To: National Aeronautics and Space Administration
Office of Scientific and Technical Information
Code U.S.
Washington, D. C. 20546

From: Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

Subject: Informal Quarterly Status Report on
EXPLORATORY POLYMER SYNTHESIS
Under NASA Grant NGL-004-001
Supplement 7 (Cont. of NsG339)

Period Covered: 1 August 1969 to 31 October 1969

By: G. F. D'Alelio, Principal Investigator

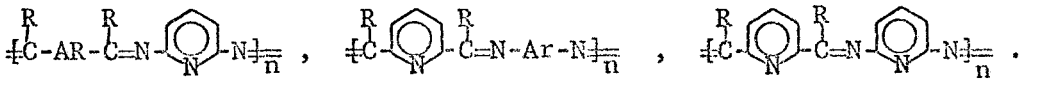
TABLE OF CONTENTS

EXPLORATORY POLYMER SYNTHESIS

NASA Grant NGL-004-001

I. Introduction.

The current research effort under this grant is being directed entirely to the synthesis of polymers of enhanced conductivity and to the exploration of the structural parameters which contribute to conductivity. As the first approach to achieving this objective, polymeric azomethines which contain hetetocyclic aromatic tertiary nitrogen atoms as part of the linear chain have been selected as candidates. These polymer systems were described in the research proposal for this grant submitted to NASA October 1, 1968. Typical polymers are the polyazomethines related to the Schiff bases in which the benzene rings are replaced by pyridine rings, for example,



It is believed that these polymers (1) satisfy the requirements as donors in charge-transfer complexes, (2) can be quaternarized permitting the attachment of short or long branches, including dipole dye molecules as branches, to the backbone, and (3) the quaternarized ionic site can be complexed with acceptors to yield charge transfer complexes.

Since it is important that the parameters that contribute to conduction be understood, and since polymer molecules themselves are complex substances in which the causes for small or subtle changes in properties are difficult to establish, it was considered essential that prototype monomeric molecules, which are similar in structure to the repeating units in the polymer molecules, be studied first and understood. For this reason the research has been divided into two parts. The first part deals with monomers, their syntheses and prototype reactions, essentially related to the reactions contemplated with

polymers, have been evaluated with the monomers.

The second part of the problem deals with the synthesis of pyridine-type Schiff base polymers and of certain specific derivatives therefrom; the synthesis will be based on chemistry established as definite by prototype studies. Some preliminary studies on polymer synthesis were performed during the early period of this study, primarily to establish that the pyridine-type Schiff base polymers could be synthesized; the preliminary data confirmed that polymers of this type were feasible and the results were summarized in the first Informal Quaterly Status Report for the period 1 February 1969 to 30 April 1969. Since April, 1969 no effort has been expended on the syntheses of polymers; all effort has been devoted to the study of the reactions of prototype molecules to assure the accuracy of the specific chemistry when it is applied to the pyridine-type Schiff-base polymers. This decision was necessitated by the fact, that the studies on the prototype molecules disclosed previously unknown chemistry for these substituted pyridines, and the type of chemistry encountered was in marked contrast with the chemistry that was expected on the basis of published pyridine chemistry.

Substantial progress has been made on the chemistry and understanding of the prototype reactions. Thus, it is expected that the synthesis of the polymers and their post-reactions will be resumed sometime during the next research quarterly period. Accordingly, it was considered advisable, at this time, to report the results of the monomer and prototype studies in substantial detail rather than to present a brief, informal status report of the effort under this grant.

II. Experimental: Monomers and Model Compounds.

A. Source of Reagents.

All of the materials used in this investigation were either prepared using standard laboratory techniques, or were obtained from commercial sources and purified, if necessary, before use.

2-Acetylpyridine, 2,6-diaminopyridine, 3,6-diaminoacridine, acriflavine, and phenosafranine were purchased from the Aldrich Chemical Company.

Methyl iodide, benzaldehyde, zinc chloride, and sodium carbonate were purchased from the J. T. Baker Corporation.

Acetonitrile was purchased from the Matheson, Coleman and Bell Company.

2-Aminopyridine and aniline were purchased from the Matheson, Coleman and Bell Division of the Matheson Company.

Tetracyanoethylene was purchased from the Eastman Kodak Company.

2,6-Diacetylpyridine was purchased from the Columbia Organic Chemicals Company.

The nitrogen used in this research was high purity, lamp grade nitrogen which contained less than two parts per million of oxygen and was purchased from the Cleveland Wire Division of the General Electric Company.

B. Physical Constants.

Melting points were determined on a Meltemp melting point apparatus and are uncorrected. Boiling points are also uncorrected.

The infrared spectra in this investigation were recorded on a Perkin-Elmer Model 457 grating spectrophotometer.

The nuclear magnetic resonance spectra were recorded on a Varian Model A60A nuclear magnetic resonance spectrometer.

All the differential thermal analyses were made on a du Pont 900 Differential Thermal Analyzer.

Elemental analyses were performed by the Midwest Microlab, Indianapolis,

Indiana.

All weighings were performed on a Mettler Balance.

C. Purification of Reagents.

1. Purification of Aniline.

Reagent grade aniline was distilled through an 18" glass-helices packed column in a nitrogen atmosphere. The fraction distilling at 97-99°C/40 mm Hg was collected and stored under nitrogen.

2. Purification of Benzaldehyde.

Reagent grade benzaldehyde was distilled through an 18" column packed with glass helices and equipped with a partial takeoff distillation head. Distillation was performed under nitrogen at a reflux ratio of five to one using a capillary bleeder. The middle fraction boiling at 80-81°C/40 mm Hg was collected and stored under nitrogen.

3. Purification of 2,6-Diaminopyridine.

2,6-Diaminopyridine was purified by recrystallization from a benzene solution containing activated charcoal. The recrystallized 2,6-diaminopyridine appeared as white platelets melting at 120-121°C (lit., mp 120°C) and was stored under nitrogen.

4. Purification of 3,6-Diaminoacridine.

3,6-Diaminoacridine was purified by recrystallization from a water solution containing activated charcoal. The recrystallized 2,6-diaminoacridine melted at 282-283°C (lit., mp 283°C) and was stored under nitrogen.

D. Syntheses.

1. Preparation of Azomethine Model Compounds Containing Aromatic Nitrogen Heterocycles.

a. Preparation of 2-(Benzylideneamino)pyridine.

Into a 50-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2-aminopyridine (2.63 g, 28 mmole),

benzaldehyde (3.26 g, 31 mmole), and 25 ml of dry benzene. The reaction mixture was heated to reflux and after twenty-four hours, 0.5 ml of water was collected in the Dean-Stark trap. Evaporation of solvent yielded a dark brown oil, which, upon vacuum distillation, yielded 2-benzylidene-aminopyridine, a light yellow oil, 4.38 g (86%), bp 102°C/0.2 mm Hg, n_{25}^{D}=1.6498 (lit., n_{21}^{D}=1.6564). Infrared spectrum (neat) (Appendix 1), 3220 cm^{-1} shoulder, weak (N-H); NMR ($CDCl_3$/TMS) 9.1δ (1,s -CH=N-), 8.5-6.9δ (10,m, aromatic protons).

Analysis: Calc'd for $C_{12}H_{10}N_2$:

C, 79.12; H, 5.49; N, 15.38.

Found: C, 77.26; H, 5.75; N, 14.20.

b. Preparation of 2-Pyridylcarboxylideneaniline.

Into a 50-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed aniline (2.52 g, 27.3 mmole), 2-pyridinecarboxaldehyde (3.02 g, 28.2 mmole), and 25 ml dry benzene. The reaction mixture was heated to reflux and after twenty-two hours, a quantitative yield of water was collected in the Dean-Stark trap. Upon evaporation of solvent a red oil formed which crystallized when cooled. Recrystallization from diethyl ether yielded 2-pyridylcarboxylideneaniline 4.35 g (88%), mp 36-37°C. Infrared spectrum (KBr disc) (Appendix 2), void 3400 cm^{-1} to 3100 cm^{-1} (N-H); NMR ($CDCl_3$/TMS), 8.6 δ (1,s -CH=N), 8.7-7.6 δ (4,m, pyridine protons), 8.4-8.2δ (5,m, phenylene protons).

Analysis: Calc'd for $C_{12}H_{10}N_2$:

C, 79.12; H, 5.49; N, 15.38.

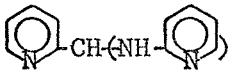
Found: C, 78.93; H, 5.76; N, 15.43.

c. Attempted Synthesis of 2-Pyridylcarboxylidene-2-aminopyridine.

i. By the Continuous Azeotropic Method.

Into a 100-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2-pyridinecarboxaldehyde (3.02 g, 28 mmole),

2-aminopyridine (2.64 g, 28 mmole), and 30 ml dry benzene. The reaction mixture was heated to reflux and after thirty-six hours 0.4 ml of water were collected. Evaporation of solvent yielded 2.36 g of a yellow-orange solid. Recrystallization from benzene yielded colorless cubical crystal, mp 121-122°C. Infrared spectrum (KBr disc) (Appendix 3), 3290 cm^{-1} amd 3240 cm^{-1} (NH). Based on the infrared spectrum and the elemental analysis, the compound wad identified as a bis derivative: 2-pyridylcarboxal-di-2-aminopyridine



.

Analysis: Calc'd for $C_{16}H_{15}N_5$:

C, 69.31; H, 5.42; N, 25.27.

Found: C, 69.10; H, 5.60; N, 25.30.

ii. By Pyrolysis of 2-Pyridylcarboxal-di-2-aminopyridine.

Into a reaction tube with side arm equipped with a nitrogen inlet capillary which extended nearly to the bottom of the tube, was placed 2-pyridylcarboxal-di-2-aminopyridine (0.76 g, 2.6 mmole). The tube was placed in an aluminum block preheated to 120°C by an electric mantle controlled by a Proportio-Null temperature controller. After three hours of heating, with a slow stream of nitrogen passing directly over the molten reactant, the reaction was stopped and the product and the condensate were both identified as starting material by thin layer chromatography.

iii. By the Hydrochloride Salt Method.

Into a 25-ml, one-neck, round-bottom flask equipped with a reflux condenser were placed 2-aminopyridine hydrochloride (1.57 g, 12 mmole), 2-pyridinecarboxaldehyde (1.29 g, 12 mmole), and 5 ml absolute ethyl alcohol. The reaction solution was heated at reflux for forty-eight hours, allowed to cool to room temperature, and neutralized at 0-5°C with sodium carbonate (0.64 g, 6 mmole). Extraction of the reaction solution with benzene and subsequent evaporation of the benzene yielded a dark oil which slowly crystallized. One

recrystallization from benzene yielded a dark red solid, mp 115-116°C. Infrared spectrum (KBr disc) 3290 and 3240 cm^{-1} (NH); based on the melting point and infrared spectrum the compound was judged to be the bis derivative, 2-pyridylcarboxal-di-2-aminopyridine.

d. Preparation of 2-Acetylpyridineketanil.

i. Attempted Preparation by Continuous Azeotropic Method.

Into a 50-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2-acetylpyridine (2.42 g, 20 mmole), aniline (1.86 g, 20 mmole), concentrated hydrochloric acid (0.148 g, 1.3% by weight reactants), and 25 ml toluene. The reaction solution was heated at reflux for forty-five hours during which time 0.2 ml of water was collected, however, thin layer chromatography indicated that little or no reaction had occurred.

ii. Preparation by the Hydrochloride Salt Method.

Into a 25-ml, one-neck, round-bottom flask equipped with a reflux condenser were placed 2-acetylpyridine (1.34 g, 11 mmole), aniline hydrochloride (1.34 g, 11 mmole), and four milliliters of absolute ethyl alcohol. The reaction solution was heated at reflux for eighteen hours, cooled to 0-5°C and neutralized with sodium carbonate (0.66 g, 11 mmole) to yield a yellow solid. Recrystallization from benzene yielded 2-acetylpyridineketanil, 0.65 g (30%), mp 189-190°C. Infrared spectrum (KBr disc) (Appendix 4), void 3200 and 3350-3500 cm^{-1} (N-H), 3310 cm^{-1} (present in 2-acetylpyridine at 3370 cm^{-1}), 1630 cm^{-1}, (C=N), 785 and 750 cm^{-1} (5 adjacent aromatic hydrogens).

Analysis: Calc'd for $C_{12}H_{12}N_2$:

C, 79.59; H, 6.13; N, 14.28.

Found : C, 80.20; H, 5.79; N, 14.01.

e. Preparation of p-Xylylidenedi-2-aminopyridine.

Into a 500-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed terephthaldehyde (1.64 g, 12.2 mmole), 2-aminopyridine (2.28 g, 24.4 mmole), and 150 ml dry toluene. The reaction mixture was heated to reflux and after twenty-four hours a quantitative yield of water was collected. Evaporation of solvent yielded yellow crystals. Recrystallization from toluene yielded p-xylylidenedi-2-aminopyridine, 2.78 g (80%), mp 208°C, (lit., 204°C). Infrared spectrum (KBr disc) (Appendix 5), void 3500 cm^{-1} to 3100 cm^{-1} (NH), 1610 cm^{-1} (C=N).

f. Preparation of N,N'-Di-2-pyridylcarboxylidene-p-phenylenediamine.

Into a 100-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed p-phenylenediamine (1.63 g, 15 mmole), 2-pyridine carboxaldehyde (3.21 g, 30 mmole), and 20 ml dry toluene. The reaction mixture was heated to reflux and after nineteen hours a quantitative yield of water was collected. Evaporation of solvent yielded yellow brown needles, recrystallization from toluene-ethanol yielded N,N'-di-2-pyridylcarboxylidene-p-phenylenediamine, 3.99 g (93%), mp (differential thermal analysis, 15°C/min) 146°C. Infrared spectrum (KBr disc) (Appendix 6), void 3500 cm^{-1} (NH), 1620 cm^{-1} (C=N); NMR ($CDCl_3$/TMS), 8.6-8.45 δ (4,m), 8.25-7.15 (10,m).

Analysis: Calc'd for $C_{18}H_{14}N_4$:

C, 75.03; H, 4.90; N, 19.58.

Found: C, 75.87; H, 5.10; N, 19.03.

g. Preparation of 2,6-Diacetylpyridinediketanil.

Into a 250-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2,6-diacetylpyridine (2.61 g, 16 mmole), aniline (3.16 g, 34 mmole), zinc chloride (0.03 g), and 50 ml dry toluene. The reaction mixture was heated to reflux under nitrogen and after fifty hours

the solution was allowed to cool and filtered. Evaporation of solvent gave a yellow solid, which, upon recrystallization from toluene yielded 2,6-diacetylpyridinediketanil, 0.93 g (19%), mp (differential thermal analysis 15°C/min) 161°C. Infrared spectrum (KBr disc) (Appendix 7), void in 3500 to 3100 cm^{-1} region (NH), void at 1700 cm^{-1} (C=O), and 1630 cm^{-1} (C=N); NMR (CDC /TMS) 2.4δ (s,6) 4.2-3.35 δ (m, 10), and 5.1-4.35δ (m, 3).

Analysis: Calc'd for $C_{21}H_{19}N_3$:

C, 80.51; H, 6.07; N, 13.42.

Found: C, 80.35; H, 6.28; N, 13.37.

h. Preparation of 3,6-Di-(benzylideneamino)acridine.

Into a 500-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 3,6-diaminoacridine (3.01 g, 14 mmole), benzaldehyde (4.20 g, 40 mmole), p-toluenesulfonic acid (0.01 g), and 250 ml dry toluene. The reaction mixture was heated to reflux and after ninety hours of reflux nearly a quantitative yield of water was collected. Evaporation of the solvent yielded a yellow-orange product, which, upon recrystallization from toluene yielded 3,6-di-(benzylideneamino)acridine, 3.36 g (57%), mp (differential thermal analysis) 212°C. Infrared spectrum (KBr disc) (Appendix 8), void in 3500 cm^{-1} to 3100 cm^{-1} region (NH), 1630 cm^{-1} (-C=N-).

Analysis: Calc'd for $C_{27}H_{19}N_3$:

C, 84.16; H, 4.94; N, 10.91.

Found: C, 83.71; H, 5.91; N, 11.03.

i. Attempted Synthesis of 2,6-Di-(benzylideneamino)pyridine.

i. By Azeotrope Condensation.

Into a 500-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2,6-diaminopyridine (15.50 g, 140 mmole), benzaldehyde (29.87 g, 280 mmole), and 250 ml dry benzene. The reaction mixture was heated for twenty-four hours, during which time 4.2 ml water were

collected in the trap. Precipitation by the addition of 200 ml hexane yielded 10.26 g of a yellow powder. Recrystallization from toluene yielded a yellow powder, mp with decomposition 258-263°C. Infrared spectrum (KBr disc), 3350 cm^{-1} broad band (N-H); vapor phase osmometry (tetrahydrofuran) yielded a molecular weight of 1200 g/mole indicating a polymeric product.

Analysis: Calc'd for $C_{19}H_{15}N_3$:

C, 79.96; H, 5.30; N, 14.72.

Found: C, 76.99; H, 5.87; N, 15.92.

ii. Condensation with Slow Addition of 2,6-Diaminopyridine.

Into a 250-ml, three-neck, round-bottom flask equipped with an injection port, a Dean-Stark trap and water condenser were placed benzaldehyde (3.68 g, 35 mmole) and 60 ml dry benzene. The system was thoroughly flushed with nitrogen and heated to reflux. 2,6-Diaminopyridine (1.0002 g, 9.1 mmole) was dissolved in 100 ml hot benzene. Seventy milliliters of this warm solution were added in ten ml aliquots by syringe over a period of six hours. The remaining solution was added over a period of seven hours in two ml aliquots.

After a total reflux time of twenty hours, a nearly quantitative yield of water was collected in the Dean-Stark trap. One hundred milliliters of benzene were distilled from the solution, then sixty milliliters of n-hexane were added to precipitate 1.38 g of a yellow powder, mp with decomposition, 258-263°C, similar to the polymeric product obtained using the azeotropic technique given immediately above.

The yellow powder was recrystallized from toluene and product was collected at various stages of solvent evaporation. The infrared spectrum of each stage contained a broad peak centered at 3380 cm^{-1} (N-H).

iii. By Amine Exchange with Dibenzylideneazine.

Into a polymerization reaction tube with side arm equipped with a nitrogen inlet and collection flask were placed 2,6-diaminopyridine (0.50 g, 4.5 mmole)

and dibenzylideneazine (0.94 g, 4.5 mmole). The system was thoroughly flushed with nitrogen and placed into a preheated block at 100°C for thirty minutes, during which time a homogeneous melt solution formed. Then, the reaction mixture was heated for fifty-minute intervals at 120, 150 and 175°C. Finally, the system was heated for three hours at 175°C with a slow stream of nitrogen passing directly over the melt solution. The solid was collected and chromatographed on silica gel. Elution with ethyl acetate failed to achieve separation of the complex mixture of reaction products, some of which were polymeric.

iv. By the Hydrochloride Salt Method.

a) Preparation of 2,6-Diaminopyridine Monohydrochloride.

Into a 500-ml Erlenmeyer flask were placed 2,6-diaminopyridine (1.000 g, 9.1 mmole) and 150 ml anhydrous diethyl ether. Hydrogen chloride was bubbled through the solution until precipitation was complete. The white product was collected by filtration, washed with diethyl ether and dried to yield 2,6-diaminopyridine monohydrochloride, 1.31 g (99%).

