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# A study of the structures of some compounds of the symmetrical triazine series by means of their ultraviolet spectra

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A STUDY OF THE STRUCTURES OF SOME  
COMPOUNDS OF THE SYMMETRICAL TRIAZINE SERIES  
BY MEANS OF THEIR ULTRAVIOLET SPECTRA

BY

ROBERT WILLIAM SCHAEFER

A thesis presented to the Department of Chemistry  
of Union College in partial fulfillment of the require-  
ments for the degree of Master of Science.

By Robert W. Schaefer

Approved by Galen W. Ewing

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I should also like to extend at this time my thanks to Dr. Peter Russell of Wellcome Research Laboratories for the samples and information which he made available.

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11. Nov. 53

Gift of Author

## ABSTRACT

The purpose of this work is to investigate the ultraviolet absorption spectra of symmetrical triazines with the outlook of correlating, on a theoretical basis, the data obtained with molecular structure.

Ultraviolet spectra have been determined for the following, 1,3,5-triazines; 2,4,6-triamino-, 2,4-diamino-6-phenyl-, 2-amino-4,6-diphenyl-, 2,4,6-triphenyl-, and 2,4,6-triazido-, both in polar and non-polar solvents where the solubility of the compounds permitted. Aqueous solutions of varying pH were determined for all but the triphenyl derivative which is insoluble in polar solvents. All spectra were determined with a model DU Beckman Spectrophotometer.

A theory has been worked out which attempts to correlate the data with that given by infra-red absorption.

## INTRODUCTION

From man's first look at a rainbow he must have marveled at the many colors present where previously there had only been what was to him ordinary light. As he looked he may have realized that these were the same colors that he saw in the rocks, flowers and foliage of nature. With his naturally curious and yet practical mind man wondered as to the origin of light and color and how it could be of use to him. We can see some of the results of this curiosity and practicality of man in the beautiful stained glass windows of the late middle age cathedrals and also in the multicolored paintings and artifacts of early man. Still man did not know what light was or the reasons for some materials being opaque while others allowed only certain colors to pass through when exposed to white light and still others did not seem to interfere at all with the passage of light.

It is well to note at this point that when the term 'light' is used herein the restriction to those radiations which are visible to the human eye is not implied but rather the term is used in its fullest extent embracing the ultraviolet and infra-red regions of the spectrum as well as the visible. This definition of the term is in accord with present ideas since the only difference between the visible light and either of the other regions mentioned is in the magnitude of the energy transition causing the radiation.

## INTRODUCTION (cont.)

Only with the fairly recent advent of wave theory and quantum mechanics together with a better understanding of the atomic structure of matter has a reasonable answer been given with regard to man's questions concerning light. Even now at our present state of knowledge there are still many unanswered questions in this field. Nevertheless, light has become for us a tool whereby we may consider the structure of substances through which it passes. This in general is what shall be attempted in this paper.

It is hoped that this work may add to our general knowledge of the relationship between chemical structure and light. If, however, nothing further is accomplished than adding new absorption data to the bulk of empirical data already at hand, the satisfaction of moving us even a little closer to the ultimate goal of understanding light absorption will be mine.

It was decided that the materials used for this study would be those known as symmetrical triazines, because of their analogy to benzene type compound, because they should be good absorbants in the ultraviolet region and because of the apparent anomalies in the interpretation of ultraviolet and infra-red spectra for cyanuric acid and melamine.

## HISTORICAL

It was recognized in early times that certain properties of a substance were not dependent upon the state of aggregation of that substance. It seemed therefore that such properties were intrinsically dependent upon the molecular structure as that does not change with the state of aggregation. As an example of this it was discovered by Biot (6, 7, 58) in 1817 that certain organic compounds exhibit optical activity not only in their solid state but also in the liquid and gaseous states. The optical activity therefore is clearly a property inherent to the individual molecules of the compound.

Miller (39) about midway through the nineteenth century built what is recognized as the first instrument for observing ultraviolet absorption. In reporting his observations in 1864 Miller (42) noted, "The most interesting fact, however, disclosed by these various experiments is the persistence of either diastatic or the absorbent property in the compound whatever be its physical state . . . . a circumstance which proves that the property under examination is intimately connected with the atomic or molecular nature of the body, and not merely with its state of aggregation."

Upon the death of Miller the instrument became the property of Hartley (25, 39) who is responsible for a large bulk of absorption spectral data. It is interesting to note at this

## HISTORICAL (cont.)

point that Hartley (24) was the first to determine absorption spectra for triazines having reported on both cyanuric acid and melamine. Others such as Baly and Henri (20, 39) joined in the race to report ultraviolet data.

The credit for the first real attempt at correlating absorption spectral data must be given to Witt (20, 61) who presented in 1876 and 1883 his theory of chromophores and auxochromes. While this theory was wholly empirical, it was valid and is still of use today in interpreting absorption spectra. Briefly, Witt said that any compound which shows selective absorption must possess what he called a chromophore, i.e., certain unsaturated groups such as the carbon-carbon double bond. He further stated that such groups as hydroxyl<sup>y</sup> or amino would augment or intensify the color resulting from the chromophores. These he called auxochromes. Henri (39) extended Witt's theory to include in the class of chromophores any group which produces a characteristic absorption peak in any region of the spectrum including the ultraviolet and the infra-red. Hartley (25) believed that the absorption was characteristic of the parent compound and was merely altered by the presence of substituent groups; i.e., that the absorption spectrum of the parent compound retained its identity from one situation to another.



## HISTORICAL (cont.)

These early theories, however, gave no explanation as to why certain wavelengths of light were absorbed and others not. Even the correlation of data was difficult in that there was no uniform way of presenting experimental results, and in that the data produced by one man's apparatus did not always correspond to that of another's.

The first approach to the modern theory was made by Baly (3, 20), Kauffmann (20, 28) and Hantzsch (20, 22) who stated that light absorption is due to valency changes in a particular molecule. Hantzsch said, "Color is due to changes in the distribution of affinity without accompanying changes in the relative positions of atoms." He called this "valency isomerism". Though vague in its statement this parallels our modern resonance theory.

Baeyer (2, 20) believed erroneously that color was caused by a tautomeric shift of some particular atom in the compound.

Campbell (13, 20), due to his paper in 1913 is credited with introducing the idea that light absorption is caused by the vibration of electrons. This was in accord with contemporary ideas on the emission of light of specific wave lengths from excited elemental substances. This idea was developed by Lewis (20, 36) and Wells (20, 57). As we shall see in the

## HISTORICAL (cont.)

theoretical discussion electronic vibrations are still believed to be the basis for light absorption by the molecules of a substance.

