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Second Annual Report
to
THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Non-Metallic Materials Branch, Materials Division
Langley Research Center
Hampton, Virginia

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Department of Chemistry
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Richmond, Virginia 23284

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THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NON-METALLIC MATERIALS BRANCH, MATERIALS DIVISION

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INSTITUTION:	VIRGINIA COMMONWEALTH UNIVERSITY Department of Chemistry School of Arts and Sciences Richmond, Virginia 23284
PRINCIPAL INVESTIGATOR:	Dr. B. L. Stump Associate Professor of Chemistry
TITLE OF RESEARCH:	"ISOMER EFFECTS ON POLYIMIDE PROPERTIES"
REPORT PERIOD COVERED:	September 16, 1973 - December 31, 1974

ABSTRACT: *An investigation of the effect of structure variation on the solubility and glass-transition temperature of polyimide polymers is continuing. The addition of alkyl substituents to an aromatic ring in the polymer molecule, the reduction in the number of imide rings per average polymer chain-length, and a variation in the symmetry of the polymer molecule are parameters being explored. The synthesis of key intermediates for the preparation of the monomers required in this investigation is reported, including 2,4,6-Tris(m-nitrobenzyl)-1,3,5-trimethyl benzene, 2,4,6-Tris(p-nitrobenzyl)-1,3,5-trimethylbenzene, and 1,4-Bis(m-nitrobenzyl)-2,3,5,6-tetramethylbenzene. The synthesis of polyimide-precursor amines that contain functional groups to allow for post-cure cross-linking constitutes another phase of the project. An example is 2,5,3'-Triaminobenzophenone. Progress made in the synthesis of key intermediates for these types of monomers is summarized.*

B. L. Stump

B. L. Stump, Principal Investigator

March 12, 1975

Second Annual Report

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I. Introduction

An investigation of the effect of modifying the structure of thermally-stable polymers like polyimides has shown that a lower glass-transition temperature can be achieved with a less symmetrical molecule. For example, the polyimide prepared from 2,4'-methylenedianiline and benzophenonetetracarboxylic acid dianhydride (BTDA) softens[1] at approximately 272 °C. Dr. Vernon L. Bell has found[2] that polyimide from BTDA and 3,3'-diaminobenzophenone softens at an even lower temperature, about 220 °C.

One phase of this study is related to the 3,3'-diaminobenzophenone--BTDA polyimide system. The low softening temperature of this polyimide is desirable from the point of view of processability. However, the need to raise the softening temperature after processing is complete *via* a post-cure cross-linking mechanism is recognized. Earlier studies carried out as part of this investigation have shown that amino groups *ortho* to the carbonyl group, as in 2,4'-diaminobenzophenone, are sufficiently deactivated that polymerization does not occur. Hence, an objective of this research is the synthesis of monomers that will have polymerizable amino groups in the *meta*- and *para*- positions in benzophenone and that will have non-polymerizable amino groups in the *ortho*-position. These *ortho*-groups would thus be available in the processed polyimide for cross-linking, and the cross-linking would conceivably raise the softening temperature. Progress on this phase of the project is summarized in the next section of this report.

The studies currently being pursued continue an exploitation of the correlation between low glass-transition temperature and lack of symmetry in the polymer molecule. Additionally, these studies are directed towards an assessment of the effect of alkyl substituents in the polymer molecule on polyimide solubility. At the same time, the possibility of achieving a lower glass-transition temperature and/or solubility by decreasing the number of imide groups in the macromolecule is being investigated. Finally, an alternate route to thermally-stable polymers through imide monomers that will polymerize or cross-link thermally is being explored. The progress made on these phases of the project are summarized in the following sections of this report.

II. Discussion

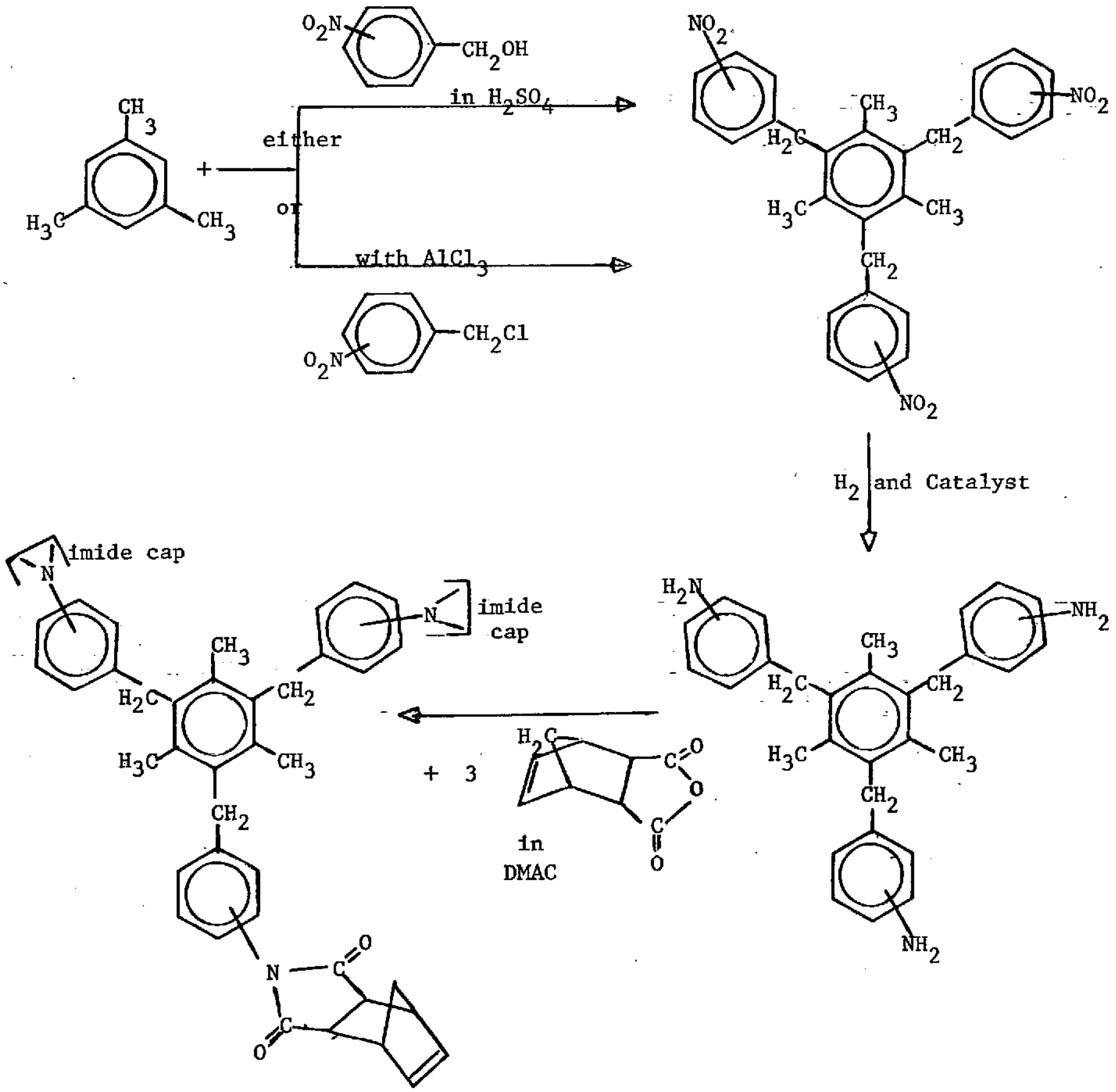
A. Imide Monomers for Addition-type Polyimides

Imide monomers for thermally-stable addition-type polyimides are being sought *via* the reaction scheme outlined in Figure 1. The nitro group on the benzyl alcohol or benzyl chloride could be in either the *ortho*, *meta*, or *para* position, and the trimethyl benzene could be either 1,3,5- or 1,2,3- or 1,2,4-trimethylbenzene. Two of the nitro compounds in the series have been synthesized via the Friedel-Crafts route: 2,4,6-tris(*m*-nitrobenzyl)-1,3,5-trimethylbenzene and 2,4,6-tris(*p*-nitrobenzyl)-1,3,5-trimethylbenzene. The preparations of these compounds are described in the Experimental Section of this report. The nmr and ir spectra of the compounds, as well as their DTA curves, are shown as Figures 2,3,4,5,6, and 7. As the investigation continues, other compounds in the series will be synthesized, while the two compounds already synthesized will be reduced to amines, reacted with 5-norbornene-2,3-dicarboxylic anhydride to form imides, and characterized as to cross-linking or addition-type polymerization properties.

B. Aromatic Diamines with Three Benzene Rings

Seeking novel diamines which could lead to thermally-stable and

Figure 1. Imide Monomers for Addition-Type Polyimides.



--The nitro group in the benzyl alcohol or benzyl chloride can be either <u>ortho</u>, <u>meta</u>, or <u>para</u>-.

--The trimethyl benzene can be either the 1,3,5-, the 1,2,3-, or the 1,2,4-isomer.

