

THE SYNTHESIS OF NITRATE SELECTIVE RESINS

by

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B. S., Cheng-Kung University, 1971.

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

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1977

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INTRODUCTION

Human nitrate poisoning was first associated in 1945 with a temporary, but sometimes fatal, blood disorder in infants.¹ Since then, approximately 2,000 cases of this disease, infantile methemoglobinemia, have been reported in North America and Europe and about 7-8 per cent of the infants died.² Nitrates, after ingestion, are reduced to nitrites by bacteria. The nitrites then convert oxyhemoglobin, the oxygen-combined blood pigment, to methemoglobin. Because this altered brownish-colored pigment can no longer transport oxygen, the physiological effect is oxygen deprivation or suffocation.³

In infants that are under the age of three months, the capability of parietal cells to secrete hydrochloric acid (gastric acid) has not completely developed and the lesser acidic (higher pH value of 5-7) environment allows microorganisms such as E. coli to reside in the deodenum and stomach. Under these conditions, the bacteria are able to reduce the nitrate before it is absorbed into circulation.³ In addition, hemoglobin F (fetal hemoglobin, the predominant form at birth), is more susceptible to methemoglobin formation than hemoglobin A, the adult form, and this fact further predisposes very young babies.³ Moreover, the activity of the enzyme (NADH-dependent methemoglobin reductase), which is responsible for the normal reduction of methemoglobin, is decreased.³ This causes

methemoglobin to accumulate. Since the ratio of total fluid intake to body weight of infants is three times that of adults, these physiological and biochemical features of early infancy could explain the increased susceptibility of infants to nitrate poisoning.

Nitrate poisoning is not limited to only humans. The earliest account of the toxic effects of excessive amounts of nitrates naturally occurring in feedlots was given in 1895. Mayo⁴ described three episodes of fatal poisoning in cattle, where they showed tremors, diuresis, cyanosis and collapse. In all cases, the cattle had been feeding on cornstalks, which were shown by chemical analyses to contain extraordinary amounts of potassium nitrate (25% by dry weight).

The sources of nitrates in water are many: industrial and municipal wastes, fertilizer, septic tanks, refuse dumps and animal feedlots including runoff and leaching. As the number and the size of feedlots increase, this source of nitrate becomes increasingly significant. For example, in the State of Kansas in 1939, 33% of dug wells showed concentration of nitrates over 45 ppm, while in 1945 it had increased to 51%.⁵

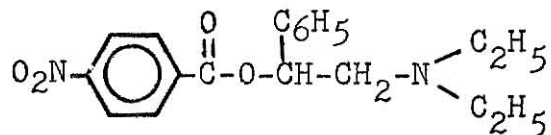
The tolerance level for nitrate in water depends on the individuals. However, the limit has been set at 45 ppm for infants and 200 ppm for adults.⁶ As for cattle, it seems to be in the range of 330 to 660 ppm,⁷ which is exceeded

in many partially dried creeks and streams. City water usually contains 15-22 ppm,⁸ but rural well water can be in excess of 440 ppm.

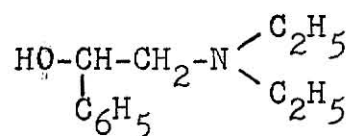
Several ion-exchange resins have been used to remove nitrate ion from water but there are serious disadvantages in using ordinary ion-exchange resins for this purpose. First, an ion-exchange resin, in addition to removing nitrate ion, will also remove other anions like chloride, carbonate, sulfate, phosphate, etc., from water. Since these ions are essential for the water to be usable for consumption, they have to be replenished. Secondly, valuable resin sites are wasted by binding anions other than nitrates.

In 1973, Meloan and Gran⁸ reported the preparation of a resin in bead form to selectively remove nitrate ion from water. The original idea was to take reagents that are specific for nitrate and attach them to a resin bead. These authors chose α -phenyl- β -diethylaminoethyl-p-nitrobenzoate (1) for their investigation, with appropriate modification in the structure (compounds 2 and 3), to allow attachment to the resin but always retaining the amine function which was the suspected essential moiety. The resins that were used to support reagents 2 and 3 were commercial Bio-Rex 70 (a cross-linked polymethacrylic acid resin) and Bio-Gel P-4 (a cross-linked polyacrylamide resin). The nitrate selectivity of these resins was

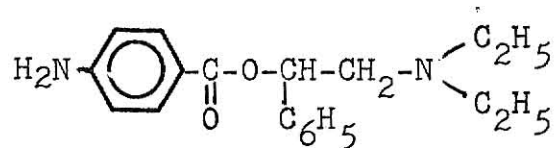
realized but the capacity was found to be about 0.1%, which was too low to be of commercial value.



1



2

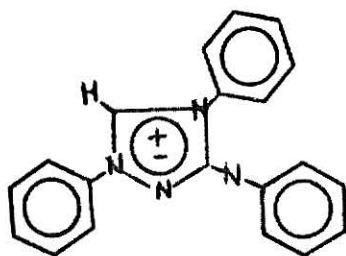


3

There are several organic bases in addition to 1 that can precipitate NO_3^- . Among these bases are a few which do not remove from water other vital anions such as CO_3^{-2} , HCO_3^- , SO_4^{-2} , PO_4^{-3} and OH^- ; these are listed in Table 1.⁹

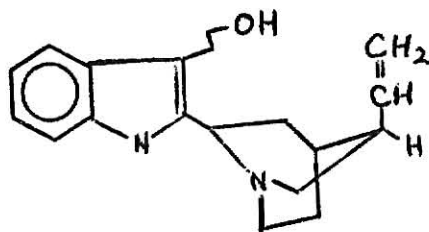
Of the compounds depicted in Table 1, nitron (4) was chosen as the reagent in this study. Nitron is also known to precipitate ClO_3^- , NO_2^- , ReO_4^- , SCN^- , I^- , BO_3^- and Br^- . Of these, only NO_3^- and NO_2^- are normally present in water, and the others are present at concentrations so low that no interference to the nitrate precipitate should be encountered.

TABLE 1
Structures of Nitrate Selective Compounds



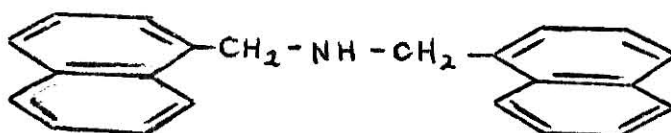
Nitron

4



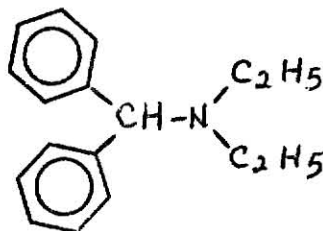
Cinchonamine

5



1,1'-Dinaphthyl-dimethylamine

6



N-Diphenylmethyl-diethylamine

7

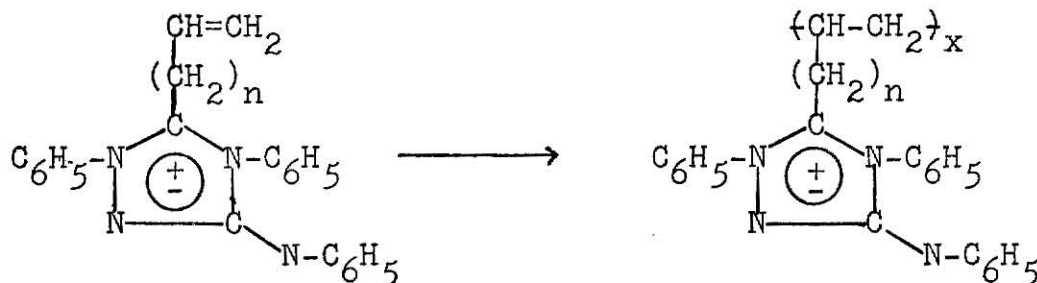
Polymer-supported reagents have come to be recognized as extremely useful in organic chemistry and there are several review articles that have been published on this subject.^{10,11} When a reagent is appended on a polymer backbone, the solubility of the reagent is decreased which would eliminate any color and taste problem for the present application. Perhaps the most important feature of a reagent supported on a polymer backbone is efficient recovery. This is a particularly important in the case of nitron, since nitron is reported to work best under slightly acidic conditions and the protonated form of nitron is sufficiently soluble to color water.¹² In addition, nitron is expensive to synthesize and hence should be recoverable.

There are two ways by which nitron could be appended on a polymer backbone. One can either introduce a 2-3 carbon "leash" on one end of the nitron molecule and affect polymerization or it is possible to attach nitron to a commercially available polymer through a chemical reaction. Both of these approaches were utilized in this work.

The general method for introduction of a 2-3 carbon leash in the nitron molecule had been reported in the literature.¹³ One of the starting materials for the synthesis of nitron is the suitable acid chloride, $R-CO-Cl$. By choosing a polymerizable function as R and affecting the polymerization, one can append nitron on a polymer backbone. In this work, attempts were made to accomplish this by two types of

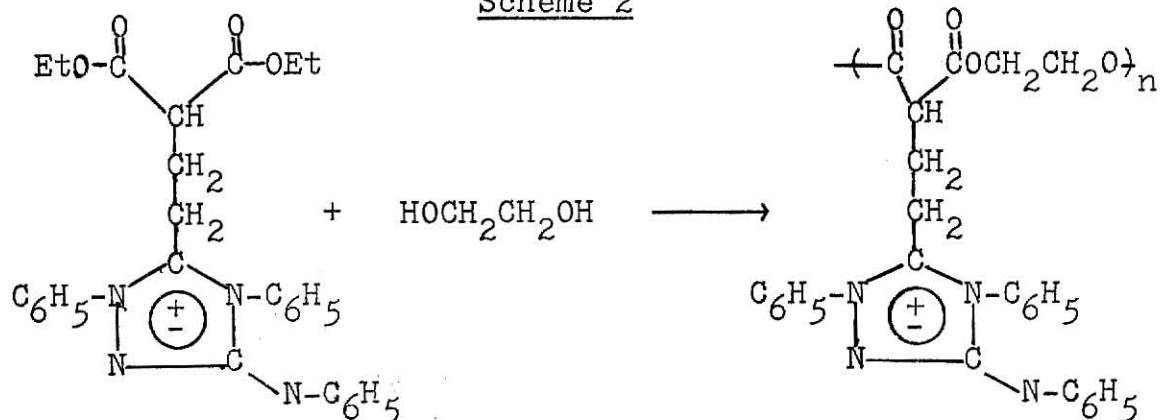
polymerization, vinylic and condensation. For vinylic polymerization the R group chosen was $(\text{CH}_2)_n\text{-CH=CH}_2$, where $n = 0, 1, 2$ or 3 (Scheme 1).

Scheme 1



For condensation polymerization R was chosen as $-\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$; the resulting diester was then reacted with ethylene glycol (Scheme 2).

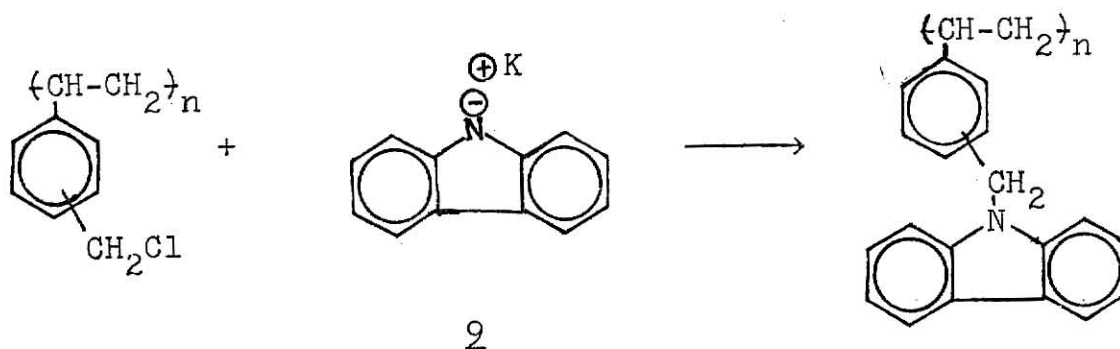
Scheme 2



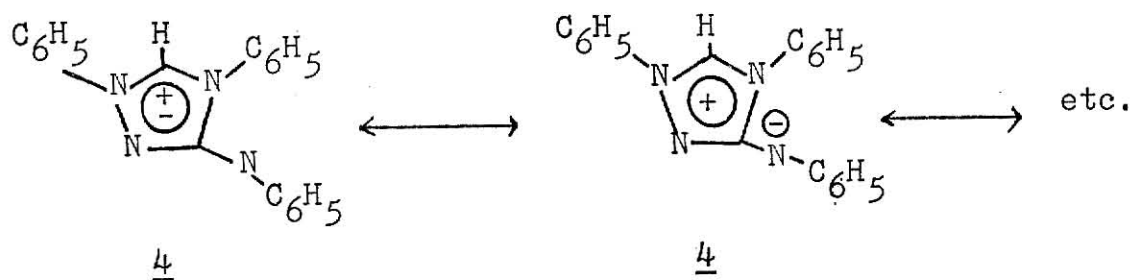
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For the second approach, i.e., attachment of nitron to commercially available polymer backbones, the polymer chosen should be insoluble in water and have very little or no crosslinking. Too much crosslinking will presumably constrain the reagent moiety excessively, thereby destroying the alignment believed necessary to achieve effective complexation.

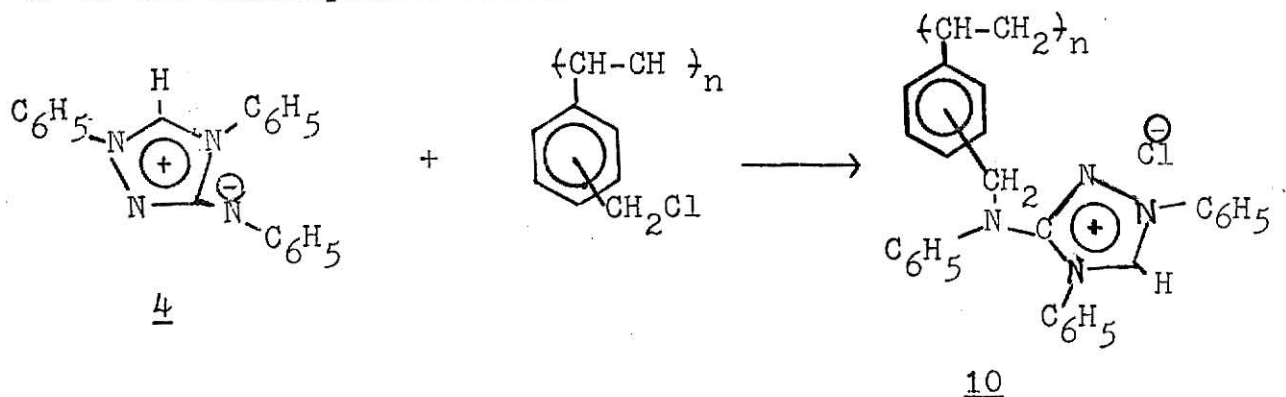
Gibson and Bailey¹⁴ have reported the reaction of potassium carbazole (9) with polyvinylbenzyl chloride. It was postulated that nitron should react in the same manner because



of the similarity in structure, i.e., the exocyclic nitrogen should behave in the capacity of a nucleophile.¹⁵ It has been



reported in the literature¹³ that nitron can be easily N-alkylated, although it was not clearly established which nitrogen was alkylated. This meant that the nitron molecule could be attached to polyvinylbenzyl chloride by a simple displacement of chloride as shown below with the exocyclic nitrogen presumed to be the nucleophilic center:

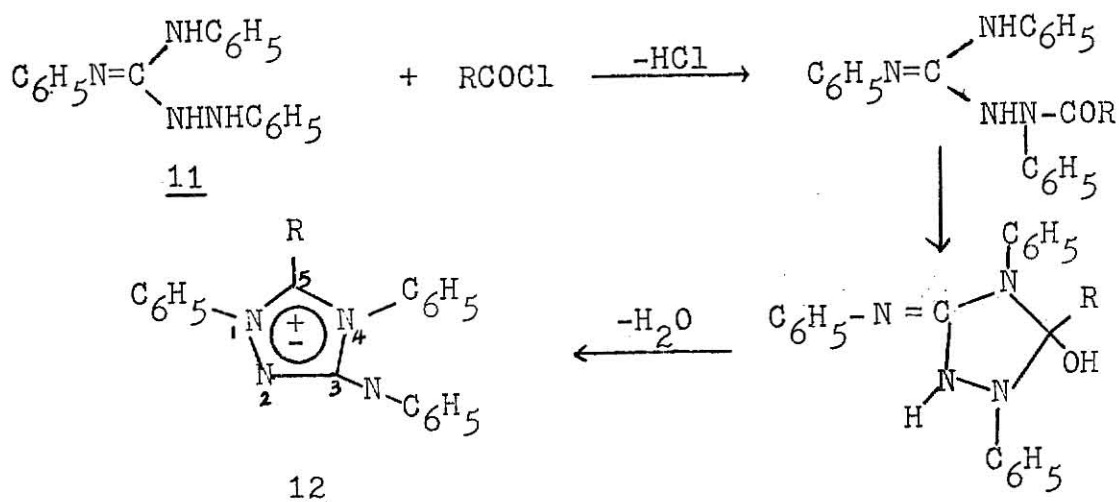


The chloride ion held by the resin (10) should be displaced by nitrate ion thereby resulting in the removal of nitrate from water.

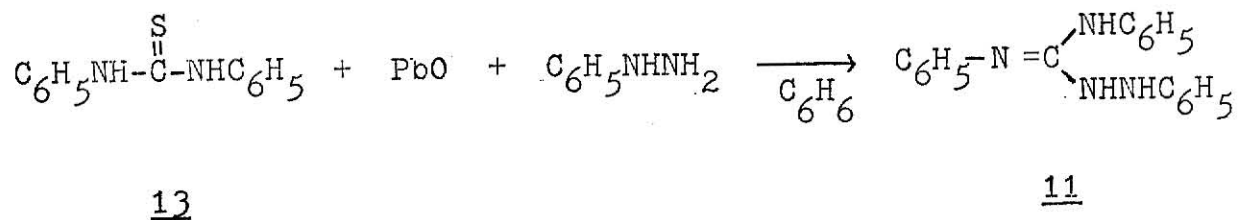
RESULTS AND DISCUSSION

Attempted Synthesis of Olefinic-Substituted Nitrons

The substituted nitrons were prepared according to Scheme 3 using a slightly modified version of the published¹³ procedure.

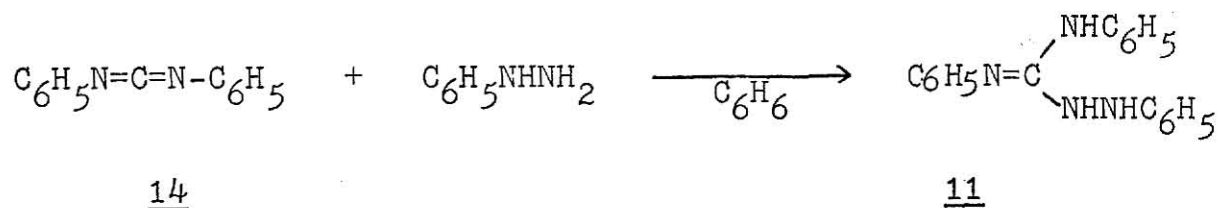
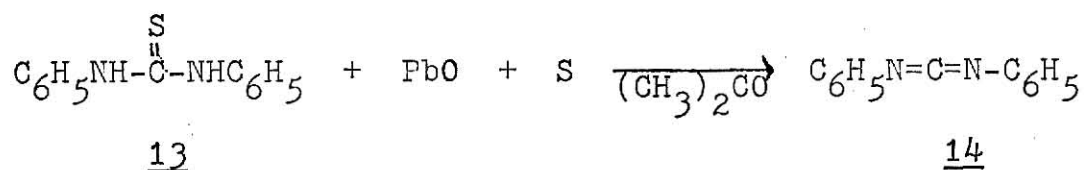
Scheme 3

In an attempt to prepare 1,3-diphenyl-2-aminophenyl-guanidine, 11, according to the method of Marckwald,¹⁶ it was found by infrared analysis that most of the product was 1,4-diphenyl-3-thiosemicarbazide. Consequently, modification had to be made in the procedure to obtain compound 11 in a pure form. Marckwald's method is depicted by Scheme 4.

Scheme 4

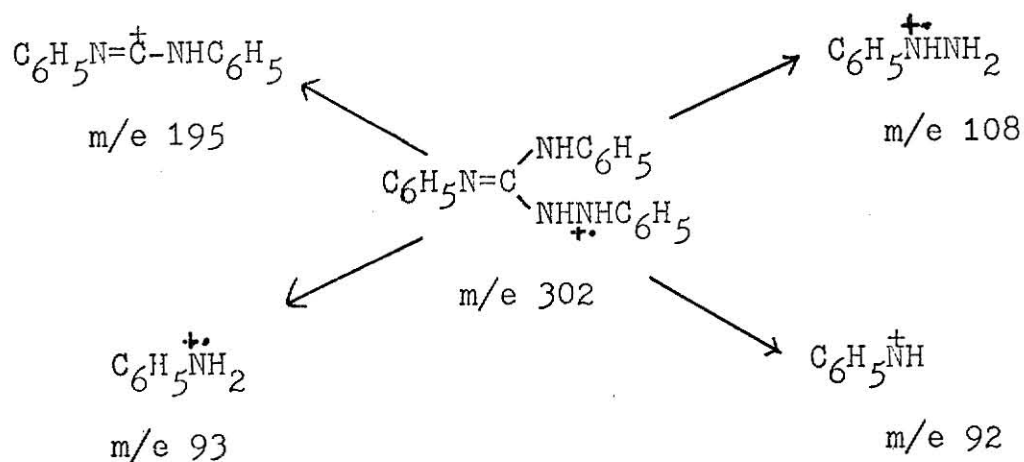
In our work, Scheme 5 was employed. Diphenylcarbodiimide, 14, was synthesized starting from 1,3-diphenylthiourea, 13, according to the procedure of Zetzsche and Nerger.¹⁷

Scheme 5



Diphenylcarbodiimide, 14, was converted to 11 by reacting with phenylhydrazine. The infrared spectrum of 11 was superimposable with the standard spectrum of 1,2,3-triphenylguanidine.¹⁸ The mass spectrum of 11 confirmed the molecular ion at m/e 302 and also the fragmentation pattern fit (Scheme 6).