Bury (12, 54) combined resonance theory taken from organic chemistry with Witt's theory to show that the groups which Witt called auxochromes augmented the possibility of resonance in the molecule which contains an unsaturated group or chromophore. This presented the basis of our modern interpretation of absorption data with regard to molecular structure.

Perhaps the greatest advance in the field of absorption spectroscopy came in 1940 with the completion of the Beckman Quartz Spectrophotometer (14). This instrument made it possible for a relatively unskilled operator to obtain absorption data which are reproducible to a high degree from one instrument to another (15). It also permitted relative ease in the investigation of the ultraviolet region of the spectrum. Since 1940 other instruments have been manufactured which have improved somewhat on the Beckman in that automatic recording devices have been employed but the bulk of good available data in this country is still that produced by the Beckman instrument.

For a more detailed history of the field of absorption spectroscopy many excellent reviews are available (20, 16, 31, 19 and others).

## THEORY

## Part One: The Theory of Light Absorption

In the early studies of emission spectroscopy it was found that when heated, elements such as sodium and barium produced certain fixed wavelengths of light. The explanation of why this occurred based on quantum mechanics is that the electrons of such atoms have certain fixed energy levels and as the electrons receive heat energy they may oscillate between these levels. As the electron proceeds from a higher level to a lower one, i.e., from  $E_2$  to  $E_1$  the energy emitted is given by:

$$E = E_2 - E_1 = h\nu$$

where  $\nu$  is the frequency of the light emitted and  $h$  is a constant known as Planck's constant.

Kirchhoff (29,39) suggested that the dark lines in the solar spectrum were absorption lines due to vapors of substances through which the light must pass between the core of the sun and the earth. These lines corresponded to the known emission lines of certain elements. Thus we can say that light of a certain frequency may be absorbed by an atom or molecule if the correct quantum energy levels are available. The absorption of light follows the same equation as that for light emission.

The theory as stated so far is good for monatomic elements but we are interested in the case of polyatomic molecules and must, therefore, consider what happens when they absorb light.

## THEORY (cont.)

In such molecules these same electronic transitions from one energy level to another are available but they are now accompanied by certain other quantized energy effects due to rotational and vibrational transitions in the energy states of the atoms. These effects require much less energy and accompany the electronic transitions in such a way that for a given sample single lines are no longer apparent but rather a series of lines so close together that usual dispersing instruments are unable to separate them. Thus instead of giving a line spectrum as in the case of atomic elements polyatomic molecules give what are known as band spectra. The equation for any one line of the band spectrum now becomes

$$E = E_2 - E_1 = E_T + E_R + E_V = h\nu;$$

where  $E_T$  is the energy due to electronic transition,  $E_R$  is that due to rotational effects and  $E_V$  is that due to vibrational effects. If we investigate the amount of energy needed to produce light of a given wavelength in the ultraviolet region we see that electron transitions are necessary.

If we recall now Witt's theory of chromophores we see that in order to absorb in the ultraviolet an unsaturated group must be present. For example, ethylene exhibits an absorption peak at 180 m $\mu$ . (8) while such compounds as ethane, pentane, hexane and other saturated hydrocarbons exhibit no such absorption in the ultraviolet. We may therefore postulate that in the satu-

## THEORY (cont.)

rated hydrocarbons the higher energy levels of the individual atoms are no longer available and therefore no ultraviolet absorption is found in any easily accessible range.

In the case of unsaturated compounds, one pair of the four bonding electrons of the unsaturated linkage is considered less fixed in position than the other pair and is relatively free or mobile. Higher energy levels for these electrons are available and therefore electronic transitions capable of absorbing ultraviolet light are possible. These electrons are often referred to as "unsaturation", "mobile", or " $\pi$ " electrons (8 pg. 108-09).

The only points which are still to be explained are the effects of resonance and auxochromes. The effects produced in each case are such that they stabilize the available energy levels for the " $\pi$ " - electrons at various positions with respect to the ground state of those electrons in the molecule. This would account for absorption of light in a region of higher wavelength for molecules where there is a possibility of resonance (as in a conjugated system of double and single bonds) or where there is an auxochrome present. The effect of resonance on absorption spectra in the case of butadiene is summarized by Vogel (19).

## THEORY (cont.)

For a more detailed account of the theory of light absorption there are many existing texts, articles and reviews (8, 9, 11, 12, 16, 20, 25, 27, 28, 31, 34, 37, 38, 39, 43).

## THEORY (cont.)

## Part Two: The Measurement of Light Absorption

The quantitative measurement of light absorption is based on two fundamental laws which are concerned with the relationship of the intensities of the incident light,  $I_0$ , and the transmitted light,  $I$ . These two laws are known as Lambert's and Beer's Laws.

Lambert's Law (33, 35) states that the proportion of the light transmitted is independent of the intensity of the light incident upon the sample and may be expressed by the equation

$$I = I_0 e^{-rl}$$

where  $r$  is a constant for each substance and  $l$  is the thickness of the sample. No exceptions to this relation have been discovered.

Beer's Law (4, 52) states that the intensity of the transmitted light is dependent only on the number of absorbing molecules through which the incident light passes for a given sample. Thus if  $c$  is the concentration and  $l$  is the thickness of the sample

$$I = I_0 e^{-\alpha cl}$$

where  $\alpha$  is a constant for the absorbing sample.

We may now combine the two relations to give us the familiar expression known as the Beer-Lambert Law

$$\log \frac{I_0}{I} = kcl$$

## THEORY (cont.)

where  $k$  is now the absorbance per unit concentration and thickness of a given sample.

The field of light absorption has been hindered by a great number of symbols and terms many of which mean nearly the same thing. This matter has been taken up by Brode (10) and by the National Bureau of Standards (46). We shall comply with the suggested nomenclature and symbols of the latter in this work. The logarithmic term of the Beer-Lambert equation then is given the name absorbency (formerly extinction or optical density) and the symbol  $A_g$  (formerly  $E$ ).

It is clearly evident that the units of the absorbency constant are dependent upon those chosen for the length of the cell and the concentration. Almost without exception the cell length is specified in centimeters. However, there is no such uniformity in the units for the expression of the concentration. The two most widely used are grams per liter and gram-moles per liter. If grams per liter are used then the proportionality constant is given the symbol  $a_g$  (formerly  $k$ ) and is known as the absorbency index (formerly the specific extinction coefficient). If gram-moles per liter are used the proportionality constant is given the symbol  $a_m$  (formerly  $\epsilon$ ) and is known as the molar absorbency index (formerly the molar extinction coefficient).



## THEORY (cont.)

It is interesting to note at this point that while there are no known cases of exception to Lambert's Law, Beer's Law is apparently not always obeyed. It is generally accepted, however, that deviations result from one of two sources, a change in the nature of the absorbing species such as would be brought about through dissociation or association of the individual molecules, or by the use of polychromatic light.