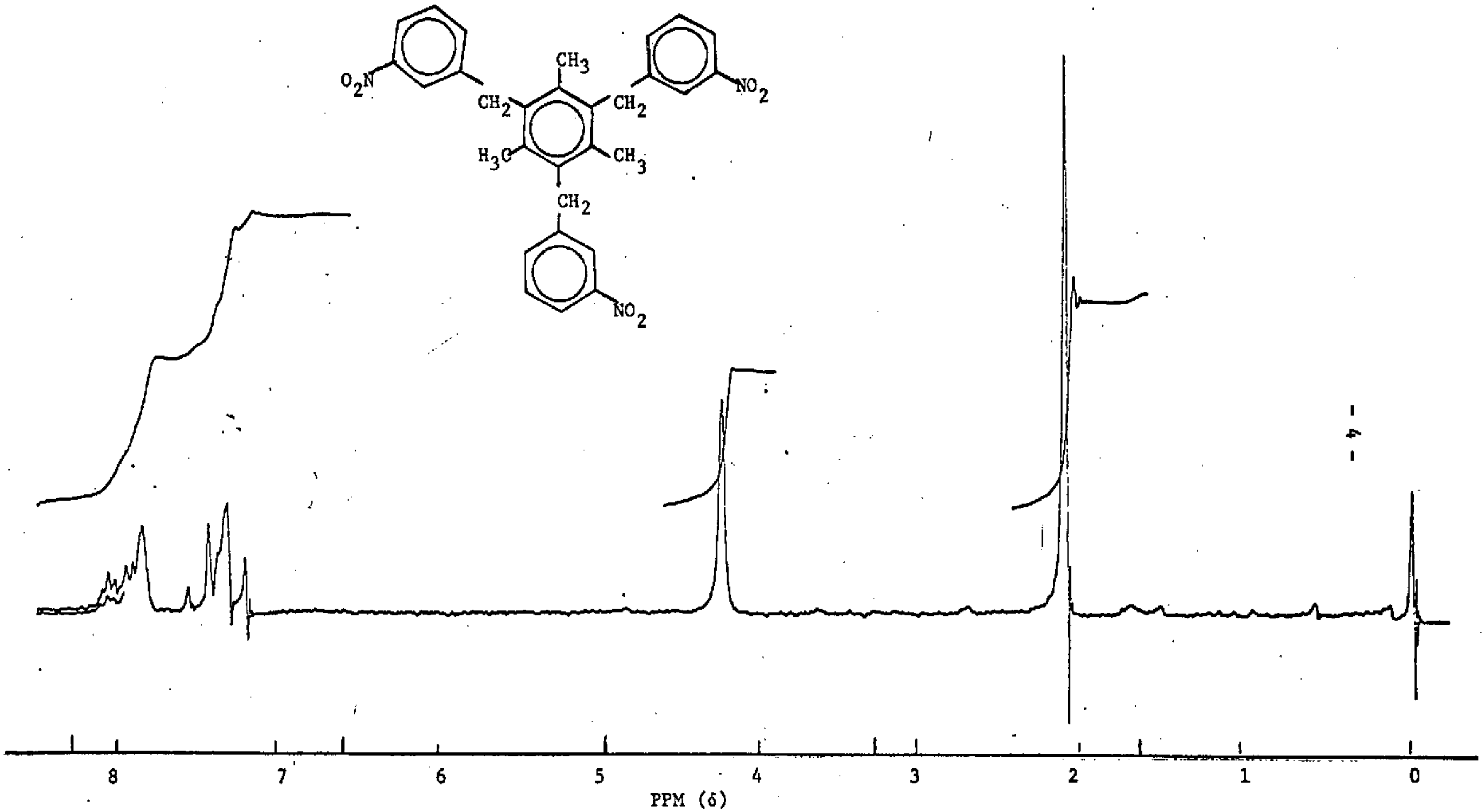


Figure 2. The nmr spectrum of 2,4,6-Tris(m-Nitrobenzyl)-1,3,5-Trimethylbenzene in $CDCl_3$.

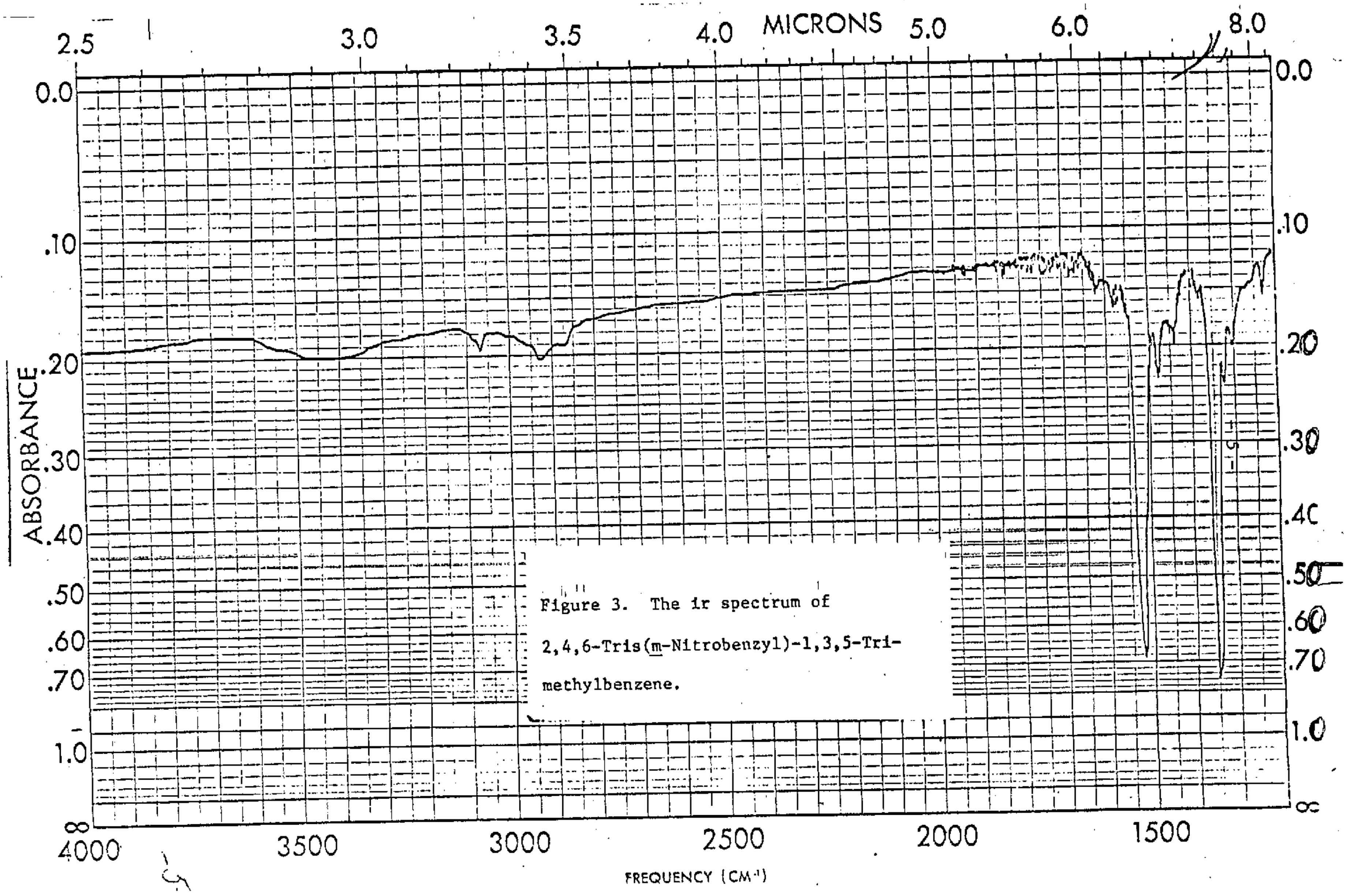


Figure 3. The ir spectrum of 2,4,6-Tris(m-Nitrobenzyl)-1,3,5-Trimethylbenzene.

