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RESEARCH GRANT NGR 47-002-041

Semi-Annual Report

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NON-METALLIC MATERIALS BRANCH, MATERIALS DIVISION

Langley Research Center

Hampton, Virginia

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TITLE OF RESEARCH: "ISOMER EFFECTS ON POLYIMIDE PROPERTIES"

REPORT PERIOD COVERED: January 1, 1975 - July 1, 1975

ABSTRACT: *The goal of this investigation is the preparation of polyimide polymers which are both thermally stable and processable. One approach being taken is the addition of alkyl substituents to an aromatic ring in the polymer backbone. The synthesis of key monomers is reported, including 2,4,6-Tris(m-aminobenzyl)-1,3,5-trimethylbenzene and 2,4,6-Tris(p-aminobenzyl)-1,3,5-trimethylbenzene. Polyimide-precursor amines containing functional groups that allow for post-cure cross-linking are being sought as another phase of this project. The preparation of a key monomer, 2,5,3'-Triaminobenzophenone, is reported.*

B. L. Stump

B. L. Stump, Principal Investigator

October 1, 1975

Semi-Annual Report

RESEARCH GRANT NGR 47-002-041

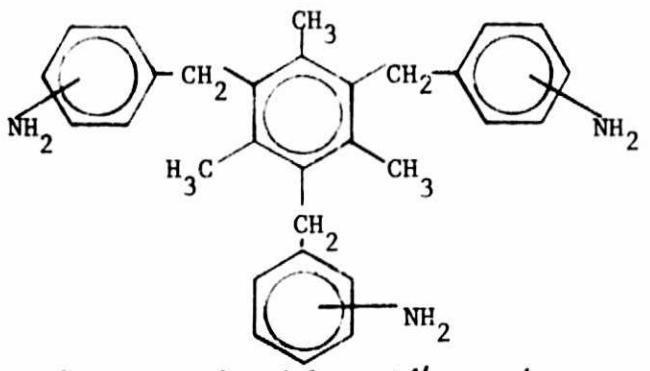
I. Introduction

Studies aimed at preparing polyimides which have high thermal stability and which are processable have continued. The main effort this report period has been in the direction of preparing amine monomers which would lead to polyimides either having enhanced solubility or a low glass transition temperature or both, and which would have extra functional groups present and available for post-cure cross-linking. The work is discussed below in three categories.

II. Discussion

A. Imide Monomers for Addition-Type Polyimides

We reported (1) earlier that compounds of the type,



where the amino group is either *ortho*, *meta*, or *para* to the methylene group, were being synthesized. At that time the syntheses of 2,4,6-*tris*(*m*-nitrobenzyl)-1,3,5-trimethyl benzene and 2,4,6-*tris*(*p*-nitrobenzyl)-1,3,5-trimethylbenzene were described. Continued efforts are described in the following paragraphs.

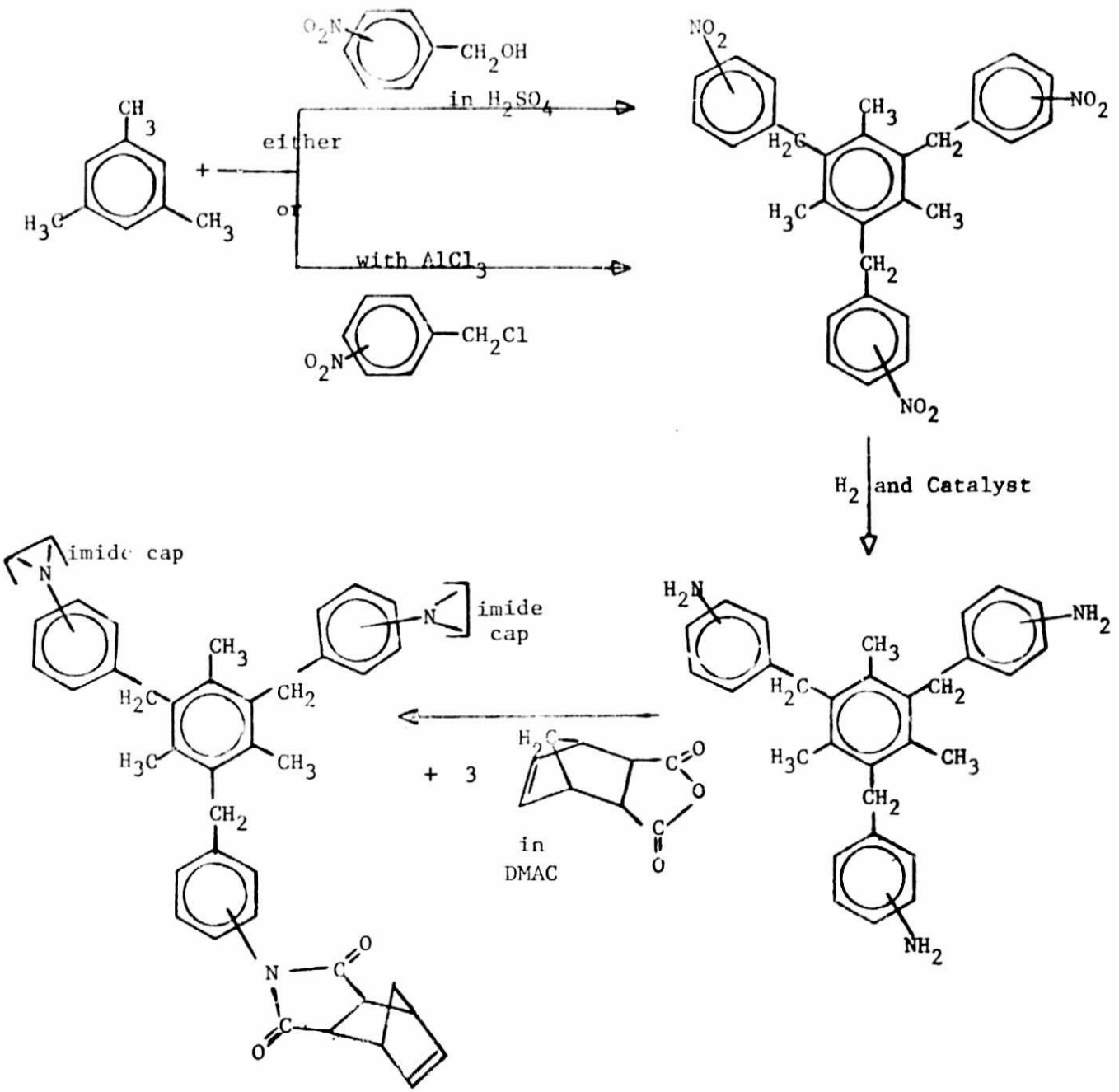
1. 2,4,6-*Tris*(*m*-nitrobenzyl)-1,3,5-trimethylbenzene. This compound has been analyzed by Galbraith Microanalytical Laboratories and the

analysis is reported here. Theory: C, 68.56; H, 5.18. Found: C, 68.22; H, 5.21.

2. 2,4,6-*Tris*(*m*-aminobenzyl)-1,3,5-trimethylbenzene. The compound from part 1 above has been reduced to the corresponding triamine via catalytic hydrogenation in ethyl acetate using 10% palladium on charcoal. The amine product melts at 181 - 183 °C. Carbon/hydrogen analyses of the triamine have not been obtained as yet. Bell (2) has prepared this compound and reports a melting point of 188 - 190 °C. for the triamine. He also has prepared an imide derivative by reacting the triamine with 5-norbornene-2,3-dicarboxylic anhydride, as shown in Figure 1. This derivative melts between 167 - 170 °C. and is soluble in benzene. When heated above its melting point, the compound apparently polymerizes via the carbon-carbon double bond in the norbornene rings. Further work with this meta triamine and its imide derivatives will be pursued by Bell and our efforts will be focused on the ortho and para analogs in this project.

3. 2,4,6-*Tris*(*p*-nitrobenzyl)-1,3,5-trimethylbenzene. This compound has been analyzed by Galbraith and the analysis is reported here. Theory: C, 68.56; H, 5.18. Found: C, 67.8; H, 5.34. The synthesis of this compound is being explored further to obtain a more economical synthetic method and/or to improve on the yield. One approach uses *p*-nitrobenzyl alcohol in concentrated sulfuric acid with mesitylene. Reaction conditions which lead to high yields of the desired product are being optimized. The second route to the product, via the Friedel-Crafts reaction, has been repeated using nitrobenzene in place of carbon disulfide as the solvent. Results at this time are

Figure 1. Imide Monomers for Addition-Type Polyimides.



--The nitro group in the benzyl alcohol or benzyl chloride can be either ortho, meta, or para-.
--The trimethyl benzene can be either the 1,3,5-, the 1,2,3-, or the 1,2,4-isomer.

inconclusive, although it does appear that a greater yield is being obtained.

4. 2,4,6-*Tris*(*p*-aminobenzyl)-1,3,5-trimethylbenzene. The title compound has been prepared via the catalytic hydrogenation of 2,4,6-*tris*-(*p*-nitrobenzyl)-1,3,5-trimethylbenzene in ethyl acetate over 10% Pd/C. The product obtained melted between 238 - 242 °C. The nmr spectrum was obtained with the triamine dissolved in $CDCl_3$ and is shown as Figure 2. The singlet at δ 2.2 integrates correctly for 9 protons in the three methyl groups on the mesitylene ring. The broad absorption band between δ 2.2 and δ 3.0 integrates for 6 protons in the three amino groups; further, this band disappears when D_2O is added to the sample. The singlet at δ 4.0 integrates correctly for the 6 protons of the three methylene groups connecting the aromatic rings. The multiplet between δ 6.4 and δ 7.3 integrates correctly for the 12 aromatic protons in the three benzyl rings. Elemental analysis has not been obtained on this material as yet. The preparation and further characterization of this material is in progress.