## EXPERIMENTAL PART

## Apparatus

The spectra described in this work were determined with a model D. U. Beckman Spectrophotometer (14), Serial Number 3210, equipped for ultraviolet measurement.

The sensitivity control of the instrument was set at its counterclockwise limit (minimum sensitivity) for all determinations, thus allowing measurements to be made down to 210 m $\mu$  wavelength. The slit widths varied from 1.6 to 0.3 mm at the extreme limits. However, in the range above 220 m $\mu$ , the average slit used was in the range of 0.5 to 0.3 mm, corresponding to a nominal band width isolation of  $1.0 \pm 0.2$  m $\mu$ . (26).

Readings were taken at 5 m $\mu$  intervals except at points of interest and near maxima or minima where readings were taken at 1 m $\mu$  intervals.

The cells used were matched and of fused silica with an inside square cross-section of 1.00 cm  $\pm$  .001 cm.

The pH of all buffer solutions was checked with a Model H-2 Beckman pH meter.

Melting point determinations were made with a simple Thiele tube apparatus calibrated at various intervals with compounds

## EXPERIMENTAL PART (cont.)

of known purity and melting points.

All weighings were accomplished on a Roller-Smith torsion type balance.

## EXPERIMENTAL PART (cont.)

## Calibration of Apparatus

The spectrophotometer was checked and calibrated against the hydrogen  $\alpha$  - line (656.3  $\mu$ m.) approximately once a month. A complete wavelength versus density test was run approximately every two months in accord with the recommendation of the National Bureau of Standards (45).

The pH meter was checked and calibrated with National Technical Laboratory concentrated buffer solutions before use each time.

## EXPERIMENTAL PART (cont.)

## Preparation of Compounds

## 1. 2-Amino-4,6-diphenyl-1,3,5-triazine.

A sample of this material was received from Dr. Peter Russell (50). The melting point of this compound after air drying at 100° C was found to be correct at 168-170° C.

## 2. 2,4-Diamino-6-phenyl-1,3,5-triazine.

A sample of this material was obtained from the Sterling-Winthrop Research Institute in the form of the monohydrochloride monohydrate. It was recrystallized from aqueous alcohol and air dried at 100° C. The melting point was found to check at 246-247° C (44).

## 3. Melamine.

A sample of melamine or 2,4,6-triamino-1,3,5-triazine was received from American Cyanamide Co. It was purified by recrystallization from aqueous alcohol and checked as to purity by spectroscopic measurements (30) and melting point, the latter of which checked at 249° C.

## 4. 2,4,6-Triazido-1,3,5-triazine.

This compound which is better known as cyanuric triazide was prepared according to the method given by Hart and Ott (23, 48) and twice recrystallized from absolute alcohol. The melting point was found to check at 94-95° C with that given by Ott (47, 49).

## EXPERIMENTAL PART (cont.)

## 5. 2,4,6-Triphenyl-1,3,5-triazine.

This compound was prepared by the method described by Schmidt and Wahl (51) and twice recrystallized from absolute alcohol. The melting point checked with that given in the above mentioned paper and found to be the same, 196° C.

## EXPERIMENTAL PART (cont.)

## Preparation of Solutions

In each case the solvents used were of spectroscopic purity and solvents of the same batch were used for the reference liquid as were used for the solution.

Due to the very limited solubility of the 2-amino-4,6-diphenyl-1,3,5-triazine and the 2,4,6-triazido-1,3,5-triazine in aqueous solution it was necessary to dissolve these first in a small amount of ethyl alcohol. About 2 ml was enough to facilitate preparation of one liter of final solution. In each case a similar amount of the ethyl alcohol was added to the reference liquid.

A check was made to test the effect of the added alcohol on the spectra of both these compounds by observing spectra of the saturated aqueous solutions. The shape of the curve was identical although the exact concentration of the solution was not determined.

Spectral determinations could not be obtained with melamine in iso-octane nor with 2,4,6-triphenyl-1,3,5-triazine in aqueous and alcoholic solutions due to their extreme insolubility.

## EXPERIMENTAL PART (cont.)

## Buffer Solutions

It was necessary to obtain suitable buffers which did not absorb in the region from 210 to 350 m $\mu$ . A series of buffers which would cover the whole range of pH and still not absorb could not be found.

However, Clark and Lubs buffers(15, 60) were found to be well suited for the job except in the range from pH 2 to pH 6 where a biphthalate salt is used which absorbs strongly in the ultraviolet. In this region Sørensen's glycine-hydrochloric acid (21, 53) buffers were found to fit rather well. The big difficulty with these solutions was that they had to be freshly prepared frequently because of the growth of fungi in them.