Scheme 6



Ring closure of triphenylaminoguanidine 11 was attempted using appropriate acid chlorides. Seven acid chlorides were used with the results listed in Table 2.

The plan of approach was first to synthesize nitrons substituted at position 5 with polymerizable vinylic groups ($R = -(CH_2)_n-CH=CH_2$ in Scheme 3). If the vinylic group is $-CH=CH_2$ ($n = 0$) then polymerization would place the nitron moieties close to each other in the polymer; this might give the complex of polymeric nitron and NO_3^- more crystallinity. On the other hand, when $n = 1$, the nitron group will have more flexibility and consequently might minimize steric hindrance during complexation with NO_3^- .

First the original method of Bush¹³ was tried using sealed tube reactions to produce the desired vinylnitrons, but these attempts proved unsuccessful. Dry benzene was then utilized as a reaction solvent in subsequent experiments. Several attempts to optimize the reaction conditions and the reactant concentrations all proved to be less successful than desired. However, in several cases, a material did result, varying in nature from a semisolid to an extremely brittle mass. The nmr spectra of these solids indicated the absence of olefinic protons. Apparently the guanidine was reacting, but after the initial amide bond formed, ring closure was not completed by reacting with the second substituted amine functional group. Possibly, the second substituted amine functional group could have reacted with the olefinic group

TABLE 2

Results of Attempts to Effect Ring Closure between 1,3-Diphenyl-2-aminophenylguanidine and RCOCl

R		Reaction Products	M.P.	Yield
-CH=CH ₂	(<u>15</u>)	Brownish solid		
-CH ₂ CH=CH ₂	(<u>16</u>)	Brownish solid		
-CH ₂ CHBrCH ₃	(<u>17</u>)	Dark solid		
-CH ₂ CH ₂ Br	(<u>18</u>)	Brownish solid		
-CH ₂ CH ₂ CH ₂ Cl	(<u>19</u>)	Substituted-nitron (<u>22</u>)	140-141	90%
-(CH ₂) ₃ CH ₂ Br	(<u>20</u>)	Substituted-nitron (<u>23</u>)	183-185	92%
-CH ₂ CH ₂ CH(CO ₂ Et) ₂	(<u>21</u>)	Substituted-nitron (<u>24</u>)	177-180	88%

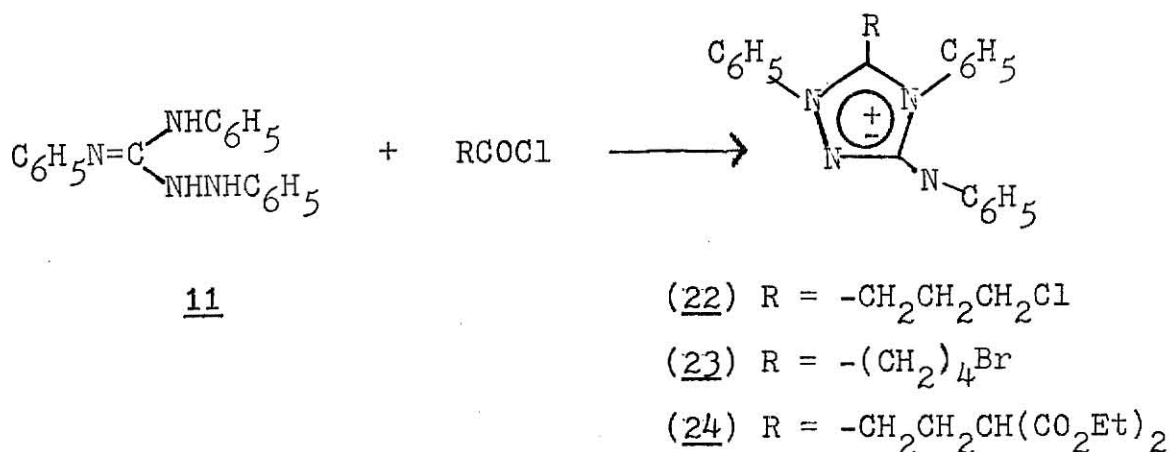
before ring closure. However, this explanation is only speculative at this stage.

The failure to form the desired substituted nitrons by the reaction of 11 and acid chlorides 15 and 16 prompted the preparation of substituted nitrons, 1,4-diphenyl-3-phenylimino-5-(3-chloropropyl)-1,2,4-triazoline (22) and 1,4-diphenyl-3-phenylimino-5-(4-bromobutyl)-1,2,4-triazoline (23), the substituents of which could be later modified to vinylic groups. The absence of C=O stretching in the infrared spectrum of 22 indicated that the second amine group had actually attacked the initially formed amide group, i.e., the ring closure had been accomplished. Also, absence of O-H stretching indicated the complete conversion to nitron, as depicted in Scheme 3. The fact that the infrared spectrum of 22 (page 49) was nearly superimposable with the standard spectrum of nitron¹⁹ in the range 6-7 μ , further confirmed the formation of the substituted nitron. The nmr spectrum (page 61) showed that the peaks corresponding to the alkyl protons were shifted slightly up-field as anticipated due to the five-membered ring being formed in place of the carbonyl group. The absence of extensive fine structure in the aromatic region of the nmr spectrum of 22 indicated much similarity in the phenyl groups in 22 compared to the unsubstituted nitron (page 68). This is presumably because substitution of a bulky group at position 5 causes the benzene rings at positions 1 and 4 to twist out of the plane of the 5-member ring. Therefore, the efficiency of

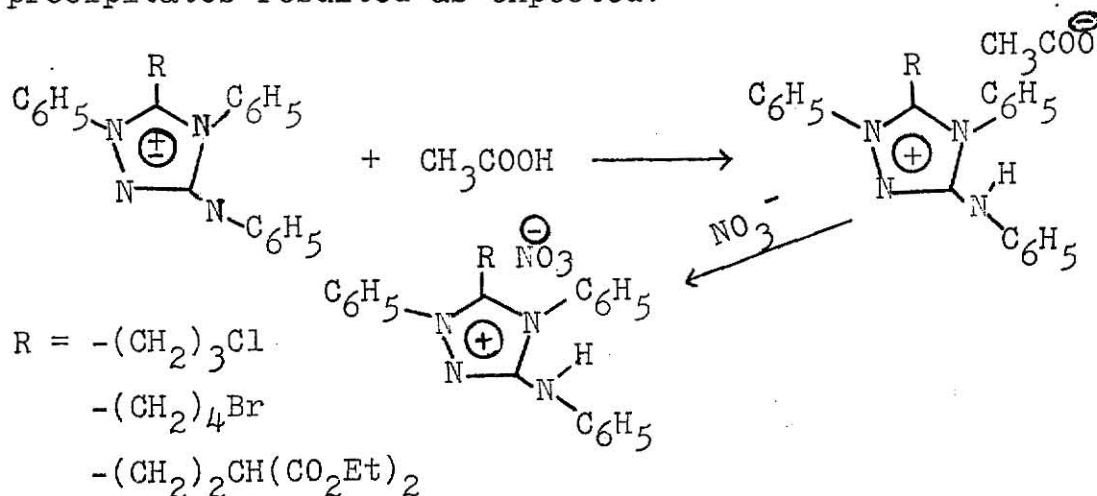
delocalization of charge into the 1- and 4- benzene rings is decreased, and consequently, the protons of these rings are more nearly equivalent as compared to those in the unsubstituted nitron. The mass spectrum of 22 (page 70) showed a weak parent ion m/e 388. The ratio of m/e 390 to m/e 388 was about 1/3 which confirmed the presence of chloride. The more intense peak at m/e 353 is due to the loss of chloride. The remaining peaks resulting from the fragmentation of nitron ring were quite similar to the pattern in nitron itself (page 74), further substantiating the structure.

The infrared and nmr spectra of 23 and 22 had similar characteristics with respect to ring closure, i.e., loss of C=O character and loss of water in the last step. The mass spectrum of 23 showed an intense peak at m/e 367 due to the loss of bromine and no parent ion at all. Also, the remaining peaks resulting from the fragmentation of nitron ring were as anticipated. Thus nitron 23 was synthesized as shown in Scheme 7.

Scheme 7



The identities of 22 and 23 were further substantiated by reacting them with nitrate ion. This was done by dissolving the compounds in dilute acetic acid and then adding aqueous potassium nitrate to the resulting solutions. In both cases precipitates resulted as expected:

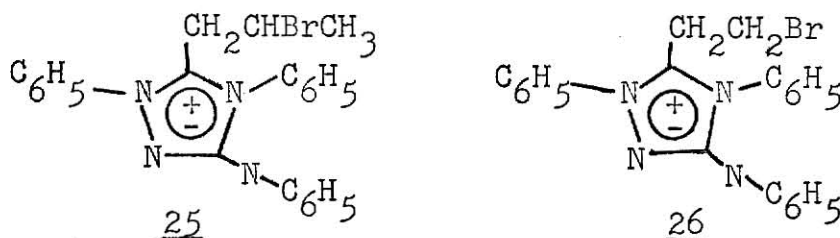


The modification of the substituents in 22 and 23 to vinylic groups was attempted by two routes: (1) dehydrohalogenation of 22 and 23 in the presence of 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) and (2) conversion of 22 and 23 into their corresponding phosphonium salts, which would then be reacted with formaldehyde (Wittig condensation) to generate the double bond.

Several attempts were made to dehydrohalogenate 22 and 23 in the presence of DBN as the base under various reported conditions.²⁰⁻²³ In all cases the nmr spectra of the products indicated the absence of olefinic protons. This failure could have been due to the fact that the halogen is primary in 22 and 23 and also the absence of any other driving force, such

as conjugation with an aryl group.

Consequently, attempts were made to react 11 with $\text{CH}_3\text{CHBrCH}_2\text{COCl}$ (17) and $\text{BrCH}_2\text{CH}_2\text{COCl}$ (18) to form the substituted nitrons 25 and 26. These attempts also proved to be unsuccessful as deduced by nmr spectroscopy.



When 22 and 23 were reacted with triphenylphosphine,^{24, 25} it was found by nmr spectroscopy that the corresponding Wittig reagents were not generated, only the starting material was detected.

In summary, attempts to introduce a vinylic functional group into the nitron molecule, either by affecting ring closure of 11 and RCOCl ($\text{R} = -(\text{CH}_2)_n\text{CH}=\text{CH}_2$) or by modifying 22 and 23, were unsuccessful and, consequently, further efforts involved condensation polymerization instead of vinylic polymerization.

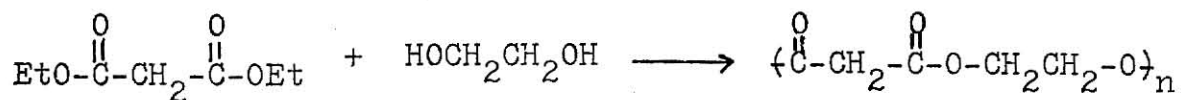
Synthesis of Diester Substituted Nitron and Subsequent Polymerization

The approach was to introduce a diester function in the nitron molecule and subsequently effect condensation polymerization with ethylene glycol as explained earlier in Scheme 2 (page 7).

The acid chloride γ,γ -dicarboethoxybutyryl chloride (21) was synthesized in good yield, and reacted with 11 yielding the substituted nitron 1,4-diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) in 88% (Scheme 7). The structure of 24 was confirmed by nmr (page 63), infrared (page 51) and mass spectral (page 72) analyses in comparison to the substituted nitrons 22 and 23. The mass spectrum was quite complicated; nevertheless, the presence of peaks at $m/e = 160, 115, 173$ and 195 , corresponding to the fragments $\text{HO}^{\dagger}=\text{C}(\text{OEt})\dot{\text{C}}\text{HCO}_2\text{Et}$, $\text{HO}^{\dagger}=\text{C}(\text{OEt})\text{CH}=\text{C}=\text{O}$, $\text{HO}^{\dagger}=\text{C}(\text{OEt})\text{C}(\text{CO}_2\text{Et})=\text{CH}_2$ and $\text{C}_6\text{H}_5-\text{N}=\text{C}^{\dagger}-\text{NH}-\text{C}_6\text{H}_5$ respectively, was sufficient evidence. The nitron character of 24 was finally confirmed by testing its capacity to form a precipitate with nitrate ion as mentioned before.

The procedure first employed for the condensation polymerization of 24 with ethylene glycol was that reported for the condensation of ethylmalonate and ethylene glycol²⁶ (Scheme 8). It was found by ir spectroscopy that the resulting

Scheme 8

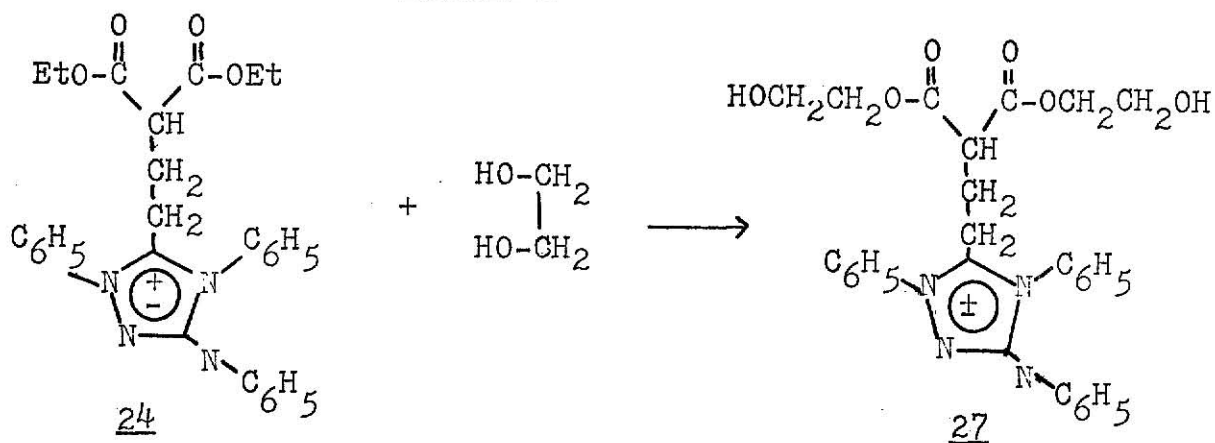


solid had lost C=O character and nitron character. Perhaps this was due to the decomposition of the nitron ring and/or the decarboxylation of the diester group at the high temperature (220°) employed.

Because of the failure to prepare the desired polymer from the above procedure, an attempt was made to use a solvent.

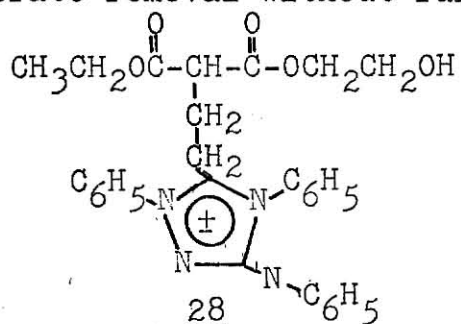
Benzene was chosen as the solvent (usually 15 ml/g of 24) and different mole ratios of reactants (24 and ethylene glycol) were employed. The nmr spectrum of the product (page 64) showed two broad peaks in the range of δ 3.40-4.36 when excess ethylene glycol was employed in the reaction. It was believed that the peak at δ 3.80-4.36 was due to the proton between RCO_2^- and $-\text{CH}_2\text{OH}$ groups and the peak at δ 3.40-3.80 was corresponding to the proton between the $\text{RCO}_2\text{CH}_2^-$ and $-\text{OH}$ groups. It was believed that condensation polymerization did not occur but instead, the ethoxy group in compound 24 had been replaced by the glycol, i.e., Scheme 9.

Scheme 9



Consequently, a 1:1 mole ratio of reactants (24 and glycol) was employed to obtain the polymer. The nmr spectrum of the product showed three broad peaks at the range of δ 3.4-4.8. It was believed that the peak at δ 4.3-4.8 was due to the protons in the polymer chain of polymer 8, i.e., $-\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2^-$, and the peaks at δ 3.4-3.8 and 3.8-4.3 were believed to have

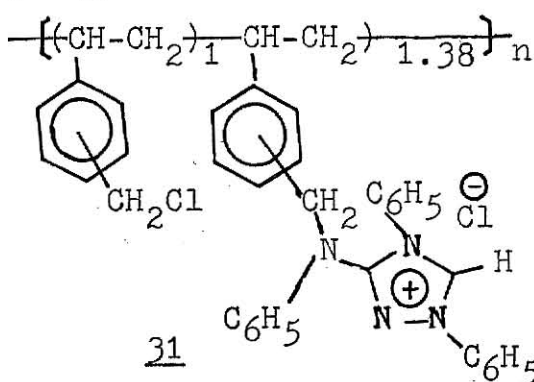
resulted from the mixture of 24, 27 and 28. Attempts to separate the mixture by chromatography were unsuccessful and it was tested for nitrate removal without further purification.



Attachment of Nitron to Polyvinylbenzyl Chloride.

The structure of nitron has been established as shown on page 8. It was postulated that the nitron molecule could be attached to polyvinylbenzyl chloride by a simple displacement of chloride with the exocyclic nitrogen. Before attempting to attach nitron to commercially available polyvinylbenzyl chloride, it was desired to make sure such a reaction would indeed take place. The reaction of nitron with methyl iodide and benzyl chloride was carried out as reported in the literature.¹³ The nmr spectrum of nitron-methyl iodide (page 66) showed a signal at δ 3.56 due to the methyl group. The peak corresponding to aromatic protons at δ 6.95-8.33 and the peak corresponding to 5-CH at δ 12.24 are worthy of comment because nitron itself has peaks corresponding to aromatic protons at δ 6.5-7.8 and 5-CH at δ 8.7. This deshielding can be explained as follows. The nitron group has a nucleophilic center at the exocyclic nitrogen as mentioned earlier on page 8. It was believed that the exocyclic nitrogen should attack methyl iodide

of nitron-benzylchloride. Elemental analysis of the purified polymer revealed that not all of the chloro groups of polyvinylbenzyl chloride had reacted. In order to match the experimental and the calculated analytical value, one has to have only 58% of nitron appended on the polyvinylbenzyl chloride, i.e., the product 31 should be $(1 \text{ C}_9\text{H}_9\text{Cl} \cdot 1.38 \text{ C}_{29}\text{H}_{25}\text{N}_4\text{Cl})_n$ (See Experimental section, page 43).



The formation of 31 can be explained as follows. The commercial polyvinylbenzyl chloride has chloromethyl groups at both ortho and para positions on the benzene ring in a 60:40 ratio.²⁷ The attachment of the bulky nitron molecule (molecular weight 312) to displace the chloride ion from the ortho chloromethyl group may be sterically hindered; consequently, the amount of nitron attached to the polymer is lowered to 58%.

Determination of Nitrate Capacity of Polymer-Supported Nitrons.

A. Capacity of Resulting Product of Condensation Polymerization of 24 and Ethylene Glycol.

A half gram sample of the product resulting from the condensation polymerization of 24 and ethylene glycol (presumably a mixture of 8, 24, 27, and 28) was packed into a column (as shown on page 34) and aqueous potassium nitrate

solution (10^{-3} M) was passed through the column. Two-ml aliquots were collected and tested for nitrate using a nitrate selective electrode. The nitrate ion-selective electrode was standardized by diluting a 0.1 M KNO_3 stock solution. The electrode response was linear from 10^{-2} M to 10^{-4} M nitrate (Figure 1). The concentration of nitrate in the effluent was determined from Figure 1 with the result depicted in Figure 2. From Figure 2 one can calculate the capacity of this resin to remove nitrate by the following equation.

$$A = (M_1 - M_2) \times L \quad (1)$$

Where: A. (mole) = mole of nitrate being absorbed by resin.

M_1 ($\frac{\text{mole}}{\text{l}}$) = concentration of NO_3^- solution being employed.

M_2 ($\frac{\text{mole}}{\text{l}}$) = concentration of NO_3^- of collected effluent.

L (l) = volume of collected effluent.