5. 2,4,6-*Tris*(*o*-nitrobenzyl)-1,3,5-trimethylbenzene. Attempts to prepare this compound, using *o*-nitrobenzyl alcohol and mesitylene in concentrated sulfuric acid, have yielded high-melting deep red crystalline material thought to be a sulfate salt, perhaps of the benzyl alcohol. The Friedel-Crafts reaction of *o*-nitrobenzyl chloride with mesitylene, in CS_2 using aluminum chloride, has produced material difficult to crystallize and relatively low melting. It is suspected that incomplete substitution on the mesitylene ring occurred. Carbon disulfide appeared to be a very poor solvent for the reaction, since two phases appeared quite early. A repeat synthesis is planned, where nitrobenzene will be

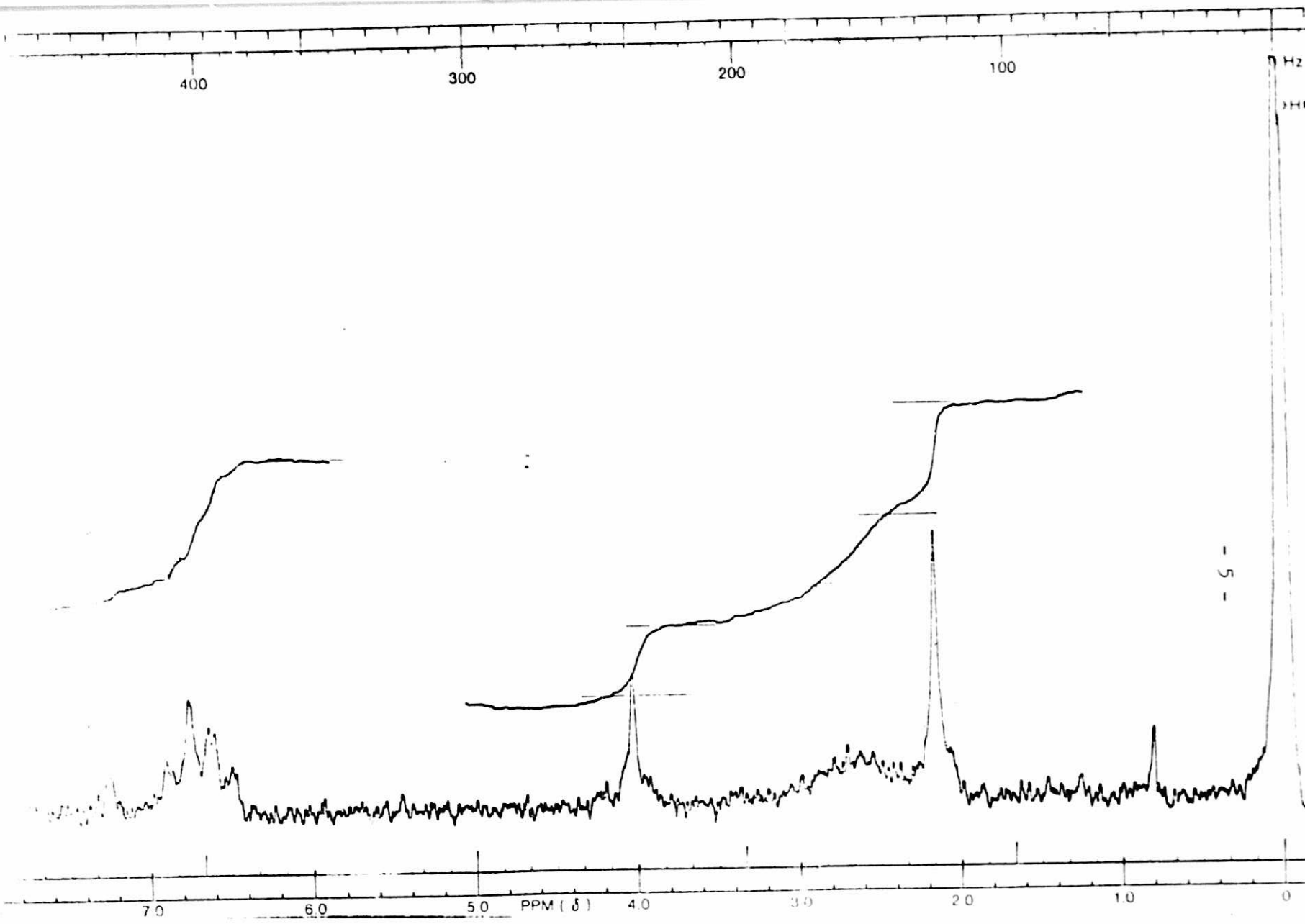


Figure 2. NMR spectrum of 2,4,6-*Tris*(*p*-aminobenzyl)-1,3,5-trimethylbenzene.

used as the solvent.

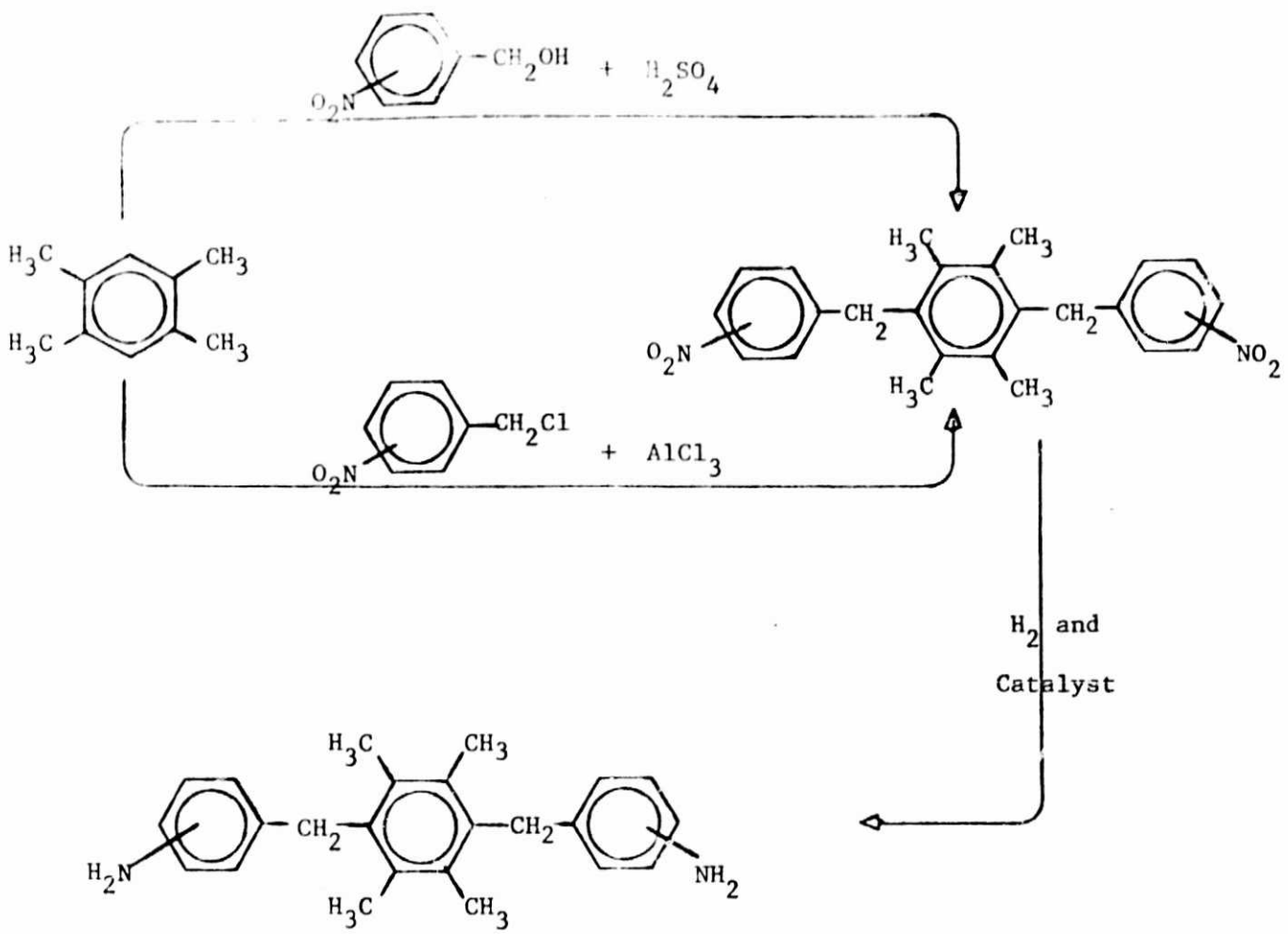
B. Aromatic Diamines with Three Benzene Rings

Amines of the type shown in Figure 3 are interesting candidates for polyimide preparation, as well as potentially interesting cross-linking agents for polyepoxides and polyurethanes. A goal of this project is to synthesize and evaluate a variety of these compounds. Little effort has been expended in this direction during the current reporting period. We reported (1) earlier on the preparation and characterization of 1,4-*bis*(*m*-nitrobenzyl)-2,3,5,6-tetramethylbenzene. The chemical analysis of this compound has been obtained and is reported here. Theory: C, 71.27; H, 5.98. Found: C, 71.18; H, 6.19.

As our studies continue, we plan to prepare the diamine of this compound and to evaluate it as a monomer for polyimide preparation. We also plan to furnish Langley Research Center personnel a sufficient amount of the material to allow for evaluation as a cross-linking agent. Other diamines described in Figure 3 will also be prepared and evaluated.

C. Diamine Monomers with Cross-Linking Potential

The preparation of a polyimide monomer like *m*,*m*'-diaminobenzophenone, which would contain a third amino group in the position *ortho* to the carbonyl group connecting the two aromatic rings, is desirable. This third amino group would be available for post-cure cross-linking to elevate the glass-transition-temperature of the processed polyimide product. A possible reaction scheme is outlined, Figure 4. The syntheses and characterization of 2-acetamidobenzophenone, 2-acetamido-5,3'-dinitrobenzophenone, and 2-acetamido-5,3'-diaminobenzophenone



--The nitro group in the benzyl alcohol or benzyl chloride can be either ortho, meta, or para-.
--The tetramethyl benzene can be either the 1,2,4,5-, the 1,2,3,5- or the 1,2,3,4-isomer.

