THE SYNTHESIS OF 1-SUBSTITUTED TETRAZOLES AND SPECTROSCOPIC STUDIES WITH TETRAZOLES

By

Frances Gertrude Fallon

A THESIS

Submitted to the College of Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1956

9-24-57
G 2407

ACKNOWLEDGMENT

The author wishes to thank Dr. Robert M. Herbst, under whose valuable guidance and help this investigation was carried out.

****

VITA

Frances Gertrude Fallon

candidate for the degree of

Doctor of Philosophy

Final examination:

Dissertation: The Synthesis of 1-Substituted Tetrazoles and Spectroscopic Studies with Tetrazoles

Outline of Studies

Major subject: Organic Chemistry

Minor subjects: Biochemistry, Physical Chemistry

Biographical Items

Born, November 2, 1923, Owing Mills, Maryland

Undergraduate Studies, Goucher College, 1942-46

Graduate Studies, Michigan State University 1950-56

Experience: Laboratory Technician, Chemistry Laboratory, Johns Hopkins Hospital, 1946-48;

Laboratory Technician, Department of Pharmacology and Experimental Therapeutics, Johns Hopkins University, 1948-50;

Graduate Assistant, Michigan State University, 1950-53, 1954-55;

American Viscose Corporation Fellowship, 1953-54.

Member of Phi Beta Kappa, Society of the Sigma Xi

THE SYNTHESIS OF 1-SUBSTITUTED TETRAZOLES AND SPECTROSCOPIC STUDIES WITH TETRAZOLES

By

Frances Gertrude Fallon

AN ABSTRACT

Submitted to the College of Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

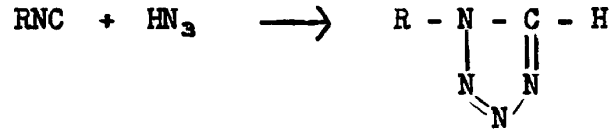
Year 1956

Approved Robert M. Herbst

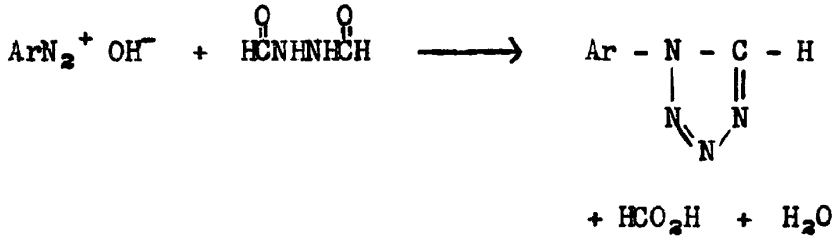
ABSTRACT

Although a great many 5-substituted tetrazoles are known, very few 1-substituted tetrazoles have been reported up to the present time. It was the purpose of this study to investigate the preparation and properties of further compounds of the 1-substituted tetrazole series. The preparation of such a series would also allow comparative spectroscopic studies, in the ultraviolet and infrared regions, of alkyl- and aryltetrazoles, including both 1- and 5-monosubstituted compounds, as well as 1,5-disubstituted tetrazoles.

Of the methods employed to obtain the seven known 1-substituted tetrazoles, three have possibilities as general methods.* Oliveri-Mandala and Alagna (1) added hydrazoic acid to various isocyanides to obtain the corresponding tetrazole.



Dimroth and DeMontmollin (2) prepared several 1-aryltetrazoles by addition of the appropriate diazonium chloride to an alkaline solution of diformylhydrazine.



*Two of these were utilized in the present investigation.

During the present study, a series of seven 1-alkyltetrazoles were prepared from the corresponding isocyanides. Attempts to prepare 1-phenyltetrazole both by the isocyanide and Dimroth methods showed that neither procedure is entirely satisfactory. Consequently a new method was developed for the synthesis of 1-aryltetrazoles. The procedure employed is an extension of the von Braun method for the preparation of 1,5-disubstituted tetrazoles (3), and consists in the reaction of phosphorus pentachloride with formanilides, followed by the addition of hydrazoic acid to the reaction mixture. A series of eight 1-aryltetrazoles was prepared by this method. The same method was successfully extended to the synthesis of 1-isobutyltetrazole from N-isobutylformamide. Six of the alkyltetrazoles and six of the aryltetrazoles prepared are new compounds.

Infrared and ultraviolet absorption spectra were obtained on all the compounds synthesized. For comparison, spectra were also obtained on other alkyl and aryltetrazoles. Tetrazole and its alkyl derivatives show little absorption in the ultraviolet region examined. The 1-aryltetrazoles show considerable absorption, with curves similar to those obtained by Wilson (4) for 5-aryltetrazoles. In both aryl series, the maxima are shifted to shorter wavelengths when steric factors interfere with the coplanarity of the phenyl and tetrazole rings.

Infrared spectra were obtained for a total of 46 tetrazoles, of which fifteen were 1-substituted, seventeen were 5-substituted, and thirteen were 1,5-disubstituted. An attempt has been made to identify bands characteristic of the tetrazole ring, and eight such bands have

been tentatively identified, three of which seem to be split into two peaks in many of the substituted compounds. This confirms and extends the conclusions of Lieber, et al. (5), who found that the region from 9 to 10 microns (1111 to 1000 cm^{-1}) contained from one to three bands characteristic of tetrazoles.

REFERENCES

1. Oliveri-Mandala, E., and Alagna, B., Gazz. chim. ital. 40, II, 441-444 (1910).

2. Dimroth, O., and DeMontmollin, G., Ber. 43, 2904-2915 (1910).

3. Von Braun, J., and Rudolph, W., Ber. 74, 264-272 (1941).

4. Wilson, K. R., The Apparent Acidic Dissociation Constants of Some 5-Aryltetrazoles, M. S. Thesis, Michigan State College, 1955.

5. Lieber, E., Levering, D. R., and Patterson, L. J., Anal. Chem. 23, 1594-1604 (1951).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

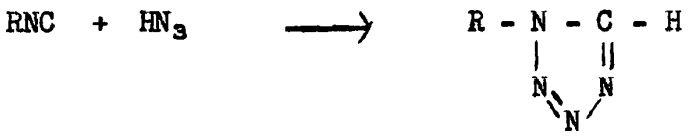
LIST OF FIGURES - Continued

INTRODUCTION

Although a great many 5-substituted tetrazoles are known, very few 1-substituted tetrazoles have been reported up to the present time. In his review of the chemistry of tetrazoles in 1947, Benson (1) lists only seven examples, including 1-hydroxytetrazole, the identity of which he questions. It was the purpose of this study to investigate the preparation and properties of further compounds of the 1-substituted tetrazole series.

The preparation of such a series would also allow comparative spectroscopic studies, in the ultraviolet and infrared regions, of alkyl- and aryltetrazoles, including both 1- and 5- monosubstituted compounds, as well as 1,5-disubstituted tetrazoles.

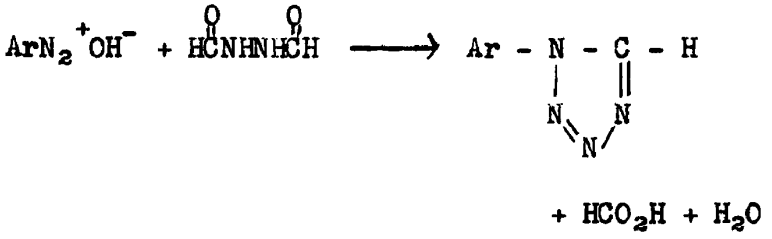
Of the methods employed to obtain the seven 1-substituted tetrazoles listed by Benson, three have possibilities as general methods, while others are special methods for preparing one particular compound. Oliveri-Mandalà and Alagna (2) obtained the 1-methyl-, 1-ethyl-, and 1-phenyltetrazoles by the addition of hydrazoic acid to the corresponding isocyanides in ether solution.



The reactants were mixed and allowed to stand overnight at room temperature or warmed several hours on the steam bath. Dilution of

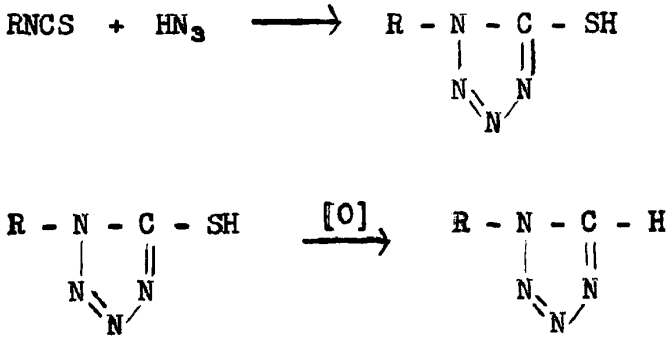
the reaction mixture with ether was found to slow the reaction.

1-Aryltetrazoles were prepared by Dimroth and De Montmollin (3) by adding the appropriate diazonium chloride to an alkaline solution of diformylhydrazine.



The 1-phenyl, 1-p-tolyl-, and 1-p-nitrophenyltetrazoles were obtained by this method.

The oxidation of 1-substituted-5-mercaptotetrazoles has furnished 1-substituted tetrazoles in two cases (4, 5). The mercaptotetrazoles were obtained by reaction of sodium azide or hydrazoic acid with an isothiocyanate, followed by cyclization through the use of heat or an alkaline reagent. Although only the 1-methyl- and 1-phenyltetrazoles have been prepared by this procedure, a number of other 1-substituted-5-mercaptotetrazoles have been reported (1).



A number of more limited methods have furnished individual compounds of this series. The alkylation of tetrazole with diazomethane furnished 1-methyltetrazole (4), while alkylation of the silver salt of tetrazole with ethyl iodide produced a mixture of 1-, and 2-ethyltetrazoles (6).

Nitration of 1-phenyltetrazole produced a 1-nitrophenyltetrazole, apparently with the nitro group in the para position, although the details of identification of this compound were not given (5). The corresponding aminophenyltetrazole was also prepared by reduction of the nitro group. Thermal decomposition of 1-phenyl-2-anilinotetrazole produced some 1-phenyltetrazole (7).

It will be noted from the above that the only 1-alkyltetrazoles previously known are the methyl and ethyl compounds. A series of seven 1-alkyltetrazoles, including 1-ethyltetrazole, has been prepared in the present study from the corresponding isocyanides.

Four 1-aryltetrazoles were known previously. Attempts to prepare 1-phenyltetrazole both by the isocyanide and Dimroth methods have shown that neither procedure is entirely satisfactory. Consequently a new method was developed for the synthesis of 1-aryltetrazoles. The procedure employed is an extension of the von Braun method for the preparation of 1,5-disubstituted tetrazoles (8), and consists in the reaction of phosphorus pentachloride with formanilides, followed by the addition of hydrazoic acid to the reaction mixture. In one instance, the same method has been successfully extended to the preparation of a 1-alkyltetrazole from an N-alkylformamide.

The infrared and ultraviolet spectra of these compounds and other alkyl- and arylsubstituted tetrazoles have been obtained. Although a number of previous workers have reported spectroscopic data on tetrazole derivatives, most of the compounds included have been 5-aminotetrazoles, where the association of spectroscopic data with structural features is complicated by the possibility of tautomerism.

DISCUSSION

Three methods for the synthesis of 1-substituted tetrazoles were employed in the course of this investigation. In the following sections, each of these procedures will be discussed individually. The reaction of an alkyl or aryl isocyanide with hydrazoic acid to form a 1-substituted tetrazole is referred to in the discussion below as the isocyanide method. The coupling of a diazonium salt with diformylhydrazine and subsequent cyclization of the product to a 1-aryltetrazole is called the Dimroth method. The treatment of a formanilide or N-alkylformamide first with phosphorus pentachloride and then with hydrazoic acid to yield the desired tetrazole is referred to as the formamide method. The work on the spectra of the compounds prepared by these methods, and of other tetrazoles, will be considered in the latter part of this discussion.

Isocyanide Method

Since the most general method of preparation for 1-substituted tetrazoles appeared to be that utilizing the corresponding isocyanides, the first phase of the study was the selection of a suitable method for obtaining these compounds. Isocyanides were first recognized as new compounds by Gautier (9,10), who obtained them from the reaction of silver cyanide with various alkyl iodides. He called attention to a number of instances in which members of the series had been

obtained previously without recognition of their identity. Almost simultaneously, Hofmann (11) reported the reaction of aniline with chloroform and alcoholic potassium hydroxide to form phenyl isocyanide.

$$C_6H_5NH_2 + 3KOH + CHCl_3 \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

Further references in the literature to the preparation of isocyanides report the use of modifications of one or the other of the above reactions. For the Hofmann method, the more detailed directions given by Nef (12) are usually cited. However, Biddle (13) suggested that the low yields usually obtained probably were due to interaction of the product with alcohol. He reported a preparation of phenyl isocyanide in which alcohol was excluded and powdered potassium hydroxide was employed as the reagent. The yield was 35-40%, in contrast to the 15% yield reported by Nef. Hammick, et al. (14) obtained a 50% yield of phenyl isocyanide by using powdered sodium hydroxide and small amounts of methanol, added only as necessary to keep the reaction going. Lindemann and Wiegrebe (15) also report a 50% yield from a similar procedure using small amounts of ethanol. Later, Malatesta (16) described a similar modification, using powdered potassium hydroxide and excess chloroform as solvent. Excellent yields were reported for both alkyl and aryl isocyanides, but more recent workers have been unable to confirm these high yields (17). In the present study, phenyl isocyanide was prepared according to Malatesta's directions. The yield in this instance was 30%, while Malatesta reported a 70% yield. Since this is a heterogeneous reaction, differences in the particle

size of the potassium hydroxide and in the degree of heating are probably responsible for the wide variations in the results.

The method described by Gautier for preparation of alkyl isocyanides proved quite successful, with slight modifications. The alkyl iodide and dry silver cyanide were heated under reflux on a steam bath for the desired reaction time. Progress of the reaction was followed by inspection. For a period of time, varying for each member of the series, no change was evident. The start of the reaction was marked by a crumbling, moist appearance in the reaction mixture. The double salt of alkyl isocyanide and silver cyanide gradually formed a syrupy layer, varying from colorless to dark red-brown, while silver iodide formed a compact lower layer.

According to Gautier, excessive heating causes marked darkening and decomposition of the double salt. In the present series of preparations, all heating was carried out on a steam bath instead of the salt water bath and oil bath described by Gautier for the higher homologues. The lengthened reaction time necessary at lower temperatures appeared to be due, at least in part, to a longer induction period. The time of total heating varied in individual cases from three to eight hours.

The double salt was decomposed by addition of water and potassium cyanide, and the product was isolated by steam distillation.

$$RI + 2AgCN \longrightarrow RNC \cdot AgCN + AgI$$

$$RNC \cdot AgCN + KCN \longrightarrow RNC + AgCN \cdot KCN$$

Crude yields by this method were excellent. Except for preliminary studies with butyl isocyanide, the products were not further purified or characterized, but were used immediately for preparation of the corresponding tetrazole. A list of the compounds prepared is given in Table I.

The selection of suitable reaction conditions was greatly simplified by the data assembled by Guillemard (18), who investigated this reaction in great detail. He studied the reaction of ethyl iodide with a variety of metallic and complex cyanides at temperatures from 80° C. to 160° C. for varying periods of time. Each reaction was carried out in a sealed tube, and the proportions of the nitrile and isocyanide formed in the reaction mixture were determined by analytical procedures. Only silver cyanide was found to form alkyl isocyanides exclusively at lower temperatures, while even in this case some nitrile was obtained at 130° C. and above. The optimum yield was obtained by heating at 80° C. for four to eight hours.

In a second series of experiments, Guillemard prepared other alkyl isocyanides by heating equal weights of the alkyl iodide and silver cyanide for four hours at temperatures from 80° to 160° C. Again, the best yields were obtained at 80° C. Although no nitrile was detected at this temperature, the higher homologues formed some nitrile at temperatures as low as 100° C. It is interesting to note that no isocyanide and only traces of nitrile were obtained from 2-iodohexane, the only secondary iodide studied by Guillemard. Gautier had noted the formation of an alkene and hydrogen cyanide in certain reactions

TABLE I

Alkyl Isocyanides

RNC

R	Moles RI	Heating Time (hrs.)	Yield Crude Product	
			Grams	Percent
C_2H_5	0.1	5	5.5[a]	100
C_3H_7	0.2	--	13.6	99
	0.2	--	12.9	93
C_4H_9-n	0.1	4	7.4[a]	89
	0.1	4	(3.2)[b]	(40)
	0.2	4	14.0	84
C_4H_9-iso	0.2	31	15.8	95
C_5H_{11}-n	0.2	5.5	9.1	47
C_5H_{11}-iso	0.1	5.5	8.8[a]	91
			(4.8)[b]	(49)
	0.2	8	11.9	61
C_6H_{13}-n	0.2	6	8.4	38
C_7H_{15}-n	0.2	8	22.8	91
	0.2	8	13.6	54

(a) Crude product.

(b) Determined by titration - see page 11.

where the alkyl iodide was probably the secondary isomer or a mixture.

Since the alkyl isocyanides in the present study were to be converted immediately to tetrazoles without purification, a rapid estimation of isocyanide content in the crude material appeared highly desirable. In preparation for the investigations described above, Guillemard developed several methods for the analysis of isocyanides. When a known amount of bromine was added dropwise to ethyl isocyanide, both reactants being diluted with the same solvent, the bromine color did not appear until exactly one molar proportion of bromine had been added. The extremely unstable compound, $C_2H_5NCBr_2$, was isolated and described. Analysis gave 73.9% bromine content, as compared to a theoretical value of 74.3%. Nef (12) had reported earlier the preparation and analysis of the more stable chlorine compounds, $RNCCl_2$, from a number of aryl isocyanides. A number of derivatives were also prepared by reaction with water, aniline, ethanol, and other reagents. The products in each case confirmed the original compound as the addition product of one mole of chlorine with one mole of isocyanide. Bromine and iodine were also said to be absorbed immediately by solutions of an isocyanide at 0° C., but the resulting products were oils and were not purified. Guillemard's method involved the reaction of the isocyanide with bromine or hypobromite and decomposition of the product in the presence of water to release carbon dioxide, which was precipitated as barium carbonate and weighed. Although Guillemard's gravimetric procedure was far too long for the purposes of the present

study, the report of instant absorption of bromine and apparently quantitative reaction suggested that a titration method might be feasible.

A number of workers have determined phenols by the reaction with bromide-bromate solution, which acts, under acid conditions, as a standard solution of bromine (19,20). Since bromine is released only on addition of acid, and since the excess is converted to bromide ion on addition of potassium iodide, bromination time is easily controlled. The addition of potassium iodide releases iodine in proportion to the excess bromine. The iodine is then determined by titration with standard thiosulfate with starch as the indicator. An attempt was made to apply this determination to isocyanides. The equations for the reactions involved are:

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$

$$RNC + Br_2 \longrightarrow RNCBr_2$$

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

The crude isocyanide was taken up in benzene, dried, and diluted to a known volume. After aliquots were removed for analysis, the remaining solution was used immediately to form the tetrazole. The method was applied to several runs, but tests on weighed samples of supposedly pure butyl isocyanide gave low results. The work is summarized in Table II. When the dilution of crude isocyanide with benzene appeared to slow the subsequent reaction with hydrazoic acid

TABLE II

Attempted Estimation of Butyl Isocyanide

Sample	Boiling Point (°C.)	Weight of Sample (g.)	Volume of Isocyanide (ml.)	Density of Isocyanide (g./ml.)	Weight of Isocyanide By Titration (g.)	Time Interval (hours)
A	--	6.19	--	--	4.57 3.91 4.11 3.54	24
A	--	6.19	--	--	2.89 2.61 2.46	36
B	121-2	0.86	1	0.86	0.46 0.46 0.38 0.55	1-3/4
C	123-4	1.58	2	0.79	1.26 1.28 1.23 1.22	1-1/3

Sample A was purified by steam distillation alone.
Samples B and C were purified by steam distillation, followed by two distillations at atmospheric pressure.

too much, further work on this analytical method was abandoned. Although it has not been possible to substantiate the validity of the method, it still appears to show promise.

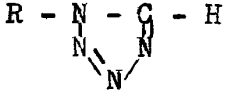
It will be noticed that the samples of butyl isocyanide used were not uniform. The dark color in crude sample B, and the higher density of the twice-distilled product probably reflect the presence of butyl iodide as a contaminant. Davis and Yelland (21) report the boiling point of n-butyl isocyanide as 124-125° C. at 761.5 mm. Gautier (10) reports the density of methyl isocyanide as 0.7557 at 4°, and that of ethyl isocyanide as 0.7591 at 4° and 0.7417 at 21.3°. He also reports a value of 0.7873 at 4° for the butyl compound he prepared, but it is doubtful whether he actually had the n-butyl isomer in hand. In any case, it may readily be seen that sample C approaches these physical constants most closely, and that it also gives the best results by titration. It seems possible that sample C is still not entirely pure, particularly since the density is somewhat higher than that expected from the values reported for other members of the series. If this is true, the value obtained may represent the actual isocyanide content. The increased precision in the determinations on sample C may be due to the insertion of one minute bromination time between addition of the acid and of the potassium iodide. This agreement of duplicate determinations performed at the same time on the same sample, and the drop in the apparent isocyanide content with time, as shown in the case of sample A, is another bit of evidence in favor of the idea that the isocyanide is actually determined by this reaction. The gradual

drop in the apparent isocyanide content is not surprising in view of the known ease with which these compounds polymerize.

In most preparations, as has already been mentioned, the crude isocyanide was isolated by steam distillation, dried briefly over sodium sulfate, and immediately mixed with a solution of hydrazoic acid in benzene for conversion to the tetrazole. The mixture was warmed on the steam bath under reflux for one to five hours, after which the solvent was removed and the residue was boiled with a strong solution of hydrochloric acid in an attempt to hydrolyze any polymeric isocyanide present. The 1-alkyltetrazoles were then purified by fractional distillation through a small Vigreux column. Several distillations were usually necessary. In early runs, both refractive index and infrared spectrum were obtained for each fraction. It soon became apparent, however, that the 1-alkyltetrazoles showed remarkable similarity to one another, both in infrared spectra and in refractive indices. Thereafter, it was only necessary to obtain infrared spectra for the fractions close to the expected refractive index. The compounds obtained are listed in Table III. Two of these gave analyses slightly outside the acceptable range, but show marked similarity in physical properties to other members of the series. It would appear that the contaminant, in the case of the isoamyl compound, is of higher refractive index than the tetrazole. Pure 1-isobutyltetrazole, obtained by the formamide method described below, has a lower refractive index than the normal isomer. Therefore, 1-isoamyltetrazole should probably have a refractive index somewhat lower than that reported.

TABLE III

1-Alkyltetrazoles



R	Boiling Point (°C./mm.)	Refractive Index at 20°C.	Molecular Formula	Analysis (e) Calculated C	H	N	Found C	H	N
C_2H_5	147-8/14	1.4601	$C_3H_6N_4$	36.72	6.17	57.11	36.79	6.32	56.93
$n\text{-}C_4H_9$	143-5/2	(1.4600)[b]	$C_5H_{10}N_4$	47.62	7.94	44.44	47.91	7.67	44.32
$iso\text{-}C_4H_9$[a]	128-132/2-3[c]	1.4590	$C_5H_{10}N_4$	47.62	7.94	44.44	Not Analyzed		
$iso\text{-}C_4H_9$[d]	121-123/1	1.4590	$C_5H_{10}N_4$	47.62	7.94	44.44	47.94	8.24	44.64
$n\text{-}C_5H_{11}$	138-9/1	1.4608	$C_6H_{12}N_4$	51.43	8.57	40.00	51.42	8.66	39.96
$iso\text{-}C_5H_{11}$[a]	143-5/1	1.4607	$C_6H_{12}N_4$	51.43	8.57	40.00	51.89 51.83	8.72 8.92	39.53 39.30
$n\text{-}C_6H_{13}$	144-6/1	1.4610	$C_7H_{14}N_4$	54.55	9.09	36.36	54.74	9.16	36.15
$n\text{-}C_7H_{15}$[a]	150-2/1	1.4613	$C_8H_{16}N_4$	57.14	9.52	33.33	57.68 57.43	9.38 9.13	32.50 32.65

(a) Impure material.
(b) Reading taken at 21°C. On the basis of a change of .0004 per degree, the refractive index at 20°C. would be 1.4604.
(c) Variations in pressure, due to decomposition of residue.
(d) Prepared from N-isobutylformamide. All other compounds listed were prepared from the corresponding isocyanide.
(e) Analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

Although yields of pure material are somewhat low, the above method is reasonably satisfactory for the preparations of 1-alkyltetrazoles. The chief difficulty is the unpleasant character of the intermediates, which are both highly toxic and difficult to obtain in pure form. It seems probable that the low yields are due chiefly to the first step.

The single aryl compound prepared by this method was 1-phenyltetrazole. The low yield of phenylisocyanide by Malatesta's modification of the Hofmann reaction has already been mentioned. The yield in the second step, calculated on the weight of crude isocyanide used, was also quite low. The method therefore appeared unsatisfactory for preparation of a series of compounds.

Dimroth Method

The procedure described by Dimroth and De Montmollin (3) appeared to be convenient for preparing the 1-aryltetrazoles. The procedure involves addition of a neutralized solution of a diazotized aromatic amine to an alkaline solution of a diacylhydrazine. Interaction of these reactants leads to the formation of a diazohydrazide and the latter undergoes cyclization to form a substituted tetrazole with elimination of a molecule of a carboxylic acid. When applied to diformylhydrazine, the end product is a 1-aryltetrazole.

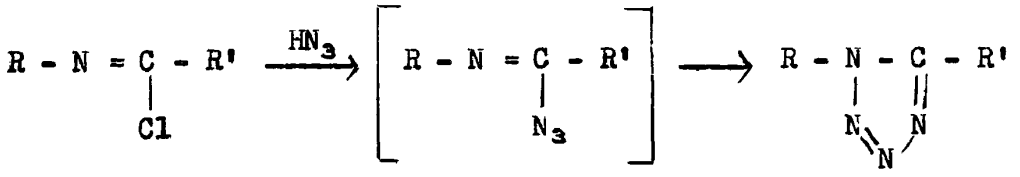
Diformylhydrazine was easily obtained from sodium formate and hydrazine sulfate according to the directions of Pellizzari (22). The finely ground solids were heated together on the steam bath,

after which the product was extracted from its mixture with sodium sulfate by means of hot alcohol. On cooling, the extract deposited white crystals of diformylhydrazine. The time of heating described by Pellizzari appeared to be inadequate for a satisfactory yield.

The chief difficulty with the Dimroth method when applied to the preparation of 1-aryltetrazoles is the marked sensitivity of the diazonium salt to both pH and temperature. Careful control of the neutralization step would appear to be an important consideration. Neutralization to litmus causes immediate darkening of the solution; neutralization to Congo Red appears to be more satisfactory. All stages of the reaction require control of the temperature below 0° C. A very small amount of impure 1-phenyltetrazole was obtained by this method. Further investigation of suitable conditions for the reaction was not carried out, since the formamide method described below proved a more convenient route to the 1-aryltetrazoles.

Formamide Method

The difficulties encountered in the synthesis of 1-aryltetrazoles by the two methods described above led to a search for a more convenient procedure. One method which had been applied successfully to the preparation of 1,5-disubstituted tetrazoles was the addition of hydrazoic acid to the appropriate imide chloride. The intermediate is believed to be an imide azide, which cyclizes to the tetrazole.



The first report of this reaction was made by Forster (23), who obtained 1-hydroxy-5-phenyltetrazole from benzhydroximic chloride and powdered sodium azide. The preparation of 1,5-diphenyltetrazole by a similar procedure was carried out by Schroeter (24), with silver azide as the reagent. Later, von Braun and Rudolph (8) pointed out that the reaction could be extended to more sensitive imide chlorides by the use of hydrazoic acid, which reacts at a lower temperature than the metal azides. With this modification, von Braun and Rudolph were able to apply the reaction successfully to the preparation of a whole series of 1,5-diaryl- and 1-alkyl-5-aryltetrazoles. No compounds were prepared containing alkyl groups in the 5-position, since von Braun's previous work on the preparation and properties of imide chlorides had shown that compounds of the type $R - N = \underset{Cl}{C} - CHR_2'$, where R is an alkyl or aryl group and R' is hydrogen or an alkyl group, are unstable and readily rearrange and condense, with loss of hydrogen chloride, to an amidine-like structure, formed from two molecules of the imide chloride (25,26).

$$CH_3 - \underset{Cl}{C} = N - C_6H_5 \longrightarrow CH_2 = \underset{Cl}{C} - NHC_6H_5$$

$$CH_3 - \underset{Cl}{C} = N - C_6H_5 + CH_2 = \underset{Cl}{C} - NHC_6H_5 \longrightarrow CH_3 - C(= N - C_6H_5) - N(C_6H_5) - \underset{Cl}{C} = CH_2 \quad + HCl$$

The imide chlorides obtained from N-substituted benzamides were found to be far more stable. At high temperatures, these compounds decompose

to a nitrile and an alkyl or aryl chloride (25).

$$Ar - \underset{Cl}{C} = N - R \longrightarrow ArCN + RCl$$

Harvill, Herbst, Schreiner and Roberts (27) showed that the reaction could be extended to 1-aryl-5-alkyltetrazoles, and even to 1,5-dialkyltetrazoles if the imide chloride was not isolated. Their procedure consisted in the treatment of an N-substituted amide in benzene solution with phosphorus pentachloride, and addition of a benzene solution of hydrazoic acid to the reaction mixture at room temperature. The reaction was brought to completion by the application of heat. The yields reported varied from 10 to 75%.

The application of this method to the synthesis of 1-aryltetrazoles would require the use of substituted formanilides as starting materials. Wallach (28) had studied the reaction of formanilide with phosphorus pentachloride and reported that the product was N, N'-diphenylformamidine:

$$C_6H_5 - N = \underset{H}{C} - \underset{H}{N} - C_6H_5$$

However, he did not use a solvent or control the temperature of the exothermic reaction. Products were frequently isolated by distillation of the reaction mixture at atmospheric pressure. Therefore, it appeared quite probable that the N, N'-diphenylformamidine was formed from thermal decomposition products of the imide chloride or formanilide. If either the imide chloride or the isocyanide formed by interaction of phosphorus pentachloride and formanilide could be stabilized by

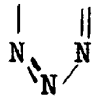
controlling the temperature and diluting the reaction mixture, the subsequent addition of hydrazoic acid could lead to formation of the desired 1-aryltetrazoles.

$$C_6H_5NHCHO + PCl_5 \longrightarrow C_6H_5NHCHCl_2 + POCl_3$$

$$C_6H_5NHCHCl_2 \longrightarrow C_6H_5N = CHCl + HCl$$

$$C_6H_5N = CHCl \longrightarrow C_6H_5N \equiv C + HCl$$

$$C_6H_5N = CHCl + HN_3 \longrightarrow C_6H_5 - N - C - H + HCl$$



$$C_6H_5N \equiv C + HN_3 \longrightarrow C_6H_5 - N - C - H$$

In the experiments reported in this thesis, toluene was used as a diluent and solvent for the reactants. The reaction mixture was kept at or below room temperature during the addition of the phosphorus pentachloride. On several occasions, stirring was stopped and the ice bath lowered during the course of the reaction. In these cases, a heavy oil, ranging from yellow to bright red, was noted below the toluene layer. With the ice bath in place, this sometimes appeared as a pasty solid on the walls of the flask. While the reaction mixture remained cold, little or no evolution of hydrogen chloride was detected at the top of the condenser. However, if the reaction mixture was allowed to reach room temperature during the first step, evolution of hydrogen chloride was noted. These observations were interpreted by assuming that the colored oil was the amide chloride, R-NH-$CHCl_2$, which

is known to be quite unstable and which decomposes to give hydrogen chloride and the imide chloride.

Cooling and stirring were continued during the addition of hydrazoic acid to the reaction mixture. Towards the end of this addition, the ice bath was removed and the solution was allowed to warm to room temperature. Vigorous evolution of hydrogen chloride occurred as soon as the addition of the hydrazoic acid was begun. Evolution of hydrogen chloride continued for hours at a gradually decreasing rate. When the addition of hydrazoic acid was complete, the reaction mixture had become homogeneous. In most of the preparations of the 1-aryl series, fine, white needles were gradually deposited. This solid was at first thought to be the 1-aryltetrazole. Attempts to filter this material at the end of the reaction showed that it was quite soluble in water in some cases, while in others treatment with water merely changed the character of the solid without dissolving all of it. The water solution was acid to litmus. These observations suggest that the white needles formed in each case might be the hydrochloride of the expected product.

To simplify the handling of the product, which appeared to occur in part as the free base in toluene solution, and in part as the easily hydrolyzed hydrochloride, the whole reaction mixture was poured over ice to destroy phosphorus oxychloride, and then made alkaline to convert all of the product to the free base. It was soon found that chilling of the resulting two-phase mixture brought both product and large quantities of inorganic material out of solution. The mixture

was therefore filtered and the filter cake washed copiously with water. In many cases, all of the solid redissolved at this point. Any solid which did not dissolve was considered as part of the crude product. The aqueous layer of the two-phase filtrate was separated, combined with the aqueous washings, and extracted with toluene. The toluene extract was combined with the toluene layer from the filtrate, and the solution was concentrated to a small volume.

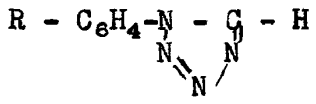
The crude product was usually contaminated with highly colored impurities. In most cases, a series of recrystallizations and treatments with decolorizing charcoal were necessary to obtain the pure, colorless material. Pure material was most easily obtained by the use of 99% isopropyl alcohol for recrystallization. However, most of the 1-aryltetrazoles are fairly soluble in both ethyl and isopropyl alcohols, so that losses during recrystallizations were large. The use of aqueous isopropyl alcohol caused less loss of material on each recrystallization, but also led to greater retention of colored impurities in the recrystallized product. Since the low-melting members of the series did not crystallize well from alcohols, cyclohexane was used for these compounds. The crude material was extracted repeatedly with small amounts of warm cyclohexane, and the two layers were separated by decantation. Although this process was tedious, the yield was far better than in the cases where low-melting compounds were recrystallized from isopropyl alcohol. Two recrystallizations from cyclohexane usually sufficed to obtain pure material, while the use of isopropyl alcohol required a number of recrystallizations, with

considerable loss of material. The 1-aryltetrazoles prepared by the formanilide method are listed in Table IV. While the yields are fairly low, the difficulty would appear to lie more in the purification of the product than in the formation of the tetrazole.

Several attempts to prepare 1-alkyltetrazoles according to the procedure used for the 1-aryl derivatives failed to yield any of the desired product. In these unsuccessful syntheses, it was noted that evolution of hydrogen chloride began before addition of hydrazoic acid. It seemed possible that the more reactive alkyl imino-chlorides might form the isocyanide before reaction with hydrazoic acid. The long stirring at room temperature would allow many side-reactions to interfere with the reaction between isocyanide and hydrazoic acid. Consequently, the reaction conditions were modified somewhat. The reagents were added with cooling and stirring as before, and stirring was continued at room temperature for one hour. The reaction mixture was then heated on the steam bath for three hours to complete the reaction. After the reaction mixture was poured over ice and made alkaline, the toluene layer was dried and distilled at reduced pressure. By this means, a 13% yield of 1-isobutyltetrazole was obtained. The product gave a satisfactory elemental analysis for the tetrazole and had the same refractive index as the best sample of 1-isobutyltetrazole obtained by the isocyanide method. The infrared spectra of the compounds prepared by these two methods are the same except in those areas believed to indicate impurities. It would appear therefore that the formamide method is also applicable, with suitable modification, to

TABLE IV

1-Aryltetrazoles



R	Melting Point (°C.)	Recryst. Solvent	Percent Yield	Molecular Formula	Analysis (a) Calculated C	H	N	Cl	Found C	H	N	Cl
H	65-66	Cyclo-hexane	15.6	$C_7H_6N_4$	57.52	4.14	38.34	--	57.47	3.91	38.60	--
m-CH_3	53-54	Cyclo-hexane	34.0	$C_8H_8N_4$	59.99	5.03	34.98	--	60.10	5.03	34.92	--
p-CH_3	93-94	Isopropyl Alcohol	28.4	$C_8H_8N_4$	59.99	5.03	34.98	--	59.76	4.92	34.92	--
o-Cl	86-87	Isopropyl Alcohol	40.8	$C_7H_5N_4Cl$	46.55	2.79	31.03	19.63	46.55	2.85	31.10	19.69
m-Cl	100.5-102	Isopropyl Alcohol	43.4	$C_7H_5N_4Cl$	46.55	2.79	31.03	19.63	46.50	2.85	31.20	19.66
p-Cl	155.5-156	Isopropyl Alcohol	32.1	$C_7H_5N_4Cl$	46.55	2.79	31.03	19.63	46.60	2.92	31.02	19.69
o-CH_3O	47.5-48.5	Cyclo-hexane	32.0	$C_8H_8N_4O$	54.54	4.58	31.81	--	54.78	4.61	32.00	--
p-CH_3O	116-117.5	Isopropyl Alcohol	34.8	$C_8H_8N_4O$	54.54	4.58	31.81	--	54.66	4.57	32.10	--

(a) Analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

the preparation of 1-alkyltetrazoles. While the yield and purity of the product appear no greater than in the isocyanide method, the advantage of the formamide method lies in the easier accessibility of the intermediates. In the aryl series, the formamide method is far more convenient than the other two methods studied.

Spectroscopic Studies

Although Benson (1) stated in 1947 that no spectroscopic studies of tetrazoles had been made up to that time, a number of workers have since reported investigations in this field. Ultraviolet spectra of a small number of compounds were reported by Havinga and Veldstra (29) and by Schueler, Wang, Featherstone and Gross (30). In the course of a study of the alkylation of 5-phenyltetrazole, Elpern and Nachod (31) used the ultraviolet spectra of the product and reference compounds as evidence that alkylation occurred in the 2-position on the tetrazole ring. Some of their results will be further discussed below in connection with those obtained in the present study.

Lieber, Levering and Patterson (32) studied the infrared spectra of thirty-eight high-nitrogen compounds, including 13 tetrazoles. Unfortunately, many of these compounds were sensitive to shock and could not be ground long enough to give sharp resolution to the spectra obtained on oil mulls. Assignments were suggested for a number of bands. The region from 9.0 to 10 microns (1111 to 1000 cm^{-1}) was considered the region in which bands characteristic of the tetrazole ring appear. Although the number of bands in this region varied from

one to three, three bands were found in most cases. These results have been confirmed by the present study.

The ultraviolet absorption of tetrazole itself and of several amino-tetrazoles has been explored by Mihina (33a) in acid, basic and neutral solution. Garrison (34) examined both ultraviolet and infrared spectra of some nitraminotetrazoles. Percival (35) studied the infrared spectra of several types of substituted aminotetrazoles and iminotetrazolines and pointed out that these types could be distinguished from one another by infrared spectra. Murphy and Picard (36) also studied both infrared and ultraviolet spectra of aminotetrazoles and iminotetrazolines. On the basis of the results obtained in these investigations, attempts have been made to establish the structure of these two groups of compounds (34,35,36), but no agreement has been reached.

More recently, Wilson (37) studied the ultraviolet spectra of a series of 5-aryltetrazoles. Since the results of the present investigation parallel and supplement those obtained by Wilson, his conclusions will be discussed more fully later on.

Ultraviolet Absorption Spectra

Ultraviolet absorption spectra were obtained for all eight of the 1-aryltetrazoles prepared, and for three members of the 1-alkyl series. Two 5-alkyl compounds were included for comparison. Wilson (37) had previously studied the ultraviolet spectra of a series of 5-aryltetrazoles. Since he had not examined the 5-m-tolyl and 5-p-tolyl derivatives, these were included in the present investigation to

complete the comparison. All of the aryltetrazoles were examined as 1×10^{-4} M solutions in 95% ethanol between 210 and 300 mμ. The absorption maxima and extinction coefficients are listed in Table V. The curves are shown in Figures 1 through 10.

A comparison of these results with those obtained by Wilson shows a marked similarity for corresponding substituents in the one and five positions. In both cases, para-substituted compounds absorb at slightly longer wavelengths than meta derivatives, while ortho derivatives show a pronounced shift to shorter wavelengths. The peak in 1-o-chlorophenyltetrazole has shifted below 210 mμ, so that only a shoulder occurs in the range examined. Although 5-o-chlorophenyltetrazole exhibits a maximum at 234 mμ, the 5-o-bromophenyl derivative shows a picture similar to the 1-o-chlorophenyl compound. The 5-aryltetrazoles have maxima at slightly longer wavelengths than the corresponding 1-aryltetrazoles. Extinction coefficients are also somewhat higher for 5-substituted compounds.

Neither tetrazole nor its monoalkyl derivatives exhibit any appreciable absorption in the range examined. The curves for 1×10^{-3} M solutions in 95% ethanol of tetrazole and its 1-butyl, 1-amyl, 1-hexyl, 5-butyl, and 5-hexyl derivatives are given in Figure 11. Although plotted on ten times the scale used for the aryl derivatives, the absorption is still not significant, and no maxima can be detected above 210 mμ. The 5-butyl and 5-hexyltetrazoles gave identical curves, within the error of the instrument. The same pattern of absorption is also shown by 5-cyclohexyltetrazole (31). These results confirm those

TABLE V

Ultraviolet Absorption Maxima of Some Aryltetrazoles

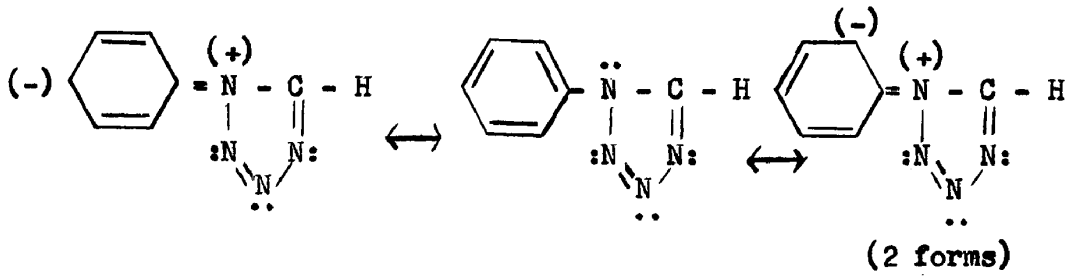
Compound	Max. (mμ)	
1-phenyltetrazole	236	9,260
1-m-tolyltetrazole	239	8,740
1-p-tolyltetrazole	243	10,100
1-o-chloro-phenyl-tetrazole	(215)[a]	(10,440)
1-m-chlorophenyl-tetrazole	238 240	8,830 8,780
1-p-chlorophenyl-tetrazole	240.5 243.5	14,040 14,050
1-o-methoxyphenyl-tetrazole	235 282.5	5,800 3,840
1-p-methoxyphenyl-tetrazole	255	10,930
5-m-tolyltetrazole	243	13,640
5-p-tolyltetrazole	246	16,720

(a) Shoulder

obtained by Mihina (33a), who examined the ultraviolet spectrum of tetrazole in acid, neutral and basic aqueous medium. The absorption in basic solution was somewhat higher than that in acidic or neutral solution, but no peak occurred in the region examined. Re-examination of the ultraviolet absorption spectrum of tetrazole in both aqueous and alcoholic solutions during the present investigation revealed slightly higher absorption in alcohol than water, but no maximum in either case.

The above results show that the tetrazole ring itself is not capable of strong absorption in the region examined. In this respect, it is similar to the carboxyl group. An analogy between these two groups has been suggested previously (33b), and has frequently proved useful. Wilson (37) explained his results with the 5-aryltetrazoles by attributing the strong absorption to resonance interaction of the phenyl and tetrazole rings. The shift to much shorter wavelengths in ortho derivatives was then explained by interference with the attainment of a coplanar configuration between the two rings, due to a bulky group in the ortho position. The results obtained here support this interpretation, and suggest further that steric hindrance may be greater in the 1-position than in the 5-position.

