

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee
of the Graduate School, have read the accompanying
thesis submitted by Glenn Earl Matthews
for the degree of Master of Science.

They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of Master of Science.

J. H. Hunter
.....
Chairman

F. H. Macdougall
.....

John T. Tate
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May 26 1921
..... 1918

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report

of

Committee on Examination

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This is to certify that we the undersigned, as a committee of the Graduate School, have given Glenn Earl Matthews final oral examination for the degree of Master of Science. We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

May 26 1921

J. H. Hunter
Chairman

F. H. MacDougall

John T. Tate

A Comparison of
the
Absorption Spectra of
Diphenylamine and Carbazole
and
Several of their Derivatives

A Thesis
Submitted to the
Faculty of the Graduate School
of the
University of Minnesota
by
Glenn Earl Matthews

In Partial Fulfillment of the Requirements
for the degree of
Master of Science
in Chemistry
May
1921.

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A Comparison of
the Absorption Spectra of
Diphenylamine and Carbazole
and
Several of their Derivatives.

I. General Discussion of the Theories of Color.

Introductory.

Color had been a subject of general interest to people for many centuries, before the beginnings of scientific investigation. This interest was centered around the application of natural dyes, like madder, purpurin, and indigo. The first artificial dyestuff was synthetically made by A.W.von Hoffman and Sir Wm. Perkin and appeared under the name of "mauve" in 1856. In the years that followed, the dye industry grew rapidly and by the time the synthesis of indigo was accomplished by A. von Baeyer in 1880, chemists had proven undeniably that any color could be reproduced if the investigators were willing to give the time and study necessary for its preparation. As the basis of structural organic chemistry, dependent on the Principles of Kekule published in 1868, was being formed at the same time, it was quite natural that an interest should be aroused in the cause of color. To facilitate an understanding of the discussion that follows, it is pointed out that the terms, "colored" and "colorless" as applied to the compounds mentioned are to be taken in the sense of visible color. We find Graebe and Liebermann recording the first observation on the subject. They concluded that the phenomenon of color in organic compounds must

1 - Ber. 1867, 1, 104.

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be associated in some way with unsaturation, as reduction as well as addition of halogens seemed to cause all known colored compounds to become colorless.

The Chromophore Theory of O.N. Witt.

Several years later, in 1876, the theory of O.N. Witt appeared.¹ According to this investigator, *color was due* to the presence of certain groups, unsaturated in character, which he termed chromophores. Those most frequently appearing are $\text{N}=\text{N}$, $\text{N}=\text{O}$, NO_2 , $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{N}$, and $\text{C}=\text{C}$. The molecule that these groups were held by was called a chromogen. It can be seen that as time passed and more colored substances were discovered, new chromophores had to be added to the list. This looseness of application of the theory is somewhat fortunate in that it is only necessary to pick out a new chromophore to explain the color of a particular substance. It does not, however, aid us materially in arriving at a definite explanation for a cause of color that will hold without additions or subtractions for all substances.

The theory has been a basis for an extended investigation of the cause of color and has served to stimulate the development of many additional theories. As chromogens may or may not be colored, it was next postulated that the addition of certain salt-forming groups to a colorless chromogen would render it colored. These groups were called auxochromes. Their addition to a chromogen caused the chromogen to become a dyestuff. Examples of auxochromes are NH_2 , OH , $\text{N}(\text{CH}_3)_2$. There is an exception to this rule, as for

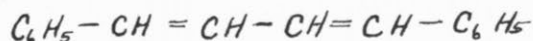
1. Ber. 1876. 9, 522.

instance, the sulphonic and carboxyl groups do not possess the ability to produce color in a chromogen when tied to it. Oftentimes a single chromophore will cause visible color to appear, but it is more often the result of a piling up or "mass effect" of several of these groups which appears to be the direct cause of color.

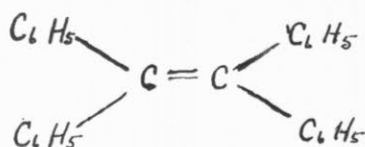
Examples of the effect of the addition of chromophores on the color of compounds appear in the following types, wherein it is to be noticed that the formulae on the right hand side possess several chromophores whereas those on the left have only one.



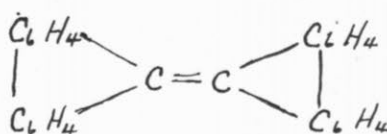
Diphenyl - Colorless



Diphenyl hexatriene - Yellow.



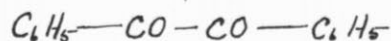
Tetraphenyl ethylene - Colorless



Bisdiphenylene ethylene
Red.



Benzophone - Colorless



Benzil - Yellow.

The group $\begin{array}{c} =C \\ \diagdown \\ C = \\ \diagup \\ =C \end{array}$ which appears in the fulvenes discovered by Thiele¹ seems to possess color carrying power. Examination of

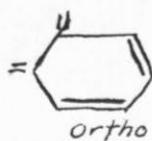
the color of many hundreds of compounds have yielded the conclusions relative to the effect of the addition of these groups as described in the next paragraph.

The C=O group does not lend color to the simpler aldehydes and ketones, but it appears, as shown above, to give this power to the more complex series. Both the N=N and the C=S groups are strong chromophores as nearly all substances in which they are found, are colored. Many nitroso compounds are characterized by

a blue or green color effect, whereas the nitro group gives yellow to some compounds, but leaves others such as the nitro-paraffins colorless. Furthermore, additions of two or more groups instead of increasing the color, sometimes diminish it. Such an effect is shown in nitro benzene which is yellow, while the di- and tri-nitro benzenes are colorless. As a result of the ability of certain chromophores, like $N=N$ and $C=S$ being able to produce color, while others like $C=O$ and $C=C$ do so only when aided by the proximity of other groups, Kauffmann separated the chromophores into two classes, the independent and the dependent chromophores. This varied nature of the chromophore group and the general looseness of the theory is probably what stimulated Armstrong and Nietzki to search for a fundamental chromophore.

The Quinonoid Theory.

Both H.E. Armstrong and Nietski published, in 1888, a theory that is now known as the "Quinonoid" theory.¹ It was an attempt to show that the essential chromophore for the production of color was of the type found in quinone, two varieties of which appear below.

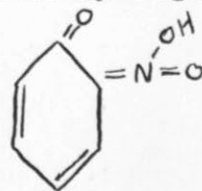


In his second paper,² Armstrong states, "although the general correctness of this view has never yet been acknowledged, a study of the literature relating to colored compounds clearly shows that it is more and more recommending itself; it should also be mentioned that Nietzki, in the introduction to his *Organische Farbstoffe*, makes ref-

1 - Armstrong. Proc.Chem. Soc. 1888, 27.
Nietzki. "Organische Farbstoffe" 1888
Springer, Berlin
2.- Armstrong. Proc.Chem. Soc. 1892. 101.

erence to the quinonoid character of a number of dyestuffs, although he does not seek to apply such a view of their structure generally. The subject has continually occupied my attention since I first brought it before the Society, and I think it justifiable that I should now state the opinion at which I have arrived, viz., that in the case of colored compounds, which have been fairly well studied, it is so generally true that a quinonoid formula is applicable, that the reconsideration of the formula of any colored substance is warranted if it is not to come within this rule. The term "quinonoid", must however, be understood to include compounds of the type of benzil; and it is to be noted that ⁱⁿ the case of closed chain compounds it appears to be essential that at least one of the quinonoid carbon atoms be associated with a dyad radical, and that the ring itself be unsaturated. The presence of two ortho or one para carbonyl group in a saturated ring apparently does not condition colour."

In the remainder of the paper, he endeavors to explain the apparent anomaly of the yellow color of the ortho nitro phenol and the colorless para derivative. He showed that the methoxy nitro benzenes prepared from both, are colorless. For several reasons, which he further states, it seems justifiable to say that these two compounds are not mere position isomers and that the formula for o-nitro phenol may be written quinoid by transferring the hydrogen from the OH group to the NO₂ group as shown.



This case has been inserted to show an example of a type of change which is resorted to many times in the literature to explain the color of a compound. As Cohen states in his "Organic Chemistry", this theory has "one important

attribute which most other theories lack; it lends itself readily to experimental proof or disproof and is accountable for a valuable extension to our knowledge of dyestuffs."

There are, however, quite a number of apparent exceptions to this theory; i.e., several colorless compounds which are most certainly quinoid and several colored substances which cannot be shifted to show a quinoid structure. Examples of the former are



Quinone diimine - Colorless



Quinoneimine - Colorless

while several examples of the latter appear in α and β nitronaphthalene, nitrodimethylquinol, the two benzal nitroanilines, that are yellow and orange, and the quinhydrone. It can be seen that this theory does not fully satisfy the conditions which a rigid color theory must.

Kauffman's Auxochrome Rule.

Kauffmann formulated a rule and published his results in 1904.¹ It may be thought of as a branch of Witt's Theory in that his conclusions state that the auxochromes tend to deepen the color when attached indirectly to the chromophore by an aromatic nucleus, which can act as a chromophore. The term "depth of color" has a different meaning than usually considered. To the color chemist, the complements of the ordinary spectrum arrangement are used and in order of depth, the colors run, - green (deepest), blue, violet, red, orange, and yellow. Kauffmann made a very extended study of the behavior of substances under the influence of Tesla radiation (high frequency current discharge).² He concluded from a comparative study of luminescent compounds that they are in the main, benzene derivatives

1 - Kauffmann. "Farbe und Constitution."

Ahrens' Vorträge. 1904, 9, 277.

2.- Ber. 1900,33, 1725; 1901,34, 682; 1902,35,3668.

containing certain groups, which he called luminophores. Benzene is regarded as the seat of the luminescence, and though only feebly luminescent itself, it becomes more so on the introduction of auxochromes, by increasing the number of aromatic nuclei (naphthalene and anthracene), and by the linking of nuclei with unsaturated carbon atoms. Many other properties appear to run parallel with luminescence as for example the tendency to oxidize to quinoid compounds which is proportional to the strength of the luminescence.

Kauffman therefore came to the conclusion that the benzene nucleus differed in different compounds. Those compounds possessing strong luminescence may be thought to possess the Dewar formula I, the non-luminous substances, the Claus diagonal ring III, and the intermediate stage characterized by moderate luminescence, the formula of Kekule II.



I.

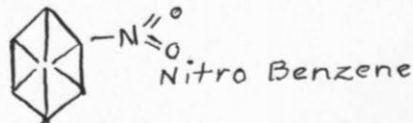


II.

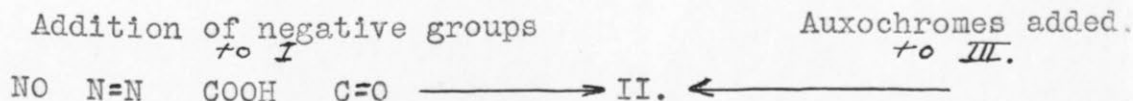


III.

An example would be of interest to show how he applied his idea. Naphthalene, which shows fairly strong luminescence under Tesla rays is concluded to possess one ring like I and the other as in II.



Nitro benzene has almost no luminosity, so it would have the Claus formula. In general, the following condition represented below was concluded to be true.

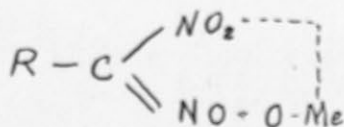


The objections raised to this theory are in the main:

- (1) Alkylation of OH groups tends to destroy their auxochromic effect.
- (2) Hydroxy groups when attached to benzoic acid do not produce color, whereas they should according to Kauffmans' theory.

Hantzsch's Theory of Chromoisomerism.

Contrary to many of Kauffman's ideas, Hantzsch has prepared a different explanation relating to the cause of color. It was while he was working on the ethers of nitrophenol that he discovered both colored and colorless forms of these substances. The colorless type was called the true nitro ether and the colored form, the aci-nitro ether. He formulated the general rule, "every appearance of color or change of color in salt formation with a colorless metallic atom is due to isomeric change." All true nitro phenols and their derivatives are therefore considered colorless and only becomes colored when converted to the aci-form. This kind of isomerism, which is accompanied by a change of color, he defined as Chromoisomerism. As attempts were made to go deeper into the problem, the question became more complex. For instance, the dinitro paraffins, as previously stated, are colored whilst the mono nitro derivatives are colorless. Hantzsch concluded that the second nitro group lends color to the compound because the subsidiary valency or residual affinity of the metal linked up with that of the nitro group as shown below.



Me - Metal.

This theory of valency isomerism, due to recent observations, led

him to propose that the nitro group could exist in three different forms: (1) a true nitro group ; (2) a simple aci-nitro group $>C=NOOH$; (3) an aci-nitro group represented by $R-C \begin{matrix} \swarrow X \\ \searrow NOOH \end{matrix}$ where X= strongly negative radicle (NO_2 , NOH etc.,). It was further found that besides different metals and organic bases producing differently colored salts, the same metal sometimes yields differently colored salts and solutions according to the solvent used. Potassium, rubidium, or caesium diphenyl violurate can each be prepared in blue and red modifications. This phenomenon he called pantochromism.¹ An added difficulty arose when it was found that different structural modifications may possess the same color and identical absorption bands in solution. He defined this effect as homochromisomerism.² There are so great a variety of colored substances that it hardly seems necessary to resort to isomerism as an explanation of all the possible changes. Many of them, no doubt, could be explained by polymorphism, while other cases may be due to the formation of a solvate or the union of solvent and solute.

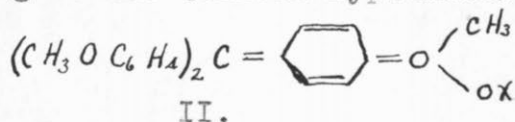
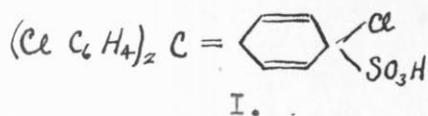
Baeyer's Theory.

