

THE SYNTHESIS AND CHARACTERIZATION
OF
NITRAMINOTETRAZOLES

By

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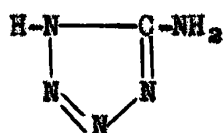
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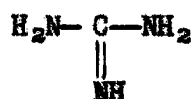
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INTRODUCTION

It has long been known that the nitric acid salts of certain amidic derivatives such as urea and guanidine can be dehydrated with the formation of nitrourea and nitroguanidine, respectively. In both instances the fundamental reaction appears to involve conversion of a substituted ammonium nitrate into a similarly substituted nitramine. The structural analogy which can be observed between 5-aminotetrazole (I) and guanidine (II) suggested the possibility that the nitric acid salt of the former might be converted by dehydration into a nitro-amino tetrazole.



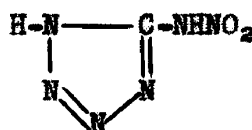
I



II

The first part of this thesis presents a study of the preparation of the nitric acid salt of 5-aminotetrazole and its conversion into 5-nitraminotetrazole. Although 5-nitraminotetrazole had already been prepared by the treatment of N-nitro-N'-aminoguanidine with nitrous acid and cyclization of the resulting guanyl azide (1), it was necessary to reconcile the recorded properties (1) of the nitraminotetrazole with those observed in this laboratory.

Tetrazole derivatives in which the hydrogen attached to the ring nitrogens has not been replaced generally behave as acidic substances (2,3). 5-Nitraminotetrazole (III)



III

is no exception and, in fact, behaves as a dibasic acid due to the presence of a second dissociable hydrogen in the nitramino group. It had been suggested without sufficient supporting evidence that the hydrogen of the nitramino group was responsible for the first dissociation (4,5). In order to establish which of the two hydrogens of 5-nitraminotetrazole was most easily dissociated, the preparation of nitraminotetrazoles in which one or the other hydrogen was replaced by a simple alkyl group was undertaken. Since 1-alkyl-5-aminotetrazoles (6) and 5-alkylaminotetrazoles (7) could be prepared by unequivocal syntheses, the nitration of compounds of these types by dehydration of their nitric acid salts was studied. The structures of the resulting compounds were supported by independent synthesis and by comparison of their physical properties including absorption spectra. The results of these studies are described in the second part of this thesis.

PART I
THE SYNTHESIS AND CHARACTERIZATION
OF 5-NITRAMINOTETRAZOLE

DISCUSSION

The similarity between 5-aminotetrazole and guanidine in certain structural features suggested that nitraminotetrazole might be prepared from 5-aminotetrazole much as nitroguanidine can be prepared from guanidine. Since it was first described by Thiele (7), 5-aminotetrazole has generally been looked upon as an acidic substance. Although the amino group can be acylated (8) and under suitable conditions diazotized (7), its salts with mineral acids are extensively hydrolyzed in aqueous solution.

5-Aminotetrazole nitrate (9) can be prepared by crystallization of 5-aminotetrazole from warm, moderately concentrated nitric acid. Presumably the amino group is involved in salt formation, although participation of the ring nitrogens cannot be excluded. Care must be taken in preparation of the nitrate since prolonged heating may result in considerable decomposition. The crude nitric acid salt may be recrystallized from water, presumably because the crude salt was not washed free of excess nitric acid.

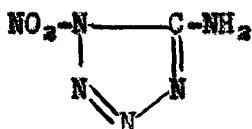
Dehydration of the nitrate with sulfuric acid at room temperature led to the formation of a nitraaminotetrazole. The reaction was quenched by addition of ice and water. After removal of most of the sulfate with barium carbonate, the product was extracted from the aqueous solution with ethyl ether. Crude nitraminotetrazole was obtained by evaporation of the ether at room temperature. On crystallization from

dioxane-benzene mixture a solvated product resulted. The loss in weight upon drying indicated that the crystalline material was either a trihydrate or a complex of two moles of nitraminotetrazole with one mole of dioxane and two moles of water. Elemental analysis of the solvated material supported the hydrated-dioxanate form. The presence of water in the solvated material was also established qualitatively by interaction with calcium carbide in anhydrous ether. Under these conditions a gas was evolved, probably acetylene, that gave a colorless precipitate when passed into an alcoholic silver nitrate solution. The anhydrous nitraminotetrazole did not cause gas evolution with calcium carbide under the same conditions. The water in the solvated product was estimated quantitatively by the Karl Fischer technique.

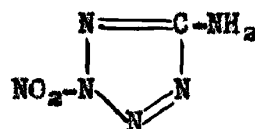
Analogy with the guanidine series suggested that 5-nitraminotetrazole (I) or 1-nitro-5-aminotetrazole (II) might be formed; however, 2-nitro-5-aminotetrazole (III) could not be excluded.



I

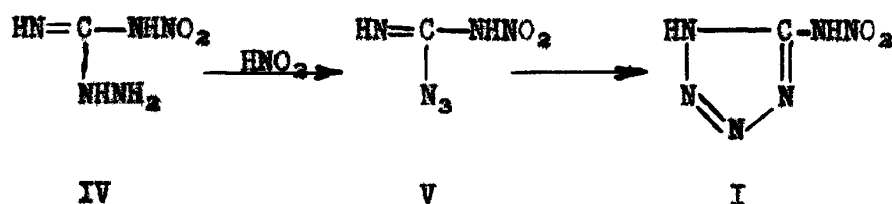


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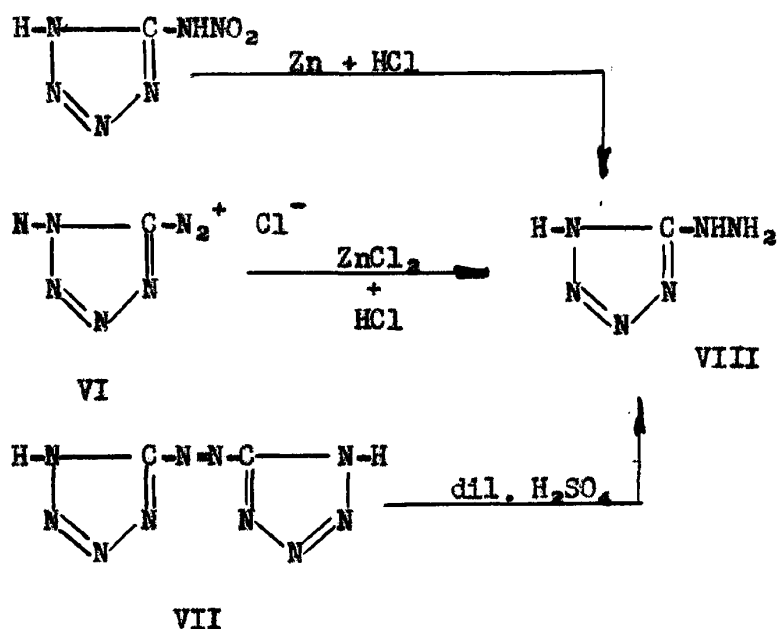


III

Lieber, *et al.* (1) have described a compound prepared by the interaction of N-nitro-N'-aminoguanidine (IV) and nitrous acid followed by cyclization of the resulting guanyl azide (V) to which they assigned the structure of 5-nitraminotetrazole (I). Assignment of structure was based on the reduction of the nitro compound to



5-tetrazolylhydrazine (VIII) which Thiele had prepared by reduction of diazotized 5-aminotetrazole (VI) (10) and by decomposition of 5-azotetrazole (VII) (11).



The nitraminotetrazole prepared from 5-aminotetrazole differed in certain respects from the compound prepared from nitroaminoguanidine. The former crystallized as a hydrated-dioxanate which lost its solvent of crystallization in three or four days at room temperature or in 8-10 hours at 60-70°C.; drying at higher temperature may be dangerous. (Although drying at 100°C. had been successful on several occasions, one sample of about 100 mg. exploded violently in the oven while being

dried at 100°C. completely pulverizing the glass vial containing the sample although the mouth of the vial was not stoppered.) Furthermore, the compound was not sensitive to shock even when struck very sharply with a hammer on an anvil. The product from nitroaminoguanidine was said to crystallize as an anhydrous solid which was sensitive to shock (1).

In order to resolve these differences the preparation of 5-nitraminotetrazole according to Lieber, et al. (1) was repeated. The product so prepared also crystallized as a hydrated-dioxanate and failed to exhibit sensitivity to shock. The previously reported shock-sensitivity may have been due to a trace of the azide as contaminant. The identity of the two products was confirmed by the preparation of several salts with organic bases. Lieber, et al. (12) had described an extensive series of such salts of 5-nitraminotetrazole. The salts with pyridine, diethylaniline, 2-aminopyridine, and ethylene diamine were found to be easily prepared. Salts prepared from the nitraminotetrazoles obtained by both procedures were identical as shown by the data recorded in Table I. In other respects, including ultraviolet absorption spectrum and potentiometric titration, the nitraminotetrazoles prepared by both methods were also identical. The ultraviolet absorption spectrum showed a maximum absorption at 277-276 mμ and a minimum absorption at 237 mμ for the solvated and anhydrous nitraminotetrazoles prepared by both methods.

On potentiometric titration 5-nitraminotetrazole behaves as a dibasic acid. The first dissociation has been described as that of a

completely dissociated strong acid (4) while the second dissociation has a pK value of 6.2. Although the results of the potentiometric titrations of solvated and anhydrous products prepared by both methods were identical, our data do not support the conclusion that the first dissociation is that of a completely dissociated strong acid. Its behavior is more comparable to that of a moderately strong dibasic acid such as oxalic acid. Our results indicate that pK_1 is 2.55, while our values for pK_2 , 6.05 and 6.04 for the two preparations, are in good agreement with the value observed by Lieber, et al. (4).

EXPERIMENTAL*

Preparation of 5-Aminotetrazole

A large scale adaptation of the preparation of 5-aminotetrazole (2) has been developed. All operations should be carried out in a good hood. Powdered dicyandiamide (328 gm.) and 528 gm. of powdered sodium azide were suspended in 800 ml. of water in a 5 l.-resin flask. The top of the flask was secured and fitted with an efficient reflux condenser, a stirrer, and a dropping-funnel. The flask was warmed to 50°C. in a water bath after which 680 ml. of concentrated hydrochloric acid was added with stirring, through the dropping-funnel at such a rate that the hydrazoic acid liberated refluxed very slowly. Addition of the acid required about an hour during which period the water bath was allowed to warm to 65-70°C. where it was maintained for six hours. The stirrer was stopped and crystallization of the product began soon after addition of the hydrochloric acid was complete. The reaction mixture was allowed to stand at room temperature overnight and then thoroughly chilled in an ice bath before the product was filtered by suction and washed with ice water. The crude product was recrystallized from 1500 ml. of boiling water from which it separated as the monohydrate. After drying at 110°C. anhydrous 5-aminotetrazole was obtained. Yield 610 gm., (90%) m.p. 206°C. with decomposition in a capillary (7).

* Carbon, hydrogen, and nitrogen analyses by Micro-Tech Laboratories, Skokie, Illinois.

Preparation of 5-Aminotetrazole Nitrate

Ten grams of 5-aminotetrazole were mixed with a solution of 16 gm. of concentrated nitric acid (sp. gr. 1.419) in 15 ml. of water. The mixture was warmed until homogeneous and then cooled immediately. (It is best to heat rapidly to attain complete solution of the 5-amino-tetrazole and to cool rapidly since prolonged heating causes decomposition and decreased yield.) The product crystallized immediately as colorless needles. It was recrystallized from water. Yield 15 gm. (97%) m.p. 178-179°C. with decomposition.

Analysis. Calculated for $\text{CH}_4\text{N}_6\text{O}_3$: C, 8.11; H, 2.72; N, 56.78. Found: C, 8.48; H, 2.91; N, 56.82.

Preparation of 5-Nitraminetetrazole

Finely divided 5-aminotetrazole nitrate (14.8 gm., 0.1 mole) was added in small portions with stirring to 20 ml. of cold concentrated sulfuric acid. The mixture should be cooled in an ice-water bath during the addition of the nitrate. After complete addition of the salt, the milky suspension was allowed to stand at room temperature until it became homogeneous.

The cold sulfuric acid solution was diluted with 250 ml. of water and ice after which slightly less than the amount of barium carbonate required to neutralize the sulfuric acid was added. The mixture was digested on a steam bath until carbon dioxide evolution ceased. The barium sulfate was removed by centrifugation and was washed twice by resuspension in hot water. The combined aqueous solutions were

evaporated to about 100 ml. under reduced pressure. The concentrate was shaken with five 100 ml. portions of ether. After evaporating the combined ethereal extracts almost to dryness in a current of air, the residue was treated with 250 ml. of benzene which caused the product to separate as colorless plates. When the crude product was recrystallized by dissolving in a small volume of 1,4-dioxane and adding a large excess of benzene, there was obtained 10.7 gm. (54%) of solvated 5-nitraminotetrazole which decomposed with a reddish flash at about 135°C. on the melting point block. In a capillary the product decomposed with gas evolution variously at 160-170°C.

The aqueous concentrate was further evaporated to about 10 ml. and extracted with three 50 ml. portions of ether. The ethereal extracts were treated as just described to give 0.8 gm. of solvated product of the same decomposition characteristics. The total yield of solvated product was 11.5 gm. (58%).

The presence of water in the solvated product was demonstrated qualitatively by the evolution of acetylene when calcium carbide was added to a solution of the material in dry ether. The gas evolved gave a colorless precipitate when passed into alcoholic silver nitrate solution. Anhydrous 5-nitraminotetrazole did not cause gas evolution under these conditions. Water was also estimated quantitatively with the Karl Fischer reagent.

Analysis. Calculated for $2\text{CH}_2\text{N}_6\text{O}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$: C, 18.8; H, 4.2; N, 43.7; H_2O , 9.4. Found: C, 19.4, 19.5; H, 4.2, 4.3; N, 43.1, 43.3; H_2O , 10.3.

Anhydrous 5-nitraminotetrazole was obtained by drying the hydrated dioxanate at 70°C. for 24 hours.

Analysis. Calculated for $2\text{CH}_2\text{N}_6\text{O}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$: $\text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$, 32.3. Found: 29.6.

When air-dried at room temperature for six days the weight loss was 30.5%.

Analysis of anhydrous 5-nitraminotetrazole. Calculated for $\text{CH}_2\text{N}_6\text{O}_2$: C, 9.2; H, 1.6; N, 64.6. Found: C, 9.6, 9.6; H, 1.7, 1.6; N, 64.7, 64.5.

Preparation of 5-Nitraminotetrazole from N-Nitro-N'-aminoguanidine

A quantity of 5-nitraminotetrazole was prepared from N-nitro-N'-aminoguanidine following the procedure of Lieber, et al. (1). The product was isolated as described by these authors and was found to be solvated.

Analysis of the hydrated dioxanate dried at 70°C. for 24 hours. Calculated for $2\text{CH}_2\text{N}_6\text{O}_2 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$: $\text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$, 32.3. Found: 29.1.

The yield of 5-nitraminotetrazole was improved substantially by the following modified procedure: To a cold solution of 9.4 gm. of sodium nitrite and 13.7 gm. of N-nitro-N'-aminoguanidine in 50 ml. of water there was added with cooling (below 15°C.) and stirring a cold mixture of 11.8 ml. of concentrated hydrochloric acid and 50 ml. of water. The mixture was allowed to come to room temperature and was filtered and evaporated to dryness in a current of air. The residue was extracted with three 100 ml. portions of ether. Evaporation of

the ether left a residue of crude nitroguanyl azide that was taken up in 100 ml. of 95% ethanol and treated with an aqueous-alcoholic solution of sodium acetate until precipitation of the sodium salt of 5-nitraminotetrazole was complete. The sodium salt was filtered and air-dried. Yield 13 gm. (75%); explodes at 210-220°C. on the melting point block.

A solution of 8.7 g. of sodium nitraminotetrazole in 30 ml. of water was treated with 25 ml. of 18% hydrochloric acid. The solution was extracted with five 100 ml. portions of ether from which 8.0 g. of solvated 5-nitraminotetrazole was isolated by concentration and precipitation with benzene. Concentration of the aqueous solution to 10 ml. and extraction with three 100 ml. portions of ether, followed by evaporation of the ether and precipitation with benzene gave 2 g. of the product. The combined fractions were recrystallized from a 1,4-dioxane-benzene mixture as before to give 9.5 g. of solvated product (86% from the sodium salt) showing the same decomposition characteristics previously described.

Preparation of Salts of 5-Nitraminotetrazole

Salts with pyridine, diethylaniline, 2-aminopyridine, and ethylene diamine were prepared from 5-nitraminotetrazole prepared by both procedures. The salts were prepared by dissolving 0.7 g. of solvated 5-nitraminotetrazole in ether and treating with an ethereal solution of the appropriate amine. The salt, which precipitated immediately, was filtered and recrystallized from an appropriate solvent.

A list of the salts prepared, the solvents used in recrystallization, melting points, and analyses are given in Table I.

TABLE I
SALTS OF 5-NITRAMINOTETRAZOLE WITH ORGANIC BASES

Amine	M.P. ^a	M.P. ^b	Formula	N% ^a	
				Calc'd	Found
Pyridine ^c	131-132	131-132	C ₆ H ₇ N ₃ O	46.18	46.70 46.70
N-Diethyl aniline ^d	124-125	124-125	C ₁₁ H ₁₇ N ₃ O	35.11	35.48 35.68
2-Amino- pyridine ^e	181-182	181-182	C ₆ H ₈ N ₃ O	49.99	49.88 50.17
Ethylene diamine ^f	239	239	C ₂ H ₁₀ N ₃ O	58.93	58.87 59.00

a. Salts of the 5-Nitraminotetrazole prepared from 5-Aminotetrazole. All compounds decompose at the melting point. Temperatures corrected.

b. Salts of the 5-Nitraminotetrazole prepared from N-nitro-N'-amino-guanidine (12). All compounds decompose at the melting point. Temperatures corrected.

c. Recrystallized from acetone.

d. Recrystallized from ethyl acetate.

e. Recrystallized from 1:1 isopropyl alcohol-ethyl alcohol.

f. Recrystallized from isopropyl alcohol-water mixture.