## EXPERIMENTAL PART (cont.)

## Experimental Results

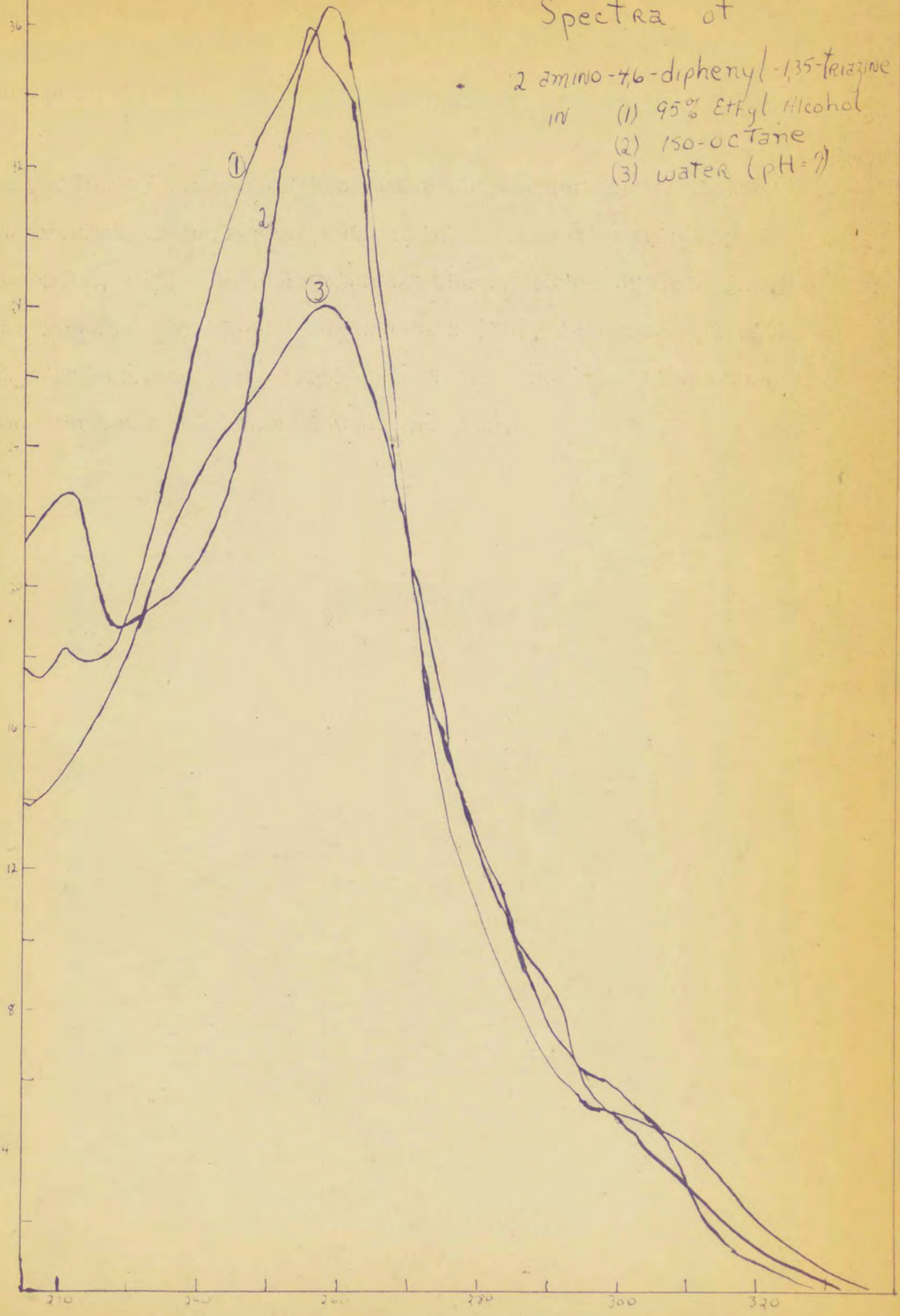
The following graphs of the solar absorptancy index plotted against wavelength represent data which have not previously been reported, with the exception of the spectrum of melamine. This was reported by Klotz and Askounis (30), in agreement with present findings. All spectral data taken from the literature have been repeated with consistent results.

# Plate # 1

## Spectra of

- 2-amino-4,6-diphenyl-1,3,5-triazine
- in (1) 95% Ethyl Alcohol
- (2) Iso-octane
- (3) water (pH=7)

$\frac{2.72 \times 10^{-3}}{\lambda}$



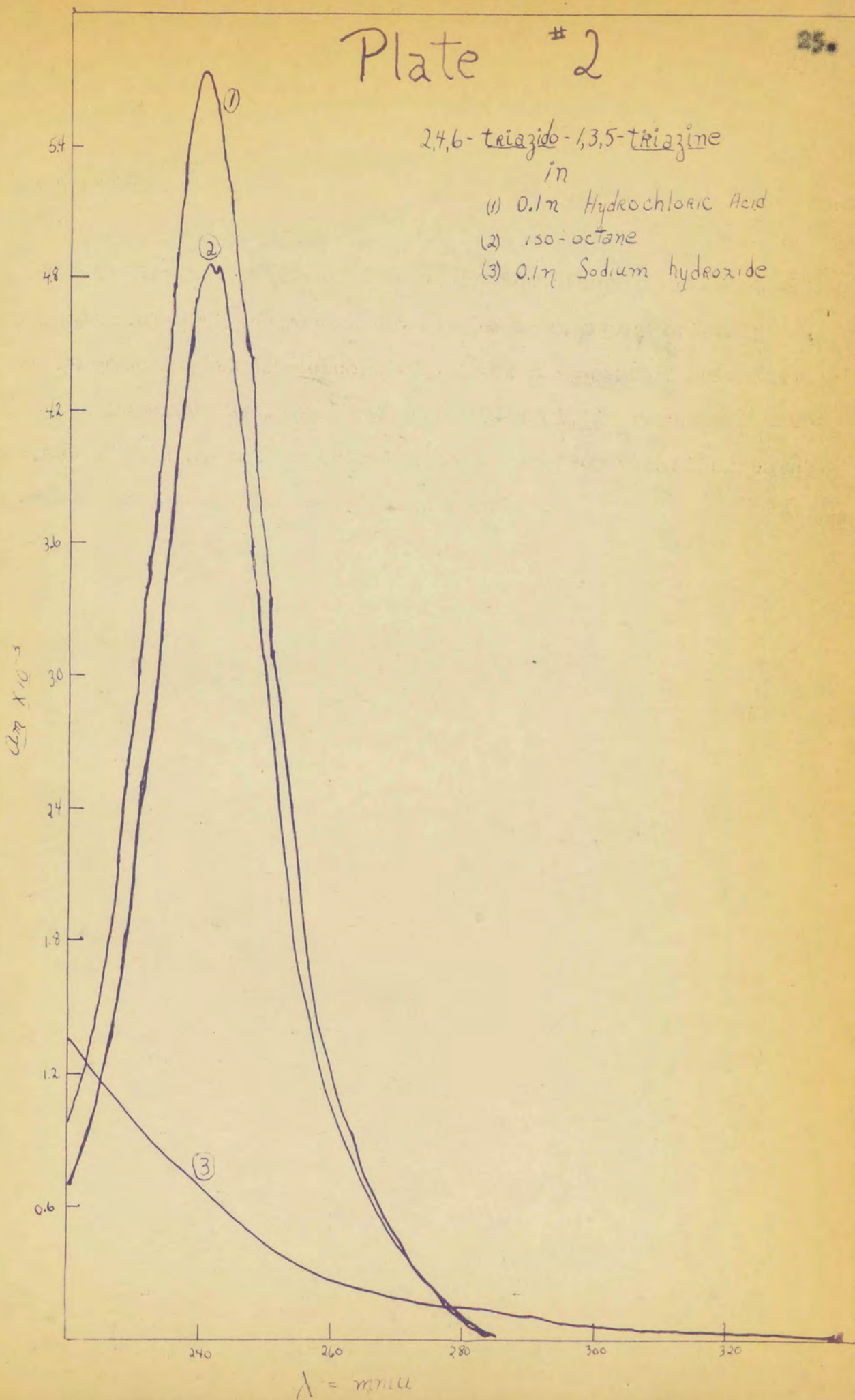
$\lambda = \text{m}\mu.$

# Plate #2

25.