The triphenylmethane series of dyes offer an interesting field to the color chemist and with the discovery of triphenyl methyl by Gomberg in 1900, interest has been centered considerably more on this series. For instance, the sulphate of p-trichlorotriphenyl carbinol may be represented by such a formula as I, as it is strongly colored. It is found, however, that the chlorine atoms possess equal stability. Introduction of methoxy groups into the nucleus enables isolation of more stable colored salts. Trianisyl nitrate

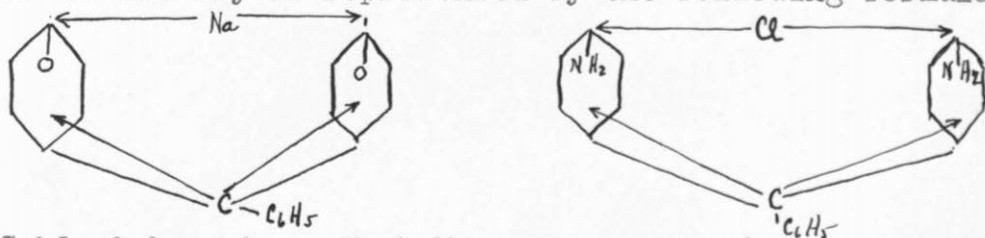
1 - Ber. 1909, 42, 966; 1910, 43, 45, 68, 82.

2 - Ber. 1910, 43, 1910; 1911, 44, 2001.

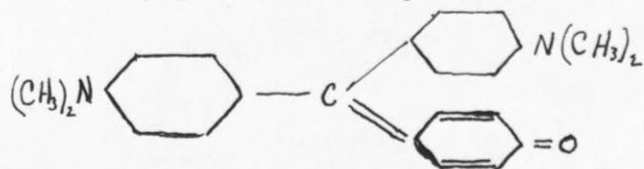
$(\text{CH}_3\text{OC}_6\text{H}_4)_3\text{NO}_3 + 1-1/2 \text{HNO}_3$ has a pronounced color. It should possess a structure like II, according to the quinoid hypothesis.



It is found, however, that the methyl group is not easily detached in comparison with the metal radicle and the trianisyl compound should react differently from the isomers with the OCH_3 groups in the ortho and meta positions. Baeyer believed this difference between the colorless and colored salts and the ionisation of the latter to be due to an oscillation of the quinonoid condition between two or more benzene nuclei.¹ He takes the stand that the quinoid structure does not explain color in this series. It is explained, preferably by the character of the oscillations, which are in turn dependent on the structure of the molecule. According to Cohen², "the benzene nuclei must be represented as alternately possessing the structure of Graebe's superoxide formula, whilst the fourth carbon valency executes, as it were, a pendulum motion between the oxygen or nitrogen atoms. The effect may be represented by the following formulae :



Schlenk has shown that there are cases where, even in the triphenyl methane series, such oscillations are impossible. He cites as an individual case, p-tetra methyl diaminofuchsone.

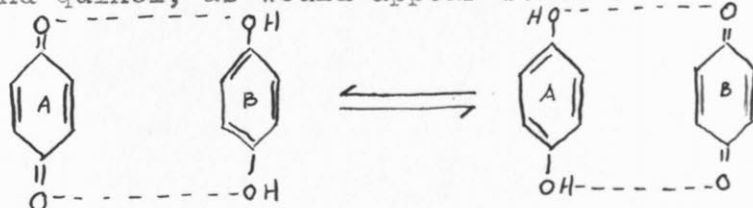


It appears that this theory, which makes use of a conception of os-
1.- Jour.Chem. Soc. Abs. 1907, i, 504.
2.- Cohen. "Organic Chemistry. Vol.II. p.119.

cillatory motion within the molecule is not of sufficient general application to justify its complete acceptance.

The Theory of Willstätter.

Willstätter made a careful study of the quinhydrones, including the colored compounds prepared by Wurster in 1897, and concluded that the color of these substances is best accounted for by assuming the saturation of the partial valencies of the oxygen atoms of the quinone and quinol, as would appear below :



He found the red compound, which Nietzki had called a quinonimine, to be a semi-quinonimine (meriquinonoid), while the full quinonimine, (Holoquinonoid) which he obtained by oxidizing amino dimethylaniline, was colorless. From further investigation, he decided that the colored form belonged to the quinhydrone series. He explained the difference between ordinary quinhydrone and Wurster's compound which exists only in a red modification, by oscillatory motion of the residual affinities, as shown above.² He postulated further that the same thing may occur in parts of the molecule, as between a quinoid and ^{an}aromatic nucleus. This conception was advanced as an explanation of the similarity of Wurster's Red and fuchsine.

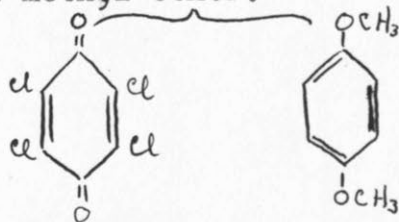
Several series of compounds have been found, since the appearance of his first paper, whose color changes seem best explained by this theory.³

- 1 - Willstätter and Piccard. Ber. 1908, 41, 1465.
- 2 - Willstätter and Piccard. Ber. 1908, 41, 1458, 3245.
- 3 - K.H.Meyer. Ber. 1909, 42, 1149; 1910, 43, 157;

Werner. Ber. 1909, 42, 4324. Hoffmann and Kirmreuther. Ber. 1910, 43, 1764.

F. Kehrman, in a series of papers, criticised strongly the views of these investigators.¹ In one of his papers, published in 1913,² he states that the triphenyl methane bases and Wurster's salts all have the auxochrome outside the quinonoid portion of the molecule, so that both may, in a wide sense, be regarded as of the meri-quinonoid type.

Schlenk has also found a pointed objection³, for he pointed out several colored compounds whose structure presents no possibility of oscillation. An example may be given in the blue compound of chloranil and quinol methyl ether.



Even though these objections possess a validity which cannot be disregarded, it should be noticed in passing, the apparently loose molecular combinations which often produce color.

Baly's Color Theory.

In the theories of both Baeyer and Willstätter, there is the development of a kinetic conception of the cause of color, dependent on an inner molecular oscillation. Baly and his collaborators have published a theory⁴ which follows somewhat along the same trend of thought. Their idea is essentially that of a force field surrounding the molecule. The opening or closing of this field is dependent on the solvent action or the energy of the light waves to

1 - F. Kehrman. Ber. 1908, 41, 2340; 3396; 1913, 46, 3036. 1915, 48, 1938; 1917, 50, 856.

2 - F. Kehrman. Ber. 1913, 46, 3036.

3 - Schlenk. Ann. 1909, 368, 271.

4 - Stewart and Baly. T. 1906, 489; 502; Baly and Tryhorn. T. 1915, 1058.

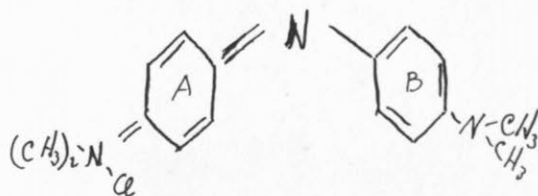
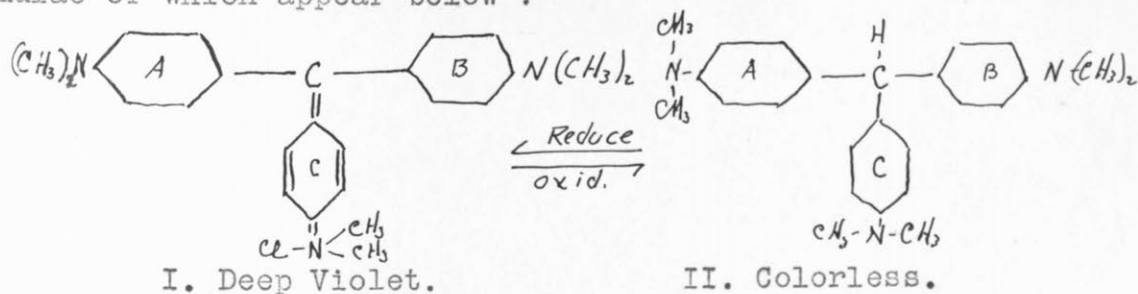
which they respond and which they absorb. This opening and closing of force fields corresponds in a general way with the inner-molecular oscillation conception of Baeyer and Willstätter so that further discussion of this theory is not deemed necessary at this point.

The Color Theory of Stieglitz.

At a recent lecture given before the Minnesota section of the American Chemical Society, Dr. Julius Stieglitz presented his electronic conception of color. He showed that the explanation of Stewart and Baly on the cause of the keto-enol change of acetoacetic ester, which is based primarily on an oscillatory motion of the hydrogen atom between the oxygen and carbon atoms, is far too slow in action to fit in with our modern idea of color. It was found that it takes three weeks for one gram mole to change from one form into the other. Rather he would choose to explain all color changes on the basis of the desire of elements to gain or lose electrons. In other words, whenever a carbon compound is oxydized, one or more of the carbon atoms lose electrons. He explains the deep color of quinhydrones, which he chooses to represent by the formula of Willstätter, appearing on page 11, as due to two electrons trying to escape from the para carbon on the right hand ring. These electrons oscillate very rapidly with the result that the quinhydrones are more deeply colored than quinone. Similarly in the series of inorganic salts, AgCl, AgBr, and AgI, the color ranges from colorless in the first salt, to yellow in the second, and deep yellow in the last. It is explained by the fact that Iodine tends to give up electrons most readily.

In an explanation of the color of dyes, he gave two exam-

ples, which were methyl violet and methylene blue, the structural formulae of which appear below :



Methylene Blue.

In I, the electrons are on the two reducing groups A and B and the result is the production of color. If maximum color is desired in the dye, an alkali is added. In the case of methylene blue B has gained electrons, thereby becoming reduced while A has lost electrons and become oxydized. As no papers have appeared yet, no referances can be given. The theory presents a very interesting and promising application of our modern theory of electron exchange.

Summary.

In an effort to arrive at a reasonable cause for the color developed in compounds organic in character, Witt has given us a theory which has been the basis of of clearer understanding of the important phenomenon and at the same time has stimulated the formation of later theories. Essentially he explained the color of organic substances as due to the presence of certain groups called chromophores attached to a grouping termed a chromogen. Further, he showed that addition of various salt-forming groups called auxochromes

to a colorless chromogen would render it colored and change it to a dyestuff. Armstrong then attempted to limit the idea of a chromophore, by showing that there was only one essential chromophore, that found in compounds of the character of quinone and that compounds which were colored and did not possess this grouping could be rearranged so that the grouping would appear. A slight variation of this limiting case was presented by Kauffmann. He proposed that the benzene nucleus, several formulae for which have been given, was different in many substances and could be explained by the luminescent reaction which compounds offered to high frequency radiation.

Differing in a large degree from the foregoing, but still adhering to the basic idea of Witt, Hantzsch concluded that the color of organic substances was best explained by the assumption of the existence of isomeric forms, one type of which were never colored and the other always colored. He called his idea, chromoisomerism. On developing the conception further, so many complications arose that he found it necessary to add new amendments and define new effects until he became somewhat entangled in the mass of his own theory.

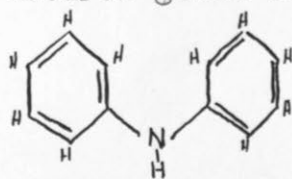
Shortly after the publication of Hantzsch's theory, two new theories based on an idea of oscillatory motion were published. These were prepared by Baeyer and Willstätter. They are practically alike in that they postulate an inner molecular strain which causes a vibration of the residual affinities of the carbon atoms that results in the production of color. The theory of Baly, although couched in different terminology, brings out the mechanism of a force field surrounding the molecule, which is essentially of the character of the two preceding theories. Stieglitz's idea, however, attacks the question from the electronic standpoint and develops the point of the loss and gain of electrons. In the end, it shows that

he virtually considers the quinonoid structure essential to the production of color in aromatic compounds.

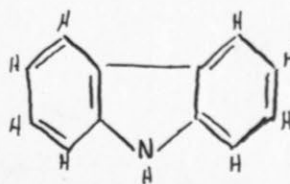
It will be seen from the review given of these theories that all are outgrowths of the fundamental chromophore theory of Witt. In a general sense, it may now be stated that any atom or group of atoms, which joined to a compound give it the property of visible color may be termed a chromophore. Relative to the depth of color produced by the addition of groups, it appears that no definite rule can be applied. It can only be mentioned that some groups such as $N=N$, $N=O$, and $C=S$ apparently are more efficient and dependable in this respect than other groups as $C=O$ or $CH=CH$. The theories have been of great value in directing and correlating the work of the color chemist.

Diphenylamine and Carbazole.

The two compounds, diphenylamine and carbazole, are now finding extensive use as important intermediates for the preparation of certain dyes. Due to this application, it would be of considerable interest to study the effect of auxochrome addition on the color of these compounds. The compounds are usually represented by the structures given below :



Diphenylamine.



Carbazole.

Both compounds are colorless in the free state. The derivatives chosen for investigation were the $N=O$, the NO_2 and the indophenols. The method of comparison was the selective absorption evidenced by these substances in the ultra-violet part of the spectrum as far as could be examined by means of the photographic plate.

II. Absorption Spectra.

a. Theory of Absorption Spectra.

With reference to the spectrum, generally speaking, there are two kinds of absorption. The first is general absorption, which consists in a general weakening of the whole spectrum. The second is selective absorption wherein parts of the spectrum disappear due to absorption. These parts may be only lines or again as is the case in most aromatic organic substances, they may be a series of lines, which would be called a band. Visible color is produced by selective absorption in the visible spectrum whereby part of the white light passing through a solution of a substance is plucked out. If a solution appears green, for example, it would indicate that all the spectrum except the green had been absorbed.