Analysis: Calc'd for $C_5H_8N_3Cl$:

C, 41.24; H, 5.49; N, 28.93; Cl, 24.39.

Found: C, 40.28; H, 5.94; N, 27.92; Cl, 23.97.

b) Reaction of 2,6-Diaminopyridine Monohydrochloride with Benzaldehyde.

Into a 100-ml Erlenmeyer flask were placed 2,6-diaminopyridine monohydrochloride (1.31 g, 8.9 mmole), benzaldehyde (2.10 g, 20 mmole), and 10 ml absolute ethanol. The solution was stirred at room temperature for two hours, cooled to 5°C, and neutralized with sodium carbonate (0.75 g, 7.1 mmole) to yield a yellow precipitate. The yellow product was dissolved in toluene, however, it would not crystallize out of the solution and upon cooling the solution became very viscous. Complete evaporation of solvent yielded a glassy, polymeric solid, mp 95-99°C, and the desired compound was not obtained.

Infrared spectrum (KBr disc) 3380 cm^{-1} broad, medium (N-H).

v. By Acetal Exchange.

Into a 25-ml, three-neck, round-bottom flask equipped with a thermometer and a reflux condenser were placed 2,6-diaminopyridine (0.55 g, 5 mmole) and benzaldehyde diethyl acetal (1.82 g, 10 mmole). The reaction solution was heated for two and one-half hours during which time the vapor temperature was recorded. The vapor temperature slowly rose to 82-84°C where it remained for forty-five minutes; then it continued to climb past 100°C at which time the reaction was halted. Thin layer chromatography indicated that some polymeric material had formed and only a trace of non-polymeric product had formed.

vi. By Direct Condensation Using Benzaldehyde as Solvent.

Into a 50-ml, three-neck, round-bottom flask equipped with a reflux condenser were placed 2,6-diaminopyridine (1.06 g, 9.7 mmole) and 25 ml of freshly distilled benzaldehyde. The solution was stirred for one hour under a nitrogen atmosphere and then 17 ml of benzaldehyde were vacuum distilled from the solution to yield a slightly viscous orange solution which hardened upon cooling to 5°C. Precipitation with hexane yielded a rubbery, polymeric yellow solid; and the infrared spectrum exhibited a broad medium peak centered at 3380 cm^{-1}.

j. Attempted Synthesis of 2,6-Di-(α-methylbenzylideneamino)pyridine.

Into a 250-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2,6-diaminopyridine (1.09 g, 10 mmole), acetophenone (2.47 g, 20 mmole), conc. hydrochloric acid (0.07 g) and 50 ml dry toluene.

The reaction solution was heated at reflux under nitrogen for two hundred thirty-six hours during which time approximately 0.2 ml water was collected in the trap. The solution was allowed to cool and filtered. Evaporation of solvent yielded a dark viscous oil which consisted of four compounds. The oil was paper chromatographed. Elution with ethyl acetate and a number of

other solvents failed to achieve separation.

k. Attempted Synthesis of 2,8-Di(benzylideneamino)-10-phenylphenazine.

i. By Condensation in Benzaldehyde.

Into a 500-ml, three-neck, round-bottom flask equipped with a reflux condenser were placed phenosafranine (4.34 g, 13.4 mmole), p-toluenesulfonic acid (0.01 g), and 100 ml benzaldehyde. The reaction mixture was thoroughly flushed with nitrogen, and heated to reflux under a nitrogen atmosphere for six hours. The water of reaction and the excess benzaldehyde were vacuum distilled from the solid yielding a purple residue. Recrystallization from 95% ethyl alcohol-water, followed by washing with boiling water gave a purple powder which did not melt upon heating to 350°C. Infrared spectrum (KBr disc) 3200 to 3420 cm^{-1} broad shoulder (N-H), 700 and 760 cm^{-1} strong (five adjacent aromatic hydrogens).

Analysis: Calc'd for $C_{32}H_{23}N_4Cl$:

C, 77.03; H, 4.64; N, 11.25; Cl, 7.08.

Found: C, 79.70; H, 5.15; N, 6.95; Cl, 2.36.

The desired compound was not obtained.

ii. By Amine Exchange.

Into a polymerization tube with side-arm equipped with a distillation adaptor and collection flask were placed phenosafranine (0.32 g, 1 mmole) and benzylideneaniline (1.81 g, 10 mmole). The reaction mixture was heated under a nitrogen atmosphere for three and one-half hours at 150°C, followed by one and one-half hours at 200°C. The system was then heated at 150°C at 0.55 mm Hg for seven and one-half hours during which time a few drops of aniline were collected in the collection flask. The reaction was cooled to room temperature, extracted twice with 50 ml boiling hexane and once with 100 ml hot benzene, dried to yield 0.29 g of a purple powder. Infrared spectrum (KBr disc) 3420 cm^{-1} and 3280 cm^{-1} (N-H), 750 and 700 cm^{-1} (5 adjacent aromatic hydrogens).

The desired compound was not obtained.

iii. Reaction of Phenosafranine with Aqueous Sodium Hydroxide.

Into a 250-ml, three-neck, round-bottom flask equipped with a reflux condenser were placed phenosafranine (1.00 g, 3.1 mmole), sodium hydroxide (0.12 g, 3.1 mmole), and 50 ml water. The reaction mixture was heated at reflux under nitrogen for one and one-half hours, allowed to cool and filtered. The residue was washed in 200 ml of hot water, filtered and dried to yield 0.23 g of a green solid, mp (differential thermal analysis, 15°C/min) 301°C. Infrared spectrum (KBr disc) (Appendix 9), 3320 and 3260 cm^{-1} (N-H), 1590 cm^{-1} (C=N).

Analysis: Calc'd for 2-amino-10-phenylphenazin-8-one, $C_{18}H_{13}N_3O$:

C, 75.00; H, 4.84; N, 14.58; O, 5.56.

Found: C, 72.27; H, 4.54; N, 14.64; O, 8.54; Cl, 0.00

1. Attempted Synthesis of 3,6-Di(benzylideneamino)-10-methylacridinium Chloride.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser were placed acriflavine (0.30 g, 0.7 mmole), p-toluenesulfonic acid (0.001 g) and 20 ml benzaldehyde. The reaction mixture was thoroughly flushed with nitrogen, heated to reflux under a nitrogen atmosphere for thirty-six hours. The system was allowed to cool and filtered yielding a brown residue which was dissolved in benzene and then precipitated with hexane twice to yield 0.06 g of a brown powder: mp (differential thermal analysis) 293°C. Infrared spectrum (KBr disc) 3380 cm^{-1} broad (N-H), 1720 cm^{-1} (C=O), 1660 cm^{-1}, 1595 cm^{-1} (C=N) and 700 and 750 cm^{-1} (5 adjacent aromatic hydrogens).

Analysis: Calc'd for $C_{28}H_{22}N_3Cl$:

C, 77.20; H, 5.00; N, 9.60; Cl, 8.10.

Found: C, 81.48; H, 4.59; N, 4.79; Cl, 3.69.

The desired compound was not obtained.

m. Attempted Preparation of α,α'-Dimethyl-p-xylylidene-di-2-aminopyridine.

Into a 100-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 1,4-diacetylbenzene (1.62 g, 10 mmole), 2-aminopyridine (1.88 g, 20 mmole), zinc chloride (0.162 g), and 20 ml dry toluene. After ninety-three hours of reflux no water was collected in the trap, so the system was cooled to room temperature. Thin layer chromatography indicated that a small amount of two reaction products had formed. The filtrate was paper chromatographed. Elution with ethyl acetate failed to achieve separation. The desired compound was not isolated.

n. Attempted Synthesis of 2,6-Di-(α-methylcarboxylidene-2-aminopyridine)pyridine.

i. By the Continuous Azeotropic Method.

Into a 500-ml, three-neck, round-bottom flask equipped with a Dean-Stark trap and water condenser were placed 2,6-diacetylpyridine (2.49 g, 15 mmole), 2-aminopyridine (2.96 g, 30 mmole), p-toluenesulfonic acid (0.028 g), and 60 ml dry toluene. The system was heated under a nitrogen atmosphere to reflux for ninety-four hours during which time only 0.1 ml of water had been collected. The solution was neutralized with sodium carbonate (0.037 g). Thin layer chromatography indicated the presence of two reaction products in addition to the reactants. The solution was chromatographed on silica gel. Elution with ethyl acetate failed to achieve separation.

ii. By the Hydrochloride Salt Method.

Into a 25-ml Erlenmeyer flask were placed 2-aminopyridine hydrochloride (1.59 g, 12 mmole), 2,6-diacetylpyridine (0.97 g, 6 mmole), and 7 ml absolute ethyl alcohol. The solution was stirred thirty-two hours at room temperature, neutralized with sodium carbonate (0.64 g, 12 mmole), to yield white crystals which were filtered and identified as 2,6-diacetylpyridine. Thin layer chromatography indicated that the mother liquor contained only starting material.

2. The Quaternary Derivatives of Pyridine-type Monomers.

a. Quaternarization of p-Xylylidene-di-2-aminopyridine with Methyl Iodide.

The following is a typical example of the procedure used to quaternarize p-xylylidene-di-2-aminopyridine.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser and thermometer were placed p-xylylidene-di-2-aminopyridine (0.25 g, 0.87 mmole), methyl iodide (0.25 g, 1.74 mmole) and 5 ml dry nitromethane. The reaction mixture was heated under a nitrogen atmosphere at 50°C for seven hours, allowed to cool, then stirred at room temperature for fourteen hours and filtered. Evaporation of the solvent yielded 0.22 g of an orange solid, mp 95-96°C. Infrared spectrum (KBr disc) (Appendix 10); specific assignments were not able to be made due to the number of moieties absorbing in similar regions. The following bands are either not present in the starting material or are shifted: 1650, 1625, 1520, 1315, 1175, 1025, 760 and 500 cm^{-1}.

Analysis: Calc'd for $C_{20}H_{20}N_4I_2$:

C, 42.11; H, 3.51; N, 9.82; I, 44.56.

Calc'd for $C_{20}H_{20}N_4I_2 \cdot CH_3NO_2$:

C, 39.94; H, 3.65; N, 11.09; I, 40.25; O, 5.07.

Calc'd for $C_{20}H_{20}N_4I_2 \cdot 2CH_3NO_2$:

C, 38.30; H, 3.75; N, 12.12; I, 36.58; O, 9.25.

Found: C, 44.34; H, 4.78; N, 12.96; I, 28.34; O, 9.58 (by diff.)

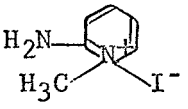
The iodide content of this product was lower than the theoretical for the desired compound; most of the product was the mono-quaternary derivative. The data of this experiment and the data of other experiments using methyl iodide as a quaternarization reagent are summarized in Table 1.

The reaction of the Schiff base with 4 moles of CH_3I was performed in CH_3NO_2 at 50°C for nine hours. The product was isolated by precipitation with benzene or ether and found to be a mixture of 25% mono-quaternary and 75% di-

quaternary derivatives complexes with 1.75 moles of CH_3NO_2. The reaction of the Schiff base with 4 moles of CH_3I was performed in CH_3NO_2 at 50°C for twenty-four hours. The precipitated product was the di-quaternarized Schiff base. Thus, the quaternarization of the di-Schiff base at 50°C was completely successful, but the product was complexed with 1.5 moles of CH_3NO_2.

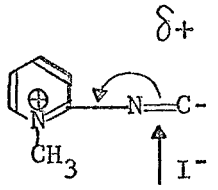
In an attempt to remove the complexed CH_3NO_2, the di-quaternarized product was extracted with dry ether in a Soxhlet apparatus for forty-eight hours. The extracted product melted at approximately 109-110°C and its infrared spectrum was identical to that of the unextracted product.

Since the attempts to extract the complexed CH NO from the product were unsuccessful, the quaternarization of this Schiff base was attempted with 2 moles and 4 moles of CH_3I respectively in DMAC. The crude sample which was precipitated by benzene was evaluated by NMR in deuterated DMSO and the integration appeared to correspond exactly to that of the desired compound. The remainder of the sample was purified twice by dissolving it in DMAC and precipitating it with benzene and dried at room temperature at 0.5 mm Hg pressure, and submitted for analysis. The elemental analysis corresponded exactly to a compound of the structure



rather than for the expected compound. Its infrared spectrum showed strong bands for the presence of $-NH_2$ and the quaternary structure. Thus, the product was not the same as that obtained when nitromethane was used as the reaction medium. Evidently, the desired product was not obtained but reductive-cleavage and hydrolysis of the -C=N- Schiff base linkage occurred when DMAC was used as the solvent and this observation was shown to be specifically true of those Schiff bases in which the amine nitrogen atoms are in the ortho position to the pyridine nitrogen, that is, the 2- or 2- and 6- positions. The probable explanation is that the positive quaternarized nitrogen withdraws

electrons from the -C=N- Schiff base linkage, leaving a partially positive charge which is then attacked by the negative iodine atom:



It appears also that DMAC participates in the reaction in some fashion which, at present, is not understood.

b. Quaternarization of p-Xylylidene-di-2-aminopyridine with Dimethylsulfate.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser and a thermometer were placed p-xylylidene-di-2-aminopyridine (0.50 g, 1.75 mmole), dimethylsulfate (0.44 g, 3.5 mmole), and 10 ml nitromethane. The reaction mixture was heated under a nitrogen atmosphere at 50°C for one and one-half hours. Evaporation of the solvent yielded 1.07 g of an orange solid.

The product was precipitated from CH_3NO_2 solution by the addition of benzene and washed with ether, yielding a light orange powder, mp 65-67°C. The product was very hygroscopic and became gummy when exposed to atmospheric moisture. Infrared spectrum (KBr disc) 1660, 1640, 1585, 1230, 1060, 1000, and 760 cm^{-1}. (Appendix 11).

Analysis: Calc'd for $C_{22}H_{26}N_4O_8S_2$:

C, 49.09; H, 4.83; N, 10.41; O, 23.79; S, 11.90.

Calc'd for $C_{22}H_{26}N_4O_8S_2 \cdot CH_3NO_2$:

C, 46.10; H, 4.90; N, 11.60; O, 26.70; S, 10.70.

Found: C, 46.69; H, 5.25; N, 11.48; O, 26.74; S, 10.06.

This data has been incorporated in Table 1.

The elemental analysis of the product indicated that the desired di-quaternarized Schiff base was obtained but that it was complexed with one mole of CH_3NO_2. The quaternarization with $(CH_3)_2SO_4$ was complete and was more

facile than with CH_3I in CH_3NO_2. The quaternarization of this Schiff base was attempted with $(CH_3)_2SO_4$ using m-cresol as the solvent and the product apparently was obtained, but the m-cresol apparently complexes even more strongly with the quaternarized product than does nitromethane.

c. Quaternarization of 2-Benzylideneaminopyridine with Methyl Iodide.

This Schiff base is very sensitive to hydrolysis and rearrangement. Therefore this Schiff base was prepared and used for the quaternarization studies immediately after its preparation.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser and thermometer were placed 2-benzylideneaminopyridine (0.5 g, 2.75 mmole), methyl iodide (0.5 g, 3.52 mmole) and 6 ml dry nitromethane. The reaction mixture was heated with stirring under a nitrogen atmosphere at 50°C for forty-eight hours. Evaporation of the solvent yielded 0.981 g of a deep orange solid. The evaporated product was reprecipitated from CH_3NO_2 with ether and washed with ether. The reprecipitated product was an orange solid, mp 129-131°C. Infrared spectrum (KBr disc) 3380 (NH-), 1650, 1590, 1520, 760 and 695 cm^{-1} (mono-substituted phenyl group).

Analysis: Calc'd for $C_{13}H_{13}N_2I$:

C, 48.15; H, 4.01; N, 8.64; I, 39.20.

Found: C, 34.71; H, 3.79; N, 11.38; I, 50.12.

Calc'd for (A) $C_6H_9N_2I$:

C, 30.50; H, 3.82; N, 11.85; I, 53.83.

Calc'd for (B) $C_{19}H_{22}N_4I_2$:

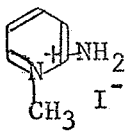
C, 40.71; H, 3.93; N, 10.00; I, 45.36.

Mixture of A and B (A:B = 56.3:43.7)

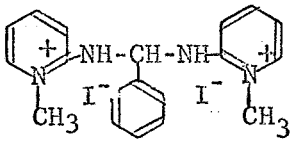
C, 34.97; H, 3.87; N, 11.05; I, 50.11.

The infrared spectrum of the product indicated a very strong absorption band for quatrnary groups at 1650 cm^{-1}, but the remainder of the spectrum was

similar to a reference sample of a bis methylene compound obtained by mild hydrolysis of the monomer, except for the absorption band of mono-substituted phenyl group at 695 cm^{-1}. Elemental analysis indicated that the product was a mixture of two hydrolyzed quaternarized products with the following structure (A : B = 56.3 : 43.7),



(A)



(B)

rather than the desired compound.

d. Quaternarization of 2-Pyridylcarboxylideneaniline.

Into a 25-ml, three-neck, round-bottom flask equipped with a thermometer and reflux condenser were placed 2-pyridylcarboxylideneaniline (0.50 g, 2.75 mmole), methyl iodide (0.50 g, 3.52 mmole), and 7 ml dimethylacetamide. The reaction solution was heated under a nitrogen atmosphere at 50°C for eight hours, allowed to cool, and then stirred at room temperature for sixteen hours. Evaporation of the solvent yielded 1.087 g (109%) of a black gummy solid. The residue was dissolved in DMAC and reprecipitated with diethyl ether to yield a black solid, mp 65-67°C. Infrared spectrum (KBr disc) (Appendix 12), 1660-1640 cm^{-1} shoulder, 1510-1490 cm^{-1}, 1325 cm^{-1}, void 480-600 cm^{-1} (C-I stretch).

Analysis: Calc'd for $C_{13}H_{13}N_2I$:

C, 48.15; H, 4.01; N, 8.64; I, 39.20.

Found: C, 47.45; H, 4.79; N, 8.59; I, 39.17.

Its infrared spectrum and elemental analysis confirmed that the desired compound was obtained. The quaternarization of this Schiff base with CH_3I was successful in DMAC.

e. Quaternarization of 2,6-Diacetylpyridinediketanil.

Into a 25-ml, three-neck, round-bottom flask equipped with a thermometer and a reflux condenser were placed 2,6-diacetylpyridinediketanil (0.40 g,

1.28 mmole), methyl iodide (0.27 g, 1.92 mmole), and 6 ml nitromethane. The solution was heated at 50°C for twenty-four hours under a nitrogen atmosphere. That the quaternarization reaction was complete was confirmed by TLC. Evaporation of the solvent yielded a brown solid, 0.62 g (107%). The melting point of the product reprecipitated from CH_3NO_2 with ether was 176-178°C. Infrared spectrum (KBr disc) 1600, 1475, 1450, 1260 and 850 cm^{-1}, void 480-600 cm^{-1} (C-I stretch); the following bands disappear as a result of the reaction, 1360, 1220, and 1175-1195 cm^{-1}. (Appendix 13).

Analysis: Calc'd for $C_{22}H_{22}N_3I$:

C, 58.02; H, 4.83; N, 9.23; I, 27.92.

Calc'd for $C_{22}H_{22}N_3I \cdot CH_3NO_2$:

C, 53.50; H, 4.86; N, 10.85; I, 24.62; O, 6.20.

Found: C, 54.64; H, 4.14; N, 8.51; I, 29.74; O, 2.97.