Ultraviolet Absorption Spectra of 5-Nitraminotetrazole

The ultraviolet absorption spectra of samples of 5-nitraminotetrazole prepared from 5-aminotetrazole and from N-nitro-N'-aminoguanidine were determined. Both anhydrous and solvated materials were examined. All spectra were observed in aqueous solutions of 1×10^{-4} to 1×10^{-6} molarity using a Beckman Model D-U Spectrophotometer. The results are given in Appendix I, and are represented graphically in Figures 1-2. No significant differences were apparent.

Potentiometric Titrations of 5-Nitraminotetrazole

Samples of anhydrous 5-nitraminotetrazole and of the solvated material prepared by both methods, from 5-aminotetrazole and from N-nitro-N'-aminoguanidine, were titrated potentiometrically using a Beckman Model G pH Meter. All titrations were carried out at $25^{\circ}\text{C}.$ [±] $0.02^{\circ}\text{C}.$ in an initial volume of 200 ml. Complete agreement was found for all compounds. Data and results are given in Appendix II, and are represented graphically in Figures 3-4.

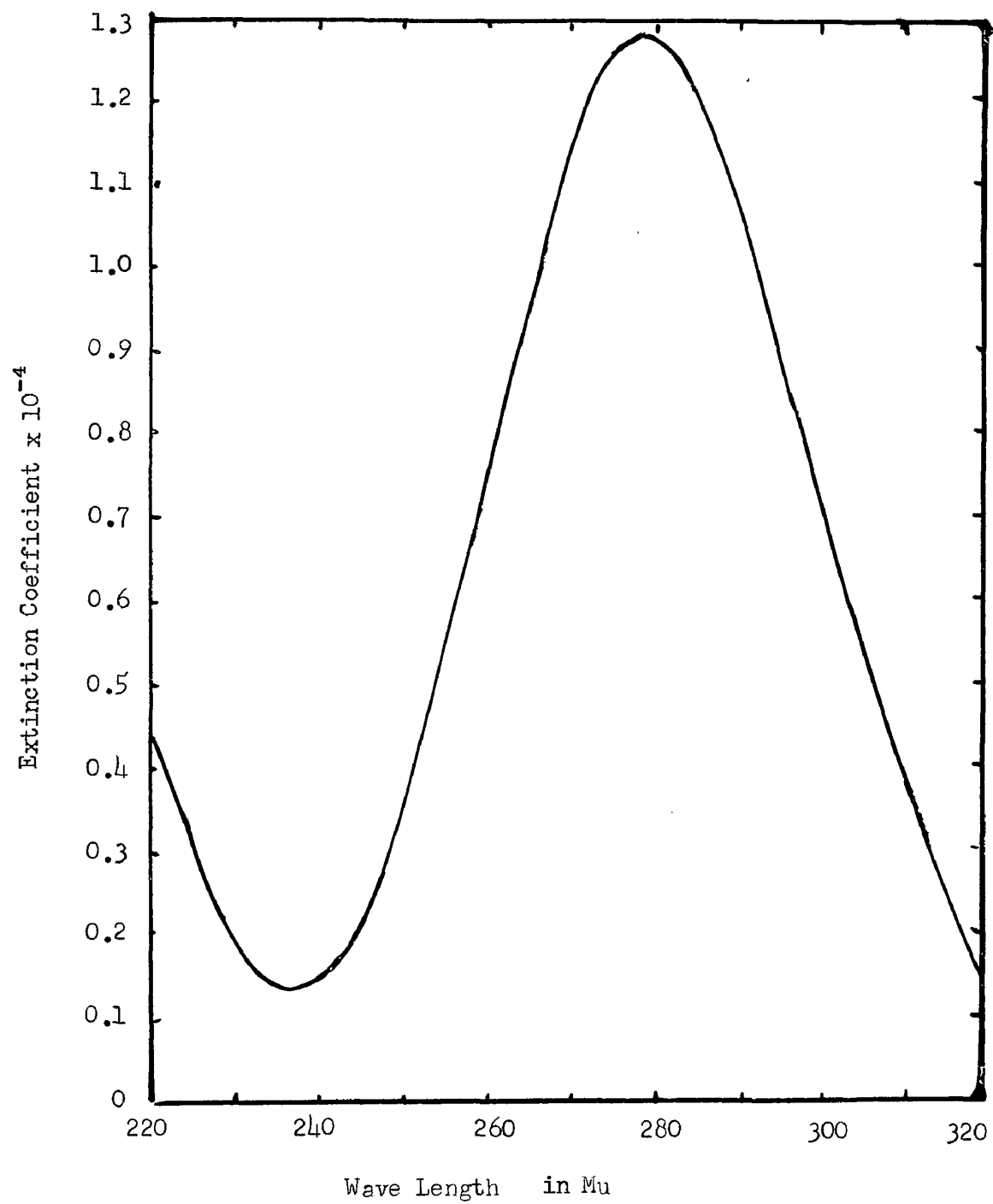


Figure 1. Ultraviolet Absorption Spectrum of 5-Nitramino-tetrazole (Anhydrous) Prepared from 5-Aminotetrazole.

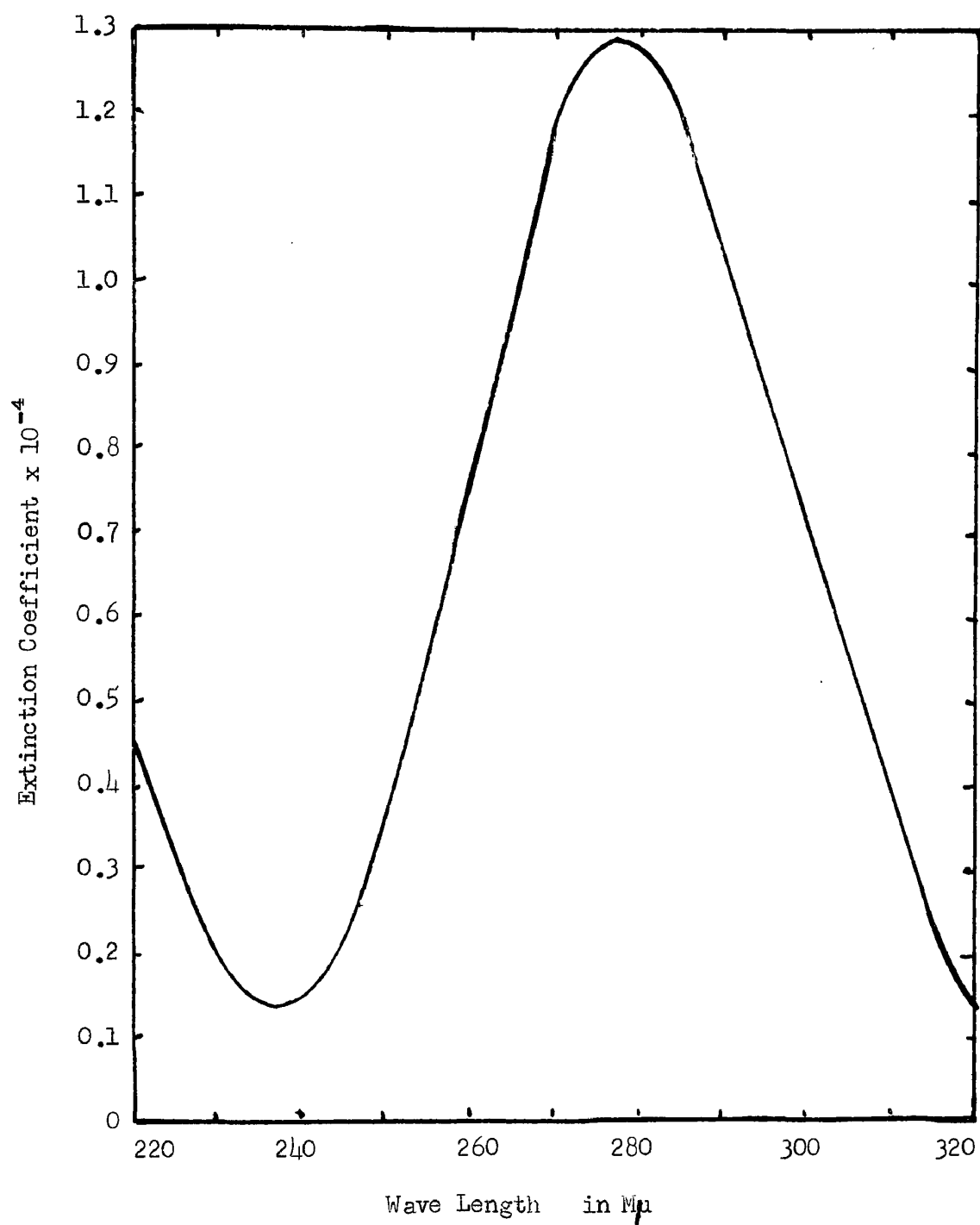


Figure 2. Ultraviolet Absorption Spectrum of 5-Nitroamino-tetrazole (Anhydrous) Prepared from N-nitro-N'-Aminoguanidine.

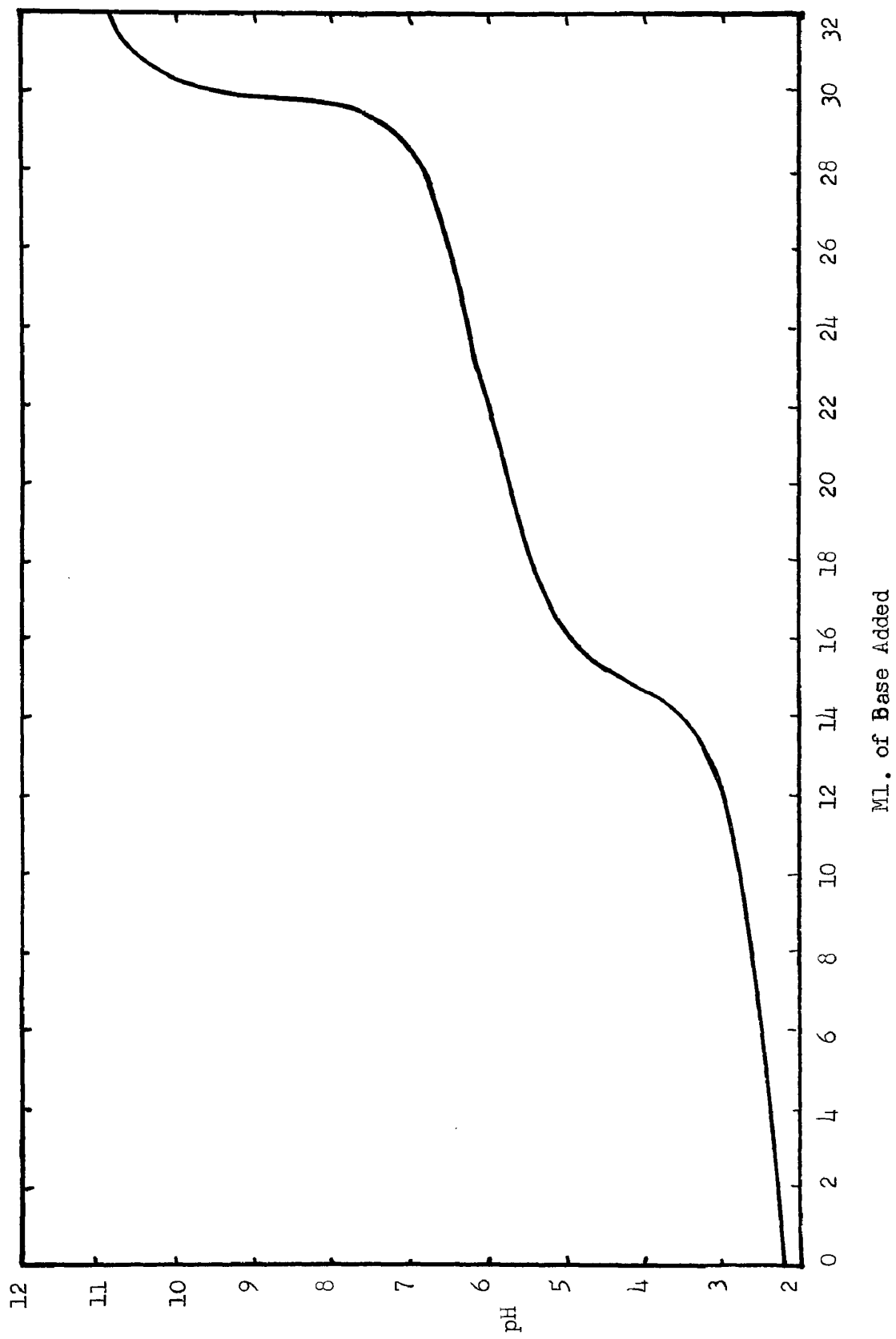


Figure 3. Potentiometric Titration Curve of 5-Nitraminotetrazole (Anhydrous) Prepared from 5-Aminotetrazole.

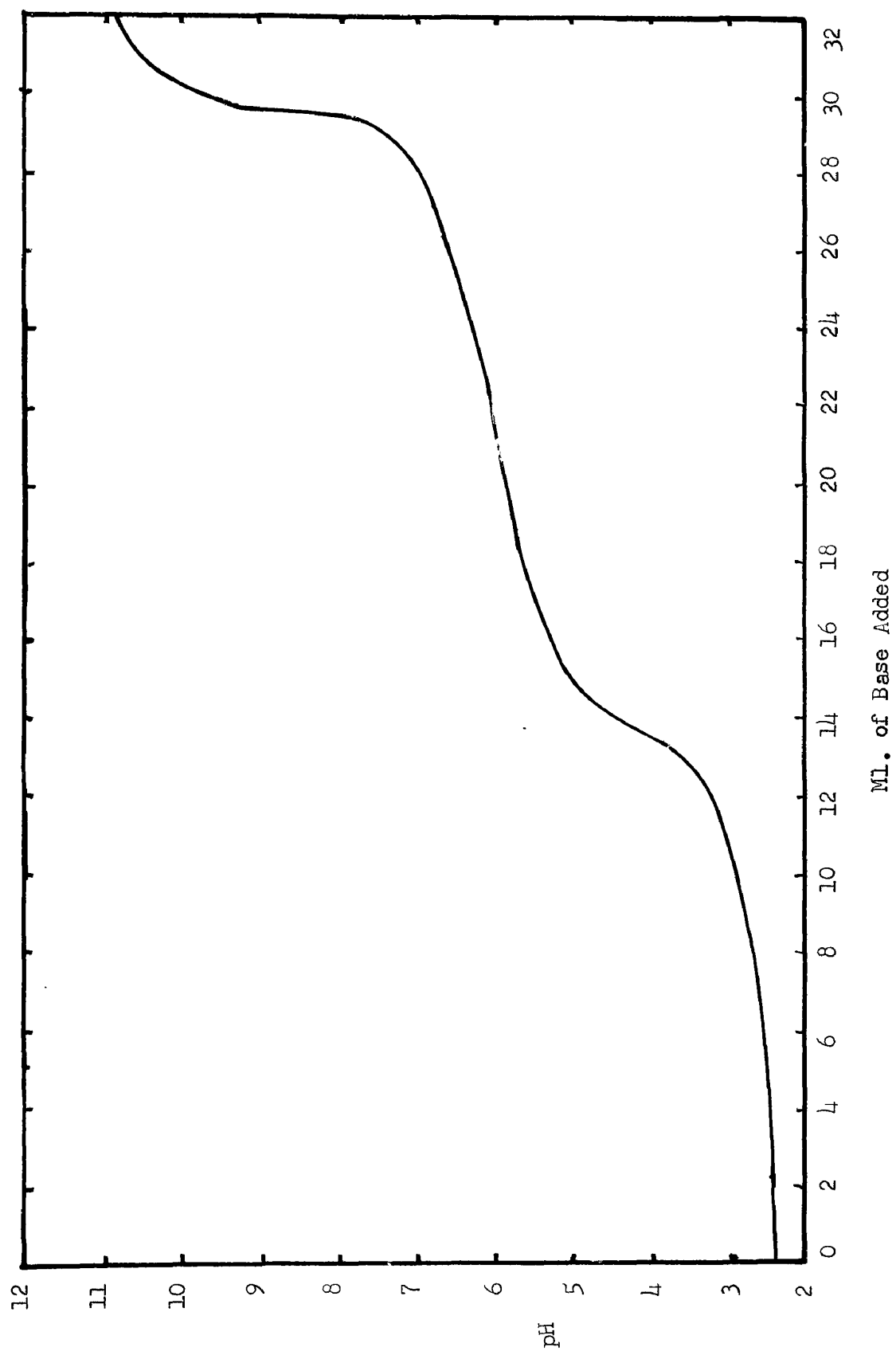


Figure 4. Potentiometric Titration, Curve of 5-Nitraminotetrazole Prepared from N-nitro-N'-aminoguanidine.

PART II

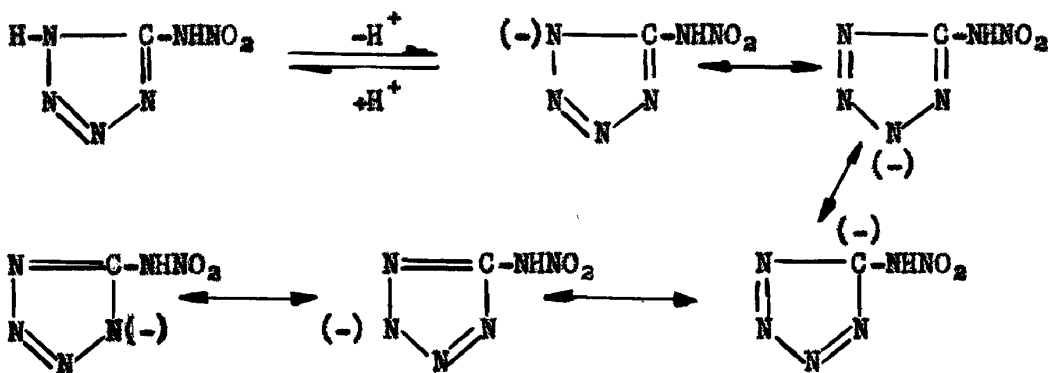
THE SYNTHESIS AND CHARACTERIZATION
OF
SOME ALKYL 5-NITRAMINOTETRAZOLES

DISCUSSION

In Part I 5-nitraminotetrazole was characterized as a dibasic acid with pK values of 2.5 and 6.1. Since the two hydrogen atoms in the structure do not necessarily occupy equivalent positions, it became of interest to determine whether the hydrogen attached to the tetrazole nucleus or the hydrogen of the nitramino group was responsible for the relatively strongly acidic character of the compound. Lieber, et al. (4,5) had assigned the stronger acid function to the hydrogen of the nitramino group. This conclusion was based on comparison of ultraviolet absorption spectra 5-nitraminotetrazole, and several of its salts, with the ultraviolet absorption spectra of N-nitro-N'-aminoguanidine and nitramide. Since corresponding data for other tetrazole derivatives were not cited and the differences in absorption maxima were quite large, it was thought that further work was needed to definitely establish which hydrogen was responsible for the first dissociation constant.