Figure 3 . Aromatic amines with Three Benzene Rings.

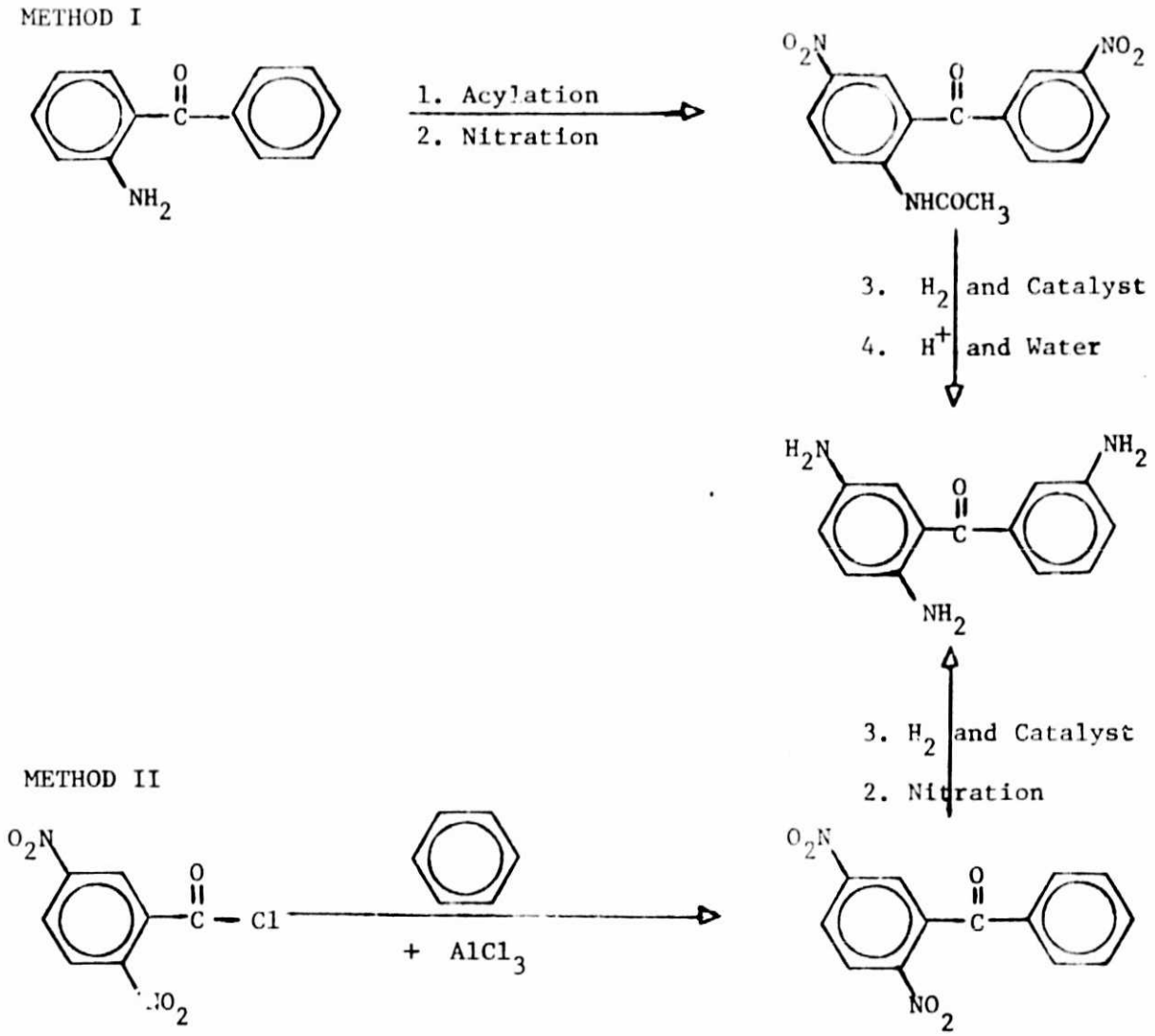


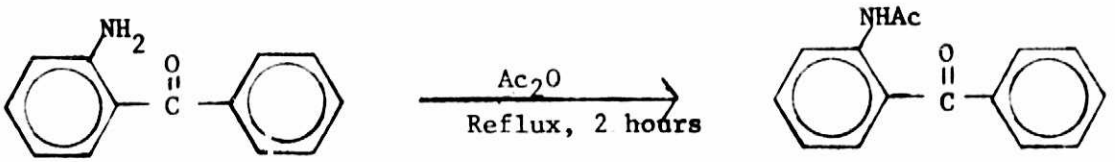
Figure 4. Synthetic scheme for preparing 2,5,3'-Triaminobenzophenone.

appear to have been accomplished and are described in the following paragraphs. Conversion of the 2-acetamido-5,3'-diaminobenzophenone to 2,5,3'-triaminobenzophenone is presenting some difficulty, and it appears that the triamine is very sensitive to oxygen and must be handled in an inert atmosphere.

In the process of working out the reaction conditions for preparing the 2,5,3'-triaminobenzophenone, several other interesting potential monomers may have been prepared. Our results are incomplete at this time, so a claim that these compounds have been prepared is not made. However, the evidence at hand suggests that these compounds may very well have been prepared: 2,3,3'-trinitrobenzophenone; 2,2',5,5'-tetranitrobenzophenone; 2,5,4'-trinitrobenzophenone; and 2,4,2',4'-tetranitrobenzophenone. A further investigation of these products is underway.

III. Experimental

A. 2-Acetamidobenzophenone. 2-Aminobenzophenone, I, (25 g, 0.13 mole), and 50 ml of freshly distilled acetic anhydride were placed in a 500 ml

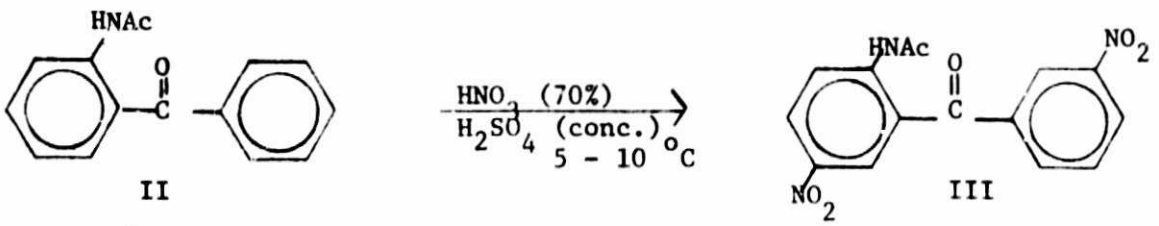


I II

round bottom flask and refluxed for 2½ hours. After reflux, the reaction mixture was cooled and poured on 1 kg of crushed ice, and an oil formed. Using a separatory funnel, the oil was removed and washed with 500 ml of distilled water. Crude oil (28 g) was crystallized by dissolving it in hot ethanol (50 ml) and adding to the solution distilled water until lingering cloudiness persisted. The solution was then placed in an ice

bath. Crystals of II were obtained which weighed 22 g (72%), m.p. 82 - 83°C; ir 3500 - 3300, 1710, 1650 cm^{-1}; nmr δ 2.2 (S; 3H), 7.5 (M, 9H), and 9.5 (S, 1H).

B. 2-Acetamido-5,3'-dinitrobenzophenone. A freshly prepared nitrating mixture, 10 ml (5 ml of 70% HNO_3 and 5 ml of conc. H_2SO_4), was placed in a 50 ml erlenmeyer flask and cooled in an ice bath with stirring. To this nitrating mixture was added solid 2-acetamidobenzophenone, II, 2 g. (0.008 mole), in portions so that the temperature remained between



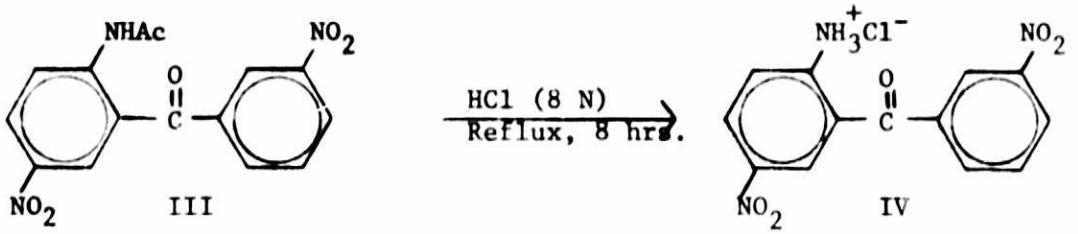
II III

5 - 10 °C. The addition of II was complete in 20 minutes. The reaction was followed by TLC (silica gel plates) using 20% ethyl acetate--benzene as solvents. After four hours, when the starting material had disappeared from the reaction mixture as determined by TLC, the contents were poured onto one kg. of crushed ice. The precipitate which formed was collected, washed with sodium carbonate solution and with distilled water. The crude product, 2.6 g, was recrystallized from methanol-acetone to afford 1.2 g (47% yield), m.p. 173 - 175 °C; ir 3500 - 3300, 1720, and 1700 cm^{-1}; nmr δ 2.2 (S, 3H), 9.2 (D, 1H), 7.9 - 9.0 (M, 8H, including the NH proton). Anal. Calc. for $C_{15}H_{11}O_6N_3$: C, 54.71; H, 3.34; N, 12.76. Found: C, 54.41; H, 3.19; N, 12.49.

The synthesis of this compound has been successfully repeated on a 30 g scale.