It was shown in Figure 2 that the concentration of NO_3^- of the first 6 ml effluent was 5×10^{-5} M, i.e., $M_2 = 5 \times 10^{-5}$ in equation 1. Therefore, the moles of nitrate being absorbed by this resin was calculated as follows.

$$\begin{aligned} A &= (1 \times 10^{-3} - 5 \times 10^{-5}) \times 6 \times 10^{-3} \\ &= 5.7 \times 10^{-6} \text{ mole.} \end{aligned}$$

The concentration of NO_3^- of each 2 ml effluent could be calculated in the same fasion and the overall capacity of this resin to remove nitrate from water was calculated to be 1.04×10^{-5} mole. Assuming the condensation polymeri-

FIGURE 1

Nitrate Standard Curve

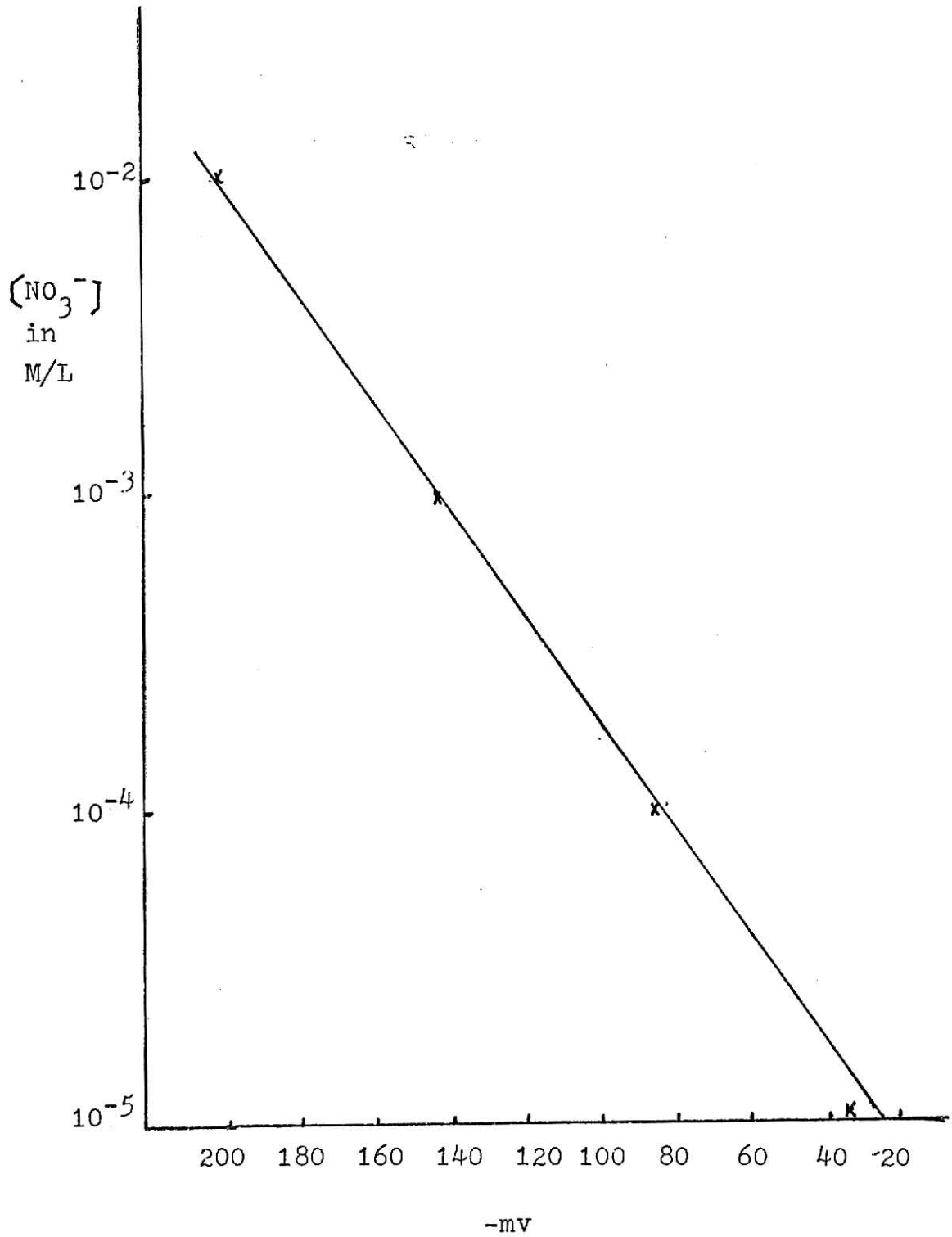
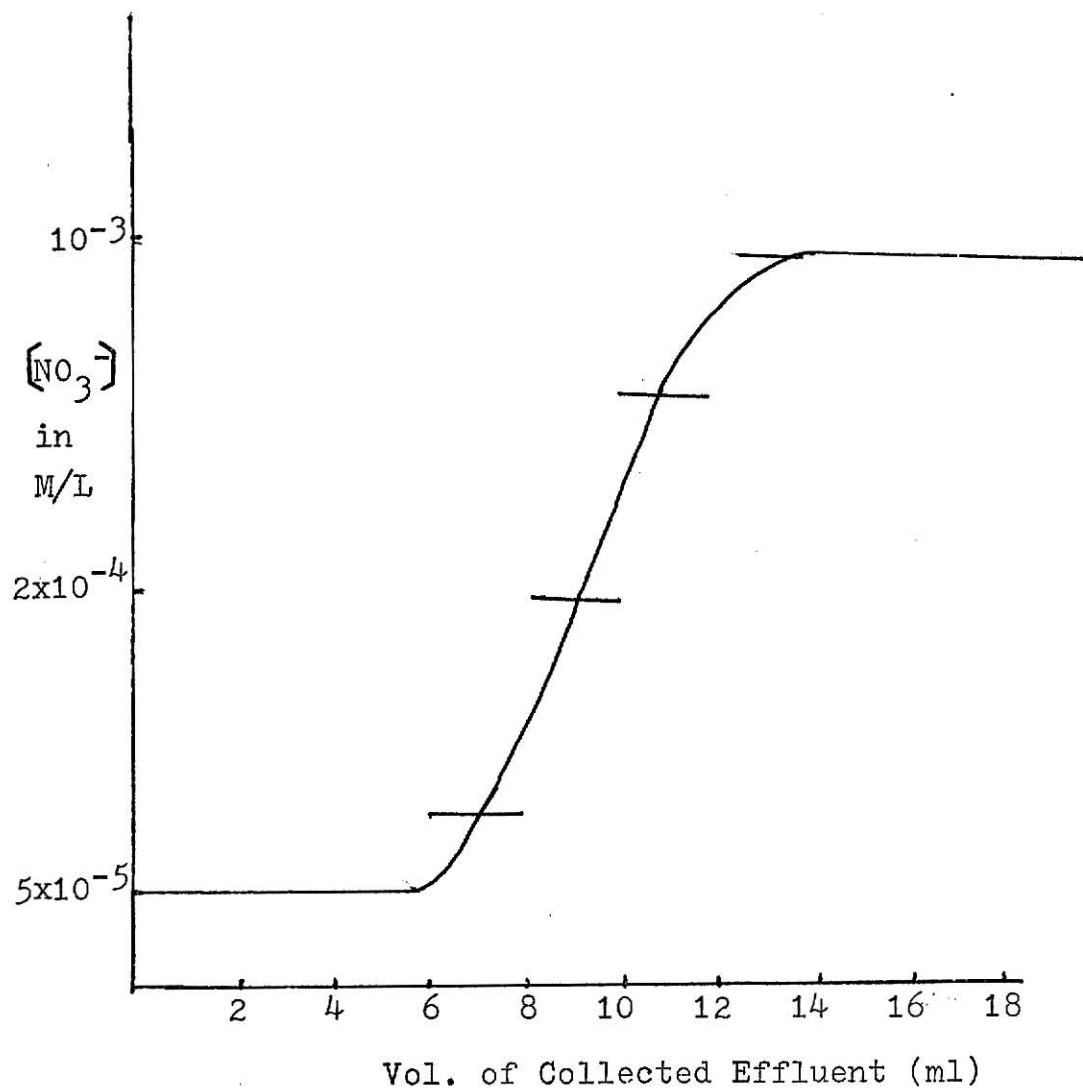


FIGURE 2.

Capacity of Resulting Product of Condensation
Polymerization of 24 (0.002 mole) and Ethylene
Glycol (0.002 mole).



zation of 24 and ethylene glycol had proceeded to completion, the nitron moiety contained in the testing resin (0.5 g) was calculated to be 1×10^{-3} mole. Therefore, the percentage of nitron moiety in the resin actually complexing with NO_3^- was calculated to be only 1.04%. The low efficiency of this compound was believed due to a very low degree of polymerization which in turn might have caused some of the nitron moiety to dissolve in the dilute acetic acid employed. The fact that coloration of the effluent occurred supported the above hypothesis.

B. Capacity of Nitron-Polyvinylbenzyl Chloride (31).

The capacity of the nitron-polyvinylbenzyl chloride, 31, to remove nitrate from water was investigated. The granulated resin become tacky when interacted with aqueous solution. To avoid this problem and to increase the effective surface area, attempts were made to coat the resin on suitable inert supports. Sand was first chosen as the support, but this attempt proved to be less successful than desired. Silica gel was then utilized as a inert support in subsequent experiment. The ratio of silica gel to 31 used was either 10:1 or 50:1 by weight. In one run, 0.465 g of 31 was deposited on 4.65 g of silica gel (resin 1). In a different run, 0.465 g of 31 was coated on 22 g of silica gel (resin 2). Both were tested as described above and the results are depicted in Figures 3 and 4. From Figures 3 and 4 one can calculate the capacity of these resins to remove nitrate from water by equation (1) to be 2.8×10^{-4} mole and 3.6×10^{-4} mole, respectively. Assuming only 58% of nitron appended on the poly-

FIGURE 3
Capacity of Resin 1 (4.65 g of silica gel
with 0.465 g of 31)

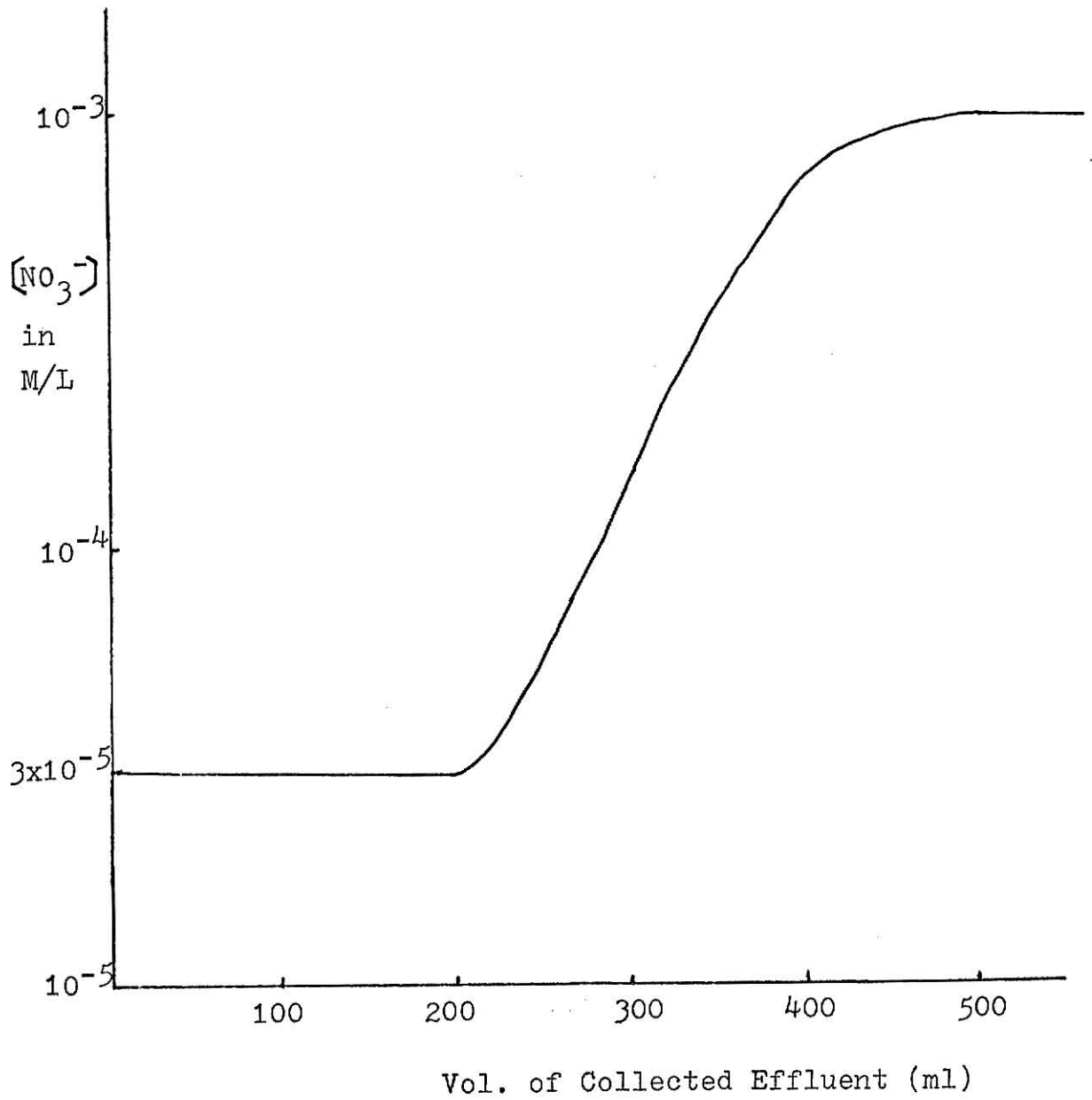
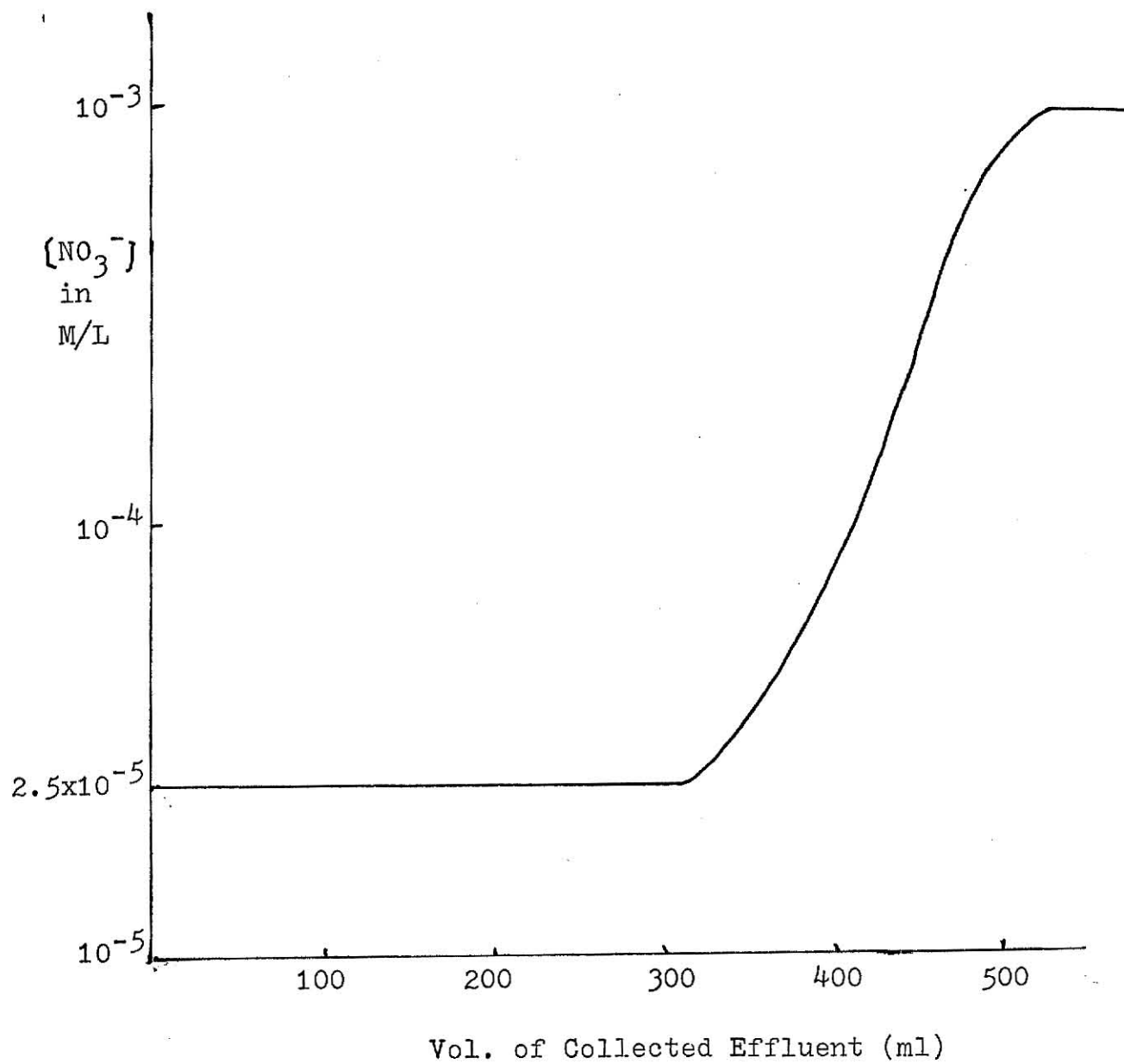


FIGURE 4
Capacity of Resin 2 (22 g of silica gel
with 0.465 g of 31)



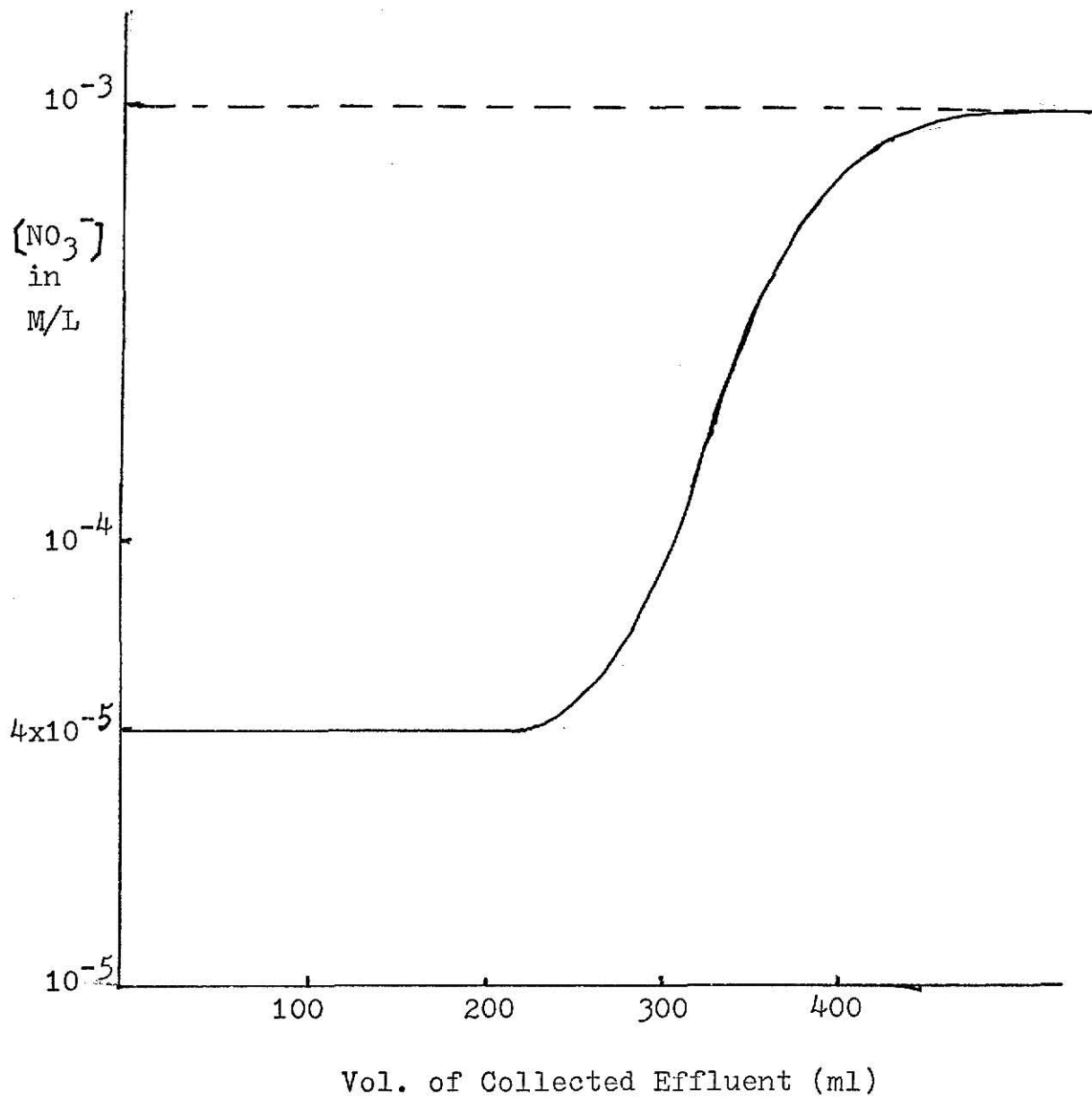
vinylbenzyl chloride, the nitron moiety containing in the testing resin was calculated to be 5.8×10^{-4} mole. The percentage of nitron moiety in resin 1 and resin 2 complexing with NO_3^- was calculated to be 48% and 62%, respectively. The capacity was increased if the ratio of silica gel to 31 was increased presumably due to an increased effective surface area. One possible explanation for the 62% efficiency is that the polymer backbone interfered with approaching nitrate anion and sterically prevented displacement of chloride from the ortho nitron-benzyl chloride.

Capacity of Regenerated Resin.

To determine the capacity of the regenerated resin, the resin was washed with 0.1 M NH_4Cl , and NO_3^- detected as discussed earlier with the result shown in Figure 5. It was found that the regenerated resin had 90% of its original efficiency. The capacity of the resin regenerated twice still retained 88% of its original efficiency.

Since one can regenerate the resin and use it again and again, this offers a good possibility for commercial use.

FIGURE 5
Capacity of Regenerated Resin 2
(22 g of silica gel with 0.465
g of 31)



CONCLUSION

The preparation of a suitable nitrate-selective resin by polymerization of nitron containing polymerizable vinyl functional groups was not realized. The compound 1,4-diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline, 24, was synthesized and a condensation polymerization with ethylene glycol was attempted. The capacity of this resin to remove nitrate was tested to be too low to be of commercial value. The low capacity may have been the result of a low degree of polymerization. A higher capacity nitrate selective resin was made by attaching nitron to commercial polyvinylbenzyl chloride; analysis indicated 58% of the nitron was appended on the polyvinylbenzyl chloride. The capacity of this synthesized resin to remove nitrate from potassium nitrate solution (1×10^{-3} M) was 62%. One possible explanation for the 62% efficiency is that the polymer backbone interferes with the approaching nitrate anion and sterically prevents the displacement of the chloride ion from the ortho nitrate-benzyl chloride.

A possible solution to the steric hindrance occurring in the syntheses and removal of nitrate could be to prepare polyvinylbenzyl chloride containing the chloromethyl groups only in the para position. It is plausible that such a polymer could append 100% nitron and it is also reasonable to assume that the capacity might approach 100%.

However, since the synthesized polymer resin, $(1 \text{ C}_9\text{H}_9\text{Cl} \cdot 1.38 \text{ C}_{29}\text{H}_{25}\text{N}_4\text{Cl})_n$, can be regenerated and used again and again,

it offers a good possibility for commercial development.

EXPERIMENTAL

Chemicals

Commercial thionyl chloride was redistilled from quinoline and boiled linseed oil²⁸ before it was used as the reagent for conversion of the acid to acid chloride. Acetone,²⁸ benzene,²⁹ N,N-dimethylformamide (DMF),²⁹ dimethylsulfoxide (DMSO),²⁹ and tetrahydrofuran (THF),²⁰ were used after distillation from sodium iodide, phosphorous pentoxide, barium oxide, calcium hydride and sodium borohydride, respectively. The other chemicals were all reagent grade and used without further purification.