This data and the data obtained from the quaternarization of 2,6-diacetylpyridinediketanil with dimethyl sulfate are summarized in Table 2.

The elemental analysis of the product showed it was high in iodide and low in nitrogen and complexed with 0.4 moles of CH_3NO_2. The reaction was carried out over a period of many hours and side reactions undoubtedly occurred. The long reaction time was used on the basis of TLC as the experiment progressed and the slow rate appears to be due to marked steric hindrance.

The quaternarization of this diketanil Schiff base was attempted with CH_3I in DMAC, but the product, mp 177-179°C, which was isolated from this reaction was not the desired compound. The analytical data indicated a reductive-cleavage in which the DMAC probably participated, had occurred in this attempt.

Next, the quaternarization of this diketanil Schiff base with $(CH_3)_2SO_4$ in CH_3NO_2 was studied. The reaction at 50°C was rapid and complete in two hours. The yield of crude evaporated product was substantially quantitative (99.3%). The melting point of the isolated product, after reprecipitation

from CH_3NO_2 solution with ether, was 171-173°C. Infrared spectrum (KBr disc) 1600 (sharp), 1450, 1250 (broad SO_3), 1060, 1000 and 750 cm^{-1}. Its infrared spectrum and elemental analysis confirmed that the desired compound was obtained.

f. Quaternarization of N,N'-Di-(2-pyridylcarboxylidene)-p-phenylenediamine.

Into a 25-ml, three-neck, round-bottom flask equipped with a thermometer and a reflux condenser were placed N,N'-di-(2-pyridylcarboxylidene)-p-phenylenediamine (0.40 g, 1.4 mmole), methyl iodide (0.80 g, 5.6 mmole), and 5 ml nitromethane. The reaction mixture was heated at 50°C for twenty-four hours under a nitrogen atmosphere.

A TLC examination showed that the reaction was not completed. Then, half of the reaction solution was subjected to paper chromatography for separation. Elution with acetone and evaporation yielded 0.034 g of a brown solid, mp 68-70°C. The product was very hygroscopic. Infrared spectrum (KBr disc) (Appendix 14) 1640, 1520, 1260, and void 600-480 cm^{-1} (C-I stretch).

Analysis: Calc'd for $C_{20}H_{20}N_4I_2$:

C, 42.11; H, 3.51; N, 9.82; I, 44.56.

Calc'd for $C_{20}H_{20}N_4I_2 \cdot CH_3NO_2$:

C, 39.94; H, 3.65; N, 11.09; I, 40.25; O, 5.07.

Calc'd for $C_{20}H_{20}N_4I_2 \cdot 2CH_3NO_2$:

C, 38.30; H, 3.75; N, 12.12; I, 36.58; O, 9.25.

Found: C, 40.62; H, 4.60; N, 7.71; I, 39.23; O, 7.84.

This data and the data obtained from the other quaternarization of N,N'-di-2(-pyridylcarboxylidene)-p-phenylenediamine with CH_3I and dimethylsulfate are summarized in Table 3. Its infrared spectrum and elemental analysis confirmed that the desired compound was obtained, but that it was complexed with 1.5 moles of CH_3NO_2.

In a separate experiment, the product quaternarized with 4 moles of CH_3I

at 50°C for one and one-half hours was found to be a mixture of 47% mono-quaternary and 53% diquaternary derivatives.

The quaternarization of the di-Schiff base with $(CH_3)_2SO_4$ was performed in CH_3NO_2. The product was precipitated from CH_3NO_2 solution with ether. The product was an orange powder, mp 58-60°C, very hygroscopic and became gummy when exposed to atmospheric moisture. Infrared spectrum (KBr disc) 1630 cm^{-1} (broad) 1510, 1450, 1250-1200 cm^{-1} (broad), 1060, 1000 and 765 cm^{-1}. Its infrared spectrum and elemental analysis confirmed that the desired compound was obtained, but the di-quaternarized product was complexed with one mole of CH_3NO_2.

g. Quaternarization of 2,6-Diacetylpyridine.

Into a 25-ml, three-neck, round-bottom flask equipped with a thermometer and reflux condenser were placed 2,6-diacetylpyridine (1.00 g, 6.1 mmole), dimethylsulfate (1.01 g, 7.98 mmole) and 10 ml nitromethane. The reaction solution was heated at 50°C for twenty-four hours and at 80°C for one hundred forty-four hours under a nitrogen atmosphere. Evaporation of the solvent yielded a black solid, 1.80 g (102%); the product was very hygroscopic and became a liquid when exposed to atmospheric moisture. Infrared spectrum (KBr disc) 1690 cm^{-1} (C=O), 1600, 1480 and 1045 cm^{-1}.

Analysis: Calc'd for $C_{11}H_{15}NO_6S$:

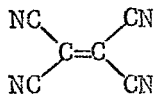
C, 45.67; H, 5.19; N, 4.84; S, 11.07; O, 33.23.

Found: C, 32.57; H, 4.77; N, 7.68; S, 14.60; O, 40.38.

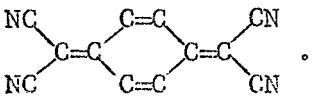
The desired compound was not obtained. This data and the data from the attempted quaternarization of 2,6-diacetylpyridine with methyl iodide are summarized in Table 4. As given in Table 4, the attempted quaternarizations of 2,6-diacetylpyridine with $(CH_3)_2SO_4$ or CH_3I were not successful, due to large steric hindrance of 2,6-diacetyl groups and lower basicity of pyridine nitrogen induced by the electron withdrawal of 2,6-diacetyl groups.

3. Charge Transfer Complexes Derived from Pyridine-Type Monomers.

Exploratory experiments have been performed to establish whether or not the prototype pyridine monomers will form charge transfer complexes with selected acceptors such as TCNE and TNCQ:



TCNE



TCNQ

a. Formation of the Charge-Transfer Complexes Between p-Xylylidene-di-2-aminopyridine (I) and Tetracyanoethylene.

The reactions of Schiff base (I) with TCNE were performed in DMAC in which both reactants were soluble. The Schiff base (I) has two pyridine rings, each of which would be expected to act as donor to at least one molecule of TCNE. Thus, the equivalent complex should be (I.2 TCNE). In efforts to establish the value of n for (I), a series of reactions were performed in DMAC using a mole ratio of 1 mole of (I) with one, two and four moles of TCNE respectively. The reaction temperature was 50°C for five hours. In all cases, a marked change in the almost colorless solution containing the monomer and the TCNE occurred within the first few minutes of the reaction; and as the reaction continued, the color darkened to a maximum and did not change further. The color of the solutions at ten minutes of reaction time and the final color for the compositions containing the various moles of TCNE per each mole of (I) were

Monomer	Moles of TCNE	Color at 10 min.	Final Color
I	1	orange	brown
I	2	brown	black
I	4	black	black

The reaction products were divided into two portions, evaporated product (A) and precipitated product (B), and examined respectively.

i. Portion A: Reaction Product Obtained by the Evaporation of the Solvent.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux

condenser and a thermometer were placed p-xylylidene-di-2-aminopyridine (0.28 g, 0.98 mmole), tetracyanoethylene (0.25 g, 1.95 mmole), and 10 ml of dimethylacetamide. The reaction mixture was maintained under a nitrogen atmosphere, heated at 50°C for five hours, allowed to cool, and stirred at room temperature for eighteen hours. The solvent was removed by evaporation at 0.5 mm Hg pressure, to yield a solid which was dried in vacuo at 50°C for three days until a constant weight was obtained. There was obtained a dark-brown solid 0.58 g (109%), mp 130-140°C. Infrared spectrum (KBr disc) (Appendix 15), 2200 cm^{-1} (C=N), broad absorption 1630-1400 cm^{-1}.

Analysis: Calc'd for $C_{30}H_{14}N_{12}$:

C, 66.42; H, 2.58; N, 31.00.

Calc'd for $C_{30}H_{14}N_{12} \cdot 3CH_3CON(CH_3)_2$:

C, 62.69; H, 3.98; N, 27.36; O, 5.97.

Found: [a] C, 63,64; H, 4.18; N, 27.83; O, 4.35 (by difference)

[a] This sample was block dried at 120°C suffering a weight loss of approximately 2.7% before analysis.

These data and the data of related experiments are summarized in Table 5.

The yield of evaporated product for the three complexes were found to be

Complex	Yield % of Theory
I 1 TCNE	100
I 2 TCNE	110
I 4 TCNE	110

Analysis of the products showed, that in the 2 TCNE and the 4 TCNE complexes, DMAC had been retained in the complex as follows:

Complex	Moles of DMAC Retained
I 1 TCNE	0.0
I 2 TCNE	1.0
I 4 TCNE	2.0

The isolated complexes were redissolved in DMAC, reprecipitated by $(C_2H_5)_2O$, isolated and dried at 50°C in a vacuum oven. Additional quantities of products

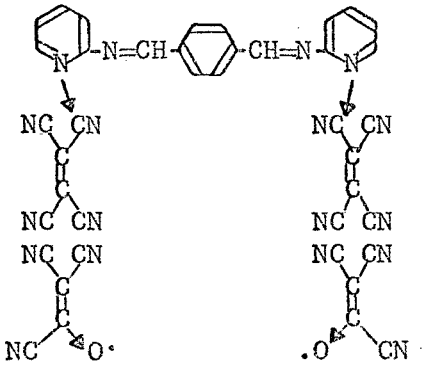
were obtained by concentration of the mother liquors and purified by redissolution in DMAC and followed by precipitation.

Elemental analysis of the precipitated I. 1 TCNE reaction product confirmed the 1:1 complex and that the product did not contain retained DMAC.

Elemental analyses of the precipitated I. 2 TCNE reaction product showed the presence of oxygen and that it appeared to complex with approximately one mole of DMAC.

Elemental analyses of the precipitated I. 4 TCNE reaction product showed the presence of large amounts of oxygen and appeared to be complexed with approximately two moles of DMAC.

It may be other than fortuitous that the elemental analyses of these complexes are close to the values expected for the complexes with DMAC. Perhaps, the retention of DMAC in the 1:2 and 1:4 products may be due to the reaction of DMAC with TCNE. Also, it is known that CN groups in charge transfer complex are very sensitive to oxygen and oxidized in air. Then the abnormally high content of oxygen in I. 4 TCNE product could be due to the fact that an uncoordinated free CN group in the complex is oxidized in air, with the elimination of CN groups, to give a stable radical, probably of the structure



The infrared spectra of the various complexes showed strong bands for CN at 2200 cm^{-1} and the spectra of the three complexes were substantially identical except that in the case of the 1:1 complex, the intensity at 2200 cm^{-1} was noticeably less than for the 1:2 of 1:4 complex. In addition, the three

complexes did not melt when heated to 360°C.

ii. Portion B: Reaction Product Obtained by Precipitation with Benzene.

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser and a thermometer were placed p-xylylidene-di-2-aminopyridine (0.56 g, 1.95 mmole), tetracyanoethylene (0.50 g, 3.91 mmole), and 20 ml dimethylacetamide. The reaction mixture was maintained under a nitrogen atmosphere at 50°C for five hours, allowed to cool, and stirred at room temperature for thirteen and one-half hours. The product was precipitated by the addition of benzene, collected by filtration, and dried at 50°C in vacuo, to yield a brown solid, 0.32 g (30%), mp $>$ 360°C. Infrared spectrum (KBr disc) (Same as Appendix 15), 2200 cm^{-1} (C=N), broad absorption 1630-1400 cm^{-1}.

Analysis: Calc'd for $C_{30}H_{14}N_{12}$:

C, 66.42; H, 2.58; N, 31.00.

Calc'd for $C_{30}H_{14}N_{12}\cdot CH_3CON(CH_3)_2$:

C, 64.83; H, 3.66; N, 28.62; O, 2.54.

Calc'd for $C_{30}H_{14}N_{12}\cdot 2CH_3CON(CH_3)_2$:

C, 63.69; H, 4.46; N, 27.37; O, 4.46.

Found:[a] C, 64.10; H, 3.73; N, 27.48; O, 4.69 (by difference).

[a]This sample was block dried at 120°C suffering a weight loss of approximately 2.7% before analysis.

These data and the data or related experiments are summarized in Table 5.

4. Charge Transfer Complexes Derived from Quaternary Derivatives of Pyridine-Type Schiff Bases.

a. Preliminary Experiments on the Preparation of Charge Transfer Complexes.

A number of preliminary qualitative experiments were performed to establish some conditions for the preparation of the charge transfer complexes from various quaternarized Schiff bases and TCNE. Dimethylformamide, dimethylacetoamide and nitromethane were found to be unsuitable as reaction media for preparation of charge transfer complexes, since they reacted strongly with TCNE.

Acetonitrile and absolute ethanol were established as more suitable solvents. The results of these experiments are summarized in Table 6. In general, the N-methyl pyridinium sulfates of the quaternarized Schiff bases were poorly soluble in acetonitrile and did not react with TCNE appreciably; for these reactions, absolute ethanol was suitable as a reaction medium.

b. Formation of the Charge Transfer Complex Derived from Di-N-Methyl-(p-Xylylidene-di-2-aminopyridinium)-Iodide and Tetracyanoethylene.

i. Charge Transfer Complex (I. 2 TCNE).

The di-quaternarized Schiff base used in this experiment was one precipitated from CH_3NO_2 solution with ether, washed with dry ether and dried in vacuum at 45°C to constant weight, and shown to be complexed with 1.5 moles CH_3NO_2, mp approximately 108-110°C.

Into a 25 ml, three-neck, round-bottom flask equipped with a reflux condenser and a thermometer were placed di-quaternarized Schiff base (0.331 g, 0.5 mmole), tetracyanoethylene (0.128 g, 1.0 mmole) and 10 ml acetonitrile.

The reaction mixture was heated under a nitrogen atmosphere at 50°C for five hours, allowed to cool, and stirred at room temperature for eighteen hours. The color of the reaction solution was dark-brown. The solvent was removed by evaporation at 0.5 mm Hg pressure to yield a black powder which was dried in vacuum at 45°C for twenty-four hours, until a constant weight was obtained. There was obtained a black solid, 0.40 g (87.2%), mp 80-82°C. Infrared spectrum (KBr disc), 2200 cm^{-1} (C≡N) 1650, 1590, 1500 cm^{-1}, and 770 cm^{-1} (broad). The evaporated product was dried at 40°C under vacuum for seventy-two hours before elemental analysis.

Analysis: Calc'd for $C_{32}H_{20}N_{12}I_2$:

C, 46.49; H, 2.42; N, 20.34; I, 30.75.

Found: C, 43.22; H, 3.08; N, 19.13; I, 29.27; O, 5.14.

The chemical composition of this product was $C_{31.4}H_{26.8}N_{11.9}I_2O_{2.79}$ and the

product was complexed with 1.4 moles of CH_3NO_2. When corrected for its nitromethane content, the chemical composition of the product is $C_{30}H_{22.6}N_{10.5}I_2$ which shows that it is somewhat low in carbon and nitrogen, compared to the composition of the expected compound, $C_{32}H_{20}N_{12}I_2$. This product was reprecipitated from CH_3CN solution by ether, washed with large amount of ether, and dried at 40°C under vacuum to afford a brown powder (yield about 30%), mp 110-112°C. Infrared spectrum (KBr disc) 2210 cm^{-1} (C=N) 1650, 1590, 1510 and 775 cm^{-1} (strong). The infrared spectrum of the reprecipitated product indicated a very strong absorption band for CN groups at 2210 cm^{-1} and was almost the same with one of diquaternarized Schiff base in other regions of the spectrum.

Analysis: Calc'd for $C_{32}H_{20}N_{12}I_2$:

C, 46.49; H, 2.42; N, 20.34; I, 30.75.

Found: C, 50.34; H, 3.40; N, 22.05; I, 16.40; O, 7.68.

Corrected*: C, 55.10; H, 3.14; N, 22.50; I, 19.30.

*For CH_3NO_2 content.

The elemental analysis indicated that precipitated product was complexed with 1.6 mmoles of CH_3NO_2 and the chemical composition of reprecipitated product, corrected for its nitromethane content was $C_{92}H_{62}N_{32}I_3$, which corresponds to a mixture composed of the following three components, $C_{20}H_{20}N_4I_2$, $C_{20}H_{20}N_4I^+$ and $C_{20}H_{20}N_4^{++}$ complexed with 5 moles of TCNE, thus: $[(C_{20}H_{20}N_4I_2 + (C_{20}H_{20}N_4I^+ \cdot TCNE^-)TCNE + (C_{20}H_{20}N_4^{++} \cdot 2TCNE^-)TCNE]$ whose elemental analysis is:

Calc'd: C, 54.9; H, 3.1; N, 22.7; I, 19.3.

This would indicate that the iodide ion of di-quaternarized Schiff base served as the electron source for the formation of $TCNE^-$ with the iodide ion being oxidized to elemental iodine; evidence of which was obtained in the filtrates from the reaction.

ii. Charge Transfer Complex (I·4 TCNE).

Into a 25-ml, three-neck, round-bottom flask equipped with a reflux condenser and a thermometer were placed di-quaternarized Schiff base (0.331 g, 0.5 mmole), tetracyanoethylene (0.256 g, 2 mmole) and 10 ml of acetonitrile. The reaction mixture was heated under a nitrogen atmosphere at 50°C for five hours, and then allowed to cool with stirring at room temperature for eighteen hours to yield a black solution. The solvent was removed by evaporation at 0.5 mm Hg pressure to yield a black powder which was dried to constant weight in a vacuum oven at 45°C for twenty-four hours, affording a black solid 0.436 g (74.5%). Infrared spectrum (KBr disc): 2210 cm^{-1} (C≡N), 1660, 1590 (broad), and 770 cm^{-1}. The product was reprecipitated from CH_3CN solution with ether, washed with a large amount of ether and dried at 40°C in vacuum oven to constant weight, yielding a black powder, 0.1288 g (20%), mp 163-165°C. Infrared spectrum (KBr disc) 2210 cm^{-1} (C≡N), 1650, 1590, 1550, 1500 and 765 cm^{-1} (broad). The infrared spectra of the evaporated and reprecipitated products showed a very sharp absorption band for CN groups at 2210 cm^{-1}.

Analysis: Calc'd for $C_{44}H_{20}N_{20}I_2$:

C, 48.80; H, 1.85; N, 25.88; I, 23.47.

Found: C, 54.94; H, 3.20; N, 22.02; I, 8.60; O, 11.24

The iodine content of the product was low and its elemental analysis corresponded to a chemical composition of the formula $C_{45.8}H_{32}N_{15.7}I_{0.677}O_{7.02}$ against the expected $C_{44}H_{20}N_{20}I_2$. The product appears to be a mixture composed of one mole of $C_{20}H_{20}N_4I^+$, 0.5 mole of $C_{20}H_{20}N_4^{++}$, and 3 moles of TCNE complexed with 1.55 moles of CH_3NO_2. In the case of this 1:4 reaction, the elimination from the quaternarized Schiff base of iodide by TCNE was more extensive than in the 1:2 reaction but it was not complete. Longer reaction times or higher temperature probably would complete the elimination. The data do appear to confirm, however, that the iodide ion of these quaternary iodides can be exchanged for a $TCNE^{\cdot-}$ anion radical.

III. Discussion.

A. Synthesis of Pyridine-Type Schiff Base Monomers.

Seven aromatic, Schiff-base type monomers have been prepared and some of their prototype reactions have been studied.