After a careful study of the visible spectrum, Prof. Stokes of Cambridge reached the conclusion that the electric spark, no matter whether it was produced by a prime conductor of an ordinary electrifying machine, or by the discharge from a Leyden jar, gave off rays of very high refrangibility, surpassing any of the solar rays.¹ Furthermore, he discovered that these rays pass freely through quartz while glass absorbs them. He therefore procured a lens and prism of quartz and on examining the solar spectrum, he discovered that an invisible region existed which extended as far beyond the previously known part as the latter extended beyond the visible. In the same year, Prof. Miller of King's College, London, published a paper describing the method by which he used a photographic plate to record

1 - Phil. Trans., 1852, 463.

this invisible or ultra-violet spectrum.¹

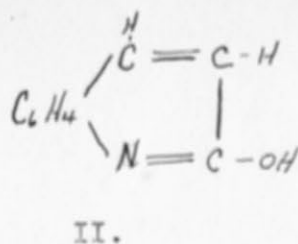
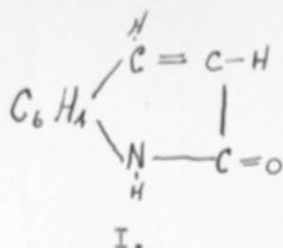
On further study of the subject, it was discovered that nearly all colorless aromatic organic substances possess absorption bands in the ultra-violet part of the spectrum, whereas addition of certain groups appears to produce an accompanying shift of the band or bands over into the visible. Therefore as Watson states, " a study of the color of a substance thus involves the examination of its entire visible and ultra-violet spectrum, and further, as Hartley and his successors have shown, of the change of the absorption with the concentration of the absorbing substance."² It should also be mentioned that there is an infra-red region of the spectrum, characterized by its heating effect and possessing rays of long wave length. Absorption in this region is measured by the heating of an electrical resistance in an instrument known as Langley's bolometer. Coblentz conducted a very comprehensive investigation of the infra-red region and has published his results in several volumes.³

After several years of investigation, it was concluded that an important use of absorption spectra was the determination of the formula of a substance whose structure was doubtful, by comparison of its spectrum with the spectrum of a substance of known structure. The work of Hartley, Dobbie, Lauder, Hantzsch, Coblentz, Baly and others has been of great value in arriving at this conclusion. An example will show more clearly the application of this principle. The chemical reactions of carbostyryl are such that it is impossible to determine whether it possesses the keto structure shown in I, or the enol structure appearing in II.

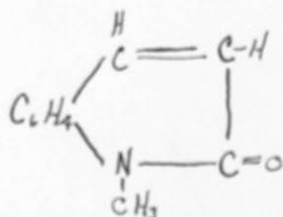
1 - Phil. Trans., 1862. Pt.2., 861.

2 - Watson. "Color in Relation to Chemical Constitution"
Longmans. 1918. p. 21.

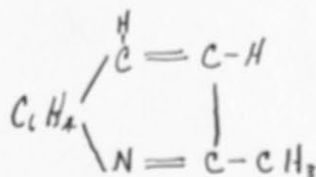
3.- Coblentz. "Infra Red Spectra." Carnegie Inst. 1905.



The methyl derivatives of both forms are known, whose formulae have the structures :



Methylpseudocarbostyryl.



Methylcarbostyryl.

The absorption curves of the three substances were examined by Hartley and Dobbie¹, and the similarity of the curve of methylpseudocarbostyryl to that of carbostyryl proved that the constitution of the latter was ketonic in character as shown in I.

Ley and Ulrich² have shown that the structure of an ortho amino acid with an open chain and one with a closed chain (betaine) can be distinguished between by means of the absorption curves. The knowledge we now possess of the complete structure of some of the alkaloids has proven the trustworthiness and the application of this method of examination.³ Lowry and Desch have investigated the relation between dynaminc isomerism and selective absorption⁴. They traced the extent to which isomeric change determines the existence of a banded spectrum. Lowry showed that by altering the solvent it was possible to vary at will the period of change, to accelerate

1 - J. Chem. Soc., 1899, 75, 640.

2 - Ber., 1909, 42, 3440.

3 - Tinkler. Trans., 1911, 99, 1340; Dobbie and Fox. *ibid.*, 1914, 105, 1639.

4 - Trans., 1909, 95, 807, 1340; 1910, 97, 900.

or retard it, or to stop it altogether. From the foregoing it can be seen the general usefulness of the study of absorption spectra.

For purposes of discussion, the effect of addition of groups on the displacement of absorption bands can best be shown by a brief summary of their effect when added to benzene, as we like to regard benzene as the parent substance of all aromatic organic compounds. Benzene itself possesses seven bands in the distant ultra-violet. On introducing alkyl groups, the bands apparently fuse together. Among the di-derivatives of benzene, the para compounds usually retain more of the benzene bands.

Halogens. Halogens produce a similar merging effect with a shifting toward the red; iodo benzene having merged all seven bands completely. Unsaturated side chains produce an analogous effect.

Amino. In the case of the amino compounds, like aniline where the nitrogen has a valence of three, the benzene bands are all united into one; however when the hydrochloride is prepared, some of benzene bands reappear in the same positions as originally found.

Hydroxyl. The OH group, as found in phenol produces a broad, deep band, which shifts toward the red end, opposite from aniline, when its sodium salt is prepared. In the case of p-amino phenol, the reverse effect is found when an acid is added.

Nitro. Nitro groups generally cause a fusion of the bands, without much displacement. When nuclear hydrogen atoms are substituted in nitro compounds by OH or NH₂ groups, several distinct bands are produced and a well-defined movement is observed.

Carboxyl. Benzoic acid produces a union in the bands, and a movement toward the red end while, the salts of the acid shift the

bands back toward the ultra-violet. As in unsaturated side chain-derivatives of benzene, similar derivatives of benzoic acid (cinnamic acid, for example) show a displacement toward the red part of the spectrum, with the production of a broad band.

As far as can be stated the usual effect of substitution in the benzene nucleus is to produce color by a gradual movement of the absorption bands from the ultra-violet into the visible. As given by Cohen¹, the order of the groups relative to their displacement effects, follows. The groups producing maximum displacement are found on the right.



B. Description of the Apparatus.

The study of the color of a substance, by means of an examination of its visible and ultra-violet spectrum is accomplished by passing white light through a liquid layer contained in a quartz-sided cell and thence through the slit of a spectrograph where the rays pass through quartz lenses and prisms, and are recorded on the surface of a photographic plate, specially sensitized to record rays of high refrangibility. For substances like benzene, for example, the spectrum appears as a series of long narrow bands in the far ultra-violet.

For the spectrum pictures which we prepared, a Hilger Spectrograph, size "C", of 24 inch focus, was used. As our source of light, we chose an iron spark. A drawing of the entire apparatus appears as Plate No. 1. The cell we employed was made of a section of glass tubing, 5/8 inches in diameter. It had a hole in the side where it was fastened on to the bottom of a graduated burette.

1 - Cohen. "Organic Chemistry." Pt. II. p. 89.

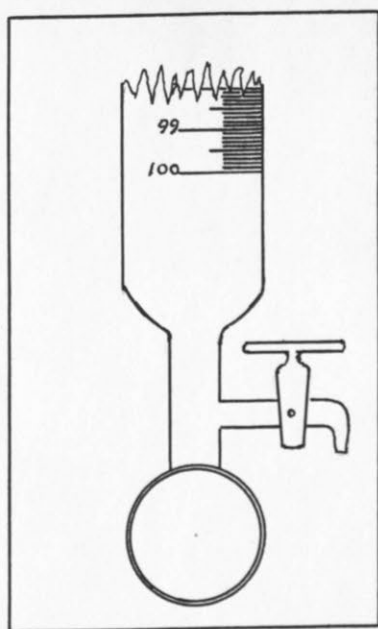
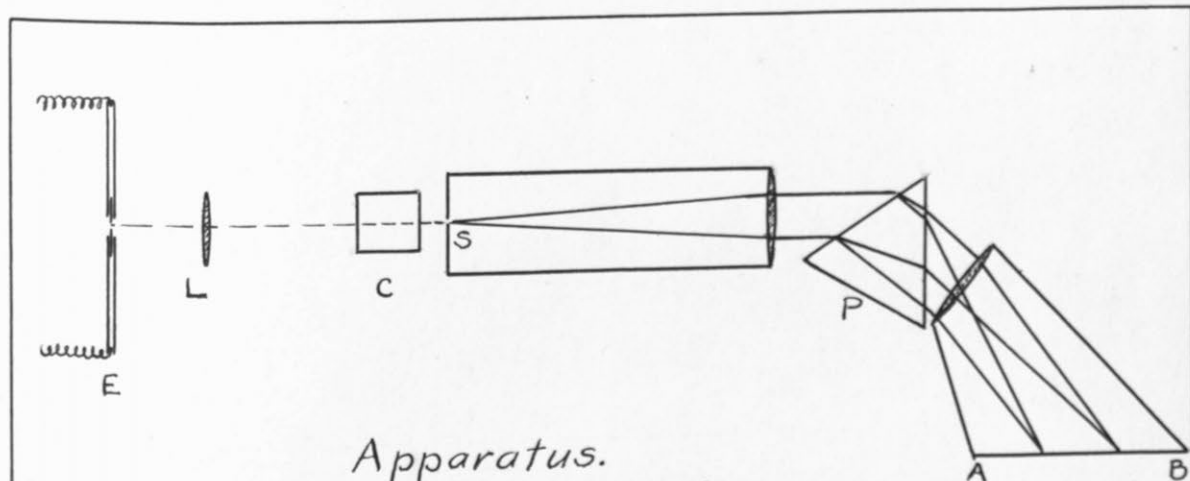


Plate No. 1.

Bottom of Burette Cell.



Apparatus.

- E = Iron Electrodes.
- L = Lens to direct rays on slit.
- C = Cell.
- S = Slit.
- P = Prism.
- AB = Photographic Plate.

In the neck, between the cell and the bottom of the burette, there was a small glass elbow, which served as a means of emptying the burette. The sides of the cell were made of two quartz plates cemented on with water glass. The distance from the inside of one quartz plate to the inside of the other, or in other words the length of the cell, was 13.8 mm. For most of the photographs, a slit of .06 mm. opening was used and an exposure of 15 seconds made. We used a logarithmic dilution instead of a linear. In this way, we obtained a spectrum at once as it would appear if plotted in the form of a curve. We believe this to be a decided improvement, as the results may be plotted much easier from the direct measurement of the photographic plate.

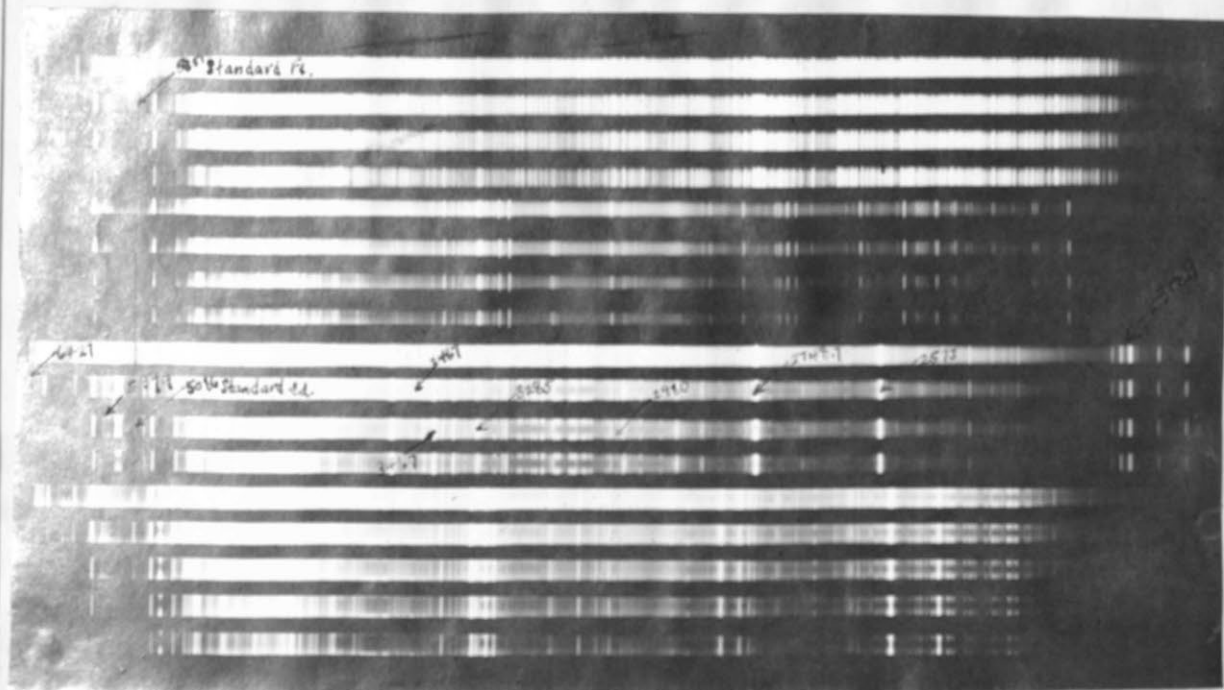
In our experiments, we sometimes used a two-thirds dilution and at other times, a five-sixths dilution, depending on the character of the absorption produced. That is, if the bands were rather hard to distinguish from a plate where a two-thirds dilution had been used, it was partly repeated using the slower dilution. All amounts of substances examined were weighed out and the solvent added so as to produce molar concentrations. In detail, a two-thirds logarithmic dilution was carried out as follows: 4 cc. of the solution being examined, was added to the cell. An exposure was made, the plate turned, and 2 cc. of the solvent added with thorough mixing. Another exposure was made, and 3 cc. of solvent added. This procedure was continued with the addition of 4.4 cc., 6.66 cc., and 10.08 cc., respectively. After an exposure at the last dilution, the solution was run out of the burette until exactly 6 cc. remained in the cell. Then the entire procedure was repeated until 18 exposures had been made. At this point the cell was carefully rinsed out, and one more

exposure made using the pure solvent. This method of emptying the cell saved considerable solvent as well as enabled a more thorough mixing to be made. The photographic plates used were the Cramer Spectrum Plate, size 4 x 10, made by the Cramer Plate Company of St. Louis, Missouri. These were developed in a metol-hydroquinone developer over a period of three minutes.

c. Reproduction of Results.