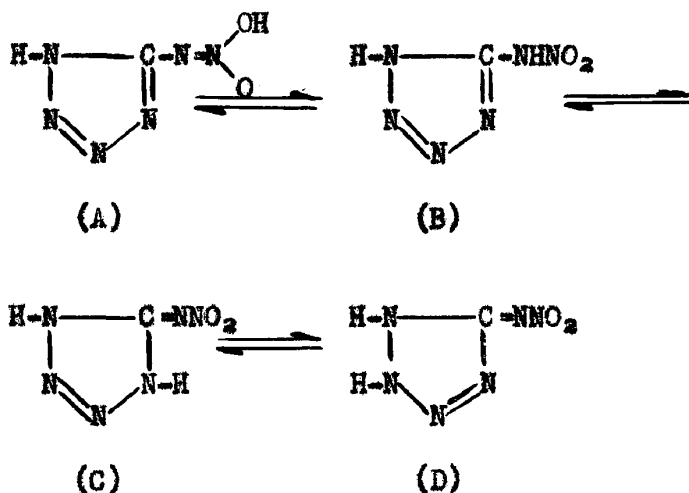
It has been shown that all tetrazole derivatives in which the hydrogen attached to the ring nitrogens has not been replaced by a substituent group may behave as acidic substances. An analogy has been developed between 5-substituted tetrazole derivatives, $R-CN_4H$, and carboxylic acids, $R-COOH$, and it has been shown in a rather extensive series of compounds that the nature of the group R affects the acidic dissociation constant of the 5-substituted tetrazoles in much the same way as it affects the dissociation constant of the carboxylic acids

(2,3,13). Baur (14) has shown that 5-aminotetrazole behaves as a weak acid ($pK=5.93$). The basicity of the amino group is largely masked by the acidic function of the tetrazole ring. Acetylation of the amino group in 5-aminotetrazole causes a marked increase in the acidic dissociation of the tetrazole group ($pK=4.53$ (15)). It would hardly be expected that the electron-withdrawing effect of the acetyl group would be sufficient to endow the amidic hydrogen with such a strongly acidic character. If the introduction of a nitro group in place of one of the amino hydrogens of 5-aminotetrazole is considered as comparable to an acylation with a strongly electron-withdrawing group, it could be anticipated that the effect upon the acidic dissociation of the tetrazole ring would be markedly greater than that produced by the acetyl group. In this event the nuclear hydrogen of the 5-nitraminetetrazole would become responsible for the relatively strong acidic dissociation of the compound. The stability of the tetrazole anion would be enhanced by resonance of the following type (Type 1). It would be observed that

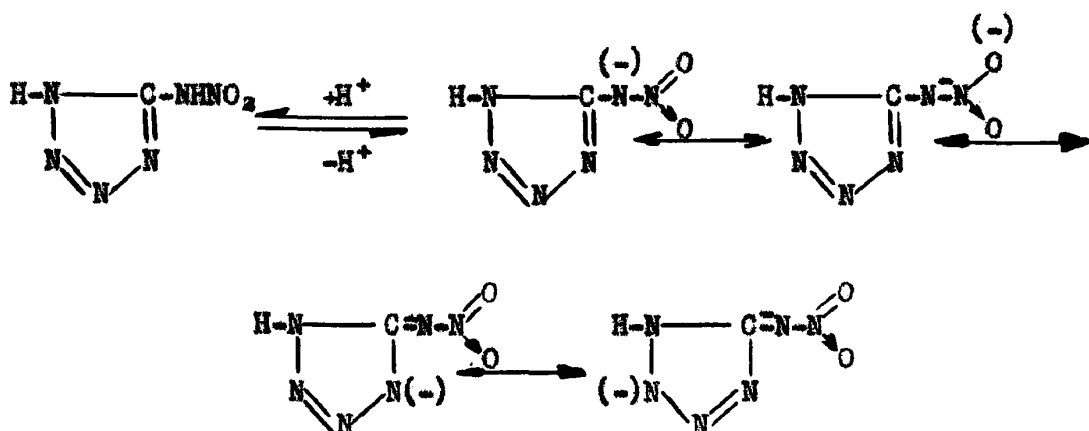


the resonance inherent in the nitro group would serve to increase the number of forms contributing to the resonance hybrid.

Dissociation and resonance of Type 1 assumes that the strongly acidic dissociation of 5-nitraminotetrazole involves the hydrogen of the tetrazole nucleus rather than the nitramino hydrogen. On the other hand, the possibility that 5-nitraminotetrazole may exist in several tautomeric forms cannot be neglected. It should be noted that both

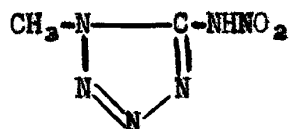


hydrogens occupy equivalent positions in tautomer (C) and that they would be indistinguishable in this instance. Assuming for the moment that the hydrogen of the nitramino group is the first to dissociate, the resulting tetrazole anion would be stabilized, not only by the resonance possibilities inherent in the ring system, but also by conjugation of the resonance of the ring structure with that of the nitro group (Type 2). As before, the resonance possibilities inherent in the nitro group would increase the number of forms contributing to the hybrid.

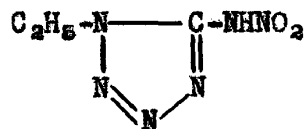


Type 2.

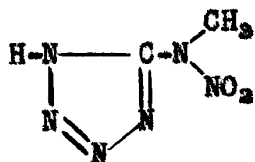
In order to determine which type of resonance predominated, two series of monoalkyl nitraminotetrazoles were prepared and their physical properties studied. The first series included 1-methyl-5-nitraminotetrazole (I) and 1-ethyl-5-nitraminotetrazole (II) in both of which dissociation and resonance of Type 1 can not exist, but dissociation and resonance of Type 2 is possible. The second series consisted of 5-methylnitraminotetrazole (III) and 5-ethylnitraminotetrazole (IV) in both of which dissociation and resonance of Type 2 is blocked while dissociation and resonance of Type 1 is unhindered.



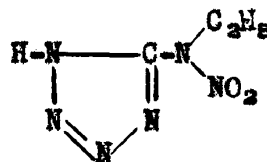
(I)



(II)



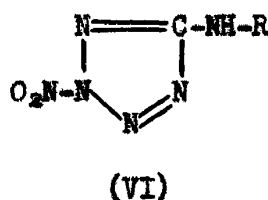
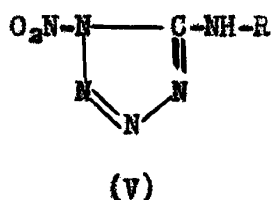
(III)



(IV)

Quantities of 1-methyl-5-aminotetrazole, 1-ethyl-5-aminotetrazole, 5-methylaminotetrazole, and 5-ethylaminotetrazole were prepared according to the methods of Garbrecht and Herbst (3,6). The corresponding alkyl 5-nitraminotetrazoles were prepared by dehydration of the appropriate alkyl 5-aminotetrazole nitrates by adaptations of the procedure described in Part I. No attempt was made to find the optimum conditions for the preparation and isolation of the alkyl nitraminotetrazoles.

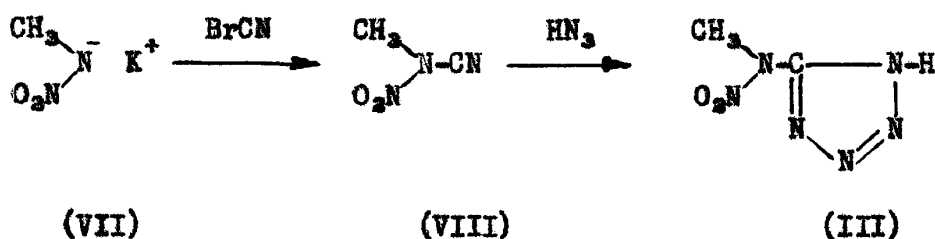
The nitration of the 5-alkylaminotetrazoles could have taken place on the tetrazole ring in positions 1- or 2- with the formation of a 1-nitro-5-alkylaminotetrazole (V) or a 2-nitro-5-alkylaminotetrazole (VI). Therefore, it was necessary to prove the structure of the product



formed by direct nitration of at least one 5-alkylaminotetrazole. Two courses were available: first, synthesis of a 5-alkylnitraminotetrazole by an independent method; second, reduction of a 5-alkylnitraminotetrazole and characterization of the reduction product.

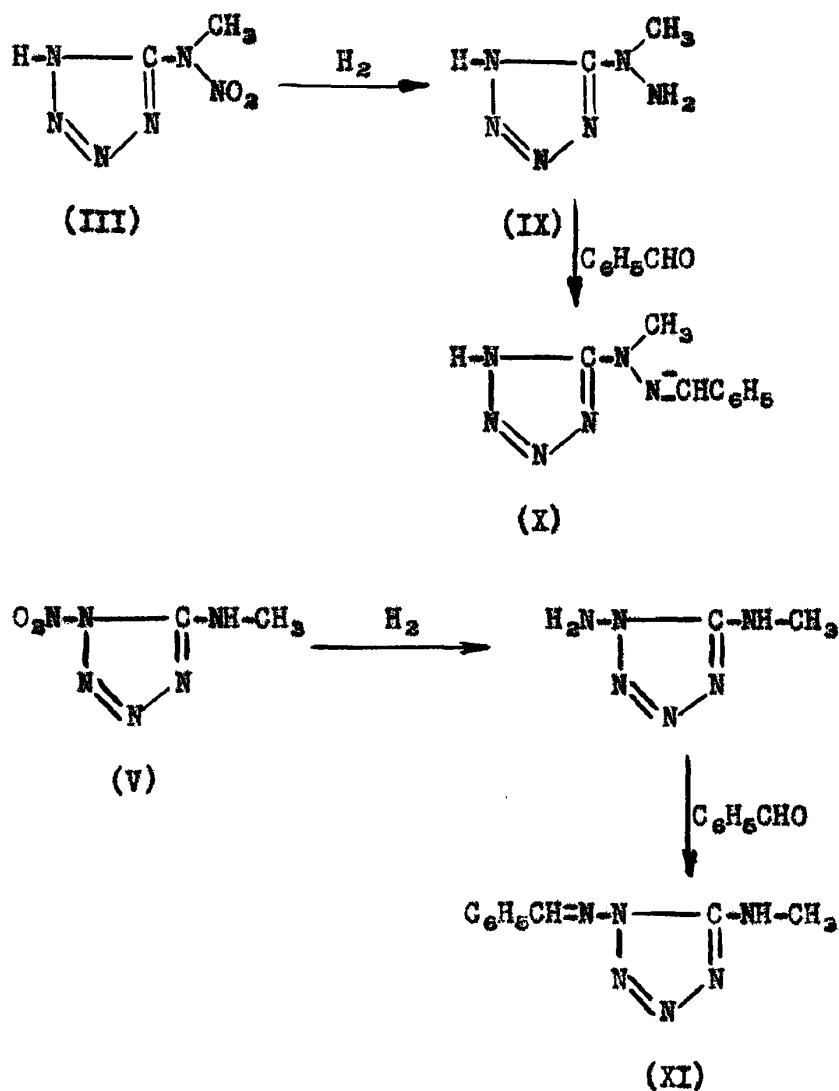
The independent synthesis was carried out as follows: Potassium methylnitramine (VII), prepared according to Franchimont (16), was treated with cyanogen bromide to form methylnitrocyanamide (VIII). After interaction of methylnitrocyanamide and hydrazoic acid,

5-methylnitraminotetrazole (III) was isolated. This was shown to be identical with the product formed by direct nitration of 5-methylamino-tetrazole by comparison of melting points, mixed melting point,



infrared absorption spectra and characterization as a salt with 2-amino-pyridine.

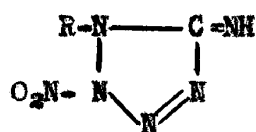
Reduction of 5-nitraminotetrazole has been shown to lead to the formation of 5-tetrazolyl hydrazine (I). The analogous reduction of 5-methylnitraminotetrazole would be expected to lead to N-methyl-N-(5-tetrazolyl)-hydrazine (IX). Subsequent condensation of the hydrazine with benzaldehyde should result in an acidic hydrazone (X). A similar series of reactions with the corresponding 1-nitro-5-methylaminotetrazole should give a neutral or basic product (XI). Similarly, a neutral product would be anticipated upon the analogous treatment of 2-nitro-5-methylaminotetrazole (VI). The product actually obtained upon reduction of the nitro 5-methylaminotetrazole was 5-methylaminotetrazole probably formed by hydrogenolysis of the intermediate hydrazine (IX). Therefore, the reduction of the nitro 5-methylaminotetrazole did not help to establish the position of nitration.



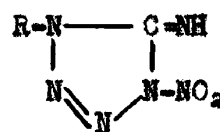
The structure of the corresponding 5-ethylnitraminetetrazole obtained by nitration of 5-ethylaminotetrazole was assumed to be correctly assigned by analogy in the method of preparation and because of the similarity of its properties.

Although the structure of 1-methyl- and 1-ethyl-5-nitraminetetrazole (I,II) was not supported by an independent synthesis, it seemed reasonable to assume that nitration of 1-methyl- and 1-ethyl-5-aminotetrazole

would follow a course analogous to that established for other 5-amino-tetrazoles. This assumption finds support in the properties of the compounds as evidenced particularly by their dissociation constants and ultraviolet absorption spectra. The 1-alkyl-5-nitraminetetrazoles are moderately strong monobasic acids ($pK = 2.7-2.8$). If nitration is assumed to take place on one of the ring nitrogens, a 1-alkyl-2-(or 4)-nitro-5-iminetetrazoline (XIIa,b) would result. Resonance



XIIa



XIIb

stabilisation of the tetrazole anion would probably be very minor in such a structure as compared with the resonance stabilization of the 5-nitramino compounds (Type 2).

The apparent dissociation constants for the alkyl nitraminetetrazoles were determined and the results are presented in Table II. A typical titration curve for each series is presented in Figures 5-6. The 1-alkyl-5-nitraminetetrazoles were found to have a pK value of about 2.7, while the 5-alkylnitraminetetrazoles have a pK value of about 2.9. The results demonstrate that resonance of either Type 1 or Type 2 could explain the relatively strong acidic dissociation of 5-nitraminetetrazole.

Since the hydrogen, both of the tetrazole nucleus and of the nitramino group, is dissociated with equal ease it became necessary

TABLE II
APPARENT DISSOCIATION CONSTANTS OF ALKYL 5-NITRAMINOTETRAZOLES

Compound	Apparent	
	pK_1	$K \times 10^3$
5-Nitraminotetrazole	2.55 (a.)	2.8 (a)
1-Methyl-5-nitraminotetrazole	2.72	1.9
1-Ethyl-5-nitraminotetrazole	2.74	1.8
5-Methylnitraminotetrazole	2.88	1.3
5-Ethylnitraminotetrazole	2.86	1.4

(a.) The values for the second apparent dissociation are
 $pK = 6.04$, $K = 9.1 \times 10^{-7}$.

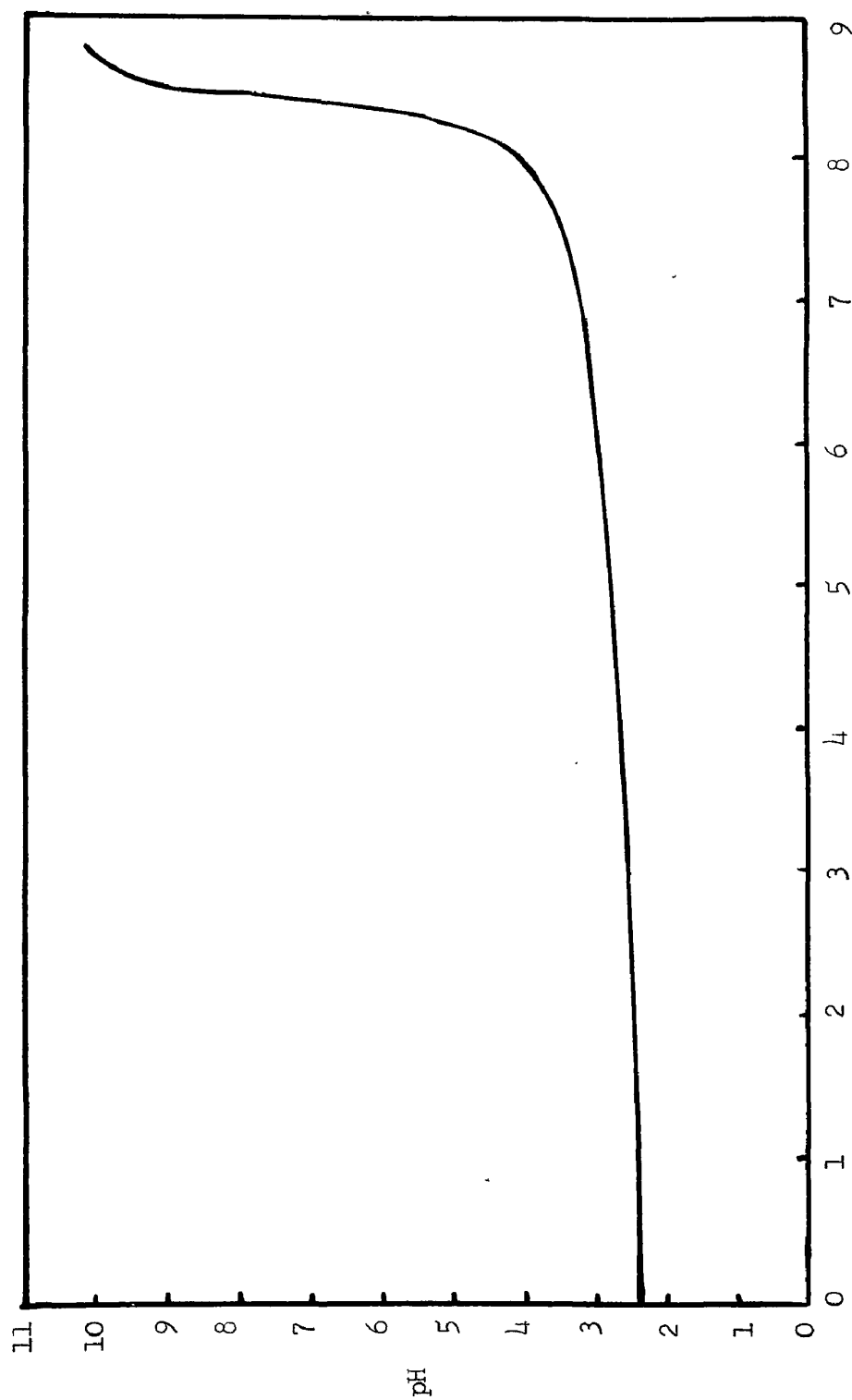


Figure 5. Potentiometric Titration Curve of 1-Methyl-5-nitraminotetrazole.