Of the seven heterocyclic Schiff bases, six were prepared by the reaction of the appropriate carbonyl compounds with selected amino compounds by a continuous azeotropic method using toluene as the azeotropic agent. In general, the yields of crude product were less than, and the rates of condensation were slower than, similar reactions reported for the synthesis of aromatic carbocyclic Schiff bases using the continuous azeotropic technique. In the synthesis of aldazomethines, a catalyst was not required for the condensation; however, the ketazomethines required the use of a Lewis acid catalyst due to the lower reactivity of the ketone moiety compared to the aldehyde function.

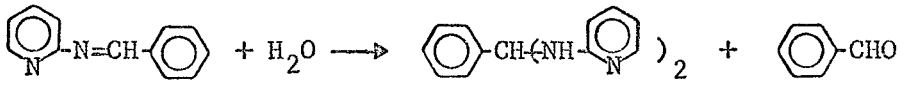
Attempts to prepare the seventh heterocyclic Schiff base by the azeotropic method were unsuccessful; it was prepared by condensing the amine hydrochloride with the appropriate carbonyl compound in alcohol as the solvent. The desired product was obtained as a precipitate upon the neutralization of the solution with aqueous sodium carbonate.

The syntheses of a number of other Schiff bases of interest in this project were not achieved, and the reasons for these failures were sought.

1. Preparation of Benzylidene-2-aminopyridine.

Benzylidene-2-aminopyridine was prepared by the condensation of benzaldehyde with 2-aminopyridine through the continuous azeotropic method. After a nearly quantitative yield of water was collected, the solvent was evaporated to yield a dark oil which was distilled under reduced pressure to give a light yellow oil, bp 102°C/0.2 mm Hg, corr. 196°C/18 mm Hg (lit., bp 200°C/18 mm Hg); n^{D}_{25}=1.6498 (lit., n^{D}_{21}=1.6564). During the purification by distillation of the product, a film consisting of a white solid, mp 108°C, formed on the walls of

the distillation apparatus. The infrared spectrum of the distilled product had a weak absorption consisting of a shoulder at 3230 cm^{-1} attributed to N-H, an absorption band at 1700 cm^{-1} attributed to carbonyl and a band for C=N at 1630 cm^{-1}. The NMR had a one proton singlet at 9.18 δ attributed to -CH=N- and a multiplet at 8.5 to 6.9 δ which according to the integration contained ten protons instead of the expected nine. These irregularities in the spectra can be attributed to impurities caused by the previously reported rapid reaction of the benzylidene-2-aminopyridine with water:



Benzylidene-2,2'-dipyridylamine, one of the products of this reaction, is a white solid, mp 109°C. The elemental analysis also confirmed that the product contained about 10% impurities; and repeated attempts at purification were unsuccessful in that the regeneration of the bis-compound continued with each attempt. Also it was found that after only two days of storage under nitrogen in a refrigerator, the same type of white solid, mp 109°C, had begun to precipitate from the light yellow oil.

2. Preparation of 2-Pyridylcarboxylideneanil.

The synthesis of 2-pyridylcarboxylideneanil was accomplished using the continuous azeotropic method by condensing 2-pyridinecarboxaldehyde with aniline; it was a red solid, mp 36-37°C. The infrared spectrum was void in the 3400-3100 cm^{-1} region (NH); the NMR had a one proton singlet at 8.6 δ, for the -CH=N- azomethine linkage, and two multiplets; one was assigned to the four pyridine ring protons at 8.7-7.6 δ and the other was assigned to the five phenylene protons at 8.4-8.2 δ. The preparation of 2-pyridylcarboxylideneanil was previously reported by Harris and Lenart, who heated 2-pyridinecarboxaldehyde with aniline at 150°C to yield a greenish oil, bp 165°C, but reported no melting point. The infrared spectrum, NMR, and the elemental analysis

support the identification of this red solid, mp 36-37°C, as 2-pyridylcarboxylideneanil.

3. The Attempted Preparation of Pyridylcarboxylidene-2-aminopyridine.

The condensation of 2-pyridine carboxaldehyde and 2-aminopyridine using the continuous azeotropic method yielded nearly colorless crystals, mp 121-122°C. The infrared spectrum was very similar to that of benzylidene -2,2'-dipyridylamine; based on this fact and on the elemental analysis, the product was identified as 2-pyridylcarboxylidene-2,2'-dipyridylamine and not the desired product.

In a second attempt to prepare the desired compound, 2-pyridylcarboxylidene-2,2'-dipyridylamine, prepared above by the azeotropic method, was heated at 120°C in an effort to pyrolyze it to 2-pyridylcarboxylidene-2-aminopyridine. During the pyrolysis experiment, some white solid condensed on the upper walls of the tube; however, a thin layer chromatography of this condensate and of the residue in the reaction flask, when compared with that of starting materials, indicated that the pyrolytic reaction had not occurred.

A third method was tried in the attempt to synthesize 2-pyridylcarboxylidene-2-aminopyridine; it involved the reaction of 2-aminopyridinium hydrochloride with 2-pyridine carboxaldehyde in refluxing ethanol. The product of the reaction was a dark red solid, mp 115-116°C; recrystallized from benzene, nearly colorless crystals, mp 121-122°C. The infrared spectrum was identical to the infrared spectrum of 2-pyridylcarboxylidene-2,2'-dipyridylamine. Thus, the attempted syntheses of 2-pyridylcarboxylidene-2-aminopyridine were not successful due to the side reaction which leads to the bis-pyridyl derivative.

4. Preparation of 2-Acetylpyridineketanil.

The synthesis of 2-acetylpyridineketanil was not successful using the continuous azeotropic method. Thin layer chromatography indicated that only a trace of product was present after forty-five hours of reaction in refluxing

toluene. However, a low yield (30%) of 2-acetylpyridineketanil was realized from the reaction of 2-acetylpyridine with anilinium hydrochloride in refluxing ethanol. The infrared spectrum was void of the amino hydrogen peaks present in aniline at 3200 cm^{-1} and 3350-3500 cm^{-1}; it contained a peak at 3310 cm^{-1} which appears in the infrared spectrum of 2-acetylpyridine at 3370 cm^{-1}. Elemental analysis lends support to the identification of this yellow solid as 2-acetylpyridineketanil.

5. Preparation of 2,6-Diacetylpyridinediketanil.

Only a very low yield (19%) of 2,6-diacetylpyridinediketanil was realized upon the condensation of 2,6-diacetylpyridine and aniline using the continuous azeotropic method. In the course of the reaction, no water was collected until a catalytic amount of zinc chloride was added to the reaction mixture. Even in the presence of zinc chloride, the reaction progressed very slowly and after fifty hours the reaction was stopped. The product of the reaction was identified by its infrared spectrum, NMR and elemental analysis to be 2,6-diacetylpyridinediketanil.

Another method was also tried in an attempt to obtain a higher yield of the desired product. A mixture fo 2,6-diacetylpyridine and anilinium hydrochloride in ethanol was stirred at room temperature for twenty-four hours, after which time the solution was neutralized with sodium carbonate; only starting materials were isolated.

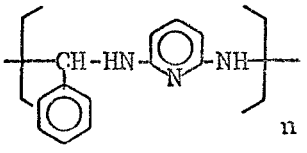
6. The Attempted Preparation of 2,6-Di-(α-methylcarboxylidene-2-aminopyridine)pyridine.

During the attempted azeotropic condensation of 2,6-diacetylpyridine with 2-aminopyridine, only a small amount of water was collected. Thin layer chromatography indicated that, in addition to starting materials, two reaction products were present in only very small amounts. Attempts to isolate these reaction products by fractional crystallization failed to give separation; after

which a chromatographic separation was tried. A concentrated portion of the reaction solution was subjected to column chromatography using silica gel as the support. The column was eluted with ethyl acetate and ten milliliter fractions were collected. The first six fractions contained only 2,6-diacetylpyridine, the next two fractions appeared to contain only solvent, and the remaining fractions collected consisted of a mixture of three compounds. However, the quantity of solid collected was insufficient to allow a second chromatographic separation.

7. The Attempted Preparation of 2,6-Di-(benzylideneamino)pyridine.

Many attempts were made to synthesize 2,6-di-(benzylideneamino)pyridine from benzaldehyde and 2,6-diaminopyridine by the continuous azeotropic method. In none of the experiments was a quantitative yield of water collected in the Dean-Stark trap. Crystals did not form during the slow evaporation of the solvent from the reaction mixture, but it was found that complete evaporation of the solvent yielded a glassy resinous residue. However, a yellow powder could be obtained by the addition of hexane to the reaction mixture. In every case, the infrared spectrum of the product isolated contained a broad peak centered at 3380 cm^{-1} which was attributed to N-H. A comparison of the infrared spectrum of the product obtained from the continuous azeotropic method with the infrared spectra of benzylidene-2,2'-dipyridylamine and 2-pyridylcarboxylidene-2,2'-dipyridylamine suggested that the structure of the product was an analogous form,



Vapor phase osmometry of the product dissolved in tetrahydrofuran yielded a molecular weight of 1200 for the product.

Many attempts were made to prevent the formation of the polymeric material during synthesis. It was believed that a large excess of benzaldehyde in the

reaction mixture would enhance the formation of Schiff base by reducing the probability of one molecule of benzaldehyde reacting with the amino groups of two different molecules. Therefore, ten millimoles of 2,6-diaminopyridine were reacted in 25 ml of benzaldehyde. Seventeen ml of benzaldehyde were removed by distillation at 50°C and 0.5 mm Hg to yield a slightly viscous solution which hardened upon cooling. Precipitation of a portion of this solution with hexane yielded a rubbery polymeric solid. The infrared spectrum of the solid was identical to the product obtained from the continuous azeotropic method.

It was speculated that the formation of the polymeric material might be prevented by the use of dibenzylideneazine or by benzaldehyde diethyl acetal in place of benzaldehyde. Accordingly, dibenzylideneazine was heated with 2,6-diaminopyridine under a slow stream of nitrogen passing over the melt solution. Thin layer chromatography indicated that the reaction yielded a complex mixture of reaction products most of which appeared to be polymeric. The mixture was column chromatographed; however, elution with ethyl acetate failed to achieve separation.

Alternately, benzaldehyde diethyl acetal was reacted with 2,6-diaminopyridine. However, thin layer chromatography indicated that polymeric material had formed and that only a trace of non-polymeric product may have formed. Isolation of the non-polymeric product was not attempted.

8. The Attempted Preparation of 2,6-Di-(α-methylbenzylideneamino)-pyridine.

The condensation of 2,6-diaminopyridine with acetophenone in the presence of HCl as the catalyst was attempted using the continuous azeotropic method. A trace amount of water was collected during the extended reflux time of two hundred thirty-six hours. Thin layer chromatography indicated that two reaction products had formed in small quantities. Crystallization did not occur during the slow evaporation of the solvent, rather, a dark brown oil was obtained.

The oil was subjected to paper chromatography and eluted with ethyl acetate. An attempt was made to cut a narrow strip thought to contain only one compound. Extraction of the strip with hot methyl alcohol yielded a few milligrams of a yellowish solid which thin layer chromatography indicated contained three compounds. No further attempts at isolation were undertaken.

9. The Attempted Preparation of α,α'-Dimethyl-p-xylylidenedi-2-aminopyridine.

During the attempted azeotropic condensation of 1,4-diacetylbenzene and 2-aminopyridine no water was collected in the Dean-Stark trap. However, thin layer chromatography indicated that two reaction products had formed in small quantities. Fractional crystallization by the slow removal of solvent yielded three crystalline fractions containing only 1,4-diacetylbenzene and 2-aminopyridine. The remaining solution was subjected to paper chromatography and eluted with ethyl acetate. An attempt was made to cut a narrow strip thought to contain only one compound. Extraction of the strip with methyl alcohol yielded a few milligrams of a solid which thin layer chromatography indicated was a mixture. No further attempt was made to isolate the products of the reaction.

10. The Attempted Synthesis of 3,6-Di-(benzylideneamino)-10-methylacridinium Chloride.

It was not possible to synthesize 3,6-di-(benzylideneamino)-10-methylacridinium chloride. An attempt was made to prepare this compound from acriflavine and benzaldehyde using the continuous azeotropic method, however, acriflavine was not soluble in toluene and only very slightly soluble in toluene containing benzaldehyde. Accordingly, acriflavine was condensed with a large excess of benzaldehyde which also acted as the solvent for the reaction mixture. The infrared spectrum of the product contained a broad peak at 3380 cm^{-1} (NH), a weak band at 1700 cm^{-1} (C=O), and bands at 700 and 750 cm^{-1} which were attributed to five adjacent aromatic hydrogens. The elemental analysis of the

product showed that much less nitrogen and chlorine were present than expected for either the mono- or the desired bis-Schiff base. It appears that HCl was eliminated during the reaction, however, it was not possible to determine clearly the structure of the final product. A similar behavior was experienced in the attempts to react phenosafranine with benzaldehyde.

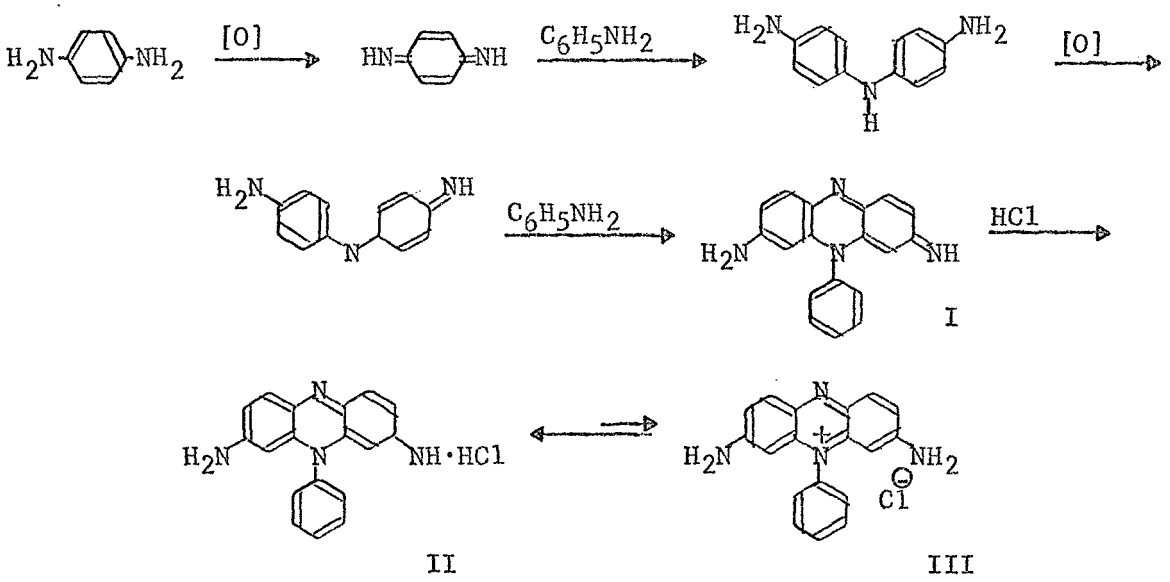
11. The Attempted Preparation of 2,8-Di-(benzylideneamino)-10-phenylphenazine Chloride.

The attempted preparation of 2,8-di-(benzylideneamino)-10-phenylphenazine chloride was not successful and paralleled that experienced in the preparation of the acriflavine derivative. The reaction of phenosafranine with benzaldehyde using benzaldehyde as the solvent produced a purple residue. The infrared spectrum of this product contained bands attributed to the presence of N-H, and peaks at 700 and 760 cm^{-1} which were attributed to five adjacent aromatic hydrogens. The elemental analysis of the product showed that much less nitrogen and chlorine were present than the theoretical amount calculated for either the mono- or the desired bis-Schiff base. It appears that HCl was eliminated from the molecule during the reaction, however, it was not possible to determine clearly the structure of the final product.

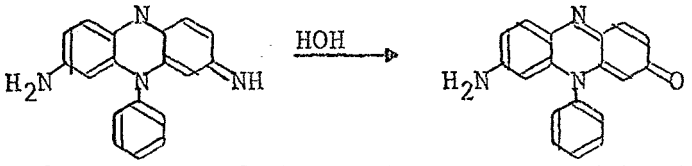
It has been stated in the literature that if one amino group of phenosafranine is attacked, the other ceases to exercise the function of an amino group. This conclusion was based on the following observations: (1) it was found to be impossible to diazotize both amino groups in solution of acid of medium concentration, (2) phenosafranine reacts with only one mole of benzaldehyde in water solution; the procedure reported in the literature for the reaction was repeated and it yielded only starting material, and (3) tetramethylphenosafranine combines with only one mole of methyl iodide.

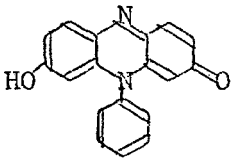
Phenosafranine is sold as the diamine, III (see equations below). It is synthesized by the addition of potassium dichromate to a cold solution of p-

phenylenediamine and aniline, as illustrated in the following equations:



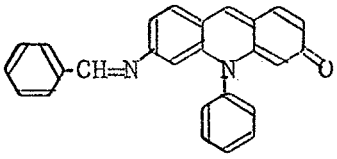
It appears that phenosafranine can exist in the tautomeric forms II and III. However, if III were the predominant form, reaction with two moles of benzaldehyde should yield the bis-Schiff base; if II were the predominant form, only the mono-Schiff base should be obtained, since the imine, C=NH, cannot react to form the Schiff base. In an attempt to show that II is the favored form, phenosafranine was refluxed with aqueous sodium hydroxide, for it was believed that elimination of HCl would occur to yield I. The elemental analysis of the final product, when compared to I, indicated that there was no chlorine present in the molecule; however, it showed that much less nitrogen was present, and that there was a considerable amount of oxygen in the product. This was taken to indicate that I had formed and then was hydrolyzed, thus:



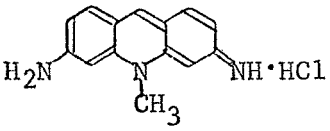
The infrared spectrum of the product contained bands at 3320 and 3260 cm^{-1} attributed to N-H, and a medium intensity shoulder at 1650 cm^{-1} which is probably due to the C=O moiety, phenosafranol,  , which would be

the next stage of the previously mentioned hydrolysis of phenosafranine with aqueous NaOH, is reported as being prepared by boiling phenosafranine with alcoholic KOH for some days.

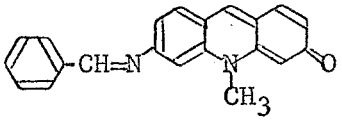
It would appear to be logical to conclude that during the condensation of phenosafranine with benzaldehyde, not only had the mono-Schiff base



formed, but that the product was contaminated with other decomposition products which had also lost some additional amino nitrogen. By analogy then, it is believed that acriflavine which has the formula



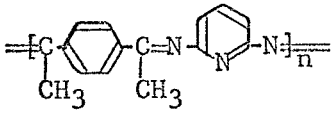
underwent a similar decomposition during the reaction with benzaldehyde to yield

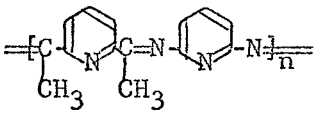


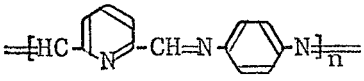
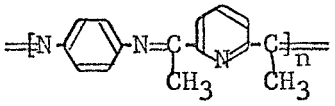
B. Conclusions on Applicability of Prototype Reactions to Polymer Syntheses.