Apparatus

A glass column (2.0 cm diameter, 50 cm length) with a glass fritted medium porous disc sealed at the bottom was used to test the synthesized resin.⁸

In a typical test, about 0.5 g of synthesized resin was packed on the top of the glass frit followed by 1 g of sand and a little glass wool as shown in Figure 6.

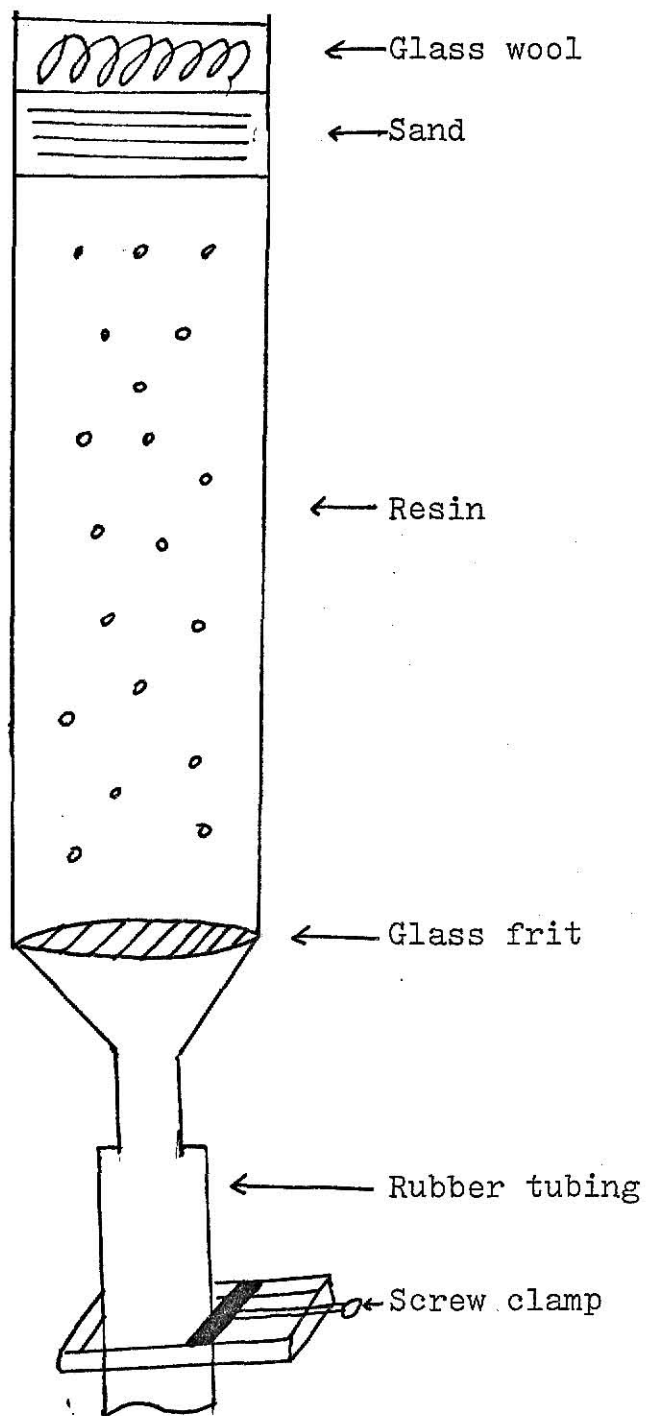
A nitrate ion selective electrode (Orion, Model 92-07, Cambridge, Mass.) was used to detect nitrate concentration as described by Shults.³⁰ The single junction sleeve type reference electrode was filled with 0.1 M KCl, since the normal filling solution contained NO_3^- and would interfere.

All melting points were obtained uncorrected using a Fisher-Johns melting point apparatus.

The infrared spectra of the compounds were recorded on

FIGURE 6

Diagram of Resin Testing Column



a Perkin-Elmer Model 137 infrared spectrophotometer. The infrared spectra of liquids were taken on films formed between two sodium chloride plates; potassium bromide was used in preparing pellets of solid samples for infrared spectra. The band 9.724μ of a polystyrene film was used as a reference peak.

The nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer. Deuterated chloroform (CDCl_3) was used as the solvent with tetramethylsilane (TMS) as the internal standard.

Mass spectral data were obtained using an AEI MS-9 mass spectrometer. Elemental analyses were performed by Chemalytics Inc. (Tempe, Arizona.).

Syntheses

1,3-diphenyl-2-aminophenylguanidine (11). Forty grams of 1,3-diphenylthiourea, 800 mg powdered sulfur, and 400 ml of dry acetone were refluxed with mechanical stirring for 40 minutes. Then, irrespective of whether or not the thiourea was completely dissolved, 70 g of lead oxide was added rapidly. After 15 minutes the mixture was filtered and the filtrate concentrated to ca. 120 ml by evaporation of the solvent under reduced pressure. The unreacted thiourea precipitated at -70° (dry ice-acetone). After evaporating the solvent, the residue was dissolved in petroleum ether (b.p. $40-60^\circ$) and allowed to stand 30 minutes in ice- H_2O to completely precipitate the thiourea or urea. The solid was filtered off and the filtrate was evaporated

to dryness to obtain 30 g of yellowish oil of 1,3-diphenylcarbodiimide, 14. This was dissolved in 50 ml of dry benzene by warming and the resulting solution was added to 20 g of phenylhydrazine. After standing at room temperature under a nitrogen atmosphere for six hours, the pale yellow crystalline precipitate which formed was filtered and washed with ether: yield 44 g (80%) of colorless crystals of 11: mp 160° (literature¹⁶ 160°); ir (KBr), distinctive absorption at 6.12, 6.3, 6.54, 6.72 and 6.90 μ ; mass spectrum m/e (rel intensity) 302(29), 208(13), 195(86), 108(91), 93(100), 92(60), 78(61). See page 48 for the ir, and page 69 for the mass spectra.

Acrylyl chloride (15). This compound was prepared from acrylic acid in 65% overall yield according to the procedure of Park.³¹ The yellow liquid had a bp of 72-74° (literature 72-74°); ir (neat), characteristic absorption at 5.65 μ (C=O).³²

Vinylacetyl chloride (16). A mixture of 8.6 g (0.1 mole) of vinylacetic acid, 28 g (0.2 mole) of benzoyl chloride, and 0.05 g of hydroquinone was distilled at a fairly rapid rate through an efficient 25 cm distilling column. The distillate was collected in a receiver containing 0.05 g of hydroquinone immersed in ice. When the temperature at the top of the column which remained between 90° and 98° for most of the distillation, had reached 106° the distillation was discontinued. The crude product was then redistilled through the same column and the fraction boiling at 96-99° at atmospheric pressure was collected. The weight of the final product was 7.1 g (68% yield) (lit.³³

bp 98-99°/774 mm). The infrared spectrum showed characteristic absorption at 5.56 μ (C=O).

4-Chlorobutyryl chloride (19). A 50 ml round bottom flask was attached to a Claisen head fitted with a condenser and an addition funnel. Thirteen grams of redistilled thionyl chloride were placed in the flask and 12 g of 4-chlorobutyric acid in the addition funnel. The flask was heated gently on a water bath and 4-chlorobutyric acid was added during the course of 25-30 minutes. When all the acid had been introduced, the mixture was refluxed for 30 minutes. The apparatus was re-arranged for distillation and the excess thionyl chloride was removed by distillation under reduced pressure (aspirator). The distillation was continued using a vacuum pump, and the fraction boiling at 66-69°/20 mm was collected (lit.³⁴ bp 58-60°/11 mm); nmr³⁵ (neat, internal TMS) δ 3.55 (t, CH₂Cl, 2H), 3.09 (t, CH₂-C=O, 2H), 2.14 (m, CH₂, 2H).

5-Bromovaleryl chloride (20). This compound was prepared from 5-bromovaleric acid in 90% yield according to the procedure of Merchant and Narvel.³⁶ The compound had a bp of 78-80°/4 mm (lit.³⁶ bp 102-104°/15 mm); nmr (neat, internal TMS) δ 3.3-3.5 (m, CH₂Br, 2H), 2.83-3.06 (m, 2-CH₂, 2H) and 1.73-2.0 (m, 3,4-CH₂, 4H). See page 56 for the nmr spectrum.

γ,γ -Dicarboethoxybutyraldehyde (32). This aldehyde was prepared from acrolein and ethyl malonate in 50% overall yield according to the procedure of Warner and Moe.³⁷ The crude product was distilled under reduced pressure and the aldehyde

was collected at 93-95°/0.1 mm (lit. ³⁷ 76-79°/0.04-0.07 mm); nmr (neat, internal TMS) δ 9.68 (s, -CHO, 1H), 4.14 (q, -OCH₂, 4H), 3.4 (t, γ -CH, 1H), 2.57 (t, α -CH₂, 2H), 2.12 (q, β -CH₂, 2H) and 1.21 (t, CH₃, 6H). See page 57 for the nmr spectrum.

γ,γ -Dicarboethoxybutyric acid (33): Twenty milliliters of water and 2.3 ml of concentrated sulfuric acid were placed in a 50 ml flask and the flask was cooled in an ice bath. When the temperature was below 12°, 4.25 g of γ,γ -dicarboethoxybutyraldehyde was added followed by 2.3 g of potassium permanganate in 0.5 g portions at such a rate that the temperature did not rise above 20°. Sodium bisulfite was introduced into the solution until the precipitated manganese dioxide just dissolved and the solution became clear. The oily layer was separated, washed with water and saturated sodium chloride solution, dried with anhydrous magnesium sulfate, and water distilled off under reduced pressure. Nmr (neat, internal TMS) δ 10.95 (s, OH, 1H), 4.14 (q, OCH₂, 4H), 3.46 (t, γ -CH, 1H), 1.85-2.7 (m, α,β -CH₂, 4H), and 1.21 (t, CH₃, 6H). See page 58 for the nmr spectrum.

γ,γ -Dicarboethoxybutyryl chloride (21): This compound was prepared from γ,γ -dicarboethoxybutyric acid by the procedure which is essentially the same as described for 4-chlorobutyryl chloride. The crude acid chloride was purified by distillation under reduced pressure: bp 115-122°/0.5 mm; nmr (neat, internal TMS) δ 4.14 (q, OCH₂, 4H), 3.23 (t, γ -CH, 1H), 3.1 (t, α -CH₂, 2H), 2.26 (t, β -CH₂, 2H) and 1.21 (t, CH₃, 6H).

See page 59 for the nmr spectrum.

2-Bromobutyryl chloride (17). This acid chloride was prepared by a method similar to that described for the preparation of 4-chlorobutyryl chloride. The acid chloride was purified by distillation under reduced pressure: bp $93-94^{\circ}/66$ mm; nmr (neat, internal TMS) δ 4.43 (m, CHBr, 1H), 3.43 (d, CH₂, 2H) and 1.73 (d, CH₃, 3H). See page 60 for the nmr spectrum.

General Procedure for the Preparation of Substituted Nitrons.

A. A mixture of the acid chloride and 1,3-diphenyl-2-aminophenylguanidine, 11,¹³ was heated in a sealed tube (46 cm in length, 1.5 cm in diameter) at 140° for 10 hours. The thick oily residue that resulted was dissolved in 95% ethanol and water was added until turbidity just appeared. At that point ethanol was added dropwise to clarify the solution. Ammonium hydroxide was added in excess to the above solution and the precipitated solid was extracted with chloroform. The combined chloroform extracts were dried over anhydrous MgSO₄ and concentrated to a small volume. The resulting solution was added dropwise to petroleum ether (bp $40-60^{\circ}$) to precipitate the solid which was recrystallized from petroleum ether-chloroform.

B. To a solution of 0.02 mole of 1,3-diphenyl-2-aminophenylguanidine, 11, in 30 ml of dry benzene was added 0.03 mole of acid chloride. The reaction mixture was heated at reflux for 24 hours. After evaporation of the solvent under reduced pressure, the resulting oily residue was treated in the same fashion as

described earlier, except changing petroleum ether to ethyl ether for the reaction of γ,γ -dicarboethoxybutyryl chloride with 1,3-diphenyl-3-aminophenylguanidine.

1,4-Diphenyl-3-phenylimino-5-(3-chloropropyl)-1,2,4-triazoline (22). This compound was prepared according to procedure B: 90%; mp 140-141^o; ir (KBr) distinctive absorptions at 6.2, 6.3, 6.48, 6.69 and 6.9 μ ; nmr (CDCl₃, internal TMS) δ 6.6-7.7 (m, aromatic, 15H), 3.1 (t, CH₂Cl, 2H), 2.65 (t, 1-CH₂, 2H) and 1.26-1.75 (m, 2-CH₂, 2H); mass spectrum m/e (rel intensity) 390(0.34), 388(1.0), 353(80), 208(1.5), 195(50), 176(100), 93(35), 92(25) and 77(50). See page 49 for the ir, page 61 for the nmr, and page 70 for the mass spectra.

1,4-Diphenyl-3-phenylimino-5-(4-bromobutyl)-1,2,4-triazoline (23) was prepared according to procedure B: 92%; mp 183-185^o; ir (KBr) distinctive absorptions at 6.2, 6.3, 6.48, 6.7 and 6.91 μ ; nmr (CDCl₃, internal TMS) δ 6.6-7.7 (m, aromatic, 15H), 3.0-3.3 (m, CH₂Br, 2H), 2.3-2.7 (m, 1-CH₂, 2H) and 1.2-1.6 (m, 2,3-CH₂, 4H); mass spectrum m/e (rel intensity) 367(100), 208 (0.59), 194(17.6), 158(35.3), 104(1.18), 93(53) and 77(59.0). See page 50 for the ir, page 62 for the nmr and page 71 for the mass spectra.

1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) was prepared according to procedure B: 88%; mp 177-180^o; ir (KBr) distinctive absorptions at 6.2, 6.3, 6.48, 6.7 and 6.9 μ ; nmr (CDCl₃, internal TMS) δ 6.5-7.7(m, aromatic, 15H), 4.0 (q, OCH₂, 4H), 2.93 (t, CH, 1H), 2.4-2.8

(m, 1-CH₂, 2H), 1.50-2.10 (m, 2-CH₂, 2H) and 1.13 (t, CH₃, 6H); mass spectrum m/e (rel intensity) 287(40), 258(11), 241(25), 213(10), 195(7), 186(17), 185(15), 174(14), 173(100), 160 (38) and 115(90). See page 51 for ir, page 63 for nmr, and page 72 for mass spectra.

Condensation Polymerization of 1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) and ethylene glycol.

A. To a solution of 0.498 g (0.001 mole) of 1,4-diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) in 30 ml of dry benzene, was added 0.62 g (0.01 mole) of ethylene glycol. The reaction mixture was heated at reflux for 12 hours. After evaporation of the solvent, the resulting residue was dissolved in 10 ml of chloroform. The resulting solution was added dropwise to ethyl ether to preprecipitate the solid. The solid was filtered, washed with ethyl ether, and recrystallized from chloroform-ethyl ether. Nmr (CDCl₃, internal TMS): δ 6.6-7.7 (m, aromatic, 15H), 3.80-4.36 (broad s, COOCH₂-, 4H), 3.40-3.80 (broad s, -CH₂O-, 4H) and 1.5-3.1 (m, -CH₂CH₂CH, 5H). See page 64 for the nmr spectrum.

B. To a solution of 1.0 g (0.002 mole) of 1,4-diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) in 15 ml of dry benzene, was added 0.124 g (0.002 mole) of ethylene glycol. The reaction mixture was refluxed for 12 hours. After evaporation of the solvent, the resulting residue was placed in a Claisen flask provided with a receiver and

condenser, and the flask was heated at 150° under vacuum (0.1 mm) for one hour. The residue was dissolved in 10 ml of chloroform and added dropwise to ethyl ether. A dark-brownish precipitate was formed. The solid was filtered, washed with ethyl ether, and recrystallized from chloroform-ethyl ether to yield 1.1 g of product: ir (KBr) distinctive absorptions at 3.1, 3.4, 5.8, 6.3-6.5, 6.78 and 6.91 μ ; nmr (CDCl₃, internal TMS) δ 6.5-7.7 (m, aromatic, 15H), 4.38-4.8 (broad s, 2H), 3.8-4.38 (m, 4H), 3.38-3.8 (broad s, 3H), 1.65-3.2 (m, 5H) and 1.18 (t, 3H). See page 52 for the ir, and page 65 for the nmr spectra.

Nitron-methyl iodide (29). This nitron salt was prepared according to the procedure described in the literature.¹³ Mp 213°; ir (KBr) distinctive absorptions at 3.4-3.5, 6.2, 6.3, 6.5, 6.7, 6.9 and 8.1 μ ; nmr (CDCl₃, internal TMS) δ 6.98-8.35 (m, aromatic, 15H), 3.57 (s, CH₃, 3H), and 12.23 (s, ring CH, 1H). See page 53 for the ir, and page 66 for the nmr spectra.

Nitron-benzyl chloride (30). This nitron salt was prepared according to the procedure of Bush.¹³ Mp 210°; ir (KBr) distinctive absorptions at 3.4, 3.5, 6.2, 6.3, 6.5, 6.7, 6.9 and 8.0 μ ; nmr (CDCl₃, internal TMS) δ 12.27 (s, ring CH, 1H), 6.8-8.4 (m, aromatic, 15H) and 5.67 (s, -CH₂-N, 2H); mass spectrum m/e (rel intensity): 403(30.2), 312(3.3), 311(3.7), 208(2.2), 195(20.8), 194(100), 92(4.9), 91(40.6) and 77(32.0). See page 54 for the ir, page 67 for the nmr and page 73 for the mass spectra.

Reaction of nitron with polyvinylbenzyl chloride (60/40 ortho/para isomer). A solution of 1.52 g (0.01 mole) of polyvinylbenzyl chloride (60/40 ortho/para isomer, Aldrich Chemical Company) in 20 ml of dry DMF was added to a stirred solution of 3.12 g (0.01 mole) of nitron in 25 ml of dry DMF. This reaction mixture was stirred at 60° for 12 hours. The gelatin-like reaction mixture was filtered and washed with water. The solid was recrystallized twice by dissolving in about 300 ml of chloroform and precipitating the solid with ether and was finally washed with 500 ml of acetone to yield a yellowish powder. After drying at 80°/2 mm the compound (31) had a melting point greater than 300°. Ir (KBr) distinctive absorptions at 3.36, 3.48, 6.3, 6.5, 6.7, 6.9 and 7.94 μ . See page 55 for the ir spectrum. Anal. Calcd. for $C_{29}H_{25}N_4Cl$: C, 74.91; H, 5.42; N, 12.05. Found: C, 74.63; H, 6.04; N, 9.74. In order to match the experimental analytical value for nitrogen, one has to have only 58% of nitron appended on the polyvinylbenzyl chloride, i.e., the resulting product should be $(1 C_9H_9Cl \cdot 1.38 C_{29}H_{25}N_4Cl)_n$. Anal. Calcd. for $1 C_9H_9Cl \cdot 1.38 C_{29}H_{25}N_4Cl$: C, 74.13; H, 5.52; N, 9.74.

Determination of Nitrate Capacity of Polymer-Supported Nitrons.

A. A 0.5 g sample of the product from the condensation polymerization of 24 and ethylene glycol was packed into a column and washed with 0.1 M acetic acid until the effluent solution reached a pH value of 1.5. The column was rinsed with 100 ml of deionized water until neutral (using pH paper). A

solution of 10^{-3} M of KNO_3 was passed through the column and 2 ml fractions were collected to be tested. The test fractions were placed in a microsample dish (Orion, Model 92-00-14) and the solution was constantly agitated by shaking the dish. The capacity was calculated as described on page 22.

B. The polymer resin 31 was dissolved in chloroform and the appropriate amount of silica gel was added. The ratio of silica gel to resin 31 used was either 50:1 or 10:1 by weight. The solvent was evaporated on a Buchi rotovapor which resulted in good mixing of 31 and silica gel. The mixture was powdered and dried in an Abderhalden drying pistol at $78^\circ/0.5$ mm. The mixture was then packed into a column and used directly for removing the nitrate ions without acidifying with acetic acid. A solution of 10^{-3} M potassium nitrate was passed through the column and 2 ml of fractions were collected to be tested. In one run, 4.65 g of silica gel was mixed with 0.465 g of polymer 31 (resin 1). In a different run, 22 g of silica gel was mixed with 0.465 g of polymer 31 (resin 2). Both were packed in the column for testing the capacity of removing nitrate from water and the results were depicted in Figures 3 and 4.

Regeneration of Column.

After the resin was saturated, it was washed with 200 ml of deionized water until the effluent solution contained no nitrate ion as determined by nitrate selective electrode. A 0.1 M NH_4Cl solution was passed through the column for regeneration of the resin by exchanging nitrate ion with chloride ion. The effluent was

TABLE 3

Result of Regeneration of Resin 2 (22 g of
silica gel with 0.465 g of 31)

<u>Bottle No.</u>	<u>Collected Volume (ml)</u>	<u>Correspond E (mv)</u>
1	10	-198
2	10	-189
3	10	-180
4	10	-172
5	10	-169
6	10	-166
7	10	-162
8	10	-160
9	10	-158
10	10	-155
11	10	-152
12	10	-150
13	10	-147
14	10	-145
15	10	-143
16	10	-141
17	10	-138
18	10	-135
19	10	-130
20	10	-128
21	10	-127

monitored with the nitrate selective electrode to determine whether the nitrate ions had been replaced by chloride ions. The results of regeneration of resin 2 are listed in Table 3. The data show that the nitrate had been replaced by chloride ions as explained as follows. The nitrate selective electrode responds to certain other anions as well as nitrate ions. In a solution containing nitrate ions and an interfering anion, electrode behavior is given by the following equation (2):³⁸

$$E = E_v - 2.3 \frac{RT}{F} \log (A_{\text{NO}_3^-} + K_x A_x^{1/n}) \quad (2)$$

Where E = electrode potential.

E_v = standard electrode potential.