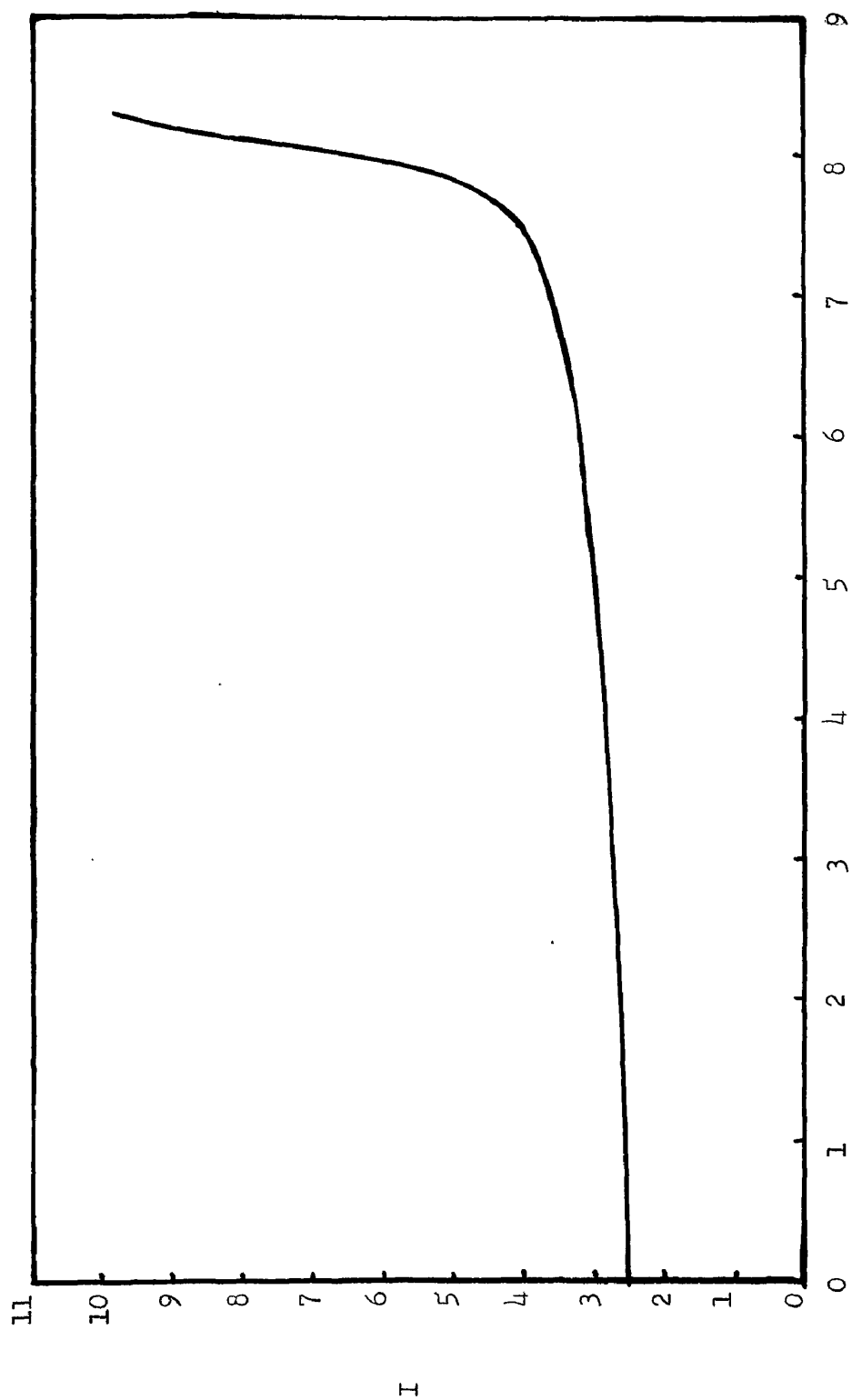
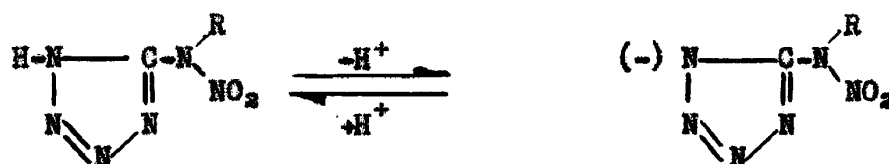


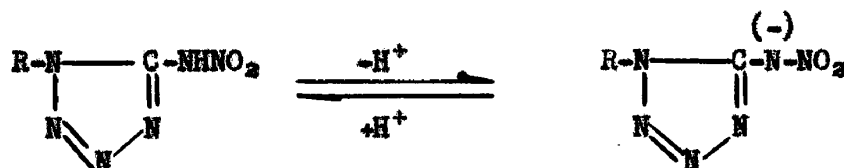
Figure 6. Potentiometric Titration Curve of 5-Methylnitraminotetrazole.

to employ methods other than measurement of dissociation constants to differentiate between dissociations of Type 1 and Type 2. 5-Nitraminotetrazole exhibits a strong absorption in the ultraviolet with a maximum at 277-278 mμ and a minimum at 237 mμ (See Part I). The 5-alkyl-nitraminotetrazoles should be almost completely dissociated in aqueous solution to the resonance hybrid of a tetrazole anion of Type 1. On



Type 1.

the other hand the 1-alkyl-5-nitraminotetrazoles should be almost completely dissociated with formation of the resonance hybrid of a tetrazole anion of Type 2. It seemed reasonable to anticipate that resonance



Type 2.

hybrids of Types 1 and 2 would show characteristic differences in their ultraviolet absorption. Furthermore, since both tetrazole anions are formed from relatively strong acids, conversion to the sodium or potassium salts should cause little, if any, change in the ultraviolet absorption. These considerations were realized. Both 1-methyl- and 1-ethyl-5-nitraminotetrazole (Figures 7-8) and their potassium salts

exhibited a maximum at 277-278 μ and a minimum at 237 μ . On the other hand, 5-methylnitramino- and 5-ethylnitraminotetrazole (Figures 9-10) and their potassium salts exhibited a maximum at 246 μ ; the minima were out of the range of the instrument. It will be noted that the maxima and minima of 5-nitraminotetrazole, 1-methyl- and 1-ethyl-5-nitraminotetrazole, both as such and as potassium salts, are identical. From this it may be concluded that the hydrogen of the nitramino group of 5-nitraminotetrazole is involved in the first dissociation of this compound (Dissociation and resonance of Type 2).

The ultraviolet absorption spectrum of 5-nitraminotetrazole (Figure 11) was also determined in a large excess of potassium hydroxide solution. In this solution 5-nitraminotetrazole exists as a doubly charged ion. It was found that the general shape of the curve is the same as observed for 5-nitraminotetrazole in aqueous solution, and for the 1-alkyl-5-nitraminotetrazaes. The maximum absorption is shifted 6 μ to 271-272 μ , and the minimum absorption is also shifted toward shorter wave lengths, 232 μ , as compared with 237 μ . These results indicate that the resonance of Type 2 is modified by the presence of the second negative charge, but is still the predominating resonance. The four alkyl-nitraminotetrazaes were further characterized by preparation of their potassium salts, their salts with 2-aminopyridine, and by their infrared absorption spectra. The infrared absorption spectra are shown in Figures 12-15. Since infrared absorption spectra for only a very few tetrazole derivatives have been published, it is not feasible to attempt to assign particular significance to absorption maxima at this time.

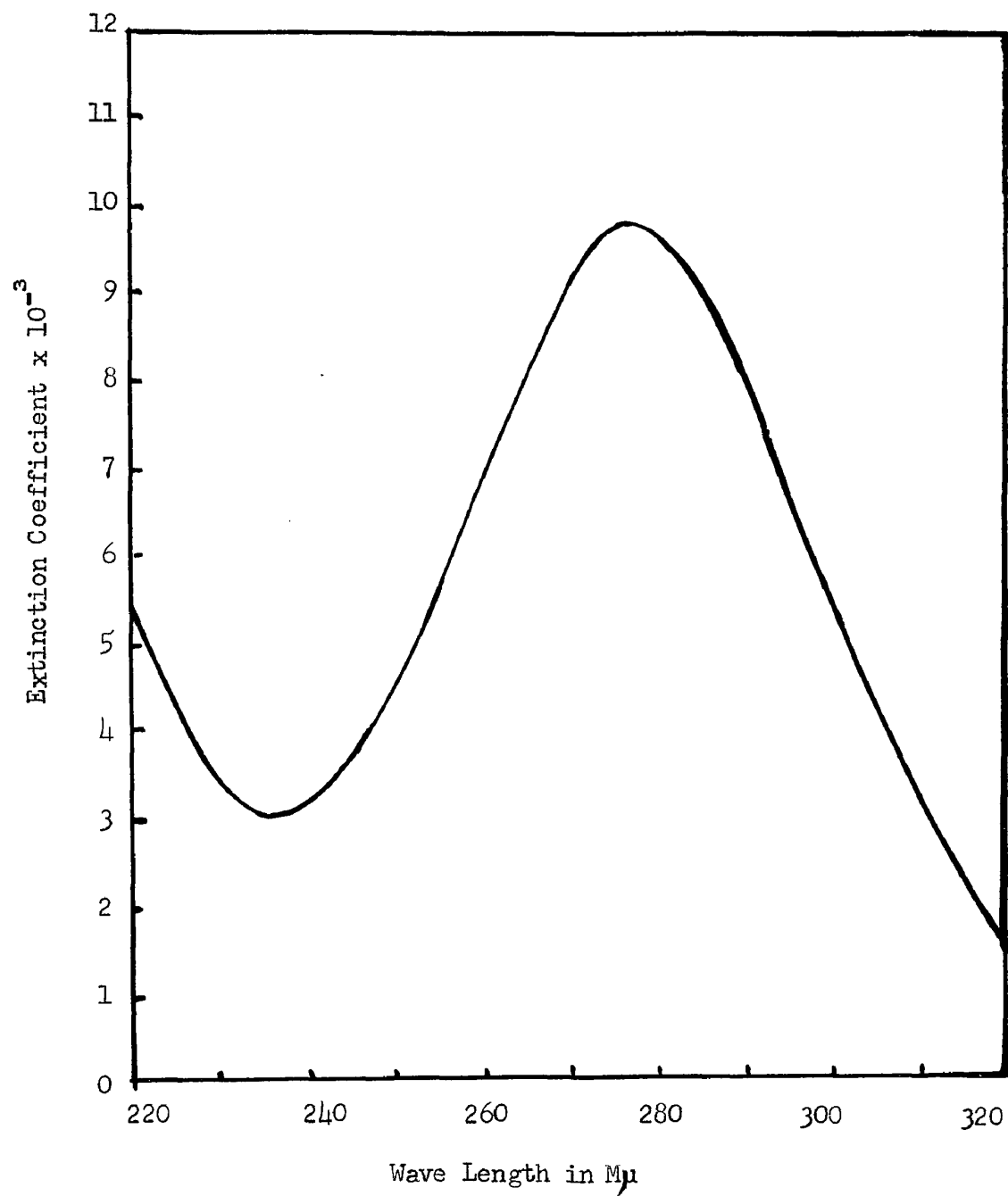


Figure 7. Ultraviolet Absorption Spectrum of 1-Methyl-5-nitraminotetrazole.

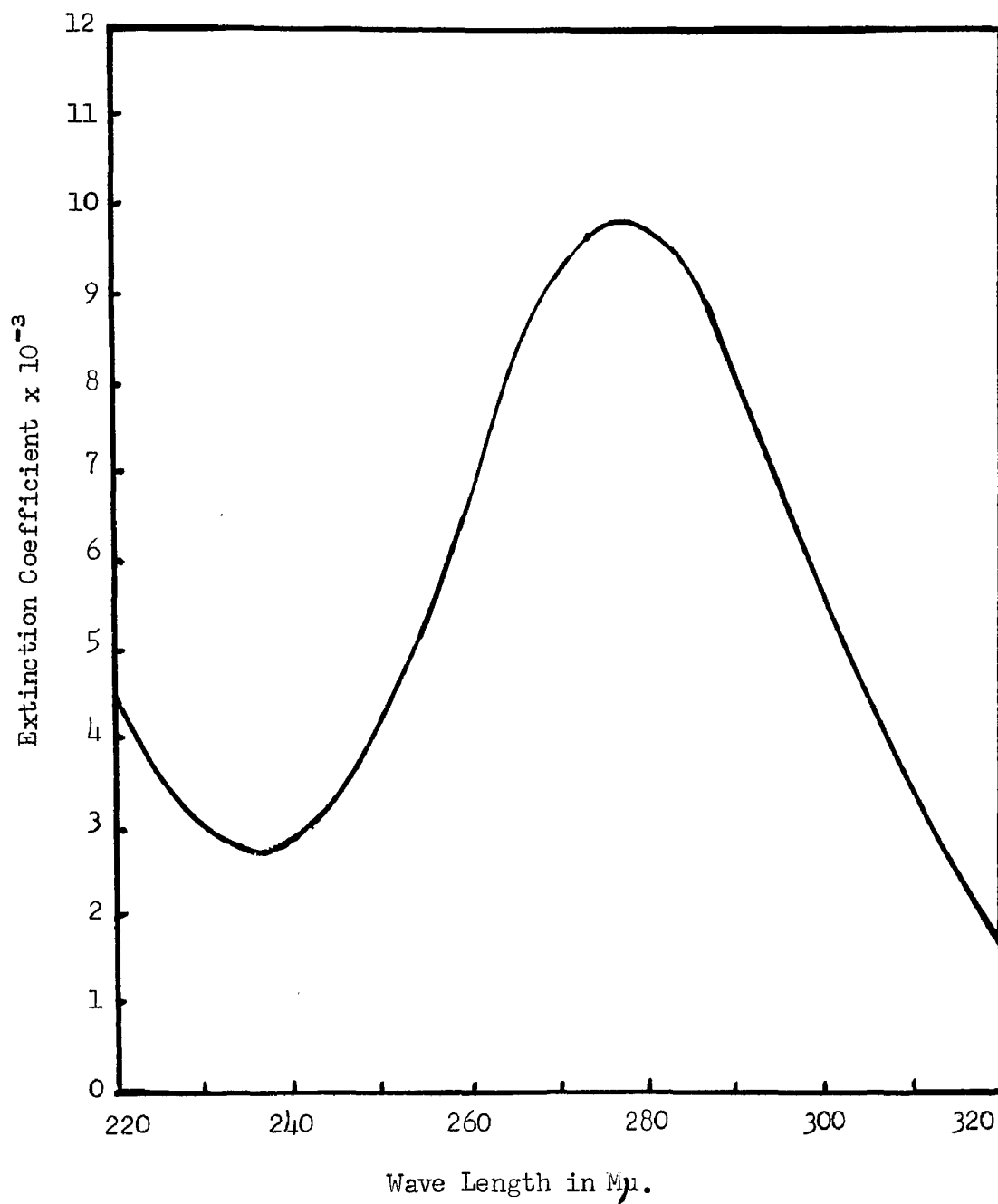


Figure 8. Ultraviolet Absorption Spectrum of 1-Ethyl-5-nitraminotetrazole.