In the measurement of the wave lengths of the edges of bands on a plate exhibiting selective absorption, considerable difficulty is encountered. The principle source of error arises from the choice of the point where the band begins. For our drawings, we have chosen the point where the first visible absorption is apparent to the eye. This is done by a careful comparison of the density of the solvent exposure with that of each of the dilution exposures. To decide this point the plate is placed on a frame and leaned against a piece of opal glass illuminated from behind by an electric light. After the points were chosen, a light line was drawn through them with a pen, marking the edges of the band.

At the present time, the method of expressing conclusions relative to the number and position of bands is by means of a curve. In the general curve, the point "a" in Figure I is defined as the head of a band. The ordinate of this point indicates the persistance of the band. Our curves were prepared using for abscissae, the wave numbers or oscillation frequencies of the spectrum at the different points. By the term, "oscillation frequency" is meant, as Baly defines it, the reciprocal of the wave length reduced to vacuum. For ordinates, we employed the logarithms of the actual thickness of the



Photograph of Spark Spectra.

1. Iron
2. Copper
3. Cadmium
4. Zinc.

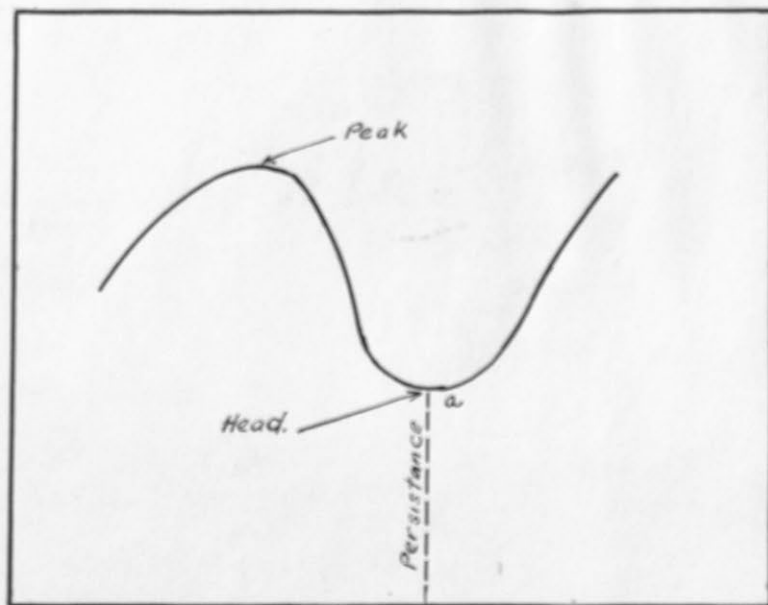
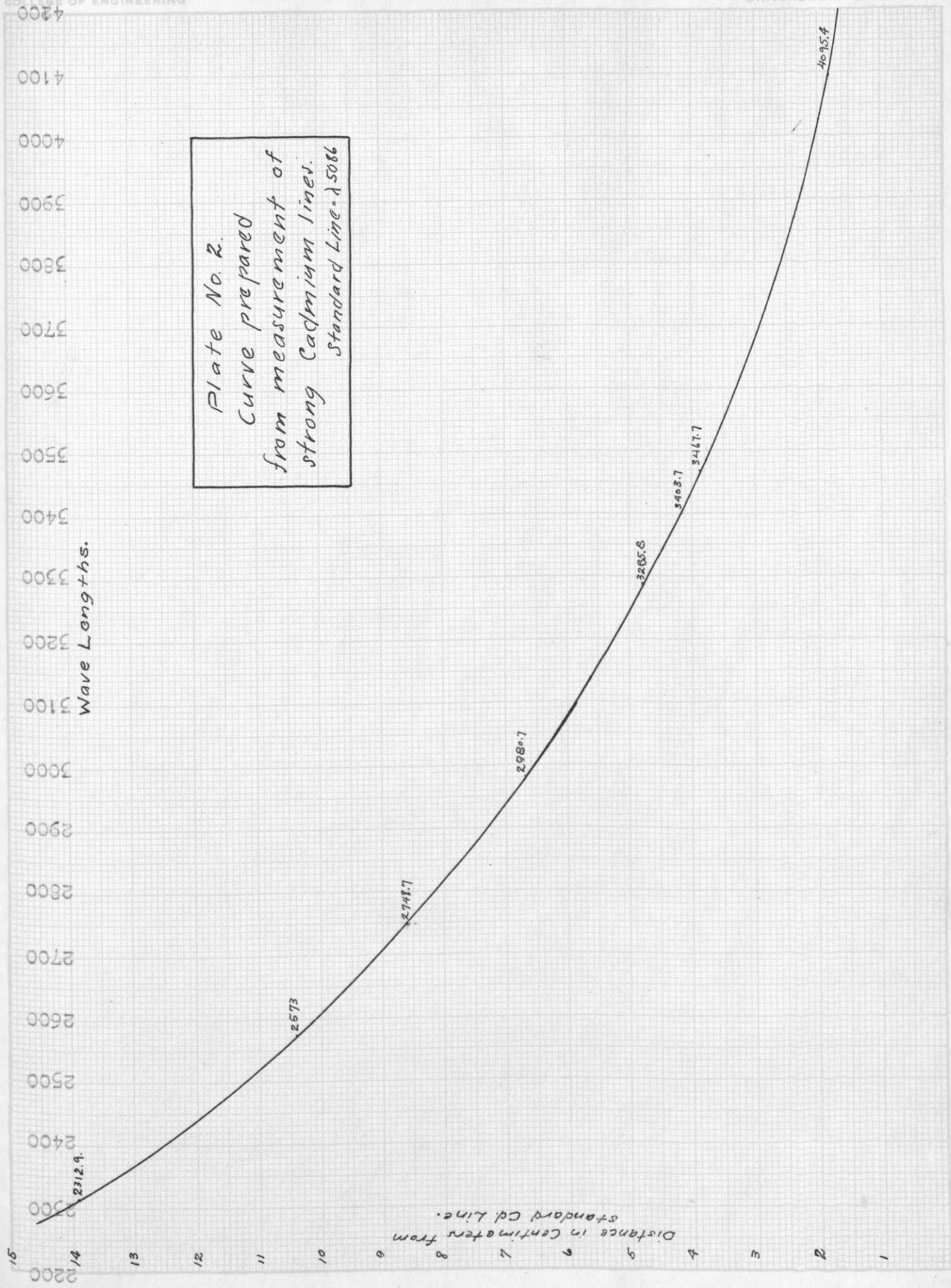


Figure No. 1.

Plate No. 2.
 Curve prepared
 from measurement of
 strong Cadmium line.
 Standard Line - 15086



of the solution as calculated from our dilutions. On the right hand side of each curve will also be found the relative thickness using 1000 as the basis of our first exposure.

In determining the wave lengths of the points, it was found that use could not be made of the scale on the spectrograph as an adjustment had thrown it out. We therefore ran a plate of several metallic spectra, such as iron, copper, cadmium and zinc. Working, after the method of Baly, with cadmium line, wave length 5086.06 which is practically identical, for purposes of measurement, with iron line 5056, cadmium lines were chosen with their respective wave lengths, and the distance in centimeters from the standard line was found. These two figures, the wave length and the distance in centimeters, were plotted using the latter as ordinates and the former as abscissae. This curve appears as Plate No. 2. Then, on preparing a curve of the absorption spectrum of a substance, the distance from the standard line to the edge of the band was measured in centimeters and by referring to our curve, we could read off directly the wave lengths. To convert the wave lengths to oscillation frequencies, we used the table of Dr. N. Rosanoff that appears in Plotnikow's "Photochemische Versuchstechnik" on page 300. In this way, a curve that faithfully represents the absorption band is produced.

III. Diphenylamine, Carbazole and Several of their Derivatives.

Discussion of the Curves.

Introduction.

1 - Baly. "Spectroscopy", p.134.

From the discussion which was taken up in the first part of the paper, it is not out of place, at this point, to make a few predictions. The only one of the group of spectra prepared that had been run before is that of Diphenylamine. Therefore this substance will not be considered here. We would expect, however, for carbazole, a spectrum influenced by the combined spectra of benzene, indol, and pyrrol. The first and last named had been run, but the second substance had not been examined. Pyrrol has only general absorption, while benzene, as stated before, possesses seven bands in the distant ultra-violet, the nearest one to the visible, having its head at $\frac{1}{\lambda}$ 3710. Therefore it could be predicted that the substance, indol, which is a combined benzene and pyrrol ring, would have quite a distinct band, the head of which would be shifted over toward the visible. Further, on adding another benzene ring to the indol structure, it would be anticipated that the effect would be a widening of the band of indol, caused by the distant ultra-violet bands of the additional benzene ring, as well as a further shift toward the visible.

On adding the nitroso group to the N position of diphenylamine, it could be thought that a shift might be produced in the one large band that this compound has, along with the appearance of one or two bands in the ultra-violet due to the influence of the group itself. If the group exerted enough influence to move the edge of the band just into the visible, it could be predicted that the color of the resulting compound would be greenish yellow to yellow. Upon preparing the para derivative, a deeper colored compound would probably result, whose spectrum should differ from the N-nitroso form. Results similar in character would be predicted for the corresponding

nitroso derivatives of carbazole.

With the nitro group, however, we would expect a stronger shifting effect. In the first place, the substance would no doubt be more highly colored, as absorption would be expected to continue over as far as the blue or blue-green part of the visible, which would produce an orange or a red-orange colored compound. The spectrum of this compound would probably have several bands in addition to the one large band extending partly into the visible.

In the indophenols, where a large colored molecule has been added (P-Nitroso Phenol), the absorption would be expected to extend over into the yellow or orange, with the production of a substance yielding a reddish-violet or indigo solution when dissolved in alcohol. Again, the influence of the spectrum of the group added may be so great as to partly hide the effect of the diphenylamine or carbazole radicle.

With these prophesies in mind we will now discuss the results as actually obtained.

a. Diphenylamine.

The spectrum of this substance had been prepared by two investigators. It was decided to run its spectrum, however, to be able to check up our instrument. Examination of the spectrum, of diphenylamine, appearing in Plate No. 3, shows that general absorption begins at about $\frac{1}{2}$ 3100, and extends in a rapidly falling curve until the head of a band appears at $\frac{1}{2}$ 3535. The logarithm of the actual thickness of a M/20000 solution at this point is .9435. The result compares favorably with that of Baker published in 1907, who

1 - Baker. Trans., 1907, 91, 1496.

- Purvis and McClelland. Trans. 1912, 101, 1517.

Oscillation Frequencies.

Logarithms of the Actual Thickness of a $\frac{M}{20000}$ Solution.