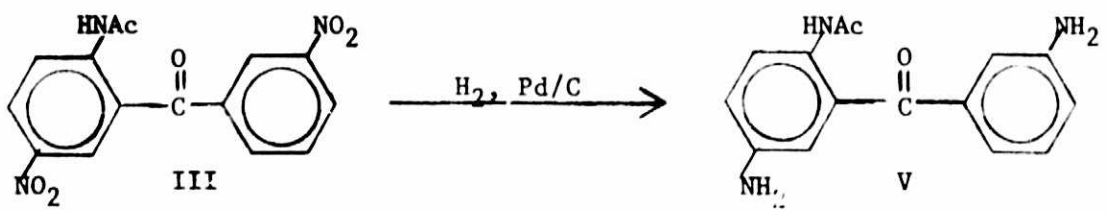
C. 2-Amino-5,3'-dinitrobenzophenone hydrochloride. 2-Acetamido-5,3'-dinitrobenzophenone, III, 1.1 g (0.0033 mole) and 30 ml of hydrochloric

acid (8 N) were placed in a flask and heated on a steam bath, and the disappearance of III was monitored by TLC. After eight hours,



when the starting material had disappeared, the mixture was poured into an ice bath and the crude precipitate (1.2 g) was collected and recrystallized from a methanol-acetone solution to give 1.1 g (97%) of product, m.p. 231 - 234 °C; ir 3400 - 3300, 1650 cm^{-1}. Anal. Calc. for $C_{13}H_{10}O_5N_3Cl$: C, 48.6; H, 3.09; N, 13.09. Found: C, 50.06; H, 2.87; N, 13.26.

D. 2-Acetamido-5,3'-diaminobenzophenone. 2-Acetamido-5,3'-dinitrobenzophenone, III, 500 mg (0.0016 mole), was dissolved in 200 ml of ethyl acetate and placed in a hydrogenation bottle with 0.10 g 10% Pd/C. Hydrogenation was carried out in the Parr low-pressure apparatus and the reaction was continued until the pressure no longer dropped.



The reaction mixture was filtered to remove the catalyst and the solvent was evaporated on a rotary evaporator. The crude product was recrystallized from ethyl acetate-petroleum ether to form 300 mg (69% yield) of crystals which melted between 122 - 123 °C; ir 3500 - 3000, 1710 and 1620 cm^{-1}; nmr δ 2.1 (M, 5H), 3.0 - 4.2 (S, broad, 2H), and 7.0 - 8.0 (M).

IV. Bibliography

(1) B. L. Stump, *Second Annual Report, NASA Grant NGR 47-002-041,* March 12, 1975.

(2) Vernon L. Bell, Private Communication.

V. Personnel

Dr. B. L. Stump, Principal Investigator

Dr. Junaid Siddiqui, Post-doctoral Research Associate

Ms. Li-Ching Shih, Graduate Research Assistant

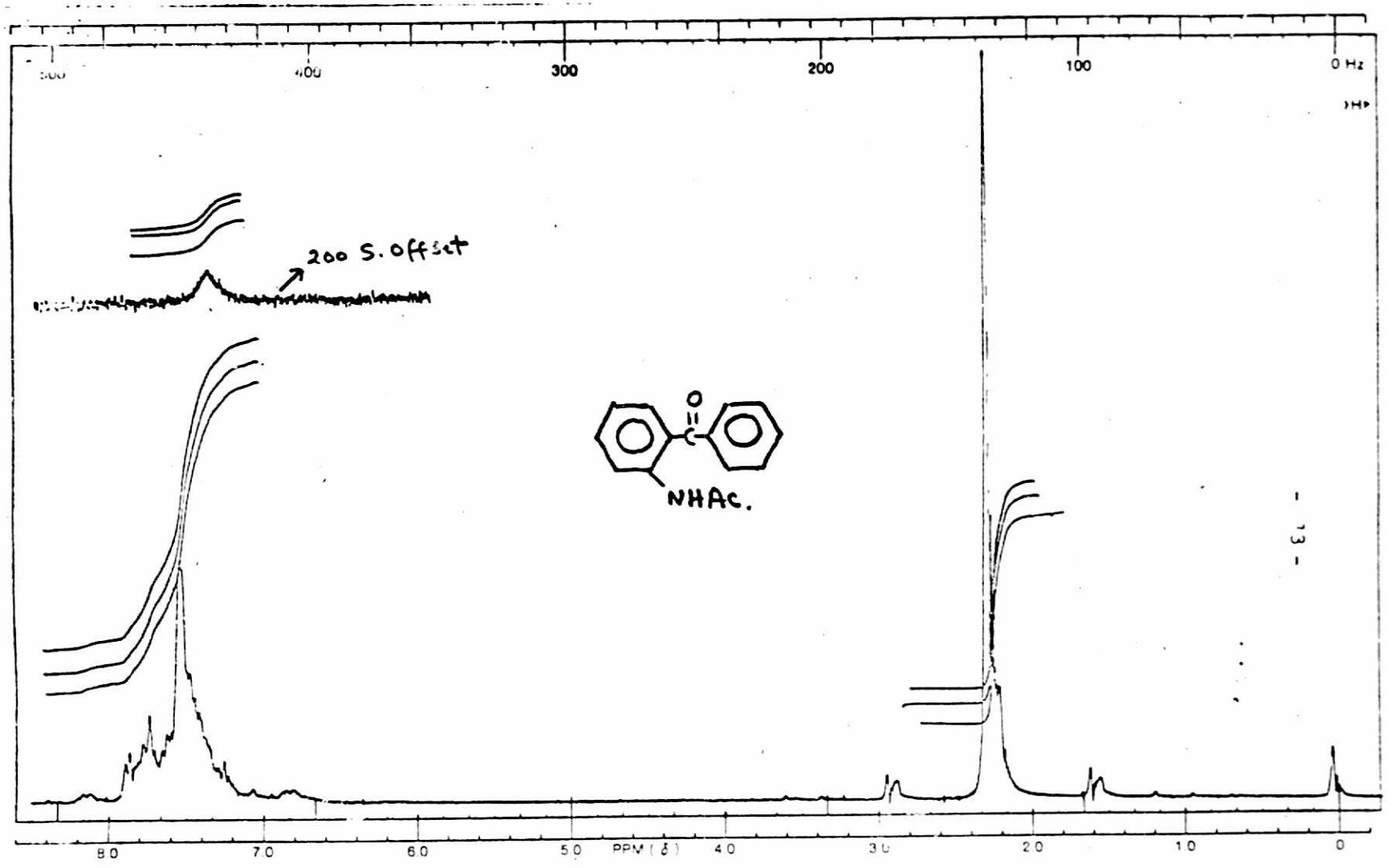


Figure 5. NMR spectrum of 2-Acetamidobenzophenone.

