for three hours. During this time 10.85 mmoles of NH_3 was evolved. Upon cooling, a solid separated from the solution. This solid was taken up completely in chloroform and reprecipitated with n-pentane. The molecular weight and elemental analysis of this solid are shown in Table 1 , Run No. 2 .

b. Deamination of β-trans-$[\phi PN(NHCH_3)]_4$

Four grams (6.57 mmoles) of β-trans-$[\phi PN(NHCH_3)]_4$, m.p. 131-2°, was heated in a nitrogen atmosphere to 280-290°C. Methylamine began to evolve at about 260°. During the course of the reaction some solid collected in the cooler part of the flask. After 24 hours at 280-290°C, 8.84 mmoles of methylamine had evolved. The glassy residue was completely soluble in chloroform The molecular weight, determined by VPO, was 1800. The product presently is being characterized further.

3. Benzene Elimination Studies

In a reaction tube 1.967 g. of deammoniated β-trans-$[\phi\ NNH_2]_4$ (sample No. 2956-46-2P45) was heated to 300°C. in a stream of helium. At this temperature some NH_3 and chloroform were collected in a liquid nitrogen trap. After no more ammonia or chloroform was collected the temperature was rapidly raised to 395°C. Between 300 and 395°C. a small amount of gas evolution was observed. The temperature was then maintained at 395°C. Gases evolved from the sample were collected in liquid N_2 and periodically transferred to a volumetric bulb, weighed and examined by infrared spectroscopy. In all cases only ammonia and benzene were observed. Heating at 395°C. was continued until no further evolution of gas from the sample was observed.

A similar run, using 1.615 g. of sample, was carried out at 475°C.

4. Model Compounds, $[\phi_5P_3N_3]_2NH$

A mixture of 0.9 mmoles of $\phi_5P_3N_3NH_2$ and 0.9 mmoles of $\phi_5P_3N_3Cl$, in 50 ml. of dry pyridine, was refluxed for 24 hrs. The solution was evaporated to dryness under reduced pressure and the residue taken up in benzene. Pyridine hydrochloride was filtered from the solution. The benzene solution then was put through a chromatographic column containing acidic alumina. Upon elution with benzene, solids were recovered that had a melting range of 230 to 236°. When combined and recrystallized a solid melting at 236° was obtained.

In 50 ml. of refluxing dry pyridine 3.2 mmoles of cis-$\phi_4P_3N_3(NH_3)_2$ (m.p. 189-191°) was treated with 3.2 mmoles of $\phi_5P_3N_3Cl$. After 24 hours the solution was evaporated to dryness and the residue taken up in benzene. The product of this reaction also melted at 236°. Elemental analysis indicates that it is $[\phi_5P_3N_3]_2NH$.

B. Methyl Phosphonitriles

1. Reaction of $(PNCl_2)_4$ and CH_3MgBr

Method (a)

To ten grams (21.55 mmoles) of $[PNCl_2]_4$, dissolved in anhydrous diethyl ether, was slowly added 94.8 mmoles of CH_3MgBr in ether (obtained from Arapahoe as a 3 Molar solution). The reaction was carried out in a helium atmosphere. The solution turned opaque but a precipitate did not form during six hours of refluxing. The solution was then poured over ice and extracted with 1 liter of benzene. The benzene solution was dried over $CaCl_2$ and evaporated to dryness. The solid residue was taken up in hexane, from which 6.5 g. of $[PNCl_2]_4$ was recovered.

Method (b)

Octachlorophosphonitrilic tetramer (11.6 g., 0.025 mole) was dissolved in 200 ml. of THF and methylmagnesium bromide in ethyl ether (71.5 ml., 0.1 mole) was added slowly during a half-hour period. The exothermic reaction started immediately and after the addition was complete the reaction mixture gave a negative Gilman Test for active organometallic compounds. The THF and ether were removed by distillation while 200 ml. of toluene was added. The heavy precipitate that formed was filtered and washed with toluene. The filtrate was concentrated by distillation of the solvent and the remaining product was a viscous oil. No crystalline product could be obtained from this oil upon further work-up. Subsequent qualitative tests of this material for magnesium established that this element is present. Figure 26 shows the infrared spectrum of the oil after attempts to isolate a product. This spectrum can be compared with the spectrum of the same material (Figure 27) prior to handling. It appears that degradation has occurred.

2. Preparation of $(MePNCl)_4$ via $(PNCl\ NMe_2)_4$

(a) Reaction of $[PNCl_2]_4$ with Dimethylamine

Method (a)

To 20 g. (43.5 mmoles) of $[PNCl_2]_4$ in 1 l. of benzene was added 0.35 mole of dimethylamine in 100 ml. of benzene. After all of the amine had been added the solution was filtered to remove the amine hydrochloride.

Upon evaporation of the filtrate an oil remained from which crystallized a solid, which after recrystallization melted at 192-4° (3.5% yield).

Part of the remaining oil was distilled at 140-150°C. at 1 to 1.5 Torr. A solid was recovered which, upon recrystallization from pentane-hexane, melts at 103-105°.

Another aliquot of the oil was absorbed on an acidic alumina column (Woelm Alumina, acidic, Type 1) using hexane as the solvent. Continued elution with hexane has given a solid melting at 103-105° (approx. 10% yield). Further elution with dioxane-hexane (1:20) gave a solids melting at 99°C. and 222-223°; however, only very small amounts of these solids were recovered.

The reaction of eight equivalents of dimethylamine with 50 g. of $[PNCl_2]_4$ was carried out in 1 l. of diethylether at 0°C. After removing the dimethylamine hydrochloride the filtrate was evaporated to dryness, leaving an oil. This oil presently is being separated.

Method (b)

Octachlorocyclophosphonitrilic tetramer $[PNCl_2]_4$, (25.0 g., 0.54 mole) was dissolved in 200 ml. of THF and the solution cooled to 0-3°C. While maintaining this temperature, dimethylamine (19.4 g., 0.43 mole) was slowly distilled into the solution. After sixteen hours the dimethylamine hydrochloride was removed by filtration and the filtrate concentrated by evaporating the THF. The product was crystallized from n-hexane. A yield of 16.5 g., (0.033 mole) of $[PNCl(NMe_2)]_4$ was obtained. The melting range of this product was 130-195°, apparently a mixture of several isomers. From this mixture less than 4 g. of the 192-4° isomer, previously reported by Shaw, was obtained.

In a similar reaction, using 23.2 g. (0.05 mole) of $[PNCl_2]_4$ and 18 g. (0.40 mole) of Me_2NH, a yield of 15 g. (0.30 mole) of mixed cyclic tetramer $[PNCl(NMe_2)]_4$ was obtained.

(b) Preparation of Non-Geminal Tetrachlorotetrakis-N-methylanilinocyclotetraphosphonitrile

Octachlorocyclotetraphosphonitrile, 25 g., (0.054 mole) was dissolved in 500 ml. of THF and 43.1 g., (0.43 mole of N-methylaniline was added during a half-hour period. The mixture was kept at reflux (65°C) for 16 hours. Solvent was then removed by distillation and 200 ml. of benzene added. The N-methylaniline hydrochloride was filtered and the product, a dark oil, was obtained when the benzene was removed by distillation. Attempts to isolate a pure tetrasubstituted compound from this product were unsuccessful.

The reaction was repeated with 10:1 mole ratio of N-methylaniline to phosphonitrile. As before, an oil was the only product. The oil has an elemental analysis as follows:

Found: %C, 40.2; %H, 4.2; %N, 14.1; %Cl, 24.5
Calc'd: %C, 95.1; %H, 4.3; %N, 15.0; %Cl, 19.0

(c) Attempted Preparation of $[PNBr\ NMe_2]_4$: Reaction of $[PN(NMe_2)_2]_4$ With HBr

Three grams (5.6 mmoles) of $[PN(NMe_2)_2]_4$ was dissolved in 50 ml. of freshly distilled glacial acetic acid. To this solution, at room temperature, was added gaseous HBr. A heavy precipitate formed which was filtered from the solution. The filtrate was evaporated to dryness leaving no residue.

The acetic acid residue was examined by infrared and n.m.r. spectroscopy. A sample of the solid when put into water resulted in an acidic solution, which upon neutralization with base gave a precipitate of $[PN(NMe_2)_2]_4$.

(d) Methylmagnesium Bromide Addition to $[PNCl(NMe_2)]_4$

Method (a)

The Grignard Reagent was prepared by slowly passing methyl bromide into a flask containing 2.4 g. (0.1 mole) of magnesium and 50 ml. of ethyl ether. After the disappearance of the magnesium, 8.4 g. (0.68 mole) of tetrachlorotetrakisdimethylamine phosphonitrilic tetramer (m.p. 192-4°) in 50 ml. of tetrahydrofuran was slowly added. There was no sign of reaction. The reaction mixture was heated to approximately 55° and stirred overnight. There was still no evidence of reaction. One hundred ml. of toluene was added and the ethyl ether and tetrahydrofuran were removed by distillation as the reaction mixture was heated to 110°. After refluxing for twenty hours at this temperature the reaction mixture gave a negative Gilman Test for Grignard Reagent. The mixture was cooled and a precipitate was removed by filtration. This solid did not show a typical PN infrared absorption peak and was soluble in dilute HCl. The filtrate was concentrated and an oil and two crystalline products were obtained.

Method (b)

Tetrachlorotetrakisdimethylamido-phosphonitrilic cyclic tetramer, $[PNCl(NMe_2)]_4$ (8.74 g., 0.0175 mole) was dissolved in 200 ml. of THF and 0.07 mole of methylmagnesium bromide, and 25 ml. of diethyl ether was added slowly. The reaction mixture was heated to reflux and held there for two hours. After this time the reaction mixture gave a negative Gilman Test (Michler's Ketone) for organometallic reagent. Toluene, 100 ml., was added and the THF was then removed by distillation. The solid product from this mixture was filtered and the precipitate washed with toluene. The filtrate was evaporated and a crystalline product precipitated. This material had a wide melting range. Recrystallizations from CCl_4, cyclohexane, benzene, and pentane were tried without success. An attempt to isolate cyclic material by distillation led to deamination of the product and the formation of a polymeric material.

3. Preparation of Bromophosphonitriles

(a) Reaction of $[PNCl_2]_4$ With PBr_3 and PBr_5

Five grams (0.0112 mole) of $[PNCl_2]_4$ was heated in 73 g. (0.27 mole) of PBr_3. No material boiling below 173° was observed during a heating period of four hours. The reaction mixture was cooled and 7.5 g. (0.047 mole) of bromine was added. No material boiling below the sublimation point of PBr_5 (sub. 105°) was observed on heating for two hours.

(b) Reaction of $[PNCl_2]_4$ With Acetylbromide

A solution of 2.3 g. (0.005 mole) of $[PNCl_2]_4$ in 50 ml. of acetyl bromide was heated at 77°C. for four hours. No material boiling below that of acetyl bromide was formed. A catalytic amount of $AlBr_3$ was added to the reaction mixture but upon reheating for a period of four hours, no evidence for the formation of acetyl chloride was observed.

(c) Reaction of $[PNCl_2]_4$ with $AlBr_3/Br_2$

To 2.3 g. (5 mmoles) of $[PNCl_2]_4$ in 50 ml. of carbon tetrachloride were added 3.2 g. (20 mmoles) of bromine and 0.1 g. of $AlBr_3$. The solution was kept at reflux (76°C) for sixteen hours. No reaction was apparent. An additional quantity of $AlBr_3$, 3.1 g. (11.65 mmoles), was added and the reaction mixture reheated to 76°C. A steady evolution of a gas ensued. The gas when collected in water gave a positive test with silver nitrate. The evolution of gas became negligible after twenty four hours.

The $AlBr_3$ was removed by addition of triethylamine and filtration of the addition compound that formed. No excess bromine was observed. The filtrate was concentrated by evaporation the solvent and excess amine. The residue, a dark gummy solid had an infrared spectrum similar to $[PNCl_2]_4$. This solid, however, was lost in attempting to purify it by recrystallization.

Octachlorocyclotetraphosphonitrile, 23.2 g. (0.05 mole) was added to a solution containing 160 g. (0.60 mole) of $AlBr_3$ and 32 g. (0.20 mole) of Br_2 in 500 ml. of CCl_4. The reaction was exothermic and the slow evolution of a brown colored gas that boiled below room temperature was observed. Presumably this was bromine monochloride (bp 5°C) but no attempt was made to further characterize this gas. The reaction mixture was heated for 128 hours then the unreacted bromine and solvent were removed by distillation. Isolation of product from the dark viscous resudue was not attempted after it became evident that there was little need for this compound.

4. Direct Preparation of Methylchlorophosphonitrilic Cyclics from Methylphosphorus Tetrachloride and Ammonium Chloride

a. Reaction of $MePCl_2$, Br_2 and NH_4Br

Methylphosphorus dichloride, (117 g., 1.00 mole) was combined with bromine (233 g., 1.46 moles) and freshly prepared ammonium bromide (196.0 g., 2.0 moles) in hexachlorobutadiene. The reaction mixture was slowly heated to 120°. Because the bromine color disappeared, additional bromine (296 g., 1.85 moles) was added and the mixture again heated. Evolution of HX started at 80°. After heating and stirring for forty-eight hours, 90% of the theoretical amount of HX had been evolved. The final temperature was approximately 140°C and after an additional two days no appreciable amount of HX evolved. The reaction products were recovered after removal of the solvent, but appeared to be primarily short chain linear compounds with relatively high halogen content. No further characterization was attempted.

b. Preparation of $MePCl_4$

The preparation of CH_3PCl_4 was accomplished by allowing 14.2 g. (0.20 mole) of liquid chlorine to distill into a carbon tetrachloride solution containing 23.4 g. (0.20 mole) of CH_3PCl_2. Exact Stoichiometry was used because of the distinct possibility that excess chlorine would attack the methyl groups. The solid that precipitated analyzed well for four equivalents of chlorine (gravimetric) or five equivalents of acid when hydrolyzed and titrated with base of pH of 7 (i.e., also one P-OH titrated). The proton n.m.r. spectrum showed a single triplet consistent with the assigned structure, CH_3PCl_4. This material is very easily hydrolyzed and must be handled in an inert atmosphere.

c. Reaction of $MePCl_4$ and NH_4Cl

A reaction was carried out with both reagents freshly prepared. Tetrachloromethylphosphorane (0.10 mole), was added to 0.78 mole of freshly prepared NH_4Cl in 200 ml. of hexachlorobutadiene in an inert atmosphere. Evolution of HCl began at 90°C and continued slowly during the next forty-eight hours. Approximately 26%, 0.11 mole, of HCl was evolved during this period. It was necessary to raise the temperature in order to maintain HCl evolution; however, even at 150°C very little further evolution of HCl took place. Upon addition of more freshly prepared NH_4Cl (0.26 mole) an additional 0.02 mole of HCl evolved during the next seven days, while the temperature was raised to 175°.

After filtering the solution to remove unreacted NH_4Cl, the filtrate was distilled. Surprisingly, there was very little residue left after distillation. An infrared spectrum of the distillate, however, indicated that some product may have come over with the hexachlorobutadiene.

Recrystallization of the material recovered from the sides of the still gave the first definite indication that methylphosphonitrilic cyclics had been prepared. Three different species were isolated from this small amount of material:

1. m.p. 175-181°, infrared spectrum indicated a phosphonitrilic halide with methyl groups. A molecular weight by vapor pressure osmometry was 363. The proton n.m.r. spectrum, with the phosphorus decoupled, showed a single methyl peak. The compound was tentatively identified as a non-geminal tetrachloro-tetramethyl cyclic tetramer.