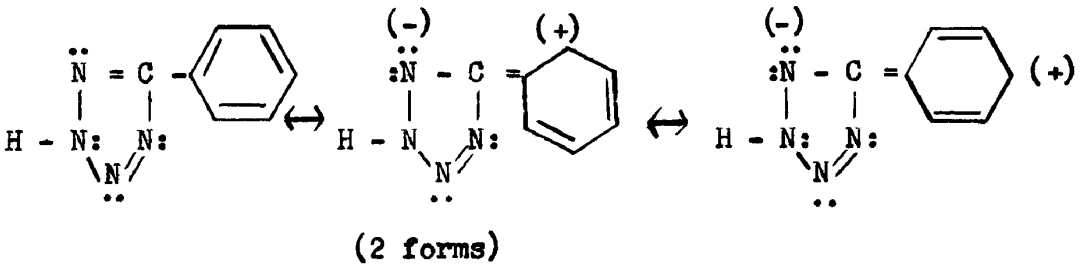
If the possibilities for resonance interaction between the two rings are examined, the following structures may be considered for 1-phenyltetrazole:



(2 forms)

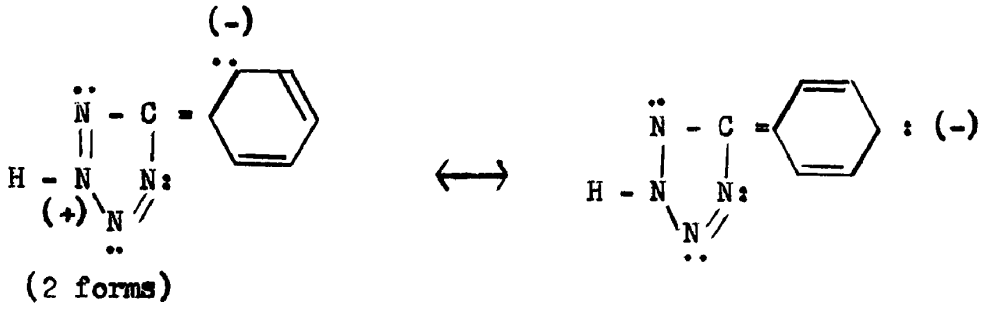
Interaction here is limited to the shift of a pair of electrons towards the phenyl ring. The unshared pairs of electrons on the ring nitrogens prevent the phenyl group from acting as an electron source.

In the five-position, the possibilities are much greater. First of all, the ring hydrogen atom might be attached to any one of the four nitrogens. Elpern and Nachod (31) suggested on the basis of spectroscopic evidence that the isomer in which the hydrogen occurs on the 2- or 3-position is the most probable structure for 5-phenyltetrazole. The structures contributing to the resonance of 5-phenyltetrazole would then include:



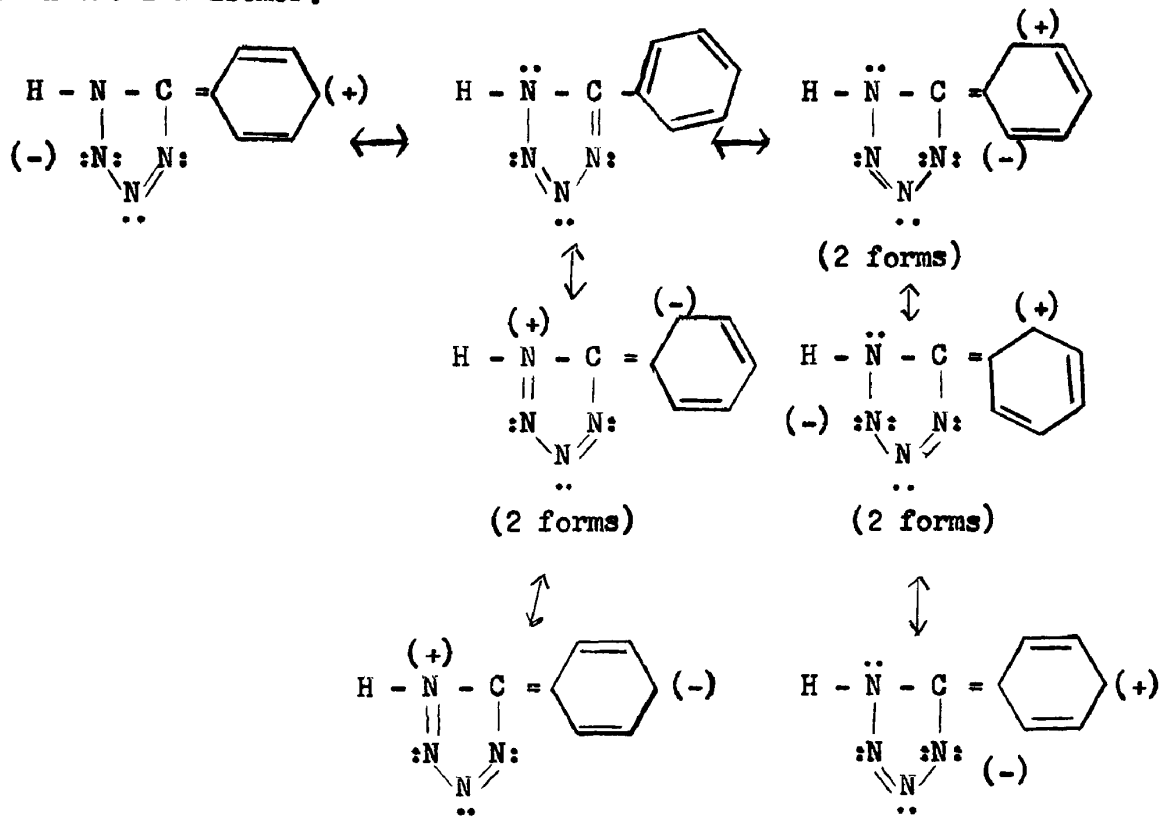
(2 forms)

In the above structures, electron shifts are towards the tetrazole ring. Structures can also be written for shift of electrons away from the tetrazole ring:



(2 forms)

The tautomer with the hydrogen at the 1 position on the ring, allows for the contribution of more forms to the resonance hybrid than the 2-H isomer.

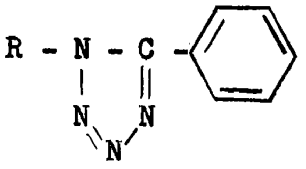


(2 forms)

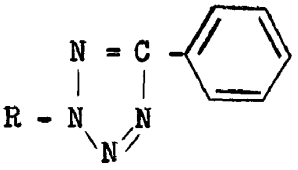
(2 forms)

(2 forms)

Elpern and Nachod (31) have pointed out that a linear-conjugated structure, such as structure I, might be expected to absorb at about 270-290 mμ, while a cross-conjugated compound, such as structure II, should absorb at shorter wavelengths.



I



II

They obtained, by methylation of 5-phenyltetrazole, a product differing in melting point from the known 1-methyl-5-phenyltetrazole. This new product showed a maximum of 240 mμ, consistent with their prediction for structure II (R = CH_3). Since 5-phenyltetrazole showed a maximum of 239 mμ, it was also considered to have structure II (R = H). However, 1-methyl-5-phenyltetrazole did not conform to the theory, since it absorbed at 232 mμ, instead of in the predicted 270-290 mu region. The authors explained this inconsistency on the basis of charge separation in solution. However, a consistent explanation can also be given on the basis of steric factors.

If the absorption in the ultraviolet region is due to the resonance interaction of the phenyl and tetrazole rings, any factors which interfere with coplanarity of the two rings should shift the absorption to lower wavelengths. Since neither ring system alone absorbs to an appreciable extent in the region examined, sufficient interference with coplanarity should shift the absorption maximum below the available range. This has already been shown to occur in the case of 1-o-chlorophenyltetrazole and 5-o-bromophenyltetrazole. It is therefore conceivable that a methyl group on the adjacent ring atom should interfere with the coplanarity of the two rings, thus shifting the maximum

to lower wavelengths, rather than to the higher value predicted for a completely planar system.

The formulation of 5-aryltetrazoles as structure II (R = H) could also be defended on steric grounds, in spite of the greater number of resonance structures which may be written for structure I (R = H). In 1-aryltetrazoles, the hydrogen on the adjacent carbon atom is firmly held, and any interference which may occur with substituents on the phenyl ring cannot be avoided. In 5-aryltetrazoles, however, interference can be avoided if the hydrogen occupies the two-position. This would explain the apparently greater degree of steric hindrance already noted for aryl substituents in the one-position as compared with the same substituents in the five-position. A difference of 3-5 mμ between the absorption peaks of corresponding isomers is noted throughout the series, except for the o-methoxyphenyltetrazoles, which differ by 11 mμ. It is interesting to note that $\lambda_{max.}$ for these latter two compounds reaches the range predicted by Elpern and Nachod. Wilson (37) has already suggested that some molecules of 5-o-methoxyphenyltetrazole may reach coplanarity through interaction of the methoxy group with the hydrogen on the tetrazole ring. The second peak at shorter wavelength in each case may represent the expected shift to shorter wavelengths due to interference between the bulky methoxyl group and the ring.

The above explanation is not intended to exclude electronic effects. Present data are not sufficient to evaluate the relative

roles of electrical and steric factors. However, the spectroscopic data so far collected can be correlated on the basis of steric considerations. It may be noted that the ultraviolet absorption maxima determined for 1-aryl-5-aminotetrazoles by Murphy and Picard (36) do not fit the above pattern at all. Factors operating in the two series would appear to be quite different.

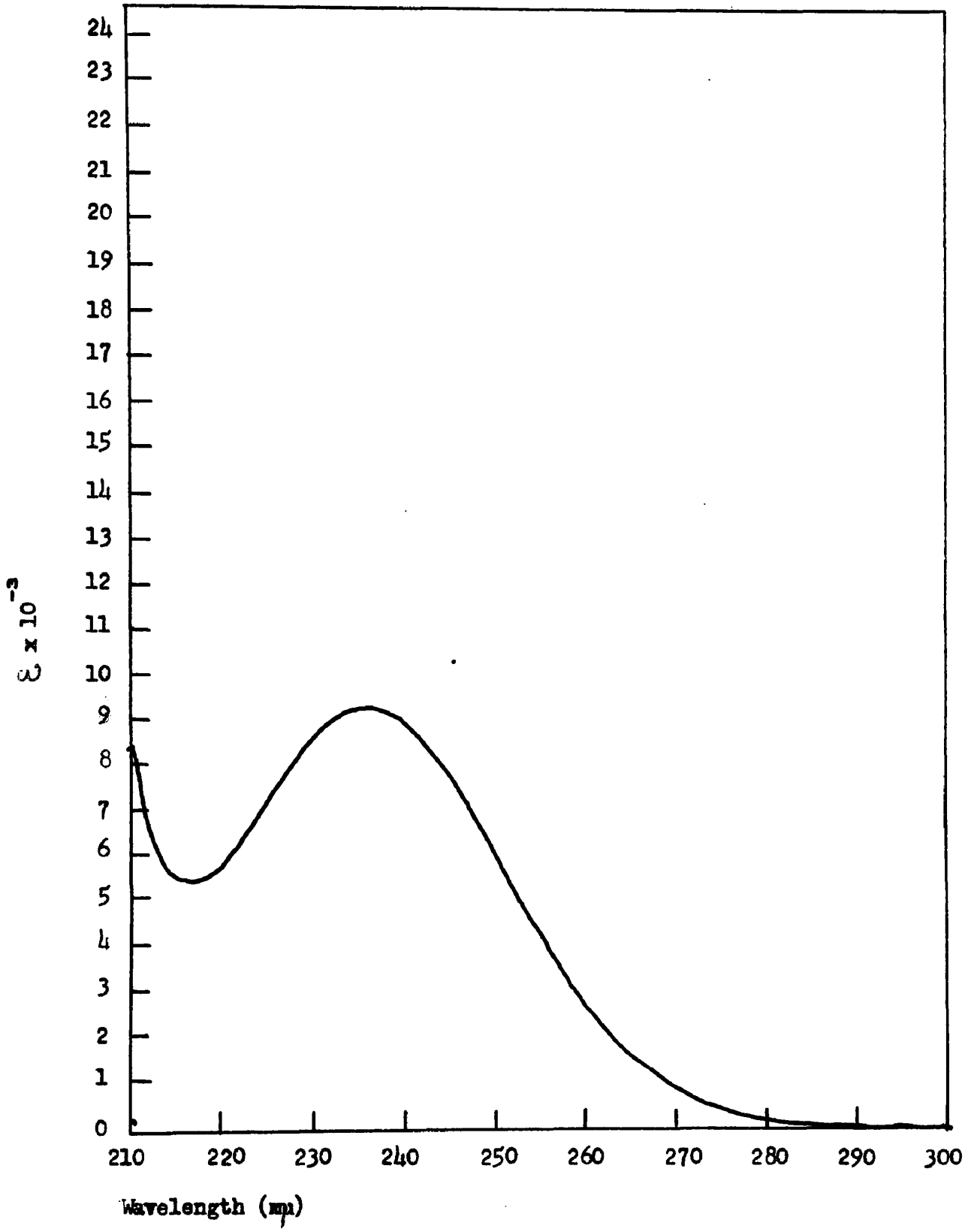


Figure 1. Ultraviolet Absorption Spectrum of 1-Phenyltetrazole.

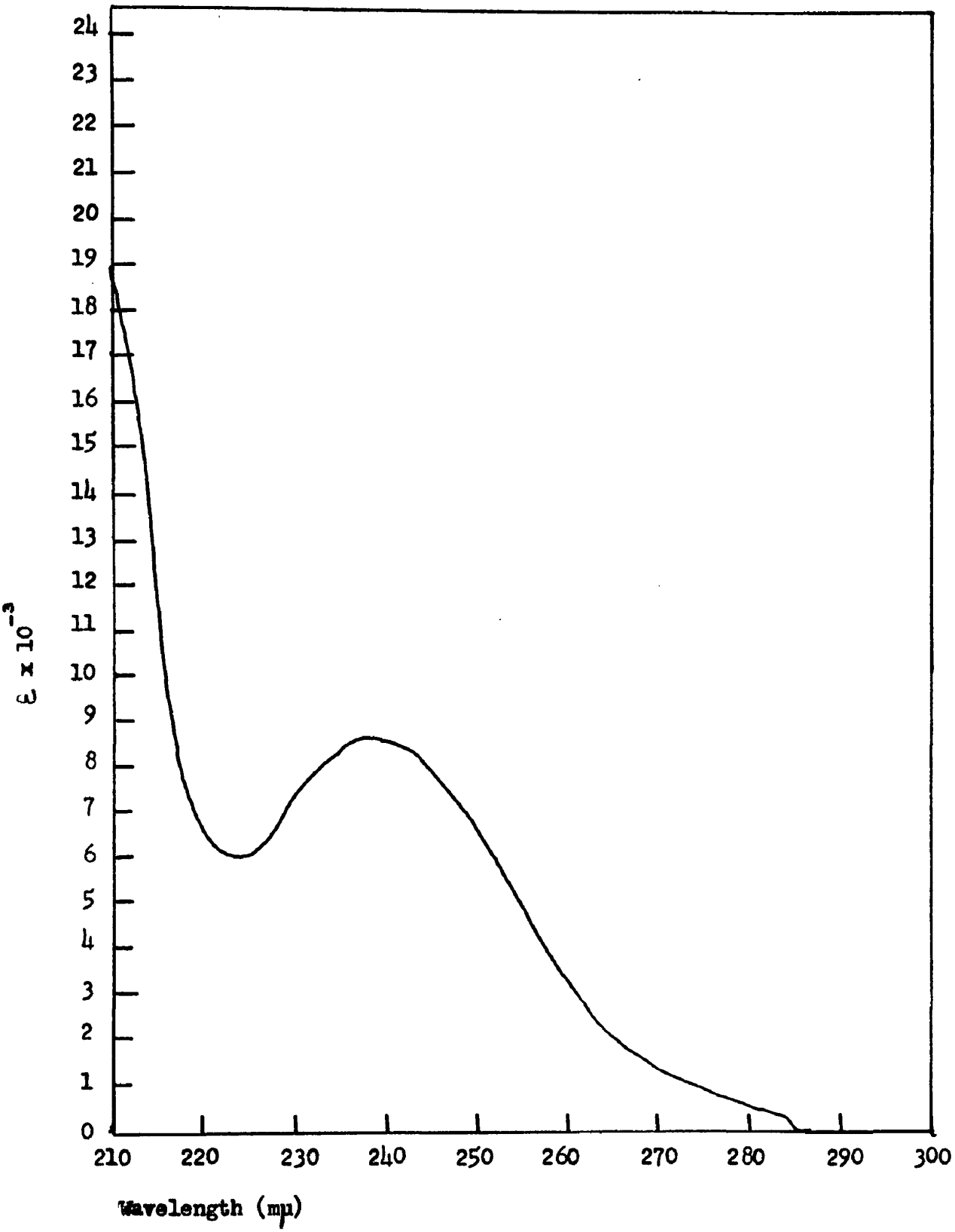


Figure 2. Ultraviolet Absorption Spectrum of 1-m-Tolyltetrazole.

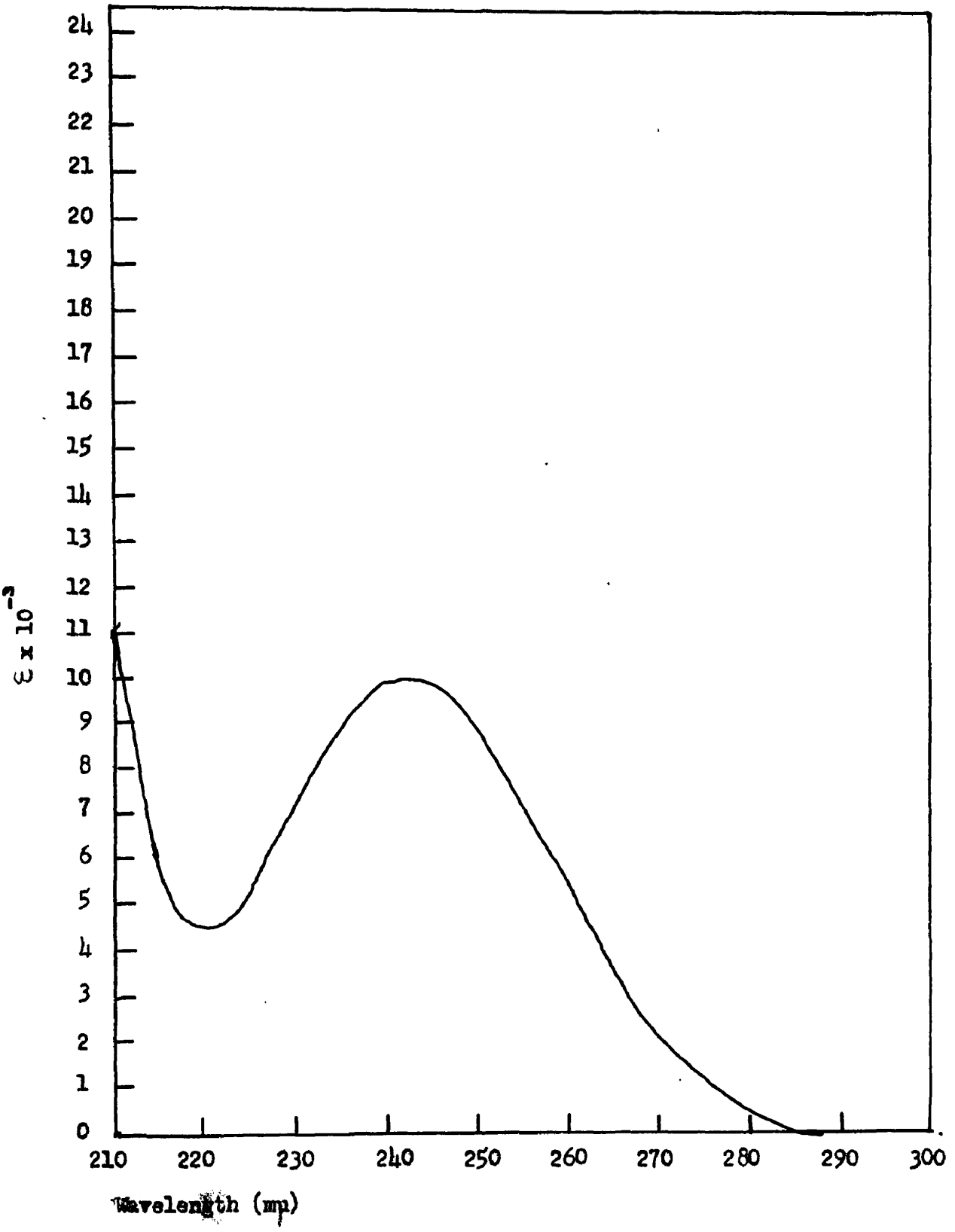


Figure 3. Ultraviolet Absorption Spectrum of 1-p-Tolyltetrazole.

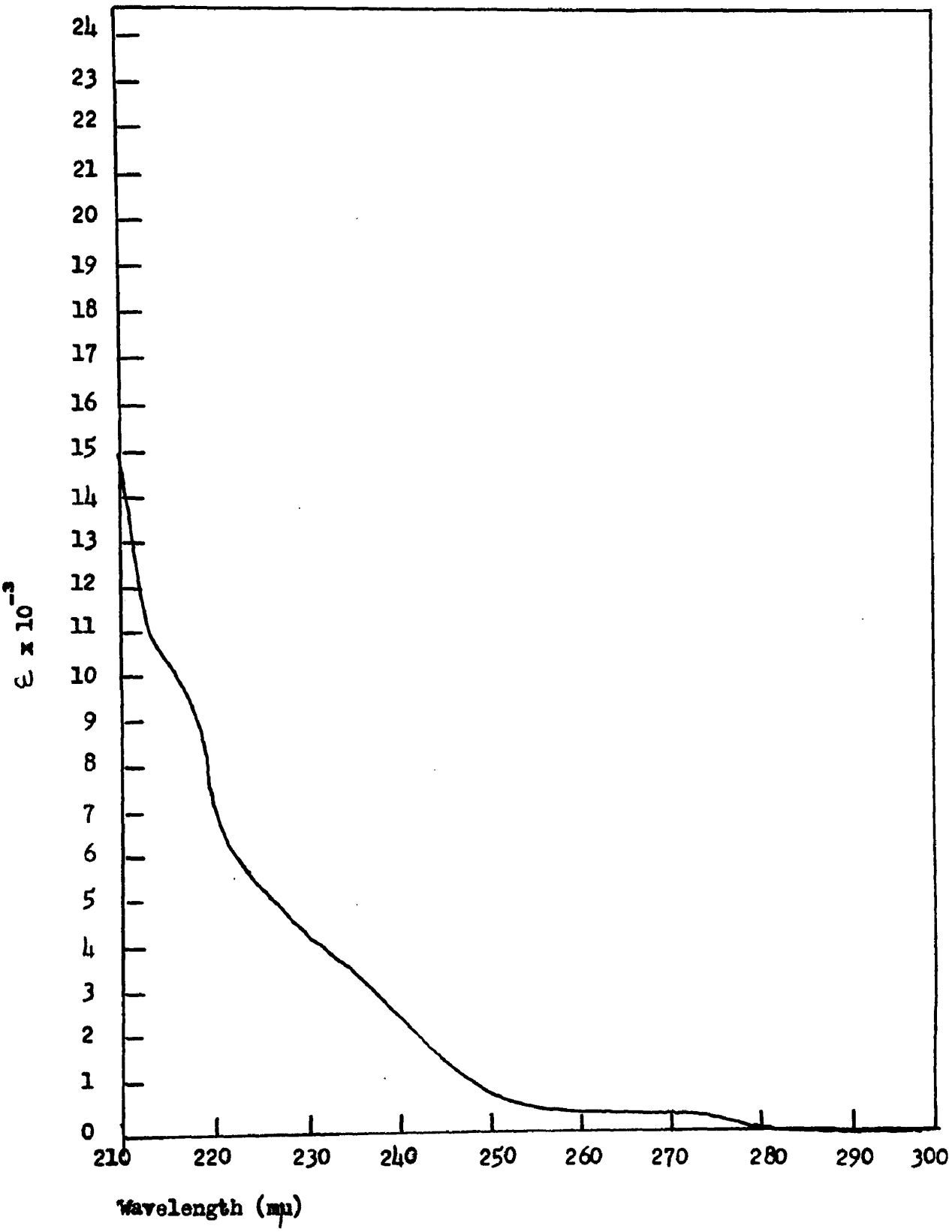


Figure 4. Ultraviolet Absorption Spectrum of 1-o-Chlorophenyltetrazole.

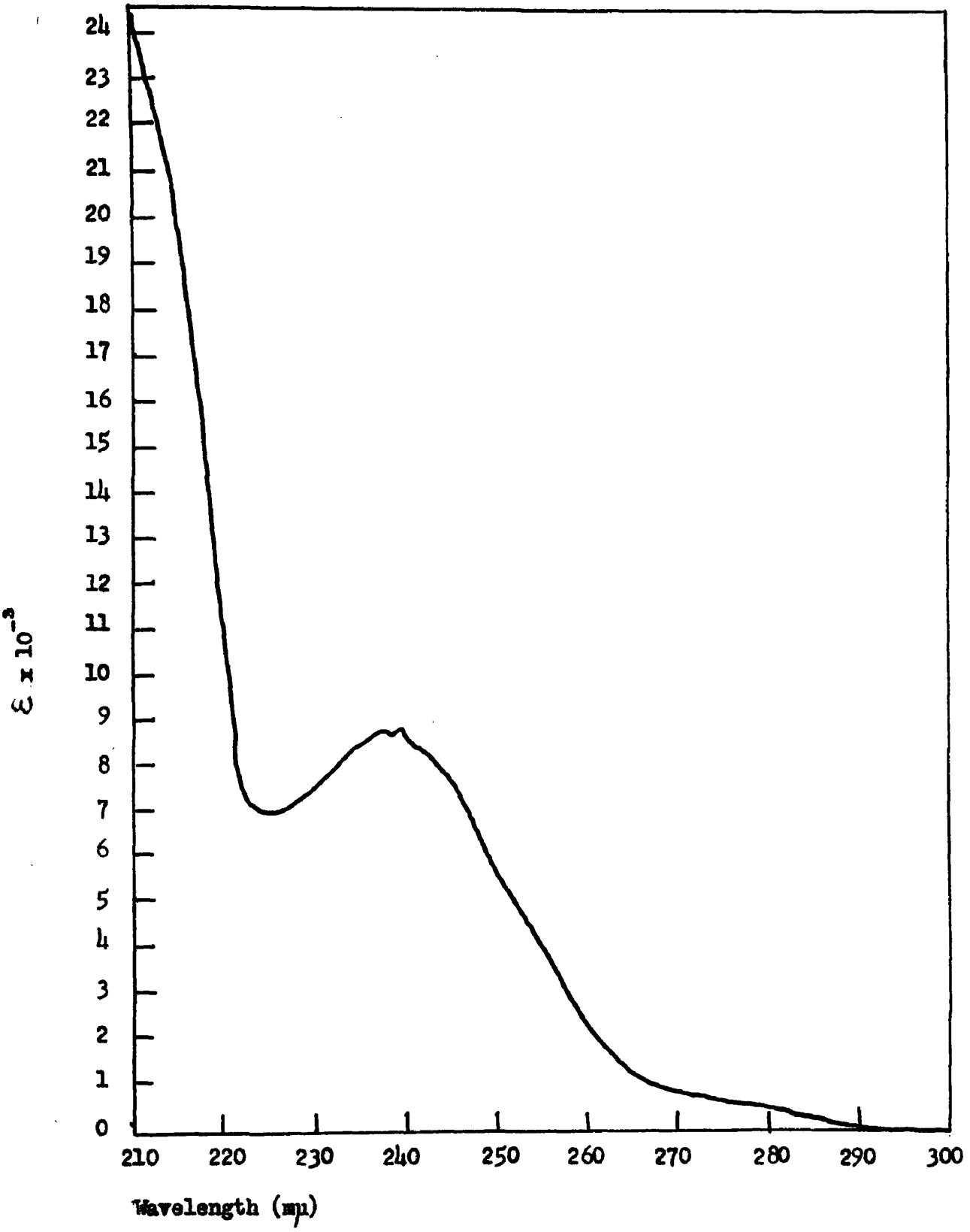


Figure 5. Ultraviolet Absorption Spectrum of 1-m-Chlorophenyltetrazole.

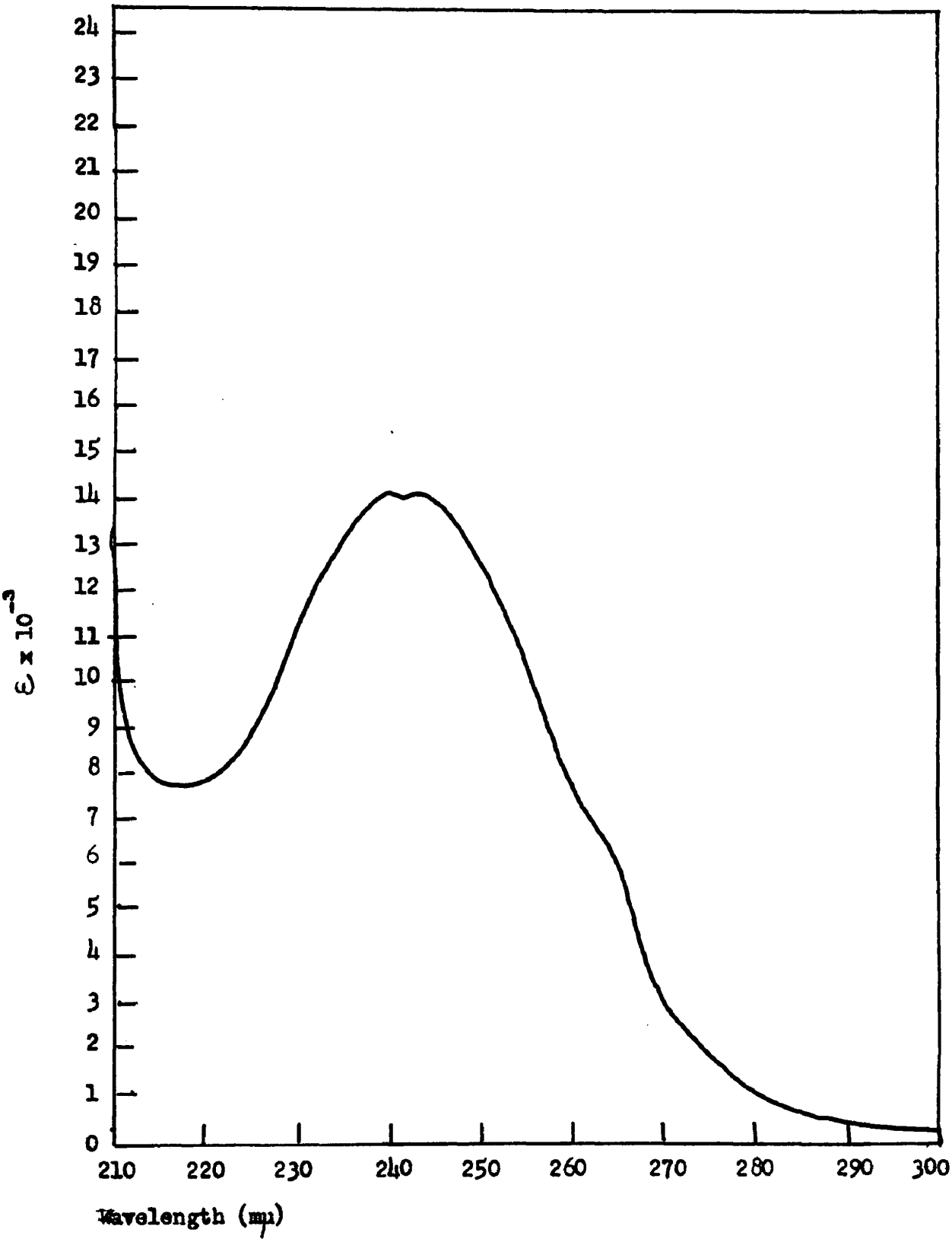


Figure 6. Ultraviolet Absorption Spectrum of 1-p-Chlorophenyltetrazole.

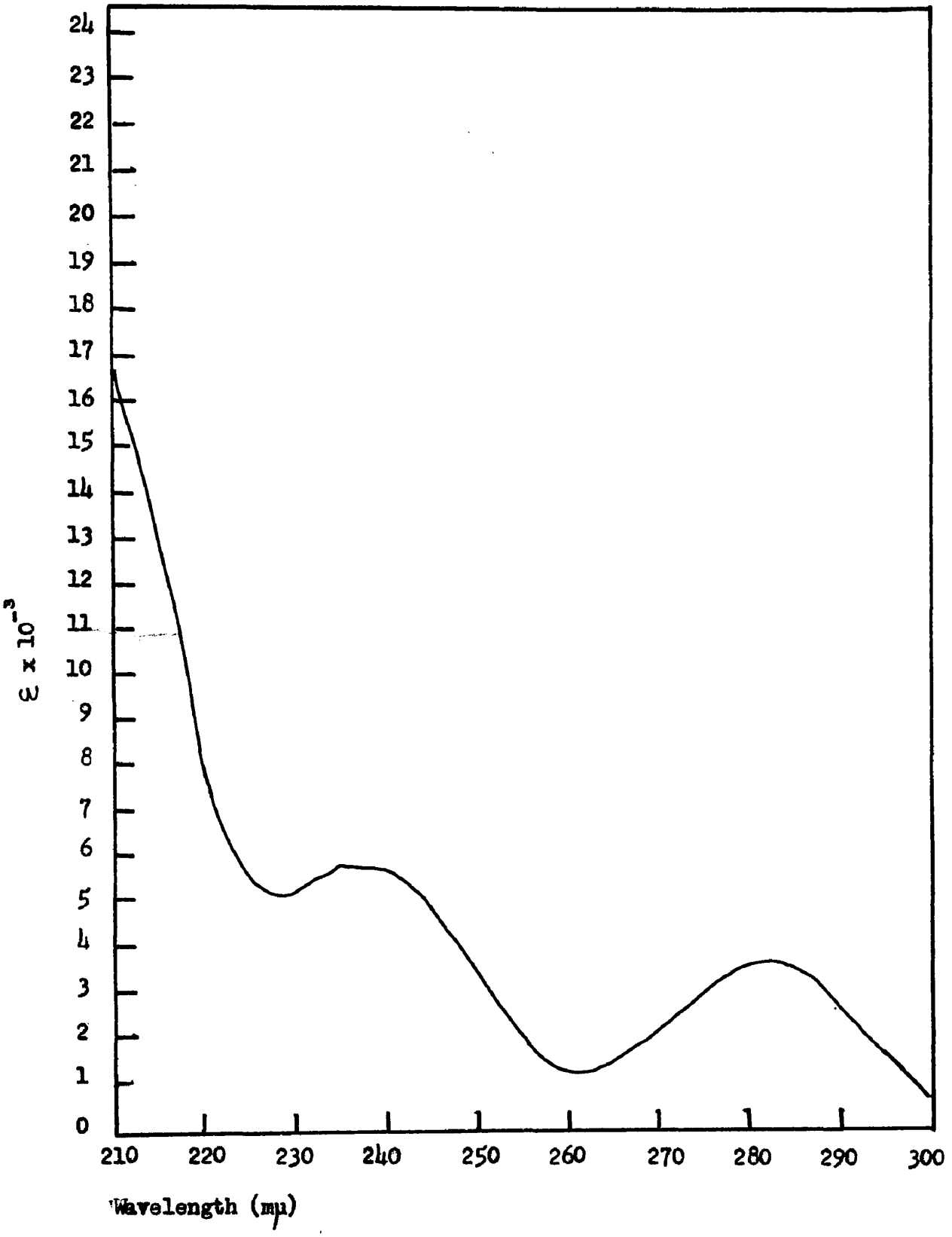


Figure 7. Ultraviolet Absorption Spectrum of 1-o-Methoxyphenyltetrazole.

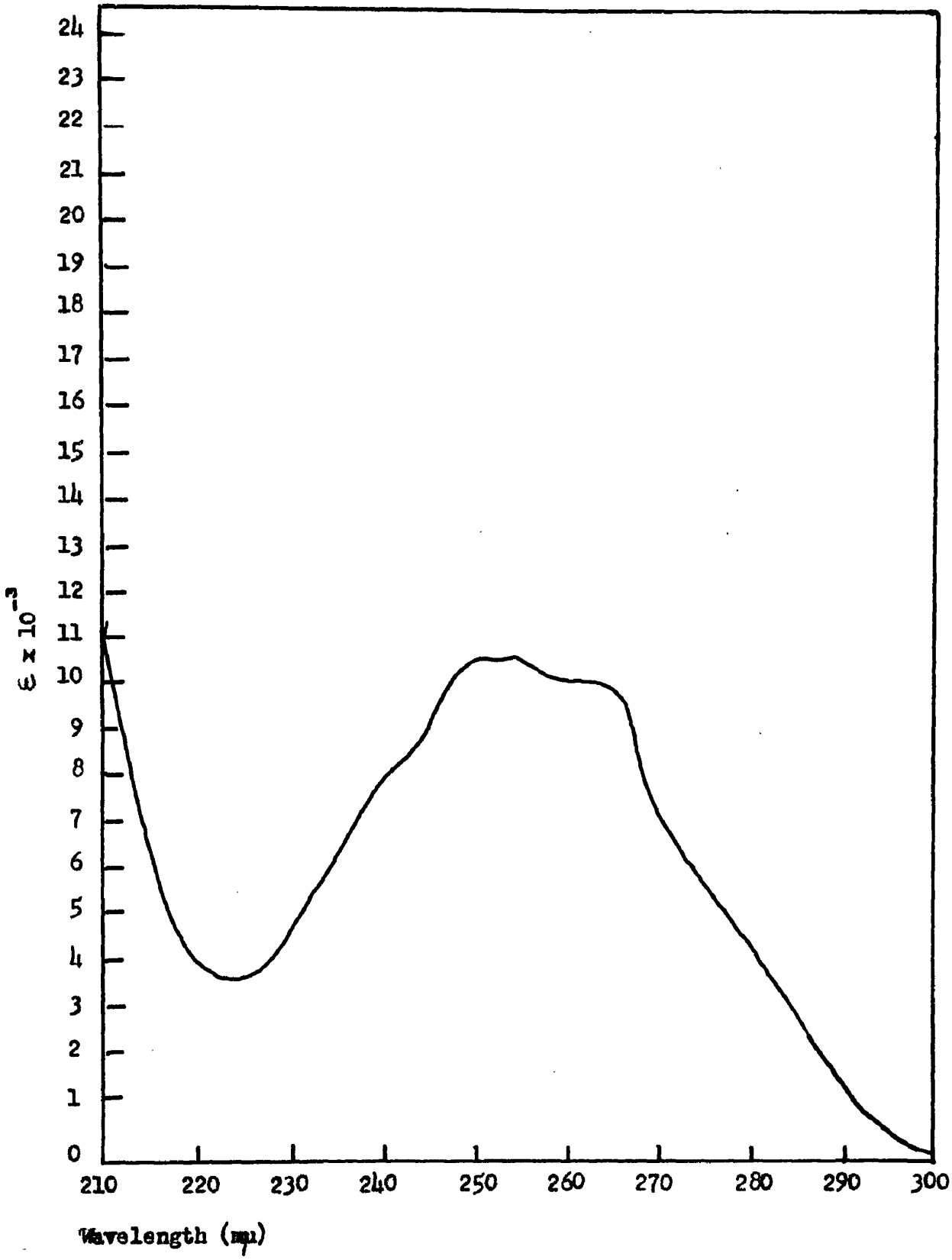


Figure 8. Ultraviolet Absorption Spectrum of 1-p-Methoxyphenyltetrazole.

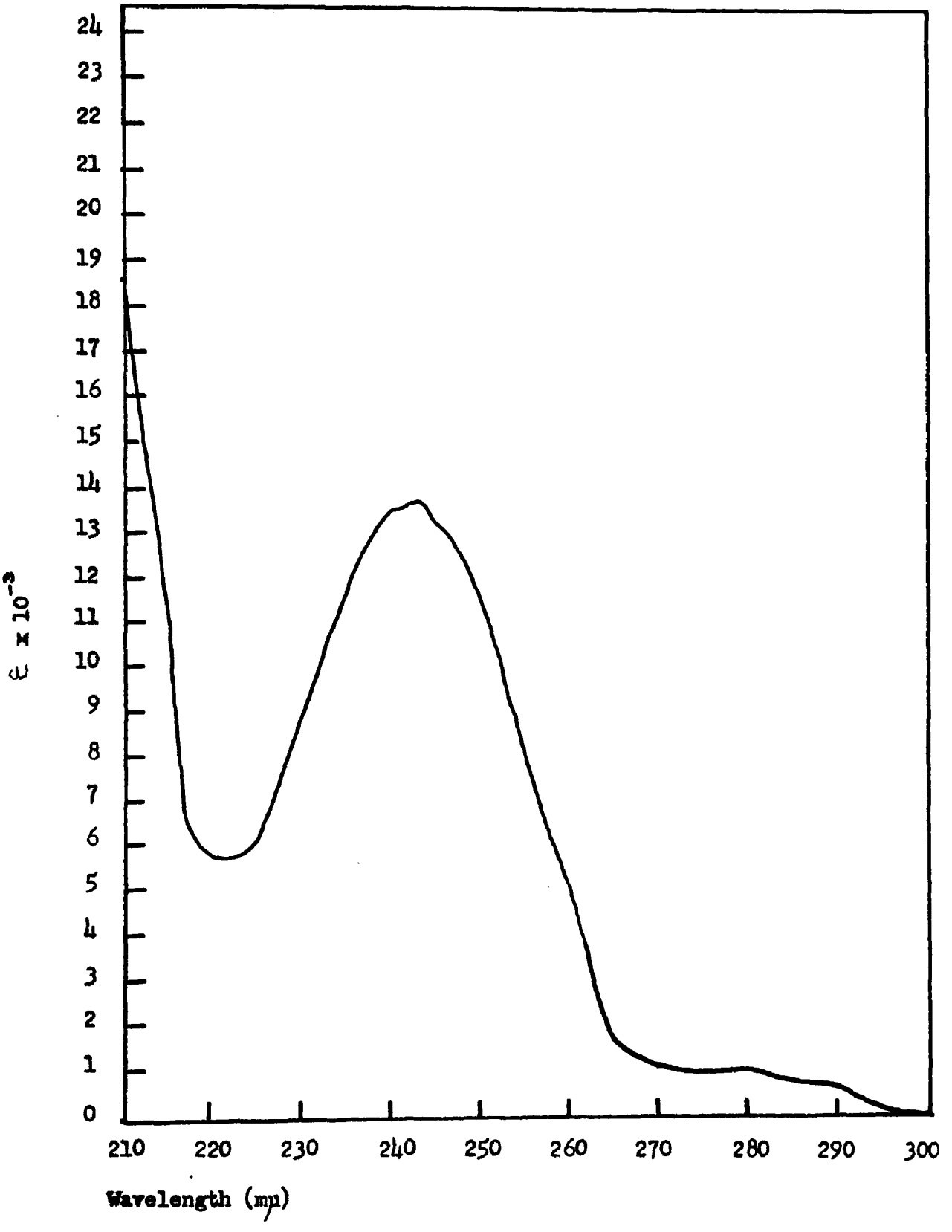


Figure 9. Ultraviolet Absorption Spectrum of 5-m-Tolyltetrazole.