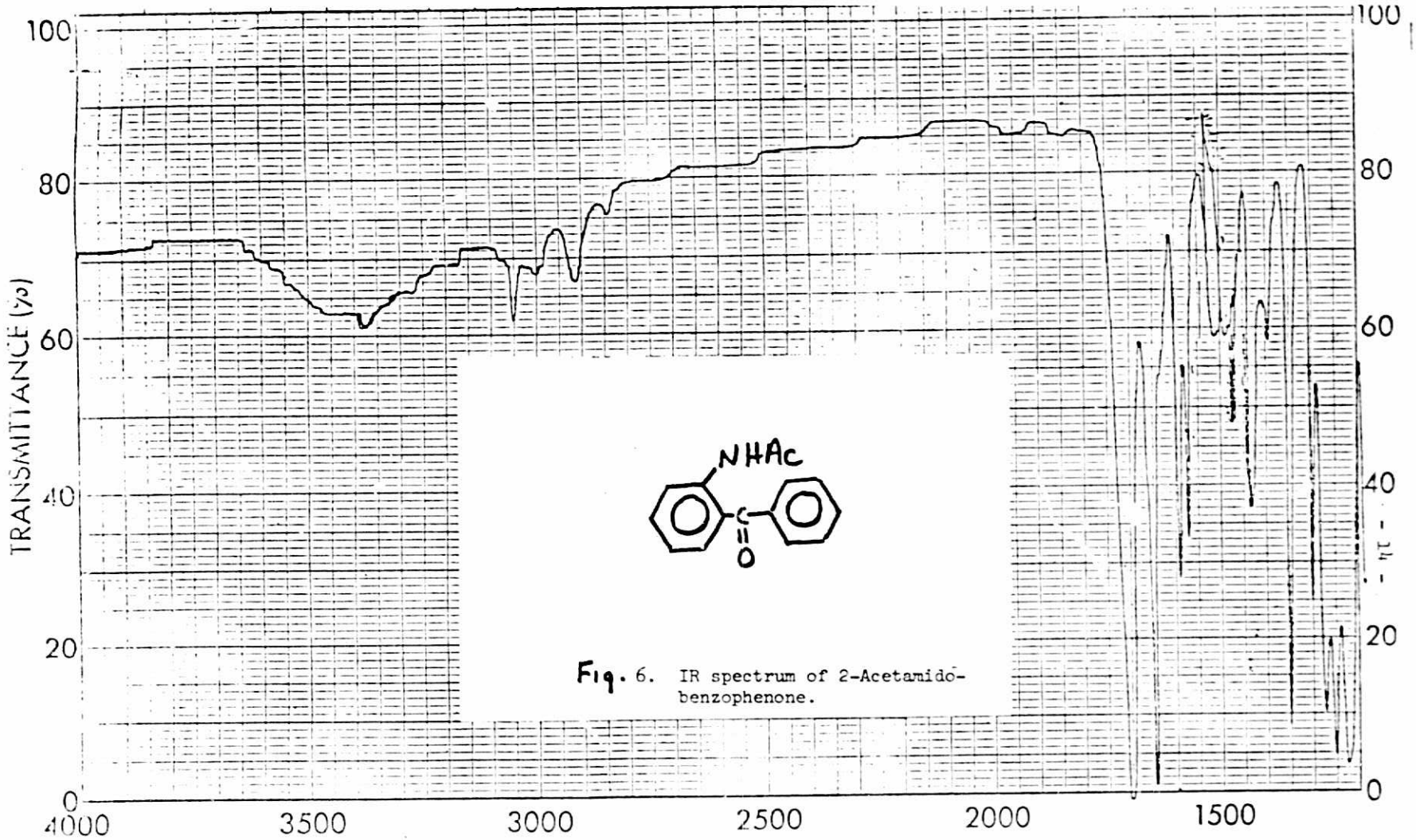
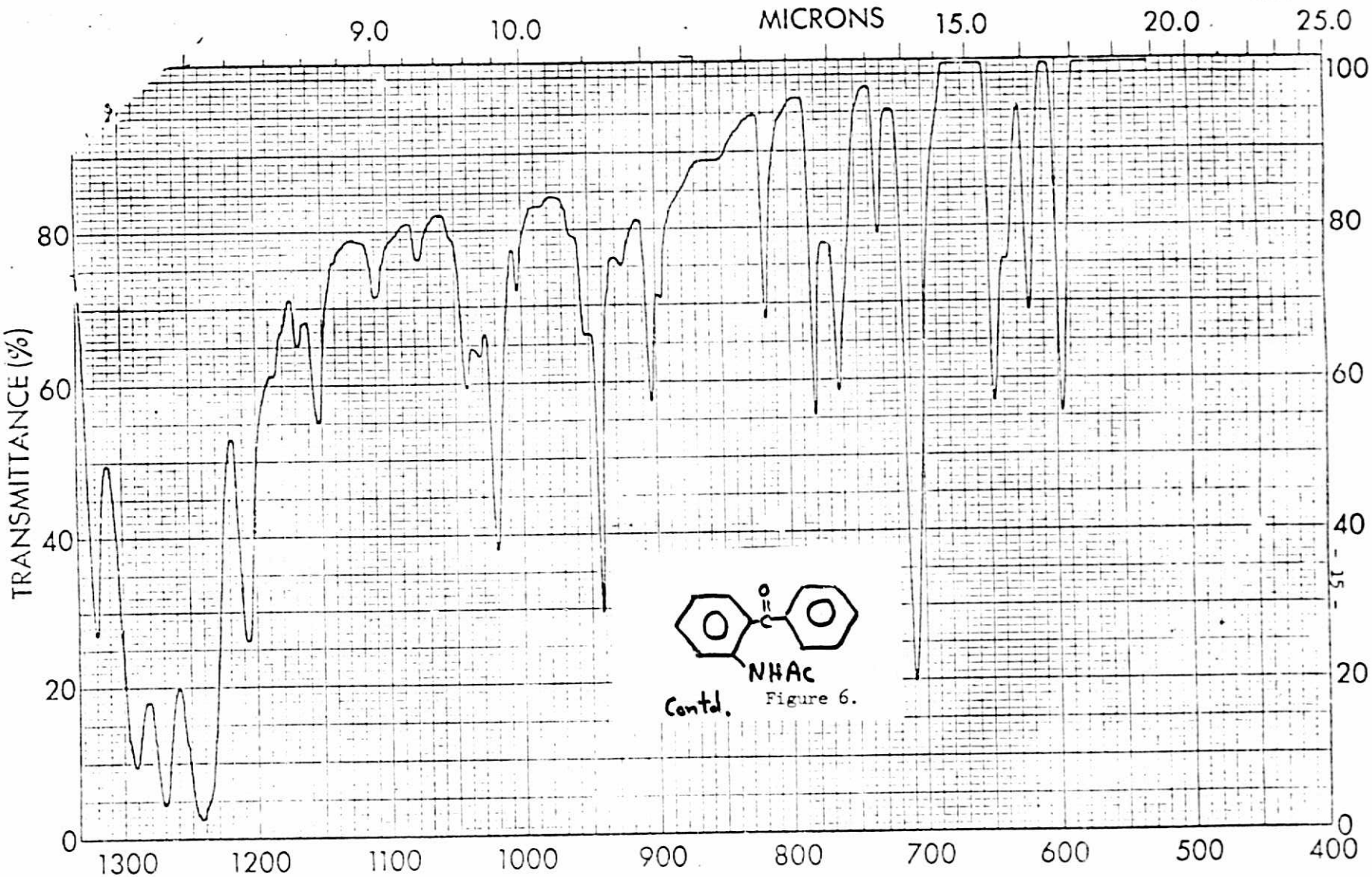


Fig. 6. IR spectrum of 2-Acetamido-benzophenone.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40
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O
C
NHAc
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Figure 6.

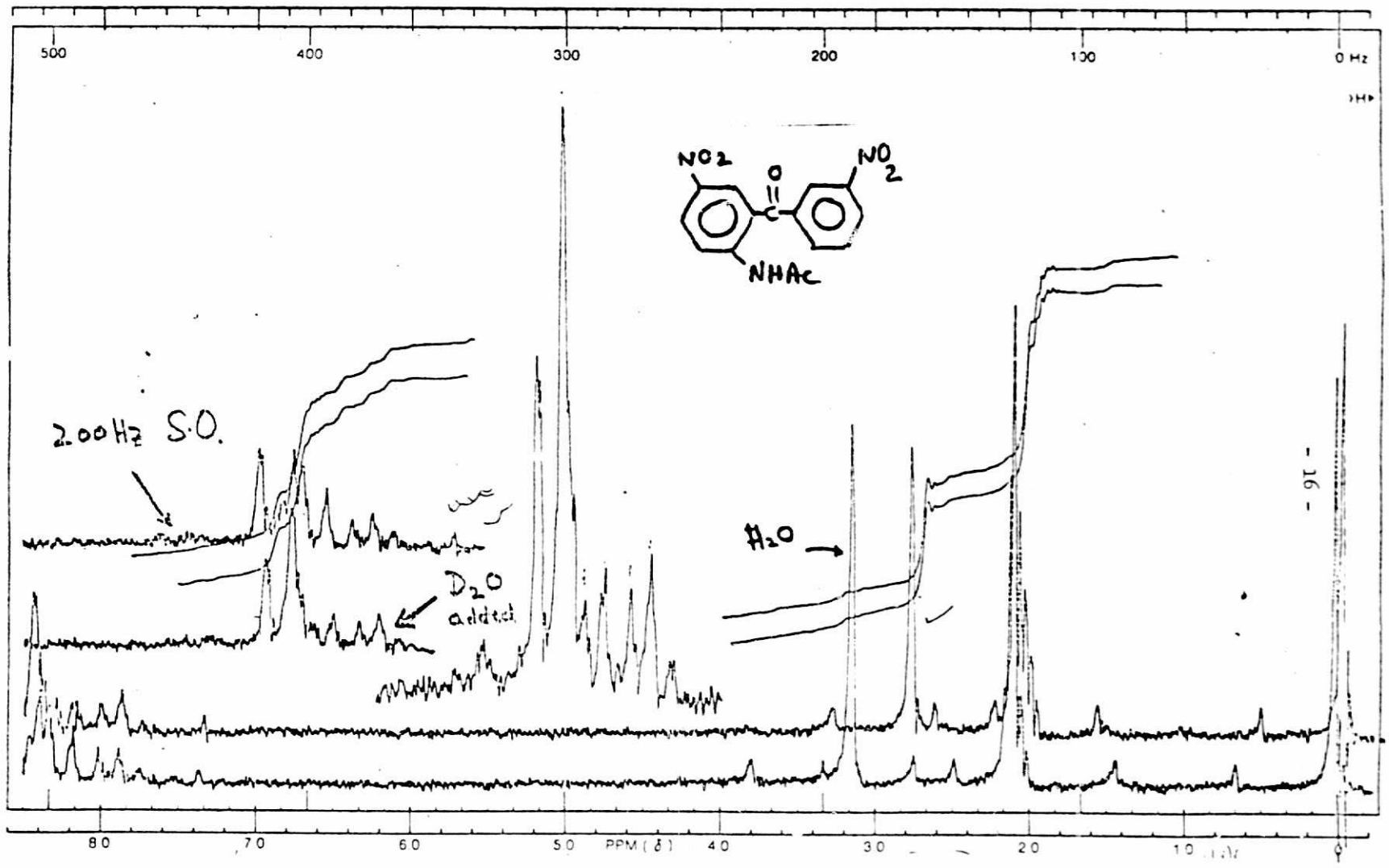


Figure 7. NMR spectrum of 2-Acetamido-5,3'-dinitrobenzophenone.