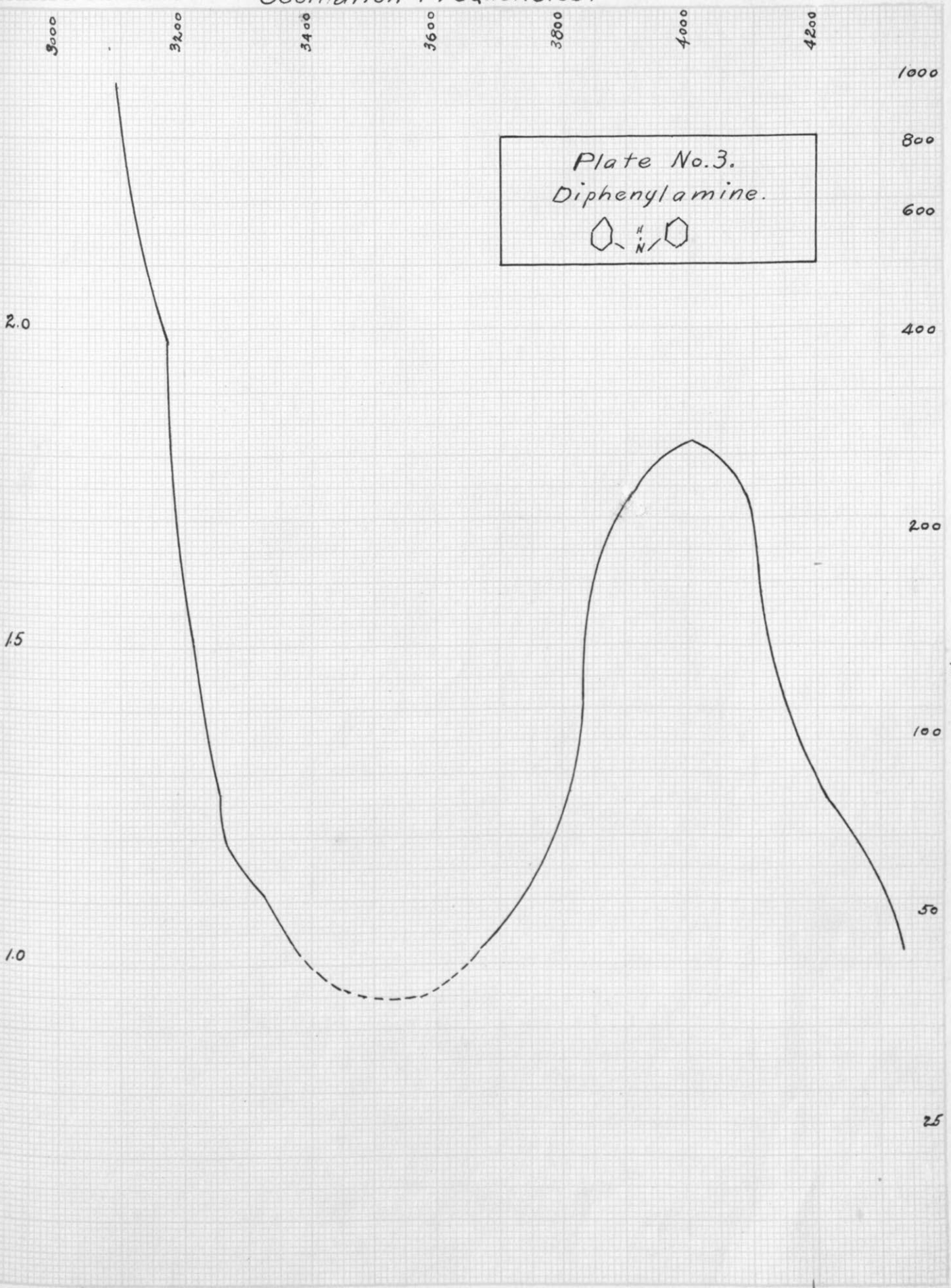
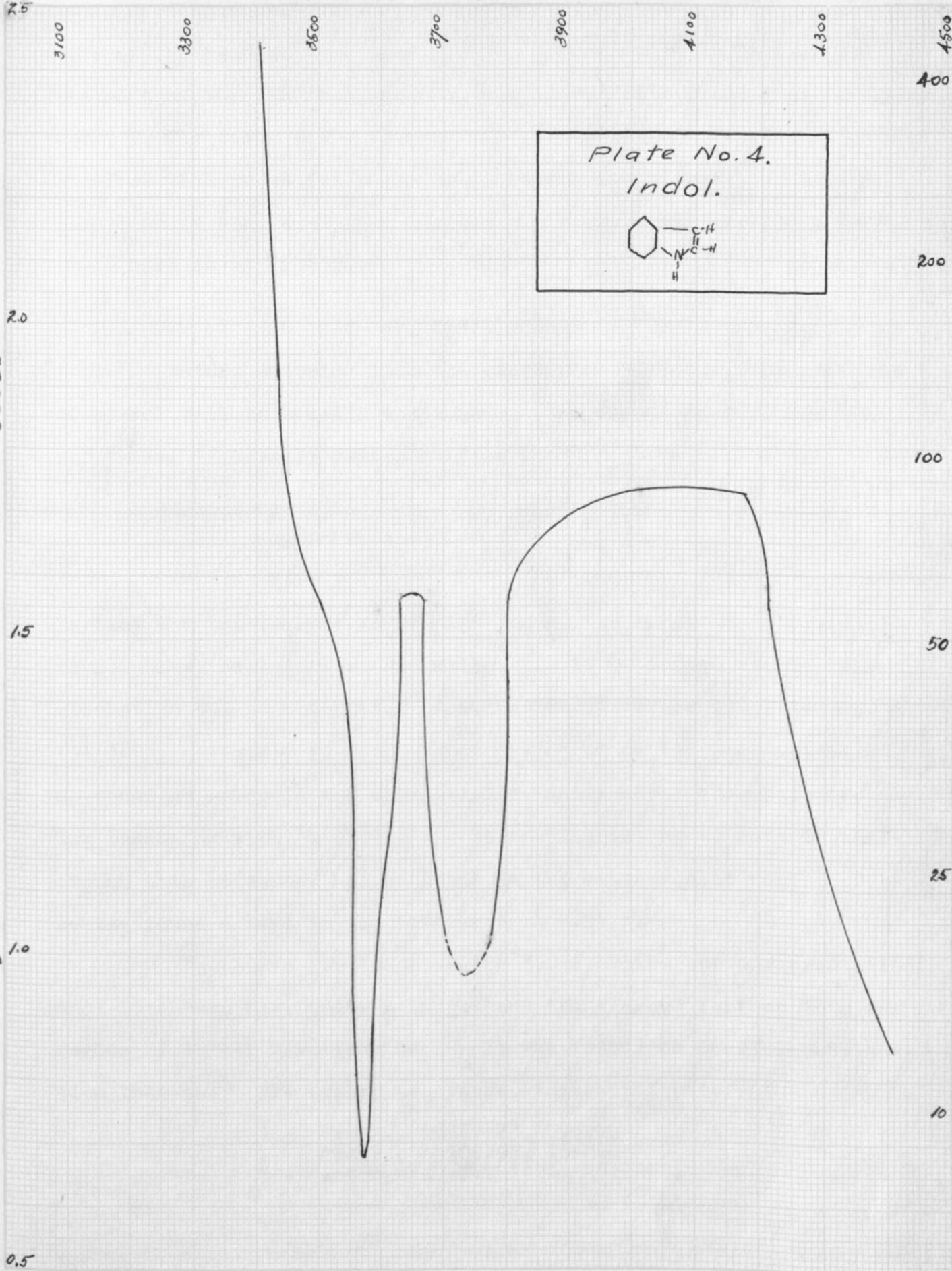


Plate No.3.
 Diphenylamine.
c1ccccc1N(c2ccccc2)

Relative Thickness

Oscillation Frequencies.

Logarithms of the Actual Thickness of a $\frac{M}{30000}$ Solution.

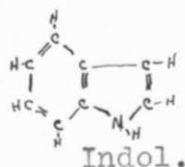
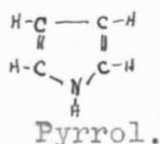


Relative Thickness.

gave as the head of this band $\frac{1}{\lambda}$ 3550. Purvis and McClelland in 1912 stated that the band had its head at $\frac{1}{\lambda}$ 3560. All results are comparable. The curve rises to a peak at $\frac{1}{\lambda}$ 4005, Log. Thickness 1.822, and from that point falls gradually toward the ultra-violet. Diphenyl amine can be said to possess one deep, wide absorption band whose head is at $\frac{1}{\lambda}$ 3535.

b. Indol.

Before entering into the discussion of indol, the spectrum of pyrrol will be briefly mentioned. The structure of these two substances is usually represented as shown.



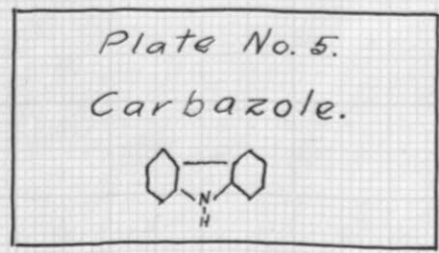
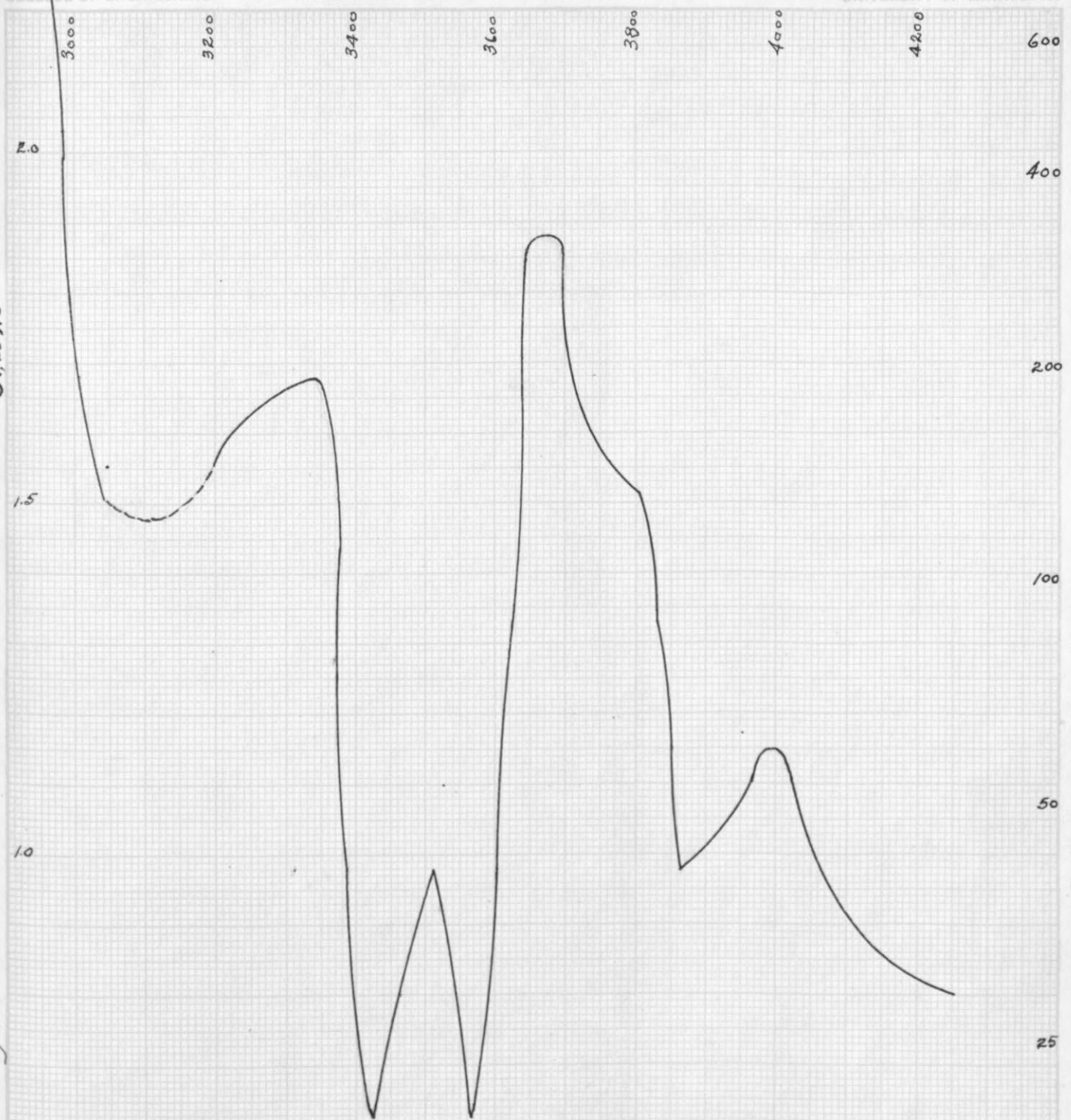
Hartley and Dobbie₁ made an examination of the spectrum of pyrrol in 1898. They came to the conclusion that it possessed strong general absorption but no absorption band. Absorption was complete beyond $\frac{1}{\lambda}$ 3893. Later, in 1910, Purvis₂ reported on the same substance. He found no bands in the ultra-violet, and general absorption appearing beginning with $\frac{1}{\lambda}$ 3781. It is interesting to note that although this substance had no bands in the ultra-violet region, Coblentz₃ found a band in the infra-red at 2.94 u.

The curve for Indol, Plate No. 4, bears out our predictions that it should have quite a large band transferred further into the region of longer wave-lengths. It was found, on careful examination that there are really two bands, instead of one. These may be

- 1 - Trans., 1898, 73, 598.
- 2 - Trans., 1910, 97, 1648.
- 3 - Astrophys. J., 1904, 20, 207.

Oscillation Frequencies.

Logarithms of the Actual Thickness of a $\frac{M}{31,257.6}$ Solution.



the merged effect of the seven benzene bands, the two strongest still remaining. The heads of these two bands are found to be at $\frac{1}{\lambda}$ 3575 and $\frac{1}{\lambda}$ 3735, respectively. The Log. Thicknesses are .675 and .965 respectively. Toward the ultra-violet, the band rises to a peak at $\frac{1}{\lambda}$ 3980, and then descends on a sharp curve.

c. Carbazole.

In the curve for carbazole, we find four distinct bands. The two bands of indol are still present, but they are not separated nearly so much as in the spectrum for that substance. Examination of Plate No. 5 shows that the heads of these two bands have been slightly shifted. They appear at $\frac{1}{\lambda}$ 3424 and $\frac{1}{\lambda}$ 3565. The persistence of both bands is the same; Log. Thickness $M/30000$, .625. Two new bands have made their appearance; one, very near the visible with its head at $\frac{1}{\lambda}$ 3105, and the other, caused probably by the benzene bands in the ultra-violet, with its head at $\frac{1}{\lambda}$ 3864. The persistence of these bands is Log. Thickness 1.480 and .9785 respectively.

These results are somewhat in accordance with the predictions. The large deep band, which is divided into two parts near its head, is the band that was anticipated. The small band in the region of the benzene bands is probably the result of the merging of the seven bands of the extra benzene nucleus added to indol. The unexpected band appearing so near the visible may be thought to be one of the reasons that carbazole is proving to be so good an intermediate. It is almost near enough to produce visible color. As will be mentioned later, the color of the nitroso derivative may, no doubt be traced directly to this band. It should be mentioned that carbazole shows a beautiful violet-blue fluorescence, especially marked when in alcoholic solution.

Oscillation Frequencies.

Logarithms of the Actual Thickness of a $\frac{M}{30,000}$ Solution.