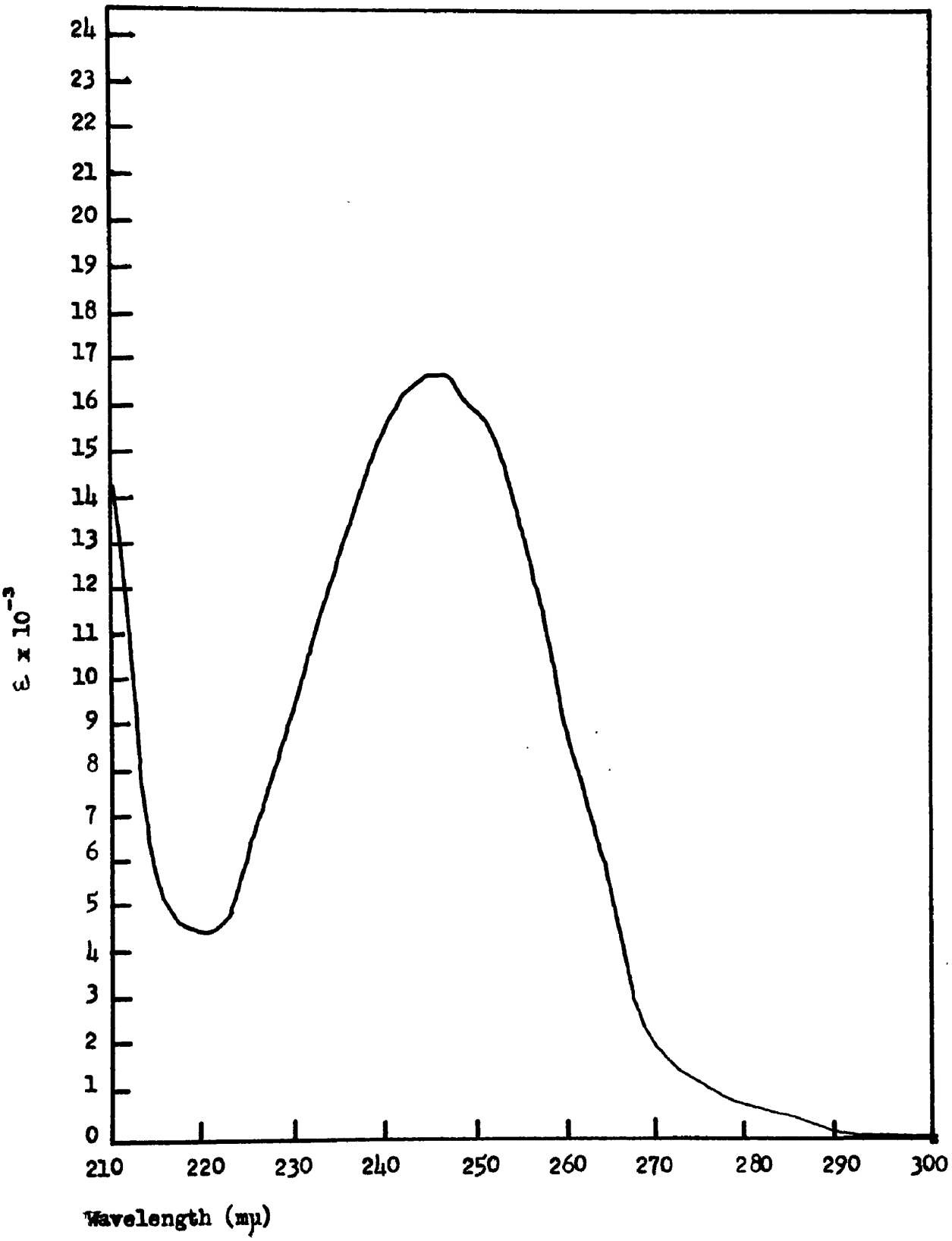


Figure 10. Ultraviolet Absorption Spectrum of 5-p-Tolyltetrazole.

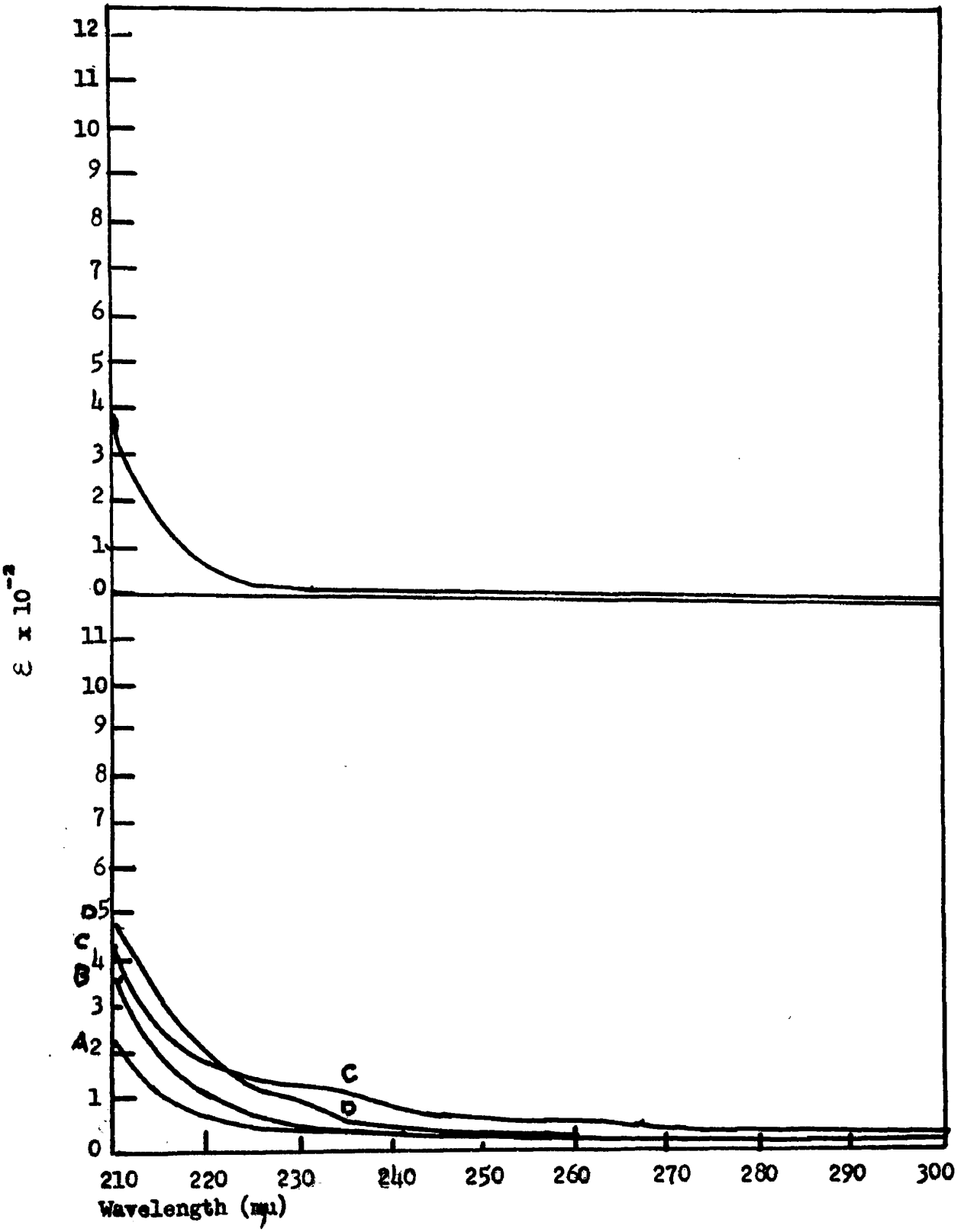


Figure 11. Ultraviolet Absorption Spectra of Tetrazole and Some Alkyltetrazoles.
Upper: 5-Butyltetrazole
5-Hexyltetrazole
Lower: A. Tetrazole
B. 1-n-Butyltetrazole
C. 1-n-Amyltetrazole
D. 1-n-Hexyltetrazole

Infrared Absorption Spectra

Infrared spectra were obtained for all fifteen of the 1-substituted tetrazoles. The solid aryl-substituted compounds were found to be sufficiently soluble in chloroform to allow spectra in solution as well as in oil mull. In two cases, a spectrum in carbon tetrachloride was also obtained. The 1-alkyl compounds were examined only as pure liquids.

For purposes of comparison, the corresponding 5-substituted tetrazoles were also examined. A total of seventeen of these compounds were available, including eight with alkyl substituents and nine with aryl substituents. A group of thirteen disubstituted tetrazoles were also included. In these groups, only the solid mulled in white mineral oil was examined, except for a single liquid example in the latter class. In all, spectra were obtained for a total of forty-six tetrazoles.

After elimination of all bands which are known to be due to the phenyl ring or to alkyl groups (38), a search was made for bands common to all members of a particular subgroup. Tables XI through XV in the Appendix contain the tabulated results. The characteristic bands found for each group of monosubstituted compounds are summarized in Tables VI through IX on both the wave length and wave number scales. The spectra vary widely in resolution, particularly among those obtained from mulls. For this reason, weaker bands might not be detectable in the poorly defined spectra. Also, single bands in some compounds may be split into two or more bands in other members of the series.

To allow for such situations, the third column in Tables VI through IX records the number of compounds in which the band appears. The fourth column in each table indicates the relative intensity of the band.

In the aryl compounds, the certain identification and elimination of all bands due to the phenyl ring was not possible, since absorptions due to the phenyl and tetrazole rings appear in the same regions, and probably overlap. In the 1600-1500 cm^{-1} region, somewhat arbitrary assignments were made, and this has been indicated by including the bands attributed to phenyl in the summary. Below 1000 cm^{-1}, the situation is less clear-cut, since vibrations due to the whole molecule occur in this region, and the spectra consequently vary more widely than at higher frequencies.

In Table X, an attempt has been made to correlate bands in the various types of compounds, and to make tentative assignments for some of these bands. These assignments are discussed in greater detail below. The assignment "ring" indicates merely that the band appears to be characteristic of some part of the tetrazole ring system, and does not necessarily involve a structural vibration of the ring as a whole. In several cases, a more definite assignment is also suggested in parentheses, based on analogies to other types of compounds.

The single numbers reported in these tables are each the mid-point of a range of values. The extent of the range is also indicated in each case. It should be noted that the wider ranges in Table X sometimes obscure differences between sub-groups. For instance,

5-alkyltetrazoles have a band at 1042 $\pm$6 cm^{-1}, while in most of the 5-aryl compounds, two bands appear, at 1053 $\pm$7 cm^{-1} and at 1037 $\pm$4 cm^{-1}. The summary includes the whole range by recording the band as 1047 $\pm$14 cm^{-1}, although variations within each sub-group are much less than this.

In the spectrum of tetrazole and in the tabulations in Tables XI to XV in the Appendix, square brackets have been used to indicate doubtful bands, which cannot be distinguished with certainty from background absorption. In many cases, this procedure has been justified by the appearance of a more definite band at the same frequency in the spectra of other members of the same series.

Tetrazole itself would theoretically be expected to show 3N - 6, or 15, fundamental bands. It seems probable that ten of these are the bands at 1543, 1508, 1328, 1252, 1140, 1081, 1044, 1005, 898, and 661 cm^{-1}. The other five may be represented by bands at 3135, 1805, 1449, 952, and 721 cm^{-1}.

In the substituted tetrazoles, the picture is not clear-cut above 2000 cm^{-1}. Resolution is comparatively poor in this region with a rock salt prism, so vibrations of different atom pairs may be grouped together here. The weak and ill-defined absorption found in the 4000 cm^{-1} region of most tetrazoles is almost certainly due to overtone or combination bands. The band near 3135 cm^{-1} in tetrazole and in both monosubstituted series is especially puzzling. The region, in general, is characterized by hydrogen-stretching vibrations, but whether C-H or N-H bonds, or both, are involved here is unknown.

TABLE VI

Summary of Characteristic Infrared Bands of
5-Alkyltetrazoles (8 Compounds)

Wave Length (μ)	Wave Number (cm^{-1})	Number of Compounds	Relative Intensity
2.32-2.47	4310 - 4049	8	weak
3.19 ± .02	3135 ± 20	8	medium
3.60-4.75	2778 - 2105	8	strong, ill-defined
5.51 ± .09	1814 ± 28	8	weak, broad
6.33 ± .02	1579 ± 4	8	medium to strong
6.44 ± .05	1553 ± 10	7	weak to medium
7.09 ± .04	1411 ± 8	7	weak to medium
7.72 ± .17	1295 ± 28	6	weak to medium
7.95 ± .06	1258 ± 10	8	variable
9.00 ± .08	1111 ± 10	8	medium to strong
9.24 ± .04	1082 ± 5	5	medium to strong
9.60 ± .05	1042 ± 6	8	variable
10.12 ± .08	988 ± 8	6	weak to medium
13.99 ± .09	715 ± 5	8	weak to medium

TABLE VII

Summary of Characteristic Infrared Bands of 5-Aryltetrazoles (9 Compounds)

Wave Length (μ)	Wave Number (cm^{-1})	Number of Compounds	Relative Intensity
2.35 - 2.45	4255 - 4082	8	weak
3.60 - 4.32	2778 - 2315	8	variable, ill-defined
5.36 - 5.43	1866 - 1842	2	weak, broad
6.22 ± .06	1607 ± 15[a]	7	weak to medium
6.36 ± .09	1573 ± 23	9	weak to medium
6.48 ± .11	1545 ± 25	9	weak to medium
7.05 ± .09	1419 ± 18	9	weak to medium
7.71 ± .15	1298 ± 26	6	weak to medium
8.00 ± .06	1250 ± 9	9	variable
8.56 ± .13	1168 ± 17	9	variable
8.97 ± .13	1115 ± 16	7	weak to medium
9.20 ± .07	1087 ± 8	7	weak to medium
9.50 ± .07	1053 ± 7	8	medium to strong
9.64 ± .04	1037 ± 4	6	medium to strong
9.86 ± .10	1014 ± 10	8	weak to medium
10.12 ± .08	988 ± 8	7	variable
13.38 ± .10	748 ± 6	8	medium to strong
13.91 ± .12	719 ± 6	5	variable
14.87 ± .51	673 ± 23	8	weak to medium

(a) Assigned to phenyl group.

TABLE VIII

Summary of Characteristic Infrared Bands of 1-Alkyltetrazoles (7 Compounds)

Wave Length (μ)	Wave Number (cm^{-1})	Number of Compounds	Relative Intensity
2.28 - 2.50	4386 - 4000	6	very weak to weak
2.82 - 2.89	3546 - 3460	5	weak
3.19 ± .03	3135 ± 20	7	medium to strong
4.50 ± .02	2222 ± 5	6	weak to medium
5.70 ± .01	1754 ± 3	4	very weak to weak
6.03 ± .11	1658 ± 32	5	very weak to weak
6.73 ± .03	1487 ± 6	7	medium to strong
6.80 ± .02	1470 ± 4	6	medium to strong
7.32 ± .05	1366 ± 9	6	medium
7.69 ± .07	1301 ± 12	7	weak
7.86 ± .05	1273 ± 7	5	very weak to medium
8.01 ± .06	1249 ± 10	7	weak to medium
8.21 ± .14	1219 ± 21	5	weak to medium
8.56 ± .03	1168 ± 4	7	strong
8.99 ± .02	1113 ± 3	7	strong
9.20 ± .10	1087 ± 12	7	variable
9.80 ± .04	1020 ± 5	7	weak to medium
10.33 ± .05	968 ± 5	7	medium to strong
11.42 ± .04	876 ± 3	7	variable
13.22 ± .15	757 ± 9	5	weak to medium
13.91 ± .06	719 ± 3	7	weak to medium
14.80 ± .04	676 ± 2	5	medium to strong
15.05 ± .08	665 ± 4	7	medium to strong
15.46 ± .03	647 ± 1	4	variable

TABLE IX

Summary of Characteristic Infrared Bands of 1-Aryltetrazoles (8 Compounds)

Wave Length (μ)	Wave Number (cm^{-1})	Number of Compounds	Relative Intensity
2.18 - 2.48	4587 - 4032	6	weak
2.73 - 2.92	3663 - 3425	8	weak to medium
3.18 ± .03	3145 ± 30	8	variable
3.76 - 4.89	2658 - 2045	8	variable
6.19 ± .10	1615 ± 25[a]	8	variable
6.44 ± .18	1554 ± 43	8	variable
6.68 ± .06	1498 ± 14[a]	8	medium to strong
6.83 ± .02	1464 ± 4	8	medium to strong
7.17 ± .04	1395 ± 8	8	variable
7.64 ± .12	1310 ± 21	7	variable
7.93 ± .09	1261 ± 15	8 (?)	variable
8.28 ± .07	1208 ± 10	8	variable
8.39 ± .08	1192 ± 11	7	variable
8.54 ± .03	1171 ± 4	8	variable
8.61 ± .01	1162 ± 1	3	weak to medium

8.98 ± .15	1114 ± 19	6	variable
9.23 ± .11	1084 ± 12	8	medium to strong
9.57 ± .13	1045 ± 14	8	variable
9.87 ± .08	1013 ± 8	6	variable
10.05 ± .05	995 ± 5	8	variable
10.46 ± .08	956 ± 7	8	variable
10.65 ± .13	939 ± 11	3	weak to medium
11.09 ± .15	902 ± 12	4	variable
11.51 ± .24	869 ± 18	8	variable
13.99 ± .02	715 ± 1	7	weak to medium
15.15 ± .28	660 ± 12	8	variable

(a) Assigned to phenyl group.

TABLE X

Summary of Characteristic Infrared Bands of Tetrazoles

Tetrazole Unsubstituted 1 Compound	5-Substituted Tetrazoles 17 Compounds	1-Substituted Tetrazoles 15 Compounds	1,5-Disubstituted Tetrazoles 13 Compounds	Tentative Assignments
4255-4082	4310-4049	4587-4000[a]	4274-4200	overtones?
		3663-3425		
3135	3135 ± 20[a]	3145 ± 30		
2760 2320	2778-2105	2658-2045		associated forms, hydrogen bonding?
1805	1826 ± 40			ring N-H
1543	1573 ± 23			ring N-H
1520 1508	1545 ± 25	1539 ± 58	1539 ± 33	ring (C = N)
1499 1449		1467 ± 7		ring C-H
	1419 ± 18	1380 ± 23	1399 ± 18	
1328	1295 ± 28	1310 ± 21	1300 ± 20	ring (C = N)
1252	1254 ± 13	1261 ± 22	1258 ± 17	ring (C-N)
		1219 ± 21 1192 ± 11[b]	1205 ± 22[a]	exocyclic C-N?
1140	1168 ± 17	1168 ± 7	1166 ± 13	ring
	1115 ± 16	1114 ± 19	1121 ± 24	
1081	1086 ± 8[a]	1085 ± 13	1081 ± 16	ring
1044	1047 ± 14	1038 ± 22[b]	1039 ± 19[a]	ring
1005	1014 ± 10[b] 988 ± 8[a]	1013 ± 8[b] 995 ± 5[b]	1010 ± 9[a] 986 ± 13	ring
952		961 ± 12	No correlations attempted	
932 898		902 ± 12[b] 869 ± 18		
721	717 ± 8	718 ± 4		
661	673 ± 23[b]	662 ± 16		

(a) Band missing in 3 or more of the compounds in the group.
(b) Band found only in aryl-substituted compounds.

The diffuse, ill-defined area of absorption between 2800 and 2100 cm^{-1} in 5-substituted compounds appears to be similar to that described for dimeric and polymeric forms of the carboxylic acids, and is there attributed to hydrogen bonding. An analogous explanation is suggested here. However, this cannot account for absorption in this region in 1-substituted tetrazoles.

Since the weak band near 1800 cm^{-1} occurs only in tetrazole and its 5-substituted derivatives, it has been assigned to the ring N-H bond. A recent study of amino acids (39) assigned a band at slightly higher frequencies (4.7 microns, or 2128 cm^{-1}) to the N-H bond in the NH_3^+ group. While a similarity between the N-H absorption in 5-substituted tetrazoles and the zwitter-ion form of amino acids was not predicted, it would not be unreasonable. In each case, the hydrogen atoms are described as "acidic", whereas the N-H bonds in amines and amides are much stronger. The difference in bond strength should be reflected in differences in position of absorption peaks.

The 1600-1500 cm^{-1} region is complicated by the presence of both phenyl and tetrazole absorption. To consider first the alkyl compounds, the 5-alkyltetrazoles show at least two peaks which are absent in the corresponding 1-substituted compounds. Both might be due to the ring N-H bond. However, it seemed possible that the band just below 1500 cm^{-1} in the 1-alkyl compounds was the counterpart of one of the above-mentioned bands, probably the one at lower frequencies. For this reason, the band at 1579 ± 4 cm^{-1} (see Table VI) was tentatively assigned to ring N-H and the bands at 1553 ± 10 cm^{-1} (Table VI) and

at 1487 ±6 cm^{-1} (Table VIII) to a ring vibration. The band at 1579 cm^{-1} is just above the range given for the amide II band in secondary amides (38). Although the origin of this band has been debated, there is good support for its assignment to an N-H deformation.

The 1-aryltetrazoles, in which no N-H bond would be present, show three bands in this region (see Table IX). Somewhat arbitrarily, the highest and lowest of these were attributed to the 1600 and 1500 cm^{-1} bands of the phenyl ring, while the center one was assigned to a tetrazole ring vibration. Although the range is much wider for this band, the midpoint coincides with that in the 5-alkyltetrazole series. These assignments seemed justified when the 1,5-disubstituted compounds also exhibited a band in this region.

A new problem arose in the 5-aryltetrazoles, where only three bands are found, instead of the four expected (see Table VII). Absorption ranges can be brought into line with the other series by assigning the 1607 cm^{-1} band to the phenyl ring, the one at 1573 cm^{-1} to ring N-H, and the one at 1545 cm^{-1} to the tetrazole ring. This involves the assumption that the band usually found in phenyl compounds at 1500 cm^{-1}, is too weak to detect, or has merged with nearby tetrazole absorption. It should be recalled that opportunity for interaction between the two rings is greater in the 5-position than in the 1-position. The three 1-alkyl-5-aryltetrazoles also lack a band at 1500 cm^{-1}, although it is present in the 1-aryl-5-alkyl series.

There appears to be some extra absorption near 1467 cm^{-1} in the 1-substituted compounds and this has been assigned to ring C-H.

However, this assignment is doubtful, since the ring carbon would not be expected to show as much single-bond character as absorption in this region suggests. No other clear-cut band due to ring C-H has been found.

From 1400 cm^{-1} to 1000 cm^{-1}, occur a series of bands which appear to be characteristic of the tetrazole ring. Some of these bands appear to be double in many of the compounds examined, so the ranges for each peak have been recorded individually. Since the band near 1400 cm^{-1} does not appear in tetrazole, it has been grouped with the one at 1300 cm^{-1} as a possible double peak. Alternatively, the former may be due to single bond C-N absorption, obscured in tetrazole by the white oil peaks nearby. Primary amides have a band near 1400 cm^{-1} assigned to the C-N bond (38).

Frequently, it has been helpful in tetrazole chemistry to draw analogies between carboxylic acids and the tetrazole ring. The systems $\underset{\underset{O}{|}}{C} = O$ and $\underset{\underset{N}{|}}{C} = N$ might also be expected to give similar absorption, since the atoms involved are close in atomic weight. Since the carboxylate ion, $\underset{\underset{O}{|}}{C} = O^{-}$, has bands at 1610-1550 cm^{-1} and at 1420-1300 cm^{-1} (38), it has been suggested in Table X that the tetrazole bands near 1540 cm^{-1} and 1300 cm^{-1} may be due to the corresponding carbon-nitrogen system. The band near 1250 cm^{-1} is in a region frequently assigned to C-O and C-N stretching vibrations, and has therefore been attributed to the C-N single bond of the tetrazole ring. Since the nearby band at 1200 cm^{-1} occurs only in the two groups containing a carbon atom attached to ring nitrogen, an exocyclic C-N vibration has been suggested.

The series of bands from 1170-1000 cm^{-1} has been assigned simply to the tetrazole ring, and many of them may well be due to vibration of the whole ring as a unit. Not all of these bands occur in every compound, and wide variations in intensity occur in different subgroups. The band near 1168 cm^{-1}, for instance, frequently exhibited the most intense absorption in the whole spectrum of 1-alkyltetrazoles, which were examined as liquids. The same band is very weak in some of the other classes, and disappears entirely in the mulls of most of the 5-alkyltetrazoles. It does, however, appear as a definite but weak band in one case, and as a slight dip in background absorption in others.

Below 1000 cm^{-1}, vibrations characteristic of the whole molecule might be expected, as well as those due to carbon-carbon bonds. Therefore, no assignments in this region will be attempted at the present time.

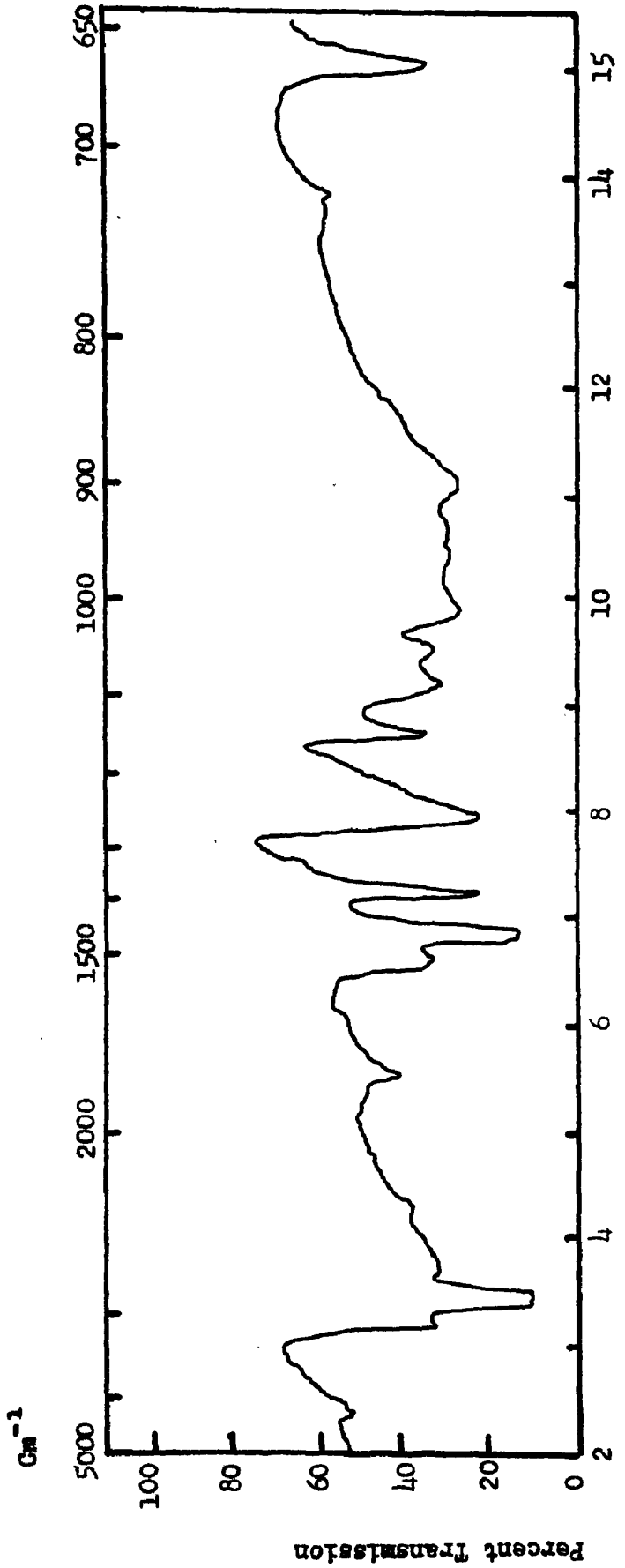


Figure 12. Infrared Absorption Spectrum of Tetrazole (Oil mull).

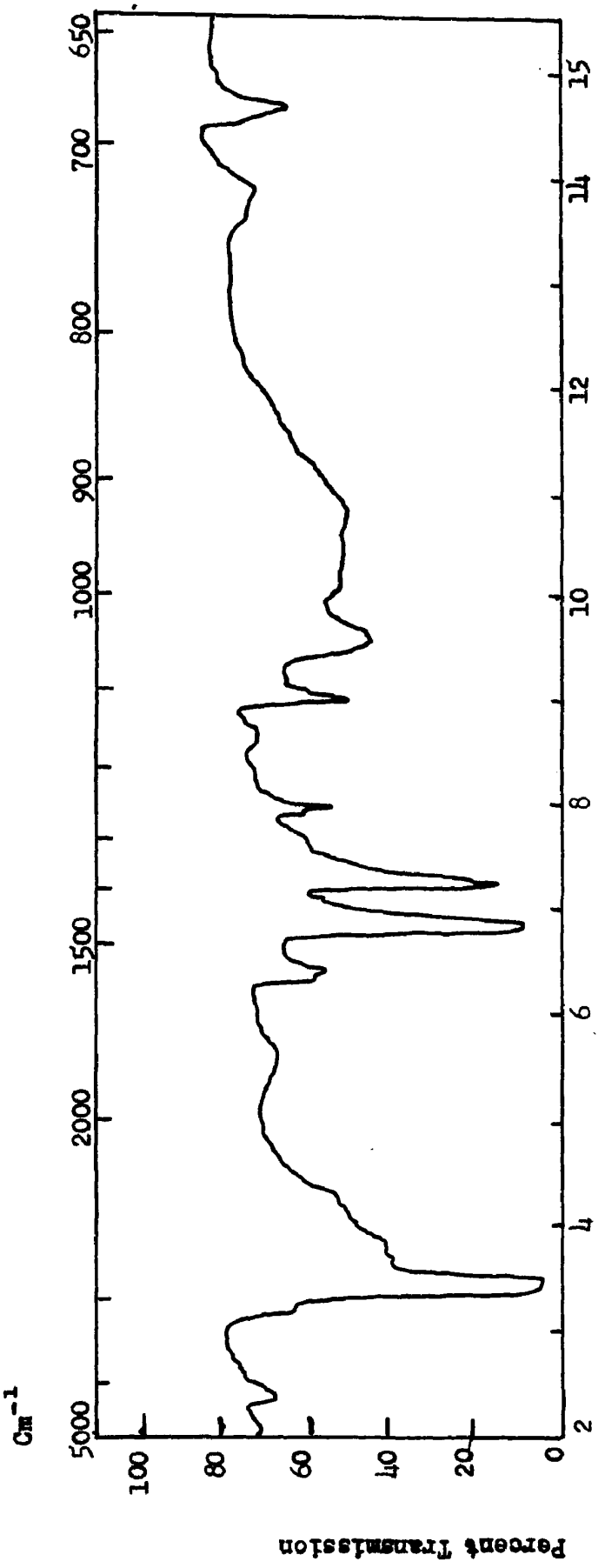


Figure 13. Infrared Absorption Spectrum of 5-Methyltetrazole (Oil mull).

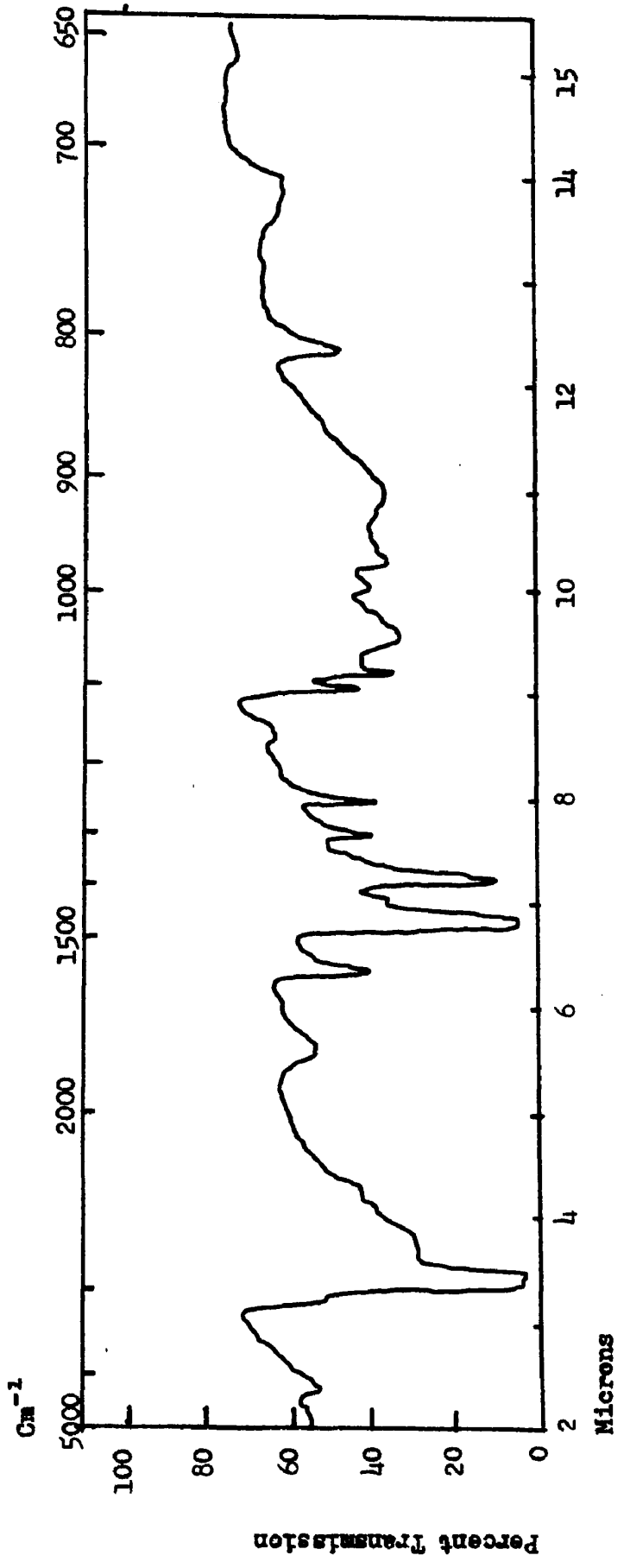


Figure 14. Infrared Absorption Spectrum of 5-Ethyltetrazole (Oil mull).

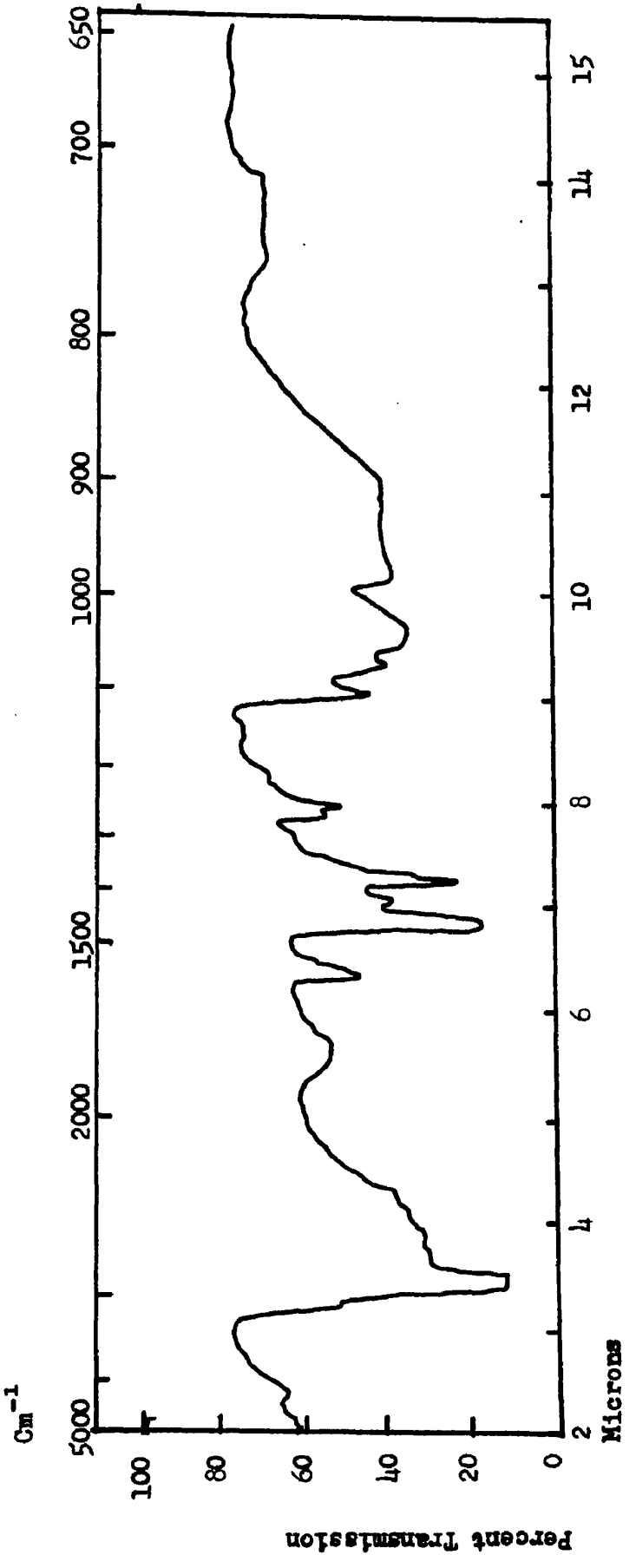


Figure 15. Infrared Absorption Spectrum of 5-n-Propyltetrazole (Oil mull).

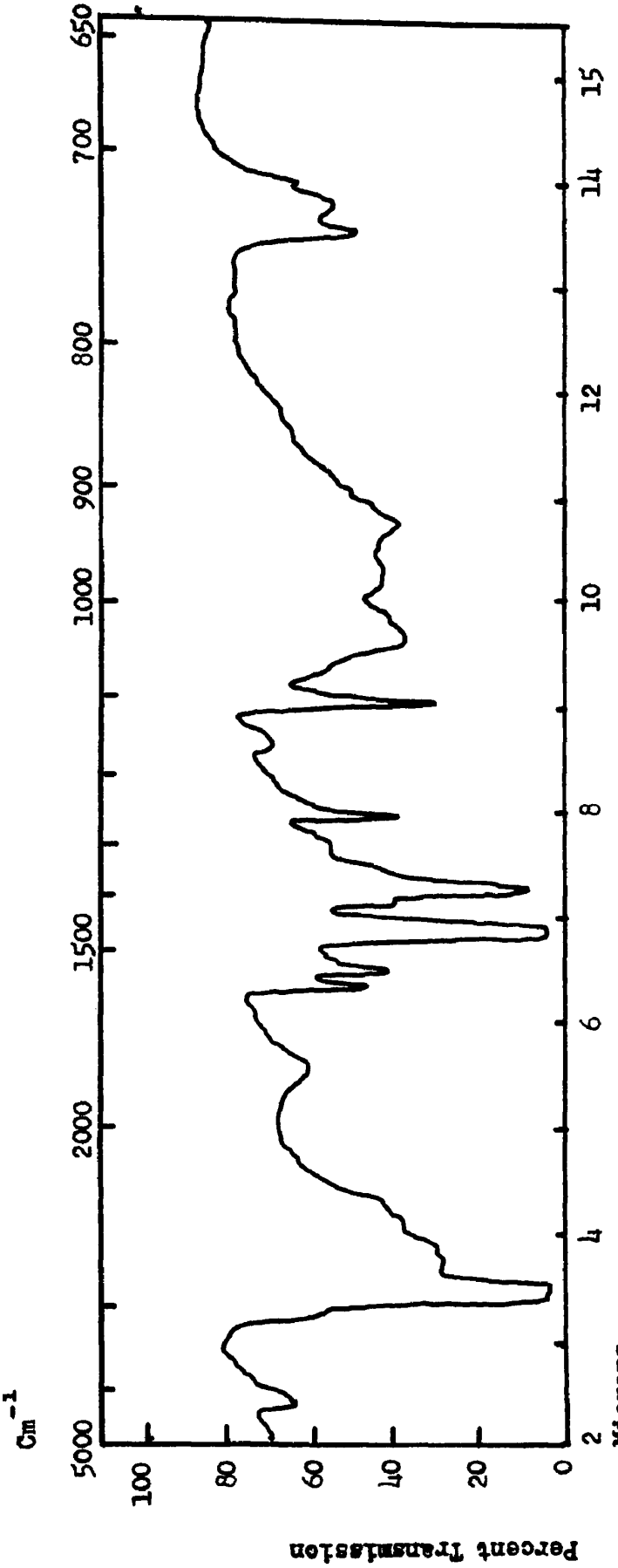


Figure 16. Infrared Absorption Spectrum of 5-n-Butyltetrazole (Oil mull).

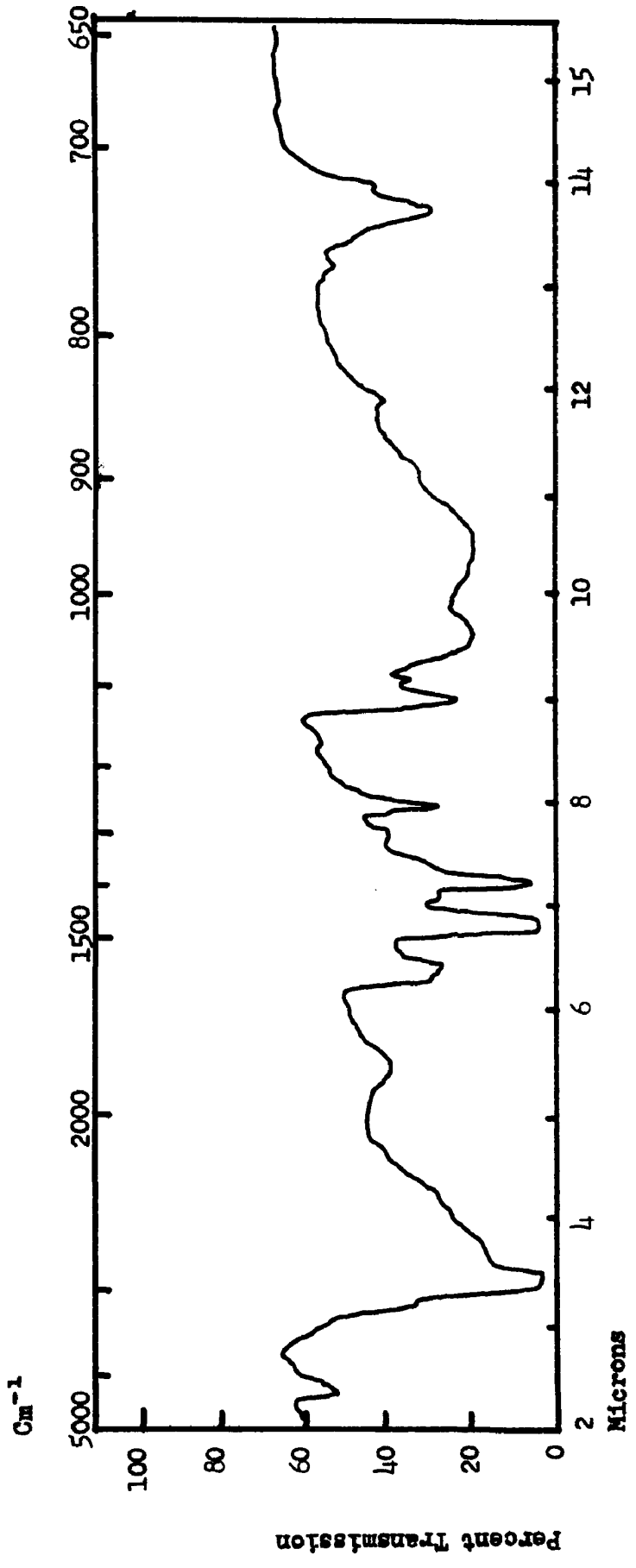


Figure 17. Infrared Absorption Spectrum of 5-n-Amyltetrazole (Oil mull).

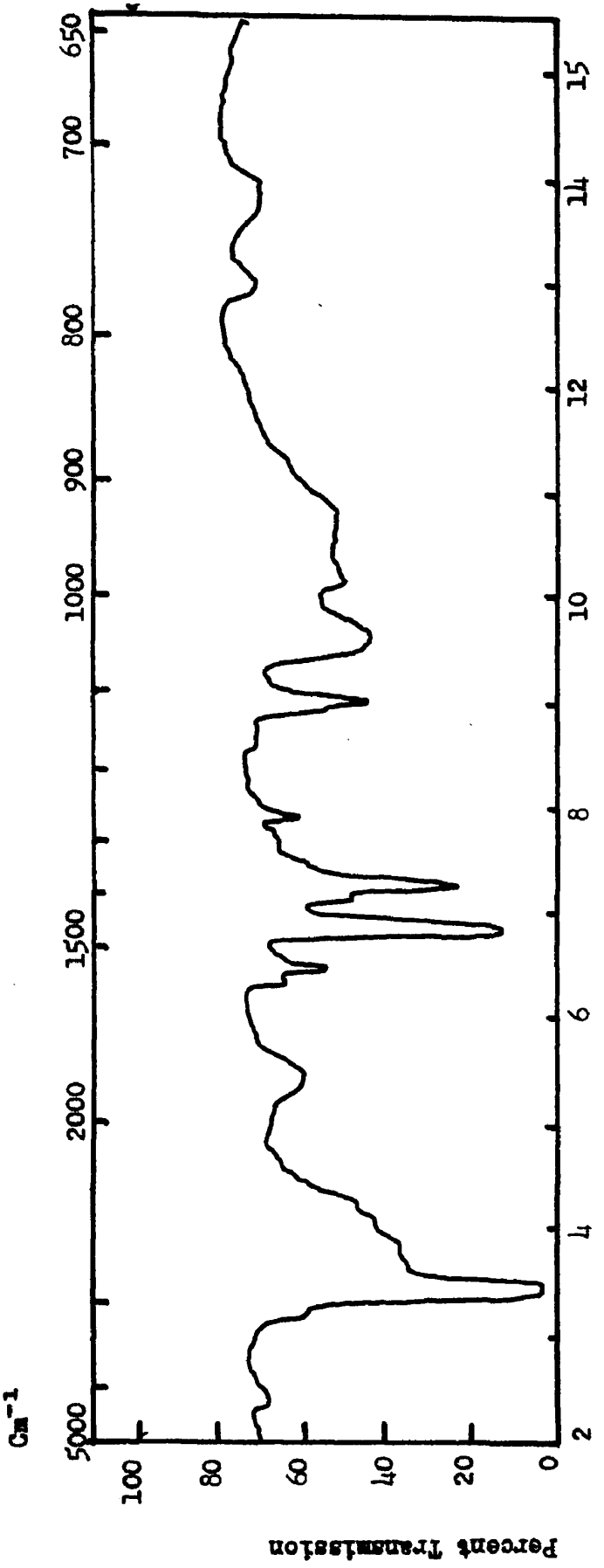


Figure 18. Infrared Absorption Spectrum of 5-Isoamyltetrazole (Oil mull).