Based on the results of the synthesis of the prototypes, it was concluded that the condensation of 2,6-diaminopyridine with aryl carbocyclic dialdehydes, such as terephthaldehyde, and with heterocyclic dialdehydes such as 2,6-pyridine dicarboxaldehyde, will not yield polyazomethines having C=N linkages. It would appear that these reactions probably would yield instead, cross-linked, three-dimensional polymers containing -HN-CH-NH- linkages in structures resembling that of the linear polymeric product obtained from 2,6-diaminopyridine and benzaldehyde.

In contrast, it appears that carbocyclic aryl diketones will yield polyketanils with 2,6-diaminopyridine. For example, the formation of



from p-diacetylbenzene and 2,6-diaminopyridine appears to be feasible, but the condensation would be a very slow process even in the presence of a catalyst. It would appear that the preparation of  would be even slower.

The successful reactions of aniline with 2-pyridine carboxaldehyde and 2-acetylpyridine led to the speculation that the polymers based on p-phenylene-diamine with 2,6-pyridine dicarboxaldehyde or 2,6-diacetylpyridine, for example  and  respectively, are feasible candidates for future polymer studies.

In spite of the fact that some of the continuous azeotropic experiments failed to yield isolable quantities of product, it still may be possible to synthesize the polymers which are structurally related to these systems by other methods, such as by (a) melt condensations at higher temperatures, or (b) by a modified Schiff base exchange method.

C. Quaternarization of the Model Compounds.

Four model Schiff base compounds containing aromatic, nitrogen heterocyclic rings were subjected to quaternarization to determine the feasibility of performing the same reaction on polyazomethines which would have repeating units of corresponding structures.

It has been reported in the literature that the reactions of 2-, 3-, and 4-aminopyridine respectively with methyl iodide and benzylhalides yield predominantly the quaternary pyridinium salts rather than the alkylaminopyridines. These results were explained by the preference of these aminopyridines to exist mainly in the amine rather than the imine form and by the greater basicity of the nuclear nitrogen atom. Based on these results, it was believed that the aromatic heterocyclic ring nitrogen would be much more basic than the azomethine linkage and, therefore, would be the site at which quaternarization would occur.

The quaternarization reactions of the pyridine-type Schiff bases were carried out in a variety of solvents using methyl iodide and dimethyl sulfate as the model quaternarization agents. It was found that quaternarization of these compounds failed to occur in non-polar solvents such as benzene or diethyl ether, but did occur in polar solvents such as N,N-dimethylacetamide or nitromethane. These results confirm the findings reported in the literature that polar solvents speed up the quaternarization reaction of pyridines. The quaternarization of the model compounds by dimethyl sulfate was more facile and produced better yields than quaternarizations with methyl iodide.

The quaternary salts, usually brown or black in color, were very hygroscopic, and retained solvent tenaciously.

Of the reactions attempted, only the reaction of 2-pyridylcarboxylideneaniline with methyl iodide was successful when dimethylacetamide was used as the solvent. In all other experiments in which DMAC was employed as the solvent, only decomposition products were isolated. These observations led to the belief that the dimethylacetamide participated in the decomposition reactions, because, when the quaternarization reactions were performed under similar conditions in nitromethane, they were successful.

1. Quaternarization of p-Xylylidene-di-2-aminopyridine with Methyl Iodide.

The reaction of p-xylylidene-di-2-aminopyridine with methyl iodide in DMAC did not produce the desired product. The elemental analysis of the product isolated from the reaction corresponded to a compound of molecular formula $C_6H_9N_2I$. The infrared spectrum of the isolated product contained peaks centered at 3300 cm^{-1} and 3140 cm^{-1} which were attributed to free NH_2. It was void in the region of 2700 to 2300 cm^{-1} which is the region of $\overset{+}{N}H_2$ stretch. Based on its elemental analysis and infrared spectrum, the product was identified as 2-amino-1-methylpyridinium iodide. Since p-xylylidene-di-2-aminopyridine is

stable in DMAC at the temperatures used in the quaternarization reaction, the product obtained would indicate that quaternarization had occurred first and that the decomposition of the quarternary salt was influenced by the DMAC. A possible explanation of these results would be that methyl iodide added to the ring nitrogen, and then this positive quaternarized nitrogen could withdraw electrons from the azomethine linkage rendering it more susceptible to subsequent decomposition.

In contrast, the reaction in nitromethane of p-xylylidene-di-2-aminopyridine with two moles of methyl iodide produced the diquaternary salt. The elemental analysis of the product indicated that nitromethane had been complexed with the diquaternary salt.

The reaction in nitromethane of p-xylylidene-di-2-aminopyridine with four moles of methyl iodide (two moles excess) also produced the diquaternary salt. The infrared spectrum of the product isolated from this experiment was identical to the infrared spectrum of the product isolated from the reaction of the bis-Schiff base with two moles of methyl iodide in nitromethane; its elemental analysis indicated also that the diquaternary salt had retained nitromethane.

2. Quaternarization of p-Xylylidene-di-2-aminopyridine with Dimethyl Sulfate.

The experimental data indicate that one mole of dimethyl sulfate was effective in quaternarizing p-xylylidene-di-2-aminopyridine when the reaction was performed in m-cresol, and that both CH_3 groups in the dimethyl sulfate had been utilized in the reaction. In this case, the counter ion for the two pyridinium groups was the divalent sulfate ion, $SO_4^{=}$. The elemental analysis of the product isolated from this reaction indicated that the quaternary salt retained approximately four moles of m-cresol.

The quaternarization of p-xylylidene-di-2-aminopyridine with two moles of dimethyl sulfate was very facile in nitromethane. In this case the counter ion

for each pyridinium group was the methyl acid sulfate ion, $CH_3SO_4^-$. The elemental analysis of the product indicated that the diquaternary salt retained approximately one mole of nitromethane.

3. Quaternarization of 2,6-Diacetylpyridinediketanil.

The reaction of 2,6-diacetylpyridinediketanil with methyl iodide in DMAC did not produce the desired diquaternary salt. The elemental analysis of the product isolated from this reaction indicated the presence of nearly twice as much iodine and considerably less carbon than required for the quaternary salt. It was obvious that the desired compound had not been obtained when the reaction was attempted in DMAC. However, the quaternary salts of 2,6-diacetylpyridinediketanil were prepared in nitromethane by reaction with methyl iodide and dimethyl sulfate respectively. The reaction was much more facile when dimethyl sulfate was used as the quaternarization agent.. The elemental analysis of both quaternary salts indicated that they had retained complexed nitromethane.

4. Quaternarization of N,N'-Di-(2-pyridylcarboxylidene)-p-phenylenediamine.

The reaction of N,N'-di-(2-pyridylcarboxylidene)-p-phenylenediamine with methyl iodide was performed in nitromethane. After two and one-half hours at 50°C, the reaction was terminated and the product isolated. The elemental analysis indicated that the quaternarization reaction was incomplete. The experiment was reported and the reaction time was increased to twenty-four hours before isolating the product. The data obtained on the product indicated that the quaternarization was successful; its elemental analysis also showed that this salt retained solvent.

The reaction of N,N'-di-(2-pyridylcarboxylidene)-p-phenylenediamine with dimethyl sulfate in nitromethane was also performed and the data indicated that this diquaternary salt formed much more readily than the corresponding iodide.

5. The Attempted Quaternarization of 2,6-Diacetylpyridine.

As a possible route to poly-Schiff bases containing a quaternary ionic site, the carbonyl component containing an aromatic, nitrogen heterocyclic ring could be quaternarized before the polycondensation with the diamino component. For this reason an attempt was made to quaternarize 2,6-diacetylpyridine.

The results obtained indicated that methyl iodide did not react with 2,6-diacetylpyridine in nitromethane. After forty-five hours at 50°C, the color of the reaction solution had not changed, and thin layer chromatography indicated that no reaction had occurred. However, when the reaction was performed in DMAC, it appeared that methyl iodide did add to the 2,6-diacetylpyridine. The elemental analysis of the product isolated from the reaction in DMAC indicated that it contained more iodine and less oxygen than required for 1-methyl-2,6-diacetylpyridinium iodide. Some preliminary efforts to determine the structure of this product were not successful.

In an effort to obtain the quaternarized derivative, dimethyl sulfate was reacted with 2,6-diacetylpyridine in nitromethane, and a product was obtained. However, the elemental analysis of this product showed that it contained more nitrogen, oxygen and sulfur, but less carbon than required for 1-methyl-2,6-diacetylpyridinium methyl sulfate. Preliminary efforts to determine the structure of this product were not successful.

D. Reaction of p-Xylylidene-di-2-aminopyridine with Tetracyanoethylene.

The experimental data showed that p-xylylidene-di-2-aminopyridine can form charge transfer complexes with one, two and four moles of tetracyanoethylene. The complexation reactions were performed in DMAC, and the products were isolated either by evaporation of the solvent or by the addition of benzene to precipitate the product. In the latter method, the yields reported refer only to the product obtained directly from the precipitation; the remaining unprecipitated product was recovered, however, by evaporating the resulting solution.

The elemental analyses of the products isolated in every experiment showed the presence of oxygen which was attributed to DMAC retained by the complex. The infrared spectra of the complexes containing one, two and four moles of tetracyanoethylene were all identical; each contained a sharp band at 2200 cm^{-1} (C≡N), and the profile of the spectra in the region between 1640 to 800 cm^{-1} appeared as one broad absorption. The 1:4 complex of p-xylylidene-di-2-aminopyridine and TCNE appears to contain oxygen of reaction with air.

E. Reaction of Quaternarized Schiff Bases with TCNE.

The experimental data show that the quaternarized Schiff bases also form complexes with TCNE but that in the presence of excess TCNE, the iodide ion is displaced and oxidized to iodine.

F. Conclusions on Applicability of the Reactions of the Model Compounds to the Polymers.

Based on the results of the quaternarization reactions of the model Schiff base compounds, it may be concluded that the quaternarization of the nitrogen of the aromatic heterocyclic rings in the corresponding poly-Schiff bases is a feasible reaction by proper choice of solvent and alkylating agent.

It may also be concluded that the poly-Schiff bases which have repeating units similar to the structure of the model compounds, will form charge-transfer complexes readily under appropriate reaction conditions.

IV. Studies in Progress.

a) Pyridine-type Schiff bases with various mole ratios of TCNE are in progress.

b) Quaternarized pyridine-type Schiff bases with various mole ratios of TCNQ are in progress.

c) Quaternarized pyridine-type Schiff base with Li(TCNQ) and $Li(TCNQ)_2$ are in progress.

V. Miscellaneous.

Thomas Daly, research associate, will terminate his appointment on this project on November 15, 1969.

The research staff consists currently of Dr. M. Nishimura, Postdoctoral Research Associate (Osaka University) full time, and Dr. O. C. Joice (Freiburg University) part time, under Professor G. F. D'Alelio, Principal Investigator.

Table 1. Data on the Quaternization of p-Xylylidene-di-2-aminopyridine.

Moles Reactant	Solvent	Temp. °C / Time hrs.	Yield % / Color	mp °C		Elemental Analysis C	H	N	I	O
$2CH_3I$	CH_3NO_2	50/7	44 Orange	95-96	Theory[a]	42.11	3.51	9.82	44.56	-
					Found[b]	44.34	4.78	12.96	28.34	9.58[d]
$2CH_3I$	DMAC	50/4	98 Yellow	151-152	Found[c]	30.75	3.90	11.68	53.51	-
$2CH_3I$	DMAC	50/8	76 Yellow	151-152	Found[c]	30.76	3.92	12.12	53.10	-
$4CH_3I$	DMAC	50/8	69 Yellow	151-152	Found[c]	30.67	3.83	12.11	53.61	-
$4CH_3I$	CH_3NO_2	50/9	109 Brown	107-109	Found[b]	40.73	4.06	11.98	33.68	8.90
$4CH_3I$	CH_3NO_2	50/24	125 Brown	107-109	Found[b]	37.64	3.72	11.71	39.64	7.56
$8CH_3I$	-	50/2	N.R.							

a. These values are for the di-quaternary salt, $C_{20}H_{20}N_4I_2$.

b. Cal'd for $C_{20}H_{20}N_4I_2 \cdot CH_3NO_2$: C,39.94; H,3.65; N,11.09; I,40.25; O,5.07.

Cal'd for $C_{20}H_{20}N_4I_2 \cdot 2CH_3NO_2$: C,38.30; H,3.75; N,12.12; I,36.58; O,9.25.

c. Compare this analysis with the theoretical values for 1-methyl-2-aminopyridinium iodide, $C_6H_9N_2I$: C,30.72; H,3.91; N,12.18; I,53.32.

d. This value was determined by difference.

Table 1. (Cont.) Data on the Quaternization of p-Xylylidene-di-2-aminopyridine.

Moles Reactant	Solvent	Temp. °C / Time hrs.	Yield % / Color	mp °C		Elemental Analysis C	H	N	S	O
$(CH_3)_2SO_4$	m-Cresol	50/7	118 Yellow	65-63	Theory[e]	58.25	4.85	13.59	7.77	15.53
					Found[f]	67.09	6.26	5.19	3.98	16.75
$2(CH_3)_2SO_4$	CH_3NO_2	50/1.5	108 Orange	65-68	Theory[g]	49.07	4.83	10.41	11.90	23.79
					Found[h]	46.69	5.25	11.48	10.06	26.74

e. These values are for the quaternary salt, $C_{20}H_{20}N_4SO_4$.

f. Cal'd for $C_{20}H_{20}N_4SO_4 \cdot 3$ m-Cresol: C,67.10; H,5.62; N,7.65; S,4.37; O,15.28.
Cal'd for $C_{20}H_{20}N_4SO_4 \cdot 4$ m-Cresol: C,68.62; H,5.72; N,6.67; S,3.82; O,15.25.

g. These values are for the quaternary salt, $C_{22}H_{26}N_4S_2O_8$.

h. Cal'd for $C_{22}H_{26}N_4S_2O_8 \cdot CH_3NO_2$: C,46.08; H,4.84; N,11.68; S,10.68; O,26.72.

Table 2. Data on the Quaternization of 2,6-Diacetylpyridinediketanil.

Moles Reactant	Solvent	Temp. °C / Time hrs.	Yield % / Color	mp °C		Elemental Analysis C	H	N	I	S	O
1.5CH_3I	CH_3NO_2	50/24	93 Brown	176-178	Theory[a]	58.02	4.83	9.23	27.92	-	-
					Found[b]	53.35	4.04	8.31	29.04	-	2.90
CH_3I	DMAC	50/44 plus 70/48	94 Black.	177-179	Found[c]	41.50	5.25	5.38	47.31	-	-
$(CH_3)_2SO_4$	CH_3NO_2	50/2	99 Brown	171-173	Theory[d]	62.87	5.69	9.57	-	7.29	14.58
					Found[e]	61.59	5.70	9.19	-	6.75	16.09

a. These values are for the quaternary salt, $C_{22}H_{22}N_3I$.
b. Cal'd for $C_{22}H_{22}N_3I \cdot CH_3NO_2$: C,53.50; H,4.86; N,10.85; I,24.62; O,6.20.
c. These values indicate that the desired compound was not obtained.
d. These values are for the quaternary salt, $C_{23}H_{25}N_3SO_4$.
e. Cal'd for $C_{23}H_{25}N_3SO_4 \cdot CH_3NO_2$: C,57.60; H,5.61; N,11.18; S,6.42; O,19.19.

Table 3. Data on the Quaternization of N,N'-Di-(2-pyridylcarboxylidene)-p-phenylenediamine.

Moles Reactant	Solvent	Temp. °C / Time hrs.	Yield % / Color	mp °C		Elemental Analysis C	H	N	I	S	O
$4CH_3I$	CH_3NO_2	50/24	5 Brown	68-69	Theory[a]	42.11	3.51	9.82	44.56	-	-
					Found[b]	40.62	4.60	7.71	39.23	-	7.84
$4CH_3I$	CH_3NO_2	50/2.5	92 Brown	95-97	Found[b]	46.07	3.94	11.62	34.91	-	3.90
$2(CH_3)_2SO_4$	CH_3NO_2	50/7	107 Red	58-60	Theory[c]	49.07	4.83	10.41	-	11.90	23.79
					Found[d]	46.30	5.29	8.61	-	11.25	28.55

a. These values are for the diquaternary salt, $C_{20}H_{20}N_4I_2$.

b. Cal'd for $C_{20}H_{20}N_4I_2 \cdot CH_3NO_2$: C,39.94; H,3.65; N,11.09; I,40.25; O,5.07.

Cal'd for $C_{20}H_{20}N_4I_2 \cdot 2CH_3NO_2$: C,38.30; H,3.75; N,12.12; I,36.58; O,9.25.

c. These values are for the di-quaternary salt, $C_{22}H_{26}N_4S_2O_8$.

d. Cal'd for $C_{22}H_{26}N_4S_2O_8 \cdot CH_3NO_2$: C,46.08; H,4.84; N,11.68; S,10.68; O,26.72.

Cal'd for $C_{22}H_{26}N_4S_2O_8 \cdot 2CH_3NO_2$: C,43.64; H,4.85; N,12.58; S, 9.70; O,29.09.

Table 4. Data on the Quaternization of 2,6-Diacetylpyridine.

Moles Reactant	Solvent	Temp. °C / Time hrs	Yield % / Color	mp °C		Elemental Analysis C	H	N	I	S	O
$(CH_3)_2SO_4$	CH_3NO_2	50/24 plus 80/144	102 Black	-	Theory[a]	45.67	5.19	4.84	-	11.07	33.23
					Found[b]	32.57	4.77	7.68	-	14.60	40.38
CH_3I	CH_3NO_2	50/4	N.R.								
CH_3I	DMAC	50/45 plus 80/120	85 Black	-	Theory[c]	39.34	3.93	4.59	41.64	-	10.49
					Found[b]	38.29	3.86	6.12	50.45	-	6.30

a. These values are for the quaternary salt, $C_{11}H_{15}NSO_6$.

b. These values indicate that the desired compound was not obtained.

c. These values are for the quaternary salt, $C_{10}H_{12}NIO_2$.

Table 5. Data on the Complexes of p-Xylylidene-di-2-aminopyridine and Tetracyanoethylene.

Moles TCNE	Solvent	Temp. °C / Time hrs.	Method of Isolation	Yield % / Color	mp °C		Elemental Analysis C	H	N	O
2	DMAC	50/5	Precipitation by Benzene	30 Dark-Brown	>360	Theory[a]	66.42	2.58	31.00	-
						Found[b,c]	64.10	3.73	27.48	4.69[d]
2	DMAC	50/5	Evaporation of Solvent	109 Dark-Brown	130-140	Found[b,c]	63.64	4.18	27.83	4.35[d]
1	DMAC	50/5	Precipitation[e] by Benzene	21 Dark-Brown	>360	Theory[f]	69.56	3.38	27.06	-
						Found[g]	66.06	4.03	26.30	3.61[d]
			Evaporation[e] of Solvent	51 Dark-Brown	130-140	Found[g]	66.70	4.56	25.31	3.43[d]

a. These values are for p-xylylidene-di-2-aminopyridine complexed with two moles of TCNE, $C_{30}H_{14}N_{12}$.

b. Sample was block dried at 120 °C suffering a weight loss of approximately 2.7% before analysis.

c. Cal'd for $C_{30}H_{14}N_{12} \cdot 2CH_3CON(CH_3)_2$: C,63.69; H,4.46; N,27.37; O,4.46.

d. This value was determined by difference.

e. In this experiment the reaction solution was divided into two parts immediately preceeding the isolation of the product. Both methods of isolation were then used; one method on one half of the solution, the other method on the remainder.

f. These values are for p-xylylidene-di-2-aminopyridine complexed with one mole of TCNE, $C_{24}H_{14}N_8$.

g. Cal'd for $C_{24}H_{14}N_8 \cdot CH_3CON(CH_3)_2$: C,67.10; H,4.59; N,25.18; O,3.19.