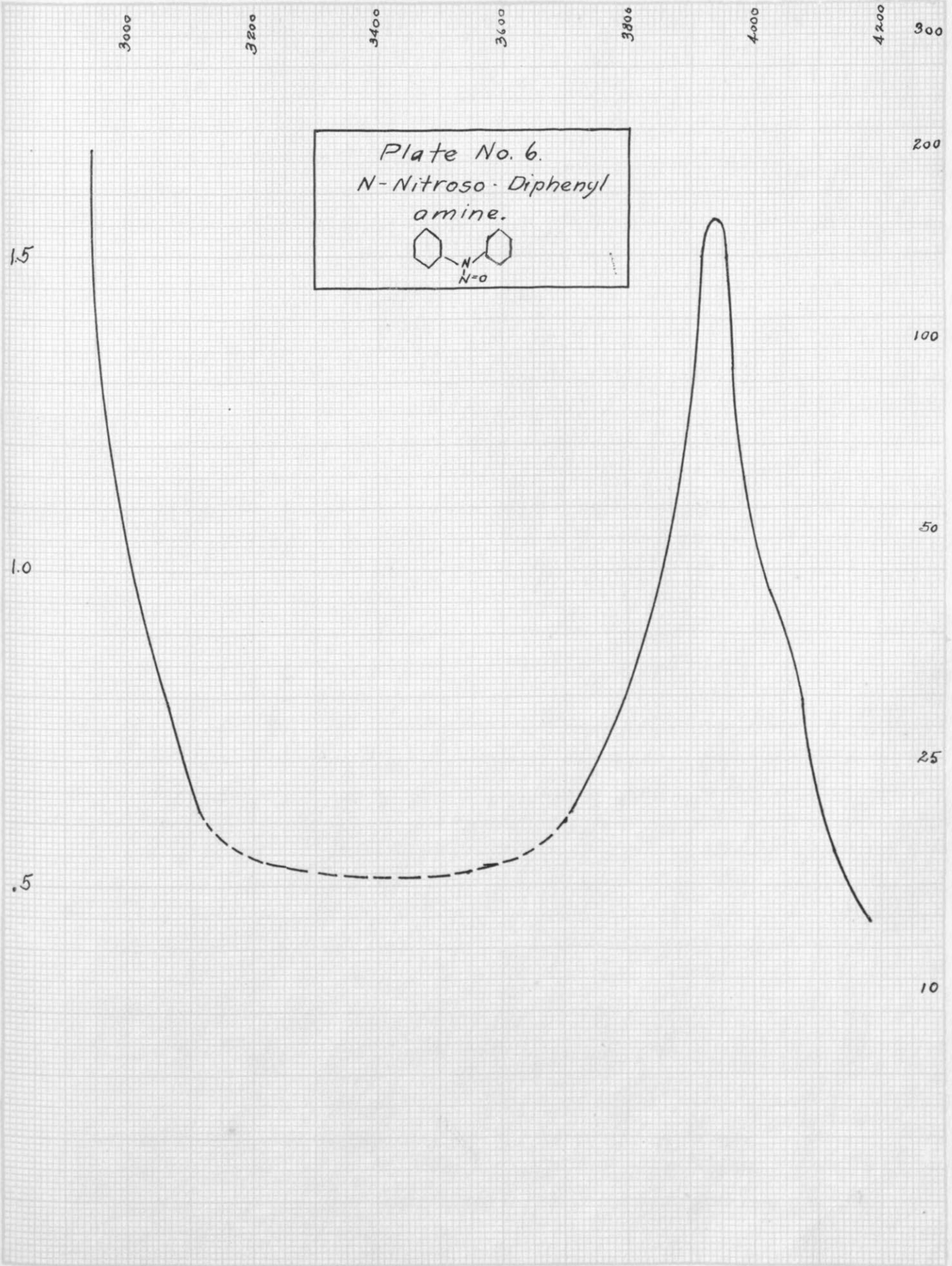
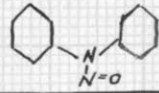


Plate No. 6.
 N-Nitroso-Diphenyl
 amine.

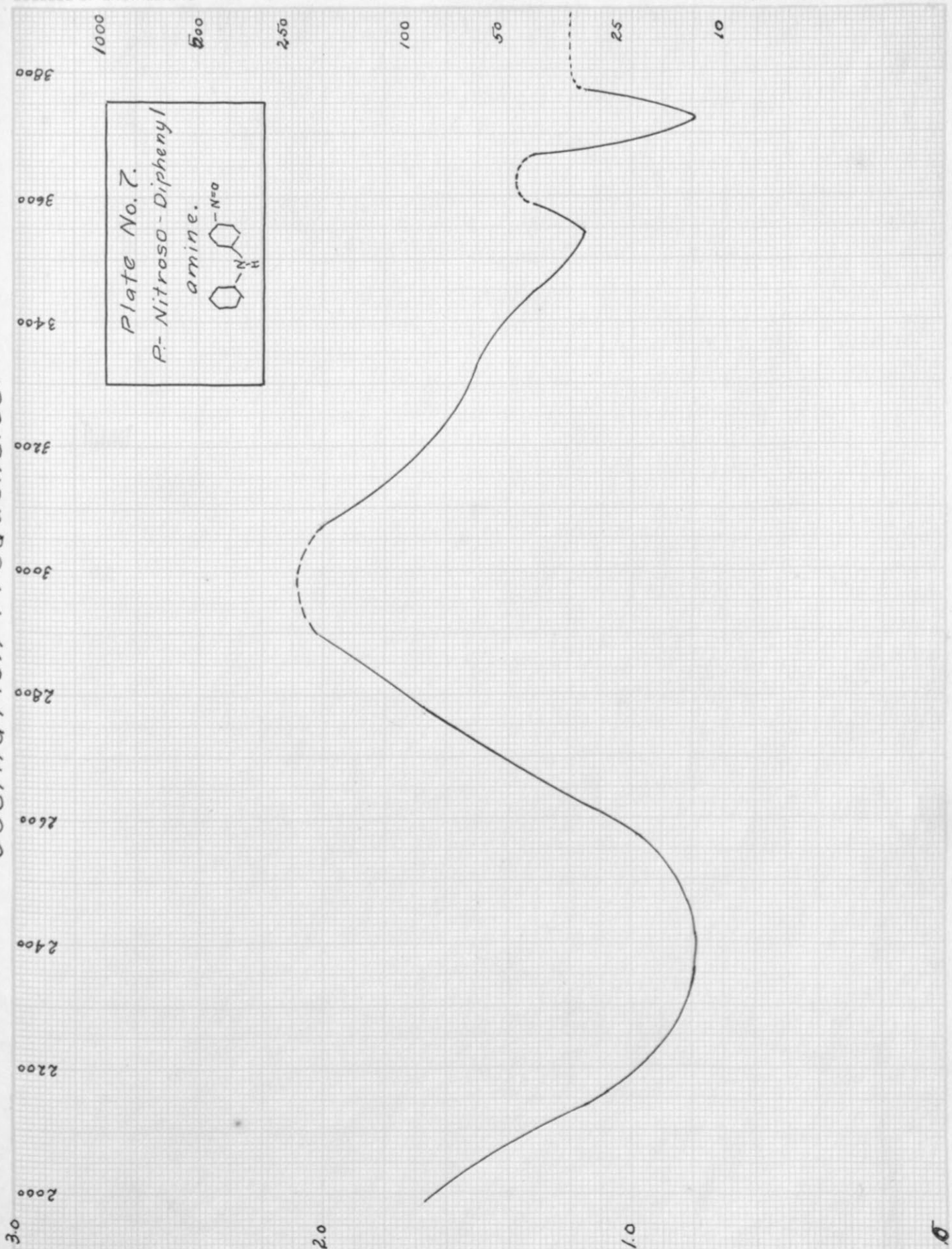
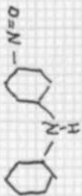


Relative Thickness

Relative Thickness.

Oscillation Frequencies.

Plate No. 7.
 P-Nitroso-Diphenyl
 amine.



Logarithms of the Actual Thickness of a 30000 M Solution.

P-Nitroso-Diphenylamine

d. The Nitroso Derivatives.

N-Nitroso Diphenylamine.

On preparing pure N-nitroso diphenylamine, it was found to be light greenish-yellow in color, substantiating the predictions. The curve for the absorption registered by this compound does not, however, wholly agree with the predictions. In the first place, it is very much like the curve for diphenylamine, with one apparent difference; that is, the main band has been considerably widened, as it now extends over into the edge of the visible blue violet. The second contradiction is that there are no small bands appearing in the distant ultra-violet as was thought might be the case due to the influence of the nitroso group itself. The head of the band has been moved slightly, as it now falls at $\frac{1}{\lambda}$ 3420, with the Log. Thickness, .516. From the peak at $\frac{1}{\lambda}$ 3930, the edge descends sharply, into the far ultra-violet. The curve appears as Plate No. 6.

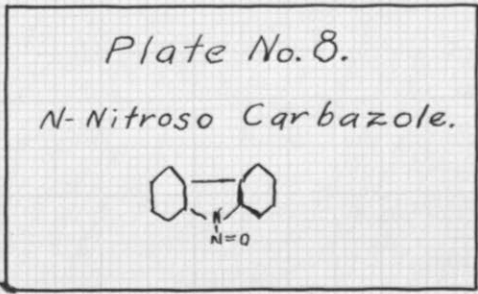
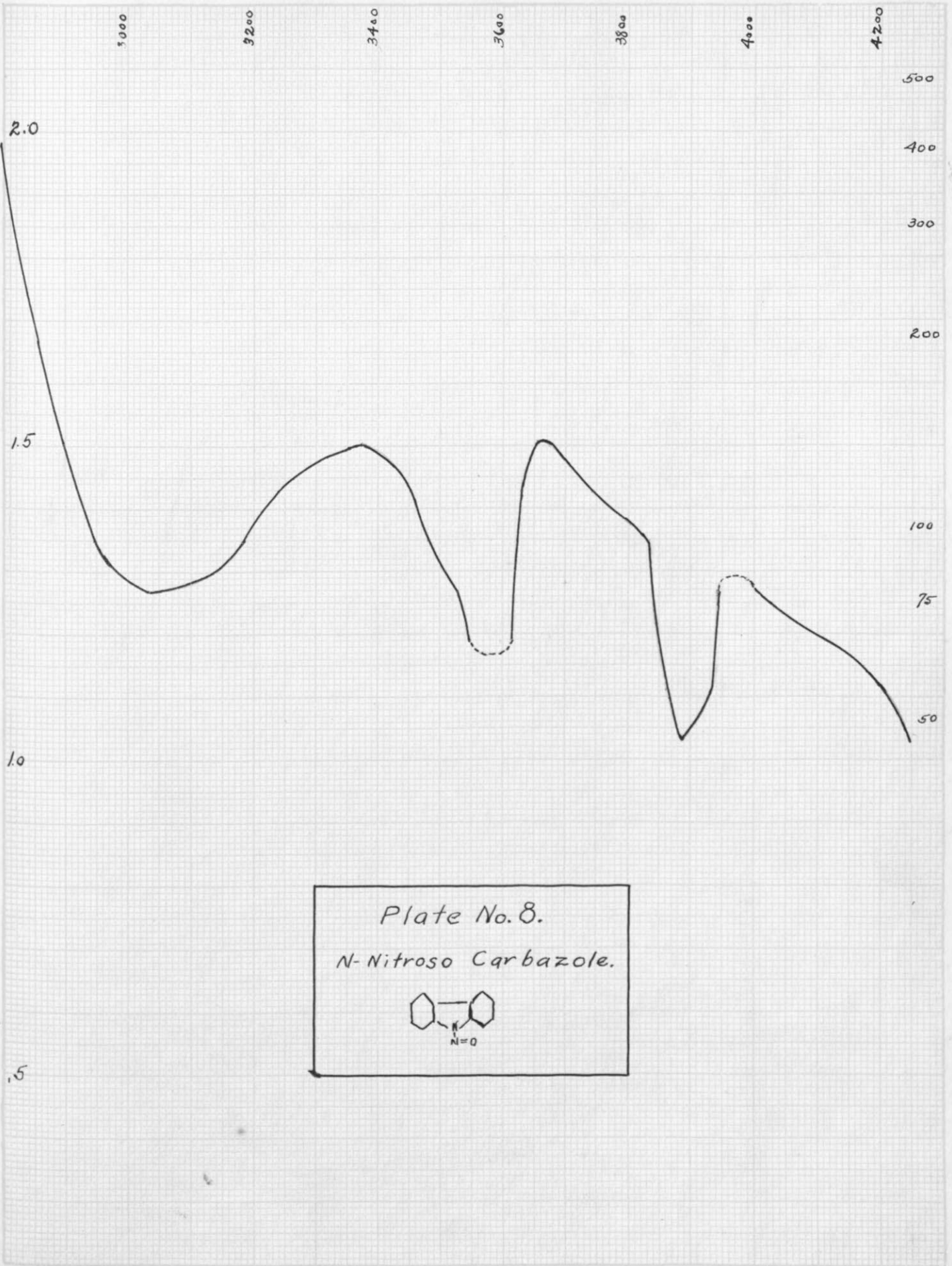
P-Nitroso Diphenylamine.

The aniline type of rearrangement which occurs when the nitroso group is shifted around from the N position to the para position appears to exert a strong influence on the color of this compound as it changes from the light yellow to a deep blue. The curve for this substance, represented by Plate No. 7, shows the effect of the strong absorption in the visible as the most prominent band is found with its head at $\frac{1}{\lambda}$ 2400, Log. Thickness, .894. The band is large and wide, rising to a peak on the right at $\frac{1}{\lambda}$ 2984. From that point, it descends in a gradually falling curve until another small band is produced with the head at $\frac{1}{\lambda}$ 3542, Log. Thickness, 1.078. This band is followed by another, slightly deeper band at $\frac{1}{\lambda}$ 3625, Log. Thickness, .898. These bands may be the ultra-violet bands which

Oscillation Frequencies.

Logarithms of the Actual Thickness of a $\frac{M}{30000}$ Solution.

Relative Thickness



were predicted for N-nitroso di-phenylamine, but did not appear. That is, the effect of the shifting of the nitroso group around the ring may be that of allowing it to exert enough influence to produce the two bands in the ultra violet.

N-Nitroso Carbazole.

When this substance was prepared in the pure state, it was found to possess a beautiful golden-yellow color, much stronger than the color of the corresponding diphenylamine derivative. As was briefly mentioned before, this difference in depth of color may be explained by the fact that carbazole possesses a band nearer the visible region than does diphenylamine. Therefore, it would probably be more deeply colored than N-nitroso diphenylamine, which is the case. The curve, as drawn in Plate No. 8, shows the presence of three distinct absorption bands. None of them are very persistent, at least not so much as the two most prominent bands of carbazole. The heads of these bands are found at $\frac{1}{\lambda}$ 3038, $\frac{1}{\lambda}$ 3580, and $\frac{1}{\lambda}$ 3888 respectively. The persistences expressed in the same order, are 1.270, 1.168, and 1.034. The edge of the band rises into the visible on the left on a rapid ascent. The last band on the right is apparently the same one as appeared in carbazole. An attempt was made to prepare the P-Nitroso Carbazole, but it did not meet with success.

e. O-Nitro Diphenylamine.