2. m.p. 80-92°, the infrared spectrum was consistent with that of a methyl phosphonitrilic cyclic tetramer. Degradation occurred during subsequent recrystallizations.

3. m.p. 163-163.5°, the infrared spectrum is consistent with methylphosphonitrilic cyclic trimer, molecular weight 307. N.m.r. spectrum had a single methyl peak. This was therefore assumed to be the non-geminal <u>cis</u> isomer of trichlorotrimethylphosphonitrilic cyclic trimer, $[MePNCl]_3$.

Methylphosphorus dichloride, 11.7 g. (0.10 mole) was dissolved in 200 ml. of carbon tetrachloride and chlorine, 7.1 g. (0.10 mole) was slowly passed through the solution. A copious precipitate of tetrachloromethylphosphorane formed. The solvent was changed by distilling the CCl_4 and adding chlorobenzene. A solution of ammonia 6.8 g. (0.40 mole) in 500 ml. $CHCl_3$ was treated with 14.6 g. of hydrochloric acid gas (0.40 mole) and ammonium chloride formed as a finely divided precipitate. The solvent was changed to chlorobenzene. The two chlorobenzene slurries were combined and then the reaction mixture was heated. At 90°C the evolution of HCl began and the temperature was slowly increased up to the reflux temperature of the solvent, 132°C. During a forty-eight hour period 0.38 moles of HCl (95% of the theoretical amount) was evolved.

The excess NH_4Cl was removed by filtration, the chlorobenzene was removed by distillation. The reaction product was recrystallized from benzene, pentane and cyclohexane. The yield of crude product, 2.1 g. represented less than a 25% yield, and obviously some of this material was a hydrolyzed species. Portions of this crude product were recrystallized from pentane and sublimed less than 0.5 g. of material with a satisfactory infrared spectrum was isolated by these techniques.

5. Reactions of Methylphosphonitriles

a. Preparation of Derivatives of $[MePNCl]_n$

(1) Preparation of $[MePN(NH_2)]_n$

Methylphosphorus dichloride, 11.7 g. (0.10 mole) was dissolved in 200 ml. of CCl_4 and then chlorine, 7.1 g. (0.10 mole) was slowly bubbled through the solution. The precipitate, $MePCl_4$ was filtered then placed in 500 ml of chlorobenzene. Ammonia, 7 g. (0.40 mole) and HCl (0.40 mole) were combined in chloroform to give ammonium chloride. This product was filtered then added to the chlorobenzene - $MePCl_4$ slurry. The reaction mixture was heated slowly to 132° and during a forty-eight hour period 32 moles

(80% of theory) of HCl was evolved. The mixture was cooled and ammonia was slowly passed through until no exothermic reaction could be detected. The mixture was filtered to remove the NH_4Cl and NH_3 (g) was again passed through for several minutes. The very small amount of NH_4Cl that was formed was filtered and the solvent was distilled. The product was recrystallized from benzene then hexane. Each successive recrystallization caused large losses without eliminating the strong infrared absorption at 950 $cm.^{-1}$. No pure, hydrolysis free product was obtained.

(2) Preparation of $[MePN(NMe_2)]_n$

Methylphosphorus tetrachloride, 18.8 g (0.10 mole), prepared in carbon tetrachloride from equi-molar quantities of chlorine and $MePCl_2$ was filtered and placed in chlorobenzene. Ammonium chloride, 21.2 g (0.40 mole), prepared from qui-molar quantities of NH_3 and HCl was added to the above slurry, and this reaction mixture was heated to 132°C. During a nine hour period 0.4 moles of HCl was evolved. The excess NH_4Cl was filtered, the solvent removed by distillation and the product dissolved in 500 ml of benzene. Dimethylamine, > 0.2 mole, was distilled into the solution and a solid presumed to be dimethylamine hydrochloride was removed by filtration. The product weighed 2.8 g. for a 27% yield of impure $[MePN(MNe_2)]_{3,4}$. A small portion of this crude product was recrystallized, m.p. 125-27°C.

b. Oxidation of $(MePNCl)_{3,4}$

A special apparatus was constructed to permit several consecutive sublimations without exposure to the atmosphere. A pyrex tube, 25 x 300 mm, was sealed at one end and then heated and slightly elongated at 50 mm intervals to form a container consisting of five bulbs in series. A small quantity of $(MePNCl)_{3,4}$ was placed in this tube and then the tube was connected to a vacuum line. The end bulb was heated in an oil bath at > 100°/0.1 Torr and the second bulb was cooled with a copper coil containing circulating water. Most of the material slowly sublimed into the second bulb. The first bulb was removed with a torch without breaking the vacuum and the process was repeated. After four such sublimations the material was pure $(MePNCl)_3$. The stability of this material to dry oxygen was measured by comparing elemental analysis, infrared and n.m.r. spectra of the material before and after a twenty-four hour exposure to a stream of oxygen that had been passed through a container of H_2SO_4 then NaOH pellets.

c. Hydrolysis of $(MePNCl)_{3,4}$

Using a similar apparatus for several consecutive sublimations, a material was obtained that analyzed for pure $(MePNCl)_3$. The stability of this cyclic towards water was assessed by passing a stream of nitrogen through a container of water and then over the material. A comparison of the elemental analyses, infrared and n.m.r. spectra showed the changes that occur when $(MePNCl)_n$ is exposed to H_2O.

d. Reaction of $[(CH_3)_2PN]_3$ with Br_2

In 50 ml. of freshly distilled carbon tetrachloride, 8.9 mmoles of bromine was added to 0.5 g. (2.22 mmoles) of $[(CH_3)_2PN]_3$ (m.p. 187-9°). The reaction was carried out in a nitrogen atmosphere. During several hours of stirring at room temperature a solid formed but the bromine color did not disappear. After heating the mixture for 2 hr. the solution was cooled and filtered. Approximately 0.25 g. of solid, m.p. 220-235°, was recovered. Upon recrystallization from chloroform this solid melted at 235-6°. Elemental analysis agrees with the formula $P_3N_3(CH_3)_5(CH_2Br)$.

FIGURES

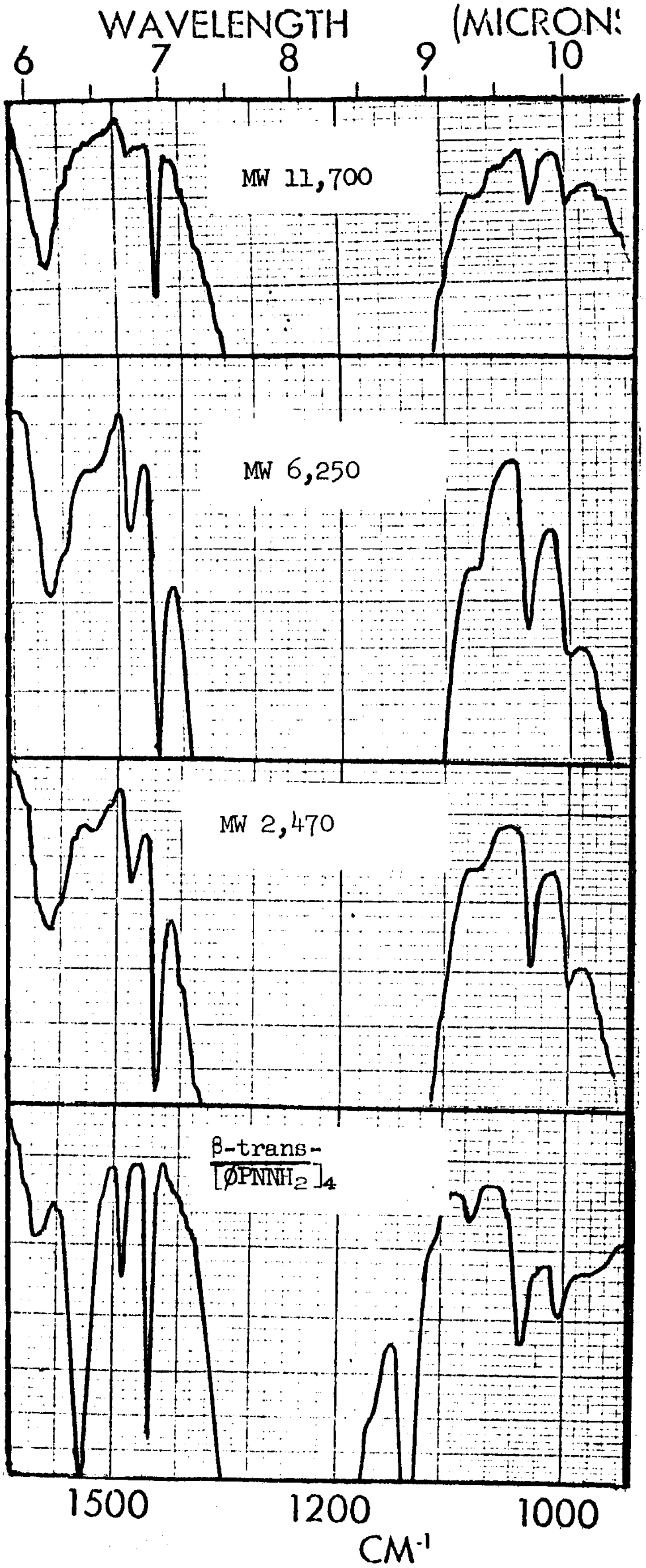


Figure 1.