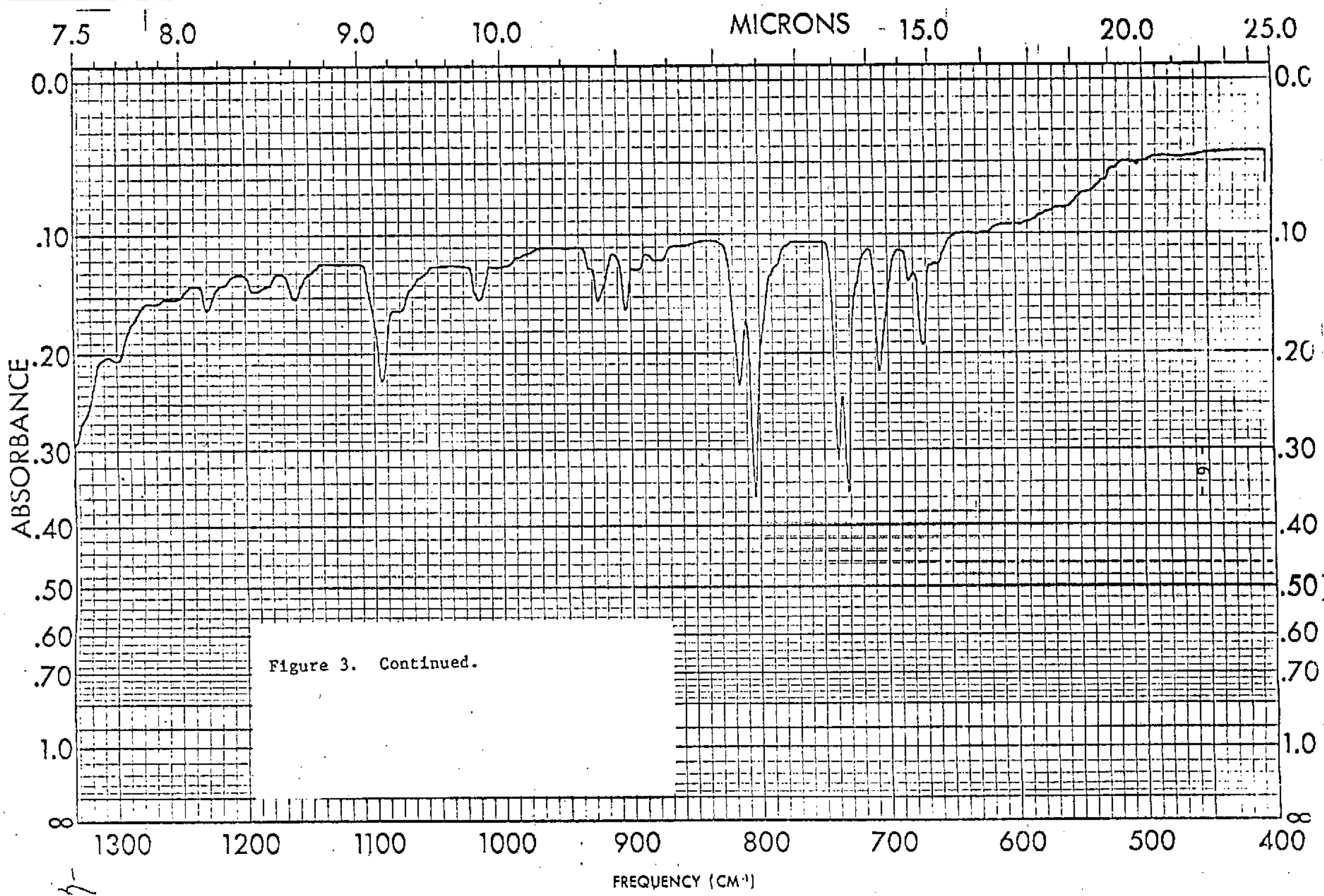


Figure 3. Continued.

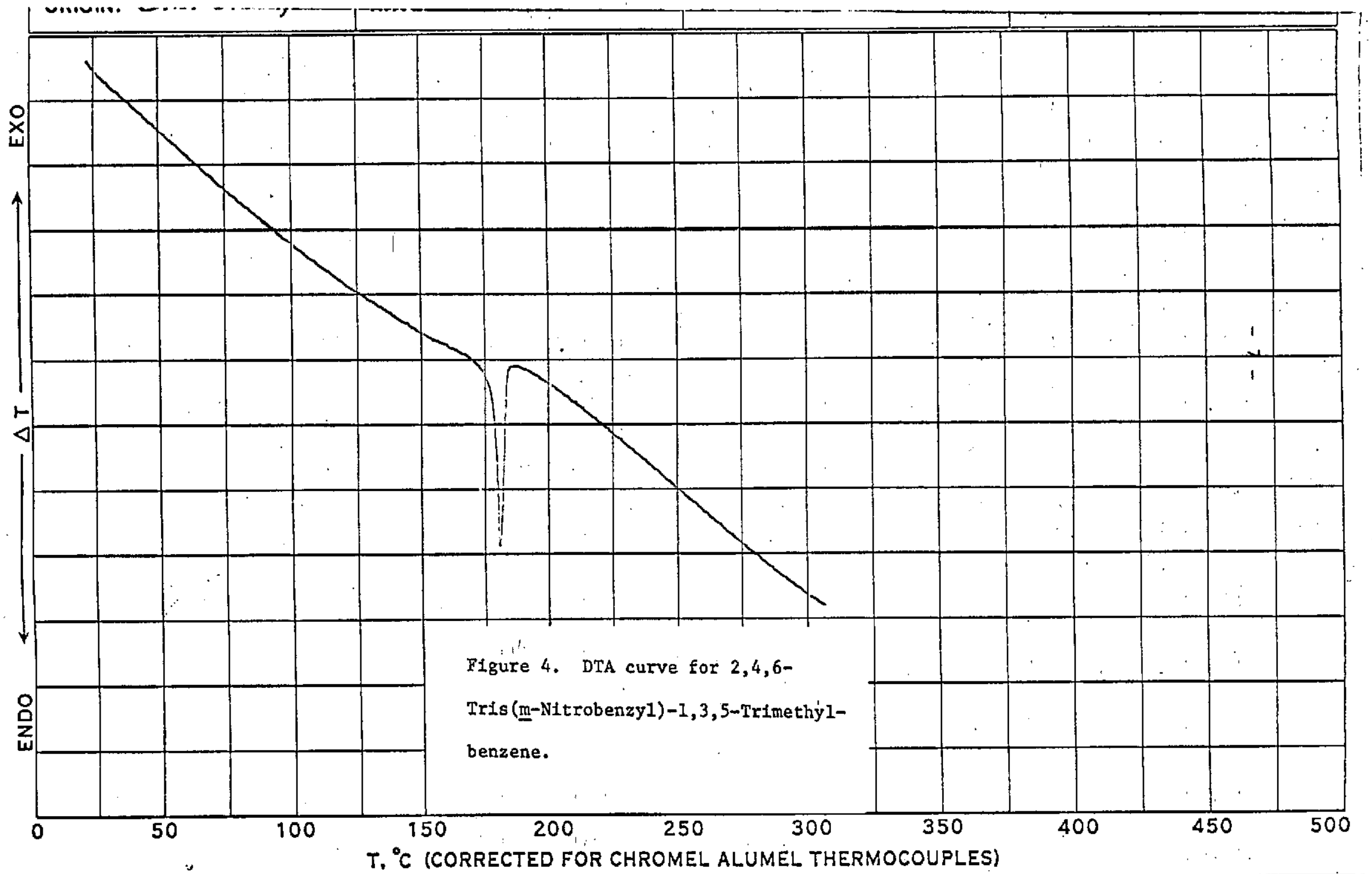


Figure 4. DTA curve for 2,4,6-Tris(m-Nitrobenzyl)-1,3,5-Trimethylbenzene.

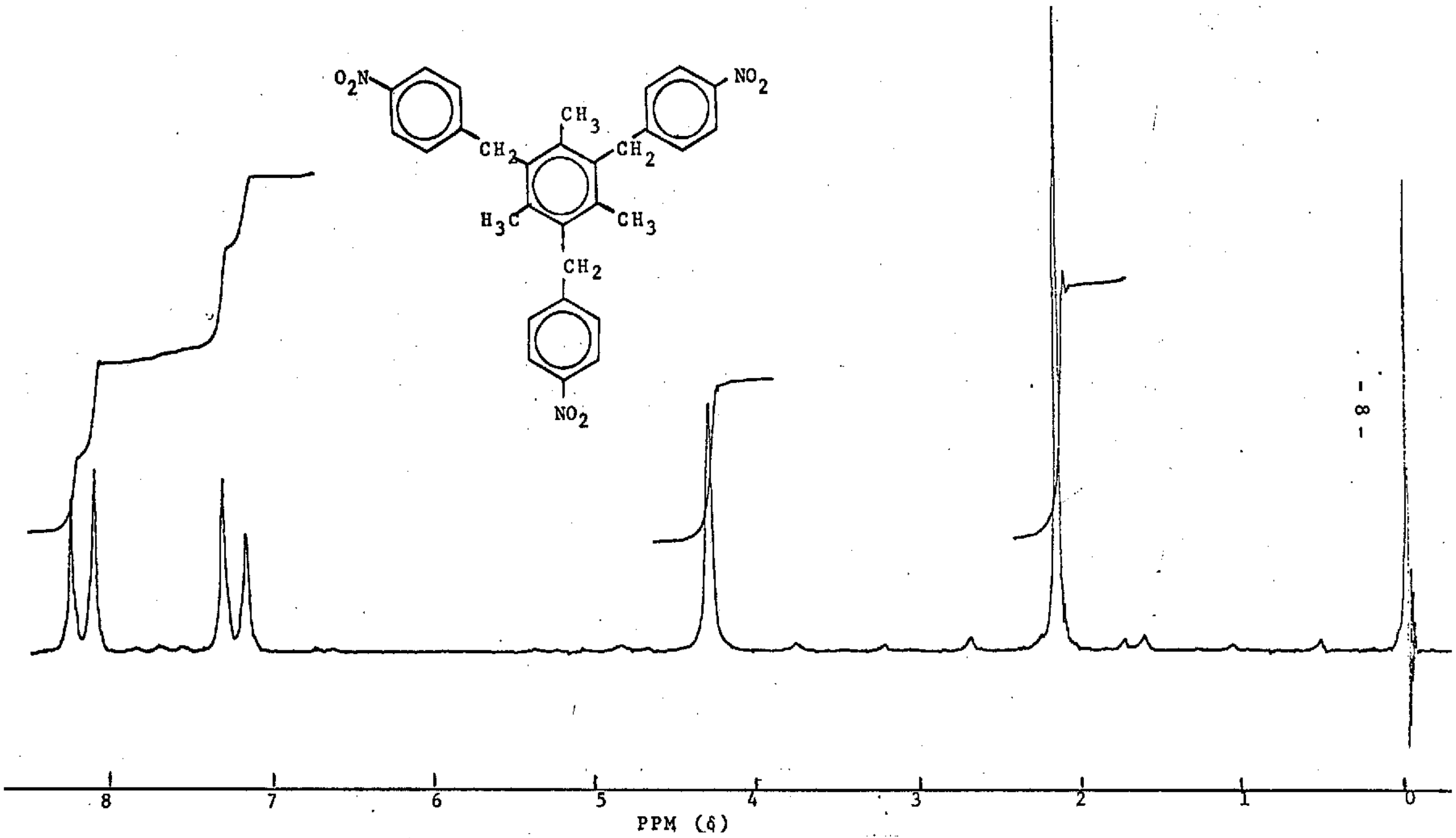


Figure 5. The nmr spectrum of 2,4,6-Tris(p-Nitrobenzyl)-1,3,5-Trimethylbenzene in $CDCl_3$.

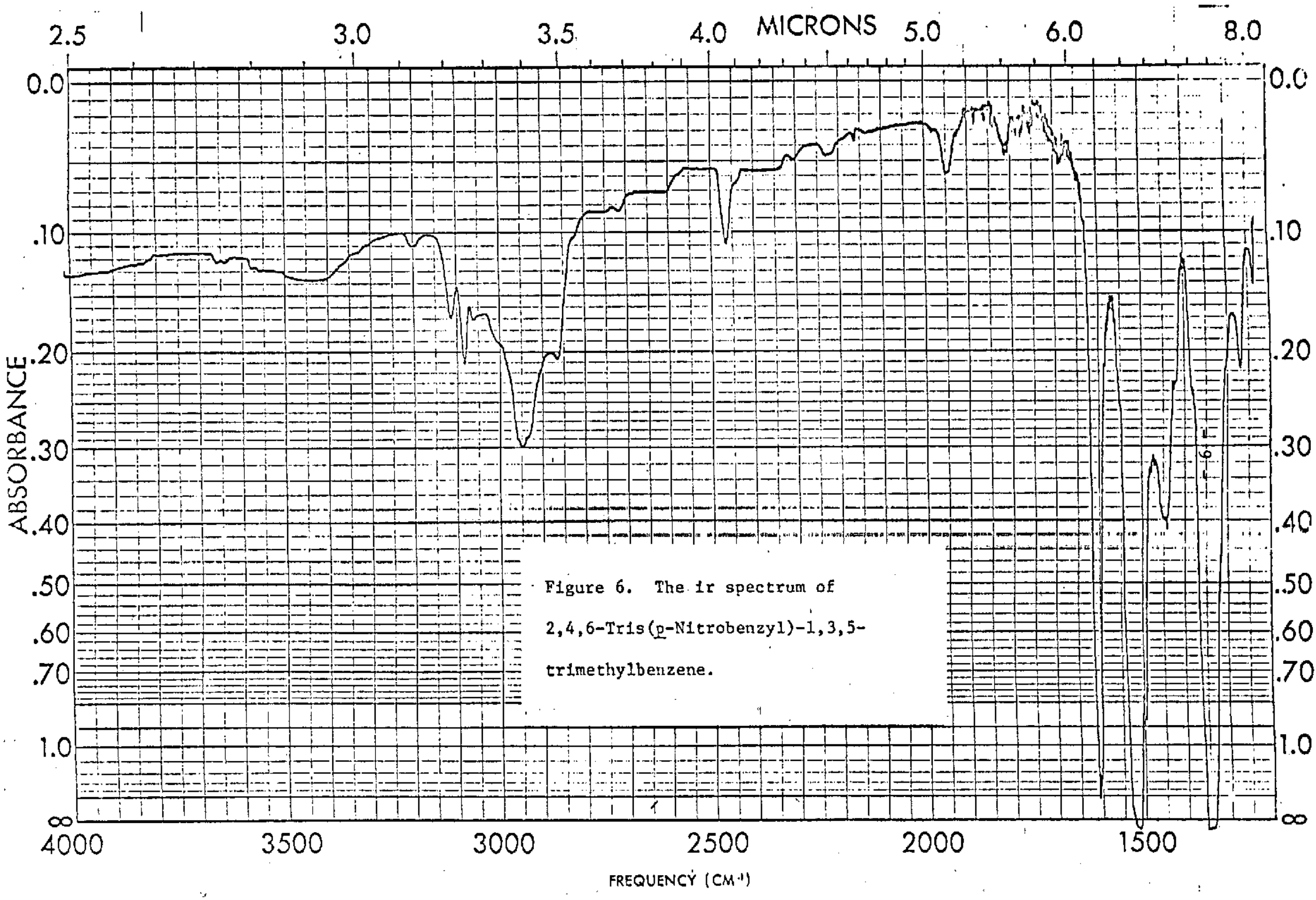


Figure 6. The ir spectrum of 2,4,6-Tris(p-Nitrobenzyl)-1,3,5-trimethylbenzene.

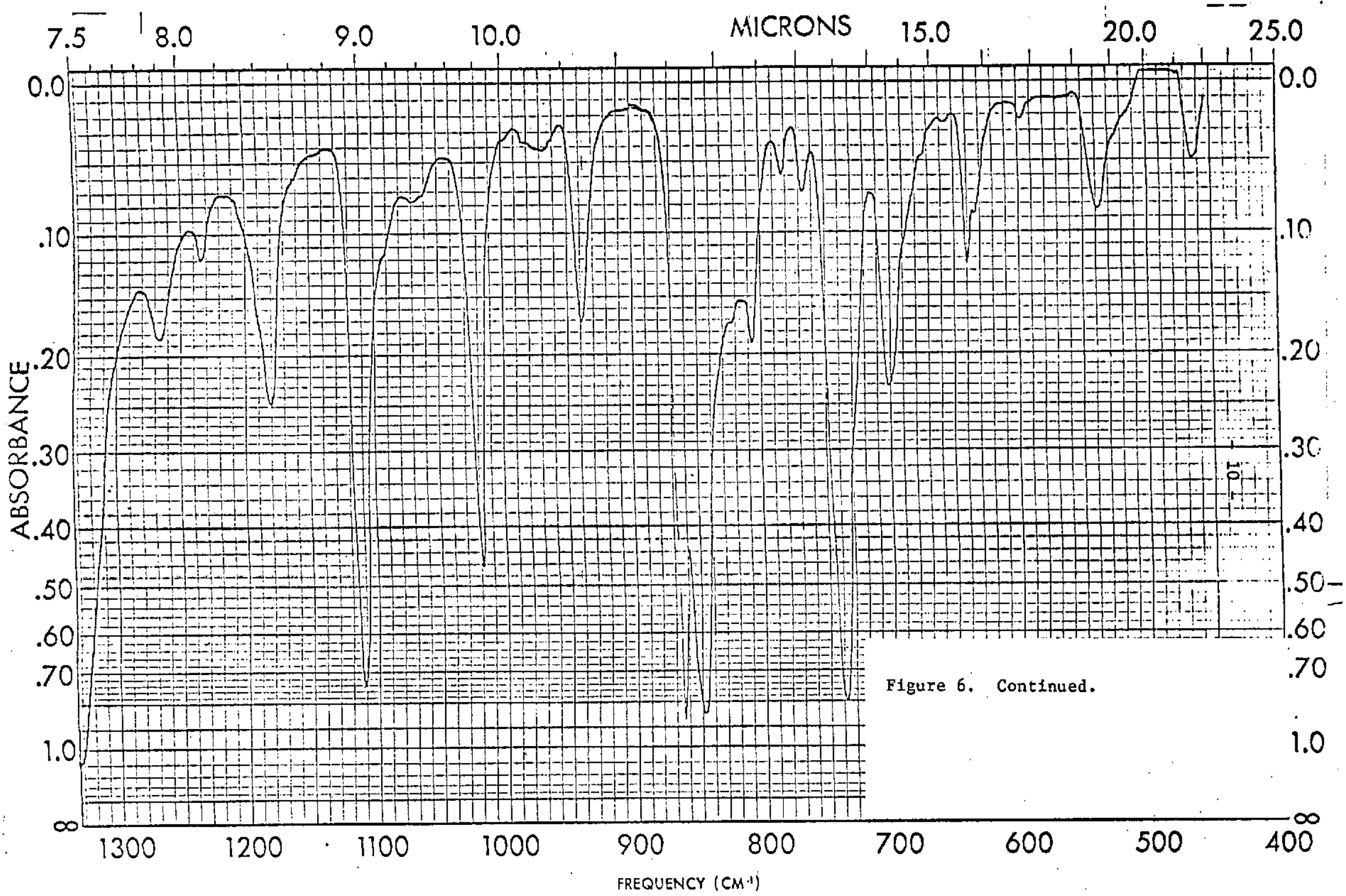


Figure 6. Continued.

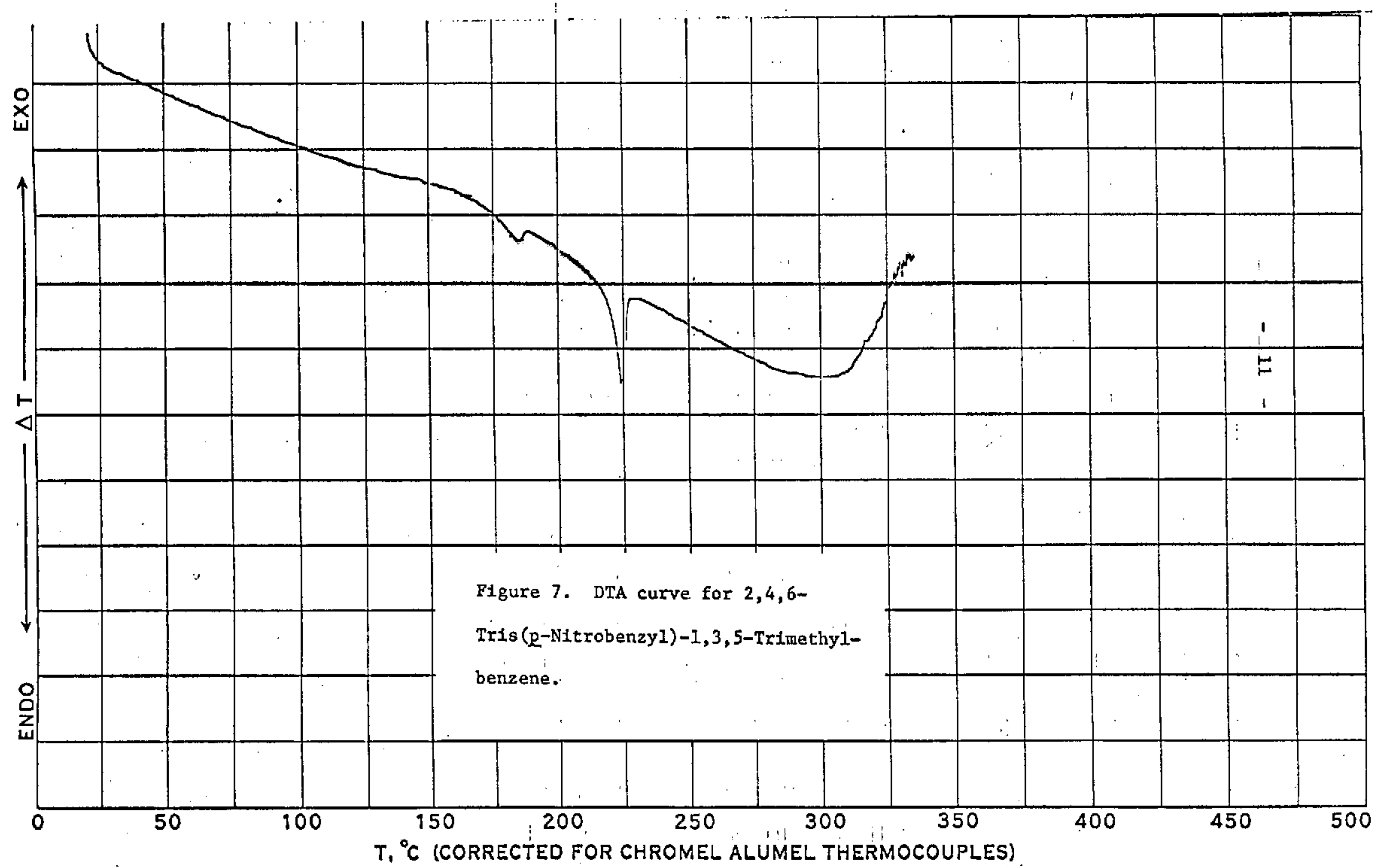
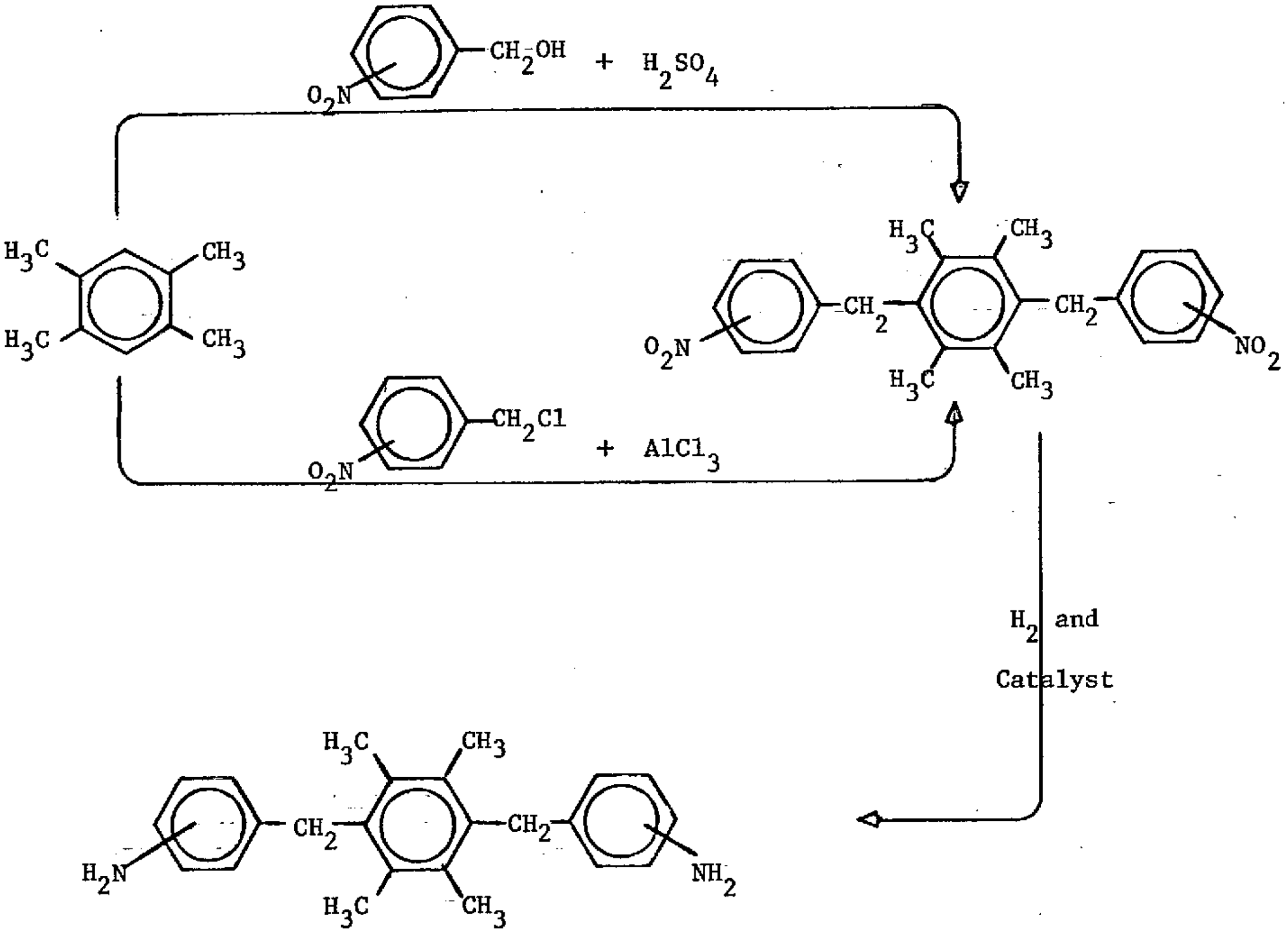


Figure 7. DTA curve for 2,4,6-Tris(p-Nitrobenzyl)-1,3,5-Trimethylbenzene.

processable polyamides and polyimides and which could also serve as cross-linking agents for polyepoxides and polyurethanes, the synthesis of a series of aminobenzyl-substituted alkyl benzenes was undertaken. The general synthetic scheme followed is shown as Figure 8. The benzyl alcohol or benzyl chloride could be either ortho-, meta-, or para-, and the tetramethyl benzene could be either the 1,2,4,5- (durene), the 1,2,3,5- (isodurene), or the 1,2,3,4-isomer. The 1,4-bis(m-nitrobenzyl)-2,3,5,6-tetramethylbenzene compound has been synthesized and partially characterized. The nmr and ir spectra and the DTA curve are shown as Figures 9, 10, and 11. The p-nitrobenzyl analog has been synthesized, but the work-up of the product is incomplete. As the investigation continues, the described dinitrocompound will be reduced to the diamine and evaluated in polymerization studies. Additional dinitro compounds as implied in Figure 8 will be synthesized.

C. Diamine Monomers with Cross-linking Potential

The activity on this phase of the project has been focused on the synthesis of the three compounds 2,5,3'-triaminobenzophenone, 2,2',5,5'-tetraaminobenzophenone, and 2,2',4,4'-tetraaminobenzophenone. The synthetic schemes being explored are summarized in Figures 12 and 13. The syntheses are in various stages and none have been completed. Those compounds which have been synthesized are described in the Experimental Section of this report.



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

Figure 8. Aromatic amines with Three Benzene Rings.

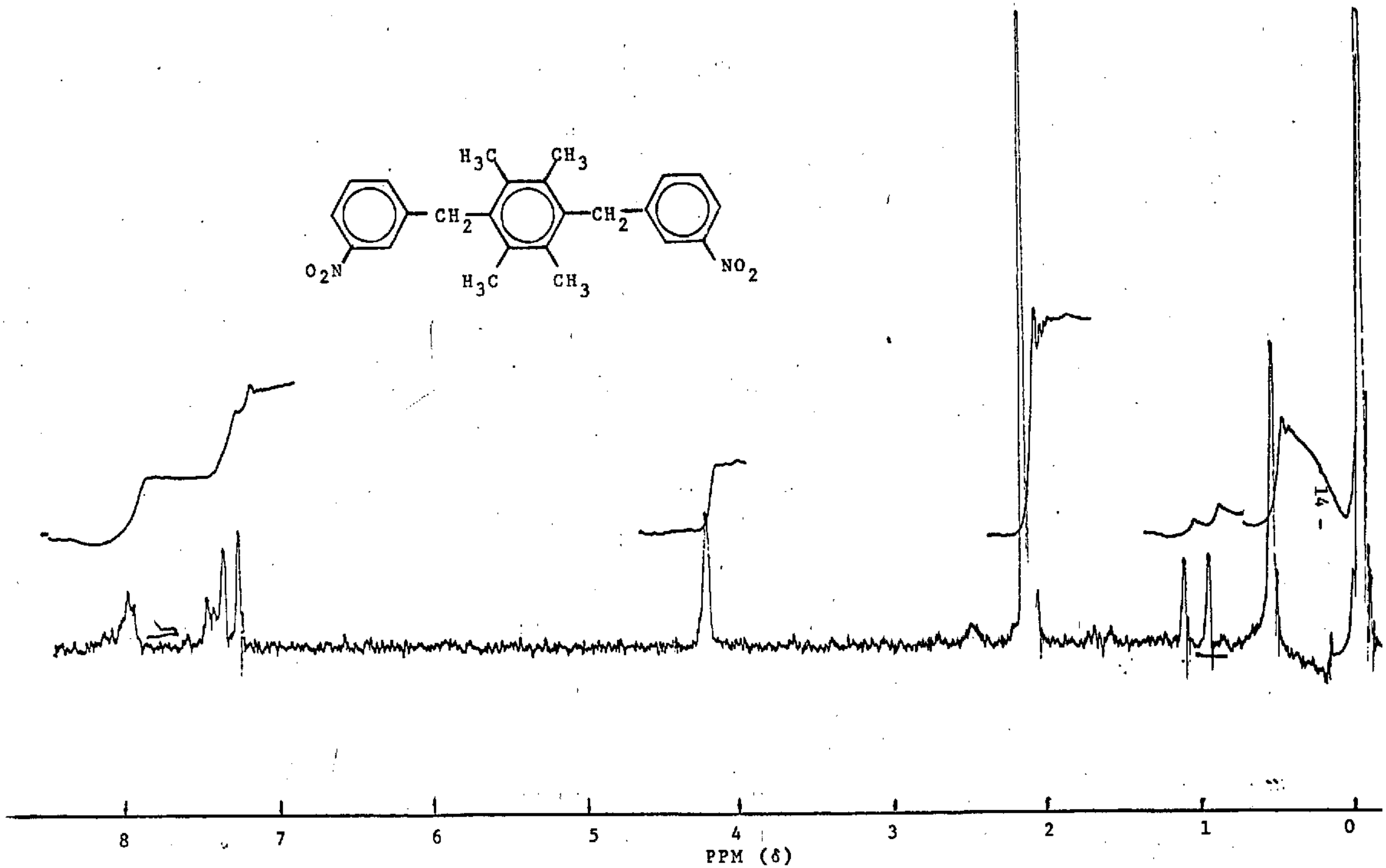


Figure 9. The nmr spectrum of 1,4-bis(*m*-Nitrobenzyl)-2,3,5,6-Tetramethyl benzene in CDCl$_3$.

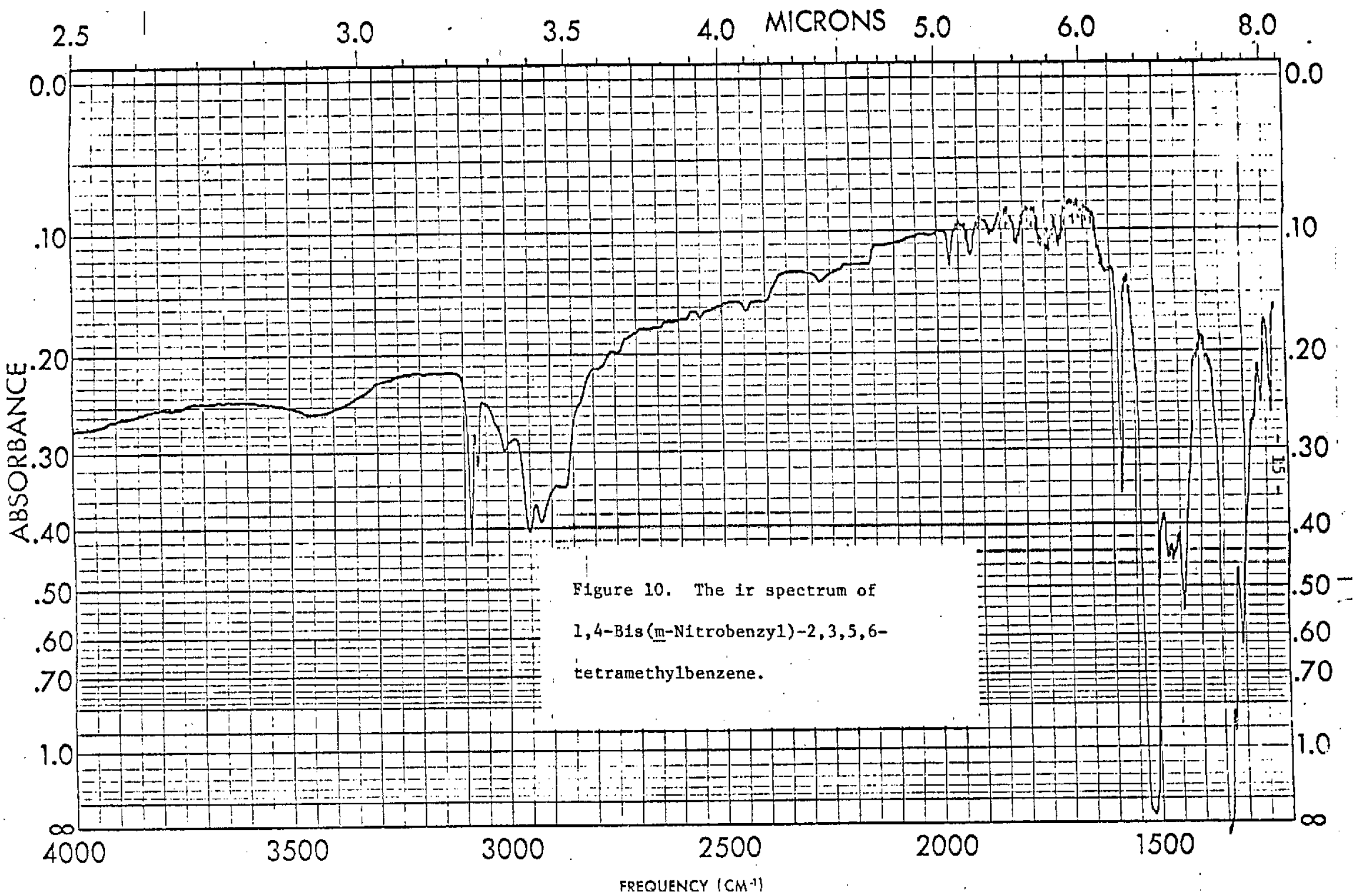


Figure 10. The ir spectrum of 1,4-Bis(m-Nitrobenzyl)-2,3,5,6-tetramethylbenzene.

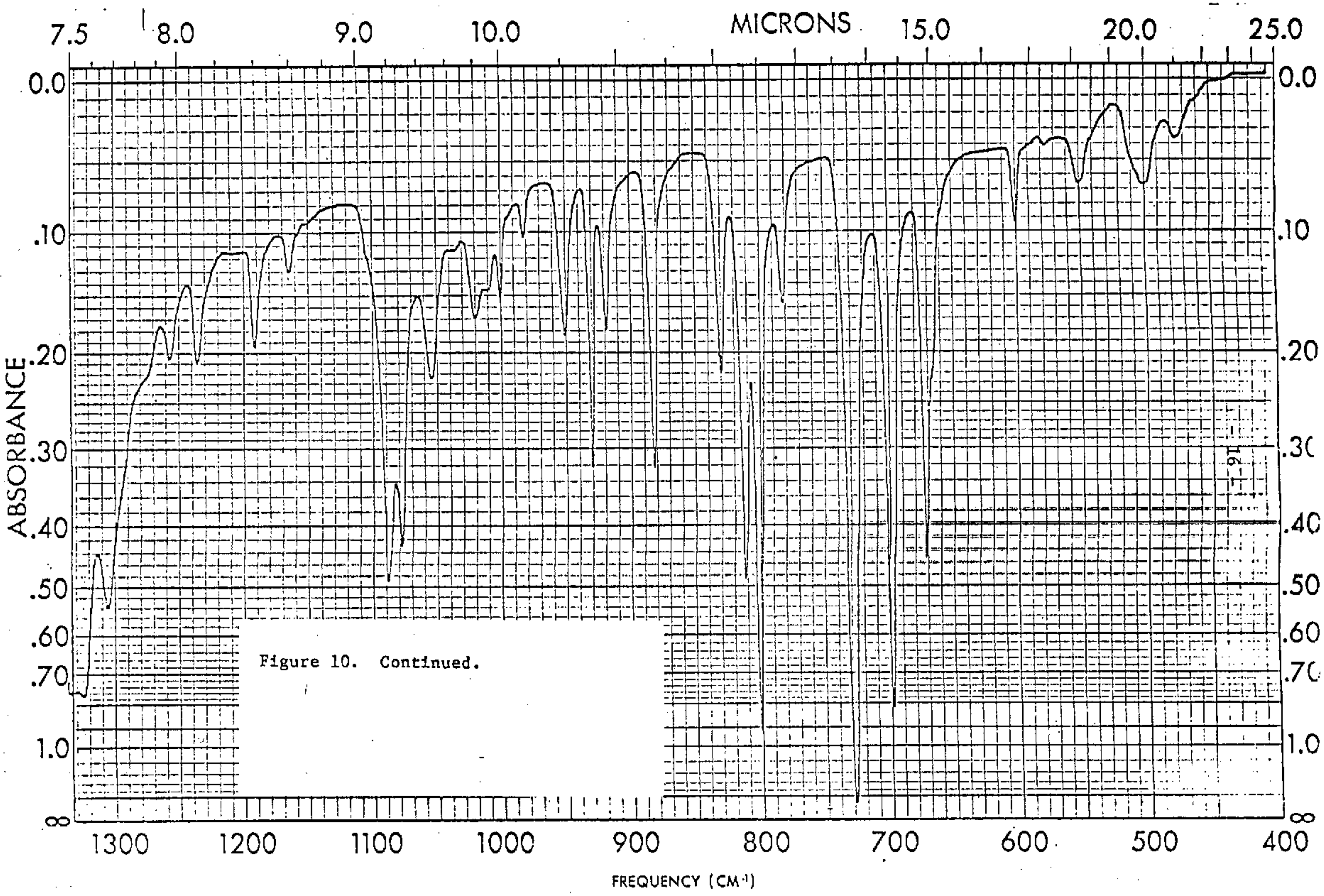


Figure 10. Continued.

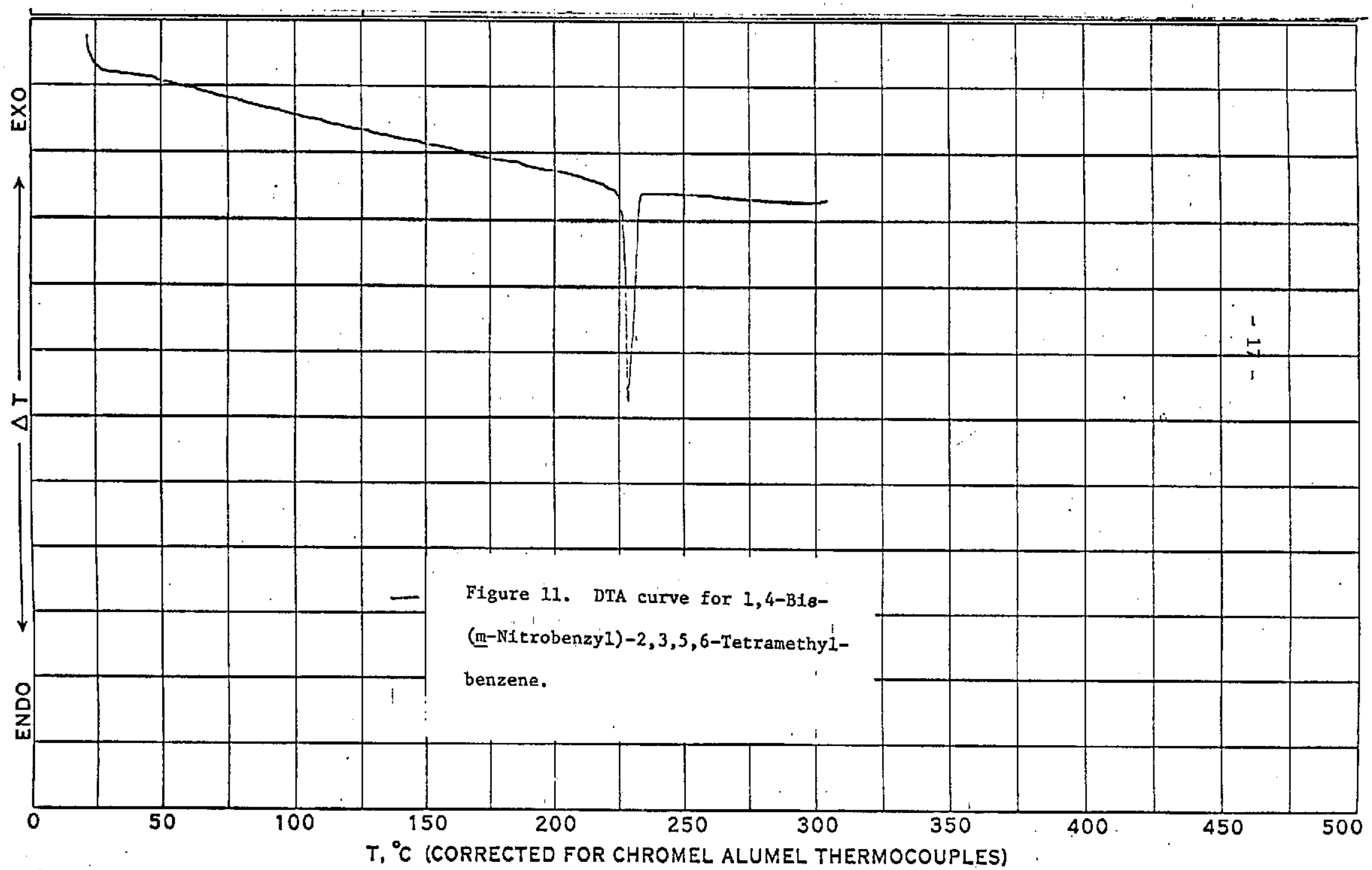


Figure 11. DTA curve for 1,4-Bis-(m-Nitrobenzyl)-2,3,5,6-Tetramethylbenzene.

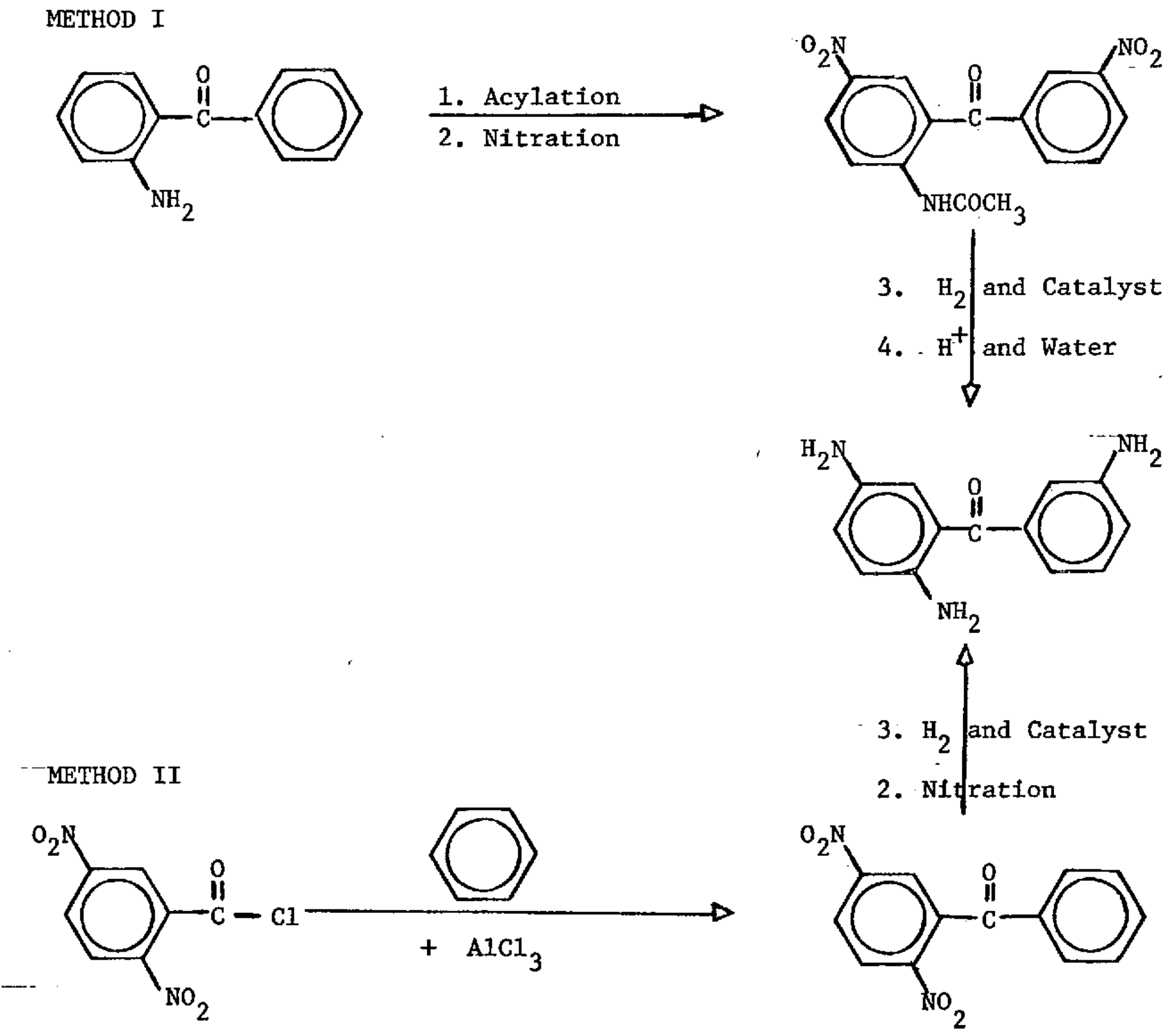


Figure 12. Synthetic scheme for preparing 2,5,3'-Triaminobenzophenone.