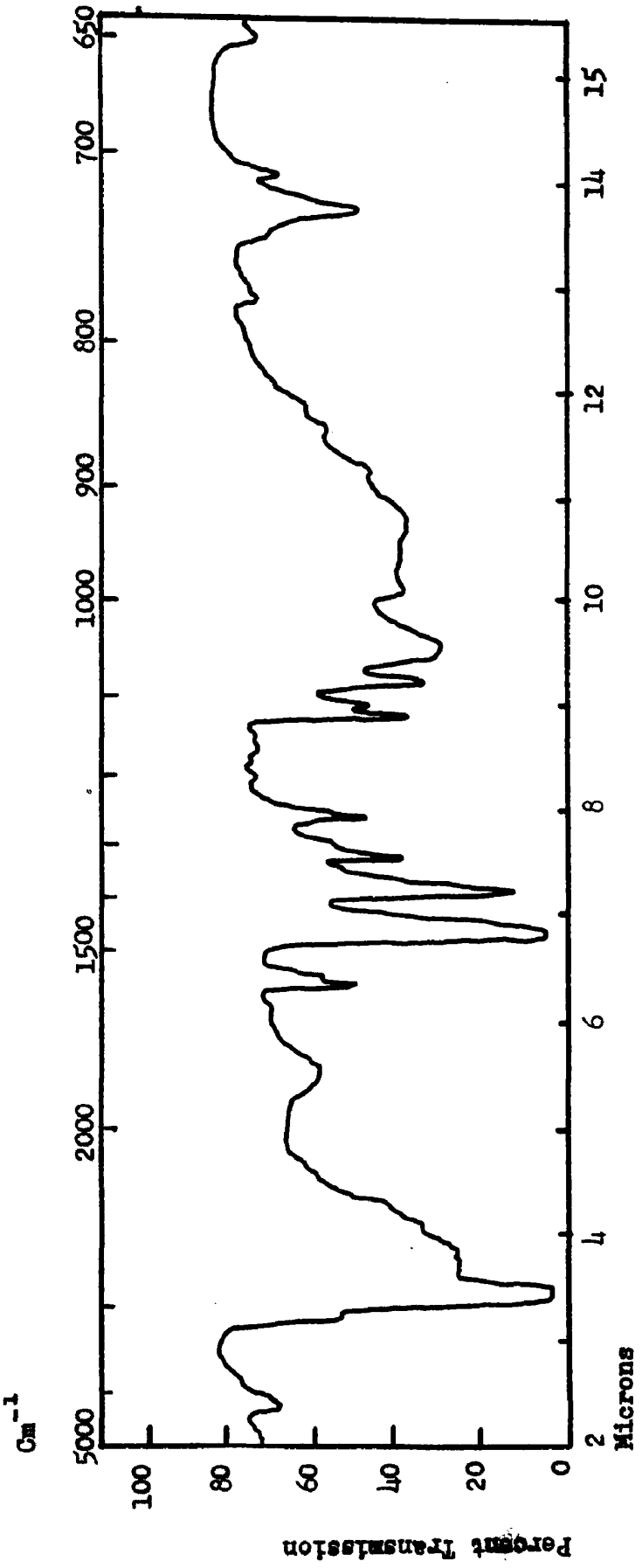


Figure 19. Infrared Absorption Spectrum of 5-n-Hexyltetrazole (Oil mull).

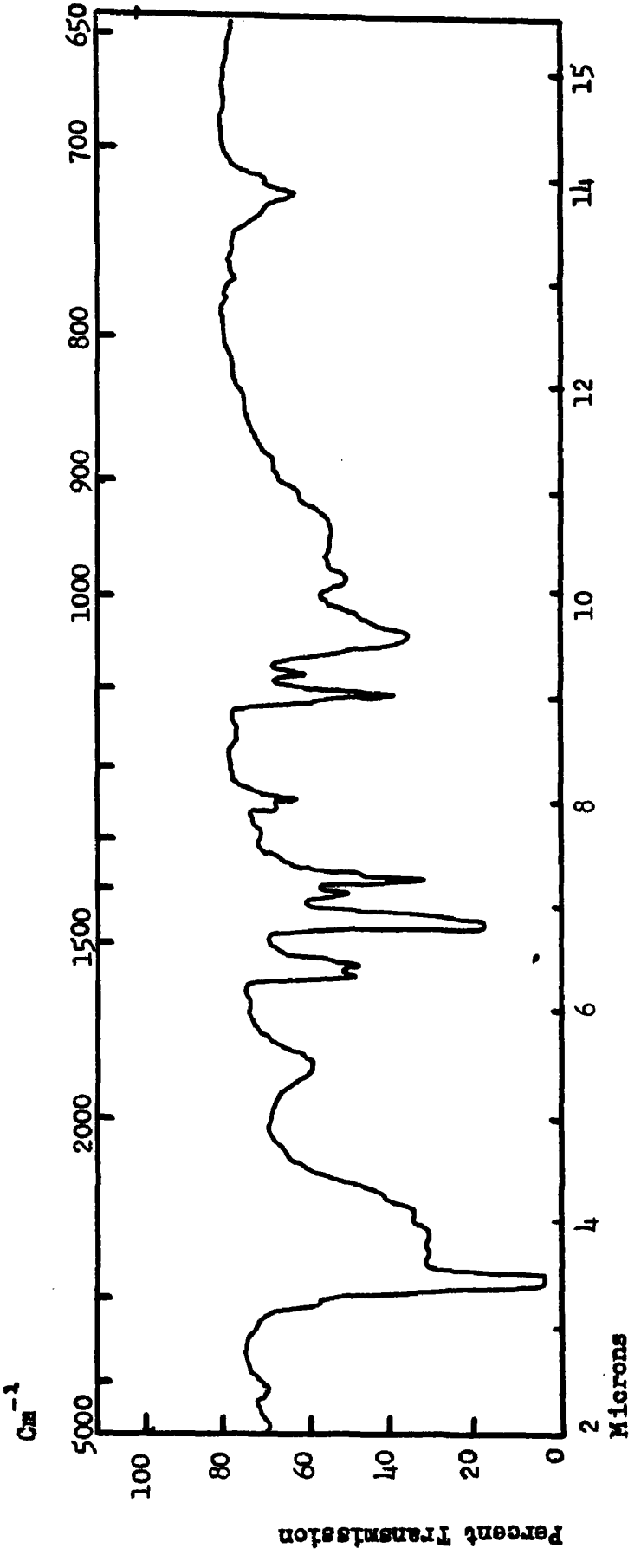


Figure 20. Infrared Absorption Spectrum of 5-n-Heptyltetrazole (Oil mull).

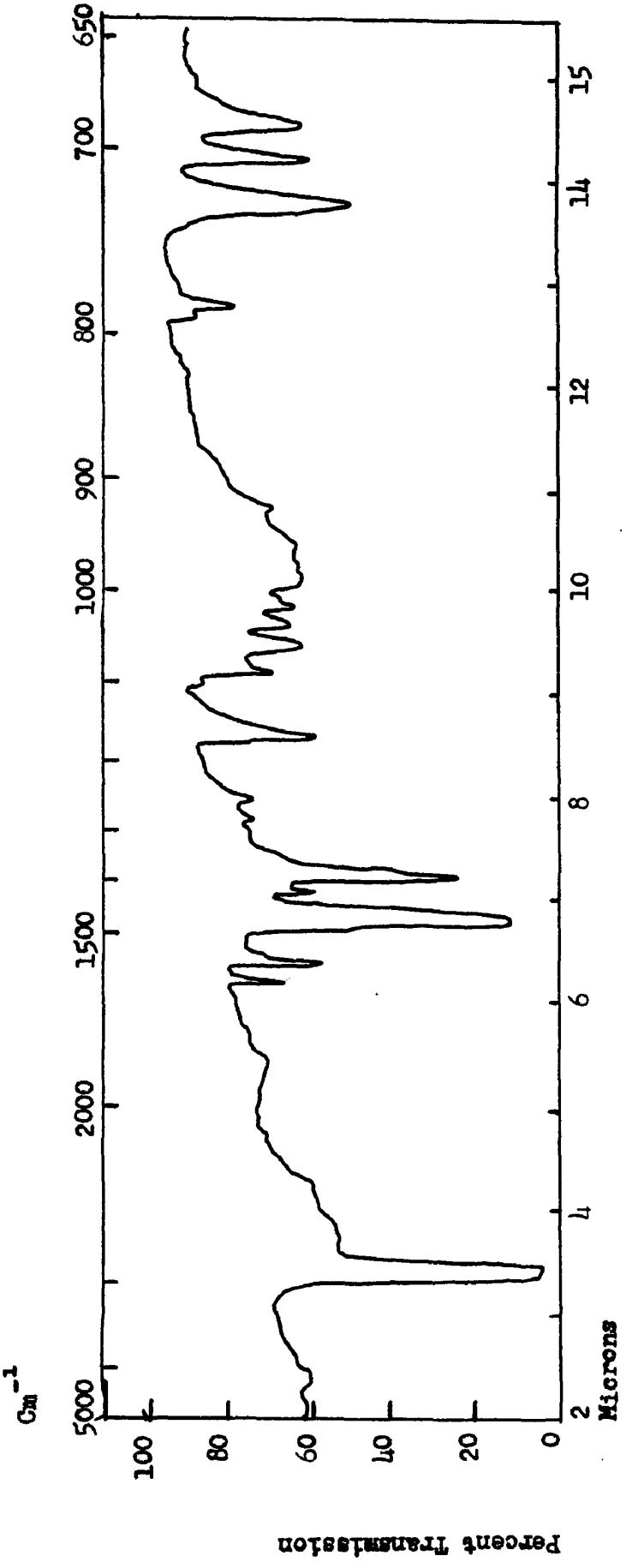


Figure 21. Infrared Absorption Spectrum of 5-Phenyltetrazole (Oil mull).

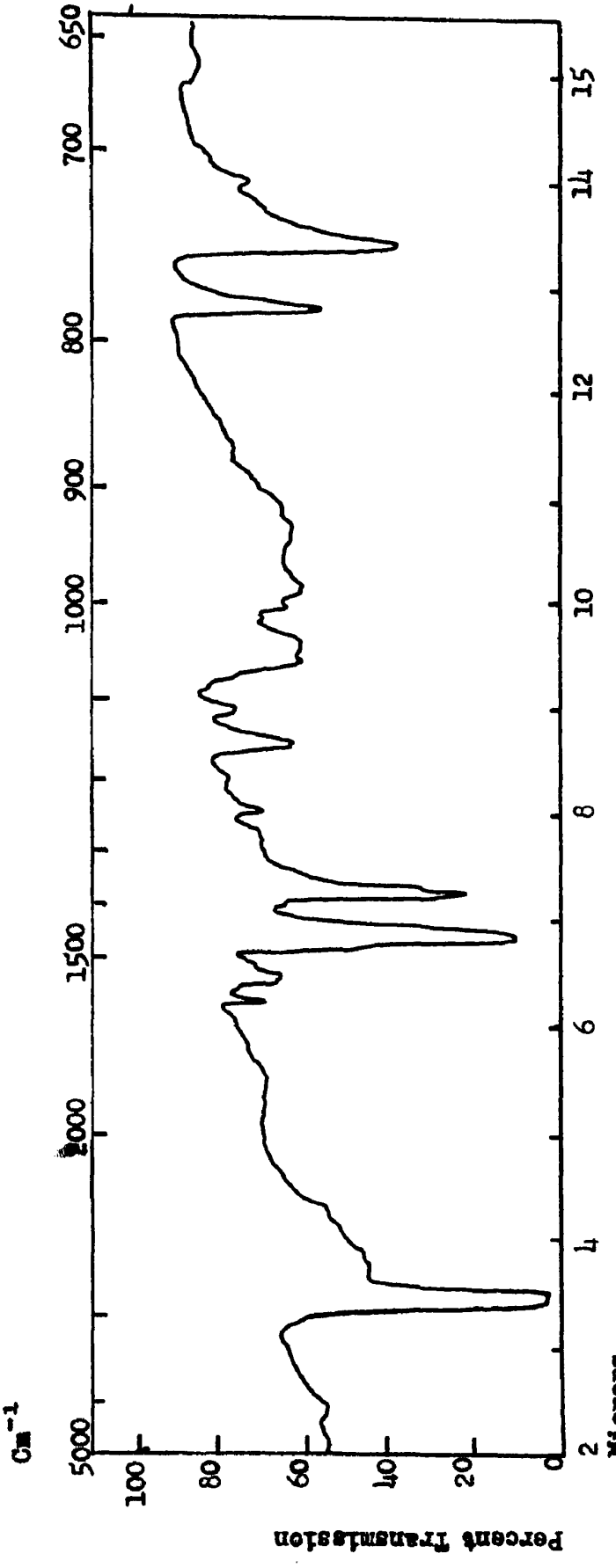


Figure 22. Infrared Absorption Spectrum of 5-o-Tolyltetrazole (Oil mull).

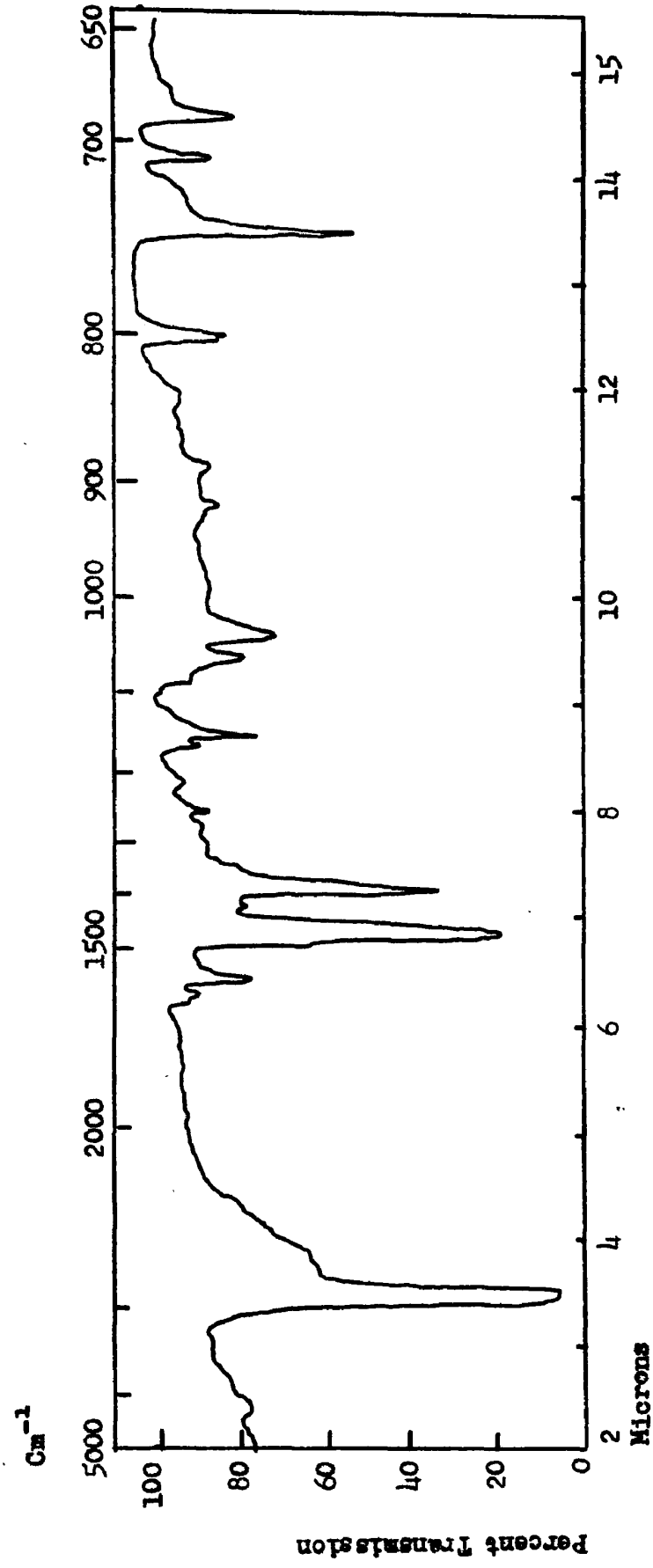


Figure 23. Infrared Absorption Spectrum of 5-m-Tolyltetrazole (Oil mull).

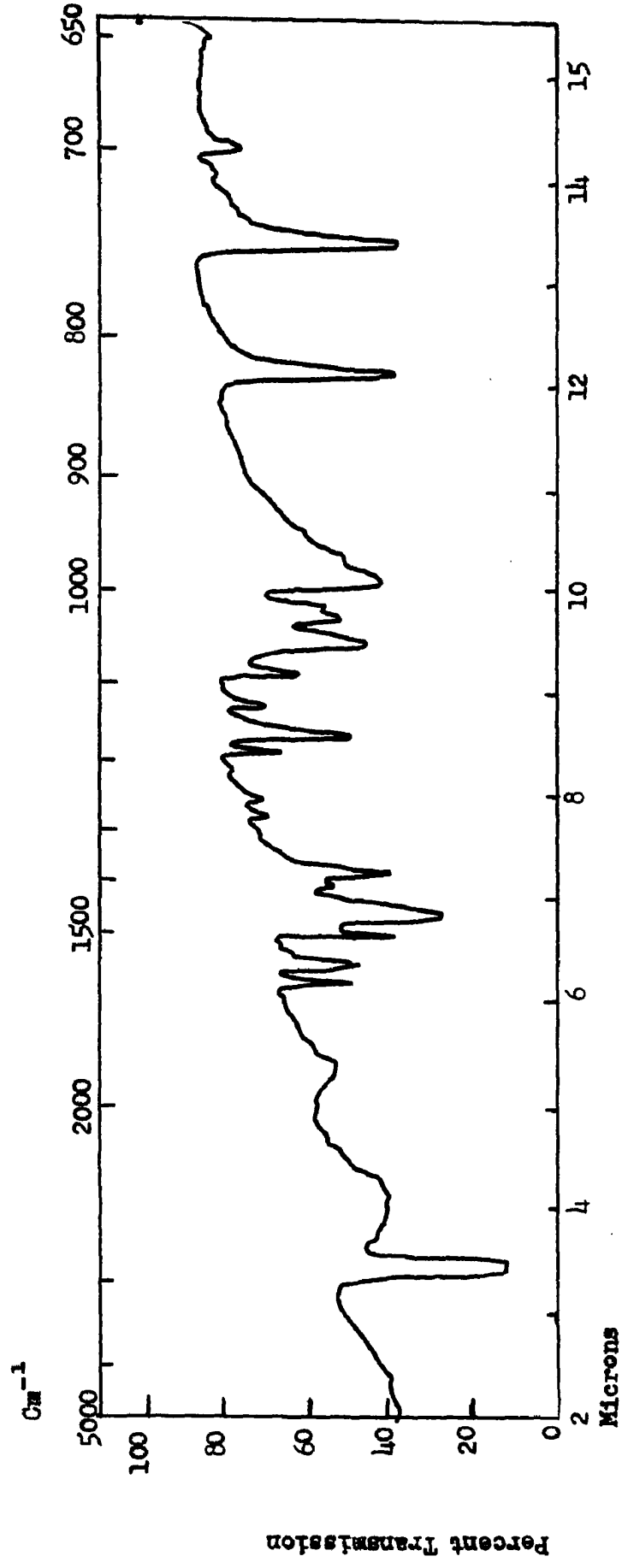


Figure 24. Infrared Absorption Spectrum of 5-p-Tolyltetrazole (Oil mull).

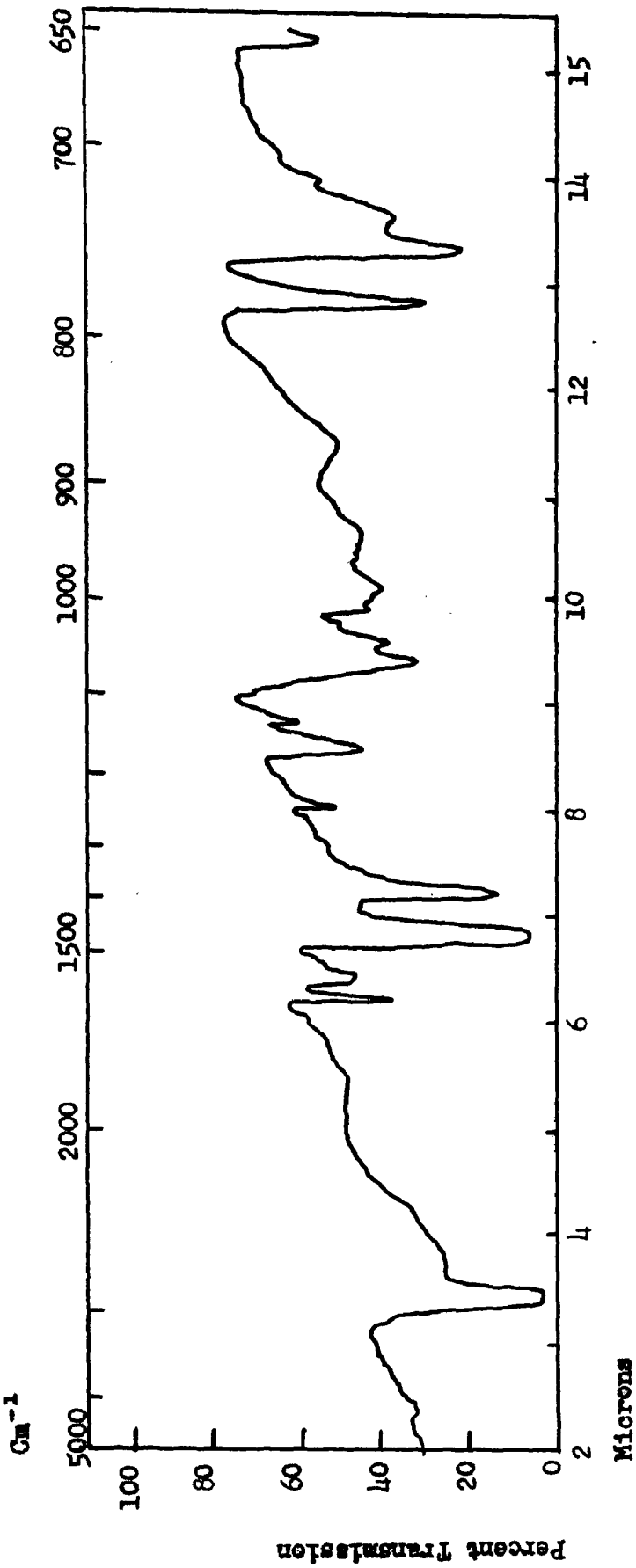


Figure 25. Infrared Absorption Spectrum of 5-o-Chlorophenyltetrazole (Oil mull).

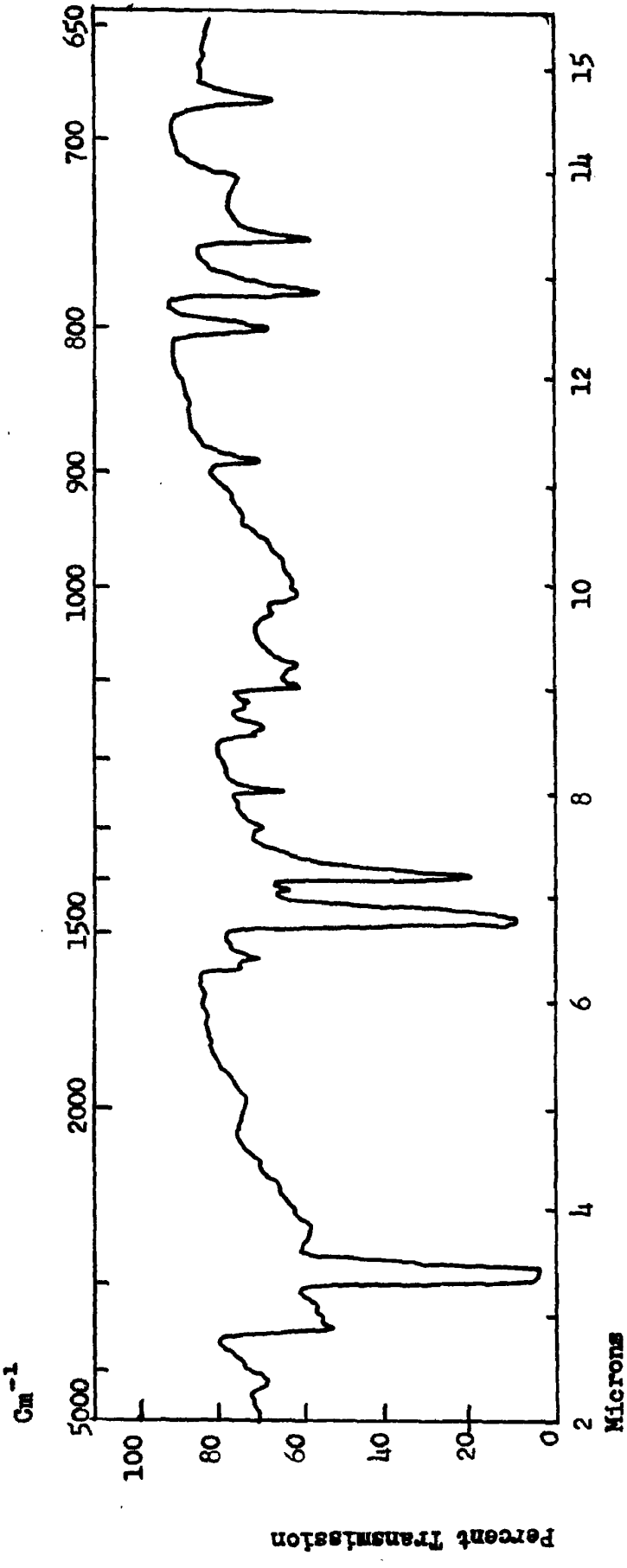


Figure 26. Infrared Absorption Spectrum of 5-m-Chlorophenyltetrazole (Oil mull).

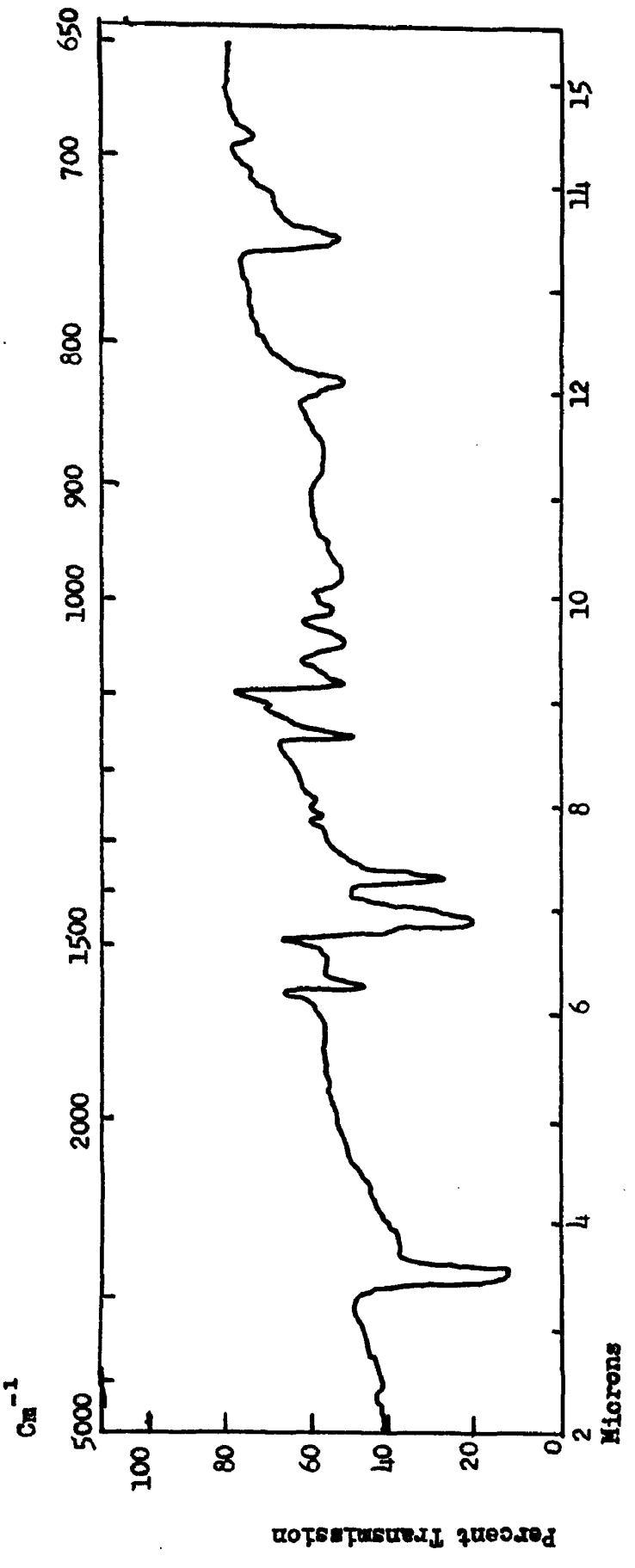


Figure 27. Infrared Absorption Spectrum of 5-p-Chlorophenyltetrazole (Oil mull).

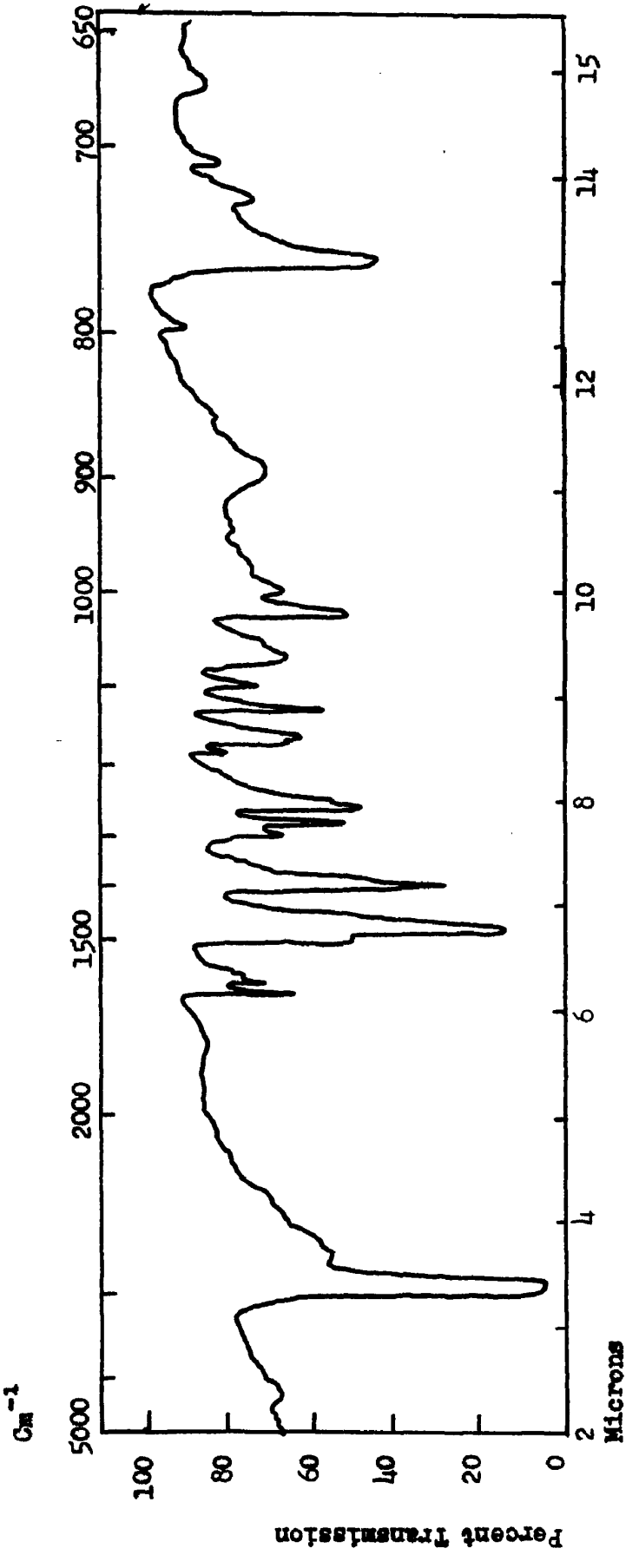


Figure 28. Infrared Absorption Spectrum of 5-o-Methoxyphenyltetrazole (Oil mull).

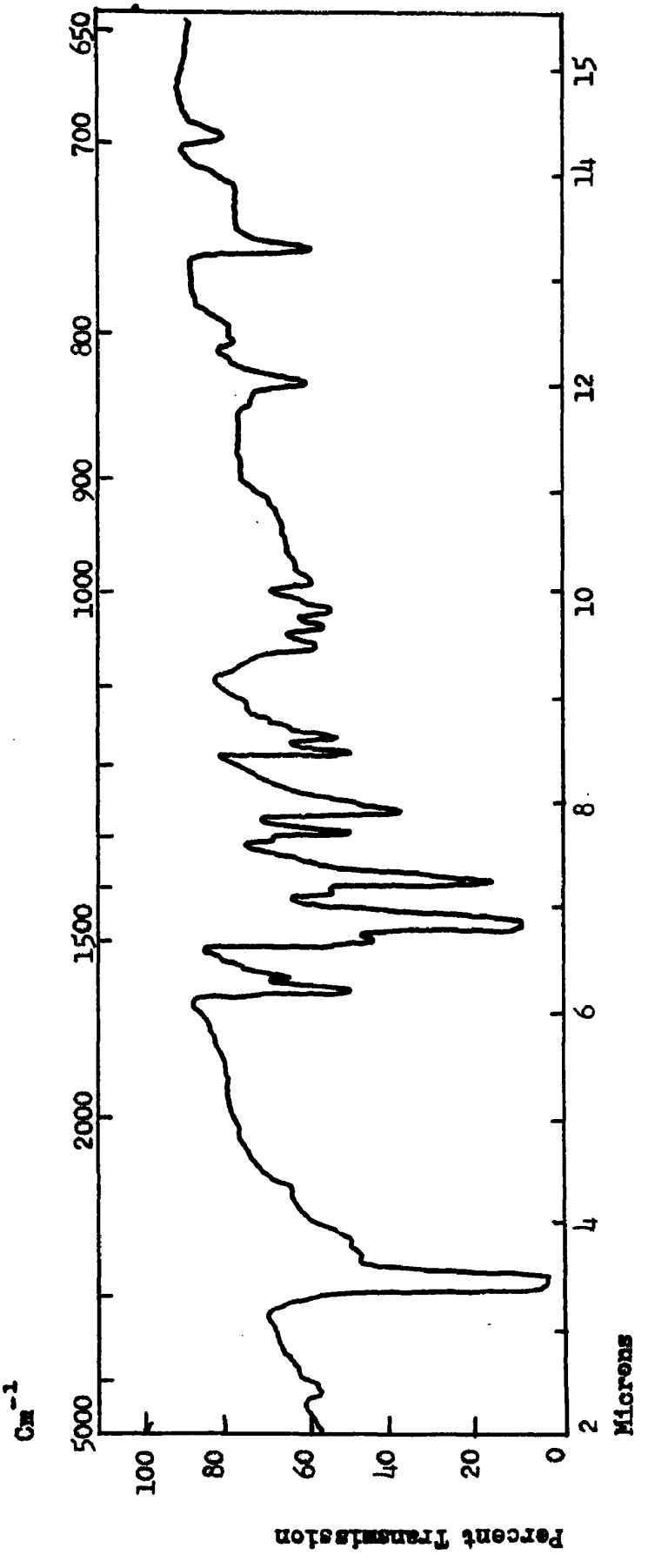


Figure 29. Infrared Absorption Spectrum of 5-p-Methoxyphenyltetrazole (Oil mull).

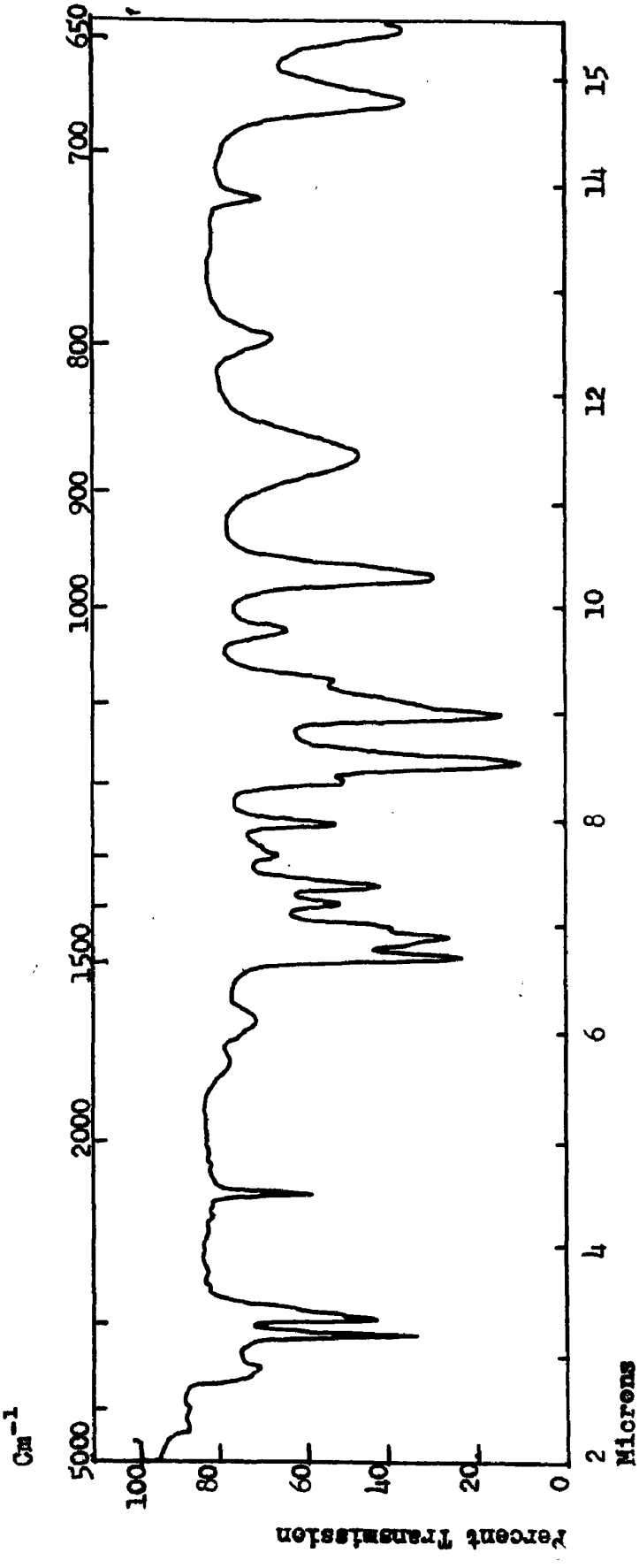


Figure 30. Infrared Absorption Spectrum of 1-Ethyltetrazole (Pure liquid).

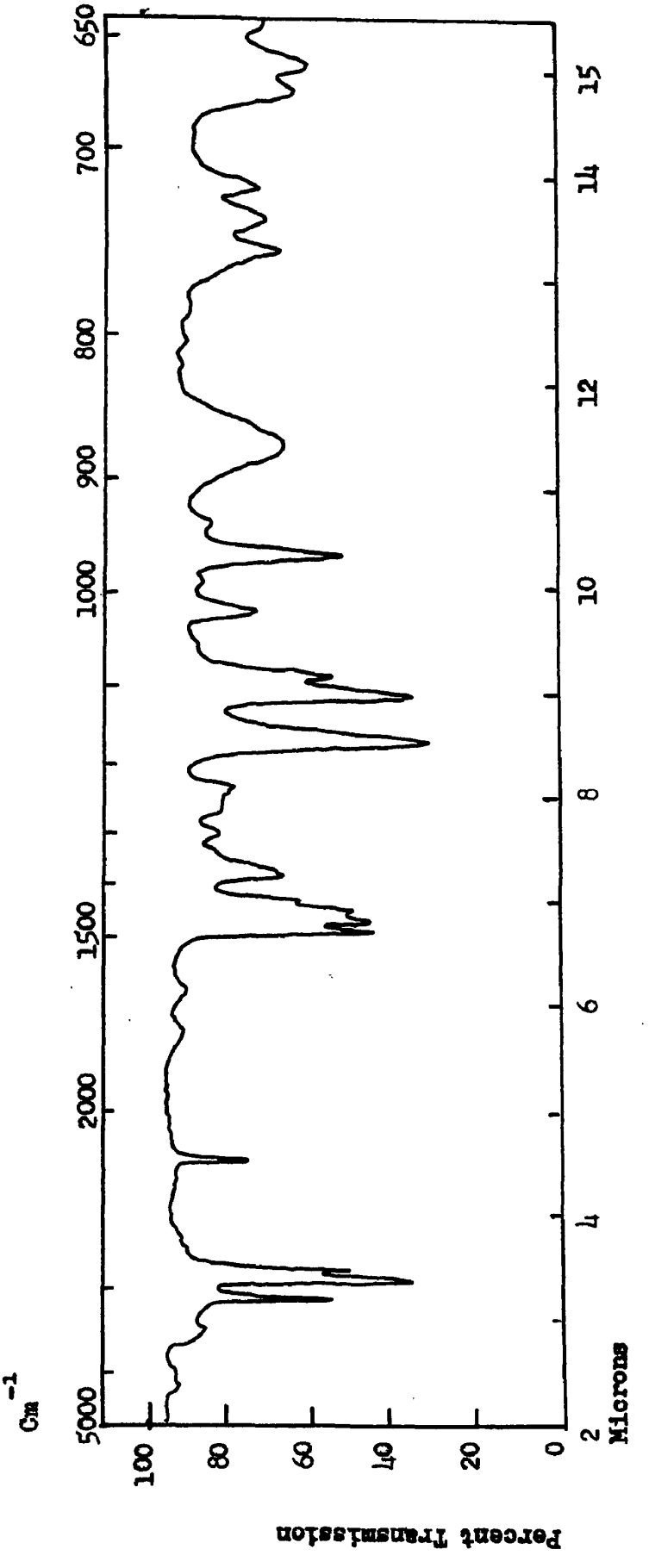


Figure 31. Infrared Absorption Spectrum of 1-n-Butyltetrazole (Pure Liquid).