Infrared Spectra of Polymers Derived From β-trans-[∅PNNH$_2$]$_4$

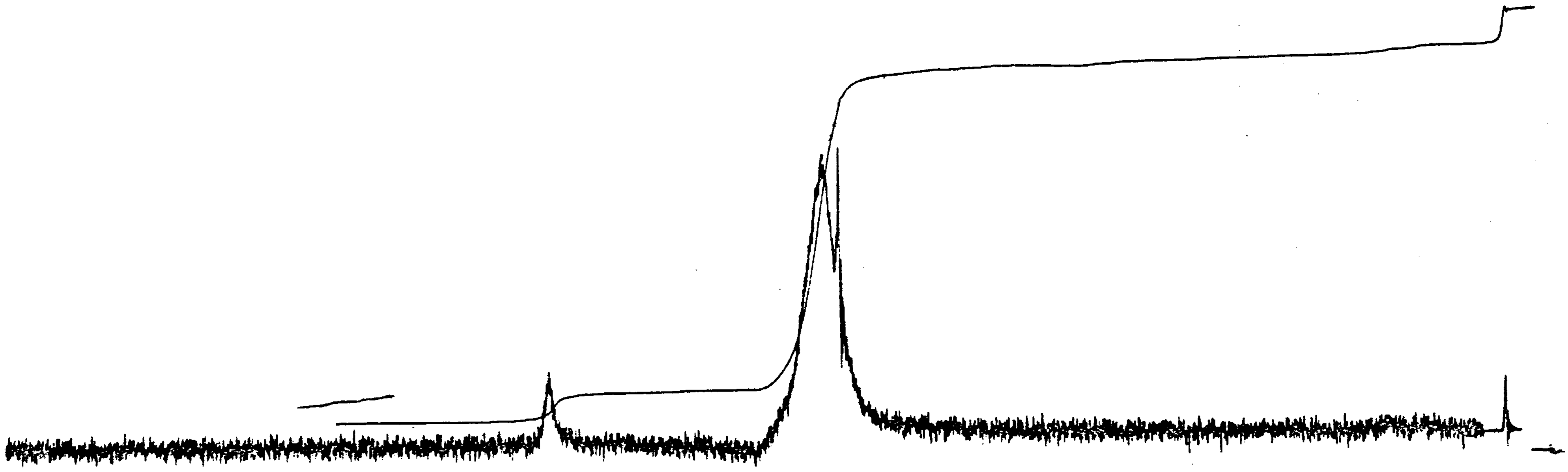


FIGURE 2

Proton n.m.r. Spectrum of Product $\phi_5P_3N_3NH_2$ + $Cl_3CC(O)NCO$

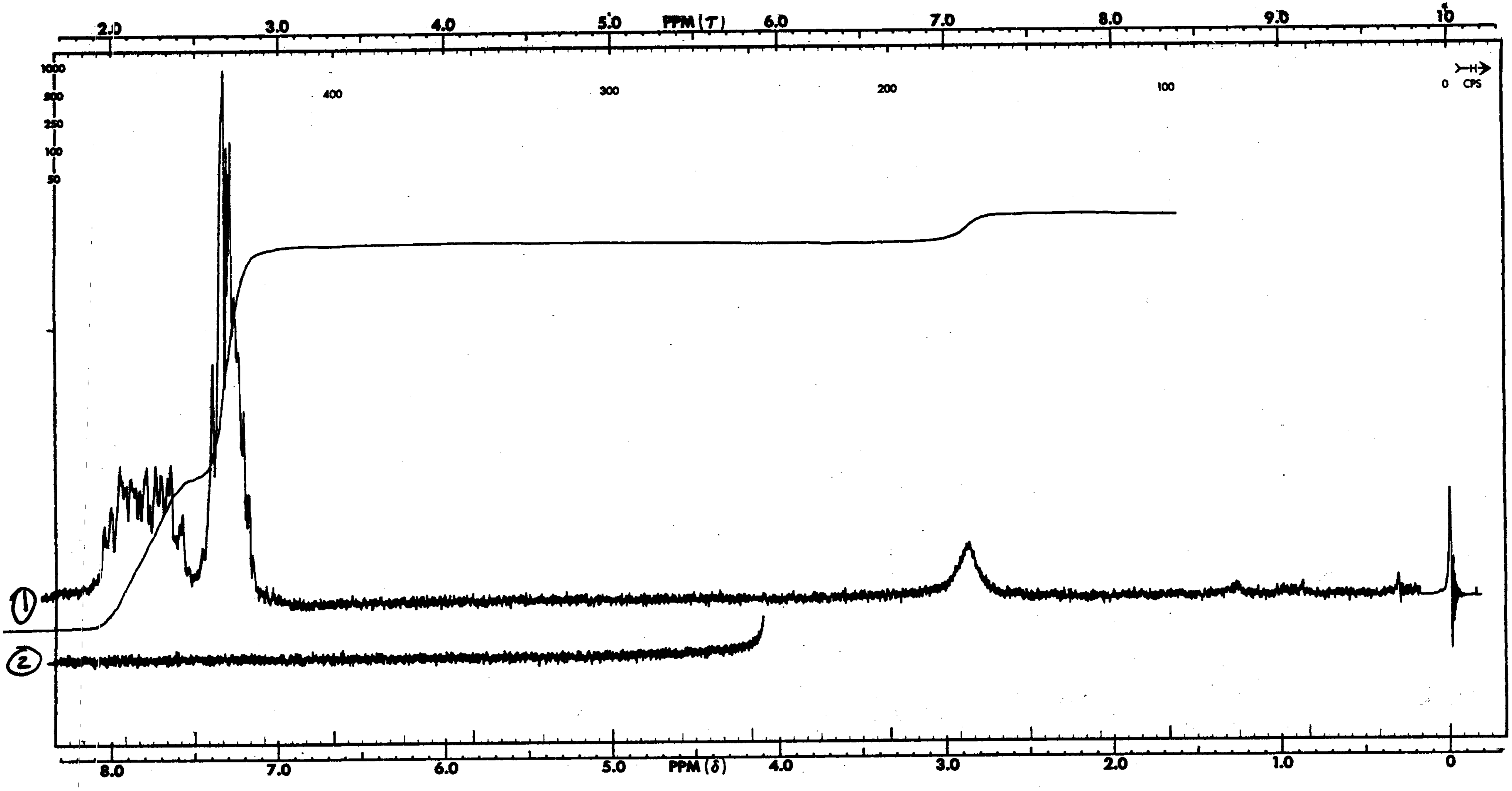
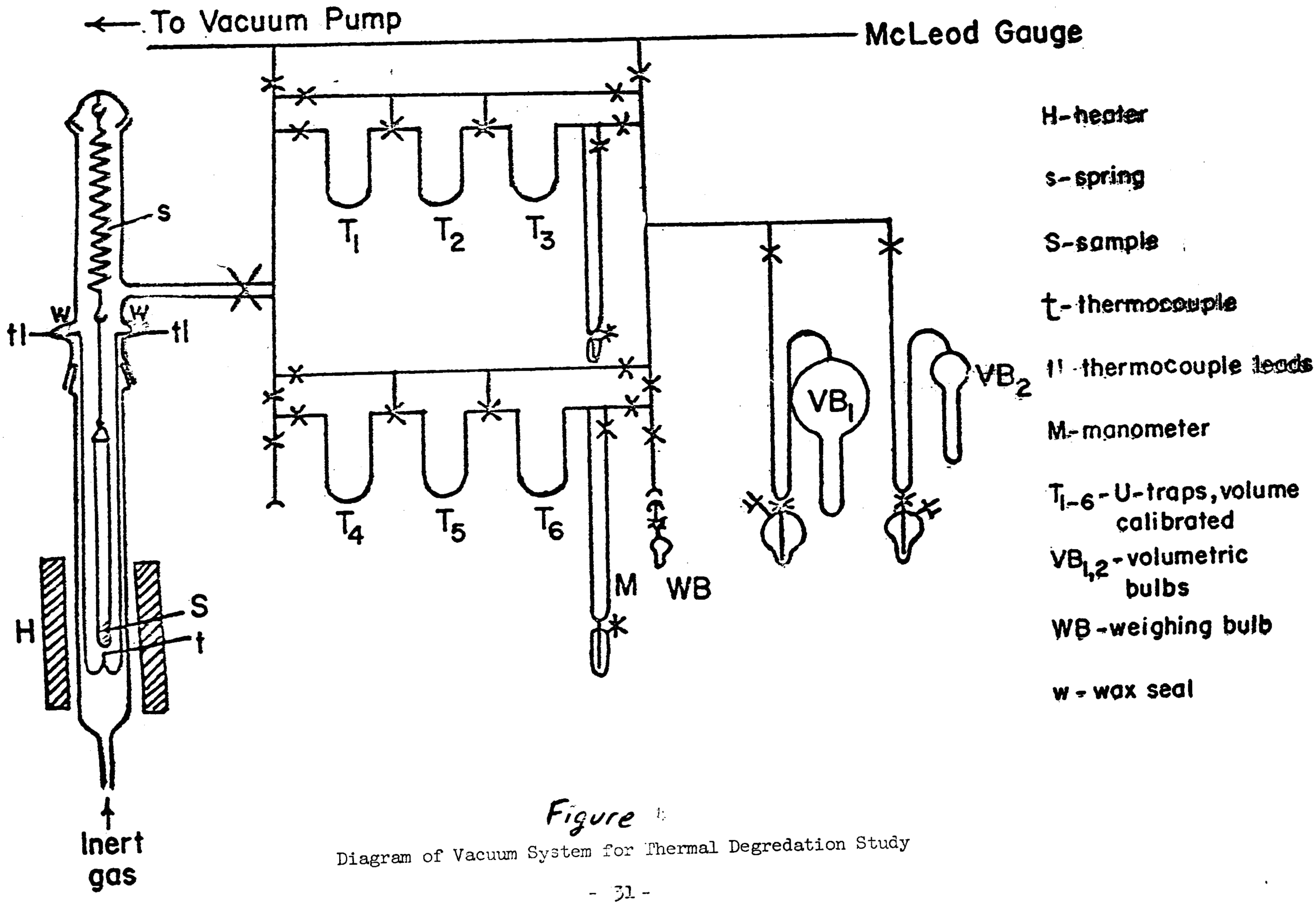


FIGURE 3

Proton n.m.r. Spectrum $\emptyset_5P_3N_3NH_2$



Figure

Diagram of Vacuum System for Thermal Degredation Study

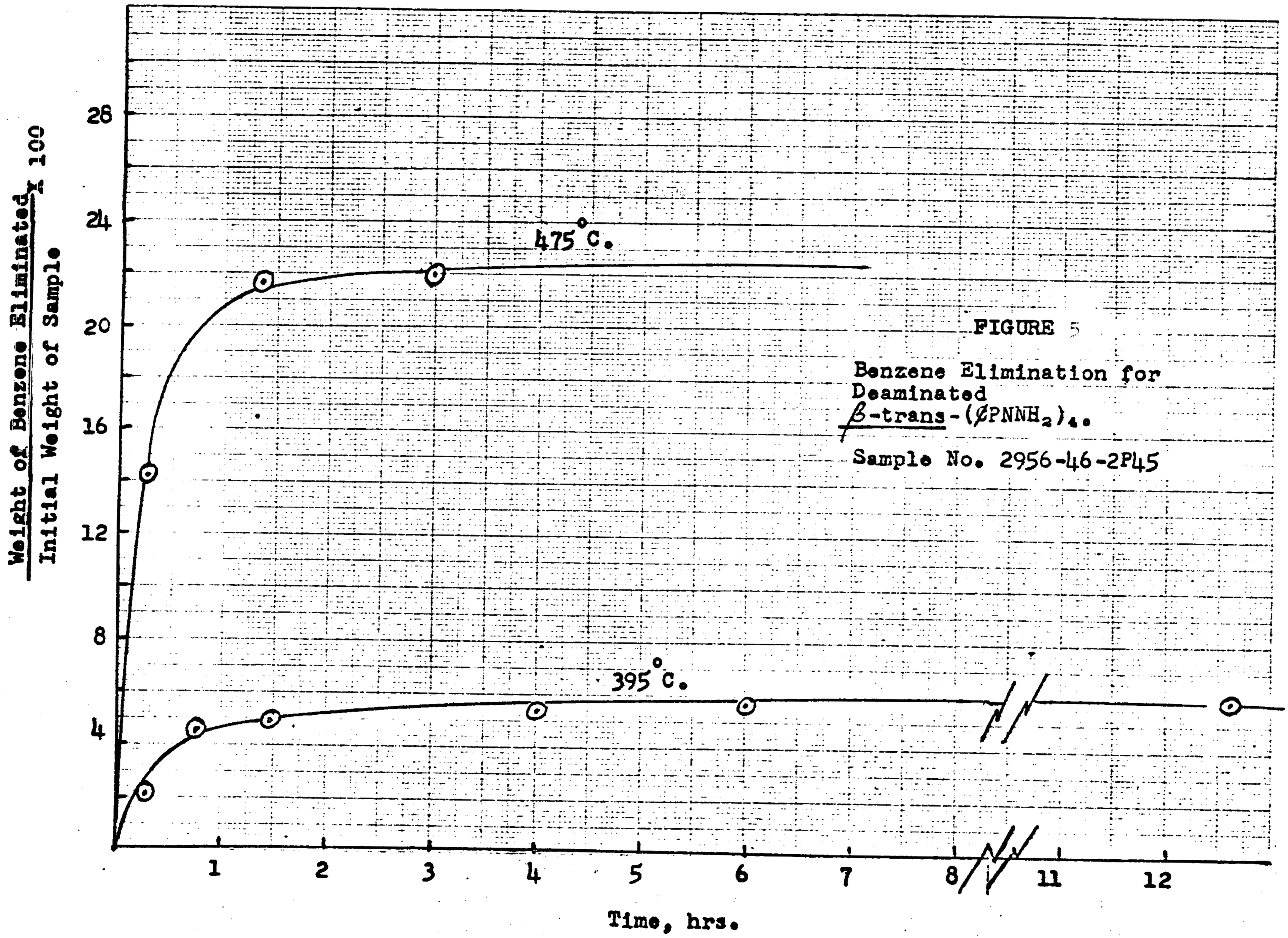


FIGURE 5

Benzene Elimination for Deaminated β-trans-$(\varnothing PNNH_2)_4$.

Sample No. 2956-46-2P45

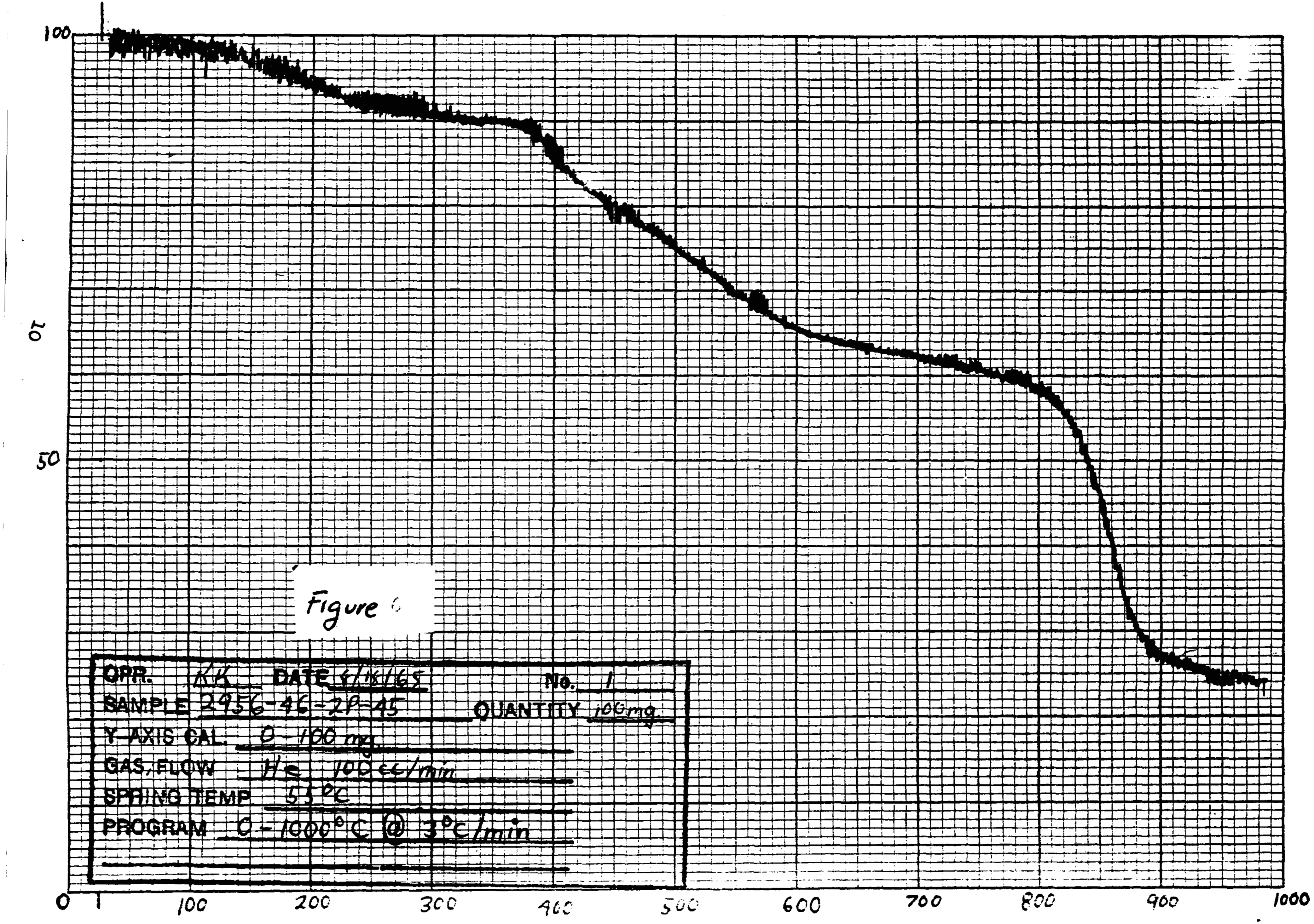
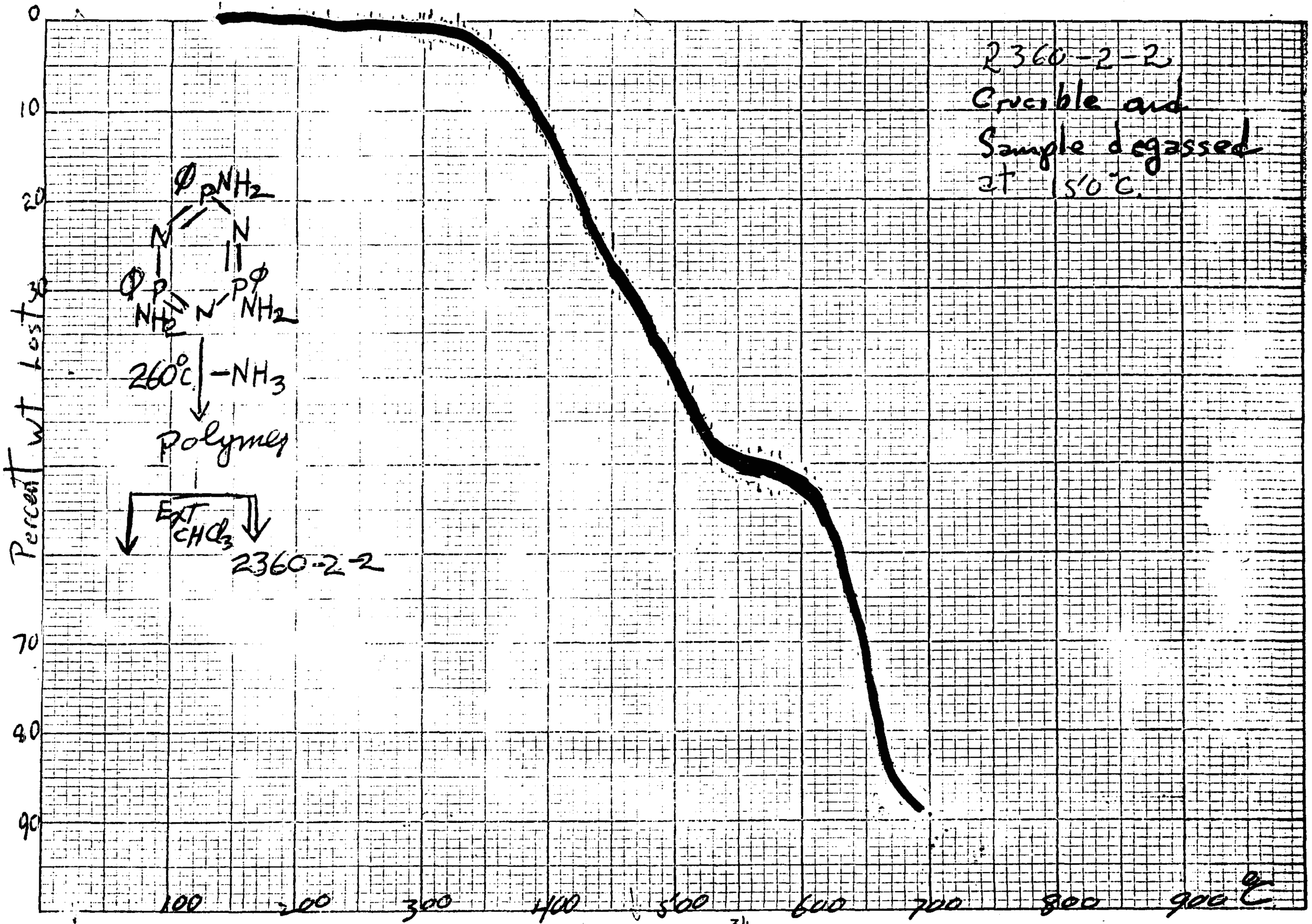