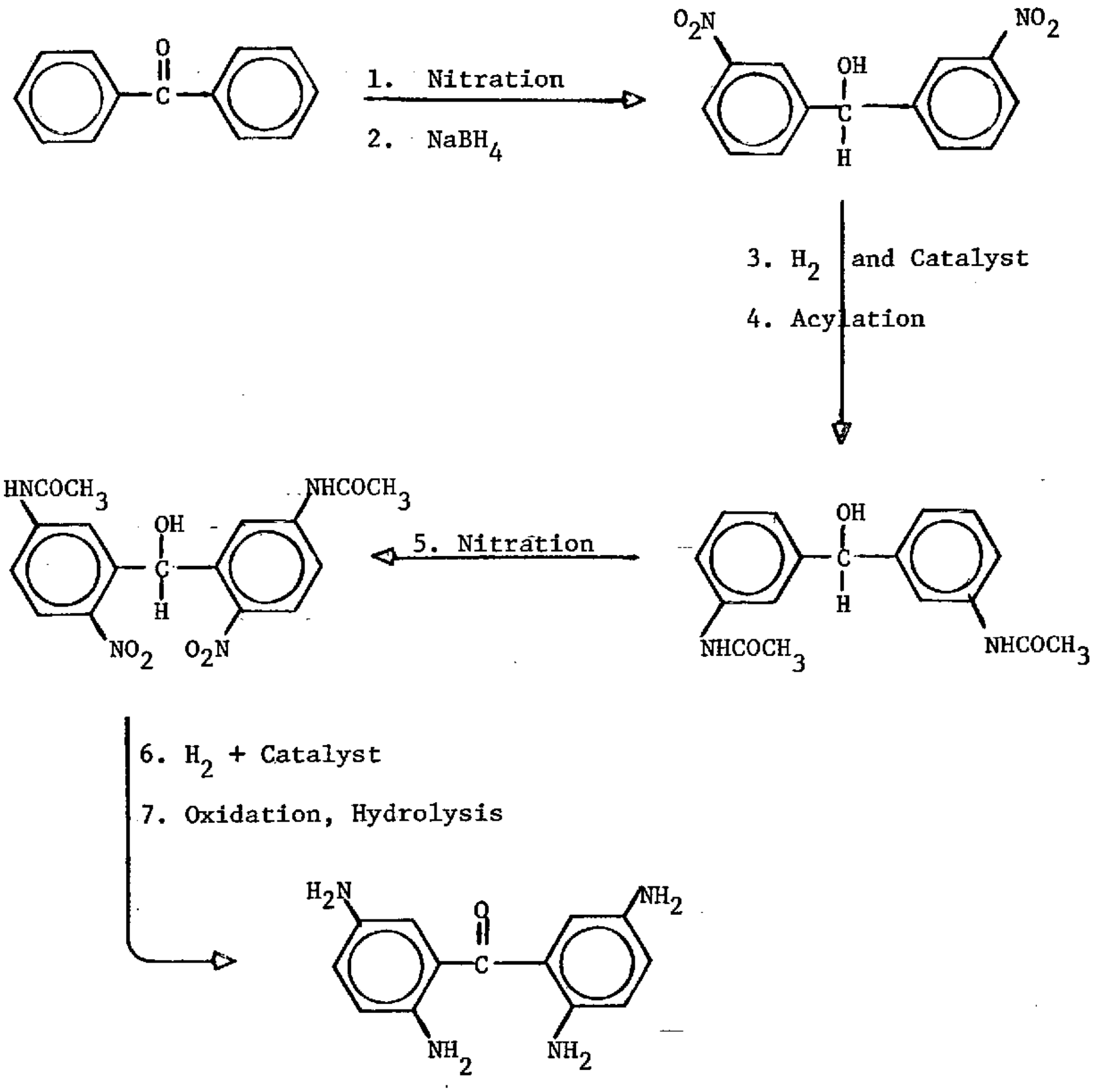


Figure 13. Synthetic scheme for preparing 2,2',5,5'-Tetraaminobenzophenone.

III. Experimental

A. *2,4,6-Tris(m-nitrobenzyl)-1,3,5-trimethylbenzene.* A solution was prepared by dissolving 17.16 g (0.1 mole) of α-chloro-m-nitrotoluene in 25 ml of carbon disulfide. This stirred solution was chilled to less than 10 °C and 14.67 g (0.11 mole) of anhydrous aluminum chloride was added at a rate such that the temperature remained below 10 °C. The mixture was allowed to warm to room temperature and a solution of 3.97 g (0.033 mole) of 1,3,5-trimethylbenzene in 4.0 ml of carbon disulfide was added dropwise. The reaction mixture was then warmed gently and the temperature was held between 30 and 35 °C until the evolution of hydrogen chloride had virtually ceased. The solution was then heated and refluxed at 45 °C for one hour. The reaction product was poured onto a mixture of crushed ice and hydrochloric acid. The brown residue present was extracted into benzene, and the benzene was washed with water, dilute base, water, dilute acid, and water. The benzene solution was dried over sodium sulfate and then decanted into a rotovapor where the benzene solvent was removed *in vacuo*. The brown solid was recrystallized from acetone to yield 4.7 g of off-white crystals which melt at 181 °C. The nmr spectrum in particular supports the assigned structure. Carbon-hydrogen analyses are being obtained.

B. *2,4,6-Tris(p-nitrobenzyl)-1,3,5-trimethylbenzene.* Essentially the same procedure as described above for the α-chloro-m-nitrotoluene reaction was used to react 17.16 g (0.1 mole) of α-chloro-p-nitrotoluene with 14.67 g (0.11 mole) of aluminum chloride and 3.97 g (0.033 mole) of 1,3,5-trimethylbenzene in carbon disulfide. Acetone and water were used to recrystallize the product and a yield of 6.98 g of white crystals was obtained. These were found to melt at 215 °C. The nmr spectrum supports the assigned structure, and carbon-hydrogen analyses are being obtained.

C. *1,4-Bis(m-nitrobenzyl)-2,3,5,6-tetramethylbenzene.* A stirred solution of 17.16 g (0.1 mole) of α-chloro-m-nitrotoluene in 50 ml of nitrobenzene was chilled in an ice bath and treated with 14.67 g (0.11 mole) of anhydrous aluminum chloride. The solution was warmed to room temperature and treated dropwise with 6.71 g (0.05 mole) of 1,2,4,5-tetramethylbenzene dissolved in 50 ml of nitrobenzene. The reaction proceeded at room temperature and stirring was continued until the evolution of hydrogen chloride appeared to be complete. The reaction mixture was poured onto crushed ice and hydrochloric acid, where the product precipitated. The precipitate was recovered by suction filtration. The nitrobenzene layer was recovered, washed with water, weak base, water, weak acid, and finally with water, and then the nitrobenzene was dried over sodium sulfate. The nitrobenzene solvent was stripped *in vacuo* and the residue was recrystallized from glacial acetic acid. The off-white crystals weighing 5.81 g melted between 228 - 230 °C. The nmr spectrum supports the assigned structure and carbon-hydrogen analyses are being obtained.

D. *2,5-Dinitrobenzoyl Chloride.* 2,5-Dinitrobenzoic acid (9.5 g, 0.046 mole) and thionyl chloride (4 ml, 0.2 mole) were placed in a round-bottom flask and refluxed for eight hours. After reflux, excess thionyl chloride was removed under vacuum. Crude 2,5-dinitrobenzoyl chloride (9.4 g) was isolated. The compound was characterized by ir and nmr spectra.

E. *2,5-Dinitrobenzophenone.* 2,5-Dinitrobenzoyl chloride (9.4 g) and 10 ml of dry benzene were charged into a round-bottom flask fitted with a condenser which was connected to a gas trap. Aluminum chloride (9.5 g) was added in small portions. During the addition of aluminum chloride, the solution was stirred with a magnetic stirrer. The addition of the aluminum chloride was complete in 30 minutes and the resulting solution was heated on a steam bath for fifteen minutes. The reaction mixture was then poured into a 500 ml beaker containing 50 g of crushed ice. The mixture was stirred until all the ice had melted and it was then transferred to a separatory funnel. The mixture was extracted with ether, and the ether was evaporated to yield 10.2 g of crude product. Column chromatography of crude material, 5.0 g., yield 1.2 g (25%) of 2,5-dinitrobenzophenone.

F. *3,3'-Dinitrobenzophenone.*[3] Benzophenone (100 g) was dissolved in fuming sulfuric acid and then nitrated with a mixture of fuming nitric acid (51 ml) and fuming sulfuric acid (140 ml) at 25 - 35 °C. The temperature was raised to 75 - 85 °C for one hour. The mixture was cooled at room temperature and then poured on ice. Pure 3,3'-dinitrobenzophenone was crystallized from acetone and glacial acetic acid mixture to yield 72 g (90% yield) of product.

G. *3,3'-Dinitrobenzhydrol.*[4] 3,3'-Dinitrobenzophenone (13.0 g) was dissolved in 250 ml of tetrahydrofuran in a 1-liter Erlenmeyer flask. In a separate flask sodium borohydride (2.8 g) was dissolved in ethanol. This solution was added slowly to the stirred solution of 3,3'-dinitrobenzophenone. Addition time was 15 minutes. Sodium hydroxide solution, 6N, 15 ml, was then added to the mixture and the solution was heated on a steam bath for 15 - 20 minutes. The reaction mixture was then poured into a 500-ml separatory funnel and extracted with ether. Evaporation of the ether yielded 12.2 g of 3,3'-dinitrobenzhydrol. Ir and nmr spectra confirmed the structure.

H. *2,2'-Dinitro-4,4'-diamino diphenylmethane.*[5] Potassium nitrate (25 g) was added during 45 minutes to a vigorously stirred solution of 4,4'-diamino diphenylmethane (25 g, 0.126 mole) in sulfuric acid (d. 1.84, 250 ml). The temperature was maintained between 0 and 5 °C during the addition and for one hour afterwards. The mixture was poured over 1 Kg of crushed ice, partially neutralized with aqueous ammonia (d. 0.088, 400 ml) and cooled to 15 °C. The precipitate which formed was recovered and crystallized from 2 N sulfuric acid to give 37.13 g of salt which melted with decomposition at 216 °C. The solid was suspended in water and neutralized with sodium bicarbonate. Crude 2,2'-dinitro-4,4'-diamino diphenylmethane was recrystallized from 95 % ethanol (30.5 g). Ir and nmr spectra confirm the structure.

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