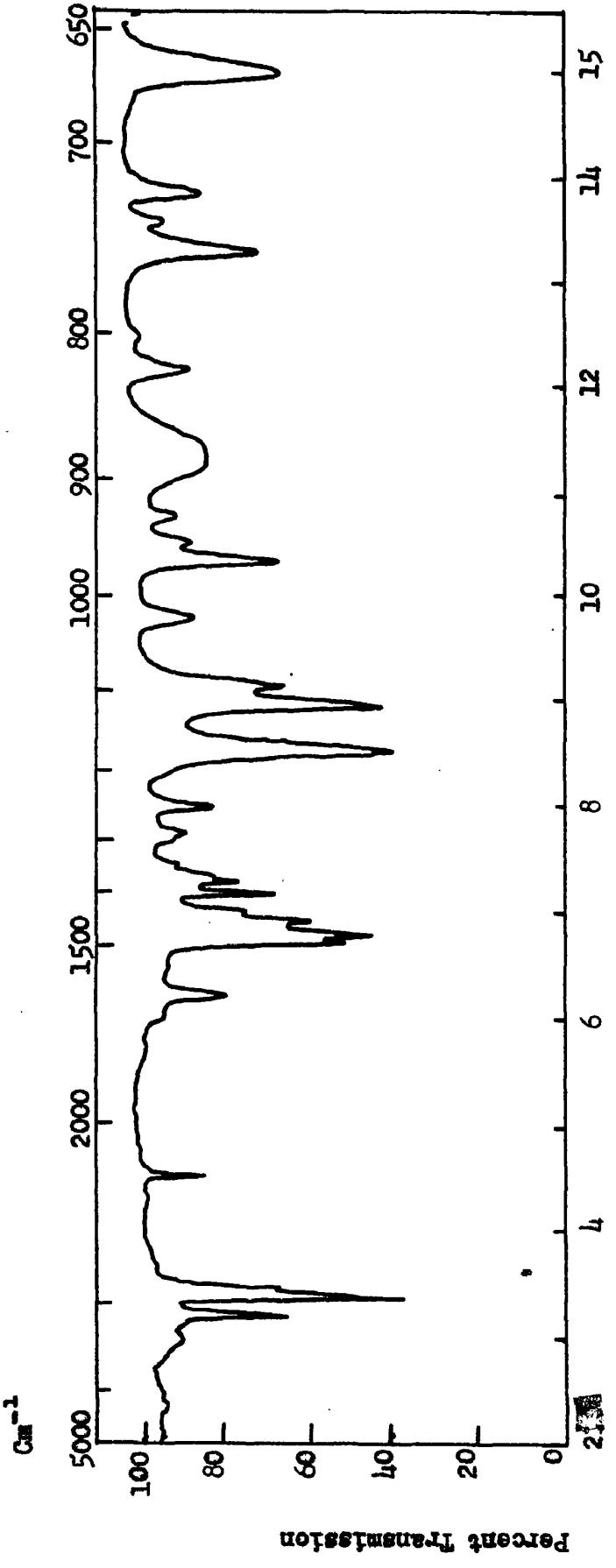


Figure 32. Infrared Absorption Spectrum of 1-Isobutyltetrazole (Isocyanide Method, Impure liquid).

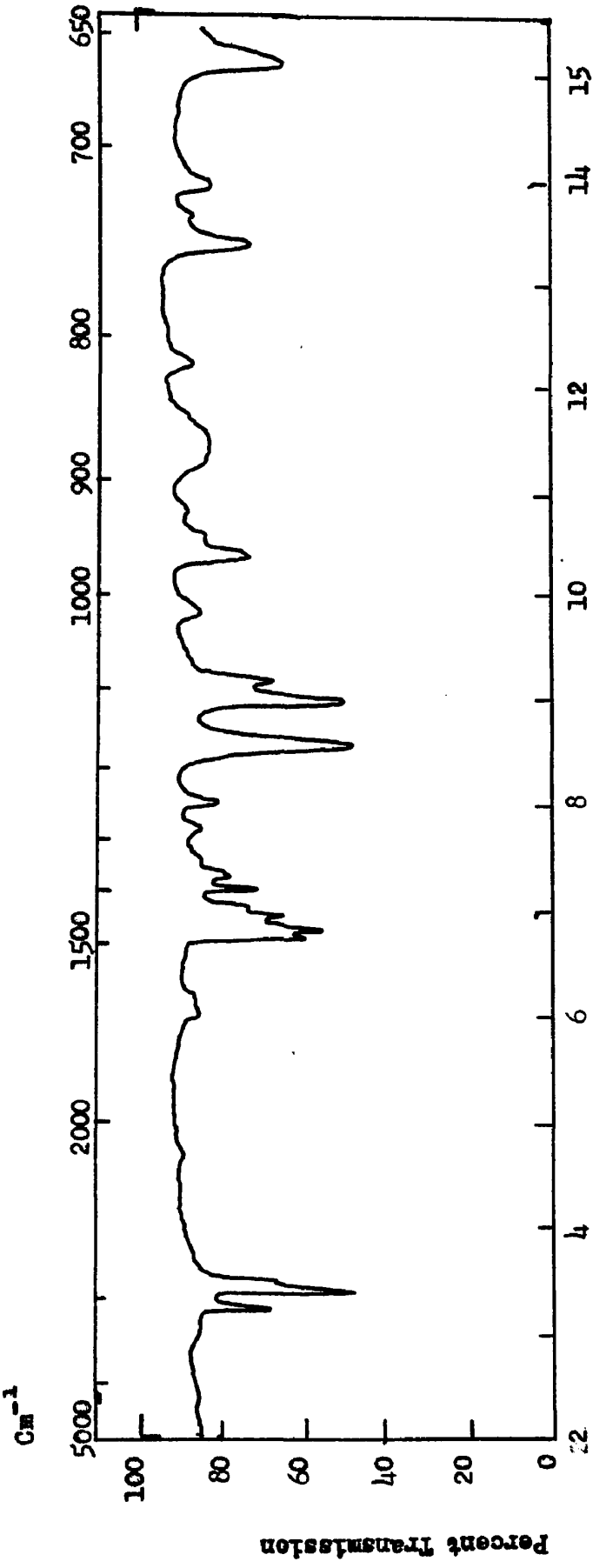


Figure 33. Infrared Absorption Spectrum of 1-Isobutyltetrazole (Formamide Method--Pure liquid).

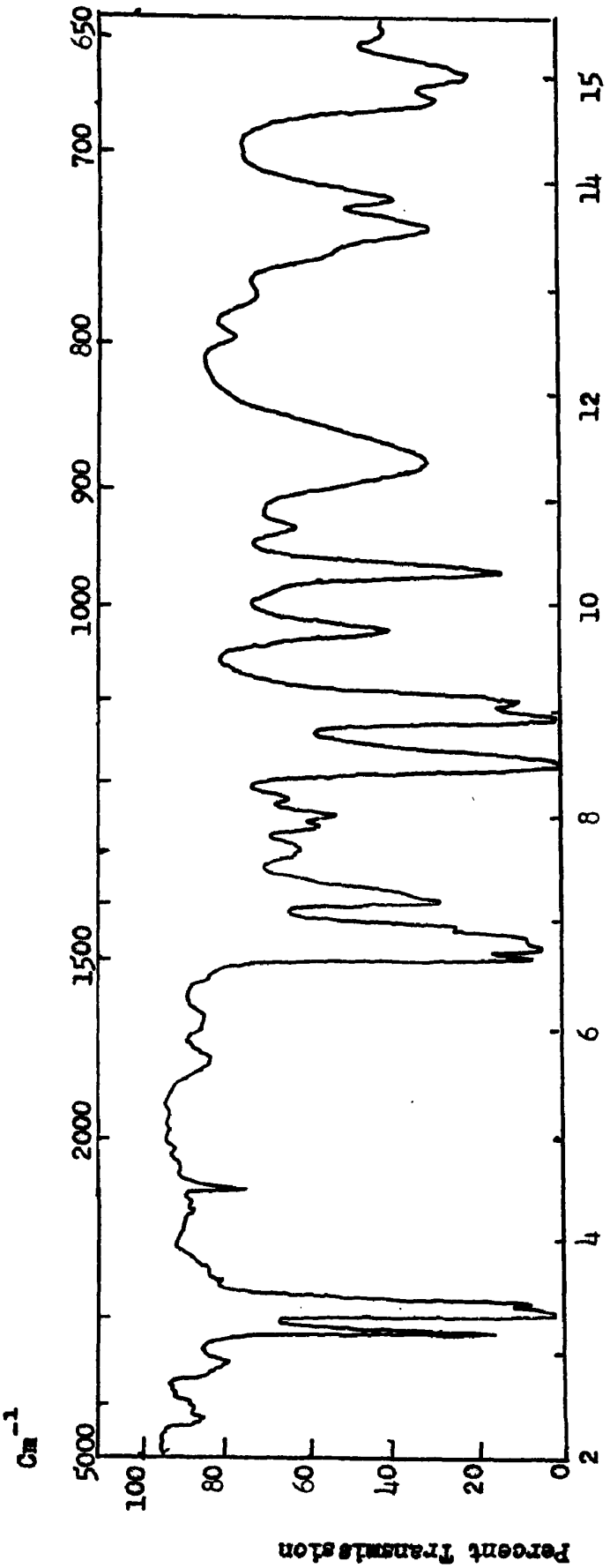


Figure 34. Infrared Absorption Spectrum of 1-n-Amyltetrazole (Pure Liquid).

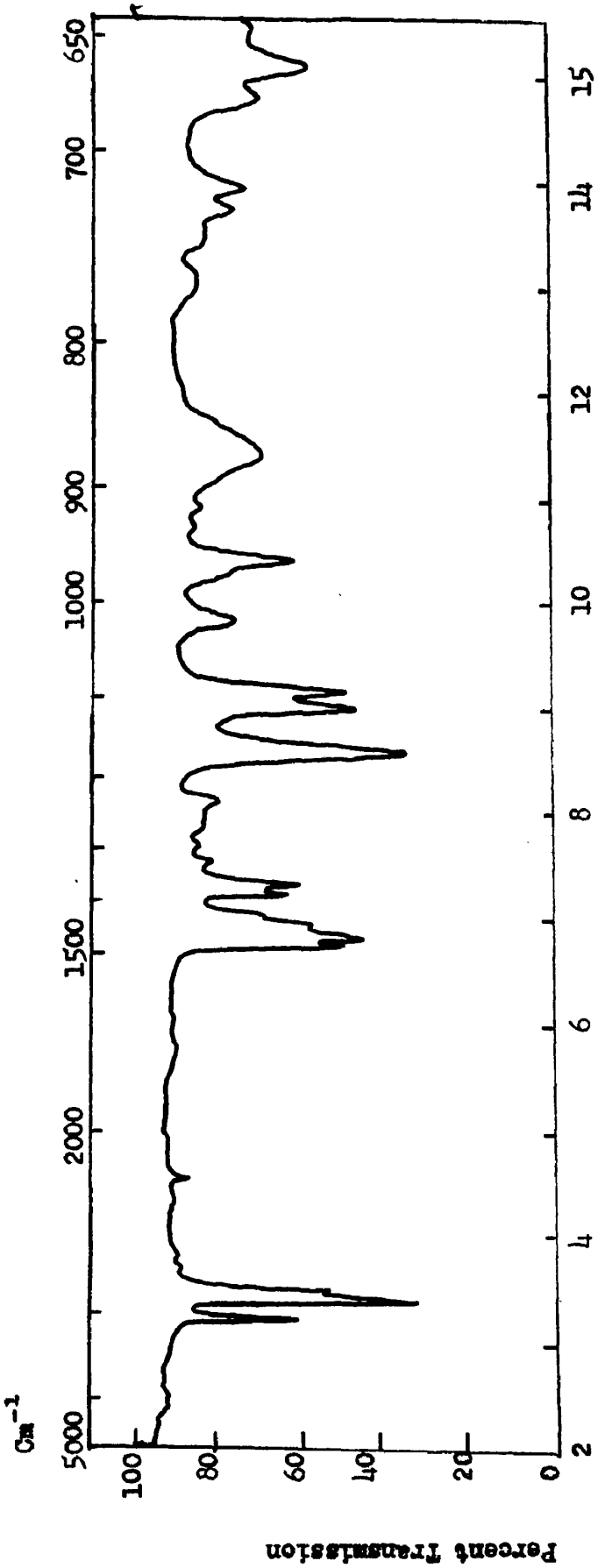


Figure 35. Infrared Absorption Spectrum of 1-Isoamyltetrazole (Impure liquid).

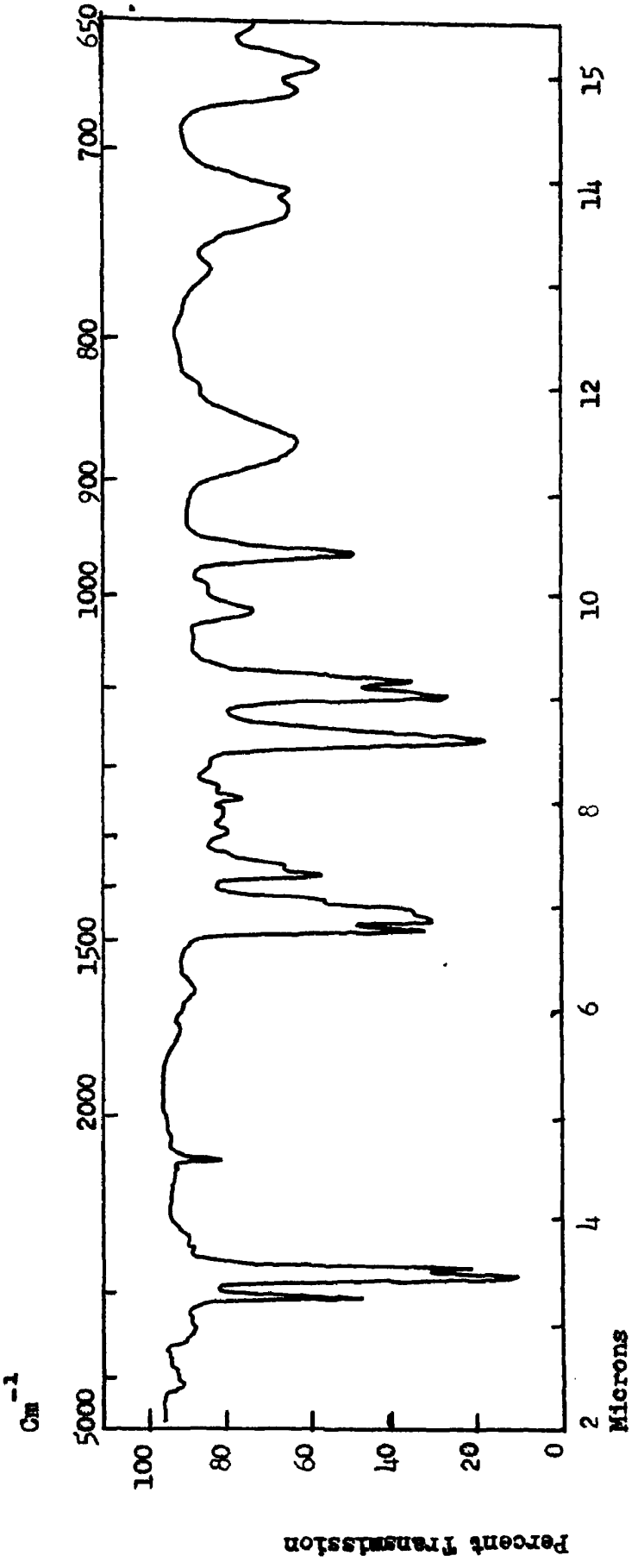


Figure 36. Infrared Absorption Spectrum of 1-n-Hexyltetrazole (Pure Liquid).

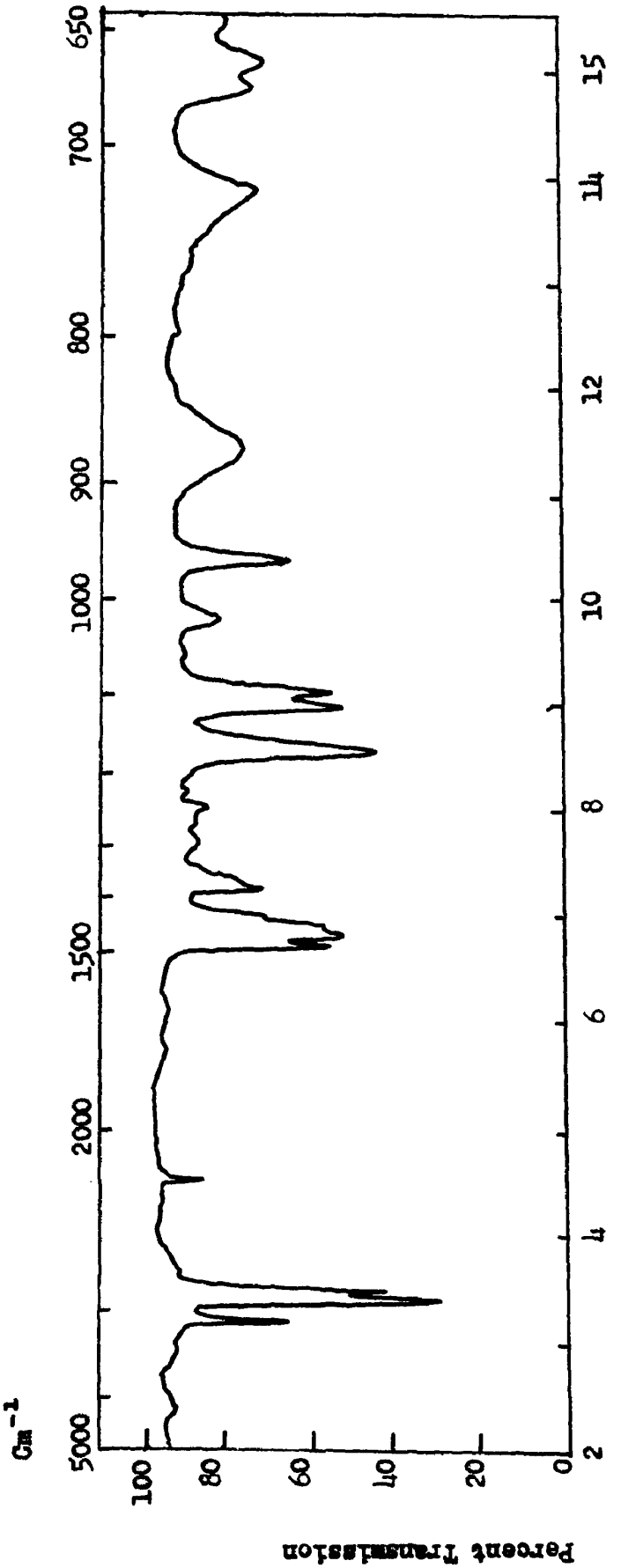


Figure 37. Infrared Absorption Spectrum of 1-n-Heptyltetrazole (Impure Liquid).

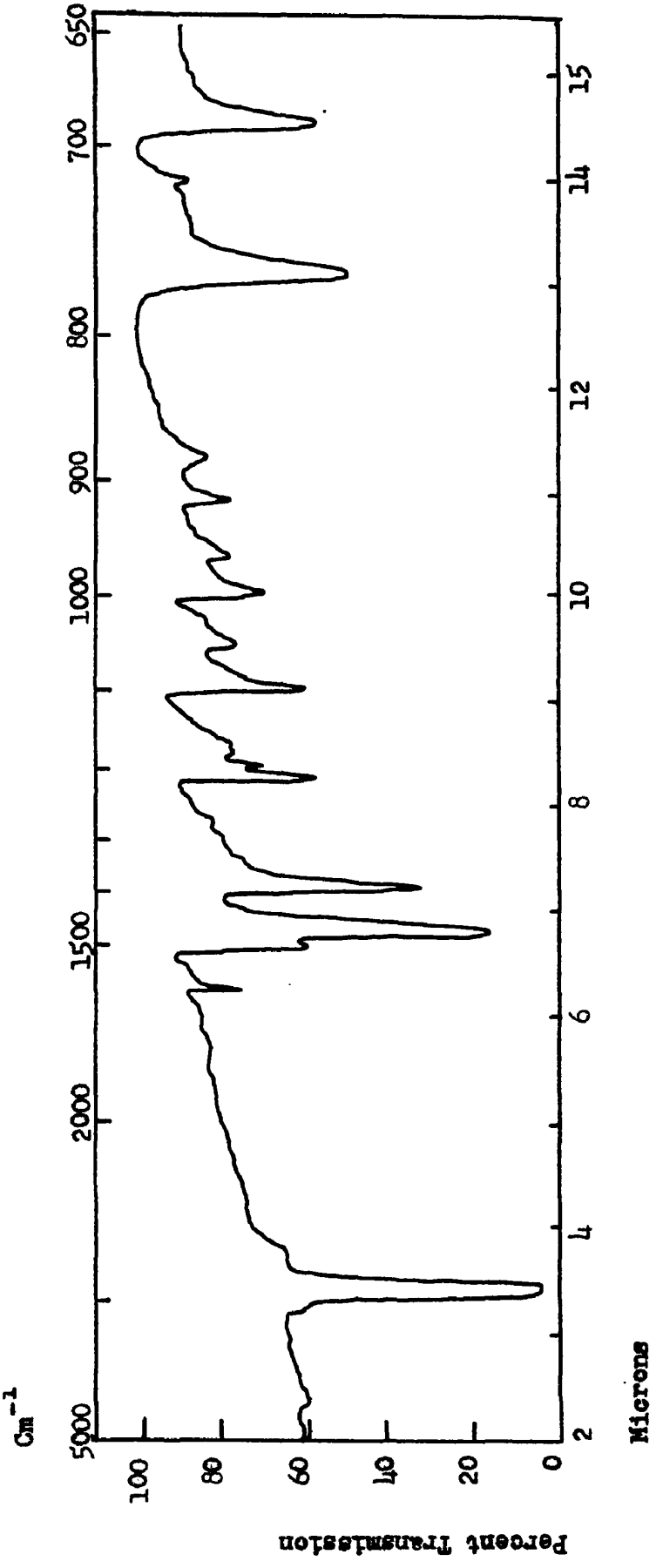


Figure 38. Infrared Absorption Spectrum of 1-Phenyltetrazole (Oil mull).

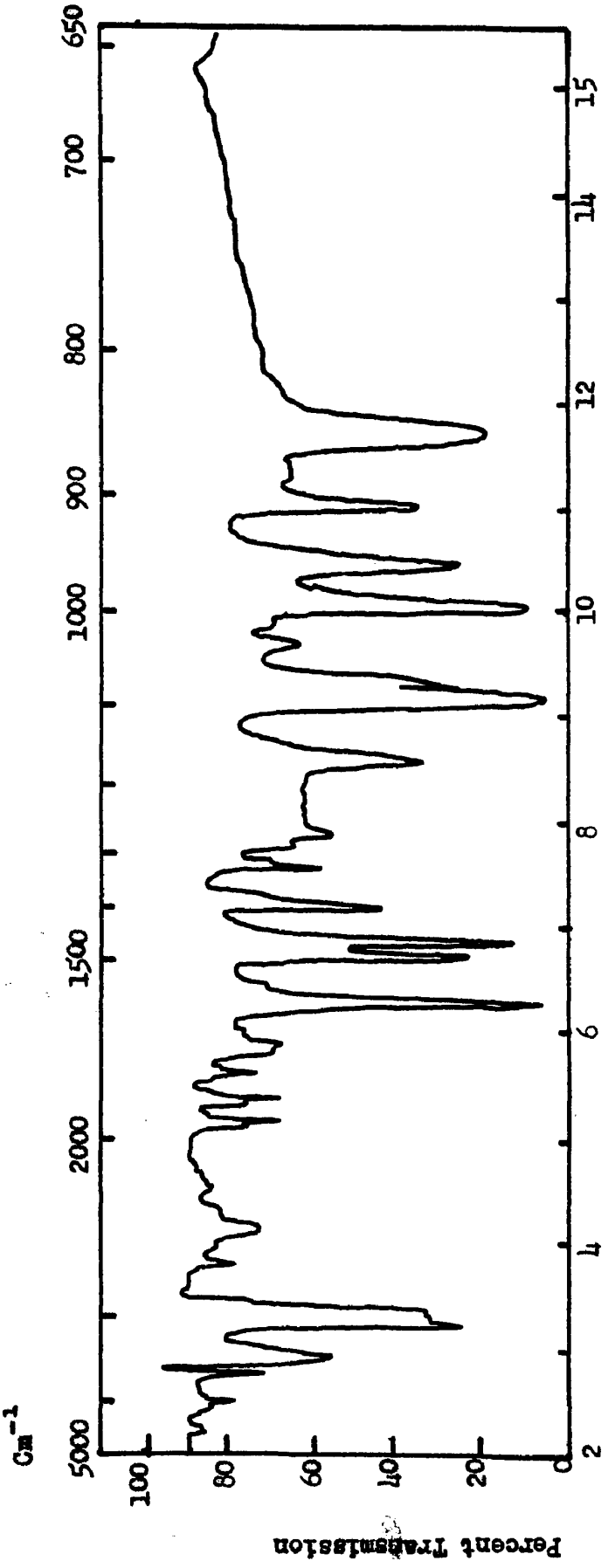


Figure 39. Infrared Absorption Spectrum of 1-Phenyltetrazole ($CHCl_3$).

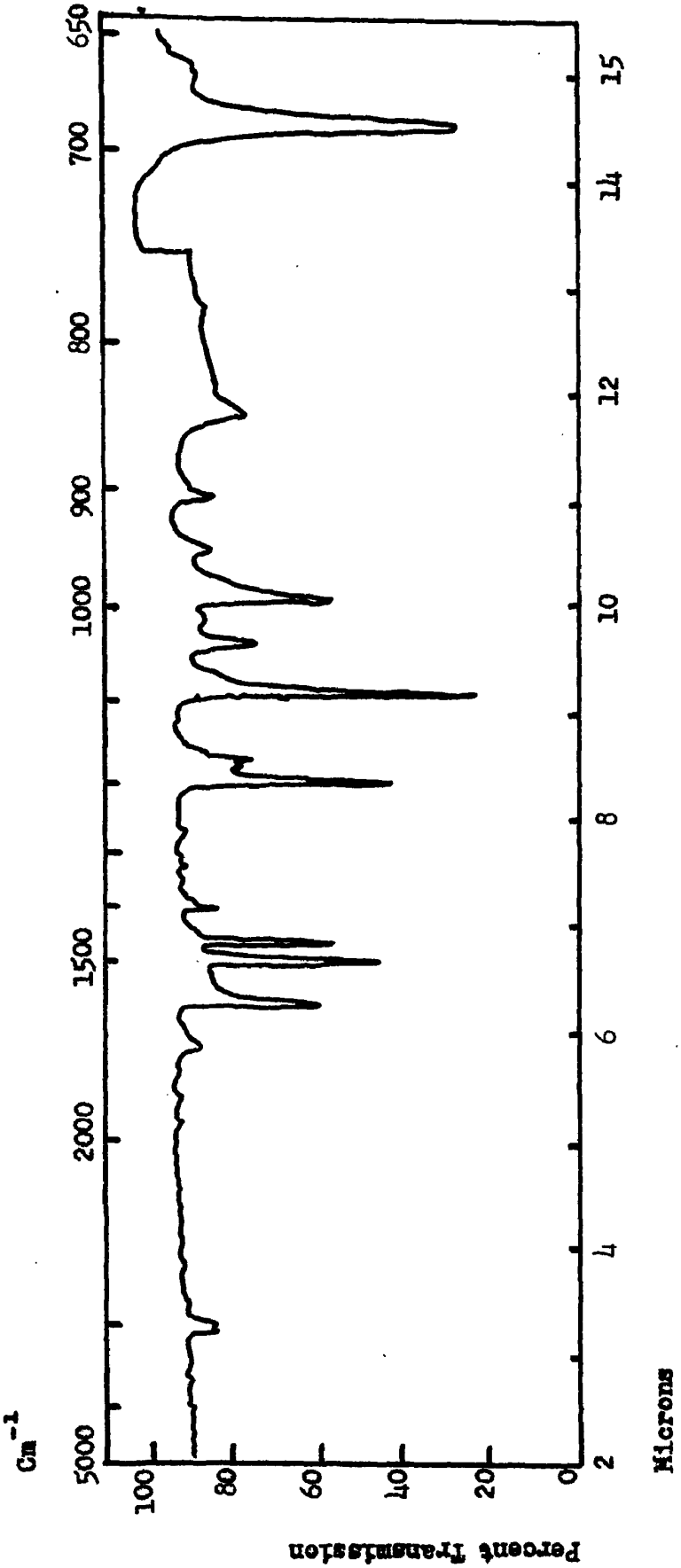


Figure 40. Infrared Absorption Spectrum of 1-Phenyltetrazole (CCl_4).

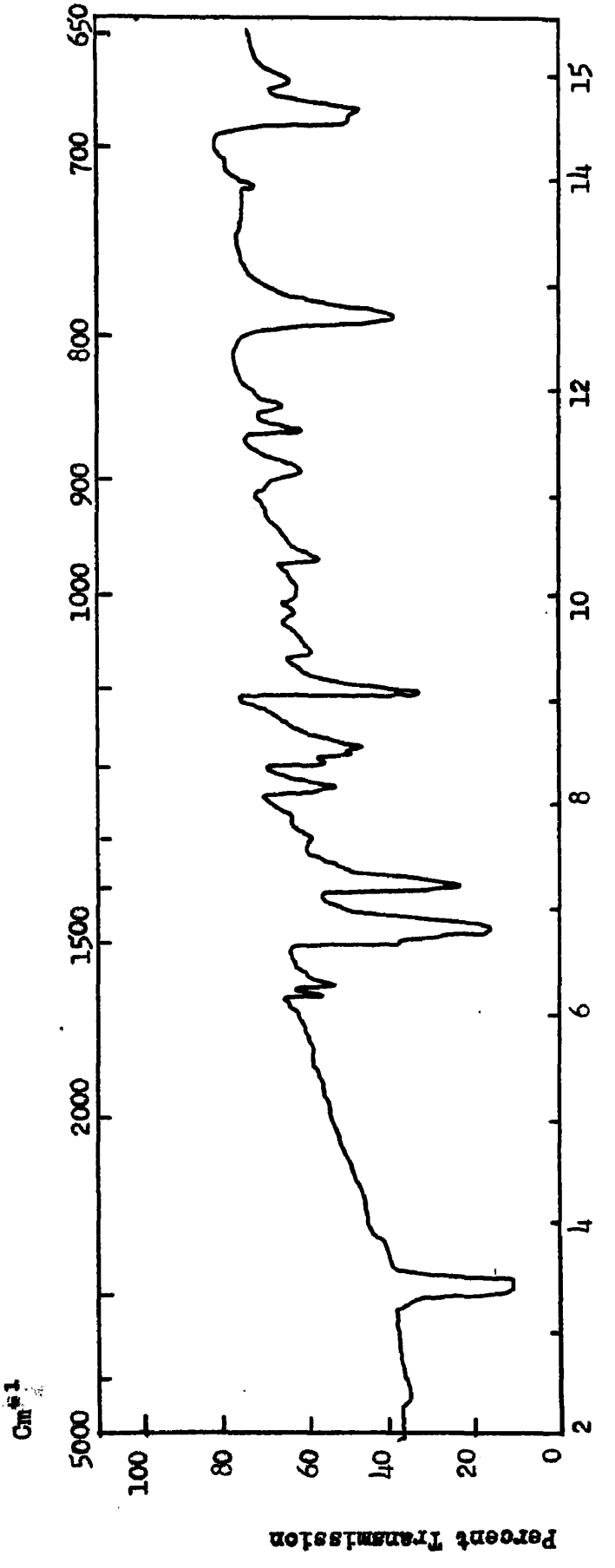


Figure 41. Infrared Absorption Spectrum of 1-m-Tolyltetrazole (Oil mull).

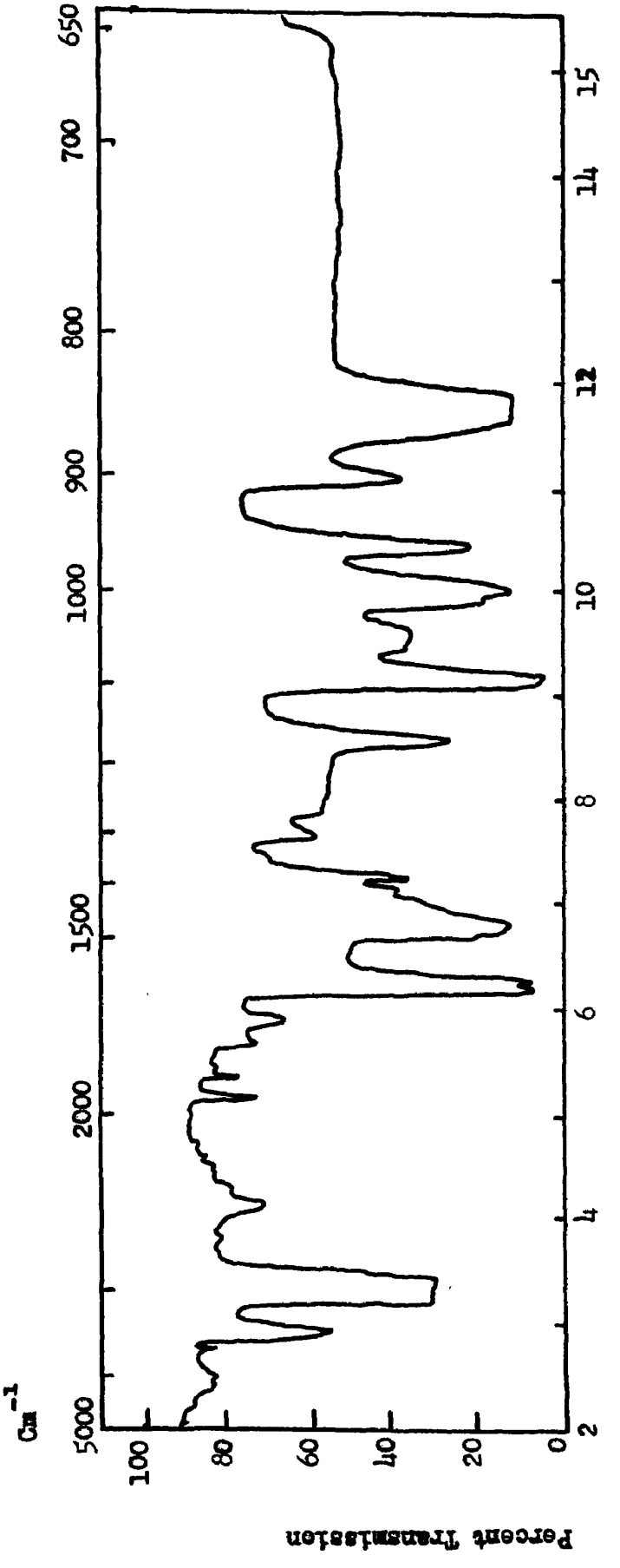


Figure 42. Infrared Absorption Spectrum of 1-m-Tolyltetrazole ($CHCl_3$).

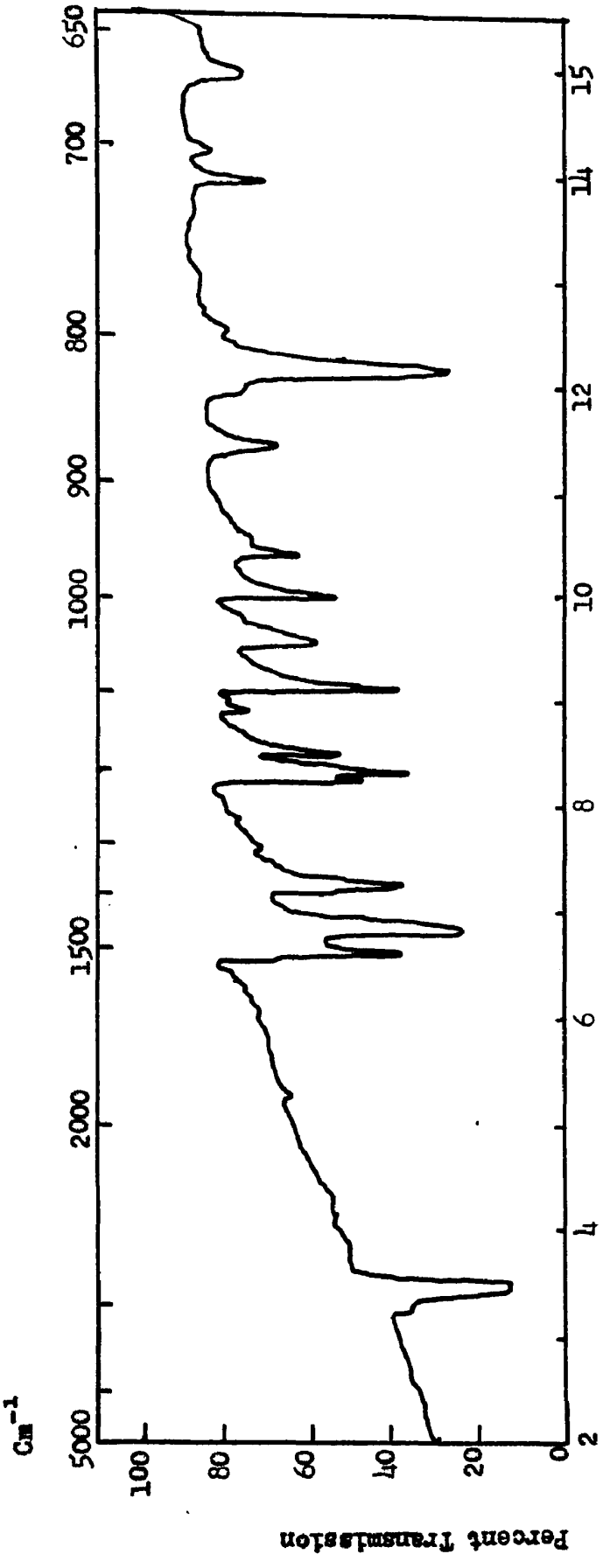


Figure 43. Infrared Absorption Spectrum of 1-p-Tolyltetrazole (Oil mull).

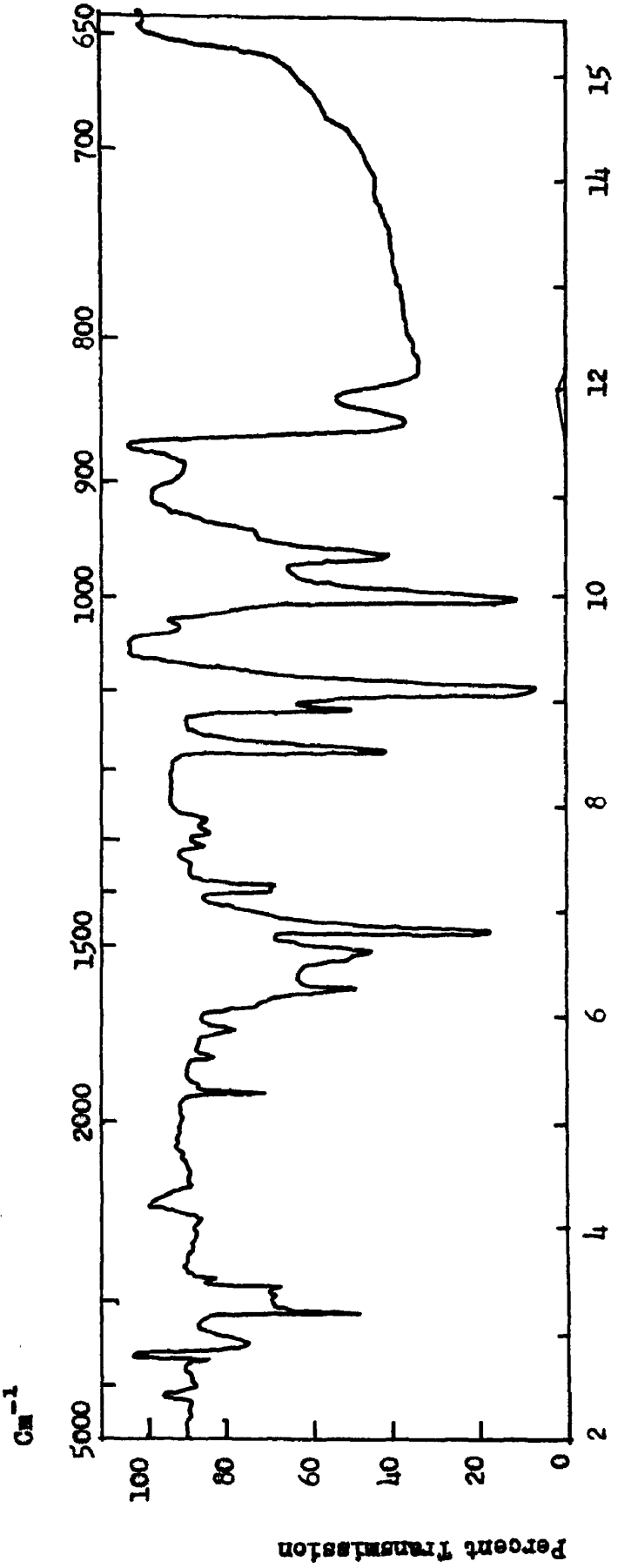


Figure 44. Infrared Absorption Spectrum of 1-p-Tolyltetrazole ($CHCl_3$).

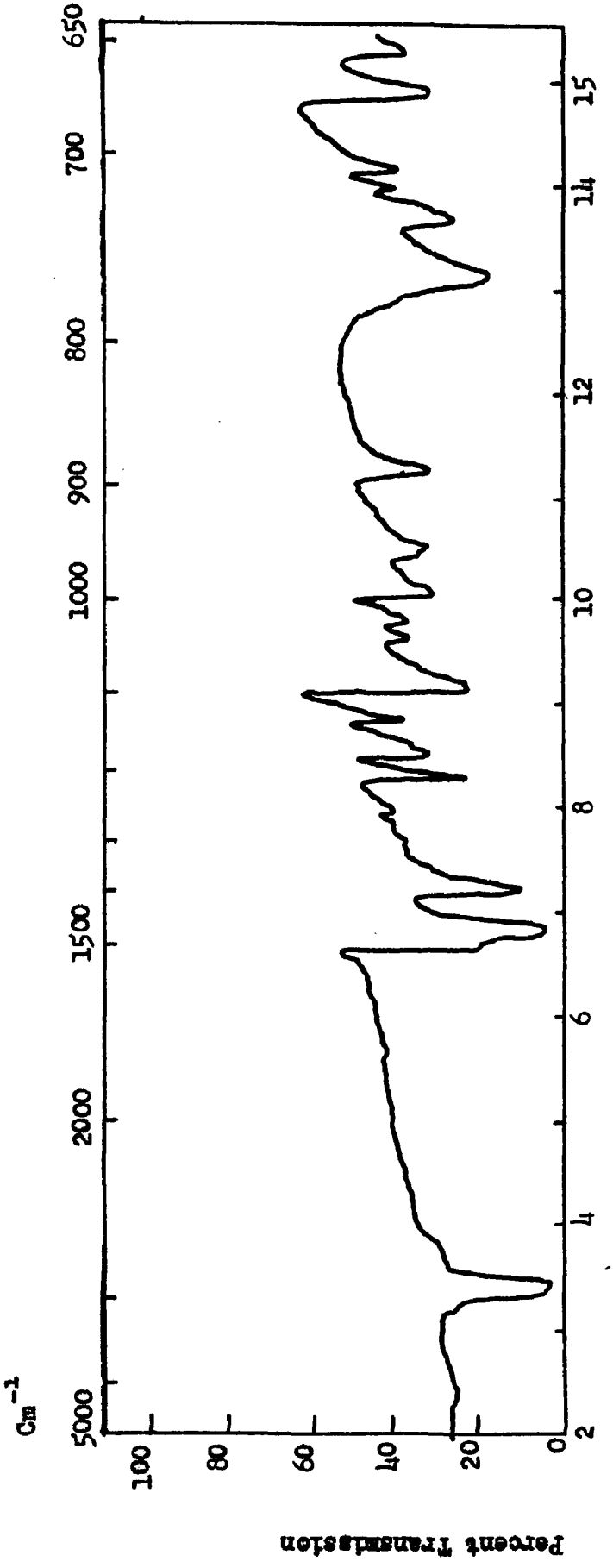


Figure 45. Infrared Absorption Spectrum of 1-o-Chlorophenyltetrazole (Oil mull).