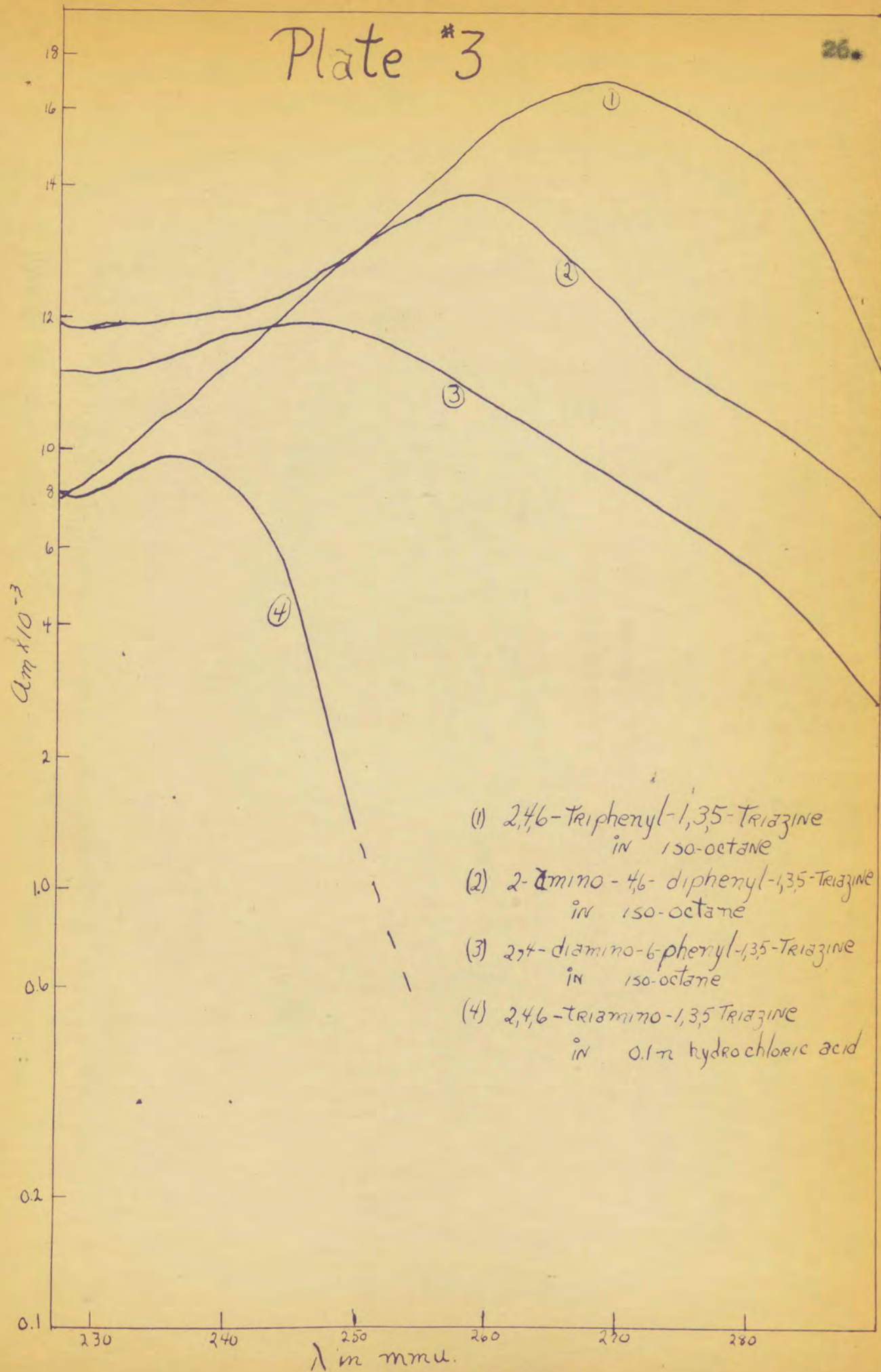
2,4,6-triazido-1,3,5-triazine  
in

- (1) 0.1N Hydrochloric Acid
- (2) iso-octane
- (3) 0.1N Sodium hydroxide



# Plate #3

26.