K_x = selectivity constant for the interfering ions,

A_x = activity of the interfering ions.

n = the charges on the interfering ions.

For chloride ions, $K_x = 4 \times 10^{-3}$, $n = 1$; therefore,

$$\begin{aligned} E &= E_v - 0.059 \log (A_{\text{NO}_3^-} + 4 \times 10^{-3} A_{\text{Cl}^-}) \\ &= E_v - 0.059 \log ([\text{NO}_3^-] + 4 \times 10^{-3} [\text{Cl}^-]) \end{aligned} \quad (3)$$

The pure solution of 0.1 M of NH_4Cl ($[\text{NO}_3^-] = 0$) should respond as:

$$\begin{aligned} E &= E_v - 0.059 \log (4 \times 10^{-3} \times 0.1) \\ &= E_v - 0.059 \log (4 \times 10^{-4}). \end{aligned}$$

In this study, E was set at -125 mv. Thereby, E_v can be calculated as follows:

$$\begin{aligned} E &= E_v - 0.059 \log (4 \times 10^{-4}) \\ E_v &= E + 0.059 \log (4 \times 10^{-4}) \\ E_v &= -125 \text{ mv} + 0.059 \times (-3.4 \text{ v}) \times 1000 \frac{\text{mv}}{\text{v}} \\ &= -325 \text{ mv}. \end{aligned}$$

It was shown in Table 3 that the electrode potential E of

the first 10 ml of collected effluent was -198 mv. From the data of E and E_v one can calculate the concentration of nitrate ions by using equation 3.

$$\begin{aligned} [\text{NO}_3^-] + 4 \times 10^{-3} \times [\text{Cl}^-] &= 10^{(E_v - E)/0.059} \\ [\text{NO}_3^-] &= 10^{(E_v - E)/0.059} - 4 \times 10^{-3} [\text{Cl}^-] \\ &= 10^{(-0.325 + 0.198)/0.059} - 4 \times 10^{-3} [\text{Cl}^-] \\ &= 7 \times 10^{-3} - 4 \times 10^{-3} [\text{Cl}^-] \end{aligned} \quad (4)$$

Because one chloride ion replaced one nitrate ion, and the original concentration of chloride ion was 0.1 M, equation 5

$$[\text{NO}_3^-] = 0.1 - [\text{Cl}^-] \quad (5)$$

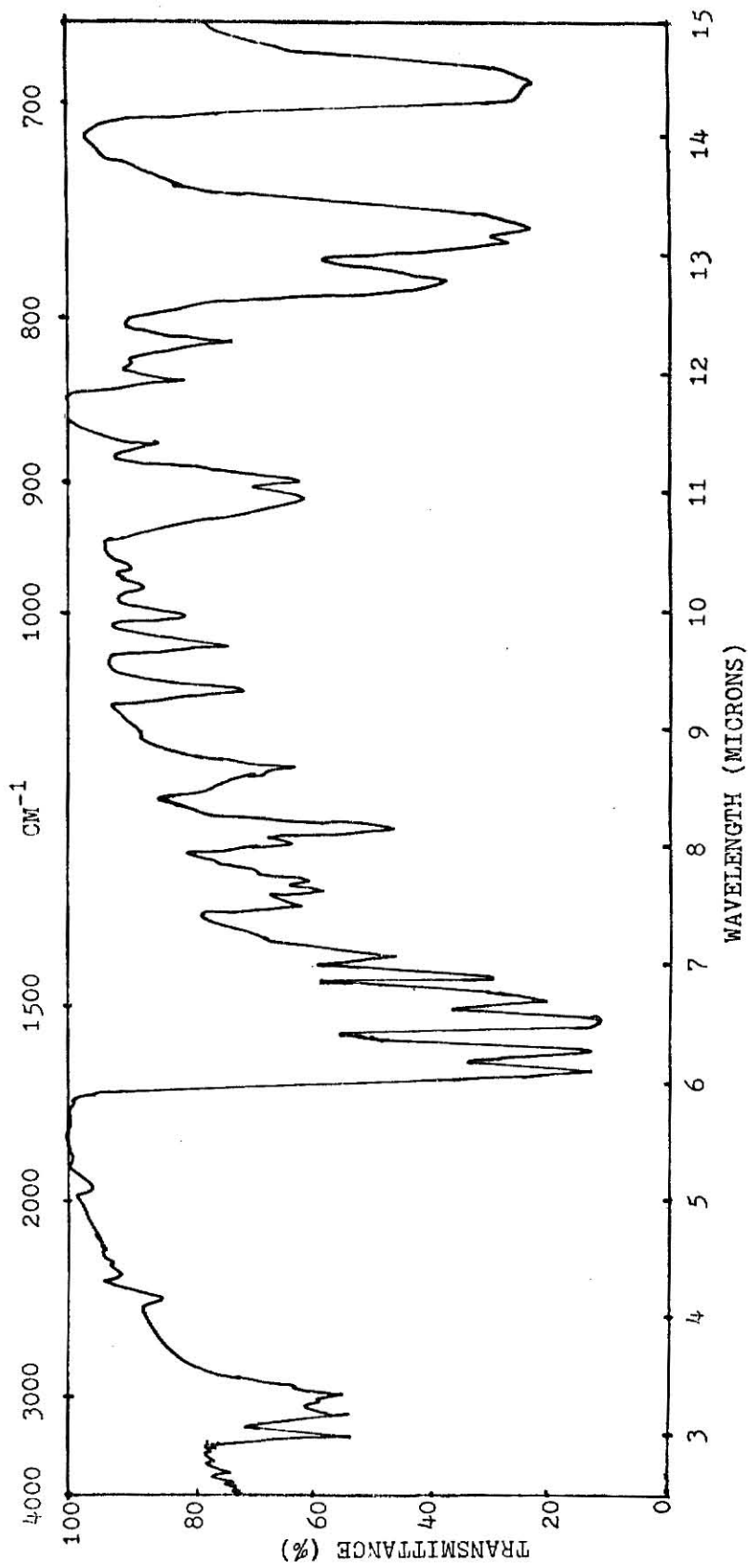
should hold for all the collected effluents. Subtracting 4×10^{-3} times equation 5 from equation 4, one has

$$[\text{NO}_3^-] = 6.6 \times 10^{-3} / (1 - 4 \times 10^{-3}) = 6.6 \times 10^{-3} \text{ M}$$

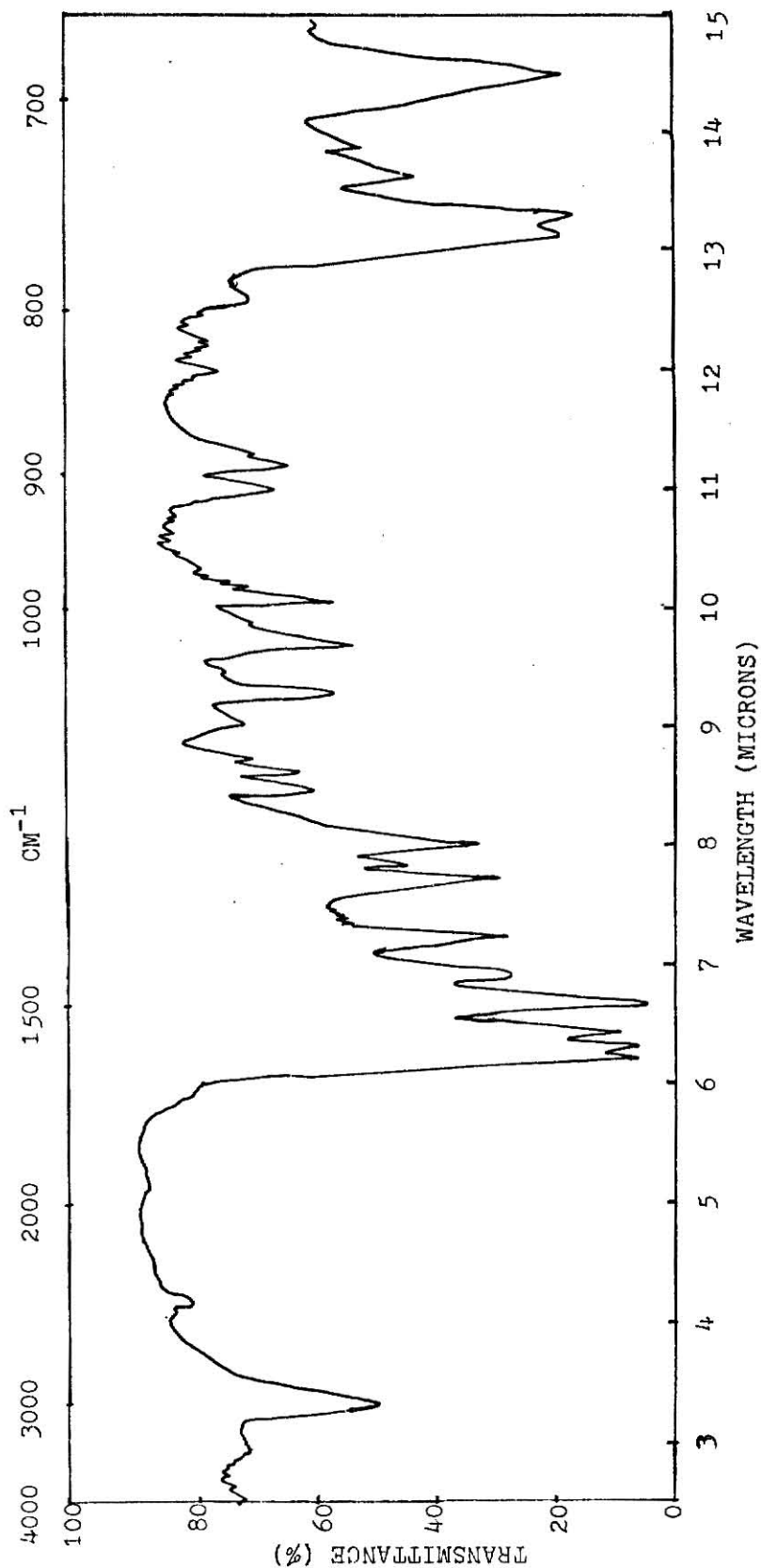
Thereby, the amount of nitrate being replaced with the first 10 ml effluent was calculated to be 6.6×10^{-5} mole. The total moles of nitrate being replaced (calculated from all the effluents) was found to be 3.2×10^{-4} mole.

Capacity of Regenerated Resin. To determine the capacity of the regenerated resin, the resin was washed with 0.1 M of NH_4Cl as mentioned above. Then it was washed with deionized water until the effluent contained no chloride ion (tested by adding silver nitrate). Aqueous KNO_3 (1×10^{-3} M) was passed through and detected as described earlier with the result shown in Figure 5. It was found that the regenerated resin had 90% of its original capacity.

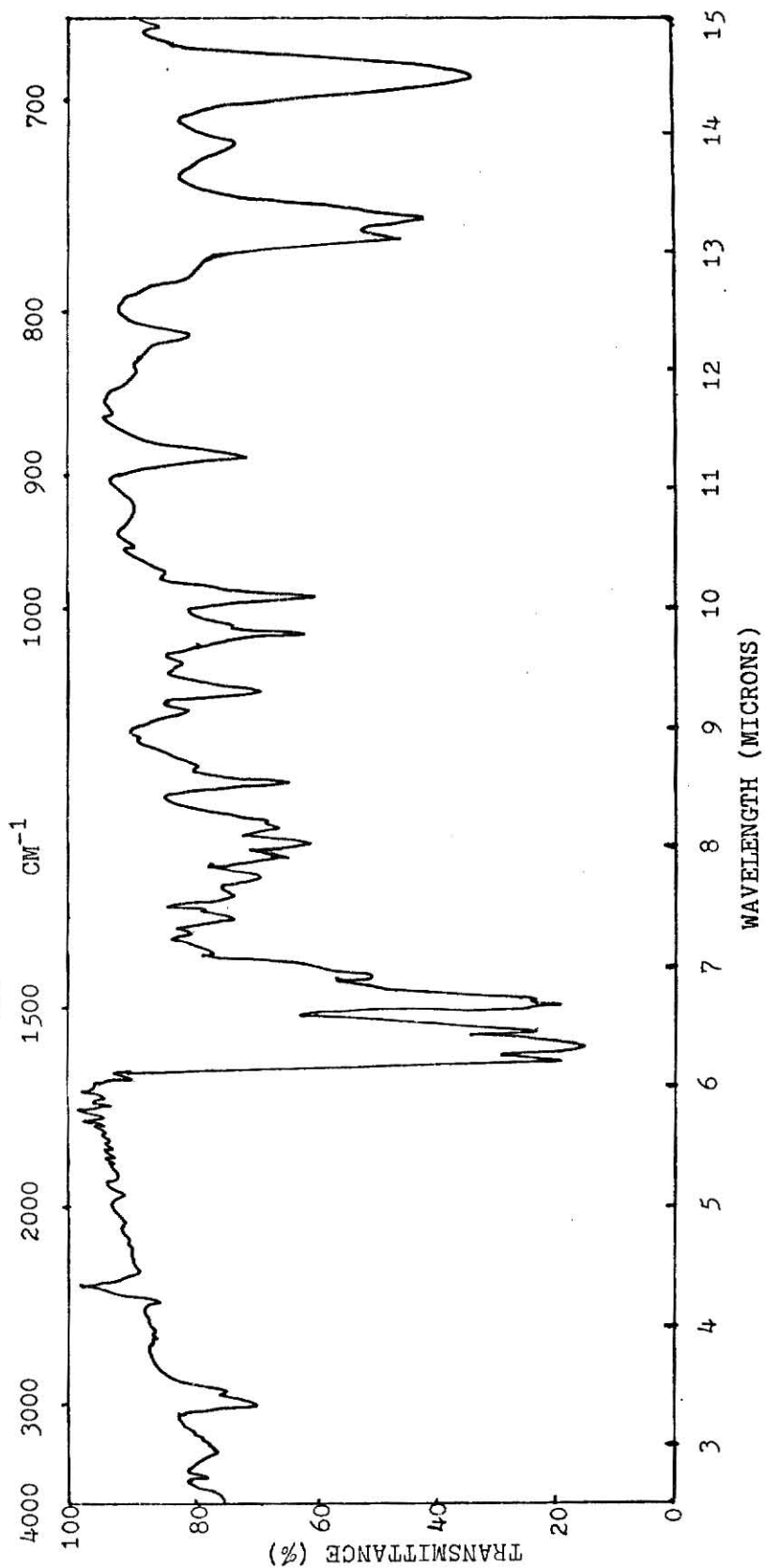
I.R. Spectrum of 1,3-Diphenyl-2-aminophenylguanidine (11) as a KBr Pellet.



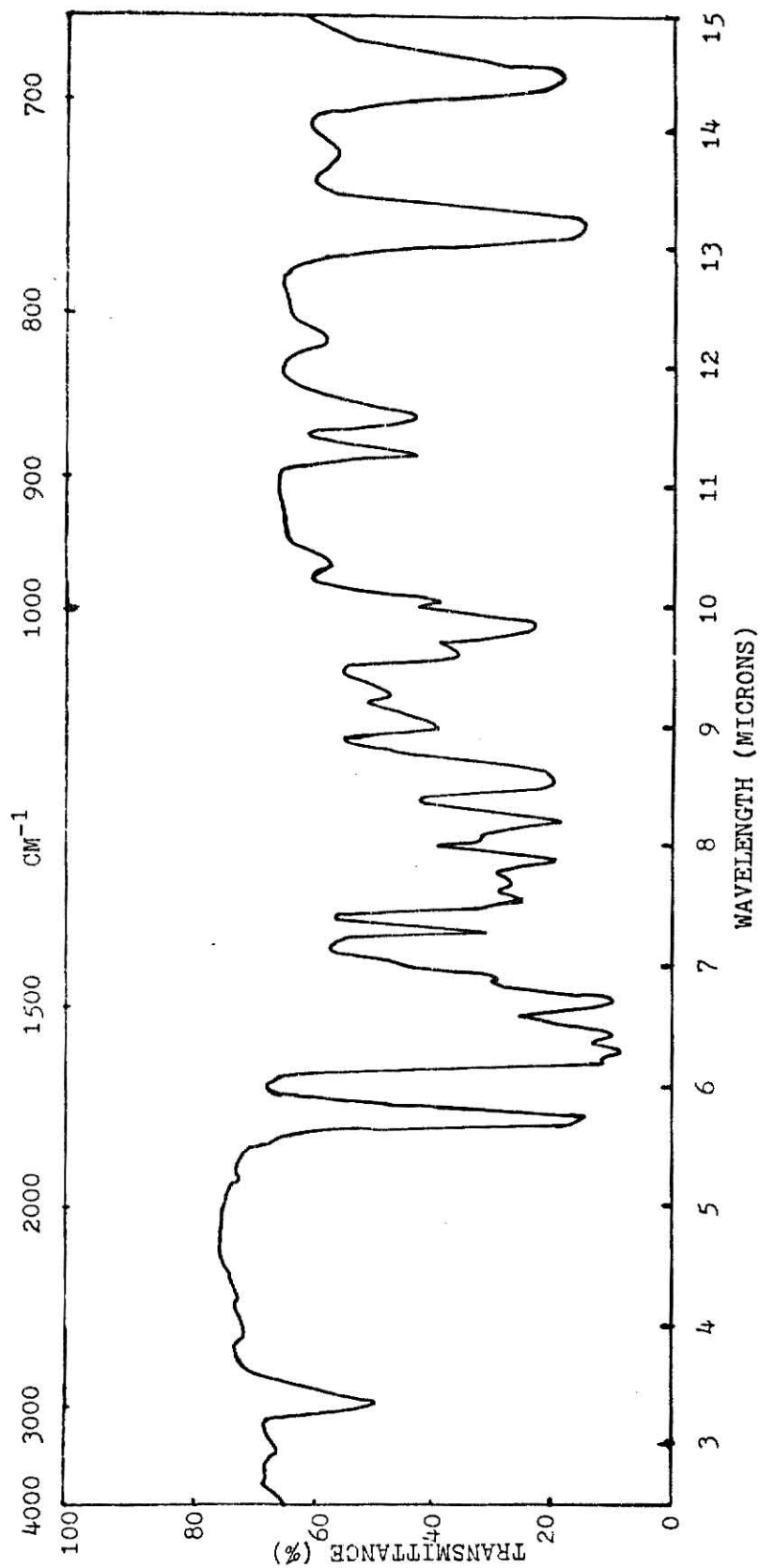
I.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(3-chloropropyl)-
triazoline (22) as a KBr Pellet.



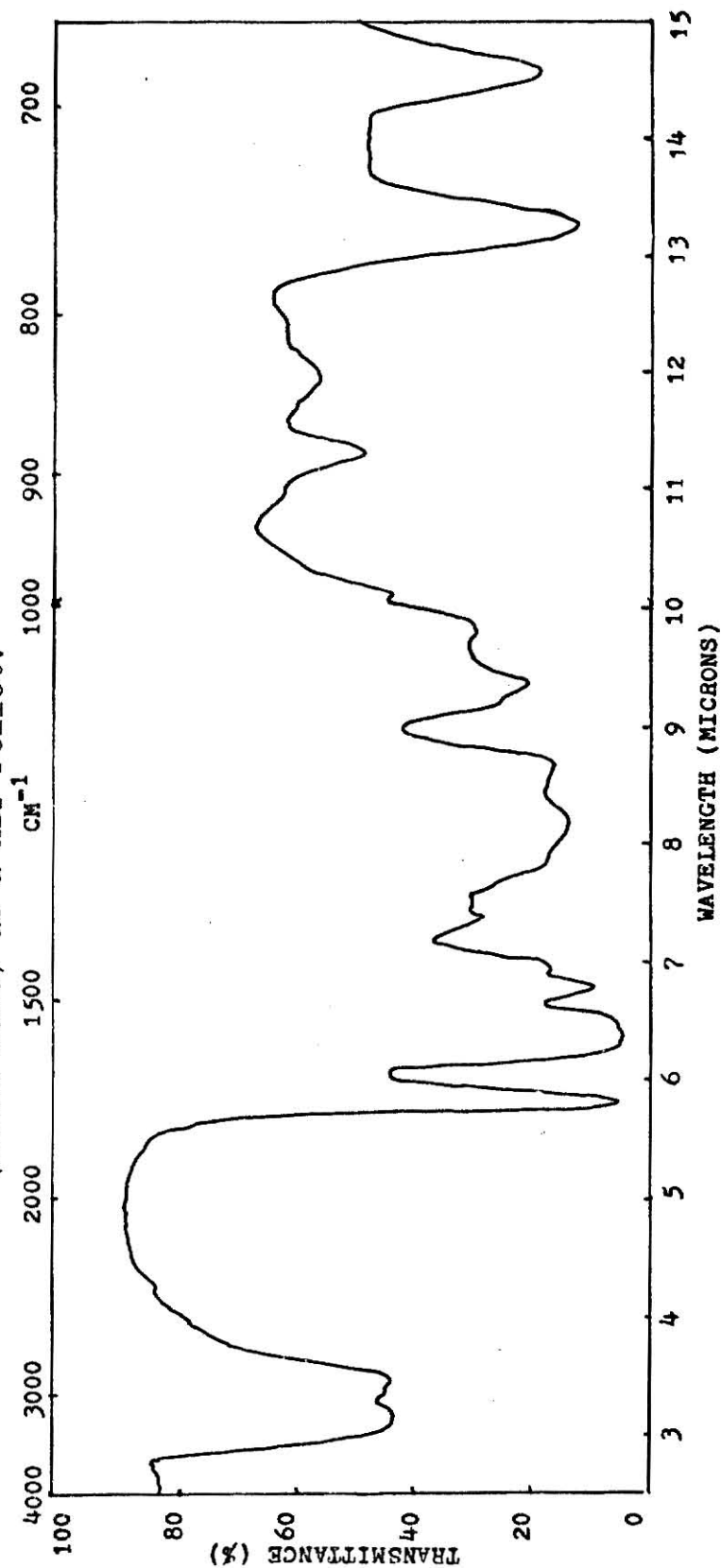
I.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(4-bromobutyl)-
triazoline (23) as a KBr Pellet.