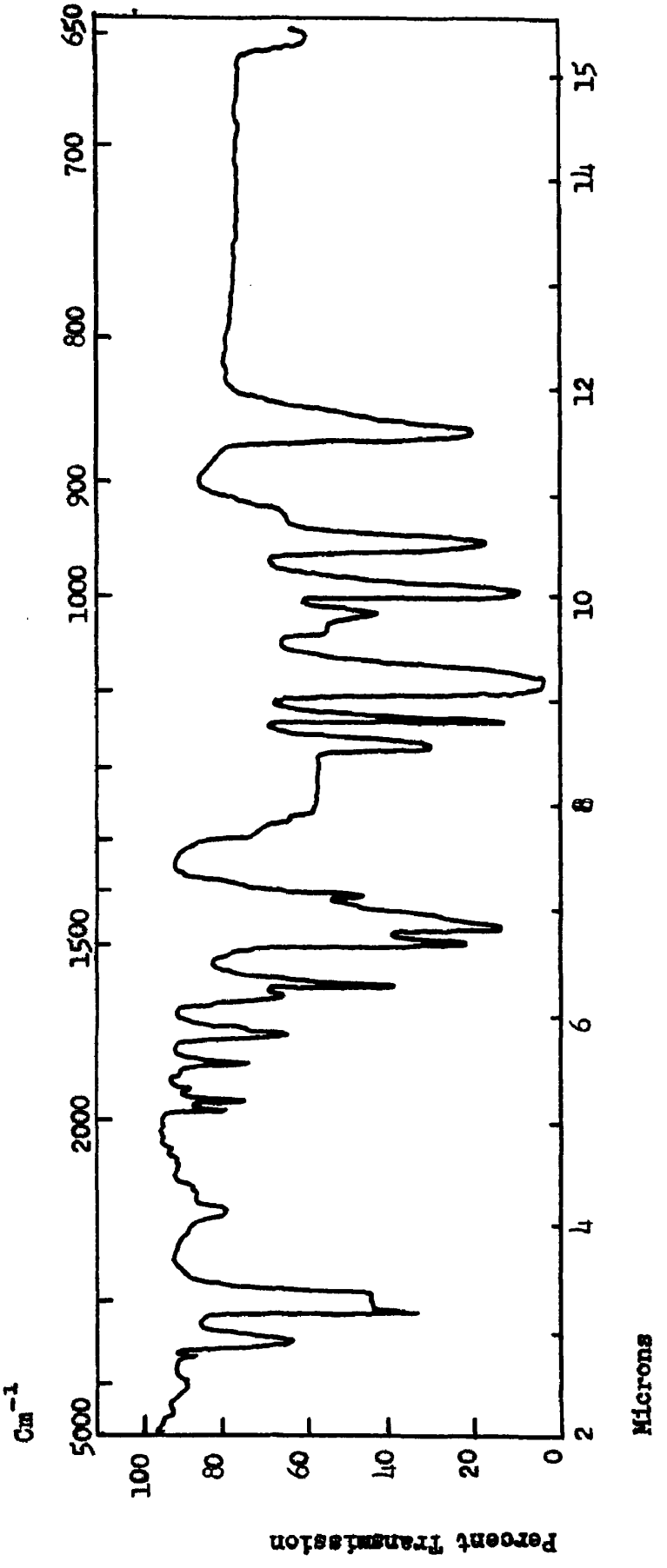


Figure 46. Infrared Absorption Spectrum of 1-o-Chlorophenyltetrazole ($CHCl_3$).

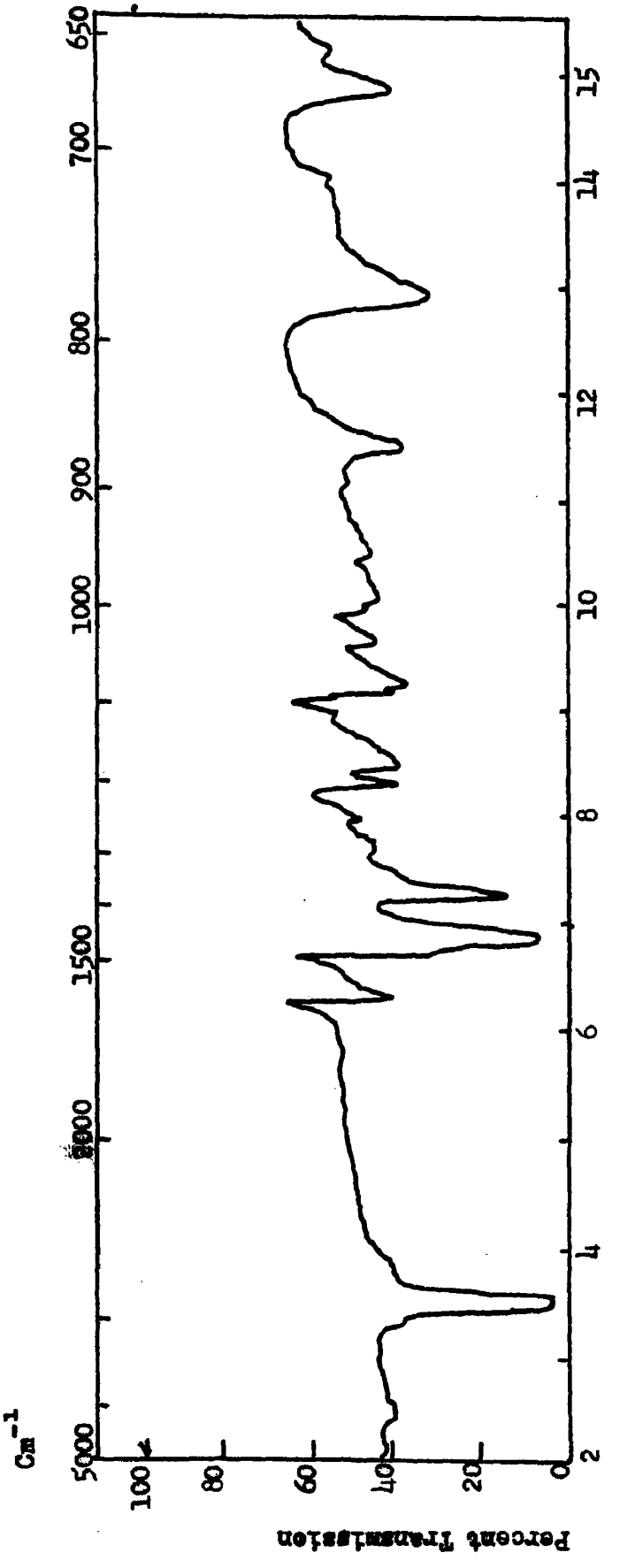


Figure 47. Infrared Absorption Spectrum of 1-m-Chlorophenyltetrazole (Oil mull).

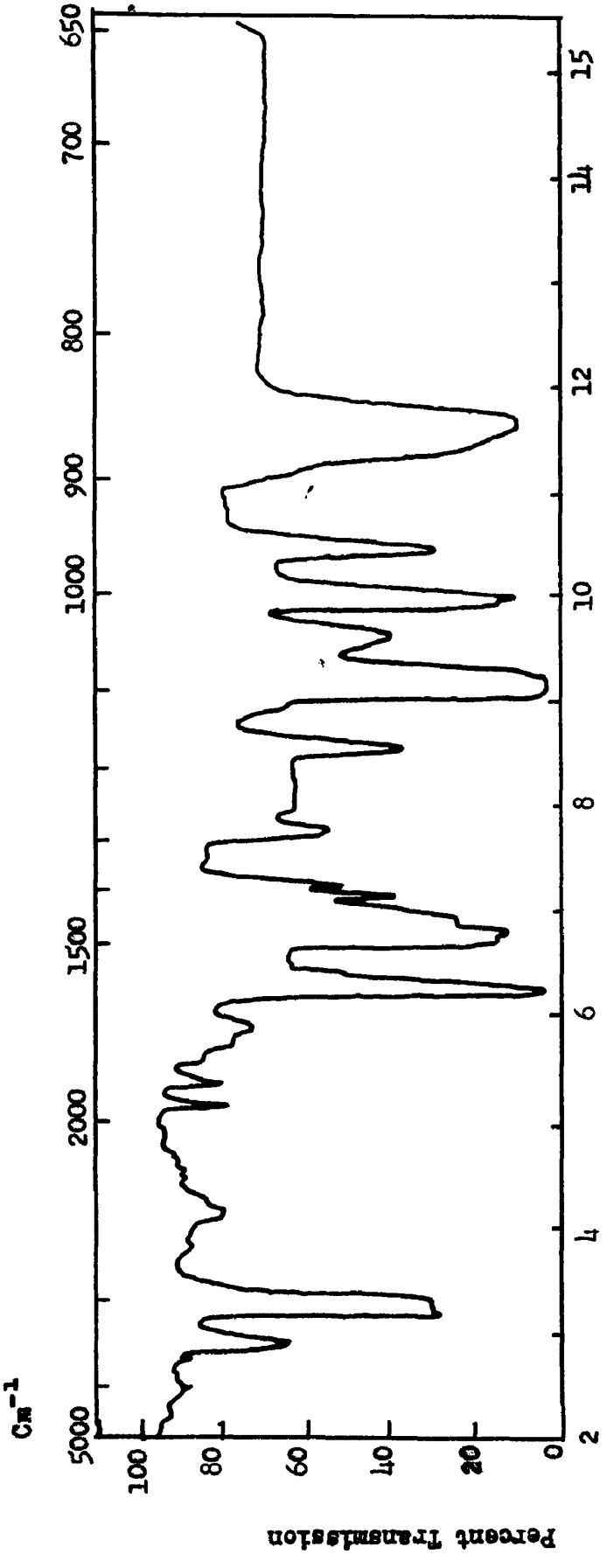


Figure 48. Infrared Absorption Spectrum of 1-m-Chlorophenyltetrazole ($CHCl_3$).

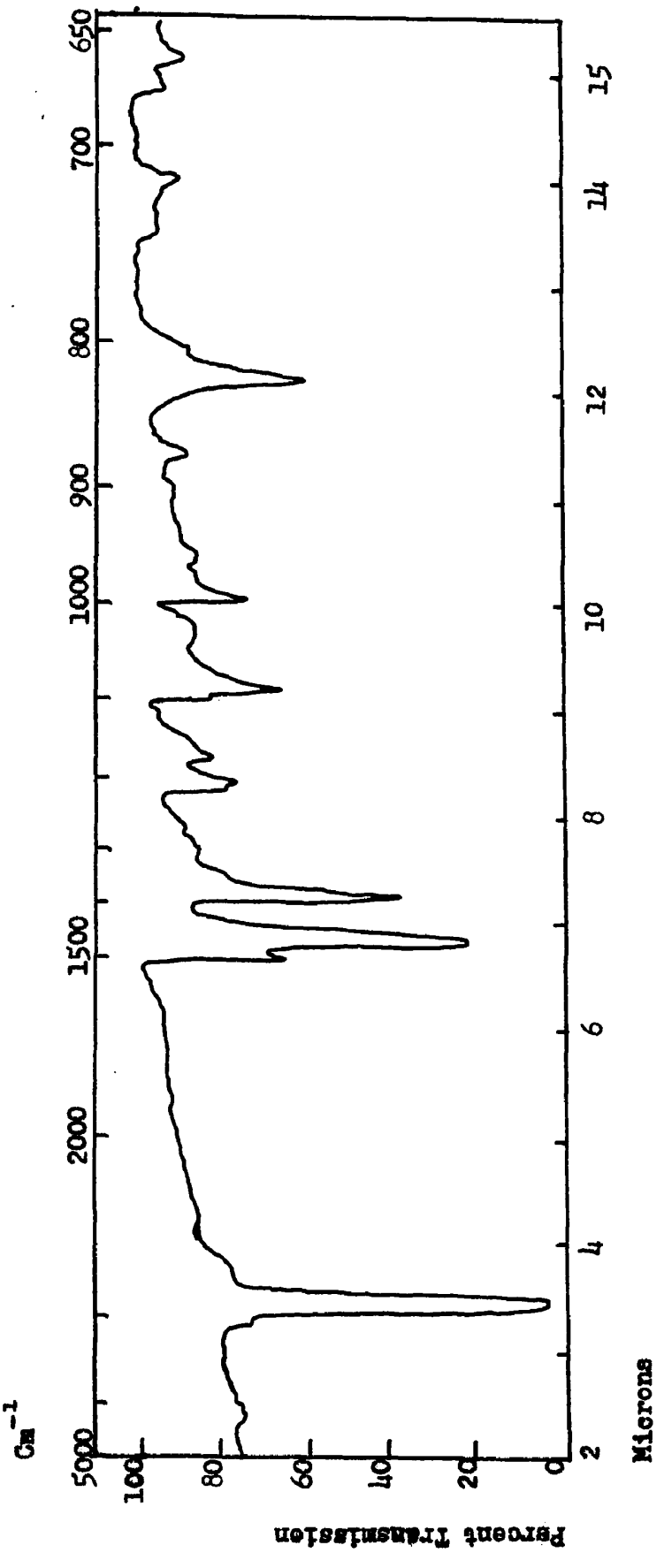


Figure 49. Infrared Absorption Spectrum of 1-p-Chlorophenyltetrazole (Oil mull).

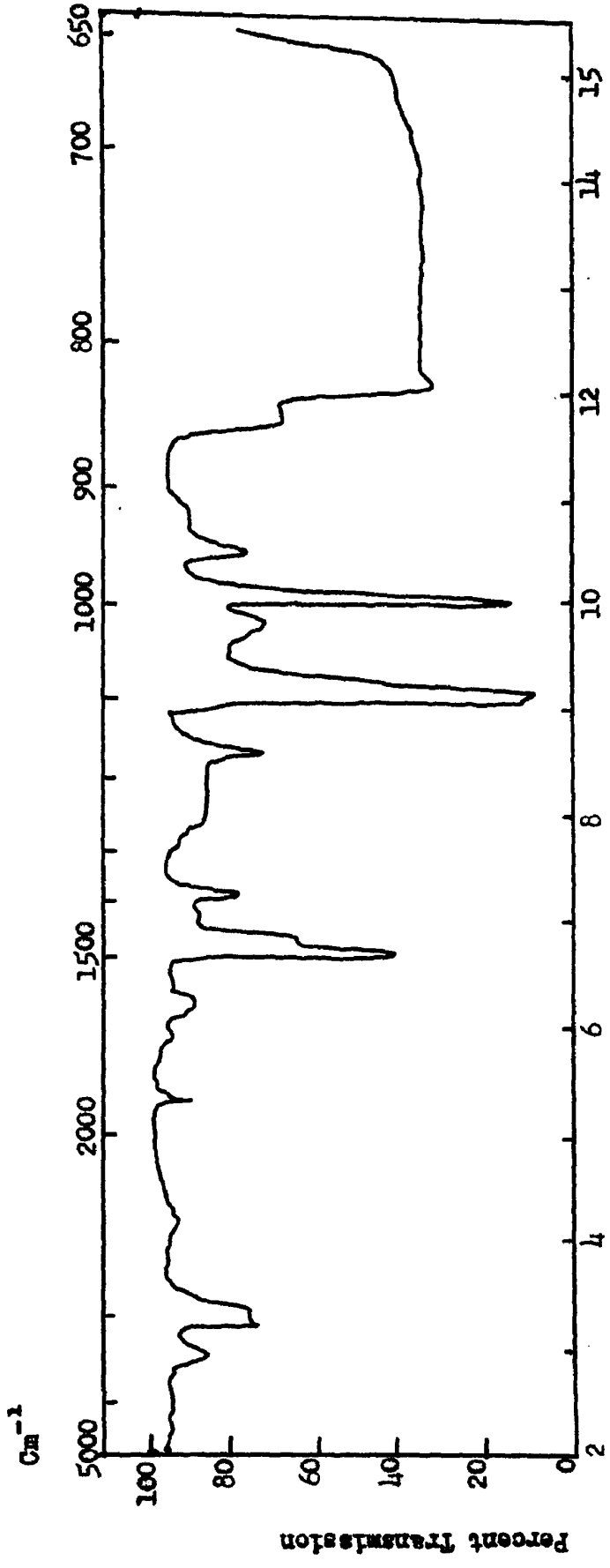


Figure 50. Infrared Absorption Spectrum of 1-p-Chlorophenyltetrazole ($CHCl_3$).

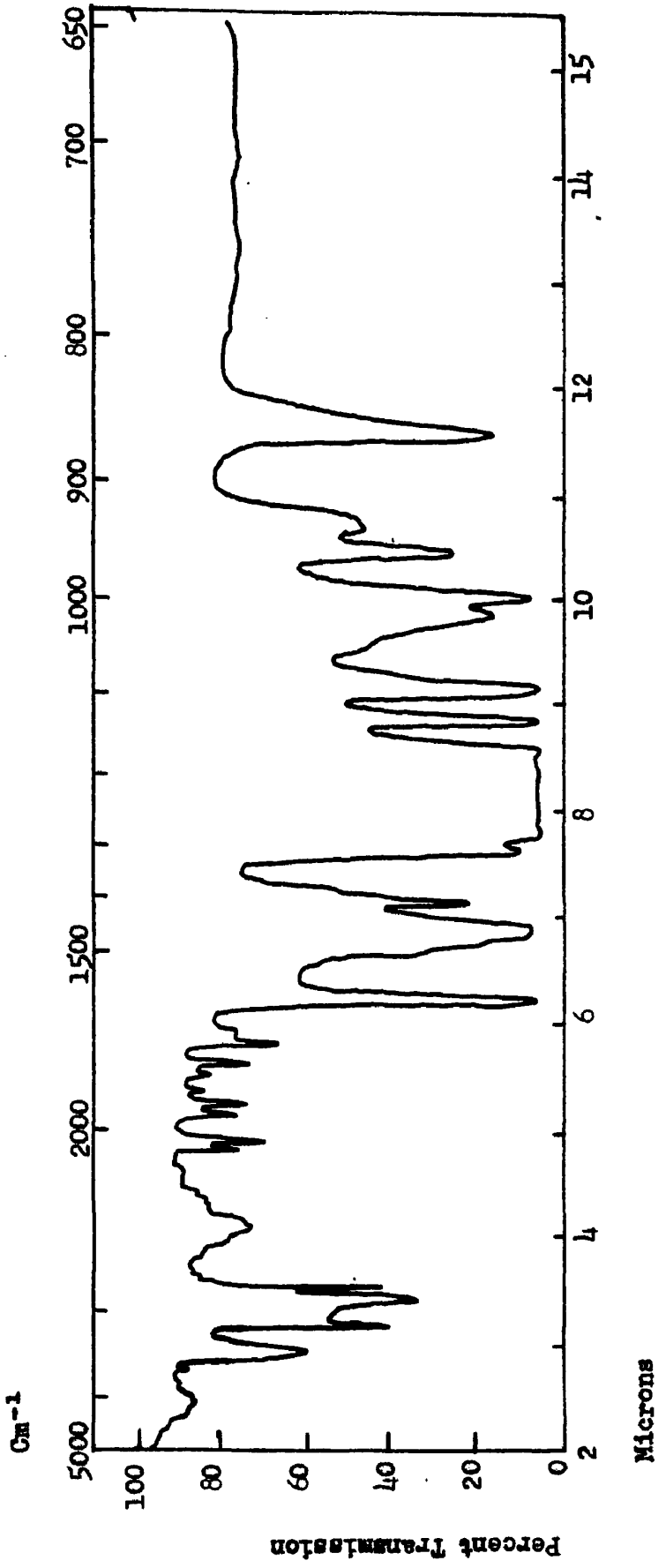


Figure 51. Infrared Absorption Spectrum of 1-o-Methoxyphenyltetrazole ($CHCl_3$).

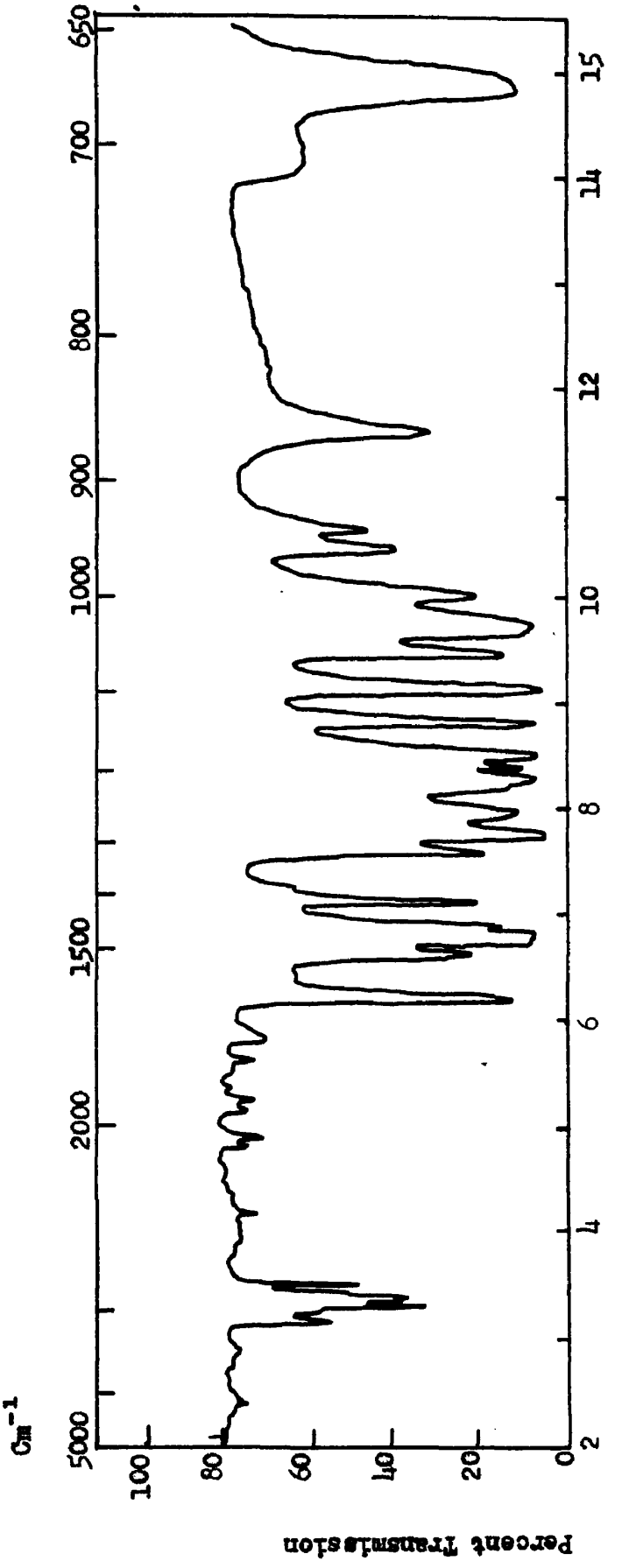


Figure 52. Infrared Absorption Spectrum of 1-o-Methoxyphenyltetrazole (CCl_4).

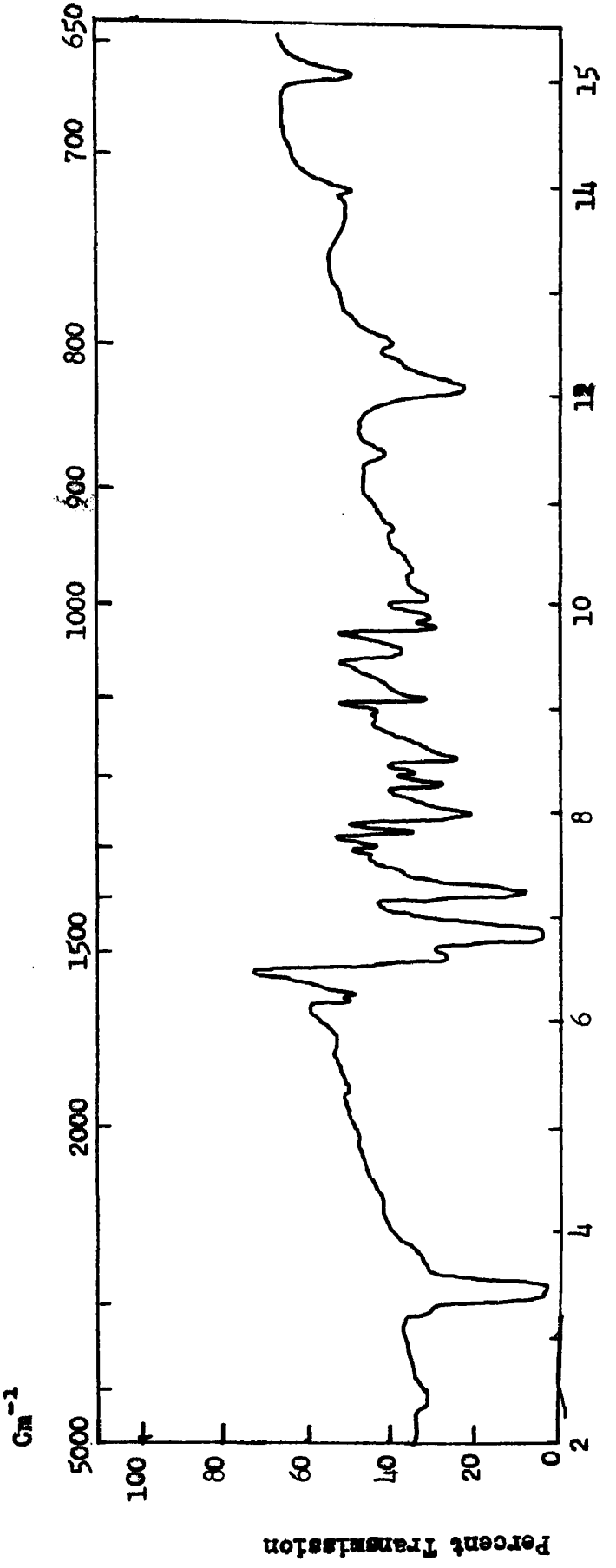


Figure 53. Infrared Absorption Spectrum of 1-p-Methoxyphenyltetrazole (Oil mull).

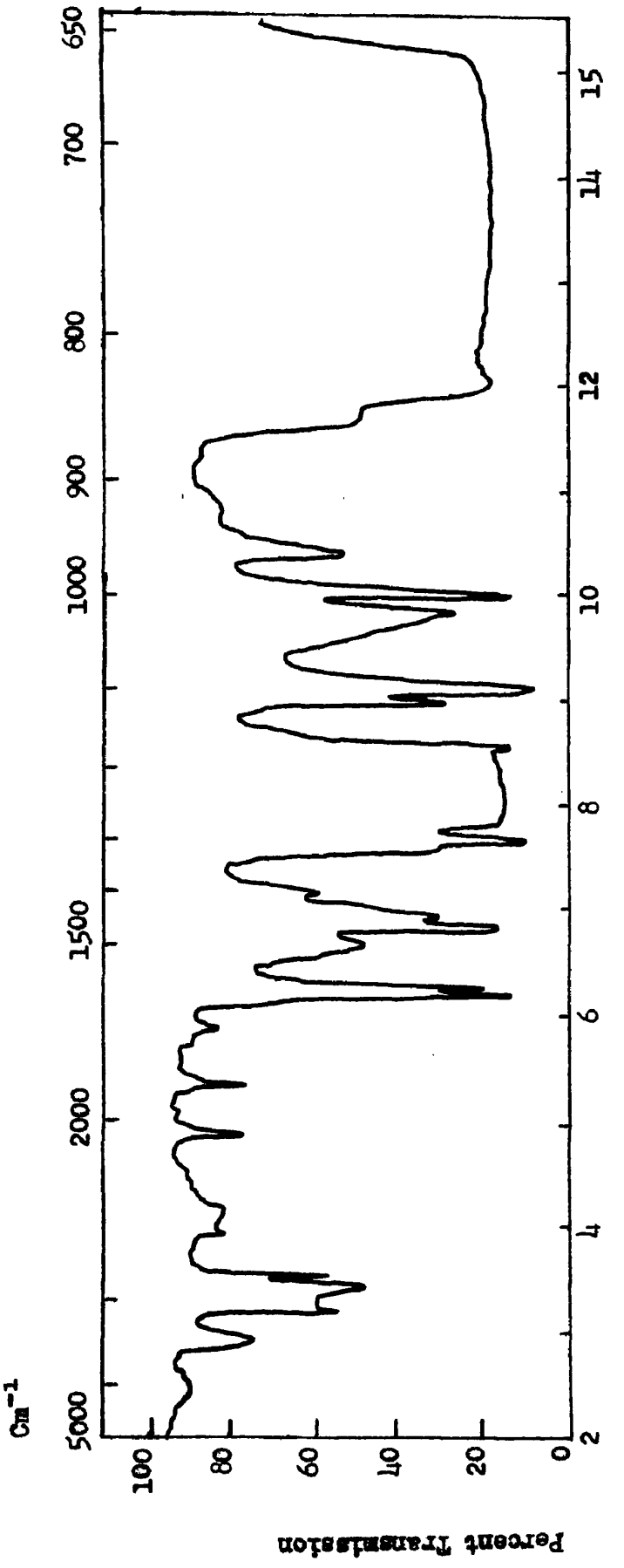


Figure 54. Infrared Absorption Spectrum of 1-p-Methoxyphenyltetrazole ($CHCl_3$).

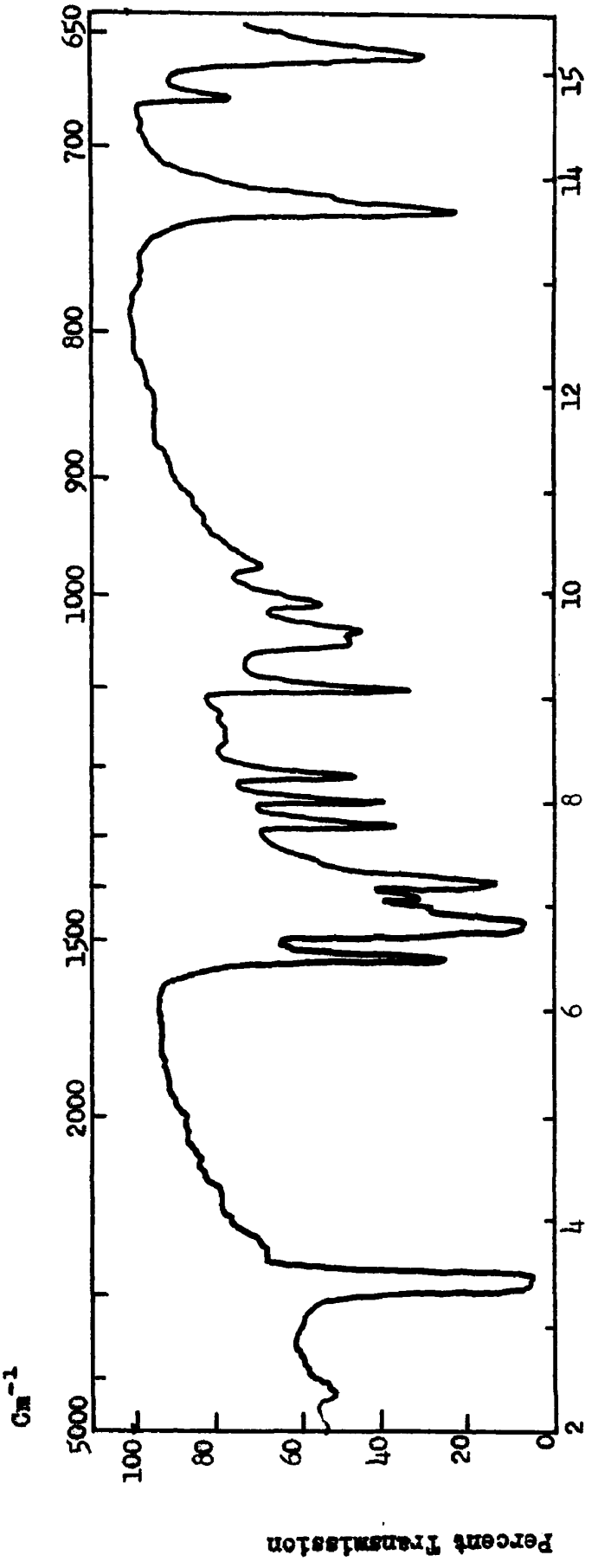


Figure 55. Infrared Absorption Spectrum of 1,5-Dimethyltetrazole (Oil mull).

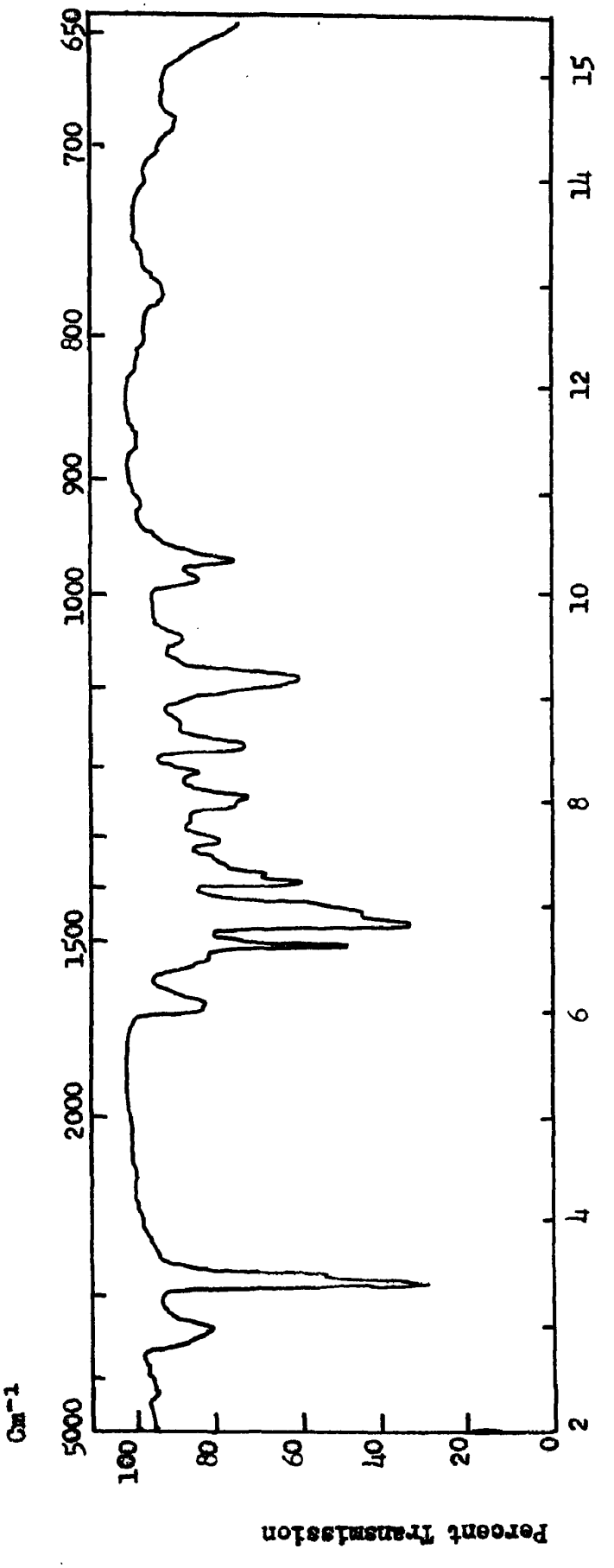


Figure 56. Infrared Absorption Spectrum of 1-Ethyl-5-Isobutyltetrazole (Pure Liquid).

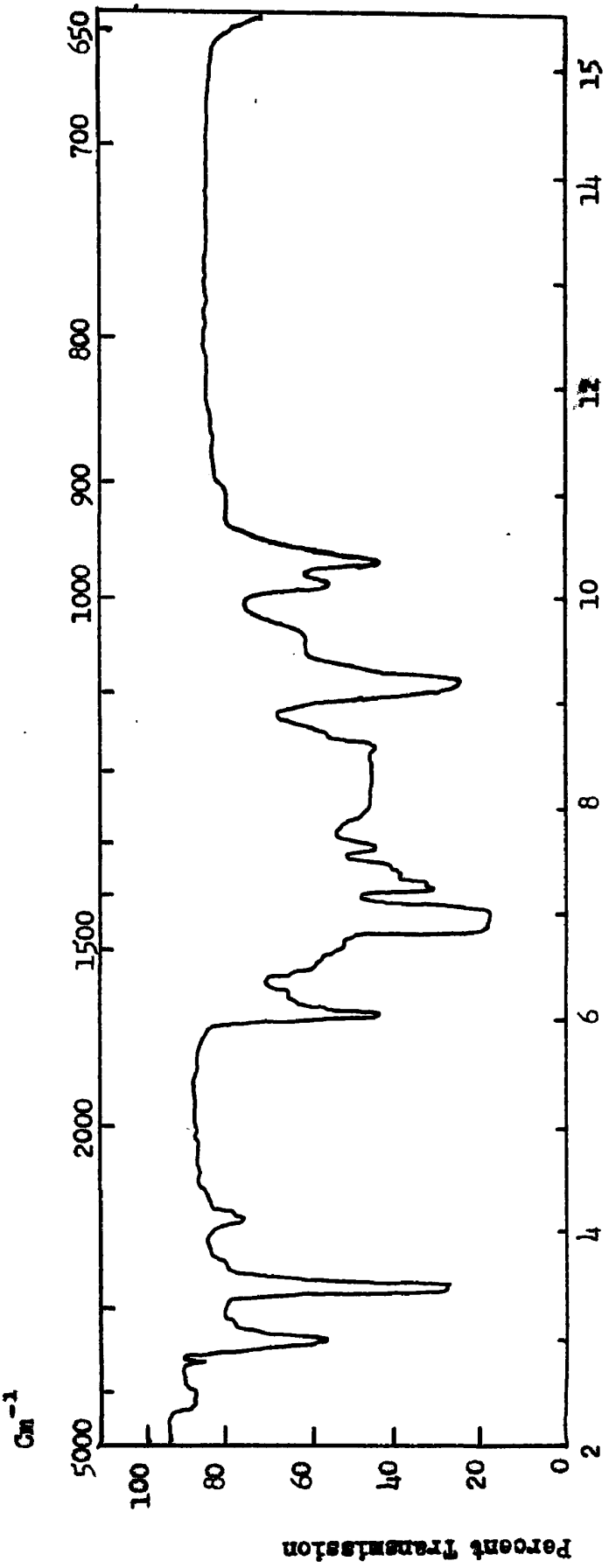


Figure 57. Infrared Absorption Spectrum of 1-Ethyl-5-Isobutyltetrazole ($CHCl_3$).

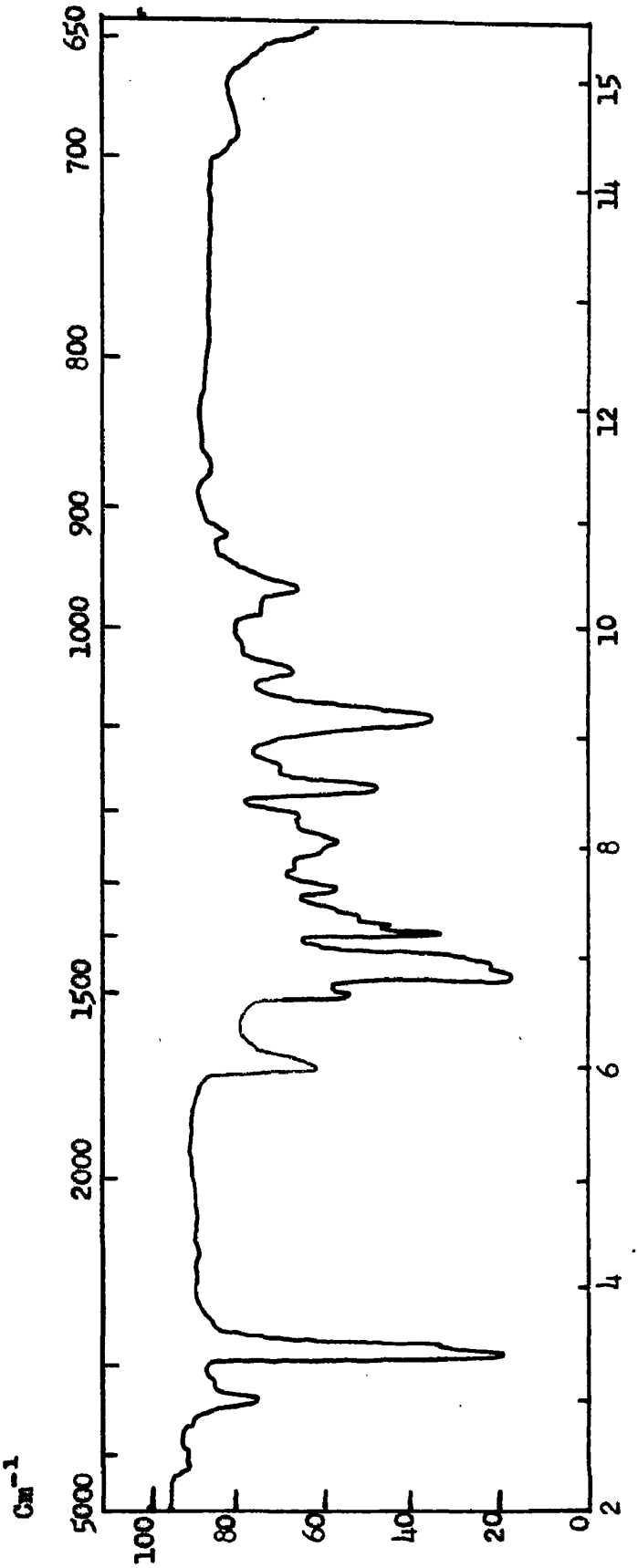


Figure 58. Infrared Absorption Spectrum of 1-Ethyl-5-Isobutyltetrazole (CCl_4).

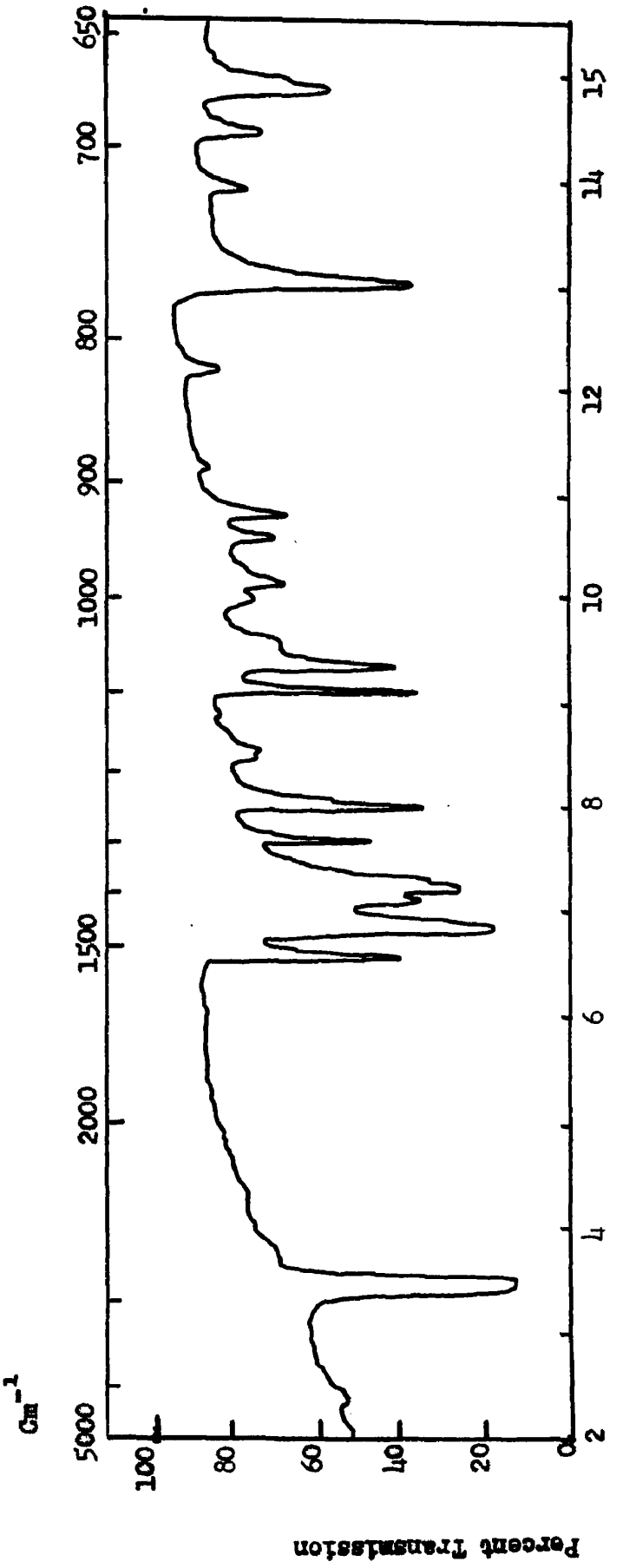


Figure 59. Infrared Absorption Spectrum of 1-Isobuyl-5-Methyltetrazole (Oil mull).