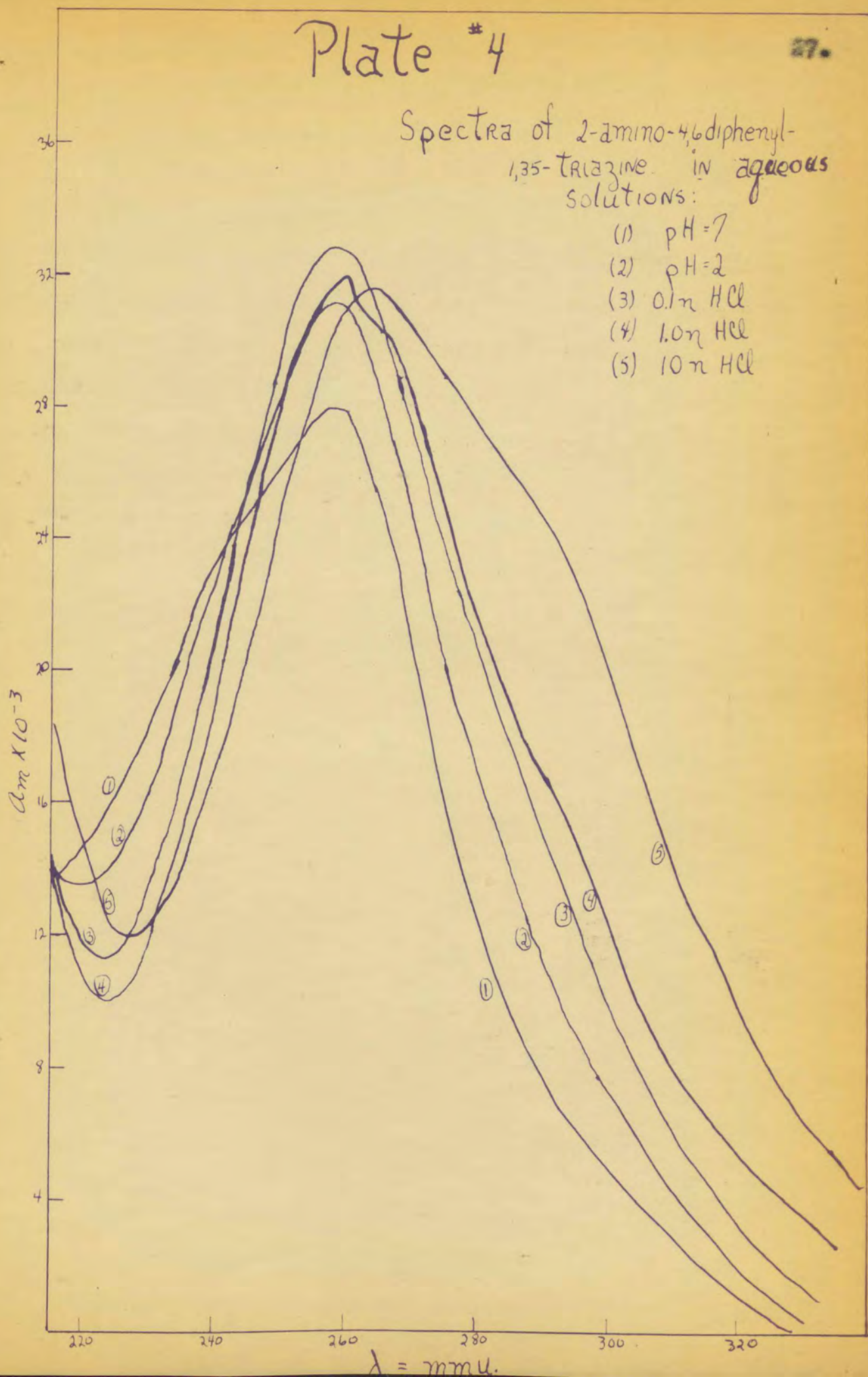


# Plate # 4

27.

Spectra of 2-amino-4,6-diphenyl-  
1,3,5-triazine in aqueous  
solutions:

- (1) pH=7
- (2) pH=2
- (3) 0.1n HCl
- (4) 1.0n HCl
- (5) 10n HCl

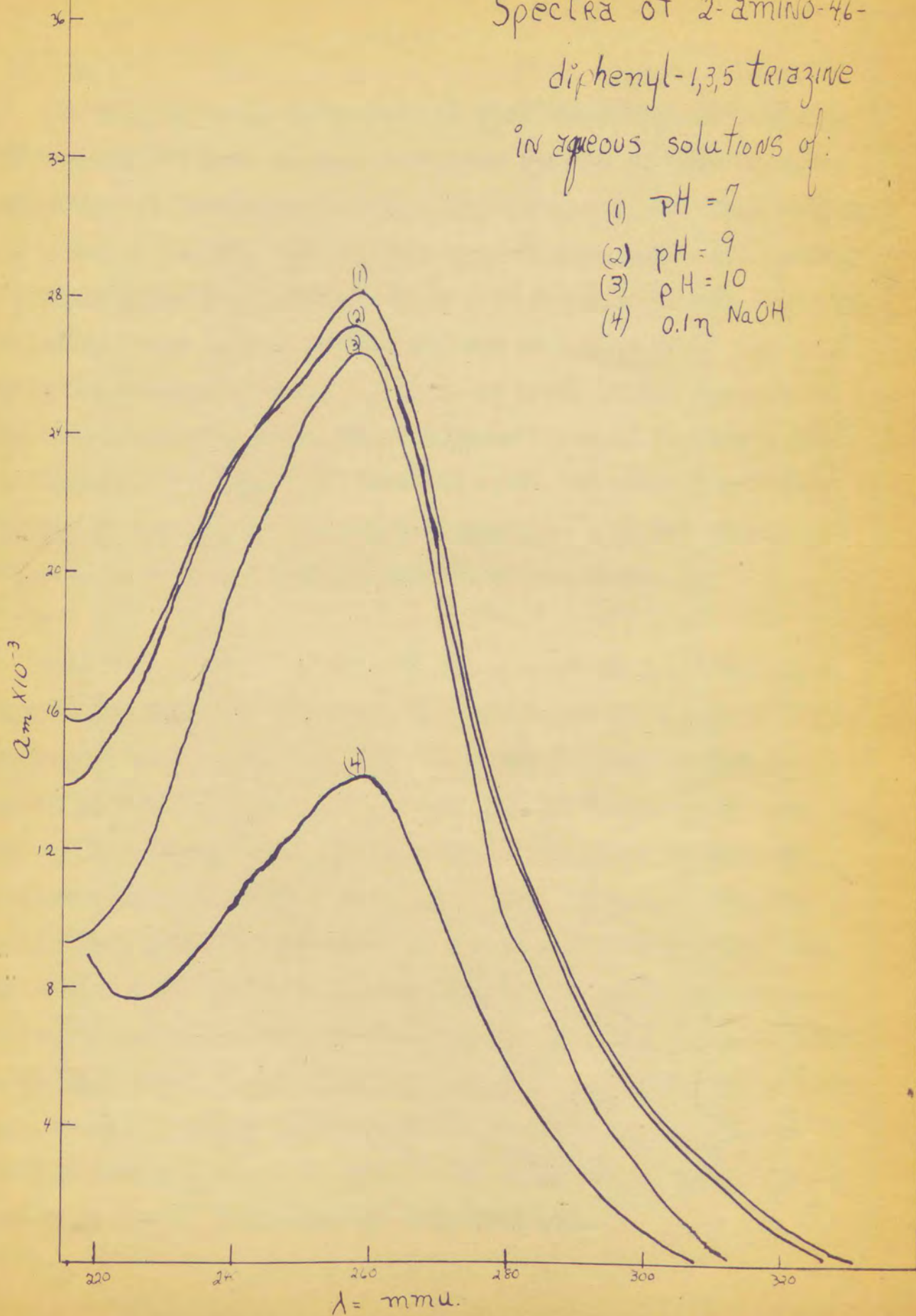


# Plate #5

28.

Spectra of 2-amino-4,6-diphenyl-1,3,5 triazine  
in aqueous solutions of:

- (1) pH = 7
- (2) pH = 9
- (3) pH = 10
- (4) 0.1N NaOH



## DISCUSSION

It will be noted from Plate #1 that the effect of solvents of varying polarity on the absorption spectra of 2-amino-4,6-diphenyl-1,3,5-triazine is not quite in accord with that normally expected (8,34). The general hypsochromic shift (9) usually found in going from polar to non-polar solvents is not observed, although there is an increase in fine structure (8). The fact that the molar absorptency index is so small at the maximum in neutral aqueous solution is of extreme interest in that a similar situation arises with melamine (30). An attempt at explanation of this will be given in connection with the effect of varying pH on the aqueous solutions of the compound.

Plate #2 gives a picture of the spectra of 2,4,6-triazido-1,3,5-triazine in a non-polar solvent, tenth normal acid (HCl) and tenth normal base (NaOH). The curve in basic solution shows that the compound has hydrolyzed, as described by Hart (23). This curve takes the form of superimposed spectra of sodium azide (55) and cyanuric acid (30). The main purpose of including this compound is to add to the evidence that the maximum present in each of these spectra is due to the presence of the benzenoid structure of the cyanuric ring. This structure must be present in this compound since it is impossible to draw resonance structures in which there is a shift of electrons either into or out of the ring. The azide group, itself, does not show strong absorption in this area (55).