Figure 6

OPR. KK DATE 6/18/65 No. 1
SAMPLE 2956-46-2P-45 QUANTITY 100mg.
Y-AXIS CAL. 0 - 100 mg.
GAS, FLOW He 100 cc/min
SPRING TEMP 53 °C
PROGRAM 0 - 1000° C @ 3°C/min

FIGURE 7


2360-2-2
Crucible and
Sample degassed
at 50°C.
Percent wt Lost
0
10
20
30
70
80
90
100
200
300
400
500
600
700
800
900 °C
260°C
$-NH_3$
Polymer
Ext $CHCl_3$
2360-2-2

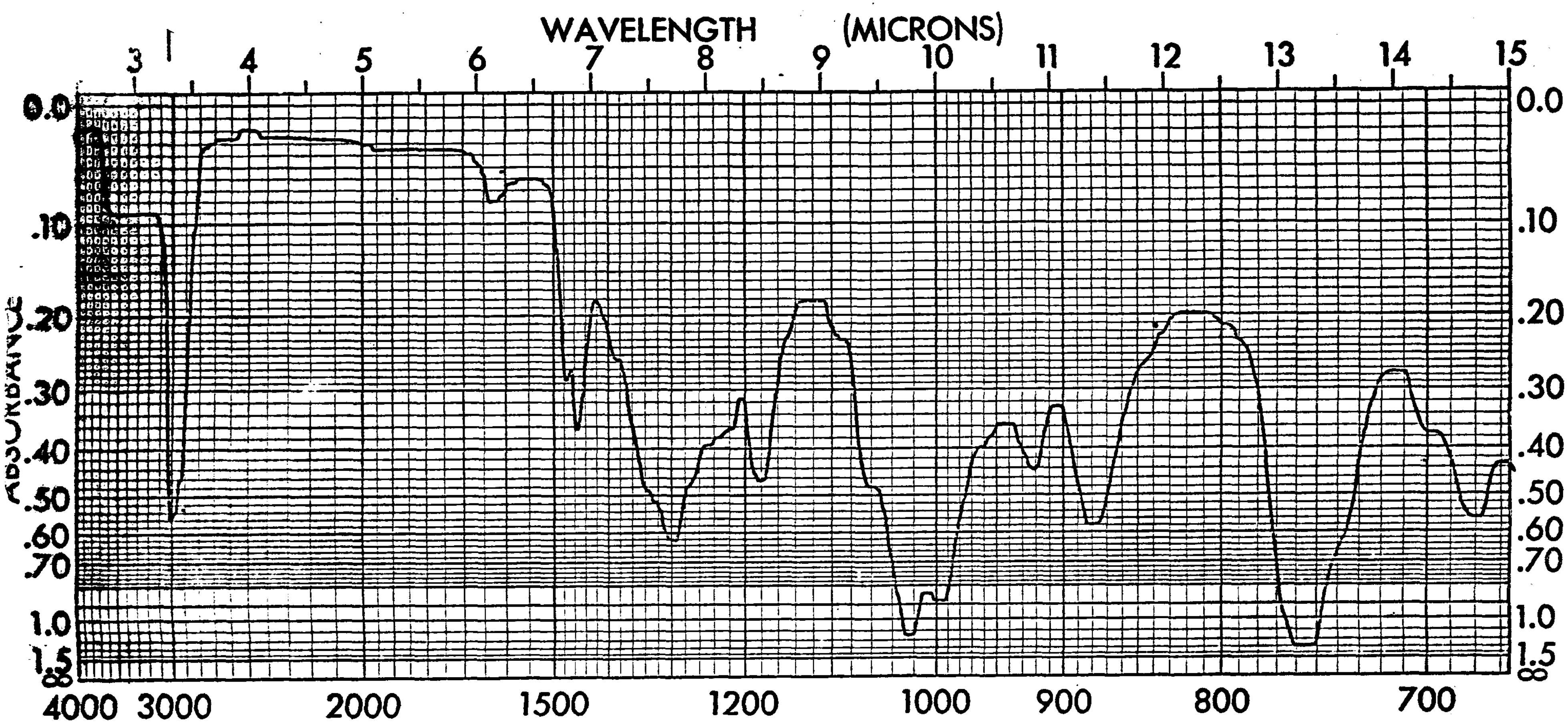


Figure 8.

Infrared Spectrum of Product, Reaction of $[PNCl_2]_4$ with CH_3MgBr

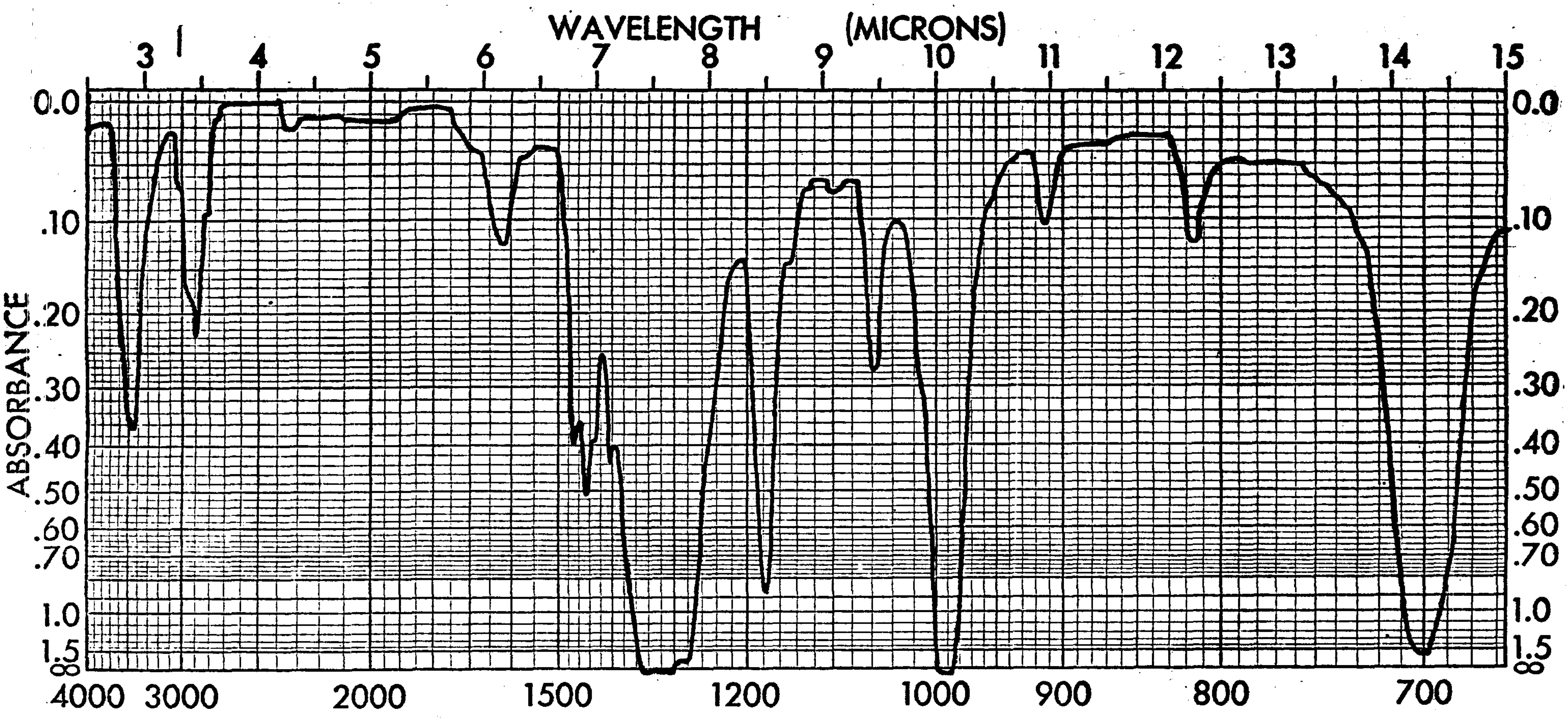


Figure 9.