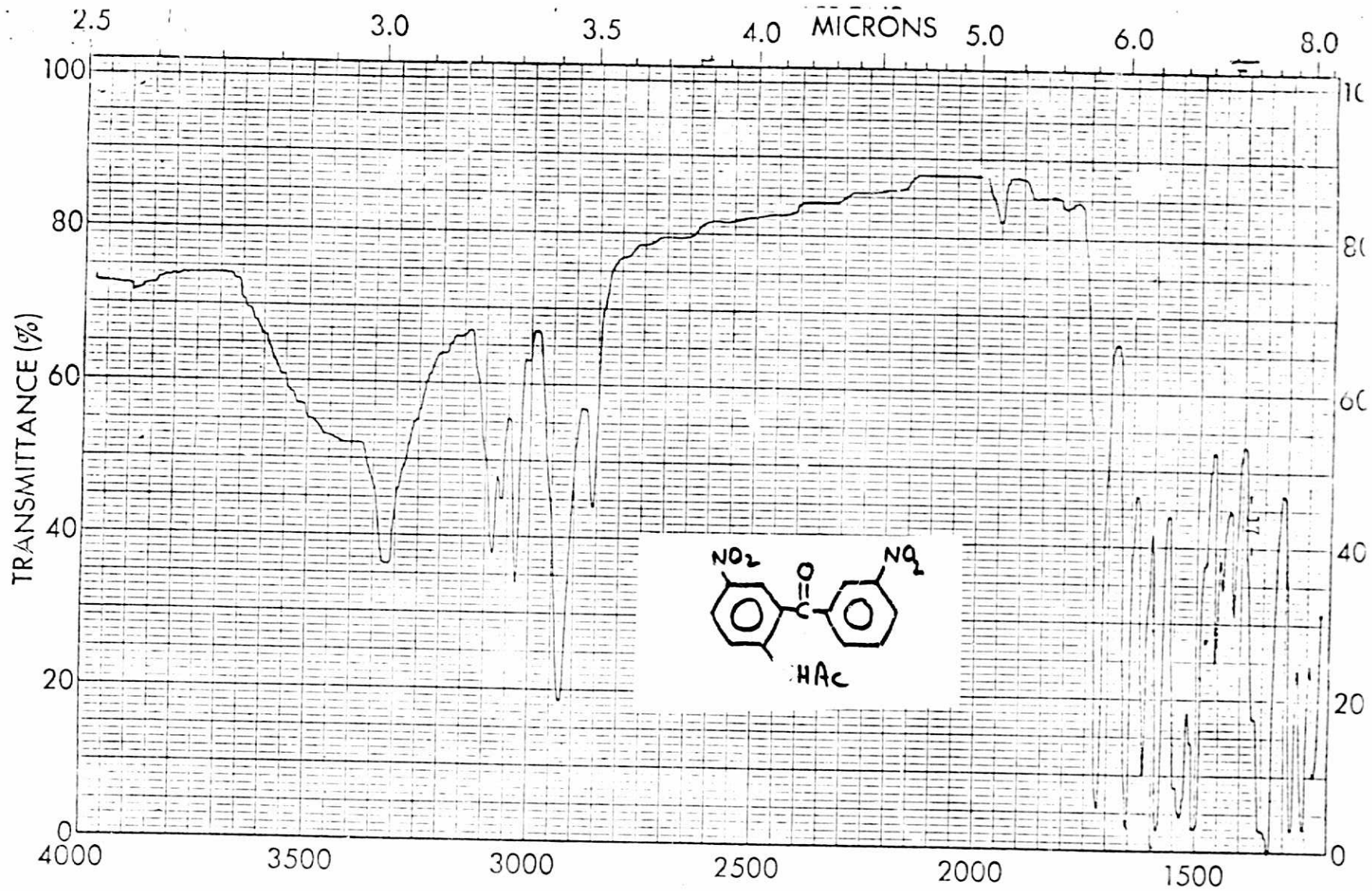
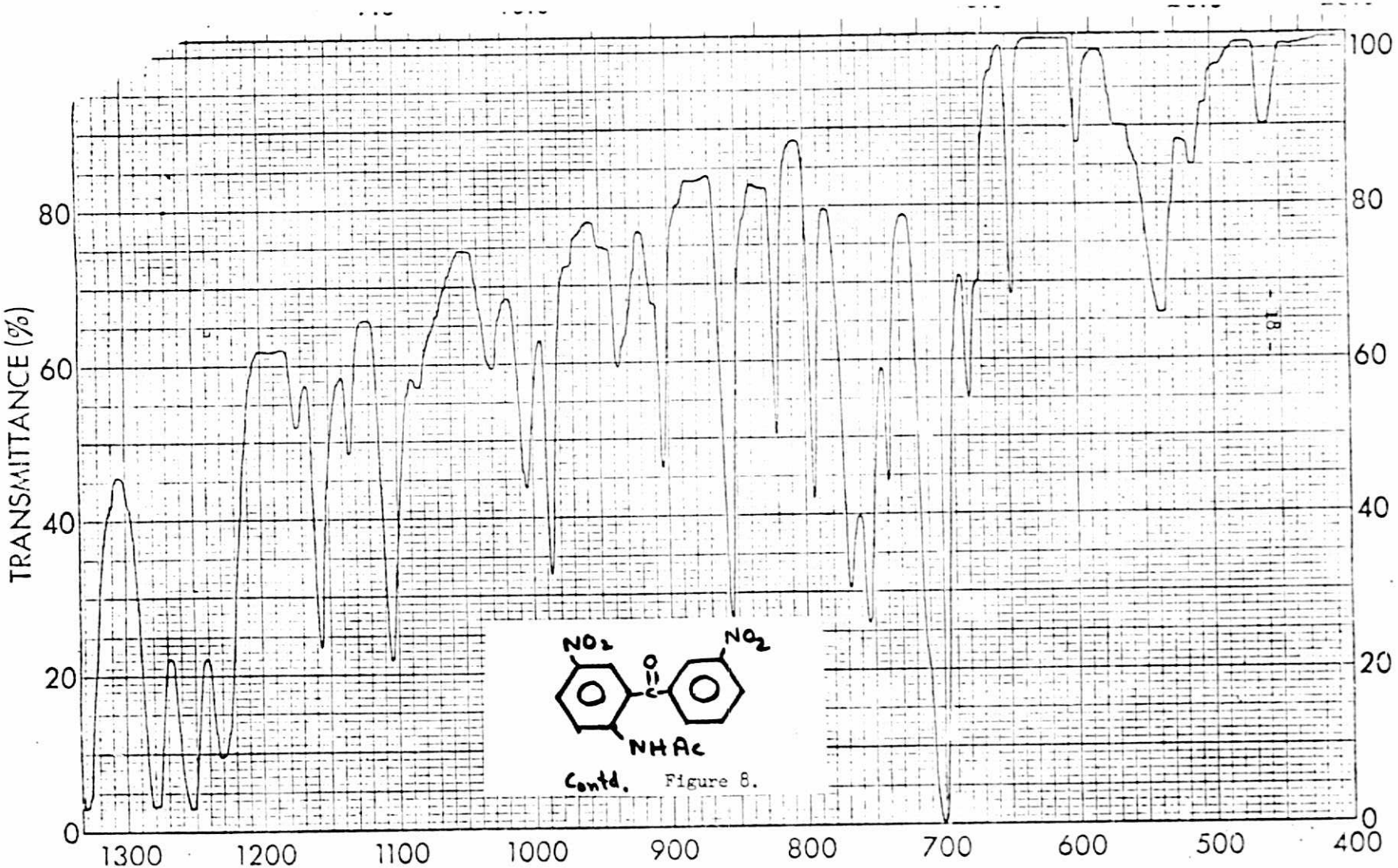
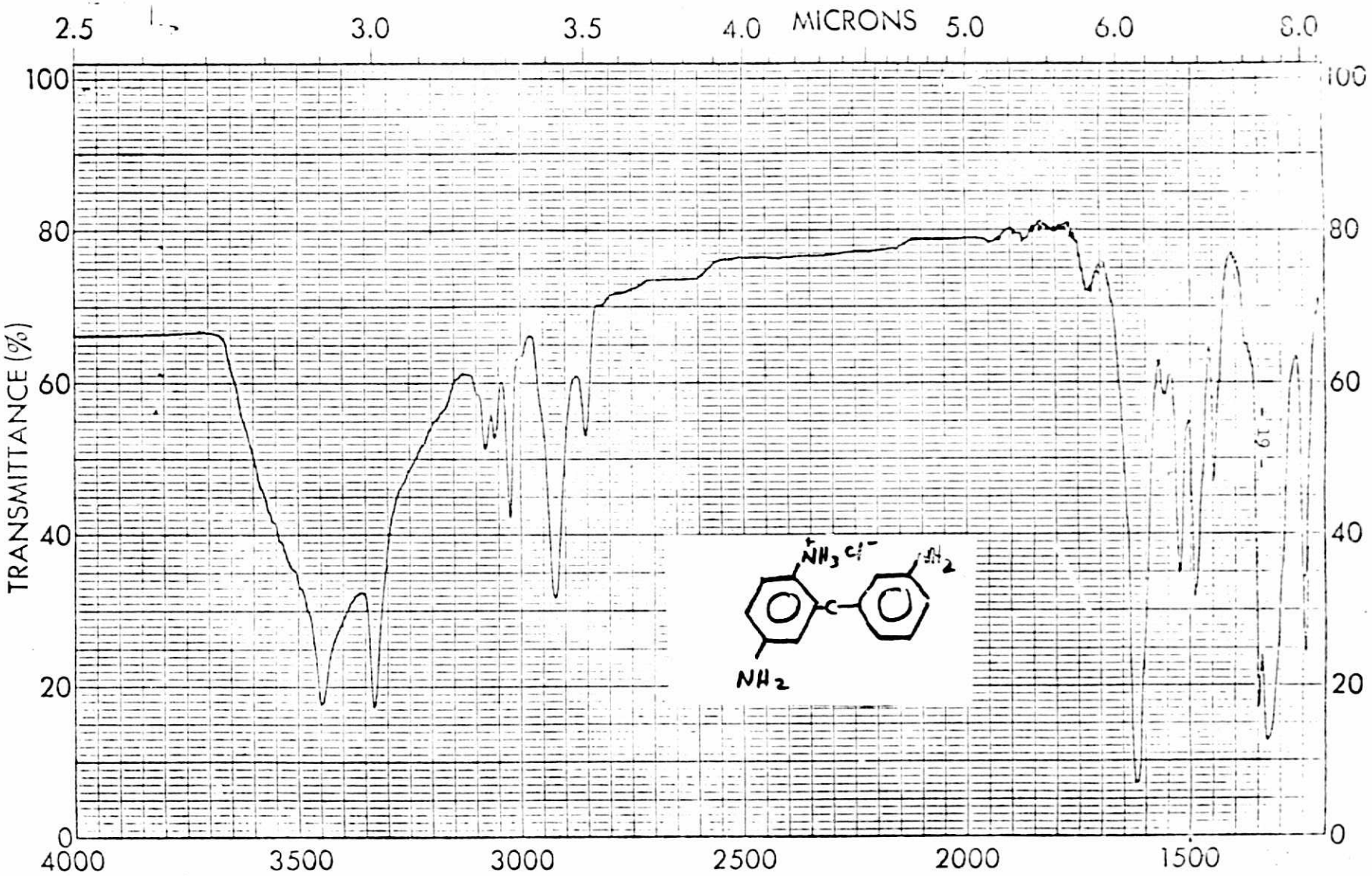