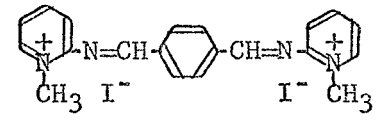
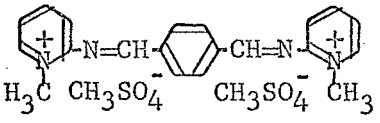
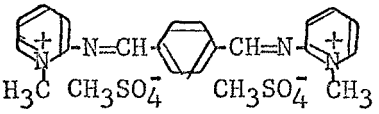
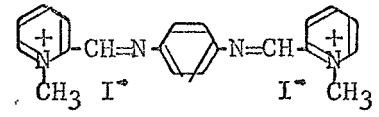
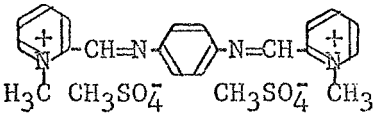
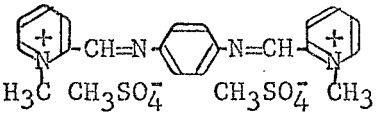
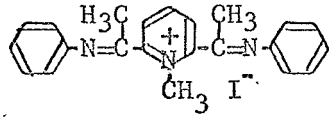
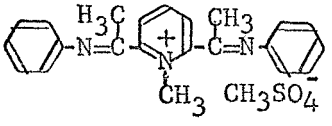
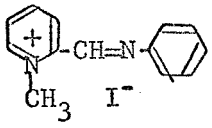
Table 5. (Cont.) Data on the Complexes of p-Xylylidene-di-2-aminopyridine and Tetracyanoethylene.

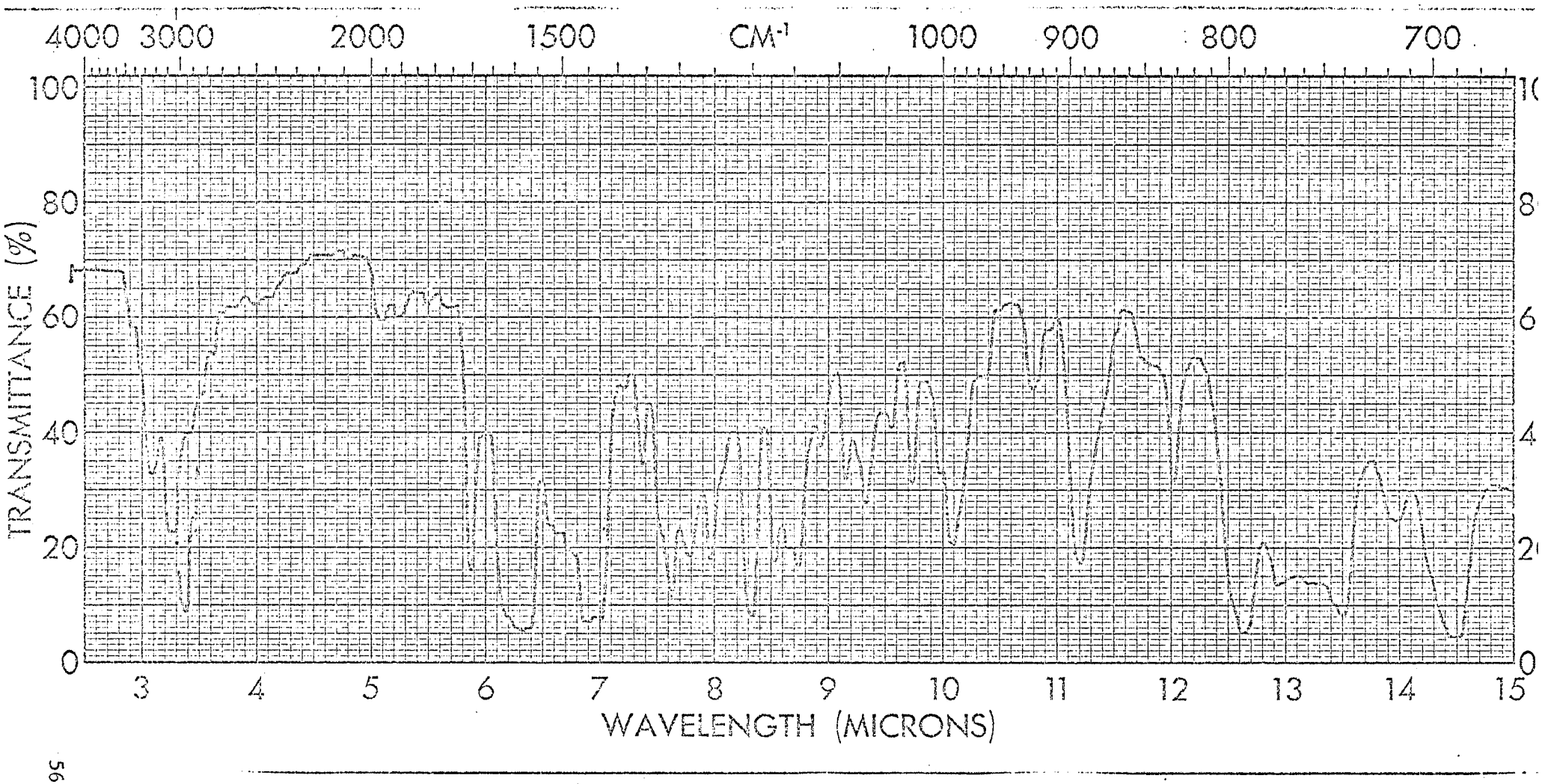
Moles TCNE	Solvent	Temp. °C / Time hrs.	Method of Isolation	Yield % / Color	mp °C		Elemental Analysis C	H	N	O
4	DMAC	50/5	Precipitation by Benzene	30 Black	360	Theory[h]	63.16	1.75	35.09	-
						Found[i]	60.23	3.48	28.66	6.19
4	DMAC	50/5	Evaporation of Solvent	113 Black	100-110	Found[i]	60.00	4.07	30.56	5.37[d]

h. These values are for p-xylylidene-di-2-aminopyridine complexed with four moles of TCNE, $C_{42}H_{14}N_{20}$.

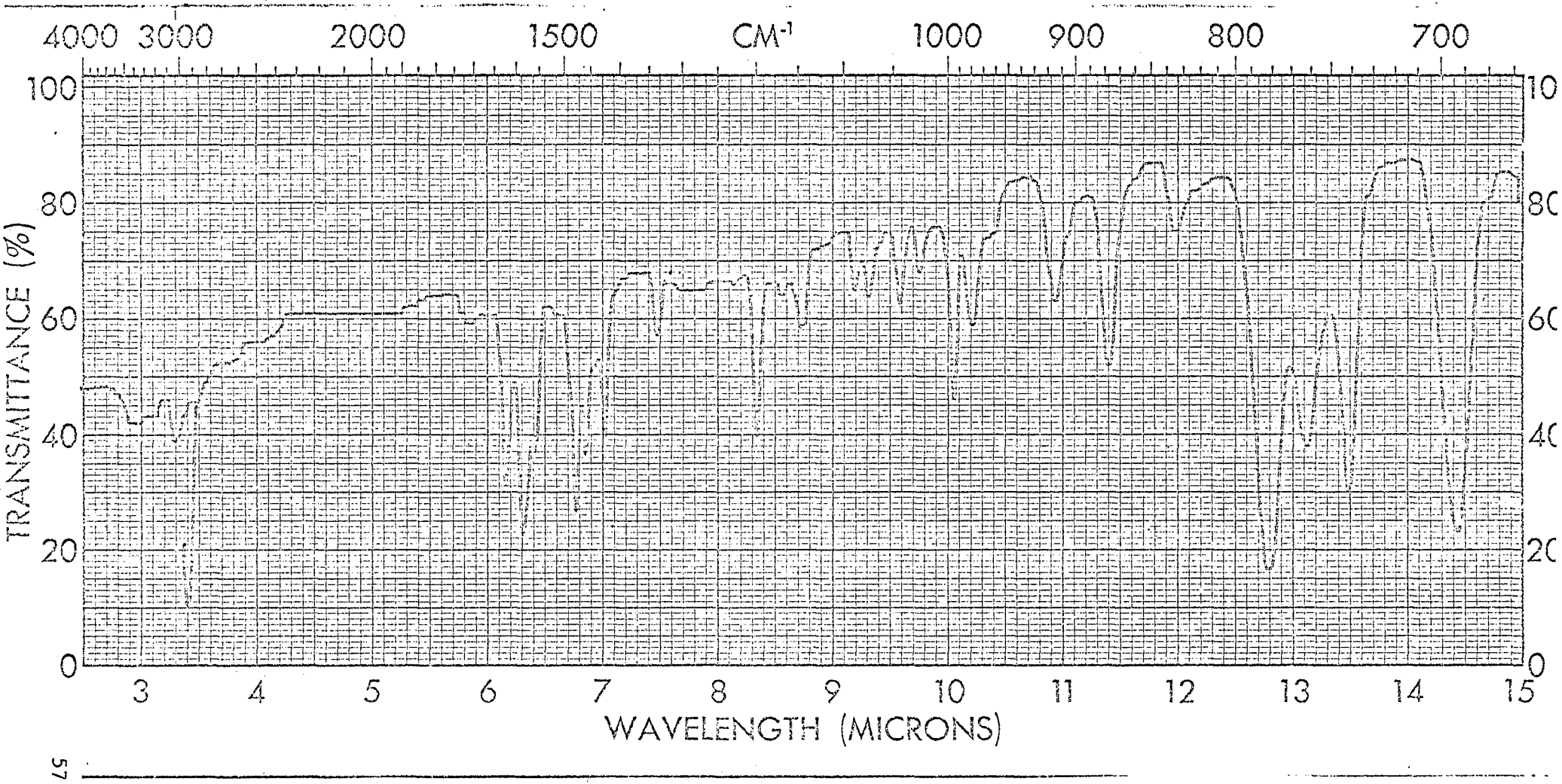
i. Cal'd for $C_{42}H_{14}N_{20}$ $4CH_3CON(CH_3)_2$: C,60.73; H,4.36; N,29.32; O,5.59.
Cal'd for $C_{42}H_{14}N_{20}$ $5CH_3CON(CH_3)_2$: C,60.34; H,4.79; N,28.39; O,6.48.

Table 6. Charge Transfer Complexes Derived from Quaternary Derivatives of Pyridine-type Schiff Bases and TCNE

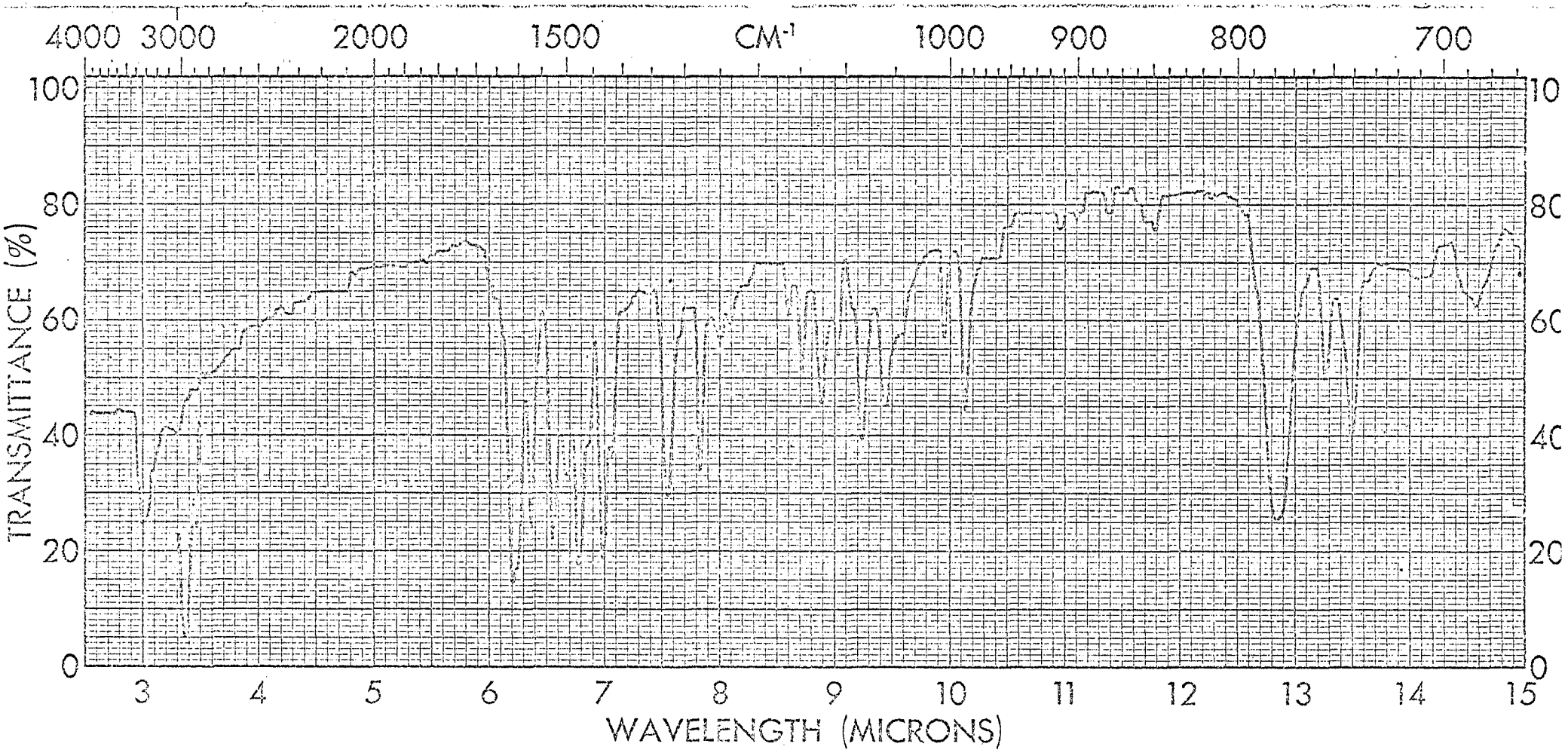
Quaternarized Schiff Base	Solvent	Color of Reaction	Method of Isolation of Complex
	CH_3CN	immediate change (dark-brown)	precipitated with ether (brown)
	CH_3CN slightly soluble	no change	did not form
	Absolute C_2H_5OH	immediate change (red)	precipitated with ether (red)
	CH_3CN	immediate change (deep-red)	precipitated with ether; low yield (red)
	CH_3CN slightly soluble	no change	did not form
	Absolute C_2H_5OH	immediate change (red)	precipitated with ether (red)
	CH_3CN	immediate change (brown)	precipitated with ether (brown)
	Absolute C_2H_5OH	immediate change (red)	precipitated with ether (red)
	CH_3CN	immediate change (dark-brown)	precipitated with ether (brown)



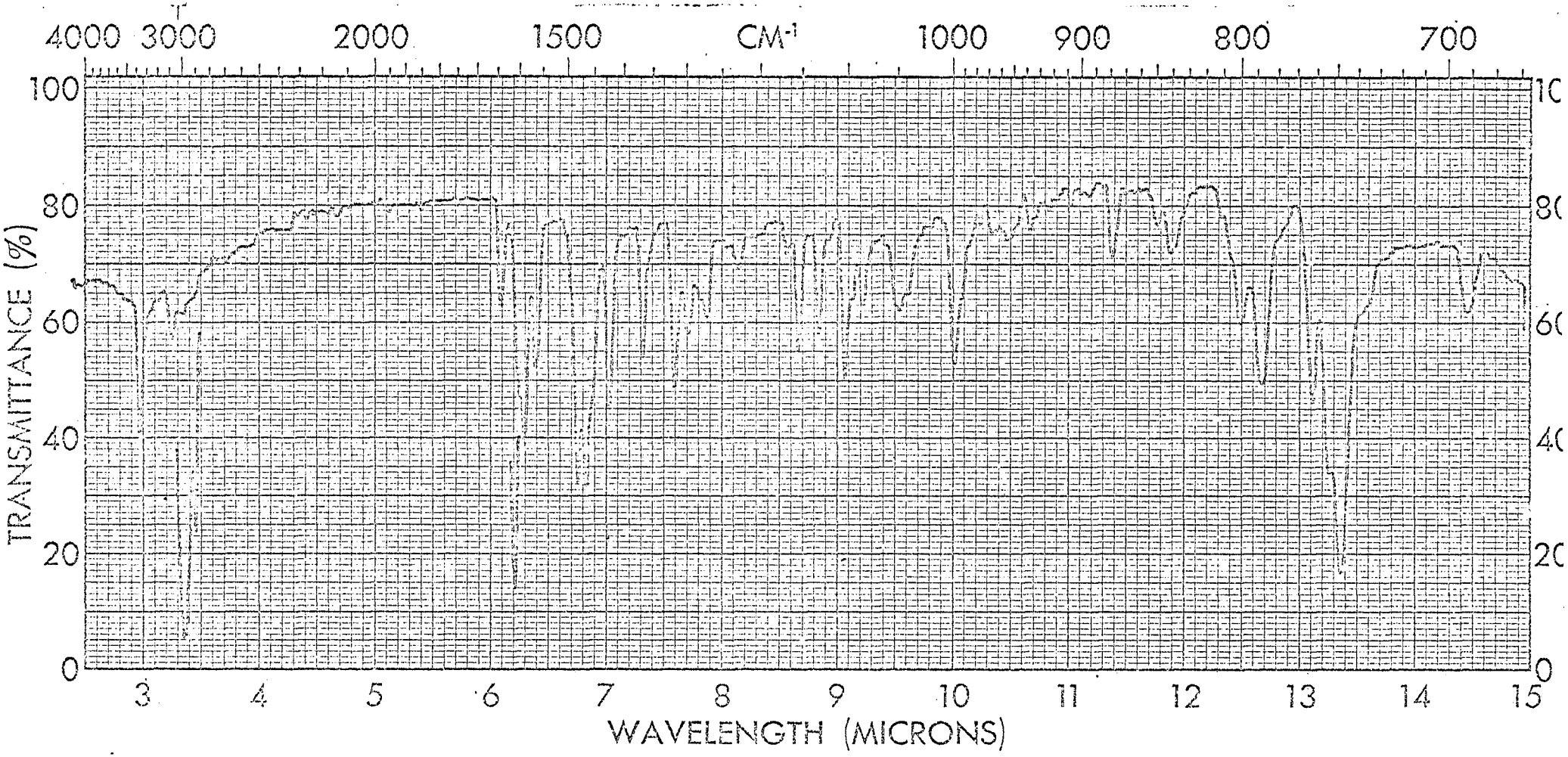
Appendix No. 1 Infrared Spectrum of 2-(Benzylideneamino)pyridine Neat