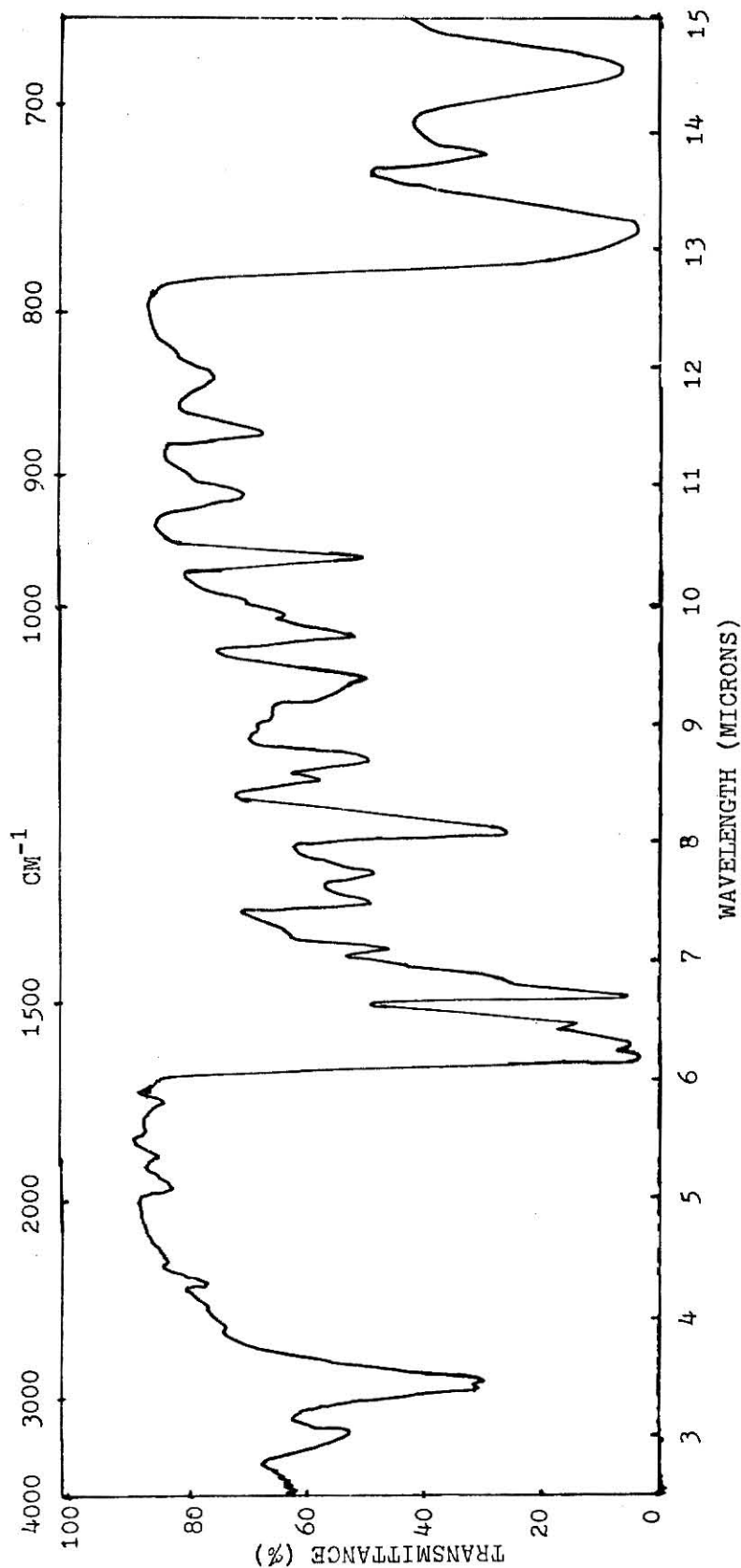
I.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-
1,2,4-triazoline (24) as a KBr Pellet.



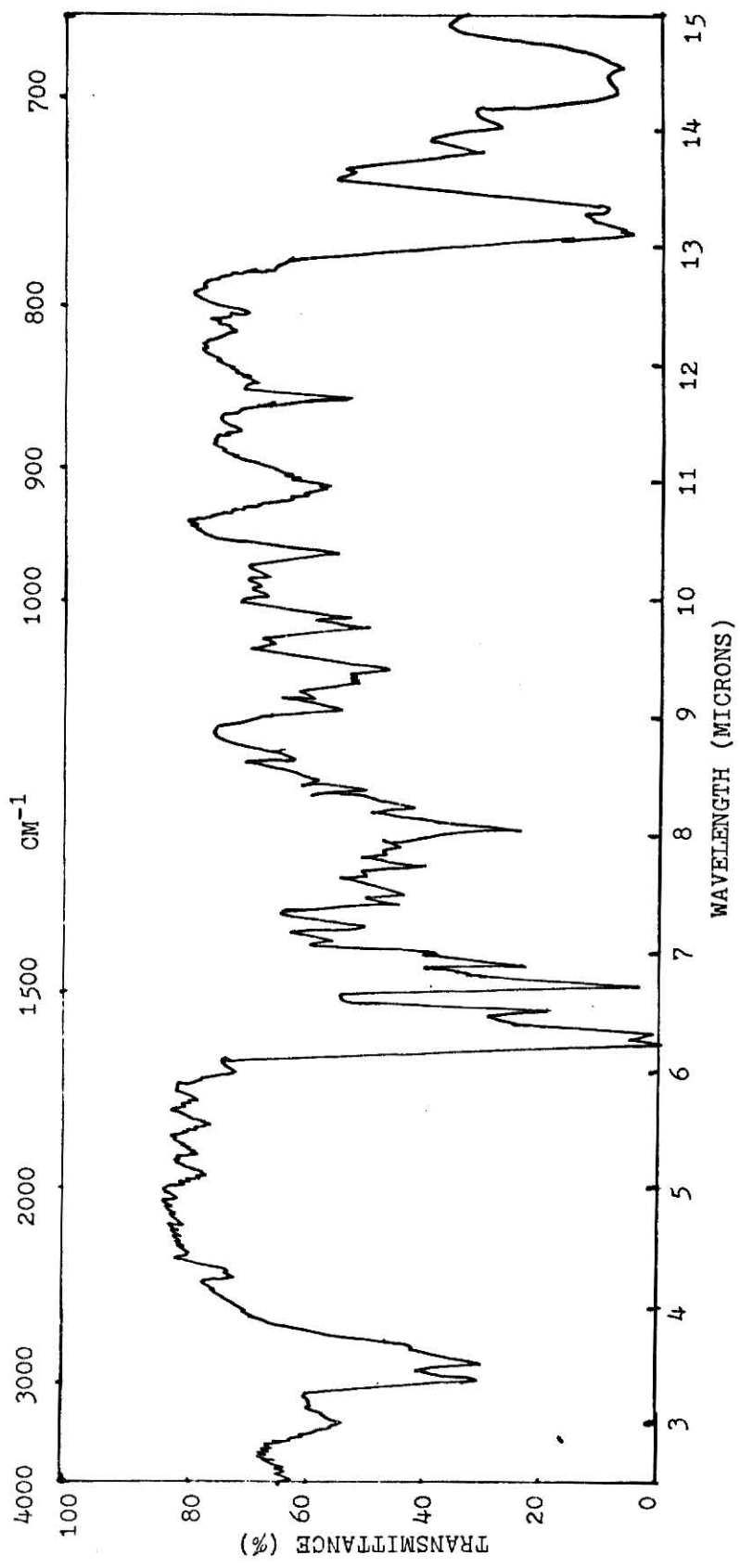
I.R. Spectrum of Resulting Product of Condensation Polymerization of
1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-
1,2,4-triazoline (24, 0.002 mole) and Ethylene Glycol
(0.002 mole) as a KBr Pellet.



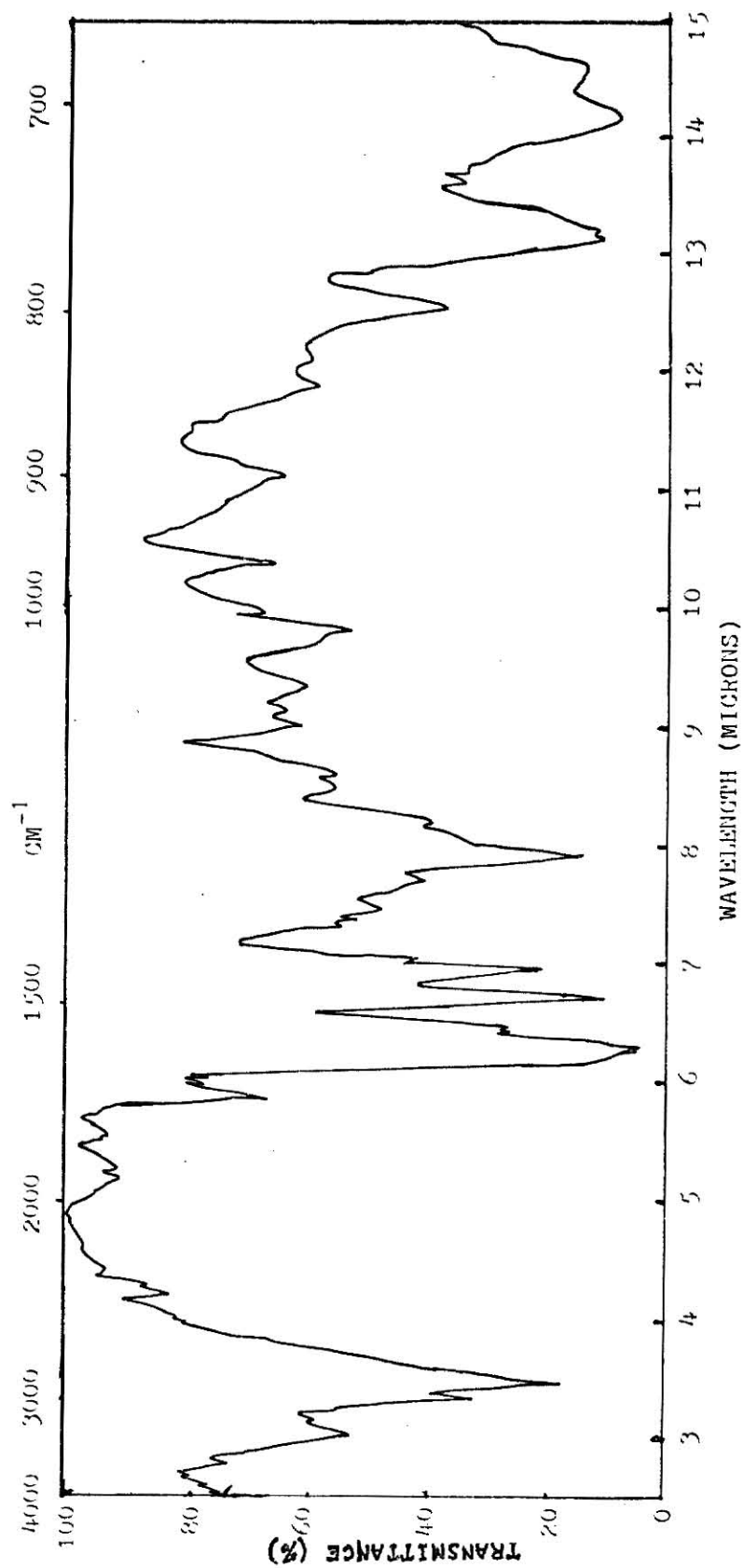
I.R. Spectrum of Nitron-methyl Iodide (22) as a KBr Pellet.

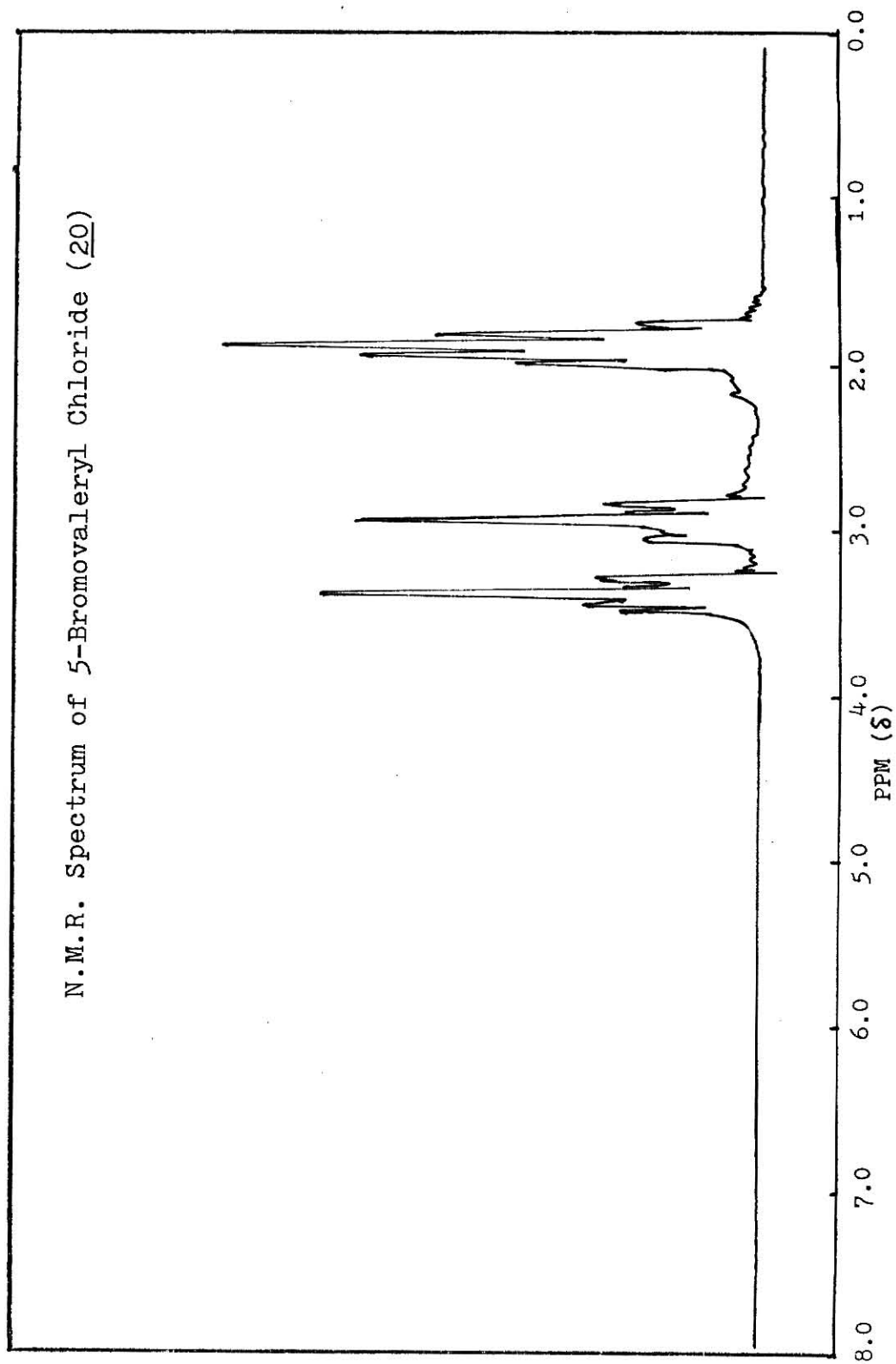


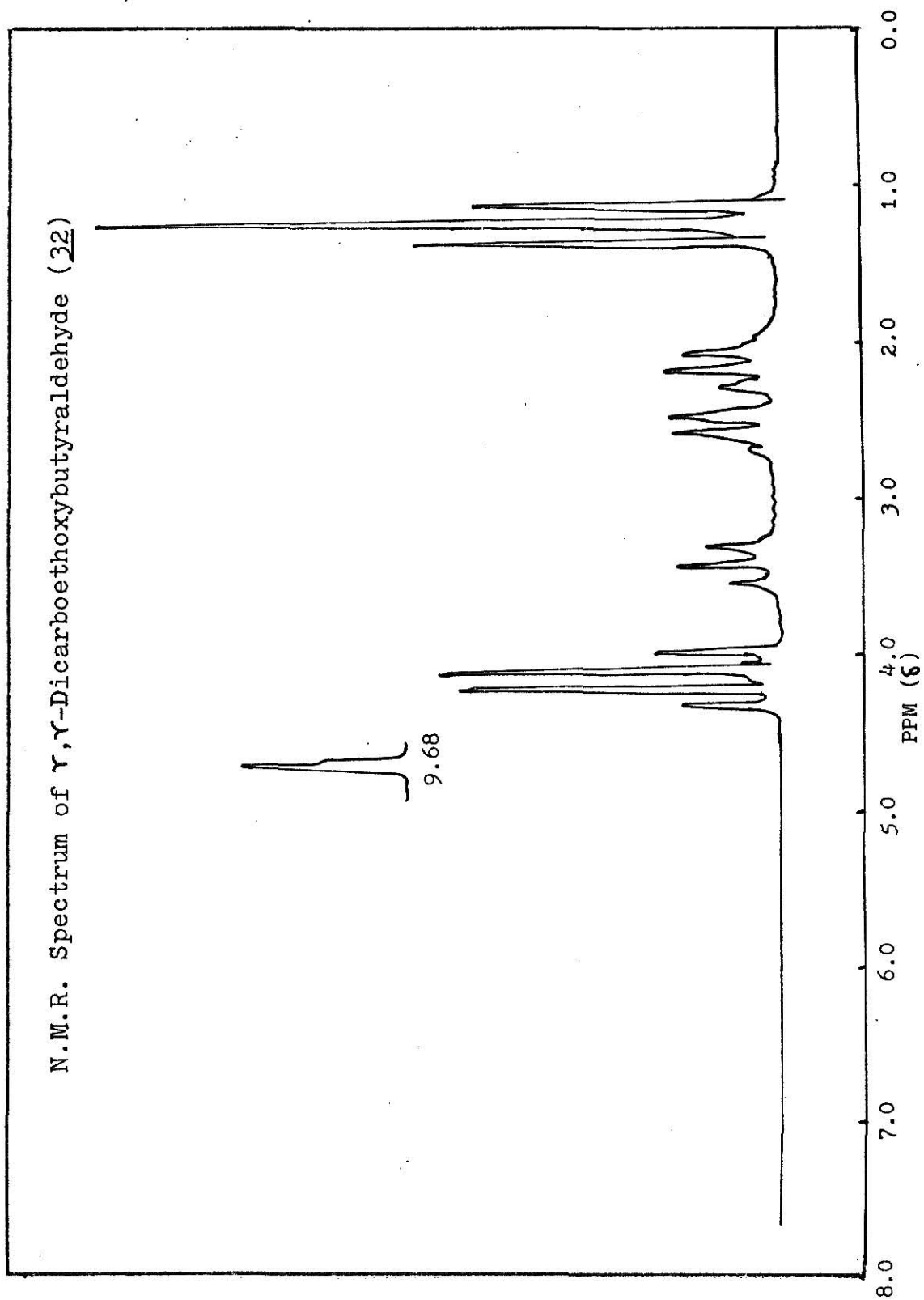
I.R. Spectrum of Nitron-benzyl Chloride (30) as a KBr Pellet.

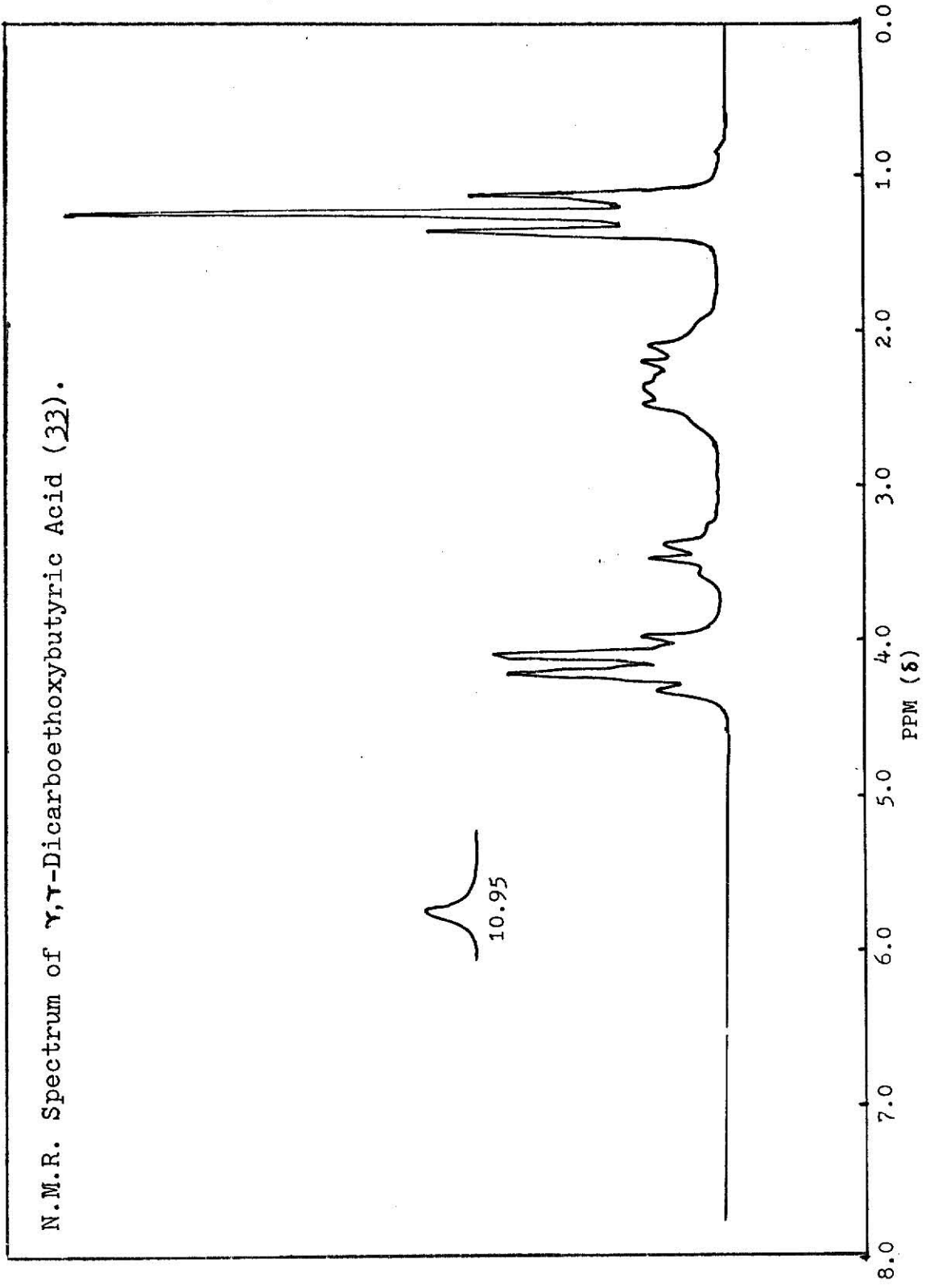


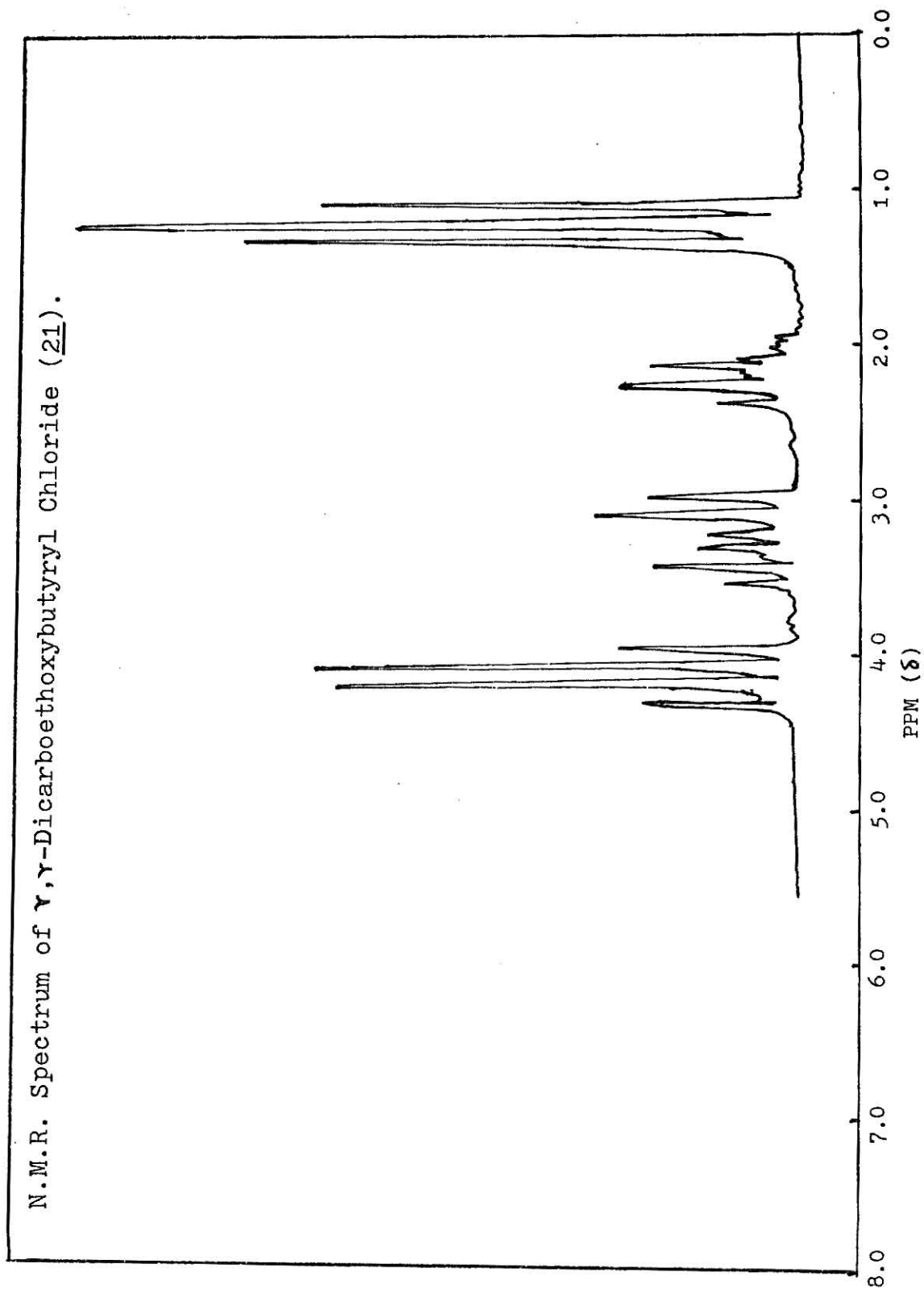
I.R. Spectrum of Resulting Product of Modification Polymerization of Nitron and Polyvinylbenzyl Chloride (31) as a KBr Pellet.

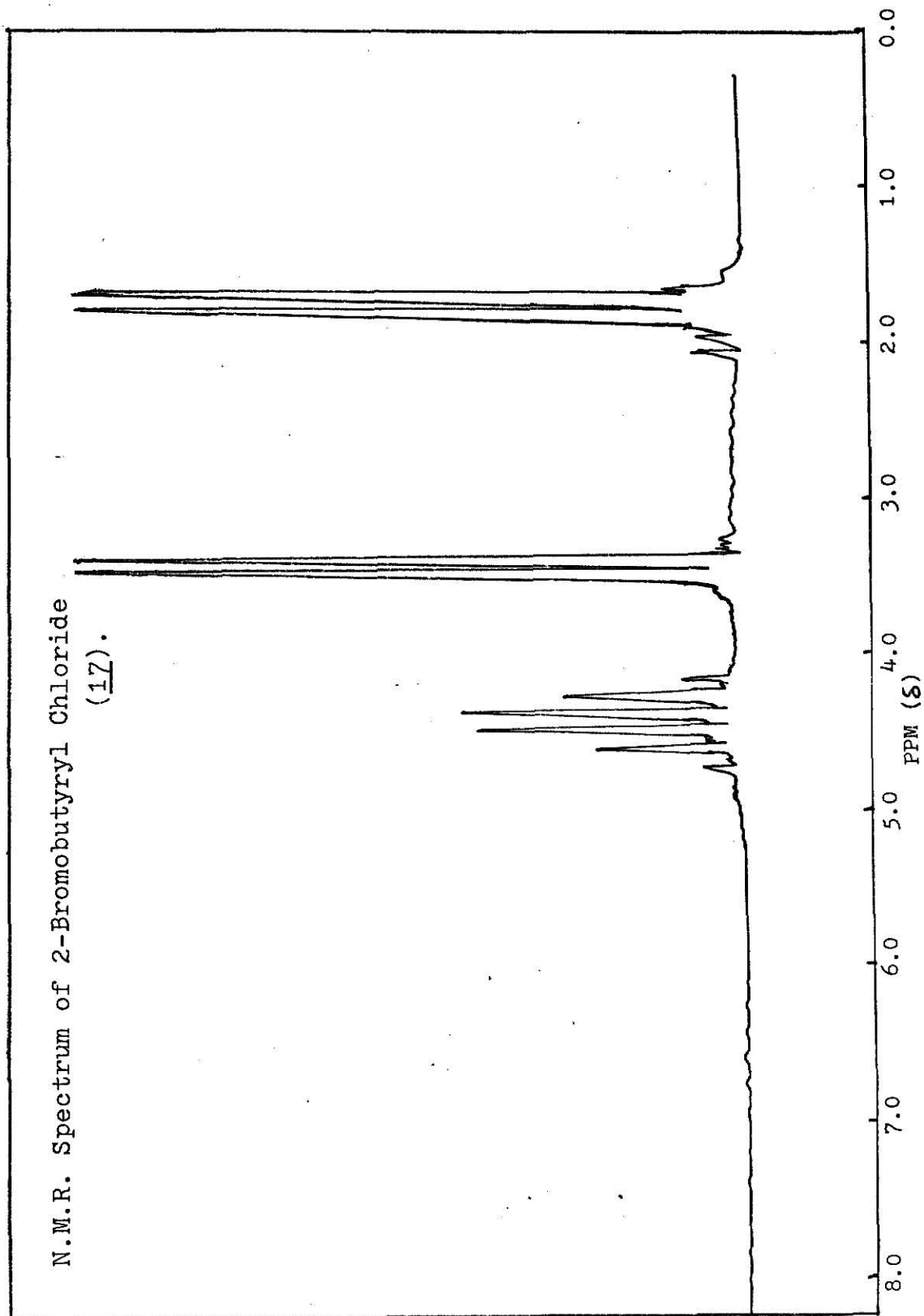




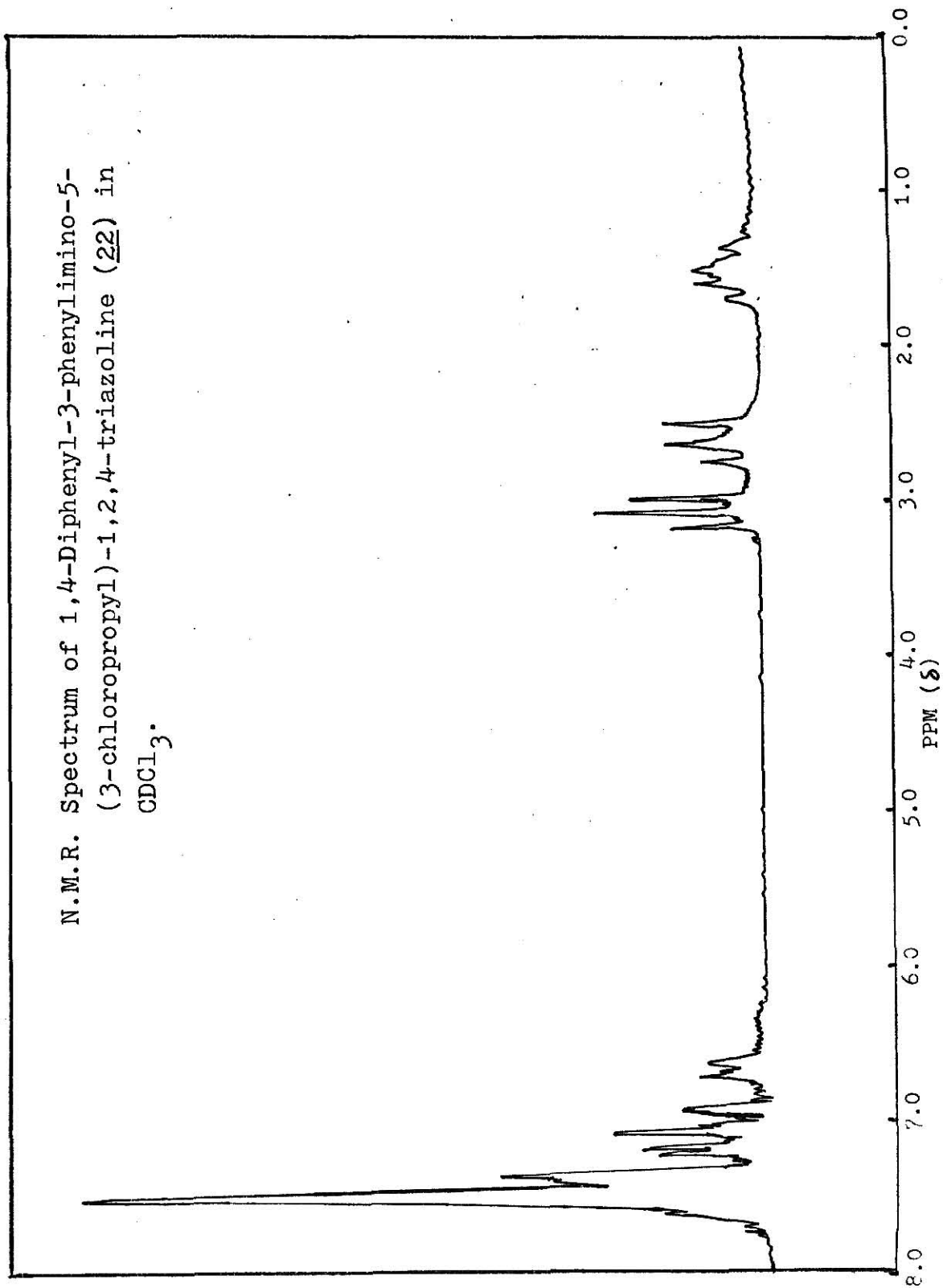


N.M.R. Spectrum of γ,γ -Dicarboethoxybutyric Acid (33).

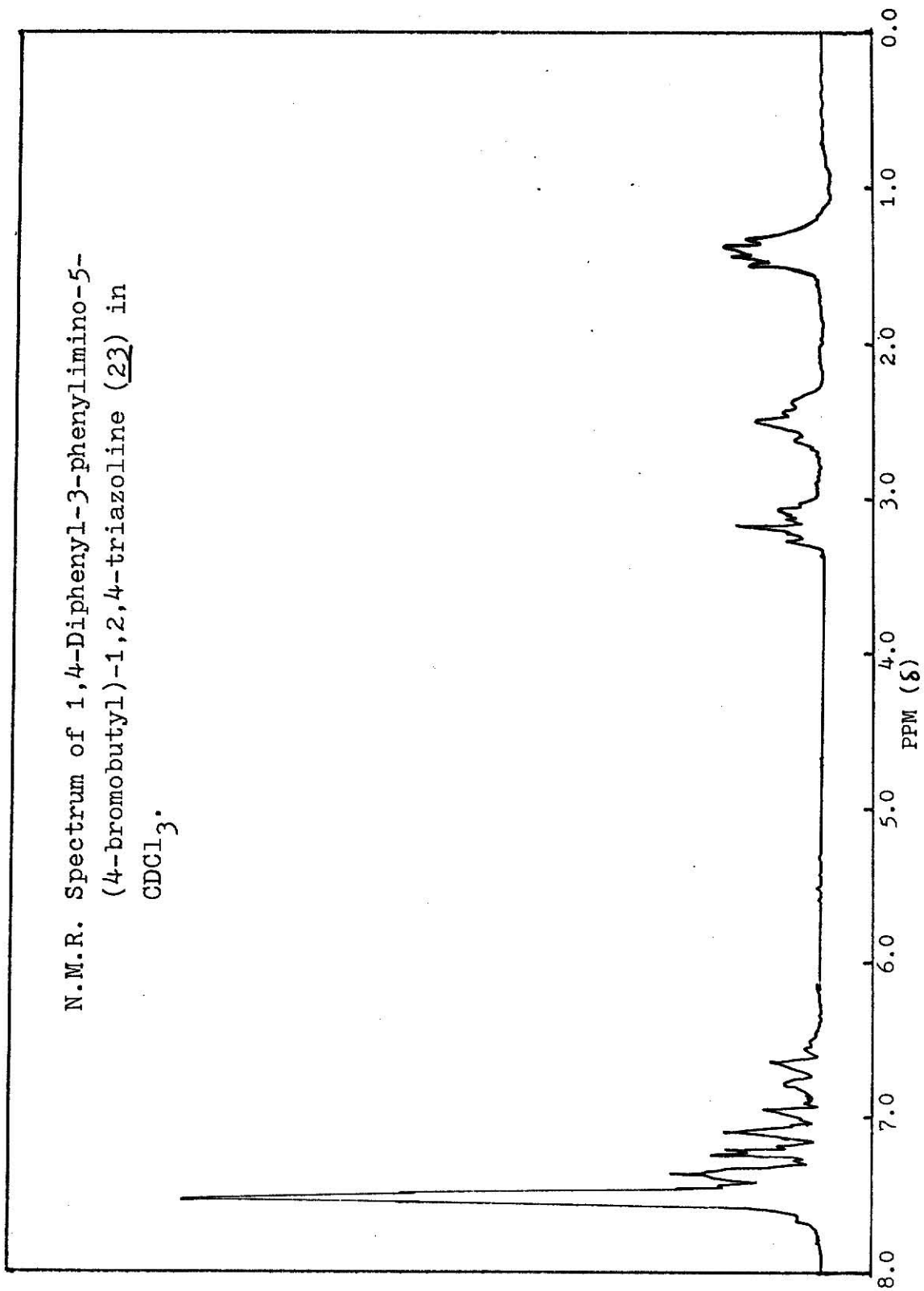




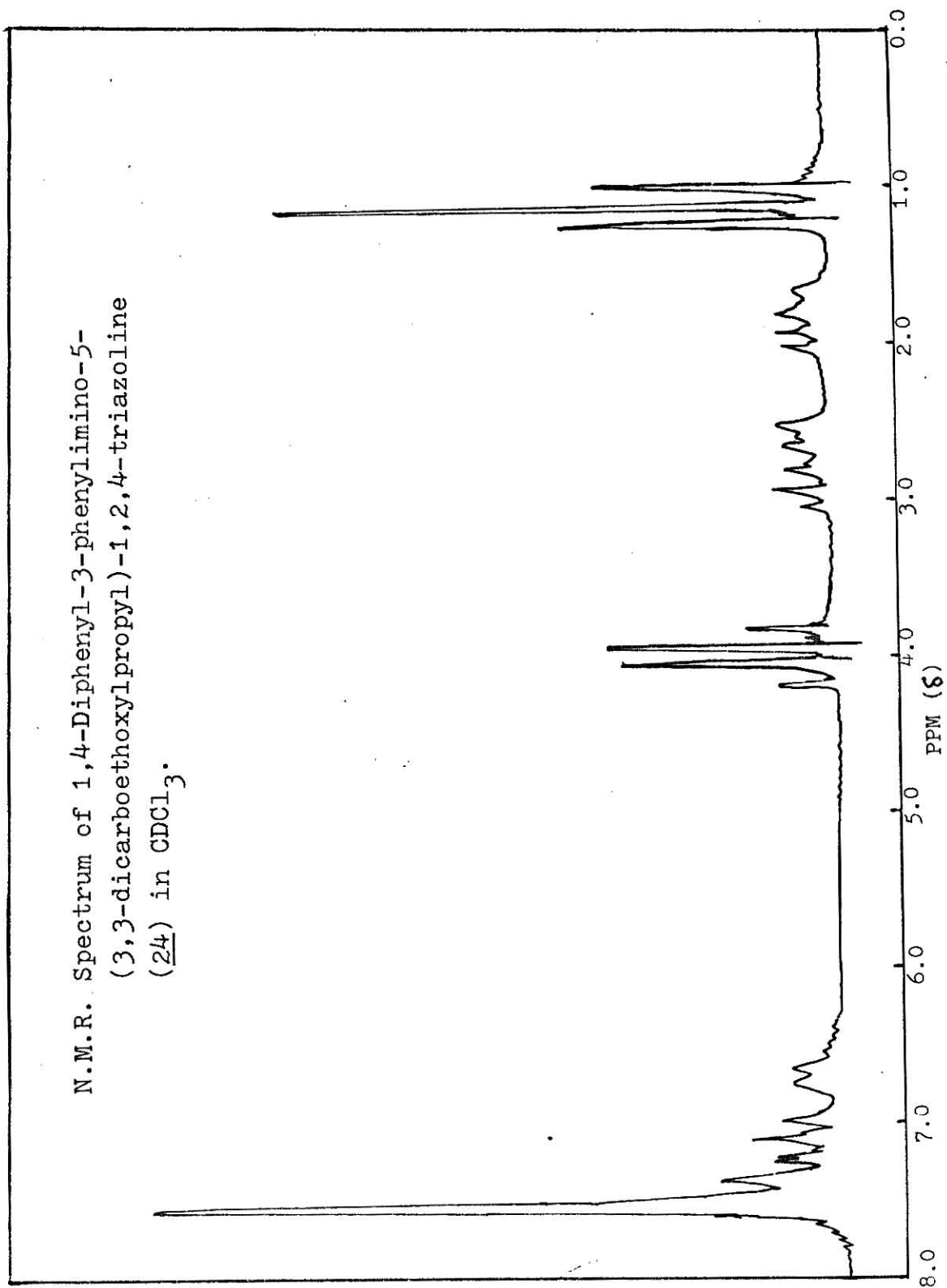
N.M.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(3-chloropropyl)-1,2,4-triazoline (22) in CDCl_3 .



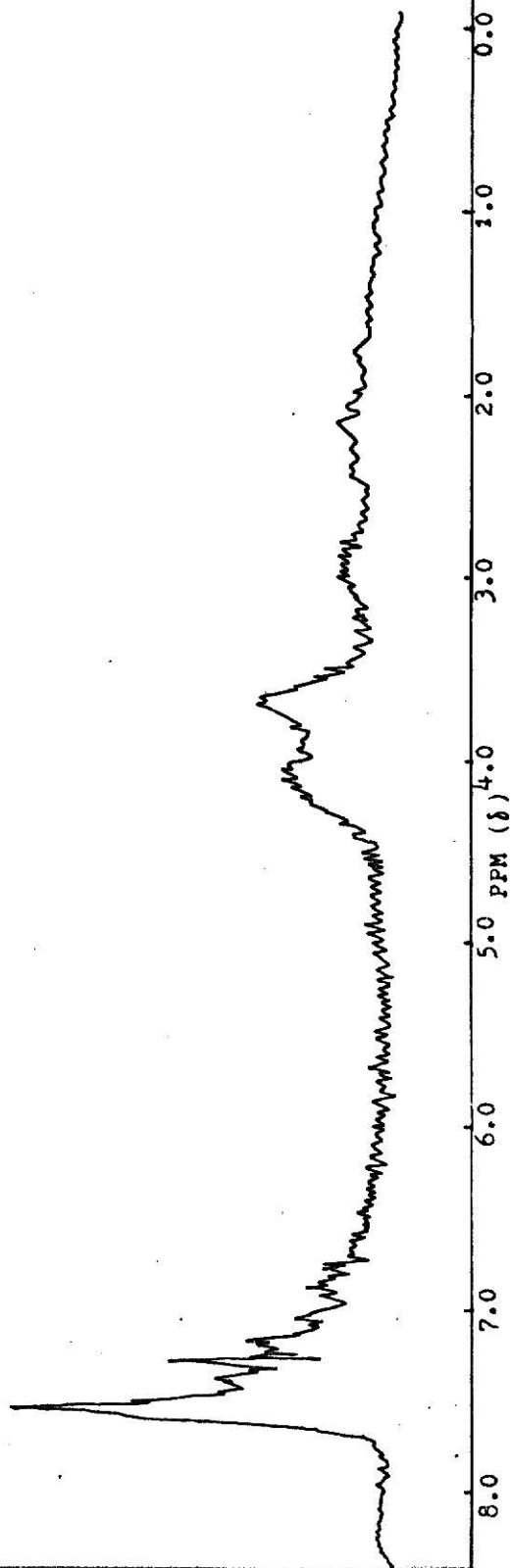
N.M.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(4-bromobutyl)-1,2,4-triazoline (23) in CDCl_3 .



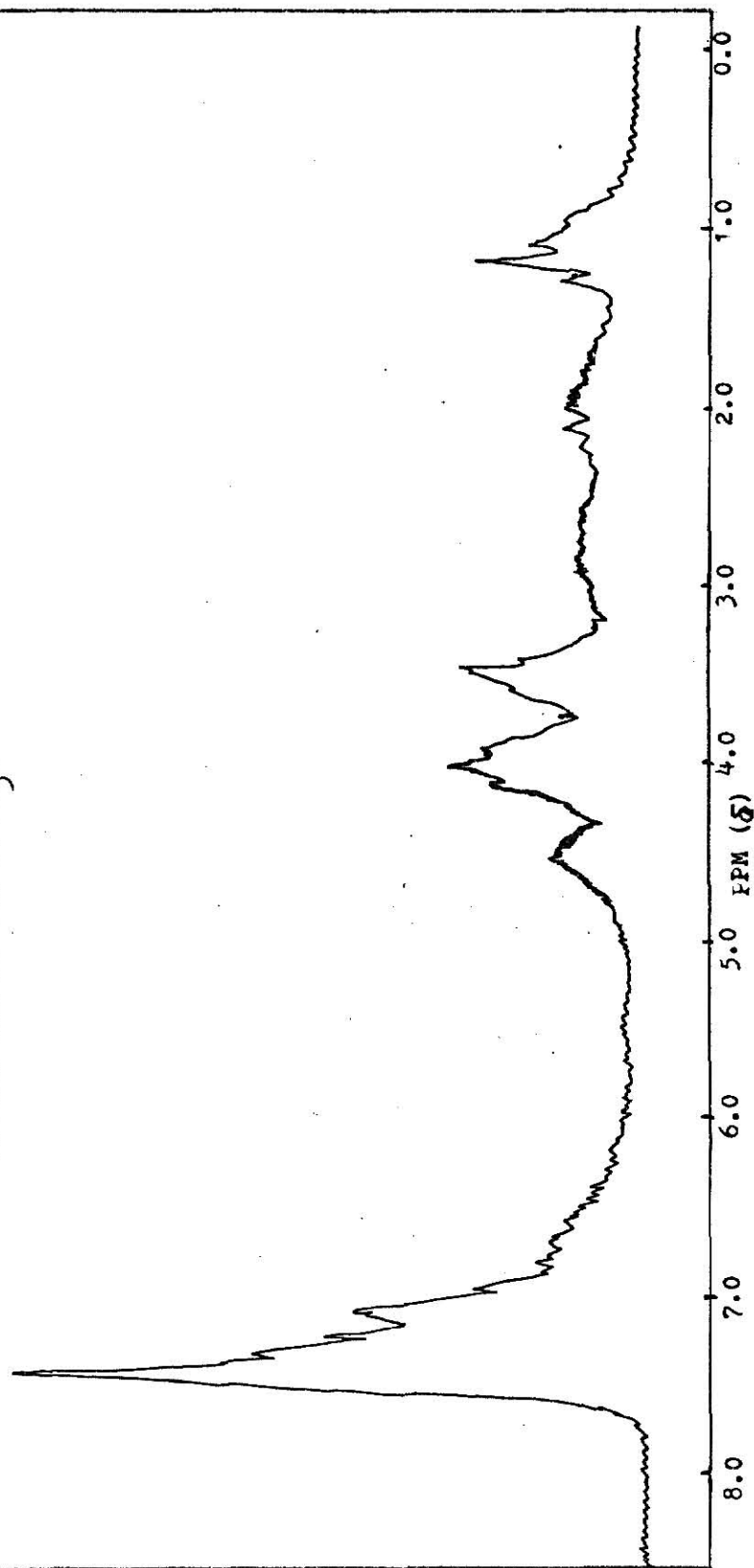
N.M.R. Spectrum of 1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline (24) in CDCl_3 .



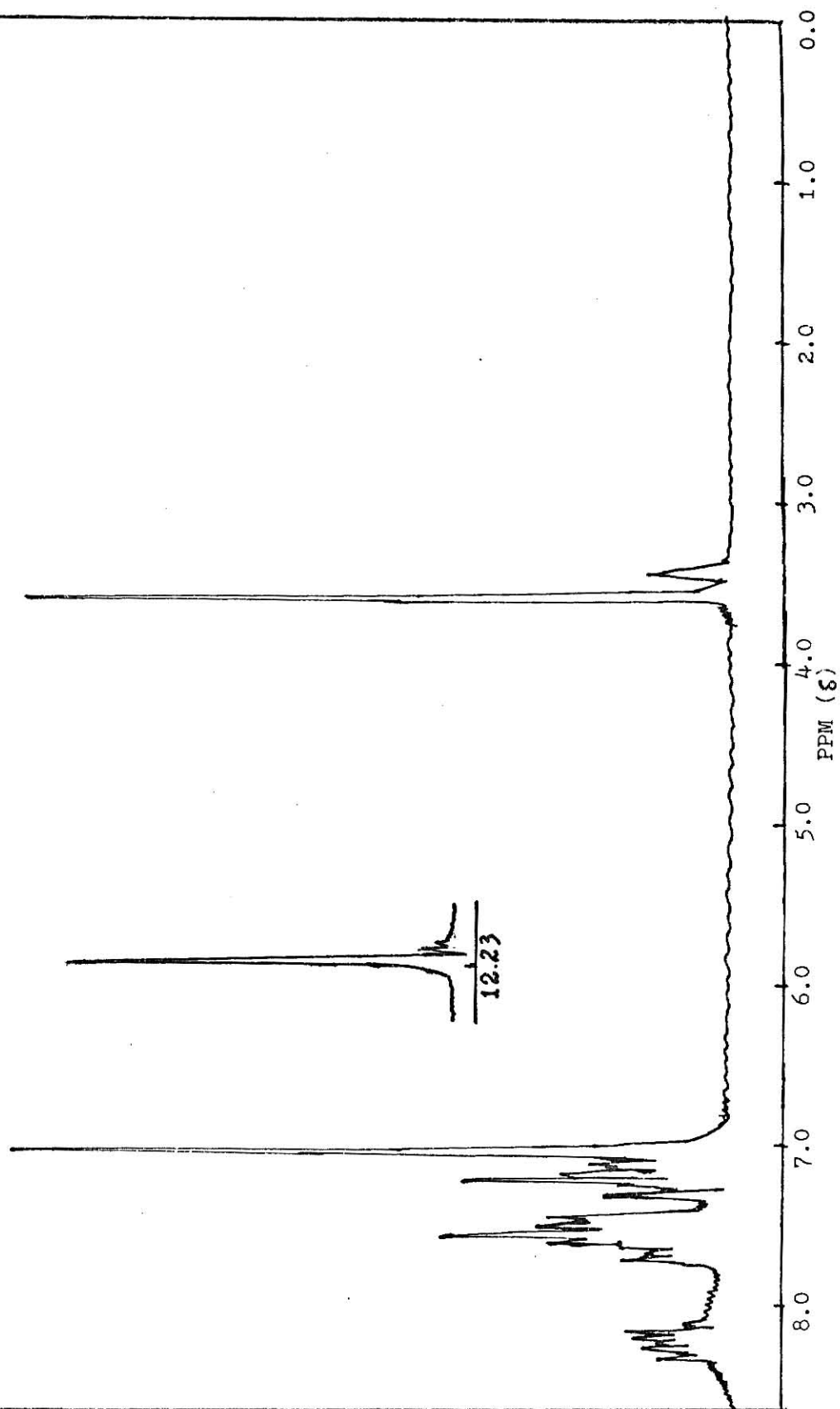
N.M.R. Spectrum of Resulting Product of Condensation Polymerization
of 1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-
1,2,4-triazoline (24, 0.001 mole) and Ethylene Glycol (0.01 mole)
in CDCl_3 .



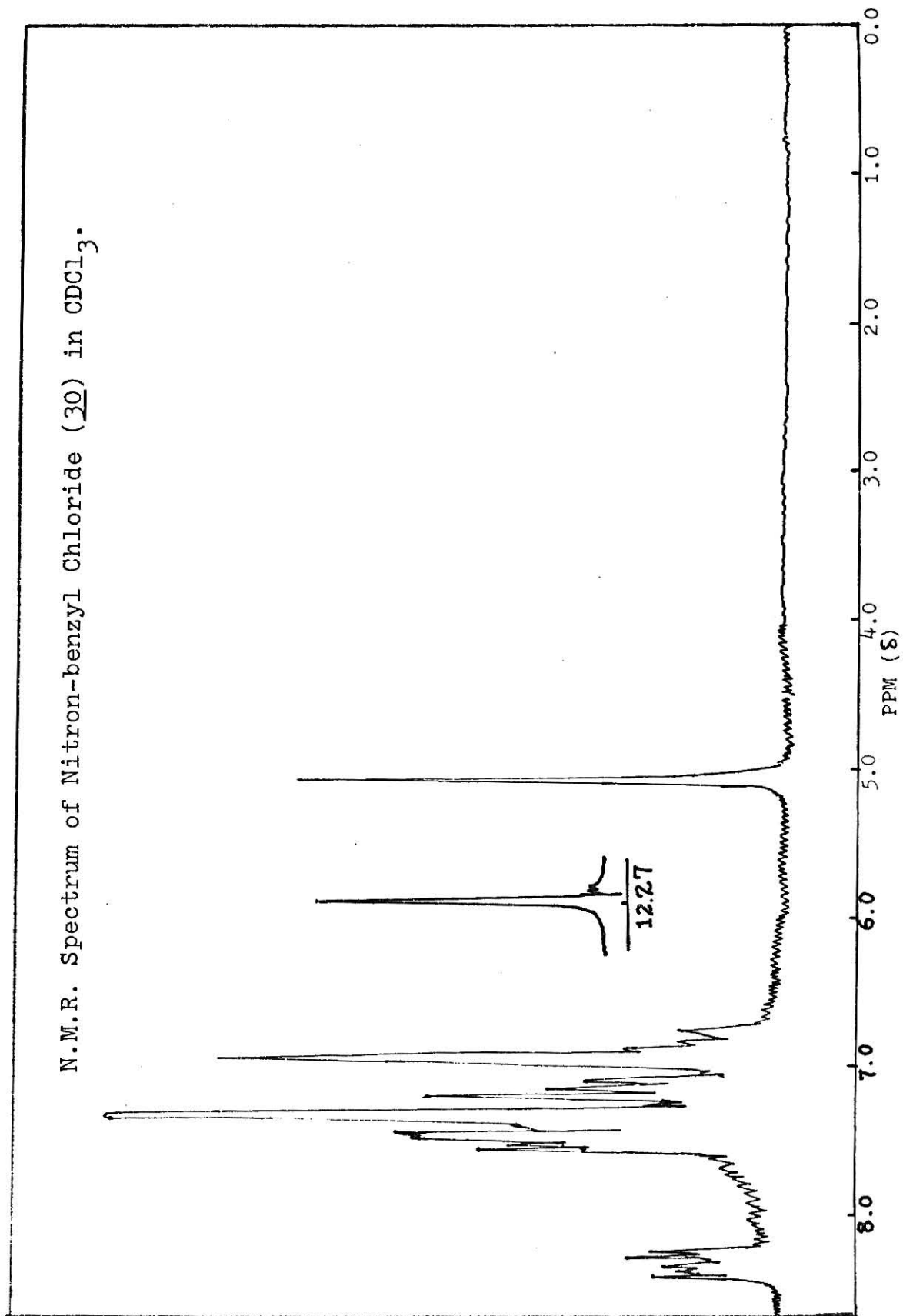
N.M.R. Spectrum of Resulting Product of Condensation Polymerization
of 1,4-Diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-
1,2,4-triazoline (24, 0.002 mole) and Ethylene Glycol
(0.002 mole) in CDCl_3 .



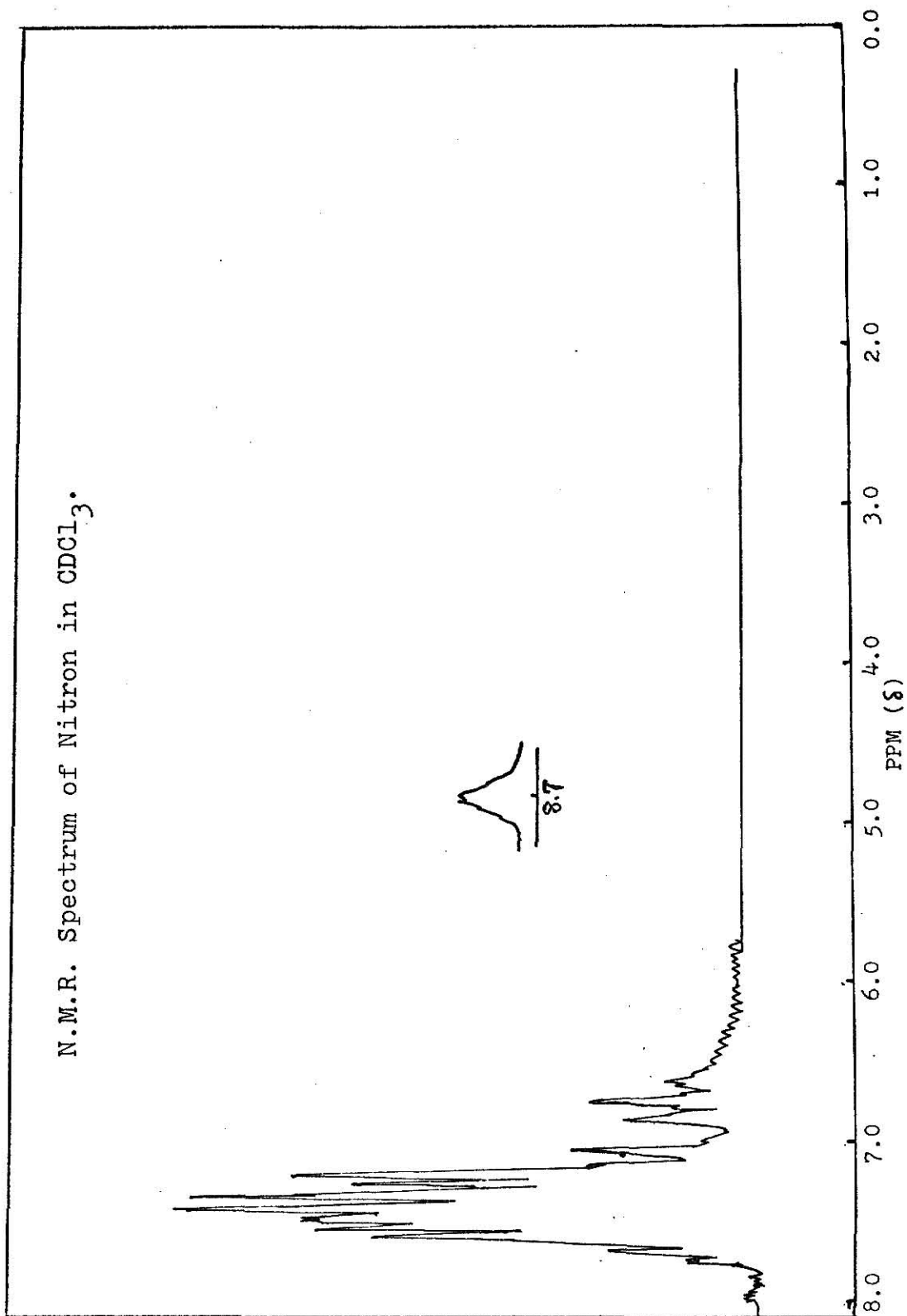
N.M.R. Spectrum of Nitron-methyl Iodide (22) in CDCl_3 .



N.M.R. Spectrum of Nitron-benzyl Chloride (30) in CDCl_3 .



N.M.R. Spectrum of Nitron in CDCl_3 .



Mass Spectral Data for
1,3-Diphenyl-2-aminophenylguanidine (11)

Peak m/e	Relative abundance (% of base peak)
302	55
287	0.5
211	15
210	6
209	11
208	13
196	11
195	86
194	15
108	91
93	100
92	60
91	28
79	17
78	61
77	5

Mass Spectral Data for
1,4-Diphenyl-3-phenylimino-5-(3-chloro-
propyl)-1,2,4-triazoline (22)

Peak m/e	Relative abundance (% of base peak)
390	0.34
389	0.45
388	1
353	80
210	1.6
208	1.5
196	10
195	50
194	10
176	100
93	35
92	25
91	10
78	10
77	50

Mass Spectral Data for
1,4-Diphenyl-3-phenylimino-5-(4-bromo-
butyl)-1,2,4-triazoline (23)

Peak m/e	Relative abundance (% of base peak)
367	100
208	0.59
194	17.6
158	35.3
104	1.18
93	53
77	59

Mass Spectral Data for
1,4-Diphenyl-3-phenylimino-5-(3,3-dicarbo-
ethoxypropyl)-1,2,4-triazoline (24)

Peak m/e	Relative abundance (% of base peak)
287	40
258	11
241	25
213	10
195	8
194	7
186	17
185	15
174	14
173	100
160	38
133	80
132	13
128	27
127	84
126	16
120	23
119	65
116	13
115	90

Mass Spectral Data for
Nitron-benzyl Chloride (30)

Peak m/e	Relative abundance (% of base peak)
405	3
404	10.3
403	30.2
312	3.3
311	3.7
208	2.2
195	20.8
194	100
180	3.3
167	2.5
126	2.4
118	4.1
105	2.2
104	3.3
103	4.1
93	1.9
92	4.9
91	40.6
78	3.6
77	32

Mass Spectral Data for

Nitron

Peak m/e	Relative abundance (% of base peak)
313	25
312	100
311	33
208	25
195	25
194	25
108	32
104	13
93	44
92	37
91	27
77	44

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ACKNOWLEDGEMENT

The author wishes to gratefully acknowledge the guidance and support of his major professor, Dr. Wayne C. Danen. His enthusiasm and direction have made a lasting impression upon the author. The author would also like to acknowledge the helpful suggestions and assistance provide by Dr. Clifton E. Meloan, Ravindra Arudi and other faculty members and graduate students at Kansas State University.

The author also would like to thank his wife, Hway-Ying, and his parents for their confidence and help.

The author thanks the State of Kansas and the Kansas Water Resources Research Institute for financial support including a research assistantship.

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He married Rita Hway-Ying (朱慧音) Chu on May 30, 1975. A son, Carl Kwan-Hsi (冠憲), was born on July 17, 1976.

In September 1974, he entered Kansas State University and began work toward the Master of Science degree.

THE SYNTHESIS OF NITRATE SELECTIVE RESINS

by

SHANG-JAW CHIOU

B. S., Cheng-Kung University, 1971

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

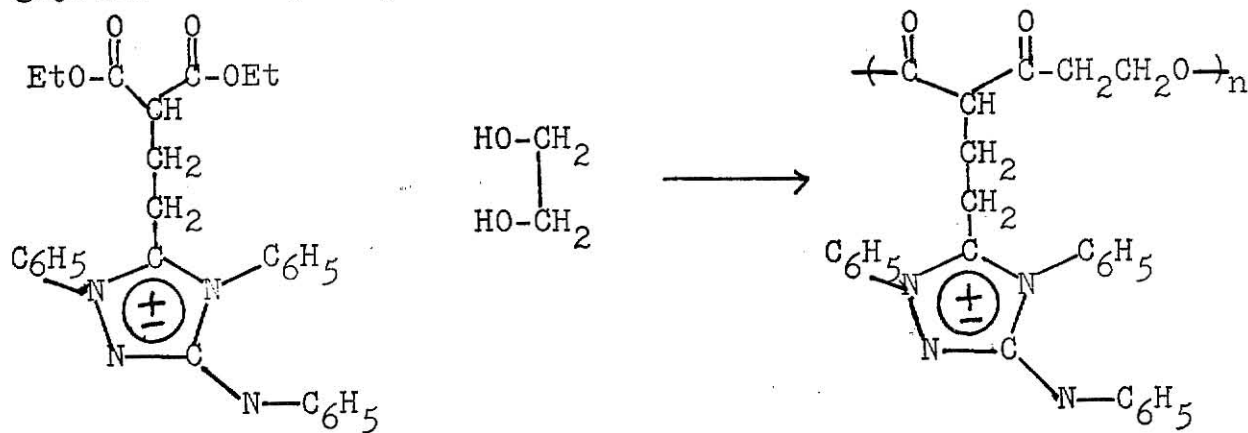
Kansas State University
Manhattan, Kansas

1977

ABSTRACT

Since first reported in 1945, human nitrate poisoning has been implicated in numerous illnesses and death of infants, especially those under three months of age. The disorder produced by excess nitrate is termed methemoglobinemia.

The objective of the research reported in this thesis was to synthesize resins to remove nitrate from water. Two separate nitrate-selective resins were synthesized and tested for nitrate removing capacity. The first resin was synthesized by condensation polymerization of 1,4-diphenyl-3-phenylimino-5-(3,3-dicarboethoxypropyl)-1,2,4-triazoline with ethylene glycol. The capacity of this resin to remove nitrate from



water was determined to be too low to be of commercial value. The low degree of polymerization made the synthesized resin partially soluble in water which contributed to the low capacity. The difficulty in synthesizing an insoluble polymer incorporating nitron prompted the preparation of such a resin by reacting nitron with commercial polyvinylbenzyl chloride (60/40 ortho/para isomer). A polymer was synthesized and the

capacity of removing nitrate was tested to be 62%. Since this polymer resin could be regenerated and used again, it offered a possibility for commercial development.