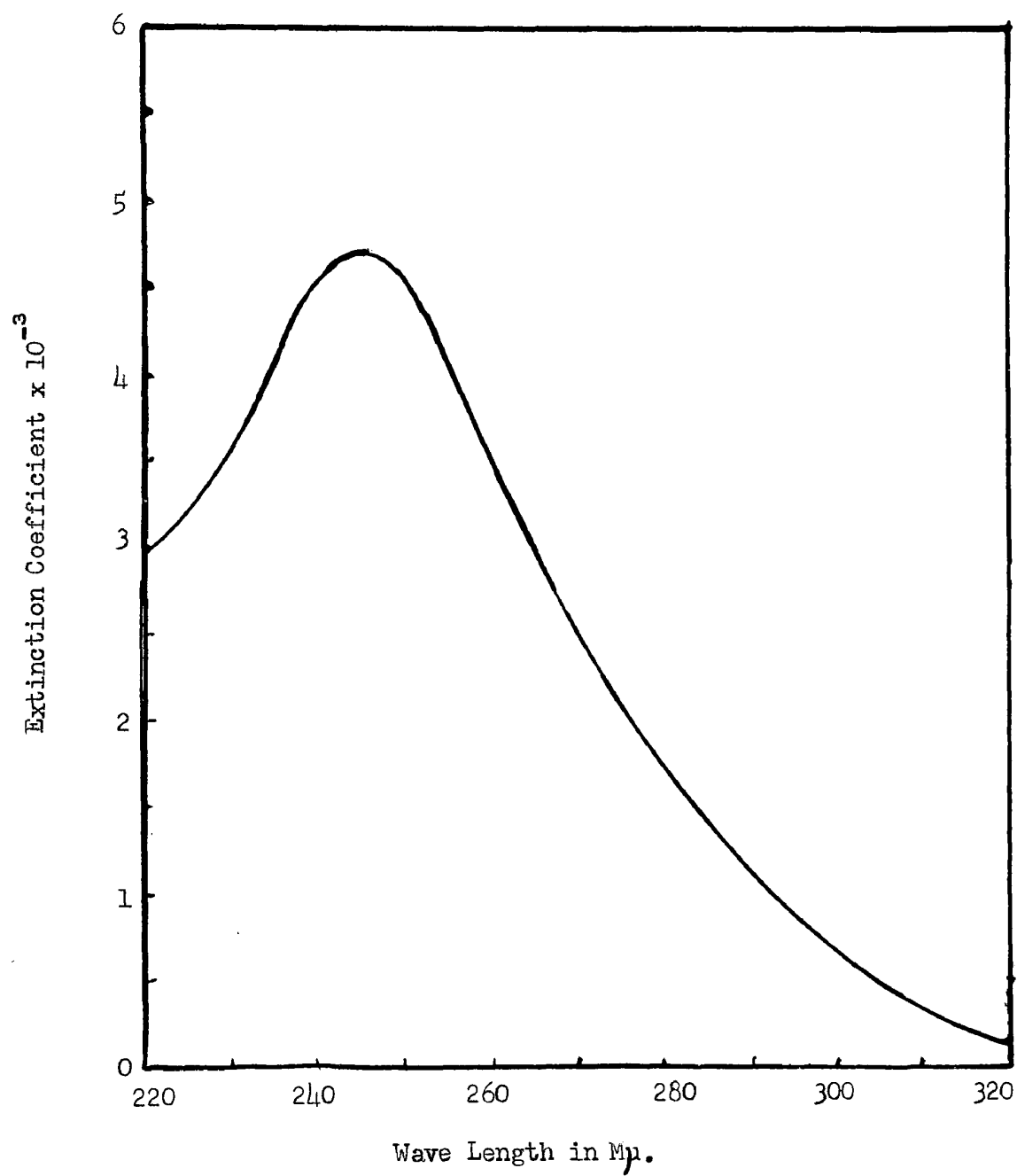


Figure 9. Ultraviolet Absorption Spectrum of 5-Methylnitraminetetrazole.

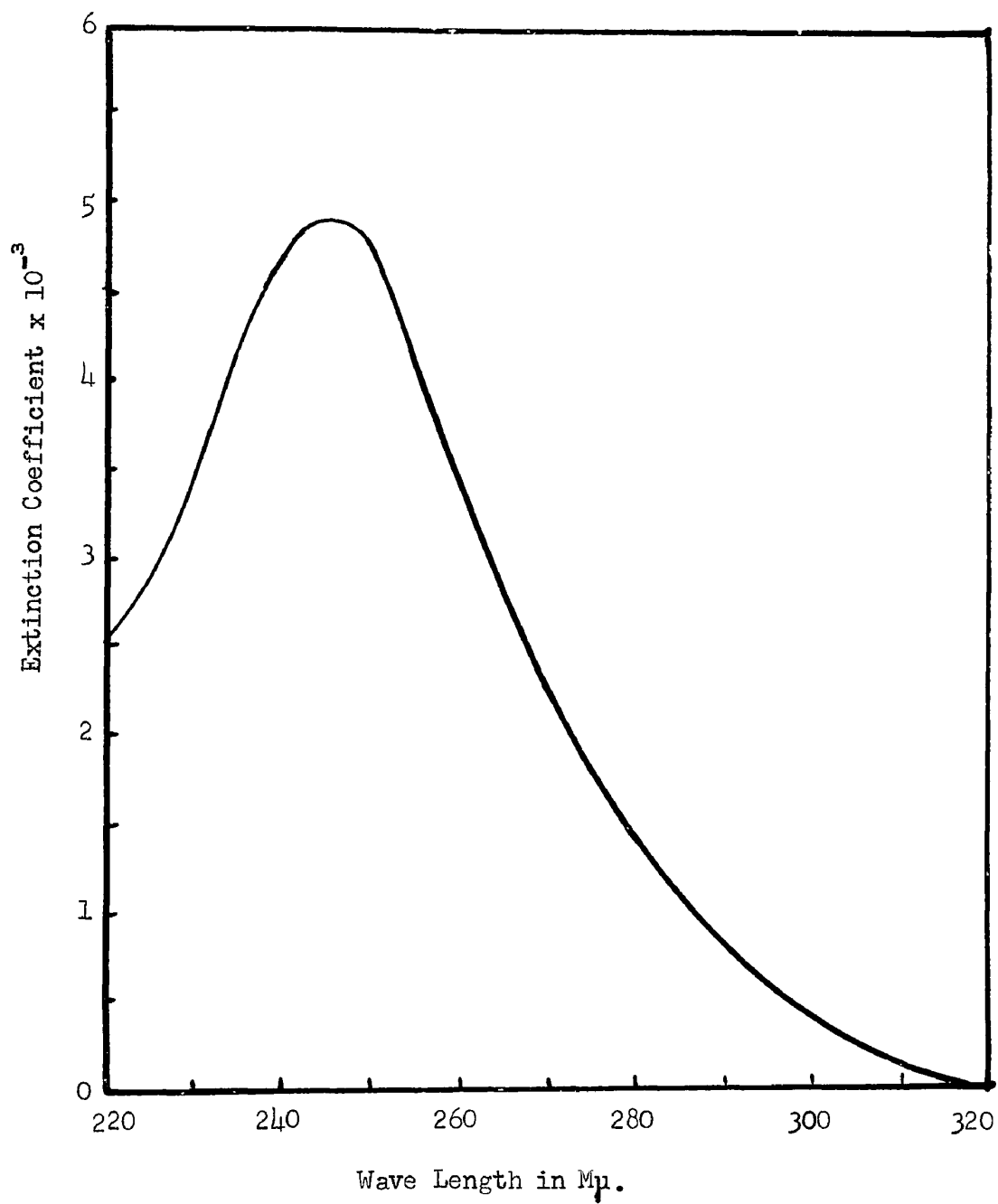


Figure 10. Ultraviolet Absorption Spectrum of 5-Ethyl-nitraminotetrazole.

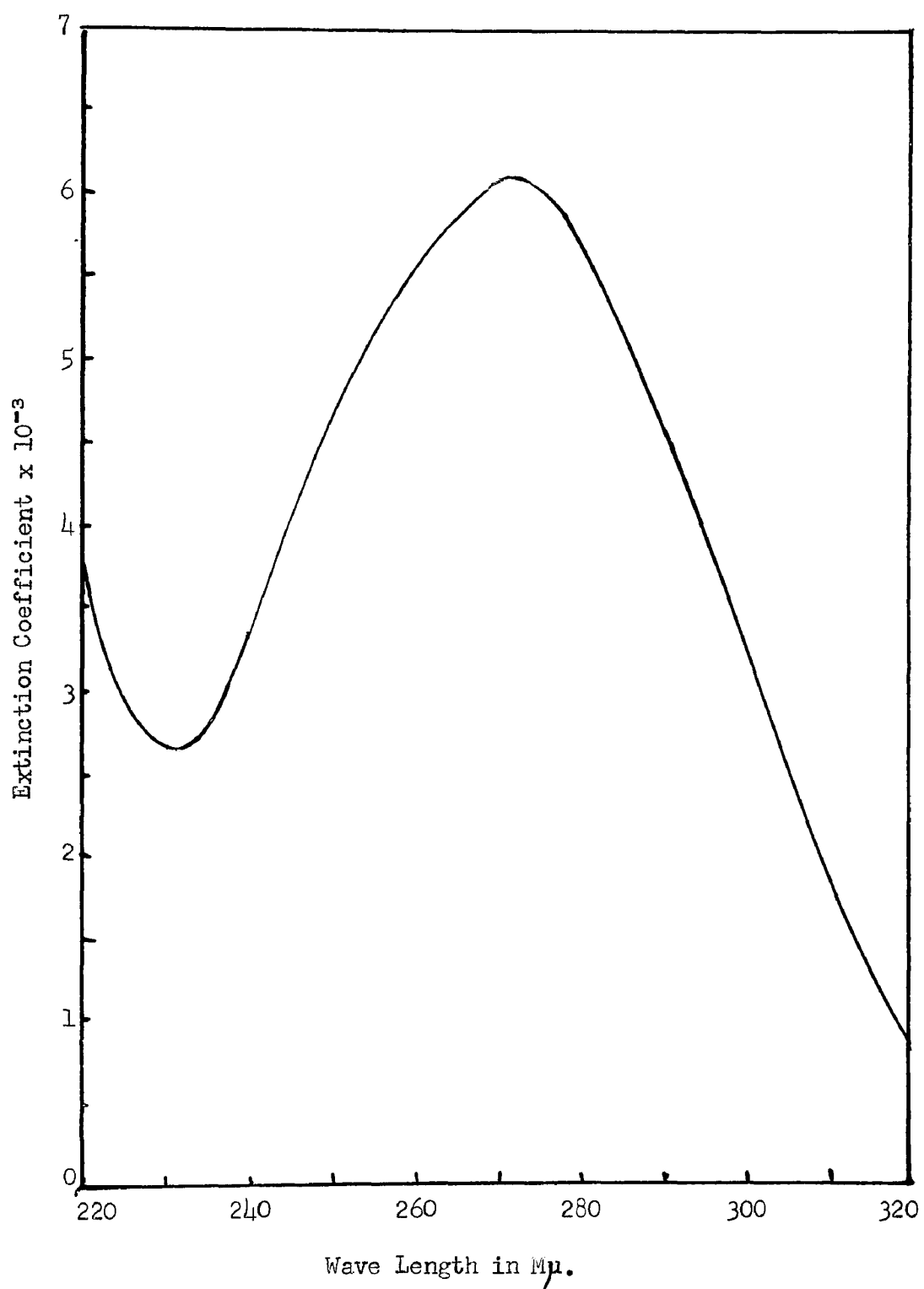


Figure 11. Ultraviolet Absorption Spectrum of Dipotassium 5-Nitraminotetrazole.

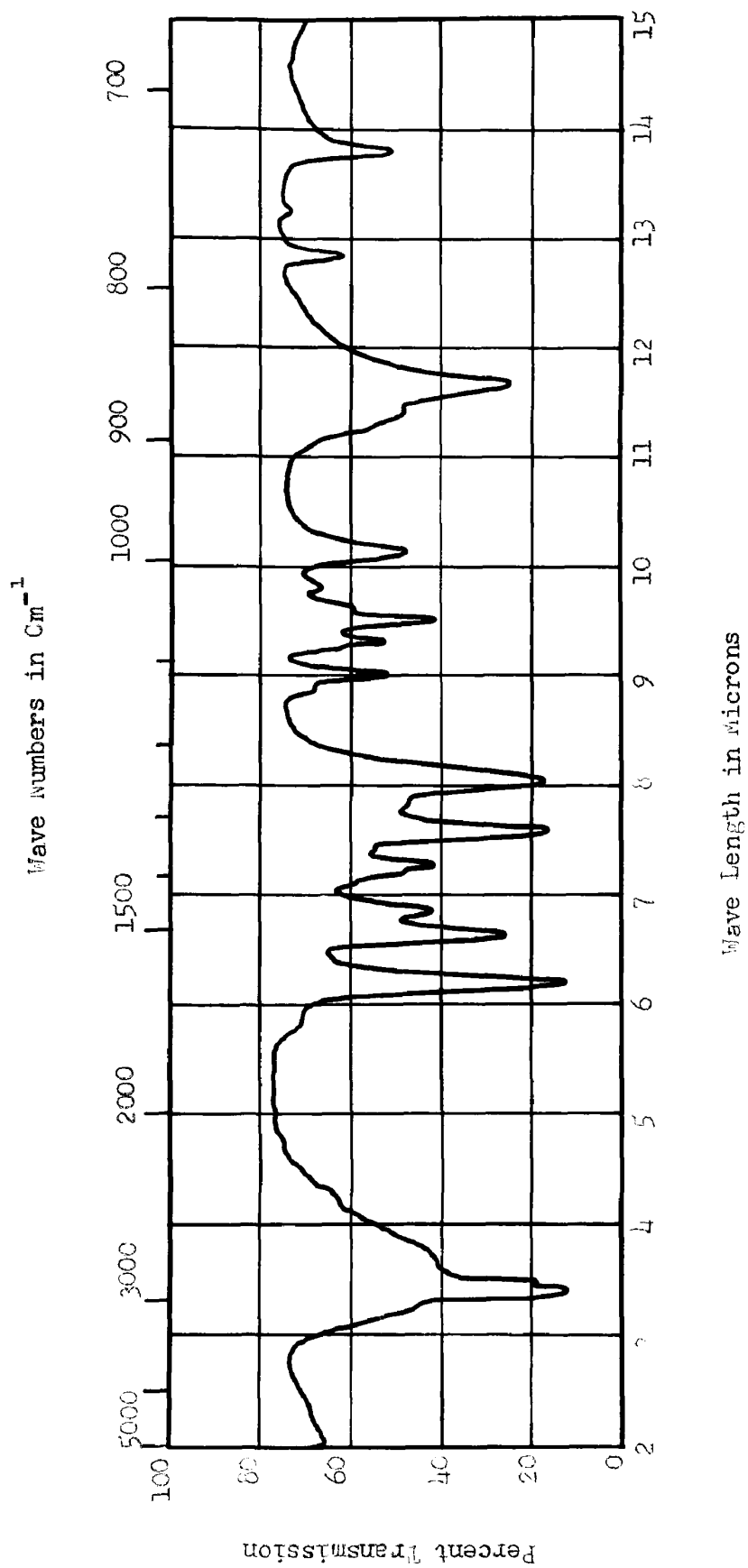


Figure 12. Infrared Absorption Spectrum of 5-nitraminotetrazole in Nujol.

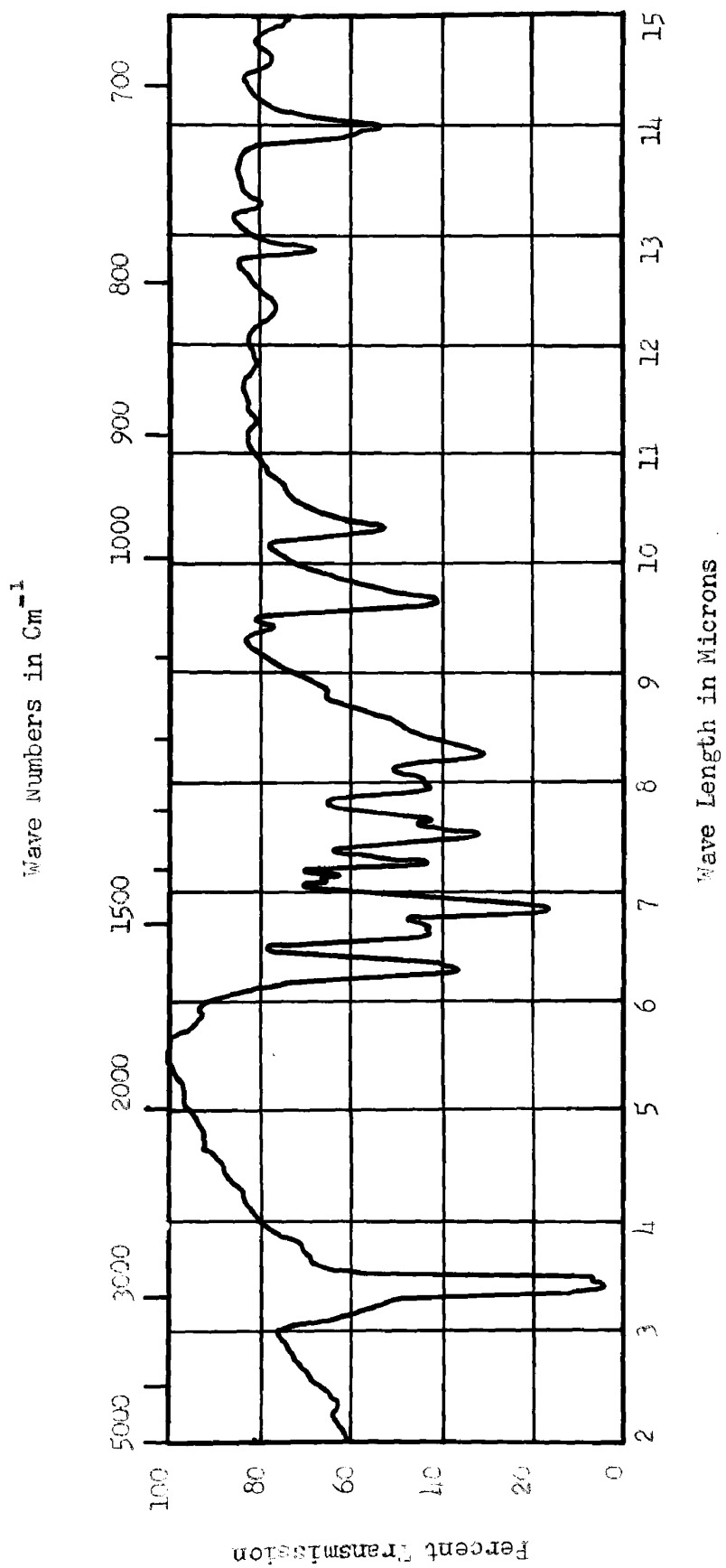


Figure 13. Infrared Absorption Spectrum of 1-Methyl-5-nitraminotetrazole in Nujol.