Relative to the color of O-nitro diphenylamine, it was found to agree closely with predictions, as it was reddish-orange. In other words, the nitro group must exert a stronger shifting influence on the absorption band in diphenylamine, than does the nitroso group. . . On measurement of the photograph and construction of

Relative Thickness.

Oscillation Frequencies

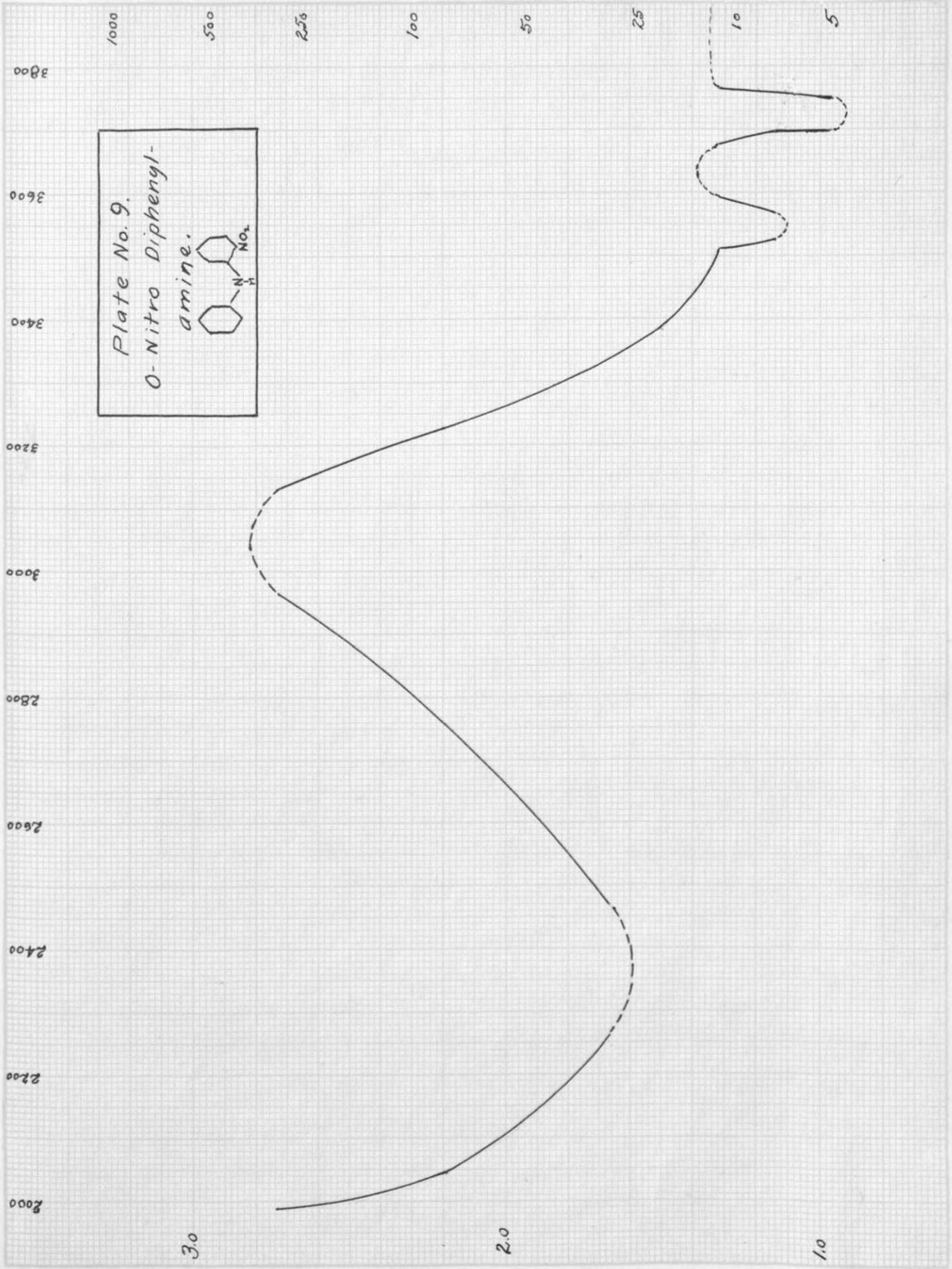
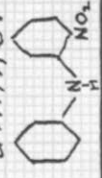


Plate No. 9.
O-Nitro Diphenyl-
amine.



Logarithms of the Actual Thickness of a 30000 Solution.

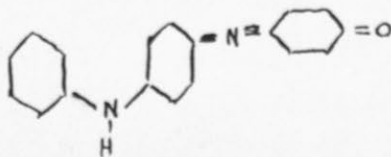
the curve, appearing as Plate No. 9, it was found that the substance is characterized by one very large, broad, deep band in the visible and two small bands in the ultra-violet. The large band has its head at $\frac{1}{\lambda} 2365$ and then rises on a smooth curve to a peak at $\frac{1}{\lambda} 3042$, from where it descends sharply to the point where the first small band appears. This band has a head at $\frac{1}{\lambda} 3550$ and the adjoining small band, slightly more persistent, at $\frac{1}{\lambda} 3725$. The large band in the visible is not as persistent as either of the two smaller bands, as the persistence of the large band is 1.590, while the two smaller, are 1.120 and .920 respectively, going from left to right. These two small bands may be due to the influence of the auxochrome, as it was suggested in the discussion of P-Nitroso Diphenylamine. An interesting fact about the curve for O-nitro diphenylamine is that it is almost identical with that of P-nitroso diphenylamine.

Several unsuccessful attempts were made to prepare the nitro derivatives of carbazole.

f. The Indophenols.

Indophenol of Diphenylamine.

The structure of the indophenol of diphenylamine is usually looked upon as

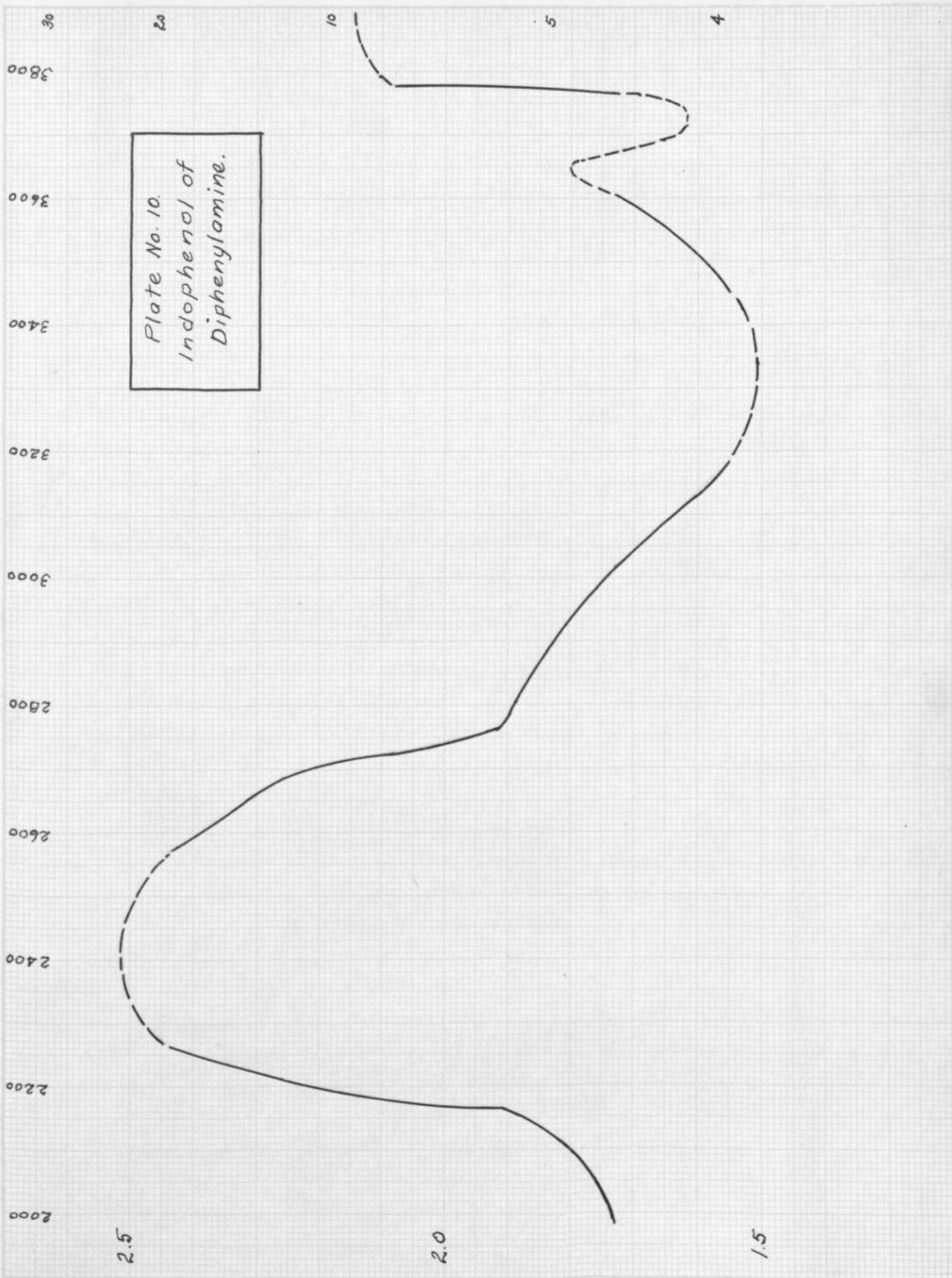


When prepared pure, in the dry state, it is a very dark blue in color. In alcoholic solution it is a deep indigo under transmitted light. The addition of the grouping, p-nitroso phenol, has apparently produced a large displacement in the absorption bands. The curve for p-nitroso phenol, prepared by Baly, Edwards, and Stewart appeared in

Relative Thickness.

Plate No. 10.
Indophenol of
Diphenylamine.

Oscillation Frequencies

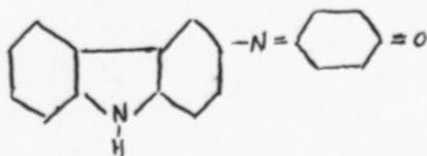


Logarithms of the Actual Thickness of a 152.572 Solution.

1906. It shows two prominent absorption bands; one at $\frac{1}{\lambda}$ 2650, and the other at $\frac{1}{\lambda}$ 3760. The first has about twice the persistency of the second. Therefore, when the large band of diphenylamine is added to this band, the effect is a marked shifting of both bands far over into the visible. The curve for this substance, Plate No. 10 shows this fact quite clearly. On the left hand side, there is part of a large band appearing in the visible. Its head would probably be at $\frac{1}{\lambda}$ 1850, which is the same as $\frac{1}{\lambda}$ 5405. From this point, the curve ascends steeply until a peak is reached at $\frac{1}{\lambda}$ 2420, or about the edge of the visible. The next band is deep and wide, and has its head at $\frac{1}{\lambda}$ 3330, with a persistency for a $M/152,572$ at Log. Thickness 1.506. A short distance beyond this band, another, smaller band makes its appearance. The head is at $\frac{1}{\lambda}$ 3728, with Log. Thickness 1.615. The right hand side of this band is an almost vertical curve which turns sharply to the ultra-violet at Log. Thickness, 2.08. From the curve, it can be seen that the effect of combination of groups has been a large shifting of the bands of both compounds.

Indophenol of Carbazole.

The structure of this substance may be considered as shown.

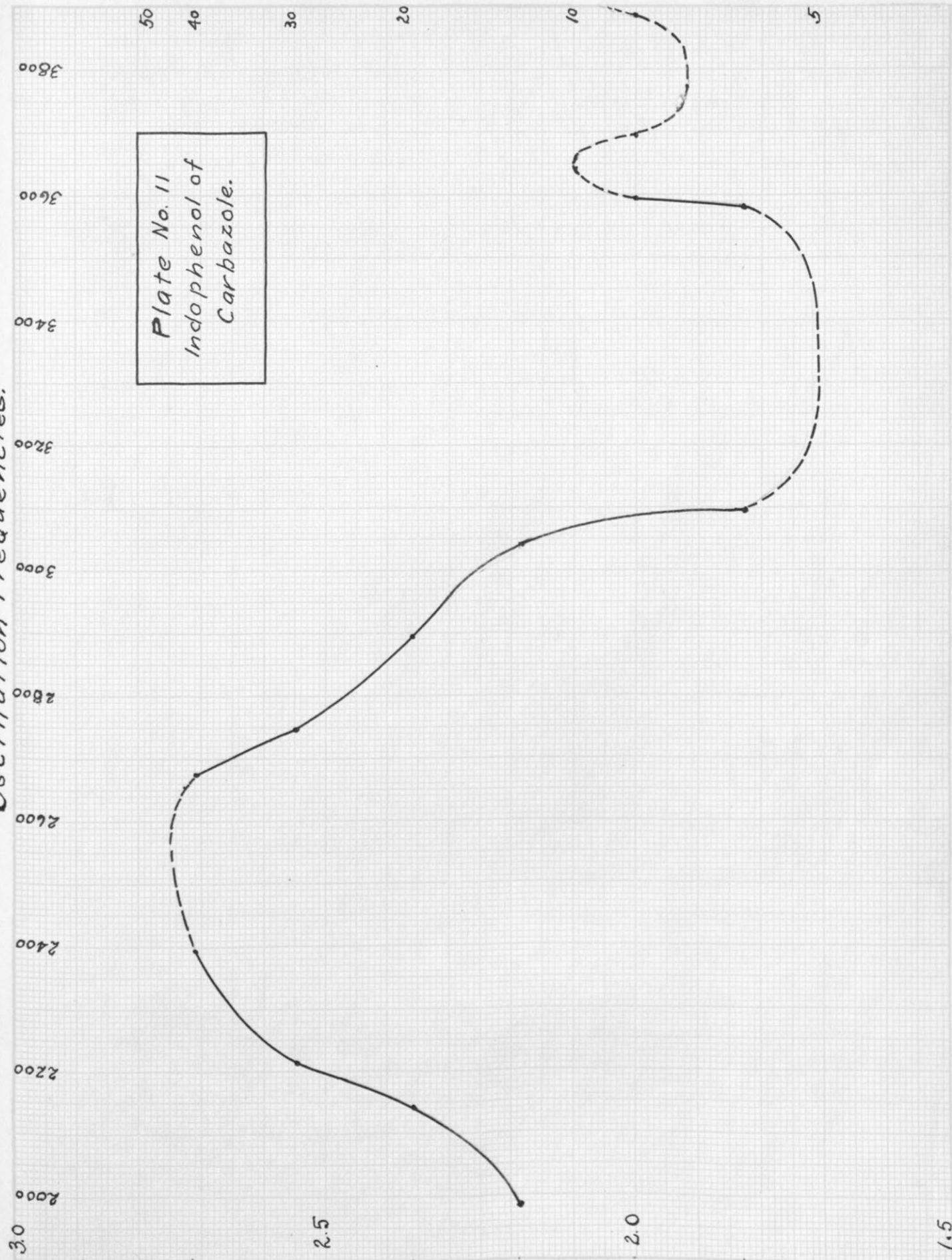


In the powdered form, when pure, the indophenol was of a very dark bluish-red color. It gave a wine-red color in alcoholic solution. The solubility was only about half that of the indophenol of diphenylamine. On preparation of the absorption curve, as shown in Plate No. 11, it appears very much like the curve for the other indo-

Relative Thickness.