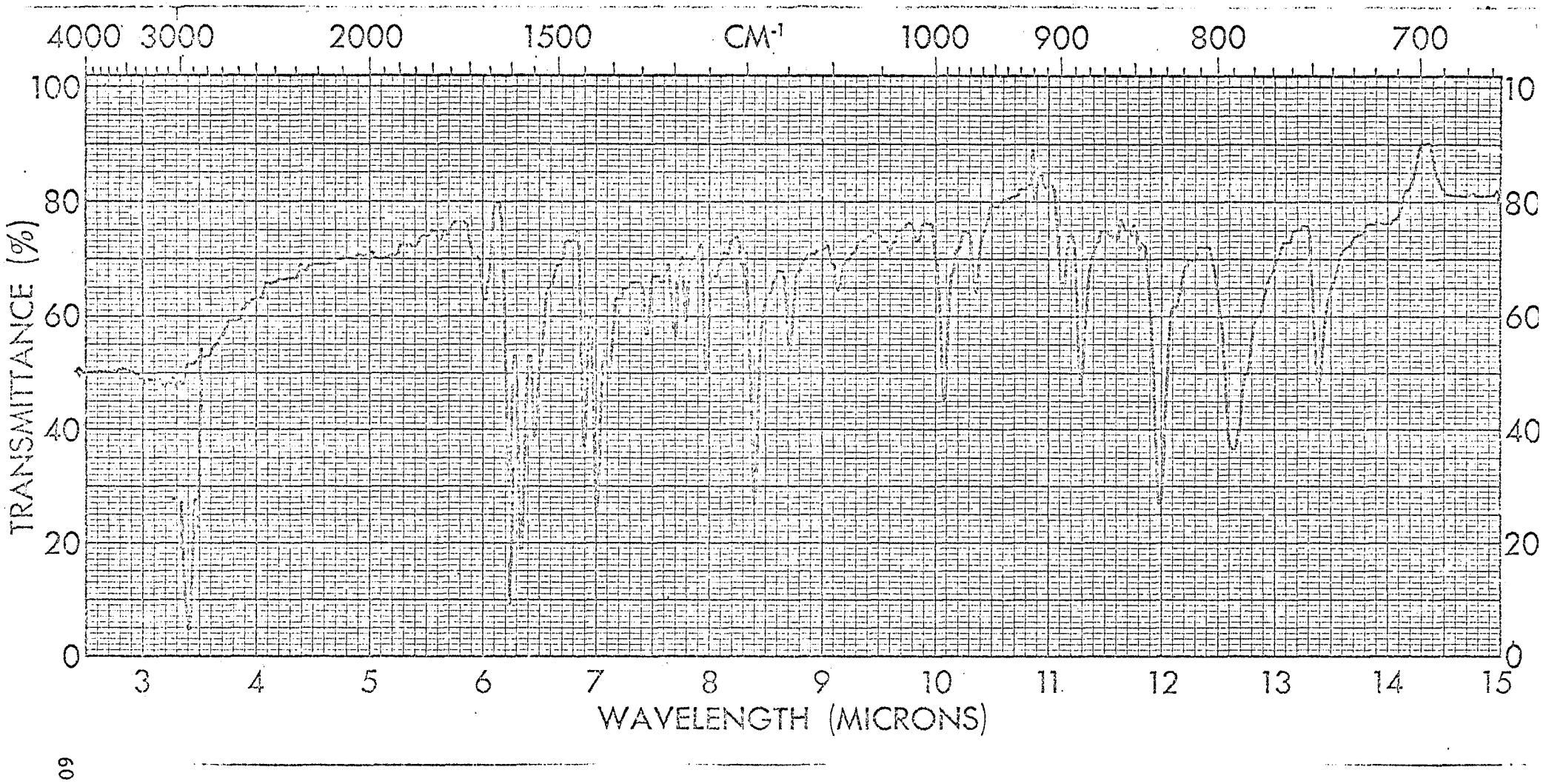
Appendix No. 2 Infrared Spectrum of 2-Pyridylcarboxylideneaniline KBr Disc



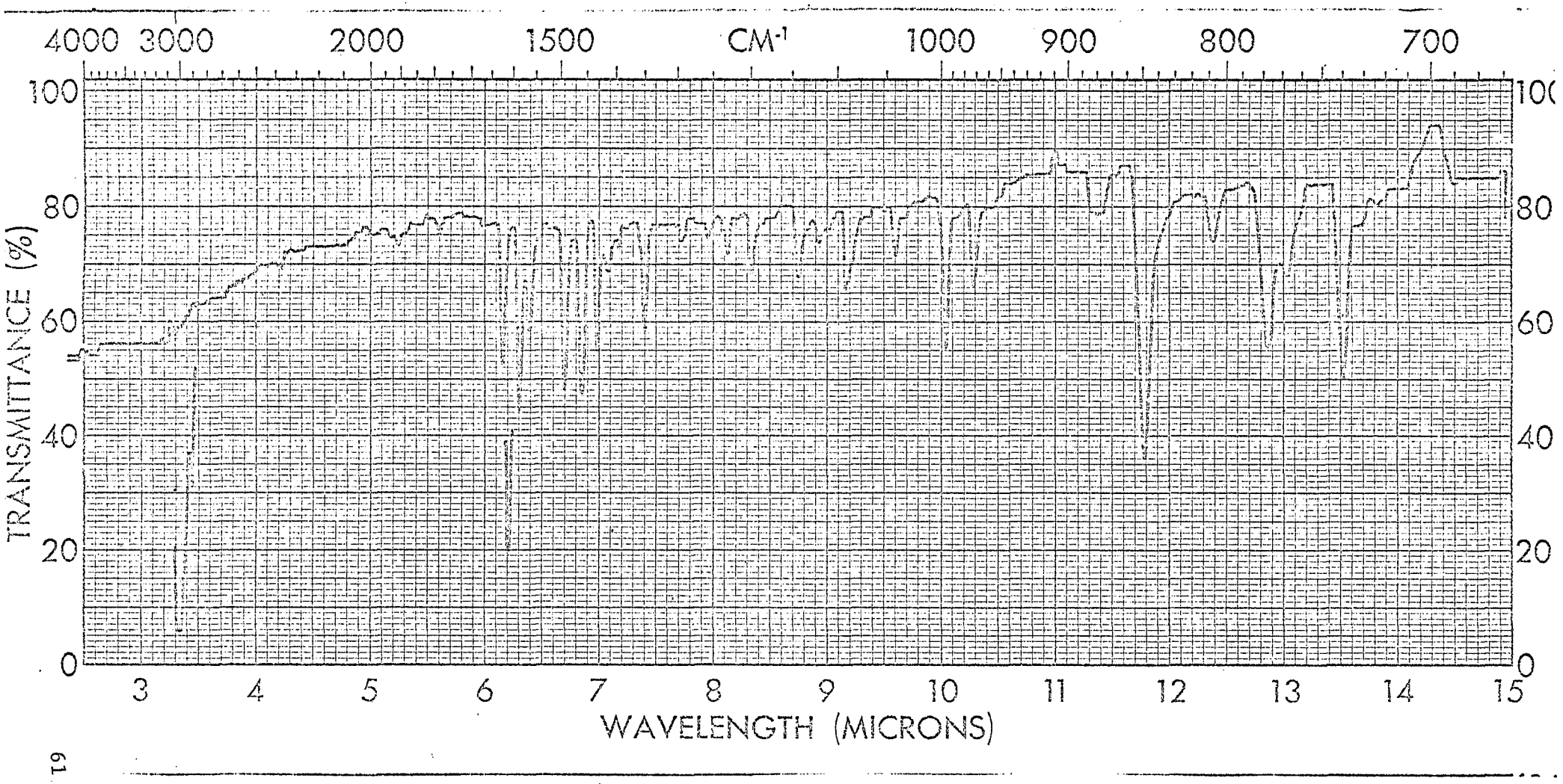
Appendix No. 3 Infrared Spectrum of 2-Pyridylcarboxal-di-2-aminopyridine KBr Disc



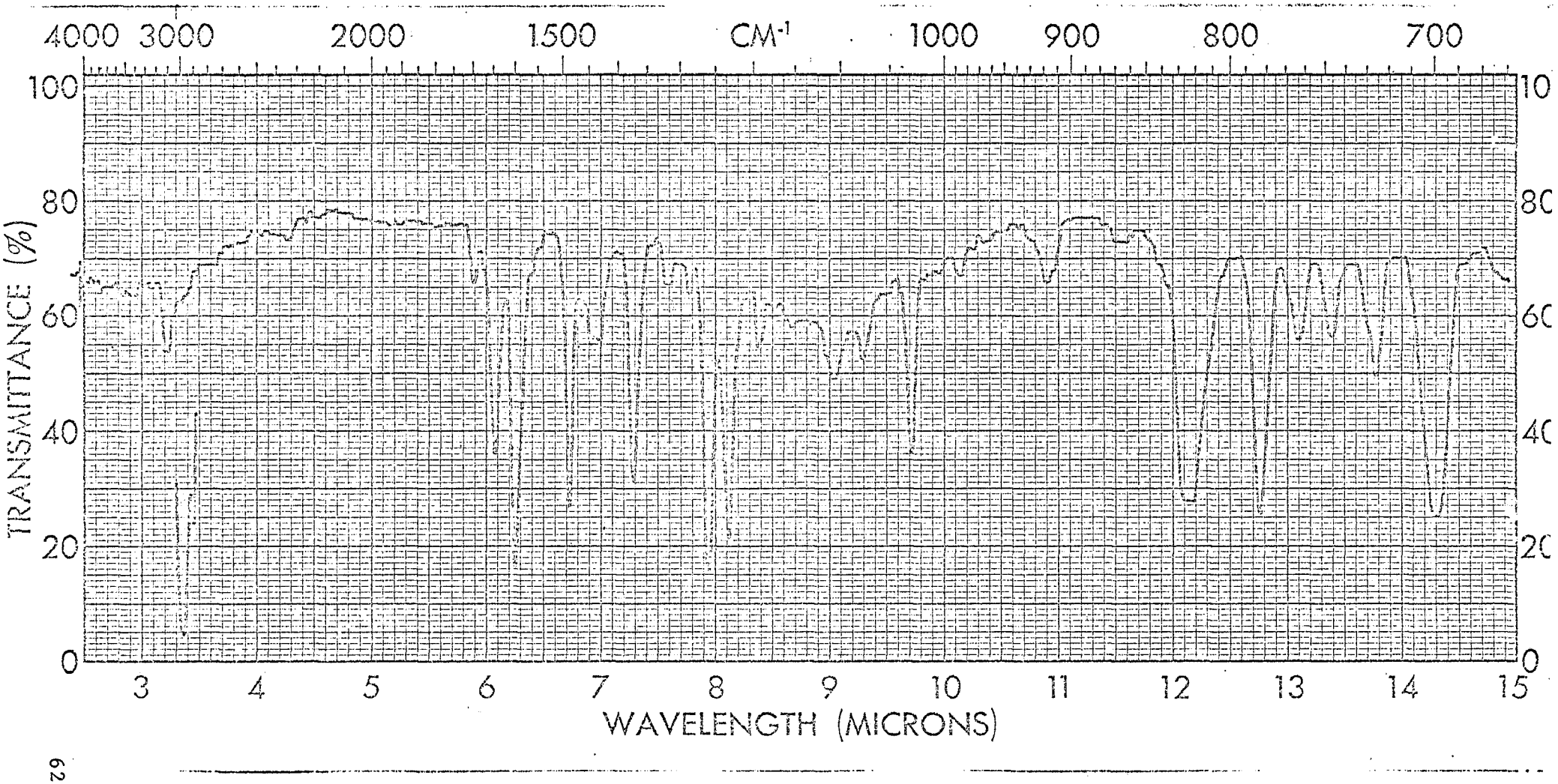
Appendix No. 4 Infrared Spectrum of 2-acetylpyridineketanil KBr Disc



Appendix No. 5 Infrared Spectrum of p-Xylylidene-di-2-aminopyridine KBr Disc

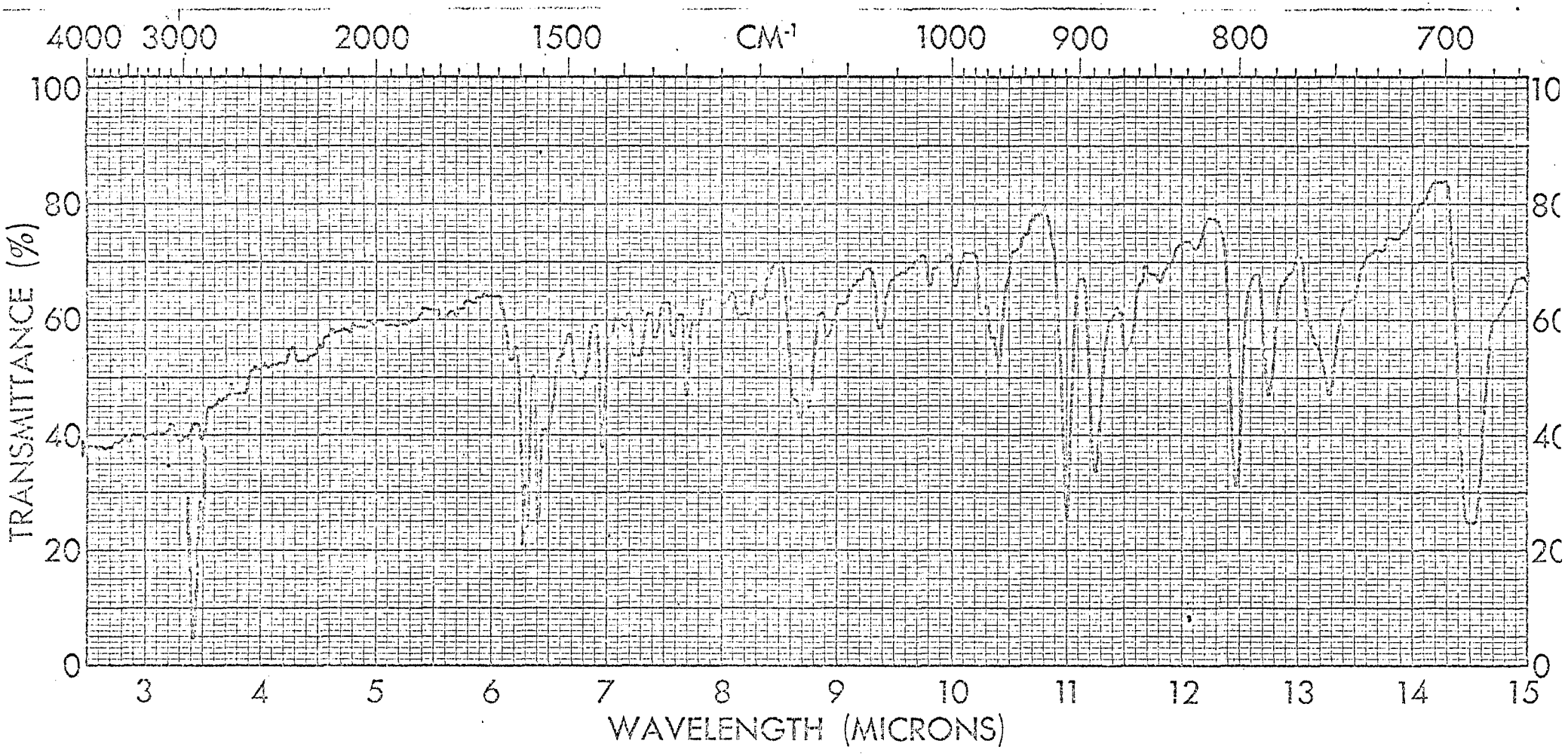


Appendix No. 6 Infrared Spectrum of N,N'-Di-2-pyridylcarboxylidene-p-phenylenediamine KBr Disc