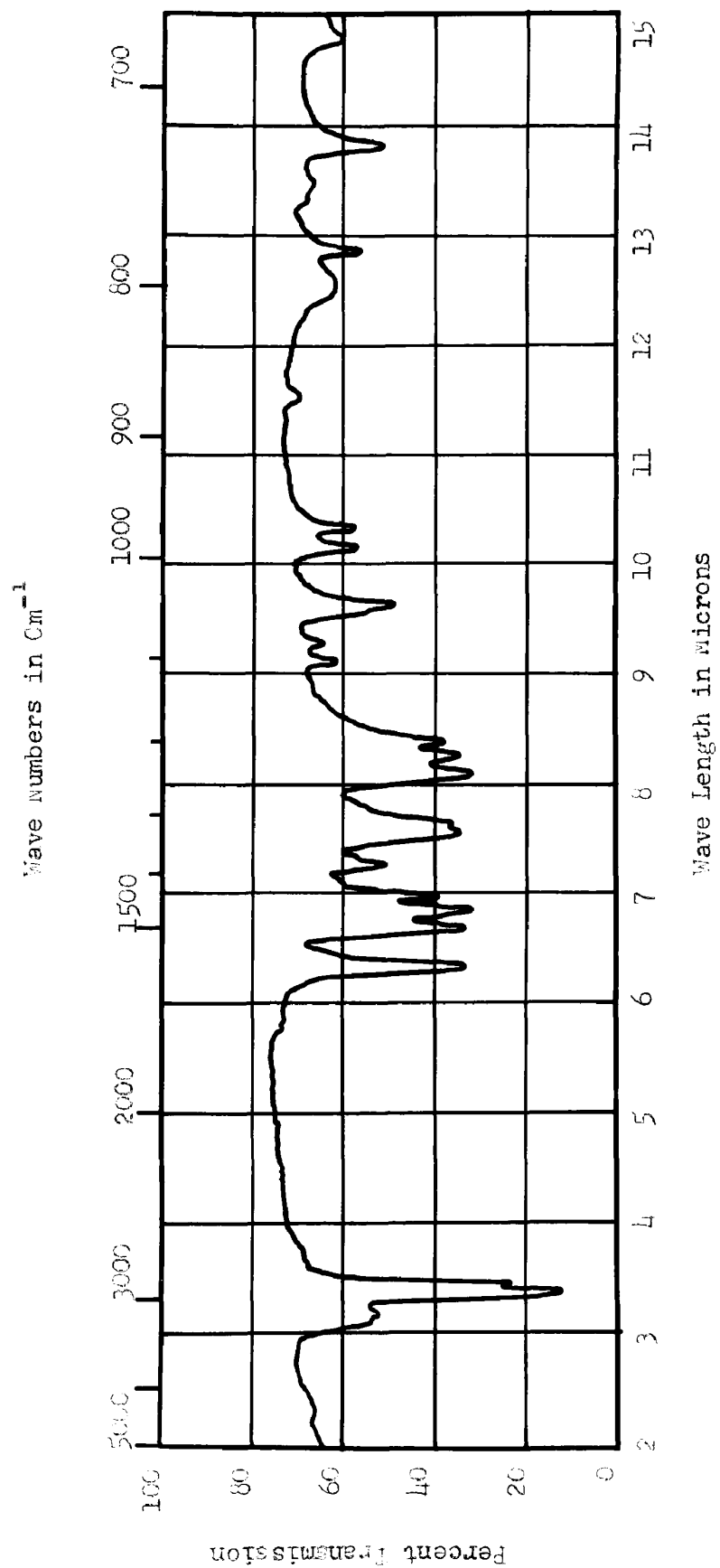


Figure 14. Infrared Absorption Spectrum of 1-Ethyl-5-nitraminotetrazole in wujol.

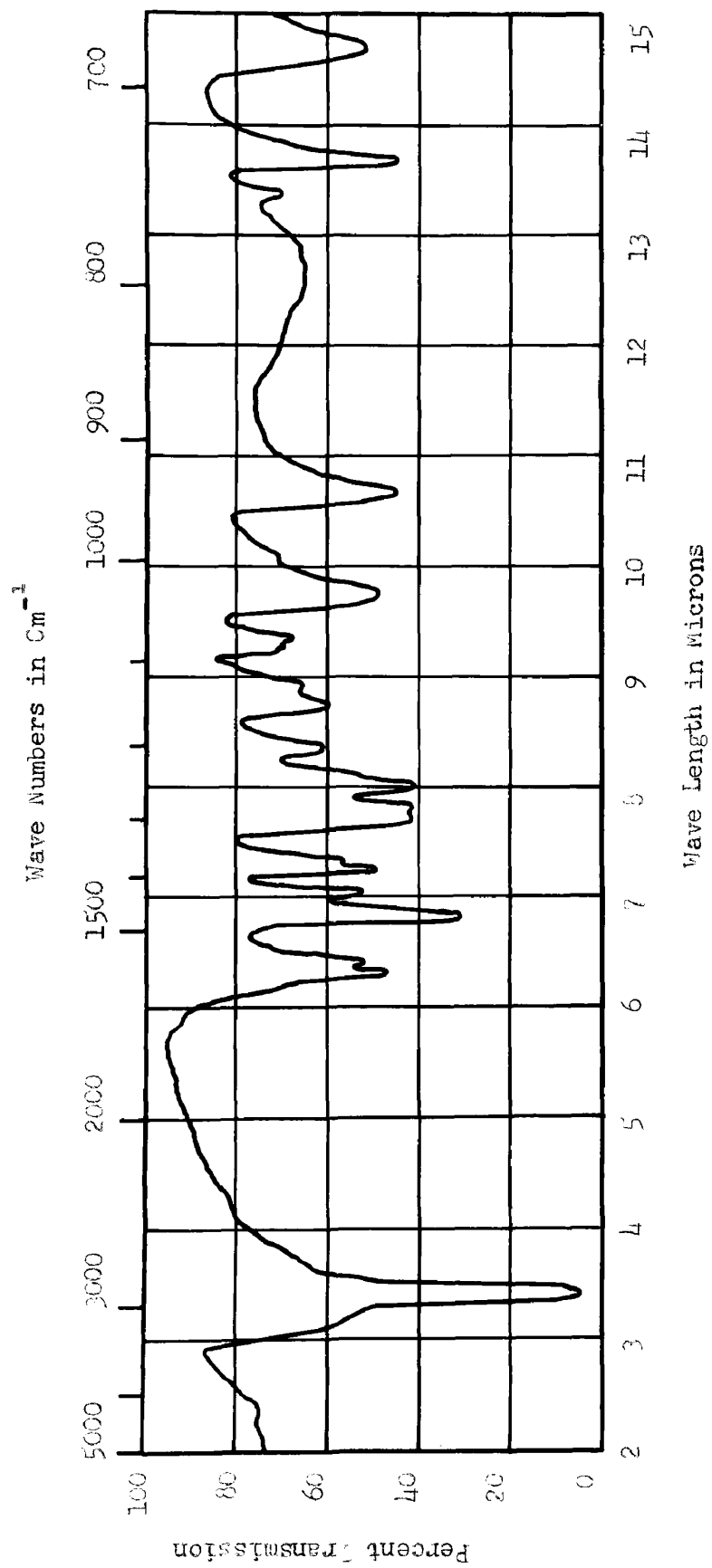


Figure 15. Infrared Absorption Spectrum of 5-Methylnitraminotetrazole in mujol.

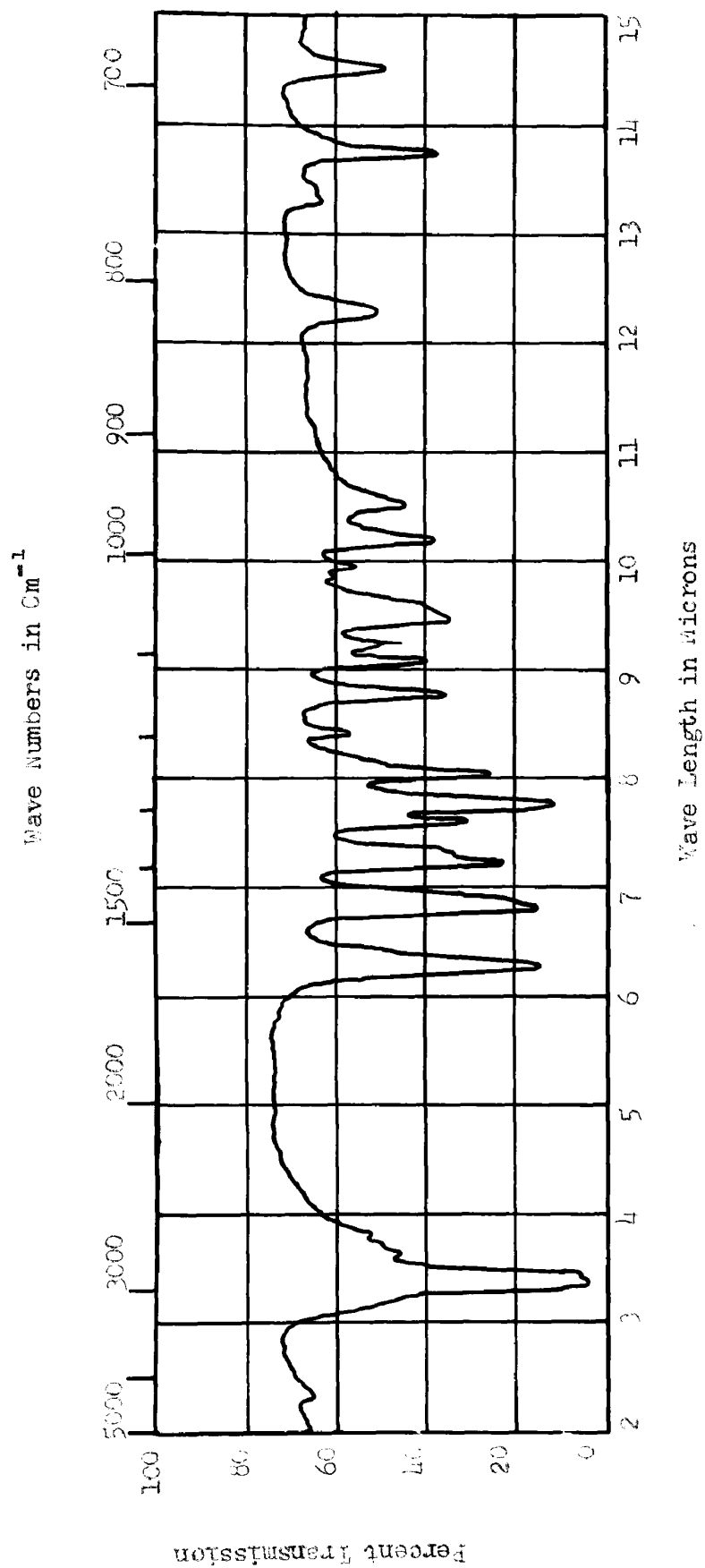


Figure 16. Infrared Absorption Spectrum of 5-Ethynitraminotetrazole in nujol.

Figure 17

Infrared Absorption Spectra
of
Nitraminotetrazoles

- A. 5-Nitraminotetrazole.
- B. 1-Methyl-5-nitraminotetrazole.
- C. 1-Ethyl-5-nitraminotetrazole.
- D. 5-Methylnitraminotetrazole.
- E. 5-Ethylnitraminotetrazole.

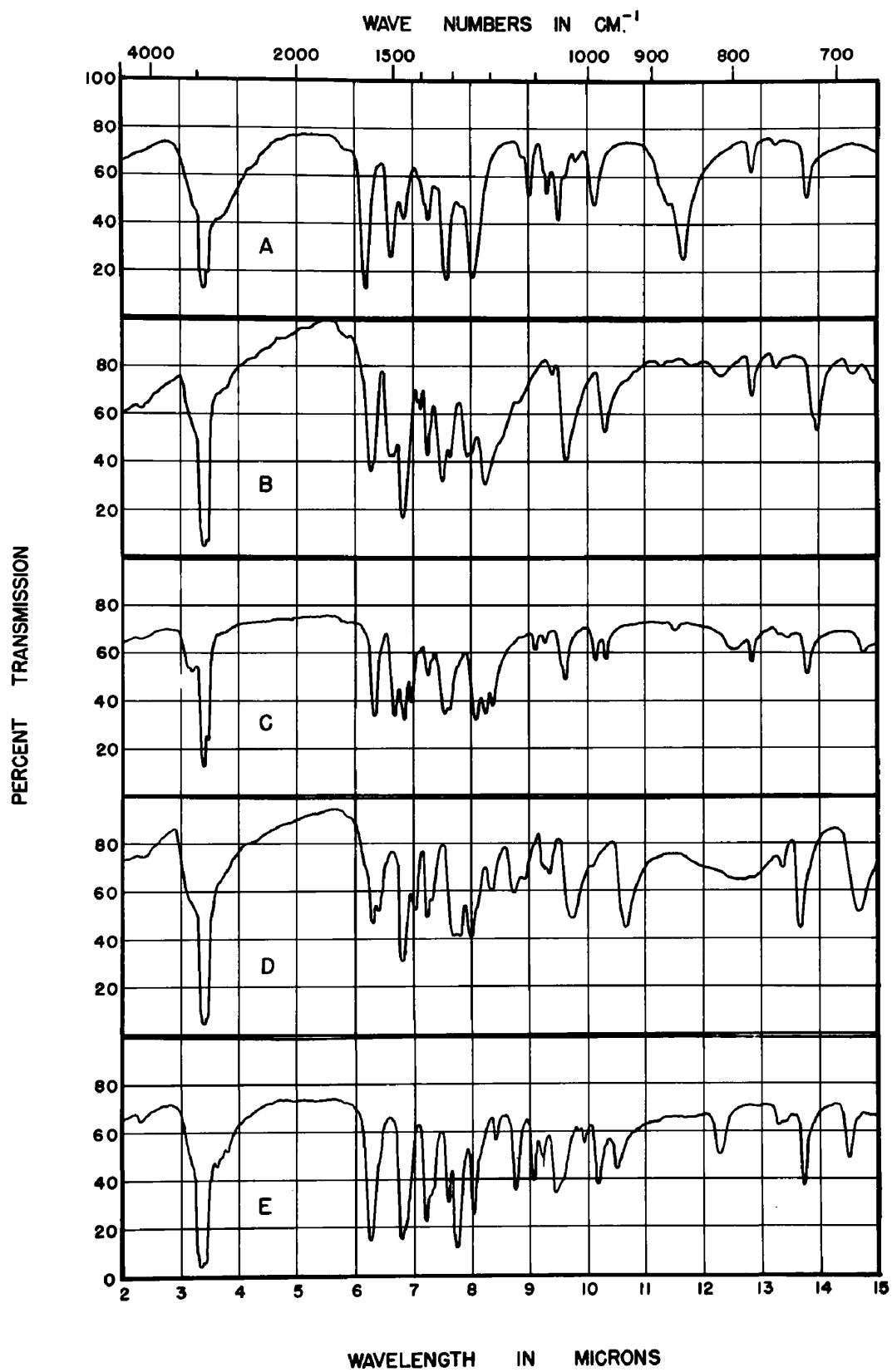


Figure 17.

EXPERIMENTAL

Preparation of Alkyl 5-Aminotetrazoles

1-Methyl-5-aminotetrazole and 1-ethyl-5-aminotetrazole were prepared from the appropriate alkyl cyanamides and hydrazoic acid as described by Garbrecht and Herbst (6). 5-Methylaminotetrazole and 5-ethylaminotetrazole were prepared by debenzylation of 5-benzylmethylamino- or 5-benzylethylaminotetrazole according to Garbrecht and Herbst (3).

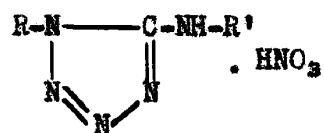
Preparation of Alkyl 5-Aminotetrazole Nitrates

One molar portion of the appropriate 1-alkyl-5-aminotetrazole, or 5-alkylaminotetrazole, was added with cooling to 1.5 molar portions of concentrated nitric acid (sp. gr. 1.419). The mixture was warmed carefully to prevent overheating until all of the tetrazole had dissolved. The nitric acid salt, which separated on cooling, was filtered and washed with ethyl ether. The salt was used without recrystallization. Melting points and analyses are given in Table III.

Preparation of 1-Methyl-5-nitraminotetrazole

(a) Five grams of 1-methyl-5-aminotetrazole nitrate were dissolved with cooling in 7.0 ml. of cold concentrated sulfuric acid. The mixture was allowed to warm to 20°C. and was poured slowly into 150 ml. of ice cold ethyl ether. The ether was removed by decantation and the sulfuric acid further extracted with one 150 ml. and two 50 ml. portions of ether. The combined ether extracts were dried over sodium sulfate and

TABLE III
ALKYL 5-AMINOTETRAZOLE NITRATES



R	R'	M.P. °C.	Molecular Formula	Analysis					
				Calculated			Found		
				C	H	N	C	H	N
CH ₃	H	158-160	C ₂ H ₆ N ₆ O ₃	14.8	3.7	51.8	15.2	3.6	51.9
C ₂ H ₅	H	125-7	C ₃ H ₈ N ₆ O ₃	20.5	4.6	47.7	20.7	4.5	47.6
H	CH ₃	70-72	C ₂ H ₆ N ₆ O ₃	14.8	3.7	51.8	14.6	3.6	51.9
H	C ₂ H ₅	68-70	C ₃ H ₈ N ₆ O ₃	20.5	4.6	47.7	20.8	4.8	47.2

evaporated to dryness at room temperature. The 1-methyl-5-nitramino-tetrazole which remained was recrystallized by dissolving in a small volume of ethyl acetate and then adding a four to five fold volume of petroleum ether. Yield 0.4 g. (9%), m.p. 129-130°C.