## DISCUSSION (cont.)

A comparison is shown in Plate #3 of the spectra of the series of amino- and phenyl- substituted triazines, all in non-polar iso-octane with the exception of melamine which is in tenth normal aqueous acid (HCl). Due to the similarity in spectra of solutions in tenth normal acid and non-polar solvent for the phenyl and diphenyl compounds and the inability to dissolve melamine in iso-octane this curve was used for the comparison. The stepwise decrease of both the molar absorptivity index and the wavelength for the replacement of a phenyl group by an azine group should be noted. This is taken by the writer to mean that the phenyl group is acting as an auxochrome with a much more powerful effect in causing a batho-shift than the amine group. From these considerations we may still maintain that the maximum in each case is that due to the benzene-like cyanuric ring. It should be noted that Maccoll's prediction (40) of about 370  $\mu$ , for the maximum absorption of this ring appears to be too high in view of more recent work.

The absence of fine structure or at least the absence of more than one maxima in this region may be attributed to the continuous conjugation of the cyanuric ring with those of the attached phenyl rings (38). It must be remembered, however, that though there is complete conjugation (i.e. alternate double and single bonds), there is no possibility for electron shifts into or out of the cyanuric ring with respect to an attached phenyl group.



## DISCUSSION (cont.)

Up to this point we have been concerned mainly in identifying the absorption maxima shown as those due to the ring structure. Now let us consider those derivatives containing an amine group. In molecules of these compounds there are at least two tautomers possible (see structures I, II, VII, VIII, IX, X in the appendix). There has been considerable discussion in the literature concerning which of these are present in the greatest proportion in solutions of varying polarity (1, 5, 17, 32, 41, 56). X-ray and magnetic measurements show that in the solid state the amide type structure is the greatest contributor in the case of melamine (32, 56). It may be assumed that the same is true in non-polar solutions. This is supported by our spectral data in the case of 2,4-diamino-6-phenyl- and 2-amino-4,6-diphenyl-1,3,5-triazines.

We shall now examine the case of the diphenyl compound in aqueous solutions (Plates 4 and 5). In this case only two tautomers (I, II) are possible. It is noted from the curves that the molar absorptancy index at the maximum drops off in alkaline solutions and become larger in acids. From a consideration of Beer's Law this must be taken to mean that the absorbing species is decreasing in concentration with an increase in pH. This may be explained by assuming that in the polar aqueous solutions structure II is the greater contributing tautomer. This is in accord with the infra-red data (58). The worth of this assumption may be seen in a consideration of the resonance

## DISCUSSION (cont.)

structures possible for each tautomer. For the amine type tautomer we can draw three possible contributors; two Kekulé type structures for structure I and a charge separated form, III. The other tautomer shows resonance between structure II and two charge separated Kekulé structures illustrated by IV. It should be observed that IV possesses the cyanuric ring structure and a charge separation more favorable than III to the addition of a proton as the hydrochloride salt is formed in acid solutions (38). From this consideration and the assumption that II is the predominant tautomer we can say that the contribution of the two Kekulé forms of IV increases as the solution becomes more acid (decreases in pH). This accounts for the gradual increase in the molar absorptivity index at the maximum as the pH increases. The effect on the spectra would be just the opposite if the amine type structure was the tautomer present in the greatest proportion.

An alternative explanation for the observed change with pH is that the tautomeric equilibrium between structures I and II is shifted in favor of II as the pH becomes larger. This reasoning is faulty in that it does not give a complete picture and in that the dielectric constant of the solution remains essentially constant, thus leading to doubt as to whether the equilibrium would shift.

The batho-shift shown in the curves taken in one and ten

## DISCUSSION (cont.)

normal acid (HSL) is presumed to be caused by the addition of a proton. It is interesting to note that both of the tautomers lead to the same structures (V, VI) when a proton is added. Structure VI, for which another Kekulé form can be drawn, should be the greater contributor due to the ring type resonance stabilization. This is shown to be the case from the spectral data.

This line of reasoning, if valid, should be able to explain not only the spectra in aqueous solution of the diphenyl compound but also those of melamine and the diamino derivative. In the case of melamine the theory fits the curves reported by Klotz and Askounis (30) and reproduced in the present study.

However, the spectra of 2,4-diamino-6-phenyl-1,3,5-triazine in aqueous solutions reported by Machod and Steck (44) show only the expected bathochromic shift due to the addition of a proton. The maximum remains in the same position as it is in a non-polar solvent. After verification of these curves it was thought that for some reason the tautomer shown as structure X could not be the major contributor in this case. Two possible reasons for this became evident upon a comparison of the structures of the three compounds which possess the amine group. The first of these is based on the symmetry of the molecule. A plane passing through the amine group perpendicular to the plane of the ring is a plane of symmetry in the case of melamine

## DISCUSSION (cont.)

and the diphenyl compound while it is not in the case of the compound under consideration. From this we can say that it would make a difference which ring-nitrogen accepted the proton in the case of the monophenyl compound when the tautomer is formed.

The second argument involves the permanent polarity of the molecule. The resultant vector from a consideration of the electropositive phenyl group and electronegative amine groups is in the direction of the ring-nitrogen between the two amine groups (shown in structure IX). This tends to make that atom a little more negative than the other ring-nitrogens. By combining these two arguments we see that, if tautomerism is to take place, the negative ring-nitrogen would be the most likely place for the proton to attach itself. However, both the amine groups tend to give up protons to this ring-nitrogen to the same degree. It is possible that this situation results in the case where neither proton can change position and the tautomer given in structure IX must be the greater contributor.

This consideration is offered for the diamino compound only as a possible explanation of the spectra reported and is admittedly weak. It is not felt, however, that this lessens the validity of the theory used to explain the spectra of the other two compounds.

## DISCUSSION (cont.)

The theory in general is supported further in that it may be used to correlate the ultraviolet and infra-red spectral data for cyanuric acid (30, 56), which had previously been in apparent disagreement.

## SUMMARY

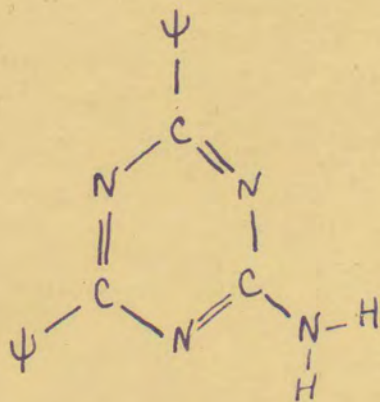
The ultraviolet absorption spectra of melamine, 2,4-diamino-6-phenyl-, 2-amino-4,6-diphenyl-, 2,4,6-triphenyl-, and 2,4,6-triazido-1,3,5-triazines have been determined in ethyl alcohol and iso-octane as well as in aqueous solutions of varying pH where ever the solubility of the compounds would allow. In addition, an attempt has been made to correlate the spectra with the molecular structures of the compounds on a theoretical basis.