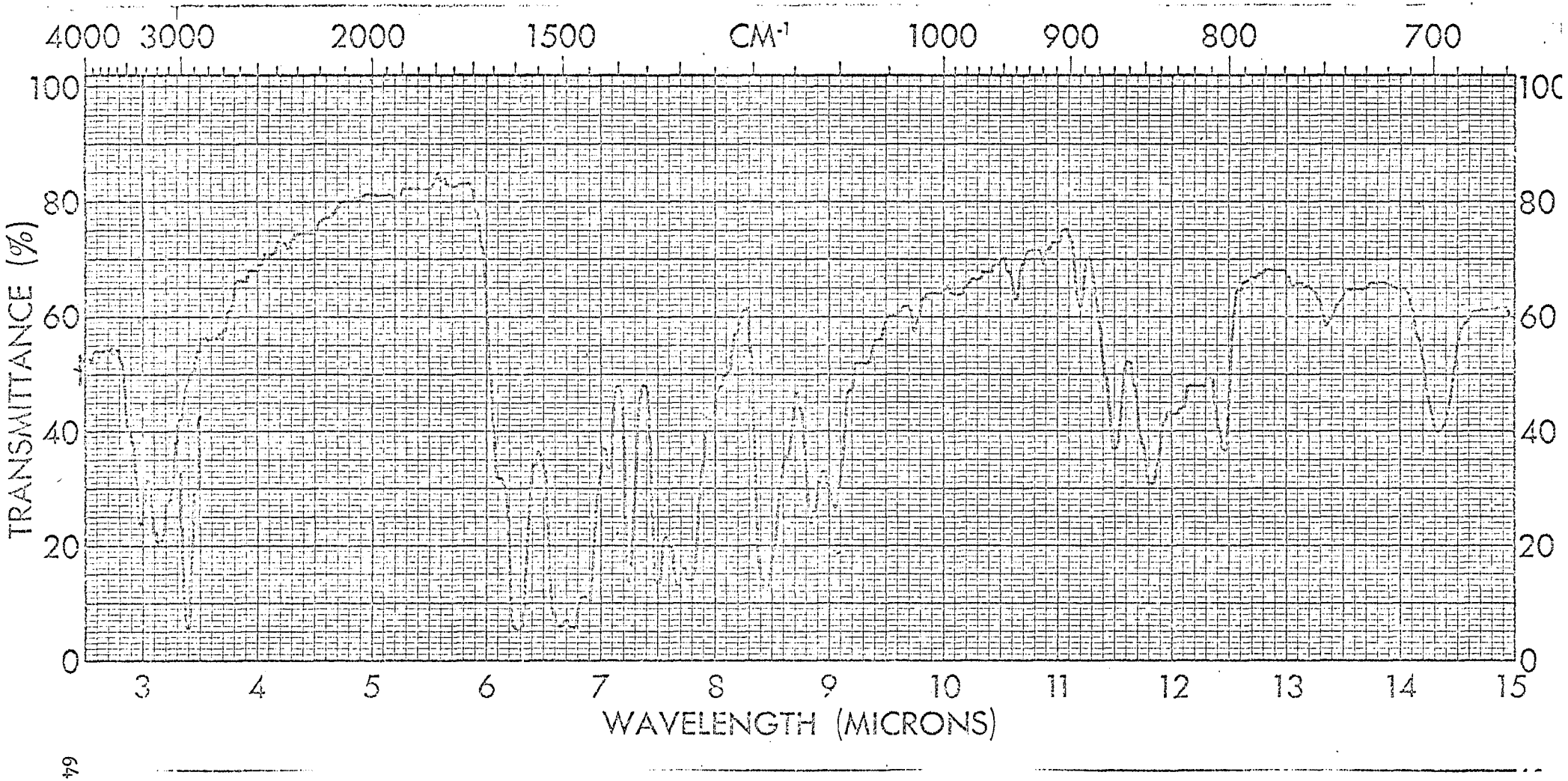


62

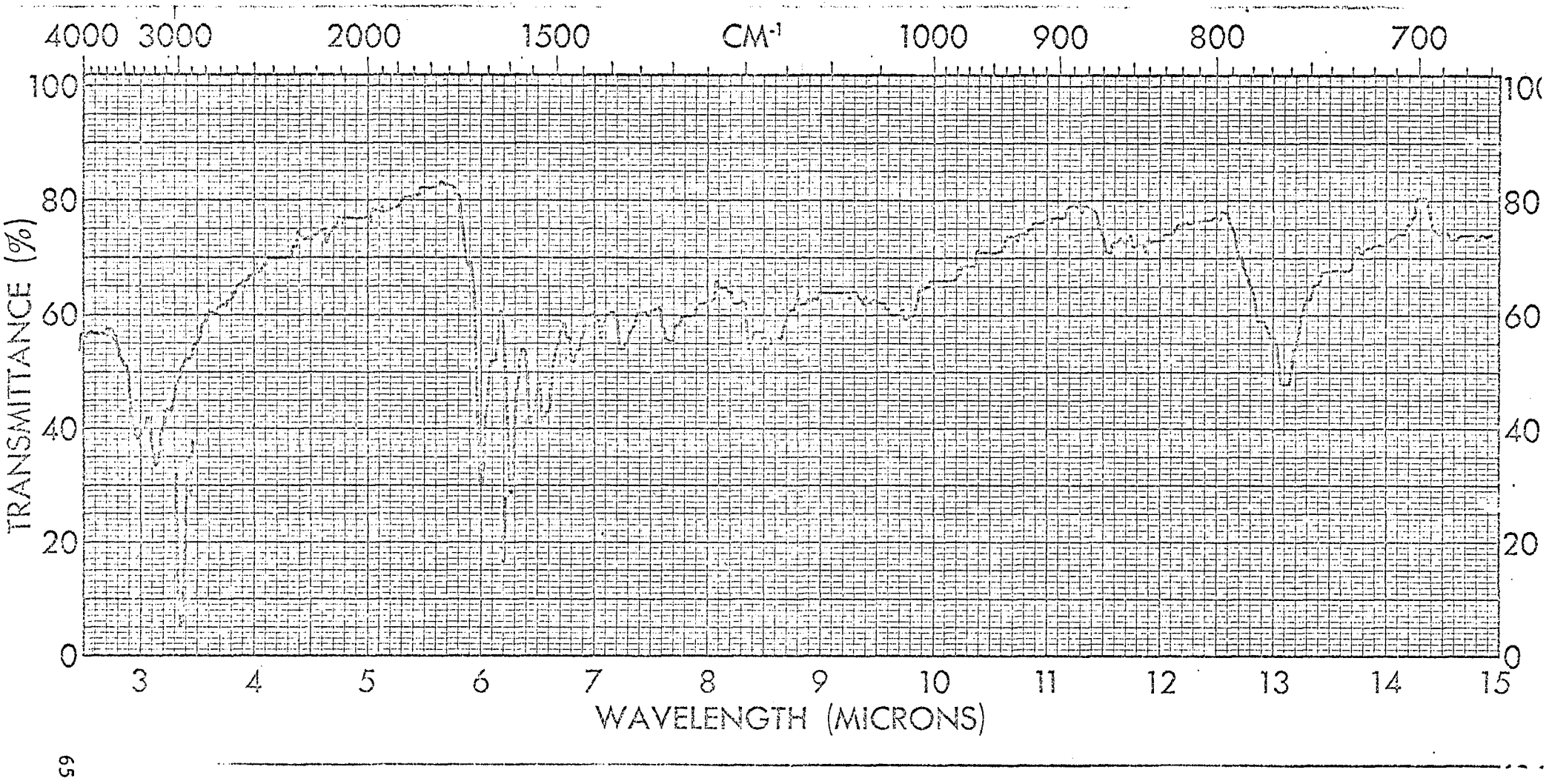
Appendix No. 7 Infrared Spectrum of 2,6-Diacetylpyridinediketanil KBr Disc



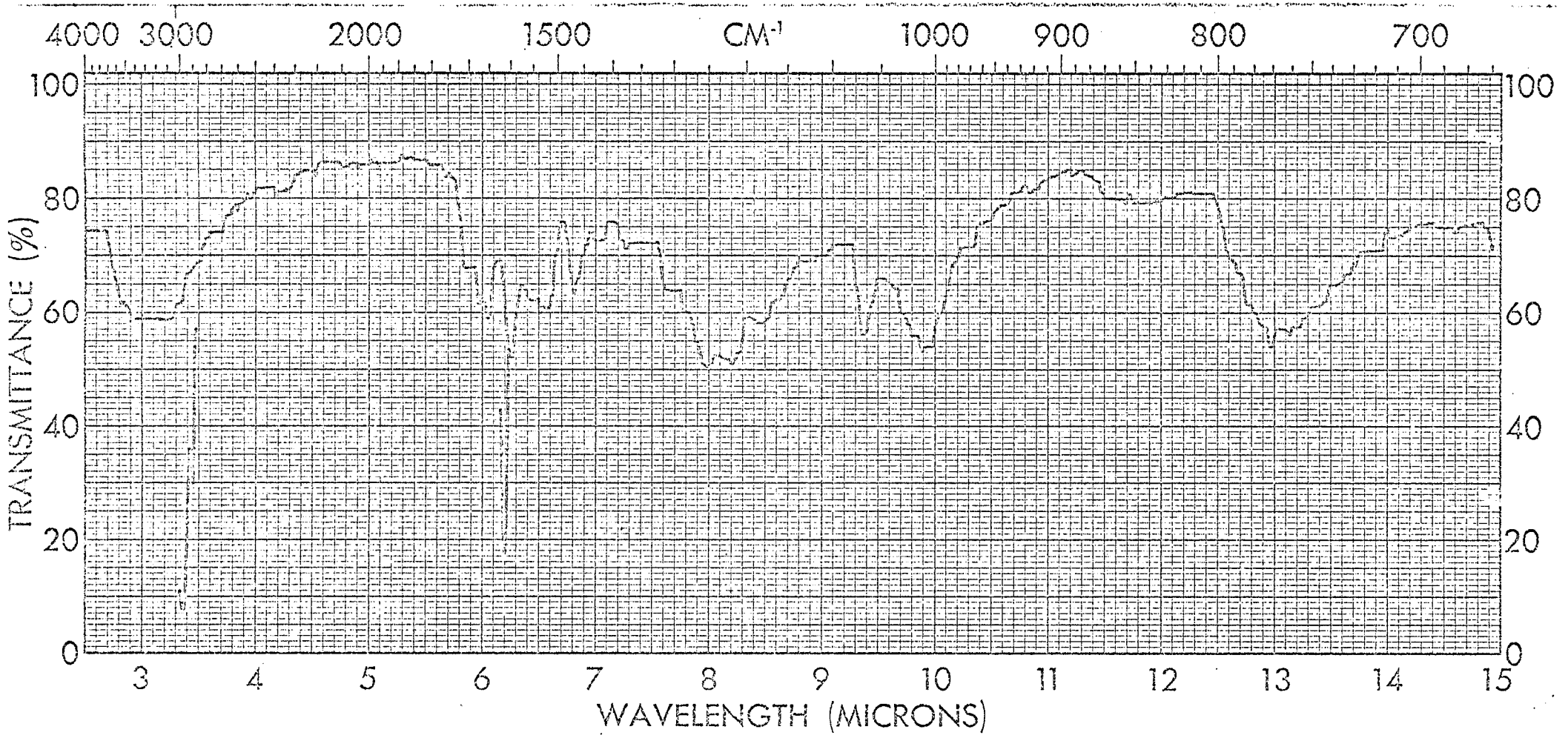
Appendix No. 8 Infrared Spectrum of 3,6-Di-(benzylideneamino)acridine KBr Disc



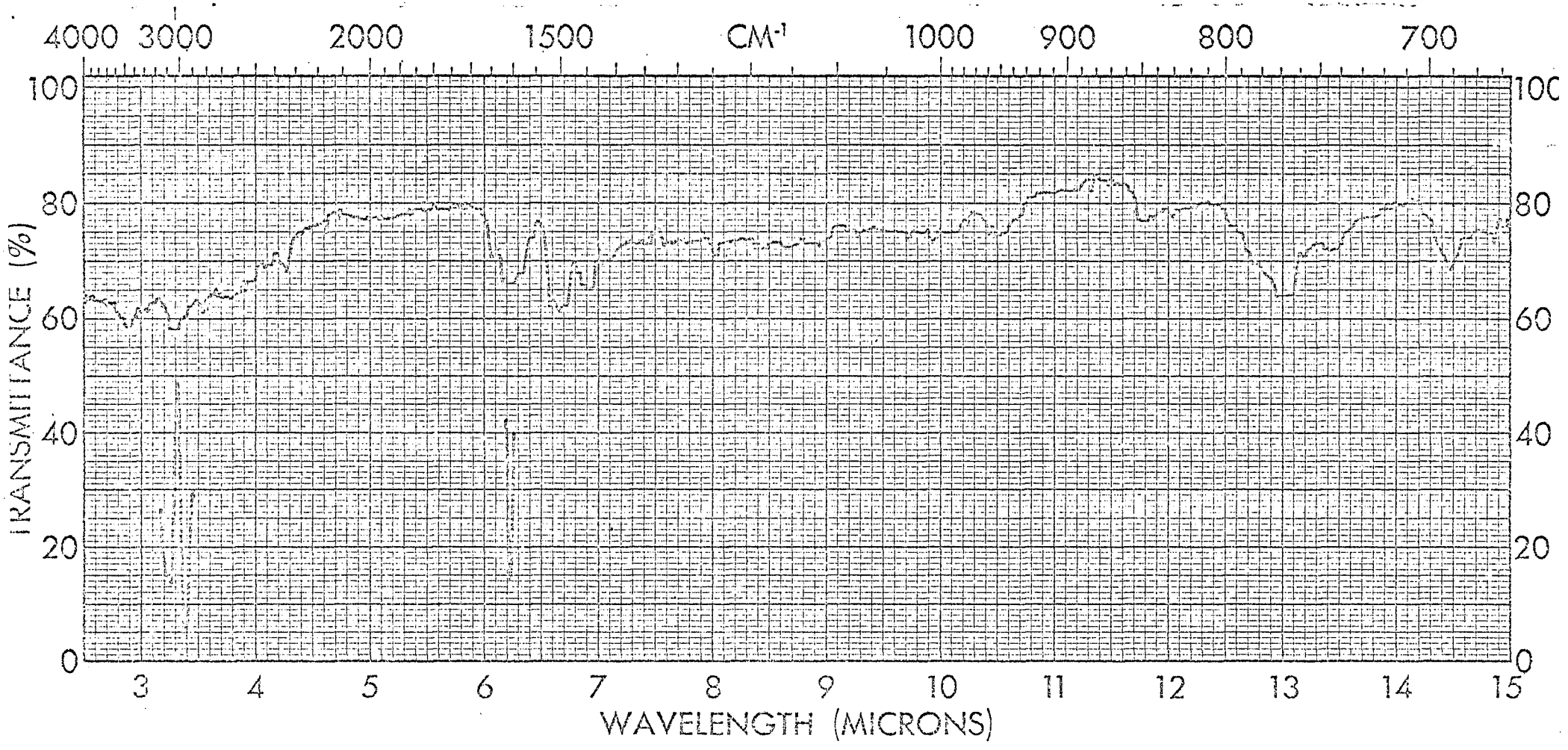
Appendix No. 9 Infrared Spectrum of Product of the Reaction of Phenosafranine and Aqueous NaOH KBr Disc



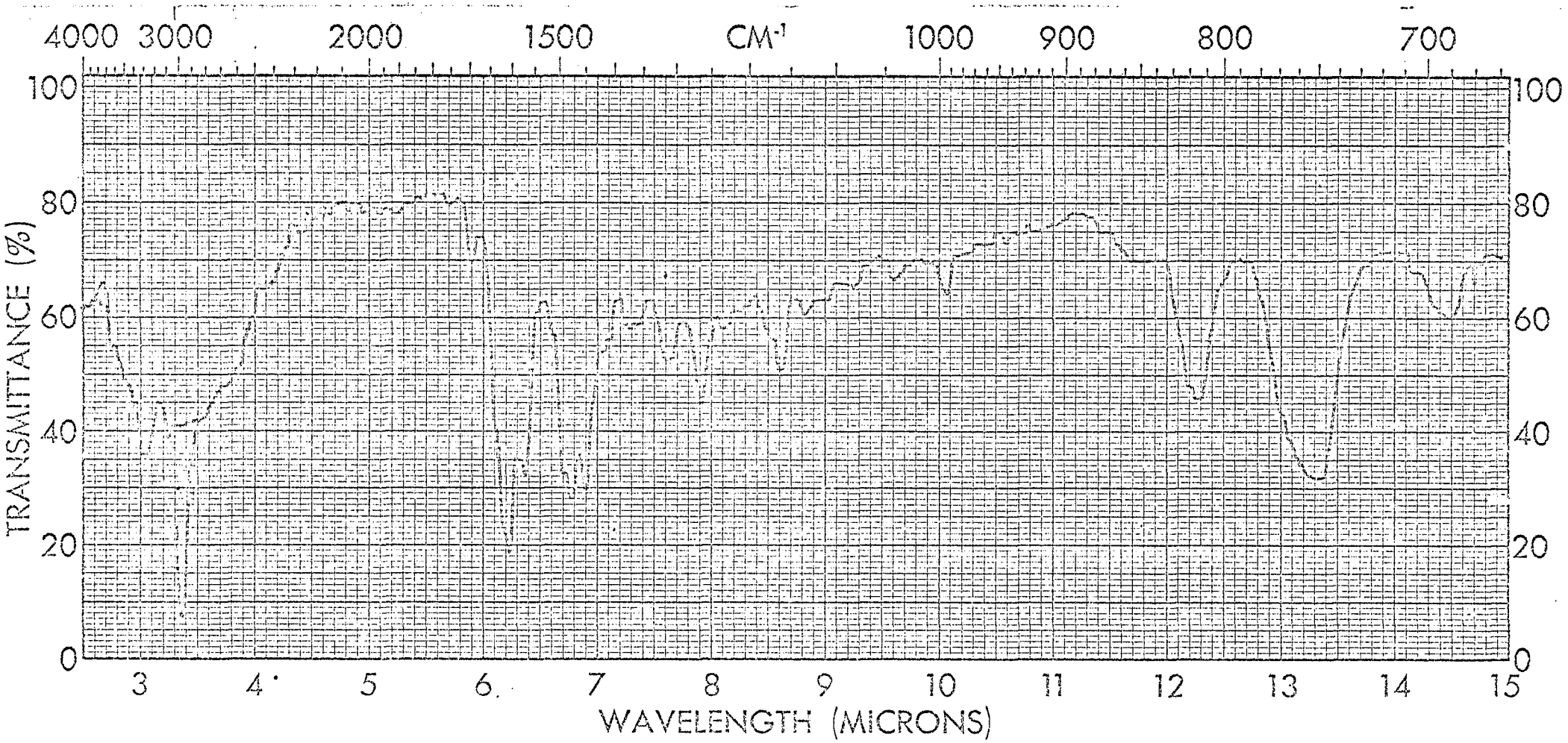
Appendix No. 10. Infrared Spectrum of the Diquaternary Salt of p-Xylylidene-di-2-aminopyridine and Methyl Iodide KBr Disc



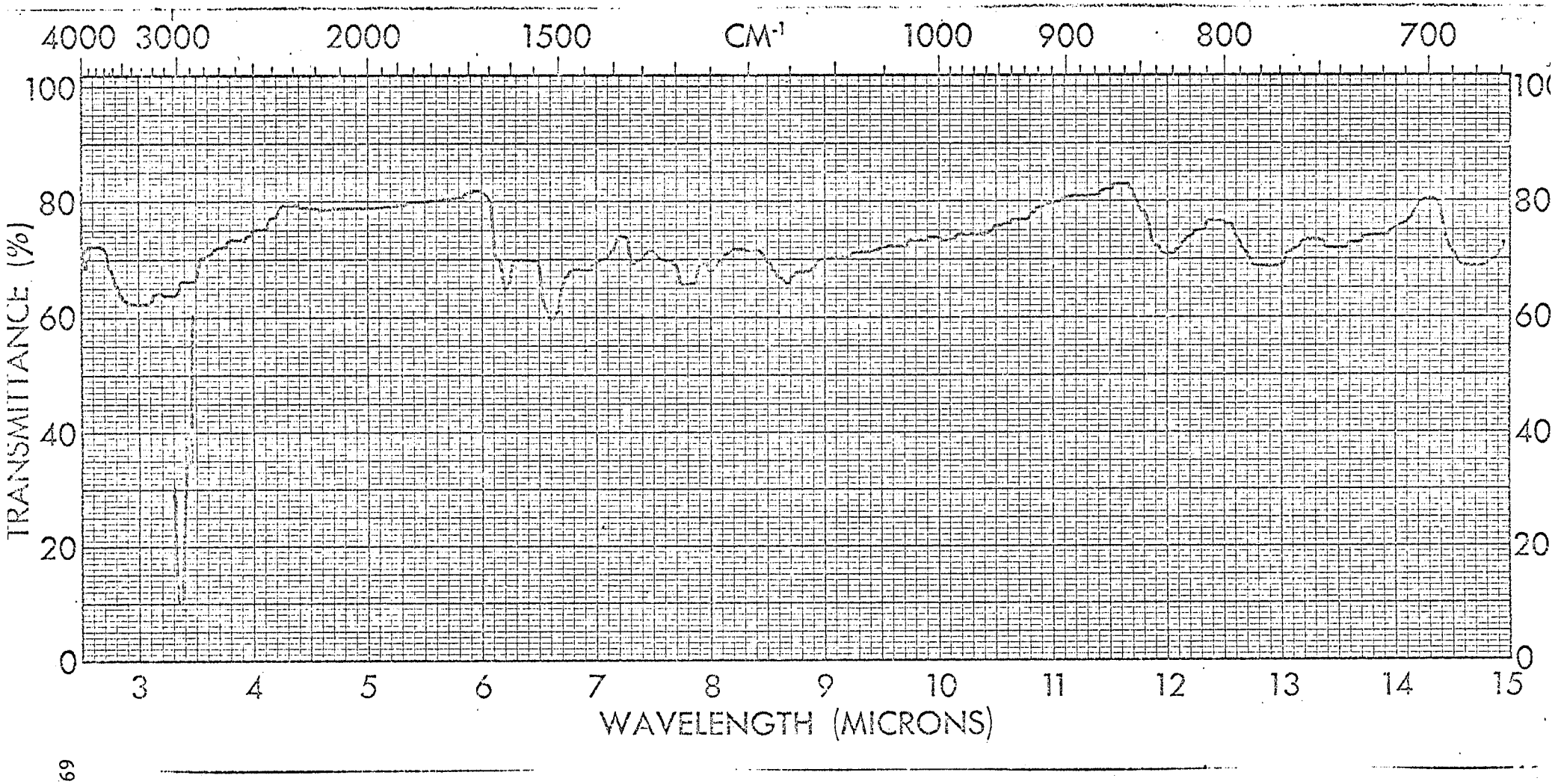
Appendix No. 11. Infrared Spectrum of the Diquaternary Salt of p-Xylylidene-di-2-aminopyridine and Dimethylsulfate KBr Disc



Appendix No. 12. Infrared Spectrum of the Quaternary Salt of 2-Pyridylcarboxylideneaniline and Methyl Iodide KBr Disc



Appendix No. 13. Infrared Spectrum of the Quaternary Salt of 2,6-Diacetylpyridinediketanil and Methyl Iodide KBr Disc



Appendix No. 14. Infrared Spectrum of the Diquaternary Salt of N,N'-Di-(2-pyridylcarboxylidene)-p-phenylenediamine and Methyl Iodide

KBr Disc