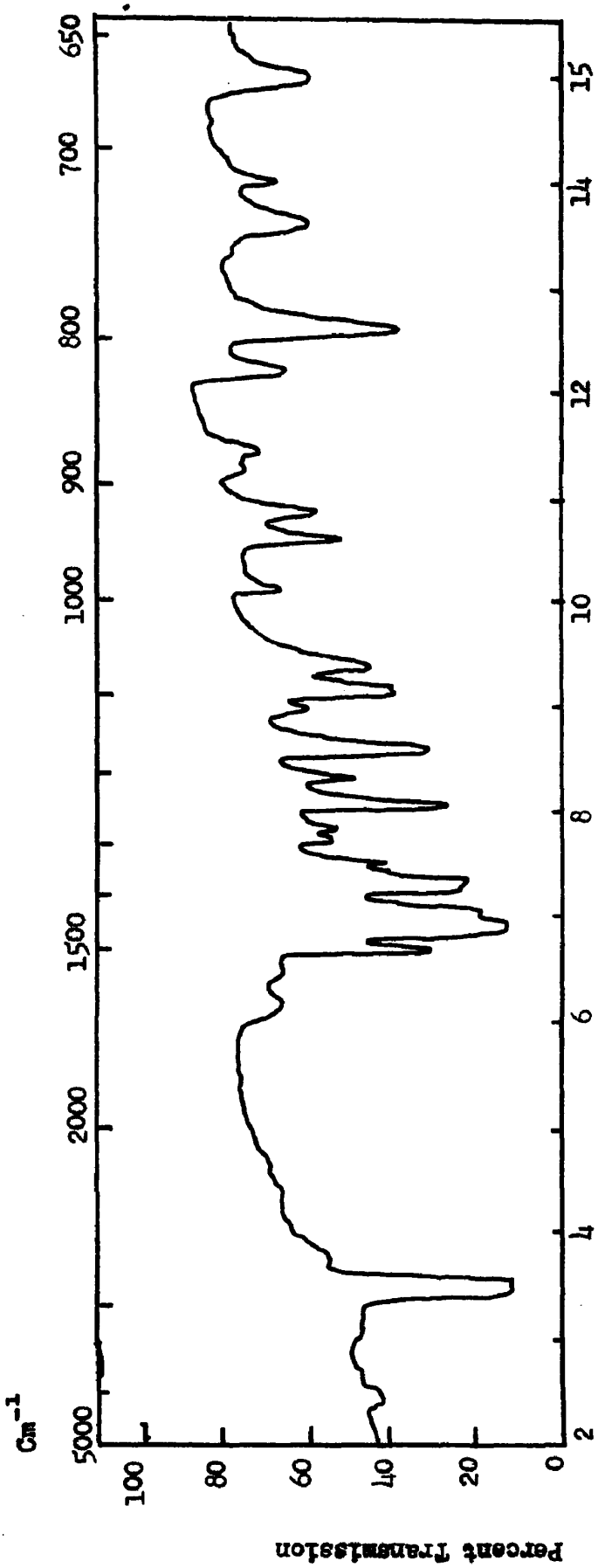


Figure 60. Infrared Absorption Spectrum of 1,5-Di-isobutyltetrasole (Oil mull).

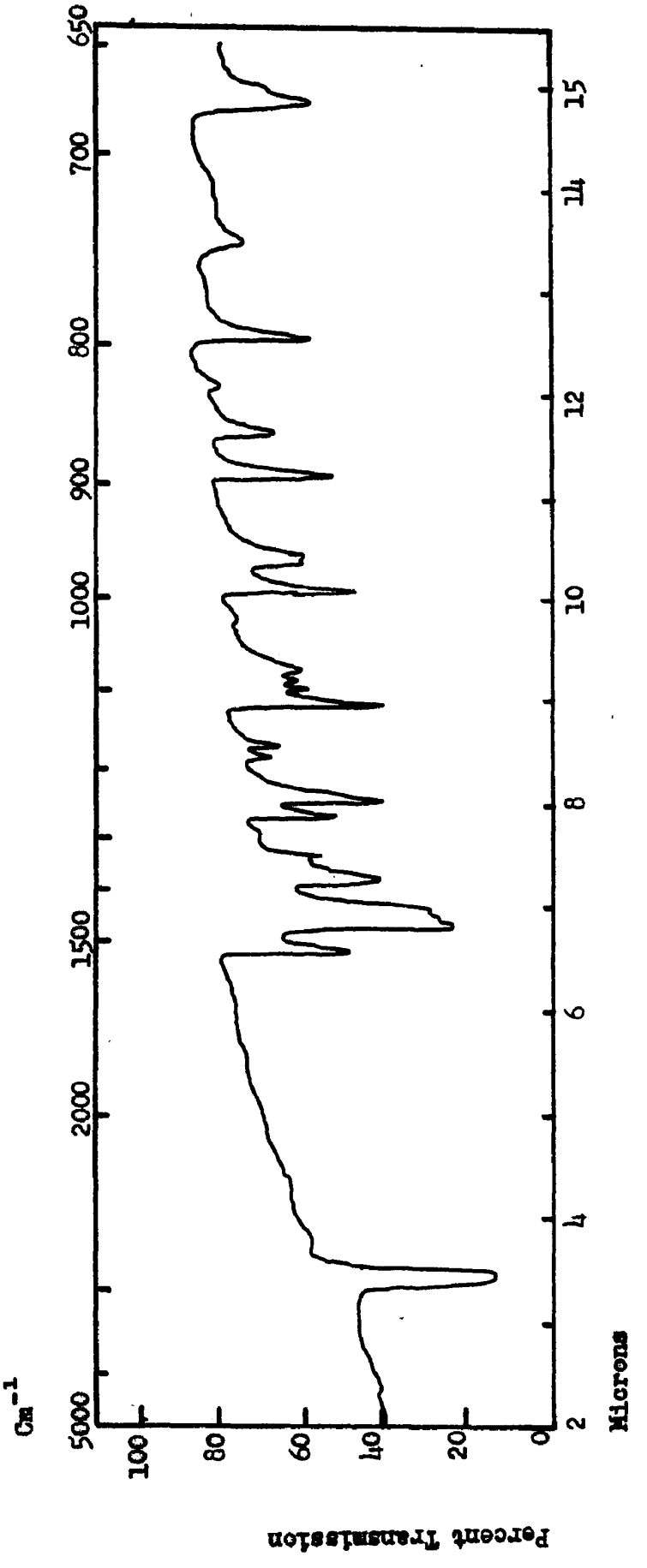


Figure 61. Infrared Absorption Spectrum of 1,5-Pentamethylenetetrazole (Oil mull).

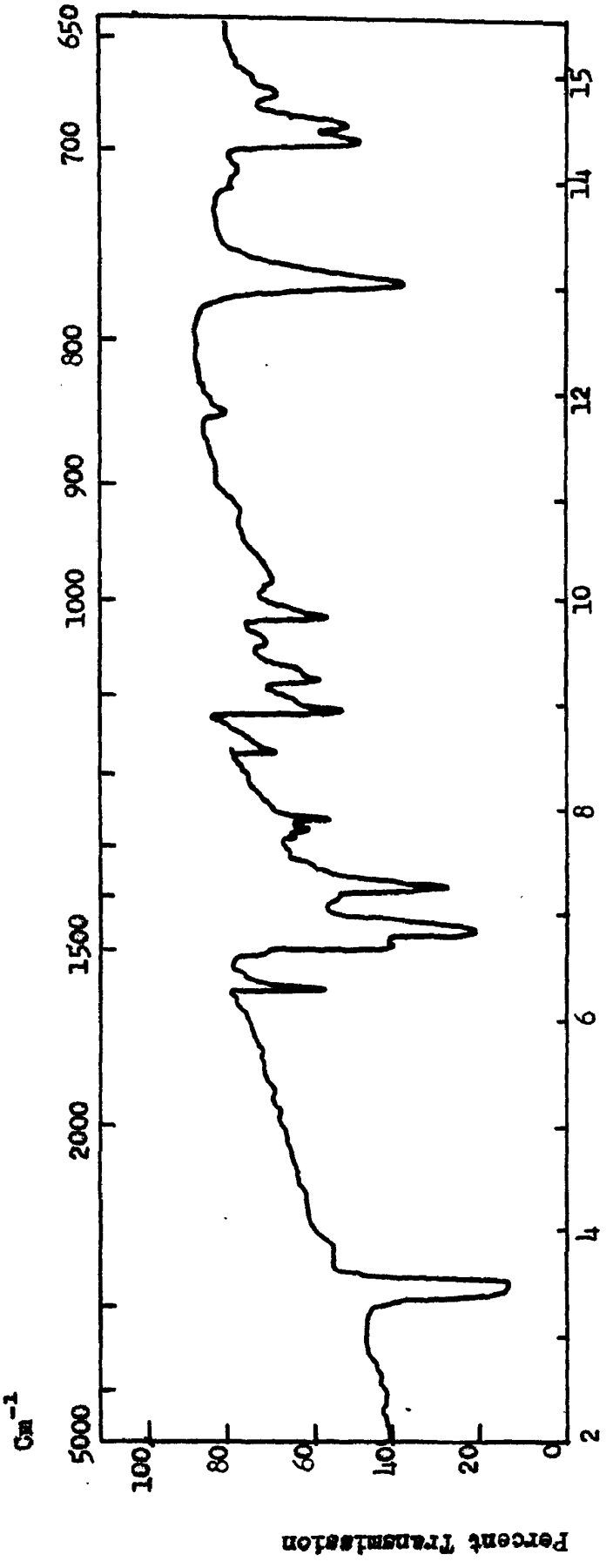


Figure 62. Infrared Absorption Spectrum of 1-Phenyl-5-Methyltetrazole (Oil mull).

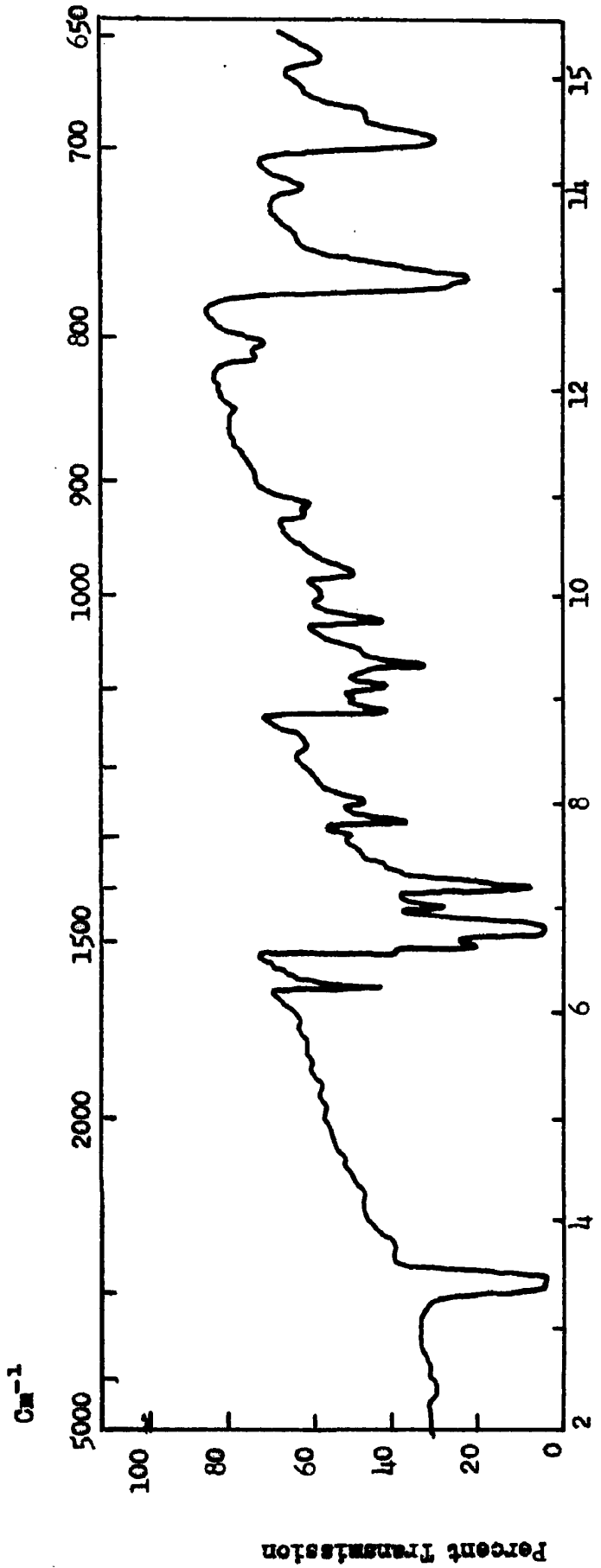


Figure 63. Infrared Absorption Spectrum of 1-Phenyl-5-Ethyltetrazole (Oil mull).

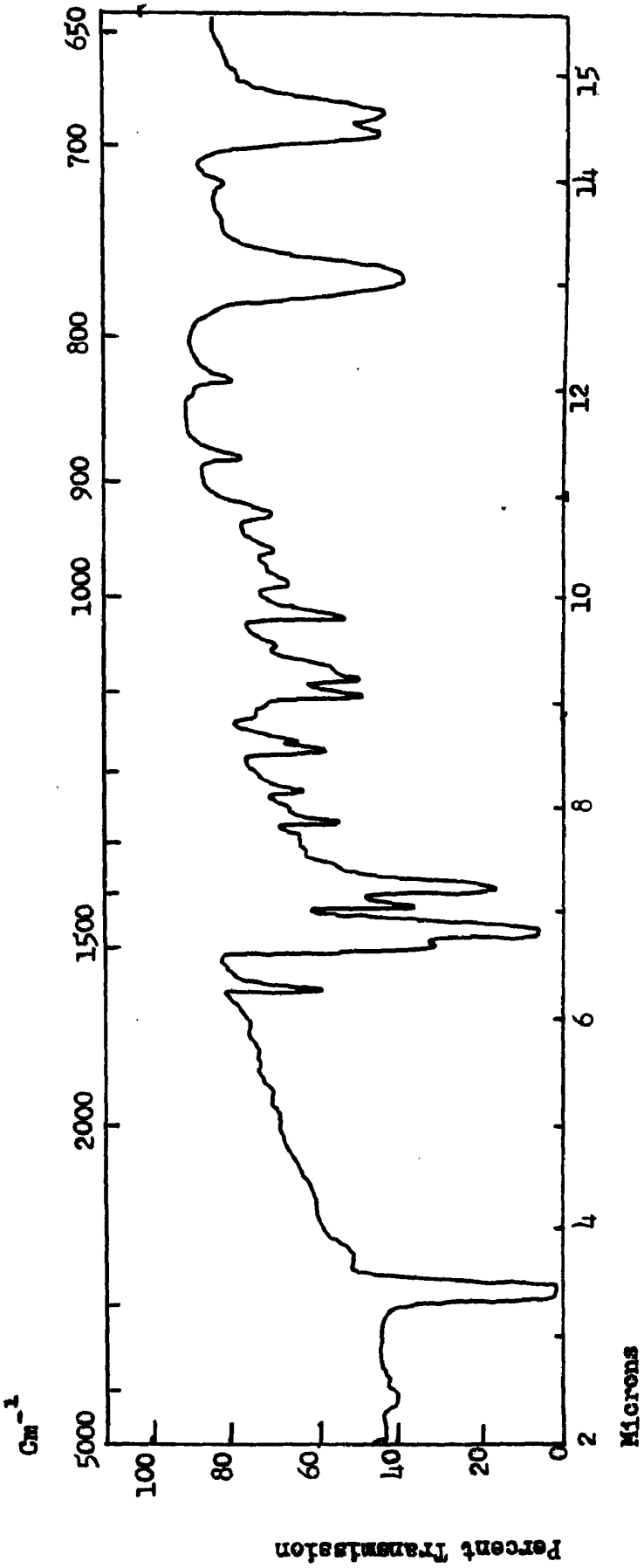


Figure 64. Infrared Absorption Spectrum of 1-Phenyl-5-Isobutyltetrazole (oil mull).

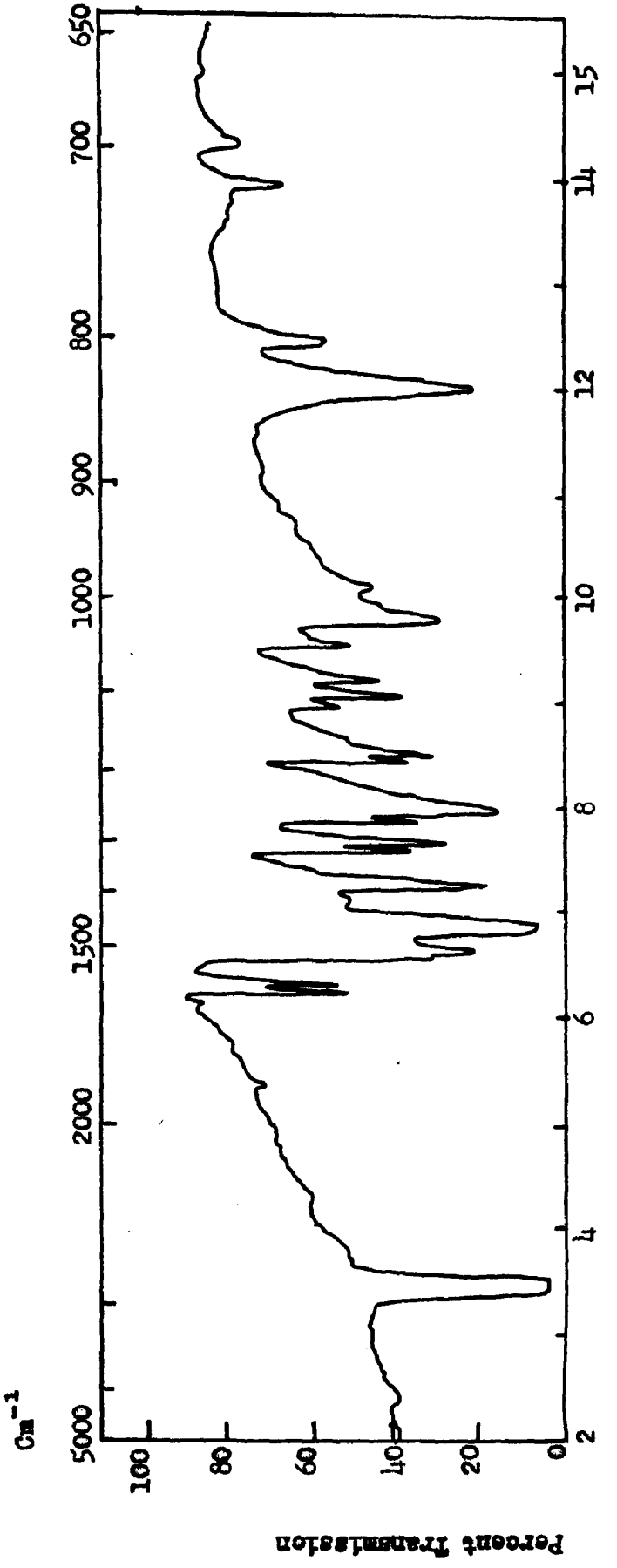


Figure 65. Infrared Absorption Spectrum of 1-(p-Methoxyphenyl)-5-Methyltetrazole (Oil mull).

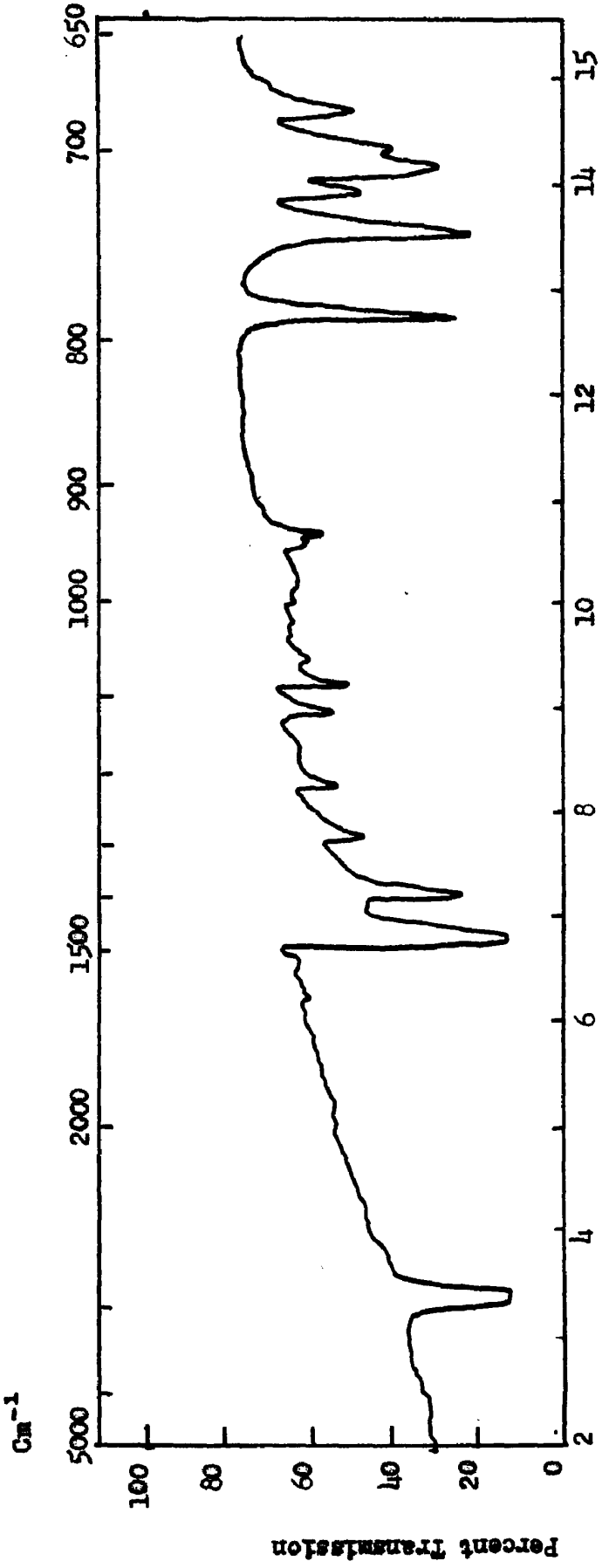


Figure 66. Infrared Absorption Spectrum of 1-Methyl-5-Phenyltetrazole (Oil mull).

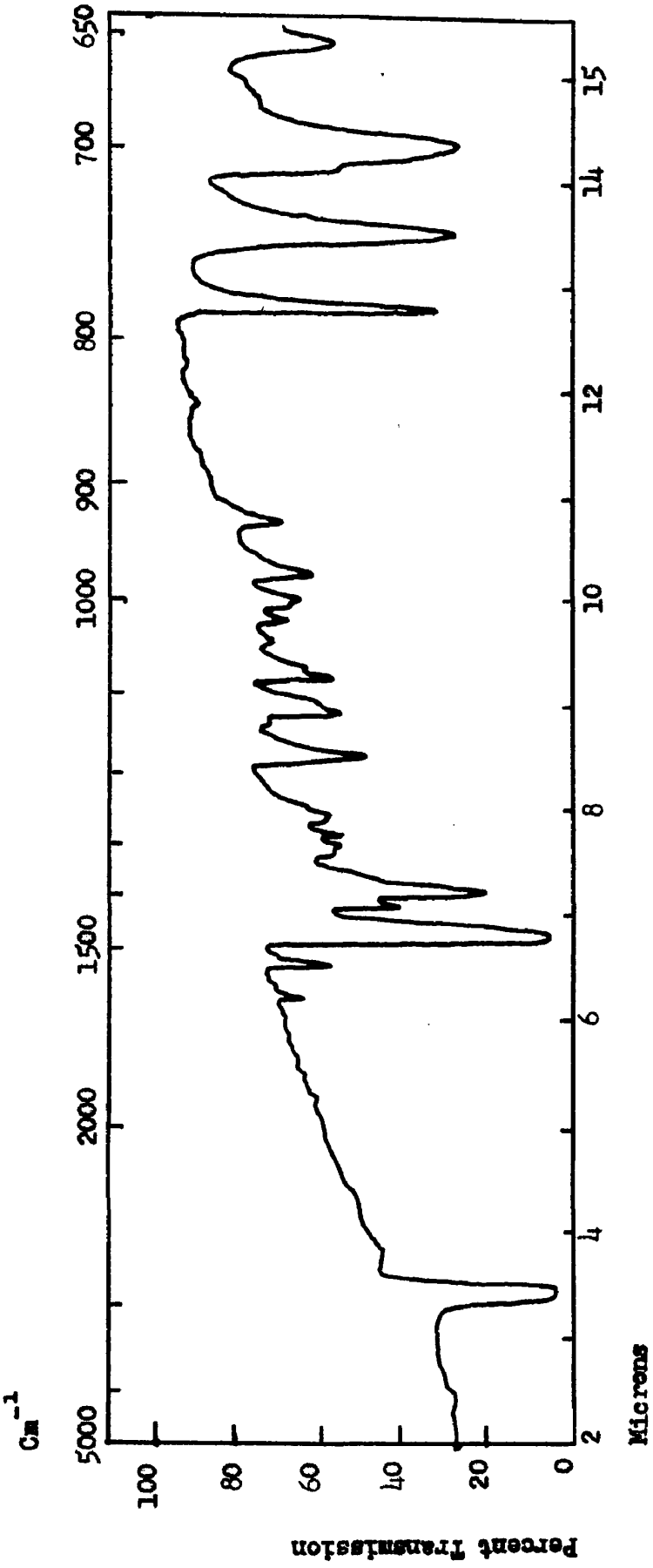


Figure 67. Infrared Absorption Spectrum of 1-Ethyl-5-Phenyltetrazole (Oil mull).

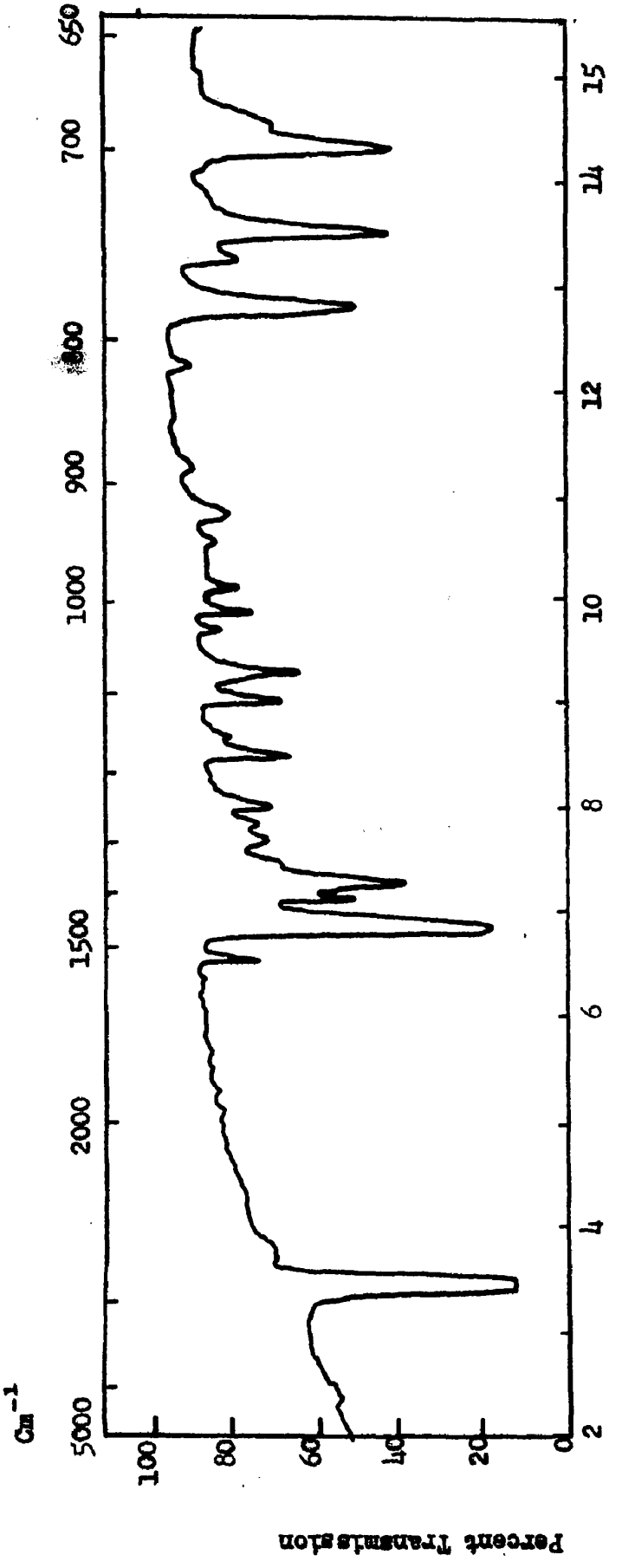


Figure 68. Infrared Absorption Spectrum of 1-Isobutyl-5-Phenyltetrazole (Oil mull).

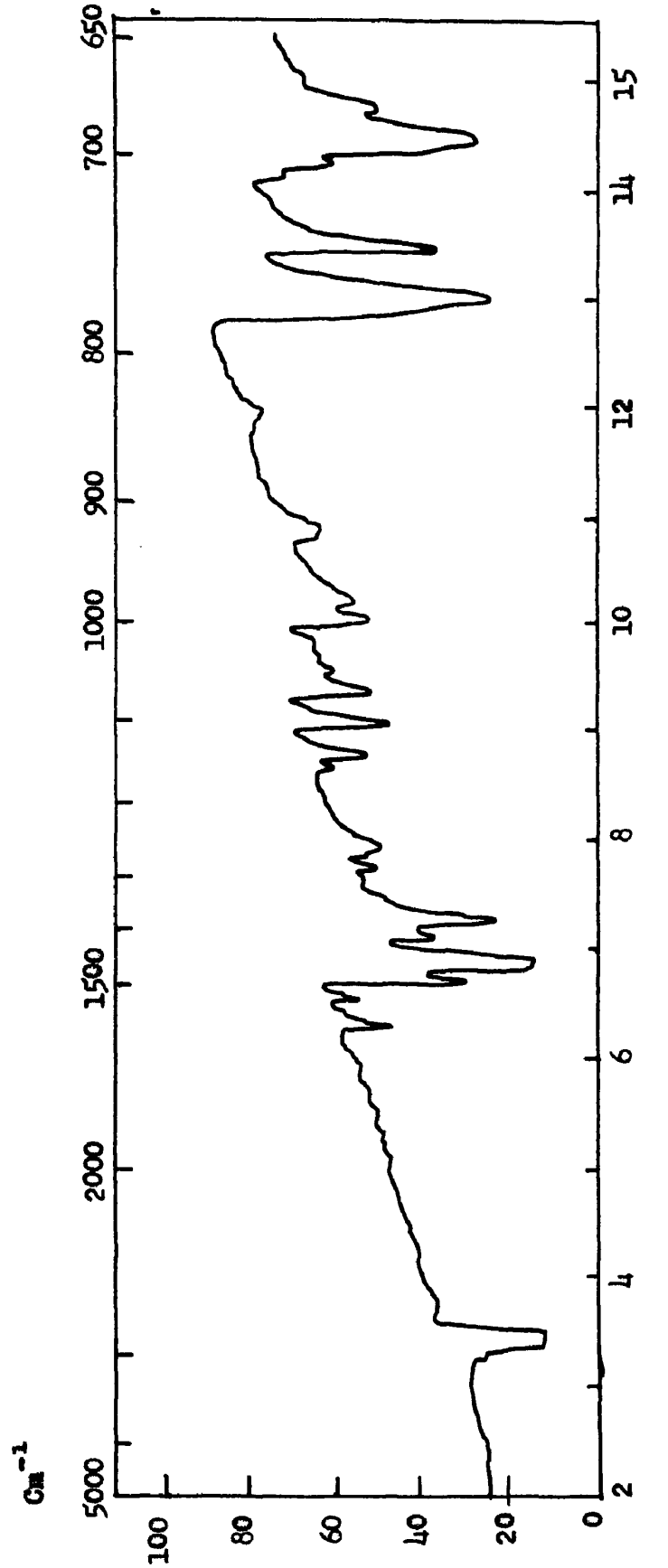


Figure 69. Infrared Absorption Spectrum of 1,5-Diphenyltetrazole (Oil mull).

EXPERIMENTAL

Preparation of Alkyl Isocyanides

All of the alkyl isocyanides were prepared by essentially the same procedure that was used by Gautier (9,10), with variations only in the time of heating. The appropriate alkyl iodide was added to solid silver cyanide in the proportions of one mole of iodide to two of cyanide. This mixture was heated under reflux on a steam bath for the desired length of time, after which water, potassium cyanide and sodium hydroxide were added to the reaction flask. The mixture was then distilled over a free flame until the distillate became clear. The aqueous solution in the distilling flask was discarded. The crude isocyanide, which formed a colorless or pale yellow-green upper layer in the distillate, was separated from the lower water layer, dried over anhydrous sodium sulfate, and used immediately to prepare the corresponding tetrazole. In a few runs, the isocyanide was taken up in benzene before drying, but this dilution appeared to slow the subsequent reaction with hydrazoic acid.

The compounds prepared by this method are listed in Table I. Since the crude products were not purified before use, only a rough estimate of the yield can be made from the weight of crude material. In a few cases, as indicated by footnotes, the weight was taken before drying over sodium sulfate. Yields calculated from bromide-bromate titrations have also been included for comparison in two cases.

Unless otherwise indicated, the weight of product is the difference between the weight of flask, sodium sulfate and product, and the weight of flask and wet sodium sulfate after decantation of the crude isocyanide. The preparation of n-butyl isocyanide is given below as an example.

n-Butyl Isocyanide

A mixture of 53.6 g. (0.4 mole) of silver cyanide and 36.8 g. (0.2 mole) of n-butyl iodide was heated under reflux on the steam bath for four hours. Water, 70 g. of potassium cyanide and 16 g. of sodium hydroxide were added, and the condenser was arranged for downward distillation. On gentle heating with a free flame, the solid mass in the distilling flask began to dissolve, and an oily layer formed above the aqueous layer. A cloudy distillate formed as the crude product steam-distilled from the reaction mixture. When the distillate became clear and the lower aqueous layer of the distillate began to increase noticeably in bulk, distillation was stopped. The distillate was transferred quickly to a small separatory funnel. After the lower aqueous layer had been drawn off and discarded, the upper layer was transferred to a tared flask, and the weight of flask and contents recorded. The weight of crude, wet n-butyl isocyanide was 16.2 g. (98%). Anhydrous sodium sulfate was added to the flask, which was stoppered, swirled, and allowed to stand a few minutes until the liquid appeared clear. During this time, the flask and contents were weighed. The dried product was decanted into a round-bottom flask and used

immediately for preparation of the tetrazole. The weight of the drying flask and wet sodium sulfate was recorded. By difference, the weight of crude n-butyl isocyanide was 14.0 g. (84%). The loss in weight during drying is not entirely due to removal of water, since some product is trapped in the moist sodium sulfate mass.

Estimation of Isocyanides by Titration

An attempt was made to estimate concentration of isocyanides in benzene solution by treatment with excess standard bromide-bromate solution, addition of potassium iodide, and back-titration with standard thiosulfate, a method which has been used successfully for determination of phenols (19). The procedure followed is essentially that used by Spliethoff (20) for the titration of phenols.

Reagents:

Approximately 0.1 N Sodium Thiosulfate

A solution of 25 g. of sodium thiosulfate in 975 ml. of water was standardized against potassium iodate. Each sample of potassium iodate was weighed into an iodine flask and treated with 30 ml. of water and 30 ml. of 10% potassium iodide. Beyond this point, the determination was completed was each sample before proceeding with the next one. Three milliliters of 6 N hydrochloric acid was added through the stopper; the solution was mixed by swirling, and immediately titrated with the sodium thiosulfate solution to a starch endpoint.

Approximately 0.1 N Bromate-Bromide Solution

A mixture of 2.8 g. of potassium bromate and 15 g. of potassium bromide was dissolved in 980 ml. of water.

10% Potassium Iodide

One hundred grams of potassium iodide was dissolved in 900 ml. of water.

Starch Solution

One gram of soluble starch was added to 100 ml. of boiling water and stirred until a clear solution was obtained.

Procedure:

The samples of isocyanide in benzene solution were transferred by pipette to 250 ml. iodine flasks; a flask containing an equal volume of benzene was used as the blank. Ten milliliters of bromate-bromide solution was added to each flask, using a volumetric pipette. Beyond this point, the determination was completed with each sample before proceeding with the next one. Five milliliters of concentrated hydrochloric acid was added through the stopper, washed down with distilled water, swirled and titrated immediately with standard sodium thiosulfate solution. From the difference between blank and sample, the isocyanide content was calculated.

Preparation of sample:

A weighed sample of n-butyl isocyanide was placed in a volumetric flask and diluted to the mark with benzene. Aliquots were

analyzed by the above procedure and the isocyanide content of the total sample was calculated. The results are summarized in Table II. The right hand column gives the time interval between purification of the sample and completion of titrations. Sample A was purified by steam distillation alone. Samples B and C were purified by steam distillation, followed by two distillations at atmospheric pressure. Sample B was dark after steam distillation, while sample C was colorless at this point. In determinations on sample C, one minute bromination time was allowed between addition of acid and addition of potassium iodide.

Preparation of 1-Alkyltetrazoles from Isocyanides

The crude isocyanide was placed in a round-bottom flask, treated with 100 ml. of approximately 16% hydrazoic acid in benzene and heated under reflux on the steam bath for one to five hours. Where the shorter heating times were used, the mixture was allowed to stand overnight at room temperature before removal of the solvent. The solvent was removed at reduced pressure and the residue was heated over a free flame for one hour with 8 ml. of water and 10 ml. of concentrated hydrochloric acid. The cooled acid solution was made alkaline with sodium hydroxide. The mixture, which now consisted of two layers, was transferred to a separatory funnel. The lower layer was drawn off, washed with ether, and discarded. The ether extract and upper layer were combined and dried over sodium sulfate. The ether was stripped off at reduced pressure, and the product was fractionally distilled

through a small Vigreux column at a pressure of 1-2 millimeters of mercury. Since the boiling points of these compounds are quite high, even at this pressure, heating was done with a free flame. Refractive indices and infrared spectra were used as criteria in selecting fractions for analysis. The 1-alkyltetrazoles obtained by this method are listed in Table III, together with their boiling points, refractive indices, and analyses. Due to the difficulties of purifying such small samples, no adequate picture of the yields could be obtained. In several cases, analysis showed the compound to be impure. However, the refractive index and infrared spectrum in each case resembled so closely those obtained on compounds which gave satisfactory analyses, that these impure products are also included in Table III.

The details of preparation of 1-n-amyltetrazole and 1-n-hexyltetrazole are given as examples. The latter is the only case in which a single distillation proved sufficient.

1-n-Amyltetrazole

A mixture of 8.6 g. of crude n-amyl isocyanide and 100 ml. of a 16% solution of hydrazoic acid in benzene was heated under reflux on the steam bath for four hours. The crude product was isolated as described above and fractionally distilled.

Fraction	Temperature (°C.)	Pressure (mm.)	Refractive Index/20°C.	Weight (g.)
1	123-128	1	1.4592	0.07
2	128-131	1	1.4603	0.58
3	128-132	1	1.4604	0.48
4	131-135	1	1.4610	3.93
5	132-135	1	1.4610	3.21
residue	--	--	--	0.51

Fractions 4 and 5 were combined and redistilled.

Fraction	Temperature (°C.)	Pressure (mm.)	Refractive Index/20°C.
6	up to 133	1-8	1.4589
7	134-136	1	1.4592
8	136-137	1	1.4600
9	138-139	1	1.4608
10	138-139	1	1.4603

Fraction 9 was shown by elemental analysis to be pure product. On the basis of refractive index, fractions 4 and 5 from the first distillation would appear to be mostly 1-n-amyltetrazole. From this data, the yield may be considered approximately 7.1 g. (37% of the theoretical yield, based on the weight of isocyanide used.)

1-n-Hexyltetrazole

A mixture of 8.0 g. of crude n-hexyl isocyanide and 100 ml. of a 16% solution of hydrazoic acid in benzene was heated under reflux

for three hours on the steam bath. The crude product was isolated as described above and fractionally distilled.

Fraction	Temperature (°C.)	Pressure (mm.)	Refractive Index/20°C.	Weight (g.)
1	126-138	1	1.4631	0.20
2	133-142	1	1.4632	0.04
3	142-145	1	1.4627	0.33
4	144-146	1	1.4610	6.31
5	148	1	1.4606	0.34

Fraction 4 was shown by elemental analysis to be pure 1-n-hexyl-tetrazole. This represents 57% of the theoretical yield, based on the weight of isocyanide used.

Preparation of Phenyl Isocyanide

Phenyl isocyanide was prepared by the method of Malatesta (16). A solution of 30 g. (0.32 mole) of aniline in 75 g. (0.64 mole) of chloroform was added very slowly to a suspension of 80 g. (1.43 moles) of powdered potassium hydroxide in 200 ml. of benzene in a three-necked flask equipped with reflux condenser, stirrer and addition funnel. The mixture was heated for 15 minutes on the steam bath, cooled, and decanted. The solid residue was washed with benzene and the washings added to the main liquid. The benzene solution was extracted with 0.12 M hydrochloric acid, then washed once with a 0.2 M solution of sodium hydroxide and repeatedly with water until the final washing was neutral to litmus. The benzene was distilled at

atmospheric pressure until the temperature rose to about 100° C. The residue was distilled at reduced pressure. The product, which boiled at 67-69° C. at 10 mm., weighed 9.9 g. (30%).

In another run, following the same procedure except that 57 g. (1.43 moles) of powdered sodium hydroxide was used in place of the potassium hydroxide, the yield was 14.2 g. (42%) of product, boiling at 62-68° C. at 12 mm.

Preparation of 1-Phenyltetrazole from Phenyl Isocyanide

A mixture of 14.2 g. of crude phenyl isocyanide (b.p. 62-68° C. at 12 mm.) and 100 ml. of an approximately 16% solution of hydrazoic acid in benzene was heated under reflux for one hour on the steam bath, then allowed to stand at room temperature for 24 hours. The solvent was removed at reduced pressure, and a few drops of phenyl isocyanide distilled at 60-68° C. at 14 mm. The residue was cooled and treated with water. Although some crystals formed, the resulting oil did not solidify completely. The water layer was decanted and the residue taken up in isopropyl alcohol. The crystals which formed were filtered and washed with water. The mother liquor was treated with water to force more of the product out of solution. This second crop was taken up in a small amount of isopropyl alcohol, filtered, and the crystals added to the first crop. The total product was washed sparingly with isopropyl alcohol and pressed out on filter paper to dry. The crude yield was 2.5 g., m.p. 56-62° C. (12.4% of the theoretical yield, based on the weight of phenyl isocyanide). One recrystallization from isopropyl alcohol gave 1.6 g., m.p. 63-64° C.

Preparation of Diformylhydrazine

A mixture of 5.2 g. (0.076 mole) of sodium formate and 4.9 g. (0.038 mole) of hydrazine sulfate was ground in a mortar, transferred to a crystallizing dish, and heated one hour on the steam bath with occasional stirring. The mass softened to a paste, then hardened again. The solid mass was extracted three times with 20 ml. portions of hot 95% ethanol. The remaining solid was discarded. On cooling, the extract deposited diformylhydrazine as white needles. The product weighed one gram (30%) and melted 157-162° C. Pellizzari (22) reports a 77% yield, m.p. 161° C. by this method.

Preparation of 1-Phenyltetrazole by the Dimroth Method

Fourteen milliliters of 7 N hydrochloric acid was added to 1.9 g. of aniline and the resulting suspension cooled to 0° C. and mechanically stirred. A solution of 1.44 g. of sodium nitrite in 5 ml. of water was added dropwise, so that the temperature remained below 5° C. This diazotized aniline solution was carefully neutralized to litmus with solid sodium carbonate and added dropwise to a well-stirred solution of 1.8 g. of diformylhydrazine in 20 ml. of 5 N sodium hydroxide and 20 ml. of water. The temperature was kept below 5° C. After standing overnight, the reaction mixture was extracted with ether. After evaporation of the ether on the steam bath, the residue was warmed with 7 N hydrochloric acid, and neutralized with sodium hydroxide. Chilling and scratching of the walls caused separation of a brown solid weighing about 90 mg. Recrystallization from aqueous

isopropyl alcohol gave a few milligrams of pale tan needles, m.p. 60-61° C.

Preparation of Formamides

The appropriate amine was mixed cautiously with an excess of 88% formic acid, and distilled until the temperature of the vapor reached 105° C. The residue then consisted of the desired product, colored impurities, and some excess formic acid. Several methods of purification were used. Liquids were distilled at reduced pressure. Solids were taken up in ethanol and poured over ice, with stirring and scratching to induce crystallization. Although crude yields were excellent, difficulty in removing the colored impurities and the tendency of these compounds to separate as oils made complete purification difficult. In many cases, the once recrystallized product still retained a faint color, but was nevertheless considered pure enough for use in the preparation of the corresponding tetrazole.