As a result of the discussion we may postulate that in non-polar solvents the amine type tautomer is the greater component in the mixture in the case of melamine, 2,4-diamino-6-phenyl-, and 2-amino-4,6-diphenyl-1,3,5-triazine. We may further postulate that in the case of melamine and 2-amino-4,6-diphenyl-1,3,5-triazine the other tautomer (i.e., those given by structures II and VIII) is the greater contributor in aqueous solution. The case of 2,4-diamino-6-phenyl-1,3,5-triazine in polar solution is uncertain but it is felt that the amine type tautomer is still the major contributor.

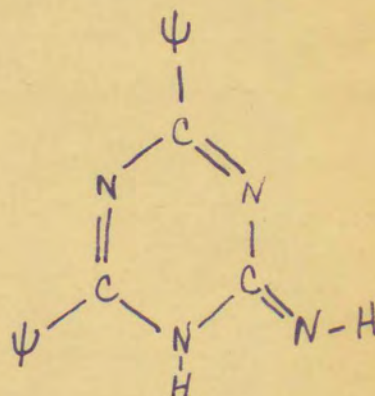
It is hoped that some insight into the structural behavior of these and related compounds may be gained through this study and that a contributions has been made to the ultimate goal of a complete understanding of the relationship between light absorption and molecular structure.

I. Tautomeric and resonance structures of  
2-amino-4,6-diphenyl-1,3,5 triazine:

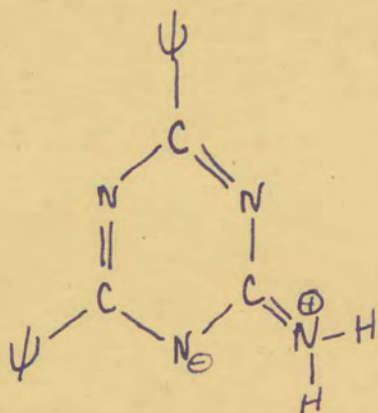
A. In neutral solutions:



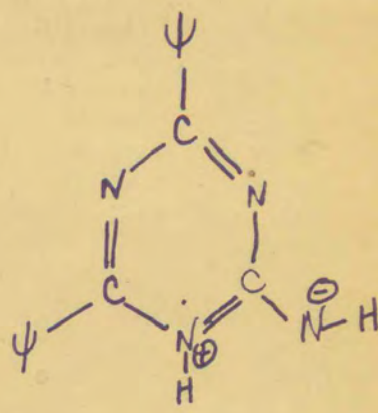
I.



II.

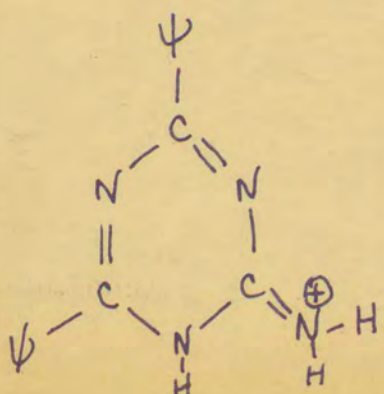


III.

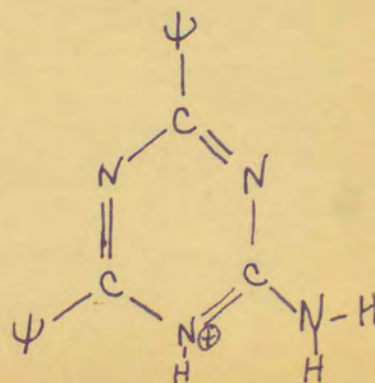


IV.

B. In acid solution:



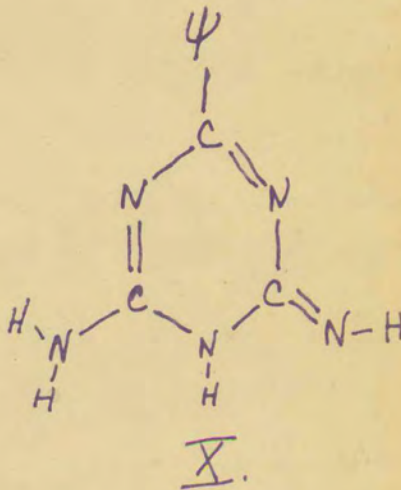
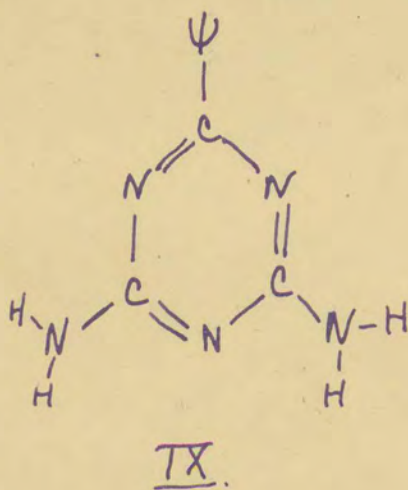
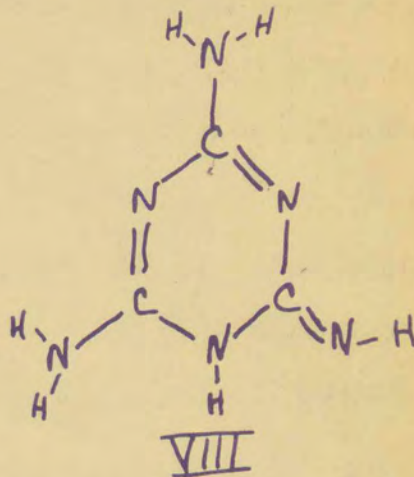
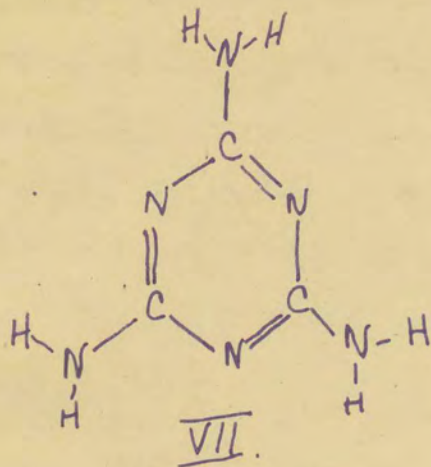
V.



VI.

# Appendix (Continued)

II Tautomeric structures of melamine and 2,4-diamino-6-phenyl-1,3,5-triazine





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