Oscillation Frequencies.

Plate No. 11
Indophenol of
Carbazole.



Logarithms of the Actual Thickness of a 360000 Solution.

phenol. There is the same general appearance relative to the number and position of absorption bands. The distinguishing difference is found in the persistency of the two substances. The indophenol first discussed possesses the stronger persistency. In this indophenol for carbazole, there is a large band in the visible which probably has a head at about $\frac{1}{\lambda}$ 1900. Two other bands are found, both in the ultra-violet; the first at $\frac{1}{\lambda}$ 3350, and the second, less persistent band at $\frac{1}{\lambda}$ 3795. The persistency of the former (Substance is M/360000) is Log. Thickness 1.71 and the latter, 1.92.

Summary.

In general, it may be said that the curves as found bear out the facts. The nitro group appears to possess a stronger influence on the displacement of bands to the left or visible part of than does the nitroso group. A para shift of the nitroso grouping apparently has quite a powerful effect on the molecule, as it becomes more deeply colored as a result of this rearrangement. In the indophenols, the spectra are so much alike that it might be thought that it is mainly the added group which is producing the effect. The two spectra resemble, in a large measure the spectrum for p-nitroso phenol, so that this fact further points to such a conclusion.

IV. Experimental Work.

a. Diphenylamine and Carbazole.

Samples of both these substances, in a very pure condition were obtained from Merck and Kahlbaum, respectively. Upon taking the melting points, diphenylamine gave 54° and Carbazole, 238° . The conclusion reached was that they were sufficiently pure to run spect-

rum photographs of. Solutions were prepared, such that the diphenylamine was M/20 and the carbazole M/30.

b. Indole Purification.

A tan colored sample of indol resisted attempts to purify it when several different solvents were used. Finally, it was decided that water might dissolve it. A small amount dissolved readily in water, was boiled with animal charcoal, and filtered. It yielded beautiful white, leafy crystals melting at 52.5° . About half the sample was treated in the same manner and the resulting purified product used for a picture. An amount equal to .0975 gms. was dissolved in 25 cc. of alcohol. This solution was M/30.

c. N-Nitroso Diphenylamine.

Following the method of E. Fischer,¹ this substance was prepared pure in the following way. 15 grams of diphenylamine was dissolved in a cold mixture of 100 cc of alcohol and 9 cc. hydrochloric acid (Sp. Gr., 1.19). To this solution was slowly added 35 parts of NaNO_2 (containing 28% N_2O_3) in a concentrated solution (2:3). With constant stirring, the liquid first appeared a dark brown color and later became a light tan. After the reaction had apparently reached an end, the yellow, granular crystals of the nitrosamine were filtered off with suction, washed with alcohol and water, and dried. The water removes any salt that may be mixed with the crystals. All of the product obtained was recrystallized twice from hot ligroin and carefully dried in a desiccator. The crystals were granular in form, of a light greenish-yellow color and melted at 66.5° . An M/30 solution was prepared by dissolving .3304 gms. in 50 cc. alcohol.

1 - Ann., 190, 174. (1878).

d. P-Nitroso Diphenylamine.

The N-nitroso diphenylamine, upon treatment in a solution in alcohol saturated with dry HCl gas, undergoes an aniline type of rearrangement, wherein the N=O group shifts from the N to the para position. Following the method of Fischer and Hepp, about 3/4 of the amount of the N compound we had left was treated in this way. The alcohol solution of Hydrogen chloride was prepared by generating HCl by dropping sulphuric acid through a separatory funnel into a suction flask, the side arm of which lead into a calcium chloride tube and thence by means of glass tubing to the surface of the alcohol. It was allowed to run two hours. The solution was then cooled in ice and the crystals of N-nitroso diphenylamine added slowly with constant stirring. The color changed slowly from light yellow to red, to dark red and finally to reddish brown. The acid salt separated out as a reddish-brown precipitate, which was filtered off, dried and added to benzene. This solution was boiled with animal charcoal, filtered and allowed to stand until the acid salt crystized out. After filtering this off, it was added to a slightly alkaline solution of sodium acetate, heated until nearly all was in solution, and then filtered. On standing, the filtrate yielded a brown powder, which was filtered off, redissolved in hot chloroform, filtered and allowed to stand. On cooling, fine, steel-blue crystals separated out, which melted at 143°. A M/30 solution was prepared by dissolving .3303 grams in 50 cc. of alcohol.

e. N-Nitroso Carbazole.

A sample of crude N-nitroso carbazole, prepared by one of the students in the laboratory after the method of Wieland,² was re-

1 - O. Rischer and E. Hepp. Ber. 19, 2994.

2 - Wieland. Ann. 393, 127- 192.

crystallized from hot ether solution several times. The crystals as finally obtained were a golden yellow in color and melted sharply at 80.5° . A M/30 solution was prepared by dissolving .3269 grams in 50 cc. of alcohol, and was used for the picture.

f. P-Nitroso Carbazole.

Following a rather meager account of preparation given by Schott, an attempt was made to prepare p-nitroso carbazole. The N-nitroso carbazole was added slowly, with constant stirring to 150 cc. of glacial acetic acid saturated with HCl. The solution was cooled by allowing to stand in contact with ice. About one minute after all the solid was added, the entire solution became suddenly thick. The color changed from a yellowish-green to a dark red in about five minutes. Upon filtering and washing with water, the mass turned light green. The salt, which we supposed we had, was dissolved in dilute alkali (NaOH). The color changed immediately to red. Weak acetic acid was added until the base was neutralized, and the precipitate that formed was filtered, washed thoroughly with water, and recrystallized from hot alcohol. The crystals were of a greyish-yellow in color and melted at 233° . On recrystallizing again from hot benzene, in the presence of animal charcoal, pure white, flaky crystals were obtained, which melted at 238° . It was concluded that the HCl had hydrolyzed off the N=O group and that we had obtained carbazole as our final product.

g. O-Nitro Diphenylamine.

In the preparation of o-nitro diphenylamine, we adopted the method of Kehrman and Havas, with slight modifications.² 10 gm.

- 1 - Chem. Zentral., 1902, II, 1165.
- 2 - Ber., 1913, 46, 341.

of o-nitro chlor benzene which had been recrystallized from alcohol, 13.8 cc. of aniline, and 5.2 gms. of anhydrous sodium acetate was heated in a round-bottomed flask with an air condenser, about 14 hours in an oil bath. The temperature, during this time was held at about 215°. Instead of steam distilling the mass, as suggested by the authors, the dark brown oily solid was treated with 20 cc. of 10% acetic acid solution and thoroughly shaken. After standing over night, the acetic acid, containing some aniline, was decanted off and the process repeated several times. The oil was allowed to run into a six inch evaporating dish and washed again with acetic and finally with water. The whole mass was then dissolved in alcohol, heated with bone charcoal and filtered. On allowing the filtrate to stand, dark reddish-brown crystals separated out. These were recrystallized from hot alcohol, from which the o-nitro diphenylamine crystallized out in glancing reddish-yellow leaflets. On carefully drying, they melted sharply at 75°. A M/30 solution was prepared by dissolving .3569 grams in 50 cc. of alcohol.

h. O-Nitro Carbazole.

Several attempts were made to prepare the 1-nitro and 3-nitro carbazoles, which were supposed to come from the same experiment according to Ziersch. All trials yielded the same product. Essentially the procedure followed was : 15 grams of carbazole was suspended in 120 cc. of glacial acetic acid, to which was added drop by drop 2.33 cc. of HNO_3 (Sp. Gr. 1.38) keeping the temperature at about 80°. In one experiment, the heating was stopped at this point, while in another, it was continued for three hours after ward

The yield was the same in both cases and the products appeared to be the same. The suspension turns dark brown and upon cooling a yellowish-brown substance separates out which according to Ziersch, melted at 205° . The o-nitro carbazole was supposed to be obtainable from the filtrate upon addition of water. According to the author, this substance melted at 164° , after crystalizing in fine yellow needles from alcohol.

The precipitate from the nitration mixture (supposedly 3-nitro carbazole) was added to 200 cc. of alcohol and heated to boiling. It was then filtered and the undissolved part added to more alcohol. From the filtrate of the first filtration, there was obtained a crop of scale-like tan colored crystals. From the other crystalizations, there was obtained needle crystals, scales, and powder. All were light brown in color and all melted within the range $229 - 232.5^{\circ}$. Evidently the compound was different entirely from that obtained by Ziersch.

The precipitate, formed on addition of water to the filtrate from the nitration mixture (stated by Ziersch to be 1-nitro carbazole), was dissolved in alcohol, filtered and allowed to stand. There appeared dark-brown rosette-like crystals which formed shortly before some light brown crystals separated out. A melting point was run on each. The dark brown rosette crystals melted at 197° and the light brown or yellow crystals at 165° . Various solvents were tried on these to see if a separation could be brought about. Benzene seemed to dissolve the light brown crystals. On boiling up in benzene and drying several times, the melting point was found to continually vary. (175° , 174° , 169°). The work had to be dropped at this point in order to continue the work on the indophenols.

i. P-Nitroso Phenol.

As none of this substance was found available, it was prepared after the method described in Meyer and Jacobson, using slight modifications to purify the product. 60 grams of phenol were dissolved in 1200 cc. of water. To this solution was added, solutions 54 grams of NaNO_2 in 150 cc. of water and 27 grams NaOH in 150 cc. of water. The beaker containing the solutions was surrounded by an ice and salt mixture. When the temperature had become 0° , a mixture of 150 grams of sulphuric acid and 400 cc. of water was added to the first solution slowly with continuous stirring. After standing two hours, the precipitate formed was filtered off, washed thoroughly with ice water, and the whole dissolved in 500 cc. of water by addition of 40 cc of NaOH solution. (added drop by drop with stirring) After adding about 8 grams of Fuller's Earth, the whole was stirred for twenty minutes with a mechanical stirrer, whereupon it was filtered with suction. The filtrate was treated with con HCl , adding the acid very carefully with constant stirring. The p-nitroso phenol separated out almost white at first, but rapidly darkened to a brown after a short time. This was filtered off, washed thoroughly and dried in a desiccator. It was a brown powder which on examination with a microscope proved to be crystalline. It melted at 130° with decomposition.

j. Indophenol of Diphenylamine,

As both the indophenols were prepared in exactly the same way, only one preparation, that of the indophenol of diphenylamine will be described. The method followed was given in Friedlander,

- 1 - Meyer and Jacobson. Vol. II. Pt. 1, p. 457.
- 2 - Friedlander., 1910-1912., 10, 301.

5 grams of diphenylamine were dissolved in 50 grams of sulphuric acid (66° Be'). A solution of 4 grams of p-nitroso phenol in 40 grams of sulphuric acid was added slowly with stirring to the first solution, the temperature being kept at about 12°. The color turned to a deep green. The mixture was next poured on cracked ice in an evaporating dish, whereupon a blue precipitate formed. This was filtered off with suction, the air drawing through it all night. It was spread upon porous plates to dry and placed in a vacuum desiccator. After leaving for about a week in the desiccator, a small sample was tested with BaCl₂ and the presence of a sulphate detected.

Conversion of Sulphate to Neutral Base.

About one-half of the total amount was treated with sodium acetate solution on a steam bath. A purplish-brown solution was formed. The solution was filtered and the residue dissolved in acetone with the production of a deep blue color. This was heated and filtered. To the filtrate was added just enough water to produce a small precipitate and then it was set aside and allowed to crystallize out of solution. The crystals, which were very finely divided were dissolved in weak caustic soda solution and precipitated with dilute acetic acid, and filtered.

Purification of Neutral Base.

The blue powder obtained in this way was dissolved in acetone solution, boiled a short time, and filtered. A small amount of water was added to the filtrate until the first noticeable precipitation occurred, when it was set aside and allowed to crystallize out. The powder so obtained was dried thoroughly in the air, then, for several hours in an oven at 40°. A solution was made up and the spectrum prepared.

The outstanding difference in the case of the indophenol of carbazole was that it was a dark reddish blue in color after the treatment with sodium acetate solution.

Acknowledgment.

We wish to express our appreciation of the many kindnesses and courtesies which have been extended to us by the members of the Physics Department, especially to Dr. Tate, in whose laboratory all the spectrum photographs were prepared. The loan of the spectrograph, an instrument which we did not possess, enabled the work to be carried out. The writer personally wishes to thank Dr. Hunter, under whose direction and by whose suggestion the research was done, for his encouraging advice and helpful assistance.