(b) To 8 ml. of cold concentrated sulfuric acid was added 6.9 g. (0.023 mole) of 1-methyl-5-aminotetrazole nitrate. The mixture was allowed to warm slowly to 20°C. and then poured over 50 g. of ice. After 90% of the sulfuric acid had been neutralized by addition of the calculated amount of potassium hydroxide, the aqueous solution was extracted with ether in a liquid-liquid continuous extractor for three days. The ether solution was then separated, dried over sodium sulfate, and evaporated to about 100 ml. on a steam bath. The remaining ether was removed under a current of air at room temperature. The solid residue was recrystallized as described above and was identical with the 1-methyl-5-nitraminetetrazole prepared above. Yield 1.9 g. (31%), m.p. 129-130°C.

Analysis. Calculated for $C_2H_4N_6O_2$: C, 16.67; H, 2.80; N, 58.33. Found: C, 16.81; H, 2.67; N, 58.08.

Preparation of 1-Ethyl-5-nitraminetetrazole

Five grams of 1-ethyl-5-aminotetrazole nitrate was dissolved in 10 ml. of cold concentrated sulfuric acid in such a manner that the temperature did not rise above 10°C. The mixture was allowed to warm slowly to 20°C. and was poured into 150 ml. of ice cold ether. The sulfuric acid was further extracted with two 150 ml. and four 50 ml.

portions of ether. The combined extracts were evaporated to dryness at room temperature. The crude residue was recrystallized from benzene. Yield 1.15 g. (26%), m.p. 102-103°C.

Analysis. Calculated for $C_3H_5N_6O_2$: C, 22.77; H, 3.82; N, 53.13.
Found: C, 23.12; H, 3.74; N, 52.95.

Preparation of 5-Methylnitraminotetrazole

(a) 5-Methylaminotetrazole nitrate (6.5 g., 0.04 mole) was added slowly with cooling and stirring to 5.5 ml. of cold concentrated sulfuric acid. The mixture was allowed to stand in an ice bath for 10-15 minutes and then poured over 30 g. of ice. (On one occasion the product crystallized from the aqueous solution; however, this could not be repeated.) The aqueous solution was extracted with two 150 ml. and three 50 ml. portions of ether. The combined ethereal extracts were dried over sodium sulfate and evaporated to dryness at room temperature. The residue, after recrystallization by dissolving in ethyl acetate and adding a three fold volume of petroleum ether, gave 2.0 g. (35%) of 5-methylnitraminotetrazole, m.p. 112-113°C.

Analysis. Calculated for $C_2H_4N_6O_2$: C, 16.67; H, 2.80; N, 58.33.
Found: C, 16.71; H, 2.95; N, 58.03.

(b) Forty grams of N,N'-dinitrodimethyloxamide (16) was treated with 160 ml. of concentrated ammonia solution (sp. gr. 0.899). The mixture warmed spontaneously to about 40°C. After cooling to room temperature, the mixture was made slightly acid to Congo red with 10%

sulfuric acid. The colorless precipitate of oxamide was removed by filtration and the filtrate extracted with three 100 ml. portions of ether. An equivalent amount of potassium hydroxide dissolved in 100 ml. of methanol was added to the ether extracts. Upon evaporation of the solution to small volume, potassium methylnitramine separated as a colorless powder. Yield 18 g. m.p. 220°C . (16).

One tenth mole (11.4 g.) of potassium methylnitramine suspended in 50 ml. of methanol was treated with 0.1 mole (10.6 g.) of cyanogen bromide in 100 ml. of ether. The solution was filtered to remove the potassium bromide and the filtrate evaporated to a small volume. At this point the mixture separated into two layers. The upper layer was insoluble in water and was assumed to be methylnitrocyanamide. Due to the possibility of decomposition, no effort was made to purify the product.

Four grams of crude methylnitrocyanamide were dissolved in 25 ml. of a 13% solution of hydrazoic acid in benzene and allowed to stand for two days. Next an additional 25 ml. of hydrazoic acid solution was added and the mixture refluxed for two hours. After cooling and evaporating to small volume, 100 ml. of petroleum ether was added. The mixture separated into two layers. The upper, petroleum ether, layer was removed by decantation and the lower layer dissolved in ethyl acetate. The ethyl acetate solution was diluted with a four fold volume of petroleum ether. Upon standing, a quantity of long, colorless needles, m.p. $113-114^{\circ}\text{C}$., separated which were identical with the

5-methylnitraminetetrazole described above as shown by mixed melting point, infrared absorption spectra, and identity of the salts with 2-aminopyridine.

Preparation of 5-Ethynitraminetetrazole

5-Ethylaminotetrazole nitrate (2.0 g.) was dissolved in 2.0 ml. of cold concentrated sulfuric acid. The cold mixture was then poured over 20 g. of ice. The aqueous solution was extracted with two 100 ml. portions of ether. The combined ethereal extracts were dried over sodium sulfate and evaporated to dryness in a current of air. The residue was taken up in ethyl acetate and a large volume of petroleum ether was added. 5-Ethynitraminetetrazole separated as colorless plates. Yield 0.7 g. (25%) m.p. 88-89°C.

Analysis. Calculated for $C_3H_6N_6O_2$: C, 22.77; H, 3.82; N, 53.13. Found: C, 22.72; H, 3.99; N, 53.23.

Reduction of 5-Methylnitraminetetrazole

A sample of 5-methylnitraminetetrazole (1.44 g., 0.01 mole) dissolved in 50 ml. of absolute ethanol was reduced under hydrogen at 50 p.s.i. using palladium oxide catalyst (The American Platinum Works). When three molar equivalents of hydrogen had been absorbed, the reduction was stopped and the catalyst was removed by filtration. To the alcoholic solution was added 1.06 g. of benzaldehyde and the solution was evaporated to dryness. The product was recrystallized from 1,4-dioxane. Elemental analysis and melting point characteristics indicated that the product was 5-methylaminotetrazole. Yield 0.5 g.

(50%), m.p. 185-187°C. (The product resolidified on further heating and remelted at 224-225°C.)

Analysis. Calculated for $C_2H_5N_5$: C, 24.2; H, 5.09; N, 70.7.

Found: C, 24.4; H, 5.07; N, 70.4.

Preparation of Potassium Salts of Alkyl Nitraminotetrazoles

The potassium salts of the alkyl nitraminotetrazoles were prepared by dissolving the tetrazole in ether and adding methanolic potassium hydroxide until precipitation was complete. The salt was removed by filtration and recrystallized from ethyl acetate. Yields were essentially quantitative. The potassium salts decompose explosively at, or near, their melting points which are as follows: 1-methyl-5-nitraminotetrazole, 170-171°C.; 1-ethyl-5-nitraminotetrazole, 205-206°C.; 5-methyl-nitraminotetrazole, 191-192°C.; 5-ethylnitraminotetrazole, 174-175°C.

Due to the explosive character of these salts, it has not been possible to obtain reliable nitrogen analyses. However, ultraviolet absorption spectra of the salts in water were identical with those of the respective tetrazoles in water or in an equivalent amount of dilute aqueous potassium hydroxide solution.

Preparation of 2-Aminopyridine Salts of Alkyl Nitraminotetrazoles

Salts with 2-aminopyridine were prepared by treating an ethereal solution of the appropriate tetrazole with an equivalent amount of 2-aminopyridine dissolved in ether. The products were recrystallized from 1:1 isopropyl alcohol-ethyl alcohol. The yields were quantitative. Melting points and analyses are listed in Table IV.

TABLE IV
SALTS OF ALKYL 5-NITRAMINOTETRAZOLES WITH 2-AMINOPYRIDINE

Tetrazole	M.P. °C.	Molecular Formula	Analysis					
			Calculated			Found		
			C	H	N	C	N	N
1-Methyl-5-nitramino-	177-8	$C_7H_{10}N_5O_2$	35.3	4.2	47.0	35.5	4.4	46.8
1-Ethyl-5-nitramino-	131-2	$C_8H_{12}N_5O_2$	38.1	4.8	44.4	38.2	4.7	44.2
5-Methyl-nitramino-	165-7	$C_7H_{10}N_5O_2$	35.3	4.2	47.0	35.1	4.2	47.1
5-Ethyl-nitramino-	139-40	$C_8H_{12}N_5O_2$	38.1	4.8	44.4	38.5	5.1	44.1

Potentiometric Titrations

Samples of 1-methyl-5-nitramino-, 1-ethyl-5-nitramino-, 5-methyl-nitramino-, and 5-ethylnitraminotetrazole were titrated potentiometrically using a Beckman Model G pH Meter. All titrations were carried out at 25°C. $\pm$ 0.02°C. The initial concentration was about 0.01 molar. The data obtained are given in Appendix II. Typical titration curve are shown in Figures 5-6. The results are summarized in Table II.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of 1-alkyl-5-nitraminotetrazoles, 5-alkylnitraminotetrazoles, and their potassium salts, and the dipotassium salt of 5-nitraminotetrazole were determined using a Beckman Model D-U Spectrophotometer. The results are given in Appendix I and are represented graphically in Figures 7-11. A summary of the location of absorption maxima and minima is given in Table V.

Infrared Absorption Spectra

The infrared absorption spectra of the following compounds were determined using a Perkin-Elmer Recording Infrared Spectrophotometer Model 21: 5-nitraminotetrazole (Figure 12), 1-methyl-5-nitraminotetrazole (Figure 13), 1-ethyl-5-nitraminotetrazole (Figure 14), 5-methylnitraminotetrazole (Figure 15), and 5-ethylnitraminotetrazole (Figure 16). For comparative purposes the infrared absorption spectra are shown together in Figure 17.

TABLE V

WAVE LENGTHS OF MAXIMUM AND MINIMUM ULTRAVIOLET ABSORPTION OF ALKYL
5-NITRAMINOTETRAZOLES AND THEIR POTASSIUM SALTS

Compound	Ultraviolet Absorption	
	Maximum	Minimum
5-Nitraminotetrazole	277	237
1-Methyl-5-nitraminotetrazole	277	237
1-Ethyl-5-nitraminotetrazole	277	237
5-Methylnitraminotetrazole	246	---
5-Ethylnitraminotetrazole	246	---
Potassium 5-Nitraminotetrazole	277	237 (5)
Potassium 1-Methyl- 5-nitraminotetrazole	277	237
Potassium 1-Ethyl- 5-nitraminotetrazole	277	237
Potassium 5-Methylnitramino- tetrazole	246	---
Potassium 5-Ethylnitramino- tetrazole	246	---
Dipotassium 5-Nitraminotetrazole	270	230

SUMMARY

It has been shown that 5-nitraminotetrazole may be prepared by nitration of 5-aminotetrazole.

The apparent dissociation constants and the ultraviolet absorption spectra of 5-nitraminotetrazole, so prepared, were determined and found to be identical with the corresponding properties of the nitraminotetrazole prepared by cyclization nitroguanyl azide. Salts with four organic bases were prepared from 5-nitraminotetrazole synthesized by both procedures and were found to be identical.

Two 1-alkyl-5-nitraminotetrazoles and two 5-alkyl-nitraminotetrazoles were prepared by nitration of the appropriate alkyl 5-aminotetrazoles and their apparent dissociation constants were determined. The compounds in both series were found to be moderately strong acids.

The structure of 5-methylnitraminotetrazole was supported by independent synthesis and comparison of physical properties, including absorption spectra.

The ultraviolet absorption spectra of the alkyl-5-nitraminotetrazoles were determined. The 1-alkyl-5-nitraminotetrazoles were found to have maximum and minimum absorption at 277-78 m μ and 237 m μ , respectively. Since 5-nitraminotetrazole has the same maximum and minimum, it was concluded that the first dissociation of 5-nitraminotetrazole involved the hydrogen of the nitramino group. The 5-alkylnitraminotetrazoles exhibited a maximum absorption at 246 m μ .

The alkyl 5-nitraminotetrazoles were further characterized by their infrared absorption spectra and by their salts with 2-aminopyridine.

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APPENDIX I

ULTRAVIOLET ABSORPTION DATA

ULTRAVIOLET ABSORPTION SPECTRUM 5-NITRAMINOTETRAZOLE (ANHYDROUS)
PREPARED FROM 5-AMINOTETRAZOLE

(0.0130 g./l. in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-4}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-4}$
220	.435	.434	272	1.21	1.215
224	.333	.332	274	1.26	1.245
228	.235	.233	276	1.28	1.275
232	.165	.163	277	1.29	1.285
234	.143	.143	278	1.29	1.285
236	.133	.132	280	1.27	1.255
237	.132	.131	282	1.24	1.245
238	.134	.133	284	1.20	1.205
239	.138	.138	288	1.12	1.115
240	.145	.144	292	.997	.996
244	.198	.197	296	.855	.856
248	.294	.293	300	.719	.717
252	.432	.439	305	.553	.550
256	.594	.593	310	.389	.388
260	.768	.777	320	.144	.143
264	.950	.946	330	.036	.036
268	1.10	1.095	340	.006	.007

ULTRAVIOLET ABSORPTION SPECTRUM 5-NITRAMINOTETRAZOLE (ANHYDROUS)
PREPARED FROM N-NITRO-N'-AMINO GUANIDINE

(0.0098 g./1. in water)

λ in μ	Optical Density	$\epsilon \times 10^{-4}$	λ in μ	Optical Density	$\epsilon \times 10^{-4}$
220	.345	.451	276	.970	1.288
226	.224	.296	277	.975	1.292
230	.156	.206	278	.975	1.292
234	.114	.149	279	.970	1.288
236	.104	.139	280	.962	1.282
237	.102	.135	282	.950	1.262
238	.103	.136	286	.880	1.169
240	.111	.146	290	.794	1.054
244	.150	.198	294	.700	.925
248	.223	.295	300	.548	.734
252	.326	.431	305	.419	.555
256	.451	.596	310	.298	.394
260	.588	.778	315	.264	.250
264	.722	.955	320	.111	.147
266	.782	1.037	325	.058	.075
270	.885	1.176	330	.028	.037
272	.922	1.222	340	.007	.008
274	.950	1.262			
275	.962	1.282			

ULTRAVIOLET ABSORPTION SPECTRUM 5-NITRAMINOTETRAZOLE (SOLVATED)
PREPARED FROM 5-AMINOTETRAZOLE

(0.0110 g./l. in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-4}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-4}$
220	.184	.308	274	.653	1.096
226	.119	.197	276	.667	1.118
230	.083	.139	277	.670	1.121
234	.062	.104	278	.670	1.121
238	.059	.097	279	.667	1.118
239	.062	.105	280	.665	1.113
240	.066	.110	282	.653	1.091
242	.077	.129	286	.612	1.024
246	.118	.197	290	.553	.927
250	.184	.308	294	.498	.812
253	.244	.407	298	.420	.696
255	.288	.480	305	.289	.482
257	.336	.561	320	.075	.101
259	.383	.643			
260	.408	.679			
263	.475	.795			
265	.520	.870			
267	.561	.940			
270	.612	1.024			
272	.637	1.067			

ULTRAVIOLET ABSORPTION SPECTRUM 1-METHYL-5-NITRAMINOTETRAZOLE

(0.01035 g./l. in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$
220	.396	5.51	275	.700	9.75
224	.324	4.51	276	.700	9.75
228	.261	3.63	277	.702	9.77
232	.227	3.16	278	.702	9.77
236	.215	2.99	279	.700	9.75
240	.228	3.17	280	.696	9.69
242	.258	3.59	282	.683	9.51
248	.304	4.23	284	.665	9.26
250	.331	4.61	288	.612	8.52
254	.394	5.49	292	.541	7.53
258	.462	6.43	296	.462	6.43
262	.533	7.42	300	.386	5.38
266	.603	8.40	305	.302	4.21
270	.658	9.16	310	.229	3.19
272	.680	9.47	320	.108	1.50
274	.694	9.66			

ULTRAVIOLET ABSORPTION SPECTRUM 1-ETHYL-5-NITRAMINOTETRAZOLE

(0.01460 g./l. in water)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.421	4.56	264	.718	7.77
224	.356	3.85	268	.802	8.68
228	.314	3.39	274	.898	9.72
232	.259	2.80	275	.900	9.74
234	.253	2.74	276	.910	9.85
235	.251	2.72	277	.915	9.90
236	.248	2.68	278	.910	9.85
237	.251	2.72	279	.908	9.83
238	.252	2.73	280	.905	9.79
240	.264	2.86	284	.868	9.39
244	.304	3.29	288	.802	8.68
248	.361	3.91	295	.633	6.85
252	.441	4.77	300	.508	5.50
256	.528	5.71	310	.298	3.23
260	.625	6.76	320	.139	1.50

ULTRAVIOLET ABSORPTION SPECTRUM 5-METHYLNITRAMINOTETRAZOLE

(0.01630 g./1. in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$
220	.338	2.99	258	.432	3.82
224	.352	3.11	262	.382	3.38
228	.378	3.34	266	.332	2.94
232	.425	3.76	270	.284	2.51
236	.472	4.17	274	.245	2.17
240	.511	4.52	278	.213	1.88
242	.523	4.62	284	.163	1.44
244	.530	4.69	288	.142	1.26
245	.532	4.70	292	.118	1.04
246	.532	4.70	296	.096	0.85
247	.529	4.68	300	.075	0.67
248	.525	4.64	305	.054	0.48
250	.514	4.54	310	.038	0.34
254	.478	4.23	320	.016	0.14

ULTRAVIOLET ABSORPTION SPECTRUM 5-ETHYLNITRAMINOTETRAZOLE

(0.01838 g./l. in water)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.324	2.54	254	.553	4.34
224	.344	2.70	258	.486	3.81
228	.403	3.16	262	.413	3.24
232	.472	3.70	266	.346	2.71
236	.548	4.30	270	.283	2.22
238	.572	4.48	272	.253	1.98
242	.617	4.84	276	.211	1.65
243	.621	4.87	280	.174	1.36
244	.625	4.90	286	.131	1.03
245	.628	4.92	290	.105	0.82
246	.632	4.95	295	.078	0.61
247	.628	4.92	300	.056	0.44
248	.618	4.85	310	.023	0.18
250	.604	4.73	320	.007	0.05

ULTRAVIOLET ABSORPTION SPECTRUM POTASSIUM
1-METHYL-5-NITRAMINOTETRAZOLE

(0.01732 g./l. in water)