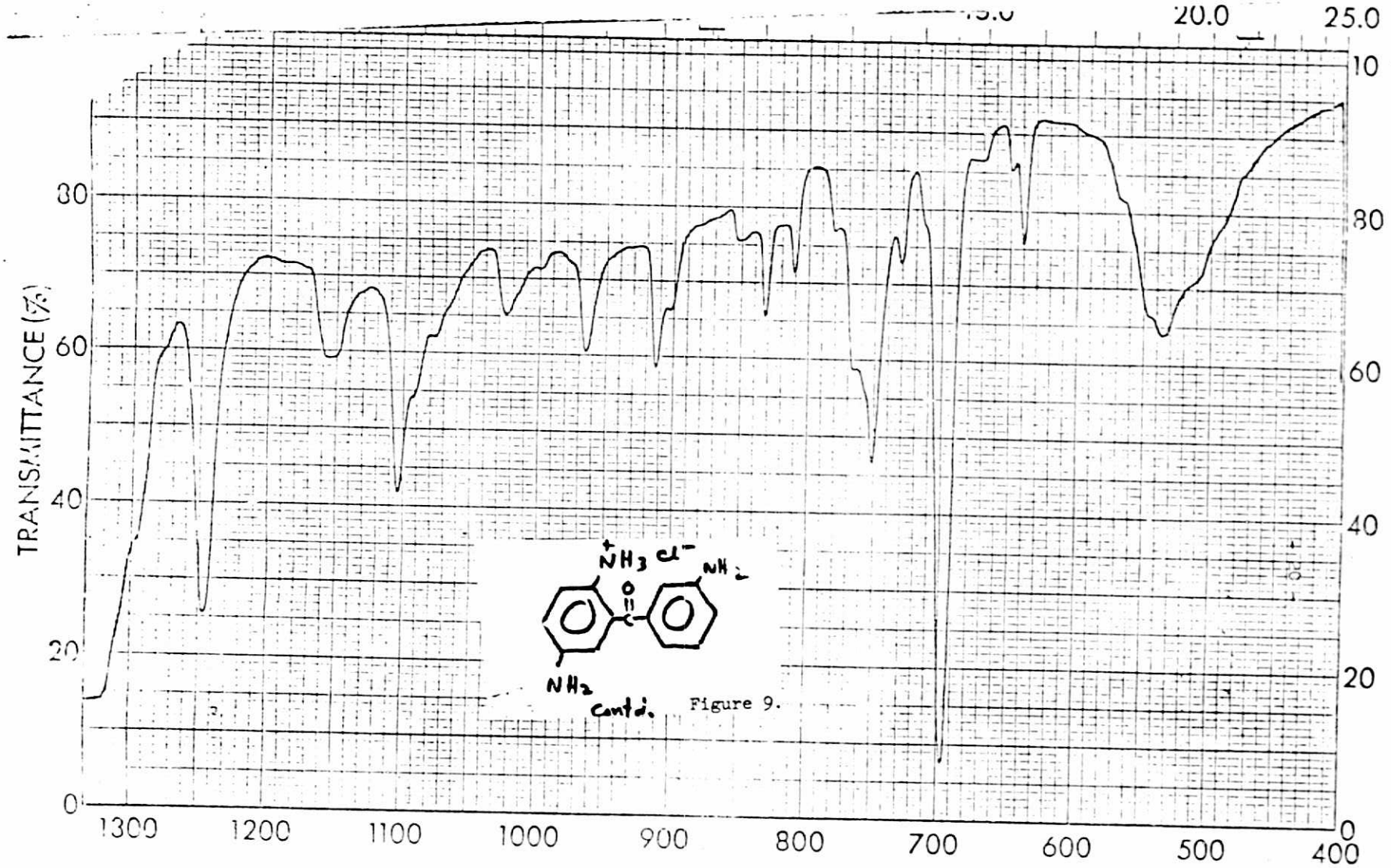
Figure 8. IR spectrum of 2-Acetamido-5,3'-dinitrobenzophenone.



Contd. Figure 8.

Figure 9. IR spectrum of 2-Amino-5,3'-dinitrobenzophenone hydrochloride.

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10
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20
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TRANSMITTANCE (%)
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NH_2
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NH_2
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Figure 9.

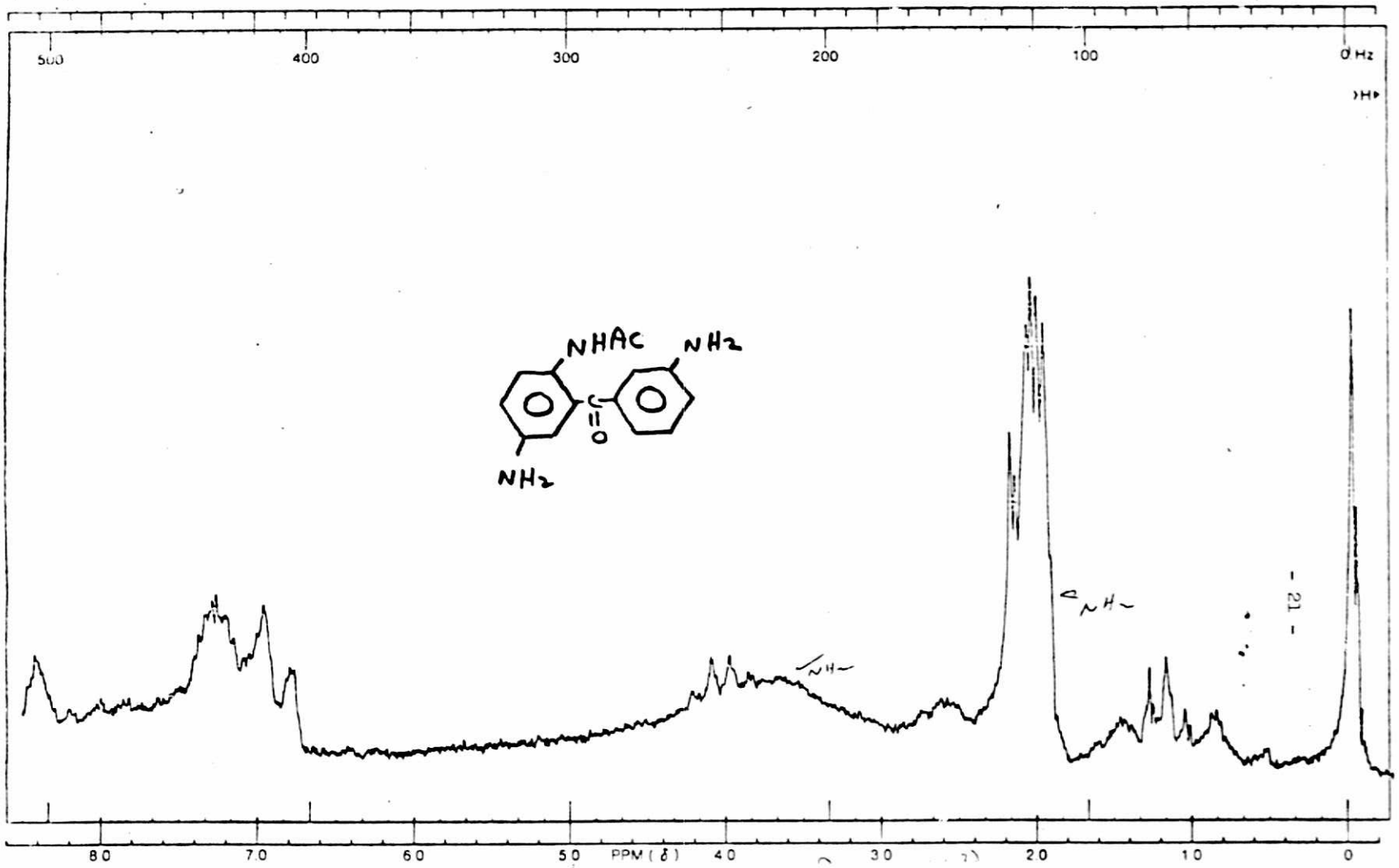


Figure 10. NMR spectrum of 2-Acetamido-5,3'-diaminobenzophenone.