Infrared Spectrum of [PNCl(NMe$_2$)]$_4$, m.p. 192-4°

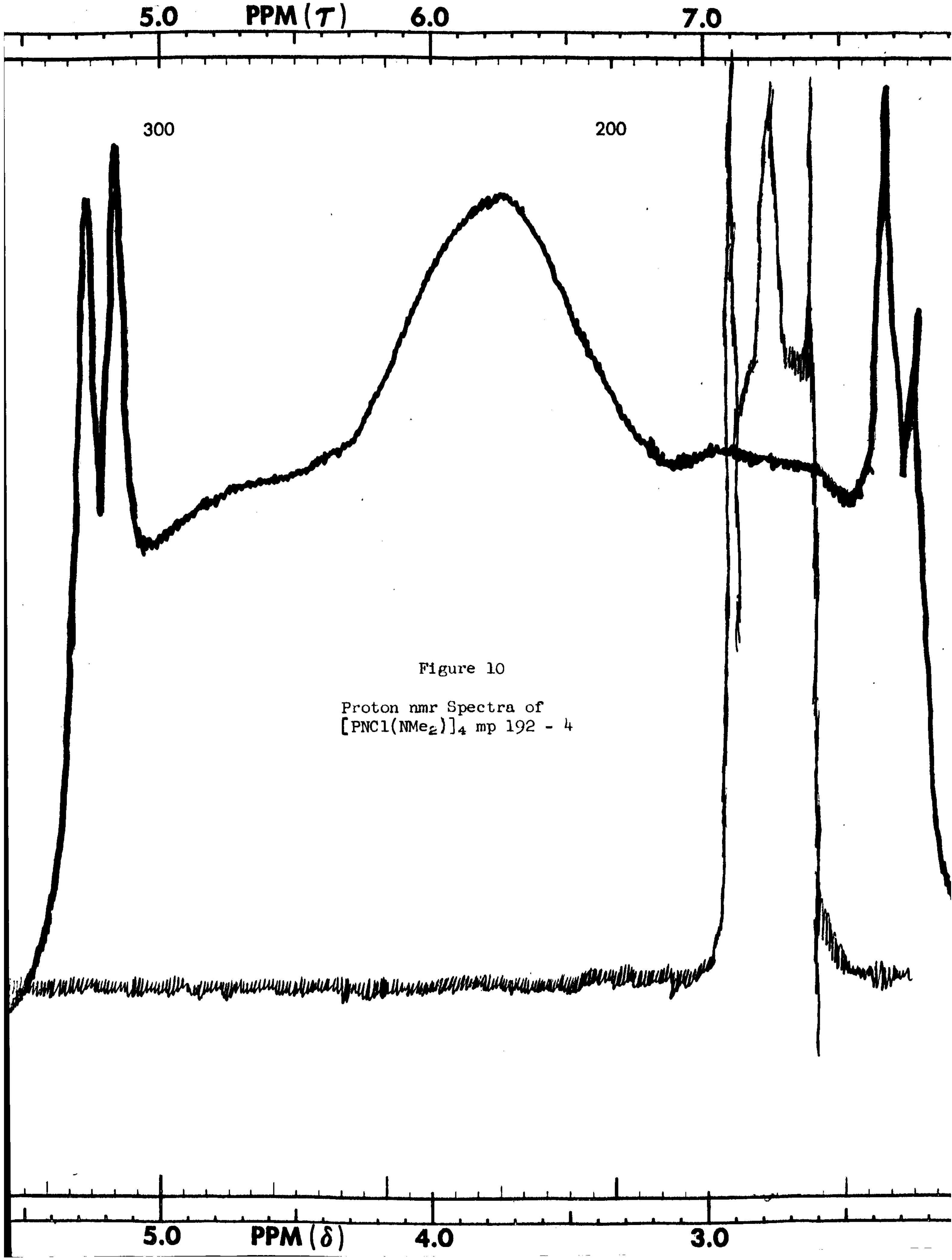


Figure 10

Proton nmr Spectra of
$[PNCl(NMe_2)]_4$ mp 192 - 4

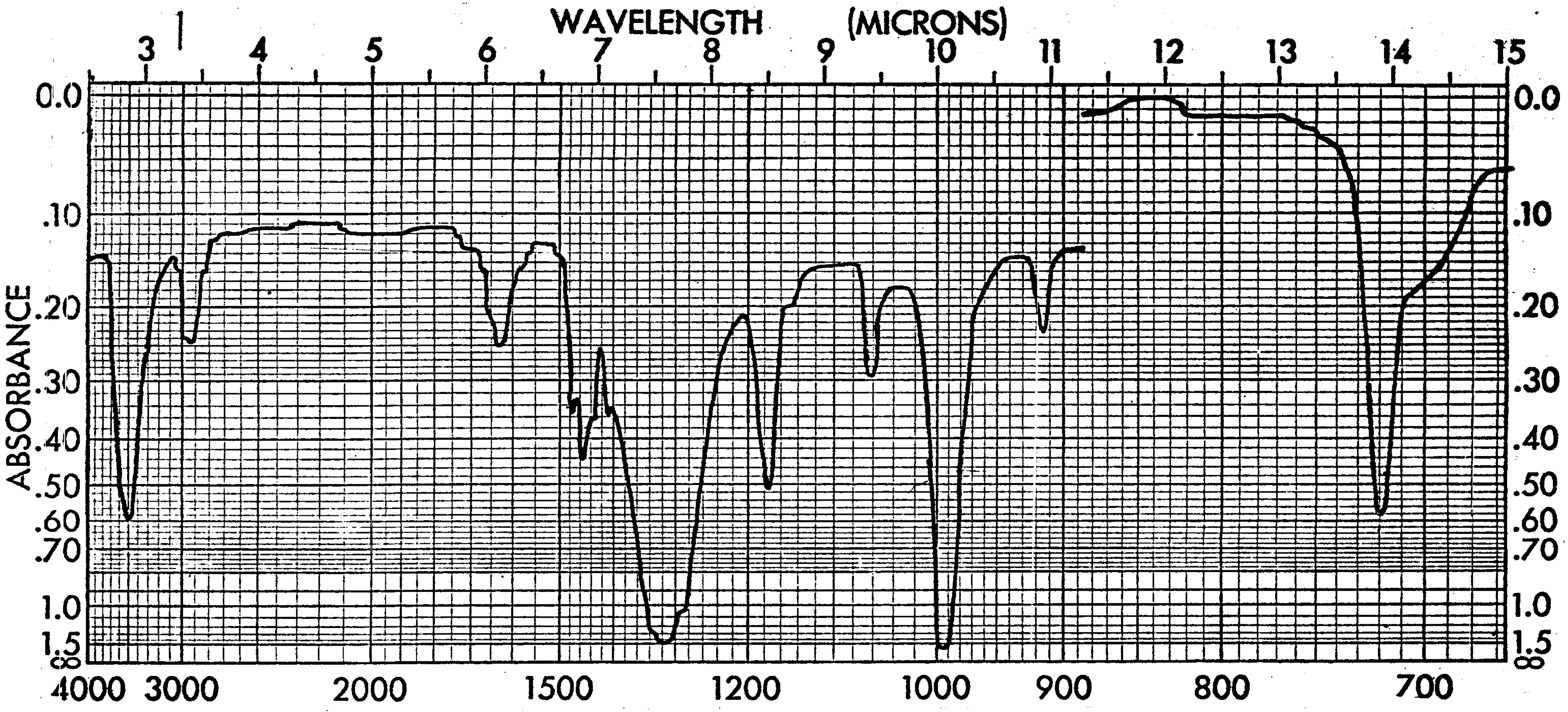


Figure 11

Infrared Spectrum of $[PNCl(NMe_2)]_4$, m.p. 156-60°

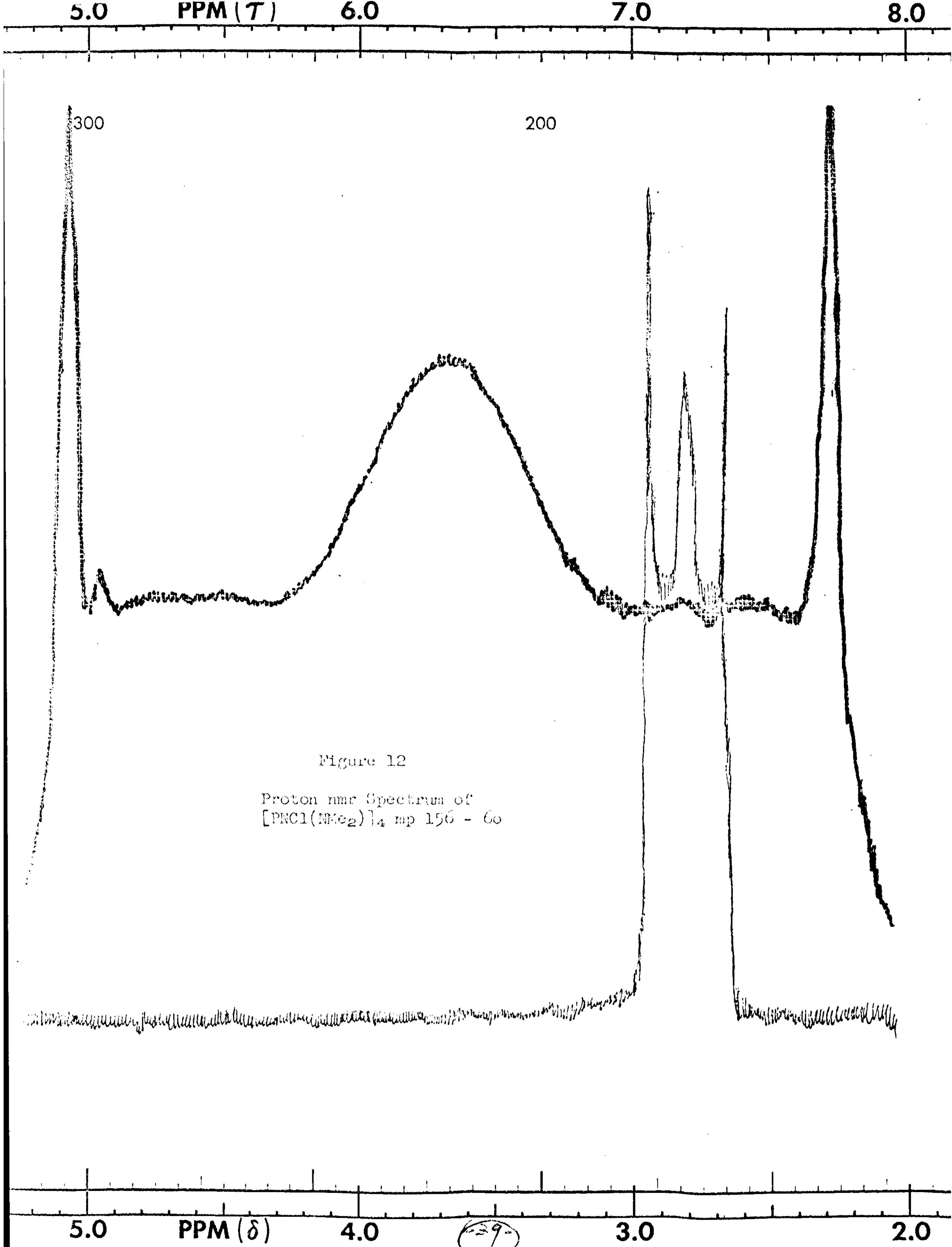
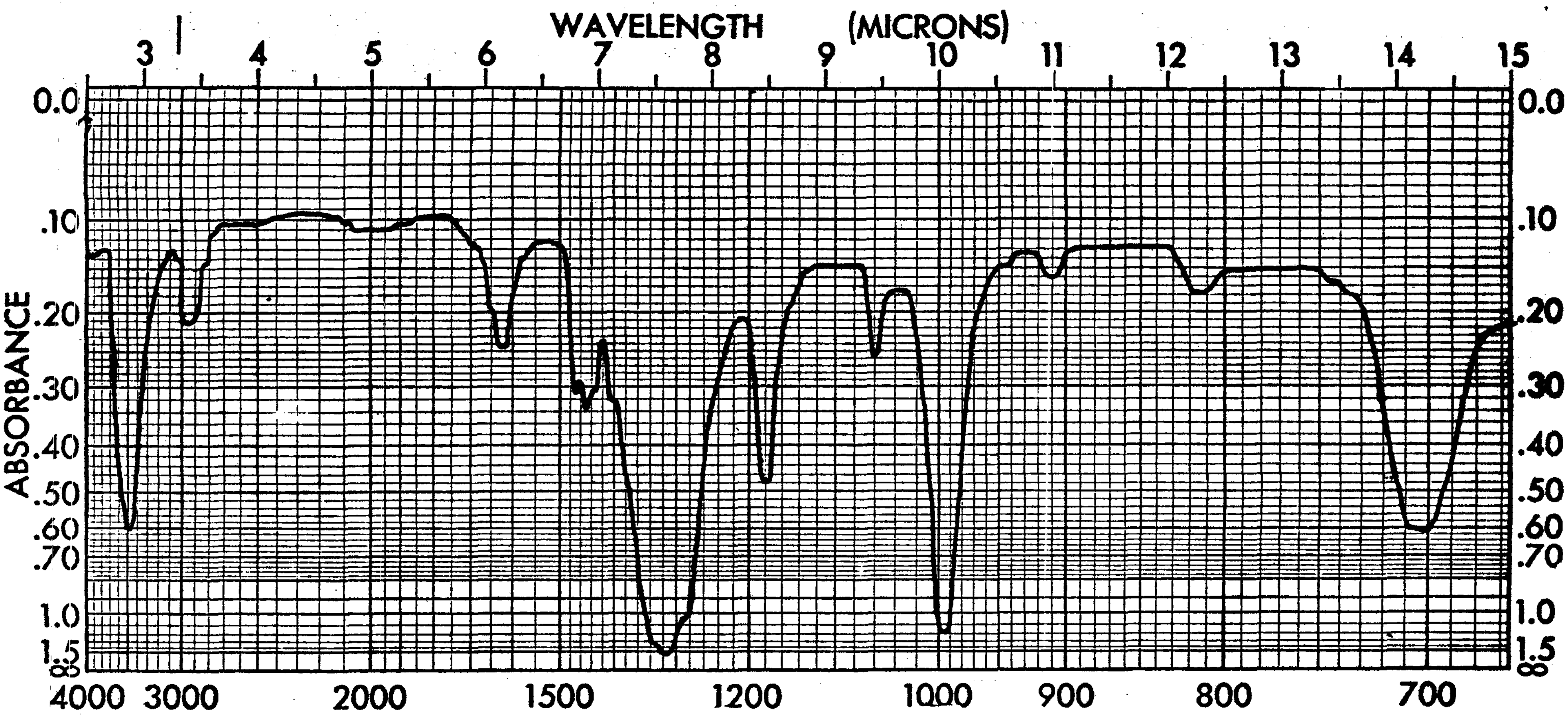


Figure 12

Proton nmr Spectrum of
$[PNCl(NMe_2)]_4$ mp 156 - 60



<u>**Figure** 13</u>

Infrared Spectrum of $[PNCl(NMe_2)]_4$, m.p. 152-177°

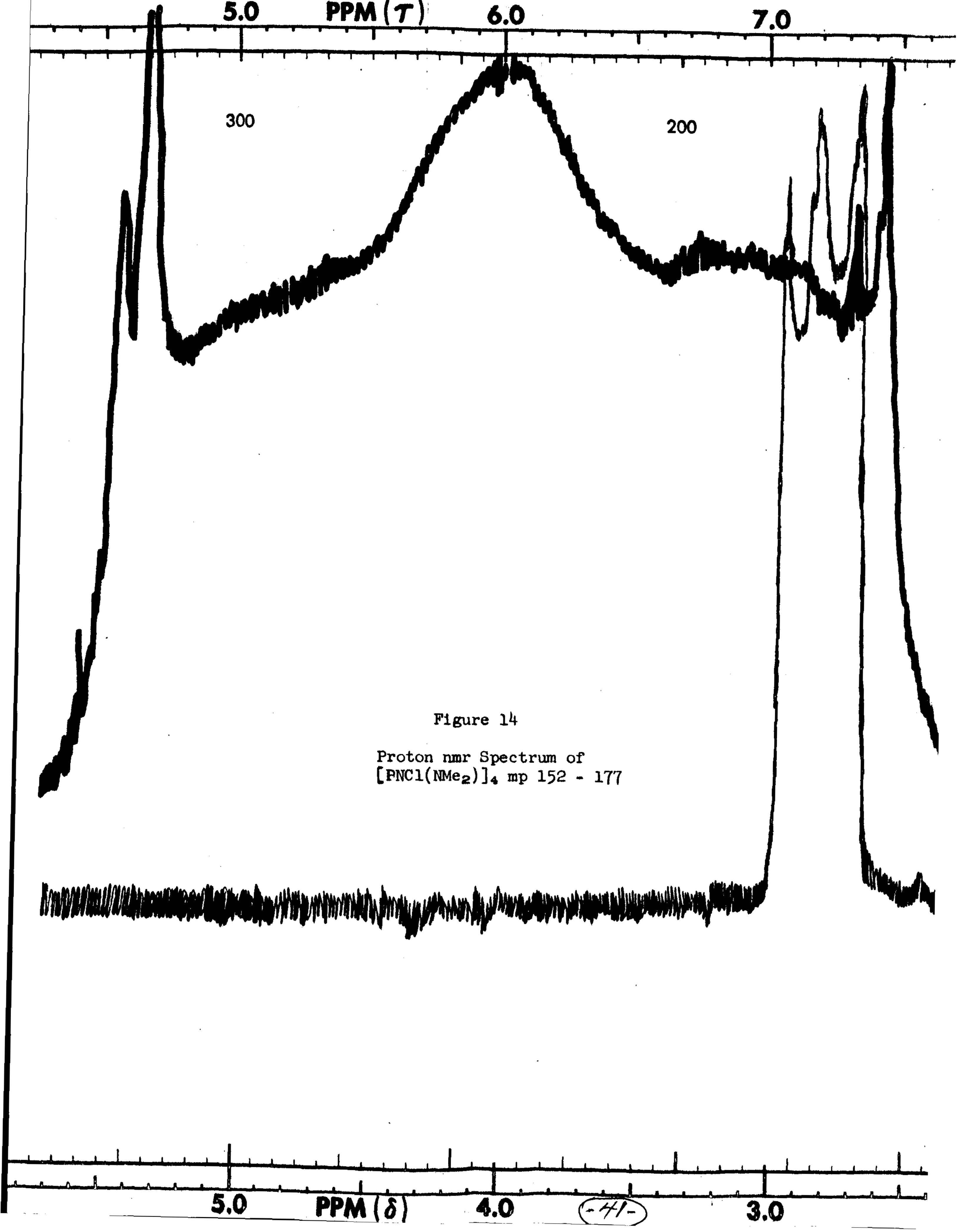


Figure 14

Proton nmr Spectrum of
[$PNCl(NMe_2)]_4$ mp 152 - 177

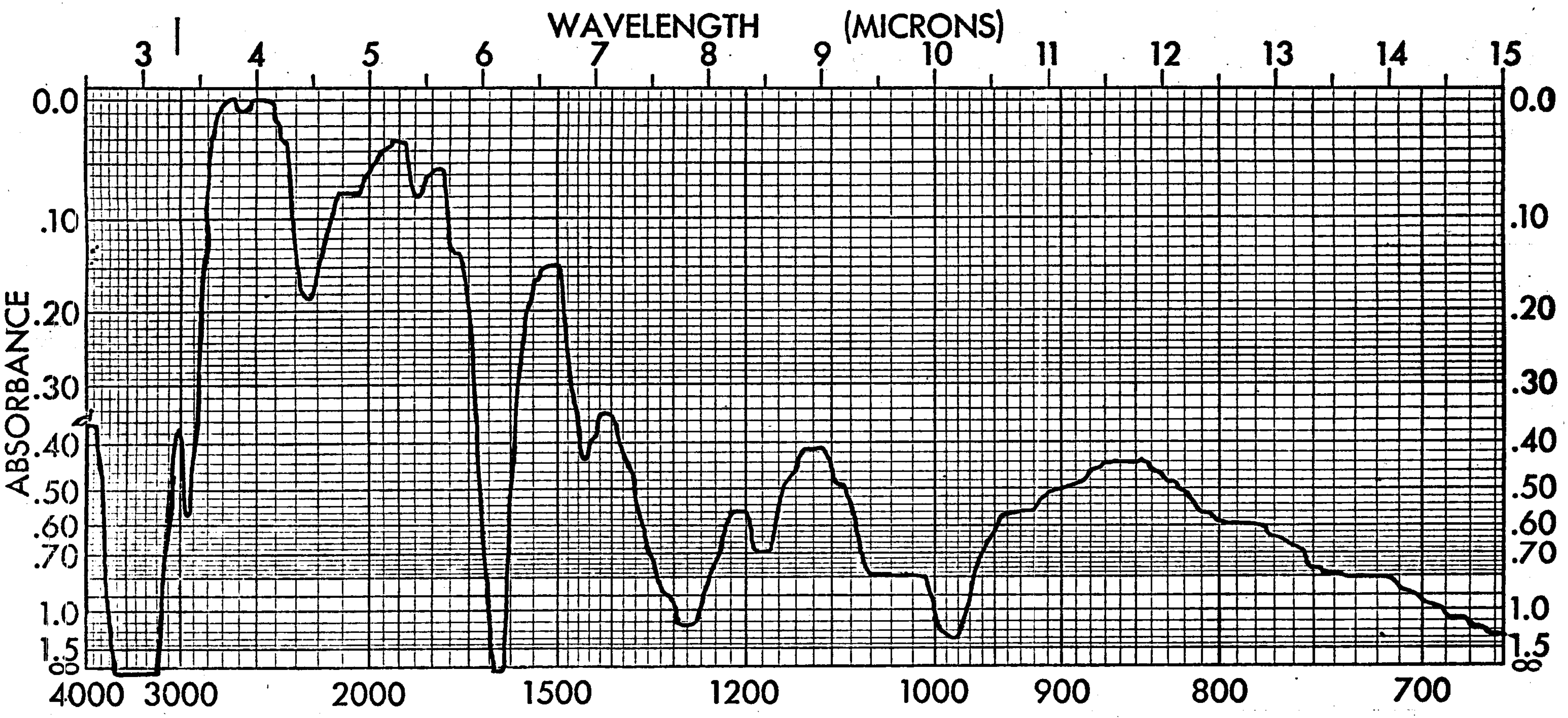


Figure 15

Infrared Spectrum of Product of Reaction of [PNCl(NMe$_2$)]$_4$ with CH$_3$MgBr

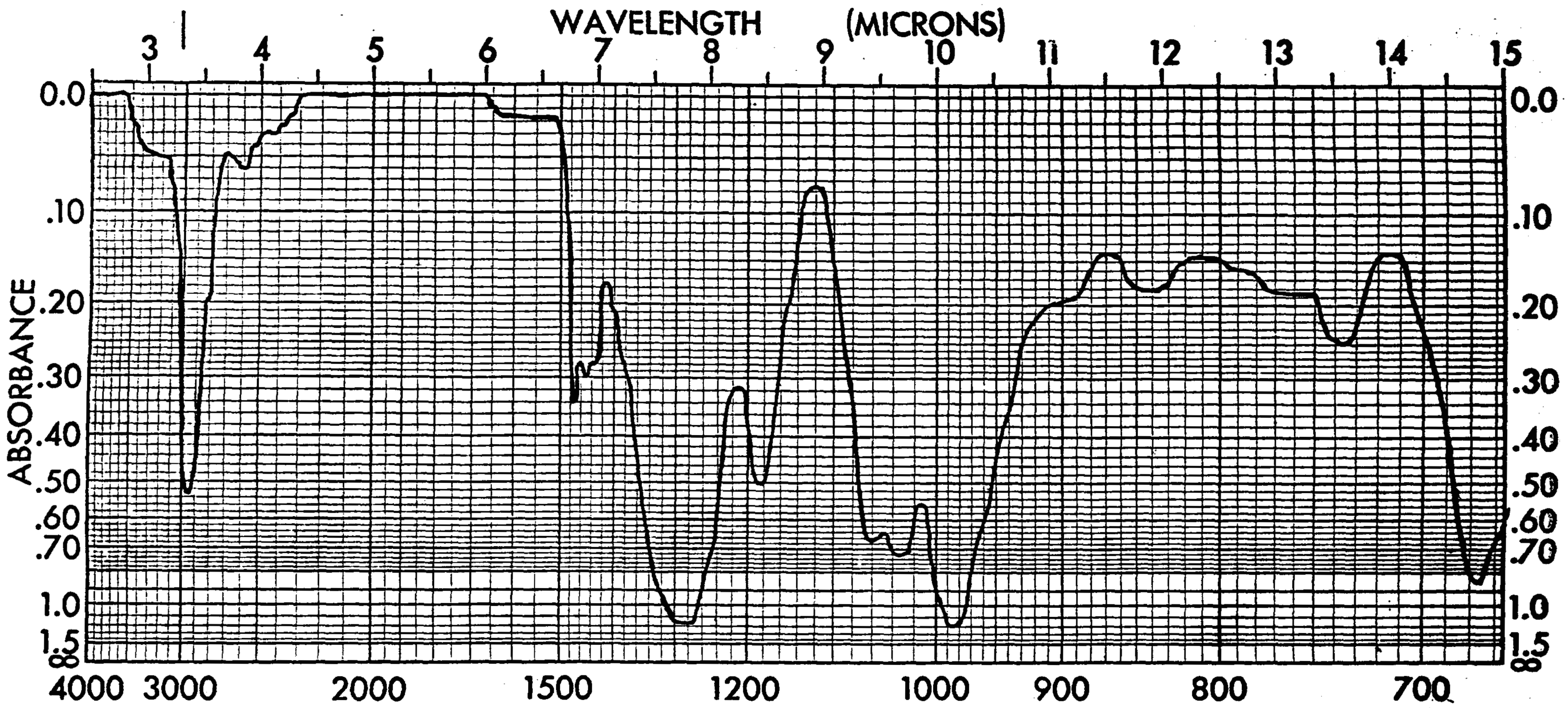


Figure 16

Infrared Spectrum of Product of Reaction of $[PNCl(NMe_2)]_4$ with CH_3MgBr

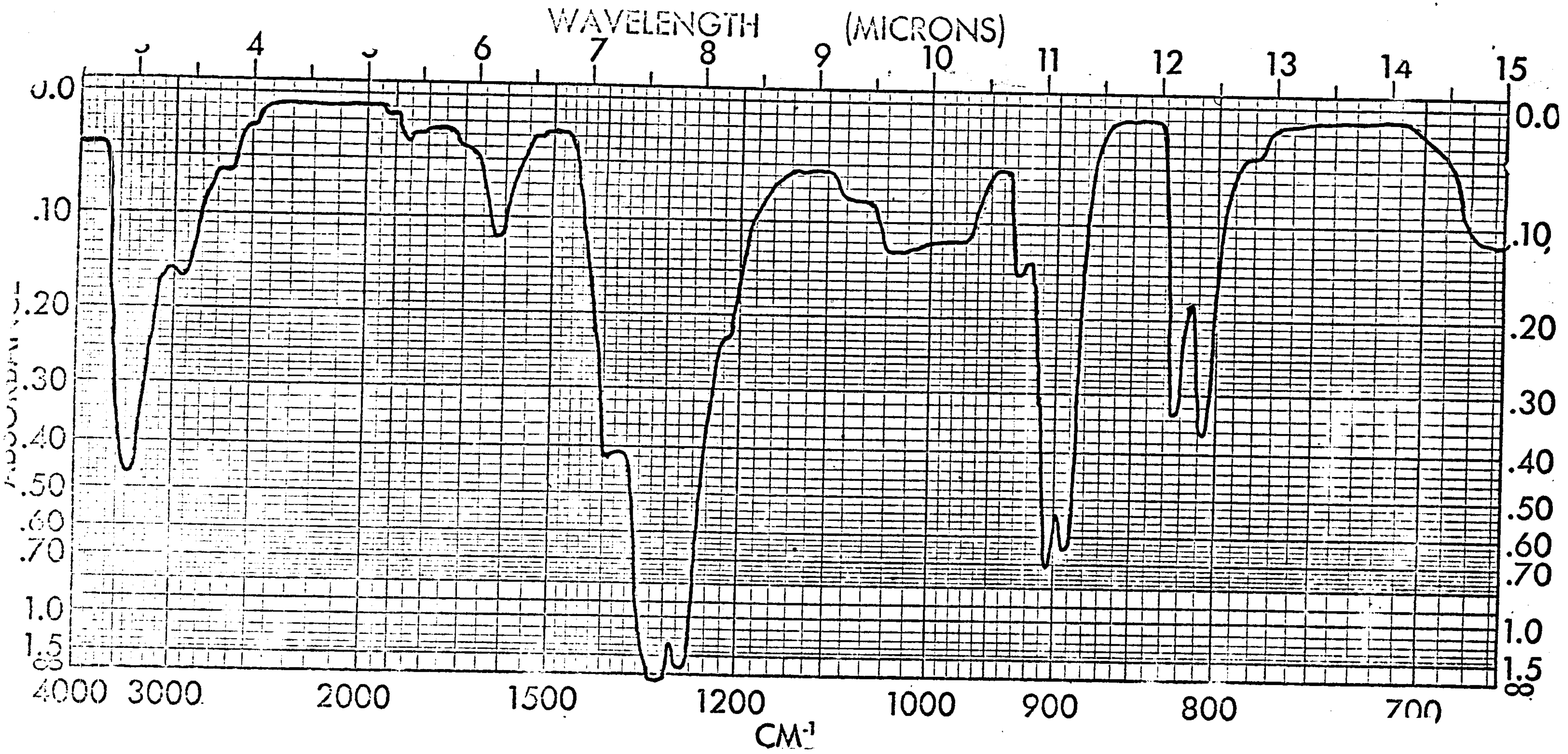


Figure 17

Infrared Spectrum of [CH_3 PNCl]$_4$ mp 175 - 181

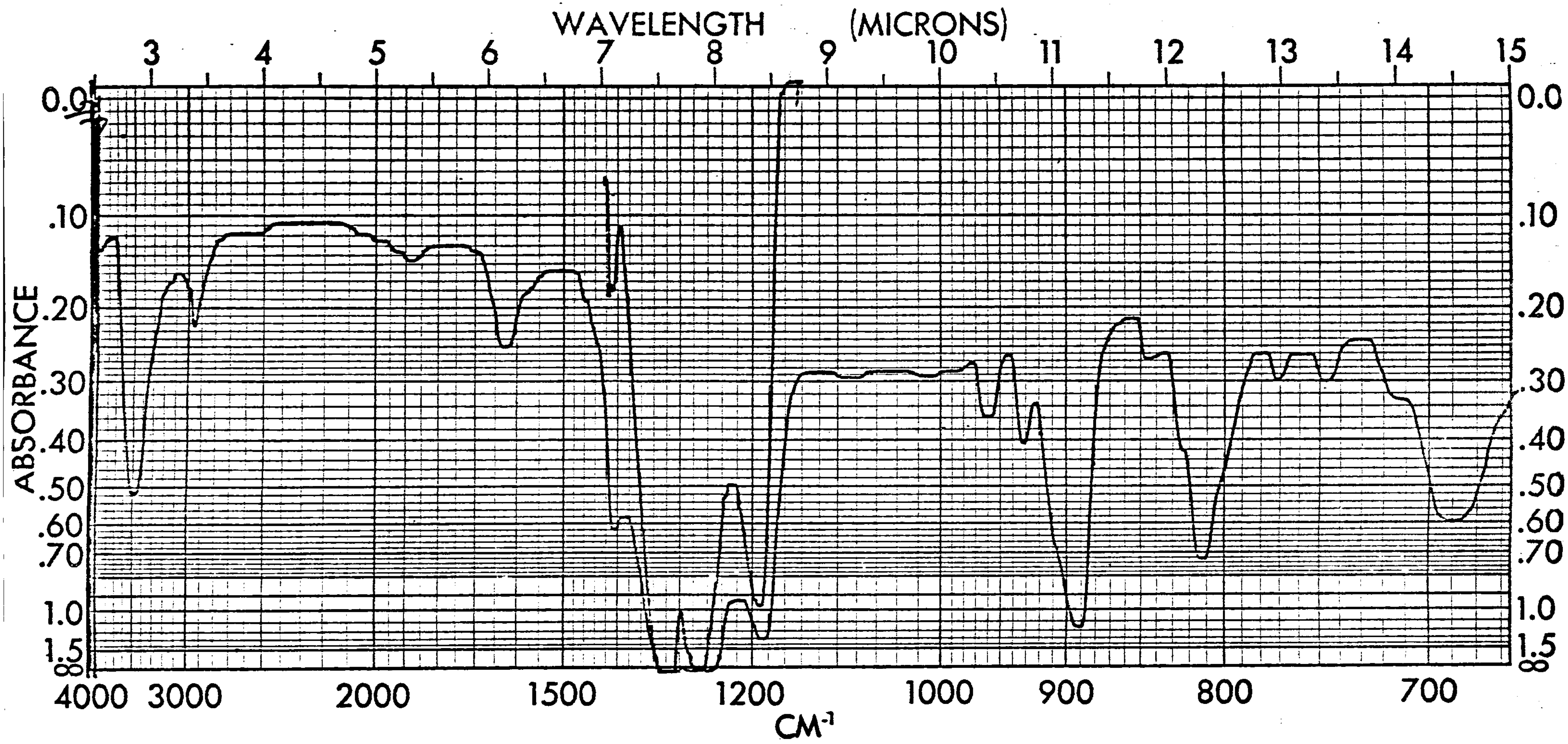


Figure 18

Infrared Spectrum of $[CH_3\ PNCl]_4$ mp 80 - 92°

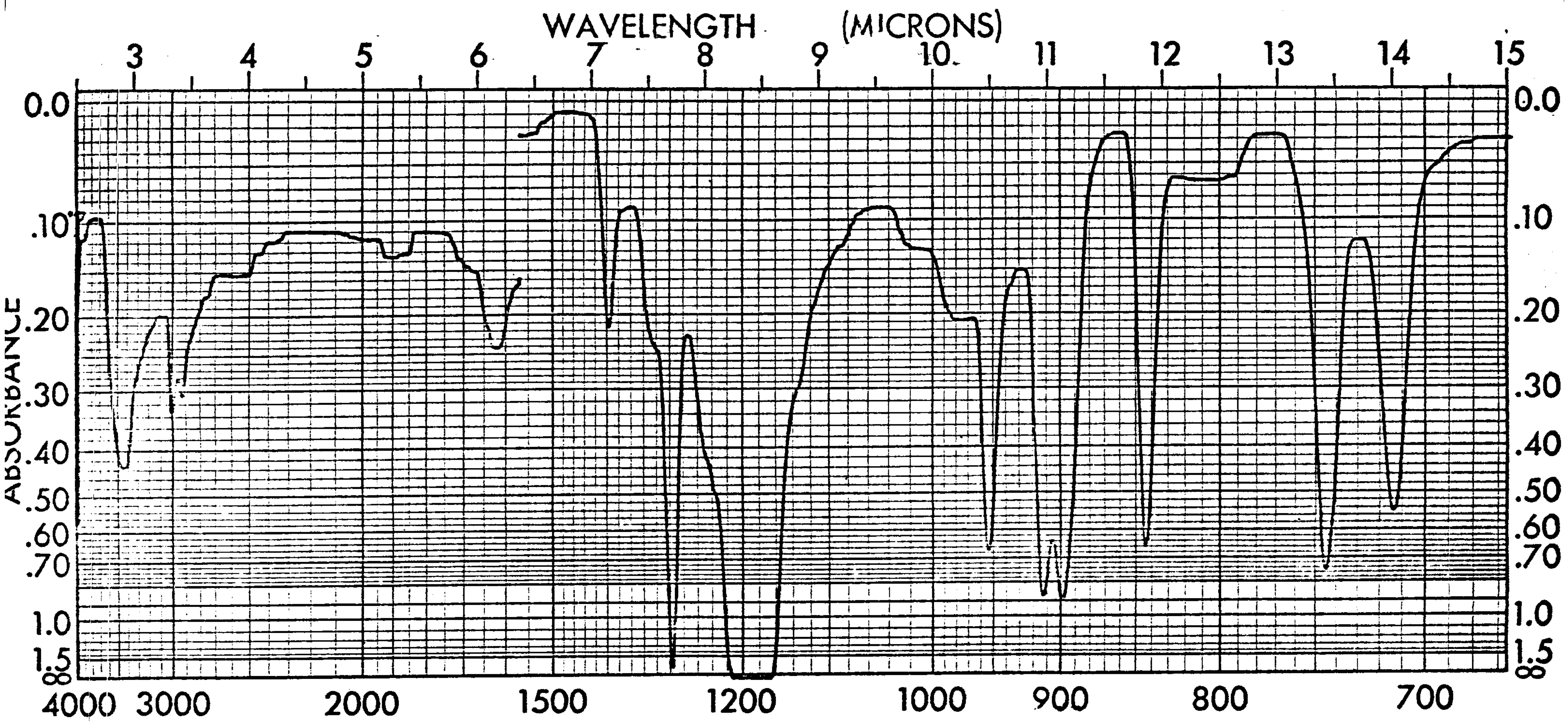


Figure 19

Infrared Sprectrum of $[CH_3\ PNCl]_3$ mp 163 - 163.5

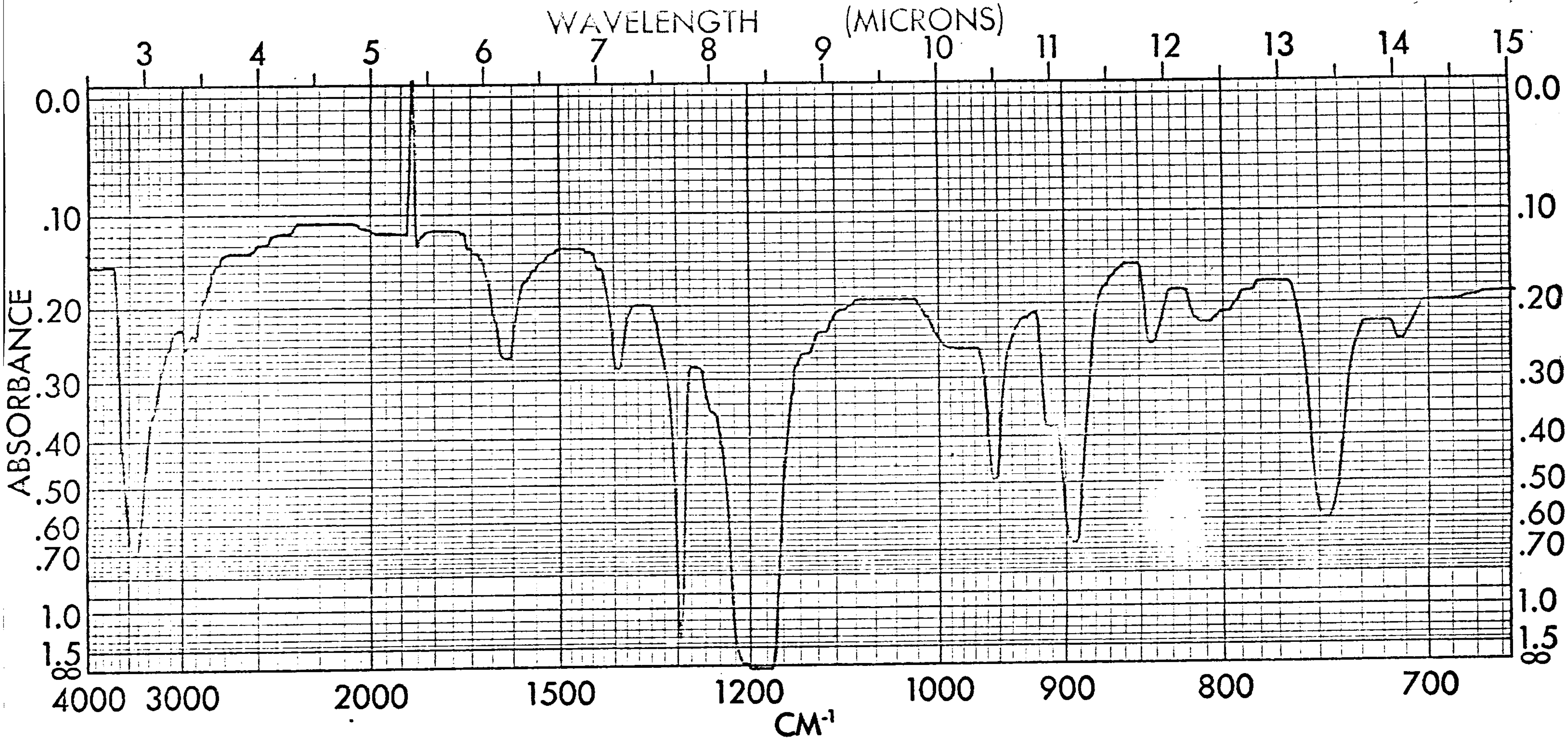


Figure 20

Infrared Spectrum of Purified $[CH_3\ PNCl]_{3,4}$ Before O_2 Oxidation

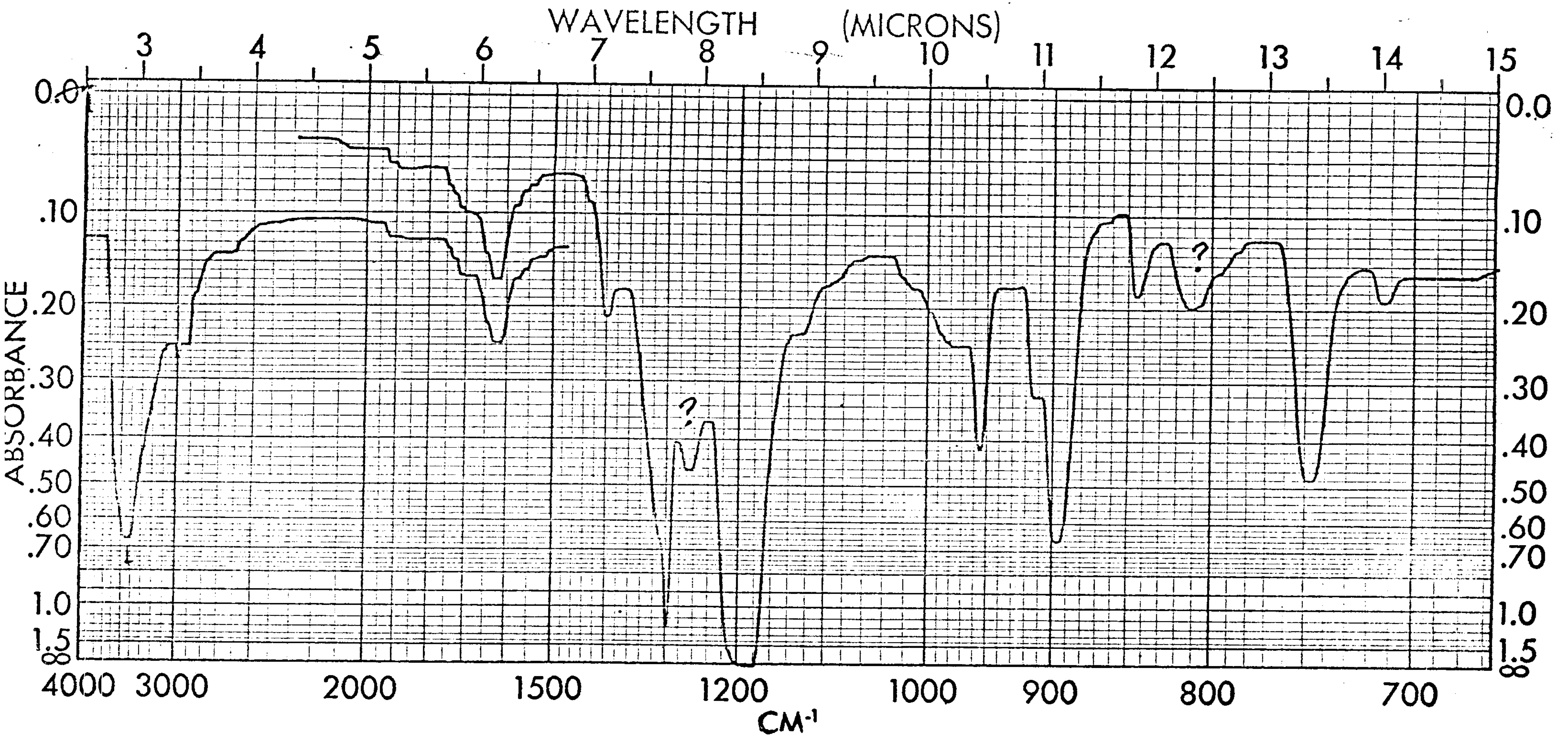


Figure 21

Infrared Spectrum of Mixed Cis-trans $[CH_3\ PNCl]_3$
Before Hydrolysis Study

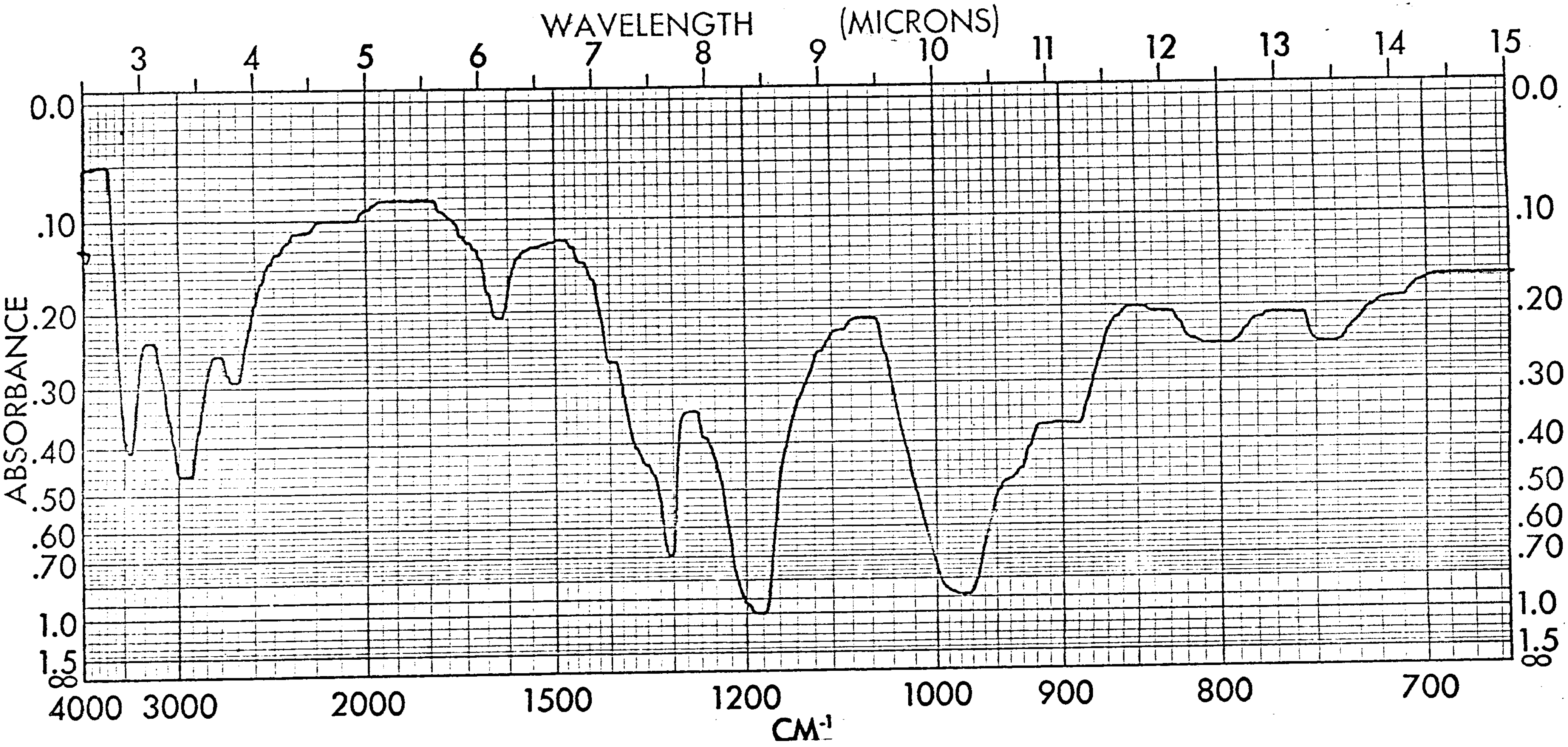


Figure 22

Infrared Spectrum of $[CH_3\ PNCl]_3$ After Hydrolysis Study

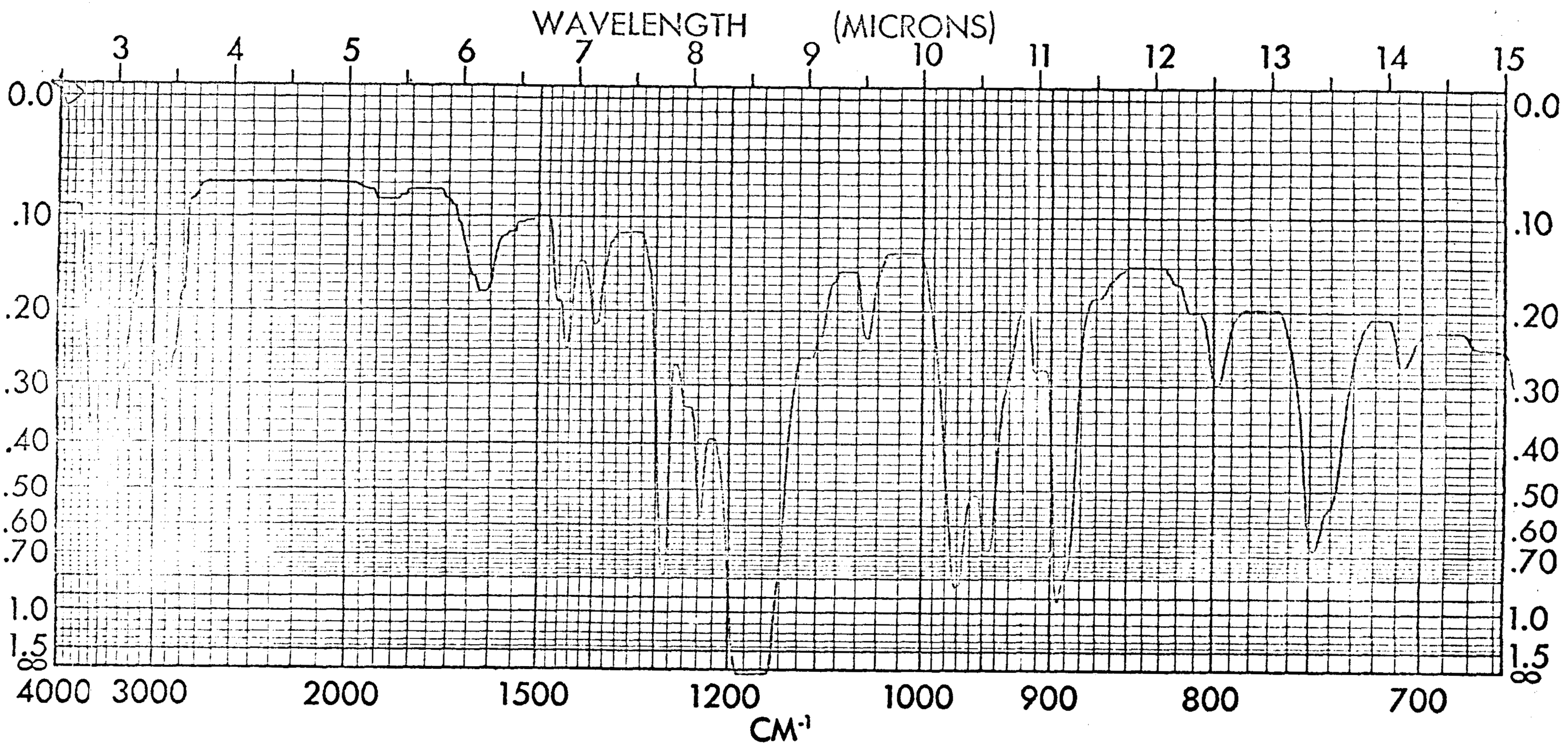


Figure 23

Infrared Spectrum of $[MePN(NMe_2)]_n$
Before Exposure to Moisture

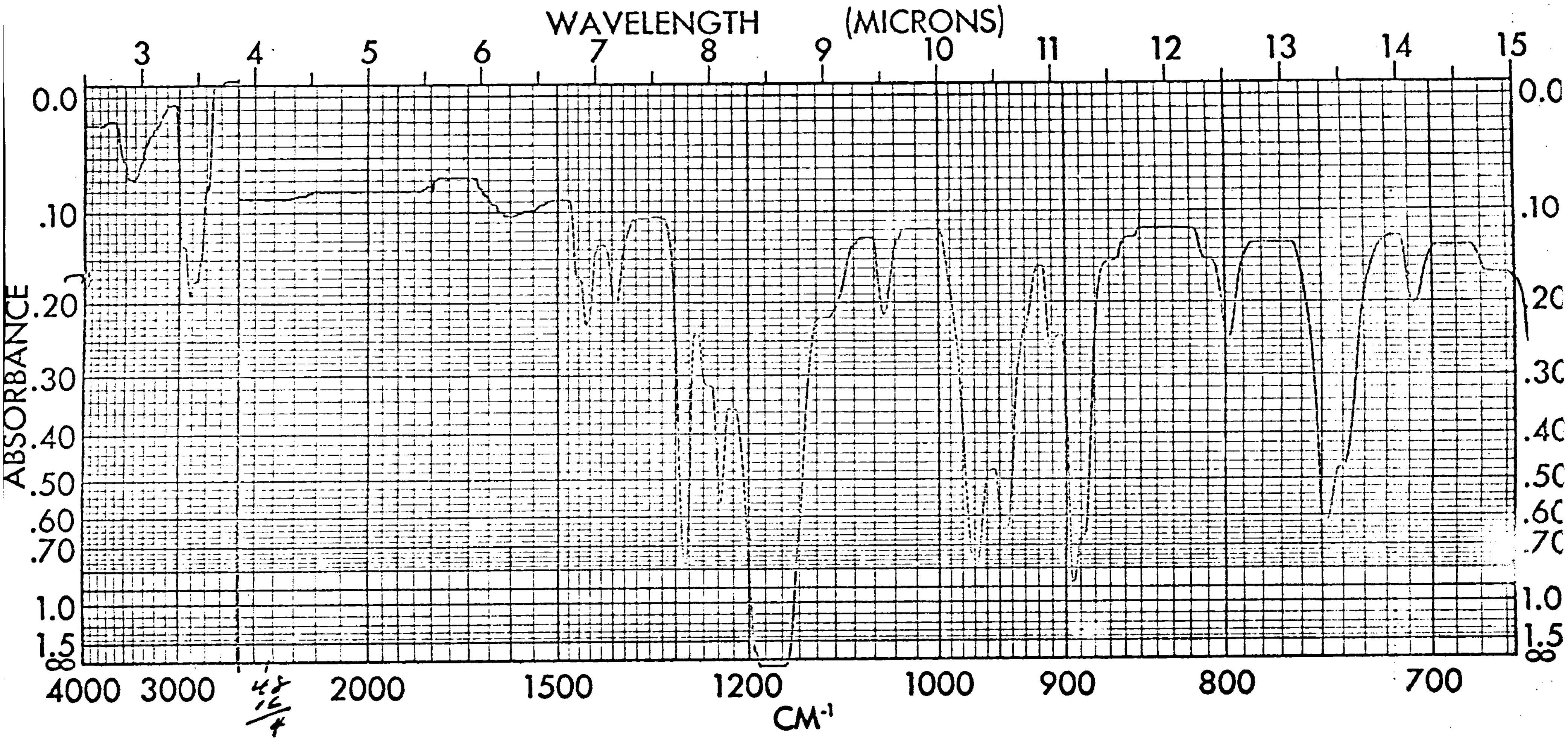


Figure 24

Infrared Spectrum of $[MePN(NMe_2)]_n$
After Exposure to Moisture

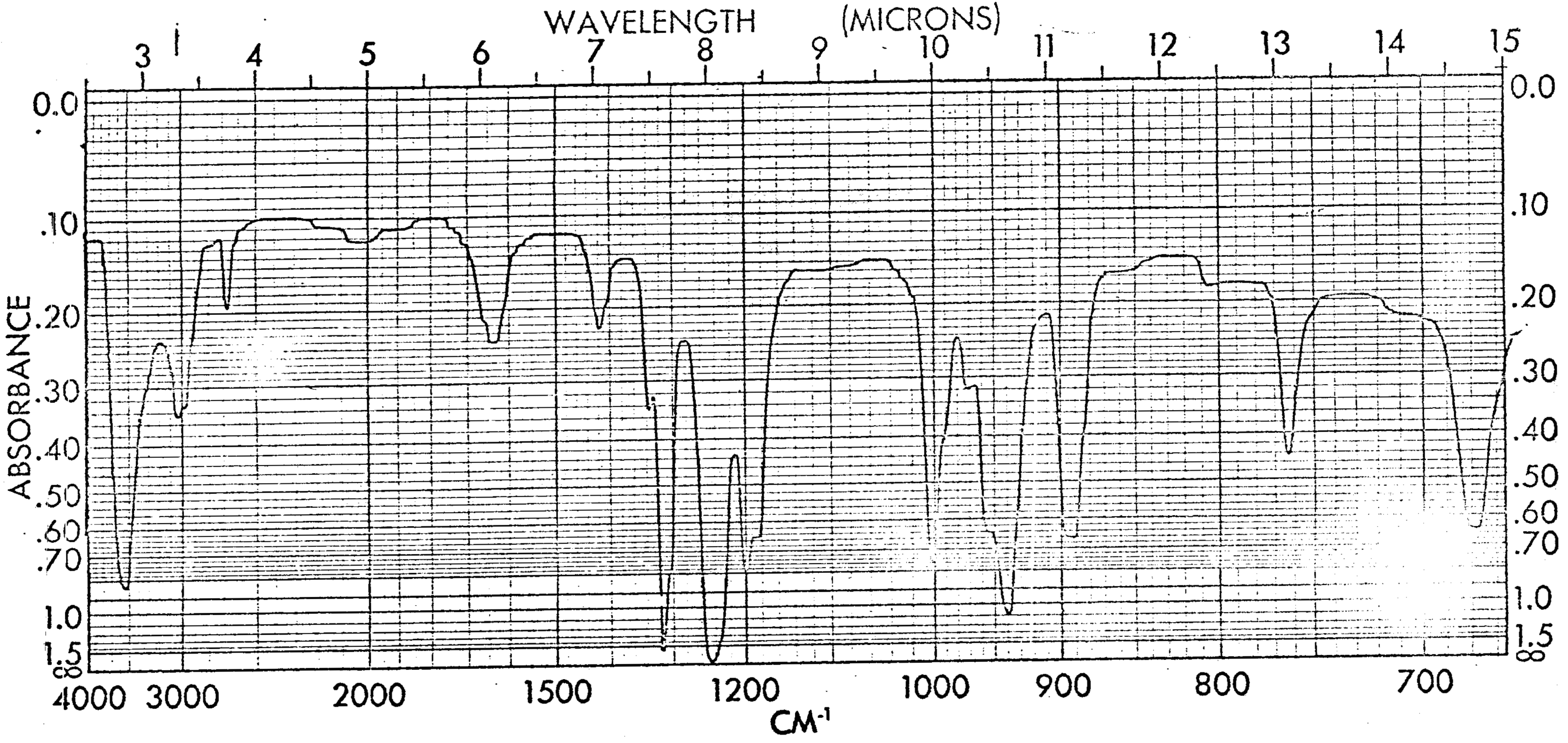


Figure 25

Infrared Spectrum of $(CH_3)_5P_3N_3CH_2Br$

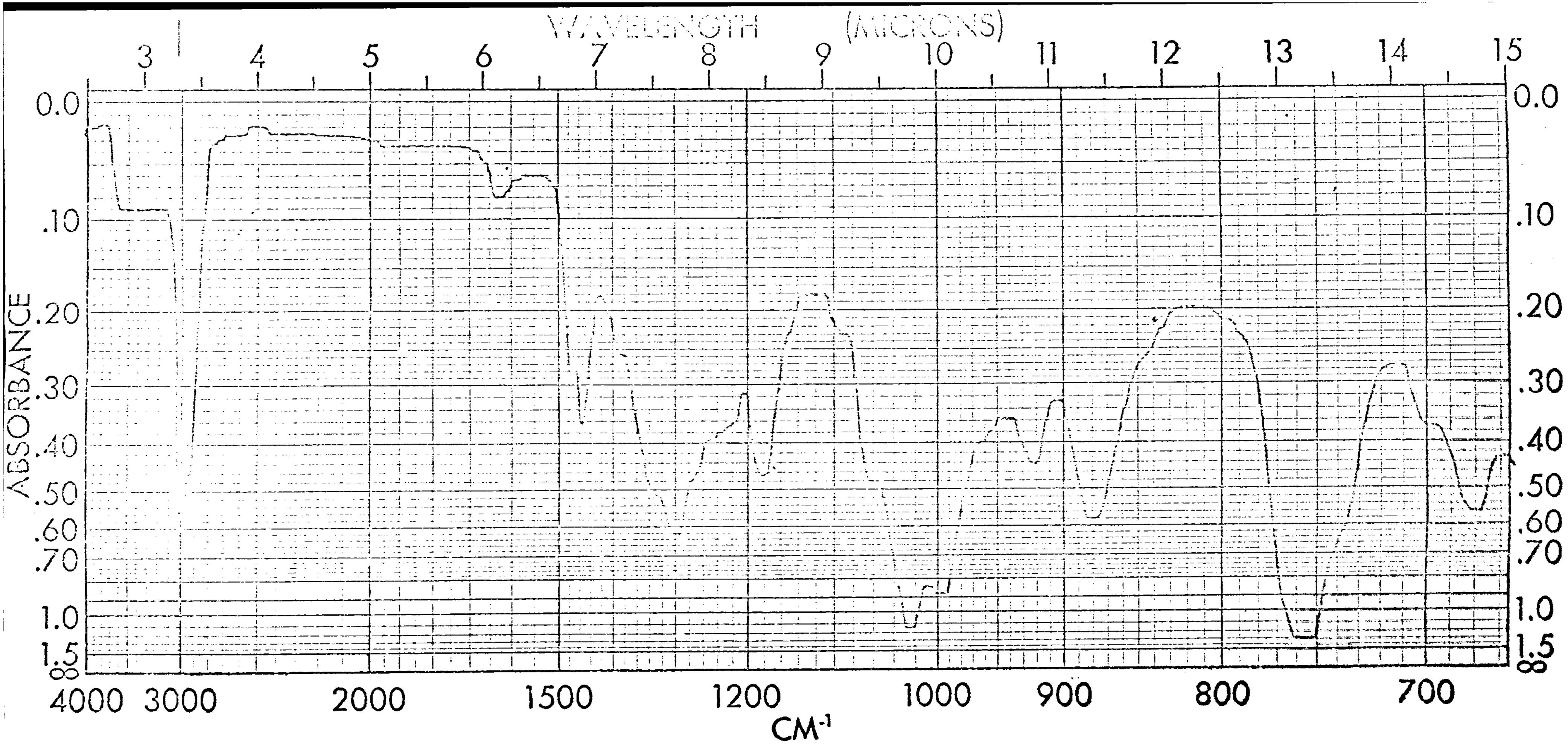


Figure 26

Infrared Spectrum of Reaction Products:
$[PNCl_2]_4$ + MeMgBr
Before Extensive Handling

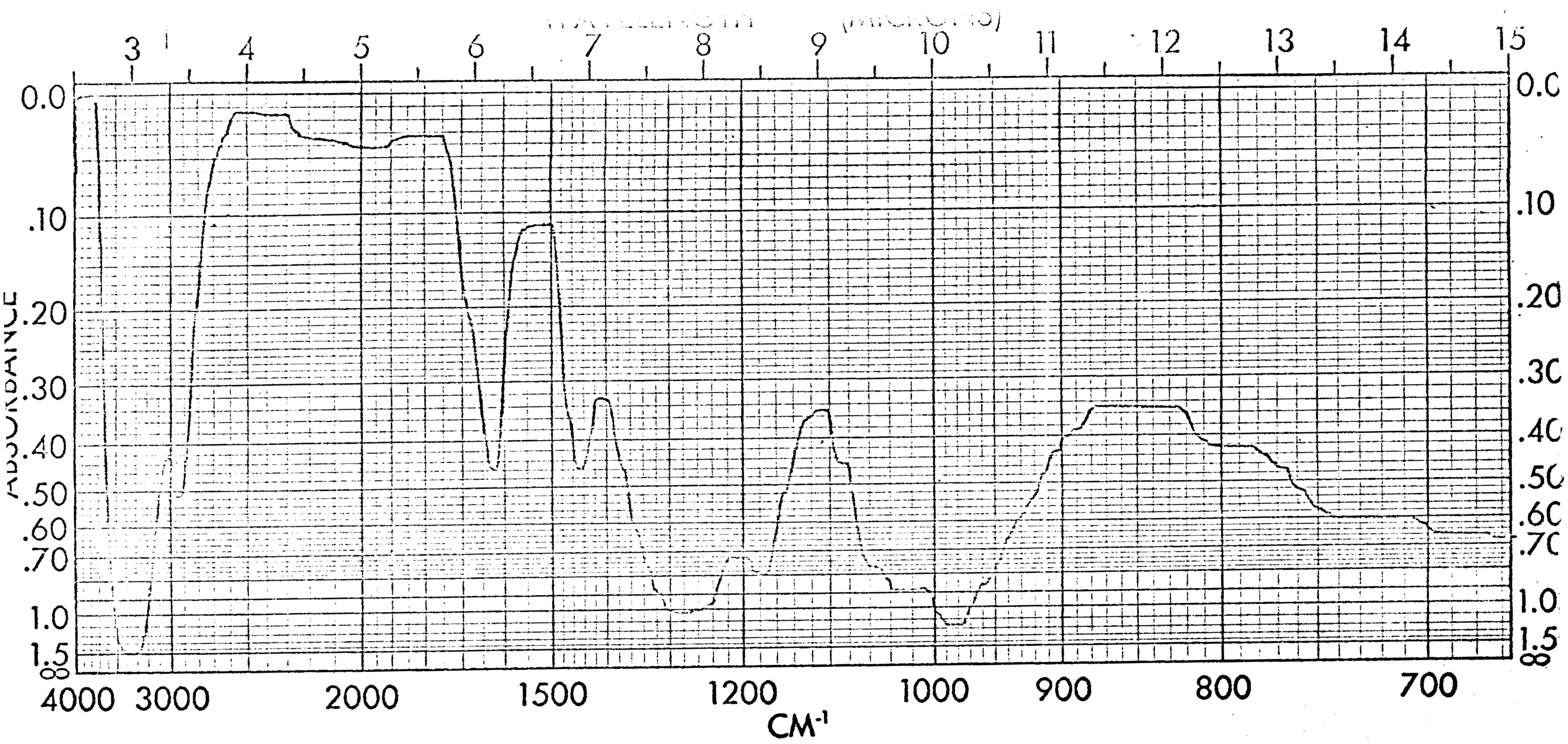


Figure 27

Infrared Spectrum of Reaction Products:
$(PNCl_2)_4$ + MeMgBr After Handling

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