λ in μ	Optical Density	$\epsilon \times 10^{-3}$	λ in μ	Optical Density	$\epsilon \times 10^{-3}$
220	.498	5.24	268	.688	7.24
224	.386	4.06	272	.742	7.81
228	.300	3.16	275	.765	8.05
232	.246	2.56	276	.768	8.08
234	.236	2.48	277	.770	8.10
235	.232	2.44	278	.768	8.08
236	.230	2.42	279	.768	8.08
237	.232	2.44	280	.765	8.05
238	.234	2.46	284	.728	7.66
240	.241	2.54	288	.670	7.05
244	.276	2.90	292	.592	6.23
248	.329	3.46	296	.508	5.34
252	.393	4.13	300	.424	4.46
256	.468	4.92	305	.330	3.47
260	.546	5.74	310	.249	2.62
264	.622	6.54	320	.118	1.24

ULTRAVIOLET ABSORPTION SPECTRUM POTASSIUM
1-ETHYL-5-NITRAMINOTETRAZOLE

(0.02189 g./l. in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$
220	.592	5.31	268	.798	7.15
224	.462	4.14	272	.858	7.69
228	.362	3.25	275	.881	7.90
232	.301	2.70	276	.883	7.91
234	.287	2.57	277	.885	7.93
235	.284	2.55	278	.885	7.93
236	.280	2.51	279	.882	7.91
237	.284	2.55	280	.880	7.89
238	.284	2.55	284	.841	7.54
240	.292	2.62	288	.778	6.97
244	.329	2.95	292	.688	6.17
248	.388	3.48	296	.592	5.31
252	.460	4.12	300	.492	4.41
256	.545	4.89	305	.386	3.46
260	.632	5.67	310	.290	2.60
264	.722	6.47	320	.136	1.22

ULTRAVIOLET ABSORPTION SPECTRUM POTASSIUM
5-METHYLNITRAMINOTETRAZOLE

(0.01708 g./l. in water)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.244	2.60	250	.482	5.14
224	.273	2.91	254	.452	4.82
228	.325	3.47	260	.385	4.11
232	.386	4.12	265	.325	3.47
236	.438	4.67	270	.267	2.85
240	.476	5.08	275	.222	2.37
242	.485	5.17	280	.184	1.96
244	.493	5.26	290	.124	1.32
245	.495	5.28	300	.074	0.79
246	.496	5.29	310	.037	0.40
247	.495	5.28	320	.018	0.19
248	.491	5.24			

ULTRAVIOLET ABSORPTION SPECTRUM POTASSIUM
5-ETHYLNITRAMINOTETRAZOLE

(0.02069 g./l. in water)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.251	2.36	250	.520	4.89
224	.292	2.74	254	.475	4.46
228	.353	3.31	260	.386	3.63
232	.423	3.97	265	.311	2.92
236	.484	4.55	270	.244	2.30
240	.527	4.95	275	.192	1.80
242	.538	5.06	280	.151	1.42
244	.542	5.09	290	.097	0.91
245	.542	5.09	300	.054	0.51
246	.542	5.09	310	.026	0.24
247	.538	5.06	320	.012	0.11
248	.532	5.00			

ULTRAVIOLET ABSORPTION SPECTRUM
1-METHYL-5-NITRAMINOTETRAZOLE

(0.00645 g./l. with an equivalent of 0.001 N KOH.)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.240	5.36	275	.440	9.83
230	.156	3.49	276	.442	9.88
234	.147	3.28	277	.444	9.92
235	.146	3.26	278	.444	9.82
236	.146	3.26	279	.442	9.88
237	.148	3.31	280	.440	9.83
240	.158	3.53	290	.367	8.20
250	.223	4.98	300	.250	5.59
260	.323	7.21	310	.150	3.35
270	.419	9.36	320	.077	1.72

ULTRAVIOLET ABSORPTION SPECTRUM 1-ETHYL-5-NITRAMINOTETRAZOLE

(0.00733 g./l. with an equivalent of 0.001 N KOH in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$
220	.226	4.88	275	.446	9.62
230	.149	3.21	276	.450	9.71
234	.142	3.06	277	.451	9.73
235	.141	3.04	278	.451	9.73
236	.141	3.04	279	.449	9.69
237	.144	3.11	280	.447	9.64
240	.155	3.34	290	.370	7.98
250	.221	4.77	300	.252	5.44
260	.323	6.97	310	.148	3.19
270	.421	9.08	320	.072	1.55

ULTRAVIOLET ABSORPTION SPECTRUM 5-METHYLNITRAMINOTETRAZOLE

(0.00597 g./l. with an equivalent of 0.001 N KOH in water)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.132	3.19	250	.218	5.26
230	.163	3.93	260	.169	4.08
240	.216	5.21	270	.118	2.85
245	.227	5.48	290	.058	1.40
246	.227	5.48	310	.023	0.56
247	.227	5.48	320	.015	0.36

ULTRAVIOLET ABSORPTION SPECTRUM 5-ETHYLNITRAMINOTETRAZOLE

(0.00710 g./l. with an equivalent of 0.001 N KOH in water)

λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$	λ in $m\mu$	Optical Density	$\epsilon \times 10^{-3}$
220	.124	2.76	250	.230	5.12
230	.164	3.65	260	.168	3.74
240	.229	5.10	270	.104	2.32
245	.240	5.34	290	.038	0.87
246	.241	5.37	310	.010	0.22
247	.241	5.37	320	.004	0.09

ULTRAVIOLET ABSORPTION SPECTRUM 5-NITRAMINOTETRAZOLE

(0.0205 g. /1. in 0.1 N KOH)

λ in m μ	Optical Density	$\epsilon \times 10^{-3}$	λ in m μ	Optical Density	$\epsilon \times 10^{-3}$
220	.598	3.79	266	.938	5.95
224	.477	3.03	268	.950	6.02
228	.422	2.68	270	.955	6.05
229	.420	2.66	271	.960	6.09
230	.416	2.64	272	.960	6.09
232	.418	2.65	273	.960	6.09
233	.420	2.66	274	.955	6.05
234	.435	2.76	278	.930	5.90
238	.487	3.09	282	.875	5.55
242	.563	3.57	286	.800	5.07
246	.642	4.07	290	.723	4.58
250	.725	4.60	294	.637	4.04
254	.790	5.01	300	.508	3.22
258	.840	5.33	310	.304	1.93
262	.890	5.64	320	.138	0.88

APPENDIX II

POTENTIOMETRIC TITRATION DATA

POTENTIOMETRIC TITRATION 5-NITRAMINOTETRAZOLE (ANHYDROUS)
PREPARED FROM 5-AMINOTETRAZOLE

Sample weight: 0.2075 g. in 200 ml. water
Potassium Hydroxide: 0.1043 N.

pH	Base Added Ml.	pH	Base Added Ml.
2.23	0.00	5.70	19.27
2.32	2.20	5.82	20.20
2.46	5.48	5.92	21.10
2.49	6.15	6.02	22.00
2.52	6.80	6.09	22.60
2.56	7.30	6.15	23.18
2.61	8.02	6.23	23.87
2.63	8.50	6.29	24.30
2.70	9.30	6.37	24.85
2.76	9.97	6.43	25.32
2.92	11.42	6.63	26.63
3.09	12.55	6.91	28.00
3.29	13.42	7.16	28.72
3.43	13.88	7.31	29.00
3.53	14.12	7.55	29.32
3.75	14.50	8.15	29.68
3.89	14.67	8.35	29.72
4.07	14.82	9.00	29.88
4.22	14.98	9.35	29.98
4.47	15.18	9.72	30.10
4.59	15.37	10.06	30.30
4.82	15.68	10.25	30.50
4.99	16.00	10.53	30.95
5.29	17.00	10.73	31.50
5.51	18.02	10.86	32.05

POTENTIOMETRIC TITRATION 5-NITRAMINOTETRAZOLE (ANHYDROUS)
PREPARED FROM N-NITRO-N'-AMINOGUANIDINE

Sample weight: 0.2167 g. in 200 ml. of water

Potassium Hydroxide: 0.1043 N

pH	Base Added Ml.	pH	Base Added Ml.
2.22	0.00	5.48	19.00
2.33	1.08	5.61	19.97
2.38	2.00	5.74	21.00
2.45	6.05	5.85	22.00
2.48	6.50	5.90	22.52
2.50	6.92	5.94	23.00
2.51	7.43	6.02	23.70
2.55	7.99	6.06	24.10
2.59	8.50	6.10	24.50
2.63	9.10	6.13	24.98
2.68	9.62	6.21	25.52
2.75	10.00	6.27	26.00
2.85	11.10	6.41	27.10
2.93	12.50	6.72	29.00
3.09	13.08	7.02	29.60
3.16	13.50	7.22	30.64
3.29	14.06	7.43	30.98
3.43	14.61	7.59	31.12
3.51	14.80	7.88	31.30
3.63	15.02	7.99	31.48
3.71	15.15	8.55	31.50
3.82	15.30	9.05	31.60
3.90	15.35	9.39	31.70
4.02	15.48	9.62	31.78
4.12	15.58	9.92	31.95
4.28	15.70	10.08	32.10
4.37	15.80	10.27	32.30
4.51	15.95	10.56	32.90
4.66	16.18	10.80	33.78
4.78	16.32	10.98	34.98
4.99	16.87	11.12	36.22
5.12	17.28		
5.22	17.00		
5.33	18.12		

POTENTIOMETRIC TITRATION 5-NITRAMINOTETRAZOLE (SOLVATED)
PREPARED FROM 5-AMINOTETRAZOLE

Sample weight: 0.2610 g. in 200 ml. of water

Potassium Hydroxide: 0.1043 N

pH	Base Added Ml.	pH	Base Added Ml.
2.42	0.00	5.95	17.98
2.48	1.76	6.00	18.48
2.69	5.93	6.08	19.00
2.72	6.43	6.15	19.58
2.76	7.08	6.20	19.93
2.81	7.68	6.40	21.48
2.82	8.06	6.72	23.53
3.23	11.18	6.98	24.68
3.51	12.18	7.22	25.43
3.71	12.58	7.65	26.08
4.14	13.13	8.12	26.38
4.53	13.43	8.86	26.50
4.83	13.78	9.82	26.73
5.08	14.16	10.22	26.98
5.43	15.16	10.52	27.33
5.85	17.18	10.73	27.78
5.90	17.66		

POTENTIOMETRIC TITRATION 5-NITRAMINOTETRAZONE (SOLVATED)
 PREPARED FROM N-NITRO-N'-AMINOGUANIDINE

Sample weight: 0.2106 g. in 200 ml. of water

Potassium Hydroxide: 0.1043 N

pH	Base Added Ml.	pH	Base Added Ml.
2.52	0.00	5.70	13.05
2.65	2.37	6.02	14.73
2.72	3.93	6.08	15.13
2.76	4.45	6.12	15.45
2.79	4.97	6.22	15.95
2.85	5.97	6.56	17.97
2.95	6.71	7.06	19.70
3.27	8.77	7.31	20.35
3.42	9.37	7.95	21.05
3.90	10.27	9.77	21.45
4.19	10.55	10.27	21.72
4.55	10.83	10.53	21.95
4.78	11.00		
4.95	11.20		
5.21	11.65		

POTENTIOMETRIC TITRATION 1-METHYL-5-NITRAMINOTETRAZOLE

Sample weight: 0.1012 g. in 100 ml. of water
 Potassium Hydroxide: 0.0830 N

Ml. Base Added	pH	Ml. Base Added	pH
0.00	2.38	4.70	2.78
1.00	2.43	4.80	2.78
2.00	2.51	4.90	2.80
3.00	2.58	5.00	2.81
3.50	2.62	6.00	2.98
3.60	2.63	7.00	3.22
3.72	2.64	8.00	3.94
3.80	2.67	8.25	4.82
3.90	2.67	8.29	5.43
4.00	2.68	8.33	5.93
4.10	2.70	8.37	6.35
4.20	2.71	8.42	6.78
4.30	2.72	8.45	7.33
4.40	2.73	8.49	8.58
4.50	2.75	8.53	9.18
4.60	2.76	8.75	10.08

POTENTIOMETRIC TITRATION 1-ETHYL-5-NITRAMINOTETRAZOLE

Sample weight: 0.1168 g. in 100 ml. of water

Potassium Hydroxide: 0.0830 N

Ml. Base Added	pH	Ml. Base Added	pH
0.00	2.39	5.00	2.79
1.00	2.45	5.50	2.88
2.00	2.52	6.00	2.95
3.00	2.60	7.00	3.16
3.50	2.63	8.00	3.56
3.60	2.65	8.15	3.66
3.70	2.66	8.30	3.79
3.80	2.67	8.42	3.96
3.90	2.68	8.55	4.20
4.00	2.70	8.62	4.52
4.10	2.71	8.67	4.83
4.30	2.73	8.72	5.52
4.40	2.73	8.76	6.13
4.50	2.75	8.80	6.79
4.60	2.75	8.83	7.28
4.70	2.76	8.88	9.13
4.80	2.78	8.92	9.45
4.90	2.79	9.00	9.88

POTENTIOMETRIC TITRATION 5-METHYLNITRAMINOTETRAZOLE

Sample weight: 0.0970 g. in 100 ml. of water
Potassium Hydroxide: 0.0830 N

Ml. Base Added	pH	Ml. Base Added	pH
0.00	2.50	6.00	3.23
1.00	2.57	6.50	3.39
2.00	2.67	7.00	3.61
3.00	2.76	7.50	3.99
3.50	2.82	7.75	4.46
3.60	2.83	7.84	4.82
3.70	2.84	7.92	5.52
3.80	2.85	7.95	5.88
3.90	2.86	8.00	6.18
4.00	2.87	8.03	6.45
4.10	2.89	8.07	6.78
4.20	2.90	8.11	7.16
4.30	2.92	8.15	8.27
4.40	2.94	8.19	9.05
4.50	2.96	8.31	9.85
5.00	3.03		

POTENTIOMETRIC TITRATION 5-ETHYLNITRAMINOTETRAZOLE

Sample weight: 0.0990 g. in 100 ml. of water
Potassium Hydroxide: 0.0830 N

Ml. Base Added	pH	Ml. Base Added	pH
0.00	2.49	4.50	2.98
1.00	2.57	5.00	3.08
2.00	2.67	6.01	3.33
3.00	2.77	6.75	3.75
3.30	2.81	7.00	4.04
3.40	2.82	7.25	5.12
3.50	2.83	7.29	5.63
3.60	2.83	7.33	6.03
3.70	2.85	7.37	6.32
3.80	2.86	7.43	6.78
3.90	2.88	7.46	7.25
4.00	2.89	7.50	8.72
4.10	2.91	7.53	9.20
4.20	2.93	7.57	9.53
4.30	2.94	8.00	10.40

THE SYNTHESIS AND CHARACTERIZATION
OF
NITRAMINOTETRAZOLES

By

James A. Garrison

AN ABSTRACT

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Approved

Robert M. Hecht

THESIS ABSTRACT

It has long been known that the nitric acid salts of certain amidic derivatives such as urea and guanidine can be dehydrated with the formation of nitrourea and nitroguanidine, respectively. In both instances the fundamental reaction appears to involve conversion of a substituted ammonium nitrate into a similarly substituted nitramine. The structural analogy which can be observed between 5-aminotetrazole (I) and guanidine (II) suggested the possibility that the nitric acid salt of the former might be converted by dehydration into a nitramino tetrazole.



I

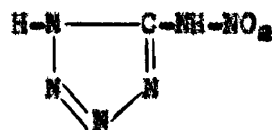


II

This work describes the preparation of the nitric acid salt of 5-aminotetrazole and its conversion into 5-nitraminotetrazole. Although 5-nitraminotetrazole had already been prepared by the treatment of N-nitro-N'-aminoguanidine with nitrous acid and cyclization of the resulting guanyl azide (1), it was necessary to reconcile the recorded properties (1) of the nitraminotetrazole with those observed in this laboratory. A sample of 5-nitraminotetrazole was prepared by the technique of Lieber, et al. (1) and its properties compared with those

of the nitraminotetrazole obtained from 5-aminotetrazole. It was found that 5-nitraminotetrazole prepared by both procedures were identical in all respects.

Tetrazole derivatives in which the hydrogen attached to the ring nitrogens has not been replaced generally behave as acidic substances (2,3). 5-Nitraminotetrazole (III) is no exception and, in fact,



III

behaves as a dibasic acid due to the presence of a second dissociable hydrogen in the nitramino group. It had been suggested without sufficient supporting evidence that the hydrogen of the nitramino group was most easily dissociated as a proton (4). In order to establish which of the two hydrogens of 5-nitraminotetrazole was most easily dissociated, the preparation of nitraminotetrazoles in which one or the other hydrogen was replaced by a simple alkyl group was undertaken. Since 1-alkyl-5-aminotetrazoles (5) and 5-alkylaminotetrazoles (3) could be prepared by unequivocal syntheses, the nitration of compounds of these types by dehydration of their nitric acid salts was studied. The structures of the resulting compounds were supported by independent synthesis and by comparison of their physical properties including absorption spectra.

The apparent dissociation constants of 1-alkyl-5-nitraminotetrazoles and the 5-alkylnitraminotetrazoles were determined. It was found that both series of compounds were moderately strong acids and that either hydrogen could have been responsible for the first dissociation of 5-nitraminotetrazole.

The ultraviolet absorption spectra of both series of alkyl 5-nitraminotetrazoles were determined. It was found that both the 1-alkyl-5-nitraminotetrazoles and their potassium salts exhibited a maximum absorption at 277-278 m μ . and a minimum absorption at 236-7 m μ . 5-Nitraminotetrazole was found to possess maximum and minimum absorption at the same wave lengths. On the other hand, 5-alkylnitraminotetrazoles and their potassium salts exhibited maximum absorption at 246 m μ . From this it was concluded that the first dissociation of 5-nitraminotetrazole involved the hydrogen of the nitramino group.

The alkyl 5-nitraminotetrazoles were characterized by their infrared absorption spectra and by preparation of salts with 2-amino-pyridine.

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