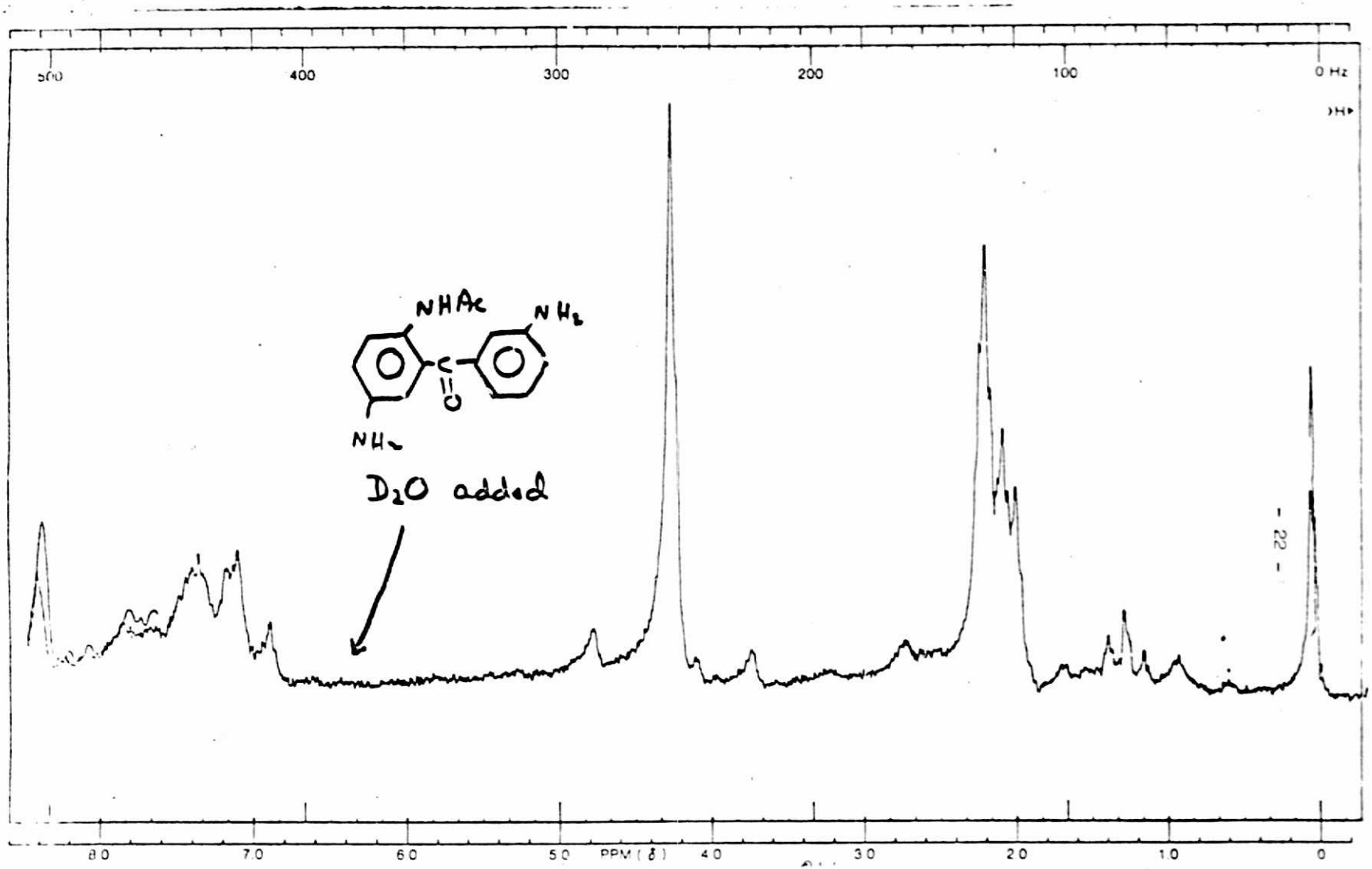


Figure 11. NMR spectrum of 2-Acetamido-5,3'-diaminobenzophenone with D_2O added.

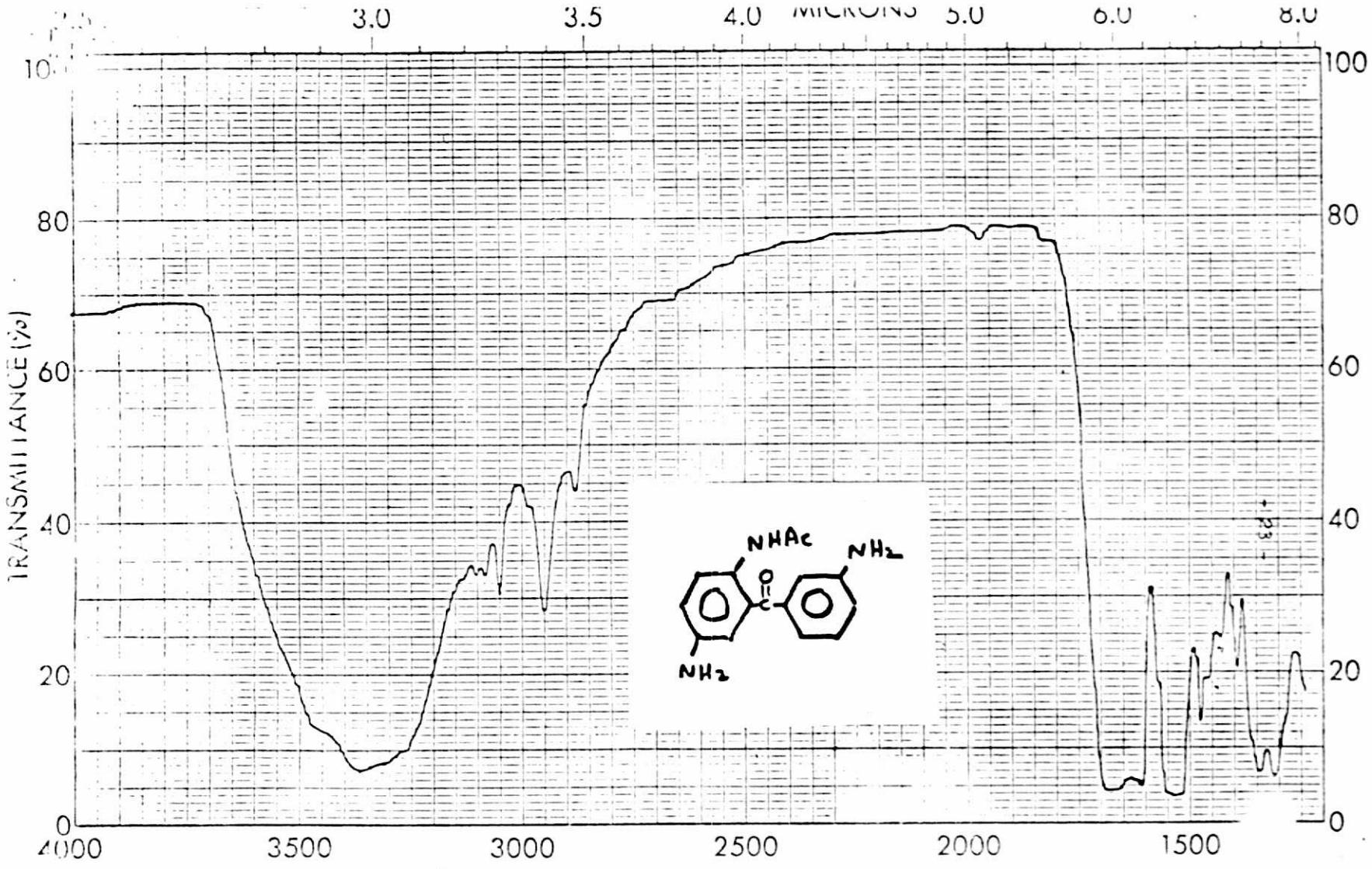
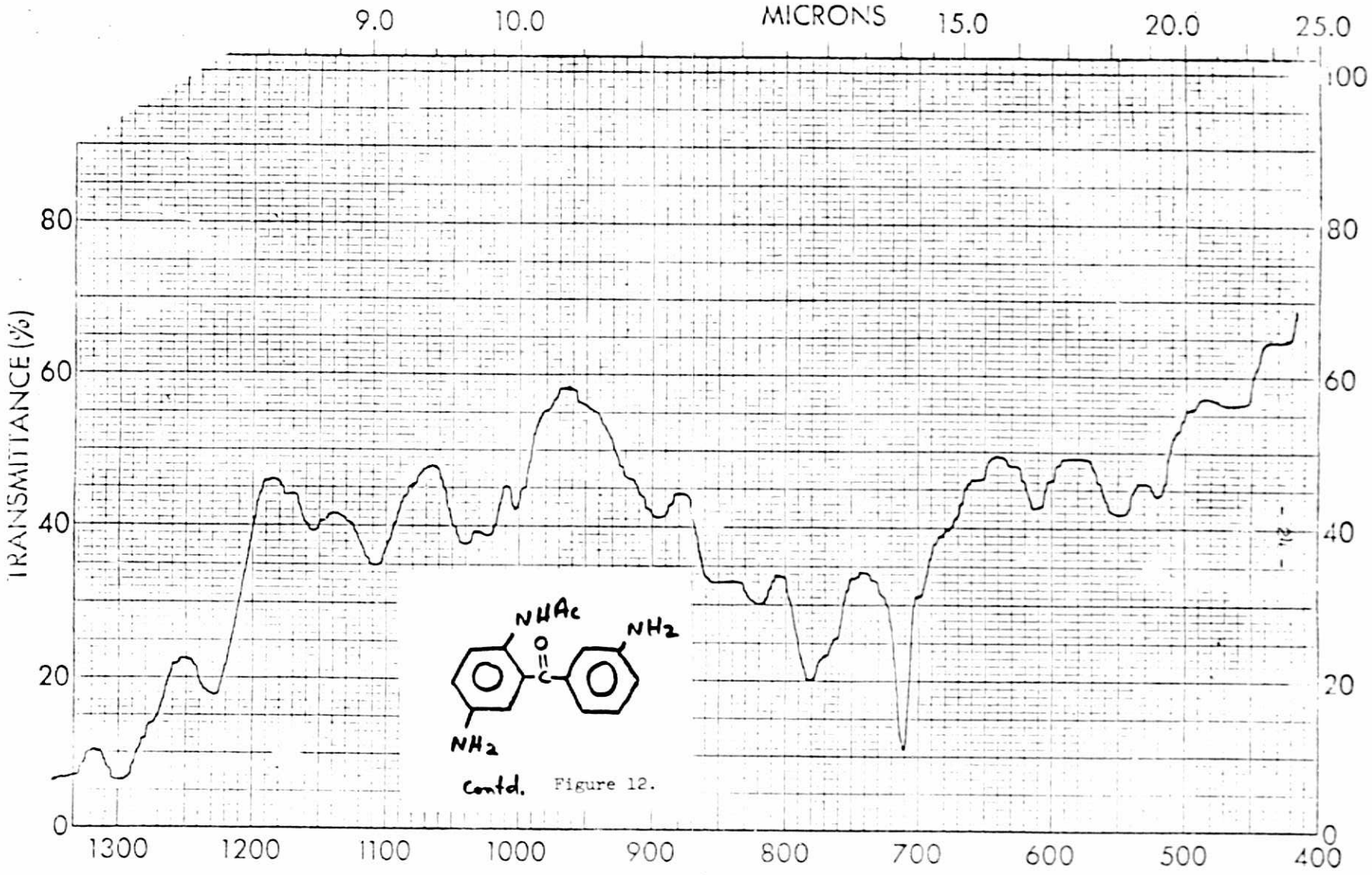


Figure 12. IR spectrum of 2-Acetamido-5,3'-diaminobenzophenone.



contd. Figure 12.