Details of preparation are given below for several compounds to illustrate the preparation of formanilides and of N-alkylformamides. All of the formamides prepared are known.

o-Formotoluidide

A mixture of 107 g. (one mole) of o-toluidine and 66 ml. of 88% formic acid was distilled until the temperature of the vapor reached 105° C. The red residue was poured into an Erlenmeyer flask and chilled. Scratching of the walls of the flask with a glass rod induced solidification. The crude product was stirred with 100 ml. of cold

ethanol, filtered and washed with a small amount of ethanol. The filtrate was treated with ice and solid sodium carbonate to give a second crop. The combined crude product weighed 117.2 g. One recrystallization from aqueous ethanol and one from carbon tetrachloride gave 47.5 g. (35%) of almost colorless material, m.p. 57-60° C. Several values for the melting point of this compound have been recorded: 62, 57-59, 56.5-57.5° C. (40,42,12).

p-Formanisidide

A mixture of 123 g. (one mole) of p-anisidine and 66 ml. of 88% formic acid was distilled until the vapor temperature reached 105° C. The residue was poured into an Erlenmeyer and chilled to induce solidification. The crude product was filtered by suction and dried. The crude product weighed 76 g., m.p. 74-80° C. The material was dissolved in warm ethanol, treated with decolorizing charcoal, filtered, and poured over ice. This once-recrystallized product weighed 67.4 g. (45%) and melted 79.5-81.5° C. The melting point given in Beilstein for p-formanisidide is 80-81° C. (41). The method described above was also used to obtain p-formotoluidide (42), o-formanisidide (43), o-chloroformanilide (44), m-chloroformanilide (45), and p-chloroformanilide (46).

N-Isobutylformamide

A mixture of 36.5 (0.5 mole) of isobutylamine and 52 g. of 88% formic acid was distilled at atmospheric pressure until the vapor temperature rose above 105° C. The residue was allowed to cool

somewhat, and then was distilled at reduced pressure. After a fore-run had been discarded, the material boiling 104-113° C. at 13 mm. was collected. The literature value for the boiling point of the product is 111° C. at 12 mm. (47). The product thus collected was a colorless liquid weighing 47.2 g. (93%). It was used without further purification for the preparation of the tetrazole. This method was also used to obtain formanilide (42), m-formotoluidide (48), N-methylformamide (10), and N-ethylformamide (49).

Preparation of 1-Aryltetrazoles from Formanilides

A solution of slurry of 0.25 mole of the formanilide in 100 ml. of toluene was placed in a three-necked flask equipped with condenser, mechanical stirrer and rubber tube connected to a flask containing powdered phosphorus pentachloride. The mixture was cooled by means of an ice bath and stirred rapidly during the gradual addition of 52.1 g. (0.25 mole) of phosphorus pentachloride. A pasty solid or a heavy oil usually appeared at this time, but there was no evidence of hydrogen chloride evolution through the condenser in most cases. After five to ten minutes further stirring, 100 ml. of an approximately 16% solution of hydrazoic acid in benzene was added slowly from an addition funnel. Vigorous evolution of hydrogen chloride was noted during this step. A clear solution formed as the hydrazoic acid was added. The ice bath was removed towards the end of this step, and the solution was stirred at room temperature for 24 hours, during which time fine white needles were deposited in quantities varying with the compound being prepared. At the end of 24 hours, the reaction

mixture was poured over ice, made alkaline with sodium hydroxide, and filtered. The filter cake was washed with water, whereupon most of it redissolved. Any solid remaining was crude product. The toluene layer was separated from the filtrate. The aqueous layer was combined with the aqueous washings and extracted with toluene. The toluene solutions were combined and evaporated to a small volume. The crude product which separated was filtered and recrystallized. High-melting members of the series were recrystallized from isopropyl alcohol, with the use of decolorizing charcoal. Cyclohexane was found to be a more suitable solvent for recrystallization of the low-melting compounds.

The 1-aryltetrazoles obtained by this method are listed in Table IV. Details of preparation are given below for 1-m-tolyltetrazole and 1-p-chlorophenyltetrazole, to illustrate successful preparations of a low-melting and a high-melting compound, respectively. Unsuccessful attempts to obtain 1-o-tolyltetrazole are also described.

1-m-Tolyltetrazole

A solution of 33.8 g. (0.25 mole) of m-formotoluidide in 100 ml. of toluene was stirred and cooled during the addition of 52.1 g. (0.25 mole) of phosphorus pentachloride. To the resulting bright yellow solution was added 100 ml. of a 16% solution of hydrazoic acid in toluene. The mixture was stirred at room temperature for 24 hours, poured over ice, made alkaline with sodium hydroxide, and filtered. The filter-cake was stirred with a solution of 4 g. of sodium hydroxide in 100 ml. of water, and filtered. The solid so obtained was stirred with 100 ml. of distilled water, filtered, and washed with water.

The aqueous washes and the water layer from the first filtrate were discarded. The toluene layer from the first filtrate was evaporated to dryness to give a second crop of crude product. The total crude product weighed 36.5 g. (91%). The two crops were combined and recrystallized from aqueous isopropyl alcohol, including treatment with decolorizing charcoal. The once recrystallized material weighed 20.1 g. and still contained colored impurities. The product was recrystallized from cyclohexane by repeated extractions with small amounts of the hot solvent. The cyclohexane layer was decanted and chilled to cause separation of colorless crystals. Only small amounts of product dissolved in each extraction, but repetition of this procedure finally left only a small amount of highly colored waxy residue. The total yield of pure 1-m-tolyltetrazole obtained in this way was 13.6 g. (34%), m.p. 53-54° C.

1-p-Chlorophenyltetrazole

A mixture of 38.9 g. (0.25 mole) of p-chloroformanilide and 100 ml. of toluene was stirred and cooled during the addition of 52.1 g. of phosphorus pentachloride, followed by the addition of 100 ml. of a 16% solution of hydrazoic acid in toluene. The reaction mixture was stirred at room temperature for 24 hours, poured over ice, made alkaline with sodium hydroxide, and filtered. The filter cake was washed by stirring with dilute sodium hydroxide, filtered and dried. The crude yield was 44.4 g. (98%) of slightly colored product, m.p. 143-150° C. The crude product was recrystallized three times from isopropyl alcohol, with the use of decolorizing charcoal in the first

two. After drying in the oven at 110° C., the pure material weighed 9.0 g. and melted 155.5-156° C. Material recovered from the recrystallization mother liquors and from evaporation of the toluene layer of the reaction mixture was recrystallized twice from isopropyl alcohol to furnish an additional 5.5 g. of pure product, m.p. 155-156° C. The total yield of pure 1-p-chlorophenyltetrazole was 14.5 g. (32%).

1-o-Tolyltetrazole

A mixture of 20.25 g. (0.15 mole) of o-formotoluidide and 60 ml. of toluene was stirred and cooled during the addition of 31.3 g. (0.15 mole) of phosphorus pentachloride, followed by the addition of 60 ml. of a 16% solution of hydrazoic acid in toluene. The reaction mixture was stirred at room temperature for 38 hours. The mixture was poured over ice, neutralized, and chilled. The water layer was separated and discarded. Removal of the toluene at reduced pressure left 23.3 g. of a dark-red oil from which no solid could be isolated. Since a survey of melting points of the other 1-aryltetrazoles on hand suggested that 1-o-tolyltetrazole might melt very close to room temperature, the preparation was repeated.

On the addition of phosphorus pentachloride in the second run, the formation of an orange lower layer was noted. After addition of the hydrazoic acid, a clear solution was obtained. The mixture was stirred for 24 hours, during which time a white precipitate appeared. The reaction mixture was worked up in the same manner as the first run. After removal of the toluene, an attempt was made to distill the residue at reduced pressure. When no distillate was obtained

even on heating to 200° C. at 1 mm., the heating was discontinued and the apparatus partially disassembled. At this point, the residue began to decompose with vigorous evolution of gas. Although no explosion occurred, it was felt that further attempts to distill this material were inadvisable.

Preparation of 1-Isobutyltetrazole by the Formamide Method

Attempts to prepare 1-isobutyltetrazole according to the procedure described above for the preparation of the 1-aryltetrazoles failed to yield the desired product. The following modification led to the formation of the expected compound in low yield.

A mixture of 17.9 g. (0.18 mole) of isobutyl formamide and 100 ml. of toluene was stirred and cooled during the addition of 37.1 g. (0.18 mole) of phosphorus pentachloride, followed by the addition of 100 ml. of a 16% solution of hydrazoic acid in toluene. The reaction mixture was stirred at room temperature for one hour, and then on the steam bath for three hours. The mixture was poured over ice, and made alkaline with sodium hydroxide. The water layer was separated, washed with toluene and discarded. After removal of solvent at reduced pressure from the combined toluene solutions, the residue was fractionated at reduced pressure. The fraction boiling at 121-123° C. at 1 mm. gave the correct elemental analysis for 1-isobutyltetrazole, and exhibited an infrared spectrum similar to that of the other 1-alkyltetrazoles. This fraction weighed 2.88 g. and had a refractive index of 1.4590 at 20° C. Further attempts to distill the residue were accompanied by evidence of decomposition and resultant variation in

the pressure. A fraction boiling at 127-130° C. at 2-3 mm. had a refractive index of 1.4587 at 20° C., and may represent a further amount of impure product. This liquid had a faint yellow tinge, in contrast to the pure product which was colorless. The impure material weighed 1.1 g. The yield might therefore be estimated as 4.0 g., or 18% crude, and as 2.9 g., or 13%, of pure material.

Ultraviolet Absorption Spectra

The ultraviolet spectra were obtained on 1 x 10^{-4} M solutions in 95% ethanol. In a few cases, spectra were also obtained for 1 x 10^{-3} M and 1 x 10^{-2} M solutions in the same solvent. Readings were made on a Beckmann Model DU Spectrophotometer using one centimeter cells, with 95% ethanol as the blank. The region from 210 to 300 mμ was scanned at five mμ intervals. Near a maximum, readings were made at intervals of one mμ.

Infrared Absorption Spectra

The infrared spectra were obtained on a Perkin-Elmer Doublebeam Recording Spectrophotometer, Model 21. The region from 2 to 15 μ was examined, using a rock salt prism. Spectra were obtained on oil mulls, solutions in chloroform or carbon tetrachloride, or pure liquid samples. Only the 1-substituted tetrazoles were prepared during the present investigation. The 5-alkyltetrazoles were prepared by Mihina (33b). The 5-aryltetrazoles were prepared by Wilson (37) and by Mihina (33b). The 1,5-disubstituted compounds were reference samples from the work of Harvill, et al. (27) except for 1,5-pentamethylene-tetrazole, which was a commercial sample of Metrazole, obtained from E. Bilhuber, Inc. and used without further purification.

SUMMARY AND CONCLUSIONS

Seven 1-alkyltetrazoles have been prepared from the corresponding isocyanides by a known method. Eight 1-aryltetrazoles have been prepared from substituted formanilides by a new method which consists in treating a toluene solution or suspension of the formanilide first with phosphorus pentachloride, and then with a solution of hydrazoic acid in toluene. One 1-alkyltetrazole has also been obtained by this new method. Of the compounds prepared, six of the 1-alkyltetrazoles and six of the 1-aryltetrazoles are new compounds.

Ultraviolet and infrared absorption spectra of the new compounds have been studied. Tetrazole and its alkyl derivatives show little absorption in the ultraviolet region examined. The aryl tetrazoles show considerable absorption, with maxima shifted to shorter wavelengths when steric factors interfere with the coplanarity of the phenyl and tetrazole rings. Infrared absorption spectra were also obtained for seventeen 5-substituted tetrazoles and for thirteen 1,5-disubstituted tetrazoles. A total of 46 tetrazoles were examined in the infrared region, and an attempt has been made to identify bands characteristic of the tetrazole ring.

REFERENCES

1. Benson, F. R., Chem. Rev. 41, 1-61 (1947).
2. Oliveri-Mandalà, E., and Alagna, B., Gazz. chim. ital. 40, II, 441-444 (1910).
3. Dimroth, O., and DeMontmollin, G., Ber. 43, 2904-2915 (1910).
4. Stollé, R., and Henke-Stark, F., J. prakt. Chem. 124, 261-300 (1930).
5. Freund, M., and Paradies, T., Ber. 34, 3110-3122 (1901).
6. Oliveri-Mandalà, E., and Passalacqua, T., Gazz. chim. ital. 43, II, 465-475 (1913).
7. Oliveri-Mandalà, E., Gazz. chim. ital. 52, II, 139-144 (1922).
8. Von Braun, J., and Rudolph, W., Ber. 74, 264-272 (1941).
9. Gautier, A., Ann. 146, 119-130 (1868).
10. Gautier, A., Ann. chim. [4], 17, 103-108; 203-260 (1869).
11. Hofmann, A. W., Ann. 146, 107-119 (1868).
12. Nef, J. U., Ann. 270, 267-335 (1892).
13. Biddle, H. C., Ann. 310, 1-24 (1900).
14. Hammick, D. L., New, R. C. A., Sidgwick, N. V., and Sutton, L. E., J. Chem. Soc. 1930, 1876-1887.
15. Lindemann, J., and Wiegrebe, L., Ber. 63B, 1650-1657 (1930).
16. Malatesta, L., Gazz. chim. ital. 77, 238-240 (1947); C. A. 42, 869 (1948).
17. Baker, R. H., and Stanonis, D., J. Am. Chem. Soc. 73, 699-702 (1951).
18. Guillemard, H., Ann. chim. et phys. [8], 14, 311-432 (1908).
19. Ruderman, I. W., Anal. Chem. 18, 753 (1946).

20. Spliethoff, W. L., The Kinetics and Mechanism of the Racemization of Phenylmethylcarbinyl Chloride by Phenols, Ph. D. Thesis, Michigan State College, 1953.

21. Davis, T. L., and Yelland, W. E., J. Am. Chem. Soc. 59, 1998-1999 (1937).

22. Pellizzari, G., Gazz. chim. ital. 39, I, 520-540 (1909).

23. Forster, M. O., J. Chem. Soc. 95, 184-191 (1909).

24. Schroeter, G., Ber. 42, 2336-2349 (1909).

25. Von Braun, J., Jostes, F., and Heymons, A., Ber. 60B, 92-102 (1927).

26. Von Braun, J., and Heymons, A., Ber. 62B, 409-413 (1929).

27. Harvill, E. K., Herbst, R. M., Schreiner, E. C., and Roberts, C. W., J. Org. Chem. 15, 662-670 (1950).

28. Wallach, O., Ann. 214, 193-202 (1882).

29. Havinga, E., and Veldstra, H., Rec. trav. chim. 66, 257-272 (1947).

30. Schueler, F. W., Wang, S. C., Featherstone, R. M., and Gross, E. G., J. Pharm. Exp. Ther. 97, 266 (1949).

31. Elpern, B., and Nachod, F. C., J. Am. Chem. Soc. 72, 3379-3382 (1950).

32. Lieber, E., Levering, D. R., and Patterson, L. J., Anal. Chem. 23, 1594-1604 (1951).

33. a) Mihina, J. S., unpublished work.
b) Mihina, J. S., and Herbst, R. M., J. Org. Chem. 15, 1082 (1950).

34. Garrison, J. A., The Synthesis and Characterization of Nitraminotetrazoles, Ph. D. Thesis, Michigan State College, 1954.

35. Percival, D. F., Alkylated 5-Aminotetrazoles, Their Preparation and Properties, Ph. D. Thesis, Michigan State College, 1955.

36. Murphy, D. B. and Picard, J. P., J. Org. Chem. 19, 1807-1814 (1954).

37. Wilson, K. R., The Apparent Acidic Dissociation Constants of Some 5-Aryltetrazoles, M. S. Thesis, Michigan State College, 1955.

38. Bellamy, L. J., The Infra-red Spectra of Complex Molecules, Methuen and Co., Ltd., London; John Wiley and Sons, Inc., New York, 1954.

39. Koegel, R. J., Greenstein, J. P., Winitz, M., Birnbaum, S. M., and McCallum, R. A., J. Am. Chem. Soc., 77, 5708-5720 (1955).

40. a) Ladenburg, A., Ber. 10, 1123-1131 (1877).
b) Hirst, H. R. and Cohen, J. B., J. Chem. Soc. 67, 829-831 (1895).

41. Froehlich, E., and Wedekind, E., Ber. 40, 1009-1013 (1907).

42. Tobias, G., Ber. 15, 2443-2452 (1882).

43. Diepolder, E., Ber. 32, 3514-3517 (1899).

44. Chattaway, F. D., and Orton, K. J. P., Ber. 33, 2396-2400 (1900).

45. Davis, O. C. M., J. Chem. Soc. 95, 1397-1403 (1909).

46. Slosson, E. E., Am. J. Chem. 29, 289-319 (1903).

47. Schmidt, O., Ber. 36, 2459-2482 (1903).

48. Von Niementowski, S., Ber. 20, 1874-1895 (1887).

49. Wurtz, A., Ann. chim. [3] 42, 43-70 (1854).

APPENDIX

Abbreviations Used in Tables XI through XV

W = weak

M = medium

S = strong

B = broad

sh = shoulder

p = plateau

[ ] = very weak, doubtful

TABLE XI

Characteristic Bands in the Infrared Spectra of 5-Alkyltetrazoles

Alkyl Group	4000 Region	3135	2800-2000	1814	1579	1553	1411
Methyl	4274W 4202Wsh	3155Msh	[2778-2326]	1812WB	1582M	1563M	[1412]sh
Ethyl	4310W 4219Wsh	3125Msh	[2778-2326]	1795W	1575M	[1541] 1563Wsh	1418M
n-Propyl	4255W	3135Msh	2717Ssh [2703-2326]	1786M	1577S		1418S
n-Butyl	4274W 4219W	3115Msh	2710Ssh 2591Ssh [2439]	1808W	1582M	1548M	1403Msh
n-Amyl	4292 4049W	3135S	[2778-2105]	1835WB	1577sh	1565sh 1555M	1408Wsh
i-Amyl	4274W 4202Wsh	3125Msh	2740S-2353M	1842WB	1582W	1550M	1403M
n-Hexyl	4274W 4202Wsh	3115Msh	2703S-2463S	1818WB	1575M	1553Wsh 1543Wsh	
n-Heptyl	4219W	3125M	2710S-2469	1832WB	1580M	1553M 1543Msh	1404M

Table XI Continued

1295	1258	1111	1082	1042	988	715
1267W	1256M	1112M 1103sh		1047		[719]
1307M	1253M	1101M	1082S	1043S	995W	[715]
[1346] [1307] 1276M	1259S	1106S	1078S	1040B	[990- 893]S	715M
	1259M	1107S		1036WB	[1015] [980]	715M
[1305]	1263sh 1253M	1110M	1087M	1036B		715Msh
	1267W	1109M		1040M	985W	[733- 716]
1323M	1267Wsh 1259M 1253Wsh	1121S 1110M	1082S	1043S	994M	710W
[1307]	1264W 1248W	1107S	1086M	1041S	986M	715Wsh

TABLE XII

Characteristic Bands in the Infrared Spectra of 5-Aryltetrazoles

Aryl Group	4000 Region	2800-2000	1850 Region	1607*	1573	1545	1419	1298	1250	1168
Phenyl	4202W 4115Wsh	[2740-2326]	1842WB	1610W	1563M	1546Wsh	1410W	1287W	1255W	1170Wsh 1163M
o-Tolyl	4255W	[2725-2315]		1605W	1577Wsh 1563Wsh	1546W 1543Wsh	[1401]sh		1248W	1159Msh 1152M
m-Tolyl	4237W	[2762-2326]		1621W	1595W	1563W	1412W		1255W	1164W 1151M
p-Tolyl		[2674] [2597-2326]	1866	1613M	1577Msh 1567M	1560Msh	1403W	1280W	1255W	1183M 1160S
o-Chloro-phenyl	[4237]	[2778-2315]		1603M	1558Wsh	1553W	[1422] [1403]		[1258] 1242W	1161M
m-Chloro-phenyl	4237W 3448-3215M	[2600]	[1969]		1580W	1553W	1410M	1292W	1244W	1164W 1155W
p-Chloro-phenyl	[4167]			1608M	1550WB	1520Wsh	1437Msh	[1272]	[1248]	1157M
o-Methoxy-phenyl	4274W 4219W	[2700]		1613M	1587W	1570sh	[1435]sh	1297M 1277M	1252M 1241Msh	1163Msh 1156M
p-Methoxy-phenyl	4219W 4082sh	[2740-2315]		1592M	1590M	1563Wsh 1543Wsh	1408M	1323Wsh 1300M	1266S [1256]	1182M 1161M

Aryl Group	1115	1087	1053	1037	1014	988	748	719	673
Phenyl	[1099]	1085W	1054M	1034M	1015M 1006Wsh	[995- 956]W		725S	686M
o-Tolyl	1114W		1058M	1041M	1004W	983W	745S	714W	
m-Tolyl		[1081]	1059W	1036M			742S		687W
p-Tolyl	1122W	1085M	1048S	1034M	1011Msh	986S	743S		696W
o-Chloro-phenyl	1129W	[1079]	1057S	1037S	1019Wsh 1006M	[995]sh 986M	746S	713M	651M
m-Chloro-phenyl	1130Wsh 1122W 1104M	1082M			[1025] 1014W		746M	[715]	679M
p-Chloro-phenyl	1119W	1092M 1082Wsh	1046W		1015W	980W	745Msh 742M	[721]sh	691W
o-Methoxy-phenyl	1121M	1094W	1060M		1016M	994W	753S		670W
p-Methoxy-phenyl			1056M	1033M	1017M	991W	752M		696W

* Assigned to phenyl.

TABLE XIII

Characteristic Bands in the Infrared Spectra of 1-Alkyltetrazoles

Alkyl Group	4000 Region	3500 Region	3135	2222	1754	1658	1487	1470
Ethyl	[4386-4000]	3546Msh 3497M	3155S	2227M	[1754]	1639W	1490S	
n-Butyl	[4237]	3472W	3155M	2227M	[1751]	[1639]	1481S	1466S
i-Butyl			3115M			1672 [1626]	1490M	1475S
n-Amyl	4274W 4065Wsh 4000Wsh	3484W	3155S	2227M	1757W	[1664] 1647W	1493S	1473S 1471Ssh
i-Amyl	[4219]		3135M	2217W			1488S	1471S
n-Hexyl	4237W	3460W	3135M	2222W	[1754]	[1689] 1642W	1490S	1468S
n-Heptyl	[4255]	[3472]	3155M	2222W			1490M	1468M

Alkyl Group	1366	1301	1273	1249	1219	1168	1113	1087
Ethyl	1357M	1304W		1258M	1198M	1170S	1112S	[1075]
n-Butyl	1374Msh	1312W	1277Wsh	1248Wsh	1239W	1170S	1114S	1092M
i-Butyl	1389M 1368W	1289W		1247W		1164S	1110	1087M
n-Amyl		1304M	1266M	1248M	1225M	1171S	1114S	1095S
i-Amyl	1372M	[1311]	[1279]	1239W		1167S	1114S	1095S

n-Hexyl	1364Msh	1311W	1280W	1256W	1238W	1168S	1114S	1095S
n-Heptyl	[1370]sh	[1307]	[1276]	1252W	[1230]	1170S	1115M	1098M

Alkyl Group	1020	968	876	757	719	676	665	647
Ethyl	1024M	973S	876M		722W		668S	648S
n-Butyl	1022M	968M	877M	754M	716M	675M	663M	646M
i-Butyl	1016W	963M	873WB	748M	718W		661M	
n-Amyl	1025M	967S	879S	748Msh	722M	675S	664S	647M
i-Amyl	1020W	965M	879M	[750]	720W	677M	663M	
n-Hexyl	1022W	966M	877M	765W	722M	674M	664M	[647]
n-Heptyl	1021W	966M	877M		722M	674M	664M	

TABLE XIV

Tabulation of Characteristic Bands in the Infrared Spectra of 1-Aryltetrazoles

Aryl Group	4000 Region	3500 Region	3145	2000 Region	1615*	1554	1498*	1464	1395
Phenyl (oil)	[4219]				1597W		1499M		
Phenyl ($CHCl_3$)	[4587] 4032W	3650W 3436M	3135S	2985-2217	1595S	1555Wsh	1490S	1462S	1401S
Phenyl (CCl_4)			3155W		1603M		1504S	1466M	1403W
m-Tolyl (oil)	[4255-4032]				1610W	1585W	1486Ssh	1458S	1374S 1351Wsh
m-Tolyl ($CHCl_3$)	[4255] 4032W	3650W 3448M	3135S	2933-2193	1613S	1595S		1468S	1403S 1381S
p-Tolyl (oil)			3115Wsh		[1590]	1527Wsh	1511S		1389Msh 1364Msh
p-Tolyl ($CHCl_3$)	[4049]	3663W 3484W	3155M	2994M 2933M	1597M	1527Msh	1513M	1468S	1395M 1383M
o-Chlorophenyl (oil)			3125Wsh				1488Msh		1377S
o-Chlorophenyl ($CHCl_3$)	4065W	3663W 3460M	3165S	2994Msh 2400W	1621M	1590S	1493S	1462	1401M
m-Chlorophenyl (oil)					1590M				
m-Chlorophenyl ($CHCl_3$)	4049W	3650W 3460M	3155S	2639-2212W	1592S	1563Msh	1484S	1466S	1401S 1381M

p-Chloro-phenyl (oil)							1502M		
p-Chloro-phenyl ($CHCl_3$)		3448W	3155W	[3125-2985]Wp	1639Wsh 1623W	1511Wsh	1495S	1466Msh	1387W
o-Methoxy-phenyl ($CHCl_3$)	[4255] 4098	3636W 3425M	3165S	2933-2045V	1600S			1460Ssh	1397S
o-Methoxy-phenyl (CCl_4)	4184W		3175M	2967-2049V	1608S	1511Ssh	1504S	1475Ssh 1464S 1458S	1401S 1377Wsh
p-Methoxy-phenyl (oil)					1610W	1595W	1511S		
p-Methoxy-phenyl ($CHCl_3$)		[3650] 3448W	3155M	2933M-2058W	1613S	1597S	1502M	1462S	1399M

Aryl Group	1310	1261	1208	1192	1171	1162	1114	1084	1045
Phenyl (oil)			1208M	1192M	1172W	1161W		1094M	1046W
Phenyl ($CHCl_3$)	1328M 1290Msh	1274M			1168S			1087S 1072S	1034M
Phenyl (CCl_4)	[1330] [1316]	[1276]	1200S	1181M	1171M			1089S 1073W	1037M
m-Tolyl (oil)	1299W		1218M	1183M	1171M	1160M		1094S	1050W
m-Tolyl ($CHCl_3$)	1312M	[1274-1190]p			1166S			1087S	1059Ssh 1046SB
p-Tolyl (oil)	[1316]	[1271]	1211M	1200S	1174M		1121W [1109]	1093S	1045M

Continued next page

TABLE XIV - Continued

Aryl Group	1310	1261	1208	1192	1171	1162	1114	1084	1045
p-Tolyl ($CHCl_3$)	1318W 1295W	1274W			1170M		1120M	1092S	1031W
o-Chlorophenyl (oil)			1202M		1170M	1157Msh	1127M	1091S 1082S	1034W
o-Chlorophenyl ($CHCl_3$)	1290Wsh	[1265-1175]Mp			1167S		1133S	1085S	1031Msh
m-Chlorophenyl (oil)	[1305] [1294]	[1259]	1208M	1182M	1174Msh		1119W 1100W	1092M 1082M	1038M
m-Chlorophenyl ($CHCl_3$)	1289M	[1260-1190]Mp			1170S		1119Msh	1089S	1037S
p-Chlorophenyl (oil)			1214Wsh	1202W	1170W		1096Wsh	1087M	
p-Chlorophenyl ($CHCl_3$)		[1271-1190]Wp			1168W		1095Ssh	1089S	1020W
o-Methoxyphenyl ($CHCl_3$)	1307S	1274S [1266-1258]Sp			1168S		1124S	1085S	1016S
o-Methoxyphenyl (CCl_4)	1312S	1282S 1247S	1198S	1182S	1167S		1126S	1086S	1049S

p-Methoxy-phenyl (oil)	1316W 1302W	1277W 1248M	1206W	1190W	1168M		[1121] [1112]	1095M	1044W
p-Methoxy-phenyl ($CHCl_3$)	1319Ssh 1304S	[1277-1176]Sp			1167S		1110S	1092S	

Aryl Group	1013	995	956	939	902	869	715	660
Phenyl (oil)		999Wsh 994M	963W		914W	882W	715W	686M
Phenyl ($CHCl_3$)	1015W	994S	957S		909S	885MB 853S		
Phenyl (CCl_4)		995M	952W		908W	850M		687S
m-Tolyl (oil)	1011W	[990]	960W		889W	859W	715W	682Msh
m-Tolyl ($CHCl_3$]	1008S	998S	959S		902S	[855-840]p		
p-Tolyl (oil)		998M	961M	[948]		874W	716W	666W
p-Tolyl ($CHCl_3$)		998S	961M	942Wsh	890W	855M		
o-Chloro-phenyl (oil)	1017W	992M	955Wsh	949M		887M	714M	670M 652M
o-Chloro-phenyl ($CHCl_3$)	1016M	993S	949S	928Msh		861S		649M

Continued next page

TABLE XIV - Continued

Aryl Group	1013	995	956	939	902	869	715	660
m-Chloro-phenyl (oil)	1006W	996W	973Wsh 954W		[899]	872M	714W	673M 657W
m-Chloro-phenyl ($CHCl_3$)	1005Ssh	997S	956S			856S		
p-Chloro-phenyl (oil)		995W				878W		672W 660W
p-Chloro-phenyl ($CHCl_3$)		996S	956W			851M		
o-Methoxy-phenyl ($CHCl_3$)		993S	955S	937		863S		
o-Methoxy-phenyl (CCl_4)	1018S	992S	952M	936M		860S		670S
p-Methoxy-phenyl (oil)	1019M 1009M	990W				872W		662M
p-Methoxy-phenyl ($CHCl_3$)	1013S	996S	961M			851MB sh		

TABLE XV

Tabulation of Characteristic Bands of 1,5-Disubstituted Tetrazoles

1-Position	5-Position	4000 Region	1593[a]	1539		1399	1300	1258
Methyl (oil)	Methyl	4274W		1531S		1425S 1406S	1284S	1247S
Ethyl (liquid)	Isobutyl	[4237]		1538Wsh 1508S		1437Ssh 1383M	1312W	1253Wsh 1242M
Ethyl ($CHCl_3$)	Isobutyl	[4274] [4115]		[1565- 1545]M	(1481-1422)S	1381M 1357Msh	1314W	[1265- 1175]p
Ethyl (CCl_4)	Isobutyl	4237W				1437S 1383S 1355Msh	1312M [1282]	1255Wsh 1242M
Isobutyl (oil)	Methyl	4274W		1527S 1511Wsh		1385S [1357]	1305M	1252S 1241Msh
Isobutyl (oil)	Isobutyl	4255W		1563W 1511S		1427S 1385Ssh 1355Msh	1307W 1300Wsh 1287W	1250S
Pentamethylene (oil)				1524M 1511Msh		1429S 1359Wsh	[1282]	1269M 1244S
Phenyl (oil)	Methyl		1590M	1506Wsh	1488S	1397Wsh	1292W	1264M
Phenyl (oil)	Ethyl		1597M	1508S	1497S	1416S 1372Ssh	1295W	1272M 1241M
Phenyl (oil)	Isobutyl	[4200]	1595M		1493S	1416S		1272M [1250]sh

p-Methoxy-phenyl	Methyl (oil)	[4202]	1608M 1590M	1524Ssh	1511S	[1410]	1319S 1309S	1272S 1253S
Methyl	Phenyl (oil)		[1603]	[1572]		[1403]	1282W	
Ethyl	Phenyl (oil)		1608W	1531M		1406M	1318M 1302M 1285M	1263Msh 1255M 1241Wsh
Isobutyl	Phenyl (oil)	[4274]	[1577]	1534W		1404M	1307W 1279W	1252W
Phenyl	Phenyl (oil)		1592M	1522W	1490M	1406M	1292W	1274W 1261W

1-Position	5-Position	1205	1166	1121	1081	1039	1010	986
Methyl	Methyl (oil)	1209M			1096S	1033M	1006M	973W
Ethyl	Isobutyl (liquid)	1209W	1168M		1086M	1044W		987W
Ethyl	Isobutyl ($CHCl_3$)	[1265-1175]p	1167M		1086S	1042Wsh		988M
Ethyl	Isobutyl (CCl_4)	1206W	1168M	1145Wsh	1085S	1040W		980Wsh
Isobutyl	Methyl (oil)	1183W	1174W	1098S	1070S	1047Wsh		987W
Isobutyl	Isobutyl (oil)	1211M	1170S	1120W 1101S	1094S 1071M			994W
Pentamethylene		1185W	1170W	1115S 1096W	1088W 1074W	[1024]		992M

Continued next page

TABLE XV - Continued

1-Position	5-Position	1205	1166	1121	1081	1039	1010	986
Phenyl (oil)	Methyl		1168W	1116M 1104Wsh	1080M	1041W	1014M	[980] 975M
Phenyl (oil)	Ethyl		1166W	1119M 1106W	1091M 1072Msh 1065S	1050Msh	1019M	[999] [992]
Phenyl (oil)	Isobutyl	1227W	1168M 1159W	1103M	1082M [1072]	[1047]	1018M	986W
p-Methoxy-phenyl (oil)	Methyl	1185S	1175S 1153Msh	1116M 1103S	1085M	1047M	1019S 1006Msh	989W
Methyl (oil)	Phenyl	1208W		1111W	1079W	[1054]		
Ethyl (oil)	Phenyl		1170M	1116M 1107Msh	1076M 1065W	1040W	1016W 1001Wsh	995W 973M
Isobutyl (oil)	Phenyl		1178M 1155W	1110M	1078M	1031W	1013W	990W
Phenyl (oil)	Phenyl		1156W	1139M 1101M	1067M	[1046]		996M 982W

TABLE XVI

Ultraviolet Absorption Spectrum of 1-Phenyltetrazole
(1×10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	.826	8,260
215	.531	5,310
220	.568	5,680
225	.709	7,090
230	.848	8,480
235	.921	9,210
236	.921	9,210
237	.925	9,250
238	.920	9,200
239	.909	9,090
240	.899	8,990
241	.881	8,810
242	.861	8,610
243	.836	8,360
244	.811	8,110
245	.783	7,830
250	.614	6,140
255	.427	4,270
260	.268	2,680
265	.159	1,590
270	.088	880
275	.046	460
280	.020	200
285	.011	110
290	.010	100
295	.009	90
300	.005	50

TABLE XVII

Ultraviolet Absorption Spectrum of 1-m-Tolyltetrazole
(1×10^{-4}M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.889	18,890
215	1.147	11,470
220	.658	6,580
225	.608	6,080
230	.732	7,320
235	.837	8,370
236	.852	8,520
237	.865	8,650
238	.870	8,700
239	.874	8,740
240	.869	8,690
241	.864	8,640
242	.854	8,540
243	.842	8,420
244	.824	8,240
245	.808	8,080
250	.675	6,750
255	.503	5,030
260	.343	3,430
265	.217	2,170
270	.144	1,440
275	.107	1,070
280	.065	650
285	.016	160
290	.014	140
295	.011	110
300	.009	90

TABLE XVIII

Ultraviolet Absorption Spectrum of 1-p-Tolyltetrazole
(1×10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.102	11,020
215	.578	5,780
220	.455	4,550
225	.545	5,450
230	.726	7,260
235	.896	8,960
237	.945	9,450
239	.981	9,810
240	1.000	10,000
241	1.001	10,010
242	1.008	10,080
243	1.010	10,100
244	1.006	10,060
245	1.002	10,020
250	.903	9,030
255	.734	7,340
260	.544	5,440
265	.362	3,620
270	.212	2,120
275	.119	1,190
280	.054	540
285	.007	70
290	-.003	0
295	-.003	0
300	-.005	0

TABLE XIX

Ultraviolet Absorption Spectrum of 1-o-Chlorophenyltetrazole
(1×10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
208	1.587	15,870
209	1.571	15,710
210	1.472	14,720
211	1.360	13,600
215	1.044	10,440
220	.746	7,460
225	.541	5,410
230	.441	4,410
235	.359	3,590
240	.261	2,610
245	.165	1,650
250	.094	940
255	.055	550
260	.046	460
265	.047	470
270	.046	460
275	.038	380
280	.015	150
290	.001	10
300	.001	10

TABLE XX

Ultraviolet Absorption Spectrum of 1-m-Chlorophenyl Tetrazole
(1×10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	2.43	24,300
215	2.01	20,100
220	1.129	11,290
225	.694	6,940
230	.746	7,460
232	.788	7,880
234	.822	8,220
235	.852	8,520
236	.857	8,570
237	.872	8,720
238	.883	8,830
239	.873	8,730
240	.878	8,780
241	.858	8,580
242	.843	8,430
243	.822	8,220
245	.784	7,840
250	.616	6,160
255	.417	4,170
260	.246	2,460
265	.130	1,300
270	.092	920
275	.073	730
280	.060	600
290	.017	170
300	.005	50

TABLE XXI

Ultraviolet Absorption Spectrum of 1-p-Chlorophenyltetrazole
(1×10^{-4} solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.247	12,470
215	.767	7,670
220	.701	7,010
225	.863	8,630
230	1.101	11,010
235	1.289	12,890
237	1.347	13,470
239	1.391	13,910
240	1.402	14,020
241	1.401	14,010
242	1.399	13,990
243	1.400	14,000
244	1.403	14,030
245	1.393	13,930
246	1.381	13,810
248	1.336	13,360
250	1.270	12,700
255	1.043	10,430
260	.773	7,730
265	.605	6,050
270	.300	3,000
275	.187	1,870
280	.102	1,020
290	.038	380
300	.025	250

TABLE XXII

Ultraviolet Absorption Spectrum of 1-o-Methoxyphenyltetrazole
(1×10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.652	16,520
215	1.277	12,770
220	.792	7,920
225	.554	5,540
230	.519	5,190
232	.547	5,470
234	.565	5,650
235	.580	5,800
236	.576	5,760
238	.575	5,750
240	.573	5,730
245	.488	4,880
250	.354	3,540
255	.213	2,130
260	.134	1,340
265	.151	1,510
270	.224	2,240
275	.314	3,140
278	.352	3,520
280	.374	3,740
281	.380	3,800
282	.384	3,840
283	.384	3,840
284	.381	3,810
285	.375	3,750
290	.294	2,940
295	.183	1,830
300	.086	860

TABLE XXIII

Ultraviolet Absorption Spectrum of 1-p-Methoxyphenyltetrazole
(1 x 10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.110	11,100
215	.656	6,560
220	.415	4,150
225	.377	3,770
230	.468	4,680
235	.633	6,330
240	.809	8,090
245	.912	9,120
250	1.075	10,750
252	1.082	10,820
254	1.086	10,860
255	1.093	10,930
256	1.079	10,790
258	1.058	10,580
260	1.040	10,400
265	1.031	10,310
270	.772	7,720
275	.623	6,230
280	.481	4,810
285	.326	3,260
290	.182	1,820
295	.070	700
300	.018	180

TABLE XXIV

Ultraviolet Absorption Spectrum of 5-m-Tolyltetrazole
(1 x 10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.839	18,390
215	1.042	10,420
220	0.553	5,530
225	0.613	6,130
233	1.064	10,640
234	1.119	11,190
235	1.166	11,660
236	1.210	12,100
237	1.248	12,480
238	1.283	12,830
239	1.319	13,190
240	1.345	13,450
241	1.348	13,480
242	1.360	13,600
243	1.364	13,640
244	1.346	13,460
245	1.332	13,320
246	1.295	12,950
247	1.265	12,650
250	1.151	11.510
255	0.789	7,890
260	0.459	4,590
265	0.154	1,540
270	0.100	1,000

TABLE XXV

Ultraviolet Absorption Spectrum of 5-p-Tolyltetrazole
(1 x 10^{-4} M solution in 95% ethanol)

Wavelength	Optical Density	ε
210	1.408	14,080
215	0.546	5,460
220	0.431	4,310
225	0.615	6,150
230	0.930	9,300
233	1.137	11,370
234	1.204	12,040
235	1.269	12,690
236	1.333	13,330
237	1.392	13,920
238	1.449	14,490
239	1.493	14,930
240	1.539	15,390
241	1.578	15,780
242	1.622	16,220
243	1.640	16,400
244	1.657	16,570
245	1.672	16,720
246	1.672	16,720
247	1.672	16,720
248	1.645	16,450
249	1.618	16,180
250	1.599	15,990
255	1.347	13,470

TABLE XXVIa

Ultraviolet Absorption Spectrum of Tetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε		
	10^{-4} M	10^{-3} M	10^{-2} M
210	350	215	181
215	310	107	87
220	310	59	36
225	350	39	14
227	370	-	-
229	380	-	-
230	370	32	5
232	360	-	-
234	350	-	-
235	340	26	2
237	280	-	-
240	270	20	2
245	210	14	1
250	160	16	1
255	210	13	1
260	200	9	1
265	120	8	1
270	110	7	1
275	110	9	1
280	120	9	1
285	70	7	-
290	70	6	0
295	70	7	-
300	60	4	0

TABLE XXVIb

Ultraviolet Absorption Spectrum of Tetrazole
(in water, at concentrations given below)

Wavelength	ε	
	10^{-4} M	10^{-2} M
210	280	118
215	130	47
220	70	17
225	30	6
230	30	3
235	40	2
240	30	1
245	30	1
250	40	1
255	20	1
260	20	1
265	20	1
270	20	1
275	30	1
280	30	1
285	20	0
290	20	0
295	20	0
300	20	0

TABLE XXVII

Ultraviolet Absorption Spectrum of 1-n-Butyltetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε		
	10^{-4} M	10^{-3} M	10^{-2} M
210	430	350	255
215	230	186	140
220	160	104	68
225	100	62	31
230	30	37	15
235	30	27	8
240	20	20	5
245	10	16	4
250	20	14	4
255	10	10	3
260	0	6	3
265	0	9	2
270	0	8	2
275	0	8	2
280	0	9	2
285	0	8	2
290	0	8	2
295	0	9	-
300	0	9	1

TABLE XXVIII

Ultraviolet Absorption Spectrum of 1-n-Amyltetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε		
	10^{-4} M	10^{-3} M	10^{-2} M
210	690	417	256
215	420	248	139
220	330	179	64
225	260	143	27
230	200	131	11
235	170	112	5
240	120	76	3
245	80	57	2
250	60	53	2
255	30	50	2
260	30	47	2
265	30	37	1
270	30	31	1
275	50	29	1
280	70	28	1
285	50	24	1
290	40	20	1
295	40	17	-
300	0	13	1

TABLE XXIX

Ultraviolet Absorption Spectrum of 1-n-Hexyltetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε	
	10^{-3} M	10^{-2} M
210	466	283
215	309	273
220	198	185
225	124	116
230	71	70
235	45	42
240	31	27
245	25	22
250	21	19
255	17	16
260	13	12
265	10	9
270	8	7
275	7	6
280	7	5
285	-	4
290	5	4
300	6	2

TABLE XXX

Ultraviolet Absorption Spectrum of 5-n-Butyltetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε	
	10^{-3} M	10^{-2} M
210	374	299
215	175	157
220	67	62
225	21	19
230	9	5
235	7	2
240	7	1
245	4	1
250	4	0
255	4	1
260	4	0
265	2	1
270	2	0
275	3	0
280	2	0
285	3	0
290	2	0
295	3	0
300	3	0

TABLE XXXI

Ultraviolet Absorption Spectrum of 5-n-Hexyltetrazole
(in 95% ethanol, at concentrations given below)

Wavelength	ε		
	10^{-4} M	10^{-3} M	10^{-2} M
210	110	377	260
215	70	167	160
220	0	66	61
225	0	22	19
230	0	8	5
235	0	6	2
240	0	3	1
245	0	1	0
250	0	1	0
255	0	1	0
260	0	1	0
265	0	1	0
270	0	0	0
275	0	0	0
280	0	2	0
285	0	0	0
290	0	1	0
